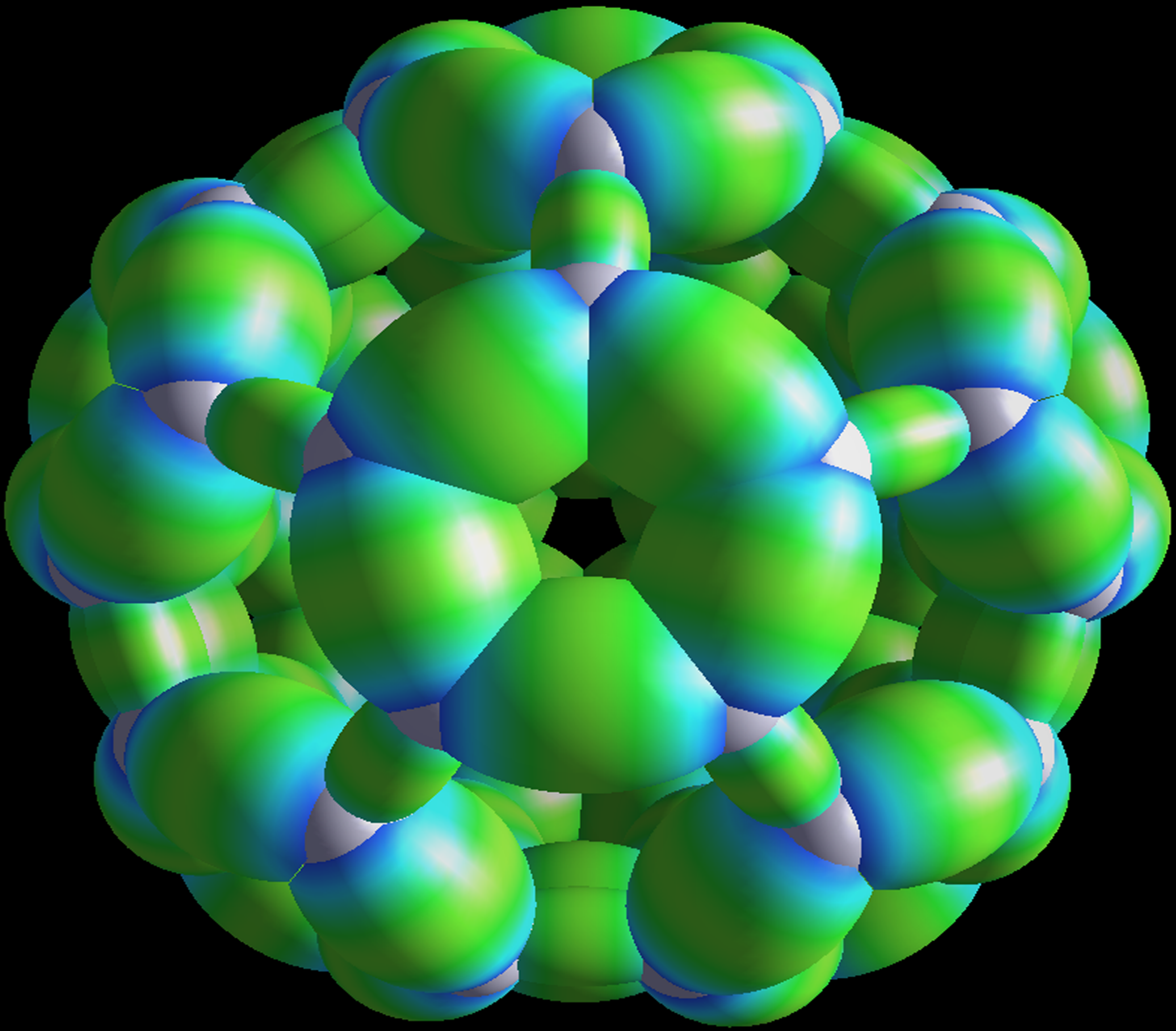
# THE GRAND UNIFIED THEORY OF CLASSICAL PHYSICS

Dr. Randell L. Mills



## VOLUME II:

Part A

## MOLECULAR PHYSICS

# *THE GRAND UNIFIED THEORY OF CLASSICAL PHYSICS*

***Volume 2A of 3***

# *THE GRAND UNIFIED THEORY OF CLASSICAL PHYSICS*

BY

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## VOLUME 2 MOLECULAR PHYSICS Part A

# Chapter 11

# THE NATURE OF THE CHEMICAL BOND OF HYDROGEN-TYPE MOLECULES AND MOLECULAR IONS

With regard to the Hydrino Theory—BlackLight Process section, the possibility of states with $n = 1/p$ is also predicted in the case of hydrogen molecular species wherein $H\left(1/p\right)$ reacts with a proton or two $H\left(1/p\right)$ atoms react to form $H_2^+\left(1/p\right)$ and $H_2\left(1/p\right)$, respectively. The natural molecular-hydrogen coordinate system based on symmetry is ellipsoidal coordinates. The magnitude of the central field in the derivations of molecular hydrogen species is taken as the general parameter $p$ wherein $p$ may be an integer which may be predictive of new possibilities. Thus, $p$ replaces the effective nuclear charge of quantum mechanics and corresponds to the physical field of a resonant photon superimposed with the field of the proton. The case with $p = 1$ is evaluated and compared with the experimental results for hydrogen species in Table 11.1, and the consequences that $p = \text{integer}$ are considered in the Nuclear Magnetic Resonance Shift section.

Two hydrogen atoms react to form a diatomic molecule, the hydrogen molecule.

$$2H\left[a_H\right] \to H_2\left[2c' = \sqrt{2}a_0\right] \tag{11.1}$$

where $2c'$ is the internuclear distance. Also, two hydrino atoms react to form a diatomic molecule, a dihydrino molecule.

$$2H\left[\frac{a_H}{p}\right] \to H_2\left[2c' = \frac{\sqrt{2}a_0}{p}\right] \tag{11.2}$$

where $p$ is an integer.

Hydrogen molecules form hydrogen molecular ions when they are singly ionized.

$$H_2\left[2c' = \sqrt{2}a_0\right] \to H_2\left[2c' = 2a_0\right]^+ + e- \tag{11.3}$$

Also, dihydrino molecules form dihydrino molecular ions when they are singly ionized.

$$H_2\left[2c' = \frac{\sqrt{2}a_0}{p}\right] \to H_2\left[2c' = \frac{2a_0}{p}\right]^+ + e- \tag{11.4}$$

## HYDROGEN-TYPE MOLECULAR IONS

Each hydrogen-type molecular ion comprises two protons and an electron where the equation of motion of the electron is determined by the central field that is $p$ times that of a proton at each focus ( $p$ is one for the hydrogen molecular ion, and $p$ is an integer greater than one for each $H_2^+\left(1/p\right)$, called a dihydrino molecular ion). The differential equations of motion in the case of a central field are [1]

$$m(\ddot{r} - r\dot{\theta}^2) = f(r) \tag{11.5}$$

$$m(2\dot{r}\dot{\theta} + r\ddot{\theta}) = 0 \tag{11.6}$$

The second or transverse equation, Eq. (11.6), gives the result that the angular momentum is constant.

$$r^2\dot{\theta} = \text{constant} = L/m \tag{11.7}$$

where $L$ is the angular momentum ( $\hbar$ in the case of the electron). The central force equations can be transformed into an orbital equation by the substitution, $u = \frac{1}{r}$. The differential equation of the orbit of a particle moving under a central force is

$$\frac{\partial^2 u}{\partial \theta^2} + u = \frac{-1}{\dfrac{mL^2u^2}{m^2}} f(u^{-1}) \tag{11.8}$$

Because the angular momentum is constant, motion in only one plane need be considered; thus, the orbital equation is given in polar coordinates. The solution of Eq. (11.8) for an inverse-squared force

$$f(r) = -\frac{k}{r^2} \tag{11.9}$$

is

$$r = r_0 \frac{1+e}{1+e\cos\theta} \tag{11.10}$$

$$e = A\frac{m\dfrac{L^2}{m^2}}{k} \tag{11.11}$$

$$r_0 = \frac{m\dfrac{L^2}{m^2}}{k(1+e)} \tag{11.12}$$

where $e$ is the eccentricity of the ellipse and $A$ is a constant. The equation of motion due to a central force can also be expressed in terms of the energies of the orbit. The square of the speed in polar coordinates is

$$v^2 = (\dot{r}^2 + r^2\dot{\theta}^2) \tag{11.13}$$

Since a central force is conservative, the total energy, $E$, is equal to the sum of the kinetic, $T$, and the potential, $V$, and is constant. The total energy is:

$$\frac{1}{2}m(\dot{r}^2 + r^2\dot{\theta}^2) + V(r) = E = \text{ constant} \tag{11.14}$$

Substitution of the variable $u = \frac{1}{r}$ and Eq. (11.7) into Eq. (11.14) gives the orbital energy equation.

$$\frac{1}{2}m\frac{L^2}{m^2}\left(\left(\frac{\partial u}{\partial \theta}\right)^2 + u^2\right) + V(u^{-1}) = E \tag{11.15}$$

Because the potential energy function $V(r)$ for an inverse-squared force field is:

$$V(r) = -\frac{k}{r} = -ku \tag{11.16}$$

the energy equation of the orbit, Eq. (11.15),

$$\frac{1}{2}m\frac{L^2}{m^2}\left(\left(\frac{\partial u}{\partial \theta}\right)^2 + u^2\right) - ku = E \tag{11.17}$$

which has the solution

$$r = \frac{m\dfrac{L^2}{m^2}k^{-1}}{1+\left(1+2Em\dfrac{L^2}{m^2}k^{-2}\right)^{1/2}\cos\theta} \tag{11.18}$$

where the eccentricity, $e$, is:

$$e = \left(1+2Em\frac{L^2}{m^2}k^{-2}\right)^{1/2} \tag{11.19}$$

Eq. (11.19) permits the classification of the orbits according to the total energy, $E$, as follows:

| | | |
|---|---|---|
| $E < 0,$ | $e < 1$ | closed orbits (ellipse or circle) |
| $E = 0,$ | $e = 1$ | parabolic orbit |
| $E > 0,$ | $e > 1$ | hyperbolic orbit |

Since $E = T + V$ and is constant, the closed orbits are those for which $T < |V|$, and the open orbits are those for which $T \geq |V|$. It can be shown that the time average of the kinetic energy, $<T>$, for elliptical motion in an inverse-squared field is $1/2$ that of the time average of the magnitude of the potential energy, $|<V>|$. $<T> = 1/2|<V>|$ [1].

As demonstrated in the One-Electron Atom section, the electric inverse-squared force is conservative; thus, the angular momentum of the electron, $\hbar$, and the energy of atomic atomic orbitals are constant. In addition, the atomic orbitals are nonradiative when the boundary condition is met.

The central force equation, Eq. (11.14), has orbital solutions, which are circular, elliptical, parabolic, or hyperbolic. The former two types of solutions are associated with atomic and molecular orbitals. These solutions are nonradiative. The boundary condition for nonradiation given in the One-Electron Atom section, is the absence of components of the spacetime Fourier transform of the current-density function synchronous with waves traveling at the speed of light. The boundary condition is met when the velocity for the charge density at every coordinate position on the atomic orbital is:

$$v_n = \frac{\hbar}{m_e r_n} \tag{11.20}$$

The allowed velocities and angular frequencies are related to $r_n$ by:

$$v_n = r_n \omega_n \tag{11.21}$$

$$\omega_n = \frac{\hbar}{m_e r_n^2} \tag{11.22}$$

As demonstrated in the One-Electron Atom section and by Eq. (11.22), this condition is met for the product function of a radial Dirac delta function and a time harmonic function where the angular frequency, $\omega$, is constant and given by Eq. (11.22).

$$\omega_n = \frac{\hbar}{m_e r_n^2} = \frac{\frac{\pi L}{m_e}}{A} \tag{11.23}$$

where $L$ is the angular momentum and $A$ is the area of the closed orbit. Consider the solution of the central force equation comprising the product of a two-dimensional ellipsoid and a time harmonic function. The spatial part of the product function is the convolution of a radial Dirac delta function with the equation of an ellipsoid. The Fourier transform of the convolution of two functions is the product of the individual Fourier transforms of the functions; thus, the boundary condition is met for an ellipsoidal-time harmonic function when,

$$\omega_n = \frac{\pi\hbar}{m_e A} = \frac{\hbar}{m_e ab} \tag{11.24}$$

where the area of an ellipse is

$$A = \pi ab \tag{11.25}$$

where $b$ and $2b$ are the lengths of the semiminor and minor axes, respectively, and $a$ and $2a$ are the lengths of the semimajor and major axes, respectively. The geometry of molecular hydrogen is ellipsoidal with the internuclear axis as the principal axis; thus, the electron orbital is a two-dimensional ellipsoidal-time harmonic function. The mass follows an elliptical path, time harmonically as determined by the central field of the protons at the foci. Rotational symmetry about the internuclear axis further determines that the orbital is a prolate spheroid. In general, ellipsoidal orbits of molecular bonding, hereafter referred to as ellipsoidal molecular orbitals (MOs), have the general equation:

$$\frac{x^2}{a^2} + \frac{y^2}{b^2} + \frac{z^2}{c^2} = 1 \tag{11.26}$$

The semiprincipal axes of the ellipsoid are $a,\ b,\ c$.

In ellipsoidal coordinates the Laplacian is:

$$(\eta - \zeta)R_\xi \frac{\partial}{\partial \xi}\left(R_\xi \frac{\partial \phi}{\partial \xi}\right) + (\zeta - \xi)R_\eta \frac{\partial}{\partial \eta}\left(R_\eta \frac{\partial \phi}{\partial \eta}\right) + (\xi - \eta)R_\zeta \frac{\partial}{\partial \zeta}\left(R_\zeta \frac{\partial \phi}{\partial \zeta}\right) = 0 \tag{11.27}$$

An ellipsoidal MO is equivalent to a charged perfect conductor (i.e. no dissipation to current flow) whose surface is given by Eq. (11.26). It is a two-dimensional equipotential membrane where each MO is supported by the outward centrifugal force due to the corresponding angular velocity, which conserves its angular momentum of $\hbar$. It satisfies the boundary conditions for a discontinuity of charge in Maxwell's equations, Eq. (11.48). It carries a total charge $q = -e$, and it's potential is a solution of the Laplacian in ellipsoidal coordinates, Eq. (11.27).

Excited states of atomic orbitals are discussed in the Excited States of the One-Electron Atom (Quantization) section. In the case of ellipsoidal MOs, excited electronic states are created when photons of discrete frequencies are trapped in the ellipsoidal resonator cavity of the MO. The photon changes the effective charge at the MO surface where the central field is ellipsoidal and arises from the protons and the effective charge of the "trapped photon" at the foci of the MO. Force balance is achieved at a series of ellipsoidal equipotential two-dimensional surfaces confocal with the ground state ellipsoid. The "trapped photons" are solutions of the Laplacian in ellipsoidal coordinates, Eq. (11.27).

As is the case with the atomic orbital, higher and lower energy states are equally valid. The photon standing wave in both cases is a solution of the Laplacian in ellipsoidal coordinates. For an ellipsoidal resonator cavity, the relationship between an allowed circumference, $4aE$, and the photon standing wavelength, $\lambda$, is:

$$4aE = n\lambda \tag{11.28}$$

where $n$ is an integer and where the elliptic integral $E$ of Eq. (11.28) is given by:

$$E(k) = \int_0^{\frac{\pi}{2}} \sqrt{1 - k^2 \sin^2 \phi}\, d\phi \tag{11.29}$$

$$k = e = \frac{\sqrt{a^2 - b^2}}{a} \tag{11.30}$$

Applying Eqs. (11.28) and (11.29-11.30), the relationship between an allowed angular frequency given by Eq. (11.24) and the photon standing wave angular frequency, $\omega$, is:

$$\frac{\pi\hbar}{m_eA}=\frac{\hbar}{m_ena_1nb_1}=\frac{\hbar}{m_ea_nb_n}=\frac{1}{n^2}\omega_1=\omega_n \tag{11.31}$$

where $n=1,2,3,4,...$ ($n=\frac{1}{2},\frac{1}{3},\frac{1}{4},...$ for molecular hydrino states); $\omega_1$ is the allowed angular frequency for $n=1$

$a_1$ and $b_1$ are the allowed semimajor and semiminor axes for $n=1$. Using the boundary conditions, the excited states are solved in the Excited States of the Hydrogen Molecular Ion and Excited States of the Hydrogen Molecule sections.

The potential, $\phi$, and distribution of charge, $\sigma$, over the conducting surface of an ellipsoidal MO are sought given the conditions: 1.) the potential is equivalent to that of a charged ellipsoidal conductor whose surface is given by Eq. (11.26), 2.) it carries a total charge $q=-e$, and 3.) initially there is no external applied field. To solve this problem, a potential function must be found which satisfies Eq. (11.27), which is regular at infinity, and which is constant over the given ellipsoid. The solution is well known and is given after Stratton [2]. Consider that the Laplacian is solved in ellipsoidal coordinates wherein $\xi$ is the parameter of a family of ellipsoids all confocal with the standard surface $\xi=0$ whose axes have the specified values $a$, $b$, $c$. The variables $\zeta$ and $\eta$ are the parameters of confocal hyperboloids and as such serve to measure position on any ellipsoid $\xi=\text{constant}$. On the surface $\xi=0$; therefore, $\phi$ must be independent of $\zeta$ and $\eta$. Due to the uniqueness property of solutions of the Laplacian, a function which satisfies Eq. (11.27), behaves properly at infinity, and depends only on $\xi$, can be adjusted to represent the potential correctly at any point outside the ellipsoid $\xi=0$.

Thus, it is assumed that $\phi=\phi(\xi)$. Then, the Laplacian reduces to:

$$\frac{\partial}{\partial\xi}\left(R_\xi\frac{\partial\phi}{\partial\xi}\right)=0 \qquad R_\xi=\sqrt{(\xi+a^2)(\xi+b^2)(\xi+c^2)} \tag{11.32}$$

which on integration leads to:

$$\phi(\xi)=C_1\int_\xi^\infty\frac{\partial\xi}{R_\xi} \tag{11.33}$$

where $C_1$ is an arbitrary constant. The upper limit is selected to ensure the proper behavior at infinity. When $\xi$ becomes very large, $R_\xi$ approaches $\xi^{3/2}$ and,

$$\phi\sim\frac{2C_1}{\sqrt{\xi}} \qquad (\xi\to\infty) \tag{11.34}$$

Furthermore, the equation of an ellipsoid can be written in the form:

$$\frac{x^2}{1+\frac{a^2}{\xi}}+\frac{y^2}{1+\frac{b^2}{\xi}}+\frac{z^2}{1+\frac{c^2}{\xi}}=\xi \tag{11.35}$$

If $r^2=x^2+y^2+z^2$ is the distance from the origin to any point on the ellipsoid $\xi$, it is apparent that as $\xi$ becomes very large $\xi\to r^2$. Thus, at great distances from the origin, the potential becomes that of a point charge at the origin:

$$\phi\sim\frac{2C_1}{r} \tag{11.36}$$

The solution Eq. (11.33) is, therefore, regular at infinity, and the constant $C_1$ is then determined. It has been shown by Stratton [2] that whatever the distribution, the dominant term of the expansion at remote points is the potential of a point charge at the origin equal to the total charge of the distribution—in this case $q$. Hence $C_1=\frac{q}{8\pi\varepsilon_o}$, and the potential at any point is:

$$\phi(\xi)=\frac{q}{8\pi\varepsilon_0}\int_\xi^\infty\frac{\partial\xi}{R_\xi} \tag{11.37}$$

The equipotential surfaces are the ellipsoids $\xi=\text{constant}$. Eq. (11.37) is an elliptic integral and its values have been tabulated [3].

Since the distance along a curvilinear coordinate $u^1$ is measured not by $du^1$ but by $h_1du^1$, the normal derivative in ellipsoidal coordinates is given by:

$$\frac{\partial\phi}{\partial n}=\frac{1}{h_1}\frac{\partial\phi}{\partial\xi}=\frac{-q}{4\pi\varepsilon_0}\frac{1}{\sqrt{(\xi-\eta)(\xi-\zeta)}} \tag{11.38}$$

where

$$h_1=\frac{1}{2}\frac{\sqrt{(\xi-\eta)(\xi-\zeta)}}{R_\xi} \tag{11.39}$$

The density of charge, $\sigma$, over the surface $\xi=0$ is:

$$\sigma = \varepsilon_0 \left( \frac{\partial \phi}{\partial n} \right)_{\xi=0} = \frac{q}{4\pi\sqrt{\eta\zeta}} \tag{11.40}$$

Defining $x, y, z$ in terms of $\xi, \eta, \zeta$ we put $\xi = 0$, it may be easily verified that,

$$\frac{x^2}{a^4} + \frac{y^2}{b^4} + \frac{z^2}{c^4} = \frac{\zeta\eta}{a^2b^2c^2} \qquad (\xi = 0) \tag{11.41}$$

Consequently, the charge density in rectangular coordinates is:

$$\sigma = \frac{q}{4\pi abc} \frac{1}{\sqrt{\frac{x^2}{a^4} + \frac{y^2}{b^4} + \frac{z^2}{c^4}}} \tag{11.42}$$

(The mass-density function of an MO is equivalent to its charge-density function where $m$ replaces $q$ of Eq. (11.42)). The equation of the plane tangent to the ellipsoid at the point $x_0, y_0, z_0$ is:

$$X\frac{x_0}{a^2} + Y\frac{y_0}{b^2} + Z\frac{z_0}{c^2} = 1 \tag{11.43}$$

where $X, Y, Z$ are running coordinates in the plane. After dividing through by the square root of the sum of the squares of the coefficients of $X$, $Y$, and $Z$, the right member is the distance $D$ from the origin to the tangent plane. That is,

$$D = \frac{1}{\sqrt{\frac{x^2}{a^4} + \frac{y^2}{b^4} + \frac{z^2}{c^4}}} \tag{11.44}$$

so that for an electron MO:

$$\sigma = \frac{-e}{4\pi abc} D \tag{11.45}$$

In other words, the surface density at any point on a charged ellipsoidal conductor is proportional to the perpendicular distance from the center of the ellipsoid to the plane tangent to the ellipsoid at the point. The charge is thus greater on the more sharply rounded ends farther away from the origin.

In the case of hydrogen-type molecules and molecular ions, rotational symmetry about the internuclear axis requires that two of the axes be equal. Thus, the MO is a spheroid, and Eq. (11.37) can be integrated in terms of elementary functions. If $a > b = c$, the spheroid is prolate, and the potential is given by:

$$\phi = \frac{1}{8\pi\varepsilon_0} \frac{-e}{\sqrt{a^2 - b^2}} \ln \frac{\sqrt{\xi + a^2} + \sqrt{a^2 - b^2}}{\sqrt{\xi + a^2} - \sqrt{a^2 - b^2}} \tag{11.46}$$

## SPHEROIDAL FORCE EQUATIONS

### ELECTRIC FORCE

The spheroidal MO is a two-dimensional surface of constant potential given by Eq. (11.46) for $\xi = 0$. For an isolated electron MO the electric field inside is zero as given by Gauss' Law:

$$\int_S \mathbf{E} dA = \int_V \frac{\rho}{\varepsilon_0} dV \tag{11.47}$$

where the charge density, $\rho$, inside the MO is zero. Gauss' Law at a two-dimensional surface with continuity of the potential across the surface according to Faraday's law in the electrostatic limit [4-6] is:

$$\mathbf{n} \bullet \left( \mathbf{E}_1 - \mathbf{E}_2 \right) = \frac{\sigma}{\varepsilon_0} \tag{11.48}$$

$\mathbf{E}_2$ is the electric field inside which is zero. The electric field of an ellipsoidal MO with semimajor and semiminor axes $a$ and $b = c$, respectively, is given by substituting $\sigma$ given by Eq. (11.38-11.42) into Eq. (11.48).

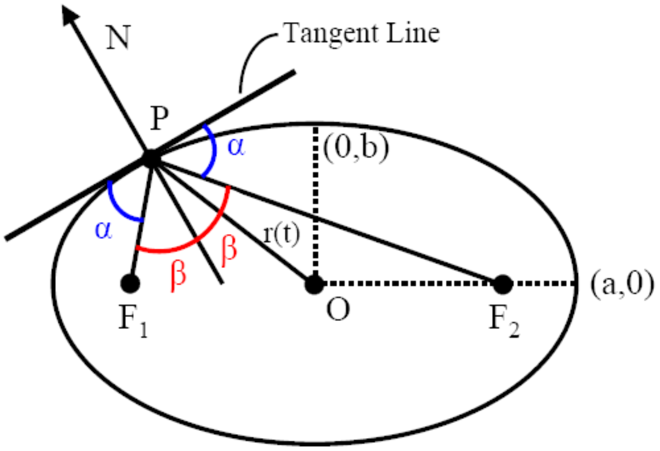
$$\mathbf{E} = \frac{\sigma}{\varepsilon_0} \mathbf{i}_\xi = \frac{-e}{4\pi\varepsilon_0} \frac{1}{\sqrt{(\xi - \eta)(\xi - \zeta)}} \mathbf{i}_\xi = \frac{-e}{4\pi\varepsilon_0 abc} D \mathbf{i}_\xi = \frac{-e}{4\pi\varepsilon_o abc} \frac{1}{\sqrt{\frac{x^2}{a^4} + \frac{y^2}{b^4} + \frac{z^2}{c^4}}} \mathbf{i}_\xi \tag{11.49}$$

wherein the ellipsoidal-coordinate parameter $\xi = 0$ at the surface of the MO and $D$ is the distance from the origin to the tangent plane given by Eq. (11.44). The electric field and thus the force and potential energy between the protons and the electron MO can be solved based on three principles: (1) Maxwell's equations require that the electron MO is an equipotential energy surface that is a function of $\xi$ alone; thus, it is a prolate spheroid, (2) stability to radiation, and conservation first principles require that the angular velocity is constant and given in polar coordinates with respect to the origin by Eq. (11.24), and (3) the equations of motion due to the central force of each proton (Eqs. (11.5-11.19) and Eqs. (11.68-11.70)) also determine that the current is ellipsoidal, and based on symmetry, the current is a prolate spheroid. Thus, based on Maxwell's equations, conservation principles, and Newton's Laws for the equations of motion, the electron MO constraints and the motion under the force of the protons both give rise to a prolate spheroid. Since the energy of motion is determined from the Coulombic central field (Eqs. (11.5-11.19), the protons give rise to a prolate spheroidal energy surface (a surface of constant energy) that is matched to the equipotential, prolate spheroidal electron MO.

*The electron cannot emit radiation; thus, it maintains the prolate spheroidal shape based on the overall conservation of angular momentum and energy (Appendix II: Stability and Absence of Self Interaction and Self Energy). Chapter 36 (Leptons) provides the conditions for the creation of an electron from a photon that forbid the electron from being severable. These properties that maintain the stability of an electron molecular orbital are invoked and provide that the integral of the physical properties such as the angular momentum of* $\hbar$ *(Eq. (11.101)) and energies in the inverse r-squared electric field originating at each focus over the entire electron match the boundary conditions. Consequently, the electron MO behaves as if it has rigidity based on the integrated conserved angular momentum of* $\hbar$ *(Eq. (11.101) as well as kinetic energy* $T$ *(Eq. (11.119)) wherein* $T$ *is one-half the magnitude of* $V_e$ *(Eq. (11.117)) as required for an inverse-squared force [1] wherein* $V_e$ *is the source of* $T$*. As in the case of an atomic orbital, a MO comprises a current density surface with flow along paths. An algorithm given in the Force Balance of Hydrogen-Type Molecules section solves the distribution wherein the velocity distribution on each path of the current distribution is variable to match the boundary conditions.*

The force balance equation between the average ellipsoidal central field of the protons at the foci and the ellipsoidal electron MO is solved to give the position of the foci. Then, the total energy is determined including the repulsive energy between the two protons at the foci to determine whether the original assumption of an elliptic orbit was valid. If the condition $E < 0$ is met, then the problem of the stable elliptic orbit is solved. In any case that this condition is not found to be met, then a stable orbit cannot be formed. The force and energy equations of a point charge (mass) (Eqs. (11.5-11.24)) are reformulated in term of densities for charge, current, mass, momentum, and potential, kinetic, and total energies. Consider an elliptical orbit shown in Figure 11.1 that applies to a point charge (mass) as well as a point on a continuous elliptical current loop that comprises a basis element of the continuous current density of the ellipsoidal MO. The tangent plane at any point on the ellipsoid makes equal angles with the foci radii at that point and the sum of the distance to the foci is a constant, $2a$. Thus, the normal is the bisector of the angle between the foci radii at that point as shown in Figure 11.1.

Figure 11.1. An elliptical current element of the prolate spheroidal MO showing the semimajor axis $a$, the semiminor axis $b$, the foci $F_1$ and $F_2$, and the vector $r(t)$ from the origin to a point $(x, y, z)$. The radial vectors from the foci to a point on the ellipse have a total length of $2a$ and make equal angles $\alpha$ with the tangent such that the normal vector is the bisector of the interior angle $2\beta$.



The unit vector normal to the ellipsoidal MO at a point $(x, y, z)$ is:

$$\hat{\mathbf{d}} = \frac{\left(\frac{x}{a^2}, \frac{y}{b^2}, \frac{z}{b^2}\right)}{\sqrt{\frac{x^2}{a^4} + \frac{y^2}{b^4} + \frac{z^2}{c^4}}} \tag{11.50}$$

$F_1(r(t))$ and $F_2(r(t))$ are defined as the components of the central forces centered on $F_1$ and $F_2$. The components of the central forces that are normal to the ellipsoidal MO in the direction of $\hat{\mathbf{d}}$, the unit vector in the $\mathbf{i}_\xi$-direction are defined as

$F_{1\perp}(r(t))$ and $F_{2\perp}(r(t))$. The normalized projections or projection factor of the sum of these central forces in the $\hat{\mathbf{d}}$-direction at the point $(x,y,z)$ is:

$$\begin{aligned}\frac{F_{1\perp}(r(t))+F_{2\perp}(r(t))}{\left|F_1(r(t))+F_2(r(t))\right|} &= \frac{(\mathbf{r}_1+\mathbf{r}_2)\cdot\hat{\mathbf{d}}}{2a} \\ &= \frac{\left((x-c,y,z)+(x+c,y,z)\right)\cdot\left(\frac{x}{a^2},\frac{y}{b^2},\frac{z}{b^2}\right)}{2a\sqrt{\frac{x^2}{a^4}+\frac{y^2}{b^4}+\frac{z^2}{c^4}}} \\ &= \frac{\left(\frac{x^2-cx}{a^2}+\frac{y^2}{b^2}+\frac{z^2}{b^2}\right)+\left(\frac{x^2+cx}{a^2}+\frac{y^2}{b^2}+\frac{z^2}{b^2}\right)}{2a\sqrt{\frac{x^2}{a^4}+\frac{y^2}{b^4}+\frac{z^2}{c^4}}} \\ &= \frac{1}{a\sqrt{\frac{x^2}{a^4}+\frac{y^2}{b^4}+\frac{z^2}{c^4}}}\end{aligned} \tag{11.51}$$

where $\mathbf{r}_1$ and $\mathbf{r}_2$ are the radial vectors of the central forces from the corresponding focus to the point $(x,y,z)$ on the ellipsoidal MO.

The polar-coordinate elliptical orbit of a point charge due to its motion in a central inverse-squared-radius field is given by Eqs. (11.10-11.12) as the solution of the polar-coordinate-force equations, Eqs. (11.5-11.19) and (11.68-11.70). The orbit is also completely specified in Cartesian coordinates by the solution of Eqs. (11.5-11.19) and (11.68-11.70) for the semimajor and semiminor axes. Then, the corresponding polar-coordinate elliptical orbit is given as a plane cross section through the foci of the Cartesian-coordinate-system ellipsoid having the same axes given by Eq. (11.26) where $c=b$. Thus, the Coulumbic central force can be determined in terms of the general Cartesian coordinates from the polar-coordinate central force equations (Eqs. (11.5-11.19)). Consider separately the elliptical solution at each focus given in polar coordinates by Eq. (11.10).

$$r_1 = a(1-e)\frac{1+e}{1+e\cos\theta} = \frac{a(1-e^2)}{1+e\cos\theta} \tag{11.52}$$

$$r_2 = \frac{a(1-e^2)}{1+e\cos(\theta+\pi)} = \frac{a(1-e^2)}{1-e\cos\theta} \tag{11.53}$$

where

$$r_0 = a-c' = a\left(1-\frac{c'}{a}\right) = a(1-e) \tag{11.54}$$

The magnitude of the sum of the central forces centered on $F_1$ and $F_2$ that are normal to the ellipsoidal MO are:

$$\begin{aligned}\left|F_1(r_1)\right|+\left|F_2(r_2)\right| &= \frac{k}{r_1^2}+\frac{k}{r_2^2} \\ &= k\frac{(1+e\cos\theta)^2+(1-e\cos\theta)^2}{a^2(1-e^2)^2} \\ &= k\frac{1+2e\cos\theta+e^2\cos^2\theta+1-2e\cos\theta+e^2\cos^2\theta}{a^2(1-e^2)^2} \\ &= k\frac{1+e^2\cos^2\theta+1+e^2\cos^2\theta}{a^2(1-e^2)^2} \\ &= k\frac{2+2e^2\cos^2\theta}{a^2(1-e^2)^2}\end{aligned} \tag{11.55}$$

The vector central forces centered on $F_1$ and $F_2$ that are normal to the ellipsoidal MO are then given by the product of the corresponding magnitude and vector projection given by Eqs. (11.55) and (11.51), respectively,

$$\mathbf{F}_{1\perp}(r_1)+\mathbf{F}_{2\perp}(r_2) = k\frac{2+2e^2\cos^2\theta}{a^2(1-e^2)^2}\frac{1}{a\sqrt{\frac{x^2}{a^4}+\frac{y^2}{b^4}+\frac{z^2}{c^4}}}\mathbf{i}_\xi \tag{11.56}$$

Eq. (11.56) is based on a single point charge $e$. For a charge-density distribution that is given as an ellipsoidal equipotential, the $\theta$-dependence must vanish. In addition to the elliptical orbit being completely specified in Cartesian coordinates by the solution of Eqs. (11.5-11.19) and Eqs. (11.68-11.70) for the semimajor and semiminor axes in Eq. (11.26), the polar-coordinate elliptical orbit is also completely specified by the total constant total energy $E$ and the angular momentum which for the electron is the constant $\hbar$. Considering Eq. (11.56), the corresponding total energy of the electron is conserved and is determined by the integration over the MO to give the average:

$$\mathbf{F}_{1\perp}(r_1)+\mathbf{F}_{2\perp}(r_2)=k\frac{2+e^2}{a^2\left(1-e^2\right)^2}\frac{1}{a\sqrt{\frac{x^2}{a^4}+\frac{y^2}{b^4}+\frac{z^2}{c^4}}}\mathbf{i}_\xi \tag{11.57}$$

Eq. (11.57) is transformed from a two-centered-central force to a one-centered-central force to match the form of the potential of the ellipsoidal MO. In this case,

$$\mathbf{r}_1,\mathbf{r}_2\rightarrow r(t)\mathbf{i}_\xi \tag{11.58}$$

In the case that

$$r_1=r_2=a \tag{11.59}$$

then,

$$r(t)=b \tag{11.60}$$

and the one-centered-central force is in the $\mathbf{i}_\xi$-direction. Consider the current motion on the great circle in the yz-plane containing the semiminor axes, each of length $b$, as shown in Figure 11.2. In order to match the average elliptic force for the condition of Eq. (11.60), Eq. (11.57) transforms as

$$\begin{aligned}\mathbf{F}_{1\perp}(r(t))+\mathbf{F}_{2\perp}(r(t))&=k\frac{\left(2+e^2\right)}{b^2\left(1-e^2\right)^2}\frac{1}{a\sqrt{\frac{x^2}{a^4}+\frac{y^2}{b^4}+\frac{z^2}{c^4}}}\\&=\frac{2+e^2}{\left(1-e^2\right)^2}k\frac{1}{ab^2\sqrt{\frac{x^2}{a^4}+\frac{y^2}{b^4}+\frac{z^2}{c^4}}}\mathbf{i}_\xi\end{aligned} \tag{11.61}$$

Eq. (11.61) has the same form as that of the electric field of the ellipsoidal MO given by Eq. (11.49), except for the scaling factor of two-centered coordinates $h_{2cc}$:

$$h_{2cc}=\frac{2+e^2}{\left(1-e^2\right)^2} \tag{11.62}$$

As shown in the case of the derivation of the Laplacian charge-density and electric field, if $r^2=x^2+y^2+z^2$ is the distance from the origin to any point on the ellipsoid $\xi$, it is apparent that as $\xi$ becomes very large $\xi\rightarrow r^2$. Thus, at great distances from the origin, the potential becomes that of a point charge at the origin as given by Eq. (11.36). The same boundary condition applies to the potential and field of the protons. The limiting case is also given as $e\rightarrow 0$. Then, to transform the scale factor to that of one-centered coordinates for an ellipsoidal MO, the reciprocal of the scaling factor multiplies the Laplacian-MO-electric-field term. The reciprocal of Eq. (11.62) is:

$$h_{2cc}^{-1}=\frac{\left(1-e^2\right)^2}{2+e^2} \tag{11.63}$$

such that as $e\rightarrow 0$, $h_{2cc}^{-1}\rightarrow\frac{1}{2}$. This transform scale factor corresponds to the interchange of the points of highest and lowest velocity on the surface and the distribution of the charge-density in the opposite manner as shown *infra*. The charge-density distribution corrects the angular variation in central force over the surface such that a solution of the central force equation of motion and the Laplacian MO are solved simultaneously. It can also be considered as a multipole normalization factor such as those of the spherical harmonics and the spherical geometric factor of atomic electrons that gives the central force as a function of $\xi$ only.

The reciprocal of the $h_{2cc}$ form-factor with the dependence of the charge density on the distance parameter $r(t)$ gives:

$$\mathbf{F}_{1\perp}(r(t))+\mathbf{F}_{2\perp}(r(t))=k\frac{\left(1-e^2\right)^2}{b^2\left(2+e^2\right)}\frac{1}{a\sqrt{\frac{x^2}{a^4}+\frac{y^2}{b^4}+\frac{z^2}{c^4}}}\mathbf{i}_\xi \tag{11.64}$$

From Eq. (11.31), the magnitude of the ellipsoidal field corresponding to a below "ground state" hydrogen-type molecular ion is an integer $p$. The integer is one in the case of the hydrogen molecular ion and an integer greater than one in the case of each dihydrino molecular ion. The central-electric-force constant, $k$, from the two protons that includes the central-field contribution due to photons of lower-energy states is:

$$k = \frac{Ze^2}{4\pi\varepsilon_0} = \frac{p2e^2}{4\pi\varepsilon_0} \tag{11.65}$$

Substitution of Eq. (11.65) for $k$ in Eq. (11.64) gives the one-center-coordinate electric force $\mathbf{F}_{ele}$ between the protons and the ellipsoidal MO:

$$\mathbf{F}_{ele} = \mathbf{F}_{1\perp}\left(r\left(t\right)\right) + \mathbf{F}_{2\perp}\left(r\left(t\right)\right) = \frac{2pe^2}{4\pi\varepsilon_0}\frac{\left(1-\left(\frac{c'}{a}\right)^2\right)^2}{ab^2\left(2+\left(\frac{c'}{a}\right)^2\right)}\frac{1}{\sqrt{\frac{x^2}{a^4}+\frac{y^2}{b^4}+\frac{z^2}{c^4}}}\mathbf{i}_\xi \tag{11.66}$$

where $e$ is the charge and with the distance from the origin to a nucleus at a focus defined as $c'$, the eccentricity, $e$, is:

$$e = \frac{c'}{a} \tag{11.67}$$

From the orbital equations in polar coordinates, Eqs. (11.10-11.12), the following relationship can be derived [1]:

$$a = \frac{m\frac{L^2}{m^2}}{k(1-e^2)} \tag{11.68}$$

For any ellipse,

$$b = a\sqrt{1-e^2} \tag{11.69}$$

thus,

$$b = a\sqrt{\frac{\frac{L^2}{m^2}m}{ka}} \quad \text{(point charge (mass) in polar coordinates)} \tag{11.70}$$

From, the equal energy condition, it can be shown that $b$ for the motion of a point charge (mass) in polar coordinates due to a proton at one focus corresponds to:

$$c' = \sqrt{a^2-b^2} \tag{11.71}$$

of the MO in ellipsoidal coordinates, and $k_1$ of one attracting focus is replaced by $k = 2k_1$ of ellipsoidal coordinates with two attracting foci. In ellipsoidal coordinates, $k$ is given by Eq. (11.65) and $L$ for the electron equals $\hbar$.

Consider the force balance equation for the point on the ellipse at the intersection of the semiminor axis $b$ with the ellipse. At this point called $\left(0,b\right)$, the distances from each focus, $r_1$ and $r_2$, to the ellipse are equal. The relationship for the sum of the distances from the foci to any point on the ellipse is:

$$r_1 + r_2 = 2a \tag{11.72}$$

Thus, at point $\left(0,b\right)$,

$$r_1 = r_2 = a \tag{11.73}$$

Using Eq. (11.5), the magnitude of the force balance in the radial ($r\left(t\right)$) direction, from the origin, is given by:

$$mr\dot{\theta}^2 = \frac{2pe^2}{4\pi\varepsilon_0 a^2}\sin\theta = \frac{2pe^2}{4\pi\varepsilon_0 a^2}\frac{b}{a} \tag{11.74}$$

wherein the $m\ddot{r}$ term of Eq. (11.5) is zero and $\theta$ is the angle from the focus to point $\left(0,b\right)$. Using Eqs. (11.24), (11.94), and (11.95), Eq. (11.74) becomes:

$$mr\omega^2 = mb\frac{\hbar^2}{m^2a^2b^2} = \frac{2pe^2}{4\pi\varepsilon_0 a^2}\frac{b}{a} \tag{11.75}$$

In order for the prolate spheroidal MO to be an equipotential surface, the mass and charge density must be according to Eq. (11.45). In this case, the mass and charge density along the ellipse is such that the magnitudes of the radial and transverse forces components at point $\left(0,b\right)$ are equivalent. Furthermore, according to Eq. (11.5), the central force of each proton at a focus is separable and symmetrical to that at the other focus. Based on symmetry, the transverse forces of the two protons are in opposite directions and the radial components are in the same direction. But, the relationship between the magnitudes must still hold wherein at point $\left(0,b\right)$ the transverse force is equivalent to that due to the sum of the charges at one focus. The sum of the magnitudes of the transverse forces which is equivalent to a force of $2e$ at each focus in turn is:

$$\left|f\left(r\right)e_\theta\right| = \frac{2pe^2}{4\pi\varepsilon_0 a^2}\cos\theta = \frac{2pe^2}{4\pi\varepsilon_0 a^2}\frac{c'}{a} \tag{11.76}$$

Thus, using the mass and charge-density scaling factor, $\frac{\frac{c'}{a}}{\frac{b}{a}} = \frac{c'}{b}$, to match the equipotential condition in Eq. (11.75) gives:

$$b\frac{\hbar^2}{m_e \frac{c'}{b} a^2 b^2} = \frac{2\frac{c'}{b} pe^2}{4\pi\varepsilon_0 a^2}\frac{b}{a} \tag{11.77}$$

$$c'^2 = \frac{\hbar^2 4\pi\varepsilon_0 a}{m_e 2pe^2} \tag{11.78}$$

Using Eq. (1.256)

$$c' = a\sqrt{\frac{\hbar^2 4\pi\varepsilon_0}{me^2 2pa}} = \sqrt{\frac{aa_0}{2p}} \tag{11.79}$$

Then, the length of the semiminor axis of the prolate spheroidal MO, $b = c$, is:

$$b = \sqrt{a^2 - c'^2} \tag{11.80}$$

Correspondingly, $c'$ is given by Eq. (11.71).

Substitution of Eq. (11.79) into Eq. (11.66) gives the electric force:

$$\begin{aligned}
\mathbf{F}_{ele} &= \frac{2pe^2}{4\pi\varepsilon_0}\frac{\left(1-\left(\frac{\sqrt{\frac{aa_0}{2p}}}{a}\right)^2\right)^2}{ab^2\left(2+\left(\frac{\sqrt{\frac{aa_0}{2p}}}{a}\right)^2\right)}\frac{1}{\sqrt{\frac{x^2}{a^4}+\frac{y^2}{b^4}+\frac{z^2}{c^4}}}\mathbf{i}_\xi \\
&= \frac{2pe^2}{4\pi\varepsilon_0}\frac{\left(1-\frac{a_0}{2ap}\right)^2}{ab^2\left(2+\frac{a_0}{2ap}\right)}\frac{1}{\sqrt{\frac{x^2}{a^4}+\frac{y^2}{b^4}+\frac{z^2}{c^4}}}\mathbf{i}_\xi \\
&= \frac{2pe^2}{4\pi\varepsilon_0}\frac{\left(1-\frac{a_0}{2ap}\right)^2}{ab^2\left(2+\frac{a_0}{2ap}\right)}D\mathbf{i}_\xi
\end{aligned} \tag{11.81}$$

## CENTRIFUGAL FORCE

The centrifugal force along the radial vector from each proton at each focus of the ellipsoid is given by the $mr\dot{\theta}^2$ term of Eq. (11.5). The tangent plane at any point on the ellipsoid makes equal angles with the foci radii at that point and the sum of the distance to the foci is a constant, $2a$. Thus, the normal is the bisector of the angle between the foci radii at that point as shown in Figure 11.1. In order to satisfy the equation of motion for an equal energy surface for both foci, the transverse component of the central force of one foci at any point on the elliptic orbit due to the central force of the other (Eq. (11.5)) must cancel on average and vice versa. Thus, the centrifugal force due to the superposition of the central forces in the direction of each foci must be normal to an ellipsoidal surface in the direction perpendicular to the direction of motion. Thus, it is in the $\xi$-direction. This can only be achieved by a time rate of change of the momentum density that compensates for the variation of the distances from each focus to each point on an elliptical cross section. Since the angular momentum must be conserved, there can be no net force in the direction transverse to the elliptical path over each orbital path. The total energy must also be conserved; thus, as shown *infra.* the distribution of the mass must also be a solution of Laplace's equation in the parameter $\xi$ only. Thus, the mass-density constraint is the same as the charge-density constraint. As further shown *infra.*, the distribution and concomitantly the centrifugal force is a function of $D$, the time-dependent distance from the center of the ellipsoid to a tangent plane given by Eq. (11.44) where $D$ and the Cartesian coordinates are the time-dependent parameters.

Each point or coordinate position on the continuous two-dimensional electron MO defines an infinitesimal mass-density element which moves along an orbit comprising an elliptical plane cross section of the spheroidal MO through the foci. The kinetic energy of the electron is conserved. Then, the corresponding radial conservative force balance equation is

$$m(\ddot{r} + C_1 r) = 0 \tag{11.82}$$

The motion is such that the eccentric angle, $\theta$, changes at a constant rate at each point. That is $\theta = \omega t$ at time $t$ where the angular velocity $\omega$ is a constant. The solution of the homogeneous equation with $C_1 = \omega^2$ is:

$$r(t) = \mathbf{i}a\cos\omega t + \mathbf{j}b\sin\omega t \tag{11.83}$$

where $a$ is the semimajor axis, $b$ is semiminor axis, and the boundary conditions of $r(t) = a$ for $\omega t = 0$ and $r(t) = b$ for $\omega t = \frac{\pi}{2}$ were applied. Eq. (11.83) is the parametric equation of the ellipse of the orbit. The velocity is given by the time derivative of the parametric position vector:

$$v(t) = \dot{r}(t) = -\mathbf{i}a\omega\sin\omega t + \mathbf{j}b\omega\cos\omega t \tag{11.84}$$

The velocity is $\frac{\pi}{2}$ out of phase with the charge density at $r(t) = a$ ($\omega t = 0$) and $r(t) = b$ ($\omega t = \frac{\pi}{2}$) such that the lowest charge density has the highest velocity and the highest charge density has the lowest velocity. In this case, it can be shown that the current is constant along each elliptical path of the MO. Recall that nonradiation results when $\omega = \text{constant}$ given by Eq. (11.24) that corresponds to a constant current, which further maintains the current continuity condition.

Consider Eq. (11.32) for the prolate spheroidal MO. From this equation, the mass and current-densities, the angular momentum, and the potential and kinetic energies are a function of $\xi$ alone, and any dependence on the orthogonal coordinate parameters averages to unity. From Eq. (11.32).

$$R_\xi \frac{\partial\phi}{\partial\xi} = C_1 \tag{11.85}$$

Substitution of Eq. (11.40) into Eq. (11.85) gives:

$$\int_\xi^\infty R_\xi h_1 \frac{e}{4\pi\sqrt{\eta\zeta}}\delta(\xi)\,d\xi = \varepsilon_0 C_1 = \frac{e}{8\pi} \tag{11.86}$$

where $C_1$ is from Eq. (11.36). Substitution of Eq. (11.39) into Eq. (11.86) gives:

$$\int_\xi^\infty R_\xi \frac{e}{4\pi\sqrt{\eta\zeta}}\frac{1}{2}\frac{\sqrt{(\xi-\eta)(\xi-\zeta)}}{R_\xi}\delta(\xi)\,d\xi = \frac{e}{8\pi} \tag{11.87}$$

Comparison of Eq. (11.86) with Eq. (11.87) demonstrates that:

$$8\pi\int_\xi^\infty R_\xi \frac{e}{4\pi\sqrt{\eta\zeta}}\frac{1}{2}\frac{\sqrt{(\xi-\eta)(\xi-\zeta)}}{R_\xi}\delta(\xi)\,d\xi = e \tag{11.88}$$

The current density $J$ is given by the product of the constant frequency (Eq. (11.24)) and the charge density (Eq. (11.40)).

$$J = \frac{\hbar}{2\pi m_e ab}\frac{e}{4\pi\sqrt{\eta\zeta}} \tag{11.89}$$

The total constant current is dependent on $\xi$ alone according to Eq. (11.32). Then, applying the result of Eq. (11.88) to Eq. (11.89) gives:

$$\mathbf{i} = 8\pi\int_\xi^\infty R_\xi \frac{\hbar}{2\pi m_e ab}\frac{e}{4\pi\sqrt{\eta\zeta}}\frac{1}{2}\frac{\sqrt{(\xi-\eta)(\xi-\zeta)}}{R_\xi}\delta(\xi)\,d\xi\;\mathbf{e}_\zeta \times \mathbf{e}_\xi = \frac{e\hbar}{2\pi m_e ab}\;\mathbf{e}_\eta \tag{11.90}$$

the constant current that is nonradiative.

If $\mathbf{a}(t)$ denotes the acceleration vector, then

$$\mathbf{a}(t) = -\omega^2 r(t)\mathbf{i}_r \tag{11.91}$$

In other words, the acceleration is centrifugal as in the case of circular motion with constant angular speed $\omega$. The dot product of $\mathbf{r}(t)$ with $\hat{\mathbf{d}}$, the unit vector normal to the ellipsoidal MO at a point $(x,y,z)$ given by Eq. (11.50), is:

$$\mathbf{r}(t)\cdot\hat{\mathbf{d}} = \frac{(x,y,z)\cdot\left(\frac{x}{a^2},\frac{y}{b^2},\frac{z}{b^2}\right)}{\sqrt{\frac{x^2}{a^4}+\frac{y^2}{b^4}+\frac{z^2}{c^4}}} = \frac{\left(\frac{x^2}{a^2}+\frac{y^2}{b^2}+\frac{z^2}{b^2}\right)}{\sqrt{\frac{x^2}{a^4}+\frac{y^2}{b^4}+\frac{z^2}{c^4}}} \tag{11.92}$$

Using Eq. (11.26), the normal component projection is:

$$\mathbf{r}(t)\cdot\hat{\mathbf{d}} = \frac{1}{\sqrt{\frac{x^2}{a^4}+\frac{y^2}{b^4}+\frac{z^2}{c^4}}} = D \tag{11.93}$$

where $D$, the distance from the origin to the tangent plane, is given by Eq. (11.44).

The centrifugal force, $\mathbf{F}_{ci}$, on mass element $m_i$ [7] given by the second term of Eq. (11.82) is:

$$\mathbf{F}_{ci} = m_i a = -m_i\omega^2 r(t) \tag{11.94}$$

Substitution of the angular velocity given by Eq. (11.24) and $m_e$ for $m$ into Eq. (11.94) gives the centrifugal force $\mathbf{F}_c$ on the electron that is normal to the MO surface according to Eq. (11.93).

$$\mathbf{F}_c = \frac{-\hbar^2}{m_e a^2 b^2}\mathbf{r}(t)\cdot \hat{\mathbf{d}}\mathbf{i}_\xi = \frac{-\hbar^2}{m_e a^2 b^2} D\mathbf{i}_\xi \tag{11.95}$$

$\mathbf{F}_c$ has an equivalent dependence on $D$ as the electric force based on the charge distribution (Eq. (11.45)). This is expected based on the invariance of $\frac{e}{m_e}$ which results in the same distribution of the mass and charge.

The equipotential charge-density distribution gives rise to the constant current condition. It also gives rise to a constant total kinetic energy condition wherein the angular velocity given by Eq. (11.24) is a constant. Recall from Eq. (11.32), that on the surface $\xi = 0$; $\phi$ must be independent of $\zeta$ and $\eta$ and depend only on $\xi$ at any point outside the ellipsoid $\xi = 0$. Since the current and total kinetic energy are also constant on the surface $\xi = 0$, the total kinetic energy depends only on $\xi$. Thus, the centrifugal force on the mass of the electron, $m_e$, must be in the same direction as the electric field corresponding to $\phi$, normal to the electron surface wherein any tangential component in Eq. (11.94) averages to zero over the electron MO by the mass distribution given by Eqs. (11.40) and (11.45) with $m_e$ replacing $e$.

The cancellation of tangential acceleration over each elliptical path maintains the charge density distribution given by Eq. (11.40) with constant current at each point on each elliptical path of the MO. Since the centrifugal force is given by Eq. (11.94), the multiplication of the mass density by the scaling factor $h_1$ and integration with respect to $\xi$ gives a constant net centrifugal force. Thus, the result matches those of the determination of the constant current (Eq. (11.90)) and angular momentum shown *infra.* (Eq. (11.101)) wherein the charge and mass densities given in Eqs. (11.90-11.91) and (11.100), respectively, were integrated over.

Specifically, consider the normal-directed centrifugal force, $\mathbf{F}_{ci}$, on mass element $m_i$:

$$\mathbf{F}_{ci} = -m_i \omega^2 D\mathbf{i}_\xi \tag{11.96}$$

The mass density is given by Eq. (11.40) with $m_e$ replacing $e$. Then, the substitution of the mass density for $m_i$ in Eq. (11.96) and using Eq. (11.24) for $\omega$ gives the centrifugal force density $\mathbf{F}_{ca}$:

$$\mathbf{F}_{ca} = \frac{m_e}{4\pi\sqrt{\eta\zeta}}\frac{\hbar^2}{m_e^2 a^2 b^2} D\mathbf{i}_\xi \tag{11.97}$$

Eq. (11.32) determines that the centrifugal force is a function of $\xi$ alone, and any dependence on the transverse coordinate parameters averages to zero. Using the result of Eq. (11.88) gives the net centrifugal force $\mathbf{F}_c$:

$$\mathbf{F}_c = 8\pi \int_\xi^\infty \frac{1}{4\pi\sqrt{\eta\zeta}}\frac{\hbar^2}{m_e a^2 b^2} R_\xi \frac{1}{2}\frac{\sqrt{(\xi-\eta)(\xi-\zeta)}}{R_\xi} D\delta(\xi)\, d\xi \mathbf{i}_\xi = \frac{\hbar^2}{m_e a^2 b^2} D\mathbf{i}_\xi \tag{11.98}$$

In the limit as the ellipsoidal coordinates go over into spherical coordinates, Eq. (11.95) reduces to the centrifugal force of the spherical atomic orbital given by Eq. (1.253) with Eq. (1.35). This condition must be and is met as a further boundary condition that parallels that of Eqs. (11.32-11.37). Using the same dependence of the total mass (charge) on the scale factor $h_1$ according to Eqs. (11.32-11.40), the further boundary conditions on the angular momentum and kinetic energy are met.

Specifically, the constant potential and current conditions and the use of Eq. (11.32) in the derivation of Eq. (11.95) also satisfy another condition, the conservation of $\hbar$ of angular momentum of the electron. The angular momentum $\mathbf{p}_i$ at each point $i$ of mass $m_i$ is

$$\begin{aligned}\mathbf{p}_i(t) &= m_i \mathbf{r}(t)\times \mathbf{v}(t)\\ &= m_i\left(\mathbf{i}a\cos\omega t + \mathbf{j}b\sin\omega t\right)\times\left(-\mathbf{i}a\omega\sin\omega t + \mathbf{j}b\omega\cos\omega t\right)\\ &= m_i ab\omega\left(\cos^2\omega t + \sin^2\omega t\right)\mathbf{i}\times\mathbf{j}\\ &= m_i ab\omega\mathbf{k}\end{aligned} \tag{11.99}$$

The mass density is given by Eq. (11.40) with $m_e$ replacing $e$. Then, substitution of $m_i$ in Eq. (11.99) by the mass density and using Eq. (11.24) for $\omega$ gives the angular momentum density $\mathbf{p}(t)$:

$$\mathbf{p}(t) = ab\omega\frac{m_e}{4\pi\sqrt{\eta\zeta}}\mathbf{k} = ab\frac{\hbar}{m_e ab}\frac{m_e}{4\pi\sqrt{\eta\zeta}}\mathbf{k} \tag{11.100}$$

Using the result of Eq. (11.88) gives the total constant angular momentum $\mathbf{L}$:

$$\mathbf{L} = 8\pi\int_\xi^\infty \hbar \frac{1}{4\pi\sqrt{\eta\zeta}} R_\xi \frac{1}{2}\frac{\sqrt{(\xi-\eta)(\xi-\zeta)}}{R_\xi}\delta(\xi)\, d\xi\mathbf{k} = \hbar\mathbf{k} \tag{11.101}$$

Eq. (11.101) demonstrates conservation of angular momentum that is a function of $\xi$ alone that parallels the case of atomic electrons where $\mathbf{L}$ conservation is a function of the radius $r$ alone as given by Eq. (1.37).

Similarly, the kinetic energy $T(t)$ at each point $i$ of mass $m_i$ is:

$$\begin{aligned} T(t) &= \frac{1}{2} m_i v(t)^2 \\ &= \frac{1}{2} m_i \left( -\mathbf{i} a\omega \sin \omega t + \mathbf{j} b\omega \cos \omega t \right)^2 \\ &= \frac{1}{2} m_i \omega^2 \left( a^2 \sin^2 \omega t + b^2 \cos^2 \omega t \right) \end{aligned} \tag{11.102}$$

In Eqs. (11.96-11.98), $m_i$ was replaced by the mass density and the $\xi$ integral was determined to give the centrifugal force in terms of the mass of the electron. The kinetic energy can also be determined from the $\xi$ integral of the centrifugal force:

$$T = h_{2cc} F_c \frac{ab^2}{2D} \int_{\xi}^{\infty} \frac{d\xi}{R_\xi} \tag{11.103}$$

The result is given in Eq. (11.119). From Eq. (11.102), the kinetic energy is time (position) dependent, but the total kinetic energy corresponding to the centrifugal force given by Eq. (11.95) satisfies the condition that the time-averaged kinetic energy is 1/2 the time-averaged potential energy for elliptic motion in an inverse-squared central force [1]. (Here, the potential and total kinetic energies are constant and correspond to the time-averaged energies of the general case.) Thus, as shown by Eqs. (11.122) (11.124), (11.262), and (11.264) energy is conserved.

## FORCE BALANCE OF HYDROGEN-TYPE MOLECULAR IONS

Consider the case of spheroidal coordinates based on the rotational symmetry about the semimajor axis [2]. In the limit, as the focal distance $2c$ and the eccentricity of the series of confocal ellipses approaches zero, spheroidal coordinates go over into spherical coordinates with $\xi \to r$ and $\eta \to \cos\theta$. The field of an equipotential two-dimensional charge surface of constant radius $r = R$ is equivalent to that of a point charge of the total charge of the spherical shell at the origin. The force balance between the centrifugal force and the central Coulomb force for spherical symmetry is given by Eq. (1.253).

Similarly, the centrifugal force is in the direction of $\xi$ and balances the central Coulombic force between the protons at the foci and the electron MO. In the case of the prolate spheroidal MO, the inhomogeneous equation given by Eq. (11.5) must hold for each fixed position of $r(t)$ since the MO is static in time due to the constant current condition. With $r(t)$ fixed, the $m\ddot{r}$ term of Eq. (11.5) is zero, and the force balanced equation is the balance between the centrifugal force and the Coulombic force which are both normal to the surface of the elliptic orbit:

$$mr\dot{\theta}^2 = f(r) \tag{11.104}$$

Substitution of Eq. (11.81) and Eq. (11.95) into Eq. (11.104) gives the force balance between the centrifugal and electric central forces:

$$\frac{\hbar^2}{m_e a^2 b^2} D = \frac{2pe^2}{4\pi\varepsilon_0} \frac{\left(1 - \frac{a_0}{2ap}\right)^2}{ab^2 \left(2 + \frac{a_0}{2ap}\right)} D \tag{11.105}$$

$$\frac{\hbar^2 4\pi\varepsilon_0}{m_e e^2 2ap} \left(2 + \frac{a_0}{2ap}\right) = \left(1 - \frac{a_0}{2ap}\right)^2 \tag{11.106}$$

$$\frac{a_0}{ap} + \left(\frac{a_0}{2ap}\right)^2 = \left(1 - \frac{a_0}{2ap}\right)^2 \tag{11.107}$$

$$\frac{a_0}{ap} + \left(\frac{a_0}{2ap}\right)^2 = 1 - \frac{a_0}{ap} + \left(\frac{a_0}{2ap}\right)^2 \tag{11.108}$$

$$a = 2\frac{a_0}{p} \tag{11.109}$$

Substitution of $a$ given by Eq. (11.109) into Eq. (11.79) gives:

$$c' = \frac{a_0}{p} \tag{11.110}$$

The internuclear distance from Eq. (11.110) is:

$$2c' = \frac{2a_0}{p} \tag{11.111}$$

Substitution of $a = \frac{2a_0}{p}$ and $c' = \frac{a_0}{p}$ into Eq. (11.80) gives the length of the semiminor axis of the prolate spheroidal MO, $b = c$:

$$b = \frac{\sqrt{3}}{p} a_0 \tag{11.112}$$

Substitution of $a = \frac{2a_0}{p}$ and $c' = \frac{a_0}{p}$ into Eq. (11.67) gives the eccentricity, $e$:

$$e = \frac{1}{2} \tag{11.113}$$

From Eqs. (11.63-11.65), the result of Eq. (11.113) can be used to the obtain the electric force $\mathbf{F}_{ele}$ between the protons and the ellipsoidal MO as:

$$\mathbf{F}_{ele} = Ze\mathbf{E}\mathbf{i}_\xi = h_{2cc}^{-1} \frac{p2e^2}{4\pi\varepsilon_0 ab^2} D\mathbf{i}_\xi = \frac{pe^2}{8\pi\varepsilon_0 ab^2} D\mathbf{i}_\xi \tag{11.114}$$

where the electric field $\mathbf{E}$ of the MO is given by Eq. (11.49). Then, the force balance of the hydrogen-type molecular ion is given by:

$$\frac{\hbar^2}{m_e a^2 b^2} D = \frac{pe^2}{8\pi\varepsilon_0 ab^2} D \tag{11.115}$$

which has the parametric solution given by Eq. (11.83) when:

$$a = \frac{2a_0}{p} \tag{11.116}$$

The solutions for the prolate spheroidal axes and eccentricity are given by Eqs. (11.109-11.113).

## ENERGIES OF HYDROGEN-TYPE MOLECULAR IONS

From Eq. (11.31), the magnitude of the ellipsoidal field corresponding to a below "ground state" hydrogen-type molecule is an integer, $p$. The force balance equation (Eq. (11.115)) applies for each point of the electron MO having non-constant charge (mass)-density and velocity over the equipotential and equal energy surface. The electron potential and kinetic energies are thus determined from an ellipsoidal integral.

The potential energy is doubled due to the transverse electric force. The force normal to the MO is given by the dot product of the sum of the force vectors from each focus with $\hat{\mathbf{d}}$ where the angle $\beta$ is $\beta = \frac{\pi}{2} - \alpha$, and the transverse forces are given by the cross product with $\hat{\mathbf{d}}$. As shown in Figure 11.1, equivalently, the transverse projection is given with the angle $\alpha$ replacing $\beta$ where the range of $\alpha$ is the same as $\beta$. The two contributions to the potential energy doubles it. The potential energy, $V_e$, of the electron MO in the field of magnitude $p$ times that of the two protons at the foci is:

$$\begin{aligned} V_e &= 2\frac{-2pe^2}{4\pi\varepsilon_0} D \frac{ab^2}{2D} \int_\xi^\infty \frac{d\xi}{R_\xi} \\ &= \frac{-4pe^2}{8\pi\varepsilon_0} \int_\xi^\infty \frac{d\xi}{(\xi+b)\sqrt{\xi+a}} \\ &= \frac{-4pe^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}} \ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} \\ &= \frac{-4pe^2}{8\pi\varepsilon_0 c'} \ln\frac{a+c'}{a-c'} \end{aligned} \tag{11.117}$$

where

$$\sqrt{a^2-b^2} = c' \tag{11.118}$$

$2c'$ is the distance between the foci which is the internuclear distance. The kinetic energy, $T$, of the electron MO follows from the same type of integral as $V_e$ using Eqs. (7-14) of Stratton [8], Eqs. (11.37-11.46), and integral #147 of Lide [9]. $T$ is given by the corresponding integral of the centrifugal force (LHS of Eq. (11.115)) with the constraint that the current motion allows the equipotential and equal energy condition with a central field due to the protons; thus, it is corrected by the scale factor $h_{2cc}$ given by Eq. (11.62). The $h_{2cc}$ correction can be considered the scaling factor of the moment of inertia such that the kinetic energy is equivalent to the rotational energy for constant angular frequency $\omega$. The kinetic energy, $T$, of the electron MO is given by

$$T = h_{2cc} \frac{-\hbar^2}{m_e a^2 b^2} D \frac{ab^2}{2D} \int_\xi^\infty \frac{d\xi}{R_\xi} = \frac{-4\hbar^2}{2m_e a} \int_\xi^\infty \frac{d\xi}{(\xi+b)\sqrt{\xi+a}} = \frac{2\hbar^2}{m_e a\sqrt{a^2-b^2}} \ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} \tag{11.119}$$

The potential energy, $V_p$, due to proton-proton repulsion in the field of magnitude $p$ times that of the protons at the foci ($\xi = 0$) is:

$$V_p = \frac{pe^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}} \tag{11.120}$$

The total energy, $E_T$, is given by the sum of the energy terms

$$E_T = V_e + V_p + T \tag{11.121}$$

Substitution of $a$ and $b$ given by Eqs. (11.109) and (11.112), respectively, into Eqs. (11.117), (11.119), (11.120), and (11.121) gives:

$$V_e = \frac{-4p^2e^2}{8\pi\varepsilon_0 a_0}\ln 3 \tag{11.122}$$

$$V_p = \frac{p^2e^2}{8\pi\varepsilon_0 a_0} \tag{11.123}$$

$$T = \frac{2p^2e^2}{8\pi\varepsilon_0 a_0}\ln 3 \tag{11.124}$$

$$E_T = -13.6\ eV(4p^2\ln 3 - p^2 - 2p^2\ln 3) = -p^2 16.28\ eV \tag{11.125}$$

The total energy, which includes the proton-proton-repulsion term is negative which justifies the original treatment of the force balance using the analytical-mechanics equations of an ellipse that considered only the binding force between the protons and the electron and the electron centrifugal force. $T$ is one-half the magnitude of $V_e$ as required for an inverse-squared force [1] wherein $V_e$ is the source of $T$.

## VIBRATION OF HYDROGEN-TYPE MOLECULAR IONS

A charge, $q$, oscillating according to $\mathbf{r}_0(t) = \mathbf{d}\sin\omega_0 t$ has a Fourier spectrum

$$\mathbf{J}(\mathbf{k},\omega) = \frac{q\omega_0 d}{2} J_m(k\cos\theta d)\{\delta[\omega-(m+1)\omega_0] + \delta[\omega-(m-1)\omega_0]\} \tag{11.126}$$

where $J_m$'s are Bessel functions of order $m$. These Fourier components can, and do, acquire phase velocities that are equal to the velocity of light [10]. The protons of hydrogen-type molecular ions and molecules oscillate as simple harmonic oscillators; thus, vibrating protons will radiate. Moreover, non-oscillating protons may be excited by one or more photons that are resonant with the oscillatory resonance frequency of the molecule or molecular ion, and oscillating protons may be further excited to higher energy vibrational states by resonant photons. The energy of a photon is quantized according to Planck's equation

$$E = \hbar\omega \tag{11.127}$$

The energy of a vibrational transition corresponds to the energy difference between the initial and final vibrational states. Each state has an electromechanical resonance frequency, and the emitted or absorbed photon is resonant with the difference in frequencies. Thus, as a general principle, quantization of the vibrational spectrum is due to the quantized energies of photons and the electromechanical resonance of the vibrationally excited ion or molecule.

It is shown by Fowles [11] that a perturbation of the orbit determined by an inverse-squared force results in simple harmonic oscillatory motion of the orbit. In a circular orbit in spherical coordinates, the transverse equation of motion gives

$$\dot{\theta} = \frac{L/m}{r^2} \tag{11.128}$$

where $L$ is the angular momentum. The radial equation of motion is:

$$m\left(\ddot{r} - r\dot{\theta}^2\right) = f(r) \tag{11.129}$$

Substitution of Eq. (11.128) into Eq. (11.129) gives:

$$m\ddot{r} - \frac{m(L/m)^2}{r^3} = f(r) \tag{11.130}$$

For a circular orbit, $r$ is a constant and $\ddot{r} = 0$. Thus, the radial equation of motion is given by:

$$-\frac{m(L/m)^2}{a^3} = f(a) \tag{11.131}$$

where $a$ is the radius of the circular orbit for central force $f(a)$ at $r = a$. A perturbation of the radial motion may be expressed in terms of a variable $x$ defined by:

$$x = r - a \tag{11.132}$$

The differential equation can then be written as

$$m\ddot{x} - m(L/m)^2(x+a)^{-3} = f(x+a) \tag{11.133}$$

Expanding the two terms involving $x+a$ as a power series in $x$, gives:

$$m\ddot{x} - m(L/m)^2 a^{-3}\left(1 - 3\frac{x}{a} + \dots\right) = f(a) + f'(a)x + \dots \tag{11.134}$$

Substitution of Eq. (11.131) into Eq. (11.134) and neglecting terms involving $x^2$ and higher powers of $x$ gives:

$$m\ddot{x}+\left[\frac{-3}{a}f(a)-f'(a)\right]x=0 \tag{11.135}$$

For an inverse-squared central field, the coefficient of $x$ in Eq. (11.135) is positive, and the equation is the same as that of the simple harmonic oscillator. In this case, the particle, if perturbed, oscillates harmonically about the circle $r=a$, and an approximation of the angular frequency of this oscillation is:

$$\omega=\sqrt{\frac{\left[\frac{-3}{a}f(a)-f'(a)\right]}{m}}=\sqrt{\frac{k}{m}} \tag{11.136}$$

An apsis is a point in an orbit at which the radius vector assumes an extreme value (maximum or minimum). The angle swept out by the radius vector between two consecutive apsides is called the apsidal angle. Thus, the apsidal angle is $\pi$ for elliptical orbits under the inverse-squared law of force. In the case of a nearly circular orbit, Eq. (11.135) shows that $r$ oscillates about the circle $r=a$, and the period of oscillation is given by:

$$\tau_r=2\pi\sqrt{\frac{m}{-\left[\frac{3}{a}f(a)+f'(a)\right]}} \tag{11.137}$$

The apsidal angle in this case is just the amount by which the polar angle $\theta$ increases during the time that $r$ oscillates from a minimum value to the succeeding maximum value which is $\tau_r$. From Eq. (11.128), $\dot{\theta}=\frac{L/m}{r^2}$; therefore, $\theta$ remains constant, and Eq. (11.131) gives:

$$\dot{\theta}\approx\frac{L/m}{a^2}=\left[-\frac{f(a)}{ma}\right]^{1/2} \tag{11.138}$$

Thus, the apsidal angle is given by

$$\psi=\frac{1}{2}\tau_r\dot{\theta}=\pi\left[3+a\frac{f'(a)}{f(a)}\right]^{-1/2} \tag{11.139}$$

Thus, the power force of $f(r)=-cr^n$ gives:

$$\psi=\pi(3+n)^{-1/2} \tag{11.140}$$

The apsidal angle is independent of the size of the orbit in this case. The orbit is re-entrant, or repetitive, in the case of the inverse-squared law ($n=-2$) for which $\psi=\pi$.

A prolate spheroid MO and the definition of axes are shown in Figures 11.5A and 11.5B, respectively. Consider the two nuclei A and B, each at a focus of the prolate spheroid MO. From Eqs. (11.115), (11.117), and (11.119), the attractive force between the electron and each nucleus at a focus is:

$$f(a)=-\frac{pe^2}{4\pi\varepsilon_0a^2} \tag{11.141}$$

and

$$f'(a)=\frac{2pe^2}{4\pi\varepsilon_0a^3} \tag{11.142}$$

In addition to the attractive force between the electron and the nuclei, there is a repulsive force between the two nuclei that is the source of a corresponding reactive force on the reentrant electron orbit. Consider an elliptical orbital plane cross section of the MO in the xy-plane with a nucleus A at (-c', 0) and a nucleus B at (c', 0). For B acting as the attractive focus, the reactive repulsive force at the point (a, 0), the positive semimajor axis, depends on the distance from (a, 0) to nucleus A at (-c', 0) (i.e. the distance from the position of the electron MO at the semimajor axis to the opposite nuclear repelling center at the opposite focus). The distance is given by the sum of the semimajor axis, $a$, and $c'$, 1/2 the internuclear distance. The contribution from the repulsive force between the two protons is:

$$f(a+c')=\frac{pe^2}{8\pi\varepsilon_0(a+c')^2} \tag{11.143}$$

and

$$f'(a+c')=-\frac{pe^2}{4\pi\varepsilon_0(a+c')^3} \tag{11.144}$$

Thus, from Eqs. (11.136) and (11.141-11.144), the angular frequency of this oscillation is:

$$\omega = \sqrt{\frac{\frac{pe^2}{4\pi\varepsilon_0 a^3} - \frac{pe^2}{8\pi\varepsilon_0 (a+c')^3}}{\mu}}$$

$$= \sqrt{\frac{\frac{pe^2}{4\pi\varepsilon_0 \left(\frac{2a_H}{p}\right)^3} - \frac{pe^2}{8\pi\varepsilon_0 \left(\frac{3a_H}{p}\right)^3}}{\mu}} \tag{11.145}$$

$$= p^2 4.44865\ X\ 10^{14}\ rad/s$$

where the semimajor axis, $a$, is $a = \frac{2a_H}{p}$ according to Eq. (11.116) and $c'$ is $c' = \frac{a_H}{p}$ according to Eq. (11.110).

In the case of a hydrogen molecule or molecular ion, the electrons which have a mass of 1/1836 that of the protons move essentially instantaneously, and the charge density is that of a continuous membrane. Thus, a stable electron orbit is maintained with oscillatory motion of the protons. Hydrogen molecules and molecular ions are symmetrical along the semimajor axis; thus, the oscillatory motion of protons is along this axis. Let $x$ be the increase in the semimajor axis due to the reentrant orbit with a corresponding displacement of the protons along the semimajor axis from the position of the initial foci of the stationary state. The equation of proton motion due to the perturbation of an orbit having a central inverse-squared central force [1] and neglecting terms involving $x^2$ and higher is given by

$$\mu\ddot{x} + kx = 0 \tag{11.146}$$

which has the solution in terms of the maximum amplitude of oscillation, $A$, the reduced nuclear mass, $\mu$, the restoring constant or spring constant, $k$, the resonance angular frequency, $\omega_0$, and the vibrational energy, $E_{vib}$, [12]

$$A\cos\omega_0 t \tag{11.147}$$

where

$$\omega_0 = \sqrt{\frac{k}{\mu}} \tag{11.148}$$

For a symmetrical displacement $x$, the potential energy corresponding to the oscillation $E_{Pvib}$ is given by:

$$E_{Pvib} = 2\left(\frac{1}{2}kx^2\right) = kx^2 \tag{11.149}$$

The total energy of the oscillating molecular ion, $E_{Totalvib}$, is given as the sum of the kinetic and potential energies

$$E_{Totalvib} = \frac{1}{2}\mu\dot{x}^2 + kx^2 \tag{11.150}$$

The velocity is zero when $x$ is the maximum amplitude, $A$. The total energy of the oscillating molecular ion, $E_{Totalvib}$, is then given as the potential energy with $x = A$

$$E_{Totalvib} = kA^2 \tag{11.151}$$

thus,

$$A = \sqrt{\frac{E_{Totalvib}}{k}} \tag{11.152}$$

It is shown in the Excited States of the One-Electron Atom (Quantization) section that the change in angular frequency of the electron atomic orbital (Eq. (2.21)) is identical to the angular frequency of the photon necessary for the excitation, $\omega_{photon}$ (Eq. (2.19)). The energy of the photon necessary to excite the equivalent transition in an electron atomic orbital is one-half of the excitation energy of the stationary cavity because the change in kinetic energy of the electron atomic orbital supplies one-half of the necessary energy. The change in the angular frequency of the atomic orbital during a transition and the angular frequency of the photon corresponding to the superposition of the free space photon and the photon corresponding to the kinetic energy change of the atomic orbital during a transition are equivalent. The correspondence principle holds. It can be demonstrated that the resonance condition between these frequencies is to be satisfied in order to have a net change of the energy field [13]. The bound electrons are excited with the oscillating protons. Thus, the mechanical resonance frequency, $\omega_0$, is only one-half that of the electromechanical frequency which is equal to the frequency of the free space photon, $\omega$, which excites the vibrational mode of the hydrogen molecule or hydrogen molecular ion. The vibrational energy, $E_{vib}$, corresponding to the photon is given by:

$$E_{vib} = \hbar\omega = \hbar\omega_0 = \hbar\sqrt{\frac{k}{\mu}} = 2kA^2 \tag{11.153}$$

where Planck's equation (Eq. (11.127)) was used. The reduced mass is given by:

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \tag{11.154}$$

Thus,

$$A = \sqrt{\frac{\hbar\omega_0}{2k}} \tag{11.155}$$

Since the protons and electron are not fixed, but vibrate about the center of mass, the maximum amplitude is given by the reduced amplitude, $A_{reduced}$, given by

$$A_{reduced} = \frac{A_1 A_2}{A_1 + A_2} \tag{11.156}$$

where $A_n$ is the amplitude $n$ if the origin is fixed. Thus, Eq. (11.155) becomes:

$$A_{reduced} = \frac{1}{2}\sqrt{\frac{\hbar\omega_0}{2k}} \tag{11.157}$$

and from Eq. (11.148), $A_{reduced}$ is:

$$A_{reduced} = \frac{1}{2}\sqrt{\frac{\hbar\omega_0}{2k}} = \frac{1}{2}\sqrt{\frac{\hbar}{2k}}\left(\frac{k}{\mu}\right)^{1/4} = \frac{\sqrt{\hbar}}{2^{3/2}\left(k\mu\right)^{1/4}} \tag{11.158}$$

Then, from Eq. (11.67), $A_{c'}$, the displacement of $c'$ is the eccentricity $e$ given by Eq. (11.113) times $A_{reduced}$ (Eq. (11.158)):

$$A_{c'} = eA_{reduced} = \frac{A_{reduced}}{2} = \frac{\sqrt{\hbar}}{2^{5/2}\left(k\mu\right)^{1/4}} \tag{11.159}$$

Thus, during bond formation, the perturbation of the orbit determined by an inverse-squared force results in simple harmonic oscillatory motion of the orbit, and the corresponding frequency, $\omega(0)$, for a hydrogen-type molecular ion $H_2^+(1/p)$ given by Eqs. (11.136) and (11.145) is

$$\omega(0) = p^2\sqrt{\frac{k(0)}{\mu}} = p^2\sqrt{\frac{165.51\ Nm^{-1}}{\mu}} = p^2 4.449\ X\ 10^{14}\ radians/s \tag{11.160}$$

where the reduced nuclear mass of hydrogen given by Eq. (11.154) is:

$$\mu = 0.5m_p \tag{11.161}$$

and the spring constant, $k(0)$, given by Eqs. (11.136) and (11.145) is:

$$k(0) = p^4 165.51\ Nm^{-1} \tag{11.162}$$

The transition-state vibrational energy, $E_{vib}(0)$, is given by Planck's equation (Eq. (11.127)):

$$E_{vib}(0) = \hbar\omega = \hbar p^2 4.44865\ X\ 10^{14}\ rad/s = p^2 0.2928\ eV \tag{11.163}$$

The amplitude of the oscillation, $A_{reduced}(0)$, given by Eq. (11.158) and Eqs. (11.161-11.162) is:

$$A_{reduced}(0) = \frac{\sqrt{\hbar}}{2^{3/2}\left(p^4 165.51\ Nm^{-1}\mu\right)^{1/4}} = \frac{5.952\ X\ 10^{-12}\ m}{p} = 0.1125\frac{a_0}{p} \tag{11.164}$$

Then, from Eq. (11.67), $A_{c'}(0)$, the displacement of $c'$ is the eccentricity $e$ given by Eq. (11.113) times $A_{reduced}(0)$ (Eq. (11.164)).

$$A_{c'}(0) = eA_{reduced}(0) = \frac{A_{reduced}(0)}{2} = \frac{\sqrt{\hbar}}{2^{5/2}\left(k\mu\right)^{1/4}} = \frac{0.05624a_0}{p} \tag{11.165}$$

The spring constant and vibrational frequency for the formed molecular ion are then obtained from Eqs. (11.136) and (11.141-11.145) using the increases in the semimajor axis and internuclear distances due to vibration in the transition state. The vibrational energy, $E_{vib}(1)$, for the $H_2^+(1/p)$ $\upsilon = 1 \rightarrow \upsilon = 0$ transition given by adding $A_{c'}(0)$ (Eq. (11.159)) to the distances $a$ and $a + c'$ in Eqs. (11.145) and (11.163) is:

$$E_{vib}(1) = p^2 0.270\ eV \tag{11.166}$$

where $\upsilon$ is the vibrational quantum number.

A harmonic oscillator is a linear system as given by Eq. (11.146). In this case, the predicted resonant vibrational frequencies and energies, spring constants, and amplitudes for $H_2^+(1/p)$ for vibrational transitions to higher energy $\upsilon_i \rightarrow \upsilon_f$ are given by $(\upsilon_f - \upsilon_i)$ times the corresponding parameters given by Eq. (11.160) and Eqs. (11.162-11.164). However, excitation of vibration of the molecular ion by external radiation causes the semimajor axis and, consequently, the internuclear distance to increase as a function of the vibrational quantum number $\upsilon$. Consequently, the vibrational energies of hydrogen-type molecular ions are nonlinear as a function of the vibrational quantum number $\upsilon$. The lines become more closely spaced and the change in amplitude, $\Delta A_{reduced}$, between successive states becomes larger as higher states are excited due to the distortion of the molecular ion in these states. The energy difference of each successive transition of the vibrational spectrum can be obtained by considering nonlinear terms corresponding to anharmonicity.

The harmonic oscillator potential energy function can be expanded about the internuclear distance and expressed as a Maclaurin series corresponding to a Morse potential after Karplus and Porter (K&P) [14] and after Eq. (11.134). Treating the Maclaurin series terms as anharmonic perturbation terms of the harmonic states, the energy corrections can be found by perturbation methods. The energy $\tilde{\nu}_{\upsilon}$ of state $\upsilon$ is:

$$\tilde{\nu}_{\upsilon} = \upsilon\omega_0 - \upsilon(\upsilon-1)\omega_0 x_0, \quad \upsilon = 0,1,2,3... \tag{11.167}$$

where

$$\omega_0 x_0 = \frac{hc\omega_0^2}{4D_0} \tag{11.168}$$

$\omega_0$ is the frequency of the $\upsilon = 1 \rightarrow \upsilon = 0$ transition corresponding to Eq. (11.166), and $D_0$ is the bond dissociation energy given by Eq. (11.198). From Eqs. (11.166), (11.168), and (11.198),

$$\omega_0 x_0 = \frac{100hc\left(8.06573X10^3 \ \frac{cm^{-1}}{eV} p^2 0.270 \ eV\right)^2}{4e\left(p^2 2.535 \ eV + p^3 0.118755 \ eV\right)} cm^{-1} \tag{11.169}$$

The vibrational energies of successive states are given by Eqs. (11.166-11.167) and (11.169).

Using Eqs. (11.145), (11.158-11.160), (11.162-11.169), and (11.199) the corresponding parameters for deuterium-type molecular ions with:

$$\mu = m_p \tag{11.170}$$

are

$$\omega(0) = p^2\sqrt{\frac{k(0)}{\mu}} = p^2\sqrt{\frac{165.65 \ Nm^{-1}}{\mu}} = p^2 3.147 \ X \ 10^{14} \ radians/s \tag{11.171}$$

$$k(0) = p^4 165.65 \ Nm^{-1} \tag{11.172}$$

$$E_{vib}(0) = p^2 0.20714 \ eV \tag{11.173}$$

$$A_{reduced}(0) = \frac{\sqrt{\hbar}}{2^{3/2}\left(p^4 165.65 \ Nm^{-1}\mu\right)^{1/4}} = \frac{5.004 \ X \ 10^{-12} \ m}{p} = 0.09457\frac{a_0}{p} \tag{11.174}$$

$$E_{vib}(1) = p^2 0.193 \ eV \tag{11.175}$$

$$\omega_0 x_0 = \frac{100hc\left(8.06573X10^3 \ \frac{cm^{-1}}{eV} p^2 0.193 \ eV\right)^2}{4e\left(p^2 2.5770 \ eV + p^3 0.118811 \ eV\right)} cm^{-1} \tag{11.176}$$

The vibrational energies of successive states are given by Eqs. (11.167) and (11.175-11.176).

## THE DOPPLER ENERGY TERM OF HYDROGEN-TYPE MOLECULAR IONS

As shown in the Vibration of Hydrogen-type Molecular Ions section, the electron orbiting the nuclei at the foci of an ellipse may be perturbed such that a stable reentrant orbit is established that gives rise to a vibrational state corresponding to time harmonic oscillation of the nuclei and electron. The perturbation is caused by a photon that is resonant with the frequency of oscillation of the nuclei wherein the radiation is electric dipole with the corresponding selection rules.

Oscillation may also occur in the transition state. The perturbation arises from the decrease in internuclear distance as the molecular bond forms. Relative to the unperturbed case given in the Force Balance of Hydrogen-type Molecular Ions section, the reentrant orbit may give rise to a decrease in the total energy while providing a transient kinetic energy to the vibrating nuclei. However, as an additional condition for stability, radiation must be considered. Regarding the potential for radiation, the nuclei may be considered point charges. A point charge undergoing periodic motion accelerates and as a consequence radiates according to the Larmor formula (cgs units) [15]:

$$P = \frac{2e^2}{3c^3}|\dot{\mathbf{v}}|^2 \tag{11.177}$$

where $e$ is the charge, $\dot{\mathbf{v}}$ is its acceleration, and $c$ is the speed of light. The radiation has a corresponding force that can be determined based on conservation of energy with radiation. The radiation reaction force, $\mathbf{F_{rad}}$, given by Jackson [16] is:

$$\mathbf{F_{rad}} = \frac{2}{3}\frac{e^2}{c^3}\ddot{\mathbf{v}} \tag{11.178}$$

Then, the Abraham-Lorentz equation of motion is given by [16]:

$$m\left(\dot{\mathbf{v}}-\frac{2}{3}\frac{e^2}{mc^3}\ddot{\mathbf{v}}\right)=\mathbf{F}_{\mathbf{ext}} \tag{11.179}$$

where $\mathbf{F}_{\mathbf{ext}}$ is the external force and $m$ is the mass. The external force for the vibrating system is given by Eq. (11.146).

$$\mathbf{F}_{\mathbf{ext}}=kx \tag{11.180}$$

where $x$ is the displacement of the protons along the semimajor axis from the position of the initial foci of the stationary state in the absence of vibration with a reentrant orbit of the electron. A nonradiative state must be achieved after the emission due to transient vibration wherein the nonradiative condition given by Eq. (11.24) must be satisfied.

As shown in the Resonant Line Shape and Lamb Shift section, the spectroscopic linewidth arises from the classical rise-time band-width relationship, and the Lamb Shift is due to conservation of energy and linear momentum and arises from the radiation reaction force between the electron and the photon. The radiation reaction force in the case of the vibration of the molecular ion in the transition state corresponds to a Doppler energy, $E_D$, that is dependent on the motion of the electron and the nuclei. The Doppler energy of the electron is given by Eq. (2.155) after Gibb [17]:

$$\overline{E}_D\cong 2\sqrt{E_K E_R}=E_{h\nu}\sqrt{\frac{2\overline{E}_K}{Mc^2}} \tag{11.181}$$

where $E_R$ is the recoil energy which arises from the photon's linear momentum given by Eq. (2.153), $E_K$ is the vibrational kinetic energy of the reentrant orbit in the transition state, and $M$ is the mass of the electron $m_e$.

As given in the Vibration of Hydrogen-Type Molecular Ions section, for an inverse-squared central field, the coefficient of $x$ in Eq. (11.135) is positive, and the equation is the same as that of the simple harmonic oscillator. Since the electron of the hydrogen molecular ion is perturbed as the internuclear separation decreases with bond formation, it oscillates harmonically about the semimajor axis given by Eq. (11.116), and an approximation of the angular frequency of this oscillation is

$$\omega=\sqrt{\frac{\left[\frac{-3}{a}f(a)-f'(a)\right]}{m_e}}=\sqrt{\frac{k}{m_e}} \tag{11.182}$$

From Eqs. (11.115), (11.117), and (11.119), the central force terms between the electron MO and the two protons are:

$$f(a)=-\frac{2pe^2}{4\pi\varepsilon_0 a^2} \tag{11.183}$$

and

$$f'(a)=\frac{4pe^2}{4\pi\varepsilon_0 a^3} \tag{11.184}$$

Thus, the angular frequency of this oscillation is:

$$\omega=\sqrt{\frac{\frac{2pe^2}{4\pi\varepsilon_0\left(\frac{2a_H}{p}\right)^3}}{m_e}}=p^2 2.06538\ X\ 10^{16}\ rad/s \tag{11.185}$$

where the semimajor axis, $a$, is $a=\frac{2a_H}{p}$ according to Eq. (11.116) including the reduced electron mass. The kinetic energy, $E_K$, is given by Planck's equation (Eq. (11.127)).

$$\overline{E}_K=\hbar\omega=\hbar p^2 2.06538\ X\ 10^{16}\ rad/s=p^2 13.594697\ eV \tag{11.186}$$

In Eq. (11.181), substitution of the total energy of the hydrogen molecular ion, $E_T$, (Eq. (11.125)) for $E_{h\nu}$, the mass of the electron, $m_e$, for $M$, and the kinetic energy given by Eq. (11.186) for $\overline{E}_K$ divided by $p^2$, the number of multipoles of a molecular hydrino state $p$ (Eq. (5.45)) gives the Doppler energy of the electron for the reentrant orbit.

$$\overline{E}_D\cong E_{h\nu}\sqrt{\frac{2\overline{E}_K}{Mc^2}}=-p^2 16.28034\ eV\sqrt{\frac{2e\left(p^2 13.594697\ eV\right)}{p^2 m_e c^2}}=-p^2 0.118755\ eV \tag{11.187}$$

The total energy of the molecular ion is decreased by $\overline{E}_D$.

In addition to the electron, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency given in the Vibration of Hydrogen-Type Molecular Ions section. On average, the total energy of vibration is equally distributed between kinetic energy and potential energy [18]. Thus, the average kinetic energy of vibration corresponding to the Doppler energy of the electrons, $\overline{E}_{Kvib}$, is 1/2 of the vibrational energy of the molecular ion given by Eq. (11.166). The decrease in the energy of the hydrogen molecular ion due to the reentrant orbit in the transition state corresponding to simple harmonic oscillation of the electron and nuclei, $\bar{E}_{osc}$, is given by the sum of the corresponding energies, $\bar{E}_D$ and $\bar{E}_{Kvib}$. Using Eq. (11.187) and $E_{vib}$ from Eq. (11.163) gives:

$$\bar{E}_{osc} = \bar{E}_D + \bar{E}_{Kvib} = \bar{E}_D + \frac{1}{2}\hbar p^2\sqrt{\frac{k}{\mu}} \tag{11.188}$$

$$\bar{E}_{osc} = -p^2 0.118755\ eV + \frac{1}{2}p^2\left(0.29282\ eV\right) \tag{11.189}$$

To the extent that the MO dimensions are the same, the electron reentrant orbital energies $\bar{E}_K$ are the same independent of the isotope of hydrogen, but the vibrational energies are related by Eq. (11.148). Thus, the differences in bond energies are essentially given by 1/2 the differences in vibrational energies. Using Eq. (11.187) with the deuterium reduced electron mass for $E_T$ and $\bar{E}_D$, and $E_{vib}$ for $D_2^+\left(1/p\right)$ given by Eq. (11.173), that corresponds to the deuterium reduced nuclear mass (Eq. (11.170)), the corresponding $\bar{E}_{osc}$ is:

$$\bar{E}_{osc} = -p^2 0.118811\ eV + \frac{1}{2}p^2\left(0.20714\ eV\right) \tag{11.190}$$

## TOTAL, IONIZATION, AND BOND ENERGIES OF HYDROGEN AND DEUTERIUM MOLECULAR IONS

The total energy of the hydrogen molecular ion which is equivalent to the negative of the ionization energy is given by the sum of $E_T$ (Eqs. (11.121) and (11.125)) and $\bar{E}_{osc}$ given by Eqs. (11.185-11.188). Thus, the total energy of the hydrogen molecular ion having a central field of $+pe$ at each focus of the prolate spheroid molecular orbital including the Doppler term is:

$$E_T = V_e + V_p + T + \bar{E}_{osc} \tag{11.191}$$

$$\begin{aligned} E_T &= -p^2\left\{ \frac{e^2}{8\pi\varepsilon_0 a_H}(4\ln 3 - 1 - 2\ln 3)\left[1+\sqrt{\frac{2\hbar\sqrt{\frac{\frac{2e^2}{4\pi\varepsilon_0\left(2a_H\right)^3}}{m_e}}}{m_e c^2}}\right] - \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right\} \\ &= -p^2 16.2803\ eV - p^2 0.118755\ eV + \frac{1}{2}p^2\hbar\sqrt{\frac{k}{\mu}} \end{aligned} \tag{11.192}$$

From Eqs. (11.189) and (11.191-11.192), the total energy for hydrogen-type molecular ions is:

$$\begin{aligned} E_T &= -p^2 16.28033\ eV + \bar{E}_{osc} \\ &= -p^2 16.28033\ eV - p^2 0.118755\ eV + \frac{1}{2}p^2\left(0.29282\ eV\right) \\ &= -p^2 16.252675\ eV \end{aligned} \tag{11.193}$$

The total energy of the deuterium molecular ion is given by the sum of $E_T$ (Eq. (11.125)) corrected for the reduced electron mass of $D$ and $\bar{E}_{osc}$ given by Eq. (11.190).

$$\begin{aligned} E_T &= -p^2 16.284\ eV + \bar{E}_{osc} \\ &= -p^2 16.284\ eV - p^2 0.118811\ eV + \frac{1}{2}p^2\left(0.20714\ eV\right) \\ &= -p^2 16.2988\ eV \end{aligned} \tag{11.194}$$

The bond dissociation energy, $E_D$, is the difference between the total energy of the corresponding hydrogen atom or $H\left(1/p\right)$ atom [19-20], called hydrino atom having a principal quantum number $1/p$ where $p$ is an integer, and $E_T$.

$$E_D = E(H\left(1/p\right)) - E_T \tag{11.195}$$

where [19]

$$E(H\left(1/p\right)) = -p^2 13.59844\ eV \tag{11.196}$$

and [20]

$$E(D\left(1/p\right)) = -p^2 13.603\ eV \tag{11.197}$$

The hydrogen molecular ion bond energy, $E_D$, is given by Eq. (11.193) with the reduced electron mass and Eqs. (11.195-11.196):

$$\begin{aligned} E_D &= -p^2 13.59844 - E_T \\ &= -p^2 13.59844 - \left(-p^2 16.252675\ eV\right) \\ &= p^2 2.65424\ eV \end{aligned} \tag{11.198}$$

The deuterium molecular ion bond energy, $E_D$, is given by Eq. (11.194) with the reduced electron mass of $D$ and Eqs. (11.195) and (11.197).

$$\begin{aligned} E_D &= -p^2 13.603 - E_T \\ &= -p^2 13.603 - \left(-p^2 16.2988\ eV\right) \\ &= p^2 2.6958\ eV \end{aligned} \tag{11.199}$$

# HYDROGEN-TYPE MOLECULES

## FORCE BALANCE OF HYDROGEN-TYPE MOLECULES

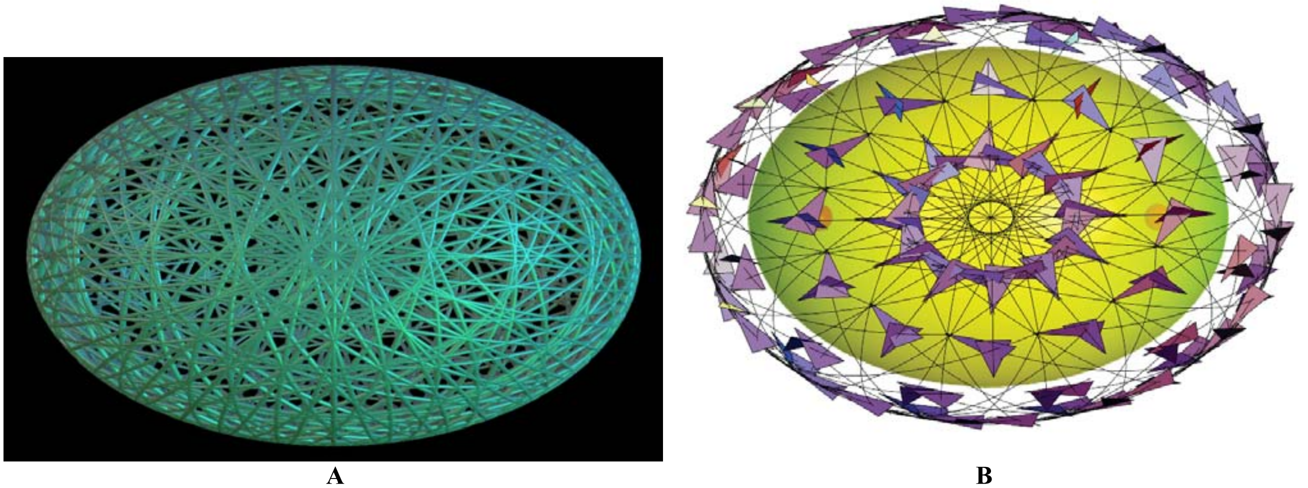
Hydrogen-type molecules comprise two indistinguishable electrons bound by an elliptic field. Each electron experiences a centrifugal force. The balancing centripetal force (on each electron) is produced by the electric force between the electron and the elliptic electric field and the magnetic force between the two electrons causing the electrons to pair wherein the interaction between the pairing electrons involves a magnetic moment of a Bohr magneton, $\mu_B$, as given in the Magnetic Moment of an Ellipsoidal MO section. The internal field is uniform along the major axis, and the far field is that of a dipole as shown in the Magnetic Field of an Ellipsoidal MO section. The magnetic force is derived by first determining the interaction of the two electrons due to the field of the outer electron 2 acting on the magnetic moments of electron 1 and vice versa. Insight into the behavior is given by considering the physics of a single bound electron in an externally applied uniform magnetic field as discussed in the Two-Electron Atoms section. The uniform current- (charge-) density function $Y_0^0(\theta,\phi)$ was given in the Atomic Orbital Equation of Motion for $\ell = 0$ Based on the Current Vector Field (CVF) section. The resultant angular momentum projections of the spherically-symmetric atomic orbital current density, $Y_0^0(\theta,\phi)$, corresponding to the interaction are $\mathbf{L}_{xy} = \frac{\hbar}{4}$ and $\mathbf{L}_z = \frac{\hbar}{2}$. As shown in the Resonant Precession of the Spin-1/2-Current-Density Function Gives Rise to the Bohr Magneton section, the electron spin angular momentum gives rise to a trapped photon with $\hbar$ of angular momentum along an $\mathbf{S}$-axis. Then, the spin state of an atomic orbital comprises a photon standing wave that is phase-matched to a spherical harmonic source current, a spherical harmonic dipole $Y_\ell^m(\theta,\phi) = \sin\theta$ with respect to the $\mathbf{S}$-axis. The dipole spins about the $\mathbf{S}$-axis at the angular velocity given by Eq. (1.36) with $\hbar$ of angular momentum. $\mathbf{S}$ rotates about the z-axis at the Larmor frequency at $\theta = \frac{\pi}{3}$ such that it has a static projection of the angular momentum of $\mathbf{S}_\parallel = \pm\hbar\cos\frac{\pi}{3} = \pm\frac{\hbar}{2}\,\mathbf{i}_{Z_R}$ as given by Eq. (1.97), and from Eq. (1.96), the projection of $\mathbf{S}$ onto the transverse plane (xy-plane) is $\mathbf{S}_\perp = \hbar\sin\frac{\pi}{3} = \pm\sqrt{\frac{3}{4}}\hbar\,\mathbf{i}_{Y_R}$. Then, the vector projection of the radiation-reaction-type magnetic force of the Two Electron Atom section given by Eqs. (7.24) and (7.31) contain the factor $\sqrt{\frac{3}{4}}\hbar$. This represents the maximum projection of the time-dependent magnetic moment onto an axis of the spherical-central-force system.

The atomic orbital can serve as a basis element to form a molecular orbital (MO). The total magnitude of the angular momentum of $\hbar$ is conserved for each member of the linear combinations of $Y_0^0(\theta,\phi)$'s in the transition from the $Y_0^0(\theta,\phi)$'s to the MO. Since the charge and current densities have the same distribution, the equipotential energy surface solution of Laplace's equation for the charge distribution also determines the current distribution. Newton's laws determine the angular frequency and the velocity of the charge motion corresponding to the current. Specifically, the further constraint from Newton's laws that the orbital surface is a constant total energy surface and the condition of nonradiation provide that the motion is periodic with a constant period and that the current is continuous and constant over a period. These boundary conditions determine the corresponding velocity function. In non-spherical coordinates, the nonuniform charge distribution given by Laplace's equation is compensated by a nonuniform velocity distribution such that the constant current condition is met. Then, the conservation of the angular momentum is provided when symmetrically stretching the current density of an atomic $Y_0^0(\theta,\phi)$ current density along the semimajor axis of the MO so formed.

The angular momentum projection may be determined by first considering the case of the hydrogen molecular ion. Specifically, the angular momentum must give the results of the Stern-Gerlach experiment as shown for atomic electrons and free electrons in the Resonant Precession of the Spin-1/2-Current-Density Function Gives Rise to the Bohr Magneton section and Stern-Gerlach Experiment section, respectively. The hydrogen-molecular-ion MO, and all MOs in general, have cylindrical symmetry along the bond axis. Then, in general, $Y_0^0(\theta,\phi)$ can serve as a basis element for an MO having cylindrical symmetry along the semimajor axis. This defines the axis for stretching the $Y_0^0(\theta,\phi)$ basis element to form the MO (Figure 11.2) while conserving the angular momentum. The charge and current distribution is normalized by applying the method given in the

Uniformity of $Y_0{}^0(\theta,\phi)$ section according to the distribution given by Eq. (11.42). This gives rise to an ellipsoidal surface comprised of the equivalent of elliptical-orbit, plane cross sections in the direction parallel to the semimajor axis with the conserved angular momentum projections along the orthogonal semiminor axes.

Figure 11.2. The bound electron MO, a prolate spheroidal two-dimensional supercurrent comprising an extended continuous distribution of charge and current completely surrounding the nuclei at the foci, obtained by stretching $Y_0^0(\theta,\phi)$ along the semimajor axis. Unlike a spinning top, there is a complex pattern of motion on its surface that generates two orthogonal components of angular momentum (Figure 11.4) that give rise to the phenomenon of electron spin. A. The z-axis view of the MO current paths having $\mathbf{L}_z = \frac{\hbar}{2}$ matching the angular momentum projection on the $\left(-\frac{1}{\sqrt{2}}\mathbf{i}_x, \frac{1}{\sqrt{2}}\mathbf{i}_y, \mathbf{i}_z\right)$-axis of the basis element $Y_0^0(\theta,\phi)$. B. A representation of the z-axis view of the continuous charge-density and supercurrent-density distributions of the MO with 144 vectors overlaid giving the direction of the currents (nuclei not to scale).

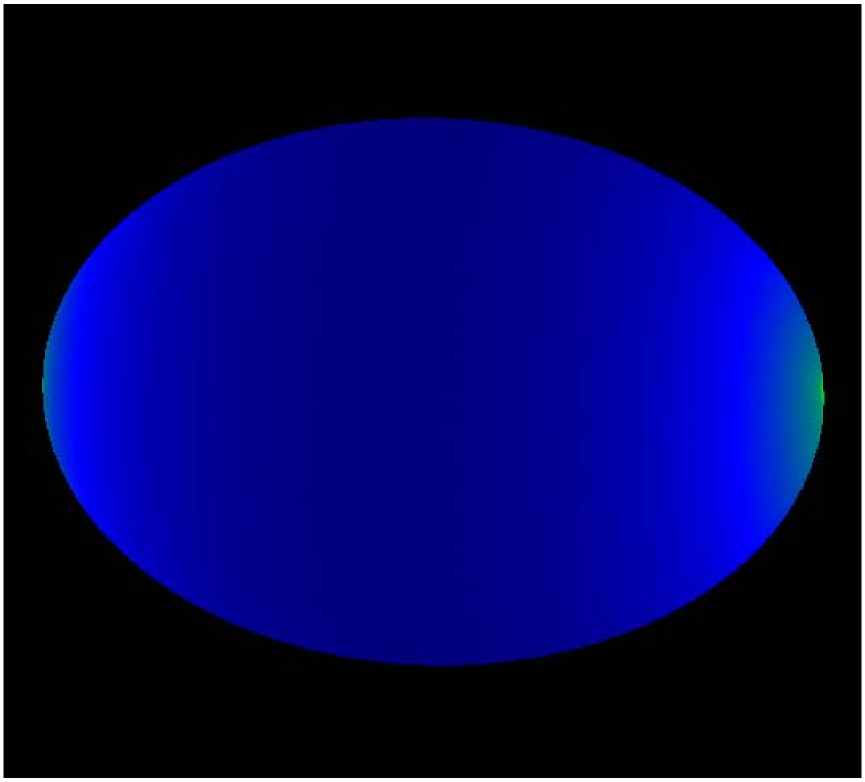


As shown in the Atomic Orbital Equation of Motion for $\ell = 0$ Based on the Current Vector Field (CVF) section, the atomic orbital is comprised of the uniform function $Y_0^0(\theta,\phi)$ with the intrinsic angular momentum directed along two orthogonal axes having three angular momentum components of $\mathbf{L}_{xy} = +/-\frac{\hbar}{4}$ and $\mathbf{L}_z = \frac{\hbar}{2}$. Then, $Y_0^0(\theta,\phi)$ serves as the basis element for the formation of a MO with conservation of the total magnitude of the angular momentum of $\hbar$ (Eq. (1.37)) and the orthogonal projections $\mathbf{L}_{xy}$ and $\mathbf{L}_z$ of $Y_0^0(\theta,\phi)$ directed along the semiminor axes of the MO. Since the direction of the stretching of the great-circle elements of $Y_0^0(\theta,\phi)$ having a radius of the semiminor axes is perpendicular to the angular momentum axes, the conserved angular momentum projections of the MO are $\mathbf{L}_y = +/-\frac{\hbar}{4}$ and $\mathbf{L}_z = \frac{\hbar}{2}$ as shown in Figure 11.4. The transform is that of a minimum energy, equipotential spherical to prolate spheroidal surface. A convenient method to perform the stretching is numerically using a computer instead of using basis elements, convolutions, and rotational matrices in ellipsoidal coordinates following the method for construction of $Y_0^0(\theta,\phi)$ given in the Generation of the Atomic Orbital CVFs section. As shown for the $Y_0^0(\theta,\phi)$ normalization algorithm in the Uniformity of $Y_0{}^0(\theta,\phi)$ section, the equipotential charge density of the MO can be obtained by stretching and weighting the total constant current on each current loop without changing the angular momentum distribution since the changes are orthogonal to the angular momentum axes. In addition, the current distribution along each loop is adjusted to achieve the equipotential charge density (Eq. (11.42)) wherein the current is constant due to a corresponding variable velocity with position on the loop (Eqs. (11.84) and (11.23-11.24) using the area A of the elliptic plane section of the prolate spheroid).

The algorithm for generating the charge and current density numerically may be an adaptation of computed tomography algorithms such as the original: Apply an Affine transform to the atomic electron current pattern to form an initial current distribution. Calculate the density at each point area from the initial distribution, substrate it from the prolate spheroid distribution, add the normalized error to the current of each contributing loop, distribute the current correction along each loop in a manner to match Eq. (11.45), and repeat over all point areas repetitively until the error goes to zero. Alternatively, a numerical spheroid to ellipsoidal transform may be applied to the numerically normalized atomic current motion wherein the angular momentum of each current loop is conserved and the constant current is based on the corresponding velocity variation on the ellipsoidal surface. Specifically, normalization was achieved using a transformation that transforms an ellipsoidal MO into the

AO atomic orbital $Y_0^0(\theta,\phi)$. Then, sample points of the normalized sphere were used to numerically perform the transform in reverse using the inverse of the ellipsoidal MO to $Y_0^0(\theta,\phi)$ transformation to give the current densities shown in Figure 11.3 [21]. The change in velocity is inherently compensated by the mass/charge density such that the overall flow of increments of mass/charge on each ellipse is constant, and the transform of each ellipse to a circle is such that the angular momentum remains the same. The radius of the sphere is the same as the semiminor axis, but could be arbitrary in the normalization algorithm since densities are computed (corresponding to the number of samples in a certain solid angle).

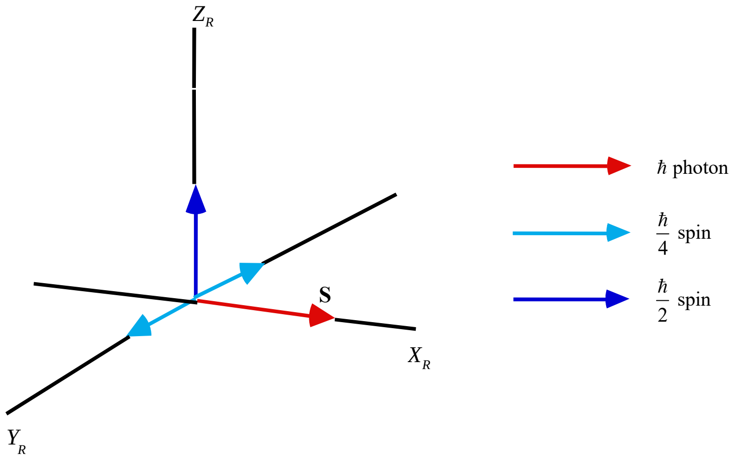
Figure 11.3. The y-axis view of the numerically normalized current density of the ellipsoidal MO using the inverse of the ellipsoidal MO to $Y_0^0(\theta,\phi)$ transformation.



Now consider the behavior of the hydrogen molecular ion in a magnetic field. As shown in the Resonant Precession of the Spin-1/2-Current-Density Function Gives Rise to the Bohr Magneton section, in general, the photon angular momentum corresponding to the resonant excitation of the Larmor excited state is $\hbar$, and the angular momentum change corresponding to the spin-flip transition is also $\hbar$. In the case of the hydrogen molecular ion, the Larmor-excitation photon carries $\hbar$ of angular momentum that gives rise to a prolate spheroidal dipole current about an $\mathbf{S}$-axis in the same manner as in the case of the spherical dipole of the Larmor excited atomic orbital shown in Figures 1.15 and 1.16. The former are given by the prolate angular function, which comprises an associated Legendre function $P_\ell^m(\eta)$ [22], and the latter comprises the spherical harmonic dipole $Y_\ell^m(\theta,\phi)=\sin\theta$. Both are with respect to the $\mathbf{S}$-axis. For hydrogen molecular ion, $\mathbf{L}_y=+/-\frac{\hbar}{4}$ and $\mathbf{L}_z=\frac{\hbar}{2}$ of intrinsic spin are along the semiminor axes of the prolate spheroidal MO and $\mathbf{S}$ is along the semimajor axis as shown in Figure 11.4. Thus, the Larmor excitation is constrained by Maxwell's equations to be along the semimajor axis. In general, all bonds are cylindrically symmetrical about the internuclear or semimajor axis; thus, the Larmor precession occurs about the bond axis of an MO wherein the intrinsic angular momentum components rotate about $\mathbf{S}$ at the Larmor frequency and are not stationary relative to the magnetic field. In the coordinate system rotating at the Larmor frequency (denoted by the axes labeled $X_R$, $Y_R$, and $Z_R$ in Figure 11.2), the angular momentum of $\mathbf{S}$ of magnitude $\hbar$ is stationary. The $Y_R$-components of magnitude $+/-\frac{\hbar}{4}$ and the $Z_R$-component of magnitude $\frac{\hbar}{2}$ rotate about $\mathbf{S}$ at the Larmor frequency. The opposing intrinsic magnetic moments of $\pm\frac{\mu_B}{4}$ along the $Y_R$-axis corresponding to the angular momentum of $\mathbf{L}_y=+/-\frac{\hbar}{4}$ (Eq. (28) of Box 1.1 and Eq. (2.65)) balances the torque on the $\frac{\hbar}{2}$ angular momentum component along the $Z_R$-axis, and all of the components have the necessary orthogonality.

Then, the $\mathbf{S}$-axis is the direction of the magnetic moment of each unpaired electron of a molecule or molecular ion. The magnetic moment of $\mathbf{S}$ of $\mu_B$ corresponding to its $\hbar$ of angular momentum is consistent with the Stern-Gerlach experiment. The Larmor excitation can only be parallel or antiparallel to the magnetic field in order to conserve the angular momentum of the electron as well as the $\hbar$ of angular momentum of each of the photon corresponding to the Larmor excitation and the photon that causes a 180° flip of the direction of $\mathbf{S}$. The result is the same as that for the atomic electron and the free electron given in the Resonant Precession of the Spin-1/2-Current-Density Function Gives Rise to the Bohr Magneton section and Stern-Gerlach Experiment section, respectively. The magnetic field is given in the Magnetic Field of an Ellipsoidal Molecular Orbital section.

Figure 11.4. The angular momentum components of the MO and $\mathbf{S}$ in the rotating coordinate system $X_R$, $Y_R$, and $Z_R$ that precesses at the Larmor frequency about $\mathbf{S}$ such that the $\mathbf{S}$ vector is stationary.



Next, consider the magnetic-pairing force of the hydrogen molecule due to the spin-angular-momentum components. The magnetic moments of electrons 1 and 2 of the hydrogen molecule cancel, as they are spin paired to form an energy minimum at the distance $\xi$ (i.e. $\xi_1 = \xi_2$). The molecular magnetic force follows from the derivation for that between the electrons of two-electron atoms as given in the Two-Electron Atoms section. The latter force was derived by first determining the interaction of the two electrons due to the field of the outer electron 2 acting on the magnetic moment of electron 1 and vice versa. It was also given by the relationship between the angular momentum, energy, and frequency for the transition of electron 2 from the continuum to the ground state of the two-electron atom. The molecular magnetic force follows from Eqs. (7.25-7.31) with the conversion to ellipsoidal coordinates. The conversion is apparent from comparing the centrifugal forces for each coordinate system given by Eq. (11.98) and Eqs. (7.1-7.2). In the present case of hydrogen-type molecules, the radiation-reaction-type magnetic force arises between the electrons, each having the components shown in Figure 11.4. With the photon angular momentum projection of $\hbar$ and the total nuclear charge (non-photon-field) of 2, the magnitude of the magnetic force between the two electrons is 1/2 that of the centrifugal force given by Eq. (11.95). This force is a term in the overall force balance.

In addition to the spin pairing force between the two electrons, the electric and centrifugal forces must be considered in the force balance. In the hydrogen-type molecule, the two electrons are bound by the central electric field as in the case of the molecular ion. The hydrogen-type molecule is formed by the binding of an electron 2 to the hydrogen-type molecular ion comprising two protons at the foci of the prolate spheroidal MO of electron 1. The ellipsoids of electron 1 and electron 2 are confocal; thus, the electric fields and the corresponding forces are normal to each MO of electron 1 and electron 2. The field of the protons is ellipsoidal on average, and the binding of electron 2 requires a quantized energy release in units of $\hbar$. The magnetic force is also quantized in terms of $\hbar$. The final bound electrons must have the same angular momentum and be paired in the same orbit; thus, they must have the same eccentricity. This is only possible according to Eq. (11.11) if they have the same central force. Consequently, to conserve angular momentum, the electric force on electron 2 must be the same as that as on electron 1. Due to the magnetic pairing force between electron 2 and electron 1 as well as the central electric force, the balance between the centrifugal force and the central field of electron 2 of the hydrogen-type molecule formed by electron 2 binding to a hydrogen-type molecular ion is the same as that given by Eq. (11.115). Then, the force balance between the centrifugal force and the sum of the Coulombic and additionally the magnetic spin-pairing forces to solve for the semimajor axis is:

$$\frac{\hbar^2}{m_e a^2 b^2} D = \frac{pe^2}{8\pi\varepsilon_0 ab^2} D + \frac{\hbar^2}{2m_e a^2 b^2} D \tag{11.200}$$

$$\frac{2a_0}{pa} - \frac{a_0}{pa} = 1 \tag{11.201}$$

$$a = \frac{a_0}{p} \tag{11.202}$$

Substitution of Eq. (11.202) into Eq. (11.79) is:

$$c' = \frac{1}{p\sqrt{2}} a_0 \tag{11.203}$$

The internuclear distance given by multiplying Eq. (11.203) by two is:

$$2c' = \frac{a_0\sqrt{2}}{p} \tag{11.204}$$

Substitution of Eqs. (11.202-11.203) into Eq. (11.80) is:

$$b = c = \frac{1}{p\sqrt{2}} a_0 \tag{11.205}$$

Substitution of Eqs. (11.202-11.203) into Eq. (11.67) is:

$$e = \frac{1}{\sqrt{2}} \tag{11.206}$$

For hydrogen, $r(t) = D$ for $\theta = n\frac{\pi}{2}$, $n = 0,1,2,3,4$. Thus, there is no dipole moment, and the molecule is not predicted to be infrared active. However, it is predicted to be Raman active due to the quadrupole moment. The liquefaction temperature of $H_2$ is also predicted to be significantly higher than isoelectronic helium.

## ENERGIES OF HYDROGEN-TYPE MOLECULES

The energy components defined previously for the molecular ion, Eqs. (11.117), (11.119), (11.120), and (11.121), apply in the case of the corresponding molecule except that all of the field lines of the protons must end on the MO comprising two-paired electrons. With spin pairing of the mirror-image-current electrons, the scaling factors due to the non-ellipsoidal variation of the electric field of the protons is unity as in the case of the sum of squares of spherical harmonics. Thus, the hydrogen-type molecular energies are given by the integral of the forces without correction. Then, each molecular-energy component is given by the integral of corresponding force in Eq. (11.200) where each energy component is the total for the two equivalent electrons with the central-force action at the position of the electron MO where the parameters $a$ and $b$ are given by Eqs. (11.202) and (11.205), respectively.

The potential energy, $V_e$, of the two-electron MO comprising equivalent electrons in the field of magnitude $p$ times that of the two protons at the foci is:

$$\begin{aligned} V_e &= 2\frac{-pe^2}{4\pi\varepsilon_0} D \frac{ab^2}{2D} \int_{\xi}^{\infty} \frac{d\xi}{R_\xi} \\ &= \frac{-2pe^2}{8\pi\varepsilon_0} \int_{\xi}^{\infty} \frac{d\xi}{(\xi + b)\sqrt{\xi + a}} \\ &= \frac{-2pe^2}{8\pi\varepsilon_0\sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} \end{aligned} \tag{11.207}$$

which is equivalent to $Ze = 2pe$ times the potential of the MO given by Eq. (11.46) after Eq. (11.114). The potential energy, $V_p$, due to proton-proton repulsion in the field of magnitude $p$ times that of the protons at the foci ($\xi = 0$) is

$$V_p = \frac{p}{8\pi\varepsilon_0} \frac{e^2}{\sqrt{a^2 - b^2}} \tag{11.208}$$

The kinetic energy, $T$, of the two-electron MO of total mass $2m_e$ is:

$$\begin{aligned} T &= 2\frac{-\hbar^2}{2m_e a^2 b^2} D \frac{ab^2}{2D} \int_{\xi}^{\infty} \frac{d\xi}{R_\xi} \\ &= \frac{-\hbar^2}{2m_e a} \int_{\xi}^{\infty} \frac{d\xi}{(\xi + b)\sqrt{\xi + a}} \\ &= \frac{\hbar^2}{2m_e a\sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} \end{aligned} \tag{11.209}$$

The magnetic energy, $V_m$, of the two-electron MO of total mass $2m_e$ corresponding to the magnetic force of Eq. (11.200) is:

$$\begin{aligned} V_m &= 2\frac{-\hbar^2}{2\left(2m_e\right)a^2b^2} D \frac{ab^2}{2D} \int_{\xi}^{\infty} \frac{d\xi}{R_\xi} \\ &= \frac{-\hbar^2}{4m_e a} \int_{\xi}^{\infty} \frac{d\xi}{\left(\xi + b\right)\sqrt{\xi + a}} \\ &= \frac{-\hbar^2}{4m_e a\sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} \end{aligned} \tag{11.210}$$

The total energy, $E_T$, is given by the sum of the energy terms (Eqs. (11.207-11.210)).

$$E_T = V_e + T + V_m + V_p \tag{11.211}$$

$$E_T = -13.60\ eV\left[\left(2p^2\sqrt{2} - p^2\sqrt{2} + \frac{p^2\sqrt{2}}{2}\right)\ln\frac{\sqrt{2}+1}{\sqrt{2}-1} - p^2\sqrt{2}\right] = -p^2 31.63 \tag{11.212}$$

where $a$ and $b$ are given by Eqs. (11.202) and (11.205), respectively. The total energy, which includes the proton-proton-repulsion term is negative which justifies the original treatment of the force balance using the analytical mechanics equation of an ellipse that considered only the binding force between the protons and the electrons and the electron centrifugal force. As shown by Eqs. (11.290) and (11.292), $T$ is one-half the magnitude of $V_e$ as required for an inverse-squared force [1] wherein $V_e$ is the source of $T$.

## VIBRATION OF HYDROGEN-TYPE MOLECULES

The vibrational energy levels of hydrogen-type molecules may be solved in the same manner as hydrogen-type molecular ions given in the Vibration of Hydrogen-type Molecular Ions section. The corresponding central force terms of Eq. (11.136) are:

$$f\left(a\right) = -\frac{pe^2}{8\pi\varepsilon_0 a^2} \tag{11.213}$$

and

$$f'\left(a\right) = \frac{pe^2}{4\pi\varepsilon_0 a^3} \tag{11.214}$$

The distance for the reactive nuclear-repulsive terms is given by the sum of the semimajor axis, $a$, and $c'$, 1/2 the internuclear distance. The contribution from the repulsive force between the two protons is:

$$f\left(a + c'\right) = \frac{pe^2}{8\pi\varepsilon_0\left(a + c'\right)^2} \tag{11.215}$$

and

$$f'\left(a + c'\right) = -\frac{pe^2}{4\pi\varepsilon_0\left(a + c'\right)^3} \tag{11.216}$$

Thus, from Eqs. (11.136) and (11.213-11.216), the angular frequency of the oscillation is:

$$\omega = \sqrt{\frac{\dfrac{pe^2}{8\pi\varepsilon_0 a^3} - \dfrac{pe^2}{8\pi\varepsilon_0\left(a + c'\right)^3}}{\mu}} = \sqrt{\frac{\dfrac{pe^2}{8\pi\varepsilon_0\left(\dfrac{a_0}{p}\right)^3} - \dfrac{pe^2}{8\pi\varepsilon_0\left(\dfrac{\left(1 + \dfrac{1}{\sqrt{2}}\right)a_0}{p}\right)^3}}{\mu}} = p^2 8.62385\ X\ 10^{14}\ rad/s \tag{11.217}$$

where the semimajor axis, $a$, is $a = \dfrac{a_0}{p}$ according to Eq. (11.202) and $c'$ is $c' = \dfrac{a_0}{p\sqrt{2}}$ according to Eq. (11.203). Thus, during bond formation, the perturbation of the orbit determined by an inverse-squared force results in simple harmonic oscillatory motion of the orbit, and the corresponding frequency, $\omega\left(0\right)$, for a hydrogen-type molecule $H_2\left(1/p\right)$ given by Eqs. (11.136) and (11.145) is:

$$\omega\left(0\right) = p^2\sqrt{\frac{k\left(0\right)}{\mu}} = p^2\sqrt{\frac{621.98\ Nm^{-1}}{\mu}} = p^2 8.62385\ X\ 10^{14}\ radians/s \tag{11.218}$$

where the reduced nuclear mass of hydrogen is given by Eq. (11.161) and the spring constant, $k(0)$, given by Eqs. (11.136) and (11.217) is:

$$k(0) = p^4 621.98\ Nm^{-1} \tag{11.219}$$

The transition-state vibrational energy, $E_{vib}(0)$, is given by Planck's equation (Eq. (11.127)):

$$E_{vib}(0) = \hbar\omega = \hbar p^2 8.62385\ X\ 10^{14}\ rad/s = p^2 0.56764\ eV \tag{11.220}$$

The amplitude of oscillation, $A_{reduced}(0)$, given by Eqs. (11.158), (11.161), and (11.219) is:

$$A_{reduced}(0) = \frac{\sqrt{\hbar}}{2^{3/2}\left(p^4 621.98\ Nm^{-1}\mu\right)^{1/4}} = \frac{4.275\ X\ 10^{-12}\ m}{p} = 0.08079\frac{a_0}{p} \tag{11.221}$$

Then, from Eq. (11.67), $A_{c'}(0)$, the displacement of $c'$ is the eccentricity $e$ given by Eq. (11.206) times $A_{reduced}(0)$ (Eq. (11.221)):

$$A_{c'}(0) = eA_{reduced}(0) = \frac{A_{reduced}(0)}{\sqrt{2}} = \frac{\sqrt{\hbar}}{4(k\mu)^{1/4}} = \frac{0.05713a_0}{p} \tag{11.222}$$

The spring constant and vibrational frequency for the formed molecule are then obtained from Eqs. (11.136) and (11.213-11.222) using the increases in the semimajor axis and internuclear distances due to vibration in the transition state. The vibrational energy, $E_{vib}(1)$, for the $H_2(1/p)$ $\upsilon = 1 \rightarrow \upsilon = 0$ transition given by adding $A_{c'}(0)$ (Eq. (11.222)) to the distances $a$ and $a + c'$ in Eqs. (11.213-11.220) is:

$$E_{vib}(1) = p^2 0.517\ eV \tag{11.223}$$

where $\upsilon$ is the vibrational quantum number. Using Eq. (11.176) with Eqs. (11.223) and (11.252), the anharmonic perturbation term, $\omega_0 x_0$, of $H_2(1/p)$ is

$$\omega_0 x_0 = \frac{100hc\left(8.06573X10^3\ \frac{cm^{-1}}{eV}\ p^2 0.517\ eV\right)^2}{4e\left(p^2 4.151\ eV + p^3 0.326469\ eV\right)} cm^{-1} \tag{11.224}$$

where $\omega_0$ is the frequency of the $\upsilon = 1 \rightarrow \upsilon = 0$ transition corresponding to Eq. (11.223) and $D_0$ is the bond dissociation energy given by Eq. (11.252). The vibrational energies of successive states are given by Eqs. (11.167) and (11.223-11.224).

Using the reduced nuclear mass given by Eq. (11.170), the corresponding parameters for deuterium-type molecules $D_2(1/p)$ (Eqs. (11.213-11.224) and (11.253)) are:

$$\omega(0) = p^2\sqrt{\frac{k(0)}{\mu}} = p^2\sqrt{\frac{621.98\ Nm^{-1}}{\mu}} = p^2 6.09798\ X\ 10^{14}\ radians/s \tag{11.225}$$

$$k(0) = p^4 621.98\ Nm^{-1} \tag{11.226}$$

$$E_{vib}(0) = p^2 0.4014\ eV \tag{11.227}$$

$$A_{reduced}(0) = \frac{\sqrt{\hbar}}{2^{3/2}\left(p^4 621.98\ Nm^{-1}\mu\right)^{1/4}} = \frac{3.595\ X\ 10^{-12}\ m}{p} = 0.06794\frac{a_0}{p} \tag{11.228}$$

$$E_{vib}(1) = p^2 0.371\ eV \tag{11.229}$$

$$\omega_0 x_0 = \frac{100hc\left(8.06573X10^3\ \frac{cm^{-1}}{eV}\ p^2 0.371\ eV\right)^2}{4e\left(p^2 4.229\ eV + p^3 0.326469\ eV\right)} cm^{-1} \tag{11.230}$$

The vibrational energies of successive states are given by Eqs. (11.167) and (11.229-11.230).

## THE DOPPLER ENERGY TERM OF HYDROGEN-TYPE MOLECULES

The radiation reaction force in the case of the vibration of the molecule in the transition state also corresponds to the Doppler energy, $E_D$, given by Eq. (11.181) that is dependent on the motion of the electrons and the nuclei. Here, a nonradiative state must also be achieved after the emission due to transient vibration wherein the nonradiative condition given by Eq. (11.24) must be satisfied. Typically, a third body is required to form hydrogen-type molecules. For example, the exothermic chemical reaction of $H+H$ to form $H_2$ does not occur with the emission of a photon. Rather, the reaction requires a collision with a third body, $M$, to remove the bond energy—$H+H+M \rightarrow H_2+M^*$ [23]. The third body distributes the energy from the exothermic reaction, and the end result is the $H_2$ molecule and an increase in the temperature of the system. Thus, a third body removes the energy corresponding to the additional force term given by Eq. (11.180). From Eqs. (11.200), (11.207) and (11.209), the central force terms between the electron MO and the two protons are:

$$f(a) = -\frac{pe^2}{4\pi\varepsilon_0 a^2} \tag{11.231}$$

and

$$f'(a) = \frac{2pe^2}{4\pi\varepsilon_0 a^3} \tag{11.232}$$

Thus, the angular frequency of this oscillation is:

$$\omega = \sqrt{\frac{\dfrac{pe^2}{4\pi\varepsilon_0 \left(\dfrac{a_0}{p}\right)^3}}{m_e}} = p^2 4.13414\ X\ 10^{16}\ rad/s \tag{11.233}$$

where the semimajor axis, $a$, is $a = \frac{a_0}{p}$ according to Eq. (11.202). The kinetic energy, $E_K$, is given by Planck's equation (Eq. (11.127)):

$$\overline{E}_K = \hbar\omega = \hbar p^2 4.13414\ X\ 10^{16}\ rad/s = p^2 27.2116\ eV \tag{11.234}$$

In Eq. (11.181), substitution of the total energy of the hydrogen molecule, $E_T$, (Eq. (11.212)) for $E_{h\nu}$, the mass of the electron, $m_e$, for $M$, and the kinetic energy given by Eq. (11.234) for $\overline{E}_K$ divided by $p^2$, the number of multipoles of a molecular hydrino state $p$ (Eq. (5.45)), gives the Doppler energy of the electrons for the reentrant orbit.

$$\overline{E}_D \cong E_{h\nu}\sqrt{\frac{2\overline{E}_K}{Mc^2}} = -31.635 p^2\ eV \sqrt{\frac{2e\left(p^2 27.2116\ eV\right)}{p^2 m_e c^2}} = -p^2 0.326469\ eV \tag{11.235}$$

The total energy of the molecule is decreased by $\overline{E}_D$.

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency given in the Vibration of Hydrogen-Type Molecules section. On average, the total energy of vibration is equally distributed between kinetic energy and potential energy [18]. Thus, the average kinetic energy of vibration corresponding to the Doppler energy of the electrons, $\overline{E}_{Kvib}$, is 1/2 of the vibrational energy of the molecule given by Eq. (11.148). The decrease in the energy of the hydrogen molecule due to the reentrant orbit in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei, $\overline{E}_{osc}$, is given by the sum of the corresponding energies, $\overline{E}_D$ and $\overline{E}_{Kvib}$. Using Eq. (11.235) and $E_{vib}$ from Eq. (11.220) gives:

$$\overline{E}_{osc} = \overline{E}_D + \overline{E}_{Kvib} = \overline{E}_D + \frac{1}{2}\hbar p^2 \sqrt{\frac{k}{\mu}} \tag{11.236}$$

$$\overline{E}_{osc} = -p^2 0.326469\ eV + \frac{1}{2} p^2 \left(0.56764\ eV\right) \tag{11.237}$$

To the extent that the MO dimensions are the same, the electron reentrant orbital energies, $\overline{E}_K$, are the same independent of the isotope of hydrogen, but the vibrational energies are related by Eq. (11.148). Thus, the differences in bond energies are essentially given by 1/2 the differences in vibrational energies. Using Eq. (11.235) and $E_{vib}$ for $D_2(1/p)$ given by Eq. (11.227), that corresponds to the deuterium reduced nuclear mass (Eq. (11.170)), the corresponding $\overline{E}_{osc}$ is:

$$\overline{E}_{osc} = -p^2 0.326469\ eV + \frac{1}{2} p^2 \left(0.401380\ eV\right) \tag{11.238}$$

## TOTAL, IONIZATION, AND BOND ENERGIES OF HYDROGEN AND DEUTERIUM MOLECULES

The total energy of the hydrogen molecule is given by the sum of $E_T$ (Eqs. (11.211-11.212)) and $\bar{E}_{osc}$ given in Eqs. (11.233-11.236). Thus, the total energy of the hydrogen molecule having a central field of $+pe$ at each focus of the prolate spheroid molecular orbital including the Doppler term is:

$$E_T = V_e + T + V_m + V_p + \bar{E}_{osc} \tag{11.239}$$

$$\begin{aligned} E_T &= -p^2 \left\{ \frac{e^2}{8\pi\varepsilon_0 a_0} \left[ \left( 2\sqrt{2} - \sqrt{2} + \frac{\sqrt{2}}{2} \right) \ln \frac{\sqrt{2}+1}{\sqrt{2}-1} - \sqrt{2} \right] \left[ 1 + \sqrt{\frac{2\hbar \sqrt{\dfrac{\dfrac{e^2}{4\pi\varepsilon_0 a_0^3}}{m_e}}}{m_e c^2}} \right] - \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \right\} \\ &= -p^2 31.635\ eV - p^2 0.326469\ eV + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \end{aligned} \tag{11.240}$$

From Eqs. (11.237) and (11.239-11.240), the total energy for hydrogen-type molecules is:

$$\begin{aligned} E_T &= -p^2 31.635\ eV + \bar{E}_{osc} \\ &= -p^2 31.635\ eV - p^2 0.326469\ eV + \frac{1}{2} p^2 \left( 0.56764\ eV \right) \\ &= -p^2 31.6775\ eV \end{aligned} \tag{11.241}$$

The total energy of the deuterium molecule is given by the sum of $E_T$ (Eq. (11.212)) and $\bar{E}_{osc}$ given by Eq. (11.238).

$$\begin{aligned} E_T &= -p^2 31.6354\ eV + \bar{E}_{osc} \\ &= -p^2 31.6354\ eV - p^2 0.326469\ eV + \frac{1}{2} p^2 \left( 0.401380\ eV \right) \\ &= -p^2 31.760\ eV \end{aligned} \tag{11.242}$$

The total energy, which includes the proton-proton-repulsion term is negative which justifies the original treatment of the force balance using the analytical mechanics equation of an ellipse that considered only the binding force between the protons and the electrons, the spin-pairing force, and the electron centrifugal force.

The first ionization energy of the hydrogen molecule, $IP_1$,

$$H_2(1/p) \to H_2^+(1/p) + e^- \tag{11.243}$$

is given by the difference of Eqs. (11.193) and (11.241).

$$\begin{aligned} IP_1 &= E_T\left(H_2^+(1/p)\right) - E_T\left(H_2(1/p)\right) \\ &= -p^2 16.2527\ eV - \left(-p^2 31.6775\ eV\right) \\ &= p^2 15.4248\ eV \end{aligned} \tag{11.244}$$

The second ionization energy, $IP_2$, is given by the negative of Eq. (11.193).

$$IP_2 = p^2 16.2527\ eV \tag{11.245}$$

The first ionization energy of the deuterium molecule, $IP_1$,

$$D_2(1/p) \to D_2^+(1/p) + e^- \tag{11.246}$$

is given by the difference of Eqs. (11.194) and (11.242).

$$\begin{aligned} IP_1 &= E_T\left(D_2^+(1/p)\right) - E_T\left(D_2(1/p)\right) \\ &= -p^2 16.2988\ eV - \left(-p^2 31.761\ eV\right) \\ &= p^2 15.4627\ eV \end{aligned} \tag{11.247}$$

The second ionization energy, $IP_2$, is given by the negative of Eq. (11.194).

$$IP_2 = p^2 16.2988\ eV \tag{11.248}$$

The bond dissociation energy, $E_D$, is the difference between the total energy of the corresponding hydrogen atoms and $E_T$

$$E_D = E(2H(1/p)) - E_T \tag{11.249}$$

where [19]:

$$E(2H(1/p)) = -p^2 27.20\ eV \tag{11.250}$$

and [20]:

$$E(2D(1/p)) = -p^2 27.206\ eV \tag{11.251}$$

The hydrogen bond energy, $E_D$, is given by Eqs. (11.249-11.250) and (11.241):

$$\begin{aligned} E_D &= -p^2 27.20\ eV - E_T \\ &= -p^2 27.20\ eV - \left(-p^2 31.677\ eV\right) \\ &= p^2 4.478\ eV \end{aligned} \tag{11.252}$$

The deuterium bond energy, $E_D$, is given by Eqs. (11.249), (11.251), and (11.242):

$$\begin{aligned} E_D &= -p^2 27.206\ eV - E_T \\ &= -p^2 27.206\ eV - \left(-p^2 31.760\ eV\right) \\ &= p^2 4.556\ eV \end{aligned} \tag{11.253}$$

# THE HYDROGEN MOLECULAR ION $\mathbf{H_2\left[2c'=2a_0\right]^+}$

## FORCE BALANCE OF HYDROGEN MOLECULAR ION

Force balance between the electric and centrifugal forces is given by Eq. (11.115) where $p=1$

$$\frac{\hbar^2}{m_e a^2 b^2} D = \frac{e^2}{8\pi\varepsilon_0 a b^2} D \tag{11.254}$$

which has the parametric solution given by Eq. (11.83) when:

$$a = 2a_0 \tag{11.255}$$

The semimajor axis, $a$, is also given by Eq. (11.116) where $p=1$. The internuclear distance, $2c'$, which is the distance between the foci is given by Eq. (11.111) where $p=1$.

$$2c' = 2a_0 \tag{11.256}$$

The experimental internuclear distance is $2a_o$. The semiminor axis is given by Eq. (11.112) where $p=1$.

$$b = \sqrt{3}a_0 \tag{11.257}$$

The eccentricity, $e$, is given by Eq. (11.113).

$$e = \frac{1}{2} \tag{11.258}$$

## ENERGIES OF THE HYDROGEN MOLECULAR ION

The potential energy, $V_e$, of the electron MO in the field of the protons at the foci ($\xi = 0$) is given by Eq. (11.117) where $p=1$

$$V_e = \frac{-4e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}} \ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} \tag{11.259}$$

The potential energy, $V_p$, due to proton-proton repulsion is given by Eq. (11.120) where $p=1$

$$V_p = \frac{e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}} \tag{11.260}$$

The kinetic energy, $T$, of the electron MO is given by Eq. (11.119) where $p=1$

$$T = \frac{2\hbar^2}{m_e a\sqrt{a^2-b^2}} \ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} \tag{11.261}$$

Substitution of $a$ and $b$ given by Eqs. (11.255) and (11.257), respectively, into Eqs. (11.259-11.261) is:

$$V_e = \frac{-4e^2}{8\pi\varepsilon_0 a_H} \ln 3 = -59.7575\ eV \tag{11.262}$$

$$V_p = \frac{e^2}{8\pi\varepsilon_0 a_H} = 13.5984\ eV \tag{11.263}$$

$$T = \frac{2e^2}{8\pi\varepsilon_0 a_H} \ln 3 = 29.8787\ eV \tag{11.264}$$

The Doppler term, $\bar{E}_{osc}$, for hydrogen and deuterium are given by Eqs. (11.189) and (11.190), respectively, where $p=1$

$$\bar{E}_{osc}\left(H_2^+\right) = \bar{E}_D + \bar{E}_{Kvib} = -0.118755\ eV + \frac{1}{2}\left(0.29282\ eV\right) = 0.027655\ eV \tag{11.265}$$

$$\bar{E}_{osc}\left(D_2^+\right) = -0.118811\ eV + \frac{1}{2}\left(0.20714\ eV\right) = -0.01524\ eV \tag{11.266}$$

The total energy, $E_T$, for the hydrogen molecular ion given by Eqs. (11.191-11.193) is:

$$\begin{aligned} E_T &= -\left\{ \frac{e^2}{8\pi e_0 a_H}(4\ln 3 - 1 - 2\ln 3)\left[1 + \sqrt{\frac{2\hbar\sqrt{\dfrac{\dfrac{2e^2}{4\pi\varepsilon_0\left(2a_H\right)^3}}{m_e}}}{m_e c^2}}\right] - \frac{1}{2}\hbar\sqrt{\frac{k}{m}} \right\} \\ &= -16.2803\ eV - 0.118755\ eV + \frac{1}{2}\left(0.29282\ eV\right) \\ &= -16.2527\ eV \end{aligned} \tag{11.267}$$

where in Eqs. (11.262-11.267), the radius of the hydrogen atom $a_H$ (Eq. (1.259)) was used in place of $a_0$ to account for the corresponding electrodynamic force between the electron and the nuclei as given in the case of the hydrogen atom by Eq. (1.252). The negative of Eq. (11.267) is the ionization energy of $H_2^+$ and the second ionization energy, $IP_2$, of $H_2$. From Eqs. (11.191-11.192) and (11.194), the total energy, $E_T$, for the deuterium molecular ion (the ionization energy of $D_2^+$ and the second ionization energy, $IP_2$, of $D_2$) is:

$$E_T = -16.284\ eV - 0.118811\ eV + \frac{1}{2}\left(0.20714\ eV\right) = -16.299\ eV \tag{11.268}$$

The bond dissociation energy, $E_D$, is the difference between the total energy of the corresponding hydrogen atom and $E_T$. The hydrogen molecular ion bond energy, $E_D$, including the reduced electron mass given by Eq. (11.198) where $p = 1$ is

$$E_D = 2.535\ eV + 0.118755\ eV = 2.654\ eV \tag{11.269}$$

The experimental bond energy of the hydrogen molecular ion [24] is:

$$E_D = 2.651\ eV \tag{11.270}$$

From Eq. (11.199) where $p = 1$, the deuterium molecular ion bond energy, $E_D$, including the reduced electron mass of $D$ is

$$E_D = 2.5770\ eV + 0.118811\ eV = 2.6958\ eV \tag{11.271}$$

The experimental bond energy of the deuterium molecular ion [25] is:

$$E_D = 2.691\ eV \tag{11.272}$$

## VIBRATION OF THE HYDROGEN MOLECULAR ION

It can be shown that a perturbation of the orbit determined by an inverse-squared force results in simple harmonic oscillatory motion of the orbit [11]. The resonant vibrational frequency for $H_2^+$ given by Eq. (11.160) is:

$$\omega(0) = \sqrt{\frac{k(0)}{\mu}} = \sqrt{\frac{165.51\ Nm^{-1}}{\mu}} = 4.449\ X\ 10^{14}\ radians/s \tag{11.273}$$

wherein $p = 1$. The spring constant, $k(0)$, for $H_2^+$ given by Eq. (11.162) is:

$$k(0) = 165.51\ Nm^{-1} \tag{11.274}$$

The vibrational energy, $E_{vib}(0)$, of $H_2^+$ during bond formation given by Eq. (11.163) is:

$$E_{vib}(0) = 0.29282\ eV \tag{11.275}$$

The amplitude of oscillation given by Eq. (11.164) is:

$$A(0) = \frac{\sqrt{\hbar}}{2^{3/2}\left(165.51\ Nm^{-1}\mu\right)^{1/4}} = 5.952\ X\ 10^{-12}\ m = 0.1125 a_o \tag{11.276}$$

The vibrational energy for the $H_2^+$ $\upsilon = 1 \rightarrow \upsilon = 0$ transition given by Eq. (11.166) is:

$$E_{vib}(1) = 0.270\ eV \tag{11.277}$$

The experimental vibrational energy of $H_2^+$ [14, 20] is:

$$E_{vib} = 0.271\ eV \tag{11.278}$$

The anharmonicity term of $H_2^+$ given by Eq. (11.169) is:

$$\omega_0 x_0 = 55.39\ cm^{-1} \tag{11.279}$$

The experimental anharmonicity term of $H_2^+$ from NIST [20] is:

$$\omega_e x_e = 66.2\ cm^{-1} \tag{11.280}$$

The vibrational energy for the $D_2^+$ $\upsilon=1\rightarrow\upsilon=0$ transition given by Eq. (11.175) is:

$$E_{vib}=0.193\ eV \tag{11.281}$$

The vibrational energy of the $D_2^+$ [20] based on calculations from experimental data is:

$$E_{vib}=0.196\ eV \tag{11.282}$$

The anharmonicity term of $D_2^+$ given by Eq. (11.176) is:

$$\omega_0 x_0=27.86\ cm^{-1} \tag{11.283}$$

The experimental anharmonicity term of $D_2^+$ for the state $X\ {}^2\sum_g{}^{+1}s\sigma$ is not given, but the term for state $B\ {}^2\sum_g{}^{+3}d\sigma$ from NIST [20] is:

$$\omega_e x_e=2.62\ cm^{-1} \tag{11.284}$$

# THE HYDROGEN MOLECULE $\mathbf{H_2\left[2c'=\sqrt{2}a_0\right]}$

## FORCE BALANCE OF THE HYDROGEN MOLECULE

The force balance equation for the hydrogen molecule is given by Eq. (11.200) where $p=1$

$$\frac{\hbar^2}{m_e a^2 b^2}D=\frac{e^2}{8\pi\varepsilon_0 ab^2}D+\frac{\hbar^2}{2m_e a^2 b^2}D \tag{11.285}$$

which has the parametric solution given by Eq. (11.83) when,

$$a=a_0 \tag{11.286}$$

The semimajor axis, $a$, is also given by Eq. (11.202) where $p=1$. The internuclear distance, $2c'$, which is the distance between the foci is given by Eq. (11.204) where $p=1$.

$$2c'=\sqrt{2}a_0 \tag{11.287}$$

The experimental internuclear distance is $\sqrt{2}a_0$. The semiminor axis is given by Eq. (11.205) where $p=1$.

$$b=\frac{1}{\sqrt{2}}a_0 \tag{11.288}$$

The eccentricity, $e$, is given by Eq. (11.206).

$$e=\frac{1}{\sqrt{2}} \tag{11.289}$$

The finite dimensions of the hydrogen molecule are evident in the plateau of the resistivity versus pressure curve of metallic hydrogen [26].

## ENERGIES OF THE HYDROGEN MOLECULE

The energies of the hydrogen molecule are given by Eqs. (11.207-11.210) where $p=1$

$$V_e=\frac{-2e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}}=-67.8358\ eV \tag{11.290}$$

$$V_p=\frac{e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}}=19.2415\ eV \tag{11.291}$$

$$T=\frac{\hbar^2}{2m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}}=33.9179\ eV \tag{11.292}$$

The energy, $V_m$, of the magnetic force is

$$V_m=\frac{-\hbar^2}{4m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}}=-16.9589\ eV \tag{11.293}$$

The Doppler terms, $\bar{E}_{osc}$, for hydrogen and deuterium molecules are given by Eqs. (11.237) and (11.238), respectively, where $p=1$

$$\bar{E}_{osc}(H_2)=\bar{E}_D+\bar{E}_{Kvib}=-0.326469\ eV+\frac{1}{2}(0.56764\ eV)=-0.042649\ eV \tag{11.294}$$

$$\bar{E}_{osc}\left(D_2\right) = -0.326469\ eV + \frac{1}{2}\left(0.401380\ eV\right) = -0.125779\ eV \tag{11.295}$$

The total energy, $E_T$, for the hydrogen molecule given by Eqs. (11.239-11.241) is

$$\begin{aligned} E_T &= -\left\{ \begin{array}{l} \\ \dfrac{e^2}{8\pi\varepsilon_0 a_0}\left[\left(2\sqrt{2}-\sqrt{2}+\dfrac{\sqrt{2}}{2}\right)\ln\dfrac{\sqrt{2}+1}{\sqrt{2}-1}-\sqrt{2}\right]\left[1+\sqrt{\dfrac{2\hbar\sqrt{\dfrac{\dfrac{e^2}{4\pi\varepsilon_0 a_0^3}}{m_e}}}{m_e c^2}}\right]-\dfrac{1}{2}\hbar\sqrt{\dfrac{k}{\mu}} \end{array} \right\} \\ &= -31.635\ eV - 0.326469\ eV + \frac{1}{2}\left(0.56764\ eV\right) \\ &= -31.6776\ eV \end{aligned} \tag{11.296}$$

From Eqs. (11.239-11.240) and (11.242), the total energy, $E_T$, for the deuterium molecule is:

$$E_T = -31.635\ eV - 0.326469\ eV + \frac{1}{2}\left(0.401380\ eV\right) = -31.7608\ eV \tag{11.297}$$

The first ionization energies of the hydrogen and deuterium molecules, $IP_1$, (Eqs. (11.243) and (11.246)) are given by the differences in the total energy of corresponding molecular ions and molecules which are given by Eqs. (11.244) and (11.247), respectively, where $p = 1$:

$$IP_1\left(H_2\right) = 15.4248\ eV \tag{11.298}$$

$$IP_1\left(D_2\right) = 15.4627\ eV \tag{11.299}$$

The bond dissociation energy, $E_D$, is the difference between the total energy of two of the corresponding hydrogen atoms and $E_T$. The hydrogen molecular bond energy, $E_D$, given by Eq. (11.252) where $p = 1$ is:

$$E_D = 4.478\ eV \tag{11.300}$$

The experimental bond energy of the hydrogen molecule [23] is:

$$E_D = 4.478\ eV \tag{11.301}$$

The deuterium molecular bond energy, $E_D$, given by Eq. (11.253) where $p = 1$ is:

$$E_D = 4.556\ eV \tag{11.302}$$

The experimental bond energy of the deuterium molecule [23] is:

$$E_D = 4.556\ eV \tag{11.303}$$

## VIBRATION OF THE HYDROGEN MOLECULE

It can be shown that a perturbation of the orbit determined by an inverse-squared force results in simple harmonic oscillatory motion of the orbit [11]. The resonant vibrational frequency for $H_2$ given by Eq. (11.218) is:

$$\omega(0) = \sqrt{\frac{k(0)}{\mu}} = \sqrt{\frac{621.98\ Nm^{-1}}{\mu}} = 8.62385\ X\ 10^{14}\ radians/s \tag{11.304}$$

The spring constant, $k(0)$, for $H_2$ given by Eq. (11.219) is:

$$k(0) = 621.98\ Nm^{-1} \tag{11.305}$$

wherein $p = 1$. The vibrational energy, $E_{vib}(0)$, of $H_2$ during bond formation given by Eq. (11.220) is:

$$E_{vib}(0) = 0.56764\ eV \tag{11.306}$$

The amplitude of oscillation given by Eq. (11.221) is:

$$A(0) = \frac{\sqrt{\hbar}}{2^{3/2}\left(621.98\ Nm^{-1}\mu\right)^{1/4}} = 4.275\ X\ 10^{-12}\ m = 0.08079 a_o \tag{11.307}$$

The vibrational energy for the $H_2$ $\upsilon = 1 \rightarrow \upsilon = 0$ transition given by Eq. (11.223) is:

$$E_{vib}(1) = 0.517\ eV \tag{11.308}$$

The experimental vibrational energy of $H_2$ [27-28] is:

$$E_{vib}\left(1\right) = 0.5159\ eV \tag{11.309}$$

The anharmonicity term of $H_2$ given by Eq. (11.224) is:

$$\omega_0 x_0 = 120.4\ cm^{-1} \tag{11.310}$$

The experimental anharmonicity term of $H_2$ from Huber and Herzberg [25] is:

$$\omega_e x_e = 121.33\ cm^{-1} \tag{11.311}$$

The vibrational energy for the $D_2$ $\upsilon = 1 \rightarrow \upsilon = 0$ transition given by Eq. (11.229) is:

$$E_{vib} = 0.371\ eV \tag{11.312}$$

The experimental vibrational energy of $D_2$ [14, 20] is:

$$E_{vib} = 0.371\ eV \tag{11.313}$$

The anharmonicity term of $D_2$ given by Eq. (11.230) is:

$$\omega_0 x_0 = 60.93\ cm^{-1} \tag{11.314}$$

The experimental anharmonicity term of $D_2$ from NIST [20] is:

$$\omega_e x_e = 61.82\ cm^{-1} \tag{11.315}$$

The results of the determination of the bond, vibrational, total, and ionization energies, and internuclear distances for hydrogen and deuterium molecules and molecular ions are given in Table 11.1. The calculated results are based on first principles and given in closed form equations containing fundamental constants only. The agreement between the experimental and calculated results is excellent.

Despite the predictions of standard quantum mechanics that preclude the imaging of a molecule orbital, the full three-dimensional structure of the outer molecular orbital of $N_2$ has been recently tomographically reconstructed [29]. The charge-density surface observed is similar to that shown in Figure 11.6 for $H_2$ which is direct evidence that electrons are not point-particle probability waves that have no form until they are “collapsed to a point” by measurement. Rather they are physical, two-dimensional equipotential charge density surfaces.

Table 11.1. The calculated and experimental parameters of $H_2$, $D_2$, $H_2^+$ and $D_2^+$.

| Parameter | Calculated | Experimental | Eqs. | Ref. for Exp. |
|---|---|---|---|---|
| $H_2$ Bond Energy | 4.478 $eV$ | 4.478 $eV$ | 11.300 | 24 |
| $D_2$ Bond Energy | 4.556 $eV$ | 4.556 $eV$ | 11.302 | 24 |
| $H_2^+$ Bond Energy | 2.654 $eV$ | 2.651 $eV$ | 11.269 | 24 |
| $D_2^+$ Bond Energy | 2.696 $eV$ | 2.691 $eV$ | 11.271 | 25 |
| $H_2$ Total Energy | 31.677 $eV$ | 31.675 $eV$ | 11.296 | 24, 30, 19[a] |
| $D_2$ Total Energy | 31.760 $eV$ | 31.760 $eV$ | 11.297 | 20, 25[b] |
| $H_2$ Ionization Energy | 15.425 $eV$ | 15.426 $eV$ | 11.298 | 30 |
| $D_2$ Ionization Energy | 15.463 $eV$ | 15.466 $eV$ | 11.299 | 25 |
| $H_2^+$ Ionization Energy | 16.253 $eV$ | 16.250 $eV$ | 11.267 | 24, 19[c] |
| $D_2^+$ Ionization Energy | 16.299 $eV$ | 16.294 $eV$ | 11.268 | 20, 25[d] |
| $H_2^+$ Spin Magnetic Moment | $0.5\mu_B$ | $0.5\mu_B$ | 12.24 | 31 |
| Absolute $H_2$ Gas-Phase NMR Shift | -28.0 ppm | -28.0 ppm | 11.416 | 32-33 |
| $H_2$ Quadrupole Moment | 0.4764 X $10^{-16}$ cm$^2$ | 0.38 0.15 X $10^{-16}$ cm$^2$ | 11.430-11.431 | 46 |
| $H_2$ Internuclear Distance | 0.7411 Å | 0.741 Å | 12.75 | 34 |
| $D_2$ Internuclear Distance | 0.7411 Å | 0.741 Å | 12.75 | 34 |
| $H_2^+$ Internuclear Distance | 1.0577 Å | 1.06 Å | 12.81 | 24 |
| $D_2^+$ Internuclear Distance | 1.0577 Å | 1.0559 Å | 12.81 | 25 |
| $H_2$ Vibrational Energy | 0.517 $eV$ | 0.516 $eV$ | 11.308 | 27, 28 |
| $D_2$ Vibrational Energy | 0.371 $eV$ | 0.371 $eV$ | 11.313 | 14, 20 |
| $H_2$ $\omega_e x_e$ | 120.4 $cm^{-1}$ | 121.33 $cm^{-1}$ | 11.310 | 25 |
| $D_2$ $\omega_e x_e$ | 60.93 $cm^{-1}$ | 61.82 $cm^{-1}$ | 11.314 | 20 |
| $H_2^+$ Vibrational Energy | 0.270 $eV$ | 0.271 $eV$ | 11.277 | 14, 20 |
| $D_2^+$ Vibrational Energy | 0.193 $eV$ | 0.196 $eV$ | 11.281 | 20 |
| $H_2$ J=1 to J=0 Rotational Energy | 0.01511 $eV$ | 0.01509 $eV$ | 12.77 | 24 |
| $D_2$ J=1 to J=0 Rotational Energy | 0.007557 $eV$ | 0.00755 $eV$ | 12.78 | 24 |
| $H_2^+$ J=1 to J=0 Rotational Energy | 0.00742 $eV$ | 0.00739 $eV$ | 12.83 | 24 |
| $D_2^+$ J=1 to J=0 Rotational Energy | 0.0037095 $eV$ | 0.003723 $eV$ | 12.84 | 25 |

[a] The experimental total energy of the hydrogen molecule is given by adding the first (15.42593 $eV$) [30] and second (16.2494 $eV$) ionization energies where the second ionization energy is given by the addition of the ionization energy of the hydrogen atom (13.59844 $eV$) [19] and the bond energy of $H_2^+$ (2.651 $eV$) [24].

[b] The experimental total energy of the deuterium molecule is given by adding the first (15.466 $eV$) [25] and second (16.294 $eV$) ionization energies where the second ionization energy is given by the addition of the ionization energy of the deuterium atom (13.603 $eV$) [20] and the bond energy of $D_2^+$ (2.692 $eV$) [25].

[c] The experimental second ionization energy of the hydrogen molecule, $IP_2$, is given by the sum of the ionization energy of the hydrogen atom (13.59844 $eV$) [19] and the bond energy of $H_2^+$ (2.651 $eV$) [24].

[d] The experimental second ionization energy of the deuterium molecule, $IP_2$, is given by the sum of the ionization energy of the deuterium atom (13.603 $eV$) [20] and the bond energy of $D_2^+$ (2.692 $eV$) [25].

## THE DIHYDRINO MOLECULAR ION $\mathbf{H_2\left[2c'=a_0\right]^+}$

### FORCE BALANCE OF THE DIHYDRINO MOLECULAR ION

Force balance between the electric and centrifugal forces of $H_2^+(1/2)$ is given by Eq. (11.115) where $p=2$

$$\frac{\hbar^2}{m_e a^2 b^2}D = \frac{2e^2}{8\pi\varepsilon_0 ab^2}D \tag{11.316}$$

which has the parametric solution given by Eq. (11.83) when:

$$a = a_0 \tag{11.317}$$

The semimajor axis, $a$, is also given by Eq. (11.116) where $p=2$. The internuclear distance, $2c'$, which is the distance between the foci is given by Eq. (11.111) where $p=2$.

$$2c' = a_0 \tag{11.318}$$

The semiminor axis is given by Eq. (11.112) where $p=2$.

$$b = \frac{\sqrt{3}}{2}a_0 \tag{11.319}$$

The eccentricity, $e$, is given by Eq. (11.113).

$$e = \frac{1}{2} \tag{11.320}$$

### ENERGIES OF THE DIHYDRINO MOLECULAR ION

The potential energy, $V_e$, of the electron MO in the field of magnitude twice that of the protons at the foci ($\xi = 0$) is given by Eq. (11.117) where $p=2$

$$V_e = \frac{-8e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} \tag{11.321}$$

The potential energy, $V_p$, due to proton-proton repulsion in the field of magnitude twice that of the protons at the foci ($\xi = 0$) is given by Eq. (11.120) where $p=2$

$$V_p = \frac{2e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}} \tag{11.322}$$

The kinetic energy, $T$, of the electron MO is given by Eq. (11.119) where $p=2$

$$T = \frac{2\hbar^2}{m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} \tag{11.323}$$

Substitution of $a$ and $b$ given by Eqs. (11.317) and (11.319), respectively, into Eqs. (11.321-11.323) and using Eqs. (11.191-11.193) with $p=2$ gives:

$$V_e = \frac{-16e^2}{8\pi\varepsilon_0 a_0}\ln 3 = -239.16\ eV \tag{11.324}$$

$$V_p = \frac{4e^2}{8\pi\varepsilon_0 a_0} = 54.42\ eV \tag{11.325}$$

$$T = \frac{8e^2}{8\pi\varepsilon_0 a_0}\ln 3 = 119.58\ eV \tag{11.326}$$

$$E_T = V_e + V_p + T + \bar{E}_{osc} \tag{11.327}$$

$$\begin{aligned} E_T &= -2^2\left\{ \frac{e^2}{8\pi\varepsilon_0 a_H}(4\ln 3 - 1 - 2\ln 3)\left[1+\sqrt{\frac{2\hbar\sqrt{\frac{\frac{2e^2}{4\pi\varepsilon_0(2a_H)^3}}{m_e}}}{p^2 m_e c^2}}\right] - \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \right\} \\ &= -2^2(16.2527\ eV) = -65.01\ eV \end{aligned} \tag{11.328}$$

where Eqs. (11.324-11.326) are equivalent to Eqs. (11.122-11.124) with $p=2$. The bond dissociation energy, $E_D$, given by Eq. (11.198) with $p=2$ is the difference between the total energy of the corresponding hydrino atom and $E_T$ given by Eq. (11.328):

$$E_D = E_T(H(1/p)) - E_T(H_2^+(1/p)) = 2^2(2.654\ eV) = 10.62\ eV \tag{11.329}$$

## VIBRATION OF THE DIHYDRINO MOLECULAR ION

It can be shown that a perturbation of the orbit determined by an inverse-squared force results in simple harmonic oscillatory motion of the orbit [11]. The resonant vibrational frequency for $H_2^+(1/2)$ from Eq. (11.160) is:

$$\omega(0) = 2^2\sqrt{\frac{165.51\ Nm^{-1}}{\mu}} = 1.78\ X\ 10^{15}\ radians/s \tag{11.330}$$

wherein $p=2$. The spring constant, $k(0)$, for $H_2^+(1/2)$ from Eq. (11.162) is:

$$k(0) = 2^4 165.51\ Nm^{-1} = 2648\ Nm^{-1} \tag{11.331}$$

The amplitude of oscillation from Eq. (11.164) is:

$$A(0) = \frac{\sqrt{\hbar}}{2^{3/2}\left(2^4(165.51)\ Nm^{-1}\mu\right)^{1/4}} = \frac{5.952\ X\ 10^{-12}\ m}{2} = \frac{0.1125a_o}{2} \tag{11.332}$$

The vibrational energy, $E_{vib}(1)$, for the $\upsilon = 1 \to \upsilon = 0$ transition given by Eq. (11.166) is:

$$E_{vib}(1) = 2^2(0.270\ eV) = 1.08\ eV \tag{11.333}$$

# THE DIHYDRINO MOLECULE $\mathbf{H_2\left[2c' = \frac{a_0}{\sqrt{2}}\right]}$

## FORCE BALANCE OF THE DIHYDRINO MOLECULE

The force balance equation for the dihydrino molecule $H_2(1/2)$ is given by Eq. (11.200) where $p=2$

$$\frac{\hbar^2}{m_e a^2 b^2}D = \frac{2e^2}{8\pi\varepsilon_0 a b^2}D + \frac{\hbar^2}{2m_e a^2 b^2}D \tag{11.334}$$

which has the parametric solution given by Eq. (11.83) when

$$a = \frac{a_0}{2} \tag{11.335}$$

The semimajor axis, $a$, is also given by Eq. (11.202) where $p=2$. The internuclear distance, $2c'$, which is the distance between the foci is given by Eq. (11.204) where $p=2$.

$$2c' = \frac{1}{\sqrt{2}}a_0 \tag{11.336}$$

The semiminor axis is given by Eq. (11.205) where $p=2$.

$$b = c = \frac{1}{2\sqrt{2}}a_0 \tag{11.337}$$

The eccentricity, $e$, is given by Eq. (11.206).

$$e = \frac{1}{\sqrt{2}} \tag{11.338}$$

## ENERGIES OF THE DIHYDRINO MOLECULE

The energies of the dihydrino molecule $H_2(1/2)$ are given by Eqs. (11.207-11.210) and Eqs. (11.239-11.241) with $p=2$

$$V_e = \frac{-4e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -271.34\ eV \tag{11.339}$$

$$V_p = \frac{2}{8\pi\varepsilon_0}\frac{e^2}{\sqrt{a^2-b^2}} = 76.97\ eV \tag{11.340}$$

$$T = \frac{\hbar^2}{2m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = 135.67\ eV \tag{11.341}$$

The energy, $V_m$, of the magnetic force is

$$V_m = \frac{-\hbar^2}{4m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -67.84\ eV \tag{11.342}$$

$$E_T = V_e + T + V_m + V_p + \bar{E}_{osc} \tag{11.343}$$

$$\begin{aligned} E_T &= -2^2 \left\{ \begin{array}{l} \dfrac{e^2}{8\pi\varepsilon_0 a_0}\left[\left(2\sqrt{2}-\sqrt{2}+\dfrac{\sqrt{2}}{2}\right)\ln\dfrac{\sqrt{2}+1}{\sqrt{2}-1}-\sqrt{2}\right]\left[1+\sqrt{\dfrac{2\hbar\sqrt{\dfrac{\dfrac{e^2}{4\pi\varepsilon_0 a_0^3}}{m_e}}}{p^2 m_e c^2}}\right]-\dfrac{1}{2}\hbar\sqrt{\dfrac{k}{\mu}} \end{array} \right\} \\ &= -2^2\left(31.677\ eV\right) \\ &= -126.71\ eV \end{aligned} \qquad (11.344)$$

where Eqs. (11.339-11.342) are equivalent to Eqs. (11.207-11.210) with $p = 2$. The bond dissociation energy, $E_D$, given by Eq. (11.252) with $p = 2$ is the difference between the total energy of the corresponding hydrino atoms and $E_T$ given by Eq. (11.344).

$$E_D = E_T(2H(1/p)) - E_T(H_2(1/p)) = 2^2\left(4.478\ eV\right) = 17.91\ eV \qquad (11.345)$$

## VIBRATION OF THE DIHYDRINO MOLECULE

It can be shown that a perturbation of the orbit determined by an inverse-squared force results in simple harmonic oscillatory motion of the orbit [11]. The resonant vibrational frequency for the $H_2(1/2)$ from Eq. (11.218) is

$$\omega(0) = 2^2\sqrt{\frac{k}{\mu}} = 2^2\sqrt{\frac{621.98\ Nm^{-1}}{\mu}} = 3.45\ X\ 10^{15}\ radians/s \qquad (11.346)$$

wherein $p = 2$. The spring constant, $k(0)$, for $H_2(1/2)$ from Eq. (11.219) is:

$$k(0) = 2^4 621.98\ Nm^{-1} = 9952\ Nm^{-1} \qquad (11.347)$$

The amplitude of oscillation from Eq. (11.221) is:

$$A(0) = \frac{\sqrt{\hbar}}{2^{3/2}\left(2^4\left(621.98\right)\ Nm^{-1}\mu\right)^{1/4}} = \frac{4.275\ X\ 10^{-12}\ m}{2} = \frac{0.08079 a_o}{2} \qquad (11.348)$$

The vibrational energy, $E_{vib}(1)$, of $H_2(1/2)$ from Eq. (11.223) is:

$$E_{vib}(1) = 2^2\left(0.517\right)\ eV = 2.07\ eV \qquad (11.349)$$

## GEOMETRY

The internuclear distance can also be determined geometrically. The spheroidal MO of the hydrogen molecule is an equipotential energy surface, which is an energy minimum surface. For the hydrogen molecule, the electric field is zero for $\xi > 0$. Consider two hydrogen atoms A and B approaching each other. Consider that the two electrons form a spheroidal MO as the two atoms overlap, and the charge is distributed such that an equipotential two-dimensional surface is formed. The electric fields of atoms A and B add vectorially as the atoms overlap. The energy at the point of intersection of the overlapping atomic orbitals decreases to a minimum as they superimpose and then rises with further overlap. When this energy is a minimum the internuclear distance is determined. It can be demonstrated [35] that when two hydrogen atomic orbitals superimpose such that the radial electric field vector from nucleus A and B makes a 45° angle with the point of intersection of the two original atomic orbitals, the electric energy of interaction between atomic orbitals given by

$$E_{\text{interaction}} = 2\ X\ \frac{1}{2}\varepsilon_0\int \Delta\mathbf{E}^2 dv \qquad (11.350)$$

is a minimum (Figure 7.1 of [35]). The MO is a minimum potential energy surface; therefore, a minimum of energy of one point on the surface is a minimum for the entire surface of the MO. Thus,

$$R_{H_2} = \sqrt{2}a_0 = 0.748\mathring{A} \qquad (11.351)$$

The experimental internuclear bond distance is $0.746\ \mathring{A}$.

## DIHYDRINO IONIZATION ENERGIES

The first ionization energy, $IP_1$, of the dihydrino molecule

$$H_2(1/p) \to H_2^+(1/p) + e^- \tag{11.352}$$

is given by Eq. (11.244) with $p = 2$.

$$IP_1 = E_T\left(H_2^+(1/p)\right) - E_T\left(H_2(1/p)\right) \tag{11.353}$$

$$IP_1 = 2^2(15.4248\ eV) = 61.70\ eV \tag{11.354}$$

The second ionization energy, $IP_2$, is given by Eq. (11.245) with $p = 2$.

$$IP_2 = 2^2(16.2527\ eV) = 65.01\ eV \tag{11.355}$$

A hydrino atom can react with a hydrogen, deuterium, or tritium nucleus to form a dihydrino molecular ion that further reacts with an electron to form a dihydrino molecule.

$$H(1/p) + H^+ + e- \to H_2(1/p) \tag{11.356}$$

The energy released is

$$E = E(H(1/p)) - E_T \tag{11.357}$$

where $E_T$ is given by Eq. (11.241).

A hydrino atom can react with a hydrogen, deuterium, or tritium atom to form a dihydrino molecule.

$$H(1/p) + H \to H_2(1/p) \tag{11.358}$$

The energy released is

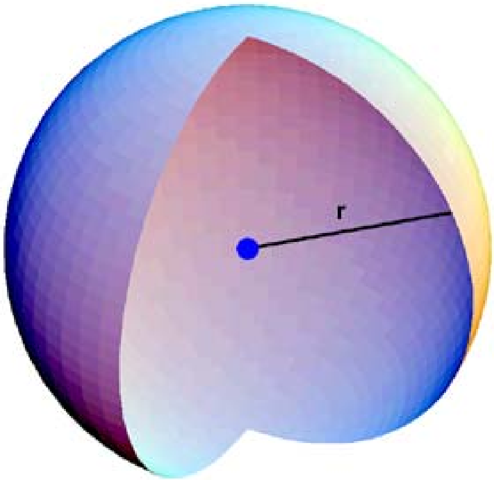
$$E = E\left(H(1/p)\right) + E(H) - E_T \tag{11.359}$$

where $E_T$ is given by Eq. (11.241).

## SIZES OF REPRESENTATIVE ATOMS AND MOLECULES

### ATOMS

Figure 11.5. Cross-section of an atomic orbital.



#### Helium Atom (He)

Helium comprises the nucleus at the origin and two electrons as a spherical shell at $r = 0.567a_0$.

#### Hydrogen Atom ($\mathbf{H}[\mathbf{a_H}]$)

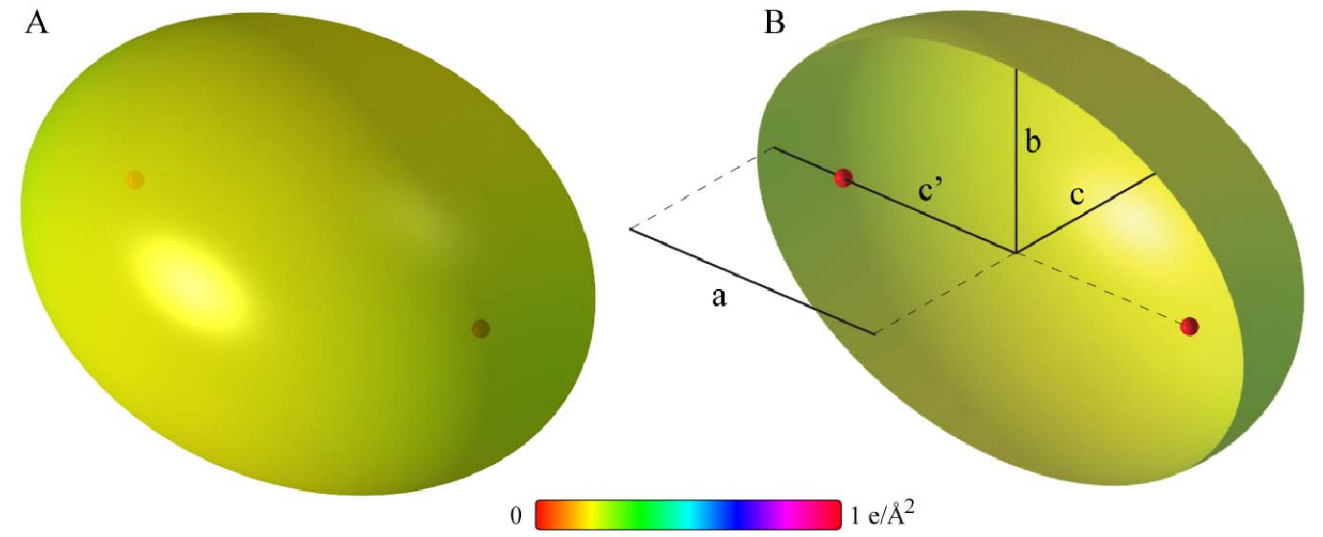
Hydrogen comprises the nucleus at the origin and the electron as a spherical shell at $r = a_H$.

#### Hydrino Atom ($\mathbf{H}\left[\frac{\mathbf{a_H}}{\mathbf{2}}\right]$)

Hydrino atom (1/2) comprises the nucleus at the origin and the electron as a spherical shell at $r = \frac{a_H}{2}$.

## MOLECULES

Figure 11.6. **A**. Prolate spheroid MO. **B**. Prolate spheroid parameters of molecules and molecular ions where $a$ is the semimajor axis, $2a$ is the total length of the molecule or molecular ion along the principal axis, $b = c$ is the semiminor axis, $2b = 2c$ is the total width of the molecule or molecular ion along the minor axis, $c'$ is the distance from the origin to a focus (nucleus), $2c'$ is the internuclear distance, and the protons are at the foci.



### Hydrogen Molecular Ion ($\mathbf{H_2[2c'=2a_0]^+}$)

$$a = 2a_0$$

$$b = c = \sqrt{3}a_0$$

$$c' = a_0$$

$$2c' = 2a_0$$

### Hydrogen Molecule ($\mathbf{H_2\left[2c'=\sqrt{2}a_0\right]}$)

$$a = a_0$$

$$b = c = \frac{1}{\sqrt{2}}a_0$$

$$c' = \frac{1}{\sqrt{2}}a_0$$

$$2c' = \sqrt{2}a_0$$

### Dihydrino Molecular Ion ($\mathbf{H_2[2c'=a_0]^+}$)

$$a = a_0$$

$$b = c = \frac{\sqrt{3}}{2}a_0$$

$$c' = \frac{1}{2}a_0$$

$$2c' = a_0$$

### Dihydrino Molecule ($\mathbf{H_2\left[2c'=\frac{1}{\sqrt{2}}a_0\right]}$)

$$a = \frac{1}{2}a_0$$

$$b = c = \frac{1}{2\sqrt{2}}a_0$$

$$c' = \frac{1}{2\sqrt{2}}a_0$$

$$2c' = \frac{1}{\sqrt{2}}a_0$$

## NUCLEAR SPIN-SPIN TRANSITION OF HYDROGEN-TYPE MOLECULES

Each proton of hydrogen-type molecules possesses a magnetic moment, which is derived in the Proton and Neutron section and is given by

$$\mu_P = \frac{\left(\frac{2}{3}\right)^2 e\hbar}{2\frac{m_p}{2\pi}} \tag{11.360}$$

The magnetic moment, $\mathbf{m}$, of the proton is given by Eq. (11.360), and the magnetic field of the proton follows from the relationship between the magnetic dipole field and the magnetic moment, $\mathbf{m}$, as given by Jackson [36] where $\mathbf{m} = \mu_P \mathbf{i_z}$.

$$\mathbf{H} = \frac{\mu_P}{r^3}(\mathbf{i}_r 2\cos\theta - \mathbf{i}_\theta \sin\theta) \tag{11.361}$$

Multiplication of Eq. (11.361) by the permeability of free space, $\mu_0$, gives the magnetic flux, $\mathbf{B}$, due to proton one at proton two.

$$\mathbf{B} = \frac{\mu_0\mu_P}{r^3}(\mathbf{i}_r 2\cos\theta - \mathbf{i}_\theta \sin\theta) \tag{11.362}$$

$\Delta E_{mag}^{\text{ortho/para}}$, the magnetic energy to flip the orientation of proton two's magnetic moments, $\mu_P$, from parallel magnetic moments to antiparallel magnetic moments with respect to the direction of the magnetic moment of proton one with corresponding magnetic flux $\mathbf{B}$ is:

$$\Delta E_{mag}^{\text{ortho/para}} = -2\mu_P\mathbf{B} = \frac{-2\mu_0{\mu_P}^2}{r^3} \tag{11.363}$$

where $r$ is the internuclear distance 2c' where c' is given by Eq. (11.204). Substitution of the internuclear distance into Eq. (11.363) for $r$ gives:

$$\Delta E_{mag}^{\text{ortho/para}} = -2\mu_P\mathbf{B} = \frac{-2\mu_0{\mu_P}^2 p^3}{\left(\sqrt{2}a_0\right)^3} \tag{11.364}$$

$\Delta E_{mag}^{\text{ortho/para}}$ corresponds to a force that causes the internuclear distance and concomitantly the other dimensions of the $H_2$ MO to change thereby having a relatively substantial effect on the energy difference of the ortho and para states. A useful parameter, the ro-vibrational ortho-para splitting, can easily be calculated from the result of Lavrov and Weber [37] for $H_2(1/4)$ using the Morse-potential expansion with an inter nuclear distance of 1/4 that of $H_2$ for $H_2(1/4)$:

$$\frac{\Delta_{H_2(1/4)}}{\Delta_{H_2}} = \frac{\frac{12(256)B_e^2}{\hbar 16\omega_e}\left(\frac{4a\hbar}{\mu 256\omega_e^2}\sqrt{\frac{2}{\mu 16 B_e}} - 1\right)}{\frac{12B_e^2}{\hbar\omega_e}\left(\frac{a\hbar}{\mu\omega_e^2}\sqrt{\frac{2}{\mu B_e}} - 1\right)} \tag{11.365}$$

In the case that $1 << \frac{a\hbar}{\mu\omega_e^2}\sqrt{\frac{2}{\mu B_e}}$, $\Delta_{H_2(1/4)} = 16\Delta_{H_2} = 4^2\Delta_{H_2} = 1418\ cm^{-1}$ where the calculated $H_2$ result of 88.61 $cm^{-1}$ (Ref. [38]) allowed for the cancellation of the curve-fit parameter $a$ and where $\omega_e$ and $B_e$ are the vibartional and rotational parameters given by Eqs. (11.217) and (12.89), respectively.

## NUCLEAR MAGNETIC RESONANCE SHIFT

The proton gyromagnetic ratio, $\gamma_p / 2\pi$, is

$$\gamma_P / 2\pi = 42.57602\ MHz\ T^{-1} \tag{11.366}$$

The NMR frequency, $f$, is the product of the proton gyromagnetic ratio given by Eq. (11.366) and the magnetic flux, $\mathbf{B}$.

$$f = \gamma_P / 2\pi\mathbf{B} = 42.57602\ MHz\ T^{-1}\mathbf{B} \tag{11.367}$$

A typical radio frequency (RF) is $400\ MHz$. According to Eq. (11.367) this corresponds to a flux of 9.39496 $T$ provided by a superconducting NMR magnet. With a constant magnetic field, the frequency is scanned to yield the spectrum where the frequency scan is typically achieved using a Fourier transform on the free induction decay signal following a radio frequency pulse. Historically, the radiofrequency was held constant, the applied magnetic field, $H_0$ ($H_0 = \frac{B}{\mu_0}$), was varied over a small range, and the frequency of energy absorption was recorded at the various values for $H_0$. By convention based on this historic mode of operation, the radiofrequency spectrum is converted into the corresponding applied magnetic field, $H_0$ ($H_0 = \frac{B}{\mu_0}$), of energy absorption and displayed as a function of increasing $H_0$. The protons that would absorb energy at a lower $H_0$ give rise to a downfield absorption peak; whereas, the protons that would absorb energy at a higher $H_0$ give rise to an upfield absorption peak. The electrons of the compound of a sample influence the field at the nucleus such that it deviates slightly from the applied value. For the case that the chemical environment has no NMR effect, the value of $H_0$ at resonance with the radiofrequency held constant at $400\ MHz$ is:

$$\frac{2\pi f}{\mu_0 \gamma_P} = \frac{(2\pi)(400\ MHz)}{\mu_0 42.57602\ MHz\ T^{-1}} = H_0 \tag{11.368}$$

In the case that the chemical environment has a NMR effect, a different value of $H_0$ is required for resonance. This chemical shift is proportional to the electronic magnetic flux charge at the nucleus due to the applied field, which in the case of each dihydrino molecule is a function of its semimajor and semiminor axes as shown *infra*.

Consider the application of a z-axis-directed uniform external magnetic flux, $\mathbf{B}_z$, to a dihydrino molecule comprising prolate spheroidal electron MOs with two spin-paired electrons. The diamagnetic reaction current increases or decreases the MO current to counteract any applied flux according to Lenz's law as shown in the Hydrino Hydride Ion Nuclear Magnetic Resonance Shift section. The current of hydrogen-type molecules is along elliptical orbits parallel to the semimajor axis. Thus, each nuclear magnetic moment must be in the direction of the semiminor axis for the electronic interaction with the nuclei. Thus, the nuclei are NMR active towards $\mathbf{B}_z$ when the orientation of the semimajor axis, $a$, is along the x-axis, and the semiminor axes, $b = c$, are along the y-axis and z-axis, respectively. The flux is applied over the time interval $\Delta t = t_i - t_f$ such that the field increases at a rate $dB/dt$. The electric field, $\mathbf{E}$, along a perpendicular elliptic path of the dihydrino MO at the plane $z = 0$ is given by

$$\oint E \cdot ds = \int \frac{dB}{dt} \cdot dA \tag{11.369}$$

The induced electric field must be constant along the path; otherwise, compensating currents would flow until the electric field is constant. Thus, Eq. (11.369) becomes

$$E = \frac{\int \frac{dB}{dt} \cdot dA}{\oint ds} = \frac{\int \frac{dB}{dt} \cdot dA}{4aE(k)} = \frac{\pi ab \frac{dB}{dt}}{4aE(k)} \tag{11.370}$$

where $E(k)$ is the elliptic integral given by:

$$E(k) = \int_0^{\frac{\pi}{2}} \sqrt{1 - k \sin^2 \phi}\, d\phi = 1.2375 \tag{11.371}$$

$$k = e = \frac{\sqrt{a^2 - b^2}}{a} = \frac{\sqrt{2}}{2} \tag{11.372}$$

the area of an ellipse, $A$, is

$$A = \pi ab \tag{11.373}$$

the perimeter of an ellipse, $s$, is:

$$s = 4aE(k) \tag{11.374}$$

$a$ is the semimajor axis given by Eq. (11.202), $b$ is the semiminor axis given by Eq. (11.205), and $e$ is the eccentricity given by Eq. (11.206). The acceleration along the path, $dv/dt$, during the application of the flux is determined by the electric force on the charge density of the electrons:

$$m_e \frac{dv}{dt} = eE = \frac{e\pi ab}{4aE(k)} \frac{dB}{dt} \tag{11.375}$$

Thus, the relationship between the change in velocity, $v$, and the change in $B$ is:

$$dv = \frac{e\pi ab}{4aE(k) m_e} dB \tag{11.376}$$

Let $\Delta v$ represent the net change in $v$ over the time interval $\Delta t = t_i - t_f$ of the application of the flux. Then,

$$\Delta v = \int_{v_0}^{v_0 + \Delta v} dv = \frac{e\pi ab}{4aE(k) m_e} \int_0^B dB = \frac{e\pi abB}{4aE(k) m_e} \tag{11.377}$$

The average current, $I$, of a charge moving in time harmonically along an ellipse is:

$$I = ef = \frac{ev}{4aE(k)} \tag{11.378}$$

where $f$ is the frequency. The corresponding magnetic moment is given by:

$$m = AI = \pi abI = \frac{\pi abev}{4aE(k)} \tag{11.379}$$

Thus, from Eqs. (11.377) and (11.379), the change in the magnetic moment, $\Delta\mathbf{m}$, due to an applied magnetic flux, $\mathbf{B}$, is [39]

$$\Delta\mathbf{m} = -\frac{(e\pi ab)^2\,\mathbf{B}}{(4aE(k))^2 m_e} \tag{11.380}$$

Next, the contribution from all plane cross-sections of the prolate spheroid MO must be integrated along the z-axis. The spheroidal surface is given by

$$\frac{x^2}{a^2} + \frac{y^2}{b^2} + \frac{z^2}{b^2} = 1 \tag{11.381}$$

The intersection of the plane $z = z'$ ($-b \le z' \le b$) with the spheroid determines the curve

$$\frac{x^2}{a^2} + \frac{y^2}{b^2} = 1 - \frac{z'^2}{b^2} \tag{11.382}$$

or

$$\frac{x^2}{a^2\left(1-\frac{z'^2}{b^2}\right)} + \frac{y^2}{b^2\left(1-\frac{z'^2}{b^2}\right)} = 1 \tag{11.383}$$

Eq. (11.383) is an ellipse with semimajor axis, $a'$, and semiminor axis, $b'$, given by:

$$a' = a\sqrt{1-\frac{z'^2}{b^2}} \tag{11.384}$$

$$b' = b\sqrt{1-\frac{z'^2}{b^2}} \tag{11.385}$$

The eccentricity, $e'$, is given by

$$e' = \frac{\sqrt{a^2\left(1-\frac{z'^2}{b^2}\right) - b^2\left(1-\frac{z'^2}{b^2}\right)}}{a\sqrt{1-\frac{z'^2}{b^2}}} = \frac{\sqrt{a^2-b^2}}{a} = e \tag{11.386}$$

where $e$ is given by Eq. (11.372). The area, $A'$, is given by:

$$A' = \pi a'b' \tag{11.387}$$

and the perimeter, $s'$, is given by

$$s' = 4a'E(k) = 4aE(k)\sqrt{1-\frac{z'^2}{b^2}} = s\sqrt{1-\frac{z'^2}{b^2}} \tag{11.388}$$

where $s$ is given by Eq. (11.374). The differential magnetic moment change along the z-axis is:

$$d\Delta\mathbf{m} = -\frac{1}{2b}\frac{(e\pi a'b')^2\,\mathbf{B}}{(4a'E(k))^2 m_e}dz' \tag{11.389}$$

Using Eq. (11.385) for the parameter $b'$, the change in magnetic moment for the dihydrino molecule is given by the integral over $-b \le b' \le b$:

$$\Delta\mathbf{m} = -\frac{1}{2b}\int_{-b}^{b}\frac{\left(e\pi a'b\sqrt{1-\frac{z'^2}{b^2}}\right)^2\mathbf{B}}{(4a'E(k))^2 m_e}dz' = -C_1\frac{1}{m_e}\left(\frac{\pi e}{4E(k)}\right)^2\mathbf{B} \tag{11.390}$$

Then, the integral to correct for the z-dependence of $b'$ is:

$$C_1 = \frac{\int_{-b}^{b}\left(b^2 - z^2\right)dz}{2b} = \frac{2}{3}b^2 = \frac{a_0^2}{3p^2} \tag{11.391}$$

where the semiminor axis, $b = \frac{a_0}{p\sqrt{2}}$, given by Eq. (11.205) was used.

The change in magnetic moment would be given by the substitution of Eq. (11.391) into Eq. (11.390), if the charge density were constant along the path of Eqs. (11.370) and (11.378), but it is not. The charge density of the MO in rectangular coordinates (Eq. (11.42)) is

$$\sigma = \frac{e}{4\pi abc}\frac{1}{\sqrt{\frac{x^2}{a^4}+\frac{y^2}{b^4}+\frac{z^2}{c^4}}} \tag{11.392}$$

(The mass-density function of an MO is equivalent to its charge-density function where $m$ replaces $q$ of Eq. (11.42)). The equation of the plane tangent to the ellipsoid at the point $x_0$, $y_0$, $z_0$ is:

$$X\frac{x_0}{a^2}+Y\frac{y_0}{b^2}+Z\frac{z_0}{c^2} = 1 \tag{11.393}$$

where $X$, $Y$, $Z$ are running coordinates in the plane. After dividing through by the square root of the sum of the squares of the coefficients of $X$, $Y$, and $Z$, the right member is the distance $D$ from the origin to the tangent plane. That is,

$$D = \frac{1}{\sqrt{\frac{x^2}{a^4}+\frac{y^2}{b^4}+\frac{z^2}{c^4}}} \tag{11.394}$$

so that

$$\sigma = \frac{e}{4\pi abc}D \tag{11.395}$$

In other words, the surface density at any point on the ellipsoidal MO is proportional to the perpendicular distance from the center of the ellipsoid to the plane tangent to the ellipsoid at the point. The charge is thus greater on the more sharply rounded ends farther away from the origin. In order to maintain current continuity, the diamagnetic velocity of Eq. (11.377) must be a constant along any given path integral corresponding to a constant electric field. Consequently, the charge density must be the minimum value of that given by Eq. (11.392). The minimum corresponds to $y = b$ and $x = z = 0$ such that the charge density is:

$$\sigma = \frac{e}{4\pi ab^2}\frac{1}{\sqrt{\frac{0^2}{a^4}+\frac{b^2}{b^4}+\frac{0^2}{b^4}}} = \frac{e}{4\pi ab} \tag{11.396}$$

The MO is an equipotential surface, and the current must be continuous over the two-dimensional surface. Continuity of the surface current density, $K$, due to the diamagnetic effect of the applied magnetic field on the MO and the equipotential boundary condition require that the current of each elliptical curve determined by the intersection of the plane $z = z'$ ($-b \le z' \le b$) with the spheroid be the same. The charge density is spheroidally symmetrical about the semimajor axis. Thus, $\lambda$, the charge density per unit length along each elliptical path cross section of Eq. (11.383) is given by distributing the surface charge density of Eq. (11.396) uniformly along the z-axis for $-b \le z' \le b$. So, $\lambda(z'=0)$, the linear charge density $\lambda$ in the plane $z'=0$, is:

$$\lambda(z'=0) = \frac{\sigma}{\frac{1}{2b}} = \frac{e}{4\pi ab}2b = \frac{e}{2\pi a} \tag{11.397}$$

And, the linear charge density must be equally distributed over each elliptical path cross-section corresponding to each plane $z = z'$. The current is independent of $z'$ when the linear charge density, $\lambda(z')$, is normalized for the path length:

$$\lambda(z') = \frac{e}{2\pi a}\frac{4aE(k)}{4a'E(k')} = \frac{e}{2\pi a'} \tag{11.398}$$

where the equality of the eccentricities of each elliptical plane cross section given by Eq. (11.386) was used. Substitution of Eq. (11.398) for the corresponding charge density, $\frac{e}{4a'E(k)}$, of Eq. (11.390) and using Eq. (11.391) gives:

$$\Delta\mathbf{m} = \frac{2}{3}\frac{e^2b^2\mathbf{B}}{4m_e} = \frac{e^2a_0^2\mathbf{B}}{12p^2m_e} \tag{11.399}$$

The two electrons are spin-paired and the velocities are mirror opposites. Thus, the change in velocity of each electron treated individually (Eq. (10.3)) due to the applied field would be equal and opposite. However, as shown in the Three Electron Atom section, the two paired electrons may be treated as one with twice the mass where $m_e$ is replaced by $2m_e$ in Eq. (11.399). In this case, the paired electrons spin together about the applied field axis, the z-axis, to cause a reduction in the applied field according to Lenz's law. Thus, from Eq. (11.399), the change in magnetic moment is given by:

$$\Delta\mathbf{m} = \frac{e^2a_0^2\mathbf{B}}{24p^2m_e} \tag{11.400}$$

The opposing diamagnetic flux is uniform, parallel, and opposite the applied field as given by Stratton [40]. Specifically, the change in magnetic flux, $\Delta\mathbf{B}$, at the nucleus due to the change in magnetic moment, $\Delta\mathbf{m}$, is:

$$\Delta\mathbf{B} = \mu_0 A_2 \Delta\mathbf{m} \tag{11.401}$$

where $\mu_0$ is the permeability of vacuum,

$$A_2 = \int_0^{\infty} \frac{ds}{\left(s+b^2\right)R_s} \tag{11.402}$$

is an elliptic integral of the second kind given by Whittaker and Watson [41], and

$$R_s = (s+b^2)\sqrt{(s+a^2)} \tag{11.403}$$

Substitution of Eq. (11.403) into Eq. (11.402) gives:

$$A_2 = \int_0^{\infty} \frac{ds}{\left(s+b^2\right)^2\left(s+a^2\right)^{1/2}} \tag{11.404}$$

From integral 154 of Lide [42]:

$$A_2 = -\left\{\frac{1}{a^2-b^2}\frac{\sqrt{s+a^2}}{s+b^2}\right\}_0^{\infty} - \frac{1}{2}\frac{1}{a^2-b^2}\int_0^{\infty}\frac{ds}{\left(s+b^2\right)\sqrt{s+a^2}} \tag{11.405}$$

The evaluation at the limits of the first integral is

$$-\left\{\frac{1}{a^2-b^2}\frac{\sqrt{s+a^2}}{s+b^2}\right\}_0^{\infty} = \frac{a}{b^2\left(a^2-b^2\right)} \tag{11.406}$$

From integral #147 of Lide [9], the second integral is:

$$-\frac{1}{2}\frac{1}{a^2-b^2}\int_0^{\infty}\frac{ds}{\left(s+b^2\right)\sqrt{s+a^2}} = \left\{\frac{1}{2}\frac{1}{\left(a^2-b^2\right)^{3/2}}\ln\frac{\sqrt{s+a^2}+\sqrt{a^2-b^2}}{\sqrt{s+a^2}-\sqrt{a^2-b^2}}\right\}_0^{\infty} \tag{11.407}$$

Evaluation at the limits of the second integral gives:

$$-\frac{1}{2}\frac{1}{\left(a^2-b^2\right)^{3/2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} \tag{11.408}$$

Combining Eq. (11.406) and Eq. (11.408) gives:

$$A_2 = \frac{a}{b^2\left(a^2-b^2\right)} - \frac{1}{2}\frac{1}{\left(a^2-b^2\right)^{3/2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = \frac{p^3 4}{a_0^3} - \frac{p^3\sqrt{2}}{a_0^3}\ln\frac{\sqrt{2}+1}{\sqrt{2}-1} \tag{11.409}$$

where the semimajor axis, $a = \frac{a_0}{p}$, given by Eq. (11.202) and the semiminor axis, $b = \frac{a_0}{p\sqrt{2}}$, given by Eq. (11.205) were used.

Substitution of Eq. (11.400) and Eq. (11.409) into Eq. (11.401) gives:

$$\Delta\mathbf{B} = -\mu_0\left(\frac{p^3 4}{a_0^3} - \frac{p^3\sqrt{2}}{a_0^3}\ln\frac{\sqrt{2}+1}{\sqrt{2}-1}\right)\frac{a_0^2 e^2 \mathbf{B}}{24 p^2 m_e} \tag{11.410}$$

Additionally, it is found both theoretically and experimentally that the dimensions, $r^2$, of the molecule corresponding to the area in Eqs. (11.369) and (11.379) used to derive Eq. (11.410) must be replaced by an average, $\left\langle r^2 \right\rangle$, that takes into account averaging over the orbits isotropically oriented. The correction of 2/3 is given by Purcell [39] (also Eq (11.391)). In the case of hydrogen-type molecules, the electronic interaction with the nuclei require that each nuclear magnetic moment is in the direction of the semiminor axis. But free rotation about each of three axes results in an isotropic averaging of 2/3 where the rotational frequencies of hydrogen-type molecules are much greater than the corresponding NMR frequency (e.g. $10^{12}$ $Hz$ versus $10^8$ $Hz$). Thus, Eq. (11.410) gives the absolute upfield chemical shift, $\frac{\Delta B}{B}$, of $H_2\left(1/p\right)$ relative to a bare proton:

$$\begin{aligned}\frac{\Delta\mathbf{B}}{\mathbf{B}} = \frac{\Delta B}{B} &= -\mu_0\left(\frac{p^3 4}{a_0^3} - \frac{p^3\sqrt{2}}{a_0^3}\ln\frac{\sqrt{2}+1}{\sqrt{2}-1}\right)\frac{a_0^2 e^2}{36 p^2 m_e} \\ &= -\mu_0\left(4-\sqrt{2}\ln\frac{\sqrt{2}+1}{\sqrt{2}-1}\right)\frac{pe^2}{36 a_0 m_e} \\ &= -p28.01\ ppm\end{aligned} \tag{11.411}$$

where $p$ is an integer.

For resonance to occur, $\Delta H_0$, the change in applied field from that given by Eq. (11.368), must compensate by an equal and opposite amount as the field due to the electrons of molecular hydrino. Compared to protons with no chemical shift, the ratio of $\Delta H_0$ for resonance of the protons of the dihydrino molecule $H_2\left(1/p\right)$ to that of $H_2$ is a positive integer. According to Eq. (11.202), the ratio of the semimajor axis of the dihydrino molecule $H_2\left(1/p\right)$ to that of the hydrogen molecule $H_2$ is the reciprocal of an integer $p$. It follows from Eqs. (11.202) and (11.411) that the diamagnetic flux (flux opposite to the applied field) at each nucleus is inversely proportional to the semimajor radius, $a = \frac{a_0}{p}$. That is, if only the size is considered, the absolute absorption peak of the dihydrino molecule (i.e. relative to a proton with no shift) occurs at a value of $\Delta H_0$ that is a multiple of $p$ times the value that is resonant for H2. However, the source current of the state must be considered in addition to the reduced geometrical dimensions.

As shown in the Stability of "Ground" and Hydrino States section, for the below "ground" (fractional quantum number) energy states of the hydrogen atom, $\sigma_{photon}$, the two-dimensional surface charge due to the "trapped photon" at the electron atomic orbital and phase-locked with the electron atomic orbital current, is given by Eqs. (5.27) and (2.11). The excited states of the hydrogen molecule are solved using the same approach as those of the excited states of atoms wherein the corresponding geometry is prolate spheroid rather than spherical and the photon fields are modeled by associated Legendre functions or ellipsoidal spherical harmonics with regard to the semimajor axis as given in the Excited States of the Hydrogen Molecule section. The total central ellipsoidal field of the molecule at the position of the molecular orbital (MO) due to the superposition of the field of the nuclei and the photon field is equivalent to an integer $p$ times that of the nuclei at the foci of the prolate spheroidal MO. The photon source current gives rise to an additional contribution to the diamagnetism of the two electrons that is a function of $p$.

As given in the Excited States of the Hydrogen Molecule section, the current of the paired electrons of the MO are phase locked to the photon field of magnitude $p$ of the dihydrino state. For the spherical harmonics, the quantum number of the electron are $p$, $\ell$, $m_\ell$, and $m_s$ as described in the Excited States of the One-Electron Atom (Quantization) section wherein the principal quantum number of excited states is replaced by $n = \frac{1}{p}$. From Eq. (5.27),

$$n = \frac{1}{p};\ \ell = 0,1,2,...,p-1;\ m_\ell = -\ell,-\ell+1,...,0,...+\ell;\ m_s = \pm\frac{1}{2} \tag{11.412}$$

In the case that the photons and corresponding source current spin in opposite directions for the two electrons, the orbital magnetic moments cancel. However, as given in the Pair Production section, a photon having an energy equivalent to that of the mass energy of the electron may undergo particle production to form an electron. To maintain continuity, the photon surface current of a dihydrino state must behave as the charge equivalent to its energy during the interaction of the electrons and the phased locked photon-field surface current with the external magnetic field such that the photon component gives rise to a proportional diamagnetic effect as well. The photon diamagnetic component is given by Eqs. (29.10-29.11) as the charge equivalent to its energy that superimposes with the diamagnetism of the two electrons. The relativistic term after Eq. (29.10) and the central field magnitude term for the dihydrino state having principle quantum number $p$ are $\alpha^2$ and $p$, respectively. The photon contribution to the change in flux $\Delta\mathbf{B}_{SR}$ for molecular hydrino $H_2(1/p)$ given by applying the corresponding relativistic factor of $\gamma_{SR} = \alpha^2$ to Eq. (11.401) is

$$\Delta\mathbf{B}_{SR} = -p\alpha^2\mu_0 A_2 \Delta\mathbf{m} \tag{11.413}$$

Thus, using Eq. (11.411) and Eq. (11.413), the upfield chemical shift, $\frac{\Delta B_{SR}}{B}$, due to the photon contribution of the molecule $H_2(1/p)$ corresponding to the lower-energy state with principal quantum energy state $p$ is given by:

$$\frac{\Delta B_{SR}}{B} = -p\alpha^2\mu_0\left(4-\sqrt{2}\ln\frac{\sqrt{2}+1}{\sqrt{2}-1}\right)\frac{pe^2}{36a_0m_e} \tag{11.414}$$

The total shift, $\frac{\Delta B_T}{B}$, for $H_2(1/p)$ is given by the sum of that of the electrons given by Eq. (11.411) and that of the photon given by Eq. (11.414):

$$\frac{\Delta B_T}{B} = -\mu_0\left(4-\sqrt{2}\ln\frac{\sqrt{2}+1}{\sqrt{2}-1}\right)\frac{pe^2}{36a_0m_e}\left(1+p\alpha^2\right) \tag{11.415}$$

$$\frac{\Delta B_T}{B} = -\left(p28.01 + p^2 1.49\ X\ 10^{-3}\right)ppm \tag{11.416}$$

where the first term applies to $H_2$ with $p=1$ and $p=$ integer >1 for $H_2(1/p)$.

$H_2$ has been characterized by gas phase $^1H$ NMR. The experimental absolute resonance shift of gas-phase TMS relative to the proton's gyromagnetic frequency is -28.5 ppm [32]. The experimental absolute resonance shift of TMS is -31.5 ppm relative to the proton's gyromagnetic frequency [43-44]. $H_2$ was observed at 0.48 ppm compared to gas phase TMS set at 0.00 ppm [33]. Thus, the corresponding absolute $H_2$ gas-phase resonance shift of -28.0 ppm (-28.5 + 0.48) ppm was in excellent agreement with the predicted absolute gas-phase shift of -28.01 ppm given by Eq. (11.411). The solution NMR of $H_2$ has a chemical shift of about +4.65 ppm relative to TMS in many solvents [45] corresponding to a solvent or matrix shift of about +1 ppm. The chemical shift of $H_2(1/p)$ is given by the difference of Eq. (11.416) and -31.5 ppm plus any solvent shift.

As given in the Parameters and Magnetic Energies Due to the Spin Magnetic Moment of $H_2(1/4)$ section $H_2(1/p)$ has an unpaired electron such that it is paramagnetic. The paramagnetism contributes to the difficulty of observing molecular hydrino NMR peaks directly. However molecular hydrino states can give rise to a matrix shift in the MAS NMR spectrum when the matrix comprises NMR active H species such as a matrix having waters of hydration or an alkaline hydroxide solid matrix wherein a local interaction with $H_2(1/p)$ causes an upfield matrix shift. This effect may be enhanced for H species capable of rapid H exchange wherein the local $H_2(1/p)$ interaction influences a larger population due to the rapid H exchange.

## QUADRUPOLE MOMENT

The quadrupole moment $Q_{33}$ of a charge distribution $\rho(\vec{r})$ along the z-axis is given by

$$Q_{zz} = \iiint d\vec{r}\rho(\vec{r})\left[3z^2 - r^2\right] \tag{11.417}$$

In cylindrical coordinates, the quadrupole moment is given by

$$Q_{zz} = \int dz \int d\phi \int drr\left[2z^2 - r^2\right]\sigma \tag{11.418}$$

wherein from Eqs. (11.26), (11.45), and (11.46) the electron charge distribution $\sigma$ is

$$\sigma = \frac{-2e}{4\pi abc}\frac{1}{\sqrt{\frac{x^2}{a^4}+\frac{y^2}{b^4}+\frac{z^2}{b^4}}}; \qquad \frac{x^2}{a^2}+\frac{y^2}{b^2}+\frac{z^2}{b^2}=1 \tag{11.419}$$

Consider that the prolate spheroid is aligned with the major axis along the z-axis such that the magnitude of the charge density of the hydrogen-type molecular orbital is

$$\sigma = \frac{-2e}{4\pi ab^2}\frac{1}{\sqrt{\frac{r^2}{b^4}+\frac{z^2}{a^4}}}; \qquad \frac{r^2}{b^2}+\frac{z^2}{a^2}=1 \tag{11.420}$$

Substitution of Eq. (11.419) into Eq. (11.418) gives the electron contribution to the quadrupole moment $Q_{zze}$:

$$Q_{zze} = \frac{-2e}{4\pi ab^2}\int_{-a}^{a}\int_{0}^{2\pi}\frac{\int_{0}^{\infty} r\left(2z^2 - r^2\right)}{\sqrt{\frac{z^2}{a^4}+\frac{r^2}{b^4}}}\delta\left(r - b\sqrt{1-\frac{z^2}{a^2}}\right)drd\phi dz \tag{11.421}$$

Integration with respect to $r$ and $\phi$ gives

$$Q_{zze} = \frac{-e}{ab^2}\int_{-a}^{a}\frac{2z^2 b\sqrt{1-\frac{z^2}{a^2}} - b^3\left(1-\frac{z^2}{a^2}\right)^{3/2}}{\sqrt{\frac{z^2}{a^4}+\frac{\left(1-\frac{z^2}{a^2}\right)}{b^2}}}dz \tag{11.422}$$

With the substitution of the semimajor axis (Eq. (11.202)), semiminor axis (Eq. (11.205)), and $z' = z/a$ into Eq. (11.422), $Q_{zze}$ becomes

$$Q_{zze} = -e\frac{a_0^2}{p^2}\int_{-1}^{1}\frac{2^{3/2}z'^2\sqrt{1-z'^2} - \frac{1}{\sqrt{2}}\left(1-z'^2\right)^{3/2}}{\sqrt{2-z'^2}}dz' \tag{11.423}$$

Integral (11.423) given by Mathematica is

$$\frac{Q_{zze}}{e} = -0.298728\frac{a_0^2}{p^2} = \frac{-8.36523X10^{-22}m^2}{p^2} = \frac{-8.36523X10^{-18}cm^2}{p^2} \tag{11.424}$$

Next, consider the quadrupole moment contribution of the two protons of hydrogen-type molecules wherein the protons are aligned along the z-axis with a separation of the internuclear distance $2c'$ given by Eq. (11.204). The quadrupole moment tensor is given by [46]:

$$Q_{ij} = \int d^3x\rho(\mathbf{x})\left(3x_i x_j - r^2\delta_{ij}\right) \tag{11.425}$$

The charge densities of the protons are given by

$$\rho(\mathbf{x}) = e\left(\delta^3\left(\mathbf{x}-c'\mathbf{k}\right)+\delta^3\left(\mathbf{x}+c'\mathbf{k}\right)\right) \tag{11.426}$$

The quadrupole moment may be easily evaluated in Cartesian coordinates wherein the Dirac delta functions become

$$\delta^3(\mathbf{x}-c'\mathbf{k})+\delta^3(\mathbf{x}+c'\mathbf{k})=\delta(z-c')\delta(x)\delta(y)+\delta(z+c')\delta(x)\delta(y) \tag{11.427}$$

Substitution of Eqs. (11.426-11.427) into Eq. (11.425) gives the proton quadrupole contribution $Q_{zzp}$:

$$\begin{aligned}Q_{zzp} &= \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} dz\rho(\mathbf{x})\left(3z^2-\left(x^2+y^2+z^2\right)\right)\\ &= e\int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} dz\left(\delta(z-c')\delta(x)\delta(y)+\delta(z+c')\delta(x)\delta(y)\right)\left(2z^2-x^2-y^2\right)\\ &= 4ec'^2\end{aligned} \tag{11.428}$$

The charge-normalized quadrupole moment of hydrogen-type molecule $\frac{Q_{zzH_2(1/p)}}{e}$ is given by the sum of the charge-normalized quadrupole moment contributions of the protons, $\frac{Q_{zzp}}{e}$ given by Eq. (11.428), and the electrons, $\frac{Q_{zze}}{e}$ given by Eq. (11.424):

$$\frac{Q_{zzH_2(1/p)}}{e}=\frac{Q_{zzp}}{e}+\frac{Q_{zze}}{e}=4c'^2-0.29873\frac{a_0^2}{p^2}=(2-0.29873)\frac{a_0^2}{p^2}=1.70127\frac{a_0^2}{p^2} \tag{11.429}$$

wherein the distance of each proton from the origin $c'$ is given by Eq. (11.203). In the case of $H_2$ wherein $p=1$, the charge-normalized quadrupole moment given by Eq. (11.429) is

$$\frac{Q_{zzH_2}}{e}=1.70127a_0^2=0.476404X10^{-16}cm^2 \tag{11.430}$$

which agrees with the experimental results of Ramsey [47]:

$$\frac{Q_{zzH_2}}{e}=0.38\pm0.15X10^{-16}cm^2 \tag{11.431}$$

In the case of $H_2(1/4)$ wherein $p=4$, the charge-normalized quadrupole moment given by Eq. (11.429) is

$$\frac{Q_{zzH_2(1/4)}}{e}=1.70127\frac{a_0^2}{4^2}=2.97752X10^{-18}cm^2 \tag{11.432}$$

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# Chapter 12

# DIATOMIC MOLECULAR ENERGY STATES

## EXCITED ELECTRONIC STATES OF ELLIPSOIDAL MOLECULAR ORBITALS

Excited states of atomic orbitals are discussed in the Excited States of the One-Electron Atom (Quantization) section and the Excited States of Helium section. In the case of ellipsoidal MOs, excited electronic states are created when photons of discrete frequencies are trapped in the ellipsoidal resonator cavity of the MO of the outer excited-state electron. The photon changes the effective charge at the MO surface where the central field is ellipsoidal and arises from both the net field of the nuclei at the foci of the inner MO and the trapped photon of the outer. The "trapped photons" are solutions of the two-dimensional Laplacian in ellipsoidal coordinates given by Eq. (11.27). The excited-state photon's electric field at the outer electron (Eq. (2.15) except ellipsoidal coordinates) superimposes that of the net field of the nuclei at the foci of the inner MO and inner MO charge such that the net electric field has a magnitude proportional to $Z/n$ in the direction of $\mathbf{i}_\xi$ at the outer electron where $n = 2,3,4,...$ for excited states. Force balance is achieved at a series of ellipsoidal equipotential two-dimensional surfaces with an increased distance $\xi$. The state geometrical parameters are solved from the force balance equation and the relationships among the ellipsoidal parameters given in the Derivation of the General Geometrical and Energy Equations of Organic Chemistry section. The force balance of the outer excited-state electron is given by balance between the centrifugal force, the central Coulombic force corresponding to the effective central field due to the superposition of photon field at the outer electron and the net field of the nuclei at the foci of the inner MO, and the magnetic forces in the case of paired electrons in the unexcited state. The energies corresponding to the excited electron are given by the prolate spheroidal energy equations given in the Derivation of the General Geometrical and Energy Equations of Organic Chemistry section except for a correction corresponding to a single electron, and the electric terms are scaled according to the effective central field.

## EXCITED STATES OF THE HYDROGEN MOLECULAR ION

### FORCE BALANCE OF THE EXCITED STATES OF THE HYDROGEN MOLECULAR ION

The excited states of the hydrogen molecular ion are determined by the same physics as those of one and two electron atoms. The excited-state photon's electric field superposes that of the protons at the foci of the MO such that the excited-state electric field has a magnitude proportional to $e/n$ in the direction of $\mathbf{i}_\xi$ at the electron MO where $n = 2,3,4,...$ for excited states. Balance between the centrifugal and the Coulomb forces is achieved at a series of MOs, ellipsoidal equipotential two-dimensional surfaces, confocal with the $n=1$-state ellipsoid MO wherein the corresponding Coulombic force that balances the centrifugal force meets the requirement that the excited-state electric field has a magnitude proportional to $e/n$ at the electron. Thus, force balance between the electric and centrifugal forces given by Eq. (11.115) where $p = 1/n$ is

$$\frac{\hbar^2}{m_e a^2 b^2} D = \frac{1}{n} \frac{e^2}{8\pi\varepsilon_0 ab^2} D \tag{12.1}$$

which has the parametric solution given by Eq. (11.83) when semimajor axis, $a$, is:

$$a = 2na_0 \tag{12.2}$$

The internuclear distance, $2c'$, which is the distance between the foci is given by Eq. (11.111) where $p = 1/n$.

$$2c' = 2na_0 \tag{12.3}$$

The semiminor axis is given by Eq. (11.112) where $p = 1/n$.

$$b = \sqrt{3}na_0 \tag{12.4}$$

The eccentricity, $e$, is given by Eq. (11.113).

$$e = \frac{1}{2} \tag{12.5}$$

## ENERGIES OF THE EXCITED STATES OF THE HYDROGEN MOLECULAR ION

The potential energy, $V_e$, of the electron MO in the field of the protons at the foci ($\xi = 0$) is given by Eq. (11.117) where $p = 1/n$

$$V_e = \frac{-\left(\frac{1}{n}\right)4e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}} \ln \frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} \tag{12.6}$$

To match the condition that electric field has a magnitude proportional to $Z/n$ in the direction of $\mathbf{i}_\xi$ at the electrons, the corresponding potential energy, $V_p$, due to proton-proton repulsion is given by Eq. (11.120) where $p = 1/n$

$$V_p = \frac{\frac{1}{n}e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}} \tag{12.7}$$

The kinetic energy, $T$, of the electron MO is given by Eq. (11.119)

$$T = \frac{2\hbar^2}{m_e a\sqrt{a^2-b^2}} \ln \frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} \tag{12.8}$$

Substitution of $a$ and $b$ given by Eqs. (12.2) and (12.4), respectively, into Eqs. (12.6-12.8) is:

$$V_e = \frac{-4e^2}{n^2 8\pi\varepsilon_0 a_H} \ln 3 = \frac{-59.7575\ eV}{n^2} \tag{12.9}$$

$$V_p = \frac{e^2}{n^2 8\pi\varepsilon_0 a_H} = \frac{13.5984\ eV}{n^2} \tag{12.10}$$

$$T = \frac{2e^2}{n^2 8\pi\varepsilon_0 a_H} \ln 3 = \frac{29.8787\ eV}{n^2} \tag{12.11}$$

The Doppler term, $\overline{E}_{osc}$, for hydrogen is given by Eq. (11.189) where $p = 1/n$

$$\overline{E}_{osc}\left(H_2^+\right) = \overline{E}_D + \overline{E}_{Kvib} = -\left(\frac{1}{n}\right)^3 0.118755\ eV + \frac{1}{2}\left(\frac{1}{n}\right)^2 \left(0.29282\ eV\right) \tag{12.12}$$

The total energy, $E_T$, for the hydrogen molecular ion given by Eqs. (11.191-11.193) is:

$$\begin{aligned} E_T &= -\left(\frac{1}{n}\right)^2 \left\{ \frac{e^2}{8\pi\varepsilon_0 a_H}(4\ln 3 - 1 - 2\ln 3)\left[1 + \left(\frac{1}{n}\right)\sqrt{\frac{2\hbar\sqrt{\frac{\frac{2e^2}{4\pi\varepsilon_0\left(2a_H\right)^3}}{m_e}}}{m_e c^2}}\right] - \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \right\} \\ &= -\left(\frac{1}{n}\right)^2 16.2803\ eV - \left(\frac{1}{n}\right)^3 0.118755\ eV + \frac{1}{2}\left(\frac{1}{n}\right)^2 \hbar\sqrt{\frac{k}{\mu}} \\ &= -\left(\frac{1}{n}\right)^2 16.13392\ eV - \left(\frac{1}{n}\right)^3 0.118755\ eV \end{aligned} \tag{12.13}$$

The negative of Eq. (12.13) is the ionization energy of the excited state of $H_2^+$. The energy $T_e$ from the $n = 1$ state (also referred to as the state X) to the energy of the $n^{th}$ excited state is given by the difference of $E_T$ given by Eq. (12.13) and the energy of unexcited $H_2^+$ given by Eq. (12.13) with $n = 1$:

$$T_e = -16.13392\ eV\left(\frac{1}{n^2} - 1\right) - 0.118755\ eV\left(\frac{1}{n^3} - 1\right) \tag{12.14}$$

These states are much higher in energy than the bond dissociation energy and cannot be observed. This result is consistent with observations wherein the excited state spectrum of $H_2^+$ comprises only excited vibrational levels and levels within a van der Waals state [1–3].

## VIBRATION OF THE EXCITED STATES OF THE HYDROGEN MOLECULAR ION

It can be shown that a perturbation of the orbit determined by an inverse-squared force results in simple harmonic oscillatory motion of the orbit [4]. The resonant vibrational frequency for $H_2^+$ given by Eq. (11.160) is

$$\omega(0)=\left(\frac{1}{n}\right)^2\sqrt{\frac{k(0)}{\mu}}=\left(\frac{1}{n}\right)^2\sqrt{\frac{165.51\ Nm^{-1}}{\mu}}=\left(\frac{1}{n}\right)^2 4.449\ \times\ 10^{14}\ radians/s \tag{12.15}$$

wherein $p=1/n$. The spring constant, $k(0)$, for $H_2^+$ excited states given by Eq. (11.162) is:

$$k(0)=\left(\frac{1}{n}\right)^4 165.51\ Nm^{-1} \tag{12.16}$$

The vibrational energy, $E_{vib}(0)$, of the $H_2^+$ excited state for the determination of $\bar{E}_{osc}$ given by Eq. (11.163) is:

$$E_{vib}(0)=\left(\frac{1}{n}\right)^2 0.2928\ eV \tag{12.17}$$

The amplitude of oscillation given by Eq. (11.164) is:

$$A_{reduced}(0)=n0.1125a_0 \tag{12.18}$$

The vibrational energy for the $H_2^+$ excited-state $\upsilon=1\rightarrow\upsilon=0$ transition given by Eq. (11.166) is:

$$E_{vib}(1)=\left(\frac{1}{n}\right)^2 0.270\ eV \tag{12.19}$$

The anharmonicity term of the $H_2^+$ excited state given by Eq. (11.169) is:

$$\omega_0 x_0=\frac{100hc\left(8.06573\times10^3\ \frac{cm^{-1}}{eV}\left(\frac{1}{n}\right)^2 0.270\ eV\right)^2}{4e\left(\left(\frac{1}{n}\right)^2 2.535\ eV+\left(\frac{1}{n}\right)^3 0.118755\ eV\right)}cm^{-1} \tag{12.20}$$

## MAGNETIC MOMENT OF AN ELLIPSOIDAL MOLECULAR ORBITAL

The magnetic dipole moment, $\mu$, of a current loop is:

$$\mu=iA \tag{12.21}$$

where $i$ is the current and $A$ is the area of the loop. For any elliptic orbital due to a central field, the frequency, $f$, is:

$$f=\frac{\frac{L}{m}}{2A}=\frac{\frac{L}{m}}{2\pi ab} \tag{12.22}$$

where $L$ is the angular momentum, $m$ is the mass, and the area $A$ of an ellipse is given by Eq. (11.25). The current, $i$, is:

$$i=ef=\frac{\frac{eL}{m_e}}{2\pi ab} \tag{12.23}$$

where $e$ is the charge. The magnetic moment is given by substitution of Eqs. (12.23) and (11.25) into Eq. (12.21) where $L=\frac{\hbar}{2}$ is the intrinsic electron angular momentum of the ellipsoidal MO given in the Force Balance of Hydrogen-type Molecules section:

$$\mu=\frac{1}{2}\frac{e\hbar}{2m_e}=\frac{\mu_B}{2} \tag{12.24}$$

where $\mu_B$ is the Bohr magneton. In a Larmor excited state, the electron gains $L=\hbar$ along the semimajor axis as the intrinsic angular momentum precesses about this axis at the Larmor frequency. The magnetic moment of the Larmor excited state of cylindrical symmetry is given by Eq. (2.65):

$$\mu=\frac{e\hbar}{2m_e}=\mu_B \tag{12.25}$$

which is the Bohr magneton.

## MAGNETIC FIELD OF AN ELLIPSOIDAL MOLECULAR ORBITAL

The magnetic field can be solved as a magnetostatic boundary value problem, which is equivalent to that of a uniformly magnetized ellipsoid. The magnetic scalar potential inside the ellipsoidal MO, $\phi^-$, [5] and outside of the MO, $\phi^+$, [6] are

$$\phi^- = \frac{e\hbar}{2m_e}\int_0^\infty \frac{ds}{(s+a^2)R_\xi} \tag{12.26}$$

and

$$\phi^+ = \frac{3e\hbar}{8\pi m_e}\frac{\xi}{a^2-b^2}\left(\frac{\eta}{2}\ln\frac{\eta+1}{\eta-1}-1\right) \tag{12.27}$$

respectively, where $R_\xi$ for a prolate spheroid given by Stratton [7] (Eq. (11.32)) is:

$$R_\xi = \left(\xi+b^2\right)\sqrt{\left(\xi+a^2\right)} \tag{12.28}$$

and the spheroidal [7] parameters for Eq. (12.27) after Chang [6] are:

$$\eta = \sqrt{\frac{1}{2}\left[\left(1+x^2+y^2+z^2\right)+\sqrt{\left(1+x^2+y^2+z^2\right)^2-4x^2}\right]} \tag{12.29}$$

$$\xi = \frac{x}{\eta} \tag{12.30}$$

The magnetic field inside the ellipsoidal MO, $\mathbf{H}_x^-$, is [5]:

$$\begin{aligned}\mathbf{H}_x^- &= -\frac{\delta\phi^-}{\delta x}\\ &= \frac{-e\hbar}{2m_e}\int_0^\infty \frac{ds}{(s+a^2)R_\xi}\\ &= \frac{-e\hbar}{2m_e}\int_0^\infty \frac{ds}{(s+b^2)(s+a^2)^{3/2}}\\ &= \frac{e\hbar}{2m_e}\frac{1}{a^3\left(1-\frac{b^2}{a^2}\right)^{3/2}}\left(2\sqrt{1-\frac{b^2}{a^2}}+\ln\frac{1+\sqrt{1-\frac{b^2}{a^2}}}{1-\sqrt{1-\frac{b^2}{a^2}}}\right)\end{aligned} \tag{12.31}$$

The magnetic field inside the ellipsoidal MO is uniform and parallel to the semimajor axis. The Cartesian-coordinate magnetic field components outside the ellipsoidal MO, $\mathbf{H}_{x,y,z}^+$, are obtained by taking the gradient of $\phi^+$ given by Eq. (12.27):

$$\mathbf{H}_{x,y,z}^+ = -\nabla\phi^+ = -\sum_{j=1}^{3}\frac{\delta\phi^+}{\delta u^j}\mathbf{i}_j \tag{12.32}$$

where

$$u^1 = x \qquad u^2 = y \qquad u^3 = z \tag{12.33}$$

Substitution of Eq. (12.27) into Eq. (12.32) gives [6]

$$\mathbf{H}_x^+ = -\frac{3e\hbar}{8\pi m_e\left(a^2-b^2\right)^{3/2}}\left(\frac{1}{2}\ln\frac{\eta+1}{\eta-1}-\frac{\eta}{\eta^2-\xi^2}\right) \tag{12.34}$$

$$\mathbf{H}_y^+ = \frac{3e\hbar}{8\pi m_e\left(a^2-b^2\right)^{3/2}}\frac{\xi\sqrt{1-\xi^2}}{\sqrt{\eta^2-1}\left(\eta^2-\xi^2\right)}\cos\theta \tag{12.35}$$

$$\mathbf{H}_z^+ = \frac{3e\hbar}{8\pi m_e\left(a^2-b^2\right)^{3/2}}\frac{\xi\sqrt{1-\xi^2}}{\sqrt{\eta^2-1}\left(\eta^2-\xi^2\right)}\sin\theta \tag{12.36}$$

where

$$\theta = \arctan\frac{z}{y} \tag{12.37}$$

A plot of the field lines of the magnetic dipole due to a resonant Larmor excitation of the prolate-spheroidal $H_2^+$ MO is shown in Figures 12.1A-C.

Figure 12.1A. The two-dimensional cross-section of the field lines of the magnetic dipole due to a resonant Larmor excitation of the prolate-spheroidal $H_2^+$ MO. The internal field is uniform, and the field external to the prolate spheroidal MO is a dipole field.

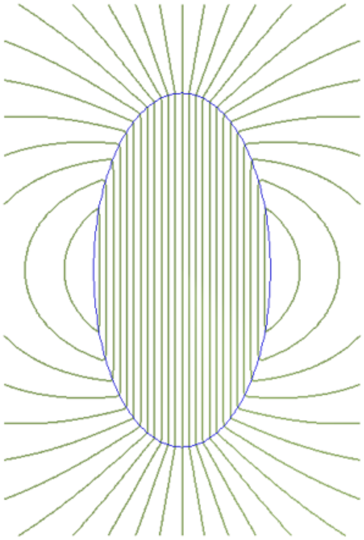


Figure 12.1B. The field lines of the magnetic dipole due to a resonant Larmor excitation of the prolate-spheroidal $H_2^+$ MO. The field external to the prolate spheroidal MO is a dipole field.

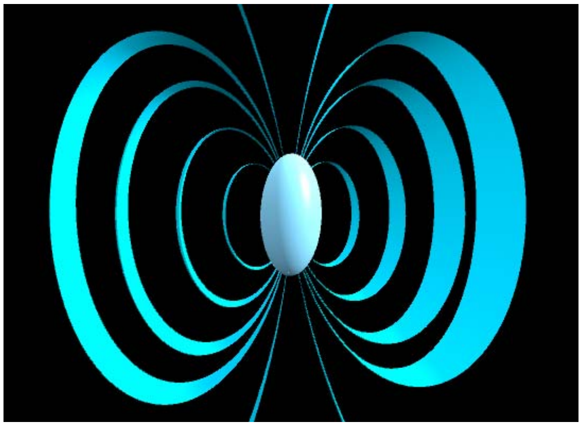
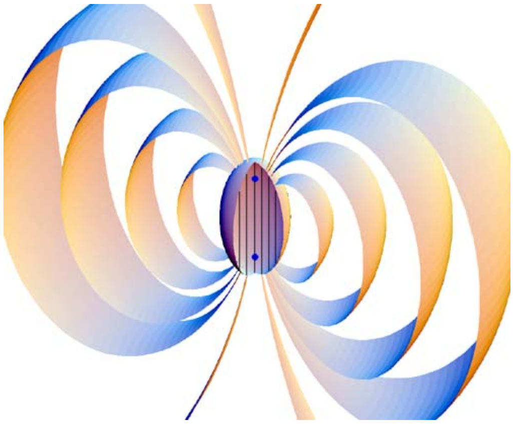


Figure 12.1C. The field lines of the magnetic dipole due to a resonant Larmor excitation of the prolate-spheroidal $H_2^+$ MO with the MO partially cut-away to show the uniform internal field lines.



# EXCITED STATES OF THE HYDROGEN MOLECULE

## FORCE BALANCE OF THE EXCITED STATES OF THE HYDROGEN MOLECULE

In the mathematical limit, as the eccentricity goes to zero the hydrogen molecule becomes the helium atom. The excited states of the hydrogen molecule are determined by the same physics as those of the helium atom. It was shown in the Excited States of Helium section that the inner atomic orbital is essentially that of $He^+$ for all excited states with the exact result upon ionization. The infinite $H_2$ excited state corresponds to a free electron with the inner MO and protons comprising $H_2^+$. Implicit in the calculation of the energy of the outer electron of each $H_2$ excited state is that the inner electron has the geometrical parameters, component energies, and the total energy of $H_2^+$ as shown to very good approximation for the inner atomic electron of helium excited states. For $H_2$, the excited-state photon's two-dimensional ellipsoidal electric field at the outer electron superimposes that of the field of the nuclei at the foci of the inner MO and inner MO charge such that the resultant electric field has a magnitude $e/n$ in the direction of $\mathbf{i}_\xi$ at the outer electron where $n = 2,3,4,...$ for excited states. Then, the force balance of the outer excited-state electron is given by the balance between the centrifugal force, the central Coulombic force corresponding to the effective central field due to the superposition of the photon field at the outer electron and the net field of the protons at the foci of the inner MO, and the magnetic forces for the particular spin and orbital state. The geometrical parameters for $H_2$ are determined from the semimajor axis given by the force balance and the relationships among the ellipsoidal parameters. The energies corresponding to the excited electron are given by the prolate spheroidal energy equations given in the Derivation of the General Geometrical and Energy Equations of Organic Chemistry section except for a 1/2 correction corresponding to a single electron, and the electric terms are scaled according to the effective central field of $1/n$.

### SINGLET EXCITED STATES

$\ell = 0$

The force balance between the electric, magnetic, and centrifugal forces of the outer electron given by Eqs. (9.10) and (11.285) is:

$$\frac{\hbar^2}{m_e a^2 b^2} D = \frac{1}{n} \frac{e^2}{8\pi\varepsilon_0 ab^2} D + \frac{1}{n} \frac{2m}{3} \frac{1}{2} \frac{\hbar^2}{2m_e a^2 b^2} D \tag{12.38}$$

where the geometrical factor due to the electron rotation about the semimajor axis is given by Eq. (11.391) and $m$ is a positive or negative integer wherein the inner and outer electron may rotate relative to each other to quantized the magnetic force such that net relative motion obeys the condition $\ell = 0$. The parametric solution given by Eq. (11.83) occurs when semimajor axis, $a$, is:

$$a = a_0\left(2n - \frac{m}{3}\right) \tag{12.39}$$

The internuclear distance, $2c'$, which is the distance between the foci is given by Eq. (11.79) where $p = 1/n$.

$$2c' = 2\sqrt{\frac{aa_0}{2p}} = 2a_0\sqrt{\frac{n\left(2n - \frac{m}{3}\right)}{2}} \tag{12.40}$$

The semiminor axis is given by Eq. (11.80).

$$b = \sqrt{a^2 - c'^2} = a_0\left(2n - \frac{m}{3}\right)\sqrt{1 - \frac{n}{2\left(2n - \frac{m}{3}\right)}} \tag{12.41}$$

The eccentricity, $e$, is given by Eq. (11.67).

$$e = \frac{c'}{a} = \sqrt{\frac{n}{2\left(2n - \frac{m}{3}\right)}} \tag{12.42}$$

$\ell \neq 0$

The excited singlet states of the hydrogen molecule for $\ell \neq 0$ are solved using the same approach as those of the excited states of the helium atom given in the corresponding section, wherein the force balance due to the $a_{Mag}(\ell, m)$ terms corresponding to prolate spheroid geometry rather than spherical are also associated Legendre functions or spherical harmonics with regard to the semimajor axis as given by Li, Kang, and Leong [8].

The magnetic forces comprise the component of Eq. (12.38) corresponding to the nondynamic current and the $a_{Mag}(\ell, m)$ component due to the time dynamic modulation current and its interaction with electron spin. The force balance between the electric, magnetic, and centrifugal forces of the outer electron given by Eqs. (12.38) and (9.52) is

$$\frac{\hbar^2}{m_e a^2 b^2} D = \frac{1}{n}\frac{e^2}{8\pi\varepsilon_0 ab^2} D + \frac{1}{n}\frac{m}{3}\frac{\hbar^2}{2m_e a^2 b^2} D - \frac{1}{n}\frac{\frac{3}{2}}{(2\ell+1)!!}\left(\frac{\ell+1}{\ell}\right)^{1/2}\frac{1}{\ell+2}\frac{1}{2}\frac{\hbar^2}{m_e a^2 b^2}\left(1-\sqrt{\frac{\ell}{\ell+1}}\right) D \tag{12.43}$$

where the $\sqrt{3/4}$ and $r^{-3}$ terms are replaced by one and $Da^{-2}b^{-2}$ as given in the Force Balance of Hydrogen-Types Molecules section. The parametric solution given by Eq. (11.83) occurs when semimajor axis, $a$, is:

$$a = a_0\left(2n - \frac{m}{3} + \frac{\frac{3}{2}}{(2\ell+1)!!}\left(\frac{\ell+1}{\ell}\right)^{1/2}\frac{1}{\ell+2}\left(1-\sqrt{\frac{\ell}{\ell+1}}\right)\right) \tag{12.44}$$

The internuclear distance, $2c'$, which is the distance between the foci is given by Eq. (11.79) where $p = 1/n$.

$$2c' = 2\sqrt{\frac{aa_0}{2p}} = 2a_0\sqrt{\frac{n\left(2n - \frac{m}{3} + \frac{\frac{3}{2}}{(2\ell+1)!!}\left(\frac{\ell+1}{\ell}\right)^{1/2}\frac{1}{\ell+2}\left(1-\sqrt{\frac{\ell}{\ell+1}}\right)\right)}{2}} \tag{12.45}$$

The semiminor axis is given by Eq. (11.80).

$$b = \sqrt{a^2 - c'^2} = a_0\left(\left(2n - \frac{m}{3} + \frac{\frac{3}{2}}{(2\ell+1)!!}\left(\frac{\ell+1}{\ell}\right)^{1/2}\frac{1}{\ell+2}\left(1-\sqrt{\frac{\ell}{\ell+1}}\right)\right)\sqrt{1 - \frac{n}{2\left(2n - \frac{m}{3} + \frac{\frac{3}{2}}{(2\ell+1)!!}\left(\frac{\ell+1}{\ell}\right)^{1/2}\frac{1}{\ell+2}\left(1-\sqrt{\frac{\ell}{\ell+1}}\right)\right)}}\right) \tag{12.46}$$

The eccentricity, $e$, is given by Eq. (11.67).

$$e = \frac{c'}{a} = \sqrt{\frac{n}{2\left(2n - \frac{m}{3} + \frac{\frac{3}{2}}{(2\ell+1)!!}\left(\frac{\ell+1}{\ell}\right)^{1/2}\frac{1}{\ell+2}\left(1-\sqrt{\frac{\ell}{\ell+1}}\right)\right)}} \tag{12.47}$$

## TRIPLET EXCITED STATES

$\ell = 0$

The force-balance equation and semimajor-axis solution of triplet excited states for $\ell = 0$ are equivalent to those of the corresponding singlet excited states given by Eqs. (12.38-12.39). However, due to the triplet spin state, the magnetic force in Eq. (12.38) is increased by a factor of two as in the case of the corresponding helium excited states given in Eq. (9.31). Thus, $m$ is replaced by $2m$. Then, the force balance between the electric, magnetic, and centrifugal forces of the outer electron is

$$\frac{\hbar^2}{m_e a^2 b^2} D = \frac{1}{n}\frac{e^2}{8\pi\varepsilon_0 ab^2} D + \frac{1}{n}\frac{4m}{3}\frac{1}{2}\frac{\hbar^2}{2m_e a^2 b^2} D \tag{12.48}$$

The parametric solution given by Eq. (11.83) occurs when semimajor axis, $a$, is:

$$a = a_0\left(2n - \frac{2m}{3}\right) \tag{12.49}$$

The internuclear distance, $2c'$, which is the distance between the foci is given by Eq. (11.79) where $p = 1/n$.

$$2c' = 2\sqrt{\frac{aa_0}{2p}} = 2a_0\sqrt{\frac{n\left(2n - \frac{2m}{3}\right)}{2}} \tag{12.50}$$

The semiminor axis is given by Eq. (11.80).

$$b = \sqrt{a^2 - c'^2} = a_0\left(2n - \frac{2m}{3}\right)\sqrt{1 - \frac{n}{2\left(2n - \frac{2m}{3}\right)}} \tag{12.51}$$

The eccentricity, $e$, is given by Eq. (11.67).

$$e = \frac{c'}{a} = \sqrt{\frac{n}{2\left(2n - \frac{2m}{3}\right)}} \tag{12.52}$$

$\ell \neq 0$

The magnetic forces of triplet excited molecular states having $\ell \neq 0$ comprise the nondynamic-current component of Eq. (12.43) with the parameter $m$ of the magnetic force of Eq. (12.38) increased by a factor of two and the $a_{Mag}(\ell, m)$ component due to the time dynamic modulation current and its interaction with electron spin. The latter is solved using the same approach as that of the triplet excited states of the helium atom given in the corresponding section. The force balance between the electric, magnetic, and centrifugal forces of the outer electron given by Eqs. (12.48) and (9.63) is

$$\frac{\hbar^2}{m_e a^2 b^2} D = \frac{1}{n}\frac{e^2}{8\pi\varepsilon_0 ab^2} D + \frac{1}{n}\frac{2m}{3}\frac{\hbar^2}{2m_e a^2 b^2} D + \frac{1}{n}\frac{\frac{3}{2}}{(2\ell+1)!!}\left(\frac{\ell+1}{\ell}\right)^{1/2}\frac{1}{\ell+2}\frac{1}{2}\frac{\hbar^2}{m_e a^2 b^2}\left(2-\sqrt{\frac{\ell}{\ell+1}}\right) D \tag{12.53}$$

where the $\sqrt{3/4}$ and $r^{-3}$ terms are replaced by one and $Da^{-2}b^{-2}$ as given in the Force Balance of Hydrogen-Types Molecules section. The parametric solution given by Eq. (11.83) occurs when semimajor axis, $a$, is:

$$a = a_0\left(2n - \frac{2m}{3} - \frac{\frac{3}{2}}{(2\ell+1)!!}\left(\frac{\ell+1}{\ell}\right)^{1/2}\frac{1}{\ell+2}\left(2-\sqrt{\frac{\ell}{\ell+1}}\right)\right) \tag{12.54}$$

The internuclear distance, $2c'$, which is the distance between the foci is given by Eq. (11.79) with the 2 factor and $p = 1/n$.

$$2c' = 2\sqrt{\frac{aa_0}{2p}} = 2a_0\sqrt{\frac{n\left(2n - \frac{2m}{3} - \frac{\frac{3}{2}}{(2\ell+1)!!}\left(\frac{\ell+1}{\ell}\right)^{1/2}\frac{1}{\ell+2}\left(2-\sqrt{\frac{\ell}{\ell+1}}\right)\right)}{2}} \tag{12.55}$$

The semiminor axis is given by Eq. (11.80).

$$b = \sqrt{a^2 - c'^2} = a_0\left(\left(2n - \frac{2m}{3} - \frac{\frac{3}{2}}{(2\ell+1)!!}\left(\frac{\ell+1}{\ell}\right)^{1/2}\frac{1}{\ell+2}\left(2-\sqrt{\frac{\ell}{\ell+1}}\right)\right)\sqrt{1 - \frac{n}{2\left(2n - \frac{2m}{3} - \frac{\frac{3}{2}}{(2\ell+1)!!}\left(\frac{\ell+1}{\ell}\right)^{1/2}\frac{1}{\ell+2}\left(2-\sqrt{\frac{\ell}{\ell+1}}\right)\right)}}\right) \tag{12.56}$$

The eccentricity, $e$, is given by Eq. (11.67).

$$e = \frac{c'}{a} = \sqrt{\frac{n}{2\left(2n - \frac{2m}{3} - \frac{\frac{3}{2}}{(2\ell+1)!!}\left(\frac{\ell+1}{\ell}\right)^{1/2}\frac{1}{\ell+2}\left(2-\sqrt{\frac{\ell}{\ell+1}}\right)\right)}} \tag{12.57}$$

## ENERGIES OF THE EXCITED STATES OF THE HYDROGEN MOLECULE

The component energies of the outer electron of the hydrogen molecule of the excited state corresponding to quantum number $n$ are given by Eqs. (11.290-11.293) and (11.233-11.236) where the energies are each multiplied by a factor of 1/2 since the outer MO comprises only one electron, and those corresponding to charge are multiplied by effective-charge factor of $1/n$:

$$V_e = \frac{1}{n}\frac{1}{2}\frac{-2e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} \tag{12.58}$$

$$V_p = 0 \tag{12.59}$$

$$T = \frac{1}{2}\frac{\hbar^2}{2m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} \tag{12.60}$$

$$V_m = \frac{1}{n}\frac{1}{2}\frac{-\hbar^2}{4m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} \tag{12.61}$$

$$\overline{E}_{osc}(H_2) = \overline{E}_D + \overline{E}_{Kvib} = -(V_e + T + V_m + V)\sqrt{\frac{2\hbar\sqrt{\frac{\frac{1}{n^4}\frac{1}{2}\frac{e^2}{4\pi\varepsilon_0 a_0^3}}{m_e}}}{m_e c^2}} + \overline{E}_{Kvib} \tag{12.62}$$

where with regard to Eq. (12.62), the angular frequency of reentrant oscillation $\omega$ and corresponding energies $E_K$, $\bar{E}_D$, and $\bar{E}_{osc}$ are given by Eqs. (11.233-11.236) with $p = 1/n$ and the factor of 1/2 was applied since the outer MO comprises only one electron. The potential energy, $V_p$, due to proton-proton repulsion (Eq. 12.59)) is zero. The repulsive term applies only to the total energy of $H_2^+$ which is implicit in the calculation of the energy of the outer electron of the $H_2$ excited state as in the case with the energy of the helium excited states given in the Excited States of Helium section. The total energy, $E_T$, for the hydrogen molecular excited state given by Eqs. (11.239-11.240) is:

$$E_T = V_e + T + V_m + V_p + \bar{E}_{osc} \tag{12.63}$$

$$E_T = -\left\{ \left( \frac{-e^2}{8\pi\varepsilon_0} - \frac{n\hbar^2}{4m_e a} + \frac{\hbar^2}{8m_e a} \right) \frac{1}{n\sqrt{a^2-b^2}} \ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} \left[ 1 + \sqrt{\frac{2\hbar\sqrt{\frac{\frac{e^2}{n^4 8\pi\varepsilon_0 a_0^3}}{m_e}}}{m_e c^2}} \right] - \bar{E}_{Kvib} \right\} \tag{12.64}$$

The negative of Eq. (12.64) is the ionization energy of the excited state of $H_2$. The energy $T_e$ from the $n = 1$ state (also referred to as the state X) to the energy of the $n^{th}$ excited state is given by the sum of $E_T$ given by Eq. (12.64) and $IP_1$ of $H_2$ given by Eq. (11.298):

$$T_e\left(H_2\right) = E_T + 15.4248\ eV \tag{12.65}$$

The geometrical (Eqs. (12.38-12.55) and energy (Eqs. (12.56-12.62)) parameters of singlet and triplet excited states of molecular hydrogen are given in Tables 12.1 and 12.2, respectively, where $\bar{E}_{Kvib}$ was given to very good approximation by $\omega_e$ of $H_2^+$ (the $n = \infty$ state) since there is a close match with $\omega_e$ of each excited state [9]. The color scale, translucent views of the charge densities of exemplary ellipsoidal spherical harmonics that modulate the time independent spin function are shown in Figure 12.2. The modulation functions propagate about the major axis as spatially and temporally harmonic charge-density waves.

Figure 12.2. Overhead-view of exemplary color scale, translucent views of the charge-densities of the inner and outer electrons of molecular-hydrogen excited states. The outer-electron orbital function modulates the time-constant (spin) function, (shown for t = 0; three-dimensional view). The inner electron is essentially that of $H_2^+$ (nuclei red, not to scale).

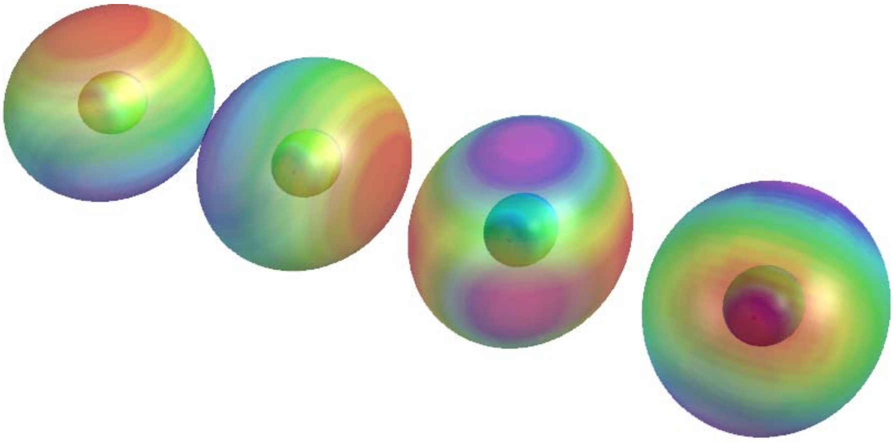


Table 12.1. The geometrical and energy parameters of the singlet excited states of molecular hydrogen compared to the experimental energies [9].

| $n$ | $m$ | $l$ | $a\ (a_0)$ | $a\ (m)$ | $b,c\ (m)$ | $c'\ (m)$ | $2c'\ (m)$ | $e$ | $V_e\ (eV)$ | $V_p\ (eV)$ | $T\ (eV)$ | $V_m\ (eV)$ | $E_T\ (H_2MO)\ (eV)$ | $\overline{E}_{Kvib}\ (eV)$ | $\omega\ (10^{15}\ rad/s)$ | $E_K\ (eV)$ | $\overline{E}_D\ (eV)$ | $\overline{E}_{osc}\ (eV)$ | $IP_1(H_2)\ (eV)$ | $Cal.\ T_e\ (eV)$ | $Exp.\ T_e\ (eV)$ | State | $Exp.\ T_e\ (cm^{-1})$ | Relative Error |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 2 | 4 | 1 | 2.73570 | 1.44767E-10 | 1.15312E-10 | 8.75257E-11 | 1.75051E-10 | 0.60460 | -5.76118 | 0 | 2.10592 | -0.52648 | -4.18174 | 0.28479 | 7.30819 | 4.81038 | -1.81447E-02 | 0.12425 | 15.424814 | 11.3673 | 11.36819 | B | 91689.9 | 0.00008 |
| 2 | 1 | 1 | 3.73570 | 1.97685E-10 | 1.69169E-10 | 1.02279E-10 | 2.04558E-10 | 0.51739 | -4.03193 | 0 | 1.07930 | -0.26982 | -3.22245 | 0.28479 | 7.30819 | 4.81038 | -1.39823E-02 | 0.12841 | 15.424814 | 12.3308 | 12.40385 | C | 100043.0 | 0.00589 |
| 2 | 0 | 0 | 4.00000 | 2.11671E-10 | 1.83312E-10 | 1.05835E-10 | 2.11671E-10 | 0.50000 | -3.73688 | 0 | 0.93422 | -0.23355 | -3.03621 | 0.28479 | 7.30819 | 4.81038 | -1.31742E-02 | 0.12922 | 15.424814 | 12.5178 | 12.40631 | E | 100062.8 | -0.00899 |
| 2 | -2 | 0 | 4.66667 | 2.46949E-10 | 2.18897E-10 | 1.14315E-10 | 2.28631E-10 | 0.46291 | -3.15548 | 0 | 0.67618 | -0.16904 | -2.64835 | 0.28479 | 7.30819 | 4.81038 | -1.14913E-02 | 0.13091 | 15.424814 | 12.9074 | 12.82999 | F | 103480 | -0.00603 |
| 3 | 4 | 0 | 4.66667 | 2.46949E-10 | 2.03426E-10 | 1.40007E-10 | 2.80014E-10 | 0.56695 | -2.20446 | 0 | 0.70858 | -0.11810 | -1.61398 | 0.28479 | 3.24809 | 2.13795 | -4.66874E-03 | 0.13773 | 15.424814 | 13.9486 | 13.96780 | K | 112657 | 0.00138 |
| 3 | 4 | 1 | 4.73570 | 2.50603E-10 | 2.07146E-10 | 1.41039E-10 | 2.82078E-10 | 0.56280 | -2.16761 | 0 | 0.68657 | -0.11443 | -1.59546 | 0.28479 | 3.24809 | 2.13795 | -4.61517E-03 | 0.13778 | 15.424814 | 13.9671 | 13.98466 | G | 112793 | 0.00125 |
| 3 | 3 | 0 | 5.00000 | 2.64589E-10 | 2.21371E-10 | 1.44921E-10 | 2.89842E-10 | 0.54772 | -2.03734 | 0 | 0.61120 | -0.10187 | -1.52801 | 0.28479 | 3.24809 | 2.13795 | -4.42004E-03 | 0.13798 | 15.424814 | 14.0348 | 14.01839 | I | 113065 | -0.00117 |
| 3 | 3 | 2 | 5.00562 | 2.64886E-10 | 2.21673E-10 | 1.45003E-10 | 2.90005E-10 | 0.54742 | -2.03474 | 0 | 0.60974 | -0.10162 | -1.52663 | 0.28479 | 3.24809 | 2.13795 | -4.41606E-03 | 0.13798 | 15.424814 | 14.0362 | 14.02818 | Q | 113144 | -0.00057 |
| 3 | 3 | 1 | 5.06904 | 2.68242E-10 | 2.25081E-10 | 1.45918E-10 | 2.91836E-10 | 0.54398 | -2.00588 | 0 | 0.59357 | -0.09893 | -1.51124 | 0.28479 | 3.24809 | 2.13795 | -4.37155E-03 | 0.13803 | 15.424814 | 14.0516 | 14.06042 | J | 113404 | 0.00063 |
| 3 | 2 | 0 | 5.33333 | 2.82228E-10 | 2.39270E-10 | 1.49674E-10 | 2.99348E-10 | 0.53033 | -1.89402 | 0 | 0.53269 | -0.08878 | -1.45011 | 0.28479 | 3.24809 | 2.13795 | -4.19471E-03 | 0.13820 | 15.424814 | 14.1129 | 14.12043 | D | 113888 | 0.00053 |
| 3 | 2 | 1 | 5.40237 | 2.85881E-10 | 2.42973E-10 | 1.50639E-10 | 3.01279E-10 | 0.52693 | -1.86685 | 0 | 0.51834 | -0.08639 | -1.43490 | 0.28479 | 3.24809 | 2.13795 | -4.15070E-03 | 0.13825 | 15.424814 | 14.1282 | 14.12055 | H | 113889 | -0.00054 |
| 3 | 1 | 0 | 5.66667 | 2.99867E-10 | 2.57134E-10 | 1.54280E-10 | 3.08561E-10 | 0.51450 | -1.76971 | 0 | 0.46845 | -0.07808 | -1.37933 | 0.28479 | 3.24809 | 2.13795 | -3.98998E-03 | 0.13841 | 15.424814 | 14.1839 | 14.19631 | L | 114500 | 0.00087 |
| 3 | 1 | 1 | 5.73570 | 3.03520E-10 | 2.60830E-10 | 1.55217E-10 | 3.10434E-10 | 0.51139 | -1.74599 | 0 | 0.45661 | -0.07610 | -1.36548 | 0.28479 | 3.24809 | 2.13795 | -3.94992E-03 | 0.13845 | 15.424814 | 14.1978 | 14.21540 | M | 114654 | 0.00124 |
| 3 | -3 | 1 | 7.06904 | 3.74077E-10 | 3.32025E-10 | 1.72316E-10 | 3.44633E-10 | 0.46064 | -1.38755 | 0 | 0.29443 | -0.04907 | -1.14219 | 0.28479 | 3.24809 | 2.13795 | -3.30401E-03 | 0.13909 | 15.424814 | 14.4217 | 14.41551 | N | 116268 | -0.00043 |
| 4 | 4 | 1 | 6.73570 | 3.56438E-10 | 2.98872E-10 | 1.94226E-10 | 3.88452E-10 | 0.54491 | -1.13268 | 0 | 0.33632 | -0.04204 | -0.83840 | 0.28479 | 1.82705 | 1.20259 | -1.81892E-03 | 0.14058 | 15.424814 | 14.7270 | 14.71581 | R | 118690 | -0.00076 |
| 4 | 1 | 2 | 7.67229 | 4.06000E-10 | 3.49094E-10 | 2.07290E-10 | 4.14580E-10 | 0.51057 | -0.97861 | 0 | 0.25510 | -0.03189 | -0.75539 | 0.28479 | 1.82705 | 1.20259 | -1.63883E-03 | 0.14076 | 15.424814 | 14.8102 | 14.81549 | T | 119494 | 0.00036 |
| 4 | 1 | 1 | 7.73570 | 4.09356E-10 | 3.52488E-10 | 2.08145E-10 | 4.16290E-10 | 0.50847 | -0.96969 | 0 | 0.25070 | -0.03134 | -0.75032 | 0.28479 | 1.82705 | 1.20259 | -1.62783E-03 | 0.14077 | 15.424814 | 14.8153 | 14.81772 | P | 119512 | 0.00017 |
| 4 | -1 | 0 | 8.33333 | 4.40981E-10 | 3.84438E-10 | 2.16036E-10 | 4.32071E-10 | 0.48990 | -0.89305 | 0 | 0.21433 | -0.02679 | -0.70551 | 0.28479 | 1.82705 | 1.20259 | -1.53061E-03 | 0.14087 | 15.424814 | 14.8602 | 14.85591 | S | 119820 | -0.00029 |
| 4 | -1 | 1 | 8.40237 | 4.44634E-10 | 3.88126E-10 | 2.16929E-10 | 4.33857E-10 | 0.48788 | -0.88497 | 0 | 0.21065 | -0.02633 | -0.70066 | 0.28479 | 1.82705 | 1.20259 | -1.52008E-03 | 0.14088 | 15.424814 | 14.8650 | 14.85975 | O | 119851 | -0.00036 |

Avg. Rel. Error -0.00035

Table 12.2. The geometrical and energy parameters of the triplet excited states of molecular hydrogen compared to the experimental energies [9].

| $n$ | $m$ | $l$ | $a\ (a_0)$ | $a\ (m)$ | $b,c\ (m)$ | $c'\ (m)$ | $2c'\ (m)$ | $e$ | $V_e\ (eV)$ | $V_p\ (eV)$ | $T\ (eV)$ | $V_m\ (eV)$ | $E_T\ (H_2MO)\ (eV)$ | $\overline{E}_{Kvib}\ (eV)$ | $\omega\ (10^{15}\ rad/s)$ | $E_K\ (eV)$ | $\overline{E}_D\ (eV)$ | $\overline{E}_{osc}\ (eV)$ | $IP_1(H_2)\ (eV)$ | $Cal.\ T_e\ (eV)$ | $Exp.\ T_e\ (eV)$ | State | $Exp.\ T_e\ (cm^{-1})$ | Relative Error |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 2 | 1 | 1 | 3.02860 | 1.60266E-10 | 1.31165E-10 | 9.20919E-11 | 1.84184E-10 | 0.57462 | -5.11612 | 0 | 1.68927 | -0.42232 | -3.84916 | 0.28479 | 7.30819 | 4.81038 | -1.67016E-02 | 0.12570 | 15.424814 | 11.7013 | 11.87084 | c | 95744 | 0.01428 |
| 2 | 1 | 0 | 3.33333 | 1.76392E-10 | 1.47580E-10 | 9.66141E-11 | 1.93228E-10 | 0.54772 | -4.58402 | 0 | 1.37520 | -0.34380 | -3.55261 | 0.28479 | 7.30819 | 4.81038 | -1.54149E-02 | 0.12698 | 15.424814 | 11.9992 | 11.89489 | a | 95938 | -0.00877 |
| 3 | 4 | 1 | 3.02860 | 1.60266E-10 | 1.13859E-10 | 1.12789E-10 | 2.25578E-10 | 0.70376 | -3.72248 | 0 | 1.84367 | -0.30728 | -2.18609 | 0.28479 | 3.24809 | 2.13795 | -6.32367E-03 | 0.13607 | 15.424814 | 13.3748 | 13.36275 | e | 107777 | -0.00090 |
| 3 | 2 | 2 | 4.63043 | 2.45032E-10 | 2.01471E-10 | 1.39462E-10 | 2.78925E-10 | 0.56916 | -2.22432 | 0 | 0.72056 | -0.12009 | -1.62386 | 0.28479 | 3.24809 | 2.13795 | -4.69732E-03 | 0.13770 | 15.424814 | 13.9387 | 13.97338 | d | 112702 | 0.00249 |
| 3 | 2 | 0 | 4.66667 | 2.46949E-10 | 2.03426E-10 | 1.40007E-10 | 2.80014E-10 | 0.56695 | -2.20446 | 0 | 0.70858 | -0.11810 | -1.61398 | 0.28479 | 3.24809 | 2.13795 | -4.66874E-03 | 0.13773 | 15.424814 | 13.9486 | 13.98181 | h | 112770 | 0.00238 |
| 3 | 1 | 1 | 5.02860 | 2.66102E-10 | 2.22908E-10 | 1.45335E-10 | 2.90670E-10 | 0.54616 | -2.02419 | 0 | 0.60380 | -0.10063 | -1.52102 | 0.28479 | 3.24809 | 2.13795 | -4.39984E-03 | 0.13800 | 15.424814 | 14.0418 | 13.98268 | g | 112777 | -0.00423 |
| 3 | 1 | 2 | 5.29710 | 2.80310E-10 | 2.37326E-10 | 1.49165E-10 | 2.98329E-10 | 0.53214 | -1.90861 | 0 | 0.54047 | -0.09008 | -1.45822 | 0.28479 | 3.24809 | 2.13795 | -4.21816E-03 | 0.13818 | 15.424814 | 14.1048 | 14.01132 | i | 113008 | -0.00667 |
| 3 | 1 | 0 | 5.33333 | 2.82228E-10 | 2.39270E-10 | 1.49674E-10 | 2.99348E-10 | 0.53033 | -1.89402 | 0 | 0.53269 | -0.08878 | -1.45011 | 0.28479 | 3.24809 | 2.13795 | -4.19471E-03 | 0.13820 | 15.424814 | 14.1129 | 14.03488 | j | 113198 | -0.00556 |
| 4 | 4 | 1 | 5.02860 | 2.66102E-10 | 2.06512E-10 | 1.67818E-10 | 3.35637E-10 | 0.63065 | -1.59277 | 0 | 0.63349 | -0.07919 | -1.03847 | 0.28479 | 1.82705 | 1.20259 | -2.25298E-03 | 0.14014 | 15.424814 | 14.5265 | 14.47007 | f | 116708 | -0.00390 |
| 4 | 3 | 1 | 5.69526 | 3.01380E-10 | 2.42762E-10 | 1.78596E-10 | 3.57193E-10 | 0.59260 | -1.37400 | 0 | 0.48251 | -0.06031 | -0.95181 | 0.28479 | 1.82705 | 1.20259 | -2.06497E-03 | 0.14033 | 15.424814 | 14.6133 | 14.66658 | v | 118293 | 0.00363 |
| 4 | 3 | 2 | 5.96376 | 3.15589E-10 | 2.57285E-10 | 1.82758E-10 | 3.65516E-10 | 0.57910 | -1.30225 | 0 | 0.43672 | -0.05459 | -0.92012 | 0.28479 | 1.82705 | 1.20259 | -1.99621E-03 | 0.14040 | 15.424814 | 14.6451 | 14.67625 | k | 118371 | 0.00212 |
| 4 | 2 | 1 | 6.36193 | 3.36659E-10 | 2.78763E-10 | 1.88760E-10 | 3.77520E-10 | 0.56069 | -1.20882 | 0 | 0.38002 | -0.04750 | -0.87630 | 0.28479 | 1.82705 | 1.20259 | -1.90115E-03 | 0.14050 | 15.424814 | 14.6890 | 14.68915 | p | 118475 | 0.00001 |
| 4 | 2 | 0 | 6.66667 | 3.52785E-10 | 2.95161E-10 | 1.93228E-10 | 3.86456E-10 | 0.54772 | -1.14600 | 0 | 0.34380 | -0.04298 | -0.84518 | 0.28479 | 1.82705 | 1.20259 | -1.83363E-03 | 0.14056 | 15.424814 | 14.7202 | 14.69250 | s | 118502 | -0.00189 |
| 4 | 1 | 1 | 7.02860 | 3.71937E-10 | 3.14600E-10 | 1.98404E-10 | 3.96808E-10 | 0.53343 | -1.07948 | 0 | 0.30717 | -0.03840 | -0.81070 | 0.28479 | 1.82705 | 1.20259 | -1.75884E-03 | 0.14064 | 15.424814 | 14.7547 | 14.70155 | r | 118575 | -0.00362 |
| 4 | 1 | 0 | 7.33333 | 3.88063E-10 | 3.30941E-10 | 2.02659E-10 | 4.05319E-10 | 0.52223 | -1.02923 | 0 | 0.28070 | -0.03509 | -0.78362 | 0.28479 | 1.82705 | 1.20259 | -1.70007E-03 | 0.14070 | 15.424814 | 14.7819 | 14.79379 | m | 119319 | 0.00080 |
| 5 | 3 | 1 | 7.69526 | 4.07216E-10 | 3.34593E-10 | 2.32104E-10 | 4.64208E-10 | 0.56998 | -0.80341 | 0 | 0.26101 | -0.02610 | -0.56850 | 0.28479 | 1.16931 | 0.76966 | -9.86698E-04 | 0.14141 | 15.424814 | 14.9977 | 14.99651 | n | 120954 | -0.00008 |
| 5 | 3 | 2 | 7.96376 | 4.21424E-10 | 3.49065E-10 | 2.36119E-10 | 4.72237E-10 | 0.56029 | -0.77238 | 0 | 0.24247 | -0.02425 | -0.55416 | 0.28479 | 1.16931 | 0.76966 | -9.61808E-04 | 0.14143 | 15.424814 | 15.0121 | 15.01449 | q | 121099 | 0.00016 |
| 5 | 2 | 1 | 8.36193 | 4.42494E-10 | 3.70488E-10 | 2.41949E-10 | 4.83898E-10 | 0.54679 | -0.73059 | 0 | 0.21843 | -0.02184 | -0.53401 | 0.28479 | 1.16931 | 0.76966 | -9.26832E-04 | 0.14147 | 15.424814 | 15.0323 | 15.03879 | t | 121295 | 0.00043 |
| 6 | -4 | 0 | 14.66667 | 7.76126E-10 | 6.92214E-10 | 3.51016E-10 | 7.02033E-10 | 0.45227 | -0.33334 | 0 | 0.06818 | -0.00568 | -0.27084 | 0.28479 | 0.812021 | 0.53449 | -3.91731E-04 | 0.14201 | 15.424814 | 15.2960 | 15.31031 | u | 123485 | 0.00094 |

Avg. Rel. Error -0.00044

## DIATOMIC MOLECULAR ROTATION

A molecule with a permanent dipole moment can resonantly absorb a photon, which excites a rotational mode about the center of mass of the molecule. Momentum must be conserved with excitation of a rotational mode. The photon carries $\hbar$ of angular momentum; thus, the rotational angular momentum of the molecule changes by $\hbar$. And, the rotational charge-density function is equivalent to the rigid rotor problem considered in the Rotational Parameters of the Electron (Angular Momentum, Rotational Energy, Moment of Inertia) section with the exception that for a diatomic molecule having atoms of masses $m_1$ and $m_2$, the moment of inertia is:

$$I = \mu r^2 \tag{12.66}$$

where $\mu$ is the reduced mass

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \tag{12.67}$$

and where $r$ is the distance between the centers of the atoms, the internuclear distance. The rotational energy levels follow from Eq. (1.71)

$$E_{rotational\ orbital} = \frac{\hbar^2}{2I} J(J+1) \tag{12.68}$$

where $J$ is an integer. For Eq. (12.68), $J = 0$ corresponds to rotation about the z-axis where the internuclear axis is along the x-axis, and $J \neq 0$ corresponds to a linear combination of rotations about the z and y-axis (Figure 11.4).

As given in the Selection Rules section, the radiation of a multipole of order ($\ell$, $m_\ell$) carries $m\hbar$ units of the z component of angular momentum per photon of energy $\hbar\omega$. Thus, the z component of the angular momentum of the corresponding excited rotational state is

$$L_z = m\hbar \tag{12.69}$$

Thus, the selection rule for rotational transitions is:

$$\Delta J = \pm 1 \tag{12.70}$$

In addition, the molecule must possess a permanent dipole moment. In the case of absorption of electromagnetic radiation, the molecule goes from a state with a quantum number $J$ to one with a quantum number of $J+1$. Using Eq. (12.68), the energy difference is:

$$\Delta E = E_{J+1} - E_J = \frac{\hbar^2}{I}\left[J+1\right] \tag{12.71}$$

## DIATOMIC MOLECULAR ROTATION OF HYDROGEN-TYPE MOLECULES

The reduced mass of hydrogen-type molecular ions and molecules, $\mu_{H_2}$, having two protons is given by Eq. (12.67) where $m_1 = m_2 = m_p$, and $m_p$ is the mass of the proton.

$$\mu_{H_2} = \frac{m_p m_p}{m_p + m_p} = \frac{1}{2} m_p \tag{12.72}$$

The moment of inertia of hydrogen-type molecules is given by substitution of the reduced mass (Eq. (12.72)) for $\mu$ of Eq. (12.66) and substitution of the internuclear distance (Eq. (11.204)) for $r$ of Eq. (12.66).

$$I = m_p \frac{a_0^2}{p^2} \tag{12.73}$$

where $p$ is an integer which corresponds to $H_2(1/p)$. The Doppler energy term, $\overline{E}_D$, of the bond energy (Eqs. (11.235), and (11.240-11.241)) decreases the internuclear distance, $r$, of Eq. (12.66), which increases the rotational energy. To determine the internuclear distance considering the correction for $\overline{E}_D$, consider that the contribution of $\overline{E}_D$ to the binding energy is one-half the magnitude of the potential energy contribution as required for an inverse-squared force [10] wherein $\overline{E}_D$ is the source of the additional binding energy term. Then, the sum of ½ $\overline{E}_D$ and the unperturbed total energy comprising the sum of the inverse-squared field terms given by Eqs. (11.207-11.211) is subtracted from the total energy given by Eqs. (11.207-11.211) with the semimajor axis $a$ comprising a variable. The difference is equated to zero, and the resulting Eq. (12.74) is solved reiteratively for the semimajor axis $a$ with the prolate other spheroidal dimensions dependent on the semimajor axis given by Eqs. (11.79-11.80) and (11.67).

$$\left\{\begin{array}{l}\left[\left(\dfrac{-2pe^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}} + \dfrac{\hbar^2}{2m_e a\sqrt{a^2-b^2}}\dfrac{-\hbar^2}{4m_e a\sqrt{a^2-b^2}}\right)\ln\dfrac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} + \dfrac{p}{8\pi\varepsilon_0}\dfrac{e^2}{\sqrt{a^2-b^2}}\right] \\ +ep^2\left(31.63536831+\left(0.5\right)p0.326469\right)\end{array}\right\} = 0 \tag{12.74}$$

internuclear distance for $p = 1$ is

$$2c' = 0.7411\ \mathring{A} \tag{12.75}$$

Eq. (12.75) is also the internuclear distance for molecular hydrogen isotopes such as $D_2$. To a high degree of accuracy, the general result for hydrogen-type molecules is

$$2c' = \frac{0.7411}{p}\ \mathring{A} \tag{12.76}$$

Using Eqs. (12.66), (12.71-12.72), and (12.76), the rotational energy absorbed by a hydrogen-type molecule with the transition from the state with the rotational quantum number $J$ to one with the rotational quantum number $J+1$ is:

$$\Delta E_{J \to J+1} = E_{J+1} - E_J = \frac{p^2\hbar^2}{0.5m_p\left(7.411X10^{-11}m\right)^2}\left[J+1\right] = p^2\left[J+1\right]0.01511\ eV\ = \left[J+1\right]p^2 121.89\ cm^{-1} \tag{12.77}$$

The result of Eq. (12.77) without the correction for centrifugal distortion compares well to the experimental value of $\Delta E = 0.01509\ eV\left(121.7\ cm^{-1}\right)$ for $p=1$ [11].

Using the reduced mass for molecular deuterium which to a high level of accuracy is twice that of molecular hydrogen given by Eq. (12.72) and the internuclear distance given by Eq. (12.76) in Eq. (12.71) gives the rotational energy of deuterium-type molecules as:

$$\Delta E_{J \to J+1} = E_{J+1} - E_J = \frac{p^2\hbar^2}{m_p\left(7.411X10^{-11}m\right)^2}\left[J+1\right] = p^2\left[J+1\right]0.007557\ eV\ = \left[J+1\right]p^2 60.95\ cm^{-1} \tag{12.78}$$

The result of Eq. (12.78) without the correction for centrifugal distortion compares well to the experimental value of $\Delta E = 0.00755\ eV\left(60.90\ cm^{-1}\right)$ for $p=1$ [11].

## DIATOMIC MOLECULAR ROTATION OF HYDROGEN-TYPE MOLECULAR IONS

The moment of inertia of hydrogen-type molecular ions is given by substitution of the reduced mass (Eq. (12.72)) for $\mu$ of Eq. (12.66) and substitution of the internuclear distance (Eq. (11.111)) for $r$ of Eq. (12.66).

$$I = m_p\frac{2a_0^2}{p^2} \tag{12.79}$$

where $p$ is an integer which corresponds to $H_2^+(1/p)$. The Doppler energy term, $\overline{E}_D$, of the bond energy (Eqs. (11.187), and (11.192-11.193)) decreases the internuclear distance, $r$, of Eq. (12.66), which increases the rotational energy. To determine the internuclear distance considering the correction for $\overline{E}_D$, consider that the contribution of $\overline{E}_D$ to the binding energy is one-half the magnitude of the potential energy contribution as required for an inverse-squared force [10] wherein $\overline{E}_D$ is the source of the additional binding energy term. Then, the sum of ½ $\overline{E}_D$ and the unperturbed total energy comprising the sum of the inverse-squared field terms given by Eqs. (11.117-11.121) with the semimajor axis given by Eq. (11.116) is subtracted from the total energy given by Eqs. (11.117-11.121) with the semimajor axis $a$ comprising a variable. The difference is equated to zero, and the resulting Eq. (12.80) is solved reiteratively for the semimajor axis $a$ with the prolate other spheroidal dimensions dependent on the semimajor axis given by Eqs. (11.79-11.80) and (11.67).

$$\left\{\begin{array}{l}\dfrac{-4pe^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}}\ln\dfrac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}}+\dfrac{pe^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}} \\ +\dfrac{2\hbar^2}{m_e a\sqrt{a^2-b^2}}\ln\dfrac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}}+ep^2\left[16.28\ eV+e\left(0.5\right)p0.11875\right]\end{array}\right\}=0 \tag{12.80}$$

internuclear distance for $p=1$ is

$$2c' = 1.0577\ \mathring{A} \tag{12.81}$$

Eq. (12.81) is also the internuclear distance for molecular hydrogen isotopes such as $D_2^+$. To a high degree of accuracy, the general result for hydrogen-type molecular ions is

$$2c' = \frac{1.0577}{p}\ \mathring{A} \tag{12.82}$$

Using Eqs. (12.66), (12.71-12.72), and (12.82), the rotational energy absorbed by a hydrogen-type molecular ion with the transition from the state with the rotational quantum number $J$ to one with the rotational quantum number $J+1$ is:

$$\begin{aligned}\Delta E_{J \to J+1} &= E_{J+1} - E_J = \frac{p^2\hbar^2}{0.5m_p\left(1.0577X10^{-10}m\right)^2}\left[J+1\right] \\ &= p^2\left[J+1\right]0.00742\ eV\ = \left[J+1\right]p^2 59.84\ cm^{-1} = \left[J+1\right]p^2 167.12\ \mu m\end{aligned} \tag{12.83}$$

The result of Eq. (12.83) without the correction for centrifugal distortion is a good match to the experimentally observed wavelength of 169 $\mu m$ [11]. The rotational wavelength for $p = 6$ is 4.7 $\mu m$. A broad 4.7 $\mu m$ solar chromospheric absorption line is observed which was previously assigned to cool carbon monoxide clouds; however, the temperature of the chromosphere, $> 6000\ K$, is higher than that at which carbon monoxide completely decomposes into carbon and oxygen, $< 4000\ K$ [12]. The assignment of the 4.7 $\mu m$ absorption line to the Doppler-broadened $J = 0$ to $J = 1$ rotational transition of $H_2\left[2c' = \frac{a_0}{3}\right]^+$ provides a resolution of the problem of cool carbon monoxide clouds.

Using the reduced mass for molecular deuterium which to a high level of accuracy is twice that of molecular hydrogen given by Eq. (12.72) and the internuclear distance given by Eq. (12.82) in Eq. (12.71) gives the rotational energy of deuterium-type molecular ions as:

$$\Delta E_{J \to J+1} = E_{J+1} - E_J = \frac{p^2 \hbar^2}{m_p \left(1.0577 X 10^{-10} m\right)^2}\left[J+1\right] = p^2\left[J+1\right] 0.0037095\ eV\ = \left[J+1\right] p^2 29.92\ cm^{-1} \tag{12.84}$$

The result of Eq. (12.84) without the correction for centrifugal distortion compares well to the experimental value of $\Delta E = 0.003723\ eV\left(30.03\ cm^{-1}\right)$ for $p = 1$ [13].

## CENTRIFUGAL DISTORTION

The equilibrium internuclear distance of the hydrogen molecular ion and hydrogen molecule can increase as a result of a centrifugal force due to rotation. Since the centrifugal distortion increases as a function of $J$, the rotational term given by Eq. (12.68) can be added as a centrifugal potential to the harmonic oscillator potential energy relationship (Eq. (11.146)) to give $E_J\left(r\right)$, a combined potential dependent on the internuclear separation [14]. From Eq. (11.146) and Eq. (12.68),

$$E_J\left(r\right) = \frac{1}{2} k_0 \left(r - r_e\right)^2 + \frac{\hbar^2}{2I} J(J+1) \tag{12.85}$$

where $r_e$ is the equilibrium internuclear distance with $J = 0$ and $k_0$ is the spring constant with $\upsilon = 0$. Let $r_e'$ be the equilibrium internuclear distance for which $E_J\left(r\right)$ is a minimum. A relationship between the distorted equilibrium internuclear distance $r_e'$ and $J$ is derived from $E_J\left(r\right)$ by taking the derivative with respect to $r$, setting the derivative equal to zero corresponding to the minimum, and evaluating the equation at $r_e'$. The result using Eq. (12.66) is:

$$\left.\frac{dE_J\left(r\right)}{dr}\right|_{r=r_e'} = k_0\left(r_e' - r_e\right) - \frac{\hbar^2}{\mu\left(r_e'\right)^3} J(J+1) = 0 \tag{12.86}$$

Since the deviation due to centrifugal distortion is small such that $\frac{r_e' - r_e}{r_e} << 1$, $r_e'$ may be determined as a function of $J$, and $r_e'$ may be solved from Eq. (12.86) by successive approximation. Little accuracy is lost by the first-order correction resulting from the substitution of $r_e' = r_e$ in the rotational term of Eq. (12.86) to give:

$$r_e' = r_e + \frac{hB_e}{2\pi^2 \nu_0^2 \mu r_e} J(J+1) \tag{12.87}$$

where

$$B_e = \frac{\hbar^2}{2I_e h} \tag{12.88}$$

and

$$\nu_0 = \frac{1}{2\pi}\left(\frac{k_0}{\mu}\right)^{1/2} \tag{12.89}$$

Then, $r_e$ can be replaced by $r_e'$ in the relationship for $E_J\left(r\right)$ (Eq. (12.85)) to determine the correction to the rotational energy due to centrifugal distortion.

$$E_J\left(r\right) = \frac{\hbar^2}{2\mu\left(r_e'\right)^2} J(J+1) + \frac{1}{2} k_0 \left(r_e' - r_e\right)^2 \tag{12.90}$$

By substitution of $r_e'$ given by Eq. (12.87) into Eq. (12.90), expanding the result in powers of $J(J+1)$, and retaining only the first two terms which are predominant, $E_J\left(r\right)$ is given by:

$$E_J = J(J+1) hc\tilde{B}_e - \left[J(J+1)\right]^2 hc\tilde{D}_e \tag{12.91}$$

where the centrifugal distortion term $\tilde{D}_e$ is given by:

$$\tilde{D}_e = \frac{4\tilde{B}_e^3}{\omega_0^2} \tag{12.92}$$

and

$$\tilde{B}_e = \frac{B_e}{c} = \frac{\hbar^2}{2I_e hc} \tag{12.93}$$

For most molecules, the corrections due to centrifugal distortion represented by $\tilde{D}_e$ are relatively small except for high $J$ values. From Eqs. (11.223), (12.72),(12.75), and (12.92-12.93), $\tilde{D}_e$ for $H_2$ is:

$$\begin{aligned} \tilde{D}_e &= \frac{4\tilde{B}_e^3}{\omega_0^2} = \frac{4\left(\dfrac{\hbar^2}{2I_e hc}\right)^3}{\omega_0^2} = \frac{\hbar^3}{10^6\left(2\right)\left(\pi\mu r_e^2 c\right)^3 \omega_0^2} \\ &= \frac{\hbar^3}{10^6\left(2\right)\left(\pi m_p\left(\sqrt{2}a_0\right)^2 c\right)^3\left(8.06573\times 10^3\ \dfrac{cm^{-1}}{eV} 0.517\ eV\right)^2} = 0.0491\ cm^{-1} \end{aligned} \tag{12.94}$$

The experimental $\tilde{D}_e$ of $H_2$ [15,16] is:

$$\tilde{D}_e = 0.0465\ cm^{-1} \tag{12.95}$$

From Eq. (11.170), (11.287), (11.312), (12.66), and (12.92-12.93), $\tilde{D}_e$ for $D_2$ is:

$$\begin{aligned} \tilde{D}_e &= \frac{4\tilde{B}_e^3}{\omega_0^2} = \frac{4\left(\dfrac{\hbar^2}{2I_e hc}\right)^3}{\omega_0^2} = \frac{\hbar^3}{10^6\left(2\right)\left(2\pi\mu r_e^2 c\right)^3 \omega_0^2} \\ &= \frac{\hbar^3}{10^6\left(2\right)\left(2\pi m_p\left(\sqrt{2}a_0\right)^2 c\right)^3\left(8.06573\times 10^3\ \dfrac{cm^{-1}}{eV} 0.371\ eV\right)^2} = 0.0119\ cm^{-1} \end{aligned} \tag{12.96}$$

The experimental $\tilde{D}_e$ of $D_2$ [15,16] is:

$$\tilde{D}_e = 0.01159\ cm^{-1} \tag{12.97}$$

There is good agreement between the calculated and experimental values of $\tilde{D}_e$.

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# Chapter 13

## GENERAL DIATOMIC AND POLYATOMIC MOLECULAR IONS AND MOLECULES

Non-hydrogen diatomic and polyatomic molecular ions and molecules can be solved using the similar principles as those used to solve hydrogen molecular ions and molecules wherein the hydrogen molecular orbitals (MOs) and hydrogen atomic orbitals serve as basis functions for the MOs of the general diatomic and polyatomic molecular ions or molecules. The MO must (1) be a solution of Laplace's equation to give a equipotential energy surface, (2) correspond to an orbital solution of the Newtonian equation of motion in an inverse-radius-squared central field having a constant total energy, (3) be stable to radiation, and (4) conserve the electron angular momentum of $\hbar$. Energy of the MO must be matched to that of the outermost atomic orbital of a bonding heteroatom in the case where a minimum energy is achieved with a direct bond to the atomic orbital (AO). In the case that an independent MO is formed, the AO force balance causes the remaining electrons to be at lower energy and a smaller radius. The atomic orbital may hybridize in order to achieve a bond at an energy minimum. At least one molecule or molecular ion representative of each of these cases was solved. Specifically, the results of the determination of bond parameters of $H_3^+$, $D_3^+$, $OH$, $OD$, $H_2O$, $D_2O$, $NH$, $ND$, $NH_2$, $ND_2$, $NH_3$, $ND_3$, $CH$, $CD$, $CH_2$, $CH_3$, $CH_4$, $N_2$, $O_2$, $F_2$, $Cl_2$, $CN$, $CO$, and $NO$ are given in Table 13.1. The calculated results for homo- and hetero-diatomic radicals and molecules, and polyatomic molecular ions and molecules are based on first principles and given in closed-form, exact equations containing fundamental constants only. The agreement between the experimental and calculated results is excellent.

## TRIATOMIC MOLECULAR HYDROGEN-TYPE ION ($H_3^+$)

The polyatomic molecular ion $H_3^+(1/p)$ is formed by the reaction of a proton with a hydrogen-type molecule

$$H_2(1/p)+H^+ \rightarrow H_3^+(1/p) \tag{13.1}$$

and by the exothermic reaction

$$H_2^+(1/p)+H_2(1/p) \rightarrow H_3^+(1/p)+H(1/p) \tag{13.2}$$

## FORCE BALANCE OF $H_3^+$-TYPE MOLECULAR IONS

$H_3^+(1/p)$-type molecular ions comprise two indistinguishable spin-paired electrons bound by three protons. The ellipsoidal molecular orbital (MO) satisfies the boundary constraints as shown in the Nature of the Chemical Bond of Hydrogen-Type Molecules section. Since the protons are indistinguishable, ellipsoidal MOs about each pair of protons taken one at a time are indistinguishable. $H_3^+(1/p)$ is then given by a superposition or linear combinations of three equivalent ellipsoidal MOs that form a equilateral triangle where the points of contact between the prolate spheroids are equivalent in energy and charge density. The outer perimeter of the superposition of three prolate spheroids is the $H_3^+(1/p)$ MO with the protons at the foci that bind and maintain the electron MO.

As in the case for $H_2^+(1/p)$ and $H_2(1/p)$ shown in the Nature of the Chemical Bond of Hydrogen-Type Molecules section, the stability of $H_3^+(1/p)$ is due to the dependence of the charge density of the distance $D$ from the origin to the tangent plane. That is,

$$D = \frac{1}{\sqrt{\frac{x^2}{a^4} + \frac{y^2}{b^4} + \frac{z^2}{c^4}}} \tag{13.3}$$

so that

$$\sigma = \frac{e}{4\pi ab^2} D \tag{13.4}$$

In other words, the surface density at any point on a charged ellipsoidal conductor is proportional to the perpendicular distance from the center of the ellipsoid to the plane tangent to the ellipsoid at the point. The charge is thus greater on the more sharply rounded ends farther away from the origin. This distribution places the charge closest to the protons to give a minimum energy.

The balanced forces also depend on $D$ as shown in the Nature of the Chemical Bond of Hydrogen-Type Molecules section. The $D$-dependence of the charge density as well as the centrifugal and Coulombic central field of two nuclei at the foci of the ellipsoid applies to each ellipsoid which is given from any other by a rotation of $|\phi| = \frac{\pi}{3}$ about an axis at a focus that is perpendicular to the plane of the equilateral triangle defined by the three foci. Since the centrifugal, Coulombic, and magnetic forces relate mass and charge densities which are interchangeable by the ratio $e/m_e$, the conditions at any point on any given ellipsoid is applicable to any other point on the ellipsoid. Furthermore, this condition can be generalized to any point of the other members of the set of three ellipsoids due to equivalence. As a further constraint to maintain the force balance between the three protons and the $H_3^+(1/p)$ MO comprising the superposition of the three $H_2(1/p)$-type ellipsoidal MOs, the total charge of the two electrons must be normalized over the three basis set $H_2(1/p)$-type ellipsoidal MOs. In this case, the parameters of each basis element $H_2(1/p)$-type ellipsoidal MO is solved, and the energies are given by the electron charge where it appears multiplied by a factor of $3/2$ (three MOs normalized by the total charge of two electrons).

Consider each $H_2(1/p)$-type ellipsoidal MO. At each point on the $H_3^+(1/p)$ MO, the electron experiences a centrifugal force, and the balancing centripetal force (on each electron) is produced by the electric force between the electron and the ellipsoidal electric field and the radiation-reaction-type magnetic force between the two electrons causing the electrons to pair. The force balance equation derived in Force Balance of Hydrogen-Type Molecules section is given by Eq. (11.200):

$$\frac{\hbar^2}{m_e a^2 b^2} D = \frac{pe^2}{8\pi\varepsilon_0 ab^2} D + \frac{\hbar^2}{2m_e a^2 b^2} D \tag{13.5}$$

$$\frac{2a_0}{pa} - \frac{a_0}{pa} = 1 \tag{13.6}$$

$$a = \frac{a_0}{p} \tag{13.7}$$

Substitution of Eq. (13.7) into Eq. (11.79) is:

$$c' = \frac{1}{p\sqrt{2}} a_0 \tag{13.8}$$

The internuclear distance given by multiplying Eq. (13.8) by two is:

$$2c' = \frac{a_0\sqrt{2}}{p} \tag{13.9}$$

Substitution of Eqs. (13.7-13.8) into Eq. (11.80) is:

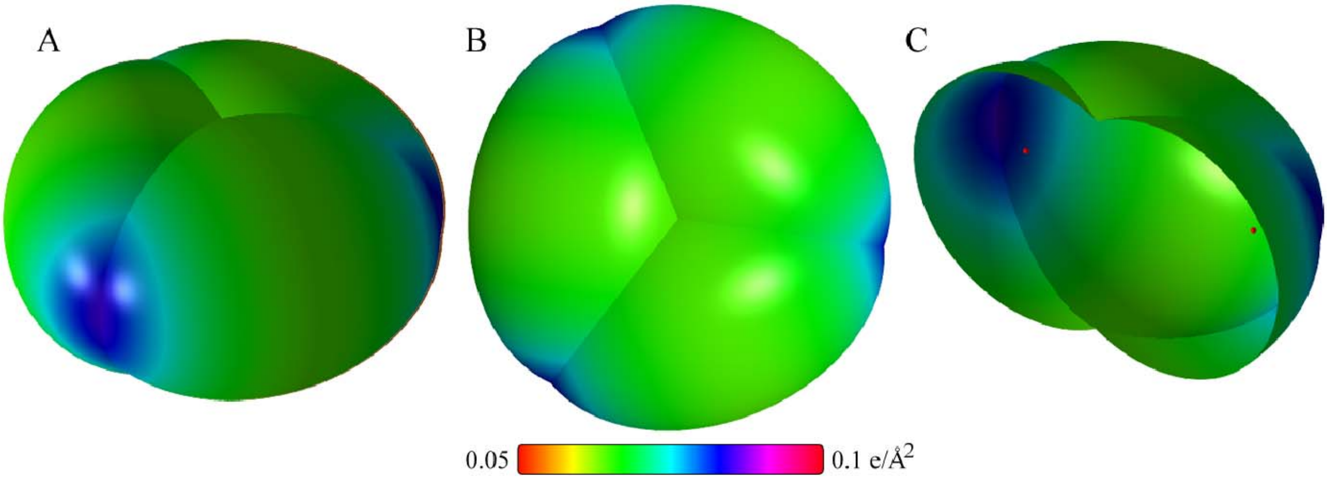
$$b = c = \frac{1}{p\sqrt{2}} a_0 \tag{13.10}$$

Substitution of Eqs. (13.7-13.8) into Eq. (11.67) is:

$$e = \frac{1}{\sqrt{2}} \tag{13.11}$$

Using the parameters given by Eqs. (13.7-13.11), the resulting $H_3^+(1/p)$ MO comprising the superposition of three $H_2(1/p)$-type ellipsoidal MOs is shown in Figure 13.1. The outer surface of the superposition comprises charge density of the MO. The equilateral triangular structure was confirmed experimentally [1]. The $H_3^+(1/p)$ MO having no distinguishable electrons is consistent with the absence of strong excited states observed for $H_3^+$ [1]. It is also consistent with the absence of a permanent dipole moment [1].

Figure 13.1. The equilateral triangular $H_3^+(1/p)$ MO formed by the superposition of three $H_2(1/p)$-type ellipsoidal MOs with the protons at the foci. (A)-(B) Oblique and top views of the charge-density shown in color scale showing the ellipsoid surfaces and the nuclei (red, not to scale). (C) Cross sectional view with one proton cut away.



## ENERGIES OF $H_3^+$-TYPE MOLECULAR IONS

Due to the equivalence of the $H_2(1/p)$-type ellipsoidal MOs and the linear superposition of their energies, the energy components defined previously for the molecule, Eqs. (11.207-11.212) apply in the case of the corresponding $H_3^+(1/p)$ molecular ion. And, each molecular energy component is given by the integral of corresponding force in Eq. (13.5). Each energy component is the total for the two equivalent electrons with the exception that the total charge of the two electrons is normalized over the three basis set $H_2(1/p)$-type ellipsoidal MOs. Thus, the energies are those given for $H_2(1/p)$ in the Energies of Hydrogen-Type Molecules section with the electron charge, where it appears, multiplied by a factor of $3/2$. In addition, the three sets of equivalent proton-proton pairs give rise to a factor of three times the proton-proton repulsion energy given by Eq. (11.208). The parameters $a$ and $b$ are given by Eqs. (13.7) and (13.10), respectively.

$$V_e = \frac{3}{2}\frac{-2pe^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} \tag{13.12}$$

$$V_p = 3\frac{p}{8\pi\varepsilon_0}\frac{e^2}{\sqrt{a^2-b^2}} \tag{13.13}$$

$$T = \frac{\hbar^2}{2m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} \tag{13.14}$$

The energy, $V_m$, corresponding to the magnetic force of Eq. (13.5) is:

$$V_m = \frac{3}{2}\frac{-\hbar^2}{4m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} \tag{13.15}$$

$$E_T = V_e + T + V_m + V_p \tag{13.16}$$

$$E_T = -\frac{e^2}{8\pi\varepsilon_0 a_0}\left[\left(3p^2\sqrt{2} - p^2\sqrt{2} + 3\frac{p^2\sqrt{2}}{4}\right)\ln\frac{\sqrt{2}+1}{\sqrt{2}-1} - 3p^2\sqrt{2}\right] = -p^2 35.54975\ eV \tag{13.17}$$

where the charge $e$ appears in the magnetic energy $V_m$ according to Eqs. (7.14-7.24) as discussed in the Force Balance of Hydrogen-Type Molecules section.

## VIBRATION OF $H_3^+$-TYPE MOLECULAR IONS

The vibrational energy levels of $H_3^+$-type molecular ions may be solved as three equivalent coupled harmonic oscillators by developing the Lagrangian, the differential equation of motion, and the eigenvalue solutions [2] wherein the spring constants are derived from the central forces as given in the Vibration of Hydrogen-Type Molecular Ions section and the Vibration of Hydrogen-Type Molecules section.

## THE DOPPLER ENERGY TERM OF $H_3^+$-TYPE MOLECULAR IONS

As shown in the Vibration of Hydrogen-type Molecular Ions section, the electron orbiting the nuclei at the foci of an ellipse may be perturbed such that a stable reentrant orbit is established that gives rise to a vibrational state corresponding to time harmonic oscillation of the nuclei and electron. The perturbation is caused by a photon that is resonant with the frequency of oscillation of the nuclei wherein the radiation is electric dipole with the corresponding selection rules.

Oscillation may also occur in the transition state. The perturbation arises from the decrease in internuclear distance as the molecular bond forms. Relative to the unperturbed case given in the Force Balance of Hydrogen-type Molecular Ions section, the reentrant orbit may give rise to a decrease in the total energy while providing a transient kinetic energy to the vibrating nuclei. However, as an additional condition for stability, radiation must be considered. A nonradiative state must be achieved after the emission due to transient vibration wherein the nonradiative condition given by Eq. (11.24) must be satisfied. The radiation reaction force due to the vibration of $H_2^+\left(1/p\right)$ and $H_2\left(1/p\right)$ in the transition state was derived in the Doppler Energy Term of Hydrogen-type Molecular Ions section and the Doppler Energy Term of Hydrogen-type Molecules section, respectively, and corresponds to a Doppler energy, $E_D$, that is dependent on the motion of the electron and the nuclei. The radiation reaction force in the case of the vibration of $H_3^+\left(1/p\right)$ in the transition state also corresponds to the Doppler energy, $E_D$, given by Eq. (11.181) that is dependent on the motion of the electrons and the nuclei. Here, a nonradiative state must also be achieved after the emission due to transient vibration wherein the nonradiative condition given by Eq. (11.24) must be satisfied. Typically, a third body is required to form $H_3^+$-type molecular ions. For example, the exothermic chemical reaction of $H+H$ to form $H_2$ does not occur with the emission of a photon. Rather, the reaction requires a collision with a third body, $M$, to remove the bond energy- $H+H+M \rightarrow H_2+M^*$ [3]. The third body distributes the energy from the exothermic reaction, and the end result is the $H_2$ molecule and an increase in the temperature of the system. Thus, a third body removes the energy corresponding to the additional force term given by Eq. (11.180).

The kinetic energy of the transient vibration is derived from the corresponding central forces. From Eqs. (13.5) and (13.12), the central force terms between the electron MO and the protons of each of the three $H_2\left(1/p\right)$-type ellipsoidal MOs are

$$f\left(a\right)=-\frac{3}{2}\frac{pe^2}{4\pi\varepsilon_0 a^2} \tag{13.18}$$

and

$$f'\left(a\right)=\frac{3}{2}\frac{2pe^2}{4\pi\varepsilon_0 a^3} \tag{13.19}$$

Thus, using Eqs. (11.136) and (13.18-13.19), the angular frequency of this oscillation is:

$$\omega=\sqrt{\frac{\frac{3}{2}\frac{pe^2}{4\pi\varepsilon_0\left(\frac{a_0}{p}\right)^3}}{m_e}}=p^2 5.06326\ X\ 10^{16}\ rad/s \tag{13.20}$$

where the semimajor axis, $a$, is $a=\frac{a_0}{p}$ according to Eq. (13.7). The kinetic energy, $E_K$, is given by Planck's equation (Eq. (11.127)):

$$\bar{E}_K=\hbar\omega=\hbar p^2 5.06326\ X\ 10^{16}\ rad/s=p^2 33.3273\ eV \tag{13.21}$$

In Eq. (11.181), substitution of the total energy of the $H_3^+$-type molecular ion, $E_T$, (Eq. (13.17)) for $E_{h\nu}$, the mass of the electron, $m_e$, for $M$, and the kinetic energy given by Eq. (13.21) for $\bar{E}_K$ gives the Doppler energy of the electrons for the reentrant orbit.

$$\bar{E}_D \cong E_{h\nu}\sqrt{\frac{2\bar{E}_K}{Mc^2}}=-35.54975p^2\ eV\sqrt{\frac{2e\left(p^2 33.3273\ eV\right)}{m_e c^2}}=-p^3 0.406013\ eV \tag{13.22}$$

The total energy of the $H_3^+$-type molecular ion is decreased by $\bar{E}_D$.

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency. On average, the total energy of vibration is equally distributed between kinetic energy and potential energy [4]. Thus, the average kinetic energy of vibration corresponding to the Doppler energy of the electrons, $\bar{E}_{Kvib}$, is 1/2 of the vibrational energy of the $H_3^+$-type molecular ion given by Eq. (11.148). The decrease in the energy of the molecular ion due to the reentrant orbit in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei, $\bar{E}_{osc}$, is given by the sum of the corresponding energies, $\bar{E}_D$ and $\bar{E}_{Kvib}$. Using Eq. (13.22) and the experimental vibrational energy $H_3^+$ of $E_{vib}=2521.31\ cm^{-1}=0.312605\ eV$ [1] gives:

$$\bar{E}_{osc} = \bar{E}_D + \bar{E}_{Kvib} = \bar{E}_D + \frac{1}{2}\hbar p^2\sqrt{\frac{k}{\mu}} \tag{13.23}$$

$$\bar{E}_{osc} = -p^3 0.406013\ eV + \frac{1}{2}p^2\left(0.312605\ eV\right) \tag{13.24}$$

The reentrant orbit for the binding of a proton to $H_2\left(1/p\right)$ causes two bonds to oscillate by increasing and decreasing in length along opposite sides of the equilateral triangle at a relative phase angle of 180°. Since the vibration and reentrant oscillation is along two lengths of the equilateral triangular MO with $E$ symmetry, $\bar{E}_{osc}$ for $H_3^+\left(1/p\right)$, $\bar{E}_{osc}\left(H_3^+\left(1/p\right)\right)$, is:

$$\bar{E}_{osc}\left(H_3^+\left(1/p\right)\right) = 2\left(\bar{E}_D + \frac{1}{2}\hbar p^2\sqrt{\frac{k}{\mu}}\right) = 2\left(-p^3 0.406013\ eV + \frac{1}{2}p^2\left(0.312605\ eV\right)\right) \tag{13.25}$$

To the extent that the MO dimensions are the same, the electron reentrant orbital energies, $\bar{E}_K$, are the same independent of the isotope of hydrogen, but the vibrational energies are related by Eq. (11.148). Thus, the differences in bond energies are essentially given by 1/2 the differences in vibrational energies per bond. Using Eq. (13.22), Eq. (13.25), and the experimental vibrational energy $D_3^+$ of $E_{vib} = 1834.67\ cm^{-1} = 0.227472\ eV$ [1], the corresponding $\bar{E}_{osc}\left(D_3^+\left(1/p\right)\right)$ is:

$$\bar{E}_{osc}\left(D_3^+\left(1/p\right)\right) = 2\left(-p^3 0.406013\ eV + \frac{1}{2}p^2\left(0.227472\ eV\right)\right) \tag{13.26}$$

## TOTAL AND BOND ENERGIES OF $H_3^+\left(1/p\right)$- AND $D_3^+\left(1/p\right)$-TYPE MOLECULAR IONS

The total energy of the $H_3^+\left(1/p\right)$-type molecular ion is given by the sum of $E_T$ (Eqs. (13.16-13.17)) and $\bar{E}_{osc}\left(H_3^+\left(1/p\right)\right)$ given Eqs. (13.20-13.25). Thus, the total energy of $H_3^+\left(1/p\right)$ having a central field of $+pe$ at each focus of the prolate spheroid molecular orbital including the Doppler term is

$$E_T = V_e + T + V_m + V_p + \bar{E}_{osc}\left(H_3^+\left(1/p\right)\right) \tag{13.27}$$

$$\begin{aligned} E_T &= -p^2\left\{ \frac{e^2}{8\pi\varepsilon_0 a_0}\left[\left(3\sqrt{2} - \sqrt{2} + \frac{3\sqrt{2}}{4}\right)\ln\frac{\sqrt{2}+1}{\sqrt{2}-1} - 3\sqrt{2}\right]\left[1 + 2p\sqrt{\frac{2\hbar\sqrt{\frac{\frac{3}{2}\frac{e^2}{4\pi\varepsilon_0 a_0^3}}{m_e}}}{m_e c^2}}\right] - 2\left(\frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right)\right\} \\ &= -p^2 35.54975 - 2p^3 0.406013\ eV + 2p^2\left(\frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right) \end{aligned} \tag{13.28}$$

From Eqs. (13.24-13.25) and (13.27-13.28), the total energy of the $H_3^+$-type molecular ion is:

$$\begin{aligned} E_T &= -p^2 35.54975\ eV + \bar{E}_{osc}\left(H_3^+\left(1/p\right)\right) \\ &= -p^2 35.54975 - 2p^3 0.406013\ eV + 2\left(\frac{1}{2}p^2\left(0.312605\ eV\right)\right) \\ &= -p^2 35.23714\ eV - p^3 0.812025\ eV \end{aligned} \tag{13.29}$$

The total energy of the $D_3^+$-type molecular ion is given by the sum of $E_T$ (Eq. (13.17)) and $\bar{E}_{osc}\left(D_3^+\left(1/p\right)\right)$ given by Eq. (13.26).

$$\begin{aligned} E_T &= -p^2 35.54975\ eV + \bar{E}_{osc}\left(D_3^+\left(1/p\right)\right) \\ &= -p^2 35.54975 - 2p^3 0.406013\ eV + 2\left(\frac{1}{2}p^2\left(0.227472\ eV\right)\right) \\ &= -p^2 35.32227\ eV - p^3 0.812025\ eV \end{aligned} \tag{13.30}$$

The bond dissociation energy, $E_D$, is the difference between the total energy of the corresponding hydrogen molecule and $E_T$

$$E_D = E(H_2\left(1/p\right)) - E_T \tag{13.31}$$

where $E\left(H_2\left(1/p\right)\right)$ is given by Eq. (11.241):

$$E\left(H_2\left(1/p\right)\right) = -p^2 31.351\ eV - p^3 0.326469\ eV \tag{13.32}$$

and $E\left(D_2\left(1/p\right)\right)$ is given by Eq. (11.242):

$$E\left(D_2\left(1/p\right)\right) = -p^2 31.4345\ eV - p^3 0.326469\ eV \tag{13.33}$$

The $H_3^+$ bond dissociation energy, $E_D$, is given by Eqs. (13.31-13.32) and (13.29):

$$\begin{aligned} E_D &= -p^2 31.351\ eV - p^3 0.326469\ eV - E_T \\ &= -p^2 31.351\ eV - p^3 0.326469\ eV - \left(-p^2 35.23714\ eV - p^3 0.812025\ eV\right) \\ &= p^2 3.88614\ eV + p^3 0.485556\ eV \end{aligned} \tag{13.34}$$

The $D_3^+$ bond dissociation energy, $E_D$, is given by Eqs. (13.31), (13.33), and (13.30):

$$\begin{aligned} E_D &= -p^2 31.4345\ eV - p^3 0.326469\ eV - E_T \\ &= -p^2 31.4345\ eV - p^3 0.326469\ eV - \left(-p^2 35.32227\ eV - p^3 0.812025\ eV\right) \\ &= p^2 3.88777\ eV + p^3 0.485556\ eV \end{aligned} \tag{13.35}$$

# THE $H_3^+$ MOLECULAR ION

## FORCE BALANCE OF THE $H_3^+$ MOLECULAR ION

The force balance equation for $H_3^+$ is given by Eq. (13.5) where $p=1$

$$\frac{\hbar^2}{m_e a^2 b^2} D = \frac{e^2}{8\pi\varepsilon_0 a b^2} D + \frac{\hbar^2}{2 m_e a^2 b^2} D \tag{13.36}$$

which has the parametric solution given by Eq. (11.83) when:

$$a = a_0 \tag{13.37}$$

The semimajor axis, $a$, is also given by Eq. (13.7) where $p=1$. The internuclear distance, $2c'$, which is the distance between the foci is given by Eq. (13.9) where $p=1$.

$$2c' = \sqrt{2} a_0 \tag{13.38}$$

The semiminor axis is given by Eq. (13.10) where $p=1$.

$$b = \frac{1}{\sqrt{2}} a_0 \tag{13.39}$$

The eccentricity, $e$, is given by Eq. (13.11).

$$e = \frac{1}{\sqrt{2}} \tag{13.40}$$

## ENERGIES OF THE $H_3^+$ MOLECULAR ION

The energies of $H_3^+$ are given by Eqs. (13.12-13.15) where $p=1$

$$V_e = \frac{3}{2} \frac{-2e^2}{8\pi\varepsilon_0 \sqrt{a^2-b^2}} \ln \frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -101.7538\ eV \tag{13.41}$$

$$V_p = 3 \frac{e^2}{8\pi\varepsilon_0 \sqrt{a^2-b^2}} = 57.7245\ eV \tag{13.42}$$

$$T = \frac{\hbar^2}{2 m_e a \sqrt{a^2-b^2}} \ln \frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = 33.9179\ eV \tag{13.43}$$

The energy, $V_m$, of the magnetic force is

$$V_m = \frac{3}{2} \frac{-\hbar^2}{4 m_e a \sqrt{a^2-b^2}} \ln \frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -25.4384\ eV \tag{13.44}$$

The Doppler terms, $\bar{E}_{osc}\left(H_3^+(1/p)\right)$ and $\bar{E}_{osc}\left(D_3^+(1/p)\right)$ are given by Eqs. (13.25) and (13.26), respectively, where $p=1$

$$\bar{E}_{osc}\left(H_2^+\right) = 2\left(\bar{E}_D + \bar{E}_{Kvib}\right) = 2\left(-0.406013\ eV + \frac{1}{2}\left(0.312605\ eV\right)\right) = -0.499420\ eV \tag{13.45}$$

$$\bar{E}_{osc}\left(D_2\right) = 2\left(-0.406013\ eV + \frac{1}{2}\left(0.227472\ eV\right)\right) = -0.584553\ eV \tag{13.46}$$

The total energy, $E_T$, for $H_3^+$ given by Eqs. (13.27-13.29) is:

$$\begin{aligned} E_T &= -\left\{ \frac{e^2}{8\pi\varepsilon_0 a_0} \left[ \left[ \left( 3\sqrt{2} - \sqrt{2} + \frac{3\sqrt{2}}{4} \right) \ln \frac{\sqrt{2}+1}{\sqrt{2}-1} - 3\sqrt{2} \right] \right] \left[ 1 + 2\sqrt{\frac{2\hbar\sqrt{\frac{\frac{3}{2}\frac{e^2}{4\pi\varepsilon_0 a_0^3}}{m_e}}}{m_e c^2}} \right] - 2\left( \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \right) \right\} \\ &= -35.54975 - 2(0.406013\ eV) + 2\left( \frac{1}{2}(0.31260516\ eV) \right) \\ &= -36.049167\ eV \end{aligned} \qquad (13.47)$$

From Eqs. (13.27-13.28) and (13.30), the total energy, $E_T$, for $D_3^+$ is:

$$E_T = -35.54975 - 2(0.406013\ eV) + 2\left( \frac{1}{2}(0.227472\ eV) \right) = -36.134300\ eV \qquad (13.48)$$

The bond dissociation energy, $E_D$, is the difference between the total energy of $H_2$ or $D_2$ and $E_T$. The $H_3^+$ molecular bond dissociation energy, $E_D$, given by the difference between the experimental total energy of $H_2$ [5-7] [1] and the total energy of $H_3^+$ (Eqs. (13.29) where $p = 1$ and (13.47)) is

$$E_D = -31.675\ eV\ - (-36.049167\ eV) = 4.374167\ eV \qquad (13.49)$$

The $H_3^+$ bond dissociation energy, $E_D$, given by Eq. (13.34) where $p = 1$ is:

$$E_D = 3.88614\ eV + 0.485556\ eV = 4.37170\ eV \qquad (13.50)$$

The experimental bond dissociation energy of $H_3^+$ [8] is:

$$E_D = 4.373\ eV \qquad (13.51)$$

The difference between the results of Eqs. (13.49) and (13.50) is within the experimental and propagated errors in the different calculations. The calculated results are based on first principles and given in closed-form equations containing fundamental constants only. The agreement between the experimental and calculated results for the $H_3^+$ bond dissociation energy is excellent.

The predicted $D_3^+$ molecular bond dissociation energy, $E_D$, given by the difference between the total energy of $D_3^+$ (Eqs. (13.30) where $p = 1$ and (13.48)) and the experimental total energy of $D_2$ [9-10][2] is:

$$E_D = -31.76\ eV - (-36.134300\ eV) = 4.374300\ eV \qquad (13.52)$$

The $D_3^+$ bond dissociation energy, $E_D$, given by Eq. (13.35) where $p = 1$ is:

$$E_D = 3.88777\ eV + 0.485556\ eV = 4.373331\ eV \qquad (13.53)$$

The results of the determination of bond parameters of $H_3^+$ are given in Table 13.1. The calculated results are based on first principles and given in closed-form, exact equations containing fundamental constants only. The agreement between the experimental and calculated results is excellent.

## HYDROXYL RADICAL ($OH$)

The water molecule can be solved by first considering the solution of the hydroxyl radical which is formed by the reaction of a hydrogen atom and an oxygen atom:

$$H + O \to OH \qquad (13.54)$$

The hydroxyl radical $OH$ can be solved using the same principles as those used to solve the hydrogen molecule wherein the diatomic molecular orbital (MO) developed in the Nature of the Chemical Bond of Hydrogen-Type Molecules and Molecular Ions section serves as basis function in linear combination with an oxygen atomic orbital (AO) to form the MO of $OH$. The MO must (1) be a solution of Laplace's equation to give a equipotential energy surface, (2) correspond to an orbital solution of the Newtonian equation of motion in an inverse-radius-squared central field having a constant total energy, (3) be stable to radiation, and (4) conserve the electron angular momentum of $\hbar$. A further constraint with the substitution of a heteroatom ($O$) for one of the hydrogen atoms is that the constant energy of the MO must match the energy of the heteroatom.

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[1] The experimental total energy of the hydrogen molecule is given by adding the first (15.42593 eV) [5] and second (16.2494 eV) ionization energies where the second ionization energy is given by the addition of the ionization energy of the hydrogen atom (13.59844 eV) [6] and the bond energy of $H_2^+$ (2.651 eV) [7].

[2] The experimental total energy of the deuterium molecule is given by adding the first (15.466 eV) [9] and second (16.294 eV) ionization energies where the second ionization energy is given by the addition of the ionization energy of the deuterium atom (13.603 eV) [10] and the bond energy of $D_2^+$ (2.692 eV) [9].

## FORCE BALANCE OF $OH$

$OH$ comprises two spin-paired electrons in a chemical bond between the oxygen atom and the hydrogen atom such that one electron on $O$ remains unpaired. The $OH$ radical MO is determined by considering properties of the binding atoms and the boundary constraints. The prolate spheroidal $H_2$ MO developed in the Nature of the Chemical Bond of Hydrogen-Type Molecules section satisfies the boundary constraints; thus, the $H$-atom electron forms a $H_2$-type ellipsoidal MO with one of the $O$-atom electrons. The $O$ electron configuration given in the Eight-Electron Atoms section is $1s^2 2s^2 2p^4$, and the orbital arrangement is:

$$\begin{array}{ccc} & \text{2p state} & \\ \underline{\uparrow\ \downarrow} & \underline{\uparrow} & \underline{\uparrow} \\ 1 & 0 & -1 \end{array} \qquad (13.55)$$

corresponding to the ground state $^3P_2$.

In determining the central forces for $O$ in the Radius and Ionization Energy of the Outer Electron of the Oxygen Atom section, it was shown that the energy is minimized with conservation of angular momentum by the cancellation of the orbital angular momentum of a $p_x$ electron by that of the $p_y$ electron with the pairing of electron eight to fill the $p_x$ orbital. Then, the diamagnetic force is given by Eq. (10.156) is that of atomic nitrogen (Eq. (10.136) corresponding to the $p_z$-orbital electron (Eq. (10.82) with $m=0$) as the source of diamagnetism with an additional contribution from the uncanceled $p_x$ electron (Eq. (10.82) with $m=1$). From Eqs. (10.83) and (10.89), the paramagnetic force, $\mathbf{F}_{mag\ 2}$, is given by Eq. (10.157) corresponding to the spin-angular-momentum contribution alone of the $p_x$ electron and the orbital angular momentum of the $p_z$ electron, respectively. The diamagnetic and paramagnetic forces cancel such that the central force is purely the Coulombic force. This central force is maintained with bond formation such that the energy of the $O2p$ shell is unchanged. Thus, the angular momentum of each electron of the $O2p$ shell is conserved with bond formation. The central paramagnetic force due to spin is provided by the spin-pairing force of the $OH$ MO that has the symmetry of an $s$ orbital that superimposes with the $2p$ orbitals such that the corresponding angular momenta of the $O2p$ orbitals are unchanged.

The $O2p_y$ electron combines with the $H1s$ electron to form a molecular orbital. The proton of the $H$ atom is along the internuclear axis. Due to symmetry, the other $O$ electrons are equivalent to point charges at the origin. (See Eqs. (19-38) of Appendix II.) Thus, the energies in the $OH$ MO involve only the $O2p_y$ and $H1s$ electrons and the change in the magnetic energy of the $O2p_y$ electron with the other $O$ electrons (Eq. (13.152)) with the formation of the $OH$ MO. The forces are determined by these energies.

As in the case of $H_2$, the MO is a prolate spheroid with the exception that the ellipsoidal MO surface cannot extend into $O$ atom for distances shorter than the radius of the $2p$ shell. Otherwise, the electric field of the other $O2p$ electrons would be perturbed, and the $2p$ shell would not be stable. The corresponding increase in energy of $O$ would not be offset by any energy decrease in the $OH$ MO based on the distance from the $O$ nucleus to the $H1s$ electron compared to those of the $O2p$ electrons. Thus, the MO surface comprises a prolate spheroid at the $H$ proton that is continuous with the $2p$ shell at the $O$ atom. The energy of the prolate spheroid is matched to that of the $O2p$ shell.

The orbital energy $E$ for each elliptical cross section of the prolate spheroidal MO is given by the sum of the kinetic $T$ and potential $V$ energies. $E=T+V$ is constant, and the closed orbits are those for which $T<|V|$, and the open orbits are those for which $T \geq |V|$. It can be shown that the time average of the kinetic energy, $<T>$, for elliptic motion in an inverse-squared field is $1/2$ that of the time average of the magnitude of the potential energy, $|<V>|$. $<T>=1/2|<V>|$ [11]. In the case of an atomic orbital (AO), $E=T+V$, and for all points on the AO, $|E|=T=1/2|V|$. As shown in the Hydrogen-type Molecular Ions section, each point or coordinate position on the continuous two-dimensional electron MO defines an infinitesimal mass-density element which moves along an orbit comprising an elliptic plane cross section of the spheroidal MO through the foci. The motion is such that eccentric angle, $\theta$, changes at a constant rate at each point. That is $\theta=\omega t$ at time $t$ where $\omega$ is a constant, and

$$r(t)=\mathbf{i}a\cos\omega t+\mathbf{j}b\sin\omega t \qquad (13.56)$$

Consider the boundary condition that the MO of $OH$ comprises a linear combination of an oxygen AO and a $H_2$-type ellipsoidal MO. The charge density of an $H_2$-type ellipsoidal MO given by Eq. (13.4) maintains that the surface is an equipotential; however, the potential and kinetic energy of a point on the surface changes as it orbits the central field. The potential energy is a maximum and the kinetic energy is a minimum at the semimajor axis, and the reverse occurs at the semiminor axis. Since the time average of the kinetic energy, $<T>$, for elliptic motion in an inverse-squared field is $1/2$ that of the time average of the magnitude of the potential energy, by symmetry, the $<T>=1/2<|V|>$ condition holds for 1/2 of the

$H_2$-type ellipsoidal MO having the $H$ focus and ending at the plane defined by the semiminor axes. The $O$ nucleus comprises the other focus of the $OH$ MO. The $O2p$ AO obeys the energy relationship for all points. Since the $H$ atomic orbital is at the Coulombic energy between the electron and proton given by Eq. (1.264), the energy matching condition is achieved while maintaining an energy match to the $O2p$ AO orbital with the charge density of 1/2e on the $O2p$ AO, corresponding to a donation of 0.25e from each MO electron. Then, the charge in the MO force balance corresponds to that of $-2(0.75)e=-1.5e$. Thus, the linear combination of the $H_2$-type ellipsoidal MO with the $O2p$ AO must involve a 25% contribution from the $H_2$-type ellipsoidal MO to the $O2p$ AO in order to match the energy relationships. Thus, the $OH$ MO must comprise 75% of a $H_2$-type ellipsoidal MO (1/2 +25%) and an oxygen AO:

$$1\, O2p_y\ AO + 0.75\ H_2\ MO \rightarrow OH\ MO \tag{13.57}$$

The force balance of the $OH$ MO is determined by the boundary conditions that arise from the linear combination of orbitals according to Eq. (13.57). The force constant $k$ of a $H_2$-type ellipsoidal MO due to the equivalent of two point charges of at the foci is given by Eq. (11.65).

$$k=\frac{2e^2}{4\pi\varepsilon_0} \tag{13.58}$$

Since the $H_2$-type ellipsoidal MO comprises 75% of the $OH$ MO, the electron charge density in Eq. (13.58) is given by $-0.75e$. Thus, $k'$ of the $H_2$-type-ellipsoidal-MO component of the $OH$ MO is

$$k'=\frac{(0.75)2e^2}{4\pi\varepsilon_0} \tag{13.59}$$

$L$ for the electron equals $\hbar$; thus, the distance from the origin of the $OH$ MO to each focus $c'$ is given by Eqs. (11.79) and (13.59):

$$c'=a\sqrt{\frac{\hbar^2 4\pi\varepsilon_0}{m_e e^2 1.5a}}=\sqrt{\frac{2aa_0}{3}} \tag{13.60}$$

The internuclear distance from Eq. (13.60) is:

$$2c'=2\sqrt{\frac{2aa_0}{3}} \tag{13.61}$$

The length of the semiminor axis of the prolate spheroidal $OH$ MO $b=c$ given by Eq. (11.80) is:

$$b=\sqrt{a^2-c'^2} \tag{13.62}$$

The eccentricity, $e$, is:

$$e=\frac{c'}{a} \tag{13.63}$$

Then, the solution of the semimajor axis $a$ allows for the solution of the other axes of the prolate spheroidal and eccentricity of the $OH$ MO.

The general equation of the ellipsoidal MO having semiprincipal axes $a$, $b$, $c$ given by:

$$\frac{x^2}{a^2}+\frac{y^2}{b^2}+\frac{z^2}{c^2}=1 \tag{13.64}$$

is also completely determined by the total energy $E$ given by Eq. (11.18):

$$r=\frac{m\frac{L^2}{m^2}k^{-1}}{1+\left(1+2Em\frac{L^2}{m^2}k^{-2}\right)^{1/2}\cos\theta} \tag{13.65}$$

The energy of the oxygen $2p$ shell is the negative of the ionization energy of the oxygen atom given by Eq. (10.163). Experimentally, the energy is [12]:

$$E(2p\ shell)=-E(ionization;\ O)=-13.6181\ eV \tag{13.66}$$

Since the prolate spheroidal MO transitions to the $O$ AO, the energy $E$ in Eq. (13.66) adds to that of the $H_2$-type ellipsoidal MO to give the total energy of the $OH$ MO. From the energy equation and the relationship between the axes given by Eqs. (13.60-13.63), the dimensions of the $OH$ MO are solved.

The energy components derived previously for the hydrogen molecule, Eqs. (11.207-11.212), apply in the case of the $H_2$-type ellipsoidal MO. As in the case of the energies of $H_3^+(1/p)$ given by Eqs. (13.12-13.16), each energy component of the $H_2$-type ellipsoidal MO is the total for the two equivalent electrons with the exception that the total charge and energies of the two electrons is normalized by the percentage composition given by Eq. (13.57):

$$V_e = \left(\frac{3}{4}\right)\frac{-2e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} \tag{13.67}$$

$$V_p = \frac{e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}} \tag{13.68}$$

$$T = \left(\frac{3}{4}\right)\frac{\hbar^2}{2m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} \tag{13.69}$$

$$V_m = \left(\frac{3}{4}\right)\frac{-\hbar^2}{4m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} \tag{13.70}$$

$$E_T = V_e + T + V_m + V_p \tag{13.71}$$

$$E_T = -\frac{e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}}\left[\left(\frac{3}{2}-\frac{3}{4}\frac{a_0}{a}+\frac{3}{8}\frac{a_0}{a}\right)\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}}-1\right] \tag{13.72}$$

$$E_T = -\frac{e^2}{8\pi\varepsilon_0 c'}\left[\left(\frac{3}{2}-\frac{3}{8}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right] \tag{13.73}$$

Since the prolate spheroidal MO transitions to the $O$ AO and the energy of the $O2p$ shell must remain constant and equal to the negative of the ionization energy given by Eq. (13.66), the total energy $E_T(OH)$ of the $OH$ MO is given by the sum of the energies of the orbitals corresponding to the composition of the linear combination of the $O$ AO and the $H_2$-type ellipsoidal MO that forms the $OH$ MO as given by Eq. (13.57):

$$E_T(OH) = E_T + E(2p\ shell) = E_T - E(ionization;\ O) = -\frac{e^2}{8\pi\varepsilon_0 c'}\left[\left(\frac{3}{2}-\frac{3}{8}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right] - 13.6181\ eV \tag{13.74}$$

To match the boundary condition that the total energy of the entire $H_2$-type ellipsoidal MO is given by Eq. (11.212):

$$E_T(H_2) = -\frac{e^2}{8\pi\varepsilon_0 a_0}\left[\left(2\sqrt{2}-\sqrt{2}+\frac{\sqrt{2}}{2}\right)\ln\frac{\sqrt{2}+1}{\sqrt{2}-1}-\sqrt{2}\right] = -31.63536831\ eV \tag{13.75}$$

$E_T(OH)$ given by Eq. (13.74) is set equal to Eq. (13.75):

$$E_T(OH) = -\frac{e^2}{8\pi\varepsilon_0 c'}\left[\left(\frac{3}{2}-\frac{3}{8}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right] - 13.6181\ eV = -31.63536831\ eV \tag{13.76}$$

From the energy relationship given by Eq. (13.76) and the relationship between the axes given by Eqs. (13.60-13.63), the dimensions of the $OH$ MO can be solved.

Substitution of Eq. (13.60) into Eq. (13.76) gives:

$$\frac{e^2}{8\pi\varepsilon_0\sqrt{\frac{2aa_0}{3}}}\left[\left(\frac{3}{2}-\frac{3}{8}\frac{a_0}{a}\right)\ln\frac{a+\sqrt{\frac{2aa_0}{3}}}{a-\sqrt{\frac{2aa_0}{3}}}-1\right] = e18.01726831 \tag{13.77}$$

The most convenient way to solve Eq. (13.77) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is:

$$a = 1.26430a_0 = 6.69039\ X\ 10^{-11}\ m \tag{13.78}$$

Substitution of Eq. (13.78) into Eq. (13.60) gives:

$$c' = 0.91808a_0 = 4.85826\ X\ 10^{-11}\ m \tag{13.79}$$

The internuclear distance given by multiplying Eq. (13.79) by two is:

$$2c' = 1.83616a_0 = 9.71651\ X\ 10^{-11}\ m \tag{13.80}$$

The experimental bond distance is [13]:

$$2c' = 9.71\ X\ 10^{-11}\ m \tag{13.81}$$

Substitution of Eqs. (13.78-13.79) into Eq. (13.62) gives:

$$b = c = 0.86925a_0 = 4.59985\ X\ 10^{-11}\ m \tag{13.82}$$

Substitution of Eqs. (13.78-13.79) into Eq. (13.63) gives:

$$e = 0.72615 \tag{13.83}$$

The nucleus of the $H$ atom and the nucleus of the $O$ atom comprise the foci of the $H_2$-type ellipsoidal MO. The parameters of the point of intersection of the $H_2$-type ellipsoidal MO and the $O2p_y$ AO can be determined from the polar equation of the ellipse (Eq. (11.10)).

$$r = r_0 \frac{1+e}{1+e\cos\theta'} \tag{13.84}$$

The radius of the $O2p_y$ AO given by Eq. (10.162) is $r_8 = a_0$, and the polar radial coordinate of the ellipse and the radius of the $O2p_y$ AO are equal at the point of intersection. Thus, Eq. (13.84) becomes:

$$r = (a-c')\frac{1+\frac{c'}{a}}{1+\frac{c'}{a}\cos\theta'} \tag{13.85}$$

where $r = a_0$ for $O$ such that the polar angle $\theta'$ is given by:

$$\theta' = \cos^{-1}\left(\frac{a}{c'}\left((a-c')\frac{1+\frac{c'}{a}}{a_0} - 1\right)\right) \tag{13.86}$$

Substitution of Eqs. (13.78-13.79) into Eq. (13.86) gives:

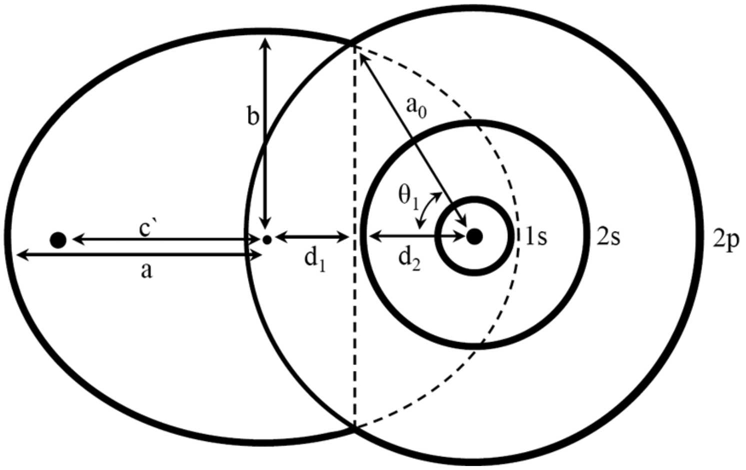
$$\theta' = 123.65° \tag{13.87}$$

Then, the angle $\theta_{O2p_yAO}$ the radial vector of the $O2p_y$ AO makes with the internuclear axis is

$$\theta_{O2p_yAO} = 180° - 123.65° = 56.35° \tag{13.88}$$

as shown in Figure 13.2.

Figure 13.2. The cross section of the $OH$ MO showing the axes, angles, and point of intersection of the $H_2$-type ellipsoidal MO with the $O2p_y$ AO. The continuation of the $H_2$-type-ellipsoidal-MO basis element beyond the intersection point with the $O2p$ shell is shown as dashed since it only serves to solve the energy match with the $O2p$ shell and does not represent charge density. Similarly, the vertical dashed line only designates the parameters of the intersection point. The actual charge density is shown by the solid lines. Legend: $a$: semimajor axis, $b$: semiminor axis, $c'$: internuclear distance, $d_1 : d_{H_2MO}$, $\theta_1 : \theta_{O2p_yAO}$, and $d_2 : d_{O2pAO}$.



The Cartesian $\mathbf{i}$-coordinate of the interception point of the MO and the AO can be calculated using the MO ellipsoidal parameters by first calculating the parametric angle in Eq. (11.83) that matches Cartesian $\mathbf{j}$-coordinate components at the point of intersection. Thus, the matching elliptic parametric angle $\omega t = \theta_{H_2MO}$ satisfies the following relationship:

$$a_0 \sin\theta_{O2p_yAO} = b\sin\theta_{H_2MO} \tag{13.89}$$

such that

$$\theta_{H_2MO} = \sin^{-1}\frac{a_0 \sin 56.35°}{b} \tag{13.90}$$

with the use of Eq. (13.88). Substitution of Eq. (13.82) into Eq. (13.90) gives:

$$\theta_{H_2MO} = 73.27° \tag{13.91}$$

Then, the distance $d_{H_2MO}$ along the internuclear axis from the origin of $H_2$-type ellipsoidal MO to the point of intersection of the orbitals is given by:

$$d_{H_2MO} = a\cos\theta_{H_2MO} \tag{13.92}$$

Substitution of Eqs. (13.78) and (13.91) into Eq. (13.92) gives:

$$d_{H_2MO} = 0.36397a_0 = 1.92606\ X\ 10^{-11}\ m \tag{13.93}$$

The distance $d_{O2pAO}$ along the internuclear axis from the origin of the $O$ atom to the point of intersection of the orbitals is given by

$$d_{O2pAO} = c' - d_{H_2MO} \tag{13.94}$$

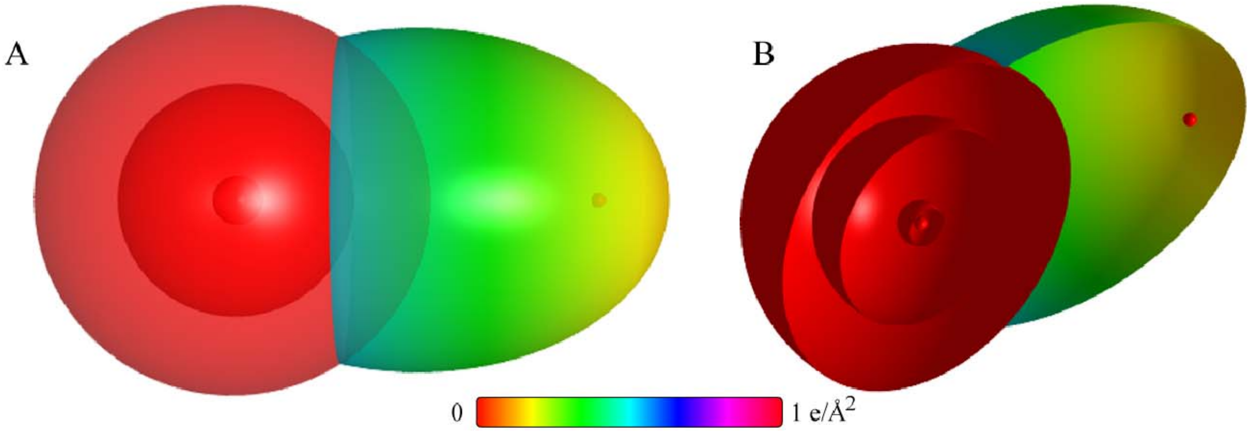
Substitution of Eqs. (13.79) and (13.93) into Eq. (13.94) gives:

$$d_{O2pAO} = 0.55411a_0 = 2.93220\ X\ 10^{-11}\ m \tag{13.95}$$

As shown in Eq. (13.57), in addition to the $p$-orbital charge-density modulation, the uniform charge-density in the $p_y$ orbital is increased by a factor of 0.25 and the $H$-atom density is decreased by a factor of 0.25. The internuclear axis of the $O-H$ bond is perpendicular to the bonding $p_y$ orbital. Using the orbital composition of $OH$ (Eq. (13.57)), the radii of $O1s = 0.12739a_0$ (Eq. (10.51)), $O2s = 0.59020a_0$ (Eq. (10.62)), and $O2p = a_0$ (Eq. (10.162)) shells, and the parameters of the $OH$ MO given by Eqs. (13.3-13.4), (13.78-13.80), (13.82-13.83), and (13.87-13.95), the dimensional diagram and charge-density of the $OH$ MO comprising the linear combination of the $H_2$-type ellipsoidal MO and the $O$ AO according to Eq. (13.57) are shown in Figures 13.2 and 13.3, respectively.

*In this case as well as in general, the current of the ellipsoidal MO and spherical AOs maintain spin pairing and current continuity. The current may comprise a linear combination of the MO current onto the AO and the AO currents that may comprise standing-wave components with current reflection at the interceptions of the surfaces. Thus, the current may flow equally in opposite directions between interception lines comprising mirror currents such that there is no net spin current. The linear combination gives a minimum equipotential energy surface of spin-paired electrons. Any asymmetrical charge distribution in the molecule corresponding to energy matching of the orbitals gives rise to a bond moment that is calculated in the Bond and Dipole Moment section.*

Figure 13.3. $OH$ MO comprising the superposition of the $H_2$-type ellipsoidal MO and the $O2p_y$ AO with a relative charge-density of 0.75 to 1.25; otherwise, the $O2p_y$ is the same as that of the oxygen atom. (A) Side-on, color scale, translucent view of the charge-density of the $OH$ MO and the nuclei (shown red, not to scale). The ellipsoidal surface of the $H_2$-type ellipsoidal MO that transitions to the $O2p_y$ AO, the $O2p$ shell, the $O2s$ shell, the $O1s$ shell, and the nuclei are shown. (B) Cut-away view showing the inner most $O1s$ shell, and moving radially, the $O2s$ shell, the $O2p$ shell, and the $H_2$-type ellipsoidal MO that transitions to the $O2p_y$ AO.



## ENERGIES OF $OH$

The energies of $OH$ given by the substitution of the semiprincipal axes (Eqs. (13.78-13.80) and (13.82)) into the energy equations (Eqs. (13.67-13.73)) are:

$$V_e = \left(\frac{3}{4}\right)\frac{-2e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -40.92709\ eV \tag{13.96}$$

$$V_p = \frac{e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}} = 14.81988\ eV \tag{13.97}$$

$$T = \left(\frac{3}{4}\right)\frac{\hbar^2}{2m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = 16.18567\ eV \tag{13.98}$$

$$V_m = \left(\frac{3}{4}\right)\frac{-\hbar^2}{4m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -8.09284\ eV \tag{13.99}$$

$$E_T\left(OH\right) = -\frac{e^2}{8\pi\varepsilon_0 c'}\left[\left(\frac{3}{2}-\frac{3}{8}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right] - 13.6181\ eV = -31.63247\ eV \tag{13.100}$$

where $E_T\left(OH\right)$ is given by Eq. (13.74) which is reiteratively matched to Eq. (13.75) within five-significant-figure round-off error.

## VIBRATION AND ROTATION OF $OH$

The vibrational energy of $OH$ may be solved in the same manner as that of hydrogen-type molecular ions and hydrogen molecules given in the Vibration of Hydrogen-type Molecular Ions section, and the Vibration of Hydrogen-type Molecules section, respectively, except that the orbital composition and the requirement that the $O2p$ shell remain at the same energy and radius in the $OH$ MO as it is in the $O$ atom must be considered. Each *p*-orbital comprises the sum of a constant function and a spherical harmonic function as given by Eq. (1.29). In addition to the *p*-orbital charge-density modulation, the uniform charge-density in $p_y$ orbital is increased by a factor of 0.25, and the *H*-atom electron density is decreased by a factor of 0.25. The force between the electron density of the $H_2$-type ellipsoidal MO and the nuclei determines the vibrational energy. With the radius of the orbit at the oxygen atom fixed at

$$r_8 = a_0 \tag{13.101}$$

according to Eq. (10.162), the central-force terms for the reentrant orbit between the electron density and the nuclei of the $H_2$-type ellipsoidal MO are given by Eqs. (11.213-11.214), except that the corresponding charge of $-0.75e$ replaces the charge of $-e$ of Eqs. (11.213-11.214). Furthermore, due to condition that the $O2p$ shell remain at the same energy and radius in the $OH$ MO as it is in the $O$ atom, the oscillation of $H_2$-type ellipsoidal is along the semiminor axis with the apsidal angle of Eq. (11.140) given by $\psi = \pi$. Thus, the semimajor axis $a$ of Eqs. (11.213-11.214) is replaced by the semiminor axis $b$:

$$f\left(b\right) = -\frac{0.75e^2}{8\pi\varepsilon_0 b^2} \tag{13.102}$$

and

$$f'\left(b\right) = \frac{0.75e^2}{4\pi\varepsilon_0 b^3} \tag{13.103}$$

Here, the force factor of 0.75 is equal to the equivalent term of Eq. (13.59). As the $H_2$-type ellipsoidal oscillates along $b$, the internuclear distance changes 180° out of phase. Thus, the distance for the reactive nuclear-repulsive terms is given by internuclear distance $2c'$ (Eq. (13.80)). Similar to that of Eqs. (11.215-11.216), the contribution from the repulsive force between the two nuclei is

$$f\left(2c'\right) = \frac{e^2}{8\pi\varepsilon_0\left(2c'\right)^2} \tag{13.104}$$

and

$$f'\left(2c'\right) = -\frac{e^2}{4\pi\varepsilon_0\left(2c'\right)^3} \tag{13.105}$$

Thus, from Eqs. (11.136), (11.213-11.217), and (13.102-13.105), the angular frequency of the oscillation is

$$\omega = \sqrt{\frac{\frac{0.75e^2}{8\pi\varepsilon_0 b^3} - \frac{e^2}{8\pi\varepsilon_0 (2c')^3}}{\mu}} = \sqrt{\frac{\frac{0.75e^2}{8\pi\varepsilon_0 (0.86925a_0)^3} - \frac{e^2}{8\pi\varepsilon_0 (1.83616a_0)^3}}{\frac{16}{17}m_p}} = 6.96269\ X\ 10^{14}\ rad/s \tag{13.106}$$

where $b$ is given by Eq. (13.82), $2c'$ is given by Eq. (13.80), and the reduced mass of $^{16}OH$ is given by:

$$\mu_{^{16}OH} = \frac{m_1 m_2}{m_1 + m_2} = \frac{(1)(16)}{1+16} m_p \tag{13.107}$$

where $m_p$ is the proton mass. Thus, during bond formation, the perturbation of the orbit determined by an inverse-squared force results in simple harmonic oscillatory motion of the orbit, and the corresponding frequency, $\omega(0)$, for $^{16}OH$ given by Eqs. (11.136), (11.148), and (13.106) is:

$$\omega(0) = \sqrt{\frac{k(0)}{\mu}} = \sqrt{\frac{763.18\ Nm^{-1}}{\mu}} = 6.96269\ X\ 10^{14}\ radians/s \tag{13.108}$$

where the reduced nuclear mass of $^{16}OH$ is given by Eq. (13.107) and the spring constant, $k(0)$, given by Eqs. (11.136) and (13.106) is:

$$k(0) = 763.18\ Nm^{-1} \tag{13.109}$$

The $^{16}OH$ transition-state vibrational energy, $E_{vib}(0)$, given by Planck's equation (Eq. (11.127)) is:

$$E_{vib}(0) = \hbar\omega = \hbar 6.96269\ X\ 10^{14}\ rad/s = 0.4583\ eV = 3696.38\ cm^{-1} \tag{13.110}$$

Zero-order or zero-point vibration is not physical and is not observed experimentally as discussed in the Diatomic Molecular Vibration section; yet, there is a term $\omega_e$ of the old point-particle-probability-wave-mechanics that can be compared to $E_{vib}(0)$. From Herzberg [14], $\omega_e$, from the experimental curve fit of the vibrational energies of $^{16}OH$ is:

$$\omega_e = 3735.21\ cm^{-1} \tag{13.111}$$

As shown in the Vibration of Hydrogen-type Molecular Ions section, the harmonic oscillator potential energy function can be expanded about the internuclear distance and expressed as a Maclaurin series corresponding to a Morse potential after Karplus and Porter (K&P) [15] and after Eq. (11.134). Treating the Maclaurin series terms as anharmonic perturbation terms of the harmonic states, the energy corrections can be found by perturbation methods. The energy $\tilde{v}_\upsilon$ of state $\upsilon$ is:

$$\tilde{v}_\upsilon = \upsilon\omega_0 - \upsilon(\upsilon-1)\omega_0 x_0, \quad \upsilon = 0,1,2,3... \tag{13.112}$$

where

$$\omega_0 x_0 = \frac{hc\omega_0^2}{4D_0} \tag{13.113}$$

$\omega_0$ is the frequency of the $\upsilon = 1 \rightarrow \upsilon = 0$ transition, and $D_0$ is the bond dissociation energy given by Eq. (13.162). From Eq. (13.112), $\omega_0$ is given by:

$$\omega_0 = E_{vib}(0) - 2\omega_0 x_0 \tag{13.114}$$

Substitution of Eq. (13.113) into Eq. (13.114) gives:

$$\omega_0 = E_{vib}(0) - 2\frac{hc\omega_0^2}{4D_0} \tag{13.115}$$

Eq. (13.115) can be expressed as:

$$\omega_0^2 + \frac{2D_0}{hc}\omega_0 - \frac{2D_0}{hc}E_{vib}(0) = 0 \tag{13.116}$$

which can be solved by the quadratic formula:

$$\omega_0 = \frac{-\frac{2D_0}{hc} \pm \sqrt{\left(\frac{2D_0}{hc}\right)^2 + 4\frac{2D_0}{hc}E_{vib}(0)}}{2} \tag{13.117}$$

Only the positive root is real, physical; thus,

$$\omega_0\left(cm^{-1}\right)=\frac{-\frac{2D_0}{100hc}+\sqrt{\left(\frac{2D_0}{100hc}\right)^2+4\frac{2D_0}{100hc}E_{vib}\left(0\right)}}{2}$$

$$=\frac{-\frac{2e\left(4.4104\ eV\right)}{100hc}+\sqrt{\left(\frac{2e\left(4.4104\ eV\right)}{100hc}\right)^2+4\frac{2e\left(4.4104\ eV\right)}{100hc}\left(3696.37\ cm^{-1}\right)}}{2} \quad (13.118)$$

$$=3522.02\ cm^{-1}$$

where $E_{vib}\left(0\right)$ is given by Eq. (13.110) and $D_0$ is given by Eq. (13.156). The corresponding $^{16}OH$ $\upsilon=1\rightarrow\upsilon=0$ vibrational energy, $E_{vib}\left(1\right)$, in electron volts is:

$$E_{vib}\left(1\right)=0.43666\ eV \quad (13.119)$$

The experimental vibrational energy of $^{16}OH$ is [16-17]:

$$E_{vib}\left(1\right)=0.4424\ eV \qquad \left(3568\ cm^{-1}\right) \quad (13.120)$$

Using Eqs. (13.118-13.119) with Eq. (13.113), the anharmonic perturbation term, $\omega_0x_0$, of $^{16}OH$ is:

$$\omega_0x_0=\frac{100hc\left(8.06573X10^3\ \frac{cm^{-1}}{eV}0.43666\ eV\right)^2}{4e\left(4.4104\ eV\right)}cm^{-1}=87.18\ cm^{-1} \quad (13.121)$$

The experimental anharmonic perturbation term, $\omega_0x_0$, of $^{16}OH$ [14] is:

$$\omega_0x_0=82.81\ cm^{-1} \quad (13.122)$$

The vibrational energies of successive states are given by Eqs. (13.110), (13.112), and (13.121).
Using the reduced nuclear mass of $^{16}OD$ given by

$$\mu_{^{16}OD}=\frac{m_1m_2}{m_1+m_2}=\frac{\left(2\right)\left(16\right)}{2+16}m_p \quad (13.123)$$

where $m_p$ is the proton mass, the corresponding parameters for deuterated hydroxyl radical $^{16}OD$ (Eqs. (13.102-13.121) and (13.162)) are:

$$\omega\left(0\right)=\sqrt{\frac{k\left(0\right)}{\mu}}=\sqrt{\frac{763.18\ Nm^{-1}}{\mu}}=5.06610\ X\ 10^{14}\ radians/s \quad (13.124)$$

$$k\left(0\right)=763.18\ Nm^{-1} \quad (13.125)$$

$$E_{vib}\left(0\right)=\hbar\omega=\hbar 5.06610\ X\ 10^{14}\ rad/s=0.33346\ eV=2689.51\ cm^{-1} \quad (13.126)$$

$$\omega_0\left(cm^{-1}\right)=\frac{-\frac{2D_0}{100hc}+\sqrt{\left(\frac{2D_0}{100hc}\right)^2+4\frac{2D_0}{100hc}E_{vib}\left(0\right)}}{2}$$

$$=\frac{-\frac{2e\left(4.4687\ eV\right)}{100hc}+\sqrt{\left(\frac{2e\left(4.4687\ eV\right)}{100hc}\right)^2+4\frac{2e\left(4.4687\ eV\right)}{100hc}\left(2689.51\ cm^{-1}\right)}}{2} \quad (13.127)$$

$$=2596.02\ cm^{-1}$$

$$E_{vib}\left(1\right)=0.3219\ eV \quad (13.128)$$

$$\omega_0x_0=\frac{100hc\left(8.06573X10^3\ \frac{cm^{-1}}{eV}0.3219\ eV\right)^2}{4e\left(4.4687\ eV\right)}cm^{-1}=46.75\ cm^{-1} \quad (13.129)$$

From Herzberg [14], $\omega_e$, from the experimental curve fit of the vibrational energies of $^{16}OD$ is:

$$\omega_e=2720.9\ cm^{-1} \quad (13.130)$$

The experimental vibrational energy of $^{16}OD$ is [16-17]:

$$E_{vib}\left(1\right)=0.3263\ eV \qquad \left(2632.1\ cm^{-1}\right) \quad (13.131)$$

and the experimental anharmonic perturbation term, $\omega_0x_0$, of $^{16}OD$ [14] is:

$$\omega_0x_0=44.2\ cm^{-1} \quad (13.132)$$

which match the predictions given by Eqs. (13.126), (13.127-13.128), and (13.129), respectively.

The $B_e$ rotational parameters for $^{16}OH$ and $^{16}OD$ are given by:

$$B_e = \frac{\hbar^2}{2I_e hc} \tag{13.133}$$

where

$$I = \mu r^2 \tag{13.134}$$

and $B_e$ is $\tilde{B}_e$ (Eq. (12.89) rather than Eq. (12.84)) to give units of $cm^{-1}$.

Using the internuclear distance, $r = 2c'$, and reduced mass of $^{16}OH$ given by Eqs. (13.80) and (13.107), respectively, the corresponding $B_e$ is:

$$B_e = 18.835\ cm^{-1} \tag{13.135}$$

The experimental $B_e$ rotational parameter of $^{16}OH$ is [14]:

$$B_e = 18.871\ cm^{-1} \tag{13.136}$$

Using the internuclear distance, $r = 2c'$, and reduced mass of $^{16}OD$ given by Eqs. (13.80) and (13.123), respectively, the corresponding $B_e$ is

$$B_e = 9.971\ cm^{-1} \tag{13.137}$$

The experimental $B_e$ rotational parameter of $^{16}OD$ is [14]:

$$B_e = 10.01\ cm^{-1} \tag{13.138}$$

## THE DOPPLER ENERGY TERMS OF $^{16}OH$ AND $^{16}OD$

The radiation reaction force in the case of the vibration of $^{16}OH$ in the transition state corresponds to the Doppler energy, $E_D$, given by Eq. (11.181) and Eq. (13.22) that is dependent on the motion of the electrons and the nuclei. The kinetic energy of the transient vibration is derived from the corresponding central forces. Following the same consideration as those used to derive Eqs. (13.102-13.103) and Eqs. (11.231-11.232), the central force terms between the electron density and the nuclei of $^{16}OH$ MO with the radius of the orbit at the oxygen atom fixed at:

$$r_8 = a_0 \tag{13.139}$$

according to Eq. (10.162) are:

$$f(b) = -\frac{0.75e^2}{4\pi\varepsilon_0 b^2} \tag{13.140}$$

and

$$f'(b) = \frac{(0.75)2e^2}{4\pi\varepsilon_0 b^3} \tag{13.141}$$

wherein the oscillation of $H_2$-type ellipsoidal MO is along the semiminor axis $b$ with the apsidal angle of Eq. (11.140) given by $\psi = \pi$ due to condition that the $O2p$ shell remain at the same energy and radius in the $OH$ MO as it is in the $O$ atom. Thus, using Eqs. (11.136) and (13.140-13.141), the angular frequency of this oscillation is:

$$\omega = \sqrt{\frac{\frac{0.75e^2}{4\pi\varepsilon_0 b^3}}{m_e}} = 4.41776\ X\ 10^{16}\ rad/s \tag{13.142}$$

The kinetic energy, $E_K$, is given by Planck's equation (Eq. (11.127)):

$$\overline{E}_K = \hbar\omega = \hbar 4.41776\ X\ 10^{16}\ rad/s = 29.07844\ eV \tag{13.143}$$

In Eq. (11.181), substitution of the total energy of $OH$, $E_T(OH)$, (Eq. (13.76)) for $E_{h\nu}$, the mass of the electron, $m_e$, for $M$, and the kinetic energy given by Eq. (13.143) for $\overline{E}_K$ gives the Doppler energy of the electrons for the reentrant orbit.

$$\overline{E}_D \cong E_{h\nu}\sqrt{\frac{2\overline{E}_K}{Mc^2}} = -31.63537\ eV\sqrt{\frac{2e(29.07844\ eV)}{m_e c^2}} = -0.33749\ eV \tag{13.144}$$

The total energy of $OH$ is decreased by $\overline{E}_D$.

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency. On average, the total energy of vibration is equally distributed between kinetic energy and potential energy [4]. Thus, the average kinetic energy of vibration corresponding to the Doppler energy of the electrons, $\overline{E}_{Kvib}$, is 1/2 of the vibrational energy of $OH$ given by Eq. (13.120). The decrease in the energy of the $OH$ due to the reentrant orbit in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei, $\overline{E}_{osc}$, is given by the sum of the corresponding energies, $\bar{E}_D$ and $\bar{E}_{Kvib}$. Using Eq. (13.144) and the experimental $^{16}OH$ $\omega_e$ of 3735.21 $cm^{-1}$ $(0.463111\ eV)$ [16-17] gives:

$$\bar{E}_{osc}\left({}^{16}OH\right) = \bar{E}_D + \bar{E}_{Kvib} = \bar{E}_D + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \tag{13.145}$$

$$\bar{E}_{osc}\left({}^{16}OH\right) = -0.33749\ eV + \frac{1}{2}\left(0.463111\ eV\right) = -0.10594\ eV \tag{13.146}$$

To the extent that the MO dimensions are the same, the electron reentrant orbital energies, $\bar{E}_K$, are the same independent of the isotope of hydrogen, but the vibrational energies are related by Eq. (11.148). Thus, the differences in bond energies are essentially given by 1/2 the differences in vibrational energies per bond. Using Eq. (13.144), Eqs. (13.145-13.146), and the experimental $^{16}OD$ $\omega_e$ of 2720.9 $cm^{-1}$ $(0.33735\ eV)$ [16-17], the corresponding $\bar{E}_{osc}\left({}^{16}OD\right)$ is:

$$\bar{E}_{osc}\left({}^{16}OD\right) = -0.33749\ eV + \frac{1}{2}\left(0.33735\ eV\right) = -0.16881\ eV \tag{13.147}$$

## TOTAL AND BOND ENERGIES OF $^{16}OH$ AND $^{16}OD$ RADICALS

$E_{T+osc}\left({}^{16}OH\right)$, the total energy of the $^{16}OH$ radical including the Doppler term, is given by the sum of $E_T\left(OH\right)$ (Eq. (13.76)) and $\bar{E}_{osc}\left({}^{16}OH\right)$ given by Eqs. (13.142-13.146):

$$E_{T+osc}\left({}^{16}OH\right) = V_e + T + V_m + V_p + E\left(2p\ shell\right) + \bar{E}_{osc}\left({}^{16}OH\right) = E_T\left(OH\right) + \bar{E}_{osc}\left({}^{16}OH\right) \tag{13.148}$$

$$\begin{aligned} E_{T+osc}\left({}^{16}OH\right) &= \left\{ \frac{-e^2}{8\pi\varepsilon_0 c'} \left[\left(\frac{3}{2} - \frac{3}{8}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'} - 1\right] - 13.6181\ eV \right\} \left[ 1 + \sqrt{\frac{2\hbar\sqrt{\frac{\frac{3}{4}\frac{e^2}{4\pi\varepsilon_0 b^3}}{m_e}}}{m_e c^2}} \right] + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \\ &= -31.63537\ eV - 0.33749\ eV + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \end{aligned} \tag{13.149}$$

From Eqs. (13.145-13.146) and (13.148-13.149), the total energy of $^{16}OH$ is:

$$\begin{aligned} E_{T+osc}\left({}^{16}OH\right) &= -31.63537\ eV + \bar{E}_{osc}\left({}^{16}OH\right) \\ &= -31.63537\ eV - 0.33749\ eV + \frac{1}{2}\left(0.463111\ eV\right) \\ &= -31.74130\ eV \end{aligned} \tag{13.150}$$

where the experimental $\omega_e$ was used for the $\hbar\sqrt{\frac{k}{\mu}}$ term. $E_{T+osc}\left({}^{16}OD\right)$, the total energy of $^{16}OD$ including the Doppler term, isgiven by the sum of $E_T\left(OD\right) = E_T\left(OH\right)$ (Eq. (13.76)) and $\bar{E}_{osc}\left({}^{16}OD\right)$ given by Eq. (13.147):

$$\begin{aligned} E_{T+osc}\left({}^{16}OD\right) &= -31.63537\ eV + \bar{E}_{osc}\left({}^{16}OD\right) \\ &= -31.63537\ eV - 0.33749\ eV + \frac{1}{2}\left(0.33735\ eV\right) \\ &= -31.80418\ eV \end{aligned} \tag{13.151}$$

where the experimental $\omega_e$ was used for the $\hbar\sqrt{\frac{k}{\mu}}$ term. The dissociation of the bond of the hydroxyl radical forms a free hydrogen atom with one unpaired electron and an oxygen atom with two unpaired electrons as shown in Eq. (13.55) which interact to stabilize the atom as shown by Eq. (10.161-10.162). The lowering of the energy of the reactants decreases the bond energy. Thus, the total energy of oxygen is reduced by the energy in the field of the two magnetic dipoles given by Eq. (7.46) and Eq. (13.101):

$$E(magnetic) = \frac{2\pi\mu_0 e^2\hbar^2}{m_e^2 a_0^3} = \frac{8\pi\mu_0\mu_B^2}{a_0^3} = 0.114411\ eV \tag{13.152}$$

The corresponding bond dissociation energy, $E_D$, is given by the sum of the total energies of the oxygen atom and the corresponding hydrogen atom minus the sum of $E_{T+osc}\left({}^{16}OH\right)$ and $E(magnetic)$:

$$E_D = E({}^{16}O) + E(H) - E_{T+osc}\left({}^{16}OH\right) - E\left(magnetic\right) \tag{13.153}$$

$E({}^{16}O)$ is given by Eq. (13.66), $E_D\left(H\right)$ [18]is:

$$E(H) = -13.59844\ eV \tag{13.154}$$

and $E_D(D)$ [19] is:

$$E(D) = -13.603\ eV \tag{13.155}$$

The ${}^{16}OH$ bond dissociation energy, $E_D\left({}^{16}OH\right)$, is given by Eqs. (13.150) and (13.152-13.155):

$$\begin{aligned} E_D\left({}^{16}OH\right) &= -(13.6181\ eV + 13.59844\ eV) - \left(E(magnetic) + E_{T+osc}\left({}^{16}OH\right)\right) \\ &= -27.21654\ eV - (0.114411\ eV - 31.74130\ eV) \\ &= 4.4104\ eV \end{aligned} \tag{13.156}$$

The experimental ${}^{16}OH$ bond dissociation energy is [20]:

$$E_D\left({}^{16}OH\right) = 4.41174\ eV \tag{13.157}$$

The ${}^{16}OD$ bond dissociation energy, $E_D\left({}^{16}OD\right)$, is given by Eqs. (13.151-13.153):

$$\begin{aligned} E_D\left({}^{16}OD\right) &= -(13.6181\ eV + 13.603\ eV) - \left(E(magnetic) + E_{T+osc}\left({}^{16}OD\right)\right) \\ &= -27.2211\ eV - (0.114411\ eV - 31.804183\ eV) \\ &= 4.4687\ eV \end{aligned} \tag{13.158}$$

The experimental ${}^{16}OD$ bond dissociation energy is [21-22]:

$$E_D\left({}^{16}OD\right) = 4.454\ eV \tag{13.159}$$

The results of the determination of bond parameters of $OH$ and $OD$ are given in Table 13.1. The calculated results are based on first principles and given in closed-form, exact equations containing fundamental constants only. The agreement between the experimental and calculated results is excellent.

## WATER MOLECULE ($H_2O$)

The water molecule $H_2O$ is formed by the reaction of a hydrogen atom with a hydroxyl radical:

$$OH + H \rightarrow H_2O \tag{13.160}$$

The water molecule can be solved using the same principles as those used to solve the hydrogen molecule, $H_3^+$, and $OH$ wherein the diatomic molecular orbital (MO) developed in the Nature of the Chemical Bond of Hydrogen-Type Molecules and Molecular Ions section serves as basis function in a linear combination with an oxygen atomic orbital (AO) to form the MO of $H_2O$. The solution is very similar to that of $OH$ except that there are two $OH$ bonds in water.

## FORCE BALANCE OF $H_2O$

$H_2O$ comprises two chemical bonds between oxygen and hydrogen. Each $O-H$ bond comprises two spin-paired electrons with one from an initially unpaired electron of the oxygen atom and the other from the hydrogen atom. The $H_2O$ MO is determined by considering properties of the binding atoms and the boundary constraints. The $H_2$ prolate spheroidal MO satisfies the boundary constraints as shown in the Nature of the Chemical Bond of Hydrogen-Type Molecules section; thus, each $H$-atom electron forms a $H_2$-type ellipsoidal MO with one of the initially unpaired $O$-atom electrons. The initial $O$ electron configuration given in the Eight-Electron Atoms section is $1s^2 2s^2 2p^4$, and the orbital arrangement is given by Eqs. (10.154) and Eq. (13.55).

As shown in the case of $OH$ in the Force Balance of $OH$ section, the forces that determine the radius and the energy of the $O2p$ shell are unchanged with bond formation. Thus, the angular momentum of each electron of the $O2p$ is conserved with bond formation. The central paramagnetic force due to spin of each $O-H$ bond is provided by the spin-pairing force of the $H_2O$ MO that has the symmetry of an $s$ orbital that superimposes with the $O2p$ orbitals such that the corresponding angular momenta are unchanged.

Each of the $O2p_z$ and $O2p_x$ electron combines with a $H1s$ electron to form a molecular orbital. The proton of the $H$ atom is along the internuclear axis. Due to symmetry, the other $O$ electrons are equivalent to point charges at the origin. (See Eqs. (19-38) of Appendix II.) Thus, the energies in the $H_2O$ MO involve only each $O2p$ and each $H1s$ electron with the formation of each $O-H$ bond. The forces are determined by these energies.

As in the case of $H_2$, each of two $O-H$-bond MOs is a prolate spheroid with the exception that the ellipsoidal MO surface cannot extend into the $O$ atom for distances shorter than the radius of the $2p$ shell. Otherwise, the electric field of the other $O2p$ electrons would be perturbed, and the $2p$ shell would not be stable. The corresponding increase in energy of $O$ would not be offset by any energy decrease in the $O-H$-bond MO based on the distance from the $O$ nucleus to the $H1s$

electron compared to those of the $O2p$ electrons. Thus, the MO surface comprises a prolate spheroid at each $H$ proton that is continuous with the $2p$ shell at the $O$ atom. The sum of the energies of the prolate spheroids is matched to that of the $2p$ shell.

The orbital energy $E$ for each elliptical cross section of the prolate spheroidal MO is given by the sum of the kinetic $T$ and potential $V$ energies. $E = T + V$ is constant, and the closed orbits are those for which $T <|V|$, and the open orbits are those for which $T \geq |V|$. It can be shown that the time average of the kinetic energy, $<T>$, for elliptic motion in an inverse-squared field is $1/2$ that of the time average of the magnitude of the potential energy, $|<V>|$. $<T> = 1/2|<V>|$ [11]. In the case of an atomic orbital (AO), $E = T + V$, and for all points on the AO, $|E| = T = 1/2|V|$. As shown in the Hydrogen-type Molecular Ions section, each point or coordinate position on the continuous two-dimensional electron MO defines an infinitesimal mass-density element which moves along an orbit comprising an elliptic plane cross section of the spheroidal MO through the foci. The motion is such that the eccentric angle, $\theta$, changes at a constant rate at each point. That is $\theta = \omega t$ at time $t$ where $\omega$ is a constant, and

$$r(t) = \mathbf{i}a\cos\omega t + \mathbf{j}b\sin\omega t \tag{13.161}$$

Consider the boundary condition that the MO of $H_2O$ comprises a linear combination of an oxygen AO and two $H_2$-type ellipsoidal MOs, one for each $O-H$-bond. The charge density of each $H_2$-type ellipsoidal MO given by Eqs. (11.44-11.45) and (13.3-13.4) maintains that the surface is an equipotential; however, the potential and kinetic energy of a point on the surface changes as it orbits the central field. The potential energy is a maximum and the kinetic energy is a minimum at the semimajor axis, and the reverse occurs at the semiminor axis. Since the time average of the kinetic energy, $<T>$, for elliptic motion in an inverse-squared field is $1/2$ that of the time average of the magnitude of the potential energy, by symmetry, the $<T> = 1/2 <|V|>$ condition holds for 1/2 of each $H_2$-type ellipsoidal MO having the $H$ focus and ending at the plane defined by the semiminor axes. The $O$ nucleus comprises the other focus of each $OH$-MO component of the $H_2O$ MO. The $O2p$ AO obeys the energy relationship for all points. Thus, the linear combination of the $H_2$-type ellipsoidal MO with the $O2p$ AO must involve a 25% contribution from the $H_2$-type ellipsoidal MO to the $O2p$ AO in order to match the energy relationships. Thus, the $H_2O$ MO must comprise two $O-H$-bonds with each comprising 75% of a $H_2$-type ellipsoidal MO (1/2 +25%) and an oxygen AO:

$$\left[1\ O2p_z\ AO + 0.75\ H_2\ MO\right] + \left[1\ O2p_y\ AO + 0.75\ H_2\ MO\right] \rightarrow H_2O\ MO \tag{13.162}$$

The force balance of the $H_2O$ MO is determined by the boundary conditions that arise from the linear combination of orbitals according to Eq. (13.162). The force constant $k$ of a $H_2$-type ellipsoidal MO due to the equivalent of two point charges at the foci is given by Eq. (11.65).

$$k = \frac{2e^2}{4\pi\varepsilon_0} \tag{13.163}$$

Since each $H_2$-type ellipsoidal MO comprises 75% of the $O-H$-bond MO, the electron charge density in Eq. (13.163) is given by $-0.75e$. Thus, $k'$ of each $H_2$-type-ellipsoidal-MO component of the $H_2O$ MO is:

$$k' = \frac{(0.75)2e^2}{4\pi\varepsilon_0} \tag{13.164}$$

$L$ for the electron equals $\hbar$; thus, the distance from the origin of each $O-H$-bond MO to each focus $c'$ is given by Eqs. (11.79) and (13.164):

$$c' = a\sqrt{\frac{\hbar^2 4\pi\varepsilon_0}{m_e e^2 1.5a}} = \sqrt{\frac{2aa_0}{3}} \tag{13.165}$$

The internuclear distance from Eq. (13.165) is:

$$2c' = 2\sqrt{\frac{2aa_0}{3}} \tag{13.166}$$

The length of the semiminor axis of the prolate spheroidal $O-H$-bond MO $b = c$ given by Eq. (11.80) is:

$$b = \sqrt{a^2 - c'^2} \tag{13.167}$$

The eccentricity, $e$, is:

$$e = \frac{c'}{a} \tag{13.168}$$

The solution of the semimajor axis $a$ then allows for the solution of the other axes of the prolate spheroid and eccentricity of the $O-H$-bond MO.

The general equation of the ellipsoidal MO having semiprincipal axes $a$, $b$, $c$ given by:

$$\frac{x^2}{a^2} + \frac{y^2}{b^2} + \frac{z^2}{c^2} = 1 \tag{13.169}$$

is also completely determined by the total energy $E$ given by Eq. (11.18).

$$r = \frac{m\frac{L^2}{m^2}k^{-1}}{1+\left(1+2Em\frac{L^2}{m^2}k^{-2}\right)^{1/2}\cos\theta} \tag{13.170}$$

The energy of the oxygen $2p$ shell is the negative of the ionization energy of the oxygen atom given by Eqs. (10.163) and (13.66). Experimentally, the energy is [12]

$$E(2p\ shell) = -E(ionization;\ O) = -13.6181\ eV \tag{13.171}$$

Since each of the two prolate spheroidal $O-H$ -bond MOs comprises a $H_2$-type-ellipsoidal MO that transitions to the $O$ AO, the energy $E$ in Eq. (13.171) adds to that of the two corresponding $H_2$-type ellipsoidal MOs to give the total energy of the $H_2O$ MO. From the energy equation and the relationship between the axes given by Eqs. (13.165-13.168), the dimensions of the $H_2O$ MO are solved.

The energy components defined previously for Hydrogen-Type Molecules, Eqs. (11.207-11.212), apply in the case of $H_2O$. Since the $H_2O$ MO comprises two equivalent $O-H$ -bond MOs, each a linear combination of a $H_2$-type-ellipsoidal MO and an $O2p$ AO, the corresponding energy component of the $H_2O$ MO is given by the linear superposition of the component energies. Thus, the energy scale factor is given as two times the force factor, the term in parentheses in Eq. (13.164). In addition to the equivalence and linearity principles, this factor also arises from the consideration of the nature of each bond and the linear combination that forms the $H_2O$ MO. Each $O-H$ -bond-energy component is the total for the two equivalent electrons with the exception that the total charge of the two electrons is normalized over the three basis set functions, two $O-H$ -bond MOs ($OH$ -type ellipsoidal MOs given in the Energies of $OH$ section) and one $O2p$ AO. Thus, the contribution of the $O-H$ -bond MOs to the $H_2O$ MO energies are those given for $H_2(1/p)$ in the Energies of Hydrogen-Type Molecules multiplied by a factor of $3/2$ as in the case with $H_3^+$ (Eqs. (13.12), (13.15), (13.18-13.20)). In addition, the two sets of equivalent nuclear-point-charge pairs give rise to a factor of two times the proton-proton repulsion energy given by Eq. (11.208). Thus, the component energies of the $H_2O$ MO are twice the corresponding energies of the $OH$ MO given by Eqs. (13.67-13.73). The parameters $a$, $b$, and $c'$ are given by Eqs. (13.165-13.167), respectively.

$$V_e = 2\left(\frac{3}{4}\right)\frac{-2e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = \left(\frac{3}{2}\right)\frac{-2e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} \tag{13.172}$$

$$V_p = 2\frac{e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}} \tag{13.173}$$

$$T = 2\left(\frac{3}{4}\right)\frac{\hbar^2}{2m_ea\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = \left(\frac{3}{2}\right)\frac{\hbar^2}{2m_ea\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} \tag{13.174}$$

$$V_m = 2\left(\frac{3}{4}\right)\frac{-\hbar^2}{4m_ea\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = \left(\frac{3}{2}\right)\frac{-\hbar^2}{4m_ea\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} \tag{13.175}$$

$$E_T = V_e + T + V_m + V_p \tag{13.176}$$

$$E_T = -\frac{e^2}{4\pi\varepsilon_0\sqrt{a^2-b^2}}\left[\left(\frac{3}{2}-\frac{3}{4}\frac{a_0}{a}+\frac{3}{8}\frac{a_0}{a}\right)\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}}-1\right] \tag{13.177}$$

$$E_T = -\frac{e^2}{4\pi\varepsilon_0 c'}\left[\left(\frac{3}{2}-\frac{3}{8}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right] \tag{13.178}$$

Since the prolate spheroidal $H_2$-type MO transitions to the $O$ AO and the energy of the $O2p$ shell must remain constant and equal to the negative of the ionization energy given by Eq. (13.171), the total energy $E_T(H_2O)$ of the $H_2O$ MO is given by the sum of the energies of the orbitals corresponding to the composition of the linear combination of the $O$ AO and the two $H_2$-type ellipsoidal MOs that forms the $H_2O$ MO as given by Eq. (13.162):

$$E_T(H_2O) = E_T + E(2p\ shell) = E_T - E(ionization;\ O) = -\frac{e^2}{4\pi\varepsilon_0 c'}\left[\left(\frac{3}{2}-\frac{3}{8}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]-13.6181\ eV \tag{13.179}$$

The two hydrogen atoms and the oxygen atom can achieve an energy minimum as a linear combination of two $H_2$-type ellipsoidal MOs each having the proton and the oxygen nucleus as the foci. Each $O-H$ -bond MO comprises the same $O2p$ shell of constant energy given by Eq. (13.171). Thus, the energy of the $H_2O$ MO is also given by the sum of that of the two

$H_2$-type ellipsoidal MOs given by Eq. (11.212) minus the energy of the redundant oxygen atom of the linear combination given by Eq. (13.171):

$$\begin{aligned} E_T\left(2H_2-O\right) &= -2\frac{e^2}{8\pi\varepsilon_0 a_0}\left[\left(2\sqrt{2}-\sqrt{2}+\frac{\sqrt{2}}{2}\right)\ln\frac{\sqrt{2}+1}{\sqrt{2}-1}-\sqrt{2}\right]-E\left(2p\ shell\right) \\ &= 2\left(-31.63536831\ eV\right)-\left(-13.6181\ eV\right) \\ &= -49.652637\ eV \end{aligned} \tag{13.180}$$

$E_T\left(H_2O\right)$ given by Eq. (13.179) is set equal to two times the energy of the $H_2$-type ellipsoidal MO minus the energy of the $O2p$ shell given by Eq. (13.180):

$$E_T\left(H_2O\right) = -\frac{e^2}{4\pi\varepsilon_0 c'}\left[\left(\frac{3}{2}-\frac{3}{8}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]-13.6181\ eV = -49.652637\ eV \tag{13.181}$$

From the energy relationship given by Eq. (13.181) and the relationship between the axes given by Eqs. (13.165-13.167), the dimensions of the $H_2O$ MO can be solved.

Substitution of Eq. (13.165) into Eq. (13.181) gives:

$$\frac{e^2}{4\pi\varepsilon_0\sqrt{\frac{2aa_0}{3}}}\left[\left(\frac{3}{2}-\frac{3}{8}\frac{a_0}{a}\right)\ln\frac{a+\sqrt{\frac{2aa_0}{3}}}{a-\sqrt{\frac{2aa_0}{3}}}-1\right] = e36.034537 \tag{13.182}$$

The most convenient way to solve Eq. (13.182) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is:

$$a = 1.2641a_0 = 6.68933\ X\ 10^{-11}\ m \tag{13.183}$$

Substitution of Eq. (13.183) into Eq. (13.165) gives:

$$c' = 0.918005a_0 = 4.85787\ X\ 10^{-11}\ m \tag{13.184}$$

The internuclear distance given by multiplying Eq. (13.184) by two is:

$$2c' = 1.83601a_0 = 9.71574\ X\ 10^{-11}\ m \tag{13.185}$$

The experimental bond distance is [23]:

$$2c' = 9.70 \pm .005\ X\ 10^{-11}\ m \tag{13.186}$$

Substitution of Eqs. (13.183-13.184) into Eq. (13.167) gives:

$$b = c = 0.869031a_0 = 4.59871\ X\ 10^{-11}\ m \tag{13.187}$$

Substitution of Eqs. (13.183-13.184) into Eq. (13.168) gives:

$$e = 0.726212 \tag{13.188}$$

The nucleus of the $H$ atom and the nucleus of the $O$ atom comprise the foci of each $H_2$-type ellipsoidal MO. The parameters of the point of intersection of each $H_2$-type ellipsoidal MO and the $O2p_y$ AO or $O2p_z$ AO can be determined from the polar equation of the ellipse (Eq. (11.10)):

$$r = r_0\frac{1+e}{1+e\cos\theta'} \tag{13.189}$$

The radius of the $O2p$ shell given by Eq. (10.162) is $r_8 = a_0$, and the polar radial coordinate of the ellipse and the radius of the $O2p$ shell are equal at the point of intersection. Thus, Eq. (13.189) becomes:

$$a_0 = \left(a-c'\right)\frac{1+\frac{c'}{a}}{1+\frac{c'}{a}\cos\theta'} \tag{13.190}$$

such that the polar angle $\theta'$ is given by

$$\theta' = \cos^{-1}\left(\frac{a}{c'}\left(\left(a-c'\right)\frac{1+\frac{c'}{a}}{a_0}-1\right)\right) \tag{13.191}$$

Substitution of Eqs. (13.183-13.184) into Eq. (13.191) gives:

$$\theta' = 123.66^\circ \tag{13.192}$$

Then, the angle $\theta_{O2pAO}$ the radial vector of the $O2p$ AO makes with the internuclear axis is:

$$\theta_{O2pAO} = 180^\circ - 123.66^\circ = 56.33^\circ \tag{13.193}$$

as shown in Figure 13.2. The Cartesian $\mathbf{i}$-coordinate of the interception point of the MO and the AO can be calculated using the MO ellipsoidal parameters by first calculating the parametric angle in Eq. (11.83) that matches Cartesian $\mathbf{j}$-coordinate components at the point of intersection. Thus, the matching elliptic parametric angle $\omega t = \theta_{H_2MO}$ satisfies the following relationship:

$$a_0 \sin \theta_{O2pAO} = b \sin \theta_{H_2MO} \tag{13.194}$$

such that

$$\theta_{H_2MO} = \sin^{-1} \frac{a_0 \sin \theta_{O2pAO}}{b} = \sin^{-1} \frac{a_0 \sin 56.33^\circ}{b} \tag{13.195}$$

with the use of Eq. (13.193). Substitution of Eq. (13.187) into Eq. (13.195) gives:

$$\theta_{H_2MO} = 73.28^\circ \tag{13.196}$$

Then, the distance $d_{H_2MO}$ along the internuclear axis from the origin of the $H_2$-type ellipsoidal MO to the point of intersection of the orbitals is given by

$$d_{H_2MO} = a \cos \theta_{H_2MO} \tag{13.197}$$

Substitution of Eqs. (13.183) and (13.196) into Eq. (13.197) gives:

$$d_{H_2MO} = 0.3637 a_0 = 1.9244\ X\ 10^{-11}\ m \tag{13.198}$$

The distance $d_{O2pAO}$ along the internuclear axis from the origin of the $O$ atom to the point of intersection of the orbitals is given by

$$d_{O2pAO} = c' - d_{H_2MO} \tag{13.199}$$

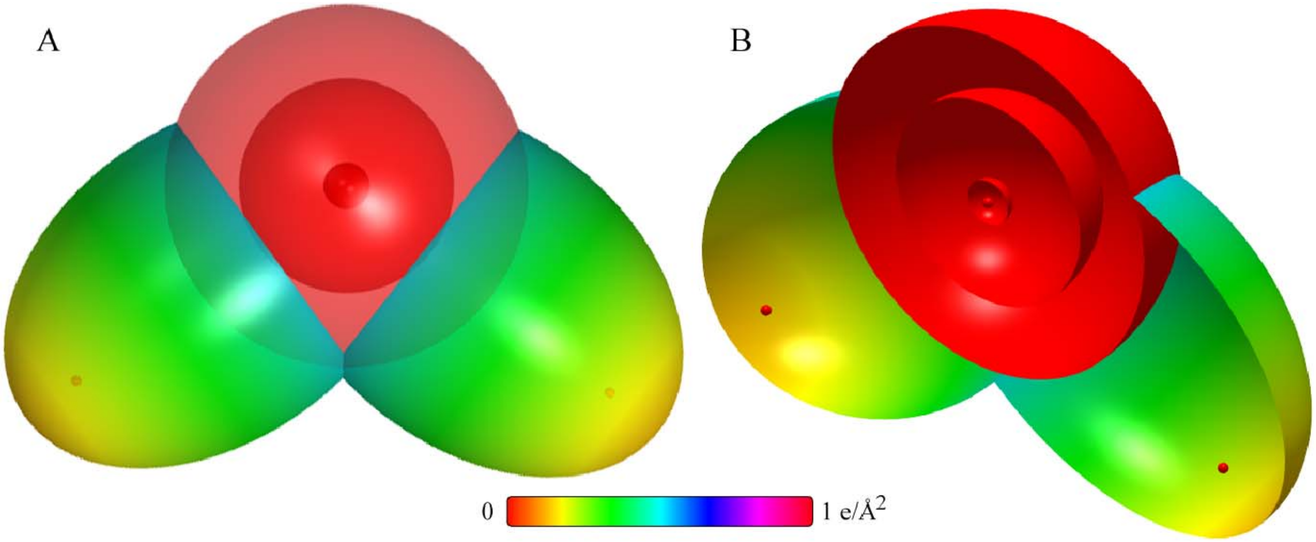
Substitution of Eqs. (13.184) and (13.198) into Eq. (13.199) gives:

$$d_{O2pAO} = 0.5543 a_0 = 2.93343\ X\ 10^{-11}\ m \tag{13.200}$$

In addition to the intersection of the $H_2$-type MO with the $O2p$ shell, two adjoining ellipsoidal $H_2$-type MOs intersect at points of equipotential. The angle and distance parameters are given by Eqs. (13.595-13.600) for the limiting methane case wherein four adjoining intersecting $H_2$-type MOs have the possibility of forming a self-contained two-dimensional equipotential surface of charge and current. Charge continuity can be obeyed for the $H_2O$ MO if the current is continuous between the adjoining $H_2$-type MOs. However, in the limiting case of methane, the existence of a separate linear combination of the $H_2$-type MOs comprising four spin-paired electrons, not connected to the bonding carbon heteroatom requires that the electron be divisible. It is possible for an electron to form time-dependent singular points or nodes having no charge as shown by Eqs. (1.28-1.29), and two-dimensional charge distributions having Laplacian potentials and one-dimensional regions of zero charge are possible for macroscopic charge densities and currents as given in Haus and Melcher [24]. However, it is not possible for single electrons to have two-dimensional discontinuities in charge based on internal forces and first principles discussed in Appendix II. Thus, at the points of intersection of the $H_2$-type MOs of methane, symmetry, electron indivisibility, current continuity, and conservation of energy and angular momentum require that the current between the points of mutual contact and the carbon atom be projected onto and flow along the radial vector to the surface of the $C2sp^3$ shell. This current designated the bisector current (BC) meets the $C2sp^3$ surface and does not travel to distances shorter than its radius. The methane result must also apply in the case of other bonds including that of the water molecule. Here, the $H_2$-type MOs intersect and the ellipsoidal current is projected onto the radial vector to the $O2p$ shell and does not travel to distances shorter than its radius as in the case of a single $O-H$ bond.

As shown in Eq. (13.162), in addition to the $p$-orbital charge-density modulation, the uniform charge-density in the $p_z$ and $p_y$ orbitals is increased by a factor of 0.25 and the $H$ atoms are each decreased by a factor of 0.25. Using the orbital composition of $H_2O$ (Eq. (13.162)), the radii of $O1s = 0.12739 a_0$ (Eq. (10.51)), $O2s = 0.59020 a_0$ (Eq. (10.62)), and $O2p = a_0$ (Eq. (10.162)) shells, and the parameters of the $H_2O$ MO given by Eqs. (13.3-13.4), (13.183-13.185), (13.187-13.188), and (13.192-13.200), the charge-density of the $H_2O$ MO comprising the linear combination of two $O-H$-bond MOs ($OH$-type ellipsoidal MOs given in the Energies of $OH$ section) according to Eq. (13.162) is shown in Figure 13.4. Each $O-H$-bond MO comprises a $H_2$-type ellipsoidal MO and an $O2p$ AO having the dimensional diagram shown in Figure 13.4.

Figure 13.4. $H_2O$ MO comprising the linear combination of two $O-H$ -bond MOs. Each $O-H$ -bond MO comprises the superposition of a $H_2$-type ellipsoidal MO and the $O2p_z$ AO or the $O2p_y$ AO with a relative charge-density of 0.75 to 1.25; otherwise, the $O2p$ orbitals are the same as those of the oxygen atom. The internuclear axis of one $O-H$ bond is perpendicular to the bonding $p_y$ orbital, and the internuclear axis of the other $O-H$ bond is perpendicular to the bonding $p_z$ orbital. (A) Color scale, translucent view of the charge-density of the $H_2O$ MO from the top. For each $O-H$ bond, the ellipsoidal surface of each $H_2$-type ellipsoidal MO transitions to the $O2p$ AO. The $O2p$ shell, the $O2s$ shell, the $O1s$ shell, and the nuclei (red, not to scale) are shown. (B) Cut-away view showing the innermost $O1s$ shell, and moving radially, the $O2s$ shell, the $O2p$ shell, and the $H_2$-type ellipsoidal MO that transitions to the $O2p$ AO for each $O-H$ bond. Bisector current not shown.



## ENERGIES OF $H_2O$

The energies of $H_2O$ given by the substitution of the semiprincipal axes (Eqs. (13.183-13.185) and (13.187)) into the energy equations (Eqs. (13.172-13.180)) are:

$$V_e = \left(\frac{3}{2}\right)\frac{-2e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -81.8715\ eV \tag{13.201}$$

$$V_p = 2\frac{e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}} = 29.6421\ eV \tag{13.202}$$

$$T = \left(\frac{3}{2}\right)\frac{\hbar^2}{2m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = 32.3833\ eV \tag{13.203}$$

$$V_m = \left(\frac{3}{2}\right)\frac{-\hbar^2}{4m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -16.1917\ eV \tag{13.204}$$

$$E_T\left(H_2O\right) = -\frac{e^2}{4\pi\varepsilon_0 c'}\left[\left(\frac{3}{2}-\frac{3}{8}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]-13.6181\ eV = -49.6558\ eV \tag{13.205}$$

where $E_T\left(H_2O\right)$ is given by Eq. (13.179) which is reiteratively matched to Eq. (13.180) within five-significant-figure round-off error.

## VIBRATION OF $H_2O$

The vibrational energy levels of $H_2O$ may be solved as two equivalent coupled harmonic oscillators by developing the Lagrangian, the differential equation of motion, and the eigenvalue solutions [2] wherein the spring constants are derived from the central forces as given in the Vibration of Hydrogen-Type Molecular Ions section and the Vibration of Hydrogen-Type Molecules section.

## THE DOPPLER ENERGY TERM OF $H_2O$

The radiation reaction force in the case of the vibration of $H_2O$ in the transition state corresponds to the Doppler energy, $E_D$, given by Eq. (11.181) and Eqs. (13.22) and (13.144) that is dependent on the motion of the electrons and the nuclei. The kinetic energy of the transient vibration is derived from the corresponding central forces. As in the case of $H_3^+$, the water molecule is a linear combination of three orbitals. The water MO comprises two $H_2$-type ellipsoidal MOs and the $O$ AO. Thus, the force factor of water in the determination of the Doppler frequency is equivalent to that of the $H_3^+$ ion given in Eqs. (13.18-13.20) and given by Eq. (13.164). From Eqs. (11.231-11.232) and (13.18-13.20), the central force terms between the electron density and the nuclei of each $O-H$ -bond MO with the radius of the orbit at the oxygen atom fixed at

$$r_8 = a_0 \tag{13.206}$$

according to Eq. (10.162) with the oscillation along the semiminor axis are:

$$f(b) = -\left(\frac{3}{2}\right)\frac{e^2}{4\pi\varepsilon_0 b^2} \tag{13.207}$$

and

$$f'(b) = \left(\frac{3}{2}\right)\frac{2e^2}{4\pi\varepsilon_0 b^3} \tag{13.208}$$

Thus, using Eqs. (11.136) and (13.207-13.208), the angular frequency of this oscillation is:

$$\omega = \sqrt{\frac{\left(\frac{3}{2}\right)\frac{e^2}{4\pi\varepsilon_0 b^3}}{m_e}} = 6.24996\ X\ 10^{16}\ rad/s \tag{13.209}$$

The kinetic energy, $E_K$, is given by Planck's equation (Eq. (11.127)):

$$\overline{E}_K = \hbar\omega = \hbar 6.24996\ X\ 10^{16}\ rad/s = 41.138334\ eV \tag{13.210}$$

The three basis elements of water, $H$, $H$, and $O$, all have the same Coulombic energy as given by Eqs. (1.264) and (10.163), respectively, such that the Doppler energy involves the total energy of the $H_2O$ MO. Thus, in Eq. (11.181), substitution of the total energy of $H_2O$, $E_T(H_2O)$, (Eqs. (13.179-13.180) and Eq. (13.181)) for $E_{h\nu}$, the mass of the electron, $m_e$, for $M$, and the kinetic energy given by Eq. (13.210) for $\overline{E}_K$ gives the Doppler energy of the electrons for the reentrant orbit:

$$\overline{E}_D \cong E_{h\nu}\sqrt{\frac{2\overline{E}_K}{Mc^2}} = -49.652637\ eV\sqrt{\frac{2e(41.138334\ eV)}{m_e c^2}} = -0.630041\ eV \tag{13.211}$$

The total energy of $H_2O$ is decreased by $\overline{E}_D$.

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency. On average, the total energy of vibration is equally distributed between kinetic energy and potential energy [4]. Thus, the average kinetic energy of vibration corresponding to the Doppler energy of the electrons, $\overline{E}_{Kvib}$, is 1/2 of the vibrational energy of $H_2O$. The decrease in the energy of $H_2O$ due to the reentrant orbit in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei, $\overline{E}_{osc}$, is given by the sum of the corresponding energies, $\overline{E}_D$ and $\overline{E}_{Kvib}$. Using Eq. (13.211) and the experimental $H^{16}OH$ vibrational energy of $E_{vib} = 3755.93\ cm^{-1} = 0.465680\ eV$ [25] gives:

$$\overline{E}'_{osc} = \overline{E}_D + \overline{E}_{Kvib} = \overline{E}_D + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \tag{13.212}$$

$$\overline{E}'_{osc} = -0.630041\ eV + \frac{1}{2}(0.465680\ eV) = -0.397201\ eV \tag{13.213}$$

per bond. As in the case for $H_3^+(1/p)$ shown in the Doppler Energy Term of $H_3^+$-type Molecular Ions section, the reentrant orbit for the binding of a hydrogen atom to a hydroxyl radical causes the bonds to oscillate by increasing and decreasing in length along the two $O-H$ bonds at a relative phase angle of 180°. Since the vibration and reentrant oscillation is along two bonds for the asymmetrical stretch ($\nu_3$), $\overline{E}_{osc}$ for $H^{16}OH$, $\overline{E}_{osc}(H^{16}OH)$, is:

$$\overline{E}_{osc}(H^{16}OH) = 2\left(\overline{E}_D + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right) = 2\left(-0.630041\ eV + \frac{1}{2}(0.465680\ eV)\right) = -0.794402\ eV \tag{13.214}$$

To the extent that the MO dimensions are the same, the electron reentrant orbital energies, $\overline{E}_K$, are the same independent of the isotope of hydrogen, but the vibrational energies are related by Eq. (11.148). Thus, the differences in bond energies are essentially given by 1/2 the differences in vibrational energies per bond. Using Eq. (13.211), Eqs. (13.212-13.214), and the experimental $D^{16}OD$ vibrational energy of $E_{vib} = 2787.92\ cm^{-1} = 0.345661\ eV$ [25], the corresponding $\bar{E}_{osc}\left(D^{16}OD\right)$ is:

$$\bar{E}_{osc}\left(D^{16}OD\right) = 2\left(-0.630041\ eV + \frac{1}{2}\left(0.345661\ eV\right)\right) = -0.914421\ eV \tag{13.215}$$

## TOTAL AND BOND ENERGIES OF $H^{16}OH$ AND $D^{16}OD$

$E_{T+osc}\left(H_2{}^{16}O\right)$, the total energy of the $H^{16}OH$ including the Doppler term, is given by the sum of $E_T\left(H_2O\right)$ (Eq. (13.181)) and $\bar{E}_{osc}\left(H^{16}OH\right)$ given Eqs. (13.207-13.214).

$$E_{T+osc}\left(H_2{}^{16}O\right) = V_e + T + V_m + V_p + E\left(O2p\right) + \bar{E}_{osc}\left(H^{16}OH\right) = E_T\left(H_2O\right) + \bar{E}_{osc}\left(H^{16}OH\right) \tag{13.216}$$

$$\begin{aligned} E_{T+osc}\left(H_2{}^{16}O\right) &= \left\{\begin{array}{l} \left(\dfrac{-e^2}{4\pi\varepsilon_0 c'}\left(\left(\dfrac{3}{2} - \dfrac{3}{8}\dfrac{a_0}{a}\right)\ln\dfrac{a+c'}{a-c'} - 1\right) - 13.6181\ eV\right)\left(1 + 2\sqrt{\dfrac{2\hbar\sqrt{\dfrac{\frac{3}{2}\frac{e^2}{4\pi\varepsilon_0 b^3}}{m_e}}}{m_e c^2}}\right) \\ +2\left(\dfrac{1}{2}\hbar\sqrt{\dfrac{k}{\mu}}\right) \end{array}\right\} \\ &= -49.652637\ eV - 2\left(0.630041\ eV - \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right) \end{aligned} \tag{13.217}$$

From Eqs. (13.214) and (13.216-13.217), the total energy of $H^{16}OH$ is:

$$\begin{aligned} E_{T+osc}\left(H_2{}^{16}O\right) &= -49.652637\ eV + \bar{E}_{osc}\left(H^{16}OH\right) \\ &= -49.652637\ eV - 2\left(0.630041\ eV - \frac{1}{2}\left(0.465680\ eV\right)\right) = -50.447039\ eV \end{aligned} \tag{13.218}$$

where the experimental vibrational energy was used for the $\hbar\sqrt{\frac{k}{\mu}}$ term. $E_{T+osc}\left(D_2{}^{16}O\right)$, the total energy of $D^{16}OD$ including the Doppler term is given by the sum of $E_T\left(D_2O\right) = E_T\left(H_2O\right)$ (Eq. (13.181)) and $\bar{E}_{osc}\left(D^{16}OD\right)$ given by Eq. (13.215):

$$\begin{aligned} E_{T+osc}\left(D_2{}^{16}O\right) &= -49.652637\ eV + \bar{E}_{osc}\left(D^{16}OD\right) \\ &= -49.652637\ eV - 2\left(0.630041\ eV - \frac{1}{2}\left(0.345661\ eV\right)\right) = -50.567058\ eV \end{aligned} \tag{13.219}$$

where the experimental vibrational energy was used for the $\hbar\sqrt{\frac{k}{\mu}}$ term. As in the case of the hydroxyl radical, the dissociation of the bond of the water molecule forms a free hydrogen atom and a hydroxyl radical, with one unpaired electron each. The lowering of the energy of the reactants due to the magnetic dipoles decreases the bond energy. Thus, the total energy of oxygen is reduced by the energy in the field of the two magnetic dipoles given by Eq. (13.152). The corresponding bond dissociation energy, $E_D$, is given by the sum of the total energies of the corresponding hydroxyl radical and hydrogen atom minus the total energy of water, $E_{T+osc}\left(H^{16}OH\right)$, and $E(magnetic)$.

