## THE

## GRAND UNIFIED THEORY OF

## CLASSICAL PHYSICS

Dr. Randell L. Mills


Part B
MOLECULAR PHYSICS

THE GRAND UNIFIED THEORY OF CLASSICAL PHYSICS

Volume 2B of 3

# THE GRAND UNIFIED THEORY OF CLASSICAL PHYSICS 

BY

Dr. Randell L. Mills

## April 2023 Edition <br> Volume 2B of 3

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# APPLICATIONS: PHARMACEUTICALS, SPECIALTY MOLECULAR FUNCTIONAL GROUPS AND MOLECULES, DIPOLE MOMENTS AND INTERACTIONS 


#### Abstract

GENERAL CONSIDERATIONS OF THE BONDING IN PHARMACEUTICALS AND SPECIALTY MOLECULES Pharmaceutical and specialty molecules comprising an arbitrary number of atoms can be solved using similar principles and procedures as those used to solve general organic molecules of arbitrary length and complexity. Pharmaceuticals and specialty molecules can be considered to be comprised of functional groups such as those of 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, $\mathrm{N}, \mathrm{N}$-dialkyl amides, ureas, 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 given in the Organic Molecular Functional Groups and Molecules section. The solutions of the functional groups can be conveniently obtained by using generalized forms of the geometrical and energy equations. The functional-group solutions can be made into a linear superposition and sum, respectively, to give the solution of any pharmaceutical or specialty molecule comprising these groups. The total bond energies of exemplary pharmaceutical or specialty molecules such as aspirin, RDX, and NaH are calculated using the functional group composition and the corresponding energies derived in the previous sections as well as those of any new component functional groups derived herein.


## ASPIRIN (ACETYLSALICYLIC ACID)

Aspirin comprises salicylic acid (ortho-hydroxybenzoic acid) with the $H$ of the phenolic $O H$ group replaced by an acetyl group. Thus, aspirin comprises the benzoic acid $C-C(O)-O H$ moiety that comprises $C=O$ and $O H$ 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 given in the Benzoic Acid Compounds section. The aromatic $C \stackrel{3 e}{=} C$ and $C-H$ functional groups are equivalent to those of benzene given in the Aromatic and Heterocyclic Compounds section. The phenolic ester $\mathrm{C}-\mathrm{O}$ functional group is equivalent to that given in the Phenol section. The acetyl $\mathrm{O}-\mathrm{C}(\mathrm{O})-\mathrm{CH}_{3}$ moiety comprises (i) $C=O$ and $C-C$ functional groups that are the same as those of carboxylic acids and esters given in the corresponding sections, (ii) a $\mathrm{CH}_{3}$ group that is equivalent to that of alkanes given in the corresponding sections, (iii) and a $C-O$ bridging the carbonyl carbon and the phenolic ester which is equivalent to that of esters given in the corresponding section.

The symbols of the functional groups of aspirin are given in Table 16.1.

The corresponding designations of aspirin are shown in Figure 16.1B. 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 aspirin are given in Tables 16.2, 16.3, and 16.4, respectively. The total energy of aspirin given in Table 16.5 was calculated as the sum over the integer multiple of each $E_{D}($ Group $)$ of Table 16.4 corresponding to functional-group composition of the molecule. The bond angle parameters of aspirin determined using Eqs. (15.88-15.117) are given in Table 16.6. The color scale, translucent view of the charge density of aspirin 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 16.1A.

Figure 16.1. (A) Color scale, translucent view of the charge density of aspirin 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 designation of aspirin.



$$
0 \square 1 \mathrm{e} / \AA^{2}
$$

Table 16.1. The symbols of functional groups of aspirin.

| Functional Group | Group Symbol |
| :--- | :--- |
| CC (aromatic bond) | $\mathrm{Ce}=\mathrm{C}$ |
| CH (aromatic) | CH |
| Aryl $\mathrm{C}-\mathrm{C}(\mathrm{O})$ | $\mathrm{C}-\mathrm{C}(\mathrm{O})$ (i) |
| Alkyl $\mathrm{C}-\mathrm{C}(\mathrm{O})$ | $\mathrm{C}-\mathrm{C}(\mathrm{O})$ (ii) |
| $\mathrm{C=O}$ (aryl carboxylic acid) | $\mathrm{C}=\mathrm{O}$ |
| Aryl $(\mathrm{O}) \mathrm{C}-\mathrm{O}$ | $\mathrm{C}-\mathrm{O}$ (i) |
| Alkyl $(\mathrm{O}) \mathrm{C}-\mathrm{O}$ | $\mathrm{C}-\mathrm{O}$ (ii) |
| Aryl $\mathrm{C}-\mathrm{O}$ | $\mathrm{C}-\mathrm{O}$ (iii) |
| OH group | OH |
| $\mathrm{CH}_{3}$ group | $\mathrm{CH}_{3}$ |

Table 16.2. The geometrical bond parameters of aspirin and experimental values of similar molecules [1].

| Parameter | $\begin{aligned} & C=C_{i}^{36} C \\ & \text { Group } \end{aligned}$ | $\begin{aligned} & \mathrm{CH} \\ & \text { Group } \end{aligned}$ | $\begin{gathered} C-C(O)(\mathrm{i}) \\ \text { Group } \\ \hline \end{gathered}$ | $\begin{gathered} C-C(O) \text { (ii) } \\ \text { Group } \end{gathered}$ | $\begin{aligned} & C=O \\ & \text { Group } \end{aligned}$ | $\begin{gathered} C-O \text { (i) } \\ \text { Group } \end{gathered}$ | $\begin{gathered} C-O \text { (ii) } \\ \text { Group } \end{gathered}$ | $\begin{gathered} C-O \text { (iii) } \\ \text { Group } \end{gathered}$ | $\begin{gathered} \mathrm{OH} \\ \text { Group } \end{gathered}$ | $\begin{gathered} \mathrm{C}-\mathrm{H}\left(\mathrm{CH}_{3}\right) \\ \text { Groupp } \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $a\left(a_{0}\right)$ | 1.47348 | 1.60061 | 1.95111 | 2.04740 | 1.29907 | 1.73490 | 1.73490 | 1.68220 | 1.26430 | 1.64920 |
| $c^{\prime}\left(a_{0}\right)$ | 1.31468 | 1.03299 | 1.39682 | 1.43087 | 1.13977 | 1.31716 | 1.31716 | 1.29700 | 0.91808 | 1.04856 |
| $\begin{gathered} \text { Bond } \\ \text { Length } \\ 2 c^{\prime}(A) \end{gathered}$ | 1.39140 | 1.09327 | 1.47833 | 1.51437 | 1.20628 | 1.39402 | 1.39402 | 1.37268 | 0.971651 | 1.10974 |
| Exp. Bond Length (A) | $\begin{gathered} 1.399 \\ \text { (benzene) } \end{gathered}$ | $\begin{gathered} 1.101 \\ \text { (bencene) } \end{gathered}$ | $\begin{gathered} 1.48[2] \\ \text { (benzoic acid) } \end{gathered}$ | $\begin{gathered} 1.520 \\ \text { (acetic acid) } \end{gathered}$ | $\begin{gathered} 1.214 \\ \text { (acetic acid) } \end{gathered}$ | 1.393 (methyl formate) | $\begin{gathered} 1.393 \\ \text { (avg. methyl } \\ \text { formate) } \end{gathered}$ | $\begin{gathered} 1.364 \\ \text { (phenol) } \end{gathered}$ | $\begin{gathered} 0.972 \\ \text { (formic acid) } \end{gathered}$ | 1.08 (methyl formate) 1.107 (C-H propanc) 1.117 $(\mathrm{C}-\mathrm{H}$ butanc) |
| $b, c\left(a_{0}\right)$ | 0.66540 | 1.22265 | 1.36225 | 1.46439 | 0.62331 | 1.12915 | 1.12915 | 1.07126 | 0.86925 | 1.27295 |
| $e$ | 0.89223 | 0.64537 | 0.71591 | 0.69887 | 0.87737 | 0.75921 | 0.75921 | 0.77101 | 0.72615 | 0.63580 |

Table 16.3. The MO to HO intercept geometrical bond parameters of aspirin. $E_{\mathrm{T}}$ is $E_{\mathrm{T}}$ (atom-atom $m s p^{3} . A O$ ).

| Bond | Atom | $\begin{gathered} \digamma_{\tau} \\ (\mathrm{eV}) \\ \text { Bond } 1 \end{gathered}$ |  |  |  | $\begin{aligned} & \text { Final Total } \\ & \text { Energy } C 2 s p^{3} \end{aligned}$ $(\mathrm{eV})$ | $\begin{aligned} & r_{\text {momv }} \\ & \left(a_{0}\right) \end{aligned}$ | $\begin{aligned} & r_{\text {mow }} \\ & \left(a_{0}\right) \end{aligned}$ | $\begin{gathered} F_{\text {Cownux }}\left(C 2 s p^{3}\right) \\ (\mathrm{eV}) \\ \text { Hinal } \\ \hline \end{gathered}$ | $\begin{gathered} E\left(C 2 s p^{3}\right) \\ (\mathrm{eV}) \\ \text { Final } \\ \hline \end{gathered}$ | $\begin{aligned} & \theta^{\prime} \\ & \left({ }^{\circ}\right) \end{aligned}$ | $\begin{aligned} & \theta_{1} \\ & \left({ }^{\circ}\right) \end{aligned}$ | $\begin{aligned} & \theta_{2} \\ & \left({ }^{\circ}\right) \end{aligned}$ | $\begin{gathered} d_{1} \\ \left(a_{0}\right) \end{gathered}$ | $\begin{gathered} d_{2} \\ \left(a_{0}\right) \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $C-H\left(C_{\text {c }} H\right)$ | $C$ | -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 |
| $C=\left(I I O O C_{s}\right) C_{b}^{3 b}=C_{c}(I I)$ | $C_{s}$ | -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 |
| $\mathrm{C}_{8} \mathrm{C}_{8}(\mathrm{O}) \mathrm{O}-\mathrm{H}$ | o | -0.92918 | 0 | 0 | 0 |  | 1.00000 | 0.86359 | -15.75493 |  | 115.09 | 64.91 | 64.12 | 0.55182 | 0.36625 |
| $\mathrm{C}_{8} C_{c}(\mathrm{O})$-OII | $\bigcirc$ | -0.92918 | 0 | 0 | 0 |  | 1.00000 | 0.86359 | -15.75493 |  | 101.32 | 78.68 | 48.58 | 1.14765 | 0.16950 |
| $C_{8} C_{0}(O)-\mathrm{OII}$ | $C_{0}$ | -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 |
| $\begin{aligned} & C_{s} C_{c}(O I I)=O \\ & O C_{e}^{\prime}\left(C_{r} H_{3}\right)=O \end{aligned}$ | $o$ | -1.34946 | 0 | 0 | 0 |  | 1.00000 | 0.84115 | -16.17521 |  | 137.27 | 42.73 | 66.31 | 0.52193 | 0.61784 |
| $C_{8} C_{6}(\mathrm{OHI})=O$ | $C_{a}$ | -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 |
| $C_{5}-C_{j}(O) O H$ | $C_{a}$ | -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 |
| $\mathrm{C}_{5}-\mathrm{C}_{0}(\mathrm{O}) \mathrm{OH}$ | $C_{5}$ | -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 |
| $C_{c}=\left(H O O C_{c}\right) C_{n}{ }_{n}^{2}=C_{c}$ | $C^{\text {s }}$ | -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 |
| $C_{d}=\left(\mathrm{CH}_{3}(\mathrm{O}) \mathrm{CO}^{2}\right) \mathrm{C}_{d}^{2}=\mathrm{C}_{b}$ | $C_{d}$ | -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 |
| $C_{c}^{2}=\left(C_{b}=\right) C_{d}^{2}-O C(O) C I I_{3}$ | O | -0.74804 | -0.92918 | 0 | 0 |  | 1.00000 | 0.82445 | -16.50297 |  | 102.93 | 77.02 | 48.60 | 1.11250 | 0.18449 |
| $\mathrm{C}_{\mathrm{c}}{ }^{3}=\left(\mathrm{C}_{b}{ }^{3}=\mathrm{C}_{d} \mathrm{O}-\mathrm{C}(\mathrm{O}) \mathrm{CH}_{3}\right.$ | $\bigcirc$ | -0.92918 | -0.74804 | 0 | 0 |  | 1.00000 | 0.82445 | -16.50297 |  | 98.22 | 81.78 | 46.27 | 1.19921 | 0.11795 |
| $\bigcirc-C_{e}(O) C_{j} / I_{3}$ | $C_{*}$ | -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 |
| $O C_{e}\left(C_{y} H_{3}\right)=O$ | $c_{\text {c }}$ | -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 |
| $O(O) C_{c}-C_{j} / I_{3}$ | $C^{\circ}$ | -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 |
| $O \mathrm{C}_{e}(\mathrm{O})-\mathrm{C}_{f} \mathrm{H}_{3}$ | $C_{\text {, }}$ | -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 |

Table 16.4. The energy parameters $(\mathrm{eV})$ of functional groups of aspirin.

| Parameters | $C_{=}^{3} C$ <br> Group | $\stackrel{\text { CII }}{\text { Ciroup }}$ | $\begin{gathered} C-C(O)(i) \\ \text { Group } \end{gathered}$ | $\begin{gathered} C-C(O)(\text { ii) } \\ \text { Group } \end{gathered}$ | $\begin{aligned} & C=O \\ & \text { Group } \end{aligned}$ | $\begin{gathered} C-O(\mathrm{i}) \\ \text { Group } \end{gathered}$ | $\begin{gathered} \text { (-O)(ii) } \\ \text { Group } \end{gathered}$ | $\begin{gathered} \text { (:-O (iii) } \\ \text { Group } \end{gathered}$ | $\begin{gathered} \text { OII } \\ \text { Group } \end{gathered}$ | $\mathrm{CH}_{3}$ <br> Group |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $f_{1}$ | 0.75 | 1 |  |  |  |  |  |  |  |  |
| $n_{1}$ | 2 | 1 | 1 | 1 | 2 | 1 | 1 | 1 | 1 | 3 |
| $n_{2}$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 2 |
| $n_{3}$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $C_{1}$ | 0.5 | 0.75 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.75 | 0.75 |
| $C_{2}$ | 0.85252 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $c_{1}$ | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 0.75 | 1 |
| $c_{2}$ | 0.85252 | 0.91771 | 0.91771 | 0.91771 | 0.85395 | 0.85395 | 0.85395 | 0.79329 | 1 | 0.91771 |
| $c_{3}$ | 0 | 1 | 0 | 0 | 2 | 0 | 0 | 0 | 1 | 0 |
| $c_{4}$ | 3 | 1 | 2 | 2 | 4 | 2 | 2 | 2 | 1 | 1 |
| $c_{5}$ | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 3 |
| $C_{10}$ | 0.5 | 0.75 | 0.5 | 1 | 0.5 | 0.5 | 0.5 | 0.5 | 0.75 | 0.75 |
| $C_{20}$ | 0.85252 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $V_{c}(\mathrm{eV})$ | -101.12679 | -37.10024 | -32.15216 | -30.19634 | -111.25473 | -35.08488 | -35.08488 | -34.04658 | -40.92709 | -107.32728 |
| $V_{p}(\mathrm{eV})$ | 20.69825 | 13.17125 | 9.74055 | 9.50874 | 23.87467 | 10.32968 | 10.32968 | 10.49024 | 14.81988 | 38.92728 |
| $T(e V)$ | 34.31559 | 11.58941 | 8.23945 | 7.37432 | 42.82081 | 10.11150 | 10.11150 | 10.11966 | 16.18567 | 32.53914 |
| $V_{\sim}(\mathrm{eV})$ | -17.15779 | -5.79470 | -4.11973 | -3.68716 | -21.41040 | -5.05575 | -5.05575 | -5.05983 | -8.09284 | -16.26957 |
| $E$ (souw) (eV) | 0 | -14.63489 | -14.63489 | -14.63489 | 0 | -14.63489 | -14.63489 | -14.63489 | -13.6181 | -15.56407 |
| $\Delta E_{M, N 0}($ (.0\%N) $(\mathrm{eV})$ | 0 | -1.13379 | -1.29147 | 0 | -2.69893 | -2.69893 | -2.69893 | -1.49608 | 0 | 0 |
|  | 0 | -13.50110 | -13.34342 | -14.63489 | 2.69893 | -11.93596 | -11.93596 | -13.13881 | -13.6181 | -15.56407 |
| $F_{T}\left(N_{2}, \omega\right)(e V)$ | -63.27075 | -31.63539 | -31.63530 | -31.63534 | -63.27074 | -31.63541 | -31.63541 | -31.63532 | -31.63247 | -67.69451 |
| $E_{l}\left(\right.$ atom - atom, $\left.\mathrm{msp}{ }^{3} \cdot \mathrm{AO}\right)(\mathrm{eV})$ | -2.26759 | -0.56690 | -1.29147 | -1.85836 | -2.69893 | -1.85836 | $-1.85836$ | -1.49608 | 0 | 0 |
| $E_{i}(\mathrm{~mol})(\mathrm{eV})$ | -65.53833 | -32.20226 | -32.92684 | -33.49373 | -65.96966 | -33.49373 | -33.49373 | -33.13145 | -31.63537 | -67.69450 |
| $\omega\left(10^{15} \mathrm{rad} / \mathrm{s}\right)$ | 49.7272 | 26.4826 | 10.7262 | 23.3291 | 59.4034 | 24.3637 | 12.7926 | 13.3984 | 44.1776 | 24.9286 |
| $E_{K}(\mathrm{eV})$ | 32.73133 | 17.43132 | 7.06019 | 15.35563 | 39.10034 | 16.03660 | 8.42030 | 8.81907 | 29.07844 | 16.40846 |
| $\bar{E}_{D}(\mathrm{eV})$ | -0.35806 | -0.26130 | -0.17309 | -0.25966 | -0.40804 | -0.26535 | -0.19228 | -0.19465 | -0.33749 | -0.25352 |
| $\bar{E}_{\text {Li, }}(\mathrm{eV})$ | $\begin{gathered} 0.19649 \\ {[3]} \end{gathered}$ | $\begin{gathered} 0.35532 \\ \text { Eq. }(13.458) \\ \hline \end{gathered}$ | $\begin{gathered} 0.10502 \\ {[4]} \end{gathered}$ | $\begin{gathered} 0.10502 \\ {[4]} \\ \hline \end{gathered}$ | $\begin{gathered} 0.21077 \\ {[5]} \\ \hline \end{gathered}$ | $\begin{gathered} 0.14010 \\ {[6]} \end{gathered}$ | $\begin{gathered} 0.14965 \\ {[7]} \\ \hline \end{gathered}$ | $\begin{gathered} 0.12808 \\ {[8]} \end{gathered}$ | $\begin{gathered} 0.46311 \\ {[9-10]} \end{gathered}$ | $\begin{gathered} 0.35532 \\ \text { (Eq. }(13.458)) \end{gathered}$ |
| $\bar{E}_{\text {ck }}(\mathrm{eV})$ | -0.25982 | -0.08364 | -0.12058 | -0.20715 | -0.30266 | -0.19530 | -0.11745 | -0.13061 | -0.10594 | -0.22757 |
| $E_{\text {mag }}(\mathrm{eV})$ | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.11441 | 0.14803 | 0.14803 | 0.14803 | 0.11441 | 0.14803 |
| $E_{r}$ (cimep) (eV) | -49.54347 | - 32.28590 | -33.04742 | -33.70088 | -66.57498 | -33.68903 | -33.61118 | -33.26206 | -31.74130 | -67.92207 |
| $E_{\text {criudu }}(\mathrm{c}$, anmol $)(\mathrm{eV})$ | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -13.6181 | -14.63489 |
|  | 0 | -13.59844 | 0 | 0 | 0 | 0 | 0 | 0 | -13.59844 | -13.59844 |
| $E_{n}\left(\operatorname{mamem}^{\prime}\right)(\mathrm{eV})$ | 5.63881 | 3.90454 | 3.77764 | 4.43110 | 7.80660 | 4.41925 | 4.34141 | 3.99228 | 4.41035 | 12.49186 |

Table 16.5. The total bond energies of salicylic acid and aspirin calculated using the functional group composition and the energies of Table 16.4 .


## CYCLOTRIMETHYLENE-TRINITRAMINE ( $\mathrm{C}_{3} \mathrm{H}_{6} \mathrm{~N}_{6} \mathrm{O}_{6}$ )

The compound cyclotrimethylene-trinitramine, commonly referred to as Cyclonite or by the code designation RDX, is a wellknown explosive. RDX comprises three methylene $\left(\mathrm{CH}_{2}\right)$ groups joined by six alkyl $\mathrm{C}-N$ secondary amine functional groups given in the corresponding section. Each of the three $N$ 's of the six-membered ring shown in Figure 16.2B is bonded to a $\mathrm{NO}_{2}$ functional group given in the Nitroalkanes section by a $N-N$ functional group. The latter requires hybridization of the nitrogen atoms in order to match the energies of the bridged groups.

Similar to the case of carbon, silicon, and aluminum, the bonding in the nitrogen of the $N-N$ functional group involves four $s p^{3}$ hybridized orbitals formed from the outer $2 p$ and $2 s$ shells. In RDX, bonds form between two $N 2 s p^{3} \operatorname{HOs}(N-N$ functional group), between a $N 2 s p^{3} \mathrm{HO}$ and a $C 2 s p^{3} \mathrm{HO}\left(C-N\right.$ functional group), and between a $N 2 s p^{3} \mathrm{HO}$ and a $O 2 p \mathrm{AO}$ (each $\mathrm{N}-\mathrm{O}$ bond of the $\mathrm{NO}_{2}$ functional group). The geometrical and energy equations of the $N-N$ functional group are given in the Derivation of the General Geometrical and Energy Equations of Organic Chemistry section wherein the energy is matched to $E\left(C, 2 s p^{3}\right)=-14.63489 \mathrm{eV}$ (Eq. (15.25)).

The $2 s p^{3}$ hybridized orbital arrangement after Eq. (13.422) is:

$$
\frac{\uparrow}{1,1}
$$

where the quantum numbers $\left(\ell, m_{\ell}\right)$ are below each electron. The total energy of the state is given by the sum over the five electrons. The sum $E_{T}\left(N, 2 s p^{3}\right)$ of experimental energies [15] of $N, N^{+}, N^{2+}, N^{3+}$, and $N^{4+}$ is:

$$
\begin{align*}
E_{T}\left(N, 2 s p^{3}\right) & =-\binom{97.8902 \mathrm{eV}+77.4735 \mathrm{eV}+47.44924 \mathrm{eV}}{+29.6013 \mathrm{eV}+14.53414 \mathrm{eV}}  \tag{16.2}\\
& =-266.94838 \mathrm{eV}
\end{align*}
$$

By considering that the central field decreases by an integer for each successive electron of the shell, the radius $r_{2 s p^{3}}$ of the $N 2 s p^{3}$ shell may be calculated from the Coulombic energy using Eq. (15.13).

$$
\begin{equation*}
r_{2 s p^{3}}=\sum_{n=2}^{6} \frac{(Z-n) e^{2}}{8 \pi \varepsilon_{0}(e 266.94838 \mathrm{eV})}=\frac{15 e^{2}}{8 \pi \varepsilon_{0}(e 266.94838 \mathrm{eV})}=0.76452 a_{0} \tag{16.3}
\end{equation*}
$$

where $Z=7$ for nitrogen. Using Eq. (15.14), the Coulombic energy $E_{\text {Coulomb }}\left(N, 2 s p^{3}\right)$ of the outer electron of the $N 2 s p^{3}$ shell is:

$$
\begin{equation*}
E_{\text {Coulomb }}\left(N, 2 s p^{3}\right)=\frac{-e^{2}}{8 \pi \varepsilon_{0} r_{2 s p^{3}}}=\frac{-e^{2}}{8 \pi \varepsilon_{0} 0.76452 a_{0}}=-17.79656 \mathrm{eV} \tag{16.4}
\end{equation*}
$$

In RDX, the $C 2 s p^{3} \mathrm{HO}$ has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of $E\left(C, 2 s p^{3}\right)=-14.63489 \mathrm{eV}$ (Eq. (15.25)), and the $N \mathrm{HO}$ has an energy of $E\left(N, 2 s p^{3}\right)=-17.79656 \mathrm{eV}$ (Eq. (16.4)). To meet the equipotential, minimum-energy condition of the union of the $N 2 s p^{3}$ and $C 2 s p^{3} \mathrm{HOs}, C_{2}=1$ in Eqs. (15.2-15.5), (15.51), and (15.61) for the $N-N$-bond MO, and $c_{2}$ given by Eqs. (15.77) and (15.79) is:

$$
\begin{equation*}
c_{2}\left(C 2 s p^{3} \mathrm{HO} \text { to } N_{b} 2 s p^{3} \mathrm{HO} \text { to } N_{a} 2 s p^{3} \mathrm{HO}\right)=\frac{E\left(C, 2 s p^{3}\right)}{E\left(N, 2 s p^{3}\right)} c_{2}\left(C 2 s p^{3} \mathrm{HO}\right)=\frac{-14.63489 \mathrm{eV}}{-17.79656 \mathrm{eV}}(0.91771)=0.75468 \tag{16.5}
\end{equation*}
$$

The energy of the $N-N$-bond MO is the sum of the component energies of the $H_{2}$-type ellipsoidal MO given in Eq. (15.51). Since the energy of the MO is matched to that of the $C 2 s p^{3} \mathrm{HO}, E(A O / H O)$ in Eqs. (15.51) and (15.61) is: $E\left(C, 2 s p^{3}\right)=-14.63489 \mathrm{eV}$ given by Eq. (15.25) and $E_{T}\left(\right.$ atom-atom, $\left.m s p^{3} . A O\right)$ is 0 eV .

The symbols of the functional groups of RDX are given in Table 16.7. 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 RDX are given in Tables 16.8, 16.9 , and 16.10 , respectively. The total energy of RDX given in Table 16.11 was calculated as the sum over the integer multiple of each $E_{D}$ (Group) of Table 16.10 corresponding to functional-group composition of the molecule. The bond angle parameters of RDX determined using Eqs. (15.88-15.117) are given in Table 16.12. The color scale charge density of RDX 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 16.2A.

Figure 16.2. (A) Color scale charge density of RDX showing the outer orbitals of the atoms at their radii and the ellipsoidal surface of each H or $\mathrm{H}_{2}$-type ellipsoidal MO that transitions to the corresponding outer shell of the atom(s) participating in each bond. (B) Chemical structure and atom designation of RDX.
A

B


$$
0 \square 1 \mathrm{e} / \AA^{2}
$$

Table 16.7. The symbols of functional groups of RDX.

|  | Functional Group |
| :--- | :--- |
| $\mathrm{NO}_{2}$ group | Group Symbol |
| $\mathrm{N}-\mathrm{N}$ | NO |
| $\mathrm{C}-\mathrm{N}$ (alkyl) | $\mathrm{N}-\mathrm{N}$ |
| $\mathrm{CH}_{2}$ group | $\mathrm{C}-\mathrm{H}\left(\mathrm{CH}_{2}\right)$ |

Table 16.8. The geometrical bond parameters of RDX and experimental values [1].
\(\left.$$
\begin{array}{|c|c|c|c|c|}\hline \text { Parameter } & \begin{array}{c}\mathrm{NO}_{2} \\
\text { Group }\end{array} & \begin{array}{c}\mathrm{N-N} \\
\text { Group }\end{array} & \begin{array}{c}\mathrm{C}-\mathrm{N} \\
\text { Group }\end{array} & \begin{array}{c}\mathrm{C}-\mathrm{H}\left(\mathrm{CH}_{2}\right) \\
\text { Group }\end{array} \\
\hline a\left(a_{0}\right) & 1.33221 & 1.68711 & 1.94862 & 1.67122 \\
\hline c^{\prime}\left(a_{0}\right) & 1.15421 & 1.29889 & 1.39593 & 1.05553 \\
\hline \begin{array}{c}\text { Bond Length } \\
2 c^{\prime}(A)\end{array} & 1.22157 & 1.37468 & 1.47739 & 1.11713 \\
\hline \text { Exp. Bond Length } & \begin{array}{c}1.224 \\
\text { (nitromethane) } \\
1.22 \text { avg. [16] } \\
\text { (RDX) }\end{array} & \begin{array}{c}1.390[16] \\
\text { (RDX) }\end{array} & \begin{array}{c}1.468[16] \\
\text { (RDX) }\end{array} & \begin{array}{c}(C-H \text { propane) } \\
1.117 \\
\text { butane) }\end{array}
$$ <br>
\hline b, c\left(a_{0}\right) \& 0.66526 \& 1.07668 \& 1.092[16] <br>

(RDX)\end{array}\right]\)| 1.35960 |
| :---: |

Table 16.9. The MO to HO intercept geometrical bond parameters of RDX. $E_{T}$ is $E_{T}$ (atom-atom,msp ${ }^{3} . A O$ ).

| Bond | Atom |  |  | $E_{T}$ $(\mathrm{cV})$ Bond 3 |  | Final Total Energy $C 2 s p^{3}$ $(\mathrm{eV})$ | $\begin{aligned} & r_{\text {miniol }} \\ & \left(a_{0}\right) \end{aligned}$ | $\begin{aligned} & r_{\text {fiaw }} \\ & \left(a_{0}\right) \end{aligned}$ | $\begin{gathered} E_{\text {Cointiont }}(\mathrm{eV}) \\ \text { Final } \end{gathered}$ | $\begin{gathered} E\left(C 2 s p^{3}\right) \\ (\mathrm{eV}) \\ \text { Final } \end{gathered}$ | $\begin{aligned} & 0^{\prime} \\ & \left({ }^{\circ}\right) \end{aligned}$ | $\begin{aligned} & \hline 0_{1} \\ & \left({ }^{\circ}\right) \end{aligned}$ | $\begin{aligned} & O_{2} \\ & \left({ }^{\circ}\right) \end{aligned}$ | $\begin{gathered} d_{1} \\ \left(a_{0}\right) \end{gathered}$ | $\begin{gathered} d_{2} \\ \left(a_{0}\right) \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $N_{6} N_{s}(O)=O$ | $O_{0}$ | -0.92918 | 0 | 0 | 0 |  | 1.00000 | 0.86359 | -15.75493 |  | 135.25 | 44.75 | 66.05 | 0.54089 | 0.61333 |
| $N_{b}, N_{a}(O)=O$ | $N_{o}$ | -0.92918 | -0.92918 | 0 | 0 |  | 0.93084 | 0.81549 | -16.68411 |  | 133.16 | 46.84 | 63.41 | 0.59640 | 0.55781 |
| $\mathrm{CH}_{2} \mathrm{~N}_{\mathrm{b}}-\mathrm{N}_{s} \mathrm{O}_{2}$ | $N_{s}$ | -0.92918 | -0.92918 | 0 | 0 |  | 0.93084 | 0.81549 | -16.68411 |  | 101.80 | 78.20 | 47.85 | 1.13213 | 0.16676 |
| $\mathrm{CH}_{2} \mathrm{~N}_{\mathrm{b}}-\mathrm{N}_{e} \mathrm{O}_{2}$ | $N_{\text {b }}$ | -0.56690 | -0.56690 | 0 | 0 |  | 0.93084 | 0.85252 | -15.95954 |  | 104.60 | 75.40 | 50.02 | 1.08404 | 0.21485 |
| $\mathrm{C}-\mathrm{H}\left(\mathrm{CH}_{2}\right)$ | $C_{0}$ | -0.56690 | $-0.56690$ | 0 | 0 | -152.74948 | 0.91771 | 0.85252 | -15.95954 | -15.76868 | 73.60 | 106.40 | 39.14 | 1.29624 | 0.24071 |
| $-\mathrm{H}_{2} \mathrm{C}_{\mathrm{a}}-\mathrm{N}_{0} \mathrm{~N}_{\mathrm{a}}$ | $N_{6}$ | -0.56690 | -0.56690 | 0 | 0 |  | 0.93084 | 0.85252 | -15.95954 |  | 80.95 | 99.05 | 38.26 | 1.53008 | 0.13415 |
| $-\mathrm{H}_{2} \mathrm{C}_{\alpha}-\mathrm{N}_{\prec} \mathrm{N}_{\alpha}$ | $C_{o}$ | -0.56690 | -0.56690 | 0 | 0 | -152.74948 | 0.91771 | 0.85252 | -15.95954 | -15.76868 | 80.95 | 99.05 | 38.26 | 1.53008 | 0.13415 |

Table 16.10. The energy parameters ( eV ) of functional groups of RDX.

| Parameters | $\mathrm{NO}_{2}$ <br> Group | $\begin{aligned} & N-N \\ & \text { Group } \end{aligned}$ | $\begin{aligned} & C-N \\ & \text { Group } \end{aligned}$ | $\mathrm{CH}_{2}$ <br> Group |
| :---: | :---: | :---: | :---: | :---: |
| $n_{1}$ | 2 | 1 | 1 | 2 |
| $n_{2}$ | 0 | 0 | 0 | 1 |
| $n_{3}$ | 0 | 0 | 0 | 0 |
| $C_{1}$ | 0.5 | 0.5 | 0.5 | 0.75 |
| $\mathrm{C}_{2}$ | 1 | 1 | 1 | 1 |
| $c_{1}$ | 1 | 1 | 1 | 1 |
| $c_{2}$ | 0.85987 | 0.75468 | 0.91140 | 0.91771 |
| $c_{3}$ | 0 | 0 | 0 | 1 |
| $c_{4}$ | 4 | 2 | 2 | 1 |
| $c_{5}$ | 0 | 0 | 0 | 2 |
| $C_{10}$ | 0.5 | 0.5 | 1 | 0.75 |
| $C_{2 o}$ | 1 | 1 | 1 | 1 |
| $V_{e}(e \mathrm{~V})$ | -106.90919 | -32.25503 | -31.98456 | -70.41425 |
| $V_{p}(e V)$ | 23.57588 | 10.47496 | 9.74677 | 25.78002 |
| $T(\mathrm{eV})$ | 40.12475 | 9.55926 | 8.20698 | 21.06675 |
| $V_{m}(\mathrm{eV})$ | -20.06238 | -4.77963 | -4.10349 | -10.53337 |
| $E($ Ао/но) $(\mathrm{eV})$ | 0 | -14.63489 | -14.63489 | -15.56407 |
| $\Delta E_{\mathrm{H}_{2} \mathrm{MO}}\left(\right.$ АО/ $^{\text {HO) }}$ ) $(\mathrm{eV})$ | 0 | 0 | -1.13379 | 0 |
| $E_{T}($ Ао/Но) $)(\mathrm{eV})$ | 0 | -14.63489 | -13.50110 | -15.56407 |
| $E_{T}\left(\mathrm{H}_{2} \mathrm{MO}\right)(\mathrm{eV})$ | -63.27093 | -31.63533 | -31.63540 | -49.66493 |
| $E_{T}\left(\right.$ atom-atom, $\left.\mathrm{msp}^{3} . \mathrm{AO}\right)(\mathrm{eV})$ | -3.71673 | 0 | -1.13379 | 0 |
| $E_{T}(\mathrm{mo})(\mathrm{eV})$ | -66.98746 | -31.63537 | -32.76916 | -49.66493 |
| $\omega\left(10^{15} \mathrm{rad} / \mathrm{s}\right)$ | 19.0113 | 26.1663 | 26.0778 | 24.2751 |
| $E_{K}(\mathrm{eV})$ | 12.51354 | 17.22313 | 17.16484 | 15.97831 |
| $\bar{E}_{D}(e V)$ | -0.23440 | -0.25974 | -0.26859 | -0.25017 |
| $\bar{E}_{\text {Kvib }}(e \mathrm{eV})$ | $\begin{gathered} 0.19342 \\ {[17]} \\ \hline \end{gathered}$ | $\begin{gathered} 0.12770 \\ {[18]} \\ \hline \end{gathered}$ | $\begin{gathered} 0.11159 \\ {[19]} \\ \hline \end{gathered}$ | $\begin{gathered} 0.35532 \\ \text { (Eq. }(13.458) \text { ) } \end{gathered}$ |
| $\bar{E}_{\text {osc }}(\mathrm{eV})$ | -0.13769 | -0.19588 | -0.21280 | -0.14502 |
| $E_{\text {mag }}(\mathrm{eV})$ | 0.11441 | 0.14803 | 0.14803 | 0.14803 |
| $E_{T}($ Group $)(\mathrm{eV})$ | -67.26284 | -31.83125 | -32.98196 | -49.80996 |
| $E_{\text {initial }}\left(c_{4}\right.$ AO/HO) $(\mathrm{eV})$ | -14.63489 | -14.63489 | -14.63489 | -14.63489 |
| $E_{\text {initial }}\left(c_{s}\right.$ АО/но) $(\mathrm{eV})$ | 0 | 0 | 0 | -13.59844 |
| $E_{D}($ Group $)(\mathrm{eV})$ | 8.72329 | 2.56147 | 3.71218 | 7.83016 |
| Exp. $E_{D}($ Group $)(\mathrm{eV})$ |  | Est. 2.86, 2.08 [20] | 3.69 [20] |  |

Table 16.11. The total bond energy of gaseous-state RDX calculated using the functional group composition and the energies of Table 16.10.

| Formula | Name | $N_{2}$ <br> Group | $N-N$ <br> Group | $\mathrm{C}-N$ <br> Group | $\mathrm{CH}_{2}$ <br> Group | Calculated <br> Total Bond <br> Energy $(\mathrm{eV})$ | Experimental <br> Total Bond <br> Energy (eV) | Relative <br> Error |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{C}_{3} \mathrm{H}_{6} \mathrm{~N}_{6} \mathrm{O}_{6}$ | RDX | 3 | 3 | 6 | 3 | 79.61783 |  |  |

Table 16.12. The bond angle parameters of RDX and experimental values [1]. $E_{T}$ is $E_{T}$ (atom-atom, $m s p^{3} . A O$ ).

| $\begin{gathered} \text { Atoms of } \\ \text { Angle } \end{gathered}$ | $\begin{gathered} 2 c^{\prime} \\ \text { Bond } 1 \\ \left(a_{0}\right) \end{gathered}$ | $\begin{array}{c\|} \hline 2 c^{\prime} \\ \text { Bond } 2\left(a_{0}\right) \end{array}$ |  | $E_{\text {Coutanto }}$ Atom I | Atom 1 Hybridization Designation (Table 15.3 | $E_{\text {Cantantic }}$ Atom 2 | Atom 2 Hybridization Designation (Table 15.3 $)$ | $\begin{gathered} c_{2} \\ \text { Atom } 1 \end{gathered}$ | $\begin{gathered} c_{2} \\ \text { Atom } 2 \end{gathered}$ | $C_{1}$ | $C_{2}$ | $c_{1}$ | $c_{2}^{\prime}$ | $\begin{gathered} E_{T} \\ (\mathrm{eV}) \end{gathered}$ | $\begin{array}{\|l\|l} \theta_{r} \\ \left({ }^{\circ}\right) \end{array}$ | $\begin{array}{\|c\|} \hline \theta_{1} \\ \left({ }^{\circ}\right) \end{array}$ | $\begin{array}{\|c\|} \hline \theta_{2} \\ \left({ }^{\circ}\right) \end{array}$ | $\begin{gathered} \text { Cal. } \theta \\ \left({ }^{\circ}\right) \end{gathered}$ | $\text { Exp. } \theta$ $\left({ }^{\circ}\right)$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\angle \mathrm{O}_{a} \mathrm{NO}_{3}$ | 2.30843 | 2.30843 | 4.1231 | $\begin{array}{c\|} \hline-16.68411 \\ O_{a} \\ \hline \end{array}$ | 25 | $\begin{gathered} -16.68411 \\ O_{k} \\ \hline \end{gathered}$ | 25 | 0.81549 | 0.81549 | 1 | 1 | 1 | 0.81549 | -1.44915 |  |  |  | 126.52 | $\begin{gathered} 125.3 \\ \text { (nitromethane) } \\ \hline \end{gathered}$ |
| $\angle N_{b} N_{0} O_{0}$ | 2.59778 | 2.27630 | 4.0988 | $\begin{gathered} \hline-17.79656 \\ N_{b} \\ \text { (Eq. (16.4)) } \end{gathered}$ |  | $\begin{gathered} -13.61806 \\ O_{o} \end{gathered}$ |  | $\begin{gathered} 0.75468 \\ \text { (Eq. (16.5)) } \end{gathered}$ | $\begin{gathered} 0.85987 \\ \text { (Eq. }(15.159) \text { ) } \end{gathered}$ | 1 | 1 | 1 | 0.80727 | -1.44915 |  |  |  | 114.32 | 116.8 [16] (RDX) |
| $\angle C N_{b} N_{\text {a }}$ | 2.79186 | 2.59778 | 4.5826 | -16.32183 | 17 | -14.53414 |  | 0.83360 | $\begin{gathered} 0.91140 \\ \text { (Eq. (15.135)) } \end{gathered}$ | 1 | 1 | 1 | 0.87250 | -1.44915 |  |  |  | 116.43 | ${ }^{116.6[16]}$ (RDX) |
| $\angle C N C$ | 2.79186 | 2.79186 | 4.6260 | -17.04640 | 33 | -17.04640 | 33 | 0.79816 | 0.79816 | 1 | 1 | 1 | 0.79816 | -1.85836 |  |  |  | 111.89 | $\begin{array}{\|c} 111.8 \\ \text { (dimethylamine) } \end{array}$ |
| Methylene $\angle H C_{\theta} H$ | 2.11106 | 2.11106 | 3.4252 | $-15.75493$ | 7 | H | H | 0.86359 | 1 | 1 | 1 | 0.75 | 1.15796 | 0 |  |  |  | 108.44 | $\begin{gathered} 107 \\ \text { (propane) } \end{gathered}$ |
| $\angle H C N$ | 2.09711 | 2.79186 | 4.0661 | -14.82575 | 1 | -14.53414 | N | 0.91771 | $\begin{gathered} 0.93383 \\ \text { (Eq. (15.136)) } \end{gathered}$ | 0.75 | 1 | 0.75 | 1.01756 | 0 |  |  |  | 111.76 | $\begin{gathered} 112 \\ \text { (dimethylamine) } \end{gathered}$ |

## SODIUM HYDRIDE MOLECULE ( $N a H$ )

Alkali hydride molecules each comprising an alkali metal atom and a hydrogen atom can be solved using similar principles and procedures as those used to solve organic molecules. The solutions of these molecules can be conveniently obtained by using generalized forms of the force balance equation given in the Force Balance of the $\sigma \mathrm{MO}$ of the Carbon Nitride Radical section and the geometrical and energy equations given in the Derivation of the General Geometrical and Energy Equations of Organic Chemistry section.

The bonding in the sodium atom involves the outer $3 s$ atomic orbital (AO), and the $N a-H$ bond forms between the $N a 3 s \mathrm{AO}$ and the $H 1 s \mathrm{AO}$. The energy of the reactive outer electron of the sodium atom is significantly less than the Coulombic energy between the electron and proton of $H$ given by Eq. (1.276). Consequently, the outer electron comprising the $N a 3 s \mathrm{AO}$ and the $H 1 s$ AO form a $\sigma-\mathrm{MO}$, and the inner AOs of $N a$ remain unaltered. The MO semimajor axis of molecular sodium hydride is determined from the force balance equation of the centrifugal, Coulombic, and magnetic forces as given in the Polyatomic Molecular Ions and Molecules section and the More Polyatomic Molecules and Hydrocarbons section. Then, the geometric and energy parameters of the MO are calculated using Eqs. (15.1-15.117) wherein the distance from the origin of the $H_{2}$-type-ellipsoidal-MO to each focus $c^{\prime}$, the internuclear distance $2 c^{\prime}$, and the length of the semiminor axis of the prolate spheroidal $H_{2}$-type MO $b=c$ are solved from the semimajor axis $a$.

The force balance of the centrifugal force equated to the Coulombic and magnetic forces is solved for the length of the semimajor axis. The Coulombic force on the pairing electron of the MO is:

$$
\begin{equation*}
\mathbf{F}_{\text {Coulomb }}=\frac{e^{2}}{8 \pi \varepsilon_{0} a b^{2}} D \mathbf{i}_{\xi} \tag{16.6}
\end{equation*}
$$

The spin pairing force is

$$
\begin{equation*}
\mathbf{F}_{\text {spin-pairing }}=\frac{\hbar^{2}}{2 m_{e} a^{2} b^{2}} D \mathbf{i}_{\xi} \tag{16.7}
\end{equation*}
$$

The diamagnetic force is:

$$
\begin{equation*}
\mathbf{F}_{\text {diamagneticMO1 }}=-\frac{n_{e} \hbar^{2}}{4 m_{e} a^{2} b^{2}} D \mathbf{i}_{\xi} \tag{16.8}
\end{equation*}
$$

where $n_{e}$ is the total number of electrons that interact with the binding $\sigma$-MO electron. The diamagnetic force $\mathbf{F}_{\text {diamagneticMO2 }}$ on the pairing electron of the $\sigma$ MO is given by the sum of the contributions over the components of angular momentum:

$$
\begin{equation*}
\mathbf{F}_{\text {diamagneticMO2 }}=-\sum_{i, j} \frac{\left|L_{i}\right| \hbar}{Z_{j} 2 m_{e} a^{2} b^{2}} D \mathbf{i}_{\xi} \tag{16.9}
\end{equation*}
$$

where $|L|$ is the magnitude of the angular momentum of each atom at a focus that is the source of the diamagnetism at the $\sigma$ MO. The centrifugal force is:

$$
\begin{equation*}
\mathbf{F}_{\text {centrifugalMO }}=-\frac{\hbar^{2}}{m_{e} a^{2} b^{2}} D \mathbf{i}_{\xi} \tag{16.10}
\end{equation*}
$$

The force balance equation for the $\sigma$-MO of the $N a-H$-bond MO with $n_{e}=2$ and $|L|=\left(2+\sqrt{\frac{3}{4}}\right) \hbar$ is:

$$
\begin{align*}
& \frac{\hbar^{2}}{m_{e} a^{2} b^{2}} D=\frac{e^{2}}{8 \pi \varepsilon_{0} a b^{2}} D+\frac{\hbar^{2}}{2 m_{e} a^{2} b^{2}} D-\left(\frac{2}{2}+\frac{2}{Z}+\frac{\sqrt{\frac{3}{4}}}{Z}\right) \frac{\hbar^{2}}{2 m_{e} a^{2} b^{2}} D  \tag{16.11}\\
& a=\left(2+\frac{2}{Z}+\frac{\sqrt{\frac{3}{4}}}{Z}\right) a_{0} \tag{16.12}
\end{align*}
$$

With $Z=11$, the semimajor axis of the $N a-H$-bond MO is:

$$
\begin{equation*}
a=2.26055 a_{0} \tag{16.13}
\end{equation*}
$$

Using the semimajor axis, 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 the Organic Molecular Functional Groups and Molecules section. For the $\mathrm{Na}-\mathrm{H}$-bond MO of the $\mathrm{NaH}, c_{1}=1, c_{2}=1$ and $C_{2}=1$ in both the geometry relationships (Eqs. (15.2-15.5)) and the energy equation (Eq. (15.61)). In NaH the molecule, the Na 3 s AO has an energy of $E(N a 3 s)=-5.139076 \mathrm{eV}$ [15] and the $H$ AO has an energy of $E(H)=-13.59844 \mathrm{eV}$ [15]. To meet the equipotential condition of the union of the Na3s AO and the $H 1 s$ AO, $c_{2}$ and $C_{2}$ of Eqs. (15.2-15.5) and Eq. (15.61) for the $N a-H$-bond MO given by Eq. (15.77) is:
$C_{2}(\mathrm{Na3s} A O$ to H 1 s AO$)=c_{2}(\mathrm{Na3s} A O$ to H 1 s AO$)=\frac{-5.139076 \mathrm{eV}}{-13.59844 \mathrm{eV}}=0.37792$
The energy of the MO is matched to that of the $N a 2 p \mathrm{AO}$ with which it intersects such that $E(A O / H O)$ is $E(N a 2 p)=-47.2864 \mathrm{eV} \quad[15]$; thus, $E_{\text {initial }}\left(c_{4} A O / H O\right)(e V)$ is given by the sum of $E(N a 2 p)=-47.2864 \mathrm{eV}$ and $E(N a 3 s)=-5.139076 \mathrm{eV}$.

The symbol of the functional group of molecular NaH is given in Table 16.13. The geometrical (Eqs. (15.1-15.5) and (16.11-16.14)), intercept (Eqs. (15.80-15.87)), and energy (Eqs. (15.61-15.65) and (16.13-16.14)) parameters of molecular NaH are given in Tables 16.14, 16.15, and 16.16, respectively. The color scale, translucent view of the charge-densities of molecular NaH comprising the concentric shells of the inner AOs of the $N a$ atom and an outer MO formed from the outer Na3s AO and the $H 1 s$ AO are shown in Figure 16.3.

Figure 16.3. Color scale, translucent view of the charge-densities of molecular NaH showing the inner orbitals of the Na atom at their radii, the ellipsoidal surface of the $H_{2}$-type ellipsoidal MO formed from the outer Na3s AO and the $H 1 s \mathrm{AO} H$, and the hydrogen nucleus (red, not to scale).


Table 16.13. The symbol of the functional group of molecular $N a H$.

|  | Functional Group |
| :--- | :---: |
| $N a H$ group | $N a-H$ |

Table 16.14. The geometrical bond parameters of molecular $N a H$ and experimental values [20].

| Parameter | $N a-H$ <br> Group |
| :--- | :---: |
| $a\left(a_{0}\right)$ | 2.26055 |
| $c^{\prime}\left(a_{0}\right)$ | 1.72939 |
| Bond Length $2 c^{\prime}(\AA)$ | 1.83031 |
| Exp. Bond Length <br> $(\AA)$ | 1.88654 <br> $(N a H)$ |
| $b, c\left(a_{0}\right)$ | 1.45577 |
| $e$ | 0.76503 |

Table 16.15. The MO to $N a 2 p$ AO intercept geometrical bond parameters of $N a H . E_{T}$ is $E_{T}\left(\right.$ atom -atom, $\left.m s p^{3} . A O\right)$.

| Bond | Atom | $\begin{gathered} E_{T} \\ (\mathrm{cV}) \\ \text { Bond } 1 \end{gathered}$ | $\begin{gathered} E_{\tau} \\ (\mathrm{cV}) \\ \text { Bond 2 } \end{gathered}$ | $\begin{gathered} E_{T} \\ (\mathrm{cV}) \\ \text { Bond 3 } \end{gathered}$ | $\begin{gathered} E_{r} \\ (\mathrm{cV}) \\ \text { Bond } 4 \end{gathered}$ | Final Total Energy Na2p (eV) | $\begin{aligned} & r_{\text {monad }} \\ & \left(a_{0}\right) \end{aligned}$ | $\begin{aligned} & r_{\text {fout }} \\ & \left(a_{0}\right) \end{aligned}$ | $\begin{gathered} E_{\text {Coulomb }}(\mathrm{Na}(\mathrm{Na} p) \\ \text { (cV) } \\ \text { Final } \end{gathered}$ | $\begin{gathered} E(\mathrm{Na2p}) \\ (\mathrm{cV}) \\ \text { Final } \end{gathered}$ | $\begin{aligned} & \theta^{\prime} \\ & \left({ }^{\circ}\right) \end{aligned}$ | $\begin{aligned} & \theta_{1} \\ & \left({ }^{\circ}\right) \end{aligned}$ | $\begin{aligned} & \theta_{2} \\ & \left({ }^{\circ}\right) \end{aligned}$ | $\begin{gathered} d_{1} \\ \left(a_{0}\right) \end{gathered}$ | $\begin{gathered} d_{2} \\ \left(a_{0}\right) \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{Na}-\mathrm{H}(\mathrm{NaH})$ | Na | 0 | 0 | 0 | 0 |  | 2.65432 | 0.56094 |  | -47.2864 | 28.66 | 151.34 | 10.65 | 2.22161 | 0.49221 |

Table 16.16. The energy parameters $(\mathrm{eV})$ of the $\mathrm{Na}-\mathrm{H}$ functional group of molecular NaH .

| Parameters | $N a-H$ Group |
| :---: | :---: |
| $n_{1}$ | 1 |
| $n_{2}$ | 0 |
| $n_{3}$ | 0 |
| $C_{1}$ | 0.37792 |
| $C_{2}$ | 1 |
| $c_{1}$ | 1 |
| $c_{2}$ | 1 |
| $c_{3}$ | 0 |
| $c_{4}$ | 1 |
| $c_{5}$ | 1 |
| $C_{1}$ o | 0.37792 |
| $C_{2 o}$ | 1 |
| $V_{e}(\mathrm{eV})$ | -31.72884 |
| $V_{p}(\mathrm{eV})$ | 7.86738 |
| $T(\mathrm{eV})$ | 7.01795 |
| $V_{m}(\mathrm{eV})$ | -3.50898 |
| $E$ (АоІно) (eV) | -47.2864 |
| $\Delta E_{\mathrm{H}_{2} \mathrm{MO}}($ АОІНО) $(\mathrm{eV})$ | 0 |
| $E_{T}($ Ао/ $/ \mathrm{O})(\mathrm{eV})$ | -47.2864 |
| $E_{T}\left(\mathrm{H}_{2} \mathrm{MO}\right)(\mathrm{eV})$ | -67.63888 |
| $E_{T}\left(\right.$ atom-atom, $\left.\mathrm{msp}^{3} . \mathrm{AO}\right)(\mathrm{eV})$ | 0 |
| $E_{T}(\mathrm{mo})(\mathrm{eV})$ | -67.63888 |
| $\omega\left(10^{15} \mathrm{rad} / \mathrm{s}\right)$ | 14.4691 [20] |
| $E_{K}(\mathrm{eV})$ | 9.52384 |
| $\bar{E}_{D}(e V)$ | -0.41296 |
| $\bar{E}_{\text {Kvib }}(\mathrm{eV})$ | 0.14534 |
| $\bar{E}_{\text {osc }}(\mathrm{eV})$ | -0.34029 |
| $E_{\text {mag }}(\mathrm{eV})$ | 0.11441 |
| $E_{T}($ Group $)(\mathrm{eV})$ | -67.97917 |
| $E_{\text {initial }}\left(c_{4}\right.$ АО/Но) $(\mathrm{eV})$ | -52.425476 |
| $E_{\text {initial }}\left(c_{5}\right.$ AO/HO) $(\mathrm{eV})$ | -13.59844 |
| $E_{D}($ Group $)(e V)$ | 1.95525 |
| Exp. $E_{D}($ Group $)(e V)$ | 1.92451 ( $\mathrm{Na}-\mathrm{H}$ [21]) |

## BOND AND DIPOLE MOMENTS

The bond moment of a functional group may be calculated by considering the charge donation between atoms of the functional group. 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 charges at the separation distance, the internuclear distance.

Using the reciprocal relationship between the orbital energies and radii, the dependence of the orbital area on the radius squared, and the relationship of the partial charge $q$ to the areas with energy matching for each electron of the MO, the bond moment $\mu$ along the internuclear axis of $A-B$ wherein $A$ is the net positively-charged atom is given by:

$$
\begin{equation*}
\mu=q d=n_{1} c e\left(1-\left(\frac{E_{A}(\text { valence })}{E_{B}(\text { valence })}\right)^{2}\right) 2 c^{\prime} \tag{16.15}
\end{equation*}
$$

wherein $n_{1}$ is the number of equivalent bonds of the MO, $c$ is energy-matching factor such as $c_{1}, c_{2}, C_{1}$, or $C_{2}$ of Eqs. (15.51) and (15.61) where $c_{1}$ and $C_{2}$ may correspond to both electrons of a MO localized on one AO or HO such as when the magnitude of the valence or Coulombic energy of the AO or HO is less than that of $E_{\text {Coulomb }}(H)=-13.605804 \mathrm{eV}$ or when the orbital may contain paired or shared electrons in a linear combination with the partner orbital, and $d$ is the charge-separation distance, the internuclear distance $2 c^{\prime} . E_{B}$ (valence) is the initial matched energy of the resultant net negatively-charged orbital of the bond that is further lowered by bonding (Eqs. (15.32) and (15.16)) to atom $A$ having an energy $E_{A}$ (valence). Typically, $E_{B}$ (valence) of a carbon-heteroatom bond is -14.63489 eV , the initial $C 2 s p^{3} \mathrm{HO}$ (Eq. (15.25)) energy to which the heteroatom is energy matched. Functional group bond moments determined using Eq. (16.15) are given in Table 16.17.

Table 16.17. The bond moments of functional groups compared to experimental values [22-87] wherein the parameters correspond to those given previously except as indicated.

| Functional Group ${ }^{\mathrm{a}}$ | $n_{1}$ | $\left(c_{1}\right) c_{2}$ | $\left(C_{1}\right) C_{2}$ | $E_{B}($ valence $)$ | $E_{A}($ valence $)$ | $\underline{q}$ | Bond <br> Length <br> $2 c^{\prime}(A)$ | Bond <br> Moment <br> $\mu(\mathrm{D})$ | Exp. Bond <br> Moment <br> $\mu(\mathrm{D})$ |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $H-C$ (alkyl) | 1 | 0.91771 | 1 | 14.63489 | 15.35946 | 0.070 | 1.11713 | 0.37 | 0.4 |
| $H-C$ (aromatic) | 1 | 0.91771 | 1 | 15.95955 | 15.95955 | 0 | 1.09327 | 0 | 0 |
| $H-N^{\mathrm{b}}$ (amine) | 1 | 0.78896 | 1 | 13.59844 | 15.81768 | 0.279 | 1.00343 | 1.34 | 1.31 |
| $H-N^{\mathrm{c}}$ (ammonia) | 1 | 0.74230 | 1 | 13.59844 | 15.81768 | 0.262 | 1.03677 | 1.30 | 1.31 |
| $H-O^{\mathrm{d}}$ (alcohol) | 1 | 0.91771 | 1 | 13.59844 | 15.81768 | 0.324 | 0.97165 | 1.51 | 1.51 |
| $H-O^{\mathrm{e} \text { (water) }}$ | 1 | 0.91419 | 1 | 13.59844 | 15.81768 | 0.323 | 0.97157 | 1.51 | 1.51 |
| $C-N$ | 1 | 0.91140 | 1 | 14.53414 | 14.82575 | 0.037 | 1.46910 | 0.26 | 0.22 |
| $C-O$ | 1 | 0.85395 | 1 | 14.63489 | 15.56407 | 0.112 | 1.41303 | 0.76 | 0.74 |
| $C-F^{\mathrm{f}}$ | 1 | 1.09254 | 1 | 14.63489 | 15.98435 | 0.211 | 1.38858 | 1.41 | 1.41 |
| $C-C l$ | 1 | 1 | $(2) 0.81317$ | 14.63489 | 15.35946 | 0.165 | 1.79005 | 1.42 | 1.46 |
| $C-B r$ | 1 | 1 | $(2) 0.74081$ | 14.63489 | 15.35946 | 0.150 | 1.93381 | 1.40 | 1.38 |
| $C-I \mathrm{~b}$ | 1 | 1 | $(2) 0.65537$ | 14.63489 | 15.28545 | 0.119 | 2.13662 | 1.22 | 1.19 |
| $C=O$ | 2 | 0.85395 | 1 | 14.63489 | 16.20002 | 0.385 | 1.20628 | 2.23 | 2.3 |
| $C \equiv N$ | 3 | 0.91140 | 1 | 14.63489 | 16.20002 | 0.616 | 1.16221 | 3.44 | 3.5 |
| $H-S^{\mathrm{h}}$ | 1 | 0.69878 | 1 | 14.63489 | 15.81768 | 0.118 | 1.34244 | 0.76 | 0.69 |
| $C-S$ | 1 | 1 | 0.91771 | 14.63489 | 15.35946 | 0.093 | 1.81460 | 0.81 | 0.9 |
| $S-O$ | 1 | 1 | 0.77641 | 14.63489 | 15.76868 | 0.125 | 1.56744 | 0.94 | 1.0 |
| $S=O^{\mathrm{i}}$ | 2 | 0.82897 | 1 | 10.36001 | 11.57099 | 0.410 | 1.49118 | 2.94 | 2.93 |
| $N-O$ | 1 | 1.06727 | 1 | 14.53414 | 14.82575 | 0.043 | 1.40582 | 0.29 | 0.30 |
| $N=O$ (nitro) | 2 | 0.91140 | 1 | 14.63489 | 15.95955 | 0.345 | 1.22157 | 2.02 | 2.01 |
| $C-P$ | 1 | 1 | 0.73885 | 14.63489 | 15.35946 | 0.075 | 1.86534 | 0.67 | 0.69 |
| $P-O$ | 1 | 0.79401 | 1 | 14.63489 | 15.35946 | 0.081 | 1.61423 | 0.62 | 0.60 |
| $P=O^{\mathrm{j}}$ | 2 | 1.25942 | 1 | 14.63489 | 15.76868 | 0.405 | 1.46521 | 2.85 | 2.825 |
| $S i-H$ | 1 | 1 | 0.75800 | 10.25487 | 11.37682 | 0.131 | 1.48797 | 0.94 | 0.99 |
| $S i-C$ | 1 | 1 | 0.70071 | 14.63489 | 15.35946 | 0.071 | 1.87675 | 0.64 | 0.60 |
| $S i-O^{\mathrm{k}}$ | 1 | 1 | 1.32796 | 10.25487 | 10.87705 | 0.166 | 1.72480 | 1.38 | 1.38 |
| $B-H^{1}$ | 1 | 1 | 11.80624 | 12.93364 | 0.172 | 1.20235 | 0.99 | 1.0 |  |
| $B-C$ | 1 | 1 | 0.80672 | 1 | 14.63489 | 15.35946 | 0.082 | 1.57443 | 0.62 |
| $B-O$ (alkoxy) | 1 | 1 | 0.79562 | 11.80624 | 12.93364 | 0.159 | 1.37009 | 1.05 | 0.69 |
| $B-N$ | 1 | 1 | 0.81231 | 11.89724 | 14.53414 | 0.400 | 1.36257 | 2.62 | 2.68 |
| $B-F^{\mathrm{m}}$ | 1 | 0.85447 | 1 | 14.88734 | 17.42282 | 0.316 | 1.29621 | 1.97 | 1.903 |
| $B-C l$ | 1 | 1 | 0.91044 | 11.80624 | 12.93364 | 0.182 | 1.76065 | 1.54 | 1.58 |

${ }^{\text {a }}$ The more positive atom is on the left.
${ }^{\mathrm{b}} c_{2}$ from Eqs. (15.77), (15.79), and Eq. (13.430) and $E_{A}\left(\right.$ valence) is given by $1 / 2$ two $H_{2}$-type ellipsoidal MOs (Eq. (11.212)).
c $c_{2}$ from Eqs. (15.77), (15.79), and the product of 0.936127 (Eq. (13.248)) and 0.92235 given by $13.59844 \mathrm{eV} /\left(13.59844 \mathrm{eV}+0.25 \cdot E_{D}\right)$ where $E_{D}$ is the $N-H$ bond energy $E_{D}\left({ }^{14} \mathrm{NH}_{3}\right)=4.57913 \mathrm{eV}$ given by Eq. (13.404) and the energy of $H$ is $13.59844 \mathrm{eV} ; E_{A}($ valence $)$ is given by $1 / 2$ two $\mathrm{H}_{2}$-type ellipsoidal MOs (Eq. (11.212)).
${ }^{\text {d }} E_{A}$ (valence) is given by $1 / 2$ two $H_{2}$-type ellipsoidal MOs (Eq. (11.212)).
e $c_{2}$ from Eqs. (15.77) given by $13.59844 \mathrm{eV} /\left(13.59844 \mathrm{eV}+0.25 \cdot E_{D}\right)$ where $E_{D}$ is the $O-H$ bond energy $E_{D}\left(H^{16} \mathrm{OH}\right)=5.1059 \mathrm{eV}$ given by Eq. (13.222) and the energy of $H$ is $13.59844 \mathrm{eV} ; E_{A}$ (valence) is given by $1 / 2$ two $H_{2}$-type ellipsoidal MOs (Eq. (11.212)).
f Eq. (15.129) with the inverse energy ratio of $E(F)=-17.42282 \mathrm{eV}$ and $E\left(C, 2 s p^{3}\right)=-14.63489 \mathrm{eV}$ corresponding to the higher binding energy of the former.
g $E_{A}$ (valence) is given by $15.35946 \mathrm{eV}-1 / 2 E_{\text {mag }}$ (Eqs. (14.150) and (15.67)).
${ }^{\mathrm{h}} c_{1}$ from Eqs. (15.79), (15.145), and (13.430); $E_{A}\left(\right.$ valence ) is given by $1 / 2$ two $H_{2}$-type ellipsoidal MOs (Eq. (11.212)).
${ }^{\mathrm{i}} c_{2}$ from the reciprocal of Eq. (15.147), $E_{A}$ (valence) is given by Eq. (15.139), and $E_{B}($ valence $)$ is $E(S)=-10.36001 \mathrm{eV}$.
$\mathrm{j}_{c_{2}}$ from the reciprocal of Eq. (15.182).
$\mathrm{k}_{c_{2}}$ from the reciprocal of Eq. (20.49).
${ }^{1} c_{2}$ from the reciprocal of Eq. (22.29).
$\mathrm{m}_{c_{2}}$ from Eq. (15.77) using $E(F)=-17.42282 \mathrm{eV}$ and $E\left(B_{B-F b o r a n e}, 2 \mathrm{sp}{ }^{3}\right)=-14.88734 \mathrm{eV}$ (Eq. (22.61)).

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 functional group bond moment stays constant from molecule to molecule and is in the vector direction of the internuclear axis. The dipole moments of water and ammonia to compare to the experimental values are given from the corresponding moments in Table 16.17. The calculated dipole moment of $\mathrm{H}_{2} \mathrm{O}$ is:

$$
\begin{equation*}
\mu_{\mathrm{H}_{2} \mathrm{O}}=2(1.51) \cos \left(\frac{106^{\circ}}{2}\right)=1.8128 D \tag{16.16}
\end{equation*}
$$

where the angle between the $\mathrm{O}-\mathrm{H}$ bond is $106^{\circ}$ given by Eq. (13.242). The experimental dipole moment of $\mathrm{H}_{2} \mathrm{O}$ is [23] :

$$
\begin{equation*}
\mu_{\mathrm{H}_{2} \mathrm{O}}=1.8546 \mathrm{D} \tag{16.17}
\end{equation*}
$$

The calculated dipole moment of $\mathrm{NH}_{3}$ is:

$$
\begin{equation*}
\mu_{N H_{3}}=3(1.30) \cos \left(68^{\circ}\right)=1.467 \mathrm{D} \tag{16.18}
\end{equation*}
$$

where the angle between each $N-H$ bond and the z-axis is $68^{\circ}$ given by Eq. (13.417). The experimental dipole moment of $\mathrm{NH}_{3}$ is [23]:

$$
\begin{equation*}
\mu_{N H_{3}}=1.4718 \mathrm{D} \tag{16.19}
\end{equation*}
$$

The charge distributions of the functional groups given in Table 16.17 facilitate the rendering of the charge distribution of molecules of unlimited complexity comprised of these functional groups. What was previously impossible to achieve using supercomputers can be readily accomplished on a personal computer (PC). The rendering of the true charge densities of the exemplary proteins insulin and lysozyme are shown in color scale, opaque view in Figures 16.4 and 16.5, respectively. The color scale, opaque view of the charge density of an exemplary double-stranded RNA helix is shown in Figure 16.6.

Figure 16.4. Color scale, opaque view of the charge density of insulin created and modeled using Millsian 2.0 on a PC.


Figure 16.5. Color scale, opaque view of the charge density of lysozyme created and modeled using Millsian 2.0 on a PC.


Figure 16.6. Color scale, opaque view of the charge density of a double-stranded DNA helix created and modeled using Millsian 2.0 on a PC.


## NATURE OF THE DIPOLE BOND: DIPOLE-DIPOLE, HYDROGEN, AND VAN DER WAALS BONDING

The boundless number and length of permutations of the functional groups can form a correspondingly infinite number of molecules. The intermolecular forces instill upon molecules their inherent properties such as state-being solid, liquid, or gas, the temperatures at which phase transitions occur, and the energy content change required to change the state. However, the types of bonding are relatively few even though the breadth of molecular compositions is infinite. Since all molecules comprise nuclei that behave on the scale of molecules as electrostatic point charges, and electrically charged electrons exist as charge and current densities that obey Maxwell's equations, the binding is determined by electrical and electrodynamics forces. These typically dominate over any magnetic forces since the latter is a relativistic effect of the former and is thus negligible as the norm. Thus, essentially all molecular bonding is Coulombic in nature. The extreme case involves ions, and ionic bonding between charged functional groups of molecules obeys the same physical principles as inorganic ions as given in the Nature of the Solid Ionic Bond of Alkali Hydrides and Halides section. Similarly, the charge-density distributions of negatively-charged electrons relative to the positively-charged nuclei of neutral molecules gives rise to Coulombic-based bonding that can be grouped into two main categories, bonding that comprises permanent dipole-dipole interactions further including an extreme case, hydrogen bonding, and bonding regarding reversible mutually induced dipole fields in near-neighbor molecules called van der Waals bonding.

The H bond is exemplary of the extreme of dipole-dipole interactions as the source of bond energy and rises from the extremely high dipole moments of $H$ bound to $F, O$, or $N$ as shown in the Bond and Dipole Moments section. The bond energies of these types of bonds are large due to the very high Coulombic energy associated with the dipole-dipole interaction between H -bonded molecules compared to those having much lower dipole moments. Still H-bond energies are typically small by the standards of covalent bonds. The differences are also reflected in the relative bond lengths. In water for example, the $O-H$ bond distance and energy are $2 c^{\prime}=0.970 \pm .005 \AA$ (Eq. (13.186)) and $E_{D}\left(H^{16} \mathrm{OH}\right)=5.1059 \mathrm{eV}$ (Eq. (13.222), respectively; whereas, those of the hydrogen bond of water are $2 c_{O \ldots H}^{\prime}=1.78 \AA$ (Eq. (16.27) and $E_{\text {vapor, } 0^{\circ} \mathrm{C}}=0.233 \mathrm{eV} / \mathrm{H}$ - bond (Eq. (16.57)), respectively. On the other end of the spectrum, van der Waals bonds are also Coulombic in nature and are between dipoles. However, the dipoles are mutually induced rather than permanent, and the mutual induction is typically small. Thus, the bond distances are on the order of angstroms and the energies in the 10 's of meV's range. The bonding between molecules gives rise to condensed matter, and the classical theory of condensed matter based on these forms of bonding is treated next.

## CONDENSED MATTER PHYSICS

Condensed matter comprises liquids and solids of atoms and molecules. It is shown infra that the geometrical parameters, energies, and properties of the latter can be solved using the same equations as those used to solve the geometrical parameters and component energies of the individual molecules as given in the Organic Molecular Functional Groups and Molecules section.

The structure and properties of liquids can be solved by first solving the unit cell of the corresponding condensed solid. The unit cell may be solved by first determining the packing that minimizes the lattice energy. In nature, there are a small, finite number of packing arrangements. The particular arrangement relates to the most efficient one giving the most objects packed into a given space with the size and shape limitations. The water molecule, for example, is small compared to the unit cell of ice; so, it will naturally assume a tetrahedral structure and hexagonal packing given the geometry of its electric dipoles with a partial positive on the $H$ 's and partial negative on the $O$. In general, a reiterative algorithm is used that optimizes the packing of the molecules and tests that packing against the unit cell parameters and lattice energy until an optimum is found. The lattice parameters can be verified by X-ray crystallography and neutron diffraction. The lattice energy can be measured using calorimetry; so, the model can be directly tested.

Bonding in neutral condensed solids and liquids arises from interactions between molecules wherein the molecules of the lattice have multipoles that give rise to corresponding Coulombic or magnetic interactions. Typically, the multipoles are electric or magnetic dipoles. Consider the former case. Since the separated partial charges that give rise to bond moments are equivalent to point charges centered on the bond nuclei as given in the Bond and Dipole Moments section, the maximum interaction energy between interacting species can be calculated using Coulomb's law with the corresponding partial monopole charges and separation distance. The energy from the interaction of the partial charges increases as the separation decreases, but concomitantly, the energy of a bond that may form between the interacting species increases as well. The equilibrium separation distance corresponds to the occurrence of the balance between the Coulombic potential energy of the interacting atoms and the energy of the bond whose formation involves the interacting atoms. Thus, the balance is at the energy threshold for the formation of a nascent bond that would replace the interacting partial charges while also destabilizing the standard bonds of the interacting molecules. Then, an optimal lattice structure corresponds to an energy minimum with an associated energy. The minimum energy structure corresponds to the highest density of interacting dipoles in their minimum energy state. A convenient method to calculate the lattice energy is to determine the electric or magnetic field in the material having an electric or magnetic polarization density, and in turn, the energy can be calculated from the energy of each dipole in the corresponding field using the electrostatic or magnetostatic form of Gauss' or Amperes' equation, respectively.

Once the $a, b$, and $c$ parameters of the unit cell are solved from the energy (force) balance between the electric monopoles and the nascent bond energy, the unit cell is determined. Then, the unit cell can be proliferated to arbitrary scale to
render the solid. Typically, only one lattice parameter needs to be determined since the additional distances can be determined from geometrical relations based on the unit cell structure. The lattice energy may be calculated from the potential between dipoles using the cell parameters. The dielectric constant and other properties may also be calculated using Maxwell's equations and other first principles.

The structures of liquids can be modeled as linear combinations of unit cells comprising perturbations of the solid unit cell. In one approach, increasing disorder is added to the solid structure in the transition from solid to liquid to gas. Complete disorder or statistical gas behavior applies in the ideal gas limit. Thus, liquid states may be modeled by adding more cells with increasing loss of order of the solid unit cell as the temperature of the liquid is increased. The disorder is due to population of translational, rotational, and vibrational levels to match the internal energy at a given temperature. Consider thermodynamics. In principle, it is possible to classically calculate the fields over all space, the exact field interactions, and the position, trajectory, momentum, and energy of every particle of a material at each instance. Then, the material properties can be determined from these parameters. However, in practice, it is impossible computationally. For the same reason, simple underlying physical principles are applied to derive statistical properties for large ensembles of particles as given in the Statistical Mechanics section. The same statistical thermodynamic methods may be applied to modeling liquids and gases using the exact solutions of the individual molecules. Using the molecular geometrical parameters, charge distributions, and corresponding interactions as input, unit cells can be computed based on the solid unit cell. Working with increasing numbers of unit cells of increasing randomness and populating the unit cells based on appropriate statistical models such as Boltzmann statistics for increasing enthalpy input and temperature, accurate models of liquids are provided. The corresponding liquid properties can be solved from each liquid structure.

A preferred approach to solving the energy and geometric parameters of ice, considered next, is to solve the separation distance of the electric monopoles comprising a partial positive on each $H$ and a partial negative charge on each $O$ as the balance between the Coulombic attraction energy between the partial charges and the repulsion energy due to the formation of a nascent $H-O$ bond between the hydrogen-bonded atoms. The nascent bond substitutes for the hydrogen bond while also removing electron density and stability from the standard water molecule bonds. Thus, it offsets the Coulombic energy and establishes the equilibrium minimum approach distance of the interacting atoms of the water molecules. Then, using Gauss's law, the energy per water molecule is calculated as the dipole energy in the electric field of the lattice of electric dipoles.

## GEOMETRICAL PARAMETERS AND ENERGIES OF THE HYDROGEN BOND OF $\mathrm{H}_{2} \mathrm{O}$

## IN THE ICE PHASE

The extraordinary properties of water are determined by hydrogen $(\mathrm{H})$ bonds, designated by the dotted bond $O-H \cdots O$, each between a participating $H$ of one water molecule and an $O$ of another. The structure of each phase of water is then determined by the number of H bonds on average per water molecule. As shown in the Bond and Dipole Moments section, the $O-H$ bond has a bond moment $\mu$ of 1.51 D corresponding to a partial charge on each $H$ of $+0.323 e$ and a component of partial charge on each $O$ per bond moment of $-0.323 e$. The thermodynamic basis of the H bond is the minimization of the Coulombic energy between the $H$ and $O$ of the hydrogen bond, limited by the formation of a nascent bond between these atoms that destabilizes the initial $O-H$ bond. The sum of the torques and forces are zero at force balance to achieve a hexagonal crystal structure that is an energy minimum. The maximum electrostatic energy of the partial charges is calculated for the components along the H bond axis. This energy is balanced by the total energy of the nascent bond that can form between the $H \cdots O$ atoms of the H bond. The bond length of the H bond, the internuclear distance between the $H$ and $O$ of the $H \cdots O$ bond, is calculated by a similar method as that used to determine the bond angle given in the Bond Angle of $\mathrm{H}_{2} \mathrm{O}$ section.

The $\mathrm{H}_{2} \mathrm{O}$ MO comprises a linear combination of two $\mathrm{O}-H$-bond MOs. Each $\mathrm{O}-H$-bond MO comprises the superposition of a $H_{2}$-type ellipsoidal MO and the $O 2 p_{z} \mathrm{AO}$ or the $O 2 p_{y} \mathrm{AO}$ with a relative $H$ partial orbital contribution to the MO of 0.75 ; otherwise, the $O 2 p$ orbitals are the same as those of the oxygen atom. The solution of the geometrical parameters and component energies are given in the Water Molecule $\left(\mathrm{H}_{2} \mathrm{O}\right)$ section and the color scale charge density of the $\mathrm{H}_{2} \mathrm{O}$ MO is shown in Figure 16.7.

Figure 16.7. $\mathrm{H}_{2} \mathrm{O}$ MO comprising the linear combination of two $O-H$-bond MOs. Each $O-H$-bond MO comprises the superposition of a $\mathrm{H}_{2}$-type ellipsoidal MO and the $\mathrm{O} 2 p_{z} \mathrm{AO}$ or the $O 2 p_{y} \mathrm{AO}$ with a relative charge-density of 0.75 to 1.25 ; otherwise, the $O 2 p$ 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 $\mathrm{H}_{2} \mathrm{O} \mathrm{MO}$ from the top. For each $\mathrm{O}-\mathrm{H}$ bond, the ellipsoidal surface of each $H_{2}$-type ellipsoidal MO transitions to the $O 2 p$ AO. The $O 2 p$ shell, the $O 2 s$ shell, the $O 1 s$ shell, and the nuclei (red, not to scale) are shown. (B) Cut-away view showing the innermost $O 1 s$ shell, and moving radially, the $O 2 s$ shell, the $O 2 p$ shell, and the $H_{2}$-type ellipsoidal MO that transitions to the $O 2 p$ AO for each $O-H$ bond. Bisector current not shown.


Rather than consider the possible bond between the two H atoms of the $\mathrm{O}-H$ bonds in the determination of the bond angle, consider that the hydrogen bond may achieve a partial bond order or partial three-centered $O-H-O$ bond as given in the Bridging Bonds of Organoaluminum Hydrides ( $A l-H-A l$ and $A l-C-A l$ ) and Bridging Bonds of Boranes ( $B-H-B$ and $B-B-B$ ) sections, and the H can become mobile between water molecules corresponding to H exchange. Such exchange of $O \cdots H-O$ to $O-H \cdots O$ bonding would decrease the initial $O-H$-bond strength since electron density would be shifted from the $O-H$ bonds to the $O \cdots H$ bond. Concomitantly, the Coulombic energy of the H bond would be eliminated. Thus, the equilibrium distance $r_{e}$ or internuclear bond distance of $O \cdots H$ designated as $2 c_{O \cdots H}^{\prime}=r_{e}$ is determined by the condition that the total energy of the nascent $H_{2}$-type ellipsoidal MO formed from the atoms of the $O \cdots H$ bond is equal to the maximum Coulombic energy between the partial charges of the $H$ and $O$ atoms of the H bond.

The $O-H$ bond moments superimpose at the central $O$. The minimum energy corresponds to the maximum separation of the $\delta^{-}$of each bond moment on the $O$ atom that occurs in space and time with $\pi$ phase. The corresponding distance is the hypotenuse of the right triangle having the distance $2 c_{o \ldots H}^{\prime}$ between the $H$ and $O$ nuclei of the $H \cdots O$ bond as one side and the radius of the oxygen atom, $r_{O 2 p}=a_{0}$ (Eq. (10.162)), as the other. Then, the maximum Coulomb energy $E_{\text {Coulomb }}(H-$ bond $)$ between the atoms of the $O \cdots H$ bond due to the two separated $\delta^{-}$'s on the oxygen atom with the $\delta^{+}$centered on the nucleus of hydrogen is:

$$
\begin{equation*}
E_{\text {Coulomb }}(H-\text { bond })=\frac{-2 \delta^{2} e^{2}}{4 \pi \varepsilon_{0} \sqrt{\left(2 c_{O \cdots H}^{\prime}\right)^{2}+\left(r_{O 2 p}\right)^{2}}} \tag{16.20}
\end{equation*}
$$

Since each H bond is between two $\mathrm{H}_{2} \mathrm{O}$ molecules and there are four H bonds per $\mathrm{H}_{2} \mathrm{O}$ molecule, the Coulomb energy per $\mathrm{H}_{2} \mathrm{O} \quad E_{\text {Coulomb }}\left(\mathrm{H}_{2} \mathrm{O}\right)$ is equivalent to two times $E_{\text {Coulomb }}(H-$ bond $)$ (Eq. (16.20)):

$$
\begin{equation*}
E_{\text {Coulomb }}\left(H_{2} \mathrm{O}\right)=\frac{-4 \delta^{2} e^{2}}{4 \pi \varepsilon_{0} \sqrt{\left(2 c_{O \cdots H}^{\prime}\right)^{2}+\left(r_{O 2 p}\right)^{2}}} \tag{16.21}
\end{equation*}
$$

Eq. (16.21) is the energy to be equated to that of the nascent covalent bonds involving the atoms of the H bonds of the water molecule. Using Eq. (15.3), the internuclear distance of this bond, $2 c_{o \cdots H}^{\prime}=r_{e}$, in terms of the corresponding semimajor axis $a_{O \cdots H}$ is:

$$
\begin{equation*}
2 c_{O \ldots H}^{\prime}=2 \sqrt{\frac{a_{O \ldots H} a_{0}}{2 C_{1} C_{2}}} \tag{16.22}
\end{equation*}
$$

The length of the semiminor axis of the prolate spheroidal MO $b=c$ is given by:

$$
\begin{equation*}
b_{O \cdots H}=\sqrt{\left(a_{O \cdots H}\right)^{2}-\left(c_{O \cdots H}^{\prime}\right)^{2}} \tag{16.23}
\end{equation*}
$$

And, the eccentricity, $e$, is:

$$
\begin{equation*}
e_{O \cdots H}=\frac{c_{O \ldots H}^{\prime}}{a_{O \cdots H}} \tag{16.24}
\end{equation*}
$$

The semimajor axis $a_{O \cdots H}$ of the $O \cdots H$ bond is determined using the general equation for determination of the bond angle between terminal atoms given by Eqs. (15.93) and (15.99) with Eqs. (15.46-15.47) except that the MO energy is matched to the Coulombic energy of the H bond (Eq. (16.21) with substitution of Eq. (15.3)) rather than being set equal to zero for zero interaction energy in the case of the bond-angle determination:

$$
=\left[\begin{array}{l}
{\left[\begin{array}{l}
-\frac{n_{1} e^{2}}{8 \pi \varepsilon_{0} \sqrt{\frac{a a_{0}}{2 C_{1} C_{2}}}}\left[c_{1} c_{2}\left(2-\frac{a_{0}}{a}\right) \ln \frac{a+\sqrt{\frac{a a_{0}}{2 C_{1} C_{2}}}}{a-\sqrt{\frac{a a_{0}}{2 C_{1} C_{2}}}}-1\right.
\end{array}\right]+E_{T}(A O / H O)}  \tag{16.25}\\
+E_{T}\left(\text { atom-atom,msp} p^{3} . A O\right)
\end{array}\right]
$$

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, $c_{2}$ is the factor that results in an equipotential energy match of the participating at least two atomic orbitals of each chemical bond, $C_{1 o}$ 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 $C_{2 o}$ 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, $E_{T}(A O / H O)$ is the total energy comprising the difference of the energy $E(A O / H O)$ of at least one atomic or hybrid orbital to which the MO is energy matched and any energy component $\Delta E_{\mathrm{H}_{2} \mathrm{MO}}(\mathrm{AO} / \mathrm{HO})$ due to the AO or HO's charge donation to the MO, $E_{T}\left(\right.$ atom - atom, $\left.m s p^{3} . A O\right)$ is the change in the energy of the AOs or HOs upon forming the bond, and $\mu$ is the reduced mass.