Thus, $E_D$ of $H^{16}OH$ is given by:

$$E_D\left(H^{16}OH\right) = E(H) + E(^{16}OH) - E_{T+osc}\left(H^{16}OH\right) - E(magnetic) \tag{13.220}$$

where $E_T(^{16}OH)$ is given by the sum of the experimental energies of $^{16}O$ (Eq. (13.171)), $H$ (Eq. (13.154)), and the negative of the bond energy of $^{16}OH$ (Eq. (13.157)):

$$E(^{16}OH) = -13.59844\ eV - 13.6181\ eV - 4.41174\ eV = -31.62828\ eV \tag{13.221}$$

From Eqs. (13.154), (13.218), and (13.220-13.221), $E_D\left(H^{16}OH\right)$ is

$$\begin{aligned} E_D(H^{16}OH) &= E(H) + E(^{16}OH) - \left(E(magnetic) + E_{T+osc}\left(H^{16}OH\right)\right) \\ &= -13.59844\ eV - 31.62828\ eV - \left(0.114411\ eV - 50.447039\ eV\right) = 5.1059\ eV \end{aligned} \tag{13.222}$$

The experimental $H^{16}OH$ bond dissociation energy is [26]:

$$E_D(H^{16}OH) = 5.0991\ eV \tag{13.223}$$

Similarly, $E_D$ of $D^{16}OD$ is given by:

$$E_D\left(D^{16}OH\right) = E(D) + E(^{16}OD) - \left(E(magnetic) + E_{T+osc}\left(D^{16}OD\right)\right) \tag{13.224}$$

where $E_T(^{16}OD)$ is given by the sum of the experimental energies of $^{16}O$ (Eq. (13.171)), $D$ (Eq. (13.155)), and the negative of the bond energy of $^{16}OD$ (Eq. (13.159)):

$$E(^{16}OD) = -13.603\ eV - 13.6181\ eV - 4.454\ eV = -31.6751\ eV \tag{13.225}$$

From Eqs. (13.155), (13.220), and (13.224-13.225), $E_D\left(D^{16}OD\right)$ is

$$E_D(D^{16}OD) = -13.603\ eV - 31.6751\ eV - \left(0.114411\ eV - 50.567058\ eV\right) = 5.178\ eV \tag{13.226}$$

The experimental $D^{16}OD$ bond dissociation energy is [27]:

$$E_D(D^{16}OD) = 5.191\ eV \tag{13.227}$$

## BOND ANGLE OF $H_2O$

The $H_2O$ MO comprises a linear combination of two $O-H$ -bond MOs. Each $O-H$ -bond MO comprises the superposition of a $H_2$-type ellipsoidal MO and the $O2p_z$ AO or the $O2p_y$ AO with a relative charge-density of 0.75 to 1.25; otherwise, the $O2p$ orbitals are the same as those of the oxygen atom. A bond is also possible between the two H atoms of the $O-H$ bonds. Such $H-H$ bonding would decrease the $O-H$ -bond strength since electron density would be shifted from the $O-H$ bonds to the $H-H$ bond. Thus, the bond angle between the two $O-H$ bonds is determined by the condition that the total energy of the $H_2$-type ellipsoidal MO between the terminal $H$ atoms of the $O-H$ bonds is zero. Since the two $H_2$-type ellipsoidal MOs comprise 75% of the $H$ electron density of $H_2$, the energies and the total energy $E_T$ of the $H-H$ bond is given by Eqs. (13.67-13.73). From Eq. (11.79), the distance from the origin to each focus of the $H-H$ ellipsoidal MO is

$$c' = a\sqrt{\frac{\hbar^2 4\pi\varepsilon_0}{m_e e^2 2a}} = \sqrt{\frac{aa_0}{2}} \tag{13.228}$$

The internuclear distance from Eq. (13.228) is:

$$2c' = 2\sqrt{\frac{aa_0}{2}} \tag{13.229}$$

The length of the semiminor axis of the prolate spheroidal $H-H$ MO $b = c$ is given by Eq. (13.167). Substitution of Eq. (13.228) into Eq. (13.73) gives:

$$E_T = -\frac{e^2}{8\pi\varepsilon_0\sqrt{\frac{aa_0}{2}}}\left[\left(\frac{3}{2} - \frac{3}{8}\frac{a_0}{a}\right)\ln\frac{a + \sqrt{\frac{aa_0}{2}}}{a - \sqrt{\frac{aa_0}{2}}} - 1\right] \tag{13.230}$$

The radiation reaction force in the case of the vibration of $H-H$ in the transition state corresponds to the Doppler energy, $E_D$, given by Eq. (11.181) that is dependent on the motion of the electrons and the nuclei. The total energy $E_T$ that includes the radiation reaction of the $H-H$ MO is given by the sum of $E_T$ (Eq. (13.73)) and $\bar{E}_{osc}\left(H_2\right)$ given by Eqs. (11.213-11.220), (11.231-11.236), and (11.239-11.240). Thus, the total energy $E_T\left(H-H\right)$ of the $H-H$ MO including the Doppler term is

$$E_T = V_e + T + V_m + V_p + \bar{E}_{osc}\left(H-H\right) \tag{13.231}$$

$$\begin{aligned} E_T &= \frac{-e^2}{8\pi\varepsilon_0\sqrt{\frac{aa_0}{2}}}\left[\left(\frac{3}{2} - \frac{3}{8}\frac{a_0}{a}\right)\ln\frac{a + \sqrt{\frac{aa_0}{2}}}{a - \sqrt{\frac{aa_0}{2}}} - 1\right]\left[1 + \sqrt{\frac{2\hbar\sqrt{\frac{\frac{0.75e^2}{4\pi\varepsilon_0 a^3}}{m_e}}}{m_e c^2}}\right] + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \\ &= \frac{-e^2}{8\pi\varepsilon_0\sqrt{\frac{aa_0}{2}}}\left[\left(\frac{3}{2} - \frac{3}{8}\frac{a_0}{a}\right)\ln\frac{a + \sqrt{\frac{aa_0}{2}}}{a - \sqrt{\frac{aa_0}{2}}} - 1\right]\left[1 + \sqrt{\frac{2\hbar\sqrt{\frac{\frac{0.75e^2}{4\pi\varepsilon_0 a^3}}{m_e}}}{m_e c^2}}\right] + \frac{1}{2}\hbar\sqrt{\frac{\frac{0.75e^2}{8\pi\varepsilon_0 a^3} - \frac{e^2}{8\pi\varepsilon_0\left(a + c'\right)^3}}{0.5m_p}} \end{aligned} \tag{13.232}$$

To match the boundary condition that the total energy of the $H-H$ ellipsoidal MO is zero, $E_T\left(H-H\right)$ given by Eq. (13.232) is set equal to zero:

$$0=\left[\begin{array}{l}\dfrac{-e^2}{8\pi\varepsilon_0\sqrt{\dfrac{aa_0}{2}}}\left[\left(\dfrac{3}{2}-\dfrac{3}{8}\dfrac{a_0}{a}\right)\ln\dfrac{a+\sqrt{\dfrac{aa_0}{2}}}{a-\sqrt{\dfrac{aa_0}{2}}}-1\right]\left[1+\sqrt{\dfrac{2\hbar\sqrt{\dfrac{\dfrac{0.75e^2}{4\pi\varepsilon_0 a^3}}{m_e}}}{m_ec^2}}\right]\\+\dfrac{1}{2}\hbar\sqrt{\dfrac{\dfrac{0.75e^2}{8\pi\varepsilon_0 a^3}-\dfrac{e^2}{8\pi\varepsilon_0\left(a+c'\right)^3}}{0.5m_p}}\end{array}\right] \tag{13.233}$$

From the energy relationship given by Eq. (13.233) and the relationship between the axes given by Eqs. (13.165-13.167), the dimensions of the $H-H$ MO can be solved.

The most convenient way to solve Eq. (13.233) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is

$$a=4.300a_0=2.275\ X\ 10^{-10}\ m \tag{13.234}$$

Substitution of Eq. (13.234) into Eq. (13.228) gives:

$$c'=1.466a_0=7.759\ X\ 10^{-11}\ m \tag{13.235}$$

The internuclear distance given by multiplying Eq. (13.235) by two is:

$$2c'=2.933a_0=1.552\ X\ 10^{-10}\ m \tag{13.236}$$

Substitution of Eqs. (13.234-13.235) into Eq. (13.167) gives:

$$b=c=4.042a_0=2.139\ X\ 10^{-10}\ m \tag{13.237}$$

Substitution of Eqs. (13.234-13.235) into Eq. (13.168) gives:

$$e=0.341 \tag{13.238}$$

Using the distance between the two $H$ atoms when the total energy of the corresponding MO is zero, the corresponding bond angle can be determined from the law of cosines:

$$A^2+B^2-2AB\text{cosine}\theta=C^2 \tag{13.239}$$

With $A=B=2c'_{O-H}$, the internuclear distance of each $O-H$ bond given by Eq. (13.185), and $C=2c'_{H-H}$, the internuclear distance of the two $H$ atoms, the bond angle between the $O-H$ bonds is given by

$$\left(2c'_{O-H}\right)^2+\left(2c'_{O-H}\right)^2-2\left(2c'_{O-H}\right)^2\text{cosine}\theta=\left(2c'_{H-H}\right)^2 \tag{13.240}$$

$$\theta=\cos^{-1}\left(\frac{2\left(2c'_{O-H}\right)^2-\left(2c'_{H-H}\right)^2}{2\left(2c'_{O-H}\right)^2}\right) \tag{13.241}$$

Substitution of Eqs. (13.185) and (13.236) into Eq. (13.241) gives:

$$\begin{aligned}\theta&=\cos^{-1}\left(\frac{2\left(1.836\right)^2-\left(2.933\right)^2}{2\left(1.836\right)^2}\right)\\&=\cos^{-1}\left(-0.2756\right)=105.998^\circ\end{aligned} \tag{13.242}$$

The experimental internuclear distance of the two $H$ atoms, $2c'_{H-H}$, is [23]:

$$2c'_{H-H}=1.55\pm0.01\ X\ 10^{-10}\ m \tag{13.243}$$

which matches Eq. (13.236) very well. The experimental angle between the $O-H$ bonds is [23]:

$$\theta=106^\circ \tag{13.244}$$

which matches the predicted angle given by Eq. (13.242).

The results of the determination of bond parameters of $H_2O$ and $D_2O$ are given in Table 13.1. The calculated results are based on first principles and given in closed-form, exact equations containing fundamental constants only. The agreement between the experimental and calculated results is excellent.

## HYDROGEN NITRIDE ($NH$)

The ammonia molecule can be solved by first considering the solution of the hydrogen and dihydrogen nitride radicals. The former is formed by the reaction of a hydrogen atom and a nitrogen atom:

$$H+N\rightarrow NH \tag{13.245}$$

The hydrogen nitride radicals, $NH$ and $NH_2$, and ammonia, $NH_3$, can be solved using the same principles as those used to solve $OH$ and $H_2O$.

## FORCE BALANCE OF $NH$

$NH$ comprises two spin-paired electrons in a chemical bond between the nitrogen atom and the hydrogen atom such that two electrons on $N$ remain unpaired. The $NH$ radical molecular orbital (MO) is determined by considering properties of the binding atoms and the boundary constraints. The prolate spheroidal $H_2$ MO developed in the Nature of the Chemical Bond of Hydrogen-Type Molecules section satisfies the boundary constraints; thus, the $H$-atom electron forms a $H_2$-type ellipsoidal MO with one of the $N$-atom electrons. The $N$ electron configuration given in the Seven-Electron Atoms section is $1s^2 2s^2 2p^3$, and the orbital arrangement is

2p state

$$\begin{array}{ccc} \underline{\ \uparrow\ } & \underline{\ \uparrow\ } & \underline{\ \uparrow\ } \\ 1 & 0 & -1 \end{array} \tag{13.246}$$

corresponding to the ground state $^4S^0_{3/2}$. The $N2p_x$ electron combines with the $H1s$ electron to form a molecular orbital. The proton of the $H$ atom is along the internuclear axis. Due to symmetry, the other $N$ electrons are equivalent to point charges at the origin. (See Eqs. (19-38) of Appendix II.) Thus, the energies in the $NH$ MO involve only the $N2p_x$ and $H1s$ electrons and the change in the magnetic energy of the $N2p_x$ electron with the other $N$ electrons (Eq. (13.305)) with the formation of the $NH$ MO. The forces are determined by these energies.

As in the case of $H_2$, the MO is a prolate spheroid with the exception that the ellipsoidal MO surface cannot extend into $N$ atom for distances shorter than the radius of the $2p$ shell. Thus, the MO surface comprises a prolate spheroid at the $H$ proton that is continuous with the $2p$ shell at the $N$ atom whose nucleus serves as the other focus. The energy of the prolate spheroid is matched to that of the $N2p$ shell. As in the case with $OH$, the linear combination of the $H_2$-type ellipsoidal MO with the $N2p$ AO must involve a 25% contribution from the $H_2$-type ellipsoidal MO to the $N2p$ atomic orbital (AO) in order to match potential, kinetic, and orbital energy relationships. Thus, the $NH$ MO must comprise 75% of a $H_2$-type ellipsoidal MO and a nitrogen AO:

$$1\, N2p_x\ AO + 0.75\ H_2\ MO \rightarrow NH\ MO \tag{13.247}$$

The force balance of the $NH$ MO is determined by the boundary conditions that arise from the linear combination of orbitals according to Eq. (13.247) and the energy matching condition between the hydrogen and nitrogen components of the MO.

Similar to the $OH$ case given by Eq. (13.59), the $H_2$-type ellipsoidal MO comprises 75% of the $NH$ MO; so, the electron charge density in Eq. (11.65) is given by $-0.75e$. Based on the condition that the electron MO is an equipotential energy surface, Eq. (11.79) gives the ellipsoidal parameter $c'$ in terms of the central force of the foci, the electron angular momentum, and the ellipsoidal parameter $a$. To meet the equipotential condition of the union of the $H_2$-type-ellipsoidal-MO and the $N$ AO, the force constant used to determine the ellipsoidal parameter $c'$ is normalized by the ratio of the ionization energy of $N$ $14.53414\ eV$ [6] and $13.605804\ eV$, the magnitude of the Coulombic energy between the electron and proton of $H$ given by Eq. (1.264). This normalizes the force to match that of the Coulombic force alone to meet the force matching condition of the $NH$ MO under the influence of the proton and the $N$ nucleus. Thus, $k'$ of Eq. (11.79) to determine $c'$ is

$$k' = \frac{(0.75)2e^2}{4\pi\varepsilon_0 \dfrac{14.53414}{13.605804}} = (0.936127)\frac{(0.75)2e^2}{4\pi\varepsilon_0} \tag{13.248}$$

$L$ for the electron equals $\hbar$; thus, the distance from the origin of the $NH$ MO to each focus $c'$ is given by Eqs. (11.79) and (13.248):

$$c' = a\sqrt{\frac{\hbar^2 4\pi\varepsilon_0}{m_e e^2 1.5a(0.936127)}} = \sqrt{\frac{2aa_0}{3(0.936127)}} = \sqrt{0.712154aa_0} \tag{13.249}$$

The internuclear distance from Eq. (13.249) is

$$2c' = 2\sqrt{0.712154aa_0} \tag{13.250}$$

The length of the semiminor axis of the prolate spheroidal $NH$ MO $b = c$ is given by Eqs. (11.80) and (13.62). The eccentricity, $e$, is given by Eq. (13.63). Then, the solution of the semimajor axis $a$ allows for the solution of the other axes of the prolate spheroidal and eccentricity of the $NH$ MO.

The energy of the nitrogen $2p$ shell is the negative of the ionization energy of the nitrogen atom given by Eq. (10.143). Experimentally, the energy is [6]:

$$E(2p\ shell) = -E(ionization;\ N) = -14.53414\ eV \tag{13.251}$$

Since the prolate spheroidal MO transitions to the $N$ AO, the energy $E$ in Eq. (13.251) adds to that of the $H_2$-type ellipsoidal MO to give the total energy of the $NH$ MO. From the energy equation and the relationship between the axes given by Eqs. (13.249-13.250) and (13.62-13.63), the dimensions of the $NH$ MO are solved.

The energy components of $V_e$, $V_p$, $T$, $V_m$, and $E_T$ are the same as those of $OH$ given by Eqs. (13.67-13.73). Similarly to $OH$, the total energy $E_T(NH)$ of the $NH$ MO is given by the sum of the energies of the orbitals corresponding to the composition of the linear combination of the $N$ AO and the $H_2$-type ellipsoidal MO that forms the $NH$ MO as given by Eq. (13.247):

$$E_T(NH) = E_T + E(2p\ shell) = E_T - E(ionization;\ N) = -\frac{e^2}{8\pi\varepsilon_0 c'}\left[\left(\frac{3}{2}-\frac{3}{8}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right] - 14.53414\ eV \tag{13.252}$$

To match the boundary condition that the total energy of the entire $H_2$-type ellipsoidal MO is given by Eqs. (11.212) and (13.75), $E_T(NH)$ given by Eq. (13.252) is set equal to Eq. (13.75):

$$E_T(NH) = -\frac{e^2}{8\pi\varepsilon_0 c'}\left[\left(\frac{3}{2}-\frac{3}{8}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right] - 14.53414\ eV = -31.63536831\ eV \tag{13.253}$$

From the energy relationship given by Eq. (13.252) and the relationship between the axes given by Eqs. (13.249-13.250) and (13.62-13.63), the dimensions of the $NH$ MO can be solved.

Substitution of Eq. (13.249) into Eq. (13.253) gives:

$$\frac{e^2}{8\pi\varepsilon_0\sqrt{0.712154aa_0}}\left[\left(\frac{3}{2}-\frac{3}{8}\frac{a_0}{a}\right)\ln\frac{a+\sqrt{0.712154aa_0}}{a-\sqrt{0.712154aa_0}}-1\right] = e17.10123 \tag{13.254}$$

The most convenient way to solve Eq. (13.254) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is

$$a = 1.36275a_0 = 7.21136\ X\ 10^{-11}\ m \tag{13.255}$$

Substitution of Eq. (13.255) into Eq. (13.249) gives:

$$c' = 0.98513a_0 = 5.21310\ X\ 10^{-11}\ m \tag{13.256}$$

The internuclear distance given by multiplying Eq. (13.256) by two is:

$$2c' = 1.97027a_0 = 1.04262\ X\ 10^{-10}\ m \tag{13.257}$$

The experimental bond distance is [28]:

$$2c' = 1.0362\ X\ 10^{-10}\ m \tag{13.258}$$

Substitution of Eqs. (13.255-13.256) into Eq. (13.62) gives:

$$b = c = 0.94159a_0 = 4.98270\ X\ 10^{-11}\ m \tag{13.259}$$

Substitution of Eqs. (13.255-13.256) into Eq. (13.63) gives:

$$e = 0.72290 \tag{13.260}$$

The nucleus of the $H$ atom and the nucleus of the $N$ atom comprise the foci of the $H_2$-type ellipsoidal MO. The parameters of the point of intersection of the $H_2$-type ellipsoidal MO and the $N2p_x$ AO are given by Eqs. (13.84-13.95). The polar intersection angle $\theta'$ is given by:

$$\theta' = \cos^{-1}\left(\frac{a}{c'}\left((a-c')\frac{1+\frac{c'}{a}}{r_n}-1\right)\right) \tag{13.261}$$

where $r_n = r_7 = 0.93084a_0$ is the radius of the $N$ atom. Substitution of Eqs. (13.255-13.256) into Eq. (13.86) gives:

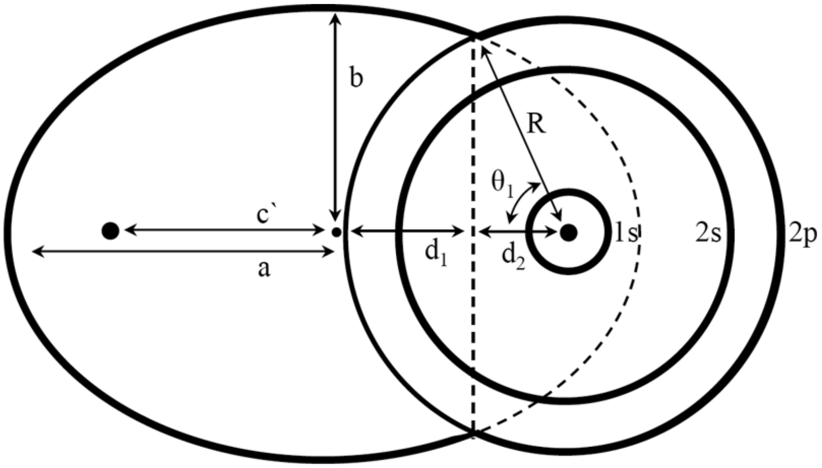
$$\theta' = 114.61^\circ \tag{13.262}$$

Then, the angle $\theta_{N2p_xAO}$ the radial vector of the $N2p_x$ AO makes with the internuclear axis is:

$$\theta_{N2p_xAO} = 180^\circ - 114.61^\circ = 65.39^\circ \tag{13.263}$$

as shown in Figure 13.5.

Figure 13.5. The cross section of the $NH$ MO showing the axes, angles, and point of intersection of the $H_2$-type ellipsoidal MO with the $N2p_x$ AO. The continuation of the $H_2$-type-ellipsoidal-MO basis element beyond the intersection point with the $N2p$ shell is shown as dashed since it only serves to solve the energy match with the $N2p$ shell and does not represent charge density. Similarly, the vertical dashed line only designates the parameters of the intersection point. The actual charge density is shown by the solid lines. Legend: $a$: semimajor axis, $b$: semiminor axis, $c'$: internuclear distance, $d_1 : d_{H_2MO}$, $\theta_1 : \theta_{N2p_xAO}$, $d_2 : d_{N2pAO}$, and $R : r_7$.



The Cartesian $\mathbf{i}$-coordinate of the interception point of the MO and the AO can be calculated using the MO ellipsoidal parameters by first calculating the parametric angle in Eq. (11.83) that matches Cartesian $\mathbf{j}$-coordinate components at the point of intersection. Thus, the matching elliptic parametric angle $\omega t = \theta_{H_2MO}$ satisfies the following relationship:

$$r_7 \sin\theta_{N2p_xAO} = 0.93084a_0 \sin\theta_{N2p_xAO} = b\sin\theta_{H_2MO} \tag{13.264}$$

such that

$$\theta_{H_2MO} = \sin^{-1}\frac{0.93084a_0 \sin\theta_{N2p_xAO}}{b} = \sin^{-1}\frac{0.93084a_0 \sin 65.39°}{b} \tag{13.265}$$

with the use of Eq. (13.263). Substitution of Eq. (13.259) into Eq. (13.265) gives:

$$\theta_{H_2MO} = 64.00° \tag{13.266}$$

Then, the distance $d_{H_2MO}$ along the internuclear axis from the origin of $H_2$-type ellipsoidal MO to the point of intersection of the orbitals is given by:

$$d_{H_2MO} = a\cos\theta_{H_2MO} \tag{13.267}$$

Substitution of Eqs. (13.255) and (13.266) into Eq. (13.267) gives:

$$d_{H_2MO} = 0.59747a_0 = 3.16166\ X\ 10^{-11}\ m \tag{13.268}$$

The distance $d_{N2pAO}$ along the internuclear axis from the origin of the $N$ atom to the point of intersection of the orbitals is given by:

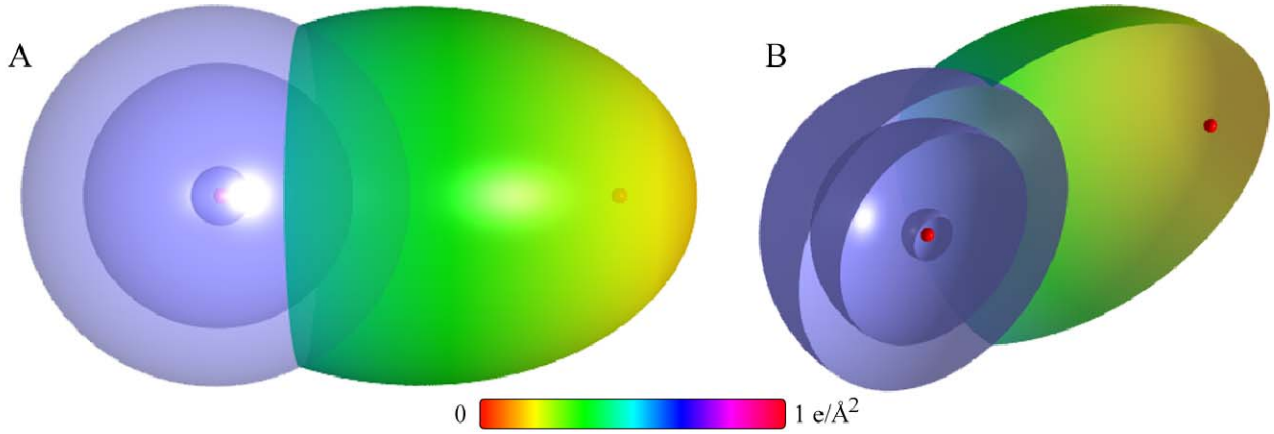
$$d_{N2pAO} = c' - d_{H_2MO} \tag{13.269}$$

Substitution of Eqs. (13.79) and (13.93) into Eq. (13.94) gives:

$$d_{N2pAO} = 0.38767a_0 = 2.05144\ X\ 10^{-11}\ m \tag{13.270}$$

As shown in Eq. (13.247), in addition to the $p$-orbital charge-density modulation, the uniform charge-density in the $p_x$ orbital is increased by a factor of 0.25 and the $H$-atom density is decreased by a factor of 0.25. The internuclear axis of the $N-H$ bond is perpendicular to the bonding $p_x$ orbital. Using the orbital composition of $NH$ (Eq. (13.27)), the radii of $N1s = 0.14605a_0$ (Eq. (10.51)), $N2s = 0.69385a_0$ (Eq. (10.62)), and $N2p = 0.93084a_0$ (Eq. (10.142)) shells, and the parameters of the $NH$ MO given by Eqs. (13.3-13.4) and (13.255-13.270), the dimensional diagram and charge-density of the $NH$ MO comprising the linear combination of the $H_2$-type ellipsoidal MO and the $N$ AO according to Eq. (13.247) are shown in Figures 13.5 and 13.6, respectively.

Figure 13.6. $NH$ MO comprising the superposition of the $H_2$-type ellipsoidal MO and the $N2p_x$ AO with a relative charge-density of 0.75 to 1.25; otherwise, the $N2p_x$ is the same as that of the nitrogen atom. (A) Side-on, color scale, translucent view of the charge-density of the $NH$ MO. The ellipsoidal surface of the $H_2$-type ellipsoidal MO that transitions to the $N2p_x$ AO, the $N2p$ shell, the $N2s$ shell, the $N1s$ shell, and the nuclei (red not to scale) are shown. (B) Cut-away view showing the inner most $N1s$ shell, and moving radially, the $N2s$ shell, the $N2p$ shell, and the $H_2$-type ellipsoidal MO that transitions to the $N2p_x$ AO.



## ENERGIES OF $NH$

The energies of $NH$ given by the substitution of the semiprincipal axes (Eqs. (13.255-13.256) and (13.259)) into the energy equations (Eqs. (13.67-13.73)) are:

$$V_e = \left(\frac{3}{4}\right)\frac{-2e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -37.85748\ eV \tag{13.271}$$

$$V_p = \frac{e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}} = 13.81113\ eV \tag{13.272}$$

$$T = \left(\frac{3}{4}\right)\frac{\hbar^2}{2m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = 13.89011\ eV \tag{13.273}$$

$$V_m = \left(\frac{3}{4}\right)\frac{-\hbar^2}{4m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -6.94505\ eV \tag{13.274}$$

$$E_T(NH) = -\frac{e^2}{8\pi\varepsilon_0 c'}\left[\left(\frac{3}{2}-\frac{3}{8}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right] - 14.53414\ eV = -31.63544\ eV \tag{13.275}$$

where $E_T(NH)$ is given by Eq. (13.253) which is reiteratively matched to Eq. (13.75) within five-significant-figure round-off error.

## VIBRATION AND ROTATION OF $NH$

The vibrational energy of $NH$ may be solved in the same manner as that of $OH$. From Eqs. (13.102-13.106) with the substitution of the $NH$ parameters, the angular frequency of the oscillation is:

$$\omega = \sqrt{\frac{\frac{0.75e^2}{8\pi\varepsilon_0 b^3}-\frac{e^2}{8\pi\varepsilon_0(2c')^3}}{\mu}} = \sqrt{\frac{\frac{0.75e^2}{8\pi\varepsilon_0(0.94159\text{a}_0)^3}-\frac{e^2}{8\pi\varepsilon_0(1.97027a_0)^3}}{\frac{14}{15}m_p}} = 6.18700\ X\ 10^{14}\ rad/s \tag{13.276}$$

where $b$ is given by Eq. (13.259), $2c'$ is given by Eq. (13.257), and the reduced mass of ${}^{14}NH$ is given by:

$$\mu_{{}^{14}NH} = \frac{m_1 m_2}{m_1+m_2} = \frac{(1)(14)}{1+14}m_p \tag{13.277}$$

where $m_p$ is the proton mass. Thus, during bond formation, the perturbation of the orbit determined by an inverse-squared force results in simple harmonic oscillatory motion of the orbit, and the corresponding frequency, $\omega(0)$, for ${}^{14}NH$ given by Eqs. (11.136), (11.148), and (13.276) is

$$\omega(0)=\sqrt{\frac{k(0)}{\mu}}=\sqrt{\frac{597.59\ Nm^{-1}}{\mu}}=6.18700\ X\ 10^{14}\ radians/s \tag{13.278}$$

where the reduced nuclear mass of $^{14}NH$ is given by Eq. (13.277) and the spring constant, $k(0)$, given by Eqs. (11.136) and (13.276) is:

$$k(0)=597.59\ Nm^{-1} \tag{13.279}$$

The $^{14}NH$ transition-state vibrational energy, $E_{vib}(0)$, given by Planck's equation (Eq. (11.127)) is:

$$E_{vib}(0)=\hbar\omega=\hbar 6.18700\ X\ 10^{14}\ rad/s=0.407239\ eV=3284.58\ cm^{-1} \tag{13.280}$$

$\omega_e$, from the experimental curve fit of the vibrational energies of $^{14}NH$ is [28]:

$$\omega_e=3282.3\ cm^{-1} \tag{13.281}$$

Using Eqs. (13.112-13.118) with $E_{vib}(0)$ given by Eq. (13.280) and $D_0$ given by Eq. (13.311), the $^{14}NH$ $\upsilon=1\rightarrow\upsilon=0$ vibrational energy, $E_{vib}(1)$ is:

$$E_{vib}(1)=0.38581\ eV \qquad \left(3111.84\ cm^{-1}\right) \tag{13.282}$$

The experimental vibrational energy of $^{14}NH$ using $\omega_e$ and $\omega_e x_e$ [28] according to K&P [15] is:

$$E_{vib}(1)=0.38752\ eV \qquad \left(3125.5\ cm^{-1}\right) \tag{13.283}$$

Using Eq. (13.113) with $E_{vib}(1)$ given by Eq. (13.282) and $D_0$ given by Eq. (13.311), the anharmonic perturbation term, $\omega_0 x_0$, of $^{14}NH$ is:

$$\omega_0 x_0=86.37\ cm^{-1} \tag{13.284}$$

The experimental anharmonic perturbation term, $\omega_0 x_0$, of $^{14}NH$ [28] is:

$$\omega_0 x_0=78.4\ cm^{-1} \tag{13.285}$$

The vibrational energies of successive states are given by Eqs. (13.280), (13.112), and (13.284).
Using $b$ given by Eq. (13.259), $2c'$ given by Eq. (13.257), $D_0$ given by Eq. (13.314), and the reduced nuclear mass of $^{14}ND$ given by

$$\mu_{^{14}ND}=\frac{m_1 m_2}{m_1+m_2}=\frac{(2)(14)}{2+14}m_p \tag{13.286}$$

where $m_p$ is the proton mass, the corresponding parameters for deuterium nitride $^{14}ND$ (Eqs. (13.102-13.121)) are:

$$\omega(0)=\sqrt{\frac{k(0)}{\mu}}=\sqrt{\frac{597.59\ Nm^{-1}}{\mu}}=4.51835\ X\ 10^{14}\ radians/s \tag{13.287}$$

$$k(0)=579.59\ Nm^{-1} \tag{13.288}$$

$$E_{vib}(0)=\hbar\omega=\hbar 4.51835\ X\ 10^{14}\ rad/s=0.29741\ eV=2398.72\ cm^{-1} \tag{13.289}$$

$$E_{vib}(1)=0.28710\ eV \qquad \left(2305.35\ cm^{-1}\right) \tag{13.290}$$

$$\omega_0 x_0=47.40\ cm^{-1} \tag{13.291}$$

$\omega_e$, from the experimental curve fit of the vibrational energies of $^{14}ND$ is [28]:

$$\omega_e=2398\ cm^{-1} \tag{13.292}$$

The experimental vibrational energy of $^{14}ND$ using $\omega_e$ and $\omega_e x_e$ [28] according to K&P [15] is:

$$E_{vib}(1)=0.2869\ eV \qquad \left(2314\ cm^{-1}\right) \tag{13.293}$$

and the experimental anharmonic perturbation term, $\omega_0 x_0$, of $^{14}ND$ [28] is:

$$\omega_0 x_0=42\ cm^{-1} \tag{13.294}$$

which match the predictions given by Eqs. (13.289), (13.290) and (13.291), respectively.

Using Eqs. (13.133-13.134) and the internuclear distance, $r=2c'$, and reduced mass of $^{14}NH$ given by Eqs. (13.257) and (13.277), respectively, the corresponding $B_e$ is:

$$B_e=16.495\ cm^{-1} \tag{13.295}$$

The experimental $B_e$ rotational parameter of $^{14}NH$ is [28]:

$$B_e=16.6993\ cm^{-1} \tag{13.296}$$

Using the internuclear distance, $r = 2c'$, and reduced mass of $^{14}ND$ given by Eqs. (13.257) and (13.286), respectively, the corresponding $B_e$ is:

$$B_e = 8.797\ cm^{-1} \tag{13.297}$$

The experimental $B_e$ rotational parameter of $^{14}ND$ is [28]:

$$B_e = 8.7913\ cm^{-1} \tag{13.298}$$

## THE DOPPLER ENERGY TERMS OF $^{14}NH$ AND $^{14}ND$

The equations of the radiation reaction force of hydrogen and deuterium nitride are the same as those of the corresponding hydroxyl radicals with the substitution of the hydrogen and deuterium nitride parameters. Using Eqs. (11.136) and (13.140-13.141), the angular frequency of the reentrant oscillation in the transition state is

$$\omega = \sqrt{\frac{\frac{0.75e^2}{4\pi\varepsilon_0 b^3}}{m_e}} = 3.91850\ X\ 10^{16}\ rad/s \tag{13.299}$$

where $b$ is given by Eq. (13.259). The kinetic energy, $E_K$, is given by Planck's equation (Eq. (11.127)):

$$\overline{E}_K = \hbar\omega = \hbar 3.91850\ X\ 10^{16}\ rad/s = 25.79224\ eV \tag{13.300}$$

In Eq. (11.181), substitution of the total energy of $NH$, $E_T(NH)$, (Eq. (13.253)) for $E_{h\nu}$, the mass of the electron, $m_e$, for $M$, and the kinetic energy given by Eq. (13.300) for $\overline{E}_K$ gives the Doppler energy of the electrons for the reentrant orbit:

$$\overline{E}_D \cong E_{h\nu}\sqrt{\frac{2\overline{E}_K}{Mc^2}} = -31.63537\ eV\sqrt{\frac{2e(25.79224\ eV)}{m_e c^2}} = -0.31785\ eV \tag{13.301}$$

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency. The decrease in the energy of $NH$ due to the reentrant orbit in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei, $\overline{E}_{osc}$, is given by the sum of the corresponding energies, $\overline{E}_D$ given by Eq. (13.301) and $\overline{E}_{Kvib}$, the average kinetic energy of vibration which is 1/2 of the vibrational energy of $NH$. Using the experimental $^{14}NH$ $\omega_e$ of $3282.3\ cm^{-1}$ $(0.40696\ eV)$ [28] $\overline{E}_{osc}(^{14}NH)$ is:

$$\overline{E}_{osc}(^{14}NH) = \overline{E}_D + \overline{E}_{Kvib} = \overline{E}_D + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \tag{13.302}$$

$$\overline{E}_{osc}(^{14}NH) = -0.31785\ eV + \frac{1}{2}(0.40696\ eV) = -0.11437\ eV \tag{13.303}$$

Using Eqs. (13.301) and the experimental $^{14}ND$ $\omega_e$ of $2398\ cm^{-1}$ $(0.29732\ eV)$ [28] $\overline{E}_{osc}(^{14}ND)$ is:

$$\overline{E}_{osc}(^{14}ND) = -0.31785\ eV + \frac{1}{2}(0.29732\ eV) = -0.16919\ eV \tag{13.304}$$

## TOTAL AND BOND ENERGIES OF $^{14}NH$ AND $^{14}ND$

$E_{T+osc}(NH)$, the total energy of the $^{14}NH$ radical including the Doppler term, is given by the sum of $E_T(NH)$ (Eq. (13.253)) and $\overline{E}_{osc}(^{14}NH)$ given by Eq. (13.303):

$$\begin{aligned} E_{T+osc}(NH) &= V_e + T + V_m + V_p + E(2p\ shell) + \overline{E}_{osc}(^{14}NH) \\ &= E_T(NH) + \overline{E}_{osc}(^{14}NH) \end{aligned} \tag{13.305}$$

$$\begin{aligned} E_{T+osc}(NH) &= \left\{\frac{-e^2}{8\pi\varepsilon_0 c'}\left[\left(\frac{3}{2} - \frac{3}{8}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'} - 1\right] - 14.53414\ eV\right\}\left[1 + \sqrt{\frac{2\hbar\sqrt{\frac{\frac{3}{4}\frac{e^2}{4\pi\varepsilon_0 b^3}}{m_e}}}{m_e c^2}}\right] + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \\ &= -31.63537\ eV - 0.31785\ eV + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \end{aligned} \tag{13.306}$$

From Eqs. (13.302-13.303) and (13.305-13.306), the total energy of $^{14}NH$ is:

$$\begin{aligned} E_{T+osc}\left(NH\right) &= -31.63537\ eV + \bar{E}_{osc}\left({}^{14}NH\right) \\ &= -31.63537\ eV - 0.31785\ eV + \frac{1}{2}\left(0.40696\ eV\right) \\ &= -31.74974\ eV \end{aligned} \tag{13.307}$$

where the experimental $\omega_e$ was used for the $\hbar\sqrt{\frac{k}{\mu}}$ term. $E_{T+osc}\left(ND\right)$, the total energy of ${}^{14}ND$ including the Doppler term, is given by the sum of $E_T\left(ND\right)=E_T\left(NH\right)$ (Eq. (13.253)) and $\bar{E}_{osc}\left({}^{14}ND\right)$ given by Eq. (13.304):

$$\begin{aligned} E_{T+osc}\left(ND\right) &= -31.63537\ eV + \bar{E}_{osc}\left({}^{14}ND\right) \\ &= -31.63537\ eV - 0.31785\ eV + \frac{1}{2}\left(0.29732\ eV\right) \\ &= -31.80456\ eV \end{aligned} \tag{13.308}$$

where the experimental $\omega_e$ was used for the $\hbar\sqrt{\frac{k}{\mu}}$ term. The dissociation of the bond of the hydrogen nitride forms a free hydrogen atom with one unpaired electron and a nitrogen atom with three unpaired electrons as shown in Eq. (13.246). The $p_x$ and $p_y$ fields cancel and the magnetic energy (Eq. (7.46)) with $r_7 = 0.93084a_0$ is subtracted due to the one component of $E_{mag}$ given by Eq. (10.137):

$$E(magnetic) = \frac{2\pi\mu_0 e^2\hbar^2}{m_e^2\left(0.93084a_0\right)^3} = \frac{8\pi\mu_0\mu_B^2}{\left(0.93084a_0\right)^3} = 0.14185\ eV \tag{13.309}$$

The corresponding bond dissociation energy, $E_D$, is given by the sum of the total energies of the nitrogen atom and the corresponding hydrogen atom minus the sum of $E_{T+osc}\left(NH\right)$ and $E(magnetic)$:

$$E_D = E({}^{14}N) + E(H) - E_{T+osc}\left(NH\right) - E\left(magnetic\right) \tag{13.310}$$

$E({}^{14}N)$ is given by Eq. (13.251), $E_D\left(H\right)$ is given by Eq. (13.154), and $E_D\left(D\right)$ is given by Eq. (13.155). The ${}^{14}NH$ bond dissociation energy, $E_D\left({}^{14}NH\right)$, is given by Eqs. (13.154), (13.251), (13.307), and (13.309-13.310):

$$\begin{aligned} E_D\left({}^{14}NH\right) &= -\left(14.53414\ eV + 13.59844\ eV\right) - \left(E\left(magnetic\right) + E_{T+osc}\left(NH\right)\right) \\ &= -28.13258\ eV - \left(0.14185 - 31.74974\ eV\right) \\ &= 3.47530\ eV \end{aligned} \tag{13.311}$$

The experimental ${}^{14}NH$ bond dissociation energy from Ref. [29] and Ref. [30] is:

$$E_D\left({}^{14}NH\right) = 3.42\ eV \tag{13.312}$$

$$E_D\left({}^{14}NH\right) \leq 3.47\ eV \tag{13.313}$$

The ${}^{14}ND$ bond dissociation energy, $E_D\left({}^{14}ND\right)$, is given by Eqs. (13.155), (13.251), (13.308), and (13.309-13.310):

$$\begin{aligned} E_D\left({}^{14}ND\right) &= -\left(14.53414\ eV + 13.603\ eV\right) - \left(E\left(magnetic\right) + E_{T+osc}\left(ND\right)\right) \\ &= -28.13714\ eV - \left(0.14185 - 31.80456\ eV\right) \\ &= 3.5256\ eV \end{aligned} \tag{13.314}$$

The experimental ${}^{14}ND$ bond dissociation energy from Ref. [31] and Ref. [30] is:

$$E_{D_{298}}\left({}^{14}ND\right) \leq 339\ kJ\,/\,mol = 3.513\ eV \tag{13.315}$$

$$E_D\left({}^{14}ND\right) \leq 3.54\ eV \tag{13.316}$$

The results of the determination of bond parameters of $NH$ and $ND$ are given in Table 13.1. The calculated results are based on first principles and given in closed-form, exact equations containing fundamental constants only. The agreement between the experimental and calculated results is excellent.

## DIHYDROGEN NITRIDE ($NH_2$)

The dihydrogen nitride radical $NH_2$ is formed by the reaction of a hydrogen atom with a hydrogen nitride radical:

$$NH + H \rightarrow NH_2 \tag{13.317}$$

$NH_2$ can be solved using the same principles as those used to solve $H_2O$. Two diatomic molecular orbitals (MOs) developed in the Nature of the Chemical Bond of Hydrogen-Type Molecules and Molecular Ions section serve as basis functions in a linear combination with two nitrogen atomic orbitals (AOs) to form the MO of $NH_2$. The solution is very similar to that of $NH$ except that there are two $NH$ bonds in $NH_2$.

## FORCE BALANCE OF $NH_2$

$NH_2$ comprises two chemical bonds between nitrogen and hydrogen. Each $N-H$ bond comprises two spin-paired electrons with one from an initially unpaired electron of the nitrogen atom and the other from the hydrogen atom. Each $H$-atom electron forms a $H_2$-type ellipsoidal MO with one of the initially unpaired $N$-atom electrons, $2p_x$ or $2p_y$, such that the proton and the $N$ nucleus serve as the foci. The initial $N$ electron configuration given in the Seven-Electron Atoms section is $1s^2 2s^2 2p^3$, and the orbital arrangement is given by Eqs. (10.134) and (13.246). The radius and the energy of the $N2p$ shell are unchanged with bond formation. The central paramagnetic force due to spin of each $N-H$ bond is provided by the spin-pairing force of the $NH_2$ MO that has the symmetry of an $s$ orbital that superimposes with the $N2p$ orbitals such that the corresponding angular momenta are unchanged.

As in the case of $H_2$, each of two $N-H$-bond MOs is a prolate spheroid with the exception that the ellipsoidal MO surface cannot extend into $N$ atom for distances shorter than the radius of the $2p$ shell since it is energetically unfavorable. Thus, the MO surface comprises a prolate spheroid at each $H$ proton that is continuous with the $2p$ shell at the $N$ atom. The energies in the $NH_2$ MO involve only each $N2p$ and each $H1s$ electron with the formation of each $N-H$ bond. The sum of the energies of the prolate spheroids is matched to that of the $2p$ shell. The forces are determined by these energies. As in the case of $NH$, the linear combination of each $H_2$-type ellipsoidal MO with each $N2p$ AO must involve a 25% contribution from the $H_2$-type ellipsoidal MO to the $N2p$ AO in order to match potential, kinetic, and orbital energy relationships. Thus, the $NH_2$ MO must comprise two $N-H$ bonds with each comprising 75% of a $H_2$-type ellipsoidal MO (1/2 +25%) and a nitrogen AO:

$$\left[1\,N2p_x\ AO + 0.75\ H_2\ MO\right] + \left[1\,N2p_y\ AO + 0.75\ H_2\ MO\right] \rightarrow NH_2\ MO \tag{13.318}$$

The force constant $k'$ of each $H_2$-type-ellipsoidal-MO component of the $NH_2$ MO is given by Eq. (13.248). The distance from the origin of each $N-H$-bond MO to each focus $c'$ is given by Eq. (13.249). The internuclear distance is given by Eq. (13.250). The length of the semiminor axis of the prolate spheroidal $N-H$-bond MO $b=c$ is given by Eq. (13.62). The eccentricity, $e$, is given by Eq. (13.63). The solution of the semimajor axis $a$ then allows for the solution of the other axes of each prolate spheroid and eccentricity of each $N-H$-bond MO. Since each of the two prolate spheroidal $N-H$-bond MOs comprises a $H_2$-type-ellipsoidal MO that transitions to the $N$ AO, the energy $E$ in Eq. (13.251) adds to that of the two corresponding $H_2$-type ellipsoidal MOs to give the total energy of the $NH_2$ MO. From the energy equation and the relationship between the axes, the dimensions of the $NH_2$ MO are solved.

The energy components of $V_e$, $V_p$, $T$, $V_m$, and $E_T$ are twice those of $OH$ and $NH$ given by Eqs. (13.67-13.73) and equal to those of $H_2O$ given by Eqs. (13.172-13.178). Similarly to $H_2O$, since each prolate spheroidal $H_2$-type MO transitions to the $N$ AO and the energy of the $N2p$ shell must remain constant and equal to the negative of the ionization energy given by Eq. (13.251), the total energy $E_T\left(NH_2\right)$ of the $NH_2$ MO is given by the sum of the energies of the orbitals corresponding to the composition of the linear combination of the $N$ AO and the two $H_2$-type ellipsoidal MOs that forms the $NH_2$ MO as given by Eq. (13.318):

$$\begin{aligned} E_T\left(NH_2\right) &= E_T + E\left(2p\ shell\right) = E_T - E(ionization;\ N) \\ &= -\frac{e^2}{4\pi\varepsilon_0 c'}\left[\left(\frac{3}{2}-\frac{3}{8}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right] - 14.53414\ eV \end{aligned} \tag{13.319}$$

The two hydrogen atoms and the nitrogen atom can achieve an energy minimum as a linear combination of two $H_2$-type ellipsoidal MOs each having the proton and the nitrogen nucleus as the foci. Each $N-H$-bond MO comprises the same $N2p$ shell of constant energy given by Eq. (13.251). Thus, the energy of the $NH_2$ MO is also given by the sum of that of the two $H_2$-type ellipsoidal MOs given by Eq. (11.212) minus the energy of the redundant nitrogen atom of the linear combination given by Eq. (13.251):

$$\begin{aligned} E_T\left(2H_2-N\right) &= -2\frac{e^2}{8\pi\varepsilon_0 a_0}\left[\left(2\sqrt{2}-\sqrt{2}+\frac{\sqrt{2}}{2}\right)\ln\frac{\sqrt{2}+1}{\sqrt{2}-1}-\sqrt{2}\right]-E\left(2p\ shell\right) \\ &= 2\left(-31.63536831\ eV\right)-\left(-14.53414\ eV\right)=-48.73660\ eV \end{aligned} \tag{13.320}$$

$E_T\left(NH_2\right)$ given by Eq. (13.319) is set equal to two times the energy of the $H_2$-type ellipsoidal MO minus the energy of the $N2p$ shell given by Eq. (13.320):

$$E_T\left(NH_2\right)=-\frac{e^2}{4\pi\varepsilon_0 c'}\left[\left(\frac{3}{2}-\frac{3}{8}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]-14.53414\ eV=-48.73660\ eV \tag{13.321}$$

From the energy relationship given by Eq. (13.321) and the relationship between the axes given by Eqs. (13.248-13.250) and (13.62-13.63), the dimensions of the $NH_2$ MO can be solved.

Substitution of Eq. (13.249) into Eq. (13.321) gives:

$$\frac{e^2}{4\pi\varepsilon_0\sqrt{0.712154aa_0}}\left[\left(\frac{3}{2}-\frac{3}{8}\frac{a_0}{a}\right)\ln\frac{a+\sqrt{0.712154aa_0}}{a-\sqrt{0.712154aa_0}}-1\right]=e34.20246 \tag{13.322}$$

The most convenient way to solve Eq. (13.322) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is

$$a=1.36276a_0=7.21141\ X\ 10^{-11}\ m \tag{13.323}$$

Substitution of Eq. (13.323) into Eq. (13.249) gives:

$$c'=0.98514a_0=5.21312\ X\ 10^{-11}\ m \tag{13.324}$$

The internuclear distance given by multiplying Eq. (13.324) by two is:

$$2c'=1.97027a_0=1.04262\ X\ 10^{-10}\ m \tag{13.325}$$

The experimental bond distance is [32]:

$$2c'=1.024\ X\ 10^{-10}\ m \tag{13.326}$$

Substitution of Eqs. (13.323-13.324) into Eq. (13.62) gives:

$$b=c=0.94160a_0=4.98276\ X\ 10^{-11}\ m \tag{13.327}$$

Substitution of Eqs. (13.323-13.324) into Eq. (13.63) gives:

$$e=0.72290 \tag{13.328}$$

The nucleus of the $H$ atom and the nucleus of the $N$ atom comprise the foci of the $H_2$-type ellipsoidal MO. The parameters of the point of intersection of each $H_2$-type ellipsoidal MO and the $N2p_x$ AO or $N2p_y$ AO are given by Eqs. (13.84-13.95) and (13.261-13.270). Using Eqs. (13.323-13.325) and (13.327-13.328), the polar intersection angle $\theta'$ given by Eq. (13.261) with $r_n=r_7=0.93084a_0$ is

$$\theta'=114.61^\circ \tag{13.329}$$

Then, the angle $\theta_{N2pAO}$ the radial vector of the $N2p_x$ AO or $N2p_y$ AO makes with the internuclear axis is

$$\theta_{N2pAO}=180^\circ-114.61^\circ=65.39^\circ \tag{13.330}$$

as shown in Figure 13.5. The parametric angle $\theta_{H_2MO}$ given by Eqs. (13.264-13.265), (13.327), and (13.330) is:

$$\theta_{H_2MO}=64.00^\circ \tag{13.331}$$

Then, the distance $d_{H_2MO}$ along the internuclear axis from the origin of $H_2$-type ellipsoidal MO to the point of intersection of the orbitals given by Eqs. (13.267), (13.323), and (13.331) is:

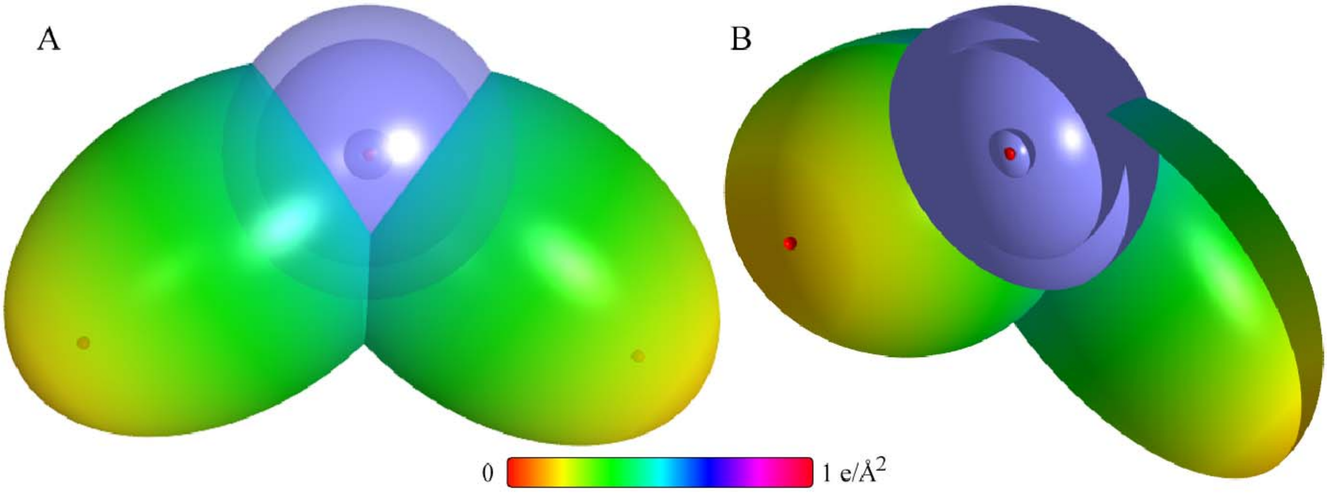
$$d_{H_2MO}=0.59748a_0=3.16175\ X\ 10^{-11}\ m \tag{13.332}$$

The distance $d_{N2pAO}$ along the internuclear axis from the origin of the $N$ atom to the point of intersection of the orbitals given by Eqs. (13.269), (13.324), and (13.332) is:

$$d_{N2pAO}=0.38765a_0=2.05137\ X\ 10^{-11}\ m \tag{13.333}$$

As shown in Eq. (13.318), in addition to the $p$-orbital charge-density modulation, the uniform charge-density in the $p_x$ and $p_y$ orbitals is increased by a factor of 0.25 and the $H$ atoms are each decreased by a factor of 0.25. Using the orbital composition of $NH_2$ (Eq. (13.318)), the radii of $N1s=0.14605a_0$ (Eq. (10.51)), $N2s=0.69385a_0$ (Eq. (10.62)), and $N2p=0.93084a_0$ (Eq. (10.142)) shells, and the parameters of the $NH_2$ MO given by Eqs. (13.3-13.4) and (13.323-13.333), the charge-density of the $NH_2$ MO comprising the linear combination of two $N-H$-bond MOs ($NH$-type ellipsoidal MOs given in the Energies of $NH$ section) according to Eq. (13.318) is shown in Figure 13.7. Each $N-H$-bond MO comprises a $H_2$-type ellipsoidal MO and an $N2p$ AO having the dimensional diagram shown in Figure 13.5.

Figure 13.7. $NH_2$ MO comprising the linear combination of two $N-H$-bond MOs. Each $N-H$-bond MO comprises the superposition of a $H_2$-type ellipsoidal MO and the $N2p_x$ AO or the $N2p_y$ AO with a relative charge-density of 0.75 to 1.25; otherwise, the $N2p$ orbitals are the same as those of the nitrogen atom. The internuclear axis of one $N-H$ bond is perpendicular to the bonding $p_x$ orbital, and the internuclear axis of the other $N-H$ bond is perpendicular to the bonding $p_y$ orbital. (A) Color scale, translucent view of the charge-density of the $NH_2$ MO from the top. For each $N-H$ bond, the ellipsoidal surface of each $H_2$-type ellipsoidal MO transitions to a $N2p$ AO. The $N2p$ shell, the $N2s$ shell, the $N1s$ shell, and the nuclei (red, not to scale) are shown. (B) Cut-away view showing the inner most $N1s$ shell, and moving radially, the $N2s$ shell, the $N2p$ shell, and the $H_2$-type ellipsoidal MO that transitions to a $N2p$ AO for each $N-H$ bond. Bisector current not shown.



## ENERGIES OF $NH_2$

The energies of $NH_2$ given by the substitution of the semiprincipal axes ((Eqs. (13.323-13.325) and (13.327)) into the energy equations (Eqs. (13.172-13.176)) are:

$$V_e = \left(\frac{3}{2}\right)\frac{-2e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -75.71422\ eV \tag{13.334}$$

$$V_p = 2\frac{e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}} = 27.62216\ eV \tag{13.335}$$

$$T = \left(\frac{3}{2}\right)\frac{\hbar^2}{2m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = 27.77974\ eV \tag{13.336}$$

$$V_m = \left(\frac{3}{2}\right)\frac{-\hbar^2}{4m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -13.88987\ eV \tag{13.337}$$

$$E_T\left(NH_2\right) = -\frac{e^2}{4\pi\varepsilon_0 c'}\left[\left(\frac{3}{2}-\frac{3}{8}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]-14.53414\ eV = -48.73633\ eV \tag{13.338}$$

where $E_T\left(NH_2\right)$ is given by Eq. (13.319) which is reiteratively matched to Eq. (13.320) within five-significant-figure round-off error.

## VIBRATION OF $NH_2$

The vibrational energy levels of $NH_2$ may be solved as two equivalent coupled harmonic oscillators by developing the Lagrangian, the differential equation of motion, and the eigenvalue solutions [2] wherein the spring constants are derived from the central forces as given in the Vibration of Hydrogen-Type Molecular Ions section and the Vibration of Hydrogen-Type Molecules section.

## THE DOPPLER ENERGY TERM OF $NH_2$

The radiation reaction force in the case of the vibration of $NH_2$ in the transition state corresponds to the Doppler energy, $E_D$, given by Eq. (11.181) and Eqs. (13.22) and (13.144) that is dependent on the motion of the electrons and the nuclei. The kinetic energy of the transient vibration is derived from the corresponding central forces. The equations of the radiation reaction force of dihydrogen and dideuterium nitride are the same as those of the corresponding water molecules with the substitution of the dihydrogen and dideuterium nitride parameters. Using Eqs. (11.136) and (13.207-13.209), the angular frequency of the reentrant oscillation in the transition state is

$$\omega = \sqrt{\frac{\left(\frac{3}{2}\right)\frac{e^2}{4\pi\varepsilon_0 b^3}}{m_e}} = 5.54150\ X\ 10^{16}\ rad/s \tag{13.339}$$

where $b$ is given by Eq. (13.327). The kinetic energy, $E_K$, is given by Planck's equation (Eq. (11.127)):

$$\overline{E}_K = \hbar\omega = \hbar 5.54150\ X\ 10^{16}\ rad/s = 36.47512\ eV \tag{13.340}$$

In Eq. (11.181), substitution of $E_T(H_2)$ (Eqs. (11.212) and (13.75)), the maximum total energy of each $H_2$-type MO, for $E_{h\nu}$, the mass of the electron, $m_e$, for $M$, and the kinetic energy given by Eq. (13.340) for $\overline{E}_K$ gives the Doppler energy of the electrons for the reentrant orbit:

$$\begin{aligned}\overline{E}_D &\cong E_{h\nu}\sqrt{\frac{2\overline{E}_K}{Mc^2}}\\ &= -31.63537\ eV\sqrt{\frac{2e(36.47512\ eV)}{m_e c^2}}\\ &= -0.37798\ eV\end{aligned} \tag{13.341}$$

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency. The decrease in the energy of $NH_2$ due to the reentrant orbit in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei, $\overline{E}_{osc}$, is given by the sum of the corresponding energies, $\overline{E}_D$ given by Eq. (13.341) and $\overline{E}_{Kvib}$, the average kinetic energy of vibration which is 1/2 of the vibrational energy of $NH_2$. Using the experimental $^{14}NH_2$ vibrational energy of $E_{vib} = 3301.110\ cm^{-1} = 0.40929\ eV$ [33] gives:

$$\overline{E}'_{osc} = \overline{E}_D + \overline{E}_{Kvib} = \overline{E}_D + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \tag{13.342}$$

$$\begin{aligned}\overline{E}'_{osc} &= -0.37798\ eV + \frac{1}{2}(0.40929\ eV)\\ &= -0.17334\ eV\end{aligned} \tag{13.343}$$

per bond. As in the case for $H_2O$, the reentrant orbit for the binding of a hydrogen atom to a $NH$ radical causes the bonds to oscillate by increasing and decreasing in length along the two $N-H$ bonds at a relative phase angle of 180°. Since the vibration and reentrant oscillation is along two bonds for the asymmetrical stretch ($v_3$), $\overline{E}_{osc}$ for $^{14}NH_2$, $\overline{E}_{osc}\left(^{14}NH_2\right)$, is:

$$\begin{aligned}\overline{E}_{osc}\left(^{14}NH_2\right) &= 2\left(\overline{E}_D + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right)\\ &= 2\left(-0.37798\ eV + \frac{1}{2}(0.40929\ eV)\right)\\ &= -0.34668\ eV\end{aligned} \tag{13.344}$$

Using Eq. (13.341), Eqs. (13.342-13.344), and the $^{14}ND_2$ vibrational energy of $E_{vib} = 2410.79\ cm^{-1} = 0.29890\ eV$, calculated from the experimental $^{14}NH_2$ vibrational energy using Eq. (11.148), the corresponding $\overline{E}_{osc}\left(^{14}ND_2\right)$ is:

$$\begin{aligned}\overline{E}_{osc}\left(^{14}ND_2\right) &= 2\left(-0.37798\ eV + \frac{1}{2}(0.29890\ eV)\right)\\ &= -0.45707\ eV\end{aligned} \tag{13.345}$$

## TOTAL AND BOND ENERGIES OF $^{14}NH_2$ AND $^{14}ND_2$

$E_{T+osc}\left({}^{14}NH_2\right)$, the total energy of the $^{14}NH_2$ including the Doppler term, is given by the sum of $E_T\left(NH_2\right)$ (Eq. (13.321)) and $\bar{E}_{osc}\left({}^{14}NH_2\right)$ given Eqs. (13.339-13.344):

$$E_{T+osc}\left({}^{14}NH_2\right) = V_e + T + V_m + V_p + E\left(N2p\right) + \bar{E}_{osc}\left({}^{14}NH_2\right) = E_T\left(NH_2\right) + \bar{E}_{osc}\left({}^{14}NH_2\right) \quad (13.346)$$

$$\begin{aligned} E_{T+osc}\left({}^{14}NH_2\right) &= \left\{ \begin{array}{l} \left( \dfrac{-e^2}{4\pi\varepsilon_0 c'} \left[ \left( \dfrac{3}{2} - \dfrac{3}{8}\dfrac{a_0}{a} \right) \ln\dfrac{a+c'}{a-c'} - 1 \right] - 14.53414\ eV \right) \\ -2\left( \left(31.63536831\ eV\right) \sqrt{\dfrac{2\hbar\sqrt{\dfrac{\dfrac{3}{2}\dfrac{e^2}{4\pi\varepsilon_0 b^3}}{m_e}}}{m_ec^2}} - \dfrac{1}{2}\hbar\sqrt{\dfrac{k}{\mu}} \right) \end{array} \right\} \\ &= -48.73660\ eV - 2\left( 0.37798\ eV - \dfrac{1}{2}\hbar\sqrt{\dfrac{k}{\mu}} \right) \end{aligned} \quad (13.347)$$

From Eqs. (13.344) and (13.346-13.347), the total energy of $^{14}NH_2$ is:

$$\begin{aligned} E_{T+osc}\left({}^{14}NH_2\right) &= -48.73660\ eV + \bar{E}_{osc}\left({}^{14}NH_2\right) \\ &= -48.73660\ eV - 2\left( 0.37798\ eV - \frac{1}{2}\left(0.40929\ eV\right) \right) \\ &= -49.08328\ eV \end{aligned} \quad (13.348)$$

where the experimental $^{14}NH_2$ vibrational energy was used for the $\hbar\sqrt{\frac{k}{\mu}}$ term. $E_{T+osc}\left({}^{14}ND_2\right)$, the total energy of $^{14}ND_2$ including the Doppler term is given by the sum of $E_T\left(ND_2\right) = E_T\left(NH_2\right)$ (Eq. (13.321)) and $\bar{E}_{osc}\left({}^{14}ND_2\right)$ given by Eq. (13.345).

$$\begin{aligned} E_{T+osc}\left({}^{14}ND_2\right) &= -48.73660\ eV + \bar{E}_{osc}\left({}^{14}ND_2\right) \\ &= -48.73660\ eV - 2\left( 0.37798\ eV - \frac{1}{2}\left(0.29890\ eV\right) \right) \\ &= -49.19366\ eV \end{aligned} \quad (13.349)$$

where the experimental $^{14}NH_2$ vibrational energy corrected for the reduced mass difference of hydrogen and deuterium was used for the $\hbar\sqrt{\frac{k}{\mu}}$ term. The corresponding bond dissociation energy, $E_D$, is given by the sum of the total energies of the corresponding hydrogen nitride radical and hydrogen atom minus the total energy of dihydrogen nitride, $E_{T+osc}\left({}^{14}NH_2\right)$.

Thus, $E_D$ of $^{14}NH_2$ is given by:

$$E_D\left({}^{14}NH_2\right) = E(H) + E({}^{14}NH) - E_{T+osc}\left({}^{14}NH_2\right) \quad (13.350)$$

where $E_T({}^{14}NH)$ is given by the of the sum of the experimental energies of $^{14}N$ (Eq. (13.251)), $H$ (Eq. (13.154)), and the negative of the bond energy of $^{14}NH$ (Eq. (13.312)):

$$E({}^{14}NH) = -13.59844\ eV - 14.53414\ eV - 3.42\ eV = -31.55258\ eV \quad (13.351)$$

From Eqs. (13.154), (13.348), and (13.350-13.351), $E_D\left({}^{14}NH_2\right)$ is:

$$\begin{aligned} E_D\left({}^{14}NH_2\right) &= E(H) + E({}^{14}NH) - E_{T+osc}\left({}^{14}NH_2\right) \\ &= -13.59844\ eV - 31.55258\ eV - \left(-49.08328\ eV\right) \\ &= 3.9323\ eV \end{aligned} \quad (13.352)$$

The experimental $^{14}NH_2$ bond dissociation energy from Ref. [34] and Ref. [35] is:

$$E_D({}^{14}NH_2) = 88 \pm 4\ kcal/mole = 3.8160\ eV \quad (13.353)$$

$$E_D({}^{14}NH_2) = 91.0 \pm 0.5\ kcal/mole = 3.9461\ eV \quad (13.354)$$

Similarly, $E_D$ of $^{14}ND_2$ is given by:

$$E_D\left({}^{14}ND_2\right) = E(D) + E({}^{14}ND) - \left(E_{T+osc}\left({}^{14}ND_2\right)\right) \quad (13.355)$$

where $E_T(^{14}ND)$ is given by the of the sum of the experimental energies of $^{14}N$ (Eq. (13.251)), $D$ (Eq. (13.155)), and the negative of the bond energy of $^{14}ND$ (Eq. (13.315)):

$$E(^{14}ND) = -13.603\ eV - 14.53414\ eV - 3.513\ eV = -31.6506\ eV \tag{13.356}$$

From Eqs. (13.155), (13.349), and (13.355-13.356), $E_D\left(^{14}ND_2\right)$ is

$$E_D(^{14}ND_2) = -13.603\ eV - 31.6506\ eV - \left(-49.19366\ eV\right) = 3.9401\ eV \tag{13.357}$$

The $^{14}ND_2$ bond dissociation energy calculated from the average of the experimental bond energies [34-35] and vibrational energy of $^{14}NH_2$ [33] is:

$$\begin{aligned} E_D(^{14}ND_2) &= E_D(^{14}NH_2) + \frac{1}{2}\left(E_{vib\ (^{14}NH_2)} - E_{vib\ (^{14}ND_2)}\right) \\ &= \frac{1}{2}\left(3.8160\ eV + 3.9461\ eV\right) + \frac{1}{2}\left(0.40929\ eV - 0.29890\ eV\right) = 3.9362\ eV \end{aligned} \tag{13.358}$$

## BOND ANGLE OF $NH_2$

The $NH_2$ MO comprises a linear combination of two $N-H$-bond MOs. Each $N-H$-bond MO comprises the superposition of a $H_2$-type ellipsoidal MO and the $N2p_x$ AO or the $N2p_y$ AO with a relative charge density of 0.75 to 1.25; otherwise, the $N2p$ AOs are the same as those of the nitrogen atom. A bond is also possible between the two H atoms of the $N-H$ bonds. Such $H-H$ bonding would decrease the $N-H$ bond strength since electron density would be shifted from the $N-H$ bonds to the $H-H$ bond. Thus, the bond angle between the two $N-H$ bonds is determined by the condition that the total energy of the $H_2$-type ellipsoidal MO between the terminal $H$ atoms of the $N-H$ bonds is zero. From Eqs. (11.79) and (13.228), the distance from the origin to each focus of the $H-H$ ellipsoidal MO is

$$c' = a\sqrt{\frac{\hbar^2 4\pi\varepsilon_0}{m_e e^2 2a}} = \sqrt{\frac{aa_0}{2}} \tag{13.359}$$

The internuclear distance from Eq. (13.229) is:

$$2c' = 2\sqrt{\frac{aa_0}{2}} \tag{13.360}$$

The length of the semiminor axis of the prolate spheroidal $H-H$ MO $b=c$ is given by Eq. (13.167).

Since the two $H_2$-type ellipsoidal MOs comprise 75% of the $H$ electron density of $H_2$ and the energy of each $H_2$-type ellipsoidal MO is matched to that of the $N2p$ AO; the component energies and the total energy $E_T$ of the $H-H$ bond are given by Eqs. (13.67-13.73) except that $V_e$, $T$, and $V_m$ are corrected for the energy matching factor of 0.93613 given in Eq. (13.248). Substitution of Eq. (13.359) into Eq. (13.233) with the energy-matching factor gives:

$$0 = \left[\begin{array}{l} \dfrac{-e^2}{8\pi\varepsilon_0\sqrt{\dfrac{aa_0}{2}}}\left[(0.93613)^{-1}\left(\dfrac{3}{2}-\dfrac{3}{8}\dfrac{a_0}{a}\right)\ln\dfrac{a+\sqrt{\dfrac{aa_0}{2}}}{a-\sqrt{\dfrac{aa_0}{2}}}-1\right]\left[1+\sqrt{\dfrac{2\hbar\sqrt{\dfrac{\dfrac{0.75e^2}{4\pi\varepsilon_0 a^3}}{m_e}}}{m_e c^2}}\right] \\ +\dfrac{1}{2}\hbar\sqrt{\dfrac{\dfrac{0.75e^2}{8\pi\varepsilon_0 a^3}-\dfrac{e^2}{8\pi\varepsilon_0\left(a+c'\right)^3}}{0.5m_p}} \end{array}\right] \tag{13.361}$$

From the energy relationship given by Eq. (13.361) and the relationship between the axes given by Eqs. (13.359-13.360) and (13.167-13.168), the dimensions of the $H-H$ MO can be solved.

The most convenient way to solve Eq. (13.361) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is:

$$a = 4.9500a_0 = 2.6194\ X\ 10^{-10}\ m \tag{13.362}$$

Substitution of Eq. (13.362) into Eq. (13.359) gives:

$$c' = 1.5732a_0 = 8.3251\ X\ 10^{-11}\ m \tag{13.363}$$

The internuclear distance given by multiplying Eq. (13.363) by two is:

$$2c' = 3.1464a_0 = 1.6650\ X\ 10^{-10}\ m \tag{13.364}$$

Substitution of Eqs. (13.362-13.363) into Eq. (13.167) gives:

$$b = c = 4.6933a_0 = 2.4836\ X\ 10^{-10}\ m \tag{13.365}$$

Substitution of Eqs. (13.362-13.363) into Eq. (13.168) gives:

$$e = 0.3178 \tag{13.366}$$

Using, $2c'_{H-H}$ (Eq. (13.364)), the distance between the two $H$ atoms when the total energy of the corresponding MO is zero (Eq. (13.361)), and $2c'_{N-H}$ (Eq. (13.325)), the internuclear distance of each $N-H$ bond, the corresponding bond angle can be determined from the law of cosines. Using, Eq. (13.242), the bond angle $\theta$ between the $N-H$ bonds is:

$$\theta = \cos^{-1}\left( \frac{2(1.9703)^2 - (3.1464)^2}{2(1.9703)^2} \right) = \cos^{-1}(-0.2751) = 105.969° \tag{13.367}$$

The experimental angle between the $N-H$ bonds is [32]:

$$\theta = 103.3° \tag{13.368}$$

The results of the determination of bond parameters of $NH_2$ and $ND_2$ are given in Table 13.1. The calculated results are based on first principles and given in closed-form, exact equations containing fundamental constants only. The agreement between the experimental and calculated results is excellent.

## AMMONIA ($NH_3$)

Ammonia ($NH_3$) is formed by the reaction of a hydrogen atom with a dihydrogen nitride radical:

$$NH_2 + H \to NH_3 \tag{13.369}$$

$NH_3$ can be solved using the same principles as those used to solve $NH_2$ except that three rather than two $H_2$-type prolate spheroidal molecular orbitals (MOs) serve as basis functions in a linear combination with nitrogen atomic orbitals (AOs) to form the MO of $NH_3$.

## FORCE BALANCE OF $NH_3$

$NH_3$ comprises three chemical bonds between nitrogen and hydrogen. Each $N-H$ bond comprises two spin-paired electrons with one from an initially unpaired electron of the nitrogen atom and the other from the hydrogen atom. Each $H$-atom electron forms a $H_2$-type ellipsoidal MO with one of the initially unpaired $N$-atom electrons, $2p_x$, $2p_y$, or $2p_z$, such that the proton and the $N$ nucleus serve as the foci. The initial $N$ electron configuration given in the Seven-Electron Atoms section is $1s^2 2s^2 2p^3$, and the orbital arrangement is given by Eqs. (10.134) and (13.246). The radius and the energy of the $N2p$ shell are unchanged with bond formation. The central paramagnetic force due to spin of each $N-H$ bond is provided by the spin-paring force of the $NH_3$ MO that has the symmetry of an $s$ orbital that superimposes with the $N2p$ orbitals such that the corresponding angular momenta are unchanged.

As in the case of $H_2$, each of three $N-H$-bond MOs is a prolate spheroid with the exception that the ellipsoidal MO surface cannot extend into the $N$ atom for distances shorter than the radius of the $2p$ shell since it is energetically unfavorable. Thus, the MO surface comprises a prolate spheroid at each $H$ proton that is continuous with the $2p$ shell at the $N$ atom. The energies in the $NH_3$ MO involve only each $N2p$ and each $H1s$ electron with the formation of each $N-H$ bond. The sum of the energies of the prolate spheroids is matched to that of the $2p$ shell. The forces are determined by these energies. As in the cases of $NH$ and $NH_2$, the linear combination of each $H_2$-type ellipsoidal MO with each $N2p$ AO must involve a 25% contribution from the $H_2$-type ellipsoidal MO to the $N2p$ AO in order to match potential, kinetic, and orbital energy relationships. Thus, the $NH_3$ MO must comprise three $N-H$ bonds with each comprising 75% of a $H_2$-type ellipsoidal MO (1/2 +25%) and a nitrogen AO:

$$[1\,N2p_x\ AO + 0.75\ H_2\ MO] + [1\,N2p_y\ AO + 0.75\ H_2\ MO] + [1\,N2p_z\ AO + 0.75\ H_2\ MO] \to NH_3\ MO \tag{13.370}$$

The force constant $k'$ of each $H_2$-type-ellipsoidal-MO component of the $NH_3$ MO is given by Eq. (13.248). The distance from the origin of each $N-H$-bond MO to each focus $c'$ is given by Eq. (13.249). The internuclear distance is given by Eq. (13.250). The length of the semiminor axis of the prolate spheroidal $N-H$-bond MO $b=c$ is given by Eq. (13.62). The eccentricity, $e$, is given by Eq. (13.63). The solution of the semimajor axis $a$ then allows for the solution of the other axes of each prolate spheroid and eccentricity of each $N-H$-bond MO. Since each of the three prolate spheroidal $N-H$-bond MOs comprises a $H_2$-type-ellipsoidal MO that transitions to the $N$ AO, the energy $E$ in Eq. (13.251) adds to that of the three corresponding $H_2$-type ellipsoidal MOs to give the total energy of the $NH_3$ MO. From the energy equation and the relationship between the axes, the dimensions of the $NH_3$ MO are solved.

The energy components of $V_e$, $V_p$, $T$, $V_m$, and $E_T$ are three times those of $OH$ and $NH$ given by Eqs. (13.67-13.73) and 1.5 times those of $H_2O$ given by Eqs. (13.172-13.178). Similarly to $H_2O$, since each prolate spheroidal $H_2$-type MO transitions to the $N$ AO and the energy of the $N2p$ shell must remain constant and equal to the negative of the ionization energy given by Eq. (13.251), the total energy $E_T(NH_3)$ of the $NH_3$ MO is given by the sum of the energies of the orbitals corresponding to the composition of the linear combination of the $N$ AO and the three $H_2$-type ellipsoidal MOs that forms the $NH_3$ MO as given by Eq. (13.370):

$$\begin{aligned} E_T\left(NH_3\right) &= E_T + E\left(2p\ shell\right) \\ &= E_T - E(ionization;\ N) \\ &= -3\frac{e^2}{8\pi\varepsilon_0 c'}\left[\left(\frac{3}{2}-\frac{3}{8}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]-14.53414\ eV \end{aligned} \tag{13.371}$$

The three hydrogen atoms and the nitrogen atom can achieve an energy minimum as a linear combination of three $H_2$-type ellipsoidal MOs each having the proton and the nitrogen nucleus as the foci. Each $N-H$-bond MO comprises the same $N2p$ shell of constant energy given by Eq. (13.251). Thus, an energy term of the $NH_3$ MO is given by the sum of the three $H_2$-type ellipsoidal MOs given by Eq. (11.212) minus the energy of the redundant nitrogen atom of the linear combination given by Eq. (13.251). The total sum is determined by the energy matching condition of the binding atoms.

In Eq. (13.248), the equipotential condition of the union of each $H_2$-type-ellipsoidal-MO and the $N$ AO was met when the force constant used to determine the ellipsoidal parameter $c'$ was normalized by the ratio of the ionization energy of $N$ $14.53414\ eV$ [6] and $13.605804\ eV$, the magnitude of the Coulombic energy between the electron and proton of $H$ given by Eq. (1.264). This normalized the force to match that of the Coulombic force alone to meet the force matching condition of the $NH$ MO under the influence of the proton and the $N$ nucleus. The minimum total energy of the $NH_3$ MO from the sum of energies of a linear combination from four atoms is determined using the energy matching condition of Eq. (13.248). Since each of the three prolate spheroidal $N-H$-bond MOs of $NH_3$ comprises a $H_2$-type-ellipsoidal MO that transitions to the $N$ AO and the energy matching condition is met, the nitrogen energy $E$ (Eq. (13.251)) and the energy (Eq. (1.264)) of a hydrogen atomic orbital ($H$ AO), $E_{Coulomb}\left(H\right)$, corresponding to the Coulombic force of $+e$ from the nitrogen nucleus is subtracted from the sum of the energies of the three corresponding $H_2$-type ellipsoidal MOs to given an energy minimum. From another perspective, the electron configuration of $NH_2$ is equivalent to that of $OH$ and is given by Eq. (10.174). $NH_2$ serves as a one-electron atom that is energy matched by the $H$ AO as a basis element to minimize the energy of $NH_3$ in the formation of the third $N-H$-bond.

$$\begin{aligned} E_T\left(3H_2-N-H\right) &= \left\{\begin{matrix} -3\dfrac{e^2}{8\pi\varepsilon_0 a_0}\left[\left(2\sqrt{2}-\sqrt{2}+\dfrac{\sqrt{2}}{2}\right)\ln\dfrac{\sqrt{2}+1}{\sqrt{2}-1}-\sqrt{2}\right] \\ -E\left(N2p\ shell\right)-E_{Coulomb}\left(H\right) \end{matrix}\right\} \\ &= 3\left(-31.63536831\ eV\right)-\left(-14.53414\ eV-13.605804eV\right) = -66.76616\ eV \end{aligned} \tag{13.372}$$

$E_T\left(NH_3\right)$ given by Eq. (13.371) is set equal to Eq. (13.372), three times the energy of the $H_2$-type ellipsoidal MO minus the energy of the $N2p$ shell and the $H$ AO:

$$E_T\left(NH_3\right) = -3\frac{e^2}{8\pi\varepsilon_0 c'}\left[\left(\frac{3}{2}-\frac{3}{8}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]-14.53414\ eV = -66.76616\ eV \tag{13.373}$$

From the energy relationship given by Eq. (13.373) and the relationship between the axes given by Eqs. (13.248-13.250) and (13.62-13.63), the dimensions of the $NH_3$ MO can be solved.

Substitution of Eq. (13.249) into Eq. (13.373) gives:

$$\frac{3e^2}{8\pi\varepsilon_0\sqrt{0.712154aa_0}}\left[\left(\frac{3}{2}-\frac{3}{8}\frac{a_0}{a}\right)\ln\frac{a+\sqrt{0.712154aa_0}}{a-\sqrt{0.712154aa_0}}-1\right] = e52.23202 \tag{13.374}$$

The most convenient way to solve Eq. (13.374) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is:

$$a = 1.34750a_0 = 7.13066\ X\ 10^{-11}\ m \tag{13.375}$$

Substitution of Eq. (13.375) into Eq. (13.249) gives:

$$c' = 0.97961a_0 = 5.18385\ X\ 10^{-11}\ m \tag{13.376}$$

The internuclear distance given by multiplying Eq. (13.376) by two is:

$$2c' = 1.95921a_0 = 1.03677\ X\ 10^{-10}\ m \tag{13.377}$$

The experimental bond distance is [32]:

$$2c' = 1.012\ X\ 10^{-10}\ m \tag{13.378}$$

Substitution of Eqs. (13.375-13.376) into Eq. (13.62) gives:

$$b = c = 0.92527a_0 = 4.89633\ X\ 10^{-11}\ m \tag{13.379}$$

Substitution of Eqs. (13.375-13.376) into Eq. (13.63) gives:

$$e = 0.72698 \qquad (13.380)$$

The nucleus of the $H$ atom and the nucleus of the $N$ atom comprise the foci of the $H_2$-type ellipsoidal MO. The parameters of the point of intersection of each $H_2$-type ellipsoidal MO and the $N2p_x$, $N2p_y$, or $N2p_z$ AO are given by Eqs. (13.84-13.95), (13.261-13.270), and (13.261-13.270). Using Eqs. (13.375-13.377) and (13.379-13.380), the polar intersection angle $\theta'$ given by Eq. (13.261) with $r_n = r_7 = 0.93084a_0$ is:

$$\theta' = 115.89° \qquad (13.381)$$

Then, the angle $\theta_{N2pAO}$ the radial vector of the $N2p_x$, $N2p_y$, or $N2p_z$ AO makes with the internuclear axis is

$$\theta_{N2pAO} = 180° - 115.89° = 64.11° \qquad (13.382)$$

as shown in Figure 13.5. The parametric angle $\theta_{H_2MO}$ given by Eqs. (13.264-13.265), (13.379), and (13.382) is:

$$\theta_{H_2MO} = 64.83° \qquad (13.383)$$

Then, the distance $d_{H_2MO}$ along the internuclear axis from the origin of $H_2$-type ellipsoidal MO to the point of intersection of the orbitals given by Eqs. (13.267), (13.375), and (13.383) is:

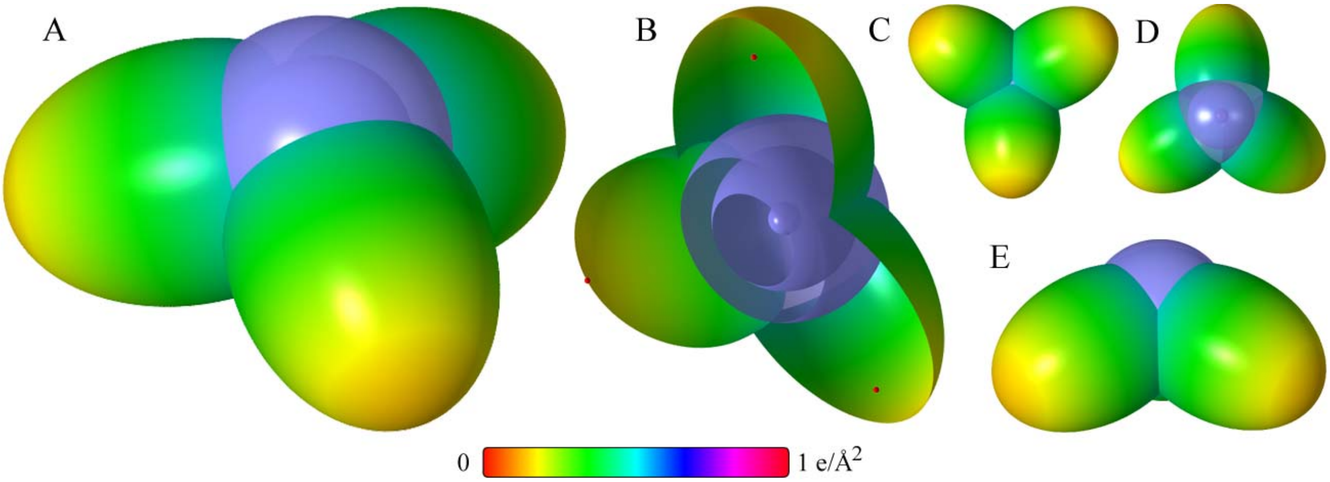
$$d_{H_2MO} = 0.57314a_0 = 3.03292\ X\ 10^{-11}\ m \qquad (13.384)$$

The distance $d_{N2pAO}$ along the internuclear axis from the origin of the $N$ atom to the point of intersection of the orbitals given by Eqs. (13.269), (13.376), and (13.384) is:

$$d_{N2pAO} = 0.40647a_0 = 2.15093\ X\ 10^{-11}\ m \qquad (13.385)$$

As shown in Eq. (13.370), in addition to the $p$-orbital charge-density modulation, the uniform charge-density in the $p_x$, $p_y$, and $p_z$ orbitals is increased by a factor of 0.25 and the $H$ atoms are each decreased by a factor of 0.25. Using the orbital composition of $NH_3$ (Eq. (13.370)), the radii of $N1s = 0.14605a_0$ (Eq. (10.51)), $N2s = 0.69385a_0$ (Eq. (10.62)), and $N2p = 0.93084a_0$ (Eq. (10.142)) shells, and the parameters of the $NH_3$ MO given by Eqs. (13.3-13.4) and (13.375-13.385), the charge-density of the $NH_3$ MO comprising the linear combination of three $N-H$-bond MOs ($NH$-type ellipsoidal MOs given in the Energies of $NH$ section) according to Eq. (13.370) is shown in Figure 13.8. Each $N-H$-bond MO comprises a $H_2$-type ellipsoidal MO and an $N2p$ AO having the dimensional diagram shown in Figure 13.5.

Figure 13.8. $NH_3$ MO comprising the linear combination of three $N-H$-bonds. Each $N-H$-bond MO comprises the superposition of a $H_2$-type ellipsoidal MO and the $N2p_x$, $N2p_y$, or $N2p_z$ AO with a relative charge-density of 0.75 to 1.25; otherwise, the $N2p$ orbitals are the same as those of the nitrogen atom. The each internuclear axis of one $N-H$ bond is perpendicular to the bonding $p$ orbital. (A) Color scale, translucent view of the charge-density of the $NH_3$ MO shown obliquely from the top. For each $N-H$ bond, the ellipsoidal surface of each $H_2$-type ellipsoidal MO transitions to a $N2p$ AO. The $N2p$ shell, the $N2s$ shell, the $N1s$ shell, and the nuclei (red, not to scale) are shown. (B) Off-center cut-away view showing the complete inner most $N1s$ shell, and moving radially, the cross section of the $N2s$ shell, the $N2p$ shell, and the $H_2$-type ellipsoidal MO that transitions to a $N2p$ AO for each $N-H$ bond. Bisector current not shown. (C)-(E) Color scale, side-on, top, and bottom translucent views of the charge-density of the $NH_3$ MO, respectively.



## ENERGIES OF $NH_3$

The energies of $NH_3$ given by the substitution of the semiprincipal axes ((Eqs. (13.375-13.377) and (13.379)) into the energy equations (Eqs. (13.67-13.73)) multiplied by three are:

$$V_e = 3\left(\frac{3}{4}\right)\frac{-2e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -115.28799\ eV \tag{13.386}$$

$$V_p = 3\frac{e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}} = 41.66718\ eV \tag{13.387}$$

$$T = 3\left(\frac{3}{4}\right)\frac{\hbar^2}{2m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = 42.77848\ eV \tag{13.388}$$

$$V_m = 3\left(\frac{3}{4}\right)\frac{-\hbar^2}{4m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -21.38924\ eV \tag{13.389}$$

$$E_T\left(NH_3\right) = -3\frac{e^2}{8\pi\varepsilon_0 c'}\left[\left(\frac{3}{2}-\frac{3}{8}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right] - 14.53414\ eV = -66.76571\ eV \tag{13.390}$$

where $E_T\left(NH_3\right)$ is given by Eq. (13.371) which is reiteratively matched to Eq. (13.372) within five-significant-figure round-off error.

## VIBRATION OF $NH_3$

The vibrational energy levels of $NH_3$ may be solved as three equivalent coupled harmonic oscillators by developing the Lagrangian, the differential equation of motion, and the eigenvalue solutions [2] wherein the spring constants are derived from the central forces as given in the Vibration of Hydrogen-Type Molecular Ions section and the Vibration of Hydrogen-Type Molecules section.

## THE DOPPLER ENERGY TERM OF $NH_3$

The radiation reaction force in the case of the vibration of $NH_3$ in the transition state corresponds to the Doppler energy, $E_D$, given by Eq. (11.181) and Eqs. (13.22) and (13.144) that is dependent on the motion of the electrons and the nuclei. The kinetic energy of the transient vibration is derived from the corresponding central forces. The equations of the radiation reaction force of ammonia are the same as those of the corresponding water and dihydrogen and dideuterium nitride radicals with the substitution of the ammonia parameters. Using Eqs. (11.136) and (13.207-13.209), the angular frequency of the reentrant oscillation in the transition state is

$$\omega = \sqrt{\frac{\left(\frac{3}{2}\right)\frac{e^2}{4\pi\varepsilon_0 b^3}}{m_e}} = 5.68887\ X\ 10^{16}\ rad/s \tag{13.391}$$

where $b$ is given by Eq. (13.379). The kinetic energy, $E_K$, is given by Planck's equation (Eq. (11.127)):

$$\overline{E}_K = \hbar\omega = \hbar 5.68887\ X\ 10^{16}\ rad/s = 37.44514\ eV \tag{13.392}$$

In Eq. (11.181), substitution of $E_T\left(H_2\right)$ (Eqs. (11.212) and (13.75)), the maximum total energy of each $H_2$-type MO acting independently due to the $D_{3h}$ symmetry point group, for $E_{h\nu}$, the mass of the electron, $m_e$, for $M$, and the kinetic energy given by Eq. (13.392) for $\overline{E}_K$ gives the Doppler energy of the electrons of each of the three bonds for the reentrant orbit:

$$\overline{E}_D \cong E_{h\nu}\sqrt{\frac{2\overline{E}_K}{Mc^2}} = -31.6353683\ eV\sqrt{\frac{2e\left(37.44514\ eV\right)}{m_e c^2}} = -0.38298\ eV \tag{13.393}$$

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency. The decrease in the energy of $NH_3$ due to the reentrant orbit in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei, $\overline{E}_{osc}$, is given by the sum of the corresponding energies, $\overline{E}_D$ given by Eq. (13.393) and $\overline{E}_{Kvib}$, the average kinetic energy of vibration which is 1/2 of the vibrational energy of $NH_3$. Using the experimental ${}^{14}NH_3$ vibrational energy of $E_{vib} = 3443.59\ cm^{-1} = 0.426954\ eV$ [36] gives:

$$\overline{E}'_{osc} = \overline{E}_D + \overline{E}_{Kvib} = \overline{E}_D + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \tag{13.394}$$

$$\bar{E}'_{osc} = -0.38298\ eV + \frac{1}{2}\left(0.426954\ eV\right) = -0.16950\ eV \tag{13.395}$$

per bond. The reentrant orbit for the binding of a hydrogen atom to a $NH_2$ radical involves three $N-H$ bonds. Since the vibration and reentrant oscillation is along three bonds, $\bar{E}_{osc}$ for $^{14}NH_3$, $\bar{E}_{osc}\left({}^{14}NH_3\right)$, is:

$$\bar{E}_{osc}\left({}^{14}NH_3\right) = 3\left(\bar{E}_D + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right) = 3\left(-0.38298\ eV + \frac{1}{2}\left(0.426954\ eV\right)\right) = -0.50850\ eV \tag{13.396}$$

Using Eq. (13.393), Eqs. (13.394-13.396), and the $^{14}ND_3$ experimental vibrational energy of $E_{vib} = 2563.96\ cm^{-1} = 0.317893\ eV$ [36], the corresponding $\bar{E}_{osc}\left({}^{14}ND_2\right)$ is:

$$\bar{E}_{osc}\left({}^{14}ND_3\right) = 3\left(-0.38298\ eV + \frac{1}{2}\left(0.317893\ eV\right)\right) = -0.67209\ eV \tag{13.397}$$

## TOTAL AND BOND ENERGIES OF $^{14}NH_3$ AND $^{14}ND_3$

$E_{T+osc}\left({}^{14}NH_3\right)$, the total energy of the $^{14}NH_3$ including the Doppler term, is given by the sum of $E_T\left(NH_3\right)$ (Eq. (13.373)) and $\bar{E}_{osc}\left({}^{14}NH_3\right)$ given Eqs. (13.391-13.396):

$$E_{T+osc}\left({}^{14}NH_3\right) = V_e + T + V_m + V_p + E\left(N2p\right) + \bar{E}_{osc}\left({}^{14}NH_3\right) = E_T\left(NH_3\right) + \bar{E}_{osc}\left({}^{14}NH_3\right) \tag{13.398}$$

$$\begin{aligned} E_{T+osc}\left({}^{14}NH_3\right) &= \left\{ \begin{array}{l} \left(3\dfrac{-e^2}{8\pi\varepsilon_0 c'}\left[\left(\dfrac{3}{2}-\dfrac{3}{8}\dfrac{a_0}{a}\right)\ln\dfrac{a+c'}{a-c'}-1\right]-14.53414\ eV\right) \\ -3\left(\left(31.63536831\ eV\right)\sqrt{\dfrac{2\hbar\sqrt{\dfrac{\frac{3}{2}\frac{e^2}{4\pi\varepsilon_0 b^3}}{m_e}}}{m_ec^2}}-\dfrac{1}{2}\hbar\sqrt{\dfrac{k}{\mu}}\right) \end{array} \right\} \\ &= -66.76616\ eV - 3\left(0.38298\ eV - \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right) \end{aligned} \tag{13.399}$$

From Eqs. (13.396) and (13.398-13.399), the total energy of $^{14}NH_2$ is:

$$\begin{aligned} E_{T+osc}\left({}^{14}NH_3\right) &= -66.76616\ eV + \bar{E}_{osc}\left({}^{14}NH_3\right) \\ &= -66.76616\ eV - 3\left(0.38298\ eV - \frac{1}{2}\left(0.426954\ eV\right)\right) \\ &= -67.27466\ eV \end{aligned} \tag{13.400}$$

where the experimental $^{14}NH_3$ vibrational energy was used for the $\hbar\sqrt{\frac{k}{\mu}}$ term. $E_{T+osc}\left({}^{14}ND_3\right)$, the total energy of $^{14}ND_3$ including the Doppler term is given by the sum of $E_T\left(ND_3\right) = E_T\left(NH_3\right)$ (Eq. (13.373)) and $\bar{E}_{osc}\left({}^{14}ND_3\right)$ given by Eq. (13.397):

$$\begin{aligned} E_{T+osc}\left({}^{14}ND_3\right) &= -66.76616\ eV + \bar{E}_{osc}\left({}^{14}ND_3\right) \\ &= -66.76616\ eV - 3\left(0.38298\ eV - \frac{1}{2}\left(0.317893\ eV\right)\right) \\ &= -67.43780\ eV \end{aligned} \tag{13.401}$$

where the experimental $^{14}ND_3$ vibrational energy was used for the $\hbar\sqrt{\frac{k}{\mu}}$ term. The corresponding bond dissociation energy, $E_D$, is given by the sum of the total energies of the corresponding dihydrogen nitride radical and hydrogen atom minus the total energy of ammonia, $E_{T+osc}\left({}^{14}NH_3\right)$.

Thus, $E_D$ of $^{14}NH_3$ is given by:

$$E_D\left({}^{14}NH_3\right) = E(H) + E({}^{14}NH_2) - E_{T+osc}\left({}^{14}NH_3\right) \tag{13.402}$$

where $E_T({}^{14}NH_2)$ is given by the of the sum of the experimental energies of $^{14}N$ (Eq. (13.251)), two $H$ (Eq. (13.154)), and the negative of the bond energies of $^{14}NH$ (Eq. (13.312)) and $^{14}NH_2$ (Eq. (13.354)):

$$E({}^{14}NH_2) = 2\left(-13.59844\ eV\right) - 14.53414\ eV - 3.42\ eV - 3.946\ eV = -49.09709\ eV \tag{13.403}$$

From Eqs. (13.154), (13.400), and (13.402-13.403), $E_D\left({}^{14}NH_2\right)$ is:

$$\begin{aligned} E_D\left({}^{14}NH_3\right) &= E(H) + E({}^{14}NH_2) - E_{T+osc}\left({}^{14}NH_3\right) \\ &= -13.59844\ eV - 49.09709\ eV - \left(-67.27466\ eV\right) = 4.57913\ eV \end{aligned} \tag{13.404}$$

The experimental ${}^{14}NH_3$ bond dissociation energy [37] is:

$$E_D({}^{14}NH_3) = 4.60155\ eV \tag{13.405}$$

Similarly, $E_D$ of ${}^{14}ND_3$ is given by:

$$E_D\left({}^{14}ND_3\right) = E(D) + E({}^{14}ND_2) - \left(E_{T+osc}\left({}^{14}ND_3\right)\right) \tag{13.406}$$

where $E_T({}^{14}ND_2)$ is given by the of the sum of the experimental energies of ${}^{14}N$ (Eq. (13.251)), two times the energy of $D$ (Eq. (13.155)), and the negative of the bond energies of ${}^{14}ND$ (Eq. (13.315)) and ${}^{14}ND_2$ (Eq. (13.358)):

$$E({}^{14}ND_2) = 2\left(-13.603\ eV\right) - 14.53414\ eV - 3.5134\ eV - 3.9362\ eV = -49.18981\ eV \tag{13.407}$$

From Eqs. (13.155), (13.401), and (13.406-13.407), $E_D\left({}^{14}ND_3\right)$ is:

$$E_D({}^{14}ND_3) = -13.603\ eV - 49.18981\ eV - \left(-67.43780\ eV\right) = 4.64499\ eV \tag{13.408}$$

The experimental ${}^{14}ND_3$ bond dissociation energy [37] is:

$$E_D({}^{14}ND_3) = 4.71252\ eV \tag{13.409}$$

## BOND ANGLE OF $NH_3$

Using, $2c'_{H-H}$ (Eq. (13.364)), the distance between the two $H$ atoms when the total energy of the corresponding MO is zero (Eq. (13.361)), and $2c'_{N-H}$, the internuclear distance of each $N-H$ bond (Eq. (13.377)), the corresponding bond angle can be determined from the law of cosines. Using Eq. (13.367), the bond angle $\theta$ between the $N-H$ bonds is:

$$\theta = \cos^{-1}\left(\frac{2\left(1.95921\right)^2 - \left(3.14643\right)^2}{2\left(1.95921\right)^2}\right) = \cos^{-1}\left(-0.28956\right) = 106.67° \tag{13.410}$$

The experimental angle between the $N-H$ bonds is [36]:

$$\theta = 106.67° \tag{13.411}$$

The $NH_3$ molecule has a pyramidal structure with the nitrogen atom along the z-axis at the apex and the hydrogen atoms at the base in the xy-plane. Since any two $N-H$ bonds form an isosceles triangle, the distance $d_{origin-H}$ from the origin to the nucleus of a hydrogen atom is given by:

$$d_{origin-H} = \frac{2c'_{H-H}}{2\sin 60°} \tag{13.412}$$

Substitution of Eq. (13.364) into Eq. (13.412) gives:

$$d_{origin-H} = 1.81659a_0 \tag{13.413}$$

The height along the z-axis of the pyramid from the origin to $N$ nucleus $d_{height}$ is given by:

$$d_{height} = \sqrt{\left(2c'_{N-H}\right)^2 - \left(d_{origin-H}\right)^2} \tag{13.414}$$

Substitution of Eqs. (13.377) and (13.413) into Eq. (13.414) gives:

$$d_{height} = 0.73383a_0 \tag{13.415}$$

The angle $\theta_v$ of each $N-H$ bond from the z-axis is given by:

$$\theta_v = \tan^{-1}\left(\frac{d_{origin-H}}{d_{height}}\right) \tag{13.416}$$

Substitution of Eqs. (13.413) and (13.415) into Eq. (13.416) gives:

$$\theta_v = 68.00° \tag{13.417}$$

The $NH_3$ MO shown in Figure 13.8 was rendered using these parameters.

The results of the determination of bond parameters of $NH_3$ and $ND_3$ are given in Table 13.1. The calculated results are based on first principles and given in closed-form, exact equations containing fundamental constants only. The agreement between the experimental and calculated results is excellent.

## HYDROGEN CARBIDE ($CH$)

The methane molecule can be solved by first considering the solution of the hydrogen carbide, dihydrogen carbide, and methyl radicals. The former is formed by the reaction of a hydrogen atom and a carbon atom:

$$H + C \rightarrow CH \tag{13.418}$$

The hydrogen carbide radicals, $CH$ and $CH_2$, methyl radical, $CH_3$, and methane, $CH_4$, can be solved using the same principles as those used to solve $OH$, $H_2O$, $NH$, $NH_2$, and $NH_3$ with the exception that the carbon $2s$ and $2p$ shells hybridize to form a single $2sp^3$ shell as an energy minimum.

## FORCE BALANCE OF $CH$

$CH$ comprises two spin-paired electrons in a chemical bond between the carbon atom and the hydrogen atom. The $CH$ radical molecular orbital (MO) is determined by considering properties of the binding atoms and the boundary constraints. The prolate spheroidal $H_2$ MO developed in the Nature of the Chemical Bond of Hydrogen-Type Molecules section satisfies the boundary constraints; thus, the $H$-atom electron forms a $H_2$-type ellipsoidal MO with one of the $C$-atom electrons. However, such a bond is not possible with the outer $C$ electrons in their ground state since the resulting $H_2$-type ellipsoidal MO would have a shorter internuclear distance than the radius of the carbon $2p$ shell, which is not energetically stable. Thus, when bonding the carbon $2s$ and $2p$ shells hybridize to form a single $2sp^3$ shell as an energy minimum.

The $C$ electron configuration given in the Six-Electron Atoms section is $1s^2 2s^2 2p^2$, and the orbital arrangement is:

$$\begin{array}{ccc} & \text{2p state} & \\ \underline{\uparrow} & \underline{\uparrow} & \underline{\quad} \\ 1 & 0 & -1 \end{array} \tag{13.419}$$

corresponding to the ground state ${}^3P_0$. The radius $r_6$ of the $2p$ shell given by Eq. (10.122) is:

$$r_6 = 1.20654a_0 \tag{13.420}$$

The energy of the carbon $2p$ shell is the negative of the ionization energy of the carbon atom given by Eq. (10.123). Experimentally, the energy is [12]

$$E(C, 2p\ shell) = -E(ionization;\ C) = -11.2603\ eV \tag{13.421}$$

The $C2s$ atomic orbital (AO) combines with the $C2p$ AOs to form a single $2sp^3$ hybridized orbital (HO) with the orbital arrangement:

$$\begin{array}{cccc} & \text{2sp}^3 \text{ state} & & \\ \underline{\uparrow} & \underline{\uparrow} & \underline{\uparrow} & \underline{\uparrow} \\ 0,0 & 1,-1 & 1,0 & 1,1 \end{array} \tag{13.422}$$

where the quantum numbers ($\ell, m_\ell$) are below each electron. The total energy of the state is given by the sum over the four electrons. The sum $E_T\left(C, 2sp^3\right)$ of calculated energies of $C$, $C^+$, $C^{2+}$, and $C^{3+}$ from Eqs. (10.123), (10.113-10.114), (10.68), and (10.48), respectively, is:

$$E_T\left(C, 2sp^3\right) = 64.3921\ eV + 48.3125\ eV + 24.2762\ eV + 11.27671\ eV = 148.25751\ eV \tag{13.423}$$

which agrees well with the sum of 148.02532 $eV$ from the experimental [6] values. The orbital-angular-momentum interactions cancel such that the energy of the $E_T\left(C, 2sp^3\right)$ is purely Coulombic. By considering that the central field decreases by an integer for each successive electron of the shell, the radius $r_{2sp^3}$ of the $C2sp^3$ shell may be calculated from the Coulombic energy using Eq. (10.102).

$$\begin{aligned} r_{2sp^3} &= \sum_{n=2}^{5} \frac{(Z-n)e^2}{8\pi\varepsilon_0 \left(e148.25751\ eV\right)} \\ &= \frac{10e^2}{8\pi\varepsilon_0 \left(e148.25751\ eV\right)} \\ &= 0.91771a_0 \end{aligned} \tag{13.424}$$

Using Eqs. (10.102) and (13.424), the Coulombic energy $E_{Coulomb}\left(C,2sp^3\right)$ of the outer electron of the $C2sp^3$ shell is:

$$\begin{aligned} E_{Coulomb}\left(C,2sp^3\right) &= \frac{-e^2}{8\pi\varepsilon_0 r_{2sp^3}} \\ &= \frac{-e^2}{8\pi\varepsilon_0 0.91771a_0} = -14.82575\ eV \end{aligned} \tag{13.425}$$

During hybridization, the spin-paired $2s$ electrons are promoted to the $C2sp^3$ shell as unpaired electrons. The energy for the promotion is the magnetic energy given by Eq. (13.152) at the initial radius of the $2s$ electrons. From Eq. (10.62) with $Z=6$, the radius $r_3$ of the $C2s$ shell is

$$r_3 = 0.84317a_0 \tag{13.426}$$

Using Eqs. (13.152) and (13.426), the unpairing energy is:

$$E(magnetic) = \frac{2\pi\mu_0 e^2\hbar^2}{m_e^2\left(r_3\right)^3} = \frac{8\pi\mu_0\mu_B^2}{\left(0.84317a_0\right)^3} = 0.19086\ eV \tag{13.427}$$

Using Eqs. (13.425) and (13.427), the energy $E\left(C,2sp^3\right)$ of the outer electron of the $C2sp^3$ shell is:

$$\begin{aligned} E\left(C,2sp^3\right) &= \frac{-e^2}{8\pi\varepsilon_0 r_{2sp^3}} + \frac{2\pi\mu_0 e^2\hbar^2}{m_e^2\left(r_3\right)^3} \\ &= -14.82575\ eV + 0.19086\ eV = -14.63489\ eV \end{aligned} \tag{13.428}$$

The nitrogen atom's $2p$-shell electron configuration given by Eq. (10.134) is the same as that of the $C2sp^3$ shell, and nitrogen's calculated energy of $14.61664\ eV$ given by Eq. (10.143) is a close match with $E\left(C,2sp^3\right)$. Thus, the binding should be very similar except that four bonds to hydrogen can occur with carbon.

The carbon $C2sp^3$ electron combines with the $H1s$ electron to form a molecular orbital. The proton of the $H$ atom and the nucleus of the $C$ atom are along the internuclear axis and serve as the foci. Due to symmetry, the other $C$ electrons are equivalent to point charges at the origin. (See Eqs. (19-38) of Appendix II.) Thus, the energies in the $CH$ MO involve only the $C2sp^3$ and $H1s$ electrons. The forces are determined by these energies.

As in the case of $H_2$, the MO is a prolate spheroid with the exception that the ellipsoidal MO surface cannot extend into the $C2sp^3$ HO for distances shorter than the radius of the $C2sp^3$ shell. Thus, the MO surface comprises a prolate spheroid at the $H$ proton that is continuous with the $C2sp^3$ shell at the $C$ atom whose nucleus serves as the other focus. The energy of the $H_2$-type ellipsoidal MO is matched to that of the $C2sp^3$ shell. As in the case with $OH$ and $NH$, the linear combination of the $H_2$-type ellipsoidal MO with the $C2sp^3$ HO must involve a 25% contribution from the $H_2$-type ellipsoidal MO to the $C2sp^3$ HO in order to match potential, kinetic, and orbital energy relationships. Thus, the $CH$ MO must comprise 75% of a $H_2$-type ellipsoidal MO and a $C2sp^3$ HO:

$$1\ C2sp^3 + 0.75\ H_2\ MO \rightarrow CH\ MO \tag{13.429}$$

The force balance of the $CH$ MO is determined by the boundary conditions that arise from the linear combination of orbitals according to Eq. (13.429) and the energy matching condition between the hydrogen and $C2sp^3$ HO components of the MO.

As in the case with $OH$ (Eq. (13.57)), the $H_2$-type ellipsoidal MO comprises 75% of the $CH$ MO; so, the electron charge density in Eq. (11.65) is given by $-0.75e$. The force constant $k'$ to determine the ellipsoidal parameter $c'$ in terms of the central force of the foci is given by Eq. (13.59). The distance from the origin to each focus $c'$ is given by Eq. (13.60). The internuclear distance is given by Eq. (13.61). The length of the semiminor axis of the prolate spheroidal $C-H$-bond MO $b=c$ is given by Eq. (13.62). The eccentricity, $e$, is given by Eq. (13.63). The solution of the semimajor axis $a$ then allows for the solution of the other axes of each prolate spheroid and eccentricity of the $CH$ MO. Since the $CH$ MO comprises a $H_2$-type-ellipsoidal MO that transitions to the $C2sp^3$ HO, the energy $E\left(C,2sp^3\right)$ in Eq. (13.428) adds to that of the $H_2$-type ellipsoidal MO to give the total energy of the $CH$ MO. From the energy equation and the relationship between the axes, the dimensions of the $CH$ MO are solved.

The energy components of $V_e$, $V_p$, $T$, and $V_m$ are those of $H_2$ (Eqs. (11.207-11.212)) except that they are corrected for electron hybridization. Hybridization gives rise to the $C2sp^3$ HO-shell Coulombic energy $E_{Coulomb}\left(C,2sp^3\right)$ given by Eq. (13.425). To meet the equipotential condition of the union of the $H_2$-type-ellipsoidal-MO and the $C2sp^3$ HO, the electron energies are normalized by the ratio of $14.82575\ eV$, the magnitude of $E_{Coulomb}\left(C,2sp^3\right)$ given by Eq. (13.425), and $13.605804\ eV$, the magnitude of the Coulombic energy between the electron and proton of $H$ given by Eq. (1.264). This normalizes the energies to match that of the Coulombic energy alone to meet the energy matching condition of the $CH$ MO under the influence of the proton and the $C$ nucleus. The hybridization energy factor $C_{C2sp^3HO}$ is

$$C_{C2sp^3HO} = \frac{\frac{e^2}{8\pi\varepsilon_0 a_0}}{\frac{e^2}{8\pi\varepsilon_0 r_{2sp^3}}} = \frac{\frac{e^2}{8\pi\varepsilon_0 a_0}}{\frac{e^2}{8\pi\varepsilon_0 0.91771 a_0}} = \frac{13.605804\ eV}{14.82575\ eV} = 0.91771 \tag{13.430}$$

The total energy $E_T(CH)$ of the $CH$ MO is given by the sum of the energies of the orbitals, the $H_2$-type ellipsoidal MO and the $C2sp^3$ HO, that form the hybridized $CH$ MO. $E_T(CH)$ follows from Eq. (13.74) for $OH$, but the energy of the $C2sp^3$ HO given by Eq. (13.428) is substituted for the energy of $O$ and the $H_2$-type-ellipsoidal-MO energies are those of $H_2$ (Eqs. (11.207-11.212)) multiplied by the electron hybridization factor rather than by the factor of $0.75$:

$$\begin{aligned} E_T(CH) &= E_T + E\left(C,2sp^3\right) \\ &= -\frac{e^2}{8\pi\varepsilon_0 c'}\left[(0.91771)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right] - 14.63489\ eV \end{aligned} \tag{13.431}$$

To match the boundary condition that the total energy of the entire the $H_2$-type ellipsoidal MO is given by Eqs. (11.212) and (13.75), $E_T(CH)$ given by Eq. (13.431) is set equal to Eq. (13.75).

$$E_T(CH) = -\frac{e^2}{8\pi\varepsilon_0 c'}\left[(0.91771)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right] - 14.63489\ eV = -31.63536831\ eV \tag{13.432}$$

From the energy relationship given by Eq. (13.432) and the relationship between the axes given by Eqs. (13.60-13.63), the dimensions of the $CH$ MO can be solved.

Substitution of Eq. (13.60) into Eq. (13.432) gives:

$$\frac{e^2}{8\pi\varepsilon_0\sqrt{\frac{2aa_0}{3}}}\left[(0.91771)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+\sqrt{\frac{2aa_0}{3}}}{a-\sqrt{\frac{2aa_0}{3}}}-1\right] = e17.00048 \tag{13.433}$$

The most convenient way to solve Eq. (13.433) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is:

$$a = 1.67465a_0 = 8.86186\ X\ 10^{-11}\ m \tag{13.434}$$

Substitution of Eq. (13.434) into Eq. (13.60) gives:

$$c' = 1.05661a_0 = 5.59136\ X\ 10^{-11}\ m \tag{13.435}$$

The internuclear distance given by multiplying Eq. (13.435) by two is:

$$2c' = 2.11323a_0 = 1.11827\ X\ 10^{-10}\ m \tag{13.436}$$

The experimental bond distance is [14]:

$$2c' = 1.1198\ X\ 10^{-10}\ m \tag{13.437}$$

Substitution of Eqs. (13.434-13.435) into Eq. (13.62) gives:

$$b = c = 1.29924a_0 = 6.87527\ X\ 10^{-11}\ m \tag{13.438}$$

Substitution of Eqs. (13.434-13.435) into Eq. (13.63) gives:

$$e = 0.63095 \tag{13.439}$$

The nucleus of the $H$ atom and the nucleus of the $C$ atom comprise the foci of the $H_2$-type ellipsoidal MO. The parameters of the point of intersection of the $H_2$-type ellipsoidal MO and the $C2sp^3$ HO are given by Eqs. (13.84-13.95) and (13.261-13.270). The polar intersection angle $\theta'$ is given by Eq. (13.261) where $r_n = r_{2sp^3} = 0.91771a_0$ is the radius of the $C2sp^3$ shell. Substitution of Eqs. (13.434-13.435) into Eq. (13.261) gives:

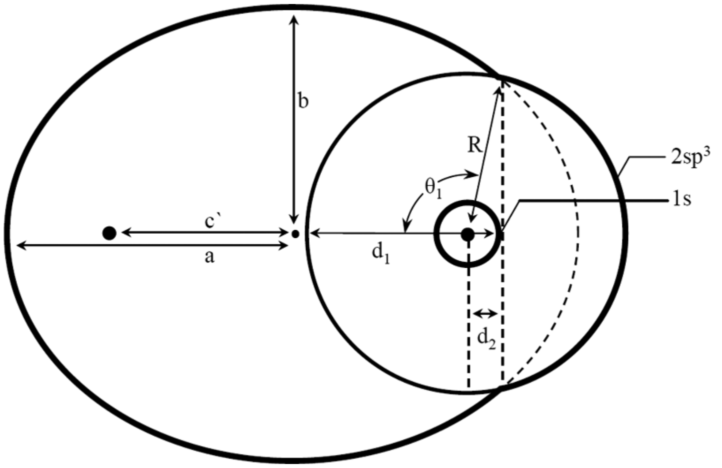
$$\theta' = 81.03° \tag{13.440}$$

Then, the angle $\theta_{C2sp^3HO}$ the radial vector of the $C2sp^3$ HO makes with the internuclear axis is:

$$\theta_{C2sp^3HO} = 180° - 81.03° = 98.97° \tag{13.441}$$

as shown in Figure 13.9.

Figure 13.9. The cross section of the $CH$ MO showing the axes, angles, and point of intersection of the $H_2$-type ellipsoidal MO with the $C2sp^3$ HO. The continuation of the $H_2$-type-ellipsoidal-MO basis element beyond the intersection point with the $C2sp^3$ shell is shown as dashed since it only serves to solve the energy match with the $C2sp^3$ shell and does not represent charge density. Similarly, the vertical dashed line only designates the parameters of the intersection point. The actual charge density is shown by the solid lines. Legend: $a$: semimajor axis, $b$: semiminor axis, $c'$: internuclear distance, $d_1 : d_{H_2MO}$, $\theta_1 : \theta_{C2sp^3HO}$, $d_2 : d_{C2sp^3HO}$, and $R : r_{2sp^3}$.



The Cartesian $\mathbf{i}$-coordinate of the interception point of the MO and the AO can be calculated using the MO ellipsoidal parameters by first calculating the parametric angle in Eq. (11.83) that matches Cartesian $\mathbf{j}$-coordinate components at the point of intersection. Thus, the matching elliptic parametric angle $\omega t = \theta_{H_2MO}$ satisfies the following relationship:

$$r_{2sp^3} \sin\theta_{C2sp^3HO} = 0.91771 a_0 \sin\theta_{C2sp^3HO} = b \sin\theta_{H_2MO} \tag{13.442}$$

such that

$$\begin{aligned} \theta_{H_2MO} &= \sin^{-1} \frac{0.91771 a_0 \sin\theta_{C2sp^3HO}}{b} \\ &= \sin^{-1} \frac{0.91771 a_0 \sin 98.97^\circ}{b} \end{aligned} \tag{13.443}$$

with the use of Eq. (13.441). Substitution of Eq. (13.438) into Eq. (13.443) gives:

$$\theta_{H_2MO} = 44.24^\circ \tag{13.444}$$

Then, the distance $d_{H_2MO}$ along the internuclear axis from the origin of $H_2$-type ellipsoidal MO to the point of intersection of the orbitals is given by

$$d_{H_2MO} = a \cos\theta_{H_2MO} \tag{13.445}$$

Substitution of Eqs. (13.434) and (13.444) into Eq. (13.445) gives:

$$d_{H_2MO} = 1.19968 a_0 = 6.34845 \ X \ 10^{-11} \ m \tag{13.446}$$

The distance $d_{C2sp^3HO}$ along the internuclear axis from the origin of the $C$ atom to the point of intersection of the orbitals is given by:

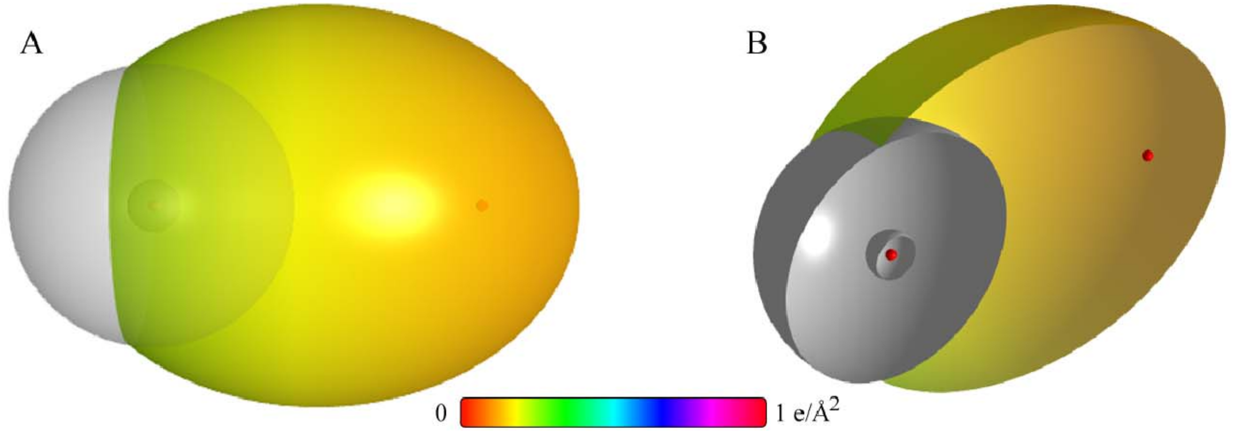
$$d_{C2sp^3HO} = d_{H_2MO} - c' \tag{13.447}$$

Substitution of Eqs. (13.435) and (13.446) into Eq. (13.447) gives:

$$d_{C2sp^3HO} = 0.14307 a_0 = 7.57090 \ X \ 10^{-12} \ m \tag{13.448}$$

As shown in Eq. (13.429), the uniform charge-density in the $C2sp^3$ HO is increased by a factor of 0.25 and the $H$-atom density is decreased by a factor of 0.25. Using the orbital composition of $CH$ (Eq. (13.429)), the radii of $C1s = 0.17113 a_0$ (Eq. (10.51)) and $C2sp^3 = 0.91771 a_0$ (Eq. (13.424)) shells, and the parameters of the $CH$ MO given by Eqs. (13.3-13.4), (13.434-13.436), and (13.438-13.448), the dimensional diagram and charge-density of the $CH$ MO comprising the linear combination of the $H_2$-type ellipsoidal MO and the $C2sp^3$ HO according to Eq. (13.429) are shown in Figures 13.9 and 13.10, respectively.

Figure 13.10. $CH$ MO comprising the superposition of the $H_2$-type ellipsoidal MO and the $C2sp^3$ HO with a relative charge-density of 0.75 to 1.25; otherwise, the $C2sp^3$ HO is unchanged. (A) Side-on, color scale, translucent view of the charge-density of the $CH$ MO. The ellipsoidal surface of the $H_2$-type ellipsoidal MO that transitions to the $C2sp^3$ HO, the $C2sp^3$ HO shell, $C1s$ shell, and the nuclei (red, not to scale) are shown. (B) Cut-away view showing the inner most $C1s$ shell, and moving radially, the $C2sp^3$ shell, and the $H_2$-type ellipsoidal MO that transitions to the $C2sp^3$ HO.



## ENERGIES OF $CH$

The energies of $CH$ are given by the substitution of the semiprincipal axes (Eqs. (13.434-13.435) and (13.438)) into the energy equations (Eq. (13.431) and Eqs. (11.207-11.211)) that are corrected for electron hybridization using Eq. (13.430).

$$V_e = (0.91771)\frac{-2e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -35.12015\ eV \tag{13.449}$$

$$V_p = \frac{e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}} = 12.87680\ eV \tag{13.450}$$

$$T = (0.91771)\frac{\hbar^2}{2m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = 10.48582\ eV \tag{13.451}$$

$$V_m = (0.91771)\frac{-\hbar^2}{4m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -5.24291\ eV \tag{13.452}$$

$$E_T(CH) = -\frac{e^2}{8\pi\varepsilon_0 c'}\left[(0.91771)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]-14.63489\ eV = -31.63533\ eV \tag{13.453}$$

where $E_T(CH)$ is given by Eq. (13.431) which is reiteratively matched to Eq. (13.75) within five-significant-figure round-off error.

## VIBRATION AND ROTATION OF $CH$

The vibrational energy of $CH$ may be solved in the same manner as that of $OH$ and $NH$ except that the force between the electrons and the foci given by Eq. (13.102) is doubled due to electron hybridization of the two shells of carbon after Eq. (11.141). From Eqs. (13.102-13.106) with the substitution of the $CH$ parameters, the angular frequency of the oscillation is

$$\omega = \sqrt{\frac{\frac{0.75e^2}{4\pi\varepsilon_0 b^3}-\frac{e^2}{8\pi\varepsilon_0(2c')^3}}{\mu}} = \sqrt{\frac{\frac{0.75e^2}{4\pi\varepsilon_0(1.29924a_0)^3}-\frac{e^2}{8\pi\varepsilon_0(2.11323a_0)^3}}{\frac{12}{13}m_p}} = 5.39828\ X\ 10^{14}\ rad/s \tag{13.454}$$

where $b$ is given by Eq. (13.438), $2c'$ is given by Eq. (13.436), and the reduced mass of $^{12}CH$ is given by:

$$\mu_{^{12}CH} = \frac{m_1 m_2}{m_1+m_2} = \frac{(1)(12)}{1+12}m_p \tag{13.455}$$

where $m_p$ is the proton mass. Thus, during bond formation, the perturbation of the orbit determined by an inverse-squared force results in simple harmonic oscillatory motion of the orbit, and the corresponding frequency, $\omega(0)$, for $^{12}CH$ given by Eqs. (11.136), (11.148), and (13.454) is:

$$\omega(0) = \sqrt{\frac{k(0)}{\mu}} = \sqrt{\frac{449.94\ Nm^{-1}}{\mu}} = 5.39828\ X\ 10^{14}\ radians/s \tag{13.456}$$

where the reduced nuclear mass of $^{12}CH$ is given by Eq. (13.455) and the spring constant, $k(0)$, given by Eqs. (11.136) and (13.454) is:

$$k(0) = 449.94\ Nm^{-1} \tag{13.457}$$

The $^{12}CH$ transition-state vibrational energy, $E_{vib}(0)$, given by Planck's equation (Eq. (11.127)) is:

$$E_{vib}(0) = \hbar\omega = \hbar 5.39828\ X\ 10^{14}\ rad/s = 0.35532\ eV = 2865.86\ cm^{-1} \tag{13.458}$$

$\omega_e$, from the experimental curve fit of the vibrational energies of $^{12}CH$ is [14] :

$$\omega_e = 2861.6\ cm^{-1} \tag{13.459}$$

Using Eqs. (13.112-13.118) with $E_{vib}(0)$ given by Eq. (13.458) and $D_0$ given by Eq. (13.488), the $^{12}CH$ $\upsilon = 1 \to \upsilon = 0$ vibrational energy, $E_{vib}(1)$ is:

$$E_{vib}(1) = 0.33879\ eV \qquad (2732.61\ cm^{-1}) \tag{13.460}$$

The experimental vibrational energy of $^{12}CH$ using $\omega_e$ and $\omega_e x_e$ [14] according to K&P [15] is:

$$E_{vib}(1) = 0.33885\ eV \qquad (2733\ cm^{-1}) \tag{13.461}$$

Using Eq. (13.113) with $E_{vib}(1)$ given by Eq. (13.460) and $D_0$ given by Eq. (13.488), the anharmonic perturbation term, $\omega_0 x_0$, of $^{12}CH$ is:

$$\omega_0 x_0 = 66.624\ cm^{-1} \tag{13.462}$$

The experimental anharmonic perturbation term, $\omega_0 x_0$, of $^{12}CH$ [14] is:

$$\omega_0 x_0 = 64.3\ cm^{-1} \tag{13.463}$$

The vibrational energies of successive states are given by Eqs. (13.458), (13.112), and (13.462).
Using $b$ given by Eq. (13.438), $2c'$ given by Eq. (13.436), $D_0$ given by Eq. (13.490), and the reduced nuclear mass of $^{12}CD$ given by:

$$\mu_{^{12}CD} = \frac{m_1 m_2}{m_1 + m_2} = \frac{(2)(12)}{2+12} m_p \tag{13.464}$$

where $m_p$ is the proton mass, the corresponding parameters for deuterium carbide $^{12}CD$ (Eqs. (13.102-13.121)) are:

$$\omega(0) = \sqrt{\frac{k(0)}{\mu}} = \sqrt{\frac{449.94\ Nm^{-1}}{\mu}} = 3.96126\ X\ 10^{14}\ radians/s \tag{13.465}$$

$$k(0) = 449.94\ Nm^{-1} \tag{13.466}$$

$$E_{vib}(0) = \hbar\omega = \hbar 3.96126\ X\ 10^{14}\ rad/s = 0.26074\ eV = 2102.97\ cm^{-1} \tag{13.467}$$

$$E_{vib}(1) = 0.25173\ eV \qquad (2030.30\ cm^{-1}) \tag{13.468}$$

$$\omega_0 x_0 = 36.335\ cm^{-1} \tag{13.469}$$

$\omega_e$, from the experimental curve fit of the vibrational energies of $^{12}CD$ is [14] :

$$\omega_e = 2101.0\ cm^{-1} \tag{13.470}$$

The experimental vibrational energy of $^{12}CD$ using $\omega_e$ and $\omega_e x_e$ [14] according to K&P [15] is:

$$E_{vib}(1) = 0.25189\ eV \qquad (2031.6\ cm^{-1}) \tag{13.471}$$

and the experimental anharmonic perturbation term, $\omega_0 x_0$, of $^{12}CD$ is [14] :

$$\omega_0 x_0 = 34.7\ cm^{-1} \tag{13.472}$$

which match the predictions given by Eqs. (13.467), (13.468) and (13.469), respectively.

Using Eqs. (13.133-13.134) and the internuclear distance, $r = 2c'$, and reduced mass of $^{12}CH$ given by Eqs. (13.436) and (13.455), respectively, the corresponding $B_e$ is:

$$B_e = 14.498\ cm^{-1} \tag{13.473}$$

The experimental $B_e$ rotational parameter of $^{12}CH$ is [14]:

$$B_e = 14.457\ cm^{-1} \tag{13.474}$$

Using the internuclear distance, $r = 2c'$, and reduced mass of $^{12}CD$ given by Eqs. (13.436) and (13.464), respectively, the corresponding $B_e$ is:

$$B_e = 7.807\ cm^{-1} \tag{13.475}$$

The experimental $B_e$ rotational parameter of $^{12}CD$ is [14]:

$$B_e = 7.808\ cm^{-1} \tag{13.476}$$

## THE DOPPLER ENERGY TERMS OF $^{12}CH$ AND $^{12}CD$

The equations of the radiation reaction force of hydrogen and deuterium carbide are the same as those of the corresponding hydroxyl and hydrogen nitride radicals with the substitution of the hydrogen and deuterium carbide parameters. Using Eqs. (11.136) and (13.140-13.142), the angular frequency of the reentrant oscillation in the transition state is

$$\omega = \sqrt{\frac{\frac{0.75e^2}{4\pi\varepsilon_0 b^3}}{m_e}} = 2.41759\ X\ 10^{16}\ rad/s \tag{13.477}$$

where $b$ is given by Eq. (13.438). The kinetic energy, $E_K$, is given by Planck's equation (Eq. (11.127)):

$$\bar{E}_K = \hbar\omega = \hbar 2.41759\ X\ 10^{16}\ rad/s = 15.91299\ eV \tag{13.478}$$

In Eq. (11.181), substitution of the total energy of $CH$, $E_T(CH)$, (Eq. (13.432)) for $E_{h\nu}$, the mass of the electron, $m_e$, for $M$, and the kinetic energy given by Eq. (13.478) for $\bar{E}_K$ gives the Doppler energy of the electrons for the reentrant orbit:

$$\bar{E}_D \cong E_{h\nu}\sqrt{\frac{2\bar{E}_K}{Mc^2}} = -31.63537\ eV\sqrt{\frac{2e(15.91299\ eV)}{m_e c^2}} = -0.24966\ eV \tag{13.479}$$

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency. The decrease in the energy of $CH$ due to the reentrant orbit in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei, $\bar{E}_{osc}$, is given by the sum of the corresponding energies, $\bar{E}_D$ given by Eq. (13.479) and $\bar{E}_{Kvib}$, the average kinetic energy of vibration which is 1/2 of the vibrational energy of $CH$. The experimental $^{12}CH$ $\omega_e$ is $2861.6\ cm^{-1}$ $(0.35480\ eV)$ [14] which matches the predicted $\omega_e$ of $2865.86\ cm^{-1}$ $(0.35532\ eV)$ given by Eq. (13.458). Using the predicted $\omega_e$ for $\bar{E}_{Kvib}$ of the transition state, $\bar{E}_{osc}\left(^{12}CH\right)$ is:

$$\bar{E}_{osc}\left(^{12}CH\right) = \bar{E}_D + \bar{E}_{Kvib} = \bar{E}_D + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \tag{13.480}$$

$$\bar{E}_{osc}\left(^{12}CH\right) = -0.24966\ eV + \frac{1}{2}(0.35532\ eV) = -0.07200\ eV \tag{13.481}$$

The experimental $^{12}CD$ $\omega_e$ is $2101.0\ cm^{-1}$ $(0.26049\ eV)$ [14] which matches the predicted $\omega_e$ of $2102.97\ cm^{-1}$ $(0.26074\ eV)$ given by Eq. (13.467). Using Eq. (13.479) and the predicted $\omega_e$ for $\bar{E}_{Kvib}$ of the transition state, $\bar{E}_{osc}\left(^{12}CD\right)$ is:

$$\bar{E}_{osc}\left(^{12}CD\right) = -0.24966\ eV + \frac{1}{2}(0.26074\ eV) = -0.11929\ eV \tag{13.482}$$

## TOTAL AND BOND ENERGIES OF $^{12}CH$ AND $^{12}CD$

$E_{T+osc}\left(^{12}CH\right)$, the total energy of the $^{12}CH$ radical including the Doppler term, is given by the sum of $E_T(CH)$ (Eq. (13.432)) and $\bar{E}_{osc}\left(^{12}CH\right)$ given by Eq. (13.481):

$$E_{T+osc}\left(^{12}CH\right) = V_e + T + V_m + V_p + E\left(C, 2sp^3\right) + \bar{E}_{osc}\left(^{12}CH\right) = E_T(CH) + \bar{E}_{osc}\left(^{12}CH\right) \tag{13.483}$$

$$\begin{aligned} E_{T+osc}\left(^{12}CH\right) &= \left\{ \begin{array}{l} \left( \frac{-e^2}{8\pi\varepsilon_0 c'} \left[ (0.91771)\left(2 - \frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'} - 1 \right] - 14.63489\ eV \right) \\ \left( 1 + \sqrt{\frac{2\hbar\sqrt{\frac{\frac{3}{4}\frac{e^2}{4\pi\varepsilon_0 b^3}}{m_e}}}{m_e c^2}} \right) + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \end{array} \right\} \\ &= -31.63537\ eV - 0.24966\ eV + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \end{aligned} \tag{13.484}$$

From Eqs. (13.480-13.481) and (13.483-13.484), the total energy of $^{12}CH$ is:

$$\begin{aligned} E_{T+osc}\left({}^{12}CH\right) &= -31.63537\ eV + \bar{E}_{osc}\left({}^{12}CH\right) \\ &= -31.63537\ eV - 0.24966\ eV + \frac{1}{2}\left(0.35532\ eV\right) \\ &= -31.70737\ eV \end{aligned} \tag{13.485}$$

where the predicted $\omega_e$ (Eq. (13.458)) was used for the $\hbar\sqrt{\frac{k}{\mu}}$ term. $E_{T+osc}\left({}^{12}CD\right)$, the total energy of $^{12}CD$ including the Doppler term, is given by the sum of $E_T\left(CD\right) = E_T\left(CH\right)$ (Eq. (13.432)) and $\bar{E}_{osc}\left({}^{12}CD\right)$ given by Eq. (13.482).

$$\begin{aligned} E_{T+osc}\left({}^{12}CD\right) &= -31.63537\ eV + \bar{E}_{osc}\left({}^{12}CD\right) \\ &= -31.63537\ eV - 0.24966\ eV + \frac{1}{2}\left(0.26074\ eV\right) \\ &= -31.75462\ eV \end{aligned} \tag{13.486}$$

where the predicted $\omega_e$ (Eq. (13.467)) was used for the $\hbar\sqrt{\frac{k}{\mu}}$ term.

The $CH$ bond dissociation energy, $E_D\left({}^{12}CH\right)$, is given by the sum of the total energies of the $C2sp^3$ HO and the hydrogen atom minus $E_{T+osc}\left({}^{12}CH\right)$[3]:

$$E_D\left({}^{12}CH\right) = E\left(C, 2sp^3\right) + E(H) - E_{T+osc}\left({}^{12}CH\right) \tag{13.487}$$

$E\left(C, 2sp^3\right)$ is given by Eq. (13.428), and $E_D\left(H\right)$ is given by Eq. (13.154). Thus, the $^{12}CH$ bond dissociation energy, $E_D\left({}^{12}CH\right)$, given by Eqs. (13.154), (13.428), (13.485), and (13.487) is:

$$\begin{aligned} E_D\left({}^{12}CH\right) &= -\left(14.63489\ eV + 13.59844\ eV\right) - E_{T+osc}\left(CH\right) \\ &= -28.23333\ eV - \left(-31.70737\ eV\right) \\ &= 3.47404\ eV \end{aligned} \tag{13.488}$$

The experimental $^{12}CH$ bond dissociation energy is [14]:

$$E_D\left({}^{12}CH\right) = 3.47\ eV \tag{13.489}$$

which is a close match to that of $NH$ as predicted based on the match between the $N$ and $C2sp^3$ HO energies and electron configurations.

The $^{12}CD$ bond dissociation energy, $E_D\left({}^{12}CD\right)$, is given by the sum of the total energies of the $C2sp^3$ HO and the deuterium atom minus $E_{T+osc}\left(CD\right)$:

$$E_D\left({}^{12}CD\right) = E\left(C, 2sp^3\right) + E(D) - E_{T+osc}\left({}^{12}CD\right) \tag{13.490}$$

$E\left(C, 2sp^3\right)$ is given by Eq. (13.428), and $E_D\left(D\right)$ is given by Eq. (13.155). Thus, the $^{12}CD$ bond dissociation energy, $E_D\left({}^{12}CD\right)$, given by Eqs. (13.155), (13.428), (13.486), and (13.490) is:

$$\begin{aligned} E_D\left({}^{12}CD\right) &= -\left(14.63489\ eV + 13.603\ eV\right) - E_{T+osc}\left({}^{12}CD\right) \\ &= -28.23789\ eV - \left(-31.75462\ eV\right) \\ &= 3.51673\ eV \end{aligned} \tag{13.491}$$

The experimental $^{12}CD$ bond dissociation energy is [14]:

$$E_D\left({}^{12}CD\right) = 3.52\ eV \tag{13.492}$$

The results of the determination of bond parameters of $CH$ and $CD$ are given in Table 13.1. The calculated results are based on first principles and given in closed-form, exact equations containing fundamental constants only. The agreement between the experimental and calculated results is excellent.

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[3] The hybridization energy is the difference between $E\left(C, 2p\ shell\right)$ given by Eq. (13.421) and $E\left(C, 2sp^3\right)$ given by Eq. (13.428). Since this term adds to $E\left(C, 2p\ shell\right)$ to give the total energy from which $E_{T+osc}\left({}^{12}CH\right)$ is subtracted to give $E_D\left({}^{12}CH\right)$, it is more convenient to simply use $E\left(C, 2sp^3\right)$ directly in Eq. (13.487).

## DIHYDROGEN CARBIDE ($CH_2$)

The dihydrogen carbide radical $CH_2$ is formed by the reaction of a hydrogen atom with a hydrogen carbide radical:

$$CH + H \rightarrow CH_2 \tag{13.493}$$

$CH_2$ can be solved using the same principles as those used to solve $H_2O$ and $NH_2$ with the exception that the carbon $2s$ and $2p$ shells hybridize to form a single $2sp^3$ shell as an energy minimum. Two diatomic molecular orbitals (MOs) developed in the Nature of the Chemical Bond of Hydrogen-Type Molecules and Molecular Ions section serve as basis functions in a linear combination with two carbon $2sp^3$ hybridized orbitals (HOs) to form the MO of $CH_2$. The solution is very similar to that of $CH$ except that there are two $CH$ bonds in $CH_2$.

## FORCE BALANCE OF $CH_2$

$CH_2$ comprises two chemical bonds between carbon and hydrogen atoms. Each $C-H$ bond comprises two spin-paired electrons with one from an initially unpaired electron of the carbon atom and the other from the hydrogen atom. Each $H$-atom electron forms a $H_2$-type ellipsoidal MO with an unpaired $C$-atom electrons. However, such a bond is not possible with the outer two $C$ electrons in their ground state since the resulting $H_2$-type ellipsoidal MO would have a shorter internuclear distance than the radius of the carbon $2p$ shell, which is not energetically stable. Thus, when bonding the carbon $2s$ and $2p$ shells hybridize to form a single $2sp^3$ shell as an energy minimum. The electron configuration and the energy, $E\left(C,2sp^3\right)$, of the $C2sp^3$ shell is given by Eqs. (13.422), and (13.428), respectively.

For each $C-H$ bond, a $C2sp^3$ electron combines with the $H1s$ electron to form a molecular orbital. The proton of the $H$ atom and the nucleus of the $C$ atom are along each internuclear axis and serve as the foci. As in the case of $H_2$, each of the two $C-H$-bond MOs is a prolate spheroid with the exception that the ellipsoidal MO surface cannot extend into the $C2sp^3$ HO for distances shorter than the radius of the $C2sp^3$ shell since it is energetically unfavorable. Thus, each MO surface comprises a prolate spheroid at the $H$ proton that is continuous with the $C2sp^3$ shell at the $C$ atom whose nucleus serves as the other focus. The radius and the energy of the $C2sp^3$ shell are unchanged with bond formation. The central paramagnetic force due to spin of each $C-H$ bond is provided by the spin-pairing force of the $CH_2$ MO that has the symmetry of an $s$ orbital that superimposes with the $C2sp^3$ orbitals such that the corresponding angular momenta are unchanged.

The energies in the $CH_2$ MO involve only each $C2sp^3$ and each $H1s$ electron with the formation of each $C-H$ bond. The sum of the energies of the $H_2$-type ellipsoidal MOs is matched to that of the $C2sp^3$ shell. As in the cases of $OH$, $H_2O$, $NH$, $NH_2$, $NH_3$, and $CH$ the linear combination of each $H_2$-type ellipsoidal MO with the $C2sp^3$ HO must involve a 25% contribution from the $H_2$-type ellipsoidal MO to the $C2sp^3$ HO in order to match potential, kinetic, and orbital energy relationships. Thus, the $CH_2$ MO must comprise two $C-H$ bonds with each comprising 75% of a $H_2$-type ellipsoidal MO and a $C2sp^3$ HO:

$$\left[1\ C2sp^3 + 0.75\ H_2\ MO\right] + \left[1\ C2sp^3 + 0.75\ H_2\ MO\right] \rightarrow CH_2\ MO \tag{13.494}$$

The force balance of the $CH_2$ MO is determined by the boundary conditions that arise from the linear combination of orbitals according to Eq. (13.494) and the energy matching condition between the hydrogen and $C2sp^3$ HO components of the MO.

The force constant $k'$ to determine the ellipsoidal parameter $c'$ of the each $H_2$-type-ellipsoidal-MO component of the $CH_2$ MO in terms of the central force of the foci is given by Eq. (13.59). The distance from the origin of each $C-H$-bond MO to each focus $c'$ is given by Eq. (13.60). The internuclear distance is given by Eq. (13.61). The length of the semiminor axis of the prolate spheroidal $C-H$-bond MO $b=c$ is given by Eq. (13.62). The eccentricity, $e$, is given by Eq. (13.63). The solution of the semimajor axis $a$ then allows for the solution of the other axes of each prolate spheroid and eccentricity of each $C-H$-bond MO. Since each of the two prolate spheroidal $C-H$-bond MOs comprises a $H_2$-type-ellipsoidal MO that transitions to the $C2sp^3$ HO, the energy $E\left(C,2sp^3\right)$ in Eq. (13.428) adds to that of the two corresponding $H_2$-type ellipsoidal MOs to give the total energy of the $CH_2$ MO. From the energy equation and the relationship between the axes, the dimensions of the $CH_2$ MO are solved.

The energy components of $V_e$, $V_p$, $T$, and $V_m$ are twice those of $CH$ corresponding to the two $C-H$ bonds. Since each prolate spheroidal $H_2$-type MO transitions to the $C2sp^3$ HO and the energy of the $C2sp^3$ shell must remain constant and equal to the $E\left(C,2sp^3\right)$ given by Eq. (13.428), the total energy $E_T\left(CH_2\right)$ of the $CH_2$ MO is given by the sum of the energies of the orbitals corresponding to the composition of the linear combination of the $C2sp^3$ HO and the two $H_2$-type ellipsoidal MOs that forms the $CH_2$ MO as given by Eq. (13.494). Using Eq. (13.431), $E_T(CH_2)$ is given by:

$$E_T(CH_2) = E_T + E(C,2sp^3) = -\frac{e^2}{4\pi\varepsilon_0 c'}\left[(0.91771)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]-14.63489\ eV \tag{13.495}$$

The two hydrogen atoms and the hybridized carbon atom can achieve an energy minimum as a linear combination of two $H_2$-type ellipsoidal MOs each having the proton and the carbon nucleus as the foci. Hybridization gives rise to the $C2sp^3$ HO-shell Coulombic energy $E_{Coulomb}(C,2sp^3)$ given by Eq. (13.425). To meet the equipotential condition of the union of the $H_2$-type-ellipsoidal-MO and the $C2sp^3$ HO, the electron energies in Eq. (13.495) were normalized by the ratio of $14.82575\ eV$, the magnitude of $E_{Coulomb}(C,2sp^3)$ given by Eq. (13.425), and $13.605804\ eV$, the magnitude of the Coulombic energy between the electron and proton of $H$ given by Eq. (1.264). The factor given by Eq. (13.430) normalized the energies to match that of the Coulombic energy alone to meet the energy matching condition of each $C-H$-bond MO under the influence of the proton and the $C$ nucleus. Each $C-H$-bond MO comprises the same $C2sp^3$ shell having its energy normalized to that of the Coulombic energy between the electron and a charge of $+e$ at the carbon focus of the $CH_2$ MO. Thus, the energy of the $CH_2$ MO is also given by the sum of that of the two $H_2$-type ellipsoidal MOs given by Eq. (11.212) minus the Coulombic energy, $E_{Coulomb}(H) = -13.605804\ eV$, of the redundant $+e$ of the linear combination:

$$\begin{aligned} E_T(2H_2 - H) &= -\frac{e^2}{4\pi\varepsilon_0 a_0}\left[\left(2\sqrt{2}-\sqrt{2}+\frac{\sqrt{2}}{2}\right)\ln\frac{\sqrt{2}+1}{\sqrt{2}-1}-\sqrt{2}\right]-E_{Coulomb}(H) \\ &= 2(-31.63536831\ eV)-(-13.605804\ eV) \\ &= -49.66493\ eV \end{aligned} \tag{13.496}$$

$E_T(CH_2)$ given by Eq. (13.495) is set equal to two times the energy of the $H_2$-type ellipsoidal MO minus the Coulombic energy of $H$ given by Eq. (13.496):

$$\begin{aligned} E_T(CH_2) &= -\frac{e^2}{4\pi\varepsilon_0 c'}\left[(0.91771)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]-14.63489\ eV \\ &= -49.66493\ eV \end{aligned} \tag{13.497}$$

From the energy relationship given by Eq. (13.497) and the relationship between the axes given by Eqs. (13.60-13.63), the dimensions of the $CH_2$ MO can be solved.

Substitution of Eq. (13.60) into Eq. (13.497) gives:

$$\frac{e^2}{4\pi\varepsilon_0\sqrt{\frac{2aa_0}{3}}}\left[(0.91771)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+\sqrt{\frac{2aa_0}{3}}}{a-\sqrt{\frac{2aa_0}{3}}}-1\right] = e35.03004 \tag{13.498}$$

The most convenient way to solve Eq. (13.498) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is

$$a = 1.64010a_0 = 8.67903\ X\ 10^{-11}\ m \tag{13.499}$$

Substitution of Eq. (13.499) into Eq. (13.60) gives:

$$c' = 1.04566a_0 = 5.53338\ X\ 10^{-11}\ m \tag{13.500}$$

The internuclear distance given by multiplying Eq. (13.500) by two is:

$$2c' = 2.09132a_0 = 1.10668\ X\ 10^{-10}\ m \tag{13.501}$$

The experimental bond distance is [38]:

$$2c' = 1.111\ X\ 10^{-10}\ m \tag{13.502}$$

Substitution of Eqs. (13.499-13.500) into Eq. (13.62) gives:

$$b = c = 1.26354a_0 = 6.68635\ X\ 10^{-11}\ m \tag{13.503}$$

Substitution of Eqs. (13.499-13.500) into Eq. (13.63) gives:

$$e = 0.63756 \tag{13.504}$$

The nucleus of the $H$ atom and the nucleus of the $C$ atom comprise the foci of each $H_2$-type ellipsoidal MO. The parameters of the point of intersection of each $H_2$-type ellipsoidal MO and the $C2sp^3$ HO are given by Eqs. (13.84-13.95), (13.261-

13.270), and (13.440-13.448). The polar intersection angle $\theta'$ is given by Eq. (13.261) where $r_n = r_{2sp^3} = 0.91771a_0$ is the radius of the $C2sp^3$ shell. Substitution of Eqs. (13.499-13.500) into Eq. (13.261) gives:

$$\theta' = 84.54° \tag{13.505}$$

Then, the angle $\theta_{C2sp^3HO}$ the radial vector of the $C2sp^3$ HO makes with the internuclear axis is:

$$\theta_{C2sp^3HO} = 180° - 84.54° = 95.46° \tag{13.506}$$

as shown in Figure 13.9. The parametric angle $\theta_{H_2MO}$ given by Eqs. (13.442-13.443), (13.503), and (13.506) is:

$$\theta_{H_2MO} = 46.30° \tag{13.507}$$

Then, the distance $d_{H_2MO}$ along the internuclear axis from the origin of $H_2$-type ellipsoidal MO to the point of intersection of the orbitals given by Eqs. (13.445), (13.499), and (13.507) is:

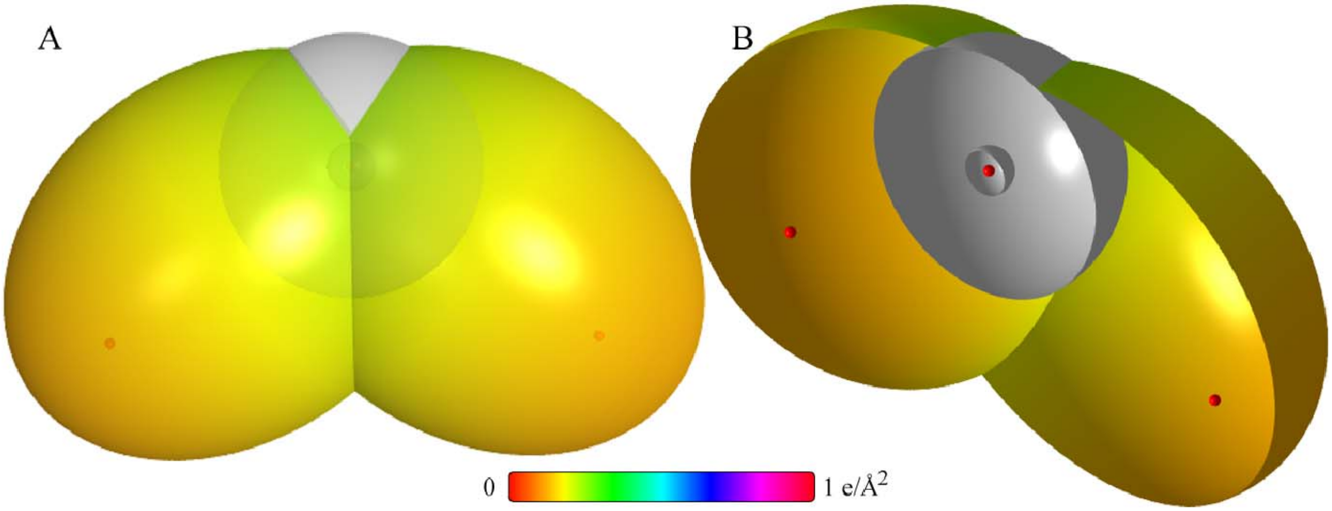
$$\begin{aligned} d_{H_2MO} &= 1.13305a_0 \\ &= 5.99585\ X\ 10^{-11}\ m \end{aligned} \tag{13.508}$$

The distance $d_{C2sp^3HO}$ along the internuclear axis from the origin of the $C$ atom to the point of intersection of the orbitals given by Eqs. (13.447), (13.500), and (13.508) is:

$$\begin{aligned} d_{C2sp^3HO} &= 0.08739a_0 \\ &= 4.62472\ X\ 10^{-12}\ m \end{aligned} \tag{13.509}$$

As shown in Eq. (13.494), the uniform charge-density in the $C2sp^3$ HO is increased by a factor of 0.25 and the $H$-atom density is decreased by a factor of 0.25 for by each $C-H$ bond. Using the orbital composition of $CH_2$ (Eq. (13.494)), the radii of $C1s = 0.17113a_0$ (Eq. (10.51)) and $C2sp^3 = 0.91771a_0$ (Eq. (13.424)) shells, and the parameters of the $CH_2$ MO given by Eqs. (13.3-13.4), (13.499-13.501), and (13.503-13.509), the charge-density of the $CH_2$ MO comprising the linear combination of two $C-H$-bond MOs is shown in Figure 13.11. Each $C-H$-bond MO comprises a $H_2$-type ellipsoidal MO and a $C2sp^3$ HO having the dimensional diagram shown in Figure 13.9.

Figure 13.11. $CH_2$ MO comprising the linear combination of two $C-H$-bond MOs. Each $C-H$-bond MO comprises the superposition of a $H_2$-type ellipsoidal MO and a $C2sp^3$ HO with a relative charge-density of 0.75 to 1.25; otherwise, the $C2sp^3$ HO shell is unchanged. (A) Color scale, translucent view of the charge-density of the $CH_2$ MO from the top. For each $C-H$ bond, the ellipsoidal surface of the $H_2$-type ellipsoidal MO that transitions to the $C2sp^3$ HO, the $C2sp^3$ HO shell, $C1s$ shell, and the nuclei (red, not to scale) are shown. (B) Cut-away view showing the inner most $C1s$ shell, and moving radially, the $C2sp^3$ shell, and the $H_2$-type ellipsoidal MO that transitions to the $C2sp^3$ HO for each $C-H$ bond. Bisector current not shown.



## ENERGIES OF $CH_2$

The energies of $CH_2$ are two times those of $CH$ and are given by the substitution of the semiprincipal axes (Eqs. (13.499-13.500) and (13.503)) into the energy equations Eq. (13.495) and (Eqs. (13.449-13.452)) that are multiplied by two:

$$V_e = (0.91771)\frac{-2e^2}{4\pi\varepsilon_0\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -72.03287\ eV \tag{13.510}$$

$$V_p = \frac{e^2}{4\pi\varepsilon_0\sqrt{a^2-b^2}} = 26.02344\ eV \tag{13.511}$$

$$T = (0.91771)\frac{\hbar^2}{m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = 21.95990\ eV \tag{13.512}$$

$$V_m = (0.91771)\frac{-\hbar^2}{2m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -10.97995\ eV \tag{13.513}$$

$$E_T(CH_2) = -\frac{e^2}{4\pi\varepsilon_0 c'}\left[(0.91771)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]-14.63489\ eV = -49.66437\ eV \tag{13.514}$$

where $E_T(CH_2)$ is given by Eq. (13.495) which is reiteratively matched to Eq. (13.496) within five-significant-figure round-off error.

## VIBRATION OF $CH_2$

The vibrational energy levels of $CH_2$ may be solved as two equivalent coupled harmonic oscillators by developing the Lagrangian, the differential equation of motion, and the eigenvalue solutions [2] wherein the spring constants are derived from the central forces as given in the Vibration of Hydrogen-Type Molecular Ions section and the Vibration of Hydrogen-Type Molecules section.

## THE DOPPLER ENERGY TERMS OF $^{12}CH_2$

The reentrant oscillation of hybridized orbitals in the transition state is not coupled. Therefore, the equations of the radiation reaction force of dihydrogen and dideuterium carbide are the same as those of the corresponding hydrogen carbide radicals with the substitution of the dihydrogen and dideuterium carbide parameters. Using Eqs. (11.136) and (13.140-13.142), the angular frequency of the reentrant oscillation in the transition state is

$$\omega = \sqrt{\frac{\frac{0.75e^2}{4\pi\varepsilon_0 b^3}}{m_e}} = 2.52077\ X\ 10^{16}\ rad/s \tag{13.515}$$

where $b$ is given by Eq. (13.503). The kinetic energy, $E_K$, is given by Planck's equation (Eq. (11.127)):

$$\bar{E}_K = \hbar\omega = \hbar 2.52077\ X\ 10^{16}\ rad/s = 16.59214\ eV \tag{13.516}$$

In Eq. (11.181), substitution of $E_T(H_2)$ (Eqs. (11.212) and (13.75)), the maximum total energy of each $H_2$-type MO, for $E_{h\nu}$, the mass of the electron, $m_e$, for $M$, and the kinetic energy given by Eq. (13.516) for $\bar{E}_K$ gives the Doppler energy of the electrons of each of the two bonds for the reentrant orbit:

$$\bar{E}_D \cong E_{h\nu}\sqrt{\frac{2\bar{E}_K}{Mc^2}} = -31.63537\ eV\sqrt{\frac{2e(16.59214\ eV)}{m_e c^2}} = -0.25493\ eV \tag{13.517}$$

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency. The decrease in the energy of $CH_2$ due to the reentrant orbit of each bond in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei, $\bar{E}_{osc}$, is given by the sum of the corresponding energies, $\bar{E}_D$ given by Eq. (13.517) and $\bar{E}_{Kvib}$, the average kinetic energy of vibration which is 1/2 of the vibrational energy of each $C-H$ bond. Using $\omega_e$ given by Eq. (13.458) for $\bar{E}_{Kvib}$ of the transition state having two independent bonds, $\bar{E}'_{osc}(^{12}CH_2)$ per bond is:

$$\bar{E}'_{osc}(^{12}CH_2) = \bar{E}_D + \bar{E}_{Kvib} = \bar{E}_D + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \tag{13.518}$$

$$\bar{E}'_{osc}(^{12}CH_2) = -0.25493\ eV + \frac{1}{2}(0.35532\ eV) = -0.07727\ eV \tag{13.519}$$

Given that the vibration and reentrant oscillation is for two $C-H$ bonds, $\bar{E}_{osc}(^{12}CH_2)$, is:

$$\begin{aligned}\bar{E}_{osc}\left({}^{12}CH_2\right) &= 2\left(\bar{E}_D + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right)\\ &= 2\left(-0.25493\ eV + \frac{1}{2}\left(0.35532\ eV\right)\right) = -0.15454\ eV\end{aligned} \tag{13.520}$$

## TOTAL AND BOND ENERGIES OF ${}^{12}CH_2$

$E_{T+osc}\left({}^{12}CH_2\right)$, the total energy of the ${}^{12}CH_2$ radical including the Doppler term, is given by the sum of $E_T\left(CH_2\right)$ (Eq. (13.497)) and $\bar{E}_{osc}\left({}^{12}CH_2\right)$ given by Eq. (13.520).

$$\begin{aligned}E_{T+osc}\left(CH_2\right) &= V_e + T + V_m + V_p + E\left(C,2sp^3\right) + \bar{E}_{osc}\left({}^{12}CH_2\right)\\ &= E_T\left(CH_2\right) + \bar{E}_{osc}\left({}^{12}CH_2\right)\end{aligned} \tag{13.521}$$

$$\begin{aligned}E_{T+osc}\left({}^{12}CH_2\right) &= \left\{\begin{array}{l}\left(\dfrac{-e^2}{4\pi\varepsilon_0 c'}\left[\left(0.91771\right)\left(2-\dfrac{1}{2}\dfrac{a_0}{a}\right)\ln\dfrac{a+c'}{a-c'}-1\right]-14.63489\ eV\right)\\ -2\left(\left(31.63536831\ eV\right)\sqrt{\dfrac{2\hbar\sqrt{\dfrac{\frac{3}{4}\frac{e^2}{4\pi\varepsilon_0 b^3}}{m_e}}}{m_e c^2}}-\dfrac{1}{2}\hbar\sqrt{\dfrac{k}{\mu}}\right)\end{array}\right\}\\ &= -49.66493\ eV - 2\left(0.25493\ eV - \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right)\end{aligned} \tag{13.522}$$

From Eqs. (13.518-13.522), the total energy of ${}^{12}CH_2$ is:

$$\begin{aligned}E_{T+osc}\left({}^{12}CH_2\right) &= -49.66493\ eV + \bar{E}_{osc}\left({}^{12}CH_2\right)\\ &= -49.66493\ eV - 2\left(0.25493\ eV - \frac{1}{2}\left(0.35532\ eV\right)\right) = -49.81948\ eV\end{aligned} \tag{13.523}$$

where $\omega_e$ given by Eq. (13.458) was used for the $\hbar\sqrt{\frac{k}{\mu}}$ term.

${}^{12}CH_2$ has the same electronic configuration as ${}^{14}NH$. The dissociation of the bond of the dihydrogen carbide radical forms a free hydrogen atom with one unpaired electron and a $C2sp^3$ HO with three unpaired electrons as shown in Eq. (13.422) wherein the magnetic moments cannot all cancel. Thus, the bond dissociation of ${}^{12}CH_2$ gives rise to ${}^{12}CH$ with the same electronic configuration as $N$ as given by Eq. (10.134). The $N$ configuration is more stable than $H$ as shown in Eqs. (10.141-10.143). The lowering of the energy of the reactants decreases the bond energy. The total energy of carbon is reduced by the energy in the field of the two magnetic dipoles given by Eq. (7.46) and Eq. (13.424).

$$E(magnetic) = \frac{2\pi\mu_0 e^2\hbar^2}{m_e^2\left(r_{2sp^3}\right)^3} = \frac{8\pi\mu_0\mu_B^2}{\left(0.91771a_0\right)^3} = 0.14803\ eV \tag{13.524}$$

The $CH_2$ bond dissociation energy, $E_D\left({}^{12}CH_2\right)$, is given by the sum of the total energies of the $CH$ radical and the hydrogen atom minus the sum of $E_{T+osc}\left({}^{12}CH_2\right)$ and $E(magnetic)$:

$$E_D\left({}^{12}CH_2\right) = E\left({}^{12}CH\right) + E(H) - E_{T+osc}\left({}^{12}CH_2\right) - E\left(magnetic\right) \tag{13.525}$$

where $E_T({}^{12}CH)$ is given by the sum of the energies of the $C2sp^3$ HO, $E\left(C,2sp^3\right)$ given by Eq. (13.428), $E_D\left(H\right)$ given by Eq. (13.154), and the negative of the bond energy of ${}^{12}CH$ given by Eq. (13.489):

$$E({}^{12}CH) = -13.59844\ eV - 14.63489\ eV - 3.47\ eV = -31.70333\ eV \tag{13.526}$$

Thus, the ${}^{12}CH_2$ bond dissociation energy, $E_D\left({}^{12}CH_2\right)$, given by Eqs. (13.154), and (13.523-13.526) is:

$$\begin{aligned}E_D\left({}^{12}CH_2\right) &= -\left(31.70333\ eV + 13.59844\ eV\right) - \left(E_{T+osc}\left({}^{12}CH_2\right) + E\left(magnetic\right)\right)\\ &= -45.30177\ eV - \left(-49.81948\ eV + 0.14803\ eV\right) = 4.36968\ eV\end{aligned} \tag{13.527}$$

The experimental ${}^{12}CH_2$ bond dissociation energy is [39]:

$$E_D\left({}^{12}CH_2\right) = 4.33064\ eV \tag{13.528}$$

## BOND ANGLE OF $^{12}CH_2$

The $CH_2$ MO comprises a linear combination of two $C-H$-bond MOs. Each $C-H$-bond MO comprises the superposition of a $H_2$-type ellipsoidal MO and the $C2sp^3$ HO with a relative charge density of 0.75 to 1.25; otherwise, the $C2sp^3$ shell is unchanged. A bond is also possible between the two H atoms of the $C-H$ bonds. Such $H-H$ bonding would decrease the $C-H$ bond strength since electron density would be shifted from the $C-H$ bonds to the $H-H$ bond. Thus, the bond angle between the two $C-H$ bonds is determined by the condition that the total energy of the $H_2$-type ellipsoidal MO between the terminal $H$ atoms of the $C-H$ bonds is zero. From Eqs. (11.79) and (13.228), the distance from the origin to each focus of the $H-H$ ellipsoidal MO is

$$c' = a\sqrt{\frac{\hbar^2 4\pi\varepsilon_0}{m_e e^2 2a}} = \sqrt{\frac{aa_0}{2}} \tag{13.529}$$

The internuclear distance from Eq. (13.229) is:

$$2c' = 2\sqrt{\frac{aa_0}{2}} \tag{13.530}$$

The length of the semiminor axis of the prolate spheroidal $H-H$ MO $b=c$ is given by Eq. (13.62).

The bond angle of $CH_2$ is derived by using the orbital composition and an energy matching factor as in the case with $NH_2$ and $NH_3$. Since the two $H_2$-type ellipsoidal MOs comprise 75% of the $H$ electron density of $H_2$ and the energy of each $H_2$-type ellipsoidal MO is matched to that of the $C2sp^3$ HO; the component energies and the total energy $E_T$ of the $H-H$ bond are given by Eqs. (13.67-13.73) except that $V_e$, $T$, and $V_m$ are corrected for the hybridization-energy-matching factor of $0.91771$ given by Eq. (13.430). Substitution of Eq. (13.529) into Eq. (13.233) with the hybridization factor gives:

$$0 = \left[ \begin{array}{l} \dfrac{-e^2}{8\pi\varepsilon_0\sqrt{\dfrac{aa_0}{2}}} \left[ (0.91771)^{-1}\left(\dfrac{3}{2}-\dfrac{3}{8}\dfrac{a_0}{a}\right)\ln\dfrac{a+\sqrt{\dfrac{aa_0}{2}}}{a-\sqrt{\dfrac{aa_0}{2}}}-1\right]\left[1+\sqrt{\dfrac{2\hbar\sqrt{\dfrac{\dfrac{0.75e^2}{4\pi\varepsilon_0 a^3}}{m_e}}}{m_e c^2}}\right] \\ +\dfrac{1}{2}\hbar\sqrt{\dfrac{\dfrac{0.75e^2}{8\pi\varepsilon_0 a^3}-\dfrac{e^2}{8\pi\varepsilon_0 (a+c')^3}}{0.5m_p}} \end{array} \right] \tag{13.531}$$

From the energy relationship given by Eq. (13.531) and the relationship between the axes given by Eqs. (13.529-13.530) and (13.62-13.63), the dimensions of the $H-H$ MO can be solved.

The most convenient way to solve Eq. (13.531) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is:

$$a = 5.1500a_0 = 2.7253\ X\ 10^{-10}\ m \tag{13.532}$$

Substitution of Eq. (13.532) into Eq. (13.529) gives:

$$c' = 1.6047a_0 = 8.4916\ X\ 10^{-11}\ m \tag{13.533}$$

The internuclear distance given by multiplying Eq. (13.533) by two is:

$$2c' = 3.2094a_0 = 1.6983\ X\ 10^{-10}\ m \tag{13.534}$$

Substitution of Eqs. (13.532-13.533) into Eq. (13.62) gives:

$$b = c = 4.8936a_0 = 2.5896\ X\ 10^{-10}\ m \tag{13.535}$$

Substitution of Eqs. (13.532-13.533) into Eq. (13.63) gives:

$$e = 0.3116 \tag{13.536}$$

Using, $2c'_{H-H}$ (Eq. (13.534)), the distance between the two $H$ atoms when the total energy of the corresponding MO is zero (Eq. (13.531)), and $2c'_{C-H}$ (Eq. (13.501)), the internuclear distance of each $C-H$ bond, the corresponding bond angle can be determined from the law of cosines. Using, Eq. (13.242), the bond angle $\theta$ between the $C-H$ bonds is:

$$\theta = \cos^{-1}\left(\frac{2(2.09132)^2-(3.2094)^2}{2(2.09132)^2}\right) = \cos^{-1}(-0.1775) = 100.22° \tag{13.537}$$

The experimental angle between the $C-H$ bonds is [38]:

$$\theta = 102.4° \tag{13.538}$$

The results of the determination of bond parameters of $CH_2$ are given in Table 13.1. The calculated results are based on first principles and given in closed-form, exact equations containing fundamental constants only. The agreement between the experimental and calculated results is excellent.

## METHYL RADICAL ($CH_3$)

The methyl radical $CH_3$ is formed by the reaction of a hydrogen atom with a dihydrogen carbide radical:

$$CH_2 + H \rightarrow CH_3 \tag{13.539}$$

$CH_3$ can be solved using the same principles as those used to solve $NH_3$ with the exception that the carbon $2s$ and $2p$ shells hybridize to form a single $2sp^3$ shell as an energy minimum. Three diatomic molecular orbitals (MOs) developed in the Nature of the Chemical Bond of Hydrogen-Type Molecules and Molecular Ions section serve as basis functions in a linear combination with three carbon $2sp^3$ hybridized orbitals (HOs) to form the MO of $CH_3$. The solution is very similar to that of $CH_2$ except that there are three $CH$ bonds in $CH_3$.

## FORCE BALANCE OF $CH_3$

$CH_3$ comprises three chemical bonds between carbon and hydrogen atoms. Each $C-H$ bond comprises two spin-paired electrons with one from an initially unpaired electron of the carbon atom and the other from the hydrogen atom. Each $H$-atom electron forms an $H_2$-type ellipsoidal MO with an unpaired $C$-atom electron. However, such a bond is not possible with the outer two $C$ electrons in their ground state since the resulting $H_2$-type ellipsoidal MO would have a shorter internuclear distance than the radius of the carbon $2p$ shell which is not energetically stable, and only two electrons are unpaired. Thus, when bonding the carbon $2s$ and $2p$ shells hybridize to form a single $2sp^3$ shell as an energy minimum. The electron configuration and the energy, $E\left(C,2sp^3\right)$, of the $C2sp^3$ shell is given by Eqs. (13.422), and (13.428), respectively.

For each $C-H$ bond, a $C2sp^3$ electron combines with the $H1s$ electron to form a molecular orbital. The proton of the $H$ atom and the nucleus of the $C$ atom are along each internuclear axis and serve as the foci. As in the case of $H_2$, each of the three $C-H$-bond MOs is a prolate spheroid with the exception that the ellipsoidal MO surface cannot extend into $C2sp^3$ HO for distances shorter than the radius of the $C2sp^3$ shell since it is energetically unfavorable. Thus, each MO surface comprises a prolate spheroid at the $H$ proton that is continuous with the $C2sp^3$ shell at the $C$ atom whose nucleus serves as the other focus. The radius and the energy of the $C2sp^3$ shell are unchanged with bond formation. The central paramagnetic force due to spin of each $C-H$ bond is provided by the spin-pairing force of the $CH_3$ MO that has the symmetry of an $s$ orbital that superimposes with the $C2sp^3$ orbitals such that the corresponding angular momenta are unchanged.

The energies in the $CH_3$ MO involve only each $C2sp^3$ and each $H1s$ electron with the formation of each $C-H$ bond. The sum of the energies of the $H_2$-type ellipsoidal MOs is matched to that of the $C2sp^3$ shell. As in the cases of $OH$, $H_2O$, $NH$, $NH_2$, $NH_3$, $CH$, and $CH_2$ the linear combination of each $H_2$-type ellipsoidal MO with the $C2sp^3$ HO must involve a 25% contribution from the $H_2$-type ellipsoidal MO to the $C2sp^3$ HO in order to match potential, kinetic, and orbital energy relationships. Thus, the $CH_3$ MO must comprise three $C-H$ bonds with each comprising 75% of a $H_2$-type ellipsoidal MO and a $C2sp^3$ HO:

$$3\left[1\ C2sp^3 + 0.75\ H_2\ MO\right] \rightarrow CH_3\ MO \tag{13.540}$$

The force balance of the $CH_3$ MO is determined by the boundary conditions that arise from the linear combination of orbitals according to Eq. (13.540) and the energy matching condition between the hydrogen and $C2sp^3$ HO components of the MO.

The force constant $k'$ to determine the ellipsoidal parameter $c'$ of each $H_2$-type-ellipsoidal-MO component of the $CH_3$ MO in terms of the central force of the foci is given by Eq. (13.59). The distance from the origin of each $C-H$-bond MO to each focus $c'$ is given by Eq. (13.60). The internuclear distance is given by Eq. (13.61). The length of the semiminor axis of the prolate spheroidal $C-H$-bond MO $b=c$ is given by Eq. (13.62). The eccentricity, $e$, is given by Eq. (13.63). The solution of the semimajor axis $a$ then allows for the solution of the other axes of each prolate spheroid and eccentricity of each $C-H$-bond MO. Since each of the three prolate spheroidal $C-H$-bond MOs comprises a $H_2$-type-ellipsoidal MO that transitions to the $C2sp^3$ HO, the energy $E\left(C,2sp^3\right)$ in Eq. (13.428) adds to that of the three corresponding $H_2$-type ellipsoidal MOs to give the total energy of the $CH_3$ MO. From the energy equation and the relationship between the axes, the dimensions of the $CH_3$ MO are solved.

The energy components of $V_e$, $V_p$, $T$, and $V_m$ are three times those of $CH$ corresponding to the three $C-H$ bonds. Since each prolate spheroidal $H_2$-type MO transitions to the $C2sp^3$ HO and the energy of the $C2sp^3$ shell must remain constant and equal to the $E\left(C,2sp^3\right)$ given by Eq. (13.428), the total energy $E_T\left(CH_3\right)$ of the $CH_3$ MO is given by the sum of the energies of the orbitals corresponding to the composition of the linear combination of the $C2sp^3$ HO and the three $H_2$-type ellipsoidal MOs that forms the $CH_3$ MO as given by Eq. (13.540). Using Eq. (13.431), $E_T\left(CH_3\right)$ is given by:

$$\begin{aligned}E_T\left(CH_3\right) &= E_T + E\left(C,2sp^3\right)\\ &= -\frac{3e^2}{8\pi\varepsilon_0 c'}\left[\left(0.91771\right)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]-14.63489\ eV\end{aligned} \tag{13.541}$$

The three hydrogen atoms and the hybridized carbon atom can achieve an energy minimum as a linear combination of three $H_2$-type ellipsoidal MOs each having the proton and the carbon nucleus as the foci. Hybridization gives rise to the $C2sp^3$ HO-shell Coulombic energy $E_{Coulomb}\left(C,2sp^3\right)$ given by Eq. (13.425). To meet the equipotential condition of the union of the $H_2$-type-ellipsoidal-MO and the $C2sp^3$ HO, the electron energies in Eqs. (13.431), (13.495), and (13.541) were normalized by the ratio of 14.82575 $eV$, the magnitude of $E_{Coulomb}\left(C,2sp^3\right)$ given by Eq. (13.425), and 13.605804 $eV$, the magnitude of the Coulombic energy between the electron and proton of $H$ given by Eq. (1.224). The factor given by Eq. (13.430) normalized the energies to match that of the Coulombic energy alone to meet the energy matching condition of each $C-H$-bond MO under the influence of the proton and the $C$ nucleus. Each $C-H$-bond MO comprises the same $C2sp^3$ shell having its energy normalized to that of the Coulombic energy between the electron and a charge of $+e$ at the carbon focus of the $CH_3$ MO. Thus, the energy of the $CH_3$ MO is also given by the sum of that of the three $H_2$-type ellipsoidal MOs given by Eq. (11.212) minus two times the Coulombic energy, $E_{Coulomb}\left(H\right)=-13.605804\ eV$, of the two redundant $+e$'s of the linear combination:

$$\begin{aligned}E_T\left(3H_2-2H\right) &= -\frac{3e^2}{8\pi\varepsilon_0 a_0}\left[\left(2\sqrt{2}-\sqrt{2}+\frac{\sqrt{2}}{2}\right)\ln\frac{\sqrt{2}+1}{\sqrt{2}-1}-\sqrt{2}\right]-2E_{Coulomb}\left(H\right)\\ &= 3\left(-31.63536831\ eV\right)-2\left(-13.605804\ eV\right)=-67.69450\ eV\end{aligned} \tag{13.542}$$

$E_T\left(CH_3\right)$ given by Eq. (13.541) is set equal to three times the energy of the $H_2$-type ellipsoidal MO minus two times the Coulombic energy of $H$ given by Eq. (13.542).

$$\begin{aligned}E_T\left(CH_3\right) &= -\frac{3e^2}{8\pi\varepsilon_0 c'}\left[\left(0.91771\right)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]-14.63489\ eV\\ &= -67.69450\ eV\end{aligned} \tag{13.543}$$

From the energy relationship given by Eq. (13.543) and the relationship between the axes given by Eqs. (13.60-13.63), the dimensions of the $CH_3$ MO can be solved.

Substitution of Eq. (13.60) into Eq. (13.543) gives:

$$\frac{3e^2}{8\pi\varepsilon_0\sqrt{\frac{2aa_0}{3}}}\left[\left(0.91771\right)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+\sqrt{\frac{2aa_0}{3}}}{a-\sqrt{\frac{2aa_0}{3}}}-1\right]=e53.05961 \tag{13.544}$$

The most convenient way to solve Eq. (13.544) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is

$$a=1.62893a_0=8.61990\ X\ 10^{-11}\ m \tag{13.545}$$

Substitution of Eq. (13.545) into Eq. (13.60) gives:

$$c'=1.04209a_0=5.51450\ X\ 10^{-11}\ m \tag{13.546}$$

The internuclear distance given by multiplying Eq. (13.546) by two is:

$$2c'=2.08418a_0=1.10290\ X\ 10^{-10}\ m \tag{13.547}$$

The experimental bond distance is [38]:

$$2c'=1.079\ X\ 10^{-10}\ m \tag{13.548}$$

Substitution of Eqs. (13.545-13.546) into Eq. (13.62) gives:

$$b=c=1.25198a_0=6.62518\ X\ 10^{-11}\ m \tag{13.549}$$

Substitution of Eqs. (13.545-13.546) into Eq. (13.63) gives:

$$e=0.63974 \tag{13.550}$$

The nucleus of the $H$ atom and the nucleus of the $C$ atom comprise the foci of each $H_2$-type ellipsoidal MO. The parameters of the point of intersection of each $H_2$-type ellipsoidal MO and the $C2sp^3$ HO are given by Eqs. (13.84-13.95), (13.261-13.270), and (13.434-13.442). The polar intersection angle $\theta'$ is given by Eq. (13.261) where $r_n = r_{2sp^3} = 0.91771a_0$ is the radius of the $C2sp^3$ shell. Substitution of Eqs. (13.545-13.546) into Eq. (13.261) gives:

$$\theta' = 85.65° \tag{13.551}$$

Then, the angle $\theta_{C2sp^3HO}$ the radial vector of the $C2sp^3$ HO makes with the internuclear axis is:

$$\theta_{C2sp^3HO} = 180° - 85.65° = 94.35° \tag{13.552}$$

as shown in Figure 13.9. The parametric angle $\theta_{H_2MO}$ given by Eqs. (13.442-13.443), (13.549), and (13.552) is:

$$\theta_{H_2MO} = 46.96° \tag{13.553}$$

Then, the distance $d_{H_2MO}$ along the internuclear axis from the origin of $H_2$-type ellipsoidal MO to the point of intersection of the orbitals given by Eqs. (13.445), (13.545), and (13.553) is:

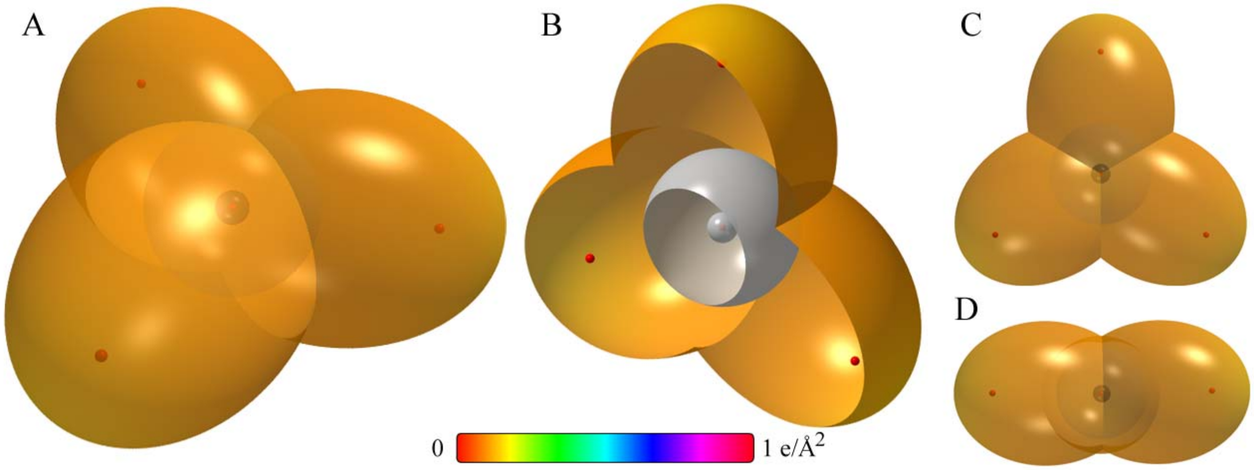
$$\begin{aligned} d_{H_2MO} &= 1.11172a_0 \\ &= 5.88295\ X\ 10^{-11}\ m \end{aligned} \tag{13.554}$$

The distance $d_{C2sp^3HO}$ along the internuclear axis from the origin of the $C$ atom to the point of intersection of the orbitals given by Eqs. (13.447), (13.546), and (13.554) is:

$$d_{C2sp^3HO} = 0.06963a_0 = 3.68457\ X\ 10^{-12}\ m \tag{13.555}$$

As shown in Eq. (13.540), the uniform charge-density in the $C2sp^3$ HO is increased by a factor of 0.25 and the $H$-atom density is decreased by a factor of 0.25 for each $C-H$ bond. Using the orbital composition of $CH_3$ (Eq. (13.540)), the radii of $C1s = 0.17113a_0$ (Eq. (10.51)) and $C2sp^3 = 0.91771a_0$ (Eq. (13.424)) shells, and the parameters of the $CH_3$ MO given by Eqs. (13.3-13.4), (13.545-13.547), and (13.549-13.555), the charge-density of the $CH_3$ MO comprising the linear combination of three $C-H$-bond MOs is shown in Figure 13.12. Each $C-H$-bond MO comprises a $H_2$-type ellipsoidal MO and a $C2sp^3$ HO having the dimensional diagram shown in Figure 13.9.

Figure 13.12. $CH_3$ MO comprising the linear combination of three $C-H$-bond MOs. Each $C-H$-bond MO comprises the superposition of a $H_2$-type ellipsoidal MO and a $C2sp^3$ HO with a relative charge-density of 0.75 to 1.25; otherwise, the $C2sp^3$ HO shell is unchanged. (A) Color scale, translucent view of the charge-density of the $CH_3$ MO from the top. For each $C-H$ bond, the ellipsoidal surface of the $H_2$-type ellipsoidal MO that transitions to the $C2sp^3$ HO, the $C2sp^3$ HO shell, $C1s$ shell, and the nuclei (red, not to scale) are shown. (B) Cut-away view showing the inner most $C1s$ shell, and moving radially, the $C2sp^3$ shell, and the $H_2$-type ellipsoidal MO that transitions to the $C2sp^3$ HO for each $C-H$ bond. Bisector current not shown. (C)-(D) Color scale, bottom, top, and side-on translucent views of the charge-density of the $CH_3$ MO, respectively.



## ENERGIES OF $CH_3$

The energies of $CH_3$ are three times those of $CH$ and are given by the substitution of the semiprincipal axes (Eqs. (13.545-13.546) and (13.549)) into the energy equations Eq. (13.541) and (Eqs. (13.449-13.452)) that are multiplied by three:

$$V_e = 3\left(0.91771\right)\frac{-2e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -108.94944\ eV \tag{13.556}$$

$$V_p = \frac{3e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}} = 39.16883\ eV \tag{13.557}$$

$$T = 3\left(0.91771\right)\frac{\hbar^2}{2m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = 33.44213\ eV \tag{13.558}$$

$$V_m = 3\left(0.91771\right)\frac{-\hbar^2}{4m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -16.72107\ eV \tag{13.559}$$

$$E_T\left(CH_3\right) = -\frac{3e^2}{8\pi\varepsilon_0 c'}\left[\left(0.91771\right)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right] - 14.63489\ eV = -67.69444\ eV \tag{13.560}$$

where $E_T\left(CH_3\right)$ is given by Eq. (13.541) which is reiteratively matched to Eq. (13.542) within five-significant-figure-round-off-error.

## VIBRATION OF $CH_3$

The vibrational energy levels of $CH_3$ may be solved as three equivalent coupled harmonic oscillators by developing the Lagrangian, the differential equation of motion, and the eigenvalue solutions [2] wherein the spring constants are derived from the central forces as given in the Vibration of Hydrogen-Type Molecular Ions section and the Vibration of Hydrogen-Type Molecules section.

## THE DOPPLER ENERGY TERMS OF $^{12}CH_3$

The reentrant oscillation of hybridized orbitals in the transition state is not coupled. Therefore, the equations of the radiation reaction force of methyl radical are the same as those of the corresponding hydrogen carbide radicals with the substitution of the methyl radical parameters. Using Eqs. (11.136) and (13.140-13.142), the angular frequency of the reentrant oscillation in the transition state is:

$$\omega = \sqrt{\frac{\frac{0.75e^2}{4\pi\varepsilon_0 b^3}}{m_e}} = 2.55577\ X\ 10^{16}\ rad/s \tag{13.561}$$

where $b$ is given by Eq. (13.549). The kinetic energy, $E_K$, is given by Planck's equation (Eq. (11.127)):

$$\bar{E}_K = \hbar\omega = \hbar 2.55577\ X\ 10^{16}\ rad/s = 16.82249\ eV \tag{13.562}$$

In Eq. (11.181), substitution of $E_T\left(H_2\right)$ (Eqs. (11.212) and (13.75)), the maximum total energy of each $H_2$-type MO, for $E_{h\nu}$, the mass of the electron, $m_e$, for $M$, and the kinetic energy given by Eq. (13.562) for $\bar{E}_K$ gives the Doppler energy of the electrons of each of the three bonds for the reentrant orbit:

$$\begin{aligned}\bar{E}_D &\cong E_{h\nu}\sqrt{\frac{2\bar{E}_K}{Mc^2}}\\ &= -31.63537\ eV\sqrt{\frac{2e\left(16.82249\ eV\right)}{m_e c^2}} = -0.25670\ eV\end{aligned} \tag{13.563}$$

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency. The decrease in the energy of $CH_3$ due to the reentrant orbit of each bond in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei, $\bar{E}_{osc}$, is given by the sum of the corresponding energies, $\bar{E}_D$ given by Eq. (13.563) and $\bar{E}_{Kvib}$, the average kinetic energy of vibration which is 1/2 of the vibrational energy of each $C-H$ bond. Using $\omega_e$ given by Eq. (13.458) for $\bar{E}_{Kvib}$ of the transition state having three independent bonds, $\bar{E}'_{osc}\left({}^{12}CH_3\right)$ per bond is

$$\bar{E}'_{osc}\left({}^{12}CH_3\right) = \bar{E}_D + \bar{E}_{Kvib} = \bar{E}_D + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \tag{13.564}$$

$$\bar{E}'_{osc}\left({}^{12}CH_3\right) = -0.25670\ eV + \frac{1}{2}\left(0.35532\ eV\right) = -0.07904\ eV \tag{13.565}$$

Given that the vibration and reentrant oscillation is for three $C-H$ bonds, $\bar{E}_{osc}\left({}^{12}CH_3\right)$, is:

$$\begin{aligned}\bar{E}_{osc}\left({}^{12}CH_3\right) &= 3\left(\bar{E}_D + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right) \\ &= 3\left(-0.25670\ eV + \frac{1}{2}\left(0.35532\ eV\right)\right) = -0.23711\ eV\end{aligned} \tag{13.566}$$

## TOTAL AND BOND ENERGIES OF ${}^{12}CH_3$

$E_{T+osc}\left({}^{12}CH_3\right)$, the total energy of the ${}^{12}CH_3$ radical including the Doppler term, is given by the sum of $E_T\left(CH_3\right)$ (Eq. (13.543)) and $\bar{E}_{osc}\left({}^{12}CH_3\right)$ given by Eq. (13.566).

$$E_{T+osc}\left(CH_3\right) = V_e + T + V_m + V_p + E\left(C,2sp^3\right) + \bar{E}_{osc}\left({}^{12}CH_3\right) = E_T\left(CH_3\right) + \bar{E}_{osc}\left({}^{12}CH_3\right) \tag{13.567}$$

$$\begin{aligned}E_{T+osc}\left({}^{12}CH_3\right) &= \left\{\begin{array}{l}\left(\dfrac{-3e^2}{8\pi\varepsilon_0 c'}\left[\left(0.91771\right)\left(2-\dfrac{1}{2}\dfrac{a_0}{a}\right)\ln\dfrac{a+c'}{a-c'}-1\right]-14.63489\ eV\right) \\ -3\left(\left(31.63536831\ eV\right)\sqrt{\dfrac{2\hbar\sqrt{\dfrac{\frac{3}{4}\frac{e^2}{4\pi\varepsilon_0 b^3}}{m_e}}}{m_e c^2}}-\dfrac{1}{2}\hbar\sqrt{\dfrac{k}{\mu}}\right)\end{array}\right\} \\ &= -67.69450\ eV - 3\left(0.25670\ eV - \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right)\end{aligned} \tag{13.568}$$

From Eqs. (13.564-13.568), the total energy of ${}^{12}CH_3$ is:

$$\begin{aligned}E_{T+osc}\left({}^{12}CH_3\right) &= -67.69450\ eV + \bar{E}_{osc}\left({}^{12}CH_3\right) \\ &= -67.69450\ eV - 3\left(0.25670\ eV - \frac{1}{2}\left(0.35532\ eV\right)\right) \\ &= -67.93160\ eV\end{aligned} \tag{13.569}$$

where $\omega_e$ given by Eq. (13.458) was used for the $\hbar\sqrt{\frac{k}{\mu}}$ term.

The $CH_3$ bond dissociation energy, $E_D\left({}^{12}CH_3\right)$, is given by the sum of the total energies of the $CH_2$ radical and the hydrogen atom minus $E_{T+osc}\left({}^{12}CH_3\right)$:

$$E_D\left({}^{12}CH_3\right) = E\left({}^{12}CH_2\right) + E(H) - E_{T+osc}\left({}^{12}CH_3\right) \tag{13.570}$$

where $E_T({}^{12}CH_2)$ is given by the sum of the energies of the $C2sp^3$ HO, $E\left(C,2sp^3\right)$ given by Eq. (13.428), $2E_D\left(H\right)$ given by Eq. (13.154), and the negative of the bond energies of ${}^{12}CH$ given by Eq. (13.489) and ${}^{12}CH_2$ given by Eq. (13.528):

$$\begin{aligned}E({}^{12}CH_2) &= 2\left(-13.59844\ eV\right) - 14.63489\ eV - 3.47\ eV - 4.33064\ eV \\ &= -49.63241\ eV\end{aligned} \tag{13.571}$$

Thus, the ${}^{12}CH_3$ bond dissociation energy, $E_D\left({}^{12}CH_3\right)$, given by Eqs. (13.154), and (13.569-13.571) is:

$$\begin{aligned}E_D\left({}^{12}CH_3\right) &= +\left(-49.63241\ \ eV - 13.59844\ eV\right) - E_{T+osc}\left({}^{12}CH_3\right) \\ &= -63.23085 eV - \left(-67.93160\ eV\right) \\ &= 4.70075\ eV\end{aligned} \tag{13.572}$$

The experimental ${}^{12}CH_3$ bond dissociation energy is [40]

$$E_D\left({}^{12}CH_3\right) = 4.72444\ eV \tag{13.573}$$

## BOND ANGLE OF $^{12}CH_3$

Consider the case that all of the MOs can participate in a superposition involving bonding of the terminal atoms. Then, solving for $2c'_{H-H} = 3.61109a_0$, the distance between any adjacent two $H$ atoms when the total energy of the corresponding MO is zero given by Eq. (13.531) with the replacement of the hybridization factor and energy terms with $(0.91771)\left(2-\frac{1}{2}\frac{a_0}{a}\right)$ of Eq. (13.568), and $2c'_{C-H}$, the internuclear distance of each $C-H$ bond (Eq. (13.547)), the corresponding bond angle can be determined from the law of cosines. Using Eq. (13.537), the bond angle $\theta$ between the $C-H$ bonds is:

$$\theta = \cos^{-1}\left(\frac{2(2.08418)^2-(3.61109)^2}{2(2.08418)^2}\right) = \cos^{-1}(-0.50099) = 120° \qquad (13.574)$$

which is in agreement with $D_{3h}$ symmetry [38].

The $CH_3$ radical has a pyramidal structure with the carbon atom along the z-axis at the apex and the hydrogen atoms at the base in the xy-plane. The distance $d_{origin-H}$ from the origin to the nucleus of a hydrogen atom given by Eqs. (13.534) and (13.412) is:

$$d_{origin-H} = 2.0848a_0 \qquad (13.575)$$

The height along the z-axis of the pyramid from the origin to the $C$ nucleus is $d_{height}$ given by Eqs. (13.414), (13.547), and (13.575) is:

$$d_{height} = 0a_0 \qquad (13.576)$$

The angle $\theta_v$ of each $C-H$ bond from the z-axis given by Eqs. (13.416), (13.575), and (13.576) is:

$$\theta_v = 90° \qquad (13.577)$$

The $CH_3$ MO shown in Figure 13.12 was rendered using these parameters.

The results of the determination of bond parameters of $CH_3$ are given in Table 13.1. The calculated results are based on first principles and given in closed-form, exact equations containing fundamental constants only. The agreement between the experimental and calculated results is excellent.

## METHANE MOLECULE ($CH_4$)

The methane molecule $CH_4$ is formed by the reaction of a hydrogen atom with a methyl radical:

$$CH_3 + H \rightarrow CH_4 \qquad (13.578)$$

$CH_4$ can be solved using the same principles as those used to solve and $CH_3$ wherein the carbon $2s$ and $2p$ shells hybridize to form a single $2sp^3$ shell as an energy minimum. Four diatomic molecular orbitals (MOs) developed in the Nature of the Chemical Bond of Hydrogen-Type Molecules and Molecular Ions section serve as basis functions in a linear combination with four carbon $2sp^3$ hybridized orbitals (HOs) to form the MO of $CH_4$. The solution is very similar to that of $CH_3$ except that there are four $CH$ bonds in $CH_4$. Methane is the simplest hydrocarbon that can be solved using the results for $CH_3$. From the solution of $CH_2$ as well as $CH_3$, more complex hydrocarbons can be solved using these radicals as basis elements with bonding between the $C2sp^3$ hybridized carbons.

## FORCE BALANCE OF $CH_4$

$CH_4$ comprises four chemical bonds between carbon and hydrogen atoms. Each $C-H$ bond comprises two spin-paired electrons with one from an initially unpaired electron of the carbon atom and the other from the hydrogen atom. Each $H$-atom electron forms a $H_2$-type ellipsoidal MO with an unpaired $C$-atom electrons. However, such a bond is not possible with the outer two $C$ electrons in their ground state since the resulting $H_2$-type ellipsoidal MO would have a shorter internuclear distance than the radius of the carbon $2p$ shell which is not energetically stable, and only two electrons are unpaired. Thus, when bonding the carbon $2s$ and $2p$ shells hybridize to form a single $2sp^3$ shell as an energy minimum. The electron configuration and the energy, $E(C,2sp^3)$, of the $C2sp^3$ shell is given by Eqs. (13.422), and (13.428), respectively.

For each $C-H$ bond, a $C2sp^3$ electron combines with the $H1s$ electron to form a molecular orbital. The proton of the $H$ atom and the nucleus of the $C$ atom are along each internuclear axis and serve as the foci. As in the case of $H_2$, each of the four $C-H$-bond MOs is a prolate spheroid with the exception that the ellipsoidal MO surface cannot extend into the $C2sp^3$ HO for distances shorter than the radius of the $C2sp^3$ shell since it is energetically unfavorable. Thus, each MO surface comprises a prolate spheroid at the $H$ proton that can be solved as being continuous with the $C2sp^3$ shell at the $C$ atom whose nucleus serves as the other focus. The radius and the energy of the $C2sp^3$ shell are unchanged with bond formation. The central paramagnetic force due to spin of each $C-H$ bond is provided by the spin-pairing force of the $CH_4$ MO that has the symmetry of an $s$ orbital that superimposes with the $C2sp^3$ orbitals such that the corresponding angular momenta are unchanged.

The energies in the $CH_4$ MO involve only each $C2sp^3$ and each $H1s$ electron with the formation of each $C-H$ bond. The sum of the energies of the $H_2$-type ellipsoidal MOs is matched to that of the $C2sp^3$ shell. As in the cases of $OH$, $H_2O$, $NH$, $NH_2$, $NH_3$, $CH$, $CH_2$, and $CH_3$ the $CH_4$ MO must comprise four $C-H$ bonds with each having 75% of a $H_2$-type ellipsoidal MO and a $C2sp^3$ HO in a linear combination in order to match potential, kinetic, and orbital energy relationships:

$$4\left[1\ C2sp^3 + 0.75\ H_2\ MO\right] \rightarrow CH_4\ MO \tag{13.579}$$

The force balance of the $CH_4$ MO is determined by the boundary conditions that arise from the linear combination of orbitals according to Eq. (13.579) and the energy matching condition between the hydrogen and $C2sp^3$ HO components of the MO.

The force constant $k'$ to determine the ellipsoidal parameter $c'$ of the each $H_2$-type-ellipsoidal-MO component of the $CH_4$ MO in terms of the central force of the foci is given by Eq. (13.59). The distance from the origin of each $C-H$-bond MO to each focus $c'$ is given by Eq. (13.60). The internuclear distance is given by Eq. (13.61). The length of the semiminor axis of the prolate spheroidal $C-H$-bond MO $b=c$ is given by Eq. (13.62). The eccentricity, $e$, is given by Eq. (13.63). The solution of the semimajor axis $a$ then allows for the solution of the other axes of each prolate spheroid and eccentricity of each $C-H$-bond MO. Since each of the four prolate spheroidal $C-H$-bond MOs comprises a $H_2$-type-ellipsoidal MO that transitions to the $C2sp^3$ HO, the energy $E\left(C,2sp^3\right)$ in Eq. (13.428) adds to that of the four corresponding $H_2$-type ellipsoidal MOs to give the total energy of the $CH_4$ MO. From the energy equation and the relationship between the axes, the dimensions of the $CH_4$ MO are solved.

The energy components of $V_e$, $V_p$, $T$, and $V_m$ are four times those of $CH$ corresponding to the four $C-H$ bonds. Since each prolate spheroidal $H_2$-type MO transitions to the $C2sp^3$ HO and the energy of the $C2sp^3$ shell must remain constant and equal to the $E\left(C,2sp^3\right)$ given by Eq. (13.428), the total energy $E_T\left(CH_4\right)$ of the $CH_4$ MO is given by the sum of the energies of the orbitals corresponding to the composition of the linear combination of the $C2sp^3$ HO and the four $H_2$-type ellipsoidal MOs that forms the $CH_4$ MO as given by Eq. (13.579). Using Eq. (13.431), $E_T\left(CH_4\right)$ is given by:

$$E_T\left(CH_4\right) = E_T + E\left(C,2sp^3\right) = -\frac{4e^2}{8\pi\varepsilon_0 c'}\left[(0.91771)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]-14.63489\ eV \tag{13.580}$$

The four hydrogen atoms and the hybridized carbon atom can achieve an energy minimum as a linear combination of four $H_2$-type ellipsoidal MOs each having the proton and the carbon nucleus as the foci. Hybridization gives rise to the $C2sp^3$ HO-shell Coulombic energy $E_{Coulomb}\left(C,2sp^3\right)$ given by Eq. (13.435). To meet the equipotential condition of the union of the $H_2$-type-ellipsoidal-MO and the $C2sp^3$ HO, the electron energies in Eqs. (13.431), (13.495), (13.541), and (13.580) were normalized by the ratio of $14.82575\ eV$, the magnitude of $E_{Coulomb}\left(C,2sp^3\right)$ given by Eq. (13.425), and $13.605804\ eV$, the magnitude of the Coulombic energy between the electron and proton of $H$ given by Eq. (1.264). The factor given by Eq. (13.430) normalized the energies to match that of the Coulombic energy alone to meet the energy matching condition of each $C-H$-bond MO under the influence of the proton and the $C$ nucleus. Each $C-H$-bond MO comprises the same $C2sp^3$ shell having its energy normalized to that of the Coulombic energy between the electron and a charge of $+e$ at the carbon focus of the $CH_4$ MO. Thus, the energy of the $CH_4$ MO is also given by the sum of that of the four $H_2$-type ellipsoidal MOs given by Eq. (11.212) minus three times the Coulombic energy, $E_{Coulomb}\left(H\right) = -13.605804\ eV$, of the three redundant $+e$'s of the linear combination:

$$\begin{aligned} E_T\left(4H_2-3H\right) &= -\frac{4e^2}{8\pi\varepsilon_0 a_0}\left[\left(2\sqrt{2}-\sqrt{2}+\frac{\sqrt{2}}{2}\right)\ln\frac{\sqrt{2}+1}{\sqrt{2}-1}-\sqrt{2}\right]-3E_{Coulomb}\left(H\right) \\ &= 4\left(-31.63536831\ eV\right)-3\left(-13.605804\ eV\right) \\ &= -85.72406\ eV \end{aligned} \tag{13.581}$$

$E_T\left(CH_4\right)$ given by Eq. (13.580) is set equal to four times the energy of the $H_2$-type ellipsoidal MO minus three times the Coulombic energy of $H$ given by Eq. (13.581):

$$E_T\left(CH_4\right) = -\frac{4e^2}{8\pi\varepsilon_0 c'}\left[(0.91771)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]-14.63489\ eV = -85.72406\ eV \tag{13.582}$$

From the energy relationship given by Eq. (13.582) and the relationship between the axes given by Eqs. (13.60-13.63), the dimensions of the $CH_4$ MO can be solved.

Substitution of Eq. (13.60) into Eq. (13.543) gives:

$$\frac{4e^2}{8\pi\varepsilon_0\sqrt{\frac{2aa_0}{3}}}\left[(0.91771)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+\sqrt{\frac{2aa_0}{3}}}{a-\sqrt{\frac{2aa_0}{3}}}-1\right]=e71.08917 \qquad (13.583)$$

The most convenient way to solve Eq. (13.583) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is

$$a=1.62340a_0=8.59066\ X\ 10^{-11}\ m \qquad (13.584)$$

Substitution of Eq. (13.584) into Eq. (13.60) gives:

$$c'=1.04032a_0=5.50514\ X\ 10^{-11}\ m \qquad (13.585)$$

The internuclear distance given by multiplying Eq. (13.585) by two is:

$$2c'=2.08064a_0=1.10103\ X\ 10^{-10}\ m \qquad (13.586)$$

The experimental bond distance is [41] :

$$2c'=1.087\ X\ 10^{-10}\ m \qquad (13.587)$$

Substitution of Eqs. (13.584-13.585) into Eq. (13.62) gives:

$$b=c=1.24626a_0=6.59492\ X\ 10^{-11}\ m \qquad (13.588)$$

Substitution of Eqs. (13.584-13.585) into Eq. (13.63) gives:

$$e=0.64083 \qquad (13.589)$$

The nucleus of the $H$ atom and the nucleus of the $C$ atom comprise the foci of each $H_2$-type ellipsoidal MO. The parameters of the point of intersection of each $H_2$-type ellipsoidal MO and the $C2sp^3$ HO in the absence of the other three are given by Eqs. (13.84-13.95), (13.261-13.270), (13.434-13.442), and (13.551-13.555). The polar intersection angle $\theta'$ is given by Eq. (13.261) where $r_n=r_{2sp^3}=0.91771a_0$ is the radius of the $C2sp^3$ shell. Substitution of Eqs. (13.584-13.585) into Eq. (13.261) gives:

$$\theta'=86.20° \qquad (13.590)$$

Then, the angle $\theta_{C2sp^3HO}$ the radial vector of the $C2sp^3$ HO makes with the internuclear axis is:

$$\theta_{C2sp^3HO}=180°-86.20°=93.80° \qquad (13.591)$$

as shown in Figure 13.9. The parametric angle $\theta_{H_2MO}$ given by Eqs. (13.442-13.443), (13.588), and (13.591) is:

$$\theta_{H_2MO}=47.29° \qquad (13.592)$$

Then, the distance $d_{H_2MO}$ along the internuclear axis from the origin of $H_2$-type ellipsoidal MO to the point of intersection of the orbitals given by Eqs. (13.445), (13.584), and (13.592) is:

$$d_{H_2MO}=1.10121a_0=5.82734\ X\ 10^{-11}\ m \qquad (13.593)$$

The distance $d_{C2sp^3HO}$ along the internuclear axis from the origin of the $C$ atom to the point of intersection of the orbitals given by Eqs. (13.447), (13.585), and (13.593) is:

$$d_{C2sp^3HO}=0.06089a_0=3.22208\ X\ 10^{-12}\ m \qquad (13.594)$$

The $H_2$-type ellipsoidal MOs do not actually directly contact the $C2sp^3$ HO. As discussed in the Force Balance of $H_2O$ section, with the addition of the fourth $C-H$ bond, the $H_2$-type ellipsoidal MOs may linearly combine to form a continuous two-dimensional surface of equipotential equivalent to that of the MOs if they did contact the $C2sp^3$ HO. However, Eqs. (13.579-13.580) must hold based on conservation of momentum and the potential, kinetic, and total energy relationships. In order that there is current continuity given the constraints of Eqs. (13.579-13.580), the existence of a self-contained, continuous-current, linear-combination of the $H_2$-type ellipsoidal MOs requires that electrons are divisible between the combination $H_2$-type MO and the $C2sp^3$ HO. This is not possible.

*Thus, at the points of intersection of the $H_2$-type MOs of methane symmetry, and in similar geometries such as that of $CH_3$, representative of the general case, electron indivisibility, current continuity, and conservation of energy and angular momentum require that the current between the $C2sp^3$ shell and points of mutual contact is projected onto and flows along the radial vector to the surface of $C2sp^3$ shell. This current designated the bisector current (BC) meets the $C2sp^3$ surface and does not travel to distances shorter than its radius.*

Moreover, an energy minimum is obtained when the $H$-atom charge-density of each $C-H$-bond MO is decreased by a factor of 0.25 with a corresponding 0.25 increase in that of the three other $C-H$-bond MOs. In this case, the angular momentum components of the transferred current mutually cancel. The geometry of the equivalent bonds is tetrahedral. The symmetry point group is $T_d$. This geometry is equivalent to the indistinguishable bonds positioned uniformly on a spherical surface or also at the apexes of a cube. The predicted angle $\theta$ between the $C-H$ bonds is:

$$\theta = 109.5° \tag{13.595}$$

The experimental bond angle is [41]:

$$\theta = 109.5° \tag{13.596}$$

The polar angle $\phi$ at which the $H_2$-type ellipsoidal MOs intersect is given by the bisector of the angle $\theta$ between the $C-H$ bonds:

$$\phi = \frac{109.5}{2} = 54.75° \tag{13.597}$$

With the carbon nucleus defined as the origin and one of the $C-H$ bonds defined as the positive x-axis, the polar-coordinate angle of the intersection occurs at:

$$\phi' = 54.75° + 180° = 234.75° \tag{13.598}$$

The polar radius $r_i$ at this angle is given by Eqs. (13.84-13.85):

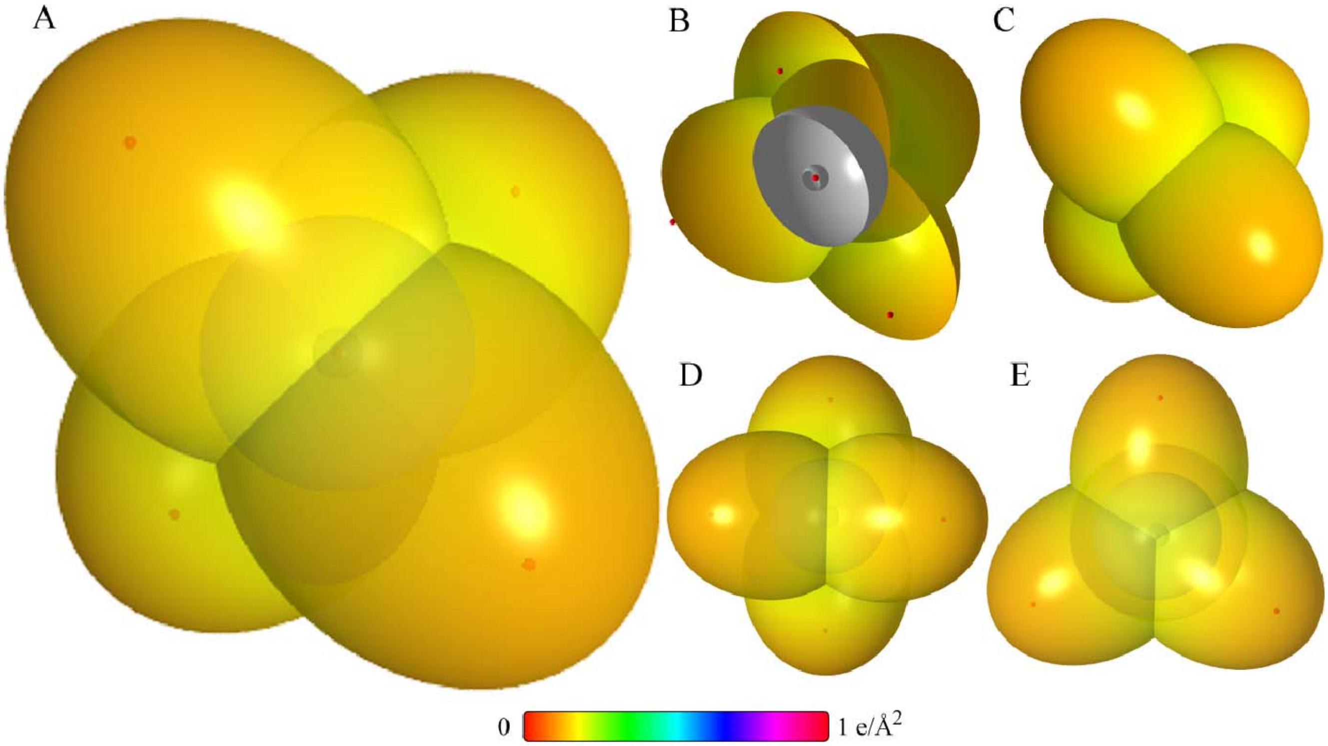
$$r_i = (a-c')\frac{1+\frac{c'}{a}}{1+\frac{c'}{a}\cos\phi'} \tag{13.599}$$

Substitution of Eqs. (13.584-13.585) and (13.589) into Eq. (13.599) gives:

$$r_i = 1.52223a_0 = 8.05530\ X\ 10^{-11}\ m \tag{13.600}$$

Using the orbital composition of $CH_4$ (Eq. (13.579)), the radii of $C1s = 0.17113a_0$ (Eq. (10.51)) and $C2sp^3 = 0.91771a_0$ (Eq. (13.424)) shells, and the parameters of the $CH_4$ MO given by Eqs. (13.3-13.4), (13.584-13.586), and (13.588-13.600), the charge-density of the $CH_4$ MO comprising the linear combination of four $C-H$-bond MOs is shown in Figure 13.13. Each $C-H$-bond MO having the dimensional diagram shown in Figure 13.9 comprises a $H_2$-type ellipsoidal MO and a $C2sp^3$ HO according to Eq. (13.579). But, based on the $T_d$ symmetry of the $H_2$-type MOs, the charge is distributed 1:1 between the $H_2$-type MOs and the $C2sp^3$ shell.

Figure 13.13. $CH_4$ MO comprising the linear combination of four $C-H$-bond MOs formed by the superposition of a $H_2$-type ellipsoidal MO and a $C2sp^3$ HO. (A) Color scale, translucent view of the charge-density of the $CH_4$ MO. The combined surface of the four $H_2$-type ellipsoidal MOs from each $C-H$ bond that surrounds the $C2sp^3$ HO, the $C2sp^3$ HO shell, $C1s$ shell, and the nuclei (red, not to scale) are shown. (B) Off-center cut-away view showing the complete inner most $C1s$ shell, and moving radially, the $C2sp^3$ shell, and the $H_2$-type ellipsoidal MOs that surround the $C2sp^3$ HO. Bisector current not shown. (C) Opaque view. (D)-(E) Additional translucent views.



## ENERGIES OF $CH_4$

The energies of $CH_4$ are four times those of $CH$ and are given by the substitution of the semiprincipal axes (Eqs. (13.584-13.585) and (13.588)) into the energy equations Eq. (13.580) and (Eqs. (13.449-13.452)) that are multiplied by four:

$$V_e = 4(0.91771)\frac{-2e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -145.86691\ eV \tag{13.601}$$

$$V_p = \frac{4e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}} = 52.31390\ eV \tag{13.602}$$

$$T = 4(0.91771)\frac{\hbar^2}{2m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = 44.92637\ eV \tag{13.603}$$

$$V_m = 4(0.91771)\frac{-\hbar^2}{4m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -22.46318\ eV \tag{13.604}$$

$$\begin{aligned} E_T(CH_4) &= -\frac{4e^2}{8\pi\varepsilon_0 c'}\left[(0.91771)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]-14.63489\ eV \\ &= -85.72472\ eV \end{aligned} \tag{13.605}$$

where $E_T(CH_4)$ is given by Eq. (13.580) which is reiteratively matched to Eq. (13.581) within five-significant-figure round-off error.

## VIBRATION OF $CH_4$

The vibrational energy levels of $CH_4$ may be solved as four equivalent coupled harmonic oscillators by developing the Lagrangian, the differential equation of motion, and the eigenvalue solutions [2] wherein the spring constants are derived from the central forces as given in the Vibration of Hydrogen-Type Molecular Ions section and the Vibration of Hydrogen-Type Molecules section.

## THE DOPPLER ENERGY TERMS OF $^{12}CH_4$

The reentrant oscillation of hybridized orbitals in the transition state is not coupled. Therefore, the equations of the radiation reaction force of methane are the same as those of $OH$, $CH$, $CH_2$, and $CH_3$ with the substitution of the methane parameters. Using Eqs. (11.136) and (13.140-13.142), the angular frequency of the reentrant oscillation in the transition state is:

$$\omega = \sqrt{\frac{\frac{0.75e^2}{4\pi\varepsilon_0 b^3}}{m_e}} = 2.57338\ X\ 10^{16}\ rad/s \tag{13.606}$$

where $b$ is given by Eq. (13.588). The kinetic energy, $E_K$, is given by Planck's equation (Eq. (11.127)).

$$\overline{E}_K = \hbar\omega = \hbar 2.57338\ X\ 10^{16}\ rad/s = 16.93841\ eV \tag{13.607}$$

In Eq. (11.181), substitution of $E_T(H_2)$ (Eqs. (11.212) and (13.75)), the maximum total energy of each $H_2$-type MO, for $E_{h\nu}$, the mass of the electron, $m_e$, for $M$, and the kinetic energy given by Eq. (13.607) for $\overline{E}_K$ gives the Doppler energy of the electrons of each of the four bonds for the reentrant orbit:

$$\begin{aligned}\overline{E}_D &\cong E_{h\nu}\sqrt{\frac{2\overline{E}_K}{Mc^2}}\\ &= -31.63537\ eV\sqrt{\frac{2e(16.93841\ eV)}{m_e c^2}} = -0.25758\ eV\end{aligned} \tag{13.608}$$

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency. The decrease in the energy of $CH_4$ due to the reentrant orbit of each bond in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei, $\overline{E}_{osc}$, is given by the sum of the corresponding energies, $\overline{E}_D$ given by Eq. (13.608) and $\overline{E}_{Kvib}$, the average kinetic energy of vibration which is 1/2 of the vibrational energy of each $C-H$ bond. Using $\omega_e$ given by Eq. (13.458) for $\overline{E}_{Kvib}$ of the transition state having four independent bonds, $\overline{E}'_{osc}\left({}^{12}CH_4\right)$ per bond is:

$$\overline{E}'_{osc}\left({}^{12}CH_4\right) = \overline{E}_D + \overline{E}_{Kvib} = \overline{E}_D + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \tag{13.609}$$

$$\overline{E}'_{osc}\left({}^{12}CH_4\right) = -0.25758\ eV + \frac{1}{2}(0.35532\ eV) = -0.07992\ eV \tag{13.610}$$

The reentrant orbit for the binding of a hydrogen atom to a $CH_3$ radical involves four $C-H$ bonds. Since the vibration and reentrant oscillation is along four bonds, $\overline{E}_{osc}$ for $^{12}CH_4$, $\overline{E}_{osc}\left({}^{12}CH_4\right)$, is:

$$\begin{aligned}\overline{E}_{osc}\left({}^{12}CH_4\right) &= 4\left(\overline{E}_D + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right)\\ &= 4\left(-0.25758\ eV + \frac{1}{2}(0.35532\ eV)\right) = -0.31967\ eV\end{aligned} \tag{13.611}$$

## TOTAL AND BOND ENERGIES OF $^{12}CH_4$

$E_{T+osc}\left(^{12}CH_4\right)$, the total energy of the $^{12}CH_4$ radical including the Doppler term, is given by the sum of $E_T\left(CH_4\right)$ (Eq. (13.582)) and $\bar{E}_{osc}\left(^{12}CH_4\right)$ given by Eq. (13.611).

$$E_{T+osc}\left(CH_4\right) = V_e + T + V_m + V_p + E\left(C,2sp^3\right) + \bar{E}_{osc}\left(^{12}CH_4\right) = E_T\left(CH_4\right) + \bar{E}_{osc}\left(^{12}CH_4\right) \tag{13.612}$$

$$\begin{aligned} E_{T+osc}\left(^{12}CH_4\right) &= \left\{ \begin{array}{l} \left( \left(\frac{-4e^2}{8\pi\varepsilon_0 c'}\right) \left[\left(0.91771\right)\left(2 - \frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'} - 1\right] - 14.63489\ eV \right) \\ -4\left( \left(31.63536831\ eV\right)\sqrt{\frac{2\hbar\sqrt{\frac{\frac{3}{4}\frac{e^2}{4\pi\varepsilon_0 b^3}}{m_e}}}{m_e c^2}} - \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \right) \end{array} \right\} \\ &= -85.72406\ eV - 4\left(0.25758\ eV - \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right) \end{aligned} \tag{13.613}$$

From Eqs. (13.609-13.613), the total energy of $^{12}CH_4$ is:

$$\begin{aligned} E_{T+osc}\left(^{12}CH_4\right) &= -85.72406\ eV + \bar{E}_{osc}\left(^{12}CH_4\right) \\ &= -85.72406\ eV - 4\left(0.25758\ eV - \frac{1}{2}\left(0.35532\ eV\right)\right) = -86.04373\ eV \end{aligned} \tag{13.614}$$

where $\omega_e$ given by Eq. (13.458) was used for the $\hbar\sqrt{\frac{k}{\mu}}$ term.

The $CH_4$ bond dissociation energy, $E_D\left(^{12}CH_4\right)$, is given by the sum of the total energies of the $CH_3$ radical and the hydrogen atom minus $E_{T+osc}\left(^{12}CH_4\right)$:

$$E_D\left(^{12}CH_4\right) = E\left(^{12}CH_3\right) + E(H) - E_{T+osc}\left(^{12}CH_4\right) \tag{13.615}$$

where $E_T(^{12}CH_3)$ is given by the sum of the energies of the $C2sp^3$ HO, $E\left(C,2sp^3\right)$ given by Eq. (13.428), $3E_D\left(H\right)$ given by Eq. (13.154), and the negative of the bond energies of $^{12}CH$ given by Eq. (13.489), $^{12}CH_2$ given by Eq. (13.528), and $^{12}CH_3$ given by Eq. (13.573):

$$E(^{12}CH_3) = \left( \begin{array}{l} 3\left(-13.59844\ eV\right) - 14.63489\ eV \\ -3.47\ eV - 4.33064\ eV - 4.72444\ eV \end{array} \right) = -67.95529\ eV \tag{13.616}$$

Thus, the $^{12}CH_4$ bond dissociation energy, $E_D\left(^{12}CH_4\right)$, given by Eqs. (13.154), and (13.614-13.616) is:

$$\begin{aligned} E_D\left(^{12}CH_4\right) &= -\left(67.95529\ \ eV + 13.59844\ eV\right) - E_{T+osc}\left(^{12}CH_4\right) \\ &= -81.55373\ eV - \left(-86.04373\ eV\right) = 4.4900\ eV \end{aligned} \tag{13.617}$$

The experimental $^{12}CH_4$ bond dissociation energy is [40] :

$$E_D\left(^{12}CH_4\right) = 4.48464\ eV \tag{13.618}$$

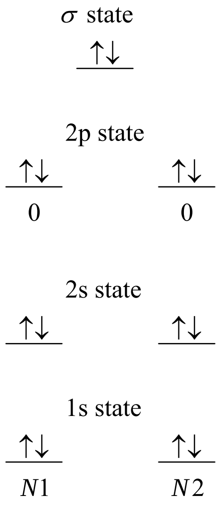
The results of the determination of bond parameters of $CH_4$ are given in Table 13.1. The calculated results are based on first principles and given in closed-form, exact equations containing fundamental constants only. The agreement between the experimental and calculated results is excellent.

## NITROGEN MOLECULE

The nitrogen molecule can be formed by the reaction of two nitrogen atoms:

$$N + N \rightarrow N_2 \tag{13.619}$$

The bond in the nitrogen molecule comprises a $H_2$-type molecular orbital (MO) with two paired electrons. The force balance equation and radius $r_7$ of the $2p$ shell of $N$ is derived in the Seven-Electron Atoms section. With the formation of the $H_2$-type MO by the contribution of a $2p$ electron from each $N$ atom, a diamagnetic force arises between the remaining $2p$ electrons and the $H_2$-type MO. This force from each $N$ causes the $H_2$-type MO to move to greater principal axes than would result with the Coulombic force alone. But, the integer increase of the central field and the resulting increased Coulombic as well as magnetic central forces on the remaining $2p$ electrons of each $N$ decrease the radius of the corresponding shell such that the energy minimum is achieved that is lower than that of the reactant atoms. The resulting electron configuration of $N_2$ is $1s_1^2 1s_2^2 2s_1^2 2s_2^2 2p_1^2 2p_2^2 \sigma_{1,2}^2$ where the subscript designates the $N$ atom, 1 or 2, $\sigma$ designates the $H_2$-type MO, and the orbital arrangement is:



(13.620)

Nitrogen is predicted to be diamagnetic in agreement with observations.

## FORCE BALANCE OF THE $2p$ SHELL OF THE NITROGEN ATOMS OF THE NITROGEN MOLECULE

For each $N$ atom, force balance for the outermost $2p$ electron of $N_2$ (electron 6) is achieved between the centrifugal force and the Coulombic and magnetic forces that arise due to interactions between electron 6 and the other $2p$-shell as well as the $2s$-shell electrons due to spin and orbital angular momentum. The forces used are derived in the Seven-Electron Atoms section. The central Coulomb force on the outer-most $2p$ shell electron of $N_2$ (electron 6) due to the nucleus and the inner five electrons is given by Eq. (10.70) with the appropriate charge and radius:

$$\mathbf{F}_{ele} = \frac{(Z-5)e^2}{4\pi\varepsilon_0 r_6^2}\mathbf{i_r} \tag{13.621}$$

for $r > r_5$. The $2p$ shell possess an external electric field given by Eq. (10.92) for $r > r_6$. The energy is minimized with conservation of angular momentum. This condition is met when the diamagnetic force, $\mathbf{F}_{diamagnetic}$, of Eq. (10.82) due to the $p$-orbital contribution is the same as that of the reactant nitrogen atoms given by Eq. (10.136) with $r_6$ replacing $r_7$:

$$\begin{aligned}\mathbf{F}_{diamagnetic} &= -\left(\frac{1}{3}\right)\frac{\hbar^2}{4m_e r_6^2 r_3}\sqrt{s(s+1)}\mathbf{i_r}\\ &= -\frac{\hbar^2}{12m_e r_6^2 r_3}\sqrt{\frac{3}{4}}\mathbf{i_r}\end{aligned} \tag{13.622}$$

And, $\mathbf{F}_{mag\ 2}$ corresponding to the conserved orbital angular momentum of the three orbitals is given by Eq. (10.89).

$$\mathbf{F}_{mag\ 2} = \frac{1}{Z}\frac{3\hbar^2}{m_e r_6^2 r_3}\sqrt{s(s+1)}\mathbf{i_r} \tag{13.623}$$

The electric field external to the $2p$ shell given by Eq. (10.92) for $r > r_6$ gives rise to a second diamagnetic force,

$\mathbf{F}_{diamagnetic\ 2}$, given by Eq. (10.93). $\mathbf{F}_{diamagnetic\ 2}$ due to the binding of the p-orbital electron having an electric field of +1 outside of its radius is:

$$\mathbf{F}_{diamagnetic\ 2} = -\left[\frac{Z-6}{Z-5}\right]\left(1-\frac{\sqrt{2}}{2}\right)\frac{r_3\hbar^2}{m_e r_6^4}10\sqrt{s(s+1)}\mathbf{i_r} \tag{13.624}$$

In addition, the contribution of a $2p$ electron from each $N$ atom in the formation of the $\sigma$ MO gives rise to a paramagnetic force on the remaining two $2p$ electrons that pair. The force, $\mathbf{F}_{mag\ 3}$, follows from Eq. (10.11) wherein the two radii are equal to $r_6$ and the direction is positive, central:

$$\mathbf{F}_{mag\ 3} = \frac{\hbar^2}{4m_e r_6^3}\sqrt{s(s+1)}\mathbf{i_r} \tag{13.625}$$

$\mathbf{F}_{mag\ 3}$ is present in additional diatomic molecules where its contribution minimizes the energy. This AO spin-pairing force reduces the radius directly to reduce the energy, and it can also cancel the contribution of the corresponding electron to $\mathbf{F}_{diamagnetic}$ to further reduce the energy.

The radius of the $2p$ shell is calculated by equating the outward centrifugal force to the sum of the electric (Eq. (13.621)) and diamagnetic (Eqs. (13.622) and (13.624)), and paramagnetic (Eqs. (13.623) and (13.625)) forces as follows:

$$\frac{m_e v_6^2}{r_6} = \left(\begin{array}{l} \frac{(Z-5)e^2}{4\pi\varepsilon_0 r_6^2} - \frac{\hbar^2}{12 m_e r_6^2 r_3}\sqrt{s(s+1)} + \frac{3\hbar^2}{Z m_e r_6^2 r_3}\sqrt{s(s+1)} \\ -\left[\frac{Z-6}{Z-5}\right]\left(1-\frac{\sqrt{2}}{2}\right)\frac{r_3\hbar^2}{r_6^4 m_e}10\sqrt{s(s+1)} + \frac{\hbar^2}{4m_e r_6^3}\sqrt{s(s+1)} \end{array}\right) \tag{13.626}$$

Substitution of $v_6 = \frac{\hbar}{m_e r_6}$ (Eq. (1.35)) and $s = \frac{1}{2}$ into Eq. (13.626) gives:

$$\frac{\hbar^2}{m_e r_6^3} - \frac{\hbar^2}{4m_e r_6^3}\sqrt{\frac{3}{4}} = \frac{(Z-5)e^2}{4\pi\varepsilon_0 r_6^2} - \frac{\hbar^2}{12 m_e r_6^2 r_3}\sqrt{\frac{3}{4}} + \frac{3\hbar^2}{Z m_e r_6^2 r_3}\sqrt{\frac{3}{4}} - \left[\frac{Z-6}{Z-5}\right]\left(1-\frac{\sqrt{2}}{2}\right)\frac{r_3\hbar^2}{r_6^4 m_e}10\sqrt{\frac{3}{4}} \tag{13.627}$$

The quadratic equation corresponding to Eq. (13.627) is:

$$r_6^2 - \frac{\frac{\hbar^2}{m_e}\left(1-\frac{\sqrt{3}}{8}\right)}{\left(\frac{(Z-5)e^2}{4\pi\varepsilon_0} - \left(\frac{1}{12}-\frac{3}{Z}\right)\frac{\hbar^2}{m_e r_3}\sqrt{\frac{3}{4}}\right)} r_6 - \frac{\frac{\hbar^2}{m_e}\left[\frac{Z-6}{Z-5}\right]\left(1-\frac{\sqrt{2}}{2}\right) r_3 10\sqrt{\frac{3}{4}}}{\left(\frac{(Z-5)e^2}{4\pi\varepsilon_0} - \left(\frac{1}{12}-\frac{3}{Z}\right)\frac{\hbar^2}{m_e r_3}\sqrt{\frac{3}{4}}\right)} = 0 \tag{13.628}$$

The solution of Eq. (13.628) using the quadratic formula is:

$$r_6 = \frac{\frac{a_0\left(1-\frac{\sqrt{3}}{8}\right)}{\left((Z-5)-\left(\frac{1}{12}-\frac{3}{Z}\right)\frac{\sqrt{3}}{2r_3}\right)} \pm a_0\sqrt{\left(\frac{1-\frac{\sqrt{3}}{8}}{\left((Z-5)-\left(\frac{1}{12}-\frac{3}{Z}\right)\frac{\sqrt{3}}{2r_3}\right)}\right)^2 + \frac{20\sqrt{3}\left(\left[\frac{Z-6}{Z-5}\right]\left(1-\frac{\sqrt{2}}{2}\right)r_3\right)}{\left((Z-5)-\left(\frac{1}{12}-\frac{3}{Z}\right)\frac{\sqrt{3}}{2r_3}\right)}}}{2},\ r_3 \textit{ in units of } a_0 \tag{13.629}$$

The positive root of Eq. (13.629) must be taken in order that $r_6 > 0$. Substitution of $\frac{r_3}{a_0} = 0.69385$ (Eq. (10.62) with $Z = 7$) into Eq. (13.629) gives:

$$r_6 = 0.78402a_0 \tag{13.630}$$

## ENERGIES OF THE $2p$ SHELL OF THE NITROGEN ATOMS OF THE NITROGEN MOLECULE

The central forces on the $2p$ shell of each $N$ are increased with the formation of the $\sigma$ MO, which reduces the shell's radius and increases its total energy. The Coulombic energy terms of the total energy of the two $N$ atoms at the new radius are calculated and added to the energy of the $\sigma$ MO to give the total energy of $N_2$. Then, the bond energy is determined from the total $N_2$ energy.

The radius $r_7$ of each nitrogen atom before bonding is given by Eq. (10.142).

$$r_7 = 0.93084 a_0 \tag{13.631}$$

Using the initial radius $r_7$ of each $N$ atom and the final radius $r_6$ of the $N2p$ shell of $N_2$ (Eq. (13.630)) and by considering that the central Coulombic field decreases by an integer for each successive electron of the shell, the sum $E_T(N_2,2p)$ of the Coulombic energy change of the $N2p$ electrons of both atoms is determined using Eq. (10.102).

$$E_T(N_2,2p) = -2\sum_{n=4}^{5} \frac{(Z-n)e^2}{8\pi\varepsilon_0}\left(\frac{1}{r_6}-\frac{1}{r_7}\right) = -2(13.60580\ eV)(0.20118)(2+3) = -27.37174\ eV \tag{13.632}$$

## FORCE BALANCE OF THE $\sigma$ MO OF THE NITROGEN MOLECULE

The $2p$ shell gives rise to two diamagnetic forces on the $\sigma$ MO. As given for the hydrogen molecule in the Hydrogen-Type Molecules section, the $\sigma$ MO comprises two electrons, $\sigma$ electron 1 and $\sigma$ electron 2, that are bound at $\xi = 0$ as a equipotential prolate spheroidal MO by the central Coulombic field due to the nitrogen atoms at the foci and the spin pairing force on $\sigma$ electron 2 due to $\sigma$ electron 1 that initially has smaller semiprincipal axes. The spin-pairing force given in Eq. (11.200) is equal to one half the centrifugal force of the two electrons. The spin-pairing electron of the $\sigma$ MO is also repelled by the remaining $2p$ electrons of each $N$ according to Lenz law, and the force is based on the total number of these electrons $n_e$ that interact with the binding $\sigma$-MO electron. This diamagnetic force $\mathbf{F}_{diamagneticMO1}$ is of the same form as the molecular spin-pairing force but in the opposite direction. The force follows from the derivations of Eqs. (10.219) and (11.200) which gives:

$$\mathbf{F}_{diamagneticMO1} = \frac{n_e \hbar^2}{4m_e a^2 b^2} D\mathbf{i}_\xi \tag{13.633}$$

In addition, there is a relativistically corrected Lorentz force $\mathbf{F}_{diamagneticMO2}$ on the pairing electron of the $\sigma$ MO that follows from Eqs. (7.15) and (11.200):

$$\mathbf{F}_{diamagneticMO2} = \frac{1}{Z}\frac{|L|\hbar}{2m_e a^2 b^2} D\mathbf{i}_\xi \tag{13.634}$$

where $|L|$ is the magnitude of the angular momentum of each $N$ atom at a focus that is the source of the diamagnetism at the $\sigma$-MO.

The force balance equation for the $\sigma$-MO of the nitrogen molecule given by Eq. (11.200) and Eqs. (13.633-13.634) with $n_e = 2$ and $|L| = \hbar$ is:

$$\frac{\hbar^2}{m_e a^2 b^2} D = \frac{e^2}{8\pi\varepsilon_0 a b^2} D + \frac{\hbar^2}{2m_e a^2 b^2} D - \left(1+\frac{1}{Z}\right)\frac{\hbar^2}{2m_e a^2 b^2} D \tag{13.635}$$

$$\frac{\hbar^2}{m_e a^2 b^2} D = \frac{e^2}{8\pi\varepsilon_0 a b^2} D - \frac{1}{Z}\frac{\hbar^2}{2m_e a^2 b^2} D \tag{13.636}$$

$$\left(2+\frac{1}{Z}\right)\frac{\hbar^2}{2m_e a^2 b^2} D = \frac{e^2}{8\pi\varepsilon_0 a b^2} D \tag{13.637}$$

$$a = \left(2+\frac{1}{Z}\right) a_0 \tag{13.638}$$

Substitution of $Z = 7$ into Eq. (13.638) gives:

$$a = 2.14286 a_0 = 1.13395\ X\ 10^{-10}\ m \tag{13.639}$$

Substitution of Eq. (13.639) into Eq. (11.79) is:

$$c' = 1.03510 a_0 = 5.47750\ X\ 10^{-11}\ m \tag{13.640}$$

The internuclear distance given by multiplying Eq. (13.640) by two is:

$$2c' = 2.07020 a_0 = 1.09550\ X\ 10^{-10}\ m \tag{13.641}$$

The experimental bond distance from Ref. [28] and Ref. [43] is:

$$2c' = 1.09769\ X\ 10^{-10}\ m \tag{13.642}$$

$$2c' = 1.094\ X\ 10^{-10}\ m \tag{13.643}$$

Substitution of Eqs. (13.639-13.640) into Eq. (11.80) is:

$$b = c = 1.87628a_0 = 9.92882\ X\ 10^{-11}\ m \tag{13.644}$$

Substitution of Eqs. (13.639-13.640) into Eq. (11.67) is:

$$e = 0.48305 \tag{13.645}$$

Using the electron configuration of $N_2$ (Eq. (13.620)), the radii of the $N1s = 0.14605a_0$ (Eq. (10.51)), $N2s = 0.69385a_0$ (Eq. (10.62)), and $N2p = 0.78402a_0$ (Eq. (13.630)) shells and the parameters of the $\sigma$ MO of $N_2$ given by Eqs. (13.3-13.4), (13.639-13.641), and (13.644-13.645), the dimensional diagram and charge-density of the $N_2$ MO are shown in Figures 13.14 and 13.15, respectively.

Despite the predictions of standard quantum mechanics that preclude the imaging of a molecular orbital, the full three-dimensional structure of the outer molecular orbital of $N_2$ has been recently tomographically reconstructed [44]. The charge-density surface observed is consistent with that shown in Figure 13.15. This result constitutes direct evidence that electrons are not point-particle probability waves that have no form until they are "collapsed to a point" by measurement. Rather they are physical, two-dimensional equipotential charge density surfaces.

Figure 13.14. The cross section of the $N_2$ MO showing the axes, $\sigma$ MO ($H_2$-type ellipsoidal MO), with the $N$ $1s$, $2s$, and $2p$ atomic orbitals (AOs). Legend: $a$: semimajor axis, $b$: semiminor axis, $c'$: internuclear distance, $r_6$: radius of the $N2p$ shell having two paired electrons.

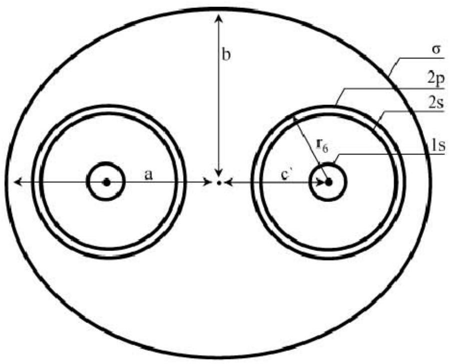
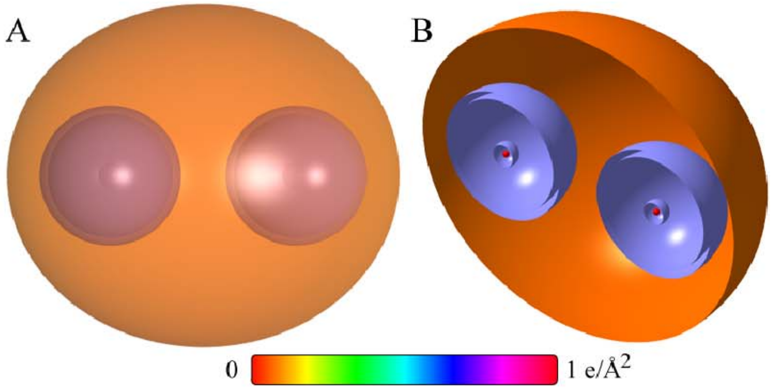


Figure 13.15. $N_2$ MO comprising the $\sigma$ MO ($H_2$-type MO) with $N$ atoms at the foci that have each donated an electron to the $\sigma$ MO and have smaller radii and higher binding energies as a consequence. (A) Color scale, translucent view of the charge-density of the $N_2$ MO. (B) Off-center cut-away view showing the complete inner most $N1s$ shell, and moving radially, the $N2s$ shell, the $N2p$ shell, and the $\sigma$ prolate spheroidal MO that have the $N$ atoms as the foci.



## Sum of the Energies of the $\sigma$ MO and the AOS of the Nitrogen Molecule

The energies of the $N_2$ $\sigma$ MO are given by the substitution of the semiprincipal axes (Eqs. (13.639-13.640) and (13.644)) into the energy equations (Eqs. (11.207-11.212)) of $H_2$:

$$V_e = \frac{-2e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -27.70586\ eV \tag{13.646}$$

$$V_p = \frac{e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}} = 13.14446\ eV \tag{13.647}$$

$$T = \frac{\hbar^2}{2m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = 6.46470\ eV \tag{13.648}$$

$$V_m = \frac{-\hbar^2}{4m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -3.23235\ eV \tag{13.649}$$

$$E_T = V_e + T + V_m + V_p \tag{13.650}$$

Substitution of Eqs. (11.79) and (13.646-13.649) into Eq. (13.650) gives:

$$\begin{aligned} E_T(N_2,\sigma) &= \frac{-e^2}{8\pi\varepsilon_0\sqrt{\frac{aa_0}{2}}}\left(\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+\sqrt{\frac{aa_0}{2}}}{a-\sqrt{\frac{aa_0}{2}}}-1\right) \\ &= -11.32906\ eV \end{aligned} \tag{13.651}$$

where $E_T(N_2,\sigma)$ is the total energy of the $\sigma$ MO of $N_2$. The sum, $E_T(N_2)$, of $E_T(N_2,2p)$, the $2p$ (AO) contribution given by Eq. (13.632), and $E_T(N_2,\sigma)$, the $\sigma$ MO contribution given by Eq. (13.651) is:

$$\begin{aligned} E_T(N_2) &= E_T(N_2,2p)+E_T(N_2,\sigma) \\ &= -27.37174\ eV - 11.32906\ eV = -38.70080\ eV \end{aligned} \tag{13.652}$$

## VIBRATION OF $N_2$

The vibrational energy levels of $N_2$ may be solved by determining the Morse potential curve from the energy relationships for the transition from two $N$ atoms whose parameters are given by Eqs. (10.134-10.143) to the two $N$ atoms whose parameter $r_6$ is given by Eq. (13.630) and the $\sigma$ MO whose parameters are given by Eqs. (13.639-13.641) and (13.644-13.645). As shown in the Vibration of Hydrogen-type Molecular Ions section, the harmonic oscillator potential energy function can be expanded about the internuclear distance and expressed as a Maclaurin series corresponding to a Morse potential after Karplus and Porter (K&P) [15] and after Eq. (11.134). Treating the Maclaurin series terms as anharmonic perturbation terms of the harmonic states, the energy corrections can be found by perturbation methods.

## THE DOPPLER ENERGY TERMS OF THE NITROGEN MOLECULE

The equations of the radiation reaction force of nitrogen are the same as those of $H_2$ with the substitution of the nitrogen parameters. Using Eqs. (11.231-11.233), the angular frequency of the reentrant oscillation in the transition state is:

$$\begin{aligned} \omega &= \sqrt{\frac{\frac{e^2}{4\pi\varepsilon_0 a^3}}{m_e}} \\ &= 1.31794\ X\ 10^{16}\ rad/s \end{aligned} \tag{13.653}$$

where $a$ is given by Eq. (13.639). The kinetic energy, $E_K$, is given by Planck's equation (Eq. (11.127)):

$$\begin{aligned} \bar{E}_K &= \hbar\omega \\ &= \hbar 1.31794\ X\ 10^{16}\ rad/s = 8.67490\ eV \end{aligned} \tag{13.654}$$

In Eq. (11.181), substitution of $E_T(N_2)$ for $E_{h\nu}$, the mass of the electron, $m_e$, for $M$, and the kinetic energy given by Eq. (13.654) for $\bar{E}_K$ gives the Doppler energy of the electrons of the reentrant orbit:

$$\begin{aligned} \bar{E}_D &\cong E_{h\nu}\sqrt{\frac{2\bar{E}_K}{Mc^2}} \\ &= -38.70080\ eV\sqrt{\frac{2e(8.67490\ eV)}{m_e c^2}} = -0.22550\ eV \end{aligned} \tag{13.655}$$

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency. The decrease in the energy of the $N_2$ MO due to the reentrant orbit in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei, $\bar{E}_{osc}$, is given by the sum of the corresponding energies, $\bar{E}_D$ given by Eq. (13.655) and $\bar{E}_{Kvib}$, the average kinetic energy of vibration which is 1/2 of the vibrational energy. Using the experimental $N_2$ $\omega_e$ of 2358.57 $cm^{-1}$ $(0.29243\ eV)$ [28] for $\bar{E}_{Kvib}$ of the transition state, $\bar{E}_{osc}(N_2)$ is:

$$\bar{E}_{osc}(N_2) = \bar{E}_D + \bar{E}_{Kvib} = \bar{E}_D + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \tag{13.656}$$

$$\begin{aligned} \bar{E}_{osc}(N_2) &= -0.22550\ eV + \frac{1}{2}(0.29243\ eV) \\ &= -0.07929\ eV \end{aligned} \tag{13.657}$$

## TOTAL AND BOND ENERGIES OF THE NITROGEN MOLECULE

$E_{T+osc}(N_2)$, the total energy of $N_2$ including the Doppler term, is given by the sum of $E_T(N_2)$ (Eq. (13.652)) and $\bar{E}_{osc}(N_2)$ given by Eq. (13.657):

$$\begin{aligned} E_{T+osc}(N_2) &= V_e + T + V_m + V_p + E_T(N_2, 2p) + \bar{E}_{osc}(N_2) \\ &= E_T(N_2, \sigma) + E_T(N_2, 2p) + \bar{E}_{osc}(N_2) = E_T(N_2) + \bar{E}_{osc}(N_2) \end{aligned} \tag{13.658}$$

$$\begin{aligned} E_{T+osc}(N_2) &= \left\{ \begin{array}{l} \left( \dfrac{-e^2}{8\pi\varepsilon_0\sqrt{\dfrac{aa_0}{2}}} \left( \left(2 - \dfrac{1}{2}\dfrac{a_0}{a}\right) \ln \dfrac{a + \sqrt{\dfrac{aa_0}{2}}}{a - \sqrt{\dfrac{aa_0}{2}}} - 1 \right) - 2\displaystyle\sum_{n=4}^{5} \dfrac{(Z-n)e^2}{8\pi\varepsilon_0} \left( \dfrac{1}{r_6} - \dfrac{1}{r_7} \right) \right) \\ \left( 1 + \sqrt{\dfrac{2\hbar\sqrt{\dfrac{\dfrac{e^2}{4\pi\varepsilon_0 a^3}}{m_e}}}{m_e c^2}} \right) + \dfrac{1}{2}\hbar\sqrt{\dfrac{k}{\mu}} \end{array} \right\} \\ &= -38.70080\ eV - 0.22550\ eV + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \end{aligned} \tag{13.659}$$

From Eqs. (13.656-13.659), the total energy of the $N_2$ MO is:

$$\begin{aligned} E_{T+osc}(N_2) &= -38.70080\ eV + \bar{E}_{osc}(N_2) \\ &= -38.70080\ eV - 0.22550\ eV + \frac{1}{2}(0.29243\ eV) = -38.78009\ eV \end{aligned} \tag{13.660}$$

where the experimental $\omega_e$ was used for the $\hbar\sqrt{\dfrac{k}{\mu}}$ term.

The $N_2$ bond dissociation energy, $E_D(N_2)$, is given by the difference in the total energies of the two $N$ atoms and $E_{T+osc}(N_2)$:

$$E_D(N_2) = 2E(N) - E_{T+osc}(N_2) \tag{13.661}$$

where the energy of a nitrogen atom is [6] :

$$E(N) = -14.53414\ eV \tag{13.662}$$

Thus, the $N_2$ bond dissociation energy, $E_D(N_2)$, given by Eqs. (13.660-13.662) is:

$$E_D(N_2) = -2(14.53414\ eV) - E_{T+osc}(N_2) = -29.06828\ eV - (-38.78009\ eV) = 9.71181\ eV \tag{13.663}$$

The experimental $N_2$ bond dissociation energy from Ref. [43] and Ref. [45] is:

$$E_D(N_2) = 9.756\ eV \tag{13.664}$$

$$E_D(N_2) = 9.764\ eV \tag{13.665}$$

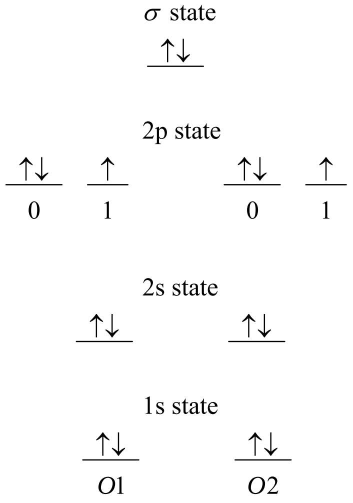
The results of the determination of bond parameters of $N_2$ are given in Table 13.1. The calculated results are based on first principles and given in closed-form, exact equations containing fundamental constants only. The agreement between the experimental and calculated results is excellent.

## OXYGEN MOLECULE

The oxygen molecule can be formed by the reaction of two oxygen atoms:

$$O + O \rightarrow O_2 \tag{13.666}$$

The bond in the oxygen molecule comprises a $H_2$-type molecular orbital (MO) with two paired electrons. The force balance equation and radius $r_8$ of the $2p$ shell of $O$ is derived in the Eight-Electron Atoms section. With the formation of the $H_2$-type MO by the contribution of a $2p$ electron from each $O$ atom, a diamagnetic force arises between the remaining $2p$ electrons and the $H_2$-type MO. This force from each $O$ causes the $H_2$-type MO to move to greater principal axes than would result with the Coulombic force alone. But, the integer increase of the central field and the resulting increased Coulombic as well as magnetic central forces on the remaining $2p$ electrons of each $O$ decrease the radius of the corresponding shell such that the energy minimum is achieved that is lower than that of the reactant atoms. The resulting electron configuration of $O_2$ is $1s_1^2 1s_2^2 2s_1^2 2s_2^2 2p_1^3 2p_2^3 \sigma_{1,2}^2$ where the subscript designates the $O$ atom, 1 or 2, $\sigma$ designates the $H_2$-type MO, and the orbital arrangement is:



(13.667)

Oxygen is predicted to be paramagnetic in agreement with observations [42].

## FORCE BALANCE OF THE $2p$ SHELL OF THE OXYGEN ATOMS OF THE OXYGEN MOLECULE

For each $O$ atom, force balance for the outermost $2p$ electron of $O_2$ (electron 7) is achieved between the centrifugal force and the Coulombic and magnetic forces that arise due to interactions between electron 7 and the other $2p$-shell as well as the $2s$-shell electrons due to spin and orbital angular momentum. The forces used are derived in the Eight-Electron Atoms section. The central Coulomb force on the outer-most $2p$ shell electron of $O_2$ (electron 7) due to the nucleus and the inner six electrons is given by Eq. (10.70) with the appropriate charge and radius:

$$\mathbf{F}_{ele} = \frac{(Z-6)e^2}{4\pi\varepsilon_0 r_7^2}\mathbf{i_r} \tag{13.668}$$

for $r > r_6$. The $2p$ shell possess an external electric field given by Eq. (10.92) for $r > r_7$. The energy is minimized with conservation of angular momentum. This condition is met when the magnetic forces are the same as those of the reactant oxygen atoms with $r_7$ replacing $r_8$. The diamagnetic force, $\mathbf{F}_{diamagnetic}$, of Eq. (10.82) due to the $p$-orbital contributions is given by Eq. (10.156):

$$\mathbf{F}_{diamagnetic} = -\left(\frac{1}{3}+\frac{2}{3}\right)\frac{\hbar^2}{4m_e r_7^2 r_3}\sqrt{s(s+1)}\mathbf{i_r} = -\frac{3\hbar^2}{12m_e r_7^2 r_3}\sqrt{\frac{3}{4}}\mathbf{i_r} \tag{13.669}$$

And, $\mathbf{F}_{mag\ 2}$ corresponding to the conserved spin and orbital angular momentum given by Eq. (10.157) is:

$$\mathbf{F}_{mag\ 2} = \frac{1}{Z}\frac{2\hbar^2}{m_e r_7^2 r_3}\sqrt{s(s+1)}\mathbf{i_r} \tag{13.670}$$

The electric field external to the $2p$ shell given by Eq. (10.92) for $r > r_7$ gives rise to a second diamagnetic force, $\mathbf{F}_{diamagnetic\ 2}$, given by Eq. (10.93). $\mathbf{F}_{diamagnetic\ 2}$ due to the binding of the p-orbital electron having an electric field of +1 outside of its radius is :

$$\mathbf{F}_{diamagnetic\ 2} = -\left[\frac{Z-7}{Z-6}\right]\left(1-\frac{\sqrt{2}}{2}\right)\frac{r_3\hbar^2}{m_e r_7^4}10\sqrt{s(s+1)}\mathbf{i_r} \tag{13.671}$$

The radius of the $2p$ shell is calculated by equating the outward centrifugal force to the sum of the electric (Eq. (13.688)) and diamagnetic (Eqs. (13.669) and (13.671)), and paramagnetic (Eq. (13.670)) forces as follows:

$$\frac{m_e v_7^2}{r_7} = \left(\begin{array}{l} \frac{(Z-6)e^2}{4\pi\varepsilon_0 r_7^2} - \frac{3\hbar^2}{12m_e r_7^2 r_3}\sqrt{s(s+1)} + \frac{2\hbar^2}{Zm_e r_7^2 r_3}\sqrt{s(s+1)} \\ -\left[\frac{Z-7}{Z-6}\right]\left(1-\frac{\sqrt{2}}{2}\right)\frac{r_3\hbar^2}{r_7^4 m_e}10\sqrt{s(s+1)} \end{array}\right) \tag{13.672}$$

Substitution of $v_7 = \frac{\hbar}{m_e r_7}$ (Eq. (1.35)) and $s = \frac{1}{2}$ into Eq. (13.672) gives:

$$\frac{\hbar^2}{m_e r_7^3} = \frac{(Z-6)e^2}{4\pi\varepsilon_0 r_7^2} - \frac{3\hbar^2}{12m_e r_7^2 r_3}\sqrt{\frac{3}{4}} + \frac{2\hbar^2}{Zm_e r_7^2 r_3}\sqrt{\frac{3}{4}} - \left[\frac{Z-7}{Z-6}\right]\left(1-\frac{\sqrt{2}}{2}\right)\frac{r_3\hbar^2}{r_7^4 m_e}10\sqrt{\frac{3}{4}} \tag{13.673}$$

The quadratic equation corresponding to Eq. (13.673) is:

$$r_7^2 - \frac{\dfrac{\hbar^2}{m_e}}{\left(\dfrac{(Z-6)e^2}{4\pi\varepsilon_0} - \left(\dfrac{3}{12}-\dfrac{2}{Z}\right)\dfrac{\hbar^2}{m_e r_3}\sqrt{\dfrac{3}{4}}\right)} r_7 - \frac{\dfrac{\hbar^2}{m_e}\left[\dfrac{Z-7}{Z-6}\right]\left(1-\dfrac{\sqrt{2}}{2}\right) r_3 10\sqrt{\dfrac{3}{4}}}{\left(\dfrac{(Z-6)e^2}{4\pi\varepsilon_0} - \left(\dfrac{3}{12}-\dfrac{2}{Z}\right)\dfrac{\hbar^2}{m_e r_3}\sqrt{\dfrac{3}{4}}\right)} = 0 \quad (13.674)$$

The solution of Eq. (13.674) using the quadratic formula is:

$$r_7 = \frac{\dfrac{a_0}{\left((Z-6)-\left(\dfrac{3}{12}-\dfrac{2}{Z}\right)\dfrac{\sqrt{3}}{2r_3}\right)} \pm a_0 \sqrt{\left(\dfrac{1}{\left((Z-6)-\left(\dfrac{3}{12}-\dfrac{2}{Z}\right)\dfrac{\sqrt{3}}{2r_3}\right)}\right)^2 + \dfrac{20\sqrt{3}\left(\left[\dfrac{Z-7}{Z-6}\right]\left(1-\dfrac{\sqrt{2}}{2}\right)r_3\right)}{\left((Z-6)-\left(\dfrac{3}{12}-\dfrac{2}{Z}\right)\dfrac{\sqrt{3}}{2r_3}\right)}}}{2}, \; r_3 \textit{ in units of } a_0 \quad (13.675)$$

The positive root of Eq. (13.675) must be taken in order that $r_7 > 0$. Substitution of $\frac{r_3}{a_0} = 0.59020$ (Eq. (10.62) with $Z = 8$) into Eq. (13.675) gives:

$$r_7 = 0.91088 a_0 \quad (13.676)$$

## ENERGIES OF THE $2p$ SHELL OF THE OXYGEN ATOMS OF THE OXYGEN MOLECULE

The central forces on the $2p$ shell of each $O$ are increased with the formation of the $\sigma$ MO, which reduces the shell's radius and increases its total energy. The Coulombic energy terms of the total energy of the two $O$ atoms at the new radius are calculated and added to the energy of the $\sigma$ MO to give the total energy of $O_2$. Then, the bond energy is determined from the total $O_2$ energy.

The radius $r_8$ of each oxygen atom before bonding is given by Eq. (10.162).

$$r_8 = a_0 \quad (13.677)$$

Using the initial radius $r_8$ of each $O$ atom and the final radius $r_7$ of the $O2p$ shell of $O_2$ (Eq. (13.676)) and by considering that the central Coulombic field decreases by an integer for each successive electron of the shell, the sum $E_T(O_2, 2p)$ of the Coulombic energy change of the $O2p$ electrons of both atoms is determined using Eq. (10.102):

$$\begin{aligned} E_T(O_2, 2p) &= -2\sum_{n=4}^{6} \frac{(Z-n)e^2}{8\pi\varepsilon_0}\left(\frac{1}{r_7}-\frac{1}{r_8}\right) \\ &= -2(13.60580\ eV)(0.09784)(2+3+4) = -23.96074\ eV \end{aligned} \quad (13.678)$$

## FORCE BALANCE OF THE $\sigma$ MO OF THE OXYGEN MOLECULE

The force balance equation for the $\sigma$-MO of the oxygen molecule given by Eq. (11.200) and Eqs. (13.633-13.634) with $n_e = 3$ and $|L| = \sqrt{\frac{3}{4}}\hbar$ is:

$$\frac{\hbar^2}{m_e a^2 b^2} D = \frac{e^2}{8\pi\varepsilon_0 a b^2} D + \frac{\hbar^2}{2m_e a^2 b^2} D - \left(\frac{3}{2} + \frac{\sqrt{\frac{3}{4}}}{Z}\right)\frac{\hbar^2}{2m_e a^2 b^2} D \quad (13.679)$$

$$\frac{\hbar^2}{m_e a^2 b^2} D = \frac{e^2}{8\pi\varepsilon_0 a b^2} D - \left(\frac{1}{2} + \frac{\sqrt{\frac{3}{4}}}{Z}\right)\frac{\hbar^2}{2m_e a^2 b^2} D \quad (13.680)$$

$$\left(\frac{5}{2}+\frac{\sqrt{\frac{3}{4}}}{Z}\right)\frac{\hbar^2}{2m_e a^2 b^2}D=\frac{e^2}{8\pi\varepsilon_0 ab^2}D \tag{13.681}$$

$$a=\left(\frac{5}{2}+\frac{\sqrt{\frac{3}{4}}}{Z}\right)a_0 \tag{13.682}$$

Substitution of $Z=8$ into Eq. (13.682) gives:

$$a=2.60825a_0=1.38023\ X\ 10^{-10}\ m \tag{13.683}$$

Substitution of Eq. (13.683) into Eq. (11.79) is:

$$c'=1.14198a_0=6.04312\ X\ 10^{-11}\ m \tag{13.684}$$

The internuclear distance given by multiplying Eq. (13.684) by two is:

$$2c'=2.28397a_0=1.20862\ X\ 10^{-10}\ m \tag{13.685}$$

The experimental bond distance is [28] :

$$2c'=1.20752\ X\ 10^{-10}\ m \tag{13.686}$$

Substitution of Eqs. (13.683-13.684) into Eq. (11.80) is:

$$\begin{aligned} b=c&=2.34496a_0\\ &=1.24090\ X\ 10^{-10}\ m \end{aligned} \tag{13.687}$$

Substitution of Eqs. (13.683-13.684) into Eq. (11.67) is:

$$e=0.43783 \tag{13.688}$$

Using the electron configuration of $O_2$ (Eq. (13.667)), the radii of the $O1s=0.12739a_0$ (Eq. (10.51)), $O2s=0.59020a_0$ (Eq. (10.62)), and $O2p=0.91088a_0$ (Eq. (13.676)) shells and the parameters of the $\sigma$ MO of $O_2$ given by Eqs. (13.3-13.4), (13.683-13.685), and (13.687-13.688), the dimensional diagram and charge-density of the $O_2$ MO are shown in Figures 13.16 and 13.17, respectively.

Figure 13.16. The cross section of the $O_2$ MO showing the axes, $\sigma$ MO ($H_2$-type ellipsoidal MO), with the $O$ $1s$, $2s$, and $2p$ atomic orbitals (AOs). Legend: $a$: semimajor axis, $b$: semiminor axis, $c'$: internuclear distance, $r_7$: radius of the $O2p$ shell having two paired electrons.

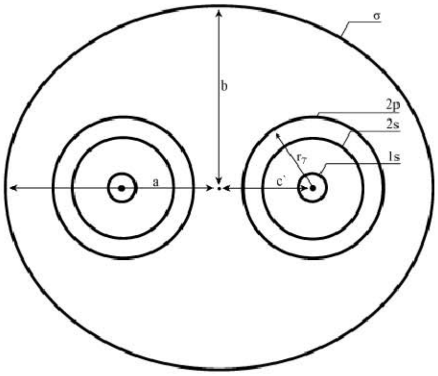
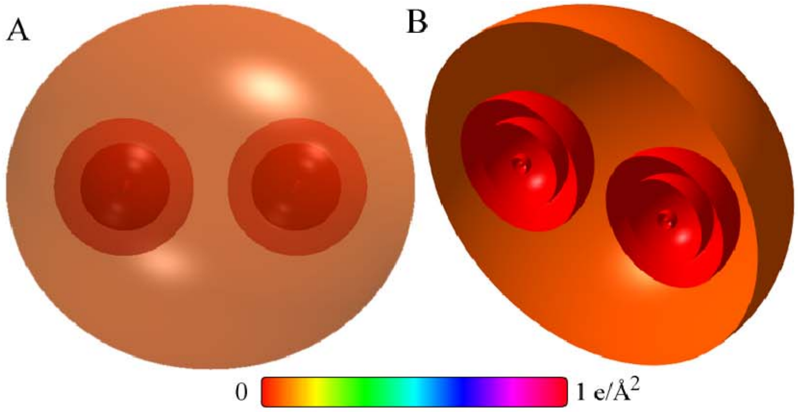


Figure 13.17. $O_2$ MO comprising the $\sigma$ MO ($H_2$-type MO) with $O$ atoms at the foci that have each donated an electron to the $\sigma$ MO and have smaller radii and higher binding energies as a consequence. (A) Color scale, translucent view of the charge-density of the $O_2$ MO. (B) Off-center cut-away view showing the complete inner most $O1s$ shell, and moving radially, the $O2s$ shell, the $O2p$ shell, and the $\sigma$ prolate spheroidal MO that have the $O$ atoms as the foci.



## SUM OF THE ENERGIES OF THE $\sigma$ MO AND THE AOs OF THE OXYGEN MOLECULE

The energies of the $O_2$ $\sigma$ MO are given by the substitution of the semiprincipal axes (Eqs. (13.683-13.684) and (13.687)) into the energy equations (Eqs. (11.207-11.212)) of $H_2$:

$$V_e = \frac{-2e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}} \ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -22.37716\ eV \tag{13.689}$$

$$V_p = \frac{e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}} = 11.91418\ eV \tag{13.690}$$

$$T = \frac{\hbar^2}{2m_e a\sqrt{a^2-b^2}} \ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = 4.28968\ eV \tag{13.691}$$

$$V_m = \frac{-\hbar^2}{4m_e a\sqrt{a^2-b^2}} \ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -2.14484\ eV \tag{13.692}$$

$$E_T = V_e + T + V_m + V_p \tag{13.693}$$

Substitution of Eqs. (11.79) and (13.689-13.692) into Eq. (13.693) gives:

$$E_T\left(O_2,\sigma\right) = \frac{-e^2}{8\pi\varepsilon_0\sqrt{\frac{aa_0}{2}}}\left(\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+\sqrt{\frac{aa_0}{2}}}{a-\sqrt{\frac{aa_0}{2}}}-1\right) \tag{13.694}$$
$$= -8.31814\ eV$$

where $E_T\left(O_2,\sigma\right)$ is the total energy of the $\sigma$ MO of $O_2$. The sum, $E_T\left(O_2\right)$, of $E_T\left(O_2,2p\right)$, the $2p$ AO contribution given by: Eq. (13.678), and $E_T\left(O_2,\sigma\right)$, the $\sigma$ MO contribution given by Eq. (13.694) is:

$$E_T\left(O_2\right) = E_T\left(O_2,2p\right) + E_T\left(O_2,\sigma\right) = -23.96074\ eV - 8.31814\ eV = -32.27888\ eV \tag{13.695}$$

## VIBRATION OF $O_2$

The vibrational energy levels of $O_2$ may be solved by determining the Morse potential curve from the energy relationships for the transition from two $O$ atoms whose parameters are given by Eqs. (10.154-10.163) to the two $O$ atoms whose parameter $r_7$ is given by Eq. (13.676) and the $\sigma$ MO whose parameters are given by Eqs. (13.683-13.685) and (13.687-13.688). As shown in the Vibration of Hydrogen-type Molecular Ions section, the harmonic oscillator potential energy function can be expanded about the internuclear distance and expressed as a Maclaurin series corresponding to a Morse potential after Karplus and Porter (K&P) [15] and after Eq. (11.134). Treating the Maclaurin series terms as anharmonic perturbation terms of the harmonic states, the energy corrections can be found by perturbation methods.

## THE DOPPLER ENERGY TERMS OF THE OXYGEN MOLECULE

The equations of the radiation reaction force of oxygen are the same as those of $H_2$ with the substitution of the oxygen parameters. Using Eqs. (11.231-11.233), the angular frequency of the reentrant oscillation in the transition state is:

$$\omega = \sqrt{\frac{\frac{e^2}{4\pi\varepsilon_0 a^3}}{m_e}} = 9.81432\ X\ 10^{16}\ rad/s \tag{13.696}$$

where $a$ is given by Eq. (13.683). The kinetic energy, $E_K$, is given by Planck's equation (Eq. (11.127)).

$$\overline{E}_K = \hbar\omega = \hbar 9.81432\ X\ 10^{16}\ rad/s = 6.45996\ eV \tag{13.697}$$

In Eq. (11.181), substitution of $E_T\left(O_2\right)$ for $E_{h\nu}$, the mass of the electron, $m_e$, for $M$, and the kinetic energy given by Eq. (13.697) for $\overline{E}_K$ gives the Doppler energy of the electrons of the reentrant orbit:

$$\overline{E}_D \cong E_{h\nu}\sqrt{\frac{2\overline{E}_K}{Mc^2}} = -32.27888\ eV\sqrt{\frac{2e\left(6.45996\ eV\right)}{m_e c^2}} = -0.16231\ eV \tag{13.698}$$

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency. The decrease in the energy of the $O_2$ MO due to the reentrant orbit in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei, $\bar{E}_{osc}$, is given by the sum of the corresponding energies, $\bar{E}_D$ given by Eq. (13.698) and $\bar{E}_{Kvib}$, the average kinetic energy of vibration which is 1/2 of the vibrational energy. Using the experimental $O_2$ $\omega_e$ of 1580.19 $cm^{-1}$ $(0.19592\ eV)$ [28] for $\bar{E}_{Kvib}$ of the transition state, $\bar{E}_{osc}(O_2)$ is:

$$\bar{E}_{osc}(O_2) = \bar{E}_D + \bar{E}_{Kvib} = \bar{E}_D + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \tag{13.699}$$

$$\bar{E}_{osc}(O_2) = -0.16231\ eV + \frac{1}{2}(0.19592\ eV) = -0.06435\ eV \tag{13.700}$$

## TOTAL AND BOND ENERGIES OF THE OXYGEN MOLECULE

$E_{T+osc}(O_2)$, the total energy of $O_2$ including the Doppler term, is given by the sum of $E_T(O_2)$ (Eq. (13.695)) and $\bar{E}_{osc}(O_2)$ given by Eq. (13.700):

$$\begin{aligned} E_{T+osc}(O_2) &= V_e + T + V_m + V_p + E_T(O_2, 2p) + \bar{E}_{osc}(O_2) \\ &= E_T(O_2, \sigma) + E_T(O_2, 2p) + \bar{E}_{osc}(O_2) \\ &= E_T(O_2) + \bar{E}_{osc}(O_2) \end{aligned} \tag{13.701}$$

$$\begin{aligned} E_{T+osc}(O_2) &= \left\{ \begin{array}{l} \left( \dfrac{-e^2}{8\pi\varepsilon_0\sqrt{\dfrac{aa_0}{2}}} \left( \left(2 - \dfrac{1}{2}\dfrac{a_0}{a}\right) \ln \dfrac{a + \sqrt{\dfrac{aa_0}{2}}}{a - \sqrt{\dfrac{aa_0}{2}}} - 1 \right) - 2\sum_{n=4}^{6} \dfrac{(Z-n)e^2}{8\pi\varepsilon_0}\left(\dfrac{1}{r_7} - \dfrac{1}{r_8}\right) \right) \\ \left( 1 + \sqrt{\dfrac{2\hbar\sqrt{\dfrac{\dfrac{e^2}{4\pi\varepsilon_0 a^3}}{m_e}}}{m_e c^2}} \right) + \dfrac{1}{2}\hbar\sqrt{\dfrac{k}{\mu}} \end{array} \right\} \\ &= -32.27888\ eV - 0.16231\ eV + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \end{aligned} \tag{13.702}$$

From Eqs. (13.699-13.702), the total energy of the $O_2$ MO is:

$$\begin{aligned} E_{T+osc}(O_2) &= -32.27888\ eV + \bar{E}_{osc}(O_2) \\ &= -32.27888\ eV - 0.16231\ eV + \frac{1}{2}(0.19592\ eV) \\ &= -32.34323\ eV \end{aligned} \tag{13.703}$$

where the experimental $\omega_e$ was used for the $\hbar\sqrt{\frac{k}{\mu}}$ term.

The $O_2$ bond dissociation energy, $E_D(O_2)$, is given by the difference in the total energies of the two $O$ atoms and $E_{T+osc}(O_2)$:

$$E_D(O_2) = 2E(O) - E_{T+osc}(O_2) \tag{13.704}$$

where the energy of an oxygen atom is [6]:

$$E(O) = -13.61806\ eV \tag{13.705}$$

Thus, the $O_2$ bond dissociation energy, $E_D(O_2)$, given by Eqs. (13.703-13.705) is:

$$E_D(O_2) = -2(13.61806\ eV) - E_{T+osc}(O_2) = -27.23612\ eV - (-32.34323\ eV) = 5.10711\ eV \tag{13.706}$$

The experimental $O_2$ bond dissociation energy from Ref. [46] and Ref. [47] is:

$$E_D(O_2) = 5.11665\ eV \tag{13.707}$$

$$E_D(O_2) = 5.116696\ eV \tag{13.708}$$

The results of the determination of bond parameters of $O_2$ are given in Table 13.1. The calculated results are based on first principles and given in closed-form, exact equations containing fundamental constants only. The agreement between the experimental and calculated results is excellent.

## FLUORINE MOLECULE

The fluorine molecule can be formed by the reaction of two fluorine atoms:

$$F + F \to F_2 \tag{13.709}$$

The bond in the fluorine molecule comprises a $H_2$-type molecular orbital (MO) with two paired electrons. The force balance equation and radius $r_9$ of the $2p$ shell of $F$ is derived in the Nine-Electron Atoms section. With the formation of the $H_2$-type MO by the contribution of a $2p$ electron from each $F$ atom, a diamagnetic force arises between the remaining $2p$ electrons and the $H_2$-type MO. This force from each $F$ causes the $H_2$-type MO to move to greater principal axes than would result with the Coulombic force alone. But, the integer increase of the central field and the resulting increased Coulombic as well as magnetic central forces on the remaining $2p$ electrons of each $F$ decrease the radius of the corresponding shell such that the energy minimum is achieved that is lower than that of the reactant atoms. The resulting electron configuration of $F_2$ is $1s_1^2 1s_2^2 2s_1^2 2s_2^2 2p_1^4 2p_2^4 \sigma_{1,2}^2$ where the subscript designates the $F$ atom, 1 or 2, $\sigma$ designates the $H_2$-type MO, and the orbital arrangement is:

$\sigma$ state
↑↓

2p state
↑↓ ↑↓ ↑↓ ↑↓
0 1 0 1
(13.710)

2s state
↑↓ ↑↓

1s state
↑↓ ↑↓
$F1$ $F2$

Fluorine is predicted to be diamagnetic in agreement with observations [42].

## FORCE BALANCE OF THE $2p$ SHELL OF THE FLUORINE ATOMS OF THE FLUORINE MOLECULE

For each $F$ atom, force balance for the outermost $2p$ electron of $F_2$ (electron 8) is achieved between the centrifugal force and the Coulombic and magnetic forces that arise due to interactions between electron 8 and the other $2p$-shell as well as the $2s$-shell electrons due to spin and orbital angular momentum. The forces used are derived in the Nine-Electron Atoms section. The central Coulomb force on the outer-most $2p$ shell electron of $F_2$ (electron 8) due to the nucleus and the inner seven electrons is given by Eq. (10.70) with the appropriate charge and radius:

$$\mathbf{F}_{ele} = \frac{(Z-7)e^2}{4\pi\varepsilon_0 r_8^2}\mathbf{i_r} \tag{13.711}$$

for $r > r_7$. The $2p$ shell possess an external electric field given by Eq. (10.92) for $r > r_8$. The energy is minimized with conservation of angular momentum. This condition is met when the diamagnetic force, $\mathbf{F}_{diamagnetic}$, of Eq. (10.82) due to the $p$-orbital contributions is the same as that of the reactant fluorine atoms given by Eq. (10.176) with $r_8$ replacing $r_9$:

$$\begin{aligned} \mathbf{F}_{diamagnetic} &= -\left(\frac{2}{3}\right)\frac{\hbar^2}{4m_e r_8^2 r_3}\sqrt{s(s+1)}\mathbf{i_r} \\ &= -\frac{2\hbar^2}{12m_e r_8^2 r_3}\sqrt{\frac{3}{4}}\mathbf{i_r} \end{aligned} \tag{13.712}$$

Thus, $\mathbf{F}_{diamagnetic}$ due to the two filled $2p$ orbitals per $F$ atom is twice that of $N_2$ given by Eq. (13.622) having one filled $2p$ orbital per $N$ atom. $\mathbf{F}_{mag\ 2}$ corresponding to the conserved spin and orbital angular momentum is also the same as that of the reactant fluorine atoms given by Eq. (10.177) and that of $N_2$ given by Eq. (13.623) where the outer radius of the $2p$ shell of the

$F$ atoms of $F_2$ is $r_8$.

$$\mathbf{F}_{mag\ 2} = \frac{1}{Z}\frac{3\hbar^2}{m_e r_8^2 r_3}\sqrt{s(s+1)}\mathbf{i_r} \tag{13.713}$$

The electric field external to the $2p$ shell given by Eq. (10.92) for $r > r_8$ gives rise to a second diamagnetic force, $\mathbf{F}_{diamagnetic\ 2}$, given by Eq. (10.93). $\mathbf{F}_{diamagnetic\ 2}$ due to the binding of the p-orbital electron having an electric field of +1 outside of its radius is :

$$\mathbf{F}_{diamagnetic\ 2} = -\left[\frac{Z-8}{Z-7}\right]\left(1-\frac{\sqrt{2}}{2}\right)\frac{r_3\hbar^2}{m_e r_8^4}10\sqrt{s(s+1)}\mathbf{i_r} \tag{13.714}$$

In addition, the contribution of a $2p$ electron from each $F$ atom in the formation of the $\sigma$ MO gives rise to a paramagnetic force on the remaining paired $2p$ electrons. The force $\mathbf{F}_{mag\ 3}$ is given by Eq. (13.625) wherein the radius is $r_8$:

$$\mathbf{F}_{mag\ 3} = \frac{\hbar^2}{4m_e r_8^3}\sqrt{s(s+1)}\mathbf{i_r} \tag{13.715}$$

The radius of the $2p$ shell is calculated by equating the outward centrifugal force to the sum of the electric (Eq. (13.711)) and diamagnetic (Eqs. (13.712) and (13.714)), and paramagnetic (Eqs. (13.713) and (13.715)) forces as follows:

$$\frac{m_e v_8^2}{r_8} = \left(\begin{array}{c} \frac{(Z-7)e^2}{4\pi\varepsilon_0 r_8^2} - \frac{2\hbar^2}{12 m_e r_8^2 r_3}\sqrt{s(s+1)} + \frac{3\hbar^2}{Z m_e r_8^2 r_3}\sqrt{s(s+1)} \\ -\left[\frac{Z-8}{Z-7}\right]\left(1-\frac{\sqrt{2}}{2}\right)\frac{r_3\hbar^2}{r_8^4 m_e}10\sqrt{s(s+1)} + \frac{\hbar^2}{4m_e r_8^3}\sqrt{s(s+1)} \end{array}\right) \tag{13.716}$$

Substitution of $v_8 = \frac{\hbar}{m_e r_8}$ (Eq. (1.35)) and $s = \frac{1}{2}$ into Eq. (13.716) gives:

$$\frac{\hbar^2}{m_e r_8^3} - \frac{\hbar^2}{4m_e r_8^3}\sqrt{\frac{3}{4}} = \frac{(Z-7)e^2}{4\pi\varepsilon_0 r_8^2} - \frac{2\hbar^2}{12 m_e r_8^2 r_3}\sqrt{\frac{3}{4}} + \frac{3\hbar^2}{Z m_e r_8^2 r_3}\sqrt{\frac{3}{4}} - \left[\frac{Z-8}{Z-7}\right]\left(1-\frac{\sqrt{2}}{2}\right)\frac{r_3\hbar^2}{r_8^4 m_e}10\sqrt{\frac{3}{4}} \tag{13.717}$$

The quadratic equation corresponding to Eq. (13.717) is:

$$r_8^2 - \frac{\frac{\hbar^2}{m_e}\left(1-\frac{\sqrt{3}}{8}\right)}{\left(\frac{(Z-7)e^2}{4\pi\varepsilon_0} - \left(\frac{2}{12}-\frac{3}{Z}\right)\frac{\hbar^2}{m_e r_3}\sqrt{\frac{3}{4}}\right)} r_8 - \frac{\frac{\hbar^2}{m_e}\left[\frac{Z-8}{Z-7}\right]\left(1-\frac{\sqrt{2}}{2}\right) r_3 10\sqrt{\frac{3}{4}}}{\left(\frac{(Z-7)e^2}{4\pi\varepsilon_0} - \left(\frac{2}{12}-\frac{3}{Z}\right)\frac{\hbar^2}{m_e r_3}\sqrt{\frac{3}{4}}\right)} = 0 \tag{13.718}$$

The solution of Eq. (13.718) using the quadratic formula is:

$$r_8 = \frac{\frac{a_0\left(1-\frac{\sqrt{3}}{8}\right)}{\left((Z-7)-\left(\frac{2}{12}-\frac{3}{Z}\right)\frac{\sqrt{3}}{2r_3}\right)} \pm a_0\sqrt{\left(\frac{1-\frac{\sqrt{3}}{8}}{\left((Z-7)-\left(\frac{2}{12}-\frac{3}{Z}\right)\frac{\sqrt{3}}{2r_3}\right)}\right)^2 + \frac{20\sqrt{3}\left(\left[\frac{Z-8}{Z-7}\right]\left(1-\frac{\sqrt{2}}{2}\right)r_3\right)}{\left((Z-7)-\left(\frac{2}{12}-\frac{3}{Z}\right)\frac{\sqrt{3}}{2r_3}\right)}}}{2}, \ r_3 \ in\ units\ of\ a_0 \tag{13.719}$$

The positive root of Eq. (13.719) must be taken in order that $r_8 > 0$. Substitution of $\frac{r_3}{a_0} = 0.51382$ (Eq. (10.62) with $Z = 9$) into Eq. (13.719) gives:

$$r_8 = 0.73318 a_0 \tag{13.720}$$

## ENERGIES OF THE $2p$ SHELL OF THE FLUORINE ATOMS OF THE FLUORINE MOLECULE

The central forces on the $2p$ shell of each $F$ are increased with the formation of the $\sigma$ MO, which reduces the shell's radius and increases its total energy. The Coulombic energy terms of the total energy of the two $F$ atoms at the new radius are calculated and added to the energy of the $\sigma$ MO to give the total energy of $F_2$. Then, the bond energy is determined from the total $F_2$ energy.

The radius $r_9$ of each fluorine atom before bonding is given by Eq. (10.182):

$$r_9 = 0.78069a_0 \tag{13.721}$$

Using the initial radius $r_9$ of each $F$ atom and the final radius $r_8$ of the $F2p$ shell of $F_2$ (Eq. (13.720)) and by considering that the central Coulombic field decreases by an integer for each successive electron of the shell, the sum $E_T\left(F_2,2p\right)$ of the Coulombic energy change of the $F2p$ electrons of both atoms is determined using Eq. (10.102).

$$\begin{aligned} E_T\left(F_2,2p\right) &= -2\sum_{n=4}^{7}\frac{(Z-n)e^2}{8\pi\varepsilon_0}\left(\frac{1}{r_8}-\frac{1}{r_9}\right) \\ &= -2\left(13.60580\ eV\right)\left(0.08301\right)\left(2+3+4+5\right) = -31.62353\ eV \end{aligned} \tag{13.722}$$

## FORCE BALANCE OF THE $\sigma$ MO OF THE FLUORINE MOLECULE

The relativistic diamagnetic force $\mathbf{F}_{diamagneticMO2}$ of $F_2$ is one half that of $N_2$ due to the two versus one filled $2p$ orbitals per atom at the focus. The force balance equation for the $\sigma$-MO of the fluorine molecule is given by Eq. (11.200) and Eqs. (13.633-13.634) with the correction of 1/2 due the two $2p$ orbitals per $F$ after Eqs. (10.2-10.11), $n_e = 5$, and $\left|L\right| = \hbar$:

$$\frac{\hbar^2}{m_e a^2 b^2}D = \frac{e^2}{8\pi\varepsilon_0 ab^2}D + \frac{\hbar^2}{2m_e a^2 b^2}D - \left(\frac{5}{2}+\frac{1}{2Z}\right)\frac{\hbar^2}{2m_e a^2 b^2}D \tag{13.723}$$

$$\frac{\hbar^2}{m_e a^2 b^2}D = \frac{e^2}{8\pi\varepsilon_0 ab^2}D - \left(\frac{3}{2}+\frac{1}{2Z}\right)\frac{\hbar^2}{2m_e a^2 b^2}D \tag{13.724}$$

$$\left(\frac{7}{2}+\frac{1}{2Z}\right)\frac{\hbar^2}{2m_e a^2 b^2}D = \frac{e^2}{8\pi\varepsilon_0 ab^2}D \tag{13.725}$$

$$a = \left(\frac{7}{2}+\frac{1}{2Z}\right)a_0 \tag{13.726}$$

Substitution of $Z = 9$ into Eq. (13.726) gives:

$$a = 3.55556a_0 = 1.88152\ X\ 10^{-10}\ m \tag{13.727}$$

Substitution of Eq. (13.727) into Eq. (11.79) is:

$$c' = 1.33333a_0 = 7.05569\ X\ 10^{-11}\ m \tag{13.728}$$

The internuclear distance given by multiplying Eq. (13.728) by two is:

$$2c' = 2.66667a_0 = 1.41114\ X\ 10^{-10}\ m \tag{13.729}$$

The experimental bond distance is [28] :

$$2c' = 1.41193\ X\ 10^{-10}\ m \tag{13.730}$$

Substitution of Eqs. (13.727-13.728) into Eq. (11.80) is:

$$b = c = 3.29609a_0 = 1.74421\ X\ 10^{-10}\ m \tag{13.731}$$

Substitution of Eqs. (13.727-13.728) into Eq. (11.67) is:

$$e = 0.37500 \tag{13.732}$$

Using the electron configuration of $F_2$ (Eq. (13.710)), the radii of the $F1s = 0.11297a_0$ (Eq. (10.51)), $F2s = 0.51382a_0$ (Eq. (10.62)), and $F2p = 0.73318a_0$ (Eq. (13.720)) shells and the parameters of the $\sigma$ MO of $F_2$ given by Eqs. (13.3-13.4), (13.727-13.728), and (13.731-13.732), the dimensional diagram and charge-density of the $F_2$ MO are shown in Figures 13.18 and 13.19, respectively.

Figure 13.18. The cross section of the $F_2$ MO showing the axes, $\sigma$ MO ($H_2$-type ellipsoidal MO), with the $F$ $1s$, $2s$, and $2p$ atomic orbitals (AOs). Legend: $a$: semimajor axis, $b$: semiminor axis, $c'$: internuclear distance, $r_8$: radius of the $F2p$ shell having two paired electrons.

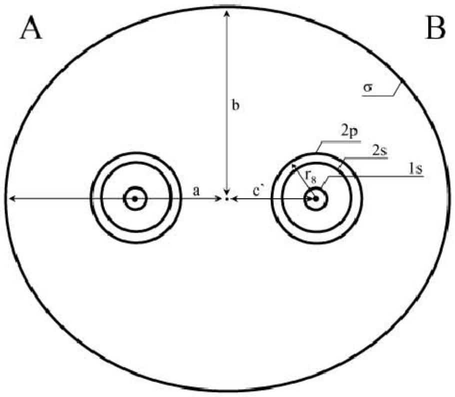
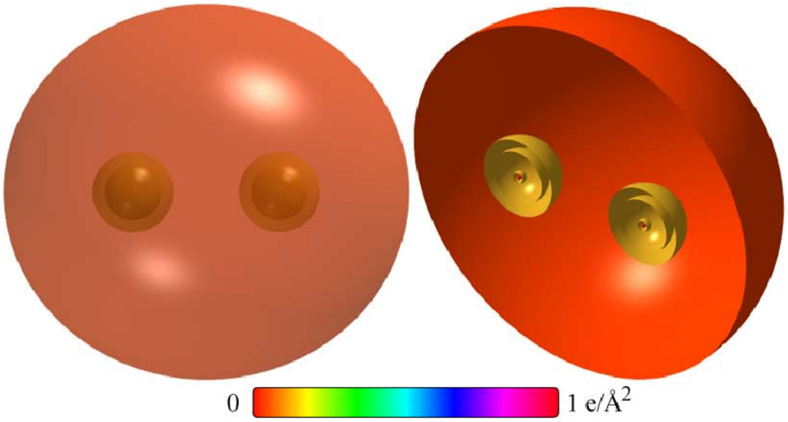


Figure 13.19. $F_2$ MO comprising the $\sigma$ MO ($H_2$-type MO) with $F$ atoms at the foci that have each donated an electron to the $\sigma$ MO and have smaller radii and higher binding energies as a consequence. (A) Color scale, translucent view of the charge-density of the $F_2$ MO. (B) Off-center cut-away view showing the complete inner most $F1s$ shell, and moving radially, the $F2s$ shell, the $F2p$ shell, and the $\sigma$ prolate spheroidal MO that have the $F$ atoms as the foci.



## SUM OF THE ENERGIES OF THE $\sigma$ MO AND THE AOs OF THE FLUORINE MOLECULE

The energies of the $F_2$ $\sigma$ MO are given by the substitution of the semiprincipal axes (Eqs. (13.683-13.684) and (13.687)) into the energy equations (Eqs. (11.207-11.212)) of $H_2$:

$$V_e = \frac{-2e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -16.09139\ eV \tag{13.733}$$

$$V_p = \frac{e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}} = 10.20435\ eV \tag{13.734}$$

$$T = \frac{\hbar^2}{2m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = 2.26285\ eV \tag{13.735}$$

$$V_m = \frac{-\hbar^2}{4m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -1.13143\ eV \tag{13.736}$$

$$E_T = V_e + T + V_m + V_p \tag{13.737}$$

Substitution of Eqs. (11.79) and (13.733-13.736) into Eq. (13.737) gives:

$$\begin{aligned} E_T(F_2,\sigma) &= \frac{-e^2}{8\pi\varepsilon_0\sqrt{\frac{aa_0}{2}}}\left[\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+\sqrt{\frac{aa_0}{2}}}{a-\sqrt{\frac{aa_0}{2}}}-1\right] \\ &= -4.75562\ eV \end{aligned} \tag{13.738}$$

where $E_T(F_2,\sigma)$ is the total energy of the $\sigma$ MO of $F_2$. The sum, $E_T(F_2)$, of $E_T(F_2,2p)$, the $2p$ AO contribution given by Eq. (13.722), and $E_T(F_2,\sigma)$, the $\sigma$ MO contribution given by Eq. (13.738) is:

$$\begin{aligned} E_T(F_2) &= E_T(F_2,2p) + E_T(F_2,\sigma) \\ &= -31.62353\ eV - 4.75562\ eV = -36.37915\ eV \end{aligned} \tag{13.739}$$

## VIBRATION OF $F_2$

The vibrational energy levels of $F_2$ may be solved by determining the Morse potential curve from the energy relationships for the transition from two $F$ atoms whose parameters are given by Eqs. (10.174-10.183) to the two $F$ atoms whose parameter $r_8$ is given by Eq. (13.720) and the $\sigma$ MO whose parameters are given by Eqs. (13.727-13.729) and (13.731-13.732). As shown in the Vibration of Hydrogen-type Molecular Ions section, the harmonic oscillator potential energy function can be expanded about the internuclear distance and expressed as a Maclaurin series corresponding to a Morse potential after Karplus and Porter (K&P) [15] and after Eq. (11.134). Treating the Maclaurin series terms as anharmonic perturbation terms of the harmonic states, the energy corrections can be found by perturbation methods.

## THE DOPPLER ENERGY TERMS OF THE FLUORINE MOLECULE

The equations of the radiation reaction force of fluorine are the same as those of $H_2$ with the substitution of the fluorine parameters. Using Eqs. (11.231-11.233), the angular frequency of the reentrant oscillation in the transition state is:

$$\omega = \sqrt{\frac{\frac{e^2}{4\pi\varepsilon_0 a^3}}{m_e}} = 6.16629\ X\ 10^{15}\ rad/s \tag{13.740}$$

where $a$ is given by Eq. (13.727). The kinetic energy, $E_K$, is given by Planck's equation (Eq. (11.127)):

$$\overline{E}_K = \hbar\omega = \hbar 6.16629\ X\ 10^{15}\ rad/s = 4.05876\ eV \tag{13.741}$$

In Eq. (11.181), substitution of $E_T(F_2)$ for $E_{h\nu}$, the mass of the electron, $m_e$, for $M$, and the kinetic energy given by Eq. (13.741) for $\overline{E}_K$ gives the Doppler energy of the electrons of the reentrant orbit:

$$\overline{E}_D \cong E_{h\nu}\sqrt{\frac{2\overline{E}_K}{Mc^2}} = -36.37915\ eV\sqrt{\frac{2e(4.05876\ eV)}{m_e c^2}} = -0.14499\ eV \tag{13.742}$$

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency. The decrease in the energy of the $F_2$ MO due to the reentrant orbit in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei, $\overline{E}_{osc}$, is given by the sum of the corresponding energies, $\overline{E}_D$ given by Eq. (13.742) and $\overline{E}_{Kvib}$, the average kinetic energy of vibration which is 1/2 of the vibrational energy. Using the experimental $F_2$ $\omega_e$ of $916.64\ cm^{-1}$ $(0.11365\ eV)$ [28] for $\overline{E}_{Kvib}$ of the transition state, $\overline{E}_{osc}(F_2)$ is:

$$\overline{E}_{osc}(F_2) = \overline{E}_D + \overline{E}_{Kvib} = \overline{E}_D + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \tag{13.743}$$

$$\overline{E}_{osc}(F_2) = -0.14499\ eV + \frac{1}{2}(0.11365\ eV) = -0.08817\ eV \tag{13.744}$$

## TOTAL AND BOND ENERGIES OF THE FLUORINE MOLECULE

$E_{T+osc}(F_2)$, the total energy of $F_2$ including the Doppler term, is given by the sum of $E_T(F_2)$ (Eq. (13.739)) and $\overline{E}_{osc}(F_2)$ given by Eq. (13.744):

$$\begin{aligned} E_{T+osc}(F_2) &= V_e + T + V_m + V_p + E_T(F_2, 2p) + \overline{E}_{osc}(F_2) \\ &= E_T(F_2,\sigma) + E_T(F_2,2p) + \overline{E}_{osc}(F_2) \\ &= E_T(F_2) + \overline{E}_{osc}(F_2) \end{aligned} \tag{13.745}$$

$$\begin{aligned} E_{T+osc}(F_2) &= \left\{ \begin{array}{l} \left( \frac{-e^2}{8\pi\varepsilon_0\sqrt{\frac{aa_0}{2}}} \left( \left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+\sqrt{\frac{aa_0}{2}}}{a-\sqrt{\frac{aa_0}{2}}} - 1 \right) - 2\sum_{n=4}^{7}\frac{(Z-n)e^2}{8\pi\varepsilon_0}\left(\frac{1}{r_8}-\frac{1}{r_9}\right) \right) \\ \left( 1+\sqrt{\frac{2\hbar\sqrt{\frac{\frac{e^2}{4\pi\varepsilon_0 a^3}}{m_e}}}{m_e c^2}} \right) + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \end{array} \right\} \\ &= -36.37915\ eV - 0.14499\ eV + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \end{aligned} \tag{13.746}$$

From Eqs. (13.743-13.746), the total energy of the $F_2$ MO is:

$$E_{T+osc}\left(F_2\right) = -36.37915\ eV + \bar{E}_{osc}\left(F_2\right) = -36.37915\ eV - 0.14499\ eV + \frac{1}{2}\left(0.11365\ eV\right) = -36.46732\ eV \tag{13.747}$$

where the experimental $\omega_e$ was used for the $\hbar\sqrt{\frac{k}{\mu}}$ term.

The $F_2$ bond dissociation energy, $E_D\left(F_2\right)$, is given by the difference in the total energies of the two $F$ atoms and $E_{T+osc}\left(F_2\right)$:

$$E_D\left(F_2\right) = 2E\left(F\right) - E_{T+osc}\left(F_2\right) \tag{13.748}$$

where the energy of a fluorine atom is [6]:

$$E(F) = -17.42282\ eV \tag{13.749}$$

Thus, the $F_2$ bond dissociation energy, $E_D\left(F_2\right)$, given by Eqs. (13.747-13.749) is:

$$E_D\left(F_2\right) = -2\left(17.42282\ eV\right) - E_{T+osc}\left(F_2\right) = -34.84564\ eV - \left(-36.46732\ eV\right) = 1.62168\ eV \tag{13.750}$$

The experimental $F_2$ bond dissociation energy is [48]:

$$E_D\left(F_2\right) = 1.606\ eV \tag{13.751}$$

The results of the determination of bond parameters of $F_2$ are given in Table 13.1. The calculated results are based on first principles and given in closed-form, exact equations containing fundamental constants only. The agreement between the experimental and calculated results is excellent.

## CHLORINE MOLECULE

The chlorine molecule can be formed by the reaction of two chlorine atoms:

$$Cl + Cl \to Cl_2 \tag{13.752}$$

The chlorine molecule can be solved by using the hybridization approach used to solve the methane series $CH_{n=1,2,3,4}$. In the methane series, the $2s$ and $2p$ shells of carbon hybridize to form a single $2sp^3$ shell to achieve an energy minimum, and in a likewise manner, the $3s$ and $3p$ shells of chlorine hybridize to form a single $3sp^3$ shell which forms the bonding orbital of $Cl_2$.

### FORCE BALANCE OF $Cl_2$

$Cl_2$ has two spin-paired electrons in a chemical bond between the chlorine atoms. The $Cl_2$ molecular orbital (MO) is determined by considering properties of the binding atoms and the boundary constraints. The prolate spheroidal $H_2$ MO developed in the Nature of the Chemical Bond of Hydrogen-Type Molecules section satisfies the boundary constraints; thus, each $Cl$ atom could contribute a $3p$ electron to form a $\sigma$ MO ($H_2$-type ellipsoidal MO) as in the case of $N_2$, $O_2$, and $F_2$. However, such a bond is not possible with the outer $Cl$ electrons in their ground state since the resulting $3p$ shells of chlorine atoms would overlap which is not energetically stable. Thus, when bonding, the chlorine $3s$ and $3p$ shells hybridize to form a single $3sp^3$ shell to achieve an energy minimum.

The $Cl$ electron configuration given in the Seventeen-Electron Atoms section is $1s^2 2s^2 2p^6 3s^2 3p^5$, and the orbital arrangement is:

$$\begin{array}{ccc} \multicolumn{3}{c}{\text{3p state}} \\ \underline{\uparrow\ \downarrow} & \underline{\uparrow\ \downarrow} & \underline{\ \uparrow\ } \\ 1 & 0 & -1 \end{array} \tag{13.753}$$

corresponding to the ground state ${}^2P^0_{3/2}$. The radius $r_{17}$ of the $3p$ shell given by Eq. (10.363) is:

$$r_{17} = 1.05158a_0 \tag{13.754}$$

The energy of the chlorine $3p$ shell is the negative of the ionization energy of the chlorine atom given by Eq. (10.364). Experimentally, the energy is [6]:

$$E\left(3p\ shell\right) = -E(ionization;\ Cl) = -12.96764\ eV \tag{13.755}$$

The $Cl3s$ atomic orbital (AO) combines with the $Cl3p$ AOs to form a single $3sp^3$ hybridized orbital (HO) with the orbital arrangement.

$$\begin{array}{cccc} \multicolumn{4}{c}{\text{3sp}^3\text{ state}} \\ \underline{\uparrow\ \downarrow} & \underline{\uparrow\ \downarrow} & \underline{\uparrow\ \downarrow} & \underline{\ \uparrow\ } \\ 0,0 & 1,-1 & 1,0 & 1,1 \end{array} \tag{13.756}$$

where the quantum numbers ($\ell, m_\ell$) are below each electron. The total energy of the state is given by the sum over the seven electrons. Using only the largest-force terms of the outer most and next inner shell, the calculated energies for the chlorine atom and the ions: $Cl$, $Cl^+$, $Cl^{2+}$, $Cl^{3+}$, $Cl^{4+}$, $Cl^{5+}$ and $Cl^{6+}$ are given in Eqs. (10.363-10.364), (10.353-10.354), (10.331-10.332), (10.309-10.310), (10.288-10.289), (10.255-10.256), and (10.235-10.236), respectively. The sum $E_T\left(Cl,3sp^3\right)$ of the experimental energies of $Cl$ and these ions is [6]:

$$E_T\left(Cl,3sp^3\right)=\begin{pmatrix}12.96764\ eV+23.814\ eV+39.61\ eV+53.4652\ eV\\ +67.8\ eV+97.03\ eV+114.1958\ eV\end{pmatrix}=408.88264\ eV \tag{13.757}$$

The spin and orbital-angular-momentum interactions cancel such that the energy of the $E_T\left(Cl,3sp^3\right)$ is purely Coulombic. By considering that the central field decreases by an integer for each successive electron of the shell, the radius $r_{3sp^3}$ of the $Cl3sp^3$ shell may be calculated from the Coulombic energy using Eq. (10.102):

$$r_{3sp^3}=\sum_{n=10}^{16}\frac{(Z-n)e^2}{8\pi\varepsilon_0\left(e408.8826\ eV\right)}=\frac{28e^2}{8\pi\varepsilon_0\left(e408.8826\ eV\right)}=0.93172a_0 \tag{13.758}$$

where $Z=17$. Using Eqs. (10.102) and (13.758), the Coulombic energy $E_{Coulomb}\left(Cl,3sp^3\right)$ of the outer electron of the $Cl3sp^3$ shell is:

$$E_{Coulomb}\left(Cl,3sp^3\right)=\frac{-e^2}{8\pi\varepsilon_0 r_{3sp^3}}=\frac{-e^2}{8\pi\varepsilon_0 0.93172a_0}=-14.60295\ eV \tag{13.759}$$

The calculated energy of the $C2sp^3$ shell of $14.63489\ eV$ given by Eq. (13.428), and nitrogen's calculated energy of $14.61664\ eV$ given by Eq. (10.143) is a close match with $E_{Coulomb}\left(Cl,3sp^3\right)$.

The unpaired $Cl3sp^3$ electrons from each of two chlorine atoms combine to form a molecular orbital. The nuclei of the $Cl$ atoms are along the internuclear axis and serve as the foci. Due to symmetry, the other $Cl$ electrons are equivalent to point charges at the origin. (See Eqs. (19-38) of Appendix II.) Thus, the energies in the $Cl$ MO involve only the two $Cl3sp^3$ electrons. The forces are determined by these energies.

As in the case of $H_2$, the MO is a prolate spheroid with the exception that the ellipsoidal MO surface cannot extend into $Cl3sp^3$ HO for distances shorter than the radius of the $Cl3sp^3$ shell of each atom. Thus, the MO surface comprises a partial prolate spheroid in between the nuclei and is continuous with the $Cl3sp^3$ shell at each $Cl$ atom. The energy of the $H_2$-type ellipsoidal MO is matched to that of the $Cl3sp^3$ shell. As in the case with $OH$, $NH$, and $CH$ (where the latter also demonstrates $sp^3$ hybridization) the linear combination of the $H_2$-type ellipsoidal MO with each $Cl3sp^3$ HO must involve a 25% contribution from the $H_2$-type ellipsoidal MO to the $Cl3sp^3$ HO in order to match potential, kinetic, and orbital energy relationships. Thus, the $Cl_2$ MO must comprise two $Cl3sp^3$ HOs and 75% of a $H_2$-type ellipsoidal MO divided between the two $Cl3sp^3$ HOs:

$$2\ Cl3sp^3+0.75\ H_2\ MO\rightarrow Cl_2\ MO \tag{13.760}$$

The force balance of the $Cl_2$ MO is determined by the boundary conditions that arise from the linear combination of orbitals according to Eq. (13.760) and the energy matching condition between the $H_2$-type-ellipsoidal-MO and $Cl3sp^3$-HO components of the MO.

As in the case with $OH$ (Eq. (13.57)), $NH$ (Eq. (13.247)), and $CH$ (Eq. (13.429)), the $H_2$-type ellipsoidal MO comprises 75% of the $Cl_2$ MO; so, the electron charge density in Eq. (11.65) is given by $-0.75e$. Since the chlorine atoms of $Cl_2$ are hybridized and the $k$ parameter is different from unity in order to meet the boundary constraints, both $k$ and $k'$ must comprise the corresponding hybridization factors. (In contrast, the chlorine atom of a $C-Cl$ bond of an alkyl chloride is not hybridized, and only $k'$ must comprise the corresponding hybridization factor.) The force constant $k'$ to determine the ellipsoidal parameter $c'$ in terms of the central force of the foci is given by Eq. (13.59), except that $k'$ is divided by two since the $H_2$-type-ellipsoidal-MO is physically divided between two $Cl3sp^3$ HOs. In addition, the energy matching at both $Cl3sp^3$ HOs further requires that $k'$ be corrected with the hybridization factor given by Eq. (13.762). Thus, $k'$ of the $H_2$-type-ellipsoidal-MO component of the $Cl_2$ MO is:

$$k'=C_{Cl3sp^3HO}\frac{(0.75)}{2}\frac{2e^2}{4\pi\varepsilon_0}=0.93172\frac{(0.75)}{2}\frac{2e^2}{4\pi\varepsilon_0} \tag{13.761}$$

The distance from the origin to each focus $c'$ is given by Eq. (13.60). The internuclear distance is given by Eq. (13.61). The length of the semiminor axis of the prolate spheroidal $Cl-Cl$-bond $b=c$ is given by Eq. (13.62). The eccentricity, $e$, is given by Eq. (13.63). The solution of the semimajor axis $a$ then allows for the solution of the other axes of each prolate spheroid and eccentricity of the $Cl_2$ MO. Since the $Cl_2$ MO comprises a $H_2$-type-ellipsoidal MO that transitions to the $Cl3sp^3$ HOs at each end of the molecule, the energy $E\left(Cl,3sp^3\right)$ in Eq. (13.759) adds to that of the $H_2$-type ellipsoidal MO to give the total energy of the $Cl_2$ MO. From the energy equation and the relationship between the axes, the dimensions of the $Cl_2$ MO are solved.

The energy components of $V_e$, $V_p$, $T$, and $V_m$ are those of $H_2$ (Eqs. (11.207-11.211)) except that they are corrected for electron hybridization. Hybridization gives rise to the $Cl3sp^3$ HO-shell Coulombic energy $E_{Coulomb}\left(Cl,3sp^3\right)$ given by Eq. (13.759). To meet the equipotential condition of the union of the $H_2$-type-ellipsoidal-MO with each $Cl3sp^3$ HO, the electron energies are normalized by the ratio of $14.60295\ eV$, the magnitude of $E_{Coulomb}\left(Cl,3sp^3\right)$ given by Eq. (13.759), and $13.605804\ eV$, the magnitude of the Coulombic energy between the electron and proton of $H$ given by Eq. (1.264). This normalizes the energies to match that of the Coulombic energy alone to meet the energy matching condition of the $Cl_2$ MO under the influence of the two $Cl3sp^3$ HOs bridged by the $H_2$-type-ellipsoidal MO. The hybridization energy factor $C_{Cl3sp^3HO}$ is:

$$C_{Cl3sp^3HO}=\frac{\frac{e^2}{8\pi\varepsilon_0 a_0}}{\frac{e^2}{8\pi\varepsilon_0 r_{3sp^3}}}=\frac{\frac{e^2}{8\pi\varepsilon_0 a_0}}{\frac{e^2}{8\pi\varepsilon_0 0.93172 a_0}}=\frac{13.605804\ eV}{14.60295\ eV}=0.93172 \tag{13.762}$$

The total energy $E_T\left(Cl_2\right)$ of the $Cl_2$ MO is given by the sum of the energies of the orbitals, the $H_2$-type ellipsoidal MO and the two $Cl3sp^3$ HOs, that form the hybridized $Cl_2$ MO. $E_T\left(Cl_2\right)$ follows from Eq. (13.74) for $OH$, but the energy of the $Cl3sp^3$ HO given by Eq. (13.759) is substituted for the energy of $O$ and the $H_2$-type-ellipsoidal-MO energies are those of $H_2$ (Eqs. (11.207-11.212)) multiplied by the electron hybridization factor rather than by the factor of $0.75$:

$$\begin{aligned}E_T\left(Cl_2\right)&=E_T+E_{Coulomb}\left(Cl,3sp^3\right)\\&=-\frac{e^2}{8\pi\varepsilon_0 c'}\left[\left(0.93172\right)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]-14.60295\ eV\end{aligned} \tag{13.763}$$

To match the boundary condition that the total energy of the entire the $H_2$-type ellipsoidal MO is given by Eqs. (11.212) and (13.75), $E_T\left(Cl_2\right)$ given by Eq. (13.763) is set equal to Eq. (13.75):

$$\begin{aligned}E_T\left(Cl_2\right)&=-\frac{e^2}{8\pi\varepsilon_0 c'}\left[\left(0.93172\right)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]-14.60295\ eV\\&=-31.63537\ eV\end{aligned} \tag{13.764}$$

From the energy relationship given by Eq. (13.764) and the relationship between the axes given by Eqs. (13.60-13.63), the dimensions of the $Cl_2$ MO can be solved.

Substitution of Eqs. (13.60) and (13.761) into Eq. (13.764) gives:

$$\frac{e^2}{8\pi\varepsilon_0\sqrt{\frac{4aa_0}{3\left(0.93172\right)}}}\left[\left(0.93172\right)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+\sqrt{\frac{4aa_0}{3\left(0.93172\right)}}}{a-\sqrt{\frac{4aa_0}{3\left(0.93172\right)}}}-1\right]=e17.03242 \tag{13.765}$$

The most convenient way to solve Eq. (13.765) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is:

$$a=2.46500a_0=1.30442\ X\ 10^{-10}\ m \tag{13.766}$$

Substitution of Eq. (13.766) into Eq. (13.60) gives:

$$c'=1.87817a_0=9.93887\ X\ 10^{-11}\ m \tag{13.767}$$

The internuclear distance given by multiplying Eq. (13.767) by two is:

$$2c' = 3.75635a_0 = 1.98777 \; X \; 10^{-10} \; m \qquad (13.768)$$

The experimental bond distance is [28] :

$$2c' = 1.988 \; X \; 10^{-10} \; m \qquad (13.769)$$

Substitution of Eqs. (13.766-13.767) into Eq. (13.62) gives:

$$b = c = 1.59646a_0 = 8.44810 \; X \; 10^{-11} \; m \qquad (13.770)$$

Substitution of Eqs. (13.766-13.767) into Eq. (13.63) gives:

$$e = 0.76194 \qquad (13.771)$$

The $Cl$ nuclei comprise the foci of the $H_2$-type ellipsoidal MO. The parameters of the point of intersection of the $H_2$-type ellipsoidal MO and the $Cl3sp^3$ HO are given by Eqs. (13.84-13.95) and (13.261-13.270). The polar intersection angle $\theta'$ is given by Eq. (13.261) where $r_n = r_{3sp^3} = 0.93172a_0$ is the radius of the $Cl3sp^3$ shell. Substitution of Eqs. (13.766-13.767) into Eq. (13.261) gives

$$\theta' = 81.72° \qquad (13.772)$$

Then, the angle $\theta_{Cl3sp^3HO}$ the radial vector of the $Cl3sp^3$ HO makes with the internuclear axis is:

$$\theta_{Cl3sp^3HO} = 180° - 81.72° = 98.28° \qquad (13.773)$$

as shown in Figure 13.20. The Cartesian $\mathbf{i}$-coordinate of the interception point of the MO and the AO can be calculated using the MO ellipsoidal parameters by first calculating the parametric angle in Eq. (11.83) that matches Cartesian $\mathbf{j}$-coordinate components at the point of intersection. Thus, the matching elliptic parametric angle $\omega t = \theta_{H_2MO}$ satisfies the following relationship:

$$r_{3sp^3} \sin\theta_{Cl3sp^3HO} = 0.93172a_0 \sin\theta_{Cl3sp^3HO} = b \sin\theta_{H_2MO} \qquad (13.774)$$

such that

$$\theta_{H_2MO} = \sin^{-1}\frac{0.93172a_0 \sin\theta_{Cl3sp^3HO}}{b} = \sin^{-1}\frac{0.93172a_0 \sin 98.28°}{b} \qquad (13.775)$$

with the use of Eq. (13.773). Substitution of Eq. (13.770) into Eq. (13.775) gives:

$$\theta_{H_2MO} = 35.28° \qquad (13.776)$$

Then, the distance $d_{H_2MO}$ along the internuclear axis from the origin of $H_2$-type ellipsoidal MO to the point of intersection of the orbitals is given by:

$$d_{H_2MO} = a \cos\theta_{H_2MO} \qquad (13.777)$$

Substitution of Eqs. (13.766) and (13.776) into Eq. (13.777) gives:

$$d_{H_2MO} = 2.01235a_0 = 1.06489 \; X \; 10^{-10} \; m \qquad (13.778)$$

The distance $d_{Cl3sp^3HO}$ along the internuclear axis from the origin of each $Cl$ atom to the point of intersection of the orbitals is given by:

$$d_{Cl3sp^3HO} = d_{H_2MO} - c' \qquad (13.779)$$

Substitution of Eqs. (13.768) and (13.778) into Eq. (13.779) gives:

$$d_{Cl3sp^3HO} = 0.13417a_0 = 7.10022 \; X \; 10^{-12} \; m \qquad (13.780)$$

As shown in Eq. (13.760), a factor of 0.25 of the charge-density of the $H_2$-type ellipsoidal MO is distributed on each $Cl3sp^3$ HO. Using the orbital composition of $Cl_2$ (Eq. (13.760)), the radii of the $Cl1s = 0.05932a_0$ (Eq. (10.51)), $Cl2s = 0.25344a_0$ (Eq. (10.62)), $Cl2p = 0.31190a_0$ (Eq. (10.212)), and $Cl3sp^3 = 0.93172a_0$ (Eq. (13.758)) shells, and the parameters of the $Cl_2$ MO given by Eqs. (13.3-13.4), (13.766-13.768), and (13.770-13.771), the dimensional diagram and charge-density of the $Cl_2$ MO comprising the linear combination of the $H_2$-type ellipsoidal MO and two $Cl3sp^3$ HOs according to Eq. (13.760) are shown in Figures 13.20 and 13.21, respectively.

Figure 13.20. The cross section of the $Cl_2$ MO showing the axes, angles, and point of intersection of the $H_2$-type ellipsoidal MO with the two $Cl3sp^3$ HOs. The continuation of the $H_2$-type-ellipsoidal-MO basis element beyond the intersection point with each $Cl3sp^3$ shell is shown as dashed since it only serves to solve the energy match with each $Cl3sp^3$ shell and does not represent charge density. Similarly, the vertical dashed line only designates the parameters of the intersection points. The actual charge density is shown by the solid lines. Legend: $a$: semimajor axis, $b$: semiminor axis, $c'$: internuclear distance, $d_1 : d_{H_2MO}$, $\theta_1 : \theta_{Cl3sp^3HO}$, $d_2 : d_{Cl3sp^3HO}$, and $R : r_{3sp^3}$.

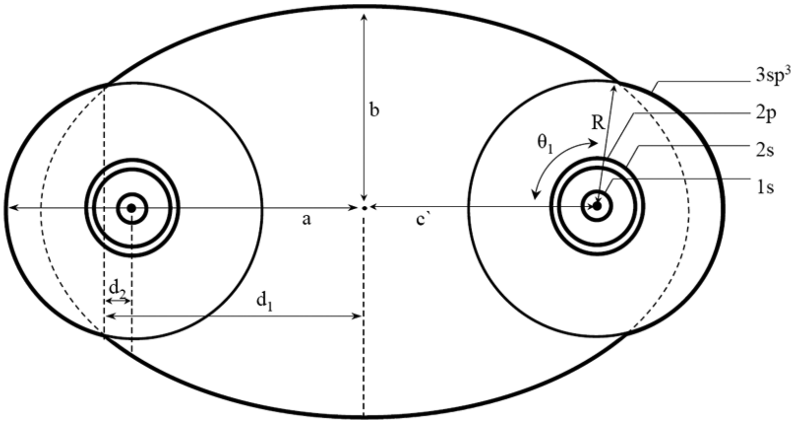
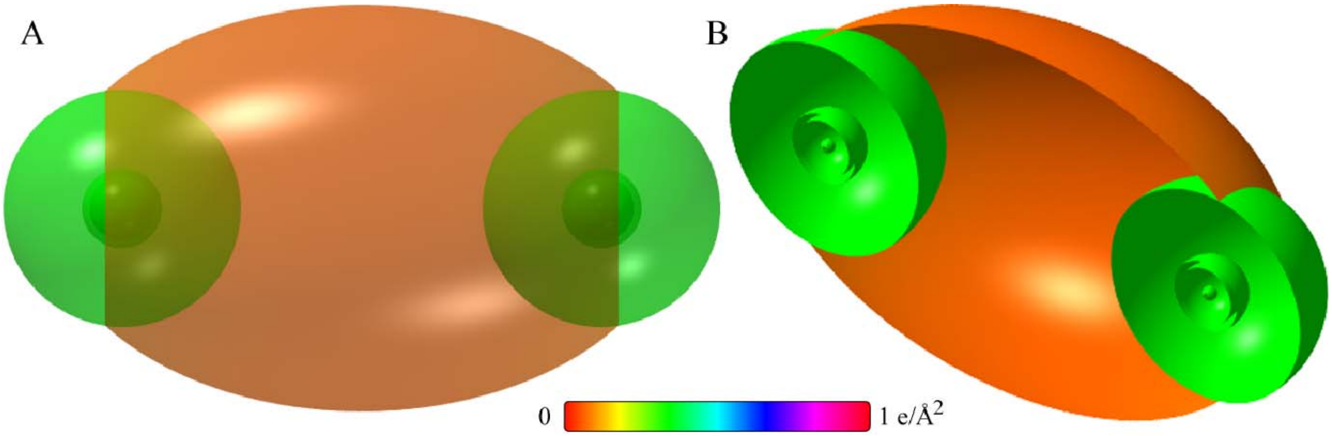


Figure 13.21. $Cl_2$ MO comprising the superposition of the $H_2$-type ellipsoidal MO and the two $Cl3sp^3$ HOs, each with a relative charge-density of 0.75 to 1.25 divided between the former and the latter; otherwise, the $Cl3sp^3$ HO is unchanged. (A) Side-on, color scale, translucent view of the charge-density of the $Cl_2$ MO. The ellipsoidal surface of the $H_2$-type ellipsoidal MO that transitions to the $Cl3sp^3$ HO, the $Cl3sp^3$ HO, and the $Cl1s$, $Cl2s$ , and $Cl2p$ shells of each $Cl$ atom are shown. (B) Cut-away view showing the inner most $Cl1s$ shell, and moving radially, the $Cl2s$, $Cl2p$, and $Cl3sp^3$ shells, and the $H_2$-type ellipsoidal MO that transitions to the $Cl3sp^3$ HOs.



## ENERGIES OF $Cl_2$

The energies of $Cl_2$ are given by the substitution of the semiprincipal axes (Eqs. (13.766-13.767) and (13.770)) into the energy equations, (Eq. (13.763) and Eqs. (11.207-11.211) of $H_2$) that are corrected for electron hybridization using Eq. (13.762).

$$V_e = (0.93172)\frac{-2e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -27.02007\ eV \tag{13.781}$$

$$V_p = \frac{e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}} = 7.24416\ eV \tag{13.782}$$

$$T = (0.93172)\frac{\hbar^2}{2m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = 5.48074\ eV \tag{13.783}$$

$$V_m = (0.93172)\frac{-\hbar^2}{4m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -2.74037\ eV \tag{13.784}$$

$$E_T\left({}^{35}Cl_2\right) = -\frac{e^2}{8\pi\varepsilon_0 c'}\left[(0.93172)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]-14.60295\ eV = -31.63537\ eV \tag{13.785}$$

where $E_T(Cl_2)$ is given by Eq. (13.763) which is reiteratively matched to Eq. (13.75) within five-significant-figure round-off error.

## VIBRATION AND ROTATION OF $Cl_2$

In $Cl_2$, the division of the $H_2$-type ellipsoidal MO between the two $Cl3sp^3$ HOs and the hybridization must be considered in determining the vibrational parameters. One approach is to use Eq. (13.761) for the force constant and $r_{3sp^3}$ given by Eq. (13.758) for the distance parameter of the central force in Eq. (11.213) since the $H_2$-type ellipsoidal MO is energy matched to the $Cl3sp^3$ HOs. With the substitution of the $Cl_2$ parameters in Eqs. (11.213-11.217), the angular frequency of the oscillation is:

$$\begin{aligned}\omega &= \sqrt{\frac{0.93172\frac{(0.75)}{2}\frac{e^2}{8\pi\varepsilon_0\left(r_{3sp^3}\right)^3}-\frac{e^2}{8\pi\varepsilon_0\left(r_{3sp^3}+c'\right)^3}}{\mu}} \\ &= \sqrt{\frac{0.93172\frac{(0.75)}{2}\frac{e^2}{8\pi\varepsilon_0(0.93172)^3}-\frac{e^2}{8\pi\varepsilon_0(0.93172a_0+1.87817a_0)^3}}{\frac{35}{2}m_p}} = 1.01438\ X\ 10^{14}\ rad/s\end{aligned} \tag{13.786}$$

where $c'$ is given by Eq. (13.767), and the reduced mass of ${}^{35}Cl_2$ is given by:

$$\mu_{{}^{35}Cl_2} = \frac{m_1m_2}{m_1+m_2} = \frac{(35)(35)}{35+35}m_p \tag{13.787}$$

where $m_p$ is the proton mass. Thus, during bond formation, the perturbation of the orbit determined by an inverse-squared force results in simple harmonic oscillatory motion of the orbit, and the corresponding frequency, $\omega(0)$, for ${}^{35}Cl_2$ given by Eqs. (11.136), (11.148), and (13.786) is:

$$\omega(0) = \sqrt{\frac{k(0)}{\mu}} = \sqrt{\frac{301.19\ Nm^{-1}}{\mu}} = 1.01438\ X\ 10^{14}\ radians/s \tag{13.788}$$

where the reduced nuclear mass of ${}^{35}Cl_2$ is given by Eq. (13.787) and the spring constant, $k(0)$, given by Eqs. (11.136) and (13.786) is:

$$k(0) = 301.19\ Nm^{-1} \tag{13.789}$$

The ${}^{35}Cl_2$ transition-state vibrational energy, $E_{vib}(0)$ or $\omega_e$, given by Planck's equation (Eq. (11.127)) is:

$$E_{vib}(0) = \omega_e = \hbar\omega = \hbar 1.01438\ X\ 10^{14}\ rad/s = 0.06677\ eV = 538.52\ cm^{-1} \tag{13.790}$$

$\omega_e$, from the experimental curve fit of the vibrational energies of $^{35}Cl_2$ is [28] :

$$\omega_e = 559.7\ cm^{-1} \tag{13.791}$$

Using Eqs. (13.112-13.118) with $E_{vib}(0)$ given by Eq. (13.790) and $D_0$ given by Eq. (13.807), the $^{35}Cl_2$ $\upsilon = 1 \rightarrow \upsilon = 0$ vibrational energy, $E_{vib}(1)$ is:

$$E_{vib}(1) = 0.0659\ eV \qquad \left(531.70\ cm^{-1}\right) \tag{13.792}$$

The experimental vibrational energy of $^{35}Cl_2$ using $\omega_e$ and $\omega_e x_e$ [28] according to K&P [15] is:

$$E_{vib}(1) = 0.0664\ eV \qquad \left(535.55\ cm^{-1}\right) \tag{13.793}$$

Using Eq. (13.113) with $E_{vib}(1)$ given by Eq. (13.792) and $D_0$ given by Eq. (13.807), the anharmonic perturbation term, $\omega_0 x_0$, of $^{35}Cl_2$ is:

$$\omega_0 x_0 = 3.41\ cm^{-1} \tag{13.794}$$

The experimental anharmonic perturbation term, $\omega_0 x_0$, of $^{35}Cl_2$ [28] is:

$$\omega_0 x_0 = 2.68\ cm^{-1} \tag{13.795}$$

The vibrational energies of successive states are given by Eqs. (13.790), (13.112), and (13.794).

Using Eqs. (13.133-13.134) and the internuclear distance, $r = 2c'$, and reduced mass of $^{35}Cl_2$ given by Eqs. (13.768) and (13.787), respectively, the corresponding $B_e$ is:

$$B_e = 0.2420\ cm^{-1} \tag{13.796}$$

The experimental $B_e$ rotational parameter of $^{35}Cl_2$ is [28]:

$$B_e = 0.2440\ cm^{-1} \tag{13.797}$$

## THE DOPPLER ENERGY TERMS OF $Cl_2$

The equations of the radiation reaction force of the symmetrical $Cl_2$ MO are the given by Eqs. (11.231-11.233) with the substitution of the $Cl_2$ parameters and the substitution of the force factor of Eq. (13.761). The angular frequency of the reentrant oscillation in the transition state is:

$$\omega = \sqrt{\frac{0.93172\frac{(0.75)}{2}\frac{e^2}{4\pi\varepsilon_0 a^3}}{m_e}} = 6.31418\ X\ 10^{15}\ rad/s \tag{13.798}$$

where $a$ is given by Eq. (13.766). The kinetic energy, $E_K$, is given by Planck's equation (Eq. (11.127)).

$$\overline{E}_K = \hbar\omega = \hbar 1.6.31418\ X\ 10^{15}\ rad/s = 4.15610\ eV \tag{13.799}$$

In Eq. (11.181), substitution of the total energy of $Cl_2$, $E_T(Cl_2)$, (Eq. (13.764)) for $E_{h\nu}$, the mass of the electron, $m_e$, for $M$, and the kinetic energy given by Eq. (13.799) for $\overline{E}_K$ gives the Doppler energy of the electrons for the reentrant orbit:

$$\overline{E}_D \cong E_{h\nu}\sqrt{\frac{2\overline{E}_K}{Mc^2}} = -31.63537\ eV\sqrt{\frac{2e(4.15610\ eV)}{m_e c^2}} = -0.12759\ eV \tag{13.800}$$

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency. The decrease in the energy of $Cl_2$ due to the reentrant orbit in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei, $\overline{E}_{osc}$, is given by the sum of the corresponding energies, $\overline{E}_D$ given by Eq. (13.800) and $\overline{E}_{Kvib}$, the average kinetic energy of vibration which is 1/2 of the vibrational energy of $Cl_2$. Using the experimental $^{35}Cl_2$ $\omega_e$ of $559.7\ cm^{-1}$ $(0.06939\ eV)$ [28] for $\overline{E}_{Kvib}$ of the transition state, $\overline{E}_{osc}\left(^{35}Cl_2\right)$ is:

$$\overline{E}_{osc}\left(^{35}Cl_2\right) = \overline{E}_D + \overline{E}_{Kvib} = \overline{E}_D + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \tag{13.801}$$

$$\overline{E}_{osc}\left(^{35}Cl_2\right) = -0.12759\ eV + \frac{1}{2}(0.06939\ eV) = -0.09289\ eV \tag{13.802}$$

## TOTAL AND BOND ENERGIES OF $Cl_2$

$E_{T+osc}\left({}^{35}Cl_2\right)$, the total energy of the ${}^{35}Cl_2$ radical including the Doppler term, is given by the sum of $E_T\left(Cl_2\right)$ (Eq. (13.764)) and $\bar{E}_{osc}\left({}^{35}Cl_2\right)$ given by Eq. (13.802).

$$E_{T+osc}\left({}^{35}Cl_2\right) = V_e + T + V_m + V_p + E_{Coulomb}\left(Cl,3sp^3\right) + \bar{E}_{osc}\left({}^{35}Cl_2\right) = E_T\left(Cl_2\right) + \bar{E}_{osc}\left({}^{35}Cl_2\right) \tag{13.803}$$

$$\begin{aligned} E_{T+osc}\left({}^{35}Cl_2\right) &= \left\{ \begin{array}{l} \left( \dfrac{-e^2}{8\pi\varepsilon_0 c'} \left[ (0.93172)\left(2 - \dfrac{1}{2}\dfrac{a_0}{a}\right)\ln\dfrac{a+c'}{a-c'} - 1 \right] - 14.60295\ eV \right) \\ \left( 1 + \sqrt{\dfrac{2\hbar\sqrt{\dfrac{0.93172\dfrac{(0.75)}{2}\dfrac{e^2}{4\pi\varepsilon_0 a^3}}{m_e}}}{m_e c^2}} \right) + \dfrac{1}{2}\hbar\sqrt{\dfrac{k}{\mu}} \end{array} \right\} \\ &= -31.63537\ eV - 0.12759\ eV + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \end{aligned} \tag{13.804}$$

From Eqs. (13.801-13.804), the total energy of ${}^{35}Cl_2$ is:

$$\begin{aligned} E_{T+osc}\left({}^{35}Cl_2\right) &= -31.63537\ eV + \bar{E}_{osc}\left({}^{35}Cl_2\right) \\ &= -31.63537\ eV - 0.12759\ eV + \frac{1}{2}\left(0.06939\ eV\right) = -31.72826\ eV \end{aligned} \tag{13.805}$$

where the experimental $\omega_e$ (Eq. (13.791)) was used for the $\hbar\sqrt{\frac{k}{\mu}}$ term.

The $Cl_2$ bond dissociation energy, $E_D\left({}^{35}Cl_2\right)$, is given by the difference between the total energies of the two $Cl3sp^3$ HOs and $E_{T+osc}\left({}^{35}Cl_2\right)$:

$$E_D\left({}^{35}Cl_2\right) = 2E_{Coulomb}\left(Cl,3sp^3\right) - E_{T+osc}\left({}^{35}Cl_2\right) \tag{13.806}$$

$E_{Coulomb}\left(Cl,3sp^3\right)$ is given by Eq. (13.759); thus, the ${}^{35}Cl_2$ bond dissociation energy, $E_D\left({}^{35}Cl_2\right)$, given by Eqs. (13.759) and (13.805-13.806) is

$$E_D\left({}^{35}Cl_2\right) = -2\left(14.60295\ eV\right) - E_{T+osc}\left({}^{35}Cl_2\right) = -29.20590\ eV - \left(-31.72826\ eV\right) = 2.52236\ eV \tag{13.807}$$

The experimental ${}^{35}Cl_2$ bond dissociation energy is [49]:

$$E_D\left({}^{35}Cl_2\right) = 2.51412\ eV \tag{13.808}$$

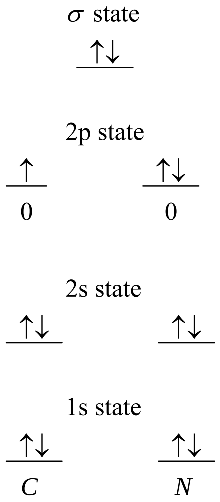
The results of the determination of bond parameters of $Cl_2$ are given in Table 13.1. The calculated results are based on first principles and given in closed-form, exact equations containing fundamental constants only. The agreement between the experimental and calculated results is excellent.

## CARBON NITRIDE RADICAL

The carbon nitride radical can be formed by the reaction of carbon and nitrogen atoms:

$$C + N \rightarrow CN \tag{13.809}$$

The bond in carbon nitride radical comprises a $H_2$-type molecular orbital (MO) with two paired electrons. The force balance equations and radii, $r_6$ and $r_7$, of the $2p$ shell of $C$ and $N$ are derived in the Six-Electron Atoms section and Seven-Electron Atoms section, respectively. With the formation of the $H_2$-type MO by the contribution of a $2p$ electron from each of the $C$ and $N$ atoms, a diamagnetic force arises between the remaining $2p$ electrons of each atom and the $H_2$-type MO. This force from each atom causes the $H_2$-type MO to move to greater principal axes than would result with the Coulombic force alone. But, the integer increase of the central field and the resulting increased Coulombic as well as magnetic central forces on the remaining $2p$ electrons of each atom decrease the radii of the corresponding shells such that the energy minimum is achieved that is lower than that of the reactant atoms. The resulting electron configuration of $CN$ is $C1s^2N1s^2C2s^2N2s^2C2p^1N2p^2\sigma_{C,N}^2$ where $\sigma$ designates the $H_2$-type MO, and the orbital arrangement is:



(13.810)

The carbon nitride radical is predicted to be weakly paramagnetic.

## FORCE BALANCE OF THE $2p$ SHELL OF THE CARBON ATOM OF THE CARBON NITRIDE RADICAL

For the $C$ atom, force balance for the outermost $2p$ electron of $CN$ (electron 5) is achieved between the centrifugal force and the Coulombic and magnetic forces that arise due to interactions between electron 5 and the $2s$-shell electrons due to spin and orbital angular momentum. The forces used are derived in the Six-Electron Atoms section. The central Coulomb force on the outer-most $2p$ shell electron of $CN$ (electron 5) due to the nucleus and the inner four electrons is given by Eq. (10.70) with the appropriate charge and radius:

$$\mathbf{F}_{ele} = \frac{(Z-4)e^2}{4\pi\varepsilon_0 r_5^2}\mathbf{i_r} \tag{13.811}$$

for $r > r_4$. The $2p$ shell possess an external electric field given by Eq. (10.92) for $r > r_5$.

The single unpaired carbon $2p$ electron gives rise to a diamagnetic force on the $\sigma$-MO as given by Eqs. (13.835-13.839). The corresponding Newtonian reaction force cancels $\mathbf{F}_{diamagnetic}$, of Eq. (10.82). The energy is minimized with conservation of angular momentum. This condition is met when:

$$\mathbf{F}_{diamagnetic} = 0 \tag{13.812}$$

And, $\mathbf{F}_{mag\ 2}$ corresponding to the maximum orbital angular momentum of the three $2p$ orbitals given by Eq. (10.89) is:

$$\mathbf{F}_{mag\ 2} = \frac{1}{Z}\frac{3\hbar^2}{m_e r_5^2 r_3}\sqrt{s(s+1)}\mathbf{i_r} \tag{13.813}$$

The electric field external to the $2p$ shell given by Eq. (10.92) for $r > r_5$ gives rise to a second diamagnetic force, $\mathbf{F}_{diamagnetic\ 2}$, given by Eq. (10.93). $\mathbf{F}_{diamagnetic\ 2}$ due to the binding of the p-orbital electron having an electric field of +1 outside of its radius is:

$$\mathbf{F}_{diamagnetic\ 2} = -\left[\frac{Z-5}{Z-4}\right]\left(1-\frac{\sqrt{2}}{2}\right)\frac{r_3\hbar^2}{m_e r_5^4}10\sqrt{s(s+1)}\mathbf{i_r} \tag{13.814}$$

The radius of the $2p$ shell is calculated by equating the outward centrifugal force to the sum of the electric (Eq. (13.811)) and diamagnetic (Eqs. (13.812) and (13.814)), and paramagnetic (Eq. (13.813)) forces as follows:

$$\frac{m_e v_5^2}{r_5} = \begin{pmatrix} \dfrac{(Z-4)e^2}{4\pi\varepsilon_0 r_5^2} + \dfrac{3\hbar^2}{Z m_e r_5^2 r_3}\sqrt{s(s+1)} \\ -\left[\dfrac{Z-5}{Z-4}\right]\left(1-\dfrac{\sqrt{2}}{2}\right)\dfrac{r_3\hbar^2}{r_5^4 m_e}10\sqrt{s(s+1)} \end{pmatrix} \tag{13.815}$$

Substitution of $v_5 = \frac{\hbar}{m_e r_5}$ (Eq. (1.35)) and $s = \frac{1}{2}$ into Eq. (13.815) gives:

$$\frac{\hbar^2}{m_e r_5^3} = \frac{(Z-4)e^2}{4\pi\varepsilon_0 r_5^2} + \frac{3\hbar^2}{Z m_e r_5^2 r_3}\sqrt{\frac{3}{4}} - \left[\frac{Z-5}{Z-4}\right]\left(1-\frac{\sqrt{2}}{2}\right)\frac{r_3\hbar^2}{r_5^4 m_e}10\sqrt{\frac{3}{4}} \tag{13.816}$$

The quadratic equation corresponding to Eq. (13.816) is:

$$r_5^2 - \frac{\frac{\hbar^2}{m_e}}{\left(\frac{(Z-4)e^2}{4\pi\varepsilon_0} + \frac{3\hbar^2}{Zm_e r_3}\sqrt{\frac{3}{4}}\right)} r_5 - \frac{\frac{\hbar^2}{m_e}\left[\frac{Z-5}{Z-4}\right]\left(1-\frac{\sqrt{2}}{2}\right) r_3 10\sqrt{\frac{3}{4}}}{\left(\frac{(Z-4)e^2}{4\pi\varepsilon_0} + \frac{3\hbar^2}{Zm_e r_3}\sqrt{\frac{3}{4}}\right)} = 0 \tag{13.817}$$

The solution of Eq. (13.817) using the quadratic formula is:

$$r_5 = \frac{\frac{a_0}{\left((Z-4)+\frac{3\sqrt{3}}{Z2r_3}\right)} \pm a_0 \sqrt{\left(\frac{1}{\left((Z-4)+\frac{3\sqrt{3}}{Z2r_3}\right)}\right)^2 + \frac{20\sqrt{3}\left(\left[\frac{Z-5}{Z-4}\right]\left(1-\frac{\sqrt{2}}{2}\right)r_3\right)}{\left((Z-4)+\frac{3\sqrt{3}}{Z2r_3}\right)}}}{2},\ r_3 \textit{ in units of } a_0 \tag{13.818}$$

The positive root of Eq. (13.818) must be taken in order that $r_5 > 0$. Substitution of $\frac{r_3}{a_0} = 0.84317$ (Eq. (10.62) with $Z = 6$) into Eq. (13.818) gives:

$$r_5 = 0.88084a_0 \tag{13.819}$$

## FORCE BALANCE OF THE $2p$ SHELL OF THE NITROGEN ATOM OF THE CARBON NITRIDE RADICAL

For the $N$ atom, force balance for the outermost $2p$ electron of $CN$ (electron 6) is achieved between the centrifugal force and the Coulombic and magnetic forces that arise due to interactions between electron 6 and the other $2p$-shell as well as the $2s$-shell electrons due to spin and orbital angular momentum. The forces used are derived in the Seven-Electron Atoms section. The central Coulomb force on the outer-most $2p$ shell electron of $CN$ (electron 6) due to the nucleus and the inner five electrons is given by Eq. (10.70) with the appropriate charge and radius:

$$\mathbf{F}_{ele} = \frac{(Z-5)e^2}{4\pi\varepsilon_0 r_6^2}\mathbf{i_r} \tag{13.820}$$

for $r > r_5$. The $2p$ shell possess an external electric field given by Eq. (10.92) for $r > r_6$.

The forces to determine the radius of the $N2p$ shell of $N$ in $CN$ are the same as those of $N$ in $N_2$ except that in $CN$ there is a contribution from the Newtonian reaction force that arises from the single unpaired carbon $2p$ electron. The energy is minimized with conservation of angular momentum. This condition is met when $\mathbf{F}_{diamagnetic}$ of $N$ in $CN$ is canceled by the $\sigma$-MO -reaction force. Eq. (13.622) becomes:

$$\mathbf{F}_{diamagnetic} = 0 \tag{13.821}$$

And, $\mathbf{F}_{mag\ 2}$ corresponding to the conserved orbital angular momentum of the three orbitals given by Eq. (10.89) is:

$$\mathbf{F}_{mag\ 2} = \frac{1}{Z}\frac{3\hbar^2}{m_e r_6^2 r_3}\sqrt{s(s+1)}\mathbf{i_r} \tag{13.822}$$

The electric field external to the $2p$ shell given by Eq. (10.92) for $r > r_6$ gives rise to a second diamagnetic force, $\mathbf{F}_{diamagnetic\ 2}$, given by Eq. (10.93). $\mathbf{F}_{diamagnetic\ 2}$ due to the binding of the p-orbital electron having an electric field of +1 outside of its radius is:

$$\mathbf{F}_{diamagnetic\ 2} = -\left[\frac{Z-6}{Z-5}\right]\left(1-\frac{\sqrt{2}}{2}\right)\frac{r_3\hbar^2}{m_e r_6^4}10\sqrt{s(s+1)}\mathbf{i_r} \tag{13.823}$$

The $N$ forces $\mathbf{F}_{ele}$, $\mathbf{F}_{mag\ 2}$, $\mathbf{F}_{diamagnetic\ 2}$, and $\mathbf{F}_{mag\ 3}$ of $CN$ are the same as those of $N_2$ given by Eqs. (13.621) and (13.623-13.624), respectively. In both cases, the contribution of a $2p$ electron from the $N$ atom in the formation of the $\sigma$ MO gives rise to a paramagnetic force on the remaining two $2p$ electrons that pair. Thus, the force, $\mathbf{F}_{mag\ 3}$ of $CN$, given by Eq. (13.625) is:

$$\mathbf{F}_{mag\ 3} = \frac{\hbar^2}{4m_e r_6^3}\sqrt{s(s+1)}\mathbf{i_r} \tag{13.824}$$

The radius of the $2p$ shell is calculated by equating the outward centrifugal force to the sum of the electric (Eq. (13.820)) and diamagnetic (Eqs. (13.821) and (13.823)), and paramagnetic (Eqs. (13.822) and (13.824)) forces as follows:

$$\frac{m_e v_6^2}{r_6} = \left( \begin{array}{l} \frac{(Z-5)e^2}{4\pi\varepsilon_0 r_6^2} + \frac{3\hbar^2}{Zm_e r_6^2 r_3}\sqrt{s(s+1)} \\ -\left[\frac{Z-6}{Z-5}\right]\left(1-\frac{\sqrt{2}}{2}\right)\frac{r_3\hbar^2}{r_6^4 m_e}10\sqrt{s(s+1)} + \frac{\hbar^2}{4m_e r_6^3}\sqrt{s(s+1)} \end{array} \right) \tag{13.825}$$

Substitution of $v_6 = \frac{\hbar}{m_e r_6}$ (Eq. (1.35)) and $s = \frac{1}{2}$ into Eq. (13.626) gives:

$$\frac{\hbar^2}{m_e r_6^3} - \frac{\hbar^2}{4m_e r_6^3}\sqrt{\frac{3}{4}} = \frac{(Z-5)e^2}{4\pi\varepsilon_0 r_6^2} + \frac{3\hbar^2}{Zm_e r_6^2 r_3}\sqrt{\frac{3}{4}} - \left[\frac{Z-6}{Z-5}\right]\left(1-\frac{\sqrt{2}}{2}\right)\frac{r_3\hbar^2}{r_6^4 m_e}10\sqrt{\frac{3}{4}} \tag{13.826}$$

The quadratic equation corresponding to Eq. (13.826) is

$$r_6^2 - \frac{\frac{\hbar^2}{m_e}\left(1-\frac{\sqrt{3}}{8}\right)}{\left(\frac{(Z-5)e^2}{4\pi\varepsilon_0} + \frac{3\hbar^2}{Zm_e r_3}\sqrt{\frac{3}{4}}\right)} r_6 - \frac{\frac{\hbar^2}{m_e}\left[\frac{Z-6}{Z-5}\right]\left(1-\frac{\sqrt{2}}{2}\right) r_3 10\sqrt{\frac{3}{4}}}{\left(\frac{(Z-5)e^2}{4\pi\varepsilon_0} + \frac{3\hbar^2}{Zm_e r_3}\sqrt{\frac{3}{4}}\right)} = 0 \tag{13.827}$$

The solution of Eq. (13.827) using the quadratic formula is:

$$r_6 = \frac{\frac{a_0\left(1-\frac{\sqrt{3}}{8}\right)}{\left((Z-5)+\frac{3\sqrt{3}}{Z2r_3}\right)} \pm a_0\sqrt{\left(\frac{1-\frac{\sqrt{3}}{8}}{\left((Z-5)+\frac{3\sqrt{3}}{Z2r_3}\right)}\right)^2 + \frac{20\sqrt{3}\left(\left[\frac{Z-6}{Z-5}\right]\left(1-\frac{\sqrt{2}}{2}\right)r_3\right)}{\left((Z-5)+\frac{3\sqrt{3}}{Z2r_3}\right)}}}{2},\ r_3 \textit{ in units of } a_0 \tag{13.828}$$

The positive root of Eq. (13.828) must be taken in order that $r_6 > 0$. Substitution of $\frac{r_3}{a_0} = 0.69385$ (Eq. (10.62) with $Z = 7$) into Eq. (13.828) gives:

$$r_6 = 0.76366a_0 \tag{13.829}$$

## ENERGIES OF THE $2p$ SHELLS OF THE CARBON AND NITROGEN ATOMS OF THE CARBON NITRIDE RADICAL

The central forces on the $2p$ shell of the $C$ and $N$ atoms are increased with the formation of the $\sigma$ MO which reduces each shell's radius and increases its total energy. The Coulombic energy terms of the total energy of the $C$ and $N$ atoms at the new radii are calculated and added to the energy of the $\sigma$ MO to give the total energy of $CN$. Then, the bond energy is determined from the total $CN$ energy.

The radius $r_6$ of the carbon atom before bonding is given by Eq. (10.122):

$$r_6 = 1.20654a_0 \tag{13.830}$$

Using the initial radius $r_6$ of the $C$ atom and the final radius $r_5$ of the $C2p$ shell of $CN$ (Eq. (13.819)) and by considering that the central Coulombic field decreases by an integer for each successive electron of the shell, the sum $E_T(CN, C2p)$ of the Coulombic energy change of the $C2p$ electron is determined using Eq. (10.102):

$$E_T\left(CN,C2p\right)=-\sum_{n=4}^{4}\frac{(Z-n)e^2}{8\pi\varepsilon_0}\left(\frac{1}{r_5}-\frac{1}{r_6}\right) =-\left(13.60580\ eV\right)\left(0.30647\right)\left(2\right)=-8.33948\ eV \tag{13.831}$$

The radius $r_7$ of the nitrogen atom before bonding is given by Eq. (10.142).

$$r_7=0.93084a_0 \tag{13.832}$$

Using the initial radius $r_7$ of the $N$ atom and the final radius $r_6$ of the $N2p$ shell of $CN$ (Eq. (13.829)) and by considering that the central Coulombic field decreases by an integer for each successive electron of the shell, the sum $E_T\left(CN,N2p\right)$ of the Coulombic energy change of the $N2p$ electron is determined using Eq. (10.102):

$$E_T\left(CN,N2p\right)=-\sum_{n=4}^{5}\frac{(Z-n)e^2}{8\pi\varepsilon_0}\left(\frac{1}{r_6}-\frac{1}{r_7}\right)=-\left(13.60580\ eV\right)\left(0.23518\right)\left(2+3\right)=-15.99929\ eV \tag{13.833}$$

## FORCE BALANCE OF THE $\sigma$ MO OF THE CARBON NITRIDE RADICAL

The diamagnetic force $\mathbf{F}_{diamagneticMO1}$ for the $\sigma$-MO of the $CN$ molecule due to the two paired electrons in the $N2p$ shell given by Eq. (13.633) with $n_e=2$ is:

$$\mathbf{F}_{diamagneticMO1}=\frac{\hbar^2}{2m_ea^2b^2}D\mathbf{i}_\xi \tag{13.834}$$

The force $\mathbf{F}_{diamagneticMO2}$ is given by Eq. (13.634) except that the force is summed over the individual diamagnetic-force terms due to each component of angular momentum $\left|L_i\right|$ acting on the electrons of the $\sigma$-MO from each atom having a nucleus of charge $Z_j$ at one of the foci of the $\sigma$-MO:

$$\mathbf{F}_{diamagneticMO2}=\sum_{i,j}\frac{\left|L_i\right|\hbar}{Z_j2m_ea^2b^2}D\mathbf{i}_\xi \tag{13.835}$$

Using Eqs. (11.200), (13.633-13.634), and (13.834-13.835), the force balance for the $\sigma$-MO of the carbon nitride radical comprising carbon with charge $Z_1=6$ and $\left|L_1\right|=\hbar$ and $\left|L_2\right|=\sqrt{\frac{3}{4}}\hbar$ and nitrogen with $Z_2=7$ and $\left|L_3\right|=\hbar$ is:

$$\frac{\hbar^2}{m_ea^2b^2}D=\frac{e^2}{8\pi\varepsilon_0ab^2}D+\frac{\hbar^2}{2m_ea^2b^2}D-\left(1+\frac{1}{Z_1}+\frac{\sqrt{\frac{3}{4}}}{Z_1}+\frac{1}{Z_2}\right)\frac{\hbar^2}{2m_ea^2b^2}D \tag{13.836}$$

$$\frac{\hbar^2}{m_ea^2b^2}D=\frac{e^2}{8\pi\varepsilon_0ab^2}D-\left(\frac{1}{Z_1}+\frac{\sqrt{\frac{3}{4}}}{Z_1}+\frac{1}{Z_2}\right)\frac{\hbar^2}{2m_ea^2b^2}D \tag{13.837}$$

$$\left(2+\frac{1}{Z_1}+\frac{\sqrt{\frac{3}{4}}}{Z_1}+\frac{1}{Z_2}\right)\frac{\hbar^2}{2m_ea^2b^2}D=\frac{e^2}{8\pi\varepsilon_0ab^2}D \tag{13.838}$$

$$a=\left(2+\frac{1}{Z_1}+\frac{\sqrt{\frac{3}{4}}}{Z_1}+\frac{1}{Z_2}\right)a_0 \tag{13.839}$$

Substitution of $Z_1=6$ and $Z_2=7$ into Eq. (13.839) gives:

$$a=2.45386a_0=1.29853\ X\ 10^{-10}\ m \tag{13.840}$$

Substitution of Eq. (13.840) into Eq. (11.79) is:

$$c'=1.10767a_0=5.86153\ X\ 10^{-11}\ m \tag{13.841}$$

The internuclear distance given by multiplying Eq. (13.841) by two is:

$$2c'=2.21534a_0=1.17231\ X\ 10^{-10}\ m \tag{13.842}$$

The experimental bond distance from Ref. [28] is:

$$2c'=1.17181\ X\ 10^{-10}\ m \tag{13.843}$$

Substitution of Eqs. (13.840-13.841) into Eq. (11.80) is:

$$b = c = 2.18964a_0 = 1.15871\ X\ 10^{-10}\ m \tag{13.844}$$

Substitution of Eqs. (13.840-13.841) into Eq. (11.67) is:

$$e = 0.45140 \tag{13.845}$$

Using the electron configuration of $CN$ (Eq. (13.810)), the radii of the $C1s = 0.17113a_0$ (Eq. (10.51)), $C2s = 0.84317a_0$ (Eq. (10.62)), $C2p = 0.88084a_0$ (Eq. (13.819)), $N1s = 0.14605a_0$ (Eq. (10.51)), $N2s = 0.69385a_0$ (Eq. (10.62)), and $N2p = 0.76366a_0$ (Eq. (13.829)) shells and the parameters of the $\sigma$ MO of $CN$ given by Eqs. (13.3-13.4), (13.840-13.842), and (13.844-13.845), the dimensional diagram and charge-density of the $CN$ MO are shown in Figures 13.22 and 13.23, respectively.

Figure 13.22. The cross section of the $CN$ MO showing the axes, $\sigma$ MO ($H_2$-type ellipsoidal MO), with the $C$ $1s$, $2s$, and $2p$ atomic orbitals (AOs) and the $N$ $1s$, $2s$, and $2p$ AOs. Legend: $a$: semimajor axis, $b$: semiminor axis, $c'$: internuclear distance, $r_5$: radius of the $C2p$ shell having one unpaired electron, $r_6$: radius of the $N2p$ shell having two paired electrons.

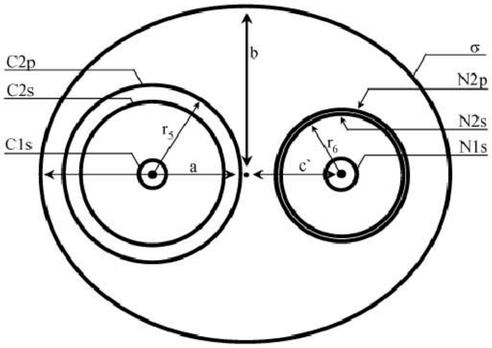
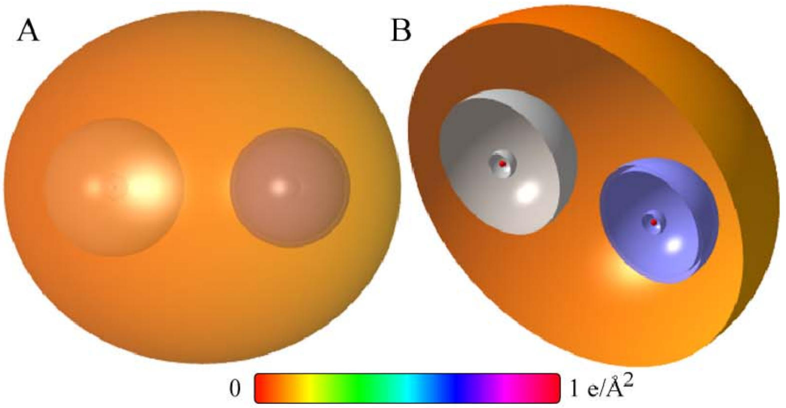


Figure 13.23. $CN$ MO comprising the $\sigma$ MO ($H_2$-type MO) with $C$ and $N$ atoms at the foci that have each donated an electron to the $\sigma$ MO and have smaller radii and higher binding energies as a consequence. (A) Color scale, translucent view of the charge-density of the $CN$ MO. (B) Off-center cut-away view showing the complete inner most $C1s$ shell, and moving radially, the $C2s$ shell, the $C2p$ shell, and the $\sigma$ prolate spheroidal MO that has the $C$ atom as a focus. Moving radially from the nitrogen-atom focus, the complete inner most $N1s$ shell, the $N2s$ shell, the $N2p$ shell, and the $\sigma$ prolate spheroidal MO are shown.



## SUM OF THE ENERGIES OF THE $\sigma$ MO AND THE AOs OF THE CARBON NITRIDE RADICAL

The energies of the $CN$ $\sigma$ MO are given by the substitution of the semiprincipal axes (Eqs. (13.840-13.841) and (13.844)) into the energy equations (Eqs. (11.207-11.212)) of $H_2$:

$$V_e = \frac{-2e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}} \ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -23.90105\ eV \tag{13.846}$$

$$V_p = \frac{e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}} = 12.28328\ eV \tag{13.847}$$

$$T = \frac{\hbar^2}{2m_e a\sqrt{a^2-b^2}} \ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = 4.87009\ eV \tag{13.848}$$

$$V_m = \frac{-\hbar^2}{4m_e a\sqrt{a^2-b^2}} \ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -2.43504\ eV \tag{13.849}$$

$$E_T = V_e + T + V_m + V_p \tag{13.850}$$

Substitution of Eqs. (11.79) and (13.846-13.849) into Eq. (13.850) gives:

$$E_T\left(CN,\sigma\right)=\frac{-e^2}{8\pi\varepsilon_0\sqrt{\frac{aa_0}{2}}}\left(\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+\sqrt{\frac{aa_0}{2}}}{a-\sqrt{\frac{aa_0}{2}}}-1\right)=-9.18273\ eV \tag{13.851}$$

where $E_T\left(CN,\sigma\right)$ is the total energy of the $\sigma$ MO of $CN$. The sum, $E_T\left(CN\right)$, of $E_T\left(CN,C2p\right)$, the $C2p$ AO contribution given by Eq. (13.831), $E_T\left(CN,N2p\right)$, the $N2p$ AO contribution given by Eq. (13.833), and $E_T\left(CN,\sigma\right)$, the $\sigma$ MO contribution given by Eq. (13.851) is:

$$\begin{aligned}E_T\left(CN\right)&=E_T\left(CN,C2p\right)+E_T\left(CN,N2p\right)+E_T\left(N_2,\sigma\right)\\&=-8.33948\ eV-15.99929\ eV-9.18273\ eV\\&=-33.52149\ eV\end{aligned} \tag{13.852}$$

## VIBRATION OF $CN$

The vibrational energy levels of $CN$ may be solved by determining the Morse potential curve from the energy relationships for the transition from a $C$ atom and $N$ atom whose parameters are given by Eqs. (10.115-10.123) and (10.134-10.143), respectively, to a $C$ atom whose parameter $r_5$ is given by Eq. (10.819), a $N$ atom whose parameter $r_6$ is given by Eq. (13.829), and the $\sigma$ MO whose parameters are given by Eqs. (13.840-13.842) and (13.844-13.845). As shown in the Vibration of Hydrogen-type Molecular Ions section, the harmonic oscillator potential energy function can be expanded about the internuclear distance and expressed as a Maclaurin series corresponding to a Morse potential after Karplus and Porter (K&P) [15] and after Eq. (11.134). Treating the Maclaurin series terms as anharmonic perturbation terms of the harmonic states, the energy corrections can be found by perturbation methods.

## THE DOPPLER ENERGY TERMS OF THE CARBON NITRIDE RADICAL

The equations of the radiation reaction force of $CN$ are the same as those of $H_2$ with the substitution of the $CN$ parameters. Using Eqs. (11.231-11.233), the angular frequency of the reentrant oscillation in the transition state is:

$$\omega=\sqrt{\frac{\frac{e^2}{4\pi\varepsilon_0 a^3}}{m_e}}=1.07550\ X\ 10^{16}\ rad/s \tag{13.853}$$

where $a$ is given by Eq. (13.840). The kinetic energy, $E_K$, is given by Planck's equation (Eq. (11.127)).

$$\overline{E}_K=\hbar\omega=\hbar 1.07550\ X\ 10^{16}\ rad/s=7.07912\ eV \tag{13.854}$$

In Eq. (11.181), substitution of $E_T\left(CN\right)$ for $E_{h\nu}$, the mass of the electron, $m_e$, for $M$, and the kinetic energy given by Eq. (13.854) for $\overline{E}_K$ gives the Doppler energy of the electrons of the reentrant orbit:

$$\begin{aligned}\overline{E}_D&\cong E_{h\nu}\sqrt{\frac{2\overline{E}_K}{Mc^2}}=-33.59603\ eV\sqrt{\frac{2e\left(7.07912\ eV\right)}{m_ec^2}}\\&=-0.17684\ eV\end{aligned} \tag{13.855}$$

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency. The decrease in the energy of the $CN$ MO due to the reentrant orbit in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei, $\overline{E}_{osc}$, is given by the sum of the corresponding energies, $\overline{E}_D$ given by Eq. (13.855) and $\overline{E}_{Kvib}$, the average kinetic energy of vibration which is 1/2 of the vibrational energy. Using the experimental $CN$ $\omega_e$ of 2068.59 $cm^{-1}$ $\left(0.25647\ eV\right)$ [28] for $\overline{E}_{Kvib}$ of the transition state, $\overline{E}_{osc}\left(CN\right)$ is:

$$\begin{aligned}\overline{E}_{osc}\left(CN\right)&=\overline{E}_D+\overline{E}_{Kvib}\\&=\overline{E}_D+\frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\end{aligned} \tag{13.856}$$

$$\begin{aligned}\overline{E}_{osc}\left(CN\right)&=-0.17684\ eV+\frac{1}{2}\left(0.25647\ eV\right)\\&=-0.04860\ eV\end{aligned} \tag{13.857}$$

## TOTAL AND BOND ENERGIES OF THE CARBON NITRIDE RADICAL

$E_{T+osc}(CN)$, the total energy of $CN$ including the Doppler term, is given by the sum of $E_T(CN)$ (Eq. (13.852)) and $\bar{E}_{osc}(CN)$ given by Eq. (13.857):

$$\begin{aligned} E_{T+osc}(CN) &= V_e + T + V_m + V_p + E_T(CN,C2p) + E_T(CN,N2p) + \bar{E}_{osc}(CN) \\ &= E_T(CN,\sigma) + E_T(CN,C2p) + E_T(CN,N2p) + \bar{E}_{osc}(CN) \\ &= E_T(CN) + \bar{E}_{osc}(CN) \end{aligned} \tag{13.858}$$

$$E_{T+osc}(CN) = \left\{ \begin{array}{l} \left( \begin{array}{l} \dfrac{-e^2}{8\pi\varepsilon_0\sqrt{\dfrac{aa_0}{2}}} \left( \left(2 - \dfrac{1}{2}\dfrac{a_0}{a}\right) \ln \dfrac{a + \sqrt{\dfrac{aa_0}{2}}}{a - \sqrt{\dfrac{aa_0}{2}}} - 1 \right) \\ - \displaystyle\sum_{C,n=4}^{4} \dfrac{(Z-n)e^2}{8\pi\varepsilon_0}\left(\dfrac{1}{r_5} - \dfrac{1}{r_6}\right) - \displaystyle\sum_{N,n=4}^{5} \dfrac{(Z-n)e^2}{8\pi\varepsilon_0}\left(\dfrac{1}{r_6} - \dfrac{1}{r_7}\right) \end{array} \right) \\ \left( 1 + \sqrt{\dfrac{2\hbar\sqrt{\dfrac{\dfrac{e^2}{4\pi\varepsilon_o a^3}}{m_e}}}{m_e c^2}} \right) + \dfrac{1}{2}\hbar\sqrt{\dfrac{k}{\mu}} \end{array} \right\} \tag{13.859}$$

$$= -33.52149\ eV - 0.17684\ eV + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}$$

From Eqs. (13.856-13.859), the total energy of the $CN$ MO is:

$$\begin{aligned} E_{T+osc}(CN) &= -33.52149\ eV + \bar{E}_{osc}(CN) \\ &= -33.52149\ eV - 0.17684\ eV + \frac{1}{2}(0.25647\ eV) \\ &= -33.56970\ eV \end{aligned} \tag{13.860}$$

where the experimental $\omega_e$ was used for the $\hbar\sqrt{\frac{k}{\mu}}$ term.

The $CN$ bond dissociation energy, $E_D(CN)$, is given by the difference between the sum of the energies of the $C$ and $N$ atoms and $E_{T+osc}(CN)$:

$$E_D(CN) = E(C) + E(N) - E_{T+osc}(CN) \tag{13.861}$$

where the energy of a carbon atom is [6]:

$$E(C) = -11.26030\ eV \tag{13.862}$$

and the energy of a nitrogen atom is [6]:

$$E(N) = -14.53414\ eV \tag{13.863}$$

Thus, the $CN$ bond dissociation energy, $E_D(CN)$, given by Eqs. (13.860-13.863) is:

$$\begin{aligned} E_D(CN) &= -(11.26030\ eV + 14.53414\ eV) - E_{T+osc}(CN) \\ &= -25.79444\ eV - (-33.56970\ eV) \\ &= 7.77526\ eV \end{aligned} \tag{13.864}$$

The experimental $CN$ bond dissociation energy is [50]:

$$E_{D298}(CN) = 7.7731\ eV \tag{13.865}$$

The results of the determination of bond parameters of $CN$ are given in Table 13.1. The calculated results are based on first principles and given in closed-form, exact equations containing fundamental constants only. The agreement between the experimental and calculated results is excellent.

## CARBON MONOXIDE MOLECULE

The carbon monoxide molecule can be formed by the reaction of carbon and oxygen atoms:

$$C+O\rightarrow CO \tag{13.866}$$

The bond in the carbon monoxide molecule comprises a double bond, a $H_2$-type molecular orbital (MO) with four paired electrons. The force balance equation and radius $r_6$ of the $2p$ shell of $C$ is derived in the Six-Electron Atoms section. The force balance equation and radius $r_8$ of the $2p$ shell of $O$ is derived in the Eight-Electron Atoms section. With the formation of the $H_2$-type MO by the contribution of two $2p$ electrons from each of the $C$ and $O$ atoms, a diamagnetic force arises between the remaining outer shell atomic electrons, the $2s$ electrons of $C$ and the $2p$ electrons of $O$, and the $H_2$-type MO. This force from $C$ and $O$ causes the $H_2$-type MO to move to greater principal axes than would result with the Coulombic force alone. But, the factor of two increase of the central field and the resulting increased Coulombic as well as magnetic central forces on the remaining $O2p$ electrons decrease the radius of the corresponding shell such that the energy minimum is achieved that is lower than that of the reactant atoms. The resulting electron configuration of $CO$ is $C1s^2O1s^2C2s^2O2s^2O2p^2\sigma_{C,O}^4$ where $\sigma$ designates the $H_2$-type MO, and the orbital arrangement is:

$\sigma$ state
↑ ↓ ↑ ↓

2p state
↑↓
0
2s state
↑↓ ↑↓ (13.867)

1s state
↑↓ ↑↓
$C$ $O$

Carbon monoxide is predicted to be diamagnetic in agreement with observations [42].

## FORCE BALANCE OF THE $2p$ SHELL OF THE OXYGEN ATOM OF THE CARBON MONOXIDE MOLECULE

For the $O$ atom, force balance for the outermost $2p$ electron of $CO$ (electron 6) is achieved between the centrifugal force and the Coulombic and magnetic forces that arise due to interactions between electron 6 and the other $2p$ electron as well as the $2s$-shell electrons due to spin and orbital angular momentum. The forces used are derived in the Eight-Electron Atoms section. The central Coulomb force on the outer-most $2p$ shell electron of $CO$ (electron 6) due to the nucleus and the inner five electrons is given by Eq. (10.70) with the appropriate charge and radius:

$$\mathbf{F}_{ele}=\frac{(Z-5)e^2}{4\pi\varepsilon_0 r_6^2}\mathbf{i_r} \tag{13.868}$$

for $r>r_5$. The $2p$ shell possesses a +2 external electric field given by Eq. (10.92) for $r>r_6$. The energy is minimized with conservation of angular momentum. This condition is met when the diamagnetic force, $\mathbf{F}_{diamagnetic}$, of Eq. (10.82) due to the $p$-orbital contribution is given by:

$$\begin{aligned}\mathbf{F}_{diamagnetic}&=-\left(\frac{1}{3}\right)\frac{\hbar^2}{4m_e r_6^2 r_3}\sqrt{s(s+1)}\mathbf{i_r}\\&=-\frac{\hbar^2}{12m_e r_6^2 r_3}\sqrt{\frac{3}{4}}\mathbf{i_r}\end{aligned} \tag{13.869}$$

And, $\mathbf{F}_{mag\ 2}$ corresponding to the conserved spin and orbital angular momentum given by Eq. (10.157) is:

$$\mathbf{F}_{mag\ 2}=\frac{1}{Z}\frac{2\hbar^2}{m_e r_6^2 r_3}\sqrt{s(s+1)}\mathbf{i_r} \tag{13.870}$$

The electric field external to the $2p$ shell given by Eq. (10.92) for $r > r_6$ gives rise to a second diamagnetic force, $\mathbf{F}_{diamagnetic\ 2}$, given by Eq. (10.93). $\mathbf{F}_{diamagnetic\ 2}$ due to the binding of the p-orbital electron having an electric field of +2 outside of its radius is:

$$\mathbf{F}_{diamagnetic\ 2} = -\left[\frac{Z-6}{Z-5}\right]\left(1-\frac{\sqrt{2}}{2}\right)\frac{r_3\hbar^2}{m_e r_6^4}10\sqrt{s(s+1)}\mathbf{i_r} \tag{13.871}$$

In addition, the contribution of two $2p$ electrons in the formation of the $\sigma$ molecular orbital (MO) gives rise to a paramagnetic force on the remaining paired $2p$ electrons. The force $\mathbf{F}_{mag\ 3}$ is given by Eq. (13.625) wherein the radius is $r_6$:

$$\mathbf{F}_{mag\ 3} = \frac{\hbar^2}{4m_e r_6^3}\sqrt{s(s+1)}\mathbf{i_r} \tag{13.872}$$

The radius of the $2p$ shell is calculated by equating the outward centrifugal force to the sum of the electric (Eq. (13.868)) and diamagnetic (Eqs. (13.869) and (13.871)), and paramagnetic (Eqs. (13.870) and (13.872)) forces as follows:

$$\frac{m_e v_6^2}{r_6} = \left(\begin{array}{l} \dfrac{(Z-5)e^2}{4\pi\varepsilon_0 r_6^2} - \dfrac{\hbar^2}{12m_e r_6^2 r_3}\sqrt{s(s+1)} + \dfrac{2\hbar^2}{Zm_e r_6^2 r_3}\sqrt{s(s+1)} \\ -\left[\dfrac{Z-6}{Z-5}\right]\left(1-\dfrac{\sqrt{2}}{2}\right)\dfrac{r_3\hbar^2}{r_6^4 m_e}10\sqrt{s(s+1)} + \dfrac{\hbar^2}{4m_e r_6^3}\sqrt{s(s+1)} \end{array}\right) \tag{13.873}$$

Substitution of $v_6 = \dfrac{\hbar}{m_e r_6}$ (Eq. (1.35)) and $s = \dfrac{1}{2}$ into Eq. (13.873) gives:

$$\frac{\hbar^2}{m_e r_6^3} - \frac{\hbar^2}{4m_e r_6^3}\sqrt{\frac{3}{4}} = \frac{(Z-5)e^2}{4\pi\varepsilon_0 r_6^2} - \frac{\hbar^2}{12m_e r_6^2 r_3}\sqrt{\frac{3}{4}} + \frac{2\hbar^2}{Zm_e r_6^2 r_3}\sqrt{\frac{3}{4}} - \left[\frac{Z-6}{Z-5}\right]\left(1-\frac{\sqrt{2}}{2}\right)\frac{r_3\hbar^2}{r_6^4 m_e}10\sqrt{\frac{3}{4}} \tag{13.874}$$

The quadratic equation corresponding to Eq. (13.874) is

$$r_6^2 - \frac{\dfrac{\hbar^2}{m_e}\left(1-\dfrac{\sqrt{3}}{8}\right)}{\left(\dfrac{(Z-5)e^2}{4\pi\varepsilon_0} - \left(\dfrac{1}{12}-\dfrac{2}{Z}\right)\dfrac{\hbar^2}{m_e r_3}\sqrt{\dfrac{3}{4}}\right)}r_6 - \frac{\dfrac{\hbar^2}{m_e}\left[\dfrac{Z-6}{Z-5}\right]\left(1-\dfrac{\sqrt{2}}{2}\right)r_3 10\sqrt{\dfrac{3}{4}}}{\left(\dfrac{(Z-5)e^2}{4\pi\varepsilon_0} - \left(\dfrac{1}{12}-\dfrac{2}{Z}\right)\dfrac{\hbar^2}{m_e r_3}\sqrt{\dfrac{3}{4}}\right)} = 0 \tag{13.875}$$

The solution of Eq. (13.875) using the quadratic formula is:

$$r_6 = \frac{\dfrac{a_0\left(1-\dfrac{\sqrt{3}}{8}\right)}{\left((Z-5)-\left(\dfrac{1}{12}-\dfrac{2}{Z}\right)\dfrac{\sqrt{3}}{2r_3}\right)} \pm a_0\sqrt{\left(\dfrac{1-\dfrac{\sqrt{3}}{8}}{\left((Z-5)-\left(\dfrac{1}{12}-\dfrac{2}{Z}\right)\dfrac{\sqrt{3}}{2r_3}\right)}\right)^2 + \dfrac{20\sqrt{3}\left(\left[\dfrac{Z-6}{Z-5}\right]\left(1-\dfrac{\sqrt{2}}{2}\right)r_3\right)}{\left((Z-5)-\left(\dfrac{1}{12}-\dfrac{2}{Z}\right)\dfrac{\sqrt{3}}{2r_3}\right)}}}{2}, \; r_3 \textit{ in units of } a_0 \tag{13.876}$$

The positive root of Eq. (13.876) must be taken in order that $r_6 > 0$. Substitution of $\dfrac{r_3}{a_0} = 0.59020$ (Eq. (10.62) with $Z = 8$) into Eq. (13.876) gives:

$$r_6 = 0.68835a_0 \tag{13.877}$$

## ENERGIES OF THE $2s$ AND $2p$ SHELLS OF THE CARBON ATOM AND THE $2p$ SHELL OF THE OXYGEN ATOM OF THE CARBON MONOXIDE MOLECULE

With the formation of the $H_2$-type MO by the contribution of two $2p$ electrons from the $C$ atom, the remaining outer-shell atomic electrons comprise the $2s$ electrons, which are unchanged by bonding with oxygen. However, the total energy of the $CO$ molecule, which is subtracted from the sum of the energies of the carbon and oxygen atoms to determine the bond energy, is increased by the ionization energies of $C^+$ and $O^+$ given by Eqs. (10.113-10.114) and (10.152-10.153), respectively. Experimentally, the energies are [6] :

$$E(ionization;\ C^+) = 24.38332\ eV \tag{13.878}$$

$$E(ionization;\ O^+) = 35.11730\ eV \tag{13.879}$$

In addition, the central forces on the $2p$ shell of the $O$ atom are increased with the formation of the $\sigma$ MO, which reduces the shell's radius and increases its total energy. The Coulombic energy terms of the total energy of the $O$ atom at the new radius are calculated and added to the ionization energies of $C^+$ and $O^+$, and the energy of the $\sigma$ MO to give the total energy of $CO$. Then, the bond energy is determined from the total $CO$ energy.

The radius $r_8$ of the oxygen atom before bonding is given by Eq. (10.162):

$$r_8 = a_0 \tag{13.880}$$

Using the initial radius $r_8$ of the $O$ atom and the final radius $r_6$ of the $O2p$ shell (Eq. (13.877)) and by considering that the central Coulombic field decreases by an integer for each successive electron of the shell, the sum $E_T\left(O,2p\right)$ of the Coulombic energy change of the $O2p$ electrons of the $O$ atom is determined using Eq. (10.102):

$$E_T\left(O,2p\right) = -\sum_{n=4}^{5} \frac{(Z-n)e^2}{8\pi\varepsilon_0}\left(\frac{1}{r_6}-\frac{1}{r_8}\right) = -\left(13.60580\ eV\right)\left(0.45275\right)\left(3+4\right) = -43.11996\ eV \tag{13.881}$$

## FORCE BALANCE OF THE $\sigma$ MO OF THE CARBON MONOXIDE MOLECULE

The force balance can be considered due to a second pair of two electrons binding to a molecular ion having $+2e$ at each focus and a first bound pair. Then, the forces are the same as those of a molecule ion having $+e$ at each focus. The diamagnetic force $\mathbf{F}_{diamagneticMO1}$ for the $\sigma$-MO of the $CO$ molecule due to the two paired electrons in each of the $C2s$ and $O2p$ shells is given by Eq. (13.633) with $n_e = 2$:

$$\mathbf{F}_{diamagneticMO1} = \frac{\hbar^2}{2m_e a^2 b^2} D\mathbf{i}_\xi \tag{13.882}$$

The force $\mathbf{F}_{diamagneticMO2}$ is given by Eqs. (13.634) and (13.835) as the sum of the contributions due to carbon with $Z = Z_1$ and oxygen with $Z = Z_2$. $\mathbf{F}_{diamagneticMO1}$ for $CO$ with $\left|L_i\right| = \hbar$ is:

$$\mathbf{F}_{diamagneticMO2} = \left(\frac{1}{Z_1}+\frac{1}{Z_2}\right)\frac{\hbar^2}{2m_e a^2 b^2} D\mathbf{i}_\xi \tag{13.883}$$

The force balance equation for the $\sigma$-MO of the carbon monoxide molecule given by Eqs. (11.200), (13.633-13.634), and (13.882-13.883) is:

$$\frac{\hbar^2}{m_e a^2 b^2} D = \frac{e^2}{8\pi\varepsilon_0 a b^2} D + \frac{\hbar^2}{2m_e a^2 b^2} D - \left(1+\left(\frac{1}{Z_1}+\frac{1}{Z_2}\right)\right)\frac{\hbar^2}{2m_e a^2 b^2} D \tag{13.884}$$

$$\frac{\hbar^2}{m_e a^2 b^2} D = \frac{e^2}{8\pi\varepsilon_0 a b^2} D - \left(\frac{1}{Z_1}+\frac{1}{Z_2}\right)\frac{\hbar^2}{2m_e a^2 b^2} D \tag{13.885}$$

$$\left(2+\frac{1}{Z_1}+\frac{1}{Z_2}\right)\frac{\hbar^2}{2m_e a^2 b^2} D = \frac{e^2}{8\pi\varepsilon_0 a b^2} D \tag{13.886}$$

$$a = \left(2+\frac{1}{Z_1}+\frac{1}{Z_2}\right) a_0 \tag{13.887}$$

Substitution of $Z_1 = 6$ and $Z_2 = 8$ into Eq. (13.887) gives:

$$a = 2.29167 a_0 = 1.21270\ X\ 10^{-10}\ m \tag{13.888}$$

Substitution of Eq. (13.888) into Eq. (11.79) is:

$$c' = 1.07044a_0 = 5.66450\ X\ 10^{-11}\ m \tag{13.889}$$

The internuclear distance given by multiplying Eq. (13.889) by two is:

$$2c' = 2.14087a_0 = 1.13290\ X\ 10^{-10}\ m \tag{13.890}$$

The experimental bond distance is [28]:

$$2c' = 1.12823\ X\ 10^{-10}\ m \tag{13.891}$$

Substitution of Eqs. (13.888-13.889) into Eq. (11.80) is:

$$b = c = 2.02630a_0 = 1.07227\ X\ 10^{-10}\ m \tag{13.892}$$

Substitution of Eqs. (13.888-13.889) into Eq. (11.67) is:

$$e = 0.46710 \tag{13.893}$$

Using the electron configuration of $CO$ (Eq. (13.867)), the radii of the $C1s = 0.17113a_0$ (Eq. (10.51)), $C2s = 0.84317a_0$ (Eq. (10.62)), $O1s = 0.12739a_0$ (Eq. (10.51)), $O2s = 0.59020a_0$ (Eq. (10.62)), and $O2p = 0.68835a_0$ (Eq. (13.877)) shells and the parameters of the $\sigma$ MO of $CO$ given by Eqs. (13.3-13.4), (13.888-13.890), and (13.892-13.893), the dimensional diagram and charge-density of the $CO$ MO are shown in Figures 13.24 and 13.25, respectively.

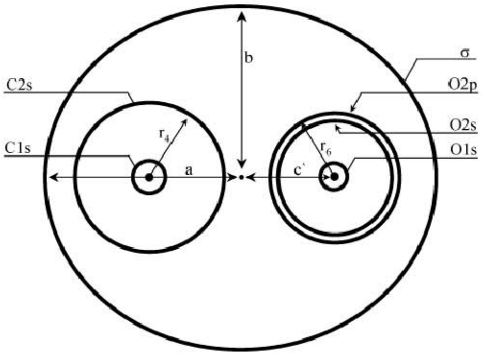


Figure 13.24. The cross section of the $CO$ MO showing the axes, $\sigma$ MO ($H_2$-type ellipsoidal MO) with four paired electrons, with the $C$ $1s$ and $2s$ atomic orbitals (AOs) and the $O$ $1s$, $2s$, and $2p$ AOs. Legend: $a$: semimajor axis, $b$: semiminor axis, $c'$: internuclear distance, $r_4$: radius of the $C2s$ shell having two paired electrons, $r_6$: radius of the $O2p$ shell having two paired electrons.

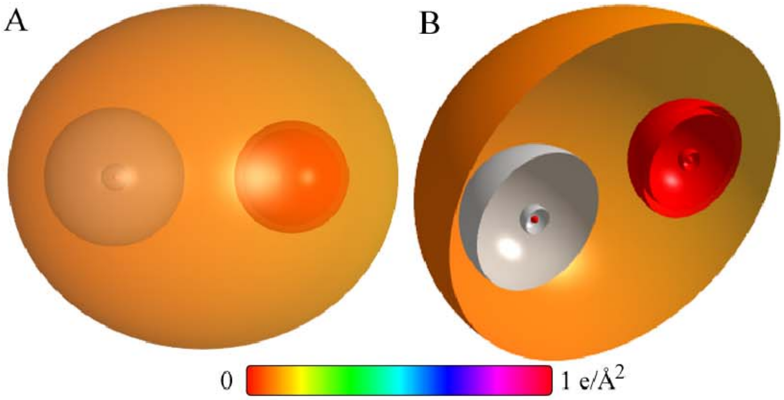


Figure 13.25. $CO$ MO comprising the $\sigma$ MO ($H_2$-type MO) with $C$ and $O$ atoms at the foci that have each donated two electrons to the $\sigma$ MO. Consequently, the outer electrons of the carbon atom comprise the $C2s$ shell, and the $O2p$ shell has a smaller radius and a higher binding energy. (A) Color scale, translucent view of the charge-density of the $CO$ MO. (B) Off-center cut-away view showing the complete inner most $O1s$ shell, and moving radially, the $O2s$ shell, the $O2p$ shell, and the $\sigma$ prolate spheroidal MO that has the $O$ atom as a focus. Moving radially from the carbon-atom focus, the complete inner most $C1s$ shell, the $C2s$ shell, and the $\sigma$ prolate spheroidal MO are shown.

## SUM OF THE ENERGIES OF THE $\sigma$ MO AND THE AOs OF THE CARBON MONOXIDE MOLECULE

The energies of the $CO$ $\sigma$ MO are given by the substitution of the semiprincipal axes (Eqs. (13.888-13.889) and (13.892)) into the energy equations (Eqs. (11.207-11.212)) of $H_2$ except that the terms based on charge are multiplied by four and the kinetic energy term is multiplied by two due to the $\sigma$-MO double bond with two pairs of paired electrons:

$$V_e = 2^2 \frac{-2e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}} \ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -102.97635\ eV \tag{13.894}$$

$$V_p = 2^2 \frac{e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}} = 50.84210\ eV \tag{13.895}$$

$$T = 2\frac{\hbar^2}{2m_e a\sqrt{a^2-b^2}} \ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = 11.23379\ eV \tag{13.896}$$

$$V_m = 2^2 \frac{-\hbar^2}{4m_e a\sqrt{a^2-b^2}} \ln \frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -11.23379\ eV \tag{13.897}$$

$$E_T = V_e + T + V_m + V_p \tag{13.898}$$

Substitution of Eqs. (11.79) and (13.894-13.897) into Eq. (13.898) gives:

$$E_T\left(CO,\sigma\right) = \frac{-e^2}{8\pi\varepsilon_0\sqrt{\frac{aa_0}{2}}}\left(8\ln\frac{a+\sqrt{\frac{aa_0}{2}}}{a-\sqrt{\frac{aa_0}{2}}}-4\right) = -52.13425\ eV \tag{13.899}$$

where $E_T\left(CO,\sigma\right)$ is the total energy of the $\sigma$ MO of $CO$. The total energy of $CO$, $E_T\left(CO\right)$, is given by the sum of $E(ionization;\ C^+)$, the energy of the second electron of carbon (Eq. (13.878)) donated to the double bond, $E(ionization;\ O^+)$, the energy of the second electron of oxygen (Eq. (13.879)) donated to the double bond, $E_T\left(O,2p\right)$, the $O2p$ AO contribution due to the decrease in radius with bond formation (Eq. (13.881)), and $E_T\left(CO,\sigma\right)$, the $\sigma$ MO contribution given by Eq. (13.899):

$$\begin{aligned} E_T\left(CO\right) &= E(ionization;\ C^+) + E(ionization;\ O^+) + E_T\left(O,2p\right) + E_T\left(CO,\sigma\right) \\ &= 24.38332\ eV + 35.11730\ eV - 43.11996\ eV - 52.13425\ eV \\ &= -35.75359\ eV \end{aligned} \tag{13.900}$$

## VIBRATION OF $CO$

The vibrational energy levels of $CO$ may be solved by determining the Morse potential curve from the energy relationships for the transition from a $C$ atom and $O$ atom whose parameters are given by Eqs. (10.115-10.123) and (10.154-10.163), respectively, to a $C$ atom whose parameter $r_4$ is given by Eq. (10.61), an $O$ atom whose parameter $r_6$ is given by Eq. (13.877), and the $\sigma$ MO whose parameters are given by Eqs. (13.888-13.890) and (13.892-13.893). As shown in the Vibration of Hydrogen-type Molecular Ions section, the harmonic oscillator potential energy function can be expanded about the internuclear distance and expressed as a Maclaurin series corresponding to a Morse potential after Karplus and Porter (K&P) [15] and after Eq. (11.134). Treating the Maclaurin series terms as anharmonic perturbation terms of the harmonic states, the energy corrections can be found by perturbation methods.

## THE DOPPLER ENERGY TERMS OF THE CARBON MONOXIDE MOLECULE

The equations of the radiation reaction force of carbon monoxide are the same as those of $H_2$ with the substitution of the $CO$ parameters except that there is a factor of four increase in the central force in Eq. (11.231) due to the double bond. Using Eqs. (11.231-11.233), the angular frequency of the reentrant oscillation in the transition state is

$$\omega = \sqrt{\frac{\frac{4e^2}{4\pi\varepsilon_0 a^3}}{m_e}} = 2.38335\ X\ 10^{16}\ rad/s \tag{13.901}$$

where $a$ is given by Eq. (13.888). The kinetic energy, $E_K$, is given by Planck's equation (Eq. (11.127)).

$$\begin{aligned} \overline{E}_K &= \hbar\omega = \hbar 2.38335\ X\ 10^{16}\ rad/s \\ &= 15.68762\ eV \end{aligned} \tag{13.902}$$

In Eq. (11.181), substitution of $E_T\left(CO\right)$ for $E_{h\nu}$, the mass of the electron, $m_e$, for $M$, and the kinetic energy given by Eq. (13.902) for $\overline{E}_K$ gives the Doppler energy of the electrons of the reentrant orbit:

$$\begin{aligned} \overline{E}_D &\cong E_{h\nu}\sqrt{\frac{2\overline{E}_K}{Mc^2}} \\ &= -35.75359\ eV\sqrt{\frac{2e\left(15.68762\ eV\right)}{m_e c^2}} = -0.28016\ eV \end{aligned} \tag{13.903}$$

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency. The decrease in the energy of the $CO$ MO due to the reentrant orbit in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei, $\overline{E}_{osc}$, is given by the sum of the corresponding energies, $\overline{E}_D$ given by Eq. (13.903) and $\overline{E}_{Kvib}$, the average kinetic energy of vibration which is 1/2 of the vibrational energy. Using the experimental $CO$ $\omega_e$ of 2169.81 $cm^{-1}$ $\left(0.26902\ eV\right)$ [28] for $\overline{E}_{Kvib}$ of the transition state, $\overline{E}'_{osc}\left(CO\right)$ per bond is:

$$\bar{E}'_{osc}(CO) = \bar{E}_D + \bar{E}_{Kvib} = \bar{E}_D + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \tag{13.904}$$

$$\bar{E}'_{osc}(CO) = -0.28016\ eV + \frac{1}{2}(0.26902\ eV) = -0.14564\ eV \tag{13.905}$$

Since the $\sigma$ MO bond is a double bond with twice a many electrons as a single bond, $\bar{E}'_{osc}(CO)$ is multiplied by two to give:

$$\bar{E}_{osc}(CO) = -0.29129\ eV \tag{13.906}$$

## TOTAL AND BOND ENERGIES OF THE CARBON MONOXIDE MOLECULE

$E_{T+osc}(CO)$, the total energy of $CO$ including the Doppler term, is given by the sum of $E_T(CO)$ (Eq. (13.900)) and $\bar{E}_{osc}(CO)$ given by Eq. (13.906):

$$\begin{aligned} E_{T+osc}(CO) &= \begin{pmatrix} V_e + T + V_m + V_p + E(ionization;\ C^+) \\ +E(ionization;\ O^+) + E_T(O,2p) + \bar{E}_{osc}(CO) \end{pmatrix} \\ &= \begin{pmatrix} E_T(CO,\sigma) + E(ionization;\ C^+) + E(ionization;\ O^+) \\ +E_T(O,2p) + \bar{E}_{osc}(CO) \end{pmatrix} \\ &= E_T(CO) + \bar{E}_{osc}(CO) \end{aligned} \tag{13.907}$$

$$\begin{aligned} E_{T+osc}(CO) &= \left\{ \begin{array}{l} \left( \begin{array}{l} \dfrac{-e^2}{8\pi\varepsilon_0\sqrt{\dfrac{aa_0}{2}}} \left( 8\ln\dfrac{a+\sqrt{\dfrac{aa_0}{2}}}{a-\sqrt{\dfrac{aa_0}{2}}} - 4 \right) + E\left(ionization;\ C^+\right) \\ +E\left(ionization;\ O^+\right) - \displaystyle\sum_{O,n=4}^{5} \frac{(Z-n)e^2}{8\pi\varepsilon_0}\left(\frac{1}{r_6} - \frac{1}{r_8}\right) \end{array} \right) \\ \left( 1 + 2\sqrt{\dfrac{2\hbar\sqrt{\dfrac{\frac{4e^2}{4\pi\varepsilon_0 a^3}}{m_e}}}{m_e c^2}} \right) + 2\left(\dfrac{1}{2}\hbar\sqrt{\dfrac{k}{\mu}}\right) \end{array} \right\} \\ &= -35.75359\ eV - 2(0.28016\ eV) + 2\left(\frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right) \end{aligned} \tag{13.908}$$

From Eqs. (13.906-13.908), the total energy of the $CO$ MO is:

$$\begin{aligned} E_{T+osc}(CO) &= -35.75359\ eV + \bar{E}_{osc}(CO) \\ &= -35.75359\ eV + (-0.29129\ eV) = -36.04488\ eV \end{aligned} \tag{13.909}$$

where the experimental $\omega_e$ was used for the $\hbar\sqrt{\frac{k}{\mu}}$ term.

The $CO$ bond dissociation energy, $E_D(CO)$, is given by the difference between the sum of the energies of the $C$ and $O$ atoms and $E_{T+osc}(CO)$:

$$E_D(CO) = E(C) + E(O) - E_{T+osc}(CO) \tag{13.910}$$

where the energy of a carbon atom is [6]:

$$E(C) = -11.26030\ eV \tag{13.911}$$

and the energy of an oxygen atom is [6]:

$$E(O) = -13.61806\ eV \tag{13.912}$$

Thus, the $CO$ bond dissociation energy, $E_D(CO)$, given by Eqs. (13.909-13.912) is:

$$\begin{aligned} E_D(CO) &= -(11.26030\ eV + 13.61806\ eV) - E_{T+osc}(CO) \\ &= -24.87836\ eV - (-36.04488\ eV) = 11.16652\ eV \end{aligned} \tag{13.913}$$

The experimental $CO$ bond dissociation energy is [49]:

$$E_{D298}(CO) = 11.15696\ eV \tag{13.914}$$

The results of the determination of bond parameters of $CO$ are given in Table 13.1. The calculated results are based on first principles and given in closed-form, exact equations containing fundamental constants only. The agreement between the experimental and calculated results is excellent.

## NITRIC OXIDE RADICAL

The nitric oxide radical can be formed by the reaction of nitrogen and oxygen atoms:

$$N + O \rightarrow NO \tag{13.915}$$

The bond in the nitric oxide radical comprises a double bond, a $H_2$-type molecular orbital (MO) with four paired electrons. The force balance equation and radius $r_7$ of the $2p$ shell of $N$ is derived in the Seven-Electron Atoms section. The force balance equation and radius $r_8$ of the $2p$ shell of $O$ is derived in the Eight-Electron Atoms section. With the formation of the $H_2$-type MO by the contribution of two $2p$ electrons from each of the $N$ and $O$ atoms, a diamagnetic force arises between the remaining outer shell atomic electrons, the $2s$ and $2p$ electrons of $N$ and $O$, and the $H_2$-type MO. This force from $N$ and $O$ causes the $H_2$-type MO to move to greater principal axes than would result with the Coulombic force alone. But, the factor of two increase of the central field and the resulting increased Coulombic as well as magnetic central forces on the remaining $N$ and $O$ electrons decrease the radii of the corresponding shells such that the energy minimum is achieved that is lower than that of the reactant atoms. The resulting electron configuration of $NO$ is $N1s^2O1s^2N2s^2O2s^2N2p^1O2p^2\sigma_{N,O}^4$ where $\sigma$ designates the $H_2$-type MO, and the orbital arrangement is:

$$\begin{array}{cc}
\multicolumn{2}{c}{\sigma \text{ state}} \\
\multicolumn{2}{c}{\underline{\uparrow\ \downarrow}\ \ \underline{\uparrow\ \downarrow}} \\
\multicolumn{2}{c}{2\text{p state}} \\
\underline{\uparrow} & \underline{\uparrow\downarrow} \\
0 & 0 \\
\multicolumn{2}{c}{2\text{s state}} \\
\underline{\uparrow\downarrow} & \underline{\uparrow\downarrow} \\
\multicolumn{2}{c}{1\text{s state}} \\
\underline{\uparrow\downarrow} & \underline{\uparrow\downarrow} \\
N & O
\end{array} \tag{13.916}$$

Nitric oxide is predicted to be weakly paramagnetic in agreement with observations [42].