For the determination of the H-bond distance, the energy parameters are the same as those of water given in the Water Molecule $\left(\mathrm{H}_{2} \mathrm{O}\right)$ section except that any parameters due to matching AO's, $E_{T}(\mathrm{AO} / \mathrm{HO})$ and $E_{T}\left(\right.$ atom - atom, msp $\left.{ }^{3} . \mathrm{AO}\right)$, is zero since only the energies of the MO electrons to form the $O \cdots H$ MO are considered. The partial charge $\delta=q / e$ from Table 16.17 is 0.323 , and the reduced mass is $\mu=\frac{16}{17}$. The parameters are summarized in Table 16.18 and Eq. (16.26).

Table 16.18. The energy parameters $(\mathrm{eV})$ of the $O \cdots H$ functional group of the hydrogen bond of Type I ice.

| Parameters | $O \cdots H$ Group |
| :---: | :---: |
| $\delta$ | 0.323 |
| $n_{1}$ | 2 |
| $C_{1}$ | 0.75 |
| $C_{2}$ | 1 |
| $c_{1}$ | 0.75 |
| $c_{2}$ | 1 |
| $C_{1 o}$ | 1.5 |
| $C_{2 o}$ | 1 |
| $V_{e}(e V)$ | -20.30177 |
| $V_{p}(e V)$ | 16.15958 |
| $T(e V)$ | 2.38652 |
| $V_{m}(\mathrm{eV})$ | -1.19326 |
| $E$ (аонно) (eV) | 0 |
| $\Delta E_{\mathrm{H}_{2} \text { МО }}($ АО/НО) $(\mathrm{eV})$ | 0 |
| $E_{T}($ АО/Но) $)(e V)$ | 0 |
| $E_{T}\left(\mathrm{H}_{2} \mathrm{MO}\right)(\mathrm{eV})$ | -2.94892 |
| $E_{T}\left(\right.$ atom - atom, $\left.\mathrm{msp}^{3} . \mathrm{AO}\right)(\mathrm{eV})$ | 0 |
| $E_{T}($ мо) $(\mathrm{eV})$ | -2.94892 |
| $\omega\left(10^{15} \mathrm{rad} / \mathrm{s}\right)$ | 6.55917 |
| $E_{K}(\mathrm{eV})$ | 4.31736 |
| $\bar{E}_{D}(\mathrm{eV})$ | -0.012122 |
| $\bar{E}_{\text {Kvi }}(\mathrm{eV})$ | 0.03263 |
| $\bar{E}_{\text {osc }}(\mathrm{eV})$ | 0.004191 |
| $E_{T}($ Group $)(\mathrm{eV})$ | -2.94054 |

Substitution of the parameters of Table 16.18, the internuclear distance $2 c_{O-H}^{\prime}$ given by Eq. (13.185), and $R$ given by Eq. (16.23) and (16.22) into Eq. (16.25) gives:

(16.26)

From the energy relationship given by Eq. (16.26) and the relationships between the axes given by Eqs. (16.22-16.24), the dimensions of the $O \cdots H$ MO can be solved.

The most convenient way to solve Eq. (16.26) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is:

$$
\begin{equation*}
a_{O \cdots H}=4.25343 a_{0}=2.25082 \times 10^{-10} \mathrm{~m} \tag{16.27}
\end{equation*}
$$

The component energy parameters at this condition are given in Table 16.18. Substitution of Eq. (16.27) into Eq. (16.22) gives

$$
\begin{equation*}
c_{O \cdots H}^{\prime}=1.68393 a_{0}=8.91097 \times 10^{-11} \mathrm{~m} \tag{16.28}
\end{equation*}
$$

and internuclear distance of the H bond:

$$
\begin{equation*}
2 c_{O \cdots H}^{\prime}=3.36786 a_{0}=1.78219 \times 10^{-10} m=1.78219 \AA \tag{16.29}
\end{equation*}
$$

The internuclear distance of the $O-H$ given by Eq. (13.185) is:

$$
\begin{equation*}
2 c^{\prime}=1.83601 a_{0}=9.71574 \times 10^{-11} \mathrm{~m} \tag{16.30}
\end{equation*}
$$

The internuclear distance $2 c_{O-H}^{\prime}$ of the $O-H$ bond added to $2 c_{O-H}^{\prime}$ gives the internuclear distance $2 c_{O \cdots H O}^{\prime}$ between the oxygen atoms of the group $O-H \cdots O$ :

$$
\begin{equation*}
2 c_{O \cdots H O}^{\prime}=2 c_{O \cdots H}^{\prime}+2 c_{O-H}^{\prime} \tag{16.31}
\end{equation*}
$$

Substitution of $2 c_{O-H}^{\prime}$ (Eq. (16.29)) and $2 c_{O-H}^{\prime}$ (Eq. (13.185)) into Eq. (16.31) gives the nearest-neighbor separation, the internuclear distance $2 c_{O \cdots H O}^{\prime}$ between the oxygen atoms of the $O-H \cdots O$ bond in Type I ice:

$$
\begin{equation*}
2 c_{O \cdots H O}^{\prime}=2 c_{O \cdots H}^{\prime}+2 c_{O-H}^{\prime}=1.78219 \times 10^{-10} m+9.71574 \times 10^{-11} m=2.75377 \times 10^{-10} m=2.75377 \AA \tag{16.32}
\end{equation*}
$$

The experimental oxygen nearest-neighbor separation distance $2 c_{O \cdots H O}^{\prime}$ is [88]:

$$
\begin{equation*}
2 c_{O \cdots H O}^{\prime}=2.75 \AA \tag{16.33}
\end{equation*}
$$

The experimental internuclear distance of the $\mathrm{O}-\mathrm{H}$ bond of $\mathrm{H}_{2} \mathrm{O}$ is [89]:

$$
\begin{equation*}
2 c^{\prime}=9.70 \pm .005 \times 10^{-11} \mathrm{~m} \tag{16.34}
\end{equation*}
$$

Using Eqs. (16.33) and (16.34), the experimental $H$ bond distance $2 c_{O-H}^{\prime}$ in Type I ice is [88, 89]:

$$
\begin{equation*}
2 c_{O \cdots H}^{\prime}=1.78 \AA \tag{16.35}
\end{equation*}
$$

The other H-bond MO parameters can also be determined by the relationships among the parameters. Substitution of Eqs. (16.27) and (16.28) into Eq. (16.23) gives:

$$
\begin{equation*}
b_{O \cdots H}=c_{O \cdots H}=3.90590 a_{0}=2.06691 \times 10^{-10} \mathrm{~m} \tag{16.36}
\end{equation*}
$$

Substitution of Eqs. (16.27) and (16.28) into Eq. (16.24) gives:

$$
\begin{equation*}
e_{O \cdots H}=0.39590 \tag{16.37}
\end{equation*}
$$

Since water is a hexagonal crystal system in common with the carbon allotrope diamond, the internuclear distance of the two terminal O atoms of a set of three $\mathrm{H}_{2} \mathrm{O}$ 's corresponding to the hexagonal lattice parameter $a_{l}$ is calculated using the same approach as that given by Eqs. (17.1-17.3) using the law of cosines:

$$
\begin{equation*}
s_{1}^{2}+s_{2}^{2}-2 s_{1} s_{2} \operatorname{cosine} \theta=s_{3}^{2} \tag{16.38}
\end{equation*}
$$

where $s_{3}=a_{l}$ is the hypotenuse of the isosceles triangle having equivalent sides of length equal to $2 c_{O \cdots H O}^{\prime}$. With the bond angle between three water molecules formed by the two corresponding H bonds given by $\theta_{\angle \mathrm{H}_{2} \mathrm{O}, \mathrm{H}_{2} \mathrm{O}, \mathrm{H}_{2} \mathrm{O}}=109.5^{\circ}$ [90] and $s_{1}=s_{2}=2 c_{O \cdot H O}^{\prime}$ given by Eq. (16.32), the distance between the oxygen atoms of the terminal water molecules along the hypotenuse, $s_{3}=2 c_{\mathrm{H}_{2} \mathrm{O}-\mathrm{H}_{2} \mathrm{O}}^{\prime}=a_{l}$, is:

$$
\begin{equation*}
a_{l}=2 c_{H_{2} \mathrm{O}-\mathrm{H}_{2} \mathrm{O}}^{\prime}=\sqrt{2\left(2 c_{O \ldots \mathrm{HO}}^{\prime}\right)^{2}\left(1-\operatorname{cosine}\left(109.5^{\circ}\right)\right)}=\sqrt{2(2.75377 \AA)^{2}\left(1-\operatorname{cosine}\left(109.5^{\circ}\right)\right)}=4.49768 \AA \tag{16.39}
\end{equation*}
$$

Due to the tetrahedral structure shown in Figure 16.8, four water molecules form a pyramidal structure with a central $\mathrm{H}_{2} \mathrm{O}(1)$ at the apex designated as on the z-axis, and the three other water molecules, $\mathrm{H}_{2} \mathrm{O}(n) n=2,3,4$, form the base in the xy-plane. As further shown in Figure 16.8, a fifth $H_{2} O(5)$ is positioned a distance $2 c_{O \cdots H O}^{\prime}$ along the z -axis. Twice the height along the z-axis from the base of the pyramid to the fifth $\mathrm{H}_{2} \mathrm{O}$ comprises the Type I ice unit cell parameter $\mathcal{C}$ which is determined next using Eqs. (13.412-13.417).

Since any two $O-H \cdots O$ bonds having the internuclear distance $2 c_{O \cdots H O}^{\prime}$ between the oxygen atoms of Type I ice form an isosceles triangle having the hypotenuse $a_{l}$ between the terminal oxygens, the distance $d_{\text {origin-O }}$ from the origin of the pyramidal base to the nucleus of a terminal oxygen atom is given by:

$$
\begin{equation*}
d_{\text {origin-O }}=\frac{a_{l}}{2 \sin 60^{\circ}} \tag{16.40}
\end{equation*}
$$

Substitution of Eq. (16.39) into Eq. (16.40) gives

$$
\begin{equation*}
d_{\text {origin }-O}=2.59674 a_{0} \tag{16.41}
\end{equation*}
$$

The height $d_{\text {height }}$ along the z-axis of the pyramid from the origin to the O nucleus of $\mathrm{H}_{2} \mathrm{O}(1)$ is given by:

$$
\begin{equation*}
d_{\text {height }}=\sqrt{\left(2 c_{O \cdots H O}^{\prime}\right)^{2}-\left(d_{\text {origin }-O}\right)^{2}} \tag{16.42}
\end{equation*}
$$

Substitution of Eqs. (16.32) and (16.41) into Eq. (16.42) gives:

$$
\begin{equation*}
d_{\text {height }}=0.91662 a_{0} \tag{16.43}
\end{equation*}
$$

The angle $\theta_{v}$ of each $O-H \cdots O$ bond from the z-axis is given by:

$$
\begin{equation*}
\theta_{v}=\tan ^{-1}\left(\frac{d_{\text {origin }-O}}{d_{\text {height }}}\right) \tag{16.44}
\end{equation*}
$$

Substitution of Eqs. (16.41) and (16.43) into Eq. (16.44) gives:

$$
\begin{equation*}
\theta_{v}=70.56^{\circ} \tag{16.45}
\end{equation*}
$$

Using Eqs. (16.32) and (16.43), the hexagonal lattice parameter $c_{l}$ for Type I ice given by twice the height along the z -axis from the base of the pyramid to the fifth water, $\mathrm{H}_{2} \mathrm{O}(5)$, is

$$
\begin{equation*}
c_{l}=2\left(2 c_{O \ldots H O}^{\prime}+d_{\text {height }}\right)=2(2.75377 \AA+0.91662 \AA)=7.34077 \AA \tag{16.46}
\end{equation*}
$$

The experimental lattice parameters $a_{l}$ and $c_{l}$ for Type I ice are [90, 91]:

$$
\begin{align*}
& a_{l}=4.49 \AA  \tag{16.47}\\
& a_{l}=4.5212 \AA
\end{align*}
$$

and [91, 92] :
$c_{l}=7.31 \AA$
$c_{l}=7.3666 \AA$
The tetrahedral unit cell and the ideal hexagonal lattice structure of Type I ice are shown in Figures 16.8-16.10, using the color scale charge density of each water molecule.

Figure 16.8. Tetrahedral unit cell structure of Type I ice using the transparent color scale charge density of each $H_{2} \mathrm{O}$ MO comprising the linear combination of two $O-H$-bond MOs. (A) Each dipole-dipole bond that is Coulombic in nature is depicted by connecting sticks. (B) Bond representation removed.


Figure 16.9. C-axis view of the ideal hexagonal lattice structure of Type I ice using the opaque color scale charge density of each $\mathrm{H}_{2} \mathrm{O}$ MO comprising the linear combination of two $\mathrm{O}-\mathrm{H}$-bond MOs. Each dipole-dipole bond that is Coulombic in nature is depicted by connecting sticks.


Figure 16.10. An off-angle view of the ideal hexagonal lattice structure of Type I ice using the opaque color scale charge density of each $\mathrm{H}_{2} \mathrm{O}$ MO comprising the linear combination of two $\mathrm{O}-\mathrm{H}$-bond MOs. Each dipole-dipole bond that is Coulombic in nature is depicted by connecting sticks.


A convenient method to calculate the lattice energy is to determine the electric field in ice having an electric polarization density corresponding to the aligned molecular water dipoles moments, and in turn, the energy can be calculated from the energy of each dipole in the corresponding field using the electrostatic form of Gauss' equation. The electric field inside of a material having a uniform polarization density $P_{0}$ given by Eq. (6.3.3.15) of Haus and Melcher [93] is:

$$
\begin{equation*}
\mathbf{E}\left(H_{2} O\right)=\frac{P_{0}}{3 \varepsilon_{0}}\left(-\cos \theta \mathbf{i}_{r}+\sin \theta \mathbf{i}_{\theta}\right) \tag{16.49}
\end{equation*}
$$

The polarization density $P_{0}$ given by Eq. (6.3.3.3) of Haus and Melcher [93] is:

$$
\begin{equation*}
P_{0}=N \mu_{H_{2} O} \tag{16.50}
\end{equation*}
$$

where $\mu_{H_{2} \mathrm{O}}$ is the dipole moment of water and $N$ is the number density of water dipoles given by the density $\rho_{\text {ice }}$ divided by the molecular weight $M W$ and multiplied by the Avogadro constant $N_{A}$ :

$$
\begin{equation*}
N=\frac{\rho_{i c e}}{M W} N_{A} \tag{16.51}
\end{equation*}
$$

Substitution of Eqs. (16.50) and (16.51) into Eq. (16.49) gives:

$$
\begin{equation*}
\mathbf{E}\left(H_{2} O\right)=\frac{\mu_{H_{2} O} \frac{\rho_{\text {ice }}}{M W} N_{A}}{3 \varepsilon_{0}}\left(-\cos \theta \mathbf{i}_{r}+\sin \theta \mathbf{i}_{\theta}\right) \tag{16.52}
\end{equation*}
$$

The energy of forming the condensed phase is that of the alignment of the water dipoles each comprised of two $O-H$ component dipoles where the angular dependence along the z -axis in ice is unity, and this condition applies even in the case of the local order in water. The corresponding energy $U\left(\mathrm{H}_{2} \mathrm{O}\right)$ per water dipole due to the polarization electric field of the lattice of hexagonal dipoles is given by:

$$
\begin{equation*}
U\left(\mathrm{H}_{2} \mathrm{O}\right)=2 \mu_{\mathrm{H}_{2} \mathrm{O}} \cdot \mathbf{E}\left(\mathrm{H}_{2} \mathrm{O}\right)=\frac{-2\left(\mu_{\mathrm{H}_{2} \mathrm{O}}\right)^{2} \frac{\rho_{\text {ice }}}{M W} N_{A}}{3 \varepsilon_{0}} \tag{16.53}
\end{equation*}
$$

Substitution of the density of ice $\rho=\frac{0.92 \mathrm{~g}}{1 \times 10^{-6} \mathrm{~m}^{3}}$ [90], the $M W=18 \mathrm{~g} /$ mole, $N_{A}=6.0221415 \times 10^{23}$ molecules / mole, and the water dipole moment given by Eq. (16.16) with the predicted and experimental hexagonal bond angle of ice, $\theta_{\angle \mathrm{H}_{2} \mathrm{O}}=109.5^{\circ}$ [90]:

$$
\begin{equation*}
\mu_{\mathrm{H}_{2} \mathrm{O}}=2(1.51) \cos \left(109.5 / 2^{\circ}\right)=5.79898 \times 10^{-30} \mathrm{C} \cdot \mathrm{~m} \tag{16.54}
\end{equation*}
$$

into Eq. (16.53) gives

$$
\begin{align*}
U\left(\mathrm{H}_{2} \mathrm{O}\right) & =\frac{-2\left(5.79898 \times 10^{-30} \mathrm{C} \cdot \mathrm{~m}\right)^{2} \frac{\frac{0.92 \mathrm{~g}}{1 X 10^{-6} \mathrm{~m}^{3}}}{18 \mathrm{~g} / \mathrm{mole}} 6.0221415 \times 10^{23} \text { molecules } / \mathrm{mole}}{3 \varepsilon_{0}}  \tag{16.55}\\
& =-0.48643 \mathrm{eV}(-46.934 \mathrm{~kJ} / \text { mole })
\end{align*}
$$

$U\left(\mathrm{H}_{2} \mathrm{O}\right)$ is also the negative of $E_{\text {vapor, } 0^{\circ} \mathrm{C}}$, the energy of water initially at $0{ }^{\circ} \mathrm{C}$ or the energy of vaporization of water at $0{ }^{\circ} \mathrm{C}$ :

$$
\begin{equation*}
E_{\text {vapor }, 0^{\circ} \mathrm{C}}=-U\left(\mathrm{H}_{2} \mathrm{O}\right)=0.48643 \mathrm{eV}(46.934 \mathrm{~kJ} / \text { mole }) \tag{16.56}
\end{equation*}
$$

The experimental energy of vaporization of water at $0^{\circ} \mathrm{C}$ (Type I ice) is [94] :

$$
\begin{equation*}
E_{\text {vapor }, 0^{\circ} \mathrm{C}}=45.054 \mathrm{~kJ} / \mathrm{mole} \tag{16.57}
\end{equation*}
$$

The calculated results based on first principles and given analytical equations are summarized in Table 16.19.

Table 16.19. The calculated and experimental geometrical and energy parameters of the H bond of water of Type I ice.

| Parameter | Calculated | Experimental | Ref. for <br> Exp. |
| :--- | :---: | :---: | :---: |
| H Bond Length $2 c_{O-H}^{\prime}$ <br> Nearest Neighbor <br> Distance $2 c_{O \cdots H O}^{\prime}$ | $1.78219 \AA$ | $1.78 \AA$ | 88,89 |
| $\mathrm{H}_{2} \mathrm{O}$ Lattice Parameter $a_{l}$ | $2.75377 \AA$ | $2.75 \AA$ | 88 |
| $\mathrm{H}_{2} \mathrm{O}$ Lattice Parameter $c_{l}$ | $4.49768 \AA$ | $4.49 \AA$ | 90 |
| Energy of Vaporization of Water <br> at $0{ }^{\circ} \mathrm{C}$ | $7.54077 \AA$ | $7.31 \AA$ | 91 |

As the temperature increases, the corresponding molecular kinetic energy can excite a vibrational mode along the H bond axis. Concomitantly, the $O-H$ bond elongates and decreases in energy. As a consequence, the hydrogen bond achieves a partial bond order or partial three-centered $O-H-O$ bond, and the $H$ can undergo exchange between water molecules. The time-average effect of exchange is to decrease the statistical equilibrium separation distance of water molecules. In competition with the separation-distance decreasing effect of exchange is the increasing effect due to collisional impact and recoil as a function of increasing temperature. The former effect dominates from the temperature of ice to $4^{\circ} \mathrm{C}$ at which point water assumes a maximum density. Thereafter, the momentum imparted with water-water collisions overwhelms the decrease due to exchange, and the molecular separation statistically increases with temperature until a totally gaseous state is achieved at atmospheric pressure at $100^{\circ} \mathrm{C}$. Unit cells with increasing entropy can be derived from the ice unit cell by populating translational, rotational, and vibrational levels of molecules within the cells to match the internal energy at a given temperature. Using statistical mechanical models such as Boltzmann statistics to populate an increasing number of basis units cells of increasing disorder and based on the ice unit cell, the behavior of water as a function of temperature can be modeled over the range of states from ice to liquid to steam. The structure of each phase of water is then determined by the number of H bonds on average per water molecule. Based on the $10 \%$ energy change in the heat of vaporization in going from ice at $0^{\circ} \mathrm{C}$ to water at $100^{\circ} \mathrm{C}$ [94], the average number of H bonds per water molecule in boiling water is 3.6 . The H bond distance is calculated next using the enthalpy to form steam from boiling water.

## GEOMETRICAL PARAMETERS AND ENERGIES OF THE HYDROGEN BOND OF $\mathrm{H}_{2} \mathrm{O}$ IN THE VAPOR PHASE

Two or more water molecules can interact along the $O \cdots H$ or $H$ bond axis. In the gas phase, the maximum energy of interaction between water molecules of steam is equivalent to the negative of the heat of vaporization of water at the boiling point, $100^{\circ} \mathrm{C}$; otherwise, water vapor would form the corresponding condensed state. For the determination of the H -bond distance, the energy parameters, partial charge, and reduced mass are the same as those of the water molecules of ice given in Eq. (16.26) except that the negative of the experimental $E_{\text {vapor }, 100^{\circ} \mathrm{C}}=0.42137 \mathrm{eV}(40.657 \mathrm{~kJ} / \mathrm{mole})$ [94] is equated to the nascent covalent bond energy. The parameters are summarized in Table 16.20 and Eq. (16.58).

Table 16.20. The energy parameters $(\mathrm{eV})$ of the $O \cdots H$ functional group of the hydrogen bond of water vapor.

| Parameters | $O \cdots H$ Group |
| :---: | :---: |
| $\delta$ | 0.323 |
| $n_{1}$ | 2 |
| $C_{1}$ | 0.75 |
| $C_{2}$ | 1 |
| $c_{1}$ | 0.75 |
| $c_{2}$ | 1 |
| $C_{1 o}$ | 1.5 |
| $C_{2 o}$ | 1 |
| $V_{e}(\mathrm{eV})$ | -15.20020 |
| $V_{p}(\mathrm{eV})$ | 14.08285 |
| $T(e V)$ | 1.35707 |
| $V_{m}(\mathrm{eV})$ | -0.67853 |
| $E$ (Аогно) (eV) | 0 |
| $\Delta E_{\mathrm{H}_{2} \mathrm{MO}}($ АО/ HO$)(\mathrm{eV})$ | 0 |
| $E_{T}($ АО/ $/ \mathrm{HO})(\mathrm{eV})$ | 0 |
| $E_{T}\left(\mathrm{H}_{2} \mathrm{MO}\right)(\mathrm{eV})$ | -0.43882 |
| $E_{T}\left(\right.$ atom - atom, $\left.\mathrm{msp}^{3} . \mathrm{AO}\right)(\mathrm{eV})$ | 0 |
| $E_{T}($ мо) $(\mathrm{eV})$ | -0.43882 |
| $\omega\left(10^{15} \mathrm{rad} / \mathrm{s}\right)$ | 4.20131 |
| $E_{K}(\mathrm{eV})$ | 2.76538 |
| $\bar{E}_{D}(e V)$ | -0.001444 |
| $\bar{E}_{\text {Kıı }}(\mathrm{eV})$ | 0.02033 |
| $\bar{E}_{\text {osc }}(\mathrm{eV})$ | 0.008724 |
| $E_{T}($ Group $)(e V)$ | -0.42137 |

Substitution of the parameters of Table 16.20 and $-E_{\text {vapor }, 0^{\circ} \mathrm{C}}$ (Eq. (16.57)) into Eq. (16.26) gives:


From the energy relationship given by Eq. (16.58) and the relationships between the axes given by Eqs. (16.22-16.24), the dimensions of the $O \cdots H$ MO can be solved.

The most convenient way to solve Eq. (16.58) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is:

$$
\begin{equation*}
a_{O \cdots H}=5.60039 a_{0}=2.96360 \times 10^{-10} \mathrm{~m} \tag{16.59}
\end{equation*}
$$

The component energy parameters at this condition are given in Table 16.20. Substitution of Eq. (16.59) into Eq. (16.22) gives

$$
\begin{equation*}
c_{O \cdots H}^{\prime}=1.93225 a_{0}=1.02250 \times 10^{-10} \mathrm{~m} \tag{16.60}
\end{equation*}
$$

and internuclear distance of the H bond:

$$
\begin{equation*}
2 c_{O \cdots H}^{\prime}=3.86450 a_{0}=2.04501 \times 10^{-10} \mathrm{~m} \tag{16.61}
\end{equation*}
$$

The experimental $H$ bond distance $2 c_{O-H}^{\prime}$ in the gas phase is [95]:

$$
\begin{equation*}
2 c_{O \cdots H}^{\prime}=2.02 \times 10^{-10} \mathrm{~m} \tag{16.62}
\end{equation*}
$$

and [96]

$$
\begin{equation*}
2 c_{O \cdot H}^{\prime}=2.05 \times 10^{-10} \mathrm{~m} \tag{16.63}
\end{equation*}
$$

The other H-bond MO parameters can also be determined by the relationships among the parameters. Substitution of Eqs. (16.59) and (16.60) into Eq. (16.23) gives:

$$
\begin{equation*}
b_{O \cdots H}=c_{O \cdots H}=5.25650 a_{0}=2.78162 \times 10^{-10} \mathrm{~m} \tag{16.64}
\end{equation*}
$$

Substitution of Eqs. (16.59) and (16.60) into Eq. (16.24) gives:

$$
\begin{equation*}
e_{O \cdots H}=0.34502 \tag{16.65}
\end{equation*}
$$

Substitution of $2 c_{O-H}^{\prime}$ (Eq. (16.61)) and $2 c_{O-H}^{\prime}$ (Eq. (13.185)) into Eq. (16.31) gives the nearest neighbor separation, the internuclear distance $2 c_{O \cdots H O}^{\prime}$ between the oxygen atoms of the $O-H \cdots O$ bond of water vapor:

$$
\begin{equation*}
2 c_{O-H O}^{\prime}=2 c_{O \cdots H}^{\prime}+2 c_{O-H}^{\prime}=2.04501 \times 10^{-10} m+9.71574 \times 10^{-11} m=3.01658 \times 10^{-10} m=3.01658 \AA \tag{16.66}
\end{equation*}
$$

Using Eqs. (16.31), (16.34), and (16.63), the experimental nearest neighbor separation $2 c_{O \cdot H O}^{\prime}$ is [89, 96]:

$$
\begin{equation*}
2 c_{O \cdots H O}^{\prime}=2 c_{O \cdots H}^{\prime}+2 c_{O-H}^{\prime}=2.05 \times 10^{-10} m+9.70 \times 10^{-11} m=3.02 \times 10^{-10} m=3.02 \AA \tag{16.67}
\end{equation*}
$$

H -bonded water vapor molecules in steam are shown in Figure 16.11 using the color scale charge density of each water molecule.

Figure 16.11. Structure of steam. (A). Ensemble of gaseous water molecules undergoing elastic hard-sphere collisions. (B). H-bonded water vapor molecules using the color scale charge density of each $\mathrm{H}_{2} \mathrm{O}$ MO comprising the linear combination of two $O-H$-bond MOs.


The calculated results based on first principles and given by analytical equations are summarized in Table 16.21.
Table 16.21. The calculated and experimental geometrical and energy parameters of the H bond of steam.

| Parameter | Calculated | Experimental | Ref. for Exp. |
| :--- | :--- | :--- | :---: | :---: |
| H Bond Length $2 c_{O-H}^{\prime}$ | $2.04501 \AA$ | $2.02 \AA$ | 95,96 |
| Nearest <br> $2 c_{O-H O}^{\prime}$ |  | $2.05 \AA$ |  |

## GEOMETRICAL PARAMETERS AND ENERGIES OF THE HYDROGEN BOND OF $\mathrm{H}_{2} \mathrm{O}$ AND $\mathrm{NH}_{3}$

Similar to the water molecule, the ammonia molecule has a strong dipole moment along each of its $\mathrm{N}-\mathrm{H}$-bonds. The $\mathrm{NH}_{3}$ MO comprises the linear combination of three $N-H$-bond MOs. Each $N-H$-bond MO comprises the superposition of a $H_{2}$-type ellipsoidal MO and the $N 2 p_{x}, N 2 p_{y}$, or $N 2 p_{z}$ AO with a relative $H$ partial orbital contribution to the MO of 0.75 . The solution of the geometrical parameters and component energies are given in the Ammonia $\left(\mathrm{NH}_{3}\right)$ section, and the color scale charge density of the $\mathrm{NH}_{3}$ MO is shown in Figure 16.12.

Figure 16.12. $N H_{3}$ 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 $N 2 p_{x}, N 2 p_{y}$, or $N 2 p_{z}$ AO. (A) Color scale, translucent view of the charge density of the $\mathrm{NH}_{3}$ MO shown obliquely from the top. For each $\mathrm{N}-\mathrm{H}$ bond, the ellipsoidal surface of each $H_{2}$-type ellipsoidal MO transitions to a $N 2 p$ AO. The $N 2 p$ shell, the $N 2 s$ shell, the $N 1 s$ shell, and the nuclei (red, not to scale) are shown. (B) Off-center cut-away view showing the complete inner most $N 1 s$ shell, and moving radially, the cross section of the $N 2 s$ shell, the $N 2 p$ shell, and the $H_{2}$-type ellipsoidal MO that transitions to a $N 2 p$ AO for each $N-H$ bond. (C)-(E) Color scale, sideon, top, and bottom translucent views of the charge density of the $\mathrm{NH}_{3} \mathrm{MO}$, respectively.


Due to the interacting dipoles, hydrogen bonds also form between the nitrogen of ammonia and the hydrogen of water molecules. Water hydrogen bonds to ammonia molecules by interaction along the $N \cdots H O$ or $H$ bond axis. As shown in the Bond and Dipole Moments section, each $N-H$ bond of ammonia has a bond moment $\mu$ of 1.30 D corresponding to a $N$ component of partial charge of $-0.262 e$, and the $O-H$ bond has a bond moment $\mu$ of 1.51 D corresponding to a $H$ partial charge of +0.323 e . The thermodynamic basis of the H bond is the minimization of the Coulombic energy between the hydrogen bonded H of $\mathrm{H}_{2} \mathrm{O}$ and N of ammonia, limited by the formation of a nascent $N-H$ bond between these atoms that destabilizes the initial $O-H$ bond of the water molecule partner. As in the case of ice, the maximum electrostatic energy of the partial charges is calculated for the components along the H-bond axis. This energy is balanced by the total energy of the nascent bond that can form between the $N \cdots H$ atoms of the H bond. The bond length of the H bond, the internuclear distance between the $N$ and $H$ of the $N \cdots H$ bond, is calculated using Eq. (16.25) by a similar method as that used to calculate the $O \cdots H$ bond distance of ice. According to the method given in the Geometrical Parameters and Energies of the Hydrogen Bond of $\mathrm{H}_{2} \mathrm{O}$ section, the equilibrium distance $r_{e}$ or internuclear bond distance of $N \cdots H$ designated as $2 c_{N \cdots H}^{\prime}=r_{e}$ is determined by the condition that the total energy of the nascent $H_{2}$-type ellipsoidal MO formed from the atoms of the $N \cdots H$ bond is equal to the maximum Coulombic energy between the partial charges of the $N$ and $H$ atoms of the H bond.

The maximum Coulumbic energy corresponds to the minimum separation distance of $N$ and $H$ atoms corresponding to the alignment along the $N \cdots H$ bond axis. The corresponding distance from the $\delta^{+}$of the $H_{2} \mathrm{OH}$ and the $\mathrm{NH}_{3} \mathrm{~N}$ is the
distance $2 c_{N \cdots H}^{\prime}$ between the $N$ and $H$ nuclei of the $N \cdots H$ bond. Then, the maximum Coulomb energy $E_{\text {Coulomb }}(H-b o n d)$ between the atoms of the $N \cdots H$ bond due to the $\delta^{-}$on the nitrogen atom with the $\delta^{+}$centered on the nucleus of hydrogen is:

$$
\begin{equation*}
E_{\text {Coulomb }}(H-\text { bond })=\frac{-\delta_{N}^{-} \delta_{H}^{+} e^{2}}{4 \pi \varepsilon_{0} 2 c_{N \cdots H}^{\prime}} \tag{16.68}
\end{equation*}
$$

Eq. (16.68) is the energy to be equated to that of the nascent bonds involving the atoms of the H bond.
For the determination of the H -bond distance, the energy parameters of the nascent $N-H$ bond are the same as those of ammonia given in the Ammonia $\left(\mathrm{NH}_{3}\right)$ section except that any parameter due to matching AO's, $E_{T}(\mathrm{AO} / \mathrm{HO})$ and $E_{T}\left(\right.$ atom-atom, $\left.m s p^{3} . A O\right)$, is zero since only the energies of the MO electrons to form the $N \cdots H$ MO are considered. The energy of Eq. (16.68) is multiplied by three to match the total energy of the three $N-H$ bond MOs of ammonia. The partial charges $\delta=q / e$ from Table 16.17 are -0.262 and +0.323 , and the reduced mass is $\mu=\frac{14}{15}$. The parameters are summarized in Table 16.22 and Eq. (16.69).

Table 16.22. The energy parameters (eV) of the $N \cdots H$ functional group of the hydrogen bond of the ammonia-water molecular dimer.

| Parameters | $\begin{aligned} & N \cdots H \\ & \text { Group } \end{aligned}$ |
| :---: | :---: |
| $\delta_{N}$ | 0.262 |
| $\delta_{H}^{+}$ | 0.323 |
| $n_{1}$ | 3 |
| $C_{1}$ | 0.75 |
| $C_{2}$ | 0.93613 |
| $c_{1}$ | 0.75 |
| $c_{2}$ | 1 |
| $C_{1 o}$ | 1.5 |
| $C_{2 o}$ | 1 |
| $V_{e}(\mathrm{eV})$ | -23.60741 |
| $V_{p}(\mathrm{eV})$ | 20.75035 |
| $T(e V)$ | 2.17246 |
| $V_{m}(\mathrm{eV})$ | -1.08623 |
| $E$ (Ао/но) (eV) | 0 |
| $\Delta E_{\mathrm{H}_{2} \mathrm{MO}}($ АОІ HO$)(\mathrm{eV})$ | 0 |
| $E_{T}($ Ао/Но) $)(\mathrm{eV})$ | 0 |
| $E_{T}\left(\mathrm{H}_{2} \mathrm{MO}\right)(\mathrm{eV})$ | -1.77083 |
| $E_{T}\left(\right.$ atom - atom, $\left.\mathrm{msp}{ }^{3} . \mathrm{AO}\right)(\mathrm{eV})$ | 0 |
| $E_{T}($ мо $)(\mathrm{eV})$ | -1.77083 |
| $\omega\left(10^{15} \mathrm{rad} / \mathrm{s}\right)$ | 4.44215 |
| $E_{K}(\mathrm{eV})$ | 2.92390 |
| $\bar{E}_{D}(e V)$ | -0.00599 |
| $\bar{E}_{\text {Kiv }}(\mathrm{eV})$ | 0.021843 |
| $\bar{E}_{\text {osc }}(\mathrm{eV})$ | 0.00493 |
| $E_{T}($ Group $)(\mathrm{eV})$ | 1.75603 |
| $E_{T}$ (Group) $(\mathrm{eV})$ per $\mathrm{N}-\mathrm{H}$ | 0.58534 |

Substitution of the parameters of Table 16.22 into Eq. (16.25) with $R=a_{N \cdots H}$ gives:

From the energy relationship given by Eq. (16.69) and the relationships between the axes given by Eqs. (16.22-16.24), the dimensions of the $N \cdots H$ MO can be solved.

The most convenient way to solve Eq. (16.69) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is:

$$
\begin{equation*}
a_{N \cdots H}=5.43333 a_{0}=2.87519 \times 10^{-10} \mathrm{~m} \tag{16.70}
\end{equation*}
$$

The component energy parameters at this condition are given in Table 16.22. Substitution of Eq. (16.70) into Eq. (16.22) gives

$$
\begin{equation*}
c_{N \ldots H}^{\prime}=1.96707 a_{0}=1.04093 \times 10^{-10} \mathrm{~m} \tag{16.71}
\end{equation*}
$$

and internuclear distance of the H bond:

$$
\begin{equation*}
2 c_{N \ldots H}^{\prime}=3.93414 a_{0}=2.08186 \times 10^{-10} m=2.08186 A \tag{16.72}
\end{equation*}
$$

The experimental H bond distance $2 c_{N \cdots H}^{\prime}$ in the gas phase is [96, 97]:

$$
\begin{equation*}
2 c_{N \cdots H O}^{\prime}=2.02 \times 10^{-10} \mathrm{~m} \tag{16.73}
\end{equation*}
$$

The other H-bond MO parameters can also be determined by the relationships among the parameters. Substitution of Eqs. (16.70) and (16.71) into Eq. (16.23) gives

$$
\begin{equation*}
b_{N \cdots H}=c_{N \cdots H}=5.06475 a_{0}=2.68015 \times 10^{-10} \mathrm{~m} \tag{16.74}
\end{equation*}
$$

Substitution of Eqs. (16.70) and (16.71) into Eq. (16.24) gives:

$$
\begin{equation*}
e_{N \cdots H}=0.36204 \tag{16.75}
\end{equation*}
$$

The addition of $2 c_{N \cdots H}^{\prime}$ (Eq. (16.72)) and $2 c_{O-H}^{\prime}$ (Eq. (13.185)) gives the nearest neighbor separation, the internuclear distance $2 c_{N \cdots H O}^{\prime}$ between the nitrogen and oxygen atoms of the $N \cdots H-O$ bond of the ammonia-water molecular dimer:

$$
\begin{align*}
2 c_{N . H O}^{\prime} & =2 c_{N . H}^{\prime}+2 c_{O-H}^{\prime}=2.08186 \times 10^{-10} \mathrm{~m}+9.71574 \times 10^{-11} \mathrm{~m}  \tag{16.76}\\
& =3.05343 \times 10^{-10} \mathrm{~m}=3.05343 \AA
\end{align*}
$$

The addition of the experimental $2 c_{N \cdots H}^{\prime}$ (Eq. (16.73)) and $2 c_{O-H}^{\prime}$ (Eq. (13.185)) gives the experimental nearest neighbor separation $2 c_{N . H O}^{\prime}[96,89]$ :

$$
\begin{align*}
2 c_{N . H O}^{\prime} & =2 c_{N . H}^{\prime}+2 c_{O-H}^{\prime}=2.02 \times 10^{-10} m+9.70 \times 10^{-11} \mathrm{~m}  \tag{16.77}\\
& =2.99 \times 10^{-10} \mathrm{~m}=2.99 A
\end{align*}
$$

H-bonded ammonia-water molecular dimer is shown in Figure 16.13 using the color scale charge density of each molecule.

Figure 16.13. Structure of the $H_{3} N \cdots H-O H$ H bond. The H-bonded ammonia-water vapor molecular dimer using the color scale charge density of each $\mathrm{NH}_{3}$ and $\mathrm{H}_{2} \mathrm{O}$ MO comprising the linear combination of three $\mathrm{N}-\mathrm{H}$ and two $\mathrm{O}-\mathrm{H}$-bond MOs, respectively.


The energy of forming the dimer in the gas phase is that of the alignment of the ammonia dipole moment in the electric field of the $H-O$ water dipole. Using $\mu_{H_{3} N}=1.467 \mathrm{D}=4.89196 \mathrm{X} 10^{-30} \mathrm{C} \cdot \mathrm{m} \quad$ Eq. (16.18), $\mu_{H-O, H_{2} O}=1.51 D=5.02385 \times 10^{-30} C \cdot m$ (Table 16.17), and the $N \cdots H$ distance, $2 c_{N \cdots H}^{\prime}=2.08186 \times 10^{-10} m$ (Eq. (16.72)), the $N \cdots H$ bond dissociation energy $E_{D}(N \cdots H)$ of the ammonia-water molecular dimer is:

$$
\begin{align*}
E_{D}(N \cdots H) & =\mu_{H_{3} N} \cdot \frac{2 \mu_{H-O, H_{2} \mathrm{O}}}{4 \pi \varepsilon_{0}\left(2 c_{N \cdots H}^{\prime}\right)^{3}} \\
& =\frac{\left(4.89196 \times 10^{-30} \mathrm{C} \cdot \mathrm{~m}\right)\left(5.02385 \times 10^{-30} \mathrm{C} \cdot \mathrm{~m}\right)}{4 \pi \varepsilon_{0}\left(2.08186 \times 10^{-10} \mathrm{~m}\right)^{2}}=29.48 \mathrm{~kJ} \tag{16.78}
\end{align*}
$$

The experimental $N \cdots H$ bond dissociation energy between amino $N$ and hydroxyl $H$ is approximately [98]:

$$
\begin{equation*}
E_{D}(N \cdots H)=29 k J \tag{16.79}
\end{equation*}
$$

The calculated results based on first principles and given by analytical equations are summarized in Table 16.23.
Table 16.23. The calculated and experimental geometrical and energy parameters of the H-bonded ammonia-water vapor molecular dimer.

| Parameter | Calculated | Experimental | Ref. for Exp. |
| :---: | :---: | :---: | :---: |
| H Bond Length $2 c_{N \cdots H}^{\prime}$ | 2.08186 A | $2.02 \AA$ | 96, 97 |
| Nearest Neighbor Separation Distance $2 c_{N \ldots H O}^{\prime}$ | 3.05343 Å | 2.99 Å | 96, 89 |
| $N \cdots H$ Bond Dissociation Energy | $29.48 \mathrm{~kJ} / \mathrm{mole}$ | $29 \mathrm{~kJ} / \mathrm{mole}$ | 98 |

## GEOMETRICAL PARAMETERS DUE TO THE INTERPLANE VAN DER WAALS COHESIVE ENERGY OF GRAPHITE

Eq. (16.25) can be applied to other solids such as graphite. Graphite is an allotrope of carbon that comprises planar sheets of covalently bound carbon atoms arranged in hexagonal aromatic rings of a macromolecule of indefinite size. The structure of graphite is shown in Figures 16.14A and B. The structure shown in Figure 16.14 has been confirmed directly by TEM imaging, and the Pi cloud predicted by quantum mechanics has been dispatched [99].

Figure 16.14. The structure of graphite. (A) Single plane of macromolecule of indefinite size. (B) Layers of graphitic planes.


As given in the Graphite section, the structure of the indefinite network of aromatic hexagons of a sheet of graphite is solved using a linear combination of aromatic $C \stackrel{3 e}{=} C$ aromatic bonds comprising $(0.75)(4)=3$ electrons according to Eq. (15.161). 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 graphite at a vertex-atom comprises 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 bond. 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 $C \stackrel{8 / 3 e}{=} C$ functional group of graphite comprises the aromatic bond with the exception that the electron-number per bond is $\frac{8}{3}$. The sheets, in turn, are bound together by weaker intermolecular van der Waals forces. The geometrical and energy parameters of graphite are calculated using Eq. (16.25) with the van der Waals energy equated to the nascent bond energy.

The van der Waals energy is due to mutually induced nonpermanent dipoles in near-neighbor bonds. Albeit, the $C \stackrel{8 / 3 e}{=} C$ functional group is symmetrical such that it lacks a permanent dipole moment, a reversible dipole can be induced upon van der Waals bonding. The parameters of the $C \stackrel{8 / 3 e}{=} C$ functional group are the same as those of the aromatic $C \stackrel{3 e}{=} C$

(16.15) wherein $C_{2}$ of Eq. (15.51) for the aromatic $C=C$-bond MO is $C_{2}\left(\right.$ aromatic $\left.C 2 s p^{3} \mathrm{HO}\right)=c_{2}\left(\right.$ aromatic $\left.C 2 s p^{3} \mathrm{HO}\right)=0.85252$ (Eq. (15.162)) and $E_{\text {Coulomb }}\left(C_{\text {benzene }}, 2 s p^{3}\right)$ is 15.95955 eV (Eq. (14.245)), $E\left(C, 2 s p^{3}\right)=-14.63489 \mathrm{eV}$ (Eq. (14.143)) and $2 c^{\prime}=1.39140 \times 10^{-10} \mathrm{~m}$ (Table 15.214), the van der Waals dipole of graphite is given in Table 16.24.

Table 16.24. The parameters and van der Waals dipole bond moment of the $C \stackrel{8 / 3 e}{=} C$ functional group of graphite.

| Functional <br> Group | $n_{1}$ | $\left(c_{1}\right) c_{2}$ | $\left(C_{1}\right)$ <br> $C_{2}$ | $E_{B}$ (valence $)$ | $E_{A}($ valence $)$ | $\frac{q}{e}$ | Bond Length <br> $2 c^{\prime}(A)$ | Bond Moment <br> $\mu(\mathrm{D})$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |


| $C \stackrel{8 / 3 e}{=} C$ | $\frac{8}{3}$ | 0.85252 | 1 | 14.82575 | 15.95955 | 0.36101 | 1.3914 | 2.41270 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |

The interaction between a dipole in one plane with the nearest neighbor in another plane is zero in the case that the aromatic rings of one layer are aligned such that they would superimpose as the interlayer separation goes to zero. But, the energy of interaction is nonzero when one plane is translated relative to a neighboring plane. A minimum equal-energy is achieved throughout the graphite structure when each layer is displaced by $2 c_{c^{\prime 3 e}}$, the bond length of $C \stackrel{8 / 3 e}{=} C$, along an intra-planar $C_{2}$ axis relative to the next as shown in Figure 16.14B. Then, a pair of dipoles exists for each dipole of a given plane with one dipole above and one below in neighboring planes such that all planes can be equivalently bound by van der Waals forces. In this case, the distance $r_{\mu_{1} . . \mu_{2}}$ between dipole $\mu_{1}$ in one plane and its nearest neighbor $\mu_{2}$ above or below on a neighboring and $2 c^{\prime} c^{\prime 3 e}=C-$ displaced plane is:

$$
r_{\mu_{1} \ldots \mu_{2}}=\sqrt{\left(\begin{array}{c}
\left.2 c_{\substack{\prime 3 \\
C=C}}\right)^{2}+\left(2 c_{C \ldots C}^{\prime}\right)^{2} \tag{16.80}
\end{array}\right) .{ }^{2}}
$$

where $2 c_{C-C}^{\prime}$ is the interplane distance. The alignment angle $\theta_{\mu_{1} \ldots \mu_{2}}$ between the dipoles is:

$$
\begin{equation*}
\theta_{\mu_{1} \ldots \mu_{2}}=\sin ^{-1} \frac{2 c_{C \ldots C}^{\prime}}{r_{\mu_{1} \ldots \mu_{2}}}=\sin ^{-1} \frac{2 c_{C \ldots C}^{\prime}}{\sqrt{\binom{c^{\prime}}{C_{=C}^{3 e}}^{2}+\left(2 c_{C \ldots C}^{\prime}\right)^{2}}} \tag{16.81}
\end{equation*}
$$

The van der Waals energy is the potential energy between interacting neighboring pairs of $C \stackrel{8 / 3 e}{=} C$ induced dipoles. Using Eqs. (16.80-16.81), $\quad \mu_{C}^{8 /{ }^{83 e}} C=2.41270 D=8.04790 \times 10^{-30} C \cdot m \quad$ (Table 16.24), and the $C \stackrel{8 / 3 e}{=} C$ distance, $2 c_{C}^{\prime} \underset{=}{8 / 30}{ }_{C}=1.39140 \times 10^{-10} \mathrm{~m}$ (Table 15.214), the van der Waals energy of graphite between two planes at a vertex atom is:

$$
\begin{align*}
& E_{\text {van der Waals }}(\text { graphite })=(3) \frac{2\left(\mu_{C}{ }_{=}^{83 c}\right)^{2}}{4 \pi \varepsilon_{0}\left(r_{\mu_{1} \ldots \mu_{2}}\right)^{3}} \cos \theta_{\mu_{1} \ldots \mu_{2}} \\
&=\left(\begin{array}{c}
6\left(8.04790 \times 10^{-30} C \cdot m\right)^{2} \\
4 \pi \varepsilon_{0}\left(\left(1.39140 \times 10^{-10} m\right)^{2}+\left(2 \sqrt{\frac{a_{C \ldots C} a_{0}}{2 C_{1} C_{2}}}\right)^{2}\right)^{1.5}
\end{array}\right.  \tag{16.82}\\
&\left.\operatorname{cos\operatorname {sin}^{-1}\frac {2\sqrt {\frac {a_{C\ldots C}a_{0}}{2C_{1}C_{2}}}}{\sqrt {(1.39140\times 10^{-10}m)^{2}+(2\sqrt {\frac {a_{C\ldots C}a_{0}}{2C_{1}C_{2}}})^{2}}}}\right)
\end{align*}
$$

where there are three bonds at each vertex atom.
The graphite inter-plane distance of $3.5 \AA[100]$ is calculated using Eq. (16.25) with the van der Waals energy (Eq. (16.82)) between dipoles of two neighboring planes equated to the nascent bond energy. The energy matching parameter $c_{2}$ is the same that of the graphite sheet corresponding to the aromatic carbons as given in the Graphite section, and the reduced mass is $\mu=6$. The parameters are summarized in Table 16.25 and Eq. (16.83).

Table 16.25. The energy parameters ( eV ) of the graphite interplanar functional group ( $C_{\text {aromatic }} \cdots C_{\text {aromatic }}$ ).

| Parameters | $\begin{gathered} C_{\text {aromatic }} \cdots C_{\text {aromatic }} \\ \text { Group } \end{gathered}$ |
| :---: | :---: |
| $n_{1}$ | 1 |
| $C_{1}$ | 0.5 |
| $C_{2}$ | 1 |
| $c_{1}$ | 1 |
| $c_{2}$ | 0.85252 |
| $C_{1 o}$ | 0.5 |
| $C_{2 o}$ | 1 |
| $V_{e}(e V)$ | -4.35014 |
| $V_{p}(\mathrm{eV})$ | 4.10093 |
| $T(e V)$ | 0.19760 |
| $V_{m}(\mathrm{eV})$ | -0.09880 |
| $E$ (Аогно) (eV) | 0 |
| $\Delta E_{\mathrm{H}_{2} \text { МО }}($ АО/НО) $(\mathrm{eV})$ | 0 |
| $E_{T}($ АО/Но) $)(e V)$ | 0 |
| $E_{T}\left(\mathrm{H}_{2} \mathrm{MO}\right)(\mathrm{eV})$ | -0.15042 |
| $E_{T}\left(\right.$ atom - atom, msp $\left.{ }^{3} \cdot \mathrm{AO}\right)(\mathrm{eV})$ | 0 |
| $E_{T}($ мо) $(\mathrm{eV})$ | -0.15042 |
| $\omega\left(10^{15} \mathrm{rad} / \mathrm{s}\right)$ | 0.800466 |
| $E_{K}(\mathrm{eV})$ | 0.52688 |
| $\bar{E}_{D}(e V)$ | -0.00022 |
| $\bar{E}_{\text {Kıı }}(\mathrm{eV})$ | 0.00317 |
| $\bar{E}_{\text {osc }}(\mathrm{eV})$ | 0.00137 |
| $E_{T}($ Group $)(\mathrm{eV})$ | -0.14905 |

Substitution of the parameters of Table 16.25 and the interlayer cohesive energy of graphite (Eq. (16.82)) into Eq. (16.25) with $R=a_{C-C}$ gives:


From the energy relationship given by Eq. (16.83) and the relationships between the axes given by Eqs. (16.22-16.24), the dimensions of the $C \cdots C$ MO can be solved.

The most convenient way to solve Eq. (16.83) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is:

$$
\begin{equation*}
a_{C \ldots C}=11.00740 a_{0}=5.82486 \times 10^{-10} \mathrm{~m} \tag{16.84}
\end{equation*}
$$

The component energy parameters at this condition are given in Table 16.25. Substitution of Eq. (16.84) into Eq. (16.22) gives:

$$
\begin{equation*}
c_{C \cdots C}^{\prime}=3.31774 a_{0}=1.75567 \times 10^{-10} \mathrm{~m} \tag{16.85}
\end{equation*}
$$

and internuclear distance of the graphite interplane bond at vacuum ambient pressure:

$$
\begin{equation*}
2 c_{C \ldots C}^{\prime}=6.63548 a_{0}=3.51134 \times 10^{-10} m=3.51134 \AA \tag{16.86}
\end{equation*}
$$

The experimental graphite interplane distance $2 c_{C-C}^{\prime}$ is [100]:

$$
\begin{equation*}
2 c_{C \ldots C}^{\prime}=3.5 \times 10^{-10} m=3.5 \AA \tag{16.87}
\end{equation*}
$$

The other interplane bond MO parameters can also be determined by the relationships among the parameters. Substitution of Eqs. (16.84) and (16.85) into Eq. (16.23) gives:

$$
\begin{equation*}
b_{C \cdots C}=c_{C \cdots C}=10.49550 a_{0}=5.55398 \times 10^{-10} \mathrm{~m} \tag{16.88}
\end{equation*}
$$

Substitution of Eqs. (16.84) and (16.85) into Eq. (16.25) gives:

$$
\begin{equation*}
e_{C-C}=0.30141 \tag{16.89}
\end{equation*}
$$

Using Eqs. (16.80) and (16.86), the distance $r_{\mu_{1} \ldots \mu_{2}}$ between dipole $\mu_{1}$ on one plane and its nearest neighbor $\mu_{2}$ above or below on a juxtaposed and $2 c_{c_{3 e}^{\prime}}^{c_{=C}}$-displaced plane is:

$$
\begin{equation*}
r_{\mu_{1} . . \mu_{2}}=3.77697 \times 10^{-10} \mathrm{~m} \tag{16.90}
\end{equation*}
$$

Using Eqs. (16.81) and (16.86), the alignment angle $\theta_{\mu_{1} . . \mu_{2}}$ between the dipoles is:

$$
\begin{equation*}
\theta_{\mu_{1} . . \mu_{2}}=68.38365^{\circ} \tag{16.91}
\end{equation*}
$$

Using Eqs. (16.82) and (16.90-91), the van der Waals energy per carbon atom is:

$$
\begin{equation*}
E_{\text {van der Waals }}(\text { graphite } / C)=0.04968 \mathrm{eV} \tag{16.92}
\end{equation*}
$$

The experimental van der Waals energy per carbon atom is [101]:

$$
\begin{equation*}
E_{\text {van der Waals }}(\text { graphite } / C)=0.052 \mathrm{eV} \tag{16.93}
\end{equation*}
$$

The calculated results based on first principles and given by analytical equations are summarized in Table 16.26.

Table 16.26. The calculated and experimental geometrical parameters and interplane van der Waals cohesive energy of graphite.

| Parameter | Calculated | Experimental | Ref. for Exp. |
| :--- | :---: | :---: | :---: |
| Graphite Interplane Distance $2 C_{C-C}^{\prime}$ | $3.51134 \AA$ | $3.5 \AA$ | 100 |
| van der Waals Energy per Carbon Atom | 0.04968 eV | 0.052 eV | 101 |

Graphite has a high cohesive energy due to its significant van der Waals dipole bond moment of 2.41270D. Other species such as atoms and molecules having mirror symmetry and consequently no permanent dipole moment also form reversible van der Waals dipole bond moments. Different phases can be achieved according to the extent of the van der Waals dipole bonding as the internal energy as a function of temperature and pressure changes analogously to the H -bonded system water that can exist as ice, water, and steam. Thus, the factors in the van der Waals bonding can give rise to numerous material behaviors. In the case of atoms such as noble gas atoms and certain diatomic molecules such as hydrogen, the moments, their interaction energies, and the corresponding nascent bond energies are much smaller. Thus, except at cryogenic temperatures, these elements exist as gases, and even at temperatures approaching absolute zero, solidification of helium has not been achieved in the absence of high pressure. This is due to the nature of the induced dipoles and van der Waals phenomena in helium. Since this system is a good example of van der Waals forces in atoms, it will be treated next.

## GEOMETRICAL PARAMETERS AND ENERGIES DUE TO THE INTERATOMIC VAN DER WAALS COHESIVE ENERGY OF LIQUID HELIUM

Noble gases such as helium are typically gaseous and comprised of non-interacting atoms having no electric or magnetic multipoles. But, at very low temperatures it is possible to form diffuse diatomic molecules, or alternatively, these gases may be condensed with the formation of mutually induced van der Waals dipole interactions. As a measure of the nascent bond between two noble gas atoms used to calculate the limiting separation for condensation, consider that the experimental bond energies of diatomic molecules of helium and argon, for example, are only 49.7 meV and 49 meV , respectively [21]. This is a factor of about 100 smaller than the bond energy of a carbon-carbon bond that is the form of nascent bond in graphite. Thus, the corresponding energy of the interspecies interaction is smaller and the van der Waals spacing is larger, except wherein the nascent bond energy as a function of separation distance mitigates this relationship to some extent. The nature of the helium bonding is solved using the same approach as that of other functional groups given in the Organic Molecular Functional Groups and Molecules section.
Helium is a two-electron neutral atom with both electrons paired as mirror-image current densities in a shell of radius
$0.566987 \mathrm{a}_{0}$ (Eq. (7.35)). Thus, in isolation or at sufficient separation, there is no energy between helium atoms. The absence of
any force such as so-called long-range London forces having a $r^{-n} ; n>2$ dependency is confirmed by elastic electron scattering from helium atoms as shown in the Electron Scattering Equation for the Helium Atom Based on the Atomic Orbital Model section. However, reversible mutual van der Waals dipoles may be induced by collisions when the atoms are in close proximity such that helium gas can condense into a liquid. The physics is similar to the case of graphite except that the dipoles are atomic rather than molecular, and in both cases the limiting separation is based on the formation of a nascent bond to replace the dipoledipole interaction. Thus, Eq. (16.25) can also be applied to atoms such as helium.

The van der Waals bonding in the helium atom involves hybridizing the one $1 s \mathrm{AO}$ into $1 s^{1} \mathrm{HO}$ orbitals containing two electrons. The total energy of the state is given by the sum over the two electrons. The sum $E_{T}\left(H e, 1 s^{1}\right)$ of experimental energies [15] of He and $\mathrm{He}^{+}$is:

$$
\begin{align*}
E_{T}\left(H e, 1 s^{1}\right) & =54.41776 \mathrm{eV}+24.587387 \mathrm{eV}  \tag{16.94}\\
& =79.005147 \mathrm{eV}
\end{align*}
$$

By considering that the central field decreases by an integer for each successive electron of the shell, the radius $r_{1 s^{1}}$ of the Hels ${ }^{1}$ shell may be calculated from the Coulombic energy using Eq. (15.13):

$$
\begin{equation*}
r_{1 s^{1}}=\sum_{n=0}^{1} \frac{(Z-n) e^{2}}{8 \pi \varepsilon_{0}(e 79.005147 \mathrm{eV})}=\frac{3 e^{2}}{8 \pi \varepsilon_{0}(e 79.005147 \mathrm{eV})}=0.51664 a_{0} \tag{16.95}
\end{equation*}
$$

where $Z=2$ for helium. Using Eq. (15.14), the Coulombic energy $E_{\text {Coulomb }}\left(H e, 1 s^{1}\right)$ of the outer electron of the van der Waals bound Hels ${ }^{1}$ shell is:

$$
\begin{equation*}
E_{\text {Coulomb }}\left(H e, 1 s^{1}\right)=\frac{-e^{2}}{8 \pi \varepsilon_{0} r_{1 s^{1}}}=\frac{-e^{2}}{8 \pi \varepsilon_{0} 0.51664 a_{0}}=-26.335049 \mathrm{eV} \tag{16.96}
\end{equation*}
$$

To meet the equipotential condition of the union of the two $\mathrm{Hels}{ }^{1} \mathrm{HOs}$ in a nascent bond, $\mathrm{c}_{2}$ of Eqs. (15.2-15.5) and Eq. (15.61) for the nascent $H e-H e$-bond MO is given by Eq. (15.75) as the ratio of the valance energy of the He AO , $E(H e)=-24.587387 \mathrm{eV}$ and the magnitude of $E_{\text {Coulomb }}\left(H e, 1 s^{1}\right)$ (Eq. (16.96)):

$$
\begin{equation*}
c_{2}\left(H e-H e, H e 1 s^{1} \mathrm{HO}\right)=\frac{24.587387 \mathrm{eV}}{26.33505 \mathrm{eV}}=0.93364 \tag{16.97}
\end{equation*}
$$

The opposite charge distributions act as symmetrical point charges at the point of maximum separation, each being centered at $1 / 2$ the He -atom radius from the origin. Using the parameters of Eq. (16.97) and $2 c^{\prime}=0.51664 a_{0}=2.73395 \times 10^{-11} \mathrm{~m}$ (Eq. (16.95)), the van der Waals dipole of helium is given in Table 16.27.

Table 16.27. The parameters and van der Waals dipole bond moment of the $H e$ functional group of liquid helium.

| Functional <br> Group | $n_{1}$ | $\left(c_{1}\right) c_{2}$ | $\left(C_{1}\right) C_{2}$ | $E_{B}($ valence $)$ | $E_{A}($ valence $)$ | $\frac{q}{e}$ | Bond <br> Length <br> $2 c^{\prime}(\AA)$ | Bond <br> Moment <br> $\mu(D)$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| He | 1 | 0.93364 | 1 | 24.587387 | 26.33505 | 0.13744 | 0.273395 | 0.18049 |

As in the case with graphite, the van der Waals energy is the potential energy between interacting neighboring induced dipoles. Using $\mu_{H e}=0.18049 D=6.02040 \times 10^{-31} C \cdot m$ (Table 16.27), the van der Waals energy is:

$$
\begin{equation*}
E_{\text {van der Waals }}(H e)=2 \frac{2\left(\mu_{H e}\right)^{2}}{4 \pi \varepsilon_{0}\left(r_{\text {He...He }}\right)^{3}}=\left(\frac{2\left(6.02040 X 10^{-31} C \cdot m\right)^{2}}{4 \pi \varepsilon_{0}\left(2 \sqrt{\frac{a_{H e . . H e} a_{0}}{2 C_{1} C_{2}}}\right)^{3}}\right) \tag{16.98}
\end{equation*}
$$

where there are two bonds at each vertex atom.
The helium interatomic distance is calculated using Eq. (16.25) with the van der Waals energy (Eq. (16.98)) between neighboring dipoles equated to the nascent bond energy. The energy matching parameter $c_{2}$ is the same as that of the helium dipole, and the reduced mass is $\mu=2$. The parameters are summarized in Table 16.28 and Eq. (16.99).

Table 16.28. The energy parameters ( eV ) of the helium functional group ( $\mathrm{He} \cdots \mathrm{He}$ ).

| Parameters | $\overline{\mathrm{He} \cdots \mathrm{He}}$ Group |
| :---: | :---: |
| $n_{1}$ | 1 |
| $C_{1}$ | 0.5 |
| $C_{2}$ | $0.93364^{-1}$ |
| $c_{1}$ | 1 |
| $c_{2}$ | 0.93364 |
| $C_{1 o}$ | 0.5 |
| $C_{2 o}$ | $0.93364^{-1}$ |
| $V_{e}(\mathrm{eV})$ | -3.96489 |
| $V_{p}(\mathrm{eV})$ | 3.88560 |
| $T(e V)$ | 0.15095 |
| $V_{m}(\mathrm{eV})$ | -0.07548 |
| $E$ (Аогно) (eV) | 0 |
| $\Delta E_{\mathrm{H}_{2} \mathrm{MO}}($ АОІ HO$)(\mathrm{eV})$ | 0 |
| $E_{T}($ АО/ $/ \mathrm{HO})(\mathrm{eV})$ | 0 |
| $E_{T}\left(\mathrm{H}_{2} \mathrm{MO}\right)(\mathrm{eV})$ | -0.00382 |
| $E_{T}\left(\right.$ atom - atom, $\left.\mathrm{msp}{ }^{3} . \mathrm{AO}\right)(\mathrm{eV})$ | 0 |
| $E_{T}($ мо $)(\mathrm{eV})$ | -0.00382 |
| $\omega\left(10^{15} \mathrm{rad} / \mathrm{s}\right)$ | 0.635696 |
| $E_{K}(e V)$ | 0.41843 |
| $\bar{E}_{D}(e V)$ | 0.00000 |
| $\bar{E}_{\text {Kıi }}(\mathrm{eV})$ | 0.00443 |
| $\bar{E}_{\text {osc }}(\mathrm{eV})$ | 0.00221 |
| $E_{T}($ Group $)(\mathrm{eV})$ | -0.00160 |

Substitution of the parameters of Table 16.28 and the interatomic cohesive energy of helium (Eq. (16.98)) into Eq. (16.25) with $R=a_{H e-H e}$ gives:
$\frac{-4\left(6.02040 \times 10^{-31} C \cdot m\right)^{2}}{4 \pi \varepsilon_{0}\left(2 \sqrt{\frac{a_{\text {He }}{ }^{2} a_{0}}{2(0.5)(0.93364)^{-1}}}\right)^{3}}$

From the energy relationship given by Eq. (16.99) and the relationships between the axes given by Eqs. (16.22-16.24), the dimensions of the $\mathrm{He} \cdots \mathrm{He}$ MO can be solved.

The most convenient way to solve Eq. (16.99) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is:

$$
\begin{equation*}
a_{H e-H e}=13.13271 a_{0}=6.94953 \times 10^{-10} \mathrm{~m} \tag{16.100}
\end{equation*}
$$

The component energy parameters at this condition are given in Table 16.28. Substitution of Eq. (16.100) into Eq. (16.22) gives

$$
\begin{equation*}
c_{H e-H e}^{\prime}=3.50160 a_{0}=1.85297 \times 10^{-10} \mathrm{~m} \tag{16.101}
\end{equation*}
$$

and internuclear distance between neighboring helium atoms:

$$
\begin{equation*}
2 c_{H e-H e}^{\prime}=7.00320 a_{0}=3.70593 \times 10^{-10} m=3.70593 \AA \tag{16.102}
\end{equation*}
$$

The experimental helium interatomic distance $2 c_{C-C}^{\prime}$ at 4.24 K and $<2.25 \mathrm{~K}$ are [102]:

$$
\begin{align*}
& 2 c_{H \text { HeHe }}^{\prime}(4.24 \mathrm{~K})=3.72 \times 10^{-10} \mathrm{~m}=3.72 \AA \\
& 2 c_{H e-H e}^{\prime}(<2.25 \mathrm{~K})=3.70 \times 10^{-10} \mathrm{~m}=3.70 \AA \tag{16.103}
\end{align*}
$$

The other interatomic bond MO parameters can also be determined by the relationships among the parameters. Substitution of Eqs. (16.100) and (16.101) into Eq. (16.23) gives

$$
\begin{equation*}
b_{H e-H e}=c_{H e \cdot-H e}=12.65729 a_{0}=6.69795 \times 10^{-10} \mathrm{~m} \tag{16.104}
\end{equation*}
$$

Substitution of Eqs. (16.100) and (16.101) into Eq. (16.25) gives:

$$
\begin{equation*}
e_{H e-H e}=0.26663 \tag{16.105}
\end{equation*}
$$

Using Eqs. (16.99) and (16.102) and the relationship that there are two van der Waals bonds per helium atom and two atoms per bond, the van der Waals energy per helium atom is:

$$
\begin{equation*}
E_{\text {van der Waals }}(\text { liquid } \mathrm{He} / \mathrm{He})=0.000799 \mathrm{eV} \tag{16.106}
\end{equation*}
$$

The experimental van der Waals energy calculated from the heat of vaporization per helium atom is [103]:

$$
\begin{equation*}
E_{\text {van der Waals }}(\text { liquid He })=E_{\text {vapor }, 4221 K}=0.0829 \mathrm{~kJ} / \text { mole }=0.000859 \mathrm{eV} / \mathrm{He} \tag{16.107}
\end{equation*}
$$

At 1.7 K , the viscosity of liquid helium is close to zero, and a characteristic roton scattering dominates over phonon scattering at this temperature and below [104]. The van der Waals bond energy is also equivalent to the roton energy [105, 106]

$$
\begin{equation*}
E_{\text {roton }}(\text { liquid } \mathrm{He})=8.7 \mathrm{~K}=0.00075 \mathrm{eV} \tag{16.108}
\end{equation*}
$$

and the roton is localized within a region of radius $\approx 3.7-4.0 \AA[104,106-108]$ that matches the $H e \cdots H e$ van der Waals bond distance (Eq. (16.102)). The origin of the roton energy and its cross section as belonging to the van der Waals bond resolves its nature. Independent of this result, the modern view of the roton is that it is not considered associated with the excitation of
vorticity as it was historically; rather it is considered to be due to short-wavelength phonon excitations [105]. Its role in scattering free electrons in superfluid helium is discussed in the Free Electrons in Superfluid Helium are Real in the Absence of Measurement Requiring a Connection of $\psi$ to Physical Reality section. The calculated results based on first principles and given by analytical equations are summarized in Table 16.29.

Table 16.29. The calculated and experimental geometrical parameters and interatomic van der Waals cohesive energy of liquid helium.

| Parameter | Calculated | Experimental | Ref. for Exp. |
| :--- | :---: | :---: | :---: |
| Liquid Helium Interatomic Distance $2 c_{C-C C}^{\prime}$ | $3.70593 \AA$ | $3.72 \AA(\mathrm{~T}=4.24 \mathrm{~K})$ | 102 |
| Roton Length Scale | $3.70593 \AA$ | $3.70(\mathrm{~T}<2.25 \mathrm{~K})$ | $104,106-108$ |
| van der Waals Energy per Helium Atom | 0.000799 eV | 0.000859 eV | 103 |
| (4.221 K) | 0.000799 eV | 0.00075 eV | 105,106 |
| Roton Energy |  |  |  |

Helium exhibits unique behavior due to its possible phases based on the interplay of the factors that determine the van der Waals bonding at a given temperature and pressure to achieve an energy minimum. In extreme cases of sufficient ultra-low temperatures with the atoms driven in phase with an external excitation field such that the formation of a van der Waals-dipolebound macromolecular state or other forms of bonding, such as metallic bonding in the case of alkali metals or van der Waals bonding in meta-stable helium atoms, are suppressed, a pure statistical thermodynamic state called a Bose-Einstein condensate [109] (BEC) ${ }^{1}$ can form having a predominant population of the atoms in a single, lowest-energy translational state in the trap. Since helium has only two electrons in an outer s-shell having a small diameter, the dipole moment is too weak to form transverse dipoles associated with packing. Specifically, with the angular dependence of packed dipoles interactions, the van der Waals energy $E_{\text {van der Waals }}(H e)$ (Eqs. (16.98) and (16.99)) between neighboring dipoles becomes less than the vibrational energy in the transition state ( $\bar{E}_{\text {Kib }}$ term of Eq. (16.99) from Eq. (15.53)). Consequently, helium can only mutually induce and form linear dipole-dipole bonds having end-to-end interactions as an energy minimum. Interposed atoms can form a non-bonded phase having correlated translational motion and obeying Bose-Einstein statistics. This phase forms a Bose-Einstein condensate (BEC) as an energy minimum wherein the translations are synchronous. Since a phase comprised of linearly ordered unit cells held together by dipole interactions, specifically van der Waals dipole interactions, can exist with a BEC phase, super-fluidity can arise wherein the lines of bound dipoles move without friction relative to the BEC phase having correlated-translational motion. The linear bonding is also the origin of quantized vortex rings that enter as quantized vortex lines to form rings.

The van der Waals bonds undergo breakage and formation and exist on a time-average basis depending on the internal energy and pressure as in the case of liquid water. The van der Waals bonding exhibits a maximum extent as the temperature is lowered below the boiling point, and the BEC phase comprises the balance of the atoms as the temperature is further lowered to absolute zero. Helium cannot form a solid without application of high pressure to decrease the interatomic separation and permit energetically favorable transverse dipole interactions as well as linear ones. In contrast, other noble gases such as $\mathrm{Ne}, \mathrm{Ar}, \mathrm{Kr}$ , and $X e$ each possess additional shells including an outer $p$-shell having a relatively larger radius that gives rise to a significant bond moment supportive of dipole packing interactions; thus, these gases can form solids without the application of high pressure.

## GEOMETRICAL PARAMETERS AND ENERGIES DUE TO THE INTERATOMIC VAN DER WAALS COHESIVE ENERGY OF SOLID NEON

Neon is a ten-electron neutral atom having the electron configuration $1 s^{2} 2 s^{2} 2 p^{6}$ with the electrons of each shell paired as mirrorimage current densities in a shell wherein the radius of the outer shell is $r_{10}=0.63659 a_{0}$ (Eq. (10.202)). Thus, in isolation or at sufficient separation, there is no energy between neon atoms. However, reversible mutual van der Waals dipoles may be induced by collisions when the atoms are in close proximity such that neon gas can condense into a liquid and further solidify at sufficiently low temperatures due to the strong dipole moment that accommodates close packing. As in the case of helium, the dipoles are atomic rather than molecular, and the limiting separation is based on the formation of a nascent bond to replace the dipole-dipole interaction. Thus, Eq. (16.25) can also be applied to neon atoms.

[^0]The van der Waals bonding in the neon atom involves hybridizing the three $2 p$ AOs into $2 p^{3} \mathrm{HO}$ orbitals containing six electrons. The total energy of the state is given by the sum over the six electrons. The sum $E_{T}\left(N e, 2 p^{3}\right)$ of experimental energies [15] of $\mathrm{Ne}, N e^{+}, N e^{2+}, N e^{3+}, N e^{4+}$, and $N e^{5+}$ is

$$
\begin{equation*}
E_{T}\left(N e, 2 p^{3}\right)=\binom{157.93 \mathrm{eV}+126.21 \mathrm{eV}+97.12 \mathrm{eV}}{+63.45 \mathrm{eV}+40.96296 \mathrm{eV}+21.56454 \mathrm{eV}}=507.2375 \mathrm{eV} \tag{16.109}
\end{equation*}
$$

By considering that the central field decreases by an integer for each successive electron of the shell, the radius $r_{2 p^{3}}$ of the $N e 2 p^{3}$ shell may be calculated from the Coulombic energy using Eq. (15.13).

$$
\begin{equation*}
r_{2 p^{3}}=\sum_{n=4}^{9} \frac{(Z-n) e^{2}}{8 \pi \varepsilon_{0}(e 507.2375 \mathrm{eV})}=\frac{21 e^{2}}{8 \pi \varepsilon_{0}(e 507.2375 \mathrm{eV})}=0.56329 a_{0} \tag{16.110}
\end{equation*}
$$

where $Z=10$ for neon. Using Eq. (15.14), the Coulombic energy $E_{\text {Coulomb }}\left(N e, 2 p^{3}\right)$ of the outer electron of the van der Waals bound $N e 2 p^{3}$ shell is:

$$
\begin{equation*}
E_{\text {Coulomb }}\left(N e, 2 p^{3}\right)=\frac{-e^{2}}{8 \pi \varepsilon_{0} r_{2 p^{3}}}=\frac{-e^{2}}{8 \pi \varepsilon_{0} 0.56329 a_{0}}=-24.154167 \mathrm{eV} \tag{16.111}
\end{equation*}
$$

To meet the equipotential condition of the union of the two $N e 2 p^{3}$ HOs in a nascent bond, $c_{2}$ of Eqs. (15.2-15.5) and Eq. (15.61) for the nascent $N e-N e$-bond MO is given by Eq. (15.75) as the ratio of the valance energy of the $N e \mathrm{AO}$, $E(N e)=-21.56454 \mathrm{eV}$ and the magnitude of $E_{\text {Coulomb }}\left(N e, 2 p^{3}\right)$ (Eq. (16.111)).

$$
\begin{equation*}
c_{2}\left(\mathrm{Ne}-\mathrm{Ne}, \mathrm{Ne} 2 \mathrm{p}^{3} \mathrm{HO}\right)=\frac{21.56454 \mathrm{eV}}{24.154167 \mathrm{eV}}=0.89279 \tag{16.112}
\end{equation*}
$$

The opposite charge distributions act as symmetrical point charges at the point of maximum separation, each being centered at $1 / 2$ the $N e$-atom radius from the origin. Using the parameters of Eq. (16.112) and $2 c^{\prime}=0.56329 a_{0}=2.98080 X 10^{-11} \mathrm{~m}$ (Eq. (16.110)), the van der Waals dipole of neon is given in Table 16.30.

Table 16.30. The parameters and van der Waals dipole bond moment of the $N e$ functional group of solid neon.

| Functional <br> Group | $n_{1}$ | $\left(c_{1}\right) c_{2}$ | $\left(C_{1}\right) C_{2}$ | $E_{B}($ valence $)$ | $E_{A}($ valence $)$ | $\frac{q}{e}$ | Bond <br> Length <br> $2 c^{\prime}(A)$ | Bond <br> Moment <br> $\mu(\mathrm{D})$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $N e$ | 1 | 0.89279 | 1 | 21.56454 | 24.15417 | 0.22730 | 0.298080 | 0.32544 |

The minimum-energy packing of neon dipoles is face-centered cubic also called cubic close packing. In this case, each neon atom has 12 nearest neighbors and the angle between the aligned dipoles is $\frac{\pi}{4}$ radians. As in the case with graphite, the van der Waals energy is the potential energy between interacting neighboring induced dipoles. Using $\mu_{N e}=0.32544 D=1.08554 X 10^{-30} \mathrm{C} \cdot \mathrm{m}$ (Table 16.30), the van der Waals energy is:

$$
\begin{equation*}
E_{\text {van der Waals }}(N e)=12 \frac{2\left(\mu_{N e}\right)^{2}}{4 \pi \varepsilon_{0}\left(r_{\text {Ne...Ne }}\right)^{3}} \cos \left(\frac{\pi}{4}\right)=\left(\frac{24\left(1.08554 X 10^{-30} C \cdot m\right)^{2}}{4 \pi \varepsilon_{0}\left(2 \sqrt{\frac{a_{\text {Ne...Ne }} a_{0}}{2 C_{1} C_{2}}}\right)^{3}}\right) \cos \left(\frac{\pi}{4}\right) \tag{16.113}
\end{equation*}
$$

The neon interatomic distance is calculated using Eq. (16.25) with the van der Waals energy (Eq. (16.113)) between neighboring dipoles equated to the nascent bond energy. The energy matching parameter $c_{2}$ is the same as that of the neon dipole, and the reduced mass is $\mu=10$. The parameters are summarized in Table 16.31 and Eq. (16.114).

Table 16.31. The energy parameters (eV) of the neon functional group ( $N e \cdots N e$ ).

| Parameters | $\mathrm{Ne} \cdots \mathrm{Ne}$ Group |
| :---: | :---: |
| $n_{1}$ | 1 |
| $C_{1}$ | 0.5 |
| $C_{2}$ | $0.89279^{-1}$ |
| $c_{1}$ | 1 |
| $c_{2}$ | 0.89279 |
| $C_{1 o}$ | 0.5 |
| $C_{2 o}$ | $0.89279^{-1}$ |
| $V_{e}(\mathrm{eV})$ | -4.40464 |
| $V_{p}(\mathrm{eV})$ | 4.27694 |
| $T(e V)$ | 0.19429 |
| $V_{m}(\mathrm{eV})$ | -0.09714 |
| $E$ (логно) (eV) | 0 |
| $\Delta E_{\mathrm{H}_{2} \mathrm{MO}}($ АО/ HO$)(\mathrm{eV})$ | 0 |
| $E_{T}($ АО/ $/ \mathrm{HO})(\mathrm{eV})$ | 0 |
| $E_{T}\left(\mathrm{H}_{2} \mathrm{MO}\right)(\mathrm{eV})$ | -0.03055 |
| $E_{T}\left(\right.$ atom - atom, $\left.\mathrm{msp}{ }^{3} . \mathrm{AO}\right)(\mathrm{eV})$ | 0 |
| $E_{T}($ мо $)(\mathrm{eV})$ | -0.03055 |
| $\omega\left(10^{15} \mathrm{rad} / \mathrm{s}\right)$ | 0.810674 |
| $E_{K}(\mathrm{eV})$ | 0.53360 |
| $\bar{E}_{D}(\mathrm{eV})$ | -0.00004 |
| $\bar{E}_{\text {Kıi }}(\mathrm{eV})$ | 0.00240 |
| $\bar{E}_{\text {osc }}(\mathrm{eV})$ | 0.00116 |
| $E_{T}($ Group $)(\mathrm{eV})$ | -0.02939 |

Substitution of the parameters of Table 16.31 and the interatomic cohesive energy of neon (Eq. (16.113)) into Eq. (16.25) with $R=a_{N e-N e}$ gives:

$$
\begin{aligned}
& \frac{-24\left(1.08554 \times 10^{-30} C \cdot m\right)^{2}}{4 \pi \varepsilon_{0}\left(2 \sqrt{\frac{a_{\text {Ne...Ne }} a_{0}}{2(0.5)(0.89279)^{-1}}}\right)^{3}} \cos \left(\frac{\pi}{4}\right)
\end{aligned}
$$

From the energy relationship given by Eq. (16.114) and the relationships between the axes given by Eqs. (16.22-16.24), the dimensions of the $N e \cdots N e$ MO can be solved.

The most convenient way to solve Eq. (16.114) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is:

$$
\begin{equation*}
a_{N e-N e}=11.33530 a_{0}=5.99838 \times 10^{-10} \mathrm{~m} \tag{16.115}
\end{equation*}
$$

The component energy parameters at this condition are given in Table 16.31. Substitution of Eq. (16.115) into Eq. (16.22) gives

$$
\begin{equation*}
c_{N e-N e}^{\prime}=3.18120 a_{0}=1.68342 \times 10^{-10} \mathrm{~m} \tag{16.116}
\end{equation*}
$$

and internuclear distance between neighboring neon atoms:

$$
\begin{equation*}
2 c_{N e \cdots N e}^{\prime}=6.36239 a_{0}=3.36683 \times 10^{-10} m=3.36683 \AA \tag{16.117}
\end{equation*}
$$

The experimental neon interatomic distance $2 c_{C-C}^{\prime}$ at the melting point of 24.48 K is [112, 113]:

$$
\begin{equation*}
2 c_{N e . N e}^{\prime}(24.48 K)=3.21 \times 10^{-10} m=3.21 \AA \tag{16.118}
\end{equation*}
$$

The other interatomic bond MO parameters can also be determined by the relationships among the parameters. Substitution of Eqs. (16.115) and (16.116) into Eq. (16.23) gives:

$$
\begin{equation*}
b_{N e \cdots N e}=c_{N e \cdot N e}=10.87975 a_{0}=5.75732 \times 10^{-10} \mathrm{~m} \tag{16.119}
\end{equation*}
$$

Substitution of Eqs. (16.115) and (16.116) into Eq. (16.25) gives:

$$
\begin{equation*}
e_{N e-N e}=0.28065 \tag{16.120}
\end{equation*}
$$

A convenient method to calculate the lattice energy is to determine the electric field in solid neon having an electric polarization density corresponding to the aligned dipoles moments, and in turn, the energy can be calculated from the energy of each dipole in the corresponding field using the electrostatic form of Gauss' equation. Substitution of the density of solid neon at the melting point $\rho=\frac{1.433 \mathrm{~g}}{1 \times 10^{-6} \mathrm{~m}^{3}}$ [113], the $M W=20.179 \mathrm{~g} /$ mole,$N_{A}=6.0221415 \times 10^{23}$ molecules / mole, and the neon dipole moment given in Table 16.30 into Eq. (16.53) gives:

$$
\begin{align*}
U(N e) & =\frac{-2\left(\mu_{N e}\right)^{2} \frac{\rho_{\text {solid Ne }}}{M W} N_{A}}{3 \varepsilon_{0}}=\frac{-2\left(1.08554 \times 10^{-30} \mathrm{C} \cdot \mathrm{~m}\right)^{2} \frac{\frac{1.433 \mathrm{~g}}{1 X 10^{-6} \mathrm{~m}^{3}}}{20.179 \mathrm{~g} / \mathrm{mole}} 6.0221415 \times 10^{23} \text { molecules / mole }}{3 \varepsilon_{0}}  \tag{16.121}\\
& =-0.02368 \mathrm{eV}(-2.285 \mathrm{~kJ} / \text { mole })
\end{align*}
$$

$U(N e)$ is also the negative of $E_{\text {van der Waals }}$, the van der Waals energy per neon atom:

$$
\begin{equation*}
E_{\text {van der Waals }}(\text { solid } \mathrm{Ne} / \mathrm{Ne})=0.02368 \mathrm{eV}=2.285 \mathrm{~kJ} / \text { mole } \tag{16.122}
\end{equation*}
$$

The experimental van der Waals energy calculated from the heat of vaporization and fusion per neon atom at the boiling point and triple point, respectively, is [103] :

$$
\begin{equation*}
E_{\text {van der Waals }}(\text { solid Ne })=E_{\text {vapor }}+E_{\text {fusion }}=0.02125 \mathrm{eV} / \mathrm{Ne}=2.0502 \mathrm{~kJ} / \mathrm{mole} \tag{16.123}
\end{equation*}
$$

The calculated results based on first principles and given by analytical equations are summarized in Table 16.32. Using neon the atomic radius (Eq. (16.110)) and the nearest-neighbor distance (Eq. (16.117)), the lattice structure of neon is shown in Figure 16.17A. The charge density of the van der Waals dipoles of the crystalline lattice is shown in Figure 16.18A.

Table 16.32. The calculated and experimental geometrical parameters and interatomic van der Waals cohesive energy of solid neon.

| Parameter | Calculated | Experimental | Ref. for Exp. |
| :--- | :---: | :---: | :---: |
| Solid Neon Interatomic Distance $2 c_{C-C}^{\prime}$ | $3.36683 \AA$ | $3.21 \AA(\mathrm{~T}=24.48 \mathrm{~K})$ | 113 |
| van der Waals Energy per Neon Atom | 0.02368 eV | 0.02125 eV | 103 |

## GEOMETRICAL PARAMETERS AND ENERGIES DUE TO THE INTERATOMIC VAN DER WAALS COHESIVE ENERGY OF SOLID ARGON

Argon is an eighteen-electron neutral atom having the electron configuration $1 s^{2} 2 s^{2} 2 p^{6} 3 s^{2} 3 p^{6}$ with the electrons of each shell paired as mirror-image current densities in a shell wherein the radius of the outer shell is $r_{18}=0.86680 a_{0}$ (Eq. (10.386)). Thus, in isolation or at sufficient separation, there is no energy between argon atoms. However, reversible mutual van der Waals dipoles may be induced by collisions when the atoms are in close proximity such that argon gas can condense into a liquid and further solidify at sufficiently low temperatures due to the strong dipole moment that accommodates close packing. As in the case of helium, the dipoles are atomic rather than molecular, and the limiting separation is based on the formation of a nascent bond to replace the dipole-dipole interaction. Thus, Eq. (16.25) can also be applied to argon atoms.

The van der Waals bonding in the argon atom involves hybridizing the three $3 p$ AOs into $3 p^{3} \mathrm{HO}$ orbitals containing six electrons. The total energy of the state is given by the sum over the six electrons. The sum $E_{T}\left(A r, 3 p^{3}\right)$ of experimental energies [15] of $A r, A r^{+}, A r^{2+}, A r^{3+}, A r^{4+}$, and $A r^{5+}$ is:

$$
\begin{equation*}
E_{T}\left(A r, 3 p^{3}\right)=\binom{91.009 \mathrm{eV}+75.02 \mathrm{eV}+59.81 \mathrm{eV}}{+40.74 \mathrm{eV}+27.62966 \mathrm{eV}+15.75961 \mathrm{eV}}=309.96827 \mathrm{eV} \tag{16.124}
\end{equation*}
$$

By considering that the central field decreases by an integer for each successive electron of the shell, the radius $r_{3 p^{3}}$ of the $A r 3 p^{3}$ shell may be calculated from the Coulombic energy using Eq. (15.13).

$$
\begin{equation*}
r_{3 p^{3}}=\sum_{n=12}^{17} \frac{(Z-n) e^{2}}{8 \pi \varepsilon_{0}(e 309.96827 \mathrm{eV})}=\frac{21 e^{2}}{8 \pi \varepsilon_{0}(e 309.96827 \mathrm{eV})}=0.92178 a_{0} \tag{16.125}
\end{equation*}
$$

where $Z=18$ for argon. Using Eq. (15.14), the Coulombic energy $E_{\text {Coulomb }}\left(A r, 3 p^{3}\right)$ of the outer electron of the van der Waals bound $\operatorname{Ar} 3 p^{3}$ shell is

$$
\begin{equation*}
E_{\text {Coulomb }}\left(A r, 3 p^{3}\right)=\frac{-e^{2}}{8 \pi \varepsilon_{0} r_{3 p^{3}}}=\frac{-e^{2}}{8 \pi \varepsilon_{0} 0.92178 a_{0}}=-14.760394 \mathrm{eV} \tag{16.126}
\end{equation*}
$$

To meet the equipotential condition of the union of the two $A r 3 p^{3}$ HOs in a nascent bond, $c_{2}$ of Eqs. (15.2-15.5) and Eq. (15.61) for the nascent $A r-A r$-bond MO is given by Eq. (15.75) as the ratio of the valance energy of the $A r$ AO, $E(A r)=-15.75961 \mathrm{eV}$ and the magnitude of $E_{\text {Coulomb }}\left(A r, 3 p^{3}\right)$ (Eq. (16.126)).

$$
\begin{equation*}
c_{2}\left(A r-A r, A r 3 p^{3} H O\right)=\frac{14.760394 \mathrm{eV}}{15.75961 \mathrm{eV}}=0.93660 \tag{16.127}
\end{equation*}
$$

Since the outer $\operatorname{Ar} 3 p^{3}$ HO shell is at a lower energy and greater radius than the non-polarized $3 p$ shell, the inner shells are polarized as well. The dipole of the outer shell can polarize the inner shells to the limit that the sum of the primary and secondary dipoles is twice the primary scaled by the energy matching factors of the van der Waals bond given in Eq. (16.15). Thus, the limiting dipole due to polarization of the inner shells is given by:

$$
\begin{align*}
\mu_{A r}<2 c_{1}^{-1} q C_{2} 2 c^{\prime} & =2(0.93660)^{-1}(0.13110) e(0.93660)^{-1}\left(4.87784 \times 10^{-11} \mathrm{~m}\right)  \tag{16.128}\\
& =2.49410 \times 10^{-30} \mathrm{C} \cdot \mathrm{~m}=0.74771 \mathrm{D}
\end{align*}
$$

The condition of Eq. (16.128) is matched by the participation of the outer four shells as given in Table 16.33. At each shell, opposite charge distributions act as symmetrical point charges at the point of maximum separation, each being centered at $1 / 2$ the shell radius from the origin. Using the parameters of Eq. (16.127) and $2 c^{\prime}=0.92178 a_{0}=4.87784 X 10^{-11} m$ (Eq. (16.125)) as well as the radii of the inner shells of argon (Table 10.17), the van der Waals dipole of argon is given in Table 16.33 as the sum of the moments of each participating shell.

Table 16.33. The parameters and van der Waals dipole bond moment of the $A r$ functional group of solid argon.

| Functional Group | $n_{1}$ | $\begin{gathered} \left(c_{1}\right) \\ c_{2} \end{gathered}$ | $\begin{gathered} \left(C_{1}\right) \\ C_{2} \end{gathered}$ | $E_{B}$ (valence) | $E_{A}($ valence $)$ | $\frac{q}{e}$ | Bond <br> Length $2 c^{\prime}(\AA)$ | Bond Moment $\mu$ (D) |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Ar | 1 | 0.93660 | 1 | 14.76039 | 15.75961 | 0.13110 | $\begin{gathered} A r 3 p^{3} \text { HO } 0.48778 \\ A r 3 s \text { AO } 0.41422 \\ A r 2 p \text { AO } 0.15282 \\ A r 2 s \text { AO } 0.12615 \end{gathered}$ | 0.74366 |

The minimum-energy packing of argon dipoles is face-centered cubic also called cubic close packing. In this case, each argon atom has 12 nearest neighbors and the angle between the aligned dipoles is $\frac{\pi}{4}$ radians. As in the case with graphite, the van der Waals energy is the potential energy between interacting neighboring induced dipoles. Using $\mu_{A r}=0.74366 D=2.48058 \times 10^{-30} \mathrm{C} \cdot m$ (Table 16.33), the van der Waals energy is:

$$
\begin{equation*}
E_{\text {van der Waals }}(A r)=12 \frac{2\left(\mu_{A r}\right)^{2}}{4 \pi \varepsilon_{0}\left(r_{A r \ldots A r}\right)^{3}} \cos \left(\frac{\pi}{4}\right)=\left(\frac{24\left(2.48058 X 10^{-30} C \cdot m\right)^{2}}{4 \pi \varepsilon_{0}\left(2 \sqrt{\frac{a_{A r \ldots A r} a_{0}}{2 C_{1} C_{2}}}\right)^{3}}\right) \cos \left(\frac{\pi}{4}\right) \tag{16.129}
\end{equation*}
$$

The argon interatomic distance is calculated using Eq. (16.25) with the van der Waals energy (Eq. (16.129)) between neighboring dipoles equated to the nascent bond energy. The energy matching parameter $c_{2}$ is the same as that of the argon dipole, and the reduced mass is $\mu=20$. The parameters are summarized in Table 16.34 and Eq. (16.130).

Table 16.34. The energy parameters $(\mathrm{eV})$ of the argon functional group ( $A r \cdots A r$ ).

| Parameters | $A r \cdots \mathrm{Ar}$ Group |
| :--- | :---: |
| $n_{1}$ | 1 |
| $C_{1}$ | 0.5 |
| $C_{2}$ | $0.93660^{-1}$ |
| $c_{1}$ | 1 |
| $c_{2}$ | 0.93660 |
| $C_{1 o}$ | 0.5 |
| $C_{2 o}$ | $0.93660^{-1}$ |
| $V_{e}(\mathrm{eV})$ | -4.18356 |
| $V_{p}(\mathrm{eV})$ | 3.97600 |
| $T(\mathrm{eV})$ | 0.16731 |
| $V_{m}(\mathrm{eV})$ | -0.08365 |
| $E_{(\text {AO/Ho })(\mathrm{eV})}$ | 0 |
| $\Delta E_{H_{2} M O}(\mathrm{AO/HO})(\mathrm{eV})$ | 0 |
| $E_{T}($ AO/HO) $(\mathrm{eV})$ | 0 |
| $E_{T}\left(\mathrm{H}_{2} M O\right)(\mathrm{eV})$ | -0.12391 |
| $E_{T}\left(\right.$ atom $\left.-\mathrm{atom}, \mathrm{msp}^{3} . \mathrm{AO}\right)(\mathrm{eV})$ | 0 |
| $E_{T}($ мO $)(\mathrm{eV})$ | -0.12391 |
| $\omega\left(10^{15} \mathrm{rad} / \mathrm{s}\right)$ | 0.683262 |
| $E_{K}(\mathrm{eV})$ | 0.44974 |
| $\bar{E}_{D}(\mathrm{eV})$ | -0.00016 |
| $\bar{E}_{\text {Kvib }}(\mathrm{eV})$ | 0.00153 |
| $\bar{E}_{\text {osc }}(\mathrm{eV})$ | 0.00060 |
| $E_{T}(\mathrm{Group})(\mathrm{eV})$ | -0.12331 |
|  |  |

Substitution of the parameters of Table 16.34 and the interatomic cohesive energy of argon (Eq. (16.129)) into Eq. (16.25) with $R=a_{A r \ldots \text { Ar }}$ gives:

$$
\frac{-24\left(2.48058 \times 10^{-30} C \cdot m\right)^{2}}{4 \pi \varepsilon_{0}\left(2 \sqrt{\frac{a_{A r . . A r} a_{0}}{2(0.5)(0.93660)^{-1}}}\right)^{3}} \cos \left(\frac{\pi}{4}\right)
$$

$$
\left\{\begin{array}{l}
\left(\begin{array}{l}
\left(\frac{-e^{2}}{8 \pi \varepsilon_{0} \sqrt{\frac{a_{A r . A r} a_{0}}{2(0.5)(0.93660)^{-1}}}}(0.93660)\left(2-\frac{1}{2} \frac{a_{0}}{a_{A r \ldots A r}}\right) \ln \frac{a+\sqrt{\frac{a_{A r \ldots A r} a_{0}}{2(0.5)(0.93660)^{-1}}}}{a-\sqrt{\frac{a_{A r \ldots A r} a_{0}}{2(0.5)(0.93660)^{-1}}}}\right.
\end{array}\right)
\end{array}\right) .1\left(\begin{array}{l}
\left(1+2 \sqrt{\frac{2 \hbar \sqrt{\frac{(0.5)(0.93660)^{-1} \frac{e^{2}}{4 \pi \varepsilon_{o}\left(a_{A r \ldots A r}\right)^{3}}}{m_{e}}}}{m_{e} c^{2}}}\right)  \tag{16.130}\\
+\left(\frac{1}{2}\right) \hbar \sqrt{\frac{e^{2}}{\frac{(0.93660) e^{2}}{8 \pi \varepsilon_{o}\left(a_{A r \ldots A r}\right)^{3}}-\frac{e^{2}}{8 \pi \varepsilon_{o}\left(a_{A r \ldots A r}+\sqrt{\frac{a_{A r . . . A r} a_{0}}{2(0.5)(0.93660)^{-1}}}\right)^{3}}}}
\end{array}\right.
$$

From the energy relationship given by Eq. (16.130) and the relationships between the axes given by Eqs. (16.22-16.24), the dimensions of the $A r \cdots A r$ MO can be solved.

The most convenient way to solve Eq. (16.130) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is:

$$
\begin{equation*}
a_{A r . . . A r}=12.50271 a_{0}=6.61615 \times 10^{-10} \mathrm{~m} \tag{16.131}
\end{equation*}
$$

The component energy parameters at this condition are given in Table 16.34. Substitution of Eq. (16.131) into Eq. (16.22) gives

$$
\begin{equation*}
c_{A r \cdots A r}^{\prime}=3.42199 a_{0}=1.81084 \times 10^{-10} \mathrm{~m} \tag{16.132}
\end{equation*}
$$

and internuclear distance between neighboring argon atoms:

$$
\begin{equation*}
2 c_{A r \cdots A r}^{\prime}(0 K)=6.84397 a_{0}=3.62167 \times 10^{-10} m=3.62167 \AA \tag{16.133}
\end{equation*}
$$

The experimental argon interatomic distance $2 c_{C-C}^{\prime}$ is [114]

$$
\begin{equation*}
2 c_{A r \cdot A r}^{\prime}(4.2 K)=3.71 \times 10^{-10} m=3.71 \AA \tag{16.134}
\end{equation*}
$$

The other interatomic bond MO parameters can also be determined by the relationships among the parameters. Substitution of Eqs. (16.131) and (16.132) into Eq. (16.23) gives:

$$
\begin{equation*}
b_{A r . . A r}=c_{A r \ldots A r}=12.02530 a_{0}=6.36351 \times 10^{-10} \mathrm{~m} \tag{16.135}
\end{equation*}
$$

Substitution of Eqs. (16.131) and (16.132) into Eq. (16.25) gives:

$$
\begin{equation*}
e_{A r \ldots A r}=0.27370 \tag{16.136}
\end{equation*}
$$

A convenient method to calculate the lattice energy is to determine the electric field in solid argon having an electric polarization density corresponding to the aligned dipoles moments, and in turn, the energy can be calculated from the energy of each dipole in the corresponding field using the electrostatic form of Gauss' equation. Substitution of the density of solid argon at $4.2 \mathrm{~K} \rho=\frac{1.83 \mathrm{~g}}{1 X 10^{-6} \mathrm{~m}^{3}}$ [114], the $M W=39.948 \mathrm{~g} / \mathrm{mole}, N_{A}=6.0221415 \times 10^{23}$ molecules / mole, and the argon dipole moment given in Table 16.33 into Eq. (16.53) gives:

$$
\begin{align*}
U(A r) & =\frac{-2\left(\mu_{A r}\right)^{2} \frac{\rho_{\text {solid Ar }}}{M W} N_{A}}{3 \varepsilon_{0}} \\
& =\frac{-2\left(2.48058 \times 10^{-30} \mathrm{C} \cdot \mathrm{~m}\right)^{2} \frac{\frac{1.83 \mathrm{~g}}{1 \times 10^{-6} \mathrm{~m}^{3}}}{39.948 \mathrm{~g} / \mathrm{mole}^{2}} 6.0221415 \times 10^{23} \text { molecules / mole }}{3 \varepsilon_{0}}  \tag{16.137}\\
& =-0.07977 \mathrm{eV}(-7.697 \mathrm{~kJ} / \text { mole })
\end{align*}
$$

$U(A r)$ is also the negative of $E_{\text {vander Waals }}$, the van der Waals energy per argon atom:

$$
\begin{equation*}
E_{\text {van der Waals }}(\text { solid } \mathrm{Ar}, 4.2 \mathrm{~K} / \mathrm{Ar})=0.07977 \mathrm{eV}=7.697 \mathrm{~kJ} / \text { mole } \tag{16.138}
\end{equation*}
$$

The experimental van der Waals energy is the cohesive energy [115]:

$$
\begin{equation*}
E_{\text {van der Waals }}(\text { solid } \mathrm{Ar}, 0 \mathrm{~K})=0.08022 \mathrm{eV} / \mathrm{Ar}=7.74 \mathrm{~kJ} / \text { mole } \tag{16.139}
\end{equation*}
$$

The calculated results based on first principles and given by analytical equations are summarized in Table 16.35. Using argon the atomic radius (Eq. (16.125)) and the nearest-neighbor distance (Eq. (16.133)), the lattice structure of argon is shown in Figure 16.17B. The charge density of the van der Waals dipoles of the crystalline lattice is shown in Figure 16.18B.

Table 16.35. The calculated and experimental geometrical parameters and interatomic van der Waals cohesive energy of solid argon.

| Parameter | Calculated | Experimental | Ref. for Exp. |
| :--- | :---: | :---: | :---: |
| Solid Argon Interatomic Distance $2 c_{C-C}^{\prime}$ | $3.62167 \AA(\mathrm{~T}=0 \mathrm{~K})$ | $3.71 \AA(\mathrm{~T}=4.2 \mathrm{~K})$ | 114 |
| van der Waals Energy per Argon Atom | $0.07977 \mathrm{eV}(\mathrm{T}=4.2 \mathrm{~K})$ | $0.08022 \mathrm{eV}(\mathrm{T}=0 \mathrm{~K})$ | 115 |

## GEOMETRICAL PARAMETERS AND ENERGIES DUE TO THE INTERATOMIC VAN DER WAALS COHESIVE ENERGY OF SOLID KRYPTON

Krypton is a thirty-six-electron neutral atom having the electron configuration $1 s^{2} 2 s^{2} 2 p^{6} 3 s^{2} 3 p^{6} 3 d^{10} 4 s^{2} 4 p^{6}$ with the electrons of each shell paired as mirror-image current densities in a shell wherein the radius of the outer shell is $r_{36}=0.97187 a_{0}$ (Eq. (10.102)). Thus, in isolation or at sufficient separation, there is no energy between krypton atoms. However, reversible mutual van der Waals dipoles may be induced by collisions when the atoms are in close proximity such that krypton gas can condense into a liquid and further solidify at sufficiently low temperatures due to the strong dipole moment that accommodates close packing. As in the case of helium, the dipoles are atomic rather than molecular, and the limiting separation is based on the formation of a nascent bond to replace the dipole-dipole interaction. Thus, Eq. (16.25) can also be applied to krypton atoms.

The van der Waals bonding in the krypton atom involves hybridizing the three $4 p$ AOs into $4 p^{3}$ HO orbitals containing six electrons. The total energy of the state is given by the sum over the six electrons. The sum $E_{T}\left(K r, 4 p^{3}\right)$ of experimental energies $[15,116-119]$ of $\mathrm{Kr}, \mathrm{Kr}^{+}, \mathrm{Kr}^{2+}, \mathrm{Kr}^{3+}, \mathrm{Kr}^{4+}$, and $\mathrm{Kr}^{5+}$ is:

$$
\begin{equation*}
E_{T}\left(K r, 4 p^{3}\right)=\binom{78.5 \mathrm{eV}+64.7 \mathrm{eV}+52.5 \mathrm{eV}}{+36.950 \mathrm{eV}+24.35984 \mathrm{eV}+13.99961 \mathrm{eV}}=271.00945 \mathrm{eV} \tag{16.140}
\end{equation*}
$$

By considering that the central field decreases by an integer for each successive electron of the shell, the radius $r_{4 p^{3}}$ of the $K r 4 p^{3}$ shell may be calculated from the Coulombic energy using Eq. (15.13).

$$
\begin{equation*}
r_{4 p^{3}}=\sum_{n=30}^{35} \frac{(Z-n) e^{2}}{8 \pi \varepsilon_{0}(e 271.00945 \mathrm{eV})}=\frac{21 e^{2}}{8 \pi \varepsilon_{0}(e 271.00945 \mathrm{eV})}=1.05429 a_{0} \tag{16.141}
\end{equation*}
$$

where $Z=36$ for krypton. Using Eq. (15.14), the Coulombic energy $E_{\text {Coulomb }}\left(K r, 4 p^{3}\right)$ of the outer electron of the van der Waals bound $K r 4 p^{3}$ shell is:

$$
\begin{equation*}
E_{\text {Coulomb }}\left(K r, 4 p^{3}\right)=\frac{-e^{2}}{8 \pi \varepsilon_{0} r_{4 p^{3}}}=\frac{-e^{2}}{8 \pi \varepsilon_{0} 1.05429 a_{0}}=-12.905212 \mathrm{eV} \tag{16.142}
\end{equation*}
$$

To meet the equipotential condition of the union of the two $K r 4 p^{3}$ HOs in a nascent bond, $c_{2}$ of Eqs. (15.2-15.5) and Eq. (15.61) for the nascent $K r-K r$-bond MO is given by Eq. (15.75) as the ratio of the valance energy of the $K r$ AO, $E(K r)=-13.99961 \mathrm{eV}$ and the magnitude of $E_{\text {Coulomb }}\left(K r, 4 p^{3}\right)$ (Eq. (16.142)).

$$
\begin{equation*}
c_{2}\left(K r-K r, K r 4 p^{3} \mathrm{HO}\right)=\frac{12.905212 \mathrm{eV}}{13.99961 \mathrm{eV}}=0.92183 \tag{16.143}
\end{equation*}
$$

Since the outer $K r 4 p^{3}$ HO shell is at a lower energy and greater radius than the non-polarized $4 p$ shell, the inner shells are polarized as well. The dipole of the outer shell can polarize the inner shells to the limit that the sum of the primary and secondary dipoles is twice the primary scaled by the energy matching factors of the van der Waals bond given in Eq. (16.15). Thus, the limiting dipole due to polarization of the inner shells is given by:

$$
\begin{align*}
\mu_{K r}<2 c_{1}^{-1} q C_{2} 2 c^{\prime} & =2(0.16298) e(0.92183)^{-1}\left(5.57905 \times 10^{-11} \mathrm{~m}\right)  \tag{16.144}\\
& =3.42870 \times 10^{-30} C \cdot m=1.02790 \mathrm{D}
\end{align*}
$$

The condition of Eq. (16.144) is matched by the participation of the outer three shells as given in Table 16.36. At each shell, opposite charge distributions act as symmetrical point charges at the point of maximum separation, each being centered at $1 / 2$ the
shell radius from the origin. Using the parameters of Eq. (16.143) and $2 c^{\prime}=1.05429 a_{0}=5.57905 \times 10^{-11} \mathrm{~m}$ (Eq. (16.141)) as well as the radii of the inner shells of krypton (Eq. (10.102)), the van der Waals dipole of krypton is given in Table 16.36 as the sum of the moments of each participating shell.

Table 16.36. The parameters and van der Waals dipole bond moment of the $K r$ functional group (FG) of solid krypton.

| FG | $n_{1}$ | $\left(c_{1}\right)$ | $\left(C_{1}\right)$ | $E_{B}($ valence $)$ | $E_{A}($ valence $)$ | $\frac{q}{e}$ | Ion/IP/Z <br> $[116-119]$ | Bond <br> Length <br> $c_{2}$ |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |

The minimum-energy packing of krypton dipoles is face-centered cubic also called cubic close packing. In this case, each krypton atom has 12 nearest neighbors and the angle between the aligned dipoles is $\frac{\pi}{4}$ radians. As in the case with graphite, the van der Waals energy is the potential energy between interacting neighboring induced dipoles. Using $\mu_{K r}=1.01129 D=3.37329 \times 10^{-30} C \cdot m$ (Table 16.36), the van der Waals energy is:

$$
\begin{equation*}
E_{\text {van der Waals }}(K r)=12 \frac{2\left(\mu_{K r}\right)^{2}}{4 \pi \varepsilon_{0}\left(r_{K r . . . K r}\right)^{3}} \cos \left(\frac{\pi}{4}\right)=\left(\frac{24\left(3.37329 X 10^{-30} C \cdot m\right)^{2}}{4 \pi \varepsilon_{0}\left(2 \sqrt{\frac{a_{K r . . K r} a_{0}}{2 C_{1} C_{2}}}\right)^{3}}\right) \cos \left(\frac{\pi}{4}\right) \tag{16.145}
\end{equation*}
$$

The krypton interatomic distance is calculated using Eq. (16.25) with the van der Waals energy (Eq. (16.145)) between neighboring dipoles equated to the nascent bond energy. The energy matching parameter $c_{2}$ is the same as that of the krypton dipole, and the reduced mass is $\mu=42$. The parameters are summarized in Table 16.37 and Eq. (16.146).

Table 16.37. The energy parameters (eV) of the krypton functional group ( $\mathrm{Kr} \cdots \mathrm{Kr}$ ).

| Parameters | $\begin{gathered} K r \cdots K r \\ \text { Group } \end{gathered}$ |
| :---: | :---: |
| $n_{1}$ | 1 |
| $C_{1}$ | 0.5 |
| $C_{2}$ | 0.92183 |
| $c_{1}$ | 1 |
| $c_{2}$ | 0.92183 |
| $C_{1 o}$ | 0.5 |
| $C_{2 o}$ | 0.92183 |
| $V_{e}(\mathrm{eV})$ | -3.75058 |
| $V_{p}(e V)$ | 3.52342 |
| $T(e V)$ | 0.13643 |
| $V_{m}(\mathrm{eV})$ | -0.06821 |
| $E$ (Аогно) (eV) | 0 |
| $\Delta E_{\mathrm{H}_{2} \mathrm{MO}}($ АОІНО) $(\mathrm{eV})$ | 0 |
| $E_{T}($ АоІН) $(\mathrm{eV})$ | 0 |
| $E_{T}\left(\mathrm{H}_{2} \mathrm{MO}\right)(\mathrm{eV})$ | -0.15895 |
| $E_{T}\left(\right.$ atom-atom, $\left.\mathrm{msp}^{3} \cdot \mathrm{AO}\right)(\mathrm{eV})$ | 0 |
| $E_{T}($ мо $)(\mathrm{eV})$ | -0.15895 |
| $\omega\left(10^{15} \mathrm{rad} / \mathrm{s}\right)$ | 0.550731 |
| $E_{K}(\mathrm{eV})$ | 0.36250 |
| $\bar{E}_{D}(e V)$ | -0.00019 |
| $\bar{E}_{\text {Kiv }}(\mathrm{eV})$ | 0.00091 |
| $\bar{E}_{\text {osc }}(\mathrm{eV})$ | 0.00026 |
| $E_{T}($ Group $)(\mathrm{eV})$ | -0.15869 |

Substitution of the parameters of Table 16.37 and the interatomic cohesive energy of krypton (Eq. (16.145)) into Eq. (16.25) with $R=a_{K r \ldots K r}$ gives:

$$
\begin{align*}
& \frac{-24\left(3.37329 \times 10^{-31} C \cdot m\right)^{2}}{4 \pi \varepsilon_{0}\left(2 \sqrt{\frac{a_{K r-K} x_{0}}{2(0.5)(0.92183)}}\right)^{3}} \cos \left(\frac{\pi}{4}\right) \\
& \left(\left(\frac{-e^{2}}{8 \pi \varepsilon_{0} \sqrt{\frac{a_{K r-K r} a_{0}}{2(0.5)(0.92183)}}}\left((0.92183)\left(2-\frac{1}{2} \frac{a_{0}}{a_{K r-K r}}\right) \ln \frac{a+\sqrt{\frac{a_{K-K-K} a_{0}}{2(0.5)(0.92183)}}}{a-\sqrt{\frac{a_{K r-K} a_{0}}{2(0.5)(0.92183)}}}-1\right)\right)\right. \\
& =\left\{\begin{array}{l}
\left(1+2 \sqrt{\frac{2 \hbar \sqrt{\frac{(0.5)(0.92183) \frac{e^{2}}{4 \pi \varepsilon_{o}\left(a_{K r-K r}\right)^{3}}}{m_{e}}}}{m_{e} c^{2}}}\right) \\
+\left(\frac{1}{2}\right) \hbar \sqrt{\frac{(0.92183) e^{2}}{8 \pi \varepsilon_{o}\left(a_{K r-K r}\right)^{3}}-\frac{e^{2}}{\frac{e^{2}}{8 \pi \varepsilon_{o}\left(a_{K r-K r}+\sqrt{\frac{a_{K r-K r} a_{0}}{2(0.5)(0.92183)}}\right)^{3}}} 42}
\end{array}\right. \tag{16.146}
\end{align*}
$$

From the energy relationship given by Eq. (16.146) and the relationships between the axes given by Eqs. (16.22-16.24), the dimensions of the $K r \cdots K r$ MO can be solved.

The most convenient way to solve Eq. (16.146) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is:

$$
\begin{equation*}
a_{K r \cdot K r}=13.74580 a_{0}=7.27396 \times 10^{-10} \mathrm{~m} \tag{16.147}
\end{equation*}
$$

The component energy parameters at this condition are given in Table 16.37. Substitution of Eq. (16.147) into Eq. (16.22) gives

$$
\begin{equation*}
c_{K r \cdots K r}^{\prime}=3.86154 a_{0}=2.04344 \times 10^{-10} \mathrm{~m} \tag{16.148}
\end{equation*}
$$

and internuclear distance between neighboring krypton atoms:

$$
\begin{equation*}
2 c_{K r \ldots K r}^{\prime}(0 K)=7.72308 a_{0}=4.08688 \times 10^{-10} m=4.08688 \AA \tag{16.149}
\end{equation*}
$$

The experimental krypton interatomic distance $2 c_{C-C}^{\prime}$ is [113]

$$
\begin{equation*}
2 c_{K r \cdot K r}^{\prime}(0 K)=3.992 \times 10^{-10} m=3.992 \AA \tag{16.150}
\end{equation*}
$$

The other interatomic bond MO parameters can also be determined by the relationships among the parameters. Substitution of Eqs. (16.147) and (16.148) into Eq. (16.23) gives:

$$
\begin{equation*}
b_{K r \cdots K r}=c_{K r \cdots K r}=13.19225 a_{0}=6.98104 \times 10^{-10} \mathrm{~m} \tag{16.151}
\end{equation*}
$$

Substitution of Eqs. (16.147) and (16.148) into Eq. (16.25) gives:

$$
\begin{equation*}
e_{K r \cdots K r}=0.28092 \tag{16.152}
\end{equation*}
$$

A convenient method to calculate the lattice energy is to determine the electric field in solid krypton having an electric polarization density corresponding to the aligned dipoles moments, and in turn, the energy can be calculated from the energy of each dipole in the corresponding field using the electrostatic form of Gauss' equation. Substitution of the density of solid krypton at $4.2 \mathrm{~K} \rho=\frac{3.094 \mathrm{~g}}{1 \times 10^{-6} \mathrm{~m}^{3}}$ [113], the $M W=83.80 \mathrm{~g} /$ mole,$N_{A}=6.0221415 \times 10^{23}$ molecules / mole, and the krypton dipole moment given in Table 16.36 into Eq. (16.53) gives:

$$
\begin{align*}
U(K r) & =\frac{-2\left(\mu_{K r}\right)^{2} \frac{\rho_{\text {solid } K r}}{M W} N_{A}}{3 \varepsilon_{0}} \\
& =\frac{-2\left(3.37329 \times 10^{-30} \mathrm{C} \cdot \mathrm{~m}\right)^{2} \frac{\frac{3.094 \mathrm{~g}}{1 \times 10^{-6} \mathrm{~m}^{3}}}{83.80 \mathrm{~g} / \mathrm{mole}} 6.0221415 \times 10^{23} \text { molecules / mole }}{3 \varepsilon_{0}}  \tag{16.153}\\
& =-0.11890 \mathrm{eV}(-11.472 \mathrm{~kJ} / \text { mole })
\end{align*}
$$

[ $U(K r)$ ] is also the negative of $E_{\text {van der Waals }}$, the van der Waals energy per krypton atom:

$$
\begin{equation*}
E_{\text {van der Waals }}(\text { solid } \mathrm{Kr}, 0 \mathrm{~K} / \mathrm{Kr})=0.11890 \mathrm{eV}=11.472 \mathrm{~kJ} / \text { mole } \tag{16.154}
\end{equation*}
$$

The experimental van der Waals energy is the cohesive energy [120]:

$$
\begin{equation*}
E_{\text {van der Waals }}(\text { solid } K r, 0 K / K r)=0.11561 \mathrm{eV}=11.15454 \mathrm{~kJ} / \text { mole } \tag{16.155}
\end{equation*}
$$

The calculated results based on first principles and given by analytical equations $(0 \mathrm{~K})$ are summarized in Table 16.38. Using krypton the atomic radius (Eq. (16.141)) and the nearest-neighbor distance (Eq. (16.149)), the lattice structure of krypton is shown in Figure 16.15C. The charge density of the van der Waals dipoles of the crystalline lattice is shown in Figure 16.16C.

Table 16.38. The calculated and experimental geometrical parameters and interatomic van der Waals cohesive energy ( 0 K ) of solid krypton.

| Parameter | Calculated | Experimental | Ref. for Exp. |
| :--- | :---: | :---: | :---: |
| Solid Krypton Interatomic Distance $2 C_{C-C}^{\prime}$ | $4.08688 \AA$ | $3.992 \AA$ | 113 |
| van der Waals Energy per Krypton Atom | 0.11890 eV | 0.11561 eV | 120 |

## GEOMETRICAL PARAMETERS AND ENERGIES DUE TO THE INTERATOMIC VAN DER WAALS COHESIVE ENERGY OF SOLID XENON

Xenon is a fifty-four-electron neutral atom having the electron configuration $1 s^{2} 2 s^{2} 2 p^{6} 3 s^{2} 3 p^{6} 3 d^{10} 4 s^{2} 4 p^{6} 4 d^{10} 5 s^{2} 5 p^{6}$ with the electrons of each shell paired as mirror-image current densities in a shell wherein the radius of the outer shell is $r_{54}=1.12168 a_{0}$ (Eq. (10.102)). Thus, in isolation or at sufficient separation, there is no energy between xenon atoms. However, reversible mutual van der Waals dipoles may be induced by collisions when the atoms are in close proximity such that xenon gas can condense into a liquid and further solidify at sufficiently low temperatures due to the strong dipole moment that accommodates close packing. As in the case of helium, the dipoles are atomic rather than molecular, and the limiting separation is based on the formation of a nascent bond to replace the dipole-dipole interaction. Thus, Eq. (16.25) can also be applied to xenon atoms.

The van der Waals bonding in the xenon atom involves hybridizing the three $5 p$ AOs into $5 p^{3}$ HO orbitals containing six electrons. The total energy of the state is given by the sum over the six electrons. The sum $E_{T}\left(X e, 5 p^{3}\right)$ of experimental energies [15, 121-122] of $X e, X e^{+}, X e^{2+}, X e^{3+}, X e^{4+}$, and $X e^{5+}$ is:

$$
\begin{equation*}
E_{T}\left(X e, 5 p^{3}\right)=\binom{66.703 \mathrm{eV}+54.14 \mathrm{eV}+40.9 \mathrm{eV}}{+31.050 \mathrm{eV}+20.975 \mathrm{eV}+12.129842 \mathrm{eV}}=225.89784 \mathrm{eV} \tag{16.156}
\end{equation*}
$$

By considering that the central field decreases by an integer for each successive electron of the shell, the radius $r_{5 p^{3}}$ of the $X e 5 p^{3}$ shell may be calculated from the Coulombic energy using Eq. (15.13).

$$
\begin{equation*}
r_{5 p^{3}}=\sum_{n=48}^{53} \frac{(Z-n) e^{2}}{8 \pi \varepsilon_{0}(e 225.897842 \mathrm{eV})}=\frac{21 e^{2}}{8 \pi \varepsilon_{0}(e 225.897842 \mathrm{eV})}=1.26483 a_{0} \tag{16.157}
\end{equation*}
$$

where $Z=54$ for xenon. Using Eq. (15.14), the Coulombic energy $E_{\text {Coulomb }}\left(X e, 5 p^{3}\right)$ of the outer electron of the van der Waals bound $X e 5 p^{3}$ shell is:

$$
\begin{equation*}
E_{\text {Coulomb }}\left(X e, 5 p^{3}\right)=\frac{-e^{2}}{8 \pi \varepsilon_{0} r_{5 p^{3}}}=\frac{-e^{2}}{8 \pi \varepsilon_{0} 1.26483 a_{0}}=-10.757040 \mathrm{eV} \tag{16.158}
\end{equation*}
$$

To meet the equipotential condition of the union of the two $X e 5 p^{3}$ HOs in a nascent bond, $c_{2}$ of Eqs. (15.2-15.5) and Eq. (15.61) for the nascent $X e-X e$-bond MO is given by Eq. (15.75) as the ratio of the valance energy of the $X e \mathrm{AO}$, $E(X e)=-12.129842 \mathrm{eV}$ and the magnitude of $E_{\text {Coulomb }}\left(X e, 5 p^{3}\right)$ (Eq. (16.158)).

$$
\begin{equation*}
c_{2}\left(X e-X e, X e 5 p^{3} H O\right)=\frac{10.75704 \mathrm{eV}}{12.129842 \mathrm{eV}}=0.88682 \tag{16.159}
\end{equation*}
$$

Since the outer $X e 5 p^{3}$ HO shell is at a lower energy and greater radius than the non-polarized $5 p$ shell, the inner shells are polarized as well. The dipole of the outer shell can polarize the inner shells to the limit that the sum of the primary and secondary dipoles is twice the primary scaled by the energy matching factors of the van der Waals bond given in Eq. (16.15). Thus, the limiting dipole due to polarization of the inner shells is given by:

$$
\begin{equation*}
\mu_{X e}<2 c_{1}^{-1} q C_{2} 2 c^{\prime}=2(0.24079) e(0.88682)\left(6.69318 \times 10^{-11} \mathrm{~m}\right)=5.16444 \times 10^{-30} \mathrm{C} \cdot \mathrm{~m}=1.54826 \mathrm{D} \tag{16.160}
\end{equation*}
$$

The condition of Eq. (16.160) is matched by the participation of the outer two shells as given in Table 16.39. At each shell, opposite charge distributions act as symmetrical point charges at the point of maximum separation, each being centered at $1 / 2$ the shell radius from the origin. Using the parameters of Eq. (16.159) and $2 c^{\prime}=1.26483 a_{0}=6.69318 \times 10^{-11} \mathrm{~m}$ (Eq. (16.157)) as
well as the radius of the inner $5 s$ shell of xenon (Eq. (10.102)), the van der Waals dipole of xenon is given in Table 16.39 as the sum of the moments of each participating shell.

Table 16.39. The parameters and van der Waals dipole bond moment of the $X e$ functional group (FG) of solid xenon.

| FG | $n_{1}$ | $\begin{gathered} \left(c_{1}\right) \\ c_{2} \end{gathered}$ | $\begin{gathered} \left(C_{1}\right) \\ C_{2} \end{gathered}$ | $E_{B}($ valence $)$ | $E_{A}($ valence $)$ | $\frac{q}{e}$ | $\begin{gathered} \text { Ion / IP / Z } \\ \text { [121-122] } \end{gathered}$ | ```Bond Length \(2 c^{\prime}(A)\) (Eqs. (16.157) and (10.102))``` | Bond Moment $\mu$ (D) |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Xe | 1 | 0.88682 | 1 | 10.75704 | 12.12984 | 0.24079 | $\begin{gathered} X e^{6+} \\ 91.6 \\ 7 \end{gathered}$ | $\begin{gathered} X e 5 p^{3} \mathrm{HO} \\ 0.66932 \\ \\ X e 5 s \mathrm{AO} \\ 0.55021 \end{gathered}$ | 1.41050 |

The minimum-energy packing of xenon dipoles is face-centered cubic also called cubic close packing. In this case, each xenon atom has 12 nearest neighbors and the angle between the aligned dipoles is $\frac{\pi}{4}$ radians. As in the case with graphite, the van der Waals energy is the potential energy between interacting neighboring induced dipoles. Using $\mu_{X e}=1.41050 D=4.70492 \times 10^{-30} C \cdot m$ (Table 16.39), the van der Waals energy is:

$$
\begin{equation*}
E_{\text {van der Waals }}(X e)=12 \frac{2\left(\mu_{X e}\right)^{2}}{4 \pi \varepsilon_{0}\left(r_{X e . . . X e}\right)^{3}} \cos \left(\frac{\pi}{4}\right)=\left(\frac{24\left(4.70492 X 10^{-30} C \cdot m\right)^{2}}{4 \pi \varepsilon_{0}\left(2 \sqrt{\frac{a_{X e . . . e_{e}} a_{0}}{2 C_{1} C_{2}}}\right)^{3}}\right) \cos \left(\frac{\pi}{4}\right) \tag{16.161}
\end{equation*}
$$

The xenon interatomic distance is calculated using Eq. (16.25) with the van der Waals energy (Eq. (16.161)) between neighboring dipoles equated to the nascent bond energy. The energy matching parameter $c_{2}$ is the same that of the xenon dipole, and the reduced mass is $\mu=65$. The parameters are summarized in Table 16.40 and Eq. (16.162).

Table 16.40. The energy parameters $(e V)$ of the xenon functional group ( $X e \cdots X e$ ).

| Parameters | Xe $\cdots X e$ Group |
| :---: | :---: |
| $n_{1}$ | 1 |
| $C_{1}$ | 0.5 |
| $C_{2}$ | 0.88682 |
| $c_{1}$ | 1 |
| $c_{2}$ | 1 |
| $C_{1 o}$ | 0.5 |
| $C_{2 o}$ | 0.88682 |
| $V_{e}(\mathrm{eV})$ | -3.49612 |
| $V_{p}(\mathrm{eV})$ | 3.20821 |
| $T(e V)$ | 0.10960 |
| $V_{m}(\mathrm{eV})$ | -0.05480 |
| $E$ (лонно) (eV) | 0 |
| $\Delta E_{\mathrm{H}_{2} \mathrm{MO}}($ AO/HO) $(\mathrm{eV})$ | 0 |
| $E_{T}($ АО/ $/ \mathrm{O})(\mathrm{eV})$ | 0 |
| $E_{T}\left(\mathrm{H}_{2} \mathrm{MO}\right)(\mathrm{eV})$ | -0.23311 |
| $E_{T}\left(\right.$ atom - atom, $\left.\mathrm{msp}^{3} . \mathrm{AO}\right)(\mathrm{eV})$ | 0 |
| $E_{T}($ мо $)(\mathrm{eV})$ | -0.23311 |
| $\omega\left(10^{15} \mathrm{rad} / \mathrm{s}\right)$ | 0.432164 |
| $E_{K}(\mathrm{eV})$ | 0.28446 |
| $\bar{E}_{D}(e V)$ | -0.00025 |
| $\bar{E}_{\text {Kiv }}(\mathrm{eV})$ | 0.00062 |
| $\bar{E}_{\text {osc }}(\mathrm{eV})$ | 0.00006 |
| $E_{T}($ Group $)(\mathrm{eV})$ | -0.23305 |

Substitution of the parameters of Table 16.40 and the interatomic cohesive energy of xenon (Eq. (16.161)) into Eq. (16.25) with $R=a_{X e . . . 才 e}$ gives:


From the energy relationship given by Eq. (16.162) and the relationships between the axes given by Eqs. (16.22-16.24), the dimensions of the $X e \cdots X e$ MO can be solved.

The most convenient way to solve Eq. (16.162) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is:

$$
\begin{equation*}
a_{X e \cdots X e}=15.94999 a_{0}=8.44037 \times 10^{-10} \mathrm{~m} \tag{16.163}
\end{equation*}
$$

The component energy parameters at this condition are given in Table 16.40. Substitution of Eq. (16.163) into Eq. (16.22) gives

$$
\begin{equation*}
c_{X e \cdots X e}^{\prime}=4.24093 a_{0}=2.24420 \times 10^{-10} \mathrm{~m} \tag{16.164}
\end{equation*}
$$

and internuclear distance between neighboring xenon atoms:

$$
\begin{equation*}
2 c_{X e \cdots X e}^{\prime}(0 K)=8.48187 a_{0}=4.48841 \times 10^{-10} m=4.48841 \AA \tag{16.165}
\end{equation*}
$$

The experimental xenon interatomic distance $2 c_{C . C}^{\prime}$ at the melting point of 161.35 K is [112, 113]:

$$
\begin{equation*}
2 c_{X e \cdots X e}^{\prime}(161.35 K)=4.492 \times 10^{-10} m=4.492 A \tag{16.166}
\end{equation*}
$$

The other interatomic bond MO parameters can also be determined by the relationships among the parameters. Substitution of Eqs. (16.163) and (16.164) into Eq. (16.23) gives:

$$
\begin{equation*}
b_{X e \cdots X e}=c_{X e \cdots X e}=15.37585 a_{0}=8.13655 \times 10^{-10} \mathrm{~m} \tag{16.167}
\end{equation*}
$$

Substitution of Eqs. (16.163) and (16.164) into Eq. (16.25) gives:

$$
\begin{equation*}
e_{X e \cdots X e}=0.26589 \tag{16.168}
\end{equation*}
$$

A convenient method to calculate the lattice energy is to determine the electric field in solid xenon having an electric polarization density corresponding to the aligned dipoles moments, and in turn, the energy can be calculated from the energy of each dipole in the corresponding field using the electrostatic form of Gauss' equation. Substitution of the density of solid xenon at $0 \mathrm{~K} \rho=\frac{3.780 \mathrm{~g}}{1 \times 10^{-6} \mathrm{~m}^{3}}$ [113], the $M W=131.29 \mathrm{~g} / \mathrm{mole}, N_{A}=6.0221415 \times 10^{23}$ molecules $/$ mole, and the xenon dipole moment given in Table 16.39 into Eq. (16.53) gives:

$$
\begin{align*}
U(X e) & =\frac{-2\left(\mu_{X e}\right)^{2} \frac{\rho_{\text {solid } X e}}{M W} N_{A}}{3 \varepsilon_{0}} \\
& =\frac{-2\left(4.70492 \times 10^{-30} \mathrm{C} \cdot \mathrm{~m}\right)^{2} \frac{\frac{3.780 \mathrm{~g}}{1 \times 10^{-6} \mathrm{~m}^{3}}}{131.29 \mathrm{~g} / \mathrm{mole}^{2}} 6.0221415 \times 10^{23} \text { molecules / mole }}{3 \varepsilon_{0}}  \tag{16.169}\\
& =-0.18037 \mathrm{eV}(-17.403 \mathrm{~kJ} / \text { mole })
\end{align*}
$$

$U(X e)$ is also the negative of $E_{\text {vander Waals }}$, the van der Waals energy per xenon atom:

$$
\begin{equation*}
E_{\text {van der Waals }}(\text { solid } X e, 0 \mathrm{~K} / \mathrm{Xe})=0.18037 \mathrm{eV}=17.403 \mathrm{~kJ} / \text { mole } \tag{16.170}
\end{equation*}
$$

The experimental van der Waals energy is the cohesive energy [123]:

$$
\begin{equation*}
E_{\text {van der Waals }}(\text { solid Xe, } 0 \mathrm{~K})=0.16608 \mathrm{eV} / \mathrm{Xe}=16.02472 \mathrm{~kJ} / \text { mole } \tag{16.171}
\end{equation*}
$$

The calculated results based on first principles and given by analytical equations are summarized in Table 16.41. Using xenon the atomic radius (Eq. (16.157)) and the nearest-neighbor distance (Eq. (16.165)), the lattice structure of xenon is shown in Figure 16.15D. The charge density of the van der Waals dipoles of the crystalline lattice is shown in Figure 16.16D.

Table 16.41. The calculated and experimental geometrical parameters and interatomic van der Waals cohesive energy of solid xenon.

| Parameter | Calculated | Experimental | Ref. for Exp. |
| :--- | :---: | :---: | :---: |
| Solid Xenon Interatomic Distance $2 c_{C-C}^{\prime}$ <br> van der Waals Energy per Xenon Atom <br> $(0 \mathrm{~K})$ | $4.4884 \AA(\mathrm{~T}=0 \mathrm{~K})$ | $4.492 \AA(\mathrm{~T}=161.35 \mathrm{~K})$ | 113 |

Figure 16.15. The face-centered cubic crystal structures of noble gas condensates, all to the same scale. (A) The crystal structure of neon. (B) The crystal structure of argon. (C) The crystal structure of krypton. (D) The crystal structure of xenon.


Figure 16.16. The charge densities of the van der Waals dipoles and face-centered cubic crystal structures of noble gas condensates, all to the same scale. (A) The charge density and crystal structure of neon. (B) The charge density and crystal structure of argon. (C) The charge density and crystal structure of krypton. (D) The charge density and crystal structure of xenon.


## GEOMETRICAL PARAMETERS AND ENERGIES DUE TO THE INTERMOLECULAR VAN DER WAALS COHESIVE ENERGIES OF $H_{2}$ DIMER, SOLID $H_{2}, H_{2}(1 / p)$ DIMER, AND SOLID $\mathrm{H}_{2}(1 / p)$

Molecular hydrogen and molecular hydrino are typically gaseous molecules having no net electric field. But, at very low temperatures it is possible to form diffuse dimers, or alternatively, these gases may be condensed with the formation of mutually induced van der Waals dipole interactions. The nature of the van der Waals bonding of molecular hydrogen and molecular hydrino is solved using the same approach as that of condensed helium atoms, except analogously with the comparison of isoelectronic helium and $\mathrm{H}_{2}$ excited states, the prolate spherical coordinate equations replace the spherical coordinate equations of the two-electron system.

Molecular hydrogen and molecular hydrino are each a two-electron neutral molecule with both electrons paired as mirror-image current densities in a prolate spheroidal shell of semimajor and minor axes given by Eqs. (11.202) and (11.205), respectively. Thus, in isolation or at sufficient separation, there is no energy between hydrogen-type molecules. However, reversible mutual van der Waals dipoles may be induced by collisions when the atoms are in close proximity such that hydrogentype gas can condense into dimers, liquid, and solid states depending on the temperature and pressure. The limiting separation of the corresponding van der Waals bonding between molecular dipoles is based on the formation of a nascent bond to replace the dipole-dipole interaction. Thus, the isoelectronic helium case of general van der Waals Eq. (16.25) given by Eq. (16.99) also applies to hydrogen-type molecules. Based on symmetry, the molecules at aligned along their semimajor axes, the induces charges act the position of the nuclei at the foci, and the dipole separation is in the direction of the semimajor axes given by the internuclear distance (Eq. (11.204)).

The van der Waals bonding in the hydrogen-type molecules involves hybridizing the $1 s$ molecular orbitals (MO) into a $1 s^{1}$ hybridized molecular orbital (HMO) containing two electrons. The total energy of the state is given by the sum over the two electrons given by Eq. (11.241). The sum $E_{T}\left(H_{2}(1 / p), 1 s^{1}\right)$ is:

$$
\begin{equation*}
E_{T}=-p^{2} 31.351 \mathrm{eV}-p^{3} 0.326469 \mathrm{eV} \tag{16.172}
\end{equation*}
$$

The HMO electron energy is equally distributed to each equivalent electron to give the Coulombic energy $E_{\text {Coulomb }}\left(H_{2}(1 / p), 1 s^{1}\right)$ of the outer electron of the van der Waals bound $H_{2}(1 / p) 1 s^{1}$ shell:

$$
\begin{align*}
E_{\text {Coulomb }}\left(H_{2}(1 / p), 1 s^{1}\right) & =\frac{-p^{2} 31.351 \mathrm{eV}-p^{3} 0.326469 \mathrm{eV}}{2}  \tag{16.173}\\
& =-p^{2} 15.6755 \mathrm{eV}-p^{3} 0.16323 \mathrm{eV}
\end{align*}
$$

To meet the equipotential condition of the union of the two $H_{2}(1 / p) 1 s^{1}$ HOs in a nascent bond, $c_{2}$ of Eqs. (15.2-15.5) and Eq. (15.61) for the nascent $H_{2}(1 / p)-H_{2}(1 / p)$-bond MO is given by Eq. (15.75) as the ratio of the valance energy of the $H_{2}(1 / p)$ MO, $E_{I P_{1}}\left(H_{2}(1 / p)\right)=p^{2} 15.2171 \mathrm{eV}+p^{3} 0.207714 \mathrm{eV}$ given by Eq. (11.244) and the magnitude of $E_{\text {Coulomb }}\left(H_{2}(1 / p), 1 s^{1}\right)$ (Eq. (16.173)):

$$
\begin{equation*}
c_{2}\left(H_{2}(1 / p)-H_{2}(1 / p), H_{2}(1 / p) 1 s^{1} H M O\right)=\frac{p^{2} 15.2171 \mathrm{eV}+p^{3} 0.207714 \mathrm{eV}}{p^{2} 15.6755 \mathrm{eV}+p^{3} 0.16323 \mathrm{eV}} \tag{16.174}
\end{equation*}
$$

The opposite charge distributions act as point charges at the foci, the position of the nuclei such that the separation distance is the internuclear distance given by Eq. (11.204).

The van der Waals dipole of $H_{2}(1 / p)$ is calculated by the same method as that of helium using the parameters of Eq. (16.174) and $2 c^{\prime}=\frac{a_{0} \sqrt{2}}{p}$ (Eq. (11.204)). As in the case with helium, the van der Waals energy is the potential energy between interacting neighboring induced dipoles. Using the van der Waals dipole of $H_{2}(1 / p)$, the van der Waals energy for a hydrogen type dimer is:

$$
\begin{equation*}
E_{\text {van der Waals }}\left(H_{2}(1 / p)\right)=\frac{2\left(\mu_{H_{2}(1 / p)}\right)^{2}}{4 \pi \varepsilon_{0}\left(r_{\left.H_{2}(1 / p)\right) . . H_{2}(1 / p)}\right)^{3}} \tag{16.175}
\end{equation*}
$$

The dimer interatomic distance is calculated using Eq. (16.25) with the van der Waals energy (Eq. (16.175)) between neighboring dipoles equated to the nascent bond energy. From the energy relationship given by Eq. (16.25) and the relationships between the axes given by Eqs. (16.22-16.24), the dimensions of the $H_{2}(1 / p) \cdots H_{2}(1 / p)$ MO can be solved.

## PARAMETERS AND ENERGIES DUE TO THE INTERMOLECULAR VAN DER WAALS COHESIVE ENERGIES OF H ${ }_{2}$ DIMER

In the case of $H_{2}, p=1$ such that the parameter $c_{2}$ is given by

$$
\begin{equation*}
c_{2}\left(H_{2}-H_{2}, H_{2} 1 s^{1} H M O\right)=\frac{1^{2} 15.2171 \mathrm{eV}+1^{3} 0.207714 \mathrm{eV}}{1^{2} 15.6755 \mathrm{eV}+1^{3} 0.16323 \mathrm{eV}}=0.9739 \tag{16.176}
\end{equation*}
$$

Using the parameters of Eq. (16.176) and $2 c^{\prime}=a_{0} \sqrt{2}$ (Eq. (11.204)), the van der Waals dipole of $H_{2}$ is given in Table 16.42.

Table 16.42 . The parameters and van der Waals dipole bond moment of the $H_{2}$ functional group of hydrogen dimer.

| Functional <br> Group | $n_{1}$ | $\left(C_{1}\right) c_{2}$ | $\left(C_{1}\right) C_{2}$ | $E_{B}$ (valence) | $E_{A}($ valence) | $\frac{q}{e}$ | Bond <br> Length <br> $2 c^{\prime}(A)$ | Bond <br> Moment <br> $\mu(D)$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $H_{2}$ | 1 | 0.9739 | 1 | 15.4248 | 15.83901 | 0.05300 | 0.748369 | 0.19053 |

The van der Waals energy is the potential energy between interacting neighboring induced dipoles. Using $\mu_{H_{2}}=0.19053 D=6.35524 \times 10^{-31} C \cdot m$ (Table 16.42), the van der Waals energy is:

$$
\begin{equation*}
E_{\text {van der Waals }}\left(H_{2}\right)=\frac{2\left(\mu_{H_{2}}\right)^{2}}{4 \pi \varepsilon_{0}\left(r_{H_{2} \cdots H_{2}}\right)^{3}}=\frac{2\left(6.35524 \times 10^{-31} C \cdot m\right)^{2}}{4 \pi \varepsilon_{0}\left(2 \sqrt{\frac{a_{H_{2} \cdots H_{2}} a_{0}}{2 C_{1} C_{2}}}\right)^{3}} \tag{16.177}
\end{equation*}
$$

The hydrogen dimer intermolecular distance is calculated using Eq. (16.25) with the van der Waals energy (Eq. (16.177)) between neighboring dipoles equated to the nascent bond energy. The energy matching parameter $c_{2}$ of $H_{2} \cdots H_{2}$ is the same as that of the $H_{2}$ dipole, and the reduced mass is $\mu=1$. The parameters are summarized in Table 16.43 and Eq. (16.178).

Table 16.43. The energy parameters (eV) of the hydrogen dimer functional group $\left(H_{2} \cdots H_{2}\right)$.

| Parameters | $H_{2} \cdots H_{2}$ <br> Group |
| :---: | :---: |
| $n_{1}$ | 1 |
| $C_{1}$ | 0.5 |
| $C_{2}$ | $0.97385^{-1}$ |
| $c_{1}$ | 1 |
| $c_{2}$ | 0.97385 |
| $C_{1 o}$ | 0.5 |
| $C_{2 o}$ | $0.97385^{-1}$ |
| $V_{e}(e V)$ | -3.64208 |
| $V_{p}(e V)$ | 3.57387 |
| $T(e V)$ | 0.12236 |
| $V_{m}(\mathrm{eV})$ | -0.06118 |
| $E$ (ао/но) (eV) | 0 |
| $\Delta E_{\mathrm{H}_{2} \mathrm{MO}}($ АО/ HO$)(\mathrm{eV})$ | 0 |
| $E_{T}($ АоІІо) $)(e V)$ | 0 |
| $E_{T}\left(\mathrm{H}_{2} \mathrm{MO}\right)(\mathrm{eV})$ | -0.00703 |
| $E_{T}\left(\right.$ atom - atom, $\left.\mathrm{msp}^{3} . \mathrm{AO}\right)(\mathrm{eV})$ | 0 |
| $E_{T}($ мо $)(\mathrm{eV})$ | -0.00703 |
| $\omega\left(10^{15} \mathrm{rad} / \mathrm{s}\right)$ | 0.515948 |
| $E_{K}(\mathrm{eV})$ | 0.33961 |
| $\bar{E}_{D}(e V)$ | 0.00001 |
| $\bar{E}_{\text {Kıi }}(\mathrm{eV})$ | 0.00028 |
| $\bar{E}_{\text {osc }}(\mathrm{eV})$ | -0.00013 |
| $E_{T}($ Group $)(e V)$ | -0.00069 |

Substitution of the parameters of Table 16.43 and the interatomic cohesive energy of hydrogen dimer (Eq. (16.177)) into Eq. (16.25) with $R=a_{H_{2}-H_{2}}$ gives:
$\frac{-2\left(6.35524 X 10^{-31} C \cdot m\right)^{2}}{4 \pi \varepsilon_{0}\left(2 \sqrt{\frac{a_{H_{2}-H_{2}} a_{0}}{2(0.5)(0.97385)^{-1}}}\right)^{3}}$

(16.178)
wherein $(0.05300)$ is $q / e$ the induced charge from Table 16.42 . From the energy relationship given by Eq. (16.178) and the relationships between the axes given by Eqs. (16.22-16.24), the dimensions of the $H_{2} \cdots H_{2}$ MO can be solved.

The most convenient way to solve Eq. (16.178) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is:

$$
\begin{equation*}
a_{H_{2} \cdot-H_{2}}=14.88260 a_{0}=7.87553 \times 10^{-10} \mathrm{~m} \tag{16.179}
\end{equation*}
$$

The component energy parameters at this condition are given in Table 16.43. Substitution of Eq. (16.179) into Eq. (16.22) gives

$$
\begin{equation*}
c_{H_{2}-H_{2}}^{\prime}=3.80702 a_{0}=2.01459 \times 10^{-10} \mathrm{~m} \tag{16.180}
\end{equation*}
$$

and internuclear distance between neighboring $H_{2}$ nuclei:

$$
\begin{equation*}
2 c_{H_{2} \cdots H_{2}}^{\prime}=7.61404 a_{0}=4.02918 \times 10^{-10} m=4.02918 \AA \tag{16.181}
\end{equation*}
$$

The other intermolecular bond MO parameters can also be determined by the relationships among the parameters. Substitution of Eqs. (16.179) and (16.180) into Eq. (16.23) gives

$$
\begin{equation*}
b_{H_{2}-H_{2}}=c_{H_{2} \cdots H_{2}}=14.38744 a_{0}=7.61350 \times 10^{-10} \mathrm{~m} \tag{16.182}
\end{equation*}
$$

Substitution of Eqs. (16.179) and (16.180) into Eq. (16.25) gives:

$$
\begin{equation*}
e_{H_{2}-H_{2}}=0.25580 \tag{16.183}
\end{equation*}
$$

Using Eqs. (16.177) and (16.181), the van der Waals energy of the hydrogen dimer is:

$$
\begin{equation*}
E_{\text {van der Waals }}\left(\left[\mathrm{H}_{2}\right]_{2}\right)=0.00069 \mathrm{eV}\left(5.59 \mathrm{~cm}^{-1}\right) \tag{16.184}
\end{equation*}
$$

The experimental $D_{0}$ is shown in Figure of Ref. [124], [125] is:

$$
\begin{equation*}
D_{0}=5.6 \mathrm{~cm}^{-1} \tag{16.185}
\end{equation*}
$$

From Table 16.43, the hydrogen dimer vibrational energy $\bar{E}_{\text {Kvib }}(\mathrm{eV})$ that matches the experimental dimer spectrum [126] is

$$
\begin{equation*}
\bar{E}_{K v i b}(e V)=0.00028 \mathrm{eV}\left(2.3 \mathrm{~cm}^{-1}\right) \tag{16.186}
\end{equation*}
$$

## PARAMETERS AND ENERGIES DUE TO THE INTERMOLECULAR VAN DER WAALS COHESIVE ENERGIES OF SOLID $\mathrm{H}_{2}$

The minimum-energy packing of $H_{2}$ dipoles is face-centered cubic also called cubic close packing. In this case, each $H_{2}$ molecule has 12 nearest neighbors and the angle between the aligned dipoles is $\frac{\pi}{4}$ radians. As in the case with hydrogen dimer, the van der Waals energy is the potential energy between interacting neighboring induced dipoles. Using $\mu_{H_{2}}=0.19053 D=6.35524 \times 10^{-31} C \cdot m$ (Table 16.42), the van der Waals energy is:
$E_{\text {van der Waals }}\left(H_{2}\right)=12 \frac{2\left(\mu_{H_{2}}\right)^{2}}{4 \pi \varepsilon_{0}\left(r_{H_{2}-H_{2}}\right)^{3}} \cos \left(\frac{\pi}{4}\right)=\frac{24\left(6.35524 X 10^{-31} C \cdot m\right)^{2}}{4 \pi \varepsilon_{0}\left(2 \sqrt{\frac{a_{H_{2}-H_{2}} a_{0}}{2 C_{1} C_{2}}}\right)^{3}} \cos \left(\frac{\pi}{4}\right)$
The hydrogen dimer intermolecular distance is calculated using Eq. (16.25) with the van der Waals energy (Eq. (16.187)) between neighboring dipoles equated to the nascent bond energy. The energy matching parameter $c_{2}$ of $H_{2} \cdots H_{2}$ is the same as that of the $H_{2}$ dipole, and the reduced mass is $\mu=1$. The parameters are summarized in Table 16.44 and Eq. (16.188).

Table 16.44. The energy parameters $(\mathrm{eV})$ of the solid hydrogen functional group ( $H_{2} \cdots H_{2}$ ).

| Parameters | $\begin{gathered} H_{2} \cdots H_{2} \\ \text { Group } \end{gathered}$ |
| :---: | :---: |
| $n_{1}$ | 1 |
| $C_{1}$ | 0.5 |
| $C_{2}$ | $0.97385^{-1}$ |
| $c_{1}$ | 1 |
| $c_{2}$ | 0.97385 |
| $C_{1 o}$ | 0.5 |
| $C_{2 o}$ | $0.97385^{-1}$ |
| $V_{e}(e V)$ | -3.63998 |
| $V_{p}(e V)$ | 3.57286 |
| $T(e V)$ | 0.12222 |
| $V_{m}(\mathrm{eV})$ | -0.06111 |
| $E$ (Ао/но) (eV) | 0 |
| $\Delta E_{\mathrm{H}_{2} \mathrm{MO}}($ АОІ HO$)(\mathrm{eV})$ | 0 |
| $E_{T}\left(\right.$ Ао/ $^{\text {/ }}$ ) $)(\mathrm{eV})$ | 0 |
| $E_{T}\left(\mathrm{H}_{2} \mathrm{MO}\right)(\mathrm{eV})$ | -0.00601 |
| $E_{T}\left(\right.$ atom - atom, $\left.\mathrm{msp}^{3} \cdot \mathrm{AO}\right)(\mathrm{eV})$ | 0 |
| $E_{T}($ мо $)(\mathrm{eV})$ | -0.00601 |
| $\omega\left(10^{15} \mathrm{rad} / \mathrm{s}\right)$ | 0.515511 |
| $E_{K}(e V)$ | 0.33932 |
| $\bar{E}_{D}(e V)$ | 0.00001 |
| $\bar{E}_{\text {Kvib }}(\mathrm{eV})$ | 0.00028 |
| $\bar{E}_{\text {osc }}(\mathrm{eV})$ | -0.00013 |
| $E_{T}($ Group $)(\mathrm{eV})$ | -0.00587 |

Substitution of the parameters of Table 16.43 and the interatomic cohesive energy of solid hydrogen (Eq. (16.187)) into Eq. (16.25) with $R=a_{H_{2} \cdots H_{2}}$ gives:
$\frac{-24\left(6.35524 \times 10^{-31} C \cdot m\right)^{2}}{4 \pi \varepsilon_{0}\left(2 \sqrt{\frac{a_{H_{2}-H_{2}} a_{0}}{2(0.5)(0.97385)^{-1}}}\right)^{3}} \cos \left(\frac{\pi}{4}\right)$

(16.188)
wherein $(0.05300)$ is $q / e$ the induced charge from Table 16.42. From the energy relationship given by Eq. (16.188) and the relationships between the axes given by Eqs. (16.22-16.24), the dimensions of the $H_{2} \cdots H_{2}$ MO can be solved.

The most convenient way to solve Eq. (16.188) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is:

$$
\begin{equation*}
a_{H_{2}-H_{2}}=14.89100 a_{0}=7.87998 \times 10^{-10} \mathrm{~m} \tag{16.189}
\end{equation*}
$$

The component energy parameters at this condition are given in Table 16.44. Substitution of Eq. (16.189) into Eq. (16.22) gives

$$
\begin{equation*}
c_{H_{2}-\cdots H_{2}}^{\prime}=3.80810 a_{0}=2.01516 \times 10^{-10} \mathrm{~m} \tag{16.190}
\end{equation*}
$$

and internuclear distance between neighboring $H_{2}$ nuclei:

$$
\begin{equation*}
2 c_{H_{2}-H_{2}}^{\prime}=7.61619 a_{0}=4.03031 \times 10^{-10} m=4.03031 \AA \tag{16.191}
\end{equation*}
$$

The other intermolecular bond MO parameters can also be determined by the relationships among the parameters. Substitution of Eqs. (16.189) and (16.190) into Eq. (16.23) gives

$$
\begin{equation*}
b_{H_{2}-H_{2}}=c_{H_{2} \cdots H_{2}}=14.39584 a_{0}=7.61795 \times 10^{-10} \mathrm{~m} \tag{16.192}
\end{equation*}
$$

Substitution of Eqs. (16.189) and (16.190) into Eq. (16.25) gives:

$$
\begin{equation*}
e_{H_{2} \cdots H_{2}}=0.25573 \tag{16.193}
\end{equation*}
$$

A convenient method to calculate the lattice energy is to determine the electric field in solid molecular hydrogen having an electric polarization density corresponding to the aligned dipoles moments, and in turn, the energy can be calculated from the energy of each dipole in the corresponding field using the electrostatic form of Gauss' equation. Substitution of the density of solid hydrogen $\rho=\frac{0.086 \mathrm{~g}}{1 \times 10^{-6} \mathrm{~m}^{3}}$ [127], the $M W=2.016 \mathrm{~g} / \mathrm{mole}, N_{A}=6.0221415 \times 10^{23}$ molecules $/ \mathrm{mole}$, and the $H_{2}$ dipole moment given in Table 16.42 into Eq. (16.53) gives:

$$
\begin{aligned}
U\left(H_{2}\right) & =\frac{-2\left(\mu_{H_{2}}\right)^{2} \frac{\rho_{\text {solid } H_{2}}}{M W} N_{A}}{3 \varepsilon_{0}} \\
& =\frac{-2\left(6.35524 \times 10^{-31} \mathrm{C} \cdot \mathrm{~m}\right)^{2} \frac{\frac{0.086 \mathrm{~g}}{1 \times 10^{-6} \mathrm{~m}^{3}}}{2.016 \mathrm{~g} / \mathrm{mole}} 6.0221415 \times 10^{23} \text { molecules / mole }}{3 \varepsilon_{0}} \\
& =-0.00488 \mathrm{eV}(-0.470 \mathrm{~kJ} / \text { mole })
\end{aligned}
$$

$$
\begin{align*}
U(N e) & =\frac{-2\left(\mu_{N e}\right)^{2} \frac{\rho_{\text {solid } N_{e}} N_{A}}{M W}}{3 \varepsilon_{0}} \\
& =\frac{-2\left(1.08554 \times 10^{-30} \mathrm{C} \cdot \mathrm{~m}\right)^{2} \frac{\frac{1.433 \mathrm{~g}}{1 \times 10^{-6} \mathrm{~m}^{3}}}{20.179 \mathrm{~g} / \mathrm{mole}} 6.0221415 \times 10^{23} \text { molecules / mole }}{3 \varepsilon_{0}}  \tag{16.194}\\
& =-0.02368 \mathrm{eV}(-2.285 \mathrm{~kJ} / \text { mole })
\end{align*}
$$

$U\left(H_{2}\right)$ is also the negative of $E_{\text {van der Waals }}$, the van der Waals energy per $H_{2}$ molecule:

$$
\begin{equation*}
E_{\text {van der Waals }}\left(\text { solid } \mathrm{H}_{2} / \mathrm{H}_{2}\right)=0.00488 \mathrm{eV}=0.470 \mathrm{~kJ} / \text { mole } \tag{16.195}
\end{equation*}
$$

The experimental van der Waals energy calculated from the heat of vaporization and fusion per hydrogen molecule [128] is

$$
\begin{align*}
E_{\text {van der Waals }}\left(\text { solid } H_{2}\right) & =E_{\text {vapor }}+E_{\text {fusion }} \\
& =0.44936 \mathrm{~kJ} / \text { mole }+0.05868 \mathrm{~kJ} / \text { mole }  \tag{16.196}\\
& =0.50804 \mathrm{~kJ} / \text { mole }
\end{align*}
$$

## PARAMETERS AND ENERGIES DUE TO THE INTERMOLECULAR VAN DER WAALS COHESIVE ENERGIES OF $\mathrm{H}_{2}(1 / 4)$ DIMER

In the case of $H_{2}, p=4$ such that the parameter $c_{2}$ is given by

$$
\begin{align*}
c_{2}\left(H_{2}(1 / 4)-H_{2}(1 / 4), H_{2}(1 / 4) 1 s^{1} H M O\right) & =\frac{4^{2} 15.2171 \mathrm{eV}+4^{3} 0.207714 \mathrm{eV}}{4^{2} 15.6755 \mathrm{eV}+4^{3} 0.16323 \mathrm{eV}}  \tag{16.197}\\
& =0.9828
\end{align*}
$$

Using the parameters of Eq. (16.197) and $2 c^{\prime}=a_{0} \frac{\sqrt{2}}{4}$ (Eq. (11.204)), the van der Waals dipole of $H_{2}(1 / 4)$ is given in Table 16.45.

Table 16.45. The parameters and van der Waals dipole bond moment of the $H_{2}(1 / 4)$ functional group of hydrogen dimer.

| Functional <br> Group | $n_{1}$ | $\left(c_{1}\right)$ | $\left(C_{1}\right)$ | $E_{B}$ (valence) | $E_{A}($ valence) | $\frac{q}{e}$ | Bond <br> $C_{2}$ | Bength <br> $2 c^{\prime}(A)$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Mond <br> $\mu(\mathrm{D})$ |  |  |  |  |  |  |  |  |
| $H_{2}(1 / 4)$ | 1 | 0.9828 | 1 | 256.767 | 261.255 | 0.03466 | 0.187092 | 0.03114 |

The van der Waals energy is the potential energy between interacting neighboring induced dipoles. Using $\mu_{H_{2}(1 / 4)}=0.03114 D=1.03885 \times 10^{-31} C \cdot m$ (Table 16.45), the van der Waals energy is:

$$
\begin{equation*}
E_{\text {van der Waals }}\left(H_{2}(1 / 4)\right)=\frac{2\left(\mu_{H_{2}(1 / 4)}\right)^{2}}{4 \pi \varepsilon_{0}\left(r_{H_{2}(1 / 4) \cdot \cdot H_{2}(1 / 4)}\right)^{3}}=\frac{2\left(1.03885 \times 10^{-31} C \cdot m\right)^{2}}{4 \pi \varepsilon_{0}\left(2 \sqrt{\frac{a_{H_{2}(1 / 4) \cdot H_{2}(1 / 4)} a_{0}}{2 C_{1} C_{2}}}\right)^{3}} \tag{16.198}
\end{equation*}
$$

The molecular hydrino dimer intermolecular distance is calculated using Eq. (16.25) with the van der Waals energy (Eq. (16.198)) between neighboring dipoles equated to the nascent bond energy. The energy matching parameter $c_{2}$ of $H_{2}(1 / 4) \cdots H_{2}(1 / 4)$ is the same as that of the $H_{2}(1 / 4)$ dipole, and the reduced mass is $\mu=1$. The parameters are summarized in Table 16.46 and Eq. (16.199).

Table 16.46. The energy parameters $(\mathrm{eV})$ of the hydrogen dimer functional group $\left(H_{2}(1 / 4) \cdots H_{2}(1 / 4)\right)$.

| Parameters | $\begin{gathered} H_{2}(1 / 4) \cdots H_{2}(1 / 4) \\ \text { Group } \end{gathered}$ |
| :---: | :---: |
| $n_{1}$ | 1 |
| $C_{1}$ | 0.5 |
| $C_{2}$ | $0.9828^{-1}$ |
| $c_{1}$ | 1 |
| $c_{2}$ | 0.9828 |
| $C_{1 o}$ | 0.5 |
| $C_{2 o}$ | $0.9828^{-1}$ |
| $V_{e}(e V)$ | -56.96364 |
| $V_{p}(e V)$ | 56.03381 |
| $T(e V)$ | 1.85462 |
| $V_{m}(\mathrm{eV})$ | -0.92731 |
| $E$ (ло/но) (eV) | 0 |
| $\Delta E_{\mathrm{H}_{2} \text { МО }}($ АО/но) $(\mathrm{eV})$ | 0 |
| $E_{T}($ Ао/Но) $)(e V)$ | 0 |
| $E_{T}\left(\mathrm{H}_{2} \mathrm{MO}\right)(\mathrm{eV})$ | -0.00253 |
| $E_{T}\left(\right.$ atom - atom, $\left.\mathrm{msp}{ }^{3} . \mathrm{AO}\right)(\mathrm{eV})$ | 0 |
| $E_{T}($ мо) $(\mathrm{eV})$ | -0.00253 |
| $\omega\left(10^{15} \mathrm{rad} / \mathrm{s}\right)$ | 7.83940 |
| $E_{K}(\mathrm{eV})$ | 5.16003 |
| $\bar{E}_{D}(e V)$ | 0.00001 |
| $\bar{E}_{\text {Kvib }}(\mathrm{eV})$ | 0.00285 |
| $\bar{E}_{\text {osc }}(\mathrm{eV})$ | -0.00141 |
| $E_{T}($ Group $)(\mathrm{eV})$ | -0.00111 |

Substitution of the parameters of Table 16.46 and the interatomic cohesive energy of hydrogen dimer (Eq. (16.198)) into Eq. (16.25) with $R=a_{H_{2}(1 / 4) \cdot H_{2}(1 / 4)}$ gives:

$$
\frac{-2\left(1.03885 \times 10^{-31} C \cdot m\right)^{2}}{4 \pi \varepsilon_{0}\left(2 \sqrt{\frac{a_{H_{2}(1 / 4) \cdot-H_{2}(1 / 4)} a_{0}}{2(0.5)(0.9828)^{-1}}}\right)^{3}}
$$


wherein $(0.03466)$ is $q / e$ the induced charge from Table 16.45 . From the energy relationship given by Eq. (16.199) and the relationships between the axes given by Eqs. (16.22-16.24), the dimensions of the $H_{2}(1 / 4) \cdots H_{2}(1 / 4) \mathrm{MO}$ can be solved.

The most convenient way to solve Eq. (16.199) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is:

$$
\begin{equation*}
a_{H_{2}(1 / 4) \cdot H_{2}(1 / 4)_{2}}=3.83931 a_{0}=2.03168 \times 10^{-10} \mathrm{~m} \tag{16.200}
\end{equation*}
$$

The component energy parameters at this condition are given in Table 16.46. Substitution of Eq. (16.200) into Eq. (16.22) gives

$$
\begin{equation*}
c_{H_{2}(1 / 4) \cdots H_{2}(1 / 4)_{2}}^{\prime}=0.97126 a_{0}=5.13967 \times 10^{-11} \mathrm{~m} \tag{16.201}
\end{equation*}
$$

and internuclear distance between neighboring $H_{2}$ nuclei:

$$
\begin{equation*}
2 c_{H_{2}(1 / 4) \cdot H_{2}(1 / 4)_{2}}^{\prime}=1.94251 a_{0}=1.02793 \times 10^{-10} m=1.02793 \AA \tag{16.202}
\end{equation*}
$$

The other intermolecular bond MO parameters can also be determined by the relationships among the parameters. Substitution of Eqs. (16.200) and (16.201) into Eq. (16.23) gives

$$
\begin{equation*}
b_{H_{2}(1 / 4) \cdot H_{2}(1 / 4)_{2}}=c_{H_{2}(1 / 4) \cdot H_{2}(1 / 4)_{2}}=3.71443 a_{0}=1.96559 \times 10^{-10} \mathrm{~m} \tag{16.203}
\end{equation*}
$$

Substitution of Eqs. (16.200) and (16.201) into Eq. (16.25) gives:

$$
\begin{equation*}
e_{H_{2}(1 / 4) \cdot H_{2}(1 / 4)_{2}}=0.25298 \tag{16.204}
\end{equation*}
$$

Using Eqs. (16.198) and (16.202), the van der Waals energy of the hydrogen dimer is:

$$
\begin{equation*}
E_{\text {van der Waals }}\left(\left[H_{2}(1 / 4)\right]_{2}\right)=0.00111 \mathrm{eV}\left(8.991 \mathrm{~cm}^{-1}\right) \tag{16.205}
\end{equation*}
$$

## PARAMETERS AND ENERGIES DUE TO THE INTERMOLECULAR VAN DER WAALS COHESIVE ENERGIES OF SOLID $\mathrm{H}_{2}(1 / 4)$

The minimum-energy packing of $H_{2}(1 / 4)$ dipoles is face-centered cubic also called cubic close packing. In this case, each $H_{2}(1 / 4)$ molecule has 12 nearest neighbors and the angle between the aligned dipoles is $\frac{\pi}{4}$ radians. As in the case with $H_{2}(1 / 4)$ dimer, the van der Waals energy is the potential energy between interacting neighboring induced dipoles. Using $\mu_{H_{2}(1 / 4)}=0.03114 D=1.03885 \times 10^{-31} \mathrm{C} \cdot m$ (Table 16.45), the van der Waals energy is:

$$
\begin{align*}
E_{\text {van der Waals }}\left(H_{2}(1 / 4)\right)= & 12 \frac{2\left(\mu_{H_{2}(1 / 4)}\right)^{2}}{4 \pi \varepsilon_{0}\left(r_{H_{2}(1 / 4) \cdot \cdot H_{2}(1 / 4)}\right)^{3}} \cos \left(\frac{\pi}{4}\right) \\
= & \frac{24\left(1.03885 \times 10^{-31} C \cdot m\right)^{2}}{4 \pi \varepsilon_{0}\left(2 \sqrt{\frac{a_{H_{2}(1 / 4) \cdot \cdot H_{2}(1 / 4)} a_{0}}{2 C_{1} C_{2}}}\right)^{3}} \cos \left(\frac{\pi}{4}\right) \tag{16.206}
\end{align*}
$$

The hydrogen dimer intermolecular distance is calculated using Eq. (16.25) with the van der Waals energy (Eq. (16.206)) between neighboring dipoles equated to the nascent bond energy. The energy matching parameter $c_{2}$ of $H_{2}(1 / 4) \cdots H_{2}(1 / 4)$ is the same as that of the $H_{2}(1 / 4)$ dipole, and the reduced mass is $\mu=1$. The parameters are summarized in Table 16.47 and Eq. (16.207).