## FORCE BALANCE OF THE $2p$ SHELL OF THE NITROGEN ATOM OF THE NITRIC OXIDE RADICAL

For the $N$ atom, force balance for the outermost $2p$ electron of $NO$ (electron 5) is achieved between the centrifugal force and the Coulombic and magnetic forces that arise due to interactions between electron 5 and the $2s$-shell electrons due to spin and orbital angular momentum. The forces used are derived in the Seven-Electron Atoms section. The central Coulomb force on the outer-most $2p$ shell electron of $NO$ (electron 5) due to the nucleus and the inner four electrons is given by Eq. (10.70) with the appropriate charge and radius:

$$\mathbf{F}_{ele} = \frac{(Z-4)e^2}{4\pi\varepsilon_0 r_5^2}\mathbf{i_r} \tag{13.917}$$

for $r > r_4$. The $2p$ shell possess a +2 external electric field given by Eq. (10.92) for $r > r_5$. The energy is minimized with conservation of angular momentum. This condition is met when the magnetic forces of $N$ in $NO$ are the same as those of $N$ in the nitrogen molecule with $r_5$ replacing $r_6$ and with an increase of the central field by an integer. The diamagnetic force, $\mathbf{F}_{diamagnetic}$, of Eq. (10.82) due to the $p$-orbital contribution is given by Eq. (13.622) with $r_5$ replacing $r_6$:

$$\mathbf{F}_{diamagnetic} = -\left(\frac{1}{3}\right)\frac{\hbar^2}{4m_e r_5^2 r_3}\sqrt{s(s+1)}\mathbf{i_r} = -\frac{\hbar^2}{12m_e r_5^2 r_3}\sqrt{\frac{3}{4}}\mathbf{i_r} \tag{13.918}$$

And, $\mathbf{F}_{mag\ 2}$ corresponding to the conserved orbital angular momentum of the three orbitals is also the same as that of $N_2$ given by Eq. (13.623) with $r_5$ replacing $r_6$:

$$\mathbf{F}_{mag\ 2} = \frac{1}{Z}\frac{3\hbar^2}{m_e r_5^2 r_3}\sqrt{s(s+1)}\mathbf{i_r} \tag{13.919}$$

The electric field external to the $2p$ shell given by Eq. (10.92) for $r > r_5$ gives rise to a second diamagnetic force, $\mathbf{F}_{diamagnetic\ 2}$, given by Eq. (10.93). $\mathbf{F}_{diamagnetic\ 2}$ due to the binding of the p-orbital electron having an electric field of +2 outside of its radius follows from Eq. (13.624).

$$\mathbf{F}_{diamagnetic\ 2} = -\left[\frac{Z-5}{Z-4}\right]\left(1-\frac{\sqrt{2}}{2}\right)\frac{r_3\hbar^2}{m_e r_5^4}10\sqrt{s(s+1)}\mathbf{i_r} \tag{13.920}$$

In addition to the $N$ forces $\mathbf{F}_{ele}$, $\mathbf{F}_{diamagnetic}$, $\mathbf{F}_{mag\ 2}$, and $\mathbf{F}_{diamagnetic\ 2}$ of $NO$ being the same as $N_2$ given by Eqs. (13.621-13.624), respectively, $\mathbf{F}_{ele}$, $\mathbf{F}_{mag\ 2}$, and $\mathbf{F}_{diamagnetic\ 2}$ are also the same as those of $CN$ (Eqs. (13.820) and (13.822-13.823)). In the $N_2$ and $CN$ cases, the contribution of a $2p$ electron from the $N$ atom in the formation of the $\sigma$ MO gives rise to an additional paramagnetic force on the remaining two $2p$ electrons that pair. However, the force, $\mathbf{F}_{mag\ 3}$, is absent in $NO$ since the single outer electron is unpaired.

The radius of the $2p$ shell is calculated by equating the outward centrifugal force to the sum of the electric (Eq. (13.917)) and diamagnetic (Eqs. (13.918) and (13.920)), and paramagnetic (Eq. (13.919)) forces as follows:

$$\frac{m_e v_5^2}{r_5} = \left(\begin{array}{l} \dfrac{(Z-4)e^2}{4\pi\varepsilon_0 r_5^2} - \dfrac{\hbar^2}{12 m_e r_5^2 r_3}\sqrt{s(s+1)} + \dfrac{3\hbar^2}{Z m_e r_5^2 r_3}\sqrt{s(s+1)} \\ -\left[\dfrac{Z-5}{Z-4}\right]\left(1-\dfrac{\sqrt{2}}{2}\right)\dfrac{r_3\hbar^2}{r_5^4 m_e}10\sqrt{s(s+1)} \end{array}\right) \tag{13.921}$$

Substitution of $v_5 = \frac{\hbar}{m_e r_5}$ (Eq. (1.35)) and $s = \frac{1}{2}$ into Eq. (13.921) gives:

$$\frac{\hbar^2}{m_e r_5^3} = \frac{(Z-4)e^2}{4\pi\varepsilon_0 r_5^2} - \frac{\hbar^2}{12 m_e r_5^2 r_3}\sqrt{\frac{3}{4}} + \frac{3\hbar^2}{Z m_e r_5^2 r_3}\sqrt{\frac{3}{4}} - \left[\frac{Z-5}{Z-4}\right]\left(1-\frac{\sqrt{2}}{2}\right)\frac{r_3\hbar^2}{r_5^4 m_e}10\sqrt{\frac{3}{4}} \tag{13.922}$$

The quadratic equation corresponding to Eq. (13.922) is

$$r_5^2 - \frac{\dfrac{\hbar^2}{m_e}}{\left(\dfrac{(Z-4)e^2}{4\pi\varepsilon_0} - \left(\dfrac{1}{12}-\dfrac{3}{Z}\right)\dfrac{\hbar^2}{m_e r_3}\sqrt{\dfrac{3}{4}}\right)} r_5 - \frac{\dfrac{\hbar^2}{m_e}\left[\dfrac{Z-5}{Z-4}\right]\left(1-\dfrac{\sqrt{2}}{2}\right) r_3 10\sqrt{\dfrac{3}{4}}}{\left(\dfrac{(Z-4)e^2}{4\pi\varepsilon_0} - \left(\dfrac{1}{12}-\dfrac{3}{Z}\right)\dfrac{\hbar^2}{m_e r_3}\sqrt{\dfrac{3}{4}}\right)} = 0 \tag{13.923}$$

The solution of Eq. (13.923) using the quadratic formula is:

$$r_5 = \frac{\dfrac{a_0}{\left((Z-4)-\left(\dfrac{1}{12}-\dfrac{3}{Z}\right)\dfrac{\sqrt{3}}{2r_3}\right)} \pm a_0\sqrt{\left(\dfrac{1}{\left((Z-4)-\left(\dfrac{1}{12}-\dfrac{3}{Z}\right)\dfrac{\sqrt{3}}{2r_3}\right)}\right)^2 + \dfrac{20\sqrt{3}\left(\left[\dfrac{Z-5}{Z-4}\right]\left(1-\dfrac{\sqrt{2}}{2}\right) r_3\right)}{\left((Z-4)-\left(\dfrac{1}{12}-\dfrac{3}{Z}\right)\dfrac{\sqrt{3}}{2r_3}\right)}}}{2},\ r_3 \textit{ in units of } a_0 \tag{13.924}$$

The positive root of Eq. (13.924) must be taken in order that $r_5 > 0$. Substitution of $\frac{r_3}{a_0} = 0.69385$ (Eq. (10.62) with $Z = 7$) into Eq. (13.924) gives:

$$r_5 = 0.74841 a_0 \tag{13.925}$$

## FORCE BALANCE OF THE $2p$ SHELL OF THE OXYGEN ATOM OF THE NITRIC OXIDE RADICAL

For the $O$ atom, force balance for the outermost $2p$ electron of $NO$ (electron 6) is achieved between the centrifugal force and the Coulombic and magnetic forces that arise due to interactions between electron 6 and the other $2p$ electron as well as the $2s$-shell electrons due to spin and orbital angular momentum. The forces used are derived in the Eight-Electron Atoms section. The central Coulomb force on the outer-most $2p$ shell electron of $NO$ (electron 6) due to the nucleus and the inner five electrons is given by Eq. (10.70) with the appropriate charge and radius:

$$\mathbf{F}_{ele} = \frac{(Z-5)e^2}{4\pi\varepsilon_0 r_6^2}\mathbf{i_r} \tag{13.926}$$

for $r > r_5$. The $2p$ shell possess an external electric field of +2 given by Eq. (10.92) for $r > r_6$. The energy is minimized with conservation of angular momentum. This condition is met when the diamagnetic force, $\mathbf{F}_{diamagnetic}$, of Eq. (10.82) due to the $p$-orbital contribution is given by:

$$\begin{aligned}\mathbf{F}_{diamagnetic} &= -\left(\frac{2}{3}\right)\frac{\hbar^2}{4m_e r_6^2 r_3}\sqrt{s(s+1)}\mathbf{i_r} \\ &= -\frac{2\hbar^2}{12m_e r_6^2 r_3}\sqrt{\frac{3}{4}}\mathbf{i_r}\end{aligned} \tag{13.927}$$

And, $\mathbf{F}_{mag\ 2}$ corresponding to the conserved spin and orbital angular momentum given by Eqs. (10.157) and (13.670) is:

$$\mathbf{F}_{mag\ 2} = \frac{1}{Z}\frac{2\hbar^2}{m_e r_6^2 r_3}\sqrt{s(s+1)}\mathbf{i_r} \tag{13.928}$$

The electric field external to the $2p$ shell given by Eq. (10.92) for $r > r_6$ gives rise to a second diamagnetic force, $\mathbf{F}_{diamagnetic\ 2}$, given by Eq. (10.93). $\mathbf{F}_{diamagnetic\ 2}$ due to the binding of the p-orbital electron having an electric field of +2 outside of its radius is:

$$\mathbf{F}_{diamagnetic\ 2} = -\left[\frac{Z-6}{Z-5}\right]\left(1-\frac{\sqrt{2}}{2}\right)\frac{r_3\hbar^2}{m_e r_6^4}10\sqrt{s(s+1)}\mathbf{i_r} \tag{13.929}$$

In addition, the contribution of two $2p$ electrons in the formation of the $\sigma$ MO gives rise to a paramagnetic force on the remaining paired $2p$ electrons. The force $\mathbf{F}_{mag\ 3}$ is given by Eq. (13.625) wherein the radius is $r_6$:

$$\mathbf{F}_{mag\ 3} = \frac{\hbar^2}{4m_e r_6^3}\sqrt{s(s+1)}\mathbf{i_r} \tag{13.930}$$

The radius of the $2p$ shell is calculated by equating the outward centrifugal force to the sum of the electric (Eq. (13.926)) and diamagnetic (Eqs. (13.927) and (13.929)), and paramagnetic (Eqs. (13.928) and (13.930)) forces as follows:

$$\frac{m_e v_6^2}{r_6} = \left(\begin{array}{l}\frac{(Z-5)e^2}{4\pi\varepsilon_0 r_6^2} - \frac{2\hbar^2}{12m_e r_6^2 r_3}\sqrt{s(s+1)} + \frac{2\hbar^2}{Zm_e r_6^2 r_3}\sqrt{s(s+1)} \\ -\left[\frac{Z-6}{Z-5}\right]\left(1-\frac{\sqrt{2}}{2}\right)\frac{r_3\hbar^2}{r_6^4 m_e}10\sqrt{s(s+1)} + \frac{\hbar^2}{4m_e r_6^3}\sqrt{s(s+1)}\end{array}\right) \tag{13.931}$$

Substitution of $v_6 = \frac{\hbar}{m_e r_6}$ (Eq. (1.35)) and $s = \frac{1}{2}$ into Eq. (13.931) gives:

$$\frac{\hbar^2}{m_e r_6^3} - \frac{\hbar^2}{4m_e r_6^3}\sqrt{\frac{3}{4}} = \frac{(Z-5)e^2}{4\pi\varepsilon_0 r_6^2} - \frac{2\hbar^2}{12m_e r_6^2 r_3}\sqrt{\frac{3}{4}} + \frac{2\hbar^2}{Zm_e r_6^2 r_3}\sqrt{\frac{3}{4}} - \left[\frac{Z-6}{Z-5}\right]\left(1-\frac{\sqrt{2}}{2}\right)\frac{r_3\hbar^2}{r_6^4 m_e}10\sqrt{\frac{3}{4}} \tag{13.932}$$

The quadratic equation corresponding to Eq. (13.932) is:

$$r_6^2 - \frac{\frac{\hbar^2}{m_e}\left(1-\frac{\sqrt{3}}{8}\right)}{\left(\frac{(Z-5)e^2}{4\pi\varepsilon_0} - \left(\frac{2}{12}-\frac{2}{Z}\right)\frac{\hbar^2}{m_e r_3}\sqrt{\frac{3}{4}}\right)}r_6 - \frac{\frac{\hbar^2}{m_e}\left[\frac{Z-6}{Z-5}\right]\left(1-\frac{\sqrt{2}}{2}\right)r_3 10\sqrt{\frac{3}{4}}}{\left(\frac{(Z-5)e^2}{4\pi\varepsilon_0} - \left(\frac{2}{12}-\frac{2}{Z}\right)\frac{\hbar^2}{m_e r_3}\sqrt{\frac{3}{4}}\right)} = 0 \tag{13.933}$$

The solution of Eq. (13.933) using the quadratic formula is:

$$r_6 = \frac{\dfrac{a_0\left(1-\dfrac{\sqrt{3}}{8}\right)}{\left((Z-5)-\left(\dfrac{2}{12}-\dfrac{2}{Z}\right)\dfrac{\sqrt{3}}{2r_3}\right)} \pm a_0\sqrt{\left(\dfrac{1-\dfrac{\sqrt{3}}{8}}{\left((Z-5)-\left(\dfrac{2}{12}-\dfrac{2}{Z}\right)\dfrac{\sqrt{3}}{2r_3}\right)}\right)^2 + \dfrac{20\sqrt{3}\left(\left[\dfrac{Z-6}{Z-5}\right]\left(1-\dfrac{\sqrt{2}}{2}\right)r_3\right)}{\left((Z-5)-\left(\dfrac{2}{12}-\dfrac{2}{Z}\right)\dfrac{\sqrt{3}}{2r_3}\right)}}}{2},\ r_3 \textit{ in units of } a_0 \tag{13.934}$$

The positive root of Eq. (13.934) must be taken in order that $r_6 > 0$. Substitution of $\frac{r_3}{a_0} = 0.59020$ (Eq. (10.62) with $Z = 8$) into Eq. (13.934) gives:

$$r_6 = 0.70460a_0 \tag{13.935}$$

## ENERGIES OF THE $2p$ SHELLS OF THE NITROGEN ATOM AND OXYGEN ATOM OF THE NITRIC OXIDE RADICAL

With the formation of the $H_2$-type MO by the contribution of two $2p$ electrons from each of the $N$ and $O$ atoms, the total energy of the $NO$ molecule, which is subtracted from the sum of the energies of the nitrogen and oxygen atoms to determine the bond energy, is increased by the ionization energies of $N^+$ and $O^+$ given by Eqs. (10.132-10.133) and (10.152-10.153), respectively. Experimentally, the energies are [6] :

$$E(ionization;\ N^+) = 29.6013\ eV \tag{13.936}$$

$$E(ionization;\ O^+) = 35.11730\ eV \tag{13.937}$$

In addition, the central forces on the $2p$ shells of the $N$ and $O$ atoms are increased with the formation of the $\sigma$ MO which reduces each shell's radius and increases its total energy. The Coulombic energy terms of the total energy of the $N$ and $O$ atoms at the new radii are calculated and added to the ionization energies of $N^+$ and $O^+$, and the energy of the $\sigma$ MO to give the total energy of $NO$. Then, the bond energy is determined from the total $NO$ energy.

The radius $r_7$ of the nitrogen atom before bonding is given by Eq. (10.142):

$$r_7 = 0.93084a_0 \tag{13.938}$$

Using the initial radius $r_7$ of the $N$ atom and the final radius $r_5$ of the $N2p$ shell (Eq. (13.925)) and by considering that the central Coulombic field decreases by an integer for each successive electron of the shell, the sum $E_T(N,2p)$ of the Coulombic energy change of the $N2p$ electrons of the $N$ atom is determined using Eq. (10.102):

$$E_T(N,2p) = -\sum_{n=4}^{4}\frac{(Z-n)e^2}{8\pi\varepsilon_0}\left(\frac{1}{r_5}-\frac{1}{r_7}\right) = -(13.60580\ eV)(0.26186)(3) = -10.68853\ eV \tag{13.939}$$

The radius $r_8$ of the oxygen atom before bonding is given by Eq. (10.162):

$$r_8 = a_0 \tag{13.940}$$

Using the initial radius $r_8$ of the $O$ atom and the final radius $r_6$ of the $O2p$ shell (Eq. (13.935)) and by considering that the central Coulombic field decreases by an integer for each successive electron of the shell, the sum $E_T(O,2p)$ of the Coulombic energy change of the $O2p$ electrons of the $O$ atom is determined using Eq. (10.102):

$$E_T(O,2p) = -\sum_{n=4}^{5}\frac{(Z-n)e^2}{8\pi\varepsilon_0}\left(\frac{1}{r_6}-\frac{1}{r_8}\right) = -(13.60580\ eV)(0.41925)(3+4) = -39.92918\ eV \tag{13.941}$$

## FORCE BALANCE OF THE $\sigma$ MO OF THE NITRIC OXIDE RADICAL

The force balance can be considered due to a second pair of two electrons binding to a molecular ion having $+2e$ at each focus and a first bound pair. Then, the forces are the same as those of a molecule ion having $+e$ at each focus. The diamagnetic force $\mathbf{F}_{diamagneticMO1}$ for the $\sigma$-MO of the $NO$ molecule due to the two paired electrons in the $O2p$ shell is given by Eq. (13.633) with: $n_e = 2$:

$$\mathbf{F}_{diamagneticMO1} = \frac{\hbar^2}{2m_e a^2 b^2} D\mathbf{i}_\xi \tag{13.942}$$

$\mathbf{F}_{diamagneticMO2}$ of the nitric oxide radical comprising nitrogen with charge $Z_1 = 7$ and $|L_1| = \hbar$ and $|L_2| = \sqrt{\frac{3}{4}}\hbar$ and oxygen with $Z_2 = 8$ and $|L_3| = \hbar$ is given by the corresponding sum of the contributions. Using Eq. (13.835), $\mathbf{F}_{diamagneticMO2}$ for $NO$ is:

$$\mathbf{F}_{diamagneticMO2} = \left( \frac{1}{Z_1} + \frac{\sqrt{\frac{3}{4}}}{Z_1} + \frac{1}{Z_2} \right) \frac{\hbar^2}{2m_e a^2 b^2} D\mathbf{i}_\xi \tag{13.943}$$

The general force balance equation for the $\sigma$-MO of the nitric oxide radical given by Eqs. (11.200), (13.633-13.634), and (13.942-13.943) is the same as that of $CN$ (Eq. (13.836)):

$$\frac{\hbar^2}{m_e a^2 b^2} D = \frac{e^2}{8\pi\varepsilon_0 ab^2} D + \frac{\hbar^2}{2m_e a^2 b^2} D - \left( 1 + \frac{1}{Z_1} + \frac{\sqrt{\frac{3}{4}}}{Z_1} + \frac{1}{Z_2} \right) \frac{\hbar^2}{2m_e a^2 b^2} D \tag{13.944}$$

$$\frac{\hbar^2}{m_e a^2 b^2} D = \frac{e^2}{8\pi\varepsilon_0 ab^2} D - \left( \frac{1}{Z_1} + \frac{\sqrt{\frac{3}{4}}}{Z_1} + \frac{1}{Z_2} \right) \frac{\hbar^2}{2m_e a^2 b^2} D \tag{13.945}$$

$$\left( 2 + \frac{1}{Z_1} + \frac{\sqrt{\frac{3}{4}}}{Z_1} + \frac{1}{Z_2} \right) \frac{\hbar^2}{2m_e a^2 b^2} D = \frac{e^2}{8\pi\varepsilon_0 ab^2} D \tag{13.946}$$

$$a = \left( 2 + \frac{1}{Z_1} + \frac{\sqrt{\frac{3}{4}}}{Z_1} + \frac{1}{Z_2} \right) a_0 \tag{13.947}$$

Substitution of $Z_1 = 7$ and $Z_2 = 8$ into Eq. (13.947) gives:

$$a = 2.39158 a_0 = 1.26557\ X\ 10^{-10}\ m \tag{13.948}$$

Substitution of Eq. (13.948) into Eq. (11.79) is:

$$c' = 1.09352 a_0 = 5.78666\ X\ 10^{-11}\ m \tag{13.949}$$

The internuclear distance given by multiplying Eq. (13.949) by two is:

$$2c' = 2.18704 a_0 = 1.15733\ X\ 10^{-10}\ m \tag{13.950}$$

The experimental bond distance is [28]:

$$2c' = 1.15077\ X\ 10^{-10}\ m \tag{13.951}$$

Substitution of Eqs. (13.948-13.949) into Eq. (11.80) is:

$$b = c = 2.12693 a_0 = 1.12552\ X\ 10^{-10}\ m \tag{13.952}$$

Substitution of Eqs. (13.948-13.949) into Eq. (11.67) is:

$$e = 0.45724 \tag{13.953}$$

Using the electron configuration of $NO$ (Eq. (13.916)), the radii of the $N1s = 0.14605 a_0$ (Eq. (10.51)), $N2s = 0.69385 a_0$ (Eq. (10.62)), $N2p = 0.74841 a_0$ (Eq. (13.925)), $O1s = 0.12739 a_0$ (Eq. (10.51)), $O2s = 0.59020 a_0$ (Eq. (10.62)), and $O2p = 0.70460 a_0$ (Eq. (13.935)) shells and the parameters of the $\sigma$ MO of $NO$ given by Eqs. (13.3-13.4), (13.948-13.950), and (13.952-13.953), the dimensional diagram and charge-density of the $NO$ MO are shown in Figures 13.26 and 13.27, respectively.

Figure 13.26. The cross section of the $NO$ MO showing the axes, $\sigma$ MO ($H_2$-type ellipsoidal MO) with four paired electrons, with the $N$ $1s$, $2s$, and $2p$ atomic orbitals (AOs) and the $O$ $1s$, $2s$, and $2p$ AOs. Legend: $a$: semimajor axis, $b$: semiminor axis, $c'$: internuclear distance, $r_5$: radius of the $N2p$ shell having two paired electrons, $r_6$: radius of the $O2p$ shell having two paired electrons.

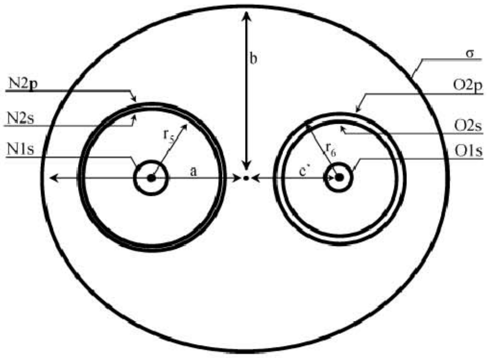
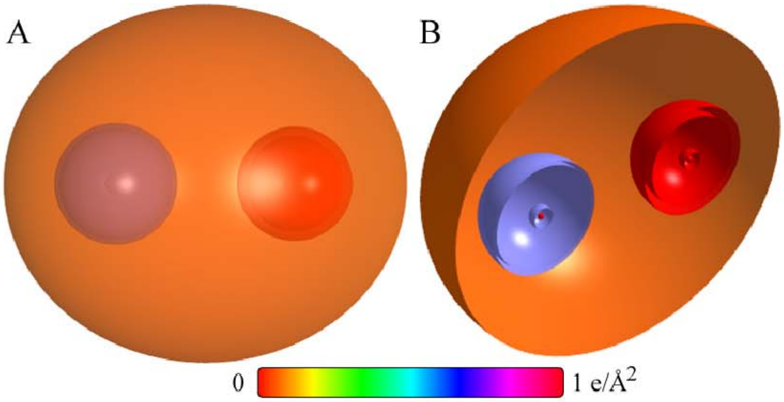


Figure 13.27. $NO$ MO comprising the $\sigma$ MO ($H_2$-type MO) with $N$ and $O$ atoms at the foci that have each donated two electrons to the $\sigma$ MO and have smaller radii and higher binding energies as a consequence. (A) Color scale, translucent view of the charge-density of the $NO$ MO. (B) Off-center cut-away view showing the complete inner most $N1s$ shell, and moving radially, the $N2s$ shell, the $N2p$ shell, and the $\sigma$ prolate spheroidal MO that has the $N$ atom as a focus. Moving radially from the oxygen-atom focus, the complete inner most $O1s$ shell, the $O2s$ shell, the $O2p$ shell, and the $\sigma$ prolate spheroidal MO are shown.



## SUM OF THE ENERGIES OF THE $\sigma$ MO AND THE AOs OF THE NITRIC OXIDE RADICAL

The energies of the $NO$ $\sigma$ MO are given by the substitution of the semiprincipal axes (Eqs. (13.948-13.949) and (13.952)) into the energy equations (Eqs. (11.207-11.212)) of $H_2$ except that the terms based on charge are multiplied by four and the kinetic energy term is multiplied by two due to the $\sigma$-MO double bond with two pairs of paired electrons:

$$V_e = 2^2 \frac{-2e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}} \ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -98.30623\ eV \tag{13.954}$$

$$V_p = 2^2 \frac{e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}} = 49.76880\ eV \tag{13.955}$$

$$T = 2\frac{\hbar^2}{2m_e a\sqrt{a^2-b^2}} \ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = 10.27631\ eV \tag{13.956}$$

$$V_m = 2^2 \frac{-\hbar^2}{4m_e a\sqrt{a^2-b^2}} \ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -10.27631\ eV \tag{13.957}$$

$$E_T = V_e + T + V_m + V_p \tag{13.958}$$

Substitution of Eqs. (11.79) and (13.954-13.957) into Eq. (13.958) gives:

$$\begin{aligned} E_T(NO,\sigma) &= \frac{-e^2}{8\pi\varepsilon_0\sqrt{\frac{aa_0}{2}}}\left(8\ln\frac{a+\sqrt{\frac{aa_0}{2}}}{a-\sqrt{\frac{aa_0}{2}}}-4\right) \\ &= -48.53743\ eV \end{aligned} \tag{13.959}$$

where $E_T(NO,\sigma)$ is the total energy of the $\sigma$ MO of $NO$. The total energy of $NO$, $E_T(NO)$, is given by the sum of $E(ionization;\ N^+)$, the energy of the second electron of nitrogen (Eq. (13.936)) donated to the double bond, $E(ionization;\ O^+)$, the energy of the second electron of oxygen (Eq. (13.937)) donated to the double bond, $E_T(N,2p)$, the $N2p$ AO contribution due to the decrease in radius with bond formation (Eq. (13.939)), $E_T(O,2p)$, the $O2p$ AO contribution due to the decrease in radius with bond formation (Eq. (13.941)), and $E_T(NO,\sigma)$, the $\sigma$ MO contribution given by Eq. (13.959).

$$\begin{aligned}E_T(NO) &= \begin{pmatrix} E(ionization;\ N^+) + E(ionization;\ O^+) \\ +E_T(N,2p) + E_T(O,2p) + E_T(NO,\sigma) \end{pmatrix} = \begin{pmatrix} 29.6013\ eV + 35.11730\ eV \\ -10.68853\ eV - 39.92918\ eV - 48.53743\ eV \end{pmatrix} \\ &= -34.43653\ eV\end{aligned} \tag{13.960}$$

## VIBRATION OF $NO$

The vibrational energy levels of $NO$ may be solved by determining the Morse potential curve from the energy relationships for the transition from a $N$ atom and $O$ atom whose parameters are given by Eqs. (10.134-10.143) and (10.154-10.163), respectively, to a $N$ atom whose parameter $r_5$ is given by Eq. (13.925), an $O$ atom whose parameter $r_6$ is given by Eq. (13.935), and the $\sigma$ MO whose parameters are given by Eqs. (13.948-13.950) and (13.952-13.953). As shown in the Vibration of Hydrogen-type Molecular Ions section, the harmonic oscillator potential energy function can be expanded about the internuclear distance and expressed as a Maclaurin series corresponding to a Morse potential after Karplus and Porter (K&P) [15] and after Eq. (11.134). Treating the Maclaurin series terms as anharmonic perturbation terms of the harmonic states, the energy corrections can be found by perturbation methods.

## THE DOPPLER ENERGY TERMS OF THE NITRIC OXIDE RADICAL

The equations of the radiation reaction force of nitric oxide are the same as those of $H_2$ with the substitution of the $NO$ parameters except that there is a factor of four increase in the central force in Eq. (11.231) due to the double bond. Using Eqs. (11.231-11.233) and (13.901), the angular frequency of the reentrant oscillation in the transition state is

$$\omega = \sqrt{\frac{\frac{4e^2}{4\pi\varepsilon_0 a^3}}{m_e}} = 2.23557\ X\ 10^{16}\ rad/s \tag{13.961}$$

where $a$ is given by Eq. (13.948). The kinetic energy, $E_K$, is given by Planck's equation (Eq. (11.127)):

$$\bar{E}_K = \hbar\omega = \hbar 2.23557\ X\ 10^{16}\ rad/s = 14.71493\ eV \tag{13.962}$$

In Eq. (11.181), substitution of $E_T(NO)$ for $E_{h\nu}$, the mass of the electron, $m_e$, for $M$, and the kinetic energy given by Eq. (13.962) for $\bar{E}_K$ gives the Doppler energy of the electrons of the reentrant orbit:

$$\bar{E}_D \cong E_{h\nu}\sqrt{\frac{2\bar{E}_K}{Mc^2}} = -34.43653\ eV\sqrt{\frac{2e(14.71493\ eV)}{m_e c^2}} = -0.26134\ eV \tag{13.963}$$

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency. The decrease in the energy of the $NO$ MO due to the reentrant orbit in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei, $\bar{E}_{osc}$, is given by the sum of the corresponding energies, $\bar{E}_D$ given by Eq. (13.963) and $\bar{E}_{Kvib}$, the average kinetic energy of vibration which is 1/2 of the vibrational energy. Using the experimental $NO$ $\omega_e$ of 1904.20 $cm^{-1}$ $(0.23609\ eV)$ [28] for $\bar{E}_{Kvib}$ of the transition state, $\bar{E}'_{osc}(NO)$ per bond is:

$$\bar{E}'_{osc}(NO) = \bar{E}_D + \bar{E}_{Kvib} = \bar{E}_D + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \tag{13.964}$$

$$\bar{E}'_{osc}(NO) = -0.26134\ eV + \frac{1}{2}(0.23609\ eV) = -0.14329\ eV \tag{13.965}$$

Since the $\sigma$ MO bond is a double bond with twice a many electrons as a single bond, $\bar{E}'_{osc}(NO)$ is multiplied by two to give:

$$\bar{E}_{osc}(NO) = -0.28658\ eV \tag{13.966}$$

## TOTAL AND BOND ENERGIES OF THE NITRIC OXIDE RADICAL

$E_{T+osc}(NO)$, the total energy of $NO$ including the Doppler term, is given by the sum of $E_T(NO)$ (Eq. (13.960)) and $\bar{E}_{osc}(NO)$ given by Eq. (13.966).

$$\begin{aligned} E_{T+osc}(NO) &= \begin{pmatrix} V_e + T + V_m + V_p + E(ionization;\ N^+) + E(ionization;\ O^+) \\ + E_T(N,2p) + E_T(O,2p) + \bar{E}_{osc}(NO) \end{pmatrix} \\ &= \begin{pmatrix} E_T(NO,\sigma) + E(ionization;\ N^+) + E(ionization;\ O^+) \\ + E_T(N,2p) + E_T(O,2p) + \bar{E}_{osc}(NO) \end{pmatrix} \\ &= E_T(NO) + \bar{E}_{osc}(NO) \end{aligned} \tag{13.967}$$

$$\begin{aligned} E_{T+osc}(NO) &= \left\{ \begin{array}{l} \left( \begin{array}{l} \dfrac{-e^2}{8\pi\varepsilon_0 \sqrt{\dfrac{aa_0}{2}}} \left( 8 \ln \dfrac{a + \sqrt{\dfrac{aa_0}{2}}}{a - \sqrt{\dfrac{aa_0}{2}}} - 4 \right) \\ + E(ionization;\ N^+) + E(ionization;\ O^+) \\ - \displaystyle\sum_{N,n=4}^{4} \frac{(Z-n)e^2}{8\pi\varepsilon_0} \left( \frac{1}{r_5} - \frac{1}{r_7} \right) - \sum_{O,n=4}^{5} \frac{(Z-n)e^2}{8\pi\varepsilon_0} \left( \frac{1}{r_6} - \frac{1}{r_8} \right) \end{array} \right) \\ \left( 1 + 2\sqrt{\dfrac{2\hbar \sqrt{\dfrac{\dfrac{4e^2}{4\pi\varepsilon_0 a^3}}{m_e}}}{m_e c^2}} \right) + 2\left( \dfrac{1}{2} \hbar \sqrt{\dfrac{k}{\mu}} \right) \end{array} \right\} \\ &= -34.43653\ eV - 2(0.26134\ eV) + 2\left( \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \right) \end{aligned} \tag{13.968}$$

From Eqs. (13.966-13.968), the total energy of the $NO$ MO is:

$$E_{T+osc}(NO) = -34.43653\ eV + \bar{E}_{osc}(NO) = -34.43653\ eV + (-0.28658) = -34.72312\ eV \tag{13.969}$$

where the experimental $\omega_e$ was used for the $\hbar\sqrt{\frac{k}{\mu}}$ term.

The $NO$ bond dissociation energy, $E_D(NO)$, is given by the difference between the sum of the energies of the $N$ and $O$ atoms and $E_{T+osc}(NO)$:

$$E_D(NO) = E(N) + E(O) - E_{T+osc}(NO) \tag{13.970}$$

where the energy of a nitrogen atom is [6]:

$$E(N) = -14.53414\ eV \tag{13.971}$$

and the energy of an oxygen atom is [6]:

$$E(O) = -13.61806\ eV \tag{13.972}$$

Thus, the $NO$ bond dissociation energy, $E_D(NO)$, given by Eqs. (13.969-13.972) is:

$$\begin{aligned} E_D(NO) &= -(14.53414\ eV + 13.61806\ eV) - E_{T+osc}(NO) \\ &= -28.15220\ eV - (-34.72312\ eV) \\ &= 6.57092\ eV \end{aligned} \tag{13.973}$$

The experimental $NO$ bond dissociation energy is [49]:

$$E_{D298}(NO) = 6.5353\ eV \tag{13.974}$$

The results of the determination of bond parameters of $NO$ are given in Table 13.1. The calculated results are based on first principles and given in closed-form, exact equations containing fundamental constants only. The agreement between the experimental and calculated results is excellent.

Table 13.1. The calculated and experimental bond parameters of $H_3^+$, $D_3^+$, $OH$, $OD$, $H_2O$, $D_2O$, $NH$, $ND$, $NH_2$, $ND_2$, $NH_3$, $ND_3$, $CH$, $CD$, $CH_2$, $CH_3$, $CH_4$, $N_2$, $O_2$, $F_2$, $Cl_2$, $CN$, $CO$, and $NO$.

| Parameter | Calculated | Experimental | Ref. for Exp. |
|---|---|---|---|
| $H_3^+$ Bond Energy | 4.373 eV | 4.373 eV | 8 |
| $D_3^+$ Bond Energy | 4.374 eV | | |
| $OH$ Bond Energy | 4.4104 eV | 4.4117 eV | 22 |
| $OD$ Bond Energy | 4.4687 eV | 4.454 eV | 23 |
| $OH$ Bond Length | 0.971651 Å | 0.971 Å | 13 |
| $OD$ Bond Length | 0.971651 Å | 0.971 Å | 13 |
| $OH$ Vibrational Energy | 0.4367 eV | 0.4424 eV | 16-17 |
| $OD$ Vibrational Energy | 0.3219 eV | 0.3263 eV | 16-17 |
| $OH$ $\omega_e$ | 3696.38 $cm^{-1}$ | 3735.21 $cm^{-1}$ | 14 |
| $OD$ $\omega_e$ | 2689.51 $cm^{-1}$ | 2720.9 $cm^{-1}$ | 14 |
| $OH$ $\omega_e x_e$ | 87.18 $cm^{-1}$ | 82.81 $cm^{-1}$ | 14 |
| $OD$ $\omega_e x_e$ | 46.75 $cm^{-1}$ | 44.2 $cm^{-1}$ | 14 |
| $OH$ $B_e$ | 18.835 $cm^{-1}$ | 18.871 $cm^{-1}$ | 14 |
| $OD$ $B_e$ | 9.971 $cm^{-1}$ | 10.01 $cm^{-1}$ | 14 |
| $H_2O$ Bond Energy | 5.1059 eV | 5.0991 eV | 26 |
| $D_2O$ Bond Energy | 5.178 eV | 5.191 eV | 31-32 |
| $H_2O$ $O-H$ Bond Length | 0.971574 Å | 0.970 $\pm$ 0.005 Å | 23 |
| $D_2O$ $O-D$ Bond Length | 0.971574 Å | 0.970 $\pm$ 0.005 Å | 23 |
| $H_2O$ $H-H$ Distance | 1.552 Å | 1.55 $\pm$ 0.01 Å | 13 |
| $D_2O$ $D-D$ Distance | 1.552 Å | 1.55 $\pm$ 0.01 Å | 13 |
| $H_2O$ Bond Angle | 106° | 106° | 23 |
| $D_2O$ Bond Angle | 106° | 106° | 23 |
| $NH$ Bond Energy | 3.47530 eV | 3.47 eV | 30 |
| $ND$ Bond Energy | 3.52556 eV | 3.5134 eV | 31 |
| $NH$ Bond Length | 1.04262 Å | 1.0362 Å | 28 |
| $ND$ Bond Length | 1.04262 Å | 1.0361 Å | 28 |
| $NH$ Vibrational Energy | 0.38581 eV | 0.38752 eV | 28 |
| $ND$ Vibrational Energy | 0.28583 eV | 0.28690 eV | 28 |
| $NH$ $\omega_e$ | 3284.58 $cm^{-1}$ | 3282.3 $cm^{-1}$ | 28 |
| $ND$ $\omega_e$ | 2398.72 $cm^{-1}$ | 2398 $cm^{-1}$ | 28 |
| $NH$ $\omega_e x_e$ | 86.37 $cm^{-1}$ | 78.4 $cm^{-1}$ | 28 |
| $ND$ $\omega_e x_e$ | 47.40 $cm^{-1}$ | 42 $cm^{-1}$ | 28 |
| $NH$ $B_e$ | 16.495 $cm^{-1}$ | 16.993 $cm^{-1}$ | 28 |
| $ND$ $B_e$ | 8.797 $cm^{-1}$ | 8.7913 $cm^{-1}$ | 28 |
| $NH_2$ Bond Energy | 3.9323 eV | 3.9461 eV | 35 |
| $ND_2$ Bond Energy | 3.9401 eV | 3.9362 eV | 33-35 |
| $NH_2$ Bond Length | 1.04262 Å | 1.0240 Å | 32 |
| $ND_2$ Bond Length | 1.04262 Å | | |
| $NH_2$ Bond Angle | 105.97° | 103.3° | 32 |
| $ND_2$ Bond Angle | 105.97° | | |
| $NH_3$ Bond Energy | 4.57913 eV | 4.60155 eV | 37 |
| $ND_3$ Bond Energy | 4.64499 eV | 4.71252 eV | 37 |
| $NH_3$ Bond Length | 1.0368 Å | 1.012 Å | 32 |
| $ND_3$ Bond Length | 1.0368 Å | | |
| $NH_3$ Bond Angle | 106.67° | 106.67° | 36 |
| $ND_3$ Bond Angle | 106.67° | 106.70° | 36 |
| $CH$ Bond Energy | 3.47404 eV | 3.47 eV | 14 |

| Parameter | Calculated | Experimental | Ref. for Exp. |
|---|---|---|---|
| $CD$ Bond Energy | 3.51673 eV | 3.52 eV | 14 |
| $CH$ Bond Length | 1.1183 Å | 1.1198 Å | 14 |
| $CD$ Bond Length | 1.1183 Å | 1.118 Å | 14 |
| $CH$ Vibrational Energy | 0.33879 eV | 0.33885 eV | 14 |
| $CD$ Vibrational Energy | 0.25173 eV | 0.25189 eV | 14 |
| $CH$ $\omega_e$ | 2865.86 $cm^{-1}$ | 2861.6 $cm^{-1}$ | 14 |
| $CD$ $\omega_e$ | 2102.97 $cm^{-1}$ | 2101.0 $cm^{-1}$ | 14 |
| $CH$ $\omega_e x_e$ | 66.624 $cm^{-1}$ | 64.3 $cm^{-1}$ | 14 |
| $CD$ $\omega_e x_e$ | 36.335 $cm^{-1}$ | 34.7 $cm^{-1}$ | 14 |
| $CH$ $B_e$ | 14.498 $cm^{-1}$ | 14.457 $cm^{-1}$ | 14 |
| $CD$ $B_e$ | 7.807 $cm^{-1}$ | 7.808 $cm^{-1}$ | 14 |
| $CH_2$ Bond Energy | 4.36968 eV | 4.33064 eV | 39 |
| $CH_2$ Bond Length | 1.1067 Å | 1.111 Å | 38 |
| $CH_2$ Bond Angle | 100.22° | 102.4° | 38 |
| $CH_3$ Bond Energy | 4.70075 eV | 4.72444 eV | 40 |
| $CH_3$ Bond Length | 1.1029 Å | 1.079 Å | 38 |
| $CH_3$ Bond Angle | 120° | 120° | 38 |
| $CH_4$ Bond Energy | 4.4900 eV | 4.48464 eV | 40 |
| $CH_4$ Bond Length | 1.1010 Å | 1.087 Å | 41 |
| $CH_4$ Bond Angle | 109.5° | 109.5° | 41 |
| $N_2$ Bond Energy | 9.71181 eV | 9.756 eV | 43 |
| $N_2$ Bond Length | 1.0955 Å | 1.094 Å | 43 |
| $O_2$ Bond Energy | 5.10711 eV | 5.11665 eV | 46 |
| $O_2$ Bond Length | 1.20862 Å | 1.20752 Å | 28 |
| $F_2$ Bond Energy | 1.62168 eV | 1.606 eV | 48 |
| $F_2$ Bond Length | 1.41114 Å | 1.41193 Å | 28 |
| $Cl_2$ Bond Energy | 2.52236 eV | 2.51412 eV | 49 |
| $Cl_2$ Bond Length | 1.988 Å | 1.988 Å | 28 |
| $Cl_2$ $\omega_e$ | 538.52 $cm^{-1}$ | 559.7 $cm^{-1}$ | 28 |
| $Cl_2$ $\omega_e x_e$ | 3.41 $cm^{-1}$ | 2.68 $cm^{-1}$ | 28 |
| $Cl_2$ $B_e$ | 0.2420 $cm^{-1}$ | 0.2440 $cm^{-1}$ | 28 |
| $CN$ Bond Energy | 7.77526 eV | 7.7731 eV | 50 |
| $CN$ Bond Length | 1.17231 Å | 1.17181 Å | 28 |
| $CO$ Bond Energy | 11.16652 eV | 11.15696 eV | 49 |
| $CO$ Bond Length | 1.13290 Å | 1.12823 Å | 28 |
| $NO$ Bond Energy | 6.57092 eV | 6.5353 eV | 49 |
| $NO$ Bond Length | 1.15733 Å | 1.15077 Å | 28 |

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# Chapter 14

## MORE POLYATOMIC MOLECULES AND HYDROCARBONS

Additional polyatomic molecules can be solved using similar principles as those used to solve hydrogen molecular ions and molecules wherein the hydrogen molecular orbitals (MOs) and hydrogen atomic orbitals serve as basis functions for the MOs. The MO must (1) be a solution of Laplace's equation to give a equipotential energy surface, (2) correspond to an orbital solution of the Newtonian equation of motion in an inverse-radius-squared central field having a constant total energy, (3) be stable to radiation, and (4) conserve the electron angular momentum of $\hbar$. Energy of the MO must be matched to that of the outermost atomic orbital of a bonding heteroatom in the case where a minimum energy is achieved with a direct bond to the AO. Alternatively, the MO is continuous with the AO containing paired electrons that do not particpate in the bond. Rather, they only provide a means for the energy matched MO to form a continuous equipotential energy surface. In the case that an independent MO is formed, the AO force balance causes the remaining electrons to be at lower energy and a smaller radius. In another case, the atomic orbital may hybridize in order to achieve a bond at an energy minimum, and the sharing of electrons between two or more such orbitals to form a MO permits the participating hybridized orbitals to decrease in energy through a decrease in the radius of one or more of the participating orbitals. Representative cases were solved. Specifically, the results of the determination of bond parameters of carbon dioxide ($CO_2$), nitrogen dioxide ($NO_2$), ethane ($CH_3CH_3$), ethylene ($CH_2CH_2$), acetylene ($CHCH$), benzene ($C_6H_6$), propane ($C_3H_8$), butane ($C_4H_{10}$), pentane ($C_5H_{12}$), hexane ($C_6H_{14}$), heptane ($C_7H_{16}$), octane ($C_8H_{18}$), nonane ($C_9H_{20}$), decane ($C_{10}H_{22}$), undecane ($C_{11}H_{24}$), dodecane ($C_{12}H_{26}$), and octadecane ($C_{18}H_{38}$) are given in Table 14.1. The calculated results are based on first principles and given in closed-form, exact equations containing fundamental constants only. The agreement between the experimental and calculated results is excellent.

## CARBON DIOXIDE MOLECULE

The carbon dioxide molecule can be formed by the reaction of carbon monoxide and an oxygen atom:

$$CO + O \rightarrow CO_2 \tag{14.1}$$

Each equivalent bond in the carbon dioxide molecule comprises a double bond that is energy-matched to the filled $C2s$ orbital. Each such bond comprises 75% of a $H_2$-type MO with four paired electrons as a basis set such that three electrons can be assigned to each $C=O$ bond. Thus, the two $C2p$ electrons combine with the four $O2p$ electrons, two from each $O$, as a linear combination to form the two $C=O$ bonds of $CO_2$. The force balance equation and radius $r_8$ of the $2p$ shell of $O$ is derived in the Eight-Electron Atoms section. With the formation of the $H_2$-type MOs by the contribution of two $2p$ electrons from each of the two $O$ atoms, a factor of two increase of the central field on the remaining $O2p$ electrons arises. The resulting increased Coulombic as well as magnetic central forces decrease the radii of the $O2p$ shells such that the energy minimum is achieved that is lower than that of the reactant atoms. The resulting electron configuration of $CO_2$ is $C1s^2O_11s^2O_21s^2C2s^2O_12s^2O_22s^2O_12p^2O_22p^2\sigma^6_{O_2,C,O_1}$ where the subscripts designate the $O$ atom, 1 or 2, $\sigma$ designates the $H_2$-type MO, and the orbital arrangement is:

$\sigma$ state

$\underline{\uparrow\ \downarrow}\ \ \underline{\uparrow\ \downarrow}\ \ \underline{\uparrow\ \downarrow}$

2p state

$\underline{\uparrow\downarrow}\qquad\qquad\qquad\underline{\uparrow\downarrow}$

0 0 (14.2)

2s state

$\underline{\uparrow\downarrow}\qquad\underline{\uparrow\downarrow}\qquad\underline{\uparrow\downarrow}$

1s state

$\underline{\uparrow\downarrow}\qquad\underline{\uparrow\downarrow}\qquad\underline{\uparrow\downarrow}$

$O\qquad C\qquad O$

Carbon dioxide is predicted to be diamagnetic in agreement with observations [1].

## FORCE BALANCE OF THE $2p$ SHELL OF THE OXYGEN ATOM OF THE CARBON DIOXIDE MOLECULE

For each $O$ atom, force balance for the outermost $2p$ electron of $CO_2$ (electron 6) is achieved between the centrifugal force and the Coulombic and magnetic forces that arise due to interactions between electron 6 and the other $2p$ electrons as well as the $2s$-shell electrons due to spin and orbital angular momentum. The forces used are derived in the Eight-Electron Atoms section. The central Coulomb force on the outer-most $2p$ shell electron of $CO$ (electron 6) due to the nucleus and the inner five electrons is given by Eq. (10.70) with the appropriate charge and radius:

$$\mathbf{F}_{ele} = \frac{(Z-5)e^2}{4\pi\varepsilon_0 r_6^2}\mathbf{i_r} \tag{14.3}$$

for $r > r_5$. The $2p$ shell possess a +2 external electric field given by Eq. (10.92) for $r > r_6$. The energy is minimized with conservation of angular momentum. This condition is met when the diamagnetic force, $\mathbf{F}_{diamagnetic}$, of Eq. (10.82) due to the $p$-orbital contribution is given by:

$$\mathbf{F}_{diamagnetic} = -\left(\frac{2}{3}\right)\frac{\hbar^2}{4m_e r_6^2 r_3}\sqrt{s(s+1)}\mathbf{i_r} = -\frac{2\hbar^2}{12m_e r_6^2 r_3}\sqrt{\frac{3}{4}}\mathbf{i_r} \tag{14.4}$$

where $s = 1/2$. And, $\mathbf{F}_{mag\ 2}$ corresponding to the conserved spin and orbital angular momentum given by Eq. (10.157) is:

$$\mathbf{F}_{mag\ 2} = \frac{1}{Z}\frac{2\hbar^2}{m_e r_6^2 r_3}\sqrt{s(s+1)}\mathbf{i_r} \tag{14.5}$$

The electric field external to the $2p$ shell given by Eq. (10.92) for $r > r_6$ gives rise to a second diamagnetic force, $\mathbf{F}_{diamagnetic\ 2}$, given by Eq. (10.93). $\mathbf{F}_{diamagnetic\ 2}$ due to the binding of the p-orbital electron having an electric field of +2 outside of its radius is:

$$\mathbf{F}_{diamagnetic\ 2} = -\left[\frac{Z-6}{Z-5}\right]\left(1-\frac{\sqrt{2}}{2}\right)\frac{r_3\hbar^2}{m_e r_6^4}10\sqrt{s(s+1)}\mathbf{i_r} \tag{14.6}$$

The radius of the $2p$ shell is calculated by equating the outward centrifugal force to the sum of the electric (Eq. (14.3)) and diamagnetic (Eqs. (14.4) and (14.6)), and paramagnetic (Eq. (14.5)) forces as follows:

$$\frac{m_e v_6^2}{r_6} = \frac{(Z-5)e^2}{4\pi\varepsilon_0 r_6^2} - \frac{2\hbar^2}{12m_e r_6^2 r_3}\sqrt{s(s+1)} + \frac{2\hbar^2}{Zm_e r_6^2 r_3}\sqrt{s(s+1)} - \left[\frac{Z-6}{Z-5}\right]\left(1-\frac{\sqrt{2}}{2}\right)\frac{r_3\hbar^2}{r_6^4 m_e}10\sqrt{s(s+1)} \tag{14.7}$$

Substitution of $v_6 = \frac{\hbar}{m_e r_6}$ (Eq. (1.35)) and $s = \frac{1}{2}$ into Eq. (14.7) gives:

$$\frac{\hbar^2}{m_e r_6^3} = \frac{(Z-5)e^2}{4\pi\varepsilon_0 r_6^2} - \frac{2\hbar^2}{12m_e r_6^2 r_3}\sqrt{\frac{3}{4}} + \frac{2\hbar^2}{Zm_e r_6^2 r_3}\sqrt{\frac{3}{4}} - \left[\frac{Z-6}{Z-5}\right]\left(1-\frac{\sqrt{2}}{2}\right)\frac{r_3\hbar^2}{r_6^4 m_e}10\sqrt{\frac{3}{4}} \tag{14.8}$$

The quadratic equation corresponding to Eq. (14.8) is:

$$r_6^2 - \frac{\frac{\hbar^2}{m_e}}{\left( \frac{(Z-5)e^2}{4\pi\varepsilon_0} - \left( \frac{2}{12} - \frac{2}{Z} \right) \frac{\hbar^2}{m_e r_3} \sqrt{\frac{3}{4}} \right)} r_6 - \frac{\frac{\hbar^2}{m_e} \left[ \frac{Z-6}{Z-5} \right] \left( 1 - \frac{\sqrt{2}}{2} \right) r_3 10 \sqrt{\frac{3}{4}}}{\left( \frac{(Z-5)e^2}{4\pi\varepsilon_0} - \left( \frac{2}{12} - \frac{2}{Z} \right) \frac{\hbar^2}{m_e r_3} \sqrt{\frac{3}{4}} \right)} = 0 \tag{14.9}$$

The solution of Eq. (14.9) using the quadratic formula is:

$$r_6 = \frac{\frac{a_0}{\left( (Z-5) - \left( \frac{2}{12} - \frac{2}{Z} \right) \frac{\sqrt{3}}{2r_3} \right)} \pm a_0 \sqrt{\left( \frac{1}{\left( (Z-5) - \left( \frac{2}{12} - \frac{2}{Z} \right) \frac{\sqrt{3}}{2r_3} \right)} \right)^2 + \frac{20\sqrt{3} \left( \left[ \frac{Z-6}{Z-5} \right] \left( 1 - \frac{\sqrt{2}}{2} \right) r_3 \right)}{\left( (Z-5) - \left( \frac{2}{12} - \frac{2}{Z} \right) \frac{\sqrt{3}}{2r_3} \right)}}}{2}, \; r_3 \textit{ in units of } a_0 \tag{14.10}$$

The positive root of Eq. (14.10) must be taken in order that $r_6 > 0$. Substitution of $\frac{r_3}{a_0} = 0.59020$ (Eq. (10.62) with $Z = 8$) into Eq. (14.10) gives:

$$r_6 = 0.74776 a_0 \tag{14.11}$$

## ENERGIES OF THE $2s$ AND $2p$ SHELLS OF THE CARBON ATOM AND THE $2p$ SHELL OF THE OXYGEN ATOMS OF THE CARBON DIOXIDE MOLECULE

Consider the determination of the total energy of $CO_2$ from the reaction of a carbon atom with two oxygen atoms. With the formation of the $H_2$-type MO by the contribution of two $2p$ electrons from the $C$ atom, the remaining outer-shell atomic electrons comprise the $2s$ electrons which are unchanged by bonding with two oxygen atoms. However, the total energy of the $CO_2$ molecule, which is subtracted from the sum of the energies of the oxygen atom and carbon monoxide molecule to determine the $O-CO$ bond energy, is increased by the ionization energies of $C$, $C^+$, $O$, and $2O^+$ given by Eqs. (14.12-14.15), respectively. Experimentally, the energies are [2]:

$$E(ionization;\ C) = 11.26030\ eV \tag{14.12}$$

$$E(ionization;\ C^+) = 24.38332\ eV \tag{14.13}$$

$$E(ionization;\ O) = 13.61806\ eV \tag{14.14}$$

$$E(ionization;\ O^+) = 35.11730\ eV \tag{14.15}$$

In addition, the central forces on the $2p$ shell of the $O$ atom are increased with the formation of the $\sigma$ MO which reduces the shell's radius and increases its total energy. The Coulombic energy terms of the total energy of each $O$ atom at the new radius are calculated and added to the ionization energies of $C$, $C^+$, $O$, and $2O^+$, and the energy of the $\sigma$ MO to give the total energy of $CO_2$. Then, the bond energy is determined from the total $CO_2$ energy.

The radius $r_8$ of each oxygen atom before bonding is given by Eq. (10.162):

$$r_8 = a_0 \tag{14.16}$$

Using the initial radius $r_8$ of each $O$ atom and the final radius $r_6$ of the $O2p$ shell (Eq. (14.11)) and by considering that the central Coulombic field decreases by an integer for each successive electron of the shell, the sum $E_T\left(O,2p\right)$ of the Coulombic energy change of the $O2p$ electrons of each $O$ atom is determined using Eq. (10.102):

$$E_T\left(O,2p\right) = -\sum_{n=4}^{5} \frac{(Z-n)e^2}{8\pi\varepsilon_0} \left( \frac{1}{r_6} - \frac{1}{r_8} \right) = -\left(13.60580\ eV\right)\left(0.33733\right)\left(3+4\right) = -32.12759\ eV \tag{14.17}$$

## FORCE BALANCE OF THE $\sigma$ MO OF THE CARBON DIOXIDE MOLECULE

As in the case of $H_2$, the $\sigma$ MO is a prolate spheroid with the exception that the ellipsoidal MO surface cannot extend into the $C$ atom for distances shorter than the radius of the $C2s$ shell; nor, can it extend into the $O$ atom for distances shorter than the radius of the $O2p$ shell. Thus, the MO surface of each $C=O$ bond comprises a prolate spheroid that bridges and is continuous with the $2s$ and $2p$ shells of the $O$ and $C$ atoms whose nuclei serve as the foci. The energy of each prolate spheroid is matched to that of the $C2s$ and $O2p$ shells. As in the case of previous examples of energy-matched MOs such as $OH$ and $NH$, the $C=O$-bond MO must comprise 75% of a $H_2$-type ellipsoidal MO in order to match potential, kinetic, and orbital energy relationships. However, the paired electrons of the $C2s$ and $O2p$ shells are not involved in bonding. Rather, the AOs permit a continuous surface comprising the two $C=O$-bond MOs having six paired electrons, two from each of the $C$ and the two $O$ atoms:

$$2\left(0.75\ H_2\ MO\right) \to CO_2\ MO \tag{14.18}$$

The force balance of the $CO_2$ MO is determined by the boundary conditions that arise from the linear combination of orbitals according to Eq. (14.18) and the energy matching condition between the carbon and oxygen components of the MO.

Similar to the $OH$ and $H_2O$ cases given by Eqs. (13.57) and (13.162), the $H_2$-type ellipsoidal MO comprises 75% of the $CO_2$ MO; so, the electron charge density in Eq. (11.65) is given by $-0.75e$. Thus, $k'$ of each $H_2$-type-ellipsoidal-MO component of the $CO_2$ MO is given by Eq. (13.59). The distance from the origin of each $C=O$-bond MO to each focus $c'$ is given by Eq. (13.60). The internuclear distance is given by Eq. (13.61). The length of the semiminor axis of the prolate spheroidal $C=O$-bond MO $b=c$ is given by Eq. (13.62). The eccentricity, $e$, is given by Eq. (13.63). Then, the solution of the semimajor axis $a$ allows for the solution of the other axes of the prolate spheroidal and eccentricity of the $CO_2$ MO.

The energy components of $V_e$, $V_p$, $T$, $V_m$, and $E_T$ of the $CO_2$ $\sigma$ MO are the same as those of $OH$ given by Eqs. (13.67-13.73), except that the terms based on charge are multiplied by four and the kinetic energy term is multiplied by two due to each $\sigma$-MO double bond:

$$E_T\left(C=O,\sigma\right) = -\frac{4e^2}{8\pi\varepsilon_0 c'}\left[\left(\frac{3}{2}\right)\ln\frac{a+c'}{a-c'}-1\right] \tag{14.19}$$

where $E_T\left(C=O,\sigma\right)$ is the total energy of each $C=O$ $\sigma$ MO of $CO_2$. The total energy of a $H_2$-type ellipsoidal MO is given by Eqs. (11.212) and (13.75). A minimum energy is obtained when each double bond of the $\sigma$ MO of $CO_2$ comprises the energy equivalent of four $H_2$-type ellipsoidal MOs. For each $C=O$ bond to match the energy of the $C2s$ orbital, the ionization energy of $C$ and $C^+$ (Eqs. (14.12-14.13)) must be added for each bond of the double bond. Thus, the total energy of each $C=O$-bond MOs is:

$$\begin{aligned} E_T\left(C=O,\sigma\right) &= 2\left(\begin{array}{l} 2\left(-\dfrac{e^2}{8\pi\varepsilon_0 a_0}\left[\left(2\sqrt{2}-\sqrt{2}+\dfrac{\sqrt{2}}{2}\right)\ln\dfrac{\sqrt{2}+1}{\sqrt{2}-1}-\sqrt{2}\right]\right) \\ +E(ionization;\ C)+E(ionization;\ C^+) \end{array}\right) \\ &= 2\left(2\left(-31.63536831\ eV\right)+11.26030\ eV+24.38332\ eV\right) \\ &= -55.25423\ eV \end{aligned} \tag{14.20}$$

$E_T\left(C=O,\sigma\right)$ given by Eq. (14.19) is set equal to Eq. (14.20):

$$\frac{4e^2}{8\pi\varepsilon_0 c'}\left[\left(\frac{3}{2}\right)\ln\frac{a+c'}{a-c'}-1\right] = e55.25423\ eV \tag{14.21}$$

From the energy relationship given by Eq. (14.21) and the relationship between the axes given by Eqs. (13.60-13.63), the dimensions of the $CO_2$ MO can be solved.

Substitution of Eq. (13.60) into Eq. (14.21) gives:

$$E_T\left(C=O,\sigma\right) = \frac{4e^2}{8\pi\varepsilon_0\sqrt{\dfrac{2aa_0}{3}}}\left[\left(\frac{3}{2}\right)\ln\frac{a+\sqrt{\dfrac{2aa_0}{3}}}{a-\sqrt{\dfrac{2aa_0}{3}}}-1\right] = e55.25423\ eV \tag{14.22}$$

The most convenient way to solve Eq. (14.22) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is

$$a = 1.80703a_0 = 9.56239\ X\ 10^{-11}\ m \tag{14.23}$$

Substitution of Eq. (14.23) into Eq. (13.60) is:

$$c' = 1.09758a_0 = 5.80815\ X\ 10^{-11}\ m \tag{14.24}$$

The internuclear distance given by multiplying Eq. (14.24) by two is:

$$2c' = 2.19516a_0 = 1.16163\ X\ 10^{-10}\ m \tag{14.25}$$

The experimental bond distance is [3]

$$2c' = 1.1600\ X\ 10^{-10}\ m \tag{14.26}$$

Substitution of Eqs. (14.23-14.24) into Eq. (13.62) is:

$$b = c = 1.43550a_0 = 7.59636\ X\ 10^{-11}\ m \tag{14.27}$$

Substitution of Eqs. (14.23-14.24) into Eq. (13.63) is:

$$e = 0.60740 \tag{14.28}$$

The $C$ and $O$ nuclei comprise the foci of each $H_2$-type ellipsoidal MO defined as $O=C=O$. Consider the left-hand $C=O$ bond of the two equivalent bonds in the absence of the right-hand bond. The parameters of the point of intersection of the $H_2$-type ellipsoidal MO and the $C2s$ AO are given by Eqs. (13.84-13.95) and (13.261-13.270). The polar intersection angle $\theta'$ is given by Eq. (13.261) where $r_n = r_4 = 0.84317a_0$ is the radius of the $C2s$ shell. Substitution of Eqs. (14.23-14.24) into Eq. (13.261) gives

$$\theta' = 54.53° \tag{14.29}$$

Then, the angle $\theta_{C2sAO}$ the radial vector of the $C2s$ AO makes with the internuclear axis is:

$$\theta_{C2sAO} = 180° - 54.53° = 125.47° \tag{14.30}$$

as shown in Figure 14.1. The Cartesian $\mathbf{i}$-coordinate of the interception point of the MO and the AO can be calculated using the MO ellipsoidal parameters by first calculating the parametric angle in Eq. (11.83) that matches Cartesian $\mathbf{j}$-coordinate components at the point of intersection. Thus, the matching elliptic parametric angle $\omega t = \theta_{H_2MO}$ satisfies the following relationship:

$$r_4 \sin\theta_{C2sAO} = 0.84317a_0 \sin\theta_{C2sAO} = b\sin\theta_{H_2MO} \tag{14.31}$$

such that

$$\theta_{H_2MO} = \sin^{-1}\frac{0.84317a_0\sin\theta_{C2sAO}}{b} = \sin^{-1}\frac{0.84317a_0\sin 125.47°}{b} \tag{14.32}$$

with the use of Eq. (14.30). Substitution of Eq. (14.27) into Eq. (14.32) gives:

$$\theta_{H_2MO} = 28.58° \tag{14.33}$$

Then, the distance $d_{H_2MO}$ along the internuclear axis from the origin of $H_2$-type ellipsoidal MO to the point of intersection of the orbitals is given by

$$d_{H_2MO} = a\cos\theta_{H_2MO} \tag{14.34}$$

Substitution of Eqs. (14.23) and (14.33) into Eq. (14.34) gives:

$$d_{H_2MO} = 1.58687a_0 = 8.39737\ X\ 10^{-11}\ m \tag{14.35}$$

The distance $d_{C2sAO}$ along the internuclear axis from the origin of the $C$ atom to the point of intersection of the orbitals is given by

$$d_{C2sAO} = d_{H_2MO} - c' \tag{14.36}$$

Substitution of Eqs. (14.24) and (14.35) into Eq. (14.36) gives:

$$d_{C2sAO} = 0.48929a_0 = 2.58922\ X\ 10^{-11}\ m \tag{14.37}$$

The $C$ and $O$ nuclei comprise the foci of each $H_2$-type ellipsoidal MO defined as $O=C=O$. Consider the right-hand $C=O$ bond of the two equivalent bonds. The parameters of the point of intersection of the $H_2$-type ellipsoidal MO and the $O2p$ AO are given by Eqs. (13.84-13.95) and (13.261-13.270). The polar intersection angle $\theta'$ is given by Eq. (13.261) where $r_n = r_6 = 0.74776a_0$ is the radius of the $O2p$ shell. Substitution of Eqs. (14.23-14.24) into Eq. (13.261) gives

$$\theta' = 30.18° \tag{14.38}$$

Then, the angle $\theta_{O2pAO}$ the radial vector of the $O2p$ AO makes with the internuclear axis is:

$$\theta_{O2pAO} = 180° - 30.18° = 149.82° \tag{14.39}$$

as shown in Figure 14.1. The Cartesian $\mathbf{i}$-coordinate of the interception point of the MO and the AO can be calculated using the MO ellipsoidal parameters by first calculating the parametric angle in Eq. (11.83) that matches Cartesian $\mathbf{j}$-coordinate components at the point of intersection. Thus, the matching elliptic parametric angle $\omega t = \theta_{H_2MO}$ satisfies the following relationship:

$$r_6 \sin\theta_{O2pAO} = 0.74776a_0 \sin\theta_{O2pAO} = b\sin\theta_{H_2MO} \tag{14.40}$$

such that

$$\theta_{H_2MO} = \sin^{-1}\frac{0.74776a_0\sin\theta_{O2pAO}}{b} = \sin^{-1}\frac{0.74776a_0\sin 149.82°}{b} \tag{14.41}$$

with the use of Eq. (14.39). Substitution of Eq. (14.27) into Eq. (14.41) gives:

$$\theta_{H_2MO} = 15.18° \tag{14.42}$$

Then, the distance $d_{H_2MO}$ along the internuclear axis from the origin of $H_2$-type ellipsoidal MO to the point of intersection of the orbitals is given by:

$$d_{H_2MO} = a\cos\theta_{H_2MO} \tag{14.43}$$

Substitution of Eqs. (14.23) and (14.42) into Eq. (14.43) gives:

$$d_{H_2MO} = 1.74396a_0 = 9.22862\ X\ 10^{-11}\ m \tag{14.44}$$

The distance $d_{O2pAO}$ along the internuclear axis from the origin of each $O$ atom to the point of intersection of the orbitals is given by:

$$d_{2pAO} = d_{H_2MO} - c' \tag{14.45}$$

Substitution of Eqs. (14.24) and (14.44) into Eq. (14.45) gives:

$$d_{O2pAO} = 0.64637a_0 = 3.42047\ X\ 10^{-11}\ m \tag{14.46}$$

As shown in Eq. (14.18), each $C = O$ bond comprises a factor of 0.75 of the charge-density of double that of the $H_2$-type ellipsoidal MO. Using the electron configuration of $CO_2$ (Eq. (14.2)), the radii of the $C1s = 0.17113a_0$ (Eq. (10.51)), $C2s = 0.84317a_0$ (Eq. (10.62)), $O1s = 0.12739a_0$ (Eq. (10.51)), $O2s = 0.59020a_0$ (Eq. (10.62)), and $O2p = 0.74776a_0$ (Eq. (14.11)) shells and the parameters of the $\sigma$ MO of $CO_2$ given by Eqs. (13.3-13.4), (14.23-14.25), and (14.27-14.28), the dimensional diagram and charge-density of the $CO_2$ MO are shown in Figures 14.1 and 14.2, respectively.

Figure 14.1. The cross section of the $CO_2$ MO showing the axes, $\sigma$ MO (two $H_2$-type ellipsoidal MOs) with six paired electrons, with the $C$ $1s$ and $2s$ AOs and the $O$ $1s$, $2s$, and $2p$ AOs. Legend: $a$: semimajor axis, $b$: semiminor axis, $c'$: internuclear distance, $r_4$: radius of the $C2s$ shell having two paired electrons, $r_6$: radius of the $O2p$ shell having two paired electrons.

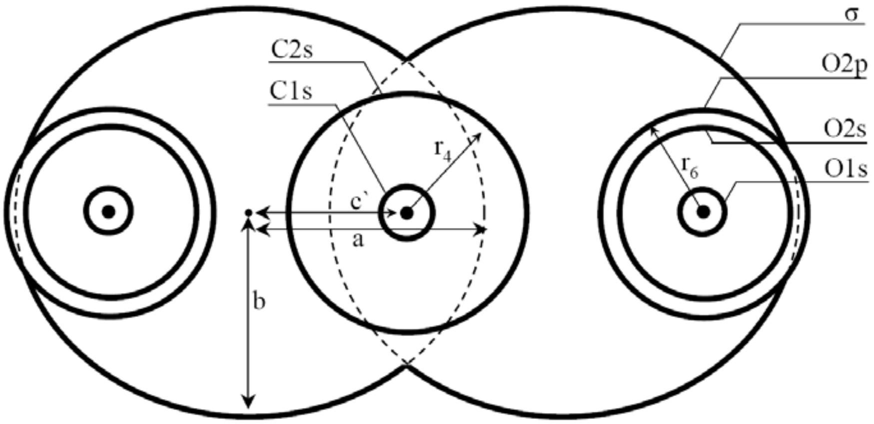
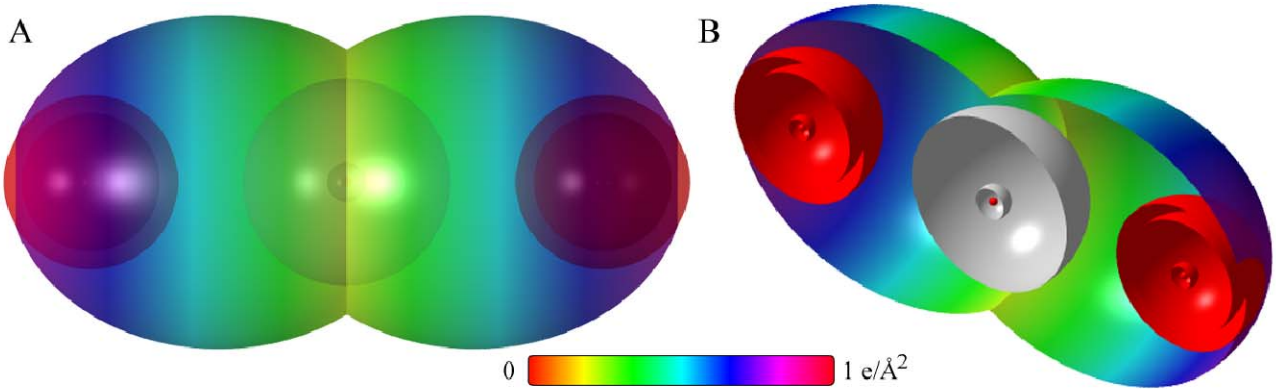


Figure 14.2. $CO_2$ MO comprising the $\sigma$ MO (two $H_2$-type MOs) with $C$ and two $O$ atoms at the foci that have each donated two electrons to the $\sigma$ MO. Consequently, the outer electrons of the carbon atom comprise the $C2s$ shell, and each $O2p$ shell has a smaller radius and a higher binding energy. (A) Color scale, translucent view of the charge-density of the $CO_2$ MO. (B) Off-center cut-away view showing each complete inner most $O1s$ shell, and moving radially, the $O2s$ shell, the $O2p$ shell, and the $\sigma$ prolate spheroidal MO that has the corresponding $O$ atom as a focus. Moving radially from the carbon-atom focus, the complete inner most $C1s$ shell, the $C2s$ shell, and the $\sigma$ prolate spheroidal MOs are shown.



## SUM OF THE ENERGIES OF THE $\sigma$ MO AND THE AOS OF THE CARBON DIOXIDE MOLECULE

The energies of the $CO_2$ $\sigma$ MO are given by the substitution of the semiprincipal axes (Eqs. (14.23-14.24) and (14.27)) into the energy equations of $OH$ (Eqs. (13.67-13.73)), except that the terms based on charge are multiplied by four and the kinetic energy term is multiplied by two due to each $\sigma$-MO double bond:

$$V_e = 2^2\left(\frac{3}{4}\right)\frac{-2e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -104.83940\ eV \tag{14.47}$$

$$V_p = 2^2\frac{e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}} = 49.58464\ eV \tag{14.48}$$

$$T = 2\left(\frac{3}{4}\right)\frac{\hbar^2}{2m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = 14.50438\ eV \tag{14.49}$$

$$V_m = 2^2\left(\frac{3}{4}\right)\frac{-\hbar^2}{4m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -14.50438\ eV \tag{14.50}$$

$$E_T = V_e + T + V_m + V_p \tag{14.51}$$

Substitution of Eqs. (13.60) and (14.47-14.50) into Eq. (14.51) gives:

$$E_T\left(C=O,\sigma\right) = V_e + T + V_m + V_p = \frac{-4e^2}{8\pi\varepsilon_0\sqrt{\frac{2aa_0}{3}}}\left[\left(\frac{3}{2}\right)\ln\frac{a+\sqrt{\frac{2aa_0}{3}}}{a-\sqrt{\frac{2aa_0}{3}}}-1\right] = -55.25476\ eV \tag{14.52}$$

where $E_T\left(C=O,\sigma\right)$ is the total energy of each $C=O$ $\sigma$ MO of $CO_2$ given by Eq. (14.19) which is reiteratively matched to Eq. (14.20) within five-significant-figure round off error.

The total energy of $CO_2$, $E_T\left(CO_2\right)$, is given by the sum of $E(ionization;\ C)$ and $E(ionization;\ C^+)$, the sum of the energies of the first and second electrons of carbon (Eqs. (14.12-14.13)) donated to each double bond, the sum of $E(ionization;\ O)$ and two times $E(ionization;\ O^+)$, the energies of the first and second electrons of oxygen (Eqs. (14.14-14.15)) donated to the double bonds, two times $E_T\left(O,2p\right)$, the $O2p$ AO contribution due to the decrease in radius with the formation of each bond (Eq. (14.17)), and two times $E_T\left(C=O,\sigma\right)$, the $\sigma$ MO contribution given by Eq. (14.22):

$$\begin{aligned}
E_T\left(CO_2\right) &= \begin{pmatrix} E(ionization;\ C)+E(ionization;\ C^+)+E(ionization;\ O) \\ +2E(ionization;\ O^+)+2E_T\left(O,2p\right)+2E_T\left(C=O,\sigma\right)\end{pmatrix} \\
&= \begin{pmatrix} 11.26030\ eV + 24.38332\ eV + 13.61806\ eV \\ +2\left(35.11730\ eV\right)+2\left(-32.12759\ eV\right) \\ -2\left(\frac{4e^2}{8\pi\varepsilon_0\sqrt{\frac{2aa_0}{3}}}\left(\left(\frac{3}{2}\right)\ln\frac{a+\sqrt{\frac{2aa_0}{3}}}{a-\sqrt{\frac{2aa_0}{3}}}-1\right)\right)\end{pmatrix} \\
&= \begin{pmatrix} 11.26030\ eV + 24.38332\ eV + 13.61806\ eV \\ +2\left(35.11730\ eV\right)+2\left(-32.12759\ eV\right)-2\left(55.25423\ eV\right)\end{pmatrix} = -55.26841\ eV
\end{aligned} \tag{14.53}$$

## VIBRATION OF $CO_2$

The vibrational energy levels of $CO_2$ may be solved by determining the Morse potential curve from the energy relationships for the transition from a $C$ atom and two $O$ atoms whose parameters are given by Eqs. (10.115-10.123) and (10.154-10.163), respectively, to a $C$ atom whose parameter $r_4$ is given by Eq. (10.61), two $O$ atoms whose parameter $r_6$ is given by Eq. (14.11), and the $\sigma$ $CO_2$ MO whose parameters are given by Eqs. (14.23-14.25) and (14.27-14.28). As shown in the Vibration of Hydrogen-type Molecular Ions section, the harmonic oscillator potential energy function can be expanded about the internuclear distance and expressed as a Maclaurin series corresponding to a Morse potential after Karplus and Porter (K&P) [4] and after Eq. (11.134). Treating the Maclaurin series terms as anharmonic perturbation terms of the harmonic states, the energy corrections can be found by perturbation methods.

## THE DOPPLER ENERGY TERMS OF THE CARBON DIOXIDE MOLECULE

The equations of the radiation reaction force of carbon dioxide are the same as those of $OH$ with the substitution of the $CO_2$ parameters except that there is a factor of four increase in the central force in Eq. (13.140) due to the double bond. Using Eqs. (13.140-13.142), the angular frequency of the reentrant oscillation in the transition state is

$$\omega = \sqrt{\frac{\frac{4(0.75)e^2}{4\pi\varepsilon_0 b^3}}{m_e}} = 4.16331\ X\ 10^{16}\ rad/s \tag{14.54}$$

where $b$ is given by Eq. (14.27). The kinetic energy, $E_K$, is given by Planck's equation (Eq. (11.127)).

$$\overline{E}_K = \hbar\omega = \hbar 4.16331\ X\ 10^{16}\ rad/s = 27.40365\ eV \tag{14.55}$$

In Eq. (11.181), substitution of $E_T(CO_2)/2$ for $E_{h\nu}$, the mass of the electron, $m_e$, for $M$, and the kinetic energy given by Eq. (14.55) for $\overline{E}_K$ gives the Doppler energy of the electrons of the reentrant orbit:

$$\overline{E}_D \cong E_{h\nu}\sqrt{\frac{2\overline{E}_K}{Mc^2}} = -27.63421\ eV\sqrt{\frac{2e(27.40365\ eV)}{m_e c^2}} = -0.28619\ eV \tag{14.56}$$

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency. The transition state comprises $O--CO$, oxygen binding to $CO$. Vibration of the linear XYZ-molecular transition state corresponds to $\upsilon_3$ [5] with the maximum kinetic energy localized to the nascent $C-O$ bond. In this case, the kinetic energy of the nuclei is the maximum for this bond. Thus, $\overline{E}_{Kvib}$ is the vibrational energy. The decrease in the energy of the $CO_2$ MO due to the reentrant orbit in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei, $\overline{E}_{osc}$, is given by the sum of the corresponding energies, $\overline{E}_D$ given by Eq. (14.56) and $\overline{E}_{Kvib}$, the vibrational energy. Using the experimental $CO_2$ $E_{vib}(\upsilon_3)$ of 2349 $cm^{-1}$ $(0.29124\ eV)$ [6] for $\overline{E}_{Kvib}$ of the transition state, $\overline{E}_{osc}(CO_2)$ is:

$$\overline{E}_{osc}(CO_2) = \overline{E}_D + \overline{E}_{Kvib} = \overline{E}_D + E_{vib} \tag{14.57}$$

$$\overline{E}_{osc}(CO_2) = -0.28619\ eV + 0.29124\ eV = 0.00505\ eV \tag{14.58}$$

## TOTAL AND BOND ENERGIES OF THE CARBON DIOXIDE MOLECULE

$E_{T+osc}(CO_2)$, the total energy of $CO_2$ including the Doppler term, is given by the sum of $E_T(CO_2)$ (Eq. (14.53)) and $\overline{E}_{osc}(CO_2)$ given by Eq. (14.58).

$$\begin{aligned} E_{T+osc}(CO_2) &= \begin{pmatrix} 2(V_e + T + V_m + V_p) + E(ionization;\ C) \\ +E(ionization;\ C^+) + E(ionization;\ O) + 2E(ionization;\ O^+) \\ +2E_T(O,2p) + \overline{E}_{osc}(CO_2) \end{pmatrix} \\ &= \begin{pmatrix} 2E_T(C=O,\sigma) + E(ionization;\ C) + E(ionization;\ C^+) \\ +E(ionization;\ O) + 2E(ionization;\ O^+) \\ +2E_T(O,2p) + \overline{E}_{osc}(CO_2) \end{pmatrix} \\ &= E_T(CO_2) + \overline{E}_{osc}(CO_2) \end{aligned} \tag{14.59}$$

$$\begin{aligned} E_{T+osc}(CO_2) &= \left\{ \begin{array}{l} \left( \begin{array}{l} 2\left( \frac{-4e^2}{8\pi\varepsilon_0\sqrt{\frac{2aa_0}{3}}} \left( \left(\frac{3}{2}\right) \ln\frac{a+\sqrt{\frac{2aa_0}{3}}}{a-\sqrt{\frac{2aa_0}{3}}} - 1 \right) \right) + E(ionization;\ C) \\ +E(ionization;\ C^+) + E(ionization;\ O) \\ +2E(ionization;\ O^+) - 2\sum_{O,n=4}^{5} \frac{(Z-n)e^2}{8\pi\varepsilon_0}\left(\frac{1}{r_6} - \frac{1}{r_8}\right) \end{array} \right) \\ \left( \left( 1 + \frac{1}{2}\sqrt{\frac{2\hbar\sqrt{\frac{\frac{4(0.75)e^2}{4\pi\varepsilon_0 b^3}}{m_e}}}{m_e c^2}} \right) \right) + E_{vib} \end{array} \right\} \\ &= -55.26841\ eV - 0.28619\ eV + E_{vib} \end{aligned} \tag{14.60}$$

From Eqs. (14.57-14.60), the total energy of the $CO_2$ MO is:

$$E_{T+osc}\left(CO_2\right) = -55.25476\ eV + \bar{E}_{osc}\left(CO_2\right) = -55.25476\ eV + 0.00505\ eV = -55.26336\ eV \tag{14.61}$$

where the experimental $E_{vib}$ was used.

As in the case of the dissociation of the bond of the hydroxyl radical, an oxygen atom is formed with dissociation of $CO_2$. $O$ has two unpaired electrons as shown in Eq. (13.55) which interact to stabilize the atom as shown by Eq. (10.161-10.162). The lowering of the energy of the reactants decreases the bond energy. Thus, the total energy of oxygen is reduced by the energy in the field of the two magnetic dipoles given by Eq. (7.46) and Eq. (13.101).

$$E(magnetic) = \frac{2\pi\mu_0 e^2\hbar^2}{m_e^2 a_0^3} = \frac{8\pi\mu_0\mu_B^2}{a_0^3} = 0.11441\ eV \tag{14.62}$$

The $CO_2$ bond dissociation energy, $E_D\left(CO_2\right)$, is given by the sum of the energies of the $CO$ and the $O$ atom minus the sum of $E_{T+osc}\left(CO_2\right)$ and $E(magnetic)$:

$$E_D\left(CO_2\right) = E\left(CO\right) + E\left(O\right) - \left(E(magnetic) + E_{T+osc}\left(CO_2\right)\right) \tag{14.63}$$

The energy of an oxygen atom is given by Eq. (14.14) and $E_T(CO)$ is given by the sum of the experimental energies of $C$ (Eq. (14.12)), $O$ (Eq. (14.14)), and the negative of the bond energy of $CO$ (Eq. (13.914)):

$$E(CO) = -11.26030\ eV - 13.618060\ eV - 11.15696\ eV = -36.03532\ eV \tag{14.64}$$

The energy of $O$ is given by the negative of the corresponding ionization energy given in Eq. (4.14). Thus, the $CO_2$ bond dissociation energy, $E_D\left(CO_2\right)$, given by the Eqs. (4.14) and (14.61-14.64) is:

$$\begin{aligned} E_D\left(CO_2\right) &= -\left(36.03532\ eV + 13.618060\ eV\right) - \left(E(magnetic) + E_{T+osc}\left(CO_2\right)\right) \\ &= -49.65338\ eV - \left(0.11441\ eV - 55.26336\ eV\right) \\ &= 5.49557\ eV \end{aligned} \tag{14.65}$$

The experimental $CO_2$ bond dissociation energy is [7]:

$$E_{D298}\left(CO_2\right) = 5.516\ eV \tag{14.66}$$

The results of the determination of bond parameters of $CO_2$ are given in Table 14.1. The calculated results are based on first principles and given in closed-form, exact equations containing fundamental constants only. The agreement between the experimental and calculated results is excellent.

## NITROGEN DIOXIDE MOLECULE

The nitrogen dioxide molecule can be formed by the reaction of nitric oxide and an oxygen atom:

$$NO + O \rightarrow NO_2 \tag{14.67}$$

The bonding in the nitrogen dioxide molecule comprises two double bonds, each a $H_2$-type MO with four paired electrons wherein the central $N$ atom is shared by both bonds such that six electrons can be assigned to the two $N=O$ bonds. Thus, two $N2p$ electrons combine with the four $O2p$ electrons, two from each $O$, as a linear combination to form the two overlapping $N=O$ bonds of $NO_2$. The force balance equation and radius $r_7$ of the $2p$ shell of $N$ is derived in the Seven-Electron Atoms section. The force balance equation and radius $r_8$ of the $2p$ shell of $O$ is derived in the Eight-Electron Atoms section. With the formation of each of the two $H_2$-type MOs by the contribution of two $2p$ electrons each from the $N$ and $O$ atoms, a diamagnetic force arises between the remaining outer shell atomic electrons, the $2s$ and $2p$ electrons of $N$ and $O$, and the $H_2$-type MO. This force from $N$ and $O$ causes the $H_2$-type MO to move to greater principal axes than would result with the Coulombic force alone. But, the factor of two increase of the central field and the resulting increased Coulombic as well as magnetic central forces on the remaining $N$ and $O$ electrons decrease the radii of the corresponding shells such that the energy minimum is achieved that is lower than that of the reactant atoms. The resulting electron configuration of $NO_2$ is $N1s^2O_11s^2O_21s^2N2s^2O_12s^2O_22s^2N2p^1O_12p^2O_22p^2\sigma^6_{O_2,N,O_1}$ where the subscripts designate the $O$ atom, 1 or 2, $\sigma$ designates the $H_2$-type MO, and the orbital arrangement is:

$$
\begin{array}{ccc}
 & \sigma \text{ state} & \\
 & \underline{\uparrow\downarrow}\ \ \underline{\uparrow\downarrow}\ \ \underline{\uparrow\downarrow} & \\
 & & \\
 & \text{2p state} & \\
\underline{\uparrow\downarrow} & \underline{\uparrow} & \underline{\uparrow\downarrow} \\
0 & 0 & 0 \\
 & \text{2s state} & \\
\underline{\uparrow\downarrow} & \underline{\uparrow\downarrow} & \underline{\uparrow\downarrow} \\
 & & \\
 & \text{1s state} & \\
\underline{\uparrow\downarrow} & \underline{\uparrow\downarrow} & \underline{\uparrow\downarrow} \\
O & N & O
\end{array}
\tag{14.68}
$$

Nitrogen dioxide is predicted to be weakly paramagnetic in agreement with observations [1].

## FORCE BALANCE OF THE $2p$ SHELL OF THE NITROGEN ATOM OF NITROGEN DIOXIDE

For the $N$ atom, force balance for the outermost $2p$ electron of $NO_2$ (electron 5) is achieved between the centrifugal force and the Coulombic and magnetic forces that arise due to interactions between electron 5 and the $2s$-shell electrons due to spin and orbital angular momentum. The forces used are derived in the Seven-Electron Atoms section. The central Coulomb force on the outer-most $2p$ shell electron of $NO$ (electron 5) due to the nucleus and the inner four electrons is given by Eq. (10.70) with the appropriate charge and radius:

$$\mathbf{F}_{ele} = \frac{(Z-4)e^2}{4\pi\varepsilon_0 r_5^2}\mathbf{i_r} \tag{14.69}$$

for $r > r_4$. The $2p$ shell possess a +2 external electric field given by Eq. (10.92) for $r > r_5$. The energy is minimized with conservation of angular momentum. This condition is met when the magnetic forces of $N$ in $NO_2$ are the same as those of $N$ in $NO$. They are also the same as those of $N$ in the nitrogen molecule with $r_5$ replacing $r_6$ and with an increase of the central field by an integer. The diamagnetic force, $\mathbf{F}_{diamagnetic}$, of Eq. (10.82) due to the $p$-orbital contribution is given by Eq. (13.918).

$$\mathbf{F}_{diamagnetic} = -\left(\frac{1}{3}\right)\frac{\hbar^2}{4m_e r_5^2 r_3}\sqrt{s(s+1)}\mathbf{i_r} = -\frac{\hbar^2}{12m_e r_5^2 r_3}\sqrt{\frac{3}{4}}\mathbf{i_r} \tag{14.70}$$

And, $\mathbf{F}_{mag\ 2}$ corresponding to the conserved orbital angular momentum of the three orbitals is also the same as that of $NO_2$ given by Eq. (13.919):

$$\mathbf{F}_{mag\ 2} = \frac{1}{Z}\frac{3\hbar^2}{m_e r_5^2 r_3}\sqrt{s(s+1)}\mathbf{i_r} \tag{14.71}$$

The electric field external to the $2p$ shell given by Eq. (10.92) for $r > r_5$ gives rise to a second diamagnetic force, $\mathbf{F}_{diamagnetic\ 2}$, given by Eq. (10.93). $\mathbf{F}_{diamagnetic\ 2}$ due to the binding of the p-orbital electron having an electric field of +2 outside of its radius is given by Eq. (13.920):

$$\mathbf{F}_{diamagnetic\ 2} = -\left[\frac{Z-5}{Z-4}\right]\left(1-\frac{\sqrt{2}}{2}\right)\frac{r_3\hbar^2}{m_e r_5^4}10\sqrt{s(s+1)}\mathbf{i_r} \tag{14.72}$$

The radius of the $2p$ shell is calculated by equating the outward centrifugal force to the sum of the electric (Eq. (14.69)) and diamagnetic (Eqs. (14.70) and (14.72)), and paramagnetic (Eq. (14.71)) forces as follows:

$$\frac{m_e v_5^2}{r_5} = \left(\begin{array}{l} \dfrac{(Z-4)e^2}{4\pi\varepsilon_0 r_5^2} - \dfrac{\hbar^2}{12m_e r_5^2 r_3}\sqrt{s(s+1)} + \dfrac{3\hbar^2}{Zm_e r_5^2 r_3}\sqrt{s(s+1)} \\ -\left[\dfrac{Z-5}{Z-4}\right]\left(1-\dfrac{\sqrt{2}}{2}\right)\dfrac{r_3\hbar^2}{r_5^4 m_e}10\sqrt{s(s+1)} \end{array}\right) \tag{14.73}$$

Substitution of $v_5 = \frac{\hbar}{m_e r_5}$ (Eq. (1.35)) and $s = \frac{1}{2}$ into Eq. (14.73) gives:

$$\frac{\hbar^2}{m_e r_5^3} = \frac{(Z-4)e^2}{4\pi\varepsilon_0 r_5^2} - \frac{\hbar^2}{12 m_e r_5^2 r_3}\sqrt{\frac{3}{4}} + \frac{3\hbar^2}{Z m_e r_5^2 r_3}\sqrt{\frac{3}{4}} - \left[\frac{Z-5}{Z-4}\right]\left(1-\frac{\sqrt{2}}{2}\right)\frac{r_3\hbar^2}{r_5^4 m_e}10\sqrt{\frac{3}{4}} \tag{14.74}$$

The quadratic equation corresponding to Eq. (14.74) is:

$$r_5^2 - \frac{\frac{\hbar^2}{m_e}}{\left(\frac{(Z-4)e^2}{4\pi\varepsilon_0} - \left(\frac{1}{12}-\frac{3}{Z}\right)\frac{\hbar^2}{m_e r_3}\sqrt{\frac{3}{4}}\right)} r_5 - \frac{\frac{\hbar^2}{m_e}\left[\frac{Z-5}{Z-4}\right]\left(1-\frac{\sqrt{2}}{2}\right) r_3 10\sqrt{\frac{3}{4}}}{\left(\frac{(Z-4)e^2}{4\pi\varepsilon_0} - \left(\frac{1}{12}-\frac{3}{Z}\right)\frac{\hbar^2}{m_e r_3}\sqrt{\frac{3}{4}}\right)} = 0 \tag{14.75}$$

The solution of Eq. (14.75) using the quadratic formula is:

$$r_5 = \frac{\frac{a_0}{\left((Z-4)-\left(\frac{1}{12}-\frac{3}{Z}\right)\frac{\sqrt{3}}{2r_3}\right)} \pm a_0\sqrt{\left(\frac{1}{\left((Z-4)-\left(\frac{1}{12}-\frac{3}{Z}\right)\frac{\sqrt{3}}{2r_3}\right)}\right)^2 + \frac{20\sqrt{3}\left(\left[\frac{Z-5}{Z-4}\right]\left(1-\frac{\sqrt{2}}{2}\right)r_3\right)}{\left((Z-4)-\left(\frac{1}{12}-\frac{3}{Z}\right)\frac{\sqrt{3}}{2r_3}\right)}}}{2}, \; r_3 \textit{ in units of } a_0 \tag{14.76}$$

The positive root of Eq. (14.76) must be taken in order that $r_5 > 0$. Substitution of $\frac{r_3}{a_0} = 0.69385$ (Eq. (10.62) with $Z = 7$) into Eq. (14.76) gives:

$$r_5 = 0.74841 a_0 \tag{14.77}$$

## FORCE BALANCE OF THE $2p$ SHELL OF EACH OXYGEN ATOM OF NITROGEN DIOXIDE

For each $O$ atom, force balance for the outermost $2p$ electron of $NO_2$ (electron 6) is achieved between the centrifugal force and the Coulombic and magnetic forces that arise due to interactions between electron 6 and the other $2p$ electron as well as the $2s$-shell electrons due to spin and orbital angular momentum. The forces used are derived in the Eight-Electron Atoms section. The central Coulomb force on the outer-most $2p$ shell electron of $NO_2$ (electron 6) due to the nucleus and the inner five electrons is given by Eq. (10.70) with the appropriate charge and radius:

$$\mathbf{F}_{ele} = \frac{(Z-5)e^2}{4\pi\varepsilon_0 r_6^2}\mathbf{i_r} \tag{14.78}$$

for $r > r_5$. The $2p$ shell possess an external electric field of +2 given by Eq. (10.92) for $r > r_6$. The energy is minimized with conservation of angular momentum. This condition is met when the magnetic forces of $O$ in $NO_2$ are the same as those of $O$ in $NO$. The diamagnetic force, $\mathbf{F}_{diamagnetic}$, of Eq. (10.82) due to the $p$-orbital contribution given by Eq. (13.927) is:

$$\mathbf{F}_{diamagnetic} = -\left(\frac{2}{3}\right)\frac{\hbar^2}{4 m_e r_6^2 r_3}\sqrt{s(s+1)}\mathbf{i_r} = -\frac{2\hbar^2}{12 m_e r_6^2 r_3}\sqrt{\frac{3}{4}}\mathbf{i_r} \tag{14.79}$$

And, $\mathbf{F}_{mag\ 2}$ corresponding to the conserved spin and orbital angular momentum given by Eq. (13.928) is:

$$\mathbf{F}_{mag\ 2} = \frac{1}{Z}\frac{2\hbar^2}{m_e r_6^2 r_3}\sqrt{s(s+1)}\mathbf{i_r} \tag{14.80}$$

The electric field external to the $2p$ shell given by Eq. (10.92) for $r > r_6$ gives rise to a second diamagnetic force, $\mathbf{F}_{diamagnetic\ 2}$, given by Eq. (10.93). $\mathbf{F}_{diamagnetic\ 2}$ due to the binding of the p-orbital electron having an electric field of +2 outside of its radius given by Eq. (13.929) is:

$$\mathbf{F}_{diamagnetic\ 2} = -\left[\frac{Z-6}{Z-5}\right]\left(1-\frac{\sqrt{2}}{2}\right)\frac{r_3\hbar^2}{m_e r_6^4}10\sqrt{s(s+1)}\mathbf{i_r} \tag{14.81}$$

In addition, the contribution of two $2p$ electrons in the formation of the $\sigma$ MO gives rise to a paramagnetic force on the remaining paired $2p$ electrons. The force $\mathbf{F}_{mag\ 3}$ is given by Eq. (13.930) is:

$$\mathbf{F}_{mag\ 3} = \frac{\hbar^2}{4m_e r_6^3}\sqrt{s(s+1)}\mathbf{i_r} \tag{14.82}$$

The radius of the $2p$ shell is calculated by equating the outward centrifugal force to the sum of the electric (Eq. (14.78)) and diamagnetic (Eqs. (14.79) and (14.81)), and paramagnetic (Eqs. (14.80) and (14.82)) forces as follows:

$$\frac{m_e v_6^2}{r_6} = \begin{pmatrix} \frac{(Z-5)e^2}{4\pi\varepsilon_0 r_6^2} - \frac{2\hbar^2}{12 m_e r_6^2 r_3}\sqrt{s(s+1)} + \frac{2\hbar^2}{Z m_e r_6^2 r_3}\sqrt{s(s+1)} \\ -\left[\frac{Z-6}{Z-5}\right]\left(1-\frac{\sqrt{2}}{2}\right)\frac{r_3\hbar^2}{r_6^4 m_e}10\sqrt{s(s+1)} + \frac{\hbar^2}{4m_e r_6^3}\sqrt{s(s+1)} \end{pmatrix} \tag{14.83}$$

Substitution of $v_6 = \frac{\hbar}{m_e r_6}$ (Eq. (1.35)) and $s = \frac{1}{2}$ into Eq. (14.83) gives:

$$\frac{\hbar^2}{m_e r_6^3} - \frac{\hbar^2}{4m_e r_6^3}\sqrt{\frac{3}{4}} = \frac{(Z-5)e^2}{4\pi\varepsilon_0 r_6^2} - \frac{2\hbar^2}{12 m_e r_6^2 r_3}\sqrt{\frac{3}{4}} + \frac{2\hbar^2}{Z m_e r_6^2 r_3}\sqrt{\frac{3}{4}} - \left[\frac{Z-6}{Z-5}\right]\left(1-\frac{\sqrt{2}}{2}\right)\frac{r_3\hbar^2}{r_6^4 m_e}10\sqrt{\frac{3}{4}} \tag{14.84}$$

The quadratic equation corresponding to Eq. (14.84) is:

$$r_6^2 - \frac{\frac{\hbar^2}{m_e}\left(1-\frac{\sqrt{3}}{8}\right)}{\left(\frac{(Z-5)e^2}{4\pi\varepsilon_0} - \left(\frac{2}{12}-\frac{2}{Z}\right)\frac{\hbar^2}{m_e r_3}\sqrt{\frac{3}{4}}\right)} r_6 - \frac{\frac{\hbar^2}{m_e}\left[\frac{Z-6}{Z-5}\right]\left(1-\frac{\sqrt{2}}{2}\right)r_3 10\sqrt{\frac{3}{4}}}{\left(\frac{(Z-5)e^2}{4\pi\varepsilon_0} - \left(\frac{2}{12}-\frac{2}{Z}\right)\frac{\hbar^2}{m_e r_3}\sqrt{\frac{3}{4}}\right)} = 0 \tag{14.85}$$

The solution of Eq. (14.85) using the quadratic formula is:

$$r_6 = \frac{\frac{a_0\left(1-\frac{\sqrt{3}}{8}\right)}{\left((Z-5)-\left(\frac{2}{12}-\frac{2}{Z}\right)\frac{\sqrt{3}}{2r_3}\right)} \pm a_0\sqrt{\left(\frac{1-\frac{\sqrt{3}}{8}}{\left((Z-5)-\left(\frac{2}{12}-\frac{2}{Z}\right)\frac{\sqrt{3}}{2r_3}\right)}\right)^2 + \frac{20\sqrt{3}\left(\left[\frac{Z-6}{Z-5}\right]\left(1-\frac{\sqrt{2}}{2}\right)r_3\right)}{\left((Z-5)-\left(\frac{2}{12}-\frac{2}{Z}\right)\frac{\sqrt{3}}{2r_3}\right)}}}{2}, \ r_3 \textit{ in units of } a_0 \tag{14.86}$$

The positive root of Eq. (14.86) must be taken in order that $r_6 > 0$. Substitution of $\frac{r_3}{a_0} = 0.59020$ (Eq. (10.62) with $Z = 8$) into Eq. (14.86) gives:

$$r_6 = 0.70460a_0 \tag{14.87}$$

## ENERGIES OF THE $2p$ SHELLS OF THE NITROGEN ATOM AND OXYGEN ATOMS OF NITROGEN DIOXIDE

Consider the determination of the total energy of $NO_2$ from the reaction of a nitrogen atom with two oxygen atoms. With the formation of each $H_2$-type MO by the contribution of two $2p$ electrons from each of the $N$ and the two $O$ atoms, the total energy of the $NO_2$ molecule, which is subtracted from the sum of the energies of the nitrogen and oxygen atoms to determine the bond energy, is increased by the ionization energies of $N$, $N^+$, $O$, and $2O^+$ given by Eqs. (14.88-14.91), respectively. Experimentally, the energies are [2]:

$$E(ionization;\ N) = 14.53414\ eV \tag{14.88}$$

$$E(ionization;\ N^+) = 29.6013\ eV \tag{14.89}$$

$$E(ionization;\ O) = 13.61806\ eV \tag{14.90}$$

$$E(ionization;\ O^+) = 35.11730\ eV \tag{14.91}$$

In addition, the central forces on the $2p$ shells of the $N$ and $O$ atoms are increased with the formation of the $\sigma$ MOs which reduces each shell's radius and increases its total energy. The change per bond is the same as that of $NO$ since the final radii given by Eq. (14.77) and (14.87) are the same for $NO$ and $NO_2$. The Coulombic energy terms of the total energy of the $N$ and $O$ atoms at the new radii are calculated and added to the ionization energies of $N$, $N^+$, $O$, and $2O^+$, and the energy of the

$\sigma$ MOs to give the total energy of $NO_2$. Then, the bond energy is determined from the total $NO_2$ energy.

The radius $r_7$ of the nitrogen atom before bonding is given by Eq. (10.142).

$$r_7 = 0.93084a_0 \tag{14.92}$$

Using the initial radius $r_7$ of the $N$ atom and the final radius $r_5$ of the $N2p$ shell (Eq. (14.77)) and by considering that the central Coulombic field decreases by an integer for each successive electron of the shell, the sum $E_T\left(N,2p\right)$ of the Coulombic energy change of the $N2p$ electrons of the $N$ atom is determined using Eq. (10.102):

$$E_T\left(N,2p\right) = -\sum_{n=4}^{4} \frac{(Z-n)e^2}{8\pi\varepsilon_0}\left(\frac{1}{r_5}-\frac{1}{r_7}\right) = -\left(13.60580\ eV\right)\left(0.26186\right)\left(3\right) = -10.68853\ eV \tag{14.93}$$

The radius $r_8$ of the oxygen atom before bonding is given by Eq. (10.162).

$$r_8 = a_0 \tag{14.94}$$

Using the initial radius $r_8$ of the $O$ atom and the final radius $r_6$ of the $O2p$ shell (Eq. (14.87)) and by considering that the central Coulombic field decreases by an integer for each successive electron of the shell, the sum $E_T\left(O,2p\right)$ of the Coulombic energy change of the $O2p$ electrons of the $O$ atom is determined using Eq. (10.102).

$$E_T\left(O,2p\right) = \sum_{n=4}^{5} \frac{(Z-n)e^2}{8\pi\varepsilon_0}\left(\frac{1}{r_6}-\frac{1}{r_8}\right) = \left(13.60580\ eV\right)\left(0.41925a_0^{-1}\right)\left(3+4\right) = -39.92918\ eV \tag{14.95}$$

## FORCE BALANCE OF THE $\sigma$ MO OF NITROGEN DIOXIDE

The force balance can be considered due to a second pair of two electrons binding to a molecular ion having $+2e$ at each focus and a first bound pair. Then, the forces are the same as those of a molecule ion having $+e$ at each focus. The diamagnetic force $\mathbf{F}_{diamagneticMO1}$ for each $\sigma$-MO of the $NO_2$ molecule due to the two, paired electrons in the $O2p$ shell is given by Eq. (13.633) with $n_e = 2$:

$$\mathbf{F}_{diamagneticMO1} = \frac{\hbar^2}{2m_e a^2 b^2} D\mathbf{i}_\xi \tag{14.96}$$

This is also the corresponding force of $NO$ given by Eq. (13.942). $\mathbf{F}_{diamagneticMO2}$ of the nitrogen dioxide molecule comprising nitrogen with charge $Z_1 = 7$ and $\left|L_1\right| = \hbar$ and $\left|L_2\right| = \sqrt{\frac{3}{4}}\hbar$ and the two oxygen atoms, each with $Z_2 = 8$ and $\left|L_3\right| = \hbar$ is given by the corresponding sum of the contributions. Using Eq. (13.835), $\mathbf{F}_{diamagneticMO2}$ for $NO_2$ is:

$$\mathbf{F}_{diamagneticMO2} = \left(\frac{1}{Z_1} + \frac{\sqrt{\frac{3}{4}}}{Z_1} + \frac{2}{Z_2}\right)\frac{\hbar^2}{2m_e a^2 b^2} D\mathbf{i}_\xi \tag{14.97}$$

This is also the corresponding force of $NO$ given by Eq. (13.943) except the term due to oxygen is twice that of $NO$ due to the two oxygen atoms of $NO_2$. The general force balance equation for the $\sigma$-MO of the nitrogen dioxide molecule given by Eqs. (11.200), and (14.97-14.98) is also the same as that of $CN$ (Eq. (14.836)) except for the doubling of the $\frac{2}{Z_2}$ term due to the two oxygen atoms:

$$\frac{\hbar^2}{m_e a^2 b^2} D = \frac{e^2}{8\pi\varepsilon_0 ab^2} D + \frac{\hbar^2}{2m_e a^2 b^2} D - \left(1 + \frac{1}{Z_1} + \frac{\sqrt{\frac{3}{4}}}{Z_1} + \frac{2}{Z_2}\right)\frac{\hbar^2}{2m_e a^2 b^2} D \tag{14.98}$$

$$\frac{\hbar^2}{m_e a^2 b^2} D = \frac{e^2}{8\pi\varepsilon_0 ab^2} D - \left(\frac{1}{Z_1} + \frac{\sqrt{\frac{3}{4}}}{Z_1} + \frac{2}{Z_2}\right)\frac{\hbar^2}{2m_e a^2 b^2} D \tag{14.99}$$

$$\left(2 + \frac{1}{Z_1} + \frac{\sqrt{\frac{3}{4}}}{Z_1} + \frac{2}{Z_2}\right)\frac{\hbar^2}{2m_e a^2 b^2} D = \frac{e^2}{8\pi\varepsilon_0 ab^2} D \tag{14.100}$$

$$a = \left( 2 + \frac{1}{Z_1} + \frac{\sqrt{\frac{3}{4}}}{Z_1} + \frac{2}{Z_2} \right) a_0 \tag{14.101}$$

Substitution of $Z_1 = 7$ and $Z_2 = 8$ into Eq. (14.101) gives:

$$a = 2.51658 a_0 = 1.33171\ X\ 10^{-10}\ m \tag{14.102}$$

Substitution of Eq. (14.102) into Eq. (11.79) is:

$$c' = 1.12173 a_0 = 5.93596\ X\ 10^{-11}\ m \tag{14.103}$$

The internuclear distance given by multiplying Eq. (14.103) by two is:

$$2c' = 2.24347 a_0 = 1.18719\ X\ 10^{-10}\ m \tag{14.104}$$

The experimental bond distance is [3]:

$$2c' = 1.193\ X\ 10^{-10}\ m \tag{14.105}$$

Substitution of Eqs. (14.102-14.103) into Eq. (11.80) is:

$$b = c = 2.25275 a_0 = 1.19210\ X\ 10^{-10}\ m \tag{14.106}$$

Substitution of Eqs. (14.102-14.103) into Eq. (11.67) is:

$$e = 0.44574 \tag{14.107}$$

The bonding in the nitrogen dioxide molecule comprises two double bonds, each a $H_2$-type MO with four paired electrons wherein the central $N$ atom is shared by both bonds such that six electrons can be assigned to the two $N = O$ bonds. Thus, two $N2p$ electrons combine with the four $O2p$ electrons, two from each $O$, as a linear combination to form the two overlapping $N = O$ bonds of $NO_2$. Using the electron configuration of $NO_2$ (Eq. (14.68)), the radii of the $N1s = 0.14605 a_0$ (Eq. (10.51)), $N2s = 0.69385 a_0$ (Eq. (10.62)), $N2p = 0.74841 a_0$ (Eq. (14.77)), $O1s = 0.12739 a_0$ (Eq. (10.51)), $O2s = 0.59020 a_0$ (Eq. (10.62)), and $O2p = 0.70460 a_0$ (Eq. (14.87)) shells and the parameters of the $\sigma$ MOs of $NO_2$ given by Eqs. (13.3-13.4), (14.102-14.104), and (14.106-14.107), the dimensional diagram and charge-density of the $NO_2$ MO are shown in Figures 14.3 and 14.4, respectively.

Figure 14.3. The cross section of the $NO_2$ MO showing the axes, $\sigma$ MOs (two $H_2$-type ellipsoidal MOs) with six paired electrons, with the $N$ $1s$, $2s$, and $2p$ AOs and the $O$ $1s$, $2s$, and $2p$ AOs. Legend: $a$: semimajor axis, $b$: semiminor axis, $c'$: internuclear distance, $r_5$: radius of the $N2p$ shell having one unpaired electron, $r_6$: radius of each $O2p$ shell having two paired electrons.

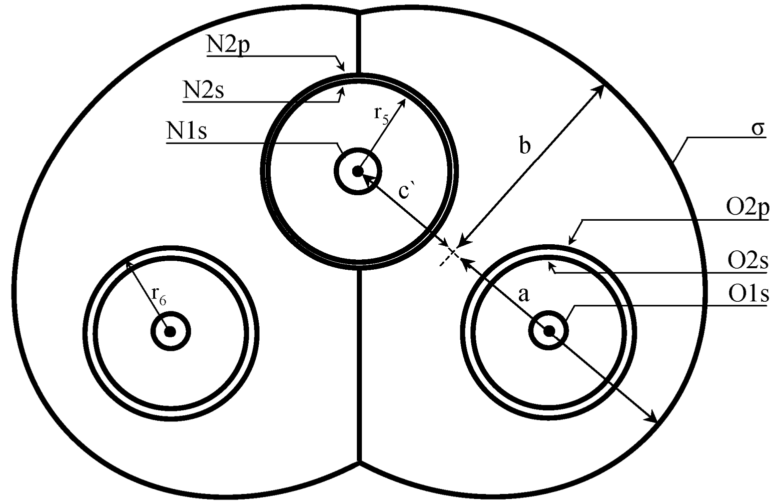
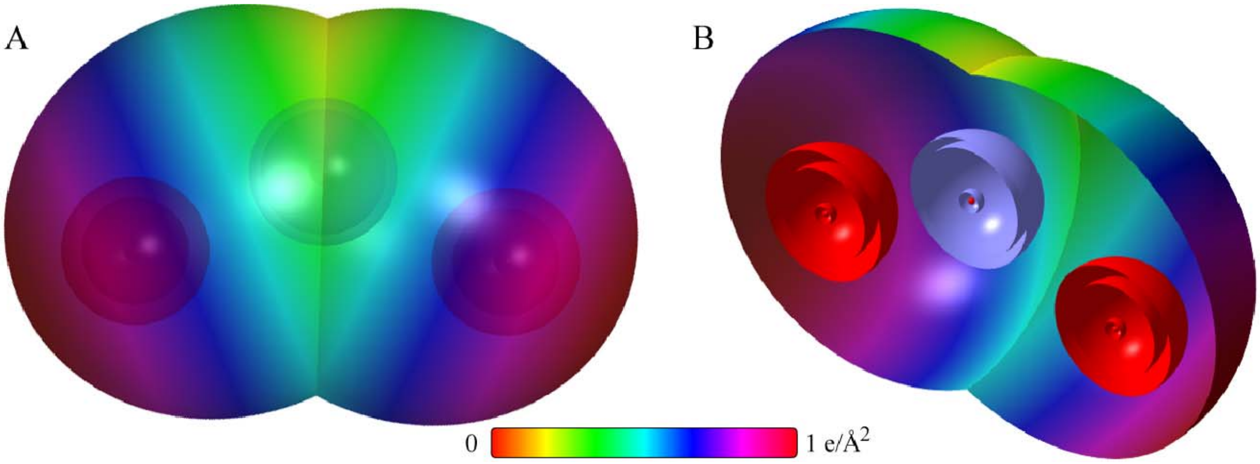


Figure 14.4. $NO_2$ MO comprising two $\sigma$ MOs ($H_2$-type MOs) with $N$ and $O$ atoms at the foci that have each donated two electrons to the $\sigma$ MOs and have smaller radii and higher binding energies as a consequence. (A)-(B) Top and side color scale, translucent views of the charge-density of the $NO_2$ MO. (C) Off-center cut-away view showing the complete inner most $N1s$ shell, and moving radially, the $N2s$ shell, the $N2p$ shell, and the $\sigma$ prolate spheroidal MOs that each have the $N$ atom as a focus. Moving radially from each oxygen-atom focus, the complete innermost $O1s$ shell, the $O2s$ shell, the $O2p$ shell, and the $\sigma$ prolate spheroidal MOs are shown.



## SUM OF THE ENERGIES OF THE $\sigma$ MOS AND THE AOS OF NITROGEN DIOXIDE

The energies of each $NO_2$ $\sigma$ MO are the same as those of $NO$ (Eqs. (13.954-13.958)). They are given by the substitution of the semiprincipal axes (Eqs. (14.102-14.103) and (14.106)) into the energy equations (Eqs. (11.207-11.212)) of $H_2$ except that the terms based on charge are multiplied by four and the kinetic energy term is multiplied by two due to the $\sigma$-MO double bond with two pairs of paired electrons:

$$V_e = 2^2 \frac{-2e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -93.03032\ eV \tag{14.108}$$

$$V_p = 2^2 \frac{e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}} = 48.51704\ eV \tag{14.109}$$

$$T = 2\frac{\hbar^2}{2m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = 9.24176\ eV \tag{14.110}$$

$$V_m = 2^2 \frac{-\hbar^2}{4m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -9.24176\ eV \tag{14.111}$$

$$E_T = V_e + T + V_m + V_p \tag{14.112}$$

Substitution of Eqs. (11.79) and (14.108-14.111) into Eq. (14.112) gives:

$$E_T\left(N=O,\sigma\right) = \frac{-e^2}{8\pi\varepsilon_0\sqrt{\frac{aa_0}{2}}}\left(8\ln\frac{a+\sqrt{\frac{aa_0}{2}}}{a-\sqrt{\frac{aa_0}{2}}}-4\right) = -44.51329\ eV \tag{14.113}$$

where $E_T\left(N=O,\sigma\right)$ is the total energy of each $\sigma$ MO of $NO_2$. The total energy of $NO_2$, $E_T\left(NO_2\right)$, is given by the sum of $E(ionization;\ N)$ and $E(ionization;\ N^+)$, the sum of the energies of the first and second electrons of nitrogen (Eqs. (14.88-14.89)) donated to each double bond, the sum of $E(ionization;\ O)$ and two times $E(ionization;\ O^+)$, the energies of the first and second electrons of oxygen (Eqs. (14.90-14.91)) donated to the double bonds, $E_T\left(N,2p\right)$, the $N2p$ AO contribution due to the decrease in radius with the formation of each bond (Eq. (14.93)), two times $E_T\left(O,2p\right)$, the $O2p$ AO contribution due to the decrease in radius with the formation of each bond (Eq. (14.95)), and two times $E_T\left(N=O,\sigma\right)$, the $\sigma$ MO contribution given by Eq. (14.113):

$$E_T\left(NO_2\right)=\begin{pmatrix}E(ionization;\ N)+E(ionization;\ N^+)\\+E(ionization;\ O)+2E(ionization;\ O^+)+E_T\left(N,2p\right)\\+2E_T\left(O,2p\right)+2E_T\left(N=O,\sigma\right)\end{pmatrix}$$
$$=\begin{pmatrix}14.53414\ eV+29.6013\ eV+13.61806\ eV\\+2\left(35.11730\ eV\right)+\left(-10.68853\ eV\right)+2\left(-39.92918\ eV\right)\\+2\left(\frac{-e^2}{8\pi\varepsilon_0\sqrt{\frac{aa_0}{2}}}\left(8\ln\frac{a+\sqrt{\frac{aa_0}{2}}}{a-\sqrt{\frac{aa_0}{2}}}-4\right)\right)\end{pmatrix}$$
$$=\begin{pmatrix}14.53414\ eV+29.6013\ eV+13.61806\ eV\\+2\left(35.11730\ eV\right)+\left(-10.68853\ eV\right)\\+2\left(-39.92918\ eV\right)+2\left(-44.51329\ eV\right)\end{pmatrix}=-51.58536\ eV \tag{14.114}$$

## VIBRATION OF $NO_2$

The vibrational energy levels of $NO_2$ may be solved by determining the Morse potential curve from the energy relationships for the transition from a $N$ atom and two $O$ atoms whose parameters are given by Eqs. (10.134-10.143) and (10.154-10.163), respectively, to a $N$ atom whose parameter $r_5$ is given by Eq. (14.77), two $O$ atoms whose parameter $r_6$ is given by Eq. (14.87), and the $\sigma$ MOs whose parameters are given by Eqs. (14.102-14.104) and (14.106-14.107). As shown in the Vibration of Hydrogen-type Molecular Ions section, the harmonic oscillator potential energy function can be expanded about the internuclear distance and expressed as a Maclaurin series corresponding to a Morse potential after Karplus and Porter (K&P) [4] and after Eq. (11.134). Treating the Maclaurin series terms as anharmonic perturbation terms of the harmonic states, the energy corrections can be found by perturbation methods.

## THE DOPPLER ENERGY TERMS OF NITROGEN DIOXIDE

The equations of the radiation reaction force of nitrogen dioxide are the same as those of $NO$ with the substitution of the $NO_2$ parameters. Using Eq. (13.961), the angular frequency of the reentrant oscillation in the transition state is:

$$\omega=\sqrt{\frac{\frac{4e^2}{4\pi\varepsilon_0 a^3}}{m_e}}=2.07110\ X\ 10^{16}\ rad/s \tag{14.115}$$

where $a$ is given by Eq. (14.102). The kinetic energy, $E_K$, is given by Planck's equation (Eq. (11.127)).

$$\overline{E}_K=\hbar\omega=\hbar 2.07110\ X\ 10^{16}\ rad/s=13.63231\ eV \tag{14.116}$$

In Eq. (11.181), substitution of $E_T\left(NO_2\right)/2$ for $E_{h\nu}$, the mass of the electron, $m_e$, for $M$, and the kinetic energy given by Eq. (14.116) for $\overline{E}_K$ gives the Doppler energy of the electrons of the reentrant orbit:

$$\overline{E}_D\cong E_{h\nu}\sqrt{\frac{2\overline{E}_K}{Mc^2}}=-25.79268\ eV\sqrt{\frac{2e\left(13.63231\ eV\right)}{m_ec^2}}=-0.18840\ eV \tag{14.117}$$

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency. The transition state comprises $O--NO$, oxygen binding to $NO$. As in the case of $CO_2$ bond formation, vibration in the transition state corresponds to $\upsilon_3$ [5] with the maximum kinetic energy localized to the nascent $N-O$ bond. In this case, the kinetic energy of the nuclei is the maximum for this bond. Thus, $\overline{E}_{Kvib}$ is the vibrational energy. The decrease in the energy of the $NO_2$ MO due to the reentrant orbit in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei, $\overline{E}_{osc}$, is given by the sum of the corresponding energies, $\overline{E}_D$ given by Eq. (14.117) and $\overline{E}_{Kvib}$, the vibrational energy. Using the experimental $NO_2$ $E_{vib}\left(\upsilon_3\right)$ of $1618\ cm^{-1}$ $\left(0.20061\ eV\right)$ [6] for $\overline{E}_{Kvib}$ of the transition state, $\overline{E}_{osc}\left(NO_2\right)$ is:

$$\overline{E}_{osc}\left(NO_2\right)=\overline{E}_D+\overline{E}_{Kvib}=\overline{E}_D+E_{vib} \tag{14.118}$$

$$\overline{E}_{osc}\left(NO_2\right)=-0.18840\ eV+0.20061\ eV=0.01221\ eV \tag{14.119}$$

## TOTAL AND BOND ENERGIES OF NITROGEN DIOXIDE

$E_{T+osc}(NO_2)$, the total energy of $NO_2$ including the Doppler term, is given by the sum of $E_T(NO_2)$ (Eq. (14.114)) and $\bar{E}_{osc}(NO_2)$ given by Eq. (14.119).

$$\begin{aligned} E_{T+osc}(NO_2) &= \begin{pmatrix} 2\left(V_e+T+V_m+V_p\right)+E(ionization;\ N)+E(ionization;\ N^+) \\ +E(ionization;\ O)+2E(ionization;\ O^+) \\ +E_T(N,2p)+2E_T(O,2p)+\bar{E}_{osc}(NO_2) \end{pmatrix} \\ &= \begin{pmatrix} 2E_T(N=O,\sigma)+E(ionization;\ N)+E(ionization;\ N^+) \\ +E(ionization;\ O)+2E(ionization;\ O^+) \\ +E_T(N,2p)+2E_T(O,2p)+\bar{E}_{osc}(NO_2) \end{pmatrix} \\ &= E_T(NO_2)+\bar{E}_{osc}(NO_2) \end{aligned} \tag{14.120}$$

$$\begin{aligned} E_{T+osc}(NO_2) &= \left\{ \begin{matrix} \begin{pmatrix} 2\left(\dfrac{-e^2}{8\pi\varepsilon_0\sqrt{\dfrac{aa_0}{2}}}\left(8\ln\dfrac{a+\sqrt{\dfrac{aa_0}{2}}}{a-\sqrt{\dfrac{aa_0}{2}}}-4\right)\right) \\ E(ionization;\ N)+E(ionization;\ N^+) \\ +E(ionization;\ O)+2E(ionization;\ O^+) \\ -\displaystyle\sum_{N,n=4}^{4}\frac{(Z-n)e^2}{8\pi\varepsilon_0}\left(\frac{1}{r_5}-\frac{1}{r_7}\right)-2\sum_{O,n=4}^{5}\frac{(Z-n)e^2}{8\pi\varepsilon_0}\left(\frac{1}{r_6}-\frac{1}{r_8}\right) \end{pmatrix} \\ \left(1+\dfrac{1}{2}\sqrt{\dfrac{2\hbar\sqrt{\dfrac{\dfrac{4e^2}{4\pi\varepsilon_0 a^3}}{m_e}}}{m_ec^2}}\right)+E_{vib} \end{matrix} \right\} \\ &= -51.58536\ eV - 0.18840\ eV + E_{vib} \end{aligned} \tag{14.121}$$

From Eqs. (14.119-14.121), the total energy of the $NO_2$ MO is:

$$\begin{aligned} E_{T+osc}(NO_2) &= -51.58536\ eV + \bar{E}_{osc}(NO_2) \\ &= -51.58536\ eV + 0.01221\ eV \\ &= -51.57315\ eV \end{aligned} \tag{14.122}$$

where the experimental $E_{vib}$ was used.

As in the case of the dissociation of the bond of the hydroxyl radical, an oxygen atom is formed with dissociation of $NO_2$. $O$ has two unpaired electrons as shown in Eq. (13.55) which interact to stabilize the atom as shown by Eq. (10.161-10.162). The lowering of the energy of the reactants decreases the bond energy. Thus, the total energy of oxygen is reduced by the energy in the field of the two magnetic dipoles given by Eq. (7.46) and Eq. (13.101).

$$E(magnetic) = \frac{2\pi\mu_0 e^2\hbar^2}{m_e^2 a_0^3} = \frac{8\pi\mu_0\mu_B^2}{a_0^3} = 0.11441\ eV \tag{14.123}$$

The $NO_2$ bond dissociation energy, $E_D(NO_2)$, is given by the sum of the energies of the $NO$ and the $O$ atom minus the sum of $E_{T+osc}(NO_2)$ and $E(magnetic)$:

$$E_D(NO_2) = E(NO) + E(O) - \left(E(magnetic) + E_{T+osc}(NO_2)\right) \tag{14.124}$$

The energy of an oxygen atom is given by the negative of Eq. (14.90), and $E_T(NO)$ is given by the sum of the experimental energies of $N$ (negative of Eq. (14.88)), $O$, and the negative of the bond energy of $NO$ (Eq. (13.974)).

$$E(NO) = -14.53414\ eV - 13.618060\ eV - 6.53529\ eV = -34.68749\ eV \tag{14.125}$$

Thus, the $NO_2$ bond dissociation energy, $E_D\left(NO_2\right)$, given by Eqs. (4.90) and (14.112-14.125) is:

$$\begin{aligned} E_D\left(NO_2\right) &= -\left(34.68749\ eV + 13.618060\ eV\right) - \left(E(magnetic) + E_{T+osc}\left(NO_2\right)\right) \\ &= -48.30555\ eV - \left(0.11441\ eV - 51.57315\ eV\right) = 3.15319\ eV \end{aligned} \tag{14.126}$$

The experimental $NO_2$ bond dissociation energy is [7]:

$$E_{D298}\left(NO_2\right) = 3.161\ eV \tag{14.127}$$

## BOND ANGLE OF $NO_2$

The $NO_2$ MO comprises a linear combination of two $N=O$-bond MOs. A bond is also possible between the two $O$ atoms of the $N=O$ bonds. Such $O=O$ bonding would decrease the $N=O$ bond strength since electron density would be shifted from the $N=O$ bonds to the $O=O$ bond. Thus, the bond angle between the two $N=O$ bonds is determined by the condition that the total energy of the $H_2$-type ellipsoidal MO between the terminal $O$ atoms of the $N=O$ bonds is zero. From Eqs. (11.79) and (13.228), the distance from the origin to each focus of the $O=O$ ellipsoidal MO is:

$$c' = a\sqrt{\frac{\hbar^2 4\pi\varepsilon_0}{m_e e^2 2a}} = \sqrt{\frac{aa_0}{2}} \tag{14.128}$$

The internuclear distance from Eq. (13.229) is:

$$2c' = 2\sqrt{\frac{aa_0}{2}} \tag{14.129}$$

The length of the semiminor axis of the prolate spheroidal $O=O$ MO $b=c$ is given by Eq. (13.167).

The component energies and the total energy $E_T$ of the $O=O$ bond are given by the energy equations (Eqs. (11.207-11.212), (11.213-11.217), and (11.239)) of $H_2$ except that the terms based on charge are multiplied by four and the kinetic energy term is multiplied by two due to the $O=O$ double bond with two pairs of paired electrons. Substitution of Eq. (14.128) into Eqs. (11.207-11.212) gives:

$$0 = \left[\begin{array}{l} \dfrac{-e^2}{8\pi\varepsilon_0\sqrt{\dfrac{aa_0}{2}}}\left(8\ln\dfrac{a+\sqrt{\dfrac{aa_0}{2}}}{a-\sqrt{\dfrac{aa_0}{2}}}-4\right)\left[1+\sqrt{\dfrac{2\hbar\sqrt{\dfrac{\dfrac{4e^2}{4\pi\varepsilon_0 a^3}}{m_e}}}{m_e c^2}}\right] \\ +\dfrac{1}{2}\hbar\sqrt{\dfrac{\dfrac{4e^2}{8\pi\varepsilon_0 a^3}-\dfrac{4e^2}{8\pi\varepsilon_0\left(a+c'\right)^3}}{8m_p}} \end{array}\right] \tag{14.130}$$

From the energy relationship given by Eq. (14.130) and the relationship between the axes given by Eqs. (14.128-14.129) and (13.167-14.168), the dimensions of the $O=O$ MO can be solved.

The most convenient way to solve Eq. (14.130) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is:

$$a = 8.3360a_0 = 4.4112\ X\ 10^{-10}\ m \tag{14.131}$$

Substitution of Eq. (14.131) into Eq. (14.128) gives:

$$c' = 2.0416a_0 = 1.0804\ X\ 10^{-10}\ m \tag{14.132}$$

The internuclear distance given by multiplying Eq. (14.132) by two is:

$$2c' = 4.0831a_0 = 2.1607\ X\ 10^{-10}\ m \tag{14.133}$$

Substitution of Eqs. (14.131-14.132) into Eq. (14.167) gives:

$$b = c = 8.0821a_0 = 4.2769\ X\ 10^{-10}\ m \tag{14.134}$$

Substitution of Eqs. (14.131-14.132) into Eq. (14.168) gives:

$$e = 0.2449 \tag{14.135}$$

From, $2c'_{C=C}$ (Eq. (14.133)), the distance between the two $O$ atoms when the total energy of the corresponding MO is zero (Eq. (14.130)), and $2c'_{N=O}$ (Eq. (14.104)), the internuclear distance of each $N=O$ bond, the corresponding bond angle can be determined from the law of cosines. Using, Eqs. (13.240-13.242), the bond angle $\theta$ between the $N=O$ bonds is:

$$\theta = \cos^{-1}\left(\frac{2(2.24347)^2-(4.0831)^2}{2(2.24347)^2}\right) = \cos^{-1}(-0.6562) = 131.012° \tag{14.136}$$

The experimental angle between the $N=O$ bonds is [3]:

$$\theta = 134.1° \tag{14.137}$$

The results of the determination of bond parameters of $NO_2$ are given in Table 14.1. The calculated results are based on first principles and given in closed-form, exact equations containing fundamental constants only. The agreement between the experimental and calculated results is excellent.

## ETHANE MOLECULE ($CH_3CH_3$)

The ethane molecule $CH_3CH_3$ is formed by the reaction of two methyl radicals:

$$CH_3 + CH_3 \rightarrow CH_3CH_3 \tag{14.138}$$

$CH_3CH_3$ can be solved using the same principles as those used to solve $CH_3$, wherein the $2s$ and $2p$ shells of each $C$ hybridize to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between two $C2sp^3$ hybridized orbitals (HOs) to form a molecular orbital (MO) permits each participating hybridized orbital to decrease in radius and energy. First, two sets of three $H$ atomic orbitals (AOs) combine with two sets of three carbon $2sp^3$ HOs to form two methyl groups comprising a linear combination of six diatomic $H_2$-type MOs developed in the Nature of the Chemical Bond of Hydrogen-Type Molecules and Molecular Ions section. Then, the two $CH_3$ groups bond by forming a $H_2$-type MO between the remaining $C2sp^3$ HO on each carbon.

## FORCE BALANCE OF THE $C-C$-BOND MO OF ETHANE

$CH_3CH_3$ comprises a chemical bond between two $CH_3$ radicals wherein each methyl radical comprises three chemical bonds between carbon and hydrogen atoms. The solution of the parameters of $CH_3$ is given in the Methyl Radical ($CH_3$) section. Each $C-H$ bond of $CH_3$ having two spin-paired electrons, one from an initially unpaired electron of the carbon atom and the other from the hydrogen atom, comprises the linear combination of 75% $H_2$-type ellipsoidal MO and 25% $C2sp^3$ HO. The proton of the $H$ atom and the nucleus of the $C$ atom are along each internuclear axis and serve as the foci. As in the case of $H_2$, each of the three $C-H$-bond MOs is a prolate spheroid with the exception that the ellipsoidal MO surface cannot extend into $C2sp^3$ HO for distances shorter than the radius of the $C2sp^3$ shell since it is energetically unfavorable. Thus, each MO surface comprises a prolate spheroid at the $H$ proton that is continuous with the $C2sp^3$ shell at the $C$ atom whose nucleus serves as the other focus. The electron configuration and the energy, $E(C,2sp^3)$, of the $C2sp^3$ shell is given by Eqs. (13.422) and (13.428), respectively. The central paramagnetic force due to spin of each $C-H$ bond is provided by the spin-pairing force of the $CH_3$ MO that has the symmetry of an $s$ orbital that superimposes with the $C2sp^3$ orbitals such that the corresponding angular momenta are unchanged.

Two $CH_3$ radicals bond to form $CH_3CH_3$ by forming a MO between the two remaining $C2sp^3$-HO electrons of the two carbon atoms. However, in this case, the sharing of electrons between two $C2sp^3$ HOs to form a molecular orbital (MO) comprising two spin-paired electrons permits each $C2sp^3$ HO to decrease in radius and energy.

As in the case of the $C-H$ bonds, the $C-C$-bond MO is a prolate-spheroidal-MO surface that cannot extend into $C2sp^3$ HO for distances shorter than the radius of the $C2sp^3$ shell of each atom. Thus, the MO surface comprises a partial prolate spheroid in between the carbon nuclei and is continuous with the $C2sp^3$ shell at each $C$ atom. The energy of the $H_2$-type ellipsoidal MO is matched to that of the $C2sp^3$ shell. As in the case of previous examples of energy-matched MOs such as those of $OH$, $NH$, $CH$, and the $C=O$-bond MO of $CO_2$, the $C-C$-bond MO of ethane must comprise 75% of a $H_2$-type ellipsoidal MO in order to match potential, kinetic, and orbital energy relationships. Thus, the $C-C$-bond MO must comprise two $C2sp^3$ HOs and 75% of a $H_2$-type ellipsoidal MO divided between the two $C2sp^3$ HOs:

$$2\ C2sp^3 + 0.75\ H_2\ MO \rightarrow C-C-bond\ MO \tag{14.139}$$

The linear combination of the $H_2$-type ellipsoidal MO with each $C2sp^3$ HO further comprises an excess 25% charge-density contribution from each $C2sp^3$ HO to the $C-C$-bond MO to achieve an energy minimum. The force balance of the $C-C$-bond

MO is determined by the boundary conditions that arise from the linear combination of orbitals according to Eq. (14.139) and the energy matching condition between the $C2sp^3$-HO components of the MO.

Similarly, the energies of each $CH_3$ MO involve each $C2sp^3$ and each $H1s$ electron with the formation of each $C-H$ bond. The sum of the energies of the $H_2$-type ellipsoidal MOs is matched to that of the $C2sp^3$ shell. This energy is determined by the considering the effect of the donation of 25% electron density from the two $C2sp^3$ HOs to the $C-C$-bond MO. The $2sp^3$ hybridized orbital arrangement given by Eq. (13.422) is:

$$\begin{array}{cccc} \multicolumn{4}{c}{2\text{sp}^3 \text{ state}} \\ \underline{\uparrow} & \underline{\uparrow} & \underline{\uparrow} & \underline{\uparrow} \\ 0,0 & 1,-1 & 1,0 & 1,1 \end{array} \tag{14.140}$$

where the quantum numbers ($\ell, m_\ell$) are below each electron. The total energy of the state is given by the sum over the four electrons. The sum $E_T\left(C,2sp^3\right)$ of calculated energies of $C$, $C^+$, $C^{2+}$, and $C^{3+}$ from Eqs. (10.123), (10.113-10.114), (10.68), and (10.48), respectively, is:

$$E_T\left(C,2sp^3\right) = 64.3921\ eV + 48.3125\ eV + 24.2762\ eV + 11.27671\ eV = 148.25751\ eV \tag{14.141}$$

which agrees well with the sum of 148.02532 $eV$ from the experimental [2] values. Consider the case of the $C2sp^3$ HO of each methyl radical. The orbital-angular-momentum interactions cancel such that the energy of the $E_T\left(C,2sp^3\right)$ is purely Coulombic. By considering that the central field decreases by an integer for each successive electron of the shell, the radius $r_{2sp^3}$ of the $C2sp^3$ shell may be calculated from the Coulombic energy using Eq. (10.102):

$$r_{2sp^3} = \sum_{n=2}^{5} \frac{(Z-n)e^2}{8\pi\varepsilon_0\left(e148.25751\ eV\right)} = \frac{10e^2}{8\pi\varepsilon_0\left(e148.25751\ eV\right)} = 0.91771a_0 \tag{14.142}$$

where $Z=6$ for carbon. Using Eqs. (10.102) and (14.142), the Coulombic energy $E_{Coulomb}\left(C,2sp^3\right)$ of the outer electron of the $C2sp^3$ shell is:

$$E_{Coulomb}\left(C,2sp^3\right) = \frac{-e^2}{8\pi\varepsilon_0 r_{2sp^3}} = \frac{-e^2}{8\pi\varepsilon_0 0.91771a_0} = -14.82575\ eV \tag{14.143}$$

During hybridization, the spin-paired $2s$ electrons are promoted to the $C2sp^3$ shell as unpaired electrons. The energy for the promotion is the magnetic energy given by Eq. (13.152) at the initial radius of the $2s$ electrons. From Eq. (10.62) with $Z=6$, the radius $r_3$ of the $C2s$ shell is:

$$r_3 = 0.84317a_0 \tag{14.144}$$

Using Eqs. (13.152) and (14.144), the unpairing energy is:

$$E(magnetic) = \frac{2\pi\mu_0 e^2\hbar^2}{m_e^2\left(r_3\right)^3} = \frac{8\pi\mu_0\mu_B^2}{\left(0.84317a_0\right)^3} = 0.19086\ eV \tag{14.145}$$

Using Eqs. (14.143) and (14.145), the energy $E\left(C,2sp^3\right)$ of the outer electron of the $C2sp^3$ shell is:

$$E\left(C,2sp^3\right) = \frac{-e^2}{8\pi\varepsilon_0 r_{2sp^3}} + \frac{2\pi\mu_0 e^2\hbar^2}{m_e^2\left(r_3\right)^3} = -14.82575\ eV + 0.19086\ eV = -14.63489\ eV \tag{14.146}$$

Next, consider the formation of the $C-C$-bond MO of ethane from two methyl radicals, each having a $C2sp^3$ electron with an energy given by Eq. (14.146). The total energy of the state is given by the sum over the four electrons. The sum $E_T\left(C_{ethane},2sp^3\right)$ of calculated energies of $C2sp^3$, $C^+$, $C^{2+}$, and $C^{3+}$ from Eqs. (10.123), (10.113-10.114), (10.68), and (10.48), respectively, is:

$$\begin{aligned} E_T\left(C_{ethane},2sp^3\right) &= -\left(64.3921\ eV + 48.3125\ eV + 24.2762\ eV + E\left(C,2sp^3\right)\right) \\ &= -\left(64.3921\ eV + 48.3125\ eV + 24.2762\ eV + 14.63489\ eV\right) \\ &= -151.61569\ eV \end{aligned} \tag{14.147}$$

where $E\left(C,2sp^3\right)$ is the sum of the energy of $C$, $-11.27671\ eV$, and the hybridization energy. The orbital-angular-momentum interactions also cancel such that the energy of the $E_T\left(C_{ethane}, 2sp^3\right)$ is purely Coulombic.

The sharing of electrons between two $C2sp^3$ HOs to form a $C-C$-bond MO permits each participating hybridized orbital to decrease in radius and energy. In order to further satisfy the potential, kinetic, and orbital energy relationships, each $C2sp^3$ HO donates an excess of 25% of its electron density to the $C-C$-bond MO to form an energy minimum. By considering this electron redistribution in the ethane molecule as well as the fact that the central field decreases by an integer for each successive electron of the shell, the radius $r_{ethane2sp^3}$ of the $C2sp^3$ shell of ethane may be calculated from the Coulombic energy using Eq. (10.102).

$$r_{ethane2sp^3} = \left(\sum_{n=2}^{5}(Z-n) - 0.25\right)\frac{e^2}{8\pi\varepsilon_0\left(e151.61569\ eV\right)} = \frac{9.75e^2}{8\pi\varepsilon_0\left(e151.61569\ eV\right)} = 0.87495a_0 \tag{14.148}$$

Using Eqs. (10.102) and (14.148), the Coulombic energy $E_{Coulomb}\left(C_{ethane}, 2sp^3\right)$ of the outer electron of the $C2sp^3$ shell is:

$$E_{Coulomb}\left(C_{ethane}, 2sp^3\right) = \frac{-e^2}{8\pi\varepsilon_0 r_{ethane2sp^3}} = \frac{-e^2}{8\pi\varepsilon_0 0.87495a_0} = -15.55033\ eV \tag{14.149}$$

During hybridization, the spin-paired $2s$ electrons are promoted to the $C2sp^3$ shell as unpaired electrons. The energy for the promotion is the magnetic energy given by Eq. (13.152). Using Eqs. (14.145) and (14.149), the energy $E\left(C_{ethane}, 2sp^3\right)$ of the outer electron of the $C2sp^3$ shell is:

$$E\left(C_{ethane}, 2sp^3\right) = \frac{-e^2}{8\pi\varepsilon_0 r_{ethane2sp^3}} + \frac{2\pi\mu_0 e^2\hbar^2}{m_e^2\left(r_3\right)^3} = -15.55033\ eV + 0.19086\ eV = -15.35946\ eV \tag{14.150}$$

Thus, $E_T\left(C-C, 2sp^3\right)$, the energy change of each $C2sp^3$ shell with the formation of the $C-C$-bond MO is given by the difference between Eq. (14.146) and Eq. (14.150).

$$E_T\left(C-C, 2sp^3\right) = E\left(C_{ethane}, 2sp^3\right) - E\left(C, 2sp^3\right) = -15.35946\ eV - \left(-14.63489\ eV\right) = -0.72457\ eV \tag{14.151}$$

The $H_2$-type ellipsoidal MO comprises 75% of the $C-C$-bond MO shared between two $C2sp^3$ HOs corresponding to the electron charge density in Eq. (11.65) of $\frac{-0.75e}{2}$. But, the additional 25% charge-density contribution to the $C-C$-bond MO causes the electron charge density in Eq. (11.65) to be $\frac{-e}{2} = -0.5e$. Thus, the force constant $k'$ to determine the ellipsoidal parameter $c'$ in terms of the central force of the foci given by Eq. (11.65) is:

$$k' = \frac{(0.5)2e^2}{4\pi\varepsilon_0} \tag{14.152}$$

The distance from the origin to each focus $c'$ is given by substitution of Eq. (14.152) into Eq. (13.60). Thus, the distance from the origin of the $C-C$-bond MO to each focus $c'$ is given by:

$$c' = a\sqrt{\frac{\hbar^2 4\pi\varepsilon_0}{m_e e^2 a}} = \sqrt{aa_0} \tag{14.153}$$

The internuclear distance from Eq. (14.153) is:

$$2c' = 2\sqrt{aa_0} \tag{14.154}$$

The length of the semiminor axis of the prolate spheroidal $C-C$-bond MO $b=c$ is given by Eq. (13.62). The eccentricity, $e$, is given by Eq. (13.63). The solution of the semimajor axis $a$ then allows for the solution of the other axes of each prolate spheroid and eccentricity of the $C-C$-bond MO. Since the $C-C$-bond MO comprises a $H_2$-type-ellipsoidal MO that transitions to the $C_{ethane}2sp^3$ HO of each carbon, the energy $E\left(C_{ethane}, 2sp^3\right)$ in Eq. (14.150) adds to that of the $H_2$-type ellipsoidal MO to give the total energy of the $C-C$-bond MO. From the energy equation and the relationship between the axes, the dimensions of the $C-C$-bond MO are solved. Similarly, $E\left(C_{ethane}, 2sp^3\right)$ is added to the energy of the $H_2$-type ellipsoidal MO of each $C-H$ bond of the methyl groups to give its total energy. From the energy equation and the relationship between the axes, the dimensions of the equivalent $C-H$-bond MOs of the methyl groups in ethane are solved.

The general equations for the energy components of $V_e$, $V_p$, $T$, $V_m$, and $E_T$ of the $C-C$-bond MO are the same as those of the $CH$ MO as well as each $C-H$-bond MO of the methyl groups except that energy of the $C_{ethane}2sp^3$ HO is used. Since the prolate spheroidal $H_2$-type MO transitions to the $C_{ethane}2sp^3$ HO of each carbon and the energy of the $C_{ethane}2sp^3$ shell must remain constant and equal to the $E\left(C_{ethane},2sp^3\right)$ given by Eq. (14.150), the total energy $E_T\left(C-C,\sigma\right)$ of the $\sigma$ component of the $C-C$-bond MO is given by the sum of the energies of the orbitals corresponding to the composition of the linear combination of the $C_{ethane}2sp^3$ HO and the $H_2$-type ellipsoidal MO that forms the $\sigma$ component of the $C-C$-bond MO as given by Eq. (14.139) with the electron charge redistribution. Using Eqs. (13.431) and (14.150), $E_T\left(C-C,\sigma\right)$ is given by:

$$E_T\left(C-C,\sigma\right)=E_T+E\left(C_{ethane},2sp^3\right)=-\frac{e^2}{8\pi\varepsilon_0 c'}\left[\left(0.91771\right)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]-15.35946\ eV \tag{14.155}$$

To match the boundary condition that the total energy of the entire the $H_2$-type ellipsoidal MO is given by Eqs. (11.212) and (13.75), $E_T\left(C-C,\sigma\right)$ given by Eq. (14.155) is set equal to Eq. (13.75):

$$E_T\left(C-C,\sigma\right)=-\frac{e^2}{8\pi\varepsilon_0 c'}\left[\left(0.91771\right)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]-15.35946\ eV=-31.63536831\ eV \tag{14.156}$$

From the energy relationship given by Eq. (14.156) and the relationship between the axes given by Eqs. (14.153-14.154) and (13.62-13.63), the dimensions of the $C-C$-bond MO can be solved.

Substitution of Eq. (14.153) into Eq. (14.156) gives:

$$\frac{e^2}{8\pi\varepsilon_0\sqrt{aa_0}}\left[\left(0.91771\right)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+\sqrt{aa_0}}{a-\sqrt{aa_0}}-1\right]=e16.27589 \tag{14.157}$$

The most convenient way to solve Eq. (14.157) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is

$$a=2.10725a_0=1.11511\ X\ 10^{-10}\ m \tag{14.158}$$

Substitution of Eq. (14.158) into Eq. (14.153) gives:

$$c'=1.45164a_0=7.68173\ X\ 10^{-11}\ m \tag{14.159}$$

The internuclear distance given by multiplying Eq. (14.159) by two is:

$$2c'=2.90327a_0=1.53635\ X\ 10^{-10}\ m \tag{14.160}$$

The experimental bond distance is [3]:

$$2c'=1.5351\ X\ 10^{-10}\ m \tag{14.161}$$

Substitution of Eqs. (14.158-14.159) into Eq. (13.62) gives:

$$b=c=1.52750a_0=8.08317\ X\ 10^{-11}\ m \tag{14.162}$$

Substitution of Eqs. (14.158-14.159) into Eq. (13.63) gives:

$$e=0.68888 \tag{14.163}$$

The nucleus of the $C$ atoms comprise the foci of the $H_2$-type ellipsoidal MO. The parameters of the point of intersection of the $H_2$-type ellipsoidal MO and the $C_{ethane}2sp^3$ HO are given by Eqs. (13.84-13.95) and (13.261-13.270). The polar intersection angle $\theta'$ is given by Eq. (13.261) where $r_n=r_{ethane2sp^3}=0.87495a_0$ is the radius of the $C_{ethane}2sp^3$ shell. Substitution of Eqs. (14.158-14.159) into Eq. (13.261) gives:

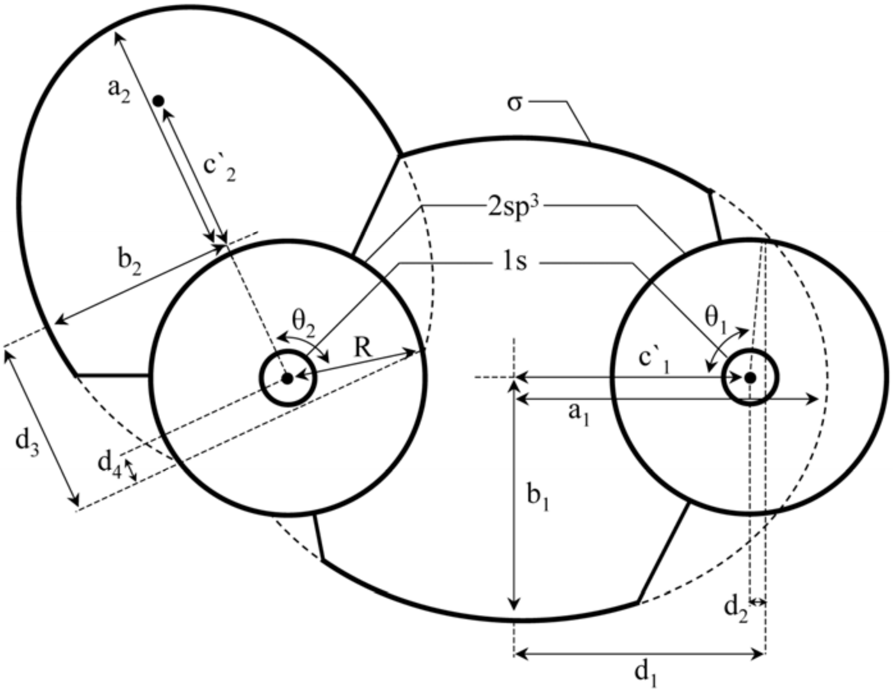
$$\theta'=67.33° \tag{14.164}$$

Then, the angle $\theta_{C-C_{ethane}2sp^3HO}$ the radial vector of the $C2sp^3$ HO makes with the internuclear axis is:

$$\theta_{C-C_{ethane}2sp^3HO}=180°-67.33°=112.67° \tag{14.165}$$

as shown in Figure 14.5.

Figure 14.5. The cross section of the $C-C$-bond MO ($\sigma$ MO) and one $C-H$-bond MO of ethane showing the axes, angles, and point of intersection of each $H_2$-type ellipsoidal MO with the corresponding $C_{ethane}2sp^3$ HO. The continuation of each $H_2$-type-ellipsoidal-MO basis element of the $C-C$ bond and the $C-H$-bond beyond the intersection point with each $C_{ethane}2sp^3$ shell and $\sigma$ MO is shown as dashed since each only serves to solve the energy match with the $C_{ethane}2sp^3$ shell and does not represent charge density. Similarly, the vertical dashed line only designates the parameters of each intersection point. The actual charge density is shown by the solid lines. Legend: $a$: semimajor axis, $b$: semiminor axis, $c'$: internuclear distance, $d_1: d_{C-C_{ethane},H_2MO}$, $\theta_1: \theta_{C-C_{ethane}2sp^3HO}$, $d_2: d_{C-C_{ethane}2sp^3HO}$, $R: r_{ethaneC2sp^3}$, $d_3: d_{C-H_{ethane},H_2MO}$, $\theta_2: \theta_{C-H_{ethane}2sp^3HO}$, and $d_4: d_{C-H_{ethane}2sp^3HO}$.



Consider the right-hand intersection point. The Cartesian $\mathbf{i}$-coordinate of the interception point of the MO and the AO can be calculated using the MO ellipsoidal parameters by first calculating the parametric angle in Eq. (11.83) that matches Cartesian $\mathbf{j}$-coordinate components at the point of intersection. Thus, the matching elliptic parametric angle $\omega t = \theta_{C-C_{ethane},H_2MO}$ satisfies the following relationship:

$$r_{ethane2sp^3}\sin\theta_{C-C_{ethane}2sp^3HO} = 0.87495a_0\sin\theta_{C-C_{ethane}2sp^3HO} = b\sin\theta_{C-C_{ethane},H_2MO} \tag{14.166}$$

such that

$$\theta_{C-C_{ethane},H_2MO} = \sin^{-1}\frac{0.87495a_0\sin\theta_{C-C_{ethane}2sp^3HO}}{b} = \sin^{-1}\frac{0.87495a_0\sin 112.67^\circ}{b} \tag{14.167}$$

with the use of Eq. (14.166). Substitution of Eq. (14.162) into Eq. (14.167) gives:

$$\theta_{C-C_{ethane},H_2MO} = 31.91^\circ \tag{14.168}$$

Then, the distance $d_{C-C_{ethane},H_2MO}$ along the internuclear axis from the origin of $H_2$-type ellipsoidal MO to the point of intersection of the orbitals is given by:

$$d_{C-C_{ethane},H_2MO} = a\cos\theta_{C-C_{ethane},H_2MO} \tag{14.169}$$

Substitution of Eqs. (14.158) and (14.168) into Eq. (14.169) gives:

$$d_{C-C_{ethane},H_2MO} = 1.78885a_0 = 9.46617\ X\ 10^{-11}\ m \tag{14.170}$$

The distance $d_{C-C_{ethane}2sp^3HO}$ along the internuclear axis from the origin of the $C$ atom to the point of intersection of the orbitals is given by:

$$d_{C-C_{ethane}2sp^3HO} = d_{C-C_{ethane},H_2MO} - c' \tag{14.171}$$

Substitution of Eqs. (14.159) and (14.170) into Eq. (14.171) gives:

$$d_{C-C_{ethane}2sp^3HO} = 0.33721a_0 = 1.78444\ X\ 10^{-11}\ m \tag{14.172}$$

## FORCE BALANCE OF THE $CH_3$ MOS OF ETHANE

Each of the two equivalent $CH_3$ MOs must comprise three $C-H$ bonds with each comprising 75% of a $H_2$-type ellipsoidal MO and a $C2sp^3$ HO as given by Eq. (13.540):

$$3\left[1\ C2sp^3 + 0.75\ H_2\ MO\right] \rightarrow CH_3\ MO \tag{14.173}$$

The force balance of the $CH_3$ MO is determined by the boundary conditions that arise from the linear combination of orbitals according to Eq. (13.540) and the energy matching condition between the hydrogen and $C2sp^3$ HO components of the MO.

The force constant $k'$ to determine the ellipsoidal parameter $c'$ of the each $H_2$-type-ellipsoidal-MO component of the $CH_3$ MO in terms of the central force of the foci is given by Eq. (13.59). The distance from the origin of each $C-H$-bond MO to each focus $c'$ is given by Eq. (13.60). The internuclear distance is given by Eq. (13.61). The length of the semiminor axis of the prolate spheroidal $C-H$-bond MO $b=c$ is given by Eq. (13.62). The eccentricity, $e$, is given by Eq. (13.63). The solution of the semimajor axis $a$ then allows for the solution of the other axes of each prolate spheroid and eccentricity of each $C-H$-bond MO. Since each of the three prolate spheroidal $C-H$-bond MOs comprises an $H_2$-type-ellipsoidal MO that transitions to the $C_{ethane}2sp^3$ HO of ethane, the energy $E\left(C_{ethane},2sp^3\right)$ of Eq. (14.150) adds to that of the three corresponding $H_2$-type ellipsoidal MOs to give the total energy of the $CH_3$ MO. From the energy equation and the relationship between the axes, the dimensions of the $CH_3$ MO are solved.

The energy components of $V_e$, $V_p$, $T$, and $V_m$ are the same as those of methyl radical, three times those of $CH$ corresponding to the three $C-H$ bonds except that energy of the $C_{ethane}2sp^3$ HO is used. Since each prolate spheroidal $H_2$-type MO transitions to the $C_{ethane}2sp^3$ HO and the energy of the $C_{ethane}2sp^3$ shell must remain constant and equal to the $E\left(C_{ethane},2sp^3\right)$ given by Eq. (14.150), the total energy $E_{T_{ethane}}\left(CH_3\right)$ of the $CH_3$ MO is given by the sum of the energies of the orbitals corresponding to the composition of the linear combination of the $C_{ethane}2sp^3$ HO and the three $H_2$-type ellipsoidal MOs that forms the $CH_3$ MO as given by Eq. (13.540). Using Eq. (13.431), $E_{T_{ethane}}\left(CH_3\right)$ is given by:

$$E_{T_{ethane}}\left(CH_3\right) = E_T + E\left(C_{ethane},2sp^3\right) = -\frac{3e^2}{8\pi\varepsilon_0 c'}\left[(0.91771)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right] - 15.35946\ eV \tag{14.174}$$

$E_{T_{ethane}}\left(CH_3\right)$ given by Eq. (14.174) is set equal to three times the energy of the $H_2$-type ellipsoidal MO minus two times the Coulombic energy of $H$ given by Eq. (13.542):

$$E_T\left(CH_3\right) = -\frac{3e^2}{8\pi\varepsilon_0 c'}\left[(0.91771)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right] - 15.35946\ eV = -67.69450\ eV \tag{14.175}$$

From the energy relationship given by Eq. (14.175) and the relationship between the axes given by Eqs. (13.60-13.63), the dimensions of the $CH_3$ MO can be solved.

Substitution of Eq. (13.60) into Eq. (14.175) gives:

$$\frac{3e^2}{8\pi\varepsilon_0\sqrt{\frac{2aa_0}{3}}}\left[(0.91771)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+\sqrt{\frac{2aa_0}{3}}}{a-\sqrt{\frac{2aa_0}{3}}}-1\right] = e52.33505 \tag{14.176}$$

The most convenient way to solve Eq. (14.176) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is:

$$a = 1.64469a_0 = 8.70331\ X\ 10^{-11}\ m \tag{14.177}$$

Substitution of Eq. (14.177) into Eq. (14.60) gives:

$$c' = 1.04712a_0 = 5.54111\ X\ 10^{-11}\ m \tag{14.178}$$

The internuclear distance given by multiplying Eq. (14.178) by two is:

$$2c' = 2.09424a_0 = 1.10822\ X\ 10^{-10}\ m \tag{14.179}$$

The experimental bond distance is [3]:

$$2c' = 1.0940\ X\ 10^{-10}\ m \tag{14.180}$$

Substitution of Eqs. (14.177-14.178) into Eq. (14.62) gives:

$$b = c = 1.26828a_0 = 6.71145\ X\ 10^{-11}\ m \tag{14.181}$$

Substitution of Eqs. (14.177-14.178) into Eq. (13.63) gives:

$$e = 0.63667 \tag{14.182}$$

The nucleus of the $H$ atom and the nucleus of the $C$ atom comprise the foci of each $H_2$-type ellipsoidal MO. The parameters of the point of intersection of the $H_2$-type ellipsoidal MO and the $C_{ethane}2sp^3$ HO are given by Eqs. (13.84-13.95) and (13.261-13.270). The polar intersection angle $\theta'$ is given by Eq. (13.261) where $r_n = r_{ethane2sp^3} = 0.87495a_0$ is the radius of the $C_{ethane}2sp^3$ shell. Substitution of Eqs. (14.177-14.178) into Eq. (13.261) gives:

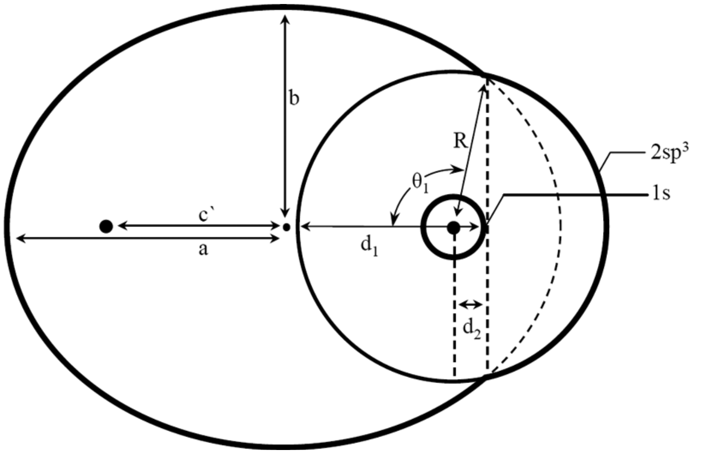
$$\theta' = 79.34° \tag{14.183}$$

Then, the angle $\theta_{C-H_{ethane}2sp^3HO}$ the radial vector of the $C2sp^3$ HO makes with the internuclear axis is:

$$\theta_{C-H_{ethane}2sp^3HO} = 180° - 79.34° = 100.66° \tag{14.184}$$

as shown in Figure 14.6.

Figure 14.6. The cross section of one $C-H$-bond MO of ethane showing the axes, angles, and point of intersection of the $H_2$-type ellipsoidal MO with the $C_{ethane}2sp^3$ HO. The continuation of the $H_2$-type-ellipsoidal-MO basis element beyond the intersection point with the $C_{ethane}2sp^3$ shell is shown as dashed since it only serves to solve the energy match with the $C_{ethane}2sp^3$ shell and does not represent charge density. Similarly, the vertical dashed line only designates the parameters of the intersection point. The actual charge density is shown by the solid lines. Legend: $a$: semimajor axis, $b$: semiminor axis, $c'$: internuclear distance, $d_1 : d_{C-H_{ethane},H_2MO}$, $\theta_1 : \theta_{C-H_{ethane}2sp^3HO}$, $d_2 : d_{C-H_{ethane}2sp^3HO}$, and $R : r_{ethane2sp^3}$.



The Cartesian $\mathbf{i}$-coordinate of the interception point of the MO and the AO can be calculated using the MO ellipsoidal parameters by first calculating the parametric angle in Eq. (11.83) that matches Cartesian $\mathbf{j}$-coordinate components at the point of intersection. Thus, the matching elliptic parametric angle $\omega t = \theta_{C-H_{ethane},H_2MO}$ satisfies the following relationship:

$$r_{ethane2sp^3} \sin\theta_{C-H_{ethane}2sp^3HO} = 0.87495a_0 \sin\theta_{C-H_{ethane}2sp^3HO} = b\sin\theta_{C-H_{ethane},H_2MO} \tag{14.185}$$

such that

$$\theta_{C-H_{ethane},H_2MO} = \sin^{-1}\frac{0.87495a_0 \sin\theta_{C-H_{ethane}2sp^3HO}}{b} = \sin^{-1}\frac{0.87495a_0 \sin 100.66°}{b} \tag{14.186}$$

with the use of Eq. (14.184). Substitution of Eq. (14.181) into Eq. (14.186) gives:

$$\theta_{C-H_{ethane},H_2MO} = 42.68° \tag{14.187}$$

Then, the distance $d_{C-H_{ethane},H_2MO}$ along the internuclear axis from the origin of $H_2$-type ellipsoidal MO to the point of intersection of the orbitals is given by:

$$d_{C-H_{ethane},H_2MO} = a\cos\theta_{C-H_{ethane},H_2MO} \tag{14.188}$$

Substitution of Eqs. (14.177) and (14.187) into Eq. (14.188) gives:

$$d_{C-H_{ethane},H_2MO} = 1.20901a_0 = 6.39780\ X\ 10^{-11}\ m \tag{14.189}$$

The distance $d_{C-H_{ethane}2sp^3HO}$ along the internuclear axis from the origin of the $C$ atom to the point of intersection of the orbitals is given by

$$d_{C-H_{ethane}2sp^3HO} = d_{C-H_{ethane},H_2MO} - c' \tag{14.190}$$

Substitution of Eqs. (14.178) and (14.189) into Eq. (14.190) gives:

$$d_{C-H_{ethane}2sp^3HO} = 0.16189a_0 = 8.56687\ X\ 10^{-12}\ m \tag{14.191}$$

## BOND ANGLE OF THE $CH_3$ GROUPS

Each $CH_3$ MO comprises a linear combination of three $C-H$-bond MOs. Each $C-H$-bond MO comprises the superposition of a $H_2$-type ellipsoidal MO and the $C_{ethane}2sp^3$ HO. A bond is also possible between the two H atoms of the $C-H$ bonds. Such $H-H$ bonding would decrease the $C-H$ bond strength since electron density would be shifted from the $C-H$ bonds to the $H-H$ bond. Thus, the bond angle between the two $C-H$ bonds is determined by the condition that the total energy of the $H_2$-type ellipsoidal MO between the terminal $H$ atoms of the $C-H$ bonds is zero. From Eqs. (11.79) and (13.228), the distance from the origin to each focus of the $H-H$ ellipsoidal MO is:

$$c' = a\sqrt{\frac{\hbar^2 4\pi\varepsilon_0}{m_e e^2 2a}} = \sqrt{\frac{aa_0}{2}} \tag{14.192}$$

The internuclear distance from Eq. (13.229) is:

$$2c' = 2\sqrt{\frac{aa_0}{2}} \tag{14.193}$$

The length of the semiminor axis of the prolate spheroidal $H-H$ MO $b=c$ is given by Eq. (14.62).

The bond angle of the $CH_3$ groups of ethane is derived by using the orbital composition and an energy matching factor as in the case with the $CH_3$ radical. Since the two $H_2$-type ellipsoidal MOs initially comprise 75% of the $H$ electron density of $H_2$ and the energy of each $H_2$-type ellipsoidal MO is matched to that of the $C_{ethane}2sp^3$ HO, the component energies and the total energy $E_T$ of the $H-H$ bond are given by Eqs. (13.67-13.73) except that $V_e$, $T$, and $V_m$ are corrected for the hybridization-energy-matching factor of $0.87495$. Hybridization with 25% electron donation to the $C-C$-bond gives rise to the $C_{ethane}2sp^3$ HO-shell Coulombic energy $E_{Coulomb}\left(C_{ethane},2sp^3\right)$ given by Eq. (14.149). The corresponding normalization factor for determining the zero of the total $H-H$ bond energy is given by the ratio of $15.55033\ eV$, the magnitude of $E_{Coulomb}\left(C_{ethane},2sp^3\right)$ given by Eq. (14.149), and $13.605804\ eV$, the magnitude of the Coulombic energy between the electron and proton of $H$ given by Eq. (1.264). The hybridization energy factor $C_{ethaneC2sp^3HO}$ is:

$$C_{ethaneC2sp^3HO} = \frac{\dfrac{e^2}{8\pi\varepsilon_0 a_0}}{\dfrac{e^2}{8\pi\varepsilon_0 r_{ethane2sp^3}}} = \frac{\dfrac{e^2}{8\pi\varepsilon_0 a_0}}{\dfrac{e^2}{8\pi\varepsilon_0 0.87495a_0}} = \frac{13.605804\ eV}{15.55033\ eV} = 0.87495 \tag{14.194}$$

Substitution of Eq. (14.152) into Eq. (13.233) with the hybridization factor of $0.87495$ gives:

$$0 = \left[\begin{array}{l} \dfrac{-e^2}{8\pi\varepsilon_0\sqrt{\dfrac{aa_0}{2}}}\left[\left(0.87495\right)^{-1}\left(\dfrac{3}{2}-\dfrac{3}{8}\dfrac{a_0}{a}\right)\ln\dfrac{a+\sqrt{\dfrac{aa_0}{2}}}{a-\sqrt{\dfrac{aa_0}{2}}}-1\right]\left[1+\sqrt{\dfrac{2\hbar\sqrt{\dfrac{\dfrac{0.75e^2}{4\pi\varepsilon_0 a^3}}{m_e}}}{m_e c^2}}\right] \\ +\hbar\sqrt{\dfrac{\dfrac{0.75e^2}{8\pi\varepsilon_0 a^3}-\dfrac{e^2}{8\pi\varepsilon_0\left(a+c'\right)^3}}{0.5m_p}} \end{array}\right] \tag{14.195}$$

From the energy relationship given by Eq. (14.195) and the relationship between the axes given by Eqs. (14.192-14.193) and (14.62-14.63), the dimensions of the $H-H$ MO can be solved.

The most convenient way to solve Eq. (14.195) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is

$$a = 5.7000a_0 = 3.0163\ X\ 10^{-10}\ m \tag{14.196}$$

Substitution of Eq. (14.196) into Eq. (14.192) gives:

$$c' = 1.6882a_0 = 8.9335\ X\ 10^{-11}\ m \tag{14.197}$$

The internuclear distance given by multiplying Eq. (14.197) by two is:

$$2c' = 3.3764a_0 = 1.7867\ X\ 10^{-10}\ m \tag{14.198}$$

Substitution of Eqs. (14.196-14.197) into Eq. (14.62) gives:

$$b = c = 5.4443a_0 = 2.8810\ X\ 10^{-10}\ m \tag{14.199}$$

Substitution of Eqs. (14.196-14.197) into Eq. (13.63) gives:

$$e = 0.2962 \tag{14.200}$$

From, $2c'_{H-H}$ (Eq. (14.198)), the distance between the two $H$ atoms when the total energy of the corresponding MO is zero (Eq. (14.195)), and $2c'_{C-H}$ (Eq. (14.179)), the internuclear distance of each $C-H$ bond, the corresponding bond angle can be determined from the law of cosines. Using, Eq. (13.242), the bond angle $\theta$ between the $C-H$ bonds is

$$\theta = \cos^{-1}\left(\frac{2(2.09424)^2 - (3.3764)^2}{2(2.09424)^2}\right) = \cos^{-1}(-0.29964) = 107.44° \tag{14.201}$$

The experimental angle between the $C-H$ bonds is [8]:

$$\theta = 107.4° \tag{14.202}$$

The $CH_3$ radical has a pyramidal structure with the carbon atom along the z-axis at the apex and the hydrogen atoms at the base in the xy-plane. The distance $d_{origin-H}$ from the origin to the nucleus of a hydrogen atom given by Eqs. (14.198) and (13.412) is:

$$d_{origin-H} = 1.94936a_0 \tag{14.203}$$

The height along the z-axis of the pyramid from the origin to $C$ nucleus $d_{height}$ given by Eqs. (13.414), (14.179), and (14.203) is

$$d_{height} = 0.76540a_0 \tag{14.204}$$

The angle $\theta_v$ of each $C-H$ bond from the z-axis given by Eqs. (13.416), (14.203), and (14.204) is:

$$\theta_v = 68.563° \tag{14.205}$$

The $C-C$ bond is along the z-axis. Thus, the bond angle $\theta_{C-C-H}$ between the internuclear axis of the $C-C$ bond and a $H$ atom of the methyl groups is given by:

$$\theta_{C-C-H} = 180 - \theta_v \tag{14.206}$$

Substitution of Eq. (14.205) into Eq. (14.206) gives:

$$\theta_{C-C-H} = 111.44° \tag{14.207}$$

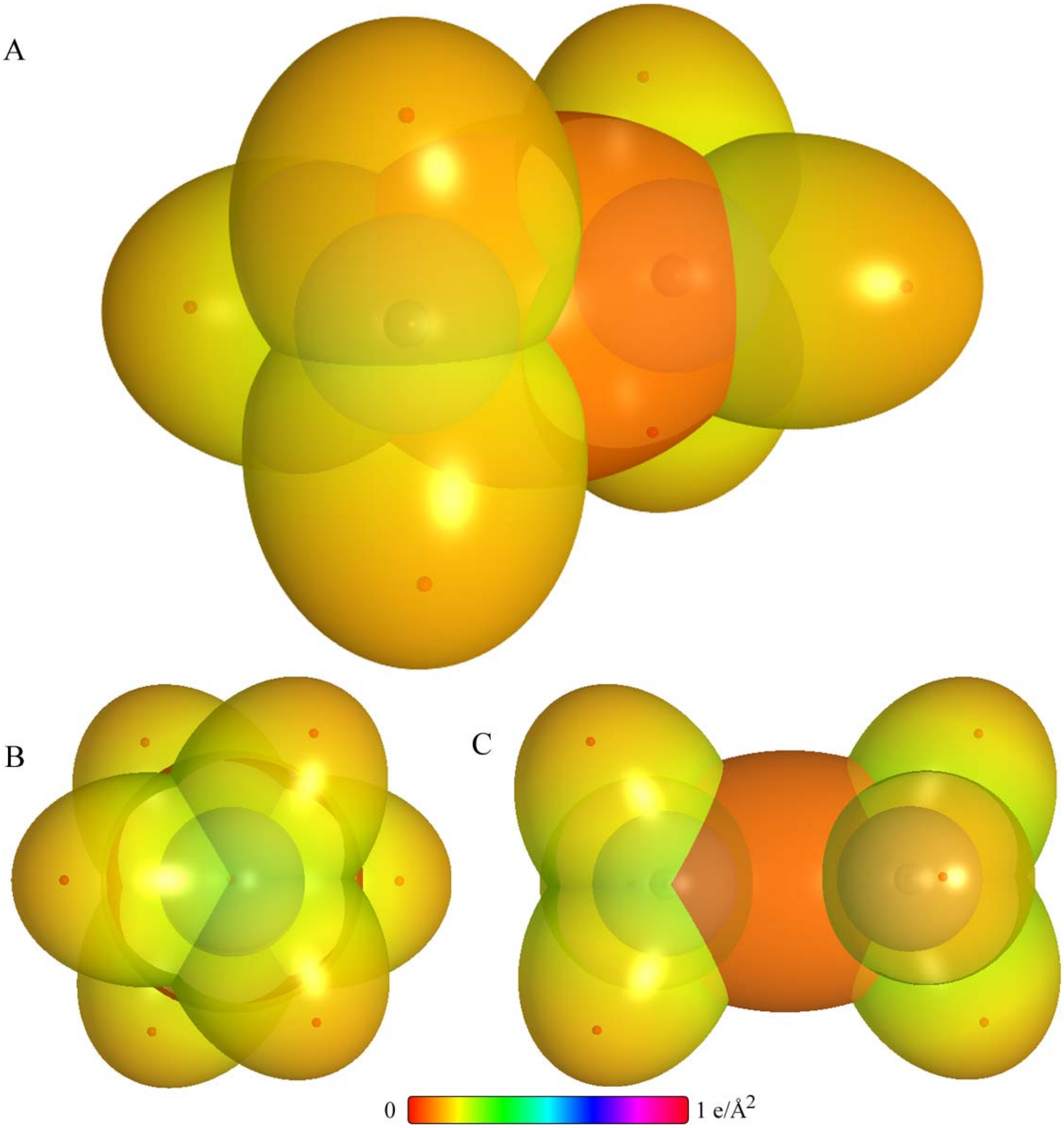
The experimental angle between the $C-C-H$ bonds is [3]:

$$\theta_{C-C-H} = 111.17° \tag{14.208}$$

The $CH_3CH_3$ MO shown in Figure 14.7 was rendered using these parameters. A minimum energy is obtained with a staggered configuration consistent with observations [3].

The charge-density in the $C-C$-bond MO is increased by a factor of 0.25 with the formation of the $C_{ethane}2sp^3$ HOs each having a smaller radius. Using the orbital composition of the $CH_3$ groups (Eq. (14.173)) and the $C-C$-bond MO (Eq. (14.139)), the radii of $C1s = 0.17113a_0$ (Eq. (10.51)) and $C_{ethane}2sp^3 = 0.87495a_0$ (Eq. (14.148)) shells, and the parameters of the $C-C$-bond (Eqs. (13.3-13.4), (14.158-14.160), and (14.162-14.172)), the parameters of the $C-H$-bond MOs (Eqs. (13.3-13.4), (14.177-14.179), and (14.181-14.191)), and the bond-angle parameters (Eqs. (14.195-14.208)), the charge-density of the $CH_3CH_3$ MO comprising the linear combination of two sets of three $C-H$-bond MOs and a $C-C$-bond MO bridging the two methyl groups is shown in Figure 14.7. Each $C-H$-bond MO comprises a $H_2$-type ellipsoidal MO and a $C_{ethane}2sp^3$ HO having the dimensional diagram shown in Figure 14.6. The $C-C$-bond MO comprises a $H_2$-type ellipsoidal MO bridging two $C_{ethane}2sp^3$ HOs having the dimensional diagram shown in Figure 14.5.

Figure 14.7. $CH_3CH_3$ MO comprising the linear combination of two sets of three $C-H$-bond MOs and a $C-C$-bond MO. (A) Color scale, translucent view of the charge-density of the $C-C$-bond MO with the $C_{ethane}2sp^3$ HOs shown transparently. The $C-C$-bond MO comprises a $H_2$-type ellipsoidal MO bridging two $C_{ethane}2sp^3$ HOs. For each $C-H$ and the $C-C$ bond, the ellipsoidal surface of the $H_2$-type ellipsoidal MO that transitions to the $C_{ethane}2sp^3$ HO, the $C_{ethane}2sp^3$ HO shell, inner most $C1s$ shell, and the nuclei (red, not to scale), are shown. (B)-(C) End-on view, translucent view high-lighting the $C-C$-bond MO, and opaque view of the charge-density of the $CH_3CH_3$ MO, respectively.



## ENERGIES OF THE $CH_3$ GROUPS

The energies of each $CH_3$ group of ethane are given by the substitution of the semiprincipal axes (Eqs. (14.177-14.178) and (14.181)) into the energy equations of the methyl radical (Eqs. (13.556-13.560)), with the exception that $E\left(C_{ethane}, 2sp^3\right)$ replaces $E\left(C, 2sp^3\right)$ in Eq. (13.560):

$$V_e = 3\left(0.91771\right)\frac{-2e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -107.68424\ eV \tag{14.209}$$

$$V_p = \frac{3e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}} = 38.98068\ eV \tag{14.210}$$

$$T = 3\left(0.91771\right)\frac{\hbar^2}{2m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = 32.73700\ eV \tag{14.211}$$

$$V_m = 3\left(0.91771\right)\frac{-\hbar^2}{4m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -16.36850\ eV \tag{14.212}$$

$$E_{T_{ethane}}\left(CH_3\right) = -\frac{3e^2}{8\pi\varepsilon_0 c'}\left[\left(0.91771\right)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]-15.35946\ eV = -67.69451\ eV \tag{14.213}$$

where $E_{T_{ethane}}\left(CH_3\right)$ is given by Eq. (14.174) which is reiteratively matched to Eq. (13.542) within five-significant-figure round off error.

## VIBRATION OF THE $^{12}CH_3$ GROUPS

The vibrational energy levels of $CH_3$ in ethane may be solved as three equivalent coupled harmonic oscillators by developing the Lagrangian, the differential equation of motion, and the eigenvalue solutions [9] wherein the spring constants are derived from the central forces as given in the Vibration of Hydrogen-Type Molecular Ions section and the Vibration of Hydrogen-Type Molecules section.

## THE DOPPLER ENERGY TERMS OF THE $^{12}CH_3$ GROUPS

The equations of the radiation reaction force of the methyl groups in ethane are the same as those of the methyl radical with the substitution of the methyl-group parameters. Using Eq. (13.561), the angular frequency of the reentrant oscillation in the transition state is

$$\omega = \sqrt{\frac{\frac{0.75e^2}{4\pi\varepsilon_0 b^3}}{m_e}} = 2.50664\ X\ 10^{16}\ rad/s \tag{14.214}$$

where $b$ is given by Eq. (14.181). The kinetic energy, $E_K$, is given by Planck's equation (Eq. (11.127)):

$$\overline{E}_K = \hbar\omega = \hbar 2.50664\ X\ 10^{16}\ rad/s = 16.49915\ eV \tag{14.215}$$

In Eq. (11.181), substitution of $E_T\left(H_2\right)$ (Eqs. (11.212) and (13.75)), the maximum total energy of each $H_2$-type MO, for $E_{h\nu}$, the mass of the electron, $m_e$, for $M$, and the kinetic energy given by Eq. (14.215) for $\overline{E}_K$ gives the Doppler energy of the electrons of each of the three bonds for the reentrant orbit:

$$\overline{E}_D \cong E_{h\nu}\sqrt{\frac{2\overline{E}_K}{Mc^2}} = -31.63537\ eV\sqrt{\frac{2e\left(16.49915\ eV\right)}{m_e c^2}} = -0.25422\ eV \tag{14.216}$$

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency. The decrease in the energy of $CH_3$ due to the reentrant orbit of each bond in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei, $\overline{E}_{osc}$, is given by the sum of the corresponding energies, $\overline{E}_D$ given by Eq. (14.216) and $\overline{E}_{Kvib}$, the average kinetic energy of vibration which is 1/2 of the vibrational energy of each $C-H$ bond. Using $\omega_e$ given by Eq. (13.458) for $\overline{E}_{Kvib}$ of the transition state having three independent bonds, $\overline{E}'_{ethane\ osc}\left(^{12}CH_3\right)$ per bond is:

$$\overline{E}'_{ethane\ osc}\left(^{12}CH_3\right) = \overline{E}_D + \overline{E}_{Kvib} = \overline{E}_D + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \tag{14.217}$$

$$\overline{E}'_{ethane\ osc}\left(^{12}CH_3\right) = -0.25422\ eV + \frac{1}{2}\left(0.35532\ eV\right) = -0.07656\ eV \tag{14.218}$$

Given that the vibration and reentrant oscillation is for three $C-H$ bonds, $\bar{E}_{ethane\ osc}\left({}^{12}CH_3\right)$, is:

$$\bar{E}_{ethane\ osc}\left({}^{12}CH_3\right)=3\left(\bar{E}_D+\frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right)=3\left(-0.25422\ eV+\frac{1}{2}\left(0.35532\ eV\right)\right)=-0.22967\ eV \tag{14.219}$$

## TOTAL AND DIFFERENCE ENERGIES OF THE $^{12}CH_3$ GROUPS

$E_{ethaneT+osc}\left({}^{12}CH_3\right)$, the total energy of each $^{12}CH_3$ group including the Doppler term, is given by the sum of $E_{T_{ethane}}\left(CH_3\right)$ (Eq. (14.213)) and $\bar{E}_{ethane\ osc}\left({}^{12}CH_3\right)$ given by Eq. (14.219).

$$\begin{aligned}E_{ethaneT+osc}\left({}^{12}CH_3\right)&=V_e+T+V_m+V_p+E\left(C_{ethane},2sp^3\right)+\bar{E}_{ethane\ osc}\left({}^{12}CH_3\right)\\&=E_{T_{ethane}}\left(CH_3\right)+\bar{E}_{ethane\ osc}\left({}^{12}CH_3\right)\end{aligned} \tag{14.220}$$

$$\begin{aligned}E_{ethaneT+osc}\left({}^{12}CH_3\right)&=\left\{\begin{array}{l}\left(\dfrac{-3e^2}{8\pi\varepsilon_0c'}\left[\left(0.91771\right)\left(2-\dfrac{1}{2}\dfrac{a_0}{a}\right)\ln\dfrac{a+c'}{a-c'}-1\right]-15.359469\ eV\right)\\-3\left(\left(31.63536831\ eV\right)\sqrt{\dfrac{2\hbar\sqrt{\dfrac{\frac{3}{4}\frac{e^2}{4\pi\varepsilon_0b^3}}{m_e}}}{m_ec^2}}-\dfrac{1}{2}\hbar\sqrt{\dfrac{k}{\mu}}\right)\end{array}\right\}\\&=-67.69450\ eV-3\left(0.25422\ eV-\frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right)\end{aligned} \tag{14.221}$$

From Eqs. (14.217-14.221), the total energy of each $^{12}CH_3$ is:

$$\begin{aligned}E_{ethaneT+osc}\left({}^{12}CH_3\right)&=-67.69450\ eV+\bar{E}_{ethane\ osc}\left({}^{12}CH_3\right)\\&=-67.69450\ eV-3\left(0.25422\ eV-\frac{1}{2}\left(0.35532\ eV\right)\right)=-67.92417\ eV\end{aligned} \tag{14.222}$$

where $\omega_e$ given by Eq. (13.458) was used for the $\hbar\sqrt{\frac{k}{\mu}}$ term.

The total energy for each methyl radical given by Eq. (13.569) is:

$$\begin{aligned}E_{radicalT+osc}\left({}^{12}CH_3\right)&=-67.69450\ eV+\bar{E}_{radical\ osc}\left({}^{12}CH_3\right)\\&=-67.69450\ eV-3\left(0.25670\ eV-\frac{1}{2}\left(0.35532\ eV\right)\right)=-67.93160\ eV\end{aligned} \tag{14.223}$$

The difference in energy between the methyl groups and the methyl radical $\Delta E_{T+osc}\left({}^{12}CH_3\right)$ is given by two times the difference between Eqs. (14.222) and (14.223):

$$\begin{aligned}\Delta E_{T+osc}\left({}^{12}CH_3\right)&=2\left(E_{ethaneT+osc}\left({}^{12}CH_3\right)-E_{radicalT+osc}\left({}^{12}CH_3\right)\right)\\&=2\left(-67.92417\ eV-\left(-67.93160\ eV\right)\right)=0.01487\ eV\end{aligned} \tag{14.224}$$

## SUM OF THE ENERGIES OF THE $C-C$ $\sigma$ MO AND THE HOS OF ETHANE

The energy components of $V_e$, $V_p$, $T$, $V_m$, and $E_T$ of the $C-C$-bond MO are the same as those of the $CH$ MO as well as each $C-H$-bond MO of the methyl groups except that energy of the $C_{ethane}2sp^3$ HO is used. The energies of each $C-C$-bond MO are given by the substitution of the semiprincipal axes (Eqs. (14.158-14.159) and (14.162)) into the energy equations of the $CH$ MO (Eqs. (13.449-13.453)), with the exception that $E\left(C_{ethane},2sp^3\right)$ replaces $E\left(C,2sp^3\right)$ in Eq. (13.453).

$$V_e=\left(0.91771\right)\frac{-2e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}}=-29.101124\ eV \tag{14.225}$$

$$V_p=\frac{e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}}=9.37273\ eV \tag{14.226}$$

$$T=\left(0.91771\right)\frac{\hbar^2}{2m_ea\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}}=6.90500\ eV \tag{14.227}$$

$$V_m = (0.91771)\frac{-\hbar^2}{4m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -3.45250\ eV \tag{14.228}$$

$$E_T(C-C,\sigma) = -\frac{e^2}{8\pi\varepsilon_0 c'}\left[(0.91771)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right] - 15.35946\ eV = -31.63535\ eV \tag{14.229}$$

where $E_T(C-C,\sigma)$ is the total energy of the $C-C$ $\sigma$ MO given by Eq. (14.155) which is reiteratively matched to Eq. (13.75) within five-significant-figure round off error.

The total energy of the $C-C$-bond MO, $E_T(C-C)$, is given by the sum of two times $E_T(C-C,2sp^3)$, the energy change of each $C2sp^3$ shell due to the decrease in radius with the formation of the $C-C$-bond MO (Eq. (14.151)), and $E_T(C-C,\sigma)$, the $\sigma$ MO contribution given by Eq. (14.156).

$$\begin{aligned} E_T(C-C) &= 2E_T(C-C,2sp^3) + E_T(C-C,\sigma) \\ &= \begin{pmatrix} 2(-0.72457\ eV) + \\ \left(-\frac{e^2}{8\pi\varepsilon_0\sqrt{aa_0}}\left[(0.91771)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+\sqrt{aa_0}}{a-\sqrt{aa_0}}-1\right] - 15.35946\ eV\right) \end{pmatrix} \\ &= 2(-0.72457\ eV) + (-31.63537\ eV) = -33.08452\ eV \end{aligned} \tag{14.230}$$

## VIBRATION OF ETHANE

The vibrational energy levels of $CH_3CH_3$ may be solved as two sets of three equivalent coupled harmonic oscillators with a bridging harmonic oscillator by developing the Lagrangian, the differential equation of motion, and the eigenvalue solutions [9] wherein the spring constants are derived from the central forces as given in the Vibration of Hydrogen-Type Molecular Ions section and the Vibration of Hydrogen-Type Molecules section.

## THE DOPPLER ENERGY TERMS OF THE $C-C$-BOND MO OF ETHANE

The equations of the radiation reaction force of the symmetrical $C-C$-bond MO are given by Eqs. (11.231-11.233), except the force-constant factor is $0.5$ based on the force constant $k'$ of Eq. (14.152), and the $C-C$-bond MO parameters are used. The angular frequency of the reentrant oscillation in the transition state is

$$\omega = \sqrt{\frac{\frac{0.5e^2}{4\pi\varepsilon_0 a^3}}{m_e}} = 9.55643\ X\ 10^{15}\ rad/s \tag{14.231}$$

where $a$ is given by Eq. (14.158). The kinetic energy, $E_K$, is given by Planck's equation (Eq. (11.127)).

$$\overline{E}_K = \hbar\omega = \hbar 9.55643\ X\ 10^{15}\ rad/s = 6.29021\ eV \tag{14.232}$$

In Eq. (11.181), substitution of $E_T(C-C)$ (Eq. (14.230)) for $E_{h\nu}$, the mass of the electron, $m_e$, for $M$, and the kinetic energy given by Eq. (14.232) for $\overline{E}_K$ gives the Doppler energy of the electrons of each of the three bonds for the reentrant orbit:

$$\overline{E}_D \cong E_{h\nu}\sqrt{\frac{2\overline{E}_K}{Mc^2}} = -33.08450\ eV\sqrt{\frac{2e(6.29021\ eV)}{m_e c^2}} = -0.16416\ eV \tag{14.233}$$

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency. The decrease in the energy of the $C-C$-bond MO due to the reentrant orbit of the bond in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei, $\overline{E}_{osc}$, is given by the sum of the corresponding energies, $\overline{E}_D$ given by Eq. (14.233) and $\overline{E}_{Kvib}$, the average kinetic energy of vibration which is 1/2 of the vibrational energy of the $C-C$ bond. Using the experimental $C-C$ $E_{vib}(\upsilon_3)$ of $993\ cm^{-1}$ $(0.12312\ eV)$ [10] for $\overline{E}_{Kvib}$ of the transition state, $\overline{E}_{osc}(C-C,\sigma)$ is:

$$\overline{E}_{osc}(C-C,\sigma) = \overline{E}_D + \overline{E}_{Kvib} = \overline{E}_D + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \tag{14.234}$$

$$\overline{E}_{osc}(C-C,\sigma) = -0.16416\ eV + \frac{1}{2}(0.12312\ eV) = -0.10260\ eV \tag{14.235}$$

## TOTAL ENERGIES OF THE $C-C$-BOND MO OF ETHANE

$E_{T+osc}\left(C-C\right)$, the total energy of the $C-C$-bond MO including the Doppler term, is given by the sum of $E_T\left(C-C\right)$ (Eq. (14.230)) and $\bar{E}_{osc}\left(C-C,\sigma\right)$ given by Eq. (14.235).

$$\begin{aligned} E_{T+osc}\left(C-C\right) &= V_e + T + V_m + V_p + E\left(C_{ethane}, 2sp^3\right) + 2E_T\left(C-C, 2sp^3\right) + \bar{E}_{osc}\left(C-C,\sigma\right) \\ &= E_T\left(C-C,\sigma\right) + 2E_T\left(C-C,2sp^3\right) + \bar{E}_{osc}\left(C-C,\sigma\right) = E_T\left(C-C\right) + \bar{E}_{osc}\left(C-C,\sigma\right) \end{aligned} \tag{14.236}$$

$$E_{T+osc}\left(C-C\right) = \left\{ \begin{array}{l} \left( \dfrac{-e^2}{8\pi\varepsilon_0 c'} \left[ \left(0.91771\right)\left(2 - \dfrac{1}{2}\dfrac{a_0}{a}\right) \ln\dfrac{a+c'}{a-c'} - 1 \right] - 15.35946\ eV + 2E_T\left(C-C,2sp^3\right) \right) \\ \left( 1 + \sqrt{\dfrac{2\hbar\sqrt{\dfrac{\dfrac{1}{2}\dfrac{e^2}{4\pi\varepsilon_0 a^3}}{m_e}}}{m_e c^2}} \right) + \dfrac{1}{2}\hbar\sqrt{\dfrac{k}{\mu}} \end{array} \right\} \tag{14.237}$$

$$= -33.08452\ eV - 0.16416\ eV + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}$$

From Eqs. (14.234-14.237), the total energy of the $C-C$-bond MO is:

$$\begin{aligned} E_{T+osc}\left(C-C\right) &= -31.63537\ eV + 2E_T\left(C-C,2sp^3\right) + \bar{E}_{osc}\left(C-C,\sigma\right) \\ &= -31.63537\ eV + 2\left(-0.72457\ eV\right) - 0.16416\ eV + \frac{1}{2}\left(0.12312\ eV\right) = -33.18712\ eV \end{aligned} \tag{14.238}$$

where the experimental $E_{vib}$ was used for the $\hbar\sqrt{\frac{k}{\mu}}$ term.

## BOND ENERGY OF THE $C-C$ BOND OF ETHANE

The dissociation energy of the $C-C$ bond of $CH_3CH_3$, $E_D\left(H_3C-CH_3\right)$, is given by two times $E\left(C,2sp^3\right)$ (Eq. (14.146)), the initial energy of the $C2sp^3$ HO of each $CH_3$ radical that bond with a single $C-C$ bond, minus the sum of $\Delta E_{T+osc}\left({}^{12}CH_3\right)$ (Eq. (14.224)), the energy change going from the methyl radicals to the methyl groups of ethane, and $E_{T+osc}\left(C-C\right)$ (Eq. (14.238)). Thus, the dissociation energy of the $C-C$ bond of $CH_3CH_3$, is:

$$\begin{aligned} E_D\left(H_3C-CH_3\right) &= 2\left(E\left(C,2sp^3\right)\right) - \left(\Delta E_{T+osc}\left({}^{12}CH_3\right) + E_{T+osc}\left(C-C\right)\right) \\ &= 2\left(-14.63489\ eV\right) - \left(0.01487\ eV - 33.18712\ eV\right) \\ &= 2\left(-14.63489\ eV\right) - \left(33.17225\ eV\right) = 3.90247\ eV \end{aligned} \tag{14.239}$$

The experimental dissociation energy of the $C-C$ bond of $CH_3CH_3$ is [6]:

$$E_D\left(H_3C-CH_3\right) = 3.89690\ eV \tag{14.240}$$

The results of the determination of bond parameters of $CH_3CH_3$ are given in Table 14.1. The calculated results are based on first principles and given in closed-form, exact equations containing fundamental constants only. The agreement between the experimental and calculated results is excellent.

# ETHYLENE MOLECULE ($CH_2CH_2$)

The ethylene molecule $CH_2CH_2$ is formed by the reaction of two dihydrogen carbide radicals:

$$CH_2 + CH_2 \rightarrow CH_2CH_2 \tag{14.241}$$

$CH_2CH_2$ can be solved using the same principles as those used to solve the methane series $CH_{n=1,2,3,4}$, wherein the $2s$ and $2p$ shells of each $C$ hybridize to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between two $C2sp^3$ hybridized orbitals (HOs) to form a molecular orbital (MO) permits each participating hybridized orbital to decrease in radius and energy. First, two sets of two $H$ atomic orbitals (AOs) combine with two sets of two carbon $2sp^3$ HOs to form two dihydrogen carbide groups comprising a linear combination of four diatomic $H_2$-type MOs developed in the Nature of the Chemical Bond of Hydrogen-Type Molecules and Molecular Ions section. Then, the two $CH_2$ groups bond by forming a $H_2$-type MO between the remaining two $C2sp^3$ HOs on each carbon atom.

## FORCE BALANCE OF THE $C=C$-BOND MO OF ETHYLENE

$CH_2CH_2$ comprises a chemical bond between two $CH_2$ radicals wherein each radical comprises two chemical bonds between carbon and hydrogen atoms. The solution of the parameters of $CH_2$ is given in the Dihydrogen Carbide ($CH_2$) section. Each $C-H$ bond of $CH_2$ having two spin-paired electrons, one from an initially unpaired electron of the carbon atom and the other from the hydrogen atom, comprises the linear combination of 75% $H_2$-type ellipsoidal MO and 25% $C2sp^3$ HO. The proton of the $H$ atom and the nucleus of the $C$ atom are along each internuclear axis and serve as the foci. As in the case of $H_2$, each of the two $C-H$-bond MOs is a prolate spheroid with the exception that the ellipsoidal MO surface cannot extend into $C2sp^3$ HO for distances shorter than the radius of the $C2sp^3$ shell since it is energetically unfavorable. Thus, each MO surface comprises a prolate spheroid at the $H$ proton that is continuous with the $C2sp^3$ shell at the $C$ atom whose nucleus serves as the other focus. The electron configuration and the energy, $E\left(C,2sp^3\right)$, of the $C2sp^3$ shell is given by Eqs. (13.422) and (13.428), respectively. The central paramagnetic force due to spin of each $C-H$ bond is provided by the spin-pairing force of the $CH_2$ MO that has the symmetry of an $s$ orbital that superimposes with the $C2sp^3$ orbitals such that the corresponding angular momenta are unchanged.

Two $CH_2$ radicals bond to form $CH_2CH_2$ by forming a MO between the two pairs of remaining $C2sp^3$-HO electrons of the two carbon atoms. However, in this case, the sharing of electrons between four $C2sp^3$ HOs to form a molecular orbital (MO) comprising four spin-paired electrons permits each $C2sp^3$ HO to decrease in radius and energy.

As in the case of the $C-H$ bonds, the $C=C$-bond MO is a prolate-spheroidal-MO surface that cannot extend into $C2sp^3$ HO for distances shorter than the radius of the $C2sp^3$ shell of each atom. Thus, the MO surface comprises a partial prolate spheroid in between the carbon nuclei and is continuous with the $C2sp^3$ shell at each $C$ atom. The energy of the $H_2$-type ellipsoidal MO is matched to that of the $C2sp^3$ shell. As in the case of previous examples of energy-matched MOs such as those of $OH$, $NH$, $CH$, the $C=O$-bond MO of $CO_2$, and the $C-C$-bond MO of $CH_3CH_3$, the $C=C$-bond MO of ethylene must comprise 75% of a $H_2$-type ellipsoidal MO in order to match potential, kinetic, and orbital energy relationships. Thus, the $C=C$-bond MO must comprise a linear combination of two MOs wherein each comprises two $C2sp^3$ HOs and 75% of a $H_2$-type ellipsoidal MO divided between the $C2sp^3$ HOs:

$$2\left(2\;C2sp^3+0.75\;H_2\;MO\right)\rightarrow C=C-bond\;MO \tag{14.242}$$

The linear combination of each $H_2$-type ellipsoidal MO with each $C2sp^3$ HO further comprises an excess 25% charge-density contribution from each $C2sp^3$ HO to the $C=C$-bond MO to achieve an energy minimum. The force balance of the $C=C$-bond MO is determined by the boundary conditions that arise from the linear combination of orbitals according to Eq. (14.242) and the energy matching condition between the $C2sp^3$-HO components of the MO.

Similarly, the energies of each $CH_2$ MO involve each $C2sp^3$ and each $H1s$ electron with the formation of each $C-H$ bond. The sum of the energies of the $H_2$-type ellipsoidal MOs is matched to that of the $C2sp^3$ shell. This energy is determined by the considering the effect of the donation of 25% electron density from the two pairs of $C2sp^3$ HOs to the $C=C$-bond MO with the formation of the $C_{ethylene}2sp^3$ HOs each having a smaller radius. The $2sp^3$ hybridized orbital arrangement is given by Eq. (14.140). The sum $E_T\left(C,2sp^3\right)$ of calculated energies of $C$, $C^+$, $C^{2+}$, and $C^{3+}$ is given by Eq. (14.141). The radius $r_{2sp^3}$ of the $C2sp^3$ shell is given by Eq. (14.142). The Coulombic energy $E_{Coulomb}\left(C,2sp^3\right)$ and the energy $E\left(C,2sp^3\right)$ of the outer electron of the $C2sp^3$ shell are given by Eqs. (14.143) and (14.146), respectively.

Next, consider the formation of the $C=C$-bond MO of ethylene from two $CH_2$ radicals, each having a $C2sp^3$ electron with an energy given by Eq. (14.146). The total energy of the state is given by the sum over the four electrons. The sum $E_T\left(C_{ethylene},2sp^3\right)$ of calculated energies of $C2sp^3$, $C^+$, $C^{2+}$, and $C^{3+}$ from Eqs. (10.123), (10.113-10.114), (10.68), and (10.48), respectively, is:

$$\begin{aligned}E_T\left(C_{ethylene},2sp^3\right)&=-\left(64.3921\;eV+48.3125\;eV+24.2762\;eV+E\left(C,2sp^3\right)\right)\\&=-\left(64.3921\;eV+48.3125\;eV+24.2762\;eV+14.63489\;eV\right)\\&=-151.61569\;eV\end{aligned} \tag{14.243}$$

where $E\left(C,2sp^3\right)$ (Eq. (14.146)) is the sum of the energy of $C$, $-11.27671\;eV$, and the hybridization energy. The orbital-angular-momentum interactions also cancel such that the energy of the $E_T\left(C_{ethylene},2sp^3\right)$ is purely Coulombic.

The sharing of electrons between two pairs of $C2sp^3$ HOs to form a $C=C$-bond MO permits each participating hybridized orbital to decrease in radius and energy. In order to further satisfy the potential, kinetic, and orbital energy relationships, each participating $C2sp^3$ HO donates an excess of 25% per bond of its electron density to the $C=C$-bond MO to form an energy minimum. By considering this electron redistribution in the ethylene molecule as well as the fact that the central field decreases by an integer for each successive electron of the shell, the radius $r_{ethylene2sp^3}$ of the $C2sp^3$ shell of ethylene may be calculated from the Coulombic energy using Eq. (10.102).

$$r_{ethylene2sp^3} = \left(\sum_{n=2}^{5}(Z-n)-0.5\right)\frac{e^2}{8\pi\varepsilon_0\left(e151.61569\ eV\right)} = \frac{9.5e^2}{8\pi\varepsilon_0\left(e151.61569\ eV\right)} = 0.85252a_0 \tag{14.244}$$

where $Z=6$ for carbon. Using Eqs. (10.102) and (14.244), the Coulombic energy $E_{Coulomb}\left(C_{ethylene},2sp^3\right)$ of the outer electron of the $C2sp^3$ shell is:

$$E_{Coulomb}\left(C_{ethylene},2sp^3\right) = \frac{-e^2}{8\pi\varepsilon_0 r_{ethylene2sp^3}} = \frac{-e^2}{8\pi\varepsilon_0 0.85252a_0} = -15.95955\ eV \tag{14.245}$$

During hybridization, the spin-paired $2s$ electrons are promoted to the $C2sp^3$ shell as unpaired electrons. The energy for the promotion is the magnetic energy given by Eq. (13.152). Using Eqs. (14.145) and (14.245), the energy $E\left(C_{ethylene},2sp^3\right)$ of the outer electron of the $C2sp^3$ shell is

$$E\left(C_{ethylene},2sp^3\right) = \frac{-e^2}{8\pi\varepsilon_0 r_{ethylene2sp^3}} + \frac{2\pi\mu_0 e^2\hbar^2}{m_e^2\left(r_3\right)^3} = -15.95955\ eV + 0.19086\ eV = -15.76868\ eV \tag{14.246}$$

Thus, $E_T\left(C=C,2sp^3\right)$, the energy change of each $C2sp^3$ shell with the formation of the $C=C$-bond MO is given by the difference between Eq. (14.146) and Eq. (14.246):

$$E_T\left(C=C,2sp^3\right) = E\left(C_{ethylene},2sp^3\right) - E\left(C,2sp^3\right) = -15.76868\ eV - \left(-14.63489\ eV\right) = -1.13380\ eV \tag{14.247}$$

As in the case of $Cl_2$, each $H_2$-type ellipsoidal MO comprises 75% of the $C=C$-bond MO shared between two $C2sp^3$ HOs corresponding to the electron charge density in Eq. (11.65) of $\frac{-0.75e}{2}$. But, the additional 25% charge-density contribution to each bond of the $C=C$-bond MO causes the electron charge density in Eq. (11.65) to be $\frac{-e}{2}=-0.5e$. The corresponding force constant $k'$ is given by Eq. (14.152). In addition, the energy matching at both $C2sp^3$ HOs further requires that $k'$ be corrected by the hybridization factor given by Eq. (13.430). Thus, the force constant $k'$ to determine the ellipsoidal parameter $c'$ in terms of the central force of the foci (Eq. (11.65)) is given by:

$$k' = C_{C2sp^3HO}\frac{(0.5)2e^2}{4\pi\varepsilon_0} = 0.91771\frac{(0.5)2e^2}{4\pi\varepsilon_0} \tag{14.248}$$

The distance from the origin to each focus $c'$ is given by substitution of Eq. (14.248) into Eq. (13.60). Thus, the distance from the origin of the component of the double $C=C$-bond MO to each focus $c'$ is given by:

$$c' = a\sqrt{\frac{\hbar^2 4\pi\varepsilon_0}{(0.91771)m_e e^2 a}} = \sqrt{\frac{aa_0}{0.91771}} \tag{14.249}$$

The internuclear distance from Eq. (14.249) is:

$$2c' = 2\sqrt{\frac{aa_0}{0.91771}} \tag{14.250}$$

The length of the semiminor axis of the prolate spheroidal $C=C$-bond MO $b=c$ is given by Eq. (13.62). The eccentricity, $e$, is given by Eq. (13.63). The solution of the semimajor axis $a$ then allows for the solution of the other axes of each prolate spheroid and eccentricity of the $C=C$-bond MO. From the energy equation and the relationship between the axes, the dimensions of the $C=C$-bond MO are solved.

The general equations for the energy components of $V_e$, $V_p$, $T$, $V_m$, and $E_T$ of the $C=C$-bond MO are the same as those of the $CH$ MO except that energy of the $C_{ethylene}2sp^3$ HO is used and the double-bond nature is considered. In the case of a single bond, the prolate spheroidal $H_2$-type MO transitions to the $C_{ethylene}2sp^3$ HO of each carbon, and the energy of the $C_{ethylene}2sp^3$ shell must remain constant and equal to the $E\left(C_{ethylene},2sp^3\right)$ given by Eq. (14.246). Thus, the energy $E\left(C_{ethylene},2sp^3\right)$ in Eq. (14.246) adds to that of the energies of the corresponding $H_2$-type ellipsoidal MO. The second bond of the double $C=C$-bond MO also transitions to the $C_{ethylene}2sp^3$ HO of each $C$. The energy of a second $H_2$-type ellipsoidal MO adds to the first energy component, and the two bonds achieve an energy minimum as a linear combination of the two $H_2$-type ellipsoidal MOs each having the carbon nuclei as the foci. Each $C-C$-bond MO comprises the same $C_{ethylene}2sp^3$ HO shells of constant energy given by Eq. (14.246). As in the case of the water, $NH_2$, and ammonia molecules given by Eqs. (13.180), (13.320), and (13.372), respectively, the energy of the redundant shell is subtracted from the total energy of the linear combination of the $\sigma$ MO. Thus, the total energy $E_T\left(C=C,\sigma\right)$ of the $\sigma$ component of the $C=C$-bond MO is given by the sum of the energies of the two bonds each comprising the linear combination of the $C_{ethylene}2sp^3$ HO and the $H_2$-type ellipsoidal MO as given by Eq. (14.242) wherein the $E_T$ terms add positively, the $E\left(C_{ethylene},2sp^3\right)$ terms cancel, and the energy matching condition between the components is provided by Eq. (14.248). Using Eqs. (13.431) and (14.246), $E_T\left(C=C,\sigma\right)$ is given by:

$$\begin{aligned} E_T\left(C=C,\sigma\right) &= E_T + E\left(C_{ethylene},2sp^3\right) - E\left(C_{ethylene},2sp^3\right) \\ &= -\frac{2e^2}{8\pi\varepsilon_0 c'}\left[\left(0.91771\right)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right] \end{aligned} \tag{14.251}$$

The total energy term of the double $C=C$-bond MO is given by the sum of the two $H_2$-type ellipsoidal MOs given by Eq. (11.212). To match this boundary condition, $E_T\left(C=C,\sigma\right)$ given by Eq. (14.251) is set equal to two times Eq. (13.75).

$$E_T\left(C=C,\sigma\right) = -\frac{2e^2}{8\pi\varepsilon_0 c'}\left[\left(0.91771\right)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right] = -63.27074\ eV \tag{14.252}$$

From the energy relationship given by Eq. (14.252) and the relationship between the axes given by Eqs. (14.249-14.250) and (13.62-13.63), the dimensions of the $C=C$-bond MO can be solved.

Substitution of Eq. (14.249) into Eq. (14.252) gives:

$$\frac{2e^2}{8\pi\varepsilon_0\sqrt{\frac{aa_0}{0.91771}}}\left[\left(0.91771\right)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+\sqrt{\frac{aa_0}{0.91771}}}{a-\sqrt{\frac{aa_0}{0.91771}}}-1\right] = e63.27074 \tag{14.253}$$

The most convenient way to solve Eq. (14.253) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is:

$$a = 1.47228a_0 = 7.79098\ X\ 10^{-11}\ m \tag{14.254}$$

Substitution of Eq. (14.254) into Eq. (14.249) gives

$$c' = 1.26661a_0 = 6.70259\ X\ 10^{-11}\ m \tag{14.255}$$

The internuclear distance given by multiplying Eq. (14.255) by two is:

$$2c' = 2.53321a_0 = 1.34052\ X\ 10^{-10}\ m \tag{14.256}$$

The experimental bond distance is [3]:

$$2c' = 1.339\ X\ 10^{-10}\ m \tag{14.257}$$

Substitution of Eqs. (14.254-14.255) into Eq. (13.62) gives:

$$b = c = 0.75055a_0 = 3.97173\ X\ 10^{-11}\ m \tag{14.258}$$

Substitution of Eqs. (14.252-14.255) into Eq. (13.63) gives:

$$e = 0.86030 \tag{14.259}$$

The nucleus of the $C$ atoms comprise the foci of the $H_2$-type ellipsoidal MO. The parameters of the point of intersection of the $H_2$-type ellipsoidal MO and the $C_{ethylene}2sp^3$ HO are given by Eqs. (13.84-13.95) and (13.261-13.270). The polar intersection angle $\theta'$ is given by Eq. (13.261) where $r_n = r_{ethylene2sp^3} = 0.85252a_0$ is the radius of the $C_{ethylene}2sp^3$ shell. Substitution of Eqs. (14.254-14.255) into Eq. (13.261) gives:

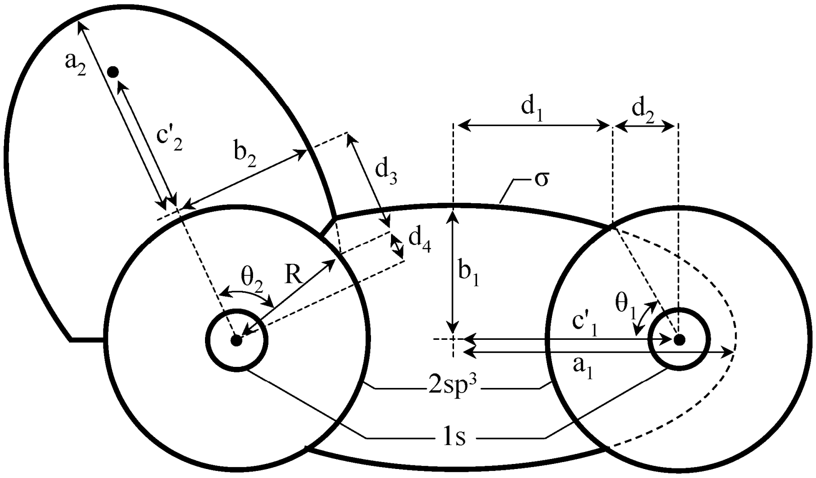
$$\theta' = 129.84° \tag{14.260}$$

Then, the angle $\theta_{C=C_{ethylene}2sp^3HO}$ the radial vector of the $C2sp^3$ HO makes with the internuclear axis is:

$$\theta_{C=C_{ethylene}2sp^3HO} = 180° - 129.84° = 50.16° \tag{14.261}$$

as shown in Figure 14.8.

Figure 14.8. The cross section of the $C=C$-bond MO ($\sigma$ MO) and one $C-H$-bond MO of ethylene showing the axes, angles, and point of intersection of each $H_2$-type ellipsoidal MO with the corresponding $C_{ethylene}2sp^3$ HO. The continuation of each $H_2$-type-ellipsoidal-MO basis element of the $C=C$ bond and the $C-H$-bond beyond the intersection point with each $C_{ethylene}2sp^3$ shell and $\sigma$ MO is shown as dashed since each only serves to solve the energy match with the $C_{ethylene}2sp^3$ shell and does not represent charge density. Similarly, the vertical dashed line only designates the parameters of each intersection point. The actual charge density is shown by the solid lines. Legend: $a$: semimajor axis, $b$: semiminor axis, $c'$: internuclear distance, $d_1 : d_{C=C_{ethylene},H_2MO}$, $\theta_1 : \theta_{C=C_{ethylene}2sp^3HO}$, $d_2 : d_{C=C_{ethylene}2sp^3HO}$, $R : r_{ethyleneC2sp^3}$, $d_3 : d_{C-H_{ethylene},H_2MO}$, $\theta_2 : \theta_{C-H_{ethylene}2sp^3HO}$, and $d_4 : d_{C-H_{ethylene}2sp^3HO}$.



Consider the right-hand intersection point. The Cartesian $\mathbf{i}$-coordinate of the interception point of the MO and the AO can be calculated using the MO ellipsoidal parameters by first calculating the parametric angle in Eq. (11.83) that matches Cartesian $\mathbf{j}$-coordinate components at the point of intersection. Thus, the matching elliptic parametric angle $\omega t = \theta_{C=C_{ethylene},H_2MO}$ satisfies the following relationship:

$$r_{ethylene2sp^3} \sin\theta_{C=C_{ethylene}2sp^3HO} = 0.85252a_0 \sin\theta_{C=C_{ethylene}2sp^3HO} = b\sin\theta_{C=C_{ethylene},H_2MO} \tag{14.262}$$

such that

$$\theta_{C=C_{ethylene},H_2MO} = \sin^{-1}\frac{0.85252a_0 \sin\theta_{C=C_{ethylene}2sp^3HO}}{b} = \sin^{-1}\frac{0.85252a_0 \sin 50.16°}{b} \tag{14.263}$$

with the use of Eq. (14.261). Substitution of Eq. (14.258) into Eq. (14.263) gives:

$$\theta_{C=C_{ethylene},H_2MO} = 60.70° \tag{14.264}$$

Then, the distance $d_{C=C_{ethylene},H_2MO}$ along the internuclear axis from the origin of $H_2$-type ellipsoidal MO to the point of intersection of the orbitals is given by:

$$d_{C=C_{ethylene},H_2MO} = a\cos\theta_{C=C_{ethylene},H_2MO} \tag{14.265}$$

Substitution of Eqs. (14.254) and (14.264) into Eq. (14.265) gives:

$$d_{C=C_{ethylene},H_2MO} = 0.72040a_0 = 3.81221 \; X \; 10^{-11} \; m \tag{14.266}$$

The distance $d_{C=C_{ethylene}2sp^3HO}$ along the internuclear axis from the origin of the $C$ atom to the point of intersection of the orbitals is given by:

$$d_{C=C_{ethylene}2sp^3HO} = c' - d_{C=C_{ethylene},H_2MO} \tag{14.267}$$

Substitution of Eqs. (14.255) and (14.266) into Eq. (14.267) gives:

$$d_{C=C_{ethylene}2sp^3HO} = 0.54620a_0 = 2.89038 \; X \; 10^{-11} \; m \tag{14.268}$$

## FORCE BALANCE OF THE $CH_2$ MOS OF ETHYLENE

Each of the two equivalent $CH_2$ MOs must comprise two $C-H$ bonds with each comprising 75% of a $H_2$-type ellipsoidal MO and a $C2sp^3$ HO as given by Eq. (13.494):

$$2\left[1\ C2sp^3 + 0.75\ H_2\ MO\right] \rightarrow CH_2\ MO \tag{14.269}$$

The force balance of the $CH_2$ MO is determined by the boundary conditions that arise from the linear combination of orbitals according to Eq. (13.494) and the energy matching condition between the hydrogen and $C2sp^3$ HO components of the MO.

The force constant $k'$ to determine the ellipsoidal parameter $c'$ of each $H_2$-type-ellipsoidal-MO component of the $CH_2$ MO in terms of the central force of the foci is given by Eq. (13.59). The distance from the origin of each $C-H$-bond MO to each focus $c'$ is given by Eq. (13.60). The internuclear distance is given by Eq. (13.61). The length of the semiminor axis of the prolate spheroidal $C-H$-bond MO $b=c$ is given by Eq. (13.62). The eccentricity, $e$, is given by Eq. (13.63). The solution of the semimajor axis $a$ then allows for the solution of the other axes of each prolate spheroid and eccentricity of each $C-H$-bond MO. From the energy equation and the relationship between the axes, the dimensions of the $CH_2$ MO are solved.

Consider the formation of the double $C=C$-bond MO of ethylene from two $CH_2$ radicals, each having a $C2sp^3$ shell with an energy given by Eq. (14.146). The energy components of $V_e$, $V_p$, $T$, $V_m$, and $E_T$ are the same as those of the dihydrogen carbide radical, two times those of $CH$ corresponding to the two $C-H$ bonds, except that two times $E_T\left(C=C,2sp^3\right)$ is subtracted from $E_T\left(CH_2\right)$ of Eq. (13.495). The subtraction of the energy change of the $C2sp^3$ shells with the formation of the $C=C$-bond MO matches the energy of the $C-H$-bond MOs to the decrease in the energy of the $C2sp^3$ HOs. Using Eqs. (13.495) and (14.247), $E_{T_{ethylene}}\left(CH_2\right)$ is given by:

$$E_{T_{ethylene}}\left(CH_2\right) = E_T + E\left(C,2sp^3\right) - 2E_T\left(C=C,2sp^3\right) = \left(\begin{array}{l} -\dfrac{2e^2}{8\pi\varepsilon_0 c'}\left[\left(0.91771\right)\left(2-\dfrac{1}{2}\dfrac{a_0}{a}\right)\ln\dfrac{a+c'}{a-c'}-1\right] \\ -14.63489\ eV - \left(-2.26758\ eV\right) \end{array}\right) \tag{14.270}$$

$E_{T_{ethylene}}\left(CH_2\right)$ given by Eq. (14.270) is set equal to two times the energy of the $H_2$-type ellipsoidal MO minus the Coulombic energy of $H$ given by Eq. (13.496):

$$E_{T_{ethylene}}\left(CH_2\right) = \left(\begin{array}{l} -\dfrac{2e^2}{8\pi\varepsilon_0 c'}\left[\left(0.91771\right)\left(2-\dfrac{1}{2}\dfrac{a_0}{a}\right)\ln\dfrac{a+c'}{a-c'}-1\right] \\ -14.63489\ eV - \left(-2.26758\ eV\right) \end{array}\right) = -49.66493\ eV \tag{14.271}$$

From the energy relationship given by Eq. (14.271) and the relationship between the axes given by Eqs. (13.60-13.63), the dimensions of the $CH_2$ MO can be solved.

Substitution of Eq. (13.60) into Eq. (14.271) gives:

$$\frac{2e^2}{8\pi\varepsilon_0\sqrt{\dfrac{2aa_0}{3}}}\left[\left(0.91771\right)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+\sqrt{\dfrac{2aa_0}{3}}}{a-\sqrt{\dfrac{2aa_0}{3}}}-1\right] = e37.29762 \tag{14.272}$$

The most convenient way to solve Eq. (14.272) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is:

$$a = 1.56946a_0 = 8.30521\ X\ 10^{-11}\ m \tag{14.273}$$

Substitution of Eq. (14.273) into Eq. (13.60) gives:

$$c' = 1.02289a_0 = 5.41290\ X\ 10^{-11}\ m \tag{14.274}$$

The internuclear distance given by multiplying Eq. (14.274) by two is:

$$2c' = 2.04578a_0 = 1.08258\ X\ 10^{-10}\ m \tag{14.275}$$

The experimental bond distance is [3]:

$$2c' = 1.087\ X\ 10^{-10}\ m \tag{14.276}$$

Substitution of Eqs. (14.273-14.274) into Eq. (14.62) gives:

$$b = c = 1.19033a_0 = 6.29897\ X\ 10^{-11}\ m \tag{14.277}$$

Substitution of Eqs. (14.273-14.274) into Eq. (14.63) gives:

$$e = 0.65175 \tag{14.278}$$

The nucleus of the $H$ atom and the nucleus of the $C$ atom comprise the foci of each $H_2$-type ellipsoidal MO. The parameters of the point of intersection of the $H_2$-type ellipsoidal MO and the $C_{ethylene}2sp^3$ HO are given by Eqs. (13.84-13.95) and (13.261-13.270). The polar intersection angle $\theta'$ is given by Eq. (13.261) where $r_n = r_{ethylene2sp^3} = 0.85252a_0$ is the radius of the $C_{etthylene}2sp^3$ shell. Substitution of Eqs. (14.273-14.274) into Eq. (13.261) gives:

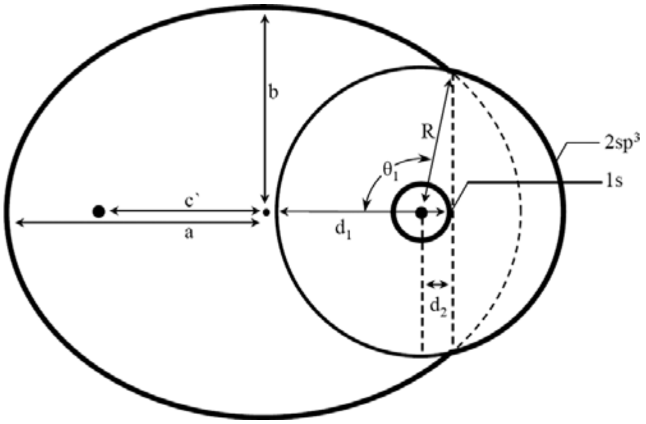
$$\theta' = 84.81° \tag{14.279}$$

Then, the angle $\theta_{C-H_{ethylene}2sp^3HO}$ the radial vector of the $C2sp^3$ HO makes with the internuclear axis is:

$$\theta_{C-H_{ethylene}2sp^3HO} = 180° - 84.81° = 95.19° \tag{14.280}$$

as shown in Figure 14.9.

Figure 14.9. The cross section of one $C-H$-bond MO of ethylene showing the axes, angles, and point of intersection of the $H_2$-type ellipsoidal MO with the $C_{ethylene}2sp^3$ HO. The continuation of the $H_2$-type-ellipsoidal-MO basis element beyond the intersection point with the $C_{ethylene}2sp^3$ shell is shown as dashed since it only serves to solve the energy match with the $C_{ethylene}2sp^3$ shell and does not represent charge density. Similarly, the vertical dashed line only designates the parameters of the intersection point. The actual charge density is shown by the solid lines. Legend: $a$: semimajor axis, $b$: semiminor axis, $c'$: internuclear distance, $d_1 : d_{C-H_{ethylene},H_2MO}$, $\theta_1 : \theta_{C-H_{ethylene}2sp^3HO}$, $d_2 : d_{C-H_{ethylene}2sp^3HO}$, and $R : r_{ethylene2sp^3}$.



The Cartesian $\mathbf{i}$-coordinate of the interception point of the MO and the AO can be calculated using the MO ellipsoidal parameters by first calculating the parametric angle in Eq. (11.83) that matches Cartesian $\mathbf{j}$-coordinate components at the point of intersection. Thus, the matching elliptic parametric angle $\omega t = \theta_{C-H_{ethylene},H_2MO}$ satisfies the following relationship:

$$r_{ethylene2sp^3} \sin\theta_{C-H_{ethylene}2sp^3HO} = 0.85252a_0 \sin\theta_{C-H_{ethylene}2sp^3HO} = b\sin\theta_{C-H,H_2MO} \tag{14.281}$$

such that

$$\theta_{C-H_{ethylene},H_2MO} = \sin^{-1}\frac{0.85252a_0\sin\theta_{C-H_{ethylene}2sp^3HO}}{b} = \sin^{-1}\frac{0.85252a_0\sin 95.19°}{b} \tag{14.282}$$

with the use of Eq. (14.280). Substitution of Eq. (14.277) into Eq. (14.282) gives:

$$\theta_{C-H_{ethylene},H_2MO} = 45.50° \tag{14.283}$$

Then, the distance $d_{C-H_{ethylene},H_2MO}$ along the internuclear axis from the origin of $H_2$-type ellipsoidal MO to the point of intersection of the orbitals is given by:

$$d_{C-H_{ethylene},H_2MO} = a\cos\theta_{C-H_{ethylene},H_2MO} \tag{14.284}$$

Substitution of Eqs. (14.273) and (14.283) into Eq. (14.284) gives:

$$d_{C-H_{ethylene},H_2MO} = 1.10002a_0 = 5.82107\ X\ 10^{-11}\ m \tag{14.285}$$

The distance $d_{C-H_{ethylene}2sp^3HO}$ along the internuclear axis from the origin of the $C$ atom to the point of intersection of the orbitals is given by:

$$d_{C-H_{ethylene}2sp^3HO} = d_{C-H_{ethylene},H_2MO} - c' \tag{14.286}$$

Substitution of Eqs. (14.274) and (14.285) into Eq. (14.286) gives:

$$d_{C-H_{ethylene}2sp^3HO} = 0.07713a_0 = 4.08171\ X\ 10^{-12}\ m \tag{14.287}$$

## BOND ANGLE OF THE $CH_2$ GROUPS

Each $CH_2$ MO comprises a linear combination of two $C-H$-bond MOs. Each $C-H$-bond MO comprises the superposition of a $H_2$-type ellipsoidal MO and the $C_{ethylene}2sp^3$ HO. A bond is also possible between the two H atoms of the $C-H$ bonds. Such $H-H$ bonding would decrease the $C-H$ bond strength since electron density would be shifted from the $C-H$ bonds to the $H-H$ bond. Thus, the bond angle between the two $C-H$ bonds is determined by the condition that the total energy of the $H_2$-type ellipsoidal MO between the terminal $H$ atoms of the $C-H$ bonds is zero. From Eqs. (11.79) and (13.228), the distance from the origin to each focus of the $H-H$ ellipsoidal MO is:

$$c' = a\sqrt{\frac{\hbar^2 4\pi\varepsilon_0}{m_e e^2 2a}} = \sqrt{\frac{aa_0}{2}} \tag{14.288}$$

The internuclear distance from Eq. (13.229) is:

$$2c' = 2\sqrt{\frac{aa_0}{2}} \tag{14.289}$$

The length of the semiminor axis of the prolate spheroidal $H-H$ MO $b=c$ is given by Eq. (14.62).

The bond angle of the $CH_2$ groups of ethane is derived by using the orbital composition and an energy matching factor as in the case with the dihydrogen carbide radical and the $CH_3$ groups of ethane. Since the two $H_2$-type ellipsoidal MOs initially comprise 75% of the $H$ electron density of $H_2$ and the energy of each $H_2$-type ellipsoidal MO is matched to that of the $C_{ethylene}2sp^3$ HO, the component energies and the total energy $E_T$ of the $H-H$ bond are given by Eqs. (13.67-13.73) except that $V_e$, $T$, and $V_m$ are corrected for the hybridization-energy-matching factor of $0.85252$. Hybridization with 25% electron donation to the $C=C$-bond gives rise to the $C_{ethylene}2sp^3$ HO-shell Coulombic energy $E_{Coulomb}\left(C_{ethylene}, 2sp^3\right)$ given by Eq. (14.245). The corresponding normalization factor for determining the zero of the total $H-H$ bond energy is given by the ratio of $15.95955\ eV$, the magnitude of $E_{Coulomb}\left(C_{ethylene}, 2sp^3\right)$ given by Eq. (14.245), and $13.605804\ eV$, the magnitude of the Coulombic energy between the electron and proton of $H$ given by Eq. (1.264). The hybridization energy factor $C_{ethyleneC2sp^3HO}$ is:

$$C_{ethyleneC2sp^3HO} = \frac{\frac{e^2}{8\pi\varepsilon_0 a_0}}{\frac{e^2}{8\pi\varepsilon_0 r_{ethylene2sp^3}}} = \frac{\frac{e^2}{8\pi\varepsilon_0 a_0}}{\frac{e^2}{8\pi\varepsilon_0 0.85252 a_0}} = \frac{13.605804\ eV}{15.95955\ eV} = 0.85252 \tag{14.290}$$

Substitution of Eq. (14.290) into Eq. (13.233) or Eq. (14.195) with the hybridization factor of $0.85252$ gives:

$$0 = \left[\begin{array}{l} \dfrac{-e^2}{8\pi\varepsilon_0\sqrt{\dfrac{aa_0}{2}}}\left[(0.85252)^{-1}\left(\dfrac{3}{2}-\dfrac{3}{8}\dfrac{a_0}{a}\right)\ln\dfrac{a+\sqrt{\dfrac{aa_0}{2}}}{a-\sqrt{\dfrac{aa_0}{2}}}-1\right]\left[1+\sqrt{\dfrac{2\hbar\sqrt{\dfrac{\dfrac{0.75e^2}{4\pi\varepsilon_0 a^3}}{m_e}}}{m_e c^2}}\right] \\ +\hbar\sqrt{\dfrac{\dfrac{0.75e^2}{8\pi\varepsilon_0 a^3}-\dfrac{e^2}{8\pi\varepsilon_0\left(a+c'\right)^3}}{0.5m_p}} \end{array}\right] \tag{14.291}$$

From the energy relationship given by Eq. (14.291) and the relationship between the axes given by Eqs. (14.192-14.193) and (14.62-14.63), the dimensions of the $H-H$ MO can be solved.

The most convenient way to solve Eq. (14.291) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is:

$$a = 6.0400a_0 = 3.1962\ X\ 10^{-10}\ m \tag{14.292}$$

Substitution of Eq. (14.292) into Eq. (14.288) gives:

$$c' = 1.7378a_0 = 9.1961\ X\ 10^{-11}\ m \tag{14.293}$$

The internuclear distance given by multiplying Eq. (14.293) by two is:

$$2c' = 3.4756a_0 = 1.8392\ X\ 10^{-10}\ m \tag{14.294}$$

Substitution of Eqs. (14.292-14.293) into Eq. (14.62) gives:

$$b = c = 5.7846a_0 = 3.0611\ X\ 10^{-10}\ m \tag{14.295}$$

Substitution of Eqs. (14.292-14.293) into Eq. (14.63) gives:

$$e = 0.2877 \tag{14.296}$$

From, $2c'_{H-H}$ (Eq. (14.294)), the distance between the two $H$ atoms when the total energy of the corresponding MO is zero (Eq. (14.291)), and $2c'_{C-H}$ (Eq. (14.275)), the internuclear distance of each $C-H$ bond, the corresponding bond angle can be determined from the law of cosines. Using, Eq. (13.242), the bond angle $\theta_{HCH}$ between the $C-H$ bonds is:

$$\theta_{HCH} = \cos^{-1}\left(\frac{2(2.04578)^2 - (3.4756)^2}{2(2.04578)^2}\right) = \cos^{-1}(-0.44318) = 116.31° \tag{14.297}$$

The experimental angle between the $C-H$ bonds is [11]:

$$\theta_{HCH} = 116.6° \tag{14.298}$$

The $C=C$ bond is along the z-axis. Thus, based on the symmetry of the equivalent bonds, the bond angle $\theta_{C=C-H}$ between the internuclear axis of the $C=C$ bond and a $H$ atom of the $CH_2$ groups is given by:

$$\theta_{C=C-H} = \frac{(360° - \theta_{HCH})}{2} \tag{14.299}$$

Substitution of Eq. (14.298) into Eq. (14.299) gives:

$$\theta_{C=C-H} = 121.85° \tag{14.300}$$

The experimental angle between the $C=C-H$ bonds is [11]:

$$\theta_{C=C-H} = 121.7° \tag{14.301}$$

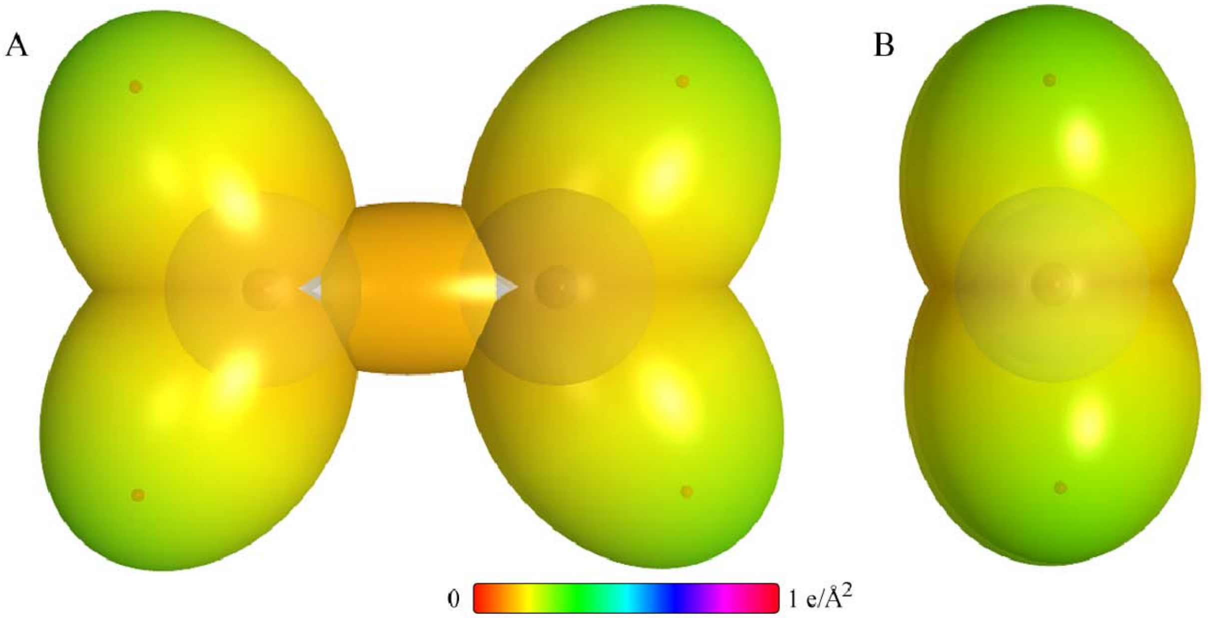
and [3]

$$\theta_{C=C-H} = 121.3° \tag{14.302}$$

The $C=C$ bond and $H$ atoms of ethylene line in a plane, and rotation about the $C=C$ is not possible due to conservation of angular momentum in the two sets of spin-paired electrons of the double bond. The $CH_2CH_2$ MO shown in Figure 14.10 was rendered using these parameters.

The charge-density in the $C=C$-bond MO is increased by a factor of 0.25 per bond with the formation of the $C_{ethylene}2sp^3$ HOs each having a smaller radius. Using the orbital composition of the $CH_2$ groups (Eq. (14.269)) and the $C=C$-bond MO (Eq. (14.242)), the radii of $C1s = 0.17113a_0$ (Eq. (10.51)) and $C_{ethylene}2sp^3 = 0.85252a_0$ (Eq. (14.244)) shells, and the parameters of the $C=C$-bond (Eqs. (13.3-13.4), (14.254-14.256), and (14.258-14.268)), the parameters of the $C-H$-bond MOs (Eqs. (13.3-13.4), (14.273-14.275), and (14.277-14.287)), and the bond-angle parameters (Eqs. (14.297-14.302)), the charge-density of the $CH_2CH_2$ MO comprising the linear combination of two sets of two $C-H$-bond MOs and a $C=C$-bond MO bridging the two $CH_2$ groups is shown in Figure 14.10. Each $C-H$-bond MO comprises a $H_2$-type ellipsoidal MO and a $C_{ethylene}2sp^3$ HO having the dimensional diagram shown in Figure 14.9. The $C=C$-bond MO comprises a $H_2$-type ellipsoidal MO bridging two $C_{ethylene}2sp^3$ HOs having the dimensional diagram shown in Figure 14.8.

Figure 14.10. $CH_2CH_2$ MO comprising the linear combination of two sets of two $C-H$-bond MOs and a $C=C$-bond MO. (A) Color scale, translucent view of the charge-density of the $C=C$-bond MO with the $C_{ethylene}2sp^3$ HOs shown transparently. The $C=C$-bond MO comprises a $H_2$-type ellipsoidal MO bridging two sets of two $C_{ethylene}2sp^3$ HOs. For each $C-H$ and the $C=C$ bond, the ellipsoidal surface of the $H_2$-type ellipsoidal MO that transitions to the $C_{ethylene}2sp^3$ HO, the $C_{ethylene}2sp^3$ HO shell, inner most $C1s$ shell, and the nuclei (red, not to scale), are shown. (B)-(D) End-on view, translucent view high-lighting the $C=C$-bond MO, and opaque view of the charge-density of the $CH_2CH_2$ MO, respectively.



## ENERGIES OF THE $CH_2$ GROUPS

The energies of each $CH_2$ group of ethylene are given by the substitution of the semiprincipal axes (Eqs. (14.273-14.274) and (14.277)) into the energy equations of dihydrogen carbide (Eqs. (13.510-13.514)), with the exception that two times $E_T\left(C=C,2sp^3\right)$ (Eq. (14.247)) is subtracted from $E_T\left(CH_2\right)$ in Eq. (13.514).

$$V_e = 2\left(0.91771\right)\frac{-2e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -76.00757\ eV \tag{14.303}$$

$$V_p = \frac{2e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}} = 26.60266\ eV \tag{14.304}$$

$$T = 2\left(0.91771\right)\frac{\hbar^2}{2m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = 24.21459\ eV \tag{14.305}$$

$$V_m = 2\left(0.91771\right)\frac{-\hbar^2}{4m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -12.10730\ eV \tag{14.306}$$

$$E_{T_{ethylene}}\left(CH_2\right) = \left(\begin{array}{l} -\dfrac{2e^2}{8\pi\varepsilon_0 c'}\left[\left(0.91771\right)\left(2-\dfrac{1}{2}\dfrac{a_0}{a}\right)\ln\dfrac{a+c'}{a-c'}-1\right] \\ -14.63489\ eV-\left(-2.26758\ eV\right) \end{array}\right) = -49.66493\ eV \tag{14.307}$$

where $E_{T_{ethylene}}\left(CH_2\right)$ is given by Eq. (14.270) which is reiteratively matched to Eq. (13.496) within five-significant-figure round off error.

## VIBRATION OF THE $^{12}CH_2$ GROUPS

The vibrational energy levels of $CH_2$ in ethylene may be solved as two equivalent coupled harmonic oscillators by developing the Lagrangian, the differential equation of motion, and the eigenvalue solutions [9] wherein the spring constants are derived from the central forces as given in the Vibration of Hydrogen-Type Molecular Ions section and the Vibration of Hydrogen-Type Molecules section.

## THE DOPPLER ENERGY TERMS OF THE $^{12}CH_2$ GROUPS

The equations of the radiation reaction force of the $CH_2$ groups in ethylene are the same as those of the dihydrogen carbide radical with the substitution of the $CH_2$-group parameters. Using Eq. (13.515), the angular frequency of the reentrant oscillation in the transition state is:

$$\omega = \sqrt{\frac{\frac{0.75e^2}{4\pi\varepsilon_0 b^3}}{m_e}} = 2.75685\ X\ 10^{16}\ rad/s \tag{14.308}$$

where $b$ is given by Eq. (14.277). The kinetic energy, $E_K$, is given by Planck's equation (Eq. (11.127)):

$$\bar{E}_K = \hbar\omega = \hbar 2.75685\ X\ 10^{16}\ rad/s = 18.14605\ eV \tag{14.309}$$

In Eq. (11.181), substitution of $E_T(H_2)$ (Eqs. (11.212) and (13.75)), the maximum total energy of each $H_2$-type MO, for $E_{h\nu}$, the mass of the electron, $m_e$, for $M$, and the kinetic energy given by Eq. (14.309) for $\bar{E}_K$ gives the Doppler energy of the electrons of each of the two bonds for the reentrant orbit:

$$\bar{E}_D \cong E_{h\nu}\sqrt{\frac{2\bar{E}_K}{Mc^2}} = -31.63537\ eV\sqrt{\frac{2e(18.14605\ eV)}{m_e c^2}} = -0.26660\ eV \tag{14.310}$$

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency. The decrease in the energy of $CH_2$ due to the reentrant orbit of each bond in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei, $\bar{E}_{osc}$, is given by the sum of the corresponding energies, $\bar{E}_D$ given by Eq. (14.310) and $\bar{E}_{Kvib}$, the average kinetic energy of vibration which is 1/2 of the vibrational energy of each $C-H$ bond. Using $\omega_e$ given by Eq. (13.458) for $\bar{E}_{Kvib}$ of the transition state having two independent bonds, $\bar{E}'_{ethylene\ osc}\left(^{12}CH_2\right)$ per bond is:

$$\bar{E}'_{ethylene\ osc}\left(^{12}CH_2\right) = \bar{E}_D + \bar{E}_{Kvib} = \bar{E}_D + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \tag{14.311}$$

$$\bar{E}'_{ethylene\ osc}\left(^{12}CH_2\right) = -0.26660\ eV + \frac{1}{2}(0.35532\ eV) = -0.08894\ eV \tag{14.312}$$

Given that the vibration and reentrant oscillation is for two $C-H$ bonds, $\bar{E}_{ethylene\ osc}\left(^{12}CH_2\right)$, is:

$$\bar{E}_{ethylene\ osc}\left(^{12}CH_2\right) = 2\left(\bar{E}_D + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right) = 2\left(-0.26660\ eV + \frac{1}{2}(0.35532\ eV)\right) = -0.17788\ eV \tag{14.313}$$

## TOTAL AND DIFFERENCE ENERGIES OF THE $^{12}CH_2$ GROUPS

$E_{ethyleneT+osc}\left(^{12}CH_2\right)$, the total energy of each $^{12}CH_2$ group including the Doppler term, is given by the sum of $E_{T_{ethylene}}(CH_2)$ (Eq. (14.307)) and $\bar{E}_{ethylene\ osc}\left(^{12}CH_2\right)$ given by Eq. (14.313):

$$\begin{aligned} E_{ethyleneT+osc}\left(^{12}CH_2\right) &= \begin{pmatrix} V_e + T + V_m + V_p + E\left(C, 2sp^3\right) \\ -2E_T\left(C=C, 2sp^3\right) + \bar{E}_{ethylene\ osc}\left(^{12}CH_2\right) \end{pmatrix} \\ &= E_{T_{ethylene}}(CH_2) + \bar{E}_{ethylene\ osc}\left(^{12}CH_2\right) \end{aligned} \tag{14.314}$$

$$E_{ethyleneT+osc}\left({}^{12}CH_2\right)=\left\{\begin{array}{l}\left(\begin{array}{l}\dfrac{-2e^2}{8\pi\varepsilon_0 c'}\left[\left(0.91771\right)\left(2-\dfrac{1}{2}\dfrac{a_0}{a}\right)\ln\dfrac{a+c'}{a-c'}-1\right]\\ -14.63489\ eV-\left(-2.26759\ eV\right)\end{array}\right)\\ -2\left(\left(31.63536831\ eV\right)\sqrt{\dfrac{2\hbar\sqrt{\dfrac{\dfrac{3}{4}\dfrac{e^2}{4\pi\varepsilon_0 b^3}}{m_e}}}{m_e c^2}}-\dfrac{1}{2}\hbar\sqrt{\dfrac{k}{\mu}}\right)\end{array}\right\}$$
$$=-49.66493\ eV-2\left(0.26660\ eV-\frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right) \tag{14.315}$$

From Eqs. (14.313-14.315), the total energy of each ${}^{12}CH_2$ is:

$$\begin{aligned}E_{ethyleneT+osc}\left({}^{12}CH_2\right)&=-49.66493\ eV+\bar{E}_{ethylene\ osc}\left({}^{12}CH_2\right)\\&=-49.66493\ eV-2\left(0.26660\ eV-\frac{1}{2}\left(0.35532\ eV\right)\right)\\&=-49.84282\ eV\end{aligned} \tag{14.316}$$

where $\omega_e$ given by Eq. (13.458) was used for the $\hbar\sqrt{\frac{k}{\mu}}$ term.

The total energy for each dihydrogen carbide radical given by Eq. (13.523) is:

$$\begin{aligned}E_{radicalT+osc}\left({}^{12}CH_2\right)&=-49.66493\ eV+\bar{E}_{radicalosc}\left({}^{12}CH_2\right)\\&=-49.66493\ eV-2\left(0.25493\ eV-\frac{1}{2}\left(0.35532\ eV\right)\right)\\&=-49.81948\ eV\end{aligned} \tag{14.317}$$

The difference in energy between the $CH_2$ groups and the dihydrogen carbide radical $\Delta E_{T+osc}\left({}^{12}CH_2\right)$ is given by two times the difference between Eqs. (14.316) and (14.317):

$$\begin{aligned}\Delta E_{T+osc}\left({}^{12}CH_2\right)&=2\left(E_{ethyleneT+osc}\left({}^{12}CH_2\right)-E_{radicalT+osc}\left({}^{12}CH_2\right)\right)\\&=2\left(-49.84282\ eV-\left(-49.81948\ eV\right)\right)\\&=-0.04667\ eV\end{aligned} \tag{14.318}$$

## SUM OF THE ENERGIES OF THE $C=C$ $\sigma$ MO AND THE HOS OF ETHYLENE

The energy components of $V_e$, $V_p$, $T$, $V_m$, and $E_T$ of the $C=C$-bond MO are the same as those of the $CH$ MO except that each term is multiplied by two corresponding to the double bond and the energy term corresponding to the $C_{ethylene}2sp^3$ HOs in the equation for $E_T$ is zero. The energies of each $C=C$-bond MO are given by the substitution of the semiprincipal axes (Eqs. (14.254-14.255) and (14.258)) into two times the energy equations of the $CH$ MO (Eqs. (13.449-13.453)), with the exception that zero replaces $E\left(C,2sp^3\right)$ in Eq. (13.453).

$$V_e=2\left(0.91771\right)\frac{-2e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}}=-102.08992\ eV \tag{14.319}$$

$$V_p=2\frac{e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}}=21.48386\ eV \tag{14.320}$$

$$T=2\left(0.91771\right)\frac{\hbar^2}{2m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}}=34.67062\ eV \tag{14.321}$$

$$V_m=2\left(0.91771\right)\frac{-\hbar^2}{4m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}}=-17.33531\ eV \tag{14.322}$$

$$E_T\left(C=C,\sigma\right)=-\frac{2e^2}{8\pi\varepsilon_0 c'}\left[\left(0.91771\right)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]=-63.27075\ eV \tag{14.323}$$

where $E_T\left(C=C,\sigma\right)$ is the total energy of the $C=C$ $\sigma$ MO given by Eq. (14.251) which is reiteratively matched to two times Eq. (13.75) within five-significant-figure round off error.

The total energy of the $C=C$-bond MO, $E_T\left(C=C\right)$, is given by the sum of two times $E_T\left(C=C,2sp^3\right)$, the energy change of each $C2sp^3$ shell due to the decrease in radius with the formation of the $C=C$-bond MO (Eq. (14.247)), and $E_T\left(C=C,\sigma\right)$, the $\sigma$ MO contribution given by Eq. (14.252).

$$\begin{aligned} E_T\left(C=C\right) &= 2E_T\left(C=C,2sp^3\right)+E_T\left(C=C,\sigma\right) \\ &= \left( \begin{array}{l} 2\left(-1.13380\ eV\right)+ \\ \left(-\frac{2e^2}{8\pi\varepsilon_0 c'}\left[\left(0.91771\right)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]\right) \end{array} \right) \\ &= 2\left(-1.13380\ eV\right)+\left(-63.27074\ eV\right) \\ &= -65.53833\ eV \end{aligned} \tag{14.324}$$

## VIBRATION OF ETHYLENE

The vibrational energy levels of $CH_2CH_2$ may be solved as two sets of two equivalent coupled harmonic oscillators with a bridging harmonic oscillator by developing the Lagrangian, the differential equation of motion, and the eigenvalue solutions [9] wherein the spring constants are derived from the central forces as given in the Vibration of Hydrogen-Type Molecular Ions section and the Vibration of Hydrogen-Type Molecules section.

## THE DOPPLER ENERGY TERMS OF THE $C=C$-BOND MO OF ETHYLENE

The equations of the radiation reaction force of the $C=C$-bond MO are given by Eq. (13.142), except the force-constant factor is $\left(0.93172\right)0.5$ based on the force constant $k'$ of Eq. (14.248), and the $C=C$-bond MO parameters are used. The angular frequency of the reentrant oscillation in the transition state is:

$$\omega=\sqrt{\frac{0.91771\frac{\left(0.5\right)e^2}{4\pi\varepsilon_0 b^3}}{m_e}}=4.30680\ X\ 10^{16}\ rad/s \tag{14.325}$$

where $b$ is given by Eq. (14.258). The kinetic energy, $E_K$, is given by Planck's equation (Eq. (11.127)).

$$\bar{E}_K=\hbar\omega=\hbar 4.30680\ X\ 10^{16}\ rad/s=28.34813\ eV \tag{14.326}$$

In Eq. (11.181), substitution of $E_T\left(C=C\right)/2$ (Eq. (14.324)) for $E_{h\nu}$, the mass of the electron, $m_e$, for $M$, and the kinetic energy given by Eq. (14.326) for $\bar{E}_K$ gives the Doppler energy of the electrons of each of the two bonds for the reentrant orbit:

$$\bar{E}_D\cong E_{h\nu}\sqrt{\frac{2\bar{E}_K}{Mc^2}}=-32.76916\ eV\sqrt{\frac{2e\left(28.34813\ eV\right)}{m_e c^2}}=-0.34517\ eV \tag{14.327}$$

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency. The decrease in the energy of the $C=C$-bond MO due to the reentrant orbit of the bond in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei, $\bar{E}_{osc}$, is given by the sum of the corresponding energies, $\bar{E}_D$ given by Eq. (14.327) and $\bar{E}_{Kvib}$, the average kinetic energy of vibration which is 1/2 of the vibrational energy of the $C=C$ bond. Using the experimental $C=C$ $E_{vib}\left(\upsilon_3\right)$ of 1443.5 $cm^{-1}$ $\left(0.17897\ eV\right)$ [12] for $\bar{E}_{Kvib}$ of the transition state having two bonds, $\bar{E}'_{osc}\left(C=C,\sigma\right)$ per bond is:

$$\bar{E}'_{osc}\left(C=C,\sigma\right)=\bar{E}_D+\bar{E}_{Kvib}=\bar{E}_D+\frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \tag{14.328}$$

$$\bar{E}'_{osc}\left(C=C,\sigma\right)=-0.34517\ eV+\frac{1}{2}\left(0.17897\ eV\right)=-0.25568\ eV \tag{14.329}$$

Given that the vibration and reentrant oscillation is for two $C-C$ bonds of the $C=C$ double bond, $\bar{E}_{ethylene\ osc}\left(C=C,\sigma\right)$, is:

$$\bar{E}_{ethylene\ osc}\left(C=C,\sigma\right)=2\left(\bar{E}_D+\frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right)=2\left(-0.34517\ eV+\frac{1}{2}\left(0.17897\ eV\right)\right)=-0.51136\ eV \tag{14.330}$$

## TOTAL ENERGIES OF THE $C=C$-BOND MO OF ETHYLENE

$E_{T+osc}(C=C)$, the total energy of the $C=C$-bond MO including the Doppler term, is given by the sum of $E_T(C=C)$ (Eq. (14.324)) and $\bar{E}_{ethylene\ osc}(C=C,\sigma)$ given by Eq. (14.330).

$$\begin{aligned} E_{T+osc}(C=C) &= V_e+T+V_m+V_p+2E_T\left(C=C,2sp^3\right)+\bar{E}_{ethylene\ osc}(C=C,\sigma) \\ &= E_T(C=C,\sigma)+2E_T\left(C=C,2sp^3\right)+\bar{E}_{ethylene\ osc}(C=C,\sigma) \\ &= E_T(C=C)+\bar{E}_{ethylene\ osc}(C=C,\sigma) \end{aligned} \tag{14.331}$$

$$\begin{aligned} E_{T+osc}(C=C) &= \left\{ \begin{array}{l} \left( \dfrac{-2e^2}{8\pi\varepsilon_0 c'}\left[(0.91771)\left(2-\dfrac{1}{2}\dfrac{a_0}{a}\right)\ln\dfrac{a+c'}{a-c'}-1\right]+2E_T\left(C=C,2sp^3\right)\right) \\ \left(1+(2)\left(\dfrac{1}{2}\right)\sqrt{\dfrac{2\hbar\sqrt{\dfrac{(0.91771)\dfrac{1}{2}\dfrac{e^2}{4\pi\varepsilon_0 b^3}}{m_e}}}{m_ec^2}}\right)+2\left(\dfrac{1}{2}\hbar\sqrt{\dfrac{k}{\mu}}\right) \end{array} \right\} \\ &= -65.53833\ eV-2\left(0.34517\ eV-\frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right) \end{aligned} \tag{14.332}$$

From Eqs. (14.330-14.332), the total energy of the $C=C$-bond MO is:

$$\begin{aligned} E_{T+osc}(C=C) &= -63.27074\ eV+2E_T\left(C=C,2sp^3\right)+\bar{E}_{ethylene\ osc}(C=C,\sigma) \\ &= -63.27074\ eV+2(-1.13380\ eV)-2\left(0.34517\ eV-\frac{1}{2}(0.17897\ eV)\right) \\ &= -66.04969\ eV \end{aligned} \tag{14.333}$$

where the experimental $E_{vib}$ was used for the $\hbar\sqrt{\frac{k}{\mu}}$ term.

## BOND ENERGY OF THE $C=C$ BOND OF ETHYLENE

The dissociation energy of the $C=C$ bond of $CH_2CH_2$, $E_D(H_2C=CH_2)$, is given by four times $E\left(C,2sp^3\right)$ (Eq. (14.146)), the initial energy of each $C2sp^3$ HO of each $CH_2$ radical that forms the double $C=C$ bond, minus the sum of $\Delta E_{T+osc}\left({}^{12}CH_2\right)$ (Eq. (14.318)), the energy change going from the dihydrogen carbide radicals to the $CH_2$ groups of ethylene, and $E_{T+osc}(C=C)$ (Eq. (14.333)). Thus, the dissociation energy of the $C=C$ bond of $CH_2CH_2$, is:

$$\begin{aligned} E_D(H_2C=CH_2) &= 4\left(E\left(C,2sp^3\right)\right)-\left(\Delta E_{T+osc}\left({}^{12}CH_2\right)+E_{T+osc}(C=C)\right) \\ &= 4(-14.63489\ eV)-(-0.04667\ eV-66.04969\ eV) \\ &= 4(-14.63489\ eV)-(-66.09636\ eV) \\ &= 7.55681\ eV \end{aligned} \tag{14.334}$$

The experimental dissociation energy of the $C=C$ bond of $CH_2CH_2$ is [7]:

$$E_D(H_2C-CH_2)=7.5969\ eV \tag{14.335}$$

The results of the determination of bond parameters of $CH_2CH_2$ are given in Table 14.1. The calculated results are based on first principles and given in closed-form, exact equations containing fundamental constants only. The agreement between the experimental and calculated results is excellent.

## ACETYLENE MOLECULE ($CHCH$)

The acetylene molecule $CHCH$ is formed by the reaction of two hydrogen carbide radicals:

$$CH + CH \rightarrow CHCH \tag{14.336}$$

$CHCH$ can be solved using the same principles as those used to solve the methane series $CH_{n=1,2,3,4}$ as well as ethane, wherein the $2s$ and $2p$ shells of each $C$ hybridize to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between two $C2sp^3$ hybridized orbitals (HOs) to form a molecular orbital (MO) permits each participating hybridized orbital to decrease in radius and energy. First, two sets of one $H$ atomic orbital (AO) combine with two sets of one carbon $2sp^3$ HO to form two hydrogen carbide groups comprising a linear combination of two diatomic $H_2$-type MOs developed in the Nature of the Chemical Bond of Hydrogen-Type Molecules and Molecular Ions section. Then, the two $CH$ groups bond by forming a $H_2$-type MO between the remaining three $C2sp^3$ HOs on each carbon atom.

## FORCE BALANCE OF THE $C \equiv C$-BOND MO OF ACETYLENE

$CHCH$ comprises a chemical bond between two $CH$ radicals wherein each radical comprises a chemical bond between a carbon and a hydrogen atom. The solution of the parameters of $CH$ is given in the Hydrogen Carbide ($CH$) section. The $C-H$ bond of $CH$ having two spin-paired electrons, one from an initially unpaired electron of the carbon atom and the other from the hydrogen atom, comprises the linear combination of 75% $H_2$-type ellipsoidal MO and 25% $C2sp^3$ HO. The proton of the $H$ atom and the nucleus of the $C$ atom are along each internuclear axis and serve as the foci. As in the case of $H_2$, the $C-H$-bond MOs is a prolate spheroid with the exception that the ellipsoidal MO surface cannot extend into $C2sp^3$ HO for distances shorter than the radius of the $C2sp^3$ shell since it is energetically unfavorable. Thus, the MO surface comprises a prolate spheroid at the $H$ proton that is continuous with the $C2sp^3$ shell at the $C$ atom whose nucleus serves as the other focus. The electron configuration and the energy, $E\left(C,2sp^3\right)$, of the $C2sp^3$ shell is given by Eqs. (13.422) and (13.428), respectively. The central paramagnetic force due to spin of the $C-H$ bond is provided by the spin-pairing force of the $CH$ MO that has the symmetry of an $s$ orbital that superimposes with the $C2sp^3$ orbitals such that the corresponding angular momenta are unchanged.

Two $CH$ radicals bond to form $CHCH$ by forming a MO between the two pairs of three remaining $C2sp^3$-HO electrons of the two carbon atoms. However, in this case, the sharing of electrons between two $C2sp^3$ HOs to form a MO comprising six spin-paired electrons permits each $C2sp^3$ HO to decrease in radius and energy.

As in the case of the $C-H$ bonds, the $C \equiv C$-bond MO is a prolate-spheroidal-MO surface that cannot extend into $C2sp^3$ HO for distances shorter than the radius of the $C2sp^3$ shell of each atom. Thus, the MO surface comprises a partial prolate spheroid in between the carbon nuclei and is continuous with the $C2sp^3$ shell at each $C$ atom. The energy of the $H_2$-type ellipsoidal MO is matched to that of the $C2sp^3$ shell. As in the case of previous examples of energy-matched MOs such as those of $OH$, $NH$, $CH$, the $C=O$-bond MO of $CO_2$, the $C-C$-bond MO of $CH_3CH_3$, and the $C=C$-bond MO of $CH_2CH_2$, the $C \equiv C$-bond MO of acetylene must comprise 75% of a $H_2$-type ellipsoidal MO in order to match potential, kinetic, and orbital energy relationships. Thus, the $C \equiv C$-bond MO must comprise a linear combination of three MOs wherein each comprises two $C2sp^3$ HOs and 75% of a $H_2$-type ellipsoidal MO divided between the $C2sp^3$ HOs:

$$3\left(2C2sp^3 + 0.75\ H_2\ MO\right) \rightarrow C \equiv C - bond\ MO \tag{14.337}$$

The linear combination of each $H_2$-type ellipsoidal MO with each $C2sp^3$ HO further comprises an excess 25% charge-density contribution from each $C2sp^3$ HO to the $C \equiv C$-bond MO to achieve an energy minimum. The force balance of the $C \equiv C$-bond MO is determined by the boundary conditions that arise from the linear combination of orbitals according to Eq. (14.337) and the energy matching condition between the $C2sp^3$-HO components of the MO.

Similarly, the energies of each $CH$ MO involve each $C2sp^3$ and each $H1s$ electron with the formation of each $C-H$ bond. The sum of the energies of the $H_2$-type ellipsoidal MOs is matched to that of the $C2sp^3$ shell. This energy is determined by the considering the effect of the donation of 25% electron density from the three pairs of $C2sp^3$ HOs to the $C \equiv C$-bond MO with the formation of the $C_{acetylene}2sp^3$ HOs each having a smaller radius. The $2sp^3$ hybridized orbital arrangement is given by Eq. (14.140). The sum $E_T\left(C,2sp^3\right)$ of calculated energies of $C$, $C^+$, $C^{2+}$, and $C^{3+}$ is given by Eq. (14.141). The radius $r_{2sp^3}$ of the $C2sp^3$ shell is given by Eq. (14.142). The Coulombic energy $E_{Coulomb}\left(C,2sp^3\right)$ and the energy $E\left(C,2sp^3\right)$ of the outer electron of the $C2sp^3$ shell are given by Eqs. (14.143) and (14.146), respectively.

Next, consider the formation of the $C \equiv C$ -bond MO of acetylene from two $CH$ radicals, each having a $C2sp^3$ electron with an energy given by Eq. (14.146). The total energy of the state is given by the sum over the four electrons. The sum $E_T\left(C_{acetylene}, 2sp^3\right)$ of calculated energies of $C2sp^3$, $C^+$, $C^{2+}$, and $C^{3+}$ from Eqs. (10.123), (10.113-10.114), (10.68), and (10.48), respectively, is

$$\begin{aligned} E_T\left(C_{acetylene}, 2sp^3\right) &= -\left(64.3921\ eV + 48.3125\ eV + 24.2762\ eV + E\left(C, 2sp^3\right)\right) \\ &= -\left(64.3921\ eV + 48.3125\ eV + 24.2762\ eV + 14.63489\ eV\right) \\ &= -151.61569\ eV \end{aligned} \tag{14.338}$$

where $E\left(C, 2sp^3\right)$ (Eq. (14.146)) is the sum of the energy of $C$, $-11.27671\ eV$, and the hybridization energy. The orbital-angular-momentum interactions also cancel such that the energy of the $E_T\left(C_{acetylene}, 2sp^3\right)$ is purely Coulombic.

The sharing of electrons between three pairs of $C2sp^3$ HOs to form a $C \equiv C$ -bond MO permits each participating hybridized orbital to decrease in radius and energy. In order to further satisfy the potential, kinetic, and orbital energy relationships, each participating $C2sp^3$ HO donates an excess of 25% of its electron density to the $C \equiv C$ -bond MO to form an energy minimum. By considering this electron redistribution in the acetylene molecule as well as the fact that the central field decreases by an integer for each successive electron of the shell, the radius $r_{acetylene2sp^3}$ of the $C2sp^3$ shell of acetylene may be calculated from the Coulombic energy using Eq. (10.102).

$$r_{acetylene2sp^3} = \left(\sum_{n=2}^{5}(Z-n) - 0.75\right)\frac{e^2}{8\pi\varepsilon_0\left(e151.61569\ eV\right)} = \frac{9.25e^2}{8\pi\varepsilon_0\left(e151.61569\ eV\right)} = 0.83008a_0 \tag{14.339}$$

where $Z = 6$ for carbon. Using Eqs. (10.102) and (14.339), the Coulombic energy $E_{Coulomb}\left(C_{acetylene}, 2sp^3\right)$ of the outer electron of the $C2sp^3$ shell is:

$$E_{Coulomb}\left(C_{acetylene}, 2sp^3\right) = \frac{-e^2}{8\pi\varepsilon_0 r_{acetylene2sp^3}} = \frac{-e^2}{8\pi\varepsilon_0 0.83008a_0} = -16.39089\ eV \tag{14.340}$$

During hybridization, the spin-paired $2s$ electrons are promoted to the $C2sp^3$ shell as unpaired electrons. The energy for the promotion is the magnetic energy given by Eq. (13.152). Using Eqs. (14.145) and (14.340), the energy $E\left(C_{acetylene}, 2sp^3\right)$ of the outer electron of the $C2sp^3$ shell is

$$E\left(C_{acetylene}, 2sp^3\right) = \frac{-e^2}{8\pi\varepsilon_0 r_{acetylene2sp^3}} + \frac{2\pi\mu_0 e^2\hbar^2}{m_e^2\left(r_3\right)^3} = -16.39089\ eV + 0.19086\ eV = -16.20002\ eV \tag{14.341}$$

Thus, $E_T\left(C \equiv C, 2sp^3\right)$, the energy change of each $C2sp^3$ shell with the formation of the $C \equiv C$ -bond MO is given by the difference between Eq. (14.146) and Eq. (14.341):

$$E_T\left(C \equiv C, 2sp^3\right) = E\left(C_{acetylene}, 2sp^3\right) - E\left(C, 2sp^3\right) = -16.20002\ eV - \left(-14.63489\ eV\right) = -1.56513\ eV \tag{14.342}$$

As in the case of $Cl_2$, each $H_2$-type ellipsoidal MO comprises 75% of the $C \equiv C$ -bond MO shared between two $C2sp^3$ HOs corresponding to the electron charge density in Eq. (11.65) of $\frac{-0.75e}{2}$. But, the additional 25% charge-density contribution to each bond of the $C \equiv C$ -bond MO causes the electron charge density in Eq. (11.65) to be $\frac{-e}{2} = -0.5e$. The corresponding force constant $k'$ to determine the ellipsoidal parameter $c'$ in terms of the central force of the foci (Eq. (11.65)) is given by Eq. (14.152). The distance from the origin to each focus $c'$ is given by Eq. (14.153). The internuclear distance is given by Eq. (14.154). The length of the semiminor axis of the prolate spheroidal $C \equiv C$ -bond MO $b = c$ is given by Eq. (13.62). The eccentricity, $e$, is given by Eq. (13.63). The solution of the semimajor axis $a$ then allows for the solution of the other axes of each prolate spheroid and eccentricity of the $C \equiv C$ -bond MO. From the energy equation and the relationship between the axes, the dimensions of the $C \equiv C$ -bond MO are solved.

The general equations for the energy components of $V_e$, $V_p$, $T$, $V_m$, and $E_T$ of the $C \equiv C$ -bond MO are the same as those of the $CH$ MO except that energy of the $C_{acetylene}2sp^3$ HO is used and the triple-bond nature is considered. In the case of a single bond, the prolate spheroidal $H_2$-type MO transitions to the $C_{acetylene}2sp^3$ HO of each carbon, and the energy of the $C_{acetylene}2sp^3$ shell must remain constant and equal to the $E\left(C_{acetylene}, 2sp^3\right)$ given by Eq. (14.391). Thus, the energy $E\left(C_{acetylene}, 2sp^3\right)$ in Eq. (14.391) adds to that of the energies of the corresponding $H_2$-type ellipsoidal MO. The second and third bonds of the triple $C \equiv C$ -bond MO also transition to each $C_{acetylene}2sp^3$ HO of each $C$. The energy of a second and a third

$H_2$-type ellipsoidal MO adds to the first energy component, and the three bonds achieve an energy minimum as a linear combination of the three $H_2$-type ellipsoidal MOs each having the carbon nuclei as the foci. Each $C-C$-bond MO comprises the same $C_{acetylene}2sp^3$ HO shells of constant energy given by Eq. (14.391). As in the case of the water, $NH_2$, ammonia, and ethylene molecules given by Eqs. (13.180), (13.320), (13.372), and (14.251), respectively, the energy of the redundant shell is subtracted from the total energy of the linear combination of the $\sigma$ MO. Thus, the total energy $E_T\left(C\equiv C,\sigma\right)$ of the $\sigma$ component of the $C\equiv C$-bond MO is given by the sum of the energies of the three bonds each comprising the linear combination of the $C_{acetylene}2sp^3$ HO and the $H_2$-type ellipsoidal MO as given by Eq. (14.337) wherein the $E_T$ terms add positively and the $E\left(C_{acetylene},2sp^3\right)$ term is positive due to the sum over a negative and two positive terms. Using Eqs. (13.431) and (14.341), $E_T\left(C\equiv C,\sigma\right)$ is given by:

$$\begin{aligned} E_T\left(C\equiv C,\sigma\right) &= E_T + E\left(C_{acetylene},2sp^3\right) - E\left(C_{acetylene},2sp^3\right) - E\left(C_{acetylene},2sp^3\right) \\ &= -\frac{3e^2}{8\pi\varepsilon_0 c'}\left[(0.91771)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right] - E\left(C_{acetylene},2sp^3\right) \\ &= -\frac{3e^2}{8\pi\varepsilon_0 c'}\left[(0.91771)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right] + 16.20002\ eV \end{aligned} \tag{14.343}$$

The total energy term of the triple $C\equiv C$-bond MO is given by the sum of the three $H_2$-type ellipsoidal MOs given by Eq. (11.212). To match this boundary condition, $E_T\left(C\equiv C,\sigma\right)$ given by Eq. (14.343) is set equal to three times Eq. (13.75):

$$E_T\left(C\equiv C,\sigma\right) = -\frac{3e^2}{8\pi\varepsilon_0 c'}\left[(0.91771)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right] + 16.20002\ eV = -94.90610\ eV \tag{14.344}$$

From the energy relationship given by Eq. (14.344) and the relationship between the axes given by Eqs. (14.153-14.154) and (13.62-13.63), the dimensions of the $C\equiv C$-bond MO can be solved.

Substitution of Eq. (14.153) into Eq. (14.344) gives:

$$\frac{3e^2}{8\pi\varepsilon_0\sqrt{aa_0}}\left[(0.91771)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+\sqrt{aa_0}}{a-\sqrt{aa_0}}-1\right] = e111.10613 \tag{14.345}$$

The most convenient way to solve Eq. (14.345) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is

$$a = 1.28714a_0 = 6.81122\ X\ 10^{-11}\ m \tag{14.346}$$

Substitution of Eq. (14.346) into Eq. (14.153) gives:

$$c' = 1.13452a_0 = 6.00362\ X\ 10^{-11}\ m \tag{14.347}$$

The internuclear distance given by multiplying Eq. (14.347) by two is:

$$2c' = 2.26904a_0 = 1.20072\ X\ 10^{-10}\ m \tag{14.348}$$

The experimental bond distance is [3]:

$$2c' = 1.203\ X\ 10^{-10}\ m \tag{14.349}$$

Substitution of Eqs. (14.346-14.347) into Eq. (13.62) gives:

$$b = c = 0.60793a_0 = 3.21704\ X\ 10^{-11}\ m \tag{14.350}$$

Substitution of Eqs. (14.346-14.347) into Eq. (13.63) gives:

$$e = 0.88143 \tag{14.351}$$

The nucleus of the $C$ atoms comprise the foci of the $H_2$-type ellipsoidal MO. The parameters of the point of intersection of the $H_2$-type ellipsoidal MO and the $C_{acetylene}2sp^3$ HO are given by Eqs. (13.84-13.95) and (13.261-13.270). The polar intersection angle $\theta'$ is given by Eq. (13.261) where $r_n = r_{acetylene2sp^3} = 0.83008a_0$ is the radius of the $C_{acetylene}2sp^3$ shell. Substitution of Eqs. (14.346-14.347) into Eq. (13.261) gives:

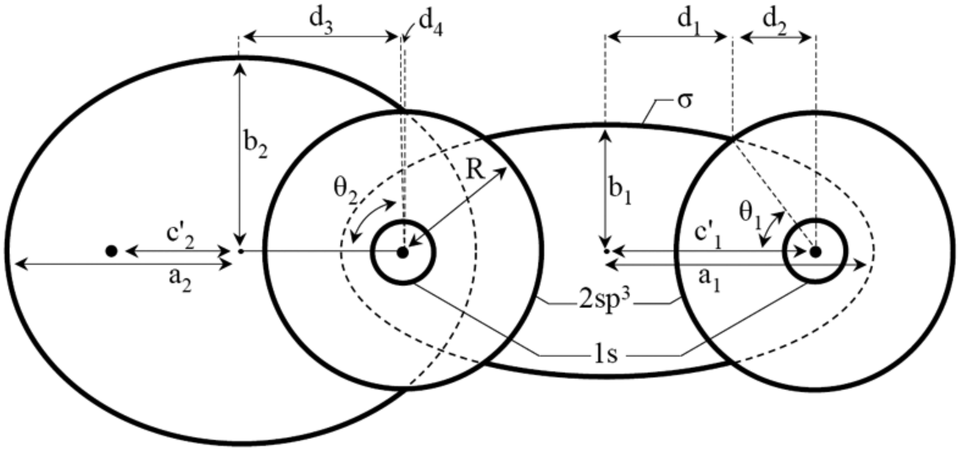
$$\theta' = 137.91^\circ \tag{14.352}$$

Then, the angle $\theta_{C\equiv C_{acetylene}2sp^3HO}$ the radial vector of the $C2sp^3$ HO makes with the internuclear axis is:

$$\theta_{C\equiv C_{acetylene}2sp^3HO} = 180^\circ - 137.91^\circ = 42.09^\circ \tag{14.353}$$

as shown in Figure 14.11.

Figure 14.11. The cross section of the $C \equiv C$-bond MO ($\sigma$ MO) and one $C-H$-bond MO of acetylene showing the axes, angles, and point of intersection of each $H_2$-type ellipsoidal MO with the corresponding $C_{acetylene}2sp^3$ HO. The continuation of each $H_2$-type-ellipsoidal-MO basis element of the $C \equiv C$ bond and the $C-H$-bond beyond the intersection point with each $C_{acetylene}2sp^3$ shell and $\sigma$ MO is shown as dashed since each only serves to solve the energy match with the $C_{acetylene}2sp^3$ shell and does not represent charge density. Similarly, the vertical dashed line only designates the parameters of each intersection point. The actual charge density is shown by the solid lines. Legend: $a$: semimajor axis, $b$: semiminor axis, $c'$: internuclear distance, $d_1 : d_{C \equiv C_{acetylene}, H_2MO}$, $\theta_1 : \theta_{C \equiv C_{acetylene}2sp^3HO}$, $d_2 : d_{C \equiv C_{acetylene}2sp^3HO}$, $R : r_{acetylene2sp^3}$, $\theta_2 : \theta_{C-H_{acetylene}2sp^3HO}$, $d_3 : d_{C-H_{acetylene}, H_2MO}$, and $d_4 : d_{C-H_{acetylene}2sp^3HO}$.



Consider the right-hand intersection point. The Cartesian $\mathbf{i}$-coordinate of the interception point of the MO and the AO can be calculated using the MO ellipsoidal parameters by first calculating the parametric angle in Eq. (11.83) that matches Cartesian $\mathbf{j}$-coordinate components at the point of intersection. Thus, the matching elliptic parametric angle $\omega t = \theta_{C \equiv C_{acetylene}, H_2MO}$ satisfies the following relationship:

$$r_{acetylene2sp^3} \sin\theta_{C \equiv C_{acetylene}2sp^3HO} = 0.83008a_0 \sin\theta_{C \equiv C_{acetylene}2sp^3HO} = b \sin\theta_{C \equiv C_{acetylene}, H_2MO} \tag{14.354}$$

such that

$$\theta_{C \equiv C_{acetylene}, H_2MO} = \sin^{-1} \frac{0.83008a_0 \sin\theta_{C \equiv C_{acetylene}2sp^3HO}}{b} = \sin^{-1} \frac{0.83008a_0 \sin 42.09°}{b} \tag{14.355}$$

with the use of Eq. (14.353). Substitution of Eq. (14.350) into Eq. (14.355) gives:

$$\theta_{C \equiv C_{acetylene}, H_2MO} = 66.24° \tag{14.356}$$

Then, the distance $d_{C \equiv C_{acetylene}, H_2MO}$ along the internuclear axis from the origin of $H_2$-type ellipsoidal MO to the point of intersection of the orbitals is given by:

$$d_{C \equiv C_{acetylene}, H_2MO} = a \cos\theta_{C \equiv C_{acetylene}, H_2MO} \tag{14.357}$$

Substitution of Eqs. (14.346) and (14.356) into Eq. (14.357) gives:

$$d_{C \equiv C_{acetylene}, H_2MO} = 0.51853a_0 = 2.74396\ X\ 10^{-11}\ m \tag{14.358}$$

The distance $d_{C \equiv C_{acetylene}2sp^3HO}$ along the internuclear axis from the origin of the $C$ atom to the point of intersection of the orbitals is given by:

$$d_{C \equiv C_{acetylene}2sp^3HO} = c' - d_{C \equiv C_{acetylene}, H_2MO} \tag{14.359}$$

Substitution of Eqs. (14.347) and (14.358) into Eq. (14.359) gives:

$$d_{C \equiv C_{acetylene}2sp^3HO} = 0.61599a_0 = 3.25966\ X\ 10^{-11}\ m \tag{14.360}$$

## FORCE BALANCE OF THE *CH* MOS OF ACETYLENE

The $C-H$ bond of each of the two equivalent $CH$ MOs must comprise 75% of a $H_2$-type ellipsoidal MO and a $C2sp^3$ HO as given by Eq. (13.429):

$$1\ C2sp^3 + 0.75\ H_2\ MO \rightarrow CH\ MO \tag{14.361}$$

The force balance of the $CH$ MO is determined by the boundary conditions that arise from the linear combination of orbitals according to Eq. (13.429) and the energy matching condition between the hydrogen and $C2sp^3$ HO components of the MO.

The force constant $k'$ to determine the ellipsoidal parameter $c'$ of the each $H_2$-type-ellipsoidal-MO component of the $CH$ MO in terms of the central force of the foci is given by Eq. (13.59). The distance from the origin of each $C-H$-bond MO to each focus $c'$ is given by Eq. (13.60). The internuclear distance is given by Eq. (13.61). The length of the semiminor axis of the prolate spheroidal $C-H$-bond MO $b=c$ is given by Eq. (13.62). The eccentricity, $e$, is given by Eq. (13.63). The solution of the semimajor axis $a$ then allows for the solution of the other axes of each prolate spheroid and eccentricity of each $C-H$-bond MO. From the energy equation and the relationship between the axes, the dimensions of the $CH$ MO are solved.

Consider the formation of the triple $C\equiv C$-bond MO of acetylene from two $CH$ radicals, each having a $C2sp^3$ shell with an energy given by Eq. (14.146). The energy components of $V_e$, $V_p$, $T$, $V_m$, and $E_T$ are the same as those of the hydrogen carbide radical, except that two times $E_T\left(C\equiv C,2sp^3\right)$ is subtracted from $E_T\left(CH\right)$ of Eq. (13.495). The subtraction of the energy change of the $C2sp^3$ shells with the formation of the $C\equiv C$-bond MO matches the energy of the $C-H$-bond MOs to the decrease in the energy of the $C2sp^3$ HOs. Using Eqs. (13.495) and (14.342), $E_{T_{acetylene}}\left(CH\right)$ is given by:

$$E_{T_{acetylene}}\left(CH\right) = E_T + E\left(C,2sp^3\right) - 2E_T\left(C\equiv C,2sp^3\right) = \left(\begin{array}{l} -\dfrac{e^2}{8\pi\varepsilon_0 c'}\left[\left(0.91771\right)\left(2-\dfrac{1}{2}\dfrac{a_0}{a}\right)\ln\dfrac{a+c'}{a-c'}-1\right] \\ -14.63489\ eV - \left(-3.13026\ eV\right) \end{array}\right) \tag{14.362}$$

$E_{T_{acetylene}}\left(CH\right)$ given by Eq. (14.362) is set equal to the energy of the $H_2$-type ellipsoidal MO given by Eq. (13.75).

$$E_{T_{acetylene}}\left(CH\right) = \left(\begin{array}{l} -\dfrac{e^2}{8\pi\varepsilon_0 c'}\left[\left(0.91771\right)\left(2-\dfrac{1}{2}\dfrac{a_0}{a}\right)\ln\dfrac{a+c'}{a-c'}-1\right] \\ -14.63489\ eV - \left(-3.13026\ eV\right) \end{array}\right) = -31.63537\ eV \tag{14.363}$$

From the energy relationship given by Eq. (14.363) and the relationship between the axes given by Eqs. (13.60-13.63), the dimensions of the $CH$ MO can be solved.

Substitution of Eq. (13.60) into Eq. (14.363) gives:

$$\frac{e^2}{8\pi\varepsilon_0\sqrt{\dfrac{2aa_0}{3}}}\left[\left(0.91771\right)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+\sqrt{\dfrac{2aa_0}{3}}}{a-\sqrt{\dfrac{2aa_0}{3}}}-1\right] = e20.13074 \tag{14.364}$$

The most convenient way to solve Eq. (14.364) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is

$$a = 1.48719a_0 = 7.86987\ X\ 10^{-11}\ m \tag{14.365}$$

Substitution of Eq. (14.365) into Eq. (14.60) gives:

$$c' = 0.99572a_0 = 5.26913\ X\ 10^{-11}\ m \tag{14.366}$$

The internuclear distance given by multiplying Eq. (14.366) by two is:

$$2c' = 1.99144a_0 = 1.05383\ X\ 10^{-10}\ m \tag{14.367}$$

The experimental bond distance is [3]:

$$2c' = 1.060\ X\ 10^{-10}\ m \tag{14.368}$$

Substitution of Eqs. (14.365-14.366) into Eq. (14.62) gives:

$$b = c = 1.10466a_0 = 5.84561\ X\ 10^{-11}\ m \tag{14.369}$$

Substitution of Eqs. (14.365-14.366) into Eq. (14.63) gives:

$$e = 0.66953 \tag{14.370}$$

The nucleus of the $H$ atom and the nucleus of the $C$ atom comprise the foci of each $H_2$-type ellipsoidal MO. The parameters of the point of intersection of the $H_2$-type ellipsoidal MO and the $C_{acetylene}2sp^3$ HO are given by Eqs. (13.84-13.95) and (13.261-13.270). The polar intersection angle $\theta'$ is given by Eq. (13.261) where $r_n = r_{acetylene2sp^3} = 0.83008a_0$ is the radius of the $C_{acetylene}2sp^3$ shell. Substitution of Eqs. (14.365-14.366) into Eq. (13.261) gives:

$$\theta' = 90.99° \tag{14.371}$$

Then, the angle $\theta_{C-H_{acetylene}2sp^3HO}$ the radial vector of the $C2sp^3$ HO makes with the internuclear axis is

$$\theta_{C-H_{acetylene}2sp^3HO} = 180° - 90.99° = 89.01° \tag{14.372}$$

as shown in Figure 14.11. The Cartesian $\mathbf{i}$-coordinate of the interception point of the MO and the AO can be calculated using the MO ellipsoidal parameters by first calculating the parametric angle in Eq. (11.83) that matches Cartesian $\mathbf{j}$-coordinate components at the point of intersection. Thus, the matching elliptic parametric angle $\omega t = \theta_{C-H_{acetylene},H_2MO}$ satisfies the following relationship:

$$r_{acetylene2sp^3} \sin\theta_{C-H_{acetylene}2sp^3HO} = 0.83008a_0 \sin\theta_{C-H_{acetylene}2sp^3HO} = b\sin\theta_{C-H_{acetylene},H_2MO} \tag{14.373}$$

such that

$$\theta_{C-H_{acetylene},H_2MO} = \sin^{-1}\frac{0.83008a_0\sin\theta_{C-H_{acetylene}2sp^3HO}}{b} = \sin^{-1}\frac{0.83008a_0\sin 89.01°}{b} \tag{14.374}$$

with the use of Eq. (14.372). Substitution of Eq. (14.369) into Eq. (14.374) gives:

$$\theta_{C-H_{acetylene},H_2MO} = 48.71° \tag{14.375}$$

Then, the distance $d_{C-H_{acetylene},H_2MO}$ along the internuclear axis from the origin of $H_2$-type ellipsoidal MO to the point of intersection of the orbitals is given by

$$d_{C-H_{acetylene},H_2MO} = a\cos\theta_{C-H_{acetylene},H_2MO} \tag{14.376}$$

Substitution of Eqs. (14.365) and (14.375) into Eq. (14.376) gives:

$$d_3 : d_{C-H_{acetylene},H_2MO} = 0.98145a_0 = 5.19359 \ X \ 10^{-11} \ m \tag{14.377}$$

The distance $d_{C-H_{acetylene}2sp^3HO}$ along the internuclear axis from the origin of the $C$ atom to the point of intersection of the orbitals is given by

$$d_{C-H_{acetylene}2sp^3HO} = c' - d_{C-H_{acetylene},H_2MO} \tag{14.378}$$

Substitution of Eqs. (14.366) and (14.377) into Eq. (14.378) gives:

$$d_4 : d_{C-H_{acetylene}2sp^3HO} = 0.01427a_0 = 7.55329 \ X \ 10^{-13} \ m \tag{14.379}$$

with the $C \equiv C$ triple bond along one axis, the minimum energy is obtained with the $C-H$-bond MO at a maximum separation. Thus, the bond angle $\theta_{C\equiv C-H}$ between the internuclear axis of the $C \equiv C$ bond and the $H$ atom of the $CH$ groups is

$$\theta_{C\equiv C-H} = 180° \tag{14.380}$$

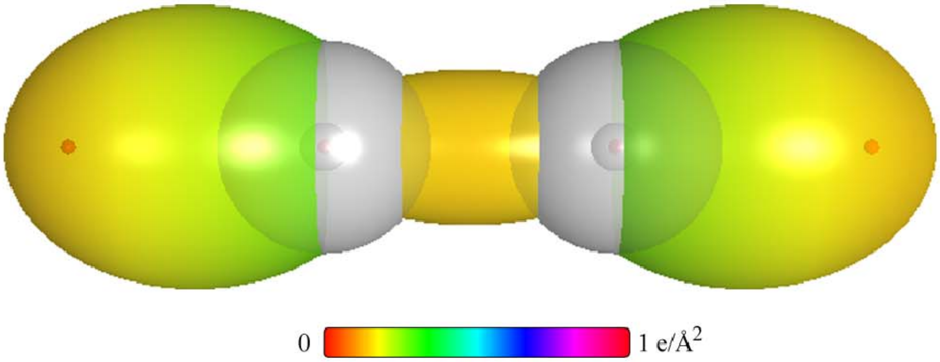
The experimental angle between the $C \equiv C - H$ bonds is [6]:

$$\theta_{C\equiv C-H} = 180° \tag{14.381}$$

The $CHCH$ MO shown in Figure 14.12 was rendered using these parameters.

The charge-density in the $C \equiv C$-bond MO is increased by a factor of 0.25 per bond with the formation of the $C_{acetylene}2sp^3$ HOs each having a smaller radius. Using the orbital composition of the $CH$ groups (Eq. (14.361)) and the $C \equiv C$-bond MO (Eq. (14.337)), the radii of $C1s = 0.17113a_0$ (Eq. (10.51)) and $C_{acetylene}2sp^3 = 0.83008a_0$ (Eq. (14.339)) shells, and the parameters of the $C \equiv C$-bond (Eqs. (13.3-13.4), (14.346-14.348), and (14.350-14.360)), the parameters of the $C-H$-bond MOs (Eqs. (13.3-13.4), (14.365-14.367), and (14.369-14.379)), and the bond-angle parameter (Eqs. (14.380-14.381)), the charge-density of the $CHCH$ MO comprising the linear combination of two $C-H$-bond MOs and a $C \equiv C$-bond MO bridging the two $CH$ groups is shown in Figure 14.12. Each $C-H$-bond MO comprises a $H_2$-type ellipsoidal MO and a $C_{acetylene}2sp^3$ HO having the dimensional diagram shown in Figure 14.11. The $C \equiv C$-bond MO comprises a $H_2$-type ellipsoidal MO bridging two $C_{acetylene}2sp^3$ HOs having the dimensional diagram also shown in Figure 14.11.

Figure 14.12. $CHCH$ MO comprising the linear combination of two $C-H$-bond MOs and a $C\equiv C$-bond MO. (A) Color scale, translucent view of the charge-density of the $C\equiv C$-bond MO with the $C_{acetylene}2sp^3$ HOs shown transparently. The $C\equiv C$-bond MO comprises a $H_2$-type ellipsoidal MO bridging two sets of three $C_{acetylene}2sp^3$ HOs. For each $C-H$ and the $C\equiv C$ bond, the ellipsoidal surface of the $H_2$-type ellipsoidal MO that transitions to the $C_{acetylene}2sp^3$ HO, the $C_{acetylene}2sp^3$ HO shell, inner most $C1s$ shell, and the nuclei (red, not to scale), are shown. (B)-(D) Translucent view high-lighting the $C\equiv C$-bond MO and end-on view of the charge-density of the $CHCH$ MO, respectively.



## ENERGIES OF THE $CH$ GROUPS

The energies of each $CH$ group of acetylene are given by the substitution of the semiprincipal axes (Eqs. (14.365-14.366) and (14.369)) into the energy equations of hydrogen carbide (Eqs. (13.510-13.514)), with the exception that two times $E_T\left(C\equiv C,2sp^3\right)$ (Eq. (14.342)) is subtracted from $E_T\left(CH\right)$ in Eq. (13.514).

$$V_e=\left(0.91771\right)\frac{-2e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}}=-40.62396\ eV \tag{14.382}$$

$$V_p=\frac{e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}}=13.66428\ eV \tag{14.383}$$

$$T=\left(0.91771\right)\frac{\hbar^2}{2m_ea\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}}=13.65796\ eV \tag{14.384}$$

$$V_m=\left(0.91771\right)\frac{-\hbar^2}{4m_ea\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}}=-6.82898\ eV \tag{14.385}$$

$$E_{T_{acetylene}}\left(CH\right)=\left(\begin{array}{l}-\frac{e^2}{8\pi\varepsilon_0c'}\left[\left(0.91771\right)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]\\-14.63489\ eV-\left(-3.13026\ eV\right)\end{array}\right)=-31.63532\ eV \tag{14.386}$$

where $E_{T_{acetylene}}\left(CH\right)$ is given by Eq. (14.362) which is reiteratively matched to Eq. (13.75) within five-significant-figure round off error.

## VIBRATION OF THE $^{12}CH$ GROUPS

The vibrational energy levels of $CH$ in acetylene may be solved using the methods given in the Vibration and Rotation of $CH$ section.

## THE DOPPLER ENERGY TERMS OF THE $^{12}CH$ GROUPS

The equations of the radiation reaction force of the $CH$ groups in acetylene are the same as those of the hydrogen carbide radical with the substitution of the $CH$-group parameters. Using Eq. (13.477), the angular frequency of the reentrant oscillation in the transition state is:

$$\omega = \sqrt{\frac{\frac{0.75e^2}{4\pi\varepsilon_0 b^3}}{m_e}} = 3.08370\ X\ 10^{16}\ rad/s \tag{14.387}$$

where $b$ is given by Eq. (14.369). The kinetic energy, $E_K$, is given by Planck's equation (Eq. (11.127)):

$$\bar{E}_K = \hbar\omega = \hbar 3.08370\ X\ 10^{16}\ rad/s = 20.29747\ eV \tag{14.388}$$

In Eq. (11.181), substitution of $E_T(H_2)$ (Eqs. (11.212) and (13.75)), the maximum total energy of each $H_2$-type MO, for $E_{h\nu}$, the mass of the electron, $m_e$, for $M$, and the kinetic energy given by Eq. (14.388) for $\bar{E}_K$ gives the Doppler energy of the electrons for the reentrant orbit:

$$\bar{E}_D \cong E_{h\nu}\sqrt{\frac{2\bar{E}_K}{Mc^2}} = -31.63537\ eV\sqrt{\frac{2e(20.29747\ eV)}{m_e c^2}} = -0.28197\ eV \tag{14.389}$$

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency. The decrease in the energy of $CH$ due to the reentrant orbit of each bond in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei, $\bar{E}_{osc}$, is given by the sum of the corresponding energies, $\bar{E}_D$ given by Eq. (14.389) and $\bar{E}_{Kvib}$, the average kinetic energy of vibration which is 1/2 of the vibrational energy of each $C-H$ bond. Using $\omega_e$ given by Eq. (13.458) for $\bar{E}_{Kvib}$ of the transition state, $\bar{E}_{acetylene\ osc}\left({}^{12}CH\right)$ is:

$$\bar{E}_{acetylene\ osc}\left({}^{12}CH\right) = \bar{E}_D + \bar{E}_{Kvib} = \bar{E}_D + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \tag{14.390}$$

$$\bar{E}_{acetylene\ osc}\left({}^{12}CH\right) = -0.28197\ eV + \frac{1}{2}(0.35532\ eV) = -0.10430\ eV \tag{14.391}$$

## TOTAL AND DIFFERENCE ENERGIES OF THE ${}^{12}CH$ GROUPS

$E_{acetyleneT+osc}\left({}^{12}CH\right)$, the total energy of each ${}^{12}CH$ group including the Doppler term, is given by the sum of $E_{T_{acetylene}}(CH)$ (Eq. (14.386)) and $\bar{E}_{acetylene\ osc}\left({}^{12}CH\right)$ given by Eq. (14.391).

$$\begin{aligned} E_{acetyleneT+osc}\left({}^{12}CH\right) &= \begin{pmatrix} V_e + T + V_m + V_p + E\left(C, 2sp^3\right) \\ -2E_T\left(C \equiv C, 2sp^3\right) + \bar{E}_{acetylene\ osc}\left({}^{12}CH\right) \end{pmatrix} \\ &= E_{T_{acetylene}}(CH) + \bar{E}_{acetylene\ osc}\left({}^{12}CH\right) \end{aligned} \tag{14.392}$$

$$\begin{aligned} E_{acetyleneT+osc}\left({}^{12}CH\right) &= \left\{ \begin{array}{l} \begin{pmatrix} \frac{-e^2}{8\pi\varepsilon_0 c'}\left[(0.91771)\left(2 - \frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'} - 1\right] \\ -14.63489\ eV - (-3.13026\ eV) \end{pmatrix} \\ -\left( (31.63536831\ eV)\sqrt{\frac{2\hbar\sqrt{\frac{\frac{3}{4}\frac{e^2}{4\pi\varepsilon_o b^3}}{m_e}}}{m_e c^2}} - \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \right) \end{array} \right\} \\ &= -31.63537\ eV - \left(0.28197\ eV - \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right) \end{aligned} \tag{14.393}$$

From Eqs. (14.391-14.393), the total energy of each ${}^{12}CH$ is:

$$\begin{aligned} E_{acetyleneT+osc}\left({}^{12}CH\right) &= -31.63537\ eV + \bar{E}_{acetylene\ osc}\left({}^{12}CH\right) \\ &= -31.63537\ eV - \left(0.28197\ eV - \frac{1}{2}(0.35532\ eV)\right) = -31.73967\ eV \end{aligned} \tag{14.394}$$

where $\omega_e$ given by Eq. (13.458) was used for the $\hbar\sqrt{\frac{k}{\mu}}$ term.

The total energy for each hydrogen carbide radical given by Eq. (13.485) is:

$$\begin{aligned} E_{radicalT+osc}\left({}^{12}CH\right) &= -31.63537\ eV + \bar{E}_{radicalosc}\left({}^{12}CH\right) \\ &= -31.63537\ eV - 0.24966\ eV + \frac{1}{2}\left(0.35532\ eV\right) \\ &= -31.70737\ eV \end{aligned} \tag{14.395}$$

The difference in energy between the $CH$ groups and the hydrogen carbide radical $\Delta E_{T+osc}\left({}^{12}CH\right)$ is given by two times the difference between Eqs. (14.394) and (14.395).

$$\begin{aligned} \Delta E_{T+osc}\left({}^{12}CH\right) &= 2\left(E_{acetyleneT+osc}\left({}^{12}CH\right) - E_{radicalT+osc}\left({}^{12}CH\right)\right) \\ &= 2\left(-31.73967\ eV - \left(-31.70737\ eV\right)\right) \\ &= -0.06460\ eV \end{aligned} \tag{14.396}$$

## SUM OF THE ENERGIES OF THE $C \equiv C$ $\sigma$ MO AND THE HOS OF ACETYLENE

The energy components of $V_e$, $V_p$, $T$, $V_m$, and $E_T$ of the $C \equiv C$-bond MO are the same as those of the $CH$ MO except that each term is multiplied by three corresponding to the triple bond and the energy term corresponding to the $C_{acetylene}2sp^3$ HOs in the equation for $E_T$ is positive. The energies of each $C \equiv C$-bond MO are given by the substitution of the semiprincipal axes (Eqs. (14.346-14.347) and (14.350)) into three times the energy equations of the $CH$ MO (Eqs. (13.449-13.453)), with the exception that $E\left(C,2sp^3\right)$ in Eq. (13.453) is positive and given by Eq. (14.341).

$$V_e = 3\left(0.91771\right)\frac{-2e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -182.53826\ eV \tag{14.397}$$

$$V_p = 3\frac{e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}} = 35.97770\ eV \tag{14.398}$$

$$T = 3\left(0.91771\right)\frac{\hbar^2}{2m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = 70.90876\ eV \tag{14.399}$$

$$V_m = 3\left(0.91771\right)\frac{-\hbar^2}{4m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -35.45438\ eV \tag{14.400}$$

$$E_T\left(C \equiv C,\sigma\right) = -\frac{3e^2}{8\pi\varepsilon_0 c'}\left[\left(0.91771\right)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]+16.20002\ eV = -94.90616\ eV \tag{14.401}$$

where $E_T\left(C \equiv C,\sigma\right)$ is the total energy of the $C \equiv C$ $\sigma$ MO given by Eq. (14.343) which is reiteratively matched to three times Eq. (13.75) within five-significant-figure round off error.

The total energy of the $C \equiv C$-bond MO, $E_T\left(C \equiv C\right)$, is given by the sum of two times $E_T\left(C \equiv C,2sp^3\right)$, the energy change of each $C2sp^3$ shell due to the decrease in radius with the formation of the $C \equiv C$-bond MO (Eq. (14.342)), and $E_T\left(C \equiv C,\sigma\right)$, the $\sigma$ MO contribution given by Eq. (14.344).

$$\begin{aligned} E_T\left(C \equiv C\right) &= 2E_T\left(C \equiv C,2sp^3\right) + E_T\left(C \equiv C,\sigma\right) \\ &= \left(\begin{array}{l} 2\left(-1.56513\ eV\right)+ \\ \left(-\frac{2e^2}{8\pi\varepsilon_0 c'}\left[\left(0.91771\right)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]+16.20002\ eV\right) \end{array}\right) \\ &= 2\left(-1.56513\ eV\right)+\left(-94.90610\ eV\right) \\ &= -98.03637\ eV \end{aligned} \tag{14.402}$$

## VIBRATION OF ACETYLENE

The vibrational energy levels of $CHCH$ may be solved as two equivalent coupled harmonic oscillators with a bridging harmonic oscillator by developing the Lagrangian, the differential equation of motion, and the eigenvalue solutions [9] wherein the spring constants are derived from the central forces as given in the Vibration of Hydrogen-Type Molecular Ions section and the Vibration of Hydrogen-Type Molecules section.

## THE DOPPLER ENERGY TERMS OF THE $C\equiv C$-BOND MO OF ACETYLENE

The equations of the radiation reaction force of the $C\equiv C$-bond MO are given by Eq. (14.231), except that the $C\equiv C$-bond MO parameters are used. The angular frequency of the reentrant oscillation in the transition state is:

$$\omega=\sqrt{\frac{\frac{0.5e^2}{4\pi\varepsilon_0 a^3}}{m_e}}=2.00186\ X\ 10^{16}\ rad/s \tag{14.403}$$

where $a$ is given by Eq. (14.346). The kinetic energy, $E_K$, is given by Planck's equation (Eq. (11.127)).

$$\overline{E}_K=\hbar\omega=\hbar 2.00186\ X\ 10^{16}\ rad/s=13.17659\ eV \tag{14.404}$$

In Eq. (11.181), substitution of $E_T\left(C\equiv C\right)/3$ (Eq. (14.402)) for $E_{h\nu}$, the mass of the electron, $m_e$, for $M$, and the kinetic energy given by Eq. (14.404) for $\overline{E}_K$ gives the Doppler energy of the electrons of each of the three bonds for the reentrant orbit:

$$\overline{E}_D\cong E_{h\nu}\sqrt{\frac{2\overline{E}_K}{Mc^2}}=-32.67879\ eV\sqrt{\frac{2e\left(13.17659\ eV\right)}{m_ec^2}}=-0.23468\ eV \tag{14.405}$$

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency. The decrease in the energy of the $C\equiv C$-bond MO due to the reentrant orbit of the bond in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei, $\overline{E}_{osc}$, is given by the sum of the corresponding energies, $\overline{E}_D$ given by Eq. (14.405) and $\overline{E}_{Kvib}$, the average kinetic energy of vibration which is 1/2 of the vibrational energy of the $C\equiv C$ bond. Using the experimental $C\equiv C$ $E_{vib}\left(\upsilon_3\right)$ of 3374 $cm^{-1}$ $\left(0.41833\ eV\right)$ [6] for $\overline{E}_{Kvib}$ of the transition state having three bonds, $\overline{E}'_{osc}\left(C\equiv C,\sigma\right)$ per bond is:

$$\overline{E}'_{osc}\left(C\equiv C,\sigma\right)=\overline{E}_D+\overline{E}_{Kvib}=\overline{E}_D+\frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \tag{14.406}$$

$$\overline{E}'_{osc}\left(C\equiv C,\sigma\right)=-0.23468\ eV+\frac{1}{2}\left(0.41833\ eV\right)=-0.02551\ eV \tag{14.407}$$

Given that the vibration and reentrant oscillation is for three $C-C$ bonds of the $C\equiv C$ triple bond, $\overline{E}_{acetylene\ osc}\left(C\equiv C,\sigma\right)$, is:

$$\begin{aligned}\overline{E}_{acetylene\ osc}\left(C\equiv C,\sigma\right)&=3\left(\overline{E}_D+\frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right)\\&=3\left(-0.23468\ eV+\frac{1}{2}\left(0.41833\ eV\right)\right)\\&=-0.07654\ eV\end{aligned} \tag{14.408}$$

## TOTAL ENERGIES OF THE $C\equiv C$-BOND MO OF ACETYLENE

$E_{T+osc}\left(C\equiv C\right)$, the total energy of the $C\equiv C$-bond MO including the Doppler term, is given by the sum of $E_T\left(C\equiv C\right)$ (Eq. (14.402)) and $\overline{E}_{acetylene\ osc}\left(C\equiv C,\sigma\right)$ given by Eq. (14.408).

$$\begin{aligned}E_{T+osc}\left(C\equiv C\right)&=\begin{pmatrix}V_e+T+V_m+V_p-E\left(C_{acetylene},2sp^3\right)\\+2E_T\left(C\equiv C,2sp^3\right)+\overline{E}_{acetylene\ osc}\left(C\equiv C,\sigma\right)\end{pmatrix}\\&=E_T\left(C\equiv C,\sigma\right)+2E_T\left(C\equiv C,2sp^3\right)+\overline{E}_{acetylene\ osc}\left(C\equiv C,\sigma\right)\\&=E_T\left(C\equiv C\right)+\overline{E}_{acetylene\ osc}\left(C\equiv C,\sigma\right)\end{aligned} \tag{14.409}$$

$$\begin{aligned}E_{T+osc}\left(C\equiv C\right)&=\left\{\begin{array}{l}\left(\begin{array}{l}\frac{-3e^2}{8\pi\varepsilon_0c'}\left[\left(0.91771\right)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]\\-E\left(C_{acetylene},2sp^3\right)+2E_T\left(C\equiv C,2sp^3\right)\end{array}\right)\\\left(1+(3)\left(\frac{1}{3}\right)\sqrt{\frac{2\hbar\sqrt{\frac{\frac{1}{2}\frac{e^2}{4\pi\varepsilon_0a^3}}{m_e}}}{m_ec^2}}\right)+3\left(\frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right)\end{array}\right\}\\&=-98.03637\ eV-3\left(0.23468\ eV-\frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right)\end{aligned} \tag{14.410}$$

From Eqs. (14.408-14.410), the total energy of the $C \equiv C$ -bond MO is:

$$\begin{aligned} E_{T+osc}\left(C \equiv C\right) &= -94.90610\ eV + 2E_T\left(C \equiv C, 2sp^3\right) + \overline{E}_{acetylene\ osc}\left(C \equiv C, \sigma\right) \\ &= -94.90610\ eV + 2\left(-1.56513\ eV\right) - 3\left(0.23468\ eV - \frac{1}{2}\left(0.41833\ eV\right)\right) \\ &= -98.11291\ eV \end{aligned} \tag{14.411}$$

where the experimental $E_{vib}$ was used for the $\hbar\sqrt{\frac{k}{\mu}}$ term.

## BOND ENERGY OF THE $C \equiv C$ BOND OF ACETYLENE

As in the case of $^{12}CH_2$ and $^{14}NH$, the dissociation of the $C \equiv C$ bond forms three unpaired electrons per central atom wherein the magnetic moments cannot all cancel. The energy per atom $E(magnetic)$ is given by Eq. (13.524). Thus, the dissociation energy of the $C \equiv C$ bond of $CHCH$, $E_D\left(HC \equiv CH\right)$, is given by six times $E\left(C, 2sp^3\right)$ (Eq. (14.146)), the initial energy of each $C2sp^3$ HO of each $CH$ radical that forms the triple $C \equiv C$ bond, minus the sum of $\Delta E_{T+osc}\left({}^{12}CH\right)$ (Eq. (14.396)), the energy change going from the hydrogen carbide radicals to the $CH$ groups of acetylene, $E_{T+osc}\left(C \equiv C\right)$ (Eq. (14.411)), and two times $E(magnetic)$ given by Eq. (13.524). Thus, the dissociation energy of the $C \equiv C$ bond of $CHCH$, is:

$$\begin{aligned} E_D\left(HC \equiv CH\right) &= 6\left(E\left(C, 2sp^3\right)\right) - \left(\Delta E_{T+osc}\left({}^{12}CH\right) + E_{T+osc}\left(C \equiv C\right) + 2E(magnetic)\right) \\ &= 6\left(-14.63489\ eV\right) - \left(-0.06460\ eV - 98.11291\ eV + 0.29606\ eV\right) \\ &= 6\left(-14.63489\ eV\right) - \left(-97.88145\ eV\right) = 10.07212\ eV \end{aligned} \tag{14.412}$$

The experimental dissociation energy of the $C \equiv C$ bond of $CHCH$ is [7]:

$$E_D\left(HC \equiv CH\right) = 10.0014\ eV \tag{14.413}$$

The results of the determination of bond parameters of $CHCH$ are given in Table 14.1. The calculated results are based on first principles and given in closed-form, exact equations containing fundamental constants only. The agreement between the experimental and calculated results is excellent.

## BENZENE MOLECULE ($C_6H_6$)

The benzene molecule $C_6H_6$ is formed by the reaction of three ethylene molecules:

$$3CH_2CH_2 \rightarrow C_6H_6 + 3H_2 \tag{14.414}$$

$C_6H_6$ can be solved using the same principles as those used to solve ethylene wherein the $2s$ and $2p$ shells of each $C$ hybridize to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between two $C2sp^3$ hybridized orbitals (HOs) to form a molecular orbital (MO) permits each participating hybridized orbital to decrease in radius and energy. Each $2sp^3$ HO of each carbon atom initially has four unpaired electrons. Thus, the $6H$ atomic orbitals (AOs) of benzene contribute six electrons and the six $sp^3$-hybridized carbon atoms contribute twenty-four electrons to form six $C-H$ bonds and six $C=C$ bonds. Each $C-H$ bond has two paired electrons with one donated from the $H$ AO and the other from the $C2sp^3$ HO. Each $C=C$ bond comprises a linear combination of a factor of $0.75$ of four paired electrons (three electrons) from two sets of two $C2sp^3$ HOs of the participating carbon atoms. Each $C-H$ and each $C=C$ bond comprises a linear combination of one and two diatomic $H_2$-type MOs developed in the Nature of the Chemical Bond of Hydrogen-Type Molecules and Molecular Ions section, respectively.

## FORCE BALANCE OF THE $C=C$-BOND MO OF BENZENE

$C_6H_6$ can be considered a linear combination of three ethylene molecules wherein a $C-H$ bond of each $CH_2$ group of $H_2C=CH_2$ is replaced by a $C=C$ bond to form a six-member ring of carbon atoms. The solution of the ethylene molecule is given in the Ethylene Molecule ($CH_2CH_2$) section. Before forming ethylene groups, the $2sp^3$ hybridized orbital arrangement of each carbon atom is given by Eq. (14.140). The sum $E_T\left(C, 2sp^3\right)$ of calculated energies of $C$, $C^+$, $C^{2+}$, and $C^{3+}$ is given by Eq. (14.141). The radius $r_{2sp^3}$ of the $C2sp^3$ shell is given by Eq. (14.142). The Coulombic energy $E_{Coulomb}\left(C, 2sp^3\right)$ and the energy $E\left(C, 2sp^3\right)$ of the outer electron of the $C2sp^3$ shell are given by Eqs. (14.143) and (14.146), respectively. Two $CH_2$ radicals bond to form $CH_2CH_2$ by forming a MO between the two pairs of remaining $C2sp^3$-HO electrons of the two carbon atoms. However, in this case, the sharing of electrons between four $C2sp^3$ HOs to form a MO comprising four spin-paired electrons permits each $C2sp^3$ HO to decrease in radius and energy. The $C=C$-bond MO is a prolate-spheroidal-MO surface that cannot extend into $C2sp^3$ HO for distances shorter than the radius of the $C2sp^3$ shell of each atom. Thus, the MO surface comprises a partial prolate spheroid in between the carbon nuclei and is continuous with the $C2sp^3$ shell at each $C$ atom. The energy of the $H_2$-type ellipsoidal MO is matched to that of each $C2sp^3$ shell. As in the case of previous examples of energy-matched MOs such as those of $OH$, $NH$, $CH$, the $C=O$-bond MO of $CO_2$, and the $C-C$-bond MO of $CH_3CH_3$, the $C=C$-bond MO of ethylene must comprise 75% of a $H_2$-type ellipsoidal MO in order to match potential, kinetic, and orbital energy relationships. Thus, the $C=C$-bond MO must comprise a linear combination of two MOs wherein each comprises two $C2sp^3$ HOs and 75% of a $H_2$-type ellipsoidal MO divided between the $C2sp^3$ HOs:

$$2\left(2\ C2sp^3+0.75\ H_2\ MO\right)\rightarrow C=C-bond\ MO \tag{14.415}$$

The linear combination of each $H_2$-type ellipsoidal MO with each $C2sp^3$ HO further comprises an excess 25% charge-density contribution from each $C2sp^3$ HO to the $C=C$-bond MO to achieve an energy minimum. The force balance of the $C=C$-bond MO is determined by the boundary conditions that arise from the linear combination of orbitals according to Eq. (14.415) and the energy matching condition between the $C2sp^3$-HO components of the MO.

The sharing of electrons between two pairs of $C2sp^3$ HOs to form a $C=C$-bond MO permits each participating hybridized orbital to decrease in radius and energy. The sum $E_T\left(C_{ethylene},2sp^3\right)$ of calculated energies of $C2sp^3$, $C^+$, $C^{2+}$, and $C^{3+}$ is given by Eq. (14.243). In order to further satisfy the potential, kinetic, and orbital energy relationships, each participating $C2sp^3$ HO donates an excess of 25% of its electron density to the $C=C$-bond MO to form an energy minimum. By considering this electron redistribution in the ethylene molecule as well as the fact that the central field decreases by an integer for each successive electron of the shell, the radius $r_{ethylene2sp^3}$ of the $C2sp^3$ shell of ethylene calculated from the Coulombic energy is given by Eq. (14.244). The Coulombic energy $E_{Coulomb}\left(C_{ethylene},2sp^3\right)$ of the outer electron of the $C2sp^3$ shell is given by Eq. (14.245). The energy $E\left(C_{ethylene},2sp^3\right)$ of the outer electron of the $C2sp^3$ shell is given by Eq. (14.246). $E_T\left(C=C,2sp^3\right)$ (Eq. (14.247)), the energy change of each $C2sp^3$ shell with the formation of the $C=C$-bond MO is given by the difference between $E\left(C_{ethylene},2sp^3\right)$ and $E\left(C,2sp^3\right)$.

Consider the case where three sets of $C=C$-bond MOs form bonds between the two carbon atoms of each molecule to form a six-member ring such that the six resulting bonds comprise eighteen paired electrons. Each bond comprises a linear combination of two MOs wherein each comprises two $C2sp^3$ HOs and 75% of a $H_2$-type ellipsoidal MO divided between the $C2sp^3$ HOs:

$$\begin{pmatrix} 3\left(2\ C2sp^3+0.75\ H_2\ MO\right)\rightarrow 3\left(C\overset{4e}{=}C\right)-ethylene-type-bond\ MO \\ \rightarrow 6\left(C\overset{3e}{=}C\right)-bond\ MO\ of\ benzene \end{pmatrix} \tag{14.416}$$

The linear combination of each $H_2$-type ellipsoidal MO with each $C2sp^3$ HO further comprises an excess 25% charge-density contribution per bond from each $C2sp^3$ HO to the $C=C$-bond MO to achieve an energy minimum. Thus, the dimensional parameters of each bond $C=C$-bond are determined using the same equations as those used to determine the same parameters of the $C=C$-bond MO of ethylene (Eqs. (14.242-14.268)) while matching the boundary conditions of the structure of benzene. The energies of each $C=C$ bond of benzene are also determined using the same equations as those of ethylene with the parameters of benzene. The result is that the energies are essentially given as $0.75$ times the energies of the $C=C$-bond MO of ethylene (Eqs. (14.251-14.253) and (14.319-14.333)).

The derivation of the dimensional parameters of benzene follows the same procedure as the determination of those of ethylene. As in the case of ethylene, each $H_2$-type ellipsoidal MO comprises 75% of the $C=C$-bond MO shared between two $C2sp^3$ HOs corresponding to the electron charge density in Eq. (11.65) of $\frac{-0.75e}{2}$. But, the additional 25% charge-density contribution to each bond of the $C=C$-bond MO causes the electron charge density in Eq. (11.65) to be $\frac{-e}{2}=-0.5e$. The corresponding force constant $k'$ is given by Eq. (14.152). In addition, the energy matching at all six $C2sp^3$ HOs further requires that $k'$ be corrected by a hybridization factor (Eq. (13.430)) as in the case of ethylene, expect that the constraint that the bonds connect a six-member ring of $C=C$ bonds of benzene rather two $C2sp^3$ HOs of ethylene decreases the hybridization factor of benzene compared to that of ethylene (Eq. (14.248)).

Since the energy of each $H_2$-type ellipsoidal MO is matched to that of all the continuously connected $C_{benzene}2sp^3$ HOs, the hybridization-energy-matching factor is $0.85252$. Hybridization with 25% electron donation to each $C=C$-bond gives rise to the $C_{benzene}2sp^3$ HO-shell Coulombic energy $E_{Coulomb}\left(C_{benzene},2sp^3\right)$ given by Eq. (14.245). The corresponding hybridization factor is given by the ratio of $15.95955\ eV$, the magnitude of $E_{Coulomb}\left(C_{benzene},2sp^3\right)$ given by Eq. (14.245), and $13.605804\ eV$, the magnitude of the Coulombic energy between the electron and proton of $H$ given by Eq. (1.264). The hybridization energy factor $C_{benzeneC2sp^3HO}$ is:

$$C_{benzeneC2sp^3HO}=\frac{\dfrac{e^2}{8\pi\varepsilon_0 a_0}}{\dfrac{e^2}{8\pi\varepsilon_0 r_{benzene2sp^3}}}=\frac{\dfrac{e^2}{8\pi\varepsilon_0 a_0}}{\dfrac{e^2}{8\pi\varepsilon_0 0.85252 a_0}}=\frac{13.605804\ eV}{15.95955\ eV}=0.85252 \tag{14.417}$$

Thus, the force constant $k'$ to determine the ellipsoidal parameter $c'$ in terms of the central force of the foci (Eq. (11.65)) is given by:

$$k'=C_{benzeneC2sp^3HO}\frac{(0.5)2e^2}{4\pi\varepsilon_0}=0.85252\frac{(0.5)2e^2}{4\pi\varepsilon_0} \tag{14.418}$$

The distance from the origin to each focus $c'$ is given by substitution of Eq. (14.418) into Eq. (13.60). Thus, the distance from the origin of the component of the double $C=C$-bond MO to each focus $c'$ is given by

$$c'=a\sqrt{\frac{\hbar^2 4\pi\varepsilon_0}{(0.85252)m_e e^2 a}}=\sqrt{\frac{aa_0}{0.85252}} \tag{14.419}$$

The internuclear distance from Eq. (14.419) is:

$$2c'=2\sqrt{\frac{aa_0}{0.85252}} \tag{14.420}$$

The length of the semiminor axis of the prolate spheroidal $C=C$-bond MO $b=c$ is given by Eq. (13.62). The eccentricity, $e$, is given by Eq. (13.63). The solution of the semimajor axis $a$ then allows for the solution of the other axes of each prolate spheroid and eccentricity of the $C=C$-bond MO. From the energy equation and the relationship between the axes, the dimensions of the $C=C$-bond MO are solved.

The general equations for the energy components of $V_e$, $V_p$, $T$, $V_m$, and $E_T$ of the $C=C$-bond MO of benzene are the same as those of the $CH_2CH_2$ MO except that energy of the $C_{benzene}2sp^3$ HO is used and the hybridization factor is given by Eq. (14.417). Using Eqs. (14.251) and (14.417), $E_T\left(C=C,\sigma\right)$ is given by:

$$E_T\left(C=C,\sigma\right)=E_T+E\left(C_{benzene},2sp^3\right)-E\left(C_{benzene},2sp^3\right)=-\frac{2e^2}{8\pi\varepsilon_0 c'}\left[(0.85252)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right] \tag{14.421}$$

The total energy term of the double $C=C$-bond MO is given by the sum of the two $H_2$-type ellipsoidal MOs given by Eq. (11.212). To match this boundary condition, $E_T\left(C=C,\sigma\right)$ given by Eq. (14.421) is set equal to two times Eq. (13.75):

$$E_T\left(C=C,\sigma\right)=-\frac{2e^2}{8\pi\varepsilon_0 c'}\left[(0.85252)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]=-63.27074\ eV \tag{14.422}$$

From the energy relationship given by Eq. (14.422) and the relationship between the axes given by Eqs. (14.419-14.420) and (13.62-13.63), the dimensions of the $C=C$-bond MO can be solved.

Substitution of Eq. (14.419) into Eq. (14.422) gives:

$$\frac{2e^2}{8\pi\varepsilon_0\sqrt{\dfrac{aa_0}{0.85252}}}\left[(0.85252)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+\sqrt{\dfrac{aa_0}{0.85252}}}{a-\sqrt{\dfrac{aa_0}{0.85252}}}-1\right]=e63.27074 \tag{14.423}$$

The most convenient way to solve Eq. (14.423) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is:

$$a=1.47348a_0=7.79733\ X\ 10^{-11}\ m \tag{14.424}$$

Substitution of Eq. (14.424) into Eq. (14.4129) gives:

$$c'=1.31468a_0=6.95699\ X\ 10^{-11}\ m \tag{14.425}$$

The internuclear distance given by multiplying Eq. (14.425) by two is:

$$2c'=2.62936a_0=1.39140\ X\ 10^{-10}\ m \tag{14.426}$$

The experimental bond distance is [3] :

$$2c' = 1.339\ X\ 10^{-10}\ m \tag{14.427}$$

Substitution of Eqs. (14.424-14.425) into Eq. (13.62) gives:

$$b = c = 0.66540a_0 = 3.52116\ X\ 10^{-11}\ m \tag{14.428}$$

Substitution of Eqs. (14.424-14.425) into Eq. (13.63) gives:

$$e = 0.89223 \tag{14.429}$$

The nucleus of the $C$ atoms comprise the foci of the $H_2$-type ellipsoidal MO. The parameters of the point of intersection of the $H_2$-type ellipsoidal MO and the $C_{benzene}2sp^3$ HO are given by Eqs. (13.84-13.95) and (13.261-13.270). Each benzene carbon atom contributes $(0.75)(-1.13380\ eV) = -0.85035\ eV$ (Eqs. (14.483) and (14.493)) to each of the two $C\overset{3e}{=}C$-bond MOs and $(0.5)(-1.13380\ eV) = -0.56690\ eV$ (Eq. (14.467)) to the corresponding $C-H$-bond MO. The energy contribution due to the charge donation at each carbon superimposes linearly. The radius of $r_{benzene2sp^3} = 0.79597a_0$ is calculated using Eq. (14.518) using the total energy donation to each bond with which it is participates in bonding. The polar intersection angle $\theta'$ is given by Eq. (13.261) where $r_n = r_{benzene2sp^3} = 0.79597a_0$ is the radius of the $C_{benzene}2sp^3$ shell. Substitution of Eqs. (14.424-14.425) into Eq. (13.261) gives:

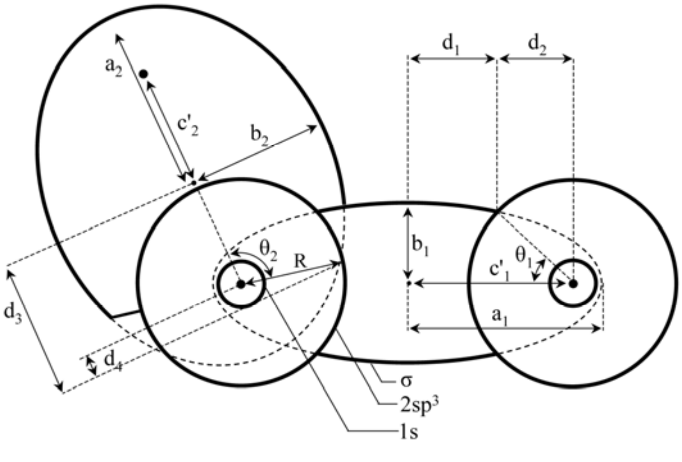
$$\theta' = 134.24° \tag{14.430}$$

Then, the angle $\theta_{C=C_{benzene}2sp^3HO}$ the radial vector of the $C2sp^3$ HO makes with the internuclear axis is:

$$\theta_{C=C_{benzene}2sp^3HO} = 180° - 134.24° = 45.76° \tag{14.431}$$

as shown in Figure 14.13.

Figure 14.13. The cross section of one $C=C$-bond MO ($\sigma$ MO) and one $C-H$-bond MO of benzene showing the axes, angles, and point of intersection of each $H_2$-type ellipsoidal MO with the corresponding $C_{benzene}2sp^3$ HO. The continuation of each $H_2$-type-ellipsoidal-MO basis element of the $C=C$ bond and the $C-H$-bond beyond the intersection point with each $C_{benzene}2sp^3$ shell and $\sigma$ MO is shown as dashed since each only serves to solve the energy match with the $C_{benzene}2sp^3$ shell and does not represent charge density. Similarly, the vertical dashed line only designates the parameters of each intersection point. The actual charge density is shown by the solid lines. Legend: $a$: semimajor axis, $b$: semiminor axis, $c'$: internuclear distance, $d_1 : d_{C=C_{benzene},H_2MO}$, $\theta_1 : \theta_{C=C_{benzene}2sp^3HO}$, $d_2 : d_{C=C_{benzene}2sp^3HO}$, $R : r_{benzeneC2sp^3}$, $d_3 : d_{C-H_{benzene},H_2MO}$, $\theta_2 : \theta_{C-H_{benzene}2sp^3HO}$, and $d_4 : d_{C-H_{benzene}2sp^3HO}$.



Consider the right-hand intersection point. The Cartesian $\mathbf{i}$-coordinate of the interception point of the MO and the AO can be calculated using the MO ellipsoidal parameters by first calculating the parametric angle in Eq. (11.83) that matches Cartesian $\mathbf{j}$-coordinate components at the point of intersection. Thus, the matching elliptic parametric angle $\omega t = \theta_{C=C_{benzene},H_2MO}$ satisfies the following relationship:

$$r_{benzene2sp^3} \sin\theta_{C=C_{benzene}2sp^3HO} = 0.79597a_0 \sin\theta_{C=C_{benzene}2sp^3HO} = b\sin\theta_{C=C_{benzene},H_2MO} \tag{14.432}$$

such that

$$\theta_{C=C_{benzene},H_2MO} = \sin^{-1}\frac{0.79597a_0 \sin\theta_{C=C_{benzene}2sp^3HO}}{b} = \sin^{-1}\frac{0.79597a_0 \sin 45.76°}{b} \tag{14.433}$$

with the use of Eq. (14.431). Substitution of Eq. (14.428) into Eq. (14.433) gives:

$$\theta_{C=C_{benzene},H_2MO} = 58.98° \tag{14.434}$$

Then, the distance $d_{C=C_{benzene},H_2MO}$ along the internuclear axis from the origin of $H_2$-type ellipsoidal MO to the point of intersection of the orbitals is given by:

$$d_{C=C_{benzene},H_2MO} = a\cos\theta_{C=C_{benzene},H_2MO} \tag{14.435}$$

Substitution of Eqs. (14.424) and (14.434) into Eq. (14.435) gives:

$$d_{C=C_{benzene},H_2MO} = 0.75935a_0 = 4.01829\ X\ 10^{-11}\ m \tag{14.436}$$

The distance $d_{C=C_{benzene}2sp^3HO}$ along the internuclear axis from the origin of the $C$ atom to the point of intersection of the orbitals is given by

$$d_{C=C_{benzene}2sp^3HO} = c' - d_{C=C_{benzene},H_2MO} \tag{14.437}$$

Substitution of Eqs. (14.425) and (14.436) into Eq. (14.437) gives:

$$d_{C=C_{benzene}2sp^3HO} = 0.55533a_0 = 2.93870\ X\ 10^{-11}\ m \tag{14.438}$$

## FORCE BALANCE OF THE $CH$ MOS OF BENZENE

Benzene can also be considered as comprising chemical bonds between six $CH$ radicals wherein each radical comprises a chemical bond between carbon and hydrogen atoms. The solution of the parameters of $CH$ is given in the Hydrogen Carbide ($CH$) section. Each $C-H$ bond of $CH$ having two spin-paired electrons, one from an initially unpaired electron of the carbon atom and the other from the hydrogen atom, comprises the linear combination of 75% $H_2$-type ellipsoidal MO and 25% $C2sp^3$ HO as given by Eq. (13.439):

$$1\ C2sp^3 + 0.75\ H_2\ MO \rightarrow CH\ MO \tag{14.439}$$

The proton of the $H$ atom and the nucleus of the $C$ atom are along each internuclear axis and serve as the foci. As in the case of $H_2$, the $C-H$-bond MO is a prolate spheroid with the exception that the ellipsoidal MO surface cannot extend into $C2sp^3$ HO for distances shorter than the radius of the $C2sp^3$ shell since it is energetically unfavorable. Thus, each MO surface comprises a prolate spheroid at the $H$ proton that is continuous with the $C2sp^3$ shell at the $C$ atom whose nucleus serves as the other focus.

The force balance of the $CH$ MO is determined by the boundary conditions that arise from the linear combination of orbitals according to Eq. (14.439) and the energy matching condition between the hydrogen and $C2sp^3$ HO components of the MO. The force constant $k'$ to determine the ellipsoidal parameter $c'$ of each $H_2$-type-ellipsoidal-MO component of the $CH$ MO in terms of the central force of the foci is given by Eq. (13.59). The distance from the origin of each $C-H$-bond MO to each focus $c'$ is given by Eq. (13.60). The internuclear distance is given by Eq. (13.61). The length of the semiminor axis of the prolate spheroidal $C-H$-bond MO $b=c$ is given by Eq. (13.62). The eccentricity, $e$, is given by Eq. (13.63). The solution of the semimajor axis $a$ then allows for the solution of the other axes of each prolate spheroid and eccentricity of each $C-H$-bond MO. From the energy equation and the relationship between the axes, the dimensions of the $CH$ MO are solved.

Consider the formation of the double $C=C$-bond MOs of benzene wherein ethylene formed from two $CH_2$ radicals, each having a $C2sp^3$ shell with an energy given by Eq. (14.146), serves as a basis element. The energy components of $V_e$, $V_p$, $T$, $V_m$, and $E_T$ are the same as those of the hydrogen carbide radical, except that $E_T\left(C=C,2sp^3\right)$ is subtracted from $E_T\left(CH\right)$ of Eq. (13.495). As in the case of the $CH_2$ groups of ethylene (Eq. (14.270)), the subtraction of the energy change of the $C2sp^3$ shell per $H$ with the formation of the $C=C$-bond MO matches the energy of each $C-H$-bond MO to the decrease in the energy of the corresponding $C2sp^3$ HO. Using Eqs. (13.431) and (14.247), $E_{T_{benzene}}\left(CH\right)$ is given by:

$$E_{T_{benzene}}\left(CH\right) = E_T + E\left(C,2sp^3\right) - E_T\left(C=C,2sp^3\right) = \begin{pmatrix} -\frac{e^2}{8\pi\varepsilon_0 c'}\left[\left(0.91771\right)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right] \\ -14.63489\ eV - \left(-1.13379\ eV\right) \end{pmatrix} \tag{14.440}$$

$E_{T_{benzene}}\left(CH\right)$ given by Eq. (14.440) is set equal to the energy of the $H_2$-type ellipsoidal MO given by Eq. (13.75).

$$E_{T_{benzene}}\left(CH\right) = \begin{pmatrix} -\frac{e^2}{8\pi\varepsilon_0 c'}\left[\left(0.91771\right)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right] \\ -14.63489\ eV - \left(-1.13379\ eV\right) \end{pmatrix} = -31.63537\ eV \tag{14.441}$$

From the energy relationship given by Eq. (14.441) and the relationship between the axes given by Eqs. (13.60-13.63), the dimensions of the $CH$ MO can be solved.

Substitution of Eq. (13.60) into Eq. (14.441) gives:

$$\frac{e^2}{8\pi\varepsilon_0\sqrt{\frac{2aa_0}{3}}}\left[(0.91771)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+\sqrt{\frac{2aa_0}{3}}}{a-\sqrt{\frac{2aa_0}{3}}}-1\right]=e18.13427 \tag{14.442}$$

The most convenient way to solve Eq. (14.442) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is

$$a=1.60061a_0=8.47006\ X\ 10^{-11}\ m \tag{14.443}$$

Substitution of Eq. (14.443) into Eq. (14.60) gives:

$$c'=1.03299a_0=5.46636\ X\ 10^{-11}\ m \tag{14.444}$$

The internuclear distance given by multiplying Eq. (14.444) by two is:

$$2c'=2.06598a_0=1.09327\ X\ 10^{-10}\ m \tag{14.445}$$

The experimental bond distance is [3]:

$$2c'=1.101\ X\ 10^{-10}\ m \tag{14.446}$$

Substitution of Eqs. (14.443-14.444) into Eq. (14.62) gives:

$$b=c=1.22265a_0=6.47000\ X\ 10^{-11}\ m \tag{14.447}$$

Substitution of Eqs. (14.443-14.444) into Eq. (14.63) gives:

$$e=0.64537 \tag{14.448}$$

The nucleus of the $H$ atom and the nucleus of the $C$ atom comprise the foci of each $H_2$-type ellipsoidal MO. The parameters of the point of intersection of the $H_2$-type ellipsoidal MO and the $C_{benzene}2sp^3$ HO are given by Eqs. (13.84-13.95) and (13.261-13.270). The polar intersection angle $\theta'$ is given by Eq. (13.261) where $r_n=r_{benzene2sp^3}=0.79597a_0$ is the radius of the $C_{benzene}2sp^3$ shell. Substitution of Eqs. (14.443-14.444) into Eq. (13.261) gives:

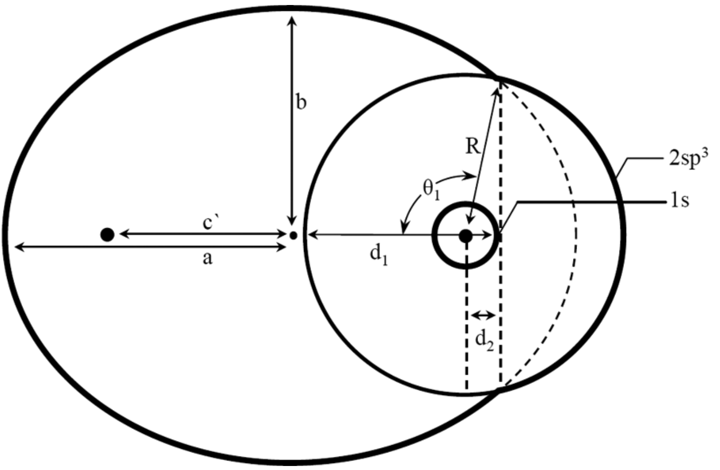
$$\theta'=74.42° \tag{14.449}$$

Then, the angle $\theta_{C-H_{benzene}2sp^3HO}$ the radial vector of the $C2sp^3$ HO makes with the internuclear axis is:

$$\theta_{C-H_{benzene}2sp^3HO}=180°-74.42°=105.58° \tag{14.450}$$

as shown in Figure 14.14.

Figure 14.14. The cross section of one $C-H$-bond MO of benzene showing the axes, angles, and point of intersection of the $H_2$-type ellipsoidal MO with the $C_{benzene}2sp^3$ HO. The continuation of the $H_2$-type-ellipsoidal-MO basis element beyond the intersection point with the $C_{benzene}2sp^3$ shell is shown as dashed since it only serves to solve the energy match with the $C_{benzene}2sp^3$ shell and does not represent charge density. Similarly, the vertical dashed line only designates the parameters of the intersection point. The actual charge density is shown by the solid lines. Legend: $a$: semimajor axis, $b$: semiminor axis, $c'$: internuclear distance, $d_1:d_{C-H_{benzene},H_2MO}$, $\theta_1:\theta_{C-H_{benzene}2sp^3HO}$, $d_2:d_{C-H_{benzene}2sp^3HO}$, and $R:r_{benzene2sp^3}$



The Cartesian $\mathbf{i}$-coordinate of the interception point of the MO and the AO can be calculated using the MO ellipsoidal parameters by first calculating the parametric angle in Eq. (11.83) that matches Cartesian $\mathbf{j}$-coordinate components at the point of intersection. Thus, the matching elliptic parametric angle $\omega t = \theta_{C-H_{benzene},H_2MO}$ satisfies the following relationship:

$$r_{benzene2sp^3} \sin\theta_{C-H_{benzene}2sp^3HO} = 0.79597a_0 \sin\theta_{C-H_{benzene}2sp^3HO} = b\sin\theta_{C-H_{benzene},H_2MO} \tag{14.451}$$

such that

$$\theta_{C-H_{benzene},H_2MO} = \sin^{-1}\frac{0.79597a_0 \sin\theta_{C-H_{benzene}2sp^3HO}}{b} = \sin^{-1}\frac{0.79597a_0 \sin 105.58°}{b} \tag{14.452}$$

with the use of Eq. (14.450). Substitution of Eq. (14.447) into Eq. (14.452) gives:

$$\theta_{C-H_{benzene},H_2MO} = 38.84° \tag{14.453}$$

Then, the distance $d_{C-H_{benzene},H_2MO}$ along the internuclear axis from the origin of $H_2$-type ellipsoidal MO to the point of intersection of the orbitals is given by:

$$d_{C-H_{benzene},H_2MO} = a\cos\theta_{C-H_{benzene},H_2MO} \tag{14.454}$$

Substitution of Eqs. (14.443) and (14.453) into Eq. (14.454) gives:

$$d_{C-H_{benzene},H_2MO} = 1.24678a_0 = 6.59767\ X\ 10^{-11}\ m \tag{14.455}$$

The distance $d_{C-H_{benzene}2sp^3HO}$ along the internuclear axis from the origin of the $C$ atom to the point of intersection of the orbitals is given by:

$$d_{C-H_{benzene}2sp^3HO} = d_{C-H_{benzene},H_2MO} - c' \tag{14.456}$$

Substitution of Eqs. (14.444) and (14.455) into Eq. (14.456) gives:

$$d_{C-H_{benzene}2sp^3HO} = 0.21379a_0 = 1.13131\ X\ 10^{-11}\ m \tag{14.457}$$

The basis set of benzene, the ethylene molecule, is planar with bond angles of approximately 120° (Eqs. (14.298-14.302)). To form a closed ring of equivalent planar bonds, the $C=C$ bonds of benzene form a planar hexagon. The bond angle $\theta_{C=C=C}$ between the internuclear axis of any two adjacent $C=C$ bonds is:

$$\theta_{C=C=C} = 120° \tag{14.458}$$

The bond angle $\theta_{C=C-H}$ between the internuclear axis of each $C=C$ bond and the corresponding $H$ atom of each $CH$ group is

$$\theta_{C=C-H} = 120° \tag{14.459}$$

The experimental angle between the $C=C=C$ bonds is [13-15]:

$$\theta_{C=C=C} = 120° \tag{14.460}$$

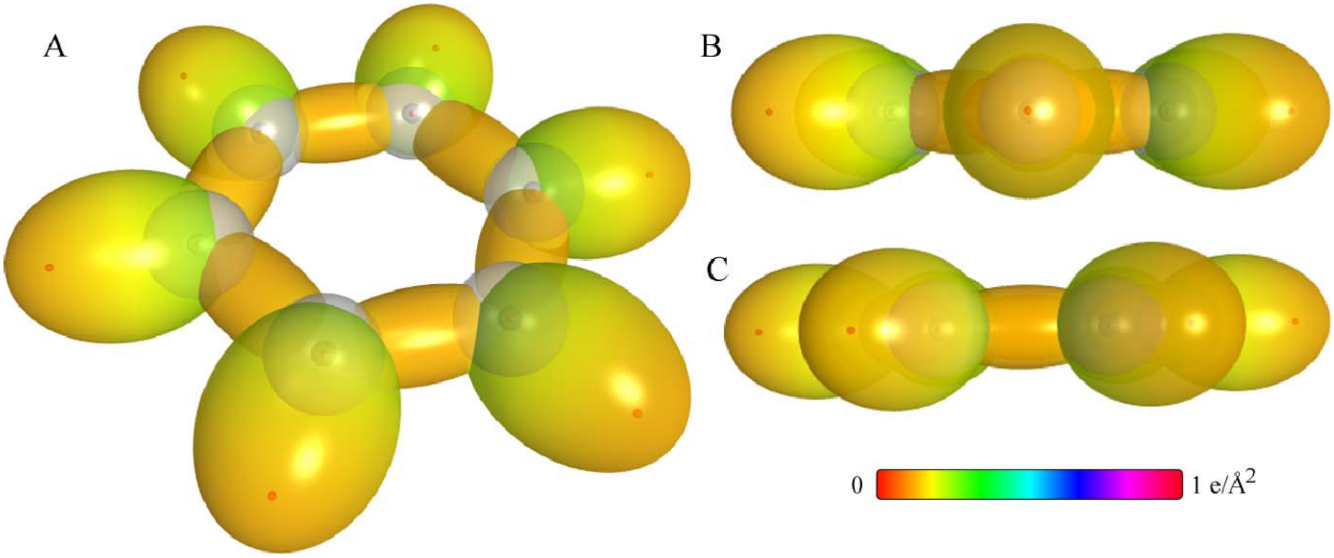
The experimental angle between the $C=C-H$ bonds is [13-15]:

$$\theta_{C=C-H} = 120° \tag{14.461}$$

The $C_6H_6$ MO shown in Figure 14.15 was rendered using these parameters.

The charge-density in the $C=C$-bond MO is increased by a factor of 0.25 per bond with the formation of the $C_{benzene}2sp^3$ HOs each having a smaller radius. Using the orbital composition of the $CH$ groups (Eq. (14.439)) and the $C=C$-bond MO (Eq. (14.416)), the radii of $C1s = 0.17113a_0$ (Eq. (10.51)) and $C_{benzene}2sp^3 = 0.79597a_0$ (Eq. (14.520)) shells, and the parameters of the $C=C$-bond (Eqs. (13.3-13.4), (14.424-14.426), and (14.428-14.438)), the parameters of the $C-H$-bond MOs (Eqs. (13.3-13.4), (14.443-14.445), and (14.447-14.457)), and the bond-angle parameters (Eqs. (14.458-14.459)), the charge-density of the $C_6H_6$ MO comprising the linear combination of six sets of $C-H$-bond MOs with bridging $C\overset{3e}{=}C$-bond MOs is shown in Figure 14.15. Each $C-H$-bond MO comprises a $H_2$-type ellipsoidal MO and a $C_{benzene}2sp^3$ HO having the dimensional diagram shown in Figure 14.14. The $C=C$-bond MO comprises a $H_2$-type ellipsoidal MO bridging two sets of two $C_{benzene}2sp^3$ HOs having the dimensional diagram shown in Figure 14.13.

Figure 14.15. $C_6H_6$ MO comprising the linear combination of six sets of $C-H$-bond MOs bridged by $C=C$-bond MOs. (A) Color scale, translucent view of the charge-density of the $C_6H_6$-bond MO with each $C_{benzene}2sp^3$ HOs shown transparently. Each $C=C$-bond MO comprises a $H_2$-type ellipsoidal MO bridging two pairs of $C_{benzene}2sp^3$ HOs. For each $C-H$ and $C=C$ bond, the ellipsoidal surface of the $H_2$-type ellipsoidal MO that transitions to the $C_{benzene}2sp^3$ HO, the $C_{benzene}2sp^3$ HO shell, inner most $C1s$ shell, and the nuclei (red, not to scale), are shown. (B)-(D) End-on view, translucent view high-lighting each $C=C$-bond MO, and opaque view of the charge-density of the $C_6H_6$ MO, respectively.



## ENERGIES OF THE $CH$ GROUPS

The energies of each $CH$ group of benzene are given by the substitution of the semiprincipal axes (Eqs. (14.443-14.444) and (14.447)) into the energy equations of hydrogen carbide (Eqs. (13.449-13.453)), with the exception that $E_T\left(C=C,2sp^3\right)$ (Eq. (14.247)) is subtracted from $E_T\left(CH\right)$ in Eq. (13.453).

$$V_e=\left(0.91771\right)\frac{-2e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}}=-37.10024\ eV \tag{14.462}$$

$$V_p=\frac{e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}}=13.17125\ eV \tag{14.463}$$

$$T=\left(0.91771\right)\frac{\hbar^2}{2m_ea\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}}=11.58941\ eV \tag{14.464}$$

$$V_m=\left(0.91771\right)\frac{-\hbar^2}{4m_ea\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}}=-5.79470\ eV \tag{14.465}$$

$$E_{T_{benzene}}\left(CH\right)=\left(\begin{array}{l}-\dfrac{e^2}{8\pi\varepsilon_0c'}\left[\left(0.91771\right)\left(2-\dfrac{1}{2}\dfrac{a_0}{a}\right)\ln\dfrac{a+c'}{a-c'}-1\right]\\ -14.63489\ eV-\left(-1.13379\ eV\right)\end{array}\right)=-31.63539\ eV \tag{14.466}$$

where $E_{T_{benzene}}\left(CH\right)$ is given by Eq. (14.440) which is reiteratively matched to Eq. (13.75) within five-significant-figure round off error.

The total energy of the $C-H$-bond MO, $E_{T_{benzene}}\left(C-H\right)$, is given by the sum of $0.5E_T\left(C=C,2sp^3\right)$, the energy change of each $C2sp^3$ shell per single bond due to the decrease in radius with the formation of the corresponding $C=C$-bond MO (Eq. (14.247)), and $E_{T_{benzene}}\left(CH\right)$, the $\sigma$ MO contribution given by Eq. (14.441).

$$E_{T_{benzene}}(C-H)=(0.5)E_T\left(C=C,2sp^3\right)+E_{T_{benzene}}(CH)$$
$$=\left(\begin{array}{l}(0.5)(-1.13379\ eV)+\\ \left(-\frac{e^2}{8\pi\varepsilon_0 c'}\left[(0.91771)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]\right)\\ -14.63489\ eV-(-1.13379\ eV)\end{array}\right) \quad (14.467)$$
$$=(0.5)(-1.13379\ eV)+(-31.63537\ eV)$$
$$=-32.20226\ eV$$

## VIBRATION OF THE $^{12}CH$ GROUPS

The vibrational energy levels of $CH$ in benzene may be solved using the methods given in the Vibration and Rotation of $CH$ section.

## THE DOPPLER ENERGY TERMS OF THE $^{12}CH$ GROUPS

The equations of the radiation reaction force of the $CH$ groups in benzene are the same as those of the hydrogen carbide radical with the substitution of the $CH$-group parameters. Using Eq. (13.477), the angular frequency of the reentrant oscillation in the transition state is

$$\omega=\sqrt{\frac{\frac{0.75e^2}{4\pi\varepsilon_0 b^3}}{m_e}}=2.64826\ X\ 10^{16}\ rad/s \quad (14.468)$$

where $b$ is given by Eq. (14.447). The kinetic energy, $E_K$, is given by Planck's equation (Eq. (11.127)).

$$\bar{E}_K=\hbar\omega=\hbar 2.64826\ X\ 10^{16}\ rad/s=17.43132\ eV \quad (14.469)$$

In Eq. (11.181), substitution of $E_T(H_2)$ (Eqs. (11.212) and (13.75)), the maximum total energy of each $H_2$-type MO, for $E_{h\nu}$, the mass of the electron, $m_e$, for $M$, and the kinetic energy given by Eq. (14.469) for $\bar{E}_K$ gives the Doppler energy of the electrons for the reentrant orbit:

$$\bar{E}_D\cong E_{h\nu}\sqrt{\frac{2\bar{E}_K}{Mc^2}}=-31.63537\ eV\sqrt{\frac{2e(17.43132\ eV)}{m_e c^2}}=-0.26130\ eV \quad (14.470)$$

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency. The decrease in the energy of $CH$ due to the reentrant orbit of each bond in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei, $\bar{E}_{osc}$, is given by the sum of the corresponding energies, $\bar{E}_D$ given by Eq. (14.470) and $\bar{E}_{Kvib}$, the average kinetic energy of vibration which is 1/2 of the vibrational energy of the $C-H$ bond. Using $\omega_e$ given by Eq. (13.458) for $\bar{E}_{Kvib}$ of the transition, $\bar{E}_{benzene\ osc}\left(^{12}CH\right)$ per bond is:

$$\bar{E}_{benzene\ osc}\left(^{12}CH\right)=\bar{E}_D+\bar{E}_{Kvib}=\bar{E}_D+\frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \quad (14.471)$$

$$\bar{E}_{benzene\ osc}\left(^{12}CH\right)=-0.26130\ eV+\frac{1}{2}(0.35532\ eV)=-0.08364\ eV \quad (14.472)$$

## TOTAL AND BOND ENERGIES OF THE $^{12}CH$ GROUPS

$E_{benzeneT+osc}\left(^{12}CH\right)$, the total energy of each $^{12}CH$ group including the Doppler term, is given by the sum of $E_{T_{benzene}}(C-H)$ (Eq. (14.467)) and $\bar{E}_{benzene\ osc}\left(^{12}CH\right)$ given by Eq. (14.472).

$$E_{benzeneT+osc}\left(^{12}CH\right)=\left(\begin{array}{l}\left(V_e+T+V_m+V_p+E\left(C,2sp^3\right)-E_T\left(C=C,2sp^3\right)\right)\\ +0.5E_T\left(C=C,2sp^3\right)+\bar{E}_{benzene\ osc}\left(^{12}CH\right)\end{array}\right) \quad (14.473)$$
$$=E_{T_{benzene}}(C-H)+\bar{E}_{benzene\ osc}\left(^{12}CH\right)$$

$$E_{benzeneT+osc}\left({}^{12}CH\right)=\left\{\begin{array}{l}\left(\begin{array}{l}\dfrac{-e^2}{8\pi\varepsilon_0 c'}\left[\left(0.91771\right)\left(2-\dfrac{1}{2}\dfrac{a_0}{a}\right)\ln\dfrac{a+c'}{a-c'}-1\right]\\-14.63489\ eV-\left(-1.13379\ eV\right)\end{array}\right)-0.5\left(1.13379\ eV\right)\\-\left(\left(31.63536831\ eV\right)\sqrt{\dfrac{2\hbar\sqrt{\dfrac{\dfrac{3}{4}\dfrac{e^2}{4\pi\varepsilon_0 b^3}}{m_e}}}{m_ec^2}}-\dfrac{1}{2}\hbar\sqrt{\dfrac{k}{\mu}}\right)\end{array}\right\}$$
$$=-32.20226\ eV-\left(0.26130\ eV-\frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right) \tag{14.474}$$

From Eqs. (14.472-14.474), the total energy of each ${}^{12}CH$ is:

$$\begin{aligned}E_{benzeneT+osc}\left({}^{12}CH\right)&=-32.20226\ eV+\bar{E}_{benzene\ osc}\left({}^{12}CH_2\right)\\&=-32.20226\ eV-\left(0.26130\ eV-\frac{1}{2}\left(0.35532\ eV\right)\right)\\&=-32.28590\ eV\end{aligned} \tag{14.475}$$

where $\omega_e$ given by Eq. (13.458) was used for the $\hbar\sqrt{\frac{k}{\mu}}$ term.

As in the case of ${}^{12}CH_2$, ${}^{14}NH$, and acetylene, the dissociation of the $C=C$ bonds forms three unpaired electrons per central atom wherein the magnetic moments cannot all cancel. The energy per atom $E(magnetic)$ is given by Eq. (13.524). Thus, the bond dissociation energy of each $CH$ group of the linear combination to form benzene, $E_{D_{benzene}}\left({}^{12}CH\right)$, is given by the sum of the total energies of the $C2sp^3$ HO and the hydrogen atom minus the sum of $E_{benzeneT+osc}\left({}^{12}CH\right)$ and $E(magnetic)$ given by Eq. (13.524):

$$E_{D_{benzene}}\left({}^{12}CH\right)=E\left(C,2sp^3\right)+E(H)-\left(E_{benzeneT+osc}\left({}^{12}CH\right)+E(magnetic)\right) \tag{14.476}$$

$E\left(C,2sp^3\right)$ is given by Eq. (13.428), $E_D\left(H\right)$ is given by Eq. (13.154), and $E(magnetic)$ is given by Eq. (13.524). Thus, $E_{D_{benzene}}\left({}^{12}CH\right)$ given by Eqs. (13.154), (13.428), (13.524), (14.475), and (14.476) is:

$$\begin{aligned}E_{D_{benzene}}\left({}^{12}CH\right)&=-\left(14.63489\ eV+13.59844\ eV\right)-\left(E_{benzeneT+osc}\left(CH\right)+E(magnetic)\right)\\&=-28.23333\ eV-\left(-32.28590\ eV+0.14803\ eV\right)\\&=3.90454\ eV\end{aligned} \tag{14.477}$$

## SUM OF THE ENERGIES OF THE $C=C$ $\sigma$ MO ELEMENT AND THE HOs OF BENZENE

The energy components of $V_e$, $V_p$, $T$, $V_m$, and $E_T$ of the $C=C$-bond MO of benzene are the same as those of the $CH_2CH_2$ MO except that the hybridization factor is given by Eq. (14.417). The energies of each $C=C$-bond MO are given by the substitution of the semiprincipal axes (Eqs. (14.424-14.425) and (14.428)) into energy equations of the $CH_2CH_2$ MO (Eqs. (14.319-14.323)), with the exception that the hybridization factor is $0.85252$ (Eq. (14.417)).

$$V_e=2\left(0.85252\right)\frac{-2e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}}=-101.12679\ eV \tag{14.478}$$

$$V_p=2\frac{e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}}=20.69825\ eV \tag{14.479}$$

$$T=2\left(0.85252\right)\frac{\hbar^2}{2m_ea\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}}=34.31559\ eV \tag{14.480}$$

$$V_m=2\left(0.85252\right)\frac{-\hbar^2}{4m_ea\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}}=-17.15779\ eV \tag{14.481}$$

$$E_T\left(C=C,\sigma\right)=-\frac{2e^2}{8\pi\varepsilon_0c'}\left[\left(0.85252\right)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]=-63.27075\ eV \tag{14.482}$$

where $E_T\left(C=C,\sigma\right)$ is the total energy of the $C=C$ $\sigma$ MO given by Eq. (14.421) which is reiteratively matched to two times Eq. (13.75) within five-significant-figure round off error.

The total energy of the $C=C$-bond MO, $E_T\left(C=C\right)$, is given by the sum of two times $E_T\left(C=C,2sp^3\right)$, the energy change of each $C2sp^3$ shell due to the decrease in radius with the formation of the $C=C$-bond MO (Eq. (14.247)), and $E_T\left(C=C,\sigma\right)$, the $\sigma$ MO contribution given by Eq. (14.422).

$$\begin{aligned} E_T\left(C=C\right) &= 2E_T\left(C=C,2sp^3\right)+E_T\left(C=C,\sigma\right) \\ &= \left(\begin{array}{l} 2\left(-1.13380\ eV\right)+ \\ \left(-\frac{2e^2}{8\pi\varepsilon_0 c'}\left[\left(0.85252\right)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]\right) \end{array}\right) \\ &= 2\left(-1.13380\ eV\right)+\left(-63.27074\ eV\right)=-65.53833\ eV \end{aligned} \tag{14.483}$$

which is the same $E_T\left(C=C,\sigma\right)$ of ethylene given by Eq. (14.324).

## VIBRATION OF BENZENE

The $C=C$ vibrational energy levels of $C_6H_6$ may be solved as six sets of equivalent coupled harmonic oscillators where each $C$ is further coupled to the corresponding $C-H$ oscillator by developing the Lagrangian, the differential equation of motion, and the eigenvalue solutions [9] wherein the spring constants are derived from the central forces as given in the Vibration of Hydrogen-Type Molecular Ions section and the Vibration of Hydrogen-Type Molecules section.

## THE DOPPLER ENERGY TERMS OF THE $C=C$-BOND MO ELEMENT OF BENZENE

The equations of the radiation reaction force of the $C=C$-bond MO of benzene are given by Eq. (13.142), except the force-constant factor is $\left(0.85252\right)0.5$ based on the force constant $k'$ of Eq. (14.418), and the $C=C$-bond MO parameters are used. The angular frequency of the reentrant oscillation in the transition state is:

$$\omega=\sqrt{\frac{0.85252\dfrac{\left(0.5\right)e^2}{4\pi\varepsilon_0 b^3}}{m_e}}=4.97272\ X\ 10^{16}\ rad/s \tag{14.484}$$

where $b$ is given by Eq. (14.428). The kinetic energy, $E_K$, is given by Planck's equation (Eq. (11.127)).

$$\overline{E}_K=\hbar\omega=\hbar 4.97272\ X\ 10^{16}\ rad/s=32.73133\ eV \tag{14.485}$$

In Eq. (11.181), substitution of $E_T\left(H_2\right)$ (Eqs. (11.212) and (13.75)), the maximum total energy of each $H_2$-type MO, for $E_{h\nu}$, the mass of the electron, $m_e$, for $M$, and the kinetic energy given by Eq. (14.485) for $\overline{E}_K$ gives the Doppler energy of the electrons for the reentrant orbit:

$$\overline{E}_D\cong E_{h\nu}\sqrt{\frac{2\overline{E}_K}{Mc^2}}=-31.63536831\ eV\sqrt{\frac{2e\left(32.73133\ eV\right)}{m_ec^2}}=-0.35806\ eV \tag{14.486}$$

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency. The decrease in the energy of the $C=C$-bond MO due to the reentrant orbit of the bond in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei, $\overline{E}_{osc}$, is given by the sum of the corresponding energies, $\overline{E}_D$ given by Eq. (14.486) and $\overline{E}_{Kvib}$, the average kinetic energy of vibration which is 1/2 of the vibrational energy of the $C=C$ bond. Using the experimental $C=C$ $E_{vib}\left(\upsilon_{16}\right)$ of $1584.8\ cm^{-1}$ $\left(0.19649\ eV\right)$ [16] for $\overline{E}_{Kvib}$ of the transition state having two bonds, $\overline{E}'_{osc}\left(C=C,\sigma\right)$ per bond is:

$$\overline{E}'_{osc}\left(C=C,\sigma\right)=\overline{E}_D+\overline{E}_{Kvib}=\overline{E}_D+\frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \tag{14.487}$$

$$\overline{E}'_{osc}\left(C=C,\sigma\right)=-0.35806\ eV+\frac{1}{2}\left(0.19649\ eV\right)=-0.25982\ eV \tag{14.488}$$

Given that the vibration and reentrant oscillation is for two $C-C$ bonds of each $C=C$ double bond, $\overline{E}_{benzene\ osc}\left(C=C,\sigma\right)$, is:

$$\overline{E}_{benzene\ osc}\left(C=C,\sigma\right)=2\left(\overline{E}_D+\frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right)=2\left(-0.35806\ eV+\frac{1}{2}\left(0.19649\ eV\right)\right)=-0.51963\ eV \tag{14.489}$$

## TOTAL ENERGIES OF THE $C=C$-BOND MO ELEMENT OF BENZENE

$E_{T+osc}(C=C)$, the total energy of the $C=C$-bond MO of benzene including the Doppler term, is given by the sum of $E_T(C=C)$ (Eq. (14.483)) and $\bar{E}_{benzene\ osc}(C=C,\sigma)$ given by Eq. (14.489).

$$\begin{aligned} E_{T+osc}(C=C) &= V_e + T + V_m + V_p + 2E_T\left(C=C,2sp^3\right) + \bar{E}_{benzene\ osc}(C=C,\sigma) \\ &= E_T(C=C,\sigma) + 2E_T\left(C=C,2sp^3\right) + \bar{E}_{benzene\ osc}(C=C,\sigma) \\ &= E_T(C=C) + \bar{E}_{benzene\ osc}(C=C,\sigma) \end{aligned} \tag{14.490}$$

$$\begin{aligned} E_{T+osc}(C=C) &= \left\{ \begin{array}{l} \left( \dfrac{-2e^2}{8\pi\varepsilon_0 c'} \left[ (0.85252)\left(2-\dfrac{1}{2}\dfrac{a_0}{a}\right)\ln\dfrac{a+c'}{a-c'} - 1 \right] + 2E_T\left(C=C,2sp^3\right) \right) \\ -2\left( (31.63536831\ eV)\sqrt{\dfrac{2\hbar\sqrt{\dfrac{(0.85252)\dfrac{1}{2}\dfrac{e^2}{4\pi\varepsilon_0 b^3}}{m_e}}}{m_e c^2}} - \dfrac{1}{2}\hbar\sqrt{\dfrac{k}{\mu}} \right) \end{array} \right\} \\ &= -65.53833\ eV - 2\left(0.35806\ eV - \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right) \end{aligned} \tag{14.491}$$

From Eqs. (14.489-14.491), the total energy of the $C=C$-bond MO is:

$$\begin{aligned} E_{T+osc}(C=C) &= -63.27074\ eV + 2E_T\left(C=C,2sp^3\right) + \bar{E}_{benzene\ osc}(C=C,\sigma) \\ &= -63.27074\ eV + 2(-1.13380\ eV) - 2\left(0.35806\ eV - \frac{1}{2}(0.19649\ eV)\right) \\ &= -66.05796\ eV \end{aligned} \tag{14.492}$$

where the experimental $E_{vib}$ was used for the $\hbar\sqrt{\frac{k}{\mu}}$ term.

## TOTAL BOND DISSOCIATION ENERGY OF BENZENE

Ethylene serves as a basis element for the $C=C$ bonding of benzene wherein each of the six $C\overset{3e}{=}C$ bonds of benzene comprises $(0.75)(4)=3$ electrons according to Eq. (14.416). The total energy of the bonds of the eighteen electrons of the $C\overset{3e}{=}C$ bonds of benzene, $E_T\left(C_6H_6,C\overset{3e}{=}C\right)$, is given by $(6)(0.75)$ times $E_{T+osc}(C=C)$ (Eq. (14.492)), the total energy of the $C=C$-bond MO of benzene including the Doppler term, minus eighteen times $E\left(C,2sp^3\right)$ (Eq. (14.146)), the initial energy of each $C2sp^3$ HO of each $C$ that forms the double $C=C$ bonds. Thus, the total energy of the six $C\overset{3e}{=}C$ bonds of benzene is:

$$\begin{aligned} E_T\left(C_6H_6,C\overset{3e}{=}C\right) &= (6)(0.75)E_{T+osc}(C=C) - 18E\left(C,2sp^3\right) \\ &= (6)(0.75)(-66.05796\ eV) - 18(-14.63489\ eV) \\ &= -297.26081\ eV - (-263.42798\ eV) \\ &= -33.83284\ eV \end{aligned} \tag{14.493}$$

Each of the $C-H$ bonds of benzene comprises two electrons according to Eq. (14.439). From the energy of each $C-H$ bond, $-E_{D_{benzene}}\left({}^{12}CH\right)$ (Eq. (14.477)), the total energy of the twelve electrons of the six $C-H$ bonds of benzene, $E_T(C_6H_6,C-H)$, is given by:

$$E_T(C_6H_6,C-H) = (6)\left(-E_{D_{benzene}}\left({}^{12}CH\right)\right) = 6(-3.90454\ eV) = -23.42724\ eV \tag{14.494}$$

The total bond dissociation energy of benzene, $E_D(C_6H_6)$, is given by the negative sum of $E_T\left(C_6H_6,C\overset{3e}{=}C\right)$ (Eq. (14.493)) and $E_T(C_6H_6,C-H)$ (Eq. (14.494)):

$$\begin{aligned} E_D(C_6H_6) &= -\left(E_T\left(C_6H_6,C\overset{3e}{=}C\right) + E_T(C_6H_6,C-H)\right) \\ &= -\left((-33.83284\ eV) + (-23.42724\ eV)\right) = 57.2601\ eV \end{aligned} \tag{14.495}$$

The experimental total bond dissociation energy of benzene, $E_T(C_6H_6)$, is given by the negative difference between the enthalpy of its formation ($\Delta H_f(benzene(gas))$) and the sum of the enthalpy of the formation of the gaseous carbons ($\Delta H_f(C(gas))$) and hydrogen ($\Delta H_f(H(gas))$) atoms. The heats of formation are [17-18]:

$$\Delta H_f(benzene(gas)) = 82.9\ kJ/mole\ (0.8592\ eV/molecule) \tag{14.496}$$

$$\Delta H_f(C(gas)) = 716.68\ kJ/mole\ (7.42774\ eV/atom) \tag{14.497}$$

$$\Delta H_f(H(gas)) = 217.998\ kJ/mole\ (2.259353\ eV/atom) \tag{14.498}$$

thus, the total bond dissociation energy of benzene, $E_D(C_6H_6)$, is:

$$\begin{aligned} E_D(C_6H_6) - E_T(C_6H_6) &= -\left(\Delta H_f(benzene(gas)) - \left(6\Delta H_f(C(gas)) + 6\Delta H_f(H(gas))\right)\right) \\ &= -\left(0.8592\ eV - 6\left(7.42774\ eV + 2.259353\ eV\right)\right) \\ &= 57.26\ eV \end{aligned} \tag{14.499}$$

where $E_T(C_6H_6)$ is the total energy of the bonds. The results of the determination of bond parameters of $C_6H_6$ are given in Table 14.1. The calculated results are based on first principles and given in closed-form, exact equations containing fundamental constants only. The agreement between the experimental and calculated results is excellent.

## CONTINUOUS-CHAIN ALKANES ($C_nH_{2n+2},\ n = 3,4,5...\infty$)

The continuous chain alkanes, $C_nH_{2n+2}$, are the homologous series comprising terminal methyl groups at each end of the chain with $n-2$ methylene ($CH_2$) groups in between:

$$CH_3(CH_2)_{n-2}CH_3 \tag{14.500}$$

$C_nH_{2n+2}$ can be solved using the same principles as those used to solve ethane and ethylene wherein the $2s$ and $2p$ shells of each $C$ hybridize to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between two $C2sp^3$ hybridized orbitals (HOs) to form a molecular orbital (MO) permits each participating hybridized orbital to decrease in radius and energy. Three $H$ AOs combine with three carbon $2sp^3$ HOs and two $H$ AOs combine with two carbon $2sp^3$ HOs to form each methyl and methylene group, respectively, where each bond comprises a $H_2$-type MO developed in the Nature of the Chemical Bond of Hydrogen-Type Molecules and Molecular Ions section. The $CH_3$ and $CH_2$ groups bond by forming $H_2$-type MOs between the remaining $C2sp^3$ HOs on the carbons such that each carbon forms four bonds involving its four $C2sp^3$ HOs.

## FORCE BALANCE OF THE $C-C$-BOND MOs OF CONTINUOUS-CHAIN ALKANES

$C_nH_{2n+2}$ comprises a chemical bond between two terminal $CH_3$ radicals and $n-2$ $CH_2$ radicals wherein each methyl and methylene radical comprises three and two chemical bonds, respectively, between carbon and hydrogen atoms. The solution of the parameters of $CH_3$ is given in the Methyl Radical ($CH_3$) section. The solution of the parameters of $CH_2$ is given in the Dihydrogen Carbide Radical ($CH_2$) section and follows the same procedure. Each $C-H$ bond having two spin-paired electrons, one from an initially unpaired electron of the carbon atom and the other from the hydrogen atom, comprises the linear combination of 75% $H_2$-type ellipsoidal MO and 25% $C2sp^3$ HO as given by Eq. (13.429):

$$1\ C2sp^3 + 0.75\ H_2\ MO \rightarrow C-H\ MO \tag{14.501}$$

The proton of the $H$ atom and the nucleus of the $C$ atom are along each internuclear axis and serve as the foci. As in the case of $H_2$, each of the $C-H$-bond MOs is a prolate spheroid with the exception that the ellipsoidal MO surface cannot extend into $C2sp^3$ HO for distances shorter than the radius of the $C2sp^3$ shell since it is energetically unfavorable. Thus, each MO surface comprises a prolate spheroid at the $H$ proton that is continuous with the $C2sp^3$ shell at the $C$ atom whose nucleus serves as the other focus. The electron configuration and the energy, $E(C,2sp^3)$, of the $C2sp^3$ shell is given by Eqs. (13.422) and (13.428), respectively. The central paramagnetic force due to spin of each $C-H$ bond is provided by the spin-pairing force of the $CH_3$ or $CH_2$ MO that has the symmetry of an $s$ orbital that superimposes with the $C2sp^3$ orbitals such that the corresponding angular momenta are unchanged. The energies of each $CH_3$ and $CH_2$ MO involve each $C2sp^3$ and each $H1s$ electron with the formation of each $C-H$ bond. The sum of the energies of the $H_2$-type ellipsoidal MOs is matched to that of the $C2sp^3$ shell.

The force balance of the $C-H$-bond MO is determined by the boundary conditions that arise from the linear combination of orbitals according to Eq. (14.139) and the energy matching condition between the $C2sp^3$-HO components of the MO.

The $CH_3$ and $CH_2$ groups form $C-C$ bonds comprising $H_2$-type MOs between the remaining $C2sp^3$ HOs on the carbons such that each carbon forms four bonds involving its four $C2sp^3$ HOs. The sharing of electrons between any two $C2sp^3$ HOs to form a molecular orbital (MO) comprising two spin-paired electrons permits each $C2sp^3$ HO to decrease in radius and energy. As in the case of the $C-H$ bonds, each $C-C$-bond MO is a prolate-spheroidal-MO surface that cannot extend into $C2sp^3$ HO for distances shorter than the radius of the $C2sp^3$ shell of each atom. Thus, the MO surface comprises a partial prolate spheroid in between the carbon nuclei and is continuous with the $C2sp^3$ shell at each $C$ atom. The energy of the $H_2$-type ellipsoidal MO is matched to that of the $C2sp^3$ shell. As in the case of previous examples of energy-matched MOs such as the $C-C$-bond MO of ethane, each $C-C$-bond MO of $C_nH_{2n+2}$ must comprise 75% of a $H_2$-type ellipsoidal MO in order to match potential, kinetic, and orbital energy relationships. Thus, the $C-C$-bond MO must comprise two $C2sp^3$ HOs and 75% of a $H_2$-type ellipsoidal MO divided between the two $C2sp^3$ HOs:

$$2\ C2sp^3 + 0.75\ H_2\ MO \rightarrow C-C-bond\ MO \tag{14.502}$$

The linear combination of the $H_2$-type ellipsoidal MO with each $C2sp^3$ HO further comprises an excess 25% charge-density contribution from each $C2sp^3$ HO to the $C-C$-bond MO to achieve an energy minimum. The force balance of the $C-C$-bond MO is determined by the boundary conditions that arise from the linear combination of orbitals according to Eq. (14.502) and the energy matching condition between the $C2sp^3$-HO components of the MO.

Before bonding, the $2sp^3$ hybridized orbital arrangement of each carbon atom is given by Eq. (14.140). The sum $E_T\left(C,2sp^3\right)$ of calculated energies of $C$, $C^+$, $C^{2+}$, and $C^{3+}$ is given by Eq. (14.141). The radius $r_{2sp^3}$ of the $C2sp^3$ shell is given by Eq. (14.142). The Coulombic energy $E_{Coulomb}\left(C,2sp^3\right)$ and the energy $E\left(C,2sp^3\right)$ of the outer electron of the $C2sp^3$ shell are given by Eqs. (14.143) and (14.146), respectively.

The formation of each $C-C$ bond of $C_nH_{2n+2}$ further requires that the energy of all $H_2$-type prolate spheroidal MOs ($\sigma$ MOs) be matched at all $C2sp^3$ HOs since they are continuous throughout the molecule. Thus, the energy of each $C2sp^3$ HO must be a linear combination of that of the $CH_3$ and $CH_2$ groups that serve as basis elements. Each $CH_3$ forms one $C-C$ bond, and each $CH_2$ group forms two. Thus, the energy of each $C2sp^3$ HO of each $CH_3$ and $CH_2$ group alone is given by that in ethane and ethylene, respectively. The parameters of ethane and ethylene are given by Eqs. (14.147-14.151) and (14.244-14.247), respectively. The alkane parameters can be determined by first reviewing those of ethane and ethylene.

With the formation of the $C-C$-bond MO of ethane from two methyl radicals, each having a $C2sp^3$ electron with an energy given by Eq. (14.146), the total energy of the state is given by the sum over the four electrons. The sum $E_T\left(C_{ethane},2sp^3\right)$ of calculated energies of $C2sp^3$, $C^+$, $C^{2+}$, and $C^{3+}$ given by Eq. (14.147), is:

$$\begin{aligned} E_T\left(C_{ethane},2sp^3\right) &= -\left(64.3921\ eV + 48.3125\ eV + 24.2762\ eV + E\left(C,2sp^3\right)\right) \\ &= -\left(64.3921\ eV + 48.3125\ eV + 24.2762\ eV + 14.63489\ eV\right) \\ &= -151.61569\ eV \end{aligned} \tag{14.503}$$

where $E\left(C,2sp^3\right)$ is the sum of the energy of $C$, $-11.27671\ eV$, and the hybridization energy. The orbital-angular-momentum interactions also cancel such that the energy of the $E_T\left(C_{ethane},2sp^3\right)$ is purely Coulombic.

The sharing of electrons between two $C2sp^3$ HOs to form a $C-C$-bond MO permits each participating hybridized orbital to decrease in radius and energy. In order to further satisfy the potential, kinetic, and orbital energy relationships, each $C2sp^3$ HO donates an excess of 25% of its electron density to the $C-C$-bond MO to form an energy minimum. By considering this electron redistribution in the ethane molecule as well as the fact that the central field decreases by an integer for each successive electron of the shell, the radius $r_{ethane2sp^3}$ of the $C2sp^3$ shell of ethane may be calculated from the Coulombic energy using Eq. (10.102).

$$r_{ethane2sp^3} = \left(\sum_{n=2}^{5}(Z-n) - 0.25\right)\frac{e^2}{8\pi\varepsilon_0\left(e151.61569\ eV\right)} = \frac{9.75e^2}{8\pi\varepsilon_0\left(e151.61569\ eV\right)} = 0.87495a_0 \tag{14.504}$$

using Eqs. (10.102) and (14.504), the Coulombic energy $E_{Coulomb}\left(C_{ethane},2sp^3\right)$ of the outer electron of the $C2sp^3$ shell is:

$$E_{Coulomb}\left(C_{ethane},2sp^3\right) = \frac{-e^2}{8\pi\varepsilon_0 r_{ethane2sp^3}} = \frac{-e^2}{8\pi\varepsilon_0 0.87495a_0} = -15.55033\ eV \tag{14.505}$$

During hybridization, one of the spin-paired $2s$ electrons is promoted to the $C2sp^3$ shell as an unpaired electron. The energy for the promotion is the magnetic energy given by Eq. (14.145). Using Eqs. (14.145) and (14.505), the energy $E\left(C_{ethane}, 2sp^3\right)$ of the outer electron of the $C2sp^3$ shell is:

$$E\left(C_{ethane}, 2sp^3\right) = \frac{-e^2}{8\pi\varepsilon_0 r_{ethane2sp^3}} + \frac{2\pi\mu_0 e^2\hbar^2}{m_e^2\left(r_3\right)^3} = -15.55033\ eV + 0.19086\ eV = -15.35946\ eV \tag{14.506}$$

thus, $E_T\left(C-C, 2sp^3\right)$, the energy change of each $C2sp^3$ shell with the formation of the $C-C$-bond MO is given by the difference between Eq. (14.146) and Eq. (14.506).

$$E_T\left(C-C, 2sp^3\right) = E\left(C_{ethane}, 2sp^3\right) - E\left(C, 2sp^3\right) = -15.35946\ eV - \left(-14.63489\ eV\right) = -0.72457\ eV \tag{14.507}$$

Next, consider the formation of the $C=C$-bond MO of ethylene from two $CH_2$ radicals, each having a $C2sp^3$ electron with an energy given by Eq. (14.146). The sum $E_T\left(C_{ethylene}, 2sp^3\right)$ of calculated energies of $C2sp^3$, $C^+$, $C^{2+}$, and $C^{3+}$ is given by Eq. (14.147). The sharing of electrons between two pairs of $C2sp^3$ HOs to form a $C=C$-bond MO permits each participating HO to decrease in radius and energy. In order to further satisfy the potential, kinetic, and orbital energy relationships, each participating $C2sp^3$ HO donates an excess of 25% of its electron density to the $C=C$-bond MO to form an energy minimum. By considering this electron redistribution in the ethylene molecule as well as the fact that the central field decreases by an integer for each successive electron of the shell, the radius $r_{ethylene2sp^3}$ of the $C2sp^3$ shell of ethylene may be calculated from the Coulombic energy using Eqs. (10.102) and (14.147):

$$\begin{aligned} r_{ethylene2sp^3} &= \left(\sum_{n=2}^{5}(Z-n) - 0.5\right)\frac{e^2}{8\pi\varepsilon_0\left(e151.61569\ eV\right)} \\ &= \frac{9.5e^2}{8\pi\varepsilon_0\left(e151.61569\ eV\right)} \\ &= 0.85252a_0 \end{aligned} \tag{14.508}$$

where $Z=6$ for carbon. Using Eqs. (10.102) and (14.508), the Coulombic energy $E_{Coulomb}\left(C_{ethylene}, 2sp^3\right)$ of the outer electron of the $C2sp^3$ shell is:

$$E_{Coulomb}\left(C_{ethylene}, 2sp^3\right) = \frac{-e^2}{8\pi\varepsilon_0 r_{ethylene2sp^3}} = \frac{-e^2}{8\pi\varepsilon_0 0.85252a_0} = -15.95955\ eV \tag{14.509}$$

During hybridization, one of the spin-paired $2s$ electrons is promoted to the $C2sp^3$ shell as an unpaired electron. The energy for the promotion is the magnetic energy given by Eq. (14.145). Using Eqs. (14.145) and (14.509), the energy $E\left(C_{ethylene}, 2sp^3\right)$ of the outer electron of the $C2sp^3$ shell is:

$$E\left(C_{ethylene}, 2sp^3\right) = \frac{-e^2}{8\pi\varepsilon_0 r_{ethylene2sp^3}} + \frac{2\pi\mu_0 e^2\hbar^2}{m_e^2\left(r_3\right)^3} = -15.95955\ eV + 0.19086\ eV = -15.76868\ eV \tag{14.510}$$

thus, $E_T\left(C=C, 2sp^3\right)$, the energy change of each $C2sp^3$ shell with the formation of the $C=C$-bond MO is given by the difference between Eq. (14.146) and Eq. (14.510):

$$\begin{aligned} E_T\left(C=C, 2sp^3\right) &= E\left(C_{ethylene}, 2sp^3\right) - E\left(C, 2sp^3\right) \\ &= -15.76868\ eV - \left(-14.63489\ eV\right) \\ &= -1.13380\ eV \end{aligned} \tag{14.511}$$

To meet the energy matching condition for all $\sigma$ MOs at all $C2sp^3$ HOs, the energy $E\left(C_{alkane}, 2sp^3\right)$ of the outer electron of the $C2sp^3$ shell of each alkane carbon atom must be the average of $E\left(C_{ethane}, 2sp^3\right)$ (Eq. (14.506)) and $E\left(C_{ethylene}, 2sp^3\right)$ (Eq. (14.510)).

$$\begin{aligned} E\left(C_{alkane}, 2sp^3\right) &= \frac{E\left(C_{ethane}, 2sp^3\right) + E\left(C_{ethylene}, 2sp^3\right)}{2} \\ &= \frac{\left(-15.35946\ eV\right) + \left(-15.76868\ eV\right)}{2} \\ &= -15.56407\ eV \end{aligned} \tag{14.512}$$

And, $E_{T_{alkane}}\left(C-C,2sp^3\right)$, the energy change of each $C2sp^3$ shell with the formation of each $C-C$-bond MO, must be the average of $E_T\left(C-C,2sp^3\right)$ (Eq. (14.507)) and $E_T\left(C=C,2sp^3\right)$ (Eq. (14.511)).

$$\begin{aligned} E_{T_{alkane}}\left(C-C,2sp^3\right) &= \frac{E_T\left(C-C,2sp^3\right)+E_T\left(C=C,2sp^3\right)}{2} \\ &= \frac{\left(-0.72457\ eV\right)+\left(-1.13379\ eV\right)}{2} \\ &= -0.92918\ eV \end{aligned} \tag{14.513}$$

using Eq. (10.102), the radius $r_{alkane2sp^3}$ of the $C2sp^3$ shell of each carbon atom of $C_nH_{2n+2}$ may be calculated from the Coulombic energy using the initial energy $E_{Coulomb}\left(C,2sp^3\right)=-14.82575\ eV$ (Eq. (14.143)) and $E_{T_{alkane}}\left(C-C,2sp^3\right)$ Eq. (14.513)), the energy change of each $C2sp^3$ shell with the formation of each $C-C$-bond MO. Consider the case of a methyl carbon which donates $E_{T_{alkane}}\left(C-C,2sp^3\right)$ Eq. (14.513)) to a single $C-C$ bond:

$$\begin{aligned} r_{alkane2sp^3} &= \frac{-e^2}{8\pi\varepsilon_0\left(E_{Coulomb}\left(C,2sp^3\right)+E_{T_{alkane}}\left(C-C,2sp^3\right)\right)} \\ &= \frac{e^2}{8\pi\varepsilon_0\left(e14.825751\ eV+e0.92918\ eV\right)} \\ &= 0.86359a_0 \end{aligned} \tag{14.514}$$

using Eqs. (10.102) and (14.514), the Coulombic energy $E_{Coulomb}\left(C_{alkane},2sp^3\right)$ of the outer electron of the $C2sp^3$ shell is:

$$E_{Coulomb}\left(C_{alkane},2sp^3\right)=\frac{-e^2}{8\pi\varepsilon_0 r_{alkane2sp^3}}=\frac{-e^2}{8\pi\varepsilon_0 0.86359a_0}=-15.75493\ eV \tag{14.515}$$

During hybridization, one of the spin-paired $2s$ electrons is promoted to the $C2sp^3$ shell as an unpaired electron. The energy for the promotion is the magnetic energy given by Eq. (14.145). Using Eqs. (14.145) and (14.515), the energy $E\left(C_{alkane},2sp^3\right)$ of the outer electron of the $C2sp^3$ shell is:

$$E\left(C_{alkane},2sp^3\right)=\frac{-e^2}{8\pi\varepsilon_0 r_{alkane2sp^3}}+\frac{2\pi\mu_0 e^2\hbar^2}{m_e^2\left(r_3\right)^3}=-15.75493\ eV+0.19086\ eV=-15.56407\ eV \tag{14.516}$$

thus, $E_{T_{alkane}}\left(C-C,2sp^3\right)$, the energy change of each $C2sp^3$ shell with the formation of each $C-C$-bond MO is given by the difference between Eq. (14.146) and Eq. (14.516):

$$E_{T_{alkane}}\left(C-C,2sp^3\right)=E\left(C_{alkane},2sp^3\right)-E\left(C,2sp^3\right)=-15.56407\ eV-\left(-14.63489\ eV\right)=-0.92918\ eV \tag{14.517}$$

which agrees with Eq. (14.513).

The energy contribution due to the charge donation at each carbon superimposes linearly. In general, the radius $r_{mol2sp^3}$ of the $C2sp^3$ HO of a carbon atom of a group of a given molecule is calculated using Eq. (14.514) by considering $\sum E_{T_{mol}}\left(MO,2sp^3\right)$, the total energy donation to each bond with which it participates in bonding. The general equation for the radius is given by:

$$\begin{aligned} r_{mol2sp^3} &= \frac{-e^2}{8\pi\varepsilon_0\left(E_{Coulomb}\left(C,2sp^3\right)+\sum E_{T_{mol}}\left(MO,2sp^3\right)\right)} \\ &= \frac{e^2}{8\pi\varepsilon_0\left(e14.825751\ eV+\sum\left|E_{T_{mol}}\left(MO,2sp^3\right)\right|\right)} \end{aligned} \tag{14.518}$$

The $C2sp^3$ HO of each methyl group of an alkane contributes $-0.92918\ eV$ to the corresponding single $C-C$ bond; thus, the corresponding $C2sp^3$ HO radius is given by Eq. (14.514). The $C2sp^3$ HO of each methylene group of $C_nH_{2n+2}$ contributes $-0.92918\ eV$ to each of the two corresponding $C-C$ bond MOs. Thus, the radius of each methylene group of an alkane is given by:

$$\begin{aligned} r_{alkaneC_{methylene}2sp^3} &= \frac{-e^2}{8\pi\varepsilon_0\left(E_{Coulomb}\left(C,2sp^3\right)+\sum E_{T_{alkane}}\left(methylene\ C-C,2sp^3\right)\right)} \\ &= \frac{e^2}{8\pi\varepsilon_0\left(e14.825751\ eV + e0.92918\ eV + e0.92918\ eV\right)} \\ &= 0.81549a_0 \end{aligned} \qquad (14.519)$$

As in the case with ethane, the $H_2$-type ellipsoidal MO comprises 75% of the $C-C$-bond MO shared between two $C2sp^3$ HOs corresponding to the electron charge density in Eq. (11.65) of $\frac{-0.75e}{2}$. But, the additional 25% charge-density contribution to the $C-C$-bond MO causes the electron charge density in Eq. (11.65) to be $\frac{-e}{2}=-0.5e$. Thus, the force constant $k'$ to determine the ellipsoidal parameter $c'$ in terms of the central force of the foci is given by Eq. (14.152). The distance from the origin of the $C-C$-bond MO to each focus $c'$ is given by Eq. (14.153). The internuclear distance from is given by Eq. (14.154). The length of the semiminor axis of the prolate spheroidal $C-C$-bond MO $b=c$ is given by Eq. (13.62). The eccentricity, $e$, is given by Eq. (13.63). The solution of the semimajor axis $a$ then allows for the solution of the other axes of each prolate spheroid and eccentricity of the $C-C$-bond MO. Since the $C-C$-bond MO comprises a $H_2$-type-ellipsoidal MO that transitions to the $C_{alkane}2sp^3$ HO of each carbon, the energy $E\left(C_{alkane},2sp^3\right)$ in Eq. (14.512) adds to that of the $H_2$-type ellipsoidal MO to give the total energy of the $C-C$-bond MO. From the energy equation and the relationship between the axes, the dimensions of the $C-C$-bond MO are solved. Similarly, $E\left(C_{alkane},2sp^3\right)$ is added to the energy of the $H_2$-type ellipsoidal MO of each $C-H$ bond of the methyl and methylene groups to give their total energy. From the energy equation and the relationship between the axes, the dimensions of the equivalent $C-H$-bond MOs of the methyl and methylene groups in the alkane are solved.

The general equations for the energy components of $V_e$, $V_p$, $T$, $V_m$, and $E_T$ of each $C-C$-bond MO are the same as those of the $CH$ MO except that energy of the $C_{alkane}2sp^3$ HO is used. The energy components at each carbon atom superimpose linearly and may be treated independently. Since each prolate spheroidal $H_2$-type MO transitions to the $C_{alkane}2sp^3$ HO of each corresponding carbon of the bond and the energy of the $C_{alkane}2sp^3$ shell treated independently must remain constant and equal to the $E\left(C_{alkane},2sp^3\right)$ given by Eq. (14.512), the total energy $E'_{T_{alkane}}\left(C-C,\sigma\right)$ of the $\sigma$ component of each $C-C$-bond MO is given by the sum of the energies of the orbitals corresponding to the composition of the linear combination of the $C_{alkane}2sp^3$ HO and the $H_2$-type ellipsoidal MO that forms the $\sigma$ component of the $C-C$-bond MO as given by Eq. (14.502) with the electron charge redistribution. The total number of $C-C$ bonds in $C_nH_{2n+2}$ is $n-1$. Using Eqs. (13.431) and (14.512), $E_{T_{alkane}}\left(C-C,\sigma\right)$ of the $n-1$ bonds is given by:

$$\begin{aligned} E_{T_{alkane}}\left(C-C,\sigma\right) &= \left(n-1\right)\left(E_T+E\left(C_{alkane},2sp^3\right)\right) \\ &= \left(n-1\right)\left(-\frac{e^2}{8\pi\varepsilon_0 c'}\left[\left(0.91771\right)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]-15.56407\ eV\right) \end{aligned} \qquad (14.520)$$

To match the boundary condition that the total energy of each $H_2$-type ellipsoidal MO is given by Eqs. (11.212) and (13.75), $E_{T_{alkane}}\left(C-C,\sigma\right)$ given by Eq. (14.520) is set equal to $\left(n-1\right)$ times Eq. (13.75).

$$E_{T_{alkane}}\left(C-C,\sigma\right)=\left(n-1\right)\left(\begin{matrix}-\frac{e^2}{8\pi\varepsilon_0 c'}\left[\left(0.91771\right)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right] \\ -15.56407\ eV\end{matrix}\right)=\left(n-1\right)\left(-31.63536831\ eV\right) \qquad (14.521)$$

From the energy relationship given by Eq. (14.521) and the relationship between the axes given by Eqs. (14.153-14.154) and (13.62-13.63), the dimensions of the $C-C$-bond MO can be solved.

Substitution of Eq. (14.153) into Eq. (14.521) gives:

$$\frac{e^2}{8\pi\varepsilon_0\sqrt{aa_0}}\left[\left(0.91771\right)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+\sqrt{aa_0}}{a-\sqrt{aa_0}}-1\right]=e16.07130 \qquad (14.522)$$

The most convenient way to solve Eq. (14.522) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is:

$$a=2.12499a_0=1.12450\ X\ 10^{-10}\ m \qquad (14.523)$$

Substitution of Eq. (14.523) into Eq. (14.155) gives:

$$c'=1.45774a_0=7.71400\ X\ 10^{-11}\ m \qquad (14.524)$$

The internuclear distance given by multiplying Eq. (14.524) by two is:

$$2c' = 2.91547a_0 = 1.54280\ X\ 10^{-10}\ m \tag{14.525}$$

The experimental $C-C$ bond distance of propane is [3]:

$$2c' = 1.532\ X\ 10^{-10}\ m \tag{14.526}$$

The experimental $C-C$ bond distance of butane is [3]:

$$2c' = 1.531\ X\ 10^{-10}\ m \tag{14.527}$$

Substitution of Eqs. (14.523-14.524) into Eq. (13.62) gives:

$$b = c = 1.54616a_0 = 8.18192\ X\ 10^{-11}\ m \tag{14.528}$$

Substitution of Eqs. (14.523-14.524) into Eq. (13.63) gives:

$$e = 0.68600 \tag{14.529}$$

The nucleus of the $C$ atoms comprise the foci of each $H_2$-type ellipsoidal MO. The parameters of the point of intersection of the $H_2$-type ellipsoidal MO and the $C_{alkane}2sp^3$ HO are given by Eqs. (13.84-13.95) and (13.261-13.270). The polar intersection angle $\theta'$ is given by Eq. (13.261) where for methylene bonds $r_n = r_{alkane2sp^3} = r_{methylene2sp^3}$=$0.81549a_0$ is the radius of the $C_{alkane}2sp^3$ shell given by Eq. (14.519). Substitution of Eqs. (14.523-14.524) into Eq. (13.261) gives:

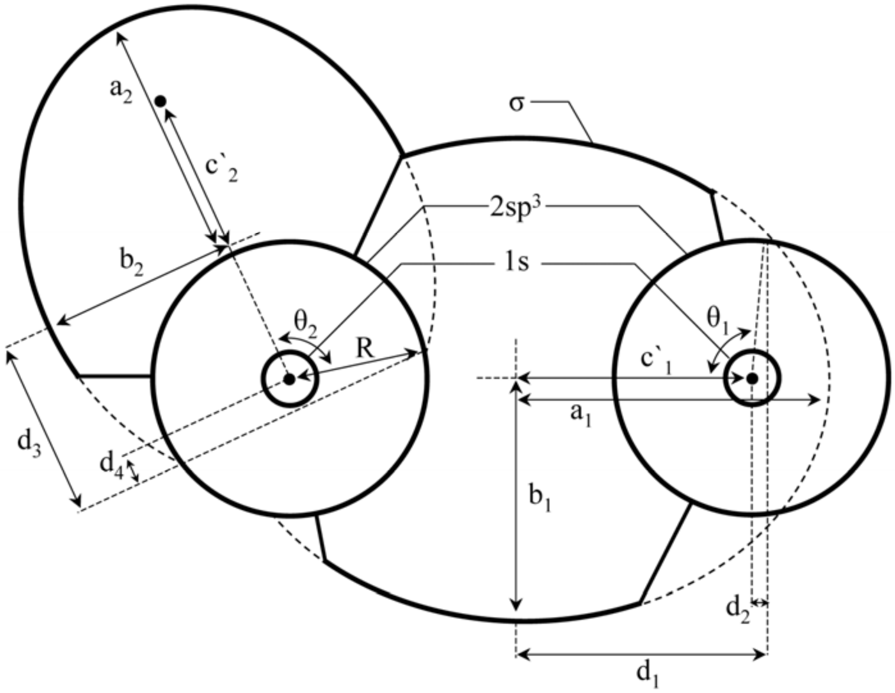
$$\theta' = 56.41° \tag{14.530}$$

Then, the angle $\theta_{C-C_{alkane}2sp^3HO}$ the radial vector of the $C2sp^3$ HO makes with the internuclear axis is:

$$\theta_{C-C_{alkane}2sp^3HO} = 180° - 56.41° = 123.59° \tag{14.531}$$

as shown in Figure 14.16.

Figure 14.16. The cross section of one $C-C$-bond MO ($\sigma$ MO) and one $C-H$-bond MO of $C_nH_{2n+2}$ showing the axes, angles, and point of intersection of each $H_2$-type ellipsoidal MO with the corresponding $C_{alkane}2sp^3$ HO. The continuation of each $H_2$-type-ellipsoidal-MO basis element of the $C-C$ bond and the $C-H$-bond beyond the intersection point with each $C_{alkane}2sp^3$ shell and $\sigma$ MO is shown as dashed since each only serves to solve the energy match with the $C_{alkane}2sp^3$ shell and does not represent charge density. Similarly, the vertical dashed line only designates the parameters of each intersection point. The actual charge density is shown by the solid lines. Legend: $a$: semimajor axis, $b$: semiminor axis, $c'$: internuclear distance, $d_1 : d_{C-C_{alkane},H_2MO}$, $\theta_1 : \theta_{C-C_{alkane}2sp^3HO}$, $d_2 : d_{C-C_{alkane}2sp^3HO}$, $R : r_{alkaneC2sp^3}$, $d_3 : d_{C-H_{alkane},H_2MO}$, $\theta_2 : \theta_{C-H_{alkane}2sp^3HO}$, and $d_4 : d_{C-H_{alkane}2sp^3HO}$.