Table 16.47. The energy parameters (eV) of the solid hydrogen functional group $\left(H_{2}(1 / 4) \cdots H_{2}(1 / 4)\right)$.

| Parameters | $\begin{gathered} H_{2}(1 / 4) \cdots H_{2}(1 / 4) \\ \text { Group } \end{gathered}$ |
| :---: | :---: |
| $n_{1}$ | 1 |
| $C_{1}$ | 0.5 |
| $C_{2}$ | $0.9828^{-1}$ |
| $c_{1}$ | 1 |
| $c_{2}$ | 0.9828 |
| $C_{1 o}$ | 0.5 |
| $C_{2 o}$ | $0.9828^{-1}$ |
| $V_{e}(e V)$ | -56.98072 |
| $V_{p}(e V)$ | 56.04202 |
| $T(e V)$ | 1.85572 |
| $V_{m}(\mathrm{eV})$ | -0.92786 |
| $E$ (Аогно) (eV) | 0 |
| $\Delta E_{\mathrm{H}_{2} \text { МО }}($ АО/НО) $(\mathrm{eV})$ | 0 |
| $E_{T}($ АО/ $/ \mathrm{O})(\mathrm{eV})$ | 0 |
| $E_{T}\left(\mathrm{H}_{2} \mathrm{MO}\right)(\mathrm{eV})$ | -0.01084 |
| $E_{T}\left(\right.$ atom - atom, $\left.\mathrm{msp}^{3} . \mathrm{AO}\right)(\mathrm{eV})$ | 0 |
| $E_{T}($ мо $)(\mathrm{eV})$ | -0.01084 |
| $\omega\left(10^{15} \mathrm{rad} / \mathrm{s}\right)$ | 7.84284 |
| $E_{K}(\mathrm{eV})$ | 5.16229 |
| $\bar{E}_{D}(\mathrm{eV})$ | 0.00005 |
| $\bar{E}_{\text {Kvib }}(\mathrm{eV})$ | 0.00285 |
| $\bar{E}_{\text {osc }}(\mathrm{eV})$ | -0.00138 |
| $E_{T}($ Group $)(\mathrm{eV})$ | -0.00946 |

Substitution of the parameters of Table 16.47 and the interatomic cohesive energy of solid hydrogen (Eq. (16.206)) into Eq. (16.25) with $R=a_{H_{2}(1 / 4) \cdot H_{2}(1 / 4)}$ gives:
$\frac{-24\left(1.03885 \times 10^{-31} C \cdot m\right)^{2}}{4 \pi \varepsilon_{0}\left(2 \sqrt{\frac{a_{H_{2}(1 / 4) \cdot H_{2}(1 / 4)} a_{0}}{2(0.5)(0.9828)^{-1}}}\right)^{3}} \cos \left(\frac{\pi}{4}\right)$

(16.207)
wherein $(0.03466)$ is $q / e$ the induced charge from Table 16.42. From the energy relationship given by Eq. (16.207) and the relationships between the axes given by Eqs. (16.22-16.24), the dimensions of the $H_{2}(1 / 4) \cdots H_{2}(1 / 4) \mathrm{MO}$ can be solved.

The most convenient way to solve Eq. (16.207) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is:

$$
\begin{equation*}
a_{H_{2}(1 / 4) \cdots H_{2}(1 / 4)}=3.83819 a_{0}=2.03108 \times 10^{-10} \mathrm{~m} \tag{16.208}
\end{equation*}
$$

The component energy parameters at this condition are given in Table 16.47. Substitution of Eq. (16.208) into Eq. (16.22) gives

$$
\begin{equation*}
c_{H_{2}(1 / 4) \cdots H_{2}(1 / 4)_{2}}^{\prime}=0.97111 a_{0}=5.13891 \times 10^{-11} \mathrm{~m} \tag{16.209}
\end{equation*}
$$

and internuclear distance between neighboring $H_{2}(1 / 4)$ nuclei:

$$
\begin{equation*}
2 c_{H_{2}(1 / 4) \cdot-H_{2}(1 / 4)}^{\prime}=1.94223 a_{0}=1.02778 \times 10^{-10} m=1.02778 \AA \tag{16.210}
\end{equation*}
$$

The other intermolecular bond MO parameters can also be determined by the relationships among the parameters. Substitution of Eqs. (16.208) and (16.209) into Eq. (16.23) gives

$$
\begin{equation*}
b_{H_{2}(1 / 4) \cdot H_{2}(1 / 4)_{2}}=c_{H_{2}(1 / 4) \cdots H_{2}(1 / 4)_{2}}=3.71330 a_{0}=1.96499 \times 10^{-10} \mathrm{~m} \tag{16.211}
\end{equation*}
$$

Substitution of Eqs. (16.208) and (16.209) into Eq. (16.25) gives:

$$
\begin{equation*}
e_{H_{2}(1 / 4) \cdot H_{2}(1 / 4)_{2}}=0.25301 \tag{16.212}
\end{equation*}
$$

A convenient method to calculate the lattice energy is to determine the electric field in solid molecular hydrogen having an electric polarization density corresponding to the aligned dipoles moments, and in turn, the energy can be calculated from the energy of each dipole in the corresponding field using the electrostatic form of Gauss' equation. The $H_{2}(1 / 4)$ number density of solid $H_{2}(1 / 4) \tilde{N}$ is given by the 4 , the number of $H_{2}(1 / 4)$ molecules per unit cell divided by the volume of the face centered cubic cell. Using the neighbor internuclear distance $2 c_{H_{2}(1 / 4)-H_{2}(1 / 4)}^{\prime}$ (Eq. (16.210)) as the length of the unit cell, $\tilde{N}$ can be approximated by

$$
\begin{equation*}
\tilde{N}=\frac{4}{\left(2 c_{H_{2}(1 / 4) \cdot \cdot \cdot H_{2}(1 / 4)}^{\prime}\right)^{3}}=\frac{4}{\left(1.02778 \times 10^{-10} \mathrm{~m}\right)^{3}}=3.684 \times 10^{30} H_{2}(1 / 4) \mathrm{m}^{-3} \tag{16.213}
\end{equation*}
$$

Substitution of number density of solid $H_{2}(1 / 4) \tilde{N}$ given by Eq. (16.213) and the $H_{2}(1 / 4)$ dipole moment given in Table 16.45 into Eq. (16.53) gives:

$$
\left.\begin{array}{rl}
U\left(H_{2}(1 / 4)\right) & =\frac{-2\left(\mu_{H_{2}(1 / 4)}\right)^{2} \tilde{N}}{3 \varepsilon_{0}} \\
& =\frac{-2\left(1.03885 \mathrm{X} 10^{-31} \mathrm{C} \cdot \mathrm{~m}\right)^{2} 3.684 \mathrm{X} 10^{30} \mathrm{H}_{2}(1 / 4) \mathrm{m}^{-3}}{3 \varepsilon_{0}} \\
& =-0.01869 \mathrm{eV}(-1.803 \mathrm{~kJ} / \mathrm{mole})
\end{array}\right] \begin{aligned}
& U\left(H_{2}(1 / 4)\right) \text { is also the negative of } E_{\text {van der Waals }} \text {, the van der Waals energy per } H_{2}(1 / 4) \text { molecule: } \\
& E_{\text {van der Waals }}\left(\text { solid } H_{2}(1 / 4) / H_{2}(1 / 4)\right)=0.01869 \mathrm{eV}(1.803 \mathrm{~kJ} / \text { mole })
\end{aligned}
$$

## PARAMETERS AND MAGNETIC ENERGIES DUE TO THE SPIN MAGNETIC MOMENT OF H2(1/4)

Molecular hydrino $H_{2}(1 / p)$ comprises (i) two electrons bound in a minimum energy, equipotential, prolate spheroidal, twodimensional current membrane comprising a molecular orbital (MO), (ii) two $Z=1$ nuclei such as two protons at the foci of the prolate spheroid, and (iii) a photon wherein the photon equation of each state is different from that of an excited $\mathrm{H}_{2}$ state given in the Excited States of the Hydrogen Molecule section, in that the photon increases the central field by an integer rather than decreasing the central prolate spheroidal field to that of a reciprocal integer of the fundamental charge at each nucleus centered on the foci of the spheroid, and the electrons of $H_{2}(1 / p)$ are paired in the same shell at the same position $\xi$ versus being in separate $\xi$ positions. The interaction of the hydrino state photon electric field with each electron gives rise to a nonradiative radial monopole such that the state is stable. In contrast, by the same mechanism, the excited $\mathrm{H}_{2}$ state photon gives rise to a radiative radial dipole at the outer excited state electron resulting in the state being unstable to radiation. For exited states, the photon electric field comprises a prolate spheroidal harmonic in space and time that modulates the constant prolate spheroidal current of the outer electron in-phase. The former corresponds to orbital angular momentum and the latter corresponds to spin angular momentum. Due to the unique stable state of molecular hydrino comprising two nonradiative electrons in a single MO, the nature of the trapped photon field, the nature of the vector photon propagation inside the molecular hydrino serving as a resonator cavity, and the nature of the electron currents are unique.

Consider the formation of a nonradiative state $\mathrm{H}_{2}$ molecule from two non-radiative $n=1$ state H atoms requiring the bond energy to be removed by a third body collision:

$$
\begin{equation*}
H+H+M \rightarrow H_{2}+M^{*} \tag{16.216a}
\end{equation*}
$$

wherein $M^{*}$ denotes the third body in an energetic state ${ }^{2}$. Molecular hydrino may form by the same nonradiative mechanism wherein, hydrino atoms and hydrino molecules comprise an additional photon component of the central field that is nonradiative by virtue of being equivalent to an integer multiple of the central field of a proton at the origin and at each focus of the prolate spheroid MO, respectively. The combination of two electrons into a single molecular orbital while maintaining the radiationless integer photonic central field gives rise to the special case of a doublet MO state in molecular hydrino rather than a singlet state. The singlet state is nonmagnetic; whereas, the doublet state has a net magnetic moment of a Bohr magneton $\mu_{B}$.

Specifically, the basis element of the current of each hydrogen-type atom is a great circle as shown in the Generation of the Atomic Orbital-CVFS section, and the great circle current basis elements transition to elliptic current basis elements in hydrogen-type molecules as shown in the Force Balance of Hydrogen-Type Molecules section. As shown in the Equation of the Electric Field inside the Atomic Orbital section, (i) photons carry electric field and comprise closed field line loops, (ii) a hydrino or a molecular hydrino each comprises a trapped photon wherein the photon field-line loops each travel along a mated great circle or elliptic current loop basis element in the same vector direction, (iii) the direction of each field line increases in the direction perpendicular to the propagation direction with relative motion as required by special relativity, and (iv) since the linear velocity of each point along a field line loop of a trapped photon is light speed $C$, the electric field direction relative to the laboratory frame is purely perpendicular to its mated current loop and it exists only at $\delta\left(r-r_{n}\right)$. The paired electrons of the hydrogen molecular orbital comprise a singlet state having no net magnetic moment. However, the photon field lines of two

[^1]Specifically, a neutrino comprises a photon having $\frac{\hbar}{2}$ angular momentum in its electric and magnetic fields (Neutrinos section). During the reaction of Eq. (16.216b), the angular momentum of the reactants is conserved in the products wherein each of the two reacting hydrino atoms are electron spin $1 / 2$, and the product molecular hydrino and electron neutrino are also each spin $1 / 2$. The neutrino emission reaction (Eq. (16.216b)) may be exploited for communication (e.g. a neutrino telecommunication system).
hydrino atoms that superimpose during the formation of a molecular hydrino can only propagate in one direction to avoid cancellation and give rise to a central field to provide force balance between the centrifugal and central forces (Eq. (11.200)). This special case gives rise to a doublet state in molecular hydrino.

The MO may be treated as a linear combination of the great ellipses that comprise the current density function of each electron as given in the Generation of the Orbitsphere-CVFS section and the Force Balance of Hydrogen-Type Molecules section. To meet the boundary conditions that each corresponding photon is matched in direction with each electron current and that the electron angular momentum is $\hbar$ are satisfied, one half of electron 1 and one half of electron 2 may be spin up and matched with the two photons of the two electrons on the MO, and the other half of electron 1 may be spin up and the other half of electron 2 may be spin down such that one half of the currents are paired and one half of the currents are unpaired. Thus, the spin of the MO is $\frac{1}{2}(\uparrow \uparrow+\downarrow \uparrow)$ where each arrow designates the spin vector of one electron. The two photons that bind the two electrons in the molecular hydrino state are phase-locked to the electron currents and circulate in opposite directions. Given the indivisibility of each electron and the condition that the MO comprises two identical electrons, the force of the two photons is transferred to the totality of the electron MO comprising a linear combination of the two identical electrons to satisfy Eq. (11.200). The resulting angular momentum and magnetic moment of the unpaired current density are $\hbar$ and a Bohr magneton $\mu_{B}$, respectively.

Due to its unpaired electron, molecular hydrino is electron paramagnetic resonance (EPR) spectroscopy active. Moreover, due to the unpaired electron in a common molecular orbital with a paired electron, the EPR spectrum is uniquely characteristic of and identifies molecular hydrino as shown infra. As given in the Electron $g$ Factor section, flux is linked by an unpaired electron in quantized units of the fluxon or magnetic flux quantum $\frac{h}{2 e}$. The electric energy, the magnetic energy, and the dissipated energy of a fluxon treading the atomic orbital given by Eqs. $(1.226-1.227)$ is

$$
\begin{equation*}
\Delta E_{\operatorname{mag} g}^{\text {spin }}=2\left(1+\frac{\alpha}{2 \pi}+\frac{2}{3} \alpha^{2}\left(\frac{\alpha}{2 \pi}\right)-\frac{4}{3}\left(\frac{\alpha}{2 \pi}\right)^{2}\right) \mu_{B} B=g \mu_{B} B \tag{16.217}
\end{equation*}
$$

In the case of the molecular hydrino, the unpaired electron is a linear combination of two electrons of the MO wherein one half of the current density is paired, and one half is unpaired. The fluxon links both interlocked electrons such that the contribution of the flux linkage terms are doubled. The corresponding $g$ factor is

$$
\begin{equation*}
g_{H_{2}(1 / p)}=2\left(1+2\left(\frac{\alpha}{2 \pi}+\frac{2}{3} \alpha^{2}\left(\frac{\alpha}{2 \pi}\right)-\frac{4}{3}\left(\frac{\alpha}{2 \pi}\right)^{2}\right)\right)=2.0046386 \tag{16.218}
\end{equation*}
$$

The energy between parallel and antiparallel levels of the unpaired electron in an applied magnetic field is

$$
\begin{equation*}
\Delta E_{\text {mag } 2.0046}^{\text {spin }}=g_{H_{2}(1 / p)} \mu_{B} B=2.0046386 \mu_{B} B \tag{16.219}
\end{equation*}
$$

The result of Eq. (16.218) was confirmed wherein the electron paramagnetic resonance peak was observed with $g$ factor of 2.00445 [131].

Molecular hydrino comprises a linear combination of an unpaired and a paired electron in a common prolate spheroidal molecular orbital (MO) wherein ellipsoidal current elements alternate in pairs of contiguous parallel and antiparallel currents. Consider the designation of the prolate spheroidal MO wherein the $y$ and $z$-axes are semiminor axes and the $x$-axis is the semimajor axis. The resulting current density comprises a prolate spheroid possessing $\frac{\hbar}{2}$ of angular momentum along either the +z -axis or -z -axis and $\frac{\hbar}{4}$ along each of the +y and -y -axes as shown in Figure 11.4 wherein the unpaired-paired intrinsic current density may occupy two degenerate distributions about either the +z -axis or -z -axis. The application of a magnetic field lifts the degeneracy. The semimajor or $x$-axis of the molecular hydrino aligns parallel or antiparallel to an applied magnetic field with capture of a photon of the Larmor frequency corresponding to the applied field-electron spin interaction energy $E_{\uparrow \uparrow / \uparrow \uparrow}$ given by the Bohr magneton $\mu_{B}$ times the applied flux $B$ :

$$
\begin{equation*}
E_{\uparrow \uparrow / \downarrow \uparrow}=\mu_{B} B \tag{16.220}
\end{equation*}
$$

The resulting cylindrical rotation of the MO current about the semimajor axis gives rise to $\hbar$ of angular momentum along either the +x or -x -axis (Figure 11.4) and causes the spin current vectors in the transverse plane containing the semiminor axes to average to zero. A $180^{\circ}$ electron spin flip transition along the semimajor axis may occur with the absorption of a resonant microwave photon having the energy given by Eqs. (16.217-16.219). The $\hbar$ of angular momentum of the spin flip photon aligns along either the +z or -z -axis in the transverse plane wherein the unpaired current $\frac{\hbar}{2}$ of angular momentum along the either the +z -axis or - z -axis quantizes the orientation of spin flip photon angular momentum. In the case that the angular momentum of the spin flip photon is opposite that of the unpaired current, the unpaired current also flips its orientation with a concomitant flip of the corresponding angular momentum by $180^{\circ}$ in the transverse plane. The semiminor axis spin flip transition lifts the degeneracy of the semimajor axis spin flip transition due to an interaction of the paired and unpaired current of the MO. The
three sources of splitting of the spin flip transition are considered: (i) the energy of interaction of the internal magnetic field of the electron MO on the proton magnetic moments, (ii) the energy of interaction of the transition between nuclear spin isomer states on the spin of the electron MO, and (iii) the coupling energy between the spin unpaired electro and the spin paired electron of the $H_{2}(1 / 4)$ electron MO.

Hydrogen-type molecules comprise a proton at each focus of the prolate spheroid molecular orbital, each with nuclear spin and a corresponding magnetic dipole moment of $\mu_{p}$. Consider that effect on the protons when a magnetic field is applied along the semimajor axis, the x-axis, that excites the Larmor precession of the unpaired electron of $H_{2}(1 / p)$ to give rise to an electron spin magnetic moment of a Bohr magneton also aligned along the semimajor axis. The intrinsic electron spin vectors along the two transverse semiminor axes, the y-axis and the z-axis, as shown in Figure 11.4 rotate around the applied magnetic field and the electron spin magnetic moment at the Larmor frequency given by Eq. (1.227). The magnetic field inside the ellipsoidal MO, $\mathbf{H}_{x}^{-}$, (Eq. (12.31)) is:

$$
\begin{equation*}
B_{x}^{-}=\mu_{0} \frac{e \hbar}{2 m_{e}} \frac{1}{a^{3}\left(1-\frac{b^{2}}{a^{2}}\right)^{3 / 2}}\left(2 \sqrt{1-\frac{b^{2}}{a^{2}}}+\ln \frac{1+\sqrt{1-\frac{b^{2}}{a^{2}}}}{1-\sqrt{1-\frac{b^{2}}{a^{2}}}}\right) \tag{16.221}
\end{equation*}
$$

Substitution of the $H_{2}(1 / 4)$ semimajor axis $a$ (Eq. (11.202)) and the $H_{2}(1 / 4)$ semiminor axis $b$ (Eq. (11.205)) into Eq. (16.221) gives

$$
\begin{equation*}
B_{x}^{-}=4.52 \times 10^{4} T \tag{16.222}
\end{equation*}
$$

This large electrodynamic field aligns parallel or antiparallel to the applied field corresponding to the direction of the Larmor electron magnetic moment. However, this electrodynamic field is transverse to the vector direction of the proton magnetic moments that must align along the direction of the magnetostatic intrinsic spin as a condition of the formation and energy stability of the $H_{2}(1 / 4)$ molecule. Thus, the nuclear magnetic moments align in the transverse plane, the yz-plane that is perpendicular to three-semimajor axis magnetic components: (i) the applied magnetic field that excites the Larmor rotation, (ii) the electron spin magnetic moment, and (iii) the electrodynamic magnetic field of the electron's Larmor rotation. The intrinsic electron spin vectors along the transverse two semiminor axes, the y-axis and the z-axis, (Figure 11.4) rotate around these threesemimajor axis magnetic components at the Larmor frequency given by Eq. (1.227). Since the nuclear magnetic moments are transverse to the three-semimajor axis magnetic components, and the Larmor-frequency rotation causes the intrinsic electron spin magnetic interaction with the nuclear spins to average to zero, the nuclear magnetic moments do not interact with the threesemimajor axis magnetic components. Then, the energy contribution of the nuclear magnetic moments to an electron spin transition depends only on the mutual interaction of the nuclear magnetic moments.

Next, the interaction between the proton nuclear magnetic moments resulting in the splitting of the quantized energy levels of the electron spin transition by the energy corresponding to the interaction is considered. In general, the potential energy of interaction $E_{\text {mag dipole }}$ of two quantized magnetic dipoles $\mathbf{m}_{1}$ and $\mathbf{m}_{2}$ separated by a distance $|\mathbf{r}|$ is given by

$$
\begin{equation*}
E_{\text {mag dipole }}=-\frac{\mu_{0}}{4 \pi|\mathbf{r}|^{3}}\left(3\left(\mathbf{m}_{1} \cdot \hat{\mathbf{r}}\right)\left(\mathbf{m}_{2} \cdot \hat{\mathbf{r}}\right)-\mathbf{m}_{1} \cdot \mathbf{m}_{2}\right) \tag{16.223}
\end{equation*}
$$

where $\mu_{0}$ is the permeability of free space and $\hat{\mathbf{r}}$ is a unit vector parallel to the line joining the centers of the two dipoles. The energy is decreased in the case of antiparallel interacting magnetic moments, and the energy is increased in the case of parallel magnetic moments. Consider the splitting energy of interaction with two parallel-aligned nuclear magnetic moments. With the substitution of the proton magnetic moment $\mu_{p}$ for each parallel-aligned nuclear magnetic moment and the $H_{2}(1 / 4)$ internuclear separation given by Eq. (11.204) for $|\mathbf{r}|$ into Eq. (16.223), the energy $E_{P \text { mag e-dipole }}$ to flip the spin direction of one proton magnetic moment of $H_{2}(1 / 4)$ relative to the other is

$$
\begin{align*}
E_{P \text { mag e-dipole }} & =\frac{2 \mu_{0} \mu_{P}^{2}}{4 \pi r^{3}}=\frac{\mu_{0}\left(1.41060671 X 10^{-26} \mathrm{JT}^{-1}\right)^{2}}{2 \pi\left(2 \frac{a_{0}}{4 \sqrt{2}}\right)^{3}}=\frac{\mu_{0}\left(1.41060671 X 10^{-26} \mathrm{JT} T^{-1}\right)^{2}}{2 \pi\left(1.870924 \times 10^{-11} \mathrm{~m}\right)^{3}}  \tag{16.224}\\
& =6.077 \times 10^{-27} \mathrm{~J}=3.793 \times 10^{-8} \mathrm{eV}=9.171 \times 10^{-3} \mathrm{GHz}
\end{align*}
$$

In order for this ortho-para nuclear spin isomer energy of Eq. (16.224) to split the electron spin transition, there must be a coupling mechanism between the nuclear and electron spins. Since the electron spin vector is along the semimajor axis, and the proton spins are transversely oriented in the plane containing the semiminor axes, there is no direct coupling mechanism. Moreover, the flux change inside of the electron MO due to the transition of the nuclear spin isomer state corresponding to Eq. (16.224) has an insignificant effect on the spin transition energy as shown by flux linkage terms of Eq. (16.217). Since the spin
transition is independent of the nuclear spin transition, the electron spin transition leaves the ortho or para nuclear spin state of $H_{2}(1 / 4)$ unchanged, and there is no nuclear spin state energy splitting.

Consider the third electron spin splitting mechanism regarding the coupling energy of the spin unpaired and paired electrons of the electron MO. The semiminor axis spin flip transition lifts the degeneracy of the semimajor axis spin flip transition due to an interaction of the paired and unpaired current of the MO. The magnetic field of the unpaired electron induces a diamagnetic current in the paired electron. The resulting magnetic moment that shifts the spin flip transition energy is opposite that of the spin magnetic moment and proportionally much smaller. In addition to the intrinsic relative motion of the linear combination of the paired and unpaired electron currents of $H_{2}(1 / 4)$ and the rotation of the electron MO about the semimajor axis corresponding to electron spin along this axis, the paired and unpaired electrons may rotate relative to each other during a spin transition similar to the case of excited-state $H_{2}$ as given in the Excited States of the Hydrogen Molecule section. The relative rotation is quantized in terms of $m$ integer units of $\hbar$ in opposite directions wherein the magnetic moments cancel, but the relativistic effect gives rise to a corresponding electron spin-orbital coupling quantum number $m$. The unpaired-paired coupling or spin-orbital coupling energy is given as the diamagnetic moment times the magnetic flux of the unpaired electron. Since flux is linked by an unpaired electron in units of the magnetic flux quantum, the spin-orbital coupling energy $E_{S / O}$ between two magnetic moments of $H_{2}(1 / 4)$ given by Eq. (2.194) can be expressed as:

$$
\begin{equation*}
E_{S / O}=\chi_{m} m\left[\frac{1}{(4 \sqrt{2})^{-3}} \alpha^{5}(2 \pi)^{2} m_{e} c^{2} \sqrt{\frac{3}{4}}\right] \tag{16.225}
\end{equation*}
$$

wherein the semiminor radius of the $H_{2}(1 / 4) \mathrm{MO}$ is given by Eq. (11.205) with $p=4$ and $\chi_{m}$ is the magnitude of the diamagnetic susceptibility of the paired electron given by Eq. (11.416):

$$
\begin{align*}
\chi_{m} & =\alpha \frac{\Delta B_{T}}{B} \sqrt{\frac{3}{4}}=\alpha \mu_{0}\left(4-\sqrt{2} \ln \frac{\sqrt{2}+1}{\sqrt{2}-1}\right) \frac{p e^{2}}{36 a_{0} m_{e}}\left(1+p \alpha^{2}\right) \sqrt{\frac{3}{4}} \\
& =\alpha\left(p 28.01+p^{2} 1.49 \times 10^{-3}\right) \sqrt{\frac{3}{4}} p p m=7.0821 \times 10^{-7} \tag{16.226}
\end{align*}
$$

In the case of spin-orbital coupling involving the intrinsic spin of $\frac{\hbar}{2}$, the electron spin-orbital coupling quantum number $m$ is $m=1 / 2$. Additional states arise due to the relative motion of the two electrons of the $H_{2}(1 / 4) \mathrm{MO}$. Consider the case of $H_{2}$ excited states given in the Excited States of the Hydrogen Molecule section wherein the relative rotational motion of the two excited state electrons corresponds to the quantum number $m$ being a positive or negative integer such that net relative motion obeys the condition $\ell=0$. The quantum number $m$ also applies to the molecular hydrino electron spin flip split by electron spin-orbital coupling wherein $m$ is a positive integer. With the substitution of Eq. (16.226) into Eq. (16.225), the unpairedpaired coupling is

$$
\begin{equation*}
E_{s / o}=m 7.0821 X 10^{-7}\left(64(2)^{1.5} \alpha^{5}(2 \pi)^{2}\right) m_{e} c^{2} \sqrt{\frac{3}{4}}=m 7.426 \times 10^{-27} \mathrm{~J} \tag{16.227}
\end{equation*}
$$

The electron paramagnetic resonance (EPR) comprises a peak at the energy equivalent position given by Eq. (16.219), that is symmetrically split into a series of pairs of peaks, one shifted downfield by the energy of Eq. (16.227), and the other shifted upfield by the energy of Eq. (16.227), wherein downfield and upfield denote lower and higher magnetic flux for a resonant transition at fixed EPR frequency, respectively.

Consider the case that the EPR frequency is 9.820295 GHz , the resonance magnetic flux $B$ for the principal peak given by Eq. (16.219) is

$$
\begin{equation*}
B=\frac{h 9.820295 G H z}{2.0046386 \mu_{B}}=0.35001 T \tag{16.228}
\end{equation*}
$$

where $h$ is Planck's constant and $\mu_{B}$ is the Bohr magneton. The resonance magnetic flux shift $\Delta B_{C}$ of a principal peak at position $B_{1}$ due to a splitting energy $E_{C}$ is given by

$$
\begin{equation*}
\Delta B_{C}=B_{1} \frac{E_{C}}{h 9.820295 G H z} \tag{16.229}
\end{equation*}
$$

Using Eqs. (16.227-16.229), the downfield and upfield shifts $\Delta B_{S / O}$ with quantized spin-orbital splitting energies $E_{S / O}$ (Eq. (16.227) and electron spin-orbital coupling quantum numbers $m=0.5,1,2,3,5 \ldots$. are given in units of Gauss by

$$
\begin{equation*}
\Delta B_{S / O}=m 0.35001\left[\frac{7.426 \times 10^{-27} \mathrm{~J}}{h 9.820295 G H z}\right] T=m 3.99427 G \tag{16.230}
\end{equation*}
$$

The spin-orbital splitting shift of $m 7.426 \times 10^{-27} J$ is independent of the applied EPR field/frequency combination for both downfield and upfield shifted peaks.

The potential energy of a superconducting quantum interference device (SQUID) given by Eq. (42.115) comprises the sum of the Josephson coupling energy of the junction and the equivalent of the magnetic energy of the loop. The free electron of $H_{2}(1 / 4)$ behaves equivalently to a superconducting quantum interference device (SQUID). In addition to the flux linked by the unpaired electron during the spin flip transition corresponding to the energy terms of the $g_{H_{2}(1 / p)}$ (Eqs. (16.218) and (16.219)), a free electron of $H_{2}(1 / 4)$ must link the magnetic flux component corresponding to spin-orbital coupling. This flux contribution increases the magnetic energy and the energy of the combined spin flip (Eq. (16.228)) and spin-orbital coupling (Eq. (16.227)) transition energy for a given spin-orbital quantum number $m$. Thus, the downfield spin-orbital splitting peaks are shifted further downfield by the corresponding magnetic energies; whereas, the upfield spin-orbital splitting peaks are not shifted since the upfield peaks correspond to emission of the spin-orbital coupling transition energies alone, and the magnetic energies thermalize. The Josephson coupling energies due to fluxon linkage during spin-orbital transitions are given by Eq. (16.227), and the magnetic energies $U_{S / O M a g}$ arising from the absorption of the corresponding spin-orbital coupling transitional flux are given by

$$
\begin{align*}
& \left.U_{\text {S/OMag }}=\frac{1}{2} U_{0}\left(\frac{2 \pi(\Delta \Phi)}{\Phi_{0}}\right)^{2}=(0.5) \frac{0.5 \Delta E_{\operatorname{mag} 2.0046}^{\text {spin }}}{g_{\left.H_{2}(1 / p)\right)} \mu_{B}}\left(\frac{2 \pi\left(\Delta B_{\text {S/O }}\right)}{0.5 \Delta E_{\text {mag } 2.0046}^{\text {spin }}}\right)^{g_{H_{2}(1 / p)} \mu_{B}}\right)^{2} \\
& =(0.5) \frac{\left(2 \pi m 0.35001\left[\frac{7.426 \times 10^{-27} J}{h 9.820295 G H z}\right]\right)^{2}}{\frac{0.5 \Delta E_{\text {mag } 2.0046}^{s p i n}}{g_{H_{2}(1 / p), p} \mu_{B}}}=(0.5) \frac{\left(2 \pi m 3.99427 \times 10^{-4}\right)^{2}}{0.5 \frac{h 9.820295 G H z}{2.0046386 \mu_{B}}}  \tag{16.231}\\
& =(0.5) \frac{\left(2 \pi m 3.99427 \times 10^{-4}\right)^{2}}{0.1750} \times 10^{4} G
\end{align*}
$$

wherein $m$ is the spin-orbital quantum number, $1 / 2$ the spin flip transition energy corresponds to the terms $U_{0}$ and $\Phi_{0}$ as given by Eqs. (16.217), (16.218), and (16.228) in units of magnetic flux (i.e. the equivalent SQUID parameters of $H_{2}(1 / 4)$ are $U_{0}=\Phi_{0}=\frac{0.5 \Delta E_{\operatorname{mig}}^{\text {spin }} 2.0046}{g_{H_{2}(1 / p)} \mu_{B}}$, and the flux change due to the transition $\Delta \Phi$ is the spin-orbital splitting energy of quantum number $m$ given in units of magnetic flux by Eqs. (16.227) and (16.230). The corresponding magnetic energies $U_{\text {S/OMag }}$ given by Eqs. (16.231), (16.217), and (16.218) in units of Joules are

$$
\begin{equation*}
U_{S / O M a g}=g_{H_{2}(1 / p)} \mu_{B}(0.5) \frac{\left(2 \pi m 3.99427 \times 10^{-4}\right)^{2}}{0.1750} J \tag{16.232}
\end{equation*}
$$

The downfield magnetic energy shifts $U_{S / O M a g}$ given by Eq. (16.232) are added to the quantized spin-orbital splitting energies $E_{S / O}\left(\Delta B_{S / O}\right)$ (Eq. (16.227)) to given combined quantized spin-orbital splitting energies $E_{S / O c o m b i n e d}$ in units of Joules:

$$
\begin{equation*}
E_{S / \text { ocombined }}=g_{H_{2}(1 / p)} \mu_{B}(0.5) \frac{\left(2 \pi m 3.99427 X 10^{-4}\right)^{2}}{0.1750} J+m 7.426 \times 10^{-27} J \tag{16.233}
\end{equation*}
$$

The downfield magnetic energy shifts $U_{S / O M a g}$ given by Eq. (16.231) are added to the quantized spin-orbital splitting energies $E_{S / O}$ (Eq. (16.230)) to given combined quantized spin-orbital downfield shift energies $\Delta B_{S / O \text { combined }}^{\text {downiel }}$ in units of Gauss:

$$
\begin{equation*}
\Delta B_{S / O \text { combinined }}^{\text {downfild }}=-\left(m 3.99427 \times 10^{-4}+(0.5) \frac{\left(2 \pi m 3.99427 X 10^{-4}\right)^{2}}{0.1750}\right) X 10^{4} G \tag{16.234}
\end{equation*}
$$

The downfield peak positions $B_{S / O c o m b i n e d}^{\text {downfild }}$ due to the combined shifts due to the magnetic energy and the spin-orbital coupling energy given by Eq. (16.228) and (16.234) are:

$$
\begin{equation*}
B_{S / O c o m b i n e d}^{\text {downfield }}=\left(0.35001-m 3.99427 \times 10^{-4}-(0.5) \frac{\left(2 \pi m 3.99427 X 10^{-4}\right)^{2}}{0.1750}\right) T \tag{16.235}
\end{equation*}
$$

There is no magnetic energy shift for upfield shift peaks corresponding to the emission of the spin-orbital coupling energy given by Eq. (16.230). Using Eq. (16.228) and Eqs. (16.227-16.230), the upfield peak positions $B_{S / O}^{\text {wfield }}$ with quantized spin-orbital
splitting energies $E_{S / O}$ (Eq. (16.227)) and electron spin-orbital coupling quantum numbers $m=0.5,1,2,3,5 \ldots$ are given by

$$
\begin{equation*}
B_{S / O}^{\text {uffield }}=0.35001\left(1+m\left[\frac{7.426 \times 10^{-27} J}{h 9.820295 G H z}\right]\right) T=\left(0.35001+m 3.99427 \times 10^{-4}\right) T \tag{16.236}
\end{equation*}
$$

The downfield shifts due to the magnetic energies in units of Joules (Eq. (16.232)) and Gauss (Eq. (16.231)), the downfield shifts due to spin-orbital coupling energies in units of Joules (Eq. (16.227) and Gauss (Eq. (16.230)) for spin-orbital coupling quantum numbers $m=0.5,1,2,3,5 \ldots$. are given in Table 16.48.

Table 16.48. The $9.820295 \mathrm{GHz} H_{2}(1 / 4)$ EPR downfield shifts due to the magnetic energies and the downfield shifts due to spin-orbital coupling energies for spin-orbital coupling quantum numbers $m=0.5,1,2,3,5$.

| m | $\begin{gathered} \text { Downfield } \\ \text { Magnetic } \\ \text { Energy Shift (J) } \end{gathered}$ | $\begin{aligned} & \text { Downfield } \\ & \text { Magnetic } \\ & \text { Energy Shift (G) } \end{aligned}$ | Spin-Orbital Shift <br> (J) | Spin-Orbital Shift (G) |
| :---: | :---: | :---: | :---: | :---: |
| 0.5 | 8.36376E-29 | 0.04499 | $3.71288 \mathrm{E}-27$ | 1.99714 |
| 1 | $3.34550 \mathrm{E}-28$ | 0.17995 | $7.42576 \mathrm{E}-27$ | 3.99427 |
| 2 | $1.33820 \mathrm{E}-27$ | 0.71981 | $1.48515 \mathrm{E}-26$ | 7.98854 |
| 3 | $3.01095 \mathrm{E}-27$ | 1.61957 | $2.22773 \mathrm{E}-26$ | 11.98281 |
| 4 | $5.35280 \mathrm{E}-27$ | 2.87924 | $2.97030 \mathrm{E}-26$ | 15.97708 |
| 5 | $8.36376 \mathrm{E}-27$ | 4.49881 | $3.71288 \mathrm{E}-26$ | 19.97135 |

The combined downfield shifts due to the magnetic and spin-orbital coupling energies in units of Joules (Eq. (16.233) and Gauss (Eq. (16.234)), the resulting downfield peak positions (Eq. (16.235), and the upfield peak positions (Eq. (16.236)) shifted only by the spin-orbital coupling energies (Eqs. (16.227) and (16.230)), for spin-orbital coupling quantum numbers $m=0.5,1,2,3,5 \ldots$. wherein the principal peak with the g-factor of 2.0046386 (Eq. (16.218)) is observed at 0.35001 T (Eq. (16.228) are given in Table 16.49.

Table 16.49. The 9.820295 GHz $H_{2}(1 / 4)$ EPR combined downfield shifts due to the magnetic and spin-orbital coupling, the resulting downfield peak positions, and the upfield peak positions shifted only by the spin-orbital coupling energies for spinorbital coupling quantum numbers $m=0.5,1,2,3,5$.

| m | Combined <br> Downfield <br> Magnetic <br> Energy Shift (J) | Combined <br> Downfield <br> Magnetic <br> Energy Shift (G) | Downfield Peak <br> Position <br> (T) |
| :---: | :---: | :---: | :---: |
| 0.5 | $3.79652 \mathrm{E}-27$ | 2.04212 | Upfield Peak <br> Position <br> $(\mathrm{T})$ |
| 1 | $7.76031 \mathrm{E}-27$ | 4.17422 | 0.34980 |
| 2 | $1.61897 \mathrm{E}-26$ | 8.70835 | 0.34959 |
| 3 | $2.52882 \mathrm{E}-26$ | 13.60238 | 0.34914 |
| 4 | $3.50559 \mathrm{E}-26$ | 18.85632 | 0.34865 |
| 5 | $4.54926 \mathrm{E}-26$ | 24.47016 | 0.34812 |

As given in the Electron $g$ Factor section, magnetic flux is linked by an unpaired electron in quantized units of the fluxon or the magnetic flux quantum $\frac{h}{2 e}$. As shown in the Hydrino Hydride Ion Hyperfine Lines section, hydrino hydride ion $H^{-}(1 / p)$ also possesses a linear combination of two electrons with one paired and the other unpaired in a common atomic orbital versus a MO. The emission spectrum of the binding of a free electron to a hydrino atom to form the corresponding hydrino hydride ion results in a series of evenly spaced emission peaks wherein the energy spacing matches that predicted for the binding electron to link the magnetic flux of the hydrino atom in units of the magnetic flux quantum in the bound-free emission spectral region. The flat intensity profile matches that of Josephson junctions such as ones of superconducting quantum interference devices (SQUIDs) that also link magnetic flux in quantized units of the magnetic flux quantum or fluxon $\frac{h}{2 e}$. The same behavior is predicted for the linkage of magnetic flux by molecular hydrino during a spin transition and the derivation of the corresponding fluxon linkage energies follows that of Eq. (7.93) of the Hydrino Hydride Ion Hyperfine Lines section.

As given by Eq. (16.218), the fluxon links both correlated electrons such that the energy contribution of the flux linkage of a fluxon by molecular hydrino is

$$
\begin{equation*}
g_{H_{2}(1 / p)}-2=2\left(1+2\left(\frac{\alpha}{2 \pi}+\frac{2}{3} \alpha^{2}\left(\frac{\alpha}{2 \pi}\right)-\frac{4}{3}\left(\frac{\alpha}{2 \pi}\right)^{2}\right)\right)-2=0.0046386 \tag{16.237}
\end{equation*}
$$

Using the energy of MO due to an applied flux given by Eq. (16.220), wherein (i) both the magnetic moments due to spin and the corresponding induced diamagnetic moment are corrected for the vector projection of $\sqrt{\frac{3}{4}}$ (Eqs. (16.226-16.227) corresponding to an increase of the energy for resonant flux linkage, (ii) the magnetic flux density $B$ is given by the ratio of the flux and the area, and (iii) the flux is linked in units of the fluxon $\Phi_{0}=\frac{h}{2 e}$, the fluxon linkage energies $E_{\Phi}$ by molecular hydrino $H_{2}(1 / 4)$ during a spin transition are

$$
\begin{align*}
E_{\Phi} & =m_{\Phi} 4\left(\frac{\alpha}{2 \pi}+\frac{2}{3} \alpha^{2}\left(\frac{\alpha}{2 \pi}\right)-\frac{4}{3}\left(\frac{\alpha}{2 \pi}\right)^{2}\right) \chi_{m \Phi} \frac{\mu_{B}}{\sqrt{s(s+1)}} B=m_{\Phi} 0.0046386 \frac{\chi_{m \Phi} \mu_{B}}{\sqrt{s(s+1)}}\left(\frac{j \Phi_{0}}{A}\right) \\
& =m_{\Phi}\left(j 0.0046386 \frac{\chi_{m \Phi} \mu_{B}}{\sqrt{s(s+1)}} \frac{\mu_{0}}{r^{3}}\left(\frac{e \hbar}{2 m_{e}}\right)\right) \tag{16.238}
\end{align*}
$$

In Eq. (16.238), the energy of flux linkage is an integer function of the components of angular moment involved in the splitting of the principal transition corresponding to the electron fluxon quantum number $m_{\Phi}$. Therefore, the electron fluxon quantum number $m_{\Phi}$ has the following integer values: (i) the electron fluxon quantum number $m_{\Phi}$ corresponding to the spin-orbital coupling involving the intrinsic spin of $\frac{\hbar}{2}$ is $m_{\Phi}=1$, (ii) the electron fluxon quantum number $m_{\Phi}$ corresponding to the spin with $m=1$ involving the semimajor axis spin is $m_{\Phi}=2$, and (iii) the electron fluxon quantum number $m_{\Phi}$ corresponding to the spin with $m>1 ;|\Delta m|=1$ involving the semimajor axis spin and relative motion of the two electrons of the $H_{2}(1 / 4)$ MO is $m_{\Phi}=3$. In addition, $j$ is an integer corresponding to the number of fluxons linked having fluxion linkage quantum number $m_{\Phi}$ , $s=1 / 2, A$ is the area of the continuous distribution of current element loops (Force Balance of Hydrogen-Type Molecules section and Figure 11.2) linked by the integer number of fluxons as given in the Electron $g$ Factor section, and the magnitude of the diamagnetic susceptibility $\chi_{n \Phi 1}$ is given by

$$
\begin{equation*}
\chi_{m \Phi}=\alpha\left(p 28.01+p^{2} 1.49 \times 10^{-3}\right) p p m=8.1777 \times 10^{-7} \tag{16.239}
\end{equation*}
$$

With the substitution of Eq. (16.239) into Eq. (16.238), $E_{\Phi}$ is

$$
\begin{equation*}
E_{\Phi}=m_{\Phi}\left(j(0.0046386) \frac{\mu_{0}\left(8.1777 \times 10^{-7}\right) \mu_{B}^{2}}{\sqrt{\frac{3}{4}}\left(\frac{a_{0}}{4 \sqrt{2}}\right)^{3}}\right)=m_{\Phi}\left(j 5.7830 \times 10^{-28} J\right) \tag{16.240}
\end{equation*}
$$

wherein the semiminor radius of the $H_{2}(1 / 4)$ MO is given by Eq. (11.205) with $p=4$. Using Eq. (16.229) with the $E_{\Phi}$, the fluxon linkage energy of $H_{2}(1 / 4)$ (Eq. (16.240)), and the spin-orbital peak positions (Eqs. (16.235) and (16.236)), the separation $\Delta B_{\Phi}$ of the integer series of peaks at each spin-orbital peak position (Table 16.49) for an EPR frequency of 9.820295 GHz is given by

$$
\begin{equation*}
\Delta B_{\Phi}^{\text {downfield }}=\left(0.35001-m 3.99427 \times 10^{-4}-(0.5) \frac{\left(2 \pi m 3.99427 X 10^{-4}\right)^{2}}{0.1750}\right)\left[\frac{m_{\Phi} 5.7830 \times 10^{-28} \mathrm{~J}}{h 9.820295 \mathrm{GHz}}\right] \times 10^{4} G \tag{16.241}
\end{equation*}
$$

and

$$
\begin{equation*}
\Delta B_{\Phi}^{\text {upfield }}=\left(0.35001+m 3.99427 \times 10^{-4}\right)\left[\frac{m_{\Phi} 5.7830 \times 10^{-28} J}{h 9.820295 G H z}\right] \times 10^{4} G \tag{16.242}
\end{equation*}
$$

The $9.820295 \mathrm{GHz} H_{2}(1 / 4)$ EPR spectral separations $\Delta B_{\Phi}$ (Eqs. (16.235) and (16.236)) of each integer series of the peaks comprising sub-splitting of the downfield and upfield peaks of Table 16.49 corresponding to the principal peak having a g-factor of 2.0046386 (Eq. (16.218)) split by quantized spin-orbital coupling energies $E_{S / O}$ (Eqs. (16.227) and (16.230)) and magnetic energies $U_{S / O M a g}$ (Eqs. (16.231) and (16.232)) for electron spin-orbital coupling quantum numbers $m=0.5,1,2,3,4,5$ and electron fluxon quantum numbers $m_{\Phi}=1,2,3$ (Eq. (16.240) are given in Table 16.50.

Table 16.50. The $9.820295 \mathrm{GHz} H_{2}(1 / 4)$ EPR spectral separation $\Delta B_{\Phi}$ of each integer series of the peaks comprising sub-splitting of the downfield and upfield peaks of Table 16.49 for electron spin-orbital coupling quantum numbers $m=0.5,1,2,3,4,5$ and electron fluxon quantum numbers $m_{\Phi}=1,2,3$.

| m | $m_{\Phi}$ | Downfield <br> Peak Position <br> $(\mathrm{T})$ | $\Delta \boldsymbol{B}_{\Phi}$ <br> $(\mathrm{G})$ | Upfield <br> Peak <br> Position <br> $(\mathrm{T})$ | $\Delta B_{\Phi}$ <br> $(\mathrm{G})$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 0.5 | 1 | 0.34980 | 0.3109 | 0.35021 | 0.3112 |
| 1 | 2 | 0.34959 | 0.6214 | 0.35041 | 0.6228 |
| 2 | 3 | 0.34914 | 0.9309 | 0.35081 | 0.9353 |
| 3 | 3 | 0.34865 | 0.9296 | 0.35121 | 0.9364 |
| 4 | 3 | 0.34812 | 0.9282 | 0.35160 | 0.9375 |
| 5 | 3 | 0.34756 | 0.9267 | 0.35200 | 0.9385 |

The spin-orbital splitting peak intensity for electron spin-orbital coupling quantum number $m=0.5$ is predicted to be dominant due to the high cross section of the spin flip transition to involve a torque about the intrinsic angular moment vector as shown in Resonant Precession of the Spin-1/2-Current-Density Function Gives Rise to the Bohr Magneton section. For integer electron spin-orbital coupling quantum number $m$ spin-orbital splitting peaks, the relative intensities are predicted to decrease with integer electron spin-orbital coupling quantum number $m$. In the case that the statistical population obeys the rules of multipole transitions, the relative peak intensities according to Eqs. (1.7-1.8) and Eq. (1.19) go as

$$
\begin{equation*}
\frac{I_{m+1}}{I_{m}}=\frac{m(m+1)}{(m+1)(m+2)}=\frac{m}{(m+2)} ; m=2,3,4 . . \tag{16.243}
\end{equation*}
$$

Furthermore, consider the relative intensities of fluxon peaks within an integer series. If the cross-sectional area of the flux linker is constant relative to the flux source, then the line intensities for the sub-splitting would be equal. However, the crosssectional area of the electron current relative to the applied field changes as the current comprising a continuous ensemble of current loops flips orientation by $180^{\circ}$. The current flowing over the surface of the prolate spheroidal to reverse the spin direction by $180^{\circ}$ is a mechanism whereby the relative intensities of the sub-splitting is higher for the center lines compared to those at the extrema. The line intensities and widths reflect the electron MO geometrical form factor in the case of $m=0.5$.

In summary, the predicted $H_{2}(1 / 4)$ EPR spectrum comprises a principal peak with a theoretical $g$-factor of 2.0046386 (Eq. (16.218)) that is split by spin-orbital coupling energies $E_{S / O}$ and corresponding magnetic energies $U_{S / O M a g}$ on the downfield side into a series of pairs of peaks with members separated by the sum of $E_{S / O}$ (Eqs. (16.227) and (16.230)) and $U_{S / O M a g}$ (Eqs. (16.231) and (16.232)) that is a function of electron spin-orbital coupling quantum number $m$. Each spin-orbital splitting peak is further sub-split into a series of equally spaced peaks of integer fluxon energy $\Delta_{\Phi}$ (Eqs. (16.241) and (16.242)) that is a function of electron fluxon quantum number $m_{\Phi}$. As given in the Hydrino Hydride Ion Hyperfine Lines section, the pattern of integer-spaced peaks predicted for the EPR spectrum of $H_{2}(1 / 4)$ is very similar to that experimentally observed on the hydrino hydride ion that also comprises a paired and unpaired electron in a common orbital, except that the orbital is an atomic orbital [132-135]. The peak separations and sub-splitting due to spin-orbital splitting energies, spin-orbital splitting magnetic energies, and fluxon energies may deviate from the values given in Tables 16.49 and 16.50 . Interactions may exist with the matrix surrounding the hydrino molecule. For example, protons of water molecules absorbed as waters of hydration of a crystalline matrix having trapped hydrino molecules could cause and external nuclear splitting effect.

The predicted EPR spectrum was confirmed experimentally [131]. The 9.820295 GHz EPR spectrum was performed on a white polymeric compound (WPC) identified by X-ray diffraction (XRD), energy-dispersive X-ray spectroscopy (EDS), transmission electron spectroscopy (TEM), scanning electron microscopy (SEM), time-of-flight secondary ionization mass spectroscopy (ToF-SIMs), Rutherford backscattering spectroscopy (RBS), and X-ray photoelectron spectroscopy (XPS) as $\mathrm{GaOOH}: \mathrm{H}_{2}(1 / 4)$. The WPC was formed by dissolving $\mathrm{Ga}_{2} \mathrm{O}_{3}$ collected from a hydrino reaction run in a SunCell® in 4 M aqueous KOH , allowing fibers to grow, and float to the surface where they were collected by filtration. The white fibers were not solution in concentrated acid or base; whereas control GaOOH is. No white fibers formed in control solutions. Control GaOOH showed no EPR spectrum. The experimental EPR was acquired by Professor Fred Hagen, TU Delft, with a high sensitivity resonator at a microwave power of -28 dB and a modulation amplitude of 0.02 G , that can be changed to 0.1 G since Dr. Hagen rigorously determined that the minimum line width is 0.15 to 0.2 G . The average error between the EPR spectrum and theory for peak positions given in Tables $16.49-16.50$ was 0.097 G . The EPR spectrum was replicated by Bruker using two instruments on two samples.

Specifically, the observed principal peak at $g=2.0045(5))$ was assigned to the theoretical peak having a g-factor of 2.0046386 (Eq. (16.218)). This principal peak was split into a series of pairs of peaks with members separated by energies
matching $E_{S / O}$ (Eqs. (16.227) and (16.230)) corresponding to each electron spin-orbital coupling quantum number $m$. The results confirmed the spin-orbital coupling between the spin magnetic moment of the unpaired electron and an orbital diamagnetic moment induced in the paired electron alone or in combination with rotational current motion about the semimajor molecular axis that shifted the flip energy of the spin magnetic moment. The data further matched the theoretically predicted one-sided tilt of the spin-orbital splitting energies wherein the downfield shift was observed to increase with quantum number $m$ due to the magnetic energies $U_{\text {S/OMag }}$ (Eqs. (16.231) and (16.232)) of the corresponding magnetic flux linked during a spinorbital transition. Each spin-orbital splitting peak was further sub-split into a series of equally spaced peaks that matched the integer fluxon energies $\Delta B_{\Phi}$ (Eqs. (16.241) and (16.242)) dependent on electron fluxon quantum number $m_{\Phi}$ corresponding to the number of angular momentum components involved in the transition. The evenly spaced series of sub-splitting peaks was assigned to flux linkage during the coupling between the paired and unpaired magnetic moments in units of the magnetic flux quantum $\frac{h}{2 e}$ while a spin flip transition occurs. The EPR spectrum recorded at different frequencies showed that the peak assigned the $g$ factor of 2.0046386 (Eq. (16.218)) remained at constant $g$ factor. Moreover, the peaks, shifted by the fixed spinorbital splitting energies relative to this true g-factor peak, exactly maintained the separation of the spin-orbital splitting energies independent of frequency as predicted.

Another consideration is that molecular hydrino can also form dimers that would alter the EPR spectrum. Consider the splitting energy of interaction with two axially aligned magnetic moments of a $H_{2}(1 / 4)$ dimer. With the substitution of a Bohr magneton $\mu_{B}$ for each axially aligned magnetic moment and the $H_{2}(1 / 4)$ dimer separation given by Eq. (16.202) for $|\mathbf{r}|$ into Eq. (16.223), the energy $E_{\operatorname{mag}\left[H_{2}(1 / 4)\right]_{2} e \text { e-dipole }}$ to flip the spin direction of two electron magnetic moments of $\left[H_{2}(1 / 4)\right]_{2}$ is

$$
\begin{align*}
E_{\text {mag }\left[H_{2}(1 / 4)\right]_{2} \text { e-dipole }} & =-\frac{2 \mu_{0} \mu_{B}^{2}}{4 \pi r^{3}} \\
& =-\frac{\mu_{0}\left(9.27400949 \times 10^{-24} \mathrm{JT}^{-1}\right)^{2}}{2 \pi\left(1.028 \times 10^{-10} \mathrm{~m}\right)^{3}}  \tag{16.244}\\
& =-1.584 \times 10^{-23} \mathrm{~J}=-9.885 \times 10^{-5} \mathrm{eV}=23.90 \mathrm{GHz}=0.7972 \mathrm{~cm}^{-1}
\end{align*}
$$

## ROTATIONAL ENERGIES DUE TO THE SPIN MAGNETIC MOMENT OF H $\mathbf{H}_{2}(1 / 4)$

Molecular hydrino $H_{2}(1 / p)$ possesses an unpaired electron that causes rotational transitions to be forbidden. This selection rule barrier to observing infrared and Raman spectra may be circumvented by application of an external magnetic field or by recording the spectrum on a compound or material with intrinsic magnetization such as one being ferromagnetic or paramagnetic. An example of the former is molecular hydrino bonded or absorbed on the surface of a nickel or iron foil. An example of the latter is a paramagnetic compound that cages the molecular hydrino such as $\mathrm{FeOOH}, \mathrm{Fe}_{2} \mathrm{O}_{3}$ or a compound that may be diamagnetic but possess paramagnetic ions in proximity to $H_{2}(1 / p)$ such as $G a^{3+}$ ions in the case of GaOOH that serves as a cage for $H_{2}(1 / p)$.

The presence of molecular hydrino in strong matrix magnetic field may result in the alignment of the free electron angular moment of $\frac{\hbar}{2}$ along the magnetic field vector direction in either the z -axis or the y -axis direction of the coordinates of $H_{2}(1 / p)$ shown in Figure 11.4. The alignment permits the excitation of a concerted transition of a rotational molecular hydrino transition coupling to the spin-orbital splitting and fluxon linkage sub-splitting of the free electron energy levels. The spin flip energy given by Eq. (16.219) with an exemplary intrinsic field of 1 T is

$$
\begin{equation*}
\Delta E_{\operatorname{mag} 2.0046}^{\text {spin }}=g_{H_{2}(1 / p)} \mu_{B} B=2.0046386 \mu_{B} B=1.85910 \times 10^{-23} J\left(0.93588 \mathrm{~cm}^{-1}\right) \tag{16.245}
\end{equation*}
$$

To conserve the photon's angular momentum of $\hbar$, rotational excitation requires $\hbar$ of angular momentum along the axis of molecular rotation, a semiminor axis being either the z-axis or y-axis. The $\hbar$ of angular momentum gives rise to a corresponding magnet moment of a Bohr magneton along this rotational angular momentum axis. Typically, the unpaired electron of $H_{2}(1 / p)$ gives rise to a Bohr magneton of magnetic moment along the internuclear axis when a magnetic field is applied. However, the molecular rotation of the hydrino molecule about one of the semiminor axes causes the excitation of the semimajor-axis Bohr magneton of magnetic moment to be forbidden. The rotational transition energy may be split by the spinorbital energy given by Eq. (16.225), except that the orbital component of spin-orbital splitting is not diamagnetically induced such that $\chi_{m}=1$ and the spin-orbital energy $E_{S / O, \text { rot }}$ due to rotational excitation is:

$$
\begin{align*}
E_{S / O, \text { rot }} & =m\left[\frac{1}{(4 \sqrt{2})^{-3}} \alpha^{5}(2 \pi)^{2} m_{e} c^{2} \sqrt{\frac{3}{4}}\right]  \tag{16.246}\\
& =m 1.04853 \times 10^{-20} J \quad\left(m 6.54434 \times 10^{-2} \mathrm{eV}, m 527.83 \mathrm{~cm}^{-1}\right)
\end{align*}
$$

wherein $m=0.5,1,2,3, \ldots$. The spin-orbital splitting energies due to rotation are given in Table 16.51.
The energies of the concerted excitation of the rotational and spin-orbital coupling transitions are sub-split by the energy corresponding to flux linkage in units of the magnetic flux quantum $\frac{h}{2 e}$. The free electron angular momentum of $\frac{\hbar}{2}$ and the rotational angular momentum of $\hbar$ add when the corresponding vectors are aligned along a common z -axis to give a resultant angular momentum of $L=\frac{3}{2} \hbar$. The energy contribution of the flux linkage of a fluxon by molecular hydrino is given by Eq. (16.238) with $\chi_{m \Phi}=1$ since the orbital component of spin-orbital coupling is not diamagnetically induced. In the case of $L=\frac{3}{2} \hbar$, the $H_{2}(1 / 4)$ fluxon linkage energies $E_{\Phi, \text { rot,concerted }}$ for fluxon sub-splitting quantum numbers $m_{\Phi 3 / 2}=0.5,1,2,3 \ldots$ due to spinorbital coupling to a molecular rotational transition are

$$
\begin{align*}
E_{\Phi, \text { rot concerted }} & =m_{\Phi 3 / 2} 4\left(\frac{\alpha}{2 \pi}+\frac{2}{3} \alpha^{2}\left(\frac{\alpha}{2 \pi}\right)-\frac{4}{3}\left(\frac{\alpha}{2 \pi}\right)^{2}\right) \frac{3}{2} \mu_{B} B \\
& =m_{\Phi 3 / 2} j \frac{3}{2}\left(j 0.0046386 \frac{\mu_{0} \mu_{B}}{r^{3}}\left(\frac{e \hbar}{2 m_{e}}\right)\right)  \tag{16.247}\\
& =m_{\Phi 3 / 2} 46.24 \mathrm{~cm}^{-1}
\end{align*}
$$

wherein $j$ is an integer corresponding to the number of fluxons linked having fluxon linkage quantum number $m_{\Phi 3 / 2}$ and the semiminor radius of the $H_{2}(1 / 4)$ MO is given by Eq. (11.205) with $p=4\left(r=\frac{a_{0}}{4 \sqrt{2}}\right)$. As in the case with spin flip transitions observable by EPR spectroscopy, the fluxon sub-splitting quantum number is determined by the number of angular momentum components active during the transition. Due to the nature of the rotation transition wherein the rotational quantum number $J$ may be arbitrarily large, the upper range of the fluxon sub-splitting quantum number is not bounded.

Alternatively, the spin component of $\frac{\hbar}{2}$ may align perpendicular to the rotational angular momentum of $\hbar$ to give a resultant z-axis angular momentum of $L=\hbar$ wherein the spin component averages to zero since it rotates about the z-axis due to molecular rotation. In the case of $L=\hbar$, the $H_{2}(1 / 4)$ fluxon linkage energies $E_{\Phi, \text { rot }}$ for fluxon sub-splitting quantum numbers $m_{\Phi}=0.5,1,2,3, \ldots$ due to spin-orbital coupling to a molecular rotational transition are

$$
\begin{align*}
E_{\Phi, \text { rot }} & =m_{\Phi}\left(j 0.0046386 \frac{\mu_{B}^{2} \mu_{0}}{r^{3}}\right)  \tag{16.248}\\
& =m_{\Phi} j 30.83 \mathrm{~cm}^{-1}
\end{align*}
$$

wherein $j$ is an integer corresponding to the number of fluxons linked having fluxon linkage quantum number $m_{\Phi}$ and the semiminor radius of the $H_{2}(1 / 4)$ MO is given by Eq. (11.205) with $p=4\left(r=\frac{a_{0}}{4 \sqrt{2}}\right)$. The fluxon linkage energies $E_{\Phi, \text { rot }}$ due to spin-orbital coupling to molecular rotation transition are given in Table 16.51.

The absorption of fluxons increases the magnetic energy of $H_{2}(1 / p)$. Using Eq. (16.231), the Josephson coupling energies due to fluxon linkage during concerted rotational-spin rotational and spin-orbital transitions are given by Eq. (16.247), and the magnetic energies $U_{\text {S/OMag, concerted }}$ arising from the absorption of the integer number of fluxons $j$ having fluxon linkage quantum number $m_{\Phi 3 / 2}$ are given by

$$
\begin{align*}
U_{\text {SIOMag,concerted }} & =\frac{1}{2} U_{0}\left(\frac{2 \pi(\Delta \Phi)}{\Phi_{0}}\right)^{2} \\
& =46.24 \mathrm{~cm}^{-1}(0.5)\left(\frac{j m_{\Phi 3 / 2} 46.24 \mathrm{~cm}^{-1}}{1950 \mathrm{~cm}^{-1}}\right)^{2}  \tag{16.249}\\
& =m_{\Phi 3 / 2}^{2} 0.0130 j^{2} \mathrm{~cm}^{-1}
\end{align*}
$$

wherein $U_{0}=46.24 \mathrm{~cm}^{-1} ; \Delta \Phi=E_{\Phi, \text { rot,concerted }}=m_{\Phi 3 / 2} 46.24 \mathrm{~cm}^{-1}$ (Eq. (16.247)), and the energy between rotational transitions corresponds to the term $\Phi_{0}$ (Eq. $(16.256, p=4)$ ). The fluxon peak spacing increases as the energy of the concerted rotationfluxon absorption transition increases and decreases in the case of emission.

Using Eq. (16.231), the magnetic energies $U_{S / O M a g}$ arising from the absorption of the integer number of fluxons $j$ having fluxon linkage quantum number $m_{\Phi}$ during concerted rotational and spin-orbital transitions are given by

$$
\begin{align*}
U_{\text {S/OMag }} & =\frac{1}{2} U_{0}\left(\frac{2 \pi(\Delta \Phi)}{\Phi_{0}}\right)^{2} \\
& =30.83 \mathrm{~cm}^{-1}(0.5)\left(\frac{j m_{\Phi 3 / 2} 30.83 \mathrm{~cm}^{-1}}{1950 \mathrm{~cm}^{-1}}\right)^{2}  \tag{16.250}\\
& =m_{\Phi 3 / 2}^{2} 0.00385 j^{2} \mathrm{~cm}^{-1}
\end{align*}
$$

wherein $U_{0}=30.83 \mathrm{~cm}^{-1} ; \Delta \Phi=E_{\Phi, \text { rot }}=m_{\Phi 3 / 2} 30.83 \mathrm{~cm}^{-1}$ (Eq. (16.248)), and the energy between rotational transitions corresponds to the term $\Phi_{0}$ (Eq. $(16.256, p=4)$ ). The fluxon peak spacing increases as the energy of the concerted rotation-fluxon absorption transition increases and decreases in the case of emission.

Table 16.51. . The electron spin-orbital coupling splitting energies and fluxon sub-splitting energies of molecular rotational transitions for spin-orbital coupling quantum numbers $m=0.5,1,2,3, \ldots, 10$ and for electron fluxon quantum numbers $m_{\Phi}=1,2,3, \ldots, 10$ and $m_{\Phi 3 / 2}=1,2,3, \ldots, 10$.

| m | Spin-Orbital <br> Splitting <br> Energy <br> $\left(\mathrm{cm}^{-1}\right)$ | $m_{\Phi}$ | Fluxon Sub- <br> Splitting Energy <br> $\left(\mathrm{cm}^{-1}\right)$ | $m_{\Phi 3 / 2}$ | Fluxon Sub- <br> Splitting <br> Energy <br> $\left(\mathrm{cm}^{-1}\right)$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 0.5 | 264 | 0.5 | 15.4 | 0.5 | 23.1 |
| 1 | 528 | 1 | 30.8 | 1 | 46.2 |
| 2 | 1056 | 2 | 61.7 | 2 | 92.5 |
| 3 | 1583 | 3 | 92.5 | 3 | 138.7 |
| 4 | 2111 | 4 | 123.3 | 4 | 185.0 |
| 5 | 2639 | 5 | 154.1 | 5 | 231.2 |
| 6 | 3167 | 6 | 185.0 | 6 | 277.5 |
| 7 | 3695 | 7 | 215.8 | 7 | 323.7 |
| 8 | 4223 | 8 | 246.6 | 8 | 370.0 |
| 9 | 4750 | 9 | 277.5 | 9 | 416.2 |
| 10 | 5278 | 10 | 308.3 | 10 | 462.4 |

The observation of spin-orbital transitions by Raman spectroscopy may be greatly enhanced by the deposition of molecular hydrinos on a metal surface to enhance the Raman spectrum. Surface enhanced Raman (SER) is very sensitive because of the surface plasmon waves set up by the stimulating wavelength. The surface plasmon field may extend about 40-60 nm below the surface, providing some depth sensitivity in the material.

The moment of inertia may be measured using rotational energy spectroscopy such as Raman spectroscopy, and using the known nuclear masses, the moment of inertia gives the nuclear separation which is characteristic of and identifies molecular hydrino of a given quantum state $p$. Specifically, for a diatomic molecule having atoms of masses $m_{1}$ and $m_{2}$, the moment of inertia is (Eq. (12.66)):

$$
\begin{equation*}
I=\mu \|^{2} \tag{16.251}
\end{equation*}
$$

where $\mu$ is the reduced mass given by (Eq. (12.67)):

$$
\begin{equation*}
\mu=\frac{m_{1} m_{2}}{m_{1}+m_{2}} \tag{16.252}
\end{equation*}
$$

and where $r$ is the distance between the centers of the atoms, the internuclear distance. The rotational energy levels follow from Eq. (1.71) and are given by (Eq. (12.68)):

$$
\begin{equation*}
E_{\text {rotational }}=\frac{\hbar^{2}}{2 I} J(J+1) \tag{16.253}
\end{equation*}
$$

where $J$ is an integer. The pure rotational energies of hydrogen type molecules for transition from the $J$ to the quantized $J^{\prime}$
rotational state are given by (Eq. (12.77)):

$$
\begin{align*}
\Delta E_{J \rightarrow J^{\prime}} & =E_{J^{\prime}}-E_{J} \\
& =\frac{p^{2} \hbar^{2}}{2\left(0.5 m_{p}\left(7.411 X 10^{-11} m\right)^{2}\right)}\left(J^{\prime}\left(J^{\prime}+1\right)-J(J+1)\right)  \tag{16.254}\\
& =\frac{\left(J^{\prime}\left(J^{\prime}+1\right)-J(J+1)\right)}{2} p^{2} 121.89 \mathrm{~cm}^{-1}
\end{align*}
$$

wherein $m_{p}$ is the mass of the proton, the moment of inertia $I=0.5 m_{p}\left(\frac{7.411 X 10^{-11} m}{p}\right)^{2}$, and the integer-squared dependence is due to the reciprocal integer dependence of the internuclear distance given by (Eq. (12.76)):

$$
\begin{equation*}
2 c^{\prime}=\frac{0.7411}{p} \AA \tag{16.255}
\end{equation*}
$$

For example, the predicted rotational energy of $H_{2}(1 / 4)$ is four squared or 16 times that of $H_{2}$ due to the internuclear distance being one fourth that of $H_{2}$ (Eq. (16.254)). At ambient laboratory temperature, molecules overwhelmingly populate the rotational state $J=0$. Then, Eq. (16.253) becomes

$$
\begin{equation*}
\Delta E_{J=0 \rightarrow J^{\prime}}=\frac{J^{\prime}\left(J^{\prime}+1\right)}{2} p^{2} 121.89 \mathrm{~cm}^{-1} \tag{16.256}
\end{equation*}
$$

Molecular hydrino $H_{2}(1 / p)$ is a diatomic molecule comprising two protons and two electrons, except that it is unique from molecular hydrogen in that it has an unpaired electron having an intrinsic angular momentum of $\frac{\hbar}{2}$. This electron spin angular momentum may align along the same axis as the rotational angular of $\hbar$ or transverse to it. Consider that the rotational energy $E_{\text {rotational }}$ of $H_{2}(1 / p)$ about z-axis which is the common axis of the intrinsic electron angular momentum of $\frac{\hbar}{2}$ and rotational angular momentum of $\hbar$. The rotational energy due to the concerted double excitation of rotation due to spin and diatomic rotation is given by the sum of the diatomic molecular rotational energy given by Eq. (16.253) and the spin rotational energy also given by Eq. (16.253) with the exception that the rotational quantum number $J$ can only change by $\pm 1$ :

$$
\begin{align*}
E_{\text {rotational }+ \text { spin }} & =\frac{\hbar^{2}}{2 I}\left(J^{\prime}\left(J^{\prime}+1\right)-J(J+1)\right)+\frac{\hbar^{2}}{I}(J+1) \\
& =\left(\frac{J^{\prime 2}+J^{\prime}-J^{2}+J+2}{2}\right) p^{2} 121.89 \mathrm{~cm}^{-1} \tag{16.257}
\end{align*}
$$

In the case that the initial rotational state is $J=0$, Eq. (16.256) becomes

$$
\begin{align*}
E_{\text {rotational }+ \text { spin }} & =\frac{\hbar^{2}}{2 I}\left(J^{\prime}\left(J^{\prime}+1\right)-J(J+1)\right)+\frac{\hbar^{2}}{I}(J+1) \\
& =\left(\frac{J^{\prime 2}+J^{\prime}+2}{2}\right) p^{2} 121.89 \mathrm{~cm}^{-1} \tag{16.258}
\end{align*}
$$

Consider that the diatomic molecular rotation is about the $z$-axis such that the corresponding rotational angular momentum of $\hbar$ is aligned along the z-axis. In the case that the axis of the intrinsic electron spin angular momentum of $\frac{\hbar}{2}$ is along the orthogonal semiminor axis, the y-axis, the rotation energy $E_{\text {rotational }}$ of $H_{2}(1 / p)$ is given by Eq. (16.255).

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 (Eq. (12.69)):

$$
\begin{equation*}
L_{z}=m \hbar \tag{16.259}
\end{equation*}
$$

Thus, the selection rule for dipole and quadrupole rotational transitions are (Eq. (12.70)):

$$
\begin{equation*}
\Delta J= \pm 1 \tag{16.260}
\end{equation*}
$$

and

$$
\begin{equation*}
\Delta J= \pm 2 \tag{12.261}
\end{equation*}
$$

Not only are the lowest energy Raman transitions for pure rotational transitions (Eq.(16.255)) and for concerted rotational-spin transition (Eq. (16.257)) allowed by each of the selection rules given by Eqs. (16.259) and (16.260), but coupling of allowed dipole and quadrupole transitions permit excitation of higher rotational energy levels. Isotopic substitution and ortho-para state occupancy also determines the section rules of Raman transitions. Exemplary transitions are given in Table 16.52.

Due to the equivalence of the two semiminor axes, a double rotational excitation comprising the superposition of the independent rotations about each may occur. The energy of the double excitation of these two rotational modes is the sum of the individual pure and concerted rotational transitions. Using Eqs. (16.256) and (16.258), the energies $E_{\text {double rotation }}$ of the combined rotational excitations are

$$
\begin{equation*}
E_{\text {double rotational }}=\left(\frac{J_{c}^{\prime 2}+J_{c}^{\prime 2}+2}{2}\right)+\frac{J_{p}^{\prime}\left(J_{p}^{\prime}+1\right)}{2} p^{2} 121.89 \mathrm{~cm}^{-1} \tag{16.262}
\end{equation*}
$$

Exemplary transitions are given in Table 16.52.

Table 16.52. $\mathrm{H}_{2}(1 / 4)$ Raman energies for (i) pure $J=0$ to $J^{\prime}=1,2,3, \ldots$ rotational transitions, (ii) concerted $J=0$ to $J^{\prime}=0,1,2,3, \ldots$ molecular rotational transition involving a spin rotation transition having the spin rotational state quantum number change from $J=0$ to $J=1$, and double transition having energies given by the sum of the independent transitions.

| J' | Pure Rotational <br> Transition $\left(\mathrm{cm}^{-1}\right)$ | Concerted Molecular <br> Rotational-Spin Rotation <br> Transition $\left(\mathrm{cm}^{-1}\right)$ |  |  |
| :---: | :---: | :---: | :---: | :---: |
| 0 | 0 | 1950 | $J_{p}^{\prime} / J_{c}^{\prime}$ | Double Rotational <br> Transition $\left(\mathrm{cm}^{-1}\right)$ |
| 1 | 1950 | 3900 | $2 / 0$ |  |
| 2 | 5851 | 7801 | $2 / 1$ | 7800 |
| 3 | 11701 | 13652 | $3 / 0$ | 9751 |
| 4 | 19502 | 21453 | $3 / 1$ | 13652 |
| 5 | 29254 | 31204 | $3 / 2$ | 15602 |
| 6 | 40955 | 42905 | $4 / 0$ | 19502 |
| 7 | 54607 | 56557 | $4 / 1$ | 21453 |
| 8 | 70209 | 72159 | $4 / 2$ | 23403 |
| 9 | 87761 | 89711 | $4 / 3$ | 33154 |
| 10 | 107263 | 109213 | $5 / 0$ | 31204 |

The rotation energies shown in Table 16.52 with spin-orbital splitting and fluxon linkage sub-splitting energy shifts were observed by Raman spectroscopy [136]. Moreover, some of the observed lines matched those of the Diffuse Interstellar Bands (DIBs) [136, 137].

## END-OVER-END ROTATION OF HYDROGEN-TYPE MOLECULAR DIMERS

The reduced masses of hydrogen-type molecular dimers having two protons $\mu_{H_{2}}$ or deuterons $\mu_{D_{2}}$ are given by Eqs. (12.67) and (12.72) where $m_{1}=m_{2}=m_{p}$ and $m_{1}=m_{2}=2 m_{p}$, respectively:

$$
\begin{align*}
& \mu_{H_{2}}=\frac{m_{p} m_{p}}{m_{p}+m_{p}}=\frac{1}{2} m_{p}  \tag{16.263}\\
& \mu_{D_{2}}=\frac{2 m_{p} 2 m_{p}}{2 m_{p}+2 m_{p}}=m_{p} \tag{16.264}
\end{align*}
$$

where $m_{p}$ is the mass of the proton. The moment of inertia of hydrogen-type molecular dimers is given by summation of the moments of inertial for two sets of nuclei, each equidistant from the center of rotation along the x -axis. The moment of inertia of the nearest neighbor nuclei is given by substitution of the reduced mass (Eqs. (16.263) or (16.264)) for $\mu$ of Eq. (12.66) and substitution of the internuclear distance $2 c^{\prime}{ }_{\text {dimer }}$ (Eq. (16.181) or (16.202))for $r$ of Eq. (12.66). The moment of inertia of the farthest neighbor nuclei is given by substitution of the reduced mass (Eqs. (16.263) or (16.264)) for $\mu$ of Eq. (12.66) and substitution of the internuclear distance $2 c^{\prime}{ }_{\text {dimer }}^{\prime}$ (Eq. (16.181) or (16.202))) plus the internuclear distance $2 c^{\prime}$ (Eq. (11.204) for $r$ of Eq. (12.66).

$$
\begin{align*}
& I\left(\left[H_{2}\right]_{2}\right)=\frac{m_{p}}{2}\left[\left(7.61404 a_{0}\right)^{2}+\left(7.61404 a_{0}+\sqrt{2} a_{0}\right)^{2}\right]  \tag{16.265}\\
& I\left(\left[D_{2}\right]_{2}\right)=m_{p}\left[\left(7.61404 a_{0}\right)^{2}+\left(7.61404 a_{0}+\sqrt{2} a_{0}\right)^{2}\right]  \tag{16.266}\\
& I\left(\left[H_{2}(1 / 4)\right]_{2}\right)=\frac{m_{p}}{2}\left[\left(1.94251 a_{0}\right)^{2}+\left(1.94251 a_{0}+\frac{\sqrt{2}}{4} a_{0}\right)^{2}\right]  \tag{16.267}\\
& I\left(\left[H_{2}(1 / 4)\right]_{2}\right)=m_{p}\left[\left(1.94251 a_{0}\right)^{2}+\left(1.94251 a_{0}+\frac{\sqrt{2}}{4} a_{0}\right)^{2}\right] \tag{16.268}
\end{align*}
$$

Using Eqs. (12.71), (12.67), and (12.74), the rotational energies absorbed by a hydrogen-type molecular dimer with the transition from the state with the rotational quantum number $J$ to one with the rotational quantum number $J+1$ are:

$$
\begin{align*}
& \Delta E\left(\left[H_{2}\right]_{2}\right)=E_{J+1}-E_{J} \\
& =\frac{\hbar^{2}}{I\left(\left[H_{2}\right]_{2}\right)}[J+1] \\
& =\frac{\hbar^{2}}{\frac{m_{p}}{2}\left[\left(7.61404 a_{0}\right)^{2}+\left(7.61404 a_{0}+\sqrt{2} a_{0}\right)^{2}\right]}  \tag{16.269}\\
& =[J+1] 1.71 \mathrm{~cm}^{-1} \\
& \Delta E\left(\left[D_{2}\right]_{2}\right)=E_{J+1}-E_{J} \\
& =\frac{\hbar^{2}}{I\left(\left[D_{2}\right]_{2}\right)}[J+1] \\
& =\frac{\hbar^{2}}{m_{p}\left[\left(7.61404 a_{0}\right)^{2}+\left(7.61404 a_{0}+\sqrt{2} a_{0}\right)^{2}\right]}  \tag{16.270}\\
& =[J+1] 0.86 \mathrm{~cm}^{-1} \\
& \Delta E\left(\left[H_{2}(1 / 4)\right]_{2}\right)=E_{J+1}-E_{J} \\
& =\frac{\hbar^{2}}{I\left(\left[H_{2}(1 / 4)\right]_{2}\right)}[J+1] \\
& =\frac{\hbar^{2}}{\frac{m_{p}}{2}\left[\left(1.94251 a_{0}\right)^{2}+\left(1.94251 a_{0}+\frac{\sqrt{2}}{4} a_{0}\right)^{2}\right]}  \tag{16.271}\\
& =[J+1] 44.30 \mathrm{~cm}^{-1} \\
& \Delta E\left(\left[D_{2}(1 / 4)\right]_{2}\right)=E_{J+1}-E_{J} \\
& =\frac{\hbar^{2}}{I\left(\left[D_{2}(1 / 4)\right]_{2}\right)}[J+1] \\
& \frac{\hbar^{2}}{m_{p}\left[\left(1.94251 a_{0}\right)^{2}+\left(1.94251 a_{0}+\frac{\sqrt{2}}{4} a_{0}\right)^{2}\right]}  \tag{16.272}\\
& =[J+1] 22.15 \mathrm{~cm}^{-1}
\end{align*}
$$

The results for $H_{2}$ and $D_{2}$ dimers (Eqs. (16.269) and (16.270)) match experimental observations [138].

## REACTION KINETICS AND THERMODYNAMICS

Reaction kinetics may be modeled using the classical solutions of reacting species and their interactions during collisions wherein the bond order of the initial and final bonds undergo a decreasing and increasing bond order, respectively, with conservation of charge and energy. Collisions can be modeled starting with the simple hard sphere model with conservation of energy and momentum. The energy distribution may be modeled using the appropriate statistical thermodynamics model such as

Maxwell-Boltzmann statistics. Low-energy collisions are elastic, but for sufficiently high energy, a reaction may occur. Hot reacting species such as molecules at the extreme of the kinetic energy distribution can achieve the transition state, the intermediate species at the cross over point in time and energy between the reactants and products. The rate function to form the transition state may depend on the collisional orientation as well as the collisional energy. Bond distortion conserves the energy and momentum of the collision from the trajectories of the reactants. For sufficient distortion due to a sufficiently energetic collision at an appropriate relative orientation, a reaction occurs wherein the products exiting the collision event are different from the reactants entering the collision. The initial reactant energy and momentum as well as those arising from any bonding energy changes are conserved in the translational, rotational, and vibrational energies of the products. The bond energy changes are given by the differences in the energies of the product and reactants molecules wherein the geometrical parameters, energies, and properties of the latter can be solved using the same equations as those used to solve the geometrical parameters and component energies of the individual molecules as given in the Organic Molecular Functional Groups and Molecules section. The bond energy changes at equilibrium determine the extent of a reaction according to the Gibbs free energy of reaction. Whereas, the corresponding dynamic reaction-trajectory parameters of translational, rotational, and vibrational energies as well as the time dependent electronic energy components such as the electron potential and kinetic energies of intermediates correspond to the reaction kinetics. Each aspect will be treated next in turn.

Consider the gas-phase reaction of two species $A$ and $B$ comprising the reactants that form one or more products $C_{n}$ where $n$ is an integer:

$$
\begin{equation*}
A+B \rightleftarrows C_{1}+\cdots+C_{n} \tag{16.273}
\end{equation*}
$$

Arising from collisional probabilities, the concentrations (denoted $[A],[B], \ldots$ ) as a function of time can be fitted to a secondorder rate law

$$
\begin{equation*}
-\frac{d[A]}{d t}=k[A][B]-k^{\prime} \prod_{i=1}^{n}\left[C_{i}\right] \tag{16.274}
\end{equation*}
$$

where $k$ and $k^{\prime}$ are the forward and reverse rate constants. The equilibrium constant $K$ corresponding to the balance between the forward and reverse reactions is given by the quotient of the forward and reverse rate constants:

$$
\begin{equation*}
K=\frac{k}{k^{\prime}} \tag{16.275}
\end{equation*}
$$

The relationship between the temperature-dependent equilibrium constant and the standard Gibbs free energy of reaction $\Delta G_{T}^{0}(T)$ at temperature $T$ is:

$$
\begin{equation*}
K=Q_{K}(T) e^{\frac{-\Delta G_{T}^{0}(T)}{R T}} \tag{16.276}
\end{equation*}
$$

where $R$ is the ideal gas constant,

$$
\begin{equation*}
Q_{K}(T)=\frac{\prod_{i=1}^{n}\left[C_{i}\right]}{[A][B]} \tag{16.277}
\end{equation*}
$$

is the reaction quotient at the standard state, and

$$
\begin{equation*}
\Delta G_{T}^{0}(T)=\Delta H_{T}^{0}(T)-T \Delta S_{T}^{0} \tag{16.278}
\end{equation*}
$$

where $\Delta H_{T}^{0}(T)$ and $\Delta S_{T}^{0}$ are the standard-state enthalpy and entropy of reaction, respectively. Rearranging Eq. (16.276) gives the free energy change upon reaction:

$$
\begin{equation*}
\Delta G=R T \ln \frac{Q_{K}}{K} \tag{16.279}
\end{equation*}
$$

If the instantaneous free energy change is zero, then the reaction is at equilibrium. An exergonic or work-producing reaction corresponds to the cases with $\Delta G_{T}^{0}(T)$ or $\Delta G$ negative, and endergonic or work consuming reactions corresponds to positive values. The enthalpy of reaction or heat of reaction at constant pressure is negative for an exothermic (heat releasing) reaction, and is positive for an endothermic (heat absorbing) reaction. The enthalpy of reaction may be calculated by Hess's law as the difference of the sum of the heats of formation of the products minus the sum of the heats of formation of the reactants wherein the individual heats of the molecules are solved using the equations given in the Organic Molecular Functional Groups and Molecules section.

## TRANSITION STATE THEORY

Transition state theory (TST) has been widely validated experimentally. It entails the application of classical trajectory calculations that allow the study of the dynamics at the microscopic level such as differential cross sections, total cross sections, and product energy distributions, as well as at the macroscopic level for the determination of thermal rate constants by solving the classical equations of motion with the formation of the transition state. The reaction trajectory parameters give rise to terms of a classical thermodynamic kinetics equation discovered in 1889 by Arrhenius and named after him. The data of the variation of the rate constant $k$ with temperature of many reactions fit the Arrhenius equation given by

$$
\begin{equation*}
k=A e^{\frac{-E_{a}}{R T}} \tag{16.280}
\end{equation*}
$$

where $E_{a}$ is the activation energy and $A$ is a preexponential or frequency factor that may have a relatively small temperature dependence compared to the exponential term of Eq. (16.244). For reactions that obey the Arrhenius equation, when $\ln k$ is plotted versus $1 / T$ in a so-called Arrhenius plot, the slope is the constant $-E_{a} / R$, and the intercept is $A$. Eq. (16.280) confirms that typically two colliding molecules require a certain minimum kinetic energy of relative motion to sufficiently distort initial reactant bonds and concomitantly allow nascent bonds to form. The crossover species from reactants to products called the transition state will proceed through the minimum energy complex involving the reactants. Thus, the activation energy can be interpreted as the minimum energy that the reactants must have in order to form the transition state and transform to product molecules. $E_{a}$ can be calculated from the total energy of the transition state relative to that of the reactants and is achieved when the thermal energy of the reactants overcomes the energy deficit between the energy of the reactants and that of the transition state. The preexponential factor corresponds to the collision frequency and energy of collisions upon which the formation of the transition state is dependent.

For bimolecular reactions, transition state theory yields [139]:

$$
\begin{equation*}
k(T)=\frac{1}{\left(k_{B} T\right) h} \gamma(T) K^{\circ} \exp \left(-\Delta G_{T}^{\ddagger \circ} / R T\right) \tag{16.281}
\end{equation*}
$$

where $\Delta G_{T}^{\ddagger \circ}$ is the quasi-thermodynamic free energy of activation, $\gamma(T)$ is a transmission coefficient, $K^{\circ}$ is the reciprocal of the concentration, $h$ is Planck's constant, and $k_{B}$ is the Boltzmann constant. The factor $\frac{1}{\left(k_{B} T\right) h}$ is obtained by dynamical classical equations of motion involving species trajectories having a statistical mechanical distribution. Specifically, the reactant molecular distribution is typically a Maxwell-Boltzmann distribution. The classical derivation of the preexponential term of the Arrhenius equation can be found in textbooks and review articles such as section 2.4 of Ref. [139]. Typically the $A$ term can be accurately determined from the Maxwell-Boltzmann-distribution-constrained classical equations of motion by sampling or by using Monte Carlo methods on many sets (usually more than ten thousand) of initial conditions for the coordinates and momenta involving the trajectories. The translational levels are a continuous distribution, and the rotational and vibrational levels are quantized according to the classical equations given, for example, in the Vibration of the Hydrogen Molecular Ion section and the Diatomic Molecular Rotation section.

## SN2 REACTION OF $\mathrm{Cl}^{-}$WITH $\mathrm{CH}_{3} \mathrm{Cl}$

Consider the $\mathrm{S}_{\mathrm{N}}$ 2 (bimolecular nucleophilic substitution) gas-phase reaction of $\mathrm{Cl}^{-}$with chloromethane through a transition state:

$$
\begin{equation*}
\mathrm{Cl}^{-}+\mathrm{CH}_{3} \mathrm{Cl} \rightarrow \mathrm{ClCH}_{3}+\mathrm{Cl}^{-} \tag{16.282}
\end{equation*}
$$

The corresponding Arrhenius equation for the reaction given by Eq. (16.280) is:

$$
\begin{equation*}
k(T)=\frac{k_{B} T}{h} \frac{Q^{\ddagger}}{\Phi^{R}} e^{\frac{-\Delta E^{\ddagger}}{k_{B} T}} \tag{16.283}
\end{equation*}
$$

where $k_{B}$ is the Boltzmann constant, $h$ is Planck's constant, $\Delta E^{\ddagger}$ is the activation energy of the transition state $\ddagger, T$ is the temperature, $\Phi^{R}$ is the reaction partition per unit volume, and $Q$ is the coordinate independent transition-state partition function. The preexponential factor $\frac{k_{B} T}{h} \frac{Q^{\ddagger}}{\Phi^{R}}$ has previously been calculated classically and shown to be in agreement with the experimental rate constant [140]. Then, only the transition state need be calculated and its geometry and energy compared to observations to confirm that classical physics is predictive of reaction kinetics. The activation energy can be calculated by determining the energy at the point that the nascent bond with the chloride ion is the same as that of the leaving chlorine wherein the negative charge is equally distributed on the chlorines. The rearrangement of bonds and the corresponding electron MOs of the reactants and products can be modeled as a continuous transition of the bond orders of the participating bonds from unity to zero and vice versa, respectively, wherein the transition state is a minimum-energy molecule having bonds between all of the reactants, $\mathrm{Cl}^{-}$and $\mathrm{CH}_{3} \mathrm{Cl}$

## TRANSITION STATE

The reaction proceeds by back-side attack of $\mathrm{Cl}^{-}$on $\mathrm{CH}_{3} \mathrm{Cl}$. Based on symmetry, the reaction pathway passes through a $D_{3 h}$ configuration having $C l^{\delta}-C-C l^{\delta}$ on the $C_{3}$ axis. The hydrogen atoms are in the $\sigma_{h}$ plane with the bond distances the same as those of the $\mathrm{CH}_{3}$ functional group given in the Alkyl Chlorides section, since this group is not involved in the substitution reaction. The transition-state group $C l^{\delta}-C-C l^{\delta}$ is treated as a three-centered-bond functional group that comprises a linear
combination of $\mathrm{Cl}^{-}$and the $\mathrm{C}-\mathrm{Cl}$ group of chloromethane ( $\mathrm{C}-\mathrm{Cl}$ (i) given in Table 15.33). It is solved using the Eq. (15.51) with the total energy matched to the sum of the $H_{2}$-type ellipsoidal MO total energy, -31.63536831 eV given by Eq. (11.212) as in the case of chloromethane, and the energy of the two outer electrons of $\mathrm{Cl}^{-}$, $E\left(C l^{-}\right)=-I P_{1}-I P_{2}=-12.96764 \mathrm{eV}-3.612724 \mathrm{eV}=-16.58036 \mathrm{eV}[15,141]$. These electrons are contributed to form the back-side-attack bond. Then, the corresponding parameter $E_{T}(А О / H O)(\mathrm{eV})$ is $-14.63489 \mathrm{eV}-16.58036 \mathrm{eV}=-31.21525 \mathrm{eV}$ due to the match of the MO energy to both $E\left(C, 2 s p^{3}\right)=-14.63489 \mathrm{eV}$ (Eq. (15.25)) and $E\left(\mathrm{Cl}^{-}\right)$, and $E_{\text {initial }}\left(c_{5} A O / H O\right)(\mathrm{eV})$ is -16.58036 eV corresponding to the initial energy of the $\mathrm{Cl}^{-}$electrons. Also, due to the two $\mathrm{C}-\mathrm{Cl}$ bonds of the $C l^{\delta}-C-C l^{\delta}$ functional group $n_{1}=2$. Otherwise all of the parameters of Eq. (15.51) remain the same as those of chloromethane given in Table 15.36. 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 16.53, 16.54, and 16.55, respectively. The color scale, translucent view of the charge density of the chloride-ion-chloromethane transition state comprising the $\mathrm{Cl}^{\delta}-\mathrm{C}^{-} \mathrm{Cl}^{\delta}$ functional group is shown in Figure 16.17. The transition state bonding comprises two paired electrons in each $C l^{\delta}-C$ MO with two from $\mathrm{Cl}^{-}$, one from Cl and one from $\mathrm{CH}_{3}$. As a symmetrical three-centered bond, the central bonding species are two Cl bound to a central $\mathrm{CH}_{3}^{+}$per $\mathrm{Cl}^{\delta}-C$ MO with a continuous current onto the $C-H$ MO at the intersection of each $\mathrm{Cl}^{\delta}-\mathrm{C}$ MO with the $\mathrm{CH}_{3}^{+}$group. Due to the four electrons and the valence of the chlorines, the latter possess a partial negative charge of $-0.5 e$ distributed on each $C l^{\delta}-C$ MO such that the far field is equivalent to that of the corresponding point charge at each $C l$ nucleus.

Figure 16.17. Color scale, translucent view of the chloride-ion-chloromethane transition state comprising the $C l^{\delta}-C-C l^{\delta}$ functional group 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 16.53. The geometrical bond parameters of the $\mathrm{Cl}^{\delta}-C-\mathrm{Cl}^{\delta}$ and $\mathrm{CH}_{3}$ functional groups of the chloride-ionchloromethane transition state.

| Parameter | $C l^{\delta^{\delta}}-\mathrm{C}-\mathrm{Cl}^{\delta^{\delta}}$ Group | $\mathrm{C}-\mathrm{H}\left(\mathrm{CH}_{3}\right)$ Group |
| :--- | :---: | :---: |
| $a\left(a_{0}\right)$ | 3.70862 | 1.64920 |
| $c^{\prime}\left(a_{0}\right)$ | 2.13558 | 1.04856 |
| Bond Length $2 c^{\prime}(\AA)$ | 2.26020 | 1.10974 |
| Literature Bond Length <br> $(\AA)$ | $2.3-2.4[140,142]$ | $1.06-1.07[140]$ |
| $b, c\left(a_{0}\right)$ | 3.03202 | 1.27295 |
| $e$ | 0.57584 | 0.63580 |

Table 16.54. The MO to HO and AO intercept geometrical bond parameters of the $-\mathrm{Cl}^{\delta^{-}}-\mathrm{C}-\mathrm{Cl}^{\circ}$ and $\mathrm{CH}_{3}$ functional groups of the chloride-ion-chloromethane transition state. $E_{T}$ is $E_{T}\left(\right.$ atom -atom, $\left.m s p^{3} . A O\right)$.

| Bond | Atom | $\begin{gathered} E_{T} \\ (\mathrm{eV}) \end{gathered}$ Bond I | $E_{T}$ (eV) Bond 2 | $E_{T}$ $(\mathrm{eV})$ <br> Bond 3 | $\begin{gathered} E_{T} \\ (\mathrm{eV}) \end{gathered}$ $\text { Bond } 4$ | Final Total <br> Energy <br> $c 2 s p^{3}$ <br> $(\mathrm{eV})$ | $r_{\left(a_{0}\right)}^{r_{0}}$ | $\begin{aligned} & r_{\text {fotal }} \\ & \left(a_{0}\right) \end{aligned}$ | $\begin{gathered} E_{\text {Camem }}(C 2 s f \\ (\mathrm{eV}) \\ \text { Final } \end{gathered}$ | $\begin{gathered} E\left(C 2 s p^{3}\right) \\ (\mathrm{eV}) \\ \text { Final } \end{gathered}$ | $\begin{aligned} & \theta^{\prime} \\ & \left({ }^{\circ}\right) \end{aligned}$ | $\begin{gathered} \theta_{1} \\ \left({ }^{\circ}\right) \end{gathered}$ | $\begin{gathered} \theta_{2} \\ \left({ }^{\circ}\right) \end{gathered}$ | $\begin{gathered} d_{1} \\ \left(a_{0}\right) \end{gathered}$ | $\begin{gathered} d_{2} \\ \left(a_{0}\right) \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{Cl}^{5}-\mathrm{C}-\mathrm{Cl}^{5}$ | C | -0.36229 | -0.36229 | 0 | 0 | -152.34026 | 0.91771 | 0.87495 | -15.55033 | -15.35946 |  |  |  |  |  |
| $\mathrm{Cl}_{0}^{5}-\mathrm{C}-\mathrm{Cl}_{6}^{5}$ | $\mathrm{Cl}_{a^{5}}$ | -0.36229 | 0 | 0 | 0 |  | 2.68720 | 0.89582 | -15.18804 |  |  |  |  |  |  |
| $\mathrm{Cl}_{a}^{5}-\mathrm{C}-\mathrm{Cl}_{6}^{5}$ | $\mathrm{Cl}_{b^{5}}$ | -0.36229 | 0 | 0 | 0 |  | 1.05158 | 0.89582 | -15.18804 |  |  |  |  |  |  |
| $\mathrm{C}-\mathrm{H}\left(\mathrm{CH}_{3}\right)$ | c | -0.36229 | $-0.36229$ | 0 | 0 | -152.34026 | 0.91771 | 0.87495 | -15.55033 | -15.35946 | 78.85 | 101.15 | 42.40 | 1.21777 | 0.16921 |

Table 16.55. The energy parameters (eV) of the $\mathrm{Cl}^{\delta}-\mathrm{C}^{-} \mathrm{Cl}^{\delta}$ and $\mathrm{CH}_{3}$ functional groups of the chloride-ionchloromethane transition state.

| Parameters | $C^{\delta}-C-C^{\delta}$ Group | $\mathrm{CH}_{3}$ Group |
| :---: | :---: | :---: |
| $n_{1}$ | 2 | 3 |
| $n_{2}$ | 0 | 2 |
| $n_{3}$ | 1 | 0 |
| $C_{1}$ | 0.5 | 0.75 |
| $C_{2}$ | 0.81317 | 1 |
| $c_{1}$ | 1 | 1 |
| $c_{2}$ | 1 | 0.91771 |
| $c_{3}$ | 1 | 0 |
| $c_{4}$ | 2 | 1 |
| $c_{5}$ | 1 | 3 |
| $C_{1 o}$ | 0.5 | 0.75 |
| $C_{2 o}$ | 0.81317 | 1 |
| $V_{e}(\mathrm{eV})$ | -33.44629 | -107.32728 |
| $V_{p}(e V)$ | 12.74200 | 38.92728 |
| $T(e V)$ | 4.50926 | 32.53914 |
| $V_{m}(\mathrm{eV})$ | -2.25463 | -16.26957 |
| $E$ (ло но) (eV) | -31.21525 | -15.56407 |
| $\Delta E_{\mathrm{H}_{2} \mathrm{MO}}\left(\right.$ АО/НО) ${ }^{\text {(eV) }}$ | -1.44915 | 0 |
| $E_{T}($ АО/ $/ \mathrm{HO})(\mathrm{eV})$ | -29.76611 | -15.56407 |
| $E\left(n_{3}\right.$, Ао/но) $(\mathrm{eV})$ | -16.58036 | 0 |
| $E_{T}\left(\mathrm{H}_{2} \mathrm{MO}\right)(\mathrm{eV})$ | -48.21577 | -67.69451 |
| $E_{T}\left(\right.$ atom - atom, $\left.\mathrm{msp}^{3} . \mathrm{AO}\right)(\mathrm{eV})$ | -1.44915 | 0 |
| $E_{T}($ мо $)(\mathrm{eV})$ | -49.66491 | -67.69450 |
| $\omega\left(10^{15} \mathrm{rad} / \mathrm{s}\right)$ | 3.69097 | 24.9286 |
| $E_{K}(\mathrm{eV})$ | 2.42946 | 16.40846 |
| $\bar{E}_{D}(e V)$ | -0.07657 | -0.25352 |
| $\bar{E}_{\text {Kvib }}(\mathrm{eV})$ | $\begin{gathered} 0.08059 \\ {[5]} \\ \hline \end{gathered}$ | $\begin{gathered} 0.35532 \\ \text { (Eq. }(13.458) \text { ) } \\ \hline \end{gathered}$ |
| $\bar{E}_{\text {osc }}(\mathrm{eV})$ | -0.03628 | -0.22757 |
| $E_{\text {mag }}(\mathrm{eV})$ | 0.14803 | 0.14803 |
| $E_{T}($ Group $)(\mathrm{eV})$ | -49.73747 | -67.92207 |
| $E_{\text {initial }}\left(c_{4}\right.$ AO/HO) $(e V)$ | -14.63489 | -14.63489 |
| $E_{\text {initial }}\left(c_{5}\right.$ AO/HO) $(\mathrm{eV})$ | -16.58036 | -13.59844 |
| $E_{D}($ Group $)(e V)$ | 3.73930 | 12.49186 |

The bond energy of the $\mathrm{C}-\mathrm{Cl}$ group of chloromethane from Table 15.36 is $E_{D}($ Group $)(\mathrm{eV})=3.77116 \mathrm{eV}$ compared to the bond energy of the $C l^{\delta}-C-C l^{\delta}$ functional group of the chloride-ion-chloromethane transition state of
$E_{D}$ (Group) $(\mathrm{eV})=3.73930 \mathrm{eV}$ (Table 16.55). Since the energies of the $\mathrm{CH}_{3}$ functional groups are unchanged, the chloride-ionchloromethane transition state is $\Delta E=+0.03186 \mathrm{eV}(+0.73473 \mathrm{kcal} / \mathrm{mole})$ higher in energy than chloromethane. Experimentally, the transition state is about $1 \pm 1 \mathrm{kcal} /$ mole higher [137]. Using this energy as the corresponding activation energy $\Delta E^{\ddagger}$ of Eq. (16.283) with the classically determined preexponential factor $\frac{k_{B} T}{h} \frac{Q^{\ddagger}}{\Phi^{R}}$ predicts the experimental reaction rate very well [140].

## NEGATIVELY-CHARGED MOLECULAR ION COMPLEX $\mathbb{C}$

In addition to the nature and energy of the transition state designated by $\ddagger$, experimental gas-phase rate constants indicate that the reaction of $\mathrm{Cl}^{-}$with $\mathrm{CH}_{3} \mathrm{Cl}$ passes through a bound state comprising the attachment of $\mathrm{Cl}^{-}$to the positive dipole of $\mathrm{CH}_{3} \mathrm{Cl}[140,142,143]$ (the dipole moment of the $\mathrm{C}-\mathrm{Cl}$ functional group is given in the Bond and Dipole Moments section). This negatively-charged molecular ion complex designated $\mathbb{C}$ exists as a more stable state in between the reactants and the transition state, and by equivalence of the chlorines, it also exists between the transition state and the products. Experimentally $\mathbb{C}$ is $12.2 \pm 2 \mathrm{kcal} /$ mole more stable than the isolated reactants and products, $\mathrm{Cl}^{-}$and $\mathrm{CH}_{3} \mathrm{Cl}$. Thus, an energy well corresponding to $\mathbb{C}$ occurs on either side of the energy barrier of the transition state $\ddagger$ that is about $1 \pm 1 \mathrm{kcal} /$ mole above the reactants and products [140, 143]. Thus, the combination of the depth of this well and the barrier height yields an intrinsic barrier to nucleophilic substitution given by the reaction of Eq. (16.282) of $13.2 \pm 2.2 \mathrm{kcal} / \mathrm{mole}$ [140, 143].

The negatively-charged molecular ion complex $\mathbb{C}$ comprises the functional groups of $\mathrm{CH}_{3} \mathrm{Cl}$ ( $\mathrm{C}-\mathrm{Cl}$ (i) and $\mathrm{CH}_{3}$ given in Table 15.33 of the Alkyl Chlorides section) and a $\mathrm{Cl}^{-} \cdot \mathrm{C}^{\delta^{+}}$functional group wherein $\mathrm{Cl}^{-}$is bound to the $\mathrm{CH}_{3} \mathrm{Cl}$ moiety by an ion-dipole bond. As given in the case of the dipole-dipole bonding of ice, liquid water, and water vapor as well as the van der Waals bonding in graphite and noble gases given in the Condensed Matter Physics section, the bond energy and bond distance of the $C^{-} \cdot C^{\delta^{+}}$functional group are determined by the limiting energy and distance of the formation of a corresponding nascent $\mathrm{Cl}^{-}-\mathrm{CH}_{3} \mathrm{Cl}$ covalent bond that destabilizes the $\mathrm{C}-\mathrm{Cl}$ bond of the $\mathrm{CH}_{3} \mathrm{Cl}$ moiety by involving charge density of its electrons in the formation the nascent bond. Subsequently, the higher energy $C l^{\delta}-C-C l^{\delta}$ functional group of the transition state is formed.

The energy and geometric parameters of the $C^{-} \cdot C^{\delta^{+}}$functional group are solved using Eq. (15.51) with the total energy matched to the $H_{2}$-type ellipsoidal MO total energy, -31.63536831 eV . The parameter $E_{T}(A O / H O)(\mathrm{eV})$ is $-14.63489 \mathrm{eV}-3.612724 \mathrm{eV}=-18.24761 \mathrm{eV}$ due to the match of the MO energy to both $E\left(C, 2 s p^{3}\right)=-14.63489 \mathrm{eV}$ (Eq. (15.25)) and the outer electron of $E\left(\mathrm{Cl}^{-}\right)\left(-I P_{1}=-3.612724 \mathrm{eV}\right)$ [141] that forms the nascent bond by the involving the electrons of the $\mathrm{C}-\mathrm{Cl}$ group of the $\mathrm{CH}_{3} \mathrm{Cl}$ moiety. Then, $E_{\text {initial }}\left(c_{5} A O / H O\right)(\mathrm{eV})$ is -3.612724 eV corresponding to the initial energy of the outer $\mathrm{Cl}^{-}$electron. Also, $E_{T}\left(\right.$ atom-atom, $\left.m s p^{3} . \mathrm{AO}\right)$ in Eq. (15.61) is -1.85836 eV due to the charge donation from the $C$ HO to the MO based on the energy match between the $C 2 s p^{3}$ HOs corresponding to the energy contribution of methylene, -0.92918 eV (Eq. (14.513)). $\quad E_{m a g}=0$ since the $\mathrm{Cl}^{-}$electrons are paired upon dissociation, and the vibrational energy of the transition state is appropriate for $C^{-} \cdot C^{\delta^{+}}$. Otherwise, all of the parameters of Eq. (15.51) remain the same as those of chloromethane given in Table 15.36. 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 16.56, 16.57, and 16.58, respectively. The color scale, translucent view of the charge density of the negatively-charged molecular ion complex $\mathbb{C}$ comprising the $C^{-} \cdot C^{\delta^{+}}$ functional group is shown in Figure 16.18. The bonding in the $\mathbb{C}$ complex comprises two paired electrons in the $C^{-} \cdot C^{\delta^{+}}$MO with $1 / 2$ of the charge density from $\mathrm{Cl}^{-}$and the other half from $\mathrm{CH}_{3}$. The central bonding species are a Cl bound to a central $\mathrm{CH}_{3}^{+}$with a continuous current onto the $\mathrm{C}-H \mathrm{MO}$ at the intersection of the $\mathrm{Cl}^{-} \cdot \mathrm{C}^{\delta^{+}} \mathrm{MO}$ with the $\mathrm{CH}_{3}^{+}$group. Due to the two electrons and the valence of the chlorine, the latter possess a negative charge of $-e$ distributed on the $C l^{-} \cdot C^{\delta^{+}}$MO such that the far field is equivalent to that of the corresponding point charge at the Cl nucleus. The bonding in the $\mathrm{CH}_{3} \mathrm{Cl}_{\text {moiety }}$ is equivalent to that of chloromethane except that the $C-H$ bonds are in a plane to accommodate the $C l^{-} \cdot C^{\delta^{+}}$MO.

Figure 16.18. Color scale, translucent view of the negatively-charged molecular ion complex $\mathbb{C}$ comprising the $C^{-} \cdot C^{\delta^{+}}$ functional group 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 16.56. The geometrical bond parameters of the $\mathrm{Cl}^{-} \cdot \mathrm{C}^{\delta^{+}}, \mathrm{C}-\mathrm{Cl}$, and $\mathrm{CH}_{3}$ functional groups of the negativelycharged molecular ion complex $\mathbb{C}$.

| Parameter | $C^{-} \cdot C^{\delta^{+}}$Group | $C-H\left(\mathrm{CH}_{3}\right)$ Group | $\begin{array}{c}C-C l(i) \\ \text { Group }\end{array}$ |
| :--- | :---: | :---: | :---: |
| $a\left(a_{0}\right)$ | 2.66434 | 1.64920 | 2.32621 |
| $c^{\prime}\left(a_{0}\right)$ | 1.81011 | 1.04856 | 1.69136 |
| $\begin{array}{l}\text { Bond Length } \\ 2 c^{\prime}(A)\end{array}$ | 1.91574 | 1.10974 | 1.79005 |
| $\begin{array}{l}\text { Literature Bond } \\ \text { Length } \\ (A)\end{array}$ | $>1.80$ |  |  |
| curve fit $[136]$ |  |  |  |\(\left.\quad 1.06-1.07[1] \begin{array}{c}1.785[1] <br>


(methyl chloride)\end{array}\right]\)| 1.95505 |
| :--- |

Table 16.57. The MO to HO and AO intercept geometrical bond parameters of the $\mathrm{Cl} \cdot \mathrm{Cl}^{\delta^{+}}, \mathrm{C}-\mathrm{Cl}$, and $\mathrm{CH}_{3}$ functional groups of the negatively-charged molecular ion complex C .

| Bond | Atom | $\begin{gathered} E_{r} \\ (\text { (eV) } \\ \text { Bond } \end{gathered}$ | $\begin{gathered} E_{r} \\ (\mathrm{eV}) \\ \text { Bond 2 } \end{gathered}$ | $\begin{gathered} E_{T} \\ (\text { eV) } \\ \text { Bond } 3 \end{gathered}$ | $\begin{gathered} E_{T} \\ (\mathrm{eV}) \\ \text { Bond } 4 \end{gathered}$ | Final Total Energy $C 2 s p^{p}$ (eV) | $\stackrel{r_{\left(a_{0}\right)}}{\left(a_{1}\right)}$ | $\begin{aligned} & r_{\text {moin }} \\ & \left(a_{0}\right) \end{aligned}$ |  | $\begin{gathered} E\left(C 2 s p^{3}\right) \\ (\text { ev) } \\ \text { Final } \end{gathered}$ | $\begin{aligned} & \theta^{\prime} \\ & \left({ }^{\circ}\right) \end{aligned}$ | $\begin{aligned} & \theta_{1} \\ & \left({ }^{\circ}\right) \end{aligned}$ | $\begin{aligned} & \theta_{2} \\ & \left({ }^{\circ}\right) \end{aligned}$ | $\begin{gathered} d_{1} \\ \left(a_{0}\right) \end{gathered}$ | $\begin{gathered} d_{2} \\ \left(a_{0}\right) \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{Cl} \cdot \mathrm{C}^{\text {b }}$ | c | $-0.82688$ | $-0.72457$ | 0 | 0 |  | 0.91771 | 0.83078 | -16.37720 | -16.18634 |  |  |  |  |  |
| $\mathrm{Cl} \cdot \mathrm{C}^{\text {b }}$ | Cl | $-0.82688$ | 0 | 0 | 0 |  | 2.68720 | 0.86923 | -15.65263 |  | 16.80 | 163.20 | 7.38 | 2.64225 | 0.83214 |
| $\mathrm{C}-\mathrm{Cl}$ | c | $-0.82688$ | $-0.72457$ | 0 | 0 | $-153.16714$ | 0.91771 | 0.83078 | -16.37720 | -16.18634 | 63.91 | 116.09 | 27.85 | 2.05675 | 0.36539 |
| C-Cl | Cl | $-0.72457$ | 0 | 0 | 0 |  | 1.05158 | 0.87495 | -15.55033 |  | 69.62 | 110.38 | 30.90 | 1.99599 | 0.30463 |
| $\mathrm{C-H}\left(\mathrm{CH}_{3}\right)$ | c | $-0.82688$ | $-0.72457$ | 0 | 0 | -153.16714 | 0.91771 | 0.83078 | -16.37720 | -16.18634 | 73.30 | 106.70 | 38.69 | 1.28725 | 0.23869 |

Table 16.58. The energy parameters (eV) of the $C^{-} \cdot C^{\delta^{+}}, C-C l$, and $\mathrm{CH}_{3}$ functional groups of the negatively-charged molecular ion complex $\mathbb{C}$.

| Parameters | $C^{-} \cdot C^{\delta^{+}}$Group | $\mathrm{CH}_{3}$ Group | $C-C l$ <br> (i) <br> Group |
| :---: | :---: | :---: | :---: |
| $n_{1}$ | 1 | 3 | 1 |
| $n_{2}$ | 0 | 2 | 0 |
| $n_{3}$ | 0 | 0 | 0 |
| $C_{1}$ | 0.5 | 0.75 | 0.5 |
| $\mathrm{C}_{2}$ | 0.81317 | 1 | 0.81317 |
| $c_{1}$ | 1 | 1 | 1 |
| $c_{2}$ | 1 | 0.91771 | 1 |
| $c_{3}$ | 0 | 0 | 1 |
| $c_{4}$ | 2 | 1 | 2 |
| $c_{5}$ | 1 | 3 | 0 |
| $C_{1 o}$ | 0.5 | 0.75 | 0.5 |
| $C_{2 o}$ | 0.81317 | 1 | 0.81317 |
| $V_{e}(\mathrm{eV})$ | -24.89394 | -107.32728 | -29.68411 |
| $V_{p}(\mathrm{eV})$ | 7.51656 | 38.92728 | 8.04432 |
| $T(\mathrm{eV})$ | 4.67169 | 32.53914 | 6.38036 |
| $V_{m}(\mathrm{eV})$ | -2.33584 | -16.26957 | -3.19018 |
| $E$ (ао/но) (eV) | -18.24761 | -15.56407 | -14.63489 |
| $\Delta E_{\mathrm{H}_{2} \mathrm{MO}}($ Ао/ HO$)(\mathrm{eV})$ | -1.65376 | 0 | -1.44915 |
| $E_{T}($ Ао/ $/ \mathrm{H})(\mathrm{eV})$ | -16.59386 | -15.56407 | -13.18574 |
| $E_{T}\left(\mathrm{H}_{2} \mathrm{MO}\right)(\mathrm{eV})$ | -31.63537 | -67.69451 | -31.63536 |
| $E_{T}\left(\right.$ atom - atom, $\left.\mathrm{msp}^{3} . \mathrm{AO}\right)(\mathrm{eV})$ | -1.65376 | 0 | -1.44915 |
| $E_{T}($ мо) $(\mathrm{eV})$ | -33.28913 | -67.69450 | -33.08452 |
| $\omega\left(10^{15} \mathrm{rad} / \mathrm{s}\right)$ | 6.06143 | 24.9286 | 7.42995 |
| $E_{K}(\mathrm{eV})$ | 3.98974 | 16.40846 | 4.89052 |
| $\bar{E}_{D}(\mathrm{eV})$ | -0.13155 | -0.25352 | -0.14475 |
| $\bar{E}_{\text {Kıib }}(\mathrm{eV})$ | $\begin{gathered} 0.02790 \\ {[144]} \\ \hline \end{gathered}$ | $\begin{gathered} 0.35532 \\ \text { (Eq. }(13.458)) \end{gathered}$ | $\begin{gathered} 0.08059 \\ {[5]} \\ \hline \end{gathered}$ |
| $\bar{E}_{\text {osc }}(e V)$ | -0.11760 | -0.22757 | -0.10445 |
| $E_{\text {mag }}(\mathrm{eV})$ | 0 | 0.14803 | 0.14803 |
| $E_{T}($ Group $)(\mathrm{eV})$ | -33.40672 | -67.92207 | -33.18897 |
| $E_{\text {initial }}\left(c_{4} A O / H O\right)(e V)$ | -14.63489 | -14.63489 | -14.63489 |
| $E_{\text {initial }}\left(c_{5}\right.$ AO/HO) $(\mathrm{eV})$ | -3.612724 | -13.59844 | 0 |
| $E_{D}($ Group $)(e V)$ | 0.52422 | 12.49186 | 3.77116 |

The bond energies of the $\mathrm{CH}_{3} \mathrm{Cl}$ moiety are unchanged to the limit of the formation of the $\mathrm{Cl}^{-} \cdot \mathrm{C}^{\delta^{+}}$functional group of the negatively-charged molecular ion complex $\mathbb{C}$. Thus, the energy of stabilization of forming the ion-dipole complex is
equivalent to the bond energy of the $C l^{-} \cdot C^{\delta^{+}}$functional group. Experimentally $\mathbb{C}$ is $12.2 \pm 2 \mathrm{kcal} /$ mole more stable than the isolated reactants and products [134, 136, 137], $\mathrm{Cl}^{-}$and $\mathrm{CH}_{3} \mathrm{Cl}$. The bond energy of the $\mathrm{Cl}^{-} \cdot \mathrm{C}^{\delta^{+}}$functional group of the negatively-charged molecular ion complex $\mathbb{C}$ of $E_{D}($ Group $)=12.08900 \mathrm{kcal} /$ mole $(0.52422 \mathrm{eV})$ given in Table 16.58 matches the experimental stabilization energy very well. A simulation of the reaction of Eq. (16.282) is available on the internet [145].

## REFERENCES

1. D. R. Lide, CRC Handbook of Chemistry and Physics, 86th Edition, CRC Press, Taylor \& Francis, Boca Raton, (2005-6), pp. 9-19 to 9-45.
2. G. A. Sim, J. M. Robertson, T. H. Goodwin, "The crystal and molecular structure of benzoic acid," Acta Cryst., Vol. 8, (1955), pp.157-164.
3. G. Herzberg, Molecular Spectra and Molecular Structure II. Infrared and Raman Spectra of Polyatomic Molecules, Van Nostrand Reinhold Company, New York, New York, (1945), pp. 362-369.
4. "Acetic acid," NIST Chemistry Handbook. http://webbook.nist.gov/.
5. G. Herzberg, Molecular Spectra and Molecular Structure II. Infrared and Raman Spectra of Polyatomic Molecules, Krieger Publishing Company, Malabar, FL, (1991), p. 195.
6. D. Lin-Vien. N. B. Colthup, W. G. Fateley, J. G. Grasselli, The Handbook of Infrared and Raman Frequencies of Organic Molecules, Academic Press, Inc., Harcourt Brace Jovanovich, Boston, (1991), p. 138.
7. "Methyl formate," NIST Chemistry Handbook. http://webbook.nist.gov/.
8. "Methanol," NIST Chemistry Handbook. http://webbook.nist.gov/.
9. K. P. Huber, G. Herzberg, Molecular Spectra and Molecular Structure, IV. Constants of Diatomic Molecules, Van Nostrand Reinhold Company, New York, (1979).
10. J. Crovisier, Molecular Database-Constants for molecules of astrophysical interest in the gas phase: photodissociation, microwave and infrared spectra, Ver. 4.2, Observatoire de Paris, Section de Meudon, Meudon, France, May 2002, pp. 34-37, available at http://www.usr.obspm.fr/~crovisie/.
11. J. D. Cox, G. Pilcher, Thermochemistry of Organometallic Compounds, Academic Press, New York, (1970), pp. 254-255.
12. W. I. F. David, R. M. Ibberson, G. A. Jeffrey, J. R. Ruble, "The structure analysis of deuterated benzene and deuterated nitromethane by pulsed-neutron powder diffraction: a comparison with single crystal neutron analysis," Physica B (1992), $180 \& 181$, pp. 597-600.
13. G. A. Jeffrey, J. R. Ruble, R. K. McMullan, J. A. Pople, "The crystal structure of deuterated benzene," Proceedings of the Royal Society of London. Series A, Mathematical and Physical Sciences, Vol. 414, No. 1846, (Nov. 9, 1987), pp. 47-57.
14. H. B. Burgi, S. C. Capelli, "Getting more out of crystal-structure analyses," Helvetica Chimica Acta, Vol. 86, (2003), pp. 1625-1640.
15. D. R. Lide, CRC Handbook of Chemistry and Physics, 86th Edition, CRC Press, Taylor \& Francis, Boca Raton, (2005-6), pp. 10-202 to 10-204.
16. C. S. Choi, E. Prince, "The crystal structure of cyclotrimethylene-trinitramine," Acta Cryst., Vol. B28, (1972), pp. 28572862.
17. D. Lin-Vien. N. B. Colthup, W. G. Fateley, J. G. Grasselli, The Handbook of Infrared and Raman Frequencies of Organic Molecules, Academic Press, Inc., Harcourt Brace Jovanovich, Boston, (1991), p. 187.
18. D. Lin-Vien. N. B. Colthup, W. G. Fateley, J. G. Grasselli, The Handbook of Infrared and Raman Frequencies of Organic Molecules, Academic Press, Inc., Harcourt Brace Jovanovich, Boston, (1991), p. 194.
19. D. Lin-Vien. N. B. Colthup, W. G. Fateley, J. G. Grasselli, The Handbook of Infrared and Raman Frequencies of Organic Molecules, Academic Press, Inc., Harcourt Brace Jovanovich, Boston, (1991), p. 482.
20. D. R. Lide, CRC Handbook of Chemistry and Physics, 86th Edition, CRC Press, Taylor \& Francis, Boca Raton, (2005-6), pp. 9-82 to 9-86.
21. D. R. Lide, CRC Handbook of Chemistry and Physics, 86th Edition, CRC Press, Taylor \& Francis, Boca Raton, (2005-6), pp. 9-54 to 9-59.
22. R. J. Fessenden, J. S. Fessenden, Organic Chemistry, Willard Grant Press. Boston, Massachusetts, (1979), p. 20.
23. D. R. Lide, CRC Handbook of Chemistry and Physics, 86th Edition, CRC Press, Taylor \& Francis, Boca Raton, (2005-6), pp. 9-47 to 9-53.
24. D. R. Lide, CRC Handbook of Chemistry and Physics, 89th Edition (Internet Version, 2009), CRC Press, Taylor and Francis, Boca Raton, (2009), 9-Dipole Moments.
25. V. H. J. Becher, "Über den Bindungszustand in Bor-Stickstoff-Verbindungen. II. Bindungsmomente in Borazanen und Borazenen," Zeitschrift für anorganische und allgemeine Chemie, Vol. 270, No. 5-6, (1952), pp. 273-286.
26. V. V. Kuznetsov, A. I. Gren, A. V. Bogatskii, S. P. Egorova, V. I. Sidorov, "Stereochemistry of heterocycles," XLIX. "Investigation of the conformation of alkyl-1,3,2-dioxaborinanes by PMR spectroscopy," Chemistry of Heterocyclic Compounds, Vol. 14, No. 1, (1978), pp. 19-22.
27. É. A. Ishmaeva, A. N. Vereshchagin, N. G. Khusainova, Z. A. Bredikhina, A. N. Pudovik, "Dipole moments of organophosphorous compounds. 15. Polarities and polarizabilities of some acetylenic compounds," Russian Chemical Bulletin, Vol. 27, No. 2, (1978), pp. 310-313.
28. O. A. Varnavskaya-Samarina, É. A. Ishmaeva, G.V. Romanov, R. Ya. Nazmutdinov, A. B. Remizov, A. N. Pudovik, "Dipole moments of organophosphorous compounds. 16. Conformations of trimethylsilyl groups in some phosphites, phosphates, and phosphonates," Russian Chemical Bulletin, Vol. 27, No. 2, (1978), pp. 313-318.
29. A. I. Echeistova, Ya. K. Syrkin, V. I. Stanko, and A. I. Klimova, "Dipole moments of halogen derivatives of ortho- and meta- carboranes," Journal of Structural Chemistry, Vol. 8, No. 5, (1967), p. 833-834.
30. V. I. Stanko, A. I. Echeistova, I. S. Astakhova, A. I. Klimova, Y. T. Struchkov, Y. K. Syrkin, "Use of dipole moments to determine the structure of halogen derivates of ortho and metacarboranes," J. Struct. Chem., Vol. 8, No. 5, (1967), pp. 829832.
31. G. J. Moody, J. D. R. Thomas, Dipole Moments in Inorganic Chemistry, Edward Arnold, London, (1971), p. 43.
32. V. I. Minkin, O. A. Osipov, Y. A. Zhdanovv, Dipole Moments in Organic Chemistry, Plenum, (1970).
33. J. G. Speight, Lange's Handbook of Chemistry, Sixteenth Edition, McGraw-Hill Professional, New York, (2004), pp. 1.171 to 1.172 .
34. J. A. Dean, Lange's Handbook of Chemistry, Fifteenth Edition, McGraw-Hill Professional, New York, (1998), pp. 4.53-4.54.
35. V. I. Minkin, O. A. Osipov, Y. A. Zhdanov, Dipole Moments in Organic Chemistry, Plenum Press, New York, (1956), p. 88.
36. J. M. Bellama, A. G. MacDiarmid, "An electric dipole moment study of methylsilyl and silylmethyl halides," J. Organomet. Chem., Vol. 24, No. 1, (1970), pp. 91-95.
37. R. Varma, A. G. MacDiarmid, J. G. Miller, "Nature of the silicon-phenyl and silicon-oxygen bond in hexaphenyldisiloxane: an electric dipole moment study," J. Organomet. Chem., Vol. 9, No. 1, (1967), pp. 77-81.
38. R. Varma, A. G. MacDiarmid, J. G. Miller, "The dipole moments and structures of disiloxane and methoxysilane," Inorg. Chem., Vol. 3, No. 12, (1964), pp. 1754-1757.
39. A. L. McClellan, Tables of Experimental Dipole Moments, W. H. Freeman and Company, San Fransico, (1963), p. 44.
40. A. L. McClellan, Tables of Experimental Dipole Moments, Volume 2, Rahara Enterprises, California, (1974).
41. A. L. McClellan, Tables of Experimental Dipole Moments, Volume 3, Rahara Enterprises, California, (1989), p. 39.
42. T. Kasuya, W. J. Lafferty, D.R. Lide, J Chem Phys., Vol. 48, (1968), pp. 1-4.
43. J. H. Hand, R. H. Schwendeman, "Microwave spectrum, molecular structure, dipole moment, and ring-bending vibration of 1,3,2-dioxaborolane," J. Chem. Phys., Vol. 45, (1966), pp. 3349-3354.
44. J. R. Weaver, R. W. Perry, "Dipole moment studies. III. The dipole moments of the methylamine boranes," Inorg. Chem., Vol. 5, No. 5, (1966), pp. 713-718.
45. NIST, "Listing of experimental data for $\mathrm{H}_{2} \mathrm{~S}$ (hydrogen sulfide)," http://cccbdb.nist.gov/exp2.asp?casno=7783064.

46. NIST, "Listing of experimental data for $\mathrm{CH}_{3} \mathrm{SCH}_{3}$ (dimethyl sulfide)," http://cccbdb.nist.gov/exp2.asp?casno=75183.
47. http://en.wikipedia.org/wiki/Trimethylphosphine.
48. Springer, http://www.springerlink.com/content/t585467172mp2263/fulltext.pdf?page=1.
49. NIST, "Listing of experimental data for $\mathrm{CH}_{3} \mathrm{SiCH}_{3}$ (dimethyl silane)," http://cccbdb.nist.gov/exp2.asp?casno=75183.
50. NIST, "Listing of experimental data for $\mathrm{SiH}_{4}$ (silane)," http://cccbdb.nist.gov/exp2.asp?casno=7803625.
51. NIST, "Listing of experimental data for $\mathrm{BHF}_{2}$ (difluoroborane)," http://cccbdb.nist.gov/exp2.asp?casno=13709836.
52. Hand, J.H., Schwendeman, R.H., J. Chem Phys., Vol. 45, (1966), p. 3349. Available at http://www.springerlink.com/content/ 1825370723216k35/fulltext.pdf?page=1.
53. S. D. Hubbard, A. P. Cox, J. Mol. Spectrosc., Vol. 115, (1986), pp. 188. Available at, http://www.springerlink.com/content/ n135855181p714r6/fulltext.pdf?page $=1$.
54. P. R. R. Langridge-Smith, R. Stevens, A. P. Cox, J. Chem. Soc., Faraday Trans. II, Vol. 75, (1979), p. 1620. Available at, http://www.springerlink.com/content/qh12341h1p157424/fulltext.pdf?page=1.
55. R. D. Nelson Jr., D. R. Lide, A. A. Maryott, "Selected Values of electric dipole moments for molecules in the gas phase," NSRDS-NBS10, (1967), p. 13.
56. R. D. Nelson Jr., D. R. Lide, A. A. Maryott, "Selected Values of electric dipole moments for molecules in the gas phase," NSRDS-NBS10, (1967), p. 26.
57. R. D. Nelson Jr., D. R. Lide, A. A. Maryott, "Selected Values of electric dipole moments for molecules in the gas phase," NSRDS-NBS10, (1967), p. 23.
58. K. K. Chatterjee, J. R. Durig, S. Bell, J. Mol. Struct., Vol. 265, (1992), p. 25.
59. J. L. Duncan, J. L. Harvie, D. C. McKean, S. Cradock, J. Mol. Struct., Vol. 145, (1986), p. 225.
60. M. Wong, I. Ozier, W. L. Meerts, J. Mol. Spectrosc., Vol. 102, (1983), p. 89.
61. S. D. Hubbard, A. P. Cox, J. Mol. Spectrosc., Vol. 115, (1986), pp. 188.
62. P. R. R. Langridge-Smith, R. Stevens, A. P. Cox, J. Chem. Soc., Faraday Trans. II, Vol. 75, (1979), p. 1620.
63. G. Kodama, J. R. Weaver, J. LaRochelle, R. W. Parry, "Dipole moment studies II. The dipole moments of the ethylphosphines," Inorg. Chem., Vol. 5, No. 5, (1966), pp. 710-713.
64. J. R. Weaver, R. W. Parry, "Dipole moment studies III. The dipole moments of the methylamine boranes," Inorg. Chem., Vol. 5, No. 5, (1966), pp. 713-718.
65. S. Bohm, O. Exner, "Prediction of molecular dipole moments from bond moments: testing of the method by DFT
calculations on isolated molecules," Phys. Chem. Chem. Phys., Vol. 6, No. 3, (2004), pp. 510-514.
66. C. W. N. Cumper, "Electric bond and group dipole moments," Tetrahedron, Vol. 25, No. 15, (1969), pp. 3131-3138.
67. O. A. Raevskii, F. G. Khalitov, "The inductive effect in a series of phosphines," Russ. Chem. Bull., Vol. 19, No. 10, (1970), pp. 2222-2224. http://www.springerlink.com/content/uw673505v7064355/.
68. E. Fluck, The Chemistry of Phosphine, Topics in Current Chemistry, Vol. 35, (1973). Available at http://www.springerlink.com/content/ y17151p8tqnq5772/.
69. M. J. S. Dewar, C. Jie, E. G. Zoebisch, "AM1 calculations for compounds containing boron," J. Organometallics, Vol. 7, No. 2, (1988), pp. 513-521.
70. J. R. Weaver, R. W. Parry, "Dipole moment studies IV. Trends in dipole moments," Inorg. Chem., Vol. 5, No. 5, (1966), pp. 718-723.
71. G. Zhou, W. Chen, Fundamentals of Structural Chemistry, World Scientific, (1993), p. 175.
72. B. A. Arbuzov, O. D. Zolova, L. K. Yuldasheva, "Dipole moments and conformation of cyclic compounds. III. Sulfites," J. Struct. Chem., Vol. 8, No. 2, (1967), pp. 249-252.
73. O. Exner, D. N. Harpp, J. G. Gleason, "Dipole moments and conformation of sultones, thiosultones and sultines," Can. J. Chem., Vol. 50, (1972), pp. 548-552.
74. O. Exner, Z. Fidlerova and V. Jehlicka, Collect. Czech. Chem. Commun., Vol. 33, (1968), pp. 2019.
75. O. Exner, P. Dembech, P. Vivarelli, "Dipole moments and conformation of sulphinic acid esters," J. Chem. Soc. B, (1970), pp. 278-281.
76. A. P. Altshuller, L. Rosenblum, "Dielectric properties of some alkylsilanes," J. Am. Chem. Soc., Vol. 77, No. 2, (1955), pp. 272-274.
77. V. A. Chetverikova, V. A. Kogan, G. I. Zelchan, M. G. Voronkov, O. A. Osipov, "Dipole moments of Si-substituted silatranes," Chem. Heterocycl. Compd., Vol. 5, No. 3, (1969), pp. 332-334.
78. J. M. Bellama, R. S. Evans, J. E. Huheey, "Bond moments, molecular moments, electronegativity, and the dipole moment of methylsilane," J. Am. Chem. Soc., Vol. 95, No. 22, (1973), pp 7242-7244.
79. L. K. Yuldasheva, R. P. Arshinova, Y. Y. Samitov, Y. P. Romadan, M. G. Voronkov, "Steric structure of 5-substituted 2,2-dimethyl-1,3,2-dioxasilanes," Russ. Chem. Bull., Vol. 23, No. 2, (1974), pp. 294-299.
80. M. G. Voronkov, T. N. Aksamentova, V. B. Modonov, L. I. Gubanova, Y. L. Frolov, V. M. Dyakov, "Dipole moments and molecular structure of (aroyloxymethyl)-trifluorosilanes and methyl(aroyloxymethyl)fluorosilanes," Russ. Chem. Bull., Vol. 33, No. 3, (1984), pp. 635-637.
81. L. K. Yuldasheva, R. P. Arshinova, S. G. Vulfson, "Dipole moments of the bonds and the unshared electron pair in sulfites and sulfoxides," Russ. Chem. Bull., Vol. 18, No. 3, (1969), pp. 495-498.
82. Y. Y. Borovikov, V. V. Pirozhenko, "Scale of additive group and bond dipole moments and dipole moments of lone pairs," Theor. Exp. Chem., Vol. 17, No. 2, (1981), pp. 136-146.
83. A. Borba, A. Gómez-Zavaglia, P. N. N. L. Simões, R. Fausto, "Matrix-isolation FT-IR spectra and theoretical study of dimethyl sulfate," Spectrochim. Acta Part A, Vol. 61, (2005), pp. 1461-1470.
84. E. N. Klimovitskii, L. K. Yuldasheva, A. N. Vereshchagin, G. N. Sergeeva, S. G. Vulfson, B. A. Arbuzov, "Sulfate group polarization and polarizability and the conformations of the dimethyl sulfates," Russ. Chem. Bull., Vol. 26, No. 1, (1977), pp. 83-85.
85. G. Wood, J. M. McIntosh, M. H. Miskow, "Conformational analysis of trimethylene sulfites. The vital importance of vicinal unshared electron pairs," Can. J. Chem., Vol. 49, (1971), pp. 1202-1208.
86. B. J. Lindberg, K. Hamrin, G. Johansson, U. Gelius, A. Fahlman, C. Nordling, K. Siegbahn, "Molecular spectroscopy by means of ESCA," Phys. Scr., Vol. 1, (1970), pp. 286-298.
87. D. Eisenberg, W. Kauzmann, The Structure and Properties of Water, Oxford University Press, London, (1969), p. 74.
88. K. Ichikawa, Y. Kameda, T. Yamaguchi, H. Wakita and M. Misawa, Neutron diffraction investigation of the intramolecular structure of a water molecule in the liquid phase at high temperatures, Mol. Phys. Vol. 73, (1991), pp. 79-86.
89. D. Eisenberg, W. Kauzmann, The Structure and Properties of Water, Oxford University Press, London, (1969), p. 85.
90. D. R. Lide, CRC Handbook of Chemistry and Physics, 86th Edition, CRC Press, Taylor \& Francis, Boca Raton, (2005-6), p. 4-151.
91. D. Eisenberg, W. Kauzmann, The Structure and Properties of Water, Oxford University Press, London, (1969), p. 83.
92. H. A. Haus, J. R. Melcher, Electromagnetic Fields and Energy, Department of Electrical Engineering and Computer Science, Massachusetts Institute of Technology, (1985), Sec. 6.3.
93. D. R. Lide, CRC Handbook of Chemistry and Physics, 79th Edition, CRC Press, Boca Raton, Florida, (1998-9), p. 6.2.
94. R. L. DeKock, H. B. Gray, Chemical Structure and Bonding, The Benjamin/Cummings Publishing Company, Menlo Park, CA, (1980), pp. 436-439.
95. G. L. Miessler, D. A. Tarr, Inorganic Chemistry, Third Edition, Pearson Prentice Hall, Upper Saddle River, New Jersey, (2004), pp. 69-71.
96. D. D. Nelson, Jr., G. T. Fraser, W. Klemperer, "Does ammonia hydrogen bond?," Science, Vol. 238, (1987), pp. 1670-674.
97. R. J. Fessenden, J. S. Fessenden, Organic Chemistry, Willard Grant Press. Boston, Massachusetts, (1979), p. 25.
98. P. F. Harris, Z. Lheng, K. Suenaga, "Imaging the atomic structure of activated carbon," J. Phys.: Condens. Matter, Vol. 20, (2008), pp. 362201-362205.
99. R. J. Fessenden, J. S. Fessenden, Organic Chemistry, Willard Grant Press. Boston, Massachusetts, (1979), pp. 744-745.
100. R. Zacharia, H. Ulbricht, T. Hertel, "Interlayer cohesive energy of graphite from thermal desorption of polyaromatic hydrocarbons," Phys. Rev. B, Vol. 69, Issue 15, (2004), pp. 155406-155412.
101. D. G. Hurst, D. G. Henshaw, "Atomic distribution in liquid helium by neutron diffraction," Phys. Rev., Vol. 100, No. 4, (1955), pp. 994-1002.
102. D. R. Lide, CRC Handbook of Chemistry and Physics, 86th Edition, CRC Press, Taylor \& Francis, Boca Raton, (2005-6), pp. 6-119 to 9-120.
103. K. W. Schwarz, R. W. Stark, Phys. Rev. Lett., Vol. 22, No. 24, (1969), pp. 1278-1280.
104. C. J. Pethick, H. Smith, Bose-Einstein Condensation in Dilute Gases, Second Edition, Cambridge University Press, Cambridge, UK, (2008), p. 8.
105. D. G. Henshaw, A. D. B. Woods, Phys. Rev. Lett., Vol. 121, (1961), p. 1266.
106. G. Baym, R. G. Barrera, C. J. Pethick, Phys. Rev. Letters, Vol. 22, No. 1, (1969), pp. 20-23.
107. F. London, Superfluids (Dover Publications, New York, 1964), Vol. III.
108. C. Pethick, H. Smith, Bose-Einstein Condensation in Dilute Gases, Cambridge University Press, Cambridge, (2008).
109. C. J. Pethick, H. Smith, Bose-Einstein Condensation in Dilute Gases, Second Edition, Cambridge University Press, Cambridge, UK, (2008), pp. 1-40.
110. R. Wynar, R. S. Freeland, D. J. Han, C. Ryu, and D. J. Heinzen, "Molecules in a Bose-Einstein condensate," Science, Vol. 287, February, 11, (2000), pp. 1016-1019.
111. J. A. Dean, Lange's Handbook of Chemistry, Fifteenth Edition, McGraw-Hill Professional, New York, (1998).
112. G. L. Pollack, "The solid state of rare gases," Rev. Mod. Phys., Vol. 36, (1964), pp. 748-791.
113. D. G. Henshaw, "Atomic distribution in liquid and solid neon and solid argon by neutron diffraction," Phys. Rev., Vol. 111, No. 6, (1958), pp. 1470-1475.
114. M. L. Klein, J. A. Venables, Rare Gas Solids, Volume 1, Academic Press, New York, (1977), p. 242.
115. J. Sugar and A. Musgrove, "Energy levels of krypton, Kr I through Kr XXXVI," J. Phys. Chem. Ref. Data, Vol. 20, No. 5, (1991), pp. 859-915. Available at http://www.nist.gov/srd/PDFfiles/jpcrd422.pdf.
116. J. Sugar and A. Musgrove, "Energy levels of krypton, Kr I through Kr XXXVI," J. Phys. Chem. Ref. Data, Vol. 20, No. 5, (1991), pp. 859-915. Available at http://www.nist.gov/srd/PDFfiles/jpcrd422.pdf.
117. E. B. Saloman, "Energy Levels and Observed Spectral Lines of Krypton, Kr I through Kr XXXVI," J. Phys. Chem. Ref. Data, Vol. 36, No. 1, (2007), pp. 215-386.
118. http://link.aip.org/link/?JPCRBU/36/215/1.
119. M. L. Klein, J. A. Venables, Rare Gas Solids, Volume 1, Academic Press, New York, (1977), p. 245.
120. E. B. Saloman, "Energy levels and observed spectral lines of xenon, Xe I through Xe LIV," J. Phys. Chem. Ref. Data, Vol. 33, No. 3, (2004), pp. 765-921. Available at http://www.nist.gov/srd/PDFfiles/jpcrd661.pdf.
121. E. B. Saloman, "Energy levels and observed spectral lines of xenon, Xe I through Xe LIV," J. Phys. Chem. Ref. Data, Vol. 33, No. 3, (2004), pp. 765-921. Available at http://www.nist.gov/srd/PDFfiles/jpcrd661.pdf.
122. M. L. Klein, J. A. Venables, Rare Gas Solids, Volume 1, Academic Press, New York, (1977), p. 250.
123. L. N. Fletcher, M. Gustafsson, G. S. Orton, "Hydrogen dimers in giant-planet infrared spectra", December 11, 2017, pp. 113, https://arxiv.org/pdf/1712.02813.pdf.
124. M. Gustafsson, "Hydrogen dimer features in low temperature collision-induced spectra," XXIII International Conference on Spectral Line Shapes, IOP Conf. Series: Journal of Physics: Conf. Series 810 (2017) 012017, doi:10.1088/17426596/810/1/012017, http://iopscience.iop.org/article/10.1088/1742-6596/810/1/012017/pdf.
125. A. R. W. McKellar," Infrared spectra of hydrogen dimers", J. Chem. Phys., Vol. 92, (1990), pp. 3261-3277.
126. https://en.wikipedia.org/wiki/Solid hydrogen
127. https://www.nuclear-power.net/hydrogen-specific-heat-latent-heat-vaporization-fusion/.
128. D. A. McQuarrie, Quantum Chemistry, University Science Books, Mill Valley, CA, (1983), pp. 238-241.
129. J. D. Jackson, Classical Electrodynamics, Second Edition, John Wiley \& Sons, New York, (1975), pp. 739-752.
130. W. R.. Hagen, R. L. Mills, " Distinguishing Electron Paramagnetic Resonance signature of molecular hydrino ", (2020), https://assets.researchsquare.com/files/rs-144403/v1_stamped.pdf.
131. R. L. Mills, P. Ray, "A Comprehensive Study of Spectra of the Bound-Free Hyperfine Levels of Novel Hydride Ion $H^{-}(1 / 2)$, Hydrogen, Nitrogen, and Air", Int. J. Hydrogen Energy, Vol. 28, No. 8, (2003), pp. 825-871.
132. R. Mills, W. Good, P. Jansson, J. He, "Stationary Inverted Lyman Populations and Free-Free and Bound-Free Emission of Lower-Energy State Hydride Ion formed by and Exothermic Catalytic Reaction of Atomic Hydrogen and Certain Group I Catalysts," Cent. Eur. J. Phys., Vol. 8, (2010), 7-16, doi: 10.2478/s11534-009-0052-6.
133. R. L. Mills, P. Ray, "Stationary Inverted Lyman Population and a Very Stable Novel Hydride Formed by a Catalytic Reaction of Atomic Hydrogen and Certain Catalysts," J. Opt. Mat., 27, (2004), 181-186.
134. R. L. Mills, P. C. Ray, R. M. Mayo, M. Nansteel, W. Good, P. Jansson, B. Dhandapani, J. He, "Hydrogen Plasmas Generated Using Certain Group I Catalysts Show Stationary Inverted Lyman Populations and Free-Free and Bound-Free Emission of Lower-Energy State Hydride," Res. J. Chem Env., Vol. 12(2), (2008), 42-72.
135. R. Mills, Z. Dong, J. Jenkins, R. Gandhi, N. S. Mehta, S. Mhatre, P. Sharma, "Hydrino states of hydrogen", https://brilliantlightpower.com/pdf/Hydrino_States of Hydrogen.pdf.
136. L. M. Hobbs, D. G. York, T. P. Snow, T. Oka, J. A. Thorburn, M. Bishof, S. D. Friedman, B. J. McCall, B. Rachford, P. Sonnentrucker, D. E. Welty, A Catalog of Diffuse Interstellar Bands in the Spectrum of HD 204827", Astrophysical Journal, Vol. 680, No. 2, (2008), pp. 1256-1270, http://dibdata.org/HD204827.pdf, https://iopscience.iop.org/article/10.1086/587930/pdf.
137. G. Danby, D. R. Flower, "Theoretical studies of van der Waals molecules: the $\mathrm{H}_{2}-\mathrm{H}_{2}$ dimer", J. Phys. B: At. Mol. Phys., Vol. 16, (1983), pp. 3411-3422.
138. A. Fernández-Ramos, J. A. Miller, S. J. Klipperstein, D. G. Truhlar, "Modeling the Kinetics of Bimolecular Reactions," Chem. Rev., Vol. 106, (2006), pp.4518-4584.
139. S. C. Tucker, D. G. Truhlar, "Ab initio calculations of the transition-state geometry and vibrational frequencies of the SN2 reaction of chloride with chloromethane," J. Phys. Chem, Vol. 93, No. 25, (1989), pp. 8138-8142.
140. D. R. Lide, CRC Handbook of Chemistry and Physics, 86th Edition, CRC Press, Taylor \& Francis, Boca Raton, (2005-6), p. 10-156.
141. S. C. Tucker, D. G. Truhlar, "A six-body potential energy surface for the SN 2 reaction $\mathrm{Cl}^{-}(\mathrm{g})+\mathrm{CH}_{3} \mathrm{Cl}(\mathrm{g})$ and a variational transition-state-theory calculation of the rate constant," J. Am. Chem. Soc., Vol. 112, No. 9, (1990), pp. 3338-3347.
142. S. E. Barlow, J. M. Van Doren, V. M. Bierbaum, "The gas phase displacement reaction of chloride ion with methyl chloride as a function of kinetic energy," J. Am. Chem. Soc., Vol. 110, No. 21, (1988), pp. 7240-7242.
143. " $\mathrm{Cl}_{3}^{-}$," NIST Chemistry Handbook. http://webbook.nist.gov/.
144. "Simulation of the gas phase displacement reaction of chloride ion with methyl chloride," at http://www.brilliantlightpower.com/, at http://www.brilliantlightpower.com/molecular-physics/.

## Chapter 17

## NATURE OF THE SOLID MOLECULAR BOND OF THE THREE ALLOTROPES OF CARBON

## GENERAL CONSIDERATIONS OF THE SOLID MOLECULAR BOND

The solid molecular bond of a material comprising an arbitrary number of atoms can be solved using similar principles and procedures as those used to solve organic molecules of arbitrary length. Molecular solids are also comprised of functional groups. Depending on the material, exemplary groups are $C-C, C=C, C-O, C-N, C-S$, and others given in the Organic Molecular Functional Groups and Molecules section. The solutions of these functional groups or any others corresponding to the particular solid can be conveniently obtained by using generalized forms of the geometrical and energy equations given in the Derivation of the General Geometrical and Energy Equations of Organic Chemistry section. The appropriate functional groups with their geometrical parameters and energies can be added as a linear sum to give the solution of any molecular solid.

## DIAMOND

It is demonstrated in this Diamond section as well as the Fullerene ( $C_{60}$ ) and Graphite sections, that very complex macromolecules can be simply solved from the groups at each vertex carbon atom of the structure. Specifically, for fullerene a $C=C$ group is bound to two $C-C$ bonds at each vertex carbon atom of $C_{60}$. The solution of the macromolecule is given by superposition of the geometrical and energy parameters of the corresponding two groups. In graphite, each sheet of joined hexagons can be constructed with a $C=C$ group bound to two $C-C$ bonds at each vertex carbon atom that hybridize to an aromatic-like functional group, $C \stackrel{8 / 3 e}{=} C$, with $\frac{8}{3}$ electron-number per bond compared to the pure aromatic functional group,
$C \stackrel{3 e}{=} C$, with 3 electron-number per bond as given in the Aromatics section. Similarly, diamond comprising, in principle, an infinite network of carbons can be solved using the functional group solutions where the task is also simple since diamond has only one functional group, the diamond $C-C$ functional group.

The diamond $C-C$ bonds are all equivalent, and each $C-C$ bond can be considered bound to a t-butyl group at the corresponding vertex carbon. Thus, the parameters of the diamond $C-C$ functional group are equivalent to those of the t-butyl $C-C$ group of branched alkanes given in the Branched Alkanes section. Based on symmetry, the parameter $R$ in Eqs. (15.56) and (15.61) is the semimajor axis $a$, and the vibrational energy in the $\bar{E}_{\text {osc }}$ term is that of diamond. Also, the $C 2 s p^{3}$ HO magnetic energy $E_{\text {mag }}$ given by Eq. (15.67) was subtracted for each t-butyl group of alkyl fluorides, alkyl chlorides, alkyl iodides, thiols, sulfides, disulfides, and nitroalkanes as given in the corresponding sections of Chapter 15 due to a set of unpaired electrons being created by bond breakage. Since each $C-C$ group of diamond bonds with a t-butyl group at each vertex carbon, $c_{3}$ of Eq. (15.65) is one, and $E_{\text {mag }}$ is given by Eq. (15.67).

The symbol of the functional group of diamond is given in Table 17.1. The geometrical (Eqs. (15.1-15.5) and (15.51)) parameters of diamond are given in Table 17.2. The lattice parameter $a_{l}$ was calculated from the bond distance using the law of cosines:

$$
\begin{equation*}
s_{1}^{2}+s_{2}^{2}-2 s_{1} s_{2} \operatorname{cosine} \theta=s_{3}^{2} \tag{17.1}
\end{equation*}
$$

With the bond angle $\theta_{\angle C C C}=109.5^{\circ}$ [1] and $s_{1}=s_{2}=2 c_{C-C}^{\prime}$, the internuclear distance of the $C-C$ bond, $s_{3}=2 c_{C_{t}-C_{t}}^{\prime}$, the internuclear distance of the two terminal $C$ atoms is given by:

$$
\begin{equation*}
2 c_{C_{t}-C_{t}}^{\prime}=\sqrt{2\left(2 c_{C-C}^{\prime}\right)^{2}\left(1-\operatorname{cosine}\left(109.5^{\circ}\right)\right)} \tag{17.2}
\end{equation*}
$$

Two times the distance $2 c_{C_{t}-C_{t}}^{\prime}$ is the hypotenuse of the isosceles triangle having equivalent sides of length equal to the lattice parameter $a_{l}$. Using Eq. (17.2) and $2 c_{C-C}^{\prime}=1.53635 \AA$ from Table 17.2, the lattice parameter $a_{l}$ for the cubic diamond structure is given by:

$$
\begin{equation*}
a_{l}=\frac{2\left(2{c_{C}}_{\prime}^{c_{l}-C_{t}}\right)}{\sqrt{2}}=\sqrt{2} \sqrt{2\left(2{C^{\prime}}_{C-C}^{\prime}\right)^{2}\left(1-\operatorname{cosine}\left(109.5^{\circ}\right)\right)}=3.54867 \AA \tag{17.3}
\end{equation*}
$$

The intercept (Eqs. (15.80-15.87)) and energy (Eqs. (15.6-15.11) and (15.17-15.65)) parameters of diamond are given in Tables 17.2, 17.3, and 17.4, respectively. The total energy of diamond given in Table 17.5 was calculated as the sum over the integer multiple of each $E_{D}$ (Group) of Table 17.4 corresponding to functional-group composition of the molecular solid. The experimental $C-C$ bond energy of diamond, $E_{D_{\text {exp }}}(C-C)$ at 298 K , is given by the difference between the enthalpy of formation of gaseous carbon atoms from graphite $\left(\Delta H_{f}\left(C_{\text {graphite }}(g a s)\right)\right.$ ) and the heat of formation of diamond $\left(\Delta H_{f}(C(\right.$ diamond $\left.))\right)$ wherein graphite has a defined heat of formation of zero $\left(\Delta H_{f}(C(\right.$ graphite $)=0)$ :

$$
\begin{equation*}
E_{D_{\text {epp }}}(C-C)=\frac{1}{2}\left[\Delta H_{f}\left(C_{\text {graphite }}(\text { gas })\right)-\Delta H_{f}(C(\text { diamond }))\right] \tag{17.4}
\end{equation*}
$$

where the heats of formation of atomic carbon and diamond are [2]:

$$
\begin{align*}
& \Delta H_{f}\left(C_{\text {graphite }}(\text { gas })\right)=716.68 \mathrm{~kJ} / \text { mole }(7.42774 \mathrm{eV} / \text { atom })  \tag{17.5}\\
& \Delta H_{f}(C(\text { diamond }))=1.9 \mathrm{~kJ} / \text { mole }(0.01969 \mathrm{eV} / \text { atom }) \tag{17.6}
\end{align*}
$$

Using Eqs. (17.4-17.6), $E_{D_{\text {exp }}}(C-C)$ is:

$$
\begin{equation*}
E_{D_{\text {exp }}}(C-C)=\frac{1}{2}[7.42774 \mathrm{eV}-0.01969 \mathrm{eV}]=3.704 \mathrm{eV} \tag{17.7}
\end{equation*}
$$

where the factor of one half corresponds to the ratio of two electrons per bond and four electrons per carbon atom. The bond angle parameters of diamond determined using Eqs. $(15.88-15.117)$ are given in Table 17.6. The structure of diamond is shown in Figure 17.1.

Figure 17.1. (A-B) The structure of diamond.


Table 17.1. The symbols of the functional group of diamond.

| Functional Group | Group Symbol |
| :--- | :---: |
| $C C$ bond (diamond- $C$ ) | $C-C$ |

Table 17.2. The geometrical bond parameters of diamond and experimental values [1, 3].

| Parameter | $C-C$ <br> Group |
| :---: | :---: |
| $a\left(a_{0}\right)$ | 2.10725 |
| $c^{\prime}\left(a_{0}\right)$ | 1.45164 |
| Bond Length $2 c^{\prime}(\AA)$ | 1.53635 |
| Exp. Bond Length $(\AA)$ | 1.54428 |
| $b, c\left(a_{0}\right)$ | 1.52750 |
| $e$ | 0.68888 |
| Lattice Parameter $a_{l}(\AA)$ | 3.54867 |
| Exp. Lattice Parameter $a_{l}(\AA)$ | 3.5670 |

Table 17.3. The MO to HO intercept geometrical bond parameters of diamond. $E_{T}$ is $E_{T}$ (atom - atom msp ${ }^{3}$. $A O$ ).

| Bond | Atom |  |  |  | $E_{T}$ (eV) Bond 4 | Final Total <br> Energy <br> $C 2 s p^{3}$ <br> $(\mathrm{eV})$ <br> 154 | $\begin{aligned} & r_{\text {minual }} \\ & \left(a_{0}\right) \end{aligned}$ | $\begin{aligned} & r_{\text {fynal }} \\ & \left(a_{0}\right) \end{aligned}$ | $\begin{gathered} E_{\text {Cantanem }}\left(C 2 s p^{3}\right) \\ (\mathrm{eV}) \\ \text { Final } \end{gathered}$ | $\begin{gathered} E\left(C 2 s p^{3}\right) \\ (\mathrm{eV}) \\ \text { Final } \end{gathered}$ | $\begin{aligned} & \theta^{\prime} \\ & \left({ }^{\circ}\right) \end{aligned}$ | $\begin{aligned} & \theta_{1} \\ & \left({ }^{\circ}\right) \end{aligned}$ | $\begin{aligned} & \theta_{2} \\ & \left({ }^{\circ}\right) \end{aligned}$ | $\begin{gathered} d_{1} \\ \left(a_{0}\right) \end{gathered}$ | $\begin{gathered} d_{2} \\ \left(a_{0}\right) \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| C-C | C | -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 17.4. The energy parameters (eV) of the functional group of diamond.

| Parameters | $\begin{aligned} & \hline C-C \\ & \text { Group } \\ & \hline \end{aligned}$ |
| :---: | :---: |
| $n_{1}$ | 1 |
| $n_{2}$ | 0 |
| $n_{3}$ | 0 |
| $C_{1}$ | 0.5 |
| $\mathrm{C}_{2}$ | 1 |
| $c_{1}$ | 1 |
| $c_{2}$ | 0.91771 |
| $c_{3}$ | 1 |
| $c_{4}$ | 2 |
| $c_{5}$ | 0 |
| $C_{10}$ | 0.5 |
| $\mathrm{C}_{2}$ 。 | 1 |
| $V_{e}(\mathrm{eV})$ | -29.10112 |
| $V_{p}(e \mathrm{~V})$ | 9.37273 |
| $T(e V)$ | 6.90500 |
| $V_{m}(\mathrm{eV})$ | -3.45250 |
| $E\left(\right.$ Ао/ Hо) $^{\text {(eV) }}$ | -15.35946 |
| $\Delta E_{\mathrm{H}_{2} \mathrm{MO}}($ АО $/ \mathrm{HO})(\mathrm{eV})$ | 0 |
|  | -15.35946 |
| $E_{T}\left(\mathrm{H}_{2} \mathrm{MO}\right)(\mathrm{eV})$ | -31.63535 |
| $E_{T}\left(\right.$ atom - atom, $\left.\mathrm{msp}^{3} . \mathrm{AO}\right)(\mathrm{eV})$ | -1.44915 |
| $E_{T}(\mathrm{mo})(\mathrm{eV})$ | -33.08452 |
| $\omega\left(10^{15} \mathrm{rad} / \mathrm{s}\right)$ | 9.55643 |
| $E_{K}(\mathrm{eV})$ | 6.29021 |
| $\bar{E}_{D}(e V)$ | -0.16416 |
| $\bar{E}_{\text {Kvib }}(\mathrm{eV})$ | $\begin{gathered} 0.16515 \\ {[4]} \\ \hline \end{gathered}$ |
| $\bar{E}_{\text {osc }}(\mathrm{eV})$ | -0.08158 |
| $E_{\text {mag }}(\mathrm{eV})$ | 0.14803 |
| $E_{T}($ Groupp $)(e V)$ | -33.16610 |
| $E_{\text {initial }}\left(c_{4}\right.$ AO/IIO) $(\mathrm{eV})$ | -14.63489 |
| $E_{\text {initial }}\left(c_{s}\right.$, Ао/но) $(\mathrm{eV})$ | 0 |
| $E_{D}($ Group) $)(\mathrm{eV})$ | 3.74829 |

Table 17.5. The total bond energy of diamond calculated using the functional group composition and the energy of Table 17.4 compared to the experimental value [1-2].

| Formula | Name | $C-C$ | Calculated <br> Total Bond <br> Energy (eV) | Experimental <br> Total Bond <br> Energy (eV) | Relative Error |  |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{C}_{\mathrm{n}}$ | Diamond |  | 1 | 3.74829 | 3.704 | -0.01 |

Table 17.6. The bond angle parameters of diamond 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 ${ }^{3} . A O$ ). The law of cosines was used to calculate the angle.

| Atoms of Angle | $\begin{gathered} 2 c^{\prime} \\ \text { Bond } 1 \\ \left(a_{0}\right) \end{gathered}$ | $\begin{gathered} 2 c^{\prime} \\ \text { Bond 2 } \\ \left(a_{0}\right) \end{gathered}$ | $\begin{gathered} 2 c^{\prime} \\ \text { Terminal } \\ \text { Atoms } \\ \left(a_{0}\right) \end{gathered}$ | $\begin{aligned} & E_{\text {Conamatic }} \text { Atom 1 } \end{aligned}$ | $\begin{gathered} \text { Atom } 1 \\ \text { Hybridization } \\ \text { Designation } \\ \text { (Table 15.3.A) } \end{gathered}$ | $E_{\text {Coulombic }}$ <br> Atom 2 | Atom 2 Hybridization Designation <br> (Table 15.3.A) | $\begin{gathered} c_{2} \\ \text { Atom } 1 \end{gathered}$ | $\begin{gathered} c_{2} \\ \text { Atom } 2 \end{gathered}$ | $C_{1}$ | $C_{2}$ | $c_{1}$ | $c_{2}^{\prime}$ | $\begin{gathered} E_{T} \\ (\mathrm{eV}) \end{gathered}$ | $\begin{aligned} & \theta_{0} \\ & \left({ }^{\circ}\right) \end{aligned}$ | $\begin{aligned} & \theta_{1} \\ & \left({ }^{\circ}\right) \end{aligned}$ | $\begin{aligned} & \theta_{2} \\ & \left({ }^{\circ}\right) \end{aligned}$ | $\begin{gathered} \text { Cal. } \theta \\ \left({ }^{\circ}\right) \end{gathered}$ | $\underset{\left({ }^{\circ}\right)}{\text { Exp. } \theta}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\underset{\text { (aromatic) }}{\angle C C C}$ | 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 | $\underset{\text { (benzene) }}{120[12-14]}$ |
| $\begin{gathered} \angle C C H \\ (\text { aromatic) } \end{gathered}$ |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  | 120.19 |  | 119.91 | $\begin{gathered} 120[12-14] \\ \text { (benzene) } \end{gathered}$ |
| $\angle C_{a} O_{b} H^{\prime}$ | 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 |  |
| $\angle C_{b} C_{a}(O)$ | 2.82796 | 2.27954 | 4.4721 | -17.17218 | 38 | -13.61806 | o | 0.79232 | $\begin{gathered} 0.8539 \\ (E q . \\ (15.114)) \end{gathered}$ | 1 | 1 | 1 | 0.82313 | -1.65376 |  |  |  | 121.86 | $\begin{aligned} & \text { (benzoic acid) } \\ & \hline 122[2] \end{aligned}$ |
| $\angle C_{b} C_{a} O$ | 2.82796 | 2.63431 | 4.6690 | -16.40067 | 20 | -13.61806 | o | 0.82959 | $\begin{aligned} & 0.8395 \\ & (\text { (Eq. } \\ & (15.114)) \end{aligned}$ | 1 | 1 | 1 | 0.84177 | -1.65376 |  |  |  | 117.43 | $\begin{gathered} 118[2] \\ \text { (benzoic acid) } \end{gathered}$ |
| $\angle(O) C_{a} O$ | 2.27954 | 2.63431 | 4.3818 | $\begin{gathered} -16.17521 \\ (O) \\ \hline \end{gathered}$ | 13 | $\begin{gathered} -15.75493 \\ O \end{gathered}$ | 7 | 0.84115 | 0.86359 | 1 | 1 | 1 | 0.85237 | -1.44915 |  |  |  | 126.03 | $\begin{gathered} 122[2] \\ \text { (benzoic acid) } \end{gathered}$ |
| $\angle C_{f} C_{c}(O)$ | 2.86175 | 2.27954 | 4.5826 | -16.68411 | 25 | -13.61806 | o | 0.81549 | $\begin{aligned} & 0.8539 \\ & (\text { (Eq. } \\ & (15.133)) \end{aligned}$ | 1 | 1 | 1 | 0.83472 | -1.65376 |  |  |  | 125.70 | $\begin{gathered} 126.6[1] \\ \text { (acetic acid) } \end{gathered}$ |
| $\angle C_{f} C_{e} O$ | 2.86175 | 2.63431 | 4.4944 | -15.75493 | 7 | -13.61806 | o | 0.86359 | $\begin{gathered} 0.85395 \\ (159 . \\ (15.133)) \end{gathered}$ | 1 | 1 | 1 | 0.85877 | -1.44915 |  |  |  | 109.65 | $\underset{\text { (acetic acid) }}{110.6[1]}$ |
| $\angle O C_{e} O$ | 2.27954 | 2.63431 | 4.3818 | $\begin{gathered} -16.17521 \\ (O) \\ \hline \end{gathered}$ | 13 | $\underset{O}{-15.75493}$ | 7 | 0.84115 | 0.86359 | 1 | 1 | 1 | 0.85237 | -1.44915 |  |  |  | 126.03 |  |
| $\angle C_{d} O C_{e}$ | 2.59399 | 2.63431 | 4.3589 | $\stackrel{-17.27448}{C_{d}}$ | 41 | $\begin{gathered} -18.03358 \\ C_{e} \\ \hline \end{gathered}$ | 56 | 0.78762 | 0.75447 | 1 | 1 | 1 | 0.77105 | -1.85836 |  |  |  | 112.96 | $\begin{gathered} 114[1] \\ \begin{array}{c} \text { (methyl } \\ \text { formate) } \end{array} \end{gathered}$ |
| $\begin{aligned} & \text { Methyl } \\ & \angle H C_{f} H \end{aligned}$ | 2.09711 | 2.09711 | 3.4252 | -15.75493 | 7 | H | H | 0.86359 | 1 | 1 | 1 | 0.75 | 1.15796 | 0 |  |  |  | 109.50 |  |

## FULLERENE ( $C_{60}$ )

$C_{60}$ comprises 60 equivalent carbon atoms that are bound as 60 single bonds and 30 double bonds in the geometric form of a truncated icosahedron: twelve pentagons and twenty hexagons joined such that no two pentagons share an edge. To achieve this minimum energy structure each equivalent carbon atom serves as a vertex incident with one double and two single bonds. Each type of bond serves as a functional group which has aromatic character. The aromatic bond is uniquely stable and requires the sharing of the electrons of multiple $\mathrm{H}_{2}$-type MOs. The results of the derivation of the parameters of the benzene molecule given in the Benzene Molecule $\left(\mathrm{C}_{6} \mathrm{H}_{6}\right)$ 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 $C=C$ bonding of the aromatic bond wherein each of the $C \stackrel{3 e}{=} C$ aromatic bonds comprises $(0.75)(4)=3$ electrons according to Eq. (15.161) wherein $C_{2}$ of Eq. (15.51) for the aromatic $C=C$-bond MO given by Eq. (15.162) is $C_{2}\left(\right.$ aromaticC2sp $\left.{ }^{3} \mathrm{HO}\right)=c_{2}\left(\right.$ aromaticC $\left.2 s p^{3} \mathrm{HO}\right)=0.85252$ and $E_{T}\left(\right.$ atom - atom, $\left.m s p^{3} \cdot \mathrm{AO}\right)=-2.26759 \mathrm{eV}$. In $C_{60}$, 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. The $C=C$ functional group of $C_{60}$ comprises the aromatic bond with the exception that it comprises four electrons. Thus, $E_{T}(G r o u p)$ and $E_{D}(G r o u p)$ are given by Eqs. (15.165) and (15.166), respectively, with $f_{1}=1, c_{4}=4$, and $\bar{E}_{\text {Kvib }}(\mathrm{eV})$ is that of $C_{60}$.