Consider the right-hand intersection point. The Cartesian $\mathbf{i}$-coordinate of the interception point of the MO and the AO can be calculated using the MO ellipsoidal parameters by first calculating the parametric angle in Eq. (11.83) that matches Cartesian $\mathbf{j}$-coordinate components at the point of intersection. Thus, the matching elliptic parametric angle $\omega t = \theta_{C-C_{alkane},H_2MO}$ satisfies the following relationship:

$$r_{alkane2sp^3}\sin\theta_{C-C_{alkane}2sp^3HO} = 0.81549a_0\sin\theta_{C-C_{alkane}2sp^3HO} = b\sin\theta_{C-C_{alkane},H_2MO} \tag{14.532}$$

such that

$$\theta_{C-C_{alkane},H_2MO} = \sin^{-1}\frac{0.81549a_0\sin\theta_{C-C_{alkane}2sp^3HO}}{b} = \sin^{-1}\frac{0.81549a_0\sin 123.59°}{b} \tag{14.533}$$

with the use of Eq. (14.531). Substitution of Eq. (14.528) into Eq. (14.533) gives:

$$\theta_{C-C_{alkane},H_2MO} = 26.06° \tag{14.534}$$

Then, the distance $d_{C-C_{alkane},H_2MO}$ along the internuclear axis from the origin of $H_2$-type ellipsoidal MO to the point of intersection of the orbitals is given by

$$d_{C-C_{alkane},H_2MO} = a\cos\theta_{C-C_{alkane},H_2MO} \tag{14.535}$$

Substitution of Eqs. (14.523) and (14.534) into Eq. (14.535) gives:

$$d_{C-C_{alkane},H_2MO} = 1.90890a_0 = 1.01015\ X\ 10^{-10}\ m \tag{14.536}$$

The distance $d_{C-C_{alkane}2sp^3HO}$ along the internuclear axis from the origin of the $C$ atom to the point of intersection of the orbitals is given by:

$$d_{C-C_{alkane}2sp^3HO} = d_{C-C_{alkane},H_2MO} - c' \tag{14.537}$$

Substitution of Eqs. (14.524) and (14.536) into Eq. (14.537) gives:

$$d_{C-C_{alkane}2sp^3HO} = 0.45117a_0 = 2.38748\ X\ 10^{-11}\ m \tag{14.538}$$

## FORCE BALANCE OF THE $CH_3$ MOs OF CONTINUOUS-CHAIN ALKANES

Each of the two $CH_3$ MOs must comprise three equivalent $C-H$ bonds with each comprising 75% of a $H_2$-type ellipsoidal MO and a $C2sp^3$ HO as given by Eq. (13.540).

$$3\left[1\ C2sp^3 + 0.75\ H_2\ MO\right] \rightarrow CH_3\ MO \tag{14.539}$$

The force balance of the $CH_3$ MO is determined by the boundary conditions that arise from the linear combination of orbitals according to Eq. (14.539) and the energy matching condition between the hydrogen and $C2sp^3$ HO components of the MO.

The force constant $k'$ to determine the ellipsoidal parameter $c'$ of the each $H_2$-type-ellipsoidal-MO component of the $CH_3$ MO in terms of the central force of the foci is given by Eq. (13.59). The distance from the origin of each $C-H$-bond MO to each focus $c'$ is given by Eq. (13.60). The internuclear distance is given by Eq. (13.61). The length of the semiminor axis of the prolate spheroidal $C-H$-bond MO $b=c$ is given by Eq. (13.62). The eccentricity, $e$, is given by Eq. (13.63). The solution of the semimajor axis $a$ then allows for the solution of the other axes of each prolate spheroid and eccentricity of each $C-H$-bond MO. Since each of the three prolate spheroidal $C-H$-bond MOs comprises an $H_2$-type-ellipsoidal MO that transitions to the $C_{alkane}2sp^3$ HO of $C_nH_{2n+2}$, the energy $E\left(C_{alkane},2sp^3\right)$ of Eq. (14.512) adds to that of the three corresponding $H_2$-type ellipsoidal MOs to give the total energy of the $CH_3$ MO. From the energy equation and the relationship between the axes, the dimensions of the $CH_3$ MO are solved.

The energy components of $V_e$, $V_p$, $T$, and $V_m$ are the same as those of methyl radical, three times those of $CH$ corresponding to the three $C-H$ bonds except that energy of the $C_{alkane}2sp^3$ HO is used. Since each prolate spheroidal $H_2$-type MO transitions to the $C_{alkane}2sp^3$ HO and the energy of the $C_{alkane}2sp^3$ shell must remain constant and equal to the $E\left(C_{alkane},2sp^3\right)$ given by Eq. (14.512), the total energy $E_{T_{alkane}}\left(CH_3\right)$ of the $CH_3$ MO is given by the sum of the energies of the orbitals corresponding to the composition of the linear combination of the $C_{alkane}2sp^3$ HO and the three $H_2$-type ellipsoidal MOs that forms the $CH_3$ MO as given by Eq. (14.539). Using Eq. (13.431) or Eq. (13.541), $E_{T_{alkane}}\left(CH_3\right)$ is given by:

$$E_{T_{alkane}}\left(CH_3\right) = E_T + E\left(C_{alkane},2sp^3\right) = -\frac{3e^2}{8\pi\varepsilon_0 c'}\left[(0.91771)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right] - 15.56407\ eV \tag{14.540}$$

$E_{T_{alkane}}\left(CH_3\right)$ given by Eq. (14.540) is set equal to three times the energy of the $H_2$-type ellipsoidal MO minus two times the Coulombic energy of $H$ given by Eq. (13.542):

$$E_T\left(CH_3\right) = -\frac{3e^2}{8\pi\varepsilon_0 c'}\left[(0.91771)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right] - 15.56407\ eV = -67.69450\ eV \tag{14.541}$$

From the energy relationship given by Eq. (14.541) and the relationship between the axes given by Eqs. (13.60-13.63), the dimensions of the $CH_3$ MO can be solved.

Substitution of Eq. (13.60) into Eq. (14.541) gives:

$$\frac{3e^2}{8\pi\varepsilon_0\sqrt{\frac{2aa_0}{3}}}\left[(0.91771)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+\sqrt{\frac{2aa_0}{3}}}{a-\sqrt{\frac{2aa_0}{3}}}-1\right]=e52.13044 \tag{14.542}$$

The most convenient way to solve Eq. (14.542) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is:

$$a=1.64920a_0=8.72720\ X\ 10^{-11}\ m \tag{14.543}$$

Substitution of Eq. (14.543) into Eq. (14.60) gives:

$$c'=1.04856a_0=5.54872\ X\ 10^{-11}\ m \tag{14.544}$$

The internuclear distance given by multiplying Eq. (14.544) by two is:

$$2c'=2.09711a_0=1.10974\ X\ 10^{-10}\ m \tag{14.545}$$

The experimental $C-H$ bond distance of propane is [3]:

$$2c'=1.107\ X\ 10^{-10}\ m \tag{14.546}$$

Substitution of Eqs. (14.543-14.544) into Eq. (14.62) gives:

$$b=c=1.27295a_0=6.73616\ X\ 10^{-11}\ m \tag{14.547}$$

Substitution of Eqs. (14.543-14.544) into Eq. (14.63) gives:

$$e=0.63580 \tag{14.548}$$

The nucleus of the $H$ atom and the nucleus of the $C$ atom comprise the foci of each $H_2$-type ellipsoidal MO. The parameters of the point of intersection of the $H_2$-type ellipsoidal MO and the $C_{alkane}2sp^3$ HO are given by Eqs. (13.84-13.95) and (13.261-13.270). The polar intersection angle $\theta'$ is given by Eq. (13.261) where $r_n=r_{alkane2sp^3}=0.86359a_0$ is the radius of the $C_{alkane}2sp^3$ shell. Substitution of Eqs. (14.543-14.544) into Eq. (13.261) gives:

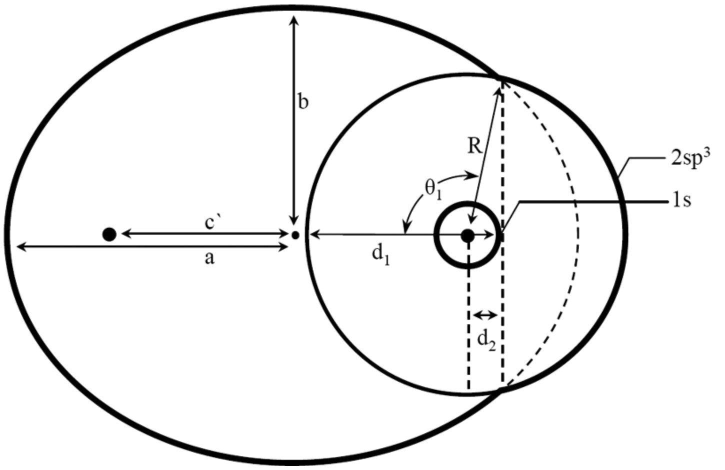
$$\theta'=77.49° \tag{14.549}$$

Then, the angle $\theta_{C-H_{alkane}2sp^3HO}$ the radial vector of the $C2sp^3$ HO makes with the internuclear axis is:

$$\theta_{C-H_{alkane}2sp^3HO}=180°-77.49°=102.51° \tag{14.550}$$

as shown in Figure 14.17.

Figure 14.17. The cross section of one $C-H$-bond MO of $C_nH_{2n+2}$ showing the axes, angles, and point of intersection of the $H_2$-type ellipsoidal MO with the $C_{alkane}2sp^3$ HO. The continuation of the $H_2$-type-ellipsoidal-MO basis element beyond the intersection point with the $C_{alkane}2sp^3$ shell is shown as dashed since it only serves to solve the energy match with the $C_{alkane}2sp^3$ shell and does not represent charge density. Similarly, the vertical dashed line only designates the parameters of the intersection point. The actual charge density is shown by the solid lines. Legend: $a$: semimajor axis, $b$: semiminor axis, $c'$: internuclear distance, $d_1 : d_{C-H_{alkane},H_2MO}$, $\theta_1 : \theta_{C-H_{alkane}2sp^3HO}$, $d_2 : d_{C-H_{alkane}2sp^3HO}$, and $R : r_{alkane2sp^3}$.



The Cartesian $\mathbf{i}$-coordinate of the interception point of the MO and the AO can be calculated using the MO ellipsoidal parameters by first calculating the parametric angle in Eq. (11.83) that matches Cartesian $\mathbf{j}$-coordinate components at the point of intersection. Thus, the matching elliptic parametric angle $\omega t = \theta_{C-H_{alkane},H_2MO}$ satisfies the following relationship:

$$r_{alkane2sp^3} \sin\theta_{C-H_{alkane}2sp^3HO} = 0.86359a_0 \sin\theta_{C-H_{alkane}2sp^3HO} = b\sin\theta_{C-H_{alkane},H_2MO} \tag{14.551}$$

such that

$$\theta_{C-H_{alkane},H_2MO} = \sin^{-1}\frac{0.86359a_0 \sin\theta_{C-H_{alkane}2sp^3HO}}{b} = \sin^{-1}\frac{0.86359a_0 \sin 102.51°}{b} \tag{14.552}$$

with the use of Eq. (14.550). Substitution of Eq. (14.547) into Eq. (14.552) gives:

$$\theta_{C-H_{alkane},H_2MO} = 41.48° \tag{14.553}$$

Then, the distance $d_{C-H_{alkane},H_2MO}$ along the internuclear axis from the origin of $H_2$-type ellipsoidal MO to the point of intersection of the orbitals is given by:

$$d_{C-H_{alkane},H_2MO} = a\cos\theta_{C-H_{alkane},H_2MO} \tag{14.554}$$

Substitution of Eqs. (14.543) and (14.553) into Eq. (14.554) gives:

$$d_{C-H_{alkane},H_2MO} = 1.23564a_0 = 6.53871\ X\ 10^{-11}\ m \tag{14.555}$$

The distance $d_{C-H_{alkane}2sp^3HO}$ along the internuclear axis from the origin of the $C$ atom to the point of intersection of the orbitals is given by

$$d_{C-H_{alkane}2sp^3HO} = d_{C-H_{alkane},H_2MO} - c' \tag{14.556}$$

Substitution of Eqs. (14.544) and (14.555) into Eq. (14.556) gives:

$$d_{C-H_{alkane}2sp^3HO} = 0.18708a_0 = 9.89999\ X\ 10^{-12}\ m \tag{14.557}$$

## BOND ANGLE OF THE $CH_3$ AND $CH_2$ GROUPS

Each $CH_3$ MO comprises a linear combination of three $C-H$-bond MOs. Each $C-H$-bond MO comprises the superposition of a $H_2$-type ellipsoidal MO and the $C_{alkane}2sp^3$ HO. A bond is also possible between the two H atoms of the $C-H$ bonds. Such $H-H$ bonding would decrease the $C-H$ bond strength since electron density would be shifted from the $C-H$ bonds to the $H-H$ bond. Thus, the bond angle between the two $C-H$ bonds is determined by the condition that the total energy of the $H_2$-type ellipsoidal MO between the terminal $H$ atoms of the $C-H$ bonds is zero. From Eqs. (11.79) and (13.228), the distance from the origin to each focus of the $H-H$ ellipsoidal MO is:

$$c' = a\sqrt{\frac{\hbar^2 4\pi\varepsilon_0}{m_e e^2 2a}} = \sqrt{\frac{aa_0}{2}} \tag{14.558}$$

The internuclear distance from Eq. (14.558) is:

$$2c' = 2\sqrt{\frac{aa_0}{2}} \tag{14.559}$$

The length of the semiminor axis of the prolate spheroidal $H-H$ MO $b=c$ is given by Eq. (14.62).

The bond angle of the $CH_3$ groups of $C_nH_{2n+2}$ is derived by using the orbital composition and an energy matching factor as in the case with the $CH_3$ radical. Since each pair of $H_2$-type ellipsoidal MOs initially comprise 75% of the $H$ electron density of $H_2$ and the energy of each $H_2$-type ellipsoidal MO is matched to that of the $C_{alkane}2sp^3$ HO, the component energies and the total energy $E_T$ of the $H-H$ bond are given by Eqs. (13.67-13.73) except that $V_e$, $T$, and $V_m$ are corrected for the hybridization-energy-matching factor of $0.86359$. Hybridization with 25% electron donation to the $C-C$-bond gives rise to the $C_{alkane}2sp^3$ HO-shell Coulombic energy $E_{Coulomb}\left(C_{alkane},2sp^3\right)$ given by Eq. (14.515). The corresponding normalization factor for determining the zero of the total $H-H$ bond energy is given by the ratio of $15.75493\ eV$, the magnitude of $E_{Coulomb}\left(C_{alkane},2sp^3\right)$ given by Eq. (14.515), and $13.605804\ eV$, the magnitude of the Coulombic energy between the electron and proton of $H$ given by Eq. (1.264). The hybridization energy factor $C_{alkaneC2sp^3HO}$ is:

$$C_{alkaneC2sp^3HO} = \frac{\dfrac{e^2}{8\pi\varepsilon_0 a_0}}{\dfrac{e^2}{8\pi\varepsilon_0 r_{alkane2sp^3}}} = \frac{\dfrac{e^2}{8\pi\varepsilon_0 a_0}}{\dfrac{e^2}{8\pi\varepsilon_0 0.86359a_0}} = \frac{13.605804\ eV}{15.75493\ eV} = 0.86359 \tag{14.560}$$

Substitution of Eq. (14.558) into Eq. (13.233) with the hybridization factor of $0.86359$ gives:

$$0=\left[\begin{array}{l}\dfrac{-e^2}{8\pi\varepsilon_0\sqrt{\dfrac{aa_0}{2}}}\left[(0.86359)^{-1}\left(\dfrac{3}{2}-\dfrac{3}{8}\dfrac{a_0}{a}\right)\ln\dfrac{a+\sqrt{\dfrac{aa_0}{2}}}{a-\sqrt{\dfrac{aa_0}{2}}}-1\right]\left[1+\sqrt{\dfrac{2\hbar\sqrt{\dfrac{\dfrac{0.75e^2}{4\pi\varepsilon_0a^3}}{m_e}}}{m_ec^2}}\right]\\ +\hbar\sqrt{\dfrac{\dfrac{0.75e^2}{8\pi\varepsilon_0a^3}-\dfrac{e^2}{8\pi\varepsilon_0(a+c')^3}}{0.5m_p}}\end{array}\right] \tag{14.561}$$

From the energy relationship given by Eq. (14.561) and the relationship between the axes given by Eqs. (14.558-14.559) and (14.62-14.63), the dimensions of the $H-H$ MO can be solved.

The most convenient way to solve Eq. (14.561) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is:

$$a=5.8660a_0=3.1042\ X\ 10^{-10}\ m \tag{14.562}$$

Substitution of Eq. (14.562) into Eq. (14.558) gives:

$$c'=1.7126a_0=9.0627\ X\ 10^{-11}\ m \tag{14.563}$$

The internuclear distance given by multiplying Eq. (14.563) by two is:

$$2c'=3.4252a_0=1.8125\ X\ 10^{-10}\ m \tag{14.564}$$

Substitution of Eqs. (14.562-14.563) into Eq. (14.62) gives:

$$b=c=5.6104a_0=2.9689\ X\ 10^{-10}\ m \tag{14.565}$$

Substitution of Eqs. (14.562-14.563) into Eq. (14.63) gives:

$$e=0.2920 \tag{14.566}$$

Using $2c'_{H-H}$ (Eq. (14.564)), the distance between the two $H$ atoms when the total energy of the corresponding MO is zero (Eq. (14.561)), and $2c'_{C-H}$, the internuclear distance of each $C-H$ bond, the corresponding bond angle can be determined from the law of cosines. Since the internuclear distance of each $C-H$ bond of $CH_3$ (Eq. (14.545)) and $CH_2$ (Eq. (14.597)) are sufficiently equivalent, the bond angle determined with either is within experimental error of being the same. Using, Eqs. (13.242), (14.545), and (14.564), the bond angle $\theta$ between the $C-H$ bonds is:

$$\theta=\cos^{-1}\left(\frac{2(2.09711)^2-(3.4252)^2}{2(2.09711)^2}\right)=\cos^{-1}(-0.33383)=109.50° \tag{14.567}$$

The experimental angle between the $C-H$ bonds is [19]:

$$\theta=109.3° \tag{14.568}$$

The $CH_3$ radical has a pyramidal structure with the carbon atom along the z-axis at the apex and the hydrogen atoms at the base in the xy-plane. The distance $d_{origin-H}$ from the origin to the nucleus of a hydrogen atom given by Eqs. (14.564) and (13.412) is:

$$d_{origin-H}=1.97754a_0 \tag{14.569}$$

The height along the z-axis of the pyramid from the origin to $C$ nucleus $d_{height}$ given by Eqs. (13.414), (14.545), and (14.569) is

$$d_{height}=0.69800a_0 \tag{14.570}$$

The angle $\theta_v$ of each $C-H$ bond from the z-axis given by Eqs. (13.416), (14.569), and (14.570) is:

$$\theta_v=70.56° \tag{14.571}$$

The $C-C$ bond is along the z-axis. Thus, the bond angle $\theta_{C-C-H}$ between the internuclear axis of the $C-C$ bond and a $H$ atom of the methyl groups is given by:

$$\theta_{C-C-H}=180-\theta_v \tag{14.572}$$

Substitution of Eq. (14.571) into Eq. (14.572) gives:

$$\theta_{C-C-H}=109.44° \tag{14.573}$$

The experimental angle between the $C-C-H$ bonds is [19]:

$$\theta_{C-C-H}=109.3° \tag{14.574}$$

The $C_nH_{2n+2}$ MOs shown in Figures 14.18-14.28 were rendered using these parameters. A minimum energy is obtained with a staggered configuration consistent with observations [3].

## ENERGIES OF THE $CH_3$ GROUPS

The energies of each $CH_3$ group of $C_nH_{2n+2}$ are given by the substitution of the semiprincipal axes (Eqs. (14.543-14.544) and (14.547)) into the energy equations of methyl radical (Eqs. (13.556-13.560)), with the exception that $E\left(C_{alkane},2sp^3\right)$ (Eq. (14.514)) replaces $E\left(C,2sp^3\right)$ in Eq. (13.560).

$$V_e = 3\left(0.91771\right)\frac{-2e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -107.32728\ eV \tag{14.575}$$

$$V_p = \frac{3e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}} = 38.92728\ eV \tag{14.576}$$

$$T = 3\left(0.91771\right)\frac{\hbar^2}{2m_ea\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = 32.53914\ eV \tag{14.577}$$

$$V_m = 3\left(0.91771\right)\frac{-\hbar^2}{4m_ea\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -16.26957\ eV \tag{14.578}$$

$$E_{T_{alkane}}\left(CH_3\right) = \left(\begin{array}{l} -\frac{3e^2}{8\pi\varepsilon_0c'}\left[\left(0.91771\right)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right] \\ -15.56407\ eV \end{array}\right) = -67.69451\ eV \tag{14.579}$$

where $E_{T_{alkane}}\left(CH_3\right)$ is given by Eq. (14.540) which is reiteratively matched to Eq. (13.542) within five-significant-figure round off error.

## VIBRATION OF THE $^{12}CH_3$ GROUPS

The vibrational energy levels of the $C-H$ bonds of $CH_3$ in $C_nH_{2n+2}$ may be solved as three equivalent coupled harmonic oscillators by developing the Lagrangian, the differential equation of motion, and the eigenvalue solutions [9] wherein the spring constants are derived from the central forces as given in the Vibration of Hydrogen-Type Molecular Ions section and the Vibration of Hydrogen-Type Molecules section.

## THE DOPPLER ENERGY TERMS OF THE $^{12}CH_3$ GROUPS

The equations of the radiation reaction force of the methyl groups in $C_nH_{2n+2}$ are the same as those of the methyl radical with the substitution of the methyl-group parameters. Using Eq. (13.561), the angular frequency of the reentrant oscillation in the transition state is:

$$\omega = \sqrt{\frac{\frac{0.75e^2}{4\pi\varepsilon_0b^3}}{m_e}} = 2.49286\ X\ 10^{16}\ rad/s \tag{14.580}$$

where $b$ is given by Eq. (14.547). The kinetic energy, $E_K$, is given by Planck's equation (Eq. (11.127)).

$$\bar{E}_K = \hbar\omega = \hbar 2.49286\ X\ 10^{16}\ rad/s = 16.40846\ eV \tag{14.581}$$

In Eq. (11.181), substitution of $E_T\left(H_2\right)$ (Eqs. (11.212) and (13.75)), the maximum total energy of each $H_2$-type MO, for $E_{h\nu}$, the mass of the electron, $m_e$, for $M$, and the kinetic energy given by Eq. (14.581) for $\bar{E}_K$ gives the Doppler energy of the electrons of each of the three bonds for the reentrant orbit:

$$\bar{E}_D \cong E_{h\nu}\sqrt{\frac{2\bar{E}_K}{Mc^2}} = -31.63537\ eV\sqrt{\frac{2e\left(16.40846\ eV\right)}{m_ec^2}} = -0.25352\ eV \tag{14.582}$$

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency. The decrease in the energy of $CH_3$ due to the reentrant orbit of each bond in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei, $\bar{E}_{osc}$, is given by the sum of the corresponding energies, $\bar{E}_D$ given by Eq. (14.582) and $\bar{E}_{Kvib}$, the average kinetic energy of vibration which is 1/2 of the vibrational energy of each $C-H$ bond. Using $\omega_e$ given by Eq. (13.458) for $\bar{E}_{Kvib}$ of the *transition* state having three independent bonds, $\bar{E}'_{alkane\ osc}\left({}^{12}CH_3\right)$ per bond is:

$$\bar{E}'_{alkane\ osc}\left({}^{12}CH_3\right) = \bar{E}_D + \bar{E}_{Kvib} = \bar{E}_D + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \tag{14.583}$$

$$\bar{E}'_{alkane\ osc}\left({}^{12}CH_3\right) = -0.25352\ eV + \frac{1}{2}\left(0.35532\ eV\right) = -0.07586\ eV \tag{14.584}$$

Given that the vibration and reentrant oscillation is for three $C-H$ bonds, $\bar{E}_{alkane\ osc}\left({}^{12}CH_3\right)$, is:

$$\bar{E}_{alkane\ osc}\left({}^{12}CH_3\right)=3\left(\bar{E}_D+\frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right)=3\left(-0.25352\ eV+\frac{1}{2}\left(0.35532\ eV\right)\right)=-0.22757\ eV \tag{14.585}$$

## TOTAL BOND ENERGIES OF THE ${}^{12}CH_3$ GROUPS

$E_{alkaneT+osc}\left({}^{12}CH_3\right)$, the total energy of each ${}^{12}CH_3$ group including the Doppler term, is given by the sum of $E_{T_{alkane}}\left(CH_3\right)$ (Eq. (14.579)) and $\bar{E}_{alkane\ osc}\left({}^{12}CH_3\right)$ given by Eq. (14.585).

$$E_{alkaneT+osc}\left({}^{12}CH_3\right)=V_e+T+V_m+V_p+E\left(C_{alkane},2sp^3\right)+\bar{E}_{alkane\ osc}\left({}^{12}CH_3\right)=E_{T_{alkane}}\left(CH_3\right)+\bar{E}_{alkane\ osc}\left({}^{12}CH_3\right) \tag{14.586}$$

$$\begin{aligned} E_{alkaneT+osc}\left({}^{12}CH_3\right)&=\left\{\begin{array}{l}\left(\dfrac{-3e^2}{8\pi\varepsilon_0 c'}\left[\left(0.91771\right)\left(2-\dfrac{1}{2}\dfrac{a_0}{a}\right)\ln\dfrac{a+c'}{a-c'}-1\right]-15.56407\ eV\right)\\ -3\left(\left(31.63536831\ eV\right)\sqrt{\dfrac{2\hbar\sqrt{\dfrac{\frac{3}{4}\frac{e^2}{4\pi\varepsilon_0 b^3}}{m_e}}}{m_ec^2}}-\dfrac{1}{2}\hbar\sqrt{\dfrac{k}{\mu}}\right)\end{array}\right\}\\ &=-67.69450\ eV-3\left(0.25352\ eV-\frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right)\end{aligned} \tag{14.587}$$

From Eqs. (14.585-14.587), the total energy of each ${}^{12}CH_3$ is:

$$\begin{aligned} E_{alkaneT+osc}\left({}^{12}CH_3\right)&=-67.69450\ eV+\bar{E}_{alkane\ osc}\left({}^{12}CH_3\right)\\ &=-67.69450\ eV-3\left(0.25352\ eV-\frac{1}{2}\left(0.35532\ eV\right)\right)=-67.92207\ eV\end{aligned} \tag{14.588}$$

where $\omega_e$ given by Eq. (13.458) was used for the $\hbar\sqrt{\frac{k}{\mu}}$ term.

The total $CH_3$ bond dissociation energy, $E_{D_{alkane}}\left({}^{12}CH_3\right)$ is given by the sum of the initial $C2sp^3$ HO energy, $E\left(C,2sp^3\right)$ (Eq. (14.146)), and three times the energy of the hydrogen atom, $E_D\left(H\right)$ (Eq. (13.154)), minus $E_{alkaneT+osc}\left({}^{12}CH_3\right)$ (Eq. (14.588)).

$$E_{D_{alkane}}\left({}^{12}CH_3\right)=E\left(C,2sp^3\right)+3E(H)-E_{alkaneT+osc}\left({}^{12}CH_3\right) \tag{14.589}$$

Thus, the total ${}^{12}CH_3$ bond dissociation energy, $E_{D_{alkane}}\left({}^{12}CH_3\right)$ is:

$$\begin{aligned} E_{D_{alkane}}\left({}^{12}CH_3\right)&=-\left(14.63489\ eV+3\left(13.59844\ eV\right)\right)-\left(E_{alkaneT+osc}\left({}^{12}CH_2\right)\right)\\ &=-55.43021\ eV-\left(-67.92207\ eV\right)=12.49186\ eV\end{aligned} \tag{14.590}$$

## FORCE BALANCE OF THE $CH_2$ MOs OF CONTINUOUS-CHAIN ALKANES

Each of the $CH_2$ MOs must comprise two equivalent $C-H$ bonds with each comprising 75% of a $H_2$-type ellipsoidal MO and a $C2sp^3$ HO as given by Eq. (13.494).

$$2\left[1\ C2sp^3+0.75\ H_2\ MO\right]\rightarrow CH_2\ MO \tag{14.591}$$

The force balance of each $CH_2$ MO is determined by the boundary conditions that arise from the linear combination of orbitals according to Eq. (14.591) and the energy matching condition between the hydrogen and $C2sp^3$ HO components of the MO.

The force constant $k'$ to determine the ellipsoidal parameter $c'$ of the each $H_2$-type-ellipsoidal-MO component of the $CH_2$ MO in terms of the central force of the foci is given by Eq. (13.59). The distance from the origin of each $C-H$-bond MO to each focus $c'$ is given by Eq. (13.60). The internuclear distance is given by Eq. (13.61). The length of the semiminor axis of the prolate spheroidal $C-H$-bond MO $b=c$ is given by Eq. (13.62). The eccentricity, $e$, is given by Eq. (13.63). The solution of the semimajor axis $a$ then allows for the solution of the other axes of each prolate spheroid and eccentricity of each $C-H$-bond MO. Since each of the two prolate spheroidal $C-H$-bond MOs comprises an $H_2$-type-ellipsoidal MO that transitions to the $C_{alkane}2sp^3$ HO of $C_nH_{2n+2}$, the energy $E\left(C_{alkane},2sp^3\right)$ of Eq. (14.512) adds to that of the two corresponding $H_2$-type ellipsoidal

MOs to give the total energy of the $CH_2$ MO. From the energy equation and the relationship between the axes, the dimensions of the $CH_2$ MO are solved.

The energy components of $V_e$, $V_p$, $T$, and $V_m$ are the same as those of dihydrogen carbide radical, two times those of $CH$ corresponding to the two $C-H$ bonds except that energy of the $C_{alkane}2sp^3$ HO is used. Since each prolate spheroidal $H_2$-type MO transitions to the $C_{alkane}2sp^3$ HO and the energy of the $C_{alkane}2sp^3$ shell treated independently must remain constant and equal to the $E\left(C_{alkane},2sp^3\right)$ given by Eq. (14.512), the total energy $E_{T_{alkane}}\left(CH_2\right)$ of the $CH_2$ MO is given by the sum of the energies of the orbitals corresponding to the composition of the linear combination of the $C_{alkane}2sp^3$ HO and the two $H_2$-type ellipsoidal MOs that forms the $CH_2$ MO as given by Eq. (14.591). Using Eq. (13.431) or Eq. (13.495), $E_{T_{alkane}}\left(CH_2\right)$ is given by:

$$E_{T_{alkane}}\left(CH_2\right)=E_T+E\left(C_{alkane},2sp^3\right)=-\frac{2e^2}{8\pi\varepsilon_0 c'}\left[\left(0.91771\right)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]-15.56407\ eV \tag{14.592}$$

$E_{T_{alkane}}\left(CH_2\right)$ given by Eq. (14.592) is set equal to two times the energy of the $H_2$-type ellipsoidal MO minus the Coulombic energy of $H$ given by Eq. (13.496).

$$E_T\left(CH_2\right)=-\frac{2e^2}{8\pi\varepsilon_0 c'}\left[\left(0.91771\right)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]-15.56407\ eV=-49.66493\ eV \tag{14.593}$$

From the energy relationship given by Eq. (14.593) and the relationship between the axes given by Eqs. (13.60-13.63), the dimensions of the $CH_2$ MO can be solved.

Substitution of Eq. (13.60) into Eq. (14.593) gives:

$$\frac{2e^2}{8\pi\varepsilon_0\sqrt{\frac{2aa_0}{3}}}\left[\left(0.91771\right)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+\sqrt{\frac{2aa_0}{3}}}{a-\sqrt{\frac{2aa_0}{3}}}-1\right]=e34.10086 \tag{14.594}$$

The most convenient way to solve Eq. (14.594) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is

$$a=1.67122a_0=8.84370\ X\ 10^{-11}\ m \tag{14.595}$$

Substitution of Eq. (14.595) into Eq. (14.60) gives:

$$c'=1.05553a_0=5.58563\ X\ 10^{-11}\ m \tag{14.596}$$

The internuclear distance given by multiplying Eq. (14.596) by two is:

$$2c'=2.11106a_0=1.11713\ X\ 10^{-10}\ m \tag{14.597}$$

The experimental $C-H$ bond distance of butane is [3]:

$$2c'=1.117\ X\ 10^{-10}\ m \tag{14.598}$$

Substitution of Eqs. (14.595-14.596) into Eq. (14.62) gives:

$$b=c=1.29569a_0=6.85652\ X\ 10^{-11}\ m \tag{14.599}$$

Substitution of Eqs. (14.595-14.596) into Eq. (14.63) gives:

$$e=0.63159 \tag{14.600}$$

The nucleus of the $H$ atom and the nucleus of the $C$ atom comprise the foci of each $H_2$-type ellipsoidal MO. The parameters of the point of intersection of the $H_2$-type ellipsoidal MO and the $C_{alkane}2sp^3$ HO are given by Eqs. (13.84-13.95) and (13.261-13.270). The polar intersection angle $\theta'$ is given by Eq. (13.261) where $r_n=r_{methylene2sp^3}=0.81549a_0$ is the radius of the $C_{methylene}2sp^3$ shell (Eq. (14.521)). Substitution of Eqs. (14.595-14.596) into Eq. (13.261) gives:

$$\theta'=68.47^\circ \tag{14.601}$$

Then, the angle $\theta_{C-H_{alkane}2sp^3HO}$ the radial vector of the $C2sp^3$ HO makes with the internuclear axis is:

$$\theta_{C-H_{alkane}2sp^3HO}=180^\circ-68.47^\circ=111.53^\circ \tag{14.602}$$

as shown in Figure 14.17. The Cartesian $\mathbf{i}$-coordinate of the interception point of the MO and the AO can be calculated using the MO ellipsoidal parameters by first calculating the parametric angle in Eq. (11.83) that matches Cartesian $\mathbf{j}$-coordinate components at the point of intersection. Thus, the matching elliptic parametric angle $\omega t=\theta_{C-H_{alkane},H_2MO}$ satisfies the following relationship:

$$r_{alkane2sp^3}\sin\theta_{C-H_{alkane}2sp^3HO}=0.81549a_0\sin\theta_{C-H_{alkane}2sp^3HO}=b\sin\theta_{C-H_{alkane},H_2MO} \tag{14.603}$$

such that

$$\theta_{C-H_{alkane},H_2MO} = \sin^{-1}\frac{0.81549a_0\sin\theta_{C-H_{alkane}2sp^3HO}}{b} = \sin^{-1}\frac{0.81549a_0\sin 111.53°}{b} \tag{14.604}$$

with the use of Eq. (14.602). Substitution of Eq. (14.599) into Eq. (14.604) gives:

$$\theta_{C-H_{alkane},H_2MO} = 35.84° \tag{14.605}$$

Then, the distance $d_{C-H_{alkane},H_2MO}$ along the internuclear axis from the origin of $H_2$-type ellipsoidal MO to the point of intersection of the orbitals is given by:

$$d_{C-H_{alkane},H_2MO} = a\cos\theta_{C-H_{alkane},H_2MO} \tag{14.606}$$

Substitution of Eqs. (14.595) and (14.605) into Eq. (14.606) gives:

$$d_{C-H_{alkane},H_2MO} = 1.35486a_0 = 7.16963\ X\ 10^{-11}\ m \tag{14.607}$$

The distance $d_{C-H_{alkane}2sp^3HO}$ along the internuclear axis from the origin of the $C$ atom to the point of intersection of the orbitals is given by:

$$d_{C-H_{alkane}2sp^3HO} = d_{C-H_{alkane},H_2MO} - c' \tag{14.608}$$

Substitution of Eqs. (14.596) and (14.605) into Eq. (14.608) gives:

$$d_{C-H_{alkane}2sp^3HO} = 0.29933a_0 = 1.58400\ X\ 10^{-11}\ m \tag{14.609}$$

The charge-density in each $C-C$-bond MO is increased by a factor of 0.25 with the formation of the $C_{alkane}2sp^3$ HOs each having a smaller radius. Using the orbital composition of the $C-C$-bond MOs (Eq. (14.504)), $CH_3$ groups (Eq. (14.539)), and the $CH_2$ groups (Eq. (14.591)), the radii of $C1s = 0.17113a_0$ (Eq. (10.51)), $C_{alkane}2sp^3 = 0.86359a_0$ (Eq. (14.514)), and $C_{alkane}2sp^3 = C_{methylene}2sp^3 = 0.81549a_0$ (Eq. (14.521)) shells, the parameters of the $C-C$-bonds (Eqs. (13.3-13.4), (14.523-14.525), and (14.528-14.538)), the parameters of the $C-H$-bond MOs of the $CH_3$ groups (Eqs. (13.3-13.4), (14.544-14.545), and (14.547-14.557)), the parameters of the $C-H$-bond MOs of the $CH_2$ groups (Eqs. (13.3-13.4), (14.595-14.597), and (14.599-14.609)), and the bond-angle parameters (Eqs. (14.562-14.574)), the charge-density of the $C_nH_{2n+2}$ MO comprising the linear combination $2n+2$ $C-H$-bond MOs and $n-1$ $C-C$-bond MOs, each bridging one or more methyl or methylene groups is shown for representative cases where data was available [17-18]. Propane, butane, pentane, hexane, heptane, octane, nonane, decane, undecane, dodecane, and octadecane are shown in Figures 14.18-14.28, respectively. Each $C-H$-bond MO comprises a $H_2$-type ellipsoidal MO and a $C_{alkane}2sp^3$ HO having the dimensional diagram shown in Figure 14.16. Each $C-C$-bond MO comprises a $H_2$-type ellipsoidal MO bridging two $C_{alkane}2sp^3$ HOs having the dimensional diagram shown in Figure 14.17.

## ENERGIES OF THE $CH_2$ GROUPS

The energies of each $CH_2$ group of $C_nH_{2n+2}$ are given by the substitution of the semiprincipal axes (Eqs. (14.595-14.596) and (14.599)) into the energy equations of dihydrogen carbide radical (Eqs. (13.510-13.514)), with the exception that $E\left(C_{alkane},2sp^3\right)$ (Eq. (14.512)) replaces $E\left(C,2sp^3\right)$ in Eq. (13.514):

$$V_e = 2\left(0.91771\right)\frac{-2e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -70.41425\ eV \tag{14.610}$$

$$V_p = \frac{2e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}} = 25.78002\ eV \tag{14.611}$$

$$T = 2\left(0.91771\right)\frac{\hbar^2}{2m_ea\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = 21.06675\ eV \tag{14.612}$$

$$V_m = 2\left(0.91771\right)\frac{-\hbar^2}{4m_ea\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -10.53337\ eV \tag{14.613}$$

$$E_{T_{alkane}}\left(CH_2\right) = -\frac{2e^2}{8\pi\varepsilon_0c'}\left[\left(0.91771\right)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right] - 15.56407\ eV = -49.66493\ eV \tag{14.614}$$

where $E_{T_{alkane}}\left(CH_2\right)$ is given by Eq. (14.592) which is reiteratively matched to Eq. (13.496) within five-significant-figure round off error.

## VIBRATION OF THE $^{12}CH_2$ GROUPS

The vibrational energy levels of the $C-H$ bonds of $CH_2$ in $C_nH_{2n+2}$ may be solved as two equivalent coupled harmonic oscillators by developing the Lagrangian, the differential equation of motion, and the eigenvalue solutions [9] wherein the spring constants are derived from the central forces as given in the Vibration of Hydrogen-Type Molecular Ions section and the Vibration of Hydrogen-Type Molecules section.

## THE DOPPLER ENERGY TERMS OF THE $^{12}CH_2$ GROUPS

The equations of the radiation reaction force of the methylene groups in $C_nH_{2n+2}$ are the same as those of the dihydrogen carbide radical with the substitution of the methylene-group parameters. Using Eq. (13.515), the angular frequency of the reentrant oscillation in the transition state is:

$$\omega = \sqrt{\frac{\frac{0.75e^2}{4\pi\varepsilon_0 b^3}}{m_e}} = 2.42751\ X\ 10^{16}\ rad/s \tag{14.615}$$

where $b$ is given by Eq. (14.599). The kinetic energy, $E_K$, is given by Planck's equation (Eq. (11.127)).

$$\overline{E}_K = \hbar\omega = \hbar 2.42751\ X\ 10^{16}\ rad/s = 15.97831\ eV \tag{14.616}$$

In Eq. (11.181), substitution of $E_T(H_2)$ (Eqs. (11.212) and (13.75)), the maximum total energy of each $H_2$-type MO, for $E_{h\nu}$, the mass of the electron, $m_e$, for $M$, and the kinetic energy given by Eq. (14.616) for $\overline{E}_K$ gives the Doppler energy of the electrons of each of the three bonds for the reentrant orbit:

$$\overline{E}_D \cong E_{h\nu}\sqrt{\frac{2\overline{E}_K}{Mc^2}} = -31.63537\ eV\sqrt{\frac{2e(15.97831\ eV)}{m_e c^2}} = -0.25017\ eV \tag{14.617}$$

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency. The decrease in the energy of $CH_2$ due to the reentrant orbit of each bond in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei, $\overline{E}_{osc}$, is given by the sum of the corresponding energies, $\overline{E}_D$ given by Eq. (14.617) and $\overline{E}_{Kvib}$, the average kinetic energy of vibration which is 1/2 of the vibrational energy of each $C-H$ bond. Using $\omega_e$ given by Eq. (13.458) for $\overline{E}_{Kvib}$ of the transition state having two independent bonds, $\overline{E}'_{alkane\ osc}\left({}^{12}CH_2\right)$ per bond is:

$$\overline{E}'_{alkane\ osc}\left({}^{12}CH_2\right) = \overline{E}_D + \overline{E}_{Kvib} = \overline{E}_D + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \tag{14.618}$$

$$\overline{E}'_{alkane\ osc}\left({}^{12}CH_2\right) = -0.25017\ eV + \frac{1}{2}(0.35532\ eV) = -0.07251\ eV \tag{14.619}$$

Given that the vibration and reentrant oscillation is for two $C-H$ bonds, $\overline{E}_{alkane\ osc}\left({}^{12}CH_2\right)$, is:

$$\overline{E}_{alkane\ osc}\left({}^{12}CH_2\right) = 2\left(\overline{E}_D + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right) = 2\left(-0.25017\ eV + \frac{1}{2}(0.35532\ eV)\right) = -0.14502\ eV \tag{14.620}$$

## TOTAL BOND ENERGIES OF THE $^{12}CH_2$ GROUPS

$E_{alkaneT+osc}\left({}^{12}CH_2\right)$, the total energy of each $^{12}CH_2$ group including the Doppler term, is given by the sum of $E_{T_{alkane}}(CH_2)$ (Eq. (14.614)) and $\overline{E}_{alkane\ osc}\left({}^{12}CH_2\right)$ given by Eq. (14.620).

$$\begin{aligned} E_{alkaneT+osc}\left({}^{12}CH_2\right) &= V_e + T + V_m + V_p + E\left(C_{alkane}, 2sp^3\right) + \overline{E}_{alkane\ osc}\left({}^{12}CH_2\right) \\ &= E_{T_{alkane}}(CH_2) + \overline{E}_{alkane\ osc}\left({}^{12}CH_2\right) \end{aligned} \tag{14.621}$$

$$\begin{aligned} E_{alkaneT+osc}\left({}^{12}CH_2\right) &= \left\{ \begin{array}{l} \left(\frac{-2e^2}{8\pi\varepsilon_0 c'}\left[(0.91771)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right] - 15.56407\ eV\right) \\ -2\left((31.63536831\ eV)\sqrt{\frac{2\hbar\sqrt{\frac{\frac{3}{4}\frac{e^2}{4\pi\varepsilon_0 b^3}}{m_e}}}{m_e c^2}} - \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right) \end{array} \right\} \\ &= -49.66493\ eV - 2\left(0.25017\ eV - \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right) \end{aligned} \tag{14.622}$$

From Eqs. (14.620-14.622), the total energy of each $^{12}CH_2$ is:

$$\begin{aligned} E_{alkaneT+osc}\left(^{12}CH_2\right) &= -49.66493\ eV + \bar{E}_{alkane\ osc}\left(^{12}CH_2\right) \\ &= -49.66493\ eV - 2\left(0.25017\ eV - \frac{1}{2}\left(0.35532\ eV\right)\right) = -49.80996\ eV \end{aligned} \tag{14.623}$$

where $\omega_e$ given by Eq. (13.458) was used for the $\hbar\sqrt{\frac{k}{\mu}}$ term.

The derivation of the total $CH_2$ bond dissociation energy, $E_{D_{alkane}}\left(^{12}CH_2\right)$ follows from that of the bond dissociation energy of dihydrogen carbide radical, $E_D\left(^{12}CH_2\right)$, given by Eqs. (13.524-13.527). $E_{D_{alkane}}\left(^{12}CH_2\right)$ is given by the sum of the initial $C2sp^3$ HO energy, $E\left(C,2sp^3\right)$ (Eq. (14.146)), and two times the energy of the hydrogen atom, $E(H)$ (Eq. (13.154)), minus the sum of $E_{alkaneT+osc}\left(^{12}CH_2\right)$ (Eq. (14.623)) and $E(magnetic)$ (Eq. (13.524)):

$$E_{D_{alkane}}\left(^{12}CH_2\right) = E\left(C,2sp^3\right) + 2E(H) - E_{alkaneT+osc}\left(^{12}CH_2\right) - E\left(magnetic\right) \tag{14.624}$$

Thus, the total $^{12}CH_2$ bond dissociation energy, $E_{D_{alkane}}\left(^{12}CH_2\right)$ is:

$$\begin{aligned} E_{D_{alkane}}\left(^{12}CH_2\right) &= -\left(14.63489\ eV + 2\left(13.59844\ eV\right)\right) - \left(E_{alkaneT+osc}\left(^{12}CH_2\right) + E\left(magnetic\right)\right) \\ &= -41.83177\ eV - \left(-49.80996\ eV + 0.14803\ eV\right) = 7.83016\ eV \end{aligned} \tag{14.625}$$

## SUM OF THE ENERGIES OF THE $C-C$ $\sigma$ MOs AND THE HOs OF CONTINUOUS-CHAIN ALKANES

The energy components of $V_e$, $V_p$, $T$, $V_m$, and $E_T$ of the $C-C$-bond MOs are the same as those of the $CH$ MO except that energy of the $C_{alkane}2sp^3$ HO is used. The energies of each $C-C$-bond MO are given by the substitution of the semiprincipal axes (Eqs. (14.523-14.524) and (14.528)) into the energy equations of the $CH$ MO (Eqs. (13.449-13.453)), with the exception that $E\left(C_{alkane},2sp^3\right)$ (Eq. (14.512)) replaces $E\left(C,2sp^3\right)$ in Eq. (13.453). The total number of $C-C$ bonds of $C_nH_{2n+2}$ is $n-1$. Thus, the energies of the $n-1$ bonds is given by:

$$V_e = \left(n-1\right)\left(0.91771\right)\frac{-2e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -\left(n-1\right)28.79214\ eV \tag{14.626}$$

$$V_p = \frac{\left(n-1\right)e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}} = \left(n-1\right)9.33352\ eV \tag{14.627}$$

$$T = \left(n-1\right)\left(0.91771\right)\frac{\hbar^2}{2m_ea\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = \left(n-1\right)6.77464\ eV \tag{14.628}$$

$$V_m = \left(n-1\right)\left(0.91771\right)\frac{-\hbar^2}{4m_ea\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -\left(n-1\right)3.38732\ eV \tag{14.629}$$

$$E_{T_{alkane}}\left(C-C,\sigma\right) = -\frac{\left(n-1\right)e^2}{8\pi\varepsilon_0c'}\left[\left(0.91771\right)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right] - 15.56407\ eV = -\left(n-1\right)31.63537\ eV \tag{14.630}$$

where $E_{T_{alkane}}\left(C-C,\sigma\right)$ is the total energy of the $C-C$ $\sigma$ MOs given by Eq. (14.520) which is reiteratively matched to Eq. (13.75) within five-significant-figure round off error.

Since there are two carbon atoms per bond, the number of $C-C$ bonds is $n-1$, and the energy change of each $C2sp^3$ shell due to the decrease in radius with the formation of each $C-C$-bond MO is $E_{T_{alkane}}\left(C-C,2sp^3\right)$ (Eq. (14.517)), the total energy of the $C-C$-bond MOs, $E_{T_{alkane}}\left(C-C\right)$, is given by the sum of $2\left(n-1\right)E_{T_{alkane}}\left(C-C,2sp^3\right)$ and $E_{T_{alkane}}\left(C-C,\sigma\right)$, the $\sigma$ MO contribution given by Eq. (14.630).

$$\begin{aligned} E_{T_{alkane}}(C-C) &= 2(n-1)E_{T_{alkane}}\left(C-C,2sp^3\right)+E_{T_{alkane}}(C-C,\sigma) \\ &= (n-1)\left(\begin{array}{l} 2(-0.92918\ eV) \\ +\left(\begin{array}{l} -\dfrac{e^2}{8\pi\varepsilon_0\sqrt{aa_0}}\left[(0.91771)\left(2-\dfrac{1}{2}\dfrac{a_0}{a}\right)\ln\dfrac{a+\sqrt{aa_0}}{a-\sqrt{aa_0}}-1\right] \\ -15.56407\ eV \end{array}\right) \end{array}\right) \\ &= (n-1)\left(2(-0.92918\ eV)+(-31.63537\ eV)\right) = -(n-1)33.49373\ eV \end{aligned} \tag{14.631}$$

## VIBRATION OF CONTINUOUS-CHAIN ALKANES

The vibrational energy levels of the $C-C$ bonds of $C_nH_{2n+2}$ may be solved as $n-1$ sets of coupled carbon harmonic oscillators wherein each carbon is further coupled to two or three equivalent $H$ harmonic oscillators by developing the Lagrangian, the differential equation of motion, and the eigenvalue solutions [9] wherein the spring constants are derived from the central forces as given in the Vibration of Hydrogen-Type Molecular Ions section and the Vibration of Hydrogen-Type Molecules section.

## THE DOPPLER ENERGY TERMS OF THE $C-C$-BOND MOs OF CONTINUOUS-CHAIN ALKANES

The equations of the radiation reaction force of each symmetrical $C-C$-bond MO are given by Eqs. (11.231-11.233), except the force-constant factor is $0.5$ based on the force constant $k'$ of Eq. (14.152), and the $C-C$-bond MO parameters are used. The angular frequency of the reentrant oscillation in the transition state is:

$$\omega = \sqrt{\frac{\dfrac{0.5e^2}{4\pi\varepsilon_0 a^3}}{m_e}} = 9.43699\ X\ 10^{15}\ rad/s \tag{14.632}$$

where $a$ is given by Eq. (14.523). The kinetic energy, $E_K$, is given by Planck's equation (Eq. (11.127)).

$$\bar{E}_K = \hbar\omega = \hbar 9.43699\ X\ 10^{15}\ rad/s = 6.21159\ eV \tag{14.633}$$

In Eq. (11.181), substitution of $E_{T_{alkane}}(C-C)$ (Eq. (14.631)) with $n=2$ for $E_{h\nu}$, the mass of the electron, $m_e$, for $M$, and the kinetic energy given by Eq. (14.633) for $\bar{E}_K$ gives the Doppler energy of the electrons of each of the bonds for the reentrant orbit:

$$\bar{E}_D \cong E_{h\nu}\sqrt{\frac{2\bar{E}_K}{Mc^2}} = -33.49373\ eV\sqrt{\frac{2e(6.21159\ eV)}{m_ec^2}} = -0.16515\ eV \tag{14.634}$$

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency. The decrease in the energy of each $C-C$-bond MO due to the reentrant orbit of the bond in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei, $\bar{E}_{osc}$, is given by the sum of the corresponding energies, $\bar{E}_D$ given by Eq. (14.634) and $\bar{E}_{Kvib}$, the average kinetic energy of vibration which is 1/2 of the vibrational energy of each $C-C$ bond. Using the ethane experimental $C-C$ $E_{vib}(\upsilon_3)$ of 993 $cm^{-1}$ $(0.12312\ eV)$ [10] for $\bar{E}_{Kvib}$ of the transition state having $n-1$ independent bonds, $\bar{E}'_{alkane\ osc}(C-C,\sigma)$ per bond is:

$$\bar{E}'_{alkane\ osc}(C-C,\sigma) = \bar{E}_D + \bar{E}_{Kvib} = \bar{E}_D + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \tag{14.635}$$

$$\bar{E}'_{alkane\ osc}(C-C,\sigma) = -0.16515\ eV + \frac{1}{2}(0.12312\ eV) = -0.10359\ eV \tag{14.636}$$

Given that the vibration and reentrant oscillation is for $n-1$ $C-C$ bonds, $\bar{E}_{alkane\ osc}(C-C,\sigma)$, is:

$$\begin{aligned} \bar{E}_{alkane\ osc}(C-C,\sigma) &= (n-1)\left(\bar{E}_D + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right) \\ &= (n-1)\left(-0.16515\ eV + \frac{1}{2}(0.12312\ eV)\right) = -(n-1)0.10359\ eV \end{aligned} \tag{14.637}$$

## TOTAL ENERGIES OF THE $C-C$-BOND MOs OF CONTINUOUS-CHAIN ALKANES

$E_{alkaneT+osc}(C-C)$, the total energy of the $n-1$ bonds of the $C-C$-bond MOs including the Doppler term, is given by the sum of $E_{T_{alkane}}(C-C)$ (Eq. (14.631)) and $\bar{E}_{alkane\ osc}(C-C,\sigma)$ given by Eq. (14.637).

$$\begin{aligned}E_{alkaneT+osc}\left(C-C\right)&=\left(\left(n-1\right)\begin{pmatrix}V_e+T+V_m+V_p+E\left(C_{alkane},2sp^3\right)\\+2E_{T_{alkane}}\left(C-C,2sp^3\right)\end{pmatrix}+\bar{E}_{alkane\ osc}\left(C-C,\sigma\right)\right)\\&=E_{T_{alkane}}\left(C-C,\sigma\right)+2\left(n-1\right)E_{T_{alkane}}\left(C-C,2sp^3\right)+\bar{E}_{alkane\ osc}\left(C-C,\sigma\right)\\&=E_{T_{alkane}}\left(C-C\right)+\bar{E}_{alkane\ osc}\left(C-C,\sigma\right)\end{aligned}\tag{14.638}$$

$$\begin{aligned}E_{alkaneT+osc}\left(C-C\right)&=\left(n-1\right)\left\{\begin{matrix}\left(\begin{matrix}\dfrac{-e^2}{8\pi\varepsilon_0c'}\left[\left(0.91771\right)\left(2-\dfrac{1}{2}\dfrac{a_0}{a}\right)\ln\dfrac{a+c'}{a-c'}-1\right]\\-15.56407\ eV+2E_{T_{alkane}}\left(C-C,2sp^3\right)\end{matrix}\right)\\\left(\left(1+\sqrt{\dfrac{2\hbar\sqrt{\dfrac{\frac{1}{2}\frac{e^2}{4\pi\varepsilon_0a^3}}{m_e}}}{m_ec^2}}\right)+\dfrac{1}{2}\hbar\sqrt{\dfrac{k}{\mu}}\right)\end{matrix}\right\}\\&=\left(n-1\right)\left(-33.49373\ eV-0.16515\ eV+\frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right)\end{aligned}\tag{14.639}$$

From Eqs. (14.637-14.639), the total energy of the $n-1$ bonds of the $C-C$-bond MOs is:

$$\begin{aligned}E_{alkaneT+osc}\left(C-C\right)&=\left(n-1\right)\left(-31.63537\ eV+2E_{T_{alkane}}\left(C-C,2sp^3\right)\right)+\bar{E}_{alkane\ osc}\left(C-C,\sigma\right)\\&=\left(n-1\right)\begin{pmatrix}-31.63537\ eV+2\left(-0.92918\ eV\right)\\-0.16515\ eV+\dfrac{1}{2}\left(0.12312\ eV\right)\end{pmatrix}=-\left(n-1\right)33.59732\ eV\end{aligned}\tag{14.640}$$

where the experimental $E_{vib}$ was used for the $\hbar\sqrt{\frac{k}{\mu}}$ term.

## TOTAL BOND ENERGY OF THE $C-C$ BONDS OF CONTINUOUS-CHAIN ALKANES

Since there are two carbon atoms per bond and the number of $C-C$ bonds is $n-1$, the total bond energy of the $C-C$ bonds of $C_nH_{2n+2}$, $E_D\left(C-C\right)_{n-1}$, is given by $2\left(n-1\right)E\left(C,2sp^3\right)$ minus $E_{alkaneT+osc}\left(C-C\right)$ (Eq. (14.640)) where $E\left(C,2sp^3\right)$ (Eq. (14.146)) is the initial energy of each $C2sp^3$ HO of the $CH_3$ and $CH_2$ groups that bond to the $C-C$ bonds. Thus, the total dissociation energy of the $C-C$ bonds of $C_nH_{2n+2}$, is:

$$\begin{aligned}E_D\left(C-C\right)_{n-1}&=2\left(n-1\right)\left(E\left(C,2sp^3\right)\right)-\left(E_{alakneT+osc}\left(C-C\right)\right)\\&=2\left(n-1\right)\left(-14.63489\ eV\right)-\left(n-1\right)\left(-33.59732\ eV\right)\\&=\left(n-1\right)\left(2\left(-14.63489\ eV\right)-\left(-33.59732\ eV\right)\right)=\left(n-1\right)\left(4.32754\ eV\right)\end{aligned}\tag{14.641}$$

## TOTAL ENERGY OF CONTINUOUS-CHAIN ALKANES

$E_D\left(C_nH_{2n+2}\right)$, the total bond dissociation energy of $C_nH_{2n+2}$, is given as the sum of the energy components due to the two methyl groups, $n-2$ methylene groups, and $n-1$ $C-C$ bonds where each energy component is given by Eqs. (14.590), (14.625), and (14.641), respectively. Thus, the total bond dissociation energy of $C_nH_{2n+2}$ is:

$$\begin{aligned}E_D\left(C_nH_{2n+2}\right)&=E_D\left(C-C\right)_{n-1}+2E_{D_{alkane}}\left({}^{12}CH_3\right)+\left(n-2\right)E_{D_{alkane}}\left({}^{12}CH_2\right)\\&=\left(n-1\right)\left(4.32754\ eV\right)+2\left(12.49186\ eV\right)+\left(n-2\right)\left(7.83016\ eV\right)\end{aligned}\tag{14.642}$$

The experimental total bond dissociation energy of $C_nH_{2n+2}$, $E_{D_{exp}}\left(C_nH_{2n+2}\right)$, is given by the negative difference between the enthalpy of its formation ($\Delta H_f\left(C_nH_{2n+2}\left(gas\right)\right)$) and the sum of the enthalpy of the formation of the reactant gaseous carbons ($\Delta H_f\left(C\left(gas\right)\right)$) and hydrogen ($\Delta H_f\left(H\left(gas\right)\right)$) atoms:

$$\begin{aligned}E_{D_{exp}}\left(C_nH_{2n+2}\right)&=-\left\{\Delta H_f\left(C_nH_{2n+2}\left(gas\right)\right)-\left[n\Delta H_f\left(C\left(gas\right)\right)+\left(2n+2\right)\Delta H_f\left(H\left(gas\right)\right)\right]\right\}\\&=-\left\{\Delta H_f\left(C_nH_{2n+2}\left(gas\right)\right)-\left[n7.42774\ eV+\left(2n+2\right)2.259353\ eV\right]\right\}\end{aligned}\tag{14.643}$$

where the heats of formation atomic carbon and hydrogen gas are given by [17-18]:

$$\Delta H_f\left(C\left(gas\right)\right)=716.68\ kJ/mole\ \left(7.42774\ eV/atom\right)\tag{14.644}$$

$$\Delta H_f\left(H\left(gas\right)\right)=217.998\ kJ\ /\ mole\ \left(2.259353\ eV\ /\ atom\right) \tag{14.645}$$

Using the corresponding experimental $\Delta H_f\left(C_nH_{2n+2}\left(gas\right)\right)$ [18], $E_D\left(C_nH_{2n+2}\right)$ was determined for propane, butane, pentane, hexane, heptane, octane, nonane, decane, undecane, dodecane, and octadecane in the corresponding sections, and the results of the determination of the total energies are given in Table 14.1. The calculated results are based on first principles and given in closed-form, exact equations containing fundamental constants only. The agreement between the experimental and calculated results is excellent.

Using the results for $C_nH_{2n+2}$ and the functional groups as basis sets that are linearly combined, the exact solution for the dimensional parameters, charge density functions, and energies of all molecules can be obtained. For example, one or more of the hydrogen atoms of the solution for $C_nH_{2n+2}$ can be substituted with one or more of the previously solved functional groups or derivative functional groups to give a desired molecule. The solution is given by energy matching each group to $C_nH_{2n+2}$. Substitution of one or more $H$ 's of $C_nH_{2n+2}$ with functional groups from the list of $CH_3$, other $C_nH_{2n+2}$ groups, $H_2C=CH_2$, $HC\equiv CH$, $F$, $Cl$, $O$, $OH$, $NH$, $NH_2$, $CN$, $NO$, $NO_2$, $CO$, $CO_2$, and $C_6H_6$ give the solutions of branched alkanes, alkenes, and alkynes, alkyl halides, ethers, alcohols, amides, amines, nitriles, alkyl nitrosos, alkyl nitrates, aldehydes, ketones, carbolylic acids, esters, and substituted aromatics.

## PROPANE ($C_3H_8$)

Using Eq. (14.642) with $n=3$, the total bond dissociation energy of $C_3H_8$ is:

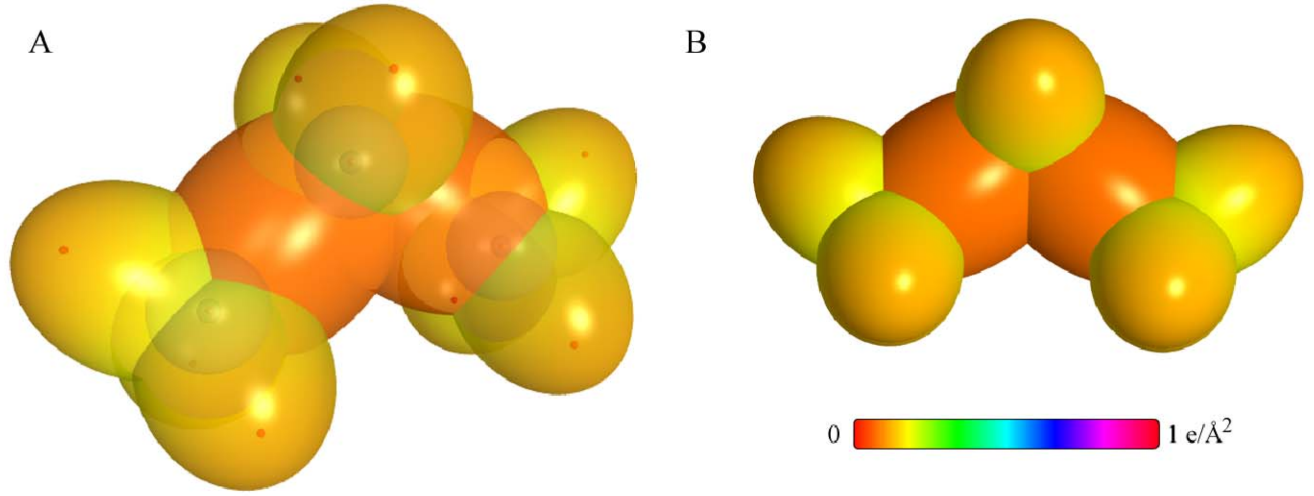
$$\begin{aligned}E_D\left(C_3H_8\right)&=E_D\left(C-C\right)_2+2E_{D_{alkane}}\left({}^{12}CH_3\right)+E_{D_{alkane}}\left({}^{12}CH_2\right)\\&=\left(2\right)\left(4.32754\ eV\right)+\left(2\right)\left(12.49186\ eV\right)+\left(1\right)\left(7.83016\ eV\right)=41.46896\ eV\end{aligned} \tag{14.646}$$

Using Eq. (14.643), the experimental total bond dissociation energy of $C_3H_8$, $E_{D_{\exp}}\left(C_3H_8\right)$, given by the negative difference between the enthalpy of its formation ($\Delta H_f\left(C_3H_8\left(gas\right)=-1.0758\ eV\right)$) [18] and the sum of the enthalpy of the formation of the gaseous carbons ($\Delta H_f\left(C\left(gas\right)\right)$) and hydrogen ($\Delta H_f\left(H\left(gas\right)\right)$) atoms is:

$$\begin{aligned}E_{D_{\exp}}\left(C_3H_8\right)&=-\left\{\Delta H_f\left(C_3H_8\left(gas\right)\right)-\left[3\Delta H_f\left(C\left(gas\right)\right)+8\Delta H_f\left(H\left(gas\right)\right)\right]\right\}\\&=-\left\{-1.0758\ eV-\left[\left(3\right)7.42774\ eV+\left(8\right)2.259353\ eV\right]\right\}=41.434\ eV\end{aligned} \tag{14.647}$$

The charge-density of the $C_3H_8$ molecular orbital (MO) comprising a linear combination of two methyl groups and one methylene group is shown in Figure 14.18.

Figure 14.18. $C_3H_8$ MO comprising a linear combination of $C-H$ -bond MOs and $C-C$ -bond MOs of the two methyl groups and one methylene group. (A) Color scale, translucent view of the charge-density of the $C-C$ -bond and $C-H$ -bond MOs and the $C_{\text{propane}}2sp^3$ HOs. Each $C-C$ -bond MO comprises a $H_2$-type ellipsoidal MO bridging two $C_{propane}2sp^3$ HOs. For each $C-H$ and the $C-C$ bond, the ellipsoidal surface of the $H_2$-type ellipsoidal MO that transitions to the $C_{propane}2sp^3$ HO, the $C_{propane}2sp^3$ HO shell, inner most $C1s$ shell, and the nuclei (red, not to scale), are shown. (B) Opaque view highlighting the $C-C$ -bond MOs of the charge-density of the $C_3H_8$ MO.



## BUTANE ($C_4H_{10}$)

Using Eq. (14.642) with $n=4$, the total bond dissociation energy of $C_4H_{10}$ is:

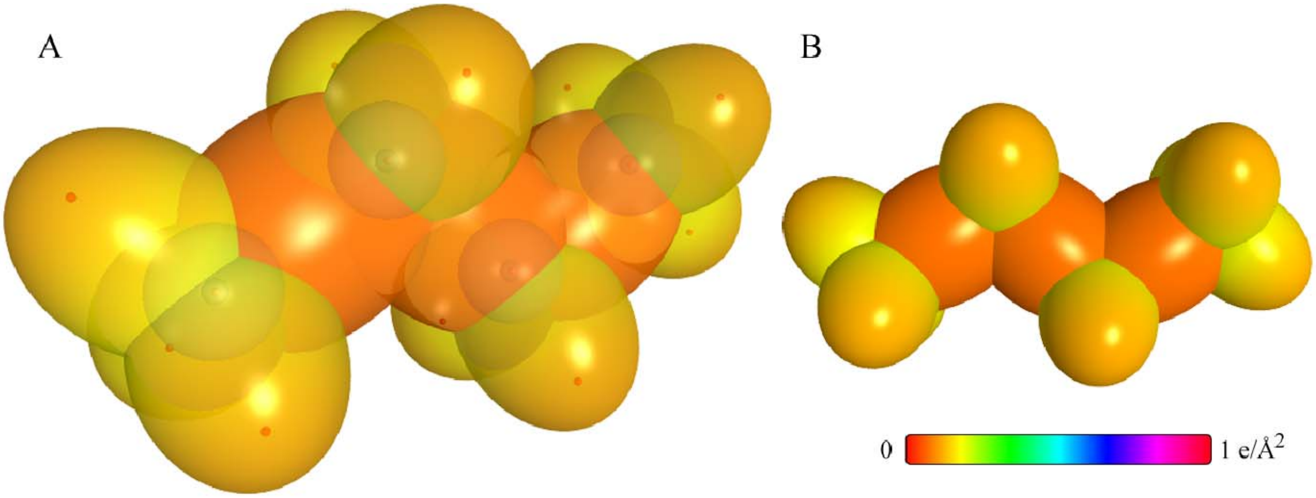
$$\begin{aligned} E_D\left(C_4H_{10}\right) &= E_D\left(C-C\right)_3 + 2E_{D_{alkane}}\left({}^{12}CH_3\right) + 2E_{D_{alkane}}\left({}^{12}CH_2\right) \\ &= (3)(4.32754\ eV) + (2)(12.49186\ eV) + (2)(7.83016\ eV) \\ &= 53.62666\ eV \end{aligned} \tag{14.648}$$

Using Eq. (14.643), the experimental total bond dissociation energy of $C_4H_{10}$, $E_{D_{\exp}}\left(C_4H_{10}\right)$, given by the negative difference between the enthalpy of its formation ($\Delta H_f\left(C_4H_{10}(gas) = -1.3028\ eV\right)$) [18] and the sum of the enthalpy of the formation of the gaseous carbons ($\Delta H_f\left(C(gas)\right)$) and hydrogen ($\Delta H_f\left(H(gas)\right)$) atoms is:

$$\begin{aligned} E_{D_{\exp}}\left(C_4H_{10}\right) &= -\left\{\Delta H_f\left(C_4H_{10}(gas)\right) - \left[4\Delta H_f\left(C(gas)\right) + 10\Delta H_f\left(H(gas)\right)\right]\right\} \\ &= -\left\{-1.3028\ eV - \left[(4)7.42774\ eV + (10)2.259353\ eV\right]\right\} \\ &= 53.61\ eV \end{aligned} \tag{14.649}$$

The charge-density of the $C_4H_{10}$ molecular orbital (MO) comprising a linear combination of two methyl and two methylene groups is shown in Figure 14.19.

Figure 14.19. $C_4H_{10}$ MO comprising a linear combination of $C-H$-bond MOs and $C-C$-bond MOs of the two methyl and two methylene groups. (A) Color scale, translucent view of the charge-density of the $C-C$-bond and $C-H$-bond MOs and the $C_{\text{butane}}2sp^3$ HOs. Each $C-C$-bond MO comprises a $H_2$-type ellipsoidal MO bridging two $C_{\text{butane}}2sp^3$ HOs. For each $C-H$ and the $C-C$ bond, the ellipsoidal surface of the $H_2$-type ellipsoidal MO that transitions to the $C_{\text{butane}}2sp^3$ HO, the $C_{\text{butane}}2sp^3$ HO shell, inner most $C1s$ shell, and the nuclei (red, not to scale), are shown. (B) Opaque view highlighting the $C-C$-bond MOs of the charge-density of the $C_4H_{10}$ MO.



## PENTANE ($C_5H_{12}$)

Using Eq. (14.642) with $n=5$, the total bond dissociation energy of $C_5H_{12}$ is:

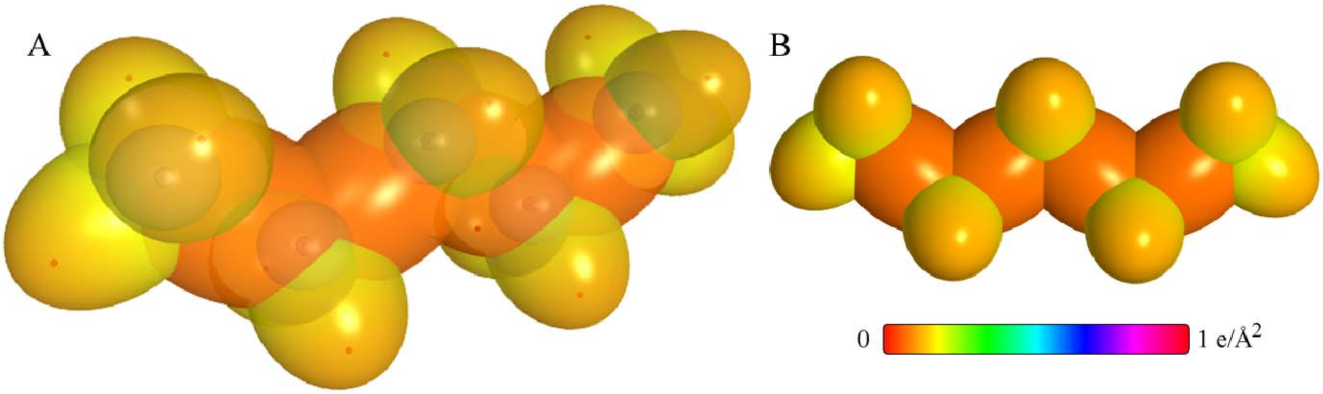
$$\begin{aligned} E_D\left(C_5H_{12}\right) &= E_D\left(C-C\right)_4 + 2E_{D_{alkane}}\left({}^{12}CH_3\right) + 3E_{D_{alkane}}\left({}^{12}CH_2\right) \\ &= (4)(4.32754\ eV) + (2)(12.49186\ eV) + (3)(7.83016\ eV) \\ &= 65.78436\ eV \end{aligned} \tag{14.650}$$

Using Eq. (14.643), the experimental total bond dissociation energy of $C_5H_{12}$, $E_{D_{\exp}}\left(C_5H_{12}\right)$, given by the negative difference between the enthalpy of its formation ($\Delta H_f\left(C_5H_{12}\left(gas\right) = -1.5225\ eV\right)$) [18] and the sum of the enthalpy of the formation of the gaseous carbons ($\Delta H_f\left(C\left(gas\right)\right)$) and hydrogen ($\Delta H_f\left(H\left(gas\right)\right)$) atoms is:

$$\begin{aligned} E_{D_{\exp}}\left(C_5H_{12}\right) &= -\left\{\Delta H_f\left(C_5H_{12}\left(gas\right)\right) - \left[5\Delta H_f\left(C\left(gas\right)\right) + 12\Delta H_f\left(H\left(gas\right)\right)\right]\right\} \\ &= -\left\{-1.5225\ eV - \left[(5)7.42774\ eV + (12)2.259353\ eV\right]\right\} \\ &= 65.77\ eV \end{aligned} \tag{14.651}$$

The charge-density of the $C_5H_{12}$ molecular orbital (MO) comprising a linear combination of two methyl and three methylene groups is shown in Figure 14.20.

Figure 14.20. $C_5H_{12}$ MO comprising a linear combination of $C-H$-bond MOs and $C-C$-bond MOs of the two methyl and three methylene groups. (A) Color scale, translucent view of the charge-density of the $C-C$-bond and $C-H$-bond MOs and the $C_{\mathrm{pentane}}2sp^3$ HOs. Each $C-C$-bond MO comprises a $H_2$-type ellipsoidal MO bridging two $C_{\mathrm{pentane}}2sp^3$ HOs. For each $C-H$ and the $C-C$ bond, the ellipsoidal surface of the $H_2$-type ellipsoidal MO that transitions to the $C_{\mathrm{pentane}}2sp^3$ HO, the $C_{\mathrm{pentane}}2sp^3$ HO shell, inner most $C1s$ shell, and the nuclei (red, not to scale), are shown. (B) Opaque view highlighting the $C-C$-bond MOs of the charge-density of the $C_5H_{12}$ MO.



## HEXANE ($C_6H_{14}$)

Using Eq. (14.642) with $n = 6$, the total bond dissociation energy of $C_6H_{14}$ is:

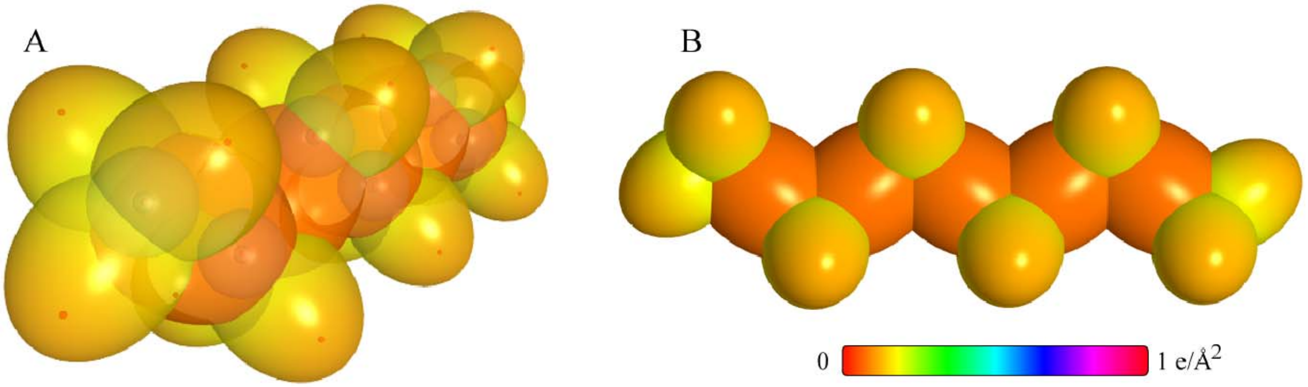
$$\begin{aligned} E_D\left(C_6H_{14}\right) &= E_D\left(C-C\right)_5 + 2E_{D_{alkane}}\left({}^{12}CH_3\right) + 4E_{D_{alkane}}\left({}^{12}CH_2\right) \\ &= (5)(4.32754\ eV) + (2)(12.49186\ eV) + (4)(7.83016\ eV) \\ &= 77.94206\ eV \end{aligned} \tag{14.652}$$

Using Eq. (14.643), the experimental total bond dissociation energy of $C_6H_{14}$, $E_{D_{\exp}}\left(C_6H_{14}\right)$, given by the negative difference between the enthalpy of its formation ($\Delta H_f\left(C_6H_{14}\left(gas\right) = -1.7298\ eV\right)$) [18] and the sum of the enthalpy of the formation of the gaseous carbons ($\Delta H_f\left(C\left(gas\right)\right)$) and hydrogen ($\Delta H_f\left(H\left(gas\right)\right)$) atoms is:

$$\begin{aligned} E_{D_{\exp}}\left(C_6H_{14}\right) &= -\left\{\Delta H_f\left(C_6H_{14}\left(gas\right)\right) - \left[6\Delta H_f\left(C\left(gas\right)\right) + 14\Delta H_f\left(H\left(gas\right)\right)\right]\right\} \\ &= -\left\{-1.7298\ eV - \left[(6)7.42774\ eV + (14)2.259353\ eV\right]\right\} \\ &= 77.93\ eV \end{aligned} \tag{14.653}$$

The charge-density of the $C_6H_{14}$ molecular orbital (MO) comprising a linear combination of two methyl and four methylene groups is shown in Figure 14.21.

Figure 14.21. $C_6H_{14}$ MO comprising a linear combination of $C-H$-bond MOs and $C-C$-bond MOs of the two methyl and four methylene groups. (A) Opaque view of the charge-density of the $C-C$-bond and $C-H$-bond MOs. Each $C-C$-bond MO comprises a $H_2$-type ellipsoidal MO bridging two $C_{\text{hexane}}2sp^3$ HOs. (B) Translucent view high-lighting the $C-C$-bond MOs of the charge-density of the $C_6H_{14}$ MO. For each $C-H$ and the $C-C$ bond, the ellipsoidal surface of the $H_2$-type ellipsoidal MO that transitions to the $C_{\text{hexane}}2sp^3$ HO, the $C_{\text{hexane}}2sp^3$ HO shell, inner most $C1s$ shell, and the nuclei (red, not to scale), are shown.



## HEPTANE ($C_7H_{16}$)

Using Eq. (14.642) with $n=7$, the total bond dissociation energy of $C_7H_{16}$ is:

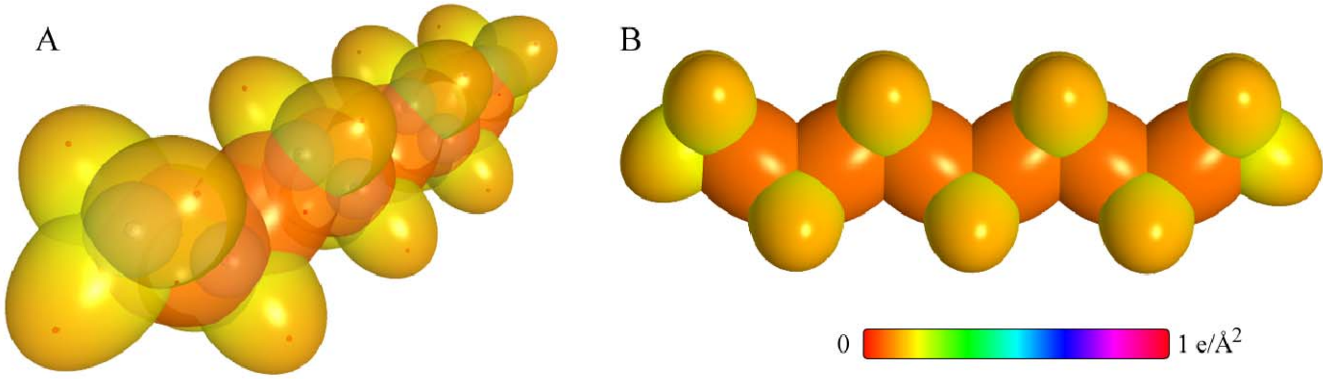
$$\begin{aligned} E_D\left(C_7H_{16}\right) &= E_D\left(C-C\right)_6 + 2E_{D_{alkane}}\left({}^{12}CH_3\right) + 5E_{D_{alkane}}\left({}^{12}CH_2\right) \\ &= (6)(4.32754\ eV) + (2)(12.49186\ eV) + (5)(7.83016\ eV) \\ &= 90.09976\ eV \end{aligned} \tag{14.654}$$

Using Eq. (14.643), the experimental total bond dissociation energy of $C_7H_{16}$, $E_{D_{\exp}}\left(C_7H_{16}\right)$, given by the negative difference between the enthalpy of its formation ($\Delta H_f\left(C_7H_{16}\left(gas\right) = -1.9443\ eV\right)$) [18] and the sum of the enthalpy of the formation of the gaseous carbons ($\Delta H_f\left(C\left(gas\right)\right)$) and hydrogen ($\Delta H_f\left(H\left(gas\right)\right)$) atoms is:

$$\begin{aligned} E_{D_{\exp}}\left(C_7H_{16}\right) &= -\left\{\Delta H_f\left(C_7H_{16}\left(gas\right)\right) - \left[7\Delta H_f\left(C\left(gas\right)\right) + 16\Delta H_f\left(H\left(gas\right)\right)\right]\right\} \\ &= -\left\{-1.9443\ eV - \left[(7)7.42774\ eV + (16)2.259353\ eV\right]\right\} \\ &= 90.09\ eV \end{aligned} \tag{14.655}$$

The charge-density of the $C_7H_{16}$ MO comprising a linear combination of two methyl and five methylene groups is shown in Figure 14.22.

Figure 14.22. $C_7H_{16}$ MO comprising a linear combination of $C-H$-bond MOs and $C-C$-bond MOs of the two methyl and five methylene groups. (A) Opaque view of the charge-density of the $C-C$-bond and $C-H$-bond MOs. Each $C-C$-bond MO comprises a $H_2$-type ellipsoidal MO bridging two $C_{\text{heptane}}2sp^3$ HOs. (B) Translucent view high-lighting the $C-C$-bond MOs of the charge-density of the $C_7H_{16}$ MO. For each $C-H$ and the $C-C$ bond, the ellipsoidal surface of the $H_2$-type ellipsoidal MO that transitions to the $C_{\text{heptane}}2sp^3$ HO, the $C_{\text{heptane}}2sp^3$ HO shell, inner most $C1s$ shell, and the nuclei (red, not to scale), are shown.



## OCTANE ($C_8H_{18}$)

Using Eq. (14.642) with $n = 8$, the total bond dissociation energy of $C_8H_{18}$ is:

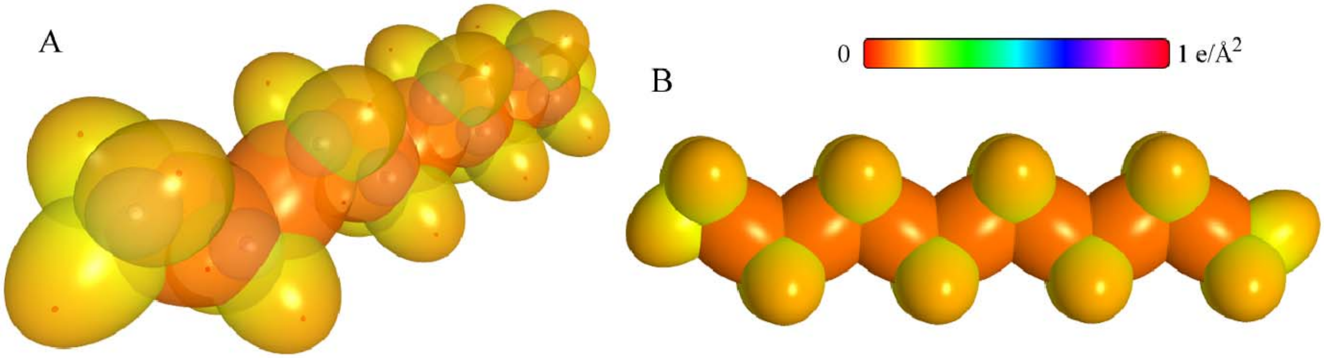
$$\begin{aligned} E_D\left(C_8H_{18}\right) &= E_D\left(C-C\right)_7 + 2E_{D_{alkane}}\left({}^{12}CH_3\right) + 6E_{D_{alkane}}\left({}^{12}CH_2\right) \\ &= (7)(4.32754\ eV) + (2)(12.49186\ eV) + (6)(7.83016\ eV) \\ &= 102.25746\ eV \end{aligned} \quad (14.656)$$

Using Eq. (14.643), the experimental total bond dissociation energy of $C_8H_{18}$, $E_{D_{\exp}}\left(C_8H_{18}\right)$, given by the negative difference between the enthalpy of its formation ($\Delta H_f\left(C_8H_{18}\left(gas\right) = -2.1609\ eV\right)$) [18] and the sum of the enthalpy of the formation of the gaseous carbons ($\Delta H_f\left(C\left(gas\right)\right)$) and hydrogen ($\Delta H_f\left(H\left(gas\right)\right)$) atoms is:

$$\begin{aligned} E_{D_{\exp}}\left(C_8H_{18}\right) &= -\left\{\Delta H_f\left(C_8H_{18}\left(gas\right)\right) - \left[8\Delta H_f\left(C\left(gas\right)\right) + 18\Delta H_f\left(H\left(gas\right)\right)\right]\right\} \\ &= -\left\{-2.1609\ eV - \left[(8)7.42774\ eV + (18)2.259353\ eV\right]\right\} \\ &= 102.25\ eV \end{aligned} \quad (14.657)$$

The charge-density of the $C_8H_{18}$ MO comprising a linear combination of two methyl and six methylene groups is shown in Figure 14.23.

Figure 14.23. $C_8H_{18}$ MO comprising a linear combination of $C-H$-bond MOs and $C-C$-bond MOs of the two methyl and six methylene groups. (A) Opaque view of the charge-density of the $C-C$-bond and $C-H$-bond MOs. Each $C-C$-bond MO comprises a $H_2$-type ellipsoidal MO bridging two $C_{\mathrm{octane}}2sp^3$ HOs. (B) Translucent view high-lighting the $C-C$-bond MOs of the charge-density of the $C_8H_{18}$ MO. For each $C-H$ and the $C-C$ bond, the ellipsoidal surface of the $H_2$-type ellipsoidal MO that transitions to the $C_{\mathrm{octane}}2sp^3$ HO, the $C_{\mathrm{octane}}2sp^3$ HO shell, inner most $C1s$ shell, and the nuclei (red, not to scale), are shown.



## NONANE ($C_9H_{20}$)

Using Eq. (14.642) with $n=9$, the total bond dissociation energy of $C_9H_{20}$ is:

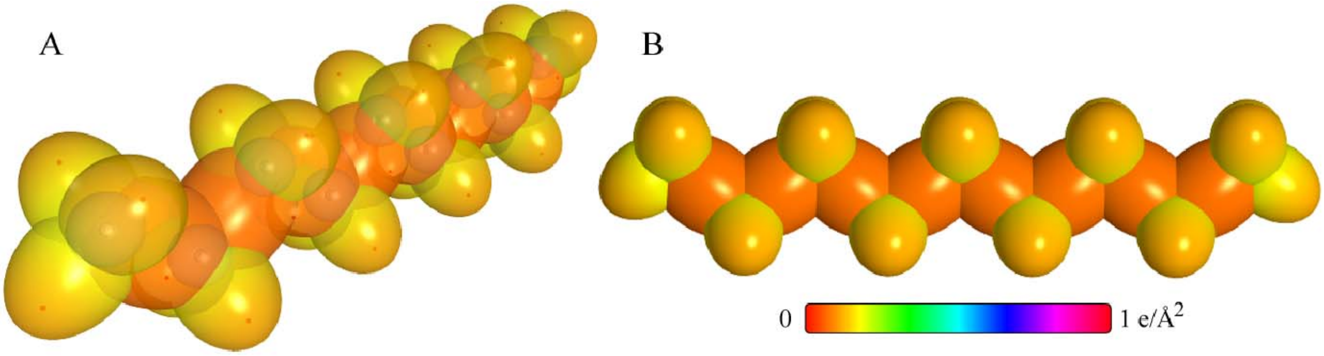
$$\begin{aligned}E_D\left(C_9H_{20}\right) &= E_D\left(C-C\right)_8 + 2E_{D_{alkane}}\left({}^{12}CH_3\right) + 7E_{D_{alkane}}\left({}^{12}CH_2\right)\\ &= (8)(4.32754\ eV) + (2)(12.49186\ eV) + (7)(7.83016\ eV)\\ &= 114.41516\ eV\end{aligned} \tag{14.658}$$

Using Eq. (14.643), the experimental total bond dissociation energy of $C_9H_{20}$, $E_{D_{\exp}}\left(C_9H_{20}\right)$, given by the negative difference between the enthalpy of its formation ($\Delta H_f\left(C_9H_{20}\left(gas\right) = -2.3651\ eV\right)$) [18] and the sum of the enthalpy of the formation of the gaseous carbons ($\Delta H_f\left(C\left(gas\right)\right)$) and hydrogen ($\Delta H_f\left(H\left(gas\right)\right)$) atoms is:

$$\begin{aligned}E_{D_{\exp}}\left(C_9H_{20}\right) &= -\left\{\Delta H_f\left(C_9H_{20}\left(gas\right)\right) - \left[9\Delta H_f\left(C\left(gas\right)\right) + 20\Delta H_f\left(H\left(gas\right)\right)\right]\right\}\\ &= -\left\{-2.3651\ eV - \left[(9)7.42774\ eV + (20)2.259353\ eV\right]\right\}\\ &= 114.40\ eV\end{aligned} \tag{14.659}$$

The charge-density of the $C_9H_{20}$ MO comprising a linear combination of two methyl and seven methylene groups is shown in Figure 14.24.

Figure 14.24. $C_9H_{20}$ MO comprising a linear combination of $C-H$-bond MOs and $C-C$-bond MOs of the two methyl and seven methylene groups. (A) Opaque view of the charge-density of the $C-C$-bond and $C-H$-bond MOs. Each $C-C$-bond MO comprises a $H_2$-type ellipsoidal MO bridging two $C_{\text{nonane}}2sp^3$ HOs. (B) Translucent view high-lighting the $C-C$-bond MOs of the charge-density of the $C_9H_{20}$ MO. For each $C-H$ and the $C-C$ bond, the ellipsoidal surface of the $H_2$-type ellipsoidal MO that transitions to the $C_{\text{nonane}}2sp^3$ HO, the $C_{\text{nonane}}2sp^3$ HO shell, inner most $C1s$ shell, and the nuclei (red, not to scale), are shown.



## DECANE ($C_{10}H_{22}$)

Using Eq. (14.642) with $n = 10$, the total bond dissociation energy of $C_{10}H_{22}$ is:

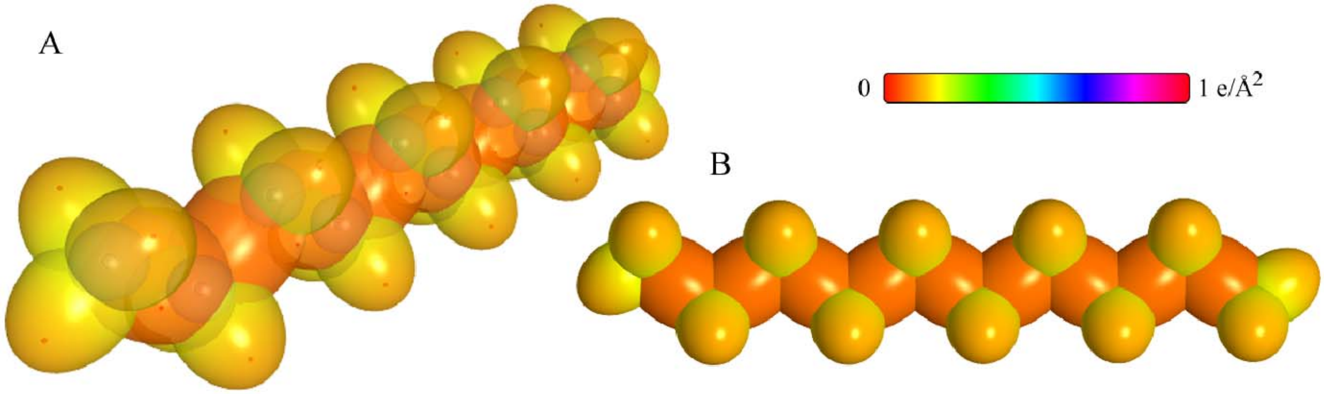
$$\begin{aligned} E_D\left(C_{10}H_{22}\right) &= E_D\left(C-C\right)_9 + 2E_{D_{alkane}}\left({}^{12}CH_3\right) + 8E_{D_{alkane}}\left({}^{12}CH_2\right) \\ &= (9)(4.32754\ eV) + (2)(12.49186\ eV) + (8)(7.83016\ eV) \\ &= 126.57286\ eV \end{aligned} \tag{14.660}$$

Using Eq. (14.643), the experimental total bond dissociation energy of $C_{10}H_{22}$, $E_{D_{\exp}}\left(C_{10}H_{22}\right)$, given by the negative difference between the enthalpy of its formation ($\Delta H_f\left(C_{10}H_{22}\left(gas\right) = -2.5858\ eV\right)$) [18] and the sum of the enthalpy of the formation of the gaseous carbons ($\Delta H_f\left(C\left(gas\right)\right)$) and hydrogen ($\Delta H_f\left(H\left(gas\right)\right)$) atoms is:

$$\begin{aligned} E_{D_{\exp}}\left(C_{10}H_{22}\right) &= -\left\{\Delta H_f\left(C_{10}H_{22}\left(gas\right)\right) - \left[10\Delta H_f\left(C\left(gas\right)\right) + 22\Delta H_f\left(H\left(gas\right)\right)\right]\right\} \\ &= -\left\{-2.5858\ eV - \left[(10)7.42774\ eV + (22)2.259353\ eV\right]\right\} \\ &= 126.57\ eV \end{aligned} \tag{14.661}$$

The charge-density of the $C_{10}H_{22}$ molecular orbital (MO) comprising a linear combination of two methyl and eight methylene groups is shown in Figure 14.25.

Figure 14.25. $C_{10}H_{22}$ MO comprising a linear combination of $C-H$-bond MOs and $C-C$-bond MOs of the two methyl and eight methylene groups. (A) Opaque view of the charge-density of the $C-C$-bond and $C-H$-bond MOs. Each $C-C$-bond MO comprises a $H_2$-type ellipsoidal MO bridging two $C_{\text{decane}}2sp^3$ HOs. (B) Translucent view high-lighting the $C-C$-bond MOs of the charge-density of the $C_{10}H_{22}$ MO. For each $C-H$ and the $C-C$ bond, the ellipsoidal surface of the $H_2$-type ellipsoidal MO that transitions to the $C_{\text{decane}}2sp^3$ HO, the $C_{\text{decane}}2sp^3$ HO shell, inner most $C1s$ shell, and the nuclei (red, not to scale), are shown.



## UNDECANE ($C_{11}H_{24}$)

Using Eq. (14.642) with $n=11$, the total bond dissociation energy of $C_{11}H_{24}$ is:

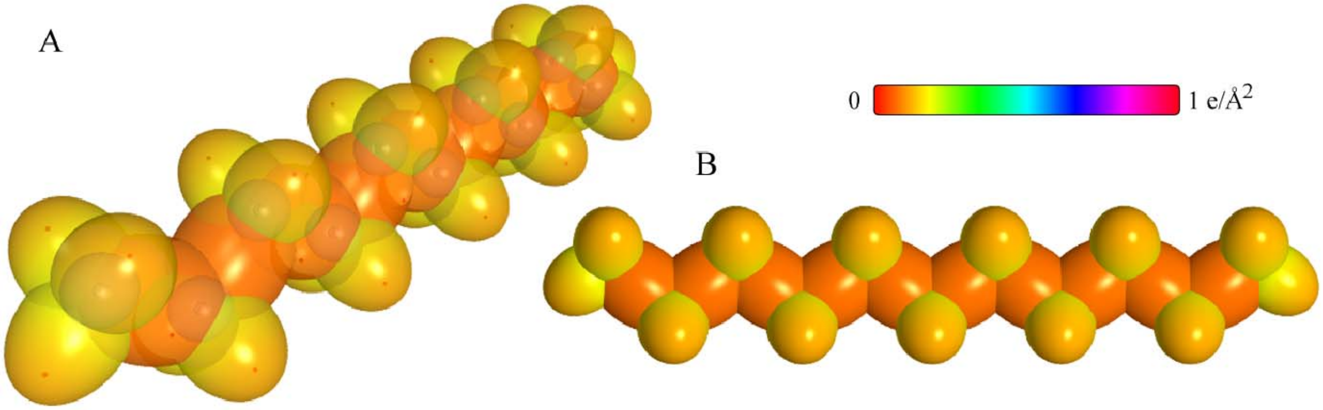
$$\begin{aligned} E_D\left(C_{11}H_{24}\right) &= E_D\left(C-C\right)_{10} + 2E_{D_{alkane}}\left({}^{12}CH_3\right) + 9E_{D_{alkane}}\left({}^{12}CH_2\right) \\ &= (10)(4.32754\ eV) + (2)(12.49186\ eV) + (9)(7.83016\ eV) \\ &= 138.73056\ eV \end{aligned} \tag{14.662}$$

Using Eq. (14.643), the experimental total bond dissociation energy of $C_{11}H_{24}$, $E_{D_{\exp}}\left(C_{11}H_{24}\right)$, given by the negative difference between the enthalpy of its formation ($\Delta H_f\left(C_{11}H_{24}\left(gas\right)=-2.8066\ eV\right)$) [18] and the sum of the enthalpy of the formation of the gaseous carbons ($\Delta H_f\left(C\left(gas\right)\right)$) and hydrogen ($\Delta H_f\left(H\left(gas\right)\right)$) atoms is:

$$\begin{aligned} E_{D_{\exp}}\left(C_{11}H_{24}\right) &= -\left\{\Delta H_f\left(C_{11}H_{24}\left(gas\right)\right) - \left[11\Delta H_f\left(C\left(gas\right)\right) + 24\Delta H_f\left(H\left(gas\right)\right)\right]\right\} \\ &= -\left\{-2.8066\ eV - \left[(11)7.42774\ eV + (24)2.259353\ eV\right]\right\} \\ &= 138.736\ eV \end{aligned} \tag{14.663}$$

The charge-density of the $C_{11}H_{24}$ MO comprising a linear combination of two methyl and nine methylene groups is shown in Figure 14.26.

Figure 14.26. $C_{11}H_{24}$ MO comprising a linear combination of $C-H$-bond MOs and $C-C$-bond MOs of the two methyl and nine methylene groups. (A) Opaque view of the charge-density of the $C-C$-bond and $C-H$-bond MOs. Each $C-C$-bond MO comprises a $H_2$-type ellipsoidal MO bridging two $C_{\mathrm{undecane}}2sp^3$ HOs. (B) Translucent view high-lighting the $C-C$-bond MOs of the charge-density of the $C_{11}H_{24}$ MO. For each $C-H$ and the $C-C$ bond, the ellipsoidal surface of the $H_2$-type ellipsoidal MO that transitions to the $C_{\mathrm{undecane}}2sp^3$ HO, the $C_{\mathrm{undecane}}2sp^3$ HO shell, inner most $C1s$ shell, and the nuclei (red, not to scale), are shown.



## DODECANE ($C_{12}H_{26}$)

Using Eq. (14.642) with $n=12$, the total bond dissociation energy of $C_{12}H_{26}$ is:

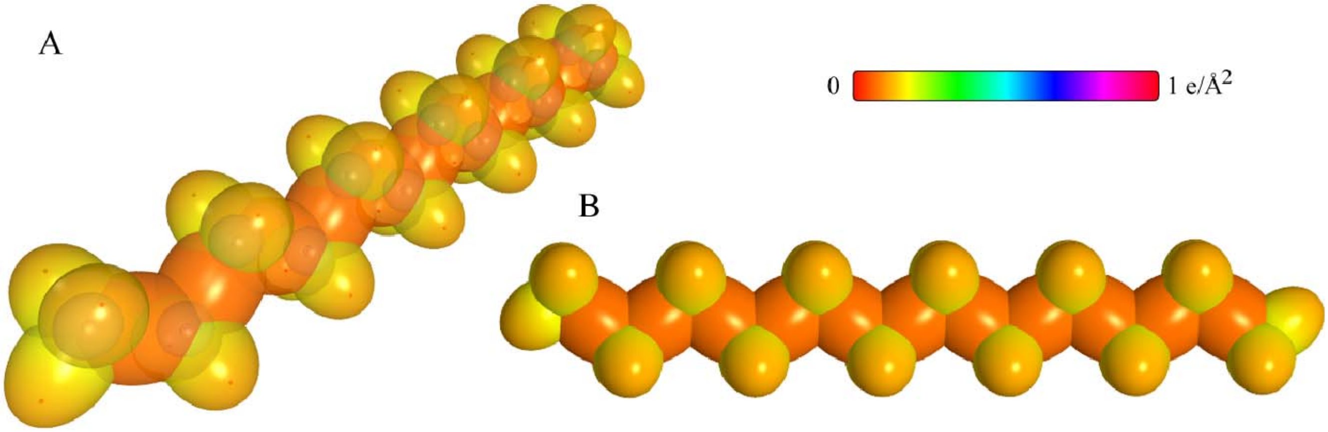
$$\begin{aligned}E_D\left(C_{12}H_{26}\right) &= E_D\left(C-C\right)_{11}+2E_{D_{alkane}}\left({}^{12}CH_3\right)+10E_{D_{alkane}}\left({}^{12}CH_2\right)\\ &=(11)(4.32754\ eV)+(2)(12.49186\ eV)+(10)(7.83016\ eV)\\ &=150.88826\ eV\end{aligned} \tag{14.664}$$

Using Eq. (14.643), the experimental total bond dissociation energy of $C_{12}H_{26}$, $E_{D_{\exp}}\left(C_{12}H_{26}\right)$, given by the negative difference between the enthalpy of its formation ($\Delta H_f\left(C_{12}H_{26}\left(gas\right)=-2.9994\ eV\right)$) [18] and the sum of the enthalpy of the formation of the gaseous carbons ($\Delta H_f\left(C\left(gas\right)\right)$) and hydrogen ($\Delta H_f\left(H\left(gas\right)\right)$) atoms is:

$$\begin{aligned}E_{D_{\exp}}\left(C_{12}H_{26}\right) &= -\left\{\Delta H_f\left(C_{12}H_{26}\left(gas\right)\right)-\left[12\Delta H_f\left(C\left(gas\right)\right)+26\Delta H_f\left(H\left(gas\right)\right)\right]\right\}\\ &=-\left\{-2.9994\ eV-\left[(12)7.42774\ eV+(26)2.259353\ eV\right]\right\}\\ &=150.88\ eV\end{aligned} \tag{14.665}$$

The charge-density of the $C_{12}H_{26}$ MO comprising a linear combination of two methyl and ten methylene groups is shown in Figure 14.27.

Figure 14.27. $C_{12}H_{26}$ MO comprising a linear combination of $C-H$-bond MOs and $C-C$-bond MOs of the two methyl and ten methylene groups. (A) Opaque view of the charge-density of the $C-C$-bond and $C-H$-bond MOs. Each $C-C$-bond MO comprises a $H_2$-type ellipsoidal MO bridging two $C_{\text{dodecane}}2sp^3$ HOs. (B) Translucent view high-lighting the $C-C$-bond MOs of the charge-density of the $C_{12}H_{26}$ MO. For each $C-H$ and the $C-C$ bond, the ellipsoidal surface of the $H_2$-type ellipsoidal MO that transitions to the $C_{\text{dodecane}}2sp^3$ HO, the $C_{\text{dodecane}}2sp^3$ HO shell, inner most $C1s$ shell, and the nuclei (red, not to scale), are shown.



## OCTADECANE ($C_{18}H_{38}$)

Using Eq. (14.642) with $n = 18$, the total bond dissociation energy of $C_{18}H_{38}$ is:

$$\begin{aligned} E_D\left(C_{18}H_{38}\right) &= E_D\left(C-C\right)_{17} + 2E_{D_{alkane}}\left({}^{12}CH_3\right) + 16E_{D_{alkane}}\left({}^{12}CH_2\right) \\ &= \left(17\right)\left(4.32754\ eV\right) + \left(2\right)\left(12.49186\ eV\right) + \left(16\right)\left(7.83016\ eV\right) \\ &= 223.83446\ eV \end{aligned} \tag{14.666}$$

Using Eq. (14.643), the experimental total bond dissociation energy of $C_{18}H_{38}$, $E_{D_{\exp}}\left(C_{18}H_{38}\right)$, given by the negative difference between the enthalpy of its formation ($\Delta H_f\left(C_{18}H_{38}\left(gas\right) = -4.2970\ eV\right)$) [18] and the sum of the enthalpy of the formation of the gaseous carbons ($\Delta H_f\left(C\left(gas\right)\right)$) and hydrogen ($\Delta H_f\left(H\left(gas\right)\right)$) atoms is:

$$\begin{aligned} E_{D_{\exp}}\left(C_{18}H_{38}\right) &= -\left\{\Delta H_f\left(C_{18}H_{38}\left(gas\right)\right) - \left[18\Delta H_f\left(C\left(gas\right)\right) + 38\Delta H_f\left(H\left(gas\right)\right)\right]\right\} \\ &= -\left\{-4.2970\ eV - \left[\left(18\right)7.42774\ eV + \left(38\right)2.259353\ eV\right]\right\} \\ &= 223.85\ eV \end{aligned} \tag{14.667}$$

The charge-density of the $C_{18}H_{38}$ molecular orbital (MO) comprising a linear combination of two methyl and sixteen methylene groups is shown in Figure 14.28.

Figure 14.28. $C_{18}H_{38}$ MO comprising a linear combination of $C-H$-bond MOs and $C-C$-bond MOs of the two methyl and sixteen methylene groups. (A) Opaque view of the charge-density of the $C-C$-bond and $C-H$-bond MOs. Each $C-C$-bond MO comprises a $H_2$-type ellipsoidal MO bridging two $C_{\text{octadecane}}2sp^3$ HOs. (B) Translucent view high-lighting the $C-C$-bond MOs of the charge-density of the $C_{18}H_{38}$ MO. For each $C-H$ and the $C-C$ bond, the ellipsoidal surface of the $H_2$-type ellipsoidal MO that transitions to the $C_{\text{octadecane}}2sp^3$ HO, the $C_{\text{octadecane}}2sp^3$ HO shell, inner most $C1s$ shell, and the nuclei (red, not to scale), are shown.

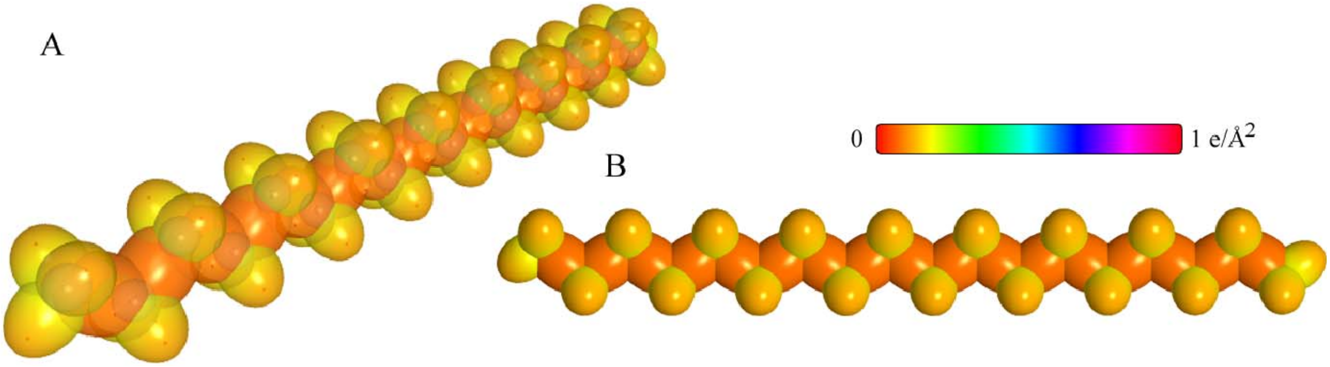


Table 14.1. The calculated and experimental bond parameters of $CO_2$, $NO_2$, $CH_3CH_3$, $CH_2CH_2$, $CHCH$, benzene, propane, butane, pentane, hexane, heptane, octane, nonane, decane, undecane, dodecane, and octadecane.

| Parameter | Calculated | Experimental | Ref. for Exp. |
|---|---|---|---|
| $CO_2$ Bond Energy | 5.49553 eV | 5.51577 eV | 7 |
| $CO_2$ Bond Length | 1.1616 Å | 1.1600 Å | 3 |
| $NO_2$ Bond Energy | 3.1532 eV | 3.161 eV | 7 |
| $NO_2$ Bond Length | 1.1872 Å | 1.193 Å | 3 |
| $NO_2$ Bond Angle | 131.012° | 134.1° | 3 |
| $H_3C-CH_3$ Bond Energy | 3.90245 eV | 3.8969 eV | 7 |
| $H_3C-CH_3$ Bond Length | 1.53635 Å | 1.5351 Å | 3 |
| $H-CH_2CH_3$ Bond Length | 1.10822 Å | 1.0940 Å | 3 |
| Ethane $H-C-H$ Bond Angle | 107.44° | 107.4° | 8 |
| Ethane $C-C-H$ Bond Angle | 111.44° | 111.17° | 3 |
| $H_2C=CH_2$ Bond Energy | 7.55681 eV | 7.597 eV | 7 |
| $H_2C=CH_2$ Bond Length | 1.3405 Å | 1.339 Å | 3 |
| $H-CHCH_2$ Bond Length | 1.0826 Å | 1.087 Å | 3 |
| Ethylene $H-C-H$ Bond Angle | 116.31° | 116.6° | 11 |
| Ethylene $C=C-H$ Bond Angle | 121.85° | 121.7° | 11 |
| $HC\equiv CH$ Bond Energy | 10.07212 eV | 10.0014 eV | 7 |
| $HC\equiv CH$ Bond Length | 1.2007 Å | 1.203 Å | 3 |
| $H-CCH$ Bond Length | 1.0538 Å | 1.060 Å | 3 |
| Acetylene $C\equiv C-H$ Bond Angle | 180° | 180° | 6 |
| $C_6H_6$ Total Bond Energy | 57.2601 eV | 57.26 eV | 17-18 |
| Benzene $C=C$ Bond Length | 1.3914 Å | 1.399 Å | 3 |
| $H-C_6H_5$ Bond Length | 1.0933 Å | 1.101 Å | 3 |
| $C_6H_6$ $C=C=C$ Bond Angle | 120° | 120° | 13-15 |
| $C_6H_6$ $C=C-H$ Bond Angle | 120° | 120° | 13-15 |
| $C_3H_8$ Total Bond Energy | 41.46896 eV | 41.434 eV | 17-18 |
| Propane $C-C$ Bond Length | 1.5428 Å | 1.532 Å | 3 |
| Propane $C-H$ Bond Length | 1.1097 Å | 1.107 Å | 3 |
| Alkane $H-C-H$ Bond Angle | 109.50° | 109.3° | 19 |
| Alkane $C-C-H$ Bond Angle | 109.44° | 109.3° | 19 |
| $C_4H_{10}$ Total Bond Energy | 53.62666 eV | 53.61 eV | 17-18 |
| Butane $C-C$ Bond Length | 1.5428 Å | 1.531 Å | 3 |
| Butane $C-H$ Bond Length | 1.11713 Å | 1.117 Å | 3 |
| $C_5H_{12}$ Total Bond Energy | 65.78436 eV | 65.77 eV | 17-18 |
| $C_6H_{14}$ Total Bond Energy | 77.94206 eV | 77.93 eV | 17-18 |
| $C_7H_{16}$ Total Bond Energy | 90.09976 eV | 90.09 eV | 17-18 |
| $C_8H_{18}$ Total Bond Energy | 102.25746 eV | 102.25 eV | 17-18 |
| $C_9H_{20}$ Total Bond Energy | 114.41516 eV | 114.40 eV | 17-18 |
| $C_{10}H_{22}$ Total Bond Energy | 126.57286 eV | 126.57 eV | 17-18 |
| $C_{11}H_{24}$ Total Bond Energy | 138.73056 eV | 138.736 eV | 17-18 |
| $C_{12}H_{26}$ Total Bond Energy | 150.88826 eV | 150.88 eV | 17-18 |
| $C_{18}H_{38}$ Total Bond Energy | 223.83446 eV | 223.85 eV | 17-18 |

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# Chapter 15

# ORGANIC MOLECULAR FUNCTIONAL GROUPS AND MOLECULES

## DERIVATION OF THE GENERAL GEOMETRICAL AND ENERGY EQUATIONS OF ORGANIC CHEMISTRY

Organic molecules comprising an arbitrary number of atoms can be solved using similar principles and procedures as those used to solve alkanes of arbitrary length. Alkanes can be considered to be comprised of the functional groups of $CH_3$, $CH_2$, and $C-C$. These groups with the corresponding geometrical parameters and energies can be added as a linear sum to give the solution of any straight chain alkane as shown in the Continuous-Chain Alkanes section. Similarly, the geometrical parameters and energies of all functional groups such as alkanes, branched alkanes, alkenes, branched alkenes, alkynes, alkyl fluorides, alkyl chlorides, alkyl bromides, alkyl iodides, alkene halides, primary alcohols, secondary alcohols, tertiary alcohols, ethers, primary amines, secondary amines, tertiary amines, aldehydes, ketones, carboxylic acids, carboxylic esters, amides, N-alkyl amides, N,N-dialkyl amides, urea, acid halides, acid anhydrides, nitriles, thiols, sulfides, disulfides, sulfoxides, sulfones, sulfites, sulfates, nitro alkanes, nitrites, nitrates, conjugated polyenes, aromatics, heterocyclic aromatics, substituted aromatics, and others can be solved. The functional-group solutions can be made into a linear superposition and sum, respectively, to give the solution of any organic molecule. The solutions of the functional groups can be conveniently obtained by using generalized forms of the geometrical and energy equations. The total bond energies of exemplary organic molecules calculated using the functional group composition and the corresponding energies derived in the following sections compared to the experimental values are given in Tables 15.410.1–15.410.43.

Consider the case wherein at least two atomic orbitals hybridize as a linear combination of electrons at the same energy in order to achieve a bond at an energy minimum, and the sharing of electrons between two or more such orbitals to form a MO permits the participating hybridized orbitals to decrease in energy through a decrease in the radius of one or more of the participating orbitals. The force-generalized constant $k'$ of a $H_2$-type ellipsoidal MO due to the equivalent of two point charges at the foci is given by:

$$k' = \frac{C_1 C_2 2e^2}{4\pi\varepsilon_0} \tag{15.1}$$

where $C_1$ is the fraction of the $H_2$-type ellipsoidal MO basis function of a chemical bond of the molecule or molecular ion which is 0.75 (Eq. (13.59)) in the case of $H$ bonding to a central atom and 0.5 (Eq. (14.152)) otherwise, and $C_2$ is the factor that results in an equipotential energy match of the participating at least two molecular or atomic orbitals of the chemical bond. From Eqs. (13.58-13.63), the distance from the origin of the MO to each focus $c'$ is given by:

$$c' = a\sqrt{\frac{\hbar^2 4\pi\varepsilon_0}{m_e e^2 2C_1C_2 a}} = \sqrt{\frac{aa_0}{2C_1C_2}} \tag{15.2}$$

The internuclear distance is

$$2c' = 2\sqrt{\frac{aa_0}{2C_1C_2}} \tag{15.3}$$

The length of the semiminor axis of the prolate spheroidal MO $b = c$ is given by:

$$b = \sqrt{a^2 - c'^2} \tag{15.4}$$

And, the eccentricity, $e$, is

$$e = \frac{c'}{a} \tag{15.5}$$

From Eqs. (11.207-11.212), the potential energy of the two electrons in the central field of the nuclei at the foci is:

$$V_e = n_1 c_1 c_2 \frac{-2e^2}{8\pi\varepsilon_0 \sqrt{a^2-b^2}} \ln \frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} \tag{15.6}$$

The potential energy of the two nuclei is:

$$V_p = n_1 \frac{e^2}{8\pi\varepsilon_0 \sqrt{a^2-b^2}} \tag{15.7}$$

The kinetic energy of the electrons is

$$T = n_1 c_1 c_2 \frac{\hbar^2}{2m_e a \sqrt{a^2-b^2}} \ln \frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} \tag{15.8}$$

And, the energy, $V_m$, of the magnetic force between the electrons is:

$$V_m = n_1 c_1 c_2 \frac{-\hbar^2}{4m_e a \sqrt{a^2-b^2}} \ln \frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} \tag{15.9}$$

The total energy of the $H_2$-type prolate spheroidal MO, $E_T\left(H_2MO\right)$, is given by the sum of the energy terms:

$$E_T\left(H_2MO\right) = V_e + T + V_m + V_p \tag{15.10}$$

$$E_T\left(H_2MO\right) = -\frac{n_1 e^2}{8\pi\varepsilon_0 \sqrt{a^2-b^2}} \left[ c_1 c_2 \left(2-\frac{a_0}{a}\right) \ln \frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} - 1 \right] = -\frac{n_1 e^2}{8\pi\varepsilon_0 c'} \left[ c_1 c_2 \left(2-\frac{a_0}{a}\right) \ln \frac{a+c'}{a-c'} - 1 \right] \tag{15.11}$$

where $n_1$ is the number of equivalent bonds of the MO and applies in the case of functional groups. In the case of independent MOs not in contact with the bonding atoms, the terms based on charge are multiplied by $c_{BO}$, the bond-order factor. It is 1 for a single bond, 4 for an independent double bond as in the case of the $CO_2$ and $NO_2$ molecules, and 9 for an independent triplet bond. Then, the kinetic energy term is multiplied by $c'_{BO}$ which is 1 for a single bond, 2 for a double bond, and 9/2 for a triple bond. $c_1$ is the fraction of the $H_2$-type ellipsoidal MO basis function of an MO which is 0.75 (Eqs. (13.67-13.73)) in the case of $H$ bonding to an unhybridized central atom and 1 otherwise, and $c_2$ is the factor that results in an equipotential energy match of the participating MO and at least two atomic orbitals of the chemical bond. Specifically, to meet the equipotential condition and energy matching conditions for the union of the $H_2$-type-ellipsoidal-MO and the HOs or AOs of the bonding atoms, the factor $c_2$ of a $H_2$-type ellipsoidal MO may given by (i) one, (ii) the ratio of the Coulombic or valence energy of the AO or HO of at least one atom of the bond and $13.605804\ eV$, the Coulombic energy between the electron and proton of $H$, (iii) the ratio of the valence energy of the AO or HO of one atom and the Coulombic energy of another, (iv) the ratio of the valence energies of the AOs or HOs of two atoms, (v) the ratio of two $c_2$ factors corresponding to any of cases (ii)-(iv), and (vi) the product of two different $c_2$ factors corresponding to any of the cases (i)-(v). Specific examples of the factor $c_2$ of a $H_2$-type ellipsoidal MO given in previous sections are:

$0.936127$, the ratio of the ionization energy of $N$ $14.53414\ eV$ and $13.605804\ eV$, the Coulombic energy between the electron and proton of $H$;

$0.91771$, the ratio of $14.82575\ eV$, $-E_{Coulomb}\left(C, 2sp^3\right)$, and $13.605804\ eV$;

$0.87495$, the ratio of $15.55033\ eV$, $-E_{Coulomb}\left(C_{ethane}, 2sp^3\right)$, and $13.605804\ eV$;

$0.85252$, the ratio of $15.95955\ eV$, $-E_{Coulomb}\left(C_{ethylene}, 2sp^3\right)$, and $13.605804\ eV$;

$0.85252$, the ratio of $15.95955\ eV$, $-E_{Coulomb}\left(C_{benzene}, 2sp^3\right)$, and $13.605804\ eV$, and

$0.86359$, the ratio of $15.55033\ eV$, $-E_{Coulomb}\left(C_{alkane}, 2sp^3\right)$, and $13.605804\ eV$.

In the generalization of the hybridization of at least two atomic-orbital shells to form a shell of hybrid orbitals, the hybridized shell comprises a linear combination of the electrons of the atomic-orbital shells. The radius of the hybridized shell is calculated from the total Coulombic energy equation by considering that the central field decreases by an integer for each successive electron of the shell and that the total energy of the shell is equal to the total Coulombic energy of the initial AO electrons. The total energy $E_T\left(atom, msp^3\right)$ ($m$ is the integer of the valence shell) of the AO electrons and the hybridized shell is given by the sum of energies of successive ions of the atom over the $n$ electrons comprising total electrons of the at least one AO shell.

$$E_T\left(atom,msp^3\right)=-\sum_{m=1}^{n}IP_m \tag{15.12}$$

where $IP_m$ is the $m$ th ionization energy (positive) of the atom. The radius $r_{msp^3}$ of the hybridized shell is given by:

$$r_{msp^3}=\sum_{q=Z-n}^{Z-1}\frac{-(Z-q)e^2}{8\pi\varepsilon_0 E_T\left(atom,msp^3\right)} \tag{15.13}$$

Then, the Coulombic energy $E_{Coulomb}\left(atom,msp^3\right)$ of the outer electron of the $atom\ msp^3$ shell is given by:

$$E_{Coulomb}\left(atom,msp^3\right)=\frac{-e^2}{8\pi\varepsilon_0 r_{msp^3}} \tag{15.14}$$

In the case that during hybridization at least one of the spin-paired AO electrons is unpaired in the hybridized orbital (HO), the energy change for the promotion to the unpaired state is the magnetic energy $E(magnetic)$ at the initial radius $r$ of the AO electron:

$$E(magnetic)=\frac{2\pi\mu_0 e^2\hbar^2}{m_e^2 r^3}=\frac{8\pi\mu_0\mu_B^2}{r^3} \tag{15.15}$$

Then, the energy $E\left(atom,msp^3\right)$ of the outer electron of the $atom\ msp^3$ shell is given by the sum of $E_{Coulomb}\left(atom,msp^3\right)$ and $E(magnetic)$:

$$E\left(atom,msp^3\right)=\frac{-e^2}{8\pi\varepsilon_0 r_{msp^3}}+\frac{2\pi\mu_0 e^2\hbar^2}{m_e^2 r^3} \tag{15.16}$$

Consider next that the at least two atomic orbitals hybridize as a linear combination of electrons at the same energy in order to achieve a bond at an energy minimum with another atomic orbital or hybridized orbital. As a further generalization of the basis of the stability of the MO, the sharing of electrons between two or more such hybridized orbitals to form a MO permits the participating hybridized orbitals to decrease in energy through a decrease in the radius of one or more of the participating orbitals. In this case, the total energy of the hybridized orbitals is given by the sum of $E\left(atom,msp^3\right)$ and the next energies of successive ions of the atom over the $n$ electrons comprising the total electrons of the at least two initial AO shells. Here, $E\left(atom,msp^3\right)$ is the sum of the first ionization energy of the atom and the hybridization energy. An example of $E\left(atom,msp^3\right)$ for $E\left(C,2sp^3\right)$ is given in Eq. (14.503) where the sum of the negative of the first ionization energy of $C$, $-11.27671\ eV$, plus the hybridization energy to form the $C2sp^3$ shell given by Eq. (14.146) is $E\left(C,2sp^3\right)=-14.63489\ eV$.

Thus, the sharing of electrons between two $atom\ msp^3$ HOs to form an atom-atom-bond MO permits each participating hybridized orbital to decrease in radius and energy. In order to further satisfy the potential, kinetic, and orbital energy relationships, each $atom\ msp^3$ HO donates an excess of 25% per bond of its electron density to the atom-atom-bond MO to form an energy minimum wherein the atom-atom bond comprises one of a single, double, or triple bond. In each case, the radius of the hybridized shell is calculated from the Coulombic energy equation by considering that the central field decreases by an integer for each successive electron of the shell and the total energy of the shell is equal to the total Coulombic energy of the initial AO electrons plus the hybridization energy. The total energy $E_T\left(mol.atom,msp^3\right)$ ($m$ is the integer of the valence shell) of the HO electrons is given by the sum of energies of successive ions of the atom over the $n$ electrons comprising total electrons of the at least one initial AO shell and the hybridization energy:

$$E_T\left(mol.atom,msp^3\right)=E\left(atom,msp^3\right)-\sum_{m=2}^{n}IP_m \tag{15.17}$$

where $IP_m$ is the $m$ th ionization energy (positive) of the atom and the sum of $-IP_1$ plus the hybridization energy is $E\left(atom,msp^3\right)$. Thus, the radius $r_{msp^3}$ of the hybridized shell due to its donation of a total charge $-Qe$ to the corresponding MO is given by:

$$r_{msp^3}=\left(\sum_{q=Z-n}^{Z-1}(Z-q)-Q\right)\frac{-e^2}{8\pi\varepsilon_0 E_T\left(mol.atom,msp^3\right)}=\left(\sum_{q=Z-n}^{Z-1}(Z-q)-s\left(0.25\right)\right)\frac{-e^2}{8\pi\varepsilon_0 E_T\left(mol.atom,msp^3\right)} \tag{15.18}$$

where $-e$ is the fundamental electron charge and $s=1,2,3$ for a single, double, and triple bond, respectively. The Coulombic energy $E_{Coulomb}\left(mol.atom,msp^3\right)$ of the outer electron of the $atom\ msp^3$ shell is given by:

$$E_{Coulomb}\left(mol.atom,msp^3\right)=\frac{-e^2}{8\pi\varepsilon_0 r_{msp^3}} \tag{15.19}$$

In the case that during hybridization at least one of the spin-paired AO electrons is unpaired in the hybridized orbital (HO), the energy change for the promotion to the unpaired state is the magnetic energy $E(magnetic)$ at the initial radius $r$ of the AO electron given by Eq. (15.15). Then, the energy $E\left(mol.atom,msp^3\right)$ of the outer electron of the $atom\ msp^3$ shell is given by the sum of $E_{Coulomb}\left(mol.atom,msp^3\right)$ and $E(magnetic)$:

$$E\left(mol.atom,msp^3\right)=\frac{-e^2}{8\pi\varepsilon_0 r_{msp^3}}+\frac{2\pi\mu_0 e^2\hbar^2}{m_e^2 r^3} \tag{15.20}$$

$E_T\left(atom-atom,msp^3\right)$, the energy change of each $atom\ msp^3$ shell with the formation of the atom-atom-bond MO is given by: the difference between $E\left(mol.atom,msp^3\right)$ and $E\left(atom,msp^3\right)$:

$$E_T\left(atom-atom,msp^3\right)=E\left(mol.atom,msp^3\right)-E\left(atom,msp^3\right) \tag{15.21}$$

As examples from prior sections, $E_{Coulomb}\left(mol.atom,msp^3\right)$ is one of:

$E_{Coulomb}\left(C_{ethylene},2sp^3\right)$, $E_{Coulomb}\left(C_{ethane},2sp^3\right)$, $E_{Coulomb}\left(C_{acetylene},2sp^3\right)$, and $E_{Coulomb}\left(C_{alkane},2sp^3\right)$;

$E_{Coulomb}\left(atom,msp^3\right)$ is one of $E_{Coulomb}\left(C,2sp^3\right)$ and $E_{Coulomb}\left(Cl,3sp^3\right)$;

$E\left(mol.atom,msp^3\right)$ is one of $E\left(C_{ethylene},2sp^3\right)$, $E\left(C_{ethane},2sp^3\right)$, $E\left(C_{acetylene},2sp^3\right)$ and $E\left(C_{alkane},2sp^3\right)$;

$E\left(atom,msp^3\right)$ is one of $E\left(C,2sp^3\right)$ and $E\left(Cl,3sp^3\right)$;

$E_T\left(atom-atom,msp^3\right)$ is one of $E\left(C-C,2sp^3\right)$, $E\left(C=C,2sp^3\right)$, and $E\left(C\equiv C,2sp^3\right)$;

$atom\ msp^3$ is one of $C2sp^3$, and $Cl3sp^3$

$E_T\left(atom-atom\left(s_1\right),msp^3\right)$ is $E_T\left(C-C,2sp^3\right)$ and $E_T\left(atom-atom\left(s_2\right),msp^3\right)$ is $E_T\left(C=C,2sp^3\right)$, and

$r_{msp^3}$ is one of $r_{C2sp^3}$, $r_{ethane2sp^3}$, $r_{ethylene2sp^3}$, $r_{acetylene2sp^3}$, $r_{alkane2sp^3}$, and $r_{Cl3sp^3}$.

In the case of the $C2sp^3$ HO, the initial parameters (Eqs. (14.142-14.146)) are:

$$r_{2sp^3}=\sum_{n=2}^{5}\frac{(Z-n)e^2}{8\pi\varepsilon_0\left(e148.25751\ eV\right)}=\frac{10e^2}{8\pi\varepsilon_0\left(e148.25751\ eV\right)}=0.91771a_0 \tag{15.22}$$

$$E_{Coulomb}\left(C,2sp^3\right)=\frac{-e^2}{8\pi\varepsilon_0 r_{2sp^3}}=\frac{-e^2}{8\pi\varepsilon_0 0.91771a_0}=-14.82575\ eV \tag{15.23}$$

$$E(magnetic)=\frac{2\pi\mu_0 e^2\hbar^2}{m_e^2\left(r_3\right)^3}=\frac{8\pi\mu_0\mu_B^2}{\left(0.84317a_0\right)^3}=0.19086\ eV \tag{15.24}$$

$$E\left(C,2sp^3\right)=\frac{-e^2}{8\pi\varepsilon_0 r_{2sp^3}}+\frac{2\pi\mu_0 e^2\hbar^2}{m_e^2\left(r_3\right)^3}=-14.82575\ eV+0.19086\ eV=-14.63489\ eV \tag{15.25}$$

In Eq. (15.18),

$$\sum_{q=Z-n}^{Z-1}(Z-q)=10 \tag{15.26}$$

Eqs. (14.147) and (15.17) gives:

$$E_T\left(mol.atom,msp^3\right)=E_T\left(C_{ethane},2sp^3\right)=-151.61569\ eV \tag{15.27}$$

Using Eqs. (15.18-15.28), the final values of $r_{C2sp^3}$, $E_{Coulomb}\left(C2sp^3\right)$, and $E\left(C2sp^3\right)$, and the resulting $E_T\left(\overset{BO}{C-C},C2sp^3\right)$ of the MO due to charge donation from the HO to the MO where $\overset{BO}{C-C}$ refers to the bond order of the carbon-carbon bond for different values of the parameter $s$ are given in Table 15.1.

Table 15.1. The final values of $r_{C2sp^3}$, $E_{Coulomb}(C2sp^3)$, and $E(C2sp^3)$ and the resulting $E_T(C \overset{BO}{-} C, C2sp^3)$ of the MO due to charge donation from the HO to the MO where $C \overset{BO}{-} C$ refers to the bond order of the carbon-carbon bond.

| MO Bond Order (BO) | $s_1$ | $s_2$ | $r_{C2sp^3}(a_0)$ Final | $E_{Coulomb}(C2sp^3)$ (eV) Final | $E(C2sp^3)$ (eV) Final | $E_T\left(C \overset{BO}{-} C, C2sp^3\right)$ (eV) |
|---|---|---|---|---|---|---|
| I | 1 | 0 | 0.87495 | -15.55033 | -15.35946 | -0.72457 |
| II | 2 | 0 | 0.85252 | -15.95955 | -15.76868 | -1.13379 |
| III | 3 | 0 | 0.83008 | -16.39089 | -16.20002 | -1.56513 |
| IV | 4 | 0 | 0.80765 | -16.84619 | -16.65532 | -2.02043 |

In another generalized case of the basis of forming a minimum-energy bond with the constraint that it must meet the energy matching condition for all MOs at all HOs or AOs, the energy $E\left(mol.atom, msp^3\right)$ of the outer electron of the $atom\ msp^3$ shell of each bonding atom must be the average of $E\left(mol.atom, msp^3\right)$ for two different values of $s$:

$$E\left(mol.atom, msp^3\right) = \frac{E\left(mol.atom\left(s_1\right), msp^3\right) + E\left(mol.atom\left(s_2\right), msp^3\right)}{2} \tag{15.28}$$

In this case, $E_T\left(atom - atom, msp^3\right)$, the energy change of each $atom\ msp^3$ shell with the formation of each atom-atom-bond MO, is average for two different values of $s$:

$$E_T\left(atom - atom, msp^3\right) = \frac{E_T\left(atom - atom\left(s_1\right), msp^3\right) + E_T\left(atom - atom\left(s_2\right), msp^3\right)}{2} \tag{15.29}$$

Consider an aromatic molecule such as benzene given in the Benzene Molecule section. Each $C = C$ double bond comprises a linear combination of a factor of $0.75$ of four paired electrons (three electrons) from two sets of two $C2sp^3$ HOs of the participating carbon atoms. Each $C - H$ bond of $CH$ having two spin-paired electrons, one from an initially unpaired electron of the carbon atom and the other from the hydrogen atom, comprises the linear combination of 75% $H_2$-type ellipsoidal MO and 25% $C2sp^3$ HO as given by Eq. (13.439). However, $E_T\left(atom - atom, msp^3\right)$ of the $C - H$-bond MO is given by $0.5E_T\left(C = C, 2sp^3\right)$ (Eq. (14.247)) corresponding to one half of a double bond that matches the condition for a single-bond order for $C - H$ that is lowered in energy due to the aromatic character of the bond.

A further general possibility is that a minimum-energy bond is achieved with satisfaction of the potential, kinetic, and orbital energy relationships by the formation of an MO comprising an allowed multiple of a linear combination of $H_2$-type ellipsoidal MOs and corresponding HOs or AOs that contribute a corresponding allowed multiple (e.g. 0.5, 0.75, 1) of the bond order given in Table 15.1. For example, the alkane MO given in the Continuous-Chain Alkanes section comprises a linear combination of factors of 0.5 of a single bond and 0.5 of a double bond.

Consider a first MO and its HOs comprising a linear combination of bond orders and a second MO that shares a HO with the first. In addition to the mutual HO, the second MO comprises another AO or HO having a single bond order or a mixed bond order. Then, in order for the two MOs to be energy matched, the bond order of the second MO and its HOs or its HO and AO is a linear combination of the terms corresponding to the bond order of the mutual HO and the bond order of the independent HO or AO. Then, in general, $E_T\left(atom - atom, msp^3\right)$, the energy change of each $atom\ msp^3$ shell with the formation of each atom-atom-bond MO, is a weighted linear sum for different values of $s$ that matches the energy of the bonded MOs, HOs, and AOs:

$$E_T\left(atom - atom, msp^3\right) = \sum_{n=1}^{N} c_{s_n} E_T\left(atom - atom\left(s_n\right), msp^3\right) \tag{15.30}$$

where $c_{s_n}$ is the multiple of the BO of $s_n$. The radius $r_{msp^3}$ of the $atom\ msp^3$ shell of each bonding atom is given by the Coulombic energy using the initial energy $E_{Coulomb}\left(atom, msp^3\right)$ and $E_T\left(atom - atom, msp^3\right)$, the energy change of each $atom\ msp^3$ shell with the formation of each atom-atom-bond MO:

$$r_{msp^3} = \frac{-e^2}{8\pi\varepsilon_0 a_0\left(E_{Coulonb}\left(atom, msp^3\right) + E_T\left(atom - atom, msp^3\right)\right)} \tag{15.31}$$

where $E_{Coulomb}\left(C2sp^3\right) = -14.825751\ eV$. The Coulombic energy $E_{Coulomb}\left(mol.atom, msp^3\right)$ of the outer electron of the $atom\ msp^3$ shell is given by Eq. (15.19). In the case that during hybridization, at least one of the spin-paired AO electrons is unpaired in the hybridized orbital (HO), the energy change for the promotion to the unpaired state is the magnetic energy $E(magnetic)$ (Eq. (15.15)) at the initial radius $r$ of the AO electron. Then, the energy $E\left(mol.atom, msp^3\right)$ of the outer electron of the *atom* $msp^3$ shell is given by the sum of $E_{Coulomb}\left(mol.atom,msp^3\right)$ and $E(magnetic)$ (Eq. (15.20)). $E_T\left(atom-atom,msp^3\right)$, the energy change of each *atom* $msp^3$ shell with the formation of the atom-atom-bond MO is given by the difference between $E\left(mol.atom,msp^3\right)$ and $E\left(atom,msp^3\right)$ given by Eq. (15.21). Using Eq. (15.23) for $E_{Coulomb}\left(C,2sp^3\right)$ in Eq. (15.31), the single bond order energies given by Eqs. (15.18-15.27) and shown in Table 15.1, and the linear combination energies (Eqs. (15.28-15.30)), the parameters of linear combinations of bond orders and linear combinations of mixed bond orders are given in Table 15.2.

Table 15.2. The final values of $r_{C2sp^3}$, $E_{Coulomb}(C2sp^3)$, and $E(C2sp^3)$ and the resulting $E_T(\overset{BO}{C-C},C2sp^3)$ of the MO comprising a linear combination of $H_2$-type ellipsoidal MOs and corresponding HOs of single or mixed bond order where $c_{s_n}$ is the multiple of the bond order parameter $E_T(atom-atom\ (s_n),\ msp^3)$ given in Table 15.1.

| MO Bond Order (BO) | $s_1$ | $c_{s_1}$ | $s_2$ | $c_{s_2}$ | $s_3$ | $c_{s_3}$ | $r_{C2sp^3}(a_0)$ Final | $E_{Coulomb}\left(C2sp^3\right)$ (eV) Final | $E\left(C2sp^3\right)$ (eV) Final | $E_T\left(\overset{BO}{C-C},C2sp^3\right)$ (eV) |
|---|---|---|---|---|---|---|---|---|---|---|
| 1/2I | 1 | 0.5 | 0 | 0 | 0 | 0 | 0.89582 | -15.18804 | -14.99717 | -0.36228 |
| 1/2II | 2 | 0.5 | 0 | 0 | 0 | 0 | 0.88392 | -15.39265 | -15.20178 | -0.56689 |
| 1/2I + 1/4II | 1 | 0.5 | 2 | 0.25 | 0 | 0 | 0.87941 | -15.47149 | -15.28062 | -0.64573 |
| 1/4II + 1/4(I + II) | 2 | 0.25 | 1 | 0.25 | 2 | 0.25 | 0.87363 | -15.57379 | -15.38293 | -0.74804 |
| 3/4II | 2 | 0.75 | 0 | 0 | 0 | 0 | 0.86793 | -15.67610 | -15.48523 | -0.85034 |
| 1/2I + 1/2II | 1 | 0.5 | 2 | 0.5 | 0 | 0 | 0.86359 | -15.75493 | -15.56407 | -0.92918 |
| 1/2I + 1/2III | 1 | 0.5 | 3 | 0.5 | 0 | 0 | 0.85193 | -15.97060 | -15.77974 | -1.14485 |
| 1/2I + 1/2IV | 1 | 0.5 | 4 | 0.5 | 0 | 0 | 0.83995 | -16.19826 | -16.00739 | -1.37250 |
| 1/2II + 1/2III | 2 | 0.5 | 3 | 0.5 | 0 | 0 | 0.84115 | -16.17521 | -15.98435 | -1.34946 |
| 1/2II + 1/2IV | 2 | 0.5 | 4 | 0.5 | 0 | 0 | 0.82948 | -16.40286 | -16.21200 | -1.57711 |
| I+1/2(I + II) | 1 | 1 | 1 | 0.5 | 2 | 0.5 | 0.82562 | -16.47951 | -16.28865 | -1.65376 |
| 1/2III + 1/2IV | 3 | 0.5 | 4 | 0.5 | 0 | 0 | 0.81871 | -16.61853 | -16.42767 | -1.79278 |
| 1/2IV + 1/2IV | 4 | 0.5 | 4 | 0.5 | 0 | 0 | 0.80765 | -16.84619 | -16.65532 | -2.02043 |
| 1/2(I + II)+II | 1 | 0.5 | 2 | 0.5 | 2 | 1 | 0.80561 | -16.88873 | -16.69786 | -2.06297 |

Consider next the radius of the AO or HO due to the contribution of charge to more than one bond. The energy contribution due to the charge donation at each atom such as carbon superimposes linearly. In general, the radius $r_{mol2sp^3}$ of the $C2sp^3$ HO of a carbon atom of a given molecule is calculated using Eq. (14.514) by considering $\sum E_{T_{mol}}\left(MO,2sp^3\right)$, the total energy donation to all bonds with which it participates in bonding. The general equation for the radius is given by:

$$r_{mol2sp^3}=\frac{-e^2}{8\pi\varepsilon_0\left(E_{Coulomb}\left(C,2sp^3\right)+\sum E_{T_{mol}}\left(MO,2sp^3\right)\right)}=\frac{e^2}{8\pi\varepsilon_0\left(e14.825751\ eV+\sum\left|E_{T_{mol}}\left(MO,2sp^3\right)\right|\right)} \tag{15.32}$$

The Coulombic energy $E_{Coulomb}\left(mol.atom,msp^3\right)$ of the outer electron of the *atom* $msp^3$ shell is given by Eq. (15.19). In the case that during hybridization, at least one of the spin-paired AO electrons is unpaired in the hybridized orbital (HO), the energy change for the promotion to the unpaired state is the magnetic energy $E(magnetic)$ (Eq. (15.15)) at the initial radius $r$ of the AO electron. Then, the energy $E\left(mol.atom,msp^3\right)$ of the outer electron of the *atom* $msp^3$ shell is given by the sum of $E_{Coulomb}\left(mol.atom,msp^3\right)$ and $E(magnetic)$ (Eq. (15.20)).

For example, the $C2sp^3$ HO of each methyl group of an alkane contributes $-0.92918\ eV$ (Eq. (14.513)) to the corresponding single $C-C$ bond; thus, the corresponding $C2sp^3$ HO radius is given by Eq. (14.514). The $C2sp^3$ HO of each methylene group of $C_nH_{2n+2}$ contributes $-0.92918\ eV$ to each of the two corresponding $C-C$ bond MOs. Thus, the radius (Eq. (15.32)), the Coulombic energy (Eq. (15.19)), and the energy (Eq. (15.20)) of each alkane methylene group are:

$$\begin{aligned} r_{alkaneC_{methylene}2sp^3} &= \frac{-e^2}{8\pi\varepsilon_0\left(E_{Coulomb}\left(C,2sp^3\right)+\sum E_{T_{alkane}}\left(methylene\ C-C,2sp^3\right)\right)} \\ &= \frac{e^2}{8\pi\varepsilon_0\left(e14.825751\ eV+e0.92918\ eV+e0.92918\ eV\right)}=0.81549a_0 \end{aligned} \tag{15.33}$$

$$E_{Coulomb}\left(C_{methylene}2sp^3\right)=\frac{-e^2}{8\pi\varepsilon_0\left(0.81549a_0\right)}=-16.68412\ eV \tag{15.34}$$

$$E\left(C_{methylene}2sp^3\right)=\frac{-e^2}{8\pi\varepsilon_0\left(0.81549a_0\right)}+\frac{2\pi\mu_0e^2\hbar^2}{m_e^2\left(0.84317a_0\right)^3}=-16.49325\ eV \tag{15.35}$$

In the determination of the parameters of functional groups, heteroatoms bonding to $C2sp^3$ HOs to form MOs are energy matched to the $C2sp^3$ HOs. Thus, the radius and the energy parameters of a bonding heteroatom are given by the same equations as those for $C2sp^3$ HOs. Using Eqs. (15.15), (15.19-15.20), (15.24), and (15.32) in a generalized fashion, the final values of the radius of the HO or AO, $r_{Atom.HO.AO}$, $E_{Coulomb}\left(mol.atom,msp^3\right)$, and $E\left(C_{mol}2sp^3\right)$ are calculated using $\sum E_{T_{group}}\left(MO,2sp^3\right)$, the total energy donation to each bond with which an atom participates in bonding corresponding to the values of $E_T\left(\overset{BO}{C-C},C2sp^3\right)$ of the MO due to charge donation from the AO or HO to the MO given in Tables 15.1 and 15.2.

Table 15.3.A. The final values of $r_{Atom.HO.AO}$, $E_{Coulomb}$ $(mol.atom,msp^3)$, and $E(C_{mol}C2sp^3)$ calculated using the values of $E_T(\overset{BO}{C-C},C2sp^3)$ given in Tables 15.1 and 15.2.

| Atom Hybridization Designation | $E_T\left(\overset{BO}{C-C},C2sp^3\right)$ | $E_T\left(\overset{BO}{C-C},C2sp^3\right)$ | $E_T\left(\overset{BO}{C-C},C2sp^3\right)$ | $E_T\left(\overset{BO}{C-C},C2sp^3\right)$ | $E_T\left(\overset{BO}{C-C},C2sp^3\right)$ | $r_{Atom.HO.AO}$ Final $(a_0)$ | $E_{Coulomb}\left(mol.atom,msp^3\right)$ (eV) Final | $E\left(C_{mol}2sp^3\right)$ (eV) Final |
|---|---|---|---|---|---|---|---|---|
| 1 | 0 | 0 | 0 | 0 | 0 | 0.91771 | -14.82575 | -14.63489 |
| 2 | -0.56690 | 0 | 0 | 0 | 0 | 0.88392 | -15.39265 | -15.20178 |
| 3 | -0.72457 | 0 | 0 | 0 | 0 | 0.87495 | -15.55033 | -15.35946 |
| 4 | -0.92918 | 0 | 0 | 0 | 0 | 0.86359 | -15.75493 | -15.56407 |
| 5 | -0.54343 | -0.54343 | 0 | 0 | 0 | 0.85503 | -15.91261 | -15.72175 |
| 6 | -1.13379 | 0 | 0 | 0 | 0 | 0.85252 | -15.95954 | -15.76868 |
| 7 | -0.60631 | -0.60631 | 0 | 0 | 0 | 0.84833 | -16.03838 | -15.84752 |
| 8 | -1.34946 | 0 | 0 | 0 | 0 | 0.84115 | -16.17521 | -15.98435 |
| 9 | -0.46459 | -0.92918 | 0 | 0 | 0 | 0.83885 | -16.21953 | -16.02866 |
| 10 | -0.72457 | -0.72457 | 0 | 0 | 0 | 0.83600 | -16.27490 | -16.08404 |
| 11 | 0 | -0.92918 | -0.56690 | 0 | 0 | 0.83360 | -16.32183 | -16.13097 |
| 12 | -0.92918 | -0.60631 | 0 | 0 | 0 | 0.83159 | -16.36125 | -16.17038 |
| 13 | 0 | -1.13379 | -0.46459 | 0 | 0 | 0.82840 | -16.42413 | -16.23327 |
| 14 | -0.92918 | -0.72457 | 0 | 0 | 0 | 0.82562 | -16.47951 | -16.28864 |
| 15 | -0.85035 | -0.85035 | 0 | 0 | 0 | 0.82327 | -16.52644 | -16.33558 |
| 16 | -0.82688 | 0 | 0 | 0 | 0 | 0.86924 | -16.58181 | -16.39095 |
| 17 | -0.92918 | -0.92918 | 0 | 0 | 0 | 0.81549 | -16.68411 | -16.49325 |
| 18 | -1.13379 | -0.72457 | 0 | 0 | 0 | 0.81549 | -16.68412 | -16.49325 |
| 19 | -0.92918 | -0.56690 | -0.46459 | 0 | 0 | 0.81052 | -16.78642 | -16.59556 |
| 20 | -1.13379 | -0.92918 | 0 | 0 | 0 | 0.80561 | -16.88873 | -16.69786 |
| 21 | -0.85035 | -0.85035 | -0.46459 | 0 | 0 | 0.80076 | -16.99103 | -16.80017 |
| 22 | 0 | -1.34946 | -0.82688 | 0 | 0 | 0.80024 | -17.00209 | -16.81123 |
| 23 | -0.85034 | -0.85034 | -0.56690 | 0 | 0 | 0.79597 | -17.09334 | -16.90247 |
| 24 | -1.13379 | -1.13380 | 0 | 0 | 0 | 0.79597 | -17.09334 | -16.90248 |
| 25 | -1.34946 | -0.92918 | 0 | 0 | 0 | 0.79546 | -17.10440 | -16.91353 |
| 26 | -0.85035 | -0.54343 | 0 | -0.92918 | 0 | 0.79340 | -17.14871 | -16.95785 |
| 27 | -0.85035 | -0.56690 | -0.92918 | 0 | 0 | 0.79232 | -17.17218 | -16.98132 |
| 28 | -0.56690 | -0.92918 | -0.92918 | 0 | 0 | 0.78870 | -17.25101 | -17.06015 |
| 29 | -0.46459 | -1.13380 | -0.92918 | 0 | 0 | 0.78405 | -17.35332 | -17.16246 |
| 30 | -0.54343 | -0.54343 | -0.56690 | -0.92918 | 0 | 0.78155 | -17.40869 | -17.21783 |
| 31 | -0.85034 | -0.28345 | -0.54343 | -0.92918 | 0 | 0.78050 | -17.43216 | -17.24130 |
| 32 | -0.92918 | -0.92918 | -0.92918 | 0 | 0 | 0.77247 | -17.61330 | -17.42243 |
| 33 | -0.85034 | -0.54343 | -0.56690 | -0.92918 | 0 | 0.76801 | -17.71560 | -17.52474 |
| 34 | -0.85034 | -0.54343 | -0.60631 | -0.92918 | 0 | 0.76631 | -17.75502 | -17.56416 |
| 35 | -1.13379 | -0.92918 | -0.92918 | 0 | 0 | 0.76360 | -17.81791 | -17.62704 |
| 36 | -1.13379 | -1.13380 | -0.72457 | 0 | 0 | 0.76360 | -17.81791 | -17.62705 |
| 37 | -0.46459 | -0.85035 | -0.85035 | -0.92918 | 0 | 0.75924 | -17.92022 | -17.72935 |
| 38 | -0.92918 | -1.34946 | -0.82688 | 0 | 0 | 0.75878 | -17.93127 | -17.74041 |
| 39 | -0.85034 | -0.54343 | -0.60631 | -1.13379 | 0 | 0.75758 | -17.95963 | -17.76877 |
| 40 | -1.13380 | -1.13379 | -0.92918 | 0 | 0 | 0.75493 | -18.02252 | -17.83166 |
| 41 | -1.13379 | -1.13379 | -1.13379 | 0 | 0 | 0.74646 | -18.22713 | -18.03627 |

Table 15.3.B. The final values of $r_{Atom.HO.AO}$, $E_{Coulomb}$ ($mol.atom,msp^3$), and $E(C_{mol}C2sp^3)$ calculated for heterocyclic groups using the values of $E_T(C\overset{BO}{-}C,C2sp^3)$ given in Tables 15.1 and 15.2.

| Atom Hybridization Designation | $E_T\left(C\overset{BO}{-}C,C2sp^3\right)$ | $E_T\left(C\overset{BO}{-}C,C2sp^3\right)$ | $E_T\left(C\overset{BO}{-}C,C2sp^3\right)$ | $E_T\left(C\overset{BO}{-}C,C2sp^3\right)$ | $E_T\left(C\overset{BO}{-}C,C2sp^3\right)$ | $r_{Atom.HO.AO}$ Final ($a_0$) | $E_{Coulomb}\left(mol.atom,msp^3\right)$ (eV) Final | $E\left(C_{mol}2sp^3\right)$ (eV) Final |
|---|---|---|---|---|---|---|---|---|
| 1 | 0 | 0 | 0 | 0 | 0 | 0.91771 | -14.82575 | -14.63489 |
| 2 | -0.56690 | 0 | 0 | 0 | 0 | 0.88392 | -15.39265 | -15.20178 |
| 3 | -0.72457 | 0 | 0 | 0 | 0 | 0.87495 | -15.55033 | -15.35946 |
| 4 | -0.92918 | 0 | 0 | 0 | 0 | 0.86359 | -15.75493 | -15.56407 |
| 5 | -0.54343 | -0.54343 | 0 | 0 | 0 | 0.85503 | -15.91261 | -15.72175 |
| 6 | -1.13379 | 0 | 0 | 0 | 0 | 0.85252 | -15.95954 | -15.76868 |
| 7 | -0.60631 | -0.60631 | 0 | 0 | 0 | 0.84833 | -16.03838 | -15.84752 |
| 8 | -1.34946 | 0 | 0 | 0 | 0 | 0.84115 | -16.17521 | -15.98435 |
| 9 | -0.46459 | -0.92918 | 0 | 0 | 0 | 0.83885 | -16.21953 | -16.02866 |
| 10 | -0.72457 | -0.72457 | 0 | 0 | 0 | 0.83600 | -16.27490 | -16.08404 |
| 11 | 0 | -0.92918 | -0.56690 | 0 | 0 | 0.83360 | -16.32183 | -16.13097 |
| 12 | -0.92918 | -0.60631 | 0 | 0 | 0 | 0.83159 | -16.36125 | -16.17038 |
| 13 | 0 | -1.13379 | -0.46459 | 0 | 0 | 0.82840 | -16.42413 | -16.23327 |
| 14 | -0.92918 | -0.72457 | 0 | 0 | 0 | 0.82562 | -16.47951 | -16.28864 |
| 15 | -0.85035 | -0.85035 | 0 | 0 | 0 | 0.82327 | -16.52644 | -16.33558 |
| 16 | -0.82688 | 0 | 0 | 0 | 0 | 0.86924 | -16.58181 | -16.39095 |
| 17 | -0.92918 | -0.92918 | 0 | 0 | 0 | 0.81549 | -16.68411 | -16.49325 |
| 18 | -1.13379 | -0.72457 | 0 | 0 | 0 | 0.81549 | -16.68412 | -16.49325 |
| 19 | -0.92918 | -0.56690 | -0.46459 | 0 | 0 | 0.81052 | -16.78642 | -16.59556 |
| 20 | -1.13379 | -0.92918 | 0 | 0 | 0 | 0.80561 | -16.88873 | -16.69786 |
| 21 | -0.85035 | -0.85035 | -0.46459 | 0 | 0 | 0.80076 | -16.99103 | -16.80017 |
| 22 | 0 | -1.34946 | -0.82688 | 0 | 0 | 0.80024 | -17.00209 | -16.81123 |
| 23 | -0.85034 | -0.85034 | -0.56690 | 0 | 0 | 0.79597 | -17.09334 | -16.90247 |
| 24 | -1.13379 | -1.13380 | 0 | 0 | 0 | 0.79597 | -17.09334 | -16.90248 |
| 25 | -1.34946 | -0.92918 | 0 | 0 | 0 | 0.79546 | -17.10440 | -16.91353 |
| 26 | -0.85035 | -0.54343 | 0 | -0.92918 | 0 | 0.79340 | -17.14871 | -16.95785 |
| 27 | -0.85035 | -0.56690 | -0.92918 | 0 | 0 | 0.79232 | -17.17218 | -16.98132 |
| 28 | -0.56690 | -0.92918 | -0.92918 | 0 | 0 | 0.78870 | -17.25101 | -17.06015 |
| 29 | -0.46459 | -1.13380 | -0.92918 | 0 | 0 | 0.78405 | -17.35332 | -17.16246 |
| 30 | -0.54343 | -0.54343 | -0.56690 | -0.92918 | 0 | 0.78155 | -17.40869 | -17.21783 |
| 31 | -0.85034 | -0.28345 | -0.54343 | -0.92918 | 0 | 0.78050 | -17.43216 | -17.24130 |
| 32 | -0.92918 | -0.92918 | -0.92918 | 0 | 0 | 0.77247 | -17.61330 | -17.42243 |
| 33 | -0.85034 | -0.54343 | -0.56690 | -0.92918 | 0 | 0.76801 | -17.71560 | -17.52474 |
| 34 | -0.85034 | -0.54343 | -0.60631 | -0.92918 | 0 | 0.76631 | -17.75502 | -17.56416 |
| 35 | -1.13379 | -0.92918 | -0.92918 | 0 | 0 | 0.76360 | -17.81791 | -17.62704 |
| 36 | -1.13379 | -1.13380 | -0.72457 | 0 | 0 | 0.76360 | -17.81791 | -17.62705 |
| 37 | -0.46459 | -0.85035 | -0.85035 | -0.92918 | 0 | 0.75924 | -17.92022 | -17.72935 |
| 38 | -0.92918 | -1.34946 | -0.82688 | 0 | 0 | 0.75878 | -17.93127 | -17.74041 |
| 39 | -0.85034 | -0.54343 | -0.60631 | -1.13379 | 0 | 0.75758 | -17.95963 | -17.76877 |
| 40 | -1.13380 | -1.13379 | -0.92918 | 0 | 0 | 0.75493 | -18.02252 | -17.83166 |
| 41 | -1.13379 | -1.13379 | -1.13379 | 0 | 0 | 0.74646 | -18.22713 | -18.03627 |

From Eq. (15.18), the general equation for the radius due to a total charge $-Qe$ of an AO or a HO that participates in bonding to form a MO is given by:

$$r_{msp^3} = \left( \sum_{q=Z-n}^{Z-1} (Z-q) - Q \right) \frac{-e^2}{8\pi\varepsilon_0 E_T\left(mol.atom,msp^3\right)} \tag{15.36}$$

By equating the radii of Eqs. (15.36) and (15.32), the total charge parameter $Q$ of the AO or HO can be calculated wherein the excess charge is on the MO:

$$Q = \left( \sum_{q=Z-n}^{Z-1} (Z-q) \right) - \frac{\left|E_T\left(mol.atom,msp^3\right)\right|}{\left(e14.825751\ eV + \sum\left|E_{T_{mol}}\left(MO,2sp^3\right)\right|\right)} \tag{15.37}$$

The modulation of the constant function by the time and spherically harmonic functions as given in Eq. (1.29) time-averages to zero such that the charge density of any HO or AO is determined by the constant function. The charge density $\sigma$ is then given by the fundamental charge $-e$ times the number of electrons $n$ divided by the area of the spherical shell of radius $r_{mol2sp^3}$ given by Eq. (15.32):

$$\sigma = \frac{(n-Q)(-e)}{\frac{4}{3}\pi r_{mol2sp^3}^2} \tag{15.38}$$

The charge density of an ellipsoidal MO in rectangular coordinates (Eqs. (11.42-11.45)) is:

$$\sigma = \frac{q}{4\pi abc}\frac{1}{\sqrt{\frac{x^2}{a^4}+\frac{y^2}{b^4}+\frac{z^2}{c^4}}} = \frac{q}{4\pi abc}D \tag{15.39}$$

where $D$ is the distance from the origin to the tangent plane. The charge $q$ is given by the fundamental electron charge $-e$ times the sum of parameter $n_1$ of Eqs. (15.51) and (15.61) and the charge donation parameter $Q$ (Eq. (15.37)) of each AO or HO to the MO. Thus, the charge density of the MO is given by:

$$\sigma = \frac{-e\left(n_1 + Q\right)}{4\pi abc}D \tag{15.40}$$

The charge density of the MO that is continuous with the surface of the AO or HO and any radial bisector current resulting from the intersection of two or more MOs as given in the Methane Molecule ($CH_4$) section is determined by the current continuity condition. Consider the continuity of the current due to the intersection of an MO with a corresponding AO or HO. The parameters of each point of intersection of each $H_2$-type ellipsoidal MO and the corresponding atom AO or HO determined from the polar equation of the ellipse are given by Eqs. (15.80-15.87). The overlap charge $\Delta q$ is given by the total charge of the prolate-spheroidal MO minus the integral of the charge density of the MO over the area between curves of intersection with the AOs or HOs that forms the MO:

$$\Delta q = -e\left(n_1 + Q\right) - \int \sigma dA = -e\left(n_1 + Q\right)\left(1 - \int \frac{D}{4\pi abc}dA\right) \tag{15.41}$$

The overlap charge of the prolate-spheroidal MO $\Delta q$ is uniformly distributed on the external spherical surface of the AO or HO of radius $r^3_{mol2sp^3}$ such that the charge density $\sigma$ from Eq. (15.41) is:

$$\sigma = \frac{\Delta q}{A} \tag{15.42}$$

where $A$ is the external surface area of the AO or HO between the curves of intersection with the MO surface.

At the curves of intersection of two or more MOs where they occur, the current between the AO or HO shell and curves of mutual contact is projected onto and flows in the direction of the radial vector to the surface of the AO or HO shell. This current designated the bisector current (BC) meets the AO or HO surface and does not travel to distances shorter than its radius. Due to symmetry, a radial axis through the AO or HO exists such that current travels from the MOs to the AO or HO along the radial vector in one direction and returns to the MO along the radial vector in the opposite direction from the AO or HO surface to conserve current flow. The MO current onto the bisector currents and the connecting current on the external surface of the AO or HO must be continuously maintained. Given the corresponding constant MO $\omega$ (Eq. (11.24)), the continuity condition requires that the charge density on these surfaces times the area ($\propto r^{-2}$) must be a constant corresponding to constant current, and this current must be matched at the inflow from the MO to the inflow bisector current, the HO or AO external surface, the outflow bisector current, and the return current on the opposite surface of the MO. Thus, $\sigma$ on each surface $s$ having charge $\Delta q_s$ is given by Eq. (15.42) wherein $\Delta q = \sum \Delta q_s$ and $\Delta q$ is given by Eq. (15.41) with the integral over the MO area between curves of intersection of the MOs. $A$ is surface area corresponding to each $\Delta q_s$ of the bisector currents and the external surface of the AO or HO between the curves of intersection of the bisector current with the AO or HO surface. Since the potential of an MO is that of a point charge at infinity (Eq. (11.36)), an asymmetry in the distribution of charge between nonequivalent HOs or AOs of the MO occurs to maintain an energy match of the MO with the bridged orbitals. The charge must redistribute between the spherical orbitals to achieve a corresponding current-density that maintains constant current at the equivalent-energy condition according to the energy-matching factor such as $c_2$ or $C_2$ of Eqs. (15.51) and (15.61). Since the orbital energy and radius are reciprocally related, the contribution scales as the square of the ratio (over unity) of the energy of the resultant net positively-charged orbital and the initial matched energy of the resultant net negatively-charged orbital of the bond multiplied by the energy-matching factor (e.g. $c_2$ or $C_2$). The partial charges on the HOs or AOs corresponding to the charge contribution are equivalent to point charges centered on the nuclei. Due to symmetry, the bond moment $\mu$ of each functional group is along the internuclear axis and is calculated from the partial changes at the separation distance, the internuclear distance. The dipole moment of a given molecule is then given by the vector sum of the bond moments in the molecule. Thus, the dipole moment is given by taking into account the magnitude and direction of the bond moment of each functional group wherein the function-group bond moment stays constant from molecule to molecule and is in the vector direction of the internuclear axis as given in the Bonds and Dipole Moments section.

The angles at which any two prolate spheroidal $A-C$ and $B-C$-bond MOs intersect can be determined using Eq. (13.85) by equating the radii of the elliptic cross sections of the MOs:

$$\left(a_1 - c_1'\right)\frac{1+\frac{c_1'}{a_1}}{1+\frac{c_1'}{a_1}\cos\theta_1'} = \left(a_2 - c_2'\right)\frac{1+\frac{c_2'}{a_2}}{1+\frac{c_2'}{a_2}\cos\theta_2'} \tag{15.43}$$

and by using the following relationship between the polar angles $\theta_1'$ and $\theta_2'$:

$$\theta_{\angle ACB} = \theta_1' + \theta_2' - 360^\circ \tag{15.44}$$

where $\theta_{\angle ACB}$ is the bond angle of atoms $A$ and $B$ with central atom $C$. From either angle, the polar radius of intersection can be determined using Eq. (13.85). An example for methane is shown in Eqs. (13.597-13.600). Using these coordinates and the radius of the AO or HO, the limits of the integrals for the determination of the charge densities as well as the regions of each charge density are determined.

The energy of the MO is matched to each of the participating outermost atomic or hybridized orbitals of the bonding atoms wherein the energy match includes the energy contribution due to the AO or HO's donation of charge to the MO. The force constant $k'$ (Eq. (15.1)) is used to determine the ellipsoidal parameter $c'$ (Eq. (15.2)) of each $H_2$-type-ellipsoidal-MO in terms of the central force of the foci. Then, $c'$ is substituted into the energy equation (from Eq. (15.11)) which is set equal to $n_1$ times the total energy of $H_2$ where $n_1$ is the number of equivalent bonds of the MO and the energy of $H_2$, $-31.63536831\ eV$, Eq. (11.212) is the minimum energy possible for a prolate spheroidal MO. From the energy equation and the relationship between the axes, the dimensions of the MO are solved. The energy equation has the semimajor axis $a$ as its only parameter. The solution of the semimajor axis $a$ then allows for the solution of the other axes of each prolate spheroid and eccentricity of each MO (Eqs. (15.3-15.5)). The parameter solutions then allow for the component and total energies of the MO to be determined.

The total energy, $E_T\,(H_2MO)$, is given by the sum of the energy terms (Eqs. (15.6-15.11)) plus $E_T\left(AO/HO\right)$:

$$E_T\,(H_2MO) = V_e + T + V_m + V_p + E_T\left(AO/HO\right) \tag{15.45}$$

$$\begin{aligned} E_T\,(H_2MO) &= -\frac{n_1 e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}}\left[c_1c_2\left(2-\frac{a_0}{a}\right)\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}}-1\right]+E_T\left(AO/HO\right) \\ &= -\frac{n_1 e^2}{8\pi\varepsilon_0 c'}\left[c_1c_2\left(2-\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]+E_T\left(AO/HO\right) \end{aligned} \tag{15.46}$$

where $n_1$ is the number of equivalent bonds of the MO, $c_1$ is the fraction of the $H_2$-type ellipsoidal MO basis function of a chemical bond of the group, $c_2$ is the factor that results in an equipotential energy match of the participating at least two atomic orbitals of each chemical bond, and $E_T\left(AO/HO\right)$ is the total energy comprising the difference of the energy $E\left(AO/HO\right)$ of at least one atomic or hybrid orbital to which the MO is energy matched and any energy component $\Delta E_{H_2MO}\left(AO/HO\right)$ due to the AO or HO's charge donation to the MO.

$$E_T\left(AO/HO\right) = E\left(AO/HO\right) - \Delta E_{H_2MO}\left(AO/HO\right) \tag{15.47}$$

As specific examples given in previous sections, $E_T\left(AO/HO\right)$ is one from the group of:

$E_T\left(AO/HO\right) = E\left(O2p\ shell\right) = -E(ionization;\ O) = -13.6181\ eV$;

$E_T\left(AO/HO\right) = E\left(N2p\ shell\right) = -E(ionization;\ N) = -14.53414\ eV$;

$E_T\left(AO/HO\right) = E\left(C,2sp^3\right) = -14.63489\ eV$;

$E_T\left(AO/HO\right) = E_{Coulomb}\left(Cl,3sp^3\right) = -14.60295\ eV$;

$E_T\left(AO/HO\right) = E(ionization;\ C) + E(ionization;\ C^+)$;

$E_T\left(AO/HO\right) = E\left(C_{ethane},2sp^3\right) = -15.35946\ eV$;

$E_T\left(AO/HO\right) = E\left(C_{ethylene},2sp^3\right) - E\left(C_{ethylene},2sp^3\right)$;

$E_T\left(AO/HO\right) = E\left(C,2sp^3\right) - 2E_T\left(C=C,2sp^3\right) = -14.63489\ eV - \left(-2.26758\ eV\right)$;

$E_T\left(AO/HO\right) = E\left(C_{acetylene},2sp^3\right) - E\left(C_{acetylene},2sp^3\right) - E\left(C_{acetylene},2sp^3\right) = 16.20002\ eV$;

$E_T\left(AO/HO\right) = E\left(C,2sp^3\right) - 2E_T\left(C\equiv C,2sp^3\right) = -14.63489\ eV - \left(-3.13026\ eV\right)$;

$E_T\left(AO/HO\right) = E\left(C_{benzene},2sp^3\right) - E\left(C_{benzene},2sp^3\right)$;

$E_T\left(AO/HO\right) = E\left(C,2sp^3\right) - E_T\left(C=C,2sp^3\right) = -14.63489\ eV - \left(-1.13379\ eV\right)$, and

$E_T\left(AO/HO\right) = E\left(C_{alkane},2sp^3\right) = -15.56407\ eV$.

To solve the bond parameters and energies, $c' = a\sqrt{\frac{\hbar^2 4\pi\varepsilon_0}{m_e e^2 2C_1C_2 a}} = \sqrt{\frac{aa_0}{2C_1C_2}}$ (Eq. (15.2)) is substituted into $E_T\,(H_2MO)$ to: give

$$
\begin{aligned}
E_T(H_2MO) &= -\frac{n_1 e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}}\left[c_1c_2\left(2-\frac{a_0}{a}\right)\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}}-1\right]+E_T\left(AO/HO\right)\\
&= -\frac{n_1 e^2}{8\pi\varepsilon_0 c'}\left[c_1c_2\left(2-\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]+E_T\left(AO/HO\right)\\
&= -\frac{n_1 e^2}{8\pi\varepsilon_0\sqrt{\frac{aa_0}{2C_1C_2}}}\left[c_1c_2\left(2-\frac{a_0}{a}\right)\ln\frac{a+\sqrt{\frac{aa_0}{2C_1C_2}}}{a-\sqrt{\frac{aa_0}{2C_1C_2}}}-1\right]+E_T\left(AO/HO\right)
\end{aligned}
\tag{15.48}
$$

The total energy is set equal to $E(basis\ energies)$ which in the most general case is given by the sum of a first integer $n_1$ times the total energy of $H_2$ minus a second integer $n_2$ times the total energy of $H$, minus a third integer $n_3$ times the valence energy of $E(AO)$ (e.g. $E(N) = -14.53414\ eV$) where the first integer can be $1,2,3...$, and each of the second and third integers can be $0,1,2,3...$.

$$E(basis\ energies) = n_1\left(-31.63536831\ eV\right) - n_2\left(-13.605804\ eV\right) - n_3 E\left(AO\right) \tag{15.49}$$

In the case that the MO bonds two atoms other than hydrogen, $E(basis\ energies)$ is $n_1$ times the total energy of $H_2$ where $n_1$ is the number of equivalent bonds of the MO and the energy of $H_2$, $-31.63536831\ eV$, Eq. (11.212) is the minimum energy possible for a prolate spheroidal MO:

$$E(basis\ energies) = n_1\left(-31.63536831\ eV\right) \tag{15.50}$$

$E_T(H_2MO)$, is set equal to $E(basis\ energies)$, and the semimajor axis $a$ is solved. Thus, the semimajor axis $a$ is solved from the equation of the form:

$$-\frac{n_1 e^2}{8\pi\varepsilon_0\sqrt{\frac{aa_0}{2C_1C_2}}}\left[c_1c_2\left(2-\frac{a_0}{a}\right)\ln\frac{a+\sqrt{\frac{aa_0}{2C_1C_2}}}{a-\sqrt{\frac{aa_0}{2C_1C_2}}}-1\right]+E_T\left(AO/HO\right) = E(basis\ energies) \tag{15.51}$$

The distance from the origin of the $H_2$-type-ellipsoidal-MO to each focus $c'$, the internuclear distance $2c'$, and the length of the semiminor axis of the prolate spheroidal $H_2$-type MO $b = c$ are solved from the semimajor axis $a$ using Eqs. (15.2-15.4). Then, the component energies are given by Eqs. (15.6-15.9) and (15.48).

The total energy of the MO of the functional group, $E_T(MO)$, is the sum of the total energy of the components comprising the energy contribution of the MO formed between the participating atoms and $E_T\left(atom-atom, msp^3.AO\right)$, the change in the energy of the AOs or HOs upon forming the bond. From Eqs. (15.48-15.49), $E_T(MO)$ is:

$$E_T(MO) = E(basis\ energies) + E_T\left(atom-atom, msp^3.AO\right) \tag{15.52}$$

During bond formation, the electrons undergo a reentrant oscillatory orbit with vibration of the nuclei, and the corresponding energy $\bar{E}_{osc}$ is the sum of the Doppler, $\bar{E}_D$, and average vibrational kinetic energies, $\bar{E}_{Kvib}$:

$$\bar{E}_{osc} = n_1\left(\bar{E}_D + \bar{E}_{Kvib}\right) = n_1\left(E_{h\nu}\sqrt{\frac{2\bar{E}_K}{m_e c^2}} + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right) \tag{15.53}$$

where $n_1$ is the number of equivalent bonds of the MO, $k$ is the spring constant of the equivalent harmonic oscillator, and $\mu$ is the reduced mass. The angular frequency of the reentrant oscillation in the transition state corresponding to $\bar{E}_D$ is determined by the force between the central field and the electrons in the transition state. The force and its derivative are given by:

$$f(R) = -c_{BO}\frac{C_{1o}C_{2o}e^2}{4\pi\varepsilon_0 R^3} \tag{15.54}$$

and

$$f'(a) = 2c_{BO}\frac{C_{1o}C_{2o}e^2}{4\pi\varepsilon_0 R^3} \tag{15.55}$$

such that the angular frequency of the oscillation in the transition state is given by:

$$\omega = \sqrt{\frac{\left[\frac{-3}{a}f(a) - f'(a)\right]}{m_e}} = \sqrt{\frac{k}{m_e}} = \sqrt{\frac{c_{BO}\frac{C_{1o}C_{2o}e^2}{4\pi\varepsilon_0 R^3}}{m_e}} \tag{15.56}$$

where $R$ is the semimajor axis $a$ or the semiminor axis $b$ depending on the eccentricity of the bond that is most representative of the oscillation in the transition state, $c_{BO}$ is the bond-order factor which is 1 for a single bond and when the MO comprises $n_1$ equivalent single bonds as in the case of functional groups. $c_{BO}$ is 4 for an independent double bond as in the case of the $CO_2$ and $NO_2$ molecules and 9 for an independent triple bond. $C_{1o}$ is the fraction of the $H_2$-type ellipsoidal MO basis function of the oscillatory transition state of a chemical bond of the group, and $C_{2o}$ is the factor that results in an equipotential energy match of the participating at least two atomic orbitals of the transition state of the chemical bond. Typically, $C_{1o} = C_1$ and $C_{2o} = C_2$. The kinetic energy, $E_K$, corresponding to $\overline{E}_D$ is given by Planck's equation for functional groups:

$$\overline{E}_K = \hbar\omega = \hbar\sqrt{\frac{\frac{C_{1o}C_{2o}e^2}{4\pi\varepsilon_0 R^3}}{m_e}} \tag{15.57}$$

The Doppler energy of the electrons of the reentrant orbit is:

$$\overline{E}_D \cong E_{h\nu}\sqrt{\frac{2\overline{E}_K}{m_e c^2}} = E_{h\nu}\sqrt{\frac{2\hbar\sqrt{\frac{\frac{C_{1o}C_{2o}e^2}{4\pi\varepsilon_0 R^3}}{m_e}}}{m_e c^2}} \tag{15.58}$$

$\overline{E}_{osc}$ given by the sum of $\overline{E}_D$ and $\overline{E}_{Kvib}$ is:

$$\overline{E}_{osc}\left(group\right) = n_1\left(\overline{E}_D + \overline{E}_{Kvib}\right) = n_1\left(E_{h\nu}\sqrt{\frac{2\hbar\sqrt{\frac{\frac{C_{1o}C_{2o}e^2}{4\pi\varepsilon_0 R^3}}{m_e}}}{m_e c^2}} + E_{vib}\right) \tag{15.59}$$

$E_{h\nu}$ of a group having $n_1$ bonds is given by $E_T\left(MO\right)/n_1$ such that:

$$\overline{E}_{osc} = n_1\left(\overline{E}_D + \overline{E}_{Kvib}\right) = n_1\left(E_T\left(MO\right)/n_1\sqrt{\frac{2\overline{E}_K}{Mc^2}} + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right) \tag{15.60}$$

$E_{T+osc}\left(Group\right)$ is given by the sum of $E_T\left(MO\right)$ (Eq. (15.51)) and $\overline{E}_{osc}$ (Eq. (15.60)).

$$\begin{aligned} E_{T+osc}\left(Group\right) = E_T\left(MO\right) + \overline{E}_{osc} &= \left(\begin{array}{l}\left(\begin{array}{l} -\frac{n_1 e^2}{8\pi\varepsilon_0\sqrt{\frac{aa_0}{2C_1C_2}}}\left[c_1c_2\left(2-\frac{a_0}{a}\right)\ln\frac{a+\sqrt{\frac{aa_0}{2C_1C_2}}}{a-\sqrt{\frac{aa_0}{2C_1C_2}}} - 1\right] \\ +E_T\left(AO/HO\right) + E_T\left(atom-atom, msp^3.AO\right)\end{array}\right) \\ \left[1+\sqrt{\frac{2\hbar\sqrt{\frac{\frac{C_{1o}C_{2o}e^2}{4\pi\varepsilon_0 R^3}}{m_e}}}{m_e c^2}}\right] + n_1\frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\end{array}\right) \\ &= \left(E(basis\ energies) + E_T\left(atom-atom, msp^3.AO\right)\right)\left[1+\sqrt{\frac{2\hbar\sqrt{\frac{\frac{C_{1o}C_{2o}e^2}{4\pi\varepsilon_0 R^3}}{m_e}}}{m_e c^2}}\right] + n_1\frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \end{aligned} \tag{15.61}$$

The total energy of the functional group $E_T\left(group\right)$ is the sum of the total energy of the components comprising the energy contribution of the MO formed between the participating atoms, $E(basis\ energies)$, the change in the energy of the AOs or HOs upon forming the bond ($E_T\left(atom-atom, msp^3.AO\right)$), the energy of oscillation in the transition state, and the change in magnetic energy with bond formation, $E_{mag}$. From Eq. (15.61), the total energy of the group $E_T\left(Group\right)$ is:

$$E_T\left(Group\right)=\left(\begin{array}{l}\left(E(basis\ energies)+E_T\left(atom-atom,msp^3.AO\right)\right)\left[1+\sqrt{\dfrac{2\hbar\sqrt{\dfrac{\dfrac{C_{1o}C_{2o}e^2}{4\pi\varepsilon_0R^3}}{m_e}}}{m_ec^2}}\right]\\+n_1\overline{E}_{Kvib}+E_{mag}\end{array}\right) \tag{15.62}$$

The change in magnetic energy $E_{mag}$ which arises due to the formation of unpaired electrons in the corresponding fragments relative to the bonded group is given by:

$$E_{mag}=c_3\frac{2\pi\mu_0e^2\hbar^2}{m_e^2r^3}=c_3\frac{8\pi\mu_0\mu_B^2}{r^3} \tag{15.63}$$

where $r$ is the radius of the atom that reacts to form the bond and $c_3$ is the number of electron pairs.

$$E_T\left(Group\right)=\left(\begin{array}{l}\left(E(basis\ energies)+E_T\left(atom-atom,msp^3.AO\right)\right)\left[1+\sqrt{\dfrac{2\hbar\sqrt{\dfrac{\dfrac{C_{1o}C_{2o}e^2}{4\pi\varepsilon_0R^3}}{m_e}}}{m_ec^2}}\right]\\+n_1\overline{E}_{Kvib}+c_3\dfrac{8\pi\mu_0\mu_B^2}{r^3}\end{array}\right) \tag{15.64}$$

The total bond energy of the group $E_D\left(Group\right)$ is the negative difference of the total energy of the group (Eq. (15.64)) and the total energy of the two starting orbitals given by the sum of $c_4E_{initial}\left(c_4\ AO/HO\right)$ and $c_5E_{initial}\left(c_5\ AO/HO\right)$:

$$E_D\left(Group\right)=-\left(\begin{array}{l}\left(E(basis\ energies)+E_T\left(atom-atom,msp^3.AO\right)\right)\left[1+\sqrt{\dfrac{2\hbar\sqrt{\dfrac{\dfrac{C_{1o}C_{2o}e^2}{4\pi\varepsilon_0R^3}}{m_e}}}{m_ec^2}}\right]\\+n_1\overline{E}_{Kvib}+c_3\dfrac{8\pi\mu_0\mu_B^2}{r^3}-\left(c_4E_{initial}\left(c_4AO/HO\right)+c_5E_{initial}\left(c_5\ AO/HO\right)\right)\end{array}\right) \tag{15.65}$$

In the case of organic molecules, the atoms of the functional groups are energy matched to the $C2sp^3$ HO such that:

$$E\left(AO/HO\right)=-14.63489\ eV \tag{15.66}$$

For examples of $E_{mag}$ from previous sections:

$$E_{mag}\left(C2sp^3\right)=c_3\frac{8\pi\mu_0\mu_B^2}{r^3}=c_3\frac{8\pi\mu_0\mu_B^2}{\left(0.91771a_0\right)^3}=c_30.14803\ eV \tag{15.67}$$

$$E_{mag}\left(O2p\right)=c_3\frac{8\pi\mu_0\mu_B^2}{r^3}=c_3\frac{8\pi\mu_0\mu_B^2}{a_0^3}=c_30.11441\ eV \tag{15.68}$$

$$E_{mag}\left(N2p\right)=c_3\frac{8\pi\mu_0\mu_B^2}{r^3}=c_3\frac{8\pi\mu_0\mu_B^2}{\left(0.93084a_0\right)^3}=c_30.14185\ eV \tag{15.69}$$

In the general case of the solution of an organic functional group, the geometric bond parameters are solved from the semimajor axis and the relationships between the parameters by first using Eq. (15.51) to arrive at $a$. Then, the remaining parameters are determined using Eqs. (15.1-15.5). Next, the energies are given by Eqs. (15.61-15.68). To meet the equipotential condition for the union of the $H_2$-type-ellipsoidal-MO and the HO or AO of the atom of a functional group, the factor $c_2$ of a $H_2$-type ellipsoidal MO in principal Eqs. (15.51) and (15.61) may given by:

**(i)** one:

$$c_2=1 \tag{15.70}$$

**(ii)** the ratio that is less than one of 13.605804 $eV$, the magnitude of the Coulombic energy between the electron and proton of $H$ given by Eq. (1.264), and the magnitude of the Coulombic energy of the participating AO or HO of the atom, $E_{Coulomb}\left(MO.atom,msp^3\right)$ given by Eqs. (15.19) and (15.31-15.32). For $\left|E_{Coulomb}\left(MO.atom,msp^3\right)\right|>13.605804\ eV$:

$$c_2 = \frac{\frac{e^2}{8\pi\varepsilon_0 a_0}}{\frac{e^2}{8\pi\varepsilon_0 r_{A-B\ AorBsp^3}}} = \frac{13.605804\ eV}{\left|E_{Coulomb}\left(MO.atom, msp^3\right)\right|} \tag{15.71}$$

For $\left|E_{Coulomb}\left(MO.atom, msp^3\right)\right| < 13.605804\ eV$:

$$c_2 = \frac{\frac{e^2}{8\pi\varepsilon_0 r_{A-B\ AorBsp^3}}}{\frac{e^2}{8\pi\varepsilon_0 a_0}} = \frac{\left|E_{Coulomb}\left(MO.atom, msp^3\right)\right|}{13.605804\ eV} \tag{15.72}$$

**(iii)** the ratio that is less than one of 13.605804 $eV$, the magnitude of the Coulombic energy between the electron and proton of $H$ given by Eq. (1.264), and the magnitude of the valence energy, $E(valence)$, of the participating AO or HO of the atom where $E(valence)$ is the ionization energy or $E\left(MO.atom, msp^3\right)$ given by Eqs. (15.20) and (15.31-15.32). For $\left|E(valence)\right| > 13.605804\ eV$:

$$c_2 = \frac{\frac{e^2}{8\pi\varepsilon_0 a_0}}{\frac{e^2}{8\pi\varepsilon_0 r_{A-B\ AorBsp^3}}} = \frac{13.605804\ eV}{\left|E(valence)\right|} \tag{15.73}$$

For $\left|E(valence)\right| < 13.605804\ eV$:

$$c_2 = \frac{\frac{e^2}{8\pi\varepsilon_0 r_{A-B\ AorBsp^3}}}{\frac{e^2}{8\pi\varepsilon_0 a_0}} = \frac{\left|E(valence)\right|}{13.605804\ eV} \tag{15.74}$$

**(iv)** the ratio that is less than one of the magnitude of the Coulombic energy of the participating AO or HO of a first atom, $E_{Coulomb}\left(MO.atom, msp^3\right)$ given by Eqs. (15.19) and (15.31-15.32), and the magnitude of the valence energy, $E(valence)$, of the participating AO or HO of a second atom to which the first is energy matched where $E(valence)$ is the ionization energy or $E\left(MO.atom, msp^3\right)$ given by Eqs. (15.20) and (15.31-15.32). For $\left|E_{Coulomb}\left(MO.atom, msp^3\right)\right| > E(valence)$:

$$c_2 = \frac{\left|E(valence)\right|}{\left|E_{Coulomb}\left(MO.atom, msp^3\right)\right|} \tag{15.75}$$

For $\left|E_{Coulomb}\left(MO.atom, msp^3\right)\right| < E(valence)$:

$$c_2 = \frac{\left|E_{Coulomb}\left(MO.atom, msp^3\right)\right|}{\left|E(valence)\right|} \tag{15.76}$$

**(v)** the ratio of the magnitude of the valence-level energies, $E_n(valence)$, of the AO or HO of the nth participating atom of two that are energy matched where $E(valence)$ is the ionization energy or $E\left(MO.atom, msp^3\right)$ given by Eqs. (15.20) and (15.31-15.32):

$$c_2 = \frac{E_1(valence)}{E_2(valence)} \tag{15.77}$$

**(vi)** the factor that is the ratio of the hybridization factor $c_2(1)$ of the valence AO or HO of a first atom and the hybridization factor $c_2(2)$ of the valence AO or HO of a second atom to which the first is energy matched where $c_2(n)$ is given by Eqs. (15.71-15.77); alternatively $c_2$ is the hybridization factor $c_2(1)$ of the valence AOs or HOs a first pair of atoms and the hybridization factor $c_2(2)$ of the valence AO or HO a third atom or second pair to which the first two are energy matched:

$$c_2 = \frac{c_2(1)}{c_2(2)} \tag{15.78}$$

**(vii)** the factor that is the product of the hybridization factor $c_2(1)$ of the valence AO or HO of a first atom and the hybridization factor $c_2(2)$ of the valence AO or HO of a second atom to which the first is energy matched where $c_2(n)$ is given by Eqs. (15.71-15.78); alternatively $c_2$ is the hybridization factor $c_2(1)$ of the valence AOs or HOs a first pair of atoms and the hybridization factor $c_2(2)$ of the valence AO or HO a third atom or second pair to which the first two are energy matched:

$$c_2 = c_2(1)c_2(2) \tag{15.79}$$

The hybridization factor $c_2$ corresponds to the force constant $k$ (Eqs. (11.65) and (13.58)). In the case that the valence or Coulombic energy of the AO or HO is less than $13.605804\ eV$, the magnitude of the Coulombic energy between the electron and proton of $H$ given by Eq. (1.264), then $C_2$ corresponding to $k'$ (Eq. (15.1)) is given by Eqs. (15.71-15.79).

Specific examples of the factors $c_2$ and $C_2$ of a $H_2$-type ellipsoidal MO of Eq. (15.60) given in following sections are:

$$c_2(C2sp^3HO\ to\ F) = \frac{E(C,2sp^3)}{E(F)}c_2(C2sp^3HO) = \frac{-14.63489\ eV}{-17.42282\ eV}(0.91771) = 0.77087;$$

$$C_2(C2sp^3HO\ to\ Cl) = \frac{E(Cl)}{E(C,2sp^3)}c_2(C2sp^3HO) = \frac{-12.96764\ eV}{-14.63489\ eV}(0.91771) = 0.81317;$$

$$C_2(C2sp^3HO\ to\ Br) = \frac{E(Br)}{E(C,2sp^3)}c_2(C2sp^3HO) = \frac{-11.81381\ eV}{-14.63489\ eV}(0.91771) = 0.74081;$$

$$C_2(C2sp^3HO\ to\ I) = \frac{E(I)}{E(C,2sp^3)}c_2(C2sp^3HO) = \frac{-10.45126\ eV}{-14.63489\ eV}(0.91771) = 0.65537;$$

$$c_2(C2sp^3HO\ to\ O) = \frac{E(O)}{E(C,2sp^3)}c_2(C2sp^3HO) = \frac{-13.61806\ eV}{-14.63489\ eV}(0.91771) = 0.85395;$$

$$c_2(H\ to\ 1°N) = \frac{E(N)}{E(C,2sp^3)} = \frac{-14.53414\ eV}{-15.35946\ eV} = 0.94627;$$

$$c_2(C2sp^3HO\ to\ N) = \frac{E(N)}{E(C,2sp^3)}c_2(C2sp^3HO) = \frac{-14.53414\ eV}{-14.63489\ eV}(0.91771) = 0.91140;$$

$$c_2(H\ to\ 2°N) = \frac{E(N)}{E(C,2sp^3)} = \frac{-14.53414\ eV}{-15.56407\ eV} = 0.93383;$$

$$C_2(S3p\ to\ H) = \frac{E(S,3p)}{E(H)} = \frac{-10.36001\ eV}{-13.60580\ eV} = 0.76144;$$

$$C_2(C2sp^3HO\ to\ \mathrm{S}) = \frac{E(S)}{E(C,2sp^3)}c_2(C2sp^3HO) = \frac{-10.36001\ eV}{-14.63489\ eV}(0.91771) = 0.64965;$$

$$c_2(O\ to\ S3sp^3\ to\ C2sp^3HO) = \frac{E(O)}{E(S)}c_2(C2sp^3HO) = \frac{-13.61806\ eV}{-10.36001\ eV}(0.91771) = 1.20632;$$

$$c_2(S3sp^3) = \frac{E_{Coulomb}(S3sp^3)}{E(H)} = \frac{-11.57099\ eV}{-13.60580\ eV} = 0.85045;$$

$$C_2(C2sp^3HO\ to\ S3sp^3) = \frac{E(S3sp^3)}{E(C,2sp^3)}c_2(S3sp^3) = \frac{-11.52126\ eV}{-14.63489\ eV}(0.85045) = 0.66951;$$

$$C_2(S3sp^3\ to\ O\ to\ C2sp^3HO) = \frac{E(S,3sp^3)}{E(O,2p)}c_2(C2sp^3HO) = \frac{-11.52126\ eV}{-13.61806\ eV}(0.91771) = 0.77641;$$

$$c_2(O\ to\ N2p\ to\ C2sp^3HO) = \frac{E(O)}{E(N)}c_2(C2sp^3HO) = \frac{-13.61806\ eV}{-14.53414\ eV}(0.91771) = 0.85987;$$

$$c_2\left(N2p\ to\ O2p\right)=\frac{c_2\left(C2sp^3HO\ to\ N\right)}{c_2\left(C2sp^3HO\ to\ O\right)}=\frac{0.91140}{0.85395}=1.06727\ \mathbf{;}$$

$$C_2\left(benzeneC2sp^3HO\right)=c_2\left(benzeneC2sp^3HO\right)=\frac{13.605804\ eV}{15.95955\ eV}=0.85252\ \mathbf{;}$$

$$c_2\left(arylC2sp^3HO\ to\ O\right)=\frac{E(O)}{E\left(C,2sp^3\right)}c_2\left(arylC2sp^3HO\right)=\frac{-13.61806\ eV}{-14.63489\ eV}\left(0.85252\right)=0.79329\ \mathbf{;}$$

$$c_2\left(H\ to\ aniline\ N\right)=\frac{E(N)}{E\left(C,2sp^3\right)}=\frac{-14.53414\ eV}{-15.76868\ eV}=0.92171;$$

$$c_2\left(arylC2sp^3HO\ to\ N\right)=\frac{E(N)}{E\left(C,2sp^3\right)}c_2\left(arylC2sp^3HO\right)=\frac{-14.53414\ eV}{-14.63489\ eV}\left(0.85252\right)=0.84665,\text{ and}$$

$$C_2\left(S3p\ to\ aryl\text{-}type\ C2sp^3HO\right)=\frac{E\left(S,3p\right)}{E\left(C,2sp^3\right)}=\frac{-10.36001\ eV}{-15.76868\ eV}=0.65700.$$

## MO INTERCEPT ANGLES AND DISTANCES

Consider the general case of Eqs. (13.84-13.95), wherein the nucleus of a $B$ atom and the nucleus of a $A$ atom comprise the foci of each $H_2$-type ellipsoidal MO of an $A-B$ bond. The parameters of the point of intersection of each $H_2$-type ellipsoidal MO and the $A$-atom AO are determined from the polar equation of the ellipse:

$$r=r_0\frac{1+e}{1+e\cos\theta'} \tag{15.80}$$

The radius of the $A$ shell is $r_A$, and the polar radial coordinate of the ellipse and the radius of the $A$ shell are equal at the point of intersection such that:

$$r_A=\left(a-c'\right)\frac{1+\frac{c'}{a}}{1+\frac{c'}{a}\cos\theta'} \tag{15.81}$$

The polar angle $\theta'$ at the intersection point is given by:

$$\theta'=\cos^{-1}\left(\frac{a}{c'}\left(\left(a-c'\right)\frac{1+\frac{c'}{a}}{r_A}-1\right)\right) \tag{15.82}$$

Then, the angle $\theta_{A\,AO}$ the radial vector of the $A$ AO makes with the internuclear axis is:

$$\theta_{A\,AO}=180°-\theta' \tag{15.83}$$

The Cartesian $\mathbf{i}$-coordinate of the interception point of the MO and the AO can be calculated using the MO ellipsoidal parameters by first calculating the parametric angle in Eq. (11.83) that matches Cartesian $\mathbf{j}$-coordinate components at the point of intersection. Thus, the matching elliptic parametric angle $\omega t=\theta_{H_2MO}$ satisfies the following relationship:

$$r_A\sin\theta_{A\,AO}=b\sin\theta_{H_2MO} \tag{15.84}$$

such that

$$\theta_{H_2MO}=\sin^{-1}\frac{r_a\sin\theta_{A\,AO}}{b} \tag{15.85}$$

The distance $d_{H_2MO}$ along the internuclear axis from the origin of $H_2$-type ellipsoidal MO to the point of intersection of the orbitals is given by:

$$d_{H_2MO}=a\cos\theta_{H_2MO} \tag{15.86}$$

The distance $d_{A\,AO}$ along the internuclear axis from the origin of the $A$ atom to the point of intersection of the orbitals is given by:

$$d_{A\,AO}=c'-d_{H_2MO} \tag{15.87}$$

## BOND ANGLES

Further consider an $ACB$ MO comprising a linear combination of $C-A$-bond and $C-B$-bond MOs where $C$ is the general central atom. A bond is also possible between the $A$ and $B$ atoms of the $C-A$ and $C-B$ bonds. Such $A-B$ bonding would decrease the $C-A$ and $C-B$ bond strengths since electron density would be shifted from the latter bonds to the former bond. Thus, the $\angle ACB$ bond angle is determined by the condition that the total energy of the $H_2$-type ellipsoidal MO between the terminal $A$ and $B$ atoms is zero. The force constant $k'$ of a $H_2$-type ellipsoidal MO due to the equivalent of two point charges at the foci is given by:

$$k' = \frac{C_1 C_2 2e^2}{4\pi\varepsilon_0} \tag{15.88}$$

where $C_1$ is the fraction of the $H_2$-type ellipsoidal MO basis function of a chemical bond of the molecule which is 0.75 (Eq. (13.59)) for a terminal $A-H$ ($A$ is $H$ or other atom) and 1 otherwise and $C_2$ is the factor that results in an equipotential energy match of the participating at least two atomic orbitals of the chemical bond and is equal to the corresponding factor of Eqs. (15.51) and (15.61). The distance from the origin of the MO to each focus $c'$ of the $A-B$ ellipsoidal MO is given by:

$$c' = a\sqrt{\frac{\hbar^2 4\pi\varepsilon_0}{m_e e^2 2C_1 C_2 a}} = \sqrt{\frac{aa_0}{2C_1 C_2}} \tag{15.89}$$

The internuclear distance is:

$$2c' = 2\sqrt{\frac{aa_0}{2C_1 C_2}} \tag{15.90}$$

The length of the semiminor axis of the prolate spheroidal $A-B$ MO $b = c$ is given by Eq. (15.4).

The component energies and the total energy, $E_T(H_2MO)$, of the $A-B$ bond are given by the energy equations (Eqs. (11.207-11.212), (11.213-11.217), and (11.239)) of $H_2$ except that the terms based on charge are multiplied by $c_{BO}$, the bond-order factor which is 1 for a single bond and when the MO comprises $n_1$ equivalent single bonds as in the case of functional groups. $c_{BO}$ is 4 for an independent double bond as in the case of the $CO_2$ and $NO_2$ molecules. The kinetic energy term is multiplied by $c'_{BO}$ which is 1 for a single bond, 2 for a double bond, and 9/2 for a triple bond. The electron energy terms are multiplied by $c_1$, the fraction of the $H_2$-type ellipsoidal MO basis function of a terminal chemical bond, which is 0.75 (Eq. (13.233)) for a terminal $A-H$ ($A$ is $H$ or other atom) and 1 otherwise. The electron energy terms are further multiplied by $c_2'$, the hybridization or energy-matching factor that results in an equipotential energy match of the participating at least two atomic orbitals of each terminal bond. Furthermore, when $A-B$ comprises atoms other than $H$, $E_T\left(atom-atom, msp^3.AO\right)$, the energy component due to the AO or HO's charge donation to the terminal MO, is added to the other energy terms to give $E_T(H_2MO)$:

$$E_T(H_2MO) = \frac{-e^2}{8\pi\varepsilon_0 c'}\left[c_1 c_2'\left(2c_{BO} - c'_{BO}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'} - 1\right] + E_T\left(atom-atom, msp^3.AO\right) \tag{15.91}$$

The radiation reaction force in the case of the vibration of $A-B$ in the transition state corresponds to the Doppler energy, $E_D$, given by Eq. (11.181) that is dependent on the motion of the electrons and the nuclei. The total energy that includes the radiation reaction of the $A-B$ MO is given by the sum of $E_T(H_2MO)$ (Eq. (15.91)) and $\overline{E}_{osc}$ given by Eqs. (11.213-11.220), (11.231-11.236), and (11.239-11.240). Thus, the total energy $E_T\left(A-B\right)$ of the $A-B$ MO including the Doppler term is:

$$E_T\left(A-B\right) = \left[\begin{array}{l} \left(\dfrac{-e^2}{8\pi\varepsilon_0 c'}\left[c_1 c_2'\left(2c_{BO} - c'_{BO}\dfrac{a_0}{a}\right)\ln\dfrac{a+c'}{a-c'} - 1\right] + E_T\left(atom-atom, msp^3.AO\right)\right) \\ \left[1 + \sqrt{\dfrac{2\hbar\sqrt{\dfrac{c_{BO}\dfrac{C_{1o}C_{2o}e^2}{4\pi\varepsilon_0 a^3}}{m_e}}}{m_e c^2}}\right] + \dfrac{1}{2}\hbar\sqrt{\dfrac{c_{BO}\dfrac{c_1 c_2' e^2}{8\pi\varepsilon_0 a^3} - \dfrac{c_{BO}e^2}{8\pi\varepsilon_0\left(a+c'\right)^3}}{\mu}} \end{array}\right] \tag{15.92}$$

where $C_{1o}$ is the fraction of the $H_2$-type ellipsoidal MO basis function of the oscillatory transition state of the $A-B$ bond which is 0.75 (Eq. (13.233)) in the case of $H$ bonding to a central atom and 1 otherwise, $C_{2o}$ is the factor that results in an equipotential energy match of the participating at least two atomic orbitals of the transition state of the chemical bond, and $\mu = \frac{m_1 m_2}{m_1 + m_2}$ is the reduced mass of the nuclei given by Eq. (11.154). To match the boundary condition that the total energy of the $A-B$ ellipsoidal MO is zero, $E_T\left(A-B\right)$ given by Eq. (15.92) is set equal to zero. Substitution of Eq. (15.90) into Eq. (15.92) gives:

$$0=\left[\begin{array}{c}\left(\dfrac{-e^2}{8\pi\varepsilon_0\sqrt{\dfrac{aa_0}{2C_1C_2}}}\left[c_1c_2'\left(2c_{BO}-c'_{BO}\dfrac{a_0}{a}\right)\ln\dfrac{a+\sqrt{\dfrac{aa_0}{2C_1C_2}}}{a-\sqrt{\dfrac{aa_0}{2C_1C_2}}}-1\right]+E_T\left(atom-atom,msp^3.AO\right)\right)\\ \left[1+\sqrt{\dfrac{2\hbar\sqrt{\dfrac{c_{BO}\dfrac{C_{1o}C_{2o}e^2}{4\pi\varepsilon_0a^3}}{m_e}}}{m_ec^2}}\right]+\dfrac{1}{2}\hbar\sqrt{\dfrac{c_{BO}\dfrac{c_1c_2'e^2}{8\pi\varepsilon_0a^3}-\dfrac{c_{BO}e^2}{8\pi\varepsilon_0\left(a+\sqrt{\dfrac{aa_0}{2C_1C_2}}\right)^3}}{\mu}}\end{array}\right] \tag{15.93}$$

The vibrational energy-term of Eq. (15.93) is determined by the forces between the central field and the electrons and those between the nuclei (Eqs. (11.141-11.145)). The electron-central-field force and its derivative are given by:

$$f\left(a\right)=-c_{BO}\frac{c_1c_2'e^2}{4\pi\varepsilon_0a^3} \tag{15.94}$$

and

$$f'\left(a\right)=2c_{BO}\frac{c_1c_2'e^2}{4\pi\varepsilon_0a^3} \tag{15.95}$$

The nuclear repulsion force and its derivative are given by:

$$f\left(a+c'\right)=\frac{e^2}{8\pi\varepsilon_0\left(a+c'\right)^2} \tag{15.96}$$

and

$$f'\left(a+c'\right)=-\frac{e^2}{4\pi\varepsilon_0\left(a+c'\right)^3} \tag{15.97}$$

such that the angular frequency of the oscillation is given by:

$$\omega=\sqrt{\frac{\left[\dfrac{-3}{a}f\left(a\right)-f'\left(a\right)\right]}{\mu}}=\sqrt{\frac{k}{m_e}}=\sqrt{\frac{c_{BO}\dfrac{c_1c_2'e^2}{4\pi\varepsilon_0a^3}-\dfrac{e^2}{8\pi\varepsilon_0\left(a+c'\right)^2}}{\mu}} \tag{15.98}$$

Since both terms of $\overline{E}_{osc}=\overline{E}_D+\overline{E}_{Kvib}$ are small due to the large values of $a$ and $c'$, to very good approximation, a convenient form of Eq. (15.93) which is evaluated to determine the bond angles of functional groups is given by:

$$0=\left[\begin{array}{c}\left(\dfrac{-e^2}{8\pi\varepsilon_0\sqrt{\dfrac{aa_0}{2C_1C_2}}}\left[c_1c_2'\left(2-\dfrac{a_0}{a}\right)\ln\dfrac{a+\sqrt{\dfrac{aa_0}{2C_1C_2}}}{a-\sqrt{\dfrac{aa_0}{2C_1C_2}}}-1\right]+E_T\left(atom-atom,msp^3.AO\right)\right)\\ \left[1+\sqrt{\dfrac{2\hbar\sqrt{\dfrac{\dfrac{c_1e^2}{4\pi\varepsilon_0a^3}}{m_e}}}{m_ec^2}}\right]+\dfrac{1}{2}\hbar\sqrt{\dfrac{\dfrac{c_1e^2}{8\pi\varepsilon_0a^3}-\dfrac{e^2}{8\pi\varepsilon_0\left(a+\sqrt{\dfrac{aa_0}{2C_1C_2}}\right)^3}}{\mu}}\end{array}\right] \tag{15.99}$$

From the energy relationship given by Eq. (15.99) and the relationship between the axes given by Eqs. (15.2-15.5), the dimensions of the $A-B$ MO can be solved. The most convenient way to solve Eq. (15.99) is by the reiterative technique using a computer.

A factor $c_2$ of a given atom in the determination of $c_2'$ for calculating the zero of the total $A-B$ bond energy is typically given by Eqs. (15.71-15.74). In the case of a $H-H$ terminal bond of an alkyl or alkenyl group, $c_2'$ is typically the ratio of $c_2$ of Eq. (15.71) for the $H-H$ bond which is one and $c_2$ of the carbon of the corresponding $C-H$ bond:

$$c_2'=\frac{1}{c_2(C2sp^3)}=\frac{E_{Coulomb}\left(C-H\ C2sp^3\right)}{13.605804\ eV} \tag{15.100}$$

In the case of the determination of the bond angle of the $ACH$ MO comprising a linear combination of $C-A$-bond and $C-H$-bond MOs where $A$ and $C$ are general, $C$ is the central atom, and $c_2$ for an atom is given by Eqs. (15.71-15.79), $c_2'$ of the

$A-H$ terminal bond is typically the ratio of $c_2$ of the $A$ atom for the $A-H$ terminal bond and $c_2$ of the $C$ atom of the corresponding $C-H$ bond:

$$c_2' = \frac{c_2(A(A-H)msp^3)}{c_2(C(C-H)msp^3)} \tag{15.101}$$

In the case of the determination of the bond angle of the $COH$ MO of an alcohol comprising a linear combination of $C-O$-bond and $O-H$-bond MOs where $C$, $O$, and $H$ are carbon, oxygen, and hydrogen, respectively, $c_2'$ of the $C-H$ terminal bond is typically $0.91771$ since the oxygen and hydrogen atoms are at the Coulomb potential of a proton and an electron (Eqs. (1.257) and (10.162), respectively) that is energy matched to the $C2sp^3$ HO.

In the determination of the hybridization factor $c_2'$ of Eq. (15.99) from Eqs. (15.71-15.79), the Coulombic energy, $E_{Coulomb}\left(MO.atom,msp^3\right)$, or the energy, $E\left(MO.atom,msp^3\right)$, the radius $r_{A-B\ AorBsp^3}$ of the $A$ or $B$ AO or HO of the heteroatom of the $A-B$ terminal bond MO such as the $C2sp^3$ HO of a terminal $C-C$ bond is calculated using Eq. (15.32) by considering $\sum E_{T_{mol}}\left(MO,2sp^3\right)$, the total energy donation to each bond with which it participates in bonding as it forms the terminal bond. The Coulombic energy $E_{Coulomb}\left(MO.atom,msp^3\right)$ of the outer electron of the $atom\ msp^3$ shell is given by Eq. (15.19). In the case that during hybridization, at least one of the spin-paired AO electrons is unpaired in the hybridized orbital (HO), the energy change for the promotion to the unpaired state is the magnetic energy $E(magnetic)$ (Eq. (15.15)) at the initial radius $r$ of the AO electron. Then, the energy $E\left(MO.atom,msp^3\right)$ of the outer electron of the $atom\ msp^3$ shell is given by the sum of $E_{Coulomb}\left(MO.atom,msp^3\right)$ and $E(magnetic)$ (Eq. (15.20)).

In the specific case of the terminal bonding of two carbon atoms, the $c_2$ factor of each carbon given by Eq. (15.71) is determined using the Coulombic energy $E_{Coulomb}\left(C-C\ C2sp^3\right)$ of the outer electron of the $C2sp^3$ shell given by Eq. (15.19) with the radius $r_{C-C\ C2sp^3}$ of each $C2sp^3$ HO of the terminal $C-C$ bond calculated using Eq. (15.32) by considering $\sum E_{T_{mol}}\left(MO,2sp^3\right)$, the total energy donation to each bond with which it participates in bonding as it forms the terminal bond including the contribution of the methylene energy, $0.92918\ eV$ (Eq. (14.513)), corresponding to the terminal $C-C$ bond. The corresponding $E_T\left(atom-atom,msp^3.AO\right)$ in Eq. (15.99) is $E_T\left(C-C\ C2sp^3\right) = -1.85836\ eV$.

In the case that the terminal atoms are carbon or other heteroatoms, the terminal bond comprises a linear combination of the HOs or AOs; thus, $c_2'$ is the average of the hybridization factors of the participating atoms corresponding to the normalized linear sum:

$$c_2' = \frac{1}{2}\left(c_2'\left(atom\ 1\right) + c_2'\left(atom\ 2\right)\right) \tag{15.102}$$

In the exemplary cases of $C-C$, $O-O$, and $N-N$ where $C$ is carbon:

$$\begin{aligned} c_2' &= \frac{1}{2}\left( \frac{\dfrac{e^2}{8\pi\varepsilon_0 a_0}}{\dfrac{e^2}{8\pi\varepsilon_0 r_{A-A\ A_1AO/HO}}} + \frac{\dfrac{e^2}{8\pi\varepsilon_0 a_0}}{\dfrac{e^2}{8\pi\varepsilon_0 r_{A-A\ \mathrm{A}_2AO/HO}}} \right) \\ &= \frac{1}{2}\left( \frac{13.605804\ eV}{E_{Coulomb}\left(A-A.A_1AO/HO\right)} + \frac{13.605804\ eV}{E_{Coulomb}\left(A-A.A_2AO/HO\right)} \right) \end{aligned} \tag{15.103}$$

In the exemplary cases of $C-N$, $C-O$, and $C-S$,

$$c_2' = \frac{1}{2}\left( \frac{13.605804\ eV}{E_{Coulomb}\left(C-B\ C2sp^3\right)} + c_2\left(C\ to\ B\right) \right) \tag{15.104}$$

where $C$ is carbon and $c_2\left(C\ to\ B\right)$ is the hybridization factor of Eqs. (15.61) and (15.93) that matches the energy of the atom $B$ to that of the atom $C$ in the group. For these cases, the corresponding $E_T\left(atom-atom,msp^3.AO\right)$ term in Eq. (15.99) depends on the hybridization and bond order of the terminal atoms in the molecule, but typical values matching those used in the determination of the bond energies (Eq. (15.65)) are:

$E_T\left(C-O\ C2sp^3.O2p\right) = -1.44915\ eV$; $E_T\left(C-O\ C2sp^3.O2p\right) = -1.65376\ eV$; $E_T\left(C-N\ C2sp^3.N2p\right) = -1.44915\ eV$;
$E_T\left(C-S\ C2sp^3.S2p\right) = -0.72457\ eV$; $E_T\left(O-O\ O2p.O2p\right) = -1.44915\ eV$; $E_T\left(O-O\ O2p.O2p\right) = -1.65376\ eV$;
$E_T\left(N-N\ N2p.N2p\right) = -1.44915\ eV$; $E_T\left(N-O\ N2p.O2p\right) = -1.44915\ eV$; $E_T\left(F-F\ F2p.F2p\right) = -1.44915\ eV$;
$E_T\left(Cl-Cl\ Cl3p.Cl3p\right) = -0.92918\ eV$; $E_T\left(Br-Br\ Br4p.Br4p\right) = -0.92918\ eV$; $E_T\left(I-I\ I5p.I5p\right) = -0.36229\ eV$;

$E_T\left(C-F\ C2sp^3.F2p\right)=-1.85836\ eV$; $E_T\left(C-Cl\ C2sp^3.Cl3p\right)=-0.92918\ eV$; $E_T\left(C-Br\ C2sp^3.Br4p\right)=-0.72457\ eV$; $E_T\left(C-I\ C2sp^3.I5p\right)=-0.36228\ eV$, and $E_T\left(O-Cl\ O2p.Cl3p\right)=-0.92918\ eV$.

In the case that the terminal bond is $X-X$ where $X$ is a halogen atom, $c_1$ is one, and $c_2'$ is the average (Eq. (15.102)) of the hybridization factors of the participating halogen atoms given by Eqs. (15.71-15.72) where $E_{Coulomb}\left(MO.atom,msp^3\right)$ is determined using Eq. (15.32) and $E_{Coulomb}\left(MO.atom,msp^3\right)=13.605804\ eV$ for $X=I$. The factor $C_1$ of Eq. (15.99) is one for all halogen atoms. The factor $C_2$ of fluorine is one since it is the only halogen wherein the ionization energy is greater than $13.605804\ eV$, the magnitude of the Coulombic energy between the electron and proton of $H$ given by Eq. (1.264). For each of the other halogens, $Cl$, $Br$, and $I$, $C_2$ is the hybridization factor of Eq. (15.61) given by Eq. (15.79) with $c_2(1)$ being that of the halogen given by Eq. (15.77) that matches the valence energy of $X$ ($E_1(valence)$) to that of the $C2sp^3$ HO ($E_2(valence)=-14.63489\ eV$, Eq. (15.25)) and to the hybridization of $C2sp^3$ HO ($c_2(2)=0.91771$, Eq. (13.430)). $E_T\left(atom-atom,msp^3.AO\right)$ of Eq. (15.99) is the maximum for the participating atoms which is $-1.44915\ eV$, $-0.92918\ eV$, $-0.92918\ eV$, and $-0.33582\ eV$ for $F$, $Cl$, $Br$, and $I$, respectively.

Consider the case that the terminal bond is $C-X$ where $C$ is a carbon atom and $X$ is a halogen atom. The factors $c_1$ and $C_1$ of Eq. (15.99) are one for all halogen atoms. For $X=F$, $c_2'$ is the average (Eq. (15.104)) of the hybridization factors of the participating carbon and $F$ atoms where $c_2$ for carbon is given by Eq. (15.71) and $c_2$ for fluorine matched to carbon is given by Eq. (15.79) with $c_2(1)$ for the fluorine atom given by Eq. (15.77) that matches the valence energy of $F$ ($E_1(valence)=-17.42282\ eV$) to that of the $C2sp^3$ HO ($E_2(valence)=-14.63489\ eV$, Eq. (15.25)) and to the hybridization of $C2sp^3$ HO ($c_2(2)=0.91771$, Eq. (13.430)). The factor $C_2$ of fluorine is one since it is the only halogen wherein the ionization energy is greater than $13.605804\ eV$, the magnitude of the Coulombic energy between the electron and proton of $H$ given by Eq. (1.264). For each of the other halogens, $Cl$, $Br$, and $I$, $c_2'$ is the hybridization factor of the participating carbon atom since the halogen atom is energy matched to the carbon atom. $C_2$ of the terminal-atom bond matches that used to determine the energies of the corresponding $C-X$-bond MO. Then, $C_2$ is the hybridization factor of Eq. (15.61) given by Eq. (15.79) with $c_2(1)$ for the halogen atom given by Eq. (15.77) that matches the valence energy of $X$ ($E_1(valence)$) to that of the $C2sp^3$ HO ($E_2(valence)=-14.63489\ eV$, Eq. (15.25)) and to the hybridization of $C2sp^3$ HO ($c_2(2)=0.91771$, Eq. (13.430)). $E_T\left(atom-atom,msp^3.AO\right)$ of Eq. (15.99) is the maximum for the participating atoms which is $-1.85836\ eV$, $-0.92918\ eV$, $-0.72457\ eV$, and $-0.33582\ eV$ for $F$, $Cl$, $Br$, and $I$, respectively.

Consider the case that the terminal bond is $H-X$ corresponding to the angle of the atoms $HCX$ where $C$ is a carbon atom and $X$ is a halogen atom. The factors $c_1$ and $C_1$ of Eq. (15.99) are 0.75 for all halogen atoms. For $X=F$, $c_2'$ is given by Eq. (15.78) with $c_2$ of the participating carbon and $F$ atoms given by Eq. (15.71) and Eq. (15.74), respectively. The factor $C_2$ of fluorine is one since it is the only halogen wherein the ionization energy is greater than $13.605804\ eV$, the magnitude of the Coulombic energy between the electron and proton of $H$ given by Eq. (1.264). For each of the other halogens, $Cl$, $Br$, and $I$, $c_2'$ is also given by Eq. (15.78) with $c_2$ of the participating carbon given by Eq. (15.71) and $c_2$ of the participating $X$ atom given by $c_2=0.91771$ (Eq. (13.430)) since the $X$ atom is energy matched to the $C2sp^3$ HO. In these cases, $C_2$ is given by Eq. (15.74) for the corresponding atom $X$ where $C_2$ matches the energy of the atom $X$ to that of $H$.

Using the distance between the two atoms $A$ and $B$ of the general molecular group $ACB$ when the total energy of the corresponding $A-B$ MO is zero, the corresponding bond angle can be determined from the law of cosines:

$$s_1^{\ 2}+s_2^{\ 2}-2s_1s_2\text{cosine}\theta=s_3^{\ 2} \tag{15.105}$$

With $s_1=2c_{C-A}'$, the internuclear distance of the $C-A$ bond, $s_2=2c_{C-B}'$, the internuclear distance of each $C-B$ bond, and $s_3=2c'_{A-B}$, the internuclear distance of the two terminal atoms, the bond angle $\theta_{\angle ACB}$ between the $C-A$ and $C-B$ bonds is given by:

$$\left(2c'_{C-A}\right)^2+\left(2c'_{C-B}\right)^2-2\left(2c'_{C-A}\right)\left(2c'_{C-B}\right)\text{cosine}\theta=\left(2c'_{A-B}\right)^2 \tag{15.106}$$

$$\theta_{\angle ACB}=\cos^{-1}\left(\frac{\left(2c'_{C-A}\right)^2+\left(2c'_{C-B}\right)^2-\left(2c'_{A-B}\right)^2}{2\left(2c'_{C-A}\right)\left(2c'_{C-B}\right)}\right) \tag{15.107}$$

Consider the exemplary structure $C_bC_a(O_a)O_b$ wherein $C_a$ is bound to $C_b$, $O_a$, and $O_b$. In the general case that the three bonds are coplanar and two of the angles are known, say $\theta_1$ and $\theta_2$, then the third $\theta_3$ can be determined geometrically:

$$\theta_3 = 360 - \theta_1 - \theta_2 \tag{15.108}$$

In the general case that two of the three coplanar bonds are equivalent and one of the angles is known, say $\theta_1$, then the second and third can be determined geometrically:

$$\theta_2 = \theta_3 = \frac{(360 - \theta_1)}{2} \tag{15.109}$$

## ANGLES AND DISTANCES FOR AN MO THAT FORMS AN ISOSCELES TRIANGLE

In the general case where the group comprises three $A-B$ bonds having $B$ as the central atom at the apex of a pyramidal structure formed by the three bonds with the $A$ atoms at the base in the xy-plane, the $C_{3v}$ axis centered on $B$ is defined as the vertical or z-axis, and any two $A-B$ bonds form an isosceles triangle. Then, the angle of the bonds and the distances from and along the z-axis are determined from the geometrical relationships given by Eqs. (13.412-13.416).

the distance $d_{origin-B}$ from the origin to the nucleus of a terminal $B$ atom is given by

$$d_{origin-B} = \frac{2c'_{B-B}}{2\sin 60°} \tag{15.110}$$

the height along the z-axis from the origin to the $A$ nucleus $d_{height}$ is given by:

$$d_{height} = \sqrt{(2c'_{A-B})^2 - (d_{origin-B})^2}\text{, and} \tag{15.111}$$

the angle $\theta_v$ of each $A-B$ bond from the z-axis is given by:

$$\theta_v = \tan^{-1}\left(\frac{d_{origin-B}}{d_{height}}\right) \tag{15.112}$$

Consider the case where the central atom $B$ is further bound to a fourth atom $C$ and the $B-C$ bond is along the z-axis. Then, the bond $\theta_{\angle ABC}$ given by Eq. (14.206) is:

$$\theta_{\angle ABC} = 180 - \theta_v \tag{15.113}$$

## DIHEDRAL ANGLE

Consider the plane defined by a general $ACA$ MO comprising a linear combination of two $C-A$-bond MOs where $C$ is the central atom. The dihedral angle $\theta_{\angle BC/ACA}$ between the $ACA$-plane and a line defined by a third bond with $C$, specifically that corresponding to a $C-B$-bond MO, is calculated from the bond angle $\theta_{\angle ACA}$ and the distances between the $A$, $B$, and $C$ atoms. The distance $d_1$ along the bisector of $\theta_{\angle ACA}$ from $C$ to the internuclear-distance line between $A$ and $A$, $2c'_{A-A}$, is given by:

$$d_1 = 2c'_{C-A}\cos\frac{\theta_{\angle ACA}}{2} \tag{15.114}$$

where $2c'_{C-A}$ is the internuclear distance between $A$ and $C$. The atoms $A$, $A$, and $B$ define the base of a pyramid. Then, the pyramidal angle $\theta_{\angle ABA}$ can be solved from the internuclear distances between $A$ and $A$, $2c'_{A-A}$, and between $A$ and $B$, $2c'_{A-B}$, using the law of cosines (Eq. (15.107)):

$$\theta_{\angle ABA} = \cos^{-1}\left(\frac{(2c'_{A-B})^2 + (2c'_{A-B})^2 - (2c'_{A-A})^2}{2(2c'_{A-B})(2c'_{A-B})}\right) \tag{15.115}$$

Then, the distance $d_2$ along the bisector of $\theta_{\angle ABA}$ from $B$ to the internuclear-distance line $2c'_{A-A}$, is given by:

$$d_2 = 2c'_{A-B}\cos\frac{\theta_{\angle ABA}}{2} \tag{15.116}$$

The lengths $d_1$, $d_2$, and $2c'_{C-B}$ define a triangle wherein the angle between $d_1$ and the internuclear distance between $B$ and $C$, $2c'_{C-B}$, is the dihedral angle $\theta_{\angle BC/ACA}$ that can be solved using the law of cosines (Eq. (15.107)):

$$\theta_{\angle BC/ACA} = \cos^{-1}\left(\frac{d_1^2 + (2c'_{C-B})^2 - d_2^2}{2d_1(2c'_{C-B})}\right) \tag{15.117}$$

## GENERAL DIHEDRAL ANGLE

Consider the plane defined by a general $ACB$ MO comprising a linear combination of $C-A$ and $C-B$-bond MOs where $C$ is the central atom. The dihedral angle $\theta_{\angle CD/ACB}$ between the $ACB$-plane and a line defined by a third bond of $C$ with $D$, specifically that corresponding to a $C-D$-bond MO, is calculated from the bond angle $\theta_{\angle ACB}$ and the distances between the $A$, $B$, $C$, and $D$ atoms. The distance $d_1$ from $C$ to the bisector of the internuclear-distance line between $A$ and $B$, $2c'_{A-B}$, is given by two equations involving the law of cosines (Eq. (15.105)). One with $s_1 = 2c'_{C-A}$, the internuclear distance of the $C-A$ bond, $s_2 = d_1$, $s_3 = \frac{2c'_{A-B}}{2}$, half the internuclear distance between $A$ and $B$, and $\theta = \theta_{\angle ACd_1}$, the angle between $d_1$ and the $C-A$ bond is given by:

$$\left(2c'_{C-A}\right)^2 + \left(d_1\right)^2 - 2\left(2c'_{C-A}\right)\left(d_1\right)\text{cosine}\theta_{\angle ACd_1} = \left(\frac{2c'_{A-B}}{2}\right)^2 \tag{15.118}$$

The other with $s_1 = 2c'_{C-B}$, the internuclear distance of the $C-B$ bond, $s_2 = d_1$, $s_3 = \frac{2c'_{A-B}}{2}$, and $\theta = \theta_{\angle ACB} - \theta_{\angle ACd_1}$ where $\theta_{\angle ACB}$ is the bond angle between the $C-A$ and $C-B$ bonds is given by:

$$\left(2c'_{C-B}\right)^2 + \left(d_1\right)^2 - 2\left(2c'_{C-B}\right)\left(d_1\right)\text{cosine}\left(\theta_{\angle ACB} - \theta_{\angle ACd_1}\right) = \left(\frac{2c'_{A-B}}{2}\right)^2 \tag{15.119}$$

Subtraction of Eq. (15.119) from Eq. (15.118) gives:

$$d_1 = \frac{\left(2c'_{C-A}\right)^2 - \left(2c'_{C-B}\right)^2}{2\left(\left(2c'_{C-A}\right)\text{cosine}\theta_{\angle ACd_1} - \left(2c'_{C-B}\right)\text{cosine}\left(\theta_{\angle ACB} - \theta_{\angle ACd_1}\right)\right)} \tag{15.120}$$

Substitution of Eq. (15.120) into Eq. (15.118) gives

$$\left(\begin{array}{l} \left(2c'_{C-A}\right)^2 + \left(\dfrac{\left(2c'_{C-A}\right)^2 - \left(2c'_{C-B}\right)^2}{2\left(\left(2c'_{C-A}\right)\text{cosine}\theta_{\angle ACd_1} - \left(2c'_{C-B}\right)\text{cosine}\left(\theta_{\angle ACB} - \theta_{\angle ACd_1}\right)\right)}\right)^2 \\ -2\left(2c'_{C-A}\right)\left(\dfrac{\left(2c'_{C-A}\right)^2 - \left(2c'_{C-B}\right)^2}{2\left(\left(2c'_{C-A}\right)\text{cosine}\theta_{\angle ACd_1} - \left(2c'_{C-B}\right)\text{cosine}\left(\theta_{\angle ACB} - \theta_{\angle ACd_1}\right)\right)}\right)\text{cosine}\theta_{\angle ACd_1} \\ -\left(\dfrac{2c'_{A-B}}{2}\right)^2 \end{array}\right) = 0 \tag{15.121}$$

The angle between $d_1$ and the $C-A$ bond, $\theta_{\angle ACd_1}$, can be solved reiteratively using Eq. (15.121), and the result can be substituted into Eq. (15.120) to give $d_1$.

The atoms $A$, $B$, and $D$ define the base of a pyramid. Then, the pyramidal angle $\theta_{\angle ADB}$ can be solved from the internuclear distances between $A$ and $D$, $2c'_{A-D}$, between $B$ and $D$, $2c'_{B-D}$, and between $A$ and $B$, $2c'_{A-B}$, using the law of cosines (Eq. (15.107)):

$$\theta_{\angle ADB} = \cos^{-1}\left(\frac{\left(2c'_{A-D}\right)^2 + \left(2c'_{B-D}\right)^2 - \left(2c'_{A-B}\right)^2}{2\left(2c'_{A-D}\right)\left(2c'_{B-D}\right)}\right) \tag{15.122}$$

Then, the distance $d_2$ from $D$ to the bisector of the internuclear-distance line between $A$ and $B$, $2c'_{A-B}$, is given by two equations involving the law of cosines (Eq. (15.105)). One with $s_1 = 2c'_{A-D}$, the internuclear distance between $A$ and $D$, $s_2 = d_2$, $s_3 = \frac{2c'_{A-B}}{2}$, half the internuclear distance between $A$ and $B$, and $\theta = \theta_{\angle ADd_2}$, the angle between $d_2$ and the $A-D$ axis is given by:

$$\left(2c'_{A-D}\right)^2 + \left(d_2\right)^2 - 2\left(2c'_{A-D}\right)\left(d_2\right)\text{cosine}\theta_{\angle ADd_2} = \left(\frac{2c'_{A-B}}{2}\right)^2 \tag{15.123}$$

The other with $s_1 = 2c'_{B-D}$, the internuclear distance between $B$ and $D$, $s_2 = d_2$, and $\theta = \theta_{\angle ADB} - \theta_{\angle ADd_2}$ where $\theta_{\angle ADB}$ is the bond angle between the $A-D$ and $B-D$ axes is given by:

$$\left(2c'_{B-D}\right)^2 + \left(d_2\right)^2 - 2\left(2c'_{B-D}\right)\left(d_2\right)\text{cosine}\left(\theta_{\angle ADB} - \theta_{\angle ADd_2}\right) = \left(\frac{2c'_{A-B}}{2}\right)^2 \tag{15.124}$$

Subtraction of Eq. (15.124) from Eq. (15.123) gives:

$$d_2 = \frac{\left(2c'_{A-D}\right)^2 - \left(2c'_{B-D}\right)^2}{2\left(\left(2c'_{A-D}\right)\text{cosine}\theta_{\angle ADd_2} - \left(2c'_{B-D}\right)\text{cosine}\left(\theta_{\angle ADB} - \theta_{\angle ADd2}\right)\right)} \tag{15.125}$$

Substitution of Eq. (15.125) into Eq. (15.123) gives:

$$\begin{pmatrix} (2c'_{A-D})^2 + \left( \dfrac{(2c'_{A-D})^2 - (2c'_{B-D})^2}{2\left((2c'_{A-D})\text{cosine}\theta_{\angle ADd_2} - (2c'_{B-D})\text{cosine}\left(\theta_{\angle ADB} - \theta_{\angle ADd_2}\right)\right)} \right)^2 \\ -2(2c'_{A-D}) \left( \dfrac{(2c'_{A-D})^2 - (2c'_{B-D})^2}{2\left((2c'_{A-D})\text{cosine}\theta_{\angle ADd_2} - (2c'_{B-D})\text{cosine}\left(\theta_{\angle ADB} - \theta_{\angle ADd_2}\right)\right)} \right) \text{cosine}\theta_{\angle ADd_2} \\ -\left( \dfrac{2c'_{A-B}}{2} \right)^2 \end{pmatrix} = 0 \tag{15.126}$$

The angle between $d_2$ and the $A-D$ axis, $\theta_{\angle ADd_2}$, can be solved reiteratively using Eq. (15.126), and the result can be substituted into Eq. (15.125) to give $d_2$.

The lengths $d_1$, $d_2$, and $2c'_{C-B}$ define a triangle wherein the angle between $d_1$ and the internuclear distance between $C$ and $D$, $2c'_{C-D}$, is the dihedral angle $\theta_{\angle CD/ACB}$ that can be solved using the law of cosines (Eq. (15.107)):

$$\theta_{\angle CD/ACB} = \cos^{-1}\left( \frac{d_1^2 + (2c'_{C-D})^2 - d_2^2}{2d_1(2c'_{C-D})} \right) \tag{15.127}$$

# SOLUTION OF GEOMETRICAL AND ENERGY PARAMETERS OF MAJOR FUNCTIONAL GROUPS AND CORRESPONDING ORGANIC MOLECULES

The exemplary molecules given in the following sections were solved using the solutions of organic chemical functional groups as basis elements wherein the structures and energies where linearly added to achieve the molecular solutions. Each functional group can be treated as a building block to form any desired molecular solution from the corresponding linear combination. Each functional group element was solved using the atomic orbital and hybrid orbital spherical atomic orbital solutions bridged by molecular orbitals comprised of the $H_2$-type prolate spheroidal solution given in the Nature of the Chemical Bond of Hydrogen-Type Molecules section. The energy of each MO was matched at the HO or AO by matching the hybridization and total energy of the MO to the AOs and HOs. The energy $E_{mag}$ (e.g. given by Eq. (15.67) for a $C2sp^3$ HO and Eq. (15.68) for an $O2p$ AO) was subtracted for each set of unpaired electrons created by bond breakage.

The bond energy is not equal to the component energy of each bond as it exists in the molecule, although, they are close. The total energy of each group is its contribution to the total energy of the molecule as a whole. The determination of the bond energies for the creation of the separate parts must take into account the energy of the formation of any radicals and any redistribution of charge density within the pieces and the corresponding energy change with bond cleavage. Also, the vibrational energy in the transition state is dependent on the other groups that are bound to a given functional group. This will affect the functional-group energy. But, because the variations in the energy based on the balance of the molecular composition are typically of the order of a few hundreds of electron volts at most, they were neglected.

The energy of each functional-group MO bonding to a given carbon HO is independently matched to the HO by subtracting the contribution to the change in the energy of the HO from the total MO energy given by the sum of the MO contributions and $E(C,2sp^3) = -14.63489\ eV$ (Eq. (13.428)). The intercept angles are determined from Eqs. (15.80-15.87) using the final radius of the HO of each atom. The final carbon-atom radius is determined using Eqs. (15.32) wherein the sum of the energy contributions of each atom to all the MOs in which it participates in bonding is determined. This final radius is used in Eqs. (15.19) and (15.20) to calculate the final valence energy of the HO of each atom at the corresponding final radius. The radius of any bonding heteroatom that contributes to a MO is calculated in the same manner, and the energy of its outermost shell is matched to that of the MO by the hybridization factor between the carbon-HO energy and the energy of the heteroatomic shell. The donation of electron density to the AOs and HOs reduces the energy. The donation of the electron density to the MO's at each AO or HO is that which causes the resulting energy to be divided equally between the participating AOs or HOs to achieve energy matching.

The molecular solutions can be used to design synthetic pathways and predict product yields based on equilibrium constants calculated from the heats of formation. New stable compositions of matter can be predicted as well as the structures of combinatorial chemistry reactions. Further important pharmaceutical applications include the ability to graphically or computationally render the structures of drugs that permit the identification of the biologically active parts of the molecules to be identified from the common spatial charge-density functions of a series of active molecules. Drugs can be designed according to geometrical parameters and bonding interactions with the data of the structure of the active site of the drug.

To calculate conformations, folding, and physical properties, the exact solutions of the charge distributions in any given molecule are used to calculate the fields, and from the fields, the interactions between groups of the same molecule or between groups on different molecules are calculated wherein the interactions are distance and relative orientation dependent. The fields and interactions can be determined using a finite-element-analysis approach of Maxwell's equations.

## CONTINUOUS-CHAIN ALKANES ($C_nH_{2n+2}$, $n=3,4,5...\infty$)

The continuous-chain alkanes, $C_nH_{2n+2}$, are the homologous series comprising terminal methyl groups at each end of the chain with $n-2$ methylene ($CH_2$) groups in between:

$$CH_3\left(CH_2\right)_{n-2}CH_3 \tag{15.128}$$

$C_nH_{2n+2}$ can be solved using the same principles as those used to solve ethane and ethylene wherein the $2s$ and $2p$ shells of each $C$ hybridize to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between two $C2sp^3$ hybridized orbitals (HOs) to form a molecular orbital (MO) permits each participating hybridized orbital to decrease in radius and energy. Three $H$ AOs combine with three carbon $2sp^3$ HOs and two $H$ AOs combine with two carbon $2sp^3$ HOs to form each methyl and methylene group, respectively, where each bond comprises a $H_2$-type MO developed in the Nature of the Chemical Bond of Hydrogen-Type Molecules and Molecular Ions section. The $CH_3$ and $CH_2$ groups bond by forming $H_2$-type MOs between the remaining $C2sp^3$ HOs on the carbons such that each carbon forms four bonds involving its four $C2sp^3$ HOs. For the alkyl $C-C$ group, $E_T\left(atom-atom,msp^3.AO\right)$ is $-1.85836\ eV$ where both energy contributions are given by Eq. (14.513). It is based on the energy match between the $C2sp^3$ HOs of the chain comprising methylene groups and terminal methyl groups.

The geometrical (Eqs. (15.1-15.5) and (15.51)), intercept (Eqs. (15.80-15.87)), and energy (Eqs. (15.6-15.11) and (15.17-15.65)) parameters of straight-chain alkanes are given in Tables 15.4, 15.5, and 15.6, respectively. The total energy of each straight-chain alkane given in Table 15.7 was calculated as the sum over the integer multiple of each $E_D\left(Group\right)$ of Table 15.6 corresponding to functional-group composition of the molecule. The bond angle parameters of straight-chain alkanes determined using Eqs. (15.88-15.117) are given in Table 15.8. In this angle table and those given in subsequent sections when $c_2'$ is given as the ratio of two values of $c_2$ designated to Atom 1 and Atom 2 and corresponding to $E_{Coulombic}$ of Atom 1 and Atom 2, respectively, then $c_2' = \dfrac{c_2\left(Atom\ 2\right)}{c_2\left(Atom\ 1\right)}$. The color scale, translucent view of the charge-density of exemplary alkane, butane comprising the concentric shells of atoms with the outer shell bridged by one or more $H_2$-type ellipsoidal MOs or joined with one or more hydrogen MOs is shown in Figure 15.1.

Figure 15.1. (A-B) Color scale, translucent and opaque views of the charge-density of butane. Each representation shows the orbitals of the atoms at their radii, the ellipsoidal surface of each $H$ or $H_2$-type ellipsoidal MO that transitions to the corresponding outer shell of the atom(s) participating in each bond, and the hydrogen nuclei (red, not to scale).

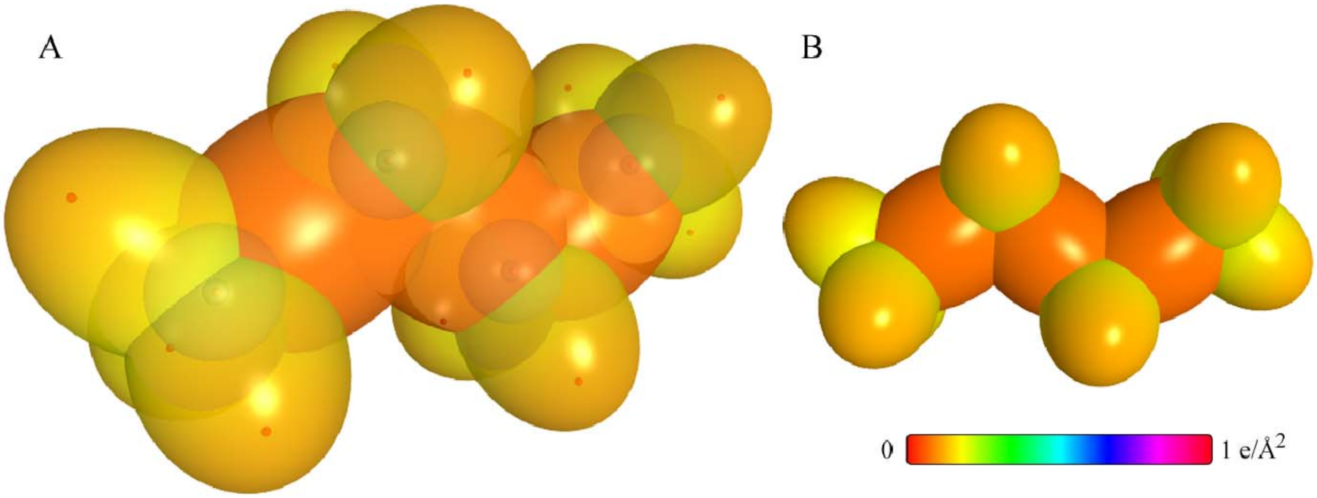


Table 15.4. The geometrical bond parameters of straight-chain alkanes and experimental values [1].

| Parameter | $C-C$ Group | $C-H\ (CH_3)$ Group | $C-H\ (CH_2)$ Group |
|---|---|---|---|
| $a\ (a_0)$ | 2.12499 | 1.64920 | 1.67122 |
| $c'\ (a_0)$ | 1.45744 | 1.04856 | 1.05553 |
| Bond Length $2c'\ (\mathring{A})$ | 1.54280 | 1.10974 | 1.11713 |
| Exp. Bond Length $(\mathring{A})$ | 1.532<br>(propane)<br>1.531<br>(butane) | 1.107<br>($C-H$ propane)<br>1.117<br>($C-H$ butane) | 1.107<br>($C-H$ propane)<br>1.117<br>($C-H$ butane) |
| $b, c\ (a_0)$ | 1.54616 | 1.27295 | 1.29569 |
| $e$ | 0.68600 | 0.63580 | 0.63159 |

**Table 15.5.** The MO to HO intercept geometrical bond parameters of straight-chain alkanes. $E_T$ is $E_T$ $(atom - atom, msp^3.AO)$.

| Bond | Atom | $E_T$ (eV) Bond 1 | $E_T$ (eV) Bond 2 | $E_T$ (eV) Bond 3 | $E_T$ (eV) Bond 4 | Final Total Energy $C2sp^3$ (eV) | $r_{initial}$ $(a_0)$ | $r_{final}$ $(a_0)$ | $E_{Coulomb}(C2sp^3)$ (eV) Final | $E(C2sp^3)$ (eV) Final | $\theta'$ $(^\circ)$ | $\theta_1$ $(^\circ)$ | $\theta_2$ $(^\circ)$ | $d_1$ $(a_0)$ | $d_2$ $(a_0)$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $C-H\ (CH_3)$ | $C$ | -0.92918 | 0 | 0 | 0 | -152.54487 | 0.91771 | 0.86359 | -15.75493 | -15.56407 | 77.49 | 102.51 | 41.48 | 1.23564 | 0.18708 |
| $C-H\ (CH_2)$ | $C$ | -0.92918 | -0.92918 | 0 | 0 | -153.47406 | 0.91771 | 0.81549 | -16.68412 | -16.49325 | 68.47 | 111.53 | 35.84 | 1.35486 | 0.29933 |
| $H_3C_a-C_bH_2CH_2$ | $C_a$ | -0.92918 | 0 | 0 | 0 | -152.54487 | 0.91771 | 0.86359 | -15.75493 | -15.56407 | 63.82 | 116.18 | 30.08 | 1.83879 | 0.38106 |
| $H_3C_a-C_bH_2CH_2$ | $C_b$ | -0.92918 | -0.92918 | 0 | 0 | -153.47406 | 0.91771 | 0.81549 | -16.68412 | -16.49325 | 56.41 | 123.59 | 26.06 | 1.90890 | 0.45117 |

Table 15.6. The energy parameters (*eV*) of functional groups of straight-chain alkanes.

| Parameters | $C-C$ Group | $CH_3$ Group | $CH_2$ Group |
|---|---|---|---|
| $n_1$ | 1 | 3 | 2 |
| $n_2$ | 0 | 2 | 1 |
| $n_3$ | 0 | 0 | 0 |
| $C_1$ | 0.5 | 0.75 | 0.75 |
| $C_2$ | 1 | 1 | 1 |
| $c_1$ | 1 | 1 | 1 |
| $c_2$ | 0.91771 | 0.91771 | 0.91771 |
| $c_3$ | 0 | 0 | 1 |
| $c_4$ | 2 | 1 | 1 |
| $c_5$ | 0 | 3 | 2 |
| $C_{1o}$ | 0.5 | 0.75 | 0.75 |
| $C_{2o}$ | 1 | 1 | 1 |
| $V_e\ (eV)$ | -28.79214 | -107.32728 | -70.41425 |
| $V_p\ (eV)$ | 9.33352 | 38.92728 | 25.78002 |
| $T\ (eV)$ | 6.77464 | 32.53914 | 21.06675 |
| $V_m\ (eV)$ | -3.38732 | -16.26957 | -10.53337 |
| $E(AO/HO)\ (eV)$ | -15.56407 | -15.56407 | -15.56407 |
| $\Delta E_{H_2MO}(AO/HO)\ (eV)$ | 0 | 0 | 0 |
| $E_T(AO/HO)\ (eV)$ | -15.56407 | -15.56407 | -15.56407 |
| $E_T(H_2MO)\ (eV)$ | -31.63537 | -67.69451 | -49.66493 |
| $E_T\left(atom-atom, msp^3.AO\right)\ (eV)$ | -1.85836 | 0 | 0 |
| $E_T(MO)\ (eV)$ | -33.49373 | -67.69450 | -49.66493 |
| $\omega\ \left(10^{15}\ rad/s\right)$ | 9.43699 | 24.9286 | 24.2751 |
| $E_K\ (eV)$ | 6.21159 | 16.40846 | 15.97831 |
| $\bar{E}_D\ (eV)$ | -0.16515 | -0.25352 | -0.25017 |
| $\bar{E}_{Kvib}\ (eV)$ | 0.12312 [2] | 0.35532 (Eq. (13.458)) | 0.35532 (Eq. (13.458)) |
| $\bar{E}_{osc}\ (eV)$ | -0.10359 | -0.22757 | -0.14502 |
| $E_{mag}\ (eV)$ | 0.14803 | 0.14803 | 0.14803 |
| $E_T(Group)\ (eV)$ | -33.59732 | -67.92207 | -49.80996 |
| $E_{initial}(c_4\ AO/HO)\ (eV)$ | -14.63489 | -14.63489 | -14.63489 |
| $E_{initial}(c_5\ AO/HO)\ (eV)$ | 0 | -13.59844 | -13.59844 |
| $E_D(Group)\ (eV)$ | 4.32754 | 12.49186 | 7.83016 |

Table 15.7. The total bond energies of n-alkanes calculated using the functional group composition and the energies of Table 15.6 compared to the experimental values [3].

| Formula | Name | $C-C$ | $CH_3$ | $CH_2$ | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|---|---|---|
| $C_3H_8$ | Propane | 2 | 2 | 1 | 41.46896 | 41.434 | -0.00085 |
| $C_4H_{10}$ | Butane | 3 | 2 | 2 | 53.62666 | 53.61 | -0.00036 |
| $C_5H_{12}$ | Pentane | 4 | 2 | 3 | 65.78436 | 65.77 | -0.00017 |
| $C_6H_{14}$ | Hexane | 5 | 2 | 4 | 77.94206 | 77.93 | -0.00019 |
| $C_7H_{16}$ | Heptane | 6 | 2 | 5 | 90.09976 | 90.09 | -0.00013 |
| $C_8H_{18}$ | Octane | 7 | 2 | 6 | 102.25746 | 102.25 | -0.00006 |
| $C_9H_{20}$ | Nonane | 8 | 2 | 7 | 114.41516 | 114.40 | -0.00012 |
| $C_{10}H_{22}$ | Decane | 9 | 2 | 8 | 126.57286 | 126.57 | -0.00003 |
| $C_{11}H_{24}$ | Undecane | 10 | 2 | 9 | 138.73056 | 138.736 | 0.00004 |
| $C_{12}H_{26}$ | Dodecane | 11 | 2 | 10 | 150.88826 | 150.88 | -0.00008 |
| $C_{18}H_{38}$ | Octadecane | 17 | 2 | 16 | 223.83446 | 223.85 | 0.00008 |

Table 15.8. The bond angle parameters of straight-chain alkanes and experimental values [1]. In the calculation of $\theta_v$, the parameters from the preceding angle were used. $E_T$ is $E_T(atom-atom, msp^3.AO)$.

| Atoms of Angle | $2c'$ Bond 1 $(a_0)$ | $2c'$ Bond 2 $(a_0)$ | $2c'$ Terminal Atoms $(a_0)$ | $E_{Coulombic}$ Atom 1 | Atom 1 Hybridization Designation (Table 15.3.A) | $E_{Coulombic}$ Atom 2 | Atom 2 Hybridization Designation (Table 15.3.A) | $c_2$ Atom 1 | $c_2$ Atom 2 | $C_1$ | $C_2$ | $c_1$ | $c_2'$ | $E_T$ (eV) | $\theta_v$ $(^\circ)$ | $\theta_1$ $(^\circ)$ | $\theta_2$ $(^\circ)$ | Cal. $\theta$ $(^\circ)$ | Exp. $\theta$ $(^\circ)$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Methylene<br>$\angle HC_aH$ | 2.11106 | 2.11106 | 3.4252 | -15.75493<br>$C_a$ | 7 | H | H | 0.86359 | 1 | 1 | 1 | 0.75 | 1.15796 | 0 | | | | 108.44 | 107<br>(propane) |
| $\angle C_aC_bC_c$ | | | | | | | | | | | | | | | 69.51 | | | 110.49 | 112<br>(propane)<br>113.8<br>(butane) |
| $\angle C_aC_bH$ | | | | | | | | | | | | | | | 69.51 | | | 110.49 | 111.0<br>(butane) |
| Methyl<br>$\angle HC_aH$ | 2.09711 | 2.09711 | 3.4252 | -15.75493<br>$C_a$ | 7 | H | H | 0.86359 | 1 | 1 | 1 | 0.75 | 1.15796 | 0 | | | | 109.50 | |
| $\angle C_aC_bC_c$ | | | | | | | | | | | | | | | 70.56 | | | 109.44 | |
| $\angle C_aC_bH$ | | | | | | | | | | | | | | | 70.56 | | | 109.44 | |

## BRANCHED ALKANES ($C_nH_{2n+2}$, $n=3,4,5...\infty$)

The branched-chain alkanes, $C_nH_{2n+2}$, comprise at least two terminal methyl groups ($CH_3$) at each end of the chain, and may comprise methylene ($CH_2$), and methylyne ($CH$) functional groups as well as $C$ bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($\left(CH_3\right)_2 CH$) and t-butyl ($\left(CH_3\right)_3 C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups. The branched-alkane groups are solved using the same principles as those used to solve the methyl and methylene functional groups wherein the $2s$ and $2p$ AOs of each $C$ hybridize to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between two $C2sp^3$ HOs to form a MO permits each participating hybridized orbital to decrease in radius and energy. $E_T\left(atom-atom,msp^3.AO\right)$ of each $C-C$-bond MO in Eq. (15.61) due to the charge donation from the $C$ atoms to the MO is $-1.85836\,eV$ or $-1.44915\,eV$ based on the energy match between the $C2sp^3$ HOs corresponding to the energy contributions equivalent to those of methylene, $-0.92918\,eV$ (Eq. (14.513)), or methyl, $-0.72457\,eV$ (Eq. (14.151)), groups, respectively.

The symbols of the functional groups of branched-chain alkanes are given in Table 15.9. The geometrical (Eqs. (15.1-15.5) and (15.51)), intercept (Eqs. (15.80-15.87)), and energy (Eqs. (15.6-15.11) and (15.17-15.65)) parameters of branched-chain alkanes are given in Tables 15.10, 15.11, and 15.12, respectively. The total energy of each branched-chain alkane given in Table 15.13 was calculated as the sum over the integer multiple of each $E_D\left(Group\right)$ of Table 15.12 corresponding to functional-group composition of the molecule. The bond angle parameters of branched-chain alkanes determined using Eqs. (15.88-15.117) are given in Table 15.14. The color scale, translucent view of the charge-density of exemplary alkane, isobutane, comprising the concentric shells of atoms with the outer shell bridged by one or more $H_2$-type ellipsoidal MOs or joined with one or more hydrogen MOs is shown in Figure 15.2.

Figure 15.2. Color scale, translucent view of the charge-density of isobutane showing the orbitals of the atoms at their radii, the ellipsoidal surface of each $H$ or $H_2$-type ellipsoidal MO that transitions to the corresponding outer shell of the atom(s) participating in each bond, and the hydrogen nuclei (red, not to scale). (A) Top view. (B) Side view.

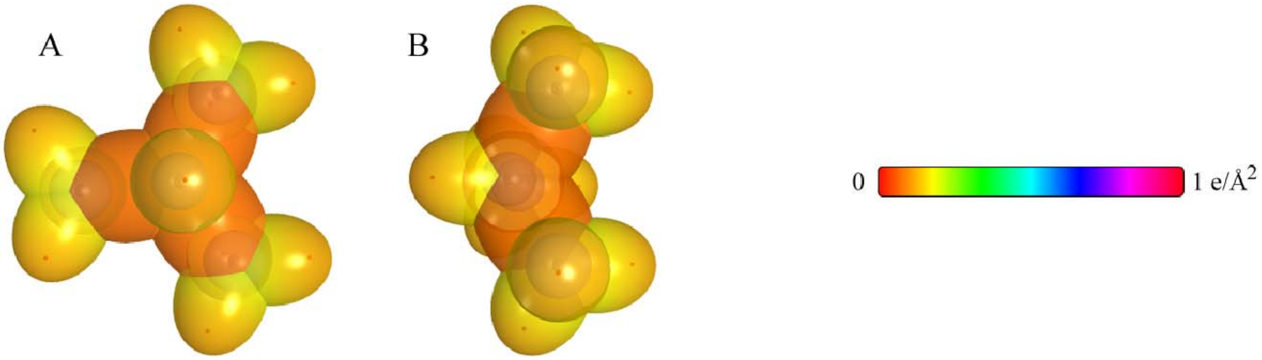


Table 15.9. The symbols of functional groups of branched alkanes.

| Functional Group | Group Symbol |
|---|---|
| $CH_3$ group | $C-H\ \left(CH_3\right)$ |
| $CH_2$ group | $C-H\ \left(CH_2\right)$ |
| $CH$ | $C-H$ |
| $CC$ bond (*n-C*) | $C-C$ (a) |
| $CC$ bond (*iso-C*) | $C-C$ (b) |
| $CC$ bond (*tert-C*) | $C-C$ (c) |
| $CC$ (*iso* to *iso-C*) | $C-C$ (d) |
| $CC$ (*t* to *t-C*) | $C-C$ (e) |
| $CC$ (*t* to *iso-C)* | $C-C$ (f) |

Table 15.10. The geometrical bond parameters of branched alkanes and experimental values [1].

| Parameter | $C-H\ (CH_3)$ Group | $C-H\ (CH_2)$ Group | $C-H$ Group | $C-C$ (a) Group | $C-C$ (b) Group | $C-C$ (c) Group | $C-C$ (d) Group | $C-C$ (e) Group | $C-C$ (f) Group |
|---|---|---|---|---|---|---|---|---|---|
| $a\ (a_0)$ | 1.64920 | 1.67122 | 1.67465 | 2.12499 | 2.12499 | 2.10725 | 2.12499 | 2.10725 | 2.10725 |
| $c'\ (a_0)$ | 1.04856 | 1.05553 | 1.05661 | 1.45744 | 1.45744 | 1.45164 | 1.45744 | 1.45164 | 1.45164 |
| Bond Length $2c'\ (Å)$ | 1.10974 | 1.11713 | 1.11827 | 1.54280 | 1.54280 | 1.53635 | 1.54280 | 1.53635 | 1.53635 |
| Exp. Bond Length $(Å)$ | 1.107<br>($C-H$ propane)<br>1.117<br>($C-H$ butane) | 1.107<br>($C-H$ propane)<br>1.117<br>($C-H$ butane) | 1.122<br>(isobutane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) |
| $b,c\ (a_0)$ | 1.27295 | 1.29569 | 1.29924 | 1.54616 | 1.54616 | 1.52750 | 1.54616 | 1.52750 | 1.52750 |
| $e$ | 0.63580 | 0.63159 | 0.63095 | 0.68600 | 0.68600 | 0.68888 | 0.68600 | 0.68888 | 0.68888 |

Table 15.11. The MO to HO intercept geometrical bond parameters of branched-chain alkanes. $R$, $R'$, $R''$ are $H$ or alkyl groups. $E_T$ is $E_T$ $(atom-atom, msp^3.AO)$.

| Bond | Atom | $E_T$ (eV) Bond 1 | $E_T$ (eV) Bond 2 | $E_T$ (eV) Bond 3 | $E_T$ (eV) Bond 4 | Final Total Energy $C2sp^3$ (eV) | $r_{initial}$ $(a_0)$ | $r_{final}$ $(a_0)$ | $E_{Coulomb}(C2sp^3)$ (eV) Final | $E(C2sp^3)$ (eV) Final | $\theta'$ (°) | $\theta_1$ (°) | $\theta_2$ (°) | $d_1$ $(a_0)$ | $d_2$ $(a_0)$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $C-H\ (CH_3)$ | $C$ | -0.92918 | 0 | 0 | 0 | -152.54487 | 0.91771 | 0.86359 | -15.75493 | -15.56407 | 77.49 | 102.51 | 41.48 | 1.23564 | 0.18708 |
| $C-H\ (CH_2)$ | $C$ | -0.92918 | -0.92918 | 0 | 0 | -153.47406 | 0.91771 | 0.81549 | -16.68412 | -16.49325 | 68.47 | 111.53 | 35.84 | 1.35486 | 0.29933 |
| $C-H\ (CH)$ | $C$ | -0.92918 | -0.92918 | -0.92918 | 0 | -154.40324 | 0.91771 | 0.77247 | -17.61330 | -17.42244 | 61.10 | 118.90 | 31.37 | 1.42988 | 0.37326 |
| $H_3C_aC_bH_2CH_2-$ $(C-C$ (a)) | $C_a$ | -0.92918 | 0 | 0 | 0 | -152.54487 | 0.91771 | 0.86359 | -15.75493 | -15.56407 | 63.82 | 116.18 | 30.08 | 1.83879 | 0.38106 |
| $H_3C_aC_bH_2CH_2-$ $(C-C$ (a)) | $C_b$ | -0.92918 | -0.92918 | 0 | 0 | -153.47406 | 0.91771 | 0.81549 | -16.68412 | -16.49325 | 56.41 | 123.59 | 26.06 | 1.90890 | 0.45117 |
| $R-H_2C_aC_b(H_2C_c-R')HCH_2-$ $(C-C$ (b)) | $C_b$ | -0.92918 | -0.92918 | -0.92918 | 0 | -154.40324 | 0.91771 | 0.77247 | -17.61330 | -17.42244 | 48.30 | 131.70 | 21.90 | 1.97162 | 0.51388 |
| $R-H_2C_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ $(C-C$ (c)) | $C_b$ | -0.92918 | -0.72457 | -0.72457 | -0.72457 | -154.71860 | 0.91771 | 0.75889 | -17.92866 | -17.73779 | 48.21 | 131.79 | 21.74 | 1.95734 | 0.50570 |
| $isoC_aC_b(H_2C_c-R')HCH_2-$ $(C-C$ (d)) | $C_b$ | -0.92918 | -0.92918 | -0.92918 | 0 | -154.40324 | 0.91771 | 0.77247 | -17.61330 | -17.42244 | 48.30 | 131.70 | 21.90 | 1.97162 | 0.51388 |
| $tertC_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ $(C-C$ (e)) | $C_b$ | -0.72457 | -0.72457 | -0.72457 | -0.72457 | -154.51399 | 0.91771 | 0.76765 | -17.92866 | -17.73779 | 50.04 | 129.96 | 22.66 | 1.94462 | 0.49298 |
| $tertC_aC_b(H_2C_c-R')HCH_2-$ $(C-C$ (f)) | $C_b$ | -0.72457 | -0.92918 | -0.92918 | 0 | -154.19863 | 0.91771 | 0.78155 | -17.40869 | -17.21783 | 52.78 | 127.22 | 24.04 | 1.92443 | 0.47279 |
| $isoC_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ $(C-C$ (f)) | $C_b$ | -0.72457 | -0.72457 | -0.72457 | -0.72457 | -154.51399 | 0.91771 | 0.76765 | -17.92866 | -17.73779 | 50.04 | 129.96 | 22.66 | 1.94462 | 0.49298 |

Table 15.12. The energy parameters $(eV)$ of functional groups of branched-chain alkanes.

| Parameters | $CH_3$ Group | $CH_2$ Group | $C-H$ Group | $C-C$ (a) Group | $C-C$ (b) Group | $C-C$ (c) Group | $C-C$ (d) Group | $C-C$ (e) Group | $C-C$ (f) Group |
|---|---|---|---|---|---|---|---|---|---|
| $n_1$ | 3 | 2 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $n_2$ | 2 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $n_3$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $C_1$ | 0.75 | 0.75 | 0.75 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| $C_2$ | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $c_1$ | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $c_2$ | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 |
| $c_3$ | 0 | 1 | 1 | 0 | 0 | 0 | 1 | 1 | 0 |
| $c_4$ | 1 | 1 | 1 | 2 | 2 | 2 | 2 | 2 | 2 |
| $c_5$ | 3 | 2 | 1 | 0 | 0 | 0 | 0 | 0 | 0 |
| $C_{1o}$ | 0.75 | 0.75 | 0.75 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| $C_{2o}$ | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $V_e\ (eV)$ | -107.32728 | -70.41425 | -35.12015 | -28.79214 | -28.79214 | -29.10112 | -28.79214 | -29.10112 | -29.10112 |
| $V_p\ (eV)$ | 38.92728 | 25.78002 | 12.87680 | 9.33352 | 9.33352 | 9.37273 | 9.33352 | 9.37273 | 9.37273 |
| $T\ (eV)$ | 32.53914 | 21.06675 | 10.48582 | 6.77464 | 6.77464 | 6.90500 | 6.77464 | 6.90500 | 6.90500 |
| $V_m\ (eV)$ | -16.26957 | -10.53337 | -5.24291 | -3.38732 | -3.38732 | -3.45250 | -3.38732 | -3.45250 | -3.45250 |
| $E(_{AO/HO})\ (eV)$ | -15.56407 | -15.56407 | -14.63489 | -15.56407 | -15.56407 | -15.35946 | -15.56407 | -15.35946 | -15.35946 |
| $\Delta E_{H_2MO}(_{AO/HO})\ (eV)$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $E_T(_{AO/HO})\ (eV)$ | -15.56407 | -15.56407 | -14.63489 | -15.56407 | -15.56407 | -15.35946 | -15.56407 | -15.35946 | -15.35946 |
| $E_T(_{H_2MO})\ (eV)$ | -67.69451 | -49.66493 | -31.63533 | -31.63537 | -31.63537 | -31.63535 | -31.63537 | -31.63535 | -31.63535 |
| $E_T\left(atom-atom, msp^3.AO\right)\ (eV)$ | 0 | 0 | 0 | -1.85836 | -1.85836 | -1.44915 | -1.85836 | -1.44915 | -1.44915 |
| $E_T(_{MO})\ (eV)$ | -67.69450 | -49.66493 | -31.63537 | -33.49373 | -33.49373 | -33.08452 | -33.49373 | -33.08452 | -33.08452 |
| $\omega\ \left(10^{15}\ rad/s\right)$ | 24.9286 | 24.2751 | 24.1759 | 9.43699 | 9.43699 | 15.4846 | 9.43699 | 9.55643 | 9.55643 |
| $E_K\ (eV)$ | 16.40846 | 15.97831 | 15.91299 | 6.21159 | 6.21159 | 10.19220 | 6.21159 | 6.29021 | 6.29021 |
| $\bar{E}_D\ (eV)$ | -0.25352 | -0.25017 | -0.24966 | -0.16515 | -0.16515 | -0.20896 | -0.16515 | -0.16416 | -0.16416 |
| $\bar{E}_{Kvib}\ (eV)$ | 0.35532 (Eq. (13.458)) | 0.35532 (Eq. (13.458)) | 0.35532 (Eq. (13.458)) | 0.12312 [2] | 0.17978 [4] | 0.09944 [5] | 0.12312 [2] | 0.12312 [2] | 0.12312 [2] |
| $\bar{E}_{osc}\ (eV)$ | -0.22757 | -0.14502 | -0.07200 | -0.10359 | -0.07526 | -0.15924 | -0.10359 | -0.10260 | -0.10260 |
| $E_{mag}\ (eV)$ | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 |
| $E_T(_{Group})\ (eV)$ | -67.92207 | -49.80996 | -31.70737 | -33.59732 | -33.49373 | -33.24376 | -33.59732 | -33.18712 | -33.18712 |
| $E_{initial}(_{c_4\ AO/HO})\ (eV)$ | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 |
| $E_{initial}(_{c_5\ AO/HO})\ (eV)$ | -13.59844 | -13.59844 | -13.59844 | 0 | 0 | 0 | 0 | 0 | 0 |
| $E_D(_{Group})\ (eV)$ | 12.49186 | 7.83016 | 3.32601 | 4.32754 | 4.29921 | 3.97398 | 4.17951 | 3.62128 | 3.91734 |

Table 15.13. The total bond energies of branched alkanes calculated using the functional group composition and the energies of Table 15.12 compared to the experimental values [3].

| Formula | Name | $CH_3$ | $CH_2$ | $CH$ | $C-C$ (a) | $C-C$ (b) | $C-C$ (c) | $C-C$ (d) | $C-C$ (e) | $C-C$ (f) | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $C_4H_{10}$ | Isobutane | 3 | 0 | 1 | 0 | 3 | 0 | 0 | 0 | 0 | 53.69922 | 53.695 | -0.00007 |
| $C_5H_{12}$ | Isopentane | 3 | 1 | 1 | 1 | 3 | 0 | 0 | 0 | 0 | 65.85692 | 65.843 | -0.00021 |
| $C_5H_{12}$ | Neopentane | 4 | 0 | 0 | 0 | 0 | 4 | 0 | 0 | 0 | 65.86336 | 65.992 | 0.00195 |
| $C_6H_{14}$ | 2-Methylpentane | 3 | 2 | 1 | 2 | 3 | 0 | 0 | 0 | 0 | 78.01462 | 78.007 | -0.00010 |
| $C_6H_{14}$ | 3-Methylpentane | 3 | 2 | 1 | 2 | 3 | 0 | 0 | 0 | 0 | 78.01462 | 77.979 | -0.00046 |
| $C_6H_{14}$ | 2,2-Dimethylbutane | 4 | 1 | 0 | 1 | 0 | 4 | 0 | 0 | 0 | 78.02106 | 78.124 | 0.00132 |
| $C_6H_{14}$ | 2,3-Dimethylbutane | 4 | 0 | 2 | 0 | 4 | 0 | 1 | 0 | 0 | 77.99581 | 78.043 | 0.00061 |
| $C_7H_{16}$ | 2-Methylhexane | 3 | 3 | 1 | 3 | 3 | 0 | 0 | 0 | 0 | 90.17232 | 90.160 | -0.00014 |
| $C_7H_{16}$ | 3-Methylhexane | 3 | 3 | 1 | 3 | 3 | 0 | 0 | 0 | 0 | 90.17232 | 90.127 | -0.00051 |
| $C_7H_{16}$ | 3-Ethylpentane | 3 | 3 | 1 | 3 | 3 | 0 | 0 | 0 | 0 | 90.17232 | 90.108 | -0.00072 |
| $C_7H_{16}$ | 2,2-Dimethylpentane | 4 | 2 | 0 | 2 | 0 | 4 | 0 | 0 | 0 | 90.17876 | 90.276 | 0.00107 |
| $C_7H_{16}$ | 2,2,3-Trimethylbutane | 5 | 0 | 1 | 0 | 2 | 3 | 0 | 0 | 1 | 90.22301 | 90.262 | 0.00044 |
| $C_7H_{16}$ | 2,4-Dimethylpentane | 4 | 1 | 2 | 0 | 6 | 0 | 0 | 0 | 0 | 90.24488 | 90.233 | -0.00013 |
| $C_7H_{16}$ | 3,3-Dimethylpentane | 4 | 2 | 0 | 2 | 0 | 4 | 0 | 0 | 0 | 90.17876 | 90.227 | 0.00054 |
| $C_8H_{18}$ | 2-Methylheptane | 3 | 4 | 1 | 4 | 3 | 0 | 0 | 0 | 0 | 102.33002 | 102.322 | -0.00008 |
| $C_8H_{18}$ | 3-Methylheptane | 3 | 4 | 1 | 4 | 3 | 0 | 0 | 0 | 0 | 102.33002 | 102.293 | -0.00036 |
| $C_8H_{18}$ | 4-Methylheptane | 3 | 4 | 1 | 4 | 3 | 0 | 0 | 0 | 0 | 102.33002 | 102.286 | -0.00043 |
| $C_8H_{18}$ | 3-Ethylhexane | 3 | 4 | 1 | 3 | 4 | 0 | 0 | 0 | 0 | 102.33002 | 102.274 | -0.00055 |
| $C_8H_{18}$ | 2,2-Dimethylhexane | 4 | 3 | 0 | 3 | 0 | 4 | 0 | 0 | 0 | 102.33646 | 102.417 | 0.00079 |
| $C_8H_{18}$ | 2,3-Dimethylhexane | 4 | 2 | 2 | 2 | 4 | 0 | 1 | 0 | 0 | 102.31121 | 102.306 | -0.00005 |
| $C_8H_{18}$ | 2,4-Dimethylhexane | 4 | 2 | 2 | 1 | 6 | 0 | 0 | 0 | 0 | 102.40258 | 102.362 | -0.00040 |
| $C_8H_{18}$ | 2,5-Dimethylhexane | 4 | 2 | 2 | 1 | 6 | 0 | 0 | 0 | 0 | 102.40258 | 102.396 | -0.00006 |
| $C_8H_{18}$ | 3,3-Dimethylhexane | 4 | 3 | 0 | 3 | 0 | 4 | 0 | 0 | 0 | 102.33646 | 102.369 | 0.00032 |
| $C_8H_{18}$ | 3,4-Dimethylhexane | 4 | 2 | 2 | 2 | 4 | 0 | 1 | 0 | 0 | 102.31121 | 102.296 | -0.00015 |
| $C_8H_{18}$ | 3-Ethyl-2-methylpentane | 4 | 2 | 2 | 2 | 4 | 0 | 1 | 0 | 0 | 102.31121 | 102.277 | -0.00033 |
| $C_8H_{18}$ | 3-Ethyl-3-methylpentane | 4 | 3 | 0 | 3 | 0 | 4 | 0 | 0 | 0 | 102.33646 | 102.317 | -0.00019 |
| $C_8H_{18}$ | 2,2,3-Trimethylpentane | 5 | 1 | 1 | 1 | 2 | 3 | 0 | 0 | 1 | 102.38071 | 102.370 | -0.00010 |
| $C_8H_{18}$ | 2,2,4-Trimethylpentane | 5 | 1 | 1 | 0 | 3 | 4 | 0 | 0 | 0 | 102.40902 | 102.412 | 0.00003 |
| $C_8H_{18}$ | 2,3,3-Trimethylpentane | 5 | 1 | 1 | 1 | 2 | 3 | 0 | 0 | 1 | 102.38071 | 102.332 | -0.00048 |
| $C_8H_{18}$ | 2,3,4-Trimethylpentane | 5 | 0 | 3 | 0 | 5 | 0 | 2 | 0 | 0 | 102.29240 | 102.342 | 0.00049 |
| $C_8H_{18}$ | 2,2,3,3-Tetramethylbutane | 6 | 0 | 0 | 0 | 0 | 6 | 0 | 1 | 0 | 102.41632 | 102.433 | 0.00016 |
| $C_9H_{20}$ | 2,3,5-Trimethylhexane | 5 | 1 | 3 | 0 | 7 | 0 | 1 | 0 | 0 | 114.54147 | 114.551 | 0.00008 |
| $C_9H_{20}$ | 3,3-Diethylpentane | 4 | 4 | 0 | 4 | 0 | 4 | 0 | 0 | 0 | 114.49416 | 114.455 | -0.00034 |
| $C_9H_{20}$ | 2,2,3,3-Tetramethylpentane | 6 | 1 | 0 | 1 | 0 | 6 | 0 | 1 | 0 | 114.57402 | 114.494 | -0.00070 |
| $C_9H_{20}$ | 2,2,3,4-Tetramethylpentane | 6 | 0 | 2 | 0 | 3 | 3 | 1 | 0 | 1 | 114.51960 | 114.492 | -0.00024 |
| $C_9H_{20}$ | 2,2,4,4-Tetramethylpentane | 6 | 1 | 0 | 0 | 0 | 8 | 0 | 0 | 0 | 114.57316 | 114.541 | -0.00028 |
| $C_9H_{20}$ | 2,3,3,4-Tetramethylpentane | 6 | 0 | 2 | 0 | 4 | 2 | 0 | 0 | 2 | 114.58266 | 114.484 | -0.00086 |
| $C_{10}H_{22}$ | 2-Methylnonane | 3 | 6 | 1 | 6 | 3 | 0 | 0 | 0 | 0 | 126.64542 | 126.680 | 0.00027 |
| $C_{10}H_{22}$ | 5-Methylnonane | 3 | 6 | 1 | 6 | 3 | 0 | 0 | 0 | 0 | 126.64542 | 126.663 | 0.00014 |

Table 15.14. The bond angle parameters of branched-chain alkanes and experimental values [1]. In the calculation of $\theta_v$, the parameters from the preceding angle were used. $E_T$ is $E_T\,(atom - atom,\ msp^3.AO)$.

| Atoms of Angle | $2c'$ Bond 1 $(a_0)$ | $2c'$ Bond 2 $(a_0)$ | $2c'$ Terminal Atoms $(a_0)$ | $E_{Coulombic}$ Atom 1 | Atom 1 Hybridization Designation (Table 15.3.A) | $E_{Coulombic}$ Atom 2 | Atom 2 Hybridization Designation (Table 15.3.A) | $c_2$ Atom 1 | $c_2$ Atom 2 | $C_1$ | $C_2$ | $c_1$ | $c'_2$ | $E_T$ (eV) | $\theta_v$ (°) | $\theta_1$ (°) | $\theta_2$ (°) | Cal. $\theta$ (°) | Exp. $\theta$ (°) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Methylene $\angle HC_aH$ | 2.11106 | 2.11106 | 3.4252 | -15.75493 | 7 | H | H | 0.86359 | 1 | 1 | 1 | 0.75 | 1.15796 | 0 | | | | 108.44 | 107 (propane) |
| $\angle C_aC_bC_c$ | | | | | | | | | | | | | | | 69.51 | | | 110.49 | 112 (propane)<br>113.8 (butane)<br>110.8 (isobutane) |
| $\angle C_aC_bH$ | | | | | | | | | | | | | | | 69.51 | | | 110.49 | 111.0 (butane)<br>111.4 (isobutane) |
| Methyl $\angle HC_aH$ | 2.09711 | 2.09711 | 3.4252 | -15.75493 | 7 | H | H | 0.86359 | 1 | 1 | 1 | 0.75 | 1.15796 | 0 | | | | 109.50 | |
| $\angle C_aC_bC_c$ | | | | | | | | | | | | | | | 70.56 | | | 109.44 | |
| $\angle C_aC_bH$ | | | | | | | | | | | | | | | 70.56 | | | 109.44 | |
| $\angle C_bC_aC_c$ iso $C_a$ | 2.91547 | 2.91547 | 4.7958 | -16.68412 $C_b$ | 26 | -16.68412 $C_c$ | 26 | 0.81549 | 0.81549 | 1 | 1 | 1 | 0.81549 | -1.85836 | | | | 110.67 | 110.8 (isobutane) |
| $\angle C_bC_aH$ iso $C_a$ | 2.91547 | 2.11323 | 4.1633 | -15.55033 $C_a$ | 5 | -14.82575 $C_b$ | 1 | 0.87495 | 0.91771 | 0.75 | 1 | 0.75 | 1.04887 | 0 | | | | 110.76 | |
| $\angle C_aC_bH$ iso $C_a$ | 2.91547 | 2.09711 | 4.1633 | -15.55033 $C_b$ | 5 | -14.82575 $C_a$ | 1 | 0.87495 | 0.91771 | 0.75 | 1 | 0.75 | 1.04887 | 0 | | | | 111.27 | 111.4 (isobutane) |
| $\angle C_bC_aC_b$ tert $C_a$ | 2.90327 | 2.90327 | 4.7958 | -16.68412 $C_b$ | 26 | -16.68412 $C_b$ | 26 | 0.81549 | 0.81549 | 1 | 1 | 1 | 0.81549 | -1.85836 | | | | 111.37 | 110.8 (isobutane) |
| $\angle C_bC_aC_d$ | | | | | | | | | | | | | | | 72.50 | | | 107.50 | |

## ALKENES ($C_nH_{2n}$, $n = 3,4,5...\infty$)

The straight and branched-chain alkenes, $C_nH_{2n}$, comprise at least one carbon-carbon double bond comprising a functional group that is solved equivalently to the double bond of ethylene. The double bond may be bound to one, two, three, or four carbon single bonds that substitute for the hydrogen atoms of ethylene. Based on the condition of energy matching of the orbital, any magnetic energy due to unpaired electrons in the constituent fragments, and differences in oscillation in the transition state, three distinct functional groups can be identified: $C$ vinyl single bond to $-C(C)=C$, $C$ vinyl single bond to $-C(H)=C$, and $C$ vinyl single bond to $-C(C)=CH_2$. In addition, $CH_2$ of the $-C=CH_2$ moiety is an alkene functional group.

The alkyl portion of the alkene may comprise at least two terminal methyl groups ($CH_3$) at each end of the chain, and may comprise methylene ($CH_2$), and methylyne ($CH$) functional groups as well as $C$ bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($(CH_3)_2CH$) and t-butyl ($(CH_3)_3C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups. The branched-chain-alkane groups in alkenes are equivalent to those in branched-chain alkanes. The solution of the functional groups comprises the hybridization of the $2s$ and $2p$ AOs of each $C$ to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between two $C2sp^3$ HOs to form a MO permits each participating hybridized orbital to decrease in radius and energy. $E_T\left(atom-atom,msp^3.AO\right)$ of the $C=C$-bond MO in Eq. (15.61) due to the charge donation from the $C$ atoms to the MO is equivalent to that of ethylene, $-2.26759\ eV$, given by Eq. (14.247). $E_T\left(atom-atom,msp^3.AO\right)$ of each $C-C$-bond MO in Eq. (15.61) is $-1.85836\ eV$ or $-1.44915\ eV$ based on the energy match between the $C2sp^3$ HOs corresponding to the energy contributions equivalent to those of methylene, $-0.92918\ eV$ (Eq. (14.513)), or methyl, $-0.72457\ eV$ (Eq. (14.151)), groups, respectively.

The symbols of the functional groups of alkenes are given in Table 15.15. The geometrical (Eqs. (15.1-15.5) and (15.41)), intercept (Eqs. (15.80-15.87)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkenes are given in Tables 15.16, 15.17, and 15.18, respectively. The total energy of each alkene given in Table 15.19 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.18 corresponding to functional-group composition of the molecule. For each set of unpaired electrons created by bond breakage, the $C2sp^3$ HO magnetic energy $E_{mag}$ that is subtracted from the weighted sum of the $E_D(Group)$ $(eV)$ values based on composition is given by Eq. (15.67). The bond angle parameters of alkenes, determined using Eqs. (15.88-15.117), are given in Table 15.20. The color scale, translucent view of the charge-density of exemplary alkene, propene, comprising the concentric shells of atoms with the outer shell bridged by one or more $H_2$-type ellipsoidal MOs or joined with one or more hydrogen MOs is shown in Figure 15.3.

Figure 15.3. Color scale, translucent view of the charge-density of propene showing the orbitals of the atoms at their radii, the ellipsoidal surface of each $H$ or $H_2$-type ellipsoidal MO that transitions to the corresponding outer shell of the atom(s) participating in each bond, and the hydrogen nuclei (red, not to scale). (A) Top view. (B) Side view.

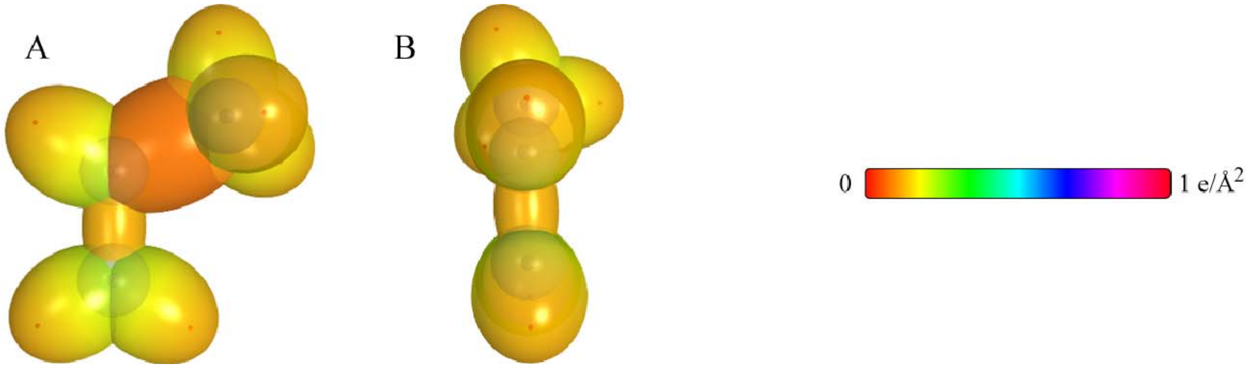


Table 15.15. The symbols of functional groups of alkenes.

| Functional Group | Group Symbol |
|---|---|
| *CC* double bond | $C=C$ |
| *C* vinyl single bond to -*C(C)=C* | $C-C$ (i) |
| *C* vinyl single bond to -*C(H)=C* | $C-C$ (ii) |
| *C* vinyl single bond to -*C(C)=CH*$_2$ | $C-C$ (iii) |
| *CH*$_2$ alkenyl group | $C-H\ (CH_2)$ (i) |
| *CH*$_3$ group | $C-H\ (CH_3)$ |
| *CH*$_2$ alkyl group | $C-H\ (CH_2)$ (ii) |
| *CH* | $C-H$ |
| *CC* bond (*n-C*) | $C-C$ (a) |
| *CC* bond (*iso-C*) | $C-C$ (b) |
| *CC* bond (*tert-C*) | $C-C$ (c) |
| *CC* (*iso* to *iso-C*) | $C-C$ (d) |
| *CC* (*t* to *t-C*) | $C-C$ (e) |
| *CC* (*t* to *iso-C*) | $C-C$ (f) |

Table 15.16. The geometrical bond parameters of alkenes and experimental values [1].

| Parameter | $C=C$ Group | $C-C$ (i) Group | $C-C$ (ii) Group | $C-C$ (iii) Group | $C-H$ $(CH_2)$ (i) Group | $C-H$ $(CH_3)$ Group | $C-H$ $(CH_2)$ (ii) Group | $C-H$ Group | $C-C$ (a) Group | $C-C$ (b) Group | $C-C$ (c) Group | $C-C$ (d) Group | $C-C$ (e) Group | $C-C$ (f) Group |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $a$ $(a_0)$ | 1.47228 | 2.04740 | 2.04740 | 2.04740 | 1.64010 | 1.64920 | 1.67122 | 1.67465 | 2.12499 | 2.12499 | 2.10725 | 2.12499 | 2.10725 | 2.10725 |
| $c'$ $(a_0)$ | 1.26661 | 1.43087 | 1.43087 | 1.43087 | 1.04566 | 1.04856 | 1.05553 | 1.05661 | 1.45744 | 1.45744 | 1.45164 | 1.45744 | 1.45164 | 1.45164 |
| Bond Length $2c'$ $(\mathring{A})$ | 1.34052 | 1.51437 | 1.51437 | 1.51437 | 1.10668 | 1.10974 | 1.11713 | 1.11827 | 1.54280 | 1.54280 | 1.53635 | 1.54280 | 1.53635 | 1.53635 |
| Exp. Bond Length $(\mathring{A})$ | 1.342<br>(2-methylpropene)<br>1.346<br>(2-butene)<br>1.349<br>(1,3-butadiene) |  | 1.508<br>(2-butene) | 1.508<br>(2-methylpropene) | 1.10<br>(2-methylpropene)<br>1.108 (avg.)<br>(1,3-butadiene) | 1.107<br>$(C-H$ propane)<br>1.117<br>$(C-H$ butane) | 1.107<br>$(C-H$ propane)<br>1.117<br>$(C-H$ butane) | 1.122<br>(isobutane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) |
| $b,c$ $(a_0)$ | 0.75055 | 1.46439 | 1.46439 | 1.46439 | 1.26354 | 1.27295 | 1.29569 | 1.29924 | 1.54616 | 1.54616 | 1.52750 | 1.54616 | 1.52750 | 1.52750 |
| $e$ | 0.86030 | 0.69887 | 0.69887 | 0.69887 | 0.63756 | 0.63580 | 0.63159 | 0.63095 | 0.68600 | 0.68600 | 0.68888 | 0.68600 | 0.68888 | 0.68888 |

Table 15.17. The MO to HO intercept geometrical bond parameters of alkenes. $R_1$ is an alkyl group and $R, R', R''$ are $H$ or alkyl groups. $E_T$ is $E_T$ $(atom-atom, msp^3.AO)$.

| Bond | Atom | $E_T$ (eV) Bond 1 | $E_T$ (eV) Bond 2 | $E_T$ (eV) Bond 3 | $E_T$ (eV) Bond 4 | Final Total Energy $C2sp^3$ (eV) | $r_{initial}$ $(a_0)$ | $r_{final}$ $(a_0)$ | $E_{Coulomb}(C2sp^3)$ (eV) Final | $E(C2sp^3)$ (eV) Final | $\theta'$ (°) | $\theta_1$ (°) | $\theta_2$ (°) | $d_1$ $(a_0)$ | $d_2$ $(a_0)$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $C_c(H)C_a=C_a(H)C_d$ | $C_a$ | -1.13380 | -0.92918 | 0 | 0 | -153.67867 | 0.91771 | 0.80561 | -16.88873 | -16.69786 | 127.61 | 52.39 | 58.24 | 0.77492 | 0.49168 |
| $C_c(H)C_a=C_bH_2$ | $C_b$ | -1.13380 | 0 | 0 | 0 | -152.74949 | 0.91771 | 0.85252 | -15.95955 | -15.76868 | 129.84 | 50.16 | 60.70 | 0.72040 | 0.54620 |
| $C_c(C_d)C_a=C_bH,C_e$ | $C_a$ | -1.13380 | -0.72457 | -0.72457 | 0 | -154.19863 | 0.91771 | 0.78155 | -17.40869 | -17.21783 | 126.39 | 53.61 | 56.95 | 0.80289 | 0.46371 |
| $R_1C_bH_2-C_a(C)=C$<br>$(C-C$ (i)) | $C_a$ | -1.13380 | -0.72457 | -0.72457 | 0 | -154.19863 | 0.91771 | 0.78155 | -17.40869 | -17.21783 | 60.88 | 119.12 | 27.79 | 1.81127 | 0.38039 |
| $R_1C_bH_2-C_a(C)=C$<br>$(C-C$ (i))<br><br>$R_1C_bH_2-C_a(C)=CH_2$<br>$(C-C$ (iii)) | $C_b$ | -0.72457 | -0.92918 | 0 | 0 | -153.26945 | 0.91771 | 0.82562 | -16.47951 | -16.28864 | 67.40 | 112.60 | 31.36 | 1.74821 | 0.31734 |
| $R_1C_bH_2-C_a(H)=C$<br>$(C-C$ (ii)) | $C_a$ | -1.13380 | -0.92918 | 0 | 0 | -153.67866 | 0.91771 | 0.80561 | -16.88873 | -16.69786 | 64.57 | 115.43 | 29.79 | 1.77684 | 0.34596 |
| $R_1C_bH_2-C_a(H)=C$<br>$(C-C$ (i)) | $C_b$ | -0.92918 | -0.92918 | 0 | 0 | -153.47405 | 0.91771 | 0.81549 | -16.68411 | -16.49325 | 65.99 | 114.01 | 30.58 | 1.76270 | 0.33183 |
| $C-H$ $(CH_2)$ (i) | $C$ | -1.13380 | 0 | 0 | 0 | -152.74949 | 0.91771 | 0.85252 | -15.95955 | -15.76868 | 77.15 | 102.85 | 41.13 | 1.23531 | 0.18965 |
| $C-H$ $(CH_3)$ | $C$ | -0.92918 | 0 | 0 | 0 | -152.54487 | 0.91771 | 0.86359 | -15.75493 | -15.56407 | 77.49 | 102.51 | 41.48 | 1.23564 | 0.18708 |
| $C-H$ $(CH_2)$ (ii) | $C$ | -0.92918 | -0.92918 | 0 | 0 | -153.47406 | 0.91771 | 0.81549 | -16.68412 | -16.49325 | 68.47 | 111.53 | 35.84 | 1.35486 | 0.29933 |
| $C-H$ $(CH)$ | $C$ | -0.92918 | -0.92918 | -0.92918 | 0 | -154.40324 | 0.91771 | 0.77247 | -17.61330 | -17.42244 | 61.10 | 118.90 | 31.37 | 1.42988 | 0.37326 |
| $H_3C_aC_bH_2CH_2-$<br>$(C-C$ (a)) | $C_a$ | -0.92918 | 0 | 0 | 0 | -152.54487 | 0.91771 | 0.86359 | -15.75493 | -15.56407 | 63.82 | 116.18 | 30.08 | 1.83879 | 0.38106 |
| $H_3C_aC_bH_2CH_2-$<br>$(C-C$ (a)) | $C_b$ | -0.92918 | -0.92918 | 0 | 0 | -153.47406 | 0.91771 | 0.81549 | -16.68412 | -16.49325 | 56.41 | 123.59 | 26.06 | 1.90890 | 0.45117 |
| $R-H_2C_aC_b(H_2C_c-R')HCH_2-$<br>$(C-C$ (b)) | $C_b$ | -0.92918 | -0.92918 | -0.92918 | 0 | -154.40324 | 0.91771 | 0.77247 | -17.61330 | -17.42244 | 48.30 | 131.70 | 21.90 | 1.97162 | 0.51388 |
| $R-H_2C_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$<br>$(C-C$ (c)) | $C_b$ | -0.92918 | -0.72457 | -0.72457 | -0.72457 | -154.71860 | 0.91771 | 0.75889 | -17.92866 | -17.73779 | 48.21 | 131.79 | 21.74 | 1.95734 | 0.50570 |
| $isoC_aC_b(H_2C_c-R')HCH_2-$<br>$(C-C$ (d)) | $C_b$ | -0.92918 | -0.92918 | -0.92918 | 0 | -154.40324 | 0.91771 | 0.77247 | -17.61330 | -17.42244 | 48.30 | 131.70 | 21.90 | 1.97162 | 0.51388 |
| $tertC_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$<br>$(C-C$ (e)) | $C_b$ | -0.72457 | -0.72457 | -0.72457 | -0.72457 | -154.51399 | 0.91771 | 0.76765 | -17.92866 | -17.73779 | 50.04 | 129.96 | 22.66 | 1.94462 | 0.49298 |
| $tertC_aC_b(H_2C_c-R')HCH_2-$<br>$(C-C$ (f)) | $C_b$ | -0.72457 | -0.92918 | -0.92918 | 0 | -154.19863 | 0.91771 | 0.78155 | -17.40869 | -17.21783 | 52.78 | 127.22 | 24.04 | 1.92443 | 0.47279 |
| $isoC_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$<br>$(C-C$ (f)) | $C_b$ | -0.72457 | -0.72457 | -0.72457 | -0.72457 | -154.51399 | 0.91771 | 0.76765 | -17.92866 | -17.73779 | 50.04 | 129.96 | 22.66 | 1.94462 | 0.49298 |

Table 15.18. The energy parameters ($eV$) of functional groups of alkenes.

| Parameters | $C=C$ Group | $C-C$ (i) Group | $C-C$ (ii) Group | $C-C$ (iii) Group | $CH_2$ (i) Group | $CH_3$ Group | $CH_2$ (ii) Group | $C-H$ Group | $C-C$ (a) Group | $C-C$ (b) Group | $C-C$ (c) Group | $C-C$ (d) Group | $C-C$ (e) Group | $C-C$ (f) Group |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $n_1$ | 2 | 1 | 1 | 1 | 2 | 3 | 2 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $n_2$ | 0 | 0 | 0 | 0 | 1 | 2 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $n_3$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $C_1$ | 0.5 | 0.5 | 0.5 | 0.5 | 0.75 | 0.75 | 0.75 | 0.75 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| $C_2$ | 0.91771 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $c_1$ | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $c_2$ | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 |
| $c_3$ | 0 | 1 | 0 | 1 | 1 | 0 | 1 | 1 | 0 | 0 | 0 | 1 | 1 | 0 |
| $c_4$ | 4 | 2 | 2 | 2 | 1 | 1 | 1 | 1 | 2 | 2 | 2 | 2 | 2 | 2 |
| $c_5$ | 0 | 0 | 0 | 0 | 2 | 3 | 2 | 1 | 0 | 0 | 0 | 0 | 0 | 0 |
| $C_{1o}$ | 0.5 | 0.5 | 0.5 | 0.5 | 0.75 | 0.75 | 0.75 | 0.75 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| $C_{2o}$ | 0.91771 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $V_e\ (eV)$ | -102.08992 | -30.19634 | -30.19634 | -30.19634 | -72.03287 | -107.32728 | -70.41425 | -35.12015 | -28.79214 | -28.79214 | -29.10112 | -28.79214 | -29.10112 | -29.10112 |
| $V_p\ (eV)$ | 21.48386 | 9.50874 | 9.50874 | 9.50874 | 26.02344 | 38.92728 | 25.78002 | 12.87680 | 9.33352 | 9.33352 | 9.37273 | 9.33352 | 9.37273 | 9.37273 |
| $T\ (eV)$ | 34.67062 | 7.37432 | 7.37432 | 7.37432 | 21.95990 | 32.53914 | 21.06675 | 10.48582 | 6.77464 | 6.77464 | 6.90500 | 6.77464 | 6.90500 | 6.90500 |
| $V_m\ (eV)$ | -17.33531 | -3.68716 | -3.68716 | -3.68716 | -10.97995 | -16.26957 | -10.53337 | -5.24291 | -3.38732 | -3.38732 | -3.45250 | -3.38732 | -3.45250 | -3.45250 |
| $E(_{AO/HO})\ (eV)$ | 0 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -15.56407 | -15.56407 | -14.63489 | -15.56407 | -15.56407 | -15.35946 | -15.56407 | -15.35946 | -15.35946 |
| $\Delta E_{H_2MO}(_{AO/HO})\ (eV)$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $E_T(_{AO/HO})\ (eV)$ | 0 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -15.56407 | -15.56407 | -14.63489 | -15.56407 | -15.56407 | -15.35946 | -15.56407 | -15.35946 | -15.35946 |
| $E_T(_{H_2MO})\ (eV)$ | -63.27075 | -31.63534 | -31.63534 | -31.63534 | -49.66437 | -67.69451 | -49.66493 | -31.63533 | -31.63537 | -31.63537 | -31.63535 | -31.63537 | -31.63535 | -31.63535 |
| $E_T\left(atom-atom, msp^3.AO\right)\ (eV)$ | -2.26759 | -1.44915 | -1.85836 | -1.44915 | 0 | 0 | 0 | 0 | -1.85836 | -1.85836 | -1.44915 | -1.85836 | -1.44915 | -1.44915 |
| $E_T(_{MO})\ (eV)$ | -65.53833 | -33.08452 | -33.49373 | -33.08452 | -49.66493 | -67.69450 | -49.66493 | -31.63537 | -33.49373 | -33.49373 | -33.08452 | -33.49373 | -33.08452 | -33.08452 |
| $\omega\ \left(10^{15}\ rad/s\right)$ | 43.0680 | 9.97851 | 16.4962 | 9.97851 | 25.2077 | 24.9286 | 24.2751 | 24.1759 | 9.43699 | 9.43699 | 15.4846 | 9.43699 | 9.55643 | 9.55643 |
| $E_K\ (eV)$ | 28.34813 | 6.56803 | 10.85807 | 6.56803 | 16.59214 | 16.40846 | 15.97831 | 15.91299 | 6.21159 | 6.21159 | 10.19220 | 6.21159 | 6.29021 | 6.29021 |
| $\bar{E}_D\ (eV)$ | -0.34517 | -0.16774 | -0.21834 | -0.16774 | -0.25493 | -0.25352 | -0.25017 | -0.24966 | -0.16515 | -0.16515 | -0.20896 | -0.16515 | -0.16416 | -0.16416 |
| $\bar{E}_{Kvib}\ (eV)$ | 0.17897<br>[6] | 0.15895<br>[7] | 0.09931<br>[8] | 0.09931<br>[8] | 0.35532<br>Eq. (13.458) | 0.35532<br>Eq. (13.458) | 0.35532<br>Eq. (13.458) | 0.35532<br>Eq. (13.458) | 0.12312<br>[2] | 0.17978<br>[4] | 0.09944<br>[5] | 0.12312<br>[2] | 0.12312<br>[2] | 0.12312<br>[2] |
| $\bar{E}_{osc}\ (eV)$ | -0.25568 | -0.08827 | -0.16869 | -0.11809 | -0.07727 | -0.22757 | -0.14502 | -0.07200 | -0.10359 | -0.07526 | -0.15924 | -0.10359 | -0.10260 | -0.10260 |
| $E_{mag}\ (eV)$ | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 |
| $E_T(_{Group})\ (eV)$ | -66.04969 | -33.17279 | -33.66242 | -33.20260 | -49.81948 | -67.92207 | -49.80996 | -31.70737 | -33.59732 | -33.49373 | -33.24376 | -33.59732 | -33.18712 | -33.18712 |
| $E_{initial}(_{c_4\ AO/HO})\ (eV)$ | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 |
| $E_{initial}(_{c_5\ AO/HO})\ (eV)$ | 0 | 0 | 0 | 0 | -13.59844 | -13.59844 | -13.59844 | -13.59844 | 0 | 0 | 0 | 0 | 0 | 0 |
| $E_D(_{Group})\ (eV)$ | 7.51014 | 3.75498 | 4.39264 | 3.78480 | 7.83968 | 12.49186 | 7.83016 | 3.32601 | 4.32754 | 4.29921 | 3.97398 | 4.17951 | 3.62128 | 3.91734 |

Table 15.19. The total bond energies of alkenes calculated using the functional group composition and the energies of Table 15.18 compared to the experimental values [3]. The magnetic energy $E_{mag}$ that is subtracted from the weighted sum of the $E_{D\,(Group)}$ $(eV)$ values based on composition is given by (15.58).

| Formula | Name | $C=C$ | $C-C$ (i) | $C-C$ (ii) | $C-C$ (iii) | $CH_2$ (i) | $CH_3$ | $CH_2$ (ii) | $CH$ | $C-C$ (a) | $C-C$ (b) | $C-C$ (c) | $C-C$ (d) | $C-C$ (e) | $C-C$ (f) | $E_{mag}$ | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $C_3H_6$ | Propene | 1 | 0 | 1 | 0 | 1 | 1 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 35.56033 | 35.63207 | 0.00201 |
| $C_4H_8$ | 1-Butene | 1 | 0 | 1 | 0 | 1 | 1 | 1 | 1 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 47.71803 | 47.78477 | 0.00140 |
| $C_4H_8$ | trans-2-Butene | 1 | 0 | 2 | 0 | 0 | 2 | 0 | 2 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 47.93116 | 47.90395 | -0.00057 |
| $C_4H_8$ | Isobutene | 1 | 0 | 0 | 2 | 1 | 2 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 47.90314 | 47.96096 | 0.00121 |
| $C_5H_{10}$ | 1-Pentene | 1 | 0 | 1 | 0 | 1 | 1 | 2 | 1 | 2 | 0 | 0 | 0 | 0 | 0 | 0 | 59.87573 | 59.95094 | 0.00125 |
| $C_5H_{10}$ | trans-2-Pentene | 1 | 0 | 2 | 0 | 0 | 2 | 1 | 2 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 60.08886 | 60.06287 | -0.00043 |
| $C_5H_{10}$ | 2-Methyl-1-butene | 1 | 0 | 0 | 2 | 1 | 2 | 1 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 60.06084 | 60.09707 | 0.00060 |
| $C_5H_{10}$ | 2-Methyl-2-butene | 1 | 2 | 1 | 0 | 0 | 3 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 60.21433 | 60.16444 | -0.00083 |
| $C_5H_{10}$ | 3-Methyl-1-butene | 1 | 0 | 1 | 0 | 1 | 2 | 0 | 2 | 0 | 2 | 0 | 0 | 0 | 0 | 0 | 59.97662 | 60.01727 | 0.00068 |
| $C_6H_{12}$ | 1-Hexene | 1 | 0 | 1 | 0 | 1 | 1 | 3 | 1 | 3 | 0 | 0 | 0 | 0 | 0 | 0 | 72.03343 | 72.12954 | 0.00133 |
| $C_6H_{12}$ | trans-2-Hexene | 1 | 0 | 2 | 0 | 0 | 2 | 2 | 2 | 2 | 0 | 0 | 0 | 0 | 0 | 0 | 72.24656 | 72.23733 | -0.00013 |
| $C_6H_{12}$ | trans-3-Hexene | 1 | 0 | 2 | 0 | 0 | 2 | 2 | 2 | 2 | 0 | 0 | 0 | 0 | 0 | 0 | 72.24656 | 72.24251 | -0.00006 |
| $C_6H_{12}$ | 2-Methyl-1-pentene | 1 | 0 | 0 | 2 | 1 | 2 | 2 | 0 | 2 | 0 | 0 | 0 | 0 | 0 | 0 | 72.21854 | 72.29433 | 0.00105 |
| $C_6H_{12}$ | 2-Methyl-2-pentene | 1 | 2 | 1 | 0 | 0 | 3 | 1 | 1 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 72.37203 | 72.37206 | 0.00000 |
| $C_6H_{12}$ | 3-Methyl-1-pentene | 1 | 0 | 1 | 0 | 1 | 2 | 1 | 2 | 1 | 2 | 0 | 0 | 0 | 0 | 0 | 72.13432 | 72.19173 | 0.00080 |
| $C_6H_{12}$ | 4-Methyl-1-pentene | 1 | 0 | 1 | 0 | 1 | 2 | 1 | 2 | 0 | 3 | 0 | 0 | 0 | 0 | 0 | 72.10599 | 72.21038 | 0.00145 |
| $C_6H_{12}$ | 3-Methyl-trans-2-pentene | 1 | 2 | 1 | 0 | 0 | 3 | 1 | 1 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 72.37203 | 72.33268 | -0.00054 |
| $C_6H_{12}$ | 4-Methyl-trans-2-pentene | 1 | 0 | 2 | 0 | 0 | 3 | 0 | 3 | 0 | 2 | 0 | 0 | 0 | 0 | 0 | 72.34745 | 72.31610 | -0.00043 |
| $C_6H_{12}$ | 2-Ethyl-1-butene | 1 | 0 | 0 | 2 | 1 | 2 | 2 | 0 | 2 | 0 | 0 | 0 | 0 | 0 | 0 | 72.21854 | 72.25909 | 0.00056 |
| $C_6H_{12}$ | 2,3-Dimethyl-1-butene | 1 | 0 | 0 | 2 | 1 | 3 | 0 | 1 | 0 | 2 | 0 | 0 | 0 | 0 | 0 | 72.31943 | 72.32543 | 0.00008 |
| $C_6H_{12}$ | 3,3-Dimethyl-1-butene | 1 | 0 | 1 | 0 | 1 | 3 | 0 | 1 | 0 | 0 | 3 | 0 | 0 | 0 | -1 | 72.31796 | 72.30366 | -0.00020 |
| $C_6H_{12}$ | 2,3-Dimethyl-2-butene | 1 | 4 | 0 | 0 | 0 | 4 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 72.49750 | 72.38450 | -0.00156 |
| $C_7H_{14}$ | 1-Heptene | 1 | 0 | 1 | 0 | 1 | 1 | 4 | 1 | 4 | 0 | 0 | 0 | 0 | 0 | 0 | 84.19113 | 84.27084 | 0.00095 |
| $C_7H_{14}$ | 5-Methyl-1-hexene | 1 | 0 | 1 | 0 | 1 | 2 | 2 | 2 | 1 | 3 | 0 | 0 | 0 | 0 | 0 | 84.26369 | 84.30608 | 0.00050 |
| $C_7H_{14}$ | trans-3-Methyl-3-hexene | 1 | 2 | 1 | 0 | 0 | 3 | 2 | 1 | 2 | 0 | 0 | 0 | 0 | 0 | 0 | 84.52973 | 84.42112 | -0.00129 |
| $C_7H_{14}$ | 2,4-Dimethyl-1-pentene | 1 | 0 | 0 | 2 | 1 | 3 | 1 | 1 | 0 | 3 | 0 | 0 | 0 | 0 | 0 | 84.44880 | 84.49367 | 0.00053 |
| $C_7H_{14}$ | 4,4-Dimethyl-1-pentene | 1 | 0 | 1 | 0 | 1 | 3 | 1 | 1 | 0 | 0 | 4 | 0 | 0 | 0 | 0 | 84.27012 | 84.47087 | 0.00238 |
| $C_7H_{14}$ | 2,4-Dimethyl-2-pentene | 1 | 2 | 1 | 0 | 0 | 4 | 0 | 2 | 0 | 2 | 0 | 0 | 0 | 0 | 0 | 84.63062 | 84.54445 | -0.00102 |
| $C_7H_{14}$ | trans-4,4-Dimethyl-2-pentene | 1 | 0 | 2 | 0 | 0 | 4 | 0 | 2 | 0 | 0 | 3 | 0 | 0 | 0 | -2 | 84.54076 | 84.54549 | 0.00006 |
| $C_7H_{14}$ | 2-Ethyl-3-methyl-1-butene | 1 | 0 | 0 | 2 | 1 | 3 | 1 | 1 | 1 | 2 | 0 | 0 | 0 | 0 | 0 | 84.47713 | 84.44910 | -0.00033 |
| $C_7H_{14}$ | 2,3,3-Trimethyl-1-butene | 1 | 0 | 0 | 2 | 1 | 4 | 0 | 0 | 0 | 0 | 3 | 0 | 0 | 0 | -2 | 84.51274 | 84.51129 | -0.00002 |
| $C_8H_{16}$ | 1-Octene | 1 | 0 | 1 | 0 | 1 | 1 | 5 | 1 | 5 | 0 | 0 | 0 | 0 | 0 | 0 | 96.34883 | 96.41421 | 0.00068 |
| $C_8H_{16}$ | trans-2,2-Dimethyl-3-hexene | 1 | 0 | 2 | 0 | 0 | 4 | 1 | 2 | 1 | 0 | 3 | 0 | 0 | 0 | -2 | 96.69846 | 96.68782 | -0.00011 |
| $C_8H_{16}$ | 3-Ethyl-2-methyl-1-pentene | 1 | 0 | 0 | 2 | 1 | 3 | 2 | 1 | 2 | 2 | 0 | 0 | 0 | 0 | 0 | 96.63483 | 96.61113 | -0.00025 |
| $C_8H_{16}$ | 2,4,4-Trimethyl-1-pentene | 1 | 0 | 0 | 2 | 1 | 4 | 1 | 0 | 0 | 0 | 4 | 0 | 0 | 0 | 0 | 96.61293 | 96.71684 | 0.00107 |
| $C_8H_{16}$ | 2,4,4-Trimethyl-2-pentene | 1 | 2 | 1 | 0 | 0 | 5 | 0 | 1 | 0 | 0 | 3 | 0 | 0 | 0 | -3 | 96.67590 | 96.65880 | -0.00018 |
| $C_{10}H_{20}$ | 1-Decene | 1 | 0 | 1 | 0 | 1 | 1 | 7 | 1 | 7 | 0 | 0 | 0 | 0 | 0 | 0 | 120.66423 | 120.74240 | 0.00065 |
| $C_{12}H_{24}$ | 1-Dodecene | 1 | 0 | 1 | 0 | 1 | 1 | 9 | 1 | 9 | 0 | 9 | 0 | 0 | 0 | 0 | 144.97963 | 145.07163 | 0.00063 |
| $C_{16}H_{32}$ | 1-Hexadecene | 1 | 0 | 1 | 0 | 1 | 1 | 13 | 1 | 13 | 0 | 0 | 0 | 0 | 0 | 0 | 193.61043 | 193.71766 | 0.00055 |

Table 15.20. The bond angle parameters of alkenes and experimental values [1]. In the calculation of $\theta_v$, the parameters from the preceding angle were used. $E_T$ is $E_T$ $(atom - atom, msp^3.AO)$.

| Atoms of Angle | 2c' Bond 1 $(a_0)$ | 2c' Bond 2 $(a_0)$ | 2c' Terminal Atoms $(a_0)$ | $E_{Coulombic}$ Atom 1 | Atom 1 Hybridization Designation (Table 15.3.A) | $E_{Coulombic}$ Atom 2 | Atom 2 Hybridization Designation (Table 15.3.A) | $c_2$ Atom 1 | $c_2$ Atom 2 | $C_1$ | $C_2$ | $c_1$ | $c_2'$ | $E_T$ (eV) | $\theta_v$ (°) | $\theta_1$ (°) | $\theta_2$ (°) | Cal. $\theta$ (°) | Exp. $\theta$ (°) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $\angle HC_aC_c$<br>$(C_c(H)C_a=C_b)$ | 2.11323 | 2.86175 | 4.2895 | -15.95955<br>$C_a$ | 10 | -14.82575<br>$C_c$ | 1 | 0.85252 | 0.91771 | 0.75 | 1 | 0.75 | 1.07647 | 0 | | | | 118.36 | |
| $\angle C_cC_aC_c$<br>$(C_c(C_c)C_a=C_b)$ | 2.86175 | 2.86175 | 4.7958 | -16.68411<br>$C_c$ | 25 | -16.68411<br>$C_c$ | 25 | 0.81549 | 0.81549 | 1 | 1 | 1 | 0.81549 | -1.85836 | | | | 113.84 | |
| $\angle C_bC_aC_c$<br>$(C_b=C_aC_c)$ | 2.53321 | 2.86175 | 4.7539 | -16.88873<br>$C_b$ | 29 | -16.68411<br>$C_c$ | 25 | 0.80561 | 0.81549 | 1 | 1 | 1 | 0.81055 | -1.85836 | | | | 123.46 | 124.4<br>(1,3,5-hexatriene CbCcCc)<br>121.7<br>(1,3,5-hexatriene CaCbCc)<br>124.4<br>(1,3-butadiene CCC)<br>125.3<br>(2-butene CbCaCc) |
| $\angle HC_aC_b$ | | | | | | | | | | | | | | | | 118.36 | 123.46 | 118.19 | |
| $\angle HC_aH$<br>$(H_2C_a=C_bC_c)$ | 2.04578 | 2.04578 | 3.4756 | -15.95955 | 10 | H | H | 0.85252 | 1 | 1 | 1 | 0.75 | 1.17300 | 0 | | | | 116.31 | 118.5<br>(2-methylpropene) |
| $\angle C_bC_aH$<br>$(H_2C_a=C_bC_c)$ | | | | | | | | | | | | | | | | 116.31 | | 121.85 | 121<br>(2-methylpropene) |
| Methylene<br>$\angle HC_aH$ | 2.11106 | 2.11106 | 3.4252 | -15.75493 | 7 | H | H | 0.86359 | 1 | 1 | 1 | 0.75 | 1.15796 | 0 | | | | 108.44 | 107<br>(propane) |
| $\angle C_aC_bC_c$ | | | | | | | | | | | | | | | 69.51 | | | 110.49 | 112<br>(propane)<br>113.8<br>(butane)<br>110.8<br>(isobutane) |
| $\angle C_aC_bH$ | | | | | | | | | | | | | | | 69.51 | | | 110.49 | 111.0<br>(butane)<br>111.4<br>(isobutane) |
| Methyl<br>$\angle HC_aH$ | 2.09711 | 2.09711 | 3.4252 | -15.75493 | 7 | H | H | 0.86359 | 1 | 1 | 1 | 0.75 | 1.15796 | 0 | | | | 109.50 | |
| $\angle C_aC_bC_c$ | | | | | | | | | | | | | | | 70.56 | | | 109.44 | |
| $\angle C_aC_bH$ | | | | | | | | | | | | | | | 70.56 | | | 109.44 | |
| $\angle C_bC_aC_c$<br>iso $C_a$ | 2.91547 | 2.91547 | 4.7958 | -16.68412<br>$C_b$ | 26 | -16.68412<br>$C_c$ | 26 | 0.81549 | 0.81549 | 1 | 1 | 1 | 0.81549 | -1.85836 | | | | 110.67 | 110.8<br>(isobutane) |
| $\angle C_bC_aH$<br>iso $C_a$ | 2.91547 | 2.11323 | 4.1633 | -15.55033<br>$C_a$ | 5 | -14.82575<br>$C_b$ | 1 | 0.87495 | 0.91771 | 0.75 | 1 | 0.75 | 1.04887 | 0 | | | | 110.76 | |
| $\angle C_aC_bH$<br>iso $C_a$ | 2.91547 | 2.09711 | 4.1633 | -15.55033<br>$C_b$ | 5 | -14.82575<br>$C_a$ | 1 | 0.87495 | 0.91771 | 0.75 | 1 | 0.75 | 1.04887 | 0 | | | | 111.27 | 111.4<br>(isobutane) |
| $\angle C_bC_aC_b$<br>tert $C_a$ | 2.90327 | 2.90327 | 4.7958 | -16.68412<br>$C_b$ | 26 | -16.68412<br>$C_b$ | 26 | 0.81549 | 0.81549 | 1 | 1 | 1 | 0.81549 | -1.85836 | | | | 111.37 | 110.8<br>(isobutane) |
| $\angle C_bC_aC_d$ | | | | | | | | | | | | | | | 72.50 | | | 107.50 | |

## ALKYNES ($C_nH_{2n-2},\ n=3,4,5...\infty$)

The straight and branched-chain alkynes, $C_nH_{2n-2}$, have at least one carbon-carbon triple bond comprising a functional group that is solved equivalently to the triple bond of acetylene. The triple bond may be bound to one or two carbon single bonds that substitute for the hydrogen atoms of acetylene. Based on the energy matching of the mutually bound $C$, these $C-C$-bond MOs are defined as primary and secondary $C-C$ functional groups, respectively, that are unique to alkynes. In addition, the corresponding terminal $CH$ of a primary alkyne comprises a functional group that is solved equivalently to the methylyne group of acetylene as given in the Acetylene Molecule section.

The alkyl portion of the alkyne may comprise at least two terminal methyl groups ($CH_3$) at each end of the chain, and may comprise methylene ($CH_2$), and methylyne ($CH$) functional groups as well as $C$ bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($(CH_3)_2CH$) and t-butyl ($(CH_3)_3C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups. The branched-chain-alkane groups in alkynes are equivalent to those in branched-chain alkanes.

The solution of the functional groups comprises the hybridization of the $2s$ and $2p$ AOs of each $C$ to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between two $C2sp^3$ HOs to form a MO permits each participating hybridized orbital to decrease in radius and energy. $E_T\left(atom-atom,msp^3.AO\right)$ of the $C\equiv C$-bond MO in Eq. (15.61) due to the charge donation from the $C$ atoms to the MO is equivalent to that of acetylene, $-3.13026\ eV$, given by Eq. (14.342). $E_T\left(atom-atom,msp^3.AO\right)$ of each -alkyl-bond MO in Eq. (15.61) is $-1.85836\ eV$ or $-1.44915\ eV$ based on the energy match between the $C2sp^3$ HOs corresponding to the energy contributions equivalent to those of methylene, $-0.92918\ eV$ (Eq. (14.513)), or methyl, $-0.72457\ eV$ (Eq. (14.151)), groups, respectively. For the $C-C$ groups each comprising a $C$ single bond to $C\equiv C$, $E_T\left(atom-atom,msp^3.AO\right)$ is $-0.72457\ eV$ based on the energy match between the $C2sp^3$ HOs for the mutually bound $C$ of the single and triple bonds. The parameter $\omega$ of each group is matched for oscillation in the transition state based on the group being primary or secondary.

The symbols of the functional groups of alkynes are given in Table 15.21. The geometrical (Eqs. (15.1-15.5) and (15.51)), intercept (Eqs. (15.80-15.87)), and energy (Eqs. (15.6-15.11) and (15.17-15.65)) parameters of alkynes are given in Tables 15.22, 15.23, and 15.24, respectively. The total energy of each alkyne given in Table 15.25 is calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.24 corresponding to functional-group composition of the molecule. The bond angle parameters of alkynes determined using Eqs. (15.88-15.117) are given in Table 15.26. Each $C$ of the $C\equiv C$ group can further bond with only one atom, and the bond is linear as a minimum of energy as in the case of acetylene. The color scale, translucent view of the charge-density of exemplary alkyne, propyne, comprising the concentric shells of atoms with the outer shell bridged by one or more $H_2$-type ellipsoidal MOs or joined with one or more hydrogen MOs is shown in Figure 15.4.

Figure 15.4. Color scale, translucent view of the charge-density of propyne showing the orbitals of the atoms at their radii, the ellipsoidal surface of each $H$ or $H_2$-type ellipsoidal MO that transitions to the corresponding outer shell of the atom(s) participating in each bond, and the hydrogen nuclei (red, not to scale).

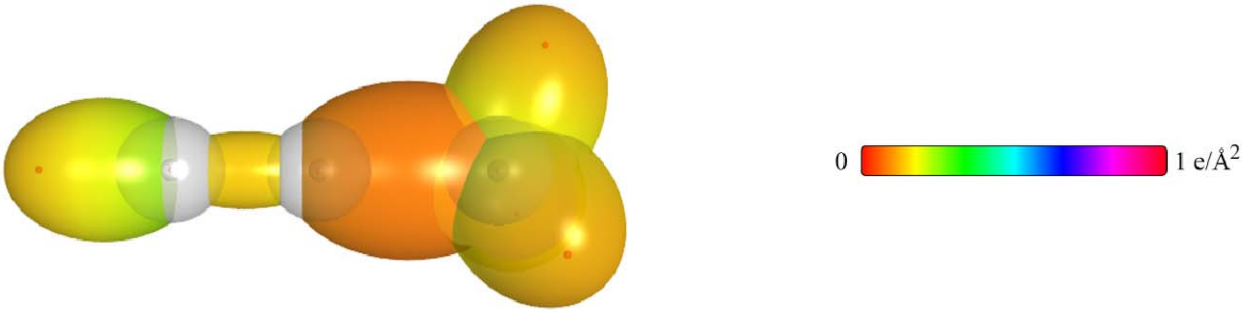


Table 15.21. The symbols of functional groups of alkynes.

| Functional Group | Group Symbol |
|---|---|
| *CC* triple bond | $C\equiv C$ |
| *C* single bond to $C\equiv C$ (1°) | $C-C$ (i) |
| *C* single bond to $C\equiv C$ (2°) | $C-C$ (ii) |
| *CH* (terminal) | $C-H$ (i) |
| $CH_3$ group | $C-H\ (CH_3)$ |
| $CH_2$ group | $C-H\ (CH_2)$ |
| *CH* (alkyl) | $C-H$ (ii) |
| *CC* bond (*n-C*) | $C-C$ (a) |
| *CC* bond (*iso-C*) | $C-C$ (b) |
| *CC* bond (*tert-C*) | $C-C$ (c) |
| *CC* (*iso* to *iso-C*) | $C-C$ (d) |
| *CC* (*t* to *t-C)* | $C-C$ (e) |
| *CC* (*t* to *iso-C*) | $C-C$ (f) |

Table 15.22. The geometrical bond parameters of alkynes and experimental values [1].

| Parameter | $C \equiv C$ Group | $C-C$ (i) Group | $C-C$ (ii) Group | $C-H$ (i) Group | $C-H$ $(CH_3)$ Group | $C-H$ $(CH_2)$ Group | $C-H$ (ii) Group | $C-C$ (a) Group | $C-C$ (b) Group | $C-C$ (c) Group | $C-C$ (d) Group | $C-C$ (e) Group | $C-C$ (f) Group |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $a$ $(a_0)$ | 1.28714 | 1.99185 | 1.99185 | 1.48719 | 1.64920 | 1.67122 | 1.67465 | 2.12499 | 2.12499 | 2.10725 | 2.12499 | 2.10725 | 2.10725 |
| $c'$ $(a_0)$ | 1.13452 | 1.41133 | 1.41133 | 0.99572 | 1.04856 | 1.05553 | 1.05661 | 1.45744 | 1.45744 | 1.45164 | 1.45744 | 1.45164 | 1.45164 |
| Bond Length $2c'$ $(\AA)$ | 1.20072 | 1.49369 | 1.49369 | 1.05383 | 1.10974 | 1.11713 | 1.11827 | 1.54280 | 1.54280 | 1.53635 | 1.54280 | 1.53635 | 1.53635 |
| Exp. Bond Length $(\AA)$ | 1.203<br>(acetylene)<br>1.208<br>(2,4-hexadiyne) | 1.450<br>(2,4-hexadiyne) | 1.450<br>(2,4-hexadiyne) | 1.060<br>(acetylene) | 1.107<br>($C-H$ propane)<br>1.117<br>($C-H$ butane) | 1.107<br>($C-H$ propane)<br>1.117<br>($C-H$ butane) | 1.122<br>(isobutane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) |
| $b,c$ $(a_0)$ | 0.60793 | 1.40557 | 1.40557 | 1.10466 | 1.27295 | 1.29569 | 1.29924 | 1.54616 | 1.54616 | 1.52750 | 1.54616 | 1.52750 | 1.52750 |
| $e$ | 0.88143 | 0.70855 | 0.70855 | 0.66953 | 0.63580 | 0.63159 | 0.63095 | 0.68600 | 0.68600 | 0.68888 | 0.68600 | 0.68888 | 0.68888 |

Table 15.23. The MO to HO intercept geometrical bond parameters of alkynes. $E_T$ is $E_T$ $(atom-atom, msp^3.AO)$.

| Bond | Atom | $E_T$ (eV) Bond 1 | $E_T$ (eV) Bond 2 | $E_T$ (eV) Bond 3 | $E_T$ (eV) Bond 4 | Final Total Energy $C2sp^3$ (eV) | $r_{initial}$ $(a_0)$ | $r_{final}$ $(a_0)$ | $E_{Coulomb}(C2sp^3)$ (eV) Final | $E(C2sp^3)$ (eV) Final | $\theta'$ (°) | $\theta_1$ (°) | $\theta_2$ (°) | $d_1$ $(a_0)$ | $d_2$ $(a_0)$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $RC_cC_bC_a-H$ | $C_a$ | -1.56513 | 0 | 0 | 0 | -153.18082 | 0.91771 | 0.83008 | -16.39088 | -16.20002 | 90.99 | 89.01 | 48.71 | 0.98144 | 0.01428 |
| $C_cC_a \equiv C_bH$ | $C_a$ | -1.56513 | -0.36229 | 0 | 0 | -153.54311 | 0.91771 | 0.81213 | -16.75317 | -16.56231 | 137.17 | 42.83 | 65.25 | 0.53890 | 0.59562 |
| $C_cC_a \equiv C_bH$ | $C_b$ | -1.56513 | 0 | 0 | 0 | -153.18082 | 0.91771 | 0.83008 | -16.39088 | -16.20002 | 137.91 | 42.09 | 66.24 | 0.51853 | 0.61599 |
| $C_c-C_a \equiv C_bH$ | $C_c$ | -0.36229 | -0.92918 | 0 | 0 | -152.90716 | 0.91771 | 0.84418 | -16.11722 | -15.92636 | 75.71 | 104.29 | 35.59 | 1.61974 | 0.20841 |
| $C-H$ $(CH_3)$ | $C$ | -0.92918 | 0 | 0 | 0 | -152.54487 | 0.91771 | 0.86359 | -15.75493 | -15.56407 | 77.49 | 102.51 | 41.48 | 1.23564 | 0.18708 |
| $C-H$ $(CH_2)$ | $C$ | -0.92918 | -0.92918 | 0 | 0 | -153.47406 | 0.91771 | 0.81549 | -16.68412 | -16.49325 | 68.47 | 111.53 | 35.84 | 1.35486 | 0.29933 |
| $C-H$ $(CH)$ | $C$ | -0.92918 | -0.92918 | -0.92918 | 0 | -154.40324 | 0.91771 | 0.77247 | -17.61330 | -17.42244 | 61.10 | 118.90 | 31.37 | 1.42988 | 0.37326 |
| $H_3C_aC_bH_2CH_2-$ $(C-C$ (a)) | $C_a$ | -0.92918 | 0 | 0 | 0 | -152.54487 | 0.91771 | 0.86359 | -15.75493 | -15.56407 | 63.82 | 116.18 | 30.08 | 1.83879 | 0.38106 |
| $H_3C_aC_bH_2CH_2-$ $(C-C$ (a)) | $C_b$ | -0.92918 | -0.92918 | 0 | 0 | -153.47406 | 0.91771 | 0.81549 | -16.68412 | -16.49325 | 56.41 | 123.59 | 26.06 | 1.90890 | 0.45117 |
| $R-H_2C_aC_b(H_2C_c-R')HCH_2-$ $(C-C$ (b)) | $C_b$ | -0.92918 | -0.92918 | -0.92918 | 0 | -154.40324 | 0.91771 | 0.77247 | -17.61330 | -17.42244 | 48.30 | 131.70 | 21.90 | 1.97162 | 0.51388 |
| $R-H_2C_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ $(C-C$ (c)) | $C_b$ | -0.92918 | -0.72457 | -0.72457 | -0.72457 | -154.71860 | 0.91771 | 0.75889 | -17.92866 | -17.73779 | 48.21 | 131.79 | 21.74 | 1.95734 | 0.50570 |
| $isoC_aC_b(H_2C_c-R')HCH_2-$ $(C-C$ (d)) | $C_b$ | -0.92918 | -0.92918 | -0.92918 | 0 | -154.40324 | 0.91771 | 0.77247 | -17.61330 | -17.42244 | 48.30 | 131.70 | 21.90 | 1.97162 | 0.51388 |
| $tertC_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ $(C-C$ (e)) | $C_b$ | -0.72457 | -0.72457 | -0.72457 | -0.72457 | -154.51399 | 0.91771 | 0.76765 | -17.92866 | -17.73779 | 50.04 | 129.96 | 22.66 | 1.94462 | 0.49298 |
| $tertC_aC_b(H_2C_c-R')HCH_2-$ $(C-C$ (f)) | $C_b$ | -0.72457 | -0.92918 | -0.92918 | 0 | -154.19863 | 0.91771 | 0.78155 | -17.40869 | -17.21783 | 52.78 | 127.22 | 24.04 | 1.92443 | 0.47279 |
| $isoC_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ $(C-C$ (f)) | $C_b$ | -0.72457 | -0.72457 | -0.72457 | -0.72457 | -154.51399 | 0.91771 | 0.76765 | -17.92866 | -17.73779 | 50.04 | 129.96 | 22.66 | 1.94462 | 0.49298 |

Table 15.24. The energy parameters ($eV$) of functional groups of alkynes.

| Parameters | $C \equiv C$ Group | $C-C$ (i) Group | $C-C$ (ii) Group | $C-H$ (i) Group | $CH_3$ Group | $CH_2$ Group | $C-H$ (ii) Group | $C-C$ (a) Group | $C-C$ (b) Group | $C-C$ (c) Group | $C-C$ (d) Group | $C-C$ (e) Group | $C-C$ (f) Group |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $n_1$ | 3 | 1 | 1 | 1 | 3 | 2 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $n_2$ | 0 | 0 | 0 | 0 | 2 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $n_3$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $C_1$ | 0.5 | 0.5 | 0.5 | 0.75 | 0.75 | 0.75 | 0.75 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| $C_2$ | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $c_1$ | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $c_2$ | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 |
| $c_3$ | 2 | 1 | 1 | 0 | 0 | 1 | 1 | 0 | 0 | 0 | 1 | 1 | 0 |
| $c_4$ | 6 | 2 | 2 | 1 | 1 | 1 | 1 | 2 | 2 | 2 | 2 | 2 | 2 |
| $c_5$ | 0 | 0 | 0 | 1 | 3 | 2 | 1 | 0 | 0 | 0 | 0 | 0 | 0 |
| $C_{1o}$ | 0.5 | 0.5 | 0.5 | 0.75 | 0.75 | 0.75 | 0.75 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| $C_{2o}$ | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $V_e\ (eV)$ | -182.53826 | -31.29307 | -31.29307 | -40.62396 | -107.32728 | -70.41425 | -35.12015 | -28.79214 | -28.79214 | -29.10112 | -28.79214 | -29.10112 | -29.10112 |
| $V_p\ (eV)$ | 35.97770 | 9.64042 | 9.64042 | 13.66428 | 38.92728 | 25.78002 | 12.87680 | 9.33352 | 9.33352 | 9.37273 | 9.33352 | 9.37273 | 9.37273 |
| $T\ (eV)$ | 70.90876 | 7.85528 | 7.85528 | 13.65796 | 32.53914 | 21.06675 | 10.48582 | 6.77464 | 6.77464 | 6.90500 | 6.77464 | 6.90500 | 6.90500 |
| $V_m\ (eV)$ | -35.45438 | -3.92764 | -3.92764 | -6.82898 | -16.26957 | -10.53337 | -5.24291 | -3.38732 | -3.38732 | -3.45250 | -3.38732 | -3.45250 | -3.45250 |
| $E(_{AO/HO})\ (eV)$ | -16.20002 | -14.63489 | -14.63489 | -14.63489 | -15.56407 | -15.56407 | -14.63489 | -15.56407 | -15.56407 | -15.35946 | -15.56407 | -15.35946 | -15.35946 |
| $\Delta E_{H_2MO}(_{AO/HO})\ (eV)$ | 0 | -0.72457 | -0.72457 | -3.130269 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $E_T(_{AO/HO})\ (eV)$ | -16.20002 | -13.91032 | -13.91032 | -11.50462 | -15.56407 | -15.56407 | -14.63489 | -15.56407 | -15.56407 | -15.35946 | -15.56407 | -15.35946 | -15.35946 |
| $E_T(_{H_2MO})\ (eV)$ | -94.90616 | -31.63533 | -31.63533 | -31.63532 | -67.69451 | -49.66493 | -31.63533 | -31.63537 | -31.63537 | -31.63535 | -31.63537 | -31.63535 | -31.63535 |
| $E_T\left(atom-atom,msp^3.AO\right)\ (eV)$ | -3.13026 | -0.72457 | -0.72457 | 0 | 0 | 0 | 0 | -1.85836 | -1.85836 | -1.44915 | -1.85836 | -1.44915 | -1.44915 |
| $E_T(_{MO})\ (eV)$ | -98.03637 | -32.35994 | -32.35994 | -31.63537 | -67.69450 | -49.66493 | -31.63537 | -33.49373 | -33.49373 | -33.08452 | -33.49373 | -33.08452 | -33.08452 |
| $\omega\ \left(10^{15}\ rad/s\right)$ | 20.0186 | 10.3988 | 17.5426 | 30.8370 | 24.9286 | 24.2751 | 24.1759 | 9.43699 | 9.43699 | 15.4846 | 9.43699 | 9.55643 | 9.55643 |
| $E_K\ (eV)$ | 13.17659 | 6.84470 | 11.54682 | 20.29747 | 16.40846 | 15.97831 | 15.91299 | 6.21159 | 6.21159 | 10.19220 | 6.21159 | 6.29021 | 6.29021 |
| $\bar{E}_D\ (eV)$ | -0.23468 | -0.16749 | -0.21754 | -0.28197 | -0.25352 | -0.25017 | -0.24966 | -0.16515 | -0.16515 | -0.20896 | -0.16515 | -0.16416 | -0.16416 |
| $\bar{E}_{Kvib}\ (eV)$ | 0.27773<br>[9] | 0.08989<br>[9] | 0.08989<br>[9] | 0.35532<br>Eq. (13.458) | 0.35532<br>Eq. (13.458) | 0.35532<br>Eq. (13.458) | 0.35532<br>Eq. (13.458) | 0.12312<br>[2] | 0.17978<br>[4] | 0.09944<br>[5] | 0.12312<br>[2] | 0.12312<br>[2] | 0.12312<br>[2] |
| $\bar{E}_{osc}\ (eV)$ | -0.09581 | -0.12255 | -0.17260 | -0.10430 | -0.22757 | -0.14502 | -0.07200 | -0.10359 | -0.07526 | -0.15924 | -0.10359 | -0.10260 | -0.10260 |
| $E_{mag}\ (eV)$ | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 |
| $E_T(_{Group})\ (eV)$ | -98.02775 | -32.48249 | -32.53254 | -31.73967 | -67.92207 | -49.80996 | -31.70737 | -33.59732 | -33.49373 | -33.24376 | -33.59732 | -33.18712 | -33.18712 |
| $E_{initial}(_{c_4\ AO/HO})\ (eV)$ | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 |
| $E_{initial}(_{c_5\ AO/HO})\ (eV)$ | 0 | 0 | 0 | -13.59844 | -13.59844 | -13.59844 | -13.59844 | 0 | 0 | 0 | 0 | 0 | 0 |
| $E_D(_{Group})\ (eV)$ | 10.21841 | 3.21271 | 3.26276 | 3.50634 | 12.49186 | 7.83016 | 3.32601 | 4.32754 | 4.29921 | 3.97398 | 4.17951 | 3.62128 | 3.91734 |

Table 15.25. The total bond energies of alkynes calculated using the functional group composition and the energies of Table 15.24 compared to the experimental values [3].

| Formula | Name | $C \equiv C$ | $C-C$ (i) | $C-C$ (ii) | $CH$ (i) | $CH_3$ | $CH_2$ | $CH$ (ii) | $C-C$ (a) | $C-C$ (b) | $C-C$ (c) | $C-C$ (d) | $C-C$ (e) | $C-C$ (f) | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $C_3H_4$ | Propyne | 1 | 1 | 0 | 1 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 29.42932 | 29.40432 | -0.00085 |
| $C_4H_6$ | 1-Butyne | 1 | 1 | 0 | 1 | 1 | 1 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 41.58702 | 41.55495 | -0.00077 |
| $C_4H_6$ | 2-Butyne | 1 | 0 | 2 | 0 | 2 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 41.72765 | 41.75705 | 0.00070 |
| $C_9H_{16}$ | 1-Nonyne | 1 | 1 | 0 | 1 | 1 | 6 | 0 | 6 | 0 | 0 | 0 | 0 | 0 | 102.37552 | 102.35367 | -0.00021 |

Table 15.26. The bond angle parameters of alkynes and experimental values [1]. In the calculation of $\theta_v$, the parameters from the preceding angle were used. $E_T$ is $E_T(atom - atom, msp^3.AO)$.

| Atoms of Angle | $2c'$ Bond 1 ($a_0$) | $2c'$ Bond 2 ($a_0$) | $2c'$ Terminal Atoms ($a_0$) | $E_{Coulombic}$ Atom 1 | Atom 1 Hybridization Designation (Table 15.3.A) | $E_{Coulombic}$ Atom 2 | Atom 2 Hybridization Designation (Table 15.3.A) | $c_2$ Atom 1 | $c_2$ Atom 2 | $C_1$ | $C_2$ | $c_1$ | $c_2'$ | $E_T$ (eV) | $\theta_v$ (°) | $\theta_1$ (°) | $\theta_2$ (°) | Cal. $\theta$ (°) | Exp. $\theta$ (°) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $\angle C_cC_aC_b$ <br> $(C_cC_a \equiv C_bH)$ | | | | | | | | | | | | | | | | | | 180 | |
| Methylene <br> $\angle HC_aH$ | 2.11106 | 2.11106 | 3.4252 | -15.75493 | 7 | H | H | 0.86359 | 1 | 1 | 1 | 0.75 | 1.15796 | 0 | | | | 108.44 | 107 <br> (propane) |
| $\angle C_aC_bC_c$ | | | | | | | | | | | | | | | 69.51 | | | 110.49 | 112 <br> (propane) <br> 113.8 <br> (butane) <br> 110.8 <br> (isobutane) |
| $\angle C_aC_bH$ | | | | | | | | | | | | | | | 69.51 | | | 110.49 | 111.0 <br> (butane) <br> 111.4 <br> (isobutane) |
| Methyl <br> $\angle HC_aH$ | 2.09711 | 2.09711 | 3.4252 | -15.75493 | 7 | H | H | 0.86359 | 1 | 1 | 1 | 0.75 | 1.15796 | 0 | | | | 109.50 | |
| $\angle C_aC_bC_c$ | | | | | | | | | | | | | | | 70.56 | | | 109.44 | |
| $\angle C_aC_bH$ | | | | | | | | | | | | | | | 70.56 | | | 109.44 | |
| $\angle C_bC_aC_c$ <br> iso $C_a$ | 2.91547 | 2.91547 | 4.7958 | -16.68412 <br> $C_b$ | 26 | -16.68412 <br> $C_c$ | 26 | 0.81549 | 0.81549 | 1 | 1 | 1 | 0.81549 | -1.85836 | | | | 110.67 | 110.8 <br> (isobutane) |
| $\angle C_bC_aH$ <br> iso $C_a$ | 2.91547 | 2.11323 | 4.1633 | -15.55033 <br> $C_a$ | 5 | -14.82575 <br> $C_b$ | 1 | 0.87495 | 0.91771 | 0.75 | 1 | 0.75 | 1.04887 | 0 | | | | 110.76 | |
| $\angle C_aC_bH$ <br> iso $C_a$ | 2.91547 | 2.09711 | 4.1633 | -15.55033 <br> $C_b$ | 5 | -14.82575 <br> $C_a$ | 1 | 0.87495 | 0.91771 | 0.75 | 1 | 0.75 | 1.04887 | 0 | | | | 111.27 | 111.4 <br> (isobutane) |
| $\angle C_bC_aC_b$ <br> tert $C_a$ | 2.90327 | 2.90327 | 4.7958 | -16.68412 <br> $C_b$ | 26 | -16.68412 <br> $C_b$ | 26 | 0.81549 | 0.81549 | 1 | 1 | 1 | 0.81549 | -1.85836 | | | | 111.37 | 110.8 <br> (isobutane) |
| $\angle C_bC_aC_d$ | | | | | | | | | | | | | | | 72.50 | | | 107.50 | |

## ALKYL FLUORIDES ($C_nH_{2n+2-m}F_m$, $n=1,2,3,4,5...\infty$ $m=1,2,3...\infty$)

The branched-chain alkyl fluorides, $C_nH_{2n+2-m}F_m$, may comprise at least two terminal methyl groups ($CH_3$) at each end of the chain, and may comprise methylene ($CH_2$), and methylyne ($CH$) functional groups as well as $C$ bound by carbon-carbon single bonds wherein at least one $H$ is replaced by a fluorine. The $C-F$ bond comprises a functional group for each case of $F$ replacing a $H$ of methane in the series $H_{4-m}C-F_m$, $m=1,2,3,4$, and $F$ replacing a $H$ of an alkane. The methyl, methylene, methylyne functional groups are equivalent to those of branched-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($(CH_3)_2CH$) and t-butyl ($(CH_3)_3C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups that are equivalent to those of branched-chain alkanes.

The solution of the $C-F$ functional groups comprises the hybridization of the $2s$ and $2p$ AOs of each $C$ to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between the $C2sp^3$ HO and the $F$ AO to form a molecular orbital (MO) permits each participating orbital to decrease in radius and energy. In alkyl fluorides, the $C2sp^3$ HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of $E(C,2sp^3)=-14.63489\ eV$ (Eq. (15.25)), and the $F$ AO has an energy of $E(F)=-17.42282\ eV$. To meet the equipotential condition of the union of the $C-F$ $H_2$-type-ellipsoidal-MO with these orbitals, the hybridization factor $c_2$ of Eq. (15.61) for the $C-F$-bond MO given by Eqs. (15.77) and (15.79) is:

$$c_2\left(C2sp^3HO\ to\ F\right)=\frac{E\left(C,2sp^3\right)}{E\left(F\right)}c_2\left(C2sp^3HO\right)=\frac{-14.63489\ eV}{-17.42282\ eV}\left(0.91771\right)=0.77087 \tag{15.129}$$

$E_T\left(atom-atom,msp^3.AO\right)$ of the $C-F$-bond MO in Eq. (15.61) based on the charge donation from $F$ to the MO is determined by the linear combination that results in a energy that is a minimum which does not exceed the energy of the AO of the $F$ atom to which it is energy matched.

The symbols of the functional groups of branched-chain alkyl fluorides are given in Table 15.27. The geometrical (Eqs. (15.1-15.5) and (15.51)), intercept (Eqs. (15.80-15.87)), and energy (Eqs. (15.6-15.11) and (15.17-15.65)) parameters of branched-chain alkyl fluorides are given in Tables 15.28, 15.29, and 15.30, respectively. The total energy of each branched-chain alkyl fluoride given in Table 15.31 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.30 corresponding to functional-group composition of the molecule. For each set of unpaired electrons created by bond breakage, the $C2sp^3$ HO magnetic energy $E_{mag}$ that is subtracted from the weighted sum of the $E_D(Group)$ $(eV)$ values based on composition is given by Eq. (15.67). In the case of trifluoromethane, $E_{mag}$ is positive since the term due to the fluorine atoms cancels that of the $CH$ group. The $C-C$ bonds to the $CHF$ group (one $H$ bond to $C$) were each treated as an iso $C-C$ bond. The $C-C$ bonds to the $CF$ group (no $H$ bonds to $C$) were each treated as a tert-butyl $C-C$. $E_{mag}$ was subtracted for each t-butyl group. The bond angle parameters of branched-chain alkyl fluorides determined using Eqs. (15.70-15.79), (15.87-15.117) and (15.129) are given in Table 15.32. The color scale, translucent view of the charge-density of exemplary alkyl fluoride, 1-fluoropropane, comprising the concentric shells of atoms with the outer shell bridged by one or more $H_2$-type ellipsoidal MOs or joined with one or more hydrogen MOs is shown in Figure 15.5.

Figure 15.5. Color scale, translucent view of the charge-density of 1-fluoropropane showing the orbitals of the atoms at their radii, the ellipsoidal surface of each $H$ or $H_2$-type ellipsoidal MO that transitions to the corresponding outer shell of the atom(s) participating in each bond, and the hydrogen nuclei (red, not to scale).

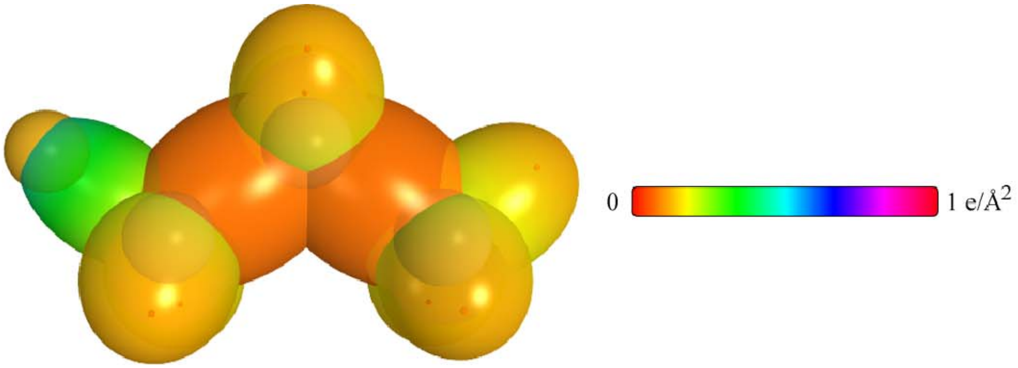


Table 15.27. The symbols of functional groups of branched-chain alkyl fluorides.

| Functional Group | Group Symbol |
|---|---|
| $CF$ of $CF_mH_{4-m}$ | $C-F$ (i) |
| $CF$ of $C_nH_{2n+2-m}F_m$ | $C-F$ (ii) |
| $CH_3$ group | $C-H$ $(CH_3)$ |
| $CH_2$ group | $C-H$ $(CH_2)$ |
| $CH$ | $C-H$ |
| $CC$ bond (*n*-$C$) | $C-C$ (a) |
| $CC$ bond (*iso*-$C$) | $C-C$ (b) |
| $CC$ bond (*tert*-$C$) | $C-C$ (c) |
| $CC$ (*iso* to *iso*-$C$) | $C-C$ (d) |
| $CC$ (*t* to *t*-$C$) | $C-C$ (e) |
| $CC$ (*t* to *iso*-$C$) | $C-C$ (f) |

Table 15.28. The geometrical bond parameters of branched-chain alkyl fluorides and experimental values [1].

| Parameter | $C-F$ (i) Group | $C-F$ (ii) Group | $C-H\ (CH_3)$ Group | $C-H\ (CH_2)$ Group | $C-H$ Group | $C-C$ (a) Group | $C-C$ (b) Group | $C-C$ (c) Group | $C-C$ (d) Group | $C-C$ (e) Group | $C-C$ (f) Group |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $a\ (a_0)$ | 1.72139 | 1.72139 | 1.64920 | 1.67122 | 1.67465 | 2.12499 | 2.12499 | 2.10725 | 2.12499 | 2.10725 | 2.10725 |
| $c'\ (a_0)$ | 1.31202 | 1.31202 | 1.04856 | 1.05553 | 1.05661 | 1.45744 | 1.45744 | 1.45164 | 1.45744 | 1.45164 | 1.45164 |
| Bond Length $2c'\ (Å)$ | 1.38858 | 1.38858 | 1.10974 | 1.11713 | 1.11827 | 1.54280 | 1.54280 | 1.53635 | 1.54280 | 1.53635 | 1.53635 |
| Exp. Bond Length $(Å)$ | 1.382 (methyl fluoride) | 1.382 (methyl fluoride) | 1.107 ($C-H$ propane)<br>1.117 ($C-H$ butane) | 1.107 ($C-H$ propane)<br>1.117 ($C-H$ butane) | 1.122 (isobutane) | 1.532 (propane)<br>1.531 (butane) | 1.532 (propane)<br>1.531 (butane) | 1.532 (propane)<br>1.531 (butane) | 1.532 (propane)<br>1.531 (butane) | 1.532 (propane)<br>1.531 (butane) | 1.532 (propane)<br>1.531 (butane) |
| $b,c\ (a_0)$ | 1.11435 | 1.11435 | 1.27295 | 1.29569 | 1.29924 | 1.54616 | 1.54616 | 1.52750 | 1.54616 | 1.52750 | 1.52750 |
| $e$ | 0.76219 | 0.76219 | 0.63580 | 0.63159 | 0.63095 | 0.68600 | 0.68600 | 0.68888 | 0.68600 | 0.68888 | 0.68888 |

Table 15.29. The MO to HO intercept geometrical bond parameters of branched-chain alkyl fluorides. *R, R′, R″* are *H* or alkyl groups. $E_T$ is $E_T$ (*atom – atom, msp*$^3$*.AO*).

| Bond | Atom | $E_T$ (eV) Bond 1 | $E_T$ (eV) Bond 2 | $E_T$ (eV) Bond 3 | $E_T$ (eV) Bond 4 | Final Total Energy $C2sp^3$ (eV) | $r_{initial}$ $(a_0)$ | $r_{final}$ $(a_0)$ | $E_{Coulomb}$ (eV) Final | $E(C2sp^3)$ (eV) Final | $\theta'$ (°) | $\theta_1$ (°) | $\theta_2$ (°) | $d_1$ $(a_0)$ | $d_2$ $(a_0)$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $H_{4-m}C_a-F_m$ $(C_a-F$ (i)) | $C_a$ | -1.34946 | 0 | 0 | 0 | -152.96515 | 0.91771 | 0.84115 | -16.17521 | -15.98435 | 100.77 | 79.23 | 47.86 | 1.15488 | 0.15714 |
| $H_{4-m}C_a-F_m$ $(C_a-F$ (i)) | $F$ | -1.34946 | 0 | 0 | 0 |  | 0.78069 | 0.84115 | -16.17521 |  | 100.77 | 79.23 | 47.86 | 1.15488 | 0.15714 |
| $-H_2C_bC_aF$ $(C_a-F$ (ii)) | $C_a$ | -1.34946 | -0.92918 | 0 | 0 | -153.89433 | 0.91771 | 0.79546 | -17.10440 | -16.91353 | 97.02 | 82.98 | 45.11 | 1.21483 | 0.09718 |
| $-H_2C_bC_aF$ $(C_a-F$ (ii)) | $F$ | -1.34946 | 0 | 0 | 0 |  | 0.78069 | 0.84115 | -16.17521 |  | 100.77 | 79.23 | 47.86 | 1.15488 | 0.15714 |
| $C-H\ (CH_3)$ | $C$ | -0.92918 | 0 | 0 | 0 | -152.54487 | 0.91771 | 0.86359 | -15.75493 | -15.56407 | 77.49 | 102.51 | 41.48 | 1.23564 | 0.18708 |
| $C-H\ (CH_2)$ | $C$ | -0.92918 | -0.92918 | 0 | 0 | -153.47406 | 0.91771 | 0.81549 | -16.68412 | -16.49325 | 68.47 | 111.53 | 35.84 | 1.35486 | 0.29933 |
| $C-H\ (CH)$ | $C$ | -0.92918 | -0.92918 | -0.92918 | 0 | -154.40324 | 0.91771 | 0.77247 | -17.61330 | -17.42244 | 61.10 | 118.90 | 31.37 | 1.42988 | 0.37326 |
| $H_3C_aC_bH_2CH_2-$ $(C-C$ (a)) | $C_a$ | -0.92918 | 0 | 0 | 0 | -152.54487 | 0.91771 | 0.86359 | -15.75493 | -15.56407 | 63.82 | 116.18 | 30.08 | 1.83879 | 0.38106 |
| $H_3C_aC_bH_2CH_2-$ $(C-C$ (a)) | $C_b$ | -0.92918 | -0.92918 | 0 | 0 | -153.47406 | 0.91771 | 0.81549 | -16.68412 | -16.49325 | 56.41 | 123.59 | 26.06 | 1.90890 | 0.45117 |
| $R-H_2C_aC_b(H_2C_c-R')HCH_2-$ $(C-C$ (b)) | $C_b$ | -0.92918 | -0.92918 | -0.92918 | 0 | -154.40324 | 0.91771 | 0.77247 | -17.61330 | -17.42244 | 48.30 | 131.70 | 21.90 | 1.97162 | 0.51388 |
| $R-H_2C_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ $(C-C$ (c)) | $C_b$ | -0.92918 | -0.72457 | -0.72457 | -0.72457 | -154.71860 | 0.91771 | 0.75889 | -17.92866 | -17.73779 | 48.21 | 131.79 | 21.74 | 1.95734 | 0.50570 |
| $isoC_aC_b(H_2C_c-R')HCH_2-$ $(C-C$ (d)) | $C_b$ | -0.92918 | -0.92918 | -0.92918 | 0 | -154.40324 | 0.91771 | 0.77247 | -17.61330 | -17.42244 | 48.30 | 131.70 | 21.90 | 1.97162 | 0.51388 |
| $tertC_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ $(C-C$ (e)) | $C_b$ | -0.72457 | -0.72457 | -0.72457 | -0.72457 | -154.51399 | 0.91771 | 0.76765 | -17.92866 | -17.73779 | 50.04 | 129.96 | 22.66 | 1.94462 | 0.49298 |
| $tertC_aC_b(H_2C_c-R')HCH_2-$ $(C-C$ (f)) | $C_b$ | -0.72457 | -0.92918 | -0.92918 | 0 | -154.19863 | 0.91771 | 0.78155 | -17.40869 | -17.21783 | 52.78 | 127.22 | 24.04 | 1.92443 | 0.47279 |
| $isoC_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ $(C-C$ (f)) | $C_b$ | -0.72457 | -0.72457 | -0.72457 | -0.72457 | -154.51399 | 0.91771 | 0.76765 | -17.92866 | -17.73779 | 50.04 | 129.96 | 22.66 | 1.94462 | 0.49298 |

Table 15.30. The energy parameters $(eV)$ of functional groups of branched-chain alkyl fluorides.

| Parameters | $C-F$ (i) Group | $C-F$ (ii) Group | $CH_3$ Group | $CH_2$ Group | $C-H$ Group | $C-C$ (a) Group | $C-C$ (b) Group | $C-C$ (c) Group | $C-C$ (d) Group | $C-C$ (e) Group | $C-C$ (f) Group |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $n_1$ | 1 | 1 | 3 | 2 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $n_2$ | 0 | 0 | 2 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $n_3$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $C_1$ | 0.5 | 0.5 | 0.75 | 0.75 | 0.75 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| $C_2$ | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $c_1$ | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $c_2$ | 0.77087 | 0.77087 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 |
| $c_3$ | 0 | 0 | 0 | 1 | 1 | 0 | 0 | 0 | 1 | 1 | 0 |
| $c_4$ | 2 | 2 | 1 | 1 | 1 | 2 | 2 | 2 | 2 | 2 | 2 |
| $c_5$ | 0 | 0 | 3 | 2 | 1 | 0 | 0 | 0 | 0 | 0 | 0 |
| $C_{1o}$ | 0.5 | 0.5 | 0.75 | 0.75 | 0.75 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| $C_{2o}$ | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $V_e\ (eV)$ | -32.02108 | -32.02108 | -107.32728 | -70.41425 | -35.12015 | -28.79214 | -28.79214 | -29.10112 | -28.79214 | -29.10112 | -29.10112 |
| $V_p\ (eV)$ | 10.37015 | 10.37015 | 38.92728 | 25.78002 | 12.87680 | 9.33352 | 9.33352 | 9.37273 | 9.33352 | 9.37273 | 9.37273 |
| $T\ (eV)$ | 9.30097 | 9.30097 | 32.53914 | 21.06675 | 10.48582 | 6.77464 | 6.77464 | 6.90500 | 6.77464 | 6.90500 | 6.90500 |
| $V_m\ (eV)$ | -4.65048 | -4.65048 | -16.26957 | -10.53337 | -5.24291 | -3.38732 | -3.38732 | -3.45250 | -3.38732 | -3.45250 | -3.45250 |
| $E(_{AO/HO})\ (eV)$ | -14.63489 | -14.63489 | -15.56407 | -15.56407 | -14.63489 | -15.56407 | -15.56407 | -15.35946 | -15.56407 | -15.35946 | -15.35946 |
| $\Delta E_{H_2MO}(_{AO/HO})\ (eV)$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $E_T(_{AO/HO})\ (eV)$ | -14.63489 | -14.63489 | -15.56407 | -15.56407 | -14.63489 | -15.56407 | -15.56407 | -15.35946 | -15.56407 | -15.35946 | -15.35946 |
| $E_T(_{H_2MO})\ (eV)$ | -31.63534 | -31.63534 | -67.69451 | -49.66493 | -31.63533 | -31.63537 | -31.63537 | -31.63535 | -31.63537 | -31.63535 | -31.63535 |
| $E_T\left(atom-atom, msp^3.AO\right)\ (eV)$ | -2.69892 | -2.69892 | 0 | 0 | 0 | -1.85836 | -1.85836 | -1.44915 | -1.85836 | -1.44915 | -1.44915 |
| $E_T(_{MO})\ (eV)$ | -34.33429 | -34.33429 | -67.69450 | -49.66493 | -31.63537 | -33.49373 | -33.49373 | -33.08452 | -33.49373 | -33.08452 | -33.08452 |
| $\omega\ \left(10^{15}\ rad/s\right)$ | 24.8506 | 12.9435 | 24.9286 | 24.2751 | 24.1759 | 9.43699 | 9.43699 | 15.4846 | 9.43699 | 9.55643 | 9.55643 |
| $E_K\ (eV)$ | 16.35707 | 8.51966 | 16.40846 | 15.97831 | 15.91299 | 6.21159 | 6.21159 | 10.19220 | 6.21159 | 6.29021 | 6.29021 |
| $\bar{E}_D\ (eV)$ | -0.27472 | -0.19826 | -0.25352 | -0.25017 | -0.24966 | -0.16515 | -0.16515 | -0.20896 | -0.16515 | -0.16416 | -0.16416 |
| $\bar{E}_{Kvib}\ (eV)$ | 0.13849 [10] | 0.10911 [11] | 0.35532 (Eq. (13.458)) | 0.35532 (Eq. (13.458)) | 0.35532 (Eq. (13.458)) | 0.12312 [2] | 0.17978 [4] | 0.09944 [5] | 0.12312 [2] | 0.12312 [2] | 0.12312 [2] |
| $\bar{E}_{osc}\ (eV)$ | -0.20547 | -0.14371 | -0.22757 | -0.14502 | -0.07200 | -0.10359 | -0.07526 | -0.15924 | -0.10359 | -0.10260 | -0.10260 |
| $E_{mag}\ (eV)$ | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 |
| $E_T(_{Group})\ (eV)$ | -34.53976 | -34.47800 | -67.92207 | -49.80996 | -31.70737 | -33.59732 | -33.49373 | -33.24376 | -33.59732 | -33.18712 | -33.18712 |
| $E_{initial}(_{c_4\ AO/HO})\ (eV)$ | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 |
| $E_{initial}(_{c_5\ AO/HO})\ (eV)$ | 0 | 0 | -13.59844 | -13.59844 | -13.59844 | 0 | 0 | 0 | 0 | 0 | 0 |
| $E_D(_{Group})\ (eV)$ | 5.26998 | 5.20822 | 12.49186 | 7.83016 | 3.32601 | 4.32754 | 4.29921 | 3.97398 | 4.17951 | 3.62128 | 3.91734 |

Table 15.31. The total bond energies of branched-chain alkyl fluorides calculated using the functional group composition and the energies of Table 15.30 compared to the experimental values [3]. The magnetic energy $E_{mag}$ that is subtracted from the weighted sum of the $E_{D\,(Group)}\ (eV)$ values based on composition is given by (15.58).

| Formula | Name | $C-F$ (i) | $C-F$ (ii) | $CH_3$ | $CH_2$ | $CH$ | $C-C$ (a) | $C-C$ (b) | $C-C$ (c) | $C-C$ (d) | $C-C$ (e) | $C-C$ (f) | $E_{mag}$ | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $CF_4$ | Tetrafluoromethane | 4 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 21.07992 | 21.016 | -0.00303 |
| $CHF_3$ | Trifluoromethane | 3 | 0 | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 19.28398 | 19.362 | 0.00405 |
| $CH_2F_2$ | Difluoromethane | 2 | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 18.37012 | 18.280 | -0.00496 |
| $C_3H_7F$ | 1-Fluoropropane | 0 | 1 | 1 | 2 | 0 | 2 | 0 | 0 | 0 | 0 | 0 | -1 | 41.86745 | 41.885 | 0.00041 |
| $C_3H_7F$ | 2-Fluoropropane | 0 | 1 | 2 | 0 | 1 | 0 | 2 | 0 | 0 | 0 | 0 | -1 | 41.96834 | 41.963 | -0.00012 |

Table 15.32. The bond angle parameters of branched-chain alkyl fluorides and experimental values [1]. In the calculation of $\theta_v$, the parameters from the preceding angle were used. $E_T$ is $E_T$ (*atom – atom, msp*$^3$*.AO*).

| Atoms of Angle | 2$c'$ Bond 1 ($a_0$) | 2$c'$ Bond 2 ($a_0$) | 2$c'$ Terminal Atoms ($a_0$) | $E_{Coulombic}$ Atom 1 | Atom 1 Hybridization Designation (Table 15.3.A) | $E_{Coulombic}$ Atom 2 | Atom 2 Hybridization Designation (Table 15.3.A) | $c_2$ Atom 1 | $c_2$ Atom 2 | $C_1$ | $C_2$ | $c_1$ | $c_2'$ | $E_T$ (eV) | $\theta_v$ (°) | $\theta_1$ (°) | $\theta_2$ (°) | Cal. $\theta$ (°) | Exp. $\theta$ (°) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $\angle FC_aF$<br>($C_a - F$ (i)) | 2.62403 | 2.62403 | 4.3128 | -16.17521<br>$F$ | 13 | -16.17521<br>$F$ | 13 | 0.84115 | 0.84115 | 1 | 1 | 1 | 0.84115 | -1.44915 | | | | 110.53 | 108.8<br>(fluoroform) |
| $\angle HC_aF$<br>($C_a - F$ (i)) | 2.11106 | 2.62403 | 3.8987 | -17.10440<br>$C_a$ | 35 | -17.42282<br>$F$ | F | 0.79546 | 0.78092<br>(Eq. (15.73)) | 0.75 | 1 | 0.75 | 0.98172 | 0 | | | | 110.38 | |
| $\angle C_bC_aF$<br>($C_a - F$ (ii)) | 2.91547 | 2.62403 | 4.5826 | -16.68412<br>$C_b$ | 26 | -17.42282<br>$F$ | F | 0.81549 | 0.77087<br>(Eq. (15.129)) | 1 | 1 | 1 | 0.79318 | -1.85836 | | | | 111.53 | 110.3<br>(1,2-difluoroethane) |
| $\angle C_bC_aH$<br>($C_a - F$ (ii)) | 2.91547 | 2.11106 | 4.1633 | -15.55033<br>$C_a$ | 5 | -14.82575<br>$C_b$ | 1 | 0.87495 | 0.91771 | 0.75 | 1 | 0.75 | 1.04887 | 0 | | | | 110.83 | 111.0<br>(1,1-difluoroethane) |
| Methylene<br>$\angle HC_aH$ | 2.11106 | 2.11106 | 3.4252 | -15.75493 | 7 | H | H | 0.86359 | 1 | 1 | 1 | 0.75 | 1.15796 | 0 | | | | 108.44 | 107<br>(propane) |
| $\angle C_aC_bC_c$ | | | | | | | | | | | | | | | 69.51 | | | 110.49 | 112<br>(propane)<br>113.8<br>(butane)<br>110.8<br>(isobutane) |
| $\angle C_aC_bH$ | | | | | | | | | | | | | | | 69.51 | | | 110.49 | 111.0<br>(butane)<br>111.4<br>(isobutane) |
| Methyl<br>$\angle HC_aH$ | 2.09711 | 2.09711 | 3.4252 | -15.75493 | 7 | H | H | 0.86359 | 1 | 1 | 1 | 0.75 | 1.15796 | 0 | | | | 109.50 | |
| $\angle C_aC_bC_c$ | | | | | | | | | | | | | | | 70.56 | | | 109.44 | |
| $\angle C_aC_bH$ | | | | | | | | | | | | | | | 70.56 | | | 109.44 | |
| $\angle C_bC_aC_c$<br>iso $C_a$ | 2.91547 | 2.91547 | 4.7958 | -16.68412<br>$C_b$ | 26 | -16.68412<br>$C_c$ | 26 | 0.81549 | 0.81549 | 1 | 1 | 1 | 0.81549 | -1.85836 | | | | 110.67 | 110.8<br>(isobutane) |
| $\angle C_bC_aH$<br>iso $C_a$ | 2.91547 | 2.11323 | 4.1633 | -15.55033<br>$C_a$ | 5 | -14.82575<br>$C_b$ | 1 | 0.87495 | 0.91771 | 0.75 | 1 | 0.75 | 1.04887 | 0 | | | | 110.76 | |
| $\angle C_aC_bH$<br>iso $C_a$ | 2.91547 | 2.09711 | 4.1633 | -15.55033<br>$C_b$ | 5 | -14.82575<br>$C_a$ | 1 | 0.87495 | 0.91771 | 0.75 | 1 | 0.75 | 1.04887 | 0 | | | | 111.27 | 111.4<br>(isobutane) |
| $\angle C_bC_aC_b$<br>tert $C_a$ | 2.90327 | 2.90327 | 4.7958 | -16.68412<br>$C_b$ | 26 | -16.68412<br>$C_b$ | 26 | 0.81549 | 0.81549 | 1 | 1 | 1 | 0.81549 | -1.85836 | | | | 111.37 | 110.8<br>(isobutane) |
| $\angle C_bC_aC_d$ | | | | | | | | | | | | | | | 72.50 | | | 107.50 | |

## ALKYL CHLORIDES ($C_nH_{2n+2-m}Cl_m,\ n=1,2,3,4,5...\infty\ \ m=1,2,3...\infty$)

The branched-chain alkyl chlorides, $C_nH_{2n+2-m}Cl_m$, may comprise at least two terminal methyl groups ($CH_3$) at each end of the chain, and may comprise methylene ($CH_2$), and methylyne ($CH$) functional groups as well as $C$ bound by carbon-carbon single bonds wherein at least one $H$ is replaced by a chlorine. The $C-Cl$ bond comprises a functional group for each case of $Cl$ replacing a $H$ of methane for the series $H_{4-m}C-Cl_m$, $m=1,2,3$, with the $C-Cl$ bond of $CCl_4$ comprising another functional group due to the limitation of the minimum energy of $Cl$ matched to that of the $C2sp^3$ HO. In addition, the $C-Cl$ bond due to $Cl$ replacing an $H$ of an alkane is a functional group. The methyl, methylene, methylyne functional groups are equivalent to those of branched-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($(CH_3)_2CH$) and t-butyl ($(CH_3)_3C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups that are equivalent to those of branched-chain alkanes.

The solution of the $C-Cl$ functional groups comprises the hybridization of the $2s$ and $2p$ AOs of each $C$ to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between the $C2sp^3$ HO and the $Cl$ AO to form a MO permits each participating orbital to decrease in radius and energy. In alkyl chlorides, the energy of chlorine is less than the Coulombic energy between the electron and proton of $H$ given by Eq. (1.264). Thus, $c_2$ in Eq. (15.61) is one, and the energy matching condition is determined by the $C_2$ parameter. Then, $C2sp^3$ HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of $E\left(C,2sp^3\right)=-14.63489\ eV$ (Eq. (15.25)), and the $Cl$ AO has an energy of $E\left(Cl\right)=-12.96764\ eV$. To meet the equipotential condition of the union of the $C-Cl$ $H_2$-type-ellipsoidal-MO with these orbitals, the hybridization factor $C_2$ of Eq. (15.61) for the $C-Cl$-bond MO given by Eqs. (15.77) and (15.79) is:

$$C_2\left(C2sp^3HO\ to\ Cl\right)=\frac{E\left(Cl\right)}{E\left(C,2sp^3\right)}c_2\left(C2sp^3HO\right)=\frac{-12.96764\ eV}{-14.63489\ eV}\left(0.91771\right)=0.81317 \tag{15.130}$$

The valence energy of the carbon $2p$ is $-11.2603\ eV$ and that of the $Cl$ AO is $-12.96764\ eV$. The energy difference is more than that of $2E_T\left(C-C,2sp^3\right)$ given by Eq. (14.151) for a single bond. Thus, $E_T\left(atom-atom,msp^3.AO\right)$ of the $C-Cl$-bond MO of $CCl_mH_{4-m}$ and $C_nH_{2n+2-m}Cl_m$ in Eq. (15.61) due to the charge donation from the $C$ and $Cl$ atoms to the MO is $-1.44915\ eV$ based on the energy match between the $C2sp^3$ HO and the $Cl$ AO corresponding to the energy contributions equivalent to those of methyl groups, $-0.72457\ eV$ (Eq. (14.151)). $E_T\left(atom-atom,msp^3.AO\right)$ of the $C-Cl$-bond MO of chloroform with four $C-Cl$ bonds is $-0.92918\ eV$ (Eq. (14.513)) based on the maximum single-bond-energy contribution of the $C2sp^3$ HO.

The symbols of the functional groups of branched-chain alkyl chlorides are given in Table 15.33. The geometrical (Eqs. (15.1-15.5) and (15.51)), intercept (Eqs. (15.80-15.87)), and energy (Eqs. (15.6-15.11) and (15.17-15.65)) parameters of branched-chain alkyl chlorides are given in Tables 15.34, 15.35, and 15.36, respectively. The total energy of each branched-chain alkyl chloride given in Table 15.37 was calculated as the sum over the integer multiple of each $E_D\left(Group\right)$ of Table 15.36 corresponding to functional-group composition of the molecule. For each set of unpaired electrons created by bond breakage, the $C2sp^3$ HO magnetic energy $E_{mag}$ that was subtracted from the weighted sum of the $E_D\left(Group\right)$ $(eV)$ values based on composition is given by Eq. (15.67). The $C-C$ bonds to the $CHCl$ group (one $H$ bond to $C$) were each treated as an iso $C-C$ bond. The $C-C$ bonds to the $CCl$ group (no $H$ bonds to $C$) were each treated as a tert-butyl $C-C$. $E_{mag}$ was subtracted for each t-butyl group. The bond angle parameters of branched-chain alkyl chlorides determined using Eqs. (15.70-15.79), (15.88-15.117) and (15.130) are given in Table 15.38. The color scale, translucent view of the charge-density of exemplary alkyl chloride, 1-chloropropane, comprising the concentric shells of atoms with the outer shell bridged by one or more $H_2$-type ellipsoidal MOs or joined with one or more hydrogen MOs is shown in Figure 15.6.

Figure 15.6. Color scale, translucent view of the charge-density of 1-chloropropane showing the orbitals of the atoms at their radii, the ellipsoidal surface of each $H$ or $H_2$-type ellipsoidal MO that transitions to the corresponding outer shell of the atom(s) participating in each bond, and the hydrogen nuclei (red, not to scale).

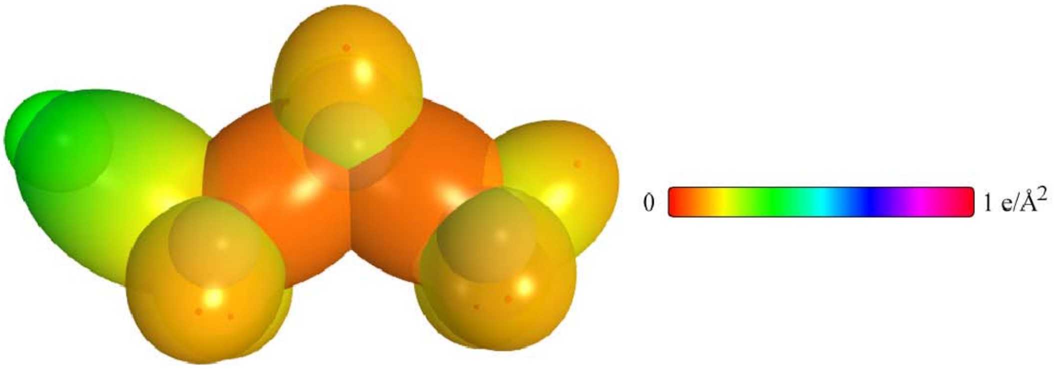


Table 15.33. The symbols of functional groups of branched-chain alkyl chlorides.

| Functional Group | Group Symbol |
|---|---|
| $CCl$ of $CCl_mH_{4-m}$ | $C-Cl$ (i) |
| $CCl$ of $CCl_4$ | $C-Cl$ (ii) |
| $CCl$ of $C_nH_{2n+2-m}Cl_m$ | $C-Cl$ (iii) |
| $CH_3$ group | $C-H\ (CH_3)$ |
| $CH_2$ group | $C-H\ (CH_2)$ |
| $CH$ | $C-H$ |
| $CC$ bond (*n-C*) | $C-C$ (a) |
| $CC$ bond (*iso-C*) | $C-C$ (b) |
| $CC$ bond (*tert-C*) | $C-C$ (c) |
| $CC$ (*iso* to *iso-C*) | $C-C$ (d) |
| $CC$ (*t* to *t-C*) | $C-C$ (e) |
| $CC$ (*t* to *iso-C*) | $C-C$ (f) |

Table 15.34. The geometrical bond parameters of branched-chain alkyl chlorides and experimental values [1].

| Parameter | $C-Cl$ (i) Group | $C-Cl$ (ii) Group | $C-Cl$ (iii) Group | $C-H\ (CH_3)$ Group | $C-H\ (CH_2)$ Group | $C-H$ Group | $C-C$ (a) Group | $C-C$ (b) Group | $C-C$ (c) Group | $C-C$ (d) Group | $C-C$ (e) Group | $C-C$ (f) Group |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $a\ (a_0)$ | 2.32621 | 2.37026 | 2.32621 | 1.64920 | 1.67122 | 1.67465 | 2.12499 | 2.12499 | 2.10725 | 2.12499 | 2.10725 | 2.10725 |
| $c'\ (a_0)$ | 1.69136 | 1.70729 | 1.69136 | 1.04856 | 1.05553 | 1.05661 | 1.45744 | 1.45744 | 1.45164 | 1.45744 | 1.45164 | 1.45164 |
| Bond Length $2c'\ (Å)$ | 1.79005 | 1.80692 | 1.79005 | 1.10974 | 1.11713 | 1.11827 | 1.54280 | 1.54280 | 1.53635 | 1.54280 | 1.53635 | 1.53635 |
| Exp. Bond Length $(Å)$ | 1.785 (methyl chloride) | 1.767 (carbon tetrachloride) | 1.802 (ethyl chloride)<br>1.790 (1,2-dichloroethane) | 1.107 ($C-H$ propane)<br>1.117 ($C-H$ butane) | 1.107 ($C-H$ propane)<br>1.117 ($C-H$ butane) | 1.122 (isobutane) | 1.532 (propane)<br>1.531 (butane) | 1.532 (propane)<br>1.531 (butane) | 1.532 (propane)<br>1.531 (butane) | 1.532 (propane)<br>1.531 (butane) | 1.532 (propane)<br>1.531 (butane) | 1.532 (propane)<br>1.531 (butane) |
| $b,c\ (a_0)$ | 1.59705 | 1.64416 | 1.59705 | 1.27295 | 1.29569 | 1.29924 | 1.54616 | 1.54616 | 1.52750 | 1.54616 | 1.52750 | 1.52750 |
| $e$ | 0.72709 | 0.72030 | 0.72709 | 0.63580 | 0.63159 | 0.63095 | 0.68600 | 0.68600 | 0.68888 | 0.68600 | 0.68888 | 0.68888 |

Table 15.35. The MO to HO intercept geometrical bond parameters of branched-chain alkyl chlorides. $R$, $R'$, $R''$ are $H$ or alkyl groups. $E_T$ is $E_T$ ($atom-atom, msp^3.AO$).

| Bond | Atom | $E_T$ (eV) Bond 1 | $E_T$ (eV) Bond 2 | $E_T$ (eV) Bond 3 | $E_T$ (eV) Bond 4 | Final Total Energy $C2sp^3$ (eV) | $r_{initial}$ $(a_0)$ | $r_{final}$ $(a_0)$ | $E_{Coulomb}$ (eV) Final | $E(C2sp^3)$ (eV) Final | $\theta'$ $(°)$ | $\theta_1$ $(°)$ | $\theta_2$ $(°)$ | $d_1$ $(a_0)$ | $d_2$ $(a_0)$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $H_{4-m}C_a-Cl_m,\ m=1,2,3,$ $(C_a-Cl$ (i)) | $C_a$ | -0.72457 | 0 | 0 | 0 | -152.34026 | 0.91771 | 0.87495 | -15.55033 | -15.35946 | 69.62 | 110.38 | 30.90 | 1.99599 | 0.30463 |
| $H_{4-m}C_a-Cl_m,\ m=1,2,3,$ $(C_a-Cl$ (i)) | $Cl$ | -0.72457 | 0 | 0 | 0 |  | 1.05158 | 0.87495 | -15.55033 |  | 69.62 | 110.38 | 30.90 | 1.99599 | 0.30463 |
| $C_aCl_4$ $(C_a-Cl$ (ii)) | $C_a$ | -0.46459 | 0 | 0 | 0 | -152.08028 | 0.91771 | 0.88983 | -15.29034 | -15.09948 | 66.98 | 113.02 | 29.87 | 2.05530 | 0.34801 |
| $C_aCl_4$ $(C_a-Cl$ (ii)) | $Cl$ | -0.46459 | 0 | 0 | 0 |  | 1.05158 | 0.88983 | -15.29034 |  | 66.98 | 113.02 | 29.87 | 2.05530 | 0.34801 |
| $-H_2C_bC_a-Cl$ $(C_a-Cl$ (iii)) | $C_a$ | -0.72457 | -0.92918 | 0 | 0 | -153.26945 | 0.91771 | 0.82562 | -16.47951 | -16.28864 | 63.18 | 116.82 | 27.48 | 2.06384 | 0.37248 |
| $-H_2C_bC_a-Cl$ $(C_a-Cl$ (iii)) | $Cl$ | -0.72457 | 0 | 0 | 0 |  | 1.05158 | 0.87495 | -15.55033 |  | 69.62 | 110.38 | 30.90 | 1.99599 | 0.30463 |
| $C-H\ (CH_3)$ | $C$ | -0.92918 | 0 | 0 | 0 | -152.54487 | 0.91771 | 0.86359 | -15.75493 | -15.56407 | 77.49 | 102.51 | 41.48 | 1.23564 | 0.18708 |
| $C-H\ (CH_2)$ | $C$ | -0.92918 | -0.92918 | 0 | 0 | -153.47406 | 0.91771 | 0.81549 | -16.68412 | -16.49325 | 68.47 | 111.53 | 35.84 | 1.35486 | 0.29933 |
| $C-H\ (CH)$ | $C$ | -0.92918 | -0.92918 | -0.92918 | 0 | -154.40324 | 0.91771 | 0.77247 | -17.61330 | -17.42244 | 61.10 | 118.90 | 31.37 | 1.42988 | 0.37326 |
| $H_3C_aC_bH_2CH_2-$ $(C-C$ (a)) | $C_a$ | -0.92918 | 0 | 0 | 0 | -152.54487 | 0.91771 | 0.86359 | -15.75493 | -15.56407 | 63.82 | 116.18 | 30.08 | 1.83879 | 0.38106 |
| $H_3C_aC_bH_2CH_2-$ $(C-C$ (a)) | $C_b$ | -0.92918 | -0.92918 | 0 | 0 | -153.47406 | 0.91771 | 0.81549 | -16.68412 | -16.49325 | 56.41 | 123.59 | 26.06 | 1.90890 | 0.45117 |
| $R-H_2C_aC_b(H_2C_c-R')HCH_2-$ $(C-C$ (b)) | $C_b$ | -0.92918 | -0.92918 | -0.92918 | 0 | -154.40324 | 0.91771 | 0.77247 | -17.61330 | -17.42244 | 48.30 | 131.70 | 21.90 | 1.97162 | 0.51388 |
| $R-H_2C_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ $(C-C$ (c)) | $C_b$ | -0.92918 | -0.72457 | -0.72457 | -0.72457 | -154.71860 | 0.91771 | 0.75889 | -17.92866 | -17.73779 | 48.21 | 131.79 | 21.74 | 1.95734 | 0.50570 |
| $isoC_aC_b(H_2C_c-R')HCH_2-$ $(C-C$ (d)) | $C_b$ | -0.92918 | -0.92918 | -0.92918 | 0 | -154.40324 | 0.91771 | 0.77247 | -17.61330 | -17.42244 | 48.30 | 131.70 | 21.90 | 1.97162 | 0.51388 |
| $tertC_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ $(C-C$ (e)) | $C_b$ | -0.72457 | -0.72457 | -0.72457 | -0.72457 | -154.51399 | 0.91771 | 0.76765 | -17.92866 | -17.73779 | 50.04 | 129.96 | 22.66 | 1.94462 | 0.49298 |
| $tertC_aC_b(H_2C_c-R')HCH_2-$ $(C-C$ (f)) | $C_b$ | -0.72457 | -0.92918 | -0.92918 | 0 | -154.19863 | 0.91771 | 0.78155 | -17.40869 | -17.21783 | 52.78 | 127.22 | 24.04 | 1.92443 | 0.47279 |
| $isoC_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ $(C-C$ (f)) | $C_b$ | -0.72457 | -0.72457 | -0.72457 | -0.72457 | -154.51399 | 0.91771 | 0.76765 | -17.92866 | -17.73779 | 50.04 | 129.96 | 22.66 | 1.94462 | 0.49298 |

Table 15.36. The energy parameters ($eV$) of functional groups of branched-chain alkyl chlorides.

| Parameters | $C-Cl$ (i) Group | $C-Cl$ (ii) Group | $C-Cl$ (iii) Group | $CH_3$ Group | $CH_2$ Group | $C-H$ Group | $C-C$ (a) Group | $C-C$ (b) Group | $C-C$ (c) Group | $C-C$ (d) Group | $C-C$ (e) Group | $C-C$ (f) Group |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $n_1$ | 1 | 1 | 1 | 3 | 2 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $n_2$ | 0 | 0 | 0 | 2 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $n_3$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $C_1$ | 0.5 | 0.5 | 0.5 | 0.75 | 0.75 | 0.75 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| $C_2$ | 0.81317 | 0.81317 | 0.81317 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $c_1$ | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $c_2$ | 1 | 1 | 1 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 |
| $c_3$ | 1 | 1 | 1 | 0 | 1 | 1 | 0 | 0 | 0 | 1 | 1 | 0 |
| $c_4$ | 2 | 2 | 2 | 1 | 1 | 1 | 2 | 2 | 2 | 2 | 2 | 2 |
| $c_5$ | 0 | 0 | 0 | 3 | 2 | 1 | 0 | 0 | 0 | 0 | 0 | 0 |
| $C_{1o}$ | 0.5 | 0.5 | 0.5 | 0.75 | 0.75 | 0.75 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| $C_{2o}$ | 0.81317 | 0.81317 | 0.81317 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $V_e\ (eV)$ | -29.68411 | -28.95265 | -29.68411 | -107.32728 | -70.41425 | -35.12015 | -28.79214 | -28.79214 | -29.10112 | -28.79214 | -29.10112 | -29.10112 |
| $V_p\ (eV)$ | 8.04432 | 7.96922 | 8.04432 | 38.92728 | 25.78002 | 12.87680 | 9.33352 | 9.33352 | 9.37273 | 9.33352 | 9.37273 | 9.37273 |
| $T\ (eV)$ | 6.38036 | 6.10748 | 6.38036 | 32.53914 | 21.06675 | 10.48582 | 6.77464 | 6.77464 | 6.90500 | 6.77464 | 6.90500 | 6.90500 |
| $V_m\ (eV)$ | -3.19018 | -3.05374 | -3.19018 | -16.26957 | -10.53337 | -5.24291 | -3.38732 | -3.38732 | -3.45250 | -3.38732 | -3.45250 | -3.45250 |
| $E(_{AO/HO})\ (eV)$ | -14.63489 | -14.63489 | -14.63489 | -15.56407 | -15.56407 | -14.63489 | -15.56407 | -15.56407 | -15.35946 | -15.56407 | -15.35946 | -15.35946 |
| $\Delta E_{H_2MO}(_{AO/HO})\ (eV)$ | -1.44915 | -0.92918 | -1.44915 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $E_T(_{AO/HO})\ (eV)$ | -13.18574 | -13.70571 | -13.18574 | -15.56407 | -15.56407 | -14.63489 | -15.56407 | -15.56407 | -15.35946 | -15.56407 | -15.35946 | -15.35946 |
| $E_T(_{H_2MO})\ (eV)$ | -31.63536 | -31.63540 | -31.63536 | -67.69451 | -49.66493 | -31.63533 | -31.63537 | -31.63537 | -31.63535 | -31.63537 | -31.63535 | -31.63535 |
| $E_T\left(atom-atom, msp^3.AO\right)\ (eV)$ | -1.44915 | -0.92918 | -1.44915 | 0 | 0 | 0 | -1.85836 | -1.85836 | -1.44915 | -1.85836 | -1.44915 | -1.44915 |
| $E_T(_{MO})\ (eV)$ | -33.08452 | -32.56455 | -33.08452 | -67.69450 | -49.66493 | -31.63537 | -33.49373 | -33.49373 | -33.08452 | -33.49373 | -33.08452 | -33.08452 |
| $\omega\ \left(10^{15}\ rad/s\right)$ | 7.42995 | 7.22380 | 13.0612 | 24.9286 | 24.2751 | 24.1759 | 9.43699 | 9.43699 | 15.4846 | 9.43699 | 9.55643 | 9.55643 |
| $E_K\ (eV)$ | 4.89052 | 4.75483 | 8.59708 | 16.40846 | 15.97831 | 15.91299 | 6.21159 | 6.21159 | 10.19220 | 6.21159 | 6.29021 | 6.29021 |
| $\bar{E}_D\ (eV)$ | -0.14475 | -0.14048 | -0.19191 | -0.25352 | -0.25017 | -0.24966 | -0.16515 | -0.16515 | -0.20896 | -0.16515 | -0.16416 | -0.16416 |
| $\bar{E}_{Kvib}\ (eV)$ | 0.08059<br>[12] | 0.08059<br>[12] | 0.09113<br>[13] | 0.35532<br>(Eq. (13.458)) | 0.35532<br>(Eq. (13.458)) | 0.35532<br>(Eq. (13.458)) | 0.12312<br>[2] | 0.17978<br>[4] | 0.09944<br>[5] | 0.12312<br>[2] | 0.12312<br>[2] | 0.12312<br>[2] |
| $\bar{E}_{osc}\ (eV)$ | -0.10445 | -0.10019 | -0.14635 | -0.22757 | -0.14502 | -0.07200 | -0.10359 | -0.07526 | -0.15924 | -0.10359 | -0.10260 | -0.10260 |
| $E_{mag}\ (eV)$ | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 |
| $E_T(_{Group})\ (eV)$ | -33.18897 | -32.66473 | -33.23086 | -67.92207 | -49.80996 | -31.70737 | -33.59732 | -33.49373 | -33.24376 | -33.59732 | -33.18712 | -33.18712 |
| $E_{initial}(_{c_4\ AO/HO})\ (eV)$ | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 |
| $E_{initial}(_{c_5\ AO/HO})\ (eV)$ | 0 | 0 | 0 | -13.59844 | -13.59844 | -13.59844 | 0 | 0 | 0 | 0 | 0 | 0 |
| $E_D(_{Group})\ (eV)$ | 3.77116 | 3.39496 | 3.96108 | 12.49186 | 7.83016 | 3.32601 | 4.32754 | 4.29921 | 3.97398 | 4.17951 | 3.62128 | 3.91734 |

Table 15.37. The total bond energies of branched-chain alkyl chlorides calculated using the functional group composition and the energies of Table 15.36 compared to the experimental values [3]. The magnetic energy $E_{mag}$ that is subtracted from the weighted sum of the $E_{D\,(Group)}$ $(eV)$ values based on composition is given by (15.58).

| Formula | Name | $C-Cl$ (i) | $C-Cl$ (ii) | $C-Cl$ (iii) | $CH_3$ | $CH_2$ | $CH$ | $C-C$ (a) | $C-C$ (b) | $C-C$ (c) | $C-C$ (d) | $C-C$ (e) | $C-C$ (f) | $E_{mag}$ | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $CCl_4$ | Tetrachloromethane | 0 | 4 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | -1 | 13.43181 | 13.448 | 0.00123 |
| $CHCl_3$ | Trichloromethane | 3 | 0 | 0 | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | -1 | 14.49146 | 14.523 | 0.00217 |
| $CH_2Cl_2$ | Dichloromethane | 2 | 0 | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 15.37248 | 15.450 | 0.00499 |
| $CH_3Cl$ | Chloromethane | 1 | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 16.26302 | 16.312 | 0.00299 |
| $C_2H_5Cl$ | Chloroethane | 0 | 0 | 1 | 1 | 1 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 28.61064 | 28.571 | -0.00138 |
| $C_3H_7Cl$ | 1-Chloropropane | 0 | 0 | 1 | 1 | 2 | 0 | 2 | 0 | 0 | 0 | 0 | 0 | 0 | 40.76834 | 40.723 | -0.00112 |
| $C_3H_7Cl$ | 2-Chloropropane | 0 | 0 | 1 | 2 | 0 | 1 | 0 | 2 | 0 | 0 | 0 | 0 | 0 | 40.86923 | 40.858 | -0.00028 |
| $C_4H_9Cl$ | 1-Chlorobutane | 0 | 0 | 1 | 1 | 3 | 0 | 3 | 0 | 0 | 0 | 0 | 0 | 0 | 52.92604 | 52.903 | -0.00044 |
| $C_4H_9Cl$ | 2-Chlorobutane | 0 | 0 | 1 | 2 | 1 | 1 | 1 | 2 | 0 | 0 | 0 | 0 | 0 | 52.02693 | 52.972 | -0.00104 |
| $C_4H_9Cl$ | 1-Chloro-2-methylpropane | 0 | 0 | 1 | 2 | 1 | 1 | 0 | 3 | 0 | 0 | 0 | 0 | 0 | 52.99860 | 52.953 | -0.00085 |
| $C_4H_9Cl$ | 2-Chloro-2-methylpropane | 0 | 0 | 1 | 3 | 0 | 0 | 0 | 0 | 3 | 0 | 0 | 0 | -1 | 53.21057 | 53.191 | -0.00037 |
| $C_5H_{11}Cl$ | 1-Chloropentane | 0 | 0 | 1 | 1 | 4 | 0 | 4 | 0 | 0 | 0 | 0 | 0 | 0 | 65.08379 | 65.061 | 0.00034 |
| $C_5H_{11}Cl$ | 1-Chloro-3-methylbutane | 0 | 0 | 1 | 2 | 2 | 1 | 1 | 3 | 0 | 0 | 0 | 0 | 0 | 65.15630 | 65.111 | -0.00069 |
| $C_5H_{11}Cl$ | 2-Chloro-2-methylbutane | 0 | 0 | 1 | 3 | 1 | 0 | 1 | 0 | 3 | 0 | 0 | 0 | -1 | 65.36827 | 65.344 | -0.00037 |
| $C_5H_{11}Cl$ | 2-Chloro-3-methylbutane | 0 | 0 | 1 | 3 | 0 | 2 | 0 | 3 | 0 | 1 | 0 | 0 | 0 | 65.16582 | 65.167 | 0.00002 |
| $C_6H_{13}Cl$ | 2-Chlorohexane | 0 | 0 | 1 | 2 | 3 | 1 | 3 | 2 | 0 | 0 | 0 | 0 | 0 | 77.34233 | 77.313 | -0.00038 |
| $C_8H_{17}Cl$ | 1-Chlorooctane | 0 | 0 | 1 | 1 | 7 | 0 | 7 | 0 | 0 | 0 | 0 | 0 | 0 | 101.55684 | 101.564 | 0.00007 |
| $C_{12}H_{25}Cl$ | 1-Chlorododecane | 0 | 0 | 1 | 1 | 11 | 0 | 11 | 0 | 0 | 0 | 0 | 0 | 0 | 150.18764 | 150.202 | 0.00009 |
| $C_{18}H_{37}Cl$ | 1-Chlorooctadecane | 0 | 0 | 1 | 1 | 17 | 0 | 17 | 0 | 0 | 0 | 0 | 0 | 0 | 223.13384 | 223.175 | 0.00018 |

Table 15.38. The bond angle parameters of branched-chain alkyl chlorides and experimental values [1]. In the calculation of $\theta_v$, the parameters from the preceding angle were used. $E_T$ is $E_T$ $(atom-atom,\ msp^3.AO)$.

| Atoms of Angle | $2c'$ Bond 1 $(a_0)$ | $2c'$ Bond 2 $(a_0)$ | $2c'$ Terminal Atoms $(a_0)$ | $E_{Coulombic}$ Atom 1 | Atom 1 Hybridization Designation (Table 15.3.A) | $E_{Coulombic}$ Atom 2 | Atom 2 Hybridization Designation (Table 15.3.A) | $c_2$ Atom 1 | $c_2$ Atom 2 | $C_1$ | $C_2$ | $c_1$ | $c_2'$ | $E_T$ (eV) | $\theta_v$ (°) | $\theta_1$ (°) | $\theta_2$ (°) | Cal. $\theta$ (°) | Exp. $\theta$ (°) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $\angle ClC_aCl$<br>$(C_a-Cl$ (i)) | 3.38271 | 3.38271 | 5.5889 | -14.82575<br>$Cl$ | 1 | -14.82575<br>$Cl$ | 1 | 0.91771 | 0.91771 | 1 | 0.81317<br>(Eq. (15.130)) | 1 | 0.91771 | -0.92918 | | | | 111.40 | 112.0<br>(dichloromethane)<br>111.3<br>(chloroform) |
| $\angle HC_aCl$<br>$(C_a-Cl$ (iii)) | 2.11106 | 3.38271 | 4.5961 | -16.27490<br>$C_a$ | 16 | -12.96764<br>$Cl$ | Cl | 0.83600 | 0.91771 | 0.75 | 0.95310<br>(Eq. (15.74)) | 0.75 | 1.09775 | 0 | | | | 111.46 | |
| $\angle HC_aH$<br>$\angle HC_bH$<br>$(C_a-Cl$ (iii)) | 2.09711 | 2.09711 | 3.4252 | -15.75493 | 7 | H | H | 0.86359 | 1 | 1 | 1 | 0.75 | 1.15796 | 0 | | | | 109.50 | 109.2<br>($\angle HC_aH$ ethyl chloride)<br>109.8<br>($\angle HC_bH$ ethyl chloride) |
| $\angle C_aC_bH_b$<br>$(C_a-Cl$ (iii)) | | | | | | | | | | | | | | | 70.56 | | | 109.44 | |
| $\angle C_bC_aCl$<br>$(C_a-Cl$ (iii)) | 2.91547 | 3.38271 | 5.1539 | -15.75493<br>$C_b$ | 7 | -12.96764<br>$Cl$ | Cl | 0.86359 | 0.86359 | 1 | 0.81317<br>(Eq. (15.130)) | 1 | 0.86359 | -0.92918 | | | | 109.61 | 110.7<br>(ethyl chloride)<br>111.0<br>(1,1-dichloroethane)<br>109.0<br>(1,2-dichloroethane)<br>109.6<br>(1,1,1-trichloroethane)<br>110.0<br>(hexachloroethane) |
| $\angle C_bC_aH_a$<br>$(C_a-Cl$ (iii)) | 2.91547 | 2.11106 | 4.1633 | -15.55033<br>$C_a$ | 5 | -14.82575<br>$C_b$ | 1 | 0.87495 | 0.91771 | 0.75 | 1 | 0.75 | 1.04887 | 0 | | | | 110.83 | 110.6<br>(ethyl chloride) |
| Methylene<br>$\angle HC_aH$ | 2.11106 | 2.11106 | 3.4252 | -15.75493 | 7 | H | H | 0.86359 | 1 | 1 | 1 | 0.75 | 1.15796 | 0 | | | | 108.44 | 107<br>(propane) |
| $\angle C_aC_bC_c$ | | | | | | | | | | | | | | | 69.51 | | | 110.49 | 112<br>(propane)<br>113.8<br>(butane)<br>110.8<br>(isobutane) |
| $\angle C_aC_bH$ | | | | | | | | | | | | | | | 69.51 | | | 110.49 | 111.0<br>(butane)<br>111.4<br>(isobutane) |
| Methyl<br>$\angle HC_aH$ | 2.09711 | 2.09711 | 3.4252 | -15.75493 | 7 | H | H | 0.86359 | 1 | 1 | 1 | 0.75 | 1.15796 | 0 | | | | 109.50 | |
| $\angle C_aC_bC_c$ | | | | | | | | | | | | | | | 70.56 | | | 109.44 | |
| $\angle C_aC_bH$ | | | | | | | | | | | | | | | 70.56 | | | 109.44 | |
| $\angle C_bC_aC_c$<br>iso $C_a$ | 2.91547 | 2.91547 | 4.7958 | -16.68412<br>$C_b$ | 26 | -16.68412<br>$C_c$ | 26 | 0.81549 | 0.81549 | 1 | 1 | 1 | 0.81549 | -1.85836 | | | | 110.67 | 110.8<br>(isobutane) |
| $\angle C_bC_aH$<br>iso $C_a$ | 2.91547 | 2.11323 | 4.1633 | -15.55033<br>$C_a$ | 5 | -14.82575<br>$C_b$ | 1 | 0.87495 | 0.91771 | 0.75 | 1 | 0.75 | 1.04887 | 0 | | | | 110.76 | |
| $\angle C_aC_bH$<br>iso $C_a$ | 2.91547 | 2.09711 | 4.1633 | -15.55033<br>$C_b$ | 5 | -14.82575<br>$C_a$ | 1 | 0.87495 | 0.91771 | 0.75 | 1 | 0.75 | 1.04887 | 0 | | | | 111.27 | 111.4<br>(isobutane) |
| $\angle C_bC_aC_b$<br>tert $C_a$ | 2.90327 | 2.90327 | 4.7958 | -16.68412<br>$C_b$ | 26 | -16.68412<br>$C_b$ | 26 | 0.81549 | 0.81549 | 1 | 1 | 1 | 0.81549 | -1.85836 | | | | 111.37 | 110.8<br>(isobutane) |
| $\angle C_bC_aC_d$ | | | | | | | | | | | | | | | 72.50 | | | 107.50 | |

## ALKYL BROMIDES ($C_nH_{2n+2-m}Br_m,\ n=1,2,3,4,5...\infty\ \ m=1,2,3...\infty$)

The branched-chain alkyl bromides, $C_nH_{2n+2-m}Br_m$, may comprise at least two terminal methyl groups ($CH_3$) at each end of the chain, and may comprise methylene ($CH_2$), and methylyne ($CH$) functional groups as well as $C$ bound by carbon-carbon single bonds wherein at least one $H$ is replaced by a bromine. The $C-Br$ bond comprises a functional group for each case of $Br$ replacing a $H$ of methane for the series $H_{4-m}C-Br_m,\ m=1,2,3,$ with the $C-Br$ bond of $CBr_4$ comprising another functional group due to the limitation of the minimum energy of $Br$ matched to that of the $C2sp^3$ HO. In addition, the $C-Br$ bond due to $Br$ replacing a $H$ of an alkane is a functional group. The methyl, methylene, methylyne functional groups are equivalent to those of branched-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($(CH_3)_2CH$) and t-butyl ($(CH_3)_3C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups that are equivalent to those of branched-chain alkanes.