In addition to the $C=C$ bond, each vertex carbon atom of $C_{60}$ is bound to two $C-C$ bonds that substitute for the aromatic $C \stackrel{3 e}{=} C$ and $C-H$ bonds. As in the case of the $C-C$-bond MO of naphthalene, to match energies within the MO that bridges single and double-bond MOs, $E(A O / H O)$ and $\Delta E_{\mathrm{H}_{2} \mathrm{MO}}(A O / \mathrm{HO})$ in Eq. $(15.51)$ are -14.63489 eV and -2.26759 eV , respectively.

To meet the equipotential condition of the union of the $C 2 s p^{3} \mathrm{HOs}$ of the $C-C$ single bond bridging double bonds, the parameters $c_{1}, C_{2}$, and $C_{20}$ of Eq. (15.51) are one for the $C-C$ group, $C_{1 o}$ and $C_{1}$ are 0.5 , and $c_{2}$ given by Eq. (13.430) is $c_{2}\left(C 2 s p^{3} \mathrm{HO}\right)=0.91771$. To match the energies of the functional groups with the electron-density shift to the double bond, $E_{T}\left(\right.$ atom-atom, $\left.m s p^{3} . A O\right)$ of each of the equivalent $C-C$-bond MOs in Eq. (15.61) due to the charge donation from the $C$ atoms to the MO can be considered a linear combination of that of $C-C$-bond MO of toluene, -1.13379 eV and that of the aromatic $C-H$-bond MO, $\frac{-1.13379 \mathrm{eV}}{2}$. Thus, $E_{T}\left(\right.$ atom-atom, $\left.m s p^{3} . A O\right)$ of each $C-C$-bond MO of $C_{60}$ is $\frac{-1.13379 \mathrm{eV}+0.5(-1.13379 \mathrm{eV})}{2}=0.75(-1.13379 \mathrm{eV})=-0.85034 \mathrm{eV}$. As in the case of the aromatic $C-H$ bond, $c_{3}=1 \mathrm{in}$ Eq. (15.65) with $E_{\text {mag }}$ given by Eq. (15.67), and $\bar{E}_{\text {Kvib }}(\mathrm{eV})$ is that of $C_{60}$.

The symbols of the functional groups of $C_{60}$ are given in Table 17.7. 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 $C_{60}$ are given in Tables $17.8,17.9$, and 17.10 , respectively. The total energy of $C_{60}$ given in Table 17.11 was calculated as the sum over the integer multiple of each $E_{D}$ (Group) of Table 17.10 corresponding to functional-group composition of the molecule. The bond angle parameters of $C_{60}$ determined using Eqs. (15.87-15.117) are given in Table 17.12. The structure of $C_{60}$ is shown in Figures 17.2 A and B . The fullerene vertex-atom group comprising a double and two single bonds can serve as a basis element to form other higher-order fullerene-type macromolecules, hyperfullerenes, and complex hybrid conjugated carbon and aromatic structures comprising a mixture of elements from the group of fullerene, graphitic, and diamond carbon described in the corresponding sections.

Figure 17.2. $C_{60}$ MO comprising a hollow cage of sixty carbon atoms bound with the linear combination of sixty sets of $C-C$-bond MOs bridged by 30 sets of $C=C$-bond MOs. A $C=C$ group is bound to two $C-C$ groups at each vertex carbon atom of $C_{60}$. Color scale, translucent pentagonal view (A), and hexagonal view (B), of the charge-density of the $C_{60}$-bond MO with each $C 2 s p^{3}$ HO shown transparently. For each $C-C$ and $C=C$ bond, the ellipsoidal surface of the $H_{2}$-type ellipsoidal MO that transitions to the $C 2 s p^{3} \mathrm{HO}$, the $C 2 s p^{3} \mathrm{HO}$ shell, inner most $C 1 s$ shell, and the nuclei (red, not to scale), are shown.


Table 17.7. The symbols of functional groups of $C_{60}$.

| Functional Group | Group Symbol |
| :--- | :--- |
| $C=C$ (aromatic-type) | $C=C$ |
| $C-C$ (bound to $C=C$ aromatic-type) | $C-C$ |

Table 17.8. The geometrical bond parameters of $C_{60}$ and experimental values [5].

| Parameter | $C=C$ <br> Group | $C-C$ <br> Group |
| :---: | :---: | :---: |
| $a\left(a_{0}\right)$ | 1.47348 | 1.88599 |
| $c^{\prime}\left(a_{0}\right)$ | 1.31468 | 1.37331 |
| Bond Length $2 c^{\prime}(\AA)$ | 1.39140 | 1.45345 |
| Exp. Bond Length | 1.391 | 1.455 |
| $(\AA)$ | $\left(C_{60}\right)$ | $\left(C_{60}\right)$ |
| $b, c\left(a_{0}\right)$ | 0.66540 | 1.29266 |
| $e$ | 0.89223 | 0.72817 |

Table 17.9. The MO to HO intercept geometrical bond parameters of $C_{60}$. $E_{T}$ is $E_{T}$ (atom - atom msp ${ }^{3} . A O$ ).

| Bond | ${ }^{\text {tom }}$ | $\begin{gathered} E_{r} \\ \substack{\text { (ev) } \\ \text { Bond } 1} \end{gathered}$ | $\begin{gathered} E_{V} \\ \text { (ev) } \\ \text { Bond } 2 \end{gathered}$ | $\begin{gathered} E_{\tau} \\ \substack{\text { eve } \\ \text { Bond } \\ \text { Bond }} \end{gathered}$ | $\begin{gathered} E_{r} \\ \text { (eve } \\ \text { Bond } 4 \end{gathered}$ | $\substack{\text { Final Total } \\ \text { Enerey } \\ \text { casp } \\ \text { (ep) } \\ \text { (ev) }}$ |  | $\begin{aligned} & r_{\text {mom }}^{\left(a_{0}\right)} \\ & \left(a_{0}\right) \end{aligned}$ |  | $\begin{gathered} E\left(C 2 s p^{1}\right) \\ \text { (ev) } \\ \text { Final } \end{gathered}$ | $\begin{aligned} & \theta^{\prime} \\ & \left({ }^{\prime}\right) \end{aligned}$ | $\begin{aligned} & \hline \theta_{1} \\ & \left({ }^{\circ}\right) \end{aligned}$ | $\begin{aligned} & \theta_{2} \\ & (0) \end{aligned}$ | $\begin{aligned} & d_{1}^{d_{1}} \\ & \left(a_{0}\right) \end{aligned}$ | $\begin{gathered} d_{2} \\ \left(a_{0}\right) \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $C=C$ <br> $C-C$ | c | $\xrightarrow{-1.13380}{ }_{\text {- }}^{-0.45517}$ | -0.42517 | $\xrightarrow{-0.42517}-1.13880$ | 0 | $\xrightarrow{-153.59983}$ | 0.91771 | 0.80939 | $-16.80989$ | - -16.61903 | $\frac{134.81}{82.53}$ | ${ }_{4}^{45.19} 9$ | 59.66 38.38 | ${ }_{0}^{0.74430}$ | $\frac{0.57338}{0.10519}$ |

Table 17.10. The energy parameters $(\mathrm{eV})$ of functional groups of $C_{60}$.

| Parameters | $\begin{aligned} & \hline C=C \\ & \text { Group } \\ & \hline \end{aligned}$ | $\begin{aligned} & \hline C-C \\ & \text { Group } \\ & \hline \end{aligned}$ |
| :---: | :---: | :---: |
| $f_{1}$ | 1 | 1 |
| $n_{1}$ | 2 | 1 |
| $n_{2}$ | 0 | 0 |
| $n_{3}$ | 0 | 0 |
| $C_{1}$ | 0.5 | 0.5 |
| $\mathrm{C}_{2}$ | 0.85252 | 1 |
| $c_{1}$ | 1 | 1 |
| $c_{2}$ | 0.85252 | 0.91771 |
| $c_{3}$ | 0 | 1 |
| $c_{4}$ | 4 | 2 |
| $c_{5}$ | 0 | 0 |
| $C_{1}$ o | 0.5 | 0.5 |
| $\mathrm{C}_{2}$ o | 0.85252 | 1 |
| $V_{e}(e \mathrm{~V})$ | -101.12679 | -33.63376 |
| $V_{p}(e \mathrm{~V})$ | 20.69825 | 9.90728 |
| $T(\mathrm{eV})$ | 34.31559 | 8.91674 |
| $V_{m}(\mathrm{eV})$ | -17.15779 | -4.45837 |
| $E$ (Аолно) (eV) | 0 | -14.63489 |
| $\Delta E_{\mathrm{H}_{2} M \text { ( }}($ АО/ HO$)(\mathrm{eV})$ | 0 | -2.26759 |
| $E_{T}($ Ао/но) $(\mathrm{eV})$ | 0 | -12.36730 |
| $E_{T}\left(H_{2} \mathrm{MO}\right)(\mathrm{eV})$ | -63.27075 | -31.63541 |
| $E_{T}\left(\right.$ atom-atom, $\left.\mathrm{msp}{ }^{3} . \mathrm{AO}\right)(\mathrm{eV})$ | -2.26759 | -0.85034 |
| $E_{T}(\mathrm{mo})(\mathrm{eV})$ | -65.53833 | -32.48571 |
| $\omega\left(10^{15} \mathrm{rad} / \mathrm{s}\right)$ | 49.7272 | 19.8904 |
| $E_{K}(\mathrm{eV})$ | 32.73133 | 13.09221 |
| $\bar{E}_{D}(\mathrm{eV})$ | -0.35806 | -0.23254 |
| $\bar{E}_{\text {Kvib }}(\mathrm{eV})$ | $\begin{gathered} 0.17727 \\ {[6]} \\ \hline \end{gathered}$ | $\begin{gathered} \hline 0.14667 \\ {[6]} \\ \hline \end{gathered}$ |
| $\bar{E}_{\text {osc }}(\mathrm{eV})$ | -0.26942 | -0.15921 |
| $E_{\text {mag }}(\mathrm{eV})$ | 0.14803 | 0.14803 |
| $E_{T}($ (Group $)(\mathrm{eV})$ | -66.07718 | -32.49689 |
| $E_{\text {ininial }}\left(\mathrm{c}_{4}\right.$ AO/ $\left./ \mathrm{HO} \mathrm{O}\right)(\mathrm{eV})$ | -14.63489 | -14.63489 |
|  | 0 | 0 |
| $E_{D}($ Group $)(e V)$ | 7.53763 | 3.22711 |

Table 17.11. The total bond energies of $C_{60}$ calculated using the functional group composition and the energies of Table 17.10 compared to the experimental values [7].

| Formula | Name | $C=C$ | $C-C$ | Calculated <br> Total Bond Energy <br> $(\mathrm{eV})$ | Experimental <br> Total Bond Energy <br> $(\mathrm{eV})$ | Relative Error |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{C}_{60}$ | Fullerene | 30 | 60 | 419.75539 | 419.73367 | -0.00005 |


| Atoms of Angle | $\begin{gathered} 2 c^{\prime} \\ \text { Bond } 1 \\ \left(a_{0}\right) \end{gathered}$ | $\begin{gathered} 2 c^{\prime} \\ \text { Bond } 2\left(a_{0}\right) \end{gathered}$ | $\begin{gathered} 2 c^{\prime} \\ \text { Terminal } \\ \text { Atoms } \\ \left(a_{0}\right) \end{gathered}$ | $\begin{aligned} & E_{\text {Conlombic }}^{\text {a }} \end{aligned}$ | Atom 1 $\begin{gathered}\text { Hybridization } \\ \text { Designation }\end{gathered}$ (Table 15.3.A) | $\begin{aligned} & E_{\text {Coulombic }}^{\text {a }} \text { Atom } 2 \end{aligned}$ | Atom 2 $\begin{gathered}\text { Hybridization } \\ \text { Designation }\end{gathered}$ (Table 15.3.A) | $\begin{gathered} c_{2} \\ \text { Atom } 1 \end{gathered}$ | $\begin{gathered} c_{2} \\ \text { Atom } 2 \end{gathered}$ | $c_{1}$ | $C_{2}$ | $c_{1}$ | $c_{2}^{\prime}$ | $\begin{gathered} E_{T} \\ (\mathrm{eV}) \end{gathered}$ | $\begin{aligned} & \theta_{v} \\ & \left({ }^{\circ}\right) \end{aligned}$ | $\begin{aligned} & \theta_{1} \\ & \left({ }^{\circ}\right) \end{aligned}$ | $\begin{aligned} & \theta_{2} \\ & \left({ }^{\circ}\right) \end{aligned}$ | $\begin{gathered} \text { Cal. } \theta \\ \left({ }^{\circ}\right) \end{gathered}$ | $\begin{gathered} \text { Exp. } \theta \\ \left({ }^{\circ}\right) \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\angle C=C-C$ | 2.62936 | 2.77663 | 4.6562 | $\xrightarrow{-17.03045}$ | 32 | -17.03045 | 32 | 0.778991 | 0.79891 | 1 | 1 | 1 | 0.79891 | -1.85836 -185836 |  |  |  | 120.00 | 120.00 |
| $\angle C-C-C$ | 2.74663 | 2.74663 | 4.4441 | -17.45563 | 47 | -17.45563 | 47 | 0.77945 | 0.77945 | 1 | 1 | 1 | 0.77945 | -1.85836 |  |  |  | 108.00 | 108.00 |

## FULLERENE DIHEDRAL ANGLES

For $C_{60}$, the bonding at each vertex atom $C_{b}$ comprises two single bonds, $C_{a}-C_{b}-C_{a}$, and a double bond, $C_{b}=C_{c}$. The dihedral angle $\theta_{\angle C=C / C-C-C}$ between the plane defined by the $C_{a}-C_{b}-C_{a}$ moiety and the line defined by the corresponding $C_{b}=C_{c}$ moiety is calculated using the results given in Table 17.12 and Eqs. (15.114-15.117). The distance $d_{1}$ along the bisector of $\theta_{\angle C_{a}-C_{b}-C a}$ from $C_{b}$ to the internuclear-distance line between one $C_{a}$ and the other $C_{a}, 2 C_{C_{a}-C_{a}}^{\prime}$, is given by:

$$
\begin{equation*}
d_{1}=2{c^{\prime}}_{C_{b}-C_{a}} \cos \frac{\theta_{\angle C_{a}-C_{b}-C a}}{2}=2.74663 a_{0} \cos \frac{108.00^{\circ}}{2}=1.61443 a_{0} \tag{17.8}
\end{equation*}
$$

where $2{c^{\prime}}_{C_{b}-C_{a}}$ is the internuclear distance between $C_{b}$ and $C_{a}$. The atoms $C_{a}, C_{a}$, and $C_{c}$ define the base of a pyramid. Then, the pyramidal angle $\theta_{\angle C_{a} C_{c} C_{a}}$ can be solved from the internuclear distances between $C_{c}$ and $C_{a}, 2 c^{\prime}{ }_{C_{c}-C_{a}}$, and between $C_{a}$ and $C_{a}, 2{C^{\prime}}_{C_{a}-C_{a}}$, using the law of cosines (Eq. (15.115)).

$$
\begin{equation*}
=57.01^{\circ} \tag{17.9}
\end{equation*}
$$

Then, the distance $d_{2}$ along the bisector of $\theta_{\angle C_{a} C_{c} C_{a}}$ from $C_{c}$ to the internuclear-distance line $2 c^{\prime}{ }_{C_{a}-C_{a}}$, is given by:

$$
\begin{equation*}
d_{2}=2 c_{C_{c}-C_{a}}^{\prime} \cos \frac{\theta_{\angle C_{a} C_{c} C_{a}}}{2}=4.65618 a_{0} \cos \frac{57.01^{\circ}}{2}=4.09176 a_{0} \tag{17.10}
\end{equation*}
$$

The lengths $d_{1}, d_{2}$, and $2 c^{\prime} C_{b}=C_{c}$ define a triangle wherein the angle between $d_{1}$ and the internuclear distance between $C_{b}$ and $C_{c}, 2 c^{\prime}{ }_{C_{b}=C_{c}}$, is the dihedral angle $\theta_{\angle C=C / C-C-C}$ that can be solved using the law of cosines (Eq. (15.117)).

$$
\begin{align*}
\theta_{\angle C=C / C-C-C} & =\cos ^{-1}\left(\frac{d_{1}^{2}+\left(2 c_{C_{b}=C_{c}}^{\prime}\right)^{2}-d_{2}^{2}}{2 d_{1}\left(2 c_{C_{b}=C_{c}}^{\prime}\right)}\right)=\cos ^{-1}\left(\frac{\left(1.61443 \mathrm{a}_{0}\right)^{2}+\left(2.62936 \mathrm{a}_{0}\right)^{2}-\left(4.09176 \mathrm{a}_{0}\right)^{2}}{2\left(1.61443 \mathrm{a}_{0}\right)\left(2.62936 \mathrm{a}_{0}\right)}\right)  \tag{17.11}\\
& =148.29^{\circ}
\end{align*}
$$

The dihedral angle for a truncated icosahedron corresponding to $\theta_{\angle C=C / C-C-C}$ is:

$$
\begin{equation*}
\theta_{\angle C=C / C-C-C}=148.28^{\circ} \tag{17.12}
\end{equation*}
$$

The dihedral angle $\theta_{\angle C-C / C-C=C}$ between the plane defined by the $C_{a}-C_{b}=C_{c}$ moiety and the line defined by the corresponding $C_{b}-C_{a}$ moiety is calculated using the results given in Table 17.12 and Eqs. (15.118-15.127). The parameter $d_{1}$ is the distance from $C_{b}$ to the internuclear-distance line between $C_{a}$ and $C_{c}, 2 C^{\prime}{ }_{C_{a}-C_{c}}$. The angle between $d_{1}$ and the $C_{b}-C_{a}$ bond, $\theta_{\angle C_{a} C_{b} d_{1}}$, can be solved reiteratively using Eq. (15.121).

$$
\begin{align*}
& \left(\left(2.74663 \mathrm{a}_{0}\right)^{2}+\left(\frac{\left(2.74663 \mathrm{a}_{0}\right)^{2}-\left(2.62936 \mathrm{a}_{0}\right)^{2}}{2\left(\left(2.74663 \mathrm{a}_{0}\right) \operatorname{cosine} \theta_{\angle C_{a} C_{b} d_{1}}-\left(2.62936 \mathrm{a}_{0}\right) \operatorname{cosine}\left(120.00^{\circ}-\theta_{\angle C_{a} C_{b} d_{1}}\right)\right)}\right)^{2}\right. \\
& \left.\left(\begin{array}{l}
-\left(2\left(2.74663 \mathrm{a}_{0}\right)\left(\frac{\left(2.74663 \mathrm{a}_{0}\right)^{2}-\left(2.62936 \mathrm{a}_{0}\right)^{2}}{2\binom{\left(2.74663 \mathrm{a}_{0}\right) \operatorname{cosine} \theta_{\angle C_{a} C_{b} d_{1}}}{-\left(2.62936 \mathrm{a}_{0}\right) \operatorname{cosine}\left(120.00^{\circ}-\theta_{\angle C_{a} C_{b} d_{1}}\right)}}\right) \operatorname{cosine} \theta_{\angle C_{a} C_{b} d_{1}}\right.
\end{array}\right) \quad \begin{array}{l}
-\left(\frac{4.6562 \mathrm{a}_{0}}{2}\right)^{2}
\end{array}\right)=0 \tag{17.13}
\end{align*}
$$

The solution of Eq. (17.13) is:

$$
\begin{equation*}
\theta_{\angle C_{a} C_{a} d_{2}}=57.810^{\circ} \tag{17.14}
\end{equation*}
$$

Eq. (17.14) can be substituted into Eq. (15.120) to give $d_{1}$ :

$$
\begin{align*}
d_{1} & =\frac{\left(2{C^{\prime}}_{C_{b}-C_{a}}\right)^{2}-\left(2{C^{\prime}}_{C_{b}-C_{c}}\right)^{2}}{2\left(\left(2{C^{\prime}{ }_{C_{b}-C_{a}}}\right) \operatorname{cosine} \theta_{\angle C_{a} C_{b} d_{1}}-\left(2 C^{\prime}{ }_{C_{b}-C_{c}}\right) \operatorname{cosine}\left(\theta_{\angle C_{a} C_{b} C_{c}}-\theta_{\angle C_{a} C_{b} d_{1}}\right)\right)}  \tag{17.15}\\
& =\frac{\left(2.74663 \mathrm{a}_{0}\right)^{2}-\left(2.62936 \mathrm{a}_{0}\right)^{2}}{2\left(\left(2.74663 \mathrm{a}_{0}\right) \operatorname{cosine}\left(57.810^{\circ}\right)-\left(2.62936 \mathrm{a}_{0}\right) \operatorname{cosine}\left(120.00^{\circ}-57.810^{\circ}\right)\right)}=1.33278 \mathrm{a}_{0}
\end{align*}
$$

The atoms $C_{a}, C_{a}$, and $C_{c}$ define the base of a pyramid. Then, the pyramidal angle $\theta_{\left\langle C_{a} C_{a} C_{c}\right.}$ can be solved from the internuclear distances between $C_{a}$ and $C_{a}, 2{C^{\prime}}_{C_{a}-C_{a}}$, and between $C_{a}$ and $C_{c}, 2 C^{\prime}{ }_{C_{a}-C_{c}}$, using the law of cosines (Eq. (15.115)).

$$
\begin{align*}
\theta_{\angle C_{a} C_{a} C_{c}} & =\cos ^{-1}\left(\frac{\left(2 C_{C_{a}-C_{a}}^{\prime}\right)^{2}+\left(2{C^{\prime}{ }_{C_{a}-C_{c}}}\right)^{2}-\left(2{c^{\prime}}_{C_{a}-C_{c}}\right)^{2}}{2\left(2{C^{\prime}}_{C_{a}-C_{a}}\right)\left(2 C^{\prime}{ }_{C_{a}-C_{c}}\right)}\right)  \tag{17.16}\\
& =\cos ^{-1}\left(\frac{\left(4.44410 \mathrm{a}_{0}\right)^{2}+\left(4.65618 \mathrm{a}_{0}\right)^{2}-\left(4.65618 \mathrm{a}_{0}\right)^{2}}{2\left(4.44410 \mathrm{a}_{0}\right)\left(4.65618 \mathrm{a}_{0}\right)}\right)=61.50^{\circ}
\end{align*}
$$

The parameter $d_{2}$ is the distance from $C_{a}$ to the bisector of the internuclear-distance line between $C_{a}$ and $C_{c}, 2 c^{\prime}{ }_{C_{a}-C_{c}}$. The angle between $d_{2}$ and the $C_{a}-C_{a}$ axis, $\theta_{\angle C_{a} C_{a} d_{2}}$, can be solved reiteratively using Eq. (15.126).

$$
\left(\begin{array}{l}
\left.\left(4.44410 \mathrm{a}_{0}\right)^{2}+\left(\frac{\left(4.44410 \mathrm{a}_{0}\right)^{2}-\left(4.65618 \mathrm{a}_{0}\right)^{2}}{2\left(\left(4.44410 \mathrm{a}_{0}\right) \operatorname{cosine} \theta_{\angle C_{a} C_{a} d_{2}}-\left(4.65618 \mathrm{a}_{0}\right) \operatorname{cosine}\left(61.50^{\circ}-\theta_{\angle C_{a} C_{a} d_{2}}\right)\right)}\right)^{2}\right) \\
-\left(2\left(4.44410 \mathrm{a}_{0}\right)\left(\frac{\left(4.44410 \mathrm{a}_{0}\right)^{2}-\left(4.65618 \mathrm{a}_{0}\right)^{2}}{\left.2\binom{\left(4.44410 \mathrm{a}_{0}\right) \operatorname{cosine} \theta_{\angle C_{a} C_{a} d_{2}}}{-\left(4.65618 \mathrm{a}_{0}\right) \operatorname{cosine}\left(61.50^{\circ}-\theta_{\angle C_{a} C_{a} d_{2}}\right)}\right)}\right)\right. \\
-\left(\frac{4.6562 \mathrm{a}_{0}}{2}\right)^{2}
\end{array}\right)=0
$$

The solution of Eq. (17.17) is:

$$
\begin{equation*}
\theta_{\angle C_{a} C_{a} d_{2}}=31.542^{\circ} \tag{17.18}
\end{equation*}
$$

Eq. (17.18) can be substituted into Eq. (15.125) to give $d_{2}$ :

$$
\begin{align*}
d_{2} & \left.=\frac{\left(2{c^{\prime}}_{C_{a}-C_{a}}\right)^{2}-\left(2{C^{\prime}{ }_{C_{a}-C_{c}}}\right)^{2}}{2\left(\left(2{\left.\left.C^{\prime}{ }_{C_{a}-C_{a}}\right) \operatorname{cosine} \theta_{\angle C_{a} C_{a} d_{2}}-\left(2 c^{\prime}{ }_{C_{a}-C_{c}}\right) \operatorname{cosine}\left(\theta_{\angle C_{a} C_{a} C_{c}}-\theta_{\angle C_{a} C_{a} d_{2}}\right)\right)}\right.\right.} \begin{array}{rl} 
& \left(4.44410 \mathrm{a}_{0}\right)^{2}-\left(4.65618 \mathrm{a}_{0}\right)^{2} \\
& =3.91101 \mathrm{a}_{0}
\end{array} .=\left(4.44410 \mathrm{a}_{0}\right) \operatorname{cosine}\left(31.542^{\circ}\right)-\left(4.65618 \mathrm{a}_{0}\right) \operatorname{cosine}\left(61.50^{\circ}-31.542^{\circ}\right)\right) \tag{17.19}
\end{align*}
$$

The lengths $d_{1}, d_{2}$, and $2 c^{\prime} C_{b}-C_{a}$ define a triangle wherein the angle between $d_{1}$ and the internuclear distance between $C_{b}$ and $C_{a}, 2 C^{\prime}{ }_{C_{b}-C_{a}}$, is the dihedral angle $\theta_{\angle C-C / C-C=C}$ that can be solved using the law of cosines (Eq. (15.117)).

$$
\begin{align*}
\theta_{\angle C-C / C-C=C} & =\cos ^{-1}\left(\frac{d_{1}^{2}+\left(2{c^{\prime}}_{C_{b}-C_{a}}^{\prime}\right)^{2}-d_{2}^{2}}{2 d_{1}\left(2 c_{C_{b}-C_{a}}\right)}\right)  \tag{17.20}\\
& =\cos ^{-1}\left(\frac{\left(1.33278 \mathrm{a}_{0}\right)^{2}+\left(2.74663 \mathrm{a}_{0}\right)^{2}-\left(3.91101 \mathrm{a}_{0}\right)^{2}}{2\left(1.33278 \mathrm{a}_{0}\right)\left(2.74663 \mathrm{a}_{0}\right)}\right)=144.71^{\circ}
\end{align*}
$$

The dihedral angle for a truncated icosahedron corresponding to $\theta_{\angle C-C / C-C=C}$ is:

$$
\begin{equation*}
\theta_{\angle C-C / C-C=C}=144.24^{\circ} \tag{17.21}
\end{equation*}
$$

## GRAPHENE AND GRAPHITE

In addition to fullerene and diamond described in the corresponding sections, graphite is the third allotrope of carbon. It comprises planar sheets of covalently bound carbon atoms arranged in hexagonal aromatic rings of a macromolecule of indefinite size. Each sheet comprises graphene. The sheets, in turn, are bound together by weaker intermolecular forces. It was demonstrated in the Fullerene $\left(C_{60}\right)$ section, that a very complex macromolecule, fullerene, could be simply solved from the groups at each vertex carbon atom of the structure. Specifically, a $C=C$ group is bound to two $C-C$ bonds at each vertex carbon atom of $C_{60}$. The solution of the macromolecule is given by superposition of the geometrical and energy parameters of the corresponding two groups. Similarly, diamond comprising, in principle, an infinite network of carbons was also solved in the Diamond section using the functional group solutions, the diamond $C-C$ functional group which is the only functional group of diamond.

The structure of the indefinite network of aromatic hexagons of a sheet of graphite can also be solved by considering the vertex atom. As in the case of fullerene, each sheet of joined hexagons can be constructed with a $C=C$ group bound to two $C-C$ bonds at each vertex carbon atom of graphite. However, an alternative bonding to that of $C_{60}$ is possible for graphite due to the structure comprising repeating hexagonal units. In this case, the lowest energy structure is achieved with a single functional group, one which has aromatic character. The aromatic bond is uniquely stable and requires the sharing of the electrons of multiple $\mathrm{H}_{2}$-type MOs. The results of the derivation of the parameters of the benzene molecule given in the Benzene Molecule ( $\mathrm{C}_{6} \mathrm{H}_{6}$ ) 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 $C \stackrel{3 e}{=} C$ bonding of the aromatic bond wherein each of the $C \stackrel{3 e}{=} C$ aromatic bonds comprises $(0.75)(4)=3$ electrons according to Eq. (15.161) wherein $C_{2}$ of Eq. (15.51) for the aromatic $C^{3 e}=C$-bond MO given by Eq. (15.162) is $C_{2}\left(\operatorname{aromaticC} 2 s p^{3} \mathrm{HO}\right)=c_{2}\left(\operatorname{aromaticC} 2 s p^{3} \mathrm{HO}\right)=0.85252$ and $E_{T}\left(\right.$ atom-atom, $\left.\mathrm{msp}^{3} . A O\right)=-2.26759 \mathrm{eV}$.

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 $C \stackrel{8 / 3 e}{=} C$ functional group of graphite comprises the aromatic bond with the exception that the electron-number per bond is $\frac{8}{3}$. $E_{T}$ (Group) and $E_{D}$ (Group) are given by Eqs. (15.165) and (15.166), respectively, with $f_{1}=\frac{2}{3}$ and $c_{4}=\frac{8}{3}$. As in the case of diamond comprising equivalent carbon atoms, the $C 2 s p^{3} \mathrm{HO}$ magnetic energy $E_{\text {mag }}$ given by Eq. (15.67) was subtracted due to a set of unpaired electrons being created by bond breakage such that $c_{3}$ of Eqs. (15.165) and (15.166) is one.

The symbol of the functional group of graphite is given in Table 17.13. 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 graphite are given in Tables 17.14, 17.15, and 17.16, respectively. The total energy of graphite given in Table 17.17 was calculated as the sum over the integer multiple of each $E_{D}$ (Group) of Table 17.16 corresponding to functional-group composition of the molecular solid. The experimental $C \stackrel{8 / 3 e}{=} C$ bond energy of graphite at $0 \mathrm{~K}, E_{D_{\text {exp }}}(C \stackrel{8 / 3 e}{=} C)$, is given by the difference between the enthalpy of formation of gaseous carbon atoms from graphite, $\Delta H_{f}\left(C_{\text {graphite }}(g a s)\right)$, and the interplanar binding energy, $E_{x}$, wherein graphite solid has a defined heat of formation of zero $\left(\Delta H_{f}(C(\right.$ graphite $)=0)$ :

$$
\begin{equation*}
E_{D_{\text {exp }}}(C \stackrel{8 / 3 e}{=} C)=\frac{2}{3}\left[\Delta H_{f}\left(C_{\text {graphite }}(\text { gas })\right)-E_{x}\right] \tag{17.22}
\end{equation*}
$$

The factor of $\frac{2}{3}$ corresponds to the ratio of $\frac{8}{3}$ electrons per bond and 4 electrons per carbon atom. The heats of formation of atomic carbon from graphite [9] and $E_{x}$ [10] are:

$$
\begin{align*}
& \Delta H_{f}\left(C_{\text {graphite }}(\text { gas })\right)=711.185 \mathrm{~kJ} / \text { mole }(7.37079 \mathrm{eV} / \text { atom })  \tag{17.23}\\
& E_{x}=0.0228 \mathrm{eV} / \text { atom } \tag{17.24}
\end{align*}
$$

Using Eqs. (17.21-17.23), $E_{D_{\text {exp }}}(C \stackrel{8 / 3 e}{=} C)$ is:

$$
\begin{equation*}
E_{D_{\text {exp }}}(C \stackrel{8 / 3 e}{=} C)=\frac{2}{3}[7.37079 \mathrm{eV}-0.0228 \mathrm{eV}]=4.89866 \mathrm{eV} \tag{17.25}
\end{equation*}
$$

The bond angle parameters of graphite determined using Eqs. (15.87-15.117) are given in Table 17.18. The inter-plane distance for graphite of $3.5 \AA$ is calculated in the Geometrical Parameters Due to the Interplane van der Waals Cohesive Energy of Graphite section. The structure of graphite is shown in Figure 17.3 A and B. The graphite $C \stackrel{8 / 3 e}{=} C$ functional group can serve as a basis element to form additional complex polycyclic aromatic carbon structures such as nanotubes [11-15].

Figure 17.3. The structure of graphite. (A) Single plane of macromolecule of indefinite size. (B) Layers of graphitic planes.
(A)

(B)


Table 17.13. The symbols of the functional group of graphite.

| Functional Group | Group Symbol |
| :--- | :---: |
| $C C$ bond (graphite- $C$ ) | $C \stackrel{8 / 3 e}{=} C$ |

Table 17.14. The geometrical bond parameters of graphite and experimental values.

| Parameter | $C \stackrel{8 / 3 e}{=}$ <br> Group |
| :---: | :---: |
| $a\left(a_{0}\right)$ | 1.47348 |
| $c^{\prime}\left(a_{0}\right)$ | 1.31468 |
| Bond Length $2 c^{\prime}(\AA)$ | 1.39140 |
| Exp. Bond Length $(\AA)$ | 1.42 <br> (graphite) $[11]$ <br> 1.399 <br> (benzene) $[16]$ |
| $b, c\left(a_{0}\right)$ | 0.66540 |
| $e$ | 0.89223 |

Table 17.15. The MO to HO intercept geometrical bond parameters of graphite. $E_{T}$ is $E_{T}$ (atom-atom $m s p^{3} . A O$ ).

| Bond | Atom | $\begin{gathered} E_{T} \\ (\mathrm{eV}) \\ \text { Bond } 1 \end{gathered}$ | $\begin{gathered} E_{T} \\ (\mathrm{eV}) \\ \text { Bond } 2 \end{gathered}$ | $\begin{gathered} E_{7} \\ (\mathrm{eV}) \\ \text { Bond } \end{gathered}$ | $\begin{gathered} E_{T} \\ (\mathrm{eV}) \\ \text { Bond } 4 \end{gathered}$ | Final Total <br> Energy <br> $C 2 s p^{3}$ <br> (ev) | $\begin{aligned} & r_{\text {matal }} \\ & \left(a_{0}\right) \end{aligned}$ | $r_{\text {mant }}$ $\left(a_{0}\right)$ | $\begin{gathered} E_{\text {Coumomom }}\left(C 2 s p^{3}\right) \\ \text { (eV) } \\ \text { Final } \end{gathered}$ | $\begin{gathered} E\left(C 2 s p^{3}\right) \\ (\mathrm{eV}) \\ \text { Final } \end{gathered}$ | $\begin{aligned} & \theta^{\prime} \\ & \left({ }^{\circ}\right) \end{aligned}$ | $\begin{aligned} & \theta_{1} \\ & \left({ }^{\circ}\right) \end{aligned}$ | $\begin{aligned} & \theta_{2} \\ & \left({ }^{\circ}\right) \end{aligned}$ | $\begin{gathered} d_{1} \\ \left(a_{0}\right) \end{gathered}$ | $\begin{gathered} d_{2} \\ \left(a_{0}\right) \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $C \stackrel{836}{=} C$ | C | -0.75586 | $-0.75586$ | -0.75586 | 0 | $-153.88328$ | 0.91771 | 0.79597 | -17.09334 | -16.90248 | 134.24 | 45.76 | 58.98 | 0.75935 | 0.55533 |

Table 17.16. The energy parameters $(e V)$ of the functional group of graphite.

| Parameters | $C=C$ <br> Group |
| :---: | :---: |
| $f_{1}$ | 2/3 |
| $n_{1}$ | 2 |
| $n_{2}$ | 0 |
| $n_{3}$ | 0 |
| $C_{1}$ | 0.5 |
| $C_{2}$ | 0.85252 |
| $c_{1}$ | 1 |
| $c_{2}$ | 0.85252 |
| $c_{3}$ | 1 |
| $c_{4}$ | 8/3 |
| $c_{5}$ | 0 |
| $C_{10}$ | 0.5 |
| $C_{2 o}$ | 0.85252 |
| $V_{e}(\mathrm{eV})$ | -101.12679 |
| $V_{p}(e \mathrm{~V})$ | 20.69825 |
| $T(e V)$ | 34.31559 |
| $V_{m}(\mathrm{eV})$ | -17.15779 |
| $E($ Ао/но) $(\mathrm{eV})$ | 0 |
| $\Delta E_{\mathrm{H}_{2} \mathrm{MO}}($ АО/ HO$)(\mathrm{eV})$ | 0 |
| $E_{T}($ Ао/ $/ \mathrm{H})(\mathrm{eV})$ | 0 |
| $E_{T}\left(\mathrm{H}_{2} \mathrm{MO}\right)(\mathrm{eV})$ | -63.27075 |
| $E_{T}\left(\right.$ atom - atom, $\left.\mathrm{msp}{ }^{3} . \mathrm{AO}\right)(\mathrm{eV})$ | -2.26759 |
| $E_{T}($ мо) $(\mathrm{eV})$ | -65.53833 |
| $\omega\left(10^{15} \mathrm{rad} / \mathrm{s}\right)$ | 49.7272 |
| $E_{K}(\mathrm{eV})$ | 32.73133 |
| $\bar{E}_{D}(e V)$ | -0.35806 |
| $\bar{E}_{\text {Kvib }}(\mathrm{eV})$ | $\begin{gathered} 0.19649 \\ {[17]} \\ \hline \end{gathered}$ |
| $\bar{E}_{\text {osc }}(\mathrm{eV})$ | -0.25982 |
| $E_{\text {mag }}(\mathrm{eV})$ | 0.14803 |
| $E_{T}($ Group $)(\mathrm{eV})$ | -43.93995 |
| $E_{\text {initial }}\left(c_{4}\right.$ AO/ $/$ HO) $(\mathrm{eV})$ | -14.63489 |
| $E_{\text {initial }}\left(c_{5}\right.$ АО $/$ но) $)(\mathrm{eV})$ | 0 |
| $E_{D}($ Group $)(\mathrm{eV})$ | 4.91359 |

Table 17.17. The total bond energy of graphite calculated using the functional group composition and the energy of Table 17.16 compared to the experimental value [9-10].

| Formula | Name | $8 / 3 e$ <br> $=$ <br> $C$ | Calculated <br> Total Bond <br> Energy (eV) | Experimental <br> Total Bond <br> Energy (eV) | Relative Error |  |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{C}_{\mathrm{n}}$ | Graphite |  | 1 | 4.91359 | 4.89866 | -0.00305 |


| Atoms of Angle | $\begin{gathered} 2 c^{\prime} \\ \text { Bond } 1 \\ \left(a_{0}\right) \end{gathered}$ | $\begin{array}{c\|} \hline 2 c^{\prime} \\ \text { Bond 2 } \\ \left(a_{0}\right) \end{array}$ | $\begin{array}{c\|} 2 c^{\prime} \\ \text { Terminal } \\ \text { Atoms }\left(a_{0}\right) \end{array}$ | $E_{\text {Coulombic }}$ | Atom 1 Hybridization Designation (Table 15.3.A) | $E_{\text {Coulomintic }}$ | Atom 2 Hybridization Designation <br> (Table 15.3.A) | $\begin{gathered} c_{2} \\ \text { Atom } 1 \end{gathered}$ | $\begin{gathered} c_{2} \\ \text { Atom } 2 \end{gathered}$ | $C_{1}$ | $C_{2}$ | $c_{1}$ | $c_{2}^{\prime}$ | $\begin{gathered} E_{T} \\ (\mathrm{eV}) \end{gathered}$ | $\begin{aligned} & \theta_{v} \\ & \left({ }^{\circ}\right) \end{aligned}$ | $\begin{aligned} & \hline \theta_{1} \\ & \left({ }^{\circ}\right) \end{aligned}$ | $\begin{aligned} & \theta_{2} \\ & \left({ }^{\circ}\right) \end{aligned}$ | $\begin{gathered} \text { Cal. } \theta \\ \left({ }^{\circ}\right) \end{gathered}$ | $\begin{gathered} \text { Exp. } \theta \\ \left({ }^{\circ}\right) \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\underset{(\text { aromatic })}{\angle C C C}$ | 2.62936 | 2.62936 | 4.5387 | -17.26666 | 40 | -17.26666 | 40 | 0.78798 | 0.78798 | 1 | 1 | 1 | 0.78798 | -1.85836 |  |  |  | 119.33 | $\begin{gathered} 120 \\ \begin{array}{c} \text { (graphite) } \\ 1218] \\ \text { (benzene) }[19-21] \end{array} \end{gathered}$ |

Table 17.19. The calculated and experimental total bond energies of allotropes of carbon using closed-form equations having integers and fundamental constants only.

| Formula | Name | Calculated <br> Total Bond Energy <br> $(\mathrm{eV})$ | Experimental <br> Total Bond Energy <br> $(\mathrm{eV})$ | Relative Error |
| :--- | :--- | :---: | :---: | :---: |
| $\mathrm{C}_{\mathrm{n}}$ | diamond | 3.74829 | 3.704 | -0.01 |
| $\mathrm{C}_{60}$ | fullerene | 419.75539 | 419.73367 | -0.00005 |
| $\mathrm{C}_{\mathrm{n}}$ | graphite | 4.91359 | 4.89866 | -0.00305 |

## REFERENCES

1. http://newton.ex.ac.uk/research/qsystems/people/sque/diamond/.
2. D. R. Lide, CRC Handbook of Chemistry and Physics, 86th Edition, CRC Press, Taylor \& Francis, Boca Raton, (2005-6), pp. 5-18; 5-45.
3. D. R. Lide, CRC Handbook of Chemistry and Physics, 86th Edition, CRC Press, Taylor \& Francis, Boca Raton, (2005-6), p. 4-150.
4. J. Wagner, Ch. Wild, P. Koidl, "Resonance effects in scattering from polycrystalline diamond films," Appl. Phys. Lett. Vol. 59, (1991), pp. 779-781.
5. W. I. F. David, R. M. Ibberson, J. C. Matthewman, K. Prassides, T. J. S. Dennis, J. P. Hare, H. W. Kroto, R. Taylor, D. R. M. Walton, "Crystal structure and bonding of $C_{60}$," Nature, Vol. 353, (1991), pp. 147-149.
6. B. Chase, N. Herron, E. Holler, "Vibrational spectroscopy of $C_{60}$ and $C_{70}$ temperature-dependent studies," J. Phys. Chem., Vol. 96, (1992), pp. 4262-4266.
7. D. R. Lide, CRC Handbook of Chemistry and Physics, 86th Edition, CRC Press, Taylor \& Francis, Boca Raton, (2005-6), pp. 9-63; 5-18 to 5-42.
8. J. M. Hawkins, "Osmylation of $C_{60}$ : proof and characterization of the soccer-ball framework," Acc. Chem. Res., (1992), Vol. 25, pp. 150-156.
9. M. W. Chase, Jr., C. A. Davies, J. R. Downey, Jr., D. J. Frurip, R. A. McDonald, A. N. Syverud, JANAF Thermochemical Tables, Third Edition, Part II, Cr-Zr, J. Phys. Chem. Ref. Data, Vol. 14, Suppl. 1, (1985), p. 536.
10. M. C. Schabel, J. L. Martins, "Energetics of interplanar binding in graphite," Phys. Rev. B, Vol. 46, No. 11, (1992), pp. 7185-7188.
11. J. -C. Charlier, J. -P. Michenaud, "Energetics of multilayered carbon tubules," Phys. Rev. Ltts., Vol. 70, No. 12, (19930, pp. 1858-1861.
12. J. P. Lu, "Elastic properties of carbon nanotubes and nanoropes," Phys. Rev. Letts., (1997), Vol. 79, No. 7, pp. 1297-1300.
13. G. Zhang, X. Jiang, E. Wang, "Tubular graphite cones," Science, (2003), vol. 300, pp. 472-474.
14. A. N. Kolmogorov, V. H. Crespi, M. H. Schleier-Smith, J. C. Ellenbogen, "Nanotube-substrate interactions: Distinguishing carbon nanotubes by the helical angle," Phys. Rev. Letts., (2004), Vol. 92, No. 8, pp. 085503-1-085503-4.
15. J.W. Jiang, H. Tang, B.S. Wang, Z.B. Su, "A lattice dynamical treatment for the total potential of single-walled carbon nanontubes and its applications: Relaxed equilibrium structure, elastic properties, and vibrational modes of ultra-narrow tubes," J. Phys. Condens. Matter, Vol. 20, (2008), p. 045228.
16. D. R. Lide, CRC Handbook of Chemistry and Physics, 86th Edition, CRC Press, Taylor \& Francis, Boca Raton, (2005-6), p. 9-29.
17. G. Herzberg, Molecular Spectra and Molecular Structure II. Infrared and Raman Spectra of Polyatomic Molecules, Van Nostrand Reinhold Company, New York, New York, (1945), pp. 362-369.
18. D. R. McKenzie, D. Muller, B. A. Pailthorpe, "Compressive-stress-induced formation of thin-film tetrahedral amorphous carbon," Phys. Rev. Lett., (1991), Vol. 67, No. 6, pp. 773-776.
19. W. I. F. David, R. M. Ibberson, G. A. Jeffrey, J. R. Ruble, "The structure analysis of deuterated benzene and deuterated nitromethane by pulsed-neutron powder diffraction: a comparison with single crystal neutron analysis," Physica B (1992), 180 \& 181, pp. 597-600.
20. G. A. Jeffrey, J. R. Ruble, R. K. McMullan, J. A. Pople, "The crystal structure of deuterated benzene," Proceedings of the Royal Society of London. Series A, Mathematical and Physical Sciences, Vol. 414, No. 1846, (Nov. 9, 1987), pp. 47-57.
21. H. B. Burgi, S. C. Capelli, "Getting more out of crystal-structure analyses," Helvetica Chimica Acta, Vol. 86, (2003), pp. 1625-1640.

# Chapter 18 

## NATURE OF THE IONIC BOND OF ALKALI HYDRIDES AND HALIDES

## ALKALI-HYDRIDE CRYSTAL STRUCTURES

The alkali hydrides are lithium hydride ( $L i H$ ), sodium hydride ( NaH ), potassium hydride ( KH ), rubidium hydride ( RbH ), and cesium hydride ( CsH ). These saline or salt-like alkali-metal hydrides each comprise an equal number of alkali cations and hydride ions [1] in unit cells of a crystalline lattice. The crystal structure of these ionic compounds is the face-centered cubic NaCl structure [2]. This close-packed structure is expected since it gives the optimal approach of the positive and negative ions [3]. The structure comprises face-centered cubes of both $M^{+}$and $H^{-}$ions combined, but offset by half a unit cell length in one direction so that $M^{+}$ions are centered in the edges of the $H^{-}$lattice and vice versa. Each $M^{+}$is surrounded by six nearest neighbor $H^{-}$ions and vice versa. The resulting unit cell consists of anions (or cations) at the midpoint of each edge and at the center of the cell such that the unit cell contains four cations and four anions.

The interionic radius of each hydride can be derived by considering the radii of the alkali ion and the hydride ion, the electron energies at these radii, and the conditions for stability of the ions as the internuclear distance changes and the ions are mutually influenced by Coulombic forces. Then, the lattice energy is given by the sum over the crystal of the minimum energy of the interacting ion pairs at the radius of minimum approach for which the ions are stable. The sum is further over all Coulombic interactions of the ions of the crystal.

Each hydride $M H$ ( $M=L i, N a, K, R b, C s)$ is comprised of $M^{+}$and $H^{-}$ions. From Coulomb's Law, the lattice energy $\Delta U$ for point charges is given by the Born-Mayer equation [3]

$$
\begin{equation*}
\Delta U=N M_{c} Z_{+} Z_{-} \frac{e^{2}}{4 \pi \varepsilon_{0} r_{0}}\left(1-\frac{\rho}{r_{0}}\right) \tag{18.1}
\end{equation*}
$$

where $N$ is Avogadro's number, $M_{c}$ is the Madelung constant (the convergent sum of all Coulombic interactions of any given ion with the lattice of ions), $Z_{+}$and $Z_{-}$are the ionic charges in elementary charge units, $r_{0}$ is the distance between ion centers, and $\rho$ is a constant that corrects for higher-order terms (e.g. $1 / r_{0}^{6}$ to $1 / r_{0}^{12}$ terms) in repulsion between close neighbor ions. The $M-H$ distance can be calculated from the minimum energy packing of the ions, which is stable. Each ion is surrounded in a symmetrical octahedral field of six counterions. From Eq. (18.1), the lattice energy increases as the interionic distance decreases. But, the interionic distance cannot be the sum of the contact radii. This is easily appreciated by considering that the energies of the outer electron of $M^{+}$and the outer two electrons of $H^{-}$are very different. For sufficiently small interionic distances, the most energetic reaction that can occur which eliminates the cation and consequently the lattice energy is the following :

$$
\begin{equation*}
M^{+}+e^{-} \rightarrow M \tag{18.2}
\end{equation*}
$$

For shorter distances, the spherically symmetrical ${ }^{1} S_{0}$ state of the hydride ion is distorted by $M^{+}$, and it is not stable in the ionic crystal when the $M-H$ distance is given by the condition that the total Coulombic energy of attractive terms of $H^{-}$in the field of $M^{+}$as well as the repulsive terms between like-charged ions is equal to the binding energy of $M, B E(M)$, for the cations of the crystal. Then, the lattice energy is given by the product of Avogadro's number, $B E(M)$, and the Madelung constant which takes into account all inverse $r_{0}$ (point-like) Coulombic interactions of the crystal:

$$
\begin{equation*}
\Delta U=N M_{c} B E(M) \tag{18.3}
\end{equation*}
$$

Thus, $M_{c}$ is the factor of stability of forming the crystal from $M^{+}$and $H^{-}$ions. The value for the NaCl structure is $M_{c}=1.74756$ [3].

Since the Coulombic potential of the ions is equivalent to that of point charges with some higher order ion-ion-interaction repulsive terms, the $M-H$ distance $r_{0}(M H)$ given using Eq. (18.1), Eq. (18.3), and $B E(M)$ is:

$$
\begin{equation*}
r_{0}(M H)=\frac{\frac{Z_{+} Z_{-} e^{2}}{B E(M) 4 \pi \varepsilon_{0}}+\sqrt{\left(\frac{Z_{+} Z_{-} e^{2}}{B E(M) 4 \pi \varepsilon_{0}}\right)^{2}-\frac{4 \rho Z_{+} Z_{-} e^{2}}{B E(M) 4 \pi \varepsilon_{0}}}}{2} \tag{18.4}
\end{equation*}
$$

wherein $\rho=0.4 \times 10^{-10} \mathrm{~m}$ for alkali hydrides [4-5]. The parameters of the hydride ion are given in the corresponding section.

## LITHIUM HYDRIDE

The calculated ionic radii for $\mathrm{Li}^{+}$and $\mathrm{H}^{-}$ions given in Tables 7.1 and 7.2 are $0.35566 a_{0}$ and $1.8660 a_{0}$, respectively. But, the interionic distance cannot be the sum of the contact radii since the calculated ionization energies of $\mathrm{Li}^{+}$(Eqs. (7.35), (7.45-7.46), and (7.63)) and $H^{-}$(Eq. (7.69)) are 75.665 eV and 0.75471 eV , respectively. Furthermore, since the calculated ionization energy (Eq. (10.25)) of Li to $\mathrm{Li}^{+}$is 5.40381 eV as shown in Table 10.1 and the ionization energy (Eq. (7.69)) of $\mathrm{H}^{-}$to $H$ is $0.75471 \mathrm{eV}\left(1.20836 \times 10^{-19} \mathrm{~J}\right)$, for sufficiently small interionic distances, the lithium ion may be reduced.

Substitution of $B E(L i)=8.65786 \times 10^{-19} \mathrm{~J}$ into Eq. (18.3) gives the calculated lattice energy of
$\Delta U=N M_{c} B E(L i)=1.74756 N 8.65786 \times 10^{-19} \mathrm{~J}=911.1 \mathrm{~kJ} / \mathrm{mole}(217.8 \mathrm{kcal} / \mathrm{mole})$
This agrees well with the experimental lattice energy of $\Delta U=217.95 \mathrm{kcal} / \mathrm{mole}$ [1] and confirms that the ionic compound LiH comprises a precise packing of discrete ions.

The calculated radius of Li (Eq. (10.13)) given in Table 10.1 is $2.55606 a_{0}$, and the calculated binding energy is $5.40381 \mathrm{eV}\left(8.65786 \times 10^{-19} \mathrm{~J}\right)$ (Eq. (10.25)). The $L i-H$ distance, $r_{0}(L i H)$, calculated using Eq. (18.4) with the substitution of $B E(L i)=8.65786 \times 10^{-19} \mathrm{~J}$ is:

$$
\begin{equation*}
r_{0}(L i H)=2.17 \times 10^{-10} \mathrm{~m} \tag{18.6}
\end{equation*}
$$

The calculated $L i-H$ is in reasonable agreement with the experimental distance of $r_{0}(L i H)=2.04 X 10^{-10} \mathrm{~m}$ [1] given the experimental difficulty of performing X-ray diffraction on lithium and hydrogen due to the low electron densities. Furthermore, there is a $15 \%$ variation in experimental measurements of the density of LiH [1] that affects the internuclear spacing. Using the $\mathrm{Li}-\mathrm{H}$ distance and the calculated ionic radii, the lattice structure of LiH is shown in Figure 18.1A.

## SODIUM HYDRIDE

The calculated ionic radii for $\mathrm{Na}^{+}$and $\mathrm{H}^{-}$ions given in Tables 10.8 and 7.2 are $0.560945 a_{0}$ and $1.8660 a_{0}$, respectively. But, the interionic distance can not be the sum of the contact radii since the calculated ionization energies of $\mathrm{Na}^{+}$(Eqs. (10.21210.213)) and $H^{-}$(Eq. (7.69)) are 48.5103 eV and 0.75471 eV , respectively. Furthermore, since the calculated ionization energy (Eqs. (10.226-10.227)) of Na to $\mathrm{Na}^{+}$is 5.12592 eV as shown in Table 10.10 and the ionization energy (Eq. (7.69)) of $H^{-}$to $H$ is $0.75471 \mathrm{eV}\left(1.20836 \times 10^{-19} \mathrm{~J}\right)$, for sufficiently small interionic distances, the sodium ion may be reduced.

Substitution of $B E(N a)=8.21263 \times 10^{-19} J$ into Eq. (18.3) gives the calculated lattice energy of

$$
\begin{equation*}
\Delta U=N M_{c} B E(N a)=1.74756 N 8.21263 \times 10^{-19} \mathrm{~J}=864.3 \mathrm{~kJ} / \mathrm{mole}(206.6 \mathrm{kcal} / \mathrm{mole}) \tag{18.7}
\end{equation*}
$$

This agrees well with the experimental lattice energy of $\Delta U=202.0 \mathrm{kcal} / \mathrm{mole}$ [2] and confirms that the ionic compound NaH comprises a precise packing of discrete ions.

The calculated radius of Na (Eq. (10.226)) given in Table 10.10 is $2.65432 a_{0}$, and the calculated binding energy is $5.12592 \mathrm{eV}\left(8.21263 \times 10^{-19} \mathrm{~J}\right)$ (Eqs. (10.226-10.227)). The $N a-H$ distance, $r_{0}(N a H)$, calculated using Eq. (18.4) with the substitution of $B E(N a)=8.21263 \times 10^{-19} \mathrm{~J}$ is:

$$
\begin{equation*}
r_{0}(\mathrm{NaH})=2.33 \times 10^{-10} \mathrm{~m} \tag{18.8}
\end{equation*}
$$

The calculated $N a-H$ is in good agreement with the experimental distance of $r_{0}(N a H)=2.44 \times 10^{-10} \mathrm{~m}$ [2]. Using the $\mathrm{Na}-H$ distance and the calculated ionic radii, the lattice structure of $N a H$ is shown in Figure 18.1B.

Figure 18.1. The crystal structures of $M H$ all to the same scale. $\left(L i^{+}=\right.$green, $N a^{+}=$yellow, $K^{+}=$purple, and $H^{-}$and $H^{-}\left(\frac{1}{4}\right)=$ blue). (A) The crystal structure of LiH . (B) The crystal structure of NaH . (C) The crystal structure of KH . (D) The crystal structure of $K H\left(\frac{1}{4}\right)$.


## POTASSIUM HYDRIDE

The calculated ionic radii for $K^{+}$and $H^{-}$ions given in Tables 10.17 and 7.2 are $0.85215 a_{0}$ and $1.8660 a_{0}$, respectively. But, the interionic distance cannot be the sum of the contact radii since the calculated ionization energies of $\mathrm{K}^{+}$(Eqs. (10.39910.400)) and $\mathrm{H}^{-}$(Eq. (7.69)) are 31.9330 eV and 0.75471 eV , respectively. Furthermore, since the calculated ionization energy (Eqs. (10.414-10.415)) of $K$ to $K^{+}$is 4.33 eV as shown in Table 10.19 and the ionization energy (Eq. (7.69)) of $\mathrm{H}^{-}$to $H$ is $0.75471 \mathrm{eV}\left(1.20836 \times 10^{-19} \mathrm{~J}\right)$, for sufficiently small interionic distances, the potassium ion may be reduced.

Substitution of $B E(K)=6.93095 \times 10^{-19} J$ into Eq. (18.3) gives the calculated lattice energy of:

$$
\begin{equation*}
\Delta U=N M_{c} B E(K)=1.74756 \mathrm{~N} 6.93095 \times 10^{-19} \mathrm{~J}=729.4 \mathrm{~kJ} / \text { mole }(174.3 \mathrm{kcal} / \mathrm{mole}) \tag{18.9}
\end{equation*}
$$

This agrees well with the experimental lattice energy of $\Delta U=177.2 \mathrm{kcal} /$ mole [2] and confirms that the ionic compound $K H$ comprises a precise packing of discrete ions.

The calculated radius of $K$ (Eq. (10.414)) given in Table 10.19 is $3.14515 a_{0}$, and the calculated binding energy is $4.32596 \mathrm{eV}\left(6.93095 X 10^{-19} \mathrm{~J}\right)$ (Eqs. (10.414-10.415)). The $K-H$ distance, $r_{0}(K H)$, calculated using Eq. (18.4) with the substitution of $B E(K)=6.93095 \times 10^{-19} J$ is:

$$
\begin{equation*}
r_{0}(K H)=2.86 \times 10^{-10} \mathrm{~m} \tag{18.10}
\end{equation*}
$$

The calculated $K-H$ is in good agreement with the experimental distance of $r_{0}(K H)=2.85 \times 10^{-10} \mathrm{~m}$ [2]. Using the $K-H$ distance and the calculated ionic radii, the lattice structure of $K H$ is shown in Figure 18.1C. An aggregate crystal of unit cells is shown in Figure 18.2.

Figure 18.2. The crystal structure of $K H . \quad\left(K^{+}=\right.$purple and $H^{-}=$blue). (A) Opaque view showing the external geometrical crystal structure of an aggregate of unit cells of $K H$. (B) The crystal structure of $K H$ showing an aggregate of units cells.
A


B


## RUBIDIUM AND CESIUM HYDRIDE

As further tests of the boundary condition, the lattice energies of RbH and CsH are given by the product of Avogadro's number, the Madelung constant of $M_{c}=1.74756$, and the binding energy of $R b$ and $C s$ of 4.17713 eV and 3.89390 eV [6], respectively. Using Eq. (18.3), the calculated lattice energy of $R b H$ is:

$$
\begin{equation*}
\Delta U=1.74756 \mathrm{~N}(e 4.17713 \mathrm{eV})=704.3 \mathrm{~kJ} / \mathrm{mole}=168.3 \mathrm{kcal} / \mathrm{mole} \tag{18.11}
\end{equation*}
$$

This agrees well with the experimental lattice energy of $\Delta U=168.6 \mathrm{kcal} /$ mole [2] and confirms that the ionic compound RbH comprises a precise packing of discrete ions.

Substitution of $B E(R b)=6.6925 \times 10^{-19} J$ into Eq. (18.4) gives the $R b-H$ distance $r_{0}(R b H)$ :
$r_{0}(R b H)=2.99 X 10^{-10} \mathrm{~m}$
The calculated $R b-H$ is in good agreement with the experimental distance of $r_{0}(R b H)=3.02 \times 10^{-10} \mathrm{~m}$ [2].
Using Eq. (18.3), the calculated lattice energy of CsH is:

$$
\begin{equation*}
\Delta U=1.74756 \mathrm{~N}(e 3.89390 \mathrm{eV})=656.6 \mathrm{~kJ} / \mathrm{mole}=156.9 \mathrm{kcal} / \mathrm{mole} \tag{18.13}
\end{equation*}
$$

This agrees well with the experimental lattice energy of $\Delta U=154.46 \mathrm{kcal} / \mathrm{mole}$ [1] and $\Delta U=162.0 \mathrm{kcal} / \mathrm{mole}$ [2] and confirms that the ionic compound CsH comprises a precise packing of discrete ions.

Substitution of $B E(C s)=6.23872 \times 10^{-19} J$ into Eq. (18.4) gives the Cs $-H$ distance $r_{0}(C s H)$ :
$r_{0}(\mathrm{CsH})=3.24 \times 10^{-10} \mathrm{~m}$
The calculated $\mathrm{Cs}-\mathrm{H}$ is in good agreement with the experimental distance of $r_{0}(\mathrm{CsH})=3.19 \times 10^{-10} \mathrm{~m}$ [2].

## POTASSIUM HYDRINO HYDRIDE (KH $\left(\frac{1}{4}\right)$

The crystal structure of each alkali hydrino hydride $M H\left(\frac{1}{p}\right)$ is the same as that of the corresponding ordinary alkali hydride except that the radii of the hydride ions $H^{-}\left(\frac{1}{p}\right)$ are each a reciprocal integer times that of the ordinary hydride as given by Eq. (7.73). Thus, the lattice energy of $K H\left(\frac{1}{4}\right)$ is the same as that of $K H$ given by Eq. (18.9), and the $K-H\left(\frac{1}{4}\right)$ distance $r_{0}\left(K H\left(\frac{1}{4}\right)\right)$ is the same as that of $K H$ given by Eq. (18.10). Using the $K-H\left(\frac{1}{4}\right)$ distance (Eq. (18.10)), the radius of $K^{+}$ of $0.85215 a_{0}$ (Eq. (10.399)) and the radius of $H^{-}\left(\frac{1}{4}\right)$ of $\frac{1.8660}{4} a_{0}=0.4665 a_{0}$ (Eq. (7.73)), the lattice structure of $K H\left(\frac{1}{4}\right)$ is shown in Figure 18.1D.

## ALKALI-HALIDE CRYSTAL STRUCTURES

The alkali halides ( $M X$ ) are lithium, sodium, potassium, rubidium, and cesium cations, $M^{+}$, with fluoride, chloride, bromide, and iodide anions, $X^{-}$. These saline or salt-like alkali-metal halides each comprise an equal number of alkali cations and halide ions [3] in unit cells of a crystalline lattice. The crystal structure of these ionic compounds is the face-centered cubic NaCl structure except for $C s C l, C s B r$, and $C s I$ that have the $C s C l$ structure at ordinary temperatures and pressures [3]. These close-packed structures are expected since it gives the optimal approach of the positive and negative ions [3]. The NaCl structure comprises face-centered cubes of both $M^{+}$and $X^{-}$ions combined, but offset by half a unit cell length in one direction so that $M^{+}$ions are centered in the edges of the $X^{-}$lattice and vice versa. Each $M^{+}$is surrounded by six nearest neighbor $X^{-}$ ions and vice versa. The resulting unit cell consists of anions (or cations) at the midpoint of each edge and at the center of the cell such that the unit cell contains four cations and four anions. The CsCl structure comprises body-centered cubes of both $M^{+}$ and $X^{-}$ions wherein $M^{+}$is in the center of cubes of $X^{-}$and vice versa.

## ALKALI-HALIDE LATTICE PARAMETERS AND ENERGIES

The interionic radius of each alkali halide can be derived by considering the radii of the alkali ion and the halide ion, the electron energies at these radii, and the conditions for stability of the ions as the internuclear distance changes and the ions are mutually influenced by the Coulombic fields. Then, the lattice energy is given by the sum over the crystal of the minimum energy of the interacting ion pairs at the radius of minimum approach for which the ions are stable. The sum is further over all Coulombic interactions of the ions of the crystal.

As in the case with alkali hydrides, each alkali halide $M X(M=L i, N a, K, R b, C s$ and $X=F, C l, B r, I)$ is comprised of $M^{+}$and $X^{-}$ions. From Coulomb's law, the lattice energy $\Delta U$ for point charges is given by Eq. (18.1), the Born-Mayer equation. The $M-X$ distance can be calculated from the minimum energy packing of the ions, which is stable. Each ion of the NaCl and CsCl structure is surrounded in a symmetrical octahedral or cubic field of six or four counterions, respectively. From Eq. (18.1), the lattice energy increases as the interionic distance decreases. But, the interionic distance cannot be the sum of the contact radii. This is easily appreciated by considering that the energies of the outer electron of $M^{+}$and the outer electrons of $X^{-}$are very different. For sufficiently small interionic distances, the most energetic reaction that can occur which eliminates the cation and consequently the lattice energy is given by Eq. (18.2). For shorter distances, the spherically symmetrical ${ }^{1} S_{0}$ state of the halide ion is distorted by $M^{+}$, and it is not stable in the ionic crystal when the $M-X$ distance is sufficiently small. To first order, this distance is given by the condition that the total Coulombic energy of attractive terms of $X^{-}$in the field of $M^{+}$as well as the repulsive terms between like-charged ions is equal to the binding energy of $M, B E(M)$, for the cations of the crystal.

As in the case of the alkali hydrides, the lattice energies of alkali halides are determined by the binding energy of the corresponding metal atom. However, for each alkali halide an additional energy term arises corresponding to the effect of the electric field of the metal ion on the magnetic forces and energy of the halide ion. With the binding of the ions in both alkali hydrides and halides, the electric field lines of the metal ions end on those of the negative ions. But, each electron of the hydride ion occupies a symmetrically symmetrical $s$ orbital, and the electrons collectively comprise a filled $s$ shell only such that there is no dipole to interact with the external electric field of the positive ions. Whereas, the outer shell of the halide ions comprise $p$-orbital electrons having magnetic dipoles. These dipoles can interact with the external electric field having dipole components. Thus, the cation-anion separation in ionic compounds having electrons with magnetic dipole moments due to orbital angular momentum is dependent on the effect of the electric field on the magnetic forces of the anion.

Since the magnetic field is a relativistic effect of the electric field and the electron's charge, $e$, charge-to-mass ratio, $\frac{e}{m_{e}}$, angular momentum of $\hbar$, and the magnetic moment of $\mu_{B}$ are relativistically invariant, it is not surprising as shown in the Stark Effect section that the energy, $E_{\text {Stark }}$, of a one-electron atom in an electric field follows from that of a magnetic dipole in a magnetic field, Eqs. (2.68-2.69), with the magnetic dipole moment replaced by the electric dipole moment and the magnetic flux replaced by the electric field $\mathbf{E}_{\text {applied }}$. Thus, in alkali halides, the change in Coulombic lattice energy due to the Stark effect is given by the change in magnetic energy of the anion. The Stark-effect energy can be expressed in terms of the magnetic-dipole energy according to Eqs. (2.73-2.75):

$$
\begin{equation*}
E=\mu_{B} B \tag{18.15}
\end{equation*}
$$

The corresponding force $\mathbf{F}_{\text {Stark }}$ on the outer nth electron of the anion is given by Eqs. (7.27-7.31).

$$
\begin{equation*}
\mathbf{F}_{\text {Stark }}=\frac{1}{Z} \frac{\hbar^{2}}{m_{e} r_{n}^{3}} \sqrt{s(s+1)} \mathbf{i}_{r} \tag{18.16}
\end{equation*}
$$

From the radius change and the magnetic energy change, the Stark energy component $\Delta E$ (ionization; $X^{-}$) is calculated. Then, the lattice energy is given by the product of Avogadro's number, the Madelung constant which takes into account all inverse $r_{0}$ (point-like) Coulombic interactions of the crystal, and the sum of $B E(M)$, and $\Delta E$ (ionization; $X^{-}$):

$$
\begin{equation*}
\Delta U=N M_{c}\left(B E(M)+\Delta E\left(\text { ionization; } X^{-}\right)\right) \tag{18.17}
\end{equation*}
$$

Thus, $M_{c}$ is the factor of stability of forming the crystal from $M^{+}$and $X^{-}$ions. The values for the NaCl and CsCl structures are $M_{c}=1.74756$ and $M_{c}=1.76267$ [3], respectively.

Since the Coulombic potential of the ions is equivalent to that of point charges with some higher order ion-ion-interaction repulsive terms, the $M-X$ distance $r_{0}(M X)$ given using Eq. (18.1), Eq. (18.3), $B E(M)$ and $\Delta E$ (ionization; $X^{-}$) is:

$$
\begin{equation*}
r_{0}(M X)=\frac{\left.\frac{Z_{+} Z_{-} e^{2}}{\left(B E(M)+\Delta E\left(\text { ionization } ; X^{-}\right)\right) 4 \pi \varepsilon_{0}}+\sqrt{\left(\frac{Z_{+} Z_{-} e^{2}}{\left(B E(M)+\Delta E\left(\text { ionization; } X^{-}\right)\right) 4 \pi \varepsilon_{0}}\right.}\right)^{2}}{2} \tag{18.18}
\end{equation*}
$$

wherein $\rho=0.2 \times 10^{-10} \mathrm{~m}$ for alkali halides [5, 7]. The parameters of the gas-phase halide ions are derived next following the same procedure as that used to solve multielectron atoms.

## RADIUS AND IONIZATION ENERGY OF THE OUTER ELECTRON OF THE FLUORIDE ION

The fluoride atom comprises a nine-electron atom having a central charge of $Z=9$ times that of the proton. There are two indistinguishable spin-paired electrons in an atomic orbital with radii $r_{1}$ and $r_{2}$ both given by Eq. (7.35) (Eq. (10.51)), two indistinguishable spin-paired electrons in an atomic orbital with radii $r_{3}$ and $r_{4}$ both given by Eq. (10.62), and two sets of paired and an unpaired electron in an atomic orbital at $r_{9}$ given by Eq. (10.182). The next electron which binds to form the corresponding ten-electron fluoride ion is attracted by the net magnetic force between the pairing (electron 10) and unpaired (electron 9) to form three pairs of electrons of opposite spin in $p_{x}, p_{y}$, and $p_{z}$ orbitals of an atomic orbital at the same radius $r_{10}$. The resulting electron configuration is $1 s^{2} 2 s^{2} 2 p^{6}$, and the orbital arrangement is:

\[

\]

corresponding to the ground state ${ }^{1} S_{0}$.

Unlike the case of the hydride ion comprising a filled $s$ shell only, the outer shell of the fluoride ion comprises additional orbitals to the one filled by the electron which binds to form the negative ion. The forces are purely magnetic in order to maintain the boundary conditions of an equipotential minimum energy for electrons of the additional orbitals. Thus, the central Coulomb force acts on the outer electron to cause it to bind wherein this electric force on the outer-most electron due to the nucleus and the inner nine electrons is given by Eq. (10.70) with the appropriate charge and radius:

$$
\begin{equation*}
\mathbf{F}_{e l e}=\frac{(Z-9) e^{2}}{4 \pi \varepsilon_{0} r_{10}^{2}} \mathbf{i}_{\mathbf{r}}=0 \tag{18.20}
\end{equation*}
$$

for $r>r_{9}$ with $Z=9$.
As in the case with the closed-shell $s$ orbitals, the spin-pairing force $\mathbf{F}_{\text {mag }}$ between electron 9 and electron 10 given by Eq. (7.24) is:

$$
\begin{equation*}
\mathbf{F}_{\operatorname{mag}}=\frac{1}{Z} \frac{\hbar^{2}}{m_{e} r_{10}^{3}} \sqrt{s(s+1)} \mathbf{i}_{\mathbf{r}} \tag{18.21}
\end{equation*}
$$

Due to the spin-pairing force the diamagnetic forces and paramagnetic forces are altered relative to those of the isoelectronic neon atom. The energy of the fluoride ion is minimized and the angular momentum is conserved with the pairing of electron ten to fill the $2 p_{y}$ orbital. Then, the orbital angular momentum of each set of the $2 p_{x}$ and $p_{z}$ spin-paired electrons give rise to the diamagnetic force (Eq. (10.82)), $\mathbf{F}_{\text {diamagnetic }}$ :

$$
\begin{equation*}
\mathbf{F}_{\text {diamagnetic }}=-\left(\frac{1}{3}+\frac{2}{3}\right) \frac{\hbar^{2}}{4 m_{e} r_{10}^{2} r_{3}} \sqrt{s(s+1)} \mathbf{i}_{\mathbf{r}}=-\frac{\hbar^{2}}{4 m_{e} r_{10}^{2} r_{3}} \sqrt{s(s+1)} \mathbf{i}_{\mathbf{r}} \tag{18.22}
\end{equation*}
$$

From Eq. (10.84), $\mathbf{F}_{\text {mag } 2}$ due to spin and orbital angular momentum is:

$$
\begin{equation*}
\mathbf{F}_{\operatorname{mag} 2}=\frac{1}{Z} \frac{4 \hbar^{2}}{m_{e} r_{10}^{2} r_{3}} \sqrt{s(s+1)} \mathbf{i}_{\mathbf{r}} \tag{18.23}
\end{equation*}
$$

The outward centrifugal force on electron 10 is balanced by the electric force and the magnetic forces (on electron 10). The radius of the outer electron is calculated by equating the outward centrifugal force to the sum of the electric (Eq. (18.20)), diamagnetic (Eq. (18.22)), and paramagnetic (Eqs. (18.21) and (18.23)) forces as follows:

$$
\begin{equation*}
\frac{m_{e} v_{10}^{2}}{r_{10}}=\frac{(Z-9) e^{2}}{4 \pi \varepsilon_{0} r_{10}^{2}}-\frac{\hbar^{2}}{4 m_{e} r_{10}^{2} r_{3}} \sqrt{s(s+1)}+\frac{4 \hbar^{2}}{Z m_{e} r_{10}^{2} r_{3}} \sqrt{s(s+1)}+\frac{\hbar^{2}}{Z m_{e} r_{10}^{3}} \sqrt{s(s+1)} \tag{18.24}
\end{equation*}
$$

Substitution of $v_{10}=\frac{\hbar}{m_{e} r_{10}}$ (Eq. (1.35)), $Z=9$, and $s=\frac{1}{2}$ into Eq. (18.24) gives:

$$
\begin{equation*}
\frac{\hbar^{2}}{m_{e} r_{10}^{3}}=-\frac{\hbar^{2}}{4 m_{e} r_{10}^{2} r_{3}} \sqrt{\frac{3}{4}}+\frac{4 \hbar^{2}}{9 m_{e} r_{10}^{2} r_{3}} \sqrt{\frac{3}{4}}+\frac{\hbar^{2}}{9 m_{e} r_{10}^{3}} \sqrt{\frac{3}{4}} \tag{18.25}
\end{equation*}
$$

$$
\begin{equation*}
r_{10}=\frac{\frac{\hbar^{2}}{m_{e}}\left(1-\frac{\sqrt{\frac{3}{4}}}{9}\right)}{-\frac{\hbar^{2}}{4 m_{e} r_{3}} \sqrt{\frac{3}{4}}+\frac{4 \hbar^{2}}{9 m_{e} r_{3}} \sqrt{\frac{3}{4}}} \tag{18.26}
\end{equation*}
$$

$$
\begin{equation*}
r_{10}=\frac{a_{0}\left(1-\frac{\sqrt{\frac{3}{4}}}{9}\right)}{(4} 1-\sqrt{\frac{3}{4}}, r_{3} \text { in units of } a_{0} \tag{18.27}
\end{equation*}
$$

$$
\left(\frac{4}{9}-\frac{1}{4}\right) \frac{\sqrt{\frac{-}{4}}}{r_{3}}
$$

Substitution of $\frac{r_{3}}{a_{0}}=0.51382$ (Eq. (10.62)) into Eq. (18.27) gives:

$$
\begin{equation*}
r_{10}=2.75769 a_{0} \tag{18.28}
\end{equation*}
$$

The ionization energy of the fluoride ion is given by the magnetic energy of the outer electron calculated by integrating the sum of the diamagnetic (Eq. (18.22)) and paramagnetic (Eqs. (18.21) and (18.23)) forces from $r_{10}$ to $\infty$ :

$$
\begin{equation*}
E_{\text {magwork }}=-\int_{r_{10}}^{\infty}-\frac{\hbar^{2}}{4 m_{e} r_{10}^{2} r_{3}} \sqrt{\frac{3}{4}}+\frac{4 \hbar^{2}}{Z m_{e} r_{10}^{2} r_{3}} \sqrt{\frac{3}{4}}+\frac{\hbar^{2}}{Z m_{e} r_{10}^{3}} \sqrt{\frac{3}{4}} d r=\frac{\hbar^{2} \sqrt{\frac{3}{4}}}{m_{e} r_{10}}\left(\left(\frac{4}{Z}-\frac{1}{4}\right) \frac{1}{r_{3}}+\frac{1}{2 Z r_{10}}\right) \tag{18.29}
\end{equation*}
$$

Eq. (18.29) with $r_{3}=0.51382 a_{0}$ (Eq. (10.62)), $r_{10}=2.75769 a_{0}$ (Eq. (18.28)), and $Z=9$ gives:

$$
\begin{equation*}
E\left(\text { ionization; } F^{-}\right)=3.40603 \mathrm{eV} \tag{18.30}
\end{equation*}
$$

The experimental ionization energy of the fluoride ion is [8] :

$$
\begin{equation*}
E\left(\text { ionization } ; F^{-}\right)=3.4011895 \mathrm{eV} \tag{18.31}
\end{equation*}
$$

## RADIUS AND IONIZATION ENERGY OF THE OUTER ELECTRON OF THE CHLORIDE ION

The chlorine atom comprises a seventeen-electron atom having a central charge of $Z=17$ times that of the proton. There are two indistinguishable spin-paired electrons in an atomic orbital with radii $r_{1}$ and $r_{2}$ both given by Eq. (7.35) (Eq. (10.51)), two indistinguishable spin-paired electrons in an atomic orbital with radii $r_{3}$ and $r_{4}$ both given by Eq. (10.62), three sets of paired electrons in an atomic orbital at $r_{10}$ given by Eq. (10.212), two indistinguishable spin-paired electrons in an atomic orbital with radii $r_{11}$ and $r_{12}$ both given by Eq. (10.255), and two sets of paired and an unpaired electron in an atomic orbital with radius $r_{17}$ given by Eq. (10.363). The next electron which binds to form the corresponding eighteen-electron chloride ion is attracted by the net magnetic force between the pairing (electron 18) and unpaired (electron 17) to form three pairs of electrons of opposite spin in $p_{x}, p_{y}$, and $p_{z}$ orbitals of an atomic orbital at the same radius $r_{18}$. The resulting electron configuration is $1 s^{2} 2 s^{2} 2 p^{6} 3 s^{2} 3 p^{6}$, and the orbital arrangement is: 3p state

corresponding to the ground state ${ }^{1} S_{0}$.
Unlike the case of the hydride ion, the outer shell of the chloride ion comprises additional orbitals to the one filled by the electron which binds to form the negative ion. The forces are purely magnetic in order to maintain the boundary conditions of an equipotential minimum energy for electrons of the additional orbitals. Thus, the central Coulomb force acts on the outer electron to cause it to bind wherein this electric force on the outer-most electron due to the nucleus and the inner seventeen electrons is given by Eq. (10.70) with the appropriate charge and radius:

$$
\begin{equation*}
\mathbf{F}_{\text {ele }}=\frac{(Z-17) e^{2}}{4 \pi \varepsilon_{0} r_{18}^{2}} \mathbf{i}_{\mathbf{r}}=0 \tag{18.33}
\end{equation*}
$$

for $r>r_{17}$ with $Z=17$.
As in the case with the closed-shell $s$ orbitals, the spin-pairing force $\mathbf{F}_{\text {mag }}$ between electron 18 and electron 17 given by Eq. (7.24) is

$$
\begin{equation*}
\mathbf{F}_{\operatorname{mag}}=\frac{1}{Z} \frac{\hbar^{2}}{m_{e} r_{18}^{3}} \sqrt{s(s+1)} \mathbf{i}_{\mathbf{r}} \tag{18.34}
\end{equation*}
$$

Due to the spin-pairing force the diamagnetic forces and paramagnetic forces are altered relative to those of the isoelectronic argon atom. The energy of the chloride ion is minimized and the angular momentum is conserved with the pairing of electron eighteen to fill the $3 p_{y}$ orbital when the orbital angular momentum of each set of the $p_{x}, p_{y}$, and $p_{z}$ spin-paired electrons add negatively to cancel. Then, the diamagnetic force (Eq. (10.82)), $\mathbf{F}_{\text {diamagnetic }}$, is zero as in the case of the closed- $p$ shell atom neon:

$$
\begin{equation*}
\mathbf{F}_{\text {diamagnetic }}=0 \tag{18.35}
\end{equation*}
$$

The orbital angular momentum of each set of the $3 p_{x}$ and $p_{z}$ spin-paired electrons and the spin and orbital angular momentum of electrons 17 and 18 that pair upon the binding to fill the $3 p_{y}$ shell give rise to the magnetic force $\mathbf{F}_{\text {mag } 2}$ with the corresponding contributions given by Eqs. (10.83) and (10.84), respectively:

$$
\begin{equation*}
\mathbf{F}_{\text {mag } 2}=(1+1) \frac{1}{Z} \frac{\hbar^{2}}{m_{e} r_{18}^{2} r_{12}} \sqrt{s(s+1)} \mathbf{i}_{\mathbf{r}}+\frac{1}{Z} \frac{4 \hbar^{2}}{m_{e} r_{18}^{2} r_{12}} \sqrt{s(s+1)} \mathbf{i}_{\mathrm{r}}=\frac{1}{Z} \frac{6 \hbar^{2}}{m_{e} r_{18}^{2} r_{12}} \sqrt{s(s+1)} \mathbf{i}_{\mathbf{r}} \tag{18.36}
\end{equation*}
$$

The outward centrifugal force on electron 18 is balanced by the electric force and the magnetic forces (on electron 18). The radius of the outer electron is calculated by equating the outward centrifugal force to the sum of the electric (Eq. (18.33)), diamagnetic (Eq. (18.35)), and paramagnetic (Eqs. (18.34) and (18.36)) forces as follows:

$$
\begin{equation*}
\frac{m_{e} v_{18}^{2}}{r_{18}}=\frac{(Z-17) e^{2}}{4 \pi \varepsilon_{0} r_{18}^{2}}+\frac{6 \hbar^{2}}{Z m_{e} r_{18}^{2} r_{12}} \sqrt{s(s+1)}+\frac{\hbar^{2}}{Z m_{e} r_{18}^{3}} \sqrt{s(s+1)} \tag{18.37}
\end{equation*}
$$

Substitution of $v_{18}=\frac{\hbar}{m_{e} r_{18}}$ (Eq. (1.35)), $Z=17$, and $s=\frac{1}{2}$ into Eq. (18.37) gives:

$$
\begin{align*}
& \frac{\hbar^{2}}{m_{e} r_{18}^{3}}=\frac{6 \hbar^{2}}{17 m_{e} r_{18}^{2} r_{12}} \sqrt{\frac{3}{4}}+\frac{\hbar^{2}}{17 m_{e} r_{18}^{3}} \sqrt{\frac{3}{4}}  \tag{18.38}\\
& r_{18}=\frac{\frac{\hbar^{2}}{m_{e}}\left(1-\frac{\sqrt{\frac{3}{4}}}{17}\right)}{\frac{6 \hbar^{2}}{17 m_{e} r_{12}} \sqrt{\frac{3}{4}}}  \tag{18.39}\\
& r_{18}=\frac{a_{0}\left(1-\frac{\sqrt{\frac{3}{4}}}{17}\right)}{6 \sqrt{\frac{3}{4}}}, r_{12} \text { in units of } a_{0}  \tag{18.40}\\
& 17 r_{12}
\end{align*}
$$

Substitution of $\frac{r_{12}}{a_{0}}=0.86545$ (Eq. (10.255)) into Eq. (18.40) gives:

$$
\begin{equation*}
r_{18}=2.68720 a_{0} \tag{18.41}
\end{equation*}
$$

The ionization energy of the chloride ion is given by the magnetic energy of the outer electron calculated by integrating the sum of the diamagnetic (Eq. (18.35)) and paramagnetic (Eqs. (18.34) and (18.36)) forces from $r_{18}$ to $\infty$ :

$$
\begin{equation*}
E_{\text {magwork }}=-\int_{r_{18}}^{\infty} \frac{6 \hbar^{2}}{Z m_{e} r_{18}^{2} r_{12}} \sqrt{\frac{3}{4}}+\frac{\hbar^{2}}{Z m_{e} r_{18}^{3}} \sqrt{\frac{3}{4}} d r=\frac{\hbar^{2} \sqrt{\frac{3}{4}}}{Z m_{e} r_{18}}\left(\frac{6}{r_{12}}+\frac{1}{2 r_{18}}\right) \tag{18.42}
\end{equation*}
$$

Eq. (18.42) with $r_{12}=0.86545 a_{0}$ (Eq. (10.255)), $r_{18}=2.68720 a_{0}$ (Eq. (18.41)), and $Z=17$ gives:

$$
\begin{equation*}
\text { E(ionization; } \left.\mathrm{Cl}^{-}\right)=3.67238 \mathrm{eV} \tag{18.43}
\end{equation*}
$$

The experimental ionization energy of the chloride ion is [8]:

$$
\begin{equation*}
\text { E(ionization; } \left.\mathrm{Cl}^{-}\right)=3.612724 \mathrm{eV} \tag{18.44}
\end{equation*}
$$

## CHANGE IN THE RADIUS AND IONIZATION ENERGY OF THE FLUORIDE ION DUE TO THE ION FIELD

As in the case of the alkali hydrides, the lattice energies of alkali halides are equivalent to the binding energy of the corresponding metal atom, except for an additional energy term corresponding to the Stark effect of the metal ion on the magnetic forces and energy of the halide ion. The corresponding force $\mathbf{F}_{\text {stark }}$ on the outer electron of the fluoride ion given by Eq. (18.16) is

$$
\begin{equation*}
\mathbf{F}_{\text {Stark }}=\frac{1}{Z} \frac{\hbar^{2}}{m_{e} r_{10}^{3}} \sqrt{s(s+1)} \mathbf{i}_{r} \tag{18.45}
\end{equation*}
$$

Then, the outward centrifugal force on electron 10 is balanced by the electric force and the magnetic forces (on electron 10). The radius of the outer electron is calculated by equating the outward centrifugal force to the sum of the electric (Eq. (18.20)), diamagnetic (Eq. (18.22)), and paramagnetic (Eqs. (18.21), (18.23), and (18.45)) forces as follows:

$$
\begin{equation*}
\frac{m_{e} v_{10}^{2}}{r_{10}}=\frac{(Z-9) e^{2}}{4 \pi \varepsilon_{0} r_{10}^{2}}-\frac{\hbar^{2}}{4 m_{e} r_{10}^{2} r_{3}} \sqrt{s(s+1)}+\frac{4 \hbar^{2}}{Z m_{e} r_{10}^{2} r_{3}} \sqrt{s(s+1)}+\frac{2 \hbar^{2}}{Z m_{e} r_{10}^{3}} \sqrt{s(s+1)} \tag{18.46}
\end{equation*}
$$

Substitution of $v_{10}=\frac{\hbar}{m_{e} r_{10}}$ (Eq. (1.35)), $Z=9$, and $s=\frac{1}{2}$ into Eq. (18.46) gives:

$$
\begin{equation*}
r_{10}=\frac{a_{0}\left(1-\frac{2 \sqrt{\frac{3}{4}}}{9}\right)}{\left(\frac{4}{9}-\frac{1}{4}\right) \frac{\sqrt{\frac{3}{4}}}{r_{3}}}, r_{3} \text { in units of } a_{0} \tag{18.47}
\end{equation*}
$$

Substitution of $\frac{r_{3}}{a_{0}}=0.51382$ (Eq. (10.62)) into Eq. (18.47) gives:

$$
\begin{equation*}
r_{10}=2.46408 a_{0} \tag{18.48}
\end{equation*}
$$

The ionization energy of the fluoride ion is given by the magnetic energy of the outer electron calculated by integrating the sum of the diamagnetic (Eq. (18.22)) and paramagnetic (Eqs. (18.21), (18.23), and (18.45)) forces from $r_{10}$ to $\infty$ :

$$
\begin{equation*}
E_{\text {magwork }}=-\int_{r_{10}}^{\infty}-\frac{\hbar^{2}}{4 m_{e} r_{10}^{2} r_{3}} \sqrt{\frac{3}{4}}+\frac{4 \hbar^{2}}{Z m_{e} r_{10}^{2} r_{3}} \sqrt{\frac{3}{4}}+\frac{2 \hbar^{2}}{Z m_{e} r_{10}^{3}} \sqrt{\frac{3}{4}} d r=\frac{\hbar^{2} \sqrt{\frac{3}{4}}}{m_{e} r_{10}}\left(\left(\frac{4}{Z}-\frac{1}{4}\right) \frac{1}{r_{3}}+\frac{1}{Z r_{10}}\right) \tag{18.49}
\end{equation*}
$$

Eq. (18.49) with $r_{3}=0.51382 a_{0}$ (Eq. (10.62)), $r_{10}=2.46408 a_{0}$ (Eq. (18.48)), and $Z=9$ gives:
$E\left(\right.$ ionization; $\left.F^{-}\right)=4.05046 \mathrm{eV}$
The energy change of the fluoride ion $\Delta E$ (ionization; $F^{-}$) due to the Stark effect is given by the difference between Eqs. (18.50) and (18.30):
$\Delta E\left(\right.$ ionization; $\left.F^{-}\right)=4.05046 \mathrm{eV}-3.40603 \mathrm{eV}=0.64444 \mathrm{eV}$

## CHANGE IN THE RADIUS AND IONIZATION ENERGY OF THE CHLORIDE ION DUE TO THE ION FIELD

Similar to the case of the alkali fluorides, the lattice energies of alkali chlorides are equivalent to the binding energy of the corresponding metal atom, except for those cases where there is an additional energy term corresponding to the Stark effect of the metal ion on the magnetic forces and energy of the chloride ion. The selection rules for the Stark effect in one-electron atoms given by Eq. (2.78) is:

$$
\begin{align*}
n & =1,2,3,4, \ldots \\
\ell & =n-1 \\
m_{\ell} & =-\ell,-\ell+1, \ldots, 0, \ldots,+\ell  \tag{18.52}\\
m_{s} & = \pm \frac{1}{2}
\end{align*}
$$

The corresponding energies are given in Table 2.3. For fluoride having an outer 2 p shell:

$$
\begin{equation*}
m_{\ell}=1 \tag{18.53}
\end{equation*}
$$

corresponding to the force $\mathbf{F}_{\text {Stark }}$ on the outer electron of the fluoride ion given by Eq. (18.45) and the binding energy change $\Delta E$ (ionization; $F^{-}$) given by Eq. (18.50).
In the case of the chloride ion, the outer shell is $3 p$. For cations having an outer filled $n s$ or $n p ; n<3$ shell, the interaction of the $3 p$ and $2 p$ shells of $\mathrm{Cl}^{-}$due to the field of the cation gives rise to a diamagnetic Stark force $\mathbf{F}_{\text {Stark }}$ corresponding to the selection rule:

$$
\begin{equation*}
m_{\ell}=-1 \tag{18.54}
\end{equation*}
$$

wherein the cation's electrons cannot compensate for the diamagnetism by changing orientation. Thus, for $\mathrm{Li}^{+}$and $\mathrm{Na}^{+}$

$$
\begin{equation*}
\mathbf{F}_{\text {Stark }}=-\frac{1}{Z} \frac{\hbar^{2}}{m_{e} r_{18}^{3}} \sqrt{s(s+1)} \mathbf{i}_{r} \tag{18.55}
\end{equation*}
$$

and for $\mathrm{K}^{+}, \mathrm{Rb}^{+}$, and $\mathrm{Cs}^{+}$with ns or $n p ; n \geq 3$

$$
\begin{equation*}
\mathbf{F}_{\text {Stark }}=0 \tag{18.56}
\end{equation*}
$$

Then, the outward centrifugal force on electron 18 is balanced by the electric force and the magnetic forces (on electron 18). The radius of the outer electron is calculated by equating the outward centrifugal force to the sum of the electric (Eq. (18.33)), diamagnetic (Eq. (18.35)), and paramagnetic (Eqs. (18.34), (18.36), and (18.55)) forces as follows:

$$
\begin{equation*}
\frac{m_{e} v_{18}^{2}}{r_{18}}=\frac{(Z-17) e^{2}}{4 \pi \varepsilon_{0} r_{18}^{2}}+\frac{6 \hbar^{2}}{Z m_{e} r_{18}^{2} r_{12}} \sqrt{s(s+1)} \tag{18.57}
\end{equation*}
$$

Substitution of $v_{18}=\frac{\hbar}{m_{e} r_{18}}$ (Eq. (1.35)), $Z=17$, and $s=\frac{1}{2}$ into Eq. (18.57) gives:

$$
\begin{equation*}
r_{18}=\frac{a_{0}}{\frac{6 \sqrt{\frac{3}{4}}}{17 r_{12}}}, r_{12} \text { in units of } a_{0} \tag{18.58}
\end{equation*}
$$

Substitution of $\frac{r_{12}}{a_{0}}=0.86545$ (Eq. (10.255)) into Eq. (18.58) gives:

$$
\begin{equation*}
r_{18}=2.83145 a_{0} \tag{18.59}
\end{equation*}
$$

The ionization energy of the chloride ion is given by the magnetic energy of the outer electron calculated by integrating the sum of the diamagnetic (Eq. (18.35)) and paramagnetic (Eqs. (18.34), (18.36), and (18.55)) forces from $r_{18}$ to $\infty$ :

$$
\begin{equation*}
E_{\text {magwork }}=-\int_{r_{18}}^{\infty} \frac{6 \hbar^{2}}{Z m_{e} r_{18}^{2} r_{12}} \sqrt{\frac{3}{4}} d r=\frac{6 \hbar^{2} \sqrt{\frac{3}{4}}}{Z m_{e} r_{18} r_{12}} \tag{18.60}
\end{equation*}
$$

Eq. (18.60) with $r_{12}=0.86545 a_{0}$ (Eq. (10.255)), $r_{18}=2.83145 a_{0}$ (Eq. (18.59)), and $Z=17$ gives:
$E\left(\right.$ ionization; $\left.\mathrm{Cl}^{-}\right)=3.39420 \mathrm{eV}$
For $\mathrm{Li}^{+}$and $\mathrm{Na}^{+}$chlorides, the energy change of the chloride ion $\Delta E$ (ionization; $\mathrm{Cl}^{-}$) due to the Stark effect is given by the difference between Eqs. (18.61) and (18.43).
$\Delta E\left(\right.$ ionization; $\left.\mathrm{Cl}^{-}\right)=3.39420 \mathrm{eV}-3.67238 \mathrm{eV}=-0.27818 \mathrm{eV}$

## LITHIUM FLUORIDE

The calculated ionic radii for $\mathrm{Li}^{+}$and $F^{-}$ions in $L i F$ given by Eqs. (10.49) and (18.48) are $0.35566 a_{0}$ and $2.46408 a_{0}$, respectively. But, the interionic distance cannot be the sum of the contact radii since the calculated ionization energies of $\mathrm{Li}^{+}$ (Eqs. (7.35), (7.45-7.46), and (7.63)) and $F^{-}$(Eq. (18.50)) are 75.665 eV and 4.05046 eV , respectively. Furthermore, since the calculated ionization energy (Eq. (10.25)) of Li to $\mathrm{Li}^{+}$is 5.40381 eV as shown in Table 10.1 and the ionization energy (Eq. (18.50)) of $F^{-}$to $F$ is 4.05046 eV , for sufficiently small interionic distances, the lithium ion may be reduced.

Substitution of $B E(L i)=8.65786 \times 10^{-19} \mathrm{~J}$ and $\Delta E$ (ionization; $\left.F^{-}\right)=0.64444 \mathrm{eV}\left(1.03251 \mathrm{X} 10^{-19} \mathrm{~J}\right)$ (Eq. (18.51)) into Eq. (18.17) gives the calculated lattice energy of:

$$
\begin{align*}
\Delta U & =N M_{c}\left(B E(L i)+\Delta E\left(\text { ionization } ; F^{-}\right)\right) \\
& =1.74756 \mathrm{~N}\left(8.65786 \times 10^{-19} \mathrm{~J}+1.03251 \times 10^{-19} \mathrm{~J}\right)  \tag{18.63}\\
& =1019.8 \mathrm{~kJ} / \mathrm{mole}(243.7 \mathrm{kcal} / \mathrm{mole})
\end{align*}
$$

This agrees well with the experimental lattice energy of $\Delta U=250.7 \mathrm{kcal} /$ mole [9] and confirms that the ionic compound LiF comprises a precise packing of discrete ions.

The $L i-F$ distance, $r_{0}(L i F)$, calculated using Eq. (18.18) with the substitution of $B E(L i)=8.65786 X 10^{-19} \mathrm{~J}$ and $\Delta E\left(\right.$ ionization $\left.; F^{-}\right)=1.03251 \times 10^{-19} \mathrm{~J}$ is:

$$
\begin{equation*}
r_{0}(L i F)=2.16 \times 10^{-10} \mathrm{~m} \tag{18.64}
\end{equation*}
$$

The calculated $L i-F$ is in reasonable agreement with the experimental distance of $r_{0}(L i F)=2.01 \times 10^{-10} \mathrm{~m}$ [10]. Using the $L i-F$ distance and the calculated ionic radii, the lattice structure of $L i F$ is shown in Figure 18.3A.

## SODIUM FLUORIDE

The calculated ionic radii for $\mathrm{Na}^{+}$and $\mathrm{F}^{-}$ions in NaF given by Eqs. (10.212) and (18.48) are $0.560945 a_{0}$ and $2.46408 a_{0}$, respectively. But, the interionic distance cannot be the sum of the contact radii since the calculated ionization energies of $\mathrm{Na}^{+}$ (Eqs. (10.212-10.213)) and $F^{-}$(Eq. (18.50)) are 48.5103 eV and 4.05046 eV , respectively. Furthermore, since the calculated ionization energy (Eqs. (10.226-10.227)) of Na to $\mathrm{Na}^{+}$is 5.12592 eV as shown in Table 10.10 and the ionization energy (Eq. (18.50)) of $F^{-}$to $F$ is 4.05046 eV , for sufficiently small interionic distances, the sodium ion may be reduced.

Substitution of $B E(N a)=8.21263 \times 10^{-19} J$ and $\Delta E$ (ionization; $F^{-}$) $=1.03251 \times 10^{-19} J$ (Eq. (18.51)) into Eq. (18.17) gives the calculated lattice energy of:

$$
\begin{align*}
\Delta U & =N M_{c}\left(B E(N a)+\Delta E\left(\text { ionization } ; F^{-}\right)\right) \\
& =1.74756 \mathrm{~N}\left(8.21263 \times 10^{-19} \mathrm{~J}+1.03251 \times 10^{-19} \mathrm{~J}\right)  \tag{18.65}\\
& =972.95 \mathrm{~kJ} / \mathrm{mole}(232.54 \mathrm{kcal} / \mathrm{mole})
\end{align*}
$$

This agrees well with the experimental lattice energy of $\Delta U=222 \mathrm{kcal} /$ mole [9] and confirms that the ionic compound NaF comprises a precise packing of discrete ions.

The $N a-F$ distance, $r_{0}(N a F)$, calculated using Eq. (18.18) with the substitution of $B E(N a)=8.21263 \times 10^{-19} \mathrm{~J}$ and $\Delta E\left(\right.$ ionization; $\left.F^{-}\right)=1.03251 \times 10^{-19} \mathrm{~J}$ is:

$$
\begin{equation*}
r_{0}(N a F)=2.28 \times 10^{-10} \mathrm{~m} \tag{18.66}
\end{equation*}
$$

The calculated $N a-F$ is in reasonable agreement with the experimental distance of $r_{0}(N a F)=2.32 \times 10^{-10} \mathrm{~m}$ [10]. Using the $N a-F$ distance and the calculated ionic radii, the lattice structure of $N a F$ is shown in Figure 18.3B.

Figure 18.3. The crystal structures of $M F$ all to the same scale. $\left(\mathrm{Li}^{+}=\right.$green, $\mathrm{Na}^{+}=$yellow, $\mathrm{K}^{+}=$purple, $\mathrm{Rb}^{+}=\mathrm{blue}, \mathrm{Cs}^{+}=$ red, and $F^{-}=$gold). (A) The crystal structure of LiF . (B) The crystal structure of NaF . (C) The crystal structure of KF . (D) The crystal structure of $R b F$. (E) The crystal structure of CsF .


## POTASSIUM FLUORIDE

The calculated ionic radii for $K^{+}$and $F^{-}$ions in $K F$ given by Eqs. (10.399) and (18.48) are $0.85215 a_{0}$ and $2.46408 a_{0}$, respectively. But, the interionic distance cannot be the sum of the contact radii since the calculated ionization energies of $K^{+}$ (Eqs. (10.399-10.400)) and $F^{-}$(Eq. (18.50)) are 31.9330 eV and 4.05046 eV , respectively. Furthermore, since the calculated ionization energy (Eqs. (10.414-10.415)) of $K$ to $K^{+}$is 4.33 eV as shown in Table 10.19 and the ionization energy (Eq. (18.50)) of $F^{-}$to $F$ is 4.05046 eV , for sufficiently small interionic distances, the potassium ion may be reduced.

Substitution of $B E(K)=6.93095 \times 10^{-19} J$ and $\Delta E$ (ionization; $F^{-}$) $=1.03251 \times 10^{-19} \mathrm{~J}$ (Eq. (18.51)) into Eq. (18.17) gives the calculated lattice energy of:

$$
\begin{align*}
\Delta U & =N M_{c}\left(B E(K)+\Delta E\left(\text { ionization } ; F^{-}\right)\right) \\
& =1.74756 \mathrm{~N}\left(6.93095 \times 10^{-19} \mathrm{~J}+1.03251 \times 10^{-19} \mathrm{~J}\right)  \tag{18.67}\\
& =838.06 \mathrm{~kJ} / \text { mole }(200.30 \mathrm{kcal} / \text { mole })
\end{align*}
$$

This agrees well with the experimental lattice energy of $\Delta U=198 \mathrm{kcal} /$ mole [9] and confirms that the ionic compound $K F$ comprises a precise packing of discrete ions.

The $K-F$ distance, $r_{0}(K F)$, calculated using Eq. (18.18) with the substitution of $B E(K)=6.93095 X 10^{-19} \mathrm{~J}$ and $\Delta E$ (ionization; $F^{-}$) $=1.03251 \times 10^{-19} \mathrm{~J}$ is:

$$
\begin{equation*}
r_{0}(K F)=2.68 \times 10^{-10} \mathrm{~m} \tag{18.68}
\end{equation*}
$$

The calculated $K-F$ is in reasonable agreement with the experimental distance of $r_{0}(K F)=2.67 \times 10^{-10} \mathrm{~m}$ [10]. Using the $K-F$ distance and the calculated ionic radii, the lattice structure of $K F$ is shown in Figure 18.3C.

## RUBIDIUM FLUORIDE

The $R b^{+}$ionic radius calculated using Eq. (10.102) and the experimental ionization energy of $R b^{+}, 27.2895 \mathrm{eV}$ [6] is $0.99714 a_{0}$ and the calculated ionic radius $F^{-}$ions in $R b F$ given by Eq. (18.48) is $2.46408 a_{0}$. But, the interionic distance cannot be the sum of the contact radii since the experimental and calculated ionization energies of $R b^{+}$[6] and $F^{-}$(Eq. (18.50)) are 27.2895 eV and 4.05046 eV , respectively. Furthermore, since the experimental ionization energy of $R b$ to $R b^{+}$is 4.177128 eV [6] and the ionization energy (Eq. (18.50)) of $F^{-}$to $F$ is 4.05046 eV , for sufficiently small interionic distances, the rubidium ion may be reduced.

Substitution of $B E(R b)=6.6925 \times 10^{-19} J$ and $\Delta E$ (ionization; $F^{-}$) = $1.03251 \times 10^{-19} J$ (Eq. (18.51)) into Eq. (18.17) gives the calculated lattice energy of:

$$
\begin{align*}
\Delta U & =N M_{c}\left(B E(R b)+\Delta E\left(\text { ionization; } F^{-}\right)\right) \\
& =1.74756 \mathrm{~N}\left(6.6925 \times 10^{-19} \mathrm{~J}+1.03251 \times 10^{-19} \mathrm{~J}\right)  \tag{18.69}\\
& =812.97 \mathrm{~kJ} / \text { mole }(194.30 \mathrm{kcal} / \text { mole })
\end{align*}
$$

This agrees well with the experimental lattice energy of $\Delta U=190 \mathrm{kcal} /$ mole [9] and confirms that the ionic compound $R b F$ comprises a precise packing of discrete ions.

The $R b-F$ distance, $r_{0}(R b F)$, calculated using Eq. (18.18) with the substitution of $B E(R b)=6.6925 \times 10^{-19} J$ and $\Delta E\left(\right.$ ionization; $\left.F^{-}\right)=1.03251 \times 10^{-19} \mathrm{~J}$ is:

$$
\begin{equation*}
r_{0}(R b F)=2.77 \times 10^{-10} \mathrm{~m} \tag{18.70}
\end{equation*}
$$

The calculated $R b-F$ is in reasonable agreement with the experimental distance of $r_{0}(R b F)=2.83 X 10^{-10} \mathrm{~m}$ [10]. Using the $R b-F$ distance and the ionic radii, the lattice structure of $R b F$ is shown in Figure 18.3D.

## CESIUM FLUORIDE

The $\mathrm{Cs}^{+}$ionic radius calculated using Eq. (10.102) and the experimental ionization energy of $\mathrm{Cs}^{+}, 23.15744 \mathrm{eV}$ [6] is $1.17506 a_{0}$ and the calculated ionic radius $F^{-}$ions in CsF given by Eq. (18.48) is $2.46408 a_{0}$. But, the interionic distance cannot be the sum of the contact radii since the experimental and calculated ionization energies of $\mathrm{Cs}^{+}$[6] and $\mathrm{F}^{-}$(Eq. (18.50)) are 23.15744 eV and 4.05046 eV , respectively. Furthermore, since the experimental ionization energy of $\mathrm{Cs}^{\text {to }} \mathrm{Cs}^{+}$is 3.893905 eV [6] and the ionization energy (Eq. (18.50)) of $F^{-}$to $F$ is 4.05046 eV , for sufficiently small interionic distances, the cesium ion may be reduced.

Substitution of $B E(C s)=6.23872 \times 10^{-19} J$ and $\Delta E\left(\right.$ ionization; $\left.F^{-}\right)=1.03251 \times 10^{-19} \mathrm{~J}$ (Eq. (18.51)) into Eq. (18.17) gives the calculated lattice energy of:

$$
\begin{align*}
\Delta U & =N M_{c}\left(B E(C s)+\Delta E\left(\text { ionization } ; F^{-}\right)\right) \\
& =1.74756 \mathrm{~N}\left(6.23872 \times 10^{-19} \mathrm{~J}+1.03251 \times 10^{-19} \mathrm{~J}\right)  \tag{18.71}\\
& =765.21 \mathrm{~kJ} / \text { mole }(182.89 \mathrm{kcal} / \text { mole })
\end{align*}
$$

This agrees well with the experimental lattice energy of $\Delta U=181 \mathrm{kcal} /$ mole [9] and confirms that the ionic compound CsF comprises a precise packing of discrete ions.

The $C s-F$ distance, $r_{0}(C s F)$, calculated using Eq. (18.18) with the substitution of $B E(C s)=6.23872 \times 10^{-19} J$ and $\Delta E\left(\right.$ ionization; $\left.F^{-}\right)=1.03251 \times 10^{-19} \mathrm{~J}$ is:

$$
\begin{equation*}
r_{0}(C s F)=2.96 \times 10^{-10} \mathrm{~m} \tag{18.72}
\end{equation*}
$$

The calculated $C s-F$ is in reasonable agreement with the experimental distance of $r_{0}(C s F)=3.01 X 10^{-10} \mathrm{~m}$ [10]. Using the $C s-F$ distance and the ionic radii, the lattice structure of $C s F$ is shown in Figure 18.3E.

## LITHIUM CHLORIDE

The calculated ionic radii for $\mathrm{Li}^{+}$and $\mathrm{Cl}^{-}$ions in LiCl given by Eqs. (10.49) and (18.59) are $0.35566 a_{0}$ and $2.83145 a_{0}$, respectively. But, the interionic distance cannot be the sum of the contact radii since the calculated ionization energies of $\mathrm{Li}^{+}$ (Eqs. (7.35), (7.45-7.46), and (7.63)) and $\mathrm{Cl}^{-}$(Eq. (18.61)) are 75.665 eV and 3.39420 eV , respectively. Furthermore, since
 (18.61)) of $\mathrm{Cl}^{-}$to Cl is 3.39420 eV , for sufficiently small interionic distances, the lithium ion may be reduced.

$$
\text { Substitution of } B E(L i)=8.65786 \times 10^{-19} \mathrm{~J} \text { and } \Delta E\left(\text { ionization; } \mathrm{Cl}^{-}\right)=-0.27818 \mathrm{eV}\left(-4.45691 \times 10^{-20} \mathrm{~J}\right) \quad \text { (Eq. }
$$

(18.62)) into Eq. (18.17) gives the calculated lattice energy of:

$$
\begin{align*}
\Delta U & =N M_{c}\left(B E(L i)+\Delta E\left(\text { ionization } ; \mathrm{Cl}^{-}\right)\right) \\
& =1.74756 \mathrm{~N}\left(8.65786 \times 10^{-19} \mathrm{~J}-4.45691 \times 10^{-20} \mathrm{~J}\right)  \tag{18.73}\\
& =864.24 \mathrm{~kJ} / \text { mole }(206.56 \mathrm{kcal} / \mathrm{mole})
\end{align*}
$$

This agrees well with the experimental lattice energy of $\Delta U=207 \mathrm{kcal} /$ mole [9] and confirms that the ionic compound LiCl comprises a precise packing of discrete ions.

The $\mathrm{Li}-\mathrm{Cl}$ distance, $r_{0}(\mathrm{LiCl})$, calculated using Eq. (18.18) with the substitution of $B E(L i)=8.65786 X 10^{-19} \mathrm{~J}$ and $\Delta E\left(\right.$ ionization; $\left.\mathrm{Cl}^{-}\right)=-4.45691 \times 10^{-20} \mathrm{~J}$ is:

$$
\begin{equation*}
r_{0}(L i C l)=2.59 \times 10^{-10} \mathrm{~m} \tag{18.74}
\end{equation*}
$$

The calculated $\mathrm{Li}-\mathrm{Cl}$ is in reasonable agreement with the experimental distance of $r_{0}(\mathrm{LiCl})=2.57 \mathrm{X} 10^{-10} \mathrm{~m}$ [10]. Using the $\mathrm{Li}-\mathrm{Cl}$ distance and the calculated ionic radii, the lattice structure of LiCl is shown in Figure 18.4A.

Figure 18.4. The crystal structures of MCl all to the same scale. ( $\mathrm{Li}^{+}=$green, $\mathrm{Na}^{+}=$yellow, $\mathrm{K}^{+}=$purple, $\mathrm{Rb}^{+}=$blue, $\mathrm{Cs}^{+}=$red, and $\mathrm{Cl}^{-}=$brown). (A) The crystal structure of LiCl . (B) The crystal structure of NaCl . (C) The crystal structure of $K C l$. (D) The crystal structure of RbCl . (E) The crystal structure of CsCl .


## SODIUM CHLORIDE

The calculated ionic radii for $\mathrm{Na}^{+}$and $\mathrm{Cl}^{-}$ions in NaCl given by Eqs. (10.212) and (18.59) are $0.560945 a_{0}$ and $2.83145 a_{0}$, respectively. But, the interionic distance cannot be the sum of the contact radii since the calculated ionization energies of $\mathrm{Na}^{+}$ (Eqs. (10.212-10.213)) and $\mathrm{Cl}^{-}$(Eq. (18.61)) are 48.5103 eV and 3.39420 eV , respectively. Furthermore, since the calculated ionization energy (Eqs. (10.226-10.227)) of $\mathrm{Na}^{2}$ to $\mathrm{Na}^{+}$is 5.12592 eV as shown in Table 10.10 and the ionization energy (Eq. (18.61)) of $\mathrm{Cl}^{-}$to Cl is 3.39420 eV , for sufficiently small interionic distances, the sodium ion may be reduced.

Substitution of $B E(N a)=8.21263 \times 10^{-19} \mathrm{~J}$ and $\Delta E\left(\right.$ ionization; $\left.\mathrm{Cl}^{-}\right)=-4.45691 \times 10^{-20} \mathrm{~J}$ (Eq. (18.62)) into Eq. (18.17) gives the calculated lattice energy of:

$$
\begin{align*}
\Delta U & =N M_{c}\left(B E(N a)+\Delta E\left(\text { ionization } ; \mathrm{Cl}^{-}\right)\right) \\
& =1.74756 \mathrm{~N}\left(8.21263 \times 10^{-19} \mathrm{~J}-4.45691 \times 10^{-20} \mathrm{~J}\right)  \tag{18.75}\\
& =817.38 \mathrm{~kJ} / \text { mole }(195.36 \mathrm{kcal} / \text { mole })
\end{align*}
$$

This agrees well with the experimental lattice energy of $\Delta U=189 \mathrm{kcal} /$ mole [9] and confirms that the ionic compound NaCl comprises a precise packing of discrete ions.

The $\mathrm{Na}-\mathrm{Cl}$ distance, $r_{0}(\mathrm{NaCl})$, calculated using Eq. (18.18) with the substitution of $\mathrm{BE}(\mathrm{Na})=8.21263 \mathrm{X} 10^{-19} \mathrm{~J}$ and $\Delta E$ (ionization; $\mathrm{Cl}^{-}$) $=-4.45691 \times 10^{-20} \mathrm{~J}$ is:

$$
\begin{equation*}
r_{0}(\mathrm{NaCl})=2.75 \times 10^{-10} \mathrm{~m} \tag{18.76}
\end{equation*}
$$

The calculated $\mathrm{Na}-\mathrm{Cl}$ is in reasonable agreement with the experimental distance of $r_{0}(\mathrm{NaCl})=2.82 \times 10^{-10} \mathrm{~m}$ [10]. Using the $\mathrm{Na}-\mathrm{Cl}$ distance and the calculated ionic radii, the lattice structure of NaCl is shown in Figure 18.4B.

## POTASSIUM CHLORIDE

The calculated ionic radii for $\mathrm{K}^{+}$and $\mathrm{Cl}^{-}$ions in KCl given by Eqs. (10.399) and (18.59) are $0.85215 a_{0}$ and $2.83145 a_{0}$, respectively. But, the interionic distance cannot be the sum of the contact radii since the calculated ionization energies of $\mathrm{K}^{+}$ (Eqs. (10.399-10.400)) and $\mathrm{Cl}^{-}$(Eq. (18.61)) are 31.9330 eV and 3.39420 eV , respectively. Furthermore, since the calculated ionization energy (Eqs. (10.414-10.415)) of $K$ to $K^{+}$is 4.33 eV as shown in Table 10.19 and the ionization energy (Eq. (18.61)) of $\mathrm{Cl}^{-}$to Cl is 3.39420 eV , for sufficiently small interionic distances, the potassium ion may be reduced.

Substitution of $B E(K)=6.93095 \times 10^{-19} \mathrm{~J}$ and $\Delta E\left(\right.$ ionization; $\left.\mathrm{Cl}^{-}\right)=-4.45691 \times 10^{-20} \mathrm{~J}$ (Eq. (18.62)) into Eq. (18.17) gives the calculated lattice energy of:

$$
\begin{align*}
\Delta U & =N M_{c}\left(B E(K)+\Delta E\left(\text { ionization } ; \mathrm{Cl}^{-}\right)\right) \\
& =1.74756 \mathrm{~N}\left(6.93095 \times 10^{-19} \mathrm{~J}-4.45691 \times 10^{-20} \mathrm{~J}\right)  \tag{18.77}\\
& =729.41 \mathrm{~kJ} / \text { mole }(174.33 \mathrm{kcal} / \mathrm{mole})
\end{align*}
$$

This agrees well with the experimental lattice energy of $\Delta U=172 \mathrm{kcal} /$ mole [9] and confirms that the ionic compound KCl comprises a precise packing of discrete ions.

The $K-C l$ distance, $r_{0}(K C l)$, calculated using Eq. (18.18) with the substitution of $B E(K)=6.93095 X 10^{-19} J$ and $\Delta E\left(\right.$ ionization; $\left.\mathrm{Cl}^{-}\right)=-4.45691 \times 10^{-20} \mathrm{~J}$ is:

$$
\begin{equation*}
r_{0}(\mathrm{KCl})=3.11 \times 10^{-10} \mathrm{~m} \tag{18.78}
\end{equation*}
$$

The calculated $\mathrm{K}-\mathrm{Cl}$ is in reasonable agreement with the experimental distance of $r_{0}(\mathrm{KCl})=3.15 \times 10^{-10} \mathrm{~m}$ [10]. Using the $\mathrm{K}-\mathrm{Cl}$ distance and the calculated ionic radii, the lattice structure of KCl is shown in Figure 18.4C.

## RUBIDIUM CHLORIDE

The $R b^{+}$ionic radius calculated using Eq. (10.102) and the experimental ionization energy of $R b^{+}$, 27.2895 eV [6] is $0.99714 a_{0}$ and the calculated ionic radius $\mathrm{Cl}^{-}$ions in RbCl given by Eq. (18.59) is $2.83145 a_{0}$. But, the interionic distance cannot be the sum of the contact radii since the experimental and calculated ionization energies of $\mathrm{Rb}^{+}$[6] and $\mathrm{Cl}^{-}$(Eq. (18.61)) are 27.2895 eV and 3.39420 eV , respectively. Furthermore, since the experimental ionization energy of $R b$ to $R b^{+}$is 4.177128 eV [6] and the ionization energy (Eq. (18.61)) of $\mathrm{Cl}^{-}$to Cl is 3.39420 eV , for sufficiently small interionic distances, the rubidium ion may be reduced.

Substitution of $B E(R b)=6.6925 \times 10^{-19} \mathrm{~J}$ and $\Delta E\left(\right.$ ionization; $\left.\mathrm{Cl}^{-}\right)=-4.45691 \times 10^{-20} \mathrm{~J}$ (Eq. (18.62)) into Eq. (18.17) gives the calculated lattice energy of:

$$
\begin{align*}
\Delta U & =N M_{c}\left(B E(R b)+\Delta E\left(\text { ionization; } \mathrm{Cl}^{-}\right)\right) \\
& =1.74756 \mathrm{~N}\left(6.6925 \times 10^{-19} \mathrm{~J}-4.45691 \times 10^{-20} \mathrm{~J}\right)  \tag{18.79}\\
& =704.31 \mathrm{~kJ} / \text { mole }(168.33 \mathrm{kcal} / \text { mole })
\end{align*}
$$

This agrees well with the experimental lattice energy of $\Delta U=166 \mathrm{kcal} /$ mole [9] and confirms that the ionic compound RbCl comprises a precise packing of discrete ions.

The $R b-C l$ distance, $r_{0}(R b C l)$, calculated using Eq. (18.18) with the substitution of $B E(R b)=6.6925 \times 10^{-19} \mathrm{~J}$ and $\Delta E\left(\right.$ ionization; $\left.\mathrm{Cl}^{-}\right)=-4.45691 \times 10^{-20} \mathrm{~J}$ is:

$$
\begin{equation*}
r_{0}(\mathrm{RbCl})=3.23 \times 10^{-10} \mathrm{~m} \tag{18.80}
\end{equation*}
$$

The calculated $\mathrm{Rb}-\mathrm{Cl}$ is in reasonable agreement with the experimental distance of $r_{0}(\mathrm{RbCl})=3.29 \mathrm{X} 10^{-10} \mathrm{~m}$ [10]. Using the $\mathrm{Rb}-\mathrm{Cl}$ distance and the ionic radii, the lattice structure of RbCl is shown in Figure 18.4D.

## CESIUM CHLORIDE

The $\mathrm{Cs}^{+}$ionic radius calculated using Eq. (10.102) and the experimental ionization energy of $\mathrm{Cs}^{+}, 23.15744 \mathrm{eV}$ [6] is $1.17506 a_{0}$ and the calculated ionic radius $\mathrm{Cl}^{-}$ions in CsCl given by Eq. (18.59) is $2.83145 a_{0}$. But, the interionic distance cannot be the sum of the contact radii since the experimental and calculated ionization energies of $\mathrm{Cs}^{+}$[6] and $\mathrm{Cl}^{-}$(Eq. (18.61)) are 23.15744 eV and 3.39420 eV , respectively. Furthermore, since the experimental ionization energy of $\mathrm{Cs}^{2}$ to $\mathrm{Cs}^{+}$is 3.893905 eV [6] and the ionization energy (Eq. (18.61)) of $\mathrm{Cl}^{-}$to Cl is 3.39420 eV , for sufficiently small interionic distances, the cesium ion may be reduced.

$$
\text { Substitution of } B E(C s)=6.23872 \times 10^{-19} J \text { and } \Delta E\left(\text { ionization; } C l^{-}\right)=-4.45691 \times 10^{-20} J \quad \text { (Eq. (18.62)) into Eq. }
$$

(18.17) gives the calculated lattice energy of:

$$
\begin{align*}
\Delta U & =N M_{c}\left(B E(C s)+\Delta E\left(\text { ionization; } C l^{-}\right)\right) \\
& =1.76267 N\left(6.23872 \times 10^{-19} \mathrm{~J}-4.45691 \times 10^{-20} \mathrm{~J}\right)  \tag{18.81}\\
& =662.23 \mathrm{~kJ} / \text { mole }(158.28 \mathrm{kcal} / \mathrm{mole})
\end{align*}
$$

This agrees well with the experimental lattice energy of $\Delta U=160 \mathrm{kcal} /$ mole [9] and confirms that the ionic compound CsCl comprises a precise packing of discrete ions.

The $C s-C l$ distance, $r_{0}(C s C l)$, calculated using Eq. (18.18) with the substitution of $B E(C s)=6.23872 \times 10^{-19} \mathrm{~J}$ and $\Delta E\left(\right.$ ionization; $\left.\mathrm{Cl}^{-}\right)=-4.45691 \times 10^{-20} \mathrm{~J}$ is:

$$
\begin{equation*}
r_{0}(\mathrm{CsCl})=3.49 \times 10^{-10} \mathrm{~m} \tag{18.82}
\end{equation*}
$$

The calculated $\mathrm{Cs}-\mathrm{Cl}$ is in reasonable agreement with the experimental distance of $r_{0}(\mathrm{CsCl})=3.54 X 10^{-10} \mathrm{~m}$ [10]. Using the $\mathrm{Cs}-\mathrm{Cl}$ distance and the ionic radii, the lattice structure of CsCl is shown in Figure 18.4E.

## REFERENCES

1. W. M. Muller, J. P. Blackledge, G. G. Libowitz, Metal Hydrides, Academic Press, New York, (1968), pp. 217-229.
2. J. C. Bailar, H. J. Emeleus, R. Nyholm, A. F. Trotman-Dickenson, (Editors), Comprehensive Inorganic Chemistry, Pergamon Press, (1973), p. 401.
3. G. L. Miessler, D. A. Tarr, Inorganic Chemistry, Third Edition, Pearson Prentice Hall, Upper Saddle River, New Jersey, (2004), pp. 207-222.
4. D. R. Stephens, E. M. Lilley, "Compressions of isotopic lithium hydrides," J. Appl. Phys. Vol. 39, (1968), pp. 177-180.
5. R. A. MacDonald, "Determination of the effective force constants between a substitutional impurity and its nearest neighbors in an alkali halide crystal," Phys. Rev., Vol. 150, No. 2, (1966), pp. 597-602.
6. D. R. Lide, CRC Handbook of Chemistry and Physics, 86th Edition, CRC Press, Taylor \& Francis, Boca Raton, (2005-6), pp. 10-202 to 10-204.
7. K. G. Spears, "Repulsive potentials of atomic ions, atoms, and molecules," J. Chem. Phys., Vol. 57, No. 5, (1972), pp. 18421849.
8. D. R. Lide, CRC Handbook of Chemistry and Physics, 86th Edition, CRC Press, Taylor \& Francis, Boca Raton, (2005-6), p. 10-156.
9. D. R. Lide, CRC Handbook of Chemistry and Physics, 86th Edition, CRC Press, Taylor \& Francis, Boca Raton, (2005-6), p. 12-21.
10. D. B. Sirdeshmukh, L. Lirdeshmukh, K. G. Subhadra, Alkali Halides: A Handbook of Physical Properties, Academic Press, New York, (2001).

## Chapter 19

## THE NATURE OF THE METALLIC BOND OF ALKALI METALS

## GENERALIZATION OF THE NATURE OF THE METALLIC BOND

Common metals comprise alkali, alkaline earth, and transition elements and have the properties of high electrical and thermal conductivity, opacity, surface luster, ductility, and malleability. From Maxwell's equations, the electric field inside of a metal conductor is zero. As shown in Appendix II, the bound electron exhibits this feature. The charge is confined to a twodimensional layer and the field is normal and discontinuous at the surface. The relationship between the electric field equation and the electron source charge-density function is given by Maxwell's equation in two dimensions [1-3].

$$
\begin{equation*}
\mathbf{n} \bullet\left(\mathbf{E}_{1}-\mathbf{E}_{2}\right)=\frac{\sigma}{\varepsilon_{0}} \tag{19.1}
\end{equation*}
$$

where $\mathbf{n}$ is the normal unit vector, $\mathbf{E}_{1}=0\left(\mathbf{E}_{1}\right.$ is the electric field inside of the MO), $\mathbf{E}_{2}$ is the electric field outside of the MO and $\sigma$ is the surface charge density. The properties of metals can be accounted for by the existence of free electrons bound to the corresponding lattice of positive ions. Based on symmetry, the natural coordinates are Cartesian. Then, the problem of the solution of the nature of the metal bonds reduces to a familiar electrostatics problem - the fields and the two-dimensional surface charge density induced on a planar conductor by a point charge such that a zero potential inside of the conductor is maintained according to Maxwell's equations.

There are many examples of charges located near a conductor such as an electron emitted from a cathode or a power line suspended above the conducting earth. Consider a point charge $+e$ at a position $(0,0, d)$ near an infinite planar conductor as shown in Figure 19.1.

Figure 19.1. A point charge above an infinite planar conductor.


With the potential of the conductor set equal to zero, the potential $\Phi$ in the upper half space $(z>0)$ is given by Poisson's equation (Eq. (3.9)), subject to the boundary condition that $\Phi=0$ at $z=0$ and at $z=\infty$. The potential for the point charge in free space is:

$$
\begin{equation*}
\Phi(x, y, z)=\frac{e}{4 \pi \varepsilon_{0}}\left(\frac{1}{\sqrt{x^{2}+y^{2}+(z-d)^{2}}}\right) \tag{19.2}
\end{equation*}
$$

The Poisson solution that meets the boundary condition that the potential is zero at the surface of the infinite planar conductor is
that due to the point charge and an image charge of $-e$ at the position $(0,0,-d)$ as shown in Figure 19.2.
Figure 19.2. A point charge above an infinite planar conductor and the image charge to meet the boundary condition $\Phi=0$ at $z=0$.


The potential for the corresponding electrostatic dipole in the positive half space is:

$$
\Phi(x, y, z)=\left\{\begin{array}{ll}
\frac{e}{4 \pi \varepsilon_{0}}\left(\frac{1}{\sqrt{x^{2}+y^{2}+(z-d)^{2}}}-\frac{1}{\sqrt{x^{2}+y^{2}+(z+d)^{2}}}\right) & \text { for } z>0  \tag{19.3}\\
0 & \text { for } z \leq 0
\end{array}\right\}
$$

The electric field shown in Figure 19.3 is nonzero only in the positive half space and is given by:

$$
\begin{equation*}
\mathbf{E}=-\nabla \Phi=\frac{e}{4 \pi \varepsilon_{0}}\left(\frac{x \mathbf{i}_{\mathbf{x}}+y \mathbf{i}_{y}+(z-d) \mathbf{i}_{z}}{\left(x^{2}+y^{2}+(z-d)^{2}\right)^{3 / 2}}-\frac{x \mathbf{i}_{\mathbf{x}}+y \mathbf{i}_{y}+(z+d) \mathbf{i}_{z}}{\left(x^{2}+y^{2}+(z+d)^{2}\right)^{3 / 2}}\right) \tag{19.4}
\end{equation*}
$$

Figure 19.3. Electric field lines from a positive point charge near an infinite planar conductor.


At the surface $(z=0)$, the electric field is normal to the conductor as required by Gauss' and Faraday's laws:

$$
\begin{equation*}
\mathbf{E}(x, y, 0)=\frac{-e d \mathbf{i}_{z}}{2 \pi \varepsilon_{0}\left(x^{2}+y^{2}+d^{2}\right)^{3 / 2}} \tag{19.5}
\end{equation*}
$$

The surface charge density shown in Figure 19.4 is given by Eq. (19.1) with $\mathbf{n}=\mathbf{i}_{z}$ and $\mathbf{E}_{2}=0$ :

$$
\begin{equation*}
\sigma=\frac{-e d}{2 \pi\left(x^{2}+y^{2}+d^{2}\right)^{3 / 2}}=\frac{-e d}{2 \pi\left(\rho^{2}+d^{2}\right)^{3 / 2}} \tag{19.6}
\end{equation*}
$$

Figure 19.4. The surface charge density distribution on the surface of the conduction planar conductor induced by the point charge at the position $(0,0, d)$. (A) The surface charge density $-\sigma(\rho)$ (shown in color-scale relief). (B) The cross-sectional view of the surface charge density.


The total induced charge is given by the integral of the density over the surface:

$$
\begin{align*}
q_{\text {induced }} & =\int \sigma d s \\
& =\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \frac{-e d}{2 \pi\left(x^{2}+y^{2}+d^{2}\right)^{3 / 2}} d y d x \\
& =\frac{-e d}{2 \pi} \int_{-\infty}^{\infty} \int_{-\frac{\pi}{2}}^{\frac{\pi}{2}} \frac{\cos \theta}{x^{2}+d^{2}} d \theta d x  \tag{19.7}\\
& =\frac{-e d}{\pi} \int_{-\infty}^{\infty} \frac{1}{x^{2}+d^{2}} d x \\
& =\frac{-e d}{\pi} \int_{-\frac{\pi}{2}}^{\frac{\pi}{2}} \frac{1}{d} d \theta^{\prime} \\
& =-e
\end{align*}
$$

wherein the change of variables $y=\left(x^{2}+d^{2}\right)^{\frac{1}{2}} \tan \theta$ and $x=d \tan \theta^{\prime}$ were used. The total surface charge induced on the surface of the conductor is exactly equal to the negative of the point charge located above the conductor.

Now consider the case where the infinite planar conductor is charged with a surface charge density $\sigma$ corresponding to a total charge of a single electron, $-e$, and the point charge of $+e$ is due to a metal ion $M^{+}$. Then, according to Maxwell's
equations, the potential function of $M^{+}$is given by Eq. (19.3), the electric field between $M^{+}$and $\sigma$ is given by Eqs. (19.419.5), and $\sigma$ is given by Eq. (19.6). The field lines of $M^{+}$end on $\sigma$, and the electric field is zero in the metal and in the negative half space. The potential energy between $M^{+}$and $\sigma$ at the surface ( $z=0$ ) given by the product of Eq. (19.2) and Eq. (19.6) is

$$
\begin{align*}
V & =\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \frac{e}{4 \pi \varepsilon_{0}}\left(\frac{1}{\sqrt{x^{2}+y^{2}+d^{2}}}\right)\left(\frac{-e d}{2 \pi\left(x^{2}+y^{2}+d^{2}\right)^{3 / 2}}\right) d x d y  \tag{19.8}\\
V & =\frac{-e^{2} d}{8 \pi^{2} \varepsilon_{0}} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \frac{1}{\left(x^{2}+y^{2}+d^{2}\right)^{2}} d x d y \tag{19.9}
\end{align*}
$$

Using a change of coordinates to cylindrical and integral \# 47 of Lide [4] gives:

$$
\begin{align*}
V & =\int_{0}^{\infty} \int_{0}^{2 \pi} \frac{-e^{2} d}{8 \pi^{2} \varepsilon_{0}\left(\rho^{2}+d^{2}\right)^{2}} \rho d \phi d \rho  \tag{19.10}\\
V & =\frac{-e^{2} d}{4 \pi \varepsilon_{0}} \int_{0}^{\infty} \frac{\rho}{\left(\rho^{2}+d^{2}\right)^{2}} d \rho  \tag{19.11}\\
V & =\frac{-e^{2} d}{4 \pi \varepsilon_{0}}\left(\frac{-1}{2\left(\rho^{2}+d^{2}\right)}\right)_{0}^{\infty}  \tag{19.12}\\
V & =\frac{-e^{2}}{4 \pi \varepsilon_{0}(2 d)} \tag{19.13}
\end{align*}
$$

The corresponding force from the negative gradient as well as the integral of the product of the electric field (Eq. (19.5)) and the charge density (Eq. (19.6)) is:

$$
\begin{align*}
\mathbf{F} & =-\nabla V \\
& =\int_{A} \mathbf{E}(x, y, 0) \sigma d A \\
& =\left(\frac{e^{2} d^{2}}{(2 \pi)^{2} \varepsilon_{0}} \mathbf{i}_{z}\right) \int_{0}^{\infty} \int_{0}^{2 \pi} \frac{\rho d \phi d \rho}{\left(\rho^{2}+d^{2}\right)^{3}} \\
& =2 \pi\left(\frac{e^{2} d^{2}}{(2 \pi)^{2} \varepsilon_{0}} \mathbf{i}_{z} \int_{0}^{\infty} \frac{\rho d \rho}{\left(\rho^{2}+d^{2}\right)^{3}}\right.  \tag{19.14}\\
& =2 \pi\left(\frac{e^{2} d^{2}}{(2 \pi)^{2} \varepsilon_{0}} \mathbf{i}_{z}\right) \frac{1}{4 d^{4}} \\
& =\frac{e^{2}}{8 \pi \varepsilon_{0} d^{2}} \mathbf{i}_{z}
\end{align*}
$$

where $d$ is treated as a variable to be solved as discussed below. The potential is equivalent to that of the charge and its image charge located a distance $2 d$ apart. In addition, the potential and force are equivalent to those of the charge $+e$ and an image charge $\frac{-e}{2}$ located a distance $d$ apart.

In addition to the infinite planar conductor at $z=0$ and the point charge $+e$ at a position $(0,0, d)$ near the infinite planar conductor as shown in Figure 19.1, next consider the introduction of a second infinite planar conductor located at position $z=2 d$ as shown in Figure 19.5.

Figure 19.5. A point charge located between two infinite planar conductors.


As shown, by Kong [5], an image charge at $(0,0,-d)$ meets the boundary condition of zero potential at the bottom plate, but it gives rise to a potential at the top. Similarly, an image charge at $(0,0,3 d)$, meets the boundary condition of zero potential at the top plate, but it gives rise to a potential at the bottom. Satisfaction of the boundary condition of zero potential at both plates due to the presence of the initial real charge requires an infinite series of alternating positive and negative image charges spaced a distance $d$ apart with the potential given by the summation over the real point source and its point-source image charges of $+e$ and $-e$. Since fields superimpose, by adding real charges in a periodic lattice, the image charges cancel except for one per each real charge at a distance $2 d$ apart as in the original case considered in Figure 19.1.

In the real world, the idealized infinite planar conductor is a planar metal sheet experimentally comprised of an essentially infinite lattice of metal ions $M^{+}$and free electrons that provide surface densities $\sigma$ in response to an applied external field such as that due to an external charge of $+e$ due to a metal ion $M^{+}$. Then, it is required that the solutions of the external point charge at an infinite planar conductor are also those of the metal ions and free electrons of metals based on the uniqueness of solutions of Maxwell's equations and the constraint that the individual electrons in a metal conserve the classical physical laws of the macro-scale conductor. In metals, a superposition of planar free electrons given in the Electron in Free Space section replaces the infinite planar conductor. Then, the nature of the metal bond is a lattice of metal ions with field lines that end on the corresponding lattice of electrons wherein each has the two-dimensional charge density $\sigma$ given by Eq. (19.6) to match the boundary conditions of equipotential, minimum energy, and conservation of charge and angular momentum for an ionized electron. Consider an infinite lattice of positive charges in the hollow Cartesian cavities whose walls are the intersecting planes of conductors and that each planar conductor comprises an electron. By Gauss' law, the field lines of each real charge end on each of the $n$ planar-electron walls of the cavity wherein the surface charge density of contribution of each electron is that of image charge of $\frac{-e}{n}$ equidistant across each wall from a given charge $+e$. Then, each electron contributes the charge $\frac{-e}{n}$ to the corresponding ion where each is equivalent electrostatically to an image point charge at twice the distance from the point charge of $+e$ due to $M^{+}$.

Thus, the metallic bond is equivalent to the ionic bond given in the Alkali-Hydride Crystal Structures section with a Madelung constant of one with each negative ion at a position of one half the distance between the corresponding positive ions, but electrostatically equivalent to being positioned at twice this distance, the $M^{+}-M^{+}$-separation distance. The surface charge density of a planar electron having an electric field equivalent to that of image point charge for the corresponding positive ion of the lattice is shown in Figure 19.6.

Figure 19.6. The surface charge density $-\sigma(\rho)$ of a planar electron shown in color scale.


## ALKALI-METAL CRYSTAL STRUCTURES

The alkali metals are lithium ( $L i$ ), sodium ( $N a$ ), potassium ( $K$ ), rubidium ( $R b$ ), and cesium ( $C s$ ). These alkali metals each comprise an equal number of alkali cations and electrons in unit cells of a crystalline lattice. The crystal structure of these metals is the body-centered cubic CsCl structure [6-8]. This close-packed structure is expected since it gives the optimal approach of the positive ions and negative electrons. For a body-centered cell, there is an identical atom at $x+\frac{a}{2}, y+\frac{a}{2}, z+\frac{a}{2}$ for each atom at $x, y, z$. The structure of the ions with lattice parameters $a=b=c$ and electrons at the diagonal positions centered at $\left(x+\frac{a}{4}, y+\frac{a}{4}, z+\frac{a}{4}\right)$ are shown in Figure 19.7. In this case $n=8$ electron planes per body-centered ion are perpendicular to the four diagonal axes running from each corner of the cube through the center to the opposite corner. The planes intersect these diagonals at one half the distance from each corner to the center of the body-centered atom. The mutual intersection of the planes forms a hexagonal cavity about each ion of the lattice. The length $l_{1}$ to a perpendicular electron plane along the axis from a corner atom to a body-centered atom that is the midpoint of this axis is:

$$
\begin{equation*}
l_{1}=\sqrt{\left(\frac{a}{4}\right)^{2}+\left(\frac{a}{4}\right)^{2}+\left(\frac{a}{4}\right)^{2}}=\frac{a \sqrt{3}}{4} \tag{19.15}
\end{equation*}
$$

The angle $\theta_{d}$ of each diagonal axis from the xy-plane of the unit cell is:

$$
\begin{equation*}
\theta_{d}=\tan ^{-1}\left(\frac{\frac{1}{4}}{\frac{\sqrt{2}}{4}}\right)=35.26^{\circ} \tag{19.16}
\end{equation*}
$$

The angle $\theta_{p}$ from the horizontal to the electron plane that is perpendicular to the diagonal axis is:

$$
\begin{equation*}
\theta_{p}=180^{\circ}-90^{\circ}-35.26^{\circ}=54.73^{\circ} \tag{19.17}
\end{equation*}
$$

The length $l_{3}$ along a diagonal axis in the xy-plane from a corner atom to another at which point an electron plane intersects the xy-plane is:

$$
\begin{equation*}
l_{3}=\frac{l_{1}}{\cos \theta_{d}}=\frac{\frac{a \sqrt{3}}{4}}{\cos \left(35.26^{\circ}\right)}=\frac{\frac{a \sqrt{3}}{4}}{\sqrt{\frac{2}{3}}}=a \frac{3}{4 \sqrt{2}} \tag{19.18}
\end{equation*}
$$

The length $l_{2}$ of the octagonal edge of the electron plane from a body-centered atom to the xy-plane defined by four corner atoms is:

$$
\begin{equation*}
l_{2}=l_{3} \sin \theta_{d}=a \frac{3}{4 \sqrt{2}} \sin \left(35.26^{\circ}\right)=a \frac{3}{4 \sqrt{2}} \frac{1}{\sqrt{3}}=\frac{a}{4} \sqrt{\frac{3}{2}} \tag{19.19}
\end{equation*}
$$

The length $l_{4}$ along the edge of the unit cell in the xy-plane from a corner atom to another at which point an electron plane intersects the xy-plane at this axis is:

$$
\begin{equation*}
l_{4}=\frac{l_{3}}{\cos \left(45^{\circ}\right)}=\frac{a \frac{3}{4 \sqrt{2}}}{\cos \left(45^{\circ}\right)}=\frac{3}{4} a \tag{19.20}
\end{equation*}
$$

The dimensions and angles given by Eqs. (19.15-19.20) are shown in Figure 19.7.
Each $M^{+}$is surrounded by six planar two-dimensional membranes that are comprised of electron density $\sigma$ on which the electric field lines of the positive charges end. The resulting unit cell consists cations at the end of each edge and at the center of the cell with an electron membrane as the perpendicular bisector of the axis from an identical atom at $x+\frac{a}{2}, y+\frac{a}{2}, z+\frac{a}{2}$ for each atom at $x, y, z$ such that the unit cell contains two cations and two electrons. The ions and electrons of the unit cell are also shown in Figure 19.7. The electron membranes exist throughout the metal, but they terminate on metal atomic orbitals or MOs of bonds between metal atoms and other reacted atoms such as the MOs of metal oxide bonds at the edges of the metal.

Figure 19.7. The body-centered cubic lithium metal lattice showing the electrons as planar two-dimensional membranes of zero thickness that are each an equipotential energy surface comprised of the superposition of multiple electrons. (A) and (B) The unit-cell component of the surface charge density of a planar electron having an electric field equivalent to that of an image point charge for each corresponding positive ion of the lattice. (C) Opaque view of the ions and electrons of a unit cell. (D) Transparent view of the ions and electrons of a unit cell.


The interionic radius of each cation and electron membrane can be derived by considering the electron energies at these radii and by calculating the corresponding forces of the electrons with the ions. Then, the lattice energy is given by the sum over the crystal of the energy of the interacting ion and electron pairs at the radius of force balance between the electrons and ions.

For each point charge of $+e$ due to a metal ion $M^{+}$, the planar two-dimensional membrane comprised of electrons contributes a surface charge density $\sigma$ given by Eq. (19.6) corresponding to that of a point image charge having a total charge of a single electron, $-e$. The potential of each electron is double that of Eq. (19.13) since there are two mirror-image $M^{+}$ions per planar electron membrane:

$$
\begin{equation*}
V=\frac{-e^{2}}{4 \pi \varepsilon_{0} d} \tag{19.21}
\end{equation*}
$$

where $d$ is treated as a variable to be solved. The same result is obtained from considering the integral of the product of two times the electric field (Eq. (19.5)) and the charge density (Eq. (19.6)) according to Eq. (19.14). In order to conserve angular momentum and maintain current continuity, the kinetic energy has two components. Since the free electron of a metal behaves as a point mass, one component using Eq. (1.35) with $r=d$ is:

$$
\begin{equation*}
T=\frac{1}{2} m_{e} v^{2}=\frac{1}{2} \frac{\hbar^{2}}{m_{e} d^{2}} \tag{19.22}
\end{equation*}
$$

The other component of kinetic energy is given by integrating the mass density $\sigma_{m}(r)$ (Eq. (19.6)) with $e$ replaced by $m_{e}$ and velocity $v(r)$ (Eq. (1.35)) over their radial dependence $\left(r=\sqrt{x^{2}+y^{2}+z^{2}}=\sqrt{\rho^{2}+d^{2}}\right)$ :

$$
\begin{align*}
T & =\frac{1}{2} \int \sigma v^{2} d A \\
& =\frac{1}{2} \int_{0}^{\infty} \int_{0}^{2 \pi} \frac{m_{e} d}{2 \pi\left(\rho^{2}+d^{2}\right)^{3 / 2}} \frac{\hbar^{2}}{m_{e}^{2}\left(\rho^{2}+d^{2}\right)} \rho d \phi d \rho \\
& =\frac{\hbar^{2} d}{4 \pi m_{e}} \int_{0}^{\infty} \int_{0}^{2 \pi} \frac{\rho}{\left(\rho^{2}+d^{2}\right)^{5 / 2}} d \phi d \rho  \tag{19.23}\\
& =\frac{2 \pi \hbar^{2} d}{4 \pi m_{e}}\left(\frac{-1}{2\left(\frac{3}{2}\right)\left(\rho^{2}+d^{2}\right)^{3 / 2}}\right)_{0}^{\infty} \\
& =\left(\frac{1}{3}\right)\left(\frac{1}{2} \frac{\hbar^{2}}{m_{e} d^{2}}\right)
\end{align*}
$$

where integral \#47 of Lide [4] was used. Thus, the total kinetic energy given by the sum of Eqs. (19.22) and (19.23) is:

$$
\begin{equation*}
T=\left(1+\frac{1}{3}\right)\left(\frac{1}{2} \frac{\hbar^{2}}{m_{e} d^{2}}\right)=\frac{4}{3}\left(\frac{1}{2} \frac{\hbar^{2}}{m_{e} d^{2}}\right) \tag{19.24}
\end{equation*}
$$

Each metal $M(M=L i, N a, K, R b, C s)$ is comprised of $M^{+}$and $e^{-}$ions. The structure of the ions comprises lattice parameters $a=b=c$ and electrons at the diagonal positions centered at $\left(x+\frac{a}{4}, y+\frac{a}{4}, z+\frac{a}{4}\right)$. Thus, the separation distance $d$ between each $M^{+}$and the corresponding electron membrane is:

$$
\begin{equation*}
d=\sqrt{\left(\frac{\Delta x}{2}\right)^{2}+\left(\frac{\Delta y}{2}\right)^{2}+\left(\frac{\Delta z}{2}\right)^{2}}=\sqrt{\left(\frac{1}{4} a\right)^{2}+\left(\frac{1}{4} a\right)^{2}+\left(\frac{1}{4} a\right)^{2}}=\frac{\sqrt{3}}{4} a \tag{19.25}
\end{equation*}
$$

where $\Delta x=\Delta y=\Delta z=\frac{a}{2}$. Thus, the lattice parameter $a$ is given by:

$$
\begin{equation*}
a=\frac{4 d}{\sqrt{3}} \tag{19.26}
\end{equation*}
$$

The molar metal bond energy $E_{D}$ is given by Avogadro's number $N$ times the negative sum of the potential energy, kinetic energy, and ionization or binding energy $(B E(M))$ of $M$ :

$$
\begin{equation*}
E_{D}=-N(V+T+B E(M))=N\left(\frac{e^{2}}{4 \pi \varepsilon_{0} d}-\frac{4}{3}\left(\frac{1}{2} \frac{\hbar^{2}}{m_{e} d^{2}}\right)-B E(M)\right) \tag{19.27}
\end{equation*}
$$

The separation distance $d$ between each $M^{+}$and the corresponding electron membrane is given by the force balance between the outward centrifugal force and the sum of the electric, paramagnetic and diamagnetic forces as given in the ThreeThrough Twenty-Electron Atoms section. The electric force $\mathbf{F}_{\text {ele }}$ corresponding to Eq. (19.21) given by its negative gradient is:

$$
\begin{equation*}
\mathbf{F}_{\text {ele }}=\frac{e^{2}}{4 \pi \varepsilon_{0} d^{2}} \mathbf{i}_{z} \tag{19.28}
\end{equation*}
$$

where inward is taken as the positive direction. The centrifugal force $\mathbf{F}_{\text {centrifugal }}$ is given by the negative gradient of Eq. (19.24) times two since the charge and mass density are doubled due to the presence of mirror image $M^{+}$ion pairs across the electron membrane at the origin for any given ion.

$$
\begin{equation*}
\mathbf{F}_{\text {centrifugal }}=-\frac{8}{3} \frac{\hbar^{2}}{m_{e} d^{3}} \mathbf{i}_{z} \tag{19.29}
\end{equation*}
$$

where $d$ is treated as a variable to be solved. In addition, there is an outward spin-pairing force $\mathbf{F}_{\text {mag }}$ between the electron density elements of two opposing ions that is given by Eqs. (7.24) and (10.52):

$$
\begin{equation*}
\mathbf{F}_{\text {mag }}=-\frac{1}{Z} \frac{\hbar^{2}}{m_{e} d^{3}} \sqrt{s(s+1)} \mathbf{i}_{z} \tag{19.30}
\end{equation*}
$$

where $s=\frac{1}{2}$. The remaining magnetic forces are determined by the electron configuration of the particular atom as given for the examples of lithium, sodium, and potassium metals in the corresponding sections.

## LITHIUM METAL

For $\mathrm{Li}^{+}$, there are two spin-paired electrons in an atomic orbital with:

$$
\begin{equation*}
r_{1}=r_{2}=a_{0}\left[\frac{1}{2}-\frac{\sqrt{\frac{3}{4}}}{6}\right] \tag{19.31}
\end{equation*}
$$

as given by Eq. (7.35) where $r_{n}$ is the radius of electron $n$ which has velocity $v_{n}$. For the next electron that contributes to the metal-electron membrane, the outward centrifugal force on electron 3 is balanced by the electric force and the magnetic forces (on electron 3). The radius of the metal-band electron is calculated by equating the outward centrifugal force (Eq. (19.29)) to the sum of the electric (Eq. (19.28)) and diamagnetic (Eq. (19.30)) forces as follows:

$$
\begin{align*}
& \frac{8}{3} \frac{\hbar^{2}}{m_{e} d^{3}}=\frac{e^{2}}{4 \pi \varepsilon_{0} d^{2}}-\frac{\hbar^{2}}{Z m_{e} d^{3}} \sqrt{\frac{3}{4}}  \tag{19.32}\\
& d=\left(\frac{8}{3}+\frac{\sqrt{\frac{3}{4}}}{3}\right) a_{0}=2.95534 a_{0}=1.56390 \times 10^{-10} \mathrm{~m} \tag{19.33}
\end{align*}
$$

where $Z=3$. Using Eq. (19.26), the lattice parameter $a$ is:

$$
\begin{equation*}
a=6.82507 a_{0}=3.61167 \times 10^{-10} \mathrm{~m} \tag{19.34}
\end{equation*}
$$

The experimental lattice parameter $a$ [7] is:

$$
\begin{equation*}
a=6.63162 a_{0}=3.5093 \times 10^{-10} \mathrm{~m} \tag{19.35}
\end{equation*}
$$

The calculated $\mathrm{Li}-\mathrm{Li}$ distance is in reasonable agreement with the experimental distance given the experimental difficulty of performing X-ray diffraction on lithium due to the low electron densities.

Using Eq. (19.27) and the experimental binding energy of lithium, $B E(L i)=5.39172 \mathrm{eV}=8.63849 \times 10^{-19} \mathrm{~J}$ [9], the molar metal bond energy $E_{D}$ is:

$$
\begin{aligned}
E_{D} & =N\left(\frac{e^{2}}{4 \pi \varepsilon_{0} 1.56390 \times 10^{-10} \mathrm{~m}}-\frac{4}{3}\left(\frac{1}{2} \frac{\hbar^{2}}{m_{e}\left(1.56390 \times 10^{-10} \mathrm{~m}\right)^{2}}\right)-8.63849 \times 10^{-19} \mathrm{~J}\right) \\
& =167.76 \mathrm{~kJ} / \mathrm{mole}
\end{aligned}
$$

This agrees well with the experimental lattice [10] energy of:

$$
\begin{equation*}
E_{D}=159.3 \mathrm{~kJ} / \mathrm{mole} \tag{19.37}
\end{equation*}
$$

and confirms that Li metal comprises a precise packing of discrete ions, $\mathrm{Li}^{+}$and $e^{-}$. Using the $\mathrm{Li}-\mathrm{Li}^{\text {and }} \mathrm{Li}^{+}-e^{-}$ distances and the calculated (Eq. (7.35)) $\mathrm{Li}^{+}$ionic radius of $0.35566 a_{0}=0.18821 \AA$, the crystalline lattice structure of the unit cell of Li metal is shown in Figure 19.8, a portion of the crystalline lattice of Li metal is shown in Figure 19.9, and the Li unit cell is shown relative to the other alkali metals in Figure 19.10.

Figure 19.8. The body-centered cubic metal lattice of lithium showing the unit cell of electrons and ions. (A) Diagonal view. (B) Top view.


Figure 19.9. A portion of the crystalline lattice of $L i$ metal comprising $3^{3}$ body-centered cubic unit cells of electrons and ions. (A) Rotated diagonal opaque view. (B) Rotated diagonal transparent view. (C) Side transparent view.


C

Figure 19.10. The crystalline unit cells of the alkali metals showing each lattice of ions and electrons to the same scale. ( $\mathrm{Li}^{+}=$green, $\mathrm{Na}^{+}=$yellow, $\mathrm{K}^{+}=$purple, $\mathrm{Rb}^{+}=$blue, $\mathrm{Cs}^{+}=$red). (A) The crystal structure of Li . (B) The crystal structure of $N a$. (C) The crystal structure of $K$. (D) The crystal structure of $R b$. (E) The crystal structure of Cs .


## SODIUM METAL

For $\mathrm{Na}^{+}$, there are two indistinguishable spin-paired electrons in an atomic orbital with radii $r_{1}$ and $r_{2}$ both given by Eq. (7.35) (Eq. (10.51)), two indistinguishable spin-paired electrons in an atomic orbital with radii $r_{3}$ and $r_{4}$ both given by Eq. (10.62), and three sets of paired electrons in an atomic orbital at $r_{10}$ given by Eq. (10.212). For $Z=11$, the next electron which binds to contribute to the metal electron membrane to form the metal bond is attracted by the central Coulomb field and is repelled by diamagnetic forces due to the 3 sets of spin-paired inner electrons.

In addition to the spin-spin interaction between electron pairs, the three sets of 2 p electrons are orbitally paired. The metal electron of the sodium atom produces a magnetic field at the position of the three sets of spin-paired 2 p electrons. In order for the electrons to remain spin and orbitally paired, a corresponding diamagnetic force, $\mathbf{F}_{\text {diamagnetic } 3}$, on electron eleven from the three sets of spin-paired electrons follows from Eqs. (10.83-10.84) and (10.220):

$$
\begin{equation*}
\mathbf{F}_{\text {diamagnetic } 3}=-\frac{1}{Z} \frac{10 \hbar^{2}}{m_{e} d^{3}} \sqrt{s(s+1)} \mathbf{i}_{z} \tag{19.38}
\end{equation*}
$$

corresponding to the $p_{x}$ and $p_{y}$ electrons with no spin-orbit coupling of the orthogonal $p_{z}$ electrons (Eq. (10.84)). The outward centrifugal force on electron 11 is balanced by the electric force and the magnetic forces (on electron 11). The radius of the outer electron is calculated by equating the outward centrifugal force (Eq. (19.29)) to the sum of the electric (Eq. (19.28)) and diamagnetic (Eqs. (19.30) and (19.38)) forces as follows:

$$
\begin{align*}
& \frac{8}{3} \frac{\hbar^{2}}{m_{e} d^{3}}=\frac{e^{2}}{4 \pi \varepsilon_{0} d^{2}}-\frac{\hbar^{2}}{Z m_{e} d^{3}} \sqrt{\frac{3}{4}}-\frac{1}{Z} \frac{10 \hbar^{2}}{m_{e} d^{3}} \sqrt{\frac{3}{4}}  \tag{19.39}\\
& d=\left(\frac{8}{3}+\frac{11 \sqrt{\frac{3}{4}}}{11}\right) a_{0}=3.53269 a_{0}=1.86942 \times 10^{-10} \mathrm{~m} \tag{19.40}
\end{align*}
$$

where $Z=11$ and $s=\frac{1}{2}$. Using Eq. (19.26), the lattice parameter $a$ is:

$$
\begin{equation*}
a=8.15840 a_{0}=4.31724 \times 10^{-10} \mathrm{~m} \tag{19.41}
\end{equation*}
$$

The experimental lattice parameter $a$ [7] is:

$$
\begin{equation*}
a=8.10806 a_{0}=4.2906 \times 10^{-10} \mathrm{~m} \tag{19.42}
\end{equation*}
$$

The calculated $N a$ — $N a$ distance is in good agreement with the experimental distance.
Using Eq. (19.27) and the experimental binding energy of sodium, $B E(N a)=5.13908 \mathrm{eV}=8.23371 \mathrm{X} 10^{-19} \mathrm{~J}$ [9], the molar metal bond energy $E_{D}$ is:

$$
\begin{equation*}
E_{D}=N\left(\frac{e^{2}}{4 \pi \varepsilon_{0} 1.86942 \times 10^{-10} \mathrm{~m}}-\frac{4}{3}\left(\frac{1}{2} \frac{\hbar^{2}}{m_{e}\left(1.86942 \times 10^{-10} \mathrm{~m}\right)^{2}}\right)-8.23371 \times 10^{-19} \mathrm{~J}\right)=107.10 \mathrm{~kJ} / \mathrm{mole} \tag{19.43}
\end{equation*}
$$

This agrees well with the experimental lattice [10] energy of:

$$
\begin{equation*}
E_{D}=107.5 \mathrm{~kJ} / \mathrm{mole} \tag{19.44}
\end{equation*}
$$

and confirms that Na metal comprises a precise packing of discrete ions, $\mathrm{Na}^{+}$and $\mathrm{e}^{-}$. Using the $\mathrm{Na}-\mathrm{Na}$ and $\mathrm{Na}^{+}-\mathrm{e}^{-}$ distances and the calculated (Eq. (10.212)) $\mathrm{Na}^{+}$ionic radius of $0.56094 a_{0}=0.29684 \AA$, the crystalline lattice structure of Na metal is shown in Figure 19.10B.

## POTASSIUM METAL

For $K^{+}$, there are two indistinguishable spin-paired electrons in an atomic orbital with radii $r_{1}$ and $r_{2}$ both given by Eq. (7.35) (Eq. (10.51)), two indistinguishable spin-paired electrons in an atomic orbital with radii $r_{3}$ and $r_{4}$ both given by Eq. (10.62), three sets of paired electrons in an atomic orbital at $r_{10}$ given by Eq. (10.212), two indistinguishable spin-paired electrons in an atomic orbital with radii $r_{11}$ and $r_{12}$ both given by Eq. (10.255), and three sets of paired electrons in an atomic orbital with radius $r_{18}$ given by Eq. (10.399). With $Z=19$, the next electron which binds to contribute to the metal electron membrane to form the metal bond is attracted by the central Coulomb field and is repelled by diamagnetic forces due to the 3 sets of spin-paired inner $3 p$ electrons.

The spherically symmetrical closed 3 p shell of nineteen-electron atoms produces a diamagnetic force, $\mathbf{F}_{\text {diamagnetic }}$, that is equivalent to that of a closed s shell given by Eq. (10.11) with the appropriate radii. The inner electrons remain at their initial radii, but cause a diamagnetic force according to Lenz's law that is:

$$
\begin{equation*}
\mathbf{F}_{\text {diamagnetic }}=-\frac{\hbar^{2}}{4 m_{e} d^{2} r_{18}} \sqrt{s(s+1)} \mathbf{i}_{z} \tag{19.45}
\end{equation*}
$$

The diamagnetic force, $\mathbf{F}_{\text {diamagnetic 3 }}$, on electron nineteen from the three sets of spin-paired electrons given by Eq. (10.409)
is

$$
\begin{equation*}
\mathbf{F}_{\text {diamagnetic } 3}=-\frac{1}{Z} \frac{12 \hbar^{2}}{m_{e} d^{3}} \sqrt{s(s+1)} \mathbf{i}_{z} \tag{19.46}
\end{equation*}
$$

corresponding to the $3 p_{x}, p_{y}$, and $p_{z}$ electrons.
The outward centrifugal force on electron 19 is balanced by the electric force and the magnetic forces (on electron 19). The radius of the outer electron is calculated by equating the outward centrifugal force (Eq. (19.29)) to the sum of the electric (Eq. (19.28)) and diamagnetic (Eqs. (19.30), (19.45), and (19.46)) forces as follows:

$$
\begin{equation*}
\frac{8}{3} \frac{\hbar^{2}}{m_{e} d^{3}}=\frac{e^{2}}{4 \pi \varepsilon_{0} d^{2}}-\frac{\hbar^{2}}{Z m_{e} d^{3}} \sqrt{\frac{3}{4}}-\frac{1}{Z} \frac{12 \hbar^{2}}{m_{e} d^{3}} \sqrt{\frac{3}{4}}-\frac{\hbar^{2}}{4 m_{e} d^{2} r_{18}} \sqrt{\frac{3}{4}} \tag{19.47}
\end{equation*}
$$

where $s=\frac{1}{2}$.

$$
\begin{equation*}
d=\frac{a_{0}\left(\frac{8}{3}+\frac{13}{Z} \sqrt{\frac{3}{4}}\right)}{(Z-18)-\frac{\sqrt{\frac{3}{4}}}{4 \frac{r_{18}}{a_{0}}}}=\frac{a_{0}\left(\frac{8}{3}+\frac{13}{19} \sqrt{\frac{3}{4}}\right)}{1-\frac{\sqrt{\frac{3}{4}}}{4 \frac{r_{18}}{a_{0}}}} \tag{19.48}
\end{equation*}
$$

Substitution of $\frac{r_{18}}{a_{0}}=0.85215$ (Eq. (10.399) with $Z=19$ ) into Eq. (19.48) gives:

$$
\begin{equation*}
d=4.36934 a_{0}=2.31215 \times 10^{-10} \mathrm{~m} \tag{19.49}
\end{equation*}
$$

Using Eq. (19.26), the lattice parameter $a$ is:

$$
\begin{equation*}
a=10.09055 a_{0}=5.33969 \times 10^{-10} \mathrm{~m} \tag{19.50}
\end{equation*}
$$

The experimental lattice parameter $a$ [7] is:

$$
\begin{equation*}
a=10.05524 a_{0}=5.321 \times 10^{-10} \mathrm{~m} \tag{19.51}
\end{equation*}
$$

The calculated $K-K$ distance is in good agreement with the experimental distance.
Using Eq. (19.27) and the experimental binding energy of potassium, $B E(K)=4.34066 \mathrm{eV}=6.9545 \times 10^{-19} \mathrm{~J}$ [9], the molar metal bond energy $E_{D}$ is:

$$
\begin{equation*}
E_{D}=N\left(\frac{e^{2}}{4 \pi \varepsilon_{0} 2.31215 \times 10^{-10} \mathrm{~m}}-\frac{4}{3}\left(\frac{1}{2} \frac{\hbar^{2}}{m_{e}\left(2.31215 \times 10^{-10} \mathrm{~m}\right)^{2}}\right)-6.9545 \times 10^{-19} \mathrm{~J}\right)=90.40 \mathrm{~kJ} / \mathrm{mole} \tag{19.52}
\end{equation*}
$$

This agrees well with the experimental lattice [10] energy of

$$
\begin{equation*}
E_{D}=89 \mathrm{~kJ} / \mathrm{mole} \tag{19.53}
\end{equation*}
$$

and confirms that $K$ metal comprises a precise packing of discrete ions, $K^{+}$and $e^{-}$. Using the $K-K$ and $K^{+}-e^{-}$distances and the calculated (Eq. (10.399)) $K^{+}$ionic radius of $0.85215 a_{0}=0.45094 \AA$, the crystalline lattice structure of $K$ metal is shown in Figure 19.10C.