The solution of the $C-Br$ functional groups comprises the hybridization of the $2s$ and $2p$ shells of each $C$ to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between the $C2sp^3$ hybridized orbital (HO) and the $Br$ AO to form a molecular orbital (MO) permits each participating orbital to decrease in radius and energy. In alkyl bromides, the energy of bromine is less than the Coulombic energy between the electron and proton of $H$ given by Eq. (1.264). Thus, $c_2$ in Eq. (15.61) is one, and the energy matching condition is determined by the $C_2$ parameter. Then, the $C2sp^3$ HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of $E\left(C,2sp^3\right)=-14.63489\ eV$ (Eq. (15.25)), and the $Br$ AO has an energy of $E\left(Br\right)=-11.81381\ eV$. To meet the equipotential condition of the union of the $C-Br$ $H_2$-type-ellipsoidal-MO with these orbitals, the hybridization factor $C_2$ of Eq. (15.61) for the $C-Br$-bond MO given by Eqs. (15.77) and (15.79) is:

$$C_2\left(C2sp^3HO\ to\ Br\right)=\frac{E\left(Br\right)}{E\left(C,2sp^3\right)}c_2\left(C2sp^3HO\right)=\frac{-11.81381\ eV}{-14.63489\ eV}\left(0.91771\right)=0.74081 \tag{15.131}$$

The valence energy of the carbon $2p$ is $-11.2603\ eV$ and that of the $Br$ AO is $-11.81381\ eV$. The energy difference is less than that of $E_T\left(C-C,2sp^3\right)$ given by Eq. (14.151) for a single bond. Thus, $E_T\left(atom-atom,msp^3.AO\right)$ of the alkyl $C-Br$-bond MO in Eq. (15.61) due to the charge donation from the $C$ and $Br$ atoms to the MO is $-0.92918\ eV$ (Eq. (14.513)) based on the maximum single-bond-energy contribution of the $C2sp^3$ HO. $E_T\left(atom-atom,msp^3.AO\right)$ of the series $CBr_mH_{4-m}\ m=1,2,3$ is equivalent to those of methyl groups, $-0.72457\ eV$ (Eq. (14.151)). For $CBr_4$, $E_T\left(atom-atom,msp^3.AO\right)$ of the $C-Br$-bond MO in Eq. (15.61) due to the charge donation from the $C$ and $Br$ atoms to the MO is $-0.36229\ eV$ based on the maximum charge density on the $C2sp^3$ HO. It is given by Eqs. (15.18-15.20) and Eq. (15.29) with a linear combination of $s=1$ corresponding to $E_T\left(atom-atom,msp^3.AO\right)=-0.72457\ eV$ and $s=0$ corresponding to: $E_T\left(atom-atom,msp^3.AO\right)=0$.

The symbols of the functional groups of branched-chain alkyl bromides are given in Table 15.39. The geometrical (Eqs. (15.1-15.5) and (15.51)), intercept (Eqs. (15.80-15.87)), and energy (Eqs. (15.6-15.11) and (15.17-15.65)) parameters of branched-chain alkyl bromides are given in Tables 15.49, 15.50, and 15.51, respectively. The total energy of each branched-chain alkyl bromide given in Table 15.52 was calculated as the sum over the integer multiple of each $E_D\left(Group\right)$ of Table 15.51 corresponding to functional-group composition of the molecule. For each set of unpaired electrons created by bond breakage, the $C2sp^3$ HO magnetic energy $E_{mag}$ that was subtracted from the weighted sum of the $E_D\left(Group\right)$ $\left(eV\right)$ values based on composition is given by Eq. (15.67). The $C-C$ bonds to the $CHBr$ group (one $H$ bond to $C$) were each treated as an iso $C-C$ bond. The $C-C$ bonds to the $CBr$ group (no $H$ bonds to $C$) were each treated as a tert-butyl $C-C$. The bond angle parameters of branched-chain alkyl bromides determined using Eqs. (15.70-15.79), (15.88-15.117) and (15.131) are given in Table 15.44. The color scale, translucent view of the charge-density of exemplary alkyl bromide, 1-bromopropane, comprising the concentric shells of atoms with the outer shell bridged by one or more $H_2$-type ellipsoidal MOs or joined with one or more hydrogen MOs is shown in Figure 15.7.

Figure 15.7. Color scale, translucent view of the charge-density of 1-bromopropane showing the orbitals of the atoms at their radii, the ellipsoidal surface of each $H$ or $H_2$-type ellipsoidal MO that transitions to the corresponding outer shell of the atom(s) participating in each bond, and the hydrogen nuclei (red, not to scale).

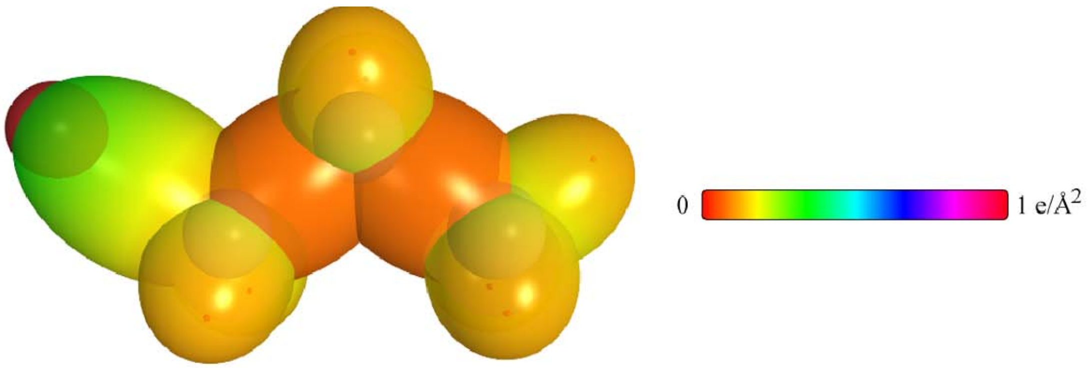


Table 15.39. The symbols of functional groups of branched-chain alkyl bromides.

| Functional Group | Group Symbol |
|---|---|
| $CBr$ of $CBr_mH_{4-m}$ | $C-Br$ (i) |
| $CBr$ of $CBr_4$ | $C-Br$ (ii) |
| $CBr$ of $C_nH_{2n+2-m}Br_m$ | $C-Br$ (iii) |
| $CH_3$ group | $C-H$ $(CH_3)$ |
| $CH_2$ group | $C-H$ $(CH_2)$ |
| $CH$ | $C-H$ |
| $CC$ bond (*n*-$C$) | $C-C$ (a) |
| $CC$ bond (*iso*-$C$) | $C-C$ (b) |
| $CC$ bond (*tert*-$C$) | $C-C$ (c) |
| $CC$ (*iso* to *iso*-$C$) | $C-C$ (d) |
| $CC$ (*t* to *t*-$C$) | $C-C$ (e) |
| $CC$ (*t* to *iso*-$C$) | $C-C$ (f) |

Table 15.40. The geometrical bond parameters of branched-chain alkyl bromides and experimental values [1].

| Parameter | $C-Br$ (i) Group | $C-Br$ (ii) Group | $C-Br$ (iii) Group | $C-H\left(CH_3\right)$ Group | $C-H\left(CH_2\right)$ Group | $C-H$ Group | $C-C$ (a) Group | $C-C$ (b) Group | $C-C$ (c) Group | $C-C$ (d) Group | $C-C$ (e) Group | $C-C$ (f) Group |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $a\left(a_0\right)$ | 2.49163 | 2.52509 | 2.47329 | 1.64920 | 1.67122 | 1.67465 | 2.12499 | 2.12499 | 2.10725 | 2.12499 | 2.10725 | 2.10725 |
| $c'\left(a_0\right)$ | 1.83395 | 1.84622 | 1.82719 | 1.04856 | 1.05553 | 1.05661 | 1.45744 | 1.45744 | 1.45164 | 1.45744 | 1.45164 | 1.45164 |
| Bond Length $2c'$ $\left(\mathring{A}\right)$ | 1.94097 | 1.95396 | 1.93381 | 1.10974 | 1.11713 | 1.11827 | 1.54280 | 1.54280 | 1.53635 | 1.54280 | 1.53635 | 1.53635 |
| Exp. Bond Length $\left(\mathring{A}\right)$ | 1.933 (methyl bromide) | 1.935 (carbon tetrabromide) | 1.93 (1,1,1-tribromoethane)<br>1.950 (1,2-dibromoethane) | 1.107 ($C-H$ propane)<br>1.117 ($C-H$ butane) | 1.107 ($C-H$ propane)<br>1.117 ($C-H$ butane) | 1.122 (isobutane) | 1.532 (propane)<br>1.531 (butane) | 1.532 (propane)<br>1.531 (butane) | 1.532 (propane)<br>1.531 (butane) | 1.532 (propane)<br>1.531 (butane) | 1.532 (propane)<br>1.531 (butane) | 1.532 (propane)<br>1.531 (butane) |
| $b,c\left(a_0\right)$ | 1.68667 | 1.72265 | 1.66689 | 1.27295 | 1.29569 | 1.29924 | 1.54616 | 1.54616 | 1.52750 | 1.54616 | 1.52750 | 1.52750 |
| $e$ | 0.73604 | 0.73115 | 0.73877 | 0.63580 | 0.63159 | 0.63095 | 0.68600 | 0.68600 | 0.68888 | 0.68600 | 0.68888 | 0.68888 |

Table 15.41. The MO to HO intercept geometrical bond parameters of branched-chain alkyl bromides. $R$, $R'$, $R''$ are $H$ or alkyl groups. $E_T$ is $E_T(atom-atom,msp^3.AO)$.

| Bond | Atom | $E_T$ (eV) Bond 1 | $E_T$ (eV) Bond 2 | $E_T$ (eV) Bond 3 | $E_T$ (eV) Bond 4 | Final Total Energy $C2sp^3$ (eV) | $r_{initial}$ $\left(a_0\right)$ | $r_{final}$ $\left(a_0\right)$ | $E_{Coulomb}$ (eV) Final | $E\left(C2sp^3\right)$ (eV) Final | $\theta'$ $\left(^\circ\right)$ | $\theta_1$ $\left(^\circ\right)$ | $\theta_2$ $\left(^\circ\right)$ | $d_1$ $\left(a_0\right)$ | $d_2$ $\left(a_0\right)$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $H_{4-m}C_a-Br_m,\ m=1,2,3,$ $(C_a-Br$ (i)) | $C_a$ | -0.36229 | 0 | 0 | 0 | -151.97798 | 0.91771 | 0.89582 | -15.18804 | -14.99717 | 68.10 | 111.90 | 29.52 | 2.16808 | 0.33413 |
| $H_{4-m}C_a-Br_m,\ m=1,2,3,$ $(C_a-Br$ (i)) | $Br$ | -0.36229 | 0 | 0 | 0 |  | 1.15169 | 0.89582 | -15.18804 |  | 68.10 | 111.90 | 29.52 | 2.16808 | 0.33413 |
| $C_aBr_4$ $(C_a-Br$ (ii)) | $C_a$ | -0.18114 | 0 | 0 | 0 | -151.79683 | 0.91771 | 0.90664 | -15.00689 | -14.81603 | 66.10 | 113.90 | 28.76 | 2.21357 | 0.36734 |
| $C_aBr_4$ $(C_a-Br$ (ii)) | $Br$ | -0.18114 | 0 | 0 | 0 |  | 1.15169 | 0.90664 | -15.00689 |  | 66.10 | 113.90 | 28.76 | 2.21357 | 0.36734 |
| $-H_2C_bC_aBr$ $(C_a-Br$ (iii)) | $C_a$ | -0.46459 | -0.92918 | 0 | 0 | -153.00946 | 0.91771 | 0.83885 | -16.21952 | -16.02866 | 62.67 | 117.33 | 26.55 | 2.21237 | 0.38518 |
| $-H_2C_bC_aBr$ $(C_a-Br$ (iii)) | $Br$ | -0.46459 | 0 | 0 | 0 |  | 1.15169 | 0.88983 | -15.29034 |  | 69.19 | 110.81 | 29.93 | 2.14337 | 0.31618 |
| $C-H\left(CH_3\right)$ | $C$ | -0.92918 | 0 | 0 | 0 | -152.54487 | 0.91771 | 0.86359 | -15.75493 | -15.56407 | 77.49 | 102.51 | 41.48 | 1.23564 | 0.18708 |
| $C-H\left(CH_2\right)$ | $C$ | -0.92918 | -0.92918 | 0 | 0 | -153.47406 | 0.91771 | 0.81549 | -16.68412 | -16.49325 | 68.47 | 111.53 | 35.84 | 1.35486 | 0.29933 |
| $C-H\left(CH\right)$ | $C$ | -0.92918 | -0.92918 | -0.92918 | 0 | -154.40324 | 0.91771 | 0.77247 | -17.61330 | -17.42244 | 61.10 | 118.90 | 31.37 | 1.42988 | 0.37326 |
| $H_3C_aC_bH_2CH_2-$ $(C-C$ (a)) | $C_a$ | -0.92918 | 0 | 0 | 0 | -152.54487 | 0.91771 | 0.86359 | -15.75493 | -15.56407 | 63.82 | 116.18 | 30.08 | 1.83879 | 0.38106 |
| $H_3C_aC_bH_2CH_2-$ $(C-C$ (a)) | $C_b$ | -0.92918 | -0.92918 | 0 | 0 | -153.47406 | 0.91771 | 0.81549 | -16.68412 | -16.49325 | 56.41 | 123.59 | 26.06 | 1.90890 | 0.45117 |
| $R-H_2C_aC_b\left(H_2C_c-R'\right)HCH_2-$ $(C-C$ (b)) | $C_b$ | -0.92918 | -0.92918 | -0.92918 | 0 | -154.40324 | 0.91771 | 0.77247 | -17.61330 | -17.42244 | 48.30 | 131.70 | 21.90 | 1.97162 | 0.51388 |
| $R-H_2C_a\left(R'-H_2C_d\right)C_b\left(R''-H_2C_c\right)CH_2-$ $(C-C$ (c)) | $C_b$ | -0.92918 | -0.72457 | -0.72457 | -0.72457 | -154.71860 | 0.91771 | 0.75889 | -17.92866 | -17.73779 | 48.21 | 131.79 | 21.74 | 1.95734 | 0.50570 |
| $isoC_aC_b\left(H_2C_c-R'\right)HCH_2-$ $(C-C$ (d)) | $C_b$ | -0.92918 | -0.92918 | -0.92918 | 0 | -154.40324 | 0.91771 | 0.77247 | -17.61330 | -17.42244 | 48.30 | 131.70 | 21.90 | 1.97162 | 0.51388 |
| $tertC_a\left(R'-H_2C_d\right)C_b\left(R''-H_2C_c\right)CH_2-$ $(C-C$ (e)) | $C_b$ | -0.72457 | -0.72457 | -0.72457 | -0.72457 | -154.51399 | 0.91771 | 0.76765 | -17.92866 | -17.73779 | 50.04 | 129.96 | 22.66 | 1.94462 | 0.49298 |
| $tertC_aC_b\left(H_2C_c-R'\right)HCH_2-$ $(C-C$ (f)) | $C_b$ | -0.72457 | -0.92918 | -0.92918 | 0- | -154.19863 | 0.91771 | 0.78155 | -17.40869 | -17.21783 | 52.78 | 127.22 | 24.04 | 1.92443 | 0.47279 |
| $isoC_a\left(R'-H_2C_d\right)C_b\left(R''-H_2C_c\right)CH_2-$ $(C-C$ (f)) | $C_b$ | -0.72457 | -0.72457 | -0.72457 | -0.72457 | -154.51399 | 0.91771 | 0.76765 | -17.92866 | -17.73779 | 50.04 | 129.96 | 22.66 | 1.94462 | 0.49298 |

Table 15.42. The energy parameters ($eV$) of functional groups of branched-chain alkyl bromides.

| Parameters | $C-Br$ (i) Group | $C-Br$ (ii) Group | $C-Br$ (iii) Group | $CH_3$ Group | $CH_2$ Group | $C-H$ Group | $C-C$ (a) Group | $C-C$ (b) Group | $C-C$ (c) Group | $C-C$ (d) Group | $C-C$ (e) Group | $C-C$ (f) Group |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $n_1$ | 1 | 1 | 1 | 3 | 2 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $n_2$ | 0 | 0 | 0 | 2 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $n_3$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $C_1$ | 0.5 | 0.5 | 0.5 | 0.75 | 0.75 | 0.75 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| $C_2$ | 0.74081 | 0.74081 | 0.74081 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $c_1$ | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $c_2$ | 1 | 1 | 1 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 |
| $c_3$ | 0 | 0 | 0 | 0 | 1 | 1 | 0 | 0 | 0 | 1 | 1 | 0 |
| $c_4$ | 2 | 2 | 2 | 1 | 1 | 1 | 2 | 2 | 2 | 2 | 2 | 2 |
| $c_5$ | 0 | 0 | 0 | 3 | 2 | 1 | 0 | 0 | 0 | 0 | 0 | 0 |
| $C_{1o}$ | 0.5 | 0.5 | 0.5 | 0.75 | 0.75 | 0.75 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| $C_{2o}$ | 0.74081 | 0.74081 | 0.74081 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $V_e\ (eV)$ | -27.94806 | -27.44996 | -28.22940 | -107.32728 | -70.41425 | -35.12015 | -28.79214 | -28.79214 | -29.10112 | -28.79214 | -29.10112 | -29.10112 |
| $V_p\ (eV)$ | 7.41885 | 7.36953 | 7.44631 | 38.92728 | 25.78002 | 12.87680 | 9.33352 | 9.33352 | 9.37273 | 9.33352 | 9.37273 | 9.37273 |
| $T\ (eV)$ | 5.60839 | 5.43544 | 5.70686 | 32.53914 | 21.06675 | 10.48582 | 6.77464 | 6.77464 | 6.90500 | 6.77464 | 6.90500 | 6.90500 |
| $V_m\ (eV)$ | -2.80419 | -2.71772 | -2.85343 | -16.26957 | -10.53337 | -5.24291 | -3.38732 | -3.38732 | -3.45250 | -3.38732 | -3.45250 | -3.45250 |
| $E(_{AO/HO})\ (eV)$ | -14.63489 | -14.63489 | -14.63489 | -15.56407 | -15.56407 | -14.63489 | -15.56407 | -15.56407 | -15.35946 | -15.56407 | -15.35946 | -15.35946 |
| $\Delta E_{H_2MO}(_{AO/HO})\ (eV)$ | -0.72457 | -0.36229 | -0.92918 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $E_T(_{AO/HO})\ (eV)$ | -13.91032 | -14.27260 | -13.70571 | -15.56407 | -15.56407 | -14.63489 | -15.56407 | -15.56407 | -15.35946 | -15.56407 | -15.35946 | -15.35946 |
| $E_T(_{H_2MO})\ (eV)$ | -31.63533 | -31.63531 | -31.63537 | -67.69451 | -49.66493 | -31.63533 | -31.63537 | -31.63537 | -31.63535 | -31.63537 | -31.63535 | -31.63535 |
| $E_T\left(atom-atom,msp^3.AO\right)(eV)$ | -0.72457 | -0.36229 | -0.92918 | 0 | 0 | 0 | -1.85836 | -1.85836 | -1.44915 | -1.85836 | -1.44915 | -1.44915 |
| $E_T(_{MO})\ (eV)$ | -32.35994 | -31.99766 | -32.56455 | -67.69450 | -49.66493 | -31.63537 | -33.49373 | -33.49373 | -33.08452 | -33.49373 | -33.08452 | -33.08452 |
| $\omega\ \left(10^{15}\ rad/s\right)$ | 6.39733 | 6.27059 | 6.46864 | 24.9286 | 24.2751 | 24.1759 | 9.43699 | 9.43699 | 15.4846 | 9.43699 | 9.55643 | 9.55643 |
| $E_K\ (eV)$ | 4.21083 | 4.12741 | 4.25777 | 16.40846 | 15.97831 | 15.91299 | 6.21159 | 6.21159 | 10.19220 | 6.21159 | 6.29021 | 6.29021 |
| $\bar{E}_D\ (eV)$ | -0.13137 | -0.12861 | -0.13293 | -0.25352 | -0.25017 | -0.24966 | -0.16515 | -0.16515 | -0.20896 | -0.16515 | -0.16416 | -0.16416 |
| $\bar{E}_{Kvib}\ (eV)$ | 0.07575<br>[14] | 0.08332<br>[15] | 0.07575<br>[14] | 0.35532<br>(Eq. (13.458)) | 0.35532<br>(Eq. (13.458)) | 0.35532<br>(Eq. (13.458)) | 0.12312<br>[2] | 0.17978<br>[4] | 0.09944<br>[5] | 0.12312<br>[2] | 0.12312<br>[2] | 0.12312<br>[2] |
| $\bar{E}_{osc}\ (eV)$ | -0.09349 | -0.08695 | -0.09506 | -0.22757 | -0.14502 | -0.07200 | -0.10359 | -0.07526 | -0.15924 | -0.10359 | -0.10260 | -0.10260 |
| $E_{mag}\ (eV)$ | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 |
| $E_T(_{Group})\ (eV)$ | -32.45343 | -32.08460 | -32.65961 | -67.92207 | -49.80996 | -31.70737 | -33.59732 | -33.49373 | -33.24376 | -33.59732 | -33.18712 | -33.18712 |
| $E_{initial}(_{c_4\ AO/HO})\ (eV)$ | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 |
| $E_{initial}(_{c_5\ AO/HO})\ (eV)$ | 0 | 0 | 0 | -13.59844 | -13.59844 | -13.59844 | 0 | 0 | 0 | 0 | 0 | 0 |
| $E_D(_{Group})\ (eV)$ | 3.18365 | 2.81482 | 3.38983 | 12.49186 | 7.83016 | 3.32601 | 4.32754 | 4.29921 | 3.97398 | 4.17951 | 3.62128 | 3.91734 |

Table 15.43. The total bond energies of branched-chain alkyl bromides calculated using the functional group composition and the energies of Table 15.42 compared to the experimental values [3]. The magnetic energy $E_{mag}$ that is subtracted from the weighted sum of the $E_D$ ($_{Group}$) ($eV$) values based on composition is given by (15.58).

| Formula | Name | $C-Br$ (i) | $C-Br$ (ii) | $C-Br$ (iii) | $CH_3$ | $CH_2$ | $CH$ (i) | $CH$ (ii) | $C-C$ (a) | $C-C$ (b) | $C-C$ (c) | $C-C$ (d) | $C-C$ (e) | $C-C$ (f) | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $CBr_4$ | Tetrabromomethane | 0 | 4 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 11.25929 | 11.196 | -0.00566 |
| $CHBr_3$ | Tribromomethane | 3 | 0 | 0 | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 12.87698 | 12.919 | 0.00323 |
| $CH_3Br$ | Bromomethane | 1 | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 15.67551 | 15.732 | 0.00360 |
| $C_2H_5Br$ | Bromoethane | 0 | 0 | 1 | 1 | 1 | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 28.03939 | 27.953 | -0.00308 |
| $C_3H_7Br$ | 1-Bromopropane | 0 | 0 | 1 | 1 | 2 | 0 | 0 | 2 | 0 | 0 | 0 | 0 | 0 | 40.19709 | 40.160 | -0.00093 |
| $C_3H_7Br$ | 2-Bromopropane | 0 | 0 | 1 | 2 | 0 | 1 | 0 | 0 | 2 | 0 | 0 | 0 | 0 | 40.29798 | 40.288 | -0.00024 |
| $C_5H_{10}Br_2$ | 2,3-Dibromo-2-methylbutane | 1 | 0 | 1 | 3 | 0 | 1 | 0 | 0 | 1 | 2 | 0 | 0 | 1 | 63.53958 | 63.477 | -0.00098 |
| $C_6H_{13}Br$ | 1-Bromohexane | 0 | 0 | 1 | 1 | 5 | 0 | 0 | 5 | 0 | 0 | 0 | 0 | 0 | 76.67019 | 76.634 | -0.00047 |
| $C_7H_{15}Br$ | 1-Bromoheptane | 0 | 0 | 1 | 1 | 6 | 0 | 0 | 6 | 0 | 0 | 0 | 0 | 0 | 88.82789 | 88.783 | 0.00051 |
| $C_8H_{17}Br$ | 1-Bromooctane | 0 | 0 | 1 | 1 | 7 | 0 | 0 | 7 | 0 | 0 | 0 | 0 | 0 | 100.98559 | 100.952 | -0.00033 |
| $C_{12}H_{25}Br$ | 1-Bromododecane | 0 | 0 | 1 | 1 | 11 | 0 | 0 | 11 | 0 | 0 | 0 | 0 | 0 | 149.61639 | 149.573 | -0.00029 |
| $C_{16}H_{33}Br$ | 1-Bromohexadecane | 0 | 0 | 1 | 1 | 15 | 0 | 0 | 15 | 0 | 0 | 0 | 0 | 0 | 198.24719 | 198.192 | -0.00028 |

Table 15.44. The bond angle parameters of branched-chain alkyl bromides and experimental values [1]. In the calculation of $\theta_v$, the parameters from the preceding angle were used. $E_T$ is $E_T(atom-atom, msp^3.AO)$.

| Atoms of Angle | $2c'$ Bond 1 ($a_0$) | $2c'$ Bond 2 ($a_0$) | $2c'$ Terminal Atoms ($a_0$) | $E_{Coulombic}$ Atom 1 | Atom 1 Hybridization Designation (Table 15.3.A) | $E_{Coulombic}$ Atom 2 | Atom 2 Hybridization Designation (Table 15.3.A) | $c_2$ Atom 1 | $c_2$ Atom 2 | $C_1$ | $C_2$ | $c_1$ | $c_2'$ | $E_T$ (eV) | $\theta_v$ (°) | $\theta_1$ (°) | $\theta_2$ (°) | Cal. $\theta$ (°) | Exp. $\theta$ (°) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $\angle BrC_aBr$ ($C_a-Br$ (i)) | 3.66790 | 3.66790 | 6.0816 | -15.18804 $Br$ | 2 | -15.18804 $Br$ | 2 | 0.89582 | 0.89582 | 1 | 0.74081 (Eq. (15.131)) | 1 | 0.89582 | -0.92918 | | | | 112.00 | 111.2 (methyl bromide)<br>113.2 (dibromomethane)<br>111.7 (bromoform) |
| $\angle HC_aBr$ ($C_a-Br$ (iii)) | 2.11106 | 3.66790 | 4.8312 | -15.55033 $C_a$ | 5 | -11.81381 $Br$ | Br | 0.87495 | 0.91771 | 0.75 | 0.86829 (Eq. (15.74)) | 0.75 | 1.04887 | 0 | | | | 110.53 | 109 (dibromomethane) |
| $\angle HC_aH$<br>$\angle HC_bH$<br>($C_a-Br$ (iii)) | 2.09711 | 2.09711 | 3.4252 | -15.75493 | 7 | H | H | 0.86359 | 1 | 1 | 1 | 0.75 | 1.15796 | 0 | | | | 109.50 | |
| $\angle C_aC_bH_b$ ($C_a-Br$ (iii)) | | | | | | | | | | | | | | | 70.56 | | | 109.44 | 110 (1,2-dibromoethane)<br>109.0 (1,1,1-tribromoethane) |
| $\angle C_bC_aBr$ ($C_a-Br$ (iii)) | 2.91547 | 3.65437 | 5.4247 | -15.75493 $C_b$ | 7 | -11.81381 $Br$ | Br | 0.86359 | 0.86359 | 1 | 0.74081 (Eq. (15.131)) | 1 | 0.86359 | -0.72457 | | | | 110.82 | 109.5 (1,1-dibromoethane) |
| Methylene $\angle HC_aH$ | 2.11106 | 2.11106 | 3.4252 | -15.75493 | 7 | H | H | 0.86359 | 1 | 1 | 1 | 0.75 | 1.15796 | 0 | | | | 108.44 | 107 (propane) |
| $\angle C_aC_bC_c$ | | | | | | | | | | | | | | | 69.51 | | | 110.49 | 112 (propane)<br>113.8 (butane)<br>110.8 (isobutane) |
| $\angle C_aC_bH$ | | | | | | | | | | | | | | | 69.51 | | | 110.49 | 111.0 (butane)<br>111.4 (isobutane) |
| Methyl $\angle HC_aH$ | 2.09711 | 2.09711 | 3.4252 | -15.75493 | 7 | H | H | 0.86359 | 1 | 1 | 1 | 0.75 | 1.15796 | 0 | | | | 109.50 | |
| $\angle C_aC_bC_c$ | | | | | | | | | | | | | | | 70.56 | | | 109.44 | |
| $\angle C_aC_bH$ | | | | | | | | | | | | | | | 70.56 | | | 109.44 | |
| $\angle C_bC_aC_c$ iso $C_a$ | 2.91547 | 2.91547 | 4.7958 | -16.68412 $C_b$ | 26 | -16.68412 $C_c$ | 26 | 0.81549 | 0.81549 | 1 | 1 | 1 | 0.81549 | -1.85836 | | | | 110.67 | 110.8 (isobutane) |
| $\angle C_bC_aH$ iso $C_a$ | 2.91547 | 2.11323 | 4.1633 | -15.55033 $C_a$ | 5 | -14.82575 $C_b$ | 1 | 0.87495 | 0.91771 | 0.75 | 1 | 0.75 | 1.04887 | 0 | | | | 110.76 | |
| $\angle C_aC_bH$ iso $C_a$ | 2.91547 | 2.09711 | 4.1633 | -15.55033 $C_b$ | 5 | -14.82575 $C_a$ | 1 | 0.87495 | 0.91771 | 0.75 | 1 | 0.75 | 1.04887 | 0 | | | | 111.27 | 111.4 (isobutane) |
| $\angle C_bC_aC_b$ tert $C_a$ | 2.90327 | 2.90327 | 4.7958 | -16.68412 $C_b$ | 26 | -16.68412 $C_b$ | 26 | 0.81549 | 0.81549 | 1 | 1 | 1 | 0.81549 | -1.85836 | | | | 111.37 | 110.8 (isobutane) |
| $\angle C_bC_aC_d$ | | | | | | | | | | | | | | | 72.50 | | | 107.50 | |

## ALKYL IODIDES ($C_nH_{2n+2-m}I_m$, $n=1,2,3,4,5...\infty$ $m=1,2,3...\infty$)

The branched-chain alkyl iodides, $C_nH_{2n+2-m}I_m$, may comprise at least two terminal methyl groups ($CH_3$) at each end of the chain, and may comprise methylene ($CH_2$), and methylyne ($CH$) functional groups as well as $C$ bound by carbon-carbon single bonds wherein at least one $H$ is replaced by an iodine atom. The $C-I$ bond comprises a functional group for $I$ replacing a $H$ of methane ($CH_3I$) or for $I$ replacing a $H$ of an alkane corresponding to the series $C_nH_{2n+2-m}I_m$. The $C-I$ bond of each of $CH_2I_2$ and $CHI_3$ comprise separate functional groups due to the limitation of the minimum energy of $I$ matched to that of the $C2sp^3$ HO. The methyl, methylene, methylyne functional groups are equivalent to those of branched-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($(CH_3)_2CH$) and t-butyl ($(CH_3)_3C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups that are equivalent to those of branched-chain alkanes.

The solution of the $C-I$ functional groups comprises the hybridization of the $2s$ and $2p$ AOs of each $C$ to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between the $C2sp^3$ HO and the $I$ AO to form a MO permits each participating orbital to decrease in radius and energy. In alkyl iodides, the energy of iodine is less than the Coulombic energy between the electron and proton of $H$ given by Eq. (1.264). Thus, $c_2$ in Eq. (15.61) is one, and the energy matching condition is determined by the $C_2$ parameter. Then, the $C2sp^3$ HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of $E(C,2sp^3)=-14.63489\ eV$ (Eq. (15.25)). The $I$ AO has an energy of $E(I)=-10.45126\ eV$. To meet the equipotential condition of the union of the $C-I$ $H_2$-type-ellipsoidal-MO with these orbitals, the hybridization factor $C_2$ of Eq. (15.60) for the $C-I$-bond MO given by Eqs. (15.77) and (15.79) is:

$$C_2\left(C2sp^3HO\ to\ I\right)=\frac{E(I)}{E\left(C,2sp^3\right)}c_2\left(C2sp^3HO\right)=\frac{-10.45126\ eV}{-14.63489\ eV}(0.91771)=0.65537 \tag{15.132}$$

The valence energy of the carbon $2p$ is $-11.2603\ eV$ and that of the $I$ AO is $-10.45126\ eV$. The energy difference is positive. Thus, based on the maximum charge density on the $C2sp^3$ HO $E_T\left(atom-atom,msp^3.AO\right)$ of the $C-I$-bond MO in Eq. (15.61) due to the charge donation from the $C$ and $I$ atoms to the MO is $-0.36229\ eV$ (Eqs. (15.18-15.20 and Eq. (15.29) with a linear combination of $s=1$, $E_T\left(atom-atom,msp^3.AO\right)=-0.72457\ eV$ and $E_T\left(atom-atom,msp^3.AO\right)=0$) for methyl and alkyl iodides, $-0.18114\ eV$ for diiodomethane, and $0$ for $CHI_3$.

The symbols of the functional groups of branched-chain alkyl iodides are given in Table 15.45. The geometrical (Eqs. (15.1-15.5) and (15.51)), intercept (Eqs. (15.80-15.87)), and energy (Eqs. (15.6-15.11) and (15.17-15.65)) parameters of branched-chain alkyl iodides are given in Tables 15.55, 15.56, and 15.57, respectively. The total energy of each branched-chain alkyl iodide given in Table 15.49 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.48 corresponding to functional-group composition of the molecule. For each set of unpaired electrons created by bond breakage, the $C2sp^3$ HO magnetic energy $E_{mag}$ that was subtracted from the weighted sum of the $E_D(Group)$ $(eV)$ values based on composition is given by Eq. (15.67). The $C-C$ bonds to the $CHI$ group (one $H$ bond to $C$) were each treated as an iso $C-C$ bond. The $C-C$ bonds to the $CI$ group (no $H$ bonds to $C$) were each treated as a tert-butyl $C-C$. $E_{mag}$ is subtracted for each t-butyl group. The bond angle parameters of branched-chain alkyl iodides determined using Eqs. (15.70-15.79), (15.88-15.117) and (15.132) are given in Table 15.50. The color scale, translucent view of the charge-density of exemplary alkyl iodide, 1-iodopropane, comprising the concentric shells of atoms with the outer shell bridged by one or more $H_2$-type ellipsoidal MOs or joined with one or more hydrogen MOs is shown in Figure 15.8.

Figure 15.8. Color scale, translucent view of the charge-density of 1-iodopropane showing the orbitals of the atoms at their radii, the ellipsoidal surface of each $H$ or $H_2$-type ellipsoidal MO that transitions to the corresponding outer shell of the atom(s) participating in each bond, and the hydrogen nuclei (red, not to scale).

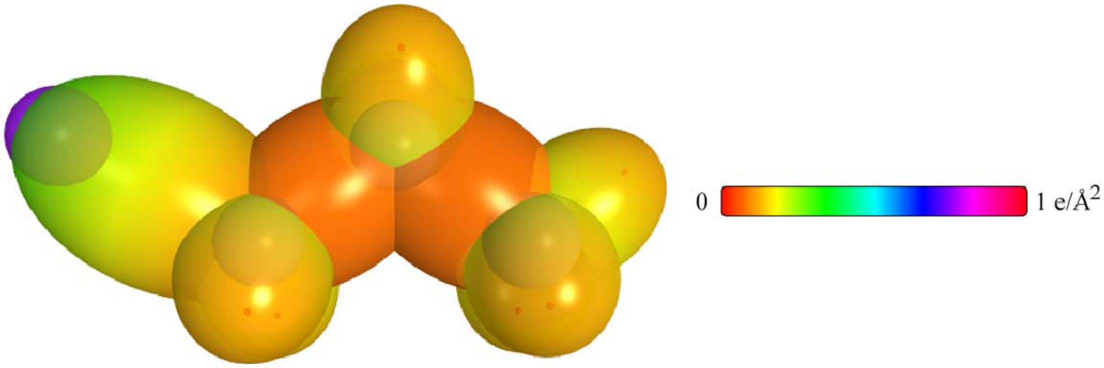


Table 15.45. The symbols of functional groups of branched-chain alkyl iodides.

| Functional Group | Group Symbol |
|---|---|
| $CI$ of $CH_3I$ and $C_nH_{2n+2-m}I_m$ | $C-I$ (i) |
| $CI$ of $CH_2I_2$ | $C-I$ (ii) |
| $CI$ of $CHI_3$ | $C-I$ (iii) |
| $CH_3$ group | $C-H\ (CH_3)$ |
| $CH_2$ group | $C-H\ (CH_2)$ |
| $CH$ | $C-H$ |
| $CC$ bond (*n-C*) | $C-C$ (a) |
| $CC$ bond (*iso-C*) | $C-C$ (b) |
| $CC$ bond (*tert-C*) | $C-C$ (c) |
| $CC$ (*iso* to *iso-C*) | $C-C$ (d) |
| $CC$ (*t* to *t-C*) | $C-C$ (e) |
| $CC$ (*t* to *iso-C*) | $C-C$ (f) |

Table 15.46. The geometrical bond parameters of branched-chain alkyl iodides and experimental values [1].

| Parameter | $C-I$ (i) Group | $C-I$ (ii) Group | $C-I$ (iii) Group | $C-H\left(CH_3\right)$ Group | $C-H\left(CH_2\right)$ Group | $C-H$ Group | $C-C$ (a) Group | $C-C$ (b) Group | $C-C$ (c) Group | $C-C$ (d) Group | $C-C$ (e) Group | $C-C$ (f) Group |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $a\left(a_0\right)$ | 2.67103 | 2.68865 | 2.70662 | 1.64920 | 1.67122 | 1.67465 | 2.12499 | 2.12499 | 2.10725 | 2.12499 | 2.10725 | 2.10725 |
| $c'\left(a_0\right)$ | 2.01881 | 2.02546 | 2.03222 | 1.04856 | 1.05553 | 1.05661 | 1.45744 | 1.45744 | 1.45164 | 1.45744 | 1.45164 | 1.45164 |
| Bond Length $2c'$ $\left(\AA\right)$ | 2.13662 | 2.14365 | 2.15081 | 1.10974 | 1.11713 | 1.11827 | 1.54280 | 1.54280 | 1.53635 | 1.54280 | 1.53635 | 1.53635 |
| Exp. Bond Length $\left(\AA\right)$ | 2.132<br>(methyl iodide) | 2.132<br>(methyl iodide) | 2.15<br>(carbon tetraiodide) | 1.107<br>($C-H$ propane)<br>1.117<br>($C-H$ butane) | 1.107<br>($C-H$ propane)<br>1.117<br>($C-H$ butane) | 1.122<br>(isobutane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) |
| $b,c\left(a_0\right)$ | 1.74894 | 1.76815 | 1.78770 | 1.27295 | 1.29569 | 1.29924 | 1.54616 | 1.54616 | 1.52750 | 1.54616 | 1.52750 | 1.52750 |
| $e$ | 0.75582 | 0.75334 | 0.75083 | 0.63580 | 0.63159 | 0.63095 | 0.68600 | 0.68600 | 0.68888 | 0.68600 | 0.68888 | 0.68888 |

Table 15.47. The MO to HO intercept geometrical bond parameters of branched-chain alkyl iodides. $R$, $R'$, $R''$ are $H$ or alkyl groups. $E_T$ is $E_T(atom - atom, msp^3.AO)$.

| Bond | Atom | $E_T$ (eV) Bond 1 | $E_T$ (eV) Bond 2 | $E_T$ (eV) Bond 3 | $E_T$ (eV) Bond 4 | Final Total Energy $C2sp^3$ (eV) | $r_{initial}$ $(a_0)$ | $r_{final}$ $(a_0)$ | $E_{Coulomb}$ (eV) Final | $E(C2sp^3)$ (eV) Final | $\theta'$ $(^\circ)$ | $\theta_1$ $(^\circ)$ | $\theta_2$ $(^\circ)$ | $d_1$ $(a_0)$ | $d_2$ $(a_0)$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $CH_3I$<br>($C_a - I$ (i)) | $C_a$ | -0.18114 | 0 | 0 | 0 | -151.79683 | 0.91771 | 0.90664 | -15.00689 | -14.81603 | 69.63 | 110.37 | 29.08 | 2.33442 | 0.31560 |
| $CH_3I$<br>($C_a - I$ (i)) | $I$ | -0.18114 | 0 | 0 | 0 |  | 1.30183 | 0.90664 | -15.00689 |  | 69.63 | 110.37 | 29.08 | 2.33442 | 0.31560 |
| $-H_2C_bC_aI$<br>($C_a - I$ (i)) | $C_a$ | -0.18114 | -0.92918 | 0 | 0 | -152.72602 | 0.91771 | 0.85377 | -15.93608 | -15.74521 | 63.16 | 116.84 | 25.82 | 2.40436 | 0.38554 |
| $-H_2C_bC_aI$<br>($C_a - I$ (i)) | $I$ | -0.18114 | 0 | 0 | 0 |  | 1.30183 | 0.90664 | -15.00689 |  | 69.63 | 110.37 | 29.08 | 2.33442 | 0.31560 |
| $C_aH_2I_2$<br>($C_a - I$ (ii)) | $C_a$ | -0.09057 | 0 | 0 | 0 | -151.70626 | 0.91771 | 0.91214 | -14.91632 | -14.72546 | 68.61 | 111.39 | 28.71 | 2.35818 | 0.33272 |
| $C_aH_2I_2$<br>($C_a - I$ (ii)) | $I$ | -0.09057 | 0 | 0 | 0 |  | 1.30183 | 0.91214 | -14.91632 |  | 68.61 | 111.39 | 28.71 | 2.35818 | 0.33272 |
| $C_aHI_3$<br>($C_a - I$ (iii)) | $C_a$ | 0 | 0 | 0 | 0 | -151.61569 | 0.91771 | 0.91771 | -14.82575 | -14.63489 | 67.56 | 112.44 | 28.32 | 2.38256 | 0.35035 |
| $C_aHI_3$<br>($C_a - I$ (iii)) | $I$ | 0 | 0 | 0 | 0 |  | 1.30183 | 0.91771 | -14.82575 | -14.63489 | 67.56 | 112.44 | 28.32 | 2.38256 | 0.35035 |
| $C-H\ (CH_3)$ | $C$ | -0.92918 | 0 | 0 | 0 | -152.54487 | 0.91771 | 0.86359 | -15.75493 | -15.56407 | 77.49 | 102.51 | 41.48 | 1.23564 | 0.18708 |
| $C-H\ (CH_2)$ | $C$ | -0.92918 | -0.92918 | 0 | 0 | -153.47406 | 0.91771 | 0.81549 | -16.68412 | -16.49325 | 68.47 | 111.53 | 35.84 | 1.35486 | 0.29933 |
| $C-H\ (CH)$ | $C$ | -0.92918 | -0.92918 | -0.92918 | 0 | -154.40324 | 0.91771 | 0.77247 | -17.61330 | -17.42244 | 61.10 | 118.90 | 31.37 | 1.42988 | 0.37326 |
| $H_3C_aC_bH_2CH_2-$<br>($C-C$ (a)) | $C_a$ | -0.92918 | 0 | 0 | 0 | -152.54487 | 0.91771 | 0.86359 | -15.75493 | -15.56407 | 63.82 | 116.18 | 30.08 | 1.83879 | 0.38106 |
| $H_3C_aC_bH_2CH_2-$<br>($C-C$ (a)) | $C_b$ | -0.92918 | -0.92918 | 0 | 0 | -153.47406 | 0.91771 | 0.81549 | -16.68412 | -16.49325 | 56.41 | 123.59 | 26.06 | 1.90890 | 0.45117 |
| $R-H_2C_aC_b(H_2C_c-R')HCH_2-$<br>($C-C$ (b)) | $C_b$ | -0.92918 | -0.92918 | -0.92918 | 0 | -154.40324 | 0.91771 | 0.77247 | -17.61330 | -17.42244 | 48.30 | 131.70 | 21.90 | 1.97162 | 0.51388 |
| $R-H_2C_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$<br>($C-C$ (c)) | $C_b$ | -0.92918 | -0.72457 | -0.72457 | -0.72457 | -154.71860 | 0.91771 | 0.75889 | -17.92866 | -17.73779 | 48.21 | 131.79 | 21.74 | 1.95734 | 0.50570 |
| $isoC_aC_b(H_2C_c-R')HCH_2-$<br>($C-C$ (d)) | $C_b$ | -0.92918 | -0.92918 | -0.92918 | 0 | -154.40324 | 0.91771 | 0.77247 | -17.61330 | -17.42244 | 48.30 | 131.70 | 21.90 | 1.97162 | 0.51388 |
| $tertC_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$<br>($C-C$ (e)) | $C_b$ | -0.72457 | -0.72457 | -0.72457 | -0.72457 | -154.51399 | 0.91771 | 0.76765 | -17.92866 | -17.73779 | 50.04 | 129.96 | 22.66 | 1.94462 | 0.49298 |
| $tertC_aC_b(H_2C_c-R')HCH_2-$<br>($C-C$ (f)) | $C_b$ | -0.72457 | -0.92918 | -0.92918 | 0- | -154.19863 | 0.91771 | 0.78155 | -17.40869 | -17.21783 | 52.78 | 127.22 | 24.04 | 1.92443 | 0.47279 |
| $isoC_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$<br>($C-C$ (f)) | $C_b$ | -0.72457 | -0.72457 | -0.72457 | -0.72457 | -154.51399 | 0.91771 | 0.76765 | -17.92866 | -17.73779 | 50.04 | 129.96 | 22.66 | 1.94462 | 0.49298 |

Table 15.48. The energy parameters ($eV$) of functional groups of branched-chain alkyl iodides.

| Parameters | $C-I$ (i) Group | $C-I$ (ii) Group | $C-I$ (iii) Group | $CH_3$ Group | $CH_2$ Group | $C-H$ Group | $C-C$ (a) Group | $C-C$ (b) Group | $C-C$ (c) Group | $C-C$ (d) Group | $C-C$ (e) Group | $C-C$ (f) Group |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $n_1$ | 1 | 1 | 1 | 3 | 2 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $n_2$ | 0 | 0 | 0 | 2 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $n_3$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $C_1$ | 0.5 | 0.5 | 0.5 | 0.75 | 0.75 | 0.75 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| $C_2$ | 0.65537 | 0.65537 | 0.65537 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $c_1$ | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $c_2$ | 1 | 1 | 1 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 |
| $c_3$ | 1 | 0 | 1 | 0 | 1 | 1 | 0 | 0 | 0 | 1 | 1 | 0 |
| $c_4$ | 2 | 2 | 2 | 1 | 1 | 1 | 2 | 2 | 2 | 2 | 2 | 2 |
| $c_5$ | 0 | 0 | 0 | 3 | 2 | 1 | 0 | 0 | 0 | 0 | 0 | 0 |
| $C_{1o}$ | 0.5 | 0.5 | 0.5 | 0.75 | 0.75 | 0.75 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| $C_{2o}$ | 0.65537 | 0.65537 | 0.65537 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $V_e\ (eV)$ | -26.59109 | -26.34902 | -26.10696 | -107.32728 | -70.41425 | -35.12015 | -28.79214 | -28.79214 | -29.10112 | -28.79214 | -29.10112 | -29.10112 |
| $V_p\ (eV)$ | 6.73951 | 6.71739 | 6.69505 | 38.92728 | 25.78002 | 12.87680 | 9.33352 | 9.33352 | 9.37273 | 9.33352 | 9.37273 | 9.37273 |
| $T\ (eV)$ | 4.97768 | 4.90005 | 4.82280 | 32.53914 | 21.06675 | 10.48582 | 6.77464 | 6.77464 | 6.90500 | 6.77464 | 6.90500 | 6.90500 |
| $V_m\ (eV)$ | -2.48884 | -2.45002 | -2.41140 | -16.26957 | -10.53337 | -5.24291 | -3.38732 | -3.38732 | -3.45250 | -3.38732 | -3.45250 | -3.45250 |
| $E(_{AO/HO})\ (eV)$ | -14.63489 | -14.63489 | -14.63489 | -15.56407 | -15.56407 | -14.63489 | -15.56407 | -15.56407 | -15.35946 | -15.56407 | -15.35946 | -15.35946 |
| $\Delta E_{H_2MO}(_{AO/HO})\ (eV)$ | -0.36229 | -0.18114 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $E_T(_{AO/HO})\ (eV)$ | -14.29907 | -14.45375 | -14.63489 | -15.56407 | -15.56407 | -14.63489 | -15.56407 | -15.56407 | -15.35946 | -15.56407 | -15.35946 | -15.35946 |
| $E_T(_{H_2MO})\ (eV)$ | -31.63534 | -31.63535 | -31.63540 | -67.69451 | -49.66493 | -31.63533 | -31.63537 | -31.63537 | -31.63535 | -31.63537 | -31.63535 | -31.63535 |
| $E_T\left(atom-atom,msp^3.AO\right)(eV)$ | -0.36229 | -0.18114 | 0 | 0 | 0 | 0 | -1.85836 | -1.85836 | -1.44915 | -1.85836 | -1.44915 | -1.44915 |
| $E_T(_{MO})\ (eV)$ | -31.99766 | -31.81651 | -31.63537 | -67.69450 | -49.66493 | -31.63537 | -33.49373 | -33.49373 | -33.08452 | -33.49373 | -33.08452 | -33.08452 |
| $\omega\ \left(10^{15}\ rad/s\right)$ | 10.2318 | 5.36799 | 9.90080 | 24.9286 | 24.2751 | 24.1759 | 9.43699 | 9.43699 | 15.4846 | 9.43699 | 9.55643 | 9.55643 |
| $E_K\ (eV)$ | 6.73472 | 3.53331 | 6.51688 | 16.40846 | 15.97831 | 15.91299 | 6.21159 | 6.21159 | 10.19220 | 6.21159 | 6.29021 | 6.29021 |
| $\bar{E}_D\ (eV)$ | -0.16428 | -0.11832 | -0.15977 | -0.25352 | -0.25017 | -0.24966 | -0.16515 | -0.16515 | -0.20896 | -0.16515 | -0.16416 | -0.16416 |
| $\bar{E}_{Kvib}\ (eV)$ | 0.06608<br>[16] | 0.06608<br>[16] | 0.06608<br>[16] | 0.35532<br>(Eq. (13.458)) | 0.35532<br>(Eq. (13.458)) | 0.35532<br>(Eq. (13.458)) | 0.12312<br>[2] | 0.17978<br>[4] | 0.09944<br>[5] | 0.12312<br>[2] | 0.12312<br>[2] | 0.12312<br>[2] |
| $\bar{E}_{osc}\ (eV)$ | -0.13124 | -0.08527 | -0.12673 | -0.22757 | -0.14502 | -0.07200 | -0.10359 | -0.07526 | -0.15924 | -0.10359 | -0.10260 | -0.10260 |
| $E_{mag}\ (eV)$ | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 |
| $E_T(_{Group})\ (eV)$ | -32.12889 | -31.90179 | -31.76210 | -67.92207 | -49.80996 | -31.70737 | -33.59732 | -33.49373 | -33.24376 | -33.59732 | -33.18712 | -33.18712 |
| $E_{initial}(_{c_4\ AO/HO})\ (eV)$ | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 |
| $E_{initial}(_{c_5\ AO/HO})\ (eV)$ | 0 | 0 | 0 | -13.59844 | -13.59844 | -13.59844 | 0 | 0 | 0 | 0 | 0 | 0 |
| $E_D(_{Group})\ (eV)$ | 2.71108 | 2.63201 | 2.34429 | 12.49186 | 7.83016 | 3.32601 | 4.32754 | 4.29921 | 3.97398 | 4.17951 | 3.62128 | 3.91734 |

Table 15.49. The total bond energies of branched-chain alkyl iodides calculated using the functional group composition and the energies of Table 15.48 compared to the experimental values [3]. The magnetic energy $E_{mag}$ that is subtracted from the weighted sum of the $E_D$ ($_{Group}$) ($eV$) values based on composition is given by (15.58).

| Formula | Name | $C-I$ (i) | $C-I$ (ii) | $C-I$ (iii) | $CH_3$ | $CH_2$ | $CH$ (i) | $CH$ (ii) | $C-C$ (a) | $C-C$ (b) | $C-C$ (c) | $C-C$ (d) | $C-C$ (e) | $C-C$ (f) | $E_{mag}$ | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $CHI_3$ | Triiodomethane | 0 | 0 | 3 | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 10.35888 | 10.405 | 0.00444 |
| $CH_2I_2$ | Diiodomethane | 0 | 2 | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | -1 | 12.94614 | 12.921 | -0.00195 |
| $CH_3I$ | Iodomethane | 1 | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 15.20294 | 15.163 | -0.00263 |
| $C_2H_5I$ | Iodoethane | 1 | 0 | 0 | 1 | 1 | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 27.36064 | 27.343 | -0.00066 |
| $C_3H_7I$ | 1-Iodopropane | 1 | 0 | 0 | 1 | 2 | 0 | 0 | 2 | 0 | 0 | 0 | 0 | 0 | 0 | 39.51834 | 39.516 | -0.00006 |
| $C_3H_7I$ | 2-Iodopropane | 1 | 0 | 0 | 2 | 0 | 1 | 0 | 0 | 2 | 0 | 0 | 0 | 0 | 0 | 39.61923 | 39.623 | 0.00009 |
| $C_4H_9I$ | 2-Iodo-2-methylpropane | 1 | 0 | 0 | 3 | 0 | 0 | 0 | 0 | 0 | 3 | 0 | 0 | 0 | -1 | 51.96057 | 51.899 | -0.00119 |

Table 15.50. The bond angle parameters of branched-chain alkyl iodides and experimental values [1]. In the calculation of $\theta_v$, the parameters from the preceding angle were used. $E_T$ is $E_T(atom-atom,msp^3.AO)$.

| Atoms of Angle | $2c'$ Bond 1 ($a_0$) | $2c'$ Bond 2 ($a_0$) | $2c'$ Terminal Atoms ($a_0$) | $E_{Coulombic}$ Atom 1 | Atom 1 Hybridization Designation (Table 15.3.A) | $E_{Coulombic}$ Atom 2 | Atom 2 Hybridization Designation (Table 15.3.A) | $c_2$ Atom 1 | $c_2$ Atom 2 | $C_1$ | $C_2$ | $c_1$ | $c_2'$ | $E_T$ (eV) | $\theta_v$ (°) | $\theta_1$ (°) | $\theta_2$ (°) | Cal. $\theta$ (°) | Exp. $\theta$ (°) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $\angle IC_aI$ ($C_a-I$ (ii)) | 4.05092 | 4.05092 | 6.7205 | -10.45126 $I$ | I | -10.45126 $I$ | I | 1 | 1 | 1 | 0.65537 (Eq. (15.132)) | 1 | 1 | -0.36228 | | | | 112.10 | |
| $\angle HC_aI$ ($C_a-I$ (i)) | 2.11106 | 4.03763 | 5.2203 | -14.82575 $C_a$ | 1 | -10.45126 $I$ | I | 0.91771 | 0.91771 | 0.75 | 0.76815 (Eq. (15.74)) | 0.75 | 1.00000 | 0 | | | | 112.39 | |
| $\angle HC_aH$<br>$\angle HC_bH$<br>($C_a-I$ (i)) | 2.09711 | 2.09711 | 3.4252 | -15.75493 | 7 | H | H | 0.86359 | 1 | 1 | 1 | 0.75 | 1.15796 | 0 | | | | 109.50 | 111.2 (methyl iodide) |
| $\angle C_aC_bH_b$ ($C_a-I$ (i)) | | | | | | | | | | | | | | | 70.56 | | | 109.44 | |
| $\angle C_bC_aI$ ($C_a-I$ (i)) | 2.91547 | 4.03763 | 5.7939 | -15.55033 $C_b$ | 5 | -10.45126 $I$ | I | 0.87495 | 0.87495 | 1 | 0.65537 (Eq. (15.132)) | 1 | 0.87495 | -0.36228 | | | | 111.86 | |
| Methylene $\angle HC_aH$ | 2.11106 | 2.11106 | 3.4252 | -15.75493 | 7 | H | H | 0.86359 | 1 | 1 | 1 | 0.75 | 1.15796 | 0 | | | | 108.44 | 107 (propane) |
| $\angle C_aC_bC_c$ | | | | | | | | | | | | | | | 69.51 | | | 110.49 | 112 (propane)<br>113.8 (butane)<br>110.8 (isobutane) |
| $\angle C_aC_bH$ | | | | | | | | | | | | | | | 69.51 | | | 110.49 | 111.0 (butane)<br>111.4 (isobutane) |
| Methyl $\angle HC_aH$ | 2.09711 | 2.09711 | 3.4252 | -15.75493 | 7 | H | H | 0.86359 | 1 | 1 | 1 | 0.75 | 1.15796 | 0 | | | | 109.50 | |
| $\angle C_aC_bC_c$ | | | | | | | | | | | | | | | 70.56 | | | 109.44 | |
| $\angle C_aC_bH$ | | | | | | | | | | | | | | | 70.56 | | | 109.44 | |
| $\angle C_bC_aC_c$ iso $C_a$ | 2.91547 | 2.91547 | 4.7958 | -16.68412 $C_b$ | 26 | -16.68412 $C_c$ | 26 | 0.81549 | 0.81549 | 1 | 1 | 1 | 0.81549 | -1.85836 | | | | 110.67 | 110.8 (isobutane) |
| $\angle C_bC_aH$ iso $C_a$ | 2.91547 | 2.11323 | 4.1633 | -15.55033 $C_a$ | 5 | -14.82575 $C_b$ | 1 | 0.87495 | 0.91771 | 0.75 | 1 | 0.75 | 1.04887 | 0 | | | | 110.76 | |
| $\angle C_aC_bH$ iso $C_a$ | 2.91547 | 2.09711 | 4.1633 | -15.55033 $C_b$ | 5 | -14.82575 $C_a$ | 1 | 0.87495 | 0.91771 | 0.75 | 1 | 0.75 | 1.04887 | 0 | | | | 111.27 | 111.4 (isobutane) |
| $\angle C_bC_aC_b$ tert $C_a$ | 2.90327 | 2.90327 | 4.7958 | -16.68412 $C_b$ | 26 | -16.68412 $C_b$ | 26 | 0.81549 | 0.81549 | 1 | 1 | 1 | 0.81549 | -1.85836 | | | | 111.37 | 110.8 (isobutane) |
| $\angle C_bC_aC_d$ | | | | | | | | | | | | | | | 72.50 | | | 107.50 | |

## ALKENYL HALIDES ($C_nH_{2n-m}X_m$, $n=3,4,5...\infty$ $m=1,2,3...\infty$)

The branched-chain alkenyl halides, $C_nH_{2n+2-m}X_m$ with $X=F,Cl,Br,I$, may comprise alkyl and alkenyl functional groups wherein at least one $H$ is replaced by a halogen atom. In the case that a halogen atom replaces an alkyl $H$, the $C-X$ bond comprises the alkyl-halogen functional groups given in their respective sections. The alkenyl halogen $C-X$ bond comprises a separate functional group for each case of $X$ bonding to the $C=C$-bond functional group given in the Alkenes section. In addition the $CH$ group of the moiety $XCH=C$ comprises a functional group unique to alkenyl halides. The straight and branched-chain alkenes, $C_nH_{2n}$, comprise at least one carbon-carbon double bond comprising a functional group that is solved equivalently to the double bond of ethylene. The double bond may be bound to one, two, three, or four carbon single bonds that substitute for the hydrogen atoms of ethylene. The three distinct functional groups given in the Alkenes section are $C$ vinyl single bond to $-C(C)=C$, $C$ vinyl single bond to $-C(H)=C$, and $C$ vinyl single bond to $-C(C)=CH_2$. In addition, $CH_2$ of the $-C=CH_2$ moiety is also an alkene functional group solved in the Alkenes section.

Consider the case where $X=Cl$ substitutes for a carbon single bond or a hydrogen atom. Based on the condition of energy matching of the orbital, any magnetic energy due to unpaired electrons in the constituent fragments, and differences in oscillation in the transition state, two distinct $C-Cl$ functional groups can be identified: $Cl$ vinyl single bond to $-C(C)=C$ and $Cl$ vinyl single bond to $-C(H)=C$. The alkenyl-halide $CH$ group is equivalent to that solved in the Hydrogen Carbide ($CH$) section except that $\Delta E_{H_2MO}\left(AO/HO\right)=-1.13379\ eV$ in order to energy match to the $C-Cl$ and $C=C$ bonds.

The alkyl portion of the alkenyl halide may comprise at least two terminal methyl groups ($CH_3$) at each end of the chain, and may comprise methylene ($CH_2$), and methylyne ($CH$) functional groups as well as $C$ bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($\left(CH_3\right)_2 CH$) and t-butyl ($\left(CH_3\right)_3 C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups. The branched-chain-alkane groups in alkene halides are equivalent to those in branched-chain alkanes.

$E_T\left(atom-atom,msp^3.AO\right)$ of the $C=C$-bond MO in Eq. (15.61) due to the charge donation from the $C$ atoms to the MO is equivalent to that of ethylene, $-2.26759\ eV$, given by Eq. (14.247). $E_T\left(atom-atom,msp^3.AO\right)$ of each $C-C$-bond MO in Eq. (15.61) is $-1.85836\ eV$ or $-1.44915\ eV$ based on the energy match between the $C2sp^3$ HOs corresponding to the energy contributions equivalent to those of methylene, $-0.92918\ eV$ (Eq. (14.513), or methyl, $-0.72457\ eV$ (Eq. (14.151)), groups, respectively.

The solution of each $C-X$ functional group comprises the hybridization of the $2s$ and $2p$ AOs of the $C$ atom to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between the $C2sp^3$ HO and the $X$ AO to form a MO permits each participating orbital to decrease in radius and energy. The alkenyl $C-X$-bond functional groups comprise single bonds and are equivalent to those of the corresponding alkyl halides except that the halogen AO and the $C-X$-bond MO are each energy matched to the alkene $C2sp^3$ HO. In alkenyl halides with $X=Cl,Br,\ or\ I$, the energy of the halogen atom is less than the Coulombic energy between the electron and proton of $H$ given by Eq. (1.264)). Thus, $c_2$ in Eq. (15.61) is one, and the energy matching condition is determined by the $C_2$ parameter. For example, the hybridization factor $C_2$ of Eq. (15.61) for the alkenyl $C-Cl$-bond MO given by Eq. (15.130) is $C_2\left(C2sp^3HO\ to\ \mathrm{Cl}\right)=0.81317$.

$E_T\left(atom-atom,msp^3.AO\right)$ of the alkenyl $C-Cl$-bond MO in Eq. (15.61) due to the charge donation from the $C$ and $Cl$ atoms to the MO is $-1.44915\ eV$ for the $Cl$ vinyl single bond to $-C(H)=C$ $C-Cl$ group and $-0.92918\ eV$ for the $Cl$ vinyl single bond to $-C(C)=C$ $C-Cl$ group. It is based on the energy match between the $Cl$ atom and the $C2sp^3$ HO of an unsubstituted vinyl group and a substituted vinyl group given by Eqs. (14.151) and (14.513), respectively.

The symbols of the functional groups of branched-chain alkenyl chlorides are given in Table 15.51. The geometrical (Eqs. (15.1-15.5) and (15.51)), intercept (Eqs. (15.80-15.87)), and energy (Eqs. (15.6-15.11) and (15.17-15.65)) parameters of branched-chain alkenyl chlorides are given in Tables 15.52, 15.53, and 15.54, respectively. The total energy of each branched-chain alkenyl chloride given in Table 15.55 was calculated as the sum over the integer multiple of each $E_D\left(Group\right)$ of Table 15.54 corresponding to functional-group composition of the molecule. The bond angle parameters of branched-chain alkenyl chlorides determined using Eqs. (15.70-15.79), (15.88-15.117) and (15.130) are given in Table 15.56. The color scale, translucent view of the charge-density of exemplary alkenyl halide, 2-chloropropene, comprising the concentric shells of atoms with the outer shell bridged by one or more $H_2$-type ellipsoidal MOs or joined with one or more hydrogen MOs is shown in Figure 15.9.

Figure 15.9. Color scale, translucent view of the charge-density of 2-chloropropene showing the orbitals of the atoms at their radii, the ellipsoidal surface of each $H$ or $H_2$-type ellipsoidal MO that transitions to the corresponding outer shell of the atom(s) participating in each bond, and the hydrogen nuclei (red, not to scale).

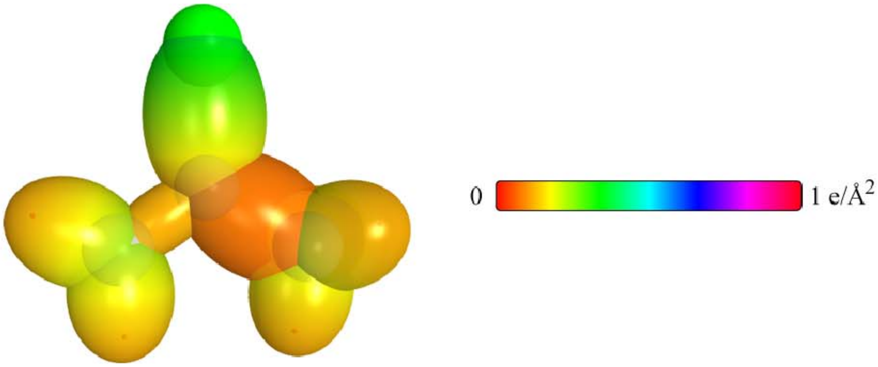


Table 15.51. The symbols of functional groups of branched-chain alkenyl chlorides.

| Functional Group | Group Symbol |
|---|---|
| $Cl$ vinyl single bond to -$C(H)=C$ | $C-Cl$ (i) |
| $Cl$ vinyl single bond to -$C(C)=C$ | $C-Cl$ (ii) |
| $CC$ double bond | $C=C$ |
| $C$ vinyl single bond to -$C(C)=C$ | $C-C$ (i) |
| $C$ vinyl single bond to -$C(H)=C$ | $C-C$ (ii) |
| $C$ vinyl single bond to -$C(C))=CH_2$ | $C-C$ (iii) |
| $CH$ (alkenyl halide) | $C-H$ (i) |
| $CH_2$ alkenyl group | $C-H\ (CH_2)$ (i) |
| $CH_3$ group | $C-H\ (CH_3)$ |
| $CH_2$ alkyl group | $C-H\ (CH_2)$ (ii) |
| $CH$ (alkyl) | $C-H$ (ii) |
| $CC$ bond (*n*-$C$) | $C-C$ (a) |
| $CC$ bond (*iso*-$C$) | $C-C$ (b) |
| $CC$ bond (*tert*-$C$) | $C-C$ (c) |
| $CC$ (*iso* to *iso*-$C$) | $C-C$ (d) |
| $CC$ (*t* to *t*-$C$) | $C-C$ (e) |
| $CC$ (*t* to *iso*-$C$) | $C-C$ (f) |

Table 15.52. The geometrical bond parameters of branched-chain alkenyl chlorides and experimental values [1].

| Parameter | $C-Cl$ (i) Group | $C-Cl$ (ii) Group | $C=C$ Group | $C-C$ (i) Group | $C-C$ (ii) Group | $C-C$ (iii) Group | $C-H\left(CH_2\right)$ (i) Group | $C-H$ (i) Group | $C-H\left(CH_3\right)$ Group | $C-H\left(CH_2\right)$ (ii) Group | $C-H$ (ii) Group | $C-C$ (a) Group | $C-C$ (b) Group | $C-C$ (c) Group | $C-C$ (d) Group | $C-C$ (e) Group | $C-C$ (f) Group |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $a\left(a_0\right)$ | 2.15818 | 2.19358 | 1.47228 | 2.04740 | 2.04740 | 2.04740 | 1.64010 | 1.60061 | 1.64920 | 1.67122 | 1.67465 | 2.12499 | 2.12499 | 2.10725 | 2.12499 | 2.10725 | 2.10725 |
| $c'\left(a_0\right)$ | 1.62912 | 1.64243 | 1.26661 | 1.43087 | 1.43087 | 1.43087 | 1.04566 | 1.03299 | 1.04856 | 1.05553 | 1.05661 | 1.45744 | 1.45744 | 1.45164 | 1.45744 | 1.45164 | 1.45164 |
| Bond Length $2c'$ $\left(\mathring{A}\right)$ | 1.72419 | 1.73827 | 1.34052 | 1.51437 | 1.51437 | 1.51437 | 1.10668 | 1.09327 | 1.10974 | 1.11713 | 1.11827 | 1.54280 | 1.54280 | 1.53635 | 1.54280 | 1.53635 | 1.53635 |
| Exp. Bond Length $\left(\mathring{A}\right)$ | 1.730 (vinyl chloride)<br>1.73 (1,1-dichloroethylene) | 1.730 (vinyl chloride)<br>1.73 (1,1-dichloroethylene) | 1.342 (2-methylpropene)<br>1.346 (2-butene)<br>1.349 (1,3-butadiene) | | 1.508 (2-butene) | 1.508 (2-methylpropene) | 1.10 (2-methylpropene)<br>1.108 (avg.) (1,3-butadiene) | 1.09 (vinyl chloride) | 1.107 ($C-H$ propane)<br>1.117 ($C-H$ butane) | 1.107 ($C-H$ propane)<br>1.117 ($C-H$ butane) | 1.122 (isobutane) | 1.532 (propane)<br>1.531 (butane) | 1.532 (propane)<br>1.531 (butane) | 1.532 (propane)<br>1.531 (butane) | 1.532 (propane)<br>1.531 (butane) | 1.532 (propane)<br>1.531 (butane) | 1.532 (propane)<br>1.531 (butane) |
| $b,c\left(a_0\right)$ | 1.41552 | 1.45403 | 0.75055 | 1.46439 | 1.46439 | 1.46439 | 1.26354 | 1.22265 | 1.27295 | 1.29569 | 1.29924 | 1.54616 | 1.54616 | 1.52750 | 1.54616 | 1.52750 | 1.52750 |
| $e$ | 0.75486 | 0.74874 | 0.86030 | 0.69887 | 0.69887 | 0.69887 | 0.63756 | 0.64537 | 0.63580 | 0.63159 | 0.63095 | 0.68600 | 0.68600 | 0.68888 | 0.68600 | 0.68888 | 0.68888 |

Table 15.53. The MO to HO intercept geometrical bond parameters of branched-chain alkenyl chlorides. $R$, $R'$, $R''$ are $H$ or alkyl groups. $E_T$ is $E_T(atom-atom,msp^3.AO)$.

| Bond | Atom | $E_T$ (eV) Bond 1 | $E_T$ (eV) Bond 2 | $E_T$ (eV) Bond 3 | $E_T$ (eV) Bond 4 | Final Total Energy $C2sp^3$ (eV) | $r_{initial}$ $(a_0)$ | $r_{final}$ $(a_0)$ | $E_{Coulomb}(C2sp^3)$ (eV) Final | $E(C2sp^3)$ (eV) Final | $\theta'$ $(^\circ)$ | $\theta_1$ $(^\circ)$ | $\theta_2$ $(^\circ)$ | $d_1$ $(a_0)$ | $d_2$ $(a_0)$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $C_b=C_a(Cl)-H\ (CH)$ (i) | $C_a$ | -1.34946 | -0.72457 | 0 | 0 | -153.47406 | 0.91771 | 0.81549 | -16.68412 | -16.49325 | 76.99 | 103.01 | 40.53 | 1.21653 | 0.18354 |
| $-C_b=C_a(H)Cl$<br>$(C_a-Cl$ (i)) | $C_a$ | -1.13379 | -0.72457 | 0 | 0 | -153.47406 | 0.91771 | 0.81549 | -16.68412 | -16.49325 | 79.43 | 100.57 | 34.49 | 1.77872 | 0.14960 |
| $-C_b=C_a(H)Cl$<br>$(C_a-Cl$ (i)) | $Cl$ | -0.72457 | 0 | 0 | 0 |  | 1.05158 | 0.87495 | -15.55033 |  | 85.36 | 94.64 | 38.03 | 1.69995 | 0.07083 |
| $-C_b=C_a(C)Cl$<br>$(C_a-Cl$ (ii)) | $C_a$ | 1.13379 | -0.46459 | -0.92918 | 0 | -154.14326 | 0.91771 | 0.78405 | -17.35332 | -17.16245 | 72.17 | 107.83 | 30.88 | 1.88253 | 0.24010 |
| $-C_b=C_a(C)Cl$<br>$(C_a-Cl$ (ii)) | $Cl$ | -0.46459 | 0 | 0 | 0 |  | 1.05158 | 0.88983 | -15.29034 |  | 83.62 | 96.38 | 37.46 | 1.74125 | 0.09882 |
| $C_c(H)C_a=C_aH,C_d$ | $C_a$ | -1.13380 | -0.92918 | 0 | 0 | -153.67867 | 0.91771 | 0.80561 | -16.88873 | -16.69786 | 127.61 | 52.39 | 58.24 | 0.77492 | 0.49168 |
| $C_c(H)C_a=C_bH_2$ | $C_b$ | -1.13380 | 0 | 0 | 0 | -152.74949 | 0.91771 | 0.85252 | -15.95955 | -15.76868 | 129.84 | 50.16 | 60.70 | 0.72040 | 0.54620 |
| $C_c(C_d)C_a=C_bH,C_e$ | $C_a$ | -1.13380 | -0.72457 | -0.72457 | 0 | -154.19863 | 0.91771 | 0.78155 | -17.40869 | -17.21783 | 126.39 | 53.61 | 56.95 | 0.80289 | 0.46371 |
| $R_1C_bH_2-C_a(C)=C$<br>$(C-C$ (i)) | $C_a$ | -1.13380 | -0.72457 | -0.72457 | 0 | -154.19863 | 0.91771 | 0.78155 | -17.40869 | -17.21783 | 60.88 | 119.12 | 27.79 | 1.81127 | 0.38039 |
| $R_1C_bH_2-C_a(C)=C$<br>$(C-C$ (i))<br>$R_1C_bH_2-C_a(C)=CH_2$<br>$(C-C$ (iii)) | $C_b$ | -0.72457 | -0.92918 | 0 | 0 | -153.26945 | 0.91771 | 0.82562 | -16.47951 | -16.28864 | 67.40 | 112.60 | 31.36 | 1.74821 | 0.31734 |
| $R_1C_bH_2-C_a(H)=C$<br>$(C-C$ (ii)) | $C_a$ | -1.13380 | -0.92918 | 0 | 0 | -153.67866 | 0.91771 | 0.80561 | -16.88873 | -16.69786 | 64.57 | 115.43 | 29.79 | 1.77684 | 0.34596 |
| $R_1C_bH_2-C_a(H)=C$<br>$(C-C$ (i)) | $C_b$ | -0.92918 | -0.92918 | 0 | 0 | -153.47405 | 0.91771 | 0.81549 | -16.68411 | -16.49325 | 65.99 | 114.01 | 30.58 | 1.76270 | 0.33183 |
| $C-H\ (CH_2)$ (i) | $C$ | -1.13380 | 0 | 0 | 0 | -152.74949 | 0.91771 | 0.85252 | -15.95955 | -15.76868 | 77.15 | 102.85 | 41.13 | 1.23531 | 0.18965 |
| $C-H\ (CH_3)$ | $C$ | -0.92918 | 0 | 0 | 0 | -152.54487 | 0.91771 | 0.86359 | -15.75493 | -15.56407 | 77.49 | 102.51 | 41.48 | 1.23564 | 0.18708 |
| $C-H\ (CH_2)$ (ii) | $C$ | -0.92918 | -0.92918 | 0 | 0 | -153.47406 | 0.91771 | 0.81549 | -16.68412 | -16.49325 | 68.47 | 111.53 | 35.84 | 1.35486 | 0.29933 |
| $C-H\ (CH)$ (ii) | $C$ | -0.92918 | -0.92918 | -0.92918 | 0 | -154.40324 | 0.91771 | 0.77247 | -17.61330 | -17.42244 | 61.10 | 118.90 | 31.37 | 1.42988 | 0.37326 |
| $H_3C_aC_bH_2CH_2-$<br>$(C-C$ (a)) | $C_a$ | -0.92918 | 0 | 0 | 0 | -152.54487 | 0.91771 | 0.86359 | -15.75493 | -15.56407 | 63.82 | 116.18 | 30.08 | 1.83879 | 0.38106 |
| $H_3C_aC_bH_2CH_2-$<br>$(C-C$ (a)) | $C_b$ | -0.92918 | -0.92918 | 0 | 0 | -153.47406 | 0.91771 | 0.81549 | -16.68412 | -16.49325 | 56.41 | 123.59 | 26.06 | 1.90890 | 0.45117 |
| $R-H_2C_aC_b(H_2C_c-R')HCH_2-$<br>$(C-C$ (b)) | $C_b$ | -0.92918 | -0.92918 | -0.92918 | 0 | -154.40324 | 0.91771 | 0.77247 | -17.61330 | -17.42244 | 48.30 | 131.70 | 21.90 | 1.97162 | 0.51388 |
| $R-H_2C_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$<br>$(C-C$ (c)) | $C_b$ | -0.92918 | -0.72457 | -0.72457 | -0.72457 | -154.71860 | 0.91771 | 0.75889 | -17.92866 | -17.73779 | 48.21 | 131.79 | 21.74 | 1.95734 | 0.50570 |
| $isoC_aC_b(H_2C_c-R')HCH_2-$<br>$(C-C$ (d)) | $C_b$ | -0.92918 | -0.92918 | -0.92918 | 0 | -154.40324 | 0.91771 | 0.77247 | -17.61330 | -17.42244 | 48.30 | 131.70 | 21.90 | 1.97162 | 0.51388 |
| $tertC_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$<br>$(C-C$ (e)) | $C_b$ | -0.72457 | -0.72457 | -0.72457 | -0.72457 | -154.51399 | 0.91771 | 0.76765 | -17.92866 | -17.73779 | 50.04 | 129.96 | 22.66 | 1.94462 | 0.49298 |
| $tertC_aC_b(H_2C_c-R')HCH_2-$<br>$(C-C$ (f)) | $C_b$ | -0.72457 | -0.92918 | -0.92918 | 0 | -154.19863 | 0.91771 | 0.78155 | -17.40869 | -17.21783 | 52.78 | 127.22 | 24.04 | 1.92443 | 0.47279 |
| $isoC_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$<br>$(C-C$ (f)) | $C_b$ | -0.72457 | -0.72457 | -0.72457 | -0.72457 | -154.51399 | 0.91771 | 0.76765 | -17.92866 | -17.73779 | 50.04 | 129.96 | 22.66 | 1.94462 | 0.49298 |

Table 15.54. The energy parameters ($eV$) of functional groups of branched-chain alkenyl chlorides.

| Parameters | $C-Cl$ (i) Group | $C-Cl$ (ii) Group | $C=C$ Group | $C-C$ (i) Group | $C-C$ (ii) Group | $C-C$ (iii) Group | $CH_2$ (i) Group | $C-H$ (i) Group | $CH_3$ Group | $CH_2$ (ii) Group | $C-H$ (ii) Group | $C-C$ (a) Group | $C-C$ (b) Group | $C-C$ (c) Group | $C-C$ (d) Group | $C-C$ (e) Group | $C-C$ (f) Group |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $n_1$ | 1 | 1 | 2 | 1 | 1 | 1 | 2 | 1 | 3 | 2 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $n_2$ | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 0 | 2 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $n_3$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $C_1$ | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.75 | 0.75 | 0.75 | 0.75 | 0.75 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| $C_2$ | 0.81317 | 0.81317 | 0.91771 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $c_1$ | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $c_2$ | 1 | 1 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 |
| $c_3$ | 1 | 0 | 0 | 1 | 0 | 1 | 1 | 1 | 0 | 1 | 1 | 0 | 0 | 0 | 1 | 1 | 0 |
| $c_4$ | 2 | 2 | 4 | 2 | 2 | 2 | 1 | 1 | 1 | 1 | 1 | 2 | 2 | 2 | 2 | 2 | 2 |
| $c_5$ | 0 | 0 | 0 | 0 | 0 | 0 | 2 | 1 | 3 | 2 | 1 | 0 | 0 | 0 | 0 | 0 | 0 |
| $C_{1o}$ | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.75 | 0.75 | 0.75 | 0.75 | 0.75 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| $C_{2o}$ | 0.81317 | 0.81317 | 0.91771 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $V_e\ (eV)$ | -32.87721 | -32.14474 | -102.08992 | -30.19634 | -30.19634 | -30.19634 | -72.03287 | -37.10024 | -107.32728 | -70.41425 | -35.12015 | -28.79214 | -28.79214 | -29.10112 | -28.79214 | -29.10112 | -29.10112 |
| $V_p\ (eV)$ | 8.35160 | 8.28394 | 21.48386 | 9.50874 | 9.50874 | 9.50874 | 26.02344 | 13.17125 | 38.92728 | 25.78002 | 12.87680 | 9.33352 | 9.33352 | 9.37273 | 9.33352 | 9.37273 | 9.37273 |
| $T\ (eV)$ | 7.61688 | 7.32700 | 34.67062 | 7.37432 | 7.37432 | 7.37432 | 21.95990 | 11.58941 | 32.53914 | 21.06675 | 10.48582 | 6.77464 | 6.77464 | 6.90500 | 6.77464 | 6.90500 | 6.90500 |
| $V_m\ (eV)$ | -3.80844 | -3.66350 | -17.33531 | -3.68716 | -3.68716 | -3.68716 | -10.97995 | -5.79470 | -16.26957 | -10.53337 | -5.24291 | -3.38732 | -3.38732 | -3.45250 | -3.38732 | -3.45250 | -3.45250 |
| $E(_{AO/HO})\ (eV)$ | -14.63489 | -14.63489 | 0 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -15.56407 | -15.56407 | -14.63489 | -15.56407 | -15.56407 | -15.35946 | -15.56407 | -15.35946 | -15.35946 |
| $\Delta E_{H_2MO}(_{AO/HO})\ (eV)$ | -3.71674 | -3.19677 | 0 | 0 | 0 | 0 | 0 | -1.13379 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $E_T(_{AO/HO})\ (eV)$ | -10.91815 | -10.97139 | 0 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -13.50110 | -15.56407 | -15.56407 | -14.63489 | -15.56407 | -15.56407 | -15.35946 | -15.56407 | -15.35946 | -15.35946 |
| $E_T(_{H_2MO})\ (eV)$ | -31.63531 | -31.63541 | -63.27075 | -31.63534 | -31.63534 | -31.63534 | -49.66437 | -31.63539 | -67.69451 | -49.66493 | -31.63533 | -31.63537 | -31.63537 | -31.63535 | -31.63537 | -31.63535 | -31.63535 |
| $E_T\left(atom-atom, msp^3.AO\right)\ (eV)$ | -1.44915 | -0.92918 | -2.26759 | -1.44915 | -1.85836 | -1.44915 | 0 | 0 | 0 | 0 | 0 | -1.85836 | -1.85836 | -1.44915 | -1.85836 | -1.44915 | -1.44915 |
| $E_T(_{MO})\ (eV)$ | -33.08452 | -32.56455 | -65.53833 | -33.08452 | -33.49373 | -33.08452 | -49.66493 | -31.63537 | -67.69450 | -49.66493 | -31.63537 | -33.49373 | -33.49373 | -33.08452 | -33.49373 | -33.08452 | -33.08452 |
| $\omega\ \left(10^{15}\ rad/s\right)$ | 8.31434 | 8.11389 | 43.0680 | 9.97851 | 16.4962 | 9.97851 | 25.2077 | 26.4826 | 24.9286 | 24.2751 | 24.1759 | 9.43699 | 9.43699 | 15.4846 | 9.43699 | 9.55643 | 9.55643 |
| $E_K\ (eV)$ | 5.47264 | 5.34070 | 28.34813 | 6.56803 | 10.85807 | 6.56803 | 16.59214 | 17.43132 | 16.40846 | 15.97831 | 15.91299 | 6.21159 | 6.21159 | 10.19220 | 6.21159 | 6.29021 | 6.29021 |
| $\bar{E}_D\ (eV)$ | -0.15312 | -0.14888 | -0.34517 | -0.16774 | -0.21834 | -0.16774 | -0.25493 | -0.26130 | -0.25352 | -0.25017 | -0.24966 | -0.16515 | -0.16515 | -0.20896 | -0.16515 | -0.16416 | -0.16416 |
| $\bar{E}_{Kvib}\ (eV)$ | 0.08059 [12] | 0.08059 [12] | 0.17897 [6] | 0.15895 [7] | 0.09931 [8] | 0.09931 [8] | 0.35532 Eq. (13.458) | 0.35532 Eq. (13.458) | 0.35532 Eq. (13.458) | 0.35532 Eq. (13.458) | 0.35532 Eq. (13.458) | 0.12312 [2] | 0.17978 [4] | 0.09944 [5] | 0.12312 [2] | 0.12312 [2] | 0.12312 [2] |
| $\bar{E}_{osc}\ (eV)$ | -0.11282 | -0.10859 | -0.25568 | -0.08827 | -0.16869 | -0.11809 | -0.07727 | -0.08364 | -0.22757 | -0.14502 | -0.07200 | -0.10359 | -0.07526 | -0.15924 | -0.10359 | -0.10260 | -0.10260 |
| $E_{mag}\ (eV)$ | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 |
| $E_T(_{Group})\ (eV)$ | -33.19734 | -32.67314 | -66.04969 | -33.17279 | -33.66242 | -33.20260 | -49.81948 | -31.71901 | -67.92207 | -49.80996 | -31.70737 | -33.59732 | -33.49373 | -33.24376 | -33.59732 | -33.18712 | -33.18712 |
| $E_{initial}(_{c_4\ AO/HO})\ (eV)$ | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 |
| $E_{initial}(_{c_5\ AO/HO})\ (eV)$ | 0 | 0 | 0 | 0 | 0 | 0 | -13.59844 | -13.59844 | -13.59844 | -13.59844 | -13.59844 | 0 | 0 | 0 | 0 | 0 | 0 |
| $E_D(_{Group})\ (eV)$ | 3.77953 | 3.40336 | 7.51014 | 3.75498 | 4.39264 | 3.78480 | 7.83968 | 3.33765 | 12.49186 | 7.83016 | 3.32601 | 4.32754 | 4.29921 | 3.97398 | 4.17951 | 3.62128 | 3.91734 |

Table 15.55. The total bond energies of branched-chain alkenyl chlorides calculated using the functional group composition and the energies of Table 15.54 compared to the experimental values [3].

| Formula | Name | $C-Cl$ (i) | $C-Cl$ (ii) | $C=C$ | $C-C$ (i) | $C-C$ (ii) | $C-C$ (iii) | $CH_2$ (i) | $CH$ (i) | $CH_3$ | $CH_2$ (ii) | $CH$ (ii) | $C-C$ (a) | $C-C$ (b) | $C-C$ (c) | $C-C$ (d) | $C-C$ (e) | $C-C$ (f) | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $C_2H_3Cl$ | Chloroethene | 1 | 0 | 1 | 0 | 0 | 0 | 1 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 22.46700 | 22.505 | 0.00170 |
| $C_3H_5Cl$ | 2-Chloropropene | 0 | 1 | 1 | 0 | 0 | 1 | 1 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 35.02984 | 35.05482 | 0.00071 |

Table 15.56. The bond angle parameters of branched-chain alkenyl chlorides and experimental values [1]. In the calculation of $\theta_v$, the parameters from the preceding angle were used. $E_T$ is $E_T(atom-atom,msp^3.AO)$.

| Atoms of Angle | 2c' Bond 1 $(a_0)$ | 2c' Bond 2 $(a_0)$ | 2c' Terminal Atoms $(a_0)$ | $E_{Coulombic}$ Atom 1 | Atom 1 Hybridization Designation (Table 15.3.A) | $E_{Coulombic}$ Atom 2 | Atom 2 Hybridization Designation (Table 15.3.A) | $c_2$ Atom 1 | $c_2$ Atom 2 | $C_1$ | $C_2$ | $c_1$ | $c_2'$ | $E_T$ (eV) | $\theta_v$ (°) | $\theta_1$ (°) | $\theta_2$ (°) | Cal. $\theta$ (°) | Exp. $\theta$ (°) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $\angle HC_aCl$<br>$(C_a-Cl$ (i)) | 2.06598 | 3.25825 | 4.5809 | -16.27490<br>$C_a$ | 16 | -12.96764<br>$Cl$ | Cl | 0.83600 | 0.91771 | 0.75 | 0.95310<br>(Eq. (15.65)) | 0.75 | 1.09775 | 0 | | | | 116.94 | |
| $\angle C_b=C_aH$<br>$(C_a-Cl$ (i)) | | | | | | | | | | | | | | | | 116.94 | | 121.53 | 124<br>(vinyl chloride) |
| $\angle C_b=C_aCl$<br>$(C_a-Cl$ (i)) | | | | | | | | | | | | | | | | 116.94 | | 121.53 | 122.5<br>(vinyl chloride)<br>123.8<br>(1,1-dichloroethylene) |
| $\angle C_b=C_aCl$<br>$(C_a-Cl$ (i)) | 2.53321 | 3.25825 | 5.1060 | -15.75493<br>$C_b$ | 7 | -12.96764<br>$Cl$ | Cl | 0.86359 | 0.86359 | 1 | 0.81317<br>(Eq. (15.111)) | 1 | 0.86359 | -0.92918 | | | | 123.19 | 123.8<br>(1,1-dichloroethylene)<br>122.5<br>(vinyl chloride) |
| $\angle HC_aC_c$<br>$(C_c(H)C_a=C_b)$ | 2.11323 | 2.86175 | 4.2895 | -15.95955<br>$C_a$ | 10 | -14.82575<br>$C_c$ | 1 | 0.85252 | 0.91771 | 0.75 | 1 | 0.75 | 1.07647 | 0 | | | | 118.36 | |
| $\angle C_cC_aC_c$<br>$(C_c(C_c)C_a=C_b)$ | 2.86175 | 2.86175 | 4.7958 | -16.68411<br>$C_c$ | 25 | -16.68411<br>$C_c$ | 25 | 0.81549 | 0.81549 | 1 | 1 | 1 | 0.81549 | -1.85836 | | | | 113.84 | |
| $\angle C_bC_aC_c$<br>$(C_b=C_aC_c)$ | 2.53321 | 2.86175 | 4.7539 | -16.88873<br>$C_b$ | 30 | -16.68411<br>$C_c$ | 25 | 0.80561 | 0.81549 | 1 | 1 | 1 | 0.81055 | -1.85836 | | | | 123.46 | 124.4<br>(1,3,5-hexatriene CbCcCc)<br>121.7<br>(1,3,5-hexatriene CaCbCc)<br>124.4<br>(1,3-butadiene CCC)<br>125.3<br>(2-butene CbCaCc) |
| $\angle HC_aC_b$ | | | | | | | | | | | | | | | | 118.36 | 123.46 | 118.19 | |
| $\angle HC_aH$<br>$(H_2C_a=C_bC_c)$ | 2.04578 | 2.04578 | 3.4756 | -15.95955 | 10 | H | H | 0.85252 | 1 | 1 | 1 | 0.75 | 1.17300 | 0 | | | | 116.31 | 118.5<br>(2-methylpropene) |
| $\angle C_bC_aH$<br>$(H_2C_a=C_bC_c)$ | | | | | | | | | | | | | | | | 116.31 | | 121.85 | 121<br>(2-methylpropene) |
| Methylene<br>$\angle HC_aH$ | 2.11106 | 2.11106 | 3.4252 | -15.75493 | 7 | H | H | 0.86359 | 1 | 1 | 1 | 0.75 | 1.15796 | 0 | | | | 108.44 | 107<br>(propane) |
| $\angle C_aC_bC_c$ | | | | | | | | | | | | | | | 69.51 | | | 110.49 | 112<br>(propane)<br>113.8<br>(butane)<br>110.8<br>(isobutane) |
| $\angle C_cC_bH$ | | | | | | | | | | | | | | | 69.51 | | | 110.49 | 111.0<br>(butane)<br>111.4<br>(isobutane) |
| Methyl<br>$\angle HC_aH$ | 2.09711 | 2.09711 | 3.4252 | -15.75493 | 7 | H | H | 0.86359 | 1 | 1 | 1 | 0.75 | 1.15796 | 0 | | | | 109.50 | |
| $\angle C_aC_bC_c$ | | | | | | | | | | | | | | | 70.56 | | | 109.44 | |
| $\angle C_aC_bH$ | | | | | | | | | | | | | | | 70.56 | | | 109.44 | |
| $\angle C_bC_aC_c$<br>iso $C_a$ | 2.91547 | 2.91547 | 4.7958 | -16.68412<br>$C_b$ | 26 | -16.68412<br>$C_c$ | 26 | 0.81549 | 0.81549 | 1 | 1 | 1 | 0.81549 | -1.85836 | | | | 110.67 | 110.8<br>(isobutane) |
| $\angle C_bC_aH$<br>iso $C_a$ | 2.91547 | 2.11323 | 4.1633 | -15.55033<br>$C_a$ | 5 | -14.82575<br>$C_b$ | 1 | 0.87495 | 0.91771 | 0.75 | 1 | 0.75 | 1.04887 | 0 | | | | 110.76 | |
| $\angle C_aC_bH$<br>iso $C_a$ | 2.91547 | 2.09711 | 4.1633 | -15.55033<br>$C_b$ | 5 | -14.82575<br>$C_a$ | 1 | 0.87495 | 0.91771 | 0.75 | 1 | 0.75 | 1.04887 | 0 | | | | 111.27 | 111.4<br>(isobutane) |
| $\angle C_bC_aC_b$<br>tert $C_a$ | 2.90327 | 2.90327 | 4.7958 | -16.68412<br>$C_b$ | 26 | -16.68412<br>$C_b$ | 26 | 0.81549 | 0.81549 | 1 | 1 | 1 | 0.81549 | -1.85836 | | | | 111.37 | 110.8<br>(isobutane) |
| $\angle C_bC_aC_d$ | | | | | | | | | | | | | | | 72.50 | | | 107.50 | |

## ALCOHOLS ($C_nH_{2n+2}O_m$, $n=1,2,3,4,5...\infty$)

The alkyl alcohols, $C_nH_{2n+2}O_m$, comprise an $OH$ functional group and two types of $C-O$ functional groups, one for methyl alcohol and the other for general alkyl alcohols. The alkyl portion of the alkyl alcohol may comprise at least two terminal methyl groups ($CH_3$) at each end of the chain, and may comprise methylene ($CH_2$), and methylyne ($CH$) functional groups as well as $C$ bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($(CH_3)_2CH$) and t-butyl ($(CH_3)_3C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups. The branched-chain-alkane groups in alcohols are equivalent to those in branched-chain alkanes.

The $OH$ functional group was solved in the Hydroxyl Radical ($OH$) section. Each $C-O$ group is solved by hybridizing the $2s$ and $2p$ AOs of the $C$ atom to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between the $C2sp^3$ HO and the $O$ AO to form a MO permits each participating orbital to decrease in radius and energy. In alkyl alcohols, the $C2sp^3$ HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of $E(C,2sp^3)=-14.63489\ eV$ (Eq. (15.25)) and the $O$ AO has an energy of $E(O)=-13.61806\ eV$. To meet the equipotential condition of the union of the $C-O$ $H_2$-type-ellipsoidal-MO with these orbitals, the hybridization factor $c_2$ of Eq. (15.61) for the $C-O$-bond MO given by Eqs. (15.77) and (15.79) is:

$$c_2\left(C2sp^3HO\ to\ O\right)=\frac{E(O)}{E\left(C,2sp^3\right)}c_2\left(C2sp^3HO\right)=\frac{-13.61806\ eV}{-14.63489\ eV}(0.91771)=0.85395 \tag{15.133}$$

$E_T\left(atom-atom,msp^3.AO\right)$ of the $C-O$-bond MO in Eq. (15.61) due to the charge donation from the $C$ and $O$ atoms to the MO is $-1.65376\ eV$ for the $CH_3-OH$ $C-O$ group. It is based on the energy match between the $OH$ group and the $C2sp^3$ HO of a methyl group and is given by the linear combination of $-0.92918\ eV$ (Eq. (14.513)) and $-0.72457\ eV$ (Eq. (14.151)), respectively. For the alkyl $C-O$ group, $E_T\left(atom-atom,msp^3.AO\right)$ is $-1.85836\ eV$. It is based on the energy match between the $O$ AO and the $C2sp^3$ HO of a methylene group where both energy contributions are given by Eq. (14.513).

The symbols of the functional groups of branched-chain alkyl alcohols are given in Table 15.66. The geometrical (Eqs. (15.1-15.5) and (15.51)), intercept (Eqs. (15.80-15.87)), and energy (Eqs. (15.6-15.11) and (15.17-15.65)) parameters of alkyl alcohols are given in Tables 15.58, 15.59, and 15.60, respectively. The total energy of each alkyl alcohol given in Table 15.61 was calculated as the sum over the integer multiple of each $E_{D\,(Group)}$ of Table 15.60 corresponding to functional-group composition of the molecule. The bond angle parameters of alkyl alcohols determined using Eqs. (15.88-15.117) are given in Table 15.62. The color scale, translucent view of the charge-density of exemplary alcohol, 1-propanol, comprising the concentric shells of atoms with the outer shell bridged by one or more $H_2$-type ellipsoidal MOs or joined with one or more hydrogen MOs is shown in Figure 15.10.

Figure 15.10. Color scale, translucent view of the charge-density of 1-propanol showing the orbitals of the atoms at their radii, the ellipsoidal surface of each $H$ or $H_2$-type ellipsoidal MO that transitions to the corresponding outer shell of the atom(s) participating in each bond, and the hydrogen nuclei (red, not to scale). (A) Side view. (B) Front view.

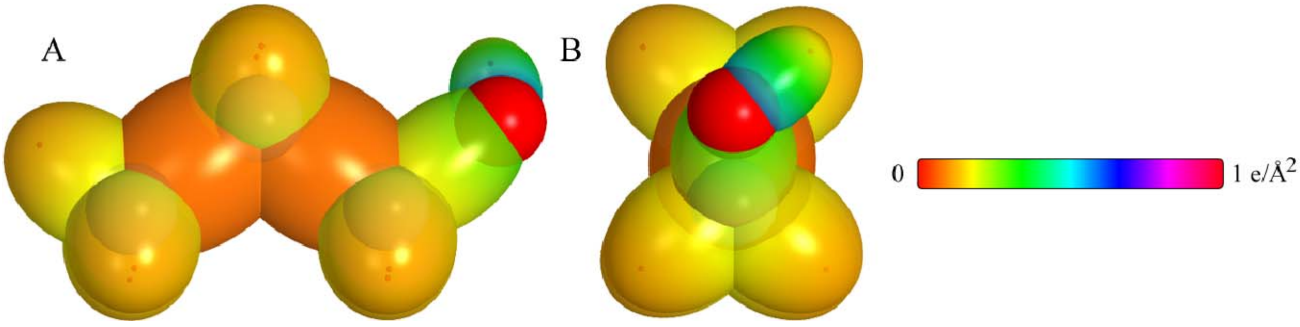


Table 15.57. The symbols of functional groups of alkyl alcohols.

| Functional Group | Group Symbol |
|---|---|
| *OH* group | $OH$ |
| $CH_3OH$ *C-O* | $C-O$ (i) |
| Alkyl *C-O* | $C-O$ (ii) |
| $CH_3$ group | $C-H\ (CH_3)$ |
| $CH_2$ group | $C-H\ (CH_2)$ |
| *CH* | $C-H$ |
| *CC* bond (*n-C*) | $C-C$ (a) |
| *CC* bond (*iso-C*) | $C-C$ (b) |
| *CC* bond (*tert-C*) | $C-C$ (c) |
| *CC* (*iso* to *iso-C*) | $C-C$ (d) |
| *CC* (*t* to *t-C*) | $C-C$ (e) |
| *CC* (*t* to iso-*C*) | $C-C$ (f) |

Table 15.58. The geometrical bond parameters of alkyl alcohols and experimental values [1].

| Parameter | $OH$ Group | $C-O$ (i) Group | $C-O$ (ii) Group | $C-H\left(CH_3\right)$ Group | $C-H\left(CH_2\right)$ Group | $C-H$ Group | $C-C$ (a) Group | $C-C$ (b) Group | $C-C$ (c) Group | $C-C$ (d) Group | $C-C$ (e) Group | $C-C$ (f) Group |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $a\left(a_0\right)$ | 1.26430 | 1.79473 | 1.78255 | 1.64920 | 1.67122 | 1.67465 | 2.12499 | 2.12499 | 2.10725 | 2.12499 | 2.10725 | 2.10725 |
| $c'\left(a_0\right)$ | 0.91808 | 1.33968 | 1.33512 | 1.04856 | 1.05553 | 1.05661 | 1.45744 | 1.45744 | 1.45164 | 1.45744 | 1.45164 | 1.45164 |
| Bond Length $2c'$ $\left(Å\right)$ | 0.971651 | 1.41785 | 1.41303 | 1.10974 | 1.11713 | 1.11827 | 1.54280 | 1.54280 | 1.53635 | 1.54280 | 1.53635 | 1.53635 |
| Exp. Bond Length $\left(Å\right)$ | 0.971 (ethanol)<br>0.9451 (methanol) | 1.4246 (methanol) | 1.431 (ethanol) | 1.107 ($C-H$ propane)<br>1.117 ($C-H$ butane) | 1.107 ($C-H$ propane)<br>1.117 ($C-H$ butane) | 1.122 (isobutane) | 1.532 (propane)<br>1.531 (butane) | 1.532 (propane)<br>1.531 (butane) | 1.532 (propane)<br>1.531 (butane) | 1.532 (propane)<br>1.531 (butane) | 1.532 (propane)<br>1.531 (butane) | 1.532 (propane)<br>1.531 (butane) |
| $b,c\left(a_0\right)$ | 0.86925 | 1.19429 | 1.18107 | 1.27295 | 1.29569 | 1.29924 | 1.54616 | 1.54616 | 1.52750 | 1.54616 | 1.52750 | 1.52750 |
| $e$ | 0.72615 | 0.74645 | 0.74900 | 0.63580 | 0.63159 | 0.63095 | 0.68600 | 0.68600 | 0.68888 | 0.68600 | 0.68888 | 0.68888 |

Table 15.59. The MO to HO intercept geometrical bond parameters of alkyl alcohols. $R$, $R'$, $R''$ are $H$ or alkyl groups. $E_T$ is $E_T(atom-atom,msp^3.AO)$.

| Bond | Atom | $E_T$ (eV) Bond 1 | $E_T$ (eV) Bond 2 | $E_T$ (eV) Bond 3 | $E_T$ (eV) Bond 4 | Final Total Energy $C2sp^3$ (eV) | $r_{initial}$ $\left(a_0\right)$ | $r_{final}$ $\left(a_0\right)$ | $E_{Coulomb}$ (eV) Final | $E\left(C2sp^3\right)$ (eV) Final | $\theta'$ $\left(°\right)$ | $\theta_1$ $\left(°\right)$ | $\theta_2$ $\left(°\right)$ | $d_1$ $\left(a_0\right)$ | $d_2$ $\left(a_0\right)$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $H_3CO-H$ | $O$ | -0.82688 | 0 | 0 | 0 |  | 1.00000 | 0.86923 | -15.65263 |  | 115.49 | 64.51 | 64.51 | 0.54405 | 0.37403 |
| $-H_2C_aO-H$ | $O$ | -0.92918 | 0 | 0 | 0 |  | 1.00000 | 0.86359 | -15.75493 |  | 115.09 | 64.91 | 64.12 | 0.55182 | 0.36625 |
| $H_3C-OH$ ($C-O$ (i)) | $C$ | -0.82688 | 0 | 0 | 0 | -152.44257 | 0.91771 | 0.86923 | -15.65263 | -15.46177 | 96.59 | 83.41 | 46.30 | 1.23986 | 0.09981 |
| $H_3C-OH$ ($C-O$ (i)) | $O$ | -0.82688 | 0 | 0 | 0 |  | 1.00000 | 0.86923 | -15.65263 |  | 96.59 | 83.41 | 46.30 | 1.23986 | 0.09981 |
| $-H_2C_a-OH$ ($C-O$ (ii)) | $C_a$ | -0.92918 | -0.92918 | 0 | 0 | -153.47405 | 0.91771 | 0.81549 | -16.68411 | -16.49325 | 93.09 | 86.91 | 43.59 | 1.29114 | 0.04398 |
| $-H_2C_a-OH$ ($C-O$ (ii)) | $O$ | -0.92918 | 0 | 0 | 0 |  | 1.00000 | 0.86359 | -15.75493 |  | 97.20 | 82.80 | 46.50 | 1.22692 | 0.10820 |
| $C-H\left(CH_3\right)$ | $C$ | -0.92918 | 0 | 0 | 0 | -152.54487 | 0.91771 | 0.86359 | -15.75493 | -15.56407 | 77.49 | 102.51 | 41.48 | 1.23564 | 0.18708 |
| $C-H\left(CH_2\right)$ | $C$ | -0.92918 | -0.92918 | 0 | 0 | -153.47406 | 0.91771 | 0.81549 | -16.68412 | -16.49325 | 68.47 | 111.53 | 35.84 | 1.35486 | 0.29933 |
| $C-H\left(CH\right)$ | $C$ | -0.92918 | -0.92918 | -0.92918 | 0 | -154.40324 | 0.91771 | 0.77247 | -17.61330 | -17.42244 | 61.10 | 118.90 | 31.37 | 1.42988 | 0.37326 |
| $H_3C_aC_bH_2CH_2-$ ($C-C$ (a)) | $C_a$ | -0.92918 | 0 | 0 | 0 | -152.54487 | 0.91771 | 0.86359 | -15.75493 | -15.56407 | 63.82 | 116.18 | 30.08 | 1.83879 | 0.38106 |
| $H_3C_aC_bH_2CH_2-$ ($C-C$ (a)) | $C_b$ | -0.92918 | -0.92918 | 0 | 0 | -153.47406 | 0.91771 | 0.81549 | -16.68412 | -16.49325 | 56.41 | 123.59 | 26.06 | 1.90890 | 0.45117 |
| $R-H_2C_aC_b\left(H_2C_c-R'\right)HCH_2-$ ($C-C$ (b)) | $C_b$ | -0.92918 | -0.92918 | -0.92918 | 0 | -154.40324 | 0.91771 | 0.77247 | -17.61330 | -17.42244 | 48.30 | 131.70 | 21.90 | 1.97162 | 0.51388 |
| $R-H_2C_a\left(R'-H_2C_d\right)C_b\left(R''-H_2C_c\right)CH_2-$ ($C-C$ (c)) | $C_b$ | -0.92918 | -0.72457 | -0.72457 | -0.72457 | -154.71860 | 0.91771 | 0.75889 | -17.92866 | -17.73779 | 48.21 | 131.79 | 21.74 | 1.95734 | 0.50570 |
| $isoC_aC_b\left(H_2C_c-R'\right)HCH_2-$ ($C-C$ (d)) | $C_b$ | -0.92918 | -0.92918 | -0.92918 | 0 | -154.40324 | 0.91771 | 0.77247 | -17.61330 | -17.42244 | 48.30 | 131.70 | 21.90 | 1.97162 | 0.51388 |
| $tertC_a\left(R'-H_2C_d\right)C_b\left(R''-H_2C_c\right)CH_2-$ ($C-C$ (e)) | $C_b$ | -0.72457 | -0.72457 | -0.72457 | -0.72457 | -154.51399 | 0.91771 | 0.76765 | -17.92866 | -17.73779 | 50.04 | 129.96 | 22.66 | 1.94462 | 0.49298 |
| $tertC_aC_b\left(H_2C_c-R'\right)HCH_2-$ ($C-C$ (f)) | $C_b$ | -0.72457 | -0.92918 | -0.92918 | 0 | -154.19863 | 0.91771 | 0.78155 | -17.40869 | -17.21783 | 52.78 | 127.22 | 24.04 | 1.92443 | 0.47279 |
| $isoC_a\left(R'-H_2C_d\right)C_b\left(R''-H_2C_c\right)CH_2-$ ($C-C$ (f)) | $C_b$ | -0.72457 | -0.72457 | -0.72457 | -0.72457 | -154.51399 | 0.91771 | 0.76765 | -17.92866 | -17.73779 | 50.04 | 129.96 | 22.66 | 1.94462 | 0.49298 |

Table 15.60. The energy parameters ($eV$) of functional groups of alkyl alcohols.

| Parameters | $OH$ Group | $C-O$ (i) Group | $C-O$ (ii) Group | $CH_3$ Group | $CH_2$ Group | $C-H$ Group | $C-C$ (a) Group | $C-C$ (b) Group | $C-C$ (c) Group | $C-C$ (d) Group | $C-C$ (e) Group | $C-C$ (f) Group |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $n_1$ | 1 | 1 | 1 | 3 | 2 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $n_2$ | 0 | 0 | 0 | 2 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $n_3$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $C_1$ | 0.75 | 0.5 | 0.5 | 0.75 | 0.75 | 0.75 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| $C_2$ | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $c_1$ | 0.75 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $c_2$ | 1 | 0.85395 | 0.85395 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 |
| $c_3$ | 1 | 0 | 0 | 0 | 1 | 1 | 0 | 0 | 0 | 1 | 1 | 0 |
| $c_4$ | 1 | 2 | 2 | 1 | 1 | 1 | 2 | 2 | 2 | 2 | 2 | 2 |
| $c_5$ | 1 | 0 | 0 | 3 | 2 | 1 | 0 | 0 | 0 | 0 | 0 | 0 |
| $C_{1o}$ | 0.75 | 0.5 | 0.5 | 0.75 | 0.75 | 0.75 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| $C_{2o}$ | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $V_e\ (eV)$ | -40.92709 | -33.47304 | -33.78820 | -107.32728 | -70.41425 | -35.12015 | -28.79214 | -28.79214 | -29.10112 | -28.79214 | -29.10112 | -29.10112 |
| $V_p\ (eV)$ | 14.81988 | 10.15605 | 10.19068 | 38.92728 | 25.78002 | 12.87680 | 9.33352 | 9.33352 | 9.37273 | 9.33352 | 9.37273 | 9.37273 |
| $T\ (eV)$ | 16.18567 | 9.32537 | 9.47749 | 32.53914 | 21.06675 | 10.48582 | 6.77464 | 6.77464 | 6.90500 | 6.77464 | 6.90500 | 6.90500 |
| $V_m\ (eV)$ | -8.09284 | -4.66268 | -4.73874 | -16.26957 | -10.53337 | -5.24291 | -3.38732 | -3.38732 | -3.45250 | -3.38732 | -3.45250 | -3.45250 |
| $E(_{AO/HO})\ (eV)$ | -13.6181 | -14.63489 | -14.63489 | -15.56407 | -15.56407 | -14.63489 | -15.56407 | -15.56407 | -15.35946 | -15.56407 | -15.35946 | -15.35946 |
| $\Delta E_{H_2MO}(_{AO/HO})\ (eV)$ | 0 | -1.65376 | -1.85836 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $E_T(_{AO/HO})\ (eV)$ | -13.6181 | -12.98113 | -12.77653 | -15.56407 | -15.56407 | -14.63489 | -15.56407 | -15.56407 | -15.35946 | -15.56407 | -15.35946 | -15.35946 |
| $E_T(_{H_2MO})\ (eV)$ | -31.63247 | -31.63544 | -31.63529 | -67.69451 | -49.66493 | -31.63533 | -31.63537 | -31.63537 | -31.63535 | -31.63537 | -31.63535 | -31.63535 |
| $E_T\left(atom-atom, msp^3.AO\right)(eV)$ | 0 | -1.65376 | -1.85836 | 0 | 0 | 0 | -1.85836 | -1.85836 | -1.44915 | -1.85836 | -1.44915 | -1.44915 |
| $E_T(_{MO})\ (eV)$ | -31.63537 | -33.28912 | -33.49373 | -67.69450 | -49.66493 | -31.63537 | -33.49373 | -33.49373 | -33.08452 | -33.49373 | -33.08452 | -33.08452 |
| $\omega\ \left(10^{15}\ rad/s\right)$ | 44.1776 | 22.3978 | 12.2831 | 24.9286 | 24.2751 | 24.1759 | 9.43699 | 9.43699 | 15.4846 | 9.43699 | 9.55643 | 9.55643 |
| $E_K\ (eV)$ | 29.07844 | 14.74264 | 8.08494 | 16.40846 | 15.97831 | 15.91299 | 6.21159 | 6.21159 | 10.19220 | 6.21159 | 6.29021 | 6.29021 |
| $\bar{E}_D\ (eV)$ | -0.33749 | -0.25287 | -0.18841 | -0.25352 | -0.25017 | -0.24966 | -0.16515 | -0.16515 | -0.20896 | -0.16515 | -0.16416 | -0.16416 |
| $\bar{E}_{Kvib}\ (eV)$ | 0.46311 [17-18] | 0.12808 [19] | 0.13328 [20] | 0.35532 (Eq. (13.458)) | 0.35532 (Eq. (13.458)) | 0.35532 (Eq. (13.458)) | 0.12312 [2] | 0.17978 [4] | 0.09944 [5] | 0.12312 [2] | 0.12312 [2] | 0.12312 [2] |
| $\bar{E}_{osc}\ (eV)$ | -0.10594 | -0.18883 | -0.12177 | -0.22757 | -0.14502 | -0.07200 | -0.10359 | -0.07526 | -0.15924 | -0.10359 | -0.10260 | -0.10260 |
| $E_{mag}\ (eV)$ | 0.11441 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 |
| $E_T(_{Group})\ (eV)$ | -31.74130 | -33.47795 | -33.61550 | -67.92207 | -49.80996 | -31.70737 | -33.59732 | -33.49373 | -33.24376 | -33.59732 | -33.18712 | -33.18712 |
| $E_{initial}(_{c_4\ AO/HO})\ (eV)$ | -13.6181 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 |
| $E_{initial}(_{c_5\ AO/HO})\ (eV)$ | -13.59844 | 0 | 0 | -13.59844 | -13.59844 | -13.59844 | 0 | 0 | 0 | 0 | 0 | 0 |
| $E_D(_{Group})\ (eV)$ | 4.41035 | 4.20817 | 4.34572 | 12.49186 | 7.83016 | 3.32601 | 4.32754 | 4.29921 | 3.97398 | 4.17951 | 3.62128 | 3.91734 |

Table 15.61. The total bond energies of alkyl alcohols calculated using the functional group composition and the energies of Table 15.60 compared to the experimental values [3].

| Formula | Name | $OH$ Group | $C-O$ (i) Group | $C-O$ (ii) Group | $CH_3$ | $CH_2$ | $CH$ | $C-C$ (a) | $C-C$ (b) | $C-C$ (c) | $C-C$ (d) | $C-C$ (e) | $C-C$ (f) | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $CH_4O$ | Methanol | 1 | 0 | 1 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 21.11038 | 21.131 | 0.00097 |
| $C_2H_6O$ | Ethanol | 1 | 0 | 1 | 1 | 1 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 33.40563 | 33.428 | 0.00066 |
| $C_3H_8O$ | 1-Propanol | 1 | 0 | 1 | 1 | 2 | 0 | 2 | 0 | 0 | 0 | 0 | 0 | 45.56333 | 45.584 | 0.00046 |
| $C_3H_8O$ | 2-Propanol | 1 | 0 | 1 | 2 | 0 | 1 | 2 | 0 | 0 | 0 | 0 | 0 | 45.72088 | 45.766 | 0.00098 |
| $C_4H_{10}O$ | 1-Butanol | 1 | 0 | 1 | 1 | 3 | 0 | 3 | 0 | 0 | 0 | 0 | 0 | 57.72103 | 57.736 | 0.00026 |
| $C_4H_{10}O$ | 2-Butanol | 1 | 0 | 1 | 2 | 1 | 1 | 3 | 0 | 0 | 0 | 0 | 0 | 57.87858 | 57.922 | 0.00074 |
| $C_4H_{10}O$ | 2-Methyl-1-propananol | 1 | 0 | 1 | 2 | 1 | 1 | 0 | 3 | 0 | 0 | 0 | 0 | 57.79359 | 57.828 | 0.00060 |
| $C_4H_{10}O$ | 2-Methyl-2-propananol | 1 | 0 | 1 | 3 | 0 | 0 | 0 | 0 | 3 | 0 | 0 | 0 | 58.15359 | 58.126 | -0.00048 |
| $C_5H_{12}O$ | 1-Pentanol | 1 | 0 | 1 | 1 | 4 | 0 | 4 | 0 | 0 | 0 | 0 | 0 | 69.87873 | 69.887 | 0.00011 |
| $C_5H_{12}O$ | 2-Pentanol | 1 | 0 | 1 | 2 | 2 | 1 | 4 | 0 | 0 | 0 | 0 | 0 | 70.03628 | 70.057 | 0.00029 |
| $C_5H_{12}O$ | 3-Pentanol | 1 | 0 | 1 | 2 | 2 | 1 | 2 | 2 | 0 | 0 | 0 | 0 | 69.97962 | 70.097 | 0.00168 |
| $C_5H_{12}O$ | 2-Methyl-1-butananol | 1 | 0 | 1 | 2 | 2 | 1 | 1 | 3 | 0 | 0 | 0 | 0 | 69.95129 | 69.957 | 0.00008 |
| $C_5H_{12}O$ | 3-Methyl-1-butananol | 1 | 0 | 1 | 2 | 2 | 1 | 1 | 3 | 0 | 0 | 0 | 0 | 69.95129 | 69.950 | -0.00002 |
| $C_5H_{12}O$ | 2-Methyl-2-butananol | 1 | 0 | 1 | 3 | 1 | 0 | 1 | 0 | 3 | 0 | 0 | 0 | 70.31129 | 70.246 | -0.00092 |
| $C_5H_{12}O$ | 3-Methyl-2-butananol | 1 | 0 | 1 | 3 | 0 | 2 | 0 | 3 | 0 | 1 | 0 | 0 | 69.96081 | 70.083 | 0.00174 |
| $C_6H_{14}O$ | 1-Hexanol | 1 | 0 | 1 | 1 | 5 | 0 | 5 | 0 | 0 | 0 | 0 | 0 | 82.03643 | 82.054 | 0.00021 |
| $C_6H_{14}O$ | 2-Hexanol | 1 | 0 | 1 | 2 | 3 | 1 | 5 | 0 | 0 | 0 | 0 | 0 | 82.19398 | 82.236 | 0.00052 |
| $C_7H_{16}O$ | 1-Heptanol | 1 | 0 | 1 | 1 | 6 | 0 | 6 | 0 | 0 | 0 | 0 | 0 | 94.19413 | 94.214 | 0.00021 |
| $C_8H_{18}O$ | 1-Octanol | 1 | 0 | 1 | 1 | 7 | 0 | 7 | 0 | 0 | 0 | 0 | 0 | 106.35183 | 106.358 | 0.00006 |
| $C_8H_{18}O$ | 2-Ethyl-1-hexananol | 1 | 0 | 1 | 2 | 5 | 1 | 4 | 3 | 0 | 0 | 0 | 0 | 106.42439 | 106.459 | 0.00032 |
| $C_9H_{20}O$ | 1-Nonanol | 1 | 0 | 1 | 1 | 8 | 0 | 8 | 0 | 0 | 0 | 0 | 0 | 118.50953 | 118.521 | 0.00010 |
| $C_{10}H_{22}O$ | 1-Decanol | 1 | 0 | 1 | 1 | 9 | 0 | 9 | 0 | 0 | 0 | 0 | 0 | 130.66723 | 130.676 | 0.00007 |
| $C_{12}H_{26}O$ | 1-Dodecanol | 1 | 0 | 1 | 1 | 11 | 0 | 11 | 0 | 0 | 0 | 0 | 0 | 154.98263 | 154.984 | 0.00001 |
| $C_{16}H_{34}O$ | 1-Hexadecanol | 1 | 0 | 1 | 1 | 15 | 0 | 15 | 0 | 0 | 0 | 0 | 0 | 203.61343 | 203.603 | -0.00005 |

Table 15.62. The bond angle parameters of alkyl alcohols and experimental values [1]. In the calculation of $\theta_v$, the parameters from the preceding angle were used. $E_T$ is $E_T(atom - atom, msp^3.AO)$.

| Atoms of Angle | $2c'$ Bond 1 $(a_0)$ | $2c'$ Bond 2 $(a_0)$ | $2c'$ Terminal Atoms $(a_0)$ | $E_{Coulombic}$ Atom 1 | Atom 1 Hybridization Designation (Table 15.3.A) | $E_{Coulombic}$ Atom 2 | Atom 2 Hybridization Designation (Table 15.3.A) | $c_2$ Atom 1 | $c_2$ Atom 2 | $C_1$ | $C_2$ | $c_1$ | $c_2'$ | $E_T$ (eV) | $\theta_v$ (°) | $\theta_1$ (°) | $\theta_2$ (°) | Cal. $\theta$ (°) | Exp. $\theta$ (°) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $\angle C_aOH$ ($C_a - O$ (i)) | 2.67935 | 1.83616 | 3.6697 | -14.82575 | 1 | -14.82575 | 1 | 1 | 0.91771 | 0.75 | 1 | 0.75 | 0.91771 | 0 | | | | 107.24 | 108.53 (methanol) |
| $\angle C_aOH$ ($C_a - O$ (ii)) | 2.67024 | 1.83616 | 3.6515 | -14.82575 | 1 | -14.82575 | 1 | 1 | 0.91771 | 0.75 | 1 | 0.75 | 0.91771 | 0 | | | | 106.78 | 105 (ethanol) |
| $\angle C_bC_aO$ ($C_a - O$ (ii)) | 2.91547 | 2.67024 | 4.5826 | -16.68412 | 26 | -13.61806 | O | 0.81549 | 0.85395 (Eq. (15.114)) | 1 | 1 | 1 | 0.83472 | -1.65376 | | | | 110.17 | 107.8 (ethanol) |
| Methylene $\angle HC_aH$ | 2.11106 | 2.11106 | 3.4252 | -15.75493 | 7 | H | H | 0.86359 | 1 | 1 | 1 | 0.75 | 1.15796 | 0 | | | | 108.44 | 107 (propane) |
| $\angle C_aC_bC_c$ | | | | | | | | | | | | | | | 69.51 | | | 110.49 | 112 (propane)<br>113.8 (butane)<br>110.8 (isobutane) |
| $\angle C_aC_bH$ | | | | | | | | | | | | | | | 69.51 | | | 110.49 | 111.0 (butane)<br>111.4 (isobutane) |
| Methyl $\angle HC_aH$ | 2.09711 | 2.09711 | 3.4252 | -15.75493 | 7 | H | H | 0.86359 | 1 | 1 | 1 | 0.75 | 1.15796 | 0 | | | | 109.50 | |
| $\angle C_aC_bC_c$ | | | | | | | | | | | | | | | 70.56 | | | 109.44 | |
| $\angle C_aC_bH$ | | | | | | | | | | | | | | | 70.56 | | | 109.44 | |
| $\angle C_bC_aC_c$ iso $C_a$ | 2.91547 | 2.91547 | 4.7958 | -16.68412 $C_b$ | 26 | -16.68412 $C_c$ | 26 | 0.81549 | 0.81549 | 1 | 1 | 1 | 0.81549 | -1.85836 | | | | 110.67 | 110.8 (isobutane) |
| $\angle C_bC_aH$ iso $C_a$ | 2.91547 | 2.11323 | 4.1633 | -15.55033 $C_a$ | 5 | -14.82575 $C_b$ | 1 | 0.87495 | 0.91771 | 0.75 | 1 | 0.75 | 1.04887 | 0 | | | | 110.76 | |
| $\angle C_aC_bH$ iso $C_a$ | 2.91547 | 2.09711 | 4.1633 | -15.55033 $C_b$ | 5 | -14.82575 $C_a$ | 1 | 0.87495 | 0.91771 | 0.75 | 1 | 0.75 | 1.04887 | 0 | | | | 111.27 | 111.4 (isobutane) |
| $\angle C_bC_aC_b$ tert $C_a$ | 2.90327 | 2.90327 | 4.7958 | -16.68412 $C_b$ | 26 | -16.68412 $C_b$ | 26 | 0.81549 | 0.81549 | 1 | 1 | 1 | 0.81549 | -1.85836 | | | | 111.37 | 110.8 (isobutane) |
| $\angle C_bC_aC_d$ | | | | | | | | | | | | | | | 72.50 | | | 107.50 | |

## ETHERS ($C_nH_{2n+2}O_m$, $n=2,3,4,5...\infty$)

The alkyl ethers, $C_nH_{2n+2}O_m$, comprise two types of $C-O$ functional groups, one for methyl or t-butyl groups corresponding to the $C$ and the other for general alkyl groups. The alkyl portion of the alkyl ether may comprise at least two terminal methyl groups ($CH_3$) at each end of the chain, and may comprise methylene ($CH_2$), and methylyne ($CH$) functional groups as well as $C$ bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($(CH_3)_2CH$) and t-butyl ($(CH_3)_3C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups. The branched-chain-alkane groups in ethers are equivalent to those in branched-chain alkanes.

Each $C-O$ group is solved by hybridizing the $2s$ and $2p$ AOs of the $C$ atom to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between the $C2sp^3$ HO and the $O$ AO to form a MO permits each participating orbital to decrease in radius and energy. In alkyl ethers, the $C2sp^3$ HO has a hybridization factor of 0.91771 (Eq. (13.430)) and an energy of $E(C,2sp^3)=-14.63489\ eV$ (Eq. (15.25)) and the $O$ AO has an energy of $E(O)=-13.61806\ eV$. To meet the equipotential condition of the union of the $C-O$ $H_2$-type-ellipsoidal-MO with these orbitals, the hybridization factor $c_2$ of Eq. (15.61) for the $C-O$-bond MO given by Eq. (15.133) is $c_2(C2sp^3HO\ to\ O)=0.85395$. $E_T(atom-atom,msp^3.AO)$ of the $C-O$-bond MO in Eq. (15.52) due to the charge donation from the $C$ and $O$ atoms to the MO is $-1.44915\ eV$ for the $CH_3-O-$ and $(CH_3)_3C-O-$ $C-O$ groups. It is based on the energy match between the $O$ AO, initially at the Coulomb potential of a proton and an electron (Eqs. (1.257) and (10.162), respectively), and the $C2sp^3$ HO of a methyl group as given by Eq. (14.151). For the alkyl $C-O$ group, $E_T(atom-atom,msp^3.AO)$ is $-1.65376\ eV$. It is based on the energy match between the $O$ AO and the $C2sp^3$ HO of a methylene group and is given by the linear combination of $-0.72457\ eV$ (Eq. (14.151)) and $-0.92918\ eV$ (Eq. (14.513)), respectively.

The symbols of the functional groups of branched-chain alkyl ethers are given in Table 15.63. The geometrical (Eqs. (15.1-15.5) and (15.51)), intercept (Eqs. (15.80-15.87)), and energy (Eqs. (15.6-15.11) and (15.17-15.65)) parameters of alkyl ethers are given in Tables 15.64, 15.65, and 15.66, respectively. The total energy of each alkyl ether given in Table 15.67 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.66 corresponding to functional-group composition of the molecule. The bond angle parameters of alkyl ethers determined using Eqs. (15.88-15.117) are given in Table 15.68. The color scale, translucent view of the charge-density of exemplary ether, diethyl ether, comprising the concentric shells of atoms with the outer shell bridged by one or more $H_2$-type ellipsoidal MOs or joined with one or more hydrogen MOs is shown in Figure 15.11.

Figure 15.11. Color scale, translucent view of the charge-density of diethyl ether showing the orbitals of the atoms at their radii, the ellipsoidal surface of each $H$ or $H_2$-type ellipsoidal MO that transitions to the corresponding outer shell of the atom(s) participating in each bond, and the hydrogen nuclei (red, not to scale). (A) Oblique view. (B) View along the nitrogen atom.

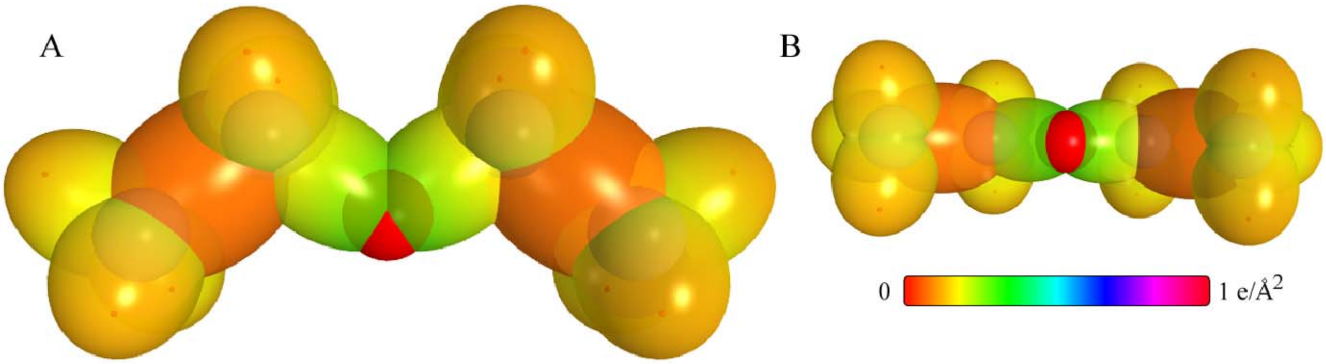


Table 15.63. The symbols of functional groups of alkyl ethers.

| Functional Group | Group Symbol |
|---|---|
| *C-O* ( $CH_3-O-$ and $\left(CH_3\right)_3C-O-$ ) | $C-O$ (i) |
| *C-O* (alkyl) | $C-O$ (ii) |
| $CH_3$ group | $C-H\ \left(CH_3\right)$ |
| $CH_2$ group | $C-H\ \left(CH_2\right)$ |
| *CH* | $C-H$ |
| *CC* bond (*n-C*) | $C-C$ (a) |
| *CC* bond (*iso-C*) | $C-C$ (b) |
| *CC* bond (*tert-C*) | $C-C$ (c) |
| *CC* (*iso to iso-C*) | $C-C$ (d) |
| *CC* (*t* to *t-C*) | $C-C$ (e) |
| *CC* (*t* to *iso-C*) | $C-C$ (f) |

Table 15.64. The geometrical bond parameters of alkyl ethers and experimental values [1].

| Parameter | $C-O$ (i) Group | $C-O$ (ii) Group | $C-H\left(CH_3\right)$ Group | $C-H\left(CH_2\right)$ Group | $C-H$ Group | $C-C$ (a) Group | $C-C$ (b) Group | $C-C$ (c) Group | $C-C$ (d) Group | $C-C$ (e) Group | $C-C$ (f) Group |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $a\left(a_0\right)$ | 1.80717 | 1.79473 | 1.64920 | 1.67122 | 1.67465 | 2.12499 | 2.12499 | 2.10725 | 2.12499 | 2.10725 | 2.10725 |
| $c'\left(a_0\right)$ | 1.34431 | 1.33968 | 1.04856 | 1.05553 | 1.05661 | 1.45744 | 1.45744 | 1.45164 | 1.45744 | 1.45164 | 1.45164 |
| Bond Length $2c'$ $\left(Å\right)$ | 1.42276 | 1.41785 | 1.10974 | 1.11713 | 1.11827 | 1.54280 | 1.54280 | 1.53635 | 1.54280 | 1.53635 | 1.53635 |
| Exp. Bond Length $\left(Å\right)$ | 1.416<br>(dimethyl ether) | 1.418<br>(ethyl methyl ether (avg.)) | 1.107<br>($C-H$ propane)<br>1.117<br>($C-H$ butane) | 1.107<br>($C-H$ propane)<br>1.117<br>($C-H$ butane) | 1.122<br>(isobutane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) |
| $b,c\left(a_0\right)$ | 1.20776 | 1.19429 | 1.27295 | 1.29569 | 1.29924 | 1.54616 | 1.54616 | 1.52750 | 1.54616 | 1.52750 | 1.52750 |
| $e$ | 0.74388 | 0.74645 | 0.63580 | 0.63159 | 0.63095 | 0.68600 | 0.68600 | 0.68888 | 0.68600 | 0.68888 | 0.68888 |

Table 15.65. The MO to HO intercept geometrical bond parameters of alkyl ethers. $R$, $R'$, $R''$ are $H$ or alkyl groups. $E_T$ is $E_T(atom-atom,msp^3.AO)$.

| Bond | Atom | $E_T$ (eV) Bond 1 | $E_T$ (eV) Bond 2 | $E_T$ (eV) Bond 3 | $E_T$ (eV) Bond 4 | Final Total Energy $C2sp^3$ (eV) | $r_{initial}$ $(a_0)$ | $r_{final}$ $(a_0)$ | $E_{Coulomb}$ (eV) Final | $E(C2sp^3)$ (eV) Final | $\theta'$ $(^\circ)$ | $\theta_1$ $(^\circ)$ | $\theta_2$ $(^\circ)$ | $d_1$ $(a_0)$ | $d_2$ $(a_0)$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $C-H\ (OC_aH_3)$ | $C_a$ | -0.72457 | 0 | 0 | 0 | -152.34026 | 0.91771 | 0.87495 | -15.55033 | -15.35946 | 78.85 | 101.15 | 42.40 | 1.21777 | 0.16921 |
| $H_3C_a-O-C_aH_3$<br>$(CH_3)_3C_a-O-C_bH_3$<br>$(CH_3)_3C_a-O-C_a(CH_3)_3$<br>$(C-O$ (i)) | $C_{a,b}$ | -0.72457 | 0 | 0 | 0 | -152.34026 | 0.91771 | 0.87495 | -15.55033 | -15.35946 | 95.98 | 84.02 | 46.10 | 1.25319 | 0.09112 |
| $H_3C_a-O-C_aH_3$<br>$(CH_3)_3C_a-O-C_bH_3$<br>$(CH_3)_3C_a-O-C_a(CH_3)_3$<br>$(C-O$ (i)) | $O$ | -0.72457 | -0.72457 | 0 | 0 |  | 1.00000 | 0.83600 | -16.27490 |  | 92.66 | 87.34 | 43.74 | 1.30555 | 0.03876 |
| $-H_2C_a-OC_b(CH_3)_3$<br>$-H_2C_a-OC_bH_3$<br>$(C-O$ (ii)) | $C_a$ | -0.82688 | -0.92918 | 0 | 0 | -153.37175 | 0.91771 | 0.82053 | -16.58181 | -16.39095 | 92.41 | 87.59 | 43.35 | 1.30512 | 0.03456 |
| $-H_2C_a-OC_b(CH_3)_3$<br>$-H_2C_a-OC_bH_3$<br>$(C-O$ (ii)) | $O$ | -0.72457 | -0.82688 | 0 | 0 |  | 1.00000 | 0.83078 | -16.37720 |  | 93.33 | 86.67 | 43.98 | 1.29138 | 0.04829 |
| $-H_2C_a-O-H_2C_a-$<br>$(C-O$ (ii)) | $O$ | -0.82688 | -0.82688 | 0 | 0 |  | 1.00000 | 0.82562 | -16.47951 |  | 92.87 | 87.13 | 43.66 | 1.29829 | 0.04138 |
| $C-H\ (CH_3)$ | $C$ | -0.92918 | 0 | 0 | 0 | -152.54487 | 0.91771 | 0.86359 | -15.75493 | -15.56407 | 77.49 | 102.51 | 41.48 | 1.23564 | 0.18708 |
| $C-H\ (CH_2)$ | $C$ | -0.92918 | -0.92918 | 0 | 0 | -153.47406 | 0.91771 | 0.81549 | -16.68412 | -16.49325 | 68.47 | 111.53 | 35.84 | 1.35486 | 0.29933 |
| $C-H\ (CH)$ | $C$ | -0.92918 | -0.92918 | -0.92918 | 0 | -154.40324 | 0.91771 | 0.77247 | -17.61330 | -17.42244 | 61.10 | 118.90 | 31.37 | 1.42988 | 0.37326 |
| $H_3C_aC_bH_2CH_2-$<br>$(C-C$ (a)) | $C_a$ | -0.92918 | 0 | 0 | 0 | -152.54487 | 0.91771 | 0.86359 | -15.75493 | -15.56407 | 63.82 | 116.18 | 30.08 | 1.83879 | 0.38106 |
| $H_3C_aC_bH_2CH_2-$<br>$(C-C$ (a)) | $C_b$ | -0.92918 | -0.92918 | 0 | 0 | -153.47406 | 0.91771 | 0.81549 | -16.68412 | -16.49325 | 56.41 | 123.59 | 26.06 | 1.90890 | 0.45117 |
| $R-H_2C_aC_b(H_2C_c-R')HCH_2-$<br>$(C-C$ (b)) | $C_b$ | -0.92918 | -0.92918 | -0.92918 | 0 | -154.40324 | 0.91771 | 0.77247 | -17.61330 | -17.42244 | 48.30 | 131.70 | 21.90 | 1.97162 | 0.51388 |
| $R-H_2C_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$<br>$(C-C$ (c)) | $C_b$ | -0.92918 | -0.72457 | -0.72457 | -0.72457 | -154.71860 | 0.91771 | 0.75889 | -17.92866 | -17.73779 | 48.21 | 131.79 | 21.74 | 1.95734 | 0.50570 |
| $isoC_aC_b(H_2C_c-R')HCH_2-$<br>$(C-C$ (d)) | $C_b$ | -0.92918 | -0.92918 | -0.92918 | 0 | -154.40324 | 0.91771 | 0.77247 | -17.61330 | -17.42244 | 48.30 | 131.70 | 21.90 | 1.97162 | 0.51388 |
| $tertC_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$<br>$(C-C$ (e)) | $C_b$ | -0.72457 | -0.72457 | -0.72457 | -0.72457 | -154.51399 | 0.91771 | 0.76765 | -17.92866 | -17.73779 | 50.04 | 129.96 | 22.66 | 1.94462 | 0.49298 |
| $tertC_aC_b(H_2C_c-R')HCH_2-$<br>$(C-C$ (f)) | $C_b$ | -0.72457 | -0.92918 | -0.92918 | 0 | -154.19863 | 0.91771 | 0.78155 | -17.40869 | -17.21783 | 52.78 | 127.22 | 24.04 | 1.92443 | 0.47279 |
| $isoC_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$<br>$(C-C$ (f)) | $C_b$ | -0.72457 | -0.72457 | -0.72457 | -0.72457 | -154.51399 | 0.91771 | 0.76765 | -17.92866 | -17.73779 | 50.04 | 129.96 | 22.66 | 1.94462 | 0.49298 |

Table 15.66. The energy parameters ($eV$) of functional groups of alkyl ethers.

| Parameters | $C-O$ (i) Group | $C-O$ (ii) Group | $CH_3$ Group | $CH_2$ Group | $C-H$ Group | $C-C$ (a) Group | $C-C$ (b) Group | $C-C$ (c) Group | $C-C$ (d) Group | $C-C$ (e) Group | $C-C$ (f) Group |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $n_1$ | 1 | 1 | 3 | 2 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $n_2$ | 0 | 0 | 2 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $n_3$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $C_1$ | 0.5 | 0.5 | 0.75 | 0.75 | 0.75 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| $C_2$ | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $c_1$ | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $c_2$ | 0.85395 | 0.85395 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 |
| $c_3$ | 0 | 0 | 0 | 1 | 1 | 0 | 0 | 0 | 1 | 1 | 0 |
| $c_4$ | 2 | 2 | 1 | 1 | 1 | 2 | 2 | 2 | 2 | 2 | 2 |
| $c_5$ | 0 | 0 | 3 | 2 | 1 | 0 | 0 | 0 | 0 | 0 | 0 |
| $C_{1o}$ | 0.5 | 0.5 | 0.75 | 0.75 | 0.75 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| $C_{2o}$ | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $V_e\ (eV)$ | -33.15757 | -33.47304 | -107.32728 | -70.41425 | -35.12015 | -28.79214 | -28.79214 | -29.10112 | -28.79214 | -29.10112 | -29.10112 |
| $V_p\ (eV)$ | 10.12103 | 10.15605 | 38.92728 | 25.78002 | 12.87680 | 9.33352 | 9.33352 | 9.37273 | 9.33352 | 9.37273 | 9.37273 |
| $T\ (eV)$ | 9.17389 | 9.32537 | 32.53914 | 21.06675 | 10.48582 | 6.77464 | 6.77464 | 6.90500 | 6.77464 | 6.90500 | 6.90500 |
| $V_m\ (eV)$ | -4.58695 | -4.66268 | -16.26957 | -10.53337 | -5.24291 | -3.38732 | -3.38732 | -3.45250 | -3.38732 | -3.45250 | -3.45250 |
| $E(_{AO/HO})\ (eV)$ | -14.63489 | -14.63489 | -15.56407 | -15.56407 | -14.63489 | -15.56407 | -15.56407 | -15.35946 | -15.56407 | -15.35946 | -15.35946 |
| $\Delta E_{H_2MO}(_{AO/HO})\ (eV)$ | -1.44915 | -1.65376 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $E_T(_{AO/HO})\ (eV)$ | -13.18574 | -12.98113 | -15.56407 | -15.56407 | -14.63489 | -15.56407 | -15.56407 | -15.35946 | -15.56407 | -15.35946 | -15.35946 |
| $E_T(_{H_2MO})\ (eV)$ | -31.63533 | -31.63544 | -67.69451 | -49.66493 | -31.63533 | -31.63537 | -31.63537 | -31.63535 | -31.63537 | -31.63535 | -31.63535 |
| $E_T\left(atom-atom,msp^3.AO\right)(eV)$ | -1.44915 | -1.65376 | 0 | 0 | 0 | -1.85836 | -1.85836 | -1.44915 | -1.85836 | -1.44915 | -1.44915 |
| $E_T(_{MO})\ (eV)$ | -33.08452 | -33.28912 | -67.69450 | -49.66493 | -31.63537 | -33.49373 | -33.49373 | -33.08452 | -33.49373 | -33.08452 | -33.08452 |
| $\omega\ \left(10^{15}\ rad/s\right)$ | 12.0329 | 12.1583 | 24.9286 | 24.2751 | 24.1759 | 9.43699 | 9.43699 | 15.4846 | 9.43699 | 9.55643 | 9.55643 |
| $E_K\ (eV)$ | 7.92028 | 8.00277 | 16.40846 | 15.97831 | 15.91299 | 6.21159 | 6.21159 | 10.19220 | 6.21159 | 6.29021 | 6.29021 |
| $\bar{E}_D\ (eV)$ | -0.18420 | -0.18631 | -0.25352 | -0.25017 | -0.24966 | -0.16515 | -0.16515 | -0.20896 | -0.16515 | -0.16416 | -0.16416 |
| $\bar{E}_{Kvib}\ (eV)$ | 0.13663 [21] | 0.16118 [4] | 0.35532 (Eq. (13.458)) | 0.35532 (Eq. (13.458)) | 0.35532 (Eq. (13.458)) | 0.12312 [2] | 0.17978 [4] | 0.09944 [5] | 0.12312 [2] | 0.12312 [2] | 0.12312 [2] |
| $\bar{E}_{osc}\ (eV)$ | -0.11589 | -0.10572 | -0.22757 | -0.14502 | -0.07200 | -0.10359 | -0.07526 | -0.15924 | -0.10359 | -0.10260 | -0.10260 |
| $E_{mag}\ (eV)$ | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 |
| $E_T(_{Group})\ (eV)$ | -33.20040 | -33.39484 | -67.92207 | -49.80996 | -31.70737 | -33.59732 | -33.49373 | -33.24376 | -33.59732 | -33.18712 | -33.18712 |
| $E_{initial}(_{c_4\ AO/HO})\ (eV)$ | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 |
| $E_{initial}(_{c_5\ AO/HO})\ (eV)$ | 0 | 0 | -13.59844 | -13.59844 | -13.59844 | 0 | 0 | 0 | 0 | 0 | 0 |
| $E_D(_{Group})\ (eV)$ | 3.93062 | 4.12506 | 12.49186 | 7.83016 | 3.32601 | 4.32754 | 4.29921 | 3.97398 | 4.17951 | 3.62128 | 3.91734 |

Table 15.67. The total bond energies of alkyl ethers calculated using the functional group composition and the energies of Table 15.66 compared to the experimental values [3].

| Formula | Name | $C-O$ (i) Group | $C-O$ (ii) Group | $CH_3$ | $CH_2$ | $CH$ | $C-C$ (a) | $C-C$ (b) | $C-C$ (c) | $C-C$ (d) | $C-C$ (e) | $C-C$ (f) | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $C_2H_6O$ | Dimethyl ether | 2 | 0 | 2 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 32.84496 | 32.902 | 0.00174 |
| $C_3H_8O$ | Ethyl methyl ether | 1 | 1 | 2 | 1 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 45.19710 | 45.183 | -0.00030 |
| $C_4H_{10}O$ | Diethyl ether | 0 | 2 | 2 | 2 | 0 | 2 | 0 | 0 | 0 | 0 | 0 | 57.54924 | 57.500 | -0.00086 |
| $C_4H_{10}O$ | Methyl propyl ether | 1 | 1 | 2 | 2 | 0 | 2 | 0 | 0 | 0 | 0 | 0 | 57.35480 | 57.355 | 0.00000 |
| $C_4H_{10}O$ | Isopropyl methyl ether | 1 | 1 | 3 | 0 | 1 | 0 | 2 | 0 | 0 | 0 | 0 | 57.45569 | 57.499 | 0.00075 |
| $C_6H_{14}O$ | Dipropyl ether | 0 | 2 | 2 | 4 | 0 | 4 | 0 | 0 | 0 | 0 | 0 | 81.86464 | 81.817 | -0.00059 |
| $C_6H_{14}O$ | Diisopropyl ether | 0 | 2 | 4 | 0 | 2 | 0 | 4 | 0 | 0 | 0 | 0 | 82.06642 | 82.088 | 0.00026 |
| $C_6H_{14}O$ | t-Butyl ethyl ether | 1 | 1 | 4 | 1 | 0 | 1 | 0 | 3 | 0 | 0 | 0 | 82.10276 | 82.033 | -0.00085 |
| $C_7H_{16}O$ | t-Butyl isopropyl ether | 1 | 1 | 5 | 0 | 1 | 0 | 2 | 3 | 0 | 0 | 0 | 94.36135 | 94.438 | 0.00081 |
| $C_8H_{18}O$ | Dibutyl ether | 0 | 2 | 2 | 6 | 0 | 6 | 0 | 0 | 0 | 0 | 0 | 106.18004 | 106.122 | -0.00055 |
| $C_8H_{18}O$ | Di-sec-butyl ether | 0 | 2 | 4 | 2 | 2 | 2 | 4 | 0 | 0 | 0 | 0 | 106.38182 | 106.410 | 0.00027 |
| $C_8H_{18}O$ | Di-t-butyl ether | 2 | 0 | 6 | 0 | 0 | 0 | 0 | 6 | 0 | 0 | 0 | 106.65628 | 106.425 | -0.00218 |
| $C_8H_{18}O$ | t-Butyl isobutyl ether | 1 | 1 | 5 | 1 | 1 | 0 | 3 | 3 | 0 | 0 | 0 | 106.49072 | 106.497 | 0.00006 |

Table 15.68. The bond angle parameters of alkyl ethers and experimental values [1]. In the calculation of $\theta_v$, the parameters from the preceding angle were used. $E_T$ is $E_T(atom-atom, msp^3.AO)$.

| Atoms of Angle | $2c'$ Bond 1 ($a_0$) | $2c'$ Bond 2 ($a_0$) | $2c'$ Terminal Atoms ($a_0$) | $E_{Coulombic}$ Atom 1 | Atom 1 Hybridization Designation (Table 15.3.A) | $E_{Coulombic}$ Atom 2 | Atom 2 Hybridization Designation (Table 15.3.A) | $c_2$ Atom 1 | $c_2$ Atom 2 | $C_1$ | $C_2$ | $c_1$ | $c_2'$ | $E_T$ (eV) | $\theta_v$ (°) | $\theta_1$ (°) | $\theta_2$ (°) | Cal. $\theta$ (°) | Exp. $\theta$ (°) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $\angle C_aOC_a$<br>($C_a-O$ (i)) | 2.68862 | 2.68862 | 4.4721 | -17.40869 | 44 | -17.40869 | 44 | 0.78155 | 0.78155 | 1 | 1 | 1 | 0.78155 | -1.85836 | | | | 112.54 | 112<br>(dimethyl ether) |
| $\angle C_aOC_b$<br>($C_a-O$ (i))<br>($C_b-O$ (ii)) | 2.68862 | 2.67935 | 4.4385 | -17.51099 | 46 | -17.51099 | 46 | 0.77699 | 0.77699 | 1 | 1 | 1 | 0.77699 | -1.85836 | | | | 111.55 | 111.9<br>(ethyl methyl ether) |
| $\angle C_bC_aO$<br>($C_a-O$ (ii)) | 2.91547 | 2.67935 | 4.5607 | -16.68412 | 26 | -13.61806 | O | 0.81549 | 0.85395<br>(Eq. (15.133)) | 1 | 1 | 1 | 0.83472 | -1.65376 | | | | 109.13 | 109.4<br>(ethyl methyl ether) |
| Methylene<br>$\angle HC_aH$ | 2.11106 | 2.11106 | 3.4252 | -15.75493 | 7 | H | H | 0.86359 | 1 | 1 | 1 | 0.75 | 1.15796 | 0 | | | | 108.44 | 107<br>(propane) |
| $\angle C_aC_bC_c$ | | | | | | | | | | | | | | | 69.51 | | | 110.49 | 112<br>(propane)<br>113.8<br>(butane)<br>110.8<br>(isobutane) |
| $\angle C_aC_bH$ | | | | | | | | | | | | | | | 69.51 | | | 110.49 | 111.0<br>(butane)<br>111.4<br>(isobutane) |
| Methyl<br>$\angle HC_aH$ | 2.09711 | 2.09711 | 3.4252 | -15.75493 | 7 | H | H | 0.86359 | 1 | 1 | 1 | 0.75 | 1.15796 | 0 | | | | 109.50 | |
| $\angle C_aC_bC_c$ | | | | | | | | | | | | | | | 70.56 | | | 109.44 | |
| $\angle C_aC_bH$ | | | | | | | | | | | | | | | 70.56 | | | 109.44 | |
| $\angle C_bC_aC_c$<br>iso $C_a$ | 2.91547 | 2.91547 | 4.7958 | -16.68412<br>$C_b$ | 26 | -16.68412<br>$C_c$ | 26 | 0.81549 | 0.81549 | 1 | 1 | 1 | 0.81549 | -1.85836 | | | | 110.67 | 110.8<br>(isobutane) |
| $\angle C_bC_aH$<br>iso $C_a$ | 2.91547 | 2.11323 | 4.1633 | -15.55033<br>$C_a$ | 5 | -14.82575<br>$C_b$ | 1 | 0.87495 | 0.91771 | 0.75 | 1 | 0.75 | 1.04887 | 0 | | | | 110.76 | |
| $\angle C_aC_bH$<br>iso $C_a$ | 2.91547 | 2.09711 | 4.1633 | -15.55033<br>$C_b$ | 5 | -14.82575<br>$C_a$ | 1 | 0.87495 | 0.91771 | 0.75 | 1 | 0.75 | 1.04887 | 0 | | | | 111.27 | 111.4<br>(isobutane) |
| $\angle C_bC_aC_b$<br>tert $C_a$ | 2.90327 | 2.90327 | 4.7958 | -16.68412<br>$C_b$ | 26 | -16.68412<br>$C_b$ | 26 | 0.81549 | 0.81549 | 1 | 1 | 1 | 0.81549 | -1.85836 | | | | 111.37 | 110.8<br>(isobutane) |
| $\angle C_bC_aC_d$ | | | | | | | | | | | | | | | 72.50 | | | 107.50 | |

## PRIMARY AMINES ($C_nH_{2n+2+m}N_m,\ n=1,2,3,4,5...\infty$)

The primary amines, $C_nH_{2n+2+m}N_m$, comprise an $NH_2$ functional group and a $C-N$ functional group. The alkyl portion of the primary amine may comprise at least two terminal methyl groups ($CH_3$) at each end of the chain, and may comprise methylene ($CH_2$), and methylyne ($CH$) functional groups as well as $C$ bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($(CH_3)_2CH$) and t-butyl ($(CH_3)_3C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups. The branched-chain-alkane groups in primary amines are equivalent to those in branched-chain alkanes.

The primary amino ($NH_2$) functional group was solved using the procedure given in the Dihydrogen Nitride ($NH_2$) section. Using the results of Eqs. (13.245-13.368), the primary amino parameters in Eq. (15.61) are $n_1=2$, $C_1=0.75$, $C_2=0.93613$ (Eqs. (13.248-13.249)), $C_{1o}=1.5$, and $c_1=0.75$. In primary amines, the $C2sp^3$ HO of the $C-NH_2$-bond MO has an energy of $E(C,2sp^3)=-15.35946\ eV$ (Eq. (15.18) with $s=1$ and Eqs. (15.19-15.20)) and the $N$ AO has an energy of $E(N)=-14.53414\ eV$. To meet the equipotential condition of the union of the $N-H$ $H_2$-type-ellipsoidal-MO with the $C2sp^3$ HO, the hybridization factor $c_2$ of Eq. (15.61) for the $N-H$-bond MO given by Eq. (15.77) is:

$$c_2(H\ to\ 1°N)=\frac{E(N)}{E(C,2sp^3)}=\frac{-14.53414\ eV}{-15.35946\ eV}=0.94627 \tag{15.134}$$

The $C-N$ group is solved by hybridizing the $2s$ and $2p$ AOs of the $C$ atom to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between the $C2sp^3$ HO and the $N$ AO to form a MO permits each participating orbital to decrease in radius and energy. In primary amines, the $C2sp^3$ HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of $E(C,2sp^3)=-14.63489\ eV$ (Eq. (15.25)), and the $N$ AO has an energy of $E(N)=-14.53414\ eV$. To meet the equipotential condition of the union of the $C-N$ $H_2$-type-ellipsoidal-MO with these orbitals, the hybridization factor $c_2$ of Eq. (15.61) for the $C-N$-bond MO given by Eqs. (15.77) and (15.79) is:

$$c_2(C2sp^3HO\ to\ N)=\frac{E(N)}{E(C,2sp^3)}c_2(C2sp^3HO)=\frac{-14.53414\ eV}{-14.63489\ eV}(0.91771)=0.91140 \tag{15.135}$$

$E_T(atom-atom,msp^3.AO)$ of the $C-N$-bond MO in Eq. (15.61) due to the charge donation from the $C$ and $N$ atoms to the MO is $-1.44915\ eV$. It is based on the energy match between the $N$ of the $NH_2$ group and the $C2sp^3$ HO corresponding to the energy contributions to the single bond that are equivalent to those of methyl groups, $-0.72457\ eV$ (Eq. (14.151)), where the $N-H$ bonds are also energy matched to the $C-N$ bond.

The symbols of the functional groups of branched-chain primary amines are given in Table 15.69. The geometrical (Eqs. (15.1-15.5) and (15.51)), intercept (Eqs. (15.80-15.87)), and energy (Eqs. (15.6-15.11) and (15.17-15.65)) parameters of primary amines are given in Tables 15.70, 15.71, and 15.72, respectively. The total energy of each primary amine given in Table 15.73 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.72 corresponding to functional-group composition of the molecule. The bond angle parameters of primary amines determined using Eqs. (15.88-15.117) are given in Table 15.74. The color scale, translucent view of the charge-density of exemplary primary amine, propylamine, comprising the concentric shells of atoms with the outer shell bridged by one or more $H_2$-type ellipsoidal MOs or joined with one or more hydrogen MOs is shown in Figure 15.12.

Figure 15.12. (A)-(B) Color scale, translucent views of the charge-density of propylamine showing the orbitals of the atoms at their radii, the ellipsoidal surface of each $H$ or $H_2$-type ellipsoidal MO that transitions to the corresponding outer shell of the atom(s) participating in each bond, and the hydrogen nuclei (red, not to scale).

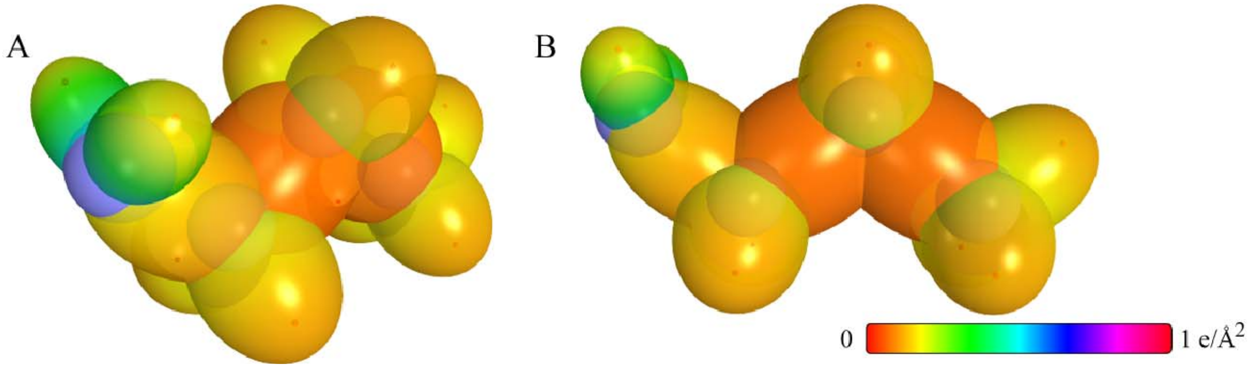


Table 15.69. The symbols of functional groups of primary amines.

| Functional Group | Group Symbol |
|---|---|
| $NH_2$ group | $NH_2$ |
| $C$-$N$ | $C-N$ |
| $CH_3$ group | $C-H\ (CH_3)$ |
| $CH_2$ group | $C-H\ (CH_2)$ |
| $CH$ | $C-H$ |
| $CC$ bond (*n*-$C$) | $C-C$ (a) |
| $CC$ bond (*iso*-$C$) | $C-C$ (b) |
| $CC$ bond (*tert*-$C$) | $C-C$ (c) |
| $CC$ (iso to *iso*-$C$) | $C-C$ (d) |
| $CC$ (*t* to *t*-$C$) | $C-C$ (e) |
| $CC$ (*t* to *iso*-$C$) | $C-C$ (f) |

Table 15.70. The geometrical bond parameters of primary amines and experimental values [1].

| Parameter | $NH_2$ Group | $C-N$ Group | $C-H\left(CH_3\right)$ Group | $C-H\left(CH_2\right)$ Group | $C-H$ Group | $C-C$ (a) Group | $C-C$ (b) Group | $C-C$ (c) Group | $C-C$ (d) Group | $C-C$ (e) Group | $C-C$ (f) Group |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $a\left(a_0\right)$ | 1.28083 | 1.92682 | 1.64920 | 1.67122 | 1.67465 | 2.12499 | 2.12499 | 2.10725 | 2.12499 | 2.10725 | 2.10725 |
| $c'\left(a_0\right)$ | 0.95506 | 1.38810 | 1.04856 | 1.05553 | 1.05661 | 1.45744 | 1.45744 | 1.45164 | 1.45744 | 1.45164 | 1.45164 |
| Bond Length $2c'$ $\left(\mathring{A}\right)$ | 1.0108 | 1.46910 | 1.10974 | 1.11713 | 1.11827 | 1.54280 | 1.54280 | 1.53635 | 1.54280 | 1.53635 | 1.53635 |
| Exp. Bond Length $\left(\mathring{A}\right)$ | 1.010<br>(methylamine) | 1.471<br>(methylamine) | 1.107<br>($C-H$ propane)<br>1.117<br>($C-H$ butane) | 1.107<br>($C-H$ propane)<br>1.117<br>($C-H$ butane) | 1.122<br>(isobutane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) |
| $b,c\left(a_0\right)$ | 0.85345 | 1.33634 | 1.27295 | 1.29569 | 1.29924 | 1.54616 | 1.54616 | 1.52750 | 1.54616 | 1.52750 | 1.52750 |
| $e$ | 0.74566 | 0.72041 | 0.63580 | 0.63159 | 0.63095 | 0.68600 | 0.68600 | 0.68888 | 0.68600 | 0.68888 | 0.68888 |

Table 15.71. The MO to HO intercept geometrical bond parameters of primary amines. $R$, $R'$, $R''$ are $H$ or alkyl groups. $E_T$ is $E_T(atom-atom,msp^3.AO)$.

| Bond | Atom | $E_T$ (eV) Bond 1 | $E_T$ (eV) Bond 2 | $E_T$ (eV) Bond 3 | $E_T$ (eV) Bond 4 | Final Total Energy $C2sp^3$ (eV) | $r_{initial}$ $\left(a_0\right)$ | $r_{final}$ $\left(a_0\right)$ | $E_{Coulomb}$ (eV) Final | $E\left(C2sp^3\right)$ (eV) Final | $\theta'$ $\left(^\circ\right)$ | $\theta_1$ $\left(^\circ\right)$ | $\theta_2$ $\left(^\circ\right)$ | $d_1$ $\left(a_0\right)$ | $d_2$ $\left(a_0\right)$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $H_3CN(H)-H$ | $N$ | -0.72457 | 0 | 0 | 0 |  | 0.93084 | 0.87495 | -15.55033 |  | 118.00 | 62.00 | 64.85 | 0.54432 | 0.41075 |
| $-H_2C_aN(H)-H$ | $N$ | -0.72457 | 0 | 0 | 0 |  | 0.93084 | 0.87495 | -15.55033 |  | 118.00 | 62.00 | 64.85 | 0.54432 | 0.41075 |
| $H_3C-NH_2$ | $C$ | -0.72457 | 0 | 0 | 0 | -152.34026 | 0.91771 | 0.87495 | -15.55033 | -15.35946 | 85.28 | 94.72 | 40.73 | 1.46010 | 0.07200 |
| $H_3C-NH_2$ | $N$ | -0.72457 | 0 | 0 | 0 |  | 0.93084 | 0.87495 | -15.55033 |  | 85.28 | 94.72 | 40.73 | 1.46010 | 0.07200 |
| $-H_2C_a-NH_2$ | $C_a$ | -0.72457 | -0.92918 | 0 | 0 | -153.26945 | 0.91771 | 0.82562 | -16.47951 | -16.28864 | 80.20 | 99.80 | 37.50 | 1.52858 | 0.14048 |
| $-H_2C_a-NH_2$ | $N$ | -0.72457 | 0 | 0 | 0 |  | 0.93084 | 0.87495 | -15.55033 |  | 85.28 | 94.72 | 40.73 | 1.46010 | 0.07200 |
| $C-H\left(CH_3\right)$ | $C$ | -0.92918 | 0 | 0 | 0 | -152.54487 | 0.91771 | 0.86359 | -15.75493 | -15.56407 | 77.49 | 102.51 | 41.48 | 1.23564 | 0.18708 |
| $C-H\left(CH_2\right)$ | $C$ | -0.92918 | -0.92918 | 0 | 0 | -153.47406 | 0.91771 | 0.81549 | -16.68412 | -16.49325 | 68.47 | 111.53 | 35.84 | 1.35486 | 0.29933 |
| $C-H\left(CH\right)$ | $C$ | -0.92918 | -0.92918 | -0.92918 | 0 | -154.40324 | 0.91771 | 0.77247 | -17.61330 | -17.42244 | 61.10 | 118.90 | 31.37 | 1.42988 | 0.37326 |
| $H_3C_aC_bH_2CH_2-$ ($C-C$ (a)) | $C_a$ | -0.92918 | 0 | 0 | 0 | -152.54487 | 0.91771 | 0.86359 | -15.75493 | -15.56407 | 63.82 | 116.18 | 30.08 | 1.83879 | 0.38106 |
| $H_3C_aC_bH_2CH_2-$ ($C-C$ (a)) | $C_b$ | -0.92918 | -0.92918 | 0 | 0 | -153.47406 | 0.91771 | 0.81549 | -16.68412 | -16.49325 | 56.41 | 123.59 | 26.06 | 1.90890 | 0.45117 |
| $R-H_2C_aC_b\left(H_2C_c-R'\right)HCH_2-$ ($C-C$ (b)) | $C_b$ | -0.92918 | -0.92918 | -0.92918 | 0 | -154.40324 | 0.91771 | 0.77247 | -17.61330 | -17.42244 | 48.30 | 131.70 | 21.90 | 1.97162 | 0.51388 |
| $R-H_2C_a\left(R'-H_2C_d\right)C_b\left(R''-H_2C_c\right)CH_2-$ ($C-C$ (c)) | $C_b$ | -0.92918 | -0.72457 | -0.72457 | -0.72457 | -154.71860 | 0.91771 | 0.75889 | -17.92866 | -17.73779 | 48.21 | 131.79 | 21.74 | 1.95734 | 0.50570 |
| $isoC_aC_b\left(H_2C_c-R'\right)HCH_2-$ ($C-C$ (d)) | $C_b$ | -0.92918 | -0.92918 | -0.92918 | 0 | -154.40324 | 0.91771 | 0.77247 | -17.61330 | -17.42244 | 48.30 | 131.70 | 21.90 | 1.97162 | 0.51388 |
| $tertC_a\left(R'-H_2C_d\right)C_b\left(R''-H_2C_c\right)CH_2-$ ($C-C$ (e)) | $C_b$ | -0.72457 | -0.72457 | -0.72457 | -0.72457 | -154.51399 | 0.91771 | 0.76765 | -17.92866 | -17.73779 | 50.04 | 129.96 | 22.66 | 1.94462 | 0.49298 |
| $tertC_aC_b\left(H_2C_c-R'\right)HCH_2-$ ($C-C$ (f)) | $C_b$ | -0.72457 | -0.92918 | -0.92918 | 0 | -154.19863 | 0.91771 | 0.78155 | -17.40869 | -17.21783 | 52.78 | 127.22 | 24.04 | 1.92443 | 0.47279 |
| $isoC_a\left(R'-H_2C_d\right)C_b\left(R''-H_2C_c\right)CH_2-$ ($C-C$ (f)) | $C_b$ | -0.72457 | -0.72457 | -0.72457 | -0.72457 | -154.51399 | 0.91771 | 0.76765 | -17.92866 | -17.73779 | 50.04 | 129.96 | 22.66 | 1.94462 | 0.49298 |

Table 15.72. The energy parameters ($eV$) of functional groups of primary amines.

| Parameters | $NH_2$ Group | $C-N$ Group | $CH_3$ Group | $CH_2$ Group | $C-H$ Group | $C-C$ (a) Group | $C-C$ (b) Group | $C-C$ (c) Group | $C-C$ (d) Group | $C-C$ (e) Group | $C-C$ (f) Group |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $n_1$ | 2 | 1 | 3 | 2 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $n_2$ | 0 | 0 | 2 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $n_3$ | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $C_1$ | 0.75 | 0.5 | 0.75 | 0.75 | 0.75 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| $C_2$ | 0.93613 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $c_1$ | 0.75 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $c_2$ | 0.94627 | 0.91140 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 |
| $c_3$ | 0 | 0 | 0 | 1 | 1 | 0 | 0 | 0 | 1 | 1 | 0 |
| $c_4$ | 1 | 2 | 1 | 1 | 1 | 2 | 2 | 2 | 2 | 2 | 2 |
| $c_5$ | 2 | 0 | 3 | 2 | 1 | 0 | 0 | 0 | 0 | 0 | 0 |
| $C_{1o}$ | 1.5 | 0.5 | 0.75 | 0.75 | 0.75 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| $C_{2o}$ | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $V_e\ (eV)$ | -77.89897 | -32.46339 | -107.32728 | -70.41425 | -35.12015 | -28.79214 | -28.79214 | -29.10112 | -28.79214 | -29.10112 | -29.10112 |
| $V_p\ (eV)$ | 28.49191 | 9.80175 | 38.92728 | 25.78002 | 12.87680 | 9.33352 | 9.33352 | 9.37273 | 9.33352 | 9.37273 | 9.37273 |
| $T\ (eV)$ | 30.40957 | 8.42409 | 32.53914 | 21.06675 | 10.48582 | 6.77464 | 6.77464 | 6.90500 | 6.77464 | 6.90500 | 6.90500 |
| $V_m\ (eV)$ | -15.20478 | -4.21204 | -16.26957 | -10.53337 | -5.24291 | -3.38732 | -3.38732 | -3.45250 | -3.38732 | -3.45250 | -3.45250 |
| $E(_{AO/HO})\ (eV)$ | -14.53414 | -14.63489 | -15.56407 | -15.56407 | -14.63489 | -15.56407 | -15.56407 | -15.35946 | -15.56407 | -15.35946 | -15.35946 |
| $\Delta E_{H_2MO}(_{AO/HO})\ (eV)$ | 0 | -1.44915 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $E_T(_{AO/HO})\ (eV)$ | -14.53414 | -13.18574 | -15.56407 | -15.56407 | -14.63489 | -15.56407 | -15.56407 | -15.35946 | -15.56407 | -15.35946 | -15.35946 |
| $E(_{n_3\ AO/HO})\ (eV)$ | -14.53414 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $E_T(_{H_2MO})\ (eV)$ | -48.73642 | -31.63534 | -67.69451 | -49.66493 | -31.63533 | -31.63537 | -31.63537 | -31.63535 | -31.63537 | -31.63535 | -31.63535 |
| $E_T\left(atom-atom,msp^3.AO\right)(eV)$ | 0 | -1.44915 | 0 | 0 | 0 | -1.85836 | -1.85836 | -1.44915 | -1.85836 | -1.44915 | -1.44915 |
| $E_T(_{MO})\ (eV)$ | -48.73660 | -33.08452 | -67.69450 | -49.66493 | -31.63537 | -33.49373 | -33.49373 | -33.08452 | -33.49373 | -33.08452 | -33.08452 |
| $\omega\ \left(10^{15}\ rad/s\right)$ | 64.2189 | 18.9231 | 24.9286 | 24.2751 | 24.1759 | 9.43699 | 9.43699 | 15.4846 | 9.43699 | 9.55643 | 9.55643 |
| $E_K\ (eV)$ | 42.27003 | 12.45552 | 16.40846 | 15.97831 | 15.91299 | 6.21159 | 6.21159 | 10.19220 | 6.21159 | 6.29021 | 6.29021 |
| $\bar{E}_D\ (eV)$ | -0.40690 | -0.23100 | -0.25352 | -0.25017 | -0.24966 | -0.16515 | -0.16515 | -0.20896 | -0.16515 | -0.16416 | -0.16416 |
| $\bar{E}_{Kvib}\ (eV)$ | 0.40929<br>[22] | 0.12944<br>[23] | 0.35532<br>(Eq. (13.458)) | 0.35532<br>(Eq. (13.458)) | 0.35532<br>(Eq. (13.458)) | 0.12312<br>[2] | 0.17978<br>[4] | 0.09944<br>[5] | 0.12312<br>[2] | 0.12312<br>[2] | 0.12312<br>[2] |
| $\bar{E}_{osc}\ (eV)$ | -0.20226 | -0.16628 | -0.22757 | -0.14502 | -0.07200 | -0.10359 | -0.07526 | -0.15924 | -0.10359 | -0.10260 | -0.10260 |
| $E_{mag}\ (eV)$ | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 |
| $E_T(_{Group})\ (eV)$ | -49.14112 | -33.25079 | -67.92207 | -49.80996 | -31.70737 | -33.59732 | -33.49373 | -33.24376 | -33.59732 | -33.18712 | -33.18712 |
| $E_{initial}(_{c_4\ AO/HO})\ (eV)$ | -14.53414 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 |
| $E_{initial}(_{c_5\ AO/HO})\ (eV)$ | -13.59844 | 0 | -13.59844 | -13.59844 | -13.59844 | 0 | 0 | 0 | 0 | 0 | 0 |
| $E_D(_{Group})\ (eV)$ | 7.41010 | 3.98101 | 12.49186 | 7.83016 | 3.32601 | 4.32754 | 4.29921 | 3.97398 | 4.17951 | 3.62128 | 3.91734 |

Table 15.73. The total bond energies of primary amines calculated using the functional group composition and the energies of Table 15.72 compared to the experimental values [3].

| Formula | Name | $NH_2$ Group | $C-N$ Group | $CH_3$ | $CH_2$ | $CH$ | $C-C$ (a) | $C-C$ (b) | $C-C$ (c) | $C-C$ (d) | $C-C$ (e) | $C-C$ (f) | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $CH_5N$ | Methylamine | 1 | 1 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 23.88297 | 23.857 | -0.00110 |
| $C_2H_7N$ | Ethylamine | 1 | 1 | 1 | 1 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 36.04067 | 36.062 | 0.00060 |
| $C_3H_9N$ | Propylamine | 1 | 1 | 1 | 2 | 0 | 2 | 0 | 0 | 0 | 0 | 0 | 48.19837 | 48.243 | 0.00092 |
| $C_4H_{11}N$ | Butylamine | 1 | 1 | 1 | 3 | 0 | 3 | 0 | 0 | 0 | 0 | 0 | 60.35607 | 60.415 | 0.00098 |
| $C_4H_{11}N$ | sec-Butylamine | 1 | 1 | 2 | 1 | 1 | 1 | 2 | 0 | 0 | 0 | 0 | 60.45696 | 60.547 | 0.00148 |
| $C_4H_{11}N$ | t-Butylamine | 1 | 1 | 3 | 0 | 0 | 0 | 0 | 3 | 0 | 0 | 0 | 60.78863 | 60.717 | -0.00118 |
| $C_4H_{11}N$ | Isobutylamine | 1 | 1 | 2 | 1 | 1 | 0 | 3 | 0 | 0 | 0 | 0 | 60.42863 | 60.486 | 0.00094 |

Table 15.74. The bond angle parameters of primary amines and experimental values [1]. In the calculation of $\theta_v$, the parameters from the preceding angle were used. $E_T$ is $E_T(atom-atom, msp^3.AO)$.

| Atoms of Angle | 2c' Bond 1 $(a_0)$ | 2c' Bond 2 $(a_0)$ | 2c' Terminal Atoms $(a_0)$ | $E_{Coulombic}$ or $E$ Atom 1 | Atom 1 Hybridization Designation (Table 15.3.A) | $E_{Coulombic}$ Atom 2 | Atom 2 Hybridization Designation (Table 15.3.A) | $c_2$ Atom 1 | $c_2$ Atom 2 | $C_1$ | $C_2$ | $c_1$ | $c_2'$ | $E_T$ (eV) | $\theta_v$ (°) | $\theta_1$ (°) | $\theta_2$ (°) | Cal. $\theta$ (°) | Exp. $\theta$ (°) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $\angle HNH$ | 1.91013 | 1.91013 | 3.0984 | -14.53414 | N | H | H | 0.94627 Eq. (15.134)) | 1 | 1 | 1 | 0.75 | 1.05679 | 0 | | | | 108.40 | 107.1 (methylamine) |
| $\angle HNC_a$ | 1.91013 | 2.77620 | 3.8816 | -14.53414 | N | -15.35946 | 5 | 0.91140 (Eq. (15.135)) | 0.88583 | 0.75 | 1 | 0.75 | 0.97194 | 0 | | | | 110.48 | 110.3 (methylamine) |
| Methylene $\angle HC_aH$ | 2.11106 | 2.11106 | 3.4252 | -15.75493 | 7 | H | H | 0.86359 | 1 | 1 | 1 | 0.75 | 1.15796 | 0 | | | | 108.44 | 108.0 (methylamine)<br>107 (propane) |
| $\angle C_aC_bC_c$ | | | | | | | | | | | | | | | 69.51 | | | 110.49 | 112 (propane)<br>113.8 (butane)<br>110.8 (isobutane) |
| $\angle C_aC_bH$ | | | | | | | | | | | | | | | 69.51 | | | 110.49 | 111.0 (butane)<br>111.4 (isobutane) |
| Methyl $\angle HC_aH$ | 2.09711 | 2.09711 | 3.4252 | -15.75493 | 7 | H | H | 0.86359 | 1 | 1 | 1 | 0.75 | 1.15796 | 0 | | | | 109.50 | |
| $\angle C_aC_bC_c$ | | | | | | | | | | | | | | | 70.56 | | | 109.44 | |
| $\angle C_aC_bH$ | | | | | | | | | | | | | | | 70.56 | | | 109.44 | |
| $\angle C_bC_aC_c$ iso $C_a$ | 2.91547 | 2.91547 | 4.7958 | -16.68412 $C_b$ | 26 | -16.68412 $C_c$ | 26 | 0.81549 | 0.81549 | 1 | 1 | 1 | 0.81549 | -1.85836 | | | | 110.67 | 110.8 (isobutane) |
| $\angle C_bC_aH$ iso $C_a$ | 2.91547 | 2.11323 | 4.1633 | -15.55033 $C_a$ | 5 | -14.82575 $C_b$ | 1 | 0.87495 | 0.91771 | 0.75 | 1 | 0.75 | 1.04887 | 0 | | | | 110.76 | |
| $\angle C_aC_bH$ iso $C_a$ | 2.91547 | 2.09711 | 4.1633 | -15.55033 $C_b$ | 5 | -14.82575 $C_a$ | 1 | 0.87495 | 0.91771 | 0.75 | 1 | 0.75 | 1.04887 | 0 | | | | 111.27 | 111.4 (isobutane) |
| $\angle C_bC_aC_b$ tert $C_a$ | 2.90327 | 2.90327 | 4.7958 | -16.68412 $C_b$ | 26 | -16.68412 $C_b$ | 26 | 0.81549 | 0.81549 | 1 | 1 | 1 | 0.81549 | -1.85836 | | | | 111.37 | 110.8 (isobutane) |
| $\angle C_bC_aC_d$ | | | | | | | | | | | | | | | 72.50 | | | 107.50 | |

## SECONDARY AMINES ($C_nH_{2n+2+m}N_m$, $n = 2,3,4,5...\infty$)

The secondary amines, $C_nH_{2n+2+m}N_m$, comprise an $NH$ functional group and two types of $C-N$ functional groups, one for the methyl group corresponding to the $C$ of $C-N$ and the other for general alkyl secondary amines. The alkyl portion of the secondary amine may comprise at least two terminal methyl groups ($CH_3$) at each end of the chain, and may comprise methylene ($CH_2$), and methylyne ($CH$) functional groups as well as $C$ bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($\left(CH_3\right)_2 CH$) and t-butyl ($\left(CH_3\right)_3 C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups. The branched-chain-alkane groups in secondary amines are equivalent to those in branched-chain alkanes.

The secondary amino ($NH$) functional group was solved using the procedure given in the Hydrogen Nitride ($NH$) section. Using the results of Eqs. (13.245-13.316), the secondary amino parameters in Eq. (15.61) are $n_1 = 1$, $C_1 = 0.75$, $C_2 = 0.93613$ (Eqs. (13.248-13.249)), $C_{1o} = 0.75$, and $c_1 = 0.75$. In secondary amines, the $C2sp^3$ HO of the $C-NH$-bond MO has an energy of $E\left(C,2sp^3\right) = -15.56407\ eV$ (Eqs. (14.514-14.516)); Eq. (15.29) with $s=1$ and $s=2$, Eq. (15.31), and Eqs. (15.19-15.20)) and the $N$ AO has an energy of $E\left(N\right) = -14.53414\ eV$ (Eq. (13.251)). To meet the equipotential condition of the union of the $N-H$ $H_2$-type-ellipsoidal-MO with the $C2sp^3$ HO, the hybridization factor $c_2$ of Eq. (15.61) for the $N-H$-bond MO given by Eq. (15.77) is:

$$c_2\left(H\ to\ 2°N\right) = \frac{E\left(N\right)}{E\left(C,2sp^3\right)} = \frac{-14.53414\ eV}{-15.56407\ eV} = 0.93383 \tag{15.136}$$

The $C-N$ group is solved by hybridizing the $2s$ and $2p$ AOs of the $C$ atom to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between the $C2sp^3$ HO and the $N$ AO to form a MO permits each participating orbital to decrease in radius and energy. In secondary amines, the $C2sp^3$ HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of $E\left(C,2sp^3\right) = -14.63489\ eV$ (Eq. (15.25)), and the $N$ AO has an energy of $E\left(N\right) = -14.53414\ eV$. To meet the equipotential condition of the union of the $C-N$ $H_2$-type-ellipsoidal-MO with these orbitals, the hybridization factor $c_2$ of Eq. (15.61) for the $C-N$-bond MO given by Eq. (15.135) is $c_2\left(C2sp^3HO\ to\ N\right) = 0.91140$.

As given in the Continuous-Chain Alkanes ($C_nH_{2n+2}$, $n = 3,4,5...\infty$) section, each methylene group forms two single bonds, and the energy of each $C2sp^3$ HO of each $CH_2$ group alone is given by that in ethylene, $-1.13379\ eV$ (Eq. (14.511)). In secondary amines, the $N$ of the $NH$ group also binds to two $C2sp^3$ HOs and the corresponding $E_T\left(atom-atom, msp^3.AO\right)$ of each $C-N$-bond MO in Eq. (15.61) due to the charge donation from the $C$ and $N$ atoms to the MO is $-1.13379\ eV$. It is based on the energy match between the $N$ of the $NH$ group to the two $C2sp^3$ HOs corresponding to the energy contributions to each of the two single bonds that are equivalent to those of independent methylene groups, $-1.13379\ eV$ (Eq. (14.511)), where the $N-H$ bond is also energy matched to the $C-N$ bonds. $E_T\left(atom-atom, msp^3.AO\right)$ of the $C-N$-bond MO in Eq. (15.61) due to the charge donation from the $C$ and $N$ atoms to the MO is $-1.13379\ eV$. It is based on the energy match between the $N$ of the $NH$ group to two $C2sp^3$ HOs corresponding to the energy contributions to the single bond that are equivalent to those of methyl groups, $-0.72457\ eV$ (Eq. (14.151)), where the $N-H$ bonds are also energy matched to the $C-N$ bond.

The symbols of the functional groups of branched-chain secondary amines are given in Table 15.75. The geometrical (Eqs. (15.1-15.5) and (15.51)), intercept (Eqs. (15.80-15.87)), and energy (Eqs. (15.6-15.11) and (15.17-15.65)) parameters of secondary amines are given in Tables 15.76, 15.77, and 15.78, respectively. As in the case of $NH_2$ (Eq. (13.339)), $C_{1o} = 2C_1$ rather than $C_{1o} = C_1$ in Eq. (15.61) for the $C-N$ bond. The total energy of each secondary amine given in Table 15.79 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.78 corresponding to functional-group composition of the molecule. The bond angle parameters of secondary amines determined using Eqs. (15.88-15.117) are given in Table 15.80. The color scale, translucent view of the charge-density of exemplary secondary amine, dimenthylamine, comprising the concentric shells of atoms with the outer shell bridged by one or more $H_2$-type ellipsoidal MOs or joined with one or more hydrogen MOs is shown in Figure 15.13.

Figure 15.13. (A)-(B) Color scale, translucent views of the charge-density of dimethylamine showing the orbitals of the atoms at their radii, the ellipsoidal surface of each $H$ or $H_2$-type ellipsoidal MO that transitions to the corresponding outer shell of the atom(s) participating in each bond, and the hydrogen nuclei (red, not to scale).

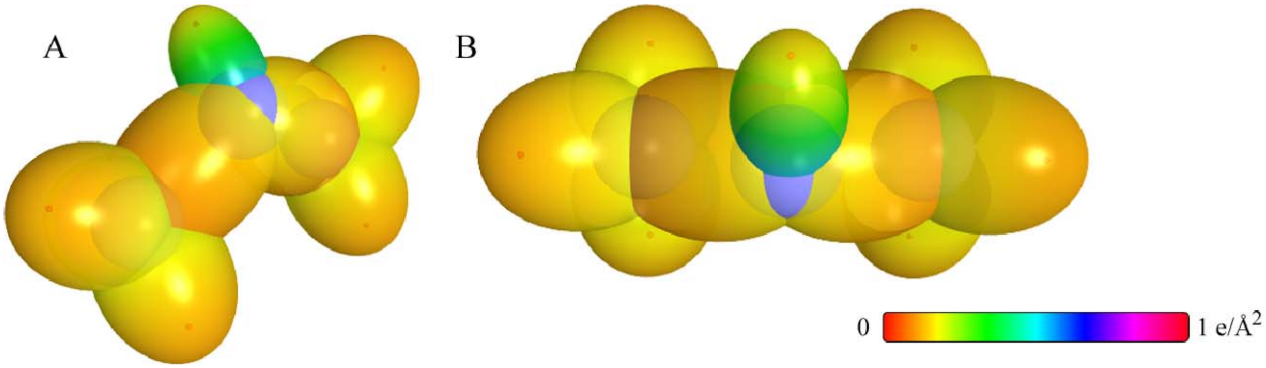


Table 15.75. The symbols of functional groups of secondary amines.

| Functional Group | Group Symbol |
|---|---|
| *NH* group | $NH$ |
| *C-N* (methyl) | $C-N$ (i) |
| *C-N* (alkyl) | $C-N$ (ii) |
| $CH_3$ group | $C-H\ (CH_3)$ |
| $CH_2$ group | $C-H\ (CH_2)$ |
| *CH* | $C-H$ |
| *CC* bond (*n-C*) | $C-C$ (a) |
| *CC* bond (*iso-C*) | $C-C$ (b) |
| *CC* bond (*tert-C*) | $C-C$ (c) |
| *CC* (*iso* to *iso-C*) | $C-C$ (d) |
| *CC* (*t* to *t-C*) | $C-C$ (e) |
| *CC* (*t* to *iso-C*) | $C-C$ (f) |

Table 15.76. The geometrical bond parameters of secondary amines and experimental values [1].

| Parameter | $NH$ Group | $C-N$ (i) Group | $C-N$ (ii) Group | $C-H\ (CH_3)$ Group | $C-H\ (CH_2)$ Group | $C-H$ Group | $C-C$ (a) Group | $C-C$ (b) Group | $C-C$ (c) Group | $C-C$ (d) Group | $C-C$ (e) Group | $C-C$ (f) Group |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $a\ (a_0)$ | 1.26224 | 1.94862 | 1.94862 | 1.64920 | 1.67122 | 1.67465 | 2.12499 | 2.12499 | 2.10725 | 2.12499 | 2.10725 | 2.10725 |
| $c'\ (a_0)$ | 0.94811 | 1.39593 | 1.39593 | 1.04856 | 1.05553 | 1.05661 | 1.45744 | 1.45744 | 1.45164 | 1.45744 | 1.45164 | 1.45164 |
| Bond Length $2c'\ (\mathring{A})$ | 1.00343 | 1.47739 | 1.47739 | 1.10974 | 1.11713 | 1.11827 | 1.54280 | 1.54280 | 1.53635 | 1.54280 | 1.53635 | 1.53635 |
| Exp. Bond Length $(\mathring{A})$ | 1.00<br>(dimethylamine) | 1.455<br>(dimethylamine) |  | 1.107<br>($C-H$ propane)<br>1.117<br>($C-H$ butane) | 1.107<br>($C-H$ propane)<br>1.117<br>($C-H$ butane) | 1.122<br>(isobutane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) |
| $b,c\ (a_0)$ | 0.83327 | 1.35960 | 1.35960 | 1.27295 | 1.29569 | 1.29924 | 1.54616 | 1.54616 | 1.52750 | 1.54616 | 1.52750 | 1.52750 |
| $e$ | 0.75113 | 0.71637 | 0.71637 | 0.63580 | 0.63159 | 0.63095 | 0.68600 | 0.68600 | 0.68888 | 0.68600 | 0.68888 | 0.68888 |

Table 15.77. The MO to HO intercept geometrical bond parameters of secondary amines. $R$, $R'$, $R''$ are $H$ or alkyl groups. $E_T$ is $E_T(atom-atom, msp^3.AO)$.

| Bond | Atom | $E_T$ (eV) Bond 1 | $E_T$ (eV) Bond 2 | $E_T$ (eV) Bond 3 | $E_T$ (eV) Bond 4 | Final Total Energy $C2sp^3$ (eV) | $r_{initial}$ $(a_0)$ | $r_{final}$ $(a_0)$ | $E_{Coulomb}$ (eV) Final | $E(C2sp^3)$ (eV) Final | $\theta'$ $(°)$ | $\theta_1$ $(°)$ | $\theta_2$ $(°)$ | $d_1$ $(a_0)$ | $d_2$ $(a_0)$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $H_3C_aN(C_bH_3)-H$ | $N$ | -0.56690 | -0.56690 | 0 | 0 |  | 0.93084 | 0.85252 | -15.95954 |  | 118.18 | 61.82 | 64.40 | 0.54546 | 0.40264 |
| $-H_2C_aN(R_{alkyl})-H$ | $N$ | -0.56690 | -0.56690 | 0 | 0 |  | 0.93084 | 0.85252 | -15.95954 |  | 118.18 | 61.82 | 64.40 | 0.54546 | 0.40264 |
| $H_3C_a-NH-C_aH_3$ | $C_a$ | -0.56690 | 0 | 0 | 0 | -152.18259 | 0.91771 | 0.88392 | -15.39265 | -15.20178 | 84.14 | 95.86 | 40.30 | 1.48625 | 0.09032 |
| $H_3C_a-NH-C_aH_3$ | $N$ | -0.56690 | -0.56690 | 0 | 0 |  | 0.93084 | 0.85252 | -15.95954 |  | 80.95 | 99.05 | 38.26 | 1.53008 | 0.13415 |
| $-H_2C_a-NH-C_bR$ | $C_a$ | -0.56690 | -0.92918 | 0 | 0 | -153.11177 | 0.91771 | 0.83360 | -16.32183 | -16.13097 | 78.89 | 101.11 | 36.99 | 1.55650 | 0.16057 |
| $-H_2C_a-NH-C_bH_2-$ | $N$ | -0.56690 | -0.56690 | 0 | 0 |  | 0.93084 | 0.85252 | -15.95954 |  | 80.95 | 99.05 | 38.26 | 1.53008 | 0.13415 |
| $C-H\ (CH_3)$ | $C$ | -0.92918 | 0 | 0 | 0 | -152.54487 | 0.91771 | 0.86359 | -15.75493 | -15.56407 | 77.49 | 102.51 | 41.48 | 1.23564 | 0.18708 |
| $C-H\ (CH_2)$ | $C$ | -0.92918 | -0.92918 | 0 | 0 | -153.47406 | 0.91771 | 0.81549 | -16.68412 | -16.49325 | 68.47 | 111.53 | 35.84 | 1.35486 | 0.29933 |
| $C-H\ (CH)$ | $C$ | -0.92918 | -0.92918 | -0.92918 | 0 | -154.40324 | 0.91771 | 0.77247 | -17.61330 | -17.42244 | 61.10 | 118.90 | 31.37 | 1.42988 | 0.37326 |
| $H_3C_aC_bH_2CH_2-$<br>($C-C$ (a)) | $C_a$ | -0.92918 | 0 | 0 | 0 | -152.54487 | 0.91771 | 0.86359 | -15.75493 | -15.56407 | 63.82 | 116.18 | 30.08 | 1.83879 | 0.38106 |
| $H_3C_aC_bH_2CH_2-$<br>($C-C$ (a)) | $C_b$ | -0.92918 | -0.92918 | 0 | 0 | -153.47406 | 0.91771 | 0.81549 | -16.68412 | -16.49325 | 56.41 | 123.59 | 26.06 | 1.90890 | 0.45117 |
| $R-H_2C_aC_b\left(H_2C_c-R'\right)HCH_2-$<br>($C-C$ (b)) | $C_b$ | -0.92918 | -0.92918 | -0.92918 | 0 | -154.40324 | 0.91771 | 0.77247 | -17.61330 | -17.42244 | 48.30 | 131.70 | 21.90 | 1.97162 | 0.51388 |
| $R-H_2C_a\left(R'-H_2C_d\right)C_b\left(R''-H_2C_c\right)CH_2-$<br>($C-C$ (c)) | $C_b$ | -0.92918 | -0.72457 | -0.72457 | -0.72457 | -154.71860 | 0.91771 | 0.75889 | -17.92866 | -17.73779 | 48.21 | 131.79 | 21.74 | 1.95734 | 0.50570 |
| $isoC_aC_b\left(H_2C_c-R'\right)HCH_2-$<br>($C-C$ (d)) | $C_b$ | -0.92918 | -0.92918 | -0.92918 | 0 | -154.40324 | 0.91771 | 0.77247 | -17.61330 | -17.42244 | 48.30 | 131.70 | 21.90 | 1.97162 | 0.51388 |
| $tertC_a\left(R'-H_2C_d\right)C_b\left(R''-H_2C_c\right)CH_2-$<br>($C-C$ (e)) | $C_b$ | -0.72457 | -0.72457 | -0.72457 | -0.72457 | -154.51399 | 0.91771 | 0.76765 | -17.92866 | -17.73779 | 50.04 | 129.96 | 22.66 | 1.94462 | 0.49298 |
| $tertC_aC_b\left(H_2C_c-R'\right)HCH_2-$<br>($C-C$ (f)) | $C_b$ | -0.72457 | -0.92918 | -0.92918 | 0 | -154.19863 | 0.91771 | 0.78155 | -17.40869 | -17.21783 | 52.78 | 127.22 | 24.04 | 1.92443 | 0.47279 |
| $isoC_a\left(R'-H_2C_d\right)C_b\left(R''-H_2C_c\right)CH_2-$<br>($C-C$ (f)) | $C_b$ | -0.72457 | -0.72457 | -0.72457 | -0.72457 | -154.51399 | 0.91771 | 0.76765 | -17.92866 | -17.73779 | 50.04 | 129.96 | 22.66 | 1.94462 | 0.49298 |

Table 15.78. The energy parameters ($eV$) of functional groups of secondary amines.

| Parameters | $NH$ Group | $C-N$ (i) Group | $C-N$ (ii) Group | $CH_3$ Group | $CH_2$ Group | $C-H$ Group | $C-C$ (a) Group | $C-C$ (b) Group | $C-C$ (c) Group | $C-C$ (d) Group | $C-C$ (e) Group | $C-C$ (f) Group |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $n_1$ | 1 | 1 | 1 | 3 | 2 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $n_2$ | 0 | 0 | 0 | 2 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $n_3$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $C_1$ | 0.75 | 0.5 | 0.5 | 0.75 | 0.75 | 0.75 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| $C_2$ | 0.93613 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $c_1$ | 0.75 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $c_2$ | 0.93383 | 0.91140 | 0.91140 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 |
| $c_3$ | 1 | 0 | 0 | 0 | 1 | 1 | 0 | 0 | 0 | 1 | 1 | 0 |
| $c_4$ | 1 | 2 | 2 | 1 | 1 | 1 | 2 | 2 | 2 | 2 | 2 | 2 |
| $c_5$ | 1 | 0 | 0 | 3 | 2 | 1 | 0 | 0 | 0 | 0 | 0 | 0 |
| $C_{1o}$ | 0.75 | 1 | 1 | 0.75 | 0.75 | 0.75 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| $C_{2o}$ | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $V_e\ (eV)$ | -39.21967 | -31.98456 | -31.98456 | -107.32728 | -70.41425 | -35.12015 | -28.79214 | -28.79214 | -29.10112 | -28.79214 | -29.10112 | -29.10112 |
| $V_p\ (eV)$ | 14.35050 | 9.74677 | 9.74677 | 38.92728 | 25.78002 | 12.87680 | 9.33352 | 9.33352 | 9.37273 | 9.33352 | 9.37273 | 9.37273 |
| $T\ (eV)$ | 15.53581 | 8.20698 | 8.20698 | 32.53914 | 21.06675 | 10.48582 | 6.77464 | 6.77464 | 6.90500 | 6.77464 | 6.90500 | 6.90500 |
| $V_m\ (eV)$ | -7.76790 | -4.10349 | -4.10349 | -16.26957 | -10.53337 | -5.24291 | -3.38732 | -3.38732 | -3.45250 | -3.38732 | -3.45250 | -3.45250 |
| $E(_{AO/HO})\ (eV)$ | -14.53414 | -14.63489 | -14.63489 | -15.56407 | -15.56407 | -14.63489 | -15.56407 | -15.56407 | -15.35946 | -15.56407 | -15.35946 | -15.35946 |
| $\Delta E_{H_2MO}(_{AO/HO})\ (eV)$ | 0 | -1.13379 | -1.13379 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $E_T(_{AO/HO})\ (eV)$ | -14.53414 | -13.50110 | -13.50110 | -15.56407 | -15.56407 | -14.63489 | -15.56407 | -15.56407 | -15.35946 | -15.56407 | -15.35946 | -15.35946 |
| $E_T(_{H_2MO})\ (eV)$ | -31.63541 | -31.63540 | -31.63540 | -67.69451 | -49.66493 | -31.63533 | -31.63537 | -31.63537 | -31.63535 | -31.63537 | -31.63535 | -31.63535 |
| $E_T\left(atom-atom,msp^3.AO\right)(eV)$ | 0 | -1.13379 | -1.13379 | 0 | 0 | 0 | -1.85836 | -1.85836 | -1.44915 | -1.85836 | -1.44915 | -1.44915 |
| $E_T(_{MO})\ (eV)$ | -31.63537 | -32.76916 | -32.76916 | -67.69450 | -49.66493 | -31.63537 | -33.49373 | -33.49373 | -33.08452 | -33.49373 | -33.08452 | -33.08452 |
| $\omega\ \left(10^{15}\ rad/s\right)$ | 47.0696 | 15.1983 | 26.0778 | 24.9286 | 24.2751 | 24.1759 | 9.43699 | 9.43699 | 15.4846 | 9.43699 | 9.55643 | 9.55643 |
| $E_K\ (eV)$ | 30.98202 | 10.00377 | 17.16484 | 16.40846 | 15.97831 | 15.91299 | 6.21159 | 6.21159 | 10.19220 | 6.21159 | 6.29021 | 6.29021 |
| $\bar{E}_D\ (eV)$ | -0.34836 | -0.20505 | -0.26859 | -0.25352 | -0.25017 | -0.24966 | -0.16515 | -0.16515 | -0.20896 | -0.16515 | -0.16416 | -0.16416 |
| $\bar{E}_{Kvib}\ (eV)$ | 0.40696<br>[24] | 0.12944<br>[23] | 0.11159<br>[25] | 0.35532<br>(Eq. (13.458)) | 0.35532<br>(Eq. (13.458)) | 0.35532<br>(Eq. (13.458)) | 0.12312<br>[2] | 0.17978<br>[4] | 0.09944<br>[5] | 0.12312<br>[2] | 0.12312<br>[2] | 0.12312<br>[2] |
| $\bar{E}_{osc}\ (eV)$ | -0.14488 | -0.14033 | -0.21280 | -0.22757 | -0.14502 | -0.07200 | -0.10359 | -0.07526 | -0.15924 | -0.10359 | -0.10260 | -0.10260 |
| $E_{mag}\ (eV)$ | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 |
| $E_T(_{Group})\ (eV)$ | -31.78025 | -32.90949 | -32.98196 | -67.92207 | -49.80996 | -31.70737 | -33.59732 | -33.49373 | -33.24376 | -33.59732 | -33.18712 | -33.18712 |
| $E_{initial}(_{c_4\ AO/HO})\ (eV)$ | -14.53414 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 |
| $E_{initial}(_{c_5\ AO/HO})\ (eV)$ | -13.59844 | 0 | 0 | -13.59844 | -13.59844 | -13.59844 | 0 | 0 | 0 | 0 | 0 | 0 |
| $E_D(_{Group})\ (eV)$ | 3.50582 | 3.63971 | 3.71218 | 12.49186 | 7.83016 | 3.32601 | 4.32754 | 4.29921 | 3.97398 | 4.17951 | 3.62128 | 3.91734 |

Table 15.79. The total bond energies of secondary amines calculated using the functional group composition and the energies of Table 15.78 compared to the experimental values [3].

| Formula | Name | $NH$ Group | $C-N$ (i) Group | $C-N$ (ii) Group | $CH_3$ | $CH_2$ | $CH$ | $C-C$ (a) | $C-C$ (b) | $C-C$ (c) | $C-C$ (d) | $C-C$ (e) | $C-C$ (f) | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $C_2H_7N$ | Dimethylamine | 1 | 2 | 0 | 2 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 35.76895 | 35.765 | -0.00012 |
| $C_4H_{11}N$ | Diethylamine | 1 | 0 | 2 | 2 | 2 | 0 | 2 | 0 | 0 | 0 | 0 | 0 | 60.22930 | 60.211 | -0.00030 |
| $C_6H_{15}N$ | Dipropylamine | 1 | 0 | 2 | 2 | 4 | 0 | 4 | 0 | 0 | 0 | 0 | 0 | 84.54470 | 84.558 | 0.00016 |
| $C_6H_{15}N$ | Diisopropylamine | 1 | 0 | 2 | 4 | 0 | 2 | 0 | 4 | 0 | 0 | 0 | 0 | 84.74648 | 84.846 | 0.00117 |
| $C_8H_{19}N$ | Dibutylamine | 1 | 0 | 2 | 2 | 6 | 0 | 6 | 0 | 0 | 0 | 0 | 0 | 108.86010 | 108.872 | 0.00011 |
| $C_8H_{19}N$ | Diisobutylamine | 1 | 0 | 2 | 4 | 2 | 2 | 0 | 6 | 0 | 0 | 0 | 0 | 109.00522 | 109.106 | 0.00092 |

Table 15.80. The bond angle parameters of secondary amines and experimental values [1]. In the calculation of $\theta_v$, the parameters from the preceding angle were used. $E_T$ is $E_T(atom - atom, msp^3.AO)$.

| Atoms of Angle | $2c'$ Bond 1 ($a_0$) | $2c'$ Bond 2 ($a_0$) | $2c'$ Terminal Atoms ($a_0$) | $E_{Coulombic}$ or $E$ Atom 1 | Atom 1 Hybridization Designation (Table 15.3.A) | $E_{Coulombic}$ Atom 2 | Atom 2 Hybridization Designation (Table 15.3.A) | $c_2$ Atom 1 | $c_2$ Atom 2 | $C_1$ | $C_2$ | $c_1$ | $c_2'$ | $E_T$ (eV) | $\theta_v$ (°) | $\theta_1$ (°) | $\theta_2$ (°) | Cal. $\theta$ (°) | Exp. $\theta$ (°) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $\angle HCN$<br>($C-N$ (i) & (ii)) | 2.09711 | 2.79186 | 4.0661 | -14.82575 | 1 | -14.53414 | N | 0.91771 | 0.93383 (Eq. (15.136)) | 0.75 | 1 | 0.75 | 1.01756 | 0 | | | | 111.76 | 112 (dimethylamine) |
| $\angle HNC_a$<br>($C-N$ (i) & (ii)) | 1.89621 | 2.79186 | 3.8123 | -14.53414 | N | -15.56407 (Eq. (15.136)) | 7 | 0.91140 (Eq. (15.135)) | 0.87418 | 0.75 | 1 | 0.75 | 0.95917 | 0 | | | | 107.27 | 107 (dimethylamine) |
| $\angle CNC$<br>($C-N$ (i) & (ii)) | 2.79186 | 2.79186 | 4.6260 | -17.04641 | 33 | -17.04641 | 33 | 0.79816 | 0.79816 | 1 | 1 | 1 | 0.79816 | -1.85836 | | | | 111.89 | 111.8 (dimethylamine) |
| Methylene<br>$\angle HC_aH$ | 2.11106 | 2.11106 | 3.4252 | -15.75493 | 7 | H | H | 0.86359 | 1 | 1 | 1 | 0.75 | 1.15796 | 0 | | | | 108.44 | 107 (dimethylamine)<br>107 (propane) |
| $\angle C_aC_bC_c$ | | | | | | | | | | | | | | | 69.51 | | | 110.49 | 112 (propane)<br>113.8 (butane)<br>110.8 (isobutane) |
| $\angle C_aC_bH$ | | | | | | | | | | | | | | | 69.51 | | | 110.49 | 111.0 (butane)<br>111.4 (isobutane) |
| Methyl<br>$\angle HC_aH$ | 2.09711 | 2.09711 | 3.4252 | -15.75493 | 7 | H | H | 0.86359 | 1 | 1 | 1 | 0.75 | 1.15796 | 0 | | | | 109.50 | |
| $\angle C_aC_bC_c$ | | | | | | | | | | | | | | | 70.56 | | | 109.44 | |
| $\angle C_aC_bH$ | | | | | | | | | | | | | | | 70.56 | | | 109.44 | |
| $\angle C_bC_aC_c$<br>iso $C_a$ | 2.91547 | 2.91547 | 4.7958 | -16.68412 $C_b$ | 26 | -16.68412 $C_c$ | 26 | 0.81549 | 0.81549 | 1 | 1 | 1 | 0.81549 | -1.85836 | | | | 110.67 | 110.8 (isobutane) |
| $\angle C_bC_aH$<br>iso $C_a$ | 2.91547 | 2.11323 | 4.1633 | -15.55033 $C_a$ | 5 | -14.82575 $C_b$ | 1 | 0.87495 | 0.91771 | 0.75 | 1 | 0.75 | 1.04887 | 0 | | | | 110.76 | |
| $\angle C_aC_bH$<br>iso $C_a$ | 2.91547 | 2.09711 | 4.1633 | -15.55033 $C_b$ | 5 | -14.82575 $C_a$ | 1 | 0.87495 | 0.91771 | 0.75 | 1 | 0.75 | 1.04887 | 0 | | | | 111.27 | 111.4 (isobutane) |
| $\angle C_bC_aC_b$<br>tert $C_a$ | 2.90327 | 2.90327 | 4.7958 | -16.68412 $C_b$ | 26 | -16.68412 $C_b$ | 26 | 0.81549 | 0.81549 | 1 | 1 | 1 | 0.81549 | -1.85836 | | | | 111.37 | 110.8 (isobutane) |
| $\angle C_bC_aC_d$ | | | | | | | | | | | | | | | 72.50 | | | 107.50 | |

## TERTIARY AMINES ($C_nH_{2n+3}N,\ n=3,4,5...\infty$)

The tertiary amines, $C_nH_{2n+3}N$, have three $C-N$ bonds to methyl or alkyl groups wherein $C-N$ comprises a functional group. The alkyl portion of the tertiary amine may comprise at least two terminal methyl groups ($CH_3$) at each end of the chain, and may comprise methylene ($CH_2$), and methylyne ($CH$) functional groups as well as $C$ bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($(CH_3)_2CH$) and t-butyl ($(CH_3)_3C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups. The branched-chain-alkane groups in tertiary amines are equivalent to those in branched-chain alkanes.

The $C-N$ group is solved by hybridizing the $2s$ and $2p$ AOs of the $C$ atom to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between the $C2sp^3$ HO and the $N$ AO to form a MO permits each participating orbital to decrease in radius and energy. In tertiary amines, the $C2sp^3$ HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of $E\left(C,2sp^3\right)=-14.63489\ eV$ (Eq. (15.25)), and the $N$ AO has an energy of $E\left(N\right)=-14.53414\ eV$. To meet the equipotential condition of the union of the $C-N$ $H_2$-type-ellipsoidal-MO with these orbitals, the hybridization factor $c_2$ of Eq. (15.61) for the $C-N$-bond MO given by Eq. (15.135) is $c_2\left(C2sp^3HO\ to\ \mathrm{N}\right)=0.91140$.

As given in the Continuous-Chain Alkanes ($C_nH_{2n+2},\ n=3,4,5...\infty$) section, the energy of each $C2sp^3$ HO must be a linear combination of that of the $CH_3$ and $CH_2$ groups that serve as basis elements. Each $CH_3$ forms one $C-C$ bond, and each $CH_2$ group forms two. Thus, the energy of each $C2sp^3$ HO of each $CH_3$ and $CH_2$ group alone is given by that in ethane, $-0.72457\ eV$ (Eq. (14.151)), and ethylene, $-1.13379\ eV$ (Eq. (14.511)), respectively. In order to match the energy of the component HOs and MOs for the entire molecule, the energy $E_{T_{alkane}}\left(C-C,2sp^3\right)$ given as a linear combination of these basis elements is $-0.92918\ eV$ (Eq. (14.513)). In tertiary amines, the $N$ binds to three $C2sp^3$ HOs and the corresponding $E_T\left(atom-atom,msp^3.AO\right)$ of each $C-N$-bond MO in Eq. (15.61) due to the charge donation from the $C$ and $N$ atoms to the MO is $-0.92918\ eV$. It comprises a linear combination of the energy for a primary amine, $-0.72457\ eV$ and a secondary amine, $-1.13379\ eV$.

The symbols of the functional groups of branched-chain tertiary amines are given in Table 15.81. The geometrical (Eqs. (15.1-15.5) and (15.51)), intercept (Eqs. (15.80-15.87)), and energy (Eqs. (15.6-15.11) and (15.17-15.65)) parameters of tertiary amines are given in Tables 15.82, 15.83, and 15.84, respectively. The total energy of each tertiary amine given in Table 15.85 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.84 corresponding to functional-group composition of the molecule. The bond angle parameters of tertiary amines determined using Eqs. (15.88-15.117) are given in Table 15.86. The color scale, translucent view of the charge-density of exemplary tertiary amine, trimethylamine, comprising the concentric shells of atoms with the outer shell bridged by one or more $H_2$-type ellipsoidal MOs or joined with one or more hydrogen MOs is shown in Figure 15.14.

Figure 15.14. Color scale, translucent view of the charge-density of trimethylamine showing the orbitals of the atoms at their radii, the ellipsoidal surface of each $H$ or $H_2$-type ellipsoidal MO that transitions to the corresponding outer shell of the atom(s) participating in each bond, and the hydrogen nuclei (red, not to scale). (A) Top view. (B) Side view.

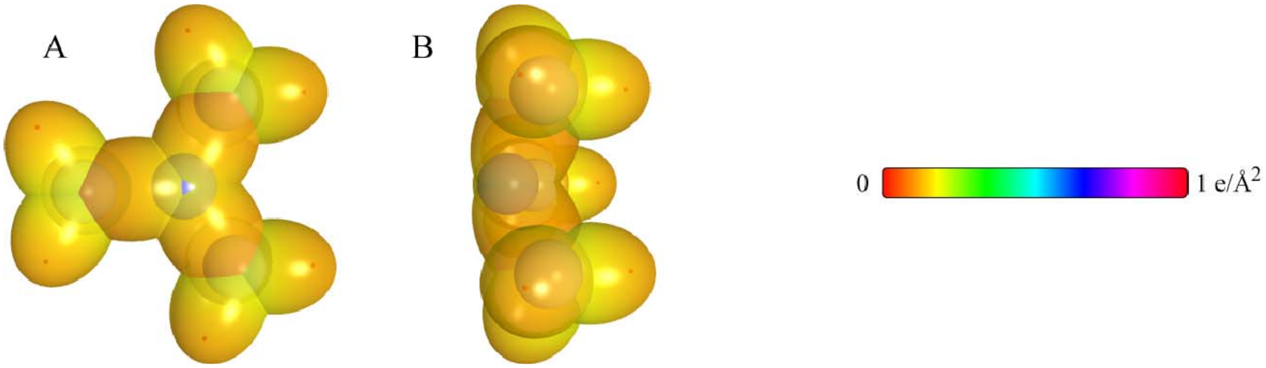


Table 15.81. The symbols of functional groups of tertiary amines.

| Functional Group | Group Symbol |
|---|---|
| *C-N* | $C-N$ |
| $CH_3$ group | $C-H\ (CH_3)$ |
| $CH_2$ group | $C-H\ (CH_2)$ |
| *CH* | $C-H$ |
| *CC* bond (*n-C*) | $C-C$ (a) |
| *CC* bond (*iso-C*) | $C-C$ (b) |
| *CC* bond (*tert-C*) | $C-C$ (c) |
| *CC* (*iso* to *iso-C*) | $C-C$ (d) |
| *CC* (*t* to *t-C*) | $C-C$ (e) |
| *CC* (*t* to *iso-C*) | $C-C$ (f) |

Table 15.82. The geometrical bond parameters of tertiary amines and experimental values [1].

| Parameter | $C-N$ Group | $C-H\ (CH_3)$ Group | $C-H\ (CH_2)$ Group | $C-H$ Group | $C-C$ (a) Group | $C-C$ (b) Group | $C-C$ (c) Group | $C-C$ (d) Group | $C-C$ (e) Group | $C-C$ (f) Group |
|---|---|---|---|---|---|---|---|---|---|---|
| $a\ (a_0)$ | 1.96313 | 1.64920 | 1.67122 | 1.67465 | 2.12499 | 2.12499 | 2.10725 | 2.12499 | 2.10725 | 2.10725 |
| $c'\ (a_0)$ | 1.40112 | 1.04856 | 1.05553 | 1.05661 | 1.45744 | 1.45744 | 1.45164 | 1.45744 | 1.45164 | 1.45164 |
| Bond Length $2c'$ ($\AA$) | 1.48288 | 1.10974 | 1.11713 | 1.11827 | 1.54280 | 1.54280 | 1.53635 | 1.54280 | 1.53635 | 1.53635 |
| Exp. Bond Length ($\AA$) | 1.458 (trimethylamine) | 1.107 ($C-H$ propane)<br>1.117 ($C-H$ butane) | 1.107 ($C-H$ propane)<br>1.117 ($C-H$ butane) | 1.122 (isobutane) | 1.532 (propane)<br>1.531 (butane) | 1.532 (propane)<br>1.531 (butane) | 1.532 (propane)<br>1.531 (butane) | 1.532 (propane)<br>1.531 (butane) | 1.532 (propane)<br>1.531 (butane) | 1.532 (propane)<br>1.531 (butane) |
| $b,c\ (a_0)$ | 1.37505 | 1.27295 | 1.29569 | 1.29924 | 1.54616 | 1.54616 | 1.52750 | 1.54616 | 1.52750 | 1.52750 |
| $e$ | 0.71372 | 0.63580 | 0.63159 | 0.63095 | 0.68600 | 0.68600 | 0.68888 | 0.68600 | 0.68888 | 0.68888 |

Table 15.83. The MO to HO intercept geometrical bond parameters of tertiary amines. $R$, $R'$, $R''$ are $H$ or alkyl groups. $E_T$ is $E_T(atom-atom, msp^3.AO)$.

| Bond | Atom | $E_T$ (eV) Bond 1 | $E_T$ (eV) Bond 2 | $E_T$ (eV) Bond 3 | $E_T$ (eV) Bond 4 | Final Total Energy $C2sp^3$ (eV) | $r_{initial}$ $(a_0)$ | $r_{final}$ $(a_0)$ | $E_{Coulomb}$ (eV) Final | $E(C2sp^3)$ (eV) Final | $\theta'$ (°) | $\theta_1$ (°) | $\theta_2$ (°) | $d_1$ $(a_0)$ | $d_2$ $(a_0)$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $N-(C_aH_3)_3$ | $C_a$ | -0.46459 |  | 0 | 0 | -152.08028 | 0.91771 | 0.88983 | -15.29034 | -15.09948 | 83.37 | 96.63 | 40.00 | 1.50383 | 0.10271 |
| $N-(C_aH_3)_3$ | $N$ | -0.46459 | -0.46459 | -0.46459 | 0 |  | 0.93084 | 0.83885 | -16.21953 |  | 78.02 | 101.98 | 36.64 | 1.57525 | 0.17413 |
| $N-(C_aH_2-)_3$ | $C_a$ | -0.46459 | -0.92918 | 0 | 0 | -153.00946 | 0.91771 | 0.83885 | -16.21953 | -16.02866 | 78.02 | 101.98 | 36.64 | 1.57525 | 0.17413 |
| $N-(C_aH_2-)_3$ | $N$ | -0.46459 | -0.46459 | -0.46459 | 0 |  | 0.93084 | 0.83885 | -16.21953 |  | 78.02 | 101.98 | 36.64 | 1.57525 | 0.17413 |
| $C-H\ (CH_3)$ | $C$ | -0.92918 | 0 | 0 | 0 | -152.54487 | 0.91771 | 0.86359 | -15.75493 | -15.56407 | 77.49 | 102.51 | 41.48 | 1.23564 | 0.18708 |
| $C-H\ (CH_2)$ | $C$ | -0.92918 | -0.92918 | 0 | 0 | -153.47406 | 0.91771 | 0.81549 | -16.68412 | -16.49325 | 68.47 | 111.53 | 35.84 | 1.35486 | 0.29933 |
| $C-H\ (CH)$ | $C$ | -0.92918 | -0.92918 | -0.92918 | 0 | -154.40324 | 0.91771 | 0.77247 | -17.61330 | -17.42244 | 61.10 | 118.90 | 31.37 | 1.42988 | 0.37326 |
| $H_3C_aC_bH_2CH_2-$ ($C-C$ (a)) | $C_a$ | -0.92918 | 0 | 0 | 0 | -152.54487 | 0.91771 | 0.86359 | -15.75493 | -15.56407 | 63.82 | 116.18 | 30.08 | 1.83879 | 0.38106 |
| $H_3C_aC_bH_2CH_2-$ ($C-C$ (a)) | $C_b$ | -0.92918 | -0.92918 | 0 | 0 | -153.47406 | 0.91771 | 0.81549 | -16.68412 | -16.49325 | 56.41 | 123.59 | 26.06 | 1.90890 | 0.45117 |
| $R-H_2C_aC_b(H_2C_c-R')HCH_2-$ ($C-C$ (b)) | $C_b$ | -0.92918 | -0.92918 | -0.92918 | 0 | -154.40324 | 0.91771 | 0.77247 | -17.61330 | -17.42244 | 48.30 | 131.70 | 21.90 | 1.97162 | 0.51388 |
| $R-H_2C_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ ($C-C$ (c)) | $C_b$ | -0.92918 | -0.72457 | -0.72457 | -0.72457 | -154.71860 | 0.91771 | 0.75889 | -17.92866 | -17.73779 | 48.21 | 131.79 | 21.74 | 1.95734 | 0.50570 |
| $isoC_aC_b(H_2C_c-R')HCH_2-$ ($C-C$ (d)) | $C_b$ | -0.92918 | -0.92918 | -0.92918 | 0 | -154.40324 | 0.91771 | 0.77247 | -17.61330 | -17.42244 | 48.30 | 131.70 | 21.90 | 1.97162 | 0.51388 |
| $tertC_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ ($C-C$ (e)) | $C_b$ | -0.72457 | -0.72457 | -0.72457 | -0.72457 | -154.51399 | 0.91771 | 0.76765 | -17.92866 | -17.73779 | 50.04 | 129.96 | 22.66 | 1.94462 | 0.49298 |
| $tertC_aC_b(H_2C_c-R')HCH_2-$ ($C-C$ (f)) | $C_b$ | -0.72457 | -0.92918 | -0.92918 | 0 | -154.19863 | 0.91771 | 0.78155 | -17.40869 | -17.21783 | 52.78 | 127.22 | 24.04 | 1.92443 | 0.47279 |
| $isoC_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ ($C-C$ (f)) | $C_b$ | -0.72457 | -0.72457 | -0.72457 | -0.72457 | -154.51399 | 0.91771 | 0.76765 | -17.92866 | -17.73779 | 50.04 | 129.96 | 22.66 | 1.94462 | 0.49298 |

Table 15.84. The energy parameters ($eV$) of functional groups of tertiary amines.

| Parameters | $C-N$ Group | $CH_3$ Group | $CH_2$ Group | $C-H$ Group | $C-C$ (a) Group | $C-C$ (b) Group | $C-C$ (c) Group | $C-C$ (d) Group | $C-C$ (e) Group | $C-C$ (f) Group |
|---|---|---|---|---|---|---|---|---|---|---|
| $n_1$ | 1 | 3 | 2 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $n_2$ | 0 | 2 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $n_3$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $C_1$ | 0.5 | 0.75 | 0.75 | 0.75 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| $C_2$ | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $c_1$ | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $c_2$ | 0.91140 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 |
| $c_3$ | 0 | 0 | 1 | 1 | 0 | 0 | 0 | 1 | 1 | 0 |
| $c_4$ | 2 | 1 | 1 | 1 | 2 | 2 | 2 | 2 | 2 | 2 |
| $c_5$ | 0 | 3 | 2 | 1 | 0 | 0 | 0 | 0 | 0 | 0 |
| $C_{1o}$ | 0.5 | 0.75 | 0.75 | 0.75 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| $C_{2o}$ | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $V_e\ (eV)$ | -31.67393 | -107.32728 | -70.41425 | -35.12015 | -28.79214 | -28.79214 | -29.10112 | -28.79214 | -29.10112 | -29.10112 |
| $V_p\ (eV)$ | 9.71067 | 38.92728 | 25.78002 | 12.87680 | 9.33352 | 9.33352 | 9.37273 | 9.33352 | 9.37273 | 9.37273 |
| $T\ (eV)$ | 8.06719 | 32.53914 | 21.06675 | 10.48582 | 6.77464 | 6.77464 | 6.90500 | 6.77464 | 6.90500 | 6.90500 |
| $V_m\ (eV)$ | -4.03359 | -16.26957 | -10.53337 | -5.24291 | -3.38732 | -3.38732 | -3.45250 | -3.38732 | -3.45250 | -3.45250 |
| $E(_{AO/HO})\ (eV)$ | -14.63489 | -15.56407 | -15.56407 | -14.63489 | -15.56407 | -15.56407 | -15.35946 | -15.56407 | -15.35946 | -15.35946 |
| $\Delta E_{H_2MO}(_{AO/HO})\ (eV)$ | -0.92918 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $E_T(_{AO/HO})\ (eV)$ | -13.70571 | -15.56407 | -15.56407 | -14.63489 | -15.56407 | -15.56407 | -15.35946 | -15.56407 | -15.35946 | -15.35946 |
| $E_T(_{H_2MO})\ (eV)$ | -31.63537 | -67.69451 | -49.66493 | -31.63533 | -31.63537 | -31.63537 | -31.63535 | -31.63537 | -31.63535 | -31.63535 |
| $E_T\left(atom-atom,msp^3.AO\right)(eV)$ | -0.92918 | 0 | 0 | 0 | -1.85836 | -1.85836 | -1.44915 | -1.85836 | -1.44915 | -1.44915 |
| $E_T(_{MO})\ (eV)$ | -32.56455 | -67.69450 | -49.66493 | -31.63537 | -33.49373 | -33.49373 | -33.08452 | -33.49373 | -33.08452 | -33.08452 |
| $\omega\ \left(10^{15}\ rad/s\right)$ | 18.1298 | 24.9286 | 24.2751 | 24.1759 | 9.43699 | 9.43699 | 15.4846 | 9.43699 | 9.55643 | 9.55643 |
| $E_K\ (eV)$ | 11.93333 | 16.40846 | 15.97831 | 15.91299 | 6.21159 | 6.21159 | 10.19220 | 6.21159 | 6.29021 | 6.29021 |
| $\bar{E}_D\ (eV)$ | -0.22255 | -0.25352 | -0.25017 | -0.24966 | -0.16515 | -0.16515 | -0.20896 | -0.16515 | -0.16416 | -0.16416 |
| $\bar{E}_{Kvib}\ (eV)$ | 0.12944<br>[23] | 0.35532<br>(Eq. (13.458)) | 0.35532<br>(Eq. (13.458)) | 0.35532<br>(Eq. (13.458)) | 0.12312<br>[2] | 0.17978<br>[4] | 0.09944<br>[5] | 0.12312<br>[2] | 0.12312<br>[2] | 0.12312<br>[2] |
| $\bar{E}_{osc}\ (eV)$ | -0.15783 | -0.22757 | -0.14502 | -0.07200 | -0.10359 | -0.07526 | -0.15924 | -0.10359 | -0.10260 | -0.10260 |
| $E_{mag}\ (eV)$ | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 |
| $E_T(_{Group})\ (eV)$ | -32.72238 | -67.92207 | -49.80996 | -31.70737 | -33.59732 | -33.49373 | -33.24376 | -33.59732 | -33.18712 | -33.18712 |
| $E_{initial}(_{c_4\ AO/HO})\ (eV)$ | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 |
| $E_{initial}(_{c_5\ AO/HO})\ (eV)$ | 0 | -13.59844 | -13.59844 | -13.59844 | 0 | 0 | 0 | 0 | 0 | 0 |
| $E_D(_{Group})\ (eV)$ | 3.45260 | 12.49186 | 7.83016 | 3.32601 | 4.32754 | 4.29921 | 3.97398 | 4.17951 | 3.62128 | 3.91734 |

Table 15.85. The total bond energies of tertiary amines calculated using the functional group composition and the energies of Table 15.84 compared to the experimental values [3].

| Formula | Name | $C-N$ Group | $CH_3$ | $CH_2$ | $CH$ | $C-C$ (a) | $C-C$ (b) | $C-C$ (c) | $C-C$ (d) | $C-C$ (e) | $C-C$ (f) | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $C_3H_9N$ | Trimethylamine | 3 | 3 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 47.83338 | 47.761 | -0.00152 |
| $C_6H_{15}N$ | Triethylamine | 3 | 3 | 3 | 0 | 3 | 0 | 0 | 0 | 0 | 0 | 84.30648 | 84.316 | 0.00012 |
| $C_9H_{21}N$ | Tripropylamine | 3 | 3 | 6 | 0 | 6 | 0 | 0 | 0 | 0 | 0 | 120.77958 | 120.864 | 0.00070 |

Table 15.86. The bond angle parameters of tertiary amines and experimental values [1]. In the calculation of $\theta_v$, the parameters from the preceding angle were used. $E_T$ is $E_T(atom - atom, msp^3.AO)$.

| Atoms of Angle | $2c'$ Bond 1 $(a_0)$ | $2c'$ Bond 2 $(a_0)$ | $2c'$ Terminal Atoms $(a_0)$ | $E_{Coulombic}$ or $E$ Atom 1 | Atom 1 Hybridization Designation (Table 15.3.A) | $E_{Coulombic}$ Atom 2 | Atom 2 Hybridization Designation (Table 15.3.A) | $c_2$ Atom 1 | $c_2$ Atom 2 | $C_1$ | $C_2$ | $c_1$ | $c_2'$ | $E_T$ (eV) | $\theta_v$ (°) | $\theta_1$ (°) | $\theta_2$ (°) | Cal. $\theta$ (°) | Exp. $\theta$ (°) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $\angle CNC$ | 2.80224 | 2.80224 | 4.6043 | -17.14871 | 36 | -17.14871 | 36 | 0.79340 | 0.79340 | 1 | 1 | 1 | 0.79340 | -1.85836 | | | | 110.48 | 110.9 (trimethylamine) |
| Methylene $\angle HC_aH$ | 2.11106 | 2.11106 | 3.4252 | -15.75493 | 7 | H | H | 0.86359 | 1 | 1 | 1 | 0.75 | 1.15796 | 0 | | | | 108.44 | 107 (dimethylamine)<br>107 (propane) |
| $\angle C_aC_bC_c$ | | | | | | | | | | | | | | | 69.51 | | | 110.49 | 112 (propane)<br>113.8 (butane)<br>110.8 (isobutane) |
| $\angle C_aC_bH$ | | | | | | | | | | | | | | | 69.51 | | | 110.49 | 111.0 (butane)<br>111.4 (isobutane) |
| Methyl $\angle HC_aH$ | 2.09711 | 2.09711 | 3.4252 | -15.75493 | 7 | H | H | 0.86359 | 1 | 1 | 1 | 0.75 | 1.15796 | 0 | | | | 109.50 | |
| $\angle C_aC_bC_c$ | | | | | | | | | | | | | | | 70.56 | | | 109.44 | |
| $\angle C_aC_bH$ | | | | | | | | | | | | | | | 70.56 | | | 109.44 | |
| $\angle C_bC_aC_c$ iso $C_a$ | 2.91547 | 2.91547 | 4.7958 | -16.68412 $C_b$ | 26 | -16.68412 $C_c$ | 26 | 0.81549 | 0.81549 | 1 | 1 | 1 | 0.81549 | -1.85836 | | | | 110.67 | 110.8 (isobutane) |
| $\angle C_bC_aH$ iso $C_a$ | 2.91547 | 2.11323 | 4.1633 | -15.55033 $C_a$ | 5 | -14.82575 $C_b$ | 1 | 0.87495 | 0.91771 | 0.75 | 1 | 0.75 | 1.04887 | 0 | | | | 110.76 | |
| $\angle C_aC_bH$ iso $C_a$ | 2.91547 | 2.09711 | 4.1633 | -15.55033 $C_b$ | 5 | -14.82575 $C_a$ | 1 | 0.87495 | 0.91771 | 0.75 | 1 | 0.75 | 1.04887 | 0 | | | | 111.27 | 111.4 (isobutane) |
| $\angle C_bC_aC_b$ tert $C_a$ | 2.90327 | 2.90327 | 4.7958 | -16.68412 $C_b$ | 26 | -16.68412 $C_b$ | 26 | 0.81549 | 0.81549 | 1 | 1 | 1 | 0.81549 | -1.85836 | | | | 111.37 | 110.8 (isobutane) |
| $\angle C_bC_aC_d$ | | | | | | | | | | | | | | | 72.50 | | | 107.50 | |

## ALDEHYDES ($C_nH_{2n}O,\ \ n=1,2,3,4,5...\infty$)

The alkyl aldehydes, $C_nH_{2n}O$, each have a $HC=O$ moiety that comprises a $C=O$ functional group and a $CH$ functional group. The single bond of carbon to the carbonyl carbon atom, $C-C(O)H$, is a functional group. In addition to the $C=O$ functional group, formaldehyde comprises a $CH_2$ functional group. The alkyl portion of the alkyl aldehyde may comprise at least two terminal methyl groups ($CH_3$) at each end of the chain, and may comprise methylene ($CH_2$), and methylyne ($CH$) functional groups as well as $C$ bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($(CH_3)_2CH$) and t-butyl ($(CH_3)_3C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups. The branched-chain-alkane groups in aldehydes are equivalent to those in branched-chain alkanes.

The $CH$ functional group was solved in the Hydrogen Carbide ($CH$) section except that $E_{mag}$ is not subtracted since unpaired electrons are not created with fragmentation of the $CH$ functional group of aldehydes. The $CH_2$ functional group of formaldehyde is solved in the Dihydrogen Carbide ($CH_2$) section except that the energy of each $C-H$ MO is matched to the initial energy of the $C2sp^3$ HO (Eq. (15.25)). The $C=O$ and $C-C(O)H$ groups are solved by hybridizing the $2s$ and $2p$ AOs of each $C$ atom to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between the $C2sp^3$ HO and the $O$ AO or between two $C2sp^3$ HOs, respectively, to form a MO permits each participating orbital to decrease in radius and energy. In alkyl aldehydes, the $C2sp^3$ HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of $E\left(C,2sp^3\right)=-14.63489\ eV$ (Eq. (15.25)) and the $O$ AO has an energy of $E\left(O\right)=-13.61806\ eV$. To meet the equipotential condition of the union of the $C=O$ $H_2$-type-ellipsoidal-MO with these orbitals, the hybridization factor $c_2$ of Eq. (15.61) for the $C=O$-bond MO given by Eq. (15.133) is $c_2\left(C2sp^3HO\ to\ O\right)=0.85395$. The unpaired electrons created by bond breakage of the double $C=O$ bond requires that two times the $O2p$ AO magnetic energy $E_{mag}$ (Eq. (15.69)) be subtracted from the total energy to give $E_{D\,(Group)}$ $(eV)$ for $C=O$.

$E_T\left(atom-atom,msp^3.AO\right)$ of the $C=O$-bond MO in Eq. (15.61) due to the charge donation from the $C$ and $O$ atoms to the MO is $-2.69893\ eV$ which is an energy minimum for the double bond between the pair of $C2sp^3$ HO electrons of the $C$ atom and the pair of AO electrons of the $O$ atom. It is given as a linear combination of the energy contributions corresponding to a double bond, $-1.13379\ eV$ (Eq. (14.247)), and a triple bond, $-1.56513\ eV$ (Eq. (14.342)). The triple bond contribution includes the $C2sp^3$ HO electron of the $C-H$ bond in addition to the pair involved directly in the double bond with $O$. $E_T\left(atom-atom,msp^3.AO\right)$ of the $C-C(O)H$ group is equivalent to that of an alkane, $-1.85836\ eV$, where both energy contributions are given by Eq. (14.513). It is based on the energy match between the $C2sp^3$ HOs of the aldehyde. In order to match energy between the groups bonded to the $C=O$, electron-density is shared. Due to the interaction in the transition state between the groups based on the sharing, $C_{1o}=2C_1$ rather than $C_{1o}=C_1$ in Eq. (15.61) for the $C-C(O)H$ bond.

The symbols of the functional groups of alkyl aldehydes are given in Table 15.87. The geometrical (Eqs. (15.1-15.5) and (15.51)), intercept (Eqs. (15.80-15.87)), and energy (Eqs. (15.6-15.11) and (15.17-15.65)) parameters of alkyl aldehydes are given in Tables 15.88, 15.89, and 15.90, respectively. The total energy of each alkyl aldehyde given in Table 15.91 was calculated as the sum over the integer multiple of each $E_{D\,(Group)}$ of Table 15.90 corresponding to functional-group composition of the molecule. The bond angle parameters of alkyl aldehydes determined using Eqs. (15.88-15.117) are given in Table 15.92. The color scale, translucent view of the charge-density of exemplary aldehyde, Propanal, comprising the concentric shells of atoms with the outer shell bridged by one or more $H_2$-type ellipsoidal MOs or joined with one or more hydrogen MOs is shown in Figure 15.15.

Figure 15.15. (A)-(B) Color scale, translucent views of the charge-density of propanal showing the orbitals of the atoms at their radii, the ellipsoidal surface of each $H$ or $H_2$-type ellipsoidal MO that transitions to the corresponding outer shell of the atom(s) participating in each bond, and the hydrogen nuclei (red, not to scale).

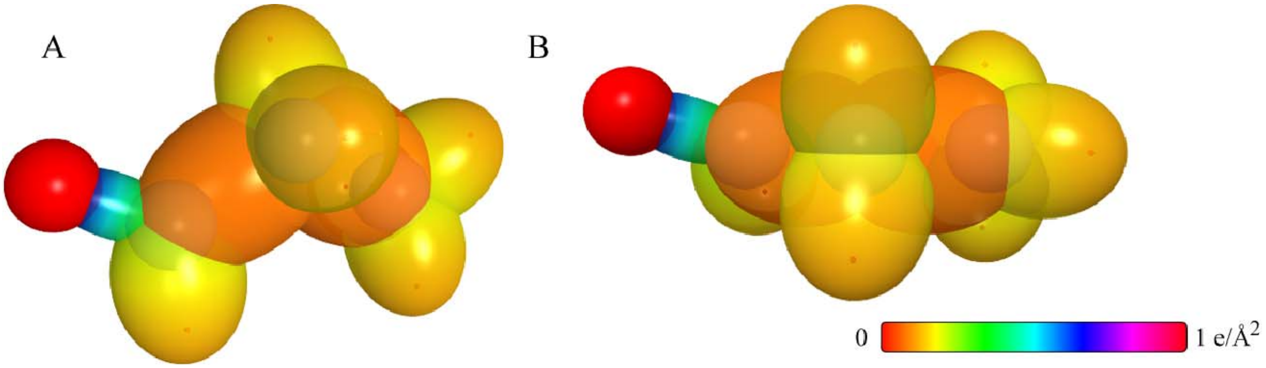


Table 15.87. The symbols of functional groups of alkyl aldehydes.

| Functional Group | Group Symbol |
|---|---|
| $CH_2$ (formaldehyde) group | $C-H\ (CH_2)$ (i) |
| $CH$ (aldehyde) group | $CH$ (i) |
| $C=O$ | $C=O$ (i) |
| $C$-$C(O)H$ | $C-C(O)H$ |
| $CH_3$ group | $C-H\ (CH_3)$ |
| $CH_2$ (alkyl) group | $C-H\ (CH_2)$ (ii) |
| $CH$ (alkyl) | $C-H$ (ii) |
| $CC$ bond (*n-C*) | $C-C$ (a) |
| $CC$ bond (*iso-C*) | $C-C$ (b) |
| $CC$ bond (*tert-C*) | $C-C$ (c) |
| $CC$ (*iso* to *iso-C*) | $C-C$ (d) |
| $CC$ (*t* to *t-C*) | $C-C$ (e) |
| $CC$ (*t* to *iso-C*) | $C-C$ (f) |

Table 15.88. The geometrical bond parameters of alkyl aldehydes and experimental values [1].

| Parameter | $C-H\left(CH_2\right)$ (i) | $CH$ (i) Group | $C=O$ Group | $C-C(O)H$ Group | $C-H\left(CH_3\right)$ Group | $C-H\left(CH_2\right)$ (ii) Group | $C-H$ (ii) Group | $C-C$ (a) Group | $C-C$ (b) Group | $C-C$ (c) Group | $C-C$ (d) Group | $C-C$ (e) Group | $C-C$ (f) Group |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $a\left(a_0\right)$ | 1.64010 | 1.67465 | 1.29907 | 2.04740 | 1.64920 | 1.67122 | 1.67465 | 2.12499 | 2.12499 | 2.10725 | 2.12499 | 2.10725 | 2.10725 |
| $c'\left(a_0\right)$ | 1.04566 | 1.05661 | 1.13977 | 1.43087 | 1.04856 | 1.05553 | 1.05661 | 1.45744 | 1.45744 | 1.45164 | 1.45744 | 1.45164 | 1.45164 |
| Bond Length $2c'$ $(\mathring{A})$ | 1.10668 | 1.11827 | 1.20628 | 1.51437 | 1.10974 | 1.11713 | 1.11827 | 1.54280 | 1.54280 | 1.53635 | 1.54280 | 1.53635 | 1.53635 |
| Exp. Bond Length $(\mathring{A})$ | 1.116 (formaldehyde) | 1.128 (acetaldehyde) | 1.208 (formaldehyde)<br>1.210 (acetaldehyde) | 1.515 (acetaldehyde) | 1.107 ($C-H$ propane)<br>1.117 ($C-H$ butane) | 1.107 ($C-H$ propane)<br>1.117 ($C-H$ butane) | 1.122 (isobutane) | 1.532 (propane)<br>1.531 (butane) | 1.532 (propane)<br>1.531 (butane) | 1.532 (propane)<br>1.531 (butane) | 1.532 (propane)<br>1.531 (butane) | 1.532 (propane)<br>1.531 (butane) | 1.532 (propane)<br>1.531 (butane) |
| $b,c\left(a_0\right)$ | 1.26354 | 1.29924 | 0.62331 | 1.46439 | 1.27295 | 1.29569 | 1.29924 | 1.54616 | 1.54616 | 1.52750 | 1.54616 | 1.52750 | 1.52750 |
| $e$ | 0.63756 | 0.63095 | 0.87737 | 0.69887 | 0.63580 | 0.63159 | 0.63095 | 0.68600 | 0.68600 | 0.68888 | 0.68600 | 0.68888 | 0.68888 |

Table 15.89. The MO to HO intercept geometrical bond parameters of alkyl aldehydes. $R$, $R'$, $R''$ are $H$ or alkyl groups. $E_T$ is $E_T$ $(atom-atom,msp^3.AO)$.

| Bond | Atom | $E_T$ (eV) Bond 1 | $E_T$ (eV) Bond 2 | $E_T$ (eV) Bond 3 | $E_T$ (eV) Bond 4 | Final Total Energy $C2sp^3$ (eV) | $r_{initial}$ $\left(a_0\right)$ | $r_{final}$ $\left(a_0\right)$ | $E_{Coulomb}$ (eV) Final | $E\left(C2sp^3\right)$ (eV) Final | $\theta'$ $\left(^{\circ}\right)$ | $\theta_1$ $\left(^{\circ}\right)$ | $\theta_2$ $\left(^{\circ}\right)$ | $d_1$ $\left(a_0\right)$ | $d_2$ $\left(a_0\right)$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $HC(O)-H\left(CH_2\right)$ (i) | $C$ | -1.34946 | 0 | 0 | 0 | -152.96515 | 0.91771 | 0.84115 | -16.17521 | -15.98435 | 75.72 | 104.28 | 40.18 | 1.25314 | 0.20748 |
| $-C_bH_2C_a(O)-H\left(CH\right)$ (i) | $C_a$ | -1.34946 | -0.92918 | 0 | 0 | -153.89434 | 0.91771 | 0.79546 | -17.10440 | -16.91353 | 64.95 | 115.05 | 33.69 | 1.39345 | 0.33684 |
| $H_2C=O$ | $O$ | -1.34946 | 0 | 0 | 0 |  | 1.00000 | 0.84115 | -16.17521 |  | 137.27 | 42.73 | 66.31 | 0.52193 | 0.61784 |
| $-C_bH_2C_a(H)=O$ | $O$ | -1.34946 | 0 | 0 | 0 |  | 1.00000 | 0.84115 | -16.17521 |  | 137.27 | 42.73 | 66.31 | 0.52193 | 0.61784 |
| $RH_2C_b-C_a(H)(O)$ | $C_a$ | -1.34946 | -0.92918 | 0 | 0 | -153.89434 | 0.91771 | 0.79546 | -17.10440 | -16.91353 | 135.34 | 44.66 | 63.78 | 0.57401 | 0.56576 |
| $H_3C_b-C_a(H)(O)$ | $C_b$ | -0.92918 | 0 | 0 | 0 | -152.54487 | 0.91771 | 0.86359 | -15.75493 | -15.56407 | 72.27 | 107.73 | 34.17 | 1.69388 | 0.26301 |
| $-C_bH_2-C_a(H)(O)$ | $C_b$ | -0.92918 | -0.92918 | 0 | 0 | -153.47405 | 0.91771 | 0.81549 | -16.68411 | -16.49325 | 65.99 | 114.01 | 30.58 | 1.76270 | 0.33183 |
| $C-H\left(CH_3\right)$ | $C$ | -0.92918 | 0 | 0 | 0 | -152.54487 | 0.91771 | 0.86359 | -15.75493 | -15.56407 | 77.49 | 102.51 | 41.48 | 1.23564 | 0.18708 |
| $C-H\left(CH_2\right)$ (ii) | $C$ | -0.92918 | -0.92918 | 0 | 0 | -153.47406 | 0.91771 | 0.81549 | -16.68412 | -16.49325 | 68.47 | 111.53 | 35.84 | 1.35486 | 0.29933 |
| $C-H\left(CH\right)$ (ii) | $C$ | -0.92918 | -0.92918 | -0.92918 | 0 | -154.40324 | 0.91771 | 0.77247 | -17.61330 | -17.42244 | 61.10 | 118.90 | 31.37 | 1.42988 | 0.37326 |
| $H_3C_aC_bH_2CH_2-$ ($C-C$ (a)) | $C_a$ | -0.92918 | 0 | 0 | 0 | -152.54487 | 0.91771 | 0.86359 | -15.75493 | -15.56407 | 63.82 | 116.18 | 30.08 | 1.83879 | 0.38106 |
| $H_3C_aC_bH_2CH_2-$ ($C-C$ (a)) | $C_b$ | -0.92918 | -0.92918 | 0 | 0 | -153.47406 | 0.91771 | 0.81549 | -16.68412 | -16.49325 | 56.41 | 123.59 | 26.06 | 1.90890 | 0.45117 |
| $R-H_2C_aC_b\left(H_2C_c-R'\right)HCH_2-$ ($C-C$ (b)) | $C_b$ | -0.92918 | -0.92918 | -0.92918 | 0 | -154.40324 | 0.91771 | 0.77247 | -17.61330 | -17.42244 | 48.30 | 131.70 | 21.90 | 1.97162 | 0.51388 |
| $R-H_2C_a\left(R'-H_2C_d\right)C_b\left(R''-H_2C_c\right)CH_2-$ ($C-C$ (c)) | $C_b$ | -0.92918 | -0.72457 | -0.72457 | -0.72457 | -154.71860 | 0.91771 | 0.75889 | -17.92866 | -17.73779 | 48.21 | 131.79 | 21.74 | 1.95734 | 0.50570 |
| $isoC_aC_b\left(H_2C_c-R'\right)HCH_2-$ ($C-C$ (d)) | $C_b$ | -0.92918 | -0.92918 | -0.92918 | 0 | -154.40324 | 0.91771 | 0.77247 | -17.61330 | -17.42244 | 48.30 | 131.70 | 21.90 | 1.97162 | 0.51388 |
| $tertC_a\left(R'-H_2C_d\right)C_b\left(R''-H_2C_c\right)CH_2-$ ($C-C$ (e)) | $C_b$ | -0.72457 | -0.72457 | -0.72457 | -0.72457 | -154.51399 | 0.91771 | 0.76765 | -17.92866 | -17.73779 | 50.04 | 129.96 | 22.66 | 1.94462 | 0.49298 |
| $tertC_aC_b\left(H_2C_c-R'\right)HCH_2-$ ($C-C$ (f)) | $C_b$ | -0.72457 | -0.92918 | -0.92918 | 0 | -154.19863 | 0.91771 | 0.78155 | -17.40869 | -17.21783 | 52.78 | 127.22 | 24.04 | 1.92443 | 0.47279 |
| $isoC_a\left(R'-H_2C_d\right)C_b\left(R''-H_2C_c\right)CH_2-$ ($C-C$ (f)) | $C_b$ | -0.72457 | -0.72457 | -0.72457 | -0.72457 | -154.51399 | 0.91771 | 0.76765 | -17.92866 | -17.73779 | 50.04 | 129.96 | 22.66 | 1.94462 | 0.49298 |

Table 15.90. The energy parameters ($eV$) of functional groups of alkyl aldehydes.

| Parameters | $CH_2$ (i) | $CH$ (i) Group | $C=O$ Group | $C-C(O)H$ Group | $CH_3$ Group | $CH_2$ (ii) Group | $C-H$ (ii) Group | $C-C$ (a) Group | $C-C$ (b) Group | $C-C$ (c) Group | $C-C$ (d) Group | $C-C$ (e) Group | $C-C$ (f) Group |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $n_1$ | 2 | 1 | 2 | 1 | 3 | 2 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $n_2$ | 1 | 0 | 0 | 0 | 2 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $n_3$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $C_1$ | 0.75 | 0.75 | 0.5 | 0.5 | 0.75 | 0.75 | 0.75 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| $C_2$ | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $c_1$ | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $c_2$ | 0.91771 | 0.91771 | 0.85395 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 |
| $c_3$ | 1 | 0 | 2 | 0 | 0 | 1 | 1 | 0 | 0 | 0 | 1 | 1 | 0 |
| $c_4$ | 1 | 1 | 4 | 2 | 1 | 1 | 1 | 2 | 2 | 2 | 2 | 2 | 2 |
| $c_5$ | 2 | 1 | 0 | 0 | 3 | 2 | 1 | 0 | 0 | 0 | 0 | 0 | 0 |
| $C_{1o}$ | 0.75 | 0.75 | 0.5 | 1 | 0.75 | 0.75 | 0.75 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| $C_{2o}$ | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $V_e\ (eV)$ | -72.03287 | -35.12015 | -111.25473 | -30.19634 | -107.32728 | -70.41425 | -35.12015 | -28.79214 | -28.79214 | -29.10112 | -28.79214 | -29.10112 | -29.10112 |
| $V_p\ (eV)$ | 26.02344 | 12.87680 | 23.87467 | 9.50874 | 38.92728 | 25.78002 | 12.87680 | 9.33352 | 9.33352 | 9.37273 | 9.33352 | 9.37273 | 9.37273 |
| $T\ (eV)$ | 21.95990 | 10.48582 | 42.82081 | 7.37432 | 32.53914 | 21.06675 | 10.48582 | 6.77464 | 6.77464 | 6.90500 | 6.77464 | 6.90500 | 6.90500 |
| $V_m\ (eV)$ | -10.97995 | -5.24291 | -21.41040 | -3.68716 | -16.26957 | -10.53337 | -5.24291 | -3.38732 | -3.38732 | -3.45250 | -3.38732 | -3.45250 | -3.45250 |
| $E(_{AO/HO})\ (eV)$ | -14.63489 | -14.63489 | 0 | -14.63489 | -15.56407 | -15.56407 | -14.63489 | -15.56407 | -15.56407 | -15.35946 | -15.56407 | -15.35946 | -15.35946 |
| $\Delta E_{H_2MO}(_{AO/HO})\ (eV)$ | 0 | 0 | -2.69893 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $E_T(_{AO/HO})\ (eV)$ | -14.63489 | -14.63489 | 2.69893 | -14.63489 | -15.56407 | -15.56407 | -14.63489 | -15.56407 | -15.56407 | -15.35946 | -15.56407 | -15.35946 | -15.35946 |
| $E_T(_{H_2MO})\ (eV)$ | -49.66437 | -31.63533 | -63.27074 | -31.63534 | -67.69451 | -49.66493 | -31.63533 | -31.63537 | -31.63537 | -31.63535 | -31.63537 | -31.63535 | -31.63535 |
| $E_T\left(atom-atom, msp^3.AO\right)(eV)$ | 0 | 0 | -2.69893 | -1.85836 | 0 | 0 | 0 | -1.85836 | -1.85836 | -1.44915 | -1.85836 | -1.44915 | -1.44915 |
| $E_T(_{MO})\ (eV)$ | -49.66493 | -31.63537 | -65.96966 | -33.49373 | -67.69450 | -49.66493 | -31.63537 | -33.49373 | -33.49373 | -33.08452 | -33.49373 | -33.08452 | -33.08452 |
| $\omega\ \left(10^{15}\ rad/s\right)$ | 25.2077 | 24.1759 | 59.4034 | 23.3291 | 24.9286 | 24.2751 | 24.1759 | 9.43699 | 9.43699 | 15.4846 | 9.43699 | 9.55643 | 9.55643 |
| $E_K\ (eV)$ | 16.59214 | 15.91299 | 39.10034 | 15.35563 | 16.40846 | 15.97831 | 15.91299 | 6.21159 | 6.21159 | 10.19220 | 6.21159 | 6.29021 | 6.29021 |
| $\bar{E}_D\ (eV)$ | -0.25493 | -0.24966 | -0.40804 | -0.25966 | -0.25352 | -0.25017 | -0.24966 | -0.16515 | -0.16515 | -0.20896 | -0.16515 | -0.16416 | -0.16416 |
| $\bar{E}_{Kvib}\ (eV)$ | 0.35532<br>(Eq. (13.458)) | 0.35532<br>(Eq. (13.458)) | 0.21077<br>[12] | 0.13800<br>[26] | 0.35532<br>(Eq. (13.458)) | 0.35532<br>(Eq. (13.458)) | 0.35532<br>(Eq. (13.458)) | 0.12312<br>[2] | 0.17978<br>[4] | 0.09944<br>[5] | 0.12312<br>[2] | 0.12312<br>[2] | 0.12312<br>[2] |
| $\bar{E}_{osc}\ (eV)$ | -0.07727 | -0.07200 | -0.30266 | -0.19066 | -0.22757 | -0.14502 | -0.07200 | -0.10359 | -0.07526 | -0.15924 | -0.10359 | -0.10260 | -0.10260 |
| $E_{mag}\ (eV)$ | 0.14803 | 0.14803 | 0.11441 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 |
| $E_T(_{Group})\ (eV)$ | -49.81948 | -31.70737 | -66.57498 | -33.68439 | -67.92207 | -49.80996 | -31.70737 | -33.59732 | -33.49373 | -33.24376 | -33.59732 | -33.18712 | -33.18712 |
| $E_{initial}(_{c_4\ AO/HO})\ (eV)$ | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 |
| $E_{initial}(_{c_5\ AO/HO})\ (eV)$ | -13.59844 | -13.59844 | 0 | 0 | -13.59844 | -13.59844 | -13.59844 | 0 | 0 | 0 | 0 | 0 | 0 |
| $E_D(_{Group})\ (eV)$ | 7.83968 | 3.47404 | 7.80660 | 4.41461 | 12.49186 | 7.83016 | 3.32601 | 4.32754 | 4.29921 | 3.97398 | 4.17951 | 3.62128 | 3.91734 |

Table 15.91. The total bond energies of alkyl aldehydes calculated using the functional group composition and the energies of Table 15.90 compared to the experimental values [3].

| Formula | Name | $CH_2$ (i) Group | $CH$ (i) Group | $C=O$ Group | $C-C(O)H$ Group | $CH_3$ | $CH_2$ (ii) | $CH$ (ii) | $C-C$ (a) | $C-C$ (b) | $C-C$ (c) | $C-C$ (d) | $C-C$ (e) | $C-C$ (f) | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $CH_2O$ | Formaldehyde | 1 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 15.64628 | 15.655 | 0.00056 |
| $C_2H_4O$ | Acetaldehyde | 0 | 1 | 1 | 1 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 28.18711 | 28.198 | 0.00039 |
| $C_3H_6O$ | Propanal | 0 | 1 | 1 | 1 | 1 | 1 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 40.34481 | 40.345 | 0.00000 |
| $C_4H_8O$ | Butanal | 0 | 1 | 1 | 1 | 1 | 2 | 0 | 2 | 0 | 0 | 0 | 0 | 0 | 52.50251 | 52.491 | -0.00022 |
| $C_4H_8O$ | Isobutanal | 0 | 1 | 1 | 1 | 2 | 0 | 1 | 0 | 2 | 0 | 0 | 0 | 0 | 52.60340 | 52.604 | 0.00001 |
| $C_5H_{10}O$ | Pentanal | 0 | 1 | 1 | 1 | 1 | 3 | 0 | 3 | 0 | 0 | 0 | 0 | 0 | 64.66021 | 64.682 | 0.00034 |
| $C_7H_{14}O$ | Heptanal | 0 | 1 | 1 | 1 | 1 | 5 | 0 | 5 | 0 | 0 | 0 | 0 | 0 | 88.97561 | 88.942 | -0.00038 |
| $C_8H_{16}O$ | Octanal | 0 | 1 | 1 | 1 | 1 | 6 | 0 | 6 | 0 | 0 | 0 | 0 | 0 | 101.13331 | 101.179 | 0.00045 |
| $C_8H_{16}O$ | 2-Ethylhexanal | 0 | 1 | 1 | 1 | 2 | 4 | 1 | 4 | 2 | 0 | 0 | 0 | 0 | 101.23420 | 101.259 | 0.00025 |

Table 15.92. The bond angle parameters of alkyl aldehydes and experimental values [1]. In the calculation of $\theta_v$, the parameters from the preceding angle were used. $E_T$ is $E_T(atom - atom, msp^3.AO)$.

| Atoms of Angle | $2c'$ Bond 1 ($a_0$) | $2c'$ Bond 2 ($a_0$) | $2c'$ Terminal Atoms ($a_0$) | $E_{Coulombic}$ Atom 1 | Atom 1 Hybridization Designation (Table 15.3.A) | $E_{Coulombic}$ Atom 2 | Atom 2 Hybridization Designation (Table 15.3.A) | $c_2$ Atom 1 | $c_2$ Atom 2 | $C_1$ | $C_2$ | $c_1$ | $c_2'$ | $E_T$ (eV) | $\theta_v$ (°) | $\theta_1$ (°) | $\theta_2$ (°) | Cal. $\theta$ (°) | Exp. $\theta$ (°) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $\angle HC_aH$ ($C_aH_2(O)$ (i)) | 2.09132 | 2.09132 | 3.5637 | -16.39089 | 19 | H | H | 0.83008 | 1 | 1 | 1 | 0.75 | 1.20470 | 0 | | | | 116.87 | 116.5 (formaldehyde) |
| $\angle C_bC_aH$ $RC_a(H)=O$ | 2.86175 | 2.11323 | 4.2269 | -15.75493 $C_a$ | 7 | -14.82575 $C_b$ | 1 | 0.86359 | 0.91771 | 0.75 | 1 | 0.75 | 1.06267 | 0 | | | | 115.52 | 115.3 (acetaldehyde) |
| $\angle C_bC_aO$ | 2.86175 | 2.27954 | 4.5826 | -16.68412 | 26 | -13.61806 | O | 0.81549 | 0.85395 (Eq. (15.133)) | 1 | 1 | 1 | 0.83472 | -1.65376 | | | | 125.70 | 124.1 (acetaldehyde) |
| Methylene $\angle HC_aH$ | 2.11106 | 2.11106 | 3.4252 | -15.75493 | 7 | H | H | 0.86359 | 1 | 1 | 1 | 0.75 | 1.15796 | 0 | | | | 108.44 | 107 (propane) |
| $\angle C_aC_bC_c$ | | | | | | | | | | | | | | | 69.51 | | | 110.49 | 112 (propane)<br>113.8 (butane)<br>110.8 (isobutane) |
| $\angle C_aC_bH$ | | | | | | | | | | | | | | | 69.51 | | | 110.49 | 111.0 (butane)<br>111.4 (isobutane) |
| Methyl $\angle HC_aH$ | 2.09711 | 2.09711 | 3.4252 | -15.75493 | 7 | H | H | 0.86359 | 1 | 1 | 1 | 0.75 | 1.15796 | 0 | | | | 109.50 | |
| $\angle C_aC_bC_c$ | | | | | | | | | | | | | | | 70.56 | | | 109.44 | |
| $\angle C_aC_bH$ | | | | | | | | | | | | | | | 70.56 | | | 109.44 | |
| $\angle C_bC_aC_c$ iso $C_a$ | 2.91547 | 2.91547 | 4.7958 | -16.68412 $C_b$ | 26 | -16.68412 $C_c$ | 26 | 0.81549 | 0.81549 | 1 | 1 | 1 | 0.81549 | -1.85836 | | | | 110.67 | 110.8 (isobutane) |
| $\angle C_bC_aH$ iso $C_a$ | 2.91547 | 2.11323 | 4.1633 | -15.55033 $C_a$ | 5 | -14.82575 $C_b$ | 1 | 0.87495 | 0.91771 | 0.75 | 1 | 0.75 | 1.04887 | 0 | | | | 110.76 | |
| $\angle C_aC_bH$ iso $C_a$ | 2.91547 | 2.09711 | 4.1633 | -15.55033 $C_b$ | 5 | -14.82575 $C_a$ | 1 | 0.87495 | 0.91771 | 0.75 | 1 | 0.75 | 1.04887 | 0 | | | | 111.27 | 111.4 (isobutane) |
| $\angle C_bC_aC_b$ tert $C_a$ | 2.90327 | 2.90327 | 4.7958 | -16.68412 $C_b$ | 26 | -16.68412 $C_b$ | 26 | 0.81549 | 0.81549 | 1 | 1 | 1 | 0.81549 | -1.85836 | | | | 111.37 | 110.8 (isobutane) |
| $\angle C_bC_aC_d$ | | | | | | | | | | | | | | | 72.50 | | | 107.50 | |

## KETONES ($C_nH_{2n}O,\ n=1,2,3,4,5...\infty$)

The alkyl ketones, $C_nH_{2n}O$, each have a $C=O$ moiety that comprises a functional group. Each of the two single bonds of carbon to the carbonyl carbon atom, $C-C(O)$, is also a functional group. The alkyl portion of the alkyl ketone may comprise at least two terminal methyl groups ($CH_3$) at each end of the chain, and may comprise methylene ($CH_2$), and methylyne ($CH$) functional groups as well as $C$ bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($\left(CH_3\right)_2CH$) and t-butyl ($\left(CH_3\right)_3C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups. The branched-chain-alkane groups in ketones are equivalent to those in branched-chain alkanes.

The $C=O$ and $C-C(O)$ groups are solved by hybridizing the $2s$ and $2p$ AOs of each $C$ atom to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between the $C2sp^3$ HO and the $O$ AO or between two $C2sp^3$ HOs, respectively, to form a MO permits each participating orbital to decrease in radius and energy. In alkyl ketones, the $C2sp^3$ HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of $E\left(C,2sp^3\right)=-14.63489\ eV$ (Eq. (15.25)) and the $O$ AO has an energy of $E\left(O\right)=-13.61806\ eV$. To meet the equipotential condition of the union of the $C=O$ $H_2$-type-ellipsoidal-MO with these orbitals, the hybridization factor $c_2$ of Eq. (15.61) for the $C=O$-bond MO given by Eq. (15.133) is $c_2\left(C2sp^3HO\ to\ O\right)=0.85395$. The unpaired electrons created by bond breakage of the double $C=O$ bond requires that two times the $O2p$ AO magnetic energy $E_{mag}$ (Eq. (15.69)) be subtracted from the total energy to give $E_D\left(Group\right)$ $(eV)$ for $C=O$.

As in the case with aldehydes, $E_T\left(atom-atom,msp^3.AO\right)$ of the $C=O$-bond MO in Eq. (15.61) due to the charge donation from the $C$ and $O$ atoms to the MO is $-2.69893\ eV$ which is an energy minimum for the double bond between the pair of $C2sp^3$ HO electrons of the $C$ atom and the pair of AO electrons of the $O$ atom. It is given as a linear combination of the energy contributions corresponding to a double bond, $-1.13379\ eV$ (Eq. (14.247)), and a triple bond, $-1.56513\ eV$ (Eq. (14.342)). The triple bond contribution includes the $C2sp^3$ HO electron of the $C-C(O)$ bond in addition to the pair involved directly in the double bond with $O$. Consequently, $E_T\left(atom-atom,msp^3.AO\right)$ of the $C-C(O)$-bond MO is $-1.44915\ eV$, corresponding to the energy contributions of the two $C2sp^3$ HOs to the single bond that are equivalent to those of methyl groups, $-0.72457\ eV$ (Eq. (14.151)). Since there are two $C-C(O)$ bonds in ketones versus one in aldehydes, $C_{1o}=C_1$ in Eq. (15.61) for each $C-C(O)$ ketone bond.

The symbols of the functional groups of alkyl ketones are given in Table 15.93. The geometrical (Eqs. (15.1-15.5) and (15.51)), intercept (Eqs. (15.80-15.87)), and energy (Eqs. (15.6-15.11) and (15.17-15.64)) parameters of alkyl ketones are given in Tables 15.94, 15.95, and 15.96, respectively. The total energy of each alkyl ketone given in Table 15.97 was calculated as the sum over the integer multiple of each $E_D\left(Group\right)$ of Table 15.96 corresponding to functional-group composition of the molecule. For each set of unpaired electrons created by bond breakage , the $C2sp^3$ HO magnetic energy $E_{mag}$ that is subtracted from the weighted sum of the $E_D\left(Group\right)$ $(eV)$ values based on composition is given by Eq. (15.67). The bond angle parameters of alkyl ketones determined using Eqs. (15.88-15.117) are given in Table 15.98. The color scale, translucent view of the charge-density of exemplary ketone, methyl ethyl ketone, comprising the concentric shells of atoms with the outer shell bridged by one or more $H_2$-type ellipsoidal MOs or joined with one or more hydrogen MOs is shown in Figure 15.16.

Figure 15.16. (A)-(B) Color scale, translucent views of the charge-density of methyl ethyl ketone showing the orbitals of the atoms at their radii, the ellipsoidal surface of each $H$ or $H_2$-type ellipsoidal MO that transitions to the corresponding outer shell of the atom(s) participating in each bond, and the hydrogen nuclei (red, not to scale).

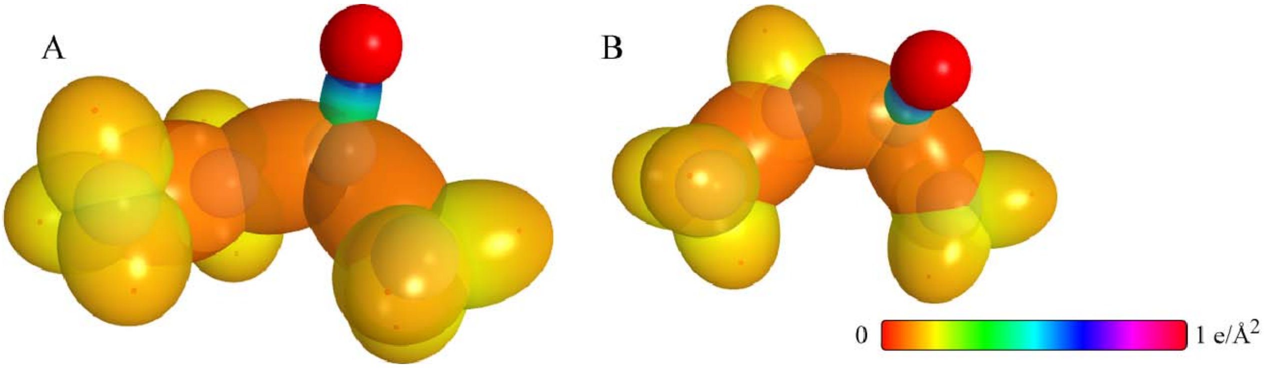


Table 15.93. The symbols of functional groups of alkyl ketones.

| Functional Group | Group Symbol |
|---|---|
| *C=O* | $C=O$ |
| *C-C(O)* | $C-C(O)$ |
| $CH_3$ group | $C-H\ (CH_3)$ |
| $CH_2$ group | $C-H\ (CH_2)$ |
| *CH* | $C-H$ |
| *CC* bond (*n-C*) | $C-C$ (a) |
| *CC* bond (*iso-C*) | $C-C$ (b) |
| *CC* bond (*tert-C*) | $C-C$ (c) |
| *CC* (*iso* to *iso-C*) | $C-C$ (d) |
| *CC* (*t* to *t-C*) | $C-C$ (e) |
| *CC* (*t* to *iso-C*) | $C-C$ (f) |

Table 15.94. The geometrical bond parameters of alkyl ketones and experimental values [1].

| Parameter | $C=O$ Group | $C-C(O)$ Group | $C-H\ (CH_3)$ Group | $C-H\ (CH_2)$ Group | $C-H$ Group | $C-C$ (a) Group | $C-C$ (b) Group | $C-C$ (c) Group | $C-C$ (d) Group | $C-C$ (e) Group | $C-C$ (f) Group |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $a\ (a_0)$ | 1.312172 | 2.04740 | 1.64920 | 1.67122 | 1.67465 | 2.12499 | 2.12499 | 2.10725 | 2.12499 | 2.10725 | 2.10725 |
| $c'\ (a_0)$ | 1.14550 | 1.43087 | 1.04856 | 1.05553 | 1.05661 | 1.45744 | 1.45744 | 1.45164 | 1.45744 | 1.45164 | 1.45164 |
| Bond Length $2c'$ ($\mathring{A}$) | 1.21235 | 1.51437 | 1.10974 | 1.11713 | 1.11827 | 1.54280 | 1.54280 | 1.53635 | 1.54280 | 1.53635 | 1.53635 |
| Exp. Bond Length ($\mathring{A}$) | 1.213<br>(acetone)<br>1.219<br>(2-butanone) | 1.520<br>(acetone)<br>1.518<br>(2-butanone) | 1.107<br>($C-H$ propane)<br>1.117<br>($C-H$ butane) | 1.107<br>($C-H$ propane)<br>1.117<br>($C-H$ butane) | 1.122<br>(isobutane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) |
| $b,c\ (a_0)$ | 0.64002 | 1.46439 | 1.27295 | 1.29569 | 1.29924 | 1.54616 | 1.54616 | 1.52750 | 1.54616 | 1.52750 | 1.52750 |
| $e$ | 0.87298 | 0.69887 | 0.63580 | 0.63159 | 0.63095 | 0.68600 | 0.68600 | 0.68888 | 0.68600 | 0.68888 | 0.68888 |

Table 15.95. The MO to HO intercept geometrical bond parameters of alkyl ketones. $R$, $R'$, $R''$ are $H$ or alkyl groups. $E_T$ is $E_T$ ($atom-atom,msp^3.AO$).

| Bond | Atom | $E_T$ (eV) Bond 1 | $E_T$ (eV) Bond 2 | $E_T$ (eV) Bond 3 | $E_T$ (eV) Bond 4 | Final Total Energy $C2sp^3$ (eV) | $r_{initial}$ $(a_0)$ | $r_{final}$ $(a_0)$ | $E_{Coulomb}$ (eV) Final | $E(C2sp^3)$ (eV) Final | $\theta'$ (°) | $\theta_1$ (°) | $\theta_2$ (°) | $d_1$ $(a_0)$ | $d_2$ $(a_0)$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $R'C_cH_2(RC_bH_2)C_a=O$ | $O$ | -1.34946 | 0 | 0 | 0 | | 1.00000 | 0.84115 | -16.17521 | | 136.09 | 43.91 | 65.72 | 0.53955 | 0.60595 |
| $R'C_cH_2(RC_bH_2)C_a=O$ | $C_a$ | -1.34946 | -0.72458 | -0.72458 | 0 | -154.41430 | 0.91771 | 0.77199 | -17.62437 | -17.43350 | 133.02 | 46.98 | 61.86 | 0.61878 | 0.52672 |
| $H_3C_b-C_a(O)(R')$ | $C_b$ | -0.72458 | 0 | 0 | 0 | -152.34026 | 0.91771 | 0.87495 | -15.55033 | -15.35946 | 73.62 | 106.38 | 34.98 | 1.67762 | 0.246675 |
| $RH_2C_c-H_2C_b-C_a(O)(R')$ | $C_b$ | -0.72458 | -0.92918 | 0 | 0 | -153.26945 | 0.91771 | 0.82562 | -16.47951 | -16.28865 | 67.40 | 112.60 | 31.36 | 1.74821 | 0.31734 |
| $C-H\ (CH_3)$ | $C$ | -0.92918 | 0 | 0 | 0 | -152.54487 | 0.91771 | 0.86359 | -15.75493 | -15.56407 | 77.49 | 102.51 | 41.48 | 1.23564 | 0.18708 |
| $C-H\ (CH_2)$ | $C$ | -0.92918 | -0.92918 | 0 | 0 | -153.47406 | 0.91771 | 0.81549 | -16.68412 | -16.49325 | 68.47 | 111.53 | 35.84 | 1.35486 | 0.29933 |
| $C-H\ (CH)$ | $C$ | -0.92918 | -0.92918 | -0.92918 | 0 | -154.40324 | 0.91771 | 0.77247 | -17.61330 | -17.42244 | 61.10 | 118.90 | 31.37 | 1.42988 | 0.37326 |
| $H_3C_aC_bH_2CH_2-$ ($C-C$ (a)) | $C_a$ | -0.92918 | 0 | 0 | 0 | -152.54487 | 0.91771 | 0.86359 | -15.75493 | -15.56407 | 63.82 | 116.18 | 30.08 | 1.83879 | 0.38106 |
| $H_3C_aC_bH_2CH_2-$ ($C-C$ (a)) | $C_b$ | -0.92918 | -0.92918 | 0 | 0 | -153.47406 | 0.91771 | 0.81549 | -16.68412 | -16.49325 | 56.41 | 123.59 | 26.06 | 1.90890 | 0.45117 |
| $R-H_2C_aC_b(H_2C_c-R')HCH_2-$ ($C-C$ (b)) | $C_b$ | -0.92918 | -0.92918 | -0.92918 | 0 | -154.40324 | 0.91771 | 0.77247 | -17.61330 | -17.42244 | 48.30 | 131.70 | 21.90 | 1.97162 | 0.51388 |
| $R-H_2C_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ ($C-C$ (c)) | $C_b$ | -0.92918 | -0.72457 | -0.72457 | -0.72457 | -154.71860 | 0.91771 | 0.75889 | -17.92866 | -17.73779 | 48.21 | 131.79 | 21.74 | 1.95734 | 0.50570 |
| $isoC_aC_b(H_2C_c-R')HCH_2-$ ($C-C$ (d)) | $C_b$ | -0.92918 | -0.92918 | -0.92918 | 0 | -154.40324 | 0.91771 | 0.77247 | -17.61330 | -17.42244 | 48.30 | 131.70 | 21.90 | 1.97162 | 0.51388 |
| $tertC_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ ($C-C$ (e)) | $C_b$ | -0.72457 | -0.72457 | -0.72457 | -0.72457 | -154.51399 | 0.91771 | 0.76765 | -17.92866 | -17.73779 | 50.04 | 129.96 | 22.66 | 1.94462 | 0.49298 |
| $tertC_aC_b(H_2C_c-R')HCH_2-$ ($C-C$ (f)) | $C_b$ | -0.72457 | -0.92918 | -0.92918 | 0 | -154.19863 | 0.91771 | 0.78155 | -17.40869 | -17.21783 | 52.78 | 127.22 | 24.04 | 1.92443 | 0.47279 |
| $isoC_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ ($C-C$ (f)) | $C_b$ | -0.72457 | -0.72457 | -0.72457 | -0.72457 | -154.51399 | 0.91771 | 0.76765 | -17.92866 | -17.73779 | 50.04 | 129.96 | 22.66 | 1.94462 | 0.49298 |

Table 15.96. The energy parameters ($eV$) of functional groups of alkyl ketones.

| Parameters | $C=O$ Group | $C-C(O)$ Group | $CH_3$ Group | $CH_2$ Group | $C-H$ Group | $C-C$ (a) Group | $C-C$ (b) Group | $C-C$ (c) Group | $C-C$ (d) Group | $C-C$ (e) Group | $C-C$ (f) Group |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $n_1$ | 2 | 1 | 3 | 2 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $n_2$ | 0 | 0 | 2 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $n_3$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $C_1$ | 0.5 | 0.5 | 0.75 | 0.75 | 0.75 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| $C_2$ | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $c_1$ | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $c_2$ | 0.85395 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 |
| $c_3$ | 2 | 0 | 0 | 1 | 1 | 0 | 0 | 0 | 1 | 1 | 0 |
| $c_4$ | 4 | 2 | 1 | 1 | 1 | 2 | 2 | 2 | 2 | 2 | 2 |
| $c_5$ | 0 | 0 | 3 | 2 | 1 | 0 | 0 | 0 | 0 | 0 | 0 |
| $C_{1o}$ | 0.5 | 1 | 0.75 | 0.75 | 0.75 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| $C_{2o}$ | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $V_e\ (eV)$ | -109.17602 | -30.19634 | -107.32728 | -70.41425 | -35.12015 | -28.79214 | -28.79214 | -29.10112 | -28.79214 | -29.10112 | -29.10112 |
| $V_p\ (eV)$ | 23.75521 | 9.50874 | 38.92728 | 25.78002 | 12.87680 | 9.33352 | 9.33352 | 9.37273 | 9.33352 | 9.37273 | 9.37273 |
| $T\ (eV)$ | 41.60126 | 7.37432 | 32.53914 | 21.06675 | 10.48582 | 6.77464 | 6.77464 | 6.90500 | 6.77464 | 6.90500 | 6.90500 |
| $V_m\ (eV)$ | -20.80063 | -3.68716 | -16.26957 | -10.53337 | -5.24291 | -3.38732 | -3.38732 | -3.45250 | -3.38732 | -3.45250 | -3.45250 |
| $E(_{AO/HO})\ (eV)$ | 0 | -14.63489 | -15.56407 | -15.56407 | -14.63489 | -15.56407 | -15.56407 | -15.35946 | -15.56407 | -15.35946 | -15.35946 |
| $\Delta E_{H_2MO}(_{AO/HO})\ (eV)$ | -1.34946 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $E_T(_{AO/HO})\ (eV)$ | 1.34946 | -14.63489 | -15.56407 | -15.56407 | -14.63489 | -15.56407 | -15.56407 | -15.35946 | -15.56407 | -15.35946 | -15.35946 |
| $E_T(_{H_2MO})\ (eV)$ | -63.27071 | -31.63534 | -67.69451 | -49.66493 | -31.63533 | -31.63537 | -31.63537 | -31.63535 | -31.63537 | -31.63535 | -31.63535 |
| $E_T\left(atom-atom,msp^3.AO\right)(eV)$ | -2.69893 | -1.44915 | 0 | 0 | 0 | -1.85836 | -1.85836 | -1.44915 | -1.85836 | -1.44915 | -1.44915 |
| $E_T(_{MO})\ (eV)$ | -65.96966 | -33.08452 | -67.69450 | -49.66493 | -31.63537 | -33.49373 | -33.49373 | -33.08452 | -33.49373 | -33.08452 | -33.08452 |
| $\omega\ \left(10^{15}\ rad/s\right)$ | 57.0928 | 16.4962 | 24.9286 | 24.2751 | 24.1759 | 9.43699 | 9.43699 | 15.4846 | 9.43699 | 9.55643 | 9.55643 |
| $E_K\ (eV)$ | 37.57947 | 10.85807 | 16.40846 | 15.97831 | 15.91299 | 6.21159 | 6.21159 | 10.19220 | 6.21159 | 6.29021 | 6.29021 |
| $\bar{E}_D\ (eV)$ | -0.40003 | -0.21568 | -0.25352 | -0.25017 | -0.24966 | -0.16515 | -0.16515 | -0.20896 | -0.16515 | -0.16416 | -0.16416 |
| $\bar{E}_{Kvib}\ (eV)$ | 0.21462 [27] | 0.14655 [28] | 0.35532 (Eq. (13.458)) | 0.35532 (Eq. (13.458)) | 0.35532 (Eq. (13.458)) | 0.12312 [2] | 0.17978 [4] | 0.09944 [5] | 0.12312 [2] | 0.12312 [2] | 0.12312 [2] |
| $\bar{E}_{osc}\ (eV)$ | -0.29272 | -0.14240 | -0.22757 | -0.14502 | -0.07200 | -0.10359 | -0.07526 | -0.15924 | -0.10359 | -0.10260 | -0.10260 |
| $E_{mag}\ (eV)$ | 0.11441 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 |
| $E_T(_{Group})\ (eV)$ | -66.55510 | -33.22692 | -67.92207 | -49.80996 | -31.70737 | -33.59732 | -33.49373 | -33.24376 | -33.59732 | -33.18712 | -33.18712 |
| $E_{initial}(_{c_4\ AO/HO})\ (eV)$ | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 |
| $E_{initial}(_{c_5\ AO/HO})\ (eV)$ | 0 | 0 | -13.59844 | -13.59844 | -13.59844 | 0 | 0 | 0 | 0 | 0 | 0 |
| $E_D(_{Group})\ (eV)$ | 7.78672 | 3.95714 | 12.49186 | 7.83016 | 3.32601 | 4.32754 | 4.29921 | 3.97398 | 4.17951 | 3.62128 | 3.91734 |

Table 15.97. The total bond energies of alkyl ketones calculated using the functional group composition and the energies of Table 15.96 compared to the experimental values [3]. The magnetic energy $E_{mag}$ that is subtracted from the weighted sum of the $E_D\,(_{Group})\,(eV)$ values based on composition is given by (15.57).

| Formula | Name | $C=O$ Group | $C-C(O)$ Group | $CH_3$ | $CH_2$ | $CH$ | $C-C$ (a) | $C-C$ (b) | $C-C$ (c) | $C-C$ (d) | $C-C$ (e) | $C-C$ (f) | $E_{mag}$ | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $C_3H_6O$ | Acetone | 1 | 2 | 2 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 40.68472 | 40.672 | -0.00031 |
| $C_4H_8O$ | 2-Butanone | 1 | 2 | 2 | 1 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 52.84242 | 52.84 | -0.00005 |
| $C_5H_{10}O$ | 2-Pentanone | 1 | 2 | 2 | 2 | 0 | 2 | 0 | 0 | 0 | 0 | 0 | 0 | 65.00012 | 64.997 | -0.00005 |
| $C_5H_{10}O$ | 3-Pentanone | 1 | 2 | 2 | 2 | 0 | 2 | 0 | 0 | 0 | 0 | 0 | 0 | 65.00012 | 64.997 | -0.00005 |
| $C_5H_{10}O$ | 3-Methyl-2-butanone | 1 | 2 | 3 | 0 | 1 | 0 | 2 | 0 | 0 | 0 | 0 | 0 | 65.10101 | 65.036 | -0.00099 |
| $C_6H_{12}O$ | 2-Hexanone | 1 | 2 | 2 | 3 | 0 | 3 | 0 | 0 | 0 | 0 | 0 | 0 | 77.15782 | 77.152 | -0.00008 |
| $C_6H_{12}O$ | 3-Hexanone | 1 | 2 | 2 | 3 | 0 | 3 | 0 | 0 | 0 | 0 | 0 | 0 | 77.15782 | 77.138 | -0.00025 |
| $C_6H_{12}O$ | 2-Methyl-3-pentanone | 1 | 2 | 3 | 1 | 1 | 1 | 2 | 0 | 0 | 0 | 0 | 0 | 77.25871 | 77.225 | -0.00043 |
| $C_6H_{12}O$ | 3,3-Dimethyl-2-butanone | 1 | 2 | 4 | 0 | 0 | 0 | 0 | 3 | 0 | 0 | 0 | -2 | 77.29432 | 77.273 | -0.00028 |
| $C_7H_{14}O$ | 3-Heptanone | 1 | 2 | 2 | 4 | 0 | 4 | 0 | 0 | 0 | 0 | 0 | 0 | 89.31552 | 89.287 | -0.00032 |
| $C_7H_{14}O$ | 4-Heptanone | 1 | 2 | 2 | 4 | 0 | 4 | 0 | 0 | 0 | 0 | 0 | 0 | 89.31552 | 89.299 | -0.00018 |
| $C_7H_{14}O$ | 2,2-Dimethyl-3-pentanone | 1 | 2 | 4 | 1 | 0 | 1 | 0 | 3 | 0 | 0 | 0 | -2 | 89.45202 | 89.458 | 0.00007 |
| $C_7H_{14}O$ | 2,4-Dimethyl-3-pentanone | 1 | 2 | 4 | 0 | 2 | 0 | 4 | 0 | 0 | 0 | 0 | 0 | 89.51730 | 89.434 | -0.00093 |
| $C_8H_{16}O$ | 2,2,4-Trimethyl-3-pentanone | 1 | 2 | 5 | 0 | 1 | 0 | 2 | 3 | 0 | 0 | 0 | -2 | 101.71061 | 101.660 | -0.00049 |
| $C_9H_{18}O$ | 2-Nonanone | 1 | 2 | 2 | 6 | 0 | 6 | 0 | 0 | 0 | 0 | 0 | 0 | 113.63092 | 113.632 | 0.00001 |
| $C_9H_{18}O$ | 5-Nonanone | 1 | 2 | 2 | 6 | 0 | 6 | 0 | 0 | 0 | 0 | 0 | 0 | 113.63092 | 113.675 | 0.00039 |
| $C_9H_{18}O$ | 2,6-Dimethyl-4-heptanone | 1 | 2 | 4 | 2 | 2 | 0 | 6 | 0 | 0 | 0 | 0 | 0 | 113.77604 | 113.807 | 0.00027 |

Table 15.98. The bond angle parameters of alkyl ketones and experimental values [1]. In the calculation of $\theta_v$, the parameters from the preceding angle were used. $E_T$ is $E_T(atom-atom,msp^3.AO)$.

| Atoms of Angle | $2c'$ Bond 1 $(a_0)$ | $2c'$ Bond 2 $(a_0)$ | $2c'$ Terminal Atoms $(a_0)$ | $E_{Coulombic}$ Atom 1 | Atom 1 Hybridization Designation (Table 15.3.A) | $E_{Coulombic}$ Atom 2 | Atom 2 Hybridization Designation (Table 15.3.A) | $c_2$ Atom 1 | $c_2$ Atom 2 | $C_1$ | $C_2$ | $c_1$ | $c_2'$ | $E_T$ (eV) | $\theta_v$ (°) | $\theta_1$ (°) | $\theta_2$ (°) | Cal. $\theta$ (°) | Exp. $\theta$ (°) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $\angle C_bC_a(O)C_c$ | 2.86175 | 2.86175 | 4.8477 | -16.68412<br>$C_b$ | 26 | -16.68412<br>$C_c$ | 26 | 0.81549 | 0.81549 | 1 | 1 | 1 | 0.81549 | -1.85836 | | | | 115.77 | 116.0<br>(acetone) |
| $\angle C_dC_bC_a(O)$ | 2.91547 | 2.86175 | 4.8374 | -16.68412<br>$C_d$ | 26 | -16.68412<br>$C_a$ | 26 | 0.81549 | 0.81549 | 1 | 1 | 1 | 0.81549 | -1.85836 | | | | 113.71 | 113.5<br>(2-butanaone) |
| $\angle C_bC_aO$ | 2.86175 | 2.29100 | 4.5166 | -15.55033 | 5 | -13.61806 | O | 0.87495 | 0.85395<br>(Eq. (15.133)) | 1 | 1 | 1 | 0.86445 | -1.44915 | | | | 122.07 | 121.9<br>(2-butanaone) |
| Methylene<br>$\angle HC_aH$ | 2.11106 | 2.11106 | 3.4252 | -15.75493 | 7 | H | H | 0.86359 | 1 | 1 | 1 | 0.75 | 1.15796 | 0 | | | | 108.44 | 107<br>(propane) |
| $\angle C_aC_bC_c$ | | | | | | | | | | | | | | | 69.51 | | | 110.49 | 112<br>(propane)<br>113.8<br>(butane)<br>110.8<br>(isobutane) |
| $\angle C_aC_bH$ | | | | | | | | | | | | | | | 69.51 | | | 110.49 | 111.0<br>(butane)<br>111.4<br>(isobutane) |
| Methyl<br>$\angle HC_aH$ | 2.09711 | 2.09711 | 3.4252 | -15.75493 | 7 | H | H | 0.86359 | 1 | 1 | 1 | 0.75 | 1.15796 | 0 | | | | 109.50 | |
| $\angle C_aC_bC_c$ | | | | | | | | | | | | | | | 70.56 | | | 109.44 | |
| $\angle C_aC_bH$ | | | | | | | | | | | | | | | 70.56 | | | 109.44 | |
| $\angle C_bC_aC_c$<br>iso $C_a$ | 2.91547 | 2.91547 | 4.7958 | -16.68412<br>$C_b$ | 26 | -16.68412<br>$C_c$ | 26 | 0.81549 | 0.81549 | 1 | 1 | 1 | 0.81549 | -1.85836 | | | | 110.67 | 110.8<br>(isobutane) |
| $\angle C_bC_aH$<br>iso $C_a$ | 2.91547 | 2.11323 | 4.1633 | -15.55033<br>$C_a$ | 5 | -14.82575<br>$C_b$ | 1 | 0.87495 | 0.91771 | 0.75 | 1 | 0.75 | 1.04887 | 0 | | | | 110.76 | |
| $\angle C_aC_bH$<br>iso $C_a$ | 2.91547 | 2.09711 | 4.1633 | -15.55033<br>$C_b$ | 5 | -14.82575<br>$C_a$ | 1 | 0.87495 | 0.91771 | 0.75 | 1 | 0.75 | 1.04887 | 0 | | | | 111.27 | 111.4<br>(isobutane) |
| $\angle C_bC_aC_b$<br>tert $C_a$ | 2.90327 | 2.90327 | 4.7958 | -16.68412<br>$C_b$ | 26 | -16.68412<br>$C_b$ | 26 | 0.81549 | 0.81549 | 1 | 1 | 1 | 0.81549 | -1.85836 | | | | 111.37 | 110.8<br>(isobutane) |
| $\angle C_bC_aC_d$ | | | | | | | | | | | | | | | 72.50 | | | 107.50 | |

## CARBOXYLIC ACIDS ($C_nH_{2n}O_2,\ n=1,2,3,4,5...\infty$)

The alkyl carboxylic acids, $C_nH_{2n}O_2$, comprise a $C=O$ functional group, and the single bond of carbon to the carbonyl carbon atom, $C-C(O)$, is also a functional group. Formic acid has a $HC=O$ moiety that comprises a more stable $C=O$ functional group and a $CH$ functional group. All carboxylic acids further comprise a $C-OH$ moiety that comprises $C-O$ and $OH$ functional groups. The alkyl portion of the alkyl carboxylic acid may comprise at least two terminal methyl groups ($CH_3$) at each end of the chain, and may comprise methylene ($CH_2$), and methylyne ($CH$) functional groups as well as $C$ bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($(CH_3)_2CH$) and t-butyl ($(CH_3)_3C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups. The branched-chain-alkane groups in carboxylic acids are equivalent to those in branched-chain alkanes.

The $CH$ functional group was solved in the Hydrogen Carbide ($CH$) section except that the energy of the $C-H$ MO is matched to the carbon-atom contribution to $\Delta E_{H_2MO}(AO/HO)$ and $E_T(atom-atom,msp^3.AO)$ of the $C-O$ group. The alkyl carboxylic acid $C=O$ and $C-C(O)$ groups are equivalent to those given in the Aldehydes section except that $\bar{E}_{Kvib}$ is that of a carboxylic acid, and $C-C(O)$ is equivalent to the n-alkane $C-C$ bond group in the case of conjugated carbonyls wherein the alkene groups when present such as the $C=C$ group are equivalent to those of the corresponding alkene. The formic acid $C=O$ group is solved equivalently to that of the alkyl carboxylic acid group, except that $\Delta E_{H_2MO}(AO/HO)$ and $E_T(atom-atom,msp^3.AO)$ correspond to a 25% increase in the donation of charge density from the orbitals of the atoms to the $C=O$ MO due to the presence of a $H$ bound to the carbonyl carbon. Also, $\bar{E}_{Kvib}$ is that corresponding to formic acid. The $C-O$ and $OH$ groups are equivalent to those of alkyl alcohols given in the corresponding section except that the energy of the $C-O$ MO is matched to that of the $C=O$ group and $\bar{E}_{Kvib}$ is that of a carboxylic acid. $\Delta E_{H_2MO}(AO/HO)$ of the $C-O$ group is equal to $E_T(atom-atom,msp^3.AO)$ of the alkyl $C=O$ group in order to match the energies of the corresponding MOs.

As in the case with aldehydes and ketones, $E_T(atom-atom,msp^3.AO)$ of the $C=O$-bond MO in Eq. (15.61) of alkyl carboxylic acids due to the charge donation from the $C$ and $O$ atoms to the MO is $-2.69893\ eV$ which is an energy minimum for the double bond between the pair of $C2sp^3$ HO electrons of the $C$ atom and the pair of AO electrons of the carbonyl $O$ atom. It is given as a linear combination of the energy contributions corresponding to a double bond, $-1.13379\ eV$ (Eq. (14.247)), and a triple bond, $-1.56513\ eV$ (Eq. (14.342)). The triple bond contribution includes the energy match of the carbonyl $C2sp^3$ HO electron with the $O$ of the $C-O$-bond MO in addition to the pair involved directly in the double bond with the carbonyl $O$.

$E_T(atom-atom,msp^3.AO)$ of the formic acid $C=O$-bond MO in Eq. (15.61) due to the charge donation from the $C$ and $O$ atoms to the MO is $-3.58557\ eV$. This is also an energy minimum for the double bond between the pair of $C2sp^3$ HO electrons of the $C$ atom and the pair of AO electrons of the carbonyl $O$ atom. It is given as a linear combination of the energy contributions corresponding to a triple bond, $-1.56513\ eV$ (Eq. (14.342)), and a quadruple bond, $-2.02043\ eV$ (Eqs. (15.18-15.21) with $s=4$)) where the bond order components are increased by an integer over that of alkyl carboxylic acids due to the presence of a $H$ bound to the carbonyl carbon.

$E_T(atom-atom,msp^3.AO)$ of the carboxylic acid $C-C(O)$ group is equivalent to that of alkanes and aldehydes, $-1.85836\ eV$, where both energy contributions are given by Eq. (14.513). It is based on the energy match between the $C2sp^3$ HOs of the carboxylic acid. As in the case of aldehydes, $C_{1o}=2C_1$ in Eq. (15.52).

$E_T(atom-atom,msp^3.AO)$ of the carboxylic acid $C-O$ group is equivalent to that of alkyl alcohols, $-1.85836\ eV$. It is based on the energy match between the $O$ AO and the $C2sp^3$ HO of a methylene group (the maximum hybridization for a single bond) where both energy contributions are given by Eq. (14.513). $E_T(atom-atom,msp^3.AO)$ of the $C-O$ group matches that of the $C-C(O)$ group.

The symbols of the functional groups of alkyl carboxylic acids are given in Table 15.99. The geometrical (Eqs. (15.1-15.5) and (15.51)), intercept (Eqs. (15.80-15.87)), and energy (Eqs. (15.6-15.11) and (15.17-15.65)) parameters of alkyl carboxylic acids are given in Tables 15.100, 15.101, and 15.102, respectively. The total energy of each alkyl carboxylic acid given in Table 15.103 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.102 corresponding to functional-group composition of the molecule. For each set of unpaired electrons created by bond breakage, the $C2sp^3$ HO magnetic energy $E_{mag}$ that is subtracted from the weighted sum of the $E_D(Group)$ $(eV)$ values based on composition is given by Eq. (15.67). The bond angle parameters of alkyl carboxylic acids determined using Eqs. (15.79-15.108) are given in Table

15.104. The color scale, translucent view of the charge-density of exemplary carboxylic acid, Propanoic acid, comprising the concentric shells of atoms with the outer shell bridged by one or more $H_2$-type ellipsoidal MOs or joined with one or more hydrogen MOs is shown in Figure 15.17.

Figure 15.17. (A)-(B) Color scale, translucent views of the charge-density of propanoic acid showing the orbitals of the atoms at their radii, the ellipsoidal surface of each $H$ or $H_2$-type ellipsoidal MO that transitions to the corresponding outer shell of the atom(s) participating in each bond, and the hydrogen nuclei (red, not to scale).

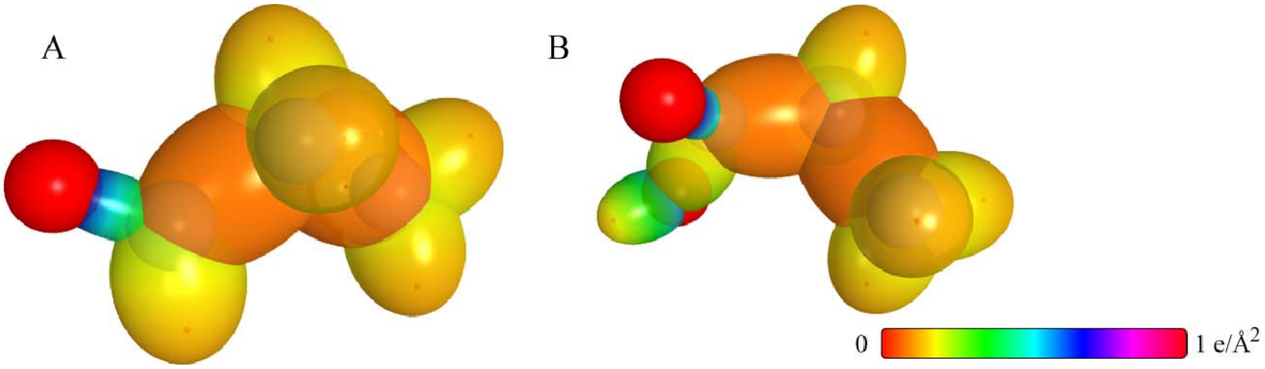


Table 15.99. The symbols of functional groups of alkyl carboxylic acids.

| Functional Group | Group Symbol |
|---|---|
| *CH* (formic acid) group | $C-H$ (i) |
| *C-C(O)* | $C-C(O)$ |
| *C=O* (formic acid) | $C=O$ (i) |
| *C=O* (alkyl carboxylic acid) | $C=O$ (ii) |
| *(O)C-O* | $C-O$ |
| *OH* group | $OH$ |
| $CH_3$ group | $C-H\ (CH_3)$ |
| $CH_2$ group | $C-H\ (CH_2)$ |
| *CH* (alkyl) group | $C-H$ (ii) |
| *CC* bond (*n-C*) | $C-C$ (a) |
| *CC* bond (*iso-C*) | $C-C$ (b) |
| *CC* bond (*tert-C*) | $C-C$ (c) |
| *CC* (*iso* to *iso-C*) | $C-C$ (d) |
| *CC* (*t* to *t-C*) | $C-C$ (e) |
| *CC* (*t* to *iso-C*) | $C-C$ (f) |
| *CC* double bond | $C=C$ |

Table 15.100. The geometrical bond parameters of alkyl carboxylic acids and experimental values [1].

| Parameter | $C-H$ (i) Group | $C-C(O)$ Group | $C=O$ (i) Group | $C=O$ (ii) Group | $C-O$ Group | $OH$ Group | $C-H\ (CH_3)$ Group | $C-H\ (CH_2)$ Group | $C-H$ (ii) Group | $C-C$ (a) Group | $C-C$ (b) Group | $C-C$ (c) Group | $C-C$ (d) Group | $C-C$ (e) Group | $C-C$ (f) Group | $C=C$ Group |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $a\ (a_0)$ | 1.61341 | 2.04740 | 1.290799 | 1.29907 | 1.73490 | 1.26430 | 1.64920 | 1.67122 | 1.67465 | 2.12499 | 2.12499 | 2.10725 | 2.12499 | 2.10725 | 2.10725 | 1.47228 |
| $c'\ (a_0)$ | 1.03711 | 1.43087 | 1.13613 | 1.13977 | 1.31716 | 0.91808 | 1.04856 | 1.05553 | 1.05661 | 1.45744 | 1.45744 | 1.45164 | 1.45744 | 1.45164 | 1.45164 | 1.26661 |
| Bond Length $2c'\ (\mathring{A})$ | 1.09763 | 1.51437 | 1.20243 | 1.20628 | 1.39402 | 0.971651 | 1.10974 | 1.11713 | 1.11827 | 1.54280 | 1.54280 | 1.53635 | 1.54280 | 1.53635 | 1.53635 | 1.34052 |
| Exp. Bond Length $(\mathring{A})$ | 1.097 (formic acid) | 1.520 (acetic acid) | 1.202 (formic acid) | 1.214 (acetic acid) | 1.393 (methyl formate) | 0.972 (formic acid) | 1.107 ($C-H$ propane)<br>1.117 ($C-H$ butane) | 1.107 ($C-H$ propane)<br>1.117 ($C-H$ butane) | 1.122 (isobutane) | 1.532 (propane)<br>1.531 (butane) | 1.532 (propane)<br>1.531 (butane) | 1.532 (propane)<br>1.531 (butane) | 1.532 (propane)<br>1.531 (butane) | 1.532 (propane)<br>1.531 (butane) | 1.532 (propane)<br>1.531 (butane) | 1.342 (2-methylpropene)<br>1.346 (2-butene)<br>1.349 (1,3-butadiene) |
| $b,c\ (a_0)$ | 1.23591 | 1.46439 | 0.61267 | 0.62331 | 1.12915 | 0.86925 | 1.27295 | 1.29569 | 1.29924 | 1.54616 | 1.54616 | 1.52750 | 1.54616 | 1.52750 | 1.52750 | 0.75055 |
| $e$ | 0.64281 | 0.69887 | 0.88018 | 0.87737 | 0.75921 | 0.72615 | 0.63580 | 0.63159 | 0.63095 | 0.68600 | 0.68600 | 0.68888 | 0.68600 | 0.68888 | 0.68888 | 0.86030 |

Table 15.101. The MO to HO intercept geometrical bond parameters of alkyl carboxylic acids. $R$, $R'$, $R''$ are $H$ or alkyl groups. $E_T$ is $E_T(atom-atom,msp^3.AO)$.

| Bond | Atom | $E_T$ (eV) Bond 1 | $E_T$ (eV) Bond 2 | $E_T$ (eV) Bond 3 | $E_T$ (eV) Bond 4 | Final Total Energy $C2sp^3$ (eV) | $r_{initial}$ $(a_0)$ | $r_{final}$ $(a_0)$ | $E_{Coulomb}$ (eV) Final | $E(C2sp^3)$ (eV) Final | $\theta'$ (°) | $\theta_1$ (°) | $\theta_2$ (°) | $d_1$ $(a_0)$ | $d_2$ $(a_0)$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $RC_a(O)O-H$ | $O$ | -0.92918 | 0 | 0 | 0 |  | 1.00000 | 0.86359 | -15.75493 |  | 115.09 | 64.91 | 64.12 | 0.55182 | 0.36625 |
| $HC_a(O)-OH$ $(C=O$ (i)) | $O$ | -0.92918 | 0 | 0 | 0 |  | 1.00000 | 0.86359 | -15.75493 |  | 101.32 | 78.68 | 48.58 | 1.14765 | 0.16950 |
| $HC_a(O)-OH$ $(C=O$ (i)) | $C_a$ | -0.92918 | -1.79278 | 0 | 0 | -154.33765 | 0.91771 | 0.77536 | -17.54772 | -17.35685 | 93.94 | 86.06 | 43.24 | 1.26386 | 0.05329 |
| $RH_2C_bC_a(O)-OH$ | $O$ | -0.92918 | 0 | 0 | 0 |  | 1.00000 | 0.86359 | -15.75493 |  | 101.32 | 78.68 | 48.58 | 1.14765 | 0.16950 |
| $RH_2C_bC_a(O)-OH$ | $C_a$ | -0.92918 | -1.34946 | -0.92918 | 0 | -154.82352 | 0.91771 | 0.75447 | -18.03358 | -17.84271 | 91.96 | 88.04 | 41.90 | 1.29138 | 0.02578 |
| $HC_a(OH)=O$ $(C=O$ (i)) | $O$ | -1.79278 | 0 | 0 | 0 |  | 1.00000 | 0.81871 | -16.61853 |  | 137.10 | 42.90 | 65.45 | 0.53635 | 0.59978 |
| $HC_a(OH)=O$ $(C=O$ (i)) | $C_a$ | -1.79278 | -0.92918 | 0 | 0 | -154.33766 | 0.91771 | 0.77536 | -17.54772 | -17.35685 | 135.24 | 44.76 | 63.02 | 0.58561 | 0.55053 |
| $RC_bH_2C_a(OH)=O$ $(C=O$ (ii)) | $O$ | -1.34946 | 0 | 0 | 0 |  | 1.00000 | 0.84115 | -16.17521 |  | 137.27 | 42.73 | 66.31 | 0.52193 | 0.61784 |
| $RC_bH_2C_a(OH)=O$ $(C=O$ (ii)) | $C_a$ | -1.34946 | -0.92918 | -0.92918 | 0 | -154.82352 | 0.91771 | 0.75447 | -18.03358 | -17.84271 | 133.47 | 46.53 | 61.46 | 0.62072 | 0.51905 |
| $H-C(O)OH$ $(CH$ (i)) | $C$ | -1.79278 | -0.92918 | 0 | 0 | -154.33766 | 0.91771 | 0.77536 | -17.54772 | -17.35685 | 69.89 | 110.11 | 36.09 | 1.30373 | 0.26662 |
| $RH_2C_b-C_a(O)OH$ | $C_a$ | -0.92918 | -1.34946 | -0.92918 | 0 | -154.82352 | 0.91771 | 0.75447 | -18.03358 | -17.84271 | 56.25 | 123.75 | 25.37 | 1.85002 | 0.41915 |
| $H_3C_b-C_a(O)OH$ | $C_b$ | -0.92918 | 0 | 0 | 0 | -152.54487 | 0.91771 | 0.86359 | -15.75493 | -15.56407 | 72.27 | 107.73 | 34.17 | 1.69388 | 0.26301 |
| $RH_2C_cH_2C_b-C_a(O)OH$ | $C_b$ | -0.92918 | -0.92918 | 0 | 0 | -153.47405 | 0.91771 | 0.81549 | -16.68411 | -16.49325 | 65.99 | 114.01 | 30.58 | 1.76270 | 0.33183 |
| $C-H\ (CH_3)$ | $C$ | -0.92918 | 0 | 0 | 0 | -152.54487 | 0.91771 | 0.86359 | -15.75493 | -15.56407 | 77.49 | 102.51 | 41.48 | 1.23564 | 0.18708 |
| $C-H\ (CH_2)$ | $C$ | -0.92918 | -0.92918 | 0 | 0 | -153.47406 | 0.91771 | 0.81549 | -16.68412 | -16.49325 | 68.47 | 111.53 | 35.84 | 1.35486 | 0.29933 |
| $C-H\ (CH)$ (ii) | $C$ | -0.92918 | -0.92918 | -0.92918 | 0 | -154.40324 | 0.91771 | 0.77247 | -17.61330 | -17.42244 | 61.10 | 118.90 | 31.37 | 1.42988 | 0.37326 |
| $H_3C_aC_bH_2CH_2-$ $(C-C$ (a)) | $C_a$ | -0.92918 | 0 | 0 | 0 | -152.54487 | 0.91771 | 0.86359 | -15.75493 | -15.56407 | 63.82 | 116.18 | 30.08 | 1.83879 | 0.38106 |
| $H_3C_aC_bH_2CH_2-$ $(C-C$ (a)) | $C_b$ | -0.92918 | -0.92918 | 0 | 0 | -153.47406 | 0.91771 | 0.81549 | -16.68412 | -16.49325 | 56.41 | 123.59 | 26.06 | 1.90890 | 0.45117 |
| $R-H_2C_aC_b(H_2C_c-R')HCH_2-$ $(C-C$ (b)) | $C_b$ | -0.92918 | -0.92918 | -0.92918 | 0 | -154.40324 | 0.91771 | 0.77247 | -17.61330 | -17.42244 | 48.30 | 131.70 | 21.90 | 1.97162 | 0.51388 |
| $R-H_2C_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ $(C-C$ (c)) | $C_b$ | -0.92918 | -0.72457 | -0.72457 | -0.72457 | -154.71860 | 0.91771 | 0.75889 | -17.92866 | -17.73779 | 48.21 | 131.79 | 21.74 | 1.95734 | 0.50570 |
| $isoC_aC_b(H_2C_c-R')HCH_2-$ $(C-C$ (d)) | $C_b$ | -0.92918 | -0.92918 | -0.92918 | 0 | -154.40324 | 0.91771 | 0.77247 | -17.61330 | -17.42244 | 48.30 | 131.70 | 21.90 | 1.97162 | 0.51388 |
| $tertC_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ $(C-C$ (e)) | $C_b$ | -0.72457 | -0.72457 | -0.72457 | -0.72457 | -154.51399 | 0.91771 | 0.76765 | -17.92866 | -17.73779 | 50.04 | 129.96 | 22.66 | 1.94462 | 0.49298 |
| $tertC_aC_b(H_2C_c-R')HCH_2-$ $(C-C$ (f)) | $C_b$ | -0.72457 | -0.92918 | -0.92918 | 0 | -154.19863 | 0.91771 | 0.78155 | -17.40869 | -17.21783 | 52.78 | 127.22 | 24.04 | 1.92443 | 0.47279 |
| $isoC_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ $(C-C$ (f)) | $C_b$ | -0.72457 | -0.72457 | -0.72457 | -0.72457 | -154.51399 | 0.91771 | 0.76765 | -17.92866 | -17.73779 | 50.04 | 129.96 | 22.66 | 1.94462 | 0.49298 |

Table 15.102. The energy parameters ($eV$) of functional groups of alkyl carboxylic acids.

| Parameters | $C-H$ (i) Group | $C-C(O)$ Group | $C=O$ (i) Group | $C=O$ (ii) Group | $C-O$ Group | $OH$ Group | $CH_3$ Group | $CH_2$ Group | $C-H$ (ii) Group | $C-C$ (a) Group | $C-C$ (b) Group | $C-C$ (c) Group | $C-C$ (d) Group | $C-C$ (e) Group | $C-C$ (f) Group | $C=C$ Group |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $n_1$ | 1 | 1 | 2 | 2 | 1 | 1 | 3 | 2 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 2 |
| $n_2$ | 0 | 0 | 0 | 0 | 0 | 0 | 2 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $n_3$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $C_1$ | 0.75 | 0.5 | 0.5 | 0.5 | 0.5 | 0.75 | 0.75 | 0.75 | 0.75 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| $C_2$ | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 0.91771 |
| $c_1$ | 1 | 1 | 1 | 1 | 1 | 0.75 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $c_2$ | 0.91771 | 0.91771 | 0.85395 | 0.85395 | 0.85395 | 1 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 |
| $c_3$ | 0 | 0 | 2 | 2 | 0 | 1 | 0 | 1 | 1 | 0 | 0 | 0 | 1 | 1 | 0 | 0 |
| $c_4$ | 1 | 2 | 4 | 4 | 2 | 1 | 1 | 1 | 1 | 2 | 2 | 2 | 2 | 2 | 2 | 4 |
| $c_5$ | 1 | 0 | 0 | 0 | 0 | 1 | 3 | 2 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $C_{1o}$ | 0.75 | 1 | 0.5 | 0.5 | 0.5 | 0.75 | 0.75 | 0.75 | 0.75 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| $C_{2o}$ | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 0.91771 |
| $V_e\ (eV)$ | -36.74167 | -30.19634 | -112.61934 | -111.25473 | -35.08488 | -40.92709 | -107.32728 | -70.41425 | -35.12015 | -28.79214 | -28.79214 | -29.10112 | -28.79214 | -29.10112 | -29.10112 | -102.08992 |
| $V_p\ (eV)$ | 13.11890 | 9.50874 | 23.95107 | 23.87467 | 10.32968 | 14.81988 | 38.92728 | 25.78002 | 12.87680 | 9.33352 | 9.33352 | 9.37273 | 9.33352 | 9.37273 | 9.37273 | 21.48386 |
| $T\ (eV)$ | 11.38634 | 7.37432 | 43.62389 | 42.82081 | 10.11150 | 16.18567 | 32.53914 | 21.06675 | 10.48582 | 6.77464 | 6.77464 | 6.90500 | 6.77464 | 6.90500 | 6.90500 | 34.67062 |
| $V_m\ (eV)$ | -5.69317 | -3.68716 | -21.81195 | -21.41040 | -5.05575 | -8.09284 | -16.26957 | -10.53337 | -5.24291 | -3.38732 | -3.38732 | -3.45250 | -3.38732 | -3.45250 | -3.45250 | -17.33531 |
| $E(_{AO/HO})\ (eV)$ | -14.63489 | -14.63489 | 0 | 0 | -14.63489 | -13.6181 | -15.56407 | -15.56407 | -14.63489 | -15.56407 | -15.56407 | -15.35946 | -15.56407 | -15.35946 | -15.35946 | 0 |
| $\Delta E_{H_2MO}(_{AO/HO})\ (eV)$ | -0.92918 | 0 | -3.58557 | -2.69893 | -2.69893 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $E_T(_{AO/HO})\ (eV)$ | -13.70571 | -14.63489 | 3.58557 | 2.69893 | -11.93596 | -13.6181 | -15.56407 | -15.56407 | -14.63489 | -15.56407 | -15.56407 | -15.35946 | -15.56407 | -15.35946 | -15.35946 | 0 |
| $E_T(_{H_2MO})\ (eV)$ | -31.63530 | -31.63534 | -63.27075 | -63.27074 | -31.63541 | -31.63247 | -67.69451 | -49.66493 | -31.63533 | -31.63537 | -31.63537 | -31.63535 | -31.63537 | -31.63535 | -31.63535 | -63.27075 |
| $E_T\left(atom-atom,msp^3.AO\right)\ (eV)$ | 0 | -1.85836 | -3.58557 | -2.69893 | -1.85836 | 0 | 0 | 0 | 0 | -1.85836 | -1.85836 | -1.44915 | -1.85836 | -1.44915 | -1.44915 | -2.26759 |
| $E_T(_{MO})\ (eV)$ | -31.63537 | -33.49373 | -66.85630 | -65.96966 | -33.49373 | -31.63537 | -67.69450 | -49.66493 | -31.63537 | -33.49373 | -33.49373 | -33.08452 | -33.49373 | -33.08452 | -33.08452 | -65.53833 |
| $\omega\ \left(10^{15}\ rad/s\right)$ | 26.0575 | 23.3291 | 60.9581 | 59.4034 | 24.3637 | 44.1776 | 24.9286 | 24.2751 | 24.1759 | 9.43699 | 9.43699 | 15.4846 | 9.43699 | 9.55643 | 9.55643 | 43.0680 |
| $E_K\ (eV)$ | 17.15150 | 15.35563 | 40.12366 | 39.10034 | 16.03660 | 29.07844 | 16.40846 | 15.97831 | 15.91299 | 6.21159 | 6.21159 | 10.19220 | 6.21159 | 6.29021 | 6.29021 | 28.34813 |
| $\bar{E}_D\ (eV)$ | -0.25920 | -0.25966 | -0.41891 | -0.40804 | -0.26535 | -0.33749 | -0.25352 | -0.25017 | -0.24966 | -0.16515 | -0.16515 | -0.20896 | -0.16515 | -0.16416 | -0.16416 | -0.34517 |
| $\bar{E}_{Kvib}\ (eV)$ | 0.35532 (Eq. (13.458)) | 0.10502 [29] | 0.21945 [30] | 0.21077 [12] | 0.14010 [31] | 0.46311 [17-18] | 0.35532 (Eq. (13.458)) | 0.35532 (Eq. (13.458)) | 0.35532 (Eq. (13.458)) | 0.12312 [2] | 0.17978 [4] | 0.09944 [5] | 0.12312 [2] | 0.12312 [2] | 0.12312 [2] | 0.17897 [6] |
| $\bar{E}_{osc}\ (eV)$ | -0.08153 | -0.20715 | -0.30918 | -0.30266 | -0.19530 | -0.10594 | -0.22757 | -0.14502 | -0.07200 | -0.10359 | -0.07526 | -0.15924 | -0.10359 | -0.10260 | -0.10260 | -0.25568 |
| $E_{mag}\ (eV)$ | 0.14803 | 0.14803 | 0.11441 | 0.11441 | 0.14803 | 0.11441 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 |
| $E_T(_{Group})\ (eV)$ | -31.71690 | -33.70088 | -67.47466 | -66.57498 | -33.68903 | -31.74130 | -67.92207 | -49.80996 | -31.70737 | -33.59732 | -33.49373 | -33.24376 | -33.59732 | -33.18712 | -33.18712 | -66.04969 |
| $E_{initial}(_{c_4\ AO/HO})\ (eV)$ | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -13.6181 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 |
| $E_{initial}(_{c_5\ AO/HO})\ (eV)$ | -13.59844 | 0 | 0 | 0 | 0 | -13.59844 | -13.59844 | -13.59844 | -13.59844 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $E_D(_{Group})\ (eV)$ | 3.48357 | 4.43110 | 8.70628 | 7.80660 | 4.41925 | 4.41035 | 12.49186 | 7.83016 | 3.32601 | 4.32754 | 4.29921 | 3.97398 | 4.17951 | 3.62128 | 3.91734 | 7.51014 |

Table 15.103. The total bond energies of alkyl carboxylic acids calculated using the functional group composition and the energies of Table 15.102 compared to the experimental values [3]. The magnetic energy $E_{mag}$ that is subtracted from the weighted sum of the $E_D$ $(_{Group})$ $(eV)$ values based on composition is given by (15.57).

| Formula | Name | $C-H$ (i) Group | $C-C(O)$ Group | $C=O$ (i) Group | $C=O$ (ii) Group | $C-O$ Group | $OH$ Group | $CH_3$ | $CH_2$ | $CH$ (ii) | $C-C$ (a) | $C-C$ (b) | $C-C$ (c) | $C-C$ (d) | $C-C$ (e) | $C-C$ (f) | $C=C$ | $E_{mag}$ | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $CH_2O_2$ | Formic acid | 1 | 0 | 1 | 0 | 1 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 21.01945 | 21.036 | 0.00079 |
| $C_2H_4O_2$ | Acetic acid | 0 | 1 | 0 | 1 | 1 | 1 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 33.55916 | 33.537 | -0.00066 |
| $C_3H_6O_2$ | Propanoic acid | 0 | 1 | 0 | 1 | 1 | 1 | 1 | 1 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 45.71686 | 45.727 | 0.00022 |
| $C_4H_8O_2$ | Butanoic acid | 0 | 1 | 0 | 1 | 1 | 1 | 1 | 2 | 0 | 2 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 57.87456 | 57.883 | 0.00015 |
| $C_4H_4O_4$ | Maleic acid | 0 | 0 | 0 | 2 | 2 | 2 | 0 | 0 | 2 | 2 | 0 | 0 | 0 | 0 | 0 | 1 | 0 | 56.08964 | 56.120 | 0.00054 |
| $C_4H_4O_4$ | Fumaric acid | 0 | 0 | 0 | 2 | 2 | 2 | 0 | 0 | 2 | 2 | 0 | 0 | 0 | 0 | 0 | 1 | 0 | 56.08964 | 56.083 | -0.00013 |
| $C_5H_{10}O_2$ | Pentanoic acid | 0 | 1 | 0 | 1 | 1 | 1 | 1 | 3 | 0 | 3 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 70.03226 | 69.995 | -0.00053 |
| $C_5H_{10}O_2$ | 3-Methylbutanoic acid | 0 | 1 | 0 | 1 | 1 | 1 | 2 | 1 | 1 | 0 | 3 | 0 | 0 | 0 | 0 | 0 | 0 | 70.10482 | 70.183 | 0.00111 |
| $C_5H_{10}O_2$ | 2,2-Dimethylpropanoic acid | 0 | 1 | 0 | 1 | 1 | 1 | 3 | 0 | 0 | 0 | 0 | 3 | 0 | 0 | 0 | 0 | -1 | 70.31679 | 69.989 | -0.00468 |
| $C_6H_{12}O_2$ | Hexanoic acid | 0 | 1 | 0 | 1 | 1 | 1 | 1 | 4 | 0 | 4 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 82.18996 | 82.149 | -0.00050 |
| $C_7H_{14}O_2$ | Heptanoic acid | 0 | 1 | 0 | 1 | 1 | 1 | 1 | 5 | 0 | 5 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 94.34766 | 94.347 | 0.00000 |
| $C_8H_{16}O_2$ | Octanoic acid | 0 | 1 | 0 | 1 | 1 | 1 | 1 | 6 | 0 | 6 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 106.50536 | 106.481 | -0.00022 |
| $C_9H_{18}O_2$ | Nonanoic acid | 0 | 1 | 0 | 1 | 1 | 1 | 1 | 7 | 0 | 7 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 118.66306 | 118.666 | 0.00003 |
| $C_{10}H_{20}O_2$ | Decanoic acid | 0 | 1 | 0 | 1 | 1 | 1 | 1 | 8 | 0 | 8 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 130.82076 | 130.795 | -0.00020 |
| $C_{12}H_{24}O_2$ | Dodecanoic acid | 0 | 1 | 0 | 1 | 1 | 1 | 1 | 10 | 0 | 10 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 155.13616 | 155.176 | 0.00026 |
| $C_{14}H_{28}O_2$ | Tetradecanoic acid | 0 | 1 | 0 | 1 | 1 | 1 | 1 | 12 | 0 | 12 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 179.45156 | 179.605 | 0.00085 |
| $C_{15}H_{30}O_2$ | Pentadecanoic acid | 0 | 1 | 0 | 1 | 1 | 1 | 1 | 13 | 0 | 13 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 191.60926 | 191.606 | -0.00002 |
| $C_{16}H_{32}O_2$ | Hexadecanoic acid | 0 | 1 | 0 | 1 | 1 | 1 | 1 | 14 | 0 | 14 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 203.76696 | 203.948 | 0.00089 |
| $C_{18}H_{36}O_2$ | Stearic acid | 0 | 1 | 0 | 1 | 1 | 1 | 1 | 16 | 0 | 16 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 228.08236 | 228.298 | 0.00094 |
| $C_{20}H_{40}O_2$ | Eicosanoic acid | 0 | 1 | 0 | 1 | 1 | 1 | 1 | 18 | 0 | 18 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 252.39776 | 252.514 | 0.00046 |

Table 15.104. The bond angle parameters of alkyl carboxylic acids and experimental values [1]. In the calculation of $\theta_v$, the parameters from the preceding angle were used. $E_T$ is $E_T(atom - atom, msp^3.AO)$.

| Atoms of Angle | $2c'$ Bond 1 ($a_0$) | $2c'$ Bond 2 ($a_0$) | $2c'$ Terminal Atoms ($a_0$) | $E_{Coulombic}$ Atom 1 | Atom 1 Hybridization Designation (Table 15.3.A) | $E_{Coulombic}$ Atom 2 | Atom 2 Hybridization Designation (Table 15.3.A) | $c_2$ Atom 1 | $c_2$ Atom 2 | $C_1$ | $C_2$ | $c_1$ | $c_2'$ | $E_T$ (eV) | $\theta_v$ (°) | $\theta_1$ (°) | $\theta_2$ (°) | Cal. $\theta$ (°) | Exp. $\theta$ (°) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $\angle HC_aO_a$ ($CH$ (i); $C=O$ (i)) | 2.06598 | 2.27227 | 3.8816 | -15.55033 $C_a$ | 5 | -13.61806 | O | 0.87495 | 0.85395 (Eq. (15.133)) | 0.75 | 1 | 0.75 | 0.97600 | 0 | | | | 126.88 | 124.1 (formic acid) |
| $\angle HC_aO_b$ ($CH$ (i)) | 2.06598 | 2.63431 | 3.8816 | -15.55033 $C_a$ | 5 | -13.61806 | O | 0.87495 | 0.85395 (Eq. (15.133)) | 0.75 | 1 | 0.75 | 0.97600 | 0 | | | | 110.76 | |
| $\angle O_aC_aO_b$ | 2.27227 | 2.63431 | 4.3243 | -16.61853 $O_a$ | 24 | -15.75493 $O_b$ | 7 | 0.81871 | 0.86359 | 1 | 1 | 1 | 0.84115 | -1.44915 | | | | 123.44 | 124.9 (formic acid) |
| $\angle C_aO_bH$ ($CH$ (i); $C=O$ (i)) | 2.63431 | 1.83616 | 3.6405 | -14.82575 | 1 | -14.82575 | 1 | 1 | 0.91771 | 0.75 | 1 | 0.75 | 0.91771 | 0 | | | | 107.71 | 106.3 (formic acid) |
| $\angle C_bC_aO_a$ | 2.86175 | 2.27954 | 4.5826 | -16.68411 | 25 | -13.61806 | O | 0.81549 | 0.85395 (Eq. (15.133)) | 1 | 1 | 1 | 0.83472 | -1.65376 | | | | 125.70 | 126.6 (acetic acid) |
| $\angle C_bC_aO_b$ | 2.86175 | 2.63431 | 4.4944 | -15.75493 | 7 | -13.61806 | O | 0.86359 | 0.85395 (Eq. (15.133)) | 1 | 1 | 1 | 0.85877 | -1.44915 | | | | 109.65 | 110.6 (acetic acid) |
| $\angle O_aC_aO_b$ | 2.27954 | 2.63431 | 4.3818 | -16.17521 $O_a$ | 13 | -15.75493 $O_b$ | 7 | 0.84115 | 0.86359 | 1 | 1 | 1 | 0.85237 | -1.44915 | | | | 126.03 | |
| Methylene $\angle HC_aH$ | 2.11106 | 2.11106 | 3.4252 | -15.75493 | 7 | H | H | 0.86359 | 1 | 1 | 1 | 0.75 | 1.15796 | 0 | | | | 108.44 | 107 (propane) |
| $\angle C_aC_bC_c$ | | | | | | | | | | | | | | | 69.51 | | | 110.49 | 112 (propane)<br>113.8 (butane)<br>110.8 (isobutane) |
| $\angle C_aC_bH$ | | | | | | | | | | | | | | | 69.51 | | | 110.49 | 111.0 (butane)<br>111.4 (isobutane) |
| Methyl $\angle HC_aH$ | 2.09711 | 2.09711 | 3.4252 | -15.75493 | 7 | H | H | 0.86359 | 1 | 1 | 1 | 0.75 | 1.15796 | 0 | | | | 109.50 | |
| $\angle C_aC_bC_c$ | | | | | | | | | | | | | | | 70.56 | | | 109.44 | |
| $\angle C_aC_bH$ | | | | | | | | | | | | | | | 70.56 | | | 109.44 | |
| $\angle C_bC_aC_c$ iso $C_a$ | 2.91547 | 2.91547 | 4.7958 | -16.68412 $C_b$ | 26 | -16.68412 $C_c$ | 26 | 0.81549 | 0.81549 | 1 | 1 | 1 | 0.81549 | -1.85836 | | | | 110.67 | 110.8 (isobutane) |
| $\angle C_bC_aH$ iso $C_a$ | 2.91547 | 2.11323 | 4.1633 | -15.55033 $C_a$ | 5 | -14.82575 $C_b$ | 1 | 0.87495 | 0.91771 | 0.75 | 1 | 0.75 | 1.04887 | 0 | | | | 110.76 | |
| $\angle C_aC_bH$ iso $C_a$ | 2.91547 | 2.09711 | 4.1633 | -15.55033 $C_b$ | 5 | -14.82575 $C_a$ | 1 | 0.87495 | 0.91771 | 0.75 | 1 | 0.75 | 1.04887 | 0 | | | | 111.27 | 111.4 (isobutane) |
| $\angle C_bC_aC_b$ tert $C_a$ | 2.90327 | 2.90327 | 4.7958 | -16.68412 $C_b$ | 26 | -16.68412 $C_b$ | 26 | 0.81549 | 0.81549 | 1 | 1 | 1 | 0.81549 | -1.85836 | | | | 111.37 | 110.8 (isobutane) |
| $\angle C_bC_aC_d$ | | | | | | | | | | | | | | | 72.50 | | | 107.50 | |

## CARBOXYLIC ACID ESTERS ($C_nH_{2n}O_2,\ n=1,2,3,4,5...\infty$)

The alkyl carboxylic acid esters, $C_nH_{2n}O_2$, comprise a $C=O$ functional group, and the single bond of carbon to the carbonyl carbon atom, $C-C(O)$, is also a functional group. Formic acid ester has a $HC=O$ moiety that comprises a more stable $C=O$ functional group and a $CH$ functional group. All carboxylic acid esters further comprise a $COR$ moiety that comprises a $C-O$ functional group and three types of $O-R$ functional groups, one for $R$ comprising methyl, one for $R$ comprising an alkyl ester group of a formate, and one for $R$ comprising an alkyl ester group of an alkyl carboxylate. The alkyl portion of the alkyl carboxylic acid ester may comprise at least two terminal methyl groups ($CH_3$) at each end of the chain, and may comprise methylene ($CH_2$), and methylyne ($CH$) functional groups as well as $C$ bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($\left(CH_3\right)_2CH$) and t-butyl ($\left(CH_3\right)_3C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups. The branched-chain-alkane groups in carboxylic acid esters are equivalent to those in branched-chain alkanes.

The $CH$ functional group is equivalent to that of formic acid. The alkyl carboxylic acid ester $C=O$ and $C-C(O)$ groups are equivalent to those given in the Carboxylic Acids section. The formic acid ester $C=O$ group is equivalent to that given in the Carboxylic Acids section except that $\overline{E}_{Kvib}$ is that corresponding to a formic acid ester. The $C-O$ group is equivalent to that given in the Carboxylic Acids section except that the parameters corresponding to oscillation of the bond in the transition state, $\overline{E}_D$ $(eV)$ and $\overline{E}_{Kvib}$, are those of a carboxylic acid ester. As in the case with the alkyl ethers, each $O-C$ group is solved by hybridizing the $2s$ and $2p$ AOs of the $C$ atom to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between the $C2sp^3$ HO and the $O$ AO to form a MO permits each participating orbital to decrease in radius and energy. To meet the equipotential condition of the union of the $O-C$ $H_2$-type-ellipsoidal-MO with other orbitals of the molecule, the hybridization factor $c_2$ of Eq. (15.60) for the $O-C$-bond MO given by Eq. (15.133) is: $c_2\left(C2sp^3HO\ to\ O\right)=0.85395$.

$E_T\left(atom-atom,msp^3.AO\right)$ (Eq. (15.61)) of (1) the $C=O$ group of alkyl carboxylic acid esters, (2) the $C=O$ group of formic acid esters, (3) the alkyl carboxylic acid ester $C-C(O)$ group, and (4) the carboxylic acid ester $C-O$ group are equivalent to those of the corresponding carboxylic acids. The values given in the Carboxylic Acids section are $-2.69893\ eV$, $-3.58557\ eV$, $-1.85836\ eV$, and $-1.85836\ eV$, respectively. $E_T\left(atom-atom,msp^3.AO\right)$ of the $C-O$ group matches that of the $C-C(O)$ group. Also, as in the case of aldehydes, $C_{1o}=2C_1$ in Eq. (15.61) for the $C-C(O)$ group.

$E_T\left(atom-atom,msp^3.AO\right)$ of the $O-C$-bond MO in Eq. (15.61) due to the charge donation from the $C$ and $O$ atoms to the MO is $-1.13379\ eV$ for the $O-CH_3$ group of formate and alkyl carboxylates, $-1.44915\ eV$ for the $O-R$ group of alkyl carboxylates, and $-1.85836\ eV$ for the $O-R$ group of alkyl formates, where $R$ is an alkyl group. Each is based on the energy match between the $O$ AO, initially at the Coulomb potential of a proton and an electron (Eqs. (1.257) and (10.162), respectively), the $C2sp^3$ HO of the methyl or alkyl ester group, and the carbonyl carbon. The increasing energy contributions to the single bond correspond to the increasing hybridization of linear combinations of increasing bond order. The energy contributions corresponding to one half of a double bond and those of the methyl-methyl and methylene-methylene bonds are $-1.13379\ eV$ (Eq. (14.247)), two times $-0.72457\ eV$ (Eq. (14.151)), and two times $-0.92918\ eV$ (Eq. (14.513)), respectively.

The symbols of the functional groups of alkyl carboxylic acid esters are given in Table 15.105. The geometrical (Eqs. (15.1-15.5) and (15.51)), intercept (Eqs. (15.80-15.87)), and energy (Eqs. (15.6-15.11) and (15.17-15.65)) parameters of alkyl carboxylic acid esters are given in Tables 15.106, 15.107, and 15.108, respectively. The total energy of each alkyl carboxylic acid ester given in Table 15.109 was calculated as the sum over the integer multiple of each $E_D\left(Group\right)$ of Table 15.108 corresponding to functional-group composition of the molecule. For each set of unpaired electrons created by bond breakage , the $C2sp^3$ HO magnetic energy $E_{mag}$ that is subtracted from the weighted sum of the $E_D\left(Group\right)$ $(eV)$ values based on composition is given by Eq. (15.67). The bond angle parameters of alkyl carboxylic acid esters determined using Eqs. (15.88-15.117) are given in Table 15.110. The color scale, translucent view of the charge-density of exemplary carboxylic acid ester, methyl acetate, comprising the concentric shells of atoms with the outer shell bridged by one or more $H_2$-type ellipsoidal MOs or joined with one or more hydrogen MOs is shown in Figure 15.18.

Figure 15.18. Color scale, translucent view of the charge-density of methyl acetate showing the orbitals of the atoms at their radii, the ellipsoidal surface of each $H$ or $H_2$-type ellipsoidal MO that transitions to the corresponding outer shell of the atom(s) participating in each bond, and the hydrogen nuclei (red, not to scale).

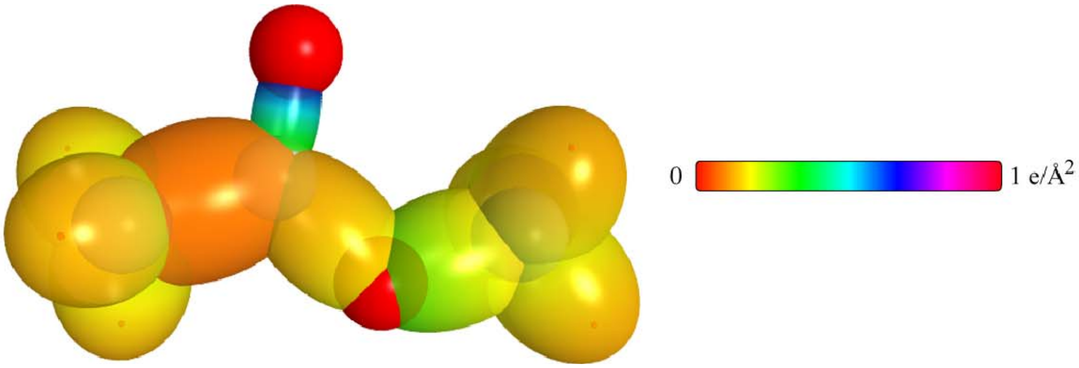


Table 15.105. The symbols of functional groups of alkyl carboxylic acid esters.

| Functional Group | Group Symbol |
|---|---|
| *CH* (formic acid ester) group | $C-H$ (i) |
| *C-C(O)* | $C-C(O)$ |
| *C=O* (formic acid ester) | $C=O$ (i) |
| *C=O* (alkyl carboxylic acid ester) | $C=O$ (ii) |
| *(O)C-O* | $C-O$ |
| $O\text{-}CH_3$ | $O-C$ (i) |
| *O-R* (formic acid ester) | $O-C$ (ii) |
| *O-R* (alkyl acid ester) | $O-C$ (iii) |
| *OH* group | $OH$ |
| $CH_3$ group | $C-H\ (CH_3)$ |
| $CH_2$ group | $C-H\ (CH_2)$ |
| *CH* (alkyl) group | $C-H$ (ii) |
| *CC* bond (*n-C*) | $C-C$ (a) |
| *CC* bond (*iso-C*) | $C-C$ (b) |
| *CC* bond (*tert-C*) | $C-C$ (c) |
| *CC* (*iso* to *iso-C*) | $C-C$ (d) |
| *CC* (*t* to *t-C*) | $C-C$ (e) |
| *CC* (*t* to *iso-C*) | $C-C$ (f) |

**Table 15.106.** The geometrical bond parameters of alkyl carboxylic acid esters and experimental values [1].

| Parameter | $C-H$ (i) Group | $C-C(O)$ Group | $C=O$ (i) Group | $C=O$ (ii) Group | $C-O$ Group | $O-C$ (i) Group | $O-C$ (ii) Group | $O-C$ (iii) Group | $C-H\left(CH_3\right)$ Group | $C-H\left(CH_2\right)$ Group | $C-H$ (ii) Group | $C-C$ (a) Group | $C-C$ (b) Group | $C-C$ (c) Group | $C-C$ (d) Group | $C-C$ (e) Group | $C-C$ (f) Group |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $a\left(a_0\right)$ | 1.61341 | 2.04740 | 1.290799 | 1.29907 | 1.73490 | 1.82683 | 1.78255 | 1.80717 | 1.64920 | 1.67122 | 1.67465 | 2.12499 | 2.12499 | 2.10725 | 2.12499 | 2.10725 | 2.10725 |
| $c'\left(a_0\right)$ | 1.03711 | 1.43087 | 1.13613 | 1.13977 | 1.31716 | 1.35160 | 1.33512 | 1.34431 | 1.04856 | 1.05553 | 1.05661 | 1.45744 | 1.45744 | 1.45164 | 1.45744 | 1.45164 | 1.45164 |
| Bond Length $2c'$ $\left(\mathring{A}\right)$ | 1.09763 | 1.51437 | 1.20243 | 1.20628 | 1.39402 | 1.43047 | 1.41303 | 1.42276 | 1.10974 | 1.11713 | 1.11827 | 1.54280 | 1.54280 | 1.53635 | 1.54280 | 1.53635 | 1.53635 |
| Exp. Bond Length $\left(\mathring{A}\right)$ | 1.101 (methyl formate) | 1.520 (acetic acid) | 1.206 (methyl formate) | 1.214 (acetic acid) | 1.393 (avg. methyl formate) | 1.393 (avg. methyl formate) | 1.393 (avg. methyl formate) | 1.393 (avg. methyl formate) | 1.08 (methyl formate)<br>1.107 ($C-H$ propane)<br>1.117 ($C-H$ butane) | 1.107 ($C-H$ propane)<br>1.117 ($C-H$ butane) | 1.122 (isobutane) | 1.532 (propane)<br>1.531 (butane) | 1.532 (propane)<br>1.531 (butane) | 1.532 (propane)<br>1.531 (butane) | 1.532 (propane)<br>1.531 (butane) | 1.532 (propane)<br>1.531 (butane) | 1.532 (propane)<br>1.531 (butane) |
| $b,c\left(a_0\right)$ | 1.23591 | 1.46439 | 0.61267 | 0.62331 | 1.12915 | 1.22901 | 1.18107 | 1.20776 | 1.27295 | 1.29569 | 1.29924 | 1.54616 | 1.54616 | 1.52750 | 1.54616 | 1.52750 | 1.52750 |
| $e$ | 0.64281 | 0.69887 | 0.88018 | 0.87737 | 0.75921 | 0.73986 | 0.74900 | 0.74388 | 0.63580 | 0.63159 | 0.63095 | 0.68600 | 0.68600 | 0.68888 | 0.68600 | 0.68888 | 0.68888 |

Table 15.107. The MO to HO intercept geometrical bond parameters of alkyl carboxylic acid esters. $R$, $R'$, $R''$ are $H$ or alkyl groups. $E_T$ is $E_T$ ($atom - atom, msp^3.AO$).

| Bond | Atom | $E_T$ (eV) Bond 1 | $E_T$ (eV) Bond 2 | $E_T$ (eV) Bond 3 | $E_T$ (eV) Bond 4 | Final Total Energy $C2sp^3$ (eV) | $r_{initial}$ $(a_0)$ | $r_{final}$ $(a_0)$ | $E_{Coulomb}$ (eV) Final | $E(C2sp^3)$ (eV) Final | $\theta'$ $(°)$ | $\theta_1$ $(°)$ | $\theta_2$ $(°)$ | $d_1$ $(a_0)$ | $d_2$ $(a_0)$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $RC_a(O)O-C_bH_3$<br>$(O-C$ (i)) | $O$ | -0.92918 | -0.56690 | 0 | 0 |  | 1.00000 | 0.83360 | -16.32183 |  | 90.63 | 89.37 | 42.70 | 1.34246 | 0.00914 |
| $RC_a(O)O-C_bH_3$<br>$(O-C$ (i)) | $C_b$ | -0.56690 | 0 | 0 | 0 | -152.18259 | 0.91771 | 0.88392 | -15.39265 | -15.20178 | 95.01 | 84.99 | 45.76 | 1.27445 | 0.07716 |
| $HC_a(O)O-C_bH_2C_cH_2R$<br>$(O-C$ (ii)) | $O$ | -0.92918 | -0.92918 | 0 | 0 |  | 1.00000 | 0.81549 | -16.68412 |  | 93.09 | 86.91 | 43.59 | 1.29113 | 0.04399 |
| $HC_a(O)O-C_bH_2C_cH_2R$<br>$(O-C$ (ii)) | $C_b$ | -0.92918 | -0.92918 | 0 | 0 | -153.47405 | 0.91771 | 0.81549 | -16.68411 | -16.49325 | 93.09 | 86.91 | 43.59 | 1.29113 | 0.04399 |
| $R'C_a(O)O-C_bH_2C_cH_2R$<br>$(O-C$ (iii)) | $O$ | -0.92918 | -0.72457 | 0 | 0 |  | 1.00000 | 0.82562 | -16.47951 |  | 91.72 | 88.28 | 43.10 | 1.31951 | 0.02480 |
| $R'C_a(O)O-C_bH_2C_cH_2R$<br>$(O-C$ (iii)) | $C_b$ | -0.72457 | -0.92918 | 0 | 0 | -153.26945 | 0.91771 | 0.82562 | -16.47951 | -16.28864 | 91.72 | 88.28 | 43.10 | 1.31951 | 0.02480 |
| $HC_a(O)-OC_bH_3$<br>$(C=O$ (i))<br>$(O-C$ (i)) | $O$ | -0.92918 | -0.56690 | 0 | 0 |  | 1.00000 | 0.83360 | -16.32183 |  | 98.97 | 81.03 | 46.82 | 1.18716 | 0.13000 |
| $HC_a(O)-OC_bH_3$<br>$(C=O$ (i))<br>$(O-C$ (i)) | $C_a$ | -0.92918 | -1.79278 | 0 | 0 | -154.33765 | 0.91771 | 0.77536 | -17.54772 | -17.35685 | 93.94 | 86.06 | 43.24 | 1.26386 | 0.05329 |
| $HC_a(O)-OR$<br>$(C=O$ (i))<br>$(O-C$ (ii)) | $O$ | -0.92918 | -0.92918 | 0 | 0 |  | 1.00000 | 0.81549 | -16.68412 |  | 97.48 | 82.52 | 45.73 | 1.21100 | 0.10616 |
| $HC_a(O)-OR$<br>$(C=O$ (i))<br>$(O-C$ (ii)) | $C_a$ | -1.79278 | -0.92918 | 0 | 0 | -154.33765 | 0.91771 | 0.77536 | -17.54772 | -17.35685 | 93.94 | 86.06 | 43.24 | 1.26386 | 0.05329 |
| $R'H_2C_bC_a(O)-OC_bH_3$<br>$(C=O$ (ii))<br>$(O-C$ (i)) | $O$ | -0.92918 | -0.56690 | 0 | 0 |  | 1.00000 | 0.83360 | -16.32183 |  | 98.97 | 81.03 | 46.82 | 1.18716 | 0.13000 |
| $R'H_2C_bC_a(O)-OC_bH_3$<br>$(C=O$ (ii))<br>$(O-C$ (i)) | $C_a$ | -0.92918 | -1.34946 | -0.92918 | 0 | -154.82352 | 0.91771 | 0.75447 | -18.03358 | -17.84271 | 91.96 | 88.04 | 41.90 | 1.29138 | 0.02578 |
| $R'H_2C_bC_a(O)-OC_bH_2C_cH_2R$<br>$(C=O$ (ii))<br>$(O-C$ (iii)) | $O$ | -0.92918 | -0.72457 | 0 | 0 |  | 1.00000 | 0.82562 | -16.47951 |  | 98.32 | 81.68 | 46.34 | 1.19766 | 0.11949 |
| $R'H_2C_bC_a(O)-OC_bH_2C_cH_2R$<br>$(C=O$ (ii))<br>$(O-C$ (iii)) | $C_a$ | -0.92918 | -1.34946 | -0.92918 | 0 | -154.82352 | 0.91771 | 0.75447 | -18.03358 | -17.84271 | 91.96 | 88.04 | 41.90 | 1.29138 | 0.02578 |
| $HC_a(OR)=O$<br>$(C=O$ (i)) | $O$ | -1.79278 | 0 | 0 | 0 |  | 1.00000 | 0.81871 | -16.61853 |  | 137.10 | 42.90 | 65.45 | 0.53635 | 0.59978 |

Table 15.107 Cont'd. The MO to HO intercept geometrical bond parameters of alkyl carboxylic acid esters. $R$, $R'$, $R''$ are $H$ or alkyl groups. $E_T$ is $E_T$ (*atom – atom,msp*$^3$.*AO*).

| Bond | Atom | $E_T$ (eV) Bond 1 | $E_T$ (eV) Bond 2 | $E_T$ (eV) Bond 3 | $E_T$ (eV) Bond 4 | Final Total Energy $C2sp^3$ (eV) | $r_{initial}$ $(a_0)$ | $r_{final}$ $(a_0)$ | $E_{Coulomb}$ (eV) Final | $E(C2sp^3)$ (eV) Final | $\theta'$ $(^\circ)$ | $\theta_1$ $(^\circ)$ | $\theta_2$ $(^\circ)$ | $d_1$ $(a_0)$ | $d_2$ $(a_0)$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $HC_a(OR)=O$ $(C=O$ (i)) | $C_a$ | -1.79278 | -0.92918 | 0 | 0 | -154.33766 | 0.91771 | 0.77536 | -17.54772 | -17.35685 | 135.24 | 44.76 | 63.02 | 0.58561 | 0.55053 |
| $R'C_bH_2C_a(OR)=O$ $(C=O$ (ii)) | $O$ | -1.34946 | 0 | 0 | 0 |  | 1.00000 | 0.84115 | -16.17521 |  | 137.27 | 42.73 | 66.31 | 0.52193 | 0.61784 |
| $R'C_bH_2C_a(OR)=O$ $(C=O$ (ii)) | $C_a$ | -1.34946 | -0.92918 | -0.92918 | 0 | -154.82352 | 0.91771 | 0.75447 | -18.03358 | -17.84272 | 133.47 | 46.53 | 61.46 | 0.62072 | 0.51905 |
| $H-C(O)OR$ $(CH$ (i)) | $C$ | -1.79278 | -0.92918 | 0 | 0 | -154.33766 | 0.91771 | 0.77536 | -17.54772 | -17.35685 | 69.89 | 110.11 | 36.09 | 1.30373 | 0.26662 |
| $R'H_2C_b-C_a(O)OR$ | $C_a$ | -0.92918 | -1.34946 | -0.92918 | 0 | -154.82352 | 0.91771 | 0.75447 | -18.03358 | -17.84272 | 56.25 | 123.75 | 25.37 | 1.85002 | 0.41915 |
| $H_3C_b-C_a(O)OR$ | $C_b$ | -0.92918 | 0 | 0 | 0 | -152.54487 | 0.91771 | 0.86359 | -15.75493 | -15.56407 | 72.27 | 107.73 | 34.17 | 1.69388 | 0.26301 |
| $R'H_2C_cH_2C_b-C_a(O)OR$ | $C_b$ | -0.92918 | -0.92918 | 0 | 0 | -153.47405 | 0.91771 | 0.81549 | -16.68411 | -16.49325 | 65.99 | 114.01 | 30.58 | 1.76270 | 0.33183 |
| $C-H$ $(CH_3)$ | $C$ | -0.92918 | 0 | 0 | 0 | -152.54487 | 0.91771 | 0.86359 | -15.75493 | -15.56407 | 77.49 | 102.51 | 41.48 | 1.23564 | 0.18708 |
| $C-H$ $(CH_2)$ | $C$ | -0.92918 | -0.92918 | 0 | 0 | -153.47406 | 0.91771 | 0.81549 | -16.68412 | -16.49325 | 68.47 | 111.53 | 35.84 | 1.35486 | 0.29933 |
| $C-H$ $(CH)$ (ii) | $C$ | -0.92918 | -0.92918 | -0.92918 | 0 | -154.40324 | 0.91771 | 0.77247 | -17.61330 | -17.42244 | 61.10 | 118.90 | 31.37 | 1.42988 | 0.37326 |
| $H_3C_aC_bH_2CH_2-$ $(C-C$ (a)) | $C_a$ | -0.92918 | 0 | 0 | 0 | -152.54487 | 0.91771 | 0.86359 | -15.75493 | -15.56407 | 63.82 | 116.18 | 30.08 | 1.83879 | 0.38106 |
| $H_3C_aC_bH_2CH_2-$ $(C-C$ (a)) | $C_b$ | -0.92918 | -0.92918 | 0 | 0 | -153.47406 | 0.91771 | 0.81549 | -16.68412 | -16.49325 | 56.41 | 123.59 | 26.06 | 1.90890 | 0.45117 |
| $R-H_2C_aC_b(H_2C_c-R')HCH_2-$ $(C-C$ (b)) | $C_b$ | -0.92918 | -0.92918 | -0.92918 | 0 | -154.40324 | 0.91771 | 0.77247 | -17.61330 | -17.42244 | 48.30 | 131.70 | 21.90 | 1.97162 | 0.51388 |
| $R-H_2C_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ $(C-C$ (c)) | $C_b$ | -0.92918 | -0.72457 | -0.72457 | -0.72457 | -154.71860 | 0.91771 | 0.75889 | -17.92866 | -17.73779 | 48.21 | 131.79 | 21.74 | 1.95734 | 0.50570 |
| $isoC_aC_b(H_2C_c-R')HCH_2-$ $(C-C$ (d)) | $C_b$ | -0.92918 | -0.92918 | -0.92918 | 0 | -154.40324 | 0.91771 | 0.77247 | -17.61330 | -17.42244 | 48.30 | 131.70 | 21.90 | 1.97162 | 0.51388 |
| $tertC_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ $(C-C$ (e)) | $C_b$ | -0.72457 | -0.72457 | -0.72457 | -0.72457 | -154.51399 | 0.91771 | 0.76765 | -17.92866 | -17.73779 | 50.04 | 129.96 | 22.66 | 1.94462 | 0.49298 |
| $tertC_aC_b(H_2C_c-R')HCH_2-$ $(C-C$ (f)) | $C_b$ | -0.72457 | -0.92918 | -0.92918 | 0 | -154.19863 | 0.91771 | 0.78155 | -17.40869 | -17.21783 | 52.78 | 127.22 | 24.04 | 1.92443 | 0.47279 |
| $isoC_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ $(C-C$ (f)) | $C_b$ | -0.72457 | -0.72457 | -0.72457 | -0.72457 | -154.51399 | 0.91771 | 0.76765 | -17.92866 | -17.73779 | 50.04 | 129.96 | 22.66 | 1.94462 | 0.49298 |

Table 15.108. The energy parameters ($eV$) of functional groups of alkyl carboxylic acid esters.

| Parameters | $C-H$ (i) Group | $C-C(O)$ Group | $C=O$ (i) Group | $C=O$ (ii) Group | $C-O$ Group | $O-C$ (i) Group | $O-C$ (ii) Group | $O-C$ (iii) Group | $CH_3$ Group | $CH_2$ Group | $C-H$ (ii) Group | $C-C$ (a) Group | $C-C$ (b) Group | $C-C$ (c) Group | $C-C$ (d) Group | $C-C$ (e) Group | $C-C$ (f) Group |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $n_1$ | 1 | 1 | 2 | 2 | 1 | 1 | 1 | 1 | 3 | 2 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $n_2$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 2 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $n_3$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $C_1$ | 0.75 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.75 | 0.75 | 0.75 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| $C_2$ | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $c_1$ | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $c_2$ | 0.91771 | 0.91771 | 0.85395 | 0.85395 | 0.85395 | 0.85395 | 0.85395 | 0.85395 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 |
| $c_3$ | 0 | 0 | 2 | 2 | 0 | 0 | 0 | 0 | 0 | 1 | 1 | 0 | 0 | 0 | 1 | 1 | 0 |
| $c_4$ | 1 | 2 | 4 | 4 | 2 | 2 | 2 | 2 | 1 | 1 | 1 | 2 | 2 | 2 | 2 | 2 | 2 |
| $c_5$ | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 3 | 2 | 1 | 0 | 0 | 0 | 0 | 0 | 0 |
| $C_{1o}$ | 0.75 | 1 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.75 | 0.75 | 0.75 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| $C_{2o}$ | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $V_e\ (eV)$ | -36.74167 | -30.19634 | -112.61934 | -111.25473 | -35.08488 | -32.67173 | -33.78830 | -33.15757 | -107.32728 | -70.41425 | -35.12015 | -28.79214 | -28.79214 | -29.10112 | -28.79214 | -29.10112 | -29.10112 |
| $V_p\ (eV)$ | 13.11890 | 9.50874 | 23.95107 | 23.87467 | 10.32968 | 10.06642 | 10.19070 | 10.12103 | 38.92728 | 25.78002 | 12.87680 | 9.33352 | 9.33352 | 9.37273 | 9.33352 | 9.37273 | 9.37273 |
| $T\ (eV)$ | 11.38634 | 7.37432 | 43.62389 | 42.82081 | 10.11150 | 8.94219 | 9.47754 | 9.17389 | 32.53914 | 21.06675 | 10.48582 | 6.77464 | 6.77464 | 6.90500 | 6.77464 | 6.90500 | 6.90500 |
| $V_m\ (eV)$ | -5.69317 | -3.68716 | -21.81195 | -21.41040 | -5.05575 | -4.47110 | -4.73877 | -4.58695 | -16.26957 | -10.53337 | -5.24291 | -3.38732 | -3.38732 | -3.45250 | -3.38732 | -3.45250 | -3.45250 |
| $E(_{AO/HO})\ (eV)$ | -14.63489 | -14.63489 | 0 | 0 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -15.56407 | -15.56407 | -14.63489 | -15.56407 | -15.56407 | -15.35946 | -15.56407 | -15.35946 | -15.35946 |
| $\Delta E_{H_2MO}(_{AO/HO})\ (eV)$ | -0.92918 | 0 | -3.58557 | -2.69893 | -2.69893 | -1.13379 | -1.85836 | -1.44915 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $E_T(_{AO/HO})\ (eV)$ | -13.70571 | -14.63489 | 3.58557 | 2.69893 | -11.93596 | -13.50110 | -12.77653 | -13.18574 | -15.56407 | -15.56407 | -14.63489 | -15.56407 | -15.56407 | -15.35946 | -15.56407 | -15.35946 | -15.35946 |
| $E_T(_{H_2MO})\ (eV)$ | -31.63530 | -31.63534 | -63.27075 | -63.27074 | -31.63541 | -31.63531 | -31.63536 | -31.63533 | -67.69451 | -49.66493 | -31.63533 | -31.63537 | -31.63537 | -31.63535 | -31.63537 | -31.63535 | -31.63535 |
| $E_T\left(atom-atom, msp^3.AO\right)\ (eV)$ | 0 | -1.85836 | -3.58557 | -2.69893 | -1.85836 | -1.13379 | -1.85836 | -1.44915 | 0 | 0 | 0 | -1.85836 | -1.85836 | -1.44915 | -1.85836 | -1.44915 | -1.44915 |
| $E_T(_{MO})\ (eV)$ | -31.63537 | -33.49373 | -66.85630 | -65.96966 | -33.49373 | -32.76916 | -33.49373 | -33.08452 | -67.69450 | -49.66493 | -31.63537 | -33.49373 | -33.49373 | -33.08452 | -33.49373 | -33.08452 | -33.08452 |
| $\omega\ \left(10^{15}\ rad/s\right)$ | 26.0575 | 23.3291 | 60.9581 | 59.4034 | 12.7926 | 21.4553 | 22.7749 | 12.0329 | 24.9286 | 24.2751 | 24.1759 | 9.43699 | 9.43699 | 15.4846 | 9.43699 | 9.55643 | 9.55643 |
| $E_K\ (eV)$ | 17.15150 | 15.35563 | 40.12366 | 39.10034 | 8.42030 | 14.12224 | 14.99085 | 7.92028 | 16.40846 | 15.97831 | 15.91299 | 6.21159 | 6.21159 | 10.19220 | 6.21159 | 6.29021 | 6.29021 |
| $\bar{E}_D\ (eV)$ | -0.25920 | -0.25966 | -0.41891 | -0.40804 | -0.19228 | -0.24362 | -0.25655 | -0.18420 | -0.25352 | -0.25017 | -0.24966 | -0.16515 | -0.16515 | -0.20896 | -0.16515 | -0.16416 | -0.16416 |
| $\bar{E}_{Kvib}\ (eV)$ | 0.35532 (Eq. (13.458)) | 0.10502 [29] | 0.21747 [32] | 0.21077 [12] | 0.14965 [32] | 0.11469 [32] | 0.11469 [32] | 0.16118 [4] | 0.35532 (Eq. (13.458)) | 0.35532 (Eq. (13.458)) | 0.35532 (Eq. (13.458)) | 0.12312 [2] | 0.17978 [4] | 0.09944 [5] | 0.12312 [2] | 0.12312 [2] | 0.12312 [2] |
| $\bar{E}_{osc}\ (eV)$ | -0.08153 | -0.20715 | -0.31017 | -0.30266 | -0.11745 | -0.18628 | -0.19921 | -0.10361 | -0.22757 | -0.14502 | -0.07200 | -0.10359 | -0.07526 | -0.15924 | -0.10359 | -0.10260 | -0.10260 |
| $E_{mag}\ (eV)$ | 0.14803 | 0.14803 | 0.11441 | 0.11441 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 |
| $E_T(_{Group})\ (eV)$ | -31.71690 | -33.70088 | -67.47664 | -66.57498 | -33.61118 | -32.95544 | -33.69294 | -33.18813 | -67.92207 | -49.80996 | -31.70737 | -33.59732 | -33.49373 | -33.24376 | -33.59732 | -33.18712 | -33.18712 |
| $E_{initial}(_{c_4\ AO/HO})\ (eV)$ | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 |
| $E_{initial}(_{c_5\ AO/HO})\ (eV)$ | -13.59844 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | -13.59844 | -13.59844 | -13.59844 | 0 | 0 | 0 | 0 | 0 | 0 |
| $E_D(_{Group})\ (eV)$ | 3.48357 | 4.43110 | 8.70826 | 7.80660 | 4.34141 | 3.68566 | 4.42316 | 3.91835 | 12.49186 | 7.83016 | 3.32601 | 4.32754 | 4.29921 | 3.97398 | 4.17951 | 3.62128 | 3.91734 |

Table 15.109. The total bond energies of alkyl carboxylic acid esters calculated using the functional group composition and the energies of Table 15.108 compared to the experimental values [3]. The magnetic energy $E_{mag}$ that is subtracted from the weighted sum of the $E_D$ ($_{Group}$) ($eV$) values based on composition is given by (15.57).

| Formula | Name | $C-H$ (i) Group | $C-C(O)$ Group | $C=O$ (i) Group | $C=O$ (ii) Group | $C-O$ Group | $O-C$ (i) Group | $O-C$ (ii) Group | $O-C$ (iii) Group | $CH_3$ | $CH_2$ | $CH$ (ii) | $C-C$ (a) | $C-C$ (b) | $C-C$ (c) | $C-C$ (d) | $C-C$ (e) | $C-C$ (f) | $E_{mag}$ | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $C_2H_4O_2$ | Methyl formate | 1 | 0 | 1 | 0 | 1 | 1 | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 32.71076 | 32.762 | 0.00156 |
| $C_3H_6O_2$ | Methyl acetate | 0 | 1 | 0 | 1 | 1 | 1 | 0 | 0 | 2 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 45.24849 | 45.288 | 0.00087 |
| $C_6H_{12}O_2$ | Methyl pentanoate | 0 | 1 | 0 | 1 | 1 | 1 | 0 | 0 | 2 | 3 | 0 | 3 | 0 | 0 | 0 | 0 | 0 | 0 | 81.72159 | 81.726 | 0.00005 |
| $C_7H_{14}O_2$ | Methyl hexanoate | 0 | 1 | 0 | 1 | 1 | 1 | 0 | 0 | 2 | 4 | 0 | 4 | 0 | 0 | 0 | 0 | 0 | 0 | 93.87929 | 93.891 | 0.00012 |
| $C_8H_{16}O_2$ | Methyl heptanoate | 0 | 1 | 0 | 1 | 1 | 1 | 0 | 0 | 2 | 5 | 0 | 5 | 0 | 0 | 0 | 0 | 0 | 0 | 106.03699 | 106.079 | 0.00040 |
| $C_9H_{18}O_2$ | Methyl octanoate | 0 | 1 | 0 | 1 | 1 | 1 | 0 | 0 | 2 | 6 | 0 | 6 | 0 | 0 | 0 | 0 | 0 | 0 | 118.19469 | 118.217 | 0.00018 |
| $C_{10}H_{20}O_2$ | Methyl nonanoate | 0 | 1 | 0 | 1 | 1 | 1 | 0 | 0 | 2 | 7 | 0 | 7 | 0 | 0 | 0 | 0 | 0 | 0 | 130.35239 | 130.373 | 0.00016 |
| $C_{11}H_{22}O_2$ | Methyl decanoate | 0 | 1 | 0 | 1 | 1 | 1 | 0 | 0 | 2 | 8 | 0 | 8 | 0 | 0 | 0 | 0 | 0 | 0 | 142.51009 | 142.523 | 0.00009 |
| $C_{12}H_{24}O_2$ | Methyl undecanoate | 0 | 1 | 0 | 1 | 1 | 1 | 0 | 0 | 2 | 9 | 0 | 9 | 0 | 0 | 0 | 0 | 0 | 0 | 154.66779 | 154.677 | 0.00006 |
| $C_{13}H_{26}O_2$ | Methyl dodecanoate | 0 | 1 | 0 | 1 | 1 | 1 | 0 | 0 | 2 | 10 | 0 | 10 | 0 | 0 | 0 | 0 | 0 | 0 | 166.82549 | 166.842 | 0.00010 |
| $C_{14}H_{28}O_2$ | Methyl tridecanoate | 0 | 1 | 0 | 1 | 1 | 1 | 0 | 0 | 2 | 11 | 0 | 11 | 0 | 0 | 0 | 0 | 0 | 0 | 178.98319 | 179.000 | 0.00009 |
| $C_{15}H_{30}O_2$ | Methyl tetradecanoate | 0 | 1 | 0 | 1 | 1 | 1 | 0 | 0 | 2 | 12 | 0 | 12 | 0 | 0 | 0 | 0 | 0 | 0 | 191.14089 | 191.170 | 0.00015 |
| $C_{16}H_{32}O_2$ | Methyl pentadecanoate | 0 | 1 | 0 | 1 | 1 | 1 | 0 | 0 | 2 | 13 | 0 | 13 | 0 | 0 | 0 | 0 | 0 | 0 | 203.29859 | 203.356 | 0.00028 |
| $C_4H_8O_2$ | Propyl formate | 1 | 0 | 1 | 0 | 1 | 0 | 1 | 0 | 1 | 2 | 0 | 2 | 0 | 0 | 0 | 0 | 0 | 0 | 57.76366 | 57.746 | -0.00030 |
| $C_4H_8O_2$ | Ethyl acetate | 0 | 1 | 0 | 1 | 1 | 0 | 0 | 1 | 2 | 1 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 57.63888 | 57.548 | -0.00157 |
| $C_5H_{10}O_2$ | Isopropyl acetate | 0 | 1 | 0 | 1 | 1 | 0 | 0 | 1 | 3 | 0 | 1 | 0 | 2 | 0 | 0 | 0 | 0 | 0 | 69.89747 | 69.889 | -0.00013 |
| $C_5H_{10}O_2$ | Ethyl propanoate | 0 | 1 | 0 | 1 | 1 | 0 | 0 | 1 | 2 | 2 | 0 | 2 | 0 | 0 | 0 | 0 | 0 | 0 | 69.79658 | 69.700 | -0.00139 |
| $C_6H_{12}O_2$ | Butyl acetate | 0 | 1 | 0 | 1 | 1 | 0 | 0 | 1 | 2 | 3 | 0 | 3 | 0 | 0 | 0 | 0 | 0 | 0 | 81.95428 | 81.873 | -0.00099 |
| $C_6H_{12}O_2$ | t-Butyl acetate | 0 | 1 | 0 | 1 | 1 | 0 | 0 | 1 | 4 | 0 | 0 | 0 | 0 | 3 | 0 | 0 | 0 | -1 | 82.23881 | 82.197 | -0.00051 |
| $C_6H_{12}O_2$ | Methyl 2,2-dimethylpropanoate | 0 | 1 | 0 | 1 | 1 | 1 | 0 | 0 | 4 | 0 | 0 | 0 | 0 | 3 | 0 | 0 | 0 | -1 | 82.00612 | 81.935 | -0.00087 |
| $C_7H_{14}O_2$ | Ethyl pentanoate | 0 | 1 | 0 | 1 | 1 | 0 | 0 | 1 | 2 | 4 | 0 | 4 | 0 | 0 | 0 | 0 | 0 | 0 | 94.11198 | 94.033 | -0.00084 |
| $C_7H_{14}O_2$ | Ethyl 3-methylbutanoate | 0 | 1 | 0 | 1 | 1 | 0 | 0 | 1 | 3 | 2 | 1 | 1 | 3 | 0 | 0 | 0 | 0 | 0 | 94.18454 | 94.252 | 0.00072 |
| $C_7H_{14}O_2$ | Ethyl 2,2-dimethylpropanoate | 0 | 1 | 0 | 1 | 1 | 0 | 0 | 1 | 4 | 1 | 0 | 1 | 0 | 3 | 0 | 0 | 0 | -1 | 94.39651 | 94.345 | -0.00054 |
| $C_8H_{16}O_2$ | Isobutyl isobutanoate | 0 | 1 | 0 | 1 | 1 | 0 | 0 | 1 | 4 | 1 | 2 | 0 | 5 | 0 | 0 | 0 | 0 | 0 | 106.44313 | 106.363 | -0.00075 |
| $C_8H_{16}O_2$ | Propyl pentanoate | 0 | 1 | 0 | 1 | 1 | 0 | 0 | 1 | 2 | 5 | 0 | 5 | 0 | 0 | 0 | 0 | 0 | 0 | 106.26968 | 106.267 | -0.00003 |
| $C_8H_{16}O_2$ | Isopropyl pentanoate | 0 | 1 | 0 | 1 | 1 | 0 | 0 | 1 | 3 | 3 | 1 | 3 | 2 | 0 | 0 | 0 | 0 | 0 | 106.37057 | 106.384 | 0.00013 |
| $C_9H_{18}O_2$ | Butyl pentanoate | 0 | 1 | 0 | 1 | 1 | 0 | 0 | 1 | 2 | 6 | 0 | 6 | 0 | 0 | 0 | 0 | 0 | 0 | 118.42738 | 118.489 | 0.00052 |
| $C_9H_{18}O_2$ | sec-Butyl pentanoate | 0 | 1 | 0 | 1 | 1 | 0 | 0 | 1 | 3 | 4 | 1 | 4 | 2 | 0 | 0 | 0 | 0 | 0 | 118.52827 | 118.624 | 0.00081 |
| $C_9H_{18}O_2$ | Isobutyl pentanoate | 0 | 1 | 0 | 1 | 1 | 0 | 0 | 1 | 3 | 4 | 1 | 3 | 3 | 0 | 0 | 0 | 0 | 0 | 118.49994 | 118.576 | 0.00064 |

Table 15.110. The bond angle parameters of alkyl carboxylic acid esters and experimental values [1]. In the calculation of $\theta_v$, the parameters from the preceding angle were used. $E_T$ is $E_T(atom - atom, msp^3.AO)$.

| Atoms of Angle | $2c'$ Bond 1 $(a_0)$ | $2c'$ Bond 2 $(a_0)$ | $2c'$ Terminal Atoms $(a_0)$ | $E_{Coulombic}$ Atom 1 | Atom 1 Hybridization Designation (Table 15.3.A) | $E_{Coulombic}$ Atom 2 | Atom 2 Hybridization Designation (Table 15.3.A) | $c_2$ Atom 1 | $c_2$ Atom 2 | $C_1$ | $C_2$ | $c_1$ | $c_2'$ | $E_T$ (eV) | $\theta_v$ (°) | $\theta_1$ (°) | $\theta_2$ (°) | Cal. $\theta$ (°) | Exp. $\theta$ (°) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $\angle HC_bO_b$<br>$(CH$ (i); $C=O$ (i)) | 2.09711 | 2.70321 | 3.9463 | -15.75493<br>$C_b$ | 7 | -13.61806 | O | 0.86359 | 0.85395<br>(Eq. (15.133)) | 0.75 | 1 | 0.75 | 0.98884 | 0 | | | | 109.95 | 110<br>(methyl formate) |
| $\angle O_aC_aO_b$<br>$(CH$ (i); $C=O$ (i)) | 2.27227 | 2.63431 | 4.4045 | -16.61853<br>$O_a$ | 24 | -16.68412<br>$O_b$ | 26 | 0.81871 | 0.81549 | 1 | 1 | 1 | 0.81710 | -1.65376 | | | | 127.56 | 127<br>(methyl formate) |
| $\angle C_bO_bC_a$<br>$(CH$ (i); $C=O$ (i)) | 2.70321 | 2.63431 | 4.4833 | -16.32183<br>$C_b$ | 17 | -18.47690<br>$C_a$ | 58 | 0.83360 | 0.73637 | 1 | 1 | 1 | 0.78498 | -1.85836 | | | | 114.27 | 114<br>(methyl formate) |
| Methylene<br>$\angle HC_aH$ | 2.11106 | 2.11106 | 3.4252 | -15.75493 | 7 | H | H | 0.86359 | 1 | 1 | 1 | 0.75 | 1.15796 | 0 | | | | 108.44 | 107<br>(propane) |
| $\angle C_aC_bC_c$ | | | | | | | | | | | | | | | 69.51 | | | 110.49 | 112<br>(propane)<br>113.8<br>(butane)<br>110.8<br>(isobutane) |
| $\angle C_aC_bH$ | | | | | | | | | | | | | | | 69.51 | | | 110.49 | 111.0<br>(butane)<br>111.4<br>(isobutane) |
| Methyl<br>$\angle HC_aH$ | 2.09711 | 2.09711 | 3.4252 | -15.75493 | 7 | H | H | 0.86359 | 1 | 1 | 1 | 0.75 | 1.15796 | 0 | | | | 109.50 | |
| $\angle C_aC_bC_c$ | | | | | | | | | | | | | | | 70.56 | | | 109.44 | |
| $\angle C_aC_bH$ | | | | | | | | | | | | | | | 70.56 | | | 109.44 | |
| $\angle C_bC_aC_c$<br>iso $C_a$ | 2.91547 | 2.91547 | 4.7958 | -16.68412<br>$C_b$ | 26 | -16.68412<br>$C_c$ | 26 | 0.81549 | 0.81549 | 1 | 1 | 1 | 0.81549 | -1.85836 | | | | 110.67 | 110.8<br>(isobutane) |
| $\angle C_bC_aH$<br>iso $C_a$ | 2.91547 | 2.11323 | 4.1633 | -15.55033<br>$C_a$ | 5 | -14.82575<br>$C_b$ | 1 | 0.87495 | 0.91771 | 0.75 | 1 | 0.75 | 1.04887 | 0 | | | | 110.76 | |
| $\angle C_aC_bH$<br>iso $C_a$ | 2.91547 | 2.09711 | 4.1633 | -15.55033<br>$C_b$ | 5 | -14.82575<br>$C_a$ | 1 | 0.87495 | 0.91771 | 0.75 | 1 | 0.75 | 1.04887 | 0 | | | | 111.27 | 111.4<br>(isobutane) |
| $\angle C_bC_aC_b$<br>tert $C_a$ | 2.90327 | 2.90327 | 4.7958 | -16.68412<br>$C_b$ | 26 | -16.68412<br>$C_b$ | 26 | 0.81549 | 0.81549 | 1 | 1 | 1 | 0.81549 | -1.85836 | | | | 111.37 | 110.8<br>(isobutane) |
| $\angle C_bC_aC_d$ | | | | | | | | | | | | | | | 72.50 | | | 107.50 | |

## AMIDES ($C_nH_{2n+1}NO,\ n=1,2,3,4,5...\infty$)

The alkyl amides, $C_nH_{2n+1}NO$, comprise a $C=O$ functional group, and the single bond of carbon to the carbonyl carbon atom, $C-C(O)$, is also a functional group. Formamide has a $HC=O$ moiety that comprises a more stable $C=O$ functional group and a $CH$ functional group that is equivalent to that of the $CH$ (i) of aldehydes given in the corresponding section. It is also equivalent to that of the iso-$CH$ group of branched-chain-alkyl portion of the alkyl amide except that $E_{mag}$ (Eq. (15.47)) is not subtracted from $E_D(_{Group})$. All amides further comprise a $C-NH_2$ moiety that comprises a $NH_2$ functional group and two types of $C-N$ functional groups, one for formamide and the other for alkyl amides ($RC(O)NH_2$ where $R$ is alkyl). The alkyl portion of the alkyl amide may comprise at least two terminal methyl groups ($CH_3$) at each end of the chain, and may comprise methylene ($CH_2$), and methylyne ($CH$) functional groups as well as $C$ bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($(CH_3)_2CH$) and t-butyl ($(CH_3)_3C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups. The branched-chain-alkane groups in amides are equivalent to those in branched-chain alkanes.

The $NH_2$ functional group was solved in the Dihydrogen Nitride ($NH_2$) section except that the energy of the $N-H$ MO is matched to the nitrogen-atom contribution to $\Delta E_{H_2MO}(AO/HO)$ and $E_T(atom-atom,msp^3.AO)$ of the $C-N$ group. Both alkyl amide $C=O$ groups and the $C-C(O)$ group are equivalent to those given in the Carboxylic Acid Esters section except that $\overline{E}_{Kvib}$ of the $C-C(O)$ group is matched to that of an amide. The $C-N$ groups are equivalent to those of alkyl amines given in the corresponding section except that the energy of the $C-N$ MO is matched to that of the $C=O$ group and $\overline{E}_{Kvib}$ is that of a amide. $\Delta E_{H_2MO}(AO/HO)$ of the $C-N$ group is equal to $E_T(atom-atom,msp^3.AO)$ of the alkyl $C=O$ and $C-N$ groups in order to match the energies of the corresponding MOs.

As in the case of primary amines, each $C-N$ group is solved by hybridizing the $2s$ and $2p$ AOs of the $C$ atom to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between the $C2sp^3$ HO and the $N$ AO to form a MO permits each participating orbital to decrease in radius and energy. To meet the equipotential condition of the union of the $C-N$ $H_2$-type-ellipsoidal-MO with other orbitals of the molecule, the hybridization factor $c_2$ of Eq. (15.52) for the $C-N$-bond MO given by Eq. (15.133) is $c_2(C2sp^3HO\ to\ N)=0.91140$.

$E_T(atom-atom,msp^3.AO)$ (Eq. (15.52)) of the $C=O$ group of alkyl amides and the $C=O$ group of formamide are equivalent to those of the corresponding carboxylic acids and esters. The values given in the Carboxylic Acids section are $-2.69893\ eV$ and $-3.58557\ eV$, respectively.

$E_T(atom-atom,msp^3.AO)$ of the amide $C-C(O)$ group is the same as alkanes, aldehydes, carboxylic acids, and carboxylic acid esters, $-1.85836\ eV$, where both energy contributions are given by Eq. (14.513). Also, as in the case of aldehydes, $C_{1o}=2C_1$ in Eq. (15.61).

In order to match energy throughout the chain of the amide molecule, $E_T(atom-atom,msp^3.AO)$ of the $C-N$-bond MO in Eq. (15.61) due to the charge donation from the $C$ and $N$ atoms to the MO is $-1.65376\ eV$. It is based on the energy match between the $C2sp^3$ HO of the carbonyl and the primary amino group $NH_2$. It is given by the linear combination of $-0.92918\ eV$ (Eq. (14.513)) which matches the contiguous $C-C(O)$ or $HC(O)$ group and $-0.72457\ eV$ (Eq. (14.151)), the contribution of a primary amino group given in the Primary Amines section.

The symbols of the functional groups of alkyl amides are given in Table 15.111. The geometrical (Eqs. (15.1-15.5) and (15.51)), intercept (Eqs. (15.80-15.87)), and energy (Eqs. (15.6-15.11) and (15.17-15.65)) parameters of alkyl amides are given in Tables 15.112, 15.113, and 15.114, respectively. The total energy of each alkyl amide given in Table 15.115 was calculated as the sum over the integer multiple of each $E_D(_{Group})$ of Table 15.114 corresponding to functional-group composition of the molecule. The bond angle parameters of alkyl amides determined using Eqs. (15.88-15.117) are given in Table 15.116. The color scale, translucent view of the charge-density of exemplary amide, propionamide, comprising the concentric shells of atoms with the outer shell bridged by one or more $H_2$-type ellipsoidal MOs or joined with one or more hydrogen MOs is shown in Figure 15.19.

Figure 15.19. (A)-(B) Color scale, translucent views of the charge-density of propionamide showing the orbitals of the atoms at their radii, the ellipsoidal surface of each $H$ or $H_2$-type ellipsoidal MO that transitions to the corresponding outer shell of the atom(s) participating in each bond, and the hydrogen nuclei (red, not to scale).

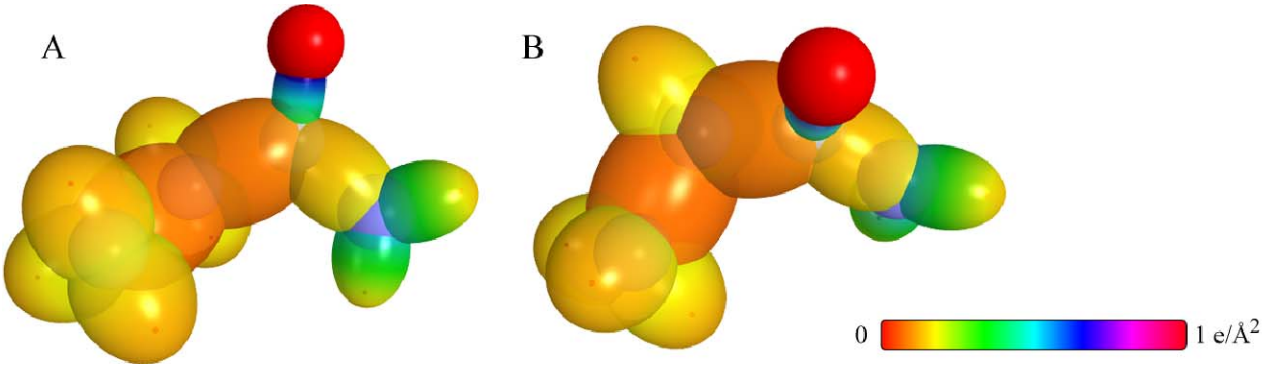


Table 15.111. The symbols of functional groups of alkyl amides.

| Functional Group | Group Symbol |
|---|---|
| *CH* (formamide) group | $C-H$ (i) |
| *C-C(O)* | $C-C(O)$ |
| *C=O* (formamide) | $C=O$ (i) |
| *C=O* (alkyl amide) | $C=O$ (ii) |
| *(O)C-N* (formamide) | $C-N$ (i) |
| *(O)C-N* (alkyl amide) | $C-N$ (ii) |
| $NH_2$ group | $NH_2$ |
| $CH_3$ group | $C-H\ (CH_3)$ |
| $CH_2$ group | $C-H\ (CH_2)$ |
| *CH* (alkyl) group | $C-H$ (ii) |
| *CC* bond (*n-C*) | $C-C$ (a) |
| *CC* bond (*iso-C*) | $C-C$ (b) |
| *CC* bond (*tert-C*) | $C-C$ (c) |
| *CC* (*iso* to *iso-C*) | $C-C$ (d) |
| *CC* (*t* to *t-C*) | $C-C$ (e) |
| *CC* (*t* to *iso-C*) | $C-C$ (f) |

Table 15.112. The geometrical bond parameters of alkyl amides and experimental values [1].

| Parameter | $C-H$ (i) Group | $C-C(O)$ Group | $C=O$ (i) Group | $C=O$ (ii) Group | $C-N$ (i) Group | $C-N$ (ii) Group | $NH_2$ Group | $C-H\ (CH_3)$ Group | $C-H\ (CH_2)$ Group | $C-H$ (ii) Group | $C-C$ (a) Group | $C-C$ (b) Group | $C-C$ (c) Group | $C-C$ (d) Group | $C-C$ (e) Group | $C-C$ (f) Group |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $a\ (a_0)$ | 1.67465 | 2.04740 | 1.290799 | 1.29907 | 1.70920 | 1.75370 | 1.32297 | 1.64920 | 1.67122 | 1.67465 | 2.12499 | 2.12499 | 2.10725 | 2.12499 | 2.10725 | 2.10725 |
| $c'\ (a_0)$ | 1.05661 | 1.43087 | 1.13613 | 1.13977 | 1.30736 | 1.32427 | 0.97065 | 1.04856 | 1.05553 | 1.05661 | 1.45744 | 1.45744 | 1.45164 | 1.45744 | 1.45164 | 1.45164 |
| Bond Length $2c'\ (Å)$ | 1.11827 | 1.51437 | 1.20243 | 1.20628 | 1.38365 | 1.40155 | 1.02729 | 1.10974 | 1.11713 | 1.11827 | 1.54280 | 1.54280 | 1.53635 | 1.54280 | 1.53635 | 1.53635 |
| Exp. Bond Length $(Å)$ | 1.125 (formamide) | 1.519 (acetamide)<br>1.520 (N-methylacetamide) | 1.212 (formamide) | 1.220 (acetamide)<br>1.225 (N-methylacetamide) | 1.368 (formamide) | 1.380 (acetamide) | 1.027 (formamide)<br>1.022 (acetamide) | 1.107 ($C-H$ propane)<br>1.117 ($C-H$ butane) | 1.107 ($C-H$ propane)<br>1.117 ($C-H$ butane) | 1.122 (isobutane) | 1.532 (propane)<br>1.531 (butane) | 1.532 (propane)<br>1.531 (butane) | 1.532 (propane)<br>1.531 (butane) | 1.532 (propane)<br>1.531 (butane) | 1.532 (propane)<br>1.531 (butane) | 1.532 (propane)<br>1.531 (butane) |
| $b,c\ (a_0)$ | 1.29924 | 1.46439 | 0.61267 | 0.62331 | 1.10098 | 1.14968 | 0.89894 | 1.27295 | 1.29569 | 1.29924 | 1.54616 | 1.54616 | 1.52750 | 1.54616 | 1.52750 | 1.52750 |
| $e$ | 0.63095 | 0.69887 | 0.88018 | 0.87737 | 0.76490 | 0.75513 | 0.73369 | 0.63580 | 0.63159 | 0.63095 | 0.68600 | 0.68600 | 0.68888 | 0.68600 | 0.68888 | 0.68888 |

Table 15.113. The MO to HO intercept geometrical bond parameters of alkyl amides. $R$, $R'$, $R''$ are $H$ or alkyl groups. $E_T$ is $E_T$ $(atom - atom, msp^3.AO)$.

| Bond | Atom | $E_T$ (eV) Bond 1 | $E_T$ (eV) Bond 2 | $E_T$ (eV) Bond 3 | $E_T$ (eV) Bond 4 | Final Total Energy $C2sp^3$ (eV) | $r_{initial}$ $(a_0)$ | $r_{final}$ $(a_0)$ | $E_{Coulomb}$ (eV) Final | $E(C2sp^3)$ (eV) Final | $\theta'$ (°) | $\theta_1$ (°) | $\theta_2$ (°) | $d_1$ $(a_0)$ | $d_2$ $(a_0)$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $RC(O)N(H)-H$<br>$(C=O$ (i) and (ii)) | $N$ | -0.82688 | 0 | 0 | 0 |  | 0.93084 | 0.86923 | -15.65263 |  | 113.90 | 66.10 | 62.13 | 0.61843 | 0.35222 |
| $HC(O)-NH_2$<br>$(C=O$ (i))<br>$(C-N$ (i)) | $N$ | -0.82688 | 0 | 0 | 0 |  | 0.93084 | 0.86923 | -15.65263 |  | 103.93 | 76.07 | 50.02 | 1.09814 | 0.20922 |
| $HC(O)-NH_2$<br>$(C=O$ (i))<br>$(C-N$ (i)) | $C$ | -0.82688 | -1.79278 | 0 | 0 | -154.23535 | 0.91771 | 0.77991 | -17.44541 | -17.25455 | 96.81 | 83.19 | 44.70 | 1.21492 | 0.09244 |
| $RH_2C_bC_a(O)-NH_2$<br>$(C=O$ (ii))<br>$(C-N$ (ii)) | $N$ | -0.82688 | 0 | 0 | 0 |  | 0.93084 | 0.86923 | -15.65263 |  | 100.14 | 79.86 | 48.10 | 1.17127 | 0.15300 |
| $RH_2C_bC_a(O)-NH_2$<br>$(C=O$ (ii))<br>$(C-N$ (ii)) | $C_a$ | -0.82688 | -1.34946 | -0.92918 | 0 | -154.72121 | 0.91771 | 0.75878 | -17.93127 | -17.74041 | 90.51 | 89.49 | 41.30 | 1.31755 | 0.00672 |
| $HC_a(NH_2)=O$<br>$(C=O$ (i)) | $O$ | -1.79278 | 0 | 0 | 0 |  | 1.00000 | 0.81871 | -16.61853 |  | 137.10 | 42.90 | 65.45 | 0.53635 | 0.59978 |
| $HC_a(NH_2)=O$<br>$(C=O$ (i)) | $C_a$ | -1.79278 | --0.82688 | 0 | 0 | -154.23535 | 0.91771 | 0.77991 | -17.44541 | -17.25455 | 135.44 | 44.56 | 63.28 | 0.58044 | 0.55569 |
| $RC_bH_2C_a(NH_2)=O$<br>$(C=O$ (ii)) | $O$ | -1.34946 | 0 | 0 | 0 |  | 1.00000 | 0.84115 | -16.17521 |  | 137.27 | 42.73 | 66.31 | 0.52193 | 0.61784 |
| $RC_bH_2C_a(NH_2)=O$<br>$(C=O$ (ii)) | $C_a$ | -1.34946 | -0.82688 | -0.92918 | 0 | -154.72121 | 0.91771 | 0.75878 | -17.93127 | -17.74041 | 133.67 | 46.33 | 61.70 | 0.61582 | 0.52395 |
| $H-C(O)NH_2$<br>$(CH$ (i)) | $C$ | -1.79278 | -0.82688 | 0 | 0 | -154.23535 | 0.91771 | 0.77991 | -17.44541 | -17.25455 | 62.39 | 117.61 | 32.13 | 1.41810 | 0.36148 |
| $RH_2C_b-C_a(O)NH_2$ | $C_a$ | -0.92918 | -1.34946 | -0.82688 | 0 | -154.72121 | 0.91771 | 0.75878 | -17.93127 | -17.74041 | 57.02 | 122.98 | 25.76 | 1.84386 | 0.41299 |
| $H_3C_b-C_a(O)NH_2$ | $C_b$ | -0.92918 | 0 | 0 | 0 | -152.54487 | 0.91771 | 0.86359 | -15.75493 | -15.56407 | 72.27 | 107.73 | 34.17 | 1.69388 | 0.26301 |
| $RH_2C_cH_2C_b-C_a(O)NH_2$ | $C_b$ | -0.92918 | -0.92918 | 0 | 0 | -153.47405 | 0.91771 | 0.81549 | -16.68411 | -16.49325 | 65.99 | 114.01 | 30.58 | 1.76270 | 0.33183 |
| $C-H$ $(CH_3)$ | $C$ | -0.92918 | 0 | 0 | 0 | -152.54487 | 0.91771 | 0.86359 | -15.75493 | -15.56407 | 77.49 | 102.51 | 41.48 | 1.23564 | 0.18708 |
| $C-H$ $(CH_2)$ | $C$ | -0.92918 | -0.92918 | 0 | 0 | -153.47406 | 0.91771 | 0.81549 | -16.68412 | -16.49325 | 68.47 | 111.53 | 35.84 | 1.35486 | 0.29933 |
| $C-H$ $(CH)$ (ii) | $C$ | -0.92918 | -0.92918 | -0.92918 | 0 | -154.40324 | 0.91771 | 0.77247 | -17.61330 | -17.42244 | 61.10 | 118.90 | 31.37 | 1.42988 | 0.37326 |
| $H_3C_aC_bH_2CH_2-$<br>$(C-C$ (a)) | $C_a$ | -0.92918 | 0 | 0 | 0 | -152.54487 | 0.91771 | 0.86359 | -15.75493 | -15.56407 | 63.82 | 116.18 | 30.08 | 1.83879 | 0.38106 |
| $H_3C_aC_bH_2CH_2-$<br>$(C-C$ (a)) | $C_b$ | -0.92918 | -0.92918 | 0 | 0 | -153.47406 | 0.91771 | 0.81549 | -16.68412 | -16.49325 | 56.41 | 123.59 | 26.06 | 1.90890 | 0.45117 |
| $R-H_2C_aC_b(H_2C_c-R')HCH_2-$<br>$(C-C$ (b)) | $C_b$ | -0.92918 | -0.92918 | -0.92918 | 0 | -154.40324 | 0.91771 | 0.77247 | -17.61330 | -17.42244 | 48.30 | 131.70 | 21.90 | 1.97162 | 0.51388 |
| $R-H_2C_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$<br>$(C-C$ (c)) | $C_b$ | -0.92918 | -0.72457 | -0.72457 | -0.72457 | -154.71860 | 0.91771 | 0.75889 | -17.92866 | -17.73779 | 48.21 | 131.79 | 21.74 | 1.95734 | 0.50570 |
| $isoC_aC_b(H_2C_c-R')HCH_2-$<br>$(C-C$ (d)) | $C_b$ | -0.92918 | -0.92918 | -0.92918 | 0 | -154.40324 | 0.91771 | 0.77247 | -17.61330 | -17.42244 | 48.30 | 131.70 | 21.90 | 1.97162 | 0.51388 |
| $tertC_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$<br>$(C-C$ (e)) | $C_b$ | -0.72457 | -0.72457 | -0.72457 | -0.72457 | -154.51399 | 0.91771 | 0.76765 | -17.92866 | -17.73779 | 50.04 | 129.96 | 22.66 | 1.94462 | 0.49298 |
| $tertC_aC_b(H_2C_c-R')HCH_2-$<br>$(C-C$ (f)) | $C_b$ | -0.72457 | -0.92918 | -0.92918 | 0- | -154.19863 | 0.91771 | 0.78155 | -17.40869 | -17.21783 | 52.78 | 127.22 | 24.04 | 1.92443 | 0.47279 |
| $isoC_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$<br>$(C-C$ (f)) | $C_b$ | -0.72457 | -0.72457 | -0.72457 | -0.72457 | -154.51399 | 0.91771 | 0.76765 | -17.92866 | -17.73779 | 50.04 | 129.96 | 22.66 | 1.94462 | 0.49298 |

Table 15.114. The energy parameters $(eV)$ of functional groups of alkyl amides.

| Parameters | $C-H$ (i) Group | $C-C(O)$ Group | $C=O$ (i) Group | $C=O$ (ii) Group | $C-N$ (i) Group | $C-N$ (ii) Group | $NH_2$ Group | $CH_3$ Group | $CH_2$ Group | $C-H$ (ii) Group | $C-C$ (a) Group | $C-C$ (b) Group | $C-C$ (c) Group | $C-C$ (d) Group | $C-C$ (e) Group | $C-C$ (f) Group |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $n_1$ | 1 | 1 | 2 | 2 | 1 | 1 | 2 | 3 | 2 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $n_2$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 2 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $n_3$ | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $C_1$ | 0.75 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.75 | 0.75 | 0.75 | 0.75 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| $C_2$ | 1 | 1 | 1 | 1 | 1 | 1 | 0.93613 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $c_1$ | 1 | 1 | 1 | 1 | 1 | 1 | 0.75 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $c_2$ | 0.91771 | 0.91771 | 0.85395 | 0.85395 | 0.91140 | 0.91140 | 1 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 |
| $c_3$ | 0 | 0 | 2 | 2 | 0 | 0 | 0 | 0 | 1 | 1 | 0 | 0 | 0 | 1 | 1 | 0 |
| $c_4$ | 1 | 2 | 4 | 4 | 2 | 2 | 1 | 1 | 1 | 1 | 2 | 2 | 2 | 2 | 2 | 2 |
| $c_5$ | 1 | 0 | 0 | 0 | 0 | 0 | 2 | 3 | 2 | 1 | 0 | 0 | 0 | 0 | 0 | 0 |
| $C_{1o}$ | 0.75 | 1 | 0.5 | 0.5 | 0.5 | 0.5 | 1.5 | 0.75 | 0.75 | 0.75 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| $C_{2o}$ | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $V_e\ (eV)$ | -35.12015 | -30.19634 | -112.61934 | -111.25473 | -38.24008 | -36.88558 | -78.77719 | -107.32728 | -70.41425 | -35.12015 | -28.79214 | -28.79214 | -29.10112 | -28.79214 | -29.10112 | -29.10112 |
| $V_p\ (eV)$ | 12.87680 | 9.50874 | 23.95107 | 23.87467 | 10.40705 | 10.27417 | 28.03446 | 38.92728 | 25.78002 | 12.87680 | 9.33352 | 9.33352 | 9.37273 | 9.33352 | 9.37273 | 9.37273 |
| $T\ (eV)$ | 10.48582 | 7.37432 | 43.62389 | 42.82081 | 11.18655 | 10.51650 | 29.77286 | 32.53914 | 21.06675 | 10.48582 | 6.77464 | 6.77464 | 6.90500 | 6.77464 | 6.90500 | 6.90500 |
| $V_m\ (eV)$ | -5.24291 | -3.68716 | -21.81195 | -21.41040 | -5.59327 | -5.25825 | -14.88643 | -16.26957 | -10.53337 | -5.24291 | -3.38732 | -3.38732 | -3.45250 | -3.38732 | -3.45250 | -3.45250 |
| $E(_{AO/HO})\ (eV)$ | -14.63489 | -14.63489 | 0 | 0 | -14.63489 | -14.63489 | -14.53414 | -15.56407 | -15.56407 | -14.63489 | -15.56407 | -15.56407 | -15.35946 | -15.56407 | -15.35946 | -15.35946 |
| $\Delta E_{H_2MO}(_{AO/HO})\ (eV)$ | 0 | 0 | -3.58557 | -2.69893 | -5.23932 | -4.35268 | -1.65376 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $E_T(_{AO/HO})\ (eV)$ | -14.63489 | -14.63489 | 3.58557 | 2.69893 | -9.39557 | -10.28221 | -12.88038 | -15.56407 | -15.56407 | -14.63489 | -15.56407 | -15.56407 | -15.35946 | -15.56407 | -15.35946 | -15.35946 |
| $E(_{n_3\ AO/HO})\ (eV)$ | 0 | 0 | 0 | 0 | 0 | 0 | -14.53414 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $E_T(_{H_2MO})\ (eV)$ | -31.63533 | -31.63534 | -63.27075 | -63.27074 | -31.63533 | -31.63537 | -48.73668 | -67.69451 | -49.66493 | -31.63533 | -31.63537 | -31.63537 | -31.63535 | -31.63537 | -31.63535 | -31.63535 |
| $E_T\left(atom-atom,msp^3.AO\right)(eV)$ | 0 | -1.85836 | -3.58557 | -2.69893 | -1.65376 | -1.65376 | 0 | 0 | 0 | 0 | -1.85836 | -1.85836 | -1.44915 | -1.85836 | -1.44915 | -1.44915 |
| $E_T(_{MO})\ (eV)$ | -31.63537 | -33.49373 | -66.85630 | -65.96966 | -33.28912 | -33.28912 | -48.73660 | -67.69450 | -49.66493 | -31.63537 | -33.49373 | -33.49373 | -33.08452 | -33.49373 | -33.08452 | -33.08452 |
| $\omega\ \left(10^{15}\ rad/s\right)$ | 24.1759 | 14.1117 | 60.9581 | 59.4034 | 13.0822 | 12.5874 | 59.4067 | 24.9286 | 24.2751 | 24.1759 | 9.43699 | 9.43699 | 15.4846 | 9.43699 | 9.55643 | 9.55643 |
| $E_K\ (eV)$ | 15.91299 | 9.28860 | 40.12366 | 39.10034 | 8.61093 | 8.28526 | 39.10250 | 16.40846 | 15.97831 | 15.91299 | 6.21159 | 6.21159 | 10.19220 | 6.21159 | 6.29021 | 6.29021 |
| $\bar{E}_D\ (eV)$ | -0.24966 | -0.20195 | -0.41891 | -0.40804 | -0.19325 | -0.18957 | -0.39136 | -0.25352 | -0.25017 | -0.24966 | -0.16515 | -0.16515 | -0.20896 | -0.16515 | -0.16416 | -0.16416 |
| $\bar{E}_{Kvib}\ (eV)$ | 0.35532 (Eq. (13.458)) | 0.14655 [28] | 0.21747 [32] | 0.21077 [12] | 0.17358 [33] | 0.17358 [33] | 0.40929 [22] | 0.35532 (Eq. (13.458)) | 0.35532 (Eq. (13.458)) | 0.35532 (Eq. (13.458)) | 0.12312 [2] | 0.17978 [4] | 0.09944 [5] | 0.12312 [2] | 0.12312 [2] | 0.12312 [2] |
| $\bar{E}_{osc}\ (eV)$ | -0.07200 | -0.12867 | -0.31017 | -0.30266 | -0.10647 | -0.10278 | -0.18672 | -0.22757 | -0.14502 | -0.07200 | -0.10359 | -0.07526 | -0.15924 | -0.10359 | -0.10260 | -0.10260 |
| $E_{mag}\ (eV)$ | 0.14803 | 0.14803 | 0.11441 | 0.11441 | 0.14803 | 0.14803 | 0.14185 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 |
| $E_T(_{Group})\ (eV)$ | -31.70737 | -33.62241 | -67.47664 | -66.57498 | -33.39559 | -33.39190 | -49.11003 | -67.92207 | -49.80996 | -31.70737 | -33.59732 | -33.49373 | -33.24376 | -33.59732 | -33.18712 | -33.18712 |
| $E_{initial}(_{c_4\ AO/HO})\ (eV)$ | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.53414 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 |
| $E_{initial}(_{c_5\ AO/HO})\ (eV)$ | -13.59844 | 0 | 0 | 0 | 0 | 0 | -13.59844 | -13.59844 | -13.59844 | -13.59844 | 0 | 0 | 0 | 0 | 0 | 0 |
| $E_D(_{Group})\ (eV)$ | 3.47404 | 4.35263 | 8.70826 | 7.80660 | 4.12581 | 4.12212 | 7.37901 | 12.49186 | 7.83016 | 3.32601 | 4.32754 | 4.29921 | 3.97398 | 4.17951 | 3.62128 | 3.91734 |

Table 15.115. The total bond energies of alkyl amides calculated using the functional group composition and the energies of Table 15.114 compared to the experimental values [3].

| Formula | Name | $C-H$ (i) Group | $C-C(O)$ Group | $C=O$ (i) Group | $C=O$ (ii) Group | $C-N$ (i) Group | $C-N$ (ii) Group | $NH_2$ Group | $CH_3$ | $CH_2$ | $CH$ (ii) | $C-C$ (a) | $C-C$ (b) | $C-C$ (c) | $C-C$ (d) | $C-C$ (e) | $C-C$ (f) | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $CH_3NO$ | Formamide | 1 | 0 | 1 | 0 | 1 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 23.68712 | 23.697 | 0.00041 |
| $C_2H_5NO$ | Acetamide | 0 | 1 | 0 | 1 | 0 | 1 | 1 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 36.15222 | 36.103 | -0.00135 |
| $C_3H_7NO$ | Propanamide | 0 | 1 | 0 | 1 | 0 | 1 | 1 | 1 | 1 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 48.30992 | 48.264 | -0.00094 |
| $C_4H_9NO$ | Butanamide | 0 | 1 | 0 | 1 | 0 | 1 | 1 | 1 | 2 | 0 | 2 | 0 | 0 | 0 | 0 | 0 | 60.46762 | 60.449 | -0.00030 |
| $C_4H_9NO$ | 2-Methylpropanamide | 0 | 0 | 0 | 1 | 0 | 1 | 1 | 2 | 0 | 1 | 0 | 3 | 0 | 0 | 0 | 0 | 60.51509 | 60.455 | -0.00099 |
| $C_5H_{11}NO$ | Pentanamide | 0 | 1 | 0 | 1 | 0 | 1 | 1 | 1 | 3 | 0 | 3 | 0 | 0 | 0 | 0 | 0 | 72.65232 | 72.481 | -0.00200 |
| $C_5H_{11}NO$ | 2,2-Dimethylpropanamide | 0 | 0 | 0 | 1 | 0 | 1 | 1 | 3 | 0 | 0 | 0 | 0 | 3 | 0 | 0 | 0 | 72.67890 | 72.718 | 0.00054 |
| $C_6H_{13}NO$ | Hexanamide | 0 | 1 | 0 | 1 | 0 | 1 | 1 | 1 | 4 | 0 | 4 | 0 | 0 | 0 | 0 | 0 | 84.78302 | 84.780 | -0.00004 |
| $C_8H_{17}NO$ | Octanamide | 0 | 1 | 0 | 1 | 0 | 1 | 1 | 1 | 6 | 0 | 6 | 0 | 0 | 0 | 0 | 0 | 109.09842 | 109.071 | -0.00025 |

Table 15.116. The bond angle parameters of alkyl amides and experimental values [1]. In the calculation of $\theta_v$, the parameters from the preceding angle were used. $E_T$ is $E_T(atom - atom, msp^3.AO)$.

| Atoms of Angle | 2c' Bond 1 ($a_0$) | 2c' Bond 2 ($a_0$) | 2c' Terminal Atoms ($a_0$) | $E_{Coulombic}$ Atom 1 | Atom 1 Hybridization Designation (Table 15.3.A) | $E_{Coulombic}$ Atom 2 | Atom 2 Hybridization Designation (Table 15.3.A) | $c_2$ Atom 1 | $c_2$ Atom 2 | $C_1$ | $C_2$ | $c_1$ | $c_2'$ | $E_T$ (eV) | $\theta_v$ (°) | $\theta_1$ (°) | $\theta_2$ (°) | Cal. $\theta$ (°) | Exp. $\theta$ (°) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $\angle HNH$ | 1.94130 | 1.94130 | 3.1464 | -14.53414 | N | H | H | 0.93613<br>Eq. (15.71)) | 1 | 1 | 1 | 0.75 | 1.06823 | 0 | | | | 108.27 | |
| $\angle C_aNH$<br>$(CH$ (i); $C_a=O$ (i)) | 2.61473 | 1.94130 | 3.9328 | -14.53414<br>$N$ | N | -14.82575<br>$C_a$ | 1 | 0.93613<br>(Eq. (15.71)) | 0.91771 | 0.75 | 1 | 0.75 | 0.98033 | 0 | | | | 118.61 | 119.2<br>(formamide) |
| $\angle HC_aN$<br>$(CH$ (i); $C_a=O$ (i)) | 2.11323 | 2.61473 | 4.0825 | -14.82575<br>$C_a$ | 1 | -14.53414<br>$N$ | N | 0.91771 | 0.93613<br>(Eq. (15.71)) | 0.75 | 1 | 0.75 | 1.02006 | 0 | | | | 119.04 | |
| $\angle HC_aO_a$<br>$(CH$ (i)) | 2.11323 | 2.27227 | 3.7238 | -14.82575<br>$C_a$ | 1 | -13.61806 | O | 0.91771 | 0.85395<br>(Eq. (15.133)) | 0.75 | 1 | 0.75 | 0.93052 | 0 | | | | 116.18 | |
| $\angle OC_aN$<br>$(C_a=O$ (i)) | 2.27227 | 2.61473 | 4.3359 | 16.17521<br>$O$ | 13 | -16.37721<br>$N$ | 18 | 0.84115 | 0.83078 | 1 | 1 | 1 | 0.83596 | -1.44915 | | | | 124.91 | 125.0<br>(formamide) |
| $\angle C_bC_aN$<br>$(C_a=O$ (ii)) | 2.86175 | 2.64855 | 4.6904 | -15.75493<br>$C_b$ | 7 | -14.53414<br>$N$ | N | 0.86359 | 0.91140<br>(Eq. (15.135)) | 1 | 1 | 1 | 0.88749 | -1.44915 | | | | 116.63 | 115.1<br>(acetamide) |
| $\angle C_bC_aO$<br>$(C_a=O$ (ii)) | 2.86175 | 2.27954 | 4.5607 | -16.68411 | 25 | -13.61806 | O | 0.81549 | 0.85395<br>(Eq. (15.133)) | 1 | 1 | 1 | 0.83472 | -1.65376 | | | | 124.63 | |
| $\angle OC_aN$<br>$(C_a=O$ (ii)) | 2.27954 | 2.64855 | 4.3128 | 16.17521<br>$O$ | 13 | -16.37721<br>$N$ | 18 | 0.84115 | 0.83078 | 1 | 1 | 1 | 0.83596 | -1.44915 | | | | 121.95 | 122.0<br>(acetamide) |
| Methylene<br>$\angle HC_aH$ | 2.11106 | 2.11106 | 3.4252 | -15.75493 | 7 | H | H | 0.86359 | 1 | 1 | 1 | 0.75 | 1.15796 | 0 | | | | 108.44 | 107<br>(propane) |
| $\angle C_aC_bC_c$ | | | | | | | | | | | | | | | 69.51 | | | 110.49 | 112<br>(propane)<br>113.8<br>(butane)<br>110.8<br>(isobutane) |
| $\angle C_aC_bH$ | | | | | | | | | | | | | | | 69.51 | | | 110.49 | 111.0<br>(butane)<br>111.4<br>(isobutane) |
| Methyl<br>$\angle HC_aH$ | 2.09711 | 2.09711 | 3.4252 | -15.75493 | 7 | H | H | 0.86359 | 1 | 1 | 1 | 0.75 | 1.15796 | 0 | | | | 109.50 | |
| $\angle C_aC_bC_c$ | | | | | | | | | | | | | | | 70.56 | | | 109.44 | |
| $\angle C_aC_bH$ | | | | | | | | | | | | | | | 70.56 | | | 109.44 | |
| $\angle C_bC_aC_c$<br>iso $C_a$ | 2.91547 | 2.91547 | 4.7958 | -16.68412<br>$C_b$ | 26 | -16.68412<br>$C_c$ | 26 | 0.81549 | 0.81549 | 1 | 1 | 1 | 0.81549 | -1.85836 | | | | 110.67 | 110.8<br>(isobutane) |
| $\angle C_bC_aH$<br>iso $C_a$ | 2.91547 | 2.11323 | 4.1633 | -15.55033<br>$C_a$ | 5 | -14.82575<br>$C_b$ | 1 | 0.87495 | 0.91771 | 0.75 | 1 | 0.75 | 1.04887 | 0 | | | | 110.76 | |
| $\angle C_aC_bH$<br>iso $C_a$ | 2.91547 | 2.09711 | 4.1633 | -15.55033<br>$C_b$ | 5 | -14.82575<br>$C_a$ | 1 | 0.87495 | 0.91771 | 0.75 | 1 | 0.75 | 1.04887 | 0 | | | | 111.27 | 111.4<br>(isobutane) |
| $\angle C_bC_aC_b$<br>tert $C_a$ | 2.90327 | 2.90327 | 4.7958 | -16.68412<br>$C_b$ | 26 | -16.68412<br>$C_b$ | 26 | 0.81549 | 0.81549 | 1 | 1 | 1 | 0.81549 | -1.85836 | | | | 111.37 | 110.8<br>(isobutane) |
| $\angle C_bC_aC_d$ | | | | | | | | | | | | | | | 72.50 | | | 107.50 | |

## N-ALKYL AND N,N-DIALKYL-AMIDES ($C_nH_{2n+1}NO,\ n=2,3,4,5...\infty$)

The N-alkyl and N,N-dialkyl amides, $C_nH_{2n+1}NO$, comprise a $C=O$ functional group, and the single bond of carbon to the carbonyl carbon atom, $C-C(O)$, is also a functional group. Formamide has a $HC=O$ moiety that comprises a more stable $C=O$ functional group and a $CH$ functional group that is equivalent to that of the iso-$CH$ group of branched-chain-alkyl portion of the N-alkyl or N,N-dialkyl amide. All amides further comprise a $C-N\left(R_1\right)R_2$ moiety that comprises two types of $C-N$ functional groups, one for formamide and the other for alkyl amides ($RC(O)N\left(R_1\right)R_2$ where $R$ is alkyl). The N or N,N-dialkyl moiety comprises three additional groups depending on the alkyl substitution of the nitrogen. In the case of a single methyl or alkyl substitution, the $NH-C$ bond and $NH$ are functional groups, and the $N-C$ bond of a di-substituted nitrogen is the third.

The alkyl portion of the N-alkyl or N,N-dialkyl amide may comprise at least two terminal methyl groups ($CH_3$) at each end of the chain, and may comprise methylene ($CH_2$), and methylyne ($CH$) functional groups as well as $C$ bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($\left(CH_3\right)_2CH$) and t-butyl ($\left(CH_3\right)_3C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups. The branched-chain-alkane groups in N-alkyl or N,N-dialkyl amides are equivalent to those in branched-chain alkanes.

The $NH$ functional group was solved in the Hydrogen Nitride ($NH$) section except that the energy of the $N-H$ MO is matched to the nitrogen-atom contribution to $\Delta E_{H_2MO}\left(AO/HO\right)$ and $E_T\left(atom-atom,msp^3.AO\right)$ of the $C-N$ group. The $C-C(O)$ group, both N-alkyl or N,N-dialkyl amide $C=O$ groups, and both $C-N$ groups are equivalent to those given in the Amides section.

As in the case of primary amines, each $N-C$ group is solved by hybridizing the $2s$ and $2p$ AOs of the $C$ atom to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between the $C2sp^3$ HO and the $N$ AO to form a MO permits each participating orbital to decrease in radius and energy. To meet the equipotential condition of the union of the $N-C$ $H_2$-type-ellipsoidal-MO with other orbitals of the molecule, the hybridization factor $c_2$ of Eq. (15.61) for the $N-C$-bond MO given by Eq. (15.133) is $c_2\left(C2sp^3HO\ to\ N\right)=0.91140$.

$E_T\left(atom-atom,msp^3.AO\right)$ of the N-substituted amide $C-C(O)$ group is the same as alkanes, aldehydes, carboxylic acids, carboxylic acid esters, and amides, $-1.85836\ eV$, where both energy contributions are given by Eq. (14.513). Also, as in the case of aldehydes, $C_{1o}=2C_1$ in Eq. (15.61).

$E_T\left(atom-atom,msp^3.AO\right)$ (Eq. (15.61)) of the $C=O$ group of N-substituted alkyl amides and the $C=O$ group of N-substituted formamide are equivalent to those of the corresponding carboxylic acids, carboxylic esters, and amides. The values given in the Carboxylic Acids section are $-2.69893\ eV$ and $-3.58557\ eV$, respectively.

$E_T\left(atom-atom,msp^3.AO\right)$ of both $C-N$ functional groups are the same as those of the corresponding groups of amides, $-1.65376\ eV$. $E_T\left(atom-atom,msp^3.AO\right)$ of the singly-substituted $NH-C$-bond MO in Eq. (15.61) due to the charge donation from the $N$ and $C$ atoms to the MO is $-0.92918\ eV$. It is equivalent to that of tertiary amines and matches the energy of the $NH-C$ group to that of the $C-N$ group wherein $E_T\left(atom-atom,msp^3.AO\right)$ of the latter is a linear combination of $-0.92918\ eV$ (Eq. (14.513)) and $-0.72457\ eV$ (Eq. (14.151)). $E_T\left(atom-atom,msp^3.AO\right)$ of the doubly-substituted $N-C$-bond MO is $-0.72457\ eV$. It is equivalent to that of the contribution of each atom of a primary amine and also matches the energy of the $N-C$ group to that of the $C-N$ group by matching one of the components of $E_T\left(atom-atom,msp^3.AO\right)$ of the latter.

The symbols of the functional groups of N-alkyl and N,N-dialkyl amides are given in Table 15.117. The geometrical (Eqs. (15.1-15.5) and (15.51)), intercept (Eqs. (15.80-15.87)), and energy (Eqs. (15.6-15.11) and (15.17-15.65)) parameters of N-alkyl and N,N-dialkyl amides are given in Tables 15.118, 15.119, and 15.120, respectively. The total energy of each N-alkyl or N,N-dialkyl amide given in Table 15.121 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.120 corresponding to functional-group composition of the molecule. The bond angle parameters of N-alkyl and N,N-dialkyl amides determined using Eqs. (15.79-15.108) are given in Table 15.122. The color scale, translucent view of the charge-density of exemplary alkyl-amide, N,N-dimethylacetamide, comprising the concentric shells of atoms with the outer shell bridged by one or more $H_2$-type ellipsoidal MOs or joined with one or more hydrogen MOs is shown in Figure 15.20.

Figure 15.20. Color scale, translucent view of the charge-density of N,N-dimethylacetamide showing the orbitals of the atoms at their radii, the ellipsoidal surface of each $H$ or $H_2$-type ellipsoidal MO that transitions to the corresponding outer shell of the atom(s) participating in each bond, and the hydrogen nuclei (red, not to scale).

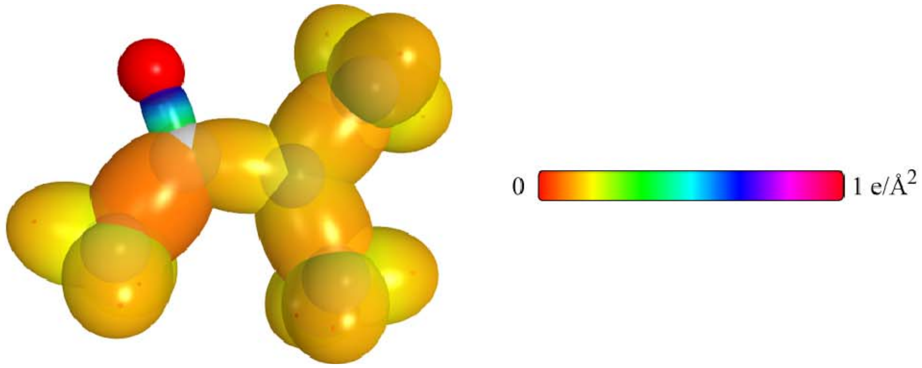


Table 15.117. The symbols of functional groups of N-alkyl and N,N-dialkyl amides.

| Functional Group | Group Symbol |
|---|---|
| *CH* (formamide) group | $C-H$ (i) |
| *C-C(O)* | $C-C(O)$ |
| *C=O* (N-alkyl and N,N-dialkyl formamide) | $C=O$ (i) |
| *C=O* (N-alkyl and N,N-dialkyl amide) | $C=O$ (ii) |
| *(O)C-N* (N-alkyl and N,N-dialkyl formamide) | $C-N$ (i) |
| *(O)C-N* (N-alkyl and N,N-dialkyl amide) | $C-N$ (ii) |
| *NH* group | $NH$ |
| *N-C* (*N*-alkyl) | $N-C$ (i) |
| *N-C (N,N*,-dialkyl) | $N-C$ (ii) |
| $CH_3$ group | $C-H\ (CH_3)$ |
| $CH_2$ group | $C-H\ (CH_2)$ |
| *CH* (alkyl) group | $C-H$ (ii) |
| *CC* bond (*n-C*) | $C-C$ (a) |
| *CC* bond (*iso-C*) | $C-C$ (b) |
| *CC* bond (*tert-C*) | $C-C$ (c) |
| *CC* (*iso* to *iso-C*) | $C-C$ (d) |
| *CC* (*t* to *t-C*) | $C-C$ (e) |
| *CC* (*t* to *iso-C*) | $C-C$ (f) |

Table 15.118. The geometrical bond parameters of N-alkyl and N,N-dialkyl amides and experimental values [1].

| Parameter | $C-H$ (i) Group | $C-C(O)$ Group | $C=O$ (i) Group | $C=O$ (ii) Group | $C-N$ (i) Group | $C-N$ (ii) Group | $NH$ Group | $N-C$ (i) Group | $N-C$ (ii) Group | $C-H\ (CH_3)$ Group | $C-H\ (CH_2)$ Group | $C-H$ (ii) Group | $C-C$ (a) Group | $C-C$ (b) Group | $C-C$ (c) Group | $C-C$ (d) Group | $C-C$ (e) Group | $C-C$ (f) Group |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $a\ (a_0)$ | 1.67465 | 2.04740 | 1.290799 | 1.29907 | 1.70920 | 1.75370 | 1.28620 | 1.96313 | 1.97794 | 1.64920 | 1.67122 | 1.67465 | 2.12499 | 2.12499 | 2.10725 | 2.12499 | 2.10725 | 2.10725 |
| $c'\ (a_0)$ | 1.05661 | 1.43087 | 1.13613 | 1.13977 | 1.30736 | 1.32427 | 0.95706 | 1.40112 | 1.40639 | 1.04856 | 1.05553 | 1.05661 | 1.45744 | 1.45744 | 1.45164 | 1.45744 | 1.45164 | 1.45164 |
| Bond Length $2c'\ (Å)$ | 1.11827 | 1.51437 | 1.20243 | 1.20628 | 1.38365 | 1.40155 | 1.01291 | 1.48288 | 1.48846 | 1.10974 | 1.11713 | 1.11827 | 1.54280 | 1.54280 | 1.53635 | 1.54280 | 1.53635 | 1.53635 |
| Exp. Bond Length $(Å)$ | 1.125 (formamide) | 1.520 (N-methyl-acetamide) | 1.212 (formamide) | 1.225 (N-methyl-acetamide) | 1.368 (formamide) | 1.380 (acetamide) | | 1.469 (N-methyl-acetamide) | | 1.107 ($C-H$ propane)<br>1.117 ($C-H$ butane) | 1.107 ($C-H$ propane)<br>1.117 ($C-H$ butane) | 1.122 (isobutane) | 1.532 (propane)<br>1.531 (butane) | 1.532 (propane)<br>1.531 (butane) | 1.532 (propane)<br>1.531 (butane) | 1.532 (propane)<br>1.531 (butane) | 1.532 (propane)<br>1.531 (butane) | 1.532 (propane)<br>1.531 (butane) |
| $b,c\ (a_0)$ | 1.29924 | 1.46439 | 0.61267 | 0.62331 | 1.10098 | 1.14968 | 0.85927 | 1.37505 | 1.39079 | 1.27295 | 1.29569 | 1.29924 | 1.54616 | 1.54616 | 1.52750 | 1.54616 | 1.52750 | 1.52750 |
| $e$ | 0.63095 | 0.69887 | 0.88018 | 0.87737 | 0.76490 | 0.75513 | 0.74410 | 0.71372 | 0.71104 | 0.63580 | 0.63159 | 0.63095 | 0.68600 | 0.68600 | 0.68888 | 0.68600 | 0.68888 | 0.68888 |

Table 15.119. The MO to HO intercept geometrical bond parameters of N-alkyl and N,N-dialkyl amides. $R$, $R'$, $R''$ are $H$ or alkyl groups. $E_T$ is $E_T(atom-atom,msp^3.AO)$.

| Bond | Atom | $E_T$ (eV) Bond 1 | $E_T$ (eV) Bond 2 | $E_T$ (eV) Bond 3 | $E_T$ (eV) Bond 4 | Final Total Energy $C2sp^3$ (eV) | $r_{initial}$ $(a_0)$ | $r_{final}$ $(a_0)$ | $E_{Coulomb}$ (eV) Final | $E(C2sp^3)$ (eV) Final | $\theta'$ $(^\circ)$ | $\theta_1$ $(^\circ)$ | $\theta_2$ $(^\circ)$ | $d_1$ $(a_0)$ | $d_2$ $(a_0)$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $R'C_a(O)N(C_bR)-H$<br>($C=O$ (i) and (ii))<br>($C-N$ (i) and (ii)) | $N$ | -0.82688 | -0.46459 | 0 | 0 |  | 0.93084 | 0.84418 | -16.11722 |  | 115.47 | 64.53 | 62.49 | 0.59403 | 0.36303 |
| $RC_a(O)N(H)-C_bH_3$<br>($C=O$ (i) and (ii))<br>($C-N$ (i) and (ii))<br>($N-C$ (i)) | $N$ | -0.82688 | -0.46459 | 0 | 0 |  | 0.93084 | 0.84418 | -16.11722 |  | 78.61 | 101.39 | 37.00 | 1.56779 | 0.16667 |
| $RC_a(O)N(H)-C_bH_3$<br>($C=O$ (i) and (ii))<br>($C-N$ (i) and (ii))<br>($N-C$ (i)) | $C_b$ | -0.46459 | 0 | 0 | 0 | -152.08028 | 0.91771 | 0.88983 | -15.29034 | -15.09948 | 83.37 | 96.63 | 40.00 | 1.50383 | 0.10271 |
| $R'C_a(O)N(H)-C_bH_2C_cH_2R$<br>($C=O$ (i) and (ii))<br>($C-N$ (i) and (ii))<br>($N-C$ (i)) | $N$ | -0.82688 | -0.46459 | 0 | 0 |  | 0.93084 | 0.84418 | -16.11722 |  | 78.61 | 101.39 | 37.00 | 1.56779 | 0.16667 |
| $R'C_a(O)N(H)-C_bH_2C_cH_2R$<br>($C=O$ (i) and (ii))<br>($C-N$ (i) and (ii))<br>($N-C$ (i)) | $C_b$ | -0.46459 | -0.92918 | 0 | 0 | -153.00946 | 0.91771 | 0.83885 | -16.21952 | -16.02866 | 78.02 | 101.39 | 36.64 | 1.57525 | 0.17413 |
| $R'C_a(O)N(C_cH_3)-C_bH_3$<br>($C=O$ (i) and (ii))<br>($C-N$ (i) and (ii))<br>($N-C$ (ii)) | $N$ | -0.82688 | -0.36229 | -0.36229 | 0 |  | 0.93084 | 0.83078 | -16.37720 |  | 75.57 | 104.43 | 35.35 | 1.61336 | 0.20697 |
| $R'C_a(O)N(C_cH_3)-C_bH_3$<br>($C=O$ (i) and (ii))<br>($C-N$ (i) and (ii))<br>($N-C$ (ii)) | $C_b$ | -0.36229 | 0 | 0 | 0 | -151.97798 | 0.91771 | 0.89582 | -15.18804 | -14.99717 | 82.59 | 97.41 | 39.70 | 1.52188 | 0.11549 |
| $R'C_a(O)N(C_cH_2C_dH_2R)-C_bH_3$<br>($C=O$ (i) and (ii))<br>($C-N$ (i) and (ii))<br>($N-C$ (ii)) | $N$ | -0.82688 | -0.36229 | -0.36229 | 0 |  | 0.93084 | 0.83078 | -16.37720 |  | 75.57 | 104.43 | 35.35 | 1.61336 | 0.20697 |
| $R'C_a(O)N(C_cH_2C_dH_2R)-C_bH_3$<br>($C=O$ (i) and (ii))<br>($C-N$ (i) and (ii))<br>($N-C$ (ii)) | $C_b$ | -0.36229 | 0 | 0 | 0 | -151.97798 | 0.91771 | 0.89582 | -15.18804 | -14.99717 | 82.59 | 97.41 | 39.70 | 1.52188 | 0.11549 |
| $R''C_a(O)N(R')-C_bH_2C_cH_2R$<br>($C=O$ (i) and (ii))<br>($C-N$ (i) and (ii))<br>($N-C$ (ii)) | $N$ | -0.82688 | -0.36229 | -0.36229 | 0 |  | 0.93084 | 0.83078 | -16.37720 |  | 75.57 | 104.43 | 35.35 | 1.61336 | 0.20697 |
| $R''C_a(O)N(R')-C_bH_2C_cH_2R$<br>($C=O$ (i) and (ii))<br>($C-N$ (i) and (ii))<br>($N-C$ (ii)) | $C_b$ | -0.36229 | -0.92918 | 0 | 0 | -152.90716 | 0.91771 | 0.84418 | -16.11722 | -15.92636 | 77.12 | 102.88 | 36.28 | 1.59451 | 0.18812 |
| $HC_a(O)-N(H)R$<br>($C=O$ (i))<br>($C-N$ (i))<br>($N-C$ (i))<br>$R = methyl\ or\ alkyl$ | $N$ | -0.82688 | -0.46459 | 0 | 0 |  | 0.93084 | 0.84418 | -16.11722 |  | 102.07 | 77.93 | 48.57 | 1.13090 | 0.17647 |
| $HC_a(O)-N(H)R$<br>($C=O$ (i))<br>($C-N$ (i))<br>($N-C$ (i))<br>$R = methyl\ or\ alkyl$ | $C_a$ | -0.82688 | -1.79278 | 0 | 0 | -154.23535 | 0.91771 | 0.77991 | -17.44541 | -17.25455 | 96.81 | 83.19 | 44.70 | 1.21492 | 0.09244 |
| $HC_a(O)-N(R')R$<br>($C=O$ (i))<br>($C-N$ (i))<br>($N-C$ (ii))<br>$R,R' = methyl\ or\ alkyl$ | $N$ | -0.82688 | -0.36229 | -0.36229 | 0 |  | 0.93084 | 0.83078 | -16.37720 |  | 101.03 | 78.97 | 47.79 | 1.14842 | 0.15895 |
| $HC_a(O)-N(R')R$<br>($C=O$ (i))<br>($C-N$ (i))<br>($N-C$ (ii))<br>$R,R' = methyl\ or\ alkyl$ | $C_a$ | -0.82688 | -1.79278 | 0 | 0 | -154.23535 | 0.91771 | 0.77991 | -17.44541 | -17.25455 | 96.81 | 83.19 | 44.70 | 1.21492 | 0.09244 |

**Table 15.119 cont'd.** The MO to HO intercept geometrical bond parameters of N-alkyl and N,N-dialkyl amides. $R$, $R'$, $R''$ are $H$ or alkyl groups. $E_T$ is $E_T$ ($atom\ atom, msp^3.AO$).

| Bond | Atom | $E_T$ (eV) Bond 1 | $E_T$ (eV) Bond 2 | $E_T$ (eV) Bond 3 | $E_T$ (eV) Bond 4 | Final Total Energy $C2sp^3$ (eV) | $r_{initial}$ $(a_0)$ | $r_{final}$ $(a_0)$ | $E_{Coulomb}$ (eV) Final | $E(C2sp^3)$ (eV) Final | $\theta'$ $(°)$ | $\theta_1$ $(°)$ | $\theta_2$ $(°)$ | $d_1$ $(a_0)$ | $d_2$ $(a_0)$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $R'H_2C_bC_a(O)-N(H)R$<br>$(C=O$ (ii)$)$<br>$(C-N$ (ii)$)$<br>$(N-C$ (i)$)$<br>$R = methyl\ or\ alkyl$ | $C_a$ | -0.82688 | -1.34946 | -0.92918 | 0 | -154.72121 | 0.91771 | 0.75878 | -17.93127 | -17.74041 | 90.51 | 89.49 | 41.30 | 1.31755 | 0.00672 |
| $R''H_2C_bC_a(O)-N(R')R$<br>$(C=O$ (ii)$)$<br>$(C-N$ (ii)$)$<br>$(N-C$ (ii)$)$<br>$R,R' = methyl\ or\ alkyl$ | $N$ | -0.82688 | -0.36229 | -0.36229 | 0 |  | 0.93084 | 0.83078 | -16.37720 |  | 97.06 | 82.94 | 45.82 | 1.22220 | 0.10207 |
| $R''H_2C_bC_a(O)-N(R')R$<br>$(C=O$ (ii)$)$<br>$(C-N$ (ii)$)$<br>$(N-C$ (ii)$)$<br>$R,R' = methyl\ or\ alkyl$ | $C_a$ | -0.82688 | -1.34946 | -0.92918 | 0 | -154.72121 | 0.91771 | 0.75878 | -17.93127 | -17.74041 | 90.51 | 89.49 | 41.30 | 1.31755 | 0.00672 |
| $HC_a(N(R'')R')=O$<br>$(C=O$ (i)$)$<br>$R',R'' = H,\ methyl,\ or\ alkyl$ | $O$ | -1.79278 | 0 | 0 | 0 |  | 1.00000 | 0.81871 | -16.61853 |  | 137.10 | 42.90 | 65.45 | 0.53635 | 0.59978 |
| $HC_a(N(R'')R')=O$<br>$(C=O$ (i)$)$<br>$R',R'' = H,\ methyl,\ or\ alkyl$ | $C_a$ | -1.79278 | --0.82688 | 0 | 0 | -154.23535 | 0.91771 | 0.77991 | -17.44541 | -17.25455 | 135.44 | 44.56 | 63.28 | 0.58044 | 0.55569 |
| $RC_bH_2C_a(N(R'')R')=O$<br>$(C=O$ (ii)$)$<br>$R',R'' = H,\ methyl,\ or\ alkyl$ | $O$ | -1.34946 | 0 | 0 | 0 |  | 1.00000 | 0.84115 | -16.17521 |  | 137.27 | 42.73 | 66.31 | 0.52193 | 0.61784 |
| $RC_bH_2C_a(N(R'')R')=O$<br>$(C=O$ (ii)$)$<br>$R',R'' = H,\ methyl,\ or\ alkyl$ | $C_a$ | -1.34946 | -0.82688 | -0.92918 | 0 | -154.72121 | 0.91771 | 0.75878 | -17.93127 | -17.74041 | 133.67 | 46.33 | 61.70 | 0.61582 | 0.52395 |
| $H-C(O)N(R'')R'$<br>$R',R'' = H,\ methyl,\ or\ alkyl$ | $C$ | -1.79278 | -0.82688 | 0 | 0 | -154.23535 | 0.91771 | 0.77991 | -17.44541 | -17.25455 | 62.39 | 117.61 | 32.13 | 1.41810 | 0.36148 |
| $RH_2C_b-C_a(O)N(R'')R'$<br>$R',R'' = H,\ methyl,\ or\ alkyl$ | $C_a$ | -0.92918 | -1.34946 | -0.82688 | 0 | -154.72121 | 0.91771 | 0.75878 | -17.93127 | -17.74041 | 57.02 | 122.98 | 25.76 | 1.84386 | 0.41299 |
| $H_3C_b-C_a(O)N(R'')R'$<br>$R',R'' = H,\ methyl,\ or\ alkyl$ | $C_b$ | -0.92918 | 0 | 0 | 0 | -152.54487 | 0.91771 | 0.86359 | -15.75493 | -15.56407 | 72.27 | 107.73 | 34.17 | 1.69388 | 0.26301 |
| $RH_2C_cH_2C_b-C_a(O)N(R'')R'$<br>$R',R'' = H,\ methyl,\ or\ alkyl$ | $C_b$ | -0.92918 | -0.92918 | 0 | 0 | -153.47405 | 0.91771 | 0.81549 | -16.68411 | -16.49325 | 65.99 | 114.01 | 30.58 | 1.76270 | 0.33183 |
| $C-H\ (CH_3)$ | $C$ | -0.92918 | 0 | 0 | 0 | -152.54487 | 0.91771 | 0.86359 | -15.75493 | -15.56407 | 77.49 | 102.51 | 41.48 | 1.23564 | 0.18708 |
| $C-H\ (CH_2)$ | $C$ | -0.92918 | -0.92918 | 0 | 0 | -153.47406 | 0.91771 | 0.81549 | -16.68412 | -16.49325 | 68.47 | 111.53 | 35.84 | 1.35486 | 0.29933 |
| $C-H\ (CH)$ (ii) | $C$ | -0.92918 | -0.92918 | -0.92918 | 0 | -154.40324 | 0.91771 | 0.77247 | -17.61330 | -17.42244 | 61.10 | 118.90 | 31.37 | 1.42988 | 0.37326 |
| $H_3C_aC_bH_2CH_2-$<br>$(C-C$ (a)$)$ | $C_a$ | -0.92918 | 0 | 0 | 0 | -152.54487 | 0.91771 | 0.86359 | -15.75493 | -15.56407 | 63.82 | 116.18 | 30.08 | 1.83879 | 0.38106 |
| $H_3C_aC_bH_2CH_2-$<br>$(C-C$ (a)$)$ | $C_b$ | -0.92918 | -0.92918 | 0 | 0 | -153.47406 | 0.91771 | 0.81549 | -16.68412 | -16.49325 | 56.41 | 123.59 | 26.06 | 1.90890 | 0.45117 |
| $R-H_2C_aC_b(H_2C_c-R')HCH_2-$<br>$(C-C$ (b)$)$ | $C_b$ | -0.92918 | -0.92918 | -0.92918 | 0 | -154.40324 | 0.91771 | 0.77247 | -17.61330 | -17.42244 | 48.30 | 131.70 | 21.90 | 1.97162 | 0.51388 |
| $R-H_2C_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$<br>$(C-C$ (c)$)$ | $C_b$ | -0.92918 | -0.72457 | -0.72457 | -0.72457 | -154.71860 | 0.91771 | 0.75889 | -17.92866 | -17.73779 | 48.21 | 131.79 | 21.74 | 1.95734 | 0.50570 |
| $isoC_aC_b(H_2C_c-R')HCH_2-$<br>$(C-C$ (d)$)$ | $C_b$ | -0.92918 | -0.92918 | -0.92918 | 0 | -154.40324 | 0.91771 | 0.77247 | -17.61330 | -17.42244 | 48.30 | 131.70 | 21.90 | 1.97162 | 0.51388 |
| $tertC_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$<br>$(C-C$ (e)$)$ | $C_b$ | -0.72457 | -0.72457 | -0.72457 | -0.72457 | -154.51399 | 0.91771 | 0.76765 | -17.92866 | -17.73779 | 50.04 | 129.96 | 22.66 | 1.94462 | 0.49298 |
| $tertC_aC_b(H_2C_c-R')HCH_2-$<br>$(C-C$ (f)$)$ | $C_b$ | -0.72457 | -0.92918 | -0.92918 | 0 | -154.19863 | 0.91771 | 0.78155 | -17.40869 | -17.21783 | 52.78 | 127.22 | 24.04 | 1.92443 | 0.47279 |
| $isoC_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$<br>$(C-C$ (f)$)$ | $C_b$ | -0.72457 | -0.72457 | -0.72457 | -0.72457 | -154.51399 | 0.91771 | 0.76765 | -17.92866 | -17.73779 | 50.04 | 129.96 | 22.66 | 1.94462 | 0.49298 |

Table 15.120. The energy parameters ($eV$) of functional groups of N-alkyl and N,N-dialkyl amides.

| Parameters | $C-H$ (i) Group | $C-C(O)$ Group | $C=O$ (i) Group | $C=O$ (ii) Group | $C-N$ (i) Group | $C-N$ (ii) Group | $NH$ Group | $N-C$ (i) | $N-C$ (ii) | $CH_3$ Group | $CH_2$ Group | $C-H$ (ii) Group | $C-C$ (a) Group | $C-C$ (b) Group | $C-C$ (c) Group | $C-C$ (d) Group | $C-C$ (e) Group | $C-C$ (f) Group |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $n_1$ | 1 | 1 | 2 | 2 | 1 | 1 | 1 | 1 | 1 | 3 | 2 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $n_2$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 2 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $n_3$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $C_1$ | 0.75 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.75 | 0.5 | 0.5 | 0.75 | 0.75 | 0.75 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| $C_2$ | 1 | 1 | 1 | 1 | 1 | 1 | 0.93613 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $c_1$ | 1 | 1 | 1 | 1 | 1 | 1 | 0.75 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $c_2$ | 0.91771 | 0.91771 | 0.85395 | 0.85395 | 0.91140 | 0.91140 | 1 | 0.91140 | 0.91140 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 |
| $c_3$ | 0 | 0 | 2 | 2 | 0 | 0 | 1 | 0 | 0 | 0 | 1 | 1 | 0 | 0 | 0 | 1 | 1 | 0 |
| $c_4$ | 1 | 2 | 4 | 4 | 2 | 2 | 1 | 2 | 2 | 1 | 1 | 1 | 2 | 2 | 2 | 2 | 2 | 2 |
| $c_5$ | 1 | 0 | 0 | 0 | 0 | 0 | 1 | 0 | 0 | 3 | 2 | 1 | 0 | 0 | 0 | 0 | 0 | 0 |
| $C_{1o}$ | 0.75 | 1 | 0.5 | 0.5 | 0.5 | 0.5 | 0.75 | 0.5 | 0.5 | 0.75 | 0.75 | 0.75 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| $C_{2o}$ | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $V_e\ (eV)$ | -35.12015 | -30.19634 | -112.61934 | -111.25473 | -38.24008 | -36.88558 | -40.92593 | -31.67393 | -31.36351 | -107.32728 | -70.41425 | -35.12015 | -28.79214 | -28.79214 | -29.10112 | -28.79214 | -29.10112 | -29.10112 |
| $V_p\ (eV)$ | 12.87680 | 9.50874 | 23.95107 | 23.87467 | 10.40705 | 10.27417 | 14.21618 | 9.71067 | 9.67426 | 38.92728 | 25.78002 | 12.87680 | 9.33352 | 9.33352 | 9.37273 | 9.33352 | 9.37273 | 9.37273 |
| $T\ (eV)$ | 10.48582 | 7.37432 | 43.62389 | 42.82081 | 11.18655 | 10.51650 | 15.90963 | 8.06719 | 7.92833 | 32.53914 | 21.06675 | 10.48582 | 6.77464 | 6.77464 | 6.90500 | 6.77464 | 6.90500 | 6.90500 |
| $V_m\ (eV)$ | -5.24291 | -3.68716 | -21.81195 | -21.41040 | -5.59327 | -5.25825 | -7.95482 | -4.03359 | -3.96416 | -16.26957 | -10.53337 | -5.24291 | -3.38732 | -3.38732 | -3.45250 | -3.38732 | -3.45250 | -3.45250 |
| $E(_{AO/HO})\ (eV)$ | -14.63489 | -14.63489 | 0 | 0 | -14.63489 | -14.63489 | -14.53414 | -14.63489 | -14.63489 | -15.56407 | -15.56407 | -14.63489 | -15.56407 | -15.56407 | -15.35946 | -15.56407 | -15.35946 | -15.35946 |
| $\Delta E_{H_2MO}(_{AO/HO})\ (eV)$ | 0 | 0 | -3.58557 | -2.69893 | -5.23932 | -4.35268 | -1.65376 | -0.92918 | -0.72457 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $E_T(_{AO/HO})\ (eV)$ | -14.63489 | -14.63489 | 3.58557 | 2.69893 | -9.39557 | -10.28221 | -12.88038 | -13.70571 | -13.91032 | -15.56407 | -15.56407 | -14.63489 | -15.56407 | -15.56407 | -15.35946 | -15.56407 | -15.35946 | -15.35946 |
| $E_T(_{H_2MO})\ (eV)$ | 0 | -31.63534 | -63.27075 | -63.27074 | -31.63533 | -31.63537 | -31.63531 | -31.63537 | -31.63540 | -67.69451 | -49.66493 | -31.63533 | -31.63537 | -31.63537 | -31.63535 | -31.63537 | -31.63535 | -31.63535 |
| $E_T\left(atom-atom,msp^3.AO\right)\ (eV)$ | -31.63533 | -1.85836 | -3.58557 | -2.69893 | -1.65376 | -1.65376 | 0 | -0.92918 | -0.72457 | 0 | 0 | 0 | -1.85836 | -1.85836 | -1.44915 | -1.85836 | -1.44915 | -1.44915 |
| $E_T(_{MO})\ (eV)$ | 0 | -33.49373 | -66.85630 | -65.96966 | -33.28912 | -33.28912 | -31.63537 | -32.56455 | -32.35994 | -67.69450 | -49.66493 | -31.63537 | -33.49373 | -33.49373 | -33.08452 | -33.49373 | -33.08452 | -33.08452 |
| $\omega\ \left(10^{15}\ rad/s\right)$ | -31.63537 | 14.1117 | 60.9581 | 59.4034 | 13.0822 | 12.5874 | 44.9494 | 10.6278 | 10.5087 | 24.9286 | 24.2751 | 24.1759 | 9.43699 | 9.43699 | 15.4846 | 9.43699 | 9.55643 | 9.55643 |
| $E_K\ (eV)$ | 24.1759 | 9.28860 | 40.12366 | 39.10034 | 8.61093 | 8.28526 | 29.58649 | 6.99543 | 6.91703 | 16.40846 | 15.97831 | 15.91299 | 6.21159 | 6.21159 | 10.19220 | 6.21159 | 6.29021 | 6.29021 |
| $\bar{E}_D\ (eV)$ | 15.91299 | -0.20195 | -0.41891 | -0.40804 | -0.19325 | -0.18957 | -0.34043 | -0.17039 | -0.16837 | -0.25352 | -0.25017 | -0.24966 | -0.16515 | -0.16515 | -0.20896 | -0.16515 | -0.16416 | -0.16416 |
| $\bar{E}_{Kvib}\ (eV)$ | -0.24966 | 0.14655 [28] | 0.21747 [32] | 0.21077 [12] | 0.17358 [33] | 0.17358 [33] | 0.40696 [24] | 0.12944 [23] | 0.12944 [23] | 0.35532 (Eq. (13.458)) | 0.35532 (Eq. (13.458)) | 0.35532 (Eq. (13.458)) | 0.12312 [2] | 0.17978 [4] | 0.09944 [5] | 0.12312 [2] | 0.12312 [2] | 0.12312 [2] |
| $\bar{E}_{osc}\ (eV)$ | 0.35532 (Eq. (13.458)) | -0.12867 | -0.31017 | -0.30266 | -0.10647 | -0.10278 | -0.13695 | -0.10567 | -0.10365 | -0.22757 | -0.14502 | -0.07200 | -0.10359 | -0.07526 | -0.15924 | -0.10359 | -0.10260 | -0.10260 |
| $E_{mag}\ (eV)$ | -0.07200 | 0.14803 | 0.11441 | 0.11441 | 0.14803 | 0.14803 | 0.14185 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 |
| $E_T(_{Group})\ (eV)$ | 0.14803 | -33.62241 | -67.47664 | -66.57498 | -33.39559 | -33.39190 | -31.77232 | -32.67022 | -32.46359 | -67.92207 | -49.80996 | -31.70737 | -33.59732 | -33.49373 | -33.24376 | -33.59732 | -33.18712 | -33.18712 |
| $E_{initial}(_{c_4\ AO/HO})\ (eV)$ | -31.70737 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.53414 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 |
| $E_{initial}(_{c_5\ AO/HO})\ (eV)$ | -14.63489 | 0 | 0 | 0 | 0 | 0 | -13.59844 | 0 | 0 | -13.59844 | -13.59844 | -13.59844 | 0 | 0 | 0 | 0 | 0 | 0 |
| $E_D(_{Group})\ (eV)$ | -13.59844 | 4.35263 | 8.70826 | 7.80660 | 4.12581 | 4.12212 | 3.49788 | 3.40044 | 3.19381 | 12.49186 | 7.83016 | 3.32601 | 4.32754 | 4.29921 | 3.97398 | 4.17951 | 3.62128 | 3.91734 |

Table 15.121. The total bond energies of N-alkyl and N,N-dialkyl amides calculated using the functional group composition and the energies of Table 15.120 compared to the experimental values [3].

| Formula | Name | $C-H$ (i) Group | $C-C(O)$ Group | $C=O$ (i) Group | $C=O$ (ii) Group | $C-N$ (i) Group | $C-N$ (ii) Group | $NH$ Group | $N-C$ (i) | $N-C$ (ii) | $CH_3$ | $CH_2$ | $CH$ (ii) | $C-C$ (a) | $C-C$ (b) | $C-C$ (c) | $C-C$ (d) | $C-C$ (e) | $C-C$ (f) | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $C_3H_7NO$ | N,N-Dimethylformamide | 1 | 0 | 1 | 0 | 1 | 0 | 0 | 0 | 2 | 2 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 47.67945 | 47.574 | 0.00221 |
| $C_4H_9NO$ | N,N-Dimethylacetamide | 0 | 1 | 0 | 1 | 0 | 1 | 0 | 0 | 2 | 3 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 60.14455 | 59.890 | -0.00426 |
| $C_6H_{13}NO$ | N-Butylacetamide | 0 | 1 | 0 | 1 | 0 | 1 | 1 | 1 | 0 | 2 | 3 | 0 | 3 | 0 | 0 | 0 | 0 | 0 | 84.63649 | 84.590 | -0.00055 |

Table 15.122. The bond angle parameters of N-alkyl and N,N-dialkyl amides and experimental values [1]. In the calculation of $\theta_v$, the parameters from the preceding angle were used. $E_T$ is $E_T(atom - atom, msp^3.AO)$.

| Atoms of Angle | $2c'$ Bond 1 ($a_0$) | $2c'$ Bond 2 ($a_0$) | $2c'$ Terminal Atoms ($a_0$) | $E_{Coulombic}$ Atom 1 | Atom 1 Hybridization Designation (Table 15.3.A) | $E_{Coulombic}$ Atom 2 | Atom 2 Hybridization Designation (Table 15.3.A) | $c_2$ Atom 1 | $c_2$ Atom 2 | $C_1$ | $C_2$ | $c_1$ | $c_2'$ | $E_T$ (eV) | $\theta_v$ (°) | $\theta_1$ (°) | $\theta_2$ (°) | Cal. $\theta$ (°) | Exp. $\theta$ (°) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $\angle OC_aN$<br>($C_a = O$ (ii)) | 2.27954 | 2.64855 | 4.3243 | 16.17521<br>$O$ | 13 | -16.11722<br>$N$ | 12 | 0.84115 | 0.84418 | 1 | 1 | 1 | 0.84266 | -1.44915 | | | | 122.51 | 121.8<br>(N-methylacetamide) |
| $\angle C_bC_aN$<br>($C_a = O$ (ii)) | 2.86175 | 2.64855 | 4.6904 | -15.75493<br>$C_b$ | 7 | -14.53414<br>$N$ | N | 0.86359 | 0.91140<br>(Eq. (15.135)) | 1 | 1 | 1 | 0.88749 | -1.44915 | | | | 116.63 | 114.1<br>(N-methylacetamide) |
| $\angle C_bC_aO$<br>($C_a = O$ (ii)) | 2.86175 | 2.27954 | 4.5607 | -16.68411 | 25 | -13.61806 | O | 0.81549 | 0.85395<br>(Eq. (15.133)) | 1 | 1 | 1 | 0.83472 | -1.65376 | | | | 124.63 | |
| $\angle C_aNC_c$<br>($C_a = O$ (ii)) | 2.64855 | 2.80224 | 4.6904 | -17.93127<br>$C_a$ | 55 | -16.21952<br>$C_c$ | 15 | 0.75878 | 0.83885 | 1 | 1 | 1 | 0.79881 | -1.85836 | | | | 118.72 | 119.7<br>(N-methylacetamide) |
| Methylene<br>$\angle HC_aH$ | 2.11106 | 2.11106 | 3.4252 | -15.75493 | 7 | H | H | 0.86359 | 1 | 1 | 1 | 0.75 | 1.15796 | 0 | | | | 108.44 | 107<br>(propane) |
| $\angle C_aC_bC_c$ | | | | | | | | | | | | | | | 69.51 | | | 110.49 | 112<br>(propane)<br>113.8<br>(butane)<br>110.8<br>(isobutane) |
| $\angle C_aC_bH$ | | | | | | | | | | | | | | | 69.51 | | | 110.49 | 111.0<br>(butane)<br>111.4<br>(isobutane) |
| Methyl<br>$\angle HC_aH$ | 2.09711 | 2.09711 | 3.4252 | -15.75493 | 7 | H | H | 0.86359 | 1 | 1 | 1 | 0.75 | 1.15796 | 0 | | | | 109.50 | |
| $\angle C_aC_bC_c$ | | | | | | | | | | | | | | | 70.56 | | | 109.44 | |
| $\angle C_aC_bH$ | | | | | | | | | | | | | | | 70.56 | | | 109.44 | |
| $\angle C_bC_aC_c$<br>iso $C_a$ | 2.91547 | 2.91547 | 4.7958 | -16.68412<br>$C_b$ | 26 | -16.68412<br>$C_c$ | 26 | 0.81549 | 0.81549 | 1 | 1 | 1 | 0.81549 | -1.85836 | | | | 110.67 | 110.8<br>(isobutane) |
| $\angle C_bC_aH$<br>iso $C_a$ | 2.91547 | 2.11323 | 4.1633 | -15.55033<br>$C_a$ | 5 | -14.82575<br>$C_b$ | 1 | 0.87495 | 0.91771 | 0.75 | 1 | 0.75 | 1.04887 | 0 | | | | 110.76 | |
| $\angle C_aC_bH$<br>iso $C_a$ | 2.91547 | 2.09711 | 4.1633 | -15.55033<br>$C_b$ | 5 | -14.82575<br>$C_a$ | 1 | 0.87495 | 0.91771 | 0.75 | 1 | 0.75 | 1.04887 | 0 | | | | 111.27 | 111.4<br>(isobutane) |
| $\angle C_bC_aC_b$<br>tert $C_a$ | 2.90327 | 2.90327 | 4.7958 | -16.68412<br>$C_b$ | 26 | -16.68412<br>$C_b$ | 26 | 0.81549 | 0.81549 | 1 | 1 | 1 | 0.81549 | -1.85836 | | | | 111.37 | 110.8<br>(isobutane) |
| $\angle C_bC_aC_d$ | | | | | | | | | | | | | | | 72.50 | | | 107.50 | |

## UREA ($CH_4N_2O$)

Urea, $CH_4N_2O$, comprises a $C=O$ functional group and two $C-NH_2$ moieties that each comprise a $NH_2$ functional group and a $C-N$ functional group. The $C=O$ group is equivalent to that given for formamide in the Amides section except that the energy terms due to oscillation in the transition state are matched to that of urea. The $NH_2$ and $C-N$ functional groups are also equivalent to those given in the Amides section. $E_T\left(atom-atom,msp^3.AO\right)$ (Eq. (15.61)) of the $C=O$ and $C-N$ groups are equivalent to those of formamide. The values given in the Amides section are $-3.58557\ eV$, and $-1.65376\ eV$, respectively.

The symbols of the functional groups of urea are given in Table 15.123. The geometrical (Eqs. (15.1-15.5) and (15.51)), intercept (Eqs. (15.80-15.87)), and energy (Eqs. (15.6-15.11) and (15.17-15.65)) parameters of urea are given in Tables 15.124, 15.125, and 15.126, respectively. The total energy of urea given in Table 15.127 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.126 corresponding to functional-group composition of the molecule. The bond angle parameters of urea determined using Eqs. (15.88-15.117) are given in Table 15.128. The color scale, translucent view of the charge-density of urea comprising the concentric shells of atoms with the outer shell bridged by one or more $H_2$-type ellipsoidal MOs or joined with one or more hydrogen MOs is shown in Figure 15.21.

Figure 15.21. Color scale, translucent view of the charge-density of urea showing the orbitals of the atoms at their radii, the ellipsoidal surface of each $H$ or $H_2$-type ellipsoidal MO that transitions to the corresponding outer shell of the atom(s) participating in each bond, and the hydrogen nuclei (red, not to scale).

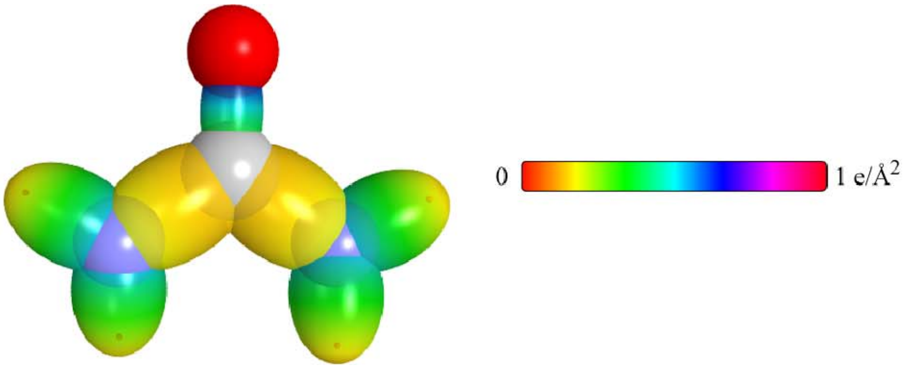


Table 15.123. The symbols of functional groups of urea.

| Functional Group | Group Symbol |
|---|---|
| *C=O* (urea) | $C=O$ |
| *(O)C-N* (urea) | $C-N$ |
| $NH_2$ *group* | $NH_2$ |

Table 15.124. The geometrical bond parameters of urea and experimental values [1].

| Parameter | $C=O$ Group | $C-N$ Group | $NH_2$ Group |
|---|---|---|---|
| $a\ (a_0)$ | 1.290799 | 1.70920 | 1.32297 |
| $c'\ (a_0)$ | 1.13613 | 1.30736 | 0.97065 |
| Bond Length $2c'$ $(Å)$ | 1.20243 | 1.38365 | 1.02729 |
| Exp. Bond Length $(Å)$ | 1.212<br>(formamide) | 1.368<br>(formamide) | 1.027<br>(formamide)<br>1.022<br>(acetamide) |
| $b,c\ (a_0)$ | 0.61267 | 1.10098 | 0.89894 |
| $e$ | 0.88018 | 0.76490 | 0.73369 |

Table 15.125. The MO to HO intercept geometrical bond parameters of urea. $E_T$ is $E_T$ ($atom - atom, msp^3.AO$).

| Bond | Atom | $E_T$ (eV) Bond 1 | $E_T$ (eV) Bond 2 | $E_T$ (eV) Bond 3 | $E_T$ (eV) Bond 4 | Final Total Energy $C2sp^3$ (eV) | $r_{initial}$ $(a_0)$ | $r_{final}$ $(a_0)$ | $E_{Coulomb}$ (eV) Final | $E(C2sp^3)$ (eV) Final | $\theta'$ (°) | $\theta_1$ (°) | $\theta_2$ (°) | $d_1$ $(a_0)$ | $d_2$ $(a_0)$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $H_2NC(O)N(H)-H$ | $N$ | -0.82688 | 0 | 0 | 0 | | 0.93084 | 0.86923 | -15.65263 | | 113.90 | 66.10 | 62.13 | 0.61843 | 0.35222 |
| $H_2NC(O)-NH_2$ | $N$ | -0.82688 | 0 | 0 | 0 | | 0.93084 | 0.86923 | -15.65263 | | 103.93 | 76.07 | 50.02 | 1.09814 | 0.20922 |
| $H_2NC(O)-NH_2$ | $C$ | -0.82688 | -1.79278 | -0.82688 | 0 | -155.06223 | 0.91771 | 0.74461 | -18.27229 | -18.08143 | 93.56 | 86.44 | 42.45 | 1.26106 | 0.04630 |
| $H_2NC_a(NH_2)=O$ | $O$ | -1.79278 | 0 | 0 | 0 | | 1.00000 | 0.81871 | -16.61853 | | 137.10 | 42.90 | 65.45 | 0.53635 | 0.59978 |
| $H_2NC_a(NH_2)=O$ | $C$ | -1.79278 | --0.82688 | -0.82688 | 0 | -155.06223 | 0.91771 | 0.74461 | -18.27229 | -18.08143 | 133.82 | 46.18 | 61.27 | 0.62054 | 0.51559 |

Table 15.126. The energy parameters ($eV$) of functional groups of urea.

| Parameters | $C=O$ Group | $C-N$ Group | $NH_2$ Group |
|---|---|---|---|
| $n_1$ | 2 | 1 | 2 |
| $n_2$ | 0 | 0 | 0 |
| $n_3$ | 0 | 0 | 1 |
| $C_1$ | 0.5 | 0.5 | 0.75 |
| $C_2$ | 1 | 1 | 0.93613 |
| $c_1$ | 1 | 1 | 0.75 |
| $c_2$ | 0.85395 | 0.91140 | 1 |
| $c_3$ | 2 | 0 | 0 |
| $c_4$ | 4 | 2 | 1 |
| $c_5$ | 0 | 0 | 2 |
| $C_{1o}$ | 0.5 | 0.5 | 1.5 |
| $C_{2o}$ | 1 | 1 | 1 |
| $V_e\ (eV)$ | -112.61934 | -38.24008 | -78.77719 |
| $V_p\ (eV)$ | 23.95107 | 10.40705 | 28.03446 |
| $T\ (eV)$ | 43.62389 | 11.18655 | 29.77286 |
| $V_m\ (eV)$ | -21.81195 | -5.59327 | -14.88643 |
| $E(AO/HO)\ (eV)$ | 0 | -14.63489 | -14.53414 |
| $\Delta E_{H_2MO}(AO/HO)\ (eV)$ | -3.58557 | -5.23932 | -1.65376 |
| $E_T(AO/HO)\ (eV)$ | 3.58557 | -9.39557 | -12.88038 |
| $E(n_3\ AO/HO)\ (eV)$ | 0 | 0 | -14.53414 |
| $E_T(H_2MO)\ (eV)$ | -63.27075 | -31.63533 | -48.73668 |
| $E_T(atom-atom, msp^3.AO)\ (eV)$ | -3.58557 | -1.65376 | 0 |
| $E_T(MO)\ (eV)$ | -66.85630 | -33.28912 | -48.73660 |
| $\omega\ (10^{15}\ rad/s)$ | 19.9334 | 13.0822 | 59.4067 |
| $E_K\ (eV)$ | 13.12053 | 8.61093 | 39.10250 |
| $\bar{E}_D\ (eV)$ | -0.23955 | -0.19325 | -0.39136 |
| $\bar{E}_{Kvib}\ (eV)$ | 0.21747 [32] | 0.17358 [33] | 0.40929 [22] |
| $\bar{E}_{osc}\ (eV)$ | -0.13081 | -0.10647 | -0.18672 |
| $E_{mag}\ (eV)$ | 0.11441 | 0.14803 | 0.14185 |
| $E_T(Group)\ (eV)$ | -67.11793 | -33.39559 | -49.11003 |
| $E_{initial}(c_4\ AO/HO)\ (eV)$ | -14.63489 | -14.63489 | -14.53414 |
| $E_{initial}(c_5\ AO/HO)\ (eV)$ | 0 | 0 | -13.59844 |
| $E_D(Group)\ (eV)$ | 8.34955 | 4.12581 | 7.37901 |

Table 15.127. The total bond energies of urea calculated using the functional group composition and the energies of Table 15.126 compared to the experimental values [3].

| Formula | Name | $C=O$ Group | $C-N$ Group | $NH_2$ Group | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|---|---|---|
| $CH_4N_2O$ | Urea | 1 | 2 | 2 | 31.35919 | 31.393 | 0.00108 |

Table 15.128. The bond angle parameters of urea and experimental values [1]. In the calculation of $\theta_v$, the parameters from the preceding angle were used. $E_T$ is $E_T(atom-atom,msp^3.AO)$.

| Atoms of Angle | 2$c'$ Bond 1 ($a_0$) | 2$c'$ Bond 2 ($a_0$) | 2$c'$ Terminal Atoms ($a_0$) | $E_{Coulombic}$ Atom 1 | Atom 1 Hybridization Designation (Table 15.3.A) | $E_{Coulombic}$ Atom 2 | Atom 2 Hybridization Designation (Table 15.3.A) | $c_2$ Atom 1 | $c_2$ Atom 2 | $C_1$ | $C_2$ | $c_1$ | $c_2'$ | $E_T$ (eV) | $\theta_v$ (°) | $\theta_1$ (°) | $\theta_2$ (°) | Cal. $\theta$ (°) | Exp. $\theta$ (°) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $\angle HNH$ | 1.94130 | 1.94130 | 3.1464 | -14.53414 | N | H | H | 0.93613 Eq. (15.71)) | 1 | 1 | 1 | 0.75 | 1.06823 | 0 | | | | 108.27 | |
| $\angle C_aNH$ | 2.61473 | 1.94130 | 3.9328 | -14.53414 $N$ | N | -14.82575 $C_a$ | 1 | 0.93613 (Eq. (15.71)) | 0.91771 | 0.75 | 1 | 0.75 | 0.98033 | 0 | | | | 118.61 | 119.2 (formamide) |
| $\angle OC_aN$ | 2.27227 | 2.61473 | 4.3359 | 16.17521 $O$ | 13 | -16.37720 $N$ | 19 | 0.84115 | 0.83078 | 1 | 1 | 1 | 0.83596 | -1.44915 | | | | 124.91 | 125.0 (formamide) |

## CARBOXYLIC ACID HALIDES ($C_nH_{2n-1}OX,\ X=F,Cl,Br,I;\ n=1,2,3,4,5...\infty$)

The alkyl carboxylic acid halides, $C_nH_{2n-1}OX$, comprise a $C=O$ functional group, and the single bond of carbon to the carbonyl carbon atom, $C-C(O)$, is also a functional group. All carboxylic acid halides further comprise a $C-X$ functional group where $X$ is a halogen atom. The alkyl portion of the alkyl carboxylic acid halide may comprise at least two terminal methyl groups ($CH_3$) at each end of the chain, and may comprise methylene ($CH_2$), and methylyne ($CH$) functional groups as well as $C$ bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($(CH_3)_2CH$) and t-butyl ($(CH_3)_3C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups. The branched-chain-alkane groups in carboxylic acids are equivalent to those in branched-chain alkanes.

The alkyl carboxylic acid halide $C=O$ and $C-C(O)$ groups are equivalent to those given in the Aldehydes section and the Ketones section, respectively. The values of $E_T\left(atom-atom,msp^3.AO\right)$ given in these sections are $-2.69893\ eV$ and $-1.44915\ eV$, respectively.

As in the case of alkyl halides, each $(O)C-X$ group is solved by hybridizing the $2s$ and $2p$ AOs of the $C$ atom to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between the $C2sp^3$ HO and the $X$ AO to form a MO permits each participating orbital to decrease in radius and energy. For example, to meet the equipotential condition of the union of the $(O)C\text{–}Cl$ $H_2$-type-ellipsoidal-MO with other orbitals of the molecule, the hybridization factor $C_2$ of Eq. (15.61) for the $(O)C\text{–}Cl$-bond MO given by Eq. (15.130) is $C_2\left(C2sp^3HO\ to\ Cl\right)=0.81317$. The solution is equivalent to that of the alkyl chloride bond except that the energy parameters corresponding to oscillation in the transition state are matched to those of a carboxylic acid chloride.

As in the case with the $C-Cl$ group of alkyl chlorides, $E_T\left(atom-atom,msp^3.AO\right)$ of the $(O)C\text{–}Cl$-bond MO in Eq. (15.61) of alkyl carboxylic acid chlorides due to the charge donation from the $C$ and $Cl$ atoms to the MO is $-1.44915\ eV$ where both energy contributions are given by Eq. (14.511). This matches the energy of the $C-C(O)$ functional group with that of the $(O)C\text{–}Cl$ group within the carboxylic acid chloride molecule.

The symbols of the functional groups of alkyl carboxylic acid chlorides are given in Table 15.129. The geometrical (Eqs. (15.1-15.5) and (15.51)), intercept (Eqs. (15.80-15.87)), and energy (Eqs. (15.6-15.11) and (15.17-15.65)) parameters of alkyl carboxylic acid chlorides are given in Tables 15.130, 15.131, and 15.132, respectively. The total energy of each alkyl carboxylic acid chloride given in Table 15.133 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.132 corresponding to functional-group composition of the molecule. The bond angle parameters of alkyl carboxylic acid chlorides determined using Eqs. (15.88-15.117) are given in Table 15.134. The color scale, translucent view of the charge-density of exemplary carboxylic acid halide, acetyl chloride, comprising the concentric shells of atoms with the outer shell bridged by one or more $H_2$-type ellipsoidal MOs or joined with one or more hydrogen MOs is shown in Figure 15.22.

Figure 15.22. Color scale, translucent view of the charge-density of acetyl chloride showing the orbitals of the atoms at their radii, the ellipsoidal surface of each $H$ or $H_2$-type ellipsoidal MO that transitions to the corresponding outer shell of the atom(s) participating in each bond, and the hydrogen nuclei (red, not to scale).

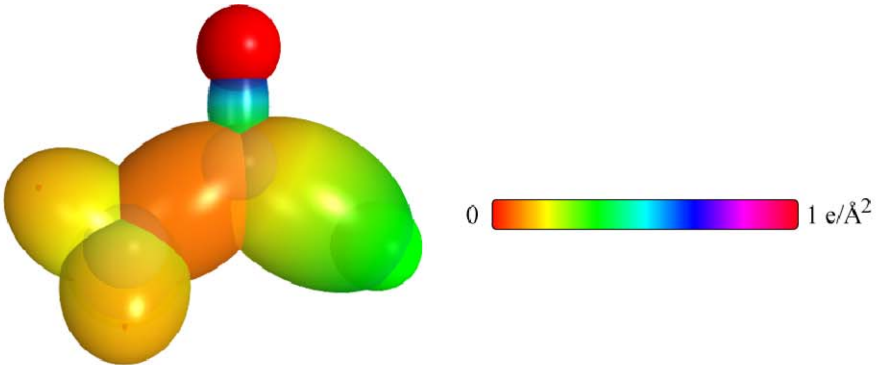


Table 15.129. The symbols of functional groups of alkyl carboxylic acid chlorides.

| Functional Group | Group Symbol |
|---|---|
| $C$-$C(O)$ | $C-C(O)$ |
| $C$=$O$ (alkyl carboxylic acid chloride) | $C=O$ |
| $(O)C$-$Cl$ | $C-Cl$ |
| $CH_3$ group | $C-H\ \left(CH_3\right)$ |
| $CH_2$ group | $C-H\ \left(CH_2\right)$ |
| $CH$ (alkyl) group | $C-H$ |
| $CC$ bond (*n*-$C$) | $C-C$ (a) |
| $CC$ bond (*iso*-$C$) | $C-C$ (b) |
| $CC$ bond (*tert*-$C$) | $C-C$ (c) |
| $CC$ (*iso* to *iso*-$C$) | $C-C$ (d) |
| $CC$ (*t* to *t*-$C$) | $C-C$ (e) |
| $CC$ (*t* to *iso*-$C$) | $C-C$ (f) |

Table 15.130. The geometrical bond parameters of alkyl carboxylic acid chlorides and experimental values [1].

| Parameter | $C-C(O)$ Group | $C=O$ Group | $C-Cl$ Group | $C-H\left(CH_3\right)$ Group | $C-H\left(CH_2\right)$ Group | $C-H$ Group | $C-C$ (a) Group | $C-C$ (b) Group | $C-C$ (c) Group | $C-C$ (d) Group | $C-C$ (e) Group | $C-C$ (f) Group |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $a\left(a_0\right)$ | 2.04740 | 1.29907 | 2.32621 | 1.64920 | 1.67122 | 1.67465 | 2.12499 | 2.12499 | 2.10725 | 2.12499 | 2.10725 | 2.10725 |
| $c'\left(a_0\right)$ | 1.43087 | 1.13977 | 1.69136 | 1.04856 | 1.05553 | 1.05661 | 1.45744 | 1.45744 | 1.45164 | 1.45744 | 1.45164 | 1.45164 |
| Bond Length $2c'$ $\left(\mathring{A}\right)$ | 1.51437 | 1.20628 | 1.79005 | 1.10974 | 1.11713 | 1.11827 | 1.54280 | 1.54280 | 1.53635 | 1.54280 | 1.53635 | 1.53635 |
| Exp. Bond Length $\left(\mathring{A}\right)$ | 1.520<br>(acetone)<br>1.518<br>(2-butanone) | 1.187<br>(acetyl chloride)<br>1.214<br>(acetic acid) | 1.798<br>(acetyl chloride) | 1.107<br>($C-H$ propane)<br>1.117<br>($C-H$ butane) | 1.107<br>($C-H$ propane)<br>1.117<br>($C-H$ butane) | 1.122<br>(isobutane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) |
| $b,c\left(a_0\right)$ | 1.46439 | 0.62331 | 1.59705 | 1.27295 | 1.29569 | 1.29924 | 1.54616 | 1.54616 | 1.52750 | 1.54616 | 1.52750 | 1.52750 |
| $e$ | 0.69887 | 0.87737 | 0.72709 | 0.63580 | 0.63159 | 0.63095 | 0.68600 | 0.68600 | 0.68888 | 0.68600 | 0.68888 | 0.68888 |

Table 15.131. The MO to HO intercept geometrical bond parameters of alkyl carboxylic acid chlorides. $R$, $R'$, $R''$ are $H$ or alkyl groups. $E_T$ is $E_T$ $(atom-atom,msp^3.AO)$.

| Bond | Atom | $E_T$ (eV) Bond 1 | $E_T$ (eV) Bond 2 | $E_T$ (eV) Bond 3 | $E_T$ (eV) Bond 4 | Final Total Energy $C2sp^3$ (eV) | $r_{initial}$ $\left(a_0\right)$ | $r_{final}$ $\left(a_0\right)$ | $E_{Coulomb}$ (eV) Final | $E\left(C2sp^3\right)$ (eV) Final | $\theta'$ $\left(^\circ\right)$ | $\theta_1$ $\left(^\circ\right)$ | $\theta_2$ $\left(^\circ\right)$ | $d_1$ $\left(a_0\right)$ | $d_2$ $\left(a_0\right)$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $H_3C_bC_a(O)-Cl$ | $Cl$ | -0.72457 | 0 | 0 | 0 |  | 1.05158 | 0.87495 | -15.55033 |  | 69.62 | 110.38 | 30.90 | 1.99599 | 0.30463 |
| $H_3C_bC_a(O)-Cl$ | $C_a$ | -1.34946 | -0.72457 | -0.72457 | 0 | -154.41430 | 0.91771 | 0.77199 | -17.62436 | -17.43350 | 54.69 | 125.31 | 23.23 | 2.13760 | 0.44625 |
| $H_3C_bC_a(Cl)=O$ | $O$ | -1.34946 | 0 | 0 | 0 |  | 1.00000 | 0.84115 | -16.17521 |  | 137.27 | 42.73 | 66.31 | 0.52193 | 0.61784 |
| $H_3C_bC_a(Cl)=O$ | $C_a$ | -1.34946 | -0.72457 | -0.72457 | 0 | -154.41430 | 0.91771 | 0.77199 | -17.62436 | -17.43350 | 134.28 | 45.72 | 62.45 | 0.60076 | 0.53901 |
| $H_3C_b-C_a(O)-Cl$ | $C_a$ | -0.72457 | -1.34946 | -0.72457 | 0 | -154.41430 | 0.91771 | 0.77199 | -17.62436 | -17.43350 | 59.30 | 120.70 | 26.96 | 1.82495 | 0.39408 |
| $H_3C_b-C_a(O)-Cl$ | $C_b$ | -0.72457 | 0 | 0 | 0 | -152.34026 | 0.91771 | 0.87495 | -15.55033 | -15.35946 | 73.62 | 106.38 | 34.98 | 1.67762 | 0.24675 |
| $C-H\left(CH_3\right)$ | $C$ | -0.92918 | 0 | 0 | 0 | -152.54487 | 0.91771 | 0.86359 | -15.75493 | -15.56407 | 77.49 | 102.51 | 41.48 | 1.23564 | 0.18708 |
| $C-H\left(CH_2\right)$ | $C$ | -0.92918 | -0.92918 | 0 | 0 | -153.47406 | 0.91771 | 0.81549 | -16.68412 | -16.49325 | 68.47 | 111.53 | 35.84 | 1.35486 | 0.29933 |
| $C-H\left(CH\right)$ (ii) | $C$ | -0.92918 | -0.92918 | -0.92918 | 0 | -154.40324 | 0.91771 | 0.77247 | -17.61330 | -17.42244 | 61.10 | 118.90 | 31.37 | 1.42988 | 0.37326 |
| $H_3C_aC_bH_2CH_2-$ ($C-C$ (a)) | $C_a$ | -0.92918 | 0 | 0 | 0 | -152.54487 | 0.91771 | 0.86359 | -15.75493 | -15.56407 | 63.82 | 116.18 | 30.08 | 1.83879 | 0.38106 |
| $H_3C_aC_bH_2CH_2-$ ($C-C$ (a)) | $C_b$ | -0.92918 | -0.92918 | 0 | 0 | -153.47406 | 0.91771 | 0.81549 | -16.68412 | -16.49325 | 56.41 | 123.59 | 26.06 | 1.90890 | 0.45117 |
| $R-H_2C_aC_b\left(H_2C_c-R'\right)HCH_2-$ ($C-C$ (b)) | $C_b$ | -0.92918 | -0.92918 | -0.92918 | 0 | -154.40324 | 0.91771 | 0.77247 | -17.61330 | -17.42244 | 48.30 | 131.70 | 21.90 | 1.97162 | 0.51388 |
| $R-H_2C_a\left(R'-H_2C_d\right)C_b\left(R''-H_2C_c\right)CH_2-$ ($C-C$ (c)) | $C_b$ | -0.92918 | -0.72457 | -0.72457 | -0.72457 | -154.71860 | 0.91771 | 0.75889 | -17.92866 | -17.73779 | 48.21 | 131.79 | 21.74 | 1.95734 | 0.50570 |
| $isoC_aC_b\left(H_2C_c-R'\right)HCH_2-$ ($C-C$ (d)) | $C_b$ | -0.92918 | -0.92918 | -0.92918 | 0 | -154.40324 | 0.91771 | 0.77247 | -17.61330 | -17.42244 | 48.30 | 131.70 | 21.90 | 1.97162 | 0.51388 |
| $tertC_a\left(R'-H_2C_d\right)C_b\left(R''-H_2C_c\right)CH_2-$ ($C-C$ (e)) | $C_b$ | -0.72457 | -0.72457 | -0.72457 | -0.72457 | -154.51399 | 0.91771 | 0.76765 | -17.92866 | -17.73779 | 50.04 | 129.96 | 22.66 | 1.94462 | 0.49298 |
| $tertC_aC_b\left(H_2C_c-R'\right)HCH_2-$ ($C-C$ (f)) | $C_b$ | -0.72457 | -0.92918 | -0.92918 | 0 | -154.19863 | 0.91771 | 0.78155 | -17.40869 | -17.21783 | 52.78 | 127.22 | 24.04 | 1.92443 | 0.47279 |
| $isoC_a\left(R'-H_2C_d\right)C_b\left(R''-H_2C_c\right)CH_2-$ ($C-C$ (f)) | $C_b$ | -0.72457 | -0.72457 | -0.72457 | -0.72457 | -154.51399 | 0.91771 | 0.76765 | -17.92866 | -17.73779 | 50.04 | 129.96 | 22.66 | 1.94462 | 0.49298 |

Table 15.132. The energy parameters $(eV)$ of functional groups of alkyl carboxylic acid chlorides.

| Parameters | $C-C(O)$ Group | $C=O$ Group | $C-Cl$ Group | $CH_3$ Group | $CH_2$ Group | $C-H$ (ii) Group | $C-C$ (a) Group | $C-C$ (b) Group | $C-C$ (c) Group | $C-C$ (d) Group | $C-C$ (e) Group | $C-C$ (f) Group |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $n_1$ | 1 | 2 | 1 | 3 | 2 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $n_2$ | 0 | 0 | 0 | 2 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $n_3$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $C_1$ | 0.5 | 0.5 | 0.5 | 0.75 | 0.75 | 0.75 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| $C_2$ | 1 | 1 | 0.81317 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $c_1$ | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $c_2$ | 0.91771 | 0.85395 | 1 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 |
| $c_3$ | 0 | 2 | 1 | 0 | 1 | 1 | 0 | 0 | 0 | 1 | 1 | 0 |
| $c_4$ | 2 | 4 | 2 | 1 | 1 | 1 | 2 | 2 | 2 | 2 | 2 | 2 |
| $c_5$ | 0 | 0 | 0 | 3 | 2 | 1 | 0 | 0 | 0 | 0 | 0 | 0 |
| $C_{1o}$ | 1 | 0.5 | 0.5 | 0.75 | 0.75 | 0.75 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| $C_{2o}$ | 1 | 1 | 0.81317 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $V_e\ (eV)$ | -30.19634 | -111.25473 | -29.68411 | -107.32728 | -70.41425 | -35.12015 | -28.79214 | -28.79214 | -29.10112 | -28.79214 | -29.10112 | -29.10112 |
| $V_p\ (eV)$ | 9.50874 | 23.87467 | 8.04432 | 38.92728 | 25.78002 | 12.87680 | 9.33352 | 9.33352 | 9.37273 | 9.33352 | 9.37273 | 9.37273 |
| $T\ (eV)$ | 7.37432 | 42.82081 | 6.38036 | 32.53914 | 21.06675 | 10.48582 | 6.77464 | 6.77464 | 6.90500 | 6.77464 | 6.90500 | 6.90500 |
| $V_m\ (eV)$ | -3.68716 | -21.41040 | -3.19018 | -16.26957 | -10.53337 | -5.24291 | -3.38732 | -3.38732 | -3.45250 | -3.38732 | -3.45250 | -3.45250 |
| $E(_{AO/HO})\ (eV)$ | -14.63489 | 0 | -14.63489 | -15.56407 | -15.56407 | -14.63489 | -15.56407 | -15.56407 | -15.35946 | -15.56407 | -15.35946 | -15.35946 |
| $\Delta E_{H_2MO}(_{AO/HO})\ (eV)$ | 0 | -2.69893 | -1.44915 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $E_T(_{AO/HO})\ (eV)$ | -14.63489 | 2.69893 | -13.18574 | -15.56407 | -15.56407 | -14.63489 | -15.56407 | -15.56407 | -15.35946 | -15.56407 | -15.35946 | -15.35946 |
| $E_T(_{H_2MO})\ (eV)$ | -31.63534 | -63.27074 | -31.63536 | -67.69451 | -49.66493 | -31.63533 | -31.63537 | -31.63537 | -31.63535 | -31.63537 | -31.63535 | -31.63535 |
| $E_T\left(atom-atom,msp^3.AO\right)(eV)$ | -1.44915 | -2.69893 | -1.44915 | 0 | 0 | 0 | -1.85836 | -1.85836 | -1.44915 | -1.85836 | -1.44915 | -1.44915 |
| $E_T(_{MO})\ (eV)$ | -33.08452 | -65.96966 | -33.08452 | -67.69450 | -49.66493 | -31.63537 | -33.49373 | -33.49373 | -33.08452 | -33.49373 | -33.08452 | -33.08452 |
| $\omega\ \left(10^{15}\ rad/s\right)$ | 16.4962 | 59.4034 | 7.42995 | 24.9286 | 24.2751 | 24.1759 | 9.43699 | 9.43699 | 15.4846 | 9.43699 | 9.55643 | 9.55643 |
| $E_K\ (eV)$ | 10.85807 | 39.10034 | 4.89052 | 16.40846 | 15.97831 | 15.91299 | 6.21159 | 6.21159 | 10.19220 | 6.21159 | 6.29021 | 6.29021 |
| $\bar{E}_D\ (eV)$ | -0.21568 | -0.40804 | -0.14475 | -0.25352 | -0.25017 | -0.24966 | -0.16515 | -0.16515 | -0.20896 | -0.16515 | -0.16416 | -0.16416 |
| $\bar{E}_{Kvib}\ (eV)$ | 0.14655 [28] | 0.21077 [12] | 0.09063 [34] | 0.35532 (Eq. (13.458)) | 0.35532 (Eq. (13.458)) | 0.35532 (Eq. (13.458)) | 0.12312 [2] | 0.17978 [4] | 0.09944 [5] | 0.12312 [2] | 0.12312 [2] | 0.12312 [2] |
| $\bar{E}_{osc}\ (eV)$ | -0.14240 | -0.30266 | -0.09943 | -0.22757 | -0.14502 | -0.07200 | -0.10359 | -0.07526 | -0.15924 | -0.10359 | -0.10260 | -0.10260 |
| $E_{mag}\ (eV)$ | 0.14803 | 0.11441 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 |
| $E_T(_{Group})\ (eV)$ | -33.22692 | -66.57498 | -33.18395 | -67.92207 | -49.80996 | -31.70737 | -33.59732 | -33.49373 | -33.24376 | -33.59732 | -33.18712 | -33.18712 |
| $E_{initial}(_{c_4\ AO/HO})\ (eV)$ | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 |
| $E_{initial}(_{c_5\ AO/HO})\ (eV)$ | 0 | 0 | 0 | -13.59844 | -13.59844 | -13.59844 | 0 | 0 | 0 | 0 | 0 | 0 |
| $E_D(_{Group})\ (eV)$ | 3.95714 | 7.80660 | 3.76614 | 12.49186 | 7.83016 | 3.32601 | 4.32754 | 4.29921 | 3.97398 | 4.17951 | 3.62128 | 3.91734 |

Table 15.133. The total bond energies of alkyl carboxylic acid chlorides calculated using the functional group composition and the energies of Table 15.132 compared to the experimental values [3].

| Formula | Name | $C-C(O)$ Group | $C=O$ Group | $C-Cl$ Group | $CH_3$ | $CH_2$ | $CH$ | $C-C$ (a) | $C-C$ (b) | $C-C$ (c) | $C-C$ (d) | $C-C$ (e) | $C-C$ (f) | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $C_2H_3ClO$ | Acetyl chloride | 1 | 1 | 1 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 28.02174 | 27.990 | -0.00115 |

Table 15.134. The bond angle parameters of alkyl carboxylic acid chlorides and experimental values [1]. In the calculation of $\theta_v$, the parameters from the preceding angle were used. $E_T$ is $E_T(atom-atom,msp^3.AO)$.

| Atoms of Angle | $2c'$ Bond 1 $(a_0)$ | $2c'$ Bond 2 $(a_0)$ | $2c'$ Terminal Atoms $(a_0)$ | $E_{Coulombic}$ Atom 1 | Atom 1 Hybridization Designation (Table 15.3.A) | $E_{Coulombic}$ Atom 2 | Atom 2 Hybridization Designation (Table 15.3.A) | $c_2$ Atom 1 | $c_2$ Atom 2 | $C_1$ | $C_2$ | $c_1$ | $c_2'$ | $E_T$ (eV) | $\theta_v$ (°) | $\theta_1$ (°) | $\theta_2$ (°) | Cal. $\theta$ (°) | Exp. $\theta$ (°) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $\angle C_bC_aO$ | 2.86175 | 2.27954 | 4.5826 | -16.68411 | 25 | -13.61806 | O | 0.81549 | 0.85395 (Eq. (15.132)) | 1 | 1 | 1 | 0.83472 | -1.65376 | | | | 125.70 | |
| $\angle C_bC_aCl$ | 2.86175 | 3.38271 | 5.1539 | -15.75493 $C_b$ | 7 | -12.96764 $Cl$ | Cl | 0.86359 | 0.86359 | 1 | 0.81317 (Eq. (15.130)) | 1 | 0.86359 | -0.92918 | | | | 110.98 | 111.6 (acetyl chloride) |
| $\angle OC_aCl$ | 2.27954 | 3.38271 | 4.9841 | -16.68412 $O$ | 26 | -15.55033 $Cl$ | 5 | 0.81549 | 0.87495 | 1 | 0.81317 (Eq. (15.130)) | 1 | 0.84522 | -0.92918 | | | | 122.13 | 121.2 (acetyl chloride) |
| Methylene $\angle HC_aH$ | 2.11106 | 2.11106 | 3.4252 | -15.75493 | 7 | H | H | 0.86359 | 1 | 1 | 1 | 0.75 | 1.15796 | 0 | | | | 108.44 | 107 (propane) |
| $\angle C_aC_bC_c$ | | | | | | | | | | | | | | | 69.51 | | | 110.49 | 112 (propane)<br>113.8 (butane)<br>110.8 (isobutane) |
| $\angle C_aC_bH$ | | | | | | | | | | | | | | | 69.51 | | | 110.49 | 111.0 (butane)<br>111.4 (isobutane) |
| Methyl $\angle HC_aH$ | 2.09711 | 2.09711 | 3.4252 | -15.75493 | 7 | H | H | 0.86359 | 1 | 1 | 1 | 0.75 | 1.15796 | 0 | | | | 109.50 | |
| $\angle C_aC_bC_c$ | | | | | | | | | | | | | | | 70.56 | | | 109.44 | |
| $\angle C_aC_bH$ | | | | | | | | | | | | | | | 70.56 | | | 109.44 | |
| $\angle C_bC_aC_c$ iso $C_a$ | 2.91547 | 2.91547 | 4.7958 | -16.68412 $C_b$ | 26 | -16.68412 $C_c$ | 26 | 0.81549 | 0.81549 | 1 | 1 | 1 | 0.81549 | -1.85836 | | | | 110.67 | 110.8 (isobutane) |
| $\angle C_bC_aH$ iso $C_a$ | 2.91547 | 2.11323 | 4.1633 | -15.55033 $C_a$ | 5 | -14.82575 $C_b$ | 1 | 0.87495 | 0.91771 | 0.75 | 1 | 0.75 | 1.04887 | 0 | | | | 110.76 | |
| $\angle C_aC_bH$ iso $C_a$ | 2.91547 | 2.09711 | 4.1633 | -15.55033 $C_b$ | 5 | -14.82575 $C_a$ | 1 | 0.87495 | 0.91771 | 0.75 | 1 | 0.75 | 1.04887 | 0 | | | | 111.27 | 111.4 (isobutane) |
| $\angle C_bC_aC_b$ tert $C_a$ | 2.90327 | 2.90327 | 4.7958 | -16.68412 $C_b$ | 26 | -16.68412 $C_b$ | 26 | 0.81549 | 0.81549 | 1 | 1 | 1 | 0.81549 | -1.85836 | | | | 111.37 | 110.8 (isobutane) |
| $\angle C_bC_aC_d$ | | | | | | | | | | | | | | | 72.50 | | | 107.50 | |

## CARBOXYLIC ACID ANHYDRIDES ($C_nH_{2n-2}O_3$, $n = 2,3,4,5...\infty$)

The alkyl carboxylic acid anhydrides, $C_nH_{2n-2}O_3$, have two $(O)C-O$ moieties that each comprise $C=O$ and $C-O$ functional groups. The single bond of carbon to the carbonyl carbon atom, $C-C(O)$, is also a functional group. The alkyl portion of the alkyl carboxylic acid anhydride may comprise at least two terminal methyl groups ($CH_3$) at each end of the chain, and may comprise methylene ($CH_2$), and methylyne ($CH$) functional groups as well as $C$ bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($(CH_3)_2CH$) and t-butyl ($(CH_3)_3C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups. The branched-chain-alkane groups in carboxylic acid anhydrides are equivalent to those in branched-chain alkanes.

The alkyl carboxylic acid anhydride $C=O$ and $C-C(O)$ groups are equivalent to those given in the Carboxylic Acid Esters section and the Ketones section, respectively. The values of $E_T\left(atom-atom,msp^3.AO\right)$ given in these sections are $-2.69893\ eV$ and $-1.44915\ eV$, respectively. The $C-O$ group is also equivalent to that given in the Carboxylic Acid Esters section except that $E_T\left(atom-atom,msp^3.AO\right)$ is equivalent to that of an alkyl ether as given in the corresponding section and the energy terms due to oscillation in the transition state are matched to that of a carboxylic acid anhydride.

For the $C-O$ group, $E_T\left(atom-atom,msp^3.AO\right)$ is $-1.65376\ eV$. It is based on the energy match between the $O$ AO and the $C2sp^3$ HO of each $C-C(O)$ group and is given by the linear combination of $-0.72457\ eV$ (Eq. (14.151)) and $-0.92918\ eV$ (Eq. (14.513)), respectively. This matches $-0.72457\ eV$, the energy contribution of each of the $C2sp^3$ HOs to each $C-C(O)$ functional group, with that of the corresponding energy component of the $C-O$ group and gives a minimum energy within the carboxylic acid anhydride molecule.

The symbols of the functional groups of alkyl carboxylic acid anhydrides are given in Table 15.135. The geometrical (Eqs. (15.1-15.5) and (15.51)), intercept (Eqs. (15.80-15.87)), and energy (Eqs. (15.6-15.11) and (15.17-15.65)) parameters of alkyl carboxylic acid anhydrides are given in Tables 15.136, 15.137, and 15.138, respectively. The total energy of each alkyl carboxylic acid anhydride given in Table 15.139 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.138 corresponding to functional-group composition of the molecule. The bond angle parameters of alkyl carboxylic acid anhydrides determined using Eqs. (15.88-15.117) are given in Table 15.140. The color scale, translucent view of the charge-density of exemplary carboxylic acid anhydride, acetic anhydride, comprising the concentric shells of atoms with the outer shell bridged by one or more $H_2$-type ellipsoidal MOs or joined with one or more hydrogen MOs is shown in Figure 15.23.

Figure 15.23. (A)-(B), color scale, translucent views of the charge-density of acetic anhydride showing the orbitals of the atoms at their radii, the ellipsoidal surface of each $H$ or $H_2$-type ellipsoidal MO that transitions to the corresponding outer shell of the atom(s) participating in each bond, and the hydrogen nuclei (red, not to scale).

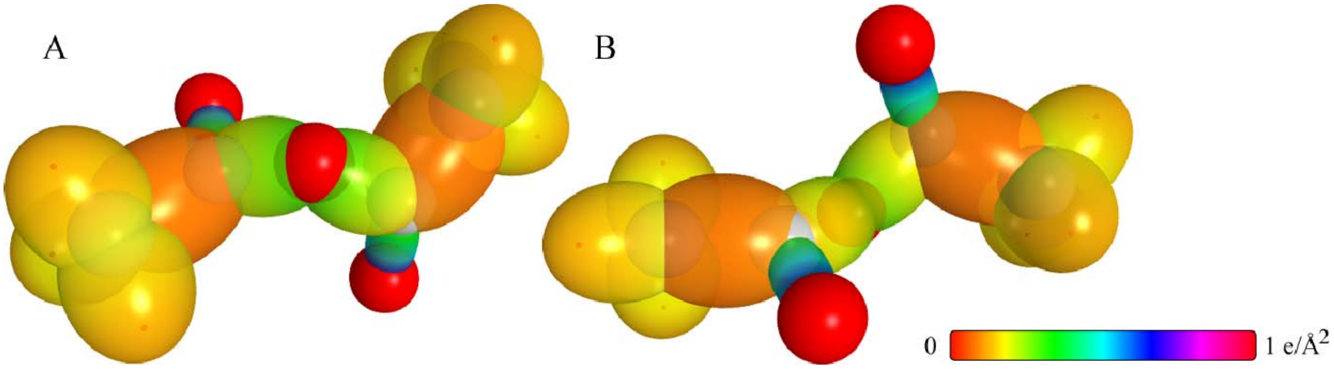


Table 15.135. The symbols of functional groups of alkyl carboxylic acid anhydrides.

| Functional Group | Group Symbol |
|---|---|
| $C$-$C(O)$ | $C-C(O)$ |
| $C$=$O$ (alkyl carboxylic acid anhydride) | $C=O$ |
| $(O)C$-$O$ | $C-O$ |
| $CH_3$ group | $C-H\ (CH_3)$ |
| $CH_2$ group | $C-H\ (CH_2)$ |
| $CH$ (alkyl) group | $C-H$ |
| $CC$ bond ($n$-$C$) | $C-C$ (a) |
| $CC$ bond ($iso$-$C$) | $C-C$ (b) |
| $CC$ bond ($tert$-$C$) | $C-C$ (c) |
| $CC$ ($iso$ to $iso$-$C$) | $C-C$ (d) |
| $CC$ ($t$ to $t$-$C$) | $C-C$ (e) |
| $CC$ ($t$ to $iso$-$C$) | $C-C$ (f) |

Table 15.136. The geometrical bond parameters of alkyl carboxylic acid anhydrides and experimental values [1].

| Parameter | $C-C(O)$ Group | $C=O$ Group | $C-O$ Group | $C-H\ (CH_3)$ Group | $C-H\ (CH_2)$ Group | $C-H$ Group | $C-C$ (a) Group | $C-C$ (b) Group | $C-C$ (c) Group | $C-C$ (d) Group | $C-C$ (e) Group | $C-C$ (f) Group |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $a\ (a_0)$ | 2.04740 | 1.29907 | 1.73490 | 1.64920 | 1.67122 | 1.67465 | 2.12499 | 2.12499 | 2.10725 | 2.12499 | 2.10725 | 2.10725 |
| $c'\ (a_0)$ | 1.43087 | 1.13977 | 1.31716 | 1.04856 | 1.05553 | 1.05661 | 1.45744 | 1.45744 | 1.45164 | 1.45744 | 1.45164 | 1.45164 |
| Bond Length $2c'$ ($\AA$) | 1.51437 | 1.20628 | 1.39402 | 1.10974 | 1.11713 | 1.11827 | 1.54280 | 1.54280 | 1.53635 | 1.54280 | 1.53635 | 1.53635 |
| Exp. Bond Length ($\AA$) | 1.520<br>(acetone)<br>1.518<br>(2-butanone) | 1.214<br>(acetic acid) | 1.393<br>(avg. methyl formate) | 1.107<br>($C-H$ propane)<br>1.117<br>($C-H$ butane) | 1.107<br>($C-H$ propane)<br>1.117<br>($C-H$ butane) | 1.122<br>(isobutane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) |
| $b,c\ (a_0)$ | 1.46439 | 0.62331 | 1.12915 | 1.27295 | 1.29569 | 1.29924 | 1.54616 | 1.54616 | 1.52750 | 1.54616 | 1.52750 | 1.52750 |
| $e$ | 0.69887 | 0.87737 | 0.75921 | 0.63580 | 0.63159 | 0.63095 | 0.68600 | 0.68600 | 0.68888 | 0.68600 | 0.68888 | 0.68888 |

Table 15.137. The MO to HO intercept geometrical bond parameters of alkyl carboxylic acid anhydrides. $R$, $R'$, $R''$ are $H$ or alkyl groups. $E_T$ is $E_T$ (*atom – atom,msp³.AO*).

| Bond | Atom | $E_T$ (eV) Bond 1 | $E_T$ (eV) Bond 2 | $E_T$ (eV) Bond 3 | $E_T$ (eV) Bond 4 | Final Total Energy $C2sp^3$ (eV) | $r_{initial}$ $(a_0)$ | $r_{final}$ $(a_0)$ | $E_{Coulomb}$ (eV) Final | $E(C2sp^3)$ (eV) Final | $\theta'$ (°) | $\theta_1$ (°) | $\theta_2$ (°) | $d_1$ $(a_0)$ | $d_2$ $(a_0)$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $RC_bH_2C_a(O)-O_a-C_a(O)C_cH_2R'$ | $O_a$ | -0.82688 | -0.82688 | 0 | 0 |  | 1.00000 | 0.82562 | -16.47951 |  | 98.32 | 81.68 | 46.34 | 1.19766 | 0.11949 |
| $RC_bH_2C_a(O)-O_a-C_a(O)C_cH_2R'$ | $C_a$ | -0.82688 | -1.34946 | -0.82688 | 0 | -154.51660 | 0.91771 | 0.76753 | -17.72667 | -17.53580 | 93.21 | 86.79 | 42.74 | 1.27417 | 0.04298 |
| $RC_bH_2(R'C_cH_2C_a(O_a)O)C_a=O_a$ | $O_a$ | -1.34946 | 0 | 0 | 0 |  | 1.00000 | 0.84115 | -16.17521 |  | 137.27 | 42.73 | 66.31 | 0.52193 | 0.61784 |
| $RC_bH_2(R'C_cH_2C_a(O_a)O)C_a=O_a$ | $C_a$ | -1.34946 | -0.72457 | -0.82688 | 0 | -154.51660 | 0.91771 | 0.76753 | -17.72667 | -17.53580 | 134.08 | 45.92 | 62.20 | 0.60583 | 0.53394 |
| $RH_2C_b-C_a(O)OC_a(O)C_cH_2R'$ | $C_a$ | -0.72457 | -1.34946 | -0.82688 | 0 | -154.51660 | 0.91771 | 0.76753 | -17.72667 | -17.53580 | 58.55 | 121.45 | 26.56 | 1.83133 | 0.40045 |
| $H_3C_b-C_a(O)OC_a(O)C_cH_2R'$ | $C_b$ | -0.72457 | 0 | 0 | 0 | -152.34026 | 0.91771 | 0.87495 | -15.55033 | -15.35946 | 73.62 | 106.38 | 34.98 | 1.67762 | 0.24675 |
| $RH_2C_b-C_a(O)OC_a(O)C_cH_2R'$<br>$R=alkyl$ | $C_b$ | -0.72457 | -0.92918 | 0 | 0 | -153.26945 | 0.91771 | 0.82562 | -16.47951 | -16.28865 | 67.40 | 112.60 | 31.36 | 1.74821 | 0.31734 |
| $C-H\ (CH_3)$ | $C$ | -0.92918 | 0 | 0 | 0 | -152.54487 | 0.91771 | 0.86359 | -15.75493 | -15.56407 | 77.49 | 102.51 | 41.48 | 1.23564 | 0.18708 |
| $C-H\ (CH_2)$ | $C$ | -0.92918 | -0.92918 | 0 | 0 | -153.47406 | 0.91771 | 0.81549 | -16.68412 | -16.49325 | 68.47 | 111.53 | 35.84 | 1.35486 | 0.29933 |
| $C-H\ (CH)$ (ii) | $C$ | -0.92918 | -0.92918 | -0.92918 | 0 | -154.40324 | 0.91771 | 0.77247 | -17.61330 | -17.42244 | 61.10 | 118.90 | 31.37 | 1.42988 | 0.37326 |
| $H_3C_aC_bH_2CH_2-$<br>($C-C$ (a)) | $C_a$ | -0.92918 | 0 | 0 | 0 | -152.54487 | 0.91771 | 0.86359 | -15.75493 | -15.56407 | 63.82 | 116.18 | 30.08 | 1.83879 | 0.38106 |
| $H_3C_aC_bH_2CH_2-$<br>($C-C$ (a)) | $C_b$ | -0.92918 | -0.92918 | 0 | 0 | -153.47406 | 0.91771 | 0.81549 | -16.68412 | -16.49325 | 56.41 | 123.59 | 26.06 | 1.90890 | 0.45117 |
| $R-H_2C_aC_b(H_2C_c-R')HCH_2-$<br>($C-C$ (b)) | $C_b$ | -0.92918 | -0.92918 | -0.92918 | 0 | -154.40324 | 0.91771 | 0.77247 | -17.61330 | -17.42244 | 48.30 | 131.70 | 21.90 | 1.97162 | 0.51388 |
| $R-H_2C_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$<br>($C-C$ (c)) | $C_b$ | -0.92918 | -0.72457 | -0.72457 | -0.72457 | -154.71860 | 0.91771 | 0.75889 | -17.92866 | -17.73779 | 48.21 | 131.79 | 21.74 | 1.95734 | 0.50570 |
| $isoC_aC_b(H_2C_c-R')HCH_2-$<br>($C-C$ (d)) | $C_b$ | -0.92918 | -0.92918 | -0.92918 | 0 | -154.40324 | 0.91771 | 0.77247 | -17.61330 | -17.42244 | 48.30 | 131.70 | 21.90 | 1.97162 | 0.51388 |
| $tertC_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$<br>($C-C$ (e)) | $C_b$ | -0.72457 | -0.72457 | -0.72457 | -0.72457 | -154.51399 | 0.91771 | 0.76765 | -17.92866 | -17.73779 | 50.04 | 129.96 | 22.66 | 1.94462 | 0.49298 |
| $tertC_aC_b(H_2C_c-R')HCH_2-$<br>($C-C$ (f)) | $C_b$ | -0.72457 | -0.92918 | -0.92918 | 0 | -154.19863 | 0.91771 | 0.78155 | -17.40869 | -17.21783 | 52.78 | 127.22 | 24.04 | 1.92443 | 0.47279 |
| $isoC_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$<br>($C-C$ (f)) | $C_b$ | -0.72457 | -0.72457 | -0.72457 | -0.72457 | -154.51399 | 0.91771 | 0.76765 | -17.92866 | -17.73779 | 50.04 | 129.96 | 22.66 | 1.94462 | 0.49298 |

Table 15.138. The energy parameters ($eV$) of functional groups of alkyl carboxylic acid anhydrides.

| Parameters | $C-C(O)$ Group | $C=O$ Group | $C-O$ Group | $CH_3$ Group | $CH_2$ Group | $C-H$ (ii) Group | $C-C$ (a) Group | $C-C$ (b) Group | $C-C$ (c) Group | $C-C$ (d) Group | $C-C$ (e) Group | $C-C$ (f) Group |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $n_1$ | 1 | 2 | 1 | 3 | 2 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $n_2$ | 0 | 0 | 0 | 2 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $n_3$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $C_1$ | 0.5 | 0.5 | 0.5 | 0.75 | 0.75 | 0.75 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| $C_2$ | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $c_1$ | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $c_2$ | 0.91771 | 0.85395 | 0.85395 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 |
| $c_3$ | 0 | 2 | 0 | 0 | 1 | 1 | 0 | 0 | 0 | 1 | 1 | 0 |
| $c_4$ | 2 | 4 | 2 | 1 | 1 | 1 | 2 | 2 | 2 | 2 | 2 | 2 |
| $c_5$ | 0 | 0 | 0 | 3 | 2 | 1 | 0 | 0 | 0 | 0 | 0 | 0 |
| $C_{1o}$ | 1 | 0.5 | 0.5 | 0.75 | 0.75 | 0.75 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| $C_{2o}$ | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $V_e\ (eV)$ | -30.19634 | -111.25473 | -35.08488 | -107.32728 | -70.41425 | -35.12015 | -28.79214 | -28.79214 | -29.10112 | -28.79214 | -29.10112 | -29.10112 |
| $V_p\ (eV)$ | 9.50874 | 23.87467 | 10.32968 | 38.92728 | 25.78002 | 12.87680 | 9.33352 | 9.33352 | 9.37273 | 9.33352 | 9.37273 | 9.37273 |
| $T\ (eV)$ | 7.37432 | 42.82081 | 10.11150 | 32.53914 | 21.06675 | 10.48582 | 6.77464 | 6.77464 | 6.90500 | 6.77464 | 6.90500 | 6.90500 |
| $V_m\ (eV)$ | -3.68716 | -21.41040 | -5.05575 | -16.26957 | -10.53337 | -5.24291 | -3.38732 | -3.38732 | -3.45250 | -3.38732 | -3.45250 | -3.45250 |
| $E(_{AO/HO})\ (eV)$ | -14.63489 | 0 | -14.63489 | -15.56407 | -15.56407 | -14.63489 | -15.56407 | -15.56407 | -15.35946 | -15.56407 | -15.35946 | -15.35946 |
| $\Delta E_{H_2MO}(_{AO/HO})\ (eV)$ | 0 | -2.69893 | -2.69893 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $E_T(_{AO/HO})\ (eV)$ | -14.63489 | 2.69893 | -11.93596 | -15.56407 | -15.56407 | -14.63489 | -15.56407 | -15.56407 | -15.35946 | -15.56407 | -15.35946 | -15.35946 |
| $E_T(_{H_2MO})\ (eV)$ | -31.63534 | -63.27074 | -31.63541 | -67.69451 | -49.66493 | -31.63533 | -31.63537 | -31.63537 | -31.63535 | -31.63537 | -31.63535 | -31.63535 |
| $E_T\left(atom-atom,msp^3.AO\right)(eV)$ | -1.44915 | -2.69893 | -1.65376 | 0 | 0 | 0 | -1.85836 | -1.85836 | -1.44915 | -1.85836 | -1.44915 | -1.44915 |
| $E_T(_{MO})\ (eV)$ | -33.08452 | -65.96966 | -33.28912 | -67.69450 | -49.66493 | -31.63537 | -33.49373 | -33.49373 | -33.08452 | -33.49373 | -33.08452 | -33.08452 |
| $\omega\ \left(10^{15}\ rad/s\right)$ | 16.4962 | 59.4034 | 24.3637 | 24.9286 | 24.2751 | 24.1759 | 9.43699 | 9.43699 | 15.4846 | 9.43699 | 9.55643 | 9.55643 |
| $E_K\ (eV)$ | 10.85807 | 39.10034 | 16.03660 | 16.40846 | 15.97831 | 15.91299 | 6.21159 | 6.21159 | 10.19220 | 6.21159 | 6.29021 | 6.29021 |
| $\bar{E}_D\ (eV)$ | -0.21568 | -0.40804 | -0.26373 | -0.25352 | -0.25017 | -0.24966 | -0.16515 | -0.16515 | -0.20896 | -0.16515 | -0.16416 | -0.16416 |
| $\bar{E}_{Kvib}\ (eV)$ | 0.14655 [28] | 0.21077 [12] | 0.13638 [35] | 0.35532 (Eq. (13.458)) | 0.35532 (Eq. (13.458)) | 0.35532 (Eq. (13.458)) | 0.12312 [2] | 0.17978 [4] | 0.09944 [5] | 0.12312 [2] | 0.12312 [2] | 0.12312 [2] |
| $\bar{E}_{osc}\ (eV)$ | -0.14240 | -0.30266 | -0.19554 | -0.22757 | -0.14502 | -0.07200 | -0.10359 | -0.07526 | -0.15924 | -0.10359 | -0.10260 | -0.10260 |
| $E_{mag}\ (eV)$ | 0.14803 | 0.11441 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 |
| $E_T(_{Group})\ (eV)$ | -33.22692 | -66.57498 | -33.48466 | -67.92207 | -49.80996 | -31.70737 | -33.59732 | -33.49373 | -33.24376 | -33.59732 | -33.18712 | -33.18712 |
| $E_{initial}(_{c_4\ AO/HO})\ (eV)$ | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 |
| $E_{initial}(_{c_5\ AO/HO})\ (eV)$ | 0 | 0 | 0 | -13.59844 | -13.59844 | -13.59844 | 0 | 0 | 0 | 0 | 0 | 0 |
| $E_D(_{Group})\ (eV)$ | 3.95714 | 7.80660 | 4.21488 | 12.49186 | 7.83016 | 3.32601 | 4.32754 | 4.29921 | 3.97398 | 4.17951 | 3.62128 | 3.91734 |

Table 15.139. The total bond energies of alkyl carboxylic acid anhydrides calculated using the functional group composition and the energies of Table 15.138 compared to the experimental values [3].

| Formula | Name | $C-C(O)$ Group | $C=O$ Group | $C-O$ Group | $CH_3$ | $CH_2$ | $CH$ | $C-C$ (a) | $C-C$ (b) | $C-C$ (c) | $C-C$ (d) | $C-C$ (e) | $C-C$ (f) | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $C_4H_6O_3$ | Acetic anhydride | 2 | 2 | 2 | 2 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 56.94096 | 56.948 | 0.00013 |
| $C_6H_{10}O_3$ | Propanoic anhydride | 2 | 2 | 2 | 2 | 2 | 0 | 2 | 0 | 0 | 0 | 0 | 0 | 81.25636 | 81.401 | 0.00177 |

Table 15.140. The bond angle parameters of alkyl carboxylic acid anhydrides and experimental values [1]. In the calculation of $\theta_v$, the parameters from the preceding angle were used. $E_T$ is $E_T(atom-atom,msp^3.AO)$.

| Atoms of Angle | $2c'$ Bond 1 ($a_0$) | $2c'$ Bond 2 ($a_0$) | $2c'$ Terminal Atoms ($a_0$) | $E_{Coulombic}$ Atom 1 | Atom 1 Hybridization Designation (Table 15.3.A) | $E_{Coulombic}$ Atom 2 | Atom 2 Hybridization Designation (Table 15.3.A) | $c_2$ Atom 1 | $c_2$ Atom 2 | $C_1$ | $C_2$ | $c_1$ | $c_2'$ | $E_T$ (eV) | $\theta_v$ (°) | $\theta_1$ (°) | $\theta_2$ (°) | Cal. $\theta$ (°) | Exp. $\theta$ (°) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $\angle O_aC_aO_b$ | 2.27954 | 2.63431 | 4.3012 | -16.17521<br>$O_a$ | 13 | -16.47951<br>$O_b$ | 22 | 0.84115 | 0.82562 | 1 | 1 | 1 | 0.83339 | -1.44915 | | | | 122.00 | 121.7 [36]<br>(acetic anhydride) |
| $\angle C_aO_bC_a$ | 2.63431 | 2.63431 | 4.4944 | -17.30638<br>$C_b$ | 42 | -17.30638<br>$C_a$ | 42 | 0.78617 | 0.78617 | 1 | 1 | 1 | 0.78617 | -1.85836 | | | | 117.09 | 115.8 [36]<br>(acetic anhydride) |
| $\angle C_bC_aO_b$ | 2.86175 | 2.63431 | 4.4944 | -15.55033 | 5 | -13.61806 | O | 0.87495 | 0.85395<br>(Eq. (15.133)) | 1 | 1 | 1 | 0.86445 | -1.44915 | | | | 109.65 | 108.3 [36]<br>(acetic anhydride) |
| $\angle C_bC_aO_a$ | 2.86175 | 2.27954 | 4.6368 | -16.47951 | 22 | -13.61806 | O | 0.82562 | 0.85395<br>(Eq. (15.133)) | 1 | 1 | 1 | 0.83979 | -1.65376 | | | | 128.46 | |
| Methylene<br>$\angle HC_aH$ | 2.11106 | 2.11106 | 3.4252 | -15.75493 | 7 | H | H | 0.86359 | 1 | 1 | 1 | 0.75 | 1.15796 | 0 | | | | 108.44 | 107<br>(propane) |
| $\angle C_aC_bC_c$ | | | | | | | | | | | | | | | 69.51 | | | 110.49 | 112<br>(propane)<br>113.8<br>(butane)<br>110.8<br>(isobutane) |
| $\angle C_aC_bH$ | | | | | | | | | | | | | | | 69.51 | | | 110.49 | 111.0<br>(butane)<br>111.4<br>(isobutane) |
| Methyl<br>$\angle HC_aH$ | 2.09711 | 2.09711 | 3.4252 | -15.75493 | 7 | H | H | 0.86359 | 1 | 1 | 1 | 0.75 | 1.15796 | 0 | | | | 109.50 | |
| $\angle C_aC_bC_c$ | | | | | | | | | | | | | | | 70.56 | | | 109.44 | |
| $\angle C_aC_bH$ | | | | | | | | | | | | | | | 70.56 | | | 109.44 | |
| $\angle C_bC_aC_c$<br>iso $C_a$ | 2.91547 | 2.91547 | 4.7958 | -16.68412<br>$C_b$ | 26 | -16.68412<br>$C_c$ | 26 | 0.81549 | 0.81549 | 1 | 1 | 1 | 0.81549 | -1.85836 | | | | 110.67 | 110.8<br>(isobutane) |
| $\angle C_bC_aH$<br>iso $C_a$ | 2.91547 | 2.11323 | 4.1633 | -15.55033<br>$C_a$ | 5 | -14.82575<br>$C_b$ | 1 | 0.87495 | 0.91771 | 0.75 | 1 | 0.75 | 1.04887 | 0 | | | | 110.76 | |
| $\angle C_aC_bH$<br>iso $C_a$ | 2.91547 | 2.09711 | 4.1633 | -15.55033<br>$C_b$ | 5 | -14.82575<br>$C_a$ | 1 | 0.87495 | 0.91771 | 0.75 | 1 | 0.75 | 1.04887 | 0 | | | | 111.27 | 111.4<br>(isobutane) |
| $\angle C_bC_aC_b$<br>tert $C_a$ | 2.90327 | 2.90327 | 4.7958 | -16.68412<br>$C_b$ | 26 | -16.68412<br>$C_b$ | 26 | 0.81549 | 0.81549 | 1 | 1 | 1 | 0.81549 | -1.85836 | | | | 111.37 | 110.8<br>(isobutane) |
| $\angle C_bC_aC_d$ | | | | | | | | | | | | | | | 72.50 | | | 107.50 | |

## NITRILES ($C_nH_{2n-1}N,\ n=2,3,4,5...\infty$)

The nitriles, $C_nH_{2n-1}N$, comprise a $C\equiv N$ functional group, and the single bond of carbon to the nitrile carbon atom, $C-CN$, is also a functional group. The alkyl portion of the nitrile may comprise at least two terminal methyl groups ($CH_3$) at each end of the chain, and may comprise methylene ($CH_2$), and methylyne ($CH$) functional groups as well as $C$ bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($(CH_3)_2CH$) and t-butyl ($(CH_3)_3C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups. The branched-chain-alkane groups in nitriles are equivalent to those in branched-chain alkanes.

The nitrile $C\equiv N$ is solved equivalently to acetylene as given in the Acetylene Molecule section except that the energy for $E(_{AO/HO})$ is two times that given in Eq. (14.343), 16.20002 $eV$, in order to match the $N$ AOs to that of the nitrile $C2sp^3$ HO having a bond order of three. $E_T\left(atom-atom,msp^3.AO\right)$ of the $C\equiv N$ functional group is $-1.56513\ eV$ (Eq. (14.342)) corresponding to the third-order bonded $C2sp^3$ HO.

The $C-CN$ functional group is equivalent to that of an alkyl $C-C$ group given in the Continuous-Chain Alkanes section except that $E_T(_{H_2MO})$ and $\overline{E}_{Kvib}$ are those corresponding to a nitrile. As given in the Continuous-Chain Alkanes section, $E_T\left(atom-atom,msp^3.AO\right)$ of the alkyl $C-C$ group is $-1.85836\ eV$ where both energy contributions are given by Eq. (14.513). It is based on energy matching within the nitrile. It corresponds to the maximum-magnitude energy contributions of a single-bonded and a third-order bonded $C2sp^3$ HO.

The symbols of the functional groups of nitriles are given in Table 15.141. The geometrical (Eqs. (15.1-15.5) and (15.51)), intercept (Eqs. (15.80-15.87)), and energy (Eqs. (15.6-15.11) and (15.17-15.65)) parameters of nitriles are given in Tables 15.142, 15.143, and 15.144, respectively. The total energy of each nitrile given in Table 15.139 was calculated as the sum over the integer multiple of each $E_D(_{Group})$ of Table 15.144 corresponding to functional-group composition of the molecule. For each set of unpaired electrons created by bond breakage, the $C2sp^3$ HO magnetic energy $E_{mag}$ that is subtracted from the weighted sum of the $E_D(_{Group})$ $(eV)$ values based on composition is given by Eq. (15.67). The bond angle parameters of nitriles determined using Eqs. (15.88-15.117) are given in Table 15.146. The $C$ of the $C\equiv N$ group can further bond with only one atom, and the bond is linear as a minimum of energy as in the case of acetylene and alkynes. The color scale, translucent view of the charge-density of exemplary nitrile, propanenitrile, comprising the concentric shells of atoms with the outer shell bridged by one or more $H_2$-type ellipsoidal MOs or joined with one or more hydrogen MOs is shown in Figure 15.24.

Figure 15.24. Color scale, translucent view of the charge-density of propanenitrile showing the orbitals of the atoms at their radii, the ellipsoidal surface of each $H$ or $H_2$-type ellipsoidal MO that transitions to the corresponding outer shell of the atom(s) participating in each bond, and the hydrogen nuclei (red, not to scale).

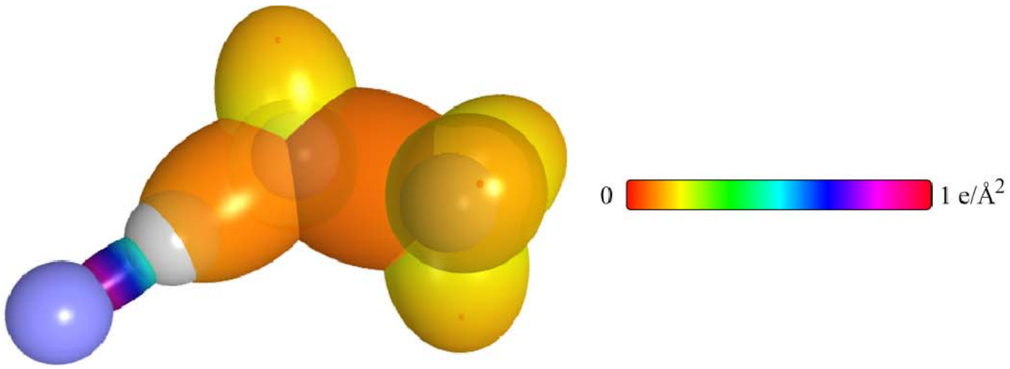


Table 15.141. The symbols of functional groups of nitriles.

| Functional Group | Group Symbol |
|---|---|
| *C-CN* | $C-C$ (i) |
| *CN* | $C\equiv N$ |
| $CH_3$ group | $C-H\ (CH_3)$ |
| $CH_2$ group | $C-H\ (CH_2)$ |
| *CH* (*alkyl*) group | $C-H$ |
| *CC* bond (*n-C*) | $C-C$ (a) |
| *CC* bond (*iso-C*) | $C-C$ (b) |
| *CC* bond (*tert-C)* | $C-C$ (c) |
| *CC* (*iso* to *iso-C*) | $C-C$ (d) |
| *CC* (*t* to *t-C*) | $C-C$ (e) |
| *CC* (*t* to iso-*C*) | $C-C$ (f) |

Table 15.142. The geometrical bond parameters of nitriles and experimental values [1].

| Parameter | $C-C$ (i) Group | $C\equiv N$ Group | $C-H\left(CH_3\right)$ Group | $C-H\left(CH_2\right)$ Group | $C-H$ Group | $C-C$ (a) Group | $C-C$ (b) Group | $C-C$ (c) Group | $C-C$ (d) Group | $C-C$ (e) Group | $C-C$ (f) Group |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $a\left(a_0\right)$ | 1.91255 | 1.20590 | 1.64920 | 1.67122 | 1.67465 | 2.12499 | 2.12499 | 2.10725 | 2.12499 | 2.10725 | 2.10725 |
| $c'\left(a_0\right)$ | 1.38295 | 1.09813 | 1.04856 | 1.05553 | 1.05661 | 1.45744 | 1.45744 | 1.45164 | 1.45744 | 1.45164 | 1.45164 |
| Bond Length $2c'$ $(\mathring{A})$ | 1.46365 | 1.16221 | 1.10974 | 1.11713 | 1.11827 | 1.54280 | 1.54280 | 1.53635 | 1.54280 | 1.53635 | 1.53635 |
| Exp. Bond Length $(\mathring{A})$ | 1.468<br>(acetonitrile) | 1.159<br>(acetonitrile) | 1.107<br>($C-H$ propane)<br>1.117<br>($C-H$ butane) | 1.107<br>($C-H$ propane)<br>1.117<br>($C-H$ butane) | 1.122<br>(isobutane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) |
| $b,c\left(a_0\right)$ | 1.382110 | 0.49828 | 1.27295 | 1.29569 | 1.29924 | 1.54616 | 1.54616 | 1.52750 | 1.54616 | 1.52750 | 1.52750 |
| $e$ | 0.72309 | 0.91064 | 0.63580 | 0.63159 | 0.63095 | 0.68600 | 0.68600 | 0.68888 | 0.68600 | 0.68888 | 0.68888 |

Table 15.143. The MO to HO intercept geometrical bond parameters of nitriles. $R$, $R'$, $R''$ are $H$ or alkyl groups. $E_T$ is $E_T(atom-atom, msp^3.AO)$.

| Bond | Atom | $E_T$ (eV) Bond 1 | $E_T$ (eV) Bond 2 | $E_T$ (eV) Bond 3 | $E_T$ (eV) Bond 4 | Final Total Energy $C2sp^3$ (eV) | $r_{initial}$ $\left(a_0\right)$ | $r_{final}$ $\left(a_0\right)$ | $E_{Coulomb}$ (eV) Final | $E\left(C2sp^3\right)$ (eV) Final | $\theta'$ $(^\circ)$ | $\theta_1$ $(^\circ)$ | $\theta_2$ $(^\circ)$ | $d_1$ $\left(a_0\right)$ | $d_2$ $\left(a_0\right)$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $RH_2C_bC_a\equiv N$ | $N$ | -0.78257 | 0 | 0 | 0 |  | 0.93084 | 0.87170 | -15.60832 |  | 147.01 | 32.99 | 72.28 | 0.36699 | 0.73114 |
| $RH_2C_bC_a\equiv N$ | $C_a$ | -0.78257 | -0.92918 | 0 | 0 | -153.32744 | 0.91771 | 0.82272 | -16.53750 | -16.34664 | 145.42 | 34.58 | 69.58 | 0.42077 | 0.67736 |
| $RH_2C_b-C_aN$ | $C_a$ | -0.92918 | -0.78257 | 0 | 0 | -153.32744 | 0.91771 | 0.82272 | -16.53750 | -16.34664 | 81.32 | 98.68 | 38.00 | 1.50718 | 0.12423 |
| $H_3C_b-C_aN$ | $C_b$ | -0.92918 | 0 | 0 | 0 | -152.54487 | 0.91771 | 0.86359 | -15.75493 | -15.56407 | 85.50 | 94.50 | 40.67 | 1.45066 | 0.06771 |
| $RH_2C_cH_2C_b-C_aN$<br>$R=alkyl$ | $C_b$ | -0.92918 | -0.92918 | 0 | 0 | -153.47406 | 0.91771 | 0.81549 | -16.68412 | -16.49325 | 80.53 | 99.47 | 37.51 | 1.51718 | 0.13423 |
| $C-H\left(CH_3\right)$ | $C$ | -0.92918 | 0 | 0 | 0 | -152.54487 | 0.91771 | 0.86359 | -15.75493 | -15.56407 | 77.49 | 102.51 | 41.48 | 1.23564 | 0.18708 |
| $C-H\left(CH_2\right)$ | $C$ | -0.92918 | -0.92918 | 0 | 0 | -153.47406 | 0.91771 | 0.81549 | -16.68412 | -16.49325 | 68.47 | 111.53 | 35.84 | 1.35486 | 0.29933 |
| $C-H\left(CH\right)$ (ii) | $C$ | -0.92918 | -0.92918 | -0.92918 | 0 | -154.40324 | 0.91771 | 0.77247 | -17.61330 | -17.42244 | 61.10 | 118.90 | 31.37 | 1.42988 | 0.37326 |
| $H_3C_aC_bH_2CH_2-$<br>$(C-C$ (a)) | $C_a$ | -0.92918 | 0 | 0 | 0 | -152.54487 | 0.91771 | 0.86359 | -15.75493 | -15.56407 | 63.82 | 116.18 | 30.08 | 1.83879 | 0.38106 |
| $H_3C_aC_bH_2CH_2-$<br>$(C-C$ (a)) | $C_b$ | -0.92918 | -0.92918 | 0 | 0 | -153.47406 | 0.91771 | 0.81549 | -16.68412 | -16.49325 | 56.41 | 123.59 | 26.06 | 1.90890 | 0.45117 |
| $R-H_2C_aC_b\left(H_2C_c-R'\right)HCH_2-$<br>$(C-C$ (b)) | $C_b$ | -0.92918 | -0.92918 | -0.92918 | 0 | -154.40324 | 0.91771 | 0.77247 | -17.61330 | -17.42244 | 48.30 | 131.70 | 21.90 | 1.97162 | 0.51388 |
| $R-H_2C_a\left(R'-H_2C_d\right)C_b\left(R''-H_2C_c\right)CH_2-$<br>$(C-C$ (c)) | $C_b$ | -0.92918 | -0.72457 | -0.72457 | -0.72457 | -154.71860 | 0.91771 | 0.75889 | -17.92866 | -17.73779 | 48.21 | 131.79 | 21.74 | 1.95734 | 0.50570 |
| $isoC_aC_b\left(H_2C_c-R'\right)HCH_2-$<br>$(C-C$ (d)) | $C_b$ | -0.92918 | -0.92918 | -0.92918 | 0 | -154.40324 | 0.91771 | 0.77247 | -17.61330 | -17.42244 | 48.30 | 131.70 | 21.90 | 1.97162 | 0.51388 |
| $tertC_a\left(R'-H_2C_d\right)C_b\left(R''-H_2C_c\right)CH_2-$<br>$(C-C$ (e)) | $C_b$ | -0.72457 | -0.72457 | -0.72457 | -0.72457 | -154.51399 | 0.91771 | 0.76765 | -17.92866 | -17.73779 | 50.04 | 129.96 | 22.66 | 1.94462 | 0.49298 |
| $tertC_aC_b\left(H_2C_c-R'\right)HCH_2-$<br>$(C-C$ (f)) | $C_b$ | -0.72457 | -0.92918 | -0.92918 | 0 | -154.19863 | 0.91771 | 0.78155 | -17.40869 | -17.21783 | 52.78 | 127.22 | 24.04 | 1.92443 | 0.47279 |
| $isoC_a\left(R'-H_2C_d\right)C_b\left(R''-H_2C_c\right)CH_2-$<br>$(C-C$ (f)) | $C_b$ | -0.72457 | -0.72457 | -0.72457 | -0.72457 | -154.51399 | 0.91771 | 0.76765 | -17.92866 | -17.73779 | 50.04 | 129.96 | 22.66 | 1.94462 | 0.49298 |

Table 15.144. The energy parameters ($eV$) of functional groups of nitriles.

| Parameters | $C-C$ (i) Group | $C\equiv N$ Group | $CH_3$ Group | $CH_2$ Group | $C-H$ Group | $C-C$ (a) Group | $C-C$ (b) Group | $C-C$ (c) Group | $C-C$ (d) Group | $C-C$ (e) Group | $C-C$ (f) Group |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $n_1$ | 1 | 3 | 3 | 2 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $n_2$ | 0 | 0 | 2 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $n_3$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $C_1$ | 0.5 | 0.5 | 0.75 | 0.75 | 0.75 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| $C_2$ | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $c_1$ | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $c_2$ | 0.91771 | 0.91140 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 |
| $c_3$ | 0 | 1 | 0 | 1 | 1 | 0 | 0 | 0 | 1 | 1 | 0 |
| $c_4$ | 2 | 6 | 1 | 1 | 1 | 2 | 2 | 2 | 2 | 2 | 2 |
| $c_5$ | 0 | 0 | 3 | 2 | 1 | 0 | 0 | 0 | 0 | 0 | 0 |
| $C_{1o}$ | 0.5 | 0.5 | 0.75 | 0.75 | 0.75 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| $C_{2o}$ | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $V_e\ (eV)$ | -33.01231 | -207.49229 | -107.32728 | -70.41425 | -35.12015 | -28.79214 | -28.79214 | -29.10112 | -28.79214 | -29.10112 | -29.10112 |
| $V_p\ (eV)$ | 9.83824 | 37.16984 | 38.92728 | 25.78002 | 12.87680 | 9.33352 | 9.33352 | 9.37273 | 9.33352 | 9.37273 | 9.37273 |
| $T\ (eV)$ | 8.63043 | 86.03250 | 32.53914 | 21.06675 | 10.48582 | 6.77464 | 6.77464 | 6.90500 | 6.77464 | 6.90500 | 6.90500 |
| $V_m\ (eV)$ | -4.31522 | -43.01625 | -16.26957 | -10.53337 | -5.24291 | -3.38732 | -3.38732 | -3.45250 | -3.38732 | -3.45250 | -3.45250 |
| $E(_{AO/HO})\ (eV)$ | -14.63489 | 32.40004 | -15.56407 | -15.56407 | -14.63489 | -15.56407 | -15.56407 | -15.35946 | -15.56407 | -15.35946 | -15.35946 |
| $\Delta E_{H_2MO}(_{AO/HO})\ (eV)$ | -1.85837 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $E_T(_{AO/HO})\ (eV)$ | -12.77652 | 32.40004 | -15.56407 | -15.56407 | -14.63489 | -15.56407 | -15.56407 | -15.35946 | -15.56407 | -15.35946 | -15.35946 |
| $E_T(_{H_2MO})\ (eV)$ | -31.63537 | -94.90616 | -67.69451 | -49.66493 | -31.63533 | -31.63537 | -31.63537 | -31.63535 | -31.63537 | -31.63535 | -31.63535 |
| $E_T\left(atom-atom,msp^3.AO\right)(eV)$ | -1.85836 | -1.56513 | 0 | 0 | 0 | -1.85836 | -1.85836 | -1.44915 | -1.85836 | -1.44915 | -1.44915 |
| $E_T(_{MO})\ (eV)$ | -33.49374 | -96.47124 | -67.69450 | -49.66493 | -31.63537 | -33.49373 | -33.49373 | -33.08452 | -33.49373 | -33.08452 | -33.08452 |
| $\omega\ \left(10^{15}\ rad/s\right)$ | 19.2516 | 22.0753 | 24.9286 | 24.2751 | 24.1759 | 9.43699 | 9.43699 | 15.4846 | 9.43699 | 9.55643 | 9.55643 |
| $E_K\ (eV)$ | 12.67172 | 14.53031 | 16.40846 | 15.97831 | 15.91299 | 6.21159 | 6.21159 | 10.19220 | 6.21159 | 6.29021 | 6.29021 |
| $\bar{E}_D\ (eV)$ | -0.23588 | -0.24250 | -0.25352 | -0.25017 | -0.24966 | -0.16515 | -0.16515 | -0.20896 | -0.16515 | -0.16416 | -0.16416 |
| $\bar{E}_{Kvib}\ (eV)$ | 0.11407<br>[37] | 0.28107<br>[37] | 0.35532<br>(Eq. (13.458)) | 0.35532<br>(Eq. (13.458)) | 0.35532<br>(Eq. (13.458)) | 0.12312<br>[2] | 0.17978<br>[4] | 0.09944<br>[5] | 0.12312<br>[2] | 0.12312<br>[2] | 0.12312<br>[2] |
| $\bar{E}_{osc}\ (eV)$ | -0.17884 | -0.10197 | -0.22757 | -0.14502 | -0.07200 | -0.10359 | -0.07526 | -0.15924 | -0.10359 | -0.10260 | -0.10260 |
| $E_{mag}\ (eV)$ | 0.14803 | 0.14185 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 |
| $E_T(_{Group})\ (eV)$ | -33.67258 | -96.77713 | -67.92207 | -49.80996 | -31.70737 | -33.59732 | -33.49373 | -33.24376 | -33.59732 | -33.18712 | -33.18712 |
| $E_{initial}(_{c_4\ AO/HO})\ (eV)$ | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 |
| $E_{initial}(_{c_5\ AO/HO})\ (eV)$ | 0 | 0 | -13.59844 | -13.59844 | -13.59844 | 0 | 0 | 0 | 0 | 0 | 0 |
| $E_D(_{Group})\ (eV)$ | 4.40280 | 8.82594 | 12.49186 | 7.83016 | 3.32601 | 4.32754 | 4.29921 | 3.97398 | 4.17951 | 3.62128 | 3.91734 |

Table 15.145. The total bond energies of nitriles calculated using the functional group composition and the energies of Table 15.144 compared to the experimental values [3]. The magnetic energy $E_{mag}$ that is subtracted from the weighted sum of the $E_D\ (_{Group})\ (eV)$ values based on composition is given by (15.58).

| Formula | Name | $C-C$ (i) Group | $C\equiv N$ Group | $CH_3$ | $CH_2$ | $CH$ | $C-C$ (a) | $C-C$ (b) | $C-C$ (c) | $C-C$ (d) | $C-C$ (e) | $C-C$ (f) | $E_{mag}$ | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $C_2H_3N$ | Acetonitrile | 1 | 1 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 25.72060 | 25.77 | 0.00174 |
| $C_3H_5N$ | Propanenitrile | 1 | 1 | 1 | 1 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 37.87830 | 37.94 | 0.00171 |
| $C_4H_7N$ | Butanenitrile | 1 | 1 | 1 | 2 | 0 | 2 | 0 | 0 | 0 | 0 | 0 | 0 | 50.03600 | 50.08 | 0.00082 |
| $C_4H_7N$ | 2-Methylpropanenitrile | 1 | 1 | 2 | 0 | 1 | 0 | 2 | 0 | 0 | 0 | 0 | 0 | 50.13689 | 50.18 | 0.00092 |
| $C_5H_9N$ | Pentanenitrile | 1 | 1 | 1 | 3 | 0 | 3 | 0 | 0 | 0 | 0 | 0 | 0 | 62.19370 | 62.26 | 0.00111 |
| $C_5H_9N$ | 2,2-Dimethylpropanenitrile | 1 | 1 | 3 | 0 | 0 | 0 | 0 | 3 | 0 | 0 | 0 | -1 | 62.47823 | 62.40 | -0.00132 |
| $C_7H_{13}N$ | Heptanenitrile | 1 | 1 | 1 | 5 | 0 | 5 | 0 | 0 | 0 | 0 | 0 | 0 | 86.50910 | 86.59 | 0.00089 |
| $C_8H_{15}N$ | Octanenitrile | 1 | 1 | 1 | 6 | 0 | 6 | 0 | 0 | 0 | 0 | 0 | 0 | 98.66680 | 98.73 | 0.00069 |
| $C_{10}H_{19}N$ | Decanenitrile | 1 | 1 | 1 | 8 | 0 | 8 | 0 | 0 | 0 | 0 | 0 | 0 | 122.98220 | 123.05 | 0.00057 |
| $C_{14}H_{27}N$ | Tetradecanenitrile | 1 | 1 | 1 | 12 | 0 | 12 | 0 | 0 | 0 | 0 | 0 | 0 | 171.61300 | 171.70 | 0.00052 |

Table 15.146. The bond angle parameters of nitriles and experimental values [1]. In the calculation of $\theta_v$, the parameters from the preceding angle were used. $E_T$ is $E_T(atom-atom,msp^3.AO)$.

| Atoms of Angle | $2c'$ Bond 1 $(a_0)$ | $2c'$ Bond 2 $(a_0)$ | $2c'$ Terminal Atoms $(a_0)$ | $E_{Coulombic}$ Atom 1 | Atom 1 Hybridization Designation (Table 15.3.A) | $E_{Coulombic}$ Atom 2 | Atom 2 Hybridization Designation (Table 15.3.A) | $c_2$ Atom 1 | $c_2$ Atom 2 | $C_1$ | $C_2$ | $c_1$ | $c_2'$ | $E_T$ (eV) | $\theta_v$ (°) | $\theta_1$ (°) | $\theta_2$ (°) | Cal. $\theta$ (°) | Exp. $\theta$ (°) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $\angle C_bC_aN$ | | | | | | | | | | | | | | | | | | 180 | |
| $\angle HC_bH$ | 2.09711 | 2.09711 | 3.4252 | -15.75493 | 7 | H | H | 0.86359 | 1 | 1 | 1 | 0.75 | 1.15796 | 0 | | | | 109.50 | |
| $\angle HC_bC_a$ | | | | | | | | | | | | | | | 70.56 | | | 109.44 | 109.7 (acetonitrile) |
| Methylene $\angle HC_aH$ | 2.11106 | 2.11106 | 3.4252 | -15.75493 | 7 | H | H | 0.86359 | 1 | 1 | 1 | 0.75 | 1.15796 | 0 | | | | 108.44 | 107 (propane) |
| $\angle C_aC_bC_c$ | | | | | | | | | | | | | | | 69.51 | | | 110.49 | 112 (propane)<br>113.8 (butane)<br>110.8 (isobutane) |
| $\angle C_aC_bH$ | | | | | | | | | | | | | | | 69.51 | | | 110.49 | 111.0 (butane)<br>111.4 (isobutane) |
| Methyl $\angle HC_aH$ | 2.09711 | 2.09711 | 3.4252 | -15.75493 | 7 | H | H | 0.86359 | 1 | 1 | 1 | 0.75 | 1.15796 | 0 | | | | 109.50 | |
| $\angle C_aC_bC_c$ | | | | | | | | | | | | | | | 70.56 | | | 109.44 | |
| $\angle C_aC_bH$ | | | | | | | | | | | | | | | 70.56 | | | 109.44 | |
| $\angle C_bC_aC_c$ iso $C_a$ | 2.91547 | 2.91547 | 4.7958 | -16.68412 $C_b$ | 26 | -16.68412 $C_c$ | 26 | 0.81549 | 0.81549 | 1 | 1 | 1 | 0.81549 | -1.85836 | | | | 110.67 | 110.8 (isobutane) |
| $\angle C_bC_aH$ iso $C_a$ | 2.91547 | 2.11323 | 4.1633 | -15.55033 $C_a$ | 5 | -14.82575 $C_b$ | 1 | 0.87495 | 0.91771 | 0.75 | 1 | 0.75 | 1.04887 | 0 | | | | 110.76 | |
| $\angle C_aC_bH$ iso $C_a$ | 2.91547 | 2.09711 | 4.1633 | -15.55033 $C_b$ | 5 | -14.82575 $C_a$ | 1 | 0.87495 | 0.91771 | 0.75 | 1 | 0.75 | 1.04887 | 0 | | | | 111.27 | 111.4 (isobutane) |
| $\angle C_bC_aC_b$ tert $C_a$ | 2.90327 | 2.90327 | 4.7958 | -16.68412 $C_b$ | 26 | -16.68412 $C_b$ | 26 | 0.81549 | 0.81549 | 1 | 1 | 1 | 0.81549 | -1.85836 | | | | 111.37 | 110.8 (isobutane) |
| $\angle C_bC_aC_d$ | | | | | | | | | | | | | | | 72.50 | | | 107.50 | |

## THIOLS ($C_nH_{2n+2}S_m$, $n=1,2,3,4,5...\infty$)

The alkyl thiols, $C_nH_{2n+2}S_m$, comprise a $SH$ functional group and a $C-S$ functional group. The alkyl portion of the alkyl thiol may comprise at least two terminal methyl groups ($CH_3$) at each end of the chain, and may comprise methylene ($CH_2$), and methylyne ($CH$) functional groups as well as $C$ bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($\left(CH_3\right)_2 CH$) and t-butyl ($\left(CH_3\right)_3 C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups. The branched-chain-alkane groups in thiols are equivalent to those in branched-chain alkanes.

The parameters of the $SH$ functional group is solved using Eq. (15.41). As in the case of the $C-H$ bonds of $CH_n$ $n=1,2,3$, the $S-H$-bond MO is a partial prolate spheroid in between the sulfur and hydrogen nuclei and is continuous with the $S3p$ shell. The energy of the $H_2$-type ellipsoidal MO is matched to that of the $S3p$ shell and comprises 75% of a $H_2$-type ellipsoidal MO in order to match potential, kinetic, and orbital energy relationships. Since the energy of $S$, $E(S)=-10.36001\ eV$, is less that that of $H$, the linear combination of the $H_2$-type ellipsoidal MO with the $S3p$ shell further comprises an excess 50% charge-density donation from $H$ to the $S3p$ shell of the $S-H$-bond MO to achieve an energy minimum. The initial total energy of the shell is given by the sum over the four $3p$ electrons. From Eq. (15.12), the sum $E_T(S,3p)$ of the energies of $S$, $S^{+}$, $S^{2+}$, and $S^{3+}$ [38] is:

$$E_T(S,3p)=10.36001\ eV+23.33788\ eV+34.79\ eV+47.222\ eV=115.70989\ eV \tag{15.137}$$

By considering that the central field decreases by an integer for each successive electron of the shell, the radius $r_{3p}$ of the $S3p$ shell may be calculated from the Coulombic energy using Eqs. (15.13) and (15.137).

$$r_{3p}=\sum_{q=12}^{15}\frac{(Z-q)e^2}{8\pi\varepsilon_0\left(e115.70989\ eV\right)}=\frac{10e^2}{8\pi\varepsilon_0\left(e115.70989\ eV\right)}=1.17585a_0 \tag{15.138}$$

where $Z=16$ for sulfur. Using Eqs. (15.14) and (15.138), the Coulombic energy $E_{Coulomb}(S,3p)$ of the outer electron of the $S3p$ shell is:

$$E_{Coulomb}(S,3p)=\frac{-e^2}{8\pi\varepsilon_0 r_{3p}}=\frac{-e^2}{8\pi\varepsilon_0 1.17585a_0}=-11.57099\ eV \tag{15.139}$$

The sharing of the electrons between the $S$ and $H$ atoms permits the formation an $S-H$-bond MO that is lowered more in energy than the participating $S3p$ orbital which consequently increases in energy. By considering the 50% electron redistribution in the $S-H$ group as well as the fact that the central field decreases by an integer for each successive electron of the shell, the radius $r_{S-H3p}$ of the $S3p$ shell may be calculated from the Coulombic energy using Eq. (15.18).

$$r_{S-H3p}=\left(\sum_{n=12}^{15}(Z-n)+2(0.25)\right)\frac{e^2}{8\pi\varepsilon_0\left(e115.70989\ eV\right)}=\frac{10.5e^2}{8\pi\varepsilon_0\left(e115.70989\ eV\right)}=1.23465a_0 \tag{15.140}$$

where the $s=-2$ in Eq. (15.18) due to the charge donation from $H$ to $S$. Using Eqs. (15.19) and (15.121), the Coulombic energy $E_{Coulomb}\left(S_{S-H},3p\right)$ of the outer electron of the $S3p$ shell is:

$$E_{Coulomb}\left(S_{S-H},3p\right)=\frac{-e^2}{8\pi\varepsilon_0 r_{S-H3p}}=\frac{-e^2}{8\pi\varepsilon_0 1.23465a_0}=-11.01999\ eV \tag{15.141}$$

Thus, $E_T(S-H,3p)$, the energy change of each $S3p$ shell with the formation of the $S-H$-bond MO is given by the difference between Eq. (15.139) and Eq. (15.141):

$$E_T(S-H,3p)=E\left(S_{S-H},3p\right)-E(S,3p)=-11.01999\ eV-\left(-11.57099\ eV\right)=0.55100\ eV \tag{15.142}$$

Then, in Eq. (15.51):

$$E_T(AO/HO)=E(S)-E_T(S-H,3p)=-10.36001\ eV-0.55100\ eV=-10.91101\ eV \tag{15.143}$$

And, in Eq. (15.65),

$$E_T\left(atom-atom,msp^3.AO\right)=0.55100\ eV \tag{15.144}$$

Due to the charge donation from $H$ to $S$, $c_1 = 1$ in both Eqs. (15.51) and (15.65). As in the case of the $C-H$-bond MO, $C_1 = 0.75$ based on the orbital composition. In alkyl thiols, the energy of sulfur is less than the Coulombic energy between the electron and proton of $H$ given by Eq. (1.264). Thus, $c_2$ in Eq. (15.61) is also one, and the energy matching condition is determined by the $C_2$ parameter. Using the energy of $S$, $E(S) = -10.36001\ eV$ in Eq. (15.74), the hybridization factor $C_2$ of Eq. (15.61) for the $S-H$-bond MO is:

$$C_2(S3p\ to\ H) = \frac{E(S,3p)}{E(H)} = \frac{-10.36001\ eV}{-13.60580\ eV} = 0.76144 \tag{15.145}$$

Since the energy of $S$ is matched to the Coulombic energy between the electron and proton of $H$, $E(H(a_0))$, $E_{initial}(c_4AO/HO) = E(H(a_0)) = -13.60580\ eV$, $E_{initial}(c_5AO/HO) = E(H) = -13.59844\ eV$, and $E_{mag}$ is that corresponding to $E(H(a_0))$ given by Eq. (15.67). $E_D(Group)$ for hydrogen sulfide is equivalent to that of the $SH$ functional group, and the $E_D(Group)$ $(eV)$ for dihydrogen sulfide follows the same derivation as that for the $SH$ functional group except that the parameters correspond to $n_1 = 2$ rather than $n_1 = 1$ in Eqs. (15.51) and (15.65).

Furthermore, with the energy of $S$ matched to the Coulombic energy between the electron and proton of $H$, the energy of the $C-S$-bond MO is the sum of the component energies of the $H_2$-type ellipsoidal MO given in Eq. (15.51) with $E(AO/HO) = 0$ and $E_T(AO/HO) = \Delta E_{H_2MO}(AO/HO)$. Then, the solution of the $C-S$ functional group comprises the hybridization of the $2s$ and $2p$ AOs of $C$ to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between the $C2sp^3$ HO and the $S$ AO to form a MO permits each participating orbital to decrease in radius and energy. Since the energy of sulfur is less than the Coulombic energy between the electron and proton of $H$ given by Eq. (1.264), $c_2$ in Eq. (15.61) is one, and the energy matching condition is determined by the $C_2$ parameter. Then, $C2sp^3$ HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of $E(C,2sp^3) = -14.63489\ eV$ (Eq. (15.25)), and the $S$ AO has an energy of $E(S) = -10.36001\ eV$. To meet the equipotential condition of the union of the $C-S$ $H_2$-type-ellipsoidal-MO with these orbitals, the hybridization factor $C_2$ of Eq. (15.60) for the $C-S$-bond MO given by Eqs. (15.77) and (15.79) is:

$$C_2(C2sp^3HO\ to\ \mathrm{S}) = \frac{E(S)}{E(C,2sp^3)} c_2(C2sp^3HO) = \frac{-10.36001\ eV}{-14.63489\ eV}(0.91771) = 0.64965 \tag{15.146}$$

Since the sulfur is energy matched to $E(H(a_0))$ in the $S-H$-bond MO, $E_T(atom-atom, msp^3.AO)$ of the $C-S$-bond MO in Eq. (15.61) due to the charge donation from the $C$ and $S$ atoms to the MO is $-0.72457\ eV$ corresponding to the energy contribution equivalent to that of a methyl group (Eq. (14.151)).

The symbols of the functional groups of branched-chain alkyl thiols are given in Table 15.147. The geometrical (Eqs. (15.1-15.5) and (15.51)), intercept (Eqs. (15.80-15.87)), and energy (Eqs. (15.6-15.11) and (15.17-15.65)) parameters of alkyl thiols are given in Tables 15.148, 15.149, and 15.150, respectively. The total energy of each alkyl thiol given in Table 15.151 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.150 corresponding to functional-group composition of the molecule. For each set of unpaired electrons created by bond breakage, the $C2sp^3$ HO magnetic energy $E_{mag}$ that is subtracted from the weighted sum of the $E_D(Group)$ $(eV)$ values based on composition is given by Eq. (15.67). The $C-C$ bonds to the $HCSH$ group (one $H$ bond to $C$) were each treated as an iso $C-C$ bond. The $C-C$ bonds to the $CSH$ group (no $H$ bonds to $C$) were each treated as a tert-butyl $C-C$. $E_{mag}$ was subtracted for each t-butyl group. The bond angle parameters of alkyl thiols determined using Eqs. (15.88-15.117) are given in Table 15.152. The color scale, translucent view of the charge-density of exemplary thiol, ethanethiol, comprising the concentric shells of atoms with the outer shell bridged by one or more $H_2$-type ellipsoidal MOs or joined with one or more hydrogen MOs is shown in Figure 15.25.

Figure 15.25. Color scale, translucent view of the charge-density of ethanethiol showing the orbitals of the atoms at their radii, the ellipsoidal surface of each $H$ or $H_2$-type ellipsoidal MO that transitions to the corresponding outer shell of the atom(s) participating in each bond, and the hydrogen nuclei (red, not to scale).

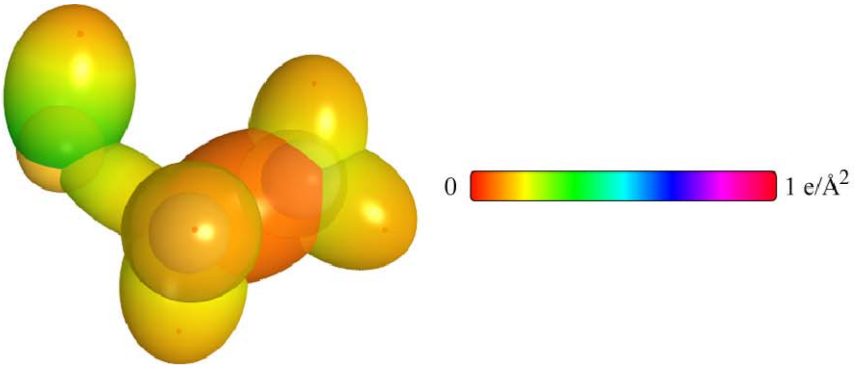


Table 15.147. The symbols of functional groups of alkyl thiols.

| Functional Group | Group Symbol |
|---|---|
| *SH* group | $SH$ |
| *H₂S* | $H_2S$ |
| *C-S* | $C-S$ |
| *CH₃* group | $C-H\ (CH_3)$ |
| *CH₂* group | $C-H\ (CH_2)$ |
| *CH* | $C-H$ |
| *CC* bond (*n-C*) | $C-C$ (a) |
| *CC* bond (*iso-C*) | $C-C$ (b) |
| *CC* bond (*tert-C*) | $C-C$ (c) |
| *CC* (*iso* to *iso-C*) | $C-C$ (d) |
| *CC* (*t* to *t-C*) | $C-C$ (e) |
| *CC* (*t* to *iso-C*) | $C-C$ (f) |

Table 15.148. The geometrical bond parameters of alkyl thiols and experimental values [1].

| Parameter | $S-H\ (H_2S)$ | $SH$ Group | $C-S$ Group | $C-H\ (CH_3)$ Group | $C-H\ (CH_2)$ Group | $C-H$ Group | $C-C$ (a) Group | $C-C$ (b) Group | $C-C$ (c) Group | $C-C$ (d) Group | $C-C$ (e) Group | $C-C$ (f) Group |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $a\ (a_0)$ | 1.83762 | 1.83762 | 1.90975 | 1.64920 | 1.67122 | 1.67465 | 2.12499 | 2.12499 | 2.10725 | 2.12499 | 2.10725 | 2.10725 |
| $c'\ (a_0)$ | 1.26842 | 1.26842 | 1.71455 | 1.04856 | 1.05553 | 1.05661 | 1.45744 | 1.45744 | 1.45164 | 1.45744 | 1.45164 | 1.45164 |
| Bond Length $2c'$ (Å) | 1.34244 | 1.34244 | 1.81460 | 1.10974 | 1.11713 | 1.11827 | 1.54280 | 1.54280 | 1.53635 | 1.54280 | 1.53635 | 1.53635 |
| Exp. Bond Length (Å) | 1.3356 | 1.34066<br>(hydrogen sulfide)<br>1.34<br>(methanethiol) | 1.819<br>(methanethiol)<br>1.829<br>(ethanethiol) | 1.107<br>($C-H$ propane)<br>1.117<br>($C-H$ butane) | 1.107<br>($C-H$ propane)<br>1.117<br>($C-H$ butane) | 1.122<br>(isobutane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) |
| $b,c\ (a_0)$ | 1.32964 | 1.32964 | 0.84112 | 1.27295 | 1.29569 | 1.29924 | 1.54616 | 1.54616 | 1.52750 | 1.54616 | 1.52750 | 1.52750 |
| $e$ | 0.69025 | 0.69025 | 0.89778 | 0.63580 | 0.63159 | 0.63095 | 0.68600 | 0.68600 | 0.68888 | 0.68600 | 0.68888 | 0.68888 |

Table 15.149. The MO to HO intercept geometrical bond parameters of alkyl thiols. $R$, $R'$, $R''$ are $H$ or alkyl groups. $E_T$ is $E_T(atom-atom,msp^3.AO)$.

| Bond | Atom | $E_T$ (eV) Bond 1 | $E_T$ (eV) Bond 2 | $E_T$ (eV) Bond 3 | $E_T$ (eV) Bond 4 | Final Total Energy $C2sp^3$ (eV) | $r_{initial}$ $(a_0)$ | $r_{final}$ $(a_0)$ | $E_{Coulomb}$ (eV) Final | $E(C2sp^3)$ (eV) Final | $\theta'$ (°) | $\theta_1$ (°) | $\theta_2$ (°) | $d_1$ $(a_0)$ | $d_2$ $(a_0)$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $S-H$<br>(hydrogen sulfide)<br>(dihydrogen sulfide) | $S$ | 0.55100 | 0 | 0 | 0 |  | 1.32010 | 1.23465 | -11.01999 |  | 108.65 | 71.35 | 61.62 | 0.87355 | 0.39487 |
| $RS-H$ | $S$ | -0.36229 | 0.55100 | 0 | 0 |  | 1.32010 | 0.92955 | -14.63704 |  | 87.09 | 92.91 | 44.28 | 1.31557 | 0.04714 |
| $C_aH_3-SH$ | $S$ | -0.36229 | 0.55100 | 0 | 0 |  | 1.32010 | 0.92955 | -14.63704 |  | 132.06 | 47.94 | 55.13 | 1.09181 | 0.62274 |
| $C_aH_3-SH$ | $C_a$ | -0.36229 | 0 | 0 | 0 | -151.97798 | 0.91771 | 0.89582 | -15.18804 | -14.99717 | 69.84 | 110.16 | 88.87 | 0.03762 | 1.67692 |
| $RC_cH_2C_bH_2-C_aH_2SH$ | $C_a$ | -0.36229 | -0.92918 | 0 | 0 | -152.90716 | 0.91771 | 0.84418 | -16.11722 | -15.92636 | 128.69 | 51.31 | 51.57 | 1.18689 | 0.52765 |
| $C-H\ (CH_3)$ | $C$ | -0.92918 | 0 | 0 | 0 | -152.54487 | 0.91771 | 0.86359 | -15.75493 | -15.56407 | 77.49 | 102.51 | 41.48 | 1.23564 | 0.18708 |
| $C-H\ (CH_2)$ | $C$ | -0.92918 | -0.92918 | 0 | 0 | -153.47406 | 0.91771 | 0.81549 | -16.68412 | -16.49325 | 68.47 | 111.53 | 35.84 | 1.35486 | 0.29933 |
| $C-H\ (CH)$ | $C$ | -0.92918 | -0.92918 | -0.92918 | 0 | -154.40324 | 0.91771 | 0.77247 | -17.61330 | -17.42244 | 61.10 | 118.90 | 31.37 | 1.42988 | 0.37326 |
| $H_3C_aC_bH_2CH_2-$<br>($C-C$ (a)) | $C_a$ | -0.92918 | 0 | 0 | 0 | -152.54487 | 0.91771 | 0.86359 | -15.75493 | -15.56407 | 63.82 | 116.18 | 30.08 | 1.83879 | 0.38106 |
| $H_3C_aC_bH_2CH_2-$<br>($C-C$ (a)) | $C_b$ | -0.92918 | -0.92918 | 0 | 0 | -153.47406 | 0.91771 | 0.81549 | -16.68412 | -16.49325 | 56.41 | 123.59 | 26.06 | 1.90890 | 0.45117 |
| $R-H_2C_aC_b(H_2C_c-R')HCH_2-$<br>($C-C$ (b)) | $C_b$ | -0.92918 | -0.92918 | -0.92918 | 0 | -154.40324 | 0.91771 | 0.77247 | -17.61330 | -17.42244 | 48.30 | 131.70 | 21.90 | 1.97162 | 0.51388 |
| $R-H_2C_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$<br>($C-C$ (c)) | $C_b$ | -0.92918 | -0.72457 | -0.72457 | -0.72457 | -154.71860 | 0.91771 | 0.75889 | -17.92866 | -17.73779 | 48.21 | 131.79 | 21.74 | 1.95734 | 0.50570 |
| $isoC_aC_b(H_2C_c-R')HCH_2-$<br>($C-C$ (d)) | $C_b$ | -0.92918 | -0.92918 | -0.92918 | 0 | -154.40324 | 0.91771 | 0.77247 | -17.61330 | -17.42244 | 48.30 | 131.70 | 21.90 | 1.97162 | 0.51388 |
| $tertC_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$<br>($C-C$ (e)) | $C_b$ | -0.72457 | -0.72457 | -0.72457 | -0.72457 | -154.51399 | 0.91771 | 0.76765 | -17.92866 | -17.73779 | 50.04 | 129.96 | 22.66 | 1.94462 | 0.49298 |
| $tertC_aC_b(H_2C_c-R')HCH_2-$<br>($C-C$ (f)) | $C_b$ | -0.72457 | -0.92918 | -0.92918 | 0 | -154.19863 | 0.91771 | 0.78155 | -17.40869 | -17.21783 | 52.78 | 127.22 | 24.04 | 1.92443 | 0.47279 |
| $isoC_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$<br>($C-C$ (f)) | $C_b$ | -0.72457 | -0.72457 | -0.72457 | -0.72457 | -154.51399 | 0.91771 | 0.76765 | -17.92866 | -17.73779 | 50.04 | 129.96 | 22.66 | 1.94462 | 0.49298 |

Table 15.150. The energy parameters ($eV$) of functional groups of alkyl thiols.

| Parameters | $H_2S$ | $SH$ Group | $C-S$ Group | $CH_3$ Group | $CH_2$ Group | $C-H$ Group | $C-C$ (a) Group | $C-C$ (b) Group | $C-C$ (c) Group | $C-C$ (d) Group | $C-C$ (e) Group | $C-C$ (f) Group |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $n_1$ | 2 | 1 | 1 | 3 | 2 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $n_2$ | 0 | 0 | 0 | 2 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $n_3$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $C_1$ | 0.75 | 0.75 | 0.5 | 0.75 | 0.75 | 0.75 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| $C_2$ | 0.76144 | 0.76144 | 0.64965 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $c_1$ | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $c_2$ | 1 | 1 | 1 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 |
| $c_3$ | 2 | 1 | 0 | 0 | 1 | 1 | 0 | 0 | 0 | 1 | 1 | 0 |
| $c_4$ | 1 | 1 | 2 | 1 | 1 | 1 | 2 | 2 | 2 | 2 | 2 | 2 |
| $c_5$ | 1 | 1 | 0 | 3 | 2 | 1 | 0 | 0 | 0 | 0 | 0 | 0 |
| $C_{1o}$ | 0.75 | 0.75 | 0.5 | 0.75 | 0.75 | 0.75 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| $C_{2o}$ | 0.76144 | 0.76144 | 0.64965 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $V_e\ (eV)$ | -72.80662 | -36.40331 | -46.36495 | -107.32728 | -70.41425 | -35.12015 | -28.79214 | -28.79214 | -29.10112 | -28.79214 | -29.10112 | -29.10112 |
| $V_p\ (eV)$ | 21.45310 | 10.72655 | 7.93551 | 38.92728 | 25.78002 | 12.87680 | 9.33352 | 9.33352 | 9.37273 | 9.33352 | 9.37273 | 9.37273 |
| $T\ (eV)$ | 19.81003 | 9.90502 | 12.13899 | 32.53914 | 21.06675 | 10.48582 | 6.77464 | 6.77464 | 6.90500 | 6.77464 | 6.90500 | 6.90500 |
| $V_m\ (eV)$ | -9.90502 | -4.95251 | -6.06949 | -16.26957 | -10.53337 | -5.24291 | -3.38732 | -3.38732 | -3.45250 | -3.38732 | -3.45250 | -3.45250 |
| $E(_{AO/HO})\ (eV)$ | -20.72002 | -10.36001 | 0 | -15.56407 | -15.56407 | -14.63489 | -15.56407 | -15.56407 | -15.35946 | -15.56407 | -15.35946 | -15.35946 |
| $\Delta E_{H_2MO}(_{AO/HO})\ (eV)$ | 1.10200 | 0.55100 | -0.72457 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $E_T(_{AO/HO})\ (eV)$ | -19.61802 | -10.91101 | 0.72457 | -15.56407 | -15.56407 | -14.63489 | -15.56407 | -15.56407 | -15.35946 | -15.56407 | -15.35946 | -15.35946 |
| $E_T(_{H_2MO})\ (eV)$ | -63.27052 | -31.63526 | -31.63537 | -67.69451 | -49.66493 | -31.63533 | -31.63537 | -31.63537 | -31.63535 | -31.63537 | -31.63535 | -31.63535 |
| $E_T\left(atom-atom, msp^3.AO\right)(eV)$ | 1.10200 | 0.55100 | -0.72457 | 0 | 0 | 0 | -1.85836 | -1.85836 | -1.44915 | -1.85836 | -1.44915 | -1.44915 |
| $E_T(_{MO})\ (eV)$ | -62.16874 | -31.08437 | -32.35994 | -67.69450 | -49.66493 | -31.63537 | -33.49373 | -33.49373 | -33.08452 | -33.49373 | -33.08452 | -33.08452 |
| $\omega\ \left(10^{15}\ rad/s\right)$ | 12.5415 | 12.5415 | 30.5436 | 24.9286 | 24.2751 | 24.1759 | 9.43699 | 9.43699 | 15.4846 | 9.43699 | 9.55643 | 9.55643 |
| $E_K\ (eV)$ | 8.25504 | 8.25504 | 20.10434 | 16.40846 | 15.97831 | 15.91299 | 6.21159 | 6.21159 | 10.19220 | 6.21159 | 6.29021 | 6.29021 |
| $\bar{E}_D\ (eV)$ | -0.17669 | -0.17669 | -0.28705 | -0.25352 | -0.25017 | -0.24966 | -0.16515 | -0.16515 | -0.20896 | -0.16515 | -0.16416 | -0.16416 |
| $\bar{E}_{Kvib}\ (eV)$ | 0.32422<br>[39] | 0.33620<br>[40] | 0.08146<br>[41] | 0.35532<br>(Eq. (13.458)) | 0.35532<br>(Eq. (13.458)) | 0.35532<br>(Eq. (13.458)) | 0.12312<br>[2] | 0.17978<br>[4] | 0.09944<br>[5] | 0.12312<br>[2] | 0.12312<br>[2] | 0.12312<br>[2] |
| $\bar{E}_{osc}\ (eV)$ | -0.01458 | -0.00859 | -0.24632 | -0.22757 | -0.14502 | -0.07200 | -0.10359 | -0.07526 | -0.15924 | -0.10359 | -0.10260 | -0.10260 |
| $E_{mag}\ (eV)$ | 0.11441 | 0.11441 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 |
| $E_T(_{Group})\ (eV)$ | -31.10493[a] | -31.09296 | -32.60626 | -67.92207 | -49.80996 | -31.70737 | -33.59732 | -33.49373 | -33.24376 | -33.59732 | -33.18712 | -33.18712 |
| $E_{initial}(_{c_4\ AO/HO})\ (eV)$ | -13.60580 | -13.60580 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 |
| $E_{initial}(_{c_5\ AO/HO})\ (eV)$ | -13.59844 | -13.59844 | 0 | -13.59844 | -13.59844 | -13.59844 | 0 | 0 | 0 | 0 | 0 | 0 |
| $E_D(_{Group})\ (eV)$ | 3.78628 | 3.77430 | 3.33648 | 12.49186 | 7.83016 | 3.32601 | 4.32754 | 4.29921 | 3.97398 | 4.17951 | 3.62128 | 3.91734 |

[a] $E_T(_{H-S,H_2S}) = E_T\ (_{H_2S}) - E_T\ (_{HS}) = 62.19789\ eV - (-31.09296\ eV)$.

Table 15.151. The total bond energies of alkyl thiols calculated using the functional group composition and the energies of Table 15.150 compared to the experimental values [3]. The magnetic energy $E_{mag}$ that is subtracted from the weighted sum of the $E_D$ $(_{Group})$ $(eV)$ values based on composition is given by (15.58).

| Formula | Name | $H_2S$ Group | $SH$ Group | $C-S$ Group | $CH_3$ | $CH_2$ | $CH$ | $C-C$ (a) | $C-C$ (b) | $C-C$ (c) | $C-C$ (d) | $C-C$ (e) | $C-C$ (f) | $E_{mag}$ | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $HS$ | Hydrogen Sulfide | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 3.77430 | 3.653 | -0.03320 |
| $H_2S$ | Dihydrogen Sulfide | 1 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 7.56058 | 7.605 | 0.00582 |
| $CH_4S$ | Methanethiol | 0 | 1 | 1 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 19.60264 | 19.575 | -0.00141 |
| $C_2H_6S$ | Ethanethiol | 0 | 1 | 1 | 1 | 1 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 31.76034 | 31.762 | 0.00005 |
| $C_3H_8S$ | 1-Propanethiol | 0 | 1 | 1 | 1 | 2 | 0 | 2 | 0 | 0 | 0 | 0 | 0 | 0 | 43.91804 | 43.933 | 0.00035 |
| $C_3H_8S$ | 2-Propanethiol | 0 | 1 | 1 | 2 | 0 | 1 | 0 | 2 | 0 | 0 | 0 | 0 | 0 | 44.01893 | 44.020 | 0.00003 |
| $C_4H_{10}S$ | 1-Butanethiol | 0 | 1 | 1 | 1 | 3 | 0 | 3 | 0 | 0 | 0 | 0 | 0 | 0 | 56.07574 | 56.089 | 0.00024 |
| $C_4H_{10}S$ | 2-Butanethiol | 0 | 1 | 1 | 2 | 1 | 1 | 1 | 2 | 0 | 0 | 0 | 0 | 0 | 56.17663 | 56.181 | 0.00009 |
| $C_4H_{10}S$ | 2-Methyl-1-propanethiol | 0 | 1 | 1 | 2 | 1 | 1 | 0 | 3 | 0 | 0 | 0 | 0 | 0 | 56.14830 | 56.186 | 0.00066 |
| $C_4H_{10}S$ | 2-Methyl-2-propanethiol | 0 | 1 | 1 | 3 | 0 | 0 | 0 | 0 | 3 | 0 | 0 | 0 | -1 | 56.36027 | 56.313 | -0.00084 |
| $C_5H_{12}S$ | 2-Methyl-1-butanethiol | 0 | 1 | 1 | 2 | 2 | 1 | 1 | 3 | 0 | 0 | 0 | 0 | 0 | 68.30600 | 68.314 | 0.00012 |
| $C_5H_{12}S$ | 1-Pentanethiol | 0 | 1 | 1 | 1 | 4 | 0 | 4 | 0 | 0 | 0 | 0 | 0 | 0 | 68.23344 | 68.264 | 0.00044 |
| $C_5H_{12}S$ | 2-Methyl-2-butanethiol | 0 | 1 | 1 | 3 | 1 | 0 | 1 | 0 | 3 | 0 | 0 | 0 | -1 | 68.51797 | 68.441 | -0.00113 |
| $C_5H_{12}S$ | 3-Methyl-2-butanethiol | 0 | 1 | 1 | 3 | 0 | 2 | 0 | 3 | 0 | 1 | 0 | 0 | 0 | 68.31552 | 68.381 | 0.00095 |
| $C_5H_{12}S$ | 2,2-Dimethyl-1-propanethiol | 0 | 1 | 1 | 3 | 1 | 0 | 1 | 0 | 3 | 0 | 0 | 0 | -1 | 68.16441 | 68.461 | 0.00433 |
| $C_6H_{14}S$ | 1-Hexanethiol | 0 | 1 | 1 | 1 | 5 | 0 | 5 | 0 | 0 | 0 | 0 | 0 | 0 | 80.39114 | 80.416 | 0.00031 |
| $C_6H_{14}S$ | 2-Methyl-2-pentanethiol | 0 | 1 | 1 | 3 | 2 | 0 | 2 | 0 | 3 | 0 | 0 | 0 | -1 | 80.67567 | 80.607 | -0.00085 |
| $C_6H_{14}S$ | 2,3-Dimethyl-2-butanethiol | 0 | 1 | 1 | 4 | 0 | 1 | 0 | 2 | 2 | 0 | 0 | 1 | -1 | 80.71992 | 80.603 | -0.00145 |
| $C_7H_{16}S$ | 1-Heptanethiol | 0 | 1 | 1 | 1 | 6 | 0 | 6 | 0 | 0 | 0 | 0 | 0 | 0 | 92.54884 | 92.570 | 0.00023 |
| $C_{10}H_{22}S$ | 1-Decanethiol | 0 | 1 | 1 | 1 | 9 | 0 | 9 | 0 | 0 | 0 | 0 | 0 | 0 | 129.02194 | 129.048 | 0.00020 |

Table 15.152. The bond angle parameters of alkyl thiols and experimental values [1]. In the calculation of $\theta_v$, the parameters from the preceding angle were used. $E_T$ is $E_T$ ($atom-atom,msp^3.AO$).

| Atoms of Angle | 2$c'$ Bond 1 ($a_0$) | 2$c'$ Bond 2 ($a_0$) | 2$c'$ Terminal Atoms ($a_0$) | $E_{Coulombic}$ Atom 1 | Atom 1 Hybridization Designation (Table 15.3.A) | $E_{Coulombic}$ Atom 2 | Atom 2 Hybridization Designation (Table 15.3.A) | $c_2$ Atom 1 | $c_2$ Atom 2 | $C_1$ | $C_2$ | $c_1$ | $c_2'$ | $E_T$ (eV) | $\theta_v$ (°) | $\theta_1$ (°) | $\theta_2$ (°) | Cal. $\theta$ (°) | Exp. $\theta$ (°) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $\angle HSC_a$ | 2.53685 | 3.42910 | 4.5166 | -10.36001<br>$S$ | S | -15.75493<br>$C_a$ | 7 | 0.76144 (Eq. 15.144)) | 0.86359 | 0.75 | 1 | 0.75 | 1.13415 | 0 | | | | 97.28 | 96.5 (methanethiol)<br>96.4 (ethanethiol) |
| $\angle C_bC_aS$ | 2.91547 | 3.42910 | 5.2344 | -16.68412<br>$C_b$ | 26 | -10.36001<br>$S$ | S | 0.81549 | 0.64965 (Eq. (15.146)) | 1 | 0.64965 (Eq. (15.146)) | 1 | 0.73257 | -0.72457 | | | | 110.92 | 108.3 (ethanethiol) |
| Methylene $\angle HC_aH$ | 2.11106 | 2.11106 | 3.4252 | -15.75493 | 7 | H | H | 0.86359 | 1 | 1 | 1 | 0.75 | 1.15796 | 0 | | | | 108.44 | 107 (propane) |
| $\angle C_aC_bC_c$ | | | | | | | | | | | | | | | 69.51 | | | 110.49 | 112 (propane)<br>113.8 (butane)<br>110.8 (isobutane) |
| $\angle C_aC_bH$ | | | | | | | | | | | | | | | 69.51 | | | 110.49 | 111.0 (butane)<br>111.4 (isobutane) |
| Methyl $\angle HC_aH$ | 2.09711 | 2.09711 | 3.4252 | -15.75493 | 7 | H | H | 0.86359 | 1 | 1 | 1 | 0.75 | 1.15796 | 0 | | | | 109.50 | |
| $\angle C_aC_bC_c$ | | | | | | | | | | | | | | | 70.56 | | | 109.44 | |
| $\angle C_aC_bH$ | | | | | | | | | | | | | | | 70.56 | | | 109.44 | |
| $\angle C_bC_aC_c$ iso $C_a$ | 2.91547 | 2.91547 | 4.7958 | -16.68412<br>$C_b$ | 26 | -16.68412<br>$C_c$ | 26 | 0.81549 | 0.81549 | 1 | 1 | 1 | 0.81549 | -1.85836 | | | | 110.67 | 110.8 (isobutane) |
| $\angle C_bC_aH$ iso $C_a$ | 2.91547 | 2.11323 | 4.1633 | -15.55033<br>$C_a$ | 5 | -14.82575<br>$C_b$ | 1 | 0.87495 | 0.91771 | 0.75 | 1 | 0.75 | 1.04887 | 0 | | | | 110.76 | |
| $\angle C_aC_bH$ iso $C_a$ | 2.91547 | 2.09711 | 4.1633 | -15.55033<br>$C_b$ | 5 | -14.82575<br>$C_a$ | 1 | 0.87495 | 0.91771 | 0.75 | 1 | 0.75 | 1.04887 | 0 | | | | 111.27 | 111.4 (isobutane) |
| $\angle C_bC_aC_b$ tert $C_a$ | 2.90327 | 2.90327 | 4.7958 | -16.68412<br>$C_b$ | 26 | -16.68412<br>$C_b$ | 26 | 0.81549 | 0.81549 | 1 | 1 | 1 | 0.81549 | -1.85836 | | | | 111.37 | 110.8 (isobutane) |
| $\angle C_bC_aC_d$ | | | | | | | | | | | | | | | 72.50 | | | 107.50 | |

## SULFIDES ($C_nH_{2n+2}S_m$, $n=2,3,4,5...\infty$)

The alkyl sulfides, $C_nH_{2n+2}S_m$, comprise two types of $C-S$ functional groups, one for t-butyl groups corresponding to the $C$ and the other for the remaining general alkyl groups including methyl. The alkyl portion of the alkyl sulfide may comprise at least two terminal methyl groups ($CH_3$) at each end of the chain, and may comprise methylene ($CH_2$), and methylyne ($CH$) functional groups as well as $C$ bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($(CH_3)_2CH$) and t-butyl ($(CH_3)_3C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups. The branched-chain-alkane groups in sulfides are equivalent to those in branched-chain alkanes.

Each $C-S$ group is solved by hybridizing the $2s$ and $2p$ AOs of the $C$ atom to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between the $C2sp^3$ HO and the $S$ AO to form a MO permits each participating orbital to decrease in radius and energy. Since the energy of sulfur is less than the Coulombic energy between the electron and proton of $H$ given by Eq. (1.264), $c_2$ in Eq. (15.61) is one, and the energy matching condition is determined by the $C_2$ parameter. As in the case of thiols, $C_2$ of Eq. (15.61) for the $C-S$-bond MO given by Eq. (15.146) is $C_2\left(C2sp^3HO\ to\ \mathrm{S}\right)=0.64965$.

The $C-S$ group of alkyl sulfides is equivalent to that of thiols where $E_T\left(atom-atom,msp^3.AO\right)$ is $-0.72457\ eV$ (Eq. (14.151)). The t-butyl-$C-S$ group is also equivalent to that of thiols except that the energy parameters corresponding to the oscillation in the transition state are matched to those of the t-butyl group.

The symbols of the functional groups of branched-chain alkyl sulfides are given in Table 15.153. The geometrical (Eqs. (15.1-15.5) and (15.51)), intercept (Eqs. (15.80-15.87)), and energy (Eqs. (15.6-15.11) and (15.17-15.65)) parameters of alkyl sulfides are given in Tables 15.154, 15.155, and 15.156, respectively. Consider that the $C-S$ bond is along the x axis in the xy-plane. The $S$ nucleus is at the focus +c and the $C$ nucleus is at the focus –c. The elliptic angle $\theta'$ is taken as counterclockwise from the x-axis for $S$ and as clockwise from the –x-axis for $C$. The total energy of each alkyl sulfide given in Table 15.157 was calculated as the sum over the integer multiple of each $E_D\left(Group\right)$ of Table 15.156 corresponding to functional-group composition of the molecule. $E_{mag}$ given by Eq. (15.67) was subtracted for each t-butyl group. The bond angle parameters of alkyl sulfides determined using Eqs. (15.88-15.117) are given in Table 15.158. The color scale, translucent view of the charge-density of exemplary sulfide, dimethyl sulfide, comprising the concentric shells of atoms with the outer shell bridged by one or more $H_2$-type ellipsoidal MOs or joined with one or more hydrogen MOs is shown in Figure 15.26.

Figure 15.26. Color scale, translucent view of the charge-density of dimethyl sulfide showing the orbitals of the atoms at their radii, the ellipsoidal surface of each $H$ or $H_2$-type ellipsoidal MO that transitions to the corresponding outer shell of the atom(s) participating in each bond, and the hydrogen nuclei (red, not to scale).

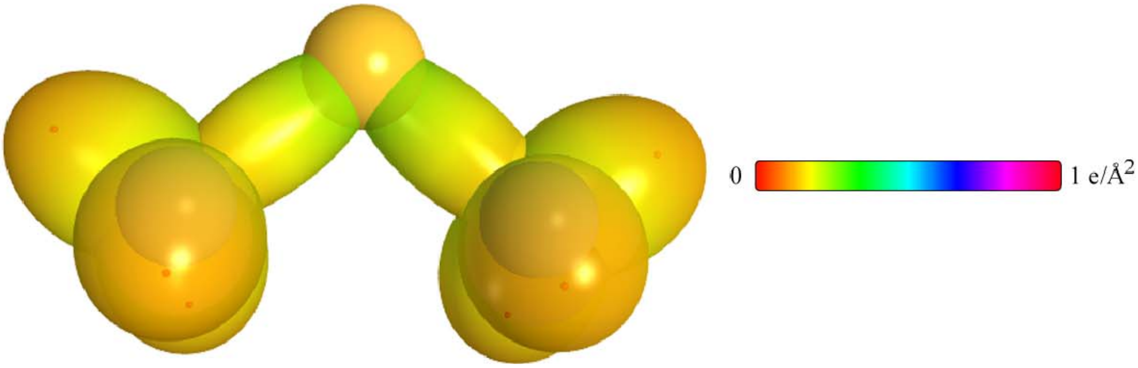


Table 15.153. The symbols of functional groups of alkyl sulfides.

| Functional Group | Group Symbol |
|---|---|
| *C-S* (*methyl, alkyl*) | $C-S$ (i) |
| *C-S* ($(CH_3)_3C-S-$) | $C-S$ (ii) |
| $CH_3$ group | $C-H$ $(CH_3)$ |
| $CH_2$ group | $C-H$ $(CH_2)$ |
| *CH* | $C-H$ |
| *CC* bond (*n-C*) | $C-C$ (a) |
| *CC* bond (*iso-C*) | $C-C$ (b) |
| *CC* bond (*tert-C*) | $C-C$ (c) |
| *CC* (*iso* to *iso-C*) | $C-C$ (d) |
| *CC* (*t* to *t-C*) | $C-C$ (e) |
| *CC* (*t* to *iso-C*) | $C-C$ (f) |

Table 15.154. The geometrical bond parameters of alkyl sulfides and experimental values [1].

| Parameter | $C-S$ (i) Group | $C-S$ (ii) Group | $C-H\ (CH_3)$ Group | $C-H\ (CH_2)$ Group | $C-H$ Group | $C-C$ (a) Group | $C-C$ (b) Group | $C-C$ (c) Group | $C-C$ (d) Group | $C-C$ (e) Group | $C-C$ (f) Group |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $a\ (a_0)$ | 1.90975 | 1.90975 | 1.64920 | 1.67122 | 1.67465 | 2.12499 | 2.12499 | 2.10725 | 2.12499 | 2.10725 | 2.10725 |
| $c'\ (a_0)$ | 1.71455 | 1.71455 | 1.04856 | 1.05553 | 1.05661 | 1.45744 | 1.45744 | 1.45164 | 1.45744 | 1.45164 | 1.45164 |
| Bond Length $2c'$ $(Å)$ | 1.81460 | 1.81460 | 1.10974 | 1.11713 | 1.11827 | 1.54280 | 1.54280 | 1.53635 | 1.54280 | 1.53635 | 1.53635 |
| Exp. Bond Length $(Å)$ | 1.807<br>(dimethyl sulfide)<br>1.813<br>(ethyl methyl sulfide, avg.) | 1.807<br>(dimethyl sulfide)<br>1.813<br>(ethyl methyl sulfide, avg.) | 1.107<br>($C-H$ propane)<br>1.117<br>($C-H$ butane) | 1.107<br>($C-H$ propane)<br>1.117<br>($C-H$ butane) | 1.122<br>(isobutane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) |
| $b,c\ (a_0)$ | 0.84112 | 0.84112 | 1.27295 | 1.29569 | 1.29924 | 1.54616 | 1.54616 | 1.52750 | 1.54616 | 1.52750 | 1.52750 |
| $e$ | 0.89778 | 0.89778 | 0.63580 | 0.63159 | 0.63095 | 0.68600 | 0.68600 | 0.68888 | 0.68600 | 0.68888 | 0.68888 |

Table 15.155. The MO to HO intercept geometrical bond parameters of alkyl sulfides. $R$, $R'$, $R''$ are $H$ or alkyl groups. $E_T$ is $E_T(atom-atom, msp^3.AO)$.

| Bond | Atom | $E_T$ (eV) Bond 1 | $E_T$ (eV) Bond 2 | $E_T$ (eV) Bond 3 | $E_T$ (eV) Bond 4 | Final Total Energy $C2sp^3$ (eV) | $r_{initial}$ $(a_0)$ | $r_{final}$ $(a_0)$ | $E_{Coulomb}$ (eV) Final | $E(C2sp^3)$ (eV) Final | $\theta'$ $(^\circ)$ | $\theta_1$ $(^\circ)$ | $\theta_2$ $(^\circ)$ | $d_1$ $(a_0)$ | $d_2$ $(a_0)$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $R-S-R$<br>($C-S$ (i) and (ii)) | $S$ | -0.36229 | -0.36229 | 0 | 0 |  | 1.32010 | 0.87495 | -15.55033 |  | 129.96 | 50.04 | 52.88 | 1.15262 | 0.56193 |
| $H_3C_a-S-C_bH_2CH_2R$<br>($C-S$ (i)) | $C_a$ | -0.36229 | 0 | 0 | 0 | -151.97798 | 0.91771 | 0.89582 | -15.18804 | -14.99717 | 130.79 | 49.21 | 53.75 | 1.12937 | 0.58518 |
| $H_3C_a-S-C_bH_2CH_2R$<br>($C-S$ (i)) | $C_b$ | -0.36229 | -0.92918 | 0 | 0 | -152.90716 | 0.91771 | 0.84418 | -16.11722 | -15.92636 | 128.69 | 51.31 | 51.57 | 1.18689 | 0.52765 |
| $H_3C_a-S-C_c(CH_3)_3$<br>($C-S$ (i) and (ii)) | $C_c$ | -0.36229 | -0.72457 | -0.72457 | -0.72457 | -154.15170 | 0.91771 | 0.78367 | -17.36176 | -17.17090 | 125.97 | 54.03 | 48.94 | 1.25430 | 0.46025 |
| $C-H\ (CH_3)$ | $C$ | -0.92918 | 0 | 0 | 0 | -152.54487 | 0.91771 | 0.86359 | -15.75493 | -15.56407 | 77.49 | 102.51 | 41.48 | 1.23564 | 0.18708 |
| $C-H\ (CH_2)$ | $C$ | -0.92918 | -0.92918 | 0 | 0 | -153.47406 | 0.91771 | 0.81549 | -16.68412 | -16.49325 | 68.47 | 111.53 | 35.84 | 1.35486 | 0.29933 |
| $C-H\ (CH)$ | $C$ | -0.92918 | -0.92918 | -0.92918 | 0 | -154.40324 | 0.91771 | 0.77247 | -17.61330 | -17.42244 | 61.10 | 118.90 | 31.37 | 1.42988 | 0.37326 |
| $H_3C_aC_bH_2CH_2-$<br>($C-C$ (a)) | $C_a$ | -0.92918 | 0 | 0 | 0 | -152.54487 | 0.91771 | 0.86359 | -15.75493 | -15.56407 | 63.82 | 116.18 | 30.08 | 1.83879 | 0.38106 |
| $H_3C_aC_bH_2CH_2-$<br>($C-C$ (a)) | $C_b$ | -0.92918 | -0.92918 | 0 | 0 | -153.47406 | 0.91771 | 0.81549 | -16.68412 | -16.49325 | 56.41 | 123.59 | 26.06 | 1.90890 | 0.45117 |
| $R-H_2C_aC_b(H_2C_c-R')HCH_2-$<br>($C-C$ (b)) | $C_b$ | -0.92918 | -0.92918 | -0.92918 | 0 | -154.40324 | 0.91771 | 0.77247 | -17.61330 | -17.42244 | 48.30 | 131.70 | 21.90 | 1.97162 | 0.51388 |
| $R-H_2C_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$<br>($C-C$ (c)) | $C_b$ | -0.92918 | -0.72457 | -0.72457 | -0.72457 | -154.71860 | 0.91771 | 0.75889 | -17.92866 | -17.73779 | 48.21 | 131.79 | 21.74 | 1.95734 | 0.50570 |
| $isoC_aC_b(H_2C_c-R')HCH_2-$<br>($C-C$ (d)) | $C_b$ | -0.92918 | -0.92918 | -0.92918 | 0 | -154.40324 | 0.91771 | 0.77247 | -17.61330 | -17.42244 | 48.30 | 131.70 | 21.90 | 1.97162 | 0.51388 |
| $tertC_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$<br>($C-C$ (e)) | $C_b$ | -0.72457 | -0.72457 | -0.72457 | -0.72457 | -154.51399 | 0.91771 | 0.76765 | -17.92866 | -17.73779 | 50.04 | 129.96 | 22.66 | 1.94462 | 0.49298 |
| $tertC_aC_b(H_2C_c-R')HCH_2-$<br>($C-C$ (f)) | $C_b$ | -0.72457 | -0.92918 | -0.92918 | 0 | -154.19863 | 0.91771 | 0.78155 | -17.40869 | -17.21783 | 52.78 | 127.22 | 24.04 | 1.92443 | 0.47279 |
| $isoC_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$<br>($C-C$ (f)) | $C_b$ | -0.72457 | -0.72457 | -0.72457 | -0.72457 | -154.51399 | 0.91771 | 0.76765 | -17.92866 | -17.73779 | 50.04 | 129.96 | 22.66 | 1.94462 | 0.49298 |

Table 15.156. The energy parameters ($eV$) of functional groups of alkyl sulfides.

| Parameters | $C-S$ (i) Group | $C-S$ (ii) Group | $CH_3$ Group | $CH_2$ Group | $C-H$ Group | $C-C$ (a) Group | $C-C$ (b) Group | $C-C$ (c) Group | $C-C$ (d) Group | $C-C$ (e) Group | $C-C$ (f) Group |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $n_1$ | 1 | 1 | 3 | 2 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $n_2$ | 0 | 0 | 2 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $n_3$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $C_1$ | 0.5 | 0.5 | 0.75 | 0.75 | 0.75 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| $C_2$ | 0.64965 | 0.64965 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $c_1$ | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $c_2$ | 1 | 1 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 |
| $c_3$ | 0 | 0 | 0 | 1 | 1 | 0 | 0 | 0 | 1 | 1 | 0 |
| $c_4$ | 2 | 2 | 1 | 1 | 1 | 2 | 2 | 2 | 2 | 2 | 2 |
| $c_5$ | 0 | 0 | 3 | 2 | 1 | 0 | 0 | 0 | 0 | 0 | 0 |
| $C_{1o}$ | 0.5 | 0.5 | 0.75 | 0.75 | 0.75 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| $C_{2o}$ | 0.64965 | 0.64965 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $V_e\ (eV)$ | -46.36495 | -46.36495 | -107.32728 | -70.41425 | -35.12015 | -28.79214 | -28.79214 | -29.10112 | -28.79214 | -29.10112 | -29.10112 |
| $V_p\ (eV)$ | 7.93551 | 7.93551 | 38.92728 | 25.78002 | 12.87680 | 9.33352 | 9.33352 | 9.37273 | 9.33352 | 9.37273 | 9.37273 |
| $T\ (eV)$ | 12.13899 | 12.13899 | 32.53914 | 21.06675 | 10.48582 | 6.77464 | 6.77464 | 6.90500 | 6.77464 | 6.90500 | 6.90500 |
| $V_m\ (eV)$ | -6.06949 | -6.06949 | -16.26957 | -10.53337 | -5.24291 | -3.38732 | -3.38732 | -3.45250 | -3.38732 | -3.45250 | -3.45250 |
| $E(_{AO/HO})\ (eV)$ | 0 | 0 | -15.56407 | -15.56407 | -14.63489 | -15.56407 | -15.56407 | -15.35946 | -15.56407 | -15.35946 | -15.35946 |
| $\Delta E_{H_2MO}(_{AO/HO})\ (eV)$ | -0.72457 | -0.72457 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $E_T(_{AO/HO})\ (eV)$ | 0.72457 | 0.72457 | -15.56407 | -15.56407 | -14.63489 | -15.56407 | -15.56407 | -15.35946 | -15.56407 | -15.35946 | -15.35946 |
| $E_T(_{H_2MO})\ (eV)$ | -31.63537 | -31.63537 | -67.69451 | -49.66493 | -31.63533 | -31.63537 | -31.63537 | -31.63535 | -31.63537 | -31.63535 | -31.63535 |
| $E_T\left(atom-atom,msp^3.AO\right)(eV)$ | -0.72457 | -0.72457 | 0 | 0 | 0 | -1.85836 | -1.85836 | -1.44915 | -1.85836 | -1.44915 | -1.44915 |
| $E_T(_{MO})\ (eV)$ | -32.35994 | -32.35994 | -67.69450 | -49.66493 | -31.63537 | -33.49373 | -33.49373 | -33.08452 | -33.49373 | -33.08452 | -33.08452 |
| $\omega\ \left(10^{15}\ rad/s\right)$ | 30.5436 | 8.92777 | 24.9286 | 24.2751 | 24.1759 | 9.43699 | 9.43699 | 15.4846 | 9.43699 | 9.55643 | 9.55643 |
| $E_K\ (eV)$ | 20.10434 | 5.87641 | 16.40846 | 15.97831 | 15.91299 | 6.21159 | 6.21159 | 10.19220 | 6.21159 | 6.29021 | 6.29021 |
| $\bar{E}_D\ (eV)$ | -0.28705 | -0.15519 | -0.25352 | -0.25017 | -0.24966 | -0.16515 | -0.16515 | -0.20896 | -0.16515 | -0.16416 | -0.16416 |
| $\bar{E}_{Kvib}\ (eV)$ | 0.08146<br>[41] | 0.08146<br>[41] | 0.35532<br>(Eq. (13.458)) | 0.35532<br>(Eq. (13.458)) | 0.35532<br>(Eq. (13.458)) | 0.12312<br>[2] | 0.17978<br>[4] | 0.09944<br>[5] | 0.12312<br>[2] | 0.12312<br>[2] | 0.12312<br>[2] |
| $\bar{E}_{osc}\ (eV)$ | -0.24632 | -0.11446 | -0.22757 | -0.14502 | -0.07200 | -0.10359 | -0.07526 | -0.15924 | -0.10359 | -0.10260 | -0.10260 |
| $E_{mag}\ (eV)$ | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 |
| $E_T(_{Group})\ (eV)$ | -32.60626 | -32.47440 | -67.92207 | -49.80996 | -31.70737 | -33.59732 | -33.49373 | -33.24376 | -33.59732 | -33.18712 | -33.18712 |
| $E_{initial}(_{c_4\ AO/HO})\ (eV)$ | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 |
| $E_{initial}(_{c_5\ AO/HO})\ (eV)$ | 0 | 0 | -13.59844 | -13.59844 | -13.59844 | 0 | 0 | 0 | 0 | 0 | 0 |
| $E_D(_{Group})\ (eV)$ | 3.33648 | 3.20462 | 12.49186 | 7.83016 | 3.32601 | 4.32754 | 4.29921 | 3.97398 | 4.17951 | 3.62128 | 3.91734 |

Table 15.157. The total bond energies of alkyl sulfides calculated using the functional group composition and the energies of Table 15.156 compared to the experimental values [3]. The magnetic energy $E_{mag}$ that is subtracted from the weighted sum of the $E_D$ $(_{Group})$ $(eV)$ values based on composition is given by (15.58).

| Formula | Name | $C-S$ (i) Group | $C-S$ (ii) Group | $CH_3$ | $CH_2$ | $CH$ | $C-C$ (a) | $C-C$ (b) | $C-C$ (c) | $C-C$ (d) | $C-C$ (e) | $C-C$ (f) | $E_{mag}$ | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $C_2H_6S$ | Dimethyl sulfide | 2 | 0 | 2 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 31.65668 | 31.672 | 0.00048 |
| $C_3H_8S$ | Ethyl methyl sulfide | 2 | 0 | 2 | 1 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 43.81438 | 43.848 | 0.00078 |
| $C_4H_{10}S$ | Diethyl sulfide | 2 | 0 | 2 | 2 | 0 | 2 | 0 | 0 | 0 | 0 | 0 | 0 | 55.97208 | 56.043 | 0.00126 |
| $C_4H_{10}S$ | Methyl propyl sulfide | 2 | 0 | 2 | 2 | 0 | 2 | 0 | 0 | 0 | 0 | 0 | 0 | 55.97208 | 56.029 | 0.00102 |
| $C_4H_{10}S$ | Isopropyl methyl sulfide | 2 | 0 | 3 | 0 | 1 | 0 | 2 | 0 | 0 | 0 | 0 | 0 | 56.07297 | 56.115 | 0.00075 |
| $C_5H_{12}S$ | Butyl methyl sulfide | 2 | 0 | 2 | 3 | 0 | 3 | 0 | 0 | 0 | 0 | 0 | 0 | 68.12978 | 68.185 | 0.00081 |
| $C_5H_{12}S$ | t-Butyl methyl sulfide | 1 | 1 | 4 | 0 | 0 | 0 | 0 | 3 | 0 | 0 | 0 | -1 | 68.28245 | 68.381 | 0.00144 |
| $C_5H_{12}S$ | Ethyl propyl sulfide | 2 | 0 | 2 | 3 | 0 | 3 | 0 | 0 | 0 | 0 | 0 | 0 | 68.12978 | 68.210 | 0.00117 |
| $C_5H_{12}S$ | Ethyl isopropyl sulfide | 2 | 0 | 3 | 1 | 1 | 1 | 2 | 0 | 0 | 0 | 0 | 0 | 68.23067 | 68.350 | 0.00174 |
| $C_6H_{14}S$ | Diisopropyl sulfide | 2 | 0 | 4 | 0 | 2 | 0 | 4 | 0 | 0 | 0 | 0 | 0 | 80.48926 | 80.542 | 0.00065 |
| $C_6H_{14}S$ | Butyl ethyl sulfide | 2 | 0 | 2 | 4 | 0 | 4 | 0 | 0 | 0 | 0 | 0 | 0 | 80.28748 | 80.395 | 0.00133 |
| $C_6H_{14}S$ | Methyl pentyl sulfide | 2 | 0 | 2 | 4 | 0 | 4 | 0 | 0 | 0 | 0 | 0 | 0 | 80.28748 | 80.332 | 0.00056 |
| $C_8H_{18}S$ | Dibutyl sulfide | 2 | 0 | 2 | 6 | 0 | 6 | 0 | 0 | 0 | 0 | 0 | 0 | 104.60288 | 104.701 | 0.00094 |
| $C_8H_{18}S$ | Di-sec-butyl sulfide | 2 | 0 | 4 | 2 | 2 | 2 | 4 | 0 | 0 | 0 | 0 | 0 | 104.80466 | 104.701 | -0.00099 |
| $C_8H_{18}S$ | Di-t-butyl sulfide | 0 | 2 | 6 | 0 | 0 | 0 | 0 | 6 | 0 | 0 | 0 | -2 | 104.90822 | 104.920 | 0.00011 |
| $C_8H_{18}S$ | Diisobutyl sulfide | 2 | 0 | 4 | 2 | 2 | 0 | 6 | 0 | 0 | 0 | 0 | 0 | 104.74800 | 104.834 | 0.00082 |
| $C_{10}H_{22}S$ | Dipentyl sulfide | 2 | 0 | 2 | 8 | 0 | 8 | 0 | 0 | 0 | 0 | 0 | 0 | 128.91828 | 128.979 | 0.00047 |
| $C_{10}H_{22}S$ | Diisopentyl sulfide | 2 | 0 | 4 | 4 | 2 | 2 | 6 | 0 | 0 | 0 | 0 | 0 | 129.06340 | 129.151 | 0.00068 |

Table 15.158. The bond angle parameters of alkyl sulfides and experimental values [1]. In the calculation of $\theta_v$, the parameters from the preceding angle were used. $E_T$ is $E_T(atom-atom, msp^3.AO)$.

| Atoms of Angle | 2c' Bond 1 ($a_0$) | 2c' Bond 2 ($a_0$) | 2c' Terminal Atoms ($a_0$) | $E_{Coulombic}$ Atom 1 | Atom 1 Hybridization Designation (Table 15.3.A) | $E_{Coulombic}$ Atom 2 | Atom 2 Hybridization Designation (Table 15.3.A) | $c_2$ Atom 1 | $c_2$ Atom 2 | $C_1$ | $C_2$ | $c_1$ | $c_2'$ | $E_T$ (eV) | $\theta_v$ (°) | $\theta_1$ (°) | $\theta_2$ (°) | Cal. $\theta$ (°) | Exp. $\theta$ (°) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $\angle C_aSC_a$<br>$(C-S$ (i)) | 3.42910 | 3.42910 | 5.2173 | -16.11722 | 12 | -16.11722 | 12 | 0.84418 | 0.84418 | 1 | 1 | 1 | 0.84418 | -1.85836 | | | | 99.06 | 99.05<br>(dimethyl sulfide) |
| $\angle C_aSC_b$<br>$(C-S$ (i)) | 3.42910 | 3.42910 | 5.1381 | -15.75493<br>methyl<br>$C_a$ | 7 | -16.68412<br>methylene<br>$C_b$ | 26 | 0.86359 | 0.81549 | 1 | 1 | 1 | 0.83954 | -1.85836 | | | | 97.04 | 97<br>(ethyl methyl sulfide) |
| $\angle SC_aC_b$<br>$(C-S$ (ii)) | 3.42910 | 2.91547 | 5.3364 | -10.36001 | S | -16.27490 | 16 | 0.64965<br>(Eq. (15.146)) | 0.83600 | 1 | 0.64965<br>(Eq. (15.146)) | 1 | 0.74282 | -0.72457 | | | | 114.27 | 114.0<br>(ethyl methyl sulfide) |
| Methylene<br>$\angle HC_aH$ | 2.11106 | 2.11106 | 3.4252 | -15.75493 | 7 | H | H | 0.86359 | 1 | 1 | 1 | 0.75 | 1.15796 | 0 | | | | 108.44 | 107<br>(propane) |
| $\angle C_aC_bC_c$ | | | | | | | | | | | | | | | 69.51 | | | 110.49 | 112<br>(propane)<br>113.8<br>(butane)<br>110.8<br>(isobutane) |
| $\angle C_aC_bH$ | | | | | | | | | | | | | | | 69.51 | | | 110.49 | 111.0<br>(butane)<br>111.4<br>(isobutane) |
| Methyl<br>$\angle HC_aH$ | 2.09711 | 2.09711 | 3.4252 | -15.75493 | 7 | H | H | 0.86359 | 1 | 1 | 1 | 0.75 | 1.15796 | 0 | | | | 109.50 | 109.3<br>(dimethyl sulfide)<br>110<br>(ethyl methyl sulfide) |
| $\angle C_aC_bC_c$ | | | | | | | | | | | | | | | 70.56 | | | 109.44 | |
| $\angle C_aC_bH$ | | | | | | | | | | | | | | | 70.56 | | | 109.44 | |
| $\angle C_bC_aC_c$<br>iso $C_a$ | 2.91547 | 2.91547 | 4.7958 | -16.68412<br>$C_b$ | 26 | -16.68412<br>$C_c$ | 26 | 0.81549 | 0.81549 | 1 | 1 | 1 | 0.81549 | -1.85836 | | | | 110.67 | 110.8<br>(isobutane) |
| $\angle C_bC_aH$<br>iso $C_a$ | 2.91547 | 2.11323 | 4.1633 | -15.55033<br>$C_a$ | 5 | -14.82575<br>$C_b$ | 1 | 0.87495 | 0.91771 | 0.75 | 1 | 0.75 | 1.04887 | 0 | | | | 110.76 | |
| $\angle C_aC_bH$<br>iso $C_a$ | 2.91547 | 2.09711 | 4.1633 | -15.55033<br>$C_b$ | 5 | -14.82575<br>$C_a$ | 1 | 0.87495 | 0.91771 | 0.75 | 1 | 0.75 | 1.04887 | 0 | | | | 111.27 | 111.4<br>(isobutane) |
| $\angle C_bC_aC_b$<br>tert $C_a$ | 2.90327 | 2.90327 | 4.7958 | -16.68412<br>$C_b$ | 26 | -16.68412<br>$C_b$ | 26 | 0.81549 | 0.81549 | 1 | 1 | 1 | 0.81549 | -1.85836 | | | | 111.37 | 110.8<br>(isobutane) |
| $\angle C_bC_aC_d$ | | | | | | | | | | | | | | | 72.50 | | | 107.50 | |

## DISULFIDES ($C_nH_{2n+2}S_{2m}$, $n=2,3,4,5...\infty$)

The alkyl disulfides, $C_nH_{2n+2}S_{2m}$, comprise $C-S$ and $S-S$ functional groups. The alkyl portion of the alkyl disulfide may comprise at least two terminal methyl groups ($CH_3$) at each end of the chain, and may comprise methylene ($CH_2$), and methylyne ($CH$) functional groups as well as $C$ bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($(CH_3)_2CH$) and t-butyl ($(CH_3)_3C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups. The branched-chain-alkane groups in disulfides are equivalent to those in branched-chain alkanes.

Each $C-S$ group is equivalent to that of general alkyl sulfides given in the corresponding section. As in the case of thiols and sulfides, $C_2$ of Eq. (15.61) for the $C-S$-bond MO given by Eq. (15.146) is $C_2\left(C2sp^3HO\ to\ \mathrm{S}\right)=0.64965$ and $E_T\left(atom-atom,msp^3.AO\right)$ is $-0.72457\ eV$ (Eq. (14.151)).

The $S-S$ group is solved as an $H_2$-type-ellipsoidal-MO that is energy matched to the energy of sulfur, $E(S)=-10.36001\ eV$, such that $E(AO/HO)=-10.36001\ eV$ in Eq. (15.51) with $E_T(AO/HO)=E(AO/HO)$. The $S-S$-bond MO is further energy matched to the $C2sp^3$ HO of the $C-S$-bond MO. $C_2$ of Eq. (15.61) for the $S-S$-bond MO given by Eq. (15.146) is also $C_2\left(C2sp^3HO\ to\ \mathrm{S}\right)=0.64965$. In order to match $E_T\left(atom-atom,msp^3.AO\right)$ of the $C-S$ group ($-0.72457\ eV$ (Eq. (14.151))), $E_T\left(atom-atom,msp^3.AO\right)$ of the $S-S$-bond MO is determined using a linear combination of the AOs corresponding to $-0.72457\ eV$ and $0\ eV$ in Eq. (15.29), Eq. (15.31), and Eqs. (15.19-15.20). The result corresponding to bond order 1/2I in Table 15.2 is $E_T\left(atom-atom,msp^3.AO\right)=-0.36229\ eV$.

The symbols of the functional groups of branched-chain alkyl disulfides are given in Table 15.159. The geometrical (Eqs. (15.1-15.5) and (15.51)), intercept (Eqs. (15.80-15.87)), and energy (Eqs. (15.6-15.11) and (15.17-15.65)) parameters of alkyl disulfides are given in Tables 15.160, 15.161, and 15.162, respectively. The total energy of each alkyl disulfide given in Table 15.163 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.162 corresponding to functional-group composition of the molecule. $E_{mag}$ given by Eq. (15.67) was subtracted for each t-butyl group. The bond angle parameters of alkyl disulfides determined using Eqs. (15.88-15.117) are given in Table 15.164. The color scale, translucent view of the charge-density of exemplary disulfide, dimethyl disulfide, comprising the concentric shells of atoms with the outer shell bridged by one or more $H_2$-type ellipsoidal MOs or joined with one or more hydrogen MOs is shown in Figure 15.27.

Figure 15.27. Color scale, translucent view of the charge-density of dimethyl disulfide showing the orbitals of the atoms at their radii, the ellipsoidal surface of each $H$ or $H_2$-type ellipsoidal MO that transitions to the corresponding outer shell of the atom(s) participating in each bond, and the hydrogen nuclei (red, not to scale).

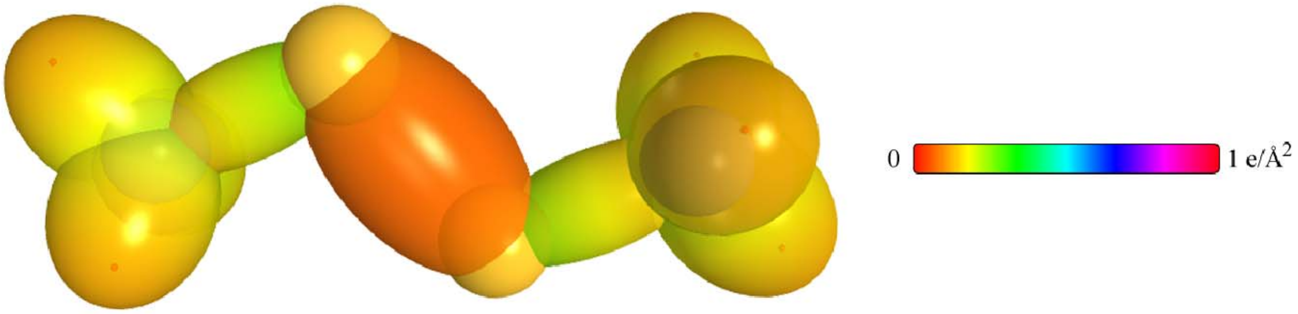


Table 15.159. The symbols of functional groups of alkyl disulfides.

| Functional Group | Group Symbol |
|---|---|
| *C-S* | $C-S$ |
| *S-S* | $S-S$ |
| $CH_3$ group | $C-H\ (CH_3)$ |
| $CH_2$ group | $C-H\ (CH_2)$ |
| *CH* | $C-H$ |
| *CC* bond (*n-C*) | $C-C$ (a) |
| *CC* bond (*iso-C*) | $C-C$ (b) |
| *CC* bond (*tert-C*) | $C-C$ (c) |
| *CC* (*iso* to *iso-C*) | $C-C$ (d) |
| *CC* (*t* to *t-C*) | $C-C$ (e) |
| *CC* (*t* to *iso-C*) | $C-C$ (f) |

Table 15.160. The geometrical bond parameters of alkyl disulfides and experimental values [1].

| Parameter | $C-S$ (i) Group | $S-S$ Group | $C-H\left(CH_3\right)$ Group | $C-H\left(CH_2\right)$ Group | $C-H$ Group | $C-C$ (a) Group | $C-C$ (b) Group | $C-C$ (c) Group | $C-C$ (d) Group | $C-C$ (e) Group | $C-C$ (f) Group |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $a\left(a_0\right)$ | 1.90975 | 2.37173 | 1.64920 | 1.67122 | 1.67465 | 2.12499 | 2.12499 | 2.10725 | 2.12499 | 2.10725 | 2.10725 |
| $c'\left(a_0\right)$ | 1.71455 | 1.91070 | 1.04856 | 1.05553 | 1.05661 | 1.45744 | 1.45744 | 1.45164 | 1.45744 | 1.45164 | 1.45164 |
| Bond Length $2c'$ $\left(\mathring{A}\right)$ | 1.81460 | 2.02220 | 1.10974 | 1.11713 | 1.11827 | 1.54280 | 1.54280 | 1.53635 | 1.54280 | 1.53635 | 1.53635 |
| Exp. Bond Length $\left(\mathring{A}\right)$ | 1.816<br>(dimethyl disulfide) | 2.029<br>(dimethyl disulfide) | 1.107<br>($C-H$ propane)<br>1.117<br>($C-H$ butane) | 1.107<br>($C-H$ propane)<br>1.117<br>($C-H$ butane) | 1.122<br>(isobutane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) |
| $b,c\left(a_0\right)$ | 0.84112 | 1.40510 | 1.27295 | 1.29569 | 1.29924 | 1.54616 | 1.54616 | 1.52750 | 1.54616 | 1.52750 | 1.52750 |
| $e$ | 0.89778 | 0.80562 | 0.63580 | 0.63159 | 0.63095 | 0.68600 | 0.68600 | 0.68888 | 0.68600 | 0.68888 | 0.68888 |

Table 15.161. The MO to HO intercept geometrical bond parameters of alkyl disulfides. $R$, $R'$, $R''$ are $H$ or alkyl groups. $E_T$ is $E_T(atom-atom, msp^3.AO)$.

| Bond | Atom | $E_T$ (eV) Bond 1 | $E_T$ (eV) Bond 2 | $E_T$ (eV) Bond 3 | $E_T$ (eV) Bond 4 | Final Total Energy $C2sp^3$ (eV) | $r_{initial}$ $\left(a_0\right)$ | $r_{final}$ $\left(a_0\right)$ | $E_{Coulomb}$ (eV) Final | $E\left(C2sp^3\right)$ (eV) Final | $\theta'$ $\left(^\circ\right)$ | $\theta_1$ $\left(^\circ\right)$ | $\theta_2$ $\left(^\circ\right)$ | $d_1$ $\left(a_0\right)$ | $d_2$ $\left(a_0\right)$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $RS-SR$<br>($C-S$ (i) and (ii)) | $S$ | -0.36229 | -0.18114 | 0 | 0 |  | 1.32010 | 0.88527 | -15.36918 |  | 94.25 | 85.75 | 38.93 | 1.84513 | 0.06558 |
| $H_3C_a-SS-C_bH_2CH_2R$ | $C_a$ | -0.36229 | 0 | 0 | 0 | -151.97798 | 0.91771 | 0.89582 | -15.18804 | -14.99717 | 130.79 | 49.21 | 53.75 | 1.12937 | 0.58518 |
| $H_3C_a-SS-C_bH_2CH_2R$<br>($C-S$ (i)) | $C_b$ | -0.36229 | -0.92918 | 0 | 0 | -152.90716 | 0.91771 | 0.84418 | -16.11722 | -15.92636 | 128.69 | 51.31 | 51.57 | 1.18689 | 0.52765 |
|  | $C_c$ | -0.36229 | -0.72457 | -0.72457 | -0.72457 | -154.15170 | 0.91771 | 0.78367 | -17.36176 | -17.17090 | 125.97 | 54.03 | 48.94 | 1.25430 | 0.46025 |
| $C-H\left(CH_3\right)$ | $C$ | -0.92918 | 0 | 0 | 0 | -152.54487 | 0.91771 | 0.86359 | -15.75493 | -15.56407 | 77.49 | 102.51 | 41.48 | 1.23564 | 0.18708 |
| $C-H\left(CH_2\right)$ | $C$ | -0.92918 | -0.92918 | 0 | 0 | -153.47406 | 0.91771 | 0.81549 | -16.68412 | -16.49325 | 68.47 | 111.53 | 35.84 | 1.35486 | 0.29933 |
| $C-H\left(CH\right)$ | $C$ | -0.92918 | -0.92918 | -0.92918 | 0 | -154.40324 | 0.91771 | 0.77247 | -17.61330 | -17.42244 | 61.10 | 118.90 | 31.37 | 1.42988 | 0.37326 |
| $H_3C_aC_bH_2CH_2-$<br>($C-C$ (a)) | $C_a$ | -0.92918 | 0 | 0 | 0 | -152.54487 | 0.91771 | 0.86359 | -15.75493 | -15.56407 | 63.82 | 116.18 | 30.08 | 1.83879 | 0.38106 |
| $H_3C_aC_bH_2CH_2-$<br>($C-C$ (a)) | $C_b$ | -0.92918 | -0.92918 | 0 | 0 | -153.47406 | 0.91771 | 0.81549 | -16.68412 | -16.49325 | 56.41 | 123.59 | 26.06 | 1.90890 | 0.45117 |
| $R-H_2C_aC_b\left(H_2C_c-R'\right)HCH_2-$<br>($C-C$ (b)) | $C_b$ | -0.92918 | -0.92918 | -0.92918 | 0 | -154.40324 | 0.91771 | 0.77247 | -17.61330 | -17.42244 | 48.30 | 131.70 | 21.90 | 1.97162 | 0.51388 |
| $R-H_2C_a\left(R'-H_2C_d\right)C_b\left(R''-H_2C_c\right)CH_2-$<br>($C-C$ (c)) | $C_b$ | -0.92918 | -0.72457 | -0.72457 | -0.72457 | -154.71860 | 0.91771 | 0.75889 | -17.92866 | -17.73779 | 48.21 | 131.79 | 21.74 | 1.95734 | 0.50570 |
| $isoC_aC_b\left(H_2C_c-R'\right)HCH_2-$<br>($C-C$ (d)) | $C_b$ | -0.92918 | -0.92918 | -0.92918 | 0 | -154.40324 | 0.91771 | 0.77247 | -17.61330 | -17.42244 | 48.30 | 131.70 | 21.90 | 1.97162 | 0.51388 |
| $tertC_a\left(R'-H_2C_d\right)C_b\left(R''-H_2C_c\right)CH_2-$<br>($C-C$ (e)) | $C_b$ | -0.72457 | -0.72457 | -0.72457 | -0.72457 | -154.51399 | 0.91771 | 0.76765 | -17.92866 | -17.73779 | 50.04 | 129.96 | 22.66 | 1.94462 | 0.49298 |
| $tertC_aC_b\left(H_2C_c-R'\right)HCH_2-$<br>($C-C$ (f)) | $C_b$ | -0.72457 | -0.92918 | -0.92918 | 0 | -154.19863 | 0.91771 | 0.78155 | -17.40869 | -17.21783 | 52.78 | 127.22 | 24.04 | 1.92443 | 0.47279 |
| $isoC_a\left(R'-H_2C_d\right)C_b\left(R''-H_2C_c\right)CH_2-$<br>($C-C$ (f)) | $C_b$ | -0.72457 | -0.72457 | -0.72457 | -0.72457 | -154.51399 | 0.91771 | 0.76765 | -17.92866 | -17.73779 | 50.04 | 129.96 | 22.66 | 1.94462 | 0.49298 |

Table 15.162. The energy parameters ($eV$) of functional groups of alkyl disulfides.

| Parameters | $C-S$ (i) Group | $S-S$ Group | $CH_3$ Group | $CH_2$ Group | $C-H$ Group | $C-C$ (a) Group | $C-C$ (b) Group | $C-C$ (c) Group | $C-C$ (d) Group | $C-C$ (e) Group | $C-C$ (f) Group |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $n_1$ | 1 | 1 | 3 | 2 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $n_2$ | 0 | 0 | 2 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $n_3$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $C_1$ | 0.5 | 0.5 | 0.75 | 0.75 | 0.75 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| $C_2$ | 0.64965 | 0.64965 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $c_1$ | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $c_2$ | 1 | 1 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 |
| $c_3$ | 0 | 0 | 0 | 1 | 1 | 0 | 0 | 0 | 1 | 1 | 0 |
| $c_4$ | 2 | 2 | 1 | 1 | 1 | 2 | 2 | 2 | 2 | 2 | 2 |
| $c_5$ | 0 | 0 | 3 | 2 | 1 | 0 | 0 | 0 | 0 | 0 | 0 |
| $C_{1o}$ | 0.5 | 0.5 | 0.75 | 0.75 | 0.75 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| $C_{2o}$ | 0.64965 | 0.64965 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $V_e\ (eV)$ | -46.36495 | -31.74215 | -107.32728 | -70.41425 | -35.12015 | -28.79214 | -28.79214 | -29.10112 | -28.79214 | -29.10112 | -29.10112 |
| $V_p\ (eV)$ | 7.93551 | 7.12083 | 38.92728 | 25.78002 | 12.87680 | 9.33352 | 9.33352 | 9.37273 | 9.33352 | 9.37273 | 9.37273 |
| $T\ (eV)$ | 12.13899 | 6.69177 | 32.53914 | 21.06675 | 10.48582 | 6.77464 | 6.77464 | 6.90500 | 6.77464 | 6.90500 | 6.90500 |
| $V_m\ (eV)$ | -6.06949 | -3.34589 | -16.26957 | -10.53337 | -5.24291 | -3.38732 | -3.38732 | -3.45250 | -3.38732 | -3.45250 | -3.45250 |
| $E(_{AO/HO})\ (eV)$ | 0 | -10.36001 | -15.56407 | -15.56407 | -14.63489 | -15.56407 | -15.56407 | -15.35946 | -15.56407 | -15.35946 | -15.35946 |
| $\Delta E_{H_2MO}(_{AO/HO})\ (eV)$ | -0.72457 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $E_T(_{AO/HO})\ (eV)$ | 0.72457 | -10.36001 | -15.56407 | -15.56407 | -14.63489 | -15.56407 | -15.56407 | -15.35946 | -15.56407 | -15.35946 | -15.35946 |
| $E_T(_{H_2MO})\ (eV)$ | -31.63537 | -31.63544 | -67.69451 | -49.66493 | -31.63533 | -31.63537 | -31.63537 | -31.63535 | -31.63537 | -31.63535 | -31.63535 |
| $E_T\left(atom-atom,msp^3.AO\right)(eV)$ | -0.72457 | -0.36229 | 0 | 0 | 0 | -1.85836 | -1.85836 | -1.44915 | -1.85836 | -1.44915 | -1.44915 |
| $E_T(_{MO})\ (eV)$ | -32.35994 | -31.99766 | -67.69450 | -49.66493 | -31.63537 | -33.49373 | -33.49373 | -33.08452 | -33.49373 | -33.08452 | -33.08452 |
| $\omega\ \left(10^{15}\ rad/s\right)$ | 30.5436 | 6.45076 | 24.9286 | 24.2751 | 24.1759 | 9.43699 | 9.43699 | 15.4846 | 9.43699 | 9.55643 | 9.55643 |
| $E_K\ (eV)$ | 20.10434 | 4.24600 | 16.40846 | 15.97831 | 15.91299 | 6.21159 | 6.21159 | 10.19220 | 6.21159 | 6.29021 | 6.29021 |
| $\bar{E}_D\ (eV)$ | -0.28705 | -0.13044 | -0.25352 | -0.25017 | -0.24966 | -0.16515 | -0.16515 | -0.20896 | -0.16515 | -0.16416 | -0.16416 |
| $\bar{E}_{Kvib}\ (eV)$ | 0.08146<br>[41] | 0.06745<br>[] | 0.35532<br>(Eq. (13.458)) | 0.35532<br>(Eq. (13.458)) | 0.35532<br>(Eq. (13.458)) | 0.12312<br>[2] | 0.17978<br>[4] | 0.09944<br>[5] | 0.12312<br>[2] | 0.12312<br>[2] | 0.12312<br>[2] |
| $\bar{E}_{osc}\ (eV)$ | -0.24632 | -0.09672 | -0.22757 | -0.14502 | -0.07200 | -0.10359 | -0.07526 | -0.15924 | -0.10359 | -0.10260 | -0.10260 |
| $E_{mag}\ (eV)$ | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 |
| $E_T(_{Group})\ (eV)$ | -32.60626 | -32.09437 | -67.92207 | -49.80996 | -31.70737 | -33.59732 | -33.49373 | -33.24376 | -33.59732 | -33.18712 | -33.18712 |
| $E_{initial}(_{c_4\ AO/HO})\ (eV)$ | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 |
| $E_{initial}(_{c_5\ AO/HO})\ (eV)$ | 0 | 0 | -13.59844 | -13.59844 | -13.59844 | 0 | 0 | 0 | 0 | 0 | 0 |
| $E_D(_{Group})\ (eV)$ | 3.33648 | 2.82459 | 12.49186 | 7.83016 | 3.32601 | 4.32754 | 4.29921 | 3.97398 | 4.17951 | 3.62128 | 3.91734 |

Table 15.163. The total bond energies of alkyl disulfides calculated using the functional group composition and the energies of Table 15.162 compared to the experimental values [3]. The magnetic energy $E_{mag}$ that is subtracted from the weighted sum of the $E_D$ $(_{Group})$ $(eV)$ values based on composition is given by (15.58).

| Formula | Name | $C-S$ Group | $S-S$ Group | $CH_3$ | $CH_2$ | $CH$ | $C-C$ (a) | $C-C$ (b) | $C-C$ (c) | $C-C$ (d) | $C-C$ (e) | $C-C$ (f) | $E_{mag}$ | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $C_2H_6S_2$ | Dimethyl disulfide | 2 | 1 | 2 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 34.48127 | 34.413 | -0.00199 |
| $C_4H_{10}S_2$ | Diethyl disulfide | 2 | 1 | 2 | 2 | 0 | 2 | 0 | 0 | 0 | 0 | 0 | 0 | 58.79667 | 58.873 | 0.00129 |
| $C_6H_{14}S_2$ | Dipropyl disulfide | 2 | 1 | 2 | 4 | 0 | 4 | 0 | 0 | 0 | 0 | 0 | 0 | 83.11207 | 83.169 | 0.00068 |
| $C_8H_{18}S_2$ | Di-t-butyl disulfide | 2 | 1 | 6 | 0 | 0 | 0 | 0 | 6 | 0 | 0 | 0 | -2 | 107.99653 | 107.919 | -0.00072 |

Table 15.164. The bond angle parameters of alkyl disulfides and experimental values [1]. In the calculation of $\theta_v$, the parameters from the preceding angle were used. $E_T$ is $E_T(atom-atom,msp^3.AO)$.

| Atoms of Angle | 2c' Bond 1 ($a_0$) | 2c' Bond 2 ($a_0$) | 2c' Terminal Atoms ($a_0$) | $E_{Coulombic}$ Atom 1 | Atom 1 Hybridization Designation (Table 15.3.A) | $E_{Coulombic}$ Atom 2 | Atom 2 Hybridization Designation (Table 15.3.A) | $c_2$ Atom 1 | $c_2$ Atom 2 | $C_1$ | $C_2$ | $c_1$ | $c_2'$ | $E_T$ (eV) | $\theta_v$ (°) | $\theta_1$ (°) | $\theta_2$ (°) | Cal. $\theta$ (°) | Exp. $\theta$ (°) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $\angle HC_aH$ | 2.09711 | 2.09711 | 3.4252 | -15.75493 | 7 | H | H | 0.86359 | 1 | 1 | 1 | 0.75 | 1.15796 | 0 | | | | 109.50 | |
| $\angle SC_aH$ | | | | | | | | | | | | | | | 70.56 | | | 109.44 | 111.3 (dimethyl disulfide) |
| $\angle HC_aS$ | 2.09711 | 3.42910 | 4.6220 | -15.55033 $C_a$ | 5 | -10.36001 $S$ | S | 0.87495 | 0.76144 (Eq. (15.145)) | 0.75 | 0.76144 (Eq. 15.145)) | 0.75 | 0.87026 | 0 | | | | 111.22 | 111.3 (dimethyl disulfide) |
| $\angle SSC_a$ | 3.82141 | 3.42910 | 5.7017 | -10.36001 $S$ | S | -14.82575 $C_a$ | 1 | 0.64965 (Eq. (15.146)) | 0.91771 | 1 | 0.64965 (Eq. (15.146)) | 1 | 0.78368 | -0.72457 | | | | 103.57 | 103.2 (dimethyl disulfide) |
| Methylene $\angle HC_aH$ | 2.11106 | 2.11106 | 3.4252 | -15.75493 | 7 | H | H | 0.86359 | 1 | 1 | 1 | 0.75 | 1.15796 | 0 | | | | 108.44 | 107 (propane) |
| $\angle C_aC_bC_c$ | | | | | | | | | | | | | | | 69.51 | | | 110.49 | 112 (propane)<br>113.8 (butane)<br>110.8 (isobutane) |
| $\angle C_aC_bH$ | | | | | | | | | | | | | | | 69.51 | | | 110.49 | 111.0 (butane)<br>111.4 (isobutane) |
| Methyl $\angle HC_aH$ | 2.09711 | 2.09711 | 3.4252 | -15.75493 | 7 | H | H | 0.86359 | 1 | 1 | 1 | 0.75 | 1.15796 | 0 | | | | 109.50 | |
| $\angle C_aC_bC_c$ | | | | | | | | | | | | | | | 70.56 | | | 109.44 | |
| $\angle C_aC_bH$ | | | | | | | | | | | | | | | 70.56 | | | 109.44 | |
| $\angle C_bC_aC_c$ iso $C_a$ | 2.91547 | 2.91547 | 4.7958 | -16.68412 $C_b$ | 26 | -16.68412 $C_c$ | 26 | 0.81549 | 0.81549 | 1 | 1 | 1 | 0.81549 | -1.85836 | | | | 110.67 | 110.8 (isobutane) |
| $\angle C_bC_aH$ iso $C_a$ | 2.91547 | 2.11323 | 4.1633 | -15.55033 $C_a$ | 5 | -14.82575 $C_b$ | 1 | 0.87495 | 0.91771 | 0.75 | 1 | 0.75 | 1.04887 | 0 | | | | 110.76 | |
| $\angle C_aC_bH$ iso $C_a$ | 2.91547 | 2.09711 | 4.1633 | -15.55033 $C_b$ | 5 | -14.82575 $C_a$ | 1 | 0.87495 | 0.91771 | 0.75 | 1 | 0.75 | 1.04887 | 0 | | | | 111.27 | 111.4 (isobutane) |
| $\angle C_bC_aC_b$ tert $C_a$ | 2.90327 | 2.90327 | 4.7958 | -16.68412 $C_b$ | 26 | -16.68412 $C_b$ | 26 | 0.81549 | 0.81549 | 1 | 1 | 1 | 0.81549 | -1.85836 | | | | 111.37 | 110.8 (isobutane) |
| $\angle C_bC_aC_d$ | | | | | | | | | | | | | | | 72.50 | | | 107.50 | |

## SULFOXIDES ($C_nH_{2n+2}\left(SO\right)_m$, $n=2,3,4,5...\infty$)

The alkyl sulfoxides, $C_nH_{2n+2}\left(SO\right)_m$, comprise a $C-SO-C$ moiety that comprises $C-S$ and $SO$ functional groups. The alkyl portion of the alkyl sulfoxide may comprise at least two terminal methyl groups ($CH_3$) at each end of the chain, and may comprise methylene ($CH_2$), and methylyne ($CH$) functional groups as well as $C$ bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($\left(CH_3\right)_2CH$) and t-butyl ($\left(CH_3\right)_3C$) groups and the isop.ropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups. The branched-chain-alkane groups in sulfoxides are equivalent to those in branched-chain alkanes.

The electron configuration of oxygen is $1s^22s^22p^4$, and the orbital arrangement given by Eq. (10.154) has two unpaired electrons corresponding to the ground state ${}^3P_2$. The $SO$ functional group comprises a double bond between the two unpaired electrons of $O$. The sulfur atom is energy matched to the $C2sp^3$ HO. In alkyl sulfoxides, the $C2sp^3$ HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of $E\left(C,2sp^3\right)=-14.63489\ eV$ (Eq. (15.25)), and the $S$ AO has an initial energy of $E\left(S\right)=-10.36001\ eV$ [38]. To meet the equipotential condition of the union of the $S=O$ $H_2$-type-ellipsoidal-MO with these orbitals, the hybridization factor $c_2$ of Eq. (15.61) for the $S=O$-bond MO given by Eqs. (15.77) and (15.79) is:

$$c_2\left(O\ to\ S3sp^3\ to\ C2sp^3HO\right)=\frac{E\left(O\right)}{E\left(S\right)}c_2\left(C2sp^3HO\right)=\frac{-13.61806\ eV}{-10.36001\ eV}\left(0.91771\right)=1.20632 \tag{15.147}$$

The $S$ atom also forms a single bond with each of the $C2sp^3$ HOs of the two $C-S$ groups. The formation of these bonds is permitted by the hybridization of the four electrons of the $S3p$ shell to give the orbital arrangement:

$$\begin{array}{cccc} \multicolumn{4}{l}{3\mathrm{sp}^3\ \text{state}} \\ \underline{\ \uparrow\ } & \underline{\ \uparrow\ } & \underline{\ \uparrow\ } & \underline{\ \uparrow\ } \\ 0,0 & 1,-1 & 1,0 & 1,1 \end{array} \tag{15.148}$$

where the quantum numbers ($\ell,m_\ell$) are below each electron. The $3s$ shell remains unchanged. Then, the Coulombic energy $E_{Coulomb}\left(S,3sp^3\right)$ of the outer electron of the $S3sp^3$ shell given by Eq. (15.137) with $r_{3sp^3}=1.17585a_0$ (Eq. (15.138)) is $-11.57099\ eV$. Using Eq. (15.16) with the radius of the sulfur atom $r_{16}=1.32010a_0$ given by Eq. (10.341), the energy $E\left(S3sp^3\right)$ of the outer electron of the $S3sp^3$ shell is given by the sum of $E_{Coulomb}\left(S3sp^3\right)$ and $E(magnetic)$:

$$\begin{aligned} E\left(S3sp^3\right) &= \frac{-e^2}{8\pi\varepsilon_0 r_{3sp^3}}+\frac{2\pi\mu_0e^2\hbar^2}{m_e^2r_{16}^3}=\frac{-e^2}{8\pi\varepsilon_0 1.17585a_0}+\frac{2\pi\mu_0e^2\hbar^2}{m_e^2\left(1.32010a_0\right)^3} \\ &= -11.57099\ eV+0.04973=-11.52126\ eV \end{aligned} \tag{15.149}$$

Then, the hybridization energy $E_{hybridization}\left(S3sp^3\right)$ of the $S3sp^3$ HO is

$$E_{hybridization}\left(S3sp^3\right)=E\left(S3sp^3\right)-E\left(S\right)=-11.52126\ eV-10.36001\ eV=-1.16125\ eV \tag{15.150}$$

The $SO$ group is matched to the $C-S$ group with which it shares the common hybridized $S$ atom. Consequently, $E_{hybridization}\left(S3sp^3\right)$ is subtracted from $E_T\left(Group\right)$ in the determination of $E_D\left(Group\right)$ (Eq. (15.65)). Furthermore, the energy of the $S=O$-bond MO is the sum of the component energies of the $H_2$-type ellipsoidal MO given in Eq. (15.51) with the energy matched to the final energy of the hybridized $S$ atom such that $E\left(AO/HO\right)=E\left(S3sp^3\right)=-11.52126\ eV$ and $\Delta E_{H_2MO}$ $\left(AO/HO\right)=E_{hybridization}\left(S3sp^3\right)=-1.16125\ eV$. Then, $E_T\left(AO/HO\right)=E\left(S\right)=-10.36001\ eV$. Also, $E_T\left(atom-atom,msp^3.AO\right)$ of the $S=O$ bond is zero since there are no bonds with a $C2sp^3$ HO.

The $C-S$ group is solved as an energy minimum by hybridizing the $2s$ and $2p$ AOs of the $C$ atom to form a single $2sp^3$ shell and by hybridizing the four $S3p$ electrons to form a $S3sp^3$ shell, and the sharing of electrons between the $C2sp^3$ HO and the $S3sp^3$ HO to form a MO permits each participating orbital to decrease in radius and energy. Using the Coulombic energy of the $S3sp^3$ shell, $E_{Coulomb}\left(S3sp^3\right)$ given by Eq. (15.139) in Eq. (15.72), the $S3sp^3$-shell hybridization factor, $c_2\left(S3sp^3\right)$, is:

$$c_2\left(S3sp^3\right)=\frac{E_{Coulomb}\left(S3sp^3\right)}{E\left(H\right)}=\frac{-11.57099\ eV}{-13.60580\ eV}=0.85045 \tag{15.151}$$

As in the case of thiols, sulfides, and disulfides, the energy of sulfur is less than the Coulombic energy between the electron and proton of $H$ given by Eq. (1.264). Thus, $c_1$ and $c_2$ are equal to one in Eq. (15.61), and the energy matching condition is determined by the $C_2$ parameter. In alkyl sulfoxides, the $C2sp^3$ HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of $E\left(C,2sp^3\right)=-14.63489\ eV$ (Eq. (15.25)) and the $S3sp^3$ HO has an energy of $E\left(S3sp^3\right)=-11.52126\ eV$ (Eq. (15.149)). To meet the equipotential condition of the union of the $C-S$ $H_2$-type-ellipsoidal-MO with these orbitals, the hybridization factor $C_2$ of Eq. (15.61) for the $C-S$-bond MO given by Eqs. (15.77) and (15.79) is:

$$C_2\left(C2sp^3HO\ to\ S3sp^3\right)=\frac{E\left(S3sp^3\right)}{E\left(C,2sp^3\right)}c_2\left(S3sp^3\right)=\frac{-11.52126\ eV}{-14.63489\ eV}(0.85045)=0.66951 \tag{15.152}$$

As in the case of thiols, sulfides, and disulfides, with the energy of $S$ matched to the Coulombic energy between the electron and proton of $H$, the energy of the $C-S$-bond MO is the sum of the component energies of the $H_2$-type ellipsoidal MO given in Eq. (15.51) with $E(_{AO/HO})=0$ and $E_T\left(AO/HO\right)=\Delta E_{H_2MO}\left(AO/HO\right)$. For sulfoxides, $\Delta E_{H_2MO}\left(AO/HO\right)=-0.72457\ eV$. Further equivalently, $E_T\left(atom-atom,msp^3.AO\right)=-0.72457\ eV$ (Eq. (14.151)).

The symbols of the functional groups of branched-chain alkyl sulfoxides are given in Table 15.165. The geometrical (Eqs. (15.1-15.5) and (15.51)), intercept (Eqs. (15.80-15.87)), and energy (Eqs. (15.6-15.11) and (15.17-15.65)) parameters of alkyl sulfoxides are given in Tables 15.166, 15.167, and 15.168, respectively. Consider that the $C-S$ bond is along the x axis in the xy-plane. The $S$ nucleus is at the focus +c and the $C$ nucleus is at the focus –c. The elliptic angle $\theta'$ is taken as counterclockwise from the x-axis for $S$ and as clockwise from the –x-axis for $C$. The total energy of each alkyl sulfoxide given in Table 15.169 was calculated as the sum over the integer multiple of each $E_D(_{Group})$ of Table 15.168 corresponding to functional-group composition of the molecule. The bond angle parameters of alkyl sulfoxides determined using Eqs. (15.88-15.117) are given in Table 15.170. The color scale, translucent view of the charge-density of exemplary sulfoxide, dimethyl sulfoxide, comprising the concentric shells of atoms with the outer shell bridged by one or more $H_2$-type ellipsoidal MOs or joined with one or more hydrogen MOs is shown in Figure 15.28.

Figure 15.28. (A)-(B) Color scale, translucent views of the charge-density of dimethyl sulfoxide showing the orbitals of the atoms at their radii, the ellipsoidal surface of each $H$ or $H_2$-type ellipsoidal MO that transitions to the corresponding outer shell of the atom(s) participating in each bond, and the hydrogen nuclei (red, not to scale).

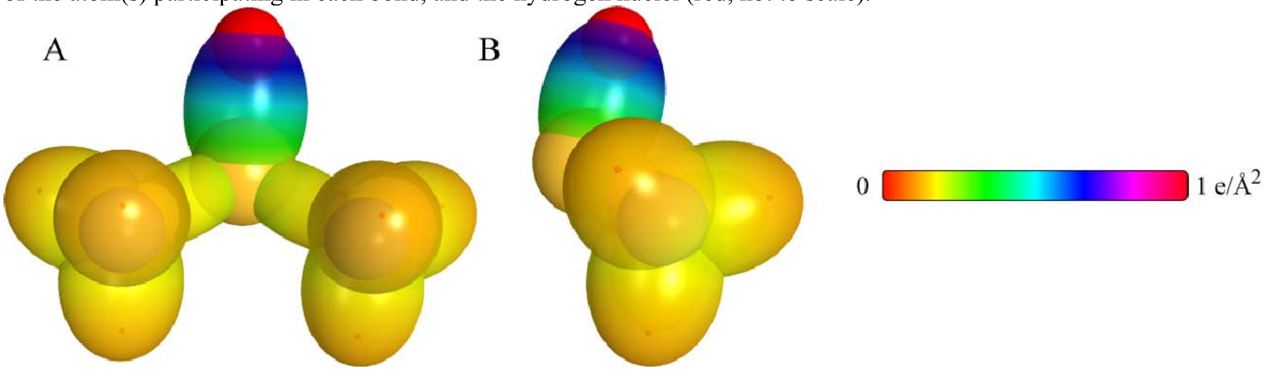


Table 15.165. The symbols of functional groups of alkyl sulfoxides.

| Functional Group | Group Symbol |
|---|---|
| *C-S* | $C-S$ |
| *SO* | $SO$ |
| $CH_3$ group | $C-H\ \left(CH_3\right)$ |
| $CH_2$ group | $C-H\ \left(CH_2\right)$ |
| *CH* | $C-H$ |
| *CC* bond (*n-C*) | $C-C$ (a) |
| *CC* bond (*iso-C*) | $C-C$ (b) |
| *CC* bond (*tert-C*) | $C-C$ (c) |
| *CC* (*iso* to *iso-C*) | $C-C$ (d) |
| *CC* (*t* to *t-C*) | $C-C$ (e) |
| *CC* (*t* to *iso-C*) | $C-C$ (f) |

Table 15.166. The geometrical bond parameters of alkyl sulfoxides and experimental values [1].

| Parameter | $C-S$ Group | $SO$ Group | $C-H\ (CH_3)$ Group | $C-H\ (CH_2)$ Group | $C-H$ Group | $C-C$ (a) Group | $C-C$ (b) Group | $C-C$ (c) Group | $C-C$ (d) Group | $C-C$ (e) Group | $C-C$ (f) Group |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $a\ (a_0)$ | 1.87325 | 1.98517 | 1.64920 | 1.67122 | 1.67465 | 2.12499 | 2.12499 | 2.10725 | 2.12499 | 2.10725 | 2.10725 |
| $c'\ (a_0)$ | 1.67271 | 1.40896 | 1.04856 | 1.05553 | 1.05661 | 1.45744 | 1.45744 | 1.45164 | 1.45744 | 1.45164 | 1.45164 |
| Bond Length $2c'$ ($\AA$) | 1.77031 | 1.49118 | 1.10974 | 1.11713 | 1.11827 | 1.54280 | 1.54280 | 1.53635 | 1.54280 | 1.53635 | 1.53635 |
| Exp. Bond Length ($\AA$) | 1.799<br>(dimethyl sulfoxide) | 1.485<br>(dimethyl sulfoxide) | 1.107<br>($C-H$ propane)<br>1.117<br>($C-H$ butane) | 1.107<br>($C-H$ propane)<br>1.117<br>($C-H$ butane) | 1.122<br>(isobutane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) |
| $b,c\ (a_0)$ | 0.84328 | 1.39847 | 1.27295 | 1.29569 | 1.29924 | 1.54616 | 1.54616 | 1.52750 | 1.54616 | 1.52750 | 1.52750 |
| $e$ | 0.89294 | 0.70974 | 0.63580 | 0.63159 | 0.63095 | 0.68600 | 0.68600 | 0.68888 | 0.68600 | 0.68888 | 0.68888 |

Table 15.167. The MO to HO intercept geometrical bond parameters of alkyl sulfoxides. $R$, $R'$, $R''$ are $H$ or alkyl groups. $E_T$ is $E_T(atom-atom,msp^3.AO)$.

| Bond | Atom | $E_T$ (eV) Bond 1 | $E_T$ (eV) Bond 2 | $E_T$ (eV) Bond 3 | $E_T$ (eV) Bond 4 | Final Total Energy $C2sp^3$ (eV) | $r_{initial}$ $(a_0)$ | $r_{final}$ $(a_0)$ | $E_{Coulomb}$ (eV) Final | $E(C2sp^3)$ (eV) Final | $\theta'$ (°) | $\theta_1$ (°) | $\theta_2$ (°) | $d_1$ $(a_0)$ | $d_2$ $(a_0)$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $R_2S=O$ | $S$ | 0 | -0.36229 | -0.36229 | 0 | | 1.32010 | 0.87495 | -15.55033 | | 79.78 | 100.22 | 38.00 | 1.56425 | 0.15529 |
| $R_2S=O$ | $O$ | 0 | 0 | 0 | 0 | | 1.00000 | 0.91771 | -14.82575 | | 84.06 | 95.94 | 40.75 | 1.50400 | 0.09504 |
| $R_2-SO$ | $S$ | -0.36229 | -0.36229 | 0 | 0 | | 1.32010 | 0.87495 | -15.55033 | | 129.35 | 50.65 | 53.36 | 1.11799 | 0.55472 |
| $H_3C_a-S(O)-C_bH_2CH_2R$ | $C_a$ | -0.36229 | 0 | 0 | 0 | -151.97798 | 0.91771 | 0.89582 | -15.18804 | -14.99717 | 130.19 | 49.81 | 54.24 | 1.09461 | 0.57809 |
| $H_3C_a-S(O)-C_bH_2CH_2R$ | $C_b$ | -0.36229 | -0.92918 | 0 | 0 | -152.90716 | 0.91771 | 0.84418 | -16.11722 | -15.92636 | 128.05 | 51.95 | 52.03 | 1.15245 | 0.52026 |
| $C-H\ (CH_3)$ | $C$ | -0.92918 | 0 | 0 | 0 | -152.54487 | 0.91771 | 0.86359 | -15.75493 | -15.56407 | 77.49 | 102.51 | 41.48 | 1.23564 | 0.18708 |
| $C-H\ (CH_2)$ | $C$ | -0.92918 | -0.92918 | 0 | 0 | -153.47406 | 0.91771 | 0.81549 | -16.68412 | -16.49325 | 68.47 | 111.53 | 35.84 | 1.35486 | 0.29933 |
| $C-H\ (CH)$ | $C$ | -0.92918 | -0.92918 | -0.92918 | 0 | -154.40324 | 0.91771 | 0.77247 | -17.61330 | -17.42244 | 61.10 | 118.90 | 31.37 | 1.42988 | 0.37326 |
| $H_3C_aC_bH_2CH_2-$ ($C-C$ (a)) | $C_a$ | -0.92918 | 0 | 0 | 0 | -152.54487 | 0.91771 | 0.86359 | -15.75493 | -15.56407 | 63.82 | 116.18 | 30.08 | 1.83879 | 0.38106 |
| $H_3C_aC_bH_2CH_2-$ ($C-C$ (a)) | $C_b$ | -0.92918 | -0.92918 | 0 | 0 | -153.47406 | 0.91771 | 0.81549 | -16.68412 | -16.49325 | 56.41 | 123.59 | 26.06 | 1.90890 | 0.45117 |
| $R-H_2C_aC_b(H_2C_c-R')HCH_2-$ ($C-C$ (b)) | $C_b$ | -0.92918 | -0.92918 | -0.92918 | 0 | -154.40324 | 0.91771 | 0.77247 | -17.61330 | -17.42244 | 48.30 | 131.70 | 21.90 | 1.97162 | 0.51388 |
| $R-H_2C_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ ($C-C$ (c)) | $C_b$ | -0.92918 | -0.72457 | -0.72457 | -0.72457 | -154.71860 | 0.91771 | 0.75889 | -17.92866 | -17.73779 | 48.21 | 131.79 | 21.74 | 1.95734 | 0.50570 |
| $isoC_aC_b(H_2C_c-R')HCH_2-$ ($C-C$ (d)) | $C_b$ | -0.92918 | -0.92918 | -0.92918 | 0 | -154.40324 | 0.91771 | 0.77247 | -17.61330 | -17.42244 | 48.30 | 131.70 | 21.90 | 1.97162 | 0.51388 |
| $tertC_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ ($C-C$ (e)) | $C_b$ | -0.72457 | -0.72457 | -0.72457 | -0.72457 | -154.51399 | 0.91771 | 0.76765 | -17.92866 | -17.73779 | 50.04 | 129.96 | 22.66 | 1.94462 | 0.49298 |
| $tertC_aC_b(H_2C_c-R')HCH_2-$ ($C-C$ (f)) | $C_b$ | -0.72457 | -0.92918 | -0.92918 | 0 | -154.19863 | 0.91771 | 0.78155 | -17.40869 | -17.21783 | 52.78 | 127.22 | 24.04 | 1.92443 | 0.47279 |
| $isoC_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ ($C-C$ (f)) | $C_b$ | -0.72457 | -0.72457 | -0.72457 | -0.72457 | -154.51399 | 0.91771 | 0.76765 | -17.92866 | -17.73779 | 50.04 | 129.96 | 22.66 | 1.94462 | 0.49298 |

Table 15.168. The energy parameters ($eV$) of functional groups of alkyl sulfoxides.

| Parameters | $C-S$ Group | $SO$ Group | $CH_3$ Group | $CH_2$ Group | $C-H$ Group | $C-C$ (a) Group | $C-C$ (b) Group | $C-C$ (c) Group | $C-C$ (d) Group | $C-C$ (e) Group | $C-C$ (f) Group |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $n_1$ | 1 | 2 | 3 | 2 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $n_2$ | 0 | 0 | 2 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $n_3$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $C_1$ | 0.5 | 0.5 | 0.75 | 0.75 | 0.75 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| $C_2$ | 0.66951 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $c_1$ | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $c_2$ | 1 | 1.20632 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 |
| $c_3$ | 0 | 0 | 0 | 1 | 1 | 0 | 0 | 0 | 1 | 1 | 0 |
| $c_4$ | 2 | 4 | 1 | 1 | 1 | 2 | 2 | 2 | 2 | 2 | 2 |
| $c_5$ | 0 | 1 | 3 | 2 | 1 | 0 | 0 | 0 | 0 | 0 | 0 |
| $C_{1o}$ | 0.5 | 0.5 | 0.75 | 0.75 | 0.75 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| $C_{2o}$ | 0.66951 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $V_e\ (eV)$ | -46.73032 | -82.63003 | -107.32728 | -70.41425 | -35.12015 | -28.79214 | -28.79214 | -29.10112 | -28.79214 | -29.10112 | -29.10112 |
| $V_p\ (eV)$ | 8.13401 | 19.31325 | 38.92728 | 25.78002 | 12.87680 | 9.33352 | 9.33352 | 9.37273 | 9.33352 | 9.37273 | 9.37273 |
| $T\ (eV)$ | 12.47306 | 20.81183 | 32.53914 | 21.06675 | 10.48582 | 6.77464 | 6.77464 | 6.90500 | 6.77464 | 6.90500 | 6.90500 |
| $V_m\ (eV)$ | -6.23653 | -10.40592 | -16.26957 | -10.53337 | -5.24291 | -3.38732 | -3.38732 | -3.45250 | -3.38732 | -3.45250 | -3.45250 |
| $E(_{AO/HO})\ (eV)$ | 0 | -11.52126 | -15.56407 | -15.56407 | -14.63489 | -15.56407 | -15.56407 | -15.35946 | -15.56407 | -15.35946 | -15.35946 |
| $\Delta E_{H_2MO}(_{AO/HO})\ (eV)$ | -0.72457 | -1.16125 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $E_T(_{AO/HO})\ (eV)$ | 0.72457 | -10.36001 | -15.56407 | -15.56407 | -14.63489 | -15.56407 | -15.56407 | -15.35946 | -15.56407 | -15.35946 | -15.35946 |
| $E_T(_{H_2MO})\ (eV)$ | -31.63521 | -63.27088 | -67.69451 | -49.66493 | -31.63533 | -31.63537 | -31.63537 | -31.63535 | -31.63537 | -31.63535 | -31.63535 |
| $E_T\left(atom-atom,msp^3.AO\right)(eV)$ | -0.72457 | 0 | 0 | 0 | 0 | -1.85836 | -1.85836 | -1.44915 | -1.85836 | -1.44915 | -1.44915 |
| $E_T(_{MO})\ (eV)$ | -32.35994 | -63.27074 | -67.69450 | -49.66493 | -31.63537 | -33.49373 | -33.49373 | -33.08452 | -33.49373 | -33.08452 | -33.08452 |
| $\omega\ \left(10^{15}\ rad/s\right)$ | 30.8880 | 17.6762 | 24.9286 | 24.2751 | 24.1759 | 9.43699 | 9.43699 | 15.4846 | 9.43699 | 9.55643 | 9.55643 |
| $E_K\ (eV)$ | 20.33104 | 11.63476 | 16.40846 | 15.97831 | 15.91299 | 6.21159 | 6.21159 | 10.19220 | 6.21159 | 6.29021 | 6.29021 |
| $\bar{E}_D\ (eV)$ | -0.28866 | -0.21348 | -0.25352 | -0.25017 | -0.24966 | -0.16515 | -0.16515 | -0.20896 | -0.16515 | -0.16416 | -0.16416 |
| $\bar{E}_{Kvib}\ (eV)$ | 0.08543<br>[42] | 0.12832<br>[43] | 0.35532<br>(Eq. (13.458)) | 0.35532<br>(Eq. (13.458)) | 0.35532<br>(Eq. (13.458)) | 0.12312<br>[2] | 0.17978<br>[4] | 0.09944<br>[5] | 0.12312<br>[2] | 0.12312<br>[2] | 0.12312<br>[2] |
| $\bar{E}_{osc}\ (eV)$ | -0.24595 | -0.14932 | -0.22757 | -0.14502 | -0.07200 | -0.10359 | -0.07526 | -0.15924 | -0.10359 | -0.10260 | -0.10260 |
| $E_{mag}\ (eV)$ | 0.14803 | 0.11441 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 |
| $E_T(_{Group})\ (eV)$ | -32.60589 | -63.56937 | -67.92207 | -49.80996 | -31.70737 | -33.59732 | -33.49373 | -33.24376 | -33.59732 | -33.18712 | -33.18712 |
| $E_{initial}(_{c_4\ AO/HO})\ (eV)$ | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 |
| $E_{initial}(_{c_5\ AO/HO})\ (eV)$ | 0 | -1.16125 | -13.59844 | -13.59844 | -13.59844 | 0 | 0 | 0 | 0 | 0 | 0 |
| $E_D(_{Group})\ (eV)$ | 3.33611 | 3.86856 | 12.49186 | 7.83016 | 3.32601 | 4.32754 | 4.29921 | 3.97398 | 4.17951 | 3.62128 | 3.91734 |

Table 15.169. The total bond energies of alkyl sulfoxides calculated using the functional group composition and the energies of Table 15.168 compared to the experimental values [3].

| Formula | Name | $C-S$ Group | $SO$ Group | $CH_3$ | $CH_2$ | $CH$ | $C-C$ (a) | $C-C$ (b) | $C-C$ (c) | $C-C$ (d) | $C-C$ (e) | $C-C$ (f) | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $C_2H_6SO$ | Dimethyl sulfoxide | 2 | 1 | 2 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 35.52450 | 35.435 | -0.00253 |
| $C_4H_{10}SO$ | Diethyl sulfoxide | 2 | 1 | 2 | 2 | 0 | 2 | 0 | 0 | 0 | 0 | 0 | 59.83990 | 59.891 | 0.00085 |
| $C_6H_{14}SO$ | Dipropyl sulfoxide | 2 | 1 | 2 | 4 | 0 | 4 | 0 | 0 | 0 | 0 | 0 | 84.15530 | 84.294 | 0.00165 |

Table 15.170. The bond angle parameters of alkyl sulfoxides and experimental values [1]. In the calculation of $\theta_v$, the parameters from the preceding angle were used. $E_T$ is $E_T$ (*atom* – *atom*,*msp*$^3$.*AO*).

| Atoms of Angle | $2c'$ Bond 1 $(a_0)$ | $2c'$ Bond 2 $(a_0)$ | $2c'$ Terminal Atoms $(a_0)$ | $E_{Coulombic}$ Atom 1 | Atom 1 Hybridization Designation (Table 15.3.A) | $E_{Coulombic}$ Atom 2 | Atom 2 Hybridization Designation (Table 15.3.A) | $c_2$ Atom 1 | $c_2$ Atom 2 | $C_1$ | $C_2$ | $c_1$ | $c_2'$ | $E_T$ (eV) | $\theta_v$ (°) | $\theta_1$ (°) | $\theta_2$ (°) | Cal. $\theta$ (°) | Exp. $\theta$ (°) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $\angle C_aSC_a$ | 3.34541 | 3.34541 | 4.9800 | -16.47951 | 22 | -16.47951 | 22 | 0.82562 | 0.82562 | 1 | 1 | 1 | 0.82562 | -1.85836 | | | | 96.20 | 96.6 (dimethyl sulfoxide) |
| $\angle C_aSO$ | 3.34541 | 2.81792 | 4.9598 | -15.18804 $C_a$ | 2 | -13.61806 $O$ | O | 0.89582 | 0.85395 (Eq. (15.133)) | 1 | 1 | 1 | 0.87489 | -1.65376 | | | | 106.88 | 106.7 (dimethyl sulfoxide) |
| Methylene $\angle HC_aH$ | 2.11106 | 2.11106 | 3.4252 | -15.75493 | 7 | H | H | 0.86359 | 1 | 1 | 1 | 0.75 | 1.15796 | 0 | | | | 108.44 | 107 (propane) |
| $\angle C_aC_bC_c$ | | | | | | | | | | | | | | | 69.51 | | | 110.49 | 112 (propane)<br>113.8 (butane)<br>110.8 (isobutane) |
| $\angle C_aC_bH$ | | | | | | | | | | | | | | | 69.51 | | | 110.49 | 111.0 (butane)<br>111.4 (isobutane) |
| Methyl $\angle HC_aH$ | 2.09711 | 2.09711 | 3.4252 | -15.75493 | 7 | H | H | 0.86359 | 1 | 1 | 1 | 0.75 | 1.15796 | 0 | | | | 109.50 | 110.3 (dimethyl sulfoxide) |
| $\angle C_aC_bC_c$ | | | | | | | | | | | | | | | 70.56 | | | 109.44 | |
| $\angle C_aC_bH$ | | | | | | | | | | | | | | | 70.56 | | | 109.44 | |
| $\angle C_bC_aC_c$ iso $C_a$ | 2.91547 | 2.91547 | 4.7958 | -16.68412 $C_b$ | 26 | -16.68412 $C_c$ | 26 | 0.81549 | 0.81549 | 1 | 1 | 1 | 0.81549 | -1.85836 | | | | 110.67 | 110.8 (isobutane) |
| $\angle C_bC_aH$ iso $C_a$ | 2.91547 | 2.11323 | 4.1633 | -15.55033 $C_a$ | 5 | -14.82575 $C_b$ | 1 | 0.87495 | 0.91771 | 0.75 | 1 | 0.75 | 1.04887 | 0 | | | | 110.76 | |
| $\angle C_aC_bH$ iso $C_a$ | 2.91547 | 2.09711 | 4.1633 | -15.55033 $C_b$ | 5 | -14.82575 $C_a$ | 1 | 0.87495 | 0.91771 | 0.75 | 1 | 0.75 | 1.04887 | 0 | | | | 111.27 | 111.4 (isobutane) |
| $\angle C_bC_aC_b$ tert $C_a$ | 2.90327 | 2.90327 | 4.7958 | -16.68412 $C_b$ | 26 | -16.68412 $C_b$ | 26 | 0.81549 | 0.81549 | 1 | 1 | 1 | 0.81549 | -1.85836 | | | | 111.37 | 110.8 (isobutane) |
| $\angle C_bC_aC_d$ | | | | | | | | | | | | | | | 72.50 | | | 107.50 | |

## DIMETHYL SULFOXIDE DIHEDRAL ANGLE

The dihedral angle $\theta_{\angle S=O/CSC}$ between the plane defined by the $CSC$ MO comprising a linear combination of two $S-C$-bond MOs and a line defined by the $S=O$-bond MO where $S$ is the central atom is calculated using the results given in Table 15.170 and Eqs. (15.114-15.117). The distance $d_1$ along the bisector of $\theta_{\angle CSC}$ from $S$ to the internuclear-distance line between $C$ and $C$, $2c'_{C-C}$, is given by:

$$d_1 = 2c'_{S-C} \cos\frac{\theta_{\angle CSC}}{2} = 4.9800a_0 \cos\frac{96.20^\circ}{2} = 2.23423a_0 \tag{15.153}$$

where $2c'_{S-C}$ is the internuclear distance between $S$ and $C$. The atoms $C$, $C$, and $O$ define the base of a pyramid. Then, the pyramidal angle $\theta_{\angle COC}$ can be solved from the internuclear distances between $C$ and $C$, $2c'_{C-C}$, and between $C$ and $O$, $2c'_{C-O}$, using the law of cosines (Eq. (15.115)):

$$\theta_{\angle COC} = \cos^{-1}\left(\frac{(2c'_{C-O})^2 + (2c'_{C-O})^2 - (2c'_{C-C})^2}{2(2c'_{C-O})(2c'_{C-O})}\right) = \cos^{-1}\left(\frac{(4.95984)^2 + (4.95984)^2 - (4.9800)^2}{2(4.95984)(4.95984)}\right) = 60.27^\circ \tag{15.154}$$

Then, the distance $d_2$ along the bisector of $\theta_{\angle COC}$ from $O$ to the internuclear-distance line $2c'_{C-C}$, is given by:

$$d_2 = 2c'_{C-O} \cos\frac{\theta_{\angle COC}}{2} = 4.95984a_0 \cos\frac{60.27^\circ}{2} = 4.28952a_0 \tag{15.155}$$

The lengths $d_1$, $d_2$, and $2c'_{S=O}$ define a triangle wherein the angle between $d_1$ and the internuclear distance between $O$ and $S$, $2c'_{S=O}$, is the dihedral angle $\theta_{\angle S=O/CSC}$ that can be solved using the law of cosines (Eq. (15.117)).

$$\theta_{\angle S=O/CSC} = \cos^{-1}\left(\frac{d_1^2 + (2c'_{S=O})^2 - d_2^2}{2d_1(2c'_{S=O})}\right) = \cos^{-1}\left(\frac{(2.23423)^2 + (2.81792)^2 - (4.28952)^2}{2(2.23423)(2.81792)}\right) = 115.74^\circ \tag{15.156}$$

The experimental [1] dihedral angle $\theta_{\angle S=O/CSC}$ is

$$\theta_{\angle S=O/CSC} = 115.5^\circ \tag{15.157}$$

## SULFONES ($C_nH_{2n+2}\left(SO_2\right)_m$, $n=2,3,4,5...\infty$)

The alkyl sulfones, $C_nH_{2n+2}\left(SO_2\right)_m$, comprise a $C-SO_2-C$ moiety that comprises $C-S$ and $SO_2$ functional groups. The alkyl portion of the alkyl sulfone may comprise at least two terminal methyl groups ($CH_3$) at each end of the chain, and may comprise methylene ($CH_2$), and methylyne ($CH$) functional groups as well as $C$ bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($\left(CH_3\right)_2CH$) and t-butyl ($\left(CH_3\right)_3C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups. The branched-chain-alkane groups in sulfones are equivalent to those in branched-chain alkanes.

The two unpaired electrons of each $O$ atom form a MO with two unpaired electrons of the sulfur atom such that the MO comprises a linear combination of two bonds, each of bond order two involving the sulfur HOs and oxygen AOs of both oxygen atoms. Due to the bonding between unpaired electrons of different oxygen atoms $E_{mag}$ (Eq. (15.68)) is subtracted from the total energy. Otherwise, the $SO_2$-bond MO of sulfones is solved in the same manner as the $SO$-bond MO of sulfoxides given in the corresponding section wherein $n_1$ in Eqs. (15.51) and (15.61) is four versus two. Also, the $C-S$-bond MO is equivalent to that of sulfoxides having $E_T\left(atom-atom,msp^3.AO\right)=-0.72457\ eV$ (Eq. (14.151)).

The symbols of the functional groups of branched-chain alkyl sulfones are given in Table 15.171. The geometrical (Eqs. (15.1-15.5) and (15.51)), intercept (Eqs. (15.80-15.87)), and energy (Eqs. (15.6-15.11) and (15.17-15.65)) parameters of alkyl sulfones are given in Tables 15.172, 15.173, and 15.174, respectively. The total energy of each alkyl sulfone given in Table 15.165 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.174 corresponding to functional-group composition of the molecule. The bond angle parameters of alkyl sulfones determined using Eqs. (15.88-15.117) are given in Table 15.176. The color scale, translucent view of the charge-density of exemplary sulfone, dimethyl sulfone, comprising the concentric shells of atoms with the outer shell bridged by one or more $H_2$-type ellipsoidal MOs or joined with one or more hydrogen MOs is shown in Figure 15.29.

Figure 15.29. (A)-(B) Color scale, translucent views of the charge-density of dimethyl sulfone showing the orbitals of the atoms at their radii, the ellipsoidal surface of each $H$ or $H_2$-type ellipsoidal MO that transitions to the corresponding outer shell of the atom(s) participating in each bond, and the hydrogen nuclei (red, not to scale).

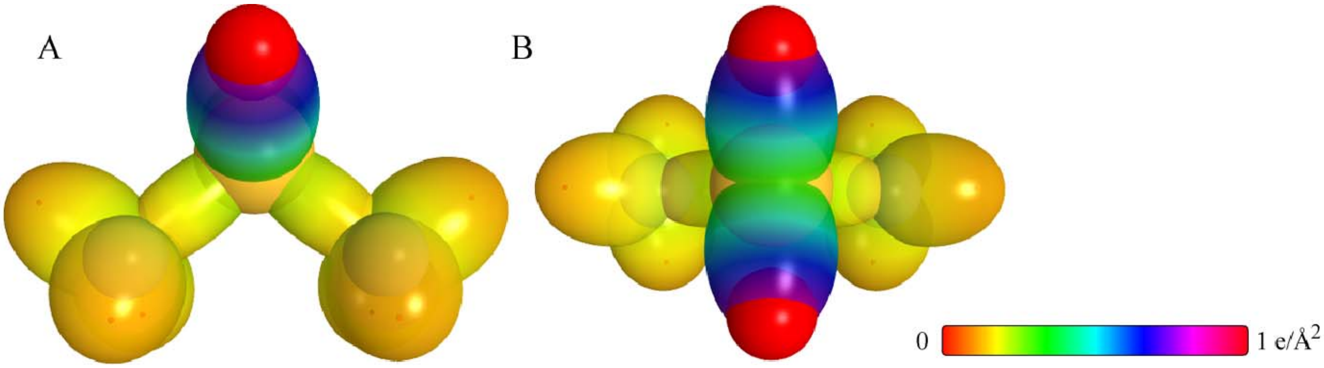


Table 15.171. The symbols of functional groups of alkyl sulfones.

| Functional Group | Group Symbol |
|---|---|
| *C-S* | $C-S$ |
| $SO_2$ | $SO_2$ |
| $CH_3$ group | $C-H\ \left(CH_3\right)$ |
| $CH_2$ group | $C-H\ \left(CH_2\right)$ |
| *CH* | $C-H$ |
| *CC* bond (*n-C*) | $C-C$ (a) |
| *CC* bond (*iso-C*) | $C-C$ (b) |
| *CC* bond (*tert-C*) | $C-C$ (c) |
| *CC* (*iso* to *iso-C*) | $C-C$ (d) |
| *CC* (*t* to *t-C*) | $C-C$ (e) |
| *CC* (*t* to *iso-C*) | $C-C$ (f) |

Table 15.172. The geometrical bond parameters of alkyl sulfones and experimental values [1].

| Parameter | $C-S$ Group | $SO_2$ Group | $C-H\left(CH_3\right)$ Group | $C-H\left(CH_2\right)$ Group | $C-H$ Group | $C-C$ (a) Group | $C-C$ (b) Group | $C-C$ (c) Group | $C-C$ (d) Group | $C-C$ (e) Group | $C-C$ (f) Group |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $a\left(a_0\right)$ | 1.87325 | 1.85851 | 1.64920 | 1.67122 | 1.67465 | 2.12499 | 2.12499 | 2.10725 | 2.12499 | 2.10725 | 2.10725 |
| $c'\left(a_0\right)$ | 1.67271 | 1.36327 | 1.04856 | 1.05553 | 1.05661 | 1.45744 | 1.45744 | 1.45164 | 1.45744 | 1.45164 | 1.45164 |
| Bond Length $2c'$ $(\AA)$ | 1.77031 | 1.44282 | 1.10974 | 1.11713 | 1.11827 | 1.54280 | 1.54280 | 1.53635 | 1.54280 | 1.53635 | 1.53635 |
| Exp. Bond Length $(\AA)$ | 1.771<br>(dimethyl sulfone) | 1.435<br>(dimethyl sulfone) | 1.107<br>($C-H$ propane)<br>1.117<br>($C-H$ butane) | 1.107<br>($C-H$ propane)<br>1.117<br>($C-H$ butane) | 1.122<br>(isobutane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) |
| $b,c\left(a_0\right)$ | 0.84328 | 1.26315 | 1.27295 | 1.29569 | 1.29924 | 1.54616 | 1.54616 | 1.52750 | 1.54616 | 1.52750 | 1.52750 |
| $e$ | 0.89294 | 0.73353 | 0.63580 | 0.63159 | 0.63095 | 0.68600 | 0.68600 | 0.68888 | 0.68600 | 0.68888 | 0.68888 |

Table 15.173. The MO to HO intercept geometrical bond parameters of alkyl sulfones. $R$, $R'$, $R''$ are $H$ or alkyl groups. $E_T$ is $E_T(atom-atom,msp^3.AO)$.

| Bond | Atom | $E_T$ (eV) Bond 1 | $E_T$ (eV) Bond 2 | $E_T$ (eV) Bond 3 | $E_T$ (eV) Bond 4 | Final Total Energy $C2sp^3$ (eV) | $r_{initial}$ $\left(a_0\right)$ | $r_{final}$ $\left(a_0\right)$ | $E_{Coulomb}$ (eV) Final | $E\left(C2sp^3\right)$ (eV) Final | $\theta'$ $\left(^\circ\right)$ | $\theta_1$ $\left(^\circ\right)$ | $\theta_2$ $\left(^\circ\right)$ | $d_1$ $\left(a_0\right)$ | $d_2$ $\left(a_0\right)$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $R_2(O)S=O$ | $S$ | 0 | 0 | -0.36229 | -0.36229 |  | 1.32010 | 0.87495 | -15.55033 |  | 91.47 | 88.53 | 43.82 | 1.34086 | 0.02242 |
| $R_2(O)S=O$ | $O$ | 0 | 0 | 0 | 0 |  | 1.00000 | 0.91771 | -14.82575 |  | 95.05 | 84.95 | 46.36 | 1.28256 | 0.08071 |
| $R_2-SO$ | $S$ | -0.36229 | -0.36229 | 0 | 0 |  | 1.32010 | 0.87495 | -15.55033 |  | 129.35 | 50.65 | 53.36 | 1.11799 | 0.55472 |
| $H_3C_a-S(O)-C_bH_2CH_2R$ | $C_a$ | -0.36229 | 0 | 0 | 0 | -151.97798 | 0.91771 | 0.89582 | -15.18804 | -14.99717 | 130.19 | 49.81 | 54.24 | 1.09461 | 0.57809 |
| $H_3C_a-S(O)-C_bH_2CH_2R$ | $C_b$ | -0.36229 | -0.92918 | 0 | 0 | -152.90716 | 0.91771 | 0.84418 | -16.11722 | -15.92636 | 128.05 | 51.95 | 52.03 | 1.15245 | 0.52026 |
| $C-H\left(CH_3\right)$ | $C$ | -0.92918 | 0 | 0 | 0 | -152.54487 | 0.91771 | 0.86359 | -15.75493 | -15.56407 | 77.49 | 102.51 | 41.48 | 1.23564 | 0.18708 |
| $C-H\left(CH_2\right)$ | $C$ | -0.92918 | -0.92918 | 0 | 0 | -153.47406 | 0.91771 | 0.81549 | -16.68412 | -16.49325 | 68.47 | 111.53 | 35.84 | 1.35486 | 0.29933 |
| $C-H\left(CH\right)$ | $C$ | -0.92918 | -0.92918 | -0.92918 | 0 | -154.40324 | 0.91771 | 0.77247 | -17.61330 | -17.42244 | 61.10 | 118.90 | 31.37 | 1.42988 | 0.37326 |
| $H_3C_aC_bH_2CH_2-$ ($C-C$ (a)) | $C_a$ | -0.92918 | 0 | 0 | 0 | -152.54487 | 0.91771 | 0.86359 | -15.75493 | -15.56407 | 63.82 | 116.18 | 30.08 | 1.83879 | 0.38106 |
| $H_3C_aC_bH_2CH_2-$ ($C-C$ (a)) | $C_b$ | -0.92918 | -0.92918 | 0 | 0 | -153.47406 | 0.91771 | 0.81549 | -16.68412 | -16.49325 | 56.41 | 123.59 | 26.06 | 1.90890 | 0.45117 |
| $R-H_2C_aC_b\left(H_2C_c-R'\right)HCH_2-$ ($C-C$ (b)) | $C_b$ | -0.92918 | -0.92918 | -0.92918 | 0 | -154.40324 | 0.91771 | 0.77247 | -17.61330 | -17.42244 | 48.30 | 131.70 | 21.90 | 1.97162 | 0.51388 |
| $R-H_2C_a\left(R'-H_2C_d\right)C_b\left(R''-H_2C_c\right)CH_2-$ ($C-C$ (c)) | $C_b$ | -0.92918 | -0.72457 | -0.72457 | -0.72457 | -154.71860 | 0.91771 | 0.75889 | -17.92866 | -17.73779 | 48.21 | 131.79 | 21.74 | 1.95734 | 0.50570 |
| $isoC_aC_b\left(H_2C_c-R'\right)HCH_2-$ ($C-C$ (d)) | $C_b$ | -0.92918 | -0.92918 | -0.92918 | 0 | -154.40324 | 0.91771 | 0.77247 | -17.61330 | -17.42244 | 48.30 | 131.70 | 21.90 | 1.97162 | 0.51388 |
| $tertC_a\left(R'-H_2C_d\right)C_b\left(R''-H_2C_c\right)CH_2-$ ($C-C$ (e)) | $C_b$ | -0.72457 | -0.72457 | -0.72457 | -0.72457 | -154.51399 | 0.91771 | 0.76765 | -17.92866 | -17.73779 | 50.04 | 129.96 | 22.66 | 1.94462 | 0.49298 |
| $tertC_aC_b\left(H_2C_c-R'\right)HCH_2-$ ($C-C$ (f)) | $C_b$ | -0.72457 | -0.92918 | -0.92918 | 0 | -154.19863 | 0.91771 | 0.78155 | -17.40869 | -17.21783 | 52.78 | 127.22 | 24.04 | 1.92443 | 0.47279 |
| $isoC_a\left(R'-H_2C_d\right)C_b\left(R''-H_2C_c\right)CH_2-$ ($C-C$ (f)) | $C_b$ | -0.72457 | -0.72457 | -0.72457 | -0.72457 | -154.51399 | 0.91771 | 0.76765 | -17.92866 | -17.73779 | 50.04 | 129.96 | 22.66 | 1.94462 | 0.49298 |

Table 15.174. The energy parameters ($eV$) of functional groups of alkyl sulfones.

| Parameters | $C-S$ Group | $SO_2$ Group | $CH_3$ Group | $CH_2$ Group | $C-H$ Group | $C-C$ (a) Group | $C-C$ (b) Group | $C-C$ (c) Group | $C-C$ (d) Group | $C-C$ (e) Group | $C-C$ (f) Group |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $n_1$ | 1 | 4 | 3 | 2 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $n_2$ | 0 | 0 | 2 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $n_3$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $C_1$ | 0.5 | 0.5 | 0.75 | 0.75 | 0.75 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| $C_2$ | 0.66951 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $c_1$ | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $c_2$ | 1 | 1.20632 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 |
| $c_3$ | 0 | 1 | 0 | 1 | 1 | 0 | 0 | 0 | 1 | 1 | 0 |
| $c_4$ | 2 | 8 | 1 | 1 | 1 | 2 | 2 | 2 | 2 | 2 | 2 |
| $c_5$ | 0 | 1 | 3 | 2 | 1 | 0 | 0 | 0 | 0 | 0 | 0 |
| $C_{1o}$ | 0.5 | 0.5 | 0.75 | 0.75 | 0.75 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| $C_{2o}$ | 0.66951 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $V_e\ (eV)$ | -46.73032 | -180.36454 | -107.32728 | -70.41425 | -35.12015 | -28.79214 | -28.79214 | -29.10112 | -28.79214 | -29.10112 | -29.10112 |
| $V_p\ (eV)$ | 8.13401 | 39.92103 | 38.92728 | 25.78002 | 12.87680 | 9.33352 | 9.33352 | 9.37273 | 9.33352 | 9.37273 | 9.37273 |
| $T\ (eV)$ | 12.47306 | 48.52397 | 32.53914 | 21.06675 | 10.48582 | 6.77464 | 6.77464 | 6.90500 | 6.77464 | 6.90500 | 6.90500 |
| $V_m\ (eV)$ | -6.23653 | -24.26198 | -16.26957 | -10.53337 | -5.24291 | -3.38732 | -3.38732 | -3.45250 | -3.38732 | -3.45250 | -3.45250 |
| $E(_{AO/HO})\ (eV)$ | 0 | -11.52126 | -15.56407 | -15.56407 | -14.63489 | -15.56407 | -15.56407 | -15.35946 | -15.56407 | -15.35946 | -15.35946 |
| $\Delta E_{H_2MO}(_{AO/HO})\ (eV)$ | -0.72457 | -1.16125 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $E_T(_{AO/HO})\ (eV)$ | 0.72457 | -10.36001 | -15.56407 | -15.56407 | -14.63489 | -15.56407 | -15.56407 | -15.35946 | -15.56407 | -15.35946 | -15.35946 |
| $E_T(_{H_2MO})\ (eV)$ | -31.63521 | -126.54154 | -67.69451 | -49.66493 | -31.63533 | -31.63537 | -31.63537 | -31.63535 | -31.63537 | -31.63535 | -31.63535 |
| $E_T\left(atom-atom,msp^3.AO\right)(eV)$ | -0.72457 | 0 | 0 | 0 | 0 | -1.85836 | -1.85836 | -1.44915 | -1.85836 | -1.44915 | -1.44915 |
| $E_T(_{MO})\ (eV)$ | -32.35994 | -126.54147 | -67.69450 | -49.66493 | -31.63537 | -33.49373 | -33.49373 | -33.08452 | -33.49373 | -33.08452 | -33.08452 |
| $\omega\ \left(10^{15}\ rad/s\right)$ | 30.8880 | 11.5378 | 24.9286 | 24.2751 | 24.1759 | 9.43699 | 9.43699 | 15.4846 | 9.43699 | 9.55643 | 9.55643 |
| $E_K\ (eV)$ | 20.33104 | 7.59437 | 16.40846 | 15.97831 | 15.91299 | 6.21159 | 6.21159 | 10.19220 | 6.21159 | 6.29021 | 6.29021 |
| $\bar{E}_D\ (eV)$ | -0.28866 | -0.17247 | -0.25352 | -0.25017 | -0.24966 | -0.16515 | -0.16515 | -0.20896 | -0.16515 | -0.16416 | -0.16416 |
| $\bar{E}_{Kvib}\ (eV)$ | 0.08543<br>[42] | 0.12832<br>[43] | 0.35532<br>(Eq. (13.458)) | 0.35532<br>(Eq. (13.458)) | 0.35532<br>(Eq. (13.458)) | 0.12312<br>[2] | 0.17978<br>[4] | 0.09944<br>[5] | 0.12312<br>[2] | 0.12312<br>[2] | 0.12312<br>[2] |
| $\bar{E}_{osc}\ (eV)$ | -0.24595 | -0.10831 | -0.22757 | -0.14502 | -0.07200 | -0.10359 | -0.07526 | -0.15924 | -0.10359 | -0.10260 | -0.10260 |
| $E_{mag}\ (eV)$ | 0.14803 | 0.11441 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 |
| $E_T(_{Group})\ (eV)$ | -32.60589 | -126.97472 | -67.92207 | -49.80996 | -31.70737 | -33.59732 | -33.49373 | -33.24376 | -33.59732 | -33.18712 | -33.18712 |
| $E_{initial}(_{c_4\ AO/HO})\ (eV)$ | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 |
| $E_{initial}(_{c_5\ AO/HO})\ (eV)$ | 0 | -1.16125 | -13.59844 | -13.59844 | -13.59844 | 0 | 0 | 0 | 0 | 0 | 0 |
| $E_D(_{Group})\ (eV)$ | 3.33611 | 8.61994 | 12.49186 | 7.83016 | 3.32601 | 4.32754 | 4.29921 | 3.97398 | 4.17951 | 3.62128 | 3.91734 |

Table 15.175. The total bond energies of alkyl sulfones calculated using the functional group composition and the energies of Table 15.174 compared to the experimental values [3].

| Formula | Name | $C-S$ Group | $SO_2$ Group | $CH_3$ | $CH_2$ | $CH$ | $C-C$ (a) | $C-C$ (b) | $C-C$ (c) | $C-C$ (d) | $C-C$ (e) | $C-C$ (f) | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $C_2H_6SO_2$ | Dimethyl sulfone | 2 | 1 | 2 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 40.27588 | 40.316 | 0.00100 |

Table 15.176. The bond angle parameters of alkyl sulfones and experimental values [1]. In the calculation of $\theta_v$, the parameters from the preceding angle were used. $E_T$ is $E_T$ $(atom - atom, msp^3.AO)$.

| Atoms of Angle | $2c'$ Bond 1 $(a_0)$ | $2c'$ Bond 2 $(a_0)$ | $2c'$ Terminal Atoms $(a_0)$ | $E_{Coulombic}$ Atom 1 | Atom 1 Hybridization Designation (Table 15.3.A) | $E_{Coulombic}$ Atom 2 | Atom 2 Hybridization Designation (Table 15.3.A) | $c_2$ Atom 1 | $c_2$ Atom 2 | $C_1$ | $C_2$ | $c_1$ | $c_2'$ | $E_T$ (eV) | $\theta_v$ (°) | $\theta_1$ (°) | $\theta_2$ (°) | Cal. $\theta$ (°) | Exp. $\theta$ (°) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $\angle O_aSO_b$ | 2.72654 | 2.72654 | 4.7539 | -15.95954 $O_a$ | 10 | -15.95954 $O_b$ | 10 | 0.85252 | 0.85252 | 1 | 1 | 1 | 0.85252 | -1.65376 | | | | 121.33 | 121 (dimethyl sulfone) |
| $\angle C_aSC_a$ | 3.34541 | 3.34541 | 5.2154 | -16.11722 | 12 | -16.11722 | 12 | 0.84418 | 0.84418 | 1 | 1 | 1 | 0.84418 | -1.85836 | | | | 102.43 | 102 (dimethyl sulfone) |
| $\angle C_aSO$ | 3.34541 | 2.72654 | 4.9193 | -15.55033 $C_a$ | 5 | -13.61806 $O$ | O | 0.87495 | 0.85395 (Eq. (15.133)) | 1 | 1 | 1 | 0.86445 | -1.65376 | | | | 107.79 | |
| Methylene $\angle HC_aH$ | 2.11106 | 2.11106 | 3.4252 | -15.75493 | 7 | H | H | 0.86359 | 1 | 1 | 1 | 0.75 | 1.15796 | 0 | | | | 108.44 | 107 (propane) |
| $\angle C_aC_bC_c$ | | | | | | | | | | | | | | | 69.51 | | | 110.49 | 112 (propane)<br>113.8 (butane)<br>110.8 (isobutane) |
| $\angle C_aC_bH$ | | | | | | | | | | | | | | | 69.51 | | | 110.49 | 111.0 (butane)<br>111.4 (isobutane) |
| Methyl $\angle HC_aH$ | 2.09711 | 2.09711 | 3.4252 | -15.75493 | 7 | H | H | 0.86359 | 1 | 1 | 1 | 0.75 | 1.15796 | 0 | | | | 109.50 | |
| $\angle C_aC_bC_c$ | | | | | | | | | | | | | | | 70.56 | | | 109.44 | |
| $\angle C_aC_bH$ | | | | | | | | | | | | | | | 70.56 | | | 109.44 | |
| $\angle C_bC_aC_c$ iso $C_a$ | 2.91547 | 2.91547 | 4.7958 | -16.68412 $C_b$ | 26 | -16.68412 $C_c$ | 26 | 0.81549 | 0.81549 | 1 | 1 | 1 | 0.81549 | -1.85836 | | | | 110.67 | 110.8 (isobutane) |
| $\angle C_bC_aH$ iso $C_a$ | 2.91547 | 2.11323 | 4.1633 | -15.55033 $C_a$ | 5 | -14.82575 $C_b$ | 1 | 0.87495 | 0.91771 | 0.75 | 1 | 0.75 | 1.04887 | 0 | | | | 110.76 | |
| $\angle C_aC_bH$ iso $C_a$ | 2.91547 | 2.09711 | 4.1633 | -15.55033 $C_b$ | 5 | -14.82575 $C_a$ | 1 | 0.87495 | 0.91771 | 0.75 | 1 | 0.75 | 1.04887 | 0 | | | | 111.27 | 111.4 (isobutane) |
| $\angle C_bC_aC_b$ tert $C_a$ | 2.90327 | 2.90327 | 4.7958 | -16.68412 $C_b$ | 26 | -16.68412 $C_b$ | 26 | 0.81549 | 0.81549 | 1 | 1 | 1 | 0.81549 | -1.85836 | | | | 111.37 | 110.8 (isobutane) |
| $\angle C_bC_aC_d$ | | | | | | | | | | | | | | | 72.50 | | | 107.50 | |

## SULFITES ($C_nH_{2n+2}\left(SO_3\right)_m$, $n=2,3,4,5...\infty$)

The alkyl sulfites, $C_nH_{2n+2}\left(SO_3\right)_m$, comprise a $C-O-SO-O-C$ moiety that comprises two types $C-O$ functional groups, one for methyl and one for alkyl, and $O-S$ and $SO$ functional groups. The alkyl portion of the alkyl sulfite may comprise at least two terminal methyl groups ($CH_3$) at each end of the chain, and may comprise methylene ($CH_2$), and methylyne ($CH$) functional groups as well as $C$ bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($\left(CH_3\right)_2CH$) and t-butyl ($\left(CH_3\right)_3C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups. The branched-chain-alkane groups in sulfites are equivalent to those in branched-chain alkanes.

The $SO$ functional group is equivalent to that of sulfoxides with $E_T\left(atom-atom,msp^3.AO\right)=0$ as given in the Sulfoxides section. The methyl and alkyl $C-O$ functional groups having $E_T\left(atom-atom,msp^3.AO\right)=-1.44915\ eV$ and $E_T\left(atom-atom,msp^3.AO\right)=-1.65376\ eV$, respectively, are equivalent to the corresponding ether groups given in the Ethers section except for the energy terms corresponding to oscillation of the bond in the transition state.

The electron configuration of oxygen is $1s^22s^22p^4$, and the orbital arrangement given by Eq. (10.154) has two unpaired electrons corresponding to the ground state ${}^3P_2$. The $SO$ functional group comprises a double bond between the $S$ atom and the two unpaired electrons of $O$. The $S$ atom also forms single bonds with two additional oxygen atoms that are each further bound to methyl or alkyl groups. The first bond-order bonding in the $O-S$ groups is between the sulfur atom and a $O2p$ AO of each oxygen of the two bonds. The formation of these four bonds with the sulfur atom is permitted by the hybridization of the four electrons of the $S3p$ shell to give the orbital arrangement given by Eq. (15.148). Then, the Coulombic energy $E_{Coulomb}\left(S,3sp^3\right)$ of the outer electron of the $S3sp^3$ shell given by Eq. (15.139) with $r_{3sp^3}=1.17585a_0$ (Eq. (15.138)) is $-11.57099\ eV$. Using Eq. (15.16) with the radius of the sulfur atom $r_{16}=1.32010a_0$ given by Eq. (10.341), the energy $E\left(S3sp^3\right)$ of the outer electron of the $S3sp^3$ shell given by the sum of $E_{Coulomb}\left(S3sp^3\right)$ and $E(magnetic)$ is $E\left(S3sp^3\right)=-11.52126\ eV$ (Eq. (15.149)).

Thus, the $O-S$ group is solved as an energy minimum by hybridizing the four $S3p$ electrons to form a $S3sp^3$ shell, and the sharing of electrons between the $O2p$ AO and the $S3sp^3$ HO to form a MO permits each participating orbital to decrease in radius and energy. As in the case of thiols, sulfides, disulfides, and sulfoxides, the energy of sulfur is less than the Coulombic energy between the electron and proton of $H$ given by Eq. (1.264). Thus, $c_1$ and $c_2$ are equal to one in Eq. (15.61), and the energy matching condition is determined by the $C_2$ parameter. Each $C2sp^3$ HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of $E\left(C,2sp^3\right)=-14.63489\ eV$ (Eq. (15.25)), and the $S$ HO has an energy of $E\left(S3sp^3\right)=-11.52126\ eV$. To meet the equipotential condition of the union of the $O-S$ $H_2$-type-ellipsoidal-MO with these orbitals with the oxygen that further bonds to a $C2sp^3$ HO, the hybridization factor $C_2$ of Eq. (15.61) for the $O-S$-bond MO given by Eqs. (15.77) and (15.79) is:

$$C_2\left(S3sp^3\ to\ O\ to\ C2sp^3HO\right)=\frac{E\left(S,3sp^3\right)}{E\left(O,2p\right)}c_2\left(C2sp^3HO\right)=\frac{-11.52126\ eV}{-13.61806\ eV}\left(0.91771\right)=0.77641 \tag{15.158}$$

As in the case of thiols, sulfides, disulfides, and sulfoxides, with the energy of $S$ matched to the Coulombic energy between the electron and proton of $H$, the energy of the $O-S$-bond MO is the sum of the component energies of the $H_2$-type ellipsoidal MO given in Eq. (15.51) with $E\left(AO/HO\right)=0$ and $E_T\left(AO/HO\right)=\Delta E_{H_2MO}\left(AO/HO\right)$. For sulfites, $\Delta E_{H_2MO}\left(AO/HO\right)=-0.92918\ eV$ and equivalently, $E_T\left(atom-atom,msp^3.AO\right)=-0.92918\ eV$ (Eq. (14.513)) due to the maximum energy match with the oxygen AO as in the case with carboxylic acid esters.

The symbols of the functional groups of branched-chain alkyl sulfites are given in Table 15.177. The geometrical (Eqs. (15.1-15.5) and (15.51)), intercept (Eqs. (15.80-15.87)), and energy (Eqs. (15.6-15.11) and (15.17-15.65)) parameters of alkyl sulfites are given in Tables 15.178, 15.179, and 15.180, respectively. The total energy of each alkyl sulfite given in Table 15.175 was calculated as the sum over the integer multiple of each $E_D\left(Group\right)$ of Table 15.180 corresponding to functional-group composition of the molecule. The bond angle parameters of alkyl sulfites determined using Eqs. (15.88-15.117) are given in Table 15.182. The color scale, translucent view of the charge-density of sulfite, dimethyl sulfite, comprising the concentric shells of atoms with the outer shell bridged by one or more $H_2$-type ellipsoidal MOs or joined with one or more hydrogen MOs is shown in Figure 15.30.

Figure 15.30. Color scale, translucent view of the charge-density of dimethyl sulfite showing the orbitals of the atoms at their radii, the ellipsoidal surface of each $H$ or $H_2$-type ellipsoidal MO that transitions to the corresponding outer shell of the atom(s) participating in each bond, and the hydrogen nuclei (red, not to scale).

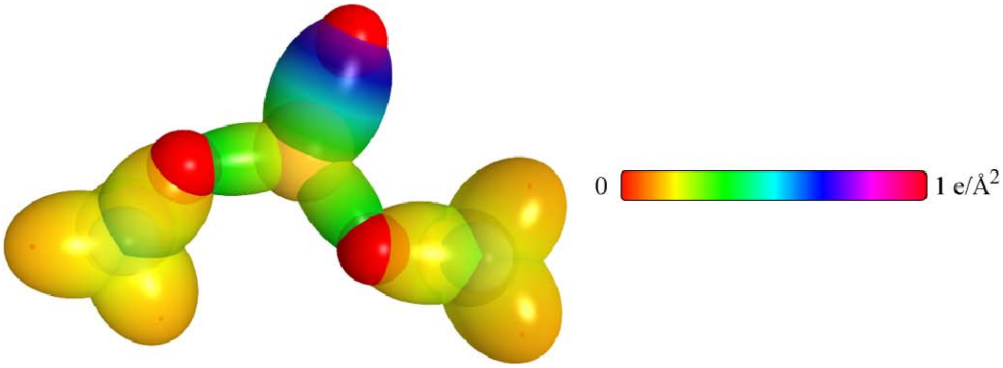


Table 15.177. The symbols of functional groups of alkyl sulfites.

| Functional Group | Group Symbol |
|---|---|
| *C-O* (*methyl*) | $C-O$ (i) |
| *C-O* (*alkyl*) | $C-O$ (ii) |
| $O\text{-}SO_2$ | $O-S$ |
| *SO* | $SO$ |
| $CH_3$ group | $C-H\ (CH_3)$ |
| $CH_2$ group | $C-H\ (CH_2)$ |
| *CH* | $C-H$ |
| *CC* bond (*n-C*) | $C-C$ (a) |
| *CC* bond (*iso-C*) | $C-C$ (b) |
| *CC* bond (*tert-C*) | $C-C$ (c) |
| *CC* (*iso* to *iso-C*) | $C-C$ (d) |
| *CC* (*t* to *t-C*) | $C-C$ (e) |
| *CC* (*t* to *iso-C*) | $C-C$ (f) |

Table 15.178. The geometrical bond parameters of alkyl sulfites and experimental values [1].

| Parameter | $C-O$ (i) Group | $C-O$ (ii) Group | $O-S$ | $SO$ | $C-H\left(CH_3\right)$ Group | $C-H\left(CH_2\right)$ Group | $C-H$ Group | $C-C$ (a) Group | $C-C$ (b) Group | $C-C$ (c) Group | $C-C$ (d) Group | $C-C$ (e) Group | $C-C$ (f) Group |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $a\left(a_0\right)$ | 1.80717 | 1.79473 | 1.70299 | 1.98517 | 1.64920 | 1.67122 | 1.67465 | 2.12499 | 2.12499 | 2.10725 | 2.12499 | 2.10725 | 2.10725 |
| $c'\left(a_0\right)$ | 1.34431 | 1.33968 | 1.48102 | 1.40896 | 1.04856 | 1.05553 | 1.05661 | 1.45744 | 1.45744 | 1.45164 | 1.45744 | 1.45164 | 1.45164 |
| Bond Length $2c'$ $\left(\mathring{A}\right)$ | 1.42276 | 1.41785 | 1.56744 | 1.49118 | 1.10974 | 1.11713 | 1.11827 | 1.54280 | 1.54280 | 1.53635 | 1.54280 | 1.53635 | 1.53635 |
| Exp. Bond Length $\left(\mathring{A}\right)$ |  |  | 1.574 ($H_2SO_4$) | 1.485 (dimethyl sulfoxide) | 1.107<br>($C-H$ propane)<br>1.117<br>($C-H$ butane) | 1.107<br>($C-H$ propane)<br>1.117<br>($C-H$ butane) | 1.122 (isobutane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) |
| $b,c\left(a_0\right)$ | 1.20776 | 1.19429 | 0.84069 | 1.39847 | 1.27295 | 1.29569 | 1.29924 | 1.54616 | 1.54616 | 1.52750 | 1.54616 | 1.52750 | 1.52750 |
| $e$ | 0.74388 | 0.74645 | 0.86966 | 0.70974 | 0.63580 | 0.63159 | 0.63095 | 0.68600 | 0.68600 | 0.68888 | 0.68600 | 0.68888 | 0.68888 |

Table 15.179. The MO to HO intercept geometrical bond parameters of alkyl sulfites. $R$, $R'$, $R''$ are $H$ or alkyl groups. $E_T$ is $E_T(atom - atom, msp^3.AO)$.

| Bond | Atom | $E_T$ (eV) Bond 1 | $E_T$ (eV) Bond 2 | $E_T$ (eV) Bond 3 | $E_T$ (eV) Bond 4 | Final Total Energy $C2sp^3$ (eV) | $r_{initial}$ $(a_0)$ | $r_{final}$ $(a_0)$ | $E_{Coulomb}$ (eV) Final | $E(C2sp^3)$ (eV) Final | $\theta'$ $(^\circ)$ | $\theta_1$ $(^\circ)$ | $\theta_2$ $(^\circ)$ | $d_1$ $(a_0)$ | $d_2$ $(a_0)$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $(RO)_2S=O_a$ | $S$ | 0 | -0.46459 | -0.46459 | 0 |  | 1.32010 | 0.86359 | -15.75493 |  | 78.56 | 101.44 | 37.25 | 1.58026 | 0.17130 |
| $(RO)_2S=O_a$ | $O_a$ | 0 | 0 | 0 | 0 |  | 1.00000 | 0.91771 | -14.82575 |  | 84.06 | 95.94 | 40.75 | 1.50400 | 0.09504 |
| $CH_3O_a-S(O)OR'$ | $S$ | -0.46459 | -0.46459 | 0 | 0 |  | 1.32010 | 0.86359 | -15.75493 |  | 126.68 | 53.32 | 55.47 | 0.96521 | 0.51581 |
| $CH_3O_a-S(O)OR'$ $(C-O$ (i)) | $O_a$ | -0.46459 | -0.72457 | 0 | 0 |  | 1.00000 | 0.84957 | -16.01492 |  | 126.03 | 53.97 | 54.81 | 0.98133 | 0.49969 |
| $RCH_2O_a-S(O)OR'$ $(C-O$ (ii)) | $O_a$ | -0.46459 | -0.82688 | 0 | 0 |  | 1.00000 | 0.84418 | -16.11722 |  | 125.77 | 54.23 | 54.56 | 0.98753 | 0.49349 |
| $H_3C_a-O_aS(O)OR$ $(C-O$ (i)) | $O_a$ | -0.72457 | -0.46459 | 0 | 0 |  | 1.00000 | 0.84957 | -16.01492 |  | 93.85 | 86.15 | 44.57 | 1.28731 | 0.05700 |
| $H_3C_a-O_aS(O)OR$ $(C-O$ (i)) | $C_a$ | -0.72457 | 0 | 0 | 0 | -152.34026 | 0.91771 | 0.87495 | -15.55033 | -15.35946 | 95.98 | 84.02 | 46.10 | 1.25319 | 0.09112 |
| $RH_2C_a-O_aS(O)OR'$ $(C-O$ (ii)) | $O_a$ | -0.82688 | -0.46459 | 0 | 0 |  | 1.00000 | 0.84418 | -16.11722 |  | 94.50 | 85.50 | 44.80 | 1.27343 | 0.06624 |
| $RH_2C_a-O_aS(O)OR'$ $(C-O$ (ii)) | $C_a$ | -0.82688 | -0.92918 | 0 | 0 | -153.37175 | 0.91771 | 0.82053 | -16.58181 | -16.39095 | 92.41 | 87.59 | 43.35 | 1.30512 | 0.03456 |
| $C-H\ (CH_3)$ | $C$ | -0.92918 | 0 | 0 | 0 | -152.54487 | 0.91771 | 0.86359 | -15.75493 | -15.56407 | 77.49 | 102.51 | 41.48 | 1.23564 | 0.18708 |
| $C-H\ (CH_2)$ | $C$ | -0.92918 | -0.92918 | 0 | 0 | -153.47406 | 0.91771 | 0.81549 | -16.68412 | -16.49325 | 68.47 | 111.53 | 35.84 | 1.35486 | 0.29933 |
| $C-H\ (CH)$ | $C$ | -0.92918 | -0.92918 | -0.92918 | 0 | -154.40324 | 0.91771 | 0.77247 | -17.61330 | -17.42244 | 61.10 | 118.90 | 31.37 | 1.42988 | 0.37326 |
| $H_3C_aC_bH_2CH_2-$ $(C-C$ (a)) | $C_a$ | -0.92918 | 0 | 0 | 0 | -152.54487 | 0.91771 | 0.86359 | -15.75493 | -15.56407 | 63.82 | 116.18 | 30.08 | 1.83879 | 0.38106 |
| $H_3C_aC_bH_2CH_2-$ $(C-C$ (a)) | $C_b$ | -0.92918 | -0.92918 | 0 | 0 | -153.47406 | 0.91771 | 0.81549 | -16.68412 | -16.49325 | 56.41 | 123.59 | 26.06 | 1.90890 | 0.45117 |
| $R-H_2C_aC_b(H_2C_c-R')HCH_2-$ $(C-C$ (b)) | $C_b$ | -0.92918 | -0.92918 | -0.92918 | 0 | -154.40324 | 0.91771 | 0.77247 | -17.61330 | -17.42244 | 48.30 | 131.70 | 21.90 | 1.97162 | 0.51388 |
| $R-H_2C_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ $(C-C$ (c)) | $C_b$ | -0.92918 | -0.72457 | -0.72457 | -0.72457 | -154.71860 | 0.91771 | 0.75889 | -17.92866 | -17.73779 | 48.21 | 131.79 | 21.74 | 1.95734 | 0.50570 |
| $isoC_aC_b(H_2C_c-R')HCH_2-$ $(C-C$ (d)) | $C_b$ | -0.92918 | -0.92918 | -0.92918 | 0 | -154.40324 | 0.91771 | 0.77247 | -17.61330 | -17.42244 | 48.30 | 131.70 | 21.90 | 1.97162 | 0.51388 |
| $tertC_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ $(C-C$ (e)) | $C_b$ | -0.72457 | -0.72457 | -0.72457 | -0.72457 | -154.51399 | 0.91771 | 0.76765 | -17.92866 | -17.73779 | 50.04 | 129.96 | 22.66 | 1.94462 | 0.49298 |
| $tertC_aC_b(H_2C_c-R')HCH_2-$ $(C-C$ (f)) | $C_b$ | -0.72457 | -0.92918 | -0.92918 | 0 | -154.19863 | 0.91771 | 0.78155 | -17.40869 | -17.21783 | 52.78 | 127.22 | 24.04 | 1.92443 | 0.47279 |
| $isoC_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ $(C-C$ (f)) | $C_b$ | -0.72457 | -0.72457 | -0.72457 | -0.72457 | -154.51399 | 0.91771 | 0.76765 | -17.92866 | -17.73779 | 50.04 | 129.96 | 22.66 | 1.94462 | 0.49298 |

Table 15.180. The energy parameters ($eV$) of functional groups of alkyl sulfites.

| Parameters | $C-O$ (i) Group | $C-O$ (ii) Group | $O-S$ Group | $SO$ Group | $CH_3$ Group | $CH_2$ Group | $C-H$ Group | $C-C$ (a) Group | $C-C$ (b) Group | $C-C$ (c) Group | $C-C$ (d) Group | $C-C$ (e) Group | $C-C$ (f) Group |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $n_1$ | 1 | 1 | 1 | 2 | 3 | 2 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $n_2$ | 0 | 0 | 0 | 0 | 2 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $n_3$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $C_1$ | 0.5 | 0.5 | 0.5 | 0.5 | 0.75 | 0.75 | 0.75 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| $C_2$ | 1 | 1 | 0.77641 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $c_1$ | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $c_2$ | 0.85395 | 0.85395 | 1 | 1.20632 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 |
| $c_3$ | 0 | 0 | 0 | 0 | 0 | 1 | 1 | 0 | 0 | 0 | 1 | 1 | 0 |
| $c_4$ | 2 | 2 | 2 | 4 | 1 | 1 | 1 | 2 | 2 | 2 | 2 | 2 | 2 |
| $c_5$ | 0 | 0 | 0 | 1 | 3 | 2 | 1 | 0 | 0 | 0 | 0 | 0 | 0 |
| $C_{1o}$ | 0.5 | 0.5 | 0.5 | 0.5 | 0.75 | 0.75 | 0.75 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| $C_{2o}$ | 1 | 1 | 0.77641 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $V_e\ (eV)$ | -33.15757 | -33.47304 | -48.93512 | -82.63003 | -107.32728 | -70.41425 | -35.12015 | -28.79214 | -28.79214 | -29.10112 | -28.79214 | -29.10112 | -29.10112 |
| $V_p\ (eV)$ | 10.12103 | 10.15605 | 9.18680 | 19.31325 | 38.92728 | 25.78002 | 12.87680 | 9.33352 | 9.33352 | 9.37273 | 9.33352 | 9.37273 | 9.37273 |
| $T\ (eV)$ | 9.17389 | 9.32537 | 14.36741 | 20.81183 | 32.53914 | 21.06675 | 10.48582 | 6.77464 | 6.77464 | 6.90500 | 6.77464 | 6.90500 | 6.90500 |
| $V_m\ (eV)$ | -4.58695 | -4.66268 | -7.18371 | -10.40592 | -16.26957 | -10.53337 | -5.24291 | -3.38732 | -3.38732 | -3.45250 | -3.38732 | -3.45250 | -3.45250 |
| $E(_{AO/HO})\ (eV)$ | -14.63489 | -14.63489 | 0 | -11.52126 | -15.56407 | -15.56407 | -14.63489 | -15.56407 | -15.56407 | -15.35946 | -15.56407 | -15.35946 | -15.35946 |
| $\Delta E_{H_2MO}(_{AO/HO})\ (eV)$ | -1.44915 | -1.65376 | -0.92918 | -1.16125 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $E_T(_{AO/HO})\ (eV)$ | -13.18574 | -12.98113 | 0.92918 | -10.36001 | -15.56407 | -15.56407 | -14.63489 | -15.56407 | -15.56407 | -15.35946 | -15.56407 | -15.35946 | -15.35946 |
| $E_T(_{H_2MO})\ (eV)$ | -31.63533 | -31.63544 | -31.63543 | -63.27088 | -67.69451 | -49.66493 | -31.63533 | -31.63537 | -31.63537 | -31.63535 | -31.63537 | -31.63535 | -31.63535 |
| $E_T\left(atom-atom,msp^3.AO\right)(eV)$ | -1.44915 | -1.65376 | -0.92918 | 0 | 0 | 0 | 0 | -1.85836 | -1.85836 | -1.44915 | -1.85836 | -1.44915 | -1.44915 |
| $E_T(_{MO})\ (eV)$ | -33.08452 | -33.28912 | -32.56455 | -63.27074 | -67.69450 | -49.66493 | -31.63537 | -33.49373 | -33.49373 | -33.08452 | -33.49373 | -33.08452 | -33.08452 |
| $\omega\ \left(10^{15}\ rad/s\right)$ | 22.0240 | 12.1583 | 33.4164 | 17.6762 | 24.9286 | 24.2751 | 24.1759 | 9.43699 | 9.43699 | 15.4846 | 9.43699 | 9.55643 | 9.55643 |
| $E_K\ (eV)$ | 14.49660 | 8.00277 | 21.99527 | 11.63476 | 16.40846 | 15.97831 | 15.91299 | 6.21159 | 6.21159 | 10.19220 | 6.21159 | 6.29021 | 6.29021 |
| $\bar{E}_D\ (eV)$ | -0.24921 | -0.18631 | -0.30214 | -0.21348 | -0.25352 | -0.25017 | -0.24966 | -0.16515 | -0.16515 | -0.20896 | -0.16515 | -0.16416 | -0.16416 |
| $\bar{E}_{Kvib}\ (eV)$ | 0.13663<br>[21] | 0.13663<br>[21] | 0.08679<br>[42] | 0.12832<br>[43] | 0.35532<br>(Eq. (13.458)) | 0.35532<br>(Eq. (13.458)) | 0.35532<br>(Eq. (13.458)) | 0.12312<br>[2] | 0.17978<br>[4] | 0.09944<br>[5] | 0.12312<br>[2] | 0.12312<br>[2] | 0.12312<br>[2] |
| $\bar{E}_{osc}\ (eV)$ | -0.18089 | -0.11799 | -0.25875 | -0.14932 | -0.22757 | -0.14502 | -0.07200 | -0.10359 | -0.07526 | -0.15924 | -0.10359 | -0.10260 | -0.10260 |
| $E_{mag}\ (eV)$ | 0.14803 | 0.14803 | 0.11441 | 0.11441 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 |
| $E_T(_{Group})\ (eV)$ | -33.26541 | -33.40711 | -32.82330 | -63.56937 | -67.92207 | -49.80996 | -31.70737 | -33.59732 | -33.49373 | -33.24376 | -33.59732 | -33.18712 | -33.18712 |
| $E_{initial}(_{c_4\ AO/HO})\ (eV)$ | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 |
| $E_{initial}(_{c_5\ AO/HO})\ (eV)$ | 0 | 0 | 0 | -1.16125 | -13.59844 | -13.59844 | -13.59844 | 0 | 0 | 0 | 0 | 0 | 0 |
| $E_D(_{Group})\ (eV)$ | 3.99563 | 4.13733 | 3.55352 | 3.86856 | 12.49186 | 7.83016 | 3.32601 | 4.32754 | 4.29921 | 3.97398 | 4.17951 | 3.62128 | 3.91734 |

Table 15.181. The total bond energies of alkyl sulfites calculated using the functional group composition and the energies of Table 15.180 compared to the experimental values [3].

| Formula | Name | $C-O$ (i) Group | $C-O$ (ii) Group | $O-S$ Group | $SO$ Group | $CH_3$ | $CH_2$ | $CH$ | $C-C$ (a) | $C-C$ (b) | $C-C$ (c) | $C-C$ (d) | $C-C$ (e) | $C-C$ (f) | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $C_2H_6SO_3$ | Dimethyl sulfite | 2 | 0 | 2 | 1 | 2 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 43.95058 | 44.042 | 0.00207 |
| $C_4H_{10}SO_3$ | Diethyl sulfite | 0 | 2 | 2 | 1 | 2 | 2 | 0 | 2 | 0 | 0 | 0 | 0 | 0 | 68.54939 | 68.648 | 0.00143 |
| $C_8H_{18}SO_3$ | Dibutyl sulfite | 0 | 2 | 2 | 1 | 2 | 6 | 0 | 6 | 0 | 0 | 0 | 0 | 0 | 117.18019 | 117.191 | 0.00009 |

Table 15.182. The bond angle parameters of alkyl sulfites and experimental values [1]. In the calculation of $\theta_v$, the parameters from the preceding angle were used. $E_T$ is $E_T(atom-atom,msp^3.AO)$.

| Atoms of Angle | 2c' Bond 1 ($a_0$) | 2c' Bond 2 ($a_0$) | 2c' Terminal Atoms ($a_0$) | $E_{Coulombic}$ Atom 1 | Atom 1 Hybridization Designation (Table 15.3.A) | $E_{Coulombic}$ Atom 2 | Atom 2 Hybridization Designation (Table 15.3.A) | $c_2$ Atom 1 | $c_2$ Atom 2 | $C_1$ | $C_2$ | $c_1$ | $c_2'$ | $E_T$ (eV) | $\theta_v$ (°) | $\theta_1$ (°) | $\theta_2$ (°) | Cal. $\theta$ (°) | Exp. $\theta$ (°) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $\angle O_aSO_b$ | 2.81792 | 2.96203 | 4.6904 | -15.95954 $O_a$ | 10 | -16.11722 $O_c$ | 12 | 0.85252 | 0.84418 | 1 | 1 | 1 | 0.84835 | -1.65376 | | | | 108.46 | |
| $\angle O_bSO_c$ | 2.96203 | 2.96203 | 4.6476 | -16.11722 $O_b$ | 12 | -16.11722 $O_c$ | 12 | 0.84418 | 0.84418 | 1 | 1 | 1 | 0.84418 | -1.65376 | | | | 103.35 | |
| $\angle C_aO_bS$ | 2.68862 | 2.96203 | 4.8416 | -15.75493 $C_a$ | 7 | -10.36001 $S$ | S | 0.86359 | 0.77641 (Eq. (15.158)) | 1 | 0.77641 (Eq. (15.158)) | 1 | 0.82000 | -0.72457 | | | | 117.84 | |
| Methylene $\angle HC_aH$ | 2.11106 | 2.11106 | 3.4252 | -15.75493 | 7 | H | H | 0.86359 | 1 | 1 | 1 | 0.75 | 1.15796 | 0 | | | | 108.44 | 107 (propane) |
| $\angle C_aC_bC_c$ | | | | | | | | | | | | | | | 69.51 | | | 110.49 | 112 (propane)<br>113.8 (butane)<br>110.8 (isobutane) |
| $\angle C_aC_bH$ | | | | | | | | | | | | | | | 69.51 | | | 110.49 | 111.0 (butane)<br>111.4 (isobutane) |
| Methyl $\angle HC_aH$ | 2.09711 | 2.09711 | 3.4252 | -15.75493 | 7 | H | H | 0.86359 | 1 | 1 | 1 | 0.75 | 1.15796 | 0 | | | | 109.50 | |
| $\angle C_aC_bC_c$ | | | | | | | | | | | | | | | 70.56 | | | 109.44 | |
| $\angle C_aC_bH$ | | | | | | | | | | | | | | | 70.56 | | | 109.44 | |
| $\angle C_bC_aC_c$ iso $C_a$ | 2.91547 | 2.91547 | 4.7958 | -16.68412 $C_b$ | 26 | -16.68412 $C_c$ | 26 | 0.81549 | 0.81549 | 1 | 1 | 1 | 0.81549 | -1.85836 | | | | 110.67 | 110.8 (isobutane) |
| $\angle C_bC_aH$ iso $C_a$ | 2.91547 | 2.11323 | 4.1633 | -15.55033 $C_a$ | 5 | -14.82575 $C_b$ | 1 | 0.87495 | 0.91771 | 0.75 | 1 | 0.75 | 1.04887 | 0 | | | | 110.76 | |
| $\angle C_aC_bH$ iso $C_a$ | 2.91547 | 2.09711 | 4.1633 | -15.55033 $C_b$ | 5 | -14.82575 $C_a$ | 1 | 0.87495 | 0.91771 | 0.75 | 1 | 0.75 | 1.04887 | 0 | | | | 111.27 | 111.4 (isobutane) |
| $\angle C_bC_aC_b$ tert $C_a$ | 2.90327 | 2.90327 | 4.7958 | -16.68412 $C_b$ | 26 | -16.68412 $C_b$ | 26 | 0.81549 | 0.81549 | 1 | 1 | 1 | 0.81549 | -1.85836 | | | | 111.37 | 110.8 (isobutane) |
| $\angle C_bC_aC_d$ | | | | | | | | | | | | | | | 72.50 | | | 107.50 | |

## SULFATES ( $C_nH_{2n+2}\left(SO_4\right)_m$, $n = 2,3,4,5...\infty$ )

The alkyl sulfates, $C_nH_{2n+2}\left(SO_4\right)_m$, comprise a $C-O-SO_2-O-C$ moiety that comprises two types $C-O$ functional groups, one for methyl and one for alkyl, and $O-S$ and $SO_2$ functional groups. The alkyl portion of the alkyl sulfate may comprise at least two terminal methyl groups ($CH_3$) at each end of the chain, and may comprise methylene ($CH_2$), and methylyne ($CH$) functional groups as well as $C$ bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($\left(CH_3\right)_2 CH$) and t-butyl ($\left(CH_3\right)_3 C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups. The branched-chain-alkane groups in sulfates are equivalent to those in branched-chain alkanes.

The methyl and alkyl $C-O$ functional groups having $E_T\left(atom-atom,msp^3.AO\right) = -1.44915\ eV$ and $E_T\left(atom-atom,msp^3.AO\right) = -1.65376\ eV$, respectively, are equivalent to the corresponding groups given in the Sulfites section. The $O-S$ functional group having $E_T\left(atom-atom,msp^3.AO\right) = -0.92918\ eV$ is equivalent to that given in the Sulfites section. The $SO_2$ functional group is equivalent to that of sulfones with $E_T\left(atom-atom,msp^3.AO\right) = 0$ as given in the Sulfones section.

The symbols of the functional groups of branched-chain alkyl sulfates are given in Table 15.183. The geometrical (Eqs. (15.1-15.5) and (15.51)), intercept (Eqs. (15.80-15.87)), and energy (Eqs. (15.6-15.11) and (15.17-15.65)) parameters of alkyl sulfates are given in Tables 15.184, 15.185, and 15.186, respectively. The total energy of each alkyl sulfate given in Table 15.187 was calculated as the sum over the integer multiple of each $E_D\left(Group\right)$ of Table 15.186 corresponding to functional-group composition of the molecule. The bond angle parameters of alkyl sulfates determined using Eqs. (15.88-15.117) are given in Table 15.188. The color scale, translucent view of the charge-density of exemplary sulfate, dimethyl sulfate, comprising the concentric shells of atoms with the outer shell bridged by one or more $H_2$-type ellipsoidal MOs or joined with one or more hydrogen MOs is shown in Figure 15.31.

Figure 15.31. (A)-(B) Color scale, translucent views of the charge-density of dimethyl sulfate showing the orbitals of the atoms at their radii, the ellipsoidal surface of each $H$ or $H_2$-type ellipsoidal MO that transitions to the corresponding outer shell of the atom(s) participating in each bond, and the hydrogen nuclei (red, not to scale).

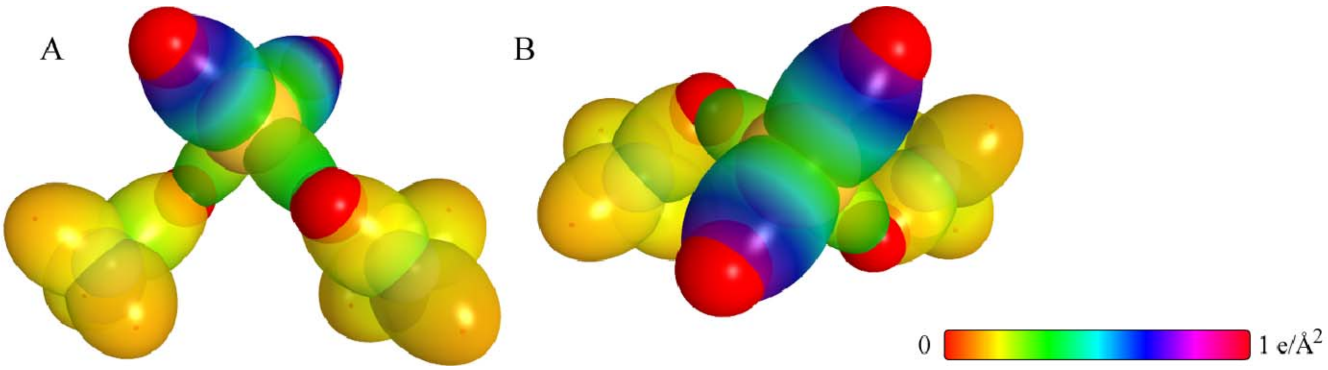


Table 15.183. The symbols of functional groups of alkyl sulfates.

| Functional Group | Group Symbol |
|---|---|
| $C$-$O$ (*methyl*) | $C-O$ (i) |
| $C$-$O$ (*alkyl*) | $C-O$ (ii) |
| $O$-$SO_3$ | $O-S$ |
| $SO_2$ | $SO_2$ |
| $CH_3$ group | $C-H\ (CH_3)$ |
| $CH_2$ group | $C-H\ (CH_2)$ |
| $CH$ | $C-H$ |
| $CC$ bond (*n*-$C$) | $C-C$ (a) |
| $CC$ bond (*iso*-$C$) | $C-C$ (b) |
| $CC$ bond (*tert*-$C$) | $C-C$ (c) |
| $CC$ (*iso* to *iso*-$C$) | $C-C$ (d) |
| $CC$ (*t* to *t*-$C$) | $C-C$ (e) |
| $CC$ (*t* to *iso*-$C$) | $C-C$ (f) |

Table 15.184. The geometrical bond parameters of alkyl sulfates and experimental values [1].

| Parameter | $C-O$ (i) Group | $C-O$ (ii) Group | $O-S$ | $SO_2$ | $C-H\left(CH_3\right)$ Group | $C-H\left(CH_2\right)$ Group | $C-H$ Group | $C-C$ (a) Group | $C-C$ (b) Group | $C-C$ (c) Group | $C-C$ (d) Group | $C-C$ (e) Group | $C-C$ (f) Group |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $a\left(a_0\right)$ | 1.80717 | 1.79473 | 1.70299 | 1.85851 | 1.64920 | 1.67122 | 1.67465 | 2.12499 | 2.12499 | 2.10725 | 2.12499 | 2.10725 | 2.10725 |
| $c'\left(a_0\right)$ | 1.34431 | 1.33968 | 1.48102 | 1.36327 | 1.04856 | 1.05553 | 1.05661 | 1.45744 | 1.45744 | 1.45164 | 1.45744 | 1.45164 | 1.45164 |
| Bond Length $2c'$ $\left(\mathring{A}\right)$ | 1.42276 | 1.41785 | 1.56744 | 1.44282 | 1.10974 | 1.11713 | 1.11827 | 1.54280 | 1.54280 | 1.53635 | 1.54280 | 1.53635 | 1.53635 |
| Exp. Bond Length $\left(\mathring{A}\right)$ |  |  | 1.574 ($H_2SO_4$) | 1.435 (dimethyl sulfone) | 1.107<br>($C-H$ propane)<br>1.117<br>($C-H$ butane) | 1.107<br>($C-H$ propane)<br>1.117<br>($C-H$ butane) | 1.122 (isobutane) | 1.532 (propane)<br>1.531 (butane) | 1.532 (propane)<br>1.531 (butane) | 1.532 (propane)<br>1.531 (butane) | 1.532 (propane)<br>1.531 (butane) | 1.532 (propane)<br>1.531 (butane) | 1.532 (propane)<br>1.531 (butane) |
| $b,c\left(a_0\right)$ | 1.20776 | 1.19429 | 0.84069 | 1.26315 | 1.27295 | 1.29569 | 1.29924 | 1.54616 | 1.54616 | 1.52750 | 1.54616 | 1.52750 | 1.52750 |
| $e$ | 0.74388 | 0.74645 | 0.86966 | 0.73353 | 0.63580 | 0.63159 | 0.63095 | 0.68600 | 0.68600 | 0.68888 | 0.68600 | 0.68888 | 0.68888 |

Table 15.185. The MO to HO intercept geometrical bond parameters of alkyl sulfates. $R$, $R'$, $R''$ are $H$ or alkyl groups. $E_T$ is $E_T(atom-atom,msp^3.AO)$.

| Bond | Atom | $E_T$ (eV) Bond 1 | $E_T$ (eV) Bond 2 | $E_T$ (eV) Bond 3 | $E_T$ (eV) Bond 4 | Final Total Energy $C2sp^3$ (eV) | $r_{initial}$ $(a_0)$ | $r_{final}$ $(a_0)$ | $E_{Coulomb}$ (eV) Final | $E(C2sp^3)$ (eV) Final | $\theta'$ $(^\circ)$ | $\theta_1$ $(^\circ)$ | $\theta_2$ $(^\circ)$ | $d_1$ $(a_0)$ | $d_2$ $(a_0)$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $(RO)_2(O_a)S=O_a$ | $S$ | 0 | 0 | -0.46459 | -0.46459 | | 1.32010 | 0.86359 | -15.75493 | | 90.46 | 89.54 | 43.13 | 1.35635 | 0.00693 |
| $(RO)_2(O_a)S=O_a$ | $O_a$ | 0 | 0 | 0 | 0 | | 1.00000 | 0.91771 | -14.82575 | | 95.05 | 84.95 | 46.36 | 1.28256 | 0.08071 |
| $CH_3O_a-S(O_2)OR'$ | $S$ | -0.46459 | -0.46459 | 0 | 0 | | 1.32010 | 0.86359 | -15.75493 | | 126.68 | 53.32 | 55.47 | 0.96521 | 0.51581 |
| $CH_3O_a-S(O_2)OR'$ $(C-O$ (i)) | $O_a$ | -0.46459 | -0.72457 | 0 | 0 | | 1.00000 | 0.84957 | -16.01492 | | 126.03 | 53.97 | 54.81 | 0.98133 | 0.49969 |
| $RCH_2O_a-S(O_2)OR'$ $(C-O$ (ii)) | $O_a$ | -0.46459 | -0.82688 | 0 | 0 | | 1.00000 | 0.84418 | -16.11722 | | 125.77 | 54.23 | 54.56 | 0.98753 | 0.49349 |
| $H_3C_a-O_aS(O_2)OR$ $(C-O$ (i)) | $O_a$ | -0.72457 | -0.46459 | 0 | 0 | | 1.00000 | 0.84957 | -16.01492 | | 93.85 | 86.15 | 44.57 | 1.28731 | 0.05700 |
| $H_3C_a-O_aS(O_2)OR$ $(C-O$ (i)) | $C_a$ | -0.72457 | 0 | 0 | 0 | -152.34026 | 0.91771 | 0.87495 | -15.55033 | -15.35946 | 95.98 | 84.02 | 46.10 | 1.25319 | 0.09112 |
| $RH_2C_a-O_aS(O_2)OR'$ $(C-O$ (ii)) | $O_a$ | -0.82688 | -0.46459 | 0 | 0 | | 1.00000 | 0.84418 | -16.11722 | | 94.50 | 85.50 | 44.80 | 1.27343 | 0.06624 |
| $RH_2C_a-O_aS(O_2)OR'$ $(C-O$ (ii)) | $C_a$ | -0.82688 | -0.92918 | 0 | 0 | -153.37175 | 0.91771 | 0.82053 | -16.58181 | -16.39095 | 92.41 | 87.59 | 43.35 | 1.30512 | 0.03456 |
| $C-H\ (CH_3)$ | $C$ | -0.92918 | 0 | 0 | 0 | -152.54487 | 0.91771 | 0.86359 | -15.75493 | -15.56407 | 77.49 | 102.51 | 41.48 | 1.23564 | 0.18708 |
| $C-H\ (CH_2)$ | $C$ | -0.92918 | -0.92918 | 0 | 0 | -153.47406 | 0.91771 | 0.81549 | -16.68412 | -16.49325 | 68.47 | 111.53 | 35.84 | 1.35486 | 0.29933 |
| $C-H\ (CH)$ | $C$ | -0.92918 | -0.92918 | -0.92918 | 0 | -154.40324 | 0.91771 | 0.77247 | -17.61330 | -17.42244 | 61.10 | 118.90 | 31.37 | 1.42988 | 0.37326 |
| $H_3C_aC_bH_2CH_2-$ $(C-C$ (a)) | $C_a$ | -0.92918 | 0 | 0 | 0 | -152.54487 | 0.91771 | 0.86359 | -15.75493 | -15.56407 | 63.82 | 116.18 | 30.08 | 1.83879 | 0.38106 |
| $H_3C_aC_bH_2CH_2-$ $(C-C$ (a)) | $C_b$ | -0.92918 | -0.92918 | 0 | 0 | -153.47406 | 0.91771 | 0.81549 | -16.68412 | -16.49325 | 56.41 | 123.59 | 26.06 | 1.90890 | 0.45117 |
| $R-H_2C_aC_b(H_2C_c-R')HCH_2-$ $(C-C$ (b)) | $C_b$ | -0.92918 | -0.92918 | -0.92918 | 0 | -154.40324 | 0.91771 | 0.77247 | -17.61330 | -17.42244 | 48.30 | 131.70 | 21.90 | 1.97162 | 0.51388 |
| $R-H_2C_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ $(C-C$ (c)) | $C_b$ | -0.92918 | -0.72457 | -0.72457 | -0.72457 | -154.71860 | 0.91771 | 0.75889 | -17.92866 | -17.73779 | 48.21 | 131.79 | 21.74 | 1.95734 | 0.50570 |
| $isoC_aC_b(H_2C_c-R')HCH_2-$ $(C-C$ (d)) | $C_b$ | -0.92918 | -0.92918 | -0.92918 | 0 | -154.40324 | 0.91771 | 0.77247 | -17.61330 | -17.42244 | 48.30 | 131.70 | 21.90 | 1.97162 | 0.51388 |
| $tertC_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ $(C-C$ (e)) | $C_b$ | -0.72457 | -0.72457 | -0.72457 | -0.72457 | -154.51399 | 0.91771 | 0.76765 | -17.92866 | -17.73779 | 50.04 | 129.96 | 22.66 | 1.94462 | 0.49298 |
| $tertC_aC_b(H_2C_c-R')HCH_2-$ $(C-C$ (f)) | $C_b$ | -0.72457 | -0.92918 | -0.92918 | 0 | -154.19863 | 0.91771 | 0.78155 | -17.40869 | -17.21783 | 52.78 | 127.22 | 24.04 | 1.92443 | 0.47279 |
| $isoC_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ $(C-C$ (f)) | $C_b$ | -0.72457 | -0.72457 | -0.72457 | -0.72457 | -154.51399 | 0.91771 | 0.76765 | -17.92866 | -17.73779 | 50.04 | 129.96 | 22.66 | 1.94462 | 0.49298 |

Table 15.186. The energy parameters ($eV$) of functional groups of alkyl sulfates.

| Parameters | $C-O$ (i) Group | $C-O$ (ii) Group | $O-S$ Group | $SO_2$ Group | $CH_3$ Group | $CH_2$ Group | $C-H$ Group | $C-C$ (a) Group | $C-C$ (b) Group | $C-C$ (c) Group | $C-C$ (d) Group | $C-C$ (e) Group | $C-C$ (f) Group |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $n_1$ | 1 | 1 | 1 | 4 | 3 | 2 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $n_2$ | 0 | 0 | 0 | 0 | 2 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $n_3$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $C_1$ | 0.5 | 0.5 | 0.5 | 0.5 | 0.75 | 0.75 | 0.75 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| $C_2$ | 1 | 1 | 0.77641 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $c_1$ | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $c_2$ | 0.85395 | 0.85395 | 1 | 1.20632 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 |
| $c_3$ | 0 | 0 | 0 | 1 | 0 | 1 | 1 | 0 | 0 | 0 | 1 | 1 | 0 |
| $c_4$ | 2 | 2 | 2 | 8 | 1 | 1 | 1 | 2 | 2 | 2 | 2 | 2 | 2 |
| $c_5$ | 0 | 0 | 0 | 1 | 3 | 2 | 1 | 0 | 0 | 0 | 0 | 0 | 0 |
| $C_{1o}$ | 0.5 | 0.5 | 0.5 | 0.5 | 0.75 | 0.75 | 0.75 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| $C_{2o}$ | 1 | 1 | 0.77641 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $V_e\ (eV)$ | -33.15757 | -33.47304 | -48.93512 | -180.36454 | -107.32728 | -70.41425 | -35.12015 | -28.79214 | -28.79214 | -29.10112 | -28.79214 | -29.10112 | -29.10112 |
| $V_p\ (eV)$ | 10.12103 | 10.15605 | 9.18680 | 39.92103 | 38.92728 | 25.78002 | 12.87680 | 9.33352 | 9.33352 | 9.37273 | 9.33352 | 9.37273 | 9.37273 |
| $T\ (eV)$ | 9.17389 | 9.32537 | 14.36741 | 48.52397 | 32.53914 | 21.06675 | 10.48582 | 6.77464 | 6.77464 | 6.90500 | 6.77464 | 6.90500 | 6.90500 |
| $V_m\ (eV)$ | -4.58695 | -4.66268 | -7.18371 | -24.26198 | -16.26957 | -10.53337 | -5.24291 | -3.38732 | -3.38732 | -3.45250 | -3.38732 | -3.45250 | -3.45250 |
| $E(_{AO/HO})\ (eV)$ | -14.63489 | -14.63489 | 0 | -11.52126 | -15.56407 | -15.56407 | -14.63489 | -15.56407 | -15.56407 | -15.35946 | -15.56407 | -15.35946 | -15.35946 |
| $\Delta E_{H_2MO}(_{AO/HO})\ (eV)$ | -1.44915 | -1.65376 | -0.92918 | -1.16125 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $E_T(_{AO/HO})\ (eV)$ | -13.18574 | -12.98113 | 0.92918 | -10.36001 | -15.56407 | -15.56407 | -14.63489 | -15.56407 | -15.56407 | -15.35946 | -15.56407 | -15.35946 | -15.35946 |
| $E_T(_{H_2MO})\ (eV)$ | -31.63533 | -31.63544 | -31.63543 | -126.54154 | -67.69451 | -49.66493 | -31.63533 | -31.63537 | -31.63537 | -31.63535 | -31.63537 | -31.63535 | -31.63535 |
| $E_T\left(atom-atom, msp^3.AO\right)(eV)$ | -1.44915 | -1.65376 | -0.92918 | 0 | 0 | 0 | 0 | -1.85836 | -1.85836 | -1.44915 | -1.85836 | -1.44915 | -1.44915 |
| $E_T(_{MO})\ (eV)$ | -33.08452 | -33.28912 | -32.56455 | -126.54147 | -67.69450 | -49.66493 | -31.63537 | -33.49373 | -33.49373 | -33.08452 | -33.49373 | -33.08452 | -33.08452 |
| $\omega\ \left(10^{15}\ rad/s\right)$ | 22.0240 | 12.1583 | 33.4164 | 11.5378 | 24.9286 | 24.2751 | 24.1759 | 9.43699 | 9.43699 | 15.4846 | 9.43699 | 9.55643 | 9.55643 |
| $E_K\ (eV)$ | 14.49660 | 8.00277 | 21.99527 | 7.59437 | 16.40846 | 15.97831 | 15.91299 | 6.21159 | 6.21159 | 10.19220 | 6.21159 | 6.29021 | 6.29021 |
| $\bar{E}_D\ (eV)$ | -0.24921 | -0.18631 | -0.30214 | -0.17247 | -0.25352 | -0.25017 | -0.24966 | -0.16515 | -0.16515 | -0.20896 | -0.16515 | -0.16416 | -0.16416 |
| $\bar{E}_{Kvib}\ (eV)$ | 0.13663<br>[21] | 0.13663<br>[21] | 0.08679<br>[42] | 0.12832<br>[43] | 0.35532<br>(Eq. (13.458)) | 0.35532<br>(Eq. (13.458)) | 0.35532<br>(Eq. (13.458)) | 0.12312<br>[2] | 0.17978<br>[4] | 0.09944<br>[5] | 0.12312<br>[2] | 0.12312<br>[2] | 0.12312<br>[2] |
| $\bar{E}_{osc}\ (eV)$ | -0.18089 | -0.11799 | -0.25875 | -0.10831 | -0.22757 | -0.14502 | -0.07200 | -0.10359 | -0.07526 | -0.15924 | -0.10359 | -0.10260 | -0.10260 |
| $E_{mag}\ (eV)$ | 0.14803 | 0.14803 | 0.11441 | 0.11441 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 |
| $E_T(_{Group})\ (eV)$ | -33.26541 | -33.40711 | -32.82330 | -126.97472 | -67.92207 | -49.80996 | -31.70737 | -33.59732 | -33.49373 | -33.24376 | -33.59732 | -33.18712 | -33.18712 |
| $E_{initial}(_{c_4\ AO/HO})\ (eV)$ | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 |
| $E_{initial}(_{c_5\ AO/HO})\ (eV)$ | 0 | 0 | 0 | -1.16125 | -13.59844 | -13.59844 | -13.59844 | 0 | 0 | 0 | 0 | 0 | 0 |
| $E_D(_{Group})\ (eV)$ | 3.99563 | 4.13733 | 3.55352 | 8.61994 | 12.49186 | 7.83016 | 3.32601 | 4.32754 | 4.29921 | 3.97398 | 4.17951 | 3.62128 | 3.91734 |

Table 15.187. The total bond energies of alkyl sulfates calculated using the functional group composition and the energies of Table 15.186 compared to the experimental values [3].

| Formula | Name | $C-O$ (i) Group | $C-O$ (ii) Group | $O-S$ Group | $SO_2$ Group | $CH_3$ | $CH_2$ | $CH$ | $C-C$ (a) | $C-C$ (b) | $C-C$ (c) | $C-C$ (d) | $C-C$ (e) | $C-C$ (f) | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $C_2H_6SO_4$ | Dimethyl sulfate | 2 | 0 | 2 | 1 | 2 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 48.70196 | 48.734 | 0.00067 |
| $C_4H_{10}SO_4$ | Diethyl sulfate | 0 | 2 | 2 | 1 | 2 | 2 | 0 | 2 | 0 | 0 | 0 | 0 | 0 | 73.30077 | 73.346 | 0.00061 |
| $C_6H_{14}SO_4$ | Dipropyl sulfate | 0 | 2 | 2 | 1 | 2 | 4 | 0 | 4 | 0 | 0 | 0 | 0 | 0 | 97.61617 | 97.609 | -0.00008 |

Table 15.188. The bond angle parameters of alkyl sulfates and experimental values [1]. In the calculation of $\theta_v$, the parameters from the preceding angle were used. $E_T$ is $E_T$ ($atom - atom, msp^3.AO$).

| Atoms of Angle | 2c' Bond 1 ($a_0$) | 2c' Bond 2 ($a_0$) | 2c' Terminal Atoms ($a_0$) | $E_{Coulombic}$ Atom 1 | Atom 1 Hybridization Designation (Table 15.3.A) | $E_{Coulombic}$ Atom 2 | Atom 2 Hybridization Designation (Table 15.3.A) | $c_2$ Atom 1 | $c_2$ Atom 2 | $C_1$ | $C_2$ | $c_1$ | $c_2'$ | $E_T$ (eV) | $\theta_v$ (°) | $\theta_1$ (°) | $\theta_2$ (°) | Cal. $\theta$ (°) | Exp. $\theta$ (°) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $\angle O_aSO_b$ | 2.72654 | 2.72654 | 4.7329 | -15.95954<br>$O_a$ | 10 | -15.95954<br>$O_b$ | 10 | 0.85252 | 0.85252 | 1 | 1 | 1 | 0.85252 | -1.65376 | | | | 120.44 | 120.9 [44]<br>(dimethyl sulfate) |
| $\angle O_aSO_c$ | 2.72654 | 2.96203 | 4.6690 | -15.95954<br>$O_a$ | 10 | -16.11722<br>$O_c$ | 12 | 0.85252 | 0.84418 | 1 | 1 | 1 | 0.84835 | -1.65376 | | | | 110.26 | 109.67 [44]<br>(dimethyl sulfate) |
| $\angle O_cSO_d$ | 2.96203 | 2.96203 | 4.6476 | -16.11722<br>$O_c$ | 12 | -16.11722<br>$O_d$ | 12 | 0.84418 | 0.84418 | 1 | 1 | 1 | 0.84418 | -1.65376 | | | | 103.35 | 103.85 [44]<br>(dimethyl sulfate) |
| $\angle C_aO_cS$ | 2.68862 | 2.96203 | 4.8416 | -15.75493<br>$C_a$ | 7 | -10.36001<br>$S$ | S | 0.86359 | 0.77641<br>(Eq. (15.158)) | 1 | 0.77641<br>(Eq. (15.158)) | 1 | 0.82000 | -0.72457 | | | | 117.84 | 117.43[44]<br>(dimethyl sulfate) |
| Methylene<br>$\angle HC_aH$ | 2.11106 | 2.11106 | 3.4252 | -15.75493 | 7 | H | H | 0.86359 | 1 | 1 | 1 | 0.75 | 1.15796 | 0 | | | | 108.44 | 107<br>(propane) |
| $\angle C_aC_bC_c$ | | | | | | | | | | | | | | | 69.51 | | | 110.49 | 112<br>(propane)<br>113.8<br>(butane)<br>110.8<br>(isobutane) |
| $\angle C_aC_bH$ | | | | | | | | | | | | | | | 69.51 | | | 110.49 | 111.0<br>(butane)<br>111.4<br>(isobutane) |
| Methyl<br>$\angle HC_aH$ | 2.09711 | 2.09711 | 3.4252 | -15.75493 | 7 | H | H | 0.86359 | 1 | 1 | 1 | 0.75 | 1.15796 | 0 | | | | 109.50 | |
| $\angle C_aC_bC_c$ | | | | | | | | | | | | | | | 70.56 | | | 109.44 | |
| $\angle C_aC_bH$ | | | | | | | | | | | | | | | 70.56 | | | 109.44 | |
| $\angle C_bC_aC_c$<br>iso $C_a$ | 2.91547 | 2.91547 | 4.7958 | -16.68412<br>$C_b$ | 26 | -16.68412<br>$C_c$ | 26 | 0.81549 | 0.81549 | 1 | 1 | 1 | 0.81549 | -1.85836 | | | | 110.67 | 110.8<br>(isobutane) |
| $\angle C_bC_aH$<br>iso $C_a$ | 2.91547 | 2.11323 | 4.1633 | -15.55033<br>$C_a$ | 5 | -14.82575<br>$C_b$ | 1 | 0.87495 | 0.91771 | 0.75 | 1 | 0.75 | 1.04887 | 0 | | | | 110.76 | |
| $\angle C_aC_bH$<br>iso $C_a$ | 2.91547 | 2.09711 | 4.1633 | -15.55033<br>$C_b$ | 5 | -14.82575<br>$C_a$ | 1 | 0.87495 | 0.91771 | 0.75 | 1 | 0.75 | 1.04887 | 0 | | | | 111.27 | 111.4<br>(isobutane) |
| $\angle C_bC_aC_b$<br>tert $C_a$ | 2.90327 | 2.90327 | 4.7958 | -16.68412<br>$C_b$ | 26 | -16.68412<br>$C_b$ | 26 | 0.81549 | 0.81549 | 1 | 1 | 1 | 0.81549 | -1.85836 | | | | 111.37 | 110.8<br>(isobutane) |
| $\angle C_bC_aC_d$ | | | | | | | | | | | | | | | 72.50 | | | 107.50 | |

## NITROALKANES ($C_nH_{2n+2-m}\left(NO_2\right)_m$, $n=1,2,3,4,5...\infty$)

The nitroalkanes, $C_nH_{2n+2-m}\left(NO_2\right)_m$, comprise a $NO_2$ functional group and a $C-N$ functional group. The alkyl portion of the nitroalkane may comprise at least two terminal methyl groups ($CH_3$) at each end of the chain, and may comprise methylene ($CH_2$), and methylyne ($CH$) functional groups as well as $C$ bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($\left(CH_3\right)_2CH$) and t-butyl ($\left(CH_3\right)_3C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups. The branched-chain-alkane groups in nitroalkanes are equivalent to those in branched-chain alkanes.

The electron configuration of oxygen is $1s^22s^22p^4$, and the orbital arrangement given by Eq. (10.154) has two unpaired electrons corresponding to the ground state ${}^3P_2$. The electron configuration of nitrogen is $1s^22s^22p^3$, and the orbital arrangement given by Eq. (10.134) has three unpaired electrons corresponding to the ground state ${}^4S^0_{3/2}$. The bonding in the nitro ($NO_2$) functional group is similar to that in the $SO_2$ group given previously. It also has similarities to the bonding in the carbonyl functional group. In the $NO_2$ group, the two unpaired electrons of the $O$ atoms form a MO with two unpaired electrons of the nitrogen atom such that the MO comprises a linear combination of two bonds, each of bond order two involving the nitrogen AOs and oxygen AOs of both oxygen atoms. The nitrogen atom is then energy matched to the $C2sp^3$ HO. In nitroalkanes, the $C2sp^3$ HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of $E\left(C,2sp^3\right)=-14.63489\ eV$ (Eq. (15.25)), the $N$ AO has an energy of $E\left(N\right)=-14.53414\ eV$, and the $O$ AO has an energy of $E\left(O\right)=-13.61806\ eV$ [38]. To meet the equipotential condition of the union of the $N=O$ $H_2$-type-ellipsoidal-MO with these orbitals, the hybridization factor $c_2$ of Eq. (15.61) for the $N=O$-bond MO given by Eqs. (15.77) and (15.79) is:

$$c_2\left(O\ to\ N2p\ to\ C2sp^3HO\right)=\frac{E\left(O\right)}{E\left(N\right)}c_2\left(C2sp^3HO\right)=\frac{-13.61806\ eV}{-14.53414\ eV}\left(0.91771\right)=0.85987 \tag{15.159}$$

Since there are two $O$ atoms in a linear combination that comprises the bonding of the $NO_2$ group, the unpaired electrons of each $O$ cancel each others effect such that $E_{mag}$ is not subtracted from the total energy of $NO_2$. Additionally, $E_T\left(atom-atom,msp^3.AO\right)=-3.71673\ eV=4\left(-0.92918\ eV\right)$ (Eq. (14.513)) is the maximum given the bonding involves four electrons comprising two bonds, each having a bond order of one.

The $C-N$ group is equivalent to that of primary amines except that the energies corresponding to vibration in the transition state are matched to a nitroalkane and $\Delta E_{H_2MO}\left(AO/HO\right)=-0.72457\ eV$ for nitroalkane and $\Delta E_{H_2MO}\left(AO/HO\right)=-1.44915\ eV$ for primary amines. Whereas, $E_T\left(atom-atom,msp^3.AO\right)=-1.44915\ eV$ for both functional groups. This condition matches the energy of the $C-N$ group with the $NO_2$ having $\Delta E_{H_2MO}\left(AO/HO\right)=0$.

The symbols of the functional groups of branched-chain nitroalkanes are given in Table 15.189. The geometrical (Eqs. (15.1-15.5) and (15.51)), intercept (Eqs. (15.80-15.87)), and energy (Eqs. (15.6-15.11) and (15.17-15.65)) parameters of nitroalkanes are given in Tables 15.190, 15.191, and 15.192, respectively. The total energy of each nitroalkane given in Table 15.193 was calculated as the sum over the integer multiple of each $E_D\left(Group\right)$ of Table 15.192 corresponding to functional-group composition of the molecule. $E_{mag}$ given by Eq. (15.67) was subtracted for each t-butyl group. The bond angle parameters of nitroalkanes determined using Eqs. (15.88-15.117) are given in Table 15.194. The color scale, translucent view of the charge-density of exemplary nitroalkane, nitroethane, comprising the concentric shells of atoms with the outer shell bridged by one or more $H_2$-type ellipsoidal MOs or joined with one or more hydrogen MOs is shown in Figure 15.32.

Figure 15.32. Color scale, translucent view of the charge-density of nitroethane showing the orbitals of the atoms at their radii, the ellipsoidal surface of each $H$ or $H_2$-type ellipsoidal MO that transitions to the corresponding outer shell of the atom(s) participating in each bond, and the hydrogen nuclei (red, not to scale).

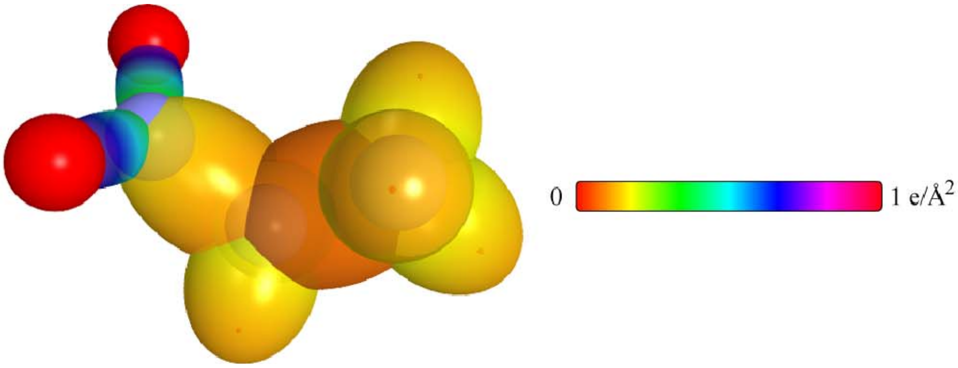


Table 15.189. The symbols of functional groups of nitroalkanes.

| Functional Group | Group Symbol |
|---|---|
| $NO_2$ group | $NO_2$ |
| *C-N* | $C-N$ |
| $CH_3$ group | $C-H\ (CH_3)$ |
| $CH_2$ group | $C-H\ (CH_2)$ |
| *CH* | $C-H$ |
| *CC* bond (*n-C*) | $C-C$ (a) |
| *CC* bond (*iso-C*) | $C-C$ (b) |
| *CC* bond (*tert-C*) | $C-C$ (c) |
| *CC* (*iso* to *iso-C*) | $C-C$ (d) |
| *CC* (*t* to *t-C*) | $C-C$ (e) |
| *CC* (*t* to *iso-C*) | $C-C$ (f) |

Table 15.190. The geometrical bond parameters of nitroalkanes and experimental values [1].

| Parameter | $NO_2$ Group | $C-N$ Group | $C-H\ (CH_3)$ Group | $C-H\ (CH_2)$ Group | $C-H$ Group | $C-C$ (a) Group | $C-C$ (b) Group | $C-C$ (c) Group | $C-C$ (d) Group | $C-C$ (e) Group | $C-C$ (f) Group |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $a\ (a_0)$ | 1.33221 | 1.97794 | 1.64920 | 1.67122 | 1.67465 | 2.12499 | 2.12499 | 2.10725 | 2.12499 | 2.10725 | 2.10725 |
| $c'\ (a_0)$ | 1.15421 | 1.40639 | 1.04856 | 1.05553 | 1.05661 | 1.45744 | 1.45744 | 1.45164 | 1.45744 | 1.45164 | 1.45164 |
| Bond Length $2c'$ ($\AA$) | 1.22157 | 1.48846 | 1.10974 | 1.11713 | 1.11827 | 1.54280 | 1.54280 | 1.53635 | 1.54280 | 1.53635 | 1.53635 |
| Exp. Bond Length ($\AA$) | 1.224 (nitromethane) | 1.489 (nitromethane) | 1.107 ($C-H$ propane)<br>1.117 ($C-H$ butane) | 1.107 ($C-H$ propane)<br>1.117 ($C-H$ butane) | 1.122 (isobutane) | 1.532 (propane)<br>1.531 (butane) | 1.532 (propane)<br>1.531 (butane) | 1.532 (propane)<br>1.531 (butane) | 1.532 (propane)<br>1.531 (butane) | 1.532 (propane)<br>1.531 (butane) | 1.532 (propane)<br>1.531 (butane) |
| $b,c\ (a_0)$ | 0.66526 | 1.39079 | 1.27295 | 1.29569 | 1.29924 | 1.54616 | 1.54616 | 1.52750 | 1.54616 | 1.52750 | 1.52750 |
| $e$ | 0.86639 | 0.71104 | 0.63580 | 0.63159 | 0.63095 | 0.68600 | 0.68600 | 0.68888 | 0.68600 | 0.68888 | 0.68888 |

Table 15.191. The MO to HO intercept geometrical bond parameters of nitroalkanes. $R$, $R'$, $R''$ are $H$ or alkyl groups. $E_T$ is $E_T(atom-atom,msp^3.AO)$.

| Bond | Atom | $E_T$ (eV) Bond 1 | $E_T$ (eV) Bond 2 | $E_T$ (eV) Bond 3 | $E_T$ (eV) Bond 4 | Final Total Energy $C2sp^3$ (eV) | $r_{initial}$ $(a_0)$ | $r_{final}$ $(a_0)$ | $E_{Coulomb}$ (eV) Final | $E(C2sp^3)$ (eV) Final | $\theta'$ $(^\circ)$ | $\theta_1$ $(^\circ)$ | $\theta_2$ $(^\circ)$ | $d_1$ $(a_0)$ | $d_2$ $(a_0)$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $RN(O)=O$ | $O$ | -0.92918 | 0 | 0 | 0 |  | 1.00000 | 0.86359 | -15.75493 |  | 135.25 | 44.75 | 66.05 | 0.54089 | 0.61333 |
| $RN(O)=O$ | $N$ | -0.92918 | -0.92918 | -0.72457 | 0 |  | 0.93084 | 0.78155 | -17.40869 |  | 131.57 | 48.43 | 61.50 | 0.63558 | 0.51864 |
| $H_3C-NO_2$ | $C$ | -0.72457 | 0 | 0 | 0 | -152.34026 | 0.91771 | 0.87495 | -15.55033 | -15.35946 | 80.47 | 99.53 | 38.35 | 1.55123 | 0.14484 |
| $RH_2C-NO_2$<br>$R=H,alkyl$ | $N$ | -0.92918 | -0.92918 | -0.72457 | 0 |  | 0.93084 | 0.78155 | -17.40869 |  | 69.30 | 110.70 | 31.71 | 1.68259 | 0.27620 |
| $-H_2C_a-NO_2$ | $C_a$ | -0.72457 | -0.92918 | 0 | 0 | -153.26945 | 0.91771 | 0.82562 | -16.47951 | -16.28864 | 74.96 | 105.04 | 34.98 | 1.62061 | 0.21422 |
| $C-H\ (CH_3)$ | $C$ | -0.92918 | 0 | 0 | 0 | -152.54487 | 0.91771 | 0.86359 | -15.75493 | -15.56407 | 77.49 | 102.51 | 41.48 | 1.23564 | 0.18708 |
| $C-H\ (CH_2)$ | $C$ | -0.92918 | -0.92918 | 0 | 0 | -153.47406 | 0.91771 | 0.81549 | -16.68412 | -16.49325 | 68.47 | 111.53 | 35.84 | 1.35486 | 0.29933 |
| $C-H\ (CH)$ | $C$ | -0.92918 | -0.92918 | -0.92918 | 0 | -154.40324 | 0.91771 | 0.77247 | -17.61330 | -17.42244 | 61.10 | 118.90 | 31.37 | 1.42988 | 0.37326 |
| $H_3C_aC_bH_2CH_2-$<br>($C-C$ (a)) | $C_a$ | -0.92918 | 0 | 0 | 0 | -152.54487 | 0.91771 | 0.86359 | -15.75493 | -15.56407 | 63.82 | 116.18 | 30.08 | 1.83879 | 0.38106 |
| $H_3C_aC_bH_2CH_2-$<br>($C-C$ (a)) | $C_b$ | -0.92918 | -0.92918 | 0 | 0 | -153.47406 | 0.91771 | 0.81549 | -16.68412 | -16.49325 | 56.41 | 123.59 | 26.06 | 1.90890 | 0.45117 |
| $R-H_2C_aC_b(H_2C_c-R')HCH_2-$<br>($C-C$ (b)) | $C_b$ | -0.92918 | -0.92918 | -0.92918 | 0 | -154.40324 | 0.91771 | 0.77247 | -17.61330 | -17.42244 | 48.30 | 131.70 | 21.90 | 1.97162 | 0.51388 |
| $R-H_2C_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$<br>($C-C$ (c)) | $C_b$ | -0.92918 | -0.72457 | -0.72457 | -0.72457 | -154.71860 | 0.91771 | 0.75889 | -17.92866 | -17.73779 | 48.21 | 131.79 | 21.74 | 1.95734 | 0.50570 |
| $isoC_aC_b(H_2C_c-R')HCH_2-$<br>($C-C$ (d)) | $C_b$ | -0.92918 | -0.92918 | -0.92918 | 0 | -154.40324 | 0.91771 | 0.77247 | -17.61330 | -17.42244 | 48.30 | 131.70 | 21.90 | 1.97162 | 0.51388 |
| $tertC_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$<br>($C-C$ (e)) | $C_b$ | -0.72457 | -0.72457 | -0.72457 | -0.72457 | -154.51399 | 0.91771 | 0.76765 | -17.92866 | -17.73779 | 50.04 | 129.96 | 22.66 | 1.94462 | 0.49298 |
| $tertC_aC_b(H_2C_c-R')HCH_2-$<br>($C-C$ (f)) | $C_b$ | -0.72457 | -0.92918 | -0.92918 | 0- | -154.19863 | 0.91771 | 0.78155 | -17.40869 | -17.21783 | 52.78 | 127.22 | 24.04 | 1.92443 | 0.47279 |
| $isoC_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$<br>($C-C$ (f)) | $C_b$ | -0.72457 | -0.72457 | -0.72457 | -0.72457 | -154.51399 | 0.91771 | 0.76765 | -17.92866 | -17.73779 | 50.04 | 129.96 | 22.66 | 1.94462 | 0.49298 |

Table 15.192. The energy parameters $(eV)$ of functional groups of nitroalkanes.

| Parameters | $NO_2$ Group | $C-N$ Group | $CH_3$ Group | $CH_2$ Group | $C-H$ Group | $C-C$ (a) Group | $C-C$ (b) Group | $C-C$ (c) Group | $C-C$ (d) Group | $C-C$ (e) Group | $C-C$ (f) Group |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $n_1$ | 2 | 1 | 3 | 2 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $n_2$ | 0 | 0 | 2 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $n_3$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $C_1$ | 0.5 | 0.5 | 0.75 | 0.75 | 0.75 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| $C_2$ | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $c_1$ | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $c_2$ | 0.85987 | 0.91140 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 |
| $c_3$ | 0 | 0 | 0 | 1 | 1 | 0 | 0 | 0 | 1 | 1 | 0 |
| $c_4$ | 4 | 2 | 1 | 1 | 1 | 2 | 2 | 2 | 2 | 2 | 2 |
| $c_5$ | 0 | 0 | 3 | 2 | 1 | 0 | 0 | 0 | 0 | 0 | 0 |
| $C_{1o}$ | 0.5 | 0.5 | 0.75 | 0.75 | 0.75 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| $C_{2o}$ | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $V_e\ (eV)$ | -106.90919 | -31.36351 | -107.32728 | -70.41425 | -35.12015 | -28.79214 | -28.79214 | -29.10112 | -28.79214 | -29.10112 | -29.10112 |
| $V_p\ (eV)$ | 23.57588 | 9.67426 | 38.92728 | 25.78002 | 12.87680 | 9.33352 | 9.33352 | 9.37273 | 9.33352 | 9.37273 | 9.37273 |
| $T\ (eV)$ | 40.12475 | 7.92833 | 32.53914 | 21.06675 | 10.48582 | 6.77464 | 6.77464 | 6.90500 | 6.77464 | 6.90500 | 6.90500 |
| $V_m\ (eV)$ | -20.06238 | -3.96416 | -16.26957 | -10.53337 | -5.24291 | -3.38732 | -3.38732 | -3.45250 | -3.38732 | -3.45250 | -3.45250 |
| $E(_{AO/HO})\ (eV)$ | 0 | -14.63489 | -15.56407 | -15.56407 | -14.63489 | -15.56407 | -15.56407 | -15.35946 | -15.56407 | -15.35946 | -15.35946 |
| $\Delta E_{H_2MO}(_{AO/HO})\ (eV)$ | 0 | -0.72457 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $E_T(_{AO/HO})\ (eV)$ | 0 | -13.91032 | -15.56407 | -15.56407 | -14.63489 | -15.56407 | -15.56407 | -15.35946 | -15.56407 | -15.35946 | -15.35946 |
| $E_T(_{H_2MO})\ (eV)$ | -63.27093 | -31.63540 | -67.69451 | -49.66493 | -31.63533 | -31.63537 | -31.63537 | -31.63535 | -31.63537 | -31.63535 | -31.63535 |
| $E_T\left(atom-atom,msp^3.AO\right)(eV)$ | -3.71673 | -1.44915 | 0 | 0 | 0 | -1.85836 | -1.85836 | -1.44915 | -1.85836 | -1.44915 | -1.44915 |
| $E_T(_{MO})\ (eV)$ | -66.98746 | -33.08452 | -67.69450 | -49.66493 | -31.63537 | -33.49373 | -33.49373 | -33.08452 | -33.49373 | -33.08452 | -33.08452 |
| $\omega\ \left(10^{15}\ rad/s\right)$ | 19.0113 | 10.5087 | 24.9286 | 24.2751 | 24.1759 | 9.43699 | 9.43699 | 15.4846 | 9.43699 | 9.55643 | 9.55643 |
| $E_K\ (eV)$ | 12.51354 | 6.91703 | 16.40846 | 15.97831 | 15.91299 | 6.21159 | 6.21159 | 10.19220 | 6.21159 | 6.29021 | 6.29021 |
| $\bar{E}_D\ (eV)$ | -0.23440 | -0.17214 | -0.25352 | -0.25017 | -0.24966 | -0.16515 | -0.16515 | -0.20896 | -0.16515 | -0.16416 | -0.16416 |
| $\bar{E}_{Kvib}\ (eV)$ | 0.19342<br>[45] | 0.10539<br>[45] | 0.35532<br>(Eq. (13.458)) | 0.35532<br>(Eq. (13.458)) | 0.35532<br>(Eq. (13.458)) | 0.12312<br>[2] | 0.17978<br>[4] | 0.09944<br>[5] | 0.12312<br>[2] | 0.12312<br>[2] | 0.12312<br>[2] |
| $\bar{E}_{osc}\ (eV)$ | -0.13769 | -0.11945 | -0.22757 | -0.14502 | -0.07200 | -0.10359 | -0.07526 | -0.15924 | -0.10359 | -0.10260 | -0.10260 |
| $E_{mag}\ (eV)$ | 0.11441 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 |
| $E_T(_{Group})\ (eV)$ | -67.26284 | -33.20397 | -67.92207 | -49.80996 | -31.70737 | -33.59732 | -33.49373 | -33.24376 | -33.59732 | -33.18712 | -33.18712 |
| $E_{initial}(_{c_4\ AO/HO})\ (eV)$ | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 |
| $E_{initial}(_{c_5\ AO/HO})\ (eV)$ | 0 | 0 | -13.59844 | -13.59844 | -13.59844 | 0 | 0 | 0 | 0 | 0 | 0 |
| $E_D(_{Group})\ (eV)$ | 8.72329 | 3.93419 | 12.49186 | 7.83016 | 3.32601 | 4.32754 | 4.29921 | 3.97398 | 4.17951 | 3.62128 | 3.91734 |

Table 15.193. The total bond energies of nitroalkanes calculated using the functional group composition and the energies of Table 15.192 compared to the experimental values [3]. The magnetic energy $E_{mag}$ that is subtracted from the weighted sum of the $E_D$ ($_{Group}$) ($eV$) values based on composition is given by (15.58).

| Formula | Name | $NO_2$ Group | $C-N$ Group | $CH_3$ | $CH_2$ | $CH$ | $C-C$ (a) | $C-C$ (b) | $C-C$ (c) | $C-C$ (d) | $C-C$ (e) | $C-C$ (f) | $E_{mag}$ | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $CH_3NO_2$ | Nitromethane | 1 | 1 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 25.14934 | 25.107 | -0.00168 |
| $C_2H_5NO_2$ | Nitroethane | 1 | 1 | 1 | 1 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 37.30704 | 37.292 | -0.00040 |
| $C_3H_7NO_2$ | 1-Nitropropane | 1 | 1 | 1 | 2 | 0 | 2 | 0 | 0 | 0 | 0 | 0 | 0 | 49.46474 | 49.451 | -0.00028 |
| $C_3H_7NO_2$ | 2-Nitropropane | 1 | 1 | 2 | 0 | 1 | 0 | 2 | 0 | 0 | 0 | 0 | 0 | 49.56563 | 49.602 | 0.00074 |
| $C_4H_9NO_2$ | 1-Nitrobutane | 1 | 1 | 1 | 3 | 0 | 3 | 0 | 0 | 0 | 0 | 0 | 0 | 61.62244 | 61.601 | -0.00036 |
| $C_4H_9NO_2$ | 2-Nitroisobutane | 1 | 1 | 3 | 0 | 0 | 0 | 0 | 3 | 0 | 0 | 0 | -1 | 61.90697 | 61.945 | 0.00061 |
| $C_5H_{11}NO_2$ | 1-Nitropentane | 1 | 1 | 1 | 4 | 0 | 4 | 0 | 0 | 0 | 0 | 0 | 0 | 73.78014 | 73.759 | -0.00028 |

Table 15.194. The bond angle parameters of nitroalkanes and experimental values [1]. In the calculation of $\theta_v$, the parameters from the preceding angle were used. $E_T$ is $E_T(atom-atom,msp^3.AO)$.

| Atoms of Angle | $2c'$ Bond 1 ($a_0$) | $2c'$ Bond 2 ($a_0$) | $2c'$ Terminal Atoms ($a_0$) | $E_{Coulombic}$ or $E$ Atom 1 | Atom 1 Hybridization Designation (Table 15.3.A) | $E_{Coulombic}$ Atom 2 | Atom 2 Hybridization Designation (Table 15.3.A) | $c_2$ Atom 1 | $c_2$ Atom 2 | $C_1$ | $C_2$ | $c_1$ | $c_2'$ | $E_T$ (eV) | $\theta_v$ (°) | $\theta_1$ (°) | $\theta_2$ (°) | Cal. $\theta$ (°) | Exp. $\theta$ (°) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $\angle NC_aH$ | 2.81279 | 2.09711 | 3.9665 | -14.82575 | 1 | -14.53414 | N | 0.91771 | 0.91140 (Eq. (15.135)) | 0.75 | 1 | 0.75 | 0.99312 | 0 | | | | 106.87 | 107 (nitromethane) |
| $\angle O_aNO_b$ | 2.30843 | 2.30843 | 4.1231 | -16.68411 $O_a$ | 25 | -16.68411 $O_b$ | 25 | 0.81549 | 0.81549 | 1 | 1 | 1 | 0.81549 | -1.44915 | | | | 126.52 | 125.3 (nitromethane) |
| Methylene $\angle HC_aH$ | 2.11106 | 2.11106 | 3.4252 | -15.75493 | 7 | H | H | 0.86359 | 1 | 1 | 1 | 0.75 | 1.15796 | 0 | | | | 108.44 | 107 (propane) |
| $\angle C_aC_bC_c$ | | | | | | | | | | | | | | | 69.51 | | | 110.49 | 112 (propane)<br>113.8 (butane)<br>110.8 (isobutane) |
| $\angle C_aC_bH$ | | | | | | | | | | | | | | | 69.51 | | | 110.49 | 111.0 (butane)<br>111.4 (isobutane) |
| Methyl $\angle HC_aH$ | 2.09711 | 2.09711 | 3.4252 | -15.75493 | 7 | H | H | 0.86359 | 1 | 1 | 1 | 0.75 | 1.15796 | 0 | | | | 109.50 | |
| $\angle C_aC_bC_c$ | | | | | | | | | | | | | | | 70.56 | | | 109.44 | |
| $\angle C_aC_bH$ | | | | | | | | | | | | | | | 70.56 | | | 109.44 | |
| $\angle C_bC_aC_c$ iso $C_a$ | 2.91547 | 2.91547 | 4.7958 | -16.68412 $C_b$ | 26 | -16.68412 $C_c$ | 26 | 0.81549 | 0.81549 | 1 | 1 | 1 | 0.81549 | -1.85836 | | | | 110.67 | 110.8 (isobutane) |
| $\angle C_bC_aH$ iso $C_a$ | 2.91547 | 2.11323 | 4.1633 | -15.55033 $C_a$ | 5 | -14.82575 $C_b$ | 1 | 0.87495 | 0.91771 | 0.75 | 1 | 0.75 | 1.04887 | 0 | | | | 110.76 | |
| $\angle C_aC_bH$ iso $C_a$ | 2.91547 | 2.09711 | 4.1633 | -15.55033 $C_b$ | 5 | -14.82575 $C_a$ | 1 | 0.87495 | 0.91771 | 0.75 | 1 | 0.75 | 1.04887 | 0 | | | | 111.27 | 111.4 (isobutane) |
| $\angle C_bC_aC_b$ tert $C_a$ | 2.90327 | 2.90327 | 4.7958 | -16.68412 $C_b$ | 26 | -16.68412 $C_b$ | 26 | 0.81549 | 0.81549 | 1 | 1 | 1 | 0.81549 | -1.85836 | | | | 111.37 | 110.8 (isobutane) |
| $\angle C_bC_aC_d$ | | | | | | | | | | | | | | | 72.50 | | | 107.50 | |

## ALKYL NITRITES ($C_nH_{2n+2-m}\left(NO_2\right)_m$, $n=1,2,3,4,5...\infty$)

The alkyl nitrites, $C_nH_{2n+2-m}\left(NO_2\right)_m$, comprise a $RC-O-NO$ moiety that comprises $C-O$, $O-N$, and $NO$ functional groups. The alkyl portion of the alkyl nitrite may comprise at least two terminal methyl groups ($CH_3$) at each end of the chain, and may comprise methylene ($CH_2$), and methylyne ($CH$) functional groups as well as $C$ bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($\left(CH_3\right)_2CH$) and t-butyl ($\left(CH_3\right)_3C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups. The branched-chain-alkane groups in alkyl nitrites are equivalent to those in branched-chain alkanes.

The electron configuration of oxygen is $1s^22s^22p^4$, and the orbital arrangement given by Eq. (10.154) has two unpaired electrons corresponding to the ground state ${}^3P_2$. The electron configuration of nitrogen is $1s^22s^22p^3$, and the orbital arrangement given by Eq. (10.134) has three unpaired electrons corresponding to the ground state ${}^4S^0_{3/2}$. The bonding in the nitro ($NO$) functional group is similar to that in the $SO$ group given previously. It also has similarities to the bonding in the carbonyl functional group. In the $NO$ group, the two unpaired electrons of the $O$ atom form a MO with two unpaired electrons of the nitrogen atom such that the MO comprises a double bond. The nitrogen atom is then energy matched to the $O-N$ functional group that is further energy matched to the $C2sp^3$ HO of the $C-O$ functional group. To meet the equipotential condition of the union of the $N=O$ $H_2$-type-ellipsoidal-MO with other orbitals of the molecule, the hybridization factor $c_2$ of Eq. (15.60) for the $N=O$-bond MO given by Eq. (15.159) is $c_2\left(O\ to\ N2p\ to\ C2sp^3HO\right)=0.85987$.

As in the case of the carbonyl group, two unpaired $O$ electrons result upon bond breakage of the $N=O$ bond which requires that two times $E_{mag}$ of oxygen (Eq. (15.68)) be subtracted from the total energy of $NO$. Additionally, $E_T\left(atom-atom,msp^3.AO\right)$ and $\Delta E_{H_2MO}\left(AO/HO\right)$ are equal to $-0.92918\ eV$ (Eq. (14.513)) which matches the energy of the $N=O$ bond with the contiguous $O-N$ bond and matches the energy contribution of an oxygen atom.

The $O-N$ functional group comprise a single-bond, $H_2$-type-ellipsoidal-MO between the remaining unpaired nitrogen electron and an unpaired electron of the second oxygen atom which further forms a single bond with the $C2sp^3$ HO of the $C-O$ functional group. In alkyl nitrites, the hybridization factor $c_2$ of Eq. (15.61) for the $C-O$-bond MO given by Eq. (15.133) is $c_2\left(C2sp^3HO\ to\ O\right)=0.85395$. The hybridization factor $c_2$ of Eq. (15.61) for a $C-N$-bond MO given by Eq. (15.135) is $c_2\left(C2sp^3HO\ to\ N\right)=0.91140$. Thus, the hybridization factor $c_2$ of Eq. (15.61) for $O-N$ that bridges the $C-O$ and $N=O$ bonds given by Eq. (15.78) is:

$$c_2\left(N2p\ to\ O2p\right)=\frac{c_2\left(C2sp^3HO\ to\ N\right)}{c_2\left(C2sp^3HO\ to\ O\right)}=\frac{0.91140}{0.85395}=1.06727 \tag{15.160}$$

$E_T\left(atom-atom,msp^3.AO\right)=-0.92918\ eV$ in order to match the energy of the $NO$ group and $E\left(AO/HO\right)=-15.35946\ eV$ in order to match the $C-O$ functional group.

The $C-O$ functional group is equivalent to that of an ether as given in the corresponding section except that $E_T\left(atom-atom,msp^3.AO\right)$ and $\Delta E_{H_2MO}\left(AO/HO\right)$ are both $-0.72457\ eV$ which matches the energy contribution of an independent $C2sp^3$ HO (Eq. (14.151)). Also, the energy terms corresponding to the oscillation of the bond in the transition state are matched to a nitrite.

The symbols of the functional groups of branched-chain alkyl nitrites are given in Table 15.195. The geometrical (Eqs. (15.1-15.5) and (15.51)), intercept (Eqs. (15.80-15.87)), and energy (Eqs. (15.6-15.11) and (15.17-15.65)) parameters of alkyl nitrites are given in Tables 15.196, 15.197, and 15.198, respectively. The total energy of each alkyl nitrite given in Table 15.199 was calculated as the sum over the integer multiple of each $E_D\left(Group\right)$ of Table 15.198 corresponding to functional-group composition of the molecule. The bond angle parameters of alkyl nitrites determined using Eqs. (15.88-15.117) are given in Table 15.200. The color scale, translucent view of the charge-density of exemplary alkyl nitrite, methyl nitrite, comprising the concentric shells of atoms with the outer shell bridged by one or more $H_2$-type ellipsoidal MOs or joined with one or more hydrogen MOs is shown in Figure 15.33.

Figure 15.33. (A)-(B) Color scale, translucent views of the charge-density of methyl nitrite showing the orbitals of the atoms at their radii, the ellipsoidal surface of each $H$ or $H_2$-type ellipsoidal MO that transitions to the corresponding outer shell of the atom(s) participating in each bond, and the hydrogen nuclei (red, not to scale).

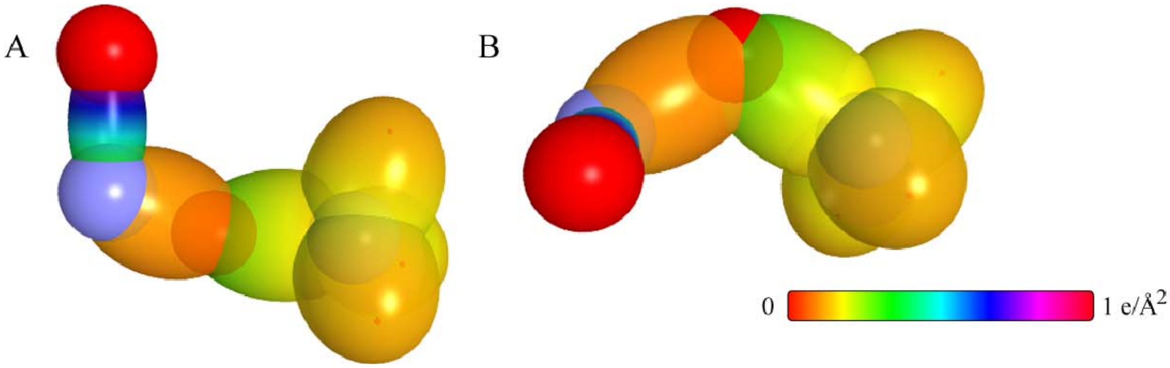


Table 15.195. The symbols of functional groups of alkyl nitrites.

| Functional Group | Group Symbol |
|---|---|
| *NO* group | $NO$ |
| *O-N* | $O-N$ |
| *C-O* | $C-O$ |
| $CH_3$ group | $C-H\ (CH_3)$ |
| $CH_2$ group | $C-H\ (CH_2)$ |
| *CH* | $C-H$ |
| *CC* bond (*n-C*) | $C-C$ (a) |
| *CC* bond (*iso-C*) | $C-C$ (b) |
| *CC* bond (*tert-C*) | $C-C$ (c) |
| *CC* (*iso* to *iso-C*) | $C-C$ (d) |
| *CC* (*t* to *t-C*) | $C-C$ (e) |
| *CC* (*t* to *iso-C*) | $C-C$ (f) |

Table 15.196. The geometrical bond parameters of alkyl nitrites and experimental values [1].

| Parameter | $NO$ Group | $O-N$ Group | $C-O$ Group | $C-H\ (CH_3)$ Group | $C-H\ (CH_2)$ Group | $C-H$ Group | $C-C$ (a) Group | $C-C$ (b) Group | $C-C$ (c) Group | $C-C$ (d) Group | $C-C$ (e) Group | $C-C$ (f) Group |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $a\ (a_0)$ | 1.32255 | 1.76440 | 1.85327 | 1.64920 | 1.67122 | 1.67465 | 2.12499 | 2.12499 | 2.10725 | 2.12499 | 2.10725 | 2.10725 |
| $c'\ (a_0)$ | 1.15002 | 1.32831 | 1.36135 | 1.04856 | 1.05553 | 1.05661 | 1.45744 | 1.45744 | 1.45164 | 1.45744 | 1.45164 | 1.45164 |
| Bond Length $2c$ (Å) | 1.21713 | 1.40582 | 1.44079 | 1.10974 | 1.11713 | 1.11827 | 1.54280 | 1.54280 | 1.53635 | 1.54280 | 1.53635 | 1.53635 |
| Exp. Bond Length (Å) | 1.205<br>(methyl nitrate)<br>1.2<br>($HNO_2$) | 1.402<br>(methyl nitrate)<br>1.432<br>($HNO_2$) | 1.437<br>(methyl nitrate) | 1.107<br>($C-H$ propane)<br>1.117<br>($C-H$ butane) | 1.107<br>($C-H$ propane)<br>1.117<br>($C-H$ butane) | 1.122<br>(isobutane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) |
| $b,c\ (a_0)$ | 0.65314 | 1.16134 | 1.25751 | 1.27295 | 1.29569 | 1.29924 | 1.54616 | 1.54616 | 1.52750 | 1.54616 | 1.52750 | 1.52750 |
| $e$ | 0.86955 | 0.75284 | 0.73457 | 0.63580 | 0.63159 | 0.63095 | 0.68600 | 0.68600 | 0.68888 | 0.68600 | 0.68888 | 0.68888 |

Table 15.197. The MO to HO intercept geometrical bond parameters of alkyl nitrites. $R$, $R'$, $R''$ are $H$ or alkyl groups. $E_T$ is $E_T(atom-atom, msp^3.AO)$.

| Bond | Atom | $E_T$ (eV) Bond 1 | $E_T$ (eV) Bond 2 | $E_T$ (eV) Bond 3 | $E_T$ (eV) Bond 4 | Final Total Energy $C2sp^3$ (eV) | $r_{initial}$ $(a_0)$ | $r_{final}$ $(a_0)$ | $E_{Coulomb}$ (eV) Final | $E(C2sp^3)$ (eV) Final | $\theta'$ (°) | $\theta_1$ (°) | $\theta_2$ (°) | $d_1$ $(a_0)$ | $d_2$ $(a_0)$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $RON=O$ | $O$ | -0.46459 | 0 | 0 | 0 |  | 1.00000 | 0.88983 | -15.29034 |  | 137.15 | 42.85 | 67.90 | 0.49764 | 0.65238 |
| $RON=O$ | $N$ | -0.46459 | -0.46459 | 0 | 0 |  | 0.93084 | 0.86359 | -15.75493 |  | 136.09 | 43.91 | 66.48 | 0.52781 | 0.62221 |
| $RO_b-NO_a$ | $O_b$ | -0.46459 | -0.36229 | 0 | 0 |  | 1.00000 | 0.86923 | -15.65263 |  | 99.22 | 80.78 | 47.63 | 1.18905 | 0.13925 |
| $RO_b-NO_a$ | $N$ | -0.46459 | -0.46459 | 0 | 0 |  | 0.93084 | 0.86359 | -15.75493 |  | 98.78 | 81.22 | 47.30 | 1.19655 | 0.13175 |
| $RH_2C_a-O_bNO_a$<br>$R=H, alkyl$ | $O_b$ | -0.36229 | -0.46459 | 0 | 0 |  | 1.00000 | 0.86923 | -15.65263 |  | 91.43 | 88.57 | 43.71 | 1.33962 | 0.02173 |
| $H_3C_a-O_bNO_a$ | $C_a$ | -0.36229 | 0 | 0 | o | -151.97798 | 0.91771 | 0.89582 | -15.18804 | -14.99717 | 93.71 | 86.29 | 45.31 | 1.30342 | 0.05793 |
| $-CH_2H_2C_a-O_bNO_a$ | $C_a$ | -0.36229 | -0.92918 | 0 | o | -152.90716 | 0.91771 | 0.84418 | -16.11722 | -15.92636 | 89.16 | 90.84 | 42.16 | 1.37373 | 0.01238 |
| $C-H\ (CH_3)$ | $C$ | -0.92918 | 0 | 0 | 0 | -152.54487 | 0.91771 | 0.86359 | -15.75493 | -15.56407 | 77.49 | 102.51 | 41.48 | 1.23564 | 0.18708 |
| $C-H\ (CH_2)$ | $C$ | -0.92918 | -0.92918 | 0 | 0 | -153.47406 | 0.91771 | 0.81549 | -16.68412 | -16.49325 | 68.47 | 111.53 | 35.84 | 1.35486 | 0.29933 |
| $C-H\ (CH)$ | $C$ | -0.92918 | -0.92918 | -0.92918 | 0 | -154.40324 | 0.91771 | 0.77247 | -17.61330 | -17.42244 | 61.10 | 118.90 | 31.37 | 1.42988 | 0.37326 |
| $H_3C_aC_bH_2CH_2-$<br>($C-C$ (a)) | $C_a$ | -0.92918 | 0 | 0 | 0 | -152.54487 | 0.91771 | 0.86359 | -15.75493 | -15.56407 | 63.82 | 116.18 | 30.08 | 1.83879 | 0.38106 |
| $H_3C_aC_bH_2CH_2-$<br>($C-C$ (a)) | $C_b$ | -0.92918 | -0.92918 | 0 | 0 | -153.47406 | 0.91771 | 0.81549 | -16.68412 | -16.49325 | 56.41 | 123.59 | 26.06 | 1.90890 | 0.45117 |
| $R-H_2C_aC_b(H_2C_c-R')HCH_2-$<br>($C-C$ (b)) | $C_b$ | -0.92918 | -0.92918 | -0.92918 | 0 | -154.40324 | 0.91771 | 0.77247 | -17.61330 | -17.42244 | 48.30 | 131.70 | 21.90 | 1.97162 | 0.51388 |
| $R-H_2C_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$<br>($C-C$ (c)) | $C_b$ | -0.92918 | -0.72457 | -0.72457 | -0.72457 | -154.71860 | 0.91771 | 0.75889 | -17.92866 | -17.73779 | 48.21 | 131.79 | 21.74 | 1.95734 | 0.50570 |
| $isoC_aC_b(H_2C_c-R')HCH_2-$<br>($C-C$ (d)) | $C_b$ | -0.92918 | -0.92918 | -0.92918 | 0 | -154.40324 | 0.91771 | 0.77247 | -17.61330 | -17.42244 | 48.30 | 131.70 | 21.90 | 1.97162 | 0.51388 |
| $tertC_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$<br>($C-C$ (e)) | $C_b$ | -0.72457 | -0.72457 | -0.72457 | -0.72457 | -154.51399 | 0.91771 | 0.76765 | -17.92866 | -17.73779 | 50.04 | 129.96 | 22.66 | 1.94462 | 0.49298 |
| $tertC_aC_b(H_2C_c-R')HCH_2-$<br>($C-C$ (f)) | $C_b$ | -0.72457 | -0.92918 | -0.92918 | 0 | -154.19863 | 0.91771 | 0.78155 | -17.40869 | -17.21783 | 52.78 | 127.22 | 24.04 | 1.92443 | 0.47279 |
| $isoC_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$<br>($C-C$ (f)) | $C_b$ | -0.72457 | -0.72457 | -0.72457 | -0.72457 | -154.51399 | 0.91771 | 0.76765 | -17.92866 | -17.73779 | 50.04 | 129.96 | 22.66 | 1.94462 | 0.49298 |

Table 15.198. The energy parameters $(eV)$ of functional groups of alkyl nitrites.

| Parameters | $NO$ Group | $O-N$ Group | $C-O$ Group | $CH_3$ Group | $CH_2$ Group | $C-H$ Group | $C-C$ (a) Group | $C-C$ (b) Group | $C-C$ (c) Group | $C-C$ (d) Group | $C-C$ (e) Group | $C-C$ (f) Group |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $n_1$ | 2 | 1 | 1 | 3 | 2 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $n_2$ | 0 | 0 | 0 | 2 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $n_3$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $C_1$ | 0.5 | 0.5 | 0.5 | 0.75 | 0.75 | 0.75 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| $C_2$ | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $c_1$ | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $c_2$ | 0.85987 | 1.06727 | 0.85395 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 |
| $c_3$ | 2 | 0 | 0 | 0 | 1 | 1 | 0 | 0 | 0 | 1 | 1 | 0 |
| $c_4$ | 4 | 2 | 2 | 1 | 1 | 1 | 2 | 2 | 2 | 2 | 2 | 2 |
| $c_5$ | 0 | 0 | 0 | 3 | 2 | 1 | 0 | 0 | 0 | 0 | 0 | 0 |
| $C_{1o}$ | 0.5 | 0.5 | 0.5 | 0.75 | 0.75 | 0.75 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| $C_{2o}$ | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $V_e\ (eV)$ | -108.34117 | -42.83043 | -32.04173 | -107.32728 | -70.41425 | -35.12015 | -28.79214 | -28.79214 | -29.10112 | -28.79214 | -29.10112 | -29.10112 |
| $V_p\ (eV)$ | 23.66182 | 20.48593 | 9.99436 | 38.92728 | 25.78002 | 12.87680 | 9.33352 | 9.33352 | 9.37273 | 9.33352 | 9.37273 | 9.37273 |
| $T\ (eV)$ | 40.95920 | 12.13739 | 8.64465 | 32.53914 | 21.06675 | 10.48582 | 6.77464 | 6.77464 | 6.90500 | 6.77464 | 6.90500 | 6.90500 |
| $V_m\ (eV)$ | -20.47960 | -6.06870 | -4.32232 | -16.26957 | -10.53337 | -5.24291 | -3.38732 | -3.38732 | -3.45250 | -3.38732 | -3.45250 | -3.45250 |
| $E(_{AO/HO})\ (eV)$ | 0 | -15.35946 | -14.63489 | -15.56407 | -15.56407 | -14.63489 | -15.56407 | -15.56407 | -15.35946 | -15.56407 | -15.35946 | -15.35946 |
| $\Delta E_{H_2MO}(_{AO/HO})\ (eV)$ | -0.92918 | 0 | -0.72457 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $E_T(_{AO/HO})\ (eV)$ | 0.92918 | -15.35946 | -13.91032 | -15.56407 | -15.56407 | -14.63489 | -15.56407 | -15.56407 | -15.35946 | -15.56407 | -15.35946 | -15.35946 |
| $E_T(_{H_2MO})\ (eV)$ | -63.27057 | -31.63527 | -31.63537 | -67.69451 | -49.66493 | -31.63533 | -31.63537 | -31.63537 | -31.63535 | -31.63537 | -31.63535 | -31.63535 |
| $E_T\left(atom-atom,msp^3.AO\right)(eV)$ | -0.92918 | -0.92918 | -0.72457 | 0 | 0 | 0 | -1.85836 | -1.85836 | -1.44915 | -1.85836 | -1.44915 | -1.44915 |
| $E_T(_{MO})\ (eV)$ | -64.19992 | -32.56455 | -32.35994 | -67.69450 | -49.66493 | -31.63537 | -33.49373 | -33.49373 | -33.08452 | -33.49373 | -33.08452 | -33.08452 |
| $\omega\ \left(10^{15}\ rad/s\right)$ | 19.2199 | 23.3578 | 20.7301 | 24.9286 | 24.2751 | 24.1759 | 9.43699 | 9.43699 | 15.4846 | 9.43699 | 9.55643 | 9.55643 |
| $E_K\ (eV)$ | 12.65089 | 15.37450 | 13.64490 | 16.40846 | 15.97831 | 15.91299 | 6.21159 | 6.21159 | 10.19220 | 6.21159 | 6.29021 | 6.29021 |
| $\bar{E}_D\ (eV)$ | -0.22587 | 0.25261 | -0.23648 | -0.25352 | -0.25017 | -0.24966 | -0.16515 | -0.16515 | -0.20896 | -0.16515 | -0.16416 | -0.16416 |
| $\bar{E}_{Kvib}\ (eV)$ | 0.20396<br>[46] | 0.10725<br>[47] | 0.13663<br>[21] | 0.35532<br>(Eq. (13.458)) | 0.35532<br>(Eq. (13.458)) | 0.35532<br>(Eq. (13.458)) | 0.12312<br>[2] | 0.17978<br>[4] | 0.09944<br>[5] | 0.12312<br>[2] | 0.12312<br>[2] | 0.12312<br>[2] |
| $\bar{E}_{osc}\ (eV)$ | -0.12390 | 0.19899 | -0.16817 | -0.22757 | -0.14502 | -0.07200 | -0.10359 | -0.07526 | -0.15924 | -0.10359 | -0.10260 | -0.10260 |
| $E_{mag}\ (eV)$ | 0.11441 | 0.11441 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 |
| $E_T(_{Group})\ (eV)$ | -64.44771 | 32.76354 | -32.52811 | -67.92207 | -49.80996 | -31.70737 | -33.59732 | -33.49373 | -33.24376 | -33.59732 | -33.18712 | -33.18712 |
| $E_{initial}(_{c_4\ AO/HO})\ (eV)$ | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 |
| $E_{initial}(_{c_5\ AO/HO})\ (eV)$ | 0 | 0 | 0 | -13.59844 | -13.59844 | -13.59844 | 0 | 0 | 0 | 0 | 0 | 0 |
| $E_D(_{Group})\ (eV)$ | 5.67933 | 3.49376 | 3.25833 | 12.49186 | 7.83016 | 3.32601 | 4.32754 | 4.29921 | 3.97398 | 4.17951 | 3.62128 | 3.91734 |

Table 15.199. The total bond energies of alkyl nitrites calculated using the functional group composition and the energies of Table 15.198 compared to the experimental values [3].

| Formula | Name | $NO$ Group | $O-N$ Group | $C-O$ Group | $CH_3$ | $CH_2$ | $CH$ | $C-C$ (a) | $C-C$ (b) | $C-C$ (c) | $C-C$ (d) | $C-C$ (e) | $C-C$ (f) | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $CH_3NO_2$ | Methyl nitrite | 1 | 1 | 1 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 24.92328 | 24.955 | 0.00126 |

Table 15.200. The bond angle parameters of alkyl nitrites and experimental values [1]. In the calculation of ❑$_v$, the parameters from the preceding angle were used. $E_T$ is $E_T$ ($atom - atom, msp^3.AO$ ).

| Atoms of Angle | $2c'$ Bond 1 ($a_0$) | $2c'$ Bond 2 ($a_0$) | $2c'$ Terminal Atoms ($a_0$) | $E_{Coulombic}$ or $E$ Atom 1 | Atom 1 Hybridization Designation (Table 15.3.A) | $E_{Coulombic}$ Atom 2 | Atom 2 Hybridization Designation (Table 15.3.A) | $c_2$ Atom 1 | $c_2$ Atom 2 | $C_1$ | $C_2$ | $c_1$ | $c_2'$ | $E_T$ (eV) | $\theta_v$ (°) | $\theta_1$ (°) | $\theta_2$ (°) | Cal. $\theta$ (°) | Exp. $\theta$ (°) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $\angle CO_bN$ | 2.72270 | 2.65661 | 4.4944 | -16.68412 $C_b$ | 26 | -14.53414 $N$ | N | 0.81549 | 0.91140 (Eq. (15.135)) | 1 | 1 | 1 | 0.86345 | -1.44915 | | | | 113.33 | |
| $\angle O_aNO_b$ | 2.30004 | 2.65661 | 4.1231 | -16.68411 $O_a$ | 25 | -16.68411 $O_b$ | 25 | 0.81549 | 0.81549 | 1 | 1 | 1 | 0.81549 | -1.44915 | | | | 112.38 | 110.7 ($HNO_3$) |
| Methylene $\angle HC_aH$ | 2.11106 | 2.11106 | 3.4252 | -15.75493 | 7 | H | H | 0.86359 | 1 | 1 | 1 | 0.75 | 1.15796 | 0 | | | | 108.44 | 107 (propane) |
| $\angle C_aC_bC_c$ | | | | | | | | | | | | | | | 69.51 | | | 110.49 | 112 (propane)<br>113.8 (butane)<br>110.8 (isobutane) |
| $\angle C_aC_bH$ | | | | | | | | | | | | | | | 69.51 | | | 110.49 | 111.0 (butane)<br>111.4 (isobutane) |
| Methyl $\angle HC_aH$ | 2.09711 | 2.09711 | 3.4252 | -15.75493 | 7 | H | H | 0.86359 | 1 | 1 | 1 | 0.75 | 1.15796 | 0 | | | | 109.50 | |
| $\angle C_aC_bC_c$ | | | | | | | | | | | | | | | 70.56 | | | 109.44 | |
| $\angle C_aC_bH$ | | | | | | | | | | | | | | | 70.56 | | | 109.44 | |
| $\angle C_bC_aC_c$ iso $C_a$ | 2.91547 | 2.91547 | 4.7958 | -16.68412 $C_b$ | 26 | -16.68412 $C_c$ | 26 | 0.81549 | 0.81549 | 1 | 1 | 1 | 0.81549 | -1.85836 | | | | 110.67 | 110.8 (isobutane) |
| $\angle C_bC_aH$ iso $C_a$ | 2.91547 | 2.11323 | 4.1633 | -15.55033 $C_a$ | 5 | -14.82575 $C_b$ | 1 | 0.87495 | 0.91771 | 0.75 | 1 | 0.75 | 1.04887 | 0 | | | | 110.76 | |
| $\angle C_aC_bH$ iso $C_a$ | 2.91547 | 2.09711 | 4.1633 | -15.55033 $C_b$ | 5 | -14.82575 $C_a$ | 1 | 0.87495 | 0.91771 | 0.75 | 1 | 0.75 | 1.04887 | 0 | | | | 111.27 | 111.4 (isobutane) |
| $\angle C_bC_aC_b$ tert $C_a$ | 2.90327 | 2.90327 | 4.7958 | -16.68412 $C_b$ | 26 | -16.68412 $C_b$ | 26 | 0.81549 | 0.81549 | 1 | 1 | 1 | 0.81549 | -1.85836 | | | | 111.37 | 110.8 (isobutane) |
| $\angle C_bC_aC_d$ | | | | | | | | | | | | | | | 72.50 | | | 107.50 | |

## ALKYL NITRATES ($C_nH_{2n+2-m}\left(NO_3\right)_m$, $n=1,2,3,4,5...\infty$)

The alkyl nitrates, $C_nH_{2n+2-m}\left(NO_3\right)_m$, comprise a $RC-O-NO_2$ moiety that comprises $C-O$, $O-N$, and $NO_2$ functional groups. The alkyl portion of the alkyl nitrate may comprise at least two terminal methyl groups ($CH_3$) at each end of the chain, and may comprise methylene ($CH_2$), and methylyne ($CH$) functional groups as well as $C$ bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($\left(CH_3\right)_2CH$) and t-butyl ($\left(CH_3\right)_3C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups. The branched-chain-alkane groups in alkyl nitrates are equivalent to those in branched-chain alkanes.

The $NO_2$ functional group is equivalent to that of nitro alkanes with the exception that $\Delta E_{H_2MO}\left(AO/HO\right)$ as well as $E_T\left(atom-atom,msp^3.AO\right)$ is equal to $-3.71673\ eV$ in order to match the group energy to that of the contiguous $O-N$ bond. Furthermore, the $O-N$ group with $E_T\left(atom-atom,msp^3.AO\right)=-0.92918\ eV$ is equivalent to that of nitrites as given in the corresponding section.

The $C-O$ functional group is equivalent to that of an ether as given in the corresponding section except that $E_T\left(atom-atom,msp^3.AO\right)$ and $\Delta E_{H_2MO}\left(AO/HO\right)$ are both $-0.92918\ eV$ which matches the energy contribution of an independent $C2sp^3$ HO (Eq. (14.513)). Also, the energy terms corresponding to the oscillation of the bond in the transition state are matched to a nitrate.

The symbols of the functional groups of branched-chain alkyl nitrates are given in Table 15.201. The geometrical (Eqs. (15.1-15.5) and (15.51)), intercept (Eqs. (15.80-15.87)), and energy (Eqs. (15.6-15.11) and (15.17-15.65)) parameters of alkyl nitrates are given in Tables 15.202, 15.203, and 15.204, respectively. The total energy of each alkyl nitrate given in Table 15.205 was calculated as the sum over the integer multiple of each $E_D\left(Group\right)$ of Table 15.204 corresponding to functional-group composition of the molecule. The bond angle parameters of alkyl nitrates determined using Eqs. (15.88-15.117) are given in Table 15.206. The color scale, translucent view of the charge-density of exemplary alkyl nitrate, ethyl nitrate, comprising the concentric shells of atoms with the outer shell bridged by one or more $H_2$-type ellipsoidal MOs or joined with one or more hydrogen MOs is shown in Figure 15.34.

Figure 15.34. (A)-(B) Color scale, translucent views of the charge-density of ethyl nitrate showing the orbitals of the atoms at their radii, the ellipsoidal surface of each $H$ or $H_2$-type ellipsoidal MO that transitions to the corresponding outer shell of the atom(s) participating in each bond, and the hydrogen nuclei (red, not to scale).

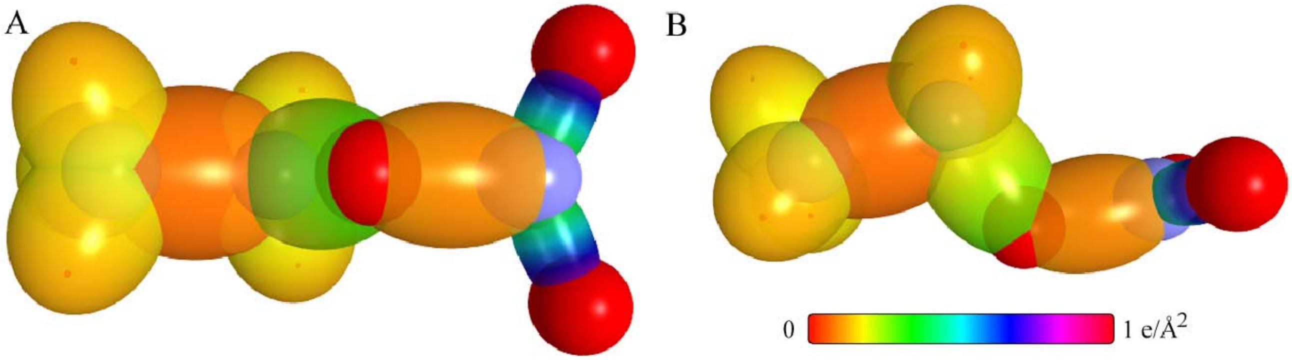


Table 15.201. The symbols of functional groups of alkyl nitrates.

| Functional Group | Group Symbol |
|---|---|
| $NO_2$ group | $NO_2$ |
| $O$-$N$ | $O-N$ |
| $C$-$O$ | $C-O$ |
| $CH_3$ group | $C-H\ (CH_3)$ |
| $CH_2$ group | $C-H\ (CH_2)$ |
| $CH$ | $C-H$ |
| $CC$ bond (*n*-$C$) | $C-C$ (a) |
| $CC$ bond (*iso*-$C$) | $C-C$ (b) |
| $CC$ bond (*tert*-$C$) | $C-C$ (c) |
| $CC$ (*iso* to *iso*-$C$) | $C-C$ (d) |
| $CC$ (*t* to *t*-$C$) | $C-C$ (e) |
| $CC$ (*t* to *iso*-$C$) | $C-C$ (f) |

Table 15.202. The geometrical bond parameters of alkyl nitrates and experimental values [1].

| Parameter | $NO_2$ Group | $O-N$ Group | $C-O$ Group | $C-H\left(CH_3\right)$ Group | $C-H\left(CH_2\right)$ Group | $C-H$ Group | $C-C$ (a) Group | $C-C$ (b) Group | $C-C$ (c) Group | $C-C$ (d) Group | $C-C$ (e) Group | $C-C$ (f) Group |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $a\left(a_0\right)$ | 1.29538 | 1.76440 | 1.83991 | 1.64920 | 1.67122 | 1.67465 | 2.12499 | 2.12499 | 2.10725 | 2.12499 | 2.10725 | 2.10725 |
| $c'\left(a_0\right)$ | 1.13815 | 1.32831 | 1.35643 | 1.04856 | 1.05553 | 1.05661 | 1.45744 | 1.45744 | 1.45164 | 1.45744 | 1.45164 | 1.45164 |
| Bond Length $2c'$ $\left(\mathring{A}\right)$ | 1.20456 | 1.40582 | 1.43559 | 1.10974 | 1.11713 | 1.11827 | 1.54280 | 1.54280 | 1.53635 | 1.54280 | 1.53635 | 1.53635 |
| Exp. Bond Length $\left(\mathring{A}\right)$ | 1.205<br>(methyl nitrate)<br>1.2<br>($HNO_2$) | 1.402<br>(methyl nitrate)<br>1.432<br>($HNO_2$) | 1.437<br>(methyl nitrate) | 1.107<br>($C-H$ propane)<br>1.117<br>($C-H$ butane) | 1.107<br>($C-H$ propane)<br>1.117<br>($C-H$ butane) | 1.122<br>(isobutane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) |
| $b,c\left(a_0\right)$ | 0.61857 | 1.16134 | 1.24312 | 1.27295 | 1.29569 | 1.29924 | 1.54616 | 1.54616 | 1.52750 | 1.54616 | 1.52750 | 1.52750 |
| $e$ | 0.87862 | 0.75284 | 0.73723 | 0.63580 | 0.63159 | 0.63095 | 0.68600 | 0.68600 | 0.68888 | 0.68600 | 0.68888 | 0.68888 |

Table 15.203. The MO to HO intercept geometrical bond parameters of alkyl nitrates. $R$, $R'$, $R''$ are $H$ or alkyl groups. $E_T$ is $E_T$ $(atom-atom,msp^3.AO)$.

| Bond | Atom | $E_T$ (eV) Bond 1 | $E_T$ (eV) Bond 2 | $E_T$ (eV) Bond 3 | $E_T$ (eV) Bond 4 | Final Total Energy $C2sp^3$ (eV) | $r_{initial}$ $\left(a_0\right)$ | $r_{final}$ $\left(a_0\right)$ | $E_{Coulomb}$ (eV) Final | $E\left(C2sp^3\right)$ (eV) Final | $\theta'$ (°) | $\theta_1$ (°) | $\theta_2$ (°) | $d_1$ $\left(a_0\right)$ | $d_2$ $\left(a_0\right)$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $RON(O)=O$ | $O$ | -0.92918 | 0 | 0 | 0 | | 1.00000 | 0.86359 | -15.75493 | | 138.49 | 41.51 | 67.70 | 0.49144 | 0.64671 |
| $RON(O)=O$ | $N$ | -0.92918 | -0.92918 | -0.46459 | 0 | | 0.93084 | 0.79340 | -17.14870 | | 135.60 | 44.40 | 63.83 | 0.57133 | 0.56682 |
| $RO_b-N\left(O_a\right)_2$ | $O_b$ | -0.46459 | -0.46459 | 0 | 0 | | 1.00000 | 0.86359 | -15.75493 | | 98.78 | 81.22 | 47.30 | 1.19655 | 0.13175 |
| $RO_b-N\left(O_a\right)_2$ | $N$ | -0.46459 | -0.92918 | -0.92918 | 0 | | 0.93084 | 0.79340 | -17.14870 | | 92.78 | 87.22 | 43.03 | 1.28978 | 0.03852 |
| $RH_2C_a-O_bN\left(O_a\right)_2$<br>$R=H,alkyl$ | $O_b$ | -0.46459 | -0.46459 | 0 | 0 | | 1.00000 | 0.86359 | -15.75493 | | 92.13 | 87.87 | 43.96 | 1.32431 | 0.03212 |
| $H_3C_a-O_bN\left(O_a\right)_2$ | $C_a$ | -0.46459 | 0 | 0 | o | -152.08028 | 0.91771 | 0.88983 | -15.29034 | -15.09948 | 94.36 | 85.64 | 45.54 | 1.28872 | 0.06771 |
| $-CH_2H_2C_a-O_bN\left(O_a\right)_2$ | $C_a$ | -0.46459 | -0.92918 | 0 | o | -153.00946 | 0.91771 | 0.83885 | -16.21952 | -16.02866 | 89.90 | 90.10 | 42.44 | 1.35787 | 0.00143 |
| $C-H\left(CH_3\right)$ | $C$ | -0.92918 | 0 | 0 | 0 | -152.54487 | 0.91771 | 0.86359 | -15.75493 | -15.56407 | 77.49 | 102.51 | 41.48 | 1.23564 | 0.18708 |
| $C-H\left(CH_2\right)$ | $C$ | -0.92918 | -0.92918 | 0 | 0 | -153.47406 | 0.91771 | 0.81549 | -16.68412 | -16.49325 | 68.47 | 111.53 | 35.84 | 1.35486 | 0.29933 |
| $C-H\left(CH\right)$ | $C$ | -0.92918 | -0.92918 | -0.92918 | 0 | -154.40324 | 0.91771 | 0.77247 | -17.61330 | -17.42244 | 61.10 | 118.90 | 31.37 | 1.42988 | 0.37326 |
| $H_3C_aC_bH_2CH_2-$<br>($C-C$ (a)) | $C_a$ | -0.92918 | 0 | 0 | 0 | -152.54487 | 0.91771 | 0.86359 | -15.75493 | -15.56407 | 63.82 | 116.18 | 30.08 | 1.83879 | 0.38106 |
| $H_3C_aC_bH_2CH_2-$<br>($C-C$ (a)) | $C_b$ | -0.92918 | -0.92918 | 0 | 0 | -153.47406 | 0.91771 | 0.81549 | -16.68412 | -16.49325 | 56.41 | 123.59 | 26.06 | 1.90890 | 0.45117 |
| $R-H_2C_aC_b\left(H_2C_c-R'\right)HCH_2-$<br>($C-C$ (b)) | $C_b$ | -0.92918 | -0.92918 | -0.92918 | 0 | -154.40324 | 0.91771 | 0.77247 | -17.61330 | -17.42244 | 48.30 | 131.70 | 21.90 | 1.97162 | 0.51388 |
| $R-H_2C_a\left(R'-H_2C_d\right)C_b\left(R''-H_2C_c\right)CH_2-$<br>($C-C$ (c)) | $C_b$ | -0.92918 | -0.72457 | -0.72457 | -0.72457 | -154.71860 | 0.91771 | 0.75889 | -17.92866 | -17.73779 | 48.21 | 131.79 | 21.74 | 1.95734 | 0.50570 |
| $isoC_aC_b\left(H_2C_c-R'\right)HCH_2-$<br>($C-C$ (d)) | $C_b$ | -0.92918 | -0.92918 | -0.92918 | 0 | -154.40324 | 0.91771 | 0.77247 | -17.61330 | -17.42244 | 48.30 | 131.70 | 21.90 | 1.97162 | 0.51388 |
| $tertC_a\left(R'-H_2C_d\right)C_b\left(R''-H_2C_c\right)CH_2-$<br>($C-C$ (e)) | $C_b$ | -0.72457 | -0.72457 | -0.72457 | -0.72457 | -154.51399 | 0.91771 | 0.76765 | -17.92866 | -17.73779 | 50.04 | 129.96 | 22.66 | 1.94462 | 0.49298 |
| $tertC_aC_b\left(H_2C_c-R'\right)HCH_2-$<br>($C-C$ (f)) | $C_b$ | -0.72457 | -0.92918 | -0.92918 | 0 | -154.19863 | 0.91771 | 0.78155 | -17.40869 | -17.21783 | 52.78 | 127.22 | 24.04 | 1.92443 | 0.47279 |
| $isoC_a\left(R'-H_2C_d\right)C_b\left(R''-H_2C_c\right)CH_2-$<br>($C-C$ (f)) | $C_b$ | -0.72457 | -0.72457 | -0.72457 | -0.72457 | -154.51399 | 0.91771 | 0.76765 | -17.92866 | -17.73779 | 50.04 | 129.96 | 22.66 | 1.94462 | 0.49298 |

Table 15.204. The energy parameters ($eV$) of functional groups of alkyl nitrates.

| Parameters | $NO_2$ Group | $O-N$ Group | $C-O$ Group | $CH_3$ Group | $CH_2$ Group | $C-H$ Group | $C-C$ (a) Group | $C-C$ (b) Group | $C-C$ (c) Group | $C-C$ (d) Group | $C-C$ (e) Group | $C-C$ (f) Group |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $n_1$ | 2 | 1 | 1 | 3 | 2 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $n_2$ | 0 | 0 | 0 | 2 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $n_3$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $C_1$ | 0.5 | 0.5 | 0.5 | 0.75 | 0.75 | 0.75 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| $C_2$ | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $c_1$ | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $c_2$ | 0.85987 | 1.06727 | 0.85395 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 |
| $c_3$ | 0 | 0 | 0 | 0 | 1 | 1 | 0 | 0 | 0 | 1 | 1 | 0 |
| $c_4$ | 4 | 2 | 2 | 1 | 1 | 1 | 2 | 2 | 2 | 2 | 2 | 2 |
| $c_5$ | 0 | 0 | 0 | 3 | 2 | 1 | 0 | 0 | 0 | 0 | 0 | 0 |
| $C_{1o}$ | 0.5 | 0.5 | 0.5 | 0.75 | 0.75 | 0.75 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| $C_{2o}$ | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $V_e\ (eV)$ | -112.63415 | -42.83043 | -32.35681 | -107.32728 | -70.41425 | -35.12015 | -28.79214 | -28.79214 | -29.10112 | -28.79214 | -29.10112 | -29.10112 |
| $V_p\ (eV)$ | 23.90868 | 20.48593 | 10.03058 | 38.92728 | 25.78002 | 12.87680 | 9.33352 | 9.33352 | 9.37273 | 9.33352 | 9.37273 | 9.37273 |
| $T\ (eV)$ | 43.47534 | 12.13739 | 8.79304 | 32.53914 | 21.06675 | 10.48582 | 6.77464 | 6.77464 | 6.90500 | 6.77464 | 6.90500 | 6.90500 |
| $V_m\ (eV)$ | -21.73767 | -6.06870 | -4.39652 | -16.26957 | -10.53337 | -5.24291 | -3.38732 | -3.38732 | -3.45250 | -3.38732 | -3.45250 | -3.45250 |
| $E(_{AO/HO})\ (eV)$ | 0 | -15.35946 | -14.63489 | -15.56407 | -15.56407 | -14.63489 | -15.56407 | -15.56407 | -15.35946 | -15.56407 | -15.35946 | -15.35946 |
| $\Delta E_{H_2MO}(_{AO/HO})\ (eV)$ | -3.71673 | 0 | -0.92918 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $E_T(_{AO/HO})\ (eV)$ | 3.71673 | -15.35946 | -13.70571 | -15.56407 | -15.56407 | -14.63489 | -15.56407 | -15.56407 | -15.35946 | -15.56407 | -15.35946 | -15.35946 |
| $E_T(_{H_2MO})\ (eV)$ | -63.27107 | -31.63527 | -31.63542 | -67.69451 | -49.66493 | -31.63533 | -31.63537 | -31.63537 | -31.63535 | -31.63537 | -31.63535 | -31.63535 |
| $E_T\left(atom-atom,msp^3.AO\right)(eV)$ | -3.71673 | -0.92918 | -0.92918 | 0 | 0 | 0 | -1.85836 | -1.85836 | -1.44915 | -1.85836 | -1.44915 | -1.44915 |
| $E_T(_{MO})\ (eV)$ | -66.98746 | -32.56455 | -32.56455 | -67.69450 | -49.66493 | -31.63537 | -33.49373 | -33.49373 | -33.08452 | -33.49373 | -33.08452 | -33.08452 |
| $\omega\ \left(10^{15}\ rad/s\right)$ | 19.8278 | 23.3578 | 21.0910 | 24.9286 | 24.2751 | 24.1759 | 9.43699 | 9.43699 | 15.4846 | 9.43699 | 9.55643 | 9.55643 |
| $E_K\ (eV)$ | 13.05099 | 15.37450 | 13.88249 | 16.40846 | 15.97831 | 15.91299 | 6.21159 | 6.21159 | 10.19220 | 6.21159 | 6.29021 | 6.29021 |
| $\bar{E}_D\ (eV)$ | -0.23938 | 0.25261 | -0.24004 | -0.25352 | -0.25017 | -0.24966 | -0.16515 | -0.16515 | -0.20896 | -0.16515 | -0.16416 | -0.16416 |
| $\bar{E}_{Kvib}\ (eV)$ | 0.19342<br>[45] | 0.10725<br>[47] | 0.13663<br>[21] | 0.35532<br>(Eq. (13.458)) | 0.35532<br>(Eq. (13.458)) | 0.35532<br>(Eq. (13.458)) | 0.12312<br>[2] | 0.17978<br>[4] | 0.09944<br>[5] | 0.12312<br>[2] | 0.12312<br>[2] | 0.12312<br>[2] |
| $\bar{E}_{osc}\ (eV)$ | -0.14267 | 0.19899 | -0.17172 | -0.22757 | -0.14502 | -0.07200 | -0.10359 | -0.07526 | -0.15924 | -0.10359 | -0.10260 | -0.10260 |
| $E_{mag}\ (eV)$ | 0.11441 | 0.11441 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 |
| $E_T(_{Group})\ (eV)$ | -67.27281 | 32.76354 | -32.73627 | -67.92207 | -49.80996 | -31.70737 | -33.59732 | -33.49373 | -33.24376 | -33.59732 | -33.18712 | -33.18712 |
| $E_{initial}(_{c_4\ AO/HO})\ (eV)$ | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 |
| $E_{initial}(_{c_5\ AO/HO})\ (eV)$ | 0 | 0 | 0 | -13.59844 | -13.59844 | -13.59844 | 0 | 0 | 0 | 0 | 0 | 0 |
| $E_D(_{Group})\ (eV)$ | 8.73325 | 3.49376 | 3.46649 | 12.49186 | 7.83016 | 3.32601 | 4.32754 | 4.29921 | 3.97398 | 4.17951 | 3.62128 | 3.91734 |

Table 15.205. The total bond energies of alkyl nitrates calculated using the functional group composition and the energies of Table 15.204 compared to the experimental values [3].

| Formula | Name | $NO_2$ Group | $O-N$ Group | $C-O$ Group | $CH_3$ | $CH_2$ | $CH$ | $C-C$ (a) | $C-C$ (b) | $C-C$ (c) | $C-C$ (d) | $C-C$ (e) | $C-C$ (f) | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $CH_3NO_3$ | Methyl nitrate | 1 | 1 | 1 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 28.18536 | 28.117 | -0.00244 |
| $C_2H_5NO_3$ | Ethyl nitrate | 1 | 1 | 1 | 1 | 1 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 40.34306 | 40.396 | 0.00131 |
| $C_3H_7NO_3$ | Propyl nitrate | 1 | 1 | 1 | 1 | 2 | 1 | 2 | 0 | 0 | 0 | 0 | 0 | 52.50076 | 52.550 | 0.00093 |
| $C_3H_7NO_3$ | Isopropyl nitrate | 1 | 1 | 1 | 2 | 0 | 1 | 0 | 2 | 0 | 0 | 0 | 0 | 52.60165 | 52.725 | 0.00233 |

Table 15.206. The bond angle parameters of alkyl nitrates and experimental values [1]. In the calculation of $\theta_v$, the parameters from the preceding angle were used. $E_T$ is $E_T(atom-atom, msp^3.AO)$.

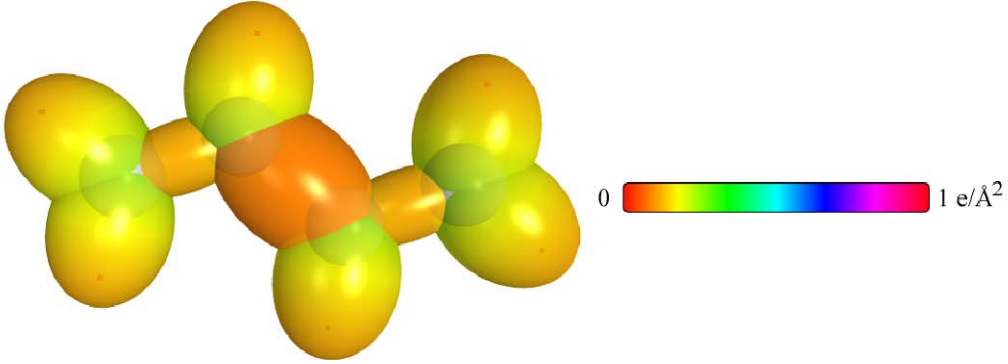
| Atoms of Angle | $2c'$ Bond 1 ($a_0$) | $2c'$ Bond 2 ($a_0$) | $2c'$ Terminal Atoms ($a_0$) | $E_{Coulombic}$ or $E$ Atom 1 | Atom 1 Hybridization Designation (Table 15.3.A) | $E_{Coulombic}$ Atom 2 | Atom 2 Hybridization Designation (Table 15.3.A) | $c_2$ Atom 1 | $c_2$ Atom 2 | $C_1$ | $C_2$ | $c_1$ | $c_2'$ | $E_T$ (eV) | $\theta_v$ (°) | $\theta_1$ (°) | $\theta_2$ (°) | Cal. $\theta$ (°) | Exp. $\theta$ (°) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Methyl<br>$\angle HC_aH$ | 2.09711 | 2.09711 | 3.4252 | -15.75493 | 7 | H | H | 0.86359 | 1 | 1 | 1 | 0.75 | 1.15796 | 0 | | | | 109.50 | |
| $\angle H_aC_aO_c$ | | | | | | | | | | | | | | | 70.56 | | | 109.44 | 110<br>(methyl nitrate) |
| $\angle H_bC_aO_c$ | 2.09711 | 2.71287 | 3.7238 | -14.82575<br>$C_a$ | 1 | -13.61806 | O | 0.91771 | 0.85395<br>(Eq. (15.133)) | 0.75 | 1 | 0.75 | 0.93052 | 0 | | | | 100.68 | 103<br>(methyl nitrate) |
| $\angle O_aNO_b$ | 2.27630 | 2.27630 | 4.1231 | -16.68411<br>$O_a$ | 25 | -16.68411<br>$O_b$ | 25 | 0.81549 | 0.81549 | 1 | 1 | 1 | 0.81549 | -1.44915 | | | | 129.83 | |
| $\angle O_aNO_c$ | | | | | | | | | | | | | | | | 129.83 | | 115.09<br>(Eq. (15.108)) | 118.1<br>(methyl nitrate) |
| $\angle O_bNO_c$ | | | | | | | | | | | | | | | | 129.83 | | 115.09<br>(Eq. (15.108)) | 112.4<br>(methyl nitrate) |
| $\angle CO_cN$ | 2.71287 | 2.65661 | 4.4721 | -16.68412<br>$C_b$ | 26 | -14.53414<br>$N$ | N | 0.81549 | 0.91140<br>(Eq. (15.135)) | 1 | 1 | 1 | 0.86345 | -1.44915 | | | | 112.79 | 112.7<br>(methyl nitrate) |
| Methylene<br>$\angle HC_aH$ | 2.11106 | 2.11106 | 3.4252 | -15.75493 | 7 | H | H | 0.86359 | 1 | 1 | 1 | 0.75 | 1.15796 | 0 | | | | 108.44 | 107<br>(propane) |
| $\angle C_aC_bC_c$ | | | | | | | | | | | | | | | 69.51 | | | 110.49 | 112<br>(propane)<br>113.8<br>(butane)<br>110.8<br>(isobutane) |
| $\angle C_aC_bH$ | | | | | | | | | | | | | | | 69.51 | | | 110.49 | 111.0<br>(butane)<br>111.4<br>(isobutane) |
| Methyl<br>$\angle HC_aH$ | 2.09711 | 2.09711 | 3.4252 | -15.75493 | 7 | H | H | 0.86359 | 1 | 1 | 1 | 0.75 | 1.15796 | 0 | | | | 109.50 | |
| $\angle C_aC_bC_c$ | | | | | | | | | | | | | | | 70.56 | | | 109.44 | |
| $\angle C_aC_bH$ | | | | | | | | | | | | | | | 70.56 | | | 109.44 | |
| $\angle C_bC_aC_c$<br>iso $C_a$ | 2.91547 | 2.91547 | 4.7958 | -16.68412<br>$C_b$ | 26 | -16.68412<br>$C_c$ | 26 | 0.81549 | 0.81549 | 1 | 1 | 1 | 0.81549 | -1.85836 | | | | 110.67 | 110.8<br>(isobutane) |
| $\angle C_bC_aH$<br>iso $C_a$ | 2.91547 | 2.11323 | 4.1633 | -15.55033<br>$C_a$ | 5 | -14.82575<br>$C_b$ | 1 | 0.87495 | 0.91771 | 0.75 | 1 | 0.75 | 1.04887 | 0 | | | | 110.76 | |
| $\angle C_aC_bH$<br>iso $C_a$ | 2.91547 | 2.09711 | 4.1633 | -15.55033<br>$C_b$ | 5 | -14.82575<br>$C_a$ | 1 | 0.87495 | 0.91771 | 0.75 | 1 | 0.75 | 1.04887 | 0 | | | | 111.27 | 111.4<br>(isobutane) |
| $\angle C_bC_aC_b$<br>tert $C_a$ | 2.90327 | 2.90327 | 4.7958 | -16.68412<br>$C_b$ | 26 | -16.68412<br>$C_b$ | 26 | 0.81549 | 0.81549 | 1 | 1 | 1 | 0.81549 | -1.85836 | | | | 111.37 | 110.8<br>(isobutane) |
| $\angle C_bC_aC_d$ | | | | | | | | | | | | | | | 72.50 | | | 107.50 | |

## CYCLIC AND CONJUGATED ALKENES ($C_nH_{2n+2-2m-2c}$, $n=3,4,5...\infty$, $m=1,2,3...$, $c=0$ *or* $1$)

The cyclic and conjugated alkenes are represented by the general formula $C_nH_{2n+2-2m-2c}$, $n=3,4,5...\infty$, $m=1,2,3...$, $c=0$ *or* 1 where $m$ is the number of double bonds and $c=0$ for a straight-chain alkene and $c=1$ for a cyclic alkene. They have at least one carbon-carbon double bond comprising a functional group that is solved equivalently to the double bond of ethylene. Consider the cyclic and conjugated alkenes 1,3-butadiene, 1,3-pentadiene, 1,4-pentadiene, 1,3-cyclopentadiene, and cyclopentene. Based on the condition of energy matching of the orbital, any magnetic energy due to unpaired electrons in the constituent fragments, and differences in oscillation in the transition state, five distinct $C-C$ functional groups can be identified as given in Table 15.208. The designation of the structure of the groups are shown in Figures 15.35A-E. In addition, $CH_2$ of any $-C=CH_2$ moiety is a conjugated alkene functional group. The alkyl portion of the cyclic or conjugated alkene may comprise at least one terminal methyl group ($CH_3$), and may comprise methylene ($CH_2$), and methylyne ($CH$) functional groups that are equivalent to those of branched-chain alkanes.

The solution of the functional groups comprises the hybridization of the $2s$ and $2p$ AOs of each $C$ to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between two $C2sp^3$ HOs to form a MO permits each participating hybridized orbital to decrease in radius and energy. The $C-C$ groups are solved in the same manner as those of the branched-chain alkanes given in the corresponding section. For example, the cyclopentene $C_a-C_b$ group is equivalent to the n-$C-C$ alkane group. Many of the corresponding energies of the molecules of this class are similar, and they can be related to one another based on the structure. For example, cyclopentadiene is formed by ring closure of 1,3-pentadiene with the elimination of $H$ from the terminal methyl and methylene groups. Thus, the energy of each of the corresponding carbon-carbon bonds in cyclopentadiene is the same as that in 1,3-pentadiene except that the difference between the energies of the 1,3-pentadiene $C_c-C_d$ and the cyclopentadiene $C_a-C_b$ groups is the magnetic energy (Eq. (15.67)) which is subtracted from the $C_a-C_b$ total bond energy according to Eqs. (13.524-13.527) due to the formation of a $CH$ group from the methylene group. The color scale, translucent view of the charge-density of exemplary cyclic and conjugated alkene, 1,3-butadiene, comprising the concentric shells of atoms with the outer shell bridged by one or more $H_2$-type ellipsoidal MOs or joined with one or more hydrogen MOs is shown in Figure 15.35.

Figure 15.35. Color scale, translucent view of the charge-density of 1,3-butadiene showing the orbitals of the atoms at their radii, the ellipsoidal surface of each $H$ or $H_2$-type ellipsoidal MO that transitions to the corresponding outer shell of the atom(s) participating in each bond, and the hydrogen nuclei (red, not to scale).



$E_T\left(atom-atom,msp^3.AO\right)$ of the $C=C$-bond MO in Eq. (15.61) due to the charge donation from the $C$ atoms to the MO is equivalent to that of ethylene, $-2.26759\ eV$, given by Eq. (14.247). $E_T\left(atom-atom,msp^3.AO\right)$ of each $C-C$-bond MO in Eq. (15.61) is $-2.26759\ eV$ or $-1.85836\ eV$ based on the energy match between the $C2sp^3$ HOs corresponding to the energy contributions equivalent to those of alkene, $-1.13379\ eV$ (Eq. (14.247)), or methylene, $-0.92918\ eV$ (Eq. (14.513)), groups, respectively, that are contiguous with the $C-C$-bond carbons. In the former case, the total energy of the $C-C$ bond MO is matched to that of the alkane energy in the determination of the bond length. The charge density of 0.5e must be donated to the $C-C$ bond in order to match the energy of the adjacent flanking double bonds. This further lowers the total energy of the $C-C$-bond MO and increases the $C-C$ bond energy. This additional lowering of the $C-C$-bond energy by additional charge donation over that of an alkane bond due to adjacent double bonds is called *conjugation*.

The symbols of the functional groups of cyclic and conjugated alkenes are given in Table 15.207. The structures of 1,3-butadiene, 1,3-pentadiene, 1,4-pentadiene, 1,3-cyclopentadiene, and cyclopentene are shown in Figures 15.35A-E, respectively. The geometrical (Eqs. (15.1-15.5) and (15.51)), intercept (Eqs. (15.80-15.87)), and energy (Eqs. (15.6-15.11) and (15.17-15.65)) parameters of cyclic and conjugated alkenes are given in Tables 15.208, 15.209, and 15.210, respectively. The total energy of each cyclic or conjugated alkenes given in Table 15.211 was calculated as the sum over the integer multiple of each $E_D(_{Group})$ of

Table 15.210 corresponding to functional-group composition of the molecule. For each set of unpaired electrons created by bond breakage, the $C2sp^3$ HO magnetic energy $E_{mag}$ that is subtracted from the weighted sum of the $E_D(_{Group})$ $(eV)$ values based on composition is given by Eq. (15.67). The bond angle parameters of cyclic and conjugated alkenes determined using Eqs. (15.88-15.117) are given in Table 15.212.

Figure 15.35A. 1,3 Butadiene

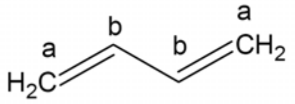


Figure 15.35B. 1,3 Pentadiene

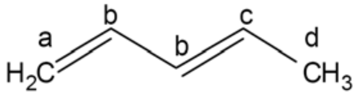


Figure 15.35C. 1,4 Pentadiene

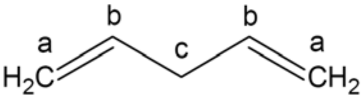


Figure 15.35D. 1,3 Cyclopentadiene

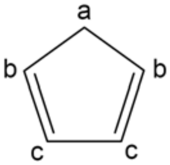


Figure 15.35E. Cyclopentene

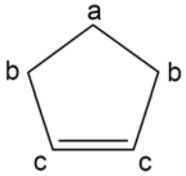


Table 15.207. The symbols of functional groups of cyclic and conjugated alkenes.

| Functional Group | Group Symbol |
|---|---|
| $CC$ double bond | $C=C$ |
| 1,3-butadiene, 1,3-pentadiene $C_b-C_b$<br>1,3-cyclopentadiene $C_c-C_c$ | $C-C$ (a) |
| 1,3-pentadiene $C_c-C_d$<br>cyclopentene $C_b-C_c$ | $C-C$ (b) |
| 1,4-pentadiene $C_b-C_c$ | $C-C$ (c) |
| 1,3-cyclopentadiene $C_a-C_b$ | $C-C$ (d) |
| cyclopentene $C_a-C_b$ | $C-C$ (e) |
| $CH_2$ alkenyl group | $C-H$ $(CH_2)$ (i) |
| $CH_3$ group | $C-H$ $(CH_3)$ |
| $CH_2$ alkyl group | $C-H$ $(CH_2)$ (ii) |
| $CH$ | $C-H$ |

Table 15.208. The geometrical bond parameters of cyclic and conjugated alkenes and experimental values [1].

| Parameter | $C=C$ Group | $C-C$ (a) Group | $C-C$ (b) Group | $C-C$ (c) Group | $C-C$ (d) Group | $C-C$ (e) Group | $C-H\left(CH_2\right)$ (i) Group | $C-H\left(CH_3\right)$ Group | $C-H\left(CH_2\right)$ (ii) Group | $C-H$ Group |
|---|---|---|---|---|---|---|---|---|---|---|
| $a\left(a_0\right)$ | 1.47228 | 1.91256 | 2.04740 | 2.04740 | 2.04740 | 2.12499 | 1.64010 | 1.64920 | 1.67122 | 1.67465 |
| $c'\left(a_0\right)$ | 1.26661 | 1.38295 | 1.43087 | 1.43087 | 1.43087 | 1.45773 | 1.04566 | 1.04856 | 1.05553 | 1.05661 |
| Bond Length $2c'$ $\left(\mathring{A}\right)$ | 1.34052 | 1.46365 | 1.51437 | 1.51437 | 1.51437 | 1.54280 | 1.10668 | 1.10974 | 1.11713 | 1.11827 |
| Exp. Bond Length $\left(\mathring{A}\right)$ | 1.349<br>(1,3-butadiene)<br>1.342<br>(1,3-cyclopentadiene)<br>1.342<br>(cyclopentene) | 1.467<br>(1,3-butadiene)<br>1.469<br>(1,3-cyclopentadiene) | 1.519<br>(cyclopentene) |  | 1.509<br>(1,3-cyclopentadiene) | 1.546<br>(cyclopentene) | 1.10<br>(2-methylpropene)<br>1.108 (avg.)<br>(1,3-butadiene) | 1.107<br>($C-H$ propane)<br>1.117<br>($C-H$ butane) | 1.107<br>($C-H$ propane)<br>1.117<br>($C-H$ butane) | 1.122<br>(isobutane) |
| $b,c\left(a_0\right)$ | 0.75055 | 1.32110 | 1.46439 | 1.46439 | 1.46439 | 1.54615 | 1.26354 | 1.27295 | 1.29569 | 1.29924 |
| $e$ | 0.86030 | 0.72309 | 0.69887 | 0.69887 | 0.69887 | 0.68600 | 0.63756 | 0.63580 | 0.63159 | 0.63095 |

Table 15.209. The MO to HO intercept geometrical bond parameters of cyclic and conjugated alkenes. $R_1$ is an alkyl group and $R$, $R'$, $R''$ are $H$ or alkyl groups. $E_T$ is $E_T$ $(atom-atom,msp^3.AO)$.

| Bond | Atom | $E_T$ (eV) Bond 1 | $E_T$ (eV) Bond 2 | $E_T$ (eV) Bond 3 | $E_T$ (eV) Bond 4 | Final Total Energy $C2sp^3$ (eV) | $r_{initial}$ $(a_0)$ | $r_{final}$ $(a_0)$ | $E_{Coulomb}(C2sp^3)$ (eV) Final | $E(C2sp^3)$ (eV) Final | $\theta'$ (°) | $\theta_1$ (°) | $\theta_2$ (°) | $d_1$ $(a_0)$ | $d_2$ $(a_0)$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $H_2C_a=C_b(H)(H)C=CR$<br>(1,3-butadiene, 1,3-pentadiene)<br>$H_2C_a=C_b(H)C_cH_2C_b(H)=C_aH_2$<br>(1,4-pentadiene) | $C_a$ | -1.13380 | 0 | 0 | 0 | -152.74949 | 0.91771 | 0.85252 | -15.95955 | -15.76868 | 129.84 | 50.16 | 60.70 | 0.72040 | 0.54620 |
| $H_2C_a=C_b(H)(H)C=CR$<br>(1,3-butadiene, 1,3-pentadiene)<br>$-HC_b=C_c(H)(H)C_c=C_bH-$<br>(1,3-cyclopentadiene) | $C_b$<br>$C_c$ | -1.13380 | -1.13380 | 0 | 0 | -153.88328 | 0.91771 | 0.79597 | -17.09334 | -16.90248 | 127.13 | 52.87 | 57.73 | 0.78613 | 0.48047 |
| $H_2C_a=C_b(H)(H)C_b=C_c(H)C_dH_3$<br>(1,3-pentadiene)<br>$H_2C_a=C_b(H)C_cH_2C_b(H)=C_aH_2$<br>(1,4-pentadiene)<br>$-HC_b=C_c(H)(H)C_c=C_bH-$<br>(1,3-cyclopentadiene)<br>$-H_2C_bC_c(H)=(H)C_cC_bH_2-$<br>(cyclopentene) | $C_c$<br>$C_b$<br>$C_b$<br>$C_c$ | -1.13380 | -0.92918 | 0 | 0 | -153.67867 | 0.91771 | 0.80561 | -16.88873 | -16.69786 | 127.61 | 52.39 | 58.24 | 0.77492 | 0.49168 |
| $RC=C_{b,c}(H)-(H)C_{b,c}=CR'$<br>$(C-C$ (a)) | $C_{b,c}$ | -1.13380 | -1.13380 | 0 | 0 | -153.88328 | 0.91771 | 0.79597 | -17.09334 | -16.90248 | 78.31 | 101.69 | 36.16 | 1.54418 | 0.16123 |
| $H_2C_a=C_b(H)(H)C_b=C_c(H)-C_dH_3$<br>(1,3-pentadiene)<br>$-H_2C_b-C_c(H)=(H)C_c-C_bH_2-$<br>(cyclopentene)<br>$(C-C$ (b)) | $C_c$<br>$C_c$ | -1.13380 | -0.92918 | 0 | 0 | -153.67867 | 0.91771 | 0.80561 | -16.88873 | -16.69786 | 64.57 | 115.43 | 29.79 | 1.77684 | 0.34596 |
| $H_2C_a=C_b(H)(H)C_b=C_c(H)-C_dH_3$<br>(1,3-pentadiene)<br>$(C-C$ (b)) | $C_d$ | -0.92918 | 0 | 0 | 0 | -152.54487 | 0.91771 | 0.86359 | -15.75493 | -15.56407 | 72.27 | 107.73 | 34.17 | 1.69388 | 0.26301 |
| $-H_2C_b-C_c(H)=(H)C_c-C_bH_2-$<br>(cyclopentene)<br>$(C-C$ (b)) | $C_b$ | -0.92918 | -0.92918 | 0 | 0 | -153.47405 | 0.91771 | 0.81549 | -16.68411 | -16.49325 | 65.99 | 114.01 | 30.58 | 1.76270 | 0.33183 |
| $H_2C_a=C_b(H)-C_cH_2C_b(H)=C_aH_2$<br>(1,4-pentadiene)<br>$(C-C$ (c))<br>$-H_2C_a-HC_b=C_c(H)(H)C_c=C_bH-$<br>(1,3-cyclopentadiene)<br>$(C-C$ (d)) | $C_b$<br>$C_b$ | -1.13380 | -0.92918 | 0 | 0 | -153.67866 | 0.91771 | 0.80561 | -16.88873 | -16.69786 | 64.57 | 115.43 | 29.79 | 1.77684 | 0.34596 |
| $H_2C_a=C_b(H)-C_cH_2C_b(H)=C_aH_2$<br>(1,4-pentadiene)<br>$(C-C$ (c))<br>$-H_2C_a-HC_b=C_c(H)(H)C_c=C_bH-$<br>(1,3-cyclopentadiene)<br>$(C-C$ (d)) | $C_c$<br>$C_a$ | -0.92918 | -0.92918 | 0 | 0 | -153.47405 | 0.91771 | 0.81549 | -16.68411 | -16.49325 | 65.99 | 114.01 | 30.58 | 1.76270 | 0.33183 |
| $-H_2C_a-H_2C_bC_c(H)=(H)C_cC_bH_2-$<br>(cyclopentene)<br>$(C-C$ (e)) | $C_a$, $C_b$ | -0.92918 | -0.92918 | 0 | 0 | -153.47405 | 0.91771 | 0.81549 | -16.68411 | -16.49325 | 56.41 | 123.59 | 26.06 | 1.90890 | 0.45116 |
| $C-H$ $(CH_2)$ (i) | $C$ | -1.13380 | 0 | 0 | 0 | -152.74949 | 0.91771 | 0.85252 | -15.95955 | -15.76868 | 77.15 | 102.85 | 41.13 | 1.23531 | 0.18965 |
| $C-H$ $(CH_3)$ | $C$ | -0.92918 | 0 | 0 | 0 | -152.54487 | 0.91771 | 0.86359 | -15.75493 | -15.56407 | 77.49 | 102.51 | 41.48 | 1.23564 | 0.18708 |
| $C-H$ $(CH_2)$ (ii) | $C$ | -0.92918 | -0.92918 | 0 | 0 | -153.47406 | 0.91771 | 0.81549 | -16.68412 | -16.49325 | 68.47 | 111.53 | 35.84 | 1.35486 | 0.29933 |
| $C-H$ $(CH)$ | $C$ | -0.92918 | -0.92918 | -0.92918 | 0 | -154.40324 | 0.91771 | 0.77247 | -17.61330 | -17.42244 | 61.10 | 118.90 | 31.37 | 1.42988 | 0.37326 |

Table 15.210. The energy parameters ($eV$) of functional groups of cyclic and conjugated alkenes.

| Parameters | $C=C$ Group | $C-C$ (a) Group | $C-C$ (b) Group | $C-C$ (c) Group | $C-C$ (d) Group | $C-C$ (e) Group | $CH_2$ (i) Group | $CH_3$ Group | $CH_2$ (ii) Group | $C-H$ Group |
|---|---|---|---|---|---|---|---|---|---|---|
| $n_1$ | 2 | 1 | 1 | 1 | 1 | 1 | 2 | 3 | 2 | 1 |
| $n_2$ | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 2 | 1 | 0 |
| $n_3$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $C_1$ | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.75 | 0.75 | 0.75 | 0.75 |
| $C_2$ | 0.91771 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $c_1$ | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $c_2$ | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 |
| $c_3$ | 0 | 0 | 0 | 0 | 1 | 0 | 1 | 0 | 1 | 1 |
| $c_4$ | 4 | 2 | 2 | 2 | 2 | 2 | 1 | 1 | 1 | 1 |
| $c_5$ | 0 | 0 | 0 | 0 | 0 | 0 | 2 | 3 | 2 | 1 |
| $C_{1o}$ | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.75 | 0.75 | 0.75 | 0.75 |
| $C_{2o}$ | 0.91771 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $V_e\ (eV)$ | -102.08992 | -33.01226 | -30.19634 | -30.19634 | -30.19634 | -28.79214 | -72.03287 | -107.32728 | -70.41425 | -35.12015 |
| $V_p\ (eV)$ | 21.48386 | 9.83824 | 9.50874 | 9.50874 | 9.50874 | 9.33352 | 26.02344 | 38.92728 | 25.78002 | 12.87680 |
| $T\ (eV)$ | 34.67062 | 8.63041 | 7.37432 | 7.37432 | 7.37432 | 6.77464 | 21.95990 | 32.53914 | 21.06675 | 10.48582 |
| $V_m\ (eV)$ | -17.33531 | -4.31520 | -3.68716 | -3.68716 | -3.68716 | -3.38732 | -10.97995 | -16.26957 | -10.53337 | -5.24291 |
| $E(_{AO/HO})\ (eV)$ | 0 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -15.56407 | -14.63489 | -15.56407 | -15.56407 | -14.63489 |
| $\Delta E_{H_2MO}(_{AO/HO})\ (eV)$ | 0 | -1.85836 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $E_T(_{AO/HO})\ (eV)$ | 0 | -12.77653 | -14.63489 | -14.63489 | -14.63489 | -15.56407 | -14.63489 | -15.56407 | -15.56407 | -14.63489 |
| $E_T(_{H_2MO})\ (eV)$ | -63.27075 | -31.63535 | -31.63534 | -31.63534 | -31.63534 | -31.63537 | -49.66437 | -67.69451 | -49.66493 | -31.63533 |
| $E_T\left(atom-atom,msp^3.AO\right)(eV)$ | -2.26759 | -2.26759 | -1.85836 | -1.85836 | -1.85836 | -1.85836 | 0 | 0 | 0 | 0 |
| $E_T(_{MO})\ (eV)$ | -65.53833 | -33.90295 | -33.49373 | -33.49373 | -33.49373 | -33.49373 | -49.66493 | -67.69450 | -49.66493 | -31.63537 |
| $\omega\ \left(10^{15}\ rad/s\right)$ | 43.0680 | 11.0522 | 9.97851 | 23.3291 | 9.97851 | 9.43699 | 25.2077 | 24.9286 | 24.2751 | 24.1759 |
| $E_K\ (eV)$ | 28.34813 | 7.27475 | 6.56803 | 15.35563 | 6.56803 | 6.21159 | 16.59214 | 16.40846 | 15.97831 | 15.91299 |
| $\bar{E}_D\ (eV)$ | -0.34517 | -0.18090 | -0.16982 | -0.25966 | -0.16982 | -0.16515 | -0.25493 | -0.25352 | -0.25017 | -0.24966 |
| $\bar{E}_{Kvib}\ (eV)$ | 0.17897<br>[6] | 0.14829<br>[48] | 0.11159<br>[12] | 0.11159<br>[12] | 0.11159<br>[12] | 0.12312<br>[2] | 0.35532<br>Eq. (13.458) | 0.35532<br>Eq. (13.458) | 0.35532<br>Eq. (13.458) | 0.35532<br>Eq. (13.458) |
| $\bar{E}_{osc}\ (eV)$ | -0.25568 | -0.10676 | -0.11402 | -0.20386 | -0.11402 | -0.10359 | -0.07727 | -0.22757 | -0.14502 | -0.07200 |
| $E_{mag}\ (eV)$ | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 |
| $E_T(_{Group})\ (eV)$ | -66.04969 | -34.00972 | -33.60776 | -33.69760 | -33.60776 | -33.59732 | -49.81948 | -67.92207 | -49.80996 | -31.70737 |
| $E_{initial}(_{c_4\ AO/HO})\ (eV)$ | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 |
| $E_{initial}(_{c_5\ AO/HO})\ (eV)$ | 0 | 0 | 0 | 0 | 0 | 0 | -13.59844 | -13.59844 | -13.59844 | -13.59844 |
| $E_D(_{Group})\ (eV)$ | 7.51014 | 4.73994 | 4.33798 | 4.42782 | 4.18995 | 4.32754 | 7.83968 | 12.49186 | 7.83016 | 3.32601 |

Table 15.211. The total bond energies of cyclic and conjugated alkenes calculated using the functional group composition and the energies of Table 15.210 compared to the experimental values [3]. The magnetic energy $E_{mag}$ that is subtracted from the weighted sum of the $E_D$ ($_{Group}$) ($eV$) values based on composition is given by (15.58).

| Formula | Name | $C=C$ | $C-C$ (a) | $C-C$ (b) | $C-C$ (c) | $C-C$ (d) | $C-C$ (e) | $CH_2$ (i) | $CH_3$ | $CH_2$ (ii) | $CH$ | $E_{mag}$ | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $C_4H_6$ | 1,3 Butadiene | 2 | 1 | 0 | 0 | 0 | 0 | 2 | 0 | 0 | 2 | 0 | 42.09159 | 42.12705 | 0.00084 |
| $C_5H_8$ | 1,3 Pentadiene | 2 | 1 | 1 | 0 | 0 | 0 | 1 | 1 | 0 | 3 | 0 | 54.40776 | 54.42484 | 0.00031 |
| $C_5H_8$ | 1,4 Pentadiene | 2 | 0 | 0 | 2 | 0 | 0 | 2 | 0 | 1 | 2 | 0 | 54.03745 | 54.11806 | 0.00149 |
| $C_5H_6$ | 1,3 Cyclopentadiene | 2 | 1 | 0 | 0 | 2 | 0 | 0 | 0 | 1 | 4 | 0 | 49.27432 | 49.30294 | 0.00058 |
| $C_5H_8$ | Cyclopentene | 1 | 0 | 2 | 0 | 0 | 2 | 0 | 0 | 3 | 2 | -1 | 54.83565 | 54.86117 | 0.00047 |

Table 15.212. The bond angle parameters of cyclic and conjugated alkenes and experimental values [1]. In the calculation of $\theta_v$, the parameters from the preceding angle were used. $E_T$ is $E_T(atom - atom,\ msp^3.AO)$.

| Atoms of Angle | $2c'$ Bond 1 ($a_0$) | $2c'$ Bond 2 ($a_0$) | $2c'$ Terminal Atoms ($a_0$) | $E_{Coulombic}$ Atom 1 | Atom 1 Hybridization Designation (Table 15.3.A) | $E_{Coulombic}$ Atom 2 | Atom 2 Hybridization Designation (Table 15.3.A) | $c_2$ Atom 1 | $c_2$ Atom 2 | $C_1$ | $C_2$ | $c_1$ | $c_2'$ | $E_T$ (eV) | $\theta_v$ (°) | $\theta_1$ (°) | $\theta_2$ (°) | Cal. $\theta$ (°) | Exp. $\theta$ (°) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $\angle HC_aH$<br>$H_2C_a = C_b$<br>1,3-butadiene | 2.09132 | 2.09132 | 3.4928 | -15.95955 | 10 | H | H | 0.85252 | 1 | 1 | 1 | 0.75 | 1.17300 | 0 | | | | 113.25 | |
| $\angle C_bC_aH_a$<br>$H_2C_a = C_b$<br>1,3-butadiene | | | | | | | | | | | | | | | | 113.25 | | 123.38 | 120.9<br>(1,3-butadiene) |
| $\angle C_bC_aH_a$<br>$H_2C_a = C_b$<br>1,3-butadiene | 2.53321 | 2.09132 | 4.0000 | -15.95954<br>$C_a$ | 10 | -15.95954<br>$C_b$ | 10 | 0.85252 | 0.85252 | 0.75 | 1 | 0.75 | 1.00000 | 0 | | | | 119.45 | 120.9<br>(1,3-butadiene) |
| $\angle C_aC_bC_b$<br>$C_a = C_bC_b$<br>1,3-butadiene | 2.53321 | 2.76590 | 4.6904 | -16.88873<br>$C_a$ | 29 | -17.09334<br>$C_b$ | 34 | 0.80561 | 0.79597 | 1 | 1 | 1 | 0.85395 | -1.85836 | | | | 124.48 | 124.4<br>(1,3-butadiene CCC)<br>124.4<br>(1,3,5-hexatriene CbCcCc)<br>121.7<br>(1,3,5-hexatriene CaCbCc)<br>125.3<br>(2-butene CbCaCc) |
| $\angle C_bC_cC_c$<br>$C_b = C_cC_c$<br>1,3-cyclopentadiene | 2.53321 | 2.76590 | 4.3012 | -17.81791<br>$C_b$ | 53 | -17.81791<br>$C_c$ | 53 | 0.76360 | 0.76360 | 1 | 1 | 1 | 0.76360 | -1.85836 | | | | 108.44 | 109.4<br>(1,3-cyclopentadiene) |
| $\angle C_aC_bC_c$<br>$C_aC_b = C_c$<br>1,3-cyclopentadiene | 2.86175 | 2.53321 | 4.3818 | -17.61330<br>$C_a$ | 49 | -17.61330<br>$C_c$ | 49 | 0.77247 | 0.77247 | 1 | 1 | 1 | 0.77247 | -1.85836 | | | | 108.47 | 109.3<br>(1,3-cyclopentadiene) |
| $\angle C_bC_aC_b$<br>$= C_bHC_aH_2C_b(H) =$<br>1,3-cyclopentadiene | 2.86175 | 2.86175 | 4.4609 | -17.40869<br>$C_b$ | 44 | -17.40869<br>$C_b$ | 44 | 0.78155 | 0.78155 | 1 | 1 | 1 | 0.78155 | -1.85836 | | | | 102.41 | 102.8<br>(1,3-cyclopentadiene) |
| $\angle C_bC_cC_c$<br>$-H_2C_bHC_c = C_cHC_bH_2-$<br>cyclopentene | 2.86175 | 2.53321 | 4.4272 | -17.40869<br>$C_b$ | 44 | -17.61330<br>$C_b$ | 49 | 0.78155 | 0.77247 | 1 | 1 | 1 | 0.77701 | -1.85836 | | | | 110.14 | 110.0<br>(cyclopentene) |
| $\angle C_aC_bC_c$<br>$-H_2C_aH_2C_bHC_c = C_cH-$<br>cyclopentene | 2.91548 | 2.86175 | 4.5166 | -17.20408<br>$C_a$ | 39 | -17.40869<br>$C_c$ | 44 | 0.79085 | 0.78155 | 1 | 1 | 1 | 0.78620 | -1.85836 | | | | 102.85 | 103.0<br>(cyclopentene) |
| $\angle C_bC_aC_b$<br>$-C_bH_2C_aH_2C_bH_2-$<br>cyclopentene | 2.91548 | 2.91548 | 4.5826 | -17.20408<br>$C_b$ | 39 | -17.20408<br>$C_b$ | 39 | 0.79085 | 0.79085 | 1 | 1 | 1 | 0.79085 | -1.85836 | | | | 103.61 | 104.0<br>(cyclopentene) |

## AROMATIC AND HETEROCYCLIC COMPOUNDS

Aromatic and heterocyclic molecules comprise at least one of an aromatic or a cyclic conjugated alkene functional group. The latter was described in the Cyclic and Conjugated Alkenes section. The aromatic bond is uniquely stable and requires the sharing of the electrons of multiple $H_2$-type MOs. The results of the derivation of the parameters of the benzene molecule given in the Benzene Molecule ($C_6H_6$) section can be generalized to any aromatic functional group(s) of aromatic and heterocyclic compounds.

$C_6H_6$ can be considered a linear combination of three ethylene molecules wherein a $C-H$ bond of each $CH_2$ group of $H_2C=CH_2$ is replaced by a $C=C$ bond to form a six-member ring of carbon atoms. The solution of the ethylene molecule is given in the Ethylene Molecule ($CH_2CH_2$) section. The radius $r_{ethylene2sp^3}$ ($0.85252a_0$) of the $C2sp^3$ shell of ethylene calculated from the Coulombic energy is given by Eq. (14.244). The Coulombic energy $E_{Coulomb}\left(C_{ethylene}, 2sp^3\right)$ ($-15.95955\ eV$) of the outer electron of the $C2sp^3$ shell is given by Eq. (14.245). The energy $E\left(C_{ethylene}, 2sp^3\right)$ ($-15.76868\ eV$) of the outer electron of the $C2sp^3$ shell is given by Eq. (14.246). $E_T\left(C=C, 2sp^3\right)$ ($-1.13380\ eV$) (Eq. (14.247)), the energy change of each $C2sp^3$ shell with the formation of the $C=C$-bond MO is given by the difference between $E\left(C_{ethylene}, 2sp^3\right)$ and $E\left(C, 2sp^3\right)$. $C_6H_6$ can be solved using the same principles as those used to solve ethylene wherein the $2s$ and $2p$ shells of each $C$ hybridize to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between two $C2sp^3$ hybridized orbitals (HOs) to form a molecular orbital (MO) permits each participating hybridized orbital to decrease in radius and energy. Each $2sp^3$ HO of each carbon atom initially has four unpaired electrons. Thus, the $6H$ atomic orbitals (AOs) of benzene contribute six electrons and the six $sp^3$-hybridized carbon atoms contribute twenty-four electrons to form six $C-H$ bonds and six $C=C$ bonds. Each $C-H$ bond has two paired electrons with one donated from the $H$ AO and the other from the $C2sp^3$ HO. Each $C=C$ bond comprises a linear combination of a factor of $0.75$ of four paired electrons (three electrons) from two sets of two $C2sp^3$ HOs of the participating carbon atoms. Each $C-H$ and each $C=C$ bond comprises a linear combination of one and two diatomic $H_2$-type MOs developed in the Nature of the Chemical Bond of Hydrogen-Type Molecules and Molecular Ions section, respectively.

Consider the case where three sets of $C=C$-bond MOs form bonds between the two carbon atoms of each molecule to form a six-member ring such that the six resulting bonds comprise eighteen paired electrons. Each bond comprises a linear combination of two MOs wherein each comprises two $C2sp^3$ HOs and 75% of a $H_2$-type ellipsoidal MO divided between the $C2sp^3$ HOs:

$$\left(\begin{array}{l} 3\left(2\ C2sp^3 + 0.75\ H_2\ MO\right) \rightarrow 3\left(C\overset{4e}{=}C\right) - ethylene - type - bond\ MO \\ \rightarrow 6\left(C\overset{3e}{=}C\right) - bond\ MO\ of\ benzene \end{array}\right) \tag{15.161}$$

The linear combination of each $H_2$-type ellipsoidal MO with each $C2sp^3$ HO further comprises an excess of 25% charge-density contribution per bond from each $C2sp^3$ HO to the $C=C$-bond MO to achieve an energy minimum. Thus, the dimensional parameters of each bond $C=C$-bond are determined using Eqs. (15.51) and (15.1-15.5) in a form that are the same equations as those used to determine the same parameters of the $C=C$-bond MO of ethylene (Eqs. (14.242-14.268)) while matching the boundary conditions of the structure of benzene.

Hybridization with 25% electron donation to each $C=C$-bond gives rise to the $C_{benzene}2sp^3$ HO-shell Coulombic energy $E_{Coulomb}\left(C_{benzene}, 2sp^3\right)$ given by Eq. (14.245). To meet the equipotential condition of the union of the six $C2sp^3$ HOs, $c_2$ and $C_2$ of Eq. (15.51) for the aromatic $C\overset{3e}{=}C$-bond MO is given by Eq. (15.71) as the ratio of $15.95955\ eV$, the magnitude of $E_{Coulomb}\left(C_{benzene}, 2sp^3\right)$ (Eq. (14.245)), and $13.605804\ eV$, the magnitude of the Coulombic energy between the electron and proton of $H$ (Eq. (1.264)):

$$C_2\left(benzeneC2sp^3HO\right) = c_2\left(benzeneC2sp^3HO\right) = \frac{13.605804\ eV}{15.95955\ eV} = 0.85252 \tag{15.162}$$

The energies of each $C\overset{3e}{=}C$ bond of benzene are also determined using the same equations as those of ethylene (Eqs. (14.251-14.253) and (14.319-14.333)) with the parameters of benzene. Ethylene serves as a basis element for the $C\overset{3e}{=}C$ bonding of benzene wherein each of the six $C\overset{3e}{=}C$ bonds of benzene comprises (0.75)(4) = 3 electrons according to Eq. (15.161). The total energy of the bonds of the eighteen electrons of the $C\overset{3e}{=}C$ bonds of benzene, $E_T\left(C_6H_6, C\overset{3e}{=}C\right)$, is given by (6)(0.75) times $E_{T+osc}\left(C=C\right)$ (Eq. (14.492)), the total energy of the $C\overset{3e}{=}C$-bond MO of benzene including the Doppler term, minus eighteen times $E\left(C, 2sp^3\right)$ (Eq. (14.146)), the initial energy of each $C2sp^3$ HO of each $C$ that forms the $C\overset{3e}{=}C$ bonds of bond order two.

Thus, the total energy of the six $C\overset{3e}{=}C$ bonds of benzene with three electron per aromatic bond given by Eq. (14.493) is:

$$\begin{aligned} E_T\left(C_6H_6, C\overset{3e}{=}C\right) &= (6)(0.75)E_{T+osc}(C=C)-(6)(3)E\left(C,2sp^3\right) \\ &= (6)(0.75)(-66.05796\ eV)-18(-14.63489\ eV) \\ &= -297.26081\ eV-(-263.42798\ eV) = -33.83284\ eV \end{aligned} \tag{15.163}$$

The results of benzene can be generalized to the class of aromatic and heterocyclic compounds. $E_{h\nu}$ of an aromatic bond is given by $E_T(H_2)$ (Eqs. (11.212) and (14.486)), the maximum total energy of each $H_2$-type MO such that:

$$\bar{E}_{osc} = n_1\left(\bar{E}_D+\bar{E}_{Kvib}\right) = n_1\left(-31.63536831\ eV\sqrt{\frac{2\bar{E}_K}{Mc^2}}+\frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right) \tag{15.164}$$

The factor of 0.75 corresponding to the three electrons per aromatic bond of bond order two given in the Benzene Molecule ($C_6H_6$) section modifies Eqs. (15.61-15.65). Multiplication of the total energy given by Eq. (15.64) by $f_1 = 0.75$ with the substitution of Eq. (15.164) gives the total energy of the aromatic bond:

$$E_T(Group) = f_1\left(\begin{array}{l} E(basis\ energies)+E_T\left(atom-atom,msp^3.AO\right) \\ -31.63536831\ eV\sqrt{\dfrac{2\hbar\sqrt{\dfrac{\frac{C_{1o}C_{2o}e^2}{4\pi\varepsilon_0 R^3}}{m_e}}}{m_ec^2}}+n_1\bar{E}_{Kvib}+c_3\dfrac{8\pi\mu_0\mu_B^2}{r^3} \end{array}\right) \tag{15.165}$$

The total bond energy of the aromatic group $E_D(Group)$ is the negative difference of the total energy of the group (Eq. (15.165)) and the total energy of the starting species given by the sum of $c_4E_{initial}\left(c_4\ AO/HO\right)$ and $c_5E_{initial}\left(c_5\ AO/HO\right)$:

$$E_D(Group) = -\left(\begin{array}{l} f_1\left(\begin{array}{l} E(basis\ energies)+E_T\left(atom-atom,msp^3.AO\right) \\ -31.63536831\ eV\sqrt{\dfrac{2\hbar\sqrt{\dfrac{\frac{C_{1o}C_{2o}e^2}{4\pi\varepsilon_0 R^3}}{m_e}}}{m_ec^2}}+n_1\bar{E}_{Kvib}+c_3\dfrac{8\pi\mu_0\mu_B^2}{r^3} \end{array}\right) \\ -\left(c_4E_{initial}\left(AO/HO\right)+c_5E_{initial}\left(c_5\ AO/HO\right)\right) \end{array}\right) \tag{15.166}$$

Since there are three electrons per aromatic bond, $c_4$ is three times the number of aromatic bonds.

Benzene can also be considered as comprising chemical bonds between six $CH$ radicals wherein each radical comprises a chemical bond between carbon and hydrogen atoms. The solution of the parameters of $CH$ is given in the Hydrogen Carbide ($CH$) section. Those of the benzene are given in the Benzene Molecule ($C_6H_6$) section. The energy components of $V_e$, $V_p$, $T$, $V_m$, and $E_T$ are the same as those of the hydrogen carbide radical, except that $E_T\left(C=C,2sp^3\right) = -1.13379\ eV$ (Eq. (14.247)) is subtracted from $E_T(CH)$ of Eq. (13.495) to match the energy of each $C-H$-bond MO to the decrease in the energy of the corresponding $C2sp^3$ HO. In the corresponding generalization of the aromatic $CH$ group, the geometrical parameters are determined using Eq. (15.51) and Eqs. (15.1-15.5) with $E_T\left(atom-atom,msp^3.AO\right) = -1.13379\ eV$.

The total energy of the benzene $C-H$-bond MO, $E_{T_{benzene}}(C-H)$, given by Eq. (14.467) is the sum of $0.5E_T\left(C=C,2sp^3\right)$, the energy change of each $C2sp^3$ shell per single bond due to the decrease in radius with the formation of the corresponding $C\overset{3e}{=}C$-bond MO (Eq. (14.247)), and $E_{T_{benzene}}(CH)$, the $\sigma$ MO contribution given by Eq. (14.441). In the corresponding generalization of the aromatic $CH$ group, the energy parameters are determined using Eqs. (15.165-15.166) with $f_1 = 1$ and $E_T\left(atom-atom,msp^3.AO\right) = \dfrac{-1.13379\ eV}{2}$. Thus, the energy contribution to the single aromatic $CH$ bond is one half that of the $C\overset{3e}{=}C$ double bond contribution. This matches the energies of the $CH$ and $C\overset{3e}{=}C$ aromatic groups, conserves the electron number with the equivalent charge density as that of $s=1$ in Eqs. (15.18-15.21), and further gives a minimum energy for the molecule. Breakage of the aromatic $C\overset{3e}{=}C$ bonds to give $CH$ groups creates unpaired electrons in these fragments that corresponds to $c_3 = 1$ in Eq. (15.65) with $E_{mag}$ given by Eq. (15.67).

Each of the $C-H$ bonds of benzene comprises two electrons according to Eq. (14.439). From the energy of each $C-H$ bond, $-E_{D_{benzene}}\left({}^{12}CH\right)$ (Eq. (14.477)), the total energy of the twelve electrons of the six $C-H$ bonds of benzene, $E_T\left(C_6H_6,C-H\right)$, given by Eq. (14.494) is:

$$E_T\left(C_6H_6,C-H\right)=(6)\left(-E_{D_{benzene}}\left({}^{12}CH\right)\right)=6\left(-3.90454\ eV\right)=-23.42724\ eV \tag{15.167}$$

The total bond dissociation energy of benzene, $E_D\left(C_6H_6\right)$, given by Eq. (14.495) is the negative sum of $E_T\left(C_6H_6,C\overset{3e}{=}C\right)$ (Eq. (14.493)) and $E_T\left(C_6H_6,C-H\right)$ (Eq. (14.494)):

$$E_D\left(C_6H_6\right)=-\left(E_T\left(C_6H_6,C\overset{3e}{=}C\right)+E_T\left(C_6H_6,C-H\right)\right)=-\left(\left(-33.83284\ eV\right)+\left(-23.42724\ eV\right)\right)=57.2601\ eV \tag{15.168}$$

Using the parameters given in Tables 15.214 and 15.216 in the general equations (Eqs. (15.51), (15.1-15.5), and (15.165-15.166)) reproduces the results for benzene given in the Benzene Molecule ($C_6H_6$) section as shown in Tables 15.214 and 15.216.

The symbols of the functional groups of aromatics and heterocyclics are given in Table 15.213. The geometrical (Eqs. (15.1-15.5) and (15.51)), intercept (Eqs. (15.80-15.87)), and energy (Eqs. (15.6-15.11), (15.17-15.65), and (15.165-15.166)) parameters of aromatics and heterocyclics are given in Tables 15.214, 15.215, and 15.216, respectively. The total energy of benzene given in Table 15.217 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.216 corresponding to functional-group composition of the molecule. The bond angle parameters of benzene determined using Eqs. (15.88-15.117) are given in Table 15.218. The color scale, translucent view of the charge-density of exemplary aromatic, benzene, comprising the concentric shells of atoms with the outer shell bridged by one or more $H_2$-type ellipsoidal MOs or joined with one or more hydrogen MOs is shown in Figure 15.36.

Figure 15.36. Color scale, translucent view of the charge-density of benzene showing the orbitals of the atoms at their radii, the ellipsoidal surface of each $H$ or $H_2$-type ellipsoidal MO that transitions to the corresponding outer shell of the atom(s) participating in each bond, and the hydrogen nuclei (red, not to scale).

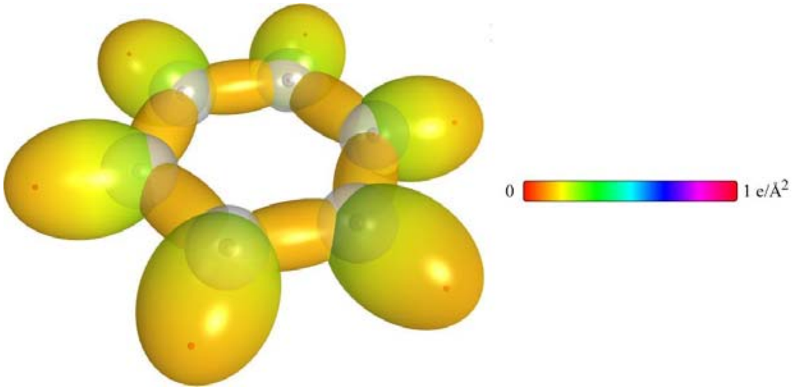


Table 15.213. The symbols of functional groups of aromatics and heterocyclics.

| Functional Group | Group Symbol |
|---|---|
| $CC$ (aromatic bond) | $C\overset{3e}{=}C$ |
| $CH$ (aromatic) | $CH$ (i) |

Table 15.214. The geometrical bond parameters of aromatics and heterocyclics and experimental values [1].

| Parameter | $C\overset{3e}{=}C$ Group | $CH$ Group |
|---|---|---|
| $a$ $(a_0)$ | 1.47348 | 1.60061 |
| $c'$ $(a_0)$ | 1.31468 | 1.03299 |
| Bond Length $2c'$ $(Å)$ | 1.39140 | 1.09327 |
| Exp. Bond Length $(Å)$ | 1.399<br>(benzene) | 1.101<br>(benzene) |
| $b,c$ $(a_0)$ | 0.66540 | 1.22265 |
| $e$ | 0.89223 | 0.64537 |

`Table 15.215.` The MO to HO intercept geometrical bond parameters of benzene. $E_T$ is $E_T$ ($atom - atom, msp^3.AO$).

| Bond | Atom | $E_T$ (eV) Bond 1 | $E_T$ (eV) Bond 2 | $E_T$ (eV) Bond 3 | $E_T$ (eV) Bond 4 | Final Total Energy $C2sp^3$ (eV) | $r_{initial}$ $(a_0)$ | $r_{final}$ $(a_0)$ | $E_{Coulomb}(C2sp^3)$ (eV) Final | $E(C2sp^3)$ (eV) Final | $\theta'$ (°) | $\theta_1$ (°) | $\theta_2$ (°) | $d_1$ $(a_0)$ | $d_2$ $(a_0)$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $C-H\ (CH)$ | $C$ | -0.85035 | -0.85035 | -0.56690 | 0 | -153.88327 | 0.91771 | 0.79597 | -17.09334 | -16.90248 | 74.42 | 105.58 | 38.84 | 1.24678 | 0.21379 |
| $C\overset{3e}{=}HC_a\overset{3e}{=}C$ | $C_a$ | -0.85035 | -0.85035 | -0.56690 | 0 | -153.88327 | 0.91771 | 0.79597 | -17.09334 | -16.90248 | 134.24 | 45.76 | 58.98 | 0.75935 | 0.55533 |

Table 15.216. The energy parameters ($eV$) of functional groups of aromatics and heterocyclics.

| Parameters | $\overset{3e}{C=C}$<br>Group | $CH$<br>Group |
|---|---|---|
| $f_1$ | 0.75 | 1 |
| $n_1$ | 2 | 1 |
| $n_2$ | 0 | 0 |
| $n_3$ | 0 | 0 |
| $C_1$ | 0.5 | 0.75 |
| $C_2$ | 0.85252 | 1 |
| $c_1$ | 1 | 1 |
| $c_2$ | 0.85252 | 0.91771 |
| $c_3$ | 0 | 1 |
| $c_4$ | 3 | 1 |
| $c_5$ | 0 | 1 |
| $C_{1o}$ | 0.5 | 0.75 |
| $C_{2o}$ | 0.85252 | 1 |
| $V_e\ (eV)$ | -101.12679 | -37.10024 |
| $V_p\ (eV)$ | 20.69825 | 13.17125 |
| $T\ (eV)$ | 34.31559 | 11.58941 |
| $V_m\ (eV)$ | -17.15779 | -5.79470 |
| $E(AO/HO)\ (eV)$ | 0 | -14.63489 |
| $\Delta E_{H_2MO}(AO/HO)\ (eV)$ | 0 | -1.13379 |
| $E_T(AO/HO)\ (eV)$ | 0 | -13.50110 |
| $E_T(H_2MO)\ (eV)$ | -63.27075 | -31.63539 |
| $E_T\left(atom-atom, msp^3.AO\right)\ (eV)$ | -2.26759 | -0.56690 |
| $E_T(MO)\ (eV)$ | -65.53833 | -32.20226 |
| $\omega\ \left(10^{15}\ rad/s\right)$ | 49.7272 | 26.4826 |
| $E_K\ (eV)$ | 32.73133 | 17.43132 |
| $\bar{E}_D\ (eV)$ | -0.35806 | -0.26130 |
| $\bar{E}_{Kvib}\ (eV)$ | 0.19649<br>[49] | 0.35532<br>Eq. (13.458) |
| $\bar{E}_{osc}\ (eV)$ | -0.25982 | -0.08364 |
| $E_{mag}\ (eV)$ | 0.14803 | 0.14803 |
| $E_T(Group)\ (eV)$ | -49.54347 | -32.28590 |
| $E_{initial}(c_4\ AO/HO)\ (eV)$ | -14.63489 | -14.63489 |
| $E_{initial}(c_5\ AO/HO)\ (eV)$ | 0 | -13.59844 |
| $E_D(Group)\ (eV)$ | 5.63881 | 3.90454 |

Table 15.217. The total bond energies of benzene calculated using the functional group composition and the energies of Table 15.216 compared to the experimental values [3].

| Formula | Name | $\overset{3e}{C=C}$ | $CH$ | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|---|---|
| $C_6H_6$ | Benzene | 6 | 6 | 57.26008 | 57.26340 | 0.00006 |

Table 15.218. The bond angle parameters of benzene and experimental values [1]. $E_T$ is $E_T$ ($atom - atom,msp^3.AO$ ).

| Atoms of Angle | $2c'$ Bond 1 ($a_0$) | $2c'$ Bond 2 ($a_0$) | $2c'$ Terminal Atoms ($a_0$) | $E_{Coulombic}$ Atom 1 | Atom 1 Hybridization Designation (Table 15.3.A) | $E_{Coulombic}$ Atom 2 | Atom 2 Hybridization Designation (Table 15.3.A) | $c_2$ Atom 1 | $c_2$ Atom 2 | $C_1$ | $C_2$ | $c_1$ | $c_2'$ | $E_T$ (eV) | $\theta_v$ (°) | $\theta_1$ (°) | $\theta_2$ (°) | Cal. $\theta$ (°) | Exp. $\theta$ (°) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $\angle CCC$ (aromatic) | 2.62936 | 2.62936 | 4.5585 | -17.17218 | 38 | -17.17218 | 38 | 0.79232 | 0.79232 | 1 | 1 | 1 | 0.79232 | -1.85836 | | | | 120.19 | 120 [50-52] (benzene) |
| $\angle CCH$ (aromatic) | | | | | | | | | | | | | | | | 120.19 | | 119.91 | 120 [50-52] (benzene) |

## NAPHTHALENE

Naphthalene has the formula $C_{10}H_8$ and comprises a planar molecule with two aromatic rings that share a common $C-C$ group. In order to be aromatic, the total number of bonding electrons must be a multiple of 3 since the number of electrons of the aromatic bond is $(0.75)(4)=3$ as shown in the Benzene section. In the case of naphthalene, the peripheral 10 carbons form the aromatic MO with the center bridged by a $C-C$ single bond. Then, 30 electrons of the 48 available form aromatic bonds, two electrons form the bridging $C-C$ single bond, and 16 electrons form the eight $C-H$ single bonds. The energies of the aromatic carbons are given by the same equations as those of benzene (Eqs. (15.51), (15.1-15.5), and (15.165-15.166)), except that there are 10 in naphthalene versus six in benzene. Since there are three electrons per aromatic bond, $c_4$ is three times ten, the number of aromatic bonds. Similarly, the aromatic $C-H$ group of naphthalene is equivalent to that of benzene.

To meet the equipotential condition of the union of the ten $C2sp^3$ HOs bridged by the $C-C$ single bond, the parameters $c_1$, $C_2$, and $C_{2o}$ of Eq. (15.51) are one for the $C-C$ group, $C_{1o}$ and $C_1$ are 0.5, and $c_2$ given by Eq. (15.161) is $c_2\left(C2sp^3HO\right)=0.85252$. Otherwise, the solutions of the $C-C$ bond parameters are equivalent to those of the replaced $C-H$ groups with $E\left(AO/HO\right)=-14.63489\ eV$ and $\Delta E_{H_2MO}\left(AO/HO\right)=-1.13379\ eV$ per carbon in Eq. (15.51). Similarly, the energy parameters are determined using Eqs. (15.61-15.65) with $E_T\left(atom-atom,msp^3.AO\right)=\frac{-1.13379\ eV}{2}$.

The symbols of the functional groups of naphthalene are given in Table 15.219. The corresponding designation of the structure is shown in Figure 15.37B. The geometrical (Eqs. (15.1-15.5) and (15.51)), intercept (Eqs. (15.80-15.87)), and energy (Eqs. (15.6-15.11), (15.17-15.65), and (15.165-15.166)) parameters of naphthalene are given in Tables 15.220, 15.221, and 15.222, respectively. The total energy of naphthalene given in Table 15.223 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.222 corresponding to functional-group composition of the molecule. The bond angle parameters of naphthalene determined using Eqs. (15.88-15.117) are given in Table 15.224. The color scale, translucent view of the charge-density of naphthalene, comprising the concentric shells of atoms with the outer shell bridged by one or more $H_2$-type ellipsoidal MOs or joined with one or more hydrogen MOs is shown in Figure 15.37A. The polycyclic aromatic hydrocarbon pentacene was imaged by atomic force microscopy using a single CO molecule as the probe [53]. The resulting breakthrough in resolution revealed that in contrast to the fuzzy images touted by quantum theoreticians as proof of the cloud model of the electron, the images showed localized bonding MOs and AOs in agreement with the classical solution as shown in Figure 15.38.

Figure 15.37. (A) Color scale, translucent view of the charge-density of naphthalene showing the orbitals of the atoms at their radii, the ellipsoidal surface of each $H$ or $H_2$-type ellipsoidal MO that transitions to the corresponding outer shell of the atom(s) participating in each bond, and the hydrogen nuclei (red, not to scale). (B) Chemical structure and atom designation of naphthalene.

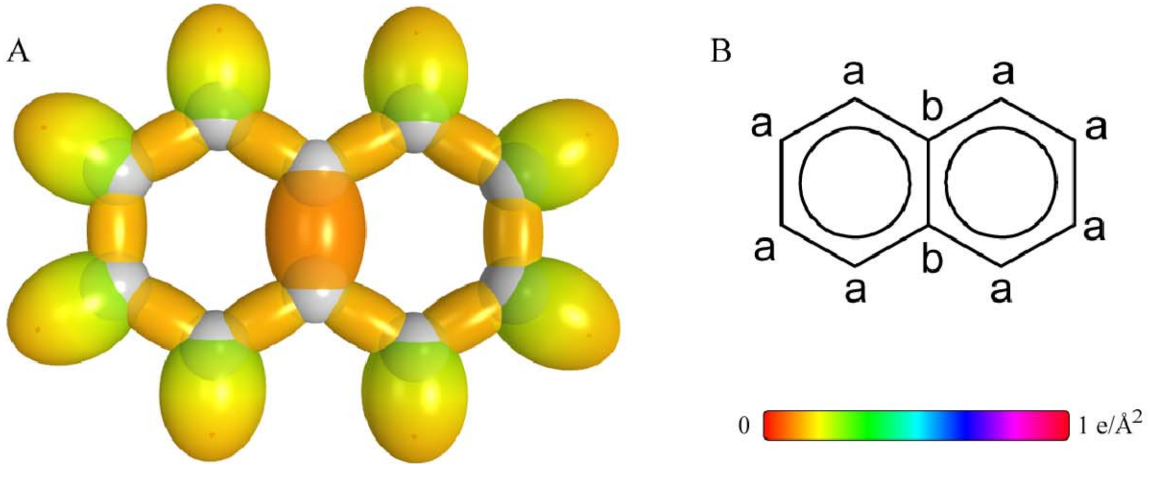


Figure 15.38. Atomic force microscopy image of pentacene by Gross et al. [53] and the superimposed analytical classical solution that matches the physical structure.

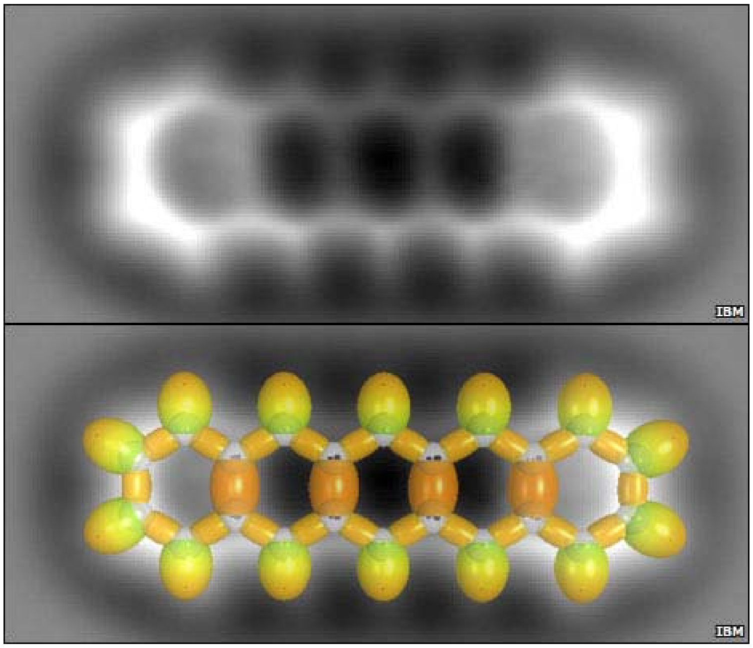


Table 15.219. The symbols of functional groups of naphthalene.

| Functional Group | Group Symbol |
|---|---|
| $C_aC_a$ (aromatic bond) | $C\overset{3e}{=}C$ |
| $CH$ (aromatic) | $CH$ (i) |
| $C_b - C_b$ (bridging bond) | $C - C$ |

Table 15.220. The geometrical bond parameters of naphthalene and experimental values [1].

| Parameter | $C\overset{3e}{=}C$ Group | $CH$ Group | $C-C$ Group |
|---|---|---|---|
| $a\ (a_0)$ | 1.47348 | 1.60061 | 1.75607 |
| $c'\ (a_0)$ | 1.31468 | 1.03299 | 1.32517 |
| Bond Length $2c'$ ($\mathring{A}$) | 1.39140 | 1.09327 | 1.40250 |
| Exp. Bond Length ($\mathring{A}$) | 1.40 (avg.) (naphthalene) | 1.101 (benzene) | 1.42 (naphthalene) |
| $b,c\ (a_0)$ | 0.66540 | 1.22265 | 1.15226 |
| $e$ | 0.89223 | 0.64537 | 0.75462 |

Table 15.221. The MO to HO intercept geometrical bond parameters of naphthalene. $E_T$ is $E_T$ ($atom - atom, msp^3.AO$).

| Bond | Atom | $E_T$ (eV) Bond 1 | $E_T$ (eV) Bond 2 | $E_T$ (eV) Bond 3 | $E_T$ (eV) Bond 4 | Final Total Energy $C2sp^3$ (eV) | $r_{initial}$ $(a_0)$ | $r_{final}$ $(a_0)$ | $E_{Coulomb}(C2sp^3)$ (eV) Final | $E(C2sp^3)$ (eV) Final | $\theta'$ (°) | $\theta_1$ (°) | $\theta_2$ (°) | $d_1$ $(a_0)$ | $d_2$ $(a_0)$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $C-H\ (CH)$ | $C$ | -0.85035 | -0.85035 | -0.56690 | 0 | -153.88327 | 0.91771 | 0.79597 | -17.09334 | -16.90248 | 74.42 | 105.58 | 38.84 | 1.24678 | 0.21379 |
| $C\overset{3e}{=}HC_a\overset{3e}{=}C$ | $C_a$ | -0.85035 | -0.85035 | -0.56690 | 0 | -153.88327 | 0.91771 | 0.79597 | -17.09334 | -16.90248 | 134.24 | 45.76 | 58.98 | 0.75935 | 0.55533 |
| $C\overset{3e}{=}C_b(C_b)\overset{3e}{=}C$ | $C_b$ | -0.85035 | -0.85035 | -0.28345 | 0 | -153.59983 | 0.91771 | 0.80939 | -16.80989 | -16.61903 | 134.81 | 45.19 | 59.66 | 0.74430 | 0.57038 |
| $(C_a)_2C_b-C_b(C_a)_2$ | $C_b$ | -0.85035 | -0.85035 | -0.28345 | 0 | -153.59983 | 0.91771 | 0.80939 | -16.80989 | -16.61903 | 99.50 | 80.50 | 47.66 | 1.18269 | 0.14248 |

Table 15.222. The energy parameters ($eV$) of functional groups of naphthalene.

| Parameters | $C\overset{3e}{=}C$ Group | $CH$ Group | $C-C$ Group |
|---|---|---|---|
| $f_1$ | 0.75 | 1 | 1 |
| $n_1$ | 2 | 1 | 1 |
| $n_2$ | 0 | 0 | 0 |
| $n_3$ | 0 | 0 | 0 |
| $C_1$ | 0.5 | 0.75 | 0.5 |
| $C_2$ | 0.85252 | 1 | 1 |
| $c_1$ | 1 | 1 | 1 |
| $c_2$ | 0.85252 | 0.91771 | 0.85252 |
| $c_3$ | 0 | 1 | 0 |
| $c_4$ | 3 | 1 | 2 |
| $c_5$ | 0 | 1 | 0 |
| $C_{1o}$ | 0.5 | 0.75 | 0.5 |
| $C_{2o}$ | 0.85252 | 1 | 1 |
| $V_e\ (eV)$ | -101.12679 | -37.10024 | -34.43791 |
| $V_p\ (eV)$ | 20.69825 | 13.17125 | 10.26723 |
| $T\ (eV)$ | 34.31559 | 11.58941 | 9.80539 |
| $V_m\ (eV)$ | -17.15779 | -5.79470 | -4.90270 |
| $E(AO/HO)\ (eV)$ | 0 | -14.63489 | -14.63489 |
| $\Delta E_{H_2MO}(AO/HO)\ (eV)$ | 0 | -1.13379 | -1.13379 |
| $E_T(AO/HO)\ (eV)$ | 0 | -13.50110 | -13.50110 |
| $E_T(H_2MO)\ (eV)$ | -63.27075 | -31.63539 | -31.63529 |
| $E_T(atom-atom,msp^3.AO)\ (eV)$ | -2.26759 | -0.56690 | -0.56690 |
| $E_T(MO)\ (eV)$ | -65.53833 | -32.20226 | -32.20226 |
| $\omega\ (10^{15}\ rad/s)$ | 49.7272 | 26.4826 | 23.6343 |
| $E_K\ (eV)$ | 32.73133 | 17.43132 | 15.55648 |
| $\bar{E}_D\ (eV)$ | -0.35806 | -0.26130 | -0.25127 |
| $\bar{E}_{Kvib}\ (eV)$ | 0.19649<br>[49] | 0.35532<br>Eq. (13.458) | 0.12312<br>[2] |
| $\bar{E}_{osc}\ (eV)$ | -0.25982 | -0.08364 | -0.18971 |
| $E_{mag}\ (eV)$ | 0.14803 | 0.14803 | 0.14803 |
| $E_T(Group)\ (eV)$ | -49.54347 | -32.28590 | -32.39198 |
| $E_{initial}(c_4\ AO/HO)\ (eV)$ | -14.63489 | -14.63489 | -14.63489 |
| $E_{initial}(c_5\ AO/HO)\ (eV)$ | 0 | -13.59844 | 0 |
| $E_D(Group)\ (eV)$ | 5.63881 | 3.90454 | 3.12220 |

Table 15.223. The total bond energies of naphthalene calculated using the functional group composition and the energies of Table 15.222 compared to the experimental values [3].

| Formula | Name | $\overset{3e}{C=C}$ | $CH$ | $C-C$ Group | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|---|---|---|
| $C_{10}H_8$ | Naphthalene | 10 | 8 | 1 | 90.74658 | 90.79143 | 0.00049 |

Table 15.224. The bond angle parameters of naphthalene and experimental values [1]. $E_T$ is $E_T(atom-atom,msp^3.AO)$.

| Atoms of Angle | $2c'$ Bond 1 $(a_0)$ | $2c'$ Bond 2 $(a_0)$ | $2c'$ Terminal Atoms $(a_0)$ | $E_{Coulombic}$ Atom 1 | Atom 1 Hybridization Designation (Table 15.3.A) | $E_{Coulombic}$ Atom 2 | Atom 2 Hybridization Designation (Table 15.3.A) | $c_2$ Atom 1 | $c_2$ Atom 2 | $C_1$ | $C_2$ | $c_1$ | $c_2'$ | $E_T$ (eV) | $\theta_v$ (°) | $\theta_1$ (°) | $\theta_2$ (°) | Cal. $\theta$ (°) | Exp. $\theta$ (°) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $\angle C_aC_cC_c$ (naphthalene) | 2.62936 | 2.65034 | 4.5585 | -17.17218 | 38 | -17.17218 | 38 | 0.79232 | 0.79232 | 1 | 1 | 1 | 0.79232 | -1.85836 | | | | 119.40 | 119.4 (naphthalene) |
| $\angle C_cC_aH$ (naphthalene) | | | | | | | | | | | | | | | | 119.40 | | 120.30 | |
| $\angle CCC$ (aromatic) | 2.62936 | 2.62936 | 4.5585 | -17.17218 | 38 | -17.17218 | 38 | 0.79232 | 0.79232 | 1 | 1 | 1 | 0.79232 | -1.85836 | | | | 120.19 | 120 [50-52] (benzene) |
| $\angle CCH$ (aromatic) | | | | | | | | | | | | | | | | 120.19 | | 119.91 | 120 [50-52] (benzene) |

## TOLUENE

Toluene has the formula $C_7H_8$ and comprises the benzene molecule with one hydrogen atom replaced by a methyl group corresponding to a $CH_3$ functional group and a $C-C$ functional group. The aromatic $C\overset{3e}{=}C$ and $C-H$ functional groups are equivalent to those of benzene given in the Aromatic and Heterocyclic Compounds section. The $CH_3$ functional group is the same as that of continuous and branched-chain alkanes given in the corresponding sections.

The bond between the methyl and aromatic ring comprises a $C-C$ functional group that is solved using the same principles as those used to solve the alkane functional groups wherein the $2s$ and $2p$ AOs of each $C$ hybridize to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between two $C2sp^3$ HOs to form a MO permits each participating hybridized orbital to decrease in radius and energy. To match energies within the MO that bridges methyl and aromatic carbons, $E(AO/HO)$ and $\Delta E_{H_2MO}(AO/HO)$ in Eq. (15.50) are $-15.35946\ eV$ (Eq. (14.155)) and $\frac{-1.13379\ eV}{2}$, respectively.

To meet the equipotential condition of the union of the aromatic and methyl $C2sp^3$ HOs of the $C-C$ single bond, the parameters $c_1$, $C_2$, and $C_{2o}$ of Eq. (15.51) are one for the $C-C$ group, $C_{1o}$ and $C_1$ are 0.5, and $c_2$ given by Eq. (13.430) is $c_2\left(C2sp^3HO\right)=0.91771$. To match the energies of the functional groups, $E_T\left(atom-atom, msp^3.AO\right)$ of the $C-C$-bond MO in Eq. (15.61) due to the charge donation from the $C$ atoms to the MO is $-1.13379\ eV$ which is the same energy per $C2sp^3$ HO as that of the replaced $C-H$ group.

The symbols of the functional groups of toluene are given in Table 15.225. The corresponding designation of the structure is shown in Figure 15.39B. The geometrical (Eqs. (15.1-15.5) and (15.51)), intercept (Eqs. (15.80-15.87)), and energy (Eqs. (15.6-15.11), (15.17-15.65), and (15.165-15.166)) parameters of toluene are given in Tables 15.226, 15.227, and 15.228, respectively. The total energy of toluene given in Table 15.229 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.228 corresponding to functional-group composition of the molecule. The bond angle parameters of toluene determined using Eqs. (15.88-15.117) are given in Table 15.230. The color scale, translucent view of the charge-density of toluene comprising the concentric shells of atoms with the outer shell bridged by one or more $H_2$-type ellipsoidal MOs or joined with one or more hydrogen MOs is shown in Figure 15.39A.

Figure 15.39. (A) Color scale, translucent view of the charge-density of toluene showing the orbitals of the atoms at their radii, the ellipsoidal surface of each $H$ or $H_2$-type ellipsoidal MO that transitions to the corresponding outer shell of the atom(s) participating in each bond, and the hydrogen nuclei (red, not to scale). (B) Chemical structure and atom designation of toluene.

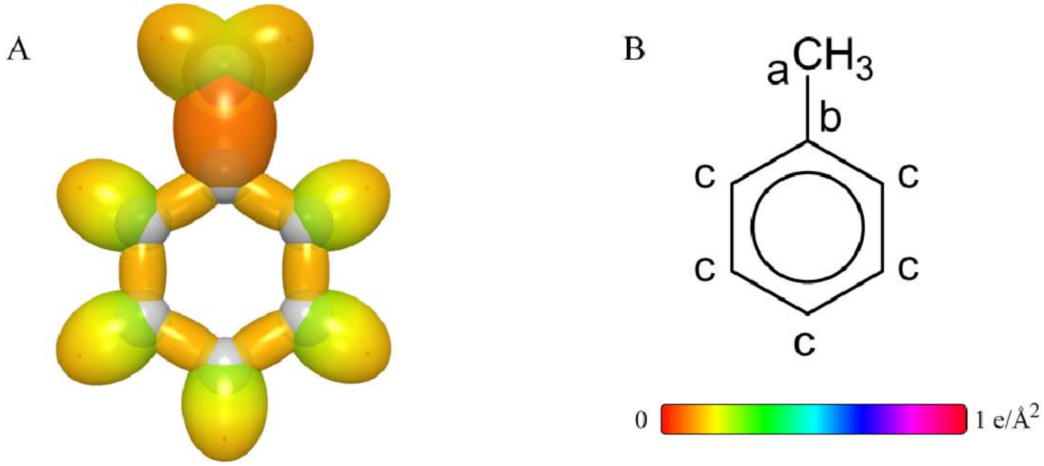


Table 15.225. The symbols of functional groups of toluene.

| Functional Group | Group Symbol |
|---|---|
| $CC$ (aromatic bond) | $C\overset{3e}{=}C$ |
| $CH$ (aromatic) | $CH$ (i) |
| $C_a - C_b$ ($CH_3$ to aromatic bond) | $C-C$ |
| $CH_3$ group | $C-H$ $(CH_3)$ |

Table 15.226. The geometrical bond parameters of toluene and experimental values [1].

| Parameter | $C\overset{3e}{=}C$ Group | $CH$ (i) Group | $C-C$ Group | $C-H$ $(CH_3)$ Group |
|---|---|---|---|---|
| $a$ $(a_0)$ | 1.47348 | 1.60061 | 2.06004 | 1.64920 |
| $c'$ $(a_0)$ | 1.31468 | 1.03299 | 1.43528 | 1.04856 |
| Bond Length $2c'$ $(\mathring{A})$ | 1.39140 | 1.09327 | 1.51904 | 1.10974 |
| Exp. Bond Length $(\mathring{A})$ | 1.399<br>(toluene) | 1.11 (avg.)<br>(toluene) | 1.524<br>(toluene) | 1.11 (avg.)<br>(toluene) |
| $b,c$ $(a_0)$ | 0.66540 | 1.22265 | 1.47774 | 1.27295 |
| $e$ | 0.89223 | 0.64537 | 0.69673 | 0.63580 |

Table 15.227. The MO to HO intercept geometrical bond parameters of toluene. $E_T$ is $E_T$ (*atom – atom,msp*$^3$*.AO*).

| Bond | Atom | $E_T$ (eV) Bond 1 | $E_T$ (eV) Bond 2 | $E_T$ (eV) Bond 3 | $E_T$ (eV) Bond 4 | Final Total Energy $C2sp^3$ (eV) | $r_{initial}$ $(a_0)$ | $r_{final}$ $(a_0)$ | $E_{Coulomb}(C2sp^3)$ (eV) Final | $E(C2sp^3)$ (eV) Final | $\theta'$ $(°)$ | $\theta_1$ $(°)$ | $\theta_2$ $(°)$ | $d_1$ $(a_0)$ | $d_2$ $(a_0)$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $C-H\ (C_aH_3)$ | $C_a$ | -0.56690 | 0 | 0 | 0 | -152.18259 | 0.91771 | 0.88392 | -15.39265 | -15.20178 | 79.89 | 101.11 | 43.13 | 1.20367 | 0.15511 |
| $C-H\ (C_cH)$ | $C_c$ | -0.85035 | -0.85035 | -0.56690 | 0 | -153.88327 | 0.91771 | 0.79597 | -17.09334 | -16.90248 | 74.42 | 105.58 | 38.84 | 1.24678 | 0.21379 |
| $C\overset{3e}{=}HC_c\overset{3e}{=}C$<br>$C\overset{3e}{=}(H_3C_a)C_b\overset{3e}{=}C$ | $C_c$<br>$C_b$ | -0.85035 | -0.85035 | -0.56690 | 0 | -153.88327 | 0.91771 | 0.79597 | -17.09334 | -16.90248 | 134.24 | 45.76 | 58.98 | 0.75935 | 0.55533 |
| $\left(C\overset{3e}{=}\right)_2 C_b-C_aH_3$ | $C_a$ | -0.56690 | 0 | 0 | 0 | -152.18259 | 0.91771 | 0.88392 | -15.39265 | -15.20178 | 73.38 | 106.62 | 34.97 | 1.68807 | 0.25279 |
| $\left(C\overset{3e}{=}\right)_2 C_b-C_aH_3$ | $C_b$ | -0.56690 | -0.85035 | -0.85035 | 0 | -153.88328 | 0.91771 | 0.79597 | -17.09334 | -16.90247 | 61.56 | 118.44 | 28.27 | 1.81430 | 0.37901 |

Table 15.228. The energy parameters ($eV$) of functional groups of toluene.

| Parameters | $\overset{3e}{C=C}$ Group | $CH$ (i) Group | $C-C$ Group | $CH_3$ Group |
|---|---|---|---|---|
| $f_1$ | 0.75 | 1 | | |
| $n_1$ | 2 | 1 | 1 | 3 |
| $n_2$ | 0 | 0 | 0 | 2 |
| $n_3$ | 0 | 0 | 0 | 0 |
| $C_1$ | 0.5 | 0.75 | 0.5 | 0.75 |
| $C_2$ | 0.85252 | 1 | 1 | 1 |
| $c_1$ | 1 | 1 | 1 | 1 |
| $c_2$ | 0.85252 | 0.91771 | 0.91771 | 0.91771 |
| $c_3$ | 0 | 1 | 0 | 0 |
| $c_4$ | 3 | 1 | 2 | 1 |
| $c_5$ | 0 | 1 | 0 | 3 |
| $C_{1o}$ | 0.5 | 0.75 | 0.5 | 0.75 |
| $C_{2o}$ | 0.85252 | 1 | 1 | 1 |
| $V_e$ $(eV)$ | -101.12679 | -37.10024 | -29.95792 | -107.32728 |
| $V_p$ $(eV)$ | 20.69825 | 13.17125 | 9.47952 | 38.92728 |
| $T$ $(eV)$ | 34.31559 | 11.58941 | 7.27120 | 32.53914 |
| $V_m$ $(eV)$ | -17.15779 | -5.79470 | -3.63560 | -16.26957 |
| $E(AO/HO)$ $(eV)$ | 0 | -14.63489 | -15.35946 | -15.56407 |
| $\Delta E_{H_2MO}(AO/HO)$ $(eV)$ | 0 | -1.13379 | -0.56690 | 0 |
| $E_T(AO/HO)$ $(eV)$ | 0 | -13.50110 | -14.79257 | -15.56407 |
| $E_T(H_2MO)$ $(eV)$ | -63.27075 | -31.63539 | -31.63537 | -67.69451 |
| $E_T\left(atom-atom, msp^3.AO\right)$ $(eV)$ | -2.26759 | -0.56690 | -1.13379 | 0 |
| $E_T(MO)$ $(eV)$ | -65.53833 | -32.20226 | -32.76916 | -67.69450 |
| $\omega$ $\left(10^{15}\ rad/s\right)$ | 49.7272 | 26.4826 | 16.2731 | 24.9286 |
| $E_K$ $(eV)$ | 32.73133 | 17.43132 | 10.71127 | 16.40846 |
| $\bar{E}_D$ $(eV)$ | -0.35806 | -0.26130 | -0.21217 | -0.25352 |
| $\bar{E}_{Kvib}$ $(eV)$ | 0.19649 [49] | 0.35532 Eq. (13.458) | 0.14940 [54] | 0.35532 (Eq. (13.458)) |
| $\bar{E}_{osc}$ $(eV)$ | -0.25982 | -0.08364 | -0.13747 | -0.22757 |
| $E_{mag}$ $(eV)$ | 0.14803 | 0.14803 | 0.14803 | 0.14803 |
| $E_T(Group)$ $(eV)$ | -49.54347 | -32.28590 | -32.90663 | -67.92207 |
| $E_{initial}(c_4\ AO/HO)$ $(eV)$ | -14.63489 | -14.63489 | -14.63489 | -14.63489 |
| $E_{initial}(c_5\ AO/HO)$ $(eV)$ | 0 | -13.59844 | 0 | -13.59844 |
| $E_D(Group)$ $(eV)$ | 5.63881 | 3.90454 | 3.63685 | 12.49186 |

Table 15.229. The total bond energies of toluene calculated using the functional group composition and the energies of Table 15.228 compared to the experimental values [3].

| Formula | Name | $C\overset{3e}{=}C$ | $CH$ (i) | $C-C$ Group | $CH_3$ | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|---|---|---|---|
| $C_7H_8$ | Toluene | 6 | 5 | 1 | 1 | 69.48425 | 69.546 | 0.00088 |

Table 15.230. The bond angle parameters of toluene and experimental values [1]. $E_T$ is $E_T$ ($atom - atom, msp^3.AO$).

| Atoms of Angle | $2c'$ Bond 1 ($a_0$) | $2c'$ Bond 2 ($a_0$) | $2c'$ Terminal Atoms ($a_0$) | $E_{Coulombic}$ Atom 1 | Atom 1 Hybridization Designation (Table 15.3.A) | $E_{Coulombic}$ Atom 2 | Atom 2 Hybridization Designation (Table 15.3.A) | $c_2$ Atom 1 | $c_2$ Atom 2 | $C_1$ | $C_2$ | $c_1$ | $c_2'$ | $E_T$ (eV) | $\theta_v$ (°) | $\theta_1$ (°) | $\theta_2$ (°) | Cal. $\theta$ (°) | Exp. $\theta$ (°) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $\angle CCC$ (aromatic) | 2.62936 | 2.62936 | 4.5585 | -17.17218 | 38 | -17.17218 | 38 | 0.79232 | 0.79232 | 1 | 1 | 1 | 0.79232 | -1.85836 | | | | 120.19 | 120 [50-52] (benzene) |
| $\angle CCH$ (aromatic) | | | | | | | | | | | | | | | | 120.19 | | 119.91 | 120 [50-52] (benzene) |

## HALOBENZENES

Halobenzenes have the formula $C_6H_{6-m}X_m$ $X = F, Cl, Br, I$ and comprise the benzene molecule with at least one hydrogen atom replaced by a halogen atom corresponding to a $C-X$ functional group. The aromatic $C\overset{3e}{=}C$ and $C-H$ functional groups are equivalent to those of benzene given in the Aromatic and Heterocyclic Compounds section. The hybridization factors of the aryl $C-X$ functional groups are equivalent to those of the corresponding alkyl halides as given in Tables 15.30, 15.36, 15.42, and 15.48, and are solved using the same principles as those used to solve the alkyl halide functional groups as given in the corresponding sections. In each case, the $2s$ and $2p$ AOs of each $C$ hybridize to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between the $C2sp^3$ HO and $X$ AO to form a MO permits each participating hybridized orbital to decrease in radius and energy. Therefore, the MO is energy matched to the $C2sp^3$ HO such that $E(AO/HO)$ in Eq. (15.51) is $-14.63489\ eV$. $E_T(atom-atom,msp^3.AO)$ of each $C-X$ functional group given in Table 15.234 that achieves matching of the energies of the AOs and HOs within the functional groups of the MOs are those of alkanes and alkenes given in Tables 15.1 and 15.2. To further match energies within each MO that bridges the halogen AO and aromatic carbon $C2sp^3$ HO, $\Delta E_{H_2MO}(AO/HO)$ in Eq. (15.51) is $E_T(atom-atom,msp^3.AO)$ of the alkene $C=C$ functional group, $-2.26759\ eV$ given by Eq. (14.247), plus the maximum possible contribution of $E_T(atom-atom,msp^3.AO)$ of the $C-X$ functional group to minimize the energy of the MO as given in Table 15.234. $E_{initial}(c_4\ AO/HO)$ is $-14.63489\ eV$ (Eq. (15.25)), except for $C-I$ due to the low ionization potential of the $I$ AO. In order to achieve an energy minimum with energy matching within iodo-aryl molecules, $E_{initial}(c_4\ AO/HO)$ of the $C-I$ functional group is $-15.76868\ eV$ (Eq. (14.246)), and $E_T(atom-atom,msp^3.AO)$ is $-1.65376\ eV$ given by the linear combination of $-0.72457\ eV$ (Eq. (14.151)) and $-0.92918\ eV$ (Eq. (14.513)), respectively.

The small differences between energies of ortho, meta, and para-dichlorobenzene is due to differences in the energies of vibration in the transition state that contribute to $E_{osc}$. Two types of $C-Cl$ functional groups can be identified based on symmetry that determine the parameter $R$ in Eq. (15.57). One corresponds to the special case of 1,3,5 substitution and the other corresponds to other cases of single or multiple substitutions of $Cl$ for $H$. P-dichlorobenzene is representative of the bonding with $R=a$. 1,2,3-trichlorobenzene is the particular case wherein $R=b$. Also, beyond the binding of three chlorides $E_{mag}$ is subtracted for each additional $Cl$ due to the formation of an unpaired electrons on each $C-Cl$ bond.

The symbols of the functional groups of halobenzenes are given in Table 15.231. The geometrical (Eqs. (15.1-15.5) and (15.51)), intercept (Eqs. (15.80-15.87)), and energy (Eqs. (15.6-15.11), (15.17-15.65), and (15.165-15.166)) parameters of halobenzenes are given in Tables 15.232, 15.233, and 15.234, respectively. The total energy of each halobenzene given in Table 15.235 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.234 corresponding to functional-group composition of the molecule. For each set of unpaired electrons created by bond breakage, the $C2sp^3$ HO magnetic energy $E_{mag}$ that is subtracted from the weighted sum of the $E_D(Group)$ $(eV)$ values based on composition is given by Eq. (15.67). The bond angle parameters of halobenzenes determined using Eqs. (15.88-15.117) are given in Table 15.236. The color scale, translucent view of the charge-density of chlorobenzene comprising the concentric shells of atoms with the outer shell bridged by one or more $H_2$-type ellipsoidal MOs or joined with one or more hydrogen MOs is shown in Figure 15.40.

Figure 15.40. Color scale, translucent view of the charge-density of chlorobenzene showing the orbitals of the atoms at their radii, the ellipsoidal surface of each $H$ or $H_2$-type ellipsoidal MO that transitions to the corresponding outer shell of the atom(s) participating in each bond, and the hydrogen nuclei (red, not to scale).

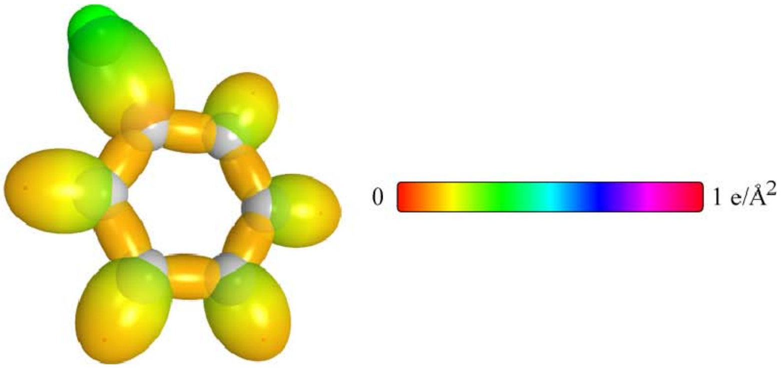


Table 15.231. The symbols of functional groups of halobenzenes.

| Functional Group | Group Symbol |
|---|---|
| $CC$ (aromatic bond) | $C\overset{3e}{=}C$ |
| $CH$ (aromatic) | $CH$ (i) |
| $F-C$ ($F$ to aromatic bond) | $C-F$ |
| $Cl-C$ ($Cl$ to aromatic bond) | $C-Cl$ (a) |
| $Cl-C$ ($Cl$ to aromatic bond of 1,3,5-trichlorobenzene) | $C-Cl$ (b) |
| $Br-C$ ($Br$ to aromatic bond) | $C-Br$ |
| $I-C$ ($I$ to aromatic bond) | $C-I$ |

Table 15.232. The geometrical bond parameters of halobenzenes and experimental values [1].

| Parameter | $\overset{3e}{C=C}$ Group | $CH$ (i) Group | $C-F$ Group | $C-Cl$ (a) Group | $C-Cl$ (b) Group | $C-Br$ Group | $C-I$ Group |
|---|---|---|---|---|---|---|---|
| $a\ (a_0)$ | 1.47348 | 1.60061 | 1.60007 | 2.20799 | 2.20799 | 2.30810 | 2.50486 |
| $c'\ (a_0)$ | 1.31468 | 1.03299 | 1.26494 | 1.64782 | 1.64782 | 1.76512 | 1.95501 |
| Bond Length $2c'$ $(Å)$ | 1.39140 | 1.09327 | 1.33875 | 1.74397 | 1.74397 | 1.86812 | 2.06909 |
| Exp. Bond Length $(Å)$ | 1.400 (chlorobenzene) | 1.083 (chlorobenzene) | 1.356 [55] (fluorobenzene) | 1.737 (chlorobenzene) | 1.737 (chlorobenzene) | 1.8674 [56] (bromobenzene) | 2.08 [57] (iodobenzene) |
| $b,c\ (a_0)$ | 0.66540 | 1.22265 | 0.97987 | 1.46967 | 1.46967 | 1.48718 | 1.56597 |
| $e$ | 0.89223 | 0.64537 | 0.79055 | 0.74630 | 0.74630 | 0.76475 | 0.78049 |

Table 15.233. The MO to HO intercept geometrical bond parameters of halobenzenes. $E_T$ is $E_T$ ($atom-atom,msp^3.AO$).

| Bond | Atom | $E_T$ (eV) Bond 1 | $E_T$ (eV) Bond 2 | $E_T$ (eV) Bond 3 | $E_T$ (eV) Bond 4 | Final Total Energy $C2sp^3$ (eV) | $r_{initial}$ $(a_0)$ | $r_{final}$ $(a_0)$ | $E_{Coulomb}(C2sp^3)$ (eV) Final | $E(C2sp^3)$ (eV) Final | $\theta'$ (°) | $\theta_1$ (°) | $\theta_2$ (°) | $d_1$ $(a_0)$ | $d_2$ $(a_0)$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $C-H\ (C_bH)$ | $C_b$ | -0.85035 | -0.85035 | -0.56690 | 0 | -153.88327 | 0.91771 | 0.79597 | -17.09334 | -16.90248 | 74.42 | 105.58 | 38.84 | 1.24678 | 0.21379 |
| $\overset{3e}{C=}HC_b\overset{3e}{=}C$ | $C_b$ | -0.85035 | -0.85035 | -0.56690 | 0 | -153.88327 | 0.91771 | 0.79597 | -17.09334 | -16.90248 | 134.24 | 45.76 | 58.98 | 0.75935 | 0.55533 |
| $\left(\overset{3e}{C=}\right)_2 C_a-F$ | $C_a$ | -1.03149 | -0.85035 | -0.85035 | 0 | -154.34787 | 0.91771 | 0.77491 | -17.55793 | -17.36707 | 106.58 | 73.42 | 49.28 | 1.04378 | 0.22116 |
| $\left(\overset{3e}{C=}\right)_2 C_a-F$ | $F$ | -1.03149 | 0 | 0 | 0 |  | 0.78069 | 0.85802 | -15.85724 |  | 112.35 | 67.65 | 54.08 | 0.93865 | 0.32629 |
| $\left(\overset{3e}{C=}\right)_2 C_a-Cl$ | $C_a$ | -0.36229 | -0.85035 | -0.85035 | 0 | -153.67867 | 0.91771 | 0.80561 | -16.88873 | -16.69786 | 73.32 | 106.68 | 31.67 | 1.87911 | 0.23129 |
| $\left(\overset{3e}{C=}\right)_2 C_a-Cl$ | $Cl$ | -0.36229 | 0 | 0 | 0 |  | 1.05158 | 0.89582 | 15.18804 |  | 82.92 | 97.08 | 37.22 | 1.75824 | 0.11042 |
| $C_b\overset{3e}{=}(Cl)C_a\overset{3e}{=}C_b$ ($C_b$ bound to $Cl$) | $C_b$ | -0.36229 | -0.85035 | -0.85035 | 0 | -153.67867 | 0.91771 | 0.80561 | -16.88873 | -16.69786 | 134.65 | 45.35 | 59.47 | 0.74854 | 0.56614 |
| $\left(\overset{3e}{C=}\right)_2 C_a-Br$ | $C_a$ | -0.18114 | -0.85035 | -0.85035 | 0 | -153.49753 | 0.91771 | 0.81435 | -16.70759 | -16.51672 | 76.64 | 103.36 | 32.19 | 1.95326 | 0.18814 |
| $\left(\overset{3e}{C=}\right)_2 C_a-Br$ | $Br$ | -0.18114 | 0 | 0 | 0 |  | 1.15169 | 0.90664 | -15.00689 |  | 85.73 | 94.27 | 37.44 | 1.83258 | 0.06746 |
| $\left(\overset{3e}{C=}\right)_2 C_a-I$ | $C_a$ | -0.82688 | -0.85035 | -0.85035 | 0 | -154.14326 | 0.91771 | 0.78405 | -17.35332 | -17.16246 | 71.42 | 108.58 | 28.33 | 2.20480 | 0.24979 |
| $\left(\overset{3e}{C=}\right)_2 C_a-I$ | $I$ | -0.82688 | 0 | 0 | 0 |  | 1.30183 | 0.86923 | -15.65263 |  | 80.69 | 99.31 | 33.21 | 2.09565 | 0.14064 |

Table 15.234. The energy parameters ($eV$) of functional groups of halobenzenes.

| Parameters | $\overset{3e}{C=C}$ Group | $CH$ (i) Group | $C-F$ Group | $C-Cl$ (a) Group | $C-Cl$ (b) Group | $C-Br$ Group | $C-I$ Group |
|---|---|---|---|---|---|---|---|
| $f_1$ | 0.75 | 1 | 1 | 1 | 1 | 1 | 1 |
| $n_1$ | 2 | 1 | 1 | 1 | 1 | 2 | 2 |
| $n_2$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $n_3$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $C_1$ | 0.5 | 0.75 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| $C_2$ | 0.85252 | 1 | 1 | 0.81317 | 0.81317 | 0.74081 | 0.65537 |
| $c_1$ | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $c_2$ | 0.85252 | 0.91771 | 0.77087 | 1 | 1 | 1 | 1 |
| $c_3$ | 0 | 1 | 0 | 0 | 0 | 0 | 0 |
| $c_4$ | 3 | 1 | 2 | 2 | 2 | 2 | 2 |
| $c_5$ | 0 | 1 | 0 | 0 | 0 | 0 | 0 |
| $C_{1o}$ | 0.5 | 0.75 | 1 | 0.5 | 0.5 | 0.5 | 0.5 |
| $C_{2o}$ | 0.85252 | 1 | 0.5 | 0.81317 | 0.81317 | 0.74081 | 0.65537 |
| $V_e\ (eV)$ | -101.12679 | -37.10024 | -35.58388 | -31.85648 | -31.85648 | -31.06557 | -29.13543 |
| $V_p\ (eV)$ | 20.69825 | 13.17125 | 10.75610 | 8.25686 | 8.25686 | 7.70816 | 6.95946 |
| $T\ (eV)$ | 34.31559 | 11.58941 | 11.11948 | 7.21391 | 7.21391 | 6.72969 | 5.81578 |
| $V_m\ (eV)$ | -17.15779 | -5.79470 | -5.55974 | -3.60695 | -3.60695 | -3.36484 | -2.90789 |
| $E(_{AO/HO})\ (eV)$ | 0 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -2.99216 | -2.26759 |
| $\Delta E_{H_2MO}(_{AO/HO})\ (eV)$ | 0 | -1.13379 | -2.26759 | -2.99216 | -2.99216 | -14.63489 | -14.63489 |
| $E_T(_{AO/HO})\ (eV)$ | 0 | -13.50110 | -12.36730 | -11.64273 | -11.64273 | -11.64273 | -12.36730 |
| $E_T(_{H_2MO})\ (eV)$ | -63.27075 | -31.63539 | -31.63535 | -31.63539 | -31.63539 | -31.63530 | -31.63538 |
| $E_T\left(atom-atom,msp^3.AO\right)\ (eV)$ | -2.26759 | -0.56690 | -2.06297 | -0.72457 | -0.72457 | -0.36229 | -1.65376 |
| $E_T(_{MO})\ (eV)$ | -65.53833 | -32.20226 | -33.69834 | -32.35994 | -32.35994 | -31.99766 | -33.28912 |
| $\omega\ \left(10^{15}\ rad/s\right)$ | 49.7272 | 26.4826 | 14.4431 | 8.03459 | 14.7956 | 7.17533 | 12.0764 |
| $E_K\ (eV)$ | 32.73133 | 17.43132 | 9.50672 | 5.28851 | 9.73870 | 4.72293 | 7.94889 |
| $\bar{E}_D\ (eV)$ | -0.35806 | -0.26130 | -0.20555 | -0.14722 | -0.19978 | -0.13757 | -0.18568 |
| $\bar{E}_{Kvib}\ (eV)$ | 0.19649<br>[49] | 0.35532<br>Eq. (13.458) | 0.10911<br>[11] | 0.08059<br>[12] | 0.08059<br>[12] | 0.08332<br>[15] | 0.06608<br>[16] |
| $\bar{E}_{osc}\ (eV)$ | -0.25982 | -0.08364 | -0.15100 | -0.10693 | -0.15949 | -0.09591 | -0.15264 |
| $E_{mag}\ (eV)$ | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 |
| $E_T(_{Group})\ (eV)$ | -49.54347 | -32.28590 | -33.84934 | -32.46687 | -32.51943 | -32.09357 | -33.44176 |
| $E_{initial}(_{c_4\ AO/HO})\ (eV)$ | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -15.76868 |
| $E_{initial}(_{c_5\ AO/HO})\ (eV)$ | 0 | -13.59844 | 0 | 0 | 0 | 0 | 0 |
| $E_D(_{Group})\ (eV)$ | 5.63881 | 3.90454 | 4.57956 | 3.19709 | 3.24965 | 2.82379 | 1.90439 |

Table 15.235. The total bond energies of halobenzenes calculated using the functional group composition and the energies of Table 15.234 compared to the experimental values [3]. The magnetic energy $E_{mag}$ that is subtracted from the weighted sum of the $E_D$ $(_{Group})$ $(eV)$ values based on composition is given by (15.58).

| Formula | Name | $C\overset{3e}{=}C$ | $CH$ (i) | $C-F$ Group | $C-Cl$ (a) Group | $C-Cl$ (b) Group | $C-Br$ Group | $C-I$ Group | $E_{mag}$ | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $C_6H_5Cl$ | Fluorobenzene | 6 | 5 | 1 | 0 | 0 | 0 | 0 | 0 | 57.93510 | 57.887 | -0.00083 |
| $C_6H_5Cl$ | Chlorobenzene | 6 | 5 |  | 1 | 0 |  |  | 0 | 56.55263 | 56.581 | 0.00051 |
| $C_6H_4Cl_2$ | m-dichlorobenzene | 6 | 4 |  | 2 | 0 |  |  | 0 | 55.84518 | 55.852 | 0.00012 |
| $C_6H_3Cl_3$ | 1,2,3-trichlorobenzene | 6 | 3 |  | 3 | 0 |  |  | 0 | 55.13773 | 55.077 | -0.00111 |
| $C_6H_3Cl_3$ | 1,3,5-trichlorobenzene | 6 | 3 |  | 0 | 3 |  |  | 0 | 55.29542 | 55.255 | -0.00073 |
| $C_6Cl_6$ | Hexachlorobenzene | 6 | 0 |  | 6 | 0 |  |  | 3 | 52.57130 | 52.477 | -0.00179 |
| $C_6H_5Br$ | Bromobenzene | 6 | 5 | 0 | 0 | 0 | 1 | 0 | 0 | 56.17932 | 56.391[a] | 0.00376 |
| $C_6H_5I$ | Iodobenzene | 6 | 5 | 0 | 0 | 0 | 0 | 1 | 0 | 55.25993 | 55.261 | 0.00001 |

[a] Liquid.

Table 15.236. The bond angle parameters of halobenzenes and experimental values [1]. $E_T$ is $E_T$ $(atom-atom,msp^3.AO)$.

| Atoms of Angle | 2$c'$ Bond 1 ($a_0$) | 2$c'$ Bond 2 ($a_0$) | 2$c'$ Terminal Atoms ($a_0$) | $E_{Coulombic}$ Atom 1 | Atom 1 Hybridization Designation (Table 15.3.A) | $E_{Coulombic}$ Atom 2 | Atom 2 Hybridization Designation (Table 15.3.A) | $c_2$ Atom 1 | $c_2$ Atom 2 | $C_1$ | $C_2$ | $c_1$ | $c_2'$ | $E_T$ (eV) | $\theta_v$ (°) | $\theta_1$ (°) | $\theta_2$ (°) | Cal. $\theta$ (°) | Exp. $\theta$ (°) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $\angle CCC$ (aromatic) | 2.62936 | 2.62936 | 4.5585 | -17.17218 | 38 | -17.17218 | 38 | 0.79232 | 0.79232 | 1 | 1 | 1 | 0.79232 | -1.85836 |  |  |  | 120.19 | 120 $(\angle CC(H)C$ chlorobenzene)<br>121.7 $(\angle CC(Cl)C$ chlorobenzene)<br>120 [50-52] (benzene) |
| $\angle CCH$<br>$\angle CCX$<br>(aromatic) |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  | 120.19 |  | 119.91 | 120 [50-52] (benzene) |

## PHENOL

Phenol has the formula $C_6H_6O$ and comprises the benzene molecule with one hydrogen atom replaced by a hydroxyl corresponding to an $OH$ functional group and a $C-O$ functional group. The aromatic $C\overset{3e}{=}C$ and $C-H$ functional groups are equivalent to those of benzene given in the Aromatic and Heterocyclic Compounds section. The $OH$ functional group is the same as that of alcohols given in the corresponding section.

The bond between the hydroxyl and aromatic ring comprises a $C-O$ functional group that is solved using the same principles as those used to solve the alcohol functional groups wherein the $2s$ and $2p$ AOs of each $C$ hybridize to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between the $C2sp^3$ HO and $O$ AO to form a MO permits each participating hybridized orbital to decrease in radius and energy. In aryl alcohols, the aromatic $C2sp^3$ HO has a hybridization factor of 0.85252 (Eq. (15.162)) with an initial energy of $E\left(C,2sp^3\right)=-14.63489\ eV$ (Eq. (15.25)) and the $O$ AO has an energy of $E\left(O\right)=-13.61806\ eV$. To meet the equipotential condition of the union of the $C-O$ $H_2$-type-ellipsoidal-MO with these orbitals, the hybridization factor $c_2$ of Eq. (15.61) for the $C-O$-bond MO given by Eqs. (15.77) and (15.79) is:

$$c_2\left(arylC2sp^3HO\ to\ O\right)=\frac{E\left(O\right)}{E\left(C,2sp^3\right)}c_2\left(arylC2sp^3HO\right)=\frac{-13.61806\ eV}{-14.63489\ eV}\left(0.85252\right)=0.79329 \tag{15.169}$$

$E_T\left(atom-atom,msp^3.AO\right)$ of the $C-O$-bond MO in Eq. (15.61) due to the charge donation from the $C$ and $O$ atoms to the MO is $-1.49608\ eV$. It is based on the energy match between the $OH$ group and the $C2sp^3$ HO of an aryl group and is given by the linear combination of $-0.92918\ eV$ (Eq. (14.513)) and $-1.13379\ eV$ (Eq. (14.247)), respectively.

The symbols of the functional groups of phenol are given in Table 15.237. The geometrical (Eqs. (15.1-15.5) and (15.51)), intercept (Eqs. (15.80-15.87)), and energy (Eqs. (15.6-15.11), (15.17-15.65), and (15.165-15.166)) parameters of phenol are given in Tables 15.238, 15.239, and 15.240, respectively. The total energy of phenol given in Table 15.241 was calculated as the sum over the integer multiple of each $E_D\left(Group\right)$ of Table 15.240 corresponding to functional-group composition of the molecule. The bond angle parameters of phenol determined using Eqs. (15.88-15.117) are given in Table 15.242. The color scale, translucent view of the charge-density of phenol comprising the concentric shells of atoms with the outer shell bridged by one or more $H_2$-type ellipsoidal MOs or joined with one or more hydrogen MOs is shown in Figure 15.41.

Figure 15.41. Color scale, translucent view of the charge-density of phenol showing the orbitals of the atoms at their radii, the ellipsoidal surface of each $H$ or $H_2$-type ellipsoidal MO that transitions to the corresponding outer shell of the atom(s) participating in each bond, and the hydrogen nuclei (red, not to scale).

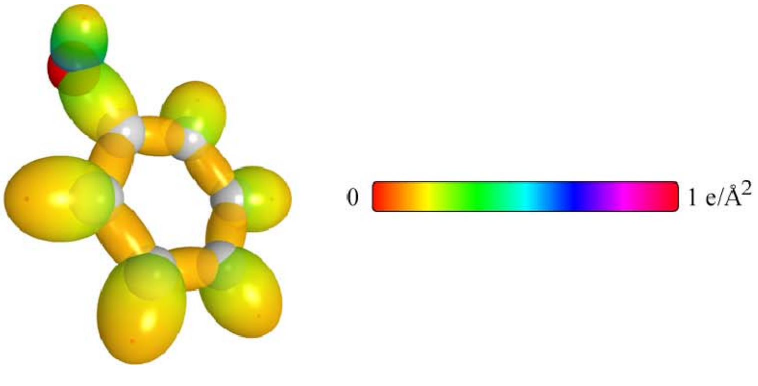


Table 15.237. The symbols of functional groups of phenol.

| Functional Group | Group Symbol |
|---|---|
| $CC$ (aromatic bond) | $C\overset{3e}{=}C$ |
| $CH$ (aromatic) | $CH$ (i) |
| Aryl $C$-$O$ | $C-O$ (a) |
| $OH$ group | $OH$ |

Table 15.238. The geometrical bond parameters of phenol and experimental values [1].

| Parameter | $\overset{3e}{C=C}$ Group | $CH$ (i) Group | $C-O$ (a) Group | $OH$ Group |
|---|---|---|---|---|
| $a\ (a_0)$ | 1.47348 | 1.60061 | 1.68220 | 1.26430 |
| $c'\ (a_0)$ | 1.31468 | 1.03299 | 1.29700 | 0.91808 |
| Bond Length $2c'$ (Å) | 1.39140 | 1.09327 | 1.37268 | 0.971651 |
| Exp. Bond Length (Å) | 1.397 avg. (phenol) | 1.084 (phenol) | 1.364 (phenol) | 0.956 (phenol) |
| $b,c\ (a_0)$ | 0.66540 | 1.22265 | 1.07126 | 0.86925 |
| $e$ | 0.89223 | 0.64537 | 0.77101 | 0.72615 |

Table 15.239. The MO to HO intercept geometrical bond parameters of phenol. $E_T$ is $E_T$ $(atom-atom,msp^3.AO)$.

| Bond | Atom | $E_T$ (eV) Bond 1 | $E_T$ (eV) Bond 2 | $E_T$ (eV) Bond 3 | $E_T$ (eV) Bond 4 | Final Total Energy $C2sp^3$ (eV) | $r_{initial}$ $(a_0)$ | $r_{final}$ $(a_0)$ | $E_{Coulomb}(C2sp^3)$ (eV) Final | $E(C2sp^3)$ (eV) Final | $\theta'$ (°) | $\theta_1$ (°) | $\theta_2$ (°) | $d_1$ $(a_0)$ | $d_2$ $(a_0)$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $C-H\ (C_bH)$ | $C_b$ | -0.85035 | -0.85035 | -0.56690 | 0 | -153.88327 | 0.91771 | 0.79597 | -17.09334 | -16.90248 | 74.42 | 105.58 | 38.84 | 1.24678 | 0.21379 |
| $\left(C_b\overset{3e}{=}\right)_2 C_aO-H$ | $O$ | -0.74804 | 0 | 0 | 0 |  | 1.00000 | 0.87363 | -15.57379 |  | 115.79 | 64.21 | 64.82 | 0.53799 | 0.38009 |
| $\left(C_b\overset{3e}{=}\right)_2 C_a-OH$ | $C_a$ | -0.74804 | -0.85035 | -0.85035 | 0 | -154.06442 | 0.91771 | 0.78762 | -17.27448 | -17.08362 | 100.00 | 80.00 | 46.39 | 1.16026 | 0.13674 |
| $\left(C_b\overset{3e}{=}\right)_2 C_a-OH$ | $O$ | -0.74804 | 0 | 0 | 0 |  | 1.00000 | 0.87363 | 15.57379 |  | 106.51 | 73.49 | 51.43 | 1.04871 | 0.24829 |
| $\left(C_b\overset{3e}{=}\right)_2 C_aOH$ | $C_a$ | -0.74804 | -0.85035 | -0.85035 | 0 | -154.06442 | 0.91771 | 0.78762 | -17.27448 | -17.08362 | 133.88 | 46.12 | 58.55 | 0.76870 | 0.54598 |
| $\left(\overset{3e}{=}(H)C_b\right)_2 C_aOH$ | $C_b$ | -0.85035 | -0.85035 | -0.56690 | 0 | -153.88327 | 0.91771 | 0.79597 | -17.09334 | -16.90248 | 134.24 | 45.76 | 58.98 | 0.75935 | 0.55533 |

Table 15.240. The energy parameters ($eV$) of functional groups of phenol.

| Parameters | $C\overset{3e}{=}C$ Group | $CH$ (i) Group | $C-O$ (a) Group | $OH$ Group |
|---|---|---|---|---|
| $f_1$ | 0.75 | 1 | | |
| $n_1$ | 2 | 1 | 1 | 1 |
| $n_2$ | 0 | 0 | 0 | 0 |
| $n_3$ | 0 | 0 | 0 | 0 |
| $C_1$ | 0.5 | 0.75 | 0.5 | 0.75 |
| $C_2$ | 0.85252 | 1 | 1 | 1 |
| $c_1$ | 1 | 1 | 1 | 0.75 |
| $c_2$ | 0.85252 | 0.91771 | 0.79329 | 1 |
| $c_3$ | 0 | 1 | 0 | 1 |
| $c_4$ | 3 | 1 | 2 | 1 |
| $c_5$ | 0 | 1 | 0 | 1 |
| $C_{1o}$ | 0.5 | 0.75 | 0.5 | 0.75 |
| $C_{2o}$ | 0.85252 | 1 | 1 | 1 |
| $V_e\ (eV)$ | -101.12679 | -37.10024 | -34.04658 | -40.92709 |
| $V_p\ (eV)$ | 20.69825 | 13.17125 | 10.49024 | 14.81988 |
| $T\ (eV)$ | 34.31559 | 11.58941 | 10.11966 | 16.18567 |
| $V_m\ (eV)$ | -17.15779 | -5.79470 | -5.05983 | -8.09284 |
| $E(AO/HO)\ (eV)$ | 0 | -14.63489 | -14.63489 | -13.6181 |
| $\Delta E_{H_2MO}(AO/HO)\ (eV)$ | 0 | -1.13379 | -1.49608 | 0 |
| $E_T(AO/HO)\ (eV)$ | 0 | -13.50110 | -13.13881 | -13.6181 |
| $E_T(H_2MO)\ (eV)$ | -63.27075 | -31.63539 | -31.63532 | -31.63247 |
| $E_T\left(atom-atom,msp^3.AO\right)(eV)$ | -2.26759 | -0.56690 | -1.49608 | 0 |
| $E_T(MO)\ (eV)$ | -65.53833 | -32.20226 | -33.13145 | -31.63537 |
| $\omega\ \left(10^{15}\ rad/s\right)$ | 49.7272 | 26.4826 | 13.3984 | 44.1776 |
| $E_K\ (eV)$ | 32.73133 | 17.43132 | 8.81907 | 29.07844 |
| $\bar{E}_D\ (eV)$ | -0.35806 | -0.26130 | -0.19465 | -0.33749 |
| $\bar{E}_{Kvib}\ (eV)$ | 0.19649<br>[49] | 0.35532<br>Eq. (13.458) | 0.12808<br>[19] | 0.46311<br>[17-18] |
| $\bar{E}_{osc}\ (eV)$ | -0.25982 | -0.08364 | -0.13061 | -0.10594 |
| $E_{mag}\ (eV)$ | 0.14803 | 0.14803 | 0.14803 | 0.11441 |
| $E_T(Group)\ (eV)$ | -49.54347 | -32.28590 | -33.26206 | -31.74130 |
| $E_{initial}(c_4\ AO/HO)\ (eV)$ | -14.63489 | -14.63489 | -14.63489 | -13.6181 |
| $E_{initial}(c_5\ AO/HO)\ (eV)$ | 0 | -13.59844 | 0 | -13.59844 |
| $E_D(Group)\ (eV)$ | 5.63881 | 3.90454 | 3.99228 | 4.41035 |

Table 15.241. The total bond energies of phenol calculated using the functional group composition and the energies of Table 15.240 compared to the experimental values [3].

| Formula | Name | $\overset{3e}{C=C}$ | $CH$ (i) | $C-O$ (a) Group | $OH$ Group | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|---|---|---|---|
| $C_6H_6O$ | Phenol | 6 | 5 | 1 | 1 | 61.75817 | 61.704 | -0.00087 |

Table 15.242. The bond angle parameters of phenol and experimental values [1]. $E_T$ is $E_T$ ($atom-atom,msp^3.AO$).

| Atoms of Angle | 2$c'$ Bond 1 ($a_0$) | 2$c'$ Bond 2 ($a_0$) | 2$c'$ Terminal Atoms ($a_0$) | $E_{Coulombic}$ Atom 1 | Atom 1 Hybridization Designation (Table 15.3.A) | $E_{Coulombic}$ Atom 2 | Atom 2 Hybridization Designation (Table 15.3.A) | $c_2$ Atom 1 | $c_2$ Atom 2 | $C_1$ | $C_2$ | $c_1$ | $c_2'$ | $E_T$ (eV) | $\theta_v$ (°) | $\theta_1$ (°) | $\theta_2$ (°) | Cal. $\theta$ (°) | Exp. $\theta$ (°) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $\angle CCC$ (aromatic) | 2.62936 | 2.62936 | 4.5585 | -17.17218 | 38 | -17.17218 | 38 | 0.79232 | 0.79232 | 1 | 1 | 1 | 0.79232 | -1.85836 | | | | 120.19 | 120 [50-52] (benzene) |
| $\angle CCH$ (aromatic) | | | | | | | | | | | | | | | | 120.19 | | 119.91 | 120 [50-52] (benzene) |
| $\angle C_aOH$ | 2.59399 | 1.83616 | 3.6515 | -14.82575 | 1 | -14.82575 | 1 | 1 | 0.91771 | 0.75 | 1 | 0.75 | 0.91771 | 0 | | | | 109.84 | 109.0 (phenol) |

## ANILINE

Aniline and methyl aniline have the formula $C_6H_7N$ and $C_7H_9N$, respectively. They comprise the benzene and toluene molecules with one hydrogen atom replaced by an amino group corresponding to an $NH_2$ functional group and a $C-N$ functional group. The aromatic $C\overset{3e}{=}C$ and $C-H$ functional groups are equivalent to those of benzene given in the Aromatic and Heterocyclic Compounds section. The $C-C$ and $CH_3$ functional groups of methyl anilines are equivalent to those of toluene given in the corresponding section.

The aryl amino ($NH_2$) functional group was solved using the procedure given in the Dihydrogen Nitride ($NH_2$) section. Using the results of Eqs. (13.245-13.368), the aryl amino parameters in Eq. (15.60) are $n_1 = 2$, $C_1 = 0.75$, $C_2 = 0.93613$ (Eqs. (13.248-13.249)), $C_{1o} = 1.5$, and $c_1 = 0.75$. In the determination of the hybridization factor $c_2$ of Eq. (15.61) for the $N-H$-bond MO of aryl amines, the $C2sp^3$ HO of the $C-NH_2$-bond MO has an energy of $E\left(C,2sp^3\right) = -15.76868\ eV$ (Eq. (15.18)) corresponding to $s = 2$ in Eqs. (15.18-15.20), and the $N$ AO has an energy of $E\left(N\right) = -14.53414\ eV$. To meet the equipotential condition of the union of the $N-H$ $H_2$-type-ellipsoidal-MO with the $C2sp^3$ HO, the hybridization factor $c_2$ given by Eq. (15.77) is:

$$c_2\left(H\ to\ aniline\ N\right) = \frac{E\left(N\right)}{E\left(C,2sp^3\right)} = \frac{-14.53414\ eV}{-15.76868\ eV} = 0.92171 \tag{15.170}$$

The bond between the amino and aromatic ring comprises a $C-N$ functional group that is the same as that of 2° amines (methylene) except that the energies corresponding to oscillation in the transition state are those of aniline. The group is solved using the same principles as those used to solve the primary and secondary-amine functional groups wherein the $2s$ and $2p$ AOs of each $C$ hybridize to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between the $C2sp^3$ HO and $N$ AO to form a MO permits each participating hybridized orbital to decrease in radius and energy. The hybridization is determined in a similar manner to that of the $C-O$ group of phenol. In anilines, the aromatic $C2sp^3$ HO has a hybridization factor of 0.85252 (Eq. (15.162)) with an initial energy of $E\left(C,2sp^3\right) = -14.63489\ eV$ (Eq. (15.25)) and the $N$ AO has an energy of $E\left(N\right) = -14.53414\ eV$. To meet the equipotential condition of the union of the $C-N$ $H_2$-type-ellipsoidal-MO with these orbitals, the hybridization factor $c_2$ of Eq. (15.60) for the $C-N$-bond MO given by Eqs. (15.77) and (15.79) is:

$$\begin{aligned} c_2\left(arylC2sp^3HO\ to\ N\right) &= \frac{E\left(N\right)}{E\left(C,2sp^3\right)} c_2\left(arylC2sp^3HO\right) \\ &= \frac{-14.53414\ eV}{-14.63489\ eV}\left(0.85252\right) \\ &= 0.84665 \end{aligned} \tag{15.171}$$

$E_T\left(atom-atom,msp^3.AO\right)$ of the $C-N$-bond MO in Eq. (15.61) due to the charge donation from the $C$ and $N$ atoms to the MO is $-1.13379\ eV$ (Eq. (14.247)). It is based on the energy match between the $NH_2$ group and the $C2sp^3$ HO of the aryl group and is twice that of the aryl $C-H$ group that it replaces.

The symbols of the functional groups of aniline and methyl-substituted anilines are given in Table 15.243. The geometrical (Eqs. (15.1-15.5) and (15.51)), intercept (Eqs. (15.80-15.87)), and energy (Eqs. (15.6-15.11), (15.17-15.65), and (15.165-15.166)) parameters of aniline and methyl-substituted anilines are given in Tables 15.244, 15.245, and 15.246, respectively. The total energy of each aniline and methyl-substituted aniline given in Table 15.247 was calculated as the sum over the integer multiple of each $E_D\left(Group\right)$ of Table 15.246 corresponding to functional-group composition of the molecule. The bond angle parameters of aniline and methyl-substituted anilines determined using Eqs. (15.88-15.117) are given in Table 15.248. The color scale, translucent view of the charge-density of aniline comprising the concentric shells of atoms with the outer shell bridged by one or more $H_2$-type ellipsoidal MOs or joined with one or more hydrogen MOs is shown in Figure 15.42.

Figure 15.42. Color scale, translucent view of the charge-density of aniline showing the orbitals of the atoms at their radii, the ellipsoidal surface of each $H$ or $H_2$-type ellipsoidal MO that transitions to the corresponding outer shell of the atom(s) participating in each bond, and the hydrogen nuclei (red, not to scale).

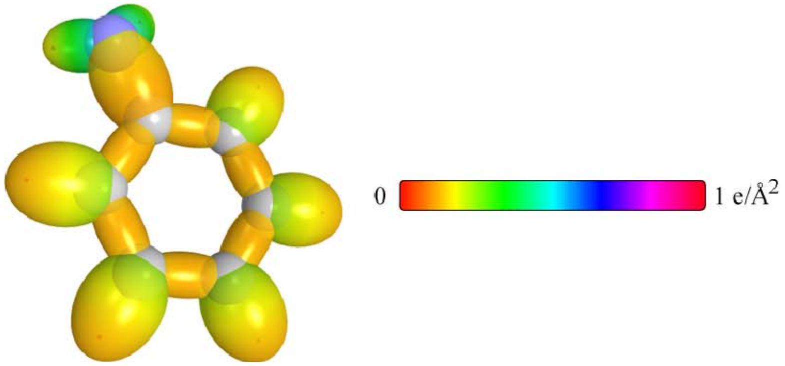


Table 15.243. The symbols of functional groups of aniline and methyl-substituted anilines.

| Functional Group | Group Symbol |
|---|---|
| $CC$ (aromatic bond) | $C\overset{3e}{=}C$ |
| $CH$ (aromatic) | $CH$ (i) |
| Aryl $C$-$N$ | $C-N$ (a) |
| $NH_2$ group | $NH_2$ |
| $C_a-C_b$ ($CH_3$ to aromatic bond) | $C-C$ (a) |
| $CH_3$ group | $C-H$ $(CH_3)$ |

Table 15.244. The geometrical bond parameters of aniline and methyl-substituted anilines and experimental values [1].

| Parameter | $C\overset{3e}{=}C$ Group | $CH$ (i) Group | $C-N$ (a) Group | $NH_2$ Group | $C-C$ (a) Group | $C-H\left(CH_3\right)$ Group |
|---|---|---|---|---|---|---|
| $a\left(a_0\right)$ | 1.47348 | 1.60061 | 1.81158 | 1.24428 | 2.06004 | 1.64920 |
| $c'\left(a_0\right)$ | 1.31468 | 1.03299 | 1.34595 | 0.94134 | 1.43528 | 1.04856 |
| Bond Length $2c'$ $\left(\AA\right)$ | 1.39140 | 1.09327 | 1.42449 | 0.99627 | 1.51904 | 1.10974 |
| Exp. Bond Length $\left(\AA\right)$ | 1.397 avg. (phenol) | 1.084 (phenol) | 1.431 (aniline) | 0.998 (aniline) | 1.524 (toluene) | 1.11 (avg.) (toluene) |
| $b,c\left(a_0\right)$ | 0.66540 | 1.22265 | 1.21254 | 0.81370 | 1.47774 | 1.27295 |
| $e$ | 0.89223 | 0.64537 | 0.74297 | 0.75653 | 0.69673 | 0.63580 |

Table 15.245. The MO to HO intercept geometrical bond parameters of aniline and methyl-substituted anilines. $E_T$ is $E_T$ ($atom - atom,msp^3.AO$).

| Bond | Atom | $E_T$ (eV) Bond 1 | $E_T$ (eV) Bond 2 | $E_T$ (eV) Bond 3 | $E_T$ (eV) Bond 4 | Final Total Energy $C2sp^3$ (eV) | $r_{initial}$ $\left(a_0\right)$ | $r_{final}$ $\left(a_0\right)$ | $E_{Coulomb}\left(C2sp^3\right)$ (eV) Final | $E\left(C2sp^3\right)$ (eV) Final | $\theta'$ $(^\circ)$ | $\theta_1$ $(^\circ)$ | $\theta_2$ $(^\circ)$ | $d_1$ $\left(a_0\right)$ | $d_2$ $\left(a_0\right)$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $C-H\ \left(C_bH\right)$ | $C_b$ | -0.85035 | -0.85035 | -0.56690 | 0 | -153.88328 | 0.91771 | 0.79597 | -17.09334 | -16.90248 | 74.42 | 105.58 | 38.84 | 1.24678 | 0.21379 |
| $C-H\ \left(C_aH_3\right)$ | $C_a$ | -0.56690 | 0 | 0 | 0 | -152.18259 | 0.91771 | 0.88392 | -15.39265 | -15.20178 | 79.89 | 101.11 | 43.13 | 1.20367 | 0.15511 |
| $\left(C_b\overset{3e}{=}\right)_2 C_aNH-H$ | $N$ | -0.56690 | 0 | 0 | 0 |  | 0.93084 | 0.88392 | -15.39265 |  | 121.74 | 58.26 | 67.49 | 0.47634 | 0.46500 |
| $\left(C_b\overset{3e}{=}\right)_2 C_a-NH_2$ | $C_a$ | -0.56690 | -0.85035 | -0.85035 | 0 | -153.88328 | 0.91771 | 0.79597 | -17.09334 | -16.90248 | 88.49 | 91.51 | 41.01 | 1.36696 | 0.02101 |
| $\left(C_b\overset{3e}{=}\right)_2 C_a-NH_2$ | $N$ | -0.56690 | 0 | 0 | 0 |  | 0.93084 | 0.88392 | -15.39265 |  | 96.32 | 83.68 | 46.43 | 1.24859 | 0.09736 |
| $\left(C\overset{3e}{=}\right)_2 C_b-C_aH_3$ | $C_a$ | -0.56690 | 0 | 0 | 0 | -152.18259 | 0.91771 | 0.88392 | -15.39265 | -15.20178 | 73.38 | 106.62 | 34.97 | 1.68807 | 0.25279 |
| $\left(C\overset{3e}{=}\right)_2 C_b-C_aH_3$ | $C_b$ | -0.56690 | -0.85035 | -0.85035 | 0 | -153.88328 | 0.91771 | 0.79597 | -17.09334 | -16.90247 | 61.56 | 118.44 | 28.27 | 1.81430 | 0.37901 |
| $C\overset{3e}{=}HC_c\overset{3e}{=}C$<br>$C\overset{3e}{=}\left(H_2N\right)C_a\overset{3e}{=}C$<br>$C\overset{3e}{=}\left(H_3C_a\right)C_b\overset{3e}{=}C$ | $C_c$<br>$C_a$<br>$C_b$ | -0.85035 | -0.85035 | -0.56690 | 0 | -153.88327 | 0.91771 | 0.79597 | -17.09334 | -16.90248 | 134.24 | 45.76 | 58.98 | 0.75935 | 0.55533 |

Table 15.246. The energy parameters ($eV$) of functional groups of aniline and methyl-substituted anilines.

| Parameters | $\overset{3e}{C=C}$ Group | $CH$ (i) Group | $C-N$ (a) Group | $NH_2$ Group | $C-C$ (a) Group | $CH_3$ Group |
|---|---|---|---|---|---|---|
| $f_1$ | 0.75 | 1 | | | | |
| $n_1$ | 2 | 1 | 1 | 2 | 1 | 3 |
| $n_2$ | 0 | 0 | 0 | 0 | 0 | 2 |
| $n_3$ | 0 | 0 | 0 | 1 | 0 | 0 |
| $C_1$ | 0.5 | 0.75 | 0.5 | 0.75 | 0.5 | 0.75 |
| $C_2$ | 0.85252 | 1 | 1 | 0.93613 | 1 | 1 |
| $c_1$ | 1 | 1 | 1 | 0.75 | 1 | 1 |
| $c_2$ | 0.85252 | 0.91771 | 0.84665 | 0.92171 | 0.91771 | 0.91771 |
| $c_3$ | 0 | 1 | 0 | 0 | 0 | 0 |
| $c_4$ | 3 | 1 | 2 | 1 | 2 | 1 |
| $c_5$ | 0 | 1 | 0 | 2 | 0 | 3 |
| $C_{1o}$ | 0.5 | 0.75 | 0.5 | 1.5 | 0.5 | 0.75 |
| $C_{2o}$ | 0.85252 | 1 | 1 | 1 | 1 | 1 |
| $V_e\ (eV)$ | -101.12679 | -37.10024 | -32.76465 | -78.97795 | -29.95792 | -107.32728 |
| $V_p\ (eV)$ | 20.69825 | 13.17125 | 10.10870 | 28.90735 | 9.47952 | 38.92728 |
| $T\ (eV)$ | 34.31559 | 11.58941 | 9.04312 | 31.73641 | 7.27120 | 32.53914 |
| $V_m\ (eV)$ | -17.15779 | -5.79470 | -4.52156 | -15.86820 | -3.63560 | -16.26957 |
| $E(_{AO/HO})\ (eV)$ | 0 | -14.63489 | -14.63489 | -14.53414 | -15.35946 | -15.56407 |
| $\Delta E_{H_2MO}(_{AO/HO})\ (eV)$ | 0 | -1.13379 | -1.13379 | 0 | -0.56690 | 0 |
| $E_T(_{AO/HO})\ (eV)$ | 0 | -13.50110 | -13.50110 | -14.53414 | -14.79257 | -15.56407 |
| $E(_{n_3\ AO/HO})\ (eV)$ | 0 | 0 | 0 | -14.53414 | 0 | 0 |
| $E_T(_{H_2MO})\ (eV)$ | -63.27075 | -31.63539 | -31.63549 | -48.73654 | -31.63537 | -67.69451 |
| $E_T\left(atom-atom,msp^3.AO\right)\ (eV)$ | -2.26759 | -0.56690 | -1.13379 | 0 | -1.13379 | 0 |
| $E_T(_{MO})\ (eV)$ | -65.53833 | -32.20226 | -32.76916 | -48.73660 | -32.76916 | -67.69450 |
| $\omega\ \left(10^{15}\ rad/s\right)$ | 49.7272 | 26.4826 | 11.9890 | 68.9812 | 16.2731 | 24.9286 |
| $E_K\ (eV)$ | 32.73133 | 17.43132 | 7.89138 | 45.40465 | 10.71127 | 16.40846 |
| $\bar{E}_D\ (eV)$ | -0.35806 | -0.26130 | -0.18211 | -0.42172 | -0.21217 | -0.25352 |
| $\bar{E}_{Kvib}\ (eV)$ | 0.19649<br>[49] | 0.35532<br>Eq. (13.458) | 0.15498<br>[58] | 0.40929<br>[22] | 0.14940<br>[54] | 0.35532<br>(Eq. (13.458)) |
| $\bar{E}_{osc}\ (eV)$ | -0.25982 | -0.08364 | -0.10462 | -0.21708 | -0.13747 | -0.22757 |
| $E_{mag}\ (eV)$ | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 |
| $E_T(_{Group})\ (eV)$ | -49.54347 | -32.28590 | -32.87379 | -49.17075 | -32.90663 | -67.92207 |
| $E_{initial}(_{c_4\ AO/HO})\ (eV)$ | -14.63489 | -14.63489 | -14.63489 | -14.53414 | -14.63489 | -14.63489 |
| $E_{initial}(_{c_5\ AO/HO})\ (eV)$ | 0 | -13.59844 | 0 | -13.59844 | 0 | -13.59844 |
| $E_D(_{Group})\ (eV)$ | 5.63881 | 3.90454 | 3.60401 | 7.43973 | 3.63685 | 12.49186 |

Table 15.247. The total bond energies of aniline and methyl-substituted anilines calculated using the functional group composition and the energies of Table 15.246 compared to the experimental values [3].

| Formula | Name | $\overset{3e}{C=C}$ | $CH$ (i) | $C-N$ (a) Group | $NH_2$ Group | $C-C$ (a) Group | $CH_3$ | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|---|---|---|---|---|---|
| $C_6H_7N$ | Aniline | 6 | 5 | 1 | 1 | 0 | 0 | 64.43373 | 64.374 | -0.00093 |
| $C_7H_9N$ | 2-methylaniline | 6 | 4 | 1 | 1 | 1 | 1 | 76.62345 | 76.643 | -0.00025 |
| $C_7H_9N$ | 3-methylaniline | 6 | 4 | 1 | 1 | 1 | 1 | 76.62345 | 76.661 | 0.00050 |
| $C_7H_9N$ | 4-methylaniline | 6 | 4 | 1 | 1 | 1 | 1 | 76.62345 | 76.654 | 0.00040 |

Table 15.248. The bond angle parameters of aniline and methyl-substituted anilines and experimental values [1]. $E_T$ is $E_T$ ($atom - atom, msp^3.AO$).

| Atoms of Angle | $2c'$ Bond 1 ($a_0$) | $2c'$ Bond 2 ($a_0$) | $2c'$ Terminal Atoms ($a_0$) | $E_{Coulombic}$ Atom 1 | Atom 1 Hybridization Designation (Table 15.3.A) | $E_{Coulombic}$ Atom 2 | Atom 2 Hybridization Designation (Table 15.3.A) | $c_2$ Atom 1 | $c_2$ Atom 2 | $C_1$ | $C_2$ | $c_1$ | $c_2'$ | $E_T$ (eV) | $\theta_v$ (°) | $\theta_1$ (°) | $\theta_2$ (°) | Cal. $\theta$ (°) | Exp. $\theta$ (°) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $\angle CCC$ (aromatic) | 2.62936 | 2.62936 | 4.5585 | -17.17218 | 38 | -17.17218 | 38 | 0.79232 | 0.79232 | 1 | 1 | 1 | 0.79232 | -1.85836 |  |  |  | 120.19 | 120 [50-52] (benzene) |
| $\angle CCH$ (aromatic) |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  | 120.19 |  | 119.91 | 120 [50-52] (benzene) |
| $\angle HNH$ | 1.88268 | 1.88268 | 3.1559 | -14.53414 | N | H | H | 0.93613 Eq. (13.248)) | 1 | 1 | 1 | 0.75 | 1.06823 | 0 |  |  |  | 113.89 | 113.9 (aniline) |
| $\angle HNC_a$ | 1.88268 | 2.69190 | 4.0332 | -14.53414 | N | -15.95955 | 10 | 0.84665 (Eq. (15.171)) | 0.86284 (Eq. (15.73)) | 0.75 | 1 | 0.75 | 1.01912 | 0 |  |  |  | 122.70 |  |

## ARYL NITRO COMPOUNDS

Aryl nitro compounds have a hydrogen of an aryl group replaced by a nitro corresponding to an $NO_2$ functional group and a $C-N$ functional group. Examples include nitrobenzene, nitrophenol, and nitroaniline with formulas $C_6H_5NO_2$, $C_6H_5NO_3$, and $C_6H_6N_2O_2$, respectively. The aromatic $C\overset{3e}{=}C$ and $C-H$ functional groups are equivalent to those of benzene given in the Aromatic and Heterocyclic Compounds section. The $OH$ and $C-O$ functional groups of nitrophenols are the same as those of phenol given in the corresponding section. The $NH_2$ and $C-N$ functional groups of nitroanilines are the same as those of aniline given in the corresponding section. The differences between the total bond energies of the nitroanilines given in Table 15.252 are due to differences in the $E_{osc}$ term. For simplicity and since the differences are small, the $E_{osc}$ terms for nitroanilines were taken as the same.

The $NO_2$ group is the same as that given in the Nitroalkanes section. The bond between the nitro and aromatic ring comprises a $C-N$ functional group that is the same as that of nitroalkanes given in the corresponding section except that $E_T\left(atom-atom,msp^3.AO\right)$ is $-0.72457\ eV$, one half of that of the $C-N$ -bond MO of nitroalkanes and equivalent to that of methyl (Eq. (14.151)) in order to maintain the independence and aromaticity of the benzene functional group. In addition, the energy terms due to oscillation in the transition state correspond to those of an aryl nitro compound.

The symbols of the functional groups of aryl nitro compounds are given in Table 15.249. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.80-15.87)), and energy (Eqs. (15.6-15.11), (15.17-15.65), and (15.165-15.166)) parameters of aryl nitro compounds are given in Tables 15.250, 15.251, and 15.252, respectively. The total energy of each aryl nitro compound given in Table 15.253 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.252 corresponding to functional-group composition of the molecule. For each set of unpaired electrons created by bond breakage, the $C2sp^3$ HO magnetic energy $E_{mag}$ that is subtracted from the weighted sum of the $E_D(Group)$ $(eV)$ values based on composition is given by Eq. (15.67). The bond angle parameters of aryl nitro compounds determined using Eqs. (15.88-15.117) are given in Table 15.254. The color scale, translucent view of the charge-density of exemplary aryl nitro, nitrobenzene, comprising the concentric shells of atoms with the outer shell bridged by one or more $H_2$-type ellipsoidal MOs or joined with one or more hydrogen MOs is shown in Figure 15.43.

Figure 15.43. Color scale, translucent view of the charge-density of nitrobenzene showing the orbitals of the atoms at their radii, the ellipsoidal surface of each $H$ or $H_2$-type ellipsoidal MO that transitions to the corresponding outer shell of the atom(s) participating in each bond, and the hydrogen nuclei (red, not to scale).

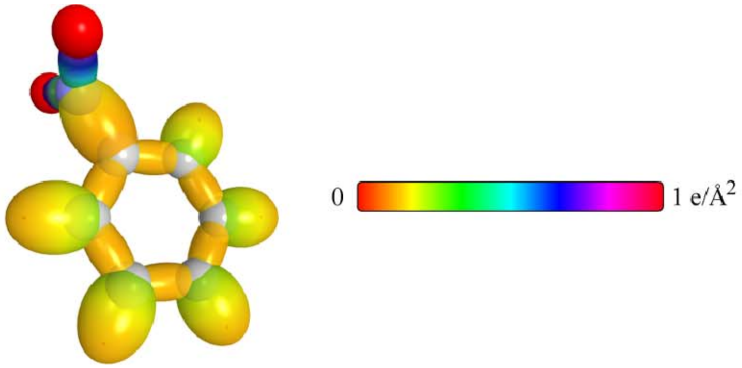


Table 15.249. The symbols of functional groups of aryl nitro compounds.

| Functional Group | Group Symbol |
|---|---|
| $CC$ (aromatic bond) | $C\overset{3e}{=}C$ |
| $CH$ (aromatic) | $CH$ (i) |
| Aryl $C$-$N$ (aniline) | $C-N$ (a) |
| Aryl $C$-$N$ (nitro) | $C-N$ (b) |
| Aryl $C$-$O$ | $C-O$ (a) |
| $NO_2$ group | $NO_2$ |
| $NH_2$ group | $NH_2$ |
| $OH$ group | $OH$ |

Table 15.250. The geometrical bond parameters of aryl nitro compounds and experimental values [1].

| Parameter | $\overset{3e}{C=C}$ Group | $CH$ (i) Group | $C-N$ (a) Group | $C-N$ (b) Group | $C-O$ (a) Group | $NO_2$ Group | $NH_2$ Group | $OH$ Group |
|---|---|---|---|---|---|---|---|---|
| $a\ (a_0)$ | 1.47348 | 1.60061 | 1.81158 | 1.97794 | 1.68220 | 1.33221 | 1.24428 | 1.26430 |
| $c'\ (a_0)$ | 1.31468 | 1.03299 | 1.34595 | 1.40639 | 1.29700 | 1.15421 | 0.94134 | 0.91808 |
| Bond Length $2c'$ ($\mathring{A}$) | 1.39140 | 1.09327 | 1.42449 | 1.48846 | 1.37268 | 1.22157 | 0.99627 | 0.971651 |
| Exp. Bond Length ($\mathring{A}$) | 1.397 avg. (phenol) | 1.084 (phenol) | 1.431 (aniline) | | 1.364 (phenol) | 1.224 (nitromethane) | 0.998 (aniline) | 0.956 (phenol) |
| $b,c\ (a_0)$ | 0.66540 | 1.22265 | 1.21254 | 1.39079 | 1.07126 | 0.66526 | 0.81370 | 0.86925 |
| $e$ | 0.89223 | 0.64537 | 0.74297 | 0.71104 | 0.77101 | 0.86639 | 0.75653 | 0.72615 |

Table 15.251. The MO to HO intercept geometrical bond parameters of aryl nitro compounds. $E_T$ is $E_T$ ($atom - atom, msp^3.AO$).

| Bond | Atom | $E_T$ (eV) Bond 1 | $E_T$ (eV) Bond 2 | $E_T$ (eV) Bond 3 | $E_T$ (eV) Bond 4 | Final Total Energy $C2sp^3$ (eV) | $r_{initial}$ $(a_0)$ | $r_{final}$ $(a_0)$ | $E_{Coulomb}(C2sp^3)$ (eV) Final | $E(C2sp^3)$ (eV) Final | $\theta'$ (°) | $\theta_1$ (°) | $\theta_2$ (°) | $d_1$ $(a_0)$ | $d_2$ $(a_0)$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $C-H\ (C_bH)$ | $C_b$ | -0.85035 | -0.85035 | -0.56690 | 0 | -153.88327 | 0.91771 | 0.79597 | -17.09334 | -16.90248 | 74.42 | 105.58 | 38.84 | 1.24678 | 0.21379 |
| $\left(C_b\overset{3e}{=}\right)_2 C_aO-H$ | $O$ | -0.74804 | 0 | 0 | 0 | | 1.00000 | 0.87363 | -15.57379 | | 115.79 | 64.21 | 64.82 | 0.53799 | 0.38009 |
| $\left(C_b\overset{3e}{=}\right)_2 C_a-OH$ | $C_a$ | -0.74804 | -0.85035 | -0.85035 | 0 | -154.06442 | 0.91771 | 0.78762 | -17.27448 | -17.08362 | 100.00 | 80.00 | 46.39 | 1.16026 | 0.13674 |
| $\left(C_b\overset{3e}{=}\right)_2 C_a-OH$ | $O$ | -0.74804 | 0 | 0 | 0 | | 1.00000 | 0.87363 | 15.57379 | | 106.51 | 73.49 | 51.43 | 1.04871 | 0.24829 |
| $\left(C_b\overset{3e}{=}\right)_2 C_aOH$ | $C_a$ | -0.74804 | -0.85035 | -0.85035 | 0 | -154.06442 | 0.91771 | 0.78762 | -17.27448 | -17.08362 | 133.88 | 46.12 | 58.55 | 0.76870 | 0.54598 |
| $C\overset{3e}{=}HC_c\overset{3e}{=}C$<br>$C\overset{3e}{=}(H_2N)C_a\overset{3e}{=}C$<br>$\left(\overset{3e}{=}(H)C_b\right)_2 C_aOH$<br>$C\overset{3e}{=}(H_3C_a)C_b\overset{3e}{=}C$ | $C_c$<br>$C_a$<br>$C_b$<br>$C_b$ | -0.85035 | -0.85035 | -0.56690 | 0 | -153.88327 | 0.91771 | 0.79597 | -17.09334 | -16.90248 | 134.24 | 45.76 | 58.98 | 0.75935 | 0.55533 |
| $\left(C_b\overset{3e}{=}\right)_2 C_aNH-H$ | $N$ | -0.56690 | 0 | 0 | 0 | | 0.93084 | 0.88392 | -15.39265 | | 121.74 | 58.26 | 67.49 | 0.47634 | 0.46500 |
| $\left(C_b\overset{3e}{=}\right)_2 C_a-NH_2$ | $C_a$ | -0.56690 | -0.85035 | -0.85035 | 0 | -153.88328 | 0.91771 | 0.79597 | -17.09334 | -16.90248 | 88.49 | 91.51 | 41.01 | 1.36696 | 0.02101 |
| $\left(C_b\overset{3e}{=}\right)_2 C_a-NH_2$ | $N$ | -0.56690 | 0 | 0 | 0 | | 0.93084 | 0.88392 | -15.39265 | | 96.32 | 83.68 | 46.43 | 1.24859 | 0.09736 |
| $\left(C\overset{3e}{=}\right)_2 C_b-C_aH_3$ | $C_a$ | -0.56690 | 0 | 0 | 0 | -152.18259 | 0.91771 | 0.88392 | -15.39265 | -15.20178 | 73.38 | 106.62 | 34.97 | 1.68807 | 0.25279 |
| $\left(C\overset{3e}{=}\right)_2 C_b-C_aH_3$ | $C_b$ | -0.56690 | -0.85035 | -0.85035 | 0 | -153.88328 | 0.91771 | 0.79597 | -17.09334 | -16.90247 | 61.56 | 118.44 | 28.27 | 1.81430 | 0.37901 |
| $RN(O)=O$ | $O$ | -0.92918 | 0 | 0 | 0 | | 1.00000 | 0.86359 | -15.75493 | | 135.25 | 44.75 | 66.05 | 0.54089 | 0.61333 |
| $RN(O)=O$ | $N$ | -0.92918 | -0.92918 | -0.36229 | 0 | | 0.93084 | 0.79816 | -17.04640 | | 132.36 | 47.64 | 62.44 | 0.61640 | 0.53781 |
| $\left(C\overset{3e}{=}\right)_2 C_a-NO_2$ | $C_a$ | -0.36229 | -0.85035 | -0.85035 | 0 | -153.67867 | 0.91771 | 0.80561 | -16.88873 | -16.69786 | 72.49 | 107.51 | 33.53 | 1.64875 | 0.24236 |
| $\left(C\overset{3e}{=}\right)_2 C_a-NO_2$ | $N$ | -0.92918 | -0.92918 | -0.36229 | 0 | | 0.93084 | 0.79816 | -17.04640 | | 71.53 | 108.47 | 32.98 | 1.65923 | 0.25284 |
| $C\overset{3e}{=}(O_2N)C_a\overset{3e}{=}C$ | $C_a$ | -0.36229 | -0.85035 | -0.85035 | 0 | -153.67867 | 0.91771 | 0.80561 | -16.88873 | -16.69786 | 134.65 | 45.35 | 59.47 | 0.74854 | 0.56614 |

Table 15.252. The energy parameters $(eV)$ of functional groups of aryl nitro compounds.

| Parameters | $C\overset{3e}{=}C$ Group | $CH$ (i) Group | $C-N$ (a) Group | $C-N$ (b) Group | $C-O$ (a) Group | $NO_2$ Group | $NH_2$ Group | $OH$ Group |
|---|---|---|---|---|---|---|---|---|
| $f_1$ | 0.75 | 1 | | | | | | |
| $n_1$ | 2 | 1 | 1 | 1 | 1 | 2 | 2 | 1 |
| $n_2$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $n_3$ | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 0 |
| $C_1$ | 0.5 | 0.75 | 0.5 | 0.5 | 0.5 | 0.5 | 0.75 | 0.75 |
| $C_2$ | 0.85252 | 1 | 1 | 1 | 1 | 1 | 0.93613 | 1 |
| $c_1$ | 1 | 1 | 1 | 1 | 1 | 1 | 0.75 | 0.75 |
| $c_2$ | 0.85252 | 0.91771 | 0.84665 | 0.91140 | 0.79329 | 0.85987 | 0.92171 | 1 |
| $c_3$ | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 1 |
| $c_4$ | 3 | 1 | 2 | 2 | 2 | 4 | 1 | 1 |
| $c_5$ | 0 | 1 | 0 | 0 | 0 | 0 | 2 | 1 |
| $C_{1o}$ | 0.5 | 0.75 | 0.5 | 0.5 | 0.5 | 0.5 | 1.5 | 0.75 |
| $C_{2o}$ | 0.85252 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $V_e$ $(eV)$ | -101.12679 | -37.10024 | -32.76465 | -31.36351 | -34.04658 | -106.90919 | -78.97795 | -40.92709 |
| $V_p$ $(eV)$ | 20.69825 | 13.17125 | 10.10870 | 9.67426 | 10.49024 | 23.57588 | 28.90735 | 14.81988 |
| $T$ $(eV)$ | 34.31559 | 11.58941 | 9.04312 | 7.92833 | 10.11966 | 40.12475 | 31.73641 | 16.18567 |
| $V_m$ $(eV)$ | -17.15779 | -5.79470 | -4.52156 | -3.96416 | -5.05983 | -20.06238 | -15.86820 | -8.09284 |
| $E(_{AO/HO})$ $(eV)$ | 0 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | 0 | -14.53414 | -13.6181 |
| $\Delta E_{H_2MO}(_{AO/HO})$ $(eV)$ | 0 | -1.13379 | -1.13379 | -0.72457 | -1.49608 | 0 | 0 | 0 |
| $E_T(_{AO/HO})$ $(eV)$ | 0 | -13.50110 | -13.50110 | -13.91032 | -13.13881 | 0 | -14.53414 | -13.6181 |
| $E(_{n_3\ AO/HO})$ $(eV)$ | 0 | 0 | 0 | 0 | 0 | 0 | -14.53414 | 0 |
| $E_T(_{H_2MO})$ $(eV)$ | -63.27075 | -31.63539 | -31.63549 | -31.63540 | -31.63532 | -63.27093 | -48.73654 | -31.63247 |
| $E_T\left(atom-atom,msp^3.AO\right)$ $(eV)$ | -2.26759 | -0.56690 | -1.13379 | -0.72457 | -1.49608 | -3.71673 | 0 | 0 |
| $E_T(_{MO})$ $(eV)$ | -65.53833 | -32.20226 | -32.76916 | -32.35994 | -33.13145 | -66.98746 | -48.73660 | -31.63537 |
| $\omega$ $\left(10^{15}\ rad/s\right)$ | 49.7272 | 26.4826 | 11.9890 | 17.8228 | 13.3984 | 19.0113 | 68.9812 | 44.1776 |
| $E_K$ $(eV)$ | 32.73133 | 17.43132 | 7.89138 | 11.73128 | 8.81907 | 12.51354 | 45.40465 | 29.07844 |
| $\bar{E}_D$ $(eV)$ | -0.35806 | -0.26130 | -0.18211 | -0.21927 | -0.19465 | -0.23440 | -0.42172 | -0.33749 |
| $\bar{E}_{Kvib}$ $(eV)$ | 0.19649<br>[49] | 0.35532<br>Eq. (13.458) | 0.15498<br>[58] | 0.10539<br>[45] | 0.12808<br>[19] | 0.19342<br>[45] | 0.40929<br>[22] | 0.46311<br>[17-18] |
| $\bar{E}_{osc}$ $(eV)$ | -0.25982 | -0.08364 | -0.10462 | -0.16658 | -0.13061 | -0.13769 | -0.21708 | -0.10594 |
| $E_{mag}$ $(eV)$ | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.11441 | 0.14803 | 0.11441 |
| $E_T(_{Group})$ $(eV)$ | -49.54347 | -32.28590 | -32.87379 | -32.52652 | -33.26206 | -67.26284 | -49.17075 | -31.74130 |
| $E_{initial}(_{c_4\ AO/HO})$ $(eV)$ | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.53414 | -13.6181 |
| $E_{initial}(_{c_5\ AO/HO})$ $(eV)$ | 0 | -13.59844 | 0 | 0 | 0 | 0 | -13.59844 | -13.59844 |
| $E_D(_{Group})$ $(eV)$ | 5.63881 | 3.90454 | 3.60401 | 3.25674 | 3.99228 | 8.72329 | 7.43973 | 4.41035 |

Table 15.253. The total bond energies of aryl nitro compounds calculated using the functional group composition and the energies of Table 15.252 compared to the experimental values [3]. The magnetic energy $E_{mag}$ that is subtracted from the weighted sum of the $E_D\,(_{Group})\,(eV)$ values based on composition is given by (15.58).

| Formula | Name | $\overset{3e}{C=C}$ | $CH$ (i) | $C-N$ (a) Group | $C-N$ (b) Group | $C-O$ (a) Group | $NO_2$ Group | $NH_2$ Group | $OH$ Group | $E_{mag}$ | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $C_6H_5NO_2$ | Nitrobenzene | 6 | 5 | 0 | 1 | 0 | 1 | 0 | 0 | 1 | 65.18754 | 65.217 | 0.00046 |
| $C_6H_4N_2O_5$ | 2,4-dinitrophenol | 6 | 4 | 0 | 2 | 1 | 2 | 0 | 1 | 2 | 77.61308 | 77.642 | 0.00037 |
| $C_6H_6N_2O_2$ | 2-nitroaniline | 6 | 4 | 1 | 1 | 0 | 1 | 1 | 0 | 0 | 72.47476 | 72.424 | -0.00070 |
| $C_6H_6N_2O_2$ | 3-nitroaniline | 6 | 4 | 1 | 1 | 0 | 1 | 1 | 0 | 0 | 72.47476 | 72.481 | -0.00009 |
| $C_6H_6N_2O_2$ | 4-nitroaniline | 6 | 4 | 1 | 1 | 0 | 1 | 1 | 0 | 0 | 72.47476 | 72.476 | -0.00002 |

Table 15.254. The bond angle parameters of aryl nitro compounds and experimental values [1]. $E_T$ is $E_T\,(atom-atom,msp^3.AO)$.

| Atoms of Angle | $2c'$ Bond 1 $(a_0)$ | $2c'$ Bond 2 $(a_0)$ | $2c'$ Terminal Atoms $(a_0)$ | $E_{Coulombic}$ Atom 1 | Atom 1 Hybridization Designation (Table 15.3.A) | $E_{Coulombic}$ Atom 2 | Atom 2 Hybridization Designation (Table 15.3.A) | $c_2$ Atom 1 | $c_2$ Atom 2 | $C_1$ | $C_2$ | $c_1$ | $c_2'$ | $E_T$ (eV) | $\theta_v$ (°) | $\theta_1$ (°) | $\theta_2$ (°) | Cal. $\theta$ (°) | Exp. $\theta$ (°) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $\angle CCC$ (aromatic) | 2.62936 | 2.62936 | 4.5585 | -17.17218 | 38 | -17.17218 | 38 | 0.79232 | 0.79232 | 1 | 1 | 1 | 0.79232 | -1.85836 | | | | 120.19 | 120 [50-52] (benzene) |
| $\angle CCH$ (aromatic) | | | | | | | | | | | | | | | | 120.19 | | 119.91 | 120 [50-52] (benzene) |
| $\angle O_aNO_b$ | 2.30843 | 2.30843 | 4.1231 | -16.68411 $O_a$ | 25 | -16.68411 $O_b$ | 25 | 0.81549 | 0.81549 | 1 | 1 | 1 | 0.81549 | -1.44915 | | | | 126.52 | 123.2 [57] (nitrobenzene)<br>125.3 (nitromethane) |
| $\angle CNO$ | 2.81279 | 2.30843 | 4.4159 | -17.45562 | 46 | -13.61806 | O | 0.77945 | 0.85395 (Eq. (15.133)) | 1 | 1 | 1 | 0.81670 | -1.65376 | | | | 118.82 | 118.5 [57] (nitrobenzene) |
| $\angle C_aOH$ | 2.59399 | 1.83616 | 3.6515 | -14.82575 | 1 | -14.82575 | 1 | 1 | 0.91771 | 0.75 | 1 | 0.75 | 0.91771 | 0 | | | | 109.84 | 109.0 (phenol) |
| $\angle HNH$ | 1.88268 | 1.88268 | 3.1559 | -14.53414 | N | H | H | 0.93613 Eq. (13.248)) | 1 | 1 | 1 | 0.75 | 1.06823 | 0 | | | | 113.89 | 113.9 (aniline) |
| $\angle C_aNH$ | 2.69190 | 1.88268 | 3.9833 | -15.95955 | 10 | -14.53414 | N | 0.84665 (Eq. (15.171)) | 0.84665 (Eq. (15.171)) | 0.75 | 1 | 0.75 | 1.00000 | 0 | | | | 120.05 | |

## BENZOIC ACID COMPOUNDS

Benzoic acid compounds have a hydrogen of an aryl group replaced by a carboxylic acid group corresponding to an $C-C(O)-OH$ moiety that comprises $C=O$ and $OH$ functional groups that are the same as those of carboxylic acids given in the corresponding section. The single bond of aryl carbon to the carbonyl carbon atom, $C-C(O)$, is also a functional group. This group is also equivalent to the same group of carboxylic acids except that $\Delta E_{H_2MO}\left(AO/HO\right)$ in Eq. (15.51) and $E_T\left(atom-atom,msp^3.AO\right)$ in Eq. (15.61) are both $-1.29147\,eV$ which is a linear combination of $\frac{-1.13379\ eV}{2}$, $E_T\left(atom-atom,msp^3.AO\right)$ of the $C-H$ group that the $C-C(O)$ group replaces, and that of an independent $C2sp^3$ HO, $-0.72457\ eV$ (Eq. (14.151)).

Examples include benzoic acid, chlorobenzoic acid, and aniline carboxylic acid with formulas $C_7H_6O_2$, $C_7H_5O_2Cl$, and $C_7H_7NO_2$, respectively. The aromatic $C\overset{3e}{=}C$ and $C-H$ functional groups are equivalent to those of benzene given in Aromatic and Heterocyclic Compounds section. The $NH_2$ and $C-N$ functional groups of aniline carboxylic acids are the same as those of aniline given in the corresponding section. The $C-Cl$ functional group of 2-chlorobenzoic acids corresponding to meta substitution is equivalent to that of chlorobenzene given in the corresponding section. The $C-Cl$ functional group of 3 or 4-chlorobenzoic acids corresponding to ortho and para substitution is also equivalent to that of chlorobenzene, except that $E_T\left(atom-atom,msp^3.AO\right)$ in Eq. (15.61) is $-0.92918\ eV$ (Eq. (14.513)) for both cases since each of these positions can form a resonance structure with the carboxylic acid group which is permissive of greater charge donation from the $C2sp^3$ HO.

The symbols of the functional groups of benzoic acid compounds are given in Table 15.255. The corresponding designations of benzoic acid is shown in Figure 15.44B. The geometrical (Eqs. (15.1-15.5) and (15.51)), intercept (Eqs. (15.80-15.87)), and energy (Eqs. (15.6-15.11), (15.17-15.65), and (15.165-15.166)) parameters of benzoic acid compounds are given in Tables 15.256, 15.257, and 15.258, respectively. The total energy of each benzoic acid compound given in Table 15.259 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.258 corresponding to functional-group composition of the molecule. The bond angle parameters of benzoic acid compounds determined using Eqs. (15.88-15.117) are given in Table 15.260. The color scale, translucent view of the charge-density of benzoic acid comprising the concentric shells of atoms with the outer shell bridged by one or more $H_2$-type ellipsoidal MOs or joined with one or more hydrogen MOs is shown in Figure 15.44A.

Figure 15.44. (A) Color scale, translucent view of the charge-density of benzoic acid showing the orbitals of the atoms at their radii, the ellipsoidal surface of each $H$ or $H_2$-type ellipsoidal MO that transitions to the corresponding outer shell of the atom(s) participating in each bond, and the hydrogen nuclei (red, not to scale). (B) Chemical structure and atom designation of benzoic acid.

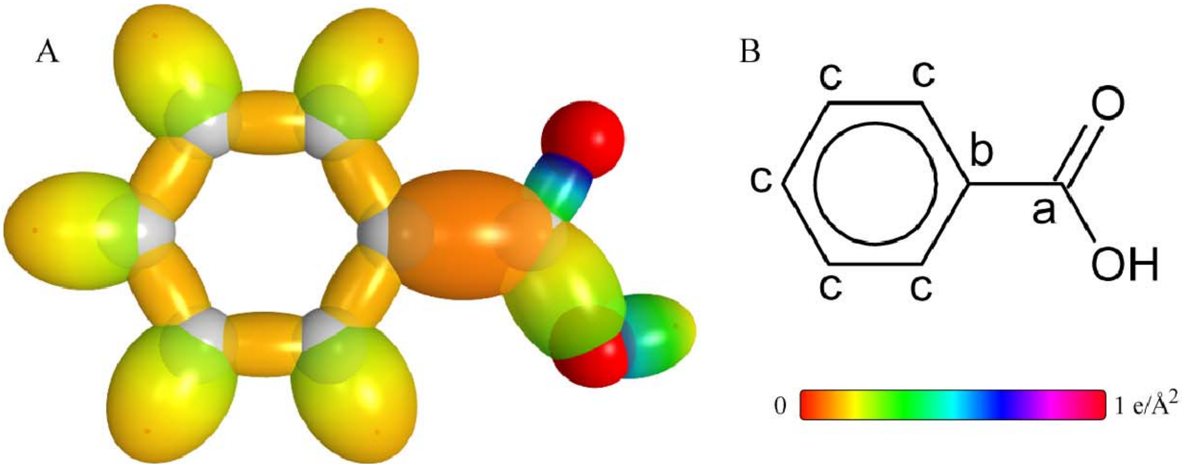


Table 15.255. The symbols of functional groups of benzoic acid compounds.

| Functional Group | Group Symbol |
|---|---|
| $CC$ (aromatic bond) | $C\overset{3e}{=}C$ |
| $CH$ (aromatic) | $CH$ (i) |
| $C$-$C(O)$ | $C-C(O)$ |
| $C=O$ (aryl carboxylic acid) | $C=O$ |
| $(O)C$-$O$ | $C-O$ |
| $OH$ group | $OH$ |
| $Cl-C$ ($Cl$ to aromatic bond of 2-chlorobenzoic acid) | $C-Cl$ (i) |
| $Cl-C$ ($Cl$ to aromatic bond of 3 or 4-chlorobenzoic acid) | $C-Cl$ (ii) |
| Aryl $C$-$N$ (aniline) | $C-N$ |
| $NH_2$ group | $NH_2$ |

Table 15.256. The geometrical bond parameters of benzoic acid compounds and experimental values [1].

| Parameters | $\overset{3e}{C=C}$ Group | $CH$ (i) Group | $C-C(O)$ Group | $C=O$ Group | $C-O$ Group | $OH$ Group | $C-Cl$ (i) Group | $C-Cl$ (ii) Group | $C-N$ Group | $NH_2$ Group |
|---|---|---|---|---|---|---|---|---|---|---|
| $f_1$ | 0.75 | 1 | | | | | | | | |
| $n_1$ | 2 | 1 | 1 | 2 | 1 | 1 | 1 | 1 | 1 | 2 |
| $n_2$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $n_3$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1 |
| $C_1$ | 0.5 | 0.75 | 0.5 | 0.5 | 0.5 | 0.75 | 0.5 | 0.5 | 0.5 | 0.75 |
| $C_2$ | 0.85252 | 1 | 1 | 1 | 1 | 1 | 0.81317 | 0.81317 | 1 | 0.93613 |
| $c_1$ | 1 | 1 | 1 | 1 | 1 | 0.75 | 1 | 1 | 1 | 0.75 |
| $c_2$ | 0.85252 | 0.91771 | 0.91771 | 0.85395 | 0.85395 | 1 | 1 | 1 | 0.84665 | 0.92171 |
| $c_3$ | 0 | 1 | 0 | 2 | 0 | 1 | 0 | 0 | 0 | 0 |
| $c_4$ | 3 | 1 | 2 | 4 | 2 | 1 | 2 | 2 | 2 | 1 |
| $c_5$ | 0 | 1 | 0 | 0 | 0 | 1 | 0 | 0 | 0 | 2 |
| $C_{1o}$ | 0.5 | 0.75 | 0.5 | 0.5 | 0.5 | 0.75 | 0.5 | 0.5 | 0.5 | 1.5 |
| $C_{2o}$ | 0.85252 | 1 | 1 | 1 | 1 | 1 | 0.81317 | 0.81317 | 1 | 1 |
| $V_e\ (eV)$ | -101.12679 | -37.10024 | -32.15216 | -111.25473 | -35.08488 | -40.92709 | -31.85648 | -32.14474 | -32.76465 | -78.97795 |
| $V_p\ (eV)$ | 20.69825 | 13.17125 | 9.74055 | 23.87467 | 10.32968 | 14.81988 | 8.25686 | 8.28394 | 10.10870 | 28.90735 |
| $T\ (eV)$ | 34.31559 | 11.58941 | 8.23945 | 42.82081 | 10.11150 | 16.18567 | 7.21391 | 7.32700 | 9.04312 | 31.73641 |
| $V_m\ (eV)$ | -17.15779 | -5.79470 | -4.11973 | -21.41040 | -5.05575 | -8.09284 | -3.60695 | -3.66350 | -4.52156 | -15.86820 |
| $E(_{AO/HO})\ (eV)$ | 0 | -14.63489 | -14.63489 | 0 | -14.63489 | -13.6181 | -14.63489 | -14.63489 | -14.63489 | -14.53414 |
| $\Delta E_{H_2MO}(_{AO/HO})\ (eV)$ | 0 | -1.13379 | -1.29147 | -2.69893 | -2.69893 | 0 | -2.99216 | -2.99216 | -1.13379 | 0 |
| $E_T(_{AO/HO})\ (eV)$ | 0 | -13.50110 | -13.34342 | 2.69893 | -11.93596 | -13.6181 | -11.64273 | -11.64273 | -13.50110 | -14.53414 |
| $E(_{n_3\ AO/HO})\ (eV)$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | -14.53414 |
| $E_T(_{H_2MO})\ (eV)$ | -63.27075 | -31.63539 | -31.63530 | -63.27074 | -31.63541 | -31.63247 | -31.63539 | -31.63542 | -31.63549 | -48.73654 |
| $E_T\left(atom-atom,msp^3.AO\right)\ (eV)$ | -2.26759 | -0.56690 | -1.29147 | -2.69893 | -1.85836 | 0 | -0.72457 | -0.92918 | -1.13379 | 0 |
| $E_T(_{MO})\ (eV)$ | -65.53833 | -32.20226 | -32.92684 | -65.96966 | -33.49373 | -31.63537 | -32.35994 | -32.56455 | -32.76916 | -48.73660 |
| $\omega\ \left(10^{15}\ rad/s\right)$ | 49.7272 | 26.4826 | 10.7262 | 59.4034 | 24.3637 | 44.1776 | 8.03459 | 8.11389 | 11.9890 | 68.9812 |
| $E_K\ (eV)$ | 32.73133 | 17.43132 | 7.06019 | 39.10034 | 16.03660 | 29.07844 | 5.28851 | 5.34070 | 7.89138 | 45.40465 |
| $\bar{E}_D\ (eV)$ | -0.35806 | -0.26130 | -0.17309 | -0.40804 | -0.26535 | -0.33749 | -0.14722 | -0.14888 | -0.18211 | -0.42172 |
| $\bar{E}_{Kvib}\ (eV)$ | 0.19649<br>[49] | 0.35532<br>Eq. (13.458) | 0.10502<br>[29] | 0.21077<br>[12] | 0.14010<br>[31] | 0.46311<br>[17-18] | 0.08059<br>[12] | 0.08059<br>[12] | 0.15498<br>[58] | 0.40929<br>[22] |
| $\bar{E}_{osc}\ (eV)$ | -0.25982 | -0.08364 | -0.12058 | -0.30266 | -0.19530 | -0.10594 | -0.10693 | -0.10859 | -0.10462 | -0.21708 |
| $E_{mag}\ (eV)$ | 0.14803 | 0.14803 | 0.14803 | 0.11441 | 0.14803 | 0.11441 | 0.14803 | 0.14803 | 0.14803 | 0.14803 |
| $E_T(_{Group})\ (eV)$ | -49.54347 | -32.28590 | -33.04742 | -66.57498 | -33.68903 | -31.74130 | -32.46687 | -32.67314 | -32.87379 | -49.17075 |
| $E_{initial}(_{c_4\ AO/HO})\ (eV)$ | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -13.6181 | -14.63489 | -14.63489 | -14.63489 | -14.53414 |
| $E_{initial}(_{c_5\ AO/HO})\ (eV)$ | 0 | -13.59844 | 0 | 0 | 0 | -13.59844 | 0 | 0 | 0 | -13.59844 |
| $E_D(_{Group})\ (eV)$ | 5.63881 | 3.90454 | 3.77764 | 7.80660 | 4.41925 | 4.41035 | 3.19709 | 3.40336 | 3.60401 | 7.43973 |

Table 15.257. The MO to HO intercept geometrical bond parameters of benzoic acid compounds. $E_T$ is $E_T$ ($atom - atom, msp^3.AO$).

| Bond | Atom | $E_T$ (eV) Bond 1 | $E_T$ (eV) Bond 2 | $E_T$ (eV) Bond 3 | $E_T$ (eV) Bond 4 | Final Total Energy $C2sp^3$ (eV) | $r_{initial}$ $(a_0)$ | $r_{final}$ $(a_0)$ | $E_{Coulomb}(C2sp^3)$ (eV) Final | $E(C2sp^3)$ (eV) Final | $\theta'$ (°) | $\theta_1$ (°) | $\theta_2$ (°) | $d_1$ $(a_0)$ | $d_2$ $(a_0)$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Aryl $C-H$ | $C_b$ | -0.85035 | -0.85035 | -0.56690 | 0 | -153.88327 | 0.91771 | 0.79597 | -17.09334 | -16.90248 | 74.42 | 105.58 | 38.84 | 1.24678 | 0.21379 |
| $C\overset{3e}{=}HC_b\overset{3e}{=}C$<br>$C\overset{3e}{=}(HOOC_a)C_b\overset{3e}{=}C_c(H)$<br>$C\overset{3e}{=}(Cl)C_a\overset{3e}{=}C_b(H)$<br>$C\overset{3e}{=}(H_2N)C_a\overset{3e}{=}C_b(H)$ | $C_b$<br>$C_c$<br>$C_b$<br>$C_b$ | -0.85035 | -0.85035 | -0.56690 | 0 | -153.88327 | 0.91771 | 0.79597 | -17.09334 | -16.90248 | 134.24 | 45.76 | 58.98 | 0.75935 | 0.55533 |
| $C_bC_a(O)O-H$ | $O$ | -0.92918 | 0 | 0 | 0 |  | 1.00000 | 0.86359 | -15.75493 |  | 115.09 | 64.91 | 64.12 | 0.55182 | 0.36625 |
| $C_bC_a(O)-OH$ | $O$ | -0.92918 | 0 | 0 | 0 |  | 1.00000 | 0.86359 | -15.75493 |  | 101.32 | 78.68 | 48.58 | 1.14765 | 0.16950 |
| $C_bC_a(O)-OH$ | $C_a$ | -0.92918 | -1.34946 | -0.64574 | 0 | -154.54007 | 0.91771 | 0.76652 | -17.75013 | -17.55927 | 93.11 | 86.89 | 42.68 | 1.27551 | 0.04165 |
| $C_bC_a(OH)=O$ | $O$ | -1.34946 | 0 | 0 | 0 |  | 1.00000 | 0.84115 | -16.17521 |  | 137.27 | 42.73 | 66.31 | 0.52193 | 0.61784 |
| $C_bC_a(OH)=O$ | $C_a$ | -1.34946 | -0.64574 | -0.92918 | 0 | -154.54007 | 0.91771 | 0.76652 | -17.75013 | -17.55927 | 134.03 | 45.97 | 62.14 | 0.60699 | 0.53278 |
| $C_b-C_a(O)OH$ | $C_a$ | -0.64574 | -1.34946 | -0.92918 | 0 | -154.54007 | 0.91771 | 0.76652 | -17.75013 | -17.55927 | 70.34 | 109.66 | 32.00 | 1.65466 | 0.25784 |
| $C_b-C_a(O)OH$ | $C_b$ | -0.64574 | -0.85035 | -0.85035 | 0 | -153.96212 | 0.91771 | 0.79232 | -17.17218 | -16.98131 | 73.74 | 106.26 | 33.94 | 1.61863 | 0.22181 |
| $C_c\overset{3e}{=}(HOOC_a)C_b\overset{3e}{=}C_c$ ($C_c$ bound to $H$, $Cl$, or $NH_2$) | $C_b$ | -0.64574 | -0.85035 | -0.85035 | 0 | -153.96212 | 0.91771 | 0.79232 | -17.17218 | -16.98132 | 134.09 | 45.91 | 58.79 | 0.76344 | 0.55124 |
| $\left(C\overset{3e}{=}\right)_2 C_a-Cl$ | $Cl$ | -0.36229 | 0 | 0 | 0 |  | 1.05158 | 0.89582 | 15.18804 |  | 82.92 | 97.08 | 37.22 | 1.75824 | 0.11042 |
| $\left(C\overset{3e}{=}\right)_2 C_a-Cl$ | $C_a$ | -0.36229 | -0.85035 | -0.85035 | 0 | -153.67867 | 0.91771 | 0.80561 | -16.88873 | -16.69786 | 73.32 | 106.68 | 31.67 | 1.87911 | 0.23129 |
| $C_b\overset{3e}{=}(Cl)C_a\overset{3e}{=}C_b$ ($C_b$ bound to $H$ or $Cl$) | $C_a$ | -0.36229 | -0.85035 | -0.85035 | 0 | -153.67867 | 0.91771 | 0.80561 | -16.88873 | -16.69786 | 134.65 | 45.35 | 59.47 | 0.74854 | 0.56614 |
| $\left(C_b\overset{3e}{=}\right)_2 C_aNH-H$ | $N$ | -0.56690 | 0 | 0 | 0 |  | 0.93084 | 0.88392 | -15.39265 |  | 121.74 | 58.26 | 67.49 | 0.47634 | 0.46500 |
| $\left(C_b\overset{3e}{=}\right)_2 C_a-NH_2$ | $C_a$ | -0.56690 | -0.85035 | -0.85035 | 0 | -153.88328 | 0.91771 | 0.79597 | -17.09334 | -16.90248 | 88.49 | 91.51 | 41.01 | 1.36696 | 0.02101 |
| $\left(C_b\overset{3e}{=}\right)_2 C_a-NH_2$ | $N$ | -0.56690 | 0 | 0 | 0 |  | 0.93084 | 0.88392 | -15.39265 |  | 96.32 | 83.68 | 46.43 | 1.24859 | 0.09736 |
| $C\overset{3e}{=}(H_2N)C_a\overset{3e}{=}C$ | $C_a$ | -0.85035 | -0.85035 | -0.56690 | 0 | -153.88327 | 0.91771 | 0.79597 | -17.09334 | -16.90248 | 134.24 | 45.76 | 58.98 | 0.75935 | 0.55533 |

Table 15.258. The energy parameters ($eV$) of functional groups of benzoic acid compounds.

| Parameters | $\overset{3e}{C=C}$ Group | $CH$ (i) Group | $C-C(O)$ Group | $C=O$ Group | $C-O$ Group | $OH$ Group | $C-Cl$ (i) Group | $C-Cl$ (ii) Group | $C-N$ Group | $NH_2$ Group |
|---|---|---|---|---|---|---|---|---|---|---|
| $f_1$ | 0.75 | 1 | | | | | | | | |
| $n_1$ | 2 | 1 | 1 | 2 | 1 | 1 | 1 | 1 | 1 | 2 |
| $n_2$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $n_3$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1 |
| $C_1$ | 0.5 | 0.75 | 0.5 | 0.5 | 0.5 | 0.75 | 0.5 | 0.5 | 0.5 | 0.75 |
| $C_2$ | 0.85252 | 1 | 1 | 1 | 1 | 1 | 0.81317 | 0.81317 | 1 | 0.93613 |
| $c_1$ | 1 | 1 | 1 | 1 | 1 | 0.75 | 1 | 1 | 1 | 0.75 |
| $c_2$ | 0.85252 | 0.91771 | 0.91771 | 0.85395 | 0.85395 | 1 | 1 | 1 | 0.84665 | 0.92171 |
| $c_3$ | 0 | 1 | 0 | 2 | 0 | 1 | 0 | 0 | 0 | 0 |
| $c_4$ | 3 | 1 | 2 | 4 | 2 | 1 | 2 | 2 | 2 | 1 |
| $c_5$ | 0 | 1 | 0 | 0 | 0 | 1 | 0 | 0 | 0 | 2 |
| $C_{1o}$ | 0.5 | 0.75 | 0.5 | 0.5 | 0.5 | 0.75 | 0.5 | 0.5 | 0.5 | 1.5 |
| $C_{2o}$ | 0.85252 | 1 | 1 | 1 | 1 | 1 | 0.81317 | 0.81317 | 1 | 1 |
| $V_e\ (eV)$ | -101.12679 | -37.10024 | -32.15216 | -111.25473 | -35.08488 | -40.92709 | -31.85648 | -32.14474 | -32.76465 | -78.97795 |
| $V_p\ (eV)$ | 20.69825 | 13.17125 | 9.74055 | 23.87467 | 10.32968 | 14.81988 | 8.25686 | 8.28394 | 10.10870 | 28.90735 |
| $T\ (eV)$ | 34.31559 | 11.58941 | 8.23945 | 42.82081 | 10.11150 | 16.18567 | 7.21391 | 7.32700 | 9.04312 | 31.73641 |
| $V_m\ (eV)$ | -17.15779 | -5.79470 | -4.11973 | -21.41040 | -5.05575 | -8.09284 | -3.60695 | -3.66350 | -4.52156 | -15.86820 |
| $E(_{AO/HO})\ (eV)$ | 0 | -14.63489 | -14.63489 | 0 | -14.63489 | -13.6181 | -14.63489 | -14.63489 | -14.63489 | -14.53414 |
| $\Delta E_{H_2MO}(_{AO/HO})\ (eV)$ | 0 | -1.13379 | -1.29147 | -2.69893 | -2.69893 | 0 | -2.99216 | -2.99216 | -1.13379 | 0 |
| $E_T(_{AO/HO})\ (eV)$ | 0 | -13.50110 | -13.34342 | 2.69893 | -11.93596 | -13.6181 | -11.64273 | -11.64273 | -13.50110 | -14.53414 |
| $E(_{n_3\ AO/HO})\ (eV)$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | -14.53414 |
| $E_T(_{H_2MO})\ (eV)$ | -63.27075 | -31.63539 | -31.63530 | -63.27074 | -31.63541 | -31.63247 | -31.63539 | -31.63542 | -31.63549 | -48.73654 |
| $E_T\left(atom-atom,msp^3.AO\right)\ (eV)$ | -2.26759 | -0.56690 | -1.29147 | -2.69893 | -1.85836 | 0 | -0.72457 | -0.92918 | -1.13379 | 0 |
| $E_T(_{MO})\ (eV)$ | -65.53833 | -32.20226 | -32.92684 | -65.96966 | -33.49373 | -31.63537 | -32.35994 | -32.56455 | -32.76916 | -48.73660 |
| $\omega\ \left(10^{15}\ rad/s\right)$ | 49.7272 | 26.4826 | 10.7262 | 59.4034 | 24.3637 | 44.1776 | 8.03459 | 8.11389 | 11.9890 | 68.9812 |
| $E_K\ (eV)$ | 32.73133 | 17.43132 | 7.06019 | 39.10034 | 16.03660 | 29.07844 | 5.28851 | 5.34070 | 7.89138 | 45.40465 |
| $\bar{E}_D\ (eV)$ | -0.35806 | -0.26130 | -0.17309 | -0.40804 | -0.26535 | -0.33749 | -0.14722 | -0.14888 | -0.18211 | -0.42172 |
| $\bar{E}_{Kvib}\ (eV)$ | 0.19649<br>[49] | 0.35532<br>Eq. (13.458) | 0.10502<br>[29] | 0.21077<br>[12] | 0.14010<br>[31] | 0.46311<br>[17-18] | 0.08059<br>[12] | 0.08059<br>[12] | 0.15498<br>[58] | 0.40929<br>[22] |
| $\bar{E}_{osc}\ (eV)$ | -0.25982 | -0.08364 | -0.12058 | -0.30266 | -0.19530 | -0.10594 | -0.10693 | -0.10859 | -0.10462 | -0.21708 |
| $E_{mag}\ (eV)$ | 0.14803 | 0.14803 | 0.14803 | 0.11441 | 0.14803 | 0.11441 | 0.14803 | 0.14803 | 0.14803 | 0.14803 |
| $E_T(_{Group})\ (eV)$ | -49.54347 | -32.28590 | -33.04742 | -66.57498 | -33.68903 | -31.74130 | -32.46687 | -32.67314 | -32.87379 | -49.17075 |
| $E_{initial}(_{c_4\ AO/HO})\ (eV)$ | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -13.6181 | -14.63489 | -14.63489 | -14.63489 | -14.53414 |
| $E_{initial}(_{c_5\ AO/HO})\ (eV)$ | 0 | -13.59844 | 0 | 0 | 0 | -13.59844 | 0 | 0 | 0 | -13.59844 |
| $E_D(_{Group})\ (eV)$ | 5.63881 | 3.90454 | 3.77764 | 7.80660 | 4.41925 | 4.41035 | 3.19709 | 3.40336 | 3.60401 | 7.43973 |

Table 15.259. The total bond energies of benzoic acid compounds calculated using the functional group composition and the energies of Table 15.258 compared to the experimental values [3].

| Formula | Name | $\overset{3e}{C=C}$ Group | $CH$ (i) Group | $C-C(O)$ Group | $C=O$ Group | $C-O$ Group | $OH$ Group | $C-Cl$ (i) Group | $C-Cl$ (ii) Group | $C-N$ Group | $NH_2$ Group | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $C_7H_6O_2$ | Benzoic acid | 6 | 5 | 1 | 1 | 1 | 1 | 0 | 0 | 0 | 0 | 73.76938 | 73.762 | -0.00009 |
| $C_7H_5ClO_2$ | 2-chlorobenzoic acid | 6 | 4 | 1 | 1 | 1 | 1 | 1 | 0 | 0 | 0 | 73.06193 | 73.082 | 0.00027 |
| $C_7H_5ClO_2$ | 3-chlorobenzoic acid | 6 | 4 | 1 | 1 | 1 | 1 | 0 | 1 | 0 | 0 | 73.26820 | 73.261 | -0.00010 |
| $C_7H_5ClO_2$ | 4-chlorobenzoic acid | 6 | 4 | 1 | 1 | 1 | 1 | 0 | 1 | 0 | 0 | 73.26820 | 73.247 | -0.00028 |
| $C_7H_7NO_2$ | Aniline-2-carboxylic acid | 6 | 4 | 1 | 1 | 1 | 1 | 0 | 0 | 1 | 1 | 80.90857 | 80.941 | 0.00041 |
| $C_7H_7NO_2$ | Aniline-3-carboxylic acid | 6 | 4 | 1 | 1 | 1 | 1 | 0 | 0 | 1 | 1 | 80.90857 | 80.813 | -0.00118 |
| $C_7H_7NO_2$ | Aniline-4-carboxylic acid | 6 | 4 | 1 | 1 | 1 | 1 | 0 | 0 | 1 | 1 | 80.90857 | 80.949 | 0.00050 |

Table 15.260. The bond angle parameters of benzoic acid compounds and experimental values [1]. $E_T$ is $E_T$ $(atom-atom,msp^3.AO)$.

| Atoms of Angle | $2c'$ Bond 1 $(a_0)$ | $2c'$ Bond 2 $(a_0)$ | $2c'$ Terminal Atoms $(a_0)$ | $E_{Coulombic}$ Atom 1 | Atom 1 Hybridization Designation (Table 15.3.A) | $E_{Coulombic}$ Atom 2 | Atom 2 Hybridization Designation (Table 15.3.A) | $c_2$ Atom 1 | $c_2$ Atom 2 | $C_1$ | $C_2$ | $c_1$ | $c_2'$ | $E_T$ (eV) | $\theta_v$ (°) | $\theta_1$ (°) | $\theta_2$ (°) | Cal. $\theta$ (°) | Exp. $\theta$ (°) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $\angle CCC$ (aromatic) | 2.62936 | 2.62936 | 4.5585 | -17.17218 | 38 | -17.17218 | 38 | 0.79232 | 0.79232 | 1 | 1 | 1 | 0.79232 | -1.85836 | | | | 120.19 | 120 [50-52] (benzene) |
| $\angle CCH$ (aromatic) | | | | | | | | | | | | | | | | 120.19 | | 119.91 | 120 [50-52] (benzene) |
| $\angle C_aO_bH$ | 2.63431 | 1.83616 | 3.6405 | -14.82575 | 1 | -14.82575 | 1 | 1 | 0.91771 | 0.75 | 1 | 0.75 | 0.91771 | 0 | | | | 107.71 | |
| $\angle C_bC_aO_a$ | 2.82796 | 2.27954 | 4.4721 | -17.17218 | 38 | -13.61806 | O | 0.79232 | 0.85395 (Eq. (15.33)) | 1 | 1 | 1 | 0.82313 | -1.65376 | | | | 121.86 | 122 [59] (benzoic acid) |
| $\angle C_bC_aO_b$ | 2.82796 | 2.63431 | 4.6690 | -16.40067 | 20 | -13.61806 | O | 0.82959 | 0.85395 (Eq. (15.133)) | 1 | 1 | 1 | 0.84177 | -1.65376 | | | | 117.43 | 118 [59] (benzoic acid) |
| $\angle O_aC_aO_b$ | 2.27954 | 2.63431 | 4.3818 | -16.17521 $O_a$ | 13 | -15.75493 $O_b$ | 7 | 0.84115 | 0.86359 | 1 | 1 | 1 | 0.85237 | -1.44915 | | | | 126.03 | 122 [59] (benzoic acid) |
| $\angle CCC$ (aromatic) | 2.62936 | 2.62936 | 4.5585 | -17.17218 | 38 | -17.17218 | 38 | 0.79232 | 0.79232 | 1 | 1 | 1 | 0.79232 | -1.85836 | | | | 120.19 | 120 ($\angle CC(H)C$ chlorobenzene)<br>121.7 ($\angle CC(Cl)C$ chlorobenzene)<br>120 [50-52] (benzene) |
| $\angle CCH$<br>$\angle CCCl$ (aromatic) | | | | | | | | | | | | | | | | 120.19 | | 119.91 | 120 [50-52] (benzene) |
| $\angle HNH$ | 1.88268 | 1.88268 | 3.1559 | -14.53414 | N | H | H | 0.93613 Eq. (13.248)) | 1 | 1 | 1 | 0.75 | 1.06823 | 0 | | | | 113.89 | 113.9 (aniline) |
| $\angle C_aNH$ | 2.69190 | 1.88268 | 3.9833 | -15.95955 | 10 | -14.53414 | N | 0.84665 (Eq. (15.171)) | 0.84665 (Eq. (15.171)) | 0.75 | 1 | 0.75 | 1.00000 | 0 | | | | 120.05 | |

## ANISOLE

Anisole has the formula $C_7H_8O$ and comprises the phenol molecule with the hydroxyl hydrogen atom replaced by the moiety $-O-CH_3$ to form an ether comprising aromatic and methyl functional groups as well as two types of $C-O$ functional groups, one for aryl carbon to oxygen and one for methyl carbon to oxygen. The aromatic $C\overset{3e}{=}C$ and $C-H$ functional groups are equivalent to those of benzene given in the Aromatic and Heterocyclic Compounds section. The $CH_3$ and methyl $C-O$ functional groups are the same as those of the corresponding ether groups given in the corresponding section.

The $C-O$ functional group comprising the bond between the ether oxygen and aromatic ring is equivalent to that of the methyl ether $C-O$ functional group except that $\Delta E_{H_2MO}\left(AO/HO\right)$ in Eq. (15.51) and $E_T\left(atom-atom,msp^3.AO\right)$ in Eq. (15.61) are both $-1.13379\ eV$ (Eq. (14.247)). $E_T\left(atom-atom,msp^3.AO\right)$ is based on the energy match between the $OCH_3$ group and the $C2sp^3$ HO of the aryl group and is twice that of the aryl $C-H$ group that it replaces.

The symbols of the functional groups of anisole are given in Table 15.261. The geometrical (Eqs. (15.1-15.5) and (15.51)), intercept (Eqs. (15.80-15.87)), and energy (Eqs. (15.6-15.11), (15.17-15.65), and (15.165-15.166)) parameters of anisole are given in Tables 15.262, 15.263, and 15.264, respectively. The total energy of anisole given in Table 15.265 was calculated as the sum over the integer multiple of each $E_D\left(Group\right)$ of Table 15.264 corresponding to functional-group composition of the molecule. The bond angle parameters of anisole determined using Eqs. (15.88-15.117) are given in Table 15.266. The color scale, translucent view of the charge-density of anisole comprising the concentric shells of atoms with the outer shell bridged by one or more $H_2$-type ellipsoidal MOs or joined with one or more hydrogen MOs is shown in Figure 15.45.

Figure 15.45. Color scale, translucent view of the charge-density of anisole showing the orbitals of the atoms at their radii, the ellipsoidal surface of each $H$ or $H_2$-type ellipsoidal MO that transitions to the corresponding outer shell of the atom(s) participating in each bond, and the hydrogen nuclei (red, not to scale).

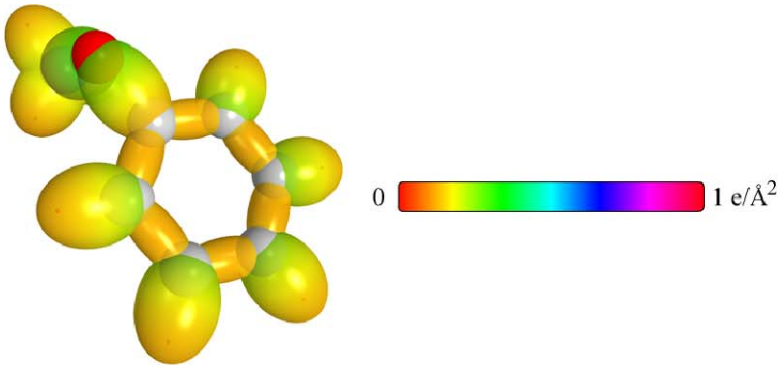


Table 15.261. The symbols of functional groups of anisole.

| Functional Group | Group Symbol |
|---|---|
| $CC$ (aromatic bond) | $C\overset{3e}{=}C$ |
| $CH$ (aromatic) | $CH$ (i) |
| Aryl $C$-$O$ | $C-O$ (a) |
| Methyl $C$-$O$ | $C-O$ (b) |
| $CH_3$ group | $C-H$ $\left(CH_3\right)$ |

Table 15.262. The geometrical bond parameters of anisole and experimental values [1].

| Parameter | $\overset{3e}{C=C}$ Group | $CH$ (i) Group | $C-O$ (a) Group | $C-O$ (b) Group | $C-H\left(CH_3\right)$ Group |
|---|---|---|---|---|---|
| $a\left(a_0\right)$ | 1.47348 | 1.60061 | 1.82682 | 1.80717 | 1.64920 |
| $c'\left(a_0\right)$ | 1.31468 | 1.03299 | 1.35160 | 1.34431 | 1.04856 |
| Bond Length $2c'$ $\left(\text{Å}\right)$ | 1.39140 | 1.09327 | 1.43047 | 1.42276 | 1.10974 |
| Exp. Bond Length $\left(\text{Å}\right)$ | 1.397 avg. (phenol) | 1.084 (phenol) | | | 1.11 (avg.) (toluene) |
| $b,c\left(a_0\right)$ | 0.66540 | 1.22265 | 1.22900 | 1.20776 | 1.27295 |
| $e$ | 0.89223 | 0.64537 | 0.73986 | 0.74388 | 0.63580 |

Table 15.263. The MO to HO intercept geometrical bond parameters of anisole. $E_T$ is $E_T$ ($atom-atom,msp^3.AO$).

| Bond | Atom | $E_T$ (eV) Bond 1 | $E_T$ (eV) Bond 2 | $E_T$ (eV) Bond 3 | $E_T$ (eV) Bond 4 | Final Total Energy $C2sp^3$ (eV) | $r_{initial}$ $(a_0)$ | $r_{final}$ $(a_0)$ | $E_{Coulomb}\left(C2sp^3\right)$ (eV) Final | $E\left(C2sp^3\right)$ (eV) Final | $\theta'$ (°) | $\theta_1$ (°) | $\theta_2$ (°) | $d_1$ $(a_0)$ | $d_2$ $(a_0)$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $C-H\ \left(C_bH\right)$ | $C_b$ | -0.85035 | -0.85035 | -0.56690 | 0 | -153.88327 | 0.91771 | 0.79597 | -17.09334 | -16.90248 | 74.42 | 105.58 | 38.84 | 1.24678 | 0.21379 |
| $C-H\ \left(OC_cH_3\right)$ | $C_c$ | -0.72457 | 0 | 0 | 0 | -152.34026 | 0.91771 | 0.87495 | -15.55033 | -15.35946 | 78.85 | 101.15 | 42.40 | 1.21777 | 0.16921 |
| $\left(C_b\overset{3e}{=}\right)_2 C_aO-C_cH_3$ | $C_c$ | -0.72457 | 0 | 0 | 0 | -152.34026 | 0.91771 | 0.87495 | -15.55033 | -15.35946 | 95.98 | 84.02 | 46.10 | 1.25319 | 0.09112 |
| $\left(C_b\overset{3e}{=}\right)_2 C_aO-C_cH_3$ | $O$ | -0.72457 | -0.56690 | 0 | 0 | | 1.00000 | 0.84418 | -16.11722 | | 93.38 | 86.62 | 44.25 | 1.29456 | 0.04975 |
| $\left(C_b\overset{3e}{=}\right)_2 C_a-OC_cH_3$ | $C_a$ | -0.56690 | -0.85035 | -0.85035 | 0 | -153.88327 | 0.91771 | 0.79597 | -17.09334 | -16.90248 | 87.00 | 93.00 | 40.30 | 1.39329 | 0.04170 |
| $\left(C_b\overset{3e}{=}\right)_2 C_a-OC_cH_3$ | $O$ | -0.56690 | -0.72457 | 0 | 0 | | 1.00000 | 0.84418 | -16.11722 | | 91.59 | 88.41 | 43.36 | 1.32814 | 0.02346 |
| $\left(C_b\overset{3e}{=}\right)_2 C_aOC_cH_3$ | $C_a$ | -0.56690 | -0.85035 | -0.85035 | 0 | -153.88327 | 0.91771 | 0.79597 | -17.09334 | -16.90248 | 134.24 | 45.76 | 58.98 | 0.75935 | 0.55533 |
| $\left(\overset{3e}{=}(H)C_b\right)_2 C_aOC_cH_3$ | $C_b$ | -0.85035 | -0.85035 | -0.56690 | 0 | -153.88327 | 0.91771 | 0.79597 | -17.09334 | -16.90248 | 134.24 | 45.76 | 58.98 | 0.75935 | 0.55533 |

Table 15.264. The energy parameters ($eV$) of functional groups of anisole.

| Parameters | $\overset{3e}{C=C}$ Group | $CH$ (i) Group | $C-O$ (a) Group | $C-O$ (b) Group | $CH_3$ Group |
|---|---|---|---|---|---|
| $f_1$ | 0.75 | 1 | | | |
| $n_1$ | 2 | 1 | 1 | 1 | 3 |
| $n_2$ | 0 | 0 | 0 | 0 | 2 |
| $n_3$ | 0 | 0 | 0 | 0 | 0 |
| $C_1$ | 0.5 | 0.75 | 0.5 | 0.5 | 0.75 |
| $C_2$ | 0.85252 | 1 | 1 | 1 | 1 |
| $c_1$ | 1 | 1 | 1 | 1 | 1 |
| $c_2$ | 0.85252 | 0.91771 | 0.85395 | 0.85395 | 0.91771 |
| $c_3$ | 0 | 1 | 0 | 0 | 0 |
| $c_4$ | 3 | 1 | 2 | 2 | 1 |
| $c_5$ | 0 | 1 | 0 | 0 | 3 |
| $C_{1o}$ | 0.5 | 0.75 | 0.5 | 0.5 | 0.75 |
| $C_{2o}$ | 0.85252 | 1 | 1 | 1 | 1 |
| $V_e\ (eV)$ | -101.12679 | -37.10024 | -32.67197 | -33.15757 | -107.32728 |
| $V_p\ (eV)$ | 20.69825 | 13.17125 | 10.06645 | 10.12103 | 38.92728 |
| $T\ (eV)$ | 34.31559 | 11.58941 | 8.94231 | 9.17389 | 32.53914 |
| $V_m\ (eV)$ | -17.15779 | -5.79470 | -4.47115 | -4.58695 | -16.26957 |
| $E(AO/HO)\ (eV)$ | 0 | -14.63489 | -14.63489 | -14.63489 | -15.56407 |
| $\Delta E_{H_2MO}(AO/HO)\ (eV)$ | 0 | -1.13379 | -1.13379 | -1.44915 | 0 |
| $E_T(AO/HO)\ (eV)$ | 0 | -13.50110 | -13.50110 | -13.18574 | -15.56407 |
| $E_T(H_2MO)\ (eV)$ | -63.27075 | -31.63539 | -31.63547 | -31.63533 | -67.69451 |
| $E_T(atom-atom, msp^3.AO)\ (eV)$ | -2.26759 | -0.56690 | -1.13379 | -1.44915 | 0 |
| $E_T(MO)\ (eV)$ | -65.53833 | -32.20226 | -32.76916 | -33.08452 | -67.69450 |
| $\omega\ (10^{15}\ rad/s)$ | 49.7272 | 26.4826 | 11.8393 | 12.0329 | 24.9286 |
| $E_K\ (eV)$ | 32.73133 | 17.43132 | 7.79284 | 7.92028 | 16.40846 |
| $\bar{E}_D\ (eV)$ | -0.35806 | -0.26130 | -0.18097 | -0.18420 | -0.25352 |
| $\bar{E}_{Kvib}\ (eV)$ | 0.19649<br>[49] | 0.35532<br>Eq. (13.458) | 0.13663<br>[21] | 0.13663<br>[21] | 0.35532<br>(Eq. (13.458)) |
| $\bar{E}_{osc}\ (eV)$ | -0.25982 | -0.08364 | -0.11266 | -0.11589 | -0.22757 |
| $E_{mag}\ (eV)$ | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 |
| $E_T(Group)\ (eV)$ | -49.54347 | -32.28590 | -32.88182 | -33.20040 | -67.92207 |
| $E_{initial}(c_4\ AO/HO)\ (eV)$ | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 |
| $E_{initial}(c_5\ AO/HO)\ (eV)$ | 0 | -13.59844 | 0 | 0 | -13.59844 |
| $E_D(Group)\ (eV)$ | 5.63881 | 3.90454 | 3.61204 | 3.93062 | 12.49186 |

Table 15.265. The total bond energies of anisole calculated using the functional group composition and the energies of Table 15.264 compared to the experimental values [3].

| Formula | Name | $\overset{3e}{C=C}$ | $CH$ (i) | $C-O$ (a) Group | $C-O$ (b) Group | $CH_3$ Group | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|---|---|---|---|---|
| $C_7H_8O$ | Anisole | 6 | 5 | 1 | 1 | 1 | 73.39006 | 73.355 | -0.00047 |

Table 15.266. The bond angle parameters of anisole and experimental values [1]. $E_T$ is $E_T$ ($atom-atom,msp^3.AO$).

| Atoms of Angle | $2c'$ Bond 1 ($a_0$) | $2c'$ Bond 2 ($a_0$) | $2c'$ Terminal Atoms ($a_0$) | $E_{Coulombic}$ Atom 1 | Atom 1 Hybridization Designation (Table 15.3.A) | $E_{Coulombic}$ Atom 2 | Atom 2 Hybridization Designation (Table 15.3.A) | $c_2$ Atom 1 | $c_2$ Atom 2 | $C_1$ | $C_2$ | $c_1$ | $c_2'$ | $E_T$ (eV) | $\theta_v$ (°) | $\theta_1$ (°) | $\theta_2$ (°) | Cal. $\theta$ (°) | Exp. $\theta$ (°) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $\angle CCC$ (aromatic) | 2.62936 | 2.62936 | 4.5585 | -17.17218 | 38 | -17.17218 | 38 | 0.79232 | 0.79232 | 1 | 1 | 1 | 0.79232 | -1.85836 | | | | 120.19 | 120 [50-52] (benzene) |
| $\angle CCH$ (aromatic) | | | | | | | | | | | | | | | | 120.19 | | 119.91 | 120 [50-52] (benzene) |

## PYRROLE

Pyrrole having the formula $C_4H_5N$ comprises the conjugated alkene 1,3-butadiene that forms a cyclic structure by terminal-atom bonding to a $NH$ functional group. The two symmetrical carbon-to-nitrogen bonds comprise the $C-N-C$ functional group. The 1,3-butadiene moiety comprises $C-C$, $C=C$, and $CH$ functional groups. The $C-C$ and $C=C$ groups are equivalent to the corresponding groups of 1,3-butadiene given in the Cyclic and Conjugated Alkenes section except that the energy terms corresponding to oscillation in the transition state match pyrrole. Furthermore, the conjugated double bonds have the same bonding as in 1,3-butadiene except that the hybridization terms $c_2$ of the $C-C$ and $C=C$ groups and $C_2$ and $C_{2o}$ of the $C=C$ group in Eqs. (15.51) and (15.61) become that of benzene given by Eq. (15.162), ($C_2\left(benzeneC2sp^3HO\right)=c_2\left(benzeneC2sp^3HO\right)=0.85252$), in the cyclic pyrrole MO which has aromatic character. The bonding in pyrrole, furan, and thiophene are the same except for the energy match to the corresponding heteroatoms. The hybridization permits double-bond character in the carbon-heteroatom bonding.

The $NH$ group is solved equivalently to that of a secondary amine as given in the corresponding section except that the hybridization term $c_2$ is that of the amino group of aniline in order provide double-bond character to match the group to the other orbitals of the molecule. Similarly, the $CH$ functional group is equivalent to that of 1,3-butadiene, except that $\Delta E_{H_2MO}\left(AO/HO\right)=-2.26758\ eV$ (Eq. (14.247)) in Eq. (15.51) in order to provide matching double-bond character.

The solution of the $C-N-C$ functional group comprises the hybridization of the $2s$ and $2p$ AOs of each $C$ to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between two $C2sp^3$ HOs and the nitrogen atom to form a MO permits each participating hybridized orbital to decrease in radius and energy. Thus, the $C-N-C$-bond MO comprising a linear combination of two single bonds is solved in the same manner as a double bond with $n_1=2$ in Eqs. (15.51) and (15.61). The hybridization factor $c_2\left(arylC2sp^3HO\ to\ N\right)=0.84665$ (Eq. (15.171)) matches the double-bond character of the $C2sp^3$ HOs to the $N$ atom of the $NH$ group, and $C_2$ and $C_{2o}$ in Eqs. (15.51) and (15.61) become that of benzene given by Eq. (15.162), $C_2\left(benzeneC2sp^3HO\right)=0.85252$. Furthermore, $\Delta E_{H_2MO}\left(AO/HO\right)$ in Eq. (15.51) and $E_T\left(atom-atom,msp^3.AO\right)$ in Eq. (15.61) are both $-0.92918\ eV$ (Eq. (14.513)) per atom corresponding to $-3.71673\ eV$ in total. This is the maximum energy for a single bond and corresponds to methylene character as given in the Continuous-Chain Alkanes section.

The symbols of the functional groups of pyrrole are given in Table 15.267. The structure of pyrrole is shown in Figure 15.46B. The geometrical (Eqs. (15.1-15.5) and (15.51)), intercept (Eqs. (15.80-15.87)), and energy (Eqs. (15.6-15.11) and (15.17-15.65)) parameters of pyrrole are given in Tables 15.268, 15.269, and 15.270, respectively. The total energy of pyrrole given in Table 15.271 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.270 corresponding to functional-group composition of the molecule. The bond angle parameters of pyrrole determined using Eqs. (15.88-15.117) are given in Table 15.272. The color scale, translucent view of the charge-density of pyrrole comprising the concentric shells of atoms with the outer shell bridged by one or more $H_2$-type ellipsoidal MOs or joined with one or more hydrogen MOs is shown in Figure 15.46A.

Figure 15.46. (A) Color scale, translucent view of the charge-density of pyrrole showing the orbitals of the atoms at their radii, the ellipsoidal surface of each $H$ or $H_2$-type ellipsoidal MO that transitions to the corresponding outer shell of the atom(s) participating in each bond, and the hydrogen nuclei (red, not to scale). (B) Chemical structure and atom designation of pyrrole.

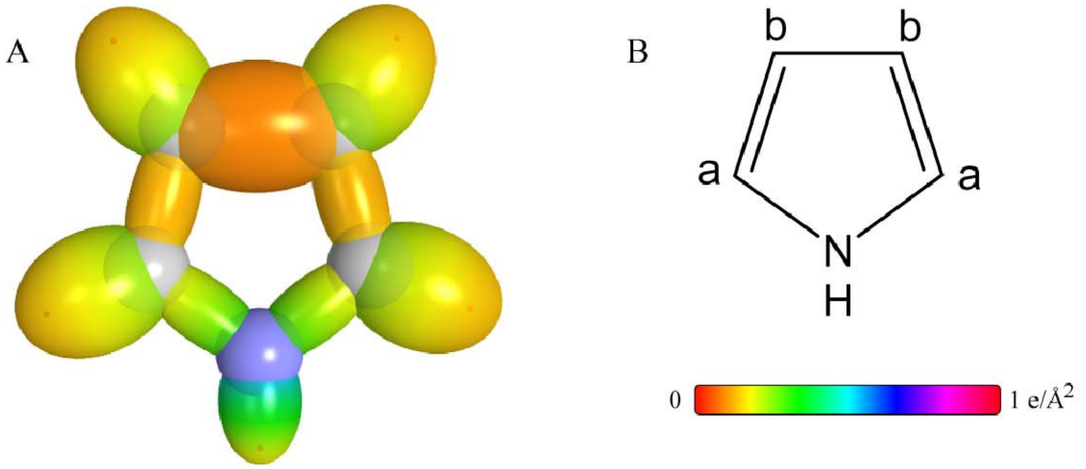


Table 15.267. The symbols of functional groups of pyrrole.

| Functional Group | Group Symbol |
|---|---|
| $C_a = C_b$ double bond | $C = C$ |
| $C_b - C_b$ | $C - C$ |
| $C_a - N - C_a$ | $C - N - C$ |
| $NH$ group | $NH$ |
| $CH$ | $CH$ |

Table 15.268. The geometrical bond parameters of pyrrole and experimental values [1].

| Parameter | $C=C$ Group | $C-C$ Group | $C-N-C$ Group | $NH$ Group | $CH$ Group |
|---|---|---|---|---|---|
| $a\ (a_0)$ | 1.45103 | 1.77965 | 1.43222 | 1.24428 | 1.53380 |
| $c'\ (a_0)$ | 1.30463 | 1.33404 | 1.29614 | 0.94134 | 1.01120 |
| Bond Length $2c'$ $(Å)$ | 1.38076 | 1.41188 | 1.37178 | 0.996270 | 1.07021 |
| Exp. Bond Length $(Å)$ | 1.382 (pyrrole) | 1.417 (pyrrole) | 1.370 (pyrrole) | 0.996 (pyrrole) | 1.076 (pyrrole) |
| $b,c\ (a_0)$ | 0.63517 | 1.17792 | 0.60931 | 0.81370 | 1.15326 |
| $e$ | 0.89910 | 0.74961 | 0.90499 | 0.75653 | 0.65928 |

Table 15.269. The MO to HO intercept geometrical bond parameters of pyrrole. $R_1$ is an alkyl group and $R, R', R''$ are $H$ or alkyl groups. $E_T$ is $E_T$ (*atom – atom,msp*$^3$*.AO*).

| Bond | Atom | $E_T$ (eV) Bond 1 | $E_T$ (eV) Bond 2 | $E_T$ (eV) Bond 3 | $E_T$ (eV) Bond 4 | Final Total Energy $C2sp^3$ (eV) | $r_{initial}$ $(a_0)$ | $r_{final}$ $(a_0)$ | $E_{Coulomb}(C2sp^3)$ (eV) Final | $E(C2sp^3)$ (eV) Final | $\theta'$ (°) | $\theta_1$ (°) | $\theta_2$ (°) | $d_1$ $(a_0)$ | $d_2$ $(a_0)$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $C-H\ (C_aH)$ | $C_a$ | -1.13380 | -0.92918 | 0 | 0 | -153.67867 | 0.91771 | 0.80561 | -16.88873 | -16.69786 | 83.35 | 96.65 | 43.94 | 1.10452 | 0.09331 |
| $C-H\ (C_bH)$ | $C_b$ | -1.13380 | -1.13380 | 0 | 0 | -153.88328 | 0.91771 | 0.79597 | -17.09334 | -16.90248 | 82.21 | 97.79 | 43.14 | 1.11914 | 0.10794 |
| $C_a=(H)C_b-C_b(H)=C_a$ | $C_b$ | -1.13380 | -1.13380 | 0 | 0 | -153.88328 | 0.91771 | 0.79597 | -17.09334 | -16.90248 | 91.57 | 88.43 | 42.49 | 1.31226 | 0.02177 |
| $C_a=C_b(H)(H)C_b=C_a$ | $C_b$ | -1.13380 | -1.13380 | 0 | 0 | -153.88328 | 0.91771 | 0.79597 | -17.09334 | -16.90248 | 136.36 | 43.64 | 59.86 | 0.72857 | 0.57606 |
| $HNC_a=C_b(H)$ | $C_a$ | -1.13380 | -0.92918 | 0 | 0 | -153.67867 | 0.91771 | 0.80561 | -16.88873 | -16.69786 | 136.75 | 43.25 | 60.35 | 0.71784 | 0.58678 |
| $C_a(H)N-C_a=C_b(H)$ | $C_a$ | -1.13380 | -0.92918 | 0 | 0 | -153.67867 | 0.91771 | 0.80561 | -16.88873 | -16.69786 | 138.54 | 41.46 | 61.09 | 0.69238 | 0.60376 |
| $C_a(H)N-C_a=C_b(H)$ | $N$ | -0.92918 | -0.92918 | 0 | 0 |  | 0.93084 | 0.81549 | -16.68411 |  | 138.92 | 41.08 | 61.59 | 0.68147 | 0.61467 |
| $N-H\ (NH)$ | $N$ | -0.92918 | -0.92918 | 0 | 0 |  | 0.93084 | 0.81549 | -16.68411 |  | 117.34 | 62.66 | 62.90 | 0.56678 | 0.37456 |

Table 15.270. The energy parameters ($eV$) of functional groups of pyrrole.

| Parameters | $C=C$ Group | $C-C$ Group | $C-N-C$ Group | $NH$ Group | $CH$ Group |
|---|---|---|---|---|---|
| $n_1$ | 2 | 1 | 2 | 1 | 1 |
| $n_2$ | 0 | 0 | 0 | 0 | 0 |
| $n_3$ | 0 | 0 | 0 | 0 | 0 |
| $C_1$ | 0.5 | 0.5 | 0.5 | 0.75 | 0.75 |
| $C_2$ | 0.85252 | 1 | 0.85252 | 0.93613 | 1 |
| $c_1$ | 1 | 1 | 1 | 0.75 | 1 |
| $c_2$ | 0.85252 | 0.85252 | 0.84665 | 0.92171 | 0.91771 |
| $c_3$ | 0 | 0 | 0 | 1 | 1 |
| $c_4$ | 4 | 2 | 4 | 1 | 1 |
| $c_5$ | 0 | 0 | 0 | 1 | 1 |
| $C_{1o}$ | 0.5 | 0.5 | 0.5 | 0.75 | 0.75 |
| $C_{2o}$ | 0.85252 | 1 | 0.85252 | 1 | 1 |
| $V_e\ (eV)$ | -104.37986 | -33.80733 | -106.58684 | -39.48897 | -39.09538 |
| $V_p\ (eV)$ | 20.85777 | 10.19898 | 20.99432 | 14.45367 | 13.45505 |
| $T\ (eV)$ | 35.96751 | 9.49831 | 37.21047 | 15.86820 | 12.74462 |
| $V_m\ (eV)$ | -17.98376 | -4.74915 | -18.60523 | -7.93410 | -6.37231 |
| $E(AO/HO)\ (eV)$ | 0 | -14.63489 | 0 | -14.53414 | -14.63489 |
| $\Delta E_{H_2MO}(AO/HO)\ (eV)$ | -2.26759 | -1.85836 | -3.71673 | 0 | -2.26758 |
| $E_T(AO/HO)\ (eV)$ | 2.26759 | -12.77653 | 3.71673 | -14.53414 | -12.36731 |
| $E_T(H_2MO)\ (eV)$ | -63.27075 | -31.63572 | -63.27056 | -31.63534 | -31.63533 |
| $E_T\left(atom-atom,msp^3.AO\right)\ (eV)$ | -2.26759 | -2.26759 | -3.71673 | 0 | 0 |
| $E_T(MO)\ (eV)$ | -65.53833 | -33.90295 | -66.98746 | -31.63537 | -31.63537 |
| $\omega\ \left(10^{15}\ rad/s\right)$ | 15.4421 | 12.3131 | 15.7474 | 48.7771 | 28.9084 |
| $E_K\ (eV)$ | 10.16428 | 8.10471 | 10.36521 | 32.10594 | 19.02803 |
| $\bar{E}_D\ (eV)$ | -0.20668 | -0.19095 | -0.21333 | -0.35462 | -0.27301 |
| $\bar{E}_{Kvib}\ (eV)$ | 0.17897<br>[6] | 0.14829<br>[48] | 0.11159<br>[12] | 0.40696<br>[24] | 0.39427<br>[59] |
| $\bar{E}_{osc}\ (eV)$ | -0.11720 | -0.11680 | -0.15754 | -0.15115 | -0.07587 |
| $E_{mag}\ (eV)$ | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 |
| $E_T(Group)\ (eV)$ | -65.77272 | -34.01976 | -67.30254 | -31.78651 | -31.71124 |
| $E_{initial}(c_4\ AO/HO)\ (eV)$ | -14.63489 | -14.63489 | -14.63489 | -14.53414 | -14.63489 |
| $E_{initial}(c_5\ AO/HO)\ (eV)$ | 0 | 0 | 0 | -13.59844 | -13.59844 |
| $E_D(Group)\ (eV)$ | 7.23317 | 4.74998 | 8.76298 | 3.51208 | 3.32988 |

Table 15.271. The total bond energies of pyrrole calculated using the functional group composition and the energies of Table 15.270 compared to the experimental values [3].

| Formula | Name | $C=C$ | $C-C$ | $C-N-C$ | $NH$ | $CH$ | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|---|---|---|---|---|
| $C_4H_5N$ | Pyrrole | 2 | 1 | 1 | 1 | 4 | 44.81090 | 44.785 | -0.00057 |

Table 15.272. The bond angle parameters of pyrrole and experimental values [1]. In the calculation of $\theta_v$, the parameters from the preceding angle were used. $E_T$ is $E_T\,(atom-atom,msp^3.AO)$.

| Atoms of Angle | 2c' Bond 1 $(a_0)$ | 2c' Bond 2 $(a_0)$ | 2c' Terminal Atoms $(a_0)$ | $E_{Coulombic}$ Atom 1 | Atom 1 Hybridization Designation (Table 15.3.B) | $E_{Coulombic}$ Atom 2 | Atom 2 Hybridization Designation (Table 15.3.B) | $c_2$ Atom 1 | $c_2$ Atom 2 | $C_1$ | $C_2$ | $c_1$ | $c_2'$ | $E_T$ (eV) | $\theta_v$ (°) | $\theta_1$ (°) | $\theta_2$ (°) | Cal. $\theta$ (°) | Exp. $\theta$ (°) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $\angle HC_aN$ | 2.02241 | 2.59228 | 4.0166 | -14.82575 | 1 | -14.53414 | N | 0.91771 | 0.92171 Eq. (15.170)) | 0.75 | 1 | 0.75 | 1.00435 | 0 | | | | 120.51 | 121.5 (pyrrole) |
| $\angle C_bC_aH_a$ | | | | | | | | | | | | | | | | 120.51 | 107.52 | 131.97 | |
| $\angle HNC_a$ | 1.88268 | 2.59228 | 3.8987 | -14.53414 | N | -16.49325 | 6 | 0.84665 (Eq. (15.171)) | 0.82493 (Eq. (15.73)) | 0.75 | 1 | 0.75 | 0.97435 | 0 | | | | 120.37 | |
| $\angle H_bC_bC_b$ | 2.02241 | 2.66807 | 4.2111 | -16.88873 $C_b$ | 20 | -15.95954 $C_b$ | 6 | 0.80561 | 0.85252 | 0.75 | 1 | 0.75 | 1.05822 | 0 | | | | 127.20 | 127.1 (pyrrole) |
| $\angle H_aC_aC_b$ | 2.02241 | 2.60925 | 4.2111 | -16.88873 $C_a$ | 20 | -15.95954 $C_b$ | 6 | 0.80561 | 0.85252 | 0.75 | 1 | 0.75 | 1.05822 | 0 | | | | 130.36 | |
| $\angle H_bC_bC_a$ | 2.02241 | 2.60925 | 4.1312 | -17.09334 $C_b$ | 24 | -16.47951 $C_a$ | 14 | 0.79597 | 0.82562 | 0.75 | 1 | 0.75 | 1.03725 | 0 | | | | 125.76 | |
| $\angle C_bC_bH_b$ | | | | | | | | | | | | | | | | 125.76 | 107.01 | 127.23 | 127.1 (pyrrole) |
| $\angle NC_aC_b$ | 2.59228 | 2.60925 | 4.1952 | -14.53414 | N | -17.09334 $C_b$ | 24 | 0.84665 (Eq. (15.171)) | 0.79597 | 1 | 1 | 1 | 0.82131 | -1.44915 | | | | 107.52 | 107.7 (pyrrole) |
| $\angle C_aNC_a$ | 2.59228 | 2.59228 | 4.2426 | -17.81791 | 35 | -17.81791 | 35 | 0.76360 | 0.76360 | 1 | 1 | 1 | 0.76360 | -1.85836 | | | | 109.83 | 109.8 (pyrrole) |
| $\angle C_aC_bC_b$ | 2.60925 | 2.66807 | 4.2426 | -17.81791 | 35 | -18.02252 | 40 | 0.76360 | 0.75493 | 1 | 1 | 1 | 0.75927 | -1.85836 | | | | 107.01 | 107.4 (pyrrole) |

## FURAN

Furan having the formula $C_4H_4O$ comprises the conjugated alkene 1,3-butadiene that forms a cyclic structure by terminal-atom bonding to an oxygen atom. The two symmetrical carbon-to-oxygen bonds comprise the $C-O-C$ functional group. The 1,3-butadiene moiety comprises $C-C$, $C=C$, and $CH$ functional groups. The $CH$, $C-C$, and $C=C$ groups are equivalent to the corresponding groups of pyrrole given in the corresponding section.

The $C-O-C$ functional group of furan is solved in a similar manner as that of the $C-N-C$ group of pyrrole. The solution of the $C-O-C$ functional group comprises the hybridization of the $2s$ and $2p$ AOs of each $C$ to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between two $C2sp^3$ HOs and the oxygen atom to form a MO permits each participating hybridized orbital to decrease in radius and energy. Thus, the $C-O-C$-bond MO comprising a linear combination of two single bonds is solved in the same manner as a double bond with $n_1=2$ in Eqs. (15.51) and (15.61). The hybridization factor $c_2\left(arylC2sp^3HO\ to\ O\right)=0.79329$ (Eq. (15.169)) matches the double-bond character of the $C2sp^3$ HOs to the $O$ atom, and $C_2$ and $C_{2o}$ in Eqs. (15.51) and (15.61) become that of benzene given by Eq. (15.162), $C_2\left(benzeneC2sp^3HO\right)=0.85252$. Furthermore, $E_T\left(atom-atom,msp^3.AO\right)$ in Eq. (15.61) is $-0.92918\ eV$ (Eq. (14.513)) per atom corresponding to $-3.71673\ eV$ in total.

The symbols of the functional groups of furan are given in Table 15.273. The structure of furan is shown in Figure 15.47B. The geometrical (Eqs. (15.1-15.5) and (15.51)), intercept (Eqs. (15.80-15.87)), and energy (Eqs. (15.6-15.11) and (15.17-15.65)) parameters of furan are given in Tables 15.274, 15.275, and 15.276, respectively. The total energy of furan given in Table 15.277 was calculated as the sum over the integer multiple of each $E_D\left(Group\right)$ of Table 15.276 corresponding to functional-group composition of the molecule. The bond angle parameters of furan determined using Eqs. (15.88-15.117) are given in Table 15.278. The color scale, translucent view of the charge-density of furan comprising the concentric shells of atoms with the outer shell bridged by one or more $H_2$-type ellipsoidal MOs or joined with one or more hydrogen MOs is shown in Figure 15.47A.

Figure 15.47. (A) Color scale, translucent view of the charge-density of furan showing the orbitals of the atoms at their radii, the ellipsoidal surface of each $H$ or $H_2$-type ellipsoidal MO that transitions to the corresponding outer shell of the atom(s) participating in each bond, and the hydrogen nuclei (red, not to scale). (B) Chemical structure and atom designation of furan.

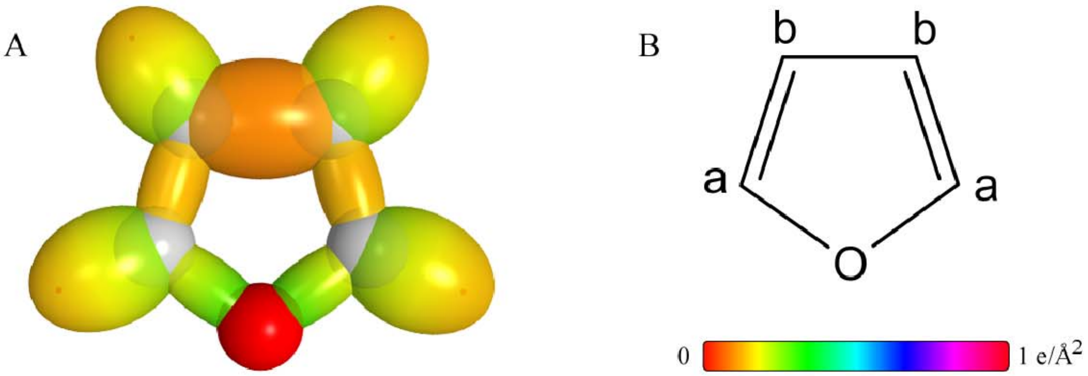


Table 15.273. The symbols of functional groups of furan.

| Functional Group | Group Symbol |
|---|---|
| $C_a=C_b$ double bond | $C=C$ |
| $C_b-C_b$ | $C-C$ |
| $C_a-O-C_a$ | $C-O-C$ |
| $CH$ | $CH$ |

Table 15.274. The geometrical bond parameters of furan and experimental values [1].

| Parameter | $C=C$ Group | $C-C$ Group | $C-O-C$ Group | $CH$ Group |
|---|---|---|---|---|
| $a\left(a_0\right)$ | 1.45103 | 1.77965 | 1.41546 | 1.53380 |
| $c'\left(a_0\right)$ | 1.30463 | 1.33404 | 1.28854 | 1.01120 |
| Bond Length $2c'$ $\left(Å\right)$ | 1.38076 | 1.41188 | 1.36373 | 1.07021 |
| Exp. Bond Length $\left(Å\right)$ | 1.361 (furan) | 1.431 (furan) | 1.362 (furan) | 1.075 (furan) |
| $b,c\left(a_0\right)$ | 0.63517 | 1.17792 | 0.58583 | 1.15326 |
| $e$ | 0.89910 | 0.74961 | 0.91033 | 0.65928 |

Table 15.275. The MO to HO intercept geometrical bond parameters of furan. $R_1$ is an alkyl group and $R, R', R''$ are $H$ or alkyl groups. $E_T$ is $E_T$ $(atom-atom, msp^3.AO)$.

| Bond | Atom | $E_T$ (eV) Bond 1 | $E_T$ (eV) Bond 2 | $E_T$ (eV) Bond 3 | $E_T$ (eV) Bond 4 | Final Total Energy $C2sp^3$ (eV) | $r_{initial}$ $\left(a_0\right)$ | $r_{final}$ $\left(a_0\right)$ | $E_{Coulomb}\left(C2sp^3\right)$ (eV) Final | $E\left(C2sp^3\right)$ (eV) Final | $\theta'$ (°) | $\theta_1$ (°) | $\theta_2$ (°) | $d_1$ $\left(a_0\right)$ | $d_2$ $\left(a_0\right)$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $C-H\ \left(C_aH\right)$ | $C_a$ | -1.13380 | -0.92918 | 0 | 0 | -153.67867 | 0.91771 | 0.80561 | -16.88873 | -16.69786 | 83.35 | 96.65 | 43.94 | 1.10452 | 0.09331 |
| $C-H\ \left(C_bH\right)$ | $C_b$ | -1.13380 | -1.13380 | 0 | 0 | -153.88328 | 0.91771 | 0.79597 | -17.09334 | -16.90248 | 82.21 | 97.79 | 43.14 | 1.11914 | 0.10794 |
| $C_a=\left(H\right)C_b-C_b\left(H\right)=C_a$ | $C_b$ | -1.13380 | -1.13380 | 0 | 0 | -153.88328 | 0.91771 | 0.79597 | -17.09334 | -16.90248 | 91.57 | 88.43 | 42.49 | 1.31226 | 0.02177 |
| $C_a=C_b\left(H\right)\left(H\right)C_b=C_a$ | $C_b$ | -1.13380 | -1.13380 | 0 | 0 | -153.88328 | 0.91771 | 0.79597 | -17.09334 | -16.90248 | 136.36 | 43.64 | 59.86 | 0.72857 | 0.57606 |
| $OC_a=C_b\left(H\right)$ | $C_a$ | -1.13380 | -0.92918 | 0 | 0 | -153.67867 | 0.91771 | 0.80561 | -16.88873 | -16.69786 | 136.75 | 43.25 | 60.35 | 0.71784 | 0.58678 |
| $C_aO-C_a=C_b\left(H\right)$ | $C_a$ | -1.13380 | -0.92918 | 0 | 0 | -153.67867 | 0.91771 | 0.80561 | -16.88873 | -16.69786 | 140.16 | 39.84 | 61.75 | 0.66992 | 0.61862 |
| $C_aO-C_a=C_b\left(H\right)$ | $O$ | -0.92918 | -0.92918 | 0 | 0 |  | 1.00000 | 0.81549 | -16.68411 |  | 140.52 | 39.48 | 62.25 | 0.65906 | 0.62947 |

Table 15.276. The energy parameters ($eV$) of functional groups of furan.

| Parameters | $C=C$ Group | $C-C$ Group | $C-O-C$ Group | $CH$ Group |
|---|---|---|---|---|
| $n_1$ | 2 | 1 | 2 | 1 |
| $n_2$ | 0 | 0 | 0 | 0 |
| $n_3$ | 0 | 0 | 0 | 0 |
| $C_1$ | 0.5 | 0.5 | 0.5 | 0.75 |
| $C_2$ | 0.85252 | 1 | 0.85252 | 1 |
| $c_1$ | 1 | 1 | 1 | 1 |
| $c_2$ | 0.85252 | 0.85252 | 0.79329 | 0.91771 |
| $c_3$ | 0 | 0 | 0 | 1 |
| $c_4$ | 4 | 2 | 4 | 1 |
| $c_5$ | 0 | 0 | 0 | 1 |
| $C_{1o}$ | 0.5 | 0.5 | 0.5 | 0.75 |
| $C_{2o}$ | 0.85252 | 1 | 0.85252 | 1 |
| $V_e\ (eV)$ | -104.37986 | -33.80733 | -102.49036 | -39.09538 |
| $V_p\ (eV)$ | 20.85777 | 10.19898 | 21.11822 | 13.45505 |
| $T\ (eV)$ | 35.96751 | 9.49831 | 36.20391 | 12.74462 |
| $V_m\ (eV)$ | -17.98376 | -4.74915 | -18.10196 | -6.37231 |
| $E(AO/HO)\ (eV)$ | 0 | -14.63489 | 0 | -14.63489 |
| $\Delta E_{H_2MO}(AO/HO)\ (eV)$ | -2.26759 | -1.85836 | 0 | -2.26758 |
| $E_T(AO/HO)\ (eV)$ | 2.26759 | -12.77653 | 0 | -12.36731 |
| $E_T(H_2MO)\ (eV)$ | -63.27075 | -31.63572 | -63.27019 | -31.63533 |
| $E_T\left(atom-atom, msp^3.AO\right)\ (eV)$ | -2.26759 | -2.26759 | -3.71673 | 0 |
| $E_T(MO)\ (eV)$ | -65.53833 | -33.90295 | -66.98746 | -31.63537 |
| $\omega\ \left(10^{15}\ rad/s\right)$ | 15.4421 | 12.3131 | 58.0664 | 28.9084 |
| $E_K\ (eV)$ | 10.16428 | 8.10471 | 38.22034 | 19.02803 |
| $\bar{E}_D\ (eV)$ | -0.20668 | -0.19095 | -0.40965 | -0.27301 |
| $\bar{E}_{Kvib}\ (eV)$ | 0.17897 [6] | 0.14829 [48] | 0.12523 [60 | 0.39427 [59] |
| $\bar{E}_{osc}\ (eV)$ | -0.11720 | -0.11680 | -0.34704 | -0.07587 |
| $E_{mag}\ (eV)$ | 0.14803 | 0.14803 | 0.14803 | 0.14803 |
| $E_T(Group)\ (eV)$ | -65.77272 | -34.01976 | -67.68154 | -31.71124 |
| $E_{initial}(c_4\ AO/HO)\ (eV)$ | -14.63489 | -14.63489 | -14.63489 | -14.63489 |
| $E_{initial}(c_5\ AO/HO)\ (eV)$ | 0 | 0 | 0 | -13.59844 |
| $E_D(Group)\ (eV)$ | 7.23317 | 4.74998 | 9.14198 | 3.32988 |

Table 15.277. The total bond energies of furan calculated using the functional group composition and the energies of Table 15.276 compared to the experimental values [3].

| Formula | Name | $C=C$ | $C-C$ | $C-O-C$ | $CH$ | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|---|---|---|---|
| $C_4H_4O$ | Furan | 2 | 1 | 1 | 4 | 41.67782 | 41.692 | 0.00033 |

Table 15.278. The bond angle parameters of furan and experimental values [1]. In the calculation of $\theta_v$, the parameters from the preceding angle were used. $E_T$ is $T$ $(atom-atom,msp^3.AO)$.

| Atoms of Angle | $2c'$ Bond 1 $(a_0)$ | $2c'$ Bond 2 $(a_0)$ | $2c'$ Terminal Atoms $(a_0)$ | $E_{Coulombic}$ Atom 1 | Atom 1 Hybridization Designation (Table 15.3.B) | $E_{Coulombic}$ Atom 2 | Atom 2 Hybridization Designation (Table 15.3.B) | $c_2$ Atom 1 | $c_2$ Atom 2 | $C_1$ | $C_2$ | $c_1$ | $c_2'$ | $E_T$ (eV) | $\theta_v$ (°) | $\theta_1$ (°) | $\theta_2$ (°) | Cal. $\theta$ (°) | Exp. $\theta$ (°) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $\angle HC_aO$ | 2.02241 | 2.57707 | 3.9328 | -16.88873 | 20 | -13.61806 | O | 0.80561 | 0.79329 Eq. (15.169)) | 0.75 | 1 | 0.75 | 0.98470 | 0 | | | | 117.02 | 115.9 (furan) |
| $\angle C_bC_aH_a$ | | | | | | | | | | | | | | | | 117.02 | 110.69 | 132.29 | |
| $\angle H_bC_bC_b$ | 2.02241 | 2.66807 | 4.2269 | -16.88873 $C_b$ | 20 | -15.95954 $C_b$ | 6 | 0.80561 | 0.85252 | 0.75 | 1 | 0.75 | 1.05822 | 0 | | | | 128.09 | 128.0 (furan) |
| $\angle H_aC_aC_b$ | 2.02241 | 2.60925 | 4.2269 | -16.88873 $C_a$ | 20 | -15.95954 $C_b$ | 6 | 0.80561 | 0.85252 | 0.75 | 1 | 0.75 | 1.05822 | 0 | | | | 131.32 | |
| $\angle H_bC_bC_a$ | 2.02241 | 2.60925 | 4.1312 | -17.09334 $C_b$ | 24 | -16.47951 $C_a$ | 14 | 0.79597 | 0.82562 | 0.75 | 1 | 0.75 | 1.03725 | 0 | | | | 125.76 | |
| $\angle C_bC_bH_b$ | | | | | | | | | | | | | | | | 125.76 | 107.01 | 127.23 | 128.0 (furan) |
| $\angle C_bC_aO$ | 2.60925 | 2.57707 | 4.2661 | -17.09334 $C_b$ | 24 | -13.61806 | O | 0.79597 | 0.79329 Eq. (15.169)) | 1 | 1 | 1 | 0.79463 | -1.65376 | | | | 110.69 | 110.7 (furan) |
| $\angle C_aOC_a$ | 2.57707 | 2.57707 | 4.1231 | -18.22713 | 41 | -18.22713 | 41 | 0.74646 | 0.74646 | 1 | 1 | 1 | 0.74646 | -1.85836 | | | | 106.25 | 106.6 (furan) |
| $\angle C_aC_bC_b$ | 2.60925 | 2.66807 | 4.2426 | -17.81791 | 35 | -18.02252 | 40 | 0.76360 | 0.75493 | 1 | 1 | 1 | 0.75927 | -1.85836 | | | | 107.01 | 106.1 (furan) |

## THIOPHENE

Thiophene having the formula $C_4H_4S$ comprises the conjugated alkene 1,3-butadiene that forms a cyclic structure by terminal-atom bonding to an oxygen atom. The two symmetrical carbon-to-sulfur bonds comprise the $C-S-C$ functional group. The 1,3-butadiene moiety comprises $C-C$, $C=C$, and $CH$ functional groups. The $CH$, $C-C$, and $C=C$ groups are equivalent to the corresponding groups of pyrrole and furan given in the corresponding sections.

The $C-S-C$ functional group of thiophene is solved in a similar manner as that of the $C-N-C$ group of pyrrole and the $C-O-C$ group of furan. The solution of the $C-S-C$ functional group comprises the hybridization of the $2s$ and $2p$ AOs of each $C$ to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between two $C2sp^3$ HOs and the sulfur atom to form a MO permits each participating hybridized orbital to decrease in radius and energy. Thus, the $C-S-C$-bond MO comprising a linear combination of two single bonds is solved in the same manner as a double bond with $n_1 = 2$ in Eqs. (15.51) and (15.61).

In thiophene, the energy of sulfur is less than the Coulombic energy between the electron and proton of $H$ given by Eq. (1.264). Thus, $c_2$ in Eq. (15.61) is $c_2\left(benzeneC2sp^3HO\right) = 0.85252$ to match the double-bond character of the $C2sp^3$ HOs, and the energy matching condition is further determined by the $C_2$ parameter. Using the energy of $S$, $E(S) = -10.36001\ eV$ in Eq. (15.77) and the $C2sp^3$ HO energy of $E\left(C,2sp^3\right) = -15.76868\ eV$ (Eq. (15.18)) corresponding to $s=2$ in Eqs. (15.18-15.20), the hybridization factor $C_2$ of Eq. (15.61) for the $C-S-C$-bond MO is:

$$C_2\left(S3p\ to\ \text{aryl-type}\ C2sp^3HO\right) = \frac{E(S,3p)}{E\left(C,2sp^3\right)} = \frac{-10.36001\ eV}{-15.76868\ eV} = 0.65700 \tag{15.172}$$

$C_{1o}$ is also given by Eq. (15.172). Furthermore, $\Delta E_{H_2MO}\left(AO/HO\right)$ of the $C-S-C$-bond MO in Eq. (15.51) and $E_T\left(atom-atom, msp^3.AO\right)$ in Eq. (15.61) are both $-0.72457\ eV$ per atom corresponding to $-2.89830\ eV$ in total. The energy contribution equivalent to that of a methyl group (Eq. (14.151)) and that of the $C-S$-bond MO of thiols given in the corresponding section matches the energy of the sulfur atom to the $C2sp^3$ HOs.

The symbols of the functional groups of thiophene are given in Table 15.279. The structure of thiophene is shown in Figure 15.48B. The geometrical (Eqs. (15.1-15.5) and (15.51)), intercept (Eqs. (15.80-15.87)), and energy (Eqs. (15.6-15.11) and (15.17-15.65)) parameters of thiophene are given in Tables 15.280, 15.281, and 15.282, respectively. The total energy of thiophene given in Table 15.283 was calculated as the sum over the integer multiple of each $E_{D}(_{Group})$ of Table 15.282 corresponding to functional-group composition of the molecule. The bond angle parameters of thiophene determined using Eqs. (15.88-15.117) are given in Table 15.284. The color scale, translucent view of the charge-density of thiophene comprising the concentric shells of atoms with the outer shell bridged by one or more $H_2$-type ellipsoidal MOs or joined with one or more hydrogen MOs is shown in Figure 15.48A.

Figure 15.48. (A) Color scale, translucent view of the charge-density of thiophene showing the orbitals of the atoms at their radii, the ellipsoidal surface of each $H$ or $H_2$-type ellipsoidal MO that transitions to the corresponding outer shell of the atom(s) participating in each bond, and the hydrogen nuclei (red, not to scale). (B) Chemical structure and atom designation of thiophene.

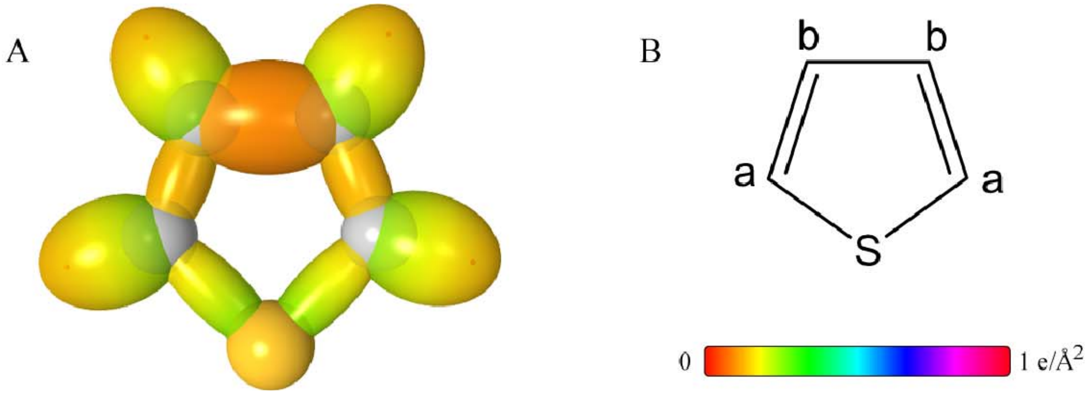


Table 15.279. The symbols of functional groups of thiophene.

| Functional Group | Group Symbol |
|---|---|
| $C_a = C_b$ double bond | $C = C$ |
| $C_b - C_b$ | $C - C$ |
| $C_a - S - C_a$ | $C - S - C$ |
| $CH$ | $CH$ |

Table 15.280. The geometrical bond parameters of thiophene and experimental values [1].

| Parameter | $C = C$ Group | $C - C$ Group | $C - S - C$ Group | $CH$ Group |
|---|---|---|---|---|
| $a$ $(a_0)$ | 1.45103 | 1.77965 | 1.74058 | 1.53380 |
| $c'$ $(a_0)$ | 1.30463 | 1.33404 | 1.62766 | 1.01120 |
| Bond Length $2c'$ $(\mathring{A})$ | 1.38076 | 1.41188 | 1.72264 | 1.07021 |
| Exp. Bond Length $(\mathring{A})$ | 1.370<br>(thiophene) | 1.423<br>(thiophene) | 1.714<br>(thiophene) | 1.078<br>(thiophene) |
| $b,c$ $(a_0)$ | 0.63517 | 1.17792 | 0.61671 | 1.15326 |
| $e$ | 0.89910 | 0.74961 | 0.93513 | 0.65928 |

Table 15.281. The MO to HO intercept geometrical bond parameters of thiophene. $R_1$ is an alkyl group and $R, R', R''$ are $H$ or alkyl groups. $E_T$ is $E_T$ ($atom - atom, msp^3.AO$).

| Bond | Atom | $E_T$ (eV) Bond 1 | $E_T$ (eV) Bond 2 | $E_T$ (eV) Bond 3 | $E_T$ (eV) Bond 4 | Final Total Energy $C2sp^3$ (eV) | $r_{initial}$ $(a_0)$ | $r_{final}$ $(a_0)$ | $E_{Coulomb}(C2sp^3)$ (eV) Final | $E(C2sp^3)$ (eV) Final | $\theta'$ (°) | $\theta_1$ (°) | $\theta_2$ (°) | $d_1$ $(a_0)$ | $d_2$ $(a_0)$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $C-H\ (C_aH)$ | $C_a$ | -1.13380 | -0.72457 | 0 | 0 | -153.47406 | 0.91771 | 0.81549 | -16.68412 | -16.49326 | 84.49 | 95.51 | 44.74 | 1.08953 | 0.07833 |
| $C-H\ (C_bH)$ | $C_b$ | -1.13380 | -1.13380 | 0 | 0 | -153.88328 | 0.91771 | 0.79597 | -17.09334 | -16.90248 | 82.21 | 97.79 | 43.14 | 1.11914 | 0.10794 |
| $C_a=(H)C_b-C_b(H)=C_a$ | $C_b$ | -1.13380 | -1.13380 | 0 | 0 | -153.88328 | 0.91771 | 0.79597 | -17.09334 | -16.90248 | 91.57 | 88.43 | 42.49 | 1.31226 | 0.02177 |
| $C_a=C_b(H)(H)C_b=C_a$ | $C_b$ | -1.13380 | -1.13380 | 0 | 0 | -153.88328 | 0.91771 | 0.79597 | -17.09334 | -16.90248 | 136.36 | 43.64 | 59.86 | 0.72857 | 0.57606 |
| $SC_a=C_b(H)$ | $C_a$ | -1.13380 | -0.72457 | 0 | 0 | -153.47406 | 0.91771 | 0.81549 | -16.68412 | -16.49326 | 137.14 | 42.86 | 60.85 | 0.70685 | 0.59777 |
| $C_aS-C_a=C_b(H)$ | $C_a$ | -1.13380 | -0.72457 | 0 | 0 | -153.47406 | 0.91771 | 0.81549 | -16.68412 | -16.49326 | 141.52 | 38.48 | 55.36 | 0.98926 | 0.63840 |
| $C_aS-C_a=C_b(H)$ | $S$ | -0.72457 | -0.72457 | 0 | 0 |  | 1.3201 | 0.83600 | -16.27490 |  | 142.17 | 37.83 | 56.24 | 0.96733 | 0.66033 |

Table 15.282. The energy parameters ($eV$) of functional groups of thiophene.

| Parameters | $C=C$ Group | $C-C$ Group | $C-S-C$ Group | $CH$ Group |
|---|---|---|---|---|
| $n_1$ | 2 | 1 | 2 | 1 |
| $n_2$ | 0 | 0 | 0 | 0 |
| $n_3$ | 0 | 0 | 0 | 0 |
| $C_1$ | 0.5 | 0.5 | 0.5 | 0.75 |
| $C_2$ | 0.85252 | 1 | 0.65700 | 1 |
| $c_1$ | 1 | 1 | 1 | 1 |
| $c_2$ | 0.85252 | 0.85252 | 0.85252 | 0.91771 |
| $c_3$ | 0 | 0 | 0 | 1 |
| $c_4$ | 4 | 2 | 4 | 1 |
| $c_5$ | 0 | 0 | 0 | 1 |
| $C_{1o}$ | 0.5 | 0.5 | 0.5 | 0.75 |
| $C_{2o}$ | 0.85252 | 1 | 0.65700 | 1 |
| $V_e\ (eV)$ | -104.37986 | -33.80733 | -96.78916 | -39.09538 |
| $V_p\ (eV)$ | 20.85777 | 10.19898 | 16.71820 | 13.45505 |
| $T\ (eV)$ | 35.96751 | 9.49831 | 27.80371 | 12.74462 |
| $V_m\ (eV)$ | -17.98376 | -4.74915 | -13.90186 | -6.37231 |
| $E(AO/HO)\ (eV)$ | 0 | -14.63489 | 0 | -14.63489 |
| $\Delta E_{H_2MO}(AO/HO)\ (eV)$ | -2.26759 | -1.85836 | -2.89830 | -2.26758 |
| $E_T(AO/HO)\ (eV)$ | 2.26759 | -12.77653 | 2.89830 | -12.36731 |
| $E_T(H_2MO)\ (eV)$ | -63.27075 | -31.63572 | -63.27080 | -31.63533 |
| $E_T\left(atom-atom,msp^3.AO\right)\ (eV)$ | -2.26759 | -2.26759 | -2.89830 | 0 |
| $E_T(MO)\ (eV)$ | -65.53833 | -33.90295 | -66.16903 | -31.63537 |
| $\omega\ \left(10^{15}\ rad/s\right)$ | 15.4421 | 12.3131 | 10.3184 | 28.9084 |
| $E_K\ (eV)$ | 10.16428 | 8.10471 | 6.79173 | 19.02803 |
| $\bar{E}_D\ (eV)$ | -0.20668 | -0.19095 | -0.17058 | -0.27301 |
| $\bar{E}_{Kvib}\ (eV)$ | 0.17897<br>[6] | 0.14829<br>[48] | 0.08146<br>[41] | 0.39427<br>[59] |
| $\bar{E}_{osc}\ (eV)$ | -0.11720 | -0.11680 | -0.12985 | -0.07587 |
| $E_{mag}\ (eV)$ | 0.14803 | 0.14803 | 0.14803 | 0.14803 |
| $E_T(Group)\ (eV)$ | -65.77272 | -34.01976 | -66.42873 | -31.71124 |
| $E_{initial}(c_4\ AO/HO)\ (eV)$ | -14.63489 | -14.63489 | -14.63489 | -14.63489 |
| $E_{initial}(c_5\ AO/HO)\ (eV)$ | 0 | 0 | 0 | -13.59844 |
| $E_D(Group)\ (eV)$ | 7.23317 | 4.74998 | 7.88917 | 3.32988 |

Table 15.283. The total bond energies of thiophene calculated using the functional group composition and the energies of Table 15.282 compared to the experimental values [3].

| Formula | Name | $C=C$ | $C-C$ | $C-S-C$ | $CH$ | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|---|---|---|---|
| $C_4H_4S$ | Thiophene | 2 | 1 | 1 | 4 | 40.42501 | 40.430 | 0.00013 |

Table 15.284. The bond angle parameters of thiophene and experimental values [1]. In the calculation of $\theta_v$, the parameters from the preceding angle were used. $E_T$ is $E_T$ $(atom-atom,msp^3.AO)$.

| Atoms of Angle | $2c'$ Bond 1 $(a_0)$ | $2c'$ Bond 2 $(a_0)$ | $2c'$ Terminal Atoms $(a_0)$ | $E_{Coulombic}$ Atom 1 | Atom 1 Hybridization Designation (Table 15.3.B) | $E_{Coulombic}$ Atom 2 | Atom 2 Hybridization Designation (Table 15.3.B) | $c_2$ Atom 1 | $c_2$ Atom 2 | $C_1$ | $C_2$ | $c_1$ | $c_2'$ | $E_T$ (eV) | $\theta_v$ (°) | $\theta_1$ (°) | $\theta_2$ (°) | Cal. $\theta$ (°) | Exp. $\theta$ (°) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $\angle HC_aS$ | 2.02241 | 3.25533 | 4.6030 | -15.55033 | 3 | -10.36001 | S | 0.87495 Eq. (15.74)) | 0.76144 (Eq. 15.145)) | 0.75 | 0.76144 (Eq. 15.145)) | 0.75 | 0.87495 | 0 | | | | 119.58 | 119.9 (thiophene) |
| $\angle C_bC_aH_a$ | | | | | | | | | | | | | | | | 119.58 | 115.84 | 124.58 | |
| $\angle H_bC_bC_b$ | 2.02241 | 2.66807 | 4.1633 | -16.68412 $C_b$ | 18 | -15.95954 $C_b$ | 6 | 0.81549 | 0.85252 | 0.75 | 1 | 0.75 | 1.04540 | 0 | | | | 124.58 | 124.3 (thiophene) |
| $\angle H_aC_aC_b$ | 2.02241 | 2.60925 | 4.1633 | -16.68412 $C_a$ | 18 | -15.95954 $C_b$ | 6 | 0.81549 | 0.85252 | 0.75 | 1 | 0.75 | 1.04540 | 0 | | | | 127.57 | |
| $\angle H_bC_bC_a$ | 2.02241 | 2.60925 | 4.0825 | -17.09334 $C_b$ | 24 | -16.68412 $C_a$ | 18 | 0.79597 | 0.81549 | 0.75 | 1 | 0.75 | 1.02453 | 0 | | | | 123.13 | |
| $\angle C_bC_bH_b$ | | | | | | | | | | | | | | | | 123.13 | 113.60 | 123.27 | 124.3 (thiophene) |
| $\angle C_bC_aS$ | 2.60925 | 3.25533 | 4.9809 | -17.81791 $C_b$ | 36 | -10.36001 | S | 0.76360 | 0.65700 Eq. (15.172)) | 1 | 0.65700 Eq. (15.172)) | 1 | 0.71030 | -0.72457 | | | | 115.84 | 115.5 (thiophene) |
| $\angle C_aSC_a$ | 3.25533 | 3.25533 | 4.7958 | -16.68412 | 18 | -16.68412 | 18 | 0.81549 | 0.81549 | 1 | 1 | 1 | 0.81549 | -1.85836 | | | | 94.89 | 92.2 (thiophene) |
| $\angle C_aC_bC_b$ | 2.60925 | 2.66807 | 4.4159 | -16.88873 | 20 | -18.02252 | 40 | 0.80561 | 0.75493 | 1 | 1 | 1 | 0.78027 | -1.85836 | | | | 113.60 | 112.5 (thiophene) |

## IMIDAZOLE

Imidazole having the formula $C_3H_4N_2$ comprises a conjugated system that is equivalent to pyrrole with one of the conjugated $CH$ groups replaced by a nitrogen atom. The $CH$, $NH$, and $C=C$ groups are equivalent to the corresponding groups of pyrrole, furan, and thiophene where present. In addition, the nitrogen substitution creates a $C-N=C$ moiety comprising $C-N$ and $N=C$ functional groups. The $C-N$ bonding is the same as that of a tertiary amine except that the hybridization term $c_2$ in Eqs. (15.51) and (15.61) is that of the amino group of aniline, $c_2\left(arylC2sp^3HO\ to\ N\right)=0.84665$ (Eq. (15.171)). The hybridization factor provides double-bond character to match the group to the other orbitals of the molecule. $\Delta E_{H_2MO}\left(AO/HO\right)$ in Eq. (15.51) and $E_T\left(atom-atom,msp^3.AO\right)$ in Eq. (15.61) are both $-0.92918\ eV$ (Eq. (14.513)). This matches the energy of the group to that of the contiguous $N=C$ group wherein $\Delta E_{H_2MO}\left(AO/HO\right)$ in Eq. (15.51) and $E_T\left(atom-atom,msp^3.AO\right)$ in Eq. (15.61) are both $-0.92918\ eV$ (Eq. (14.513)) per atom of the double bond with aromatic character as in the case of the prior heterocyclic compounds. As in the prior cases of pyrrole, furan, and thiophene, $n_1=2$ and $C_2$ and $C_{2o}$ are the same as $C_2\left(benzeneC2sp^3HO\right)=0.85252$ (Eq. (15.162)) in Eqs. (15.51) and (15.61). To match the energy of the nitrogen to the $C2sp^3$ HO, $c_2$ of the $N=C$-bond MO is also given by Eq. (15.171). These parameters also provide an energy match to the $C-N-C$ group.

As in the case of pyrrole, the $C-N-C$-bond MO comprising a linear combination of two single bonds is solved in the same manner as a double bond with $n_1=2$ in Eqs. (15.51) and (15.61). The hybridization factor $c_2\left(arylC2sp^3HO\ to\ N\right)=0.84665$ (Eq. (15.171)) matches the double-bond character of the $C2sp^3$ HOs to the $N$ atom of the $NH$ group, and $C_2$ and $C_{2o}$ in Eqs. (15.51) and (15.61) become that of benzene given by Eq. (15.162), $C_2\left(benzeneC2sp^3HO\right)=0.85252$. Furthermore, $\Delta E_{H_2MO}\left(AO/HO\right)$ in Eq. (15.51) and $E_T\left(atom-atom,msp^3.AO\right)$ in Eq. (15.61) are both $-0.92918\ eV$ (Eq. (14.513)) per atom corresponding to $-3.71673\ eV$ in total.

The symbols of the functional groups of imidazole are given in Table 15.285. The structure of imidazole is shown in Figure 15.49B. The geometrical (Eqs. (15.1-15.5) and (15.51)), intercept (Eqs. (15.80-15.87)), and energy (Eqs. (15.6-15.11) and (15.17-15.65)) parameters of imidazole are given in Tables 15.286, 15.287, and 15.288, respectively. The total energy of imidazole given in Table 15.289 was calculated as the sum over the integer multiple of each $E_D\left(Group\right)$ of Table 15.288 corresponding to functional-group composition of the molecule. The bond angle parameters of imidazole determined using Eqs. (15.88-15.117) are given in Table 15.290. The color scale, translucent view of the charge-density of imidazole, comprising the concentric shells of atoms with the outer shell bridged by one or more $H_2$-type ellipsoidal MOs or joined with one or more hydrogen MOs is shown in Figure 15.49A.

Figure 15.49. (A) Color scale, translucent view of the charge-density of imidazole showing the orbitals of the atoms at their radii, the ellipsoidal surface of each $H$ or $H_2$-type ellipsoidal MO that transitions to the corresponding outer shell of the atom(s) participating in each bond, and the hydrogen nuclei (red, not to scale). (B) Chemical structure and atom designation of imidizole.

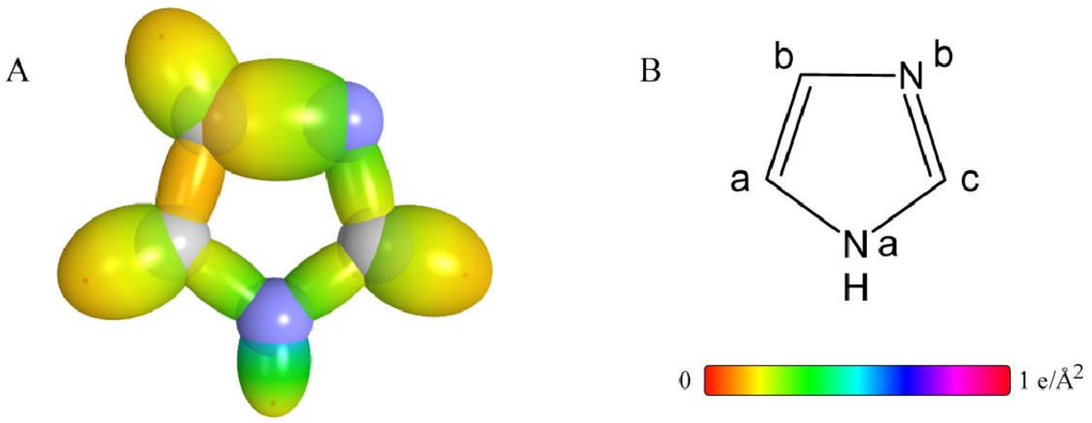


Table 15.285. The symbols of functional groups of imidazole.

| Functional Group | Group Symbol |
|---|---|
| $C_a = C_b$ double bond | $C = C$ |
| $N_b = C_c$ double bond | $N = C$ |
| $C_b - N_b$ | $C - N$ |
| $C_a - N_a - C_c$ | $C - N - C$ |
| $N_aH$ group | $NH$ |
| $CH$ | $CH$ |

Table 15.286. The geometrical bond parameters of imidazole and experimental values [1].

| Parameter | $C = C$ Group | $N = C$ Group | $C - N$ Group | $C - N - C$ Group | $NH$ Group | $CH$ Group |
|---|---|---|---|---|---|---|
| $a$ $(a_0)$ | 1.45103 | 1.44926 | 1.82450 | 1.43222 | 1.24428 | 1.53380 |
| $c'$ $(a_0)$ | 1.30463 | 1.30383 | 1.35074 | 1.29614 | 0.94134 | 1.01120 |
| Bond Length $2c'$ $(\mathring{A})$ | 1.38076 | 1.37991 | 1.42956 | 1.37178 | 0.996270 | 1.07021 |
| Exp. Bond Length $(\mathring{A})$ | 1.382 (pyrrole) | | | 1.370 (pyrrole) | 0.996 (pyrrole) | 1.076 (pyrrole) |
| $b,c$ $(a_0)$ | 0.63517 | 0.63276 | 1.22650 | 0.60931 | 0.81370 | 1.15326 |
| $e$ | 0.89910 | 0.89965 | 0.74033 | 0.90499 | 0.75653 | 0.65928 |

Table 15.287. The MO to HO intercept geometrical bond parameters of imidazole. $R_1$ is an alkyl group and $R, R', R''$ are $H$ or alkyl groups. $E_T$ is $E_T$ (*atom – atom,msp*$^3$.*AO*).

| Bond | Atom | $E_T$ (eV) Bond 1 | $E_T$ (eV) Bond 2 | $E_T$ (eV) Bond 3 | $E_T$ (eV) Bond 4 | Final Total Energy $C2sp^3$ (eV) | $r_{initial}$ $(a_0)$ | $r_{final}$ $(a_0)$ | $E_{Coulomb}(C2sp^3)$ (eV) Final | $E(C2sp^3)$ (eV) Final | $\theta'$ (°) | $\theta_1$ (°) | $\theta_2$ (°) | $d_1$ $(a_0)$ | $d_2$ $(a_0)$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $C-H\ (C_aH)$ | $C_a$ | -1.13380 | -0.92918 | 0 | 0 | -153.67867 | 0.91771 | 0.80561 | -16.88873 | -16.69786 | 83.35 | 96.65 | 43.94 | 1.10452 | 0.09331 |
| $C-H\ (C_bH)$ | $C_b$ | -1.13380 | -0.46459 | 0 | 0 | -153.21408 | 0.91771 | 0.82840 | -16.42414 | -16.23327 | 85.93 | 94.07 | 45.77 | 1.06995 | 0.05875 |
| $C-H\ (C_cH)$ | $C_c$ | -0.92918 | -0.92918 | 0 | 0 | -153.47405 | 0.91771 | 0.81549 | -16.68411 | -16.49325 | 84.49 | 95.51 | 44.47 | 1.08953 | 0.07833 |
| $C_a=(H)C_b-N_b=C_c$ | $C_b$ | -0.46459 | -1.13380 | 0 | 0 | -153.21408 | 0.91771 | 0.82840 | -16.42414 | -16.23327 | 90.36 | 89.64 | 42.49 | 1.34547 | 0.00527 |
| $C_a=(H)C_b-N_b=C_c$ | $N_b$ | -0.46459 | -0.92918 | 0 | 0 |  | 0.93084 | 0.83885 | -16.21953 |  | 91.32 | 88.68 | 43.14 | 1.33135 | 0.01939 |
| $C_a=C_b(H)N_b=C_c$ | $C_b$ | -1.13380 | -0.46459 | 0 | 0 | -153.21408 | 0.91771 | 0.82840 | -16.42414 | -16.23327 | 137.64 | 42.36 | 61.49 | 0.69250 | 0.61213 |
| $HN_aC_a=C_b(H)$ | $C_a$ | -1.13380 | -0.92918 | 0 | 0 | -153.67867 | 0.91771 | 0.80561 | -16.88873 | -16.69786 | 136.75 | 43.25 | 60.35 | 0.71784 | 0.58678 |
| $C_c(H)N_a-C_a=C_b(H)$ | $C_a$ | -1.13380 | -0.92918 | 0 | 0 | -153.67867 | 0.91771 | 0.80561 | -16.88873 | -16.69786 | 138.54 | 41.46 | 61.09 | 0.69238 | 0.60376 |
| $C_c(H)N_a-C_a=C_b(H)$ | $N_a$ | -0.92918 | -0.92918 | 0 | 0 |  | 0.93084 | 0.81549 | -16.68411 |  | 138.92 | 41.08 | 61.59 | 0.68147 | 0.61467 |
| $N-H\ (N_aH)$ | $N_a$ | -0.92918 | -0.92918 | 0 | 0 |  | 0.93084 | 0.81549 | -16.68411 |  | 117.34 | 62.66 | 62.90 | 0.56678 | 0.37456 |
| $(H)C_c-N_aC_a=C_b(H)$ | $C_c$ | -0.92918 | -0.92918 | 0 | 0 | -153.47405 | 0.91771 | 0.81549 | -16.68411 | -16.49325 | 138.92 | 41.08 | 61.59 | 0.68147 | 0.61467 |
| $C_a=(H)C_bN_b=C_c$ | $C_c$ | -0.92918 | -0.92918 | 0 | 0 | -153.47405 | 0.91771 | 0.81549 | -16.68411 | -16.49325 | 137.31 | 42.69 | 60.92 | 0.70446 | 0.59938 |
| $C_a=(H)C_bN_b=C_c$ | $N_b$ | -0.92918 | -0.46459 | 0 | 0 |  | 0.93084 | 0.83885 | -16.21953 |  | 138.20 | 41.80 | 62.08 | 0.67849 | 0.62534 |

Table 15.288. The energy parameters ($eV$) of functional groups of imidazole.

| Parameters | $C=C$ Group | $N=C$ Group | $C-N$ Group | $C-N-C$ Group | $NH$ Group | $CH$ Group |
|---|---|---|---|---|---|---|
| $n_1$ | 2 | 2 | 1 | 2 | 1 | 1 |
| $n_2$ | 0 | 0 | 0 | 0 | 0 | 0 |
| $n_3$ | 0 | 0 | 0 | 0 | 0 | 0 |
| $C_1$ | 0.5 | 0.5 | 0.5 | 0.5 | 0.75 | 0.75 |
| $C_2$ | 0.85252 | 0.85252 | 1 | 0.85252 | 0.93613 | 1 |
| $c_1$ | 1 | 1 | 1 | 1 | 0.75 | 1 |
| $c_2$ | 0.85252 | 0.84665 | 0.84665 | 0.84665 | 0.92171 | 0.91771 |
| $c_3$ | 0 | 0 | 0 | 0 | 1 | 1 |
| $c_4$ | 4 | 4 | 2 | 4 | 1 | 1 |
| $c_5$ | 0 | 0 | 0 | 0 | 1 | 1 |
| $C_{1o}$ | 0.5 | 0.5 | 0.5 | 0.5 | 0.75 | 0.75 |
| $C_{2o}$ | 0.85252 | 0.85252 | 1 | 0.85252 | 1 | 1 |
| $V_e\ (eV)$ | -104.37986 | -103.92756 | -32.44864 | -106.58684 | -39.48897 | -39.09538 |
| $V_p\ (eV)$ | 20.85777 | 20.87050 | 10.07285 | 20.99432 | 14.45367 | 13.45505 |
| $T\ (eV)$ | 35.96751 | 35.85539 | 8.89248 | 37.21047 | 15.86820 | 12.74462 |
| $V_m\ (eV)$ | -17.98376 | -17.92770 | -4.44624 | -18.60523 | -7.93410 | -6.37231 |
| $E(_{AO/HO})\ (eV)$ | 0 | 0 | -14.63489 | 0 | -14.53414 | -14.63489 |
| $\Delta E_{H_2MO}(_{AO/HO})\ (eV)$ | -2.26759 | -1.85836 | -0.92918 | -3.71673 | 0 | -2.26758 |
| $E_T(_{AO/HO})\ (eV)$ | 2.26759 | 1.85836 | -13.70571 | 3.71673 | -14.53414 | -12.36731 |
| $E_T(_{H_2MO})\ (eV)$ | -63.27075 | -63.27100 | -31.63527 | -63.27056 | -31.63534 | -31.63533 |
| $E_T\left(atom-atom, msp^3.AO\right)\ (eV)$ | -2.26759 | -1.85836 | -0.92918 | -3.71673 | 0 | 0 |
| $E_T(_{MO})\ (eV)$ | -65.53833 | -65.12910 | -32.56455 | -66.98746 | -31.63537 | -31.63537 |
| $\omega\ \left(10^{15}\ rad/s\right)$ | 15.4421 | 15.4704 | 21.5213 | 15.7474 | 48.7771 | 28.9084 |
| $E_K\ (eV)$ | 10.16428 | 10.18290 | 14.16571 | 10.36521 | 32.10594 | 19.02803 |
| $\bar{E}_D\ (eV)$ | -0.20668 | -0.20558 | -0.24248 | -0.21333 | -0.35462 | -0.27301 |
| $\bar{E}_{Kvib}\ (eV)$ | 0.17897<br>[6] | 0.20768<br>[62] | 0.12944<br>[23] | 0.11159<br>[12] | 0.40696<br>[24] | 0.39427<br>[60] |
| $\bar{E}_{osc}\ (eV)$ | -0.11720 | -0.10174 | -0.17775 | -0.15754 | -0.15115 | -0.07587 |
| $E_{mag}\ (eV)$ | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 |
| $E_T(_{Group})\ (eV)$ | -65.77272 | -65.33259 | -32.74230 | -67.30254 | -31.78651 | -31.71124 |
| $E_{initial}(_{c_4\ AO/HO})\ (eV)$ | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.53414 | -14.63489 |
| $E_{initial}(_{c_5\ AO/HO})\ (eV)$ | 0 | 0 | 0 | 0 | -13.59844 | -13.59844 |
| $E_D(_{Group})\ (eV)$ | 7.23317 | 6.79303 | 3.47253 | 8.76298 | 3.51208 | 3.32988 |

Table 15.289. The total bond energies of imidazole calculated using the functional group composition and the energies of Table 15.288 compared to the experimental values [3].

| Formula | Name | $C=C$ | $N=C$ | $C-N$ | $C-N-C$ | $NH$ | $CH$ | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|---|---|---|---|---|---|
| $C_3H_4N_2$ | Imidazole | 1 | 1 | 1 | 1 | 1 | 3 | 39.76343 | 39.74106 | -0.00056 |

Table 15.290. The bond angle parameters of imidazole and experimental values [62]. In the calculation of $\theta_v$, the parameters from the preceding angle were used. $E_T$ is $E_T\,(atom-atom, msp^3.AO)$.

| Atoms of Angle | $2c'$ Bond 1 ($a_0$) | $2c'$ Bond 2 ($a_0$) | $2c'$ Terminal Atoms ($a_0$) | $E_{Coulombic}$ Atom 1 | Atom 1 Hybridization Designation (Table 15.3B) | $E_{Coulombic}$ Atom 2 | Atom 2 Hybridization Designation (Table 15.3B) | $c_2$ Atom 1 | $c_2$ Atom 2 | $C_1$ | $C_2$ | $c_1$ | $c_2'$ | $E_T$ (eV) | $\theta_v$ (°) | $\theta_1$ (°) | $\theta_2$ (°) | Cal. $\theta$ (°) | Exp. $\theta$ (°) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $\angle HC_aN_a$ | 2.02241 | 2.59228 | 4.0166 | -14.82575 | 1 | -14.53414 | N | 0.91771 | 0.92171 Eq. (15.170)) | 0.75 | 1 | 0.75 | 1.00435 | 0 | | | | 120.51 | 117.4 (imidazole) |
| $\angle C_bC_aH_a$ | | | | | | | | | | | | | | | | 120.51 | 106.63 | 132.86 | 136.3 (imidazole) |
| $\angle HN_aC_a$ | 1.88268 | 2.59228 | 3.8987 | -14.53414 | N | -16.49325 | 25 (Table 15.3A) | 0.84665 (Eq. (15.170)) | 0.82493 (Eq. (15.73)) | 0.75 | 1 | 0.75 | 0.97435 | 0 | | | | 120.37 | 122.9 (imidazole) |
| $\angle H_aC_aC_b$ | 2.02241 | 2.60925 | 4.2895 | -16.88873 $C_a$ | 20 | -15.75493 $C_b$ | 4 | 0.80561 | 0.86359 | 0.75 | 1 | 0.75 | 1.07196 | 0 | | | | 135.30 | 136.3 (imidazole) |
| $\angle H_bC_bC_a$ | 2.02241 | 2.60925 | 4.2740 | -15.95954 $C_b$ | 6 | -14.82575 $C_a$ | 1 | 0.85252 | 0.91771 | 0.75 | 1 | 0.75 | 1.07647 | 0 | | | | 134.28 | 133.2 (imidazole) |
| $\angle N_bC_bH_b$ | | | | | | | | | | | | | | | | 134.28 | 111.18 | 114.54 | 115.8 (imidazole) |
| $\angle H_cC_cN_a$ | 2.02241 | 2.59228 | 3.8471 | -15.95954 $C_c$ | 6 | -14.53414 | N | 0.87495 | 0.84665 (Eq. (15.171)) | 0.75 | 1 | 0.75 | 0.96765 | | | | | 112.37 | 110.4 (imidazole) |
| $\angle N_bC_cH_c$ | | | | | | | | | | | | | | | | 112.37 | 109.83 | 137.80 | 138.2 (imidazole) |
| $\angle HN_aC_c$ | 1.88268 | 2.59228 | 4.0661 | -14.53414 | N | -15.76868 | 6 | 0.84665 (Eq. (15.170)) | 0.86284 (Eq. (15.73)) | 0.75 | 1 | 0.75 | 1.01912 | 0 | | | | 129.96 | 129.1 (imidazole) |
| $\angle N_aC_aC_b$ | 2.59228 | 2.60925 | 4.1952 | -14.53414 | N | -17.09334 $C_b$ | 24 | 0.84665 (Eq. (15.171)) | 0.79597 | 1 | 1 | 1 | 0.82131 | -1.44915 | | | | 107.52 | 106.3 (imidazole) |
| $\angle C_aN_aC_c$ | 2.59228 | 2.59228 | 4.2426 | -17.81791 | 35 | -17.81791 | 35 | 0.76360 | 0.76360 | 1 | 1 | 1 | 0.76360 | -1.85836 | | | | 109.83 | 107.2 (imidazole) |
| $\angle C_cN_bC_b$ | 2.60766 | 2.70148 | 4.3128 | -17.61330 | 32 | -17.61330 | 32 | 0.77247 | 0.77247 | 1 | 1 | 1 | 0.77247 | -1.85836 | | | | 108.64 | 105.4 (imidazole) |
| $\angle C_aC_bN_b$ | 2.60925 | 2.70148 | 4.3818 | -15.95955 | 6 | -14.53414 | N | 0.85252 | 0.84665 (Eq. (15.171)) | 1 | 1 | 1 | 0.84958 | -1.85836 | | | | 111.18 | 109.8 (imidazole) |
| $\angle N_aC_cN_b$ | 2.59228 | 2.60766 | 4.2544 | -16.68411 | 17 | -16.21953 | 9 | 0.81549 | 0.83885 | 1 | 1 | 1 | 0.82717 | -1.44915 | | | | 109.80 | 111.3 (imidazole) |

## PYRIDINE

Pyridine has the formula $C_5H_5N$ and comprises the benzene molecule with one $CH$ group replaced by a nitrogen atom which gives rise to a $C\overset{3e}{=}N$ functional group. The aromatic $C\overset{3e}{=}C$ and $C-H$ functional groups are equivalent to those of benzene given in the Aromatic and Heterocyclic Compounds section with the aromaticity maintained by the electrons from nitrogen in the $C\overset{3e}{=}N$ group, which is also aromatic.

As in the case of the aromatic carbons of benzene, each pyridine $C2sp^3$ HO initially has four unpaired electrons. Each $C-H$ bond has two paired electrons with one donated from the $H$ AO and the other from the $C2sp^3$ HO. In pyridine the three $N2p$ electrons are donated to the aromatic bond. Thus, as in the case of the $C\overset{3e}{=}C$ group, each $C\overset{3e}{=}N$ bond comprises a linear combination of a factor of 0.75 of four paired electrons (three electrons) from the $C2sp^3$ HO and the $N2p$ AO of the participating carbon and nitrogen atoms, respectively.

The solution of the $C\overset{3e}{=}N$ functional group comprises the hybridization of the $2s$ and $2p$ AOs of each $C$ to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between the $C2sp^3$ HO and the nitrogen atom to form a MO permits each participating hybridized orbital to decrease in radius and energy. The $C\overset{3e}{=}N$-bond MO is solved as a double bond with $n_1 = 2$ in Eqs. (15.51) and (15.166). The hybridization factor $c_2\left(C2sp^3HO\ to\ N\right) = 0.91140$ (Eq. (15.135)) matches the double-bond character of the $C2sp^3$ HO to the $N$ atom, and $C_2$ and $C_{2o}$ in Eqs. (15.51) and (15.166) are also given by Eq. (15.135) in order to match the nitrogen to the aromatic $C2sp^3$ HO such that $\Delta E_{H_2MO}\left(AO/HO\right) = 0$ in Eq. (15.51). Furthermore, $E_T\left(atom-atom, msp^3.AO\right)$ of the $C\overset{3e}{=}N$-bond MO in Eq. (15.166) due to the charge donation from the $C$ and $N$ atoms to the MO is $-1.44915\ eV$ corresponding to an energy contribution from each atom that is equivalent to that of an independent methyl group, $-0.72457\ eV$ (Eq. (14.151)). The contributions are also the same as those for a primary amine group as given in the corresponding section. As in the case of benzene, the aromatic $E_T\,(Group)$ and $E_D\,(Group)$ are given by Eqs. (15.165) and (15.166), respectively, with $f_1 = 0.75$. The breakage of the $CNC$ bonds results in three unpaired electrons on the $N$ atom. Thus, the corresponding $E_{mag}$ given by Eq. (15.69) was normalized for the two bonds per atom and for $f_1 = 0.75$ and was subtracted from the total energy of the $C\overset{3e}{=}N$-bond MO in Eq. (15.166). The pyridine vibrational energies are similar to those of benzene [63]; thus, the value for benzene was used.

The symbols of the functional groups of pyridine are given in Table 15.291. The corresponding designation of the structure is shown in Figure 15.50B. The geometrical (Eqs. (15.1-15.5) and (15.51)), intercept (Eqs. (15.80-15.87)), and energy (Eqs. (15.6-15.11), (15.17-15.65), and (15.165-15.166)) parameters of pyridine are given in Tables 15.292, 15.293, and 15.294, respectively. The total energy of pyridine given in Table 15.295 was calculated as the sum over the integer multiple of each $E_D\,(Group)$ of Table 15.294 corresponding to functional-group composition of the molecule. The bond angle parameters of pyridine determined using Eqs. (15.88-15.117) are given in Table 15.296. The color scale, translucent view of the charge-density of pyridine comprising the concentric shells of atoms with the outer shell bridged by one or more $H_2$-type ellipsoidal MOs or joined with one or more hydrogen MOs is shown in Figure 15.50A.

Figure 15.50. (A) Color scale, translucent view of the charge-density of pyridine showing the orbitals of the atoms at their radii, the ellipsoidal surface of each $H$ or $H_2$-type ellipsoidal MO that transitions to the corresponding outer shell of the atom(s) participating in each bond, and the hydrogen nuclei (red, not to scale). (B) Chemical structure and atom designation of pyridine.

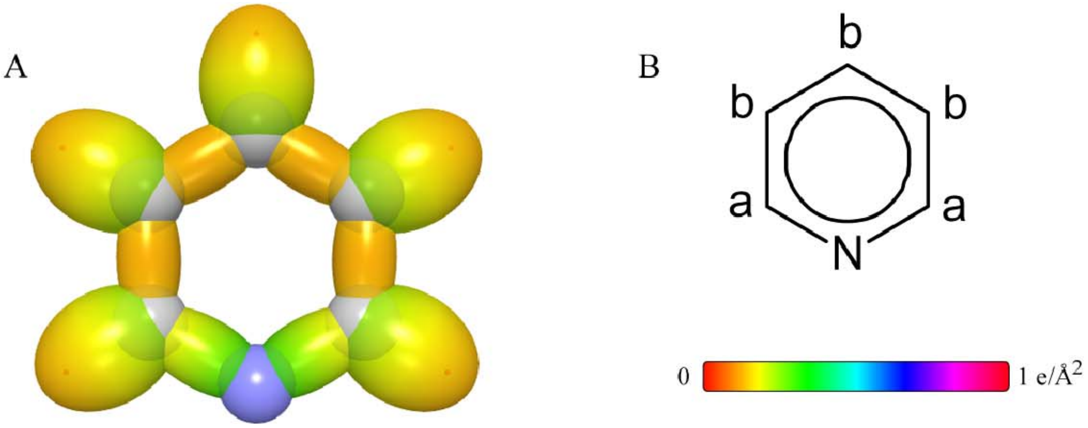


Table 15.291. The symbols of functional groups of pyridine.

| Functional Group | Group Symbol |
|---|---|
| $CC$ (aromatic bond) | $C\overset{3e}{=}C$ |
| $CH$ (aromatic) | $CH$ |
| $C_a\overset{3e}{=}N$ | $C\overset{3e}{=}N$ |

Table 15.292. The geometrical bond parameters of pyridine and experimental values [1].

| Parameter | $C\overset{3e}{=}C$ Group | $CH$ Group | $C\overset{3e}{=}N$ Group |
|---|---|---|---|
| $a\ (a_0)$ | 1.47348 | 1.60061 | 1.47169 |
| $c'\ (a_0)$ | 1.31468 | 1.03299 | 1.27073 |
| Bond Length $2c'$ $(\AA)$ | 1.39140 | 1.09327 | 1.34489 |
| Exp. Bond Length $(\AA)$ | 1.394<br>(pyridine) | 1.084<br>(pyridine) | 1.340<br>(pyridine) |
| $b,c\ (a_0)$ | 0.66540 | 1.22265 | 0.74237 |
| $e$ | 0.89223 | 0.64537 | 0.86345 |

Table 15.293. The MO to HO intercept geometrical bond parameters of pyridine. $E_T$ is $E_T$ ($atom-atom,msp^3.AO$).

| Bond | Atom | $E_T$ (eV) Bond 1 | $E_T$ (eV) Bond 2 | $E_T$ (eV) Bond 3 | $E_T$ (eV) Bond 4 | Final Total Energy $C2sp^3$ (eV) | $r_{initial}$ $(a_0)$ | $r_{final}$ $(a_0)$ | $E_{Coulomb}(C2sp^3)$ (eV) Final | $E(C2sp^3)$ (eV) Final | $\theta'$ (°) | $\theta_1$ (°) | $\theta_2$ (°) | $d_1$ $(a_0)$ | $d_2$ $(a_0)$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $C-H\ (C_aH)$ | $C_a$ | -0.54343 | -0.85035 | -0.56690 | 0 | -153.57636 | 0.91771 | 0.81052 | -16.78642 | -16.59556 | 76.35 | 103.65 | 40.11 | 1.22423 | 0.19124 |
| $C-H\ (C_bH)$ | $C_b$ | -0.85035 | -0.85035 | -0.56690 | 0 | -153.88327 | 0.91771 | 0.79597 | -17.09334 | -16.90248 | 74.42 | 105.58 | 38.84 | 1.24678 | 0.21379 |
| $(H)C_b(H)C_a\overset{3e}{=}NC_a$ | $C_a$ | -0.85035 | -0.54343 | -0.56690 | 0 | -153.57636 | 0.91771 | 0.81052 | -16.78642 | -16.59556 | 128.54 | 51.46 | 58.65 | 0.76572 | 0.50501 |
| $(H)C_b(H)C_a\overset{3e}{=}NC_a$ | $N$ | -0.54343 | -0.54343 | 0 | 0 |  | 0.93084 | 0.85503 | -15.91261 |  | 130.61 | 49.39 | 60.97 | 0.71418 | 0.55656 |
| $(H)C_b\overset{3e}{=}C_a(H)N$ | $C_a$ | -0.54343 | -0.85035 | -0.56690 | 0 | -153.57636 | 0.91771 | 0.81052 | -16.78642 | -16.59556 | 134.85 | 45.15 | 59.72 | 0.74304 | 0.57165 |
| $(H)C_b\overset{3e}{=}C_a(H)N$<br>$(H)C_b\overset{3e}{=}C_b(H)C_a(H)$ | $C_b$ | -0.85035 | -0.85035 | -0.56690 | 0 | -153.88327 | 0.91771 | 0.79597 | -17.09334 | -16.90248 | 134.24 | 45.76 | 58.98 | 0.75935 | 0.55533 |

Table 15.294. The energy parameters ($eV$) of functional groups of pyridine.

| Parameters | $\overset{3e}{C=C}$ Group | $CH$ Group | $\overset{3e}{C=N}$ Group |
|---|---|---|---|
| $f_1$ | 0.75 | 1 | 0.75 |
| $n_1$ | 2 | 1 | 2 |
| $n_2$ | 0 | 0 | 0 |
| $n_3$ | 0 | 0 | 0 |
| $C_1$ | 0.5 | 0.75 | 0.5 |
| $C_2$ | 0.85252 | 1 | 0.91140 |
| $c_1$ | 1 | 1 | 1 |
| $c_2$ | 0.85252 | 0.91771 | 0.91140 |
| $c_3$ | 0 | 1 | 0 |
| $c_4$ | 3 | 1 | 3 |
| $c_5$ | 0 | 1 | 0 |
| $C_{1o}$ | 0.5 | 0.75 | 0.5 |
| $C_{2o}$ | 0.85252 | 1 | 0.91140 |
| $V_e\ (eV)$ | -101.12679 | -37.10024 | -102.01431 |
| $V_p\ (eV)$ | 20.69825 | 13.17125 | 21.41410 |
| $T\ (eV)$ | 34.31559 | 11.58941 | 34.65890 |
| $V_m\ (eV)$ | -17.15779 | -5.79470 | -17.32945 |
| $E(AO/HO)\ (eV)$ | 0 | -14.63489 | 0 |
| $\Delta E_{H_2MO}(AO/HO)\ (eV)$ | 0 | -1.13379 | 0 |
| $E_T(AO/HO)\ (eV)$ | 0 | -13.50110 | 0 |
| $E_T(H_2MO)\ (eV)$ | -63.27075 | -31.63539 | -63.27076 |
| $E_T(atom-atom,msp^3.AO)\ (eV)$ | -2.26759 | -0.56690 | -1.44915 |
| $E_T(MO)\ (eV)$ | -65.53833 | -32.20226 | -64.71988 |
| $\omega\ (10^{15}\ rad/s)$ | 49.7272 | 26.4826 | 43.6311 |
| $E_K\ (eV)$ | 32.73133 | 17.43132 | 28.71875 |
| $\bar{E}_D\ (eV)$ | -0.35806 | -0.26130 | -0.33540 |
| $\bar{E}_{Kvib}\ (eV)$ | 0.19649<br>[49] | 0.35532<br>Eq. (13.458) | 0.19649<br>[49] |
| $\bar{E}_{osc}\ (eV)$ | -0.25982 | -0.08364 | -0.23715 |
| $E_{mag}\ (eV)$ | 0.14803 | 0.14803 | 0.09457 |
| $E_T(Group)\ (eV)$ | -49.54347 | -32.28590 | -48.82472 |
| $E_{initial}(c_4\ AO/HO)\ (eV)$ | -14.63489 | -14.63489 | -14.63489 |
| $E_{initial}(c_5\ AO/HO)\ (eV)$ | 0 | -13.59844 | 0 |
| $E_D(Group)\ (eV)$ | 5.63881 | 3.90454 | 4.92005 |

Table 15.295. The total bond energies of pyridine calculated using the functional group composition and the energies of Table 15.294 compared to the experimental values [3].

| Formula | Name | $\overset{3e}{C=C}$ | $CH$ | $\overset{3e}{C=N}$ Group | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|---|---|---|
| $C_5H_5N$ | Pyridine | 4 | 5 | 2 | 51.91802 | 51.87927 | -0.00075 |

Table 15.296. The bond angle parameters of pyridine and experimental values [1]. $E_T$ is $E_T$ ($atom - atom, msp^3.AO$).

| Atoms of Angle | $2c'$ Bond 1 ($a_0$) | $2c'$ Bond 2 ($a_0$) | $2c'$ Terminal Atoms ($a_0$) | $E_{Coulombic}$ Atom 1 | Atom 1 Hybridization Designation (Table 15.3B) | $E_{Coulombic}$ Atom 2 | Atom 2 Hybridization Designation (Table 15.3B) | $c_2$ Atom 1 | $c_2$ Atom 2 | $C_1$ | $C_2$ | $c_1$ | $c_2'$ | $E_T$ (eV) | $\theta_v$ (°) | $\theta_1$ (°) | $\theta_2$ (°) | Cal. $\theta$ (°) | Exp. $\theta$ (°) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $\angle CCC$ (aromatic) | 2.62936 | 2.62936 | 4.5585 | -17.17218 | 27 | -17.17218 | 27 | 0.79232 | 0.79232 | 1 | 1 | 1 | 0.79232 | -1.85836 |  |  |  | 120.19 | 120 [50-52] (benzene)<br>118.3 (pyridine)<br>118.5 (pyridine) |
| $\angle CCH$ (aromatic) |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  | 120.19 |  | 119.91 | 120 [50-52] (benzene)<br>121.3 (pyridine) |
| $\angle HC_aN$ | 2.06598 | 2.54147 | 3.9497 | -14.82575 | 1 | -14.53414 | N | 0.91771 | 0.91140 Eq. (15.135)) | 0.75 | 1 | 0.75 | 0.99312 | 0 |  |  |  | 117.65 | 115.9 (pyridine) |
| $\angle NC_aC_b$ | 2.54147 | 2.62936 | 4.5607 | -14.53414 | N | -16.52644 $C_b$ | 15 | 0.91140 Eq. (15.135)) | 0.82327 | 1 | 1 | 1 | 0.86734 | -1.44915 |  |  |  | 123.76 | 123.9 (pyridine) |
| $\angle C_aNC_a$ | 2.54147 | 2.54147 | 4.3359 | -17.71560 | 33 | -17.71560 | 33 | 0.76801 | 0.76801 | 1 | 1 | 1 | 0.76801 | -1.85836 |  |  |  | 117.09 | 116.8 (pyridine) |

## PYRIMIDINE

Pyrimidine has the formula $C_4H_4N_2$ and comprises the pyridine molecule with one additional $CH$ group replaced by a nitrogen atom, which gives rise to a second $C\overset{3e}{=}N$ functional group that is equivalent to that of pyridine given in the corresponding section. The aromatic $C\overset{3e}{=}C$ and $C-H$ functional groups are also equivalent to those of pyridine and benzene given in the Aromatic and Heterocyclic Compounds section with the aromaticity maintained by the electrons from nitrogen in the $C\overset{3e}{=}N$ group which is also aromatic.

The symbols of the functional groups of pyrimidine are given in Table 15.297. The corresponding designation of the structure is shown in Figure 15.51B. The geometrical (Eqs. (15.1-15.5) and (15.51)), intercept (Eqs. (15.80-15.87)), and energy (Eqs. (15.6-15.11), (15.17-15.65), and (15.165-15.166)) parameters of pyrimidine are given in Tables 15.298, 15.299, and 15.300, respectively. The total energy of pyrimidine given in Table 15.301 was calculated as the sum over the integer multiple of each $E_D\left(_{Group}\right)$ of Table 15.300 corresponding to functional-group composition of the molecule. The bond angle parameters of pyrimidine determined using Eqs. (15.88-15.117) are given in Table 15.302. The color scale, translucent view of the charge-density of pyrimidine comprising the concentric shells of atoms with the outer shell bridged by one or more $H_2$-type ellipsoidal MOs or joined with one or more hydrogen MOs is shown in Figure 15.51A.

Figure 15.51. (A) Color scale, translucent view of the charge-density of pyrimidine showing the orbitals of the atoms at their radii, the ellipsoidal surface of each $H$ or $H_2$-type ellipsoidal MO that transitions to the corresponding outer shell of the atom(s) participating in each bond, and the hydrogen nuclei (red, not to scale). (B) Chemical structure and atom designation of pyrimidine.

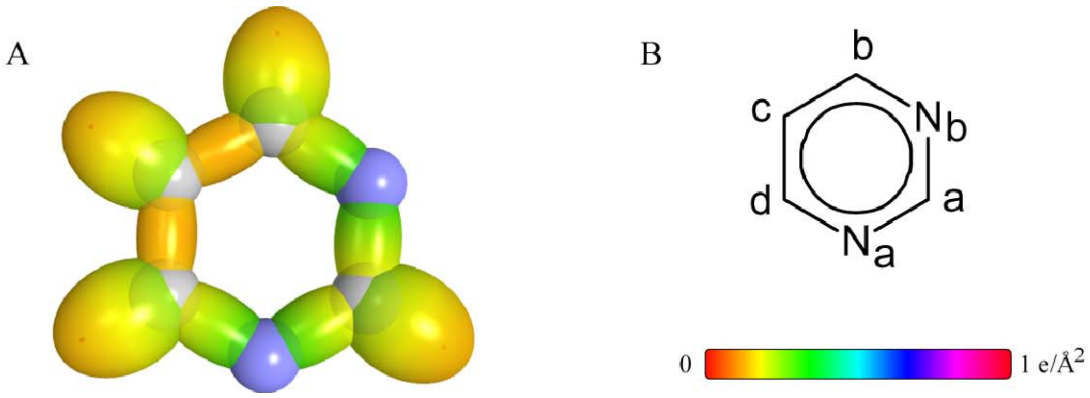


Table 15.297. The symbols of functional groups of pyrimidine.

| Functional Group | Group Symbol |
|---|---|
| $CC$ (aromatic bond) | $C\overset{3e}{=}C$ |
| $CH$ (aromatic) | $CH$ |
| $C_{a,b,d}\overset{3e}{=}N$ | $C\overset{3e}{=}N$ |

Table 15.298. The geometrical bond parameters of pyrimidine and experimental values [1].

| Parameter | $C\overset{3e}{=}C$ Group | $CH$ Group | $C\overset{3e}{=}N$ Group |
|---|---|---|---|
| $a\ (a_0)$ | 1.47348 | 1.60061 | 1.47169 |
| $c'\ (a_0)$ | 1.31468 | 1.03299 | 1.27073 |
| Bond Length $2c'\ (\mathring{A})$ | 1.39140 | 1.09327 | 1.34489 |
| Exp. Bond Length $(\mathring{A})$ | 1.393<br>(pyrimidine) | 1.084<br>(pyridine) | 1.340<br>(pyrimidine) |
| $b,c\ (a_0)$ | 0.66540 | 1.22265 | 0.74237 |
| $e$ | 0.89223 | 0.64537 | 0.86345 |

Table 15.299. The MO to HO intercept geometrical bond parameters of pyrimidine. $E_T$ is $E_T$ (*atom – atom,msp*$^3$*.AO*).

| Bond | Atom | $E_T$ (eV) Bond 1 | $E_T$ (eV) Bond 2 | $E_T$ (eV) Bond 3 | $E_T$ (eV) Bond 4 | Final Total Energy $C2sp^3$ (eV) | $r_{initial}$ $(a_0)$ | $r_{final}$ $(a_0)$ | $E_{Coulomb}\left(C2sp^3\right)$ (eV) Final | $E\left(C2sp^3\right)$ (eV) Final | $\theta'$ $(°)$ | $\theta_1$ $(°)$ | $\theta_2$ $(°)$ | $d_1$ $(a_0)$ | $d_2$ $(a_0)$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $C-H\ \left(C_aH\right)$ | $C_a$ | -0.54343 | -0.54343 | -0.56690 | 0 | -153.26945 | 0.91771 | 0.82562 | -16.47951 | -16.28864 | 78.27 | 101.73 | 41.39 | 1.20084 | 0.16785 |
| $C-H\ \left(C_{b,d}H\right)$ | $C_b$<br>$C_d$ | -0.54343 | -0.85035 | -0.56690 | 0 | -153.57636 | 0.91771 | 0.81052 | -16.78642 | -16.59556 | 76.35 | 103.65 | 40.11 | 1.22423 | 0.19124 |
| $C-H\ \left(C_cH\right)$ | $C_c$ | -0.85035 | -0.85035 | -0.56690 | 0 | -153.88327 | 0.91771 | 0.79597 | -17.09334 | -16.90248 | 74.42 | 105.58 | 38.84 | 1.24678 | 0.21379 |
| $(H)C_c(H)C_b\overset{3e}{=}N_bC_a$<br>$(H)C_c(H)C_d\overset{3e}{=}N_aC_a$ | $C_b$<br>$C_d$ | -0.85035 | -0.54343 | -0.56690 | 0 | -153.57636 | 0.91771 | 0.81052 | -16.78642 | -16.59556 | 128.54 | 51.46 | 58.65 | 0.76572 | 0.50501 |
| $(H)C_c(H)C_b\overset{3e}{=}N_bC_a$<br>$(H)C_c(H)C_d\overset{3e}{=}N_aC_a$ | $N_b$<br>$N_a$ | -0.54343 | -0.54343 | 0 | 0 |  | 0.93084 | 0.85503 | -15.91261 |  | 130.61 | 49.39 | 60.97 | 0.71418 | 0.55656 |
| $(H)C_c(H)C_bN_b\overset{3e}{=}C_a(H)$<br>$(H)C_c(H)C_dN_a\overset{3e}{=}C_a(H)$ | $C_a$ | -0.54343 | -0.54343 | -0.56690 | 0 | -153.26945 | 0.91771 | 0.82562 | -16.47951 | -16.28865 | 129.26 | 50.74 | 59.44 | 0.74824 | 0.52249 |
| $(H)C_c(H)C_bN_b\overset{3e}{=}C_a(H)$<br>$(H)C_c(H)C_dN_a\overset{3e}{=}C_a(H)$ | $N_b$<br>$N_a$ | -0.54343 | -0.54343 | 0 | 0 |  | 0.93084 | 0.85503 | -15.91261 |  | 130.61 | 49.39 | 60.97 | 0.71418 | 0.55656 |
| $N_a(H)C_d\overset{3e}{=}C_c(H)C_b$<br>$N_b(H)C_b\overset{3e}{=}C_c(H)C_d$ | $C_c$ | -0.85035 | -0.85035 | -0.56690 | 0 | -153.88327 | 0.91771 | 0.79597 | -17.09334 | -16.90248 | 134.24 | 45.76 | 58.98 | 0.75935 | 0.55533 |
| $N_a(H)C_d\overset{3e}{=}C_c(H)C_b$<br>$N_b(H)C_b\overset{3e}{=}C_c(H)C_d$ | $C_b$<br>$C_d$ | -0.85035 | -0.54343 | -0.56690 | 0 | -153.57636 | 0.91771 | 0.81052 | -16.78642 | -16.59556 | 134.85 | 45.15 | 59.72 | 0.74304 | 0.57165 |

Table 15.300. The energy parameters ($eV$) of functional groups of pyrimidine.

| Parameters | $\overset{3e}{C=C}$ Group | $CH$ Group | $\overset{3e}{C=N}$ Group |
|---|---|---|---|
| $f_1$ | 0.75 | 1 | 0.75 |
| $n_1$ | 2 | 1 | 2 |
| $n_2$ | 0 | 0 | 0 |
| $n_3$ | 0 | 0 | 0 |
| $C_1$ | 0.5 | 0.75 | 0.5 |
| $C_2$ | 0.85252 | 1 | 0.91140 |
| $c_1$ | 1 | 1 | 1 |
| $c_2$ | 0.85252 | 0.91771 | 0.91140 |
| $c_3$ | 0 | 1 | 0 |
| $c_4$ | 3 | 1 | 3 |
| $c_5$ | 0 | 1 | 0 |
| $C_{1o}$ | 0.5 | 0.75 | 0.5 |
| $C_{2o}$ | 0.85252 | 1 | 0.91140 |
| $V_e\ (eV)$ | -101.12679 | -37.10024 | -102.01431 |
| $V_p\ (eV)$ | 20.69825 | 13.17125 | 21.41410 |
| $T\ (eV)$ | 34.31559 | 11.58941 | 34.65890 |
| $V_m\ (eV)$ | -17.15779 | -5.79470 | -17.32945 |
| $E(AO/HO)\ (eV)$ | 0 | -14.63489 | 0 |
| $\Delta E_{H_2MO}(AO/HO)\ (eV)$ | 0 | -1.13379 | 0 |
| $E_T(AO/HO)\ (eV)$ | 0 | -13.50110 | 0 |
| $E_T(H_2MO)\ (eV)$ | -63.27075 | -31.63539 | -63.27076 |
| $E_T(atom-atom, msp^3.AO)\ (eV)$ | -2.26759 | -0.56690 | -1.44915 |
| $E_T(MO)\ (eV)$ | -65.53833 | -32.20226 | -64.71988 |
| $\omega\ (10^{15}\ rad/s)$ | 49.7272 | 26.4826 | 43.6311 |
| $E_K\ (eV)$ | 32.73133 | 17.43132 | 28.71875 |
| $\bar{E}_D\ (eV)$ | -0.35806 | -0.26130 | -0.33540 |
| $\bar{E}_{Kvib}\ (eV)$ | 0.19649<br>[49] | 0.35532<br>Eq. (13.458) | 0.19649<br>[49] |
| $\bar{E}_{osc}\ (eV)$ | -0.25982 | -0.08364 | -0.23715 |
| $E_{mag}\ (eV)$ | 0.14803 | 0.14803 | 0.09457 |
| $E_T(Group)\ (eV)$ | -49.54347 | -32.28590 | -48.82472 |
| $E_{initial}(c_4\ AO/HO)\ (eV)$ | -14.63489 | -14.63489 | -14.63489 |
| $E_{initial}(c_5\ AO/HO)\ (eV)$ | 0 | -13.59844 | 0 |
| $E_D(Group)\ (eV)$ | 5.63881 | 3.90454 | 4.92005 |

Table 15.301. The total bond energies of pyrimidine calculated using the functional group composition and the energies of Table 15.300 compared to the experimental values [3].

| Formula | Name | $\overset{3e}{C=C}$ | $CH$ | $\overset{3e}{C=N}$ Group | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|---|---|---|
| $C_4H_4N_2$ | Pyrimidine | 2 | 4 | 4 | 46.57597 | 46.51794 | -0.00125 |

Table 15.302. The bond angle parameters of pyrimidine and experimental values [1]. $E_T$ is $E_T$ ($atom - atom, msp^3.AO$).

| Atoms of Angle | 2$c'$ Bond 1 ($a_0$) | 2$c'$ Bond 2 ($a_0$) | 2$c'$ Terminal Atoms ($a_0$) | $E_{Coulombic}$ Atom 1 | Atom 1 Hybridization Designation (Table 15.3B) | $E_{Coulombic}$ Atom 2 | Atom 2 Hybridization Designation (Table 15.3B) | $c_2$ Atom 1 | $c_2$ Atom 2 | $C_1$ | $C_2$ | $c_1$ | $c_2'$ | $E_T$ (eV) | $\theta_v$ (°) | $\theta_1$ (°) | $\theta_2$ (°) | Cal. $\theta$ (°) | Exp. $\theta$ (°) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $\angle CCC$ (aromatic) | 2.62936 | 2.62936 | 4.5585 | -17.17218 | 27 | -17.17218 | 27 | 0.79232 | 0.79232 | 1 | 1 | 1 | 0.79232 | -1.85836 | | | | 120.19 | 120 [50-52] (benzene)<br>118.3 (pyridine)<br>118.5 (pyridine) |
| $\angle CCH$ (aromatic) | | | | | | | | | | | | | | | | 120.19 | | 119.91 | 120 [50-52] (benzene)<br>121.3 (pyridine) |
| $\angle HCN$ | 2.06598 | 2.54147 | 3.9497 | -14.82575 | 1 | -14.53414 | N | 0.91771 | 0.91140 Eq. (15.135)) | 0.75 | 1 | 0.75 | 0.99312 | 0 | | | | 117.65 | 115.9 (pyridine) |
| $\angle NCC$ | 2.54147 | 2.62936 | 4.5607 | -14.53414 | N | -16.52644 | 15 | 0.91140 Eq. (15.135)) | 0.82327 | 1 | 1 | 1 | 0.86734 | -1.44915 | | | | 123.76 | 123.9 (pyridine) |
| $\angle CNC$ | 2.54147 | 2.54147 | 4.3359 | -17.71560 | 33 | -17.71560 | 33 | 0.76801 | 0.76801 | 1 | 1 | 1 | 0.76801 | -1.85836 | | | | 117.09 | 115.5 (pyrimidine) |
| $\angle NCN$ | 2.54147 | 2.54147 | 4.5826 | -15.55033 | 3 | -15.55033 | 3 | 0.87495 | 0.87495 | 1 | 1 | 1 | 0.87495 | -1.85836 | | | | 128.73 | 127.6 (pyrimidine) |

## PYRAZINE

Pyrazine has the formula $C_4H_4N_2$ and comprises the pyrimidine molecule with para rather than ortho aromatic nitrogen atoms. The $C\overset{3e}{=}N$ functional group is equivalent to that of pyrimidine and pyridine given in the corresponding sections. The aromatic $C\overset{3e}{=}C$ and $C-H$ functional groups are also equivalent to those of pyrimidine, pyridine, and benzene given in the Aromatic and Heterocyclic Compounds section with the aromaticity maintained by the electrons from nitrogen in the $C\overset{3e}{=}N$ group, which is also aromatic.

The symbols of the functional groups of pyrazine are given in Table 15.303. The corresponding designation of the structure is shown in Figure 15.52B. The geometrical (Eqs. (15.1-15.5) and (15.51)), intercept (Eqs. (15.80-15.87)), and energy (Eqs. (15.6-15.11), (15.17-15.65), and (15.165-15.166)) parameters of pyrazine are given in Tables 15.304, 15.305, and 15.306, respectively. The total energy of pyrazine given in Table 15.307 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.306 corresponding to functional-group composition of the molecule. The bond angle parameters of pyrazine determined using Eqs. (15.88-15.117) are given in Table 15.308. The color scale, translucent view of the charge-density of pyrazine comprising the concentric shells of atoms with the outer shell bridged by one or more $H_2$-type ellipsoidal MOs or joined with one or more hydrogen MOs is shown in Figure 15.52A.

Figure 15.52. (A) Color scale, translucent view of the charge-density of pyrazine showing the orbitals of the atoms at their radii, the ellipsoidal surface of each $H$ or $H_2$-type ellipsoidal MO that transitions to the corresponding outer shell of the atom(s) participating in each bond, and the hydrogen nuclei (red, not to scale). (B) Chemical structure and atom designation of pyrazine.

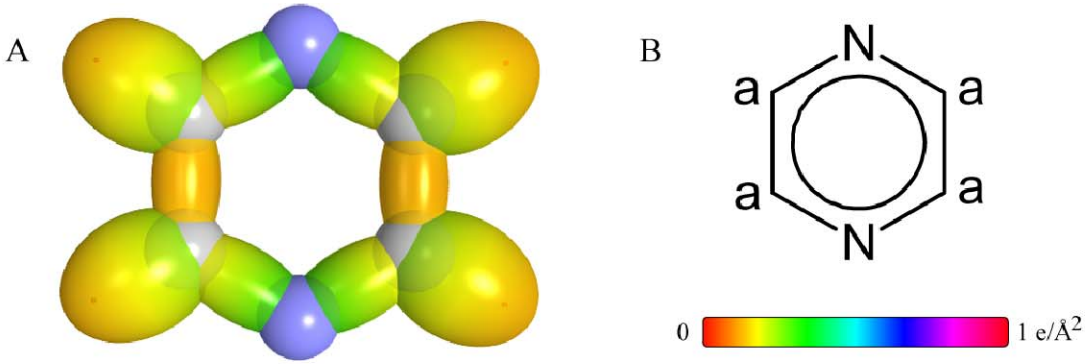


Table 15.303. The symbols of functional groups of pyrazine.

| Functional Group | Group Symbol |
|---|---|
| $CC$ (aromatic bond) | $C\overset{3e}{=}C$ |
| $CH$ (aromatic) | $CH$ |
| $C_a\overset{3e}{=}N$ | $C\overset{3e}{=}N$ |

Table 15.304. The geometrical bond parameters of pyrazine and experimental values [1].

| Parameter | $C\overset{3e}{=}C$ Group | $CH$ Group | $C\overset{3e}{=}N$ Group |
|---|---|---|---|
| $a\ (a_0)$ | 1.47348 | 1.60061 | 1.47169 |
| $c'\ (a_0)$ | 1.31468 | 1.03299 | 1.27073 |
| Bond Length $2c'$ $(Å)$ | 1.39140 | 1.09327 | 1.34489 |
| Exp. Bond Length $(Å)$ | 1.339<br>(pyrazine) | 1.115<br>(pyrazine) | 1.403<br>(pyrazine) |
| $b,c\ (a_0)$ | 0.66540 | 1.22265 | 0.74237 |
| $e$ | 0.89223 | 0.64537 | 0.86345 |

Table 15.305. The MO to HO intercept geometrical bond parameters of pyrazine. $E_T$ is $E_T$ (*atom* – *atom*,*msp*$^3$.*AO*).

| Bond | Atom | $E_T$ (eV) Bond 1 | $E_T$ (eV) Bond 2 | $E_T$ (eV) Bond 3 | $E_T$ (eV) Bond 4 | Final Total Energy $C2sp^3$ (eV) | $r_{initial}$ $(a_0)$ | $r_{final}$ $(a_0)$ | $E_{Coulomb}(C2sp^3)$ (eV) Final | $E(C2sp^3)$ (eV) Final | $\theta'$ $(^\circ)$ | $\theta_1$ $(^\circ)$ | $\theta_2$ $(^\circ)$ | $d_1$ $(a_0)$ | $d_2$ $(a_0)$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $C-H\ (C_aH)$ | $C_a$ | -0.54343 | -0.85035 | -0.56690 | 0 | -153.57636 | 0.91771 | 0.81052 | -16.78642 | -16.59556 | 76.35 | 103.65 | 40.11 | 1.22423 | 0.19124 |
| $(H)C_a(H)C_a\overset{3e}{=}NC_a$ | $C_a$ | -0.85035 | -0.54343 | -0.56690 | 0 | -153.57636 | 0.91771 | 0.81052 | -16.78642 | -16.59556 | 128.54 | 51.46 | 58.65 | 0.76572 | 0.50501 |
| $(H)C_a(H)C_a\overset{3e}{=}NC_a$ | $N$ | -0.54343 | -0.54343 | 0 | 0 |  | 0.93084 | 0.85503 | -15.91261 |  | 130.61 | 49.39 | 60.97 | 0.71418 | 0.55656 |
| $N(H)C_a\overset{3e}{=}C_a(H)N$ | $C_a$ | -0.85035 | -0.54343 | -0.56690 | 0 | -153.57636 | 0.91771 | 0.81052 | -16.78642 | -16.59556 | 134.85 | 45.15 | 59.72 | 0.74304 | 0.57165 |

Table 15.306. The energy parameters ($eV$) of functional groups of pyrazine.

| Parameters | $\overset{3e}{C=C}$ Group | $CH$ Group | $\overset{3e}{C=N}$ Group |
|---|---|---|---|
| $f_1$ | 0.75 | 1 | 0.75 |
| $n_1$ | 2 | 1 | 2 |
| $n_2$ | 0 | 0 | 0 |
| $n_3$ | 0 | 0 | 0 |
| $C_1$ | 0.5 | 0.75 | 0.5 |
| $C_2$ | 0.85252 | 1 | 0.91140 |
| $c_1$ | 1 | 1 | 1 |
| $c_2$ | 0.85252 | 0.91771 | 0.91140 |
| $c_3$ | 0 | 1 | 0 |
| $c_4$ | 3 | 1 | 3 |
| $c_5$ | 0 | 1 | 0 |
| $C_{1o}$ | 0.5 | 0.75 | 0.5 |
| $C_{2o}$ | 0.85252 | 1 | 0.91140 |
| $V_e\ (eV)$ | -101.12679 | -37.10024 | -102.01431 |
| $V_p\ (eV)$ | 20.69825 | 13.17125 | 21.41410 |
| $T\ (eV)$ | 34.31559 | 11.58941 | 34.65890 |
| $V_m\ (eV)$ | -17.15779 | -5.79470 | -17.32945 |
| $E(AO/HO)\ (eV)$ | 0 | -14.63489 | 0 |
| $\Delta E_{H_2MO}(AO/HO)\ (eV)$ | 0 | -1.13379 | 0 |
| $E_T(AO/HO)\ (eV)$ | 0 | -13.50110 | 0 |
| $E_T(H_2MO)\ (eV)$ | -63.27075 | -31.63539 | -63.27076 |
| $E_T\left(atom-atom,msp^3.AO\right)(eV)$ | -2.26759 | -0.56690 | -1.44915 |
| $E_T(MO)\ (eV)$ | -65.53833 | -32.20226 | -64.71988 |
| $\omega\ \left(10^{15}\ rad/s\right)$ | 49.7272 | 26.4826 | 43.6311 |
| $E_K\ (eV)$ | 32.73133 | 17.43132 | 28.71875 |
| $\bar{E}_D\ (eV)$ | -0.35806 | -0.26130 | -0.33540 |
| $\bar{E}_{Kvib}\ (eV)$ | 0.19649<br>[49] | 0.35532<br>Eq. (13.458) | 0.19649<br>[49] |
| $\bar{E}_{osc}\ (eV)$ | -0.25982 | -0.08364 | -0.23715 |
| $E_{mag}\ (eV)$ | 0.14803 | 0.14803 | 0.09457 |
| $E_T(Group)\ (eV)$ | -49.54347 | -32.28590 | -48.82472 |
| $E_{initial}(c_4\ AO/HO)\ (eV)$ | -14.63489 | -14.63489 | -14.63489 |
| $E_{initial}(c_5\ AO/HO)\ (eV)$ | 0 | -13.59844 | 0 |
| $E_D(Group)\ (eV)$ | 5.63881 | 3.90454 | 4.92005 |

Table 15.307. The total bond energies of pyrazine calculated using the functional group composition and the energies of Table 15.306 compared to the experimental values [3].

| Formula | Name | $\overset{3e}{C=C}$ | $CH$ | $\overset{3e}{C=N}$ Group | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|---|---|---|
| $C_4H_4N_2$ | Pyrazine | 2 | 4 | 4 | 46.57597 | 46.51380 | 0.00095 |

Table 15.308. The bond angle parameters of pyrazine and experimental values [1]. $E_T$ is $E_T$ ($atom - atom, msp^3.AO$).

| Atoms of Angle | $2c'$ Bond 1 ($a_0$) | $2c'$ Bond 2 ($a_0$) | $2c'$ Terminal Atoms ($a_0$) | $E_{Coulombic}$ Atom 1 | Atom 1 Hybridization Designation (Table 15.3B) | $E_{Coulombic}$ Atom 2 | Atom 2 Hybridization Designation (Table 15.3B) | $c_2$ Atom 1 | $c_2$ Atom 2 | $C_1$ | $C_2$ | $c_1$ | $c_2'$ | $E_T$ (eV) | $\theta_v$ (°) | $\theta_1$ (°) | $\theta_2$ (°) | Cal. $\theta$ (°) | Exp. $\theta$ (°) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $\angle CCC$ (aromatic) | 2.62936 | 2.62936 | 4.5585 | -17.17218 | 27 | -17.17218 | 27 | 0.79232 | 0.79232 | 1 | 1 | 1 | 0.79232 | -1.85836 | | | | 120.19 | 120 [50-52] (benzene)<br>118.3 (pyridine)<br>118.5 (pyridine) |
| $\angle CCH$ (aromatic) | | | | | | | | | | | | | | | | 120.19 | | 119.91 | 120 [50-52] (benzene)<br>121.3 (pyridine) |
| $\angle HCN$ | 2.06598 | 2.54147 | 3.9497 | -14.82575 | 1 | -14.53414 | N | 0.91771 | 0.91140 Eq. (15.135)) | 0.75 | 1 | 0.75 | 0.99312 | 0 | | | | 117.65 | 115.9 (pyridine) |
| $\angle CCH$ | | | | | | | | | | | | | | | | 117.65 | 116.81 | 125.54 | 123.9 (pyrazine) |
| $\angle NCC$ | 2.54147 | 2.62936 | 4.4045 | -14.53414 | N | -17.09334 | 23 | 0.91140 Eq. (15.135)) | 0.79597 | 1 | 1 | 1 | 0.85368 | -1.44915 | | | | 116.81 | 115.6 (pyrazine |
| $\angle CNC$ | 2.54147 | 2.54147 | 4.3359 | -17.71560 | 33 | -17.71560 | 33 | 0.76801 | 0.76801 | 1 | 1 | 1 | 0.76801 | -1.85836 | | | | 117.09 | 116.8 (pyrimidine) |

## QUINOLINE

Quinoline has the formula $C_9H_7N$ and comprises the naphthalene molecule with one $CH$ group replaced by a nitrogen atom which gives rise to a $C\overset{3e}{=}N$ functional group. The aromatic $C\overset{3e}{=}C$ and $C-H$ functional groups are equivalent to those of naphthalene given in the corresponding section with the aromaticity maintained by the electrons from nitrogen in the $C\overset{3e}{=}N$ group, which is also aromatic. The $C-C$ functional group is also equivalent to that of naphthalene. The bonding in quinoline can be further considered as a linear combination of the naphthalene and pyridine groups wherein the $C\overset{3e}{=}N$ group is equivalent to that of pyridine, pyrimidine, and pyrazine as given in the corresponding sections.

The symbols of the functional groups of quinoline are given in Table 15.309. The corresponding designation of the structure is shown in Figure 15.53B. The geometrical (Eqs. (15.1-15.5) and (15.51)), intercept (Eqs. (15.80-15.87)), and energy (Eqs. (15.6-15.11), (15.17-15.65), and (15.165-15.166)) parameters of quinoline are given in Tables 15.310, 15.311, and 15.312, respectively. The total energy of quinoline given in Table 15.313 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.312 corresponding to functional-group composition of the molecule. The bond angle parameters of quinoline determined using Eqs. (15.88-15.117) are given in Table 15.314. The color scale, translucent view of the charge-density of quinoline comprising the concentric shells of atoms with the outer shell bridged by one or more $H_2$-type ellipsoidal MOs or joined with one or more hydrogen MOs is shown in Figure 15.53A.

Figure 15.53. (A) Color scale, translucent view of the charge-density of quinoline showing the orbitals of the atoms at their radii, the ellipsoidal surface of each $H$ or $H_2$-type ellipsoidal MO that transitions to the corresponding outer shell of the atom(s) participating in each bond, and the hydrogen nuclei (red, not to scale). (B) Chemical structure and atom designation of quinoline.

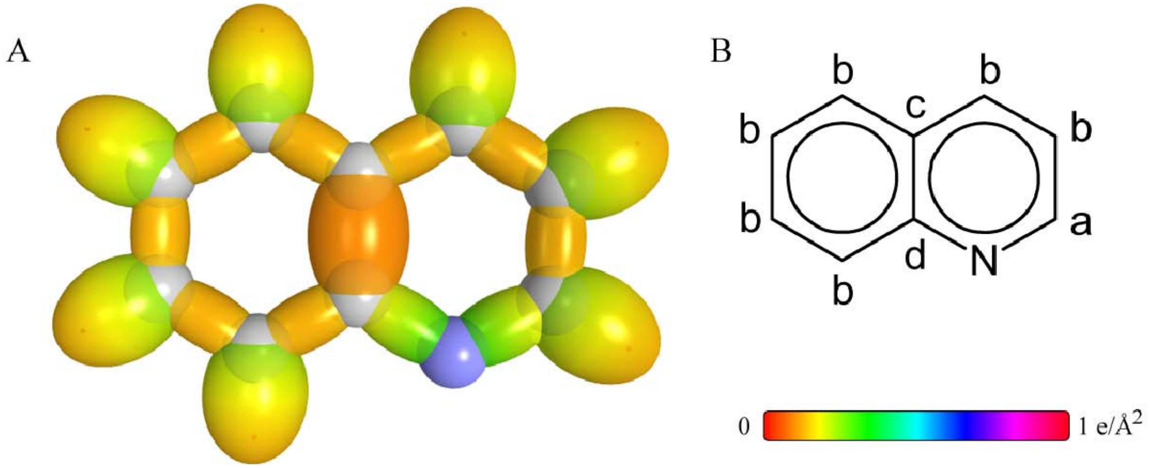


Table 15.309. The symbols of functional groups of quinoline.

| Functional Group | Group Symbol |
|---|---|
| $CC$ (aromatic bond) | $C\overset{3e}{=}C$ |
| $CH$ (aromatic) | $CH$ |
| $C_b - C_b$ (bridging bond) | $C-C$ |
| $C_{a,d}\overset{3e}{=}N$ | $C\overset{3e}{=}N$ |

Table 15.310. The geometrical bond parameters of quinoline and experimental values [1].

| Parameter | $C\overset{3e}{=}C$ Group | $CH$ Group | $C-C$ Group | $C\overset{3e}{=}N$ Group |
|---|---|---|---|---|
| $a\ (a_0)$ | 1.47348 | 1.60061 | 1.75607 | 1.47169 |
| $c'\ (a_0)$ | 1.31468 | 1.03299 | 1.32517 | 1.27073 |
| Bond Length $2c'\ (Å)$ | 1.39140 | 1.09327 | 1.40250 | 1.34489 |
| Exp. Bond Length $(Å)$ | 1.40 (avg.)<br>(naphthalene) | 1.101<br>(benzene) | 1.42<br>(naphthalene) | 1.340<br>(pyridine) |
| $b,c\ (a_0)$ | 0.66540 | 1.22265 | 1.15226 | 0.74237 |
| $e$ | 0.89223 | 0.64537 | 0.75462 | 0.86345 |

Table 15.311. The MO to HO intercept geometrical bond parameters of quinoline. $E_T$ is $E_T$ (*atom – atom,msp*$^3$.*AO*).

| Bond | Atom | $E_T$ (eV) Bond 1 | $E_T$ (eV) Bond 2 | $E_T$ (eV) Bond 3 | $E_T$ (eV) Bond 4 | Final Total Energy $C2sp^3$ (eV) | $r_{initial}$ $(a_0)$ | $r_{final}$ $(a_0)$ | $E_{Coulomb}(C2sp^3)$ (eV) Final | $E(C2sp^3)$ (eV) Final | $\theta'$ $(^\circ)$ | $\theta_1$ $(^\circ)$ | $\theta_2$ $(^\circ)$ | $d_1$ $(a_0)$ | $d_2$ $(a_0)$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $C-H\ (C_aH)$ | $C_a$ | -0.85035 | -0.54343 | -0.56690 | 0 | -153.57636 | 0.91771 | 0.81052 | -16.78642 | -16.59556 | 76.35 | 103.65 | 40.11 | 1.22423 | 0.19124 |
| $C-H\ (C_bH)$ | $C_b$ | -0.85035 | -0.85035 | -0.56690 | 0 | -153.88327 | 0.91771 | 0.79597 | -17.09334 | -16.90248 | 74.42 | 105.58 | 38.84 | 1.24678 | 0.21379 |
| $N(H)C_a \overset{3e}{=} C_b(H)$ | $C_a$ | -0.85035 | -0.54343 | -0.56690 | 0 | -153.57636 | 0.91771 | 0.81052 | -16.78642 | -16.59556 | 134.85 | 45.15 | 59.72 | 0.74304 | 0.57165 |
| $(H)C_b \overset{3e}{=} C_{a,b,c,d}(H)$ | $C_b$ | -0.85035 | -0.85035 | -0.56690 | 0 | -153.88327 | 0.91771 | 0.79597 | -17.09334 | -16.90248 | 134.24 | 45.76 | 58.98 | 0.75935 | 0.55533 |
| $(H)C_b(C_d)C_c \overset{3e}{=} C_b$ | $C_c$ | -0.85035 | -0.85035 | -0.28345 | 0 | -153.59983 | 0.91771 | 0.80939 | -16.80989 | -16.61903 | 134.81 | 45.19 | 59.66 | 0.74430 | 0.57038 |
| $N(C_c)C_d \overset{3e}{=} C_b$ | $C_d$ | -0.85035 | -0.54343 | -0.28345 | 0 | -153.29292 | 0.91771 | 0.82445 | -16.50298 | -16.31211 | 135.42 | 44.58 | 60.42 | 0.72743 | 0.58725 |
| $C_b(H)C_a \overset{3e}{=} N$ | $C_a$ | -0.85035 | -0.54343 | -0.56690 | 0 | -153.57636 | 0.91771 | 0.81052 | -16.78642 | -16.59556 | 128.54 | 51.46 | 58.65 | 0.76572 | 0.50501 |
| $C_b(H)C_a \overset{3e}{=} N$<br>$C_b(C_c)C_d \overset{3e}{=} N$ | $N$ | -0.54343 | -0.54343 | 0 | 0 |  | 0.93084 | 0.85503 | -15.91261 |  | 130.61 | 49.39 | 60.97 | 0.71418 | 0.55656 |
| $C_b(C_c)C_d \overset{3e}{=} N$ | $C_d$ | -0.85035 | -0.54343 | -0.28345 | 0 | -153.29291 | 0.91771 | 0.82445 | -16.50297 | -16.31211 | 129.21 | 50.79 | 59.38 | 0.74960 | 0.52113 |
| $\left((H)C_b \overset{3e}{=}\right)_2 C_c - C_d$ | $C_c$ | -0.85035 | -0.85035 | -0.28345 | 0 | -153.59983 | 0.91771 | 0.80939 | -16.80989 | -16.61903 | 95.01 | 84.99 | 44.41 | 1.25451 | 0.07066 |
| $N(C_b)C_d - C_c$ | $C_d$ | -0.85035 | -0.54343 | -0.28345 | 0 | -153.29292 | 0.91771 | 0.82445 | -16.50298 | -16.31211 | 96.31 | 83.69 | 45.33 | 1.23456 | 0.09061 |

Table 15.312. The energy parameters ($eV$) of functional groups of quinoline.

| Parameters | $\overset{3e}{C=C}$ Group | $CH$ Group | $C-C$ Group | $\overset{3e}{C=N}$ Group |
|---|---|---|---|---|
| $f_1$ | 0.75 | 1 | 1 | 0.75 |
| $n_1$ | 2 | 1 | 1 | 2 |
| $n_2$ | 0 | 0 | 0 | 0 |
| $n_3$ | 0 | 0 | 0 | 0 |
| $C_1$ | 0.5 | 0.75 | 0.5 | 0.5 |
| $C_2$ | 0.85252 | 1 | 1 | 0.91140 |
| $c_1$ | 1 | 1 | 1 | 1 |
| $c_2$ | 0.85252 | 0.91771 | 0.85252 | 0.91140 |
| $c_3$ | 0 | 1 | 0 | 0 |
| $c_4$ | 3 | 1 | 2 | 3 |
| $c_5$ | 0 | 1 | 0 | 0 |
| $C_{1o}$ | 0.5 | 0.75 | 0.5 | 0.5 |
| $C_{2o}$ | 0.85252 | 1 | 1 | 0.91140 |
| $V_e\ (eV)$ | -101.12679 | -37.10024 | -34.43791 | -102.01431 |
| $V_p\ (eV)$ | 20.69825 | 13.17125 | 10.26723 | 21.41410 |
| $T\ (eV)$ | 34.31559 | 11.58941 | 9.80539 | 34.65890 |
| $V_m\ (eV)$ | -17.15779 | -5.79470 | -4.90270 | -17.32945 |
| $E(_{AO/HO})\ (eV)$ | 0 | -14.63489 | -14.63489 | 0 |
| $\Delta E_{H_2MO}(_{AO/HO})\ (eV)$ | 0 | -1.13379 | -1.13379 | 0 |
| $E_T(_{AO/HO})\ (eV)$ | 0 | -13.50110 | -13.50110 | 0 |
| $E_T(_{H_2MO})\ (eV)$ | -63.27075 | -31.63539 | -31.63529 | -63.27076 |
| $E_T\left(atom-atom, msp^3.AO\right)\ (eV)$ | -2.26759 | -0.56690 | -0.56690 | -1.44915 |
| $E_T(_{MO})\ (eV)$ | -65.53833 | -32.20226 | -32.20226 | -64.71988 |
| $\omega\ \left(10^{15}\ rad/s\right)$ | 49.7272 | 26.4826 | 23.6343 | 43.6311 |
| $E_K\ (eV)$ | 32.73133 | 17.43132 | 15.55648 | 28.71875 |
| $\bar{E}_D\ (eV)$ | -0.35806 | -0.26130 | -0.25127 | -0.33540 |
| $\bar{E}_{Kvib}\ (eV)$ | 0.19649<br>[49] | 0.35532<br>Eq. (13.458) | 0.12312<br>[2] | 0.19649<br>[49] |
| $\bar{E}_{osc}\ (eV)$ | -0.25982 | -0.08364 | -0.18971 | -0.23715 |
| $E_{mag}\ (eV)$ | 0.14803 | 0.14803 | 0.14803 | 0.09457 |
| $E_T(_{Group})\ (eV)$ | -49.54347 | -32.28590 | -32.39198 | -48.82472 |
| $E_{initial}(_{c_4\ AO/HO})\ (eV)$ | -14.63489 | -14.63489 | -14.63489 | -14.63489 |
| $E_{initial}(_{c_5\ AO/HO})\ (eV)$ | 0 | -13.59844 | 0 | 0 |
| $E_D(_{Group})\ (eV)$ | 5.63881 | 3.90454 | 3.12220 | 4.92005 |

Table 15.313. The total bond energies of quinoline calculated using the functional group composition and the energies of Table 15.312 compared to the experimental values [3].

| Formula | Name | $\overset{3e}{C=C}$ | $CH$ | $C-C$ Group | $\overset{3e}{C=N}$ Group | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|---|---|---|---|
| $C_9H_7N$ | Quinoline | 8 | 7 | 1 | 2 | 85.40453 | 85.48607 | 0.00178 |

Table 15.314. The bond angle parameters of quinoline and experimental values [1]. $E_T$ is $E_T$ $(atom-atom,msp^3.AO)$.

| Atoms of Angle | $2c'$ Bond 1 $(a_0)$ | $2c'$ Bond 2 $(a_0)$ | $2c'$ Terminal Atoms $(a_0)$ | $E_{Coulombic}$ Atom 1 | Atom 1 Hybridization Designation (Table 15.3B) | $E_{Coulombic}$ Atom 2 | Atom 2 Hybridization Designation (Table 15.3B) | $c_2$ Atom 1 | $c_2$ Atom 2 | $C_1$ | $C_2$ | $c_1$ | $c_2'$ | $E_T$ (eV) | $\theta_v$ (°) | $\theta_1$ (°) | $\theta_2$ (°) | Cal. $\theta$ (°) | Exp. $\theta$ (°) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $\angle CCC$ | 2.62936 | 2.65034 | 4.5585 | -17.17218 | 27 | -17.17218 | 27 | 0.79232 | 0.79232 | 1 | 1 | 1 | 0.79232 | -1.85836 | | | | 119.40 | 119.4<br>(naphthalene) |
| $\angle CCH$ | | | | | | | | | | | | | | | | 119.40 | | 120.30 | |
| $\angle C_dNC_a$ | 2.54147 | 2.54147 | 4.3818 | -17.43216 | 31 | -17.71560 | 33 | 0.78050 | 0.76801 | 1 | 1 | 1 | 0.77426 | -1.85836 | | | | 119.10 | |

## ISOQUINOLINE

Isoquinoline has the formula $C_9H_7N$ and comprises the naphthalene molecule with one $CH$ group replaced by a nitrogen atom which gives rise to a $C\overset{3e}{=}N$ functional group. Isoquinoline is also equivalent to quinoline with the nitrogen in the meta rather than the ortho position relative to the benzene ring of the molecule. The aromatic $C\overset{3e}{=}C$ and $C-H$ functional groups are equivalent to those of naphthalene given in the corresponding section with the aromaticity maintained by the electrons from nitrogen in the $C\overset{3e}{=}N$ group which is also aromatic. The $C-C$ functional group is also equivalent to that of naphthalene. The bonding in isoquinoline can be further considered as a linear combination of the naphthalene and pyridine groups wherein the $C\overset{3e}{=}N$ group is equivalent to that of pyridine, pyrimidine, pyrazine, and quinoline as given in the corresponding sections.

The symbols of the functional groups of isoquinoline are given in Table 15.315. The corresponding designation of the structure is shown in Figure 15.54B. The geometrical (Eqs. (15.1-15.5) and (15.51)), intercept (Eqs. (15.80-15.87)), and energy (Eqs. (15.6-15.11), (15.17-15.65), and (15.165-15.166)) parameters of isoquinoline are given in Tables 15.316, 15.317, and 15.318, respectively. The total energy of isoquinoline given in Table 15.319 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.318 corresponding to functional-group composition of the molecule. The bond angle parameters of isoquinoline determined using Eqs. (15.88-15.117) are given in Table 15.320. The color scale, translucent view of the charge-density of isoquinoline comprising the concentric shells of atoms with the outer shell bridged by one or more $H_2$-type ellipsoidal MOs or joined with one or more hydrogen MOs is shown in Figure 15.54A.

Figure 15.54. (A) Color scale, translucent view of the charge-density of isoquinoline showing the orbitals of the atoms at their radii, the ellipsoidal surface of each $H$ or $H_2$-type ellipsoidal MO that transitions to the corresponding outer shell of the atom(s) participating in each bond, and the hydrogen nuclei (red, not to scale). (B) Chemical structure and atom designation of isoquinoline.

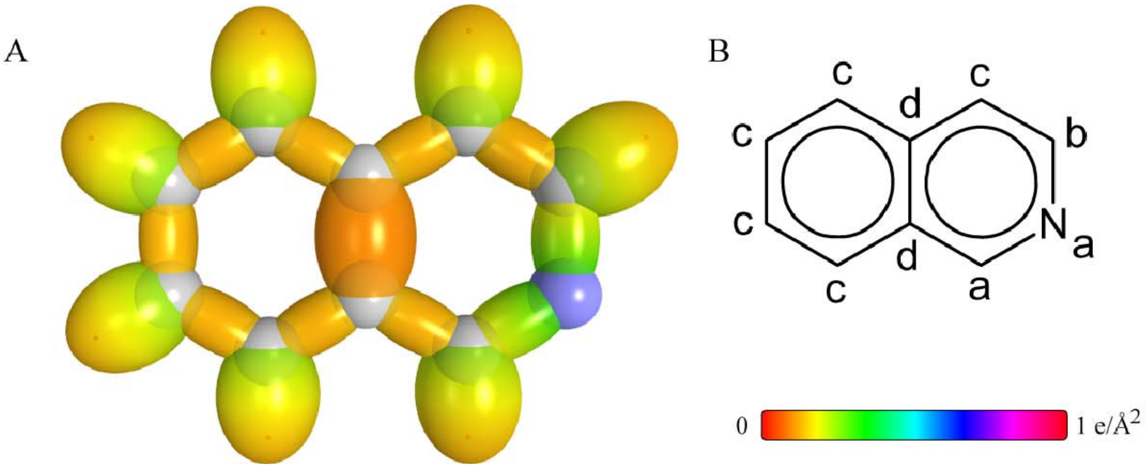


Table 15.315. The symbols of functional groups of isoquinoline.

| Functional Group | Group Symbol |
|---|---|
| $CC$ (aromatic bond) | $C\overset{3e}{=}C$ |
| $CH$ (aromatic) | $CH$ |
| $C_b - C_b$ (bridging bond) | $C-C$ |
| $C_{a,d}\overset{3e}{=}N$ | $C\overset{3e}{=}N$ |

Table 15.316. The geometrical bond parameters of isoquinoline and experimental values [1].

| Parameter | $C\overset{3e}{=}C$ Group | $CH$ Group | $C-C$ Group | $C\overset{3e}{=}N$ Group |
|---|---|---|---|---|
| $a\ (a_0)$ | 1.47348 | 1.60061 | 1.75607 | 1.47169 |
| $c'\ (a_0)$ | 1.31468 | 1.03299 | 1.32517 | 1.27073 |
| Bond Length $2c'\ (\AA)$ | 1.39140 | 1.09327 | 1.40250 | 1.34489 |
| Exp. Bond Length $(\AA)$ | 1.40 (avg.)<br>(naphthalene) | 1.101<br>(benzene) | 1.42<br>(naphthalene) | 1.340<br>(pyridine) |
| $b,c\ (a_0)$ | 0.66540 | 1.22265 | 1.15226 | 0.74237 |
| $e$ | 0.89223 | 0.64537 | 0.75462 | 0.86345 |

Table 15.317. The MO to HO intercept geometrical bond parameters of isoquinoline. $E_T$ is $E_T$ (*atom* – *atom,msp*$^3$.*AO*).

| Bond | Atom | $E_T$ (eV) Bond 1 | $E_T$ (eV) Bond 2 | $E_T$ (eV) Bond 3 | $E_T$ (eV) Bond 4 | Final Total Energy $C2sp^3$ (eV) | $r_{initial}$ $(a_0)$ | $r_{final}$ $(a_0)$ | $E_{Coulomb}(C2sp^3)$ (eV) Final | $E(C2sp^3)$ (eV) Final | $\theta'$ $(^\circ)$ | $\theta_1$ $(^\circ)$ | $\theta_2$ $(^\circ)$ | $d_1$ $(a_0)$ | $d_2$ $(a_0)$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $C-H\ (C_aH)$ | $C_a$ | -0.85035 | -0.54343 | -0.56690 | 0 | -153.57636 | 0.91771 | 0.81052 | -16.78642 | -16.59556 | 76.35 | 103.65 | 40.11 | 1.22423 | 0.19124 |
| $C-H\ (C_bH)$ | $C_b$ | -0.85035 | -0.54343 | -0.56690 | 0 | -153.57636 | 0.91771 | 0.81052 | -16.78642 | -16.59556 | 76.35 | 103.65 | 40.11 | 1.22423 | 0.19124 |
| $C-H\ (C_cH)$ | $C_c$ | -0.85035 | -0.85035 | -0.56690 | 0 | -153.88327 | 0.91771 | 0.79597 | -17.09334 | -16.90248 | 74.42 | 105.58 | 38.84 | 1.24678 | 0.21379 |
| $N(H)C_a\overset{3e}{=}C_d$<br>$N(H)C_b\overset{3e}{=}C_c$ | $C_a$<br>$C_b$ | -0.85035 | -0.54343 | -0.56690 | 0 | -153.57636 | 0.91771 | 0.81052 | -16.78642 | -16.59556 | 134.85 | 45.15 | 59.72 | 0.74304 | 0.57165 |
| $(H)C_c\overset{3e}{=}C_{b,c,d}(H)$ | $C_c$ | -0.85035 | -0.85035 | -0.56690 | 0 | -153.88327 | 0.91771 | 0.79597 | -17.09334 | -16.90248 | 134.24 | 45.76 | 58.98 | 0.75935 | 0.55533 |
| $(H)C_c(C_d)C_d\overset{3e}{=}C_{a,c}$ | $C_d$ | -0.85035 | -0.85035 | -0.28345 | 0 | -153.59983 | 0.91771 | 0.80939 | -16.80989 | -16.61903 | 134.81 | 45.19 | 59.66 | 0.74430 | 0.57038 |
| $C_d(H)C_a\overset{3e}{=}N$<br>$C_c(H)C_b\overset{3e}{=}N$ | $C_a$<br>$C_b$ | -0.85035 | -0.54343 | -0.56690 | 0 | -153.57636 | 0.91771 | 0.81052 | -16.78642 | -16.59556 | 128.54 | 51.46 | 58.65 | 0.76572 | 0.50501 |
| $C_d(H)C_a\overset{3e}{=}N$<br>$C_c(H)C_b\overset{3e}{=}N$ | $N$ | -0.54343 | -0.54343 | 0 | 0 |  | 0.93084 | 0.85503 | -15.91261 |  | 130.61 | 49.39 | 60.97 | 0.71418 | 0.55656 |
| $C_{a,c}(C_c)C_d-C_d$ | $C_d$ | -0.85035 | -0.85035 | -0.28345 | 0 | -153.59983 | 0.91771 | 0.80939 | -16.80989 | -16.61903 | 95.01 | 84.99 | 44.41 | 1.25451 | 0.07066 |

Table 15.318. The energy parameters ($eV$) of functional groups of isoquinoline.

| Parameters | $C\overset{3e}{=}C$ Group | $CH$ Group | $C-C$ Group | $C\overset{3e}{=}N$ Group |
|---|---|---|---|---|
| $f_1$ | 0.75 | 1 | 1 | 0.75 |
| $n_1$ | 2 | 1 | 1 | 2 |
| $n_2$ | 0 | 0 | 0 | 0 |
| $n_3$ | 0 | 0 | 0 | 0 |
| $C_1$ | 0.5 | 0.75 | 0.5 | 0.5 |
| $C_2$ | 0.85252 | 1 | 1 | 0.91140 |
| $c_1$ | 1 | 1 | 1 | 1 |
| $c_2$ | 0.85252 | 0.91771 | 0.85252 | 0.91140 |
| $c_3$ | 0 | 1 | 0 | 0 |
| $c_4$ | 3 | 1 | 2 | 3 |
| $c_5$ | 0 | 1 | 0 | 0 |
| $C_{1o}$ | 0.5 | 0.75 | 0.5 | 0.5 |
| $C_{2o}$ | 0.85252 | 1 | 1 | 0.91140 |
| $V_e\ (eV)$ | -101.12679 | -37.10024 | -34.43791 | -102.01431 |
| $V_p\ (eV)$ | 20.69825 | 13.17125 | 10.26723 | 21.41410 |
| $T\ (eV)$ | 34.31559 | 11.58941 | 9.80539 | 34.65890 |
| $V_m\ (eV)$ | -17.15779 | -5.79470 | -4.90270 | -17.32945 |
| $E(_{AO/HO})\ (eV)$ | 0 | -14.63489 | -14.63489 | 0 |
| $\Delta E_{H_2MO}(_{AO/HO})\ (eV)$ | 0 | -1.13379 | -1.13379 | 0 |
| $E_T(_{AO/HO})\ (eV)$ | 0 | -13.50110 | -13.50110 | 0 |
| $E_T(_{H_2MO})\ (eV)$ | -63.27075 | -31.63539 | -31.63529 | -63.27076 |
| $E_T\left(atom-atom,msp^3.AO\right)(eV)$ | -2.26759 | -0.56690 | -0.56690 | -1.44915 |
| $E_T(_{MO})\ (eV)$ | -65.53833 | -32.20226 | -32.20226 | -64.71988 |
| $\omega\ \left(10^{15}\ rad/s\right)$ | 49.7272 | 26.4826 | 23.6343 | 43.6311 |
| $E_K\ (eV)$ | 32.73133 | 17.43132 | 15.55648 | 28.71875 |
| $\bar{E}_D\ (eV)$ | -0.35806 | -0.26130 | -0.25127 | -0.33540 |
| $\bar{E}_{Kvib}\ (eV)$ | 0.19649<br>[49] | 0.35532<br>Eq. (13.458) | 0.12312<br>[2] | 0.19649<br>[49] |
| $\bar{E}_{osc}\ (eV)$ | -0.25982 | -0.08364 | -0.18971 | -0.23715 |
| $E_{mag}\ (eV)$ | 0.14803 | 0.14803 | 0.14803 | 0.09457 |
| $E_T(_{Group})\ (eV)$ | -49.54347 | -32.28590 | -32.39198 | -48.82472 |
| $E_{initial}(_{c_4\ AO/HO})\ (eV)$ | -14.63489 | -14.63489 | -14.63489 | -14.63489 |
| $E_{initial}(_{c_5\ AO/HO})\ (eV)$ | 0 | -13.59844 | 0 | 0 |
| $E_D(_{Group})\ (eV)$ | 5.63881 | 3.90454 | 3.12220 | 4.92005 |

Table 15.319. The total bond energies of isoquinoline calculated using the functional group composition and the energies of Table 15.318 compared to the experimental values [3].

| Formula | Name | $\overset{3e}{C=C}$ | $CH$ | $C-C$ Group | $\overset{3e}{C=N}$ Group | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|---|---|---|---|
| $C_9H_7N$ | Isoquinoline | 8 | 7 | 1 | 2 | 85.40453 | 85.44358 | 0.00046 |

Table 15.320. The bond angle parameters of isoquinoline and experimental values [1]. $E_T$ is $E_T$ ($atom-atom,msp^3.AO$).

| Atoms of Angle | $2c'$ Bond 1 $(a_0)$ | $2c'$ Bond 2 $(a_0)$ | $2c'$ Terminal Atoms $(a_0)$ | $E_{Coulombic}$ Atom 1 | Atom 1 Hybridization Designation (Table 15.3B) | $E_{Coulombic}$ Atom 2 | Atom 2 Hybridization Designation (Table 15.3B) | $c_2$ Atom 1 | $c_2$ Atom 2 | $C_1$ | $C_2$ | $c_1$ | $c_2'$ | $E_T$ (eV) | $\theta_v$ (°) | $\theta_1$ (°) | $\theta_2$ (°) | Cal. $\theta$ (°) | Exp. $\theta$ (°) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $\angle CCC$ | 2.62936 | 2.65034 | 4.5585 | -17.17218 | 27 | -17.17218 | 27 | 0.79232 | 0.79232 | 1 | 1 | 1 | 0.79232 | -1.85836 | | | | 119.40 | 119.4 (naphthalene) |
| $\angle CCH$ | | | | | | | | | | | | | | | | 119.40 | | 120.30 | |
| $\angle C_aNC_b$ | 2.54147 | 2.54147 | 4.3818 | -17.43216 | 31 | -17.71560 | 33 | 0.78050 | 0.76801 | 1 | 1 | 1 | 0.77426 | -1.85836 | | | | 119.10 | |

## INDOLE

Indole having the formula $C_8H_7N$ comprises a phenyl moiety with a conjugated five-membered ring which comprises pyrrole except that one of the double bonds is part of the aromatic ring. The structure is shown in Figure 15.55B. The aromatic $C\overset{3e}{=}C$ and $C-H$ functional groups of the phenyl moiety are equivalent to those of benzene given in the Aromatic and Heterocyclic Compounds section. The $CH$, $NH$, and $C_d=C_e$ groups of the pyrrole-type ring are equivalent to the corresponding groups of pyrrole, furan, and thiophene where present as given in the corresponding sections. The $C_b-C_d$ single bond of aryl carbon to the $C_d=C_e$ bond is also a functional group. This group is equivalent to the $C-C(O)$ group of benzoic acids with regard to $\Delta E_{H_2MO}(AO/HO)$ in Eq. (15.51) and $E_T\left(atom-atom,msp^3.AO\right)$ in Eq. (15.61) both being $-1.29147\ eV$. This energy is a linear combination of $\frac{-1.13379\ eV}{2}$, $E_T\left(atom-atom,msp^3.AO\right)$ of the $C-H$ group that the $C_b-C_d$ and $C-C(O)$ groups replace, and that of an independent $C2sp^3$ HO, $-0.72457\ eV$ (Eq. (14.151)). However, as in the case of pyrrole, the indole hybridization term $c_2$ is the aromatic $c_2\left(benzeneC2sp^3HO\right)=0.85252$ to match the aryl $C2sp^3$ HO, and the energy terms corresponding to oscillation in the transition state correspond to indole.

As in the case of pyrrole, the $C-N-C$-bond MO comprising a linear combination of two single bonds is solved in the same manner as a double bond with $n_1=2$ in Eqs. (15.51) and (15.61). The hybridization factor $c_2\left(arylC2sp^3HO\ to\ N\right)=0.84665$ (Eq. (15.171)) matches the aromatic character of the $C2sp^3$ HOs to the $N$ atom of the $NH$ group, and $C_2$ and $C_{2o}$ in Eqs. (15.51) and (15.61) become that of benzene given by Eq. (15.162), $C_2\left(benzeneC2sp^3HO\right)=0.85252$. Furthermore, $\Delta E_{H_2MO}(AO/HO)$ in Eq. (15.51) and $E_T\left(atom-atom,msp^3.AO\right)$ in Eq. (15.61) are both $-2.42526\ eV$ which is a linear combination of $\frac{-1.13379\ eV}{2}$, $E_T\left(atom-atom,msp^3.AO\right)$ of the $C-H$ group that the $C_c-N$ bond replaces, and $-1.85836\ eV$ (Eq. (14.513)) which is equivalent to the corresponding component of the $C-N-C$-bond of pyrrole.

The symbols of the functional groups of indole are given in Table 15.321. The geometrical (Eqs. (15.1-15.5) and (15.51)), intercept (Eqs. (15.80-15.87)), and energy (Eqs. (15.6-15.11) and (15.17-15.65)) parameters of indole are given in Tables 15.322, 15.323, and 15.324, respectively. The total energy of indole given in Table 15.325 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.324 corresponding to functional-group composition of the molecule. The bond angle parameters of indole determined using Eqs. (15.88-15.117) are given in Table 15.326. The color scale, translucent view of the charge-density of indole comprising the concentric shells of atoms with the outer shell bridged by one or more $H_2$-type ellipsoidal MOs or joined with one or more hydrogen MOs is shown in Figure 15.55A.

Figure 15.55. (A) Color scale, translucent view of the charge-density of indole showing the orbitals of the atoms at their radii, the ellipsoidal surface of each $H$ or $H_2$-type ellipsoidal MO that transitions to the corresponding outer shell of the atom(s) participating in each bond, and the hydrogen nuclei (red, not to scale). (B) Chemical structure and atom designation of indole.

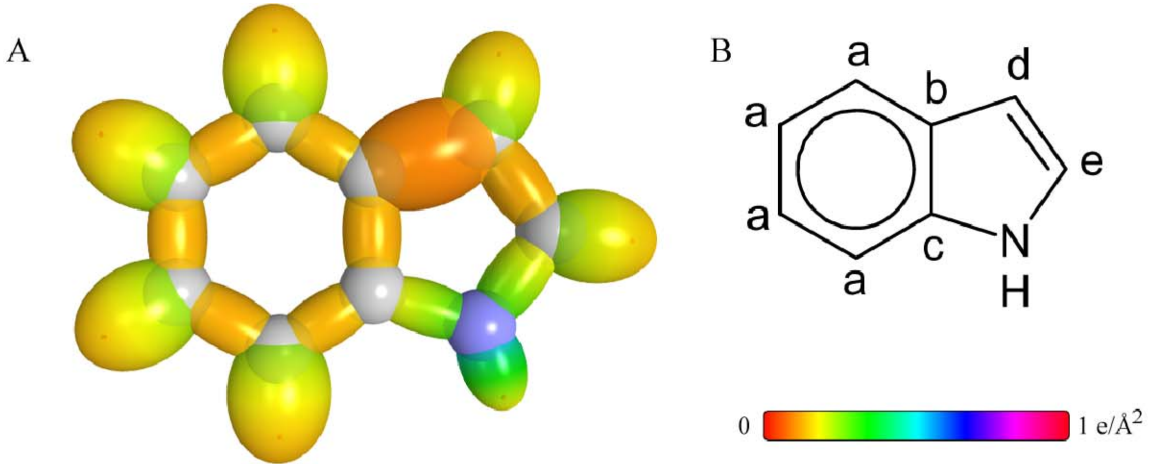


Table 15.321. The symbols of functional groups of indole.

| Functional Group | Group Symbol |
|---|---|
| $CC$ (aromatic bond) | $C\overset{3e}{=}C$ |
| $CH$ (aromatic) | $CH$ (i) |
| $C_d = C_e$ double bond | $C = C$ |
| $C_b - C_d$ | $C - C$ |
| $CH$ | $CH$ (ii) |
| $C_c - N - C_e$ | $C - N - C$ |
| $NH$ group | $NH$ |

Table 15.322. The geometrical bond parameters of indole and experimental values [1].

| Parameter | $C\overset{3e}{=}C$ Group | $CH$ (i) Group | $C=C$ Group | $CH$ (ii) Group | $C-C$ Group | $C-N-C$ Group | $NH$ Group |
|---|---|---|---|---|---|---|---|
| $a\ (a_0)$ | 1.47348 | 1.60061 | 1.45103 | 1.53380 | 1.81395 | 1.44394 | 1.24428 |
| $c'\ (a_0)$ | 1.31468 | 1.03299 | 1.30463 | 1.01120 | 1.34683 | 1.30144 | 0.94134 |
| Bond Length $2c'$ ($\AA$) | 1.39140 | 1.09327 | 1.38076 | 1.07021 | 1.42542 | 1.37738 | 0.996270 |
| Exp. Bond Length ($\AA$) | 1.399 (benzene) | 1.101 (benzene) | 1.382 (pyrrole) | 1.076 (pyrrole | 1.417 (pyrrole) | 1.370 (pyrrole) | 0.996 (pyrrole) |
| $b,c\ (a_0)$ | 0.66540 | 1.22265 | 0.63517 | 1.15326 | 1.21510 | 0.62548 | 0.81370 |
| $e$ | 0.89223 | 0.64537 | 0.89910 | 0.65928 | 0.74248 | 0.90131 | 0.75653 |

Table 15.323. The MO to HO intercept geometrical bond parameters of indole. $R_1$ is an alkyl group and $R$, $R'$, $R''$ are $H$ or alkyl groups. $E_T$ is $E_T$ ($atom - atom, msp^3.AO$).

| Bond | Atom | $E_T$ (eV) Bond 1 | $E_T$ (eV) Bond 2 | $E_T$ (eV) Bond 3 | $E_T$ (eV) Bond 4 | Final Total Energy $C2sp^3$ (eV) | $r_{initial}$ $(a_0)$ | $r_{final}$ $(a_0)$ | $E_{Coulomb}(C2sp^3)$ (eV) Final | $E(C2sp^3)$ (eV) Final | $\theta'$ $(°)$ | $\theta_1$ $(°)$ | $\theta_2$ $(°)$ | $d_1$ $(a_0)$ | $d_2$ $(a_0)$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $C-H\ (C_aH)$ | $C_a$ | -0.85035 | -0.85035 | -0.56690 | 0 | -153.88327 | 0.91771 | 0.79597 | -17.09334 | -16.90248 | 74.42 | 105.58 | 38.84 | 1.24678 | 0.21379 |
| $C_a \overset{3e}{=} HC_a \overset{3e}{=} C_{a,b,c}$ | $C_a$ | -0.85035 | -0.85035 | -0.56690 | 0 | -153.88327 | 0.91771 | 0.79597 | -17.09334 | -16.90248 | 134.24 | 45.76 | 58.98 | 0.75935 | 0.55533 |
| $C_a \overset{3e}{=} (C_d)C_b \overset{3e}{=} C_c$<br>$C_c \overset{3e}{=} (C_d)C_b \overset{3e}{=} C_a$ | $C_b$ | -0.85035 | -0.64574 | -0.85035 | 0 | -153.96212 | 0.91771 | 0.79232 | -17.17218 | -16.98132 | 134.09 | 45.91 | 58.79 | 0.76344 | 0.55124 |
| $C_a \overset{3e}{=} C_c(N)C_b$<br>$C_b \overset{3e}{=} C_c(N)C_a$ | $C_c$ | -0.60631 | -0.85035 | -0.85035 | 0 | -153.92270 | 0.91771 | 0.79414 | -17.13276 | -16.94190 | 134.16 | 45.84 | 58.89 | 0.76140 | 0.55328 |
| $C_a(H)C_b - C_d(H)C_e$ | $C_b$ | -0.85035 | -0.85035 | -0.64574 | 0 | -153.96212 | 0.91771 | 0.79232 | -17.17218 | -16.98132 | 87.89 | 92.11 | 40.66 | 1.37597 | 0.02914 |
| $C_a(H)C_b - C_d(H)C_e$ | $C_d$ | -0.64574 | -1.13379 | 0 | 0 | -153.39522 | 0.91771 | 0.81937 | -16.60528 | -16.41442 | 90.51 | 89.49 | 42.40 | 1.33953 | 0.00729 |
| $C_b(H)C_d = C_eN$ | $C_d$ | -0.64574 | -1.13379 | 0 | 0 | -153.39522 | 0.91771 | 0.81937 | -16.60528 | -16.41442 | 137.29 | 42.71 | 61.04 | 0.70255 | 0.60208 |
| $C_b(H)C_d = C_eN$ | $C_e$ | -1.13379 | -0.60631 | 0 | 0 | -153.35580 | 0.91771 | 0.82132 | -16.56586 | -16.37500 | 137.37 | 42.63 | 61.14 | 0.70038 | 0.60425 |
| $C_dC_e - NC_c$ | $C_e$ | -1.13379 | -0.60631 | 0 | 0 | -153.35580 | 0.91771 | 0.82132 | -16.56586 | -16.37500 | 138.03 | 41.97 | 61.42 | 0.69080 | 0.61064 |
| $C_dC_e - NC_c$<br>$C_aC_c - NC_e$ | $N$ | -0.60631 | -0.60631 | 0 | 0 |  | 0.93084 | 0.84833 | -16.03838 |  | 139.04 | 40.96 | 62.76 | 0.66083 | 0.64061 |
| $N-H\ (NH)$ | $N$ | -0.60631 | -0.60631 | 0 | 0 |  | 0.93084 | 0.84833 | -16.03838 |  | 119.52 | 60.48 | 65.13 | 0.52338 | 0.41796 |
| $C_aC_c - NC_e$ | $C_c$ | -0.85035 | -0.85035 | -0.60631 | 0 | -153.92269 | 0.91771 | 0.79414 | -17.13276 | -16.94189 | 136.97 | 43.03 | 60.05 | 0.72095 | 0.58048 |

Table 15.324. The energy parameters ($eV$) of functional groups of indole.

| Parameters | $\overset{3e}{C=C}$ Group | $CH$ (i) Group | $C=C$ Group | $C-C$ Group | $CH$ (ii) Group | $C-N-C$ Group | $NH$ Group |
|---|---|---|---|---|---|---|---|
| $f_1$ | 0.75 | 1 | 1 | 1 | 1 | 1 | 1 |
| $n_1$ | 2 | 1 | 2 | 1 | 1 | 2 | 1 |
| $n_2$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $n_3$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $C_1$ | 0.5 | 0.75 | 0.5 | 0.5 | 0.75 | 0.5 | 0.75 |
| $C_2$ | 0.85252 | 1 | 0.85252 | 1 | 1 | 0.85252 | 0.93613 |
| $c_1$ | 1 | 1 | 1 | 1 | 1 | 1 | 0.75 |
| $c_2$ | 0.85252 | 0.91771 | 0.85252 | 0.85252 | 0.91771 | 0.84665 | 0.92171 |
| $c_3$ | 0 | 1 | 0 | 0 | 1 | 0 | 1 |
| $c_4$ | 3 | 1 | 4 | 2 | 1 | 4 | 1 |
| $c_5$ | 0 | 1 | 0 | 0 | 1 | 0 | 1 |
| $C_{1o}$ | 0.5 | 0.75 | 0.5 | 0.5 | 0.75 | 0.5 | 0.75 |
| $C_{2o}$ | 0.85252 | 1 | 0.85252 | 1 | 1 | 0.85252 | 1 |
| $V_e\ (eV)$ | -101.12679 | -37.10024 | -104.37986 | -32.93291 | -39.09538 | -104.73877 | -39.48897 |
| $V_p\ (eV)$ | 20.69825 | 13.17125 | 20.85777 | 10.10210 | 13.45505 | 20.90891 | 14.45367 |
| $T\ (eV)$ | 34.31559 | 11.58941 | 35.96751 | 9.07768 | 12.74462 | 36.26840 | 15.86820 |
| $V_m\ (eV)$ | -17.15779 | -5.79470 | -17.98376 | -4.53884 | -6.37231 | -18.13420 | -7.93410 |
| $E(_{AO/HO})\ (eV)$ | 0 | -14.63489 | 0 | -14.63489 | -14.63489 | 0 | -14.53414 |
| $\Delta E_{H_2MO}(_{AO/HO})\ (eV)$ | 0 | -1.13379 | -2.26759 | -1.29147 | -2.26758 | -2.42526 | 0 |
| $E_T(_{AO/HO})\ (eV)$ | 0 | -13.50110 | 2.26759 | -13.34342 | -12.36731 | 2.42526 | -14.53414 |
| $E_T(_{H_2MO})\ (eV)$ | -63.27075 | -31.63539 | -63.27075 | -31.63539 | -31.63533 | -63.27040 | -31.63534 |
| $E_T\left(atom-atom, msp^3.AO\right)\ (eV)$ | -2.26759 | -0.56690 | -2.26759 | -1.29147 | 0 | -2.42526 | 0 |
| $E_T(_{MO})\ (eV)$ | -65.53833 | -32.20226 | -65.53833 | -32.92684 | -31.63537 | -65.69600 | -31.63537 |
| $\omega\ \left(10^{15}\ rad/s\right)$ | 49.7272 | 26.4826 | 15.4421 | 21.8249 | 28.9084 | 54.5632 | 48.7771 |
| $E_K\ (eV)$ | 32.73133 | 17.43132 | 10.16428 | 14.36554 | 19.02803 | 35.91442 | 32.10594 |
| $\bar{E}_D\ (eV)$ | -0.35806 | -0.26130 | -0.20668 | -0.24690 | -0.27301 | -0.38945 | -0.35462 |
| $\bar{E}_{Kvib}\ (eV)$ | 0.19649<br>[49] | 0.35532<br>Eq. (13.458) | 0.17897<br>[6] | 0.12312<br>[2] | 0.39427<br>[57] | 0.11159<br>[12] | 0.40696<br>[24] |
| $\bar{E}_{osc}\ (eV)$ | -0.25982 | -0.08364 | -0.11720 | -0.18534 | -0.07587 | -0.33365 | -0.15115 |
| $E_{mag}\ (eV)$ | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 |
| $E_T(_{Group})\ (eV)$ | -49.54347 | -32.28590 | -65.77272 | -33.11218 | -31.71124 | -66.36330 | -31.78651 |
| $E_{initial}(_{c_4\ AO/HO})\ (eV)$ | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.53414 |
| $E_{initial}(_{c_5\ AO/HO})\ (eV)$ | 0 | -13.59844 | 0 | 0 | -13.59844 | 0 | -13.59844 |
| $E_D(_{Group})\ (eV)$ | 5.63881 | 3.90454 | 7.23317 | 3.84240 | 3.32988 | 7.82374 | 3.51208 |

Table 15.325. The total bond energies of indole calculated using the functional group composition and the energies of Table 15.324 compared to the experimental values [3].

| Formula | Name | $\overset{3e}{C=C}$ | $CH$ (i) | $C=C$ | $C-C$ | $CH$ (ii) | $C-N-C$ | $NH$ | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $C_8H_7N$ | Indole | 6 | 4 | 1 | 1 | 2 | 1 | 1 | 78.52215 | 78.514 | -0.00010 |

Table 15.326. The bond angle parameters of indole and experimental values [1]. In the calculation of $\theta_v$, the parameters from the preceding angle were used. $E_T$ is $E_T$ $(atom - atom, msp^3.AO)$.

| Atoms of Angle | 2$c'$ Bond 1 ($a_0$) | 2$c'$ Bond 2 ($a_0$) | 2$c'$ Terminal Atoms ($a_0$) | $E_{Coulombic}$ Atom 1 | Atom 1 Hybridization Designation (Table 15.3B) | $E_{Coulombic}$ Atom 2 | Atom 2 Hybridization Designation (Table 15.3B) | $c_2$ Atom 1 | $c_2$ Atom 2 | $C_1$ | $C_2$ | $c_1$ | $c_2'$ | $E_T$ (eV) | $\theta_v$ (°) | $\theta_1$ (°) | $\theta_2$ (°) | Cal. $\theta$ (°) | Exp. $\theta$ (°) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $\angle CCC$ (aromatic) | 2.62936 | 2.62936 | 4.5585 | -17.17218 | 27 | -17.17218 | 27 | 0.79232 | 0.79232 | 1 | 1 | 1 | 0.79232 | -1.85836 | | | | 120.19 | 120 [50-52] (benzene) |
| $\angle CCH$ (aromatic) | | | | | | | | | | | | | | | | 120.19 | | 119.91 | 120 [50-52] (benzene) |

## ADENINE

Adenine having the formula $C_5H_5N_5$ comprises a pyrimidine moiety with an aniline-type moiety and a conjugated five-membered ring, which comprises imidazole except that one of the double bonds is part of the aromatic ring. The structure is shown in Figure 15.56B. The aromatic $C\overset{3e}{=}C$, $C-H$, and $C\overset{3e}{=}N$ functional groups of the pyrimidine moiety are equivalent to those of pyrimidine as given in the corresponding section. The $CH$, $NH$, $C_d-N_e$, and $N_e=C_e$ groups of the imidazole-type ring are equivalent to the corresponding groups of imidazole as given in the corresponding section. The $C-N-C$ functional group of the imidazole-type ring is equivalent to the corresponding group of indole having the same structure with the $C-N-C$ group bonding to aryl and alkenyl groups. The $NH_2$ and $C_a-N_a$ functional groups of the aniline-type moiety are equivalent to those of aniline as given in the corresponding section except that $\Delta E_{H_2MO}\left(AO/HO\right)$ of the $C_a-N_a$ group is equal to twice $E_T\left(atom-atom,msp^3.AO\right)$, and to meet the equipotential condition of the union of the $C-N$ $H_2$-type-ellipsoidal-MO with these orbitals, the hybridization factor $c_2$ of Eq. (15.60) for the $C-N$-bond MO given by Eqs. (15.77), (15.79), and (15.162) is:

$$c_2\left(arylC2sp^3HO\ to\ N\right)=\frac{E\left(N\right)}{E\left(C,2sp^3\right)}c_2\left(arylC2sp^3HO\right)=\frac{-14.53414\ eV}{-15.95955\ eV}\left(0.85252\right)=0.77638 \tag{15.173}$$

The symbols of the functional groups of adenine are given in Table 15.327. The geometrical (Eqs. (15.1-15.5) and (15.51)), intercept (Eqs. (15.80-15.87)), and energy (Eqs. (15.6-15.11) and (15.17-15.65)) parameters of adenine are given in Tables 15.328, 15.329, and 15.330, respectively. The total energy of adenine given in Table 15.331 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.330 corresponding to functional-group composition of the molecule. The bond angle parameters of adenine determined using Eqs. (15.88-15.117) are given in Table 15.332. The color scale, charge-density of adenine comprising atoms with the outer shell bridged by one or more $H_2$-type ellipsoidal MOs or joined with one or more hydrogen MOs is shown in Figure 15.56A.

Figure 15.56. (A) Color scale, charge-density of adenine showing the orbitals of the atoms at their radii, the ellipsoidal surface of each $H$ or $H_2$-type ellipsoidal MO that transitions to the corresponding outer shell of the atom(s) participating in each bond, and the hydrogen nuclei. (B) Chemical structure and atomic designation of adenine.

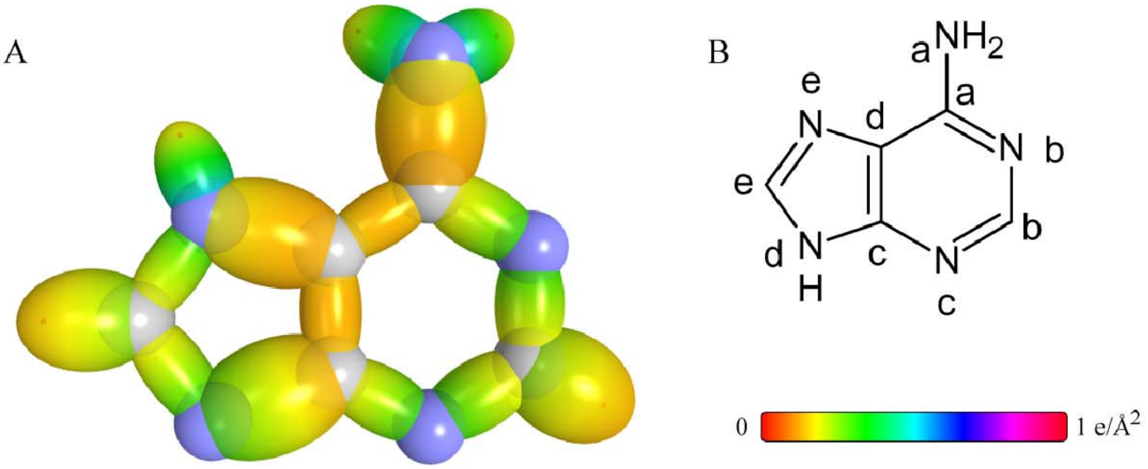


Table 15.327. The symbols of functional groups of adenine.

| Functional Group | Group Symbol |
|---|---|
| $CC$ (aromatic bond) | $C\overset{3e}{=}C$ |
| $CH$ (aromatic) | $CH$ (i) |
| $C_{b,c}\overset{3e}{=}N_c$ $\quad C_{a,b}\overset{3e}{=}N_b$ | $C\overset{3e}{=}N$ |
| $C_a-N_a$ | $C-N$ (a) |
| $NH_2$ group | $NH_2$ |
| $N_e=C_e$ double bond | $N=C$ |
| $C_d-N_e$ | $C-N$ (b) |
| $N_dH$ group | $NH$ |
| $CH$ | $CH$ (ii) |
| $C_c-N_d-C_e$ | $C-N-C$ |

Table 15.328. The geometrical bond parameters of adenine and experimental values [1].

| Parameter | $\overset{3e}{C=C}$ Group | $CH$ (i) Group | $\overset{3e}{C=N}$ Group | $C-N$ (a) Group | $NH_2$ Group | $N=C$ Group | $C-N$ (b) Group | $NH$ Group | $CH$ (ii) Group | $C-N-C$ Group |
|---|---|---|---|---|---|---|---|---|---|---|
| $a$ $(a_0)$ | 1.47348 | 1.60061 | 1.47169 | 1.61032 | 1.24428 | 1.44926 | 1.82450 | 1.24428 | 1.53380 | 1.44394 |
| $c'$ $(a_0)$ | 1.31468 | 1.03299 | 1.27073 | 1.26898 | 0.94134 | 1.30383 | 1.35074 | 0.94134 | 1.01120 | 1.30144 |
| Bond Length $2c'$ $(\AA)$ | 1.39140 | 1.09327 | 1.34489 | 1.34303 | 0.99627 | 1.37991 | 1.42956 | 0.996270 | 1.07021 | 1.37738 |
| Exp. Bond Length $(\AA)$ | 1.393 (pyrimidine) | 1.084 (pyridine) | 1.340 (pyrimidine) | 1.34 [64] (adenine) | 0.998 (aniline) | | | 0.996 (pyrrole) | 1.076 (pyrrole) | 1.370 (pyrrole) |
| $b,c$ $(a_0)$ | 0.66540 | 1.22265 | 0.74237 | 0.99137 | 0.81370 | 0.63276 | 1.22650 | 0.81370 | 1.15326 | 0.62548 |
| $e$ | 0.89223 | 0.64537 | 0.86345 | 0.78803 | 0.75653 | 0.89965 | 0.74033 | 0.75653 | 0.65928 | 0.90131 |

Table 15.329. The MO to HO intercept geometrical bond parameters of adenine. $R_1$ is an alkyl group and $R$, $R'$, $R''$ are $H$ or alkyl groups. $E_T$ is $E_T$ (*atom* – *atom,msp*$^3$*.AO*).

| Bond | Atom | $E_T$ (eV) Bond 1 | $E_T$ (eV) Bond 2 | $E_T$ (eV) Bond 3 | $E_T$ (eV) Bond 4 | Final Total Energy $C2sp^3$ (eV) | $r_{initial}$ $(a_0)$ | $r_{final}$ $(a_0)$ | $E_{Coulomb}(C2sp^3)$ (eV) Final | $E(C2sp^3)$ (eV) Final | $\theta'$ (°) | $\theta_1$ (°) | $\theta_2$ (°) | $d_1$ $(a_0)$ | $d_2$ $(a_0)$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $C_d(N_b)C_aN_aH-H$ | $N_a$ | -0.56690 | 0 | 0 | 0 | | 0.93084 | 0.88392 | -15.39265 | | 121.74 | 58.26 | 67.49 | 0.47634 | 0.46500 |
| $C_d(N_b)C_a-N_aH_2$ | $C_a$ | -0.56690 | -0.54343 | -0.85035 | 0 | -153.57636 | 0.91771 | 0.81052 | -16.78642 | -16.59556 | 108.27 | 71.73 | 50.93 | 1.01493 | 0.25406 |
| $C_d(N_b)C_a-N_aH_2$ | $N_a$ | -0.56690 | 0 | 0 | 0 | | 0.93084 | 0.88392 | -15.39265 | | 113.13 | 66.87 | 55.08 | 0.92180 | 0.34719 |
| $C-H$ $(C_bH)$ | $C_b$ | -0.54343 | -0.54343 | -0.56690 | 0 | -153.26945 | 0.91771 | 0.82562 | -16.47951 | -16.28864 | 78.27 | 101.73 | 41.39 | 1.20084 | 0.16785 |
| $C-H$ $(C_eH)$ | $C_e$ | -0.92918 | -0.60631 | 0 | 0 | -153.15119 | 0.91771 | 0.83159 | -16.36125 | -16.17038 | 86.28 | 93.72 | 46.02 | 1.06512 | 0.05392 |
| $N-H$ $(N_dH)$ | $N$ | -0.60631 | -0.60631 | 0 | 0 | | 0.93084 | 0.84833 | -16.03838 | | 119.52 | 60.48 | 65.13 | 0.52338 | 0.41796 |
| $C_d(NH_2)C_a\overset{3e}{=}N_bC_b$ | $C_a$ | -0.85035 | -0.54343 | -0.56690 | 0 | -153.57636 | 0.91771 | 0.81052 | -16.78642 | -16.59556 | 128.54 | 51.46 | 58.65 | 0.76572 | 0.50501 |
| $C_d(NH_2)C_a\overset{3e}{=}N_bC_b$<br>$N_bC_b\overset{3e}{=}N_cC_c$ | $N_b$<br>$N_c$ | -0.54343 | -0.54343 | 0 | 0 | | 0.93084 | 0.85503 | -15.91261 | | 130.61 | 49.39 | 60.97 | 0.71418 | 0.55656 |
| $N_bC_b\overset{3e}{=}N_cC_c$<br>$C_aN_b\overset{3e}{=}C_bN_c$ | $C_b$ | -0.54343 | -0.54343 | -0.56690 | 0 | -153.26945 | 0.91771 | 0.82562 | -16.47951 | -16.28865 | 129.26 | 50.74 | 59.44 | 0.74824 | 0.52249 |
| $C_d(N_dH)C_c\overset{3e}{=}N_cC_b$ | $C_c$ | -0.85035 | -0.54343 | -0.60631 | 0 | -153.61578 | 0.91771 | 0.80863 | -16.82584 | -16.63498 | 128.45 | 51.55 | 58.55 | 0.76792 | 0.50281 |
| $N_b(N_aH_2)C_a\overset{3e}{=}C_d(N_e)C_c$ | $C_a$ | -0.85035 | -0.54343 | -0.56690 | 0 | -153.57636 | 0.91771 | 0.81052 | -16.78642 | -16.59556 | 134.85 | 45.15 | 59.72 | 0.74304 | 0.57165 |
| $N_b(N_aH_2)C_a\overset{3e}{=}C_d(N_e)C_c$<br>$C_a(N_e)C_d\overset{3e}{=}C_c(N_dH)N_c$ | $C_d$ | -0.85035 | -0.85035 | -0.46459 | 0 | -153.78097 | 0.91771 | 0.80076 | -16.99103 | -16.80017 | 134.44 | 45.56 | 59.22 | 0.75398 | 0.56071 |
| $C_a(N_e)C_d\overset{3e}{=}C_c(N_dH)N_c$ | $C_c$ | -0.85035 | -0.54343 | -0.60631 | 0 | -153.61578 | 0.91771 | 0.80863 | -16.82584 | -16.63498 | 134.77 | 45.23 | 59.62 | 0.74516 | 0.56952 |
| $C_d(N_c)C_c-N_dH$ | $C_c$ | -0.85035 | -0.54343 | -0.60631 | 0 | -153.61578 | 0.91771 | 0.80863 | -16.82584 | -16.63498 | 137.54 | 42.46 | 60.78 | 0.70488 | 0.59656 |
| $C_e(H)N_d-C_c(N_c)C_d$<br>$N_e(H)C_e-N_d(H)C_c$ | $N_d$ | -0.60631 | -0.60631 | 0 | 0 | | 0.93084 | 0.84833 | -16.03838 | | 139.04 | 40.96 | 62.76 | 0.66083 | 0.64061 |
| $N_e(H)C_e-N_d(H)C_c$ | $C_e$ | -0.60631 | -0.92918 | 0 | 0 | -153.15119 | 0.91771 | 0.83159 | -16.36125 | -16.17039 | 138.42 | 41.58 | 61.93 | 0.67940 | 0.62203 |
| $C_dN_e=C_e(H)N_dH$ | $C_e$ | -0.92918 | -0.60631 | 0 | 0 | -153.15119 | 0.91771 | 0.83159 | -16.36125 | -16.17039 | 137.93 | 42.07 | 61.72 | 0.68657 | 0.61726 |
| $C_dN_e=C_e(H)N_dH$ | $N_e$ | -0.92918 | -0.46459 | 0 | 0 | | 0.93084 | 0.83885 | -16.21952 | | 138.20 | 41.80 | 62.08 | 0.67849 | 0.62534 |
| $C_a(C_c)C_d-N_eC_e$ | $N_e$ | -0.46459 | -0.92918 | 0 | 0 | | 0.93084 | 0.83885 | -16.21952 | | 91.32 | 88.68 | 43.14 | 1.33135 | 0.01939 |
| $C_a(C_c)C_d-N_eC_e$ | $C_d$ | -0.46459 | -0.85035 | -0.85035 | 0 | -153.78097 | 0.91771 | 0.80076 | -16.99103 | -16.80017 | 87.71 | 92.29 | 40.72 | 1.38280 | 0.03206 |

Table 15.330. The energy parameters ($eV$) of functional groups of adenine.

| Parameters | $\overset{3e}{C=C}$ Group | $CH$ (i) Group | $\overset{3e}{C=N}$ Group | $C-N$ (a) Group | $NH_2$ Group | $N=C$ Group | $C-N$ (b) Group | $NH$ Group | $CH$ (ii) Group | $C-N-C$ Group |
|---|---|---|---|---|---|---|---|---|---|---|
| $f_1$ | 0.75 | 1 | 0.75 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $n_1$ | 2 | 1 | 2 | 1 | 2 | 2 | 1 | 1 | 1 | 2 |
| $n_2$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $n_3$ | 0 | 0 | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 0 |
| $C_1$ | 0.5 | 0.75 | 0.5 | 0.5 | 0.75 | 0.5 | 0.5 | 0.75 | 0.75 | 0.5 |
| $C_2$ | 0.85252 | 1 | 0.91140 | 1 | 0.93613 | 0.85252 | 1 | 0.93613 | 1 | 0.85252 |
| $c_1$ | 1 | 1 | 1 | 1 | 0.75 | 1 | 1 | 0.75 | 1 | 1 |
| $c_2$ | 0.85252 | 0.91771 | 0.91140 | 0.84665 | 0.92171 | 0.84665 | 0.84665 | 0.92171 | 0.91771 | 0.84665 |
| $c_3$ | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 1 | 1 | 0 |
| $c_4$ | 3 | 1 | 3 | 2 | 1 | 4 | 2 | 1 | 1 | 4 |
| $c_5$ | 0 | 1 | 0 | 0 | 2 | 0 | 0 | 1 | 1 | 0 |
| $C_{1o}$ | 0.5 | 0.75 | 0.5 | 0.5 | 1.5 | 0.5 | 0.5 | 0.75 | 0.75 | 0.5 |
| $C_{2o}$ | 0.85252 | 1 | 0.91140 | 1 | 1 | 0.85252 | 1 | 1 | 1 | 0.85252 |
| $V_e\ (eV)$ | -101.12679 | -37.10024 | -102.01431 | -35.50149 | -78.97795 | -103.92756 | -32.44864 | -39.48897 | -39.09538 | -104.73877 |
| $V_p\ (eV)$ | 20.69825 | 13.17125 | 21.41410 | 10.72181 | 28.90735 | 20.87050 | 10.07285 | 14.45367 | 13.45505 | 20.90891 |
| $T\ (eV)$ | 34.31559 | 11.58941 | 34.65890 | 11.02312 | 31.73641 | 35.85539 | 8.89248 | 15.86820 | 12.74462 | 36.26840 |
| $V_m\ (eV)$ | -17.15779 | -5.79470 | -17.32945 | -5.51156 | -15.86820 | -17.92770 | -4.44624 | -7.93410 | -6.37231 | -18.13420 |
| $E(AO/HO)\ (eV)$ | 0 | -14.63489 | 0 | -14.63489 | -14.53414 | 0 | -14.63489 | -14.53414 | -14.63489 | 0 |
| $\Delta E_{H_2MO}(AO/HO)\ (eV)$ | 0 | -1.13379 | 0 | -2.26759 | 0 | -1.85836 | -0.92918 | 0 | -2.26758 | -2.42526 |
| $E_T(AO/HO)\ (eV)$ | 0 | -13.50110 | 0 | -12.36730 | -14.53414 | 1.85836 | -13.70571 | -14.53414 | -12.36731 | 2.42526 |
| $E(n_3\ AO/HO)\ (eV)$ | 0 | 0 | 0 | 0 | -14.53414 | 0 | 0 | 0 | 0 | 0 |
| $E_T(H_2MO)\ (eV)$ | -63.27075 | -31.63539 | -63.27076 | -31.63543 | -48.73654 | -63.27100 | -31.63527 | -31.63534 | -31.63533 | -63.27040 |
| $E_T\left(atom-atom, msp^3.AO\right)\ (eV)$ | -2.26759 | -0.56690 | -1.44915 | -1.13379 | 0 | -1.85836 | -0.92918 | 0 | 0 | -2.42526 |
| $E_T(MO)\ (eV)$ | -65.53833 | -32.20226 | -64.71988 | -32.76916 | -48.73660 | -65.12910 | -32.56455 | -31.63537 | -31.63537 | -65.69600 |
| $\omega\ \left(10^{15}\ rad/s\right)$ | 49.7272 | 26.4826 | 43.6311 | 14.3055 | 68.9812 | 15.4704 | 21.5213 | 48.7771 | 28.9084 | 54.5632 |
| $E_K\ (eV)$ | 32.73133 | 17.43132 | 28.71875 | 9.41610 | 45.40465 | 10.18290 | 14.16571 | 32.10594 | 19.02803 | 35.91442 |
| $\bar{E}_D\ (eV)$ | -0.35806 | -0.26130 | -0.33540 | -0.19893 | -0.42172 | -0.20558 | -0.24248 | -0.35462 | -0.27301 | -0.38945 |
| $\bar{E}_{Kvib}\ (eV)$ | 0.19649<br>[49] | 0.35532<br>Eq. (13.458) | 0.19649<br>[49] | 0.15498<br>[58] | 0.40929<br>[22] | 0.20768<br>[62] | 0.12944<br>[23] | 0.40696<br>[24] | 0.39427<br>[60] | 0.11159<br>[12] |
| $\bar{E}_{osc}\ (eV)$ | -0.25982 | -0.08364 | -0.23715 | -0.12144 | -0.21708 | -0.10174 | -0.17775 | -0.15115 | -0.07587 | -0.33365 |
| $E_{mag}\ (eV)$ | 0.14803 | 0.14803 | 0.09457 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 |
| $E_T(Group)\ (eV)$ | -49.54347 | -32.28590 | -48.82472 | -32.89060 | -49.17075 | -65.33259 | -32.74230 | -31.78651 | -31.71124 | -66.36330 |
| $E_{initial}(c_4\ AO/HO)\ (eV)$ | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.53414 | -14.63489 | -14.63489 | -14.53414 | -14.63489 | -14.63489 |
| $E_{initial}(c_5\ AO/HO)\ (eV)$ | 0 | -13.59844 | 0 | 0 | -13.59844 | 0 | 0 | -13.59844 | -13.59844 | 0 |
| $E_D(Group)\ (eV)$ | 5.63881 | 3.90454 | 4.92005 | 3.62082 | 7.43973 | 6.79303 | 3.47253 | 3.51208 | 3.32988 | 7.82374 |

Table 15.331. The total bond energies of adenine calculated using the functional group composition and the energies of Table 15.330 compared to the experimental values [3].

| Formula | Name | $\overset{3e}{C=C}$ | $CH$ (i) | $\overset{3e}{C=N}$ Group | $C-N$ (a) Group | $NH_2$ Group | $N=C$ | $C-N$ (b) | $NH$ | $CH$ (ii) | $C-N-C$ | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $C_5H_5N_5$ | Adenine | 2 | 1 | 4 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 70.85416 | 70.79811 | -0.00079 |

Table 15.332. The bond angle parameters of adenine and experimental values [66]. In the calculation of $\theta_v$, the parameters from the preceding angle were used. $E_T$ is $E_T$ $(atom-atom,msp^3.AO)$.

| Atoms of Angle | 2c' Bond 1 $(a_0)$ | 2c' Bond 2 $(a_0)$ | 2c' Terminal Atoms $(a_0)$ | $E_{Coulombic}$ Atom 1 | Atom 1 Hybridization Designation (Table 15.3B) | $E_{Coulombic}$ Atom 2 | Atom 2 Hybridization Designation (Table 15.3B) | $c_2$ Atom 1 | $c_2$ Atom 2 | $C_1$ | $C_2$ | $c_1$ | $c_2'$ | $E_T$ (eV) | $\theta_v$ (°) | $\theta_1$ (°) | $\theta_2$ (°) | Cal. $\theta$ (°) | Exp. $\theta$ (°) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $\angle HNH$ | 1.88268 | 1.88268 | 3.1559 | -14.53414 | N | H | H | 0.93613<br>Eq.<br>(13.248) | 1 | 1 | 1 | 0.75 | 1.06823 | 0 | | | | 113.89 | 113.9 [1]<br>(aniline) |
| $\angle C_aNH$ | 2.53797 | 1.88268 | 3.8123 | -16.78642 | 19 | -14.53414 | N | 0.81052<br>Eq.<br>(15.71) | 0.77638<br>Eq.<br>(15.173) | 0.75 | 1 | 0.75 | 0.95787 | 0 | | | | 118.42 | 118 |
| $\angle N_bC_bN_c$ | 2.54147 | 2.54147 | 4.5826 | -15.55033 | 3 | -15.55033 | 3 | 0.87495 | 0.87495 | 1 | 1 | 1 | 0.87495 | -1.44915 | | | | 128.73 | 128.9 |
| $\angle H_bC_bN_b$<br>$\angle H_bC_bN_c$ | | | | | | | | | | | | | | | | | 128.73 | 115.64<br>Eq.<br>(15.109) | 115<br>116 |
| $\angle H_eC_eN_e$ | 2.02241 | 2.60766 | 4.0661 | -16.36125 | 12 | -14.53414 | N | 0.83159 | 0.84665<br>Eq.<br>(15.171) | 0.75 | 1 | 0.75 | 1.01811 | 0 | | | | 122.35 | 126 |
| $\angle N_eC_eN_d$ | 2.60766 | 2.60287 | 4.3359 | -16.21952 | 9 | -16.03838 | 7 | 0.83885 | 0.84833 | 1 | 1 | 1 | 0.84359 | -1.44915 | | | | 112.64 | 114.4 |
| $\angle N_cC_cN_d$ | 2.54147 | 2.60287 | 4.6260 | -14.53414 | N | -14.53414 | N | 0.91140<br>Eq.<br>(15.135) | 0.84665<br>Eq.<br>(15.171) | 1 | 1 | 1 | 0.87902 | -1.44915 | | | | 128.11 | 127.8 |
| $\angle H_eC_eN_d$ | | | | | | | | | | | | | | | | 122.35 | 112.64 | 125.02 | 119 |
| $\angle H_dN_dC_e$ | 1.88268 | 2.60287 | 4.0166 | -14.53414 | N | -15.95955 | 6 | 0.84665<br>Eq.<br>(15.171) | 0.85252<br>Eq.<br>(15.162) | 0.75 | 1 | 0.75 | 1.00693 | 0 | | | | 126.39 | 127 |
| $\angle C_cN_dC_e$ | 2.60287 | 2.60287 | 4.1952 | -17.95963 | 39 | -17.95963 | 39 | 0.75758 | 0.75758 | 1 | 1 | 1 | 0.75758 | -1.85836 | | | | 107.39 | 106.1 |
| $\angle H_dN_dC_c$ | | | | | | | | | | | | | | | | 126.39 | 107.39 | 126.22 | 127 |
| $\angle N_aC_aC_d$ | 2.53797 | 2.62936 | 4.5387 | -14.53414 | N | -16.52644<br>$C_d$ | 15 | 0.91140<br>Eq.<br>(15.135) | 0.82327 | 1 | 1 | 1 | 0.86734 | -1.44915 | | | | 122.88 | 122.1 |
| $\angle N_bC_aC_d$ | 2.54147 | 2.62936 | 4.4272 | -14.53414 | N | -16.99103<br>$C_d$ | 21 | 0.91140<br>Eq.<br>(15.135) | 0.80076 | 1 | 1 | 1 | 0.85608 | -1.44915 | | | | 117.77 | 118.2 |
| $\angle N_bC_aN_a$ | | | | | | | | | | | | | | | | 122.88 | 117.77 | 119.35 | 119.4 |
| $\angle N_eC_dC_c$ | 2.70148 | 2.62936 | 4.3818 | -14.53414 | N | -15.95955<br>$C_c$ | 6 | 0.84665<br>Eq.<br>(15.171) | 0.85252 | 1 | 1 | 1 | 0.84958 | -1.44915 | | | | 110.56 | 110.4 |
| $\angle N_dC_cC_d$ | 2.60287 | 2.62936 | 4.1952 | -14.53414 | N | -16.99103<br>$C_d$ | 21 | 0.84665<br>Eq.<br>(15.171) | 0.80076 | 1 | 1 | 1 | 0.82371 | -1.44915 | | | | 106.60 | 105.9 |
| $\angle N_cC_cC_d$ | 2.54147 | 2.62936 | 4.6043 | -14.53414 | N | -16.52644<br>$C_d$ | 15 | 0.84665<br>Eq.<br>(15.171) | 0.82327 | 1 | 1 | 1 | 0.83496 | -1.65376 | | | | 125.85 | 126.4 |
| $\angle N_eC_dC_a$ | 2.70148 | 2.62936 | 4.8580 | -14.53414 | N | -16.78642<br>$C_a$ | 1 | 0.91140<br>Eq.<br>(15.135) | 0.81052 | 1 | 1 | 1 | 0.86096 | -1.65376 | | | | 131.37 | 132.8 |
| $\angle C_dN_eC_e$ | 2.70148 | 2.60766 | 4.2661 | -17.92022 | 37 | -17.92022 | 37 | 0.75924 | 0.75924 | 1 | 1 | 1 | 0.75924 | -1.85836 | | | | 106.93 | 103.3 |
| $\angle C_bN_cC_c$ | 2.54147 | 2.54147 | 4.1952 | -17.95963 | 39 | -17.95963 | 39 | 0.75758 | 0.75758 | 1 | 1 | 1 | 0.75758 | -1.85836 | | | | 111.25 | 111.3 |
| $\angle C_aN_bC_b$ | 2.54147 | 2.54147 | 4.3704 | -17.71560 | 33 | -17.40869 | 30 | 0.76801 | 0.78155 | 1 | 1 | 1 | 0.77478 | -1.85836 | | | | 118.59 | 118.6 |
| $\angle C_aC_dC_c$ | 2.62936 | 2.62936 | 4.4721 | -17.71560 | 33 | -17.14871 | 26 | 0.76801 | 0.79340 | 1 | 1 | 1 | 0.78071 | -1.85836 | | | | 116.52 | 116.7 |

## THYMINE

Thymine having the formula $C_5H_6N_2O_2$ is a pyrimidine with carbonyl substitutions at positions $C_a$ and $C_b$ and a methyl substitution at position $C_d$ further comprising a vinyl group as shown in Figure 15.57B. Each $C=O$, adjacent $C-N$, and $NH$ functional group is equivalent to the corresponding group of alkyl amides. The methyl-vinyl moiety is equivalent to the $CH_3$, $-C(C)=C$, $CH$, and $C=C$ functional groups of alkenes. Thymine further comprises $N_bH$ and $C_b-N_c-C_c$ groups that are equivalent to the corresponding groups of imidazole as given in the corresponding section. The $C_a-C_d$ bond comprises another functional group that is equivalent to the $C_a-C_d$ group of guanine.

The symbols of the functional groups of thymine are given in Table 15.333. The geometrical (Eqs. (15.1-15.5) and (15.51)), intercept (Eqs. (15.80-15.87)), and energy (Eqs. (15.6-15.11) and (15.17-15.65)) parameters of thymine are given in Tables 15.334, 15.335, and 15.336, respectively. The total energy of thymine given in Table 15.337 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.336 corresponding to functional-group composition of the molecule. The bond angle parameters of thymine determined using Eqs. (15.88-15.117) are given in Table 15.338. The color scale, charge-density of thymine comprising atoms with the outer shell bridged by one or more $H_2$-type ellipsoidal MOs or joined with one or more hydrogen MOs is shown in Figure 15.57A.

Figure 15.57. (A) Color scale, charge-density of thymine showing the orbitals of the atoms at their radii, the ellipsoidal surface of each $H$ or $H_2$-type ellipsoidal MO that transitions to the corresponding outer shell of the atom(s) participating in each bond, and the hydrogen nuclei. (B) Chemical structure and atom designation of thyamine.

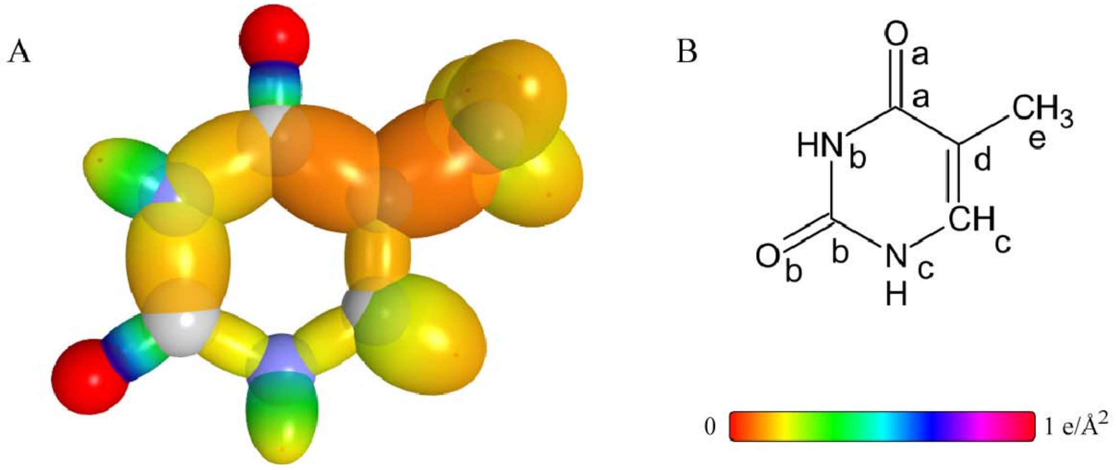


Table 15.333. The symbols of functional groups of thymine.

| Functional Group | Group Symbol |
|---|---|
| $C_a=O$ $C_b=O$ (alkyl amide) | $C=O$ |
| $C_a-N_b$ $C_b-N_b$ amide | $C-N$ |
| $N_bH$ amide group | $NH$ (i) |
| $CH_3$ group | $C-H$ $(CH_3)$ |
| $C_c=C_d$ double bond | $C=C$ |
| $C_d-C_e$ | $C-C$ (i) |
| $C_a-C_d$ | $C-C$ (ii) |
| $C_b-N_c-C_c$ | $C-N-C$ |
| $N_cH$ *group* | $NH$ (ii) |
| $C_cH$ | $CH$ |

Table 15.334. The geometrical bond parameters of thymine and experimental values [1].

| Parameter | $C=O$ Group | $C-N$ Group | $NH$ (i) Group | $C-H$ $(CH_3)$ Group | $C=C$ Group | $C-C$ (i) Group | $C-C$ (ii) Group | $C-N-C$ Group | $NH$ (ii) Group | $CH$ Group |
|---|---|---|---|---|---|---|---|---|---|---|
| $a$ $(a_0)$ | 1.29907 | 1.75370 | 1.28620 | 1.64920 | 1.47228 | 2.04740 | 1.88599 | 1.43222 | 1.24428 | 1.53380 |
| $c'$ $(a_0)$ | 1.13977 | 1.32427 | 0.95706 | 1.04856 | 1.26661 | 1.43087 | 1.37331 | 1.29614 | 0.94134 | 1.01120 |
| Bond Length $2c'$ $(Å)$ | 1.20628 | 1.40155 | 1.01291 | 1.10974 | 1.34052 | 1.51437 | 1.45345 | 1.37178 | 0.996270 | 1.07021 |
| Exp. Bond Length $(Å)$ | 1.220<br>(acetamide)<br>1.225<br>(N-methylacetamide) | 1.380<br>(acetamide) |  | 1.107<br>($C-H$ propane)<br>1.117<br>($C-H$ butane) | 1.34 [64]<br>(thymine)<br>1.342<br>(2-methylpropene)<br>1.346<br>(2-butene)<br>1.349<br>(1,3-butadiene) |  | 1.43 [65]<br>(thymine) | 1.370<br>(pyrrole) | 0.996<br>(pyrrole) | 1.076<br>(pyrrole) |
| $b,c$ $(a_0)$ | 0.62331 | 1.14968 | 0.85927 | 1.27295 | 0.75055 | 1.46439 | 1.29266 | 0.60931 | 0.81370 | 1.15326 |
| $e$ | 0.87737 | 0.75513 | 0.74410 | 0.63580 | 0.86030 | 0.69887 | 0.72817 | 0.90499 | 0.75653 | 0.65928 |

Table 15.335. The MO to HO intercept geometrical bond parameters of thymine. $R_1$ is an alkyl group and $R$, $R'$, $R''$ are $H$ or alkyl groups. $E_T$ is $E_T$ ($atom-atom,msp^3.AO$).

| Bond | Atom | $E_T$ (eV) Bond 1 | $E_T$ (eV) Bond 2 | $E_T$ (eV) Bond 3 | $E_T$ (eV) Bond 4 | Final Total Energy $C2sp^3$ (eV) | $r_{initial}$ $(a_0)$ | $r_{final}$ $(a_0)$ | $E_{Coulomb}(C2sp^3)$ (eV) Final | $E(C2sp^3)$ (eV) Final | $\theta'$ (°) | $\theta_1$ (°) | $\theta_2$ (°) | $d_1$ $(a_0)$ | $d_2$ $(a_0)$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $N_b(C_d)C_a=O$ | $O_a$ | -1.34946 | 0 | 0 | 0 |  | 1.00000 | 0.84115 | -16.17521 |  | 137.27 | 42.73 | 66.31 | 0.52193 | 0.61784 |
| $N_b(C_d)C_a=O$ | $C_a$ | -1.34946 | -0.82688 | 0 | 0 | -153.79203 | 0.91771 | 0.80024 | -17.00209 | -16.81123 | 135.55 | 44.45 | 64.05 | 0.56855 | 0.57122 |
| $N-H$ $(N_bH)$ | $N_b$ | -0.82688 | -0.82688 | 0 | 0 |  | 0.93084 | 0.82562 | -16.47951 |  | 118.03 | 61.97 | 63.59 | 0.55339 | 0.38795 |
| $C_d(O)C_a-N_bH(C_b)$ | $N_b$ | -0.82688 | -0.82688 | 0 | 0 |  | 0.93084 | 0.82562 | -16.47951 |  | 96.62 | 83.38 | 45.51 | 1.22903 | 0.09524 |
| $C_d(O)C_a-N_bH(C_b)$ | $C_a$ | -0.82688 | -1.34946 | 0 | 0 | -153.79203 | 0.91771 | 0.80024 | -17.00209 | -16.81123 | 94.42 | 85.58 | 43.95 | 1.26264 | 0.06164 |
| $C_aN_bH-C_b(O)N_cH$ | $N_b$ | -0.82688 | -0.82688 | 0 | 0 |  | 0.93084 | 0.82562 | -16.47951 |  | 96.62 | 83.38 | 45.51 | 1.22903 | 0.09524 |
| $C_aN_bH-C_b(O)N_cH$ | $C_b$ | -0.82688 | -1.34946 | -0.82688 | 0 | -154.61891 | 0.91771 | 0.76313 | -17.82897 | -17.63811 | 90.94 | 89.06 | 41.58 | 1.31179 | 0.01249 |
| $(HN_c)(HN_b)C_b=O$ | $O_b$ | -1.34946 | 0 | 0 | 0 |  | 1.00000 | 0.84115 | -16.17521 |  | 137.27 | 42.73 | 66.31 | 0.52193 | 0.61784 |
| $(HN_c)(HN_b)C_b=O$ | $C_b$ | -1.34946 | -0.82688 | -0.92918 | 0 | -154.72121 | 0.91771 | 0.75878 | -17.93127 | -17.74041 | 133.67 | 46.33 | 61.70 | 0.61582 | 0.52395 |
| $N-H$ $(N_cH)$ | $N_c$ | -0.92918 | -0.92918 | 0 | 0 |  | 0.93084 | 0.81549 | -16.68411 |  | 117.34 | 62.66 | 62.90 | 0.56678 | 0.37456 |
| $N_b(O)C_b-N_cHC_c$ | $N_c$ | -0.92918 | -0.92918 | 0 | 0 |  | 0.93084 | 0.81549 | -16.68411 |  | 138.92 | 41.08 | 61.59 | 0.68147 | 0.61467 |
| $N_b(O)C_b-N_cHC_c$ | $C_b$ | -0.92918 | -1.34946 | -0.82688 | 0 | -154.72121 | 0.91771 | 0.75878 | -17.93127 | -17.74041 | 136.68 | 43.32 | 58.70 | 0.74414 | 0.55200 |
| $C_bHN_c-HC_cC_d$ | $N_c$ | -0.92918 | -0.92918 | 0 | 0 |  | 0.93084 | 0.81549 | -16.68411 |  | 138.92 | 41.08 | 61.59 | 0.68147 | 0.61467 |
| $C_bHN_c-HC_cC_d$ | $C_c$ | -0.92918 | -1.13379 | 0 | 0 | -153.67866 | 0.91771 | 0.80561 | -16.88873 | -16.69786 | 138.54 | 41.46 | 61.09 | 0.69238 | 0.60376 |
| $C-H$ $(C_cH)$ | $C_c$ | -1.13380 | -0.92918 | 0 | 0 | -153.67867 | 0.91771 | 0.80561 | -16.88873 | -16.69786 | 83.35 | 96.65 | 43.94 | 1.10452 | 0.09331 |
| $N_cHC_c=C_dC_a(C_e)$ | $C_c$ | -1.13380 | -0.92918 | -0.72457 | 0 | -154.40324 | 0.91771 | 0.77247 | -17.61330 | -17.42244 | 125.92 | 54.08 | 56.46 | 0.81345 | 0.45316 |
| $N_cHC_c=C_dC_a(C_e)$ | $C_d$ | -1.13380 | 0 | -0.72457 | 0 | -153.47406 | 0.91771 | 0.81549 | -16.68412 | -16.49326 | 128.10 | 51.90 | 58.77 | 0.76344 | 0.50317 |
| $C-H$ $(CH_3)$ | $C_e$ | -0.72457 | 0 | 0 | 0 | -152.34026 | 0.91771 | 0.87495 | -15.55033 | -15.35946 | 78.85 | 101.15 | 42.40 | 1.21777 | 0.16921 |
| $(C_a)C_cC_d-C_eH_3$ | $C_e$ | -0.72457 | 0 | 0 | 0 | -152.34026 | 0.91771 | 0.87495 | -15.55033 | -15.35946 | 73.62 | 106.38 | 34.98 | 1.67762 | 0.24675 |
| $(C_a)C_cC_d-C_eH_3$ | $C_d$ | -0.72457 | -1.13379 | 0 | 0 | -153.47406 | 0.91771 | 0.81549 | -16.68412 | -16.49325 | 65.99 | 114.01 | 30.58 | 1.76270 | 0.33183 |
| $(C_e)C_cC_d-C_a(O)N_b$ | $C_a$ | 0 | -1.34946 | -0.82688 | 0 | -153.79203 | 0.91771 | 0.80024 | -17.00209 | -16.81123 | 81.54 | 98.46 | 37.76 | 1.49107 | 0.11776 |
| $(C_e)C_cC_d-C_a(O)N_b$ | $C_d$ | 0 | -1.13379 | -0.72457 | 0 | -153.47406 | 0.91771 | 0.81549 | -16.68412 | -16.49325 | 92.72 | 87.28 | 45.17 | 1.32975 | 0.04357 |

Table 15.336. The energy parameters ($eV$) of functional groups of thymine.

| Parameters | $C=O$ Group | $C-N$ Group | $NH$ (i) Group | $C=C$ Group | $CH_3$ Group | $C-C$ (i) Group | $C-C$ (ii) Group | $C-N-C$ Group | $NH$ (ii) Group | $CH$ Group |
|---|---|---|---|---|---|---|---|---|---|---|
| $n_1$ | 2 | 1 | 1 | 2 | 3 | 1 | 1 | 2 | 1 | 1 |
| $n_2$ | 0 | 0 | 0 | 0 | 2 | 0 | 0 | 0 | 0 | 0 |
| $n_3$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $C_1$ | 0.5 | 0.5 | 0.75 | 0.5 | 0.75 | 0.5 | 0.5 | 0.5 | 0.75 | 0.75 |
| $C_2$ | 1 | 1 | 0.93613 | 0.91771 | 1 | 1 | 1 | 0.85252 | 0.93613 | 1 |
| $c_1$ | 1 | 1 | 0.75 | 1 | 1 | 1 | 1 | 1 | 0.75 | 1 |
| $c_2$ | 0.85395 | 0.91140 | 1 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.84665 | 0.92171 | 0.91771 |
| $c_3$ | 2 | 0 | 1 | 0 | 0 | 1 | 0 | 0 | 1 | 1 |
| $c_4$ | 4 | 2 | 1 | 4 | 1 | 2 | 2 | 4 | 1 | 1 |
| $c_5$ | 0 | 0 | 1 | 0 | 3 | 0 | 0 | 0 | 1 | 1 |
| $C_{1o}$ | 0.5 | 0.5 | 0.75 | 0.5 | 0.75 | 0.5 | 0.5 | 0.5 | 0.75 | 0.75 |
| $C_{2o}$ | 1 | 1 | 1 | 0.91771 | 1 | 1 | 1 | 0.85252 | 1 | 1 |
| $V_e$ ($eV$) | -111.25473 | -36.88558 | -40.92593 | -102.08992 | -107.32728 | -30.19634 | -33.63376 | -106.58684 | -39.48897 | -39.09538 |
| $V_p$ ($eV$) | 23.87467 | 10.27417 | 14.21618 | 21.48386 | 38.92728 | 9.50874 | 9.90728 | 20.99432 | 14.45367 | 13.45505 |
| $T$ ($eV$) | 42.82081 | 10.51650 | 15.90963 | 34.67062 | 32.53914 | 7.37432 | 8.91674 | 37.21047 | 15.86820 | 12.74462 |
| $V_m$ ($eV$) | -21.41040 | -5.25825 | -7.95482 | -17.33531 | -16.26957 | -3.68716 | -4.45837 | -18.60523 | -7.93410 | -6.37231 |
| $E(_{AO/HO})$ ($eV$) | 0 | -14.63489 | -14.53414 | 0 | -15.56407 | -14.63489 | -14.63489 | 0 | -14.53414 | -14.63489 |
| $\Delta E_{H_2MO}(_{AO/HO})$ ($eV$) | -2.69893 | -4.35268 | -1.65376 | 0 | 0 | 0 | -2.26759 | -3.71673 | 0 | -2.26758 |
| $E_T(_{AO/HO})$ ($eV$) | 2.69893 | -10.28221 | -12.88038 | 0 | -15.56407 | -14.63489 | -12.36730 | 3.71673 | -14.53414 | -12.36731 |
| $E(_{n_3\ AO/HO})$ ($eV$) | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $E_T(_{H_2MO})$ ($eV$) | -63.27074 | -31.63537 | -31.63531 | -63.27075 | -67.69451 | -31.63534 | -31.63541 | -63.27056 | -31.63534 | -31.63533 |
| $E_T\left(atom-atom,msp^3.AO\right)$ ($eV$) | -2.69893 | -1.65376 | 0 | -2.26759 | 0 | -1.44915 | 0.00000 | -3.71673 | 0 | 0 |
| $E_T(_{MO})$ ($eV$) | -65.96966 | -33.28912 | -31.63537 | -65.53833 | -67.69450 | -33.08452 | -31.63537 | -66.98746 | -31.63537 | -31.63537 |
| $\omega$ $\left(10^{15}\ rad/s\right)$ | 59.4034 | 12.5874 | 44.9494 | 43.0680 | 24.9286 | 9.97851 | 19.8904 | 15.7474 | 48.7771 | 28.9084 |
| $E_K$ ($eV$) | 39.10034 | 8.28526 | 29.58649 | 28.34813 | 16.40846 | 6.56803 | 13.09221 | 10.36521 | 32.10594 | 19.02803 |
| $\bar{E}_D$ ($eV$) | -0.40804 | -0.18957 | -0.34043 | -0.34517 | -0.25352 | -0.16774 | -0.22646 | -0.21333 | -0.35462 | -0.27301 |
| $\bar{E}_{Kvib}$ ($eV$) | 0.21077<br>[12] | 0.17358<br>[33] | 0.40696<br>[24] | 0.17897<br>[6] | 0.35532<br>Eq. (13.458) | 0.15895<br>[7] | 0.14667<br>[67] | 0.11159<br>[12] | 0.40696<br>[24] | 0.39427<br>[60] |
| $\bar{E}_{osc}$ ($eV$) | -0.30266 | -0.10278 | -0.13695 | -0.25568 | -0.22757 | -0.08827 | -0.15312 | -0.15754 | -0.15115 | -0.07587 |
| $E_{mag}$ ($eV$) | 0.11441 | 0.14803 | 0.14185 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 |
| $E_T(_{Group})$ ($eV$) | -66.57498 | -33.39190 | -31.77232 | -66.04969 | -67.92207 | -33.17279 | -31.64046 | -67.30254 | -31.78651 | -31.71124 |
| $E_{initial}(_{c_4\ AO/HO})$ ($eV$) | -14.63489 | -14.63489 | -14.53414 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.53414 | -14.63489 |
| $E_{initial}(_{c_5\ AO/HO})$ ($eV$) | 0 | 0 | -13.59844 | 0 | -13.59844 | 0 | 0 | 0 | -13.59844 | -13.59844 |
| $E_D(_{Group})$ ($eV$) | 7.80660 | 4.12212 | 3.49788 | 7.51014 | 12.49186 | 3.75498 | 2.37068 | 8.76298 | 3.51208 | 3.32988 |

Table 15.337. The total gaseous bond energies of thymine calculated using the functional group composition and the energies of Table 15.336 compared to the experimental values [3].

| Formula | Name | $C=O$ Group | $C-N$ Group | $NH$ (i) Group | $C=C$ Group | $CH_3$ Group | $C-C$ (i) Group | $C-C$ (ii) Group | $C-N-C$ Group | $NH$ (ii) Group | $CH$ Group | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $C_5H_6N_2O_2$ | Thymine | 2 | 2 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 69.08792 | 69.06438 | -0.00034 |

Table 15.338. The bond angle parameters of thymine and experimental values [64]. In the calculation of $\theta_v$, the parameters from the preceding angle were used. $E_T$ is $E_T$ $(atom-atom, msp^3.AO)$.

| Atoms of Angle | $2c'$ Bond 1 $(a_0)$ | $2c'$ Bond 2 $(a_0)$ | $2c'$ Terminal Atoms $(a_0)$ | $E_{Coulombic}$ Atom 1 | Atom 1 Hybridization Designation (Table 15.3B) | $E_{Coulombic}$ Atom 2 | Atom 2 Hybridization Designation (Table 15.3B) | $c_2$ Atom 1 | $c_2$ Atom 2 | $C_1$ | $C_2$ | $c_1$ | $c_2'$ | $E_T$ (eV) | $\theta_v$ (°) | $\theta_1$ (°) | $\theta_2$ (°) | Cal. $\theta$ (°) | Exp. $\theta$ (°) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $\angle N_bC_aC_d$ | 2.64855 | 2.74663 | 4.5277 | -14.53414 | N | -16.68412<br>$C_d$ | 18 | 0.91140<br>Eq.<br>(15.135) | 0.81549 | 1 | 1 | 1 | 0.86345 | -1.44915 | | | | 114.10 | 115.7 |
| $\angle N_bC_aO$ | 2.64855 | 2.27954 | 4.2661 | -16.47951 | 14 | -16.17521 | 8 | 0.82562 | 0.84115 | 1 | 1 | 1 | 0.83339 | -1.44915 | | | | 119.73 | 119.5 |
| $\angle OC_aC_d$ | | | | | | | | | | | | | | | | 114.10 | 119.73 | 126.17 | 124.8 |
| $\angle C_bN_bC_a$ | 2.64855 | 2.64855 | 4.6904 | -17.40869 | 30 | -16.58181 | 16 | 0.78155 | 0.82053 | 1 | 1 | 1 | 0.80104 | -1.85836 | | | | 124.62 | 126.1 |
| $\angle N_bC_bN_c$ | 2.64855 | 2.59228 | 4.4497 | -16.47951 | 14 | -16.68411 | 17 | 0.82562 | 0.81549 | 1 | 1 | 1 | 0.82056 | -1.65376 | | | | 116.21 | 115.1 |
| $\angle H_bN_bC_a$ | 1.88268 | 2.64855 | 3.9158 | -14.53414 | N | -14.82575<br>$C_a$ | 1 | 0.93613<br>Eq.<br>(13.248) | 0.91771 | 0.75 | 1 | 0.75 | 0.98033 | 0 | | | | 118.60 | |
| $\angle C_bN_bH_b$ | | | | | | | | | | | | | | | | 124.62 | 118.60 | 116.78 | |
| $\angle C_bN_cC_c$ | 2.59228 | 2.59228 | 4.4944 | -17.93127 | 38 | -16.88873 | 20 | 0.75878 | 0.80561 | 1 | 1 | 1 | 0.78219 | -1.85836 | | | | 120.20 | 120.7 |
| $\angle N_cC_bO_b$ | 2.59228 | 2.27954 | 4.2661 | -16.68411 | 18 | -16.17521 | 8 | 0.81549 | 0.84115 | 1 | 1 | 1 | 0.82832 | -1.44915 | | | | 122.12 | 123.7 |
| $\angle N_bC_bO_b$ | | | | | | | | | | | | | | | | 116.21 | 122.12 | 121.67 | 121.2 |
| $\angle N_cC_cC_d$ | 2.59228 | 2.53321 | 4.5387 | -14.53414 | N | -16.68412 | 18 | 0.84665<br>Eq.<br>(15.171) | 0.81549 | 1 | 1 | 1 | 0.83107 | -1.65376 | | | | 124.63 | 122.9 |
| $\angle H_cN_cC_c$ | 1.88268 | 2.59228 | 3.8644 | -14.53414 | N | -16.68412 | 18 | 0.84665<br>Eq.<br>(15.171) | 0.81549 | 0.75 | 1 | 0.75 | 0.96320 | 0 | | | | 118.58 | |
| $\angle H_cN_cC_b$ | | | | | | | | | | | | | | | | 120.20 | 118.58 | 121.23 | |
| $\angle H_cC_cC_d$ | 2.02241 | 2.53321 | 3.9833 | -15.95955 | 6 | -15.95955 | 6 | 0.85252 | 0.85252 | 0.75 | 1 | 0.75 | 1.00000 | 0 | | | | 121.54 | |
| $\angle H_cC_cN_c$ | | | | | | | | | | | | | | | | 124.63 | 121.54 | 113.84 | |
| $\angle C_aC_dC_e$ | 2.74663 | 2.53321 | 4.5387 | -17.00209 | 22 | -17.61330 | 32 | 0.80024 | 0.77247 | 1 | 1 | 1 | 0.78636 | -1.85836 | | | | 118.49 | 118.5 |
| $\angle C_eC_dC_c$ | 2.86175 | 2.53321 | 4.7117 | -16.47951 | 14 | -17.40869 | 30 | 0.82562 | 0.78155 | 1 | 1 | 1 | 0.80359 | -1.85836 | | | | 121.58 | 123.3 |
| $\angle C_cC_dC_a$ | | | | | | | | | | | | | | | | 118.49 | 121.58 | 119.93 | 118.2 |
| Methyl<br>$\angle HC_eH$ | 2.09711 | 2.09711 | 3.4252 | -15.75493<br>$C_e$ | 4 | H | H | 0.86359 | 1 | 1 | 1 | 0.75 | 1.15796 | 0 | | | | 109.50 | |

## GUANINE

Guanine having the formula $C_5H_5N_5O$ is a purine with a carbonyl substitution at position $C_a$, and a primary amine moiety is at position $C_b$ as shown in Figure 15.58B. The carbonyl functional group is equivalent to that of alkyl amides and the $NH_2$ and $C_b-N_a$ functional groups of the primary amine moiety are equivalent to the $NH_2$ and $C_a-N_a$ functional groups of adenine. Guanine further comprises an imidazole moiety wherein the $CH$, $N_dH$, $C_d=C_c$, $C_d-N_e$, $N_e=C_e$, and $C_c-N_d-C_e$ groups of the imidazole-type ring are equivalent to the corresponding groups of imidazole as given in the corresponding section. The six-membered ring also comprises the groups $C_a-N_b-C_b$, $N_bH$, $N_c=C_c$, and $C_c-N_d$ that are equivalent to the corresponding imidazole and adenine functional groups. The $C_a-C_d$ bond comprises another functional group that is the $C_{60}$-single-bond functional group except that $E_T\left(atom-atom,msp^3.AO\right)=0$ in order to match the energies of the single and double-bonded moieties within the molecule.

The symbols of the functional groups of guanine are given in Table 15.339. The geometrical (Eqs. (15.1-15.5) and (15.51)), intercept (Eqs. (15.80-15.87)), and energy (Eqs. (15.6-15.11) and (15.17-15.65)) parameters of guanine are given in Tables 15.340, 15.341, and 15.342, respectively. The total energy of guanine given in Table 15.343 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.342 corresponding to functional-group composition of the molecule. The bond angle parameters of guanine determined using Eqs. (15.88-15.117) are given in Table 15.344. The color scale, charge-density of guanine comprising atoms with the outer shell bridged by one or more $H_2$-type ellipsoidal MOs or joined with one or more hydrogen MOs is shown in Figure 15.58A.

Figure 15.58. (A) Color scale, charge-density of guanine showing the orbitals of the atoms at their radii, the ellipsoidal surface of each $H$ or $H_2$-type ellipsoidal MO that transitions to the corresponding outer shell of the atom(s) participating in each bond, and the hydrogen nuclei. (B) Chemical structure and atomic designation of guanine.

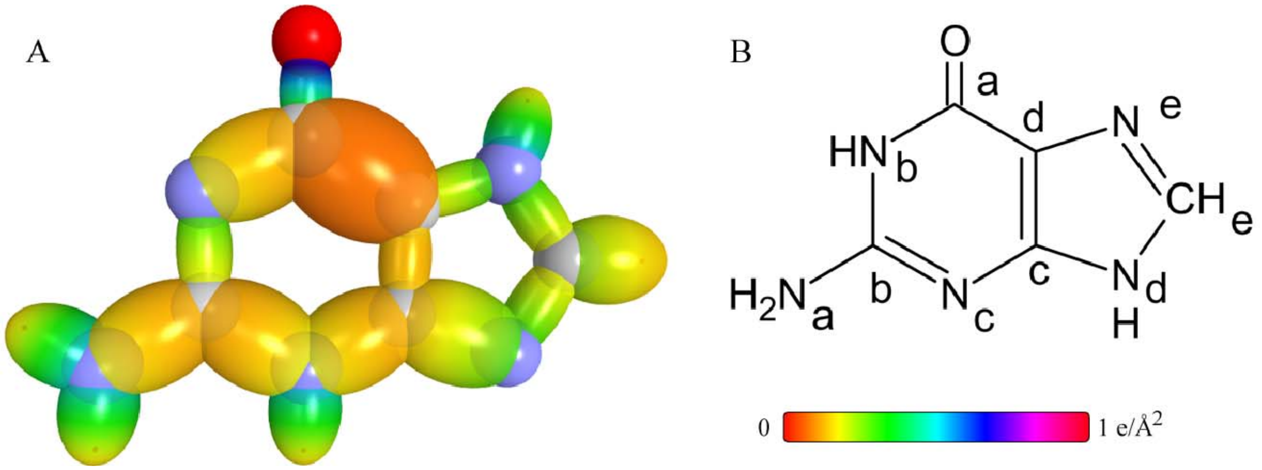


Table 15.339. The symbols of functional groups of guanine.

| Functional Group | Group Symbol |
|---|---|
| $C_a = O$ (alkyl amide) | $C = O$ |
| $C_b - N_a$ | $C - N$ (a) |
| $NH_2$ group | $NH_2$ |
| $C_c = C_d$ double bond | $C = C$ |
| $C_a - C_d$ | $C - C$ |
| $N_e = C_e$ $N_c = C_b$ double bond | $N = C$ |
| $C_d - N_e$ $C_c - N_c$ | $C - N$ (b) |
| $C_c - N_d - C_e$ $C_a - N_b - C_b$ | $C - N - C$ |
| $N_dH$ $N_bH$ *group* | $NH$ |
| $C_eH$ | $CH$ |

Table 15.340. The geometrical bond parameters of guanine and experimental values [1].

| Parameter | $C=O$ Group | $C-N$ (a) Group | $NH_2$ Group | $C=C$ Group | $C-C$ Group | $N=C$ Group | $C-N$ (b) Group | $C-N-C$ Group | $NH$ Group | $CH$ Group |
|---|---|---|---|---|---|---|---|---|---|---|
| $a\ (a_0)$ | 1.29907 | 1.61032 | 1.24428 | 1.45103 | 1.88599 | 1.44926 | 1.82450 | 1.43222 | 1.24428 | 1.53380 |
| $c'\ (a_0)$ | 1.13977 | 1.26898 | 0.94134 | 1.30463 | 1.37331 | 1.30383 | 1.35074 | 1.29614 | 0.94134 | 1.01120 |
| Bond Length $2c'$ ($\mathring{A}$) | 1.20628 | 1.34303 | 0.99627 | 1.38076 | 1.45345 | 1.37991 | 1.42956 | 1.37178 | 0.996270 | 1.07021 |
| Exp. Bond Length ($\mathring{A}$) | 1.220 (acetamide)<br>1.225 (N-methylacetamide) | 1.34 [64] (guanine) | 0.998 (aniline) | 1.382 (pyrrole) | 1.42 [64] (guanine) | | | 1.370 (pyrrole) | 0.996 (pyrrole) | 1.076 (pyrrole) |
| $b,c\ (a_0)$ | 0.62331 | 0.99137 | 0.81370 | 0.63517 | 1.29266 | 0.63276 | 1.22650 | 0.60931 | 0.81370 | 1.15326 |
| $e$ | 0.87737 | 0.78803 | 0.75653 | 0.89910 | 0.72817 | 0.89965 | 0.74033 | 0.90499 | 0.75653 | 0.65928 |

Table 15.341. The MO to HO intercept geometrical bond parameters of guanine. $R_1$ is an alkyl group and $R$, $R'$, $R''$ are $H$ or alkyl groups. $E_T$ is $E_T$ (*atom – atom,msp*$^3$*.AO*).

| Bond | Atom | $E_T$ (eV) Bond 1 | $E_T$ (eV) Bond 2 | $E_T$ (eV) Bond 3 | $E_T$ (eV) Bond 4 | Final Total Energy $C2sp^3$ (eV) | $r_{initial}$ $(a_0)$ | $r_{final}$ $(a_0)$ | $E_{Coulomb}(C2sp^3)$ (eV) Final | $E(C2sp^3)$ (eV) Final | $\theta'$ (°) | $\theta_1$ (°) | $\theta_2$ (°) | $d_1$ $(a_0)$ | $d_2$ $(a_0)$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $N_b(C_d)C_a=O$ | $O$ | -1.34946 | 0 | 0 | 0 | | 1.00000 | 0.84115 | -16.17521 | | 137.27 | 42.73 | 66.31 | 0.52193 | 0.61784 |
| $N_b(C_d)C_a=O$ | $C_a$ | -1.34946 | -0.92918 | 0 | 0 | -153.89433 | 0.91771 | 0.79546 | -17.10440 | -16.91353 | 135.34 | 44.66 | 63.78 | 0.57401 | 0.56576 |
| $N-H\ (N_bH)$ | $N_b$ | -0.92918 | -0.92918 | 0 | 0 | | 0.93084 | 0.81549 | -16.68411 | | 117.34 | 62.66 | 62.90 | 0.56678 | 0.37456 |
| $C_d(O)C_a-N_bH(C_b)$ | $N_b$ | -0.92918 | -0.92918 | 0 | 0 | | 0.93084 | 0.81549 | -16.68411 | | 138.92 | 41.08 | 61.59 | 0.68147 | 0.61467 |
| $C_d(O)C_a-N_bH(C_b)$ | $C_a$ | -1.34946 | -0.92918 | 0 | 0 | -153.89433 | 0.91771 | 0.79546 | -17.10440 | -16.91353 | 138.15 | 41.85 | 60.58 | 0.70361 | 0.59253 |
| $C_d(O)C_aN_bH-C_bN_c(N_aH_2)$ | $N_b$ | -0.92918 | -0.92918 | 0 | 0 | | 0.93084 | 0.81549 | -16.68411 | | 138.92 | 41.08 | 61.59 | 0.68147 | 0.61467 |
| $C_d(O)C_aN_bH-C_bN_c(N_aH_2)$ | $C_b$ | -0.56690 | -0.92918 | -0.92918 | 0 | -154.04095 | 0.91771 | 0.78870 | -17.25101 | -17.06015 | 137.89 | 42.11 | 60.23 | 0.71108 | 0.58506 |
| $N_c(N_b)C_bN_aH-H$ | $N_a$ | -0.56690 | 0 | 0 | 0 | | 0.93084 | 0.88392 | -15.39265 | | 121.74 | 58.26 | 67.49 | 0.47634 | 0.46500 |
| $HN_bC_b-N_aH_2(N_c)$ | $N_a$ | -0.56690 | 0 | 0 | 0 | | 0.93084 | 0.88392 | -15.39265 | | 113.13 | 66.87 | 55.08 | 0.92180 | 0.34719 |
| $HN_bC_b-N_aH_2(N_c)$ | $C_b$ | -0.56690 | -0.92918 | -0.92918 | 0 | -154.04095 | 0.91771 | 0.78870 | -17.25101 | -17.06015 | 106.68 | 73.32 | 49.65 | 1.04263 | 0.22636 |
| $HN_bC_b=N_cC_c(N_aH_2)$ | $N_c$ | -0.92918 | -0.46459 | 0 | 0 | | 0.93084 | 0.83885 | -16.21952 | | 138.20 | 41.80 | 62.08 | 0.67849 | 0.62534 |
| $HN_bC_b=N_cC_c(N_aH_2)$ | $C_b$ | -0.92918 | -0.92918 | -0.56690 | 0 | -154.04095 | 0.91771 | 0.78870 | -17.25101 | -17.06015 | 136.24 | 43.76 | 59.56 | 0.73424 | 0.56959 |
| $C_bN_c-C_cC_d(N_dH)$ | $N_c$ | -0.46459 | -0.92918 | 0 | 0 | | | 0.93084 | 0.83885 | -16.21953 | 91.32 | 88.68 | 43.14 | 1.33135 | 0.01939 |
| $C_bN_c-C_cC_d(N_dH)$ | $C_c$ | -0.46459 | -1.13380 | -0.92918 | 0 | -154.14326 | 0.91771 | 0.78405 | -17.35332 | -17.16246 | 86.00 | 94.00 | 39.62 | 1.40538 | 0.05464 |
| $N_c(N_dH)C_c=C_dN_e(C_a)$ | $C_c$ | -1.13380 | -0.92918 | -0.46459 | 0 | -154.14326 | 0.91771 | 0.78405 | -17.35332 | -17.16246 | 135.87 | 44.13 | 59.25 | 0.74183 | 0.56280 |
| $N_c(N_dH)C_c=C_dN_e(C_a)$ | $C_d$ | -1.13380 | -0.46459 | 0 | 0 | -153.21408 | 0.91771 | 0.82840 | -16.42414 | -16.23327 | 137.64 | 42.36 | 61.49 | 0.69250 | 0.61213 |
| $N-H\ (N_dH)$ | $N_d$ | -0.92918 | -0.92918 | 0 | 0 | | 0.93084 | 0.81549 | -16.68411 | | 117.34 | 62.66 | 62.90 | 0.56678 | 0.37456 |
| $(N_c)C_dC_c-N_dH(C_e)$ | $N_d$ | -0.92918 | -0.92918 | 0 | 0 | | 0.93084 | 0.81549 | -16.68411 | | 138.92 | 41.08 | 61.59 | 0.68147 | 0.61467 |
| $(N_c)C_dC_c-N_dH(C_e)$ | $C_c$ | -1.13379 | -0.92918 | -0.46459 | 0 | -154.14326 | 0.91771 | 0.78405 | -17.35332 | -17.16245 | 137.70 | 42.30 | 59.99 | 0.71622 | 0.57992 |
| $C-H\ (C_eH)$ | $C_e$ | -0.92918 | -0.92918 | 0 | 0 | -153.47405 | 0.91771 | 0.81549 | -16.68411 | -16.49325 | 84.49 | 95.51 | 44.47 | 1.08953 | 0.07833 |
| $C_cHN_dH-C_eH(N_e)$ | $N_d$ | -0.92918 | -0.92918 | 0 | 0 | | 0.93084 | 0.81549 | -16.68411 | | 138.92 | 41.08 | 61.59 | 0.68147 | 0.61467 |
| $C_cHN_dH-C_eH(N_e)$ | $C_e$ | -0.92918 | -0.92918 | 0 | 0 | -153.47405 | 0.91771 | 0.81549 | -16.68411 | -16.49325 | 138.92 | 41.08 | 61.59 | 0.68147 | 0.61467 |
| $N_d(H)C_e=N_eC_d$ | $N_e$ | -0.92918 | -0.46459 | 0 | 0 | | 0.93084 | 0.83885 | -16.21952 | | 138.20 | 41.80 | 62.08 | 0.67849 | 0.62534 |
| $N_d(H)C_e=N_eC_d$ | $C_e$ | -0.92918 | -0.92918 | 0 | 0 | -153.47405 | 0.91771 | 0.81549 | -16.68411 | -16.49325 | 137.31 | 42.69 | 60.92 | 0.70446 | 0.59938 |
| $C_eN_e-C_dC_a(C_c)$ | $N_e$ | -0.46459 | -0.92918 | 0 | 0 | | 0.93084 | 0.83885 | -16.21953 | | 91.32 | 88.68 | 43.14 | 1.33135 | 0.01939 |
| $C_eN_e-C_dC_a(C_c)$ | $C_d$ | -0.46459 | -1.13380 | 0 | 0 | -153.21408 | 0.91771 | 0.82840 | -16.42414 | -16.23327 | 90.36 | 89.64 | 42.49 | 1.34547 | 0.00527 |
| $(N_e)C_cC_d-C_a(O)N_b$ | $C_a$ | 0.00000 | -1.34946 | -0.92918 | 0 | -153.89433 | 0.91771 | 0.79546 | -17.10440 | -16.91353 | 81.01 | 98.99 | 37.43 | 1.49764 | 0.12433 |
| $(N_e)C_cC_d-C_a(O)N_b$ | $C_d$ | 0.00000 | -1.13379 | -0.46459 | 0 | -153.21407 | 0.91771 | 0.82840 | -16.42413 | -16.23327 | 92.72 | 87.28 | 45.17 | 1.32975 | 0.04357 |

Table 15.342. The energy parameters ($eV$) of functional groups of guanine.

| Parameters | $C=O$ Group | $C-N$ (a) Group | $NH_2$ Group | $C=C$ Group | $C-C$ Group | $N=C$ Group | $C-N$ (b) Group | $C-N-C$ Group | $NH$ Group | $CH$ Group |
|---|---|---|---|---|---|---|---|---|---|---|
| $n_1$ | 2 | 1 | 2 | 2 | 1 | 2 | 1 | 2 | 1 | 1 |
| $n_2$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $n_3$ | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $C_1$ | 0.5 | 0.5 | 0.75 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.75 | 0.75 |
| $C_2$ | 1 | 1 | 0.93613 | 0.85252 | 1 | 0.85252 | 1 | 0.85252 | 0.93613 | 1 |
| $c_1$ | 1 | 1 | 0.75 | 1 | 1 | 1 | 1 | 1 | 0.75 | 1 |
| $c_2$ | 0.85395 | 0.84665 | 0.92171 | 0.85252 | 0.91771 | 0.84665 | 0.84665 | 0.84665 | 0.92171 | 0.91771 |
| $c_3$ | 2 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 1 |
| $c_4$ | 4 | 2 | 1 | 4 | 2 | 4 | 2 | 4 | 1 | 1 |
| $c_5$ | 0 | 0 | 2 | 0 | 0 | 0 | 0 | 0 | 1 | 1 |
| $C_{1o}$ | 0.5 | 0.5 | 1.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.75 | 0.75 |
| $C_{2o}$ | 1 | 1 | 1 | 0.85252 | 1 | 0.85252 | 1 | 0.85252 | 1 | 1 |
| $V_e\ (eV)$ | -111.25473 | -35.50149 | -78.97795 | -104.37986 | -33.63376 | -103.92756 | -32.44864 | -106.58684 | -39.48897 | -39.09538 |
| $V_p\ (eV)$ | 23.87467 | 10.72181 | 28.90735 | 20.85777 | 9.90728 | 20.87050 | 10.07285 | 20.99432 | 14.45367 | 13.45505 |
| $T\ (eV)$ | 42.82081 | 11.02312 | 31.73641 | 35.96751 | 8.91674 | 35.85539 | 8.89248 | 37.21047 | 15.86820 | 12.74462 |
| $V_m\ (eV)$ | -21.41040 | -5.51156 | -15.86820 | -17.98376 | -4.45837 | -17.92770 | -4.44624 | -18.60523 | -7.93410 | -6.37231 |
| $E(_{AO/HO})\ (eV)$ | 0 | -14.63489 | -14.53414 | 0 | -14.63489 | 0 | -14.63489 | 0 | -14.53414 | -14.63489 |
| $\Delta E_{H_2MO}(_{AO/HO})\ (eV)$ | -2.69893 | -2.26759 | 0 | -2.26759 | -2.26759 | -1.85836 | -0.92918 | -3.71673 | 0 | -2.26758 |
| $E_T(_{AO/HO})\ (eV)$ | 2.69893 | -12.36730 | -14.53414 | 2.26759 | -12.36730 | 1.85836 | -13.70571 | 3.71673 | -14.53414 | -12.36731 |
| $E(_{n_3\ AO/HO})\ (eV)$ | 0 | 0 | -14.53414 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $E_T(_{H_2MO})\ (eV)$ | -63.27074 | -31.63543 | -48.73654 | -63.27075 | -31.63541 | -63.27100 | -31.63527 | -63.27056 | -31.63534 | -31.63533 |
| $E_T\left(atom-atom,msp^3.AO\right)\ (eV)$ | -2.69893 | -1.13379 | 0 | -2.26759 | 0.00000 | -1.85836 | -0.92918 | -3.71673 | 0 | 0 |
| $E_T(_{MO})\ (eV)$ | -65.96966 | -32.76916 | -48.73660 | -65.53833 | -31.63537 | -65.12910 | -32.56455 | -66.98746 | -31.63537 | -31.63537 |
| $\omega\ \left(10^{15}\ rad/s\right)$ | 59.4034 | 14.3055 | 68.9812 | 15.4421 | 19.8904 | 15.4704 | 21.5213 | 15.7474 | 48.7771 | 28.9084 |
| $E_K\ (eV)$ | 39.10034 | 9.41610 | 45.40465 | 10.16428 | 13.09221 | 10.18290 | 14.16571 | 10.36521 | 32.10594 | 19.02803 |
| $\bar{E}_D\ (eV)$ | -0.40804 | -0.19893 | -0.42172 | -0.20668 | -0.22646 | -0.20558 | -0.24248 | -0.21333 | -0.35462 | -0.27301 |
| $\bar{E}_{Kvib}\ (eV)$ | 0.21077<br>[12] | 0.15498<br>[58] | 0.40929<br>[22] | 0.17897<br>[6] | 0.14667<br>[67] | 0.20768<br>[62] | 0.12944<br>[23] | 0.11159<br>[12] | 0.40696<br>[24] | 0.39427<br>[60] |
| $\bar{E}_{osc}\ (eV)$ | -0.30266 | -0.12144 | -0.21708 | -0.11720 | -0.15312 | -0.10174 | -0.17775 | -0.15754 | -0.15115 | -0.07587 |
| $E_{mag}\ (eV)$ | 0.11441 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 |
| $E_T(_{Group})\ (eV)$ | -66.57498 | -32.89060 | -49.17075 | -65.77272 | -31.64046 | -65.33259 | -32.74230 | -67.30254 | -31.78651 | -31.71124 |
| $E_{initial}(_{c_4\ AO/HO})\ (eV)$ | -14.63489 | -14.63489 | -14.53414 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.53414 | -14.63489 |
| $E_{initial}(_{c_5\ AO/HO})\ (eV)$ | 0 | 0 | -13.59844 | 0 | 0 | 0 | 0 | 0 | -13.59844 | -13.59844 |
| $E_D(_{Group})\ (eV)$ | 7.80660 | 3.62082 | 7.43973 | 7.23317 | 2.37068 | 6.79303 | 3.47253 | 8.76298 | 3.51208 | 3.32988 |

Table 15.343. The total gaseous bond energies of guanine calculated using the functional group composition and the energies of Table 15.342 compared to the experimental values [3].

| Formula | Name | $C=O$ Group | $C-N$ (a) Group | $NH_2$ Group | $C=C$ Group | $C-C$ Group | $N=C$ Group | $C-N$ (b) Group | $C-N-C$ Group | $NH$ Group | $CH$ Group | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $C_5H_5N_5O$ | Guanine | 1 | 1 | 1 | 1 | 1 | 2 | 2 | 2 | 2 | 1 | 76.88212 | 77.41849[a] | 0.00693 |

[a] Crystal.

Table 15.344. The bond angle parameters of guanine and experimental values [65]. In the calculation of $\theta_v$, the parameters from the preceding angle were used. $E_T$ is $E_T(atom-atom,msp^3.AO)$.

| Atoms of Angle | 2c' Bond 1 ($a_0$) | 2c' Bond 2 ($a_0$) | 2c' Terminal Atoms ($a_0$) | $E_{Coulombic}$ Atom 1 | Atom 1 Hybridization Designation (Table 15.3B) | $E_{Coulombic}$ Atom 2 | Atom 2 Hybridization Designation (Table 15.3B) | $c_2$ Atom 1 | $c_2$ Atom 2 | $C_1$ | $C_2$ | $c_1$ | $c_2'$ | $E_T$ (eV) | $\theta_v$ (°) | $\theta_1$ (°) | $\theta_2$ (°) | Cal. $\theta$ (°) | Exp. $\theta$ (°) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $\angle N_bC_aC_d$ | 2.59228 | 2.74663 | 4.3359 | -14.53414 | N | -16.42413 $C_d$ | 13 | 0.84665 Eq. (15.171) | 0.82840 | 1 | 1 | 1 | 0.83753 | -1.44915 | | | | 108.57 | 110.8 |
| $\angle N_bC_aO$ | 2.59228 | 2.27954 | 4.2426 | -16.68411 | 18 | -16.17521 | 8 | 0.81549 | 0.84115 | 1 | 1 | 1 | 0.82832 | -1.44915 | | | | 120.98 | 120.4 |
| $\angle OC_aC_d$ | | | | | | | | | | | | | | | | 108.57 | 120.98 | 130.44 | 128.8 |
| $\angle C_bN_bC_a$ | 2.59228 | 2.59228 | 4.5826 | -17.25101 | 28 | -17.10440 | 25 | 0.78870 | 0.79546 | 1 | 1 | 1 | 0.79208 | -1.85836 | | | | 124.23 | 125.6 |
| $\angle N_bC_bN_c$ | 2.59228 | 2.60766 | 4.5166 | -15.75493 | 4 | -15.75493 | 4 | 0.86359 | 0.86359 | 1 | 1 | 1 | 0.86359 | -1.44915 | | | | 120.59 | 123.3 |
| $\angle H_bN_bC_a$ | 1.88268 | 2.64855 | 3.9158 | -14.53414 | N | -14.82575 $C_a$ | 1 | 0.93613 Eq. (13.248) | 0.91771 | 0.75 | 1 | 0.75 | 0.98033 | 0 | | | | 118.60 | |
| $\angle C_bN_bH_b$ | | | | | | | | | | | | | | | | 124.23 | 118.60 | 117.17 | |
| $\angle N_bC_bN_a$ | 2.59228 | 2.53797 | 4.3818 | -16.68411 | 18 | -15.39265 | 2 | 0.81549 | 0.88392 | 1 | 1 | 1 | 0.84971 | -1.44915 | | | | 117.32 | 115.8 |
| $\angle N_aC_bN_c$ | 2.53797 | 2.60766 | 4.4721 | -15.39265 | 2 | -16.21952 | 9 | 0.88392 | 0.83885 | 1 | 1 | 1 | 0.86138 | -1.44915 | | | | 120.71 | 120.9 |
| $\angle HN_aC_b$ | 1.88268 | 2.53797 | 3.8987 | -14.53414 | N | -16.32183 | 11 | 0.93613 Eq. (13.248) | 0.83360 | 0.75 | 1 | 0.75 | 0.98458 | 0 | | | | 123.07 | 118 [66] |
| $\angle HN_aH$ | 1.88268 | 1.88268 | 3.1559 | -14.53414 | N | H | H | 0.93613 Eq. (13.248) | 1 | 1 | 1 | 0.75 | 1.06823 | 0 | | | | 113.89 | 113.9 [1] (aniline) |
| $\angle C_bN_cC_c$ | 2.60766 | 2.70148 | 4.4721 | -17.25101 | 28 | -17.35332 | 29 | 0.78870 | 0.78405 | 1 | 1 | 1 | 0.78637 | -1.85836 | | | | 114.77 | 112.6 |
| $\angle N_cC_cN_d$ | 2.70148 | 2.59228 | 4.7117 | -14.53414 | N | -14.53414 | N | 0.84665 Eq. (15.171) | 0.84665 Eq. (15.171) | 1 | 1 | 1 | 0.84665 | -1.65376 | | | | 125.75 | 125.8 |
| $\angle N_cC_cC_d$ | 2.70148 | 2.60925 | 4.7539 | -14.53414 | N | -15.95955 | 6 | 0.84665 Eq. (15.171) | 0.85252 | 1 | 1 | 1 | 0.84958 | -1.65376 | | | | 127.05 | 128.3 |
| $\angle C_aC_dC_c$ | 2.74663 | 2.60925 | 4.6476 | -17.10440 | 25 | -16.88873 | 20 | 0.79546 | 0.80561 | 1 | 1 | 1 | 0.80054 | -1.85836 | | | | 120.38 | 119.4 |
| $\angle C_cN_dC_e$ | 2.59228 | 2.59228 | 4.2071 | -17.95963 | 39 | -17.95963 | 39 | 0.75758 | 0.75758 | 1 | 1 | 1 | 0.75758 | -1.85836 | | | | 108.48 | 108.2 |
| $\angle N_dC_cC_d$ | 2.59228 | 2.60925 | 4.1473 | -14.53414 | N | -17.35332 | 29 | 0.84665 Eq. (15.171) | 0.78405 | 1 | 1 | 1 | 0.81535 | -1.44915 | | | | 105.75 | 105.9 |
| $\angle N_eC_eN_d$ | 2.60766 | 2.60287 | 4.3359 | -16.21952 | 9 | -16.03838 | 7 | 0.83885 | 0.84833 | 1 | 1 | 1 | 0.84359 | -1.44915 | | | | 112.64 | 110.0 |
| $\angle C_eN_dH$ | 2.59228 | 1.88268 | 4.0166 | -14.53414 | N | -15.95954 | 6 | 0.84665 Eq. (15.171) | 0.85252 | 0.75 | 1 | 0.75 | 1.00693 | 0 | | | | 126.96 | 127 [66] |
| $\angle C_cN_dH$ | | | | | | | | | | | | | | | | 108.48 | 126.96 | 124.56 | 127 |
| $\angle HC_eN_e$ | 2.02241 | 2.60766 | 4.1312 | -16.68411 | 18 | -14.53414 | N | 0.81549 | 0.84665 Eq. (15.171) | 0.75 | 1 | 0.75 | 1.03820 | 0 | | | | 125.85 | 126 [66] |
| $\angle N_dC_eH$ | | | | | | | | | | | | | | | | 112.64 | 125.85 | 121.52 | 119 [66] |
| $\angle C_dN_eC_e$ | 2.70148 | 2.60766 | 4.2661 | -17.92022 | 37 | -17.92022 | 37 | 0.75924 | 0.75924 | 1 | 1 | 1 | 0.75924 | -1.85836 | | | | 106.93 | 108.0° |
| $\angle N_eC_dC_c$ | 2.70148 | 2.60925 | 4.2895 | -14.53414 | N | -16.42414 | 13 | 0.84665 Eq. (15.171) | 0.82840 | 1 | 1 | 1 | 0.83753 | -1.44915 | | | | 107.73 | 107.9 |
| $\angle C_aC_dN_e$ | 2.74663 | 2.70148 | 4.9396 | -17.10440 | 25 | -14.53414 | N | 0.79546 | 0.84665 Eq. (15.171) | 1 | 1 | 1 | 0.82105 | -1.85836 | | | | 130.10 | 133.6 |

## CYTOSINE

Cytosine having the formula $C_4H_5N_3O$ is a pyrimidine with a carbonyl substitution at position $C_b$, and a primary amine moiety is at position $C_a$ as shown in Figure 15.59B. The carbonyl and adjacent $C_b-N_b$ functional groups are equivalent to the corresponding groups of alkyl amides. The $NH_2$ and $C_a-N_a$ functional groups of the primary amine moiety are equivalent to the $NH_2$ and $C_a-N_a$ functional groups of adenine. The vinyl moiety, $HC_c=C_dH$, comprises $C=C$ and $CH$ functional groups that are equivalent to the corresponding alkene groups. Cytosine further comprises $N_b=C_a$, $N_cH$, and $C_b-N_c-C_c$ groups that are equivalent to the corresponding groups of imidazole as given in the corresponding section. The $C_a-C_d$ bond comprises another functional group that is equivalent to the $C_a-C_d$ group of guanine and thymine except that $E_T\left(atom-atom,msp^3.AO\right)$ is equivalent to the contribution of a $C2sp^3$ HO of an alkane, $-0.92918\ eV$ (Eq. (14.513)), in order to match the energies of the single and double-bonded moieties within the molecule.

The symbols of the functional groups of cytosine are given in Table 15.345. The geometrical (Eqs. (15.1-15.5) and (15.51)), intercept (Eqs. (15.80-15.87)), and energy (Eqs. (15.6-15.11) and (15.17-15.65)) parameters of cytosine are given in Tables 15.346, 15.347, and 15.348, respectively. The total energy of cytosine given in Table 15.349 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.348 corresponding to functional-group composition of the molecule. The bond angle parameters of cytosine determined using Eqs. (15.88-15.117) are given in Table 15.350. The color scale, charge-density of cytosine comprising atoms with the outer shell bridged by one or more $H_2$-type ellipsoidal MOs or joined with one or more hydrogen MOs is shown in Figure 15.59A.

Figure 15.59. (A) Color scale, charge-density of cytosine showing the orbitals of the atoms at their radii, the ellipsoidal surface of each $H$ or $H_2$-type ellipsoidal MO that transitions to the corresponding outer shell of the atom(s) participating in each bond, and the hydrogen nuclei. (B) Chemical structure and atomic designation of cytosine.

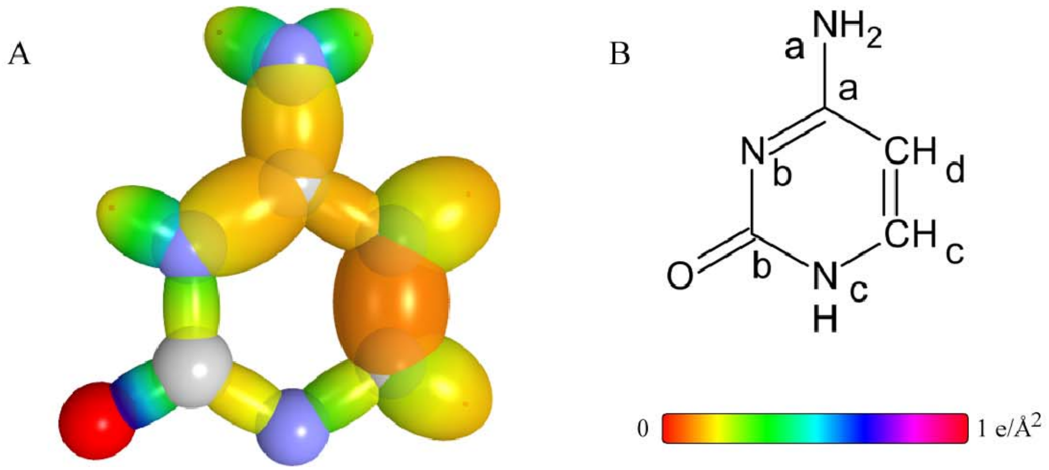


Table 15.345. The symbols of functional groups of cytosine.

| Functional Group | Group Symbol |
|---|---|
| $C_a-N_a$ | $C-N$ (a) |
| $NH_2$ group | $NH_2$ |
| $N_b=C_a$ double bond | $N=C$ |
| $C_b=O$ (alkyl amide) | $C=O$ |
| $C_b-N_b$ amide | $C-N$ (b) |
| $C_c=C_d$ double bond | $C=C$ |
| $C_cH$ $C_dH$ | $CH$ |
| $C_a-C_d$ | $C-C$ |
| $C_b-N_c-C_c$ | $C-N-C$ |
| $N_cH$ group | $NH$ |

Table 15.346. The geometrical bond parameters of cytosine and experimental values [1].

| Parameter | $C-N$ (a) Group | $NH_2$ Group | $N=C$ Group | $C=O$ Group | $C-N$ (b) Group | $C=C$ Group | $CH$ Group | $C-C$ Group | $C-N-C$ Group | $NH$ Group |
|---|---|---|---|---|---|---|---|---|---|---|
| $a$ $(a_0)$ | 1.61032 | 1.24428 | 1.44926 | 1.29907 | 1.75370 | 1.47228 | 1.53380 | 1.88599 | 1.43222 | 1.24428 |
| $c'$ $(a_0)$ | 1.26898 | 0.94134 | 1.30383 | 1.13977 | 1.32427 | 1.26661 | 1.01120 | 1.37331 | 1.29614 | 0.94134 |
| Bond Length $2c'$ $(Å)$ | 1.34303 | 0.99627 | 1.37991 | 1.20628 | 1.40155 | 1.34052 | 1.07021 | 1.45345 | 1.37178 | 0.996270 |
| Exp. Bond Length $(Å)$ | 1.34 [64]<br>(adenine) | 0.998<br>(aniline) | | 1.220<br>(acetamide)<br>1.225<br>(N-methylacetamide) | 1.380<br>(acetamide) | 1.34 [65]<br>(cytosine)<br>1.342<br>(2-methylpropene)<br>1.346<br>(2-butene)<br>1.349<br>(1,3-butadiene) | 1.076<br>(pyrrole) | 1.43 [65]<br>(cytosine) | 1.370<br>(pyrrole) | 0.996<br>(pyrrole) |
| $b,c$ $(a_0)$ | 0.99137 | 0.81370 | 0.63276 | 0.62331 | 1.14968 | 0.75055 | 1.15326 | 1.29266 | 0.60931 | 0.81370 |
| $e$ | 0.78803 | 0.75653 | 0.89965 | 0.87737 | 0.75513 | 0.86030 | 0.65928 | 0.72817 | 0.90499 | 0.75653 |

Table 15.347. The MO to HO intercept geometrical bond parameters of cytosine. $R_1$ is an alkyl group and $R$, $R'$, $R''$ are $H$ or alkyl groups. $E_T$ is $E_T$ (*atom* – *atom,msp*$^3$.*AO*).

| Bond | Atom | $E_T$ (eV) Bond 1 | $E_T$ (eV) Bond 2 | $E_T$ (eV) Bond 3 | $E_T$ (eV) Bond 4 | Final Total Energy $C2sp^3$ (eV) | $r_{initial}$ $(a_0)$ | $r_{final}$ $(a_0)$ | $E_{Coulomb}(C2sp^3)$ (eV) Final | $E(C2sp^3)$ (eV) Final | $\theta'$ (°) | $\theta_1$ (°) | $\theta_2$ (°) | $d_1$ $(a_0)$ | $d_2$ $(a_0)$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $C_d(N_b)C_aN_aH-H$ | $N_a$ | -0.56690 | 0 | 0 | 0 | | 0.93084 | 0.88392 | -15.39265 | | 121.74 | 58.26 | 67.49 | 0.47634 | 0.46500 |
| $C_d(N_b)C_a-N_aH_2$ | $N_a$ | -0.56690 | 0 | 0 | 0 | | 0.93084 | 0.88392 | -15.39265 | | 113.13 | 66.87 | 55.08 | 0.92180 | 0.34719 |
| $C_d(N_b)C_a-N_aH_2$ | $C_a$ | -0.56690 | -0.92918 | -0.46459 | 0 | -153.57636 | 0.91771 | 0.81052 | -16.78642 | -16.59556 | 108.27 | 71.73 | 50.93 | 1.01493 | 0.25406 |
| $C_d(N_a)C_a=N_bC_b$ | $N_b$ | -0.92918 | -0.82688 | 0 | 0 | | 0.93084 | 0.82053 | -16.58181 | | 137.50 | 42.50 | 61.17 | 0.69886 | 0.60497 |
| $C_d(N_a)C_a=N_bC_b$ | $C_a$ | -0.92918 | -0.56690 | -0.46459 | 0 | -153.57636 | 0.91771 | 0.81052 | -16.78642 | -16.59556 | 137.11 | 42.89 | 60.67 | 0.70998 | 0.59385 |
| $C_aN_b-C_b(O)N_c$ | $N_b$ | -0.82688 | -0.92918 | 0 | 0 | | 0.93084 | 0.82053 | -16.58181 | | 96.19 | 83.81 | 45.20 | 1.23578 | 0.08850 |
| $C_aN_b-C_b(O)N_c$ | $C_b$ | -0.82688 | -1.34946 | -0.92918 | 0 | -154.72121 | 0.91771 | 0.75878 | -17.93127 | -17.74041 | 90.51 | 89.49 | 41.30 | 1.31755 | 0.00672 |
| $N_b(N_c)C_b=O$ | $O_a$ | -1.34946 | 0 | 0 | 0 | | 1.00000 | 0.84115 | -16.17521 | | 137.27 | 42.73 | 66.31 | 0.52193 | 0.61784 |
| $N_b(N_c)C_b=O$ | $C_b$ | -1.34946 | -0.82688 | -0.92918 | 0 | -154.72121 | 0.91771 | 0.75878 | -17.93127 | -17.74041 | 133.67 | 46.33 | 61.70 | 0.61582 | 0.52395 |
| $N-H$ $(N_cH)$ | $N_c$ | -0.92918 | -0.92918 | 0 | 0 | | 0.93084 | 0.81549 | -16.68411 | | 117.34 | 62.66 | 62.90 | 0.56678 | 0.37456 |
| $C-H$ $(C_cH)$ | $C_c$ | -1.13380 | -0.92918 | 0 | 0 | -153.67867 | 0.91771 | 0.80561 | -16.88873 | -16.69786 | 83.35 | 96.65 | 43.94 | 1.10452 | 0.09331 |
| $C-H$ $(C_dH)$ | $C_d$ | -1.13380 | -0.46459 | 0 | 0 | -153.21408 | 0.91771 | 0.82840 | -16.42414 | -16.23327 | 85.93 | 94.07 | 45.77 | 1.06995 | 0.05875 |
| $N_b(O)C_b-N_cHC_c$ | $N_c$ | -0.92918 | -0.92918 | 0 | 0 | | 0.93084 | 0.81549 | -16.68411 | | 138.92 | 41.08 | 61.59 | 0.68147 | 0.61467 |
| $N_b(O)C_b-N_cHC_c$ | $C_b$ | -0.92918 | -1.34946 | -0.82688 | 0 | -154.72121 | 0.91771 | 0.75878 | -17.93127 | -17.74041 | 136.68 | 43.32 | 58.70 | 0.74414 | 0.55200 |
| $C_bHN_c-C_cHC_d$ | $N_c$ | -0.92918 | -0.92918 | 0 | 0 | | 0.93084 | 0.81549 | -16.68411 | | 138.92 | 41.08 | 61.59 | 0.68147 | 0.61467 |
| $C_bHN_c-C_cHC_d$ | $C_d$ | -0.92918 | -1.13379 | 0 | 0 | -153.67866 | 0.91771 | 0.80561 | -16.88873 | -16.69786 | 138.54 | 41.46 | 61.09 | 0.69238 | 0.60376 |
| $N_cHC_c=C_dHC_a$ | $C_c$ | -1.13380 | -0.92918 | 0.00000 | 0 | -153.67867 | 0.91771 | 0.80561 | -16.88873 | -16.69786 | 127.61 | 52.39 | 58.24 | 0.77492 | 0.49168 |
| $N_cHC_c=C_dHC_a$ | $C_d$ | -1.13380 | -0.46459 | 0.00000 | 0 | -153.21408 | 0.91771 | 0.82840 | -16.42414 | -16.23327 | 128.72 | 51.28 | 59.45 | 0.74844 | 0.51817 |
| $HC_cC_d-C_a(N_a)N_b$ | $C_a$ | -0.46459 | -0.56690 | -0.92918 | 0 | -153.57636 | 0.91771 | 0.81052 | -16.78642 | -16.59556 | 82.65 | 97.35 | 38.45 | 1.47695 | 0.10364 |
| $HC_cC_d-C_a(N_a)N_b$ | $C_d$ | -0.46459 | -1.13379 | 0 | 0 | -153.21407 | 0.91771 | 0.82840 | -16.42414 | -16.23327 | 84.52 | 95.48 | 39.64 | 1.45240 | 0.07908 |

Table 15.348. The energy parameters ($eV$) of functional groups of cytosine.

| Parameters | $C-N$ (a) Group | $NH_2$ Group | $N=C$ Group | $C=O$ Group | $C-N$ (b) Group | $C=C$ Group | $CH$ Group | $C-C$ Group | $C-N-C$ Group | $NH$ Group |
|---|---|---|---|---|---|---|---|---|---|---|
| $n_1$ | 1 | 2 | 2 | 2 | 1 | 2 | 1 | 1 | 2 | 1 |
| $n_2$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $n_3$ | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $C_1$ | 0.5 | 0.75 | 0.5 | 0.5 | 0.5 | 0.5 | 0.75 | 0.5 | 0.5 | 0.75 |
| $C_2$ | 1 | 0.93613 | 0.85252 | 1 | 1 | 0.91771 | 1 | 1 | 0.85252 | 0.93613 |
| $c_1$ | 1 | 0.75 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 0.75 |
| $c_2$ | 0.84665 | 0.92171 | 0.84665 | 0.85395 | 0.91140 | 0.91771 | 0.91771 | 0.91771 | 0.84665 | 0.92171 |
| $c_3$ | 0 | 0 | 0 | 2 | 0 | 0 | 1 | 0 | 0 | 1 |
| $c_4$ | 2 | 1 | 4 | 4 | 2 | 4 | 1 | 2 | 4 | 1 |
| $c_5$ | 0 | 2 | 0 | 0 | 0 | 0 | 1 | 0 | 0 | 1 |
| $C_{1o}$ | 0.5 | 1.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.75 | 0.5 | 0.5 | 0.75 |
| $C_{2o}$ | 1 | 1 | 0.85252 | 1 | 1 | 0.91771 | 1 | 1 | 0.85252 | 1 |
| $V_e\ (eV)$ | -35.50149 | -78.97795 | -103.92756 | -111.25473 | -36.88558 | -102.08992 | -39.09538 | -33.63376 | -106.58684 | -39.48897 |
| $V_p\ (eV)$ | 10.72181 | 28.90735 | 20.87050 | 23.87467 | 10.27417 | 21.48386 | 13.45505 | 9.90728 | 20.99432 | 14.45367 |
| $T\ (eV)$ | 11.02312 | 31.73641 | 35.85539 | 42.82081 | 10.51650 | 34.67062 | 12.74462 | 8.91674 | 37.21047 | 15.86820 |
| $V_m\ (eV)$ | -5.51156 | -15.86820 | -17.92770 | -21.41040 | -5.25825 | -17.33531 | -6.37231 | -4.45837 | -18.60523 | -7.93410 |
| $E(_{AO/HO})\ (eV)$ | -14.63489 | -14.53414 | 0 | 0 | -14.63489 | 0 | -14.63489 | -14.63489 | 0 | -14.53414 |
| $\Delta E_{H_2MO}(_{AO/HO})\ (eV)$ | -2.26759 | 0 | -1.85836 | -2.69893 | -4.35268 | 0 | -2.26758 | -2.26759 | -3.71673 | 0 |
| $E_T(_{AO/HO})\ (eV)$ | -12.36730 | -14.53414 | 1.85836 | 2.69893 | -10.28221 | 0 | -12.36731 | -12.36730 | 3.71673 | -14.53414 |
| $E(_{n_3\ AO/HO})\ (eV)$ | 0 | -14.53414 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $E_T(_{H_2MO})\ (eV)$ | -31.63543 | -48.73654 | -63.27100 | -63.27074 | -31.63537 | -63.27075 | -31.63533 | -31.63541 | -63.27056 | -31.63534 |
| $E_T\left(atom-atom, msp^3.AO\right)\ (eV)$ | -1.13379 | 0 | -1.85836 | -2.69893 | -1.65376 | -2.26759 | 0 | -0.92918 | -3.71673 | 0 |
| $E_T(_{MO})\ (eV)$ | -32.76916 | -48.73660 | -65.12910 | -65.96966 | -33.28912 | -65.53833 | -31.63537 | -32.56455 | -66.98746 | -31.63537 |
| $\omega\ \left(10^{15}\ rad/s\right)$ | 14.3055 | 68.9812 | 15.4704 | 59.4034 | 12.5874 | 43.0680 | 28.9084 | 19.8904 | 15.7474 | 48.7771 |
| $E_K\ (eV)$ | 9.41610 | 45.40465 | 10.18290 | 39.10034 | 8.28526 | 28.34813 | 19.02803 | 13.09221 | 10.36521 | 32.10594 |
| $\bar{E}_D\ (eV)$ | -0.19893 | -0.42172 | -0.20558 | -0.40804 | -0.18957 | -0.34517 | -0.27301 | -0.23311 | -0.21333 | -0.35462 |
| $\bar{E}_{Kvib}\ (eV)$ | 0.15498<br>[58] | 0.40929<br>[22] | 0.20768<br>[62] | 0.21077<br>[12] | 0.17358<br>[33] | 0.17897<br>[6] | 0.39427<br>[60] | 0.14667<br>[67] | 0.11159<br>[12] | 0.40696<br>[24] |
| $\bar{E}_{osc}\ (eV)$ | -0.12144 | -0.21708 | -0.10174 | -0.30266 | -0.10278 | -0.25568 | -0.07587 | -0.15977 | -0.15754 | -0.15115 |
| $E_{mag}\ (eV)$ | 0.14803 | 0.14803 | 0.14803 | 0.11441 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 |
| $E_T(_{Group})\ (eV)$ | -32.89060 | -49.17075 | -65.33259 | -66.57498 | -33.39190 | -66.04969 | -31.71124 | -32.57629 | -67.30254 | -31.78651 |
| $E_{initial}(_{c_4\ AO/HO})\ (eV)$ | -14.63489 | -14.53414 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.53414 |
| $E_{initial}(_{c_5\ AO/HO})\ (eV)$ | 0 | -13.59844 | 0 | 0 | 0 | 0 | -13.59844 | 0 | 0 | -13.59844 |
| $E_D(_{Group})\ (eV)$ | 3.62082 | 7.43973 | 6.79303 | 7.80660 | 4.12212 | 7.51014 | 3.32988 | 3.30651 | 8.76298 | 3.51208 |

Table 15.349. The total gaseous bond energies of cytosine calculated using the functional group composition and the energies of Table 15.348 compared to the experimental values [3].

| Formula | Name | $C-N$ (a) Group | $NH_2$ Group | $N=C$ Group | $C=O$ Group | $C-N$ (b) Group | $C=C$ Group | $CH$ Group | $C-C$ Group | $C-N-C$ Group | $NH$ Group | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $C_4H_5N_3O$ | Cytosine | 1 | 1 | 1 | 1 | 1 | 1 | 2 | 1 | 1 | 1 | 59.53378 | 60.58056 | 0.01728 |

Table 15.350. The bond angle parameters of cytosine and experimental values [64]. In the calculation of $\theta_v$, the parameters from the preceding angle were used. $E_T$ is $E_T(atom-atom,msp^3.AO)$.

| Atoms of Angle | $2c'$ Bond 1 $(a_0)$ | $2c'$ Bond 2 $(a_0)$ | $2c'$ Terminal Atoms $(a_0)$ | $E_{Coulombic}$ Atom 1 | Atom 1 Hybridization Designation (Table 15.3B) | $E_{Coulombic}$ Atom 2 | Atom 2 Hybridization Designation (Table 15.3B) | $c_2$ Atom 1 | $c_2$ Atom 2 | $C_1$ | $C_2$ | $c_1$ | $c_2'$ | $E_T$ (eV) | $\theta_v$ (°) | $\theta_1$ (°) | $\theta_2$ (°) | Cal. $\theta$ (°) | Exp. $\theta$ (°) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $\angle HNH$ | 1.88268 | 1.88268 | 3.1559 | -14.53414 | N | H | H | 0.93613 Eq. (13.248) | 1 | 1 | 1 | 0.75 | 1.06823 | 0 | | | | 113.89 | 113.9 [1] (aniline) |
| $\angle C_aNH$ | 2.53797 | 1.88268 | 3.8123 | -16.78642 | 19 | -14.53414 | N | 0.81052 Eq. (15.71) | 0.77638 Eq. (15.173) | 0.75 | 1 | 0.75 | 0.95787 | 0 | | | | 118.42 | 118 [66] |
| $\angle N_bC_aC_d$ | 2.60766 | 2.74663 | 4.6476 | -14.53414 | N | -16.42414 | 13 | 0.84665 Eq. (15.171) | 0.82840 | 1 | 1 | 1 | 0.83753 | -1.65376 | | | | 120.43 | 121.4 |
| $\angle N_bC_aN_a$ | 2.60766 | 2.53797 | 4.4272 | -15.39265 | 2 | -16.58181 | 16 | 0.88392 | 0.82053 | 1 | 1 | 1 | 0.85222 | -1.44915 | | | | 118.71 | 117.5 |
| $\angle C_dC_aN_a$ | | | | | | | | | | | | | | | | 120.43 | 118.71 | 120.85 | 121.1 |
| $\angle C_bN_bC_a$ | 2.64855 | 2.60766 | 4.4944 | -17.93127 | 38 | -16.78642 | 19 | 0.75878 | 0.81052 | 1 | 1 | 1 | 0.78465 | -1.85836 | | | | 117.53 | 120.3 |
| $\angle N_bC_bN_c$ | 2.64855 | 2.59228 | 4.4721 | -16.58181 | 16 | -16.68411 | 17 | 0.82053 | 0.81549 | 1 | 1 | 1 | 0.81801 | -1.65376 | | | | 117.15 | 118.9 |
| $\angle N_cC_bO$ | 2.59228 | 2.27954 | 4.2426 | -16.68411 | 17 | -16.17521 | 8 | 0.81549 | 0.84115 | 1 | 1 | 1 | 0.82832 | -1.44915 | | | | 120.98 | 119.8 |
| $\angle N_bC_bO$ | | | | | | | | | | | | | | | | 117.15 | 120.98 | 121.87 | 121.3 |
| $\angle C_bN_cC_c$ | 2.59228 | 2.59228 | 4.4944 | -17.93127 | 38 | -16.88873 | 20 | 0.75878 | 0.80561 | 1 | 1 | 1 | 0.78219 | -1.85836 | | | | 120.20 | 121.7 |
| $\angle N_cC_cC_d$ | 2.59228 | 2.53321 | 4.4272 | -14.53414 | N | -15.95955 | 6 | 0.84665 Eq. (15.171) | 0.85252 | 1 | 1 | 1 | 0.84958 | -1.44915 | | | | 119.48 | 121.4 |
| $\angle H_cN_cC_c$ | 1.88268 | 2.59228 | 3.8644 | -14.53414 | N | -16.68411 | 17 | 0.84665 Eq. (15.171) | 0.81549 | 0.75 | 1 | 0.75 | 0.96320 | 0 | | | | 118.58 | |
| $\angle H_cN_cC_b$ | | | | | | | | | | | | | | | | 120.20 | 118.58 | 121.23 | |
| $\angle C_aC_dC_c$ | 2.74663 | 2.53321 | 4.5166 | -16.78642 | 19 | -17.81791 | 36 | 0.81052 | 0.76360 | 1 | 1 | 1 | 0.78706 | -1.85836 | | | | 117.56 | 116.4 |
| $\angle H_cC_cC_d$ | 2.02241 | 2.53321 | 3.9833 | -15.95955 | 6 | -15.95955 | 6 | 0.85252 | 0.85252 | 0.75 | 1 | 0.75 | 1.00000 | 0 | | | | 121.54 | |
| $\angle H_cC_cN_c$ | | | | | | | | | | | | | | | | 119.48 | 121.54 | 118.99 | |
| $\angle H_dC_dC_c$ | 2.02241 | 2.53321 | 3.9833 | -15.95955 | 6 | -15.95955 | 6 | 0.85252 | 0.85252 | 0.75 | 1 | 0.75 | 1.00000 | 0 | | | | 121.54 | |
| $\angle H_dC_dC_a$ | | | | | | | | | | | | | | | | 117.56 | 121.54 | 120.90 | |

## ALKYL PHOSPHINES ($\left(\left(C_nH_{2n+1}\right)_3P,\ n=1,2,3,4,5...\infty\right)$)

The alkyl phosphines, $\left(C_nH_{2n+1}\right)_3P$, comprise a $P-C$ functional group. The alkyl portion of the alkyl phosphine may comprise at least two terminal methyl groups ($CH_3$) at each end of each chain, and may comprise methylene ($CH_2$), and methylyne ($CH$) functional groups as well as $C$ bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($\left(CH_3\right)_2CH$) and t-butyl ($\left(CH_3\right)_3C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups. The branched-chain-alkane groups in alkyl phosphines are equivalent to those in branched-chain alkanes. The $P-C$ group may further join the $P3sp^3$ HO to an aryl HO.

As in the case of carbon, the bonding in the phosphorous atom involves $sp^3$ hybridized orbitals formed, in this case, from the $3p$ and $3s$ electrons of the outer shells with five $P3sp^3$ HOs rather than four $C2sp^3$ HOs. The $P-C$ bond forms between $P3sp^3$ and $C2sp^3$ HOs to yield phosphines. The semimajor axis $a$ of the $P-C$ functional group is solved using Eq. (15.51). Using the semimajor axis and the relationships between the prolate spheroidal axes, the geometric and energy parameters of the MO are calculated using Eqs. (15.1-15.117) in the same manner as the organic functional groups given in Organic Molecular Functional Groups and Molecules section.

The energy of phosphorous is less than the Coulombic energy between the electron and proton of $H$ given by Eq. (1.264). A minimum energy is achieved while matching the potential, kinetic, and orbital energy relationships given in the Hydroxyl Radical ($OH$) section with hybridization of the phosphorous atom such that in Eqs. (15.51) and (15.61), the sum of the energies of the $H_2$-type ellipsoidal MOs is matched to that of the $P3sp^3$ shell as in the case of the corresponding carbon and silicon molecules.

The $P$ electron configuration is $[Ne]3s^23p^3$ corresponding to the ground state ${}^4S_{3/2}$, and the $3sp^3$ hybridized orbital arrangement after Eq. (13.422) is:

$$\begin{array}{cccc} \multicolumn{4}{c}{3\mathrm{sp}^3\ \text{state}} \\ \underline{\uparrow\downarrow} & \underline{\uparrow} & \underline{\uparrow} & \underline{\uparrow} \\ 0,0 & 1,\text{-}1 & 1,0 & 1,1 \end{array} \qquad (15.174)$$

where the quantum numbers ($\ell, m_\ell$) are below each electron. The total energy of the state is given by the sum over the five electrons. The sum $E_T\left(P,3sp^3\right)$ of experimental energies [38] of $P$, $P^+$, $P^{2+}$, $P^{3+}$, and $P^{4+}$ is:

$$\begin{aligned} E_T\left(P,3sp^3\right) &= 65.0251\ eV + 51.4439\ eV + 30.2027\ eV + 19.7695\ eV + 10.48669\ eV \\ &= 176.92789\ eV \end{aligned} \qquad (15.175)$$

By considering that the central field decreases by an integer for each successive electron of the shell, the radius $r_{3sp^3}$ of the $P3sp^3$ shell may be calculated from the Coulombic energy using Eq. (15.13).

$$r_{3sp^3} = \sum_{n=10}^{14} \frac{(Z-n)e^2}{8\pi\varepsilon_0\left(e176.92789\ eV\right)} = \frac{15e^2}{8\pi\varepsilon_0\left(e176.92789\ eV\right)} = 1.15350a_0 \qquad (15.176)$$

where $Z=15$ for phosphorous. Using Eq. (15.14), the Coulombic energy $E_{Coulomb}\left(P,3sp^3\right)$ of the outer electron of the $P3sp^3$ shell is:

$$E_{Coulomb}\left(P,3sp^3\right) = \frac{-e^2}{8\pi\varepsilon_0 r_{3sp^3}} = \frac{-e^2}{8\pi\varepsilon_0 1.15350a_0} = -11.79519\ eV \qquad (15.177)$$

During hybridization, the spin-paired $3s$ electrons are promoted to the $P3sp^3$ shell as paired electrons at the radius $r_{3sp^3}$ of the $P3sp^3$ shell. The energy for the promotion is the difference in the magnetic energy given by Eq. (15.15) at the initial radius of the $3s$ electrons and the final radius of the $P3sp^3$ electrons. From Eq. (10.255) with $Z=15$, the radius $r_{12}$ of $P3s$ shell is

$$r_{12} = 1.09443a_0 \qquad (15.178)$$

Using Eqs. (15.15) and (15.178), the unpairing energy is:

$$E(magnetic) = \frac{2\pi\mu_0 e^2\hbar^2}{m_e^2}\left(\frac{1}{\left(r_{12}\right)^3} - \frac{1}{\left(r_{3sp^3}\right)^3}\right) = 8\pi\mu_o\mu_B^2\left(\frac{1}{\left(1.09443a_0\right)^3} - \frac{1}{\left(1.15350a_0\right)^3}\right) = 0.01273\ eV \qquad (15.179)$$

Using Eqs. (15.177) and (15.179), the energy $E\left(P,3sp^3\right)$ of the outer electron of the $P3sp^3$ shell is:

$$E\left(P,3sp^3\right)=\frac{-e^2}{8\pi\varepsilon_0 r_{3sp^3}}+\frac{2\pi\mu_0 e^2\hbar^2}{m_e^2}\left(\frac{1}{\left(r_{12}\right)^3}-\frac{1}{\left(r_{3sp^3}\right)^3}\right)=-11.79519\ eV+0.01273\ eV=-11.78246\ eV \tag{15.180}$$

For the $P-C$ functional group, hybridization of the $2s$ and $2p$ AOs of each $C$ and the $3s$ and $3p$ AOs of each $P$ to form single $2sp^3$ and $3sp^3$ shells, respectively, forms an energy minimum, and the sharing of electrons between the $C2sp^3$ and $P3sp^3$ HOs to form a MO permits each participating orbital to decrease in radius and energy. In branched-chain alkyl phosphines, the energy of phosphorous is less than the Coulombic energy between the electron and proton of $H$ given by Eq. (1.264). Thus, $c_2$ in Eq. (15.61) is one, and the energy matching condition is determined by the $C_2$ parameter. Then, the $C2sp^3$ HO has an energy of $E\left(C,2sp^3\right)=-14.63489\ eV$ (Eq. (15.25)), and the $P3sp^3$ HO has an energy of $E\left(P,3sp^3\right)=-11.78246\ eV$ (Eq. (15.180)). To meet the equipotential condition of the union of the $P-C$ $H_2$-type-ellipsoidal-MO with these orbitals, the hybridization factor $C_2$ of Eq. (15.61) for the $P-C$-bond MO given by Eqs. (15.77), (15.79), and (13.430) is:

$$C_2\left(C2sp^3HO\ to\ P3sp^3HO\right)=\frac{E\left(P,3sp^3\right)}{E\left(C,2sp^3\right)}c_2\left(C2sp^3HO\right)=\frac{-11.78246\ eV}{-14.63489\ eV}\left(0.91771\right)=0.73885 \tag{15.181}$$

The energy of the $P-C$-bond MO is the sum of the component energies of the $H_2$-type ellipsoidal MO given in Eq. (15.51) with $E\left(AO/HO\right)=E\left(P,3sp^3\right)$ given by Eq. (15.180), and $E_T\left(atom-atom,msp^3.AO\right)$ is one half $-0.72457\ eV$ given by Eq. (14.151) in order to match the energies of the carbon and phosphorous HOs.

The symbols of the functional groups of branched-chain alkyl phosphines are given in Table 15.351. The geometrical (Eqs. (15.1-15.5) and (15.51)), intercept (Eqs. (15.80-15.87)), and energy (Eqs. (15.6-15.11) and (15.17-15.65)) parameters of alkyl phosphines are given in Tables 15.352, 15.353, and 15.354, respectively. The total energy of each alkyl phosphine given in Table 15.355 was calculated as the sum over the integer multiple of each $E_D\left(Group\right)$ of Table 15.354 corresponding to functional-group composition of the molecule. The bond angle parameters of alkyl phosphines determined using Eqs. (15.88-15.117) are given in Table 15.356. The color scale, charge-density of exemplary alkyl phosphine, triphenylphosphine, comprising atoms with the outer shell bridged by one or more $H_2$-type ellipsoidal MOs or joined with one or more hydrogen MOs is shown in Figure 15.60.

Figure 15.60. Color scale, charge-density of triphenylphosphine showing the orbitals of the atoms at their radii, the ellipsoidal surface of each $H$ or $H_2$-type ellipsoidal MO that transitions to the corresponding outer shell of the atom(s) participating in each bond, and the hydrogen nuclei. (A) Top view. (B) Side view.

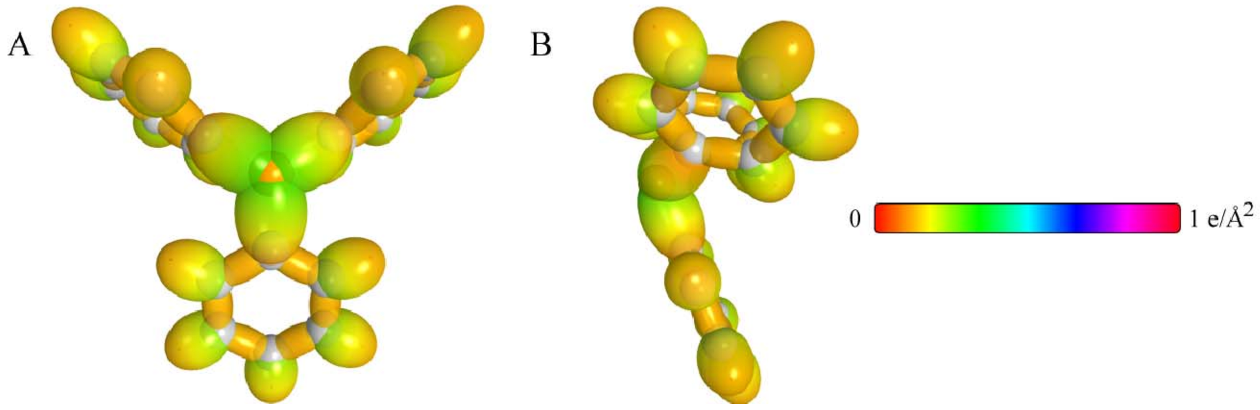


Table 15.351. The symbols of functional groups of alkyl phosphines.

| Functional Group | Group Symbol |
|---|---|
| *P-C* | $P-C$ |
| $CH_3$ group | $C-H\ (CH_3)$ |
| $CH_2$ group | $C-H\ (CH_2)$ |
| *CH* | $C-H$ (i) |
| *CC* bond (*n-C*) | $C-C$ (a) |
| *CC* bond (*iso-C*) | $C-C$ (b) |
| *CC* bond (*tert-C*) | $C-C$ (c) |
| *CC* (*iso* to *iso-C*) | $C-C$ (d) |
| *CC* (*t* to *t-C*) | $C-C$ (e) |
| *CC* (*t* to *iso-C*) | $C-C$ (f) |
| *CC* (aromatic bond) | $C\overset{3e}{=}C$ |
| *CH* (aromatic) | $CH$ (ii) |

**Table 15.352.** The geometrical bond parameters of alkyl phosphines and experimental values [1].

| Parameter | $P-C$ Group | $C-H\ (CH_3)$ Group | $C-H\ (CH_2)$ Group | $C-H$ (i) Group | $C-C$ (a) Group | $C-C$ (b) Group | $C-C$ (c) Group | $C-C$ (d) Group | $C-C$ (e) Group | $C-C$ (f) Group | $C\overset{3e}{=}C$ Group | $CH$ (ii) Group |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $a\ (a_0)$ | 2.29513 | 1.64920 | 1.67122 | 1.67465 | 2.12499 | 2.12499 | 2.10725 | 2.12499 | 2.10725 | 2.10725 | 1.47348 | 1.60061 |
| $c'\ (a_0)$ | 1.76249 | 1.04856 | 1.05553 | 1.05661 | 1.45744 | 1.45744 | 1.45164 | 1.45744 | 1.45164 | 1.45164 | 1.31468 | 1.03299 |
| Bond Length $2c'\ (\mathring{A})$ | 1.86534 | 1.10974 | 1.11713 | 1.11827 | 1.54280 | 1.54280 | 1.53635 | 1.54280 | 1.53635 | 1.53635 | 1.39140 | 1.09327 |
| Exp. Bond Length $(\mathring{A})$ | 1.847<br>$((CH_3)_2PCH_3)$<br>1.858<br>$(H_2PCH_3)$ | 1.107<br>($C-H$ propane)<br>1.117<br>($C-H$ butane) | 1.107<br>($C-H$ propane)<br>1.117<br>($C-H$ butane) | 1.122<br>(isobutane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.399<br>(benzene) | 1.101<br>(benzene) |
| $b,c\ (a_0)$ | 1.47012 | 1.27295 | 1.29569 | 1.29924 | 1.54616 | 1.54616 | 1.52750 | 1.54616 | 1.52750 | 1.52750 | 0.66540 | 1.22265 |
| $e$ | 0.76793 | 0.63580 | 0.63159 | 0.63095 | 0.68600 | 0.68600 | 0.68888 | 0.68600 | 0.68888 | 0.68888 | 0.89223 | 0.64537 |

**Table 15.353.** The MO to HO intercept geometrical bond parameters of alkyl phosphines. $R_1$ is an alkyl group and $R$, $R'$, $R''$ are $H$ or alkyl groups. $E_T$ is $E_T$ (*atom* – *atom,msp*$^3$*.AO*).

| Bond | Atom | $E_T$ (eV) Bond 1 | $E_T$ (eV) Bond 2 | $E_T$ (eV) Bond 3 | $E_T$ (eV) Bond 4 | Final Total Energy $C2sp^3$ (eV) | $r_{initial}$ $(a_0)$ | $r_{final}$ $(a_0)$ | $E_{Coulomb}$ (eV) Final | $E(C2sp^3)$ (eV) Final | $\theta'$ (°) | $\theta_1$ (°) | $\theta_2$ (°) | $d_1$ $(a_0)$ | $d_2$ $(a_0)$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $C-H\ (CH_3)$ | $C$ | -0.36229 | 0 | 0 | 0 | -151.97798 | 0.91771 | 0.89582 | -15.18804 | -14.99717 | 81.24 | 98.76 | 44.07 | 1.18494 | 0.13638 |
| $(CH_3)_2P-CH_3$ | $C$ | -0.18114 | 0 | 0 | 0 |  | 0.91771 | 0.90664 | -15.00689 | -14.81603 | 87.12 | 92.88 | 38.02 | 1.80811 | 0.04562 |
| $(CH_3)_2P-CH_3$ | $P$ | -0.18114 | -0.18114 | -0.18114 | 0 |  | 1.15350 | 0.88527 | -15.36918 |  | 85.24 | 94.76 | 36.88 | 1.83594 | 0.07345 |
| $C-H\ (CH_3)$ | $C$ | -0.92918 | 0 | 0 | 0 | -152.54487 | 0.91771 | 0.86359 | -15.75493 | -15.56407 | 77.49 | 102.51 | 41.48 | 1.23564 | 0.18708 |
| $C-H\ (CH_2)$ | $C$ | -0.92918 | -0.92918 | 0 | 0 | -153.47406 | 0.91771 | 0.81549 | -16.68412 | -16.49325 | 68.47 | 111.53 | 35.84 | 1.35486 | 0.29933 |
| $C-H\ (CH)$ | $C$ | -0.92918 | -0.92918 | -0.92918 | 0 | -154.40324 | 0.91771 | 0.77247 | -17.61330 | -17.42244 | 61.10 | 118.90 | 31.37 | 1.42988 | 0.37326 |
| $H_3C_aC_bH_2CH_2-$ $(C-C$ (a)) | $C_a$ | -0.92918 | 0 | 0 | 0 | -152.54487 | 0.91771 | 0.86359 | -15.75493 | -15.56407 | 63.82 | 116.18 | 30.08 | 1.83879 | 0.38106 |
| $H_3C_aC_bH_2CH_2-$ $(C-C$ (a)) | $C_b$ | -0.92918 | -0.92918 | 0 | 0 | -153.47406 | 0.91771 | 0.81549 | -16.68412 | -16.49325 | 56.41 | 123.59 | 26.06 | 1.90890 | 0.45117 |
| $R-H_2C_aC_b(H_2C_c-R')HCH_2-$ $(C-C$ (b)) | $C_b$ | -0.92918 | -0.92918 | -0.92918 | 0 | -154.40324 | 0.91771 | 0.77247 | -17.61330 | -17.42244 | 48.30 | 131.70 | 21.90 | 1.97162 | 0.51388 |
| $R-H_2C_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ $(C-C$ (c)) | $C_b$ | -0.92918 | -0.72457 | -0.72457 | -0.72457 | -154.71860 | 0.91771 | 0.75889 | -17.92866 | -17.73779 | 48.21 | 131.79 | 21.74 | 1.95734 | 0.50570 |
| $isoC_aC_b(H_2C_c-R')HCH_2-$ $(C-C$ (d)) | $C_b$ | -0.92918 | -0.92918 | -0.92918 | 0 | -154.40324 | 0.91771 | 0.77247 | -17.61330 | -17.42244 | 48.30 | 131.70 | 21.90 | 1.97162 | 0.51388 |
| $tertC_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ $(C-C$ (e)) | $C_b$ | -0.72457 | -0.72457 | -0.72457 | -0.72457 | -154.51399 | 0.91771 | 0.76765 | -17.92866 | -17.73779 | 50.04 | 129.96 | 22.66 | 1.94462 | 0.49298 |
| $tertC_aC_b(H_2C_c-R')HCH_2-$ $(C-C$ (f)) | $C_b$ | -0.72457 | -0.92918 | -0.92918 | 0 | -154.19863 | 0.91771 | 0.78155 | -17.40869 | -17.21783 | 52.78 | 127.22 | 24.04 | 1.92443 | 0.47279 |
| $isoC_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ $(C-C$ (f)) | $C_b$ | -0.72457 | -0.72457 | -0.72457 | -0.72457 | -154.51399 | 0.91771 | 0.76765 | -17.92866 | -17.73779 | 50.04 | 129.96 | 22.66 | 1.94462 | 0.49298 |

Table 15.354. The energy parameters ($eV$) of functional groups of alkyl phosphines.

| Parameters | $P-C$ Group | $CH_3$ Group | $CH_2$ Group | $CH$ (i) Group | $C-C$ (a) Group | $C-C$ (b) Group | $C-C$ (c) Group | $C-C$ (d) Group | $C-C$ (e) Group | $C-C$ (f) Group | $\overset{3e}{C=C}$ Group | $CH$ (ii) Group |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $f_1$ | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 0.75 | 1 |
| $n_1$ | 1 | 3 | 2 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 2 | 1 |
| $n_2$ | 0 | 2 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $n_3$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $C_1$ | 0.5 | 0.75 | 0.75 | 0.75 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.75 |
| $C_2$ | 0.73885 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 0.85252 | 1 |
| $c_1$ | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $c_2$ | 1 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.85252 | 0.91771 |
| $c_3$ | 0 | 0 | 1 | 1 | 0 | 0 | 0 | 1 | 1 | 0 | 0 | 1 |
| $c_4$ | 2 | 1 | 1 | 1 | 2 | 2 | 2 | 2 | 2 | 2 | 3 | 1 |
| $c_5$ | 0 | 3 | 2 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1 |
| $C_{1o}$ | 0.5 | 0.75 | 0.75 | 0.75 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.75 |
| $C_{2o}$ | 0.73885 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 0.85252 | 1 |
| $V_e$ $(eV)$ | -31.34959 | -107.32728 | -70.41425 | -35.12015 | -28.79214 | -28.79214 | -29.10112 | -28.79214 | -29.10112 | -29.10112 | -101.12679 | -37.10024 |
| $V_p$ $(eV)$ | 7.71965 | 38.92728 | 25.78002 | 12.87680 | 9.33352 | 9.33352 | 9.37273 | 9.33352 | 9.37273 | 9.37273 | 20.69825 | 13.17125 |
| $T$ $(eV)$ | 6.82959 | 32.53914 | 21.06675 | 10.48582 | 6.77464 | 6.77464 | 6.90500 | 6.77464 | 6.90500 | 6.90500 | 34.31559 | 11.58941 |
| $V_m$ $(eV)$ | -3.41479 | -16.26957 | -10.53337 | -5.24291 | -3.38732 | -3.38732 | -3.45250 | -3.38732 | -3.45250 | -3.45250 | -17.15779 | -5.79470 |
| $E(_{AO/HO})$ $(eV)$ | -11.78246 | -15.56407 | -15.56407 | -14.63489 | -15.56407 | -15.56407 | -15.35946 | -15.56407 | -15.35946 | -15.35946 | 0 | -14.63489 |
| $\Delta E_{H_2MO}(_{AO/HO})$ $(eV)$ | -0.36229 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | -1.13379 |
| $E_T(_{AO/HO})$ $(eV)$ | -11.42017 | -15.56407 | -15.56407 | -14.63489 | -15.56407 | -15.56407 | -15.35946 | -15.56407 | -15.35946 | -15.35946 | 0 | -13.50110 |
| $E_T(_{H_2MO})$ $(eV)$ | -31.63532 | -67.69451 | -49.66493 | -31.63533 | -31.63537 | -31.63537 | -31.63535 | -31.63537 | -31.63535 | -31.63535 | -63.27075 | -31.63539 |
| $E_T\left(atom-atom,msp^3.AO\right)$ $(eV)$ | -0.36229 | 0 | 0 | 0 | -1.85836 | -1.85836 | -1.44915 | -1.85836 | -1.44915 | -1.44915 | -2.26759 | -0.56690 |
| $E_T(_{MO})$ $(eV)$ | -31.99766 | -67.69450 | -49.66493 | -31.63537 | -33.49373 | -33.49373 | -33.08452 | -33.49373 | -33.08452 | -33.08452 | -65.53833 | -32.20226 |
| $\omega$ $\left(10^{15}\ rad/s\right)$ | 7.22663 | 24.9286 | 24.2751 | 24.1759 | 9.43699 | 9.43699 | 15.4846 | 9.43699 | 9.55643 | 9.55643 | 49.7272 | 26.4826 |
| $E_K$ $(eV)$ | 4.75669 | 16.40846 | 15.97831 | 15.91299 | 6.21159 | 6.21159 | 10.19220 | 6.21159 | 6.29021 | 6.29021 | 32.73133 | 17.43132 |
| $\bar{E}_D$ $(eV)$ | -0.13806 | -0.25352 | -0.25017 | -0.24966 | -0.16515 | -0.16515 | -0.20896 | -0.16515 | -0.16416 | -0.16416 | -0.35806 | -0.26130 |
| $\bar{E}_{Kvib}$ $(eV)$ | 0.17606<br>[68] | 0.35532<br>(Eq. (13.458)) | 0.35532<br>(Eq. (13.458)) | 0.35532<br>(Eq. (13.458)) | 0.12312<br>[2] | 0.17978<br>[4] | 0.09944<br>[5] | 0.12312<br>[2] | 0.12312<br>[2] | 0.12312<br>[2] | 0.19649<br>[49] | 0.35532<br>Eq. (13.458) |
| $\bar{E}_{osc}$ $(eV)$ | -0.05003 | -0.22757 | -0.14502 | -0.07200 | -0.10359 | -0.07526 | -0.15924 | -0.10359 | -0.10260 | -0.10260 | -0.25982 | -0.08364 |
| $E_{mag}$ $(eV)$ | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 |
| $E_T(_{Group})$ $(eV)$ | -32.04769 | -67.92207 | -49.80996 | -31.70737 | -33.59732 | -33.49373 | -33.24376 | -33.59732 | -33.18712 | -33.18712 | -49.54347 | -32.28590 |
| $E_{initial}(_{c_4\ AO/HO})$ $(eV)$ | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 |
| $E_{initial}(_{c_5\ AO/HO})$ $(eV)$ | 0 | -13.59844 | -13.59844 | -13.59844 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | -13.59844 |
| $E_D(_{Group})$ $(eV)$ | 2.77791 | 12.49186 | 7.83016 | 3.32601 | 4.32754 | 4.29921 | 3.97398 | 4.17951 | 3.62128 | 3.91734 | 5.63881 | 3.90454 |

Table 15.355. The total bond energies of alkyl phosphines calculated using the functional group composition and the energies of Table 15.354 compared to the experimental values [69].

| Formula | Name | $P-C$ | $CH_3$ | $CH_2$ | $CH$ (i) | $C-C$ (a) | $C-C$ (b) | $C-C$ (c) | $C-C$ (d) | $C-C$ (e) | $C-C$ (f) | $C\overset{3e}{=}C$ | $CH$ (ii) | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $C_3H_9P$ | Trimethylphosphine | 3 | 3 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 45.80930 | 46.87333 | 0.02270 |
| $C_6H_{15}P$ | Triethylphosphine | 3 | 3 | 3 | 0 | 3 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 82.28240 | 82.24869 | -0.00041 |
| $C_{18}H_{15}P$ | Triphenylphosphine | 3 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 18 | 15 | 168.40033 | 167.46591 | -0.00558 |

Table 15.356. The bond angle parameters of alkyl phosphines and experimental values [1]. In the calculation of $\theta_v$, the parameters from the preceding angle were used. $E_T$ is $E_T$ (*atom* – *atom*,*msp*$^3$.*AO*).

| Atoms of Angle | 2c' Bond 1 ($a_0$) | 2c' Bond 2 ($a_0$) | 2c' Terminal Atoms ($a_0$) | $E_{Coulombic}$ or $E$ Atom 1 | Atom 1 Hybridization Designation (Table 15.3.A) | $E_{Coulombic}$ Atom 2 | Atom 2 Hybridization Designation (Table 15.3.A) | $c_2$ Atom 1 | $c_2$ Atom 2 | $C_1$ | $C_2$ | $c_1$ | $c_2'$ | $E_T$ (eV) | $\theta_v$ (°) | $\theta_1$ (°) | $\theta_2$ (°) | Cal. $\theta$ (°) | Exp. $\theta$ (°) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Methyl<br>$\angle HC_aH$ | 2.09711 | 2.09711 | 3.4252 | -15.75493 | 7 | H | H | 0.86359 | 1 | 1 | 1 | 0.75 | 1.15796 | 0 | | | | 109.50 | |
| $\angle H_aC_aP$ | | | | | | | | | | | | | | | 70.56 | | | 109.44 | 110.7 (trimethyl phosphine) |
| $\angle C_aPC_b$ | 3.52498 | 3.52498 | 5.3479 | -15.93607 | 9 | -15.93607 | 9 | 0.85377 | 0.85377 | 1 | 1 | 1 | 0.85377 | -1.85836 | | | | 98.68 | 98.6 (trimethyl phosphine) |
| Methylene<br>$\angle HC_aH$ | 2.11106 | 2.11106 | 3.4252 | -15.75493 | 7 | H | H | 0.86359 | 1 | 1 | 1 | 0.75 | 1.15796 | 0 | | | | 108.44 | 107 (propane) |
| $\angle C_aC_bC_c$ | | | | | | | | | | | | | | | 69.51 | | | 110.49 | 112 (propane)<br>113.8 (butane)<br>110.8 (isobutane) |
| $\angle C_aC_bH$ | | | | | | | | | | | | | | | 69.51 | | | 110.49 | 111.0 (butane)<br>111.4 (isobutane) |
| Methyl<br>$\angle HC_aH$ | 2.09711 | 2.09711 | 3.4252 | -15.75493 | 7 | H | H | 0.86359 | 1 | 1 | 1 | 0.75 | 1.15796 | 0 | | | | 109.50 | |
| $\angle C_aC_bC_c$ | | | | | | | | | | | | | | | 70.56 | | | 109.44 | |
| $\angle C_aC_bH$ | | | | | | | | | | | | | | | 70.56 | | | 109.44 | |
| $\angle C_bC_aC_c$<br>iso $C_a$ | 2.91547 | 2.91547 | 4.7958 | -16.68412<br>$C_b$ | 26 | -16.68412<br>$C_c$ | 26 | 0.81549 | 0.81549 | 1 | 1 | 1 | 0.81549 | -1.85836 | | | | 110.67 | 110.8 (isobutane) |
| $\angle C_bC_aH$<br>iso $C_a$ | 2.91547 | 2.11323 | 4.1633 | -15.55033<br>$C_a$ | 5 | -14.82575<br>$C_b$ | 1 | 0.87495 | 0.91771 | 0.75 | 1 | 0.75 | 1.04887 | 0 | | | | 110.76 | |
| $\angle C_aC_bH$<br>iso $C_a$ | 2.91547 | 2.09711 | 4.1633 | -15.55033<br>$C_b$ | 5 | -14.82575<br>$C_a$ | 1 | 0.87495 | 0.91771 | 0.75 | 1 | 0.75 | 1.04887 | 0 | | | | 111.27 | 111.4 (isobutane) |
| $\angle C_bC_aC_b$<br>tert $C_a$ | 2.90327 | 2.90327 | 4.7958 | -16.68412<br>$C_b$ | 26 | -16.68412<br>$C_b$ | 26 | 0.81549 | 0.81549 | 1 | 1 | 1 | 0.81549 | -1.85836 | | | | 111.37 | 110.8 (isobutane) |
| $\angle C_bC_aC_d$ | | | | | | | | | | | | | | | 72.50 | | | 107.50 | |

## ALKYL PHOSPHITES ($\left(C_nH_{2n+1}O\right)_3P,\ n=1,2,3,4,5...\infty$)

The alkyl phosphites, $\left(C_nH_{2n+1}O\right)_3P$, comprise $P-O$ and $C-O$ functional groups. The alkyl portion of the alkyl phosphite may comprise at least two terminal methyl groups ($CH_3$) at each end of each chain, and may comprise methylene ($CH_2$), and methylyne ($CH$) functional groups as well as $C$ bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($\left(CH_3\right)_2CH$) and t-butyl ($\left(CH_3\right)_3C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups. The branched-chain-alkane groups in alkyl phosphites are equivalent to those in branched-chain alkanes.

The ether portion comprises two types of $C-O$ functional groups, one for methyl or t-butyl groups corresponding to the $C$, and the other for general alkyl groups that are equivalent to those in the Ethers section. The $P-O$ bond forms between the $P3sp^3$ HO and an $O2p$ AO to yield phosphites. The semimajor axis $a$ of the $P-O$ functional group is solved using Eq. (15.51). Using the semimajor axis and the relationships between the prolate spheroidal axes, the geometric and energy parameters of the MO are calculated using Eqs. (15.1-15.117) in the same manner as the organic functional groups given in Organic Molecular Functional Groups and Molecules section.

For the $P-O$ functional group, hybridization the $3s$ and $3p$ AOs of each to form a single $3sp^3$ shell forms an energy minimum, and the sharing of electrons between the $O2p$ AOs and $P3sp^3$ HOs to form a MO permits each participating orbital to decrease in radius and energy. The $O$ AO has an energy of $E(O)=-13.61805\ eV$, and the $P3sp^3$ HO has an energy of $E\left(P,3sp^3\right)=-11.78246\ eV$ (Eq. (15.180)). In branched-chain alkyl phosphites, the energy matching condition is determined by the $c_2$ and $C_2$ parameters of Eq. (15.51) given by Eqs. (15.77), (15.79), and (13.430).

$$c_2\ and\ C_2\left(O2pAO\ to\ P3sp^3HO\right)=\frac{E\left(P,3sp^3\right)}{E(O,2p)}c_2\left(C2sp^3HO\right)=\frac{-11.78246\ eV}{-13.61805\ eV}(0.91771)=0.79401 \tag{15.182}$$

The energy of the $P-O$-bond MO is the sum of the component energies of the $H_2$-type ellipsoidal MO given in Eq. (15.51) with $E(AO/HO)$ being $E\left(P,3sp^3\right)$ given by Eq. (23.180), and $E_T\left(atom-atom,msp^3.AO\right)$ is equivalent to that of single bond, $-1.44914\ eV$, given by twice Eq. (14.151) in order to match the energies of the oxygen AO with the phosphorous and carbon HOs.

The symbols of the functional groups of branched-chain alkyl phosphites are given in Table 15.357. The geometrical (Eqs. (15.1-15.5) and (15.51)), intercept (Eqs. (15.80-15.87)), and energy (Eqs. (15.6-15.11) and (15.17-15.65)) parameters of alkyl phosphites are given in Tables 15.358, 15.359, and 15.360, respectively. The total energy of each alkyl phosphite given in Table 15.361 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.360 corresponding to functional-group composition of the molecule. The bond angle parameters of alkyl phosphites determined using Eqs. (15.88-15.117) are given in Table 15.362. The color scale, charge-density of exemplary alkyl phosphite, tri-isopropyl phosphite, comprising atoms with the outer shell bridged by one or more $H_2$-type ellipsoidal MOs or joined with one or more hydrogen MOs is shown in Figure 15.61.

Figure 15.61. Color scale, charge-density of tri-isopropyl phosphite showing the orbitals of the atoms at their radii, the ellipsoidal surface of each $H$ or $H_2$-type ellipsoidal MO that transitions to the corresponding outer shell of the atom(s) participating in each bond, and the hydrogen nuclei.

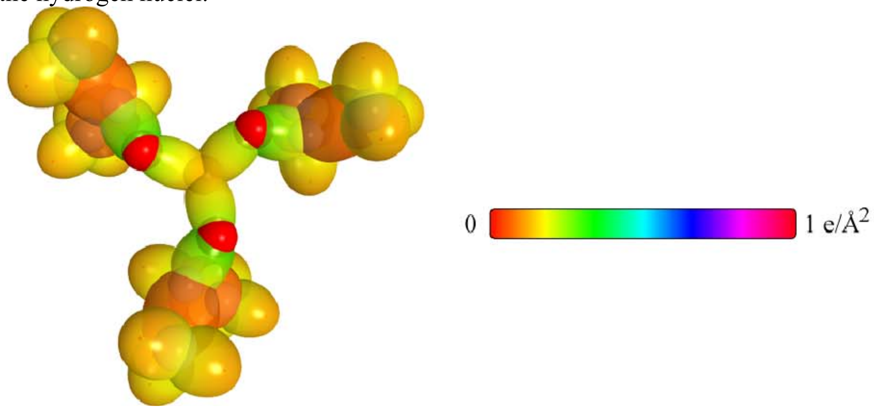


Table 15.357. The symbols of functional groups of alkyl phosphites.

| Functional Group | Group Symbol |
|---|---|
| *P-O* | $P-O$ |
| *C-O* ($CH_3-O-$ and $(CH_3)_3C-O-$) | $C-O$ (i) |
| *C-O* (alkyl) | $C-O$ (ii) |
| $CH_2$ group | $C-H$ $(CH_2)$ |
| *CH* | $C-H$ |
| *CC* bond (*n-C*) | $C-C$ (a) |
| *CC* bond (*iso-C*) | $C-C$ (b) |
| *CC* bond (*tert-C*) | $C-C$ (c) |
| *CC* (*iso* to *iso-C*) | $C-C$ (d) |
| *CC* (*t* to *t-C*) | $C-C$ (e) |
| *CC* (*t* to *iso-C*) | $C-C$ (f) |

Table 15.358. The geometrical bond parameters of alkyl phosphites and experimental values [1].

| Parameter | $P-O$ Group | $C-O$ (i) Group | $C-O$ (ii) Group | $C-H\ (CH_3)$ Group | $C-H\ (CH_2)$ Group | $C-H$ Group | $C-C$ (a) Group | $C-C$ (b) Group | $C-C$ (c) Group | $C-C$ (d) Group | $C-C$ (e) Group | $C-C$ (f) Group |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $a\ (a_0)$ | 1.84714 | 1.80717 | 1.79473 | 1.64920 | 1.67122 | 1.67465 | 2.12499 | 2.12499 | 2.10725 | 2.12499 | 2.10725 | 2.10725 |
| $c'\ (a_0)$ | 1.52523 | 1.34431 | 1.33968 | 1.04856 | 1.05553 | 1.05661 | 1.45744 | 1.45744 | 1.45164 | 1.45744 | 1.45164 | 1.45164 |
| Bond Length $2c'\ (\AA)$ | 1.61423 | 1.42276 | 1.41785 | 1.10974 | 1.11713 | 1.11827 | 1.54280 | 1.54280 | 1.53635 | 1.54280 | 1.53635 | 1.53635 |
| Exp. Bond Length $(\AA)$ | 1.631 [70]<br>(MHP)<br>1.60 [65]<br>(DNA) | 1.416<br>(dimethyl ether) | 1.418<br>(ethyl methyl ether (avg.)) | 1.107<br>($C-H$ propane)<br>1.117<br>($C-H$ butane) | 1.107<br>($C-H$ propane)<br>1.117<br>($C-H$ butane) | 1.122<br>(isobutane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) |
| $b,c\ (a_0)$ | 1.04192 | 1.20776 | 1.19429 | 1.27295 | 1.29569 | 1.29924 | 1.54616 | 1.54616 | 1.52750 | 1.54616 | 1.52750 | 1.52750 |
| $e$ | 0.82573 | 0.74388 | 0.74645 | 0.63580 | 0.63159 | 0.63095 | 0.68600 | 0.68600 | 0.68888 | 0.68600 | 0.68888 | 0.68888 |

Table 15.359. The MO to HO intercept geometrical bond parameters of alkyl phosphites. $R$, $R'$, $R''$ are $H$ or alkyl groups. $E_T$ is $E_T$ ($atom-atom,msp^3.AO$).

| Bond | Atom | $E_T$ (eV) Bond 1 | $E_T$ (eV) Bond 2 | $E_T$ (eV) Bond 3 | $E_T$ (eV) Bond 4 | Final Total Energy $C2sp^3$ (eV) | $r_{initial}$ $(a_0)$ | $r_{final}$ $(a_0)$ | $E_{Coulomb}$ (eV) Final | $E(C2sp^3)$ (eV) Final | $\theta'$ (°) | $\theta_1$ (°) | $\theta_2$ (°) | $d_1$ $(a_0)$ | $d_2$ $(a_0)$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $(CH_3O)_2P-OCH_3$<br>$(CH_3O)_2P-OC(CH_3)_3$<br>($C-O$ (i)) | $O$ | -0.72457 | -0.72457 | 0 | 0 | | 1.00000 | 0.83600 | -16.27489 | | 111.08 | 68.92 | 48.48 | 1.22455 | 0.30068 |
| $(CH_3O)_2P-OCH_3$<br>$(CH_3O)_2P-OC(CH_3)_3$<br>$(CH_3O)_2P-OCH_2R$<br>($C-O$ (i)) and ($C-O$ (ii)) | $P$ | -0.72457 | -0.72457 | -0.72457 | 0 | | 1.15350 | 0.80037 | -16.99947 | | 108.77 | 71.23 | 46.66 | 1.26770 | 0.25753 |
| $(CH_3O)_2P-OCH_2R$<br>($C-O$ (ii)) | $O$ | -0.72457 | -0.82688 | 0 | 0 | | 1.00000 | 0.83078 | -16.37720 | | 110.75 | 69.25 | 48.21 | 1.23087 | 0.29436 |
| $C-H\ (OC_aH_3)$ | $C_a$ | -0.72457 | 0 | 0 | 0 | -152.34026 | 0.91771 | 0.87495 | -15.55033 | -15.35946 | 78.85 | 101.15 | 42.40 | 1.21777 | 0.16921 |
| $(CH_3O)_2PO-C_aH_3$ | $C_a$ | -0.72457 | 0 | 0 | 0 | -152.34026 | 0.91771 | 0.87495 | -15.55033 | -15.35946 | 95.98 | 84.02 | 46.10 | 1.25319 | 0.09112 |
| $(CH_3O)_2PO-C_a(CH_3)_3$<br>($C-O$ (i)) | $C_a$ | -0.72457 | -0.72457 | -0.72457 | -0.72457 | -154.51399 | 0.91771 | 0.76765 | -17.72405 | | 86.03 | 93.97 | 39.35 | 1.39744 | 0.05313 |
| $(H_3CO)_2PO-C_aH_3$<br>$(CH_3)_3C_a-OP(OC_bH_3)_2$<br>($C-O$ (i)) | $O$ | -0.72457 | -0.72457 | 0 | 0 | | 1.00000 | 0.83600 | -16.27490 | | 92.66 | 87.34 | 43.74 | 1.30555 | 0.03876 |
| $-H_2C_a-OP(OCH_3)_2$<br>($C-O$ (ii)) | $C_a$ | -0.82688 | -0.92918 | 0 | 0 | -153.37175 | 0.91771 | 0.82053 | -16.58181 | -16.39095 | 92.41 | 87.59 | 43.35 | 1.30512 | 0.03456 |
| $(CH_3O)_2PO-C_aH(CH_3)_2$<br>($C-O$ (ii)) | $C_a$ | -0.82688 | -0.92918 | -0.92918 | 0 | -154.30093 | 0.91771 | 0.77699 | -17.51099 | -17.32013 | 88.25 | 91.75 | 40.56 | 1.36345 | 0.02377 |
| $-H_2C_a-OP(OCH_3)_2$<br>$(H_3C)_2HC_a-OP(OCH_3)_2$<br>($C-O$ (ii)) | $O$ | -0.72457 | -0.82688 | 0 | 0 | | 1.00000 | 0.83078 | -16.37720 | | 93.33 | 86.67 | 43.98 | 1.29138 | 0.04829 |
| $C-H\ (CH_3)$ | $C$ | -0.92918 | 0 | 0 | 0 | -152.54487 | 0.91771 | 0.86359 | -15.75493 | -15.56407 | 77.49 | 102.51 | 41.48 | 1.23564 | 0.18708 |
| $C-H\ (CH_2)$ | $C$ | -0.92918 | -0.92918 | 0 | 0 | -153.47406 | 0.91771 | 0.81549 | -16.68412 | -16.49325 | 68.47 | 111.53 | 35.84 | 1.35486 | 0.29933 |
| $C-H\ (CH)$ | $C$ | -0.92918 | -0.92918 | -0.92918 | 0 | -154.40324 | 0.91771 | 0.77247 | -17.61330 | -17.42244 | 61.10 | 118.90 | 31.37 | 1.42988 | 0.37326 |
| $H_3C_aC_bH_2CH_2-$<br>($C-C$ (a)) | $C_a$ | -0.92918 | 0 | 0 | 0 | -152.54487 | 0.91771 | 0.86359 | -15.75493 | -15.56407 | 63.82 | 116.18 | 30.08 | 1.83879 | 0.38106 |
| $H_3C_aC_bH_2CH_2-$<br>($C-C$ (a)) | $C_b$ | -0.92918 | -0.92918 | 0 | 0 | -153.47406 | 0.91771 | 0.81549 | -16.68412 | -16.49325 | 56.41 | 123.59 | 26.06 | 1.90890 | 0.45117 |
| $R-H_2C_aC_b(H_2C_c-R')HCH_2-$<br>($C-C$ (b)) | $C_b$ | -0.92918 | -0.92918 | -0.92918 | 0 | -154.40324 | 0.91771 | 0.77247 | -17.61330 | -17.42244 | 48.30 | 131.70 | 21.90 | 1.97162 | 0.51388 |
| $R-H_2C_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$<br>($C-C$ (c)) | $C_b$ | -0.92918 | -0.72457 | -0.72457 | -0.72457 | -154.71860 | 0.91771 | 0.75889 | -17.92866 | -17.73779 | 48.21 | 131.79 | 21.74 | 1.95734 | 0.50570 |
| $isoC_aC_b(H_2C_c-R')HCH_2-$<br>($C-C$ (d)) | $C_b$ | -0.92918 | -0.92918 | -0.92918 | 0 | -154.40324 | 0.91771 | 0.77247 | -17.61330 | -17.42244 | 48.30 | 131.70 | 21.90 | 1.97162 | 0.51388 |
| $tertC_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$<br>($C-C$ (e)) | $C_b$ | -0.72457 | -0.72457 | -0.72457 | -0.72457 | -154.51399 | 0.91771 | 0.76765 | -17.92866 | -17.73779 | 50.04 | 129.96 | 22.66 | 1.94462 | 0.49298 |
| $tertC_aC_b(H_2C_c-R')HCH_2-$<br>($C-C$ (f)) | $C_b$ | -0.72457 | -0.92918 | -0.92918 | 0 | -154.19863 | 0.91771 | 0.78155 | -17.40869 | -17.21783 | 52.78 | 127.22 | 24.04 | 1.92443 | 0.47279 |
| $isoC_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$<br>($C-C$ (f)) | $C_b$ | -0.72457 | -0.72457 | -0.72457 | -0.72457 | -154.51399 | 0.91771 | 0.76765 | -17.92866 | -17.73779 | 50.04 | 129.96 | 22.66 | 1.94462 | 0.49298 |

Table 15.360. The energy parameters ($eV$) of functional groups of alkyl phosphites.

| Parameters | $P-O$ Group | $C-O$ (i) Group | $C-O$ (ii) Group | $CH_3$ Group | $CH_2$ Group | $CH$ (i) Group | $C-C$ (a) Group | $C-C$ (b) Group | $C-C$ (c) Group | $C-C$ (d) Group | $C-C$ (e) Group | $C-C$ (f) Group |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $n_1$ | 1 | 1 | 1 | 3 | 2 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $n_2$ | 0 | 0 | 0 | 2 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $n_3$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $C_1$ | 0.5 | 0.5 | 0.5 | 0.75 | 0.75 | 0.75 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| $C_2$ | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $c_1$ | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $c_2$ | 0.79401 | 0.85395 | 0.85395 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 |
| $c_3$ | 0 | 0 | 0 | 0 | 1 | 1 | 0 | 0 | 0 | 1 | 1 | 0 |
| $c_4$ | 2 | 2 | 2 | 1 | 1 | 1 | 2 | 2 | 2 | 2 | 2 | 2 |
| $c_5$ | 0 | 0 | 0 | 3 | 2 | 1 | 0 | 0 | 0 | 0 | 0 | 0 |
| $C_{1o}$ | 0.5 | 0.5 | 0.5 | 0.75 | 0.75 | 0.75 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| $C_{2o}$ | 0.79401 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $V_e\ (eV)$ | -33.27738 | -33.15757 | -33.47304 | -107.32728 | -70.41425 | -35.12015 | -28.79214 | -28.79214 | -29.10112 | -28.79214 | -29.10112 | -29.10112 |
| $V_p\ (eV)$ | 8.92049 | 10.12103 | 10.15605 | 38.92728 | 25.78002 | 12.87680 | 9.33352 | 9.33352 | 9.37273 | 9.33352 | 9.37273 | 9.37273 |
| $T\ (eV)$ | 9.00781 | 9.17389 | 9.32537 | 32.53914 | 21.06675 | 10.48582 | 6.77464 | 6.77464 | 6.90500 | 6.77464 | 6.90500 | 6.90500 |
| $V_m\ (eV)$ | -4.50391 | -4.58695 | -4.66268 | -16.26957 | -10.53337 | -5.24291 | -3.38732 | -3.38732 | -3.45250 | -3.38732 | -3.45250 | -3.45250 |
| $E(_{AO/HO})\ (eV)$ | -11.78246 | -14.63489 | -14.63489 | -15.56407 | -15.56407 | -14.63489 | -15.56407 | -15.56407 | -15.35946 | -15.56407 | -15.35946 | -15.35946 |
| $\Delta E_{H_2MO}(_{AO/HO})\ (eV)$ | 0 | -1.44915 | -1.65376 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $E_T(_{AO/HO})\ (eV)$ | -11.78246 | -13.18574 | -12.98113 | -15.56407 | -15.56407 | -14.63489 | -15.56407 | -15.56407 | -15.35946 | -15.56407 | -15.35946 | -15.35946 |
| $E_T(_{H_2MO})\ (eV)$ | -31.63544 | -31.63533 | -31.63544 | -67.69451 | -49.66493 | -31.63533 | -31.63537 | -31.63537 | -31.63535 | -31.63537 | -31.63535 | -31.63535 |
| $E_T\left(atom-atom, msp^3.AO\right)\ (eV)$ | -1.44914 | -1.44915 | -1.65376 | 0 | 0 | 0 | -1.85836 | -1.85836 | -1.44915 | -1.85836 | -1.44915 | -1.44915 |
| $E_T(_{MO})\ (eV)$ | -33.08451 | -33.08452 | -33.28912 | -67.69450 | -49.66493 | -31.63537 | -33.49373 | -33.49373 | -33.08452 | -33.49373 | -33.08452 | -33.08452 |
| $\omega\ \left(10^{15}\ rad/s\right)$ | 10.3761 | 12.0329 | 12.1583 | 24.9286 | 24.2751 | 24.1759 | 9.43699 | 9.43699 | 15.4846 | 9.43699 | 9.55643 | 9.55643 |
| $E_K\ (eV)$ | 6.82973 | 7.92028 | 8.00277 | 16.40846 | 15.97831 | 15.91299 | 6.21159 | 6.21159 | 10.19220 | 6.21159 | 6.29021 | 6.29021 |
| $\bar{E}_D\ (eV)$ | -0.17105 | -0.18420 | -0.18631 | -0.25352 | -0.25017 | -0.24966 | -0.16515 | -0.16515 | -0.20896 | -0.16515 | -0.16416 | -0.16416 |
| $\bar{E}_{Kvib}\ (eV)$ | 0.10477<br>[71] | 0.13663<br>[21] | 0.16118<br>[4] | 0.35532<br>(Eq. (13.458)) | 0.35532<br>(Eq. (13.458)) | 0.35532<br>(Eq. (13.458)) | 0.12312<br>[2] | 0.17978<br>[4] | 0.09944<br>[5] | 0.12312<br>[2] | 0.12312<br>[2] | 0.12312<br>[2] |
| $\bar{E}_{osc}\ (eV)$ | -0.11867 | -0.11589 | -0.10572 | -0.22757 | -0.14502 | -0.07200 | -0.10359 | -0.07526 | -0.15924 | -0.10359 | -0.10260 | -0.10260 |
| $E_{mag}\ (eV)$ | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 |
| $E_T(_{Group})\ (eV)$ | -33.20318 | -33.20040 | -33.39484 | -67.92207 | -49.80996 | -31.70737 | -33.59732 | -33.49373 | -33.24376 | -33.59732 | -33.18712 | -33.18712 |
| $E_{initial}(_{c_4\ AO/HO})\ (eV)$ | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 |
| $E_{initial}(_{c_5\ AO/HO})\ (eV)$ | 0 | 0 | 0 | -13.59844 | -13.59844 | -13.59844 | 0 | 0 | 0 | 0 | 0 | 0 |
| $E_D(_{Group})\ (eV)$ | 3.93340 | 3.93062 | 4.12506 | 12.49186 | 7.83016 | 3.32601 | 4.32754 | 4.29921 | 3.97398 | 4.17951 | 3.62128 | 3.91734 |

Table 15.361. The total bond energies of alkyl phosphites calculated using the functional group composition and the energies of Table 15.360 compared to the experimental values [69].

| Formula | Name | $P-O$ | $C-O$ (i) | $C-O$ (ii) | $CH_3$ | $CH_2$ | $CH$ (i) | $C-C$ (a) | $C-C$ (b) | $C-C$ (c) | $C-C$ (d) | $C-C$ (e) | $C-C$ (f) | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $C_3H_9O_3P$ | Trimethyl phosphite | 3 | 3 | 0 | 3 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 61.06764 | 60.94329 | -0.00204 |
| $C_6H_{15}O_3P$ | Triethyl phosphite | 3 | 0 | 3 | 3 | 3 | 0 | 3 | 0 | 0 | 0 | 0 | 0 | 98.12406 | 97.97947 | -0.00148 |
| $C_9H_{21}O_3P$ | Tri-isopropyl phosphite | 3 | 0 | 3 | 6 | 0 | 3 | 0 | 6 | 0 | 0 | 0 | 0 | 134.89983 | 135.00698 | 0.00079 |

Table 15.362. The bond angle parameters of alkyl phosphites and experimental values [1]. In the calculation of $\theta_v$, the parameters from the preceding angle were used. $E_T$ is $E_T\,(atom - atom, msp^3.AO)$.

| Atoms of Angle | $2c'$ Bond 1 $(a_0)$ | $2c'$ Bond 2 $(a_0)$ | $2c'$ Terminal Atoms $(a_0)$ | $E_{Coulombic}$ or $E$ Atom 1 | Atom 1 Hybridization Designation (Table 15.3.A) | $E_{Coulombic}$ Atom 2 | Atom 2 Hybridization Designation (Table 15.3.A) | $c_2$ Atom 1 | $c_2$ Atom 2 | $C_1$ | $C_2$ | $c_1$ | $c_2'$ | $E_T$ (eV) | $\theta_v$ (°) | $\theta_1$ (°) | $\theta_2$ (°) | Cal. $\theta$ (°) | Exp. $\theta$ (°) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $\angle OPO$ | 3.05046 | 3.05046 | 4.5826 | -16.27489 | 16 | -16.27489 | 16 | 0.83600 | 0.83600 | 1 | 1 | 1 | 0.83600 | -1.65376 | | | | 97.38 | 96 [72] (triethyl phosphite) |
| $\angle POC$ | 3.05046 | 2.68862 | 4.9768 | -11.78246 | $Psp^3$ | -15.75493 | 7 | 0.73885 Eq. (23.181) | 0.86359 | 1 | 0.73885 | 1 | 0.80122 | -0.72457 | | | | 120.13 | 120 [72] (triethyl phosphite) |
| $\angle C_bC_aO$ | 2.91547 | 2.67935 | 4.5607 | -16.68412 | 26 | -13.61806 | O | 0.81549 | 0.85395 (Eq. (15.133)) | 1 | 1 | 1 | 0.83472 | -1.65376 | | | | 109.13 | 109.4 (ethyl methyl ether) |
| Methylene $\angle HC_aH$ | 2.11106 | 2.11106 | 3.4252 | -15.75493 | 7 | H | H | 0.86359 | 1 | 1 | 1 | 0.75 | 1.15796 | 0 | | | | 108.44 | 107 (propane) |
| $\angle C_aC_bC_c$ | | | | | | | | | | | | | | | 69.51 | | | 110.49 | 112 (propane)<br>113.8 (butane)<br>110.8 (isobutane) |
| $\angle C_aC_bH$ | | | | | | | | | | | | | | | 69.51 | | | 110.49 | 111.0 (butane)<br>111.4 (isobutane) |
| Methyl $\angle HC_aH$ | 2.09711 | 2.09711 | 3.4252 | -15.75493 | 7 | H | H | 0.86359 | 1 | 1 | 1 | 0.75 | 1.15796 | 0 | | | | 109.50 | |
| $\angle C_aC_bC_c$ | | | | | | | | | | | | | | | 70.56 | | | 109.44 | |
| $\angle C_aC_bH$ | | | | | | | | | | | | | | | 70.56 | | | 109.44 | |
| $\angle C_bC_aC_c$ iso $C_a$ | 2.91547 | 2.91547 | 4.7958 | -16.68412 $C_b$ | 26 | -16.68412 $C_c$ | 26 | 0.81549 | 0.81549 | 1 | 1 | 1 | 0.81549 | -1.85836 | | | | 110.67 | 110.8 (isobutane) |
| $\angle C_bC_aH$ iso $C_a$ | 2.91547 | 2.11323 | 4.1633 | -15.55033 $C_a$ | 5 | -14.82575 $C_b$ | 1 | 0.87495 | 0.91771 | 0.75 | 1 | 0.75 | 1.04887 | 0 | | | | 110.76 | |
| $\angle C_aC_bH$ iso $C_a$ | 2.91547 | 2.09711 | 4.1633 | -15.55033 $C_b$ | 5 | -14.82575 $C_a$ | 1 | 0.87495 | 0.91771 | 0.75 | 1 | 0.75 | 1.04887 | 0 | | | | 111.27 | 111.4 (isobutane) |
| $\angle C_bC_aC_b$ tert $C_a$ | 2.90327 | 2.90327 | 4.7958 | -16.68412 $C_b$ | 26 | -16.68412 $C_b$ | 26 | 0.81549 | 0.81549 | 1 | 1 | 1 | 0.81549 | -1.85836 | | | | 111.37 | 110.8 (isobutane) |
| $\angle C_bC_aC_d$ | | | | | | | | | | | | | | | 72.50 | | | 107.50 | |

## ALKYL PHOSPHINE OXIDES ($(C_nH_{2n+1})_3 P=O,\ n=1,2,3,4,5...\infty$)

The alkyl phosphine oxides, $(C_nH_{2n+1})_3 P=O$, comprise $P-C$ and $P=O$ functional groups. The alkyl portion of the alkyl phosphine oxide may comprise at least two terminal methyl groups ($CH_3$) at each end of each chain, and may comprise methylene ($CH_2$), and methylyne ($CH$) functional groups as well as $C$ bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($(CH_3)_2 CH$) and t-butyl ($(CH_3)_3 C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups. The branched-chain-alkane groups in alkyl phosphine oxides are equivalent to those in branched-chain alkanes.

The $P-C$ functional group is equivalent to that of alkyl phosphines. The $P=O$ bond forms between the $P3sp^3$ HO and an $O2p$ AO to yield phosphine oxides. The semimajor axis $a$ of the $P=O$ functional group is solved using Eq. (15.51). Using the semimajor axis and the relationships between the prolate spheroidal axes, the geometric and energy parameters of the MO are calculated using Eqs. (15.1-15.117) in the same manner as the organic functional groups given in Organic Molecular Functional Groups and Molecules section.

For the $P=O$ functional group, hybridization the $3s$ and $3p$ AOs of each $P$ to form a single $3sp^3$ shells forms an energy minimum, and the sharing of electrons between the $O2p$ AOs and $P3sp^3$ HOs to form a MO permits each participating orbital to decrease in radius and energy. In branched-chain alkyl phosphine oxides, the energy of phosphorous is less than the Coulombic energy between the electron and proton of $H$ given by Eq. (1.264). The energy matching condition is determined by the $c_2$ parameter given by Eq. (15.182). The energy of the $P=O$-bond MO is the sum of the component energies of the $H_2$-type ellipsoidal MO given in Eq. (15.51) with $E(AO/HO)$ being twice $E(P,3sp^3)$ given by Eq. (15.180) corresponding to the double bond, and $E_T(atom-atom,msp^3.AO)$ is equivalent to that of an alkene double bond, $-2.26758\ eV$, given by Eq. (14.247) in order to match the energies of the carbon and phosphorous HOs and the oxygen AO.

The symbols of the functional groups of branched-chain alkyl phosphine oxides are given in Table 15.363. The geometrical (Eqs. (15.1-15.5) and (15.51)), intercept (Eqs. (15.80-15.87)), and energy (Eqs. (15.6-15.11) and (15.17-15.65)) parameters of alkyl phosphine oxides are given in Tables 15.364, 15.365, and 15.366, respectively. The total energy of each alkyl phosphine oxide given in Table 15.367 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.366 corresponding to functional-group composition of the molecule. The bond angle parameters of alkyl phosphine oxides determined using Eqs. (15.88-15.117) are given in Table 15.368. The color scale, charge-density of exemplary alkyl phosphine oxide, trimethylphosphine oxide, comprising atoms with the outer shell bridged by one or more $H_2$-type ellipsoidal MOs or joined with one or more hydrogen MOs is shown in Figure 15.62.

Figure 15.62. Color scale, charge-density of trimethylphosphine oxide showing the orbitals of the atoms at their radii, the ellipsoidal surface of each $H$ or $H_2$-type ellipsoidal MO that transitions to the corresponding outer shell of the atom(s) participating in each bond, and the hydrogen nuclei. (A) Top view. (B) Side view.

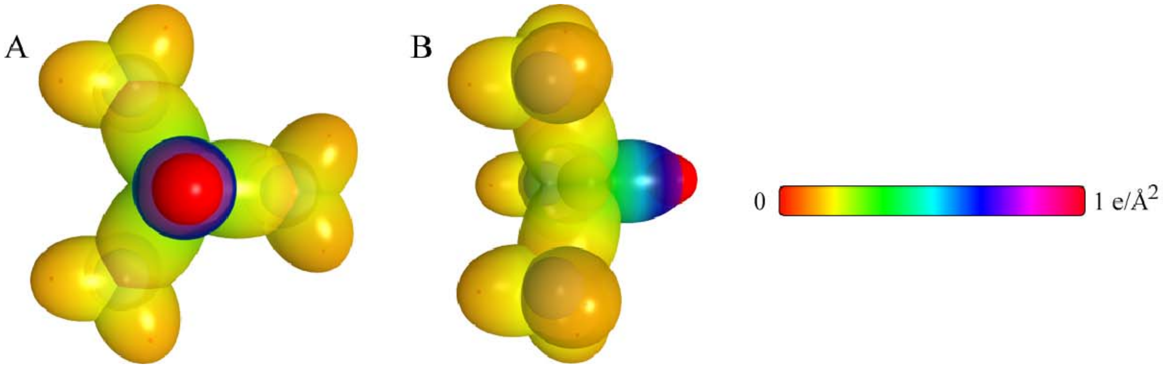


Table 15.363. The symbols of functional groups of alkyl phosphine oxides.

| Functional Group | Group Symbol |
|---|---|
| $P=O$ | $P=O$ |
| $P$-$C$ | $P-C$ |
| $CH_3$ group | $C-H\ (CH_3)$ |
| $CH_2$ group | $C-H\ (CH_2)$ |
| $CH$ | $C-H$ (i) |
| $CC$ bond (*n*-$C$) | $C-C$ (a) |
| $CC$ bond (*iso*-$C$) | $C-C$ (b) |
| $CC$ bond (*tert*-$C$) | $C-C$ (c) |
| $CC$ (*iso* to *iso*-$C$) | $C-C$ (d) |
| $CC$ (*t* to *t*-$C$) | $C-C$ (e) |
| $CC$ (*t* to *iso*-$C$) | $C-C$ (f) |
| $CC$ (aromatic bond) | $C\overset{3e}{=}C$ |
| $CH$ (aromatic) | $CH$ (ii) |

Table 15.364. The geometrical bond parameters of alkyl phosphine oxides and experimental values [1].

| Parameter | $P=O$ Group | $P-C$ Group | $C-H\ (CH_3)$ Group | $C-H\ (CH_2)$ Group | $C-H$ (i) Group | $C-C$ (a) Group | $C-C$ (b) Group | $C-C$ (c) Group | $C-C$ (d) Group | $C-C$ (e) Group | $C-C$ (f) Group | $\overset{3e}{C=C}$ Group | $CH$ (ii) Group |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $a\ (a_0)$ | 1.91663 | 2.29513 | 1.64920 | 1.67122 | 1.67465 | 2.12499 | 2.12499 | 2.10725 | 2.12499 | 2.10725 | 2.10725 | 1.47348 | 1.60061 |
| $c'\ (a_0)$ | 1.38442 | 1.76249 | 1.04856 | 1.05553 | 1.05661 | 1.45744 | 1.45744 | 1.45164 | 1.45744 | 1.45164 | 1.45164 | 1.31468 | 1.03299 |
| Bond Length $2c'\ (\AA)$ | 1.46521E-10 | 1.86534 | 1.10974 | 1.11713 | 1.11827 | 1.54280 | 1.54280 | 1.53635 | 1.54280 | 1.53635 | 1.53635 | 1.39140 | 1.09327 |
| Exp. Bond Length $(\AA)$ | 1.48 [65]<br>(DNA)<br>1.4759<br>$(PO)$ | 1.847<br>$((CH3)_2PCH_3)$<br>1.858<br>$(H_2PCH_3)$ | 1.107<br>($C-H$ propane)<br>1.117<br>($C-H$ butane) | 1.107<br>($C-H$ propane)<br>1.117<br>($C-H$ butane) | 1.122<br>(isobutane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.399<br>(benzene) | 1.101<br>(benzene) |
| $b,c\ (a_0)$ | 1.32546 | 1.47012 | 1.27295 | 1.29569 | 1.29924 | 1.54616 | 1.54616 | 1.52750 | 1.54616 | 1.52750 | 1.52750 | 0.66540 | 1.22265 |
| $e$ | 0.72232 | 0.76793 | 0.63580 | 0.63159 | 0.63095 | 0.68600 | 0.68600 | 0.68888 | 0.68600 | 0.68888 | 0.68888 | 0.89223 | 0.64537 |

Table 15.365. The MO to HO intercept geometrical bond parameters of alkyl phosphine oxides. $R$, $R'$, $R''$ are $H$ or alkyl groups. $E_T$ is $E_T$ ($atom-atom,msp^3.AO$).

| Bond | Atom | $E_T$ (eV) Bond 1 | $E_T$ (eV) Bond 2 | $E_T$ (eV) Bond 3 | $E_T$ (eV) Bond 4 | Final Total Energy $C2sp^3$ (eV) | $r_{initial}$ $(a_0)$ | $r_{final}$ $(a_0)$ | $E_{Coulomb}$ (eV) Final | $E(C2sp^3)$ (eV) Final | $\theta'$ (°) | $\theta_1$ (°) | $\theta_2$ (°) | $d_1$ $(a_0)$ | $d_2$ $(a_0)$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $(CH_3)_3P=O$ | $O$ | -1.13379 | 0 | 0 | 0 |  | 1.00000 | 0.85252 | -15.95954 |  | 84.02 | 95.98 | 39.77 | 1.47318 | 0.08876 |
| $(CH_3)_3P=O$ | $P$ | -1.13379 | -0.18114 | -0.18114 | -0.18114 |  | 1.15350 | 0.82445 | -16.50297 |  | 81.09 | 98.91 | 37.92 | 1.51205 | 0.12762 |
| $(CH_3)_2(O)P-CH_3$ | $C$ | -0.18114 | 0 | 0 | 0 |  | 0.91771 | 0.90664 | -15.00689 | -14.81603 | 87.12 | 92.88 | 38.02 | 1.80811 | 0.04562 |
| $(CH_3)_2(O)P-CH_3$ | $P$ | -0.18114 | -0.18114 | -0.18114 | -1.13379 |  | 1.15350 | 0.82445 | -16.50297 |  | 79.33 | 100.67 | 33.44 | 1.91514 | 0.15265 |
| $C-H\ (CH_3)$ | $C$ | -0.92918 | 0 | 0 | 0 | -152.54487 | 0.91771 | 0.86359 | -15.75493 | -15.56407 | 77.49 | 102.51 | 41.48 | 1.23564 | 0.18708 |
| $C-H\ (CH_2)$ | $C$ | -0.92918 | -0.92918 | 0 | 0 | -153.47406 | 0.91771 | 0.81549 | -16.68412 | -16.49325 | 68.47 | 111.53 | 35.84 | 1.35486 | 0.29933 |
| $C-H\ (CH)$ | $C$ | -0.92918 | -0.92918 | -0.92918 | 0 | -154.40324 | 0.91771 | 0.77247 | -17.61330 | -17.42244 | 61.10 | 118.90 | 31.37 | 1.42988 | 0.37326 |
| $H_3C_aC_bH_2CH_2-$ ($C-C$ (a)) | $C_a$ | -0.92918 | 0 | 0 | 0 | -152.54487 | 0.91771 | 0.86359 | -15.75493 | -15.56407 | 63.82 | 116.18 | 30.08 | 1.83879 | 0.38106 |
| $H_3C_aC_bH_2CH_2-$ ($C-C$ (a)) | $C_b$ | -0.92918 | -0.92918 | 0 | 0 | -153.47406 | 0.91771 | 0.81549 | -16.68412 | -16.49325 | 56.41 | 123.59 | 26.06 | 1.90890 | 0.45117 |
| $R-H_2C_aC_b(H_2C_c-R')HCH_2-$ ($C-C$ (b)) | $C_b$ | -0.92918 | -0.92918 | -0.92918 | 0 | -154.40324 | 0.91771 | 0.77247 | -17.61330 | -17.42244 | 48.30 | 131.70 | 21.90 | 1.97162 | 0.51388 |
| $R-H_2C_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ ($C-C$ (c)) | $C_b$ | -0.92918 | -0.72457 | -0.72457 | -0.72457 | -154.71860 | 0.91771 | 0.75889 | -17.92866 | -17.73779 | 48.21 | 131.79 | 21.74 | 1.95734 | 0.50570 |
| $isoC_aC_b(H_2C_c-R')HCH_2-$ ($C-C$ (d)) | $C_b$ | -0.92918 | -0.92918 | -0.92918 | 0 | -154.40324 | 0.91771 | 0.77247 | -17.61330 | -17.42244 | 48.30 | 131.70 | 21.90 | 1.97162 | 0.51388 |
| $tertC_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ ($C-C$ (e)) | $C_b$ | -0.72457 | -0.72457 | -0.72457 | -0.72457 | -154.51399 | 0.91771 | 0.76765 | -17.92866 | -17.73779 | 50.04 | 129.96 | 22.66 | 1.94462 | 0.49298 |
| $tertC_aC_b(H_2C_c-R')HCH_2-$ ($C-C$ (f)) | $C_b$ | -0.72457 | -0.92918 | -0.92918 | 0 | -154.19863 | 0.91771 | 0.78155 | -17.40869 | -17.21783 | 52.78 | 127.22 | 24.04 | 1.92443 | 0.47279 |
| $isoC_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ ($C-C$ (f)) | $C_b$ | -0.72457 | -0.72457 | -0.72457 | -0.72457 | -154.51399 | 0.91771 | 0.76765 | -17.92866 | -17.73779 | 50.04 | 129.96 | 22.66 | 1.94462 | 0.49298 |

Table 15.366. The energy parameters ($eV$) of functional groups of alkyl phosphine oxides.

| Parameters | $P=O$ Group | $P-C$ Group | $CH_3$ Group | $CH_2$ Group | $CH$ (i) Group | $C-C$ (a) Group | $C-C$ (b) Group | $C-C$ (c) Group | $C-C$ (d) Group | $C-C$ (e) Group | $C-C$ (f) Group | $C\overset{3e}{=}C$ Group | $CH$ (ii) Group |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $f_1$ | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 0.75 | 1 |
| $n_1$ | 2 | 1 | 3 | 2 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 2 | 1 |
| $n_2$ | 0 | 0 | 2 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $n_3$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $C_1$ | 0.5 | 0.5 | 0.75 | 0.75 | 0.75 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.75 |
| $C_2$ | 1 | 0.73885 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 0.85252 | 1 |
| $c_1$ | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $c_2$ | 0.79401 | 1 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.85252 | 0.91771 |
| $c_3$ | 0 | 0 | 0 | 1 | 1 | 0 | 0 | 0 | 1 | 1 | 0 | 0 | 1 |
| $c_4$ | 4 | 2 | 1 | 1 | 1 | 2 | 2 | 2 | 2 | 2 | 2 | 3 | 1 |
| $c_5$ | 0 | 0 | 3 | 2 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1 |
| $C_{1o}$ | 0.5 | 0.5 | 0.75 | 0.75 | 0.75 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.75 |
| $C_{2o}$ | 1 | 0.73885 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 0.85252 | 1 |
| $V_e\ (eV)$ | -56.96374 | -31.34959 | -107.32728 | -70.41425 | -35.12015 | -28.79214 | -28.79214 | -29.10112 | -28.79214 | -29.10112 | -29.10112 | -101.12679 | -37.10024 |
| $V_p\ (eV)$ | 9.82777 | 7.71965 | 38.92728 | 25.78002 | 12.87680 | 9.33352 | 9.33352 | 9.37273 | 9.33352 | 9.37273 | 9.37273 | 20.69825 | 13.17125 |
| $T\ (eV)$ | 14.86039 | 6.82959 | 32.53914 | 21.06675 | 10.48582 | 6.77464 | 6.77464 | 6.90500 | 6.77464 | 6.90500 | 6.90500 | 34.31559 | 11.58941 |
| $V_m\ (eV)$ | -7.43020 | -3.41479 | -16.26957 | -10.53337 | -5.24291 | -3.38732 | -3.38732 | -3.45250 | -3.38732 | -3.45250 | -3.45250 | -17.15779 | -5.79470 |
| $E(_{AO/HO})\ (eV)$ | -23.56492 | -11.78246 | -15.56407 | -15.56407 | -14.63489 | -15.56407 | -15.56407 | -15.35946 | -15.56407 | -15.35946 | -15.35946 | 0 | -14.63489 |
| $\Delta E_{H_2MO}(_{AO/HO})\ (eV)$ | 0 | -0.36229 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | -1.13379 |
| $E_T(_{AO/HO})\ (eV)$ | -23.56492 | -11.42017 | -15.56407 | -15.56407 | -14.63489 | -15.56407 | -15.56407 | -15.35946 | -15.56407 | -15.35946 | -15.35946 | 0 | -13.50110 |
| $E_T(_{H_2MO})\ (eV)$ | -63.27069 | -31.63532 | -67.69451 | -49.66493 | -31.63533 | -31.63537 | -31.63537 | -31.63535 | -31.63537 | -31.63535 | -31.63535 | -63.27075 | -31.63539 |
| $E_T\left(atom-atom,msp^3.AO\right)\ (eV)$ | -2.26758 | -0.36229 | 0 | 0 | 0 | -1.85836 | -1.85836 | -1.44915 | -1.85836 | -1.44915 | -1.44915 | -2.26759 | -0.56690 |
| $E_T(_{MO})\ (eV)$ | -65.53832 | -31.99766 | -67.69450 | -49.66493 | -31.63537 | -33.49373 | -33.49373 | -33.08452 | -33.49373 | -33.08452 | -33.08452 | -65.53833 | -32.20226 |
| $\omega\ \left(10^{15}\ rad/s\right)$ | 11.0170 | 7.22663 | 24.9286 | 24.2751 | 24.1759 | 9.43699 | 9.43699 | 15.4846 | 9.43699 | 9.55643 | 9.55643 | 49.7272 | 26.4826 |
| $E_K\ (eV)$ | 7.25157 | 4.75669 | 16.40846 | 15.97831 | 15.91299 | 6.21159 | 6.21159 | 10.19220 | 6.21159 | 6.29021 | 6.29021 | 32.73133 | 17.43132 |
| $\bar{E}_D\ (eV)$ | -0.17458 | -0.13806 | -0.25352 | -0.25017 | -0.24966 | -0.16515 | -0.16515 | -0.20896 | -0.16515 | -0.16416 | -0.16416 | -0.35806 | -0.26130 |
| $\bar{E}_{Kvib}\ (eV)$ | 0.15292 [24] | 0.17606 [68] | 0.35532 (Eq. (13.458)) | 0.35532 (Eq. (13.458)) | 0.35532 (Eq. (13.458)) | 0.12312 [2] | 0.17978 [4] | 0.09944 [5] | 0.12312 [2] | 0.12312 [2] | 0.12312 [2] | 0.19649 [49] | 0.35532 Eq. (13.458) |
| $\bar{E}_{osc}\ (eV)$ | -0.09812 | -0.05003 | -0.22757 | -0.14502 | -0.07200 | -0.10359 | -0.07526 | -0.15924 | -0.10359 | -0.10260 | -0.10260 | -0.25982 | -0.08364 |
| $E_{mag}\ (eV)$ | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 |
| $E_T(_{Group})\ (eV)$ | -65.73455 | -32.04769 | -67.92207 | -49.80996 | -31.70737 | -33.59732 | -33.49373 | -33.24376 | -33.59732 | -33.18712 | -33.18712 | -49.54347 | -32.28590 |
| $E_{initial}(_{c_4\ AO/HO})\ (eV)$ | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 |
| $E_{initial}(_{c_5\ AO/HO})\ (eV)$ | 0 | 0 | -13.59844 | -13.59844 | -13.59844 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | -13.59844 |
| $E_D(_{Group})\ (eV)$ | 7.19500 | 2.77791 | 12.49186 | 7.83016 | 3.32601 | 4.32754 | 4.29921 | 3.97398 | 4.17951 | 3.62128 | 3.91734 | 5.63881 | 3.90454 |

Table 15.367. The total bond energies of alkyl phosphine oxides calculated using the functional group composition and the energies of Table 15.366 compared to the experimental values [69].

| Formula | Name | $P=O$ | $P-C$ | $CH_3$ | $CH_2$ | $CH$ (i) | $C-C$ (a) | $C-C$ (b) | $C-C$ (c) | $C-C$ (d) | $C-C$ (e) | $C-C$ (f) | $C\overset{3e}{=}C$ | $CH$ (ii) | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $C_3H_9PO$ | Trimethylphosphine oxide | 1 | 3 | 3 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 53.00430 | 52.91192 | -0.00175 |

Table 15.368. The bond angle parameters of alkyl phosphine oxides and experimental values [1]. In the calculation of $\theta_v$, the parameters from the preceding angle were used. $E_T$ is $E_T$ ($atom - atom, msp^3.AO$).

| Atoms of Angle | 2c' Bond 1 ($a_0$) | 2c' Bond 2 ($a_0$) | 2c' Terminal Atoms ($a_0$) | $E_{Coulombic}$ or $E$ Atom 1 | Atom 1 Hybridization Designation (Table 15.3.A) | $E_{Coulombic}$ Atom 2 | Atom 2 Hybridization Designation (Table 15.3.A) | $c_2$ Atom 1 | $c_2$ Atom 2 | $C_1$ | $C_2$ | $c_1$ | $c_2'$ | $E_T$ (eV) | $\theta_v$ (°) | $\theta_1$ (°) | $\theta_2$ (°) | Cal. $\theta$ (°) | Exp. $\theta$ (°) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Methyl<br>$\angle HC_aH$ | 2.09711 | 2.09711 | 3.4252 | -15.75493 | 7 | H | H | 0.86359 | 1 | 1 | 1 | 0.75 | 1.15796 | 0 | | | | 109.50 | |
| $\angle H_aC_aP$ | | | | | | | | | | | | | | | 70.56 | | | 109.44 | 110.7<br>(trimethyl phosphine) |
| $\angle C_aPC_b$ | 3.52498 | 3.52498 | 5.4955 | -15.75493 | 7 | -15.75493 | 7 | 0.86359 | 0.86359 | 1 | 1 | 1 | 0.86359 | -1.85836 | | | | 102.43 | 104.31 [73]<br>($Ph_2P(O)CH_2OH$) |
| $\angle C_aPO$ | 3.52498 | 2.76885 | 5.3104 | -15.95954 | 10 | -15.95954 | 10 | 0.85252 | 0.85252 | 1 | 1 | 1 | 0.85252 | -1.85836 | | | | 114.54 | 114.03 [73]<br>($Ph_2P(O)CH_2OH$) |
| Methylene<br>$\angle HC_aH$ | 2.11106 | 2.11106 | 3.4252 | -15.75493 | 7 | H | H | 0.86359 | 1 | 1 | 1 | 0.75 | 1.15796 | 0 | | | | 108.44 | 107<br>(propane) |
| $\angle C_aC_bC_c$ | | | | | | | | | | | | | | | 69.51 | | | 110.49 | 112<br>(propane)<br>113.8<br>(butane)<br>110.8<br>(isobutane) |
| $\angle C_aC_bH$ | | | | | | | | | | | | | | | 69.51 | | | 110.49 | 111.0<br>(butane)<br>111.4<br>(isobutane) |
| Methyl<br>$\angle HC_aH$ | 2.09711 | 2.09711 | 3.4252 | -15.75493 | 7 | H | H | 0.86359 | 1 | 1 | 1 | 0.75 | 1.15796 | 0 | | | | 109.50 | |
| $\angle C_aC_bC_c$ | | | | | | | | | | | | | | | 70.56 | | | 109.44 | |
| $\angle C_aC_bH$ | | | | | | | | | | | | | | | 70.56 | | | 109.44 | |
| $\angle C_bC_aC_c$<br>iso $C_a$ | 2.91547 | 2.91547 | 4.7958 | -16.68412<br>$C_b$ | 26 | -16.68412<br>$C_c$ | 26 | 0.81549 | 0.81549 | 1 | 1 | 1 | 0.81549 | -1.85836 | | | | 110.67 | 110.8<br>(isobutane) |
| $\angle C_bC_aH$<br>iso $C_a$ | 2.91547 | 2.11323 | 4.1633 | -15.55033<br>$C_a$ | 5 | -14.82575<br>$C_b$ | 1 | 0.87495 | 0.91771 | 0.75 | 1 | 0.75 | 1.04887 | 0 | | | | 110.76 | |
| $\angle C_aC_bH$<br>iso $C_a$ | 2.91547 | 2.09711 | 4.1633 | -15.55033<br>$C_b$ | 5 | -14.82575<br>$C_a$ | 1 | 0.87495 | 0.91771 | 0.75 | 1 | 0.75 | 1.04887 | 0 | | | | 111.27 | 111.4<br>(isobutane) |
| $\angle C_bC_aC_b$<br>tert $C_a$ | 2.90327 | 2.90327 | 4.7958 | -16.68412<br>$C_b$ | 26 | -16.68412<br>$C_b$ | 26 | 0.81549 | 0.81549 | 1 | 1 | 1 | 0.81549 | -1.85836 | | | | 111.37 | 110.8<br>(isobutane) |
| $\angle C_bC_aC_d$ | | | | | | | | | | | | | | | 72.50 | | | 107.50 | |

## ALKYL PHOSPHATES ($(C_nH_{2n+1}O)_3P=O,\ n=1,2,3,4,5...\infty$)

The alkyl phosphates, $(C_nH_{2n+1}O)_3P=O$, comprise $P=O$, $P-O$, and $C-O$ functional groups. The $P=O$ functional group is equivalent to that of alkyl phosphine oxides. The $P-O$ and $C-O$ functional groups are equivalent to those of alkyl phosphites. The alkyl portion of the alkyl phosphate may comprise at least two terminal methyl groups ($CH_3$) at each end of each chain, and may comprise methylene ($CH_2$), and methylyne ($CH$) functional groups as well as $C$ bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($(CH_3)_2CH$) and t-butyl ($(CH_3)_3C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups. The branched-chain-alkane groups in alkyl phosphates are equivalent to those in branched-chain alkanes.

The symbols of the functional groups of branched-chain alkyl phosphates are given in Table 15.369. The geometrical (Eqs. (15.1-15.5) and (15.51)), intercept (Eqs. (15.80-15.87)), and energy (Eqs. (15.6-15.11) and (15.17-15.65)) parameters of alkyl phosphates are given in Tables 15.370, 15.371, and 15.372, respectively. The total energy of each alkyl phosphate given in Table 15.373 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.372 corresponding to functional-group composition of the molecule. The bond angle parameters of alkyl phosphates determined using Eqs. (15.88-15.117) are given in Table 15.374. The color scale, charge-density of exemplary alkyl phosphate, tri-isopropyl phosphate, comprising of atoms with the outer shell bridged by one or more $H_2$-type ellipsoidal MOs or joined with one or more hydrogen MOs is shown in Figure 15.63.

Figure 15.63. Color scale, charge-density of tri-isopropyl phosphate showing the orbitals of the atoms at their radii, the ellipsoidal surface of each $H$ or $H_2$-type ellipsoidal MO that transitions to the corresponding outer shell of the atom(s) participating in each bond, and the hydrogen nuclei.

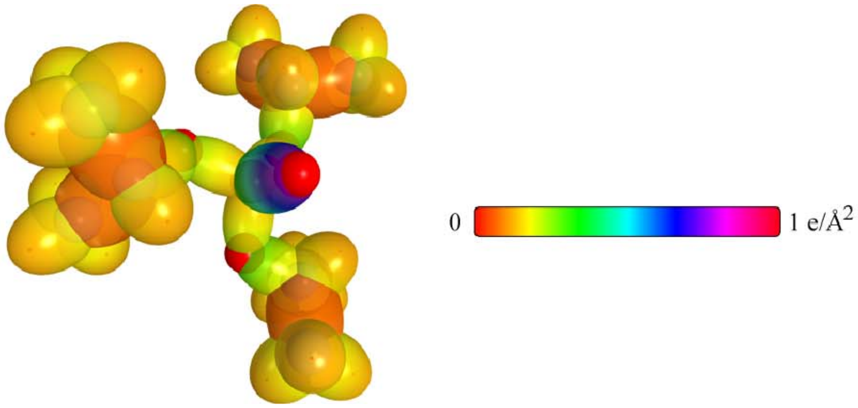


Table 15.369. The symbols of functional groups of alkyl phosphates.

| Functional Group | Group Symbol |
|---|---|
| *P=O* | $P=O$ |
| *P-O* | $P-O$ |
| *C-O* ($CH_3-O-$ and $(CH_3)_3C-O-$) | $C-O$ (i) |
| *C-O* (alkyl) | $C-O$ (ii) |
| $CH_2$ group | $C-H$ $(CH_2)$ |
| *CH* | $C-H$ |
| *CC* bond (*n-C*) | $C-C$ (a) |
| *CC* bond (*iso-C*) | $C-C$ (b) |
| *CC* bond (*tert-C*) | $C-C$ (c) |
| *CC* (*iso* to *iso-C*) | $C-C$ (d) |
| *CC* (*t* to *t-C*) | $C-C$ (e) |
| *CC* (*t* to *iso-C*) | $C-C$ (f) |

Table 15.370. The geometrical bond parameters of alkyl phosphates and experimental values [1].

| Parameter | $P=O$ Group | $P-O$ Group | $C-O$ (i) Group | $C-O$ (ii) Group | $C-H\ (CH_3)$ Group | $C-H\ (CH_2)$ Group | $C-H$ Group | $C-C$ (a) Group | $C-C$ (b) Group | $C-C$ (c) Group | $C-C$ (d) Group | $C-C$ (e) Group | $C-C$ (f) Group |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $a\ (a_0)$ | 1.91663 | 1.84714 | 1.80717 | 1.79473 | 1.64920 | 1.67122 | 1.67465 | 2.12499 | 2.12499 | 2.10725 | 2.12499 | 2.10725 | 2.10725 |
| $c'\ (a_0)$ | 1.38442 | 1.52523 | 1.34431 | 1.33968 | 1.04856 | 1.05553 | 1.05661 | 1.45744 | 1.45744 | 1.45164 | 1.45744 | 1.45164 | 1.45164 |
| Bond Length $2c'\ (Å)$ | 1.46521E-10 | 1.61423 | 1.42276 | 1.41785 | 1.10974 | 1.11713 | 1.11827 | 1.54280 | 1.54280 | 1.53635 | 1.54280 | 1.53635 | 1.53635 |
| Exp. Bond Length $(Å)$ | 1.48 [65]<br>(DNA)<br>1.4759<br>$(PO)$ | 1.631 [70]<br>(MHP)<br>1.60 [65]<br>(DNA) | 1.416<br>(dimethyl ether) | 1.418<br>(ethyl methyl ether (avg.)) | 1.107<br>($C-H$ propane)<br>1.117<br>($C-H$ butane) | 1.107<br>($C-H$ propane)<br>1.117<br>($C-H$ butane) | 1.122<br>(isobutane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) |
| $b,c\ (a_0)$ | 1.32546 | 1.04192 | 1.20776 | 1.19429 | 1.27295 | 1.29569 | 1.29924 | 1.54616 | 1.54616 | 1.52750 | 1.54616 | 1.52750 | 1.52750 |
| $e$ | 0.72232 | 0.82573 | 0.74388 | 0.74645 | 0.63580 | 0.63159 | 0.63095 | 0.68600 | 0.68600 | 0.68888 | 0.68600 | 0.68888 | 0.68888 |

Table 15.371. The MO to HO intercept geometrical bond parameters of alkyl phosphates. $R$, $R'$, $R''$ are $H$ or alkyl groups. $E_T$ is $E_T$ ($atom - atom, msp^3.AO$).

| Bond | Atom | $E_T$ (eV) Bond 1 | $E_T$ (eV) Bond 2 | $E_T$ (eV) Bond 3 | $E_T$ (eV) Bond 4 | Final Total Energy $C2sp^3$ (eV) | $r_{initial}$ $(a_0)$ | $r_{final}$ $(a_0)$ | $E_{Coulomb}$ (eV) Final | $E(C2sp^3)$ (eV) Final | $\theta'$ (°) | $\theta_1$ (°) | $\theta_2$ (°) | $d_1$ $(a_0)$ | $d_2$ $(a_0)$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $(CH_3)_3P=O$ | $O$ | -1.13379 | 0 | 0 | 0 |  | 1.00000 | 0.85252 | -15.95954 |  | 84.02 | 95.98 | 39.77 | 1.47318 | 0.08876 |
| $(CH_3O)_3P=O$ | $P$ | -1.13379 | -0.72457 | -0.72457 | -0.72457 |  | 1.15350 | 0.75032 | -18.13326 |  | 72.13 | 107.87 | 32.60 | 1.61466 | 0.23024 |
| $(CH_3O)_2(O)P-OCH_3$<br>$(CH_3O)_2(O)P-OC(CH_3)_3$<br>$(C-O$ (i)) | $O$ | -0.72457 | -0.72457 | 0 | 0 |  | 1.00000 | 0.83600 | -16.27489 |  | 111.08 | 68.92 | 48.48 | 1.22455 | 0.30068 |
| $(CH_3O)_2(O)P-OCH_3$<br>$(CH_3O)_2(O)P-OC(CH_3)_3$<br>$(CH_3O)_2(O)P-OCH_2R$<br>$(C-O$ (i)) and $(C-O$ (ii)) | $P$ | -0.72457 | -0.72457 | -0.72457 | -1.13379 |  | 1.15350 | 0.75032 | -18.13326 |  | 105.22 | 74.78 | 44.02 | 1.32831 | 0.19692 |
| $(CH_3O)_2(O)P-OCH_2R$<br>$(C-O$ (ii)) | $O$ | -0.72457 | -0.82688 | 0 | 0 |  | 1.00000 | 0.83078 | -16.37720 |  | 110.75 | 69.25 | 48.21 | 1.23087 | 0.29436 |
| $C-H\ (OC_aH_3)$ | $C_a$ | -0.72457 | 0 | 0 | 0 | -152.34026 | 0.91771 | 0.87495 | -15.55033 | -15.35946 | 78.85 | 101.15 | 42.40 | 1.21777 | 0.16921 |
| $(CH_3O)_2(O)PO-C_aH_3$ | $C_a$ | -0.72457 | 0 | 0 | 0 | -152.34026 | 0.91771 | 0.87495 | -15.55033 | -15.35946 | 95.98 | 84.02 | 46.10 | 1.25319 | 0.09112 |
| $(CH_3O)_2(O)PO-C_a(CH_3)_3$<br>$(C-O$ (i)) | $C_a$ | -0.72457 | -0.72457 | -0.72457 | -0.72457 | -154.51399 | 0.91771 | 0.76765 | -17.72405 |  | 86.03 | 93.97 | 39.35 | 1.39744 | 0.05313 |
| $(H_3CO)_2(O)PO-C_aH_3$<br>$(CH_3)_3C_a-OP(O)(OC_bH_3)_2$<br>$(C-O$ (i)) | $O$ | -0.72457 | -0.72457 | 0 | 0 |  | 1.00000 | 0.83600 | -16.27490 |  | 92.66 | 87.34 | 43.74 | 1.30555 | 0.03876 |
| $-H_2C_a-OP(O)(OCH_3)_2$<br>$(C-O$ (ii)) | $C_a$ | -0.82688 | -0.92918 | 0 | 0 | -153.37175 | 0.91771 | 0.82053 | -16.58181 | -16.39095 | 92.41 | 87.59 | 43.35 | 1.30512 | 0.03456 |
| $(CH_3O)_2(O)PO-C_aH(CH_3)_2$<br>$(C-O$ (ii)) | $C_a$ | -0.82688 | -0.92918 | -0.92918 | 0 | -154.30093 | 0.91771 | 0.77699 | -17.51099 | -17.32013 | 88.25 | 91.75 | 40.56 | 1.36345 | 0.02377 |
| $-H_2C_a-OP(O)(OCH_3)_2$<br>$(H_3C)_2HC_a-OP(O)(OCH_3)_2$<br>$(C-O$ (ii)) | $O$ | -0.72457 | -0.82688 | 0 | 0 |  | 1.00000 | 0.83078 | -16.37720 |  | 93.33 | 86.67 | 43.98 | 1.29138 | 0.04829 |
| $C-H\ (CH_3)$ | $C$ | -0.92918 | 0 | 0 | 0 | -152.54487 | 0.91771 | 0.86359 | -15.75493 | -15.56407 | 77.49 | 102.51 | 41.48 | 1.23564 | 0.18708 |
| $C-H\ (CH_2)$ | $C$ | -0.92918 | -0.92918 | 0 | 0 | -153.47406 | 0.91771 | 0.81549 | -16.68412 | -16.49325 | 68.47 | 111.53 | 35.84 | 1.35486 | 0.29933 |
| $C-H\ (CH)$ | $C$ | -0.92918 | -0.92918 | -0.92918 | 0 | -154.40324 | 0.91771 | 0.77247 | -17.61330 | -17.42244 | 61.10 | 118.90 | 31.37 | 1.42988 | 0.37326 |
| $H_3C_aC_bH_2CH_2-$<br>$(C-C$ (a)) | $C_a$ | -0.92918 | 0 | 0 | 0 | -152.54487 | 0.91771 | 0.86359 | -15.75493 | -15.56407 | 63.82 | 116.18 | 30.08 | 1.83879 | 0.38106 |
| $H_3C_aC_bH_2CH_2-$<br>$(C-C$ (a)) | $C_b$ | -0.92918 | -0.92918 | 0 | 0 | -153.47406 | 0.91771 | 0.81549 | -16.68412 | -16.49325 | 56.41 | 123.59 | 26.06 | 1.90890 | 0.45117 |
| $R-H_2C_aC_b(H_2C_c-R')HCH_2-$<br>$(C-C$ (b)) | $C_b$ | -0.92918 | -0.92918 | -0.92918 | 0 | -154.40324 | 0.91771 | 0.77247 | -17.61330 | -17.42244 | 48.30 | 131.70 | 21.90 | 1.97162 | 0.51388 |
| $R-H_2C_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$<br>$(C-C$ (c)) | $C_b$ | -0.92918 | -0.72457 | -0.72457 | -0.72457 | -154.71860 | 0.91771 | 0.75889 | -17.92866 | -17.73779 | 48.21 | 131.79 | 21.74 | 1.95734 | 0.50570 |
| $isoC_aC_b(H_2C_c-R')HCH_2-$<br>$(C-C$ (d)) | $C_b$ | -0.92918 | -0.92918 | -0.92918 | 0 | -154.40324 | 0.91771 | 0.77247 | -17.61330 | -17.42244 | 48.30 | 131.70 | 21.90 | 1.97162 | 0.51388 |
| $tertC_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$<br>$(C-C$ (e)) | $C_b$ | -0.72457 | -0.72457 | -0.72457 | -0.72457 | -154.51399 | 0.91771 | 0.76765 | -17.92866 | -17.73779 | 50.04 | 129.96 | 22.66 | 1.94462 | 0.49298 |
| $tertC_aC_b(H_2C_c-R')HCH_2-$<br>$(C-C$ (f)) | $C_b$ | -0.72457 | -0.92918 | -0.92918 | 0 | -154.19863 | 0.91771 | 0.78155 | -17.40869 | -17.21783 | 52.78 | 127.22 | 24.04 | 1.92443 | 0.47279 |
| $isoC_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$<br>$(C-C$ (f)) | $C_b$ | -0.72457 | -0.72457 | -0.72457 | -0.72457 | -154.51399 | 0.91771 | 0.76765 | -17.92866 | -17.73779 | 50.04 | 129.96 | 22.66 | 1.94462 | 0.49298 |

Table 15.372. The energy parameters ($eV$) of functional groups of alkyl phosphates.

| Parameters | $P=O$ Group | $P-O$ Group | $C-O$ (i) Group | $C-O$ (ii) Group | $CH_3$ Group | $CH_2$ Group | $CH$ (i) Group | $C-C$ (a) Group | $C-C$ (b) Group | $C-C$ (c) Group | $C-C$ (d) Group | $C-C$ (e) Group | $C-C$ (f) Group |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $n_1$ | 2 | 1 | 1 | 1 | 3 | 2 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $n_2$ | 0 | 0 | 0 | 0 | 2 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $n_3$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $C_1$ | 0.5 | 0.5 | 0.5 | 0.5 | 0.75 | 0.75 | 0.75 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| $C_2$ | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $c_1$ | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $c_2$ | 0.79401 | 0.79401 | 0.85395 | 0.85395 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 |
| $c_3$ | 0 | 0 | 0 | 0 | 0 | 1 | 1 | 0 | 0 | 0 | 1 | 1 | 0 |
| $c_4$ | 4 | 2 | 2 | 2 | 1 | 1 | 1 | 2 | 2 | 2 | 2 | 2 | 2 |
| $c_5$ | 0 | 0 | 0 | 0 | 3 | 2 | 1 | 0 | 0 | 0 | 0 | 0 | 0 |
| $C_{1o}$ | 0.5 | 0.5 | 0.5 | 0.5 | 0.75 | 0.75 | 0.75 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| $C_{2o}$ | 1 | 0.79401 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $V_e\ (eV)$ | -56.96374 | -33.27738 | -33.15757 | -33.47304 | -107.32728 | -70.41425 | -35.12015 | -28.79214 | -28.79214 | -29.10112 | -28.79214 | -29.10112 | -29.10112 |
| $V_p\ (eV)$ | 9.82777 | 8.92049 | 10.12103 | 10.15605 | 38.92728 | 25.78002 | 12.87680 | 9.33352 | 9.33352 | 9.37273 | 9.33352 | 9.37273 | 9.37273 |
| $T\ (eV)$ | 14.86039 | 9.00781 | 9.17389 | 9.32537 | 32.53914 | 21.06675 | 10.48582 | 6.77464 | 6.77464 | 6.90500 | 6.77464 | 6.90500 | 6.90500 |
| $V_m\ (eV)$ | -7.43020 | -4.50391 | -4.58695 | -4.66268 | -16.26957 | -10.53337 | -5.24291 | -3.38732 | -3.38732 | -3.45250 | -3.38732 | -3.45250 | -3.45250 |
| $E(_{AO/HO})\ (eV)$ | -23.56492 | -11.78246 | -14.63489 | -14.63489 | -15.56407 | -15.56407 | -14.63489 | -15.56407 | -15.56407 | -15.35946 | -15.56407 | -15.35946 | -15.35946 |
| $\Delta E_{H_2MO}(_{AO/HO})\ (eV)$ | 0 | 0 | -1.44915 | -1.65376 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $E_T(_{AO/HO})\ (eV)$ | -23.56492 | -11.78246 | -13.18574 | -12.98113 | -15.56407 | -15.56407 | -14.63489 | -15.56407 | -15.56407 | -15.35946 | -15.56407 | -15.35946 | -15.35946 |
| $E_T(_{H_2MO})\ (eV)$ | -63.27069 | -31.63544 | -31.63533 | -31.63544 | -67.69451 | -49.66493 | -31.63533 | -31.63537 | -31.63537 | -31.63535 | -31.63537 | -31.63535 | -31.63535 |
| $E_T\left(atom-atom,msp^3.AO\right)\ (eV)$ | -2.26758 | -1.44914 | -1.44915 | -1.65376 | 0 | 0 | 0 | -1.85836 | -1.85836 | -1.44915 | -1.85836 | -1.44915 | -1.44915 |
| $E_T(_{MO})\ (eV)$ | -65.53832 | -33.08451 | -33.08452 | -33.28912 | -67.69450 | -49.66493 | -31.63537 | -33.49373 | -33.49373 | -33.08452 | -33.49373 | -33.08452 | -33.08452 |
| $\omega\ \left(10^{15}\ rad/s\right)$ | 11.0170 | 10.3761 | 12.0329 | 12.1583 | 24.9286 | 24.2751 | 24.1759 | 9.43699 | 9.43699 | 15.4846 | 9.43699 | 9.55643 | 9.55643 |
| $E_K\ (eV)$ | 7.25157 | 6.82973 | 7.92028 | 8.00277 | 16.40846 | 15.97831 | 15.91299 | 6.21159 | 6.21159 | 10.19220 | 6.21159 | 6.29021 | 6.29021 |
| $\bar{E}_D\ (eV)$ | -0.17458 | -0.17105 | -0.18420 | -0.18631 | -0.25352 | -0.25017 | -0.24966 | -0.16515 | -0.16515 | -0.20896 | -0.16515 | -0.16416 | -0.16416 |
| $\bar{E}_{Kvib}\ (eV)$ | 0.15292 [24] | 0.10477 [71] | 0.13663 [21] | 0.16118 [4] | 0.35532 (Eq. (13.458)) | 0.35532 (Eq. (13.458)) | 0.35532 (Eq. (13.458)) | 0.12312 [2] | 0.17978 [4] | 0.09944 [5] | 0.12312 [2] | 0.12312 [2] | 0.12312 [2] |
| $\bar{E}_{osc}\ (eV)$ | -0.09812 | -0.11867 | -0.11589 | -0.10572 | -0.22757 | -0.14502 | -0.07200 | -0.10359 | -0.07526 | -0.15924 | -0.10359 | -0.10260 | -0.10260 |
| $E_{mag}\ (eV)$ | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 |
| $E_T(_{Group})\ (eV)$ | -65.73455 | -33.20318 | -33.20040 | -33.39484 | -67.92207 | -49.80996 | -31.70737 | -33.59732 | -33.49373 | -33.24376 | -33.59732 | -33.18712 | -33.18712 |
| $E_{initial}(_{c_4\ AO/HO})\ (eV)$ | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 |
| $E_{initial}(_{c_5\ AO/HO})\ (eV)$ | 0 | 0 | 0 | 0 | -13.59844 | -13.59844 | -13.59844 | 0 | 0 | 0 | 0 | 0 | 0 |
| $E_D(_{Group})\ (eV)$ | 7.19500 | 3.93340 | 3.93062 | 4.12506 | 12.49186 | 7.83016 | 3.32601 | 4.32754 | 4.29921 | 3.97398 | 4.17951 | 3.62128 | 3.91734 |

Table 15.373. The total bond energies of alkyl phosphates calculated using the functional group composition and the energies of Table 15.372 compared to the experimental values [69].

| Formula | Name | $P=O$ | $P-O$ | $C-O$ (i) | $C-O$ (ii) | $CH_3$ | $CH_2$ | $CH$ (i) | $C-C$ (a) | $C-C$ (b) | $C-C$ (c) | $C-C$ (d) | $C-C$ (e) | $C-C$ (f) | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $C_6H_{15}O_4P$ | Triethyl phosphate | 1 | 3 | 0 | 3 | 3 | 3 | 0 | 3 | 0 | 0 | 0 | 0 | 0 | 105.31906 | 104.40400 | -0.00876 |
| $C_9H_{21}O_4P$ | Tri-n-propyl phosphate | 1 | 3 | 0 | 3 | 3 | 6 | 0 | 6 | 0 | 0 | 0 | 0 | 0 | 141.79216 | 140.86778 | -0.00656 |
| $C_9H_{21}O_4P$ | Tri-isopropyl phosphate | 1 | 3 | 0 | 3 | 6 | 0 | 3 | 0 | 6 | 0 | 0 | 0 | 0 | 142.09483 | 141.42283 | -0.00475 |
| $C_9H_{27}O_4P$ | Tri-n-butyl phosphate | 1 | 3 | 0 | 3 | 3 | 9 | 0 | 9 | 0 | 0 | 0 | 0 | 0 | 178.26526 | 178.07742 | -0.00105 |

Table 15.374. The bond angle parameters of alkyl phosphates and experimental values [1]. In the calculation of $\theta_v$, the parameters from the preceding angle were used. $E_T$ is $E_T$ ($atom - atom, msp^3.AO$).

| Atoms of Angle | $2c'$ Bond 1 ($a_0$) | $2c'$ Bond 2 ($a_0$) | $2c'$ Terminal Atoms ($a_0$) | $E_{Coulombic}$ or $E$ Atom 1 | Atom 1 Hybridization Designation (Table 15.3.A) | $E_{Coulombic}$ Atom 2 | Atom 2 Hybridization Designation (Table 15.3.A) | $c_2$ Atom 1 | $c_2$ Atom 2 | $C_1$ | $C_2$ | $c_1$ | $c_2'$ | $E_T$ (eV) | $\theta_v$ (°) | $\theta_1$ (°) | $\theta_2$ (°) | Cal. $\theta$ (°) | Exp. $\theta$ (°) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $\angle POC$ | 3.05046 | 2.67935 | 4.9904 | -11.78246 | $Psp^3$ | -15.75493 | 7 | 0.73885 Eq. (15.181) | 0.86359 | 1 | 0.73885 | 1 | 0.80122 | -0.72457 | | | | 121.00 | 122.2 [70] (MHPO) |
| $\angle O_aPO_a$ | 3.05046 | 3.05046 | 4.7539 | -15.95954 | 10 | -15.95954 | 10 | 0.85252 | 0.85252 | 1 | 1 | 1 | 0.85252 | -1.65376 | | | | 102.38 | 101.4 [65] (DNA) |
| $\angle O_aPO_b$ | 3.05046 | 2.76885 | 4.7539 | -15.95954 | 10 | -15.95954 | 10 | 0.85252 | 0.85252 | 1 | 1 | 1 | 0.85395 | -1.65376 | | | | 109.46 | 109.7 [65] (DNA) |
| $\angle C_bC_aO$ ($C_a - O$ (ii)) | 2.91547 | 2.67935 | 4.5607 | -16.68412 | 26 | -13.61806 | O | 0.81549 | 0.85395 (Eq. (15.133)) | 1 | 1 | 1 | 0.83472 | -1.65376 | | | | 109.13 | 109.4 (ethyl methyl ether) |
| Methylene $\angle HC_aH$ | 2.11106 | 2.11106 | 3.4252 | -15.75493 | 7 | H | H | 0.86359 | 1 | 1 | 1 | 0.75 | 1.15796 | 0 | | | | 108.44 | 107 (propane) |
| $\angle C_aC_bC_c$ | | | | | | | | | | | | | | | 69.51 | | | 110.49 | 112 (propane)<br>113.8 (butane)<br>110.8 (isobutane) |
| $\angle C_aC_bH$ | | | | | | | | | | | | | | | 69.51 | | | 110.49 | 111.0 (butane)<br>111.4 (isobutane) |
| Methyl $\angle HC_aH$ | 2.09711 | 2.09711 | 3.4252 | -15.75493 | 7 | H | H | 0.86359 | 1 | 1 | 1 | 0.75 | 1.15796 | 0 | | | | 109.50 | |
| $\angle C_aC_bC_c$ | | | | | | | | | | | | | | | 70.56 | | | 109.44 | |
| $\angle C_aC_bH$ | | | | | | | | | | | | | | | 70.56 | | | 109.44 | |
| $\angle C_bC_aC_c$ iso $C_a$ | 2.91547 | 2.91547 | 4.7958 | -16.68412 $C_b$ | 26 | -16.68412 $C_c$ | 26 | 0.81549 | 0.81549 | 1 | 1 | 1 | 0.81549 | -1.85836 | | | | 110.67 | 110.8 (isobutane) |
| $\angle C_bC_aH$ iso $C_a$ | 2.91547 | 2.11323 | 4.1633 | -15.55033 $C_a$ | 5 | -14.82575 $C_b$ | 1 | 0.87495 | 0.91771 | 0.75 | 1 | 0.75 | 1.04887 | 0 | | | | 110.76 | |
| $\angle C_aC_bH$ iso $C_a$ | 2.91547 | 2.09711 | 4.1633 | -15.55033 $C_b$ | 5 | -14.82575 $C_a$ | 1 | 0.87495 | 0.91771 | 0.75 | 1 | 0.75 | 1.04887 | 0 | | | | 111.27 | 111.4 (isobutane) |
| $\angle C_bC_aC_b$ tert $C_a$ | 2.90327 | 2.90327 | 4.7958 | -16.68412 $C_b$ | 26 | -16.68412 $C_b$ | 26 | 0.81549 | 0.81549 | 1 | 1 | 1 | 0.81549 | -1.85836 | | | | 111.37 | 110.8 (isobutane) |
| $\angle C_bC_aC_d$ | | | | | | | | | | | | | | | 72.50 | | | 107.50 | |

# ORGANIC AND RELATED IONS ($RCO_2^-$, $ROSO_3^-$, $NO_3^-$, $(RO)_2PO_2^-$, $(RO)_3SiO^-$, $(R)_2Si(O^-)_2$, $RNH_3^+$, $R_2NH_2^+$)

Proteins comprising amino acids with amino and carboxylic acid groups are charged at physiological pH. Deoxyribonucleic acid (DNA), the genetic material of living organisms also comprises negatively charged phosphate groups. Thus, the bonding of organic ions is considered next. The molecular ions also comprise functional groups that have an additional electron or are deficient by an electron in the cases of monovalent molecular anions and cations, respectively. The molecular chemical bond typically comprises an even integer number of paired electrons, but with an excess of deficiency, the bonding may involve an odd number of electrons, and the electrons may be distributed over multiple bonds, solved as a linear combination of standard bonds. As given in the Benzene Molecule section and other sections on aromatic molecules such as naphthalene, toluene, chlorobenzene, phenol, aniline, nitrobenzene, benzoic acid, pyridine, pyrimidine, pyrazine, quinoline, isoquinoline, indole, and adenine, the paired electrons of MOs may be distributed over a linear combination of bonds such that the bonding between two atoms involves less than an integer multiple of two electrons. Specifically, the results of the derivation of the parameters of the benzene molecule given in the Benzene Molecule ($C_6H_6$) section was generalized to any aromatic functional group of aromatic and heterocyclic compounds in the Aromatic and Heterocyclic Compounds section. Ethylene serves as a basis element for the $C\overset{3e}{=}C$ bonding of the aromatic bond wherein each of the $C\overset{3e}{=}C$ aromatic bonds comprises $(0.75)(4)=3$ electrons according to Eq. (15.161). Thus, in these aromatic cases, three electrons can be assigned to a given bond between two atoms wherein the electrons of the linear combination of bonded atoms are paired and comprise an integer multiple of two.

In graphite, the minimum energy structure with equivalent carbon atoms wherein each carbon forms bonds with three other such carbons requires a redistribution of charge within an aromatic system of bonds. Considering that each carbon contributes four bonding electrons, the sum of electrons of a vertex-atom group is four from the vertex atom plus two from each of the two atoms bonded to the vertex atom where the latter also contribute two each to the juxtaposed group. These eight electrons are distributed equivalently over the three bonds of the group such that the electron number assignable to each bond is $\frac{8}{3}$. Thus, the $C\overset{8/3e}{=}C$ functional group of graphite comprises the aromatic bond with the exception that the electron-number per bond is $\frac{8}{3}$.

As given in the Bridging Bonds of Boranes section and the Bridging Bonds of Organoaluminum Hydrides section, other examples of electron deficient bonding involving two paired electrons centered on three atoms are *three-center bonds* as opposed to the typical single bond, a *two-center bond*. The $B2sp^3$ HOs comprise four orbitals containing three electrons as given by Eq. (23.1) that can form three-center as well as two-center bonds. The designation for a three-center bond involving two $B2sp^3$ HOs and a $H1s$ AO is $B-H-B$, and the designation for a three-center bond involving three $B2sp^3$ HOs is $B-B-B$. In the aluminum case, each $Al-H-Al$-bond MO and $Al-C-Al$-bond MO comprises the corresponding single bond and forms with further sharing of electrons between each $Al3sp^3$ HO and each $H1s$ AO and $C2sp^3$ HO, respectively. Thus, the geometrical and energy parameters of the three-center bond are equivalent to those of the corresponding two-center bonds except that the bond energy is increased in the former case since the donation of electron density from the unoccupied $Al3sp^3$ HO to each $Al-H-Al$-bond MO and $Al-C-Al$-bond MO permits the participating orbital to decrease in size and energy.

To match the energies of the AOs and MOs of the ionic functional group with the others within the molecular ion, the bonding in organic ions comprises a standard bond that serves as basis element and retains the same geometrical characteristics as that standard bond. In the case of organic oxyanions, the $A-O^-$ ($A=C,S,N,P,Si$) bond is intermediate between a single and double bond, and the latter serves as a basis element. Similar to the case of the $C\overset{3e}{=}C$ aromatic bond wherein ethylene is the basis element, the $A=O$-bond functional group serves as the basis element for the $A-O^-$ functional group of the oxyanion of carboxylates, sulfates, nitrates, phosphates, silanolates, and siloxanolates. This oxyanion group designated by $A\overset{3e}{=}O^-$ comprises $(0.75)(4)=3$ electrons after Eq. (15.161). Thus, the energy parameters of the $A\overset{3e}{=}O^-$ functional group are given by the factor of $(0.75)(4)=3$ times those of the corresponding $A=O$ functional group, and the geometric parameters are the same. The $C=O$, $S=O$, $N=O_2$, $P=O$, and $Si=O$ basis elements are given in the Carboxylic Acids, Sulfates, Alkyl Nitrates, Phosphates, and Silicon Oxides, Silicic Acids, Silanols, Siloxanes and Disiloxanes sections, respectively. A convenient means to obtain the final group energy parameters of $E_T\,(Group)$ and $E_D\,(Group)$ is by using Eqs. (15.165-15.166) with $f_1=0.75$:

$$E_T(Group) = f_1 \left( \begin{array}{l} E(basis\ energies) + E_T\left(atom-atom, msp^3.AO\right) \\ -31.63536831\ eV \sqrt{\frac{2\hbar\sqrt{\frac{\frac{C_{1o}C_{2o}e^2}{4\pi\varepsilon_o R^3}}{m_e}}}{m_e c^2}} + n_1\overline{E}_{Kvib} + c_3\frac{8\pi\mu_o\mu_B^2}{r^3} \end{array} \right) \tag{15.183}$$

$$E_D(Group) = -\left( \begin{array}{l} f_1 \left( \begin{array}{l} E(basis\ energies) + E_T\left(atom-atom, msp^3.AO\right) \\ -31.63536831\ eV \sqrt{\frac{2\hbar\sqrt{\frac{\frac{C_{1o}C_{2o}e^2}{4\pi\varepsilon_o R^3}}{m_e}}}{m_e c^2}} + n_1\overline{E}_{Kvib} + c_3\frac{8\pi\mu_o\mu_B^2}{r^3} \end{array} \right) \\ -\left(c_4 E_{initial}\left(AO/HO\right) + c_5 E_{initial}\left(c_5\ AO/HO\right)\right) \end{array} \right) \tag{15.184}$$

where $c_4$ is $(0.75)(4) = 3$ when $c_5 = 0$ and otherwise $c_4$ is $(0.75)(2) = 1.5$ and $c_5$ is $(0.75)(2) = 1.5$.

The nature of the bonding of the amino functional group of protonated amines is similar to that in $H_3^+$. As given in the Triatomic Molecular Hydrogen-type Ion ($H_3^+$) section, $H_3^+$ comprises two indistinguishable spin-paired electrons bound by three protons. The ellipsoidal molecular orbital (MO) satisfies the boundary constraints as shown in the Nature of the Chemical Bond of Hydrogen-Type Molecules section. Since the protons are indistinguishable, ellipsoidal MOs about each pair of protons taken one at a time are indistinguishable. $H_3^+$ is then given by a superposition or linear combinations of three equivalent ellipsoidal MOs that form an equilateral triangle where the points of contact between the prolate spheroids are equivalent in energy and charge density. Due to the equivalence of the $H_2$-type ellipsoidal MOs and the linear superposition of their energies, the energy components defined previously for the $H_2$ molecule, Eqs. (11.207-11.212) apply in the case of the corresponding $H_3^+$ molecular ion. And, each molecular energy component is given by the integral of corresponding force in Eq. (13.5). Each energy component is the total for the two equivalent electrons with the exception that the total charge of the two electrons is normalized over the three basis set $H_2$-type ellipsoidal MOs. Thus, the energies (Eqs. (13.12-13.17)) are those given in the Energies of Hydrogen-Type Molecules section with the electron charge, where it appears, multiplied by a factor of $3/2$, and the three sets of equivalent proton-proton pairs give rise to a factor of three times the proton-proton repulsion energy given by Eq. (11.208).

With the protonation of the imidogen ($NH$) functional group, the minimum energy structure with equivalent hydrogen atoms comprises two protons bound to $N$ by two paired electrons, one from $H$ and one from $N$ with the MO matched to the $N2p$ AO. These two electrons are distributed equivalently over the two $H-N$ bonds of the group such that the electron number assignable to each bond is $\frac{2}{2}$. Thus, the $NH_2^+$ functional group has the imidogen energy parameters with the exception that each energy term is multiplied by the factor $2$ due to the two bonds with electron-number per bond of $\frac{2}{2}$ and has the same geometric parameters as the $NH$ functional group given in the Secondary Amines section. A convenient means to obtain the final group energy parameters of $E_T(Group)$ and $E_D(Group)$ is by using Eqs. (15.165-15.166) (Eqs. (15.183-15.184)) with $f_1 = 2$ and $c_4$ and $c_5$ multiplied by two.

With the protonation of the amidogen ($NH_2$) functional group, the minimum energy structure with equivalent hydrogen atoms comprises three protons bound to $N$ by four paired electrons, two from $2H$ and two from $N$ with the MO matched to the $N2p$ AO. These four electrons are distributed equivalently over the three $H-N$ bonds of the group such that the electron number assignable to each bond is $\frac{4}{3}$. Thus, the $NH_3^+$ functional group has the amidogen energy parameters with the exception that each energy term is multiplied by the factor $\frac{3}{2}$ due to the three bonds with electron-number per bond of $\frac{4}{3}$ and has the same geometric parameters as the $NH_2$ functional group given in the Primary Amines section. A convenient means to obtain the final group energy parameters of $E_T(Group)$ and $E_D(Group)$ is by using Eqs. (15.165-15.166) (Eqs. (15.183-15.184)) with $f_1 = 3/2$ and $c_4$ and $c_5$ multiplied by 3/2.

The symbols of the functional groups of organic and related ions are given in Table 15.375. The geometrical (Eqs. (15.1-15.5) and (15.51)), intercept (Eqs. (15.80-15.87)), and energy (Eqs. (15.6-15.11) and (15.17-15.65)) parameters are given in Tables 15.376, 15.377, and 15.378, respectively. Due to its charge, the bond angles of the organic and related ions that minimize the total energy are those that maximize the separation of the groups. For ions having three bonds to the central atom, the angles are 120°, and ions having four bonds are tetrahedral. The color scale, charge-density of exemplary organic ion, protonated lysine, comprising atoms with the outer shell bridged by one or more $H_2$-type ellipsoidal MOs or joined with one or more hydrogen MOs is shown in Figure 15.64.

Figure 15.64. Color scale, charge-density of protonated lysine ion showing the orbitals of the atoms at their radii, the ellipsoidal surface of each $H$ or $H_2$-type ellipsoidal MO that transitions to the corresponding outer shell of the atom(s) participating in each bond, and the hydrogen nuclei.

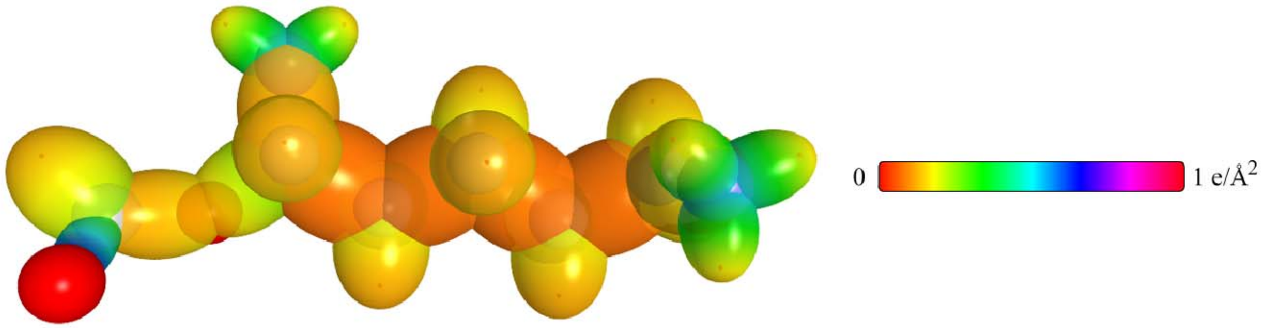


Table 15.375. The symbols of functional groups of organic and related ions.

| Functional Group | Group Symbol |
|---|---|
| $(O)C\text{-}O^-$ (alkyl carboxylate) | $C-O^-$ |
| $(RO)(O)_2S\text{-}O^-$ (alkyl sulfate) | $S-O^-$ |
| $(O)_2N\text{-}O^-$ (nitrate) | $N-O^-$ |
| $(RO)_2(O)P\text{-}O^-$ (alkyl phosphate) | $P-O^-$ |
| $(RO)_3Si\text{-}O^-$ (alkyl siloxanolate)<br>$(R)_2Si(\text{-}O^-)_2$ (alkyl silanolate) | $Si-O^-$ |
| $NH_2^+$ group | $NH_2^+$ |
| $NH_3^+$ group | $NH_3^+$ |

Table 15.376. The geometrical bond parameters of organic and related ions and experimental values of corresponding basis elements [1].

| Parameter | $C-O^-$ Group | $S-O^-$ Group | $N-O^-$ Group | $P-O^-$ Group | $Si-O^-$ Group | $NH_2^+$ Group | $NH_3^+$ Group |
|---|---|---|---|---|---|---|---|
| $a$ $(a_0)$ | 1.29907 | 1.98517 | 1.29538 | 1.91663 | 2.24744 | 1.26224 | 1.28083 |
| $c'$ $(a_0)$ | 1.13977 | 1.40896 | 1.13815 | 1.38442 | 1.41056 | 0.94811 | 0.95506 |
| Bond Length $2c'$ $(Å)$ | 1.20628 | 1.49118 | 1.20456 | 1.46521 | 1.49287 | 1.00343 | 1.0108 |
| Exp. Bond Length $(Å)$ | 1.214 (acetic acid) | 1.485 (dimethyl sulfoxide) | 1.205 (methyl nitrate)<br>1.2 ($HNO_2$) | 1.48 [65] (DNA) | 1.509 (silicon oxide) [74] | 1.00 (dimethylamine) | 1.010 (methylamine) |
| $b,c$ $(a_0)$ | 0.62331 | 1.39847 | 0.61857 | 1.32546 | 1.74966 | 0.83327 | 0.85345 |
| $e$ | 0.87737 | 0.70974 | 0.87862 | 0.72232 | 0.62763 | 0.75113 | 0.74566 |

Table 15.377. The MO to HO intercept geometrical bond parameters of organic and related ions. $E_T$ is $E_T$ $(atom-atom,msp^3.AO)$.

| Bond | Atom | $E_T$ (eV) Bond 1 | $E_T$ (eV) Bond 2 | $E_T$ (eV) Bond 3 | $E_T$ (eV) Bond 4 | Final Total Energy $C2sp^3$ (eV) | $r_{initial}$ $(a_0)$ | $r_{final}$ $(a_0)$ | $E_{Coulomb}(C2sp^3)$ (eV) Final | $E(C2sp^3)$ (eV) Final | $\theta'$ (°) | $\theta_1$ (°) | $\theta_2$ (°) | $d_1$ $(a_0)$ | $d_2$ $(a_0)$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $RH_2C_bC_a(O)-O^-$ | $O$ | -1.01210 | 0 | 0 | 0 |  | 1.00000 | 0.85907 | -15.83785 |  | 137.99 | 42.01 | 67.29 | 0.50150 | 0.63827 |
| $RH_2C_bC_a(O)-O^-$ | $C_a$ | -1.01210 | -0.92918 | -0.92918 | 0 | -154.48615 | 0.91771 | 0.76885 | -17.69621 | -17.50535 | 134.14 | 45.86 | 62.28 | 0.60433 | 0.53544 |
| $(RO)_2(O)S-O^-$ | $S$ | 0 | -0.46459 | -0.46459 | 0 |  | 1.32010 | 0.86359 | -15.75493 |  | 78.56 | 101.44 | 37.25 | 1.58026 | 0.17130 |
| $(RO)_2(O)S-O^-$ | $O$ | 0 | 0 | 0 | 0 |  | 1.00000 | 0.91771 | -14.82575 |  | 84.06 | 95.94 | 40.75 | 1.50400 | 0.09504 |
| $O_2N-O^-$ | $O$ | -0.69689 | 0 | 0 | 0 |  | 1.00000 | 0.87651 | -15.52264 |  | 135.13 | 44.87 | 63.23 | 0.58339 | 0.55475 |
| $O_2N-O^-$ | $N$ | -0.92918 | -0.92918 | -0.69689 | 0 |  | 0.93084 | 0.78280 | -17.38100 |  | 138.99 | 41.01 | 68.41 | 0.47673 | 0.66142 |
| $(RO)_2(O)P-O^-$ | $P$ | -0.72457 | -0.72457 | -1.13379 | -0.85034 |  | 1.15350 | 0.74515 | -18.25903 |  | 71.42 | 108.58 | 32.20 | 1.62182 | 0.23739 |
| $(RO)_2(O)P-O^-$ | $O$ | -0.85034 | 0 | 0 | 0 |  | 1.00000 | 0.86793 | -15.67609 |  | 85.55 | 94.45 | 40.76 | 1.45184 | 0.06742 |
| $(RO)_3Si-O^-$ | $Si$ | -1.55205 | -0.62217 | -0.62217 | -0.62217 |  | 1.31926 | 0.99082 | -13.73181 |  | 53.34 | 126.66 | 27.02 | 2.00216 | 0.59160 |
| $(RO)_3Si-O^-$ | $O$ | -1.55205 | 0 | 0 | 0 |  | 1.00000 | 0.89688 | -15.17010 |  | 34.26 | 145.74 | 16.77 | 2.15183 | 0.74128 |
| $-H_2C_aNH(R_{alkyl})-H^+$ | $N$ | -0.56690 | -0.56690 | 0 | 0 |  | 0.93084 | 0.85252 | -15.95954 |  | 118.18 | 61.82 | 64.40 | 0.54546 | 0.40264 |
| $-H_2C_aN(H_2)-H^+$ | $N$ | -0.72457 | 0 | 0 | 0 |  | 0.93084 | 0.87495 | -15.55033 |  | 118.00 | 62.00 | 64.85 | 0.54432 | 0.41075 |

Table 15.378. The energy parameters ($eV$) of functional groups of organic and related ions.

| Parameters | $C-O^-$ Group | $S-O^-$ Group | $N-O^-$ Group | $P-O^-$ Group | $Si-O^-$ Group | $NH_2^+$ Group | $NH_3^+$ Group |
|---|---|---|---|---|---|---|---|
| $f_1$ | 0.75 | 0.75 | 0.75 | 0.75 | 0.75 | 2 | 3/2 |
| $n_1$ | 2 | 2 | 2 | 2 | 2 | 1 | 2 |
| $n_2$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $n_3$ | 0 | 0 | 0 | 0 | 0 | 0 | 1 |
| $C_1$ | 0.5 | 0.5 | 0.5 | 0.5 | 0.75 | 0.75 | 0.75 |
| $C_2$ | 1 | 1 | 1 | 1 | 0.75304 | 0.93613 | 0.93613 |
| $c_1$ | 1 | 1 | 1 | 1 | 1 | 0.75 | 0.75 |
| $c_2$ | 0.85395 | 1.20632 | 0.85987 | 0.78899 | 1 | 0.93383 | 0.94627 |
| $c_3$ | 2 | 0 | 0 | 0 | 0 | 1 | 0 |
| $c_4$ | 4 | 4 | 4 | 4 | 2 | 1 | 1 |
| $c_5$ | 0 | 1 | 0 | 0 | 2 | 1 | 2 |
| $C_{1o}$ | 0.5 | 0.5 | 0.5 | 0.5 | 0.75 | 0.75 | 1.5 |
| $C_{2o}$ | 1 | 1 | 1 | 1 | 0.75304 | 1 | 1 |
| $V_e\ (eV)$ | -111.25473 | -82.63003 | -112.63415 | -56.96374 | -56.90923 | -39.21967 | -77.89897 |
| $V_p\ (eV)$ | 23.87467 | 19.31325 | 23.90868 | 9.82777 | 19.29141 | 14.35050 | 28.49191 |
| $T\ (eV)$ | 42.82081 | 20.81183 | 43.47534 | 14.86039 | 12.66092 | 15.53581 | 30.40957 |
| $V_m\ (eV)$ | -21.41040 | -10.40592 | -21.73767 | -7.43020 | -6.33046 | -7.76790 | -15.20478 |
| $E(_{AO/HO})\ (eV)$ | 0 | -11.52126 | 0 | -11.78246 | -20.50975 | -14.53414 | -14.53414 |
| $\Delta E_{H_2MO}(_{AO/HO})\ (eV)$ | -2.69893 | -1.16125 | -3.71673 | 0 | 0 | 0 | 0 |
| $E(_{n_3\ AO/HO})\ (eV)$ | 0 | 0 | 0 | 0 | 0 | 0 | -14.53414 |
| $E_T(_{AO/HO})\ (eV)$ | 2.69893 | -10.36001 | 3.71673 | -11.78246 | -20.50975 | -14.53414 | -14.53414 |
| $E_T(_{H_2MO})\ (eV)$ | -63.27074 | -63.27088 | -63.27107 | -63.27069 | -51.79710 | -31.63541 | -48.73642 |
| $E_T\left(atom-atom, msp^3.AO\right)\ (eV)$ | -2.69893 | 0 | -3.71673 | -2.26758 | -4.13881 | 0 | 0 |
| $E_T(_{MO})\ (eV)$ | -65.96966 | -63.27074 | -66.98746 | -65.53832 | -55.93591 | -31.63537 | -48.73660 |
| $\omega\ \left(10^{15}\ rad/s\right)$ | 59.4034 | 17.6762 | 19.8278 | 11.0170 | 9.22130 | 47.0696 | 64.2189 |
| $E_K\ (eV)$ | 39.10034 | 11.63476 | 13.05099 | 7.25157 | 6.06962 | 30.98202 | 42.27003 |
| $\bar{E}_D\ (eV)$ | -0.40804 | -0.21348 | -0.23938 | -0.17458 | -0.13632 | -0.34836 | -0.40690 |
| $\bar{E}_{Kvib}\ (eV)$ | 0.21077<br>[12] | 0.12832<br>[43] | 0.19342<br>[45] | 0.12337<br>[75] | 0.15393<br>[24] | 0.40696<br>[24] | 0.40929<br>[22] |
| $\bar{E}_{osc}\ (eV)$ | -0.30266 | -0.14932 | -0.14267 | -0.11289 | -0.05935 | -0.14488 | -0.20226 |
| $E_{mag}\ (eV)$ | 0.11441 | 0.11441 | 0.11441 | 0.14803 | 0.04983 | 0.14803 | 0.14803 |
| $E_T(_{Group})\ (eV)$ | -49.93123 | -47.67703 | -50.45460 | -49.32308 | -42.04096 | -63.56050 | -73.71167 |
| $E_{initial}(_{c_4\ AO/HO})\ (eV)$ | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -10.25487 | -14.53414 | -14.53414 |
| $E_{initial}(_{c_5\ AO/HO})\ (eV)$ | 0 | -1.16125 | 0 | 0 | -13.61805 | -13.59844 | -13.59844 |
| $E_D(_{Group})\ (eV)$ | 6.02656 | 2.90142 | 6.54994 | 5.41841 | 6.23157 | 7.01164 | 11.11514 |

## MONOSACCHARIDES OF DNA AND RNA

The simple sugar moiety of DNA and RNA comprises the alpha forms of 2-deoxy-D-ribose and D-ribose, respectively. The sugars comprise the alkyl $CH_2$, $CH$, and $C-C$ functional groups and the alkyl alcohol $C-O$ and $OH$ functional groups given in the Alcohols section. In addition, the alpha form of the sugars comprise the $C-O$ ether functional group given in the Ethers section, and the open-chain forms further comprise the carbon to carbonyl $C-C$, the methylyne carbon of the aldehyde carbonyl $CH$, and the aldehyde carbonyl $C=O$ functional groups given in the Aldehydes section. The total energy of each sugar given in Tables 15.379-15.382 was calculated as the sum over the integer multiple of each $E_D(_{Group})$ corresponding to the functional-group composition wherein the group identity and energy $E_D(_{Group})$ are given in each table. The color scale, charge-density of the monosaccharides, each comprising atoms with the outer shell bridged by one or more $H_2$-type ellipsoidal MOs or joined with one or more hydrogen MOs are shown in Figure 15.65.

Figure 15.65. Color scale, charge-density of riboses showing the orbitals of the atoms at their radii, the ellipsoidal surface of each $H$ or $H_2$-type ellipsoidal MO that transitions to the corresponding outer shell of the atom(s) participating in each bond, and the hydrogen nuclei. (A) 2-deoxy-D-ribose. (B) D-ribose. (C) Alpha-2-deoxy-D-ribose. (D) Alpha-D-ribose.

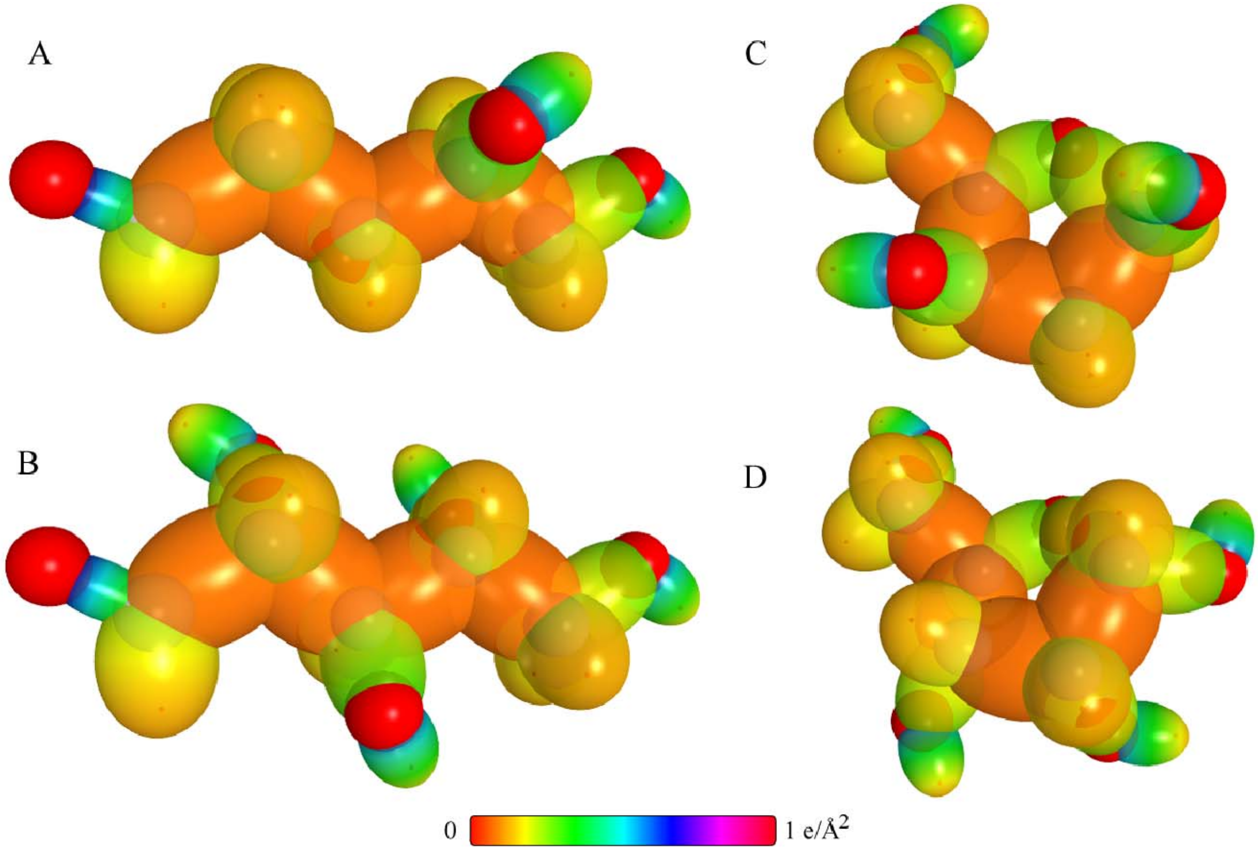


Table 15.379. The total gaseous bond energy of 2-deoxy-D-ribose ($C_5H_{10}O_4$) calculated using the functional group composition and the energies given *supra*.

| Formula | $CH_2$ Group | $CH$ (alkyl) Group | $CH$ ($HC{=}O$) Group | $C-C$ (n-C) Group | $C-C(O)$ (aldehyde) Group | $C=O$ (aldehyde) Group | $C-O$ ($C\text{-}OH$) Group | $OH$ Group | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Energies $E_D(_{Group})$ of Functional Groups (eV) | 7.83016 | 3.32601 | 3.47404 | 4.32754 | 4.41461 | 7.80660 | 4.34572 | 4.41035 | | | |
| Composition | 2 | 2 | 1 | 3 | 1 | 1 | 3 | 3 | 77.25842 | | |

Table 15.380. The total gaseous bond energy of D-ribose ($C_5H_{10}O_5$) calculated using the functional group composition and the energies given *supra*. compared to the experimental values [3].

| Formula | $CH_2$ Group | $CH$ (alkyl) Group | $CH$ ($HC{=}O$) Group | $C-C$ (n-C) Group | $C-C(O)$ (aldehyde) Group | $C=O$ (aldehyde) Group | $C-O$ ($C\text{-}OH$) Group | $OH$ Group | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Energies $E_D(_{Group})$ of Functional Groups (eV) | 7.83016 | 3.32601 | 3.47404 | 4.32754 | 4.41461 | 7.80660 | 4.34572 | 4.41035 | | | |
| Composition | 1 | 3 | 1 | 3 | 1 | 1 | 4 | 4 | 81.51034 | 83.498[a] | 0.02381 |

[a] Crystal.

Table 15.381. The total gaseous bond energy of alpha-2-deoxy-D-ribose ($C_5H_{10}O_4$) calculated using the functional group composition and the energies given *supra*.

| Formula | $CH_2$ Group | $CH$ (alkyl) Group | $C-C$ (n-C) Group | $C-O$ (alkyl ether) Group | $C-O$ ($C\text{-}OH$) Group | $OH$ Group | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|---|---|---|---|---|
| Energies $E_D(_{Group})$ of Functional Groups (eV) | 7.83016 | 3.32601 | 4.32754 | 4.12506 | 4.34572 | 4.41035 | | | |
| Composition | 2 | 3 | 4 | 2 | 3 | 3 | 77.46684 | | |

Table 15.382. The total gaseous bond energy of alpha-D-ribose ($C_5H_{10}O_5$) calculated using the functional group composition and the energies given *supra*.

| Formula | $CH_2$ Group | $CH$ (alkyl) Group | $C-C$ (n-C) Group | $C-O$ (alkyl ether) Group | $C-O$ ($C\text{-}OH$) Group | $OH$ Group | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|---|---|---|---|---|
| Energies $E_D(_{Group})$ of Functional Groups (eV) | 7.83016 | 3.32601 | 4.32754 | 4.12506 | 4.34572 | 4.41035 | | | |
| Composition | 1 | 4 | 4 | 2 | 4 | 4 | 82.31088 | | |

## NUCLEOTIDE BONDS OF DNA AND RNA

DNA and RNA comprise a backbone of alpha-2-deoxy-D-ribose and alpha-D-ribose, respectively, with a charged phosphate moiety at the 3' and 5' positions of two consecutive ribose units in the chain and a base bound at the 1' position wherein the ribose $H$ of each of the corresponding 3' or 5' $O-H$ and 1' $C-H$ bonds is replaced by $P$ and the base $N$, respectively. For the base, the $H$ of the $N-H$ at the pyrimidine 1 position or the purine 9 position is replaced by the sugar $C$. The basic repeating unit of DNA or RNA is a nucleotide that comprises a monosaccharide, a phosphate moiety and a base. The structure of the nucleotide bond is shown in Figure 15.66 with the designation of the corresponding atoms. The phosphate moiety comprises the $P=O$, $P-O$, and $C-O$ functional groups given in the Phosphates section as well as the $P-O^-$ group given in the Organic and Related Ions section. The nucleoside bond (sugar C to base N) comprises the tertiary amine $C-N$ functional group given in the corresponding section. The bases, adenine, guanine, thymine, and cytosine are equivalent to those given in the corresponding sections. The symbols of the functional groups of the nucleotide bond are given in Table 15.383. The geometrical (Eqs. (15.1-15.5) and (15.51)), intercept (Eqs. (15.80-15.87)), and energy (Eqs. (15.6-15.11) and (15.17-15.65)) parameters are given in Tables 15.384, 15.385, and 15.386, respectively. The functional group composition and the corresponding energy $E_D(Group)$ of each group of the nucleotide bond of DNA and RNA are given in Table 15.387. The bond angle parameters of the nucleoside bond determined using Eqs. (15.88-15.117) are given in Table 15.388. The color scale rendering of the charge-density of the exemplary tetra-nucleotide, (deoxy)adenosine 3'-monophosphate—5'-(deoxy)thymidine 3'-monophosphate—5'-(deoxy)guanosine 3'-monophosphate—5'-(deoxy)cytidine monophosphate (ATGC) comprising the concentric shells of atoms with the outer shell bridged by one or more $H_2$-type ellipsoidal MOs or joined with one or more hydrogen MOs is shown in Figure 15.67. Figure 15.68 shows the color scale rendering of the charge-density of the exemplary DNA fragment $\begin{array}{c}\text{ACTGACTGACTG}\\\text{TGACTGACTGAC}\end{array}$ wherein each complementary strand comprises a dodeca-nucleotide of the form (base (1)—deoxyribose) monophosphate—( base(2)—deoxyribose) monophosphate— with the phosphates bridging the 3' and 5' ribose carbons with the opposite order for the complementary stands. Figure 15.68 shows the color scale rendering of the charge-density of an exemplary double-stranded DNA helix.

Figure 15.66. Designation of the atoms of the nucleotide bond.

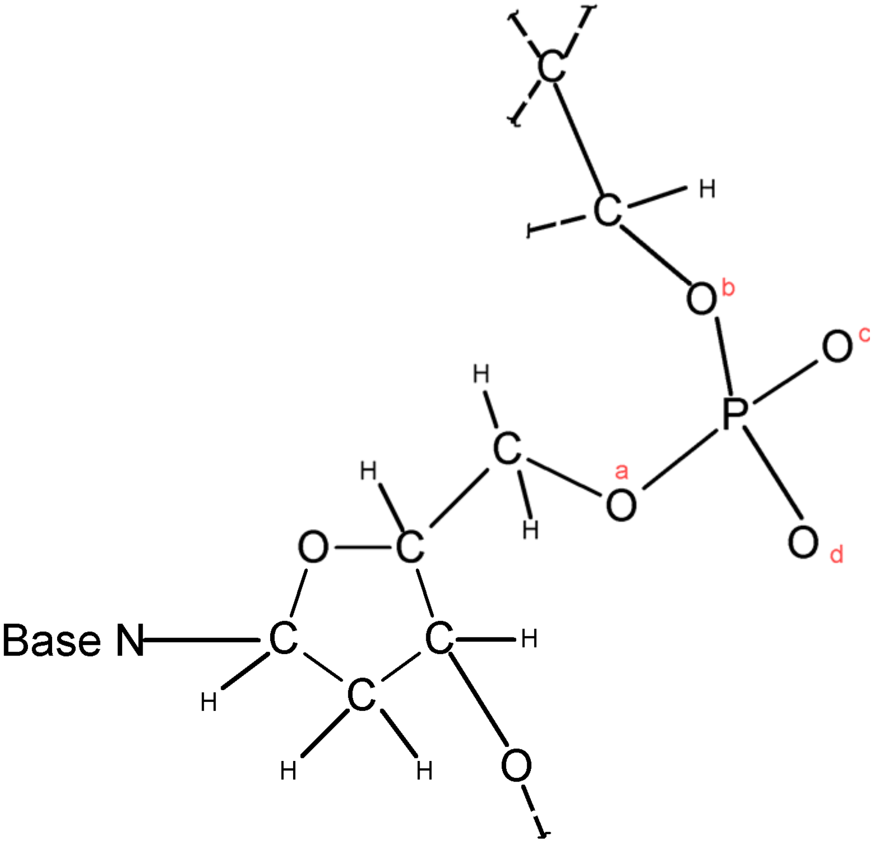


Figure 15.67. The color scale rendering of the charge-density of the exemplary tetra-nucleotide, (deoxy)adenosine monophosphate—(deoxy)thymidine monophosphate—(deoxy)guanosine monophosphate—(deoxy)cytidine monophosphate (ATGC) showing the orbitals of the atoms at their radii and the ellipsoidal surface of each $H$ or $H_2$-type ellipsoidal MO that transitions to the corresponding outer shell of the atom(s) participating in each bond.

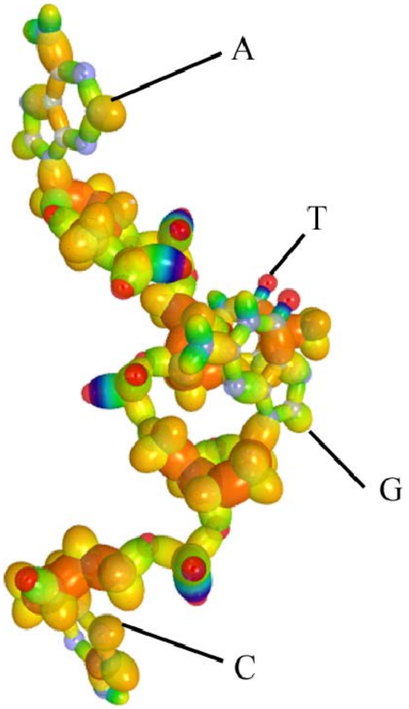


Figure 15.68. Color scale rendering of the charge-density of the DNA fragment $\begin{matrix}\text{ACTGACTGACTG}\\\text{TGACTGACTGAC}\end{matrix}$ showing the orbitals of the atoms at their radii and the ellipsoidal surface of each $H$ or $H_2$-type ellipsoidal MO that transitions to the corresponding outer shell of the atom(s) participating in each bond.

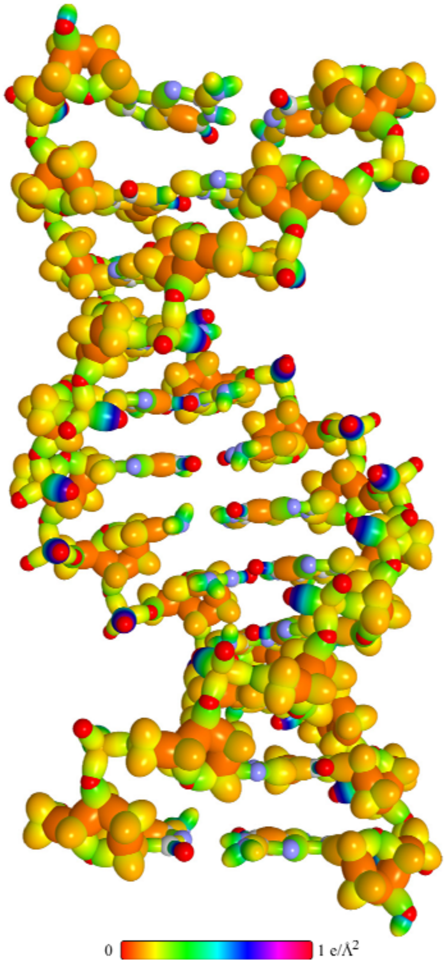


Figure 15.69. Color scale, opaque view of the charge density of a double-stranded DNA helix created and modeled using Millsian 2.0.

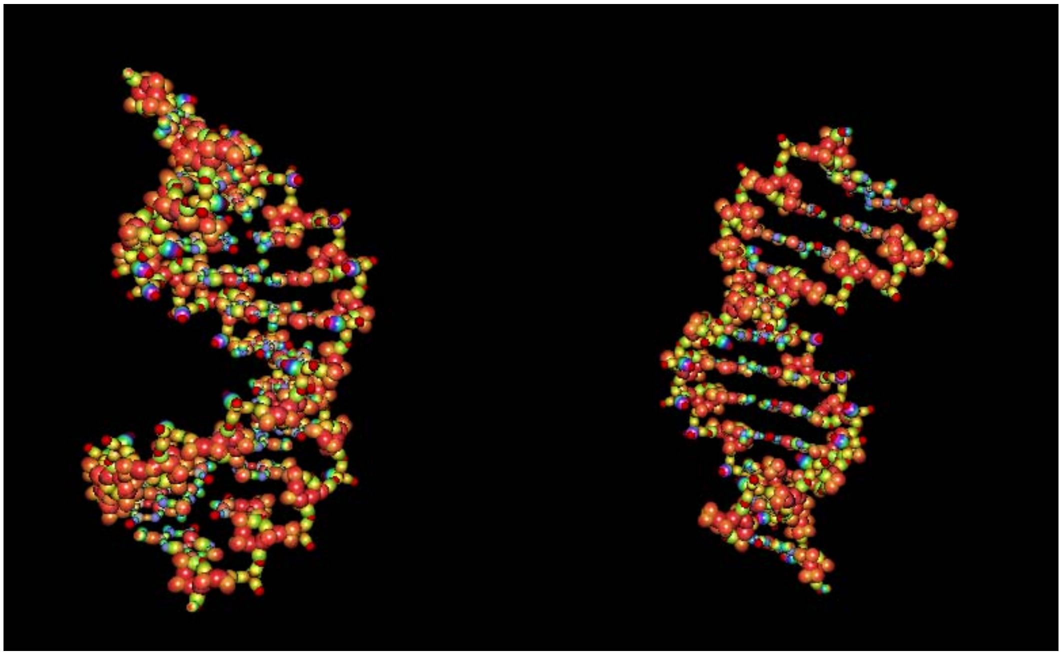


Table 15.383. The symbols of functional groups of the nucleotide bond.

| Functional Group | Group Symbol |
|---|---|
| *C-N* | $C-N$ |
| C-O (alkyl) | $C-O$ |
| *P=O* | $P=O$ |
| *P-O* | $P-O$ |
| $(RO)_2(O)P\text{-}O^-$ (alkyl phosphate) | $P-O^-$ |

Table 15.384. The geometrical bond parameters of the nucleotide bond and experimental values [1].

| Parameter | $C-N$ Group | $C-O$ Group | $P=O$ Group | $P-O$ Group | $P-O^-$ Group |
|---|---|---|---|---|---|
| $a\ (a_0)$ | 1.96313 | 1.79473 | 1.91663 | 1.84714 | 1.91663 |
| $c'\ (a_0)$ | 1.40112 | 1.33968 | 1.38442 | 1.52523 | 1.38442 |
| Bond Length $2c'\ (\AA)$ | 1.48288 | 1.41785 | 1.46521E-10 | 1.61423 | 1.46521 |
| Exp. Bond Length $(\AA)$ | 1.458<br>(trimethylamine) | 1.418<br>(ethyl methyl ether (avg.)) | 1.48 [65]<br>(DNA)<br>1.4759<br>($PO$) | 1.631 [70]<br>(MHP)<br>1.60 [65]<br>(DNA) | 1.48 [65]<br>(DNA) |
| $b,c\ (a_0)$ | 1.37505 | 1.19429 | 1.32546 | 1.04192 | 1.32546 |
| $e$ | 0.71372 | 0.74645 | 0.72232 | 0.82573 | 0.72232 |

Table 15.385. The MO to HO intercept geometrical bond parameters of the nucleotide bond. $E_T$ is $E_T$ ($atom - atom, msp^3.AO$).

| Bond | Atom | $E_T$ (eV) Bond 1 | $E_T$ (eV) Bond 2 | $E_T$ (eV) Bond 3 | $E_T$ (eV) Bond 4 | Final Total Energy $C2sp^3$ (eV) | $r_{initial}$ $(a_0)$ | $r_{final}$ $(a_0)$ | $E_{Coulomb}(C2sp^3)$ (eV) Final | $E(C2sp^3)$ (eV) Final | $\theta'$ (°) | $\theta_1$ (°) | $\theta_2$ (°) | $d_1$ $(a_0)$ | $d_2$ $(a_0)$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $C_e(H)N_d - C_c(N_c)C_d$<br>$N_e(H)C_e - N_d(H)C_c$<br>(adenine nucleoside) | $N_d$ | -0.60631 | -0.60631 | -0.46459 | 0 |  | 0.93084 | 0.82445 | -16.50297 |  | 138.15 | 41.85 | 61.57 | 0.68733 | 0.61411 |
| $C_e(H)N_d - C_c(N_c)C_d$<br>$N_e(H)C_e - N_d(H)C_c$<br>(guanine nucleoside) | $N_d$ | -0.92918 | -0.92918 | -0.46459 | 0 |  | 0.93084 | 0.79340 | -17.14871 |  | 138.07 | 41.93 | 60.47 | 0.70588 | 0.59026 |
| $N_b(O)C_b - N_cHC_c$<br>$C_bHN_c - HC_cC_d$<br>(thymine nucleoside) | $N_c$ | -0.92918 | -0.92918 | -0.46459 | 0 |  | -0.93084 | -0.79340 | -17.14871 |  | 138.07 | 41.93 | 60.47 | 0.70588 | 0.59026 |
| $N_b(O)C_b - N_cHC_c$<br>$C_bHN_c - HC_cC_d$<br>(cytosine nucleoside) | $N_c$ | -0.92918 | -0.92918 | -0.46459 | 0 |  | -0.93084 | -0.79340 | -17.14871 |  | 138.07 | 41.93 | 60.47 | 0.70588 | 0.59026 |
| $N_d - C\ ribose$<br>(adenine nucleoside) | $N_d$ | -0.46459 | -0.60631 | -0.60631 | 0 |  | 0.93084 | 0.82445 | -16.50297 |  | 76.37 | 103.63 | 35.64 | 1.59544 | 0.19432 |
| $N_d - C\ ribose$<br>(adenine nucleoside) | $C\ ribose$ | -0.46459 | -0.92918 | -0.82688 | 0 | -153.83634 | -0.91771 | -0.79816 | -17.04640 | -16.85554 | 73.17 | 106.83 | 33.75 | 1.63226 | 0.23114 |
| $N_d - C\ ribose$<br>(guanine nucleoside) | $N_d$ | -0.46459 | -0.92918 | -0.92918 | 0 |  | 0.93084 | 0.79340 | -17.14871 |  | 72.56 | 107.44 | 33.40 | 1.63893 | 0.23782 |
| $N_d - C\ ribose$<br>(guanine nucleoside) | $C\ ribose$ | -0.46459 | -0.92918 | -0.82688 | 0 | -153.83634 | -0.91771 | -0.79816 | -17.04640 | -16.85554 | 73.17 | 106.83 | 33.75 | 1.63226 | 0.23114 |
| $N_c - C\ ribose$<br>(thymine nucleoside) | $N_c$ | -0.46459 | -0.92918 | -0.92918 | 0 |  | 0.93084 | 0.79340 | -17.14871 |  | 72.56 | 107.44 | 33.40 | 1.63893 | 0.23782 |
| $N_c - C\ ribose$<br>(thymine nucleoside) | $C\ ribose$ | -0.46459 | -0.92918 | -0.82688 | 0 | -153.83634 | -0.91771 | -0.79816 | -17.04640 | -16.85554 | 73.17 | 106.83 | 33.75 | 1.63226 | 0.23114 |
| $N_c - C\ ribose$<br>(cytosine nucleoside) | $N_c$ | -0.46459 | -0.92918 | -0.92918 | 0 |  | 0.93084 | 0.79340 | -17.14871 |  | 72.56 | 107.44 | 33.40 | 1.63893 | 0.23782 |
| $N_c - C\ ribose$<br>(cytosine nucleoside) | $C\ ribose$ | -0.46459 | -0.92918 | -0.82688 | 0 | -153.83634 | -0.91771 | -0.79816 | -17.04640 | -16.85554 | 73.17 | 106.83 | 33.75 | 1.63226 | 0.23114 |

Table 15.386. The energy parameters (*eV*) of functional groups of the nucleotide bond.

| Parameters | $C-N$ Group | $C-O$ Group | $P=O$ Group | $P-O$ Group | $P-O^-$ Group |
|---|---|---|---|---|---|
| $n_1$ | 1 | 1 | 2 | 1 | 2 |
| $n_2$ | 0 | 0 | 0 | 0 | 0 |
| $n_3$ | 0 | 0 | 0 | 0 | 0 |
| $C_1$ | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| $C_2$ | 1 | 1 | 1 | 1 | 1 |
| $c_1$ | 1 | 1 | 1 | 1 | 1 |
| $c_2$ | 0.91140 | 0.85395 | 0.79401 | 0.79401 | 0.78899 |
| $c_3$ | 0 | 0 | 0 | 0 | 0 |
| $c_4$ | 2 | 2 | 4 | 2 | 4 |
| $c_5$ | 0 | 0 | 0 | 0 | 0 |
| $C_{1o}$ | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| $C_{2o}$ | 1 | 1 | 1 | 0.79401 | 1 |
| $V_e\ (eV)$ | -31.67393 | -33.47304 | -56.96374 | -33.27738 | -56.96374 |
| $V_p\ (eV)$ | 9.71067 | 10.15605 | 9.82777 | 8.92049 | 9.82777 |
| $T\ (eV)$ | 8.06719 | 9.32537 | 14.86039 | 9.00781 | 14.86039 |
| $V_m\ (eV)$ | -4.03359 | -4.66268 | -7.43020 | -4.50391 | -7.43020 |
| $E(_{AO/HO})\ (eV)$ | -14.63489 | -14.63489 | -23.56492 | -11.78246 | -11.78246 |
| $\Delta E_{H_2MO}(_{AO/HO})\ (eV)$ | -0.92918 | -1.65376 | 0 | 0 | 0 |
| $E_T(_{AO/HO})\ (eV)$ | -13.70571 | -12.98113 | -23.56492 | -11.78246 | -11.78246 |
| $E_T(_{H_2MO})\ (eV)$ | -31.63537 | -31.63544 | -63.27069 | -31.63544 | -63.27069 |
| $E_T\left(atom-atom, msp^3.AO\right)\ (eV)$ | -0.92918 | -1.65376 | -2.26758 | -1.44914 | -2.26758 |
| $E_T(_{MO})\ (eV)$ | -32.56455 | -33.28912 | -65.53832 | -33.08451 | -65.53832 |
| $\omega\ \left(10^{15}\ rad/s\right)$ | 18.1298 | 12.1583 | 11.0170 | 10.3761 | 11.0170 |
| $E_K\ (eV)$ | 11.93333 | 8.00277 | 7.25157 | 6.82973 | 7.25157 |
| $\bar{E}_D\ (eV)$ | -0.22255 | -0.18631 | -0.17458 | -0.17105 | -0.17458 |
| $\bar{E}_{Kvib}\ (eV)$ | 0.12944<br>[23] | 0.16118<br>[4] | 0.15292<br>[24] | 0.10477<br>[71] | 0.12337<br>[75] |
| $\bar{E}_{osc}\ (eV)$ | -0.15783 | -0.10572 | -0.09812 | -0.11867 | -0.11289 |
| $E_{mag}\ (eV)$ | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 |
| $E_T(_{Group})\ (eV)$ | -32.72238 | -33.39484 | -65.73455 | -33.20318 | -49.32308 |
| $E_{initial}(_{c_4\ AO/HO})\ (eV)$ | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 |
| $E_{initial}(_{c_5\ AO/HO})\ (eV)$ | 0 | 0 | 0 | 0 | 0 |
| $E_D(_{Group})\ (eV)$ | 3.45260 | 4.12506 | 7.19500 | 3.93340 | 5.41841 |

Table 15.387. The functional group composition and the energy *E<sub>D</sub>(Group)* of each group of the nucleotide bond.

| Formula | $C-N$ (3° amine) Group | $C-O$ (alkyl ether) Group | $P=O$ (phosphate) Group | $P-O$ (phosphate) Group | $P-O^-$ (organic ions) Group |
|---|---|---|---|---|---|
| Energies $E_D(_{Group})$ of Functional Groups (eV) | 3.45260 | 4.12506 | 7.19500 | 3.93340 | 5.41841 |
| Composition | 1 | 2 | 1 | 2 | 1 |

Table 15.388. The bond angle parameters of the nucleotide bond and experimental values [1]. In the calculation of $\theta_v$, the parameters from the preceding angle were used. $E_T$ is $E_T$ (*atom – atom,msp*$^3$.*AO*).

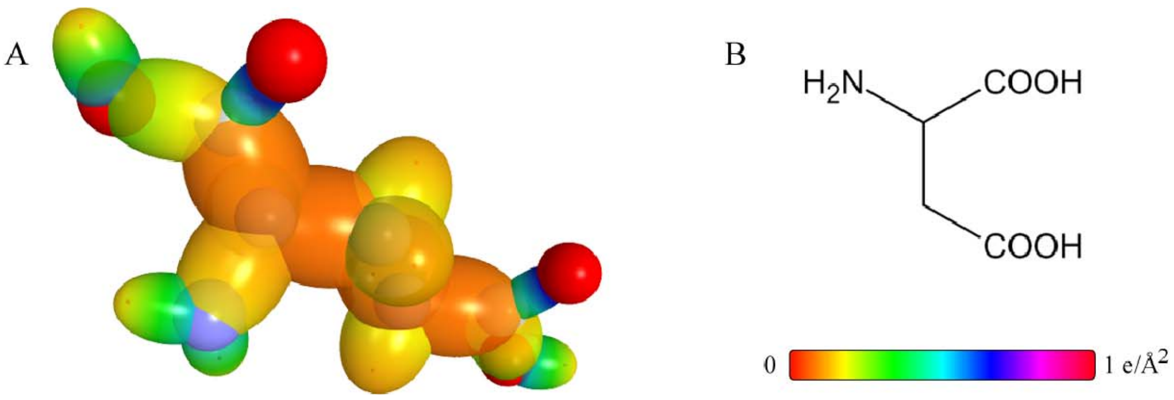
| Atoms of Angle | 2c' Bond 1 ($a_0$) | 2c' Bond 2 ($a_0$) | 2c' Terminal Atoms ($a_0$) | $E_{Coulombic}$ Atom 1 | Atom 1 Hybridization Designation (Table 15.3A) | $E_{Coulombic}$ Atom 2 | Atom 2 Hybridization Designation (Table 15.3A) | $c_2$ Atom 1 | $c_2$ Atom 2 | $C_1$ | $C_2$ | $c_1$ | $c_2'$ | $E_T$ (eV) | $\theta_v$ (°) | $\theta_1$ (°) | $\theta_2$ (°) | Cal. $\theta$ (°) | Exp. $\theta$ (°) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $\angle(P)OCN$ | 2.67935 | 2.80224 | 4.5277 | -16.47951 | 22 | -16.47951 | 22 | 0.82562 | 0.82562 | 1 | 1 | 1 | 0.82562 | -1.65376 | | | | 111.36 | 111.3 [65] |
| $\angle POC$ | 3.05046 | 2.67935 | 4.9904 | -11.78246 | $Psp^3$ | -15.75493 | 7 | 0.73885 Eq. (15.181) | 0.86359 | 1 | 0.73885 | 1 | 0.80122 | -0.72457 | | | | 121.00 | 121.3 [65] |
| $\angle O_aPO_b$ | 3.05046 | 3.05046 | 4.7539 | -15.95954 | 10 | -15.95954 | 10 | 0.85252 | 0.85252 | 1 | 1 | 1 | 0.85252 | -1.65376 | | | | 102.38 | 101.4 [65] |
| $\angle O_bPO_c$ | 3.05046 | 2.76885 | 4.7539 | -15.95954 | 10 | -15.95954 | 10 | 0.85252 | 0.85252 | 1 | 1 | 1 | 0.85395 | -1.65376 | | | | 109.46 | 109.7 [65] |
| $\angle O_cPO_d$ | 2.76885 | 2.76885 | 4.7539 | -15.95954 | 10 | -15.95954 | 10 | 0.85252 | 0.85252 | 1 | 1 | 1 | 0.85252 | -1.65376 | | | | 118.29 | 116.0 [65] |
| $\angle C_aOC_b$<br>($C_a - O$ (i))<br>($C_b - O$ (ii)) | 2.68862 | 2.67935 | 4.4385 | -17.51099 | 48 | -17.51099 | 48 | 0.77699 | 0.77699 | 1 | 1 | 1 | 0.77699 | -1.85836 | | | | 111.55 | 111.9<br>(ethyl methyl ether) |
| $\angle C_bC_aO$<br>($C_a - O$ (ii)) | 2.91547 | 2.67935 | 4.5607 | -16.68412 | 26 | -13.61806 | O | 0.81549 | 0.85395 (Eq. (15.133)) | 1 | 1 | 1 | 0.83472 | -1.65376 | | | | 109.13 | 109.4<br>(ethyl methyl ether) |
| $\angle C_aOH$<br>($C_a - O$ (ii)) | 2.67024 | 1.83616 | 3.6515 | -14.82575 | 1 | -14.82575 | 1 | 1 | 0.91771 | 0.75 | 1 | 0.75 | 0.91771 | 0 | | | | 106.78 | 105<br>(ethanol) |
| $\angle C_bC_aO$<br>($C_a - O$ (ii)) | 2.91547 | 2.67024 | 4.5826 | -16.68412 | 26 | -13.61806 | O | 0.81549 | 0.85395 (Eq. (15.114)) | 1 | 1 | 1 | 0.83472 | -1.65376 | | | | 110.17 | 107.8<br>(ethanol) |
| $\angle CNC$<br>(3° amine) | 2.80224 | 2.80224 | 4.6043 | -17.14871 | 36 | -17.14871 | 36 | 0.79340 | 0.79340 | 1 | 1 | 1 | 0.79340 | -1.85836 | | | | 110.48 | 110.9<br>(trimethyl amine) |
| Methylene<br>$\angle HC_aH$ | 2.11106 | 2.11106 | 3.4252 | -15.75493 | 7 | H | H | 0.86359 | 1 | 1 | 1 | 0.75 | 1.15796 | 0 | | | | 108.44 | 107<br>(propane) |
| $\angle C_aC_bC_c$ | | | | | | | | | | | | | | | 69.51 | | | 110.49 | 112<br>(propane)<br>113.8<br>(butane)<br>110.8<br>(isobutane) |
| $\angle C_aC_bH$ | | | | | | | | | | | | | | | 69.51 | | | 110.49 | 111.0<br>(butane)<br>111.4<br>(isobutane) |
| Methyl<br>$\angle HC_aH$ | 2.09711 | 2.09711 | 3.4252 | -15.75493 | 7 | H | H | 0.86359 | 1 | 1 | 1 | 0.75 | 1.15796 | 0 | | | | 109.50 | |
| $\angle C_aC_bC_c$ | | | | | | | | | | | | | | | 70.56 | | | 109.44 | |
| $\angle C_aC_bH$ | | | | | | | | | | | | | | | 70.56 | | | 109.44 | |
| $\angle C_bC_aC_c$<br>iso $C_a$ | 2.91547 | 2.91547 | 4.7958 | -16.68412<br>$C_b$ | 26 | -16.68412<br>$C_c$ | 26 | 0.81549 | 0.81549 | 1 | 1 | 1 | 0.81549 | -1.85836 | | | | 110.67 | 110.8<br>(isobutane) |
| $\angle C_bC_aH$<br>iso $C_a$ | 2.91547 | 2.11323 | 4.1633 | -15.55033<br>$C_a$ | 5 | -14.82575<br>$C_b$ | 1 | 0.87495 | 0.91771 | 0.75 | 1 | 0.75 | 1.04887 | 0 | | | | 110.76 | |
| $\angle C_aC_bH$<br>iso $C_a$ | 2.91547 | 2.09711 | 4.1633 | -15.55033<br>$C_b$ | 5 | -14.82575<br>$C_a$ | 1 | 0.87495 | 0.91771 | 0.75 | 1 | 0.75 | 1.04887 | 0 | | | | 111.27 | 111.4<br>(isobutane) |

## AMINO ACIDS ($H_2N-CH(R)-COOH$)

The amino acids, $H_2NCH(R)COOH$, each have a primary amine moiety comprised of $NH_2$ and $C-N$ functional groups, an alkyl carboxylic acid moiety comprised of a $C=O$ functional group, and the single bond of carbon to the carbonyl carbon atom, $C-C(O)$, is also a functional group. The carboxylic acid moiety further comprises a $C-OH$ moiety that comprises $C-O$ and $OH$ functional groups. The alpha carbon comprises a methylyne ($CH$) functional group bound to a side chain $R$ group by an isopropyl $C-C$ bond functional group. These groups common to all amino acids are given in the Primary Amines section, the Carboxylic Acids section, and the Branched Alkanes section, respectively. The $R$ group is unique for each amino acid and determines its characteristic hydrophilic, hydrophobic, acidic, and basic properties. These characteristic functional groups are given in the prior organic functional group sections. The total energy of each amino acid given in Tables 15.389-15.408 was calculated as the sum over the integer multiple of each $E_D(Group)$ corresponding to the functional-group composition of the amino acid wherein the group identity and energy $E_D(Group)$ are given in each table. The structure and the color scale, charge-density of the amino acids, each comprising atoms with the outer shell bridged by one or more $H_2$-type ellipsoidal MOs or joined with one or more hydrogen MOs are shown in Figures 15.70-15.89.

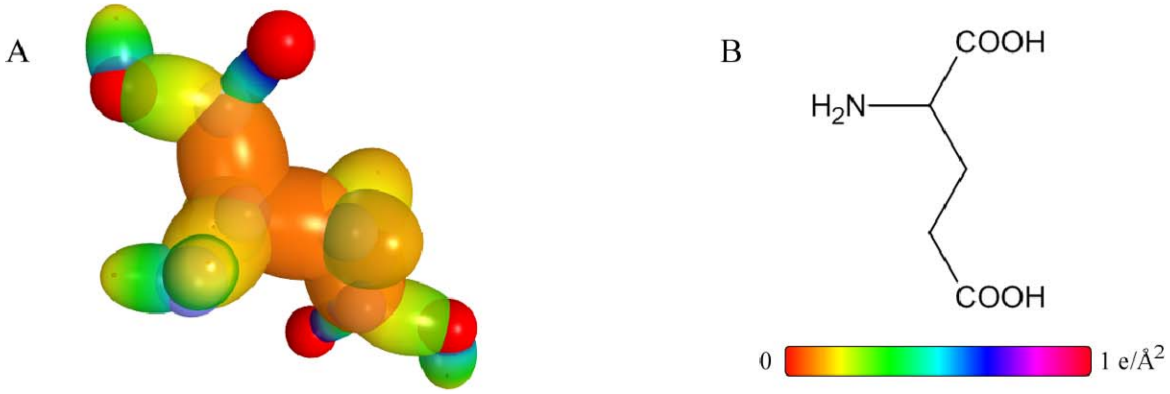
### ASPARTIC ACID

Figure 15.70. (A) Color scale, charge-density of aspartic acid showing the orbitals of the atoms at their radii, the ellipsoidal surface of each $H$ or $H_2$-type ellipsoidal MO that transitions to the corresponding outer shell of the atom(s) participating in each bond, and the hydrogen nuclei. (B) Chemical structure of aspartic acid.



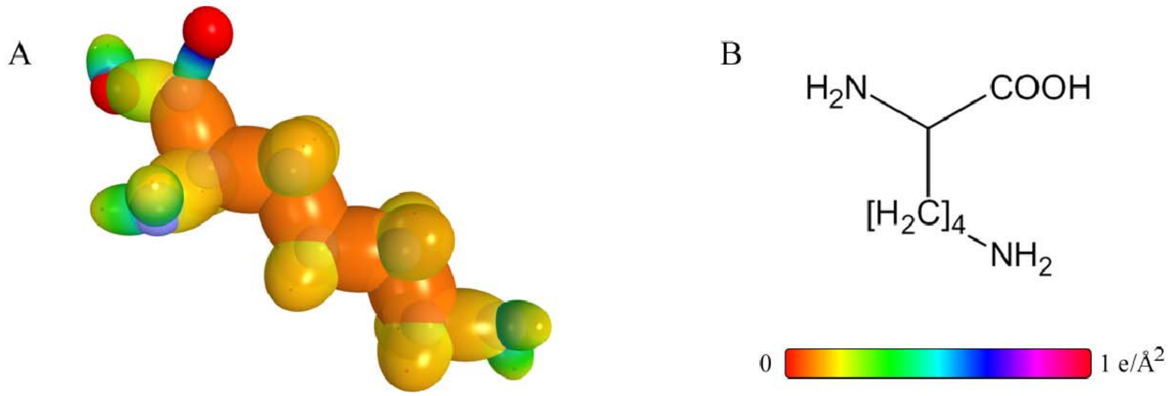
### GLUTAMIC ACID

Figure 15.71. (A) Color scale, charge-density of glutamic acid showing the orbitals of the atoms at their radii, the ellipsoidal surface of each $H$ or $H_2$-type ellipsoidal MO that transitions to the corresponding outer shell of the atom(s) participating in each bond, and the hydrogen nuclei. (B) Chemical structure of glutamic acid.



## CYSTEINE

Figure 15.72. (A) Color scale, charge-density of cysteine showing the orbitals of the atoms at their radii, the ellipsoidal surface of each $H$ or $H_2$-type ellipsoidal MO that transitions to the corresponding outer shell of the atom(s) participating in each bond, and the hydrogen nuclei. (B) Chemical structure of cysteine.



## LYSINE

Figure 15.73. (A) Color scale, charge-density of lysine showing the orbitals of the atoms at their radii, the ellipsoidal surface of each $H$ or $H_2$-type ellipsoidal MO that transitions to the corresponding outer shell of the atom(s) participating in each bond, and the hydrogen nuclei. (B) Chemical structure of lysine.

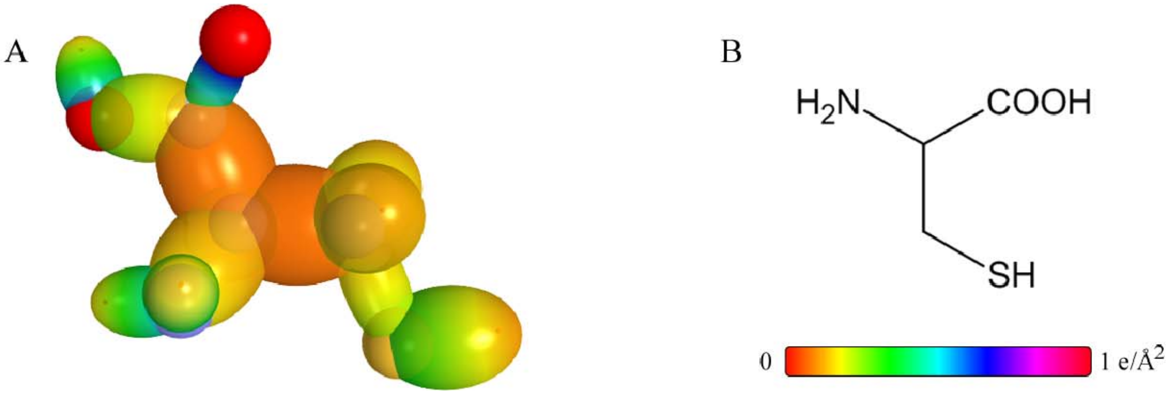


Table 15.389. The total bond energy of aspartic acid ($C_4H_7NO_4$) calculated using the functional group composition and the energies given *supra*. compared to the experimental values [3].

| Formula | $CH_2$ Group | $CH$ Group | $C-C$ (iso-C) Group | $C-C(O)$ (alkyl carboxylic acid) Group | $C=O$ (alkyl carboxylic acid) Group | $C-O$ ((O)C-O) Group | $OH$ Group | $NH_2$ Group | $C-N$ (1° amine) | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Energies $E_D(_{Group})$ of Functional Groups (eV) | 7.83016 | 3.32601 | 4.29921 | 4.43110 | 7.80660 | 4.41925 | 4.41035 | 7.41010 | 3.98101 | | | |
| Composition | 1 | 1 | 1 | 2 | 2 | 2 | 2 | 1 | 1 | 68.98109 | 70.843[a] | 0.02628 |

[a] Crystal.

Table 15.390. The total bond energy of glutamic acid ($C_5H_9NO_4$) calculated using the functional group composition and the energies given *supra*. compared to the experimental values [3].

| Formula | $CH_2$ Group | $CH$ Group | $C-C$ (n-C) Group | $C-C$ (iso-C) Group | $C-C(O)$ (alkyl carboxylic acid) Group | $C=O$ (alkyl carboxylic acid) Group | $C-O$ ((O)C-O) Group | $OH$ Group | $NH_2$ Group | $C-N$ (1° amine) | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Energies $E_D(_{Group})$ of Functional Groups (eV) | 7.83016 | 3.32601 | 4.32754 | 4.29921 | 4.43110 | 7.80660 | 4.41925 | 4.41035 | 7.41010 | 3.98101 | | | |
| Composition | 2 | 1 | 1 | 1 | 2 | 2 | 2 | 2 | 1 | 1 | 81.13879 | 83.167[a] | 0.02438 |

[a] Crystal.

Table 15.391. The total bond energy of cysteine ($C_3H_7NO_4S$) calculated using the functional group composition and the energies given *supra*. compared to the experimental values [3].

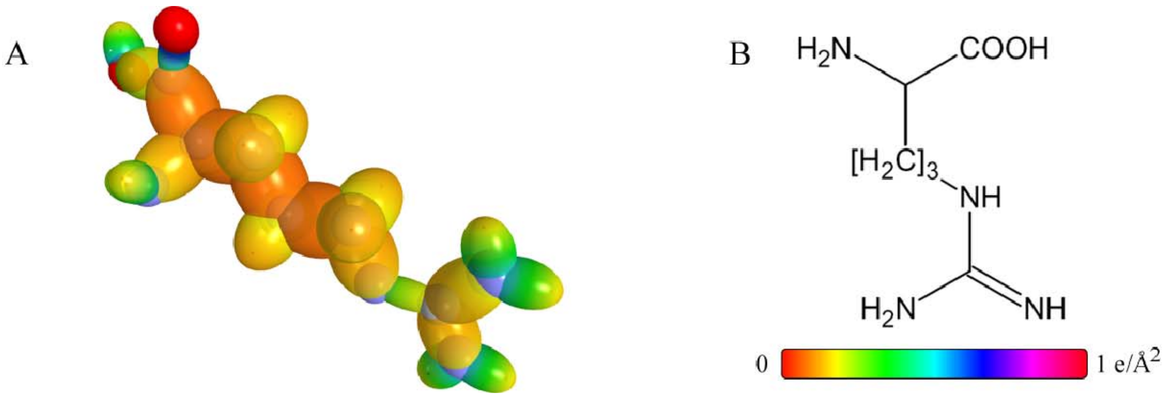
| Formula | $CH_2$ Group | $CH$ Group | $C-C$ (iso-C) Group | $C-C(O)$ (alkyl carboxylic acid) Group | $C=O$ (alkyl carboxylic acid) Group | $C-O$ ((O)C-O) Group | $OH$ Group | $NH_2$ Group | $C-N$ (1° amine) | $SH$ Group | $C-S$ (thiol) Group | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Energies $E_D(_{Group})$ of Functional Groups (eV) | 7.83016 | 3.32601 | 4.29921 | 4.43110 | 7.80660 | 4.41925 | 4.41035 | 7.41010 | 3.98101 | 3.77430 | 3.33648 | | | |
| Composition | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 55.02457 | 56.571[a] | 0.02733 |

Table 15.392. The total bond energy of lysine ($C_6H_{14}N_2O_2$) calculated using the functional group composition and the energies given *supra*. compared to the experimental values [3].

| Formula | $CH_2$ Group | $CH$ Group | $C-C$ (n-C) Group | $C-C$ (iso-C) Group | $C-C(O)$ (alkyl carboxylic acid) Group | $C=O$ (alkyl carboxylic acid) Group | $C-O$ ((O)C-O) Group | $OH$ Group | $NH_2$ Group | $C-N$ (1° amine) | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Energies $E_D(_{Group})$ of Functional Groups (eV) | 7.83016 | 3.32601 | 4.32754 | 4.29921 | 4.43110 | 7.80660 | 4.41925 | 4.41035 | 7.41010 | 3.98101 | | | |
| Composition | 4 | 1 | 3 | 1 | 1 | 1 | 1 | 1 | 2 | 2 | 95.77799 | 98.194[a] | 0.02461 |

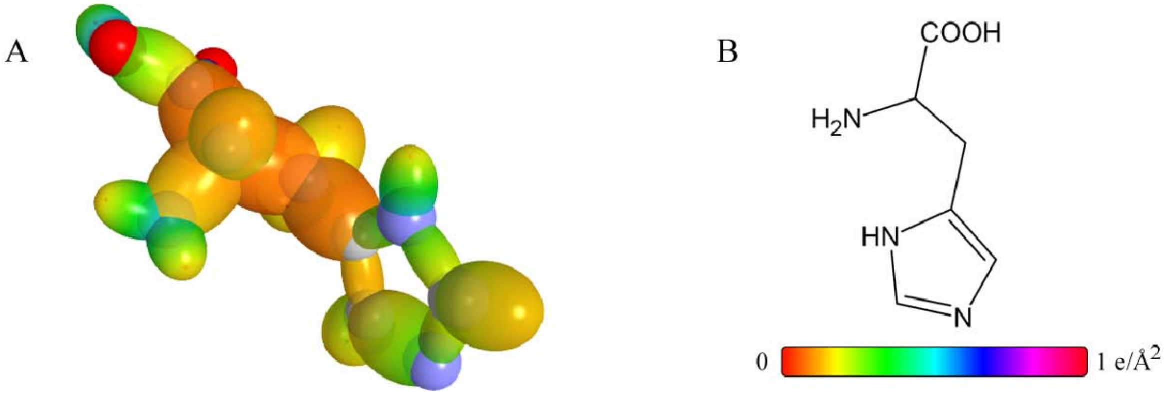
## ARGININE

Figure 15.74. (A) Color scale, charge-density of arginine showing the orbitals of the atoms at their radii, the ellipsoidal surface of each $H$ or $H_2$-type ellipsoidal MO that transitions to the corresponding outer shell of the atom(s) participating in each bond, and the hydrogen nuclei. (B) Chemical structure of arginine.



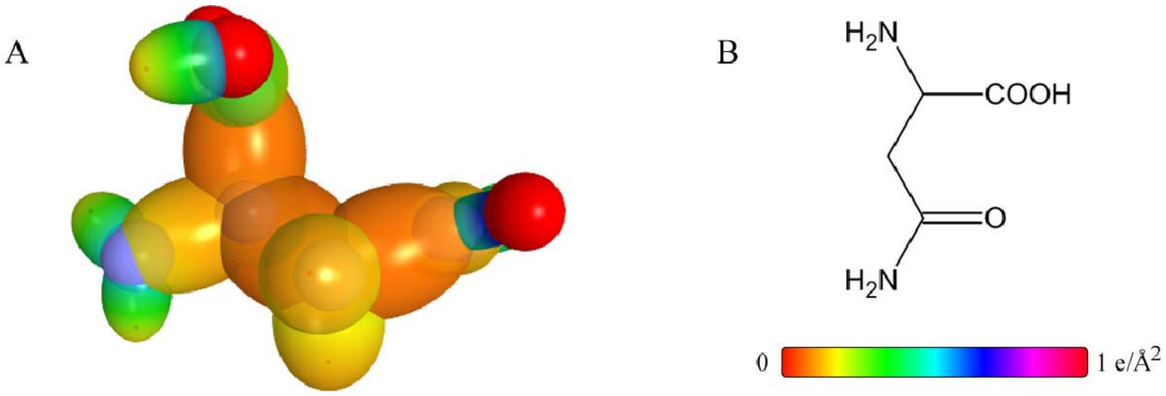
## HISTIDINE

Figure 15.75. (A) Color scale, charge-density of histidine showing the orbitals of the atoms at their radii, the ellipsoidal surface of each $H$ or $H_2$-type ellipsoidal MO that transitions to the corresponding outer shell of the atom(s) participating in each bond, and the hydrogen nuclei. (B) Chemical structure of histidine.



## ASPARAGINE

Figure 15.76. (A) Color scale, charge-density of asparagine showing the orbitals of the atoms at their radii, the ellipsoidal surface of each $H$ or $H_2$-type ellipsoidal MO that transitions to the corresponding outer shell of the atom(s) participating in each bond, and the hydrogen nuclei. (B) Chemical structure of asparagine.



## GLUTAMINE

Figure 15.77. (A) Color scale, charge-density of glutamine showing the orbitals of the atoms at their radii, the ellipsoidal surface of each $H$ or $H_2$-type ellipsoidal MO that transitions to the corresponding outer shell of the atom(s) participating in each bond, and the hydrogen nuclei. (B) Chemical structure of Glutamine.

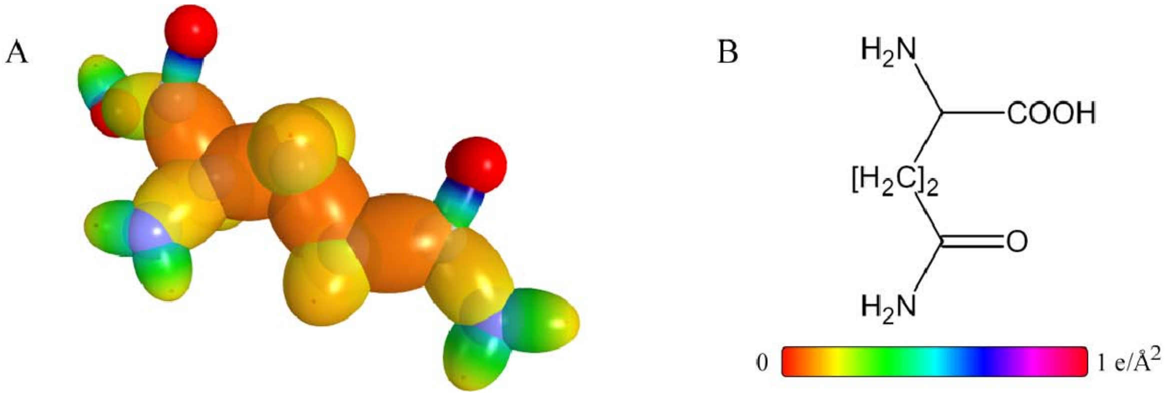


Table 15.393. The total bond energy of arginine ($C_6H_{14}N_2O_2$) calculated using the functional group composition and the energies given *supra*. compared to the experimental values [3].

| Formula | $CH_2$ Group | $CH$ Group | $C-C$ (n-C) Group | $C-C$ (iso-C) Group | $C-C(O)$ (alkyl carboxylic acid) Group | $C=O$ (alkyl carboxylic acid) Group | $C-O$ ((O)C-O) Group | $OH$ Group | $NH_2$ Group | $C-N$ (1° amine) | $N=C$ ($N_b=C_c$ imidazole) Group | $NH$ (heterocyclic imidazole) Group | $C-N$ (N alkyl amide) Group | $C-N$ ((O)C-N alkyl amide) Group | $NH_2$ (amide) Group | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Energies $E_D(_{Group})$ of Functional Groups (eV) | 7.83016 | 3.32601 | 4.32754 | 4.29921 | 4.43110 | 7.80660 | 4.41925 | 4.41035 | 7.41010 | 3.98101 | 6.79303 | 3.51208 | 3.40044 | 4.12212 | 7.37901 | | | |
| Composition | 3 | 1 | 2 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 2 | 1 | 2 | 1 | 105.07007 | 107.420[a] | 0.02188 |

Table 15.394. The total bond energy of histidine ($C_6H_9N_3O_2$) calculated using the functional group composition and the energies given *supra*. compared to the experimental values [3].

| Formula | $CH_2$ Group | $CH$ Group | $C-C$ (iso-C) Group | $C-C(O)$ (alkyl carboxylic acid) Group | $C=O$ (alkyl carboxylic acid) Group | $C-O$ ((O)C-O) Group | $OH$ Group | $NH_2$ Group | $C-N$ (1° amine) | $C-C$ (-C(C)=C) Group | $CH$ (imidazole) Group | $C=C$ ($C_a=C_b$ imidazole) Group | $N=C$ ($N_b=C_c$ imidazole) Group | $C-N$ ($C_b-N_b$ imidazole) Group | $NH$ (heterocyclic imidazole) Group | $C-N-C$ ($C_a-N_a-C_c$ imidazole) Group | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Energies $E_D(_{Group})$ of Functional Groups (eV) | 7.83016 | 3.32601 | 4.29921 | 4.43110 | 7.80660 | 4.41925 | 4.41035 | 7.41010 | 3.98101 | 3.75498 | 3.32988 | 7.23317 | 6.79303 | 3.47253 | 3.51208 | 8.76298 | | | |
| Composition | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 2 | 1 | 1 | 1 | 1 | 1 | 88.10232 | 89.599[a] | 0.01671 |

Table 15.395. The total bond energy of asparagine ($C_4H_8N_2O_2$) calculated using the functional group composition and the energies given *supra*. compared to the experimental values [3].

| Formula | $CH_2$ Group | $CH$ Group | $C-C$ (iso-C) Group | $C-C(O)$ (alkyl carboxylic acid) Group | $C=O$ (alkyl carboxylic acid) Group | $C-O$ ((O)C-O) Group | $OH$ Group | $NH_2$ Group | $C-N$ (1° amine) | $C-C(O)$ (alkyl amide) Group | $C-N$ ((O)C-N alkyl amide) Group | $NH_2$ (amide) Group | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Energies $E_D(_{Group})$ of Functional Groups (eV) | 7.83016 | 3.32601 | 4.29921 | 4.43110 | 7.80660 | 4.41925 | 4.41035 | 7.41010 | 3.98101 | 4.35263 | 4.12212 | 7.37901 | | | |
| Composition | 1 | 1 | 1 | 1 | 2 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 71.57414 | 73.513[a] | 0.02637 |

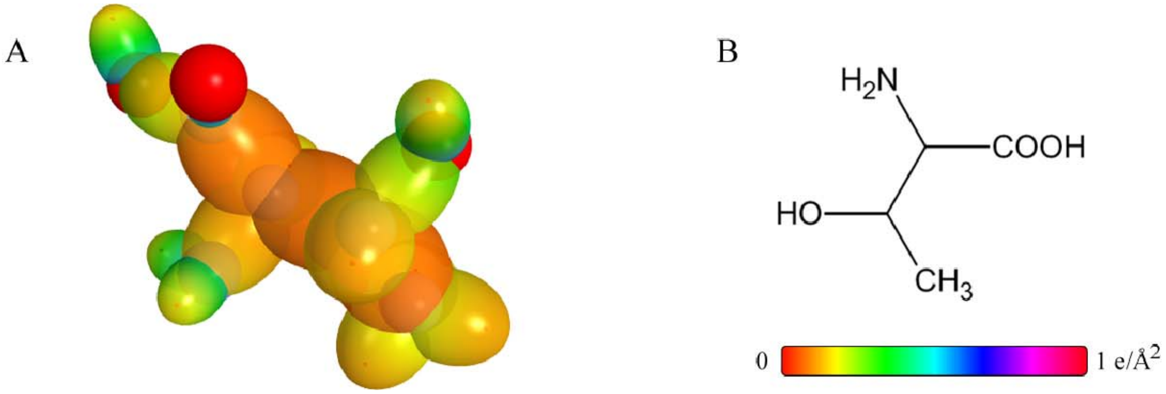
Table 15.396. The total bond energy of glutamine ($C_5H_{10}N_2O_2$) calculated using the functional group composition and the energies given *supra*. compared to the experimental values [3].

| Formula | $CH_2$ Group | $CH$ Group | $C-C$ (n-C) Group | $C-C$ (iso-C) Group | $C-C(O)$ (alkyl carboxylic acid) Group | $C=O$ (alkyl carboxylic acid) Group | $C-O$ ((O)C-O) Group | $OH$ Group | $NH_2$ Group | $C-N$ (1° amine) | $C-C(O)$ (alkyl amide) Group | $C-N$ ((O)C-N alkyl amide) Group | $NH_2$ (amide) Group | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Energies $E_D(_{Group})$ of Functional Groups (eV) | 7.83016 | 3.32601 | 4.32754 | 4.29921 | 4.43110 | 7.80660 | 4.41925 | 4.41035 | 7.41010 | 3.98101 | 4.35263 | 4.12212 | 7.37901 | | | |
| Composition | 2 | 1 | 1 | 1 | 1 | 2 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 83.73184 | 85.843[a] | 0.02459 |

[a] Crystal

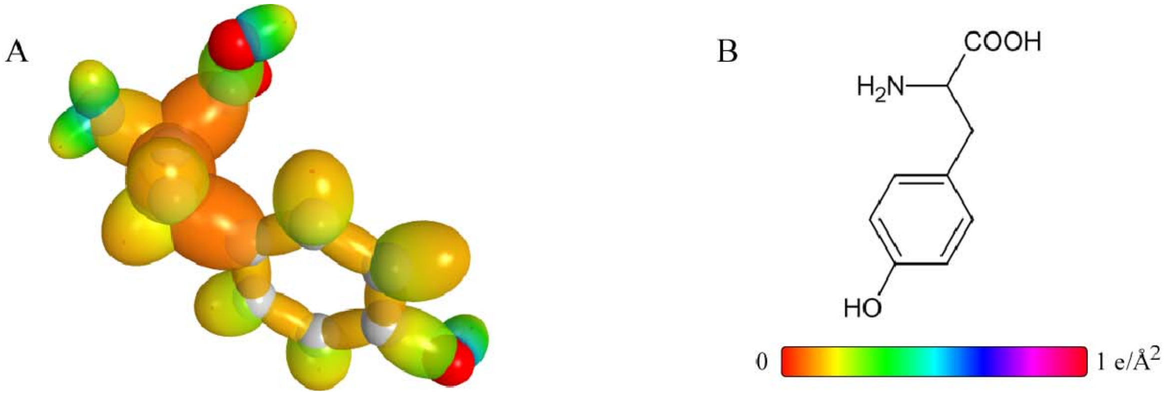
## THREONINE

Figure 15.78. (A) Color scale, charge-density of threonine showing the orbitals of the atoms at their radii, the ellipsoidal surface of each $H$ or $H_2$-type ellipsoidal MO that transitions to the corresponding outer shell of the atom(s) participating in each bond, and the hydrogen nuclei. (B) Chemical structure of threonine.



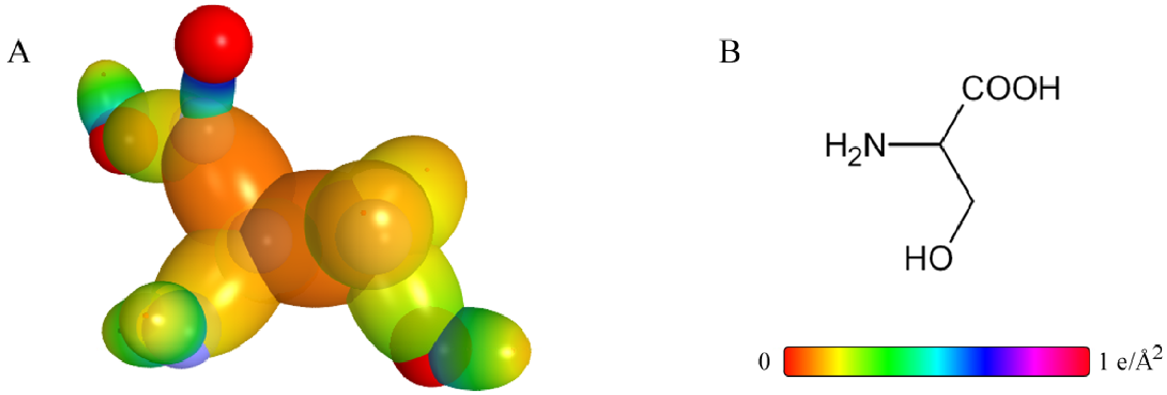
## TYROSINE

Figure 15.79. (A) Color scale, charge-density of tyrosine showing the orbitals of the atoms at their radii, the ellipsoidal surface of each $H$ or $H_2$-type ellipsoidal MO that transitions to the corresponding outer shell of the atom(s) participating in each bond, and the hydrogen nuclei. (B) Chemical structure of tyrosine.



## SERINE

Figure 15.80. (A) Color scale, charge-density of serine showing the orbitals of the atoms at their radii, the ellipsoidal surface of each $H$ or $H_2$-type ellipsoidal MO that transitions to the corresponding outer shell of the atom(s) participating in each bond, and the hydrogen nuclei. (B) Chemical structure of serine.



## TRYPTOPHAN

Figure 15.81. (A) Color scale, charge-density of tryptophan showing the orbitals of the atoms at their radii, the ellipsoidal surface of each $H$ or $H_2$-type ellipsoidal MO that transitions to the corresponding outer shell of the atom(s) participating in each bond, and the hydrogen nuclei. (B) Chemical structure of tryptophan.

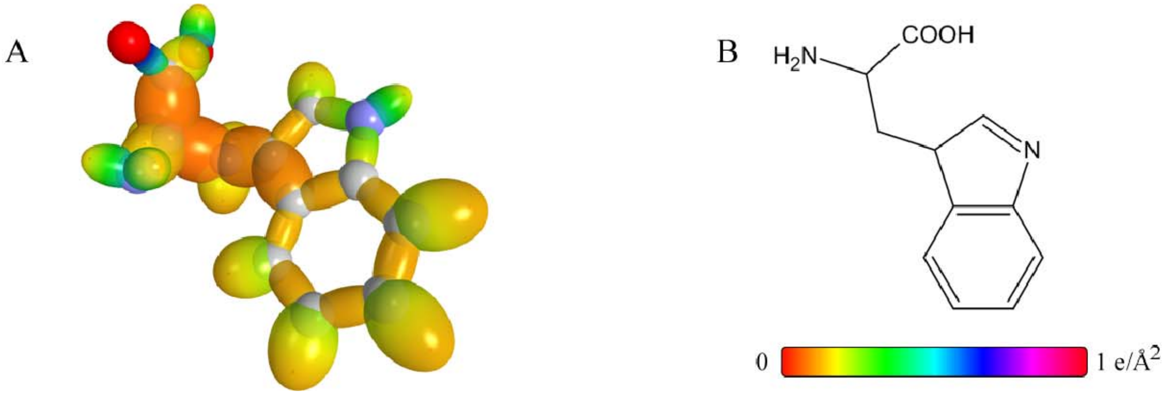


Table 15.397. The total bond energy of threonine ($C_4H_9NO_3$) calculated using the functional group composition and the energies given *supra*. compared to the experimental values [3].

| Formula | $CH_3$ Group | $CH$ Group | $C-C$ (iso-C) Group | $C-C(O)$ (alkyl carboxylic acid) Group | $C=O$ (alkyl carboxylic acid) Group | $C-O$ ((O)C-O) Group | $OH$ Group | $NH_2$ Group | $C-N$ (1° amine) | $C-O$ (alkyl alcohol) Group | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Energies $E_D(_{Group})$ of Functional Groups (eV) | 12.49186 | 3.32601 | 4.29921 | 4.43110 | 7.80660 | 4.41925 | 4.41035 | 7.41010 | 3.98101 | 4.34572 | | | |
| Composition | 1 | 2 | 2 | 1 | 1 | 1 | 2 | 1 | 1 | 1 | 68.95678 | 71.058[a] | 0.02956 |

Table 15.398. The total bond energy of tyrosine ($C_9H_{11}NO_3$) calculated using the functional group composition and the energies given *supra*. compared to the experimental values [3].

| Formula | $CH_2$ Group | $CH$ Group | $C-C$ (iso-C) Group | $C-C(O)$ (alkyl carboxylic acid) Group | $C=O$ (alkyl carboxylic acid) Group | $C-O$ ((O)C-O) Group | $OH$ Group | $NH_2$ Group | $C-N$ (1° amine) | $C\overset{3e}{=}C$ ($CC$ aromatic bond) Group | $CH$ ($CH$ aromatic) Group | $C-C$ (C alkyl to aryl toluene) Group | $C-O$ (Aryl $C$-O phenol) Group | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Energies $E_D(_{Group})$ of Functional Groups (eV) | 7.83016 | 3.32601 | 4.29921 | 4.43110 | 7.80660 | 4.41925 | 4.41035 | 7.41010 | 3.98101 | 5.63881 | 3.90454 | 3.63685 | 3.99228 | | | |
| Composition | 1 | 1 | 1 | 1 | 1 | 1 | 2 | 1 | 1 | 6 | 4 | 1 | 1 | 109.40427 | 111.450[a] | 0.01835 |

Table 15.399. The total bond energy of serine ($C_3H_7NO_3$) calculated using the functional group composition and the energies given *supra*. compared to the experimental values [3].

| Formula | $CH_2$ Group | $CH$ Group | $C-C$ (iso-C) Group | $C-C(O)$ (alkyl carboxylic acid) Group | $C=O$ (alkyl carboxylic acid) Group | $C-O$ ((O)C-O) Group | $OH$ Group | $NH_2$ Group | $C-N$ (1° amine) | $C-O$ (alkyl alcohol) Group | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Energies $E_D(_{Group})$ of Functional Groups (eV) | 7.83016 | 3.32601 | 4.29921 | 4.43110 | 7.80660 | 4.41925 | 4.41035 | 7.41010 | 3.98101 | 4.34572 | | | |
| Composition | 1 | 1 | 1 | 1 | 1 | 1 | 2 | 1 | 1 | 1 | 56.66986 | 58.339[a] | 0.02861 |

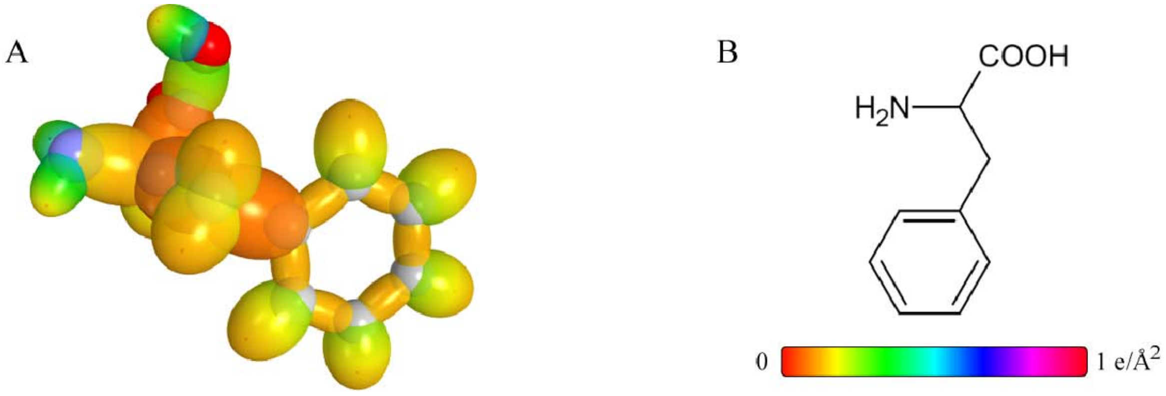
Table 15.400. The total bond energy of tryptophan ($C_{11}H_{12}N_2O_2$) calculated using the functional group composition and the energies given *supra*. compared to the experimental values [3].

| Formula | $CH_2$ Group | $CH$ Group | $C-C$ (iso-C) Group | $C-C(O)$ (alkyl carboxylic acid) Group | $C=O$ (alkyl carboxylic acid) Group | $C-O$ ((O)C-O) Group | $OH$ Group | $NH_2$ Group | $C-N$ (1° amine) | $C\overset{3e}{=}C$ ($CC$ aromatic bond) Group | $CH$ ($CH$ aromatic) Group | $C-C$ ($C_b-C_d$ indole) Group | $C=C$ ($C_d=C_e$ indole) Group | $CH$ ($CH$ indole) Group | $C-N-C$ (indole) Group | $NH$ (indole) Group | $C-C$ (C alkyl to aryl toluene) Group | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Energies $E_D(_{Group})$ of Functional Groups (eV) | 7.83016 | 3.32601 | 4.29921 | 4.43110 | 7.80660 | 4.41925 | 4.41035 | 7.41010 | 3.98101 | 5.63881 | 3.90454 | 3.47253 | 6.79303 | | | 3.63685 | 3.63685 | | | |
| Composition | 1 | 1 | 2 | 1 | 1 | 1 | 2 | 1 | 1 | 6 | 4 | 1 | 1 | 1 | 1 | 1 | 1 | 126.74291 | 128.084[a] | 0.01047 |

[a] Crystal

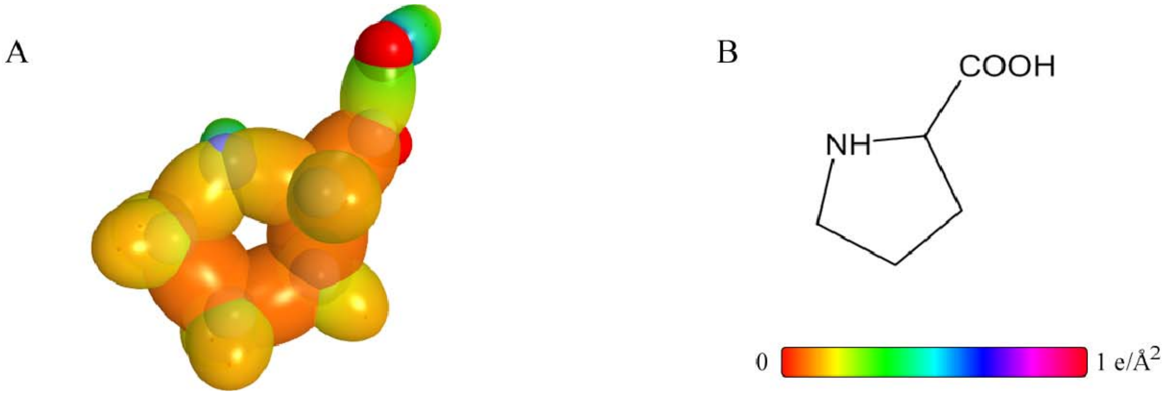
## PHENYLALANINE

Figure 15.82. (A) Color scale, charge-density of phenylalanine showing the orbitals of the atoms at their radii, the ellipsoidal surface of each $H$ or $H_2$-type ellipsoidal MO that transitions to the corresponding outer shell of the atom(s) participating in each bond, and the hydrogen nuclei. (B) Chemical structure of phenylalanine.



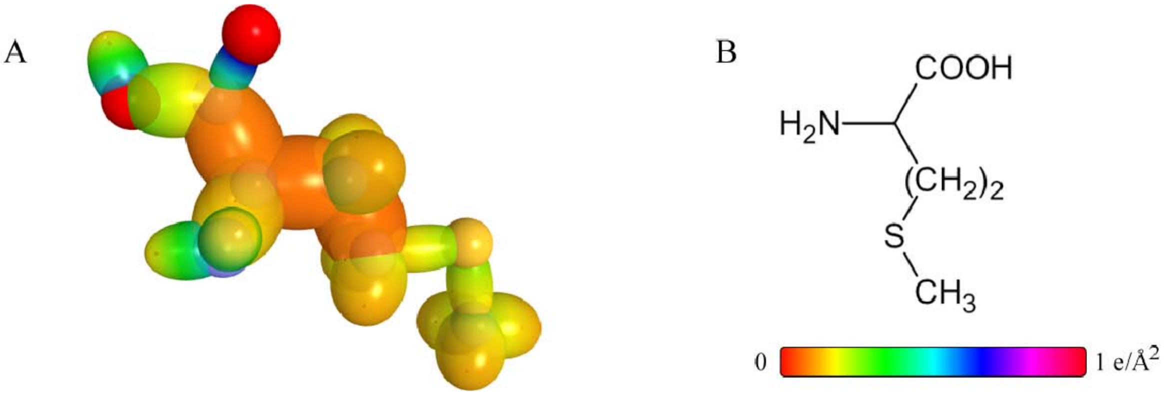
## PROLINE

Figure 15.83. (A) Color scale, charge-density of proline showing the orbitals of the atoms at their radii, the ellipsoidal surface of each $H$ or $H_2$-type ellipsoidal MO that transitions to the corresponding outer shell of the atom(s) participating in each bond, and the hydrogen nuclei. (B) Chemical structure of proline.



## METHIONINE

Figure 15.84. (A) Color scale, charge-density of methionine showing the orbitals of the atoms at their radii, the ellipsoidal surface of each $H$ or $H_2$-type ellipsoidal MO that transitions to the corresponding outer shell of the atom(s) participating in each bond, and the hydrogen nuclei. (B) Chemical structure of methionine.



## LEUCINE

Figure 15.85. (A) Color scale, charge-density of leucine showing the orbitals of the atoms at their radii, the ellipsoidal surface of each $H$ or $H_2$-type ellipsoidal MO that transitions to the corresponding outer shell of the atom(s) participating in each bond, and the hydrogen nuclei. (B) Chemical structure of leucine.

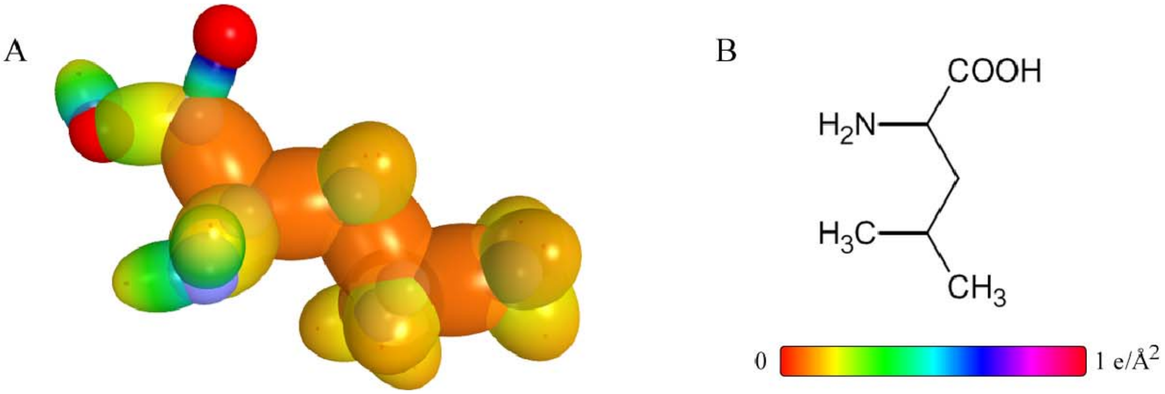


Table 15.401. The total bond energy of phenylalanine ($C_9H_{11}NO_2$) calculated using the functional group composition and the energies given *supra*. compared to the experimental values [3].

| Formula | $CH_2$ Group | $CH$ Group | $C-C$ (iso-C) Group | $C-C(O)$ (alkyl carboxylic acid) Group | $C=O$ (alkyl carboxylic acid) Group | $C-O$ ((O)C-O) Group | $OH$ Group | $NH_2$ Group | $C-N$ (1° amine) | $\overset{3e}{C=C}$ ($CC$ aromatic bond) Group | $CH$ ($CH$ aromatic) Group | $C-C$ (C alkyl to aryl toluene) Group | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Energies $E_D(_{Group})$ of Functional Groups (eV) | 7.83016 | 3.32601 | 4.29921 | 4.43110 | 7.80660 | 4.41925 | 4.41035 | 7.41010 | 3.98101 | 5.63881 | 3.90454 | 3.63685 | | | |
| Composition | 1 | 1 | 1 | 1 | 1 | 1 | 2 | 1 | 1 | 6 | 5 | 1 | 104.90618 | 105.009 | 0.00098 |

Table 15.402. The total bond energy of proline ($C_5H_9NO_2$) calculated using the functional group composition and the energies given *supra*. compared to the experimental values [3].

| Formula | $CH_2$ Group | $CH$ Group | $C-C$ (n-C) Group | $C-C$ (iso-C) Group | $C-C(O)$ (alkyl carboxylic acid) Group | $C=O$ (alkyl carboxylic acid) Group | $C-O$ ((O)C-O) Group | $OH$ Group | $NH$ (2° amine) | $C-N$ (2° amine) | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Energies $E_D(_{Group})$ of Functional Groups (eV) | 7.83016 | 3.32601 | 4.32754 | 4.29921 | 4.43110 | 7.80660 | 4.41925 | 4.41035 | 3.50582 | 3.71218 | | | |
| Composition | 3 | 1 | 2 | 1 | 1 | 1 | 1 | 1 | 1 | 2 | 71.76826 | 71.332 | -0.00611 |

Table 15.403. The total bond energy of methionine ($C_5H_{11}NO_2S$) calculated using the functional group composition and the energies given *supra*. compared to the experimental values [3].

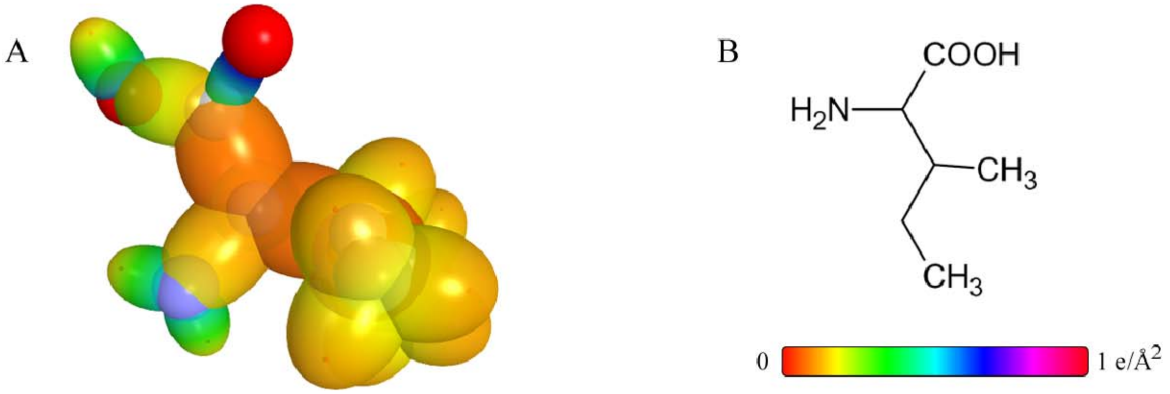
| Formula | $CH_3$ Group | $CH_2$ Group | $CH$ Group | $C-C$ (n-C) Group | $C-C$ (iso-C) Group | $C-C(O)$ (alkyl carboxylic acid) Group | $C=O$ (alkyl carboxylic acid) Group | $C-O$ ((O)C-O) Group | $OH$ Group | $NH_2$ Group | $C-N$ (1° amine) | $C-S$ (alkyl sulfide) | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Energies $E_D(_{Group})$ of Functional Groups (eV) | 12.49186 | 7.83016 | 3.32601 | 4.32754 | 4.29921 | 4.43110 | 7.80660 | 4.41925 | 4.41035 | 7.41010 | 3.98101 | 3.33648 | | | |
| Composition | 1 | 2 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 2 | 79.23631 | 79.214 | -0.00028 |

Table 15.404. The total bond energy of leucine ($C_6H_{13}NO_2$) calculated using the functional group composition and the energies given *supra*. compared to the experimental values [3].

| Formula | $CH_3$ Group | $CH_2$ Group | $CH$ Group | $C-C$ (iso-C) Group | $C-C(O)$ (alkyl carboxylic acid) Group | $C=O$ (alkyl carboxylic acid) Group | $C-O$ ((O)C-O) Group | $OH$ Group | $NH_2$ Group | $C-N$ (1° amine) | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Energies $E_D(_{Group})$ of Functional Groups (eV) | 12.49186 | 7.83016 | 3.32601 | 4.29921 | 4.43110 | 7.80660 | 4.41925 | 4.41035 | 7.41010 | 3.98101 | | | |
| Composition | 2 | 1 | 2 | 4 | 1 | 1 | 1 | 1 | 1 | 1 | 89.12115 | 89.047 | -0.00083 |

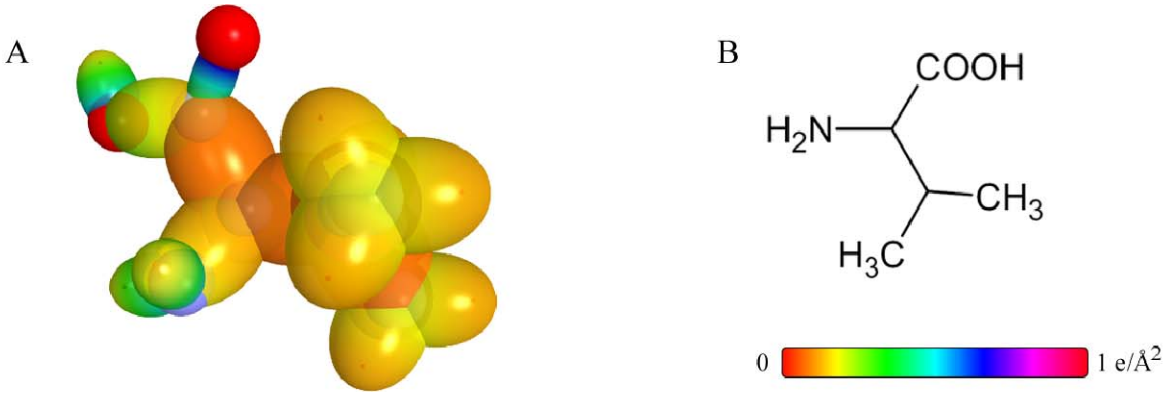
## ISOLEUCINE

Figure 15.86. (A) Color scale, charge-density of isoleucine showing the orbitals of the atoms at their radii, the ellipsoidal surface of each $H$ or $H_2$-type ellipsoidal MO that transitions to the corresponding outer shell of the atom(s) participating in each bond, and the hydrogen nuclei. (B) Chemical structure of isoleucine.



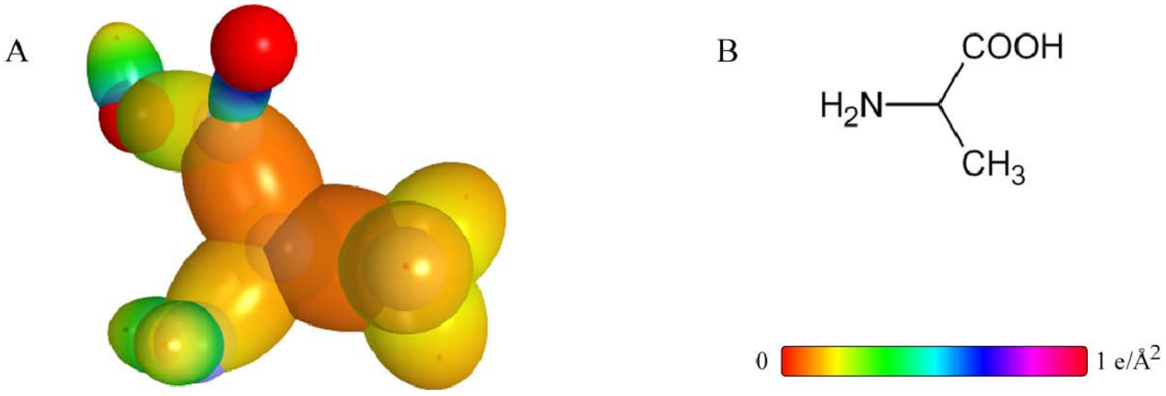
## VALINE

Figure 15.87. (A) Color scale, charge-density of valine showing the orbitals of the atoms at their radii, the ellipsoidal surface of each $H$ or $H_2$-type ellipsoidal MO that transitions to the corresponding outer shell of the atom(s) participating in each bond, and the hydrogen nuclei. (B) Chemical structure of valine.



## ALANINE

Figure 15.88. (A) Color scale, charge-density of alanine showing the orbitals of the atoms at their radii, the ellipsoidal surface of each $H$ or $H_2$-type ellipsoidal MO that transitions to the corresponding outer shell of the atom(s) participating in each bond, and the hydrogen nuclei. (B) Chemical structure of alanine.



## GLYCINE

Figure 15.89. (A) Color scale, charge-density of glycine showing the orbitals of the atoms at their radii, the ellipsoidal surface of each $H$ or $H_2$-type ellipsoidal MO that transitions to the corresponding outer shell of the atom(s) participating in each bond, and the hydrogen nuclei. (B) Chemical structure of glycine.

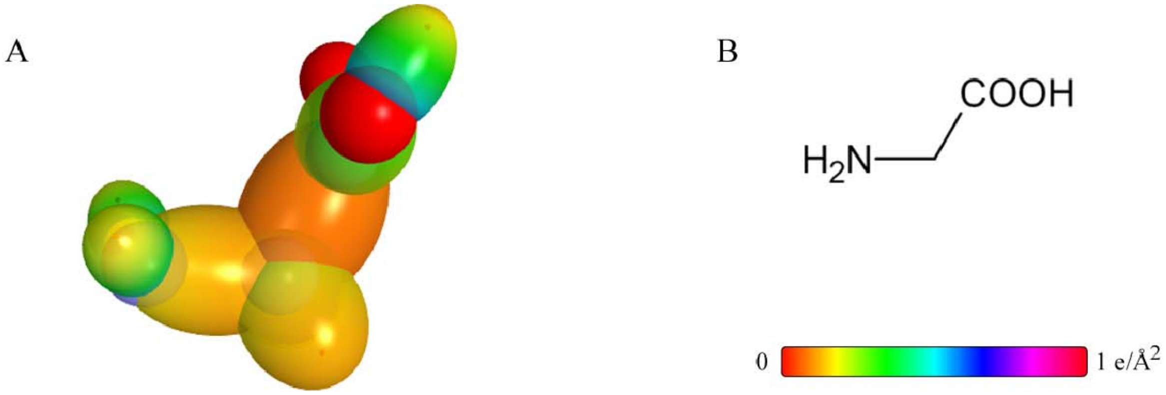


**Table 15.405.** The total bond energy of isoleucine ($C_6H_{13}NO_2$) calculated using the functional group composition and the energies given *supra*. compared to the experimental values [3].

| Formula | $CH_3$ Group | $CH_2$ Group | $CH$ Group | $C-C$ (n-C) Group | $C-C$ (iso-C) Group | $C-C(O)$ (alkyl carboxylic acid) Group | $C-C$ (iso to iso-C) Group | $C=O$ (alkyl carboxylic acid) Group | $C-O$ ((O)C-O) Group | $OH$ Group | $NH_2$ Group | $C-N$ (1° amine) | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Energies $E_D(_{Group})$ of Functional Groups (eV) | 12.49186 | 7.83016 | 3.32601 | 4.32754 | 4.29921 | 4.43110 | 4.17951 | 7.80660 | 4.41925 | 4.41035 | 7.41010 | 3.98101 | | | |
| Composition | 2 | 1 | 2 | 1 | 2 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 89.02978 | 90.612 | 0.01746 |

**Table 15.406.** The total bond energy of valine ($C_5H_{11}NO_2$) calculated using the functional group composition and the energies given *supra*. compared to the experimental values [3].

| Formula | $CH_3$ Group | $CH$ Group | $C-C$ (iso-C) Group | $C-C$ (iso to iso-C) Group | $C-C(O)$ (alkyl carboxylic acid) Group | $C=O$ (alkyl carboxylic acid) Group | $C-O$ ((O)C-O) Group | $OH$ Group | $NH_2$ Group | $C-N$ (1° amine) | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Energies $E_D(_{Group})$ of Functional Groups (eV) | 12.49186 | 3.32601 | 4.29921 | 4.17951 | 4.43110 | 7.80660 | 4.41925 | 4.41035 | 7.41010 | 3.98101 | | | |
| Composition | 2 | 2 | 2 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 76.87208 | 76.772 | -0.00130 |

**Table 15.407.** The total bond energy of alanine ($C_3H_7NO_2$) calculated using the functional group composition and the energies given *supra*. compared to the experimental values [3].

| Formula | $CH_3$ Group | $CH$ Group | $C-C$ (iso-C) Group | $C-C(O)$ (alkyl carboxylic acid) Group | $C=O$ (alkyl carboxylic acid) Group | $C-O$ ((O)C-O) Group | $OH$ Group | $NH_2$ Group | $C-N$ (1° amine) | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Energies $E_D(_{Group})$ of Functional Groups (eV) | 12.49186 | 3.32601 | 4.29921 | 4.43110 | 7.80660 | 4.41925 | 4.41035 | 7.41010 | 3.98101 | | | |
| Composition | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 52.57549 | 52.991 | 0.00785 |

**Table 15.408.** The total bond energy of glycine ($C_2H_5NO_2$) calculated using the functional group composition and the energies given *supra*. compared to the experimental values [3].

| Formula | $CH_2$ Group | $C-C(O)$ (alkyl carboxylic acid) Group | $C=O$ (alkyl carboxylic acid) Group | $C-O$ ((O)C-O) Group | $OH$ Group | $NH_2$ Group | $C-N$ (1° amine) | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|---|---|---|---|---|---|
| Energies $E_D(_{Group})$ of Functional Groups (eV) | 7.83016 | 4.43110 | 7.80660 | 4.41925 | 4.41035 | 7.41010 | 3.98101 | | | |
| Composition | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 40.28857 | 40.280 | -0.00021 |

## POLYPEPTIDES ($-\left[HN-CH(R)-C(O)\right]_n-$)

The amino acids can be polymerized by reaction of the $OH$ group from the carboxylic acid moiety of one amino acid with $H$ from the alpha-carbon $NH_2$ of another amino acid to form $H_2O$ and an amide bond as part of a polyamide chain of a polypeptide or protein. Each amide bond that forms by the condensation of two amino acids is called a peptide bond. It comprises a $C=O$ functional group, and the single bond of carbon to the carbonyl carbon atom, $C-C(O)$, is also a functional group. The peptide bond further comprises a $C-NH\left(R\right)$ moiety that comprises $NH$ and $C-N$ functional groups where $R$ is the characteristic side chain of each amino acid that is unchanged in terms of its functional group composition upon the formation of the peptide bond. From the N-Alkyl and N,N-Dialkyl-Amides section, the functional group composition and the corresponding energy $E_D\left(_{Group}\right)$ of each group of the peptide bond is given in Table 15.409. The color scale, charge-density of the exemplary polypeptide, phenylalanine-leucine-glutamine-asparic acid (phe-leu-gln-asp) comprising the atoms with the outer shell bridged by one or more $H_2$-type ellipsoidal MOs or joined with one or more hydrogen MOs is shown in Figure 15.90. The color scale, opaque view of the charge-density of the exemplary protein bovine pancreatic trypsin inhibitor (BPTI) is shown in Figure 15.91.

Figure 15.90. Color scale, charge-density of the polypeptide phenylalanine-leucine-glutamine-aspartic acid (phe-leu-gln-asp) showing the orbitals of the atoms at their radii and the ellipsoidal surface of each $H$ or $H_2$-type ellipsoidal MO that transitions to the corresponding outer shell of the atom(s) participating in each bond.

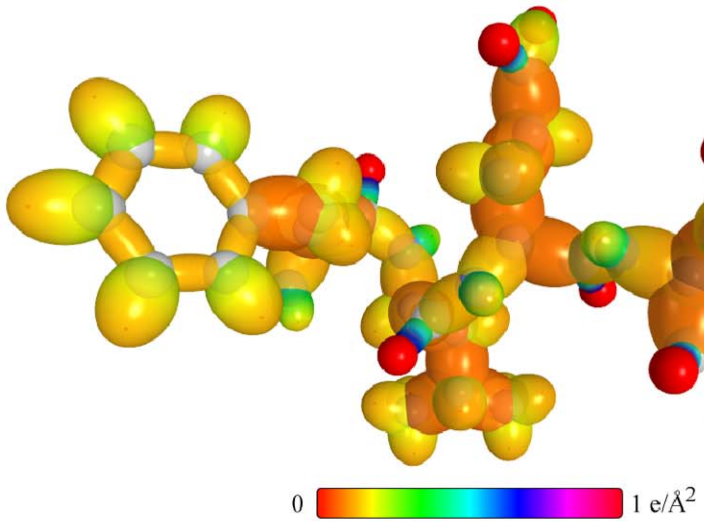


Figure 15.91. Color scale, opaque view of the charge-density of bovine pancreatic trypsin inhibitor (BPTI) protein created and modeled using Millsian 2.0. BPTI has been used as a medication administered by injection to reduce bleeding during complex surgery, such as heart and liver surgery. Its main effect is the inhibition of fibrinolysis, the process that leads to the breakdown of blood clots. The aim in its use is to decrease the need for blood transfusions during surgery, as well as end-organ damage due to hypotension (low blood pressure) as a result of marked blood loss. However, this drug was temporarily withdrawn worldwide in 2007 after studies suggested that its use increased the risk of complications or death. This protein is usually used as the benchmark for bimolecular modeling method and with accurate knowledge of its structure, it is possible to engineer it to avoid its prior side effects.

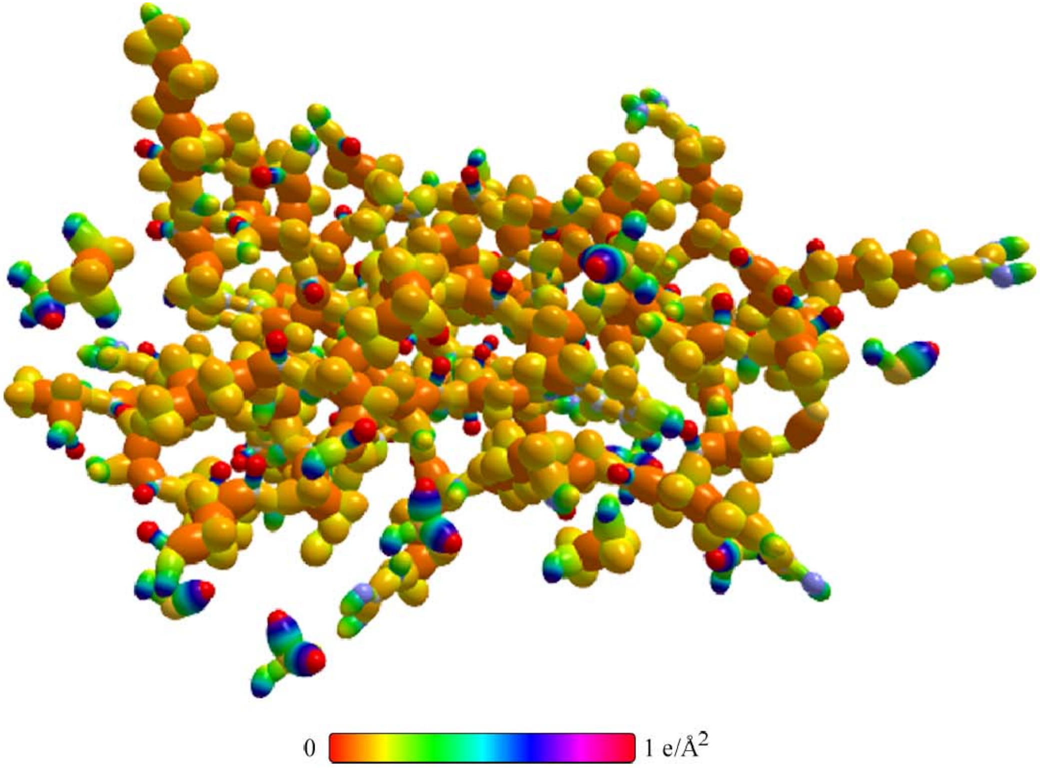


Table 15.409. The functional group composition and the energy $E_D\,(Group)$ of each group of the peptide bond.

| Formula | $C-C(O)$ (alkyl amide) Group | $C-N$ ((O)C-N alkyl amide) Group | $C-N$ (N alkyl amide) Group | $NH$ (N alkyl amide) Group |
|---|---|---|---|---|
| Energies $E_D\,(Group)$ of Functional Groups (eV) | 4.35263 | 4.12212 | 3.40044 | 3.49788 |
| Composition | 1 | 1 | 1 | 1 |

# SUMMARY TABLES OF ORGANIC MOLECULES

The bond energies, calculated using closed-form equations having integers and fundamental constants only for classes of molecules whose designation is based on the main functional group, are given in the following tables with the experimental values.

Table 15.410.1. Summary results of n-alkanes.

| Formula | Name | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|
| $C_3H_8$ | propane | 41.46896 | 41.434 | -0.00085 |
| $C_4H_{10}$ | butane | 53.62666 | 53.61 | -0.00036 |
| $C_5H_{12}$ | pentane | 65.78436 | 65.77 | -0.00017 |
| $C_6H_{14}$ | hexane | 77.94206 | 77.93 | -0.00019 |
| $C_7H_{16}$ | heptane | 90.09976 | 90.09 | -0.00013 |
| $C_8H_{18}$ | octane | 102.25746 | 102.25 | -0.00006 |
| $C_9H_{20}$ | nonane | 114.41516 | 114.40 | -0.00012 |
| $C_{10}H_{22}$ | decane | 126.57286 | 126.57 | -0.00003 |
| $C_{11}H_{24}$ | undecane | 138.73056 | 138.736 | 0.00004 |
| $C_{12}H_{26}$ | dodecane | 150.88826 | 150.88 | -0.00008 |
| $C_{18}H_{38}$ | octadecane | 223.83446 | 223.85 | 0.00008 |

Table 15.410.2. Summary results of branched alkanes.

| Formula | Name | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|
| $C_4H_{10}$ | isobutane | 53.69922 | 53.695 | -0.00007 |
| $C_5H_{12}$ | isopentane | 65.85692 | 65.843 | -0.00021 |
| $C_5H_{12}$ | neopentane | 65.86336 | 65.992 | 0.00195 |
| $C_6H_{14}$ | 2-methylpentane | 78.01462 | 78.007 | -0.00010 |
| $C_6H_{14}$ | 3-methylpentane | 78.01462 | 77.979 | -0.00046 |
| $C_6H_{14}$ | 2,2-dimethylbutane | 78.02106 | 78.124 | 0.00132 |
| $C_6H_{14}$ | 2,3-dimethylbutane | 77.99581 | 78.043 | 0.00061 |
| $C_7H_{16}$ | 2-methylhexane | 90.17232 | 90.160 | -0.00014 |
| $C_7H_{16}$ | 3-methylhexane | 90.17232 | 90.127 | -0.00051 |
| $C_7H_{16}$ | 3-ethylpentane | 90.17232 | 90.108 | -0.00072 |
| $C_7H_{16}$ | 2,2-dimethylpentane | 90.17876 | 90.276 | 0.00107 |
| $C_7H_{16}$ | 2,2,3-trimethylbutane | 90.22301 | 90.262 | 0.00044 |
| $C_7H_{16}$ | 2,4-dimethylpentane | 90.24488 | 90.233 | -0.00013 |
| $C_7H_{16}$ | 3,3-dimethylpentane | 90.17876 | 90.227 | 0.00054 |
| $C_8H_{18}$ | 2-methylheptane | 102.33002 | 102.322 | -0.00008 |
| $C_8H_{18}$ | 3-methylheptane | 102.33002 | 102.293 | -0.00036 |
| $C_8H_{18}$ | 4-methylheptane | 102.33002 | 102.286 | -0.00043 |
| $C_8H_{18}$ | 3-ethylhexane | 102.33002 | 102.274 | -0.00055 |
| $C_8H_{18}$ | 2,2-dimethylhexane | 102.33646 | 102.417 | 0.00079 |
| $C_8H_{18}$ | 2,3-dimethylhexane | 102.31121 | 102.306 | -0.00005 |
| $C_8H_{18}$ | 2,4-dimethylhexane | 102.40258 | 102.362 | -0.00040 |
| $C_8H_{18}$ | 2,5-dimethylhexane | 102.40258 | 102.396 | -0.00006 |
| $C_8H_{18}$ | 3,3-dimethylhexane | 102.33646 | 102.369 | 0.00032 |
| $C_8H_{18}$ | 3,4-dimethylhexane | 102.31121 | 102.296 | -0.00015 |
| $C_8H_{18}$ | 3-ethyl-2-methylpentane | 102.31121 | 102.277 | -0.00033 |
| $C_8H_{18}$ | 3-ethyl-3-methylpentane | 102.33646 | 102.317 | -0.00019 |
| $C_8H_{18}$ | 2,2,3-trimethylpentane | 102.38071 | 102.370 | -0.00010 |
| $C_8H_{18}$ | 2,2,4-trimethylpentane | 102.40902 | 102.412 | 0.00003 |
| $C_8H_{18}$ | 2,3,3-trimethylpentane | 102.38071 | 102.332 | -0.00048 |
| $C_8H_{18}$ | 2,3,4-trimethylpentane | 102.29240 | 102.342 | 0.00049 |
| $C_8H_{18}$ | 2,2,3,3-tetramethylbutane | 102.41632 | 102.433 | 0.00016 |
| $C_9H_{20}$ | 2,3,5-trimethylhexane | 114.54147 | 114.551 | 0.00008 |
| $C_9H_{20}$ | 3,3-diethylpentane | 114.49416 | 114.455 | -0.00034 |
| $C_9H_{20}$ | 2,2,3,3-tetramethylpentane | 114.57402 | 114.494 | -0.00070 |
| $C_9H_{20}$ | 2,2,3,4-tetramethylpentane | 114.51960 | 114.492 | -0.00024 |
| $C_9H_{20}$ | 2,2,4,4-tetramethylpentane | 114.57316 | 114.541 | -0.00028 |

| Formula | Name | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|
| $C_9H_{20}$ | 2,3,3,4-tetramethylpentane | 114.58266 | 114.484 | -0.00086 |
| $C_{10}H_{22}$ | 2-methylnonane | 126.64542 | 126.680 | 0.00027 |
| $C_{10}H_{22}$ | 5-methylnonane | 126.64542 | 126.663 | 0.00014 |

Table 15.410.3. Summary results of alkenes.

| Formula | Name | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|
| $C_3H_6$ | propene | 35.56033 | 35.63207 | 0.00201 |
| $C_4H_8$ | 1-butene | 47.71803 | 47.78477 | 0.00140 |
| $C_4H_8$ | trans-2-butene | 47.93116 | 47.90395 | -0.00057 |
| $C_4H_8$ | isobutene | 47.90314 | 47.96096 | 0.00121 |
| $C_5H_{10}$ | 1-pentene | 59.87573 | 59.95094 | 0.00125 |
| $C_5H_{10}$ | trans-2-pentene | 60.08886 | 60.06287 | -0.00043 |
| $C_5H_{10}$ | 2-methyl-1-butene | 60.06084 | 60.09707 | 0.00060 |
| $C_5H_{10}$ | 2-methyl-2-butene | 60.21433 | 60.16444 | -0.00083 |
| $C_5H_{10}$ | 3-methyl-1-butene | 59.97662 | 60.01727 | 0.00068 |
| $C_6H_{12}$ | 1-hexene | 72.03343 | 72.12954 | 0.00133 |
| $C_6H_{12}$ | trans-2-hexene | 72.24656 | 72.23733 | -0.00013 |
| $C_6H_{12}$ | trans-3-hexene | 72.24656 | 72.24251 | -0.00006 |
| $C_6H_{12}$ | 2-methyl-1-pentene | 72.21854 | 72.29433 | 0.00105 |
| $C_6H_{12}$ | 2-methyl-2-pentene | 72.37203 | 72.37206 | 0.00000 |
| $C_6H_{12}$ | 3-methyl-1-pentene | 72.13432 | 72.19173 | 0.00080 |
| $C_6H_{12}$ | 4-methyl-1-pentene | 72.10599 | 72.21038 | 0.00145 |
| $C_6H_{12}$ | 3-methyl-trans-2-pentene | 72.37203 | 72.33268 | -0.00054 |
| $C_6H_{12}$ | 4-methyl-trans-2-pentene | 72.34745 | 72.31610 | -0.00043 |
| $C_6H_{12}$ | 2-ethyl-1-butene | 72.21854 | 72.25909 | 0.00056 |
| $C_6H_{12}$ | 2,3-dimethyl-1-butene | 72.31943 | 72.32543 | 0.00008 |
| $C_6H_{12}$ | 3,3-dimethyl-1-butene | 72.31796 | 72.30366 | -0.00020 |
| $C_6H_{12}$ | 2,3-dimethyl-2-butene | 72.49750 | 72.38450 | -0.00156 |
| $C_7H_{14}$ | 1-heptene | 84.19113 | 84.27084 | 0.00095 |
| $C_7H_{14}$ | 5-methyl-1-hexene | 84.26369 | 84.30608 | 0.00050 |
| $C_7H_{14}$ | trans-3-methyl-3-hexene | 84.52973 | 84.42112 | -0.00129 |
| $C_7H_{14}$ | 2,4-dimethyl-1-pentene | 84.44880 | 84.49367 | 0.00053 |
| $C_7H_{14}$ | 4,4-dimethyl-1-pentene | 84.27012 | 84.47087 | 0.00238 |
| $C_7H_{14}$ | 2,4-dimethyl-2-pentene | 84.63062 | 84.54445 | -0.00102 |
| $C_7H_{14}$ | trans-4,4-dimethyl-2-pentene | 84.54076 | 84.54549 | 0.00006 |
| $C_7H_{14}$ | 2-ethyl-3-methyl-1-butene | 84.47713 | 84.44910 | -0.00033 |
| $C_7H_{14}$ | 2,3,3-trimethyl-1-butene | 84.51274 | 84.51129 | -0.00002 |
| $C_8H_{16}$ | 1-octene | 96.34883 | 96.41421 | 0.00068 |
| $C_8H_{16}$ | trans-2,2-dimethyl-3-hexene | 96.69846 | 96.68782 | -0.00011 |
| $C_8H_{16}$ | 3-ethyl-2-methyl-1-pentene | 96.63483 | 96.61113 | -0.00025 |
| $C_8H_{16}$ | 2,4,4-trimethyl-1-pentene | 96.61293 | 96.71684 | 0.00107 |
| $C_8H_{16}$ | 2,4,4-trimethyl-2-pentene | 96.67590 | 96.65880 | -0.00018 |
| $C_{10}H_{20}$ | 1-decene | 120.66423 | 120.74240 | 0.00065 |
| $C_{12}H_{24}$ | 1-dodecene | 144.97963 | 145.07163 | 0.00063 |
| $C_{16}H_{32}$ | 1-hexadecene | 193.61043 | 193.71766 | 0.00055 |

Table 15.410.4. Summary results of alkynes.

| Formula | Name | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|
| $C_3H_4$ | propyne | 29.42932 | 29.40432 | -0.00085 |
| $C_4H_6$ | 1-butyne | 41.58702 | 41.55495 | -0.00077 |
| $C_4H_6$ | 2-butyne | 41.72765 | 41.75705 | 0.00070 |
| $C_9H_{16}$ | 1-nonyne | 102.37552 | 102.35367 | -0.00021 |

Table 15.410.5. Summary results of alkyl fluorides.

| Formula | Name | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|
| $CF_4$ | tetrafluoromethane | 21.07992 | 21.016 | -0.00303 |
| $CHF_3$ | trifluoromethane | 19.28398 | 19.362 | 0.00405 |
| $CH_2F_2$ | difluoromethane | 18.22209 | 18.280 | 0.00314 |
| $C_3H_7F$ | 1-fluoropropane | 41.86745 | 41.885 | 0.00041 |
| $C_3H_7F$ | 2-fluoropropane | 41.96834 | 41.963 | -0.00012 |

Table 15.410.6. Summary results of alkyl chlorides.

| Formula | Name | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|
| $CCl_4$ | tetrachloromethane | 13.43181 | 13.448 | 0.00123 |
| $CHCl_3$ | trichloromethane | 14.49146 | 14.523 | 0.00217 |
| $CH_2Cl_2$ | dichloromethane | 15.37248 | 15.450 | 0.00499 |
| $CH_3Cl$ | chloromethane | 16.26302 | 16.312 | 0.00299 |
| $C_2H_5Cl$ | chloroethane | 28.61064 | 28.571 | -0.00138 |
| $C_3H_7Cl$ | 1-chloropropane | 40.76834 | 40.723 | -0.00112 |
| $C_3H_7Cl$ | 2-chloropropane | 40.86923 | 40.858 | -0.00028 |
| $C_4H_9Cl$ | 1-chlorobutane | 52.92604 | 52.903 | -0.00044 |
| $C_4H_9Cl$ | 2-chlorobutane | 53.02693 | 52.972 | -0.00104 |
| $C_4H_9Cl$ | 1-chloro-2-methylpropane | 52.99860 | 52.953 | -0.00085 |
| $C_4H_9Cl$ | 2-chloro-2-methylpropane | 53.21057 | 53.191 | -0.00037 |
| $C_5H_{11}Cl$ | 1-chloropentane | 65.08374 | 65.061 | -0.00034 |
| $C_5H_{11}Cl$ | 1-chloro-3-methylbutane | 65.15630 | 65.111 | -0.00069 |
| $C_5H_{11}Cl$ | 2-chloro-2-methylbutane | 65.36827 | 65.344 | -0.00037 |
| $C_5H_{11}Cl$ | 2-chloro-3-methylbutane | 65.16582 | 65.167 | 0.00002 |
| $C_6H_{13}Cl$ | 2-chlorohexane | 77.34233 | 77.313 | -0.00038 |
| $C_8H_{17}Cl$ | 1-chlorooctane | 101.55684 | 101.564 | 0.00007 |
| $C_{12}H_{25}Cl$ | 1-chlorododecane | 150.18764 | 150.202 | 0.00009 |
| $C_{18}H_{37}Cl$ | 1-chlorooctadecane | 223.13384 | 223.175 | 0.00018 |

Table 15.410.7. Summary results of alkyl bromides.

| Formula | Name | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|
| $CBr_4$ | tetrabromomethane | 11.25929 | 11.196 | -0.00566 |
| $CHBr_3$ | tribromomethane | 12.87698 | 12.919 | 0.00323 |
| $CH_3Br$ | bromomethane | 15.67551 | 15.732 | 0.00360 |
| $C_2H_5Br$ | bromoethane | 28.03939 | 27.953 | -0.00308 |
| $C_3H_7Br$ | 1-bromopropane | 40.19709 | 40.160 | -0.00093 |
| $C_3H_7Br$ | 2-bromopropane | 40.29798 | 40.288 | -0.00024 |
| $C_5H_{10}Br_2$ | 2,3-dibromo-2-methylbutane | 63.53958 | 63.477 | -0.00098 |
| $C_6H_{13}Br$ | 1-bromohexane | 76.67019 | 76.634 | -0.00047 |
| $C_7H_{15}Br$ | 1-bromoheptane | 88.82789 | 88.783 | -0.00051 |
| $C_8H_{17}Br$ | 1-bromooctane | 100.98559 | 100.952 | -0.00033 |
| $C_{12}H_{25}Br$ | 1-bromododecane | 149.61639 | 149.573 | -0.00029 |
| $C_{16}H_{33}Br$ | 1-bromohexadecane | 198.24719 | 198.192 | -0.00028 |

Table 15.410.8. Summary results of alkyl iodides.

| Formula | Name | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|
| $CHI_3$ | triiodomethane | 10.35888 | 10.405 | 0.00444 |
| $CH_2I_2$ | diiodomethane | 12.94614 | 12.921 | -0.00195 |
| $CH_3I$ | iodomethane | 15.20294 | 15.163 | -0.00263 |
| $C_2H_5I$ | iodoethane | 27.36064 | 27.343 | -0.00066 |
| $C_3H_7I$ | 1-iodopropane | 39.51834 | 39.516 | -0.00006 |
| $C_3H_7I$ | 2-iodopropane | 39.61923 | 39.623 | 0.00009 |
| $C_4H_9I$ | 2-iodo-2-methylpropane | 51.96057 | 51.899 | -0.00119 |

Table 15.410.9. Summary results of alkene halides.

| Formula | Name | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|
| $C_2H_3Cl$ | chloroethene | 22.46700 | 22.505 | 0.00170 |
| $C_3H_5Cl$ | 2-chloropropene | 35.02984 | 35.05482 | 0.00071 |

Table 15.410.10. Summary results of alcohols.

| Formula | Name | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|
| $CH_4O$ | methanol | 21.11038 | 21.131 | 0.00097 |
| $C_2H_6O$ | ethanol | 33.40563 | 33.428 | 0.00066 |
| $C_3H_8O$ | 1-propanol | 45.56333 | 45.584 | 0.00046 |
| $C_3H_8O$ | 2-propanol | 45.72088 | 45.766 | 0.00098 |
| $C_4H_{10}O$ | 1-butanol | 57.72103 | 57.736 | 0.00026 |
| $C_4H_{10}O$ | 2-butanol | 57.87858 | 57.922 | 0.00074 |
| $C_4H_{10}O$ | 2-methyl-1-propananol | 57.79359 | 57.828 | 0.00060 |
| $C_4H_{10}O$ | 2-methyl-2-propananol | 58.15359 | 58.126 | -0.00048 |
| $C_5H_{12}O$ | 1-pentanol | 69.87873 | 69.887 | 0.00011 |
| $C_5H_{12}O$ | 2-pentanol | 70.03628 | 70.057 | 0.00029 |
| $C_5H_{12}O$ | 3-pentanol | 70.03628 | 70.097 | 0.00087 |
| $C_5H_{12}O$ | 2-methyl-1-butananol | 69.95129 | 69.957 | 0.00008 |
| $C_5H_{12}O$ | 3-methyl-1-butananol | 69.95129 | 69.950 | -0.00002 |
| $C_5H_{12}O$ | 2-methyl-2-butananol | 70.31129 | 70.246 | -0.00092 |
| $C_5H_{12}O$ | 3-methyl-2-butananol | 69.96081 | 70.083 | 0.00174 |
| $C_6H_{14}O$ | 1-hexanol | 82.03643 | 82.054 | 0.00021 |
| $C_6H_{14}O$ | 2-hexanol | 82.19398 | 82.236 | 0.00052 |
| $C_7H_{16}O$ | 1-heptanol | 94.19413 | 94.214 | 0.00021 |
| $C_8H_{18}O$ | 1-octanol | 106.35183 | 106.358 | 0.00006 |
| $C_8H_{18}O$ | 2-ethyl-1-hexananol | 106.42439 | 106.459 | 0.00032 |
| $C_9H_{20}O$ | 1-nonanol | 118.50953 | 118.521 | 0.00010 |
| $C_{10}H_{22}O$ | 1-decanol | 130.66723 | 130.676 | 0.00007 |
| $C_{12}H_{26}O$ | 1-dodecanol | 154.98263 | 154.984 | 0.00001 |
| $C_{16}H_{34}O$ | 1-hexadecanol | 203.61343 | 203.603 | -0.00005 |

Table 15.410.11. Summary results of ethers.

| Formula | Name | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|
| $C_2H_6O$ | dimethyl ether | 32.84496 | 32.902 | 0.00174 |
| $C_3H_8O$ | ethyl methyl ether | 45.19710 | 45.183 | -0.00030 |
| $C_4H_{10}O$ | diethyl ether | 57.54924 | 57.500 | -0.00086 |
| $C_4H_{10}O$ | methyl propyl ether | 57.35480 | 57.355 | 0.00000 |
| $C_4H_{10}O$ | isopropyl methyl ether | 57.45569 | 57.499 | 0.00075 |
| $C_6H_{14}O$ | dipropyl ether | 81.86464 | 81.817 | -0.00059 |
| $C_6H_{14}O$ | diisopropyl ether | 82.06642 | 82.088 | 0.00026 |
| $C_6H_{14}O$ | t-butyl ethyl ether | 82.10276 | 82.033 | -0.00085 |
| $C_7H_{16}O$ | t-butyl isopropyl ether | 94.36135 | 94.438 | 0.00081 |
| $C_8H_{18}O$ | dibutyl ether | 106.18004 | 106.122 | -0.00055 |
| $C_8H_{18}O$ | di-sec-butyl ether | 106.38182 | 106.410 | 0.00027 |
| $C_8H_{18}O$ | di-t-butyl ether | 106.36022 | 106.425 | 0.00061 |
| $C_8H_{18}O$ | t-butyl isobutyl ether | 106.65628 | 106.497 | -0.00218 |

Table 15.410.12. Summary results of 1° amines.

| Formula | Name | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|
| $CH_5N$ | methylamine | 23.88297 | 23.857 | -0.00110 |
| $C_2H_7N$ | ethylamine | 36.04067 | 36.062 | 0.00060 |
| $C_3H_9N$ | propylamine | 48.19837 | 48.243 | 0.00092 |
| $C_4H_{11}N$ | butylamine | 60.35607 | 60.415 | 0.00098 |
| $C_4H_{11}N$ | sec-butylamine | 60.45696 | 60.547 | 0.00148 |
| $C_4H_{11}N$ | t-butylamine | 60.78863 | 60.717 | -0.00118 |
| $C_4H_{11}N$ | isobutylamine | 60.42863 | 60.486 | 0.00094 |

Table 15.410.13. Summary results of 2° amines.

| Formula | Name | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|
| $C_2H_7N$ | dimethylamine | 35.76895 | 35.765 | -0.00012 |
| $C_4H_{11}N$ | diethylamine | 60.22930 | 60.211 | -0.00030 |
| $C_6H_{15}N$ | dipropylamine | 84.54470 | 84.558 | 0.00016 |
| $C_6H_{15}N$ | diisopropylamine | 84.74648 | 84.846 | 0.00117 |
| $C_8H_{19}N$ | dibutylamine | 108.86010 | 108.872 | 0.00011 |
| $C_8H_{19}N$ | diisobutylamine | 109.00522 | 109.106 | 0.00092 |

Table 15.410.14. Summary results of 3° amines.

| Formula | Name | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|
| $C_3H_9N$ | trimethylamine | 47.83338 | 47.761 | -0.00152 |
| $C_6H_{15}N$ | triethylamine | 84.30648 | 84.316 | 0.00012 |
| $C_9H_{21}N$ | tripropylamine | 120.77958 | 120.864 | 0.00070 |

Table 15.410.15. Summary results of aldehydes.

| Formula | Name | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|
| $CH_2O$ | formaldehyde | 15.64628 | 15.655 | 0.00056 |
| $C_2H_4O$ | acetaldehyde | 28.18711 | 28.198 | 0.00039 |
| $C_3H_6O$ | propanal | 40.34481 | 40.345 | 0.00000 |
| $C_4H_8O$ | butanal | 52.50251 | 52.491 | -0.00022 |
| $C_4H_8O$ | isobutanal | 52.60340 | 52.604 | 0.00001 |
| $C_5H_{10}O$ | pentanal | 64.66021 | 64.682 | 0.00034 |
| $C_7H_{14}O$ | heptanal | 88.97561 | 88.942 | -0.00038 |
| $C_8H_{16}O$ | octanal | 101.13331 | 101.179 | 0.00045 |
| $C_8H_{16}O$ | 2-ethylhexanal | 101.23420 | 101.259 | 0.00025 |

Table 15.410.16. Summary results of ketones.

| Formula | Name | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|
| $C_3H_6O$ | acetone | 40.68472 | 40.672 | -0.00031 |
| $C_4H_8O$ | 2-butanone | 52.84242 | 52.84 | -0.00005 |
| $C_5H_{10}O$ | 2-pentanone | 65.00012 | 64.997 | -0.00005 |
| $C_5H_{10}O$ | 3-pentanone | 65.00012 | 64.988 | -0.00005 |
| $C_5H_{10}O$ | 3-methyl-2-butanone | 65.10101 | 65.036 | -0.00099 |
| $C_6H_{12}O$ | 2-hexanone | 77.15782 | 77.152 | -0.00008 |
| $C_6H_{12}O$ | 3-hexanone | 77.15782 | 77.138 | -0.00025 |
| $C_6H_{12}O$ | 2-methyl-3-pentanone | 77.25871 | 77.225 | -0.00043 |
| $C_6H_{12}O$ | 3,3-dimethyl-2-butanone | 77.29432 | 77.273 | -0.00028 |
| $C_7H_{14}O$ | 3-heptanone | 89.31552 | 89.287 | -0.00032 |
| $C_7H_{14}O$ | 4-heptanone | 89.31552 | 89.299 | -0.00018 |
| $C_7H_{14}O$ | 2,2-dimethyl-3-pentanone | 89.45202 | 89.458 | 0.00007 |

| Formula | Name | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|
| $C_7H_{14}O$ | 2,4-dimethyl-3-pentanone | 89.51730 | 89.434 | -0.00093 |
| $C_8H_{16}O$ | 2,2,4-trimethyl-3-pentanone | 101.71061 | 101.660 | -0.00049 |
| $C_9H_{18}O$ | 2-nonanone | 113.63092 | 113.632 | 0.00001 |
| $C_9H_{18}O$ | 5-nonanone | 113.63092 | 113.675 | 0.00039 |
| $C_9H_{18}O$ | 2,6-dimethyl-4-heptanone | 113.77604 | 113.807 | 0.00027 |

Table 15.410.17. Summary results of carboxylic acids.

| Formula | Name | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|
| $CH_2O_2$ | formic acid | 21.01945 | 21.036 | 0.00079 |
| $C_2H_4O_2$ | acetic acid | 33.55916 | 33.537 | -0.00066 |
| $C_3H_6O_2$ | propanoic acid | 45.71686 | 45.727 | 0.00022 |
| $C_4H_8O_2$ | butanoic acid | 57.87456 | 57.883 | 0.00015 |
| $C_5H_{10}O_2$ | pentanoic acid | 70.03226 | 69.995 | -0.00053 |
| $C_5H_{10}O_2$ | 3-methylbutanoic acid | 70.10482 | 70.183 | 0.00111 |
| $C_5H_{10}O_2$ | 2,2-dimethylpropanoic acid | 70.31679 | 69.989 | -0.00468 |
| $C_6H_{12}O_2$ | hexanoic acid | 82.18996 | 82.149 | -0.00050 |
| $C_7H_{14}O_2$ | heptanoic acid | 94.34766 | 94.347 | 0.00000 |
| $C_8H_{16}O_2$ | octanoic acid | 106.50536 | 106.481 | -0.00022 |
| $C_9H_{18}O_2$ | nonanoic acid | 118.66306 | 118.666 | 0.00003 |
| $C_{10}H_{20}O_2$ | decanoic acid | 130.82076 | 130.795 | -0.00020 |
| $C_{12}H_{24}O_2$ | dodecanoic acid | 155.13616 | 155.176 | 0.00026 |
| $C_{14}H_{28}O_2$ | tetradecanoic acid | 179.45156 | 179.605 | 0.00085 |
| $C_{15}H_{30}O_2$ | pentadecanoic acid | 191.60926 | 191.606 | -0.00002 |
| $C_{16}H_{32}O_2$ | hexadecanoic acid | 203.76696 | 203.948 | 0.00089 |
| $C_{18}H_{36}O_2$ | stearic acid | 228.08236 | 228.298 | 0.00094 |
| $C_{20}H_{40}O_2$ | eicosanoic acid | 252.39776 | 252.514 | 0.00046 |

Table 15.410.18. Summary results of carboxylic acid esters.

| Formula | Name | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|
| $C_2H_4O_2$ | methyl formate | 32.71076 | 32.762 | 0.00156 |
| $C_3H_6O_2$ | methyl acetate | 45.24849 | 45.288 | 0.00087 |
| $C_6H_{12}O_2$ | methyl pentanoate | 81.72159 | 81.726 | 0.00005 |
| $C_7H_{14}O_2$ | methyl hexanoate | 93.87929 | 93.891 | 0.00012 |
| $C_8H_{16}O_2$ | methyl heptanoate | 106.03699 | 106.079 | 0.00040 |
| $C_9H_{18}O_2$ | methyl octanoate | 118.19469 | 118.217 | 0.00018 |
| $C_{10}H_{20}O_2$ | methyl nonanoate | 130.35239 | 130.373 | 0.00016 |
| $C_{11}H_{22}O_2$ | methyl decanoate | 142.51009 | 142.523 | 0.00009 |
| $C_{12}H_{24}O_2$ | methyl undecanoate | 154.66779 | 154.677 | 0.00006 |
| $C_{13}H_{26}O_2$ | methyl dodecanoate | 166.82549 | 166.842 | 0.00010 |
| $C_{14}H_{28}O_2$ | methyl tridecanoate | 178.98319 | 179.000 | 0.00009 |
| $C_{15}H_{30}O_2$ | methyl tetradecanoate | 191.14089 | 191.170 | 0.00015 |
| $C_{16}H_{32}O_2$ | methyl pentadecanoate | 203.29859 | 203.356 | 0.00028 |
| $C_4H_8O_2$ | propyl formate | 57.76366 | 57.746 | -0.00030 |
| $C_4H_8O_2$ | ethyl acetate | 57.63888 | 57.548 | -0.00157 |
| $C_5H_{10}O_2$ | isopropyl acetate | 69.89747 | 69.889 | -0.00013 |
| $C_5H_{10}O_2$ | ethyl propanoate | 69.79658 | 69.700 | -0.00139 |
| $C_6H_{12}O_2$ | butyl acetate | 81.95428 | 81.873 | -0.00099 |
| $C_6H_{12}O_2$ | t-butyl acetate | 82.23881 | 82.197 | -0.00051 |
| $C_6H_{12}O_2$ | methyl 2,2-dimethylpropanoate | 82.00612 | 81.935 | -0.00087 |
| $C_7H_{14}O_2$ | ethyl pentanoate | 94.11198 | 94.033 | -0.00084 |
| $C_7H_{14}O_2$ | ethyl 3-methylbutanoate | 94.18454 | 94.252 | 0.00072 |
| $C_7H_{14}O_2$ | ethyl 2,2-dimethylpropanoate | 94.39651 | 94.345 | -0.00054 |
| $C_8H_{16}O_2$ | isobutyl isobutanoate | 106.44313 | 106.363 | -0.00075 |
| $C_8H_{16}O_2$ | propyl pentanoate | 106.26968 | 106.267 | -0.00003 |

| Formula | Name | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|
| $C_8H_{16}O_2$ | isopropyl pentanoate | 106.37057 | 106.384 | 0.00013 |
| $C_9H_{18}O_2$ | butyl pentanoate | 118.42738 | 118.489 | 0.00052 |
| $C_9H_{18}O_2$ | sec-butyl pentanoate | 118.52827 | 118.624 | 0.00081 |
| $C_9H_{18}O_2$ | isobutyl pentanoate | 118.49994 | 118.576 | 0.00064 |

Table 15.410.19. Summary results of amides.

| Formula | Name | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|
| $CH_3NO$ | formamide | 23.68712 | 23.697 | 0.00041 |
| $C_2H_5NO$ | acetamide | 36.15222 | 36.103 | -0.00135 |
| $C_3H_7NO$ | propanamide | 48.30992 | 48.264 | -0.00094 |
| $C_4H_9NO$ | butanamide | 60.46762 | 60.449 | -0.00030 |
| $C_4H_9NO$ | 2-methylpropanamide | 60.51509 | 60.455 | -0.00099 |
| $C_5H_{11}NO$ | pentanamide | 72.62532 | 72.481 | -0.00200 |
| $C_5H_{11}NO$ | 2,2-dimethylpropanamide | 72.67890 | 72.718 | 0.00054 |
| $C_6H_{13}NO$ | hexanamide | 84.78302 | 84.780 | -0.00004 |
| $C_8H_{17}NO$ | octanamide | 109.09842 | 109.071 | -0.00025 |

Table 15.410.20. Summary results of N-alkyl and N,N-dialkyl amides.

| Formula | Name | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|
| $C_3H_7NO$ | N,N-dimethylformamide | 47.679454 | 47.574 | 0.00221 |
| $C_4H_9NO$ | N,N-dimethylacetamide | 60.14455 | 59.890 | -0.00426 |
| $C_6H_{13}NO$ | N-butylacetamide | 84.63649 | 84.590 | -0.00055 |

Table 15.410.21. Summary results of urea.

| Formula | Name | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|
| $CH_4N_2O$ | urea | 31.35919 | 31.393 | 0.00108 |

Table 15.410.22. Summary results of acid halide.

| Formula | Name | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|
| $C_2H_3ClO$ | acetyl chloride | 28.02174 | 27.990 | -0.00115 |

Table 15.410.23. Summary results of acid anhydrides.

| Formula | Name | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|
| $C_4H_6O_3$ | acetic anhydride | 56.94096 | 56.948 | 0.00013 |
| $C_6H_{10}O_3$ | propanoic anhydride | 81.25636 | 81.401 | 0.00177 |

Table 15.410.24. Summary results of nitriles.

| Formula | Name | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|
| $C_2H_3N$ | acetonitrile | 25.72060 | 25.77 | 0.00174 |
| $C_3H_5N$ | propanenitrile | 37.87830 | 37.94 | 0.00171 |
| $C_4H_7N$ | butanenitrile | 50.03600 | 50.08 | 0.00082 |
| $C_4H_7N$ | 2-methylpropanenitrile | 50.13689 | 50.18 | 0.00092 |
| $C_5H_9N$ | pentanenitrile | 62.19370 | 62.26 | 0.00111 |
| $C_5H_9N$ | 2,2-dimethylpropanenitrile | 62.47823 | 62.40 | -0.00132 |
| $C_7H_{13}N$ | heptanenitrile | 86.50910 | 86.59 | 0.00089 |
| $C_8H_{15}N$ | octanenitrile | 98.66680 | 98.73 | 0.00069 |
| $C_{10}H_{19}N$ | decanenitrile | 122.98220 | 123.05 | 0.00057 |
| $C_{14}H_{27}N$ | tetradecanenitrile | 171.61300 | 171.70 | 0.00052 |

Table 15.410.25. Summary results of thiols.

| Formula | Name | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|
| HS | hydrogen sulfide | 3.77430 | 3.653 | -0.03320 |
| $H_2S$ | dihydrogen sulfide | 7.56058 | 7.605 | 0.00582 |
| $CH_4S$ | methanethiol | 19.60264 | 19.575 | -0.00141 |
| $C_2H_6S$ | ethanethiol | 31.76034 | 31.762 | 0.00005 |
| $C_3H_8S$ | 1-propanethiol | 43.91804 | 43.933 | 0.00035 |
| $C_3H_8S$ | 2-propanethiol | 44.01893 | 44.020 | 0.00003 |
| $C_4H_{10}S$ | 1-butanethiol | 56.07574 | 56.089 | 0.00024 |
| $C_4H_{10}S$ | 2-butanethiol | 56.17663 | 56.181 | 0.00009 |
| $C_4H_{10}S$ | 2-methyl-1-propanethiol | 56.14830 | 56.186 | 0.00066 |
| $C_4H_{10}S$ | 2-methyl-2-propanethiol | 56.36027 | 56.313 | -0.00084 |
| $C_5H_{12}S$ | 2-methyl-1-butanethiol | 68.30600 | 68.314 | 0.00012 |
| $C_5H_{12}S$ | 1-pentanethiol | 68.23344 | 68.264 | 0.00044 |
| $C_5H_{12}S$ | 2-methyl-2-butanethiol | 68.51797 | 68.441 | -0.00113 |
| $C_5H_{12}S$ | 3-methyl-2-butanethiol | 68.31552 | 68.381 | 0.00095 |
| $C_5H_{12}S$ | 2,2-dimethyl-1-propanethiol | 68.16441 | 68.461 | 0.00433 |
| $C_6H_{14}S$ | 1-hexanethiol | 80.39114 | 80.416 | 0.00031 |
| $C_6H_{14}S$ | 2-methyl-2-pentanethiol | 80.67567 | 80.607 | -0.00085 |
| $C_7H_{16}S$ | 1-heptanethiol | 92.54884 | 92.570 | 0.00023 |
| $C_{10}H_{22}S$ | 1-decanethiol | 129.02194 | 129.048 | 0.00020 |

Table 15.410.26. Summary results of sulfides.

| Formula | Name | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|
| $C_2H_6S$ | dimethyl sulfide | 31.65668 | 31.672 | 0.00048 |
| $C_3H_8S$ | ethyl methyl sulfide | 43.81438 | 43.848 | 0.00078 |
| $C_4H_{10}S$ | diethyl sulfide | 55.97208 | 56.043 | 0.00126 |
| $C_4H_{10}S$ | methyl propyl sulfide | 55.97208 | 56.029 | 0.00102 |
| $C_4H_{10}S$ | isopropyl methyl sulfide | 56.07297 | 56.115 | 0.00075 |
| $C_5H_{12}S$ | butyl methyl sulfide | 68.12978 | 68.185 | 0.00081 |
| $C_5H_{12}S$ | t-butyl methyl sulfide | 68.28245 | 68.381 | 0.00144 |
| $C_5H_{12}S$ | ethyl propyl sulfide | 68.12978 | 68.210 | 0.00117 |
| $C_5H_{12}S$ | ethyl isopropyl sulfide | 68.23067 | 68.350 | 0.00174 |
| $C_6H_{14}S$ | diisopropyl sulfide | 80.48926 | 80.542 | 0.00065 |
| $C_6H_{14}S$ | butyl ethyl sulfide | 80.28748 | 80.395 | 0.00133 |
| $C_6H_{14}S$ | methyl pentyl sulfide | 80.28748 | 80.332 | 0.00056 |
| $C_8H_{18}S$ | dibutyl sulfide | 104.60288 | 104.701 | 0.00094 |
| $C_8H_{18}S$ | di-sec-butyl sulfide | 104.80466 | 104.701 | -0.00099 |
| $C_8H_{18}S$ | di-t-butyl sulfide | 104.90822 | 104.920 | 0.00011 |
| $C_8H_{18}S$ | diisobutyl sulfide | 104.74800 | 104.834 | 0.00082 |
| $C_{10}H_{22}S$ | dipentyl sulfide | 128.91828 | 128.979 | 0.00047 |
| $C_{10}H_{22}S$ | diisopentyl sulfide | 129.06340 | 129.151 | 0.00068 |

Table 15.410.27. Summary results of disulfides.

| Formula | Name | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|
| $C_2H_6S_2$ | dimethyl disulfide | 34.48127 | 34.413 | -0.00199 |
| $C_4H_{10}S_2$ | diethyl disulfide | 58.79667 | 58.873 | 0.00129 |
| $C_6H_{14}S_2$ | dipropyl disulfide | 83.11207 | 83.169 | 0.00068 |
| $C_8H_{18}S_2$ | di-t-butyl disulfide | 107.99653 | 107.919 | -0.00072 |

Table 15.410.28. Summary results of sulfoxides.

| Formula | Name | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|
| $C_2H_6SO$ | dimethyl sulfoxide | 35.52450 | 35.435 | -0.00253 |
| $C_4H_{10}SO$ | diethyl sulfoxide | 59.83990 | 59.891 | 0.00085 |
| $C_6H_{14}SO$ | dipropyl sulfoxide | 84.15530 | 84.294 | 0.00165 |

Table 15.410.29. Summary results of sulfones.

| Formula | Name | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|
| $C_2H_6SO_2$ | dimethyl sulfone | 40.27588 | 40.316 | 0.00100 |

Table 15.410.30. Summary results of sulfites.

| Formula | Name | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|
| $C_2H_6SO_3$ | dimethyl sulfite | 43.95058 | 44.042 | 0.00207 |
| $C_4H_{10}SO_3$ | diethyl sulfite | 68.54939 | 68.648 | 0.00143 |
| $C_8H_{18}SO_3$ | dibutyl sulfite | 117.18019 | 117.191 | 0.00009 |

Table 15.410.31. Summary results of sulfates.

| Formula | Name | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|
| $C_2H_6SO_4$ | dimethyl sulfate | 48.70196 | 48.734 | 0.00067 |
| $C_4H_{10}SO_4$ | diethyl sulfate | 73.30077 | 73.346 | 0.00061 |
| $C_6H_{14}SO_4$ | dipropyl sulfate | 97.61617 | 97.609 | -0.00008 |

Table 15.410.32. Summary results of nitro alkanes.

| Formula | Name | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|
| $CH_3NO_2$ | nitromethane | 25.14934 | 25.107 | -0.00168 |
| $C_2H_5NO_2$ | nitroethane | 37.30704 | 37.292 | -0.00040 |
| $C_3H_7NO_2$ | 1-nitropropane | 49.46474 | 49.451 | -0.00028 |
| $C_3H_7NO_2$ | 2-nitropropane | 49.56563 | 49.602 | 0.00074 |
| $C_4H_9NO_2$ | 1-nitrobutane | 61.62244 | 61.601 | -0.00036 |
| $C_4H_9NO_2$ | 2-nitroisobutane | 61.90697 | 61.945 | 0.00061 |
| $C_5H_{11}NO_2$ | 1-nitropentane | 73.78014 | 73.759 | -0.00028 |

Table 15.410.33. Summary results of nitrite.

| Formula | Name | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|
| $CH_3NO_2$ | methyl nitrite | 24.92328 | 24.955 | 0.00126 |

Table 15.410.34. Summary results of nitrate.

| Formula | Name | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|
| $CH_3NO_3$ | methyl nitrate | 28.18536 | 28.117 | -0.00244 |
| $C_2H_5NO_3$ | ethyl nitrate | 40.34306 | 40.396 | 0.00131 |
| $C_3H_7NO_3$ | propyl nitrate | 52.50076 | 52.550 | 0.00093 |
| $C_3H_7NO_3$ | isopropyl nitrate | 52.60165 | 52.725 | 0.00233 |

Table 15.410.35. Summary results of conjugated alkenes.

| Formula | Name | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|
| $C_5H_8$ | cyclopentene | 54.83565 | 54.86117 | 0.00047 |
| $C_4H_6$ | 1,3 butadiene | 42.09159 | 42.12705 | 0.00084 |
| $C_5H_8$ | 1,3 pentadiene | 54.40776 | 54.42484 | 0.00031 |
| $C_5H_8$ | 1,4 pentadiene | 54.03745 | 54.11806 | 0.00149 |
| $C_5H_6$ | 1,3 cyclopentadiene | 49.27432 | 49.30294 | 0.00058 |

Table 15.410.36. Summary results of aromatics and heterocyclic aromatics.

| Formula | Name | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|
| $C_6H_6$ | benzene | 57.26008 | 57.26340 | 0.00006 |
| $C_6H_5Cl$ | fluorobenzene | 57.93510 | 57.887 | -0.00083 |
| $C_6H_5Cl$ | chlorobenzene | 56.55263 | 56.581 | 0.00051 |
| $C_6H_4Cl_2$ | m-dichlorobenzene | 55.84518 | 55.852 | 0.00012 |
| $C_6H_3Cl_3$ | 1,2,3-trichlorobenzene | 55.13773 | 55.077 | -0.00111 |
| $C_6H_3Cl_3$ | 1,3,5-trichlorobenzene | 55.29542 | 55.255 | -0.00073 |
| $C_6Cl_6$ | hexachlorobenzene | 52.57130 | 52.477 | -0.00179 |
| $C_6H_5Br$ | bromobenzene | 56.17932 | 56.391[a] | 0.00376 |
| $C_6H_5I$ | iodobenzene | 55.25993 | 55.261 | 0.00001 |
| $C_6H_5NO_2$ | nitrobenzene | 65.18754 | 65.217 | 0.00046 |
| $C_7H_8$ | toluene | 69.48425 | 69.546 | 0.00088 |
| $C_7H_6O_2$ | benzoic acid | 73.76938 | 73.762 | -0.00009 |
| $C_7H_5ClO_2$ | 2-chlorobenzoic acid | 73.06193 | 73.082 | 0.00027 |
| $C_7H_5ClO_2$ | 3-chlorobenzoic acid | 73.26820 | 73.261 | -0.00010 |
| $C_6H_7N$ | aniline | 64.43373 | 64.374 | -0.00093 |
| $C_7H_9N$ | 2-methylaniline | 76.62345 | 76.643 | -0.00025 |
| $C_7H_9N$ | 3-methylaniline | 76.62345 | 76.661 | 0.00050 |
| $C_7H_9N$ | 4-methylaniline | 76.62345 | 76.654 | 0.00040 |
| $C_6H_6N_2O_2$ | 2-nitroaniline | 72.47476 | 72.424 | -0.00070 |
| $C_6H_6N_2O_2$ | 3-nitroaniline | 72.47476 | 72.481 | -0.00009 |
| $C_6H_6N_2O_2$ | 4-nitroaniline | 72.47476 | 72.476 | -0.00002 |
| $C_7H_7NO_2$ | aniline-2-carboxylic acid | 80.90857 | 80.941 | 0.00041 |
| $C_7H_7NO_2$ | aniline-3-carboxylic acid | 80.90857 | 80.813 | -0.00118 |
| $C_7H_7NO_2$ | aniline-4-carboxylic acid | 80.90857 | 80.949 | 0.00050 |
| $C_6H_6O$ | phenol | 61.75817 | 61.704 | -0.00087 |
| $C_6H_4N_2O_5$ | 2,4-dinitrophenol | 77.61308 | 77.642 | 0.00037 |
| $C_6H_8O$ | anisole | 73.39006 | 73.355 | -0.00047 |
| $C_{10}H_8$ | naphthalene | 90.74658 | 90.79143 | 0.00049 |
| $C_4H_5N$ | pyrrole | 44.81090 | 44.785 | -0.00057 |
| $C_4H_4O$ | furan | 41.67782 | 41.692 | 0.00033 |
| $C_4H_4S$ | thiophene | 40.42501 | 40.430 | 0.00013 |
| $C_3H_4N_2$ | imidazole | 39.76343 | 39.74106 | -0.00056 |
| $C_5H_5N$ | pyridine | 51.91802 | 51.87927 | -0.00075 |
| $C_4H_4N_2$ | pyrimidine | 46.57597 | 46.51794 | -0.00125 |
| $C_4H_4N_2$ | pyrazine | 46.57597 | 46.51380 | 0.00095 |
| $C_9H_7N$ | quinoline | 85.40453 | 85.48607 | 0.00178 |
| $C_9H_7N$ | isoquinoline | 85.40453 | 85.44358 | 0.00046 |
| $C_8H_7N$ | indole | 78.52215 | 78.514 | -0.00010 |

[a] Liquid.

Table 15.410.37. Summary results of DNA bases.

| Formula | Name | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|
| $C_5H_5N_5$ | adenine | 70.85416 | 70.79811 | -0.00079 |
| $C_5H_6N_2O_2$ | thymine | 69.08792 | 69.06438 | -0.00034 |
| $C_5H_5N_5O$ | guanine | 76.88212 | 77.41849 | -0.00055 |
| $C_4H_5N_3O$ | cytosine | 59.53378 | 60.58056 | 0.01728 |

Table 15.410.38. Summary results of alkyl phosphines.

| Formula | Name | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|
| $C_3H_9P$ | trimethylphosphine | 45.80930 | 46.87333 | 0.02270 |
| $C_6H_{15}P$ | triethylphosphine | 82.28240 | 82.24869 | -0.00041 |
| $C_{18}H_{15}P$ | triphenylphosphine | 168.40033 | 167.46591 | -0.00558 |

Table 15.410.39. Summary results of alkyl phosphites.

| Formula | Name | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|
| $C_3H_9O_3P$ | trimethyl phosphite | 61.06764 | 60.94329 | -0.00204 |
| $C_6H_{15}O_3P$ | triethyl phosphite | 98.12406 | 97.97947 | -0.00148 |
| $C_9H_{21}O_3P$ | tri-isopropyl phosphite | 134.89983 | 135.00698 | 0.00079 |

Table 15.410.40. Summary results of alkyl phosphine oxides.

| Formula | Name | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|
| $C_3H_9PO$ | trimethylphosphine oxide | 53.00430 | 52.91192 | -0.00175 |

Table 15.410.41. Summary results of alkyl phosphates.

| Formula | Name | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|
| $C_6H_{15}O_4P$ | triethyl phosphate | 105.31906 | 104.40400 | -0.00876 |
| $C_9H_{21}O_4P$ | tri-n-propyl phosphate | 141.79216 | 140.86778 | -0.00656 |
| $C_9H_{21}O_4P$ | tri-isopropyl phosphate | 142.09483 | 141.42283 | -0.00475 |
| $C_9H_{27}O_4P$ | tri-n-butyl phosphate | 178.26526 | 178.07742 | -0.00105 |

Table 15.410.42. Summary results of monosaccharides of DNA and RNA.

| Formula | Name | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|
| $C_5H_{10}O_4$ | 2-deoxy-D-ribose | 77.25842 | 83.498[a] | 0.02381 |
| $C_5H_{10}O_5$ | D-ribose | 81.51034 | | |
| $C_5H_{10}O_4$ | alpha-2-deoxy-D-ribose | 77.46684 | | |
| $C_5H_{10}O_5$ | alpha-D-ribose | 82.31088 | | |

[a] Crystal

Table 15.410.43. Summary results of amino acids.

| Formula | Name | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---|---|---|---|---|
| $C_4H_7NO_4$ | aspartic acid | 68.98109 | 70.843[a] | 0.02628 |
| $C_5H_9NO_4$ | glutamic acid | 81.13879 | 83.167[a] | 0.02438 |
| $C_3H_7NO_4S$ | cysteine | 55.02457 | 56.571[a] | 0.02733 |
| $C_6H_{14}N_2O_2$ | lysine | 95.77799 | 98.194[a] | 0.02461 |
| $C_6H_{14}N_2O_2$ | arginine | 105.07007 | 107.420[a] | 0.02188 |
| $C_6H_9N_3O_2$ | histidine | 88.10232 | 89.599[a] | 0.01671 |
| $C_4H_8N_2O_2$ | asparagine | 71.57414 | 73.513[a] | 0.02637 |
| $C_5H_{10}N_2O_2$ | glutamine | 83.73184 | 85.843[a] | 0.02459 |
| $C_4H_9NO_3$ | threonine | 68.95678 | 71.058[a] | 0.02956 |
| $C_9H_{11}NO_3$ | tyrosine | 109.40427 | 111.450[a] | 0.01835 |
| $C_3H_7NO_3$ | serine | 56.66986 | 58.339[a] | 0.02861 |
| $C_{11}H_{12}N_2O_2$ | tryptophan | 126.74291 | 128.084[a] | 0.01047 |
| $C_9H_{11}NO_2$ | phenylalanine | 104.90618 | 105.009 | 0.00098 |
| $C_5H_9NO_2$ | proline | 71.76826 | 71.332 | -0.00611 |
| $C_5H_9NO_2$ | methionine | 79.23631 | 79.214 | -0.00028 |
| $C_6H_{13}NO_2$ | leucine | 89.12115 | 89.047 | -0.00083 |
| $C_6H_{13}NO_2$ | isoleucine | 89.02978 | 90.612 | 0.01746 |
| $C_6H_{13}NO_2$ | valine | 76.87208 | 76.772 | -0.00130 |
| $C_3H_7NO_2$ | alanine | 52.57549 | 52.991 | 0.00785 |
| $C_2H_5NO_2$ | glycine | 40.28857 | 40.280 | -0.00021 |

[a] Crystal

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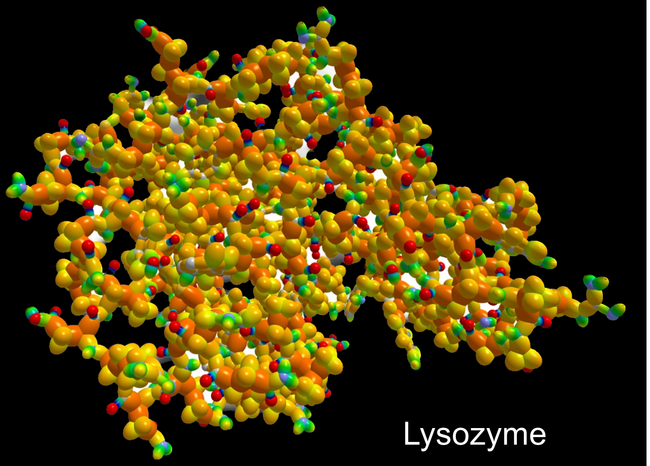
Dr. Mills has replaced the field generally known as Quantum Mechanics which postulates that classical physical laws do not apply at the atomic scale by deriving a new atomic theory of from those first principles, which unifies Maxwell's Equations, Newton's Laws, and General and Special Relativity. The central feature is that physical laws hold over all scales, from the scale of subatomic particles to that of the cosmos.

Quantum Mechanics has remained mysterious to all who have encountered it. Schrödinger postulated a boundary condition $\Psi \rightarrow 0$ as $r \rightarrow \infty$ of a wavelike positional probability for a singularity that is everywhere at once until measurement. The result was a purely algorithmic mathematical model of the hydrogen atom. In contrast, Mills solved the exact structure of matter and energy and related phenomena from known classical physics, (e.g. Maxwell's Equations wherein under special conditions, an extended distribution of charge may accelerate without radiating energy). This leads to a physical model of subatomic particles, atoms, and molecules. The closed-form solutions containing fundamental constants only agree with experimental observations demonstrating that the fundamental quantum mechanical postulate, "classical physical laws do not apply to the atomic scale", was erroneous.

From two basic equations, the key building blocks of organic chemistry have been solved, allowing the true physical structure and parameters of an infinite number of organic molecules up to infinite length and complexity to be obtained. These equations were also applied to bulk forms of matter, such as the allotropes of carbon, the solid bond of silicon and the semiconductor bond; as well as fundamental forms of matter such as the ionic bond and the metallic bond; and major fields of chemistry such as that of silicon, tin, aluminum, boron, and coordinate compounds.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Further, the Schwarzschild Metric is derived by applying Maxwell's Equations to electromagnetic and gravitational fields at particle production. This modifies General Relativity to include the conservation of spacetime and gives the origin of gravity, the families and masses of fundamental particles, the acceleration of the expansion of the universe (predicted by Dr. Mills in 1995 and since confirmed experimentally), and overturns the Big Bang model of the origin of the universe.

"Mills' theory explains the answers to some very old scientific questions, such as 'what happens to a photon upon absorption' and some very modern ones, such as 'what is dark matter.' ...Lastly, Mills has made an extremely important contribution to the philosophy of science. He has reestablished cause and effect as the basic principle of science." - **Dr. John J. Farrell**, former Chair of the Dept. of Chemistry, Franklin & Marshall College

"Mills' ingenious way of thinking creates in different physical areas astonishing results with fascinating mathematical simplicity and harmony. And his theory is strongly supported by the fact that nearly all these results are in comfortable accordance with experimental findings, sometimes with breathtaking accuracy." - **Dr Günther Landvogt,** Retired Scientist, Philips Research Lab

"Dr. Mills has apparently completed Einstein's quest for a unified field theory… without largesse from the US Government, and without the benediction of the US scientific priesthood." - **Shelby T. Brewer**, former Assistant Secretary of Energy, former CEO of ABB Combustion Engineering, MS/Ph.D. MIT - Nuclear Engineering.

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**Dr. Randell Mills** holds a Doctor of Medicine degree from Harvard, a BA degree in Chemistry from Franklin and Marshall College, and studied Electrical Engineering at MIT. He is President, Chairman and CEO of Brilliant Light Power, Inc.