## RUBIDIUM AND CESIUM METALS

Rubidium and cesium provide further examples of the nature of the bonding in alkali metals. The distance $d$ between each metal ion $M^{+}$and the corresponding electron membrane is calculated from the experimental parameter $a$, and then the molar metal bond energy $E_{D}$ is calculated using Eq. (19.27).

The experimental lattice parameter $a$ [7] for rubidium is:

$$
\begin{equation*}
a=10.78089 a_{0}=5.705 \times 10^{-10} \mathrm{~m} \tag{19.54}
\end{equation*}
$$

Using Eq. (19.25), the lattice parameter $d$ is:

$$
\begin{equation*}
d=4.66826 a_{0}=2.47034 \times 10^{-10} \mathrm{~m} \tag{19.55}
\end{equation*}
$$

Using Eqs. (19.27) and (19.55) and the experimental binding energy of rubidium, $B E(R b)=4.17713 \mathrm{eV}=6.6925 X 10^{-19} \mathrm{~J}$ [9], the molar metal bond energy $E_{D}$ is:

$$
\begin{equation*}
E_{D}=N\left(\frac{e^{2}}{4 \pi \varepsilon_{0} 2.47034 \times 10^{-10} \mathrm{~m}}-\frac{4}{3}\left(\frac{1}{2} \frac{\hbar^{2}}{m_{e}\left(2.47034 \times 10^{-10} \mathrm{~m}\right)^{2}}\right)-6.6925 \times 10^{-19} \mathrm{~J}\right)=79.06 \mathrm{~kJ} / \mathrm{mole} \tag{19.56}
\end{equation*}
$$

This agrees well with the experimental lattice [10] energy of:

$$
\begin{equation*}
E_{D}=80.9 \mathrm{~kJ} / \mathrm{mole} \tag{19.57}
\end{equation*}
$$

and confirms that $R b$ metal comprises a precise packing of discrete ions, $R b^{+}$and $e^{-}$. Using the $R b-R b$ and $R b^{+}-e^{-}$ distances and the $R b^{+}$ionic radius of $0.52766 \AA$ calculated using Eq. (10.102) and the experimental ionization energy of $R b^{+}$, 27.2895 eV [9], the crystalline lattice structure of $R b$ metal is shown in Figure 19.10D.

The experimental lattice parameter $a$ [7] for cesium is:

$$
\begin{equation*}
a=11.60481 a_{0}=6.141 \times 10^{-10} \mathrm{~m} \tag{19.58}
\end{equation*}
$$

Using Eq. (19.25), the lattice parameter $d$ is:

$$
\begin{equation*}
d=5.02503 a_{0}=2.65913 \times 10^{-10} \mathrm{~m} \tag{19.59}
\end{equation*}
$$

Using Eqs. (19.27) and (19.59) and the experimental binding energy of cesium, $B E(C s)=3.8939 \mathrm{eV}=6.23872 \times 10^{-19} \mathrm{~J}$ [9], the molar metal bond energy $E_{D}$ is:

$$
\begin{equation*}
E_{D}=N\left(\frac{e^{2}}{4 \pi \varepsilon_{0} 2.65913 \times 10^{-10} \mathrm{~m}}-\frac{4}{3}\left(\frac{1}{2} \frac{\hbar^{2}}{m_{e}\left(2.65913 \times 10^{-10} \mathrm{~m}\right)^{2}}\right)-6.23872 \times 10^{-19} \mathrm{~J}\right)=77.46 \mathrm{~kJ} / \mathrm{mole} \tag{19.60}
\end{equation*}
$$

This agrees well with the experimental lattice [10] energy of:

$$
\begin{equation*}
E_{D}=76.5 \mathrm{~kJ} / \mathrm{mole} \tag{19.61}
\end{equation*}
$$

and confirms that $C s$ metal comprises a precise packing of discrete ions, $\mathrm{Cs}^{+}$and $e^{-}$. Using the $\mathrm{Cs}-\mathrm{Cs}$ and $\mathrm{Cs}^{+}-e^{-}$ distances and the $\mathrm{Cs}^{+}$ionic radius of $0.62182 \AA$ calculated using Eq. (10.102) and the experimental ionization energy of $\mathrm{Cs}^{+}$, 23.15744 eV [9], the crystalline lattice structure of Cs metal is shown in Figure 19.10E.

Other metals can be solved in a similar manner. Iron, for example, is also a body-centered cubic lattice, and the solution of the lattice spacing and energies are given by Eqs. (19.21-19.30). The parameter $d$ is given by the iron force balance which has a corresponding form to those of alkali metals such as that of lithium given by Eqs. (19.32-19.35). In addition, the changes in radius and energy of the second $4 s$ electron due to the ionization of the first of the two $4 s$ electrons to the metal band is calculated in the similar manner as those of the atoms of diatomic molecules such as $N_{2}$ given by Eqs. (13.621-13.632). This energy term is added to those of Eq. (19.27) to give the molar metal bond energy $E_{D}$.

## PHYSICAL IMPLICATIONS OF THE NATURE OF FREE ELECTRONS IN METALS

The extension of the free-electron membrane throughout the crystalline lattice is the reason for the high thermal and electrical conductivity of metals. Electricity can be conducted on the extended electron membranes by the application of an electric field and a connection with a source of electrons to maintain current continuity. Heat can be transferred by radiation or by collisions, or by infrared-radiation-induced currents propagated through the crystal. The surface luster and opacity is due to the reflection of electromagnetic radiation by mirror currents on the surfaces of the free-planar electron membranes. Ductility and malleability result from the feature that the field lines of a given ion end on the induced electron surface charge of the planar, perfectly conducting electron membrane. Thus, layers of the metal lattice can slide over each other without juxtaposing charges of the same sign which causes ionic crystals to fracture.

The electrons in metals have surface-charge distributions that are merely equivalent to the image charges of the ions. When there is vibration of the ions, the thermal electron kinetic energy can be directed through channels of least resistance from collisions. The resulting kinetic energy distribution over the population of electrons can be modeled using Fermi Dirac statistics wherein the specific heat of a metal is dominated by the motion of the ions since the electrons behave as image charges. Based on the physical solution of the nature of the metallic bond, the small electron contribution to the specific heat of a metal is predicted to be proportional to the ratio of the temperature to the electron kinetic energy [11]. Based on Fermi-Dirac statistics, the electron contribution to the specific heat of a metal given by Eq. (23.68) is:

$$
\begin{equation*}
C_{V e}=\frac{\pi^{2}}{2}\left(\frac{k T}{\varepsilon_{F}}\right) R \tag{19.62}
\end{equation*}
$$

Now that the true structure of metals has been solved, it is interesting to relate the Fermi energy to the electron kinetic energy. The relationships between the electron velocity, the de Broglie wavelength, and the lattice spacing used to calculate the Fermi energy in the Electron-Energy Distribution section are also used in the kinetic energy derivation. The Fermi energy given by Eq. (23.61) is:

$$
\begin{equation*}
\varepsilon_{F}=\frac{h^{2}}{2 m}\left(\frac{3 N}{8 \pi V}\right)^{2 / 3}=\frac{h^{2}}{2 m_{e}}\left(\frac{3}{8 \pi}\right)^{2 / 3} n^{2 / 3} \tag{19.63}
\end{equation*}
$$

where the electron density parameter for alkali metals is two electrons per body-centered cubic cell of lattice spacing $a$. Since in the physical model, the field lines of two mirror-image ions $M^{+}$end on opposite sides per section of the two-dimensional electron membrane, the kinetic energy equivalent to the Fermi energy is twice that given by Eq. (19.24). Then, the ratio $R_{\varepsilon_{F} / T}$ of the Fermi energy to the kinetic energy provides a comparison of the statistical model to the solution of the nature of the metallic bond in the determination of electron contribution to the specific heat:

$$
\begin{equation*}
R_{\varepsilon_{F} / T}=\frac{\varepsilon_{F}}{T}=\frac{\frac{h^{2}}{2 m_{e}}\left(\frac{3}{8 \pi}\right)^{2 / 3} n^{2 / 3}}{\frac{8}{3}\left(\frac{1}{2} \frac{\hbar^{2}}{m_{e} d^{2}}\right)}=\frac{\frac{h^{2}}{2 m_{e}}\left(\frac{3}{8 \pi}\right)^{2 / 3}\left(\frac{2}{a^{3}}\right)^{2 / 3}}{\frac{8}{3}\left(\frac{1}{2} \frac{\hbar^{2}}{m_{e} d^{2}}\right)}=\frac{\frac{h^{2}}{2 m_{e}}\left(\frac{3}{8 \pi}\right)^{2 / 3}\left(\frac{2}{\left(\frac{4 d}{\sqrt{3}}\right)^{3}}\right)^{2 / 3}}{\left(\frac{8}{3}\right)\left(\frac{1}{2 \pi}\right)^{2}\left(\frac{h^{2}}{2 m_{e} d^{2}}\right)}=1.068 \tag{19.64}
\end{equation*}
$$

where Eq. (19.26) was used to convert the parameter $a$ to $d$.
From the physical nature of the current, the electrical and thermal conductivities corresponding to the currents can be determined. The electrical current is classically given by

$$
\begin{equation*}
i=e v=\sigma \frac{\varepsilon_{F}}{h e} \tag{19.65}
\end{equation*}
$$

where the energy and angular momentum of the conduction electrons are quantized according to $\hbar$ and Planck's equation (Eq. (4.8)), respectively. From Eq. (19.65), the electrical conductivity is given by:

$$
\begin{equation*}
\sigma=\frac{e^{2} h \nu}{\varepsilon_{F}} \tag{19.66}
\end{equation*}
$$

where $v$ is the frequency of the unit current carried by each electron. The thermal current is also carried by the kinetic energy of the electron plane waves. Since there are two degrees of freedom in the plane of each electron rather than three, the thermal conductivity $\kappa$ is given by:

$$
\begin{equation*}
\kappa=\frac{2}{3} \frac{C_{V e}}{N_{0} h}=\frac{\pi^{2}}{3}\left(\frac{k_{B}^{2} T}{\varepsilon_{F} / h}\right) \tag{19.67}
\end{equation*}
$$

The Wiedemann-Franz law gives the relationship of the thermal conductivity $\kappa$ to the electrical conductivity $\sigma$ and absolute temperature $T$. Thus, using Eqs. (19.66-19.67), the constant $L_{0}$ is given by:

$$
\begin{equation*}
L_{0}=\frac{\kappa}{\sigma T}=\frac{\frac{\pi^{2}}{3}\left(\frac{h k_{B}^{2}}{\varepsilon_{F}}\right)}{\frac{h e^{2}}{\varepsilon_{F}}}=\frac{\pi^{2}}{3}\left(\frac{k_{B}}{e}\right)^{2} \tag{19.68}
\end{equation*}
$$

From Eqs. (19.64) and (19.68), the statistical model is reasonably close to the physical model to be useful in modeling the specific-heat contribution of electrons in metals based on their inventory of thermal energy and the thermal-energy distribution in the crystal. However, the correct physical nature of the current carriers comprising two-dimensional electron planes is required in cases where the simplistic statistical model fails as in the case of the anisotropic violation of the Wiedemann-Franz law [12-13].

Semiconductors comprise covalent bonds wherein the electrons are of sufficiently high energy that excitation creates an ion and a free electron. The free electron forms a membrane as in the case of metals. This membrane has the same planar structure throughout the crystal. This feature accounts for the high conductivity of semiconductors when the electrons are excited by the application of external fields or electromagnetic energy that causes ion-pair ( $M^{+}-e^{-}$) formation.

Superconductors comprise free-electron membranes wherein current flows in a reduced dimensionality of two or one dimensions with the bonding being covalent along the remaining directions such that electron scattering from other planes does not interfere with the current flow. In addition, the spacing of the electrons along the membrane is such that the energy is bandpassed with respect to magnetic interactions of conducting electrons as given in the superconductivity section.

## REFERENCES

1. J. D. Jackson, Classical Electrodynamics, Second Edition, John Wiley \& Sons, New York, (1975), pp. 17-22.
2. H. A. Haus, J. R. Melcher, "Electromagnetic Fields and Energy," Department of Electrical Engineering and Computer Science, Massachusetts Institute of Technology, (1985), Sec. 5.3.
3. J. A. Stratton, Electromagnetic Theory, McGraw-Hill Book Company, (1941), p. 195.
4. D. R. Lide, CRC Handbook of Chemistry and Physics, 86th Edition, CRC Press, Taylor \& Francis, Boca Raton, (2005-6), p. A-23.
5. J. A. Kong, Electromagnetic Wave Theory, Second Edition, John Wiley \& Sons, Inc., New York, (1990), pp. 330-331.
6. A. Beiser, Concepts of Modern Physics, Fourth Edition, McGraw-Hill, New York, (1987), p. 372.
7. D. R. Lide, CRC Handbook of Chemistry and Physics, 86th Edition, CRC Press, Taylor \& Francis, Boca Raton, (2005-6), pp. 12-15 to 12-18.
8. A. K. Cheetham, P. Day, Editors, Solid State Chemistry Techniques, Clarendon Press, Oxford, (1987), pp. 52-57.
9. D. R. Lide, CRC Handbook of Chemistry and Physics, 86th Edition, CRC Press, Taylor \& Francis, Boca Raton, (2005-6), pp. 10-202 to 10-204.
10. D. R. Lide, CRC Handbook of Chemistry and Physics, 86th Edition, CRC Press, Taylor \& Francis, Boca Raton, (2005-6), pp. 5-4 to 5-18.
11. E. C. Stoner, "Collective electron specific heat and spin paramagnetism in metals," Proceedings of the Royal Society of London. Series A, Mathematical and Physical Sciences, Vol. 154, No. 883 (May 1, 1936), pp. 656-678.
12. M. A. Tanatar, J. Paglione, C. Petrovic, L. Taillefer, "Anisotropic violation of the Wiedemann-Franz law at a quantum critical point," Science, Vol. 316, (2007), pp. 1320-1322.
13. P. Coleman, "Watching electrons break up," Science, Vol. 316, (2007), pp. 1290-1291.

# Chapter 20 

## SILICON MOLECULAR FUNCTIONAL GROUPS AND MOLECULES

## GENERAL CONSIDERATIONS OF THE SILICON MOLECULAR BOND

Silane molecules comprising an arbitrary number of atoms can be solved using similar principles and procedures as those used to solve organic molecules of arbitrary length and complexity. Silanes can be considered to be comprised of functional groups such as $\mathrm{SiH}_{3}, \mathrm{SiH}_{2}, \mathrm{SiH}, \mathrm{Si}-\mathrm{Si}$, and $\mathrm{C}-\mathrm{Si}$. The solutions of these functional groups or any others corresponding to the particular silane can be conveniently obtained by using generalized forms of the force balance equation given in the Force Balance of the $\sigma$ MO of the Carbon Nitride Radical section for molecules comprised of silicon and hydrogen only and the geometrical and energy equations given in the Derivation of the General Geometrical and Energy Equations of Organic Chemistry section for silanes further comprised of heteroatoms such as carbon. The appropriate functional groups with their geometrical parameters and energies can be added as a linear sum to give the solution of any silane.

## SILANES $\left(\mathrm{Si}_{n} \mathrm{H}_{2 n+2}\right)$

As in the case of carbon, the bonding in the silicon atom involves four $s p^{3}$ hybridized orbitals formed from the $3 p$ and $3 s$ electrons of the outer shells. $\mathrm{Si}-\mathrm{Si}$ and $\mathrm{Si}-\mathrm{H}$ bonds form between $S i 3 s p^{3} \mathrm{HOs}$ and between a $S i 3 s p^{3} \mathrm{HO}$ and a $H 1 s$ AO to yield silanes. The geometrical parameters of each $\mathrm{Si}-\mathrm{Si}$ and $\mathrm{SiH}_{n=1,2,3}$ functional group is solved from the force balance equation of the electrons of the corresponding $\sigma-\mathrm{MO}$ and the relationships between the prolate spheroidal axes. Then, the sum of the energies of the $\mathrm{H}_{2}$-type ellipsoidal MOs is matched to that of the $\mathrm{Si} 3 s p^{3}$ shell as in the case of the corresponding carbon molecules. As in the case of ethane given in the Ethane Molecule section, the energy of the $\mathrm{Si}-\mathrm{Si}$ functional group is determined for the effect of the donation of $25 \%$ electron density from each participating $\mathrm{Si} 3 \mathrm{sp}{ }^{3} \mathrm{HO}$ to the $\mathrm{Si}-\mathrm{Si}$-bond MO.

The energy of silicon 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 $(\mathrm{OH})$ section with the donation of $75 \%$ electron density from the participating $\mathrm{Si} 3 \mathrm{sp}{ }^{3} \mathrm{HO}$ to each $\mathrm{Si}-\mathrm{H}$-bond MO. As in the case of acetylene given in the Acetylene Molecule section, the energy of each $\mathrm{Si}-H_{n}$ functional group is determined for the effect of the charge donation.

The $3 s p^{3}$ hybridized orbital arrangement after Eq. (13.422) is:

$$
\begin{array}{ccc} 
& 3 \mathrm{sp}^{3} \text { state } \\
\frac{\uparrow}{0,0} & \frac{\uparrow}{1,-1} & \frac{\uparrow}{1,0} \tag{20.1}
\end{array} \frac{\uparrow}{1,1}
$$

where the quantum numbers $\left(\ell, m_{\ell}\right.$ ) are below each electron. The total energy of the state is given by the sum over the four electrons. The sum $E_{T}\left(S i, 3 s p^{3}\right)$ of experimental energies [1] of $\mathrm{Si}, \mathrm{Si}^{+}, \mathrm{Si}^{2+}$, and $\mathrm{Si}^{3+}$ is:

$$
\begin{equation*}
E_{T}\left(S i, 3 s p^{3}\right)=45.14181 \mathrm{eV}+33.49302 \mathrm{eV}+16.34584 \mathrm{eV}+8.15168 \mathrm{eV}=103.13235 \mathrm{eV} \tag{20.2}
\end{equation*}
$$

By considering that the central field decreases by an integer for each successive electron of the shell, the radius $r_{3 s p^{3}}$ of the $S i 3 s p^{3}$ shell may be calculated from the Coulombic energy using Eq. (15.13).

$$
\begin{equation*}
r_{3 s p^{3}}=\sum_{n=10}^{13} \frac{(Z-n) e^{2}}{8 \pi \varepsilon_{0}(e 103.13235 \mathrm{eV})}=\frac{10 e^{2}}{8 \pi \varepsilon_{0}(e 103.13235 \mathrm{eV})}=1.31926 a_{0} \tag{20.3}
\end{equation*}
$$

where $Z=14$ for silicon. Using Eq. (15.14), the Coulombic energy $E_{\text {Coulomb }}\left(S i, 3 s p^{3}\right)$ of the outer electron of the $S i 3 s p^{3}$ shell is:

$$
\begin{equation*}
E_{\text {Coulomb }}\left(S i, 3 s p^{3}\right)=\frac{-e^{2}}{8 \pi \varepsilon_{0} r_{3 s p^{3}}}=\frac{-e^{2}}{8 \pi \varepsilon_{0} 1.31926 a_{0}}=-10.31324 \mathrm{eV} \tag{20.4}
\end{equation*}
$$

During hybridization, one of the spin-paired $3 s$ electrons is promoted to the $S i 3 s p^{3}$ shell as an unpaired electron. The energy for the promotion is the magnetic energy given by Eq. (15.15) at the initial radius of the $3 s$ electrons. From Eq. (10.255) with $Z=14$, the radius $r_{12}$ of the Si3s shell is:

$$
\begin{equation*}
r_{12}=1.25155 a_{0} \tag{20.5}
\end{equation*}
$$

Using Eqs. (15.15) and (20.5), the unpairing energy is:

$$
\begin{equation*}
E(\text { magnetic })=\frac{2 \pi \mu_{0} e^{2} \hbar^{2}}{m_{e}^{2}\left(r_{12}\right)^{3}}=\frac{8 \pi \mu_{o} \mu_{B}^{2}}{\left(1.25155 a_{0}\right)^{3}}=0.05836 \mathrm{eV} \tag{20.6}
\end{equation*}
$$

Using Eqs. (20.4) and (20.6), the energy $E\left(S i, 3 s p^{3}\right)$ of the outer electron of the $S i 3 s p^{3}$ shell is

$$
\begin{equation*}
E\left(S i, 3 s p^{3}\right)=\frac{-e^{2}}{8 \pi \varepsilon_{0} r_{3 s p^{3}}}+\frac{2 \pi \mu_{0} e^{2} \hbar^{2}}{m_{e}^{2}\left(r_{12}\right)^{3}}=-10.31324 \mathrm{eV}+0.05836 \mathrm{eV}=-10.25487 \mathrm{eV} \tag{20.7}
\end{equation*}
$$

Next, consider the formation of the $\mathrm{Si}-\mathrm{Si}$-bond MO of silanes wherein each silicon atom has a $\mathrm{Si} 3 \mathrm{sp}^{3}$ electron with an energy given by Eq. (20.7). The total energy of the state of each silicon atom is given by the sum over the four electrons. The $\operatorname{sum} E_{T}\left(S i_{\text {silane }}, 3 s p^{3}\right)$ of energies of $S i 3 s p^{3}$ (Eq. (20.7)), $S i^{+}, S i^{2+}$, and $S i^{3+}$ is:

$$
\begin{align*}
E_{T}\left(S i_{\text {silane }}, 3 s p^{3}\right) & =-\left(45.14181 \mathrm{eV}+33.49302 \mathrm{eV}+16.34584 \mathrm{eV}+E\left(S i, 3 s p^{3}\right)\right)  \tag{20.8}\\
& =-(45.14181 \mathrm{eV}+33.49302 \mathrm{eV}+16.34584 \mathrm{eV}+10.25487 \mathrm{eV})=-105.23554 \mathrm{eV}
\end{align*}
$$

where $E\left(S i, 3 s p^{3}\right)$ is the sum of the energy of $\mathrm{Si},-8.15168 \mathrm{eV}$, and the hybridization energy.
The sharing of electrons between two $\mathrm{Si} 3 s p^{3} \mathrm{HOs}$ to form a $\mathrm{Si}-\mathrm{Si}$-bond MO permits each participating orbital to decrease in size and energy. In order to further satisfy the potential, kinetic, and orbital energy relationships, each $S i 3 s p^{3} \mathrm{HO}$ donates an excess of $25 \%$ of its electron density to the Si -Si-bond MO to form an energy minimum. By considering this electron redistribution in the silane molecule as well as the fact that the central field decreases by an integer for each successive electron of the shell, the radius $r_{\text {silanessp }}$ of the $S i 3 s p^{3}$ shell may be calculated from the Coulombic energy using Eq. (15.18):

$$
\begin{equation*}
r_{\text {silane3sp }^{3}}=\left(\sum_{n=10}^{13}(Z-n)-0.25\right) \frac{e^{2}}{8 \pi \varepsilon_{0}(e 105.23554 \mathrm{eV})}=\frac{9.75 e^{2}}{8 \pi \varepsilon_{0}(\mathrm{e} 105.23554 \mathrm{eV})}=1.26057 a_{0} \tag{20.9}
\end{equation*}
$$

Using Eqs. (15.19) and (20.9), the Coulombic energy $E_{\text {Coulomb }}\left(S i_{\text {silane }}, 3 s p^{3}\right)$ of the outer electron of the $S i 3 s p^{3}$ shell is:

$$
\begin{equation*}
E_{\text {Coulomb }}\left(S i_{\text {silane }}, 3 s p^{3}\right)=\frac{-e^{2}}{8 \pi \varepsilon_{0} r_{\text {silane3sp }}{ }^{3}}=\frac{-e^{2}}{8 \pi \varepsilon_{0} 1.26057 a_{0}}=-10.79339 \mathrm{eV} \tag{20.10}
\end{equation*}
$$

During hybridization, one of the spin-paired $3 s$ electrons is promoted to the $S i 3 s p^{3}$ shell as an unpaired electron. The energy for the promotion is the magnetic energy given by Eq. (20.6). Using Eqs. (20.6) and (20.10), the energy $E\left(S i_{\text {silane }}, 3 s p^{3}\right)$ of the outer electron of the $S i 3 s p^{3}$ shell is:

$$
\begin{equation*}
E\left(S i_{\text {silane }}, 3 s p^{3}\right)=\frac{-e^{2}}{8 \pi \varepsilon_{0} r_{\text {silane } 3 s p^{3}}}+\frac{2 \pi \mu_{0} e^{2} \hbar^{2}}{m_{e}^{2}\left(r_{12}\right)^{3}}=-10.79339 \mathrm{eV}+0.05836 \mathrm{eV}=-10.73503 \mathrm{eV} \tag{20.11}
\end{equation*}
$$

Thus, $E_{T}\left(S i-S i, 3 s p^{3}\right)$, the energy change of each $S i 3 s p^{3}$ shell with the formation of the Si -Si-bond MO is given by the difference between Eq. (20.11) and Eq. (20.7):

$$
\begin{equation*}
E_{T}\left(S i-S i, 3 s p^{3}\right)=E\left(S i_{s i l a n e}, 3 s p^{3}\right)-E\left(S i, 3 s p^{3}\right)=-10.73503 \mathrm{eV}-(-10.25487 \mathrm{eV})=-0.48015 \mathrm{eV} \tag{20.12}
\end{equation*}
$$

Next, consider the formation of the $\mathrm{Si}-H$-bond MO of silanes wherein each silicon atom contributes a $S i 3 s p^{3}$ electron having the sum $E_{T}\left(S i_{\text {silane }}, 3 s p^{3}\right)$ of energies of $S i 3 s p^{3}$ (Eq. (20.7)), $S i^{+}, S i^{2+}$, and $S i^{3+}$ given by Eq. (20.8). Each $S i-H$-bond MO of each functional group $\mathrm{SiH}_{n=1,2,3}$ forms with the sharing of electrons between each $\operatorname{Si3sp}{ }^{3} \mathrm{HO}$ and each $H 1 s$ AO. As in the case of $\mathrm{C}-\mathrm{H}$, the $\mathrm{H}_{2}$-type ellipsoidal MO comprises $75 \%$ of the $\mathrm{Si}-\mathrm{H}$-bond MO according to Eq. (13.429). Furthermore, the donation of electron density from each $S i 3 s p^{3} \mathrm{HO}$ to each $\mathrm{Si}-H$-bond MO permits the participating orbital to decrease in size and energy. In order to further satisfy the potential, kinetic, and orbital energy relationships, each $\mathrm{Si}_{3} 3 p^{3} \mathrm{HO}$ donates an excess of $75 \%$ of its electron density to the $S i-H$-bond MO to form an energy minimum. By considering this electron redistribution in the silane molecule as well as the fact that the central field decreases by an integer for each successive
electron of the shell, the radius $r_{\text {silanesesp }}$ of the Si3sp ${ }^{3}$ shell may be calculated from the Coulombic energy using Eq. (15.18).

$$
\begin{equation*}
r_{\text {silanessp}}=\left(\sum_{n=10}^{13}(Z-n)-0.75\right) \frac{e^{2}}{8 \pi \varepsilon_{0}(e 105.23554 \mathrm{eV})}=\frac{9.25 e^{2}}{8 \pi \varepsilon_{0}(e 105.23554 \mathrm{eV})}=1.19592 a_{0} \tag{20.13}
\end{equation*}
$$

Using Eqs. (15.19) and (20.13), the Coulombic energy $E_{\text {Coulomb }}\left(S i_{\text {silane }}, 3 s p^{3}\right)$ of the outer electron of the $S i 3 s p^{3}$ shell is:

$$
\begin{equation*}
E_{\text {Coulomb }}\left(S i_{\text {silane }}, 3 s p^{3}\right)=\frac{-e^{2}}{8 \pi \varepsilon_{0} r_{\text {silanesspp }}}=\frac{-e^{2}}{8 \pi \varepsilon_{0} 1.19592 a_{0}}=-11.37682 \mathrm{eV} \tag{20.14}
\end{equation*}
$$

During hybridization, one of the spin-paired $3 s$ electrons is promoted to the $S i 3 s p^{3}$ shell as an unpaired electron. The energy for the promotion is the magnetic energy given by Eq. (20.6). Using Eqs. (20.6) and (20.14), the energy $E\left(S i_{\text {silane }}, 3 s p^{3}\right)$ of the outer electron of the $S i 3 s p^{3}$ shell is:

$$
\begin{equation*}
E\left(S i_{\text {silane }}, 3 s p^{3}\right)=\frac{-e^{2}}{8 \pi \varepsilon_{0} r_{\text {silane } 3 s p^{3}}}+\frac{2 \pi \mu_{0} e^{2} \hbar^{2}}{m_{e}^{2}\left(r_{12}\right)^{3}}=-11.37682 \mathrm{eV}+0.05836 \mathrm{eV}=-11.31845 \mathrm{eV} \tag{20.15}
\end{equation*}
$$

Thus, $E_{T}\left(S i-H, 3 s p^{3}\right)$, the energy change of each $S i 3 s p^{3}$ shell with the formation of the $S i-H$-bond MO is given by the difference between Eq. (20.15) and Eq. (20.7):

$$
\begin{equation*}
E_{T}\left(S i-H, 3 s p^{3}\right)=E\left(S i_{s i l a n e}, 3 s p^{3}\right)-E\left(S i, 3 s p^{3}\right)=-11.31845 \mathrm{eV}-(-10.25487 \mathrm{eV})=-1.06358 \mathrm{eV} \tag{20.16}
\end{equation*}
$$

Silane $\left(\mathrm{SiH}_{4}\right)$ involves only $\mathrm{Si}-\mathrm{H}$-bond MOs of equivalent tetrahedral structure to form a minimum energy surface involving a linear combination of all four hydrogen MOs. Here, the donation of electron density from the Si3sp ${ }^{3}$ HO to each $\mathrm{Si}-\mathrm{H}$-bond MO permits the participating orbital to decrease in size and energy as well. However, given the resulting continuous electron-density surface and the equivalent MOs, the Si3sp HO donates an excess of $100 \%$ of its electron density to the $\mathrm{Si}-\mathrm{H}$-bond MO to form an energy minimum. By considering this electron redistribution in the silane molecule as well as the fact that the central field decreases by an integer for each successive electron of the shell, the radius $r_{\text {silanessp }}$ of the $S i 3 s p^{3}$ shell may be calculated from the Coulombic energy using Eq. (15.18):

$$
\begin{equation*}
r_{\text {silane } 3 \text { sp }}{ }^{3}=\left(\sum_{n=10}^{13}(Z-n)-1\right) \frac{e^{2}}{8 \pi \varepsilon_{0}(e 105.23554 \mathrm{eV})}=\frac{9 e^{2}}{8 \pi \varepsilon_{0}(e 105.23554 \mathrm{eV})}=1.16360 a_{0} \tag{20.17}
\end{equation*}
$$

Using Eqs. (15.19) and (20.17), the Coulombic energy $E_{\text {Coulomb }}\left(S i_{\text {silane }}, 3 s p^{3}\right)$ of the outer electron of the $S i 3 s p^{3}$ shell is

$$
\begin{equation*}
E_{\text {Coulomb }}\left(S i_{\text {silane }}, 3 s p^{3}\right)=\frac{-e^{2}}{8 \pi \varepsilon_{0} r_{\text {silanessp }}{ }^{3}}=\frac{-e^{2}}{8 \pi \varepsilon_{0} 1.16360 a_{0}}=-11.69284 \mathrm{eV} \tag{20.18}
\end{equation*}
$$

During hybridization, one of the spin-paired $3 s$ electrons is promoted to the $S i 3 s p^{3}$ shell as an unpaired electron. The energy for the promotion is the magnetic energy given by Eq. (20.6). Using Eqs. (20.6) and (20.18), the energy $E\left(S i_{\text {silane }}, 3 s p^{3}\right)$ of the outer electron of the $S i 3 s p^{3}$ shell is:

$$
\begin{equation*}
E\left(S i_{\text {silane }}, 3 s p^{3}\right)=\frac{-e^{2}}{8 \pi \varepsilon_{0} r_{\text {silanessp }}}+\frac{2 \pi \mu_{0} e^{2} \hbar^{2}}{m_{e}^{2}\left(r_{12}\right)^{3}}=-11.69284 \mathrm{eV}+0.05836 \mathrm{eV}=-11.63448 \mathrm{eV} \tag{20.19}
\end{equation*}
$$

Thus, $E_{T}\left(S i-H, 3 s p^{3}\right)$, the energy change of each $S i 3 s p^{3}$ shell with the formation of the $S i-H$-bond MO is given by the difference between Eq. (20.19) and Eq. (20.7):

$$
\begin{equation*}
E_{T}\left(S i-H, 3 s p^{3}\right)=E\left(S i_{s i l a n e}, 3 s p^{3}\right)-E\left(S i, 3 s p^{3}\right)=-11.63448 \mathrm{eV}-(-10.25487 \mathrm{eV})=-1.37960 \mathrm{eV} \tag{20.20}
\end{equation*}
$$

Consider next the radius of the HO due to the contribution of charge to more than one bond. The energy contribution due to the charge donation at each silicon atom superimposes linearly. In general, the radius $r_{\text {molssp }}$ of the $\mathrm{Si3sp}^{3} \mathrm{HO}$ of a silicon atom of a given silane molecule is calculated after Eq. (15.32) by considering $\sum E_{T_{m o l}}\left(M O, 3 s p^{3}\right)$, the total energy donation to all bonds with which it participates in bonding. The general equation for the radius is given by:

$$
\begin{equation*}
r_{\text {mol } 3 s p^{3}}=\frac{-e^{2}}{8 \pi \varepsilon_{0}\left(E_{\text {Coulomb }}\left(S i, 3 s p^{3}\right)+\sum E_{T_{\text {mol }}}\left(M O, 3 s p^{3}\right)\right)}=\frac{e^{2}}{8 \pi \varepsilon_{0}\left(e 10.31324 e V+\sum\left|E_{T_{m o l}}\left(M O, 3 s p^{3}\right)\right|\right)} \tag{20.21}
\end{equation*}
$$

where $E_{\text {Coulomb }}\left(S i, 3 s p^{3}\right)$ is given by Eq. (20.4). The Coulombic energy $E_{\text {Coulomb }}\left(S i, 3 s p^{3}\right)$ of the outer electron of the $S i s p^{3}$ shell considering the charge donation to all participating bonds is given by Eq. (15.14) with Eq. (20.4). The energy $E\left(S i, 3 s p^{3}\right)$ of the outer electron of the $S i 3 s p^{3}$ shell is given by the sum of $E_{\text {Coulomb }}\left(S i, 3 s p^{3}\right)$ and $E$ (magnetic) (Eq. (20.6)). The final values of the radius of the $S i 3 s p^{3} \mathrm{HO}, r_{3 s p^{3}}, E_{\text {Coulomb }}\left(S i, 3 s p^{3}\right)$, and $E\left(S i_{\text {silane }} 3 s p^{3}\right)$ calculated using $\sum E_{T_{\text {nol }}}\left(M O, 3 s p^{3}\right)$, the total energy
donation to each bond with which an atom participates in bonding are given in Table 20.1. These hybridization parameters are used in Eqs. (15.88-15.117) for the determination of bond angles given in Table 20.7.

Table 20.1. Hybridization parameters of atoms for determination of bond angles with final values of $r_{3 s p^{3}}, E_{\text {Coulomb }}\left(S i, 3 s p^{3}\right)$, and $E\left(S i_{\text {silane }} 3 s p^{3}\right)$ calculated using the appropriate values of $\sum E_{T_{\text {mol }}}\left(M O, 3 s p^{3}\right)\left(E_{T_{\text {mol }}}\left(M O, 3 s p^{3}\right)\right.$ designated as $\left.E_{T}\right)$ for each corresponding terminal bond spanning each angle.

| Atom <br> Hybridization <br> Designation | $E_{T}$ | $E_{T}$ | $E_{T}$ | $E_{T}$ | $E_{T}$ | $r_{3 s p^{3}}$ <br> Final | $E_{\text {Coulomb }}\left(S i, 3 s p^{3}\right)$ <br> $(\mathrm{eV})$ <br> Final | $E\left(S i, 3 s p^{3}\right)$ <br> $(\mathrm{eV})$ <br> Final |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 0 | 0 | 0 | 0 | 0 | 1.31926 | -10.31324 | -10.25487 |
| 2 | -0.48015 | 0 | 0 | 0 | 0 | 1.26057 | -10.79339 | -10.73503 |

The MO semimajor axis of each functional group of silanes is determined from the force balance equation of the centrifugal, Coulombic, and magnetic forces as given in the Polyatomic Molecular Ions and Molecules section and the More Polyatomic Molecules and Hydrocarbons section. The distance from the origin of the $H_{2}$-type-ellipsoidal-MO to each focus $c^{\prime}$, the internuclear distance $2 c^{\prime}$, and the length of the semiminor axis of the prolate spheroidal $H_{2}$-type MO $b=c$ are solved from the semimajor axis $a$. Then, the geometric and energy parameters of the MO are calculated using Eqs. (15.1-15.117).

The force balance of the centrifugal force equated to the Coulombic and magnetic forces is solved for the length of the semimajor axis. The Coulombic force on the pairing electron of the MO is:

$$
\begin{equation*}
\mathbf{F}_{\text {Coulomb }}=\frac{e^{2}}{8 \pi \varepsilon_{0} a b^{2}} D \mathbf{i}_{\xi} \tag{20.22}
\end{equation*}
$$

The spin pairing force is

$$
\begin{equation*}
\mathbf{F}_{\text {spin-pairing }}=\frac{\hbar^{2}}{2 m_{e} a^{2} b^{2}} D \mathbf{i}_{\xi} \tag{20.23}
\end{equation*}
$$

The diamagnetic force is:

$$
\begin{equation*}
\mathbf{F}_{\text {diamagneticMO1 }}=-\frac{n_{e} \hbar^{2}}{4 m_{e} a^{2} b^{2}} D \mathbf{i}_{\xi} \tag{20.24}
\end{equation*}
$$

where $n_{e}$ is the total number of electrons that interact with the binding $\sigma$-MO electron. The diamagnetic force $\mathbf{F}_{\text {diamagneticмоz }}$ on the pairing electron of the $\sigma \mathrm{MO}$ is given by the sum of the contributions over the components of angular momentum:

$$
\begin{equation*}
\mathbf{F}_{\text {diamagneticMO2 }}=-\sum_{i, j} \frac{\left|L_{i}\right| \hbar^{2}}{Z_{j} 2 m_{e} a^{2} b^{2}} D \mathbf{i}_{\xi} \tag{20.25}
\end{equation*}
$$

where $|L|$ is the magnitude of the angular momentum of each atom at a focus that is the source of the diamagnetism at the $\sigma$ MO. The centrifugal force is:

$$
\begin{equation*}
\mathbf{F}_{\text {centrifiualMO }}=-\frac{\hbar^{2}}{m_{e} a^{2} b^{2}} D \mathbf{i}_{\xi} \tag{20.26}
\end{equation*}
$$

The force balance equation for the $\sigma$-MO of the $S i-S i$-bond MO with $n_{e}=3$ and $|L|=4 \sqrt{\frac{3}{4}} \hbar$ corresponding to four electrons of the $S i 3 s p^{3}$ shell is:

$$
\begin{align*}
& \frac{\hbar^{2}}{m_{e} a^{2} b^{2}} D=\frac{e^{2}}{8 \pi \varepsilon_{0} a b^{2}} D+\frac{\hbar^{2}}{2 m_{e} a^{2} b^{2}} D-\left(\frac{3}{2}+\frac{4 \sqrt{\frac{3}{4}}}{Z}\right) \frac{\hbar^{2}}{2 m_{e} a^{2} b^{2}} D  \tag{20.27}\\
& a=\left(\frac{5}{2}+\frac{4 \sqrt{\frac{3}{4}}}{Z}\right) a_{0} \tag{20.28}
\end{align*}
$$

With $Z=14$, the semimajor axis of the $S i-S i$-bond MO is:

$$
\begin{equation*}
a=2.74744 a_{0} \tag{20.29}
\end{equation*}
$$

The force balance equation for each $\sigma$-MO of the $\mathrm{Si}-H$-bond MO with $n_{e}=2$ and $|L|=4 \sqrt{\frac{3}{4}} \hbar$ corresponding to four electrons of the $S i 3 s p^{3}$ shell is:

$$
\begin{align*}
& \frac{\hbar^{2}}{m_{e} a^{2} b^{2}} D=\frac{e^{2}}{8 \pi \varepsilon_{0} a b^{2}} D+\frac{\hbar^{2}}{2 m_{e} a^{2} b^{2}} D-\left(1+\frac{4 \sqrt{\frac{3}{4}}}{Z}\right) \frac{\hbar^{2}}{2 m_{e} a^{2} b^{2}} D  \tag{20.30}\\
& a=\left(2+\frac{4 \sqrt{\frac{3}{4}}}{Z}\right) a_{0} \tag{20.31}
\end{align*}
$$

With $Z=14$, the semimajor axis of the $\mathrm{Si}-H$-bond MO is:
$a=2.24744 a_{0}$
(20.32)

Using the semimajor axis, 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 the Organic Molecular Functional Groups and Molecules section. For the $\mathrm{Si}-\mathrm{Si}$ functional group, the $\mathrm{Si3sp}{ }^{3} \mathrm{HOs}$ are equivalent; thus, $c_{1}=1$ in both the geometry relationships (Eqs. (15.2-15.5)) and the energy equation (Eq. (15.61)). In order for the bridging MO to intersect the Si3sp ${ }^{3}$ HOs while matching the potential, kinetic, and orbital energy relationships given in the $\operatorname{Hydroxyl} \operatorname{Radical}(O H)$ section, for the $\mathrm{Si}-\mathrm{Si}$ functional group, $C_{1}=\frac{0.75}{2}$ in both the geometry relationships (Eqs. (15.2-15.5)) and the energy equation (Eq. (15.61)). This is the same value as $C_{1}$ of the chlorine molecule given in the corresponding section. The hybridization factor gives the parameters $c_{2}$ and $C_{2}$ for both as well. To meet the equipotential condition of the union of the two Si3sp ${ }^{3} \mathrm{HOs}, c_{2}$ and $C_{2}$ of Eqs. (15.2-15.5) and Eq. (15.61) for the $\mathrm{Si}-\mathrm{Si}$-bond MO is given by Eq. (15.72) as the ratio of 10.31324 eV , the magnitude of $E_{\text {Coulomb }}\left(S i_{\text {silane }}, 3 s p^{3}\right)$ (Eq. (20.4)), and 13.605804 eV , the magnitude of the Coulombic energy between the electron and proton of $H$ (Eq. (1.264)):

The energy of the MO is matched to that of the $S i 3 s p^{3} \mathrm{HO}$ such that $E(A O / H O)$ is $E\left(S i, 3 s p^{3}\right)$ given by Eq. (20.7) and $E_{T}\left(\right.$ atom-atom, $\left.m s p^{3} . A O\right)$ is two times $E_{T}\left(S i-S i, 3 s p^{3}\right)$ given by Eq. (20.12).

For the $\mathrm{Si}-\mathrm{H}$-bond MO of the $\mathrm{SiH}_{n=1,2,3}$ functional groups, $c_{1}$ is one and $C_{1}=0.75$ based on the orbital composition as in the case of the $C-H$-bond MO. In silanes, the energy of silicon 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, the hybridization factor for the $\mathrm{Si}-\mathrm{H}$-bond MO given by Eq. (20.33). Since the energy of the MO is matched to that of the $S i 3 s p^{3} \mathrm{HO}, E(A O / H O)$ is $E\left(S i, 3 s p^{3}\right)$ given by Eq. (20.7) and $E_{T}\left(\right.$ atom-atom, $\left.m s p^{3} . A O\right)$ is $E_{T}\left(S i-H, 3 s p^{3}\right)$ given by Eq. (20.16). The energy $E_{D}\left(S i H_{n=1,2,3}\right)$ of the functional groups $S i H_{n=1,2,3}$ is given by the integer $n$ times that of $\mathrm{Si}-\mathrm{H}$ :

$$
\begin{equation*}
E_{D}\left(S i H_{n=1,2,3}\right)=n E_{D}(S i H) \tag{20.34}
\end{equation*}
$$

Similarly, for silane, $E_{T}\left(\right.$ atom - atom, $\left.m s p^{3} . A O\right)$ is $E_{T}\left(S i-H, 3 s p^{3}\right)$ given by Eq. (20.20). The energy $E_{D}\left(S i H_{4}\right)$ of $\mathrm{SiH}_{4}$ is given by the integer 4 times that of the $\mathrm{SiH}_{n=4}$ functional group:

$$
\begin{equation*}
E_{D}\left(\mathrm{SiH}_{4}\right)=4 E_{D}\left(S i H_{n=4}\right) \tag{20.35}
\end{equation*}
$$

The symbols of the functional groups of silanes are given in Table 20.2. The geometrical (Eqs. (15.1-15.5), (20.1-20.16), (20.29), and (20.32-20.33)), intercept (Eqs. (15.80-15.87) and (20.21)), and energy (Eqs. (15.61), (20.1-20.16), and (20.3320.35)) parameters of silanes are given in Tables 20.3, 20.4, and 20.5, respectively. The total energy of each silane given in Table 20.6 was calculated as the sum over the integer multiple of each $E_{D}$ (Group) of Table 20.5 corresponding to functional-group composition of the molecule. $E_{\text {mag }}$ of Table 20.5 is given by Eqs. (15.15) and (20.3). The bond angle parameters of silanes determined using Eqs. (15.88-15.117) are given in Table 20.7. In particular for silanes, the bond angle $\angle H S i H$ is given by Eq. (15.99) wherein $E_{T}\left(\right.$ atom - atom, $\left.m s p^{3} . A O\right)$ is given by Eq. (20.16) in order to match the energy donated from the Si3sp ${ }^{3} \mathrm{HO}$ to the $\mathrm{Si}-H$-bond MO due to the energy of silicon being less than the Coulombic energy between the electron and proton of $H$ given by Eq. (1.264). The parameter $c_{2}^{\prime}$ is given by Eq. (15.100) as in the case of a $H-H$ terminal bond of an alkyl or alkenyl group, except that $c_{2}\left(S i 3 s p^{3}\right)$ is given by Eq. (15.63) such that $c_{2}^{\prime}$ is the ratio of $c_{2}$ of Eq. (15.72) for the $H-H$ bond which is one and $c_{2}$ of the silicon of the corresponding $\mathrm{Si}-H$-bond considering the effect of the formation of the $H-H$ terminal bond:

$$
\begin{equation*}
c_{2}^{\prime}=\frac{1}{c_{2}\left(S i 3 s p^{3}\right)}=\frac{13.605804 \mathrm{eV}}{E_{\text {Coulomb }}\left(S i-H S i 3 s p^{3}\right)} \tag{20.36}
\end{equation*}
$$

The color scale, translucent view of the charge-densities of the series $\mathrm{SiH}_{n=1,2,3,4}$ comprising the concentric shells of the central Si atom of each member with the outer shell joined with one or more hydrogen MOs are shown in Figures 20.1A-D. The
charge-density of disilane is shown in Figure 20.2.

Figure 20.1. (A)-(D) Color scale, translucent view of the charge-densities of the series $\mathrm{SiH}_{n=1,2,3,4}$, showing the orbitals of each member Si atom at their radii, the ellipsoidal surface of each $H_{2}$-type ellipsoidal MO of $H$ that transitions to the outer shell of the Si atom participating in each $\mathrm{Si}-\mathrm{H}$ bond, and the hydrogen nuclei (red, not to scale).


Figure 20.2. Disilane. Color scale, translucent view of the charge-density of $\mathrm{H}_{3} \mathrm{SiSiH}_{3}$ comprising the linear combination of two sets of three $\mathrm{Si}-\mathrm{H}$-bond MOs and a $\mathrm{Si}-\mathrm{Si}$-bond MO with the $\mathrm{Si}_{\text {silane }} 3 s p^{3}$ HOs of the $\mathrm{Si}-\mathrm{Si}$-bond MO shown transparently. The $\mathrm{Si}-\mathrm{Si}$-bond MO comprises a $\mathrm{H}_{2}$-type ellipsoidal MO bridging two $\mathrm{Si}_{\text {silane }} 3 s p^{3}$ HOs. For each $\mathrm{Si}-\mathrm{H}$ and the $\mathrm{Si}-\mathrm{Si}$ bond, the ellipsoidal surface of the $H_{2}$-type ellipsoidal MO that transitions to the $S i_{\text {silane }} 3 s p^{3} \mathrm{HO}$, the $S i_{\text {silane }} 3 s p^{3} \mathrm{HO}$ shell with radius $0.97295 a_{0}$ (Eq. (20.21)), inner Si1s, $\operatorname{Si2} s$, and $\operatorname{Si} 2 p$ shells with radii of $\operatorname{Sils}=0.07216 a_{0}$ (Eq. (10.51)), $S i 2 s=0.31274 a_{0}$ (Eq. (10.62)), and Si2 $p=0.40978 a_{0}$ (Eq. (10.212)), respectively, and the nuclei (red, not to scale), are shown.


Table 20.2. The symbols of the functional groups of silanes.

| Functional Group | Group Symbol |
| :--- | :--- |
| SiH group of $\mathrm{SiH}_{n=1,2,3}$ | $\mathrm{Si}-\mathrm{H}$ (i) |
| SiH group of $\mathrm{SiH} H_{n=4}$ | $\mathrm{Si}-\mathrm{H}$ (ii) |
| SiSi bond $(n-\mathrm{Si})$ | $\mathrm{Si}-\mathrm{Si}$ |

Table 20.3. The geometrical bond parameters of silanes and experimental values [2].

| Parameter | $S i-H$ (i) and (ii) Group | $S i-S i$ Group |
| :---: | :---: | :---: |
| $a\left(a_{0}\right)$ | 2.24744 | 2.74744 |
| $c^{\prime}\left(a_{0}\right)$ | 1.40593 | 2.19835 |
| Bond Length $2 c^{\prime}(\AA)$ | 1.48797 | 2.32664 |
| Exp. Bond Length $(\AA)$ | $1.492\left(\mathrm{Si}_{2} \mathrm{H}_{6}\right)$ | $2.331\left(\mathrm{Si}_{2} \mathrm{H}_{6}\right)$ <br> $\operatorname{1.75338}$$2.32\left(\mathrm{Si}_{2} \mathrm{Cl}_{6}\right)$ |
| $b, c\left(a_{0}\right)$ | 0.62557 | 1.64792 |
| $e$ |  | 0.80015 |

Table 20.4. The MO to HO intercept geometrical bond parameters of silanes. $E_{T}$ is $E_{T}$ (atom-atom $\mathrm{msp}^{3} . A O$ ).

| Bond | Atom | $\begin{gathered} E_{T} \\ (\mathrm{eV}) \\ \text { Bond } 1 \end{gathered}$ | $\begin{gathered} E_{T} \\ (\mathrm{eV}) \\ \text { Bond } 2 \end{gathered}$ | $\begin{gathered} E_{T} \\ (\mathrm{eV}) \\ \text { Bond } 3 \end{gathered}$ | $\begin{array}{c\|} \hline E_{T} \\ (\mathrm{eV}) \\ \text { Bond } 4 \end{array}$ | (eV) | $\begin{aligned} & r_{\text {rurital }} \\ & \left(a_{0}\right) \end{aligned}$ | $\begin{aligned} & r_{\text {frnal }} \\ & \left(a_{0}\right) \end{aligned}$ | $\begin{gathered} E_{\text {Coulomb }}\left(S i 3 s p^{3}\right) \\ \text { (eV) } \\ \text { Final } \\ \hline \end{gathered}$ | $\begin{gathered} E\left(S i 3 s p^{3}\right) \\ (\mathrm{eV}) \\ \text { Final } \end{gathered}$ | $\begin{aligned} & \theta^{\prime} \\ & \left({ }^{\circ}\right) \end{aligned}$ | $\begin{gathered} \theta_{1} \\ \left({ }^{\circ}\right) \end{gathered}$ | $\begin{aligned} & \theta_{2} \\ & \left({ }^{\circ}\right) \end{aligned}$ | $\begin{gathered} d_{1} \\ \left(a_{0}\right) \end{gathered}$ | $\begin{gathered} d_{2} \\ \left(a_{0}\right) \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Si-H (SiH) | Si | -1.06358 | 0 | 0 | 0 | -106.29912 | 1.31926 | 1.19592 | -11.37682 | -11.31845 | 76.71 | 103.29 | 41.59 | 1.68089 | 0.27496 |
| $\mathrm{Si}-\mathrm{H}\left(\mathrm{SiH}_{2}\right)$ | Si | -1.06358 | -1.06358 | 0 | 0 | -107.36270 | 1.31926 | 1.09368 | -12.44040 | -12.38204 | 66.37 | 113.63 | 34.85 | 1.84433 | 0.43840 |
| $\mathrm{Si}-\mathrm{H}\left(\mathrm{SiH}_{3}\right)$ | Si | -1.06358 | -1.06358 | -1.06358 | 0 | -108.42628 | 1.31926 | 1.00754 | -13.50398 | -13.44562 | 55.12 | 124.88 | 28.13 | 1.98203 | 0.57610 |
| $\mathrm{Si}-\mathrm{H}\left(\mathrm{SiH}_{4}\right)$ | Si | -1.37960 | -1.37960 | -1.37960 | -1.37960 | -110.75395 | 1.31926 | 0.85941 | -15.83165 | -15.77329 | 18.93 | 161.07 | 9.15 | 2.21883 | 0.81290 |
| $\mathrm{H}-\left(\mathrm{H}_{2}\right) \mathrm{SiSi}-$ | Si | -1.06358 | -1.06358 | -1.06358 | -0.48015 | -108.90644 | 1.31926 | 0.97295 | -13.98413 | -13.92577 | 49.54 | 130.46 | 24.97 | 2.03733 | 0.63140 |
| $\mathrm{H}_{3} \mathrm{SiSi}(\mathrm{H})-\mathrm{HSiH}_{2}-$ | Si | -1.06358 | -1.06358 | -0.48015 | -0.48015 | -108.32301 | 1.31926 | 1.01531 | -13.40070 | -13.34234 | 56.28 | 123.72 | 28.79 | 1.96962 | 0.56369 |
| $\mathrm{H}_{3} \mathrm{Si}_{a}-\mathrm{Si}_{b} \mathrm{H}_{2} \mathrm{SiH}_{2}$ | $S i_{a}$ | -0.48015 | -1.06358 | -1.06358 | -1.06358 | -108.90644 | 1.31926 | 0.97295 | -13.98413 | -13.92577 | 88.86 | 91.14 | 36.18 | 2.21770 | 0.01935 |
| $\mathrm{H}_{3} \mathrm{Si}_{a}-\mathrm{Si}_{b} \mathrm{H}_{2} \mathrm{SiH}_{2}$ | $S i_{b}$ | -0.48015 | -0.48015 | -1.06358 | -1.06358 | -108.32301 | 1.31926 | 1.01531 | -13.40070 | -13.34234 | 91.90 | 88.10 | 38.01 | 2.16476 | 0.03359 |

Table 20.5. The energy parameters ( eV ) of the functional groups of silanes.

| Parameters | $\begin{gathered} \hline \mathrm{Si}-H \text { (i) } \\ \text { Group } \\ \hline \end{gathered}$ | $\begin{gathered} \hline \mathrm{Si}-\mathrm{H} \text { (ii) } \\ \text { Group } \\ \hline \end{gathered}$ | $\begin{aligned} & S i-S i \\ & \text { Group } \end{aligned}$ |
| :---: | :---: | :---: | :---: |
| $n_{1}$ | 1 | 1 | 1 |
| $n_{2}$ | 0 | 0 | 0 |
| $n_{3}$ | 0 | 0 | 0 |
| $C_{1}$ | 0.75 | 0.75 | 0.37500 |
| $\mathrm{C}_{2}$ | 0.75800 | 0.75800 | 0.75800 |
| $c_{1}$ | 1 | 1 | 1 |
| $c_{2}$ | 1 | 1 | 0.75800 |
| $c_{3}$ | 0 | 0 | 0 |
| $c_{4}$ | 1 | 1 | 2 |
| $c_{5}$ | 1 | 1 | 0 |
| $C_{10}$ | 0.75 | 0.75 | 0.37500 |
| $\mathrm{C}_{2}$ o | 0.75800 | 0.75800 | 0.75800 |
| $V_{e}(\mathrm{eV})$ | -28.41703 | -28.41703 | -20.62357 |
| $V_{p}(\mathrm{eV})$ | 9.67746 | 9.67746 | 6.18908 |
| $T(\mathrm{eV})$ | 6.32210 | 6.32210 | 3.75324 |
| $V_{m}(\mathrm{eV})$ | -3.16105 | -3.16105 | -1.87662 |
| $E$ (Ао/но) (eV) | -10.25487 | -10.25487 | -10.25487 |
| $\Delta E_{\mathrm{H}_{2} \text { МО }}($ АО/НО) $(\mathrm{eV})$ | 0 | 0 | 0 |
| $E_{T}($ Ао/ $/ \mathrm{Ho})(\mathrm{eV})$ | -10.25487 | -10.25487 | -10.25487 |
| $E_{T}\left(\mathrm{H}_{2} \mathrm{MO}\right)(\mathrm{eV})$ | -25.83339 | -25.83339 | -22.81274 |
| $E_{T}\left(\right.$ atom - atom, $\left.\mathrm{msp}^{3} . \mathrm{AO}\right)(\mathrm{eV})$ | -1.06358 | -1.37960 | -0.96031 |
| $E_{T}(\mathrm{mo})(\mathrm{eV})$ | -26.89697 | -27.21299 | -23.77305 |
| $\omega\left(10^{15} \mathrm{rad} / \mathrm{s}\right)$ | 13.4257 | 13.4257 | 4.83999 |
| $E_{K}(\mathrm{eV})$ | 8.83703 | 8.83703 | 3.18577 |
| $\bar{E}_{D}(\mathrm{eV})$ | -0.15818 | -0.16004 | -0.08395 |
| $\bar{E}_{\text {Kvib }}(\mathrm{eV})$ | $\begin{gathered} 0.25315 \\ {[3]} \\ \hline \end{gathered}$ | $\begin{gathered} \hline 0.25315 \\ {[3]} \\ \hline \end{gathered}$ | $\begin{gathered} \hline 0.06335 \\ {[3]} \end{gathered}$ |
| $\bar{E}_{\text {osc }}(\mathrm{eV})$ | -0.03161 | -0.03346 | -0.05227 |
| $E_{\text {mag }}(\mathrm{eV})$ | 0.04983 | 0.04983 | 0.04983 |
| $E_{T}($ Group) $(\mathrm{eV})$ | -26.92857 | -27.24646 | -23.82532 |
| $E_{\text {initial }}\left(\mathrm{c}_{\mathrm{s}}\right.$, Ао/но) $(\mathrm{eV})$ | -10.25487 | -10.25487 | -10.25487 |
| $E_{\text {initialal }}\left(c_{5}\right.$, Ао/но) $(\mathrm{eV})$ | -13.59844 | -13.59844 | 0 |
| $E_{D}($ Group $)(e \mathrm{~V})$ | 3.07526 | 3.39314 | 3.31557 |
| Exp. $E_{D}($ Group $)(\mathrm{eV})$ | 3.0398 ( Si-H [4]) |  | 3.3269 ( $\mathrm{H}_{3} \mathrm{Si}-\mathrm{SiH}_{3}$ [5]) |

Table 20.6. The total bond energies of silanes calculated using the functional group composition and the energies of Table 20.5 compared to the experimental values.

| Formula |  | Name |  |  | $\begin{gathered} \hline \mathrm{Si-H} \text { (i) } \\ \text { Group } \end{gathered}$ |  | $\begin{gathered} S i-H \text { (ii) } \\ \text { Group } \end{gathered}$ |  | $\mathrm{Si}-\mathrm{Si}$ <br> Group |  | CalculatedTotal Bond Energy (eV) |  |  | ExperimentalTotal Bond Energy (eV) |  |  |  | Relative Error |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| SiH | Silylidyne |  |  |  | 1 |  |  |  | 0 |  | 3.07526 |  |  | 3.02008 [6] |  |  |  | -0.01827 |  |
| $\mathrm{SiH}_{2}$ |  | Silylene |  |  | 2 |  | 0 |  | 0 |  | 6.15052 |  |  | 6.35523 [7] |  |  |  | 0.03221 |  |
| $\mathrm{SiH}_{3}$ |  | Silyl |  |  | 3 |  | 0 |  | 0 |  | 9.22578 |  |  | 9.36494 [7] |  |  |  | 0.01486 |  |
| $\mathrm{SiH}_{4}$ |  | Silane |  |  | 0 |  | 4 |  | 0 |  | 13.57257 |  |  | 13.34577 [6] |  |  |  | -0.01699 |  |
| $\mathrm{Si}_{2} \mathrm{H}_{6}$ |  | Trisilane |  |  | 6 |  | 0 |  | 1 |  | 21.7671331.23322 |  |  |  | 22.05 | 72 [7] |  |  | 01308 |
| $\mathrm{Si}_{3} \mathrm{H}_{8}$ |  |  |  |  | 2 |  |  |  | 30.81334 [7] |  |  |  | -0.01363 |  |
| Table 20.7. The bond angle parameters of silanes and experimental values [2]. In the calculation of $\theta_{v}$ (Eq. (15.112)), the parameters from the preceding used. $E_{T}$ is $E_{T}$ (atom - atom $m s p^{3} \cdot A O$ ). |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| $\begin{aligned} & \text { Atoms of } \\ & \text { Angle } \end{aligned}$ | $\begin{gathered} 2 c^{\prime} \\ \text { Bond } 1 \\ \left(a_{0}\right) \end{gathered}$ | $\begin{gathered} 2 c^{\prime} \\ \text { Bond } 2 \\ \left(a_{0}\right) \end{gathered}$ | $\begin{array}{\|c\|} \hline 2 c^{\prime} \\ \text { Terminal } \\ \text { Atoms }\left(a_{0}\right) \end{array}$ | $E_{\text {Columble }}$ Atom 1 |  |  | Atom 1Hybridization <br> terms(Table 20.1) |  | Atom 2 <br> Hybridization <br> terms(Table 20.1) | $\begin{gathered} c_{2} \\ \text { Atom } 1 \end{gathered}$ |  |  |  | $\begin{gathered} c_{2} \\ \text { Atom 2 } \end{gathered}$ | $C_{1}$ | $C_{2}$ | $c_{1}$ | $c_{2}^{\prime}$ | $\begin{gathered} E_{E_{r}} \\ (\mathrm{eV}) \end{gathered}$ | $\begin{aligned} & \theta_{v} \\ & \left({ }^{\circ}\right) \end{aligned}$ | $\begin{aligned} & \theta_{1} \\ & \left({ }^{\circ}\right) \end{aligned}$ | $\begin{aligned} & \theta_{2} \\ & \left({ }^{\circ}\right) \end{aligned}$ | $\begin{gathered} \text { Cal. } \theta \\ \left({ }^{\circ}\right) \end{gathered}$ | $\begin{gathered} \text { Exp. } \theta \\ \left({ }^{\circ}\right) \end{gathered}$ |
| $\begin{gathered} \text { Silyl } \\ \angle H S i_{a} H \end{gathered}$ | 2.81185 | 2.81185 | 4.5673 | $\begin{gathered} -10.79339 \\ S_{i_{a}} \\ \hline \end{gathered}$ | 2 | H | H | 0.79329 | 1 | 1 | 1 | 0.75 | 1.26057 | ${ }^{-1.06358}$ |  |  |  | 108.61 | $\begin{gathered} 108.6 \\ \text { (disilane) } \\ \hline \end{gathered}$ |
| $\angle H S i_{a} S i_{b}$ |  |  |  |  |  |  |  |  |  |  |  |  |  |  | 69.68 |  |  | 110.32 | $\begin{gathered} 110.3 \\ \text { (disilane) } \end{gathered}$ |

ALKYL SILANES AND DISILANES ( $\left.S i_{m} C_{n} H_{2(m+n)+2}, m, n=1,2,3,4,5 \ldots \infty\right)$
The branched-chain alkyl silanes and disilanes, $\mathrm{Si}_{m} \mathrm{C}_{n} \mathrm{H}_{2(m+n)+2}$, comprise at least a terminal methyl group ( $\mathrm{CH}_{3}$ ) and at least one Si bound by a carbon-silicon single bond comprising a $\mathrm{C}-\mathrm{Si}$ group, and may comprise methylene ( $\mathrm{CH}_{2}$ ), methylyne ( CH ), $\mathrm{C}-\mathrm{C}, \mathrm{SiH}_{n=1,2,3}$, and $\mathrm{Si}-\mathrm{Si}$ functional groups. 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 straightchain alkanes. In addition, the $\mathrm{C}-\mathrm{C}$ bonds within isopropyl $\left(\left(\mathrm{CH}_{3}\right)_{2} \mathrm{CH}\right)$ and t-butyl $\left(\left(\mathrm{CH}_{3}\right)_{3} \mathrm{C}\right)$ groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups. These groups in branched-chain alkyl silanes and disilanes are equivalent to those in branched-chain alkanes, and the $\mathrm{SiH}_{n=1,2,3}$ functional groups of alkyl silanes are equivalent to those in silanes $\left(S i_{n} H_{2 n+2}\right)$. The $\mathrm{Si}-\mathrm{Si}$ functional group of alkyl silanes is equivalent to that in silanes; however, in dialkyl silanes, the $S i-S i$ functional group is different due to an energy matching condition with the $C-S i$ bond having a mutual silicon atom.

For the $C-S i$ functional group, hybridization of the $2 s$ and $2 p$ AOs of each $C$ and the $3 s$ and $3 p$ AOs of each $S i$ to form single $2 s p^{3}$ and $3 s p^{3}$ shells, respectively, forms an energy minimum, and the sharing of electrons between the $C 2 s p^{3}$ and Si3sp ${ }^{3}$ HOs to form a MO permits each participating orbital to decrease in radius and energy. In branched-chain alkyl silanes, the energy of silane 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 $C 2 s p^{3} \mathrm{HO}$ has an energy of $E\left(C, 2 s p^{3}\right)=-14.63489 \mathrm{eV}$ (Eq. (15.25)), and the $S i 3 s p^{3} \mathrm{HO}$ has an energy of $E\left(S i, 3 s p^{3}\right)=-10.25487 \mathrm{eV}$ (Eq. (20.7)). To meet the equipotential condition of the union of the $\mathrm{C}-\mathrm{Si} \mathrm{H}_{2}$-type-ellipsoidal-MO with these orbitals, the hybridization factor $C_{2}$ of Eq. (15.61) for the $C-S i$-bond MO given by Eq. (15.77) is:

$$
\begin{equation*}
C_{2}\left(C 2 s p^{3} \mathrm{HO} \text { to } \mathrm{Si} 3 s p^{3} \mathrm{HO}\right)=\frac{E\left(S i, 3 s p^{3}\right)}{E\left(C, 2 s p^{3}\right)}=\frac{-10.25487 \mathrm{eV}}{-14.63489 \mathrm{eV}}=0.70071 \tag{20.37}
\end{equation*}
$$

For monosilanes, $E_{T}\left(\right.$ atom-atom, $\left.m s p^{3} . A O\right)$ of the $C-S i$-bond MO is -1.20473 eV corresponding to the single-bond contributions of carbon and silicon of -0.72457 eV given by Eq. (14.151) and -0.48015 eV given by Eq. (14.151) with $s=1 \mathrm{in}$ Eq. (15.18). The energy of the $C-S i$-bond MO is the sum of the component energies of the $H_{2}$-type ellipsoidal MO given in Eq. (15.51) with $E(A O / H O)=E\left(S i, 3 s p^{3}\right)$ given by Eq. (20.7) and $\Delta E_{H_{2} M O}(A O / H O)=E_{T}\left(\right.$ atom - atom, $\left.m s p^{3} . A O\right)$ in order to match the energies of the carbon and silicon HOs.

For the co-bonded $\mathrm{Si}-\mathrm{Si}$ group of the $\mathrm{C}-\mathrm{Si}$ group of disilanes, $E_{T}\left(\right.$ atom-atom, $\left.\mathrm{msp}{ }^{3} . \mathrm{AO}\right)$ is -0.96031 eV , two times $E_{T}\left(S i-S i, 3 s p^{3}\right)$ given by Eq. (20.12). Thus, in order to match the energy between these groups, $E_{T}\left(\right.$ atom-atom, $\left.\mathrm{msp}^{3} . \mathrm{AO}\right)$ of the $\mathrm{C}-\mathrm{Si}$-bond MO is -0.92918 eV corresponding to the single-bond methylene-type contribution of carbon given by Eq. (14.513). As in the case of monosilanes, $E(A O / H O)=E\left(S i, 3 s p^{3}\right)$ given by Eq. (20.7) and $\Delta E_{H_{2} M O}(A O / H O)=E_{T}\left(\right.$ atom -atom, $\left.m s p^{3} . A O\right)$ in order to match the energies of the carbon and silicon HOs.

The symbols of the functional groups of alkyl silanes and disilanes are given in Table 20.8. The geometrical (Eqs. (15.115.5), (20.1-20.16), (20.29), (20.32-20.33) and (20.37)) and intercept (Eqs. (15.80-15.87) and (20.21)) parameters of alkyl silanes and disilanes are given in Tables 20.9 and 20.10, respectively. Since the energy of the $\mathrm{Si} 3 s p^{3} \mathrm{HO}$ is matched to that of the $C 2 s p^{3} \mathrm{HO}$, the radius $r_{\text {mol2sp }}{ }^{3}$ of the $S i 3 s p^{3} \mathrm{HO}$ of the silicon atom and the $C 2 s p^{3} \mathrm{HO}$ of the carbon atom of a given $C-S i-$ bond MO is calculated after Eq. (15.32) by considering $\sum E_{T_{m o l}}\left(M O, 2 s p^{3}\right)$, the total energy donation to all bonds with which each atom participates in bonding. In the case that the MO does not intercept the Si HO due to the reduction of the radius from the donation of Si $3 s p^{3}$ HO charge to additional MO's, the energy of each MO is energy matched as a linear sum to the Si HO by contacting it through the bisector current of the intersecting MOs as described in the Methane Molecule ( $\mathrm{CH}_{4}$ ) section. The energy (Eqs. (15.61), (20.1-20.16), and (20.33-20.37)) parameters of alkyl silanes and disilanes are given in Table 20.11. The total energy of each alkyl silane and disilane given in Table 20.12 was calculated as the sum over the integer multiple of each $E_{D}($ Group $)$ of Table 20.11 corresponding to functional-group composition of the molecule. The bond angle parameters of alkyl silanes and disilanes determined using Eqs. (15.88-15.117) and Eq. (20.36) are given in Table 20.13. The charge-densities of exemplary alkyl silane, dimethylsilane and alkyl disilane, hexamethyldisilane 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 are shown in Figures 20.3 A and B , respectively.

Figure 20.3. (A) Dimethylsilane and (B) Hexamethyldisilane, color scale, translucent views of the charge-density of each silane showing the orbitals of the Si and C 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 atoms participating in each bond, and the hydrogen nuclei (red, not to scale).


Table 20.8. The symbols of functional groups of alkyl silanes and disilanes.

| Functional Group | Group Symbol |
| :---: | :---: |
| CSi bond (monosilanes) | $C-S i$ (i) |
| CSi bond (disilanes) | $C-S i(i i)$ |
| SiSi bond ( $n-S i$ ) | $\mathrm{Si}-\mathrm{Si}$ |
| SiH group of $\mathrm{SiH}_{n=1,2,3}$ | Si-H |
| $\mathrm{CH}_{3}$ group | $\mathrm{C}-\mathrm{H}\left(\mathrm{CH}_{3}\right)$ |
| $\mathrm{CH}_{2}$ group | $\mathrm{C}-\mathrm{H}\left(\mathrm{CH}_{2}\right)$ |
| CH | C-H |
| $C C$ bond ( $n-C$ ) | $C-C$ (a) |
| $C C$ bond (iso-C) | $C-C$ (b) |
| $C C$ bond (tert-C) | $C-C$ (c) |
| CC (iso to iso-C) | $C-C$ (d) |
| $C C$ ( $t$ to $t$ - $C$ ) | $C-C$ (e) |
| $C C$ ( $t$ to iso-C) | $C-C$ (f) |

Table 20.9. The geometrical bond parameters of alkyl silanes and disilanes and experimental values.

| Parameter | $\underset{\text { Group }}{C-S i}$ | $\begin{gathered} C-S i(\text { ii) } \\ \text { Group } \end{gathered}$ | $\begin{gathered} \mathrm{Si}-\mathrm{H} \\ \text { Group } \end{gathered}$ | $\begin{aligned} & S i-S i \\ & \text { Group } \end{aligned}$ | $\begin{gathered} \mathrm{C}-\mathrm{H}\left(\mathrm{CH}_{3}\right) \\ \text { Group } \\ \hline \end{gathered}$ | $\begin{gathered} \mathrm{C}-\mathrm{H}\left(\mathrm{CH}_{2}\right) \\ \text { Group } \\ \hline \end{gathered}$ | $\begin{aligned} & \mathrm{C}-\mathrm{H} \\ & \text { Group } \end{aligned}$ | $\begin{gathered} C-C \text { (a) } \\ \text { Group } \end{gathered}$ | $\begin{gathered} C-C(b) \\ \text { Group } \end{gathered}$ | $\begin{gathered} C-C \text { (c) } \\ \text { Group } \end{gathered}$ | $\begin{gathered} C-C \text { (d) } \\ \text { Group } \end{gathered}$ | $\begin{gathered} C-C(\mathrm{e}) \\ \text { Group } \end{gathered}$ | $\begin{gathered} C-C(\mathrm{f}) \\ \text { Group } \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $a\left(a_{0}\right)$ | 2.20339 | 2.21935 | 2.24744 | 2.74744 | 1.64920 | 1.67122 | 1.67465 | 2.12499 | 2.12499 | 2.10725 | 2.12499 | 2.10725 | 2.10725 |
| $c^{\prime}\left(a_{0}\right)$ | 1.77327 | 1.77968 | 1.40593 | 2.19835 | 1.04856 | 1.05553 | 1.05661 | 1.45744 | 1.45744 | 1.45164 | 1.45744 | 1.45164 | 1.45164 |
| $\begin{gathered} \text { Bond } \\ \text { Length } \\ 2 c^{\prime}(A) \end{gathered}$ | 1.87675 | 1.88353 | 1.48797 | 2.32664 | 1.10974 | 1.11713 | 1.11827 | 1.54280 | 1.54280 | 1.53635 | 1.54280 | 1.53635 | 1.53635 |
| Exp. Bond Length (A) | 1.867 (methylsilane) [8] 1.875 (tetramethylsilane) $[1.877$ 1.877 (methylsilane) [9] 1.871 (dimethylsilane) [9] 1.878 (trimethylsilane) [9] |  | 1.485 (methysilane) ${ }^{1.49]}$ $\left(i_{2} H_{6}\right)[8]$ 1.489 (trimethylsilane) $[9]$ |  | 1.093 (methylsilane) $[8]$ 1.115 (tetramethylsilane) $[8]$ 1.107 $(C-H$ propane) $[8]$ 1.117 $(C-H$ butane) $[8]$ | $\begin{gathered} 1.107 \\ (\mathrm{C}-\mathrm{H} \text { propane) }[8] \\ 1.117 \\ (\mathrm{C}-\mathrm{H} \text { butane })[8] \end{gathered}$ | $\begin{gathered} 1.122 \\ \text { (isobutane) [8] } \end{gathered}$ | $\begin{gathered} 1.532 \\ \text { (propane) }[8] \\ 1.531 \\ \text { (butane) }[8] \end{gathered}$ | $\begin{gathered} 1.532 \\ \text { (propane) }[8] \\ 1.531 \\ \text { (butane) }[8] \end{gathered}$ | $\begin{gathered} 1.532 \\ \text { (propane) }[8] \\ 1.531 \\ \text { (butane) }[8] \end{gathered}$ |  | $\begin{gathered} 1.532 \\ \text { (propane) }[8] \\ 1.531 \\ \text { (butane) }[8] \end{gathered}$ | $\begin{gathered} 1.532 \\ \text { (propane) }[8] \\ 1.531 \\ \text { (butane) }[8] \end{gathered}$ |
| $b, c\left(a_{0}\right)$ | 1.30783 | 1.32599 | 1.75338 | 1.64792 | 1.27295 | 1.29569 | 1.29924 | 1.54616 | 1.54616 | 1.52750 | 1.54616 | 1.52750 | 1.52750 |
| $e$ | 0.80479 | 0.80189 | 0.62557 | 0.80015 | 0.63580 | 0.63159 | 0.63095 | 0.68600 | 0.68600 | 0.68888 | 0.68600 | 0.68888 | 0.68888 |


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| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\cdots$ |  |  |  |  |  | $\begin{aligned} & \stackrel{\text { İ }}{\text { ® }} \\ & \hline \end{aligned}$ | $\begin{aligned} & \text { os } \\ & \\ & \end{aligned}$ | $\begin{aligned} & \text { İ } \\ & \text { TH } \end{aligned}$ |  | $\begin{aligned} & \tilde{n} \\ & \stackrel{\rightharpoonup}{0} \\ & \underset{\sim}{2} \end{aligned}$ | $\begin{aligned} & E \\ & E \\ & 0 \\ & 2 \end{aligned}$ | $\frac{6}{2}$ |  |  | $\stackrel{\text { त్రి }}{\stackrel{-}{i}}$ | $\begin{aligned} & \infty \\ & \stackrel{\infty}{\circ} \\ & \stackrel{y}{1} \end{aligned}$ |  | $\frac{\widehat{\alpha}}{\stackrel{O}{\infty}}$ | $\stackrel{\circ}{6}$ <br> $\stackrel{\circ}{\circ}$ <br> $\stackrel{\sim}{ـ}$ | $\begin{aligned} & \stackrel{\text { O}}{6} \\ & \underset{\sim}{n} \\ & \hline \end{aligned}$ | $\begin{aligned} & \text { Lo } \\ & \stackrel{6}{6} \end{aligned}$ | $\stackrel{n}{A}$ |  |  |  | $$ | \% | $\frac{\stackrel{\rightharpoonup}{O}}{\widehat{a}}$ | 苟 | $\frac{\stackrel{O}{0}}{2}$ | $\begin{aligned} & \underset{\square}{2} \\ & \stackrel{y}{2} \\ & \hline \end{aligned}$ | 等 | 年 |
| 00 |  |  |  | $\begin{aligned} & \infty \\ & \stackrel{\infty}{\infty} \end{aligned}$ | 畜 | $\begin{aligned} & 8 \\ & \hline \mathbf{0} \end{aligned}$ | $\frac{\pi}{\Gamma}$ | $\stackrel{\mathscr{\infty}}{\underset{\sim}{+}}$ | $\stackrel{\dddot{8}}{2}$ | $\begin{aligned} & \stackrel{\rightharpoonup}{c} \\ & \dot{d} \end{aligned}$ | $\underset{\substack{\infty \\ \underset{\sim}{2} \\ \hline}}{ }$ |  | $\frac{\infty}{e}$ |  | $\stackrel{8}{8}$ | $$ | $\frac{\circ}{\text { d }}$ | $\stackrel{\rightharpoonup}{9}$ | $\begin{gathered} \infty \\ \underset{\sim}{\infty} \\ \hline \end{gathered}$ | $\stackrel{\infty}{\stackrel{\infty}{\infty}}$ | $\stackrel{8}{7}$ | $\frac{9}{8}$ | $\stackrel{\infty}{\underset{\sim}{2}}$ | $\begin{aligned} & \vec{\sim} \\ & \underset{\sim}{\circ} \\ & \hline \end{aligned}$ | $\frac{\sqrt{2}}{m}$ | $\begin{aligned} & \text { oib } \\ & \hline 0 \end{aligned}$ | $\begin{gathered} \underset{\sim}{\circ} \\ \underset{\sim}{n} \end{gathered}$ | 음 | $\stackrel{\pi}{\sim}$ | $\frac{8}{\mathrm{~N}}$ | $\begin{aligned} & \stackrel{\text { ® }}{4} \end{aligned}$ | $\begin{aligned} & \text { d } \\ & \text { d } \end{aligned}$ | ＊ |
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Table 20.11. The energy parameters $(\mathrm{eV})$ of functional groups of alkyl silanes and disilanes





Table 20.12. The total bond energies of alkyl silanes and disilanes calculated using the functional group composition and the energies of Table 20.11 compared to the
experimental valu

Table 20．13．The bond angle parameters of alkyl silanes and disilanes and experimental values．In the calculation of $\theta_{v}$ ，the parameters from the preceding angle were used．$E_{T}$ is $E_{T}\left(\right.$ atom－atom $\left.m s p^{3} . A O\right)$ ．

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|  | $\sim \overparen{\text { © }}$ |  | $\text { in } \stackrel{\substack{\underset{\sim}{c}\\}}{ }$ |  |  |  |  |  |  |  | $\cdots \stackrel{\substack{e \\ \stackrel{\sim}{6}}}{ }$ |  |  | $\stackrel{\sim}{\sim}$ | in | in $\stackrel{\substack{e \\=}}{ }$ | ¢ ¢ ¢ |  |
|  |  |  | $\begin{aligned} & \text { लि } \\ & \hat{N} 0^{\circ} \\ & \stackrel{n}{1} \end{aligned}$ |  |  |  |  |  |  |  | $\begin{aligned} & \underset{\sim}{\underset{\sim}{2}} \\ & \stackrel{\sim}{n} \\ & \stackrel{i}{n} \end{aligned}$ |  |  |  | $\begin{aligned} & \text { लि } \\ & \stackrel{N}{n} \\ & \stackrel{n}{1} \end{aligned}$ | $\begin{aligned} & \stackrel{n}{n} \\ & \stackrel{n}{n} \\ & \stackrel{n}{n} \end{aligned}$ |  |  |
|  | $\begin{gathered} n \\ \stackrel{6}{6} \end{gathered}$ |  | $\begin{aligned} & \stackrel{\circ}{\mathscr{N}} \\ & \stackrel{\infty}{n} \end{aligned}$ |  | $\begin{aligned} & \text { Ñ } \\ & \underset{\sim}{r} \end{aligned}$ |  |  | $\begin{gathered} \tilde{\jmath} \\ \underset{\sim}{\text { rin }} \end{gathered}$ |  |  | $\begin{gathered} \tilde{\sim} \\ \underset{\sim}{c} \end{gathered}$ |  |  | $\stackrel{\infty}{\stackrel{\infty}{\sim}}$ | $\stackrel{\substack{\hat{O} \\ \hdashline}}{ }$ | $\stackrel{\text { N}}{\substack{\text { ¢ }}}$ | $\stackrel{\substack{\circ \\ \underset{\sim}{\sim}}}{\sim}$ |  |
| 드를 | $\stackrel{\curvearrowleft}{\stackrel{\infty}{\infty}}$ |  |  |  | $\begin{aligned} & \overline{\text { F }} \\ & \text { ì } \end{aligned}$ |  |  | $\stackrel{\bullet}{\vdots}$ |  |  | $\begin{aligned} & \overline{\hat{O}} \\ & \text { ì } \end{aligned}$ |  |  | $\begin{aligned} & \text { fे } \\ & \frac{\mathrm{N}}{\mathrm{i}} \end{aligned}$ | $\begin{aligned} & \text { त্} \\ & \stackrel{N}{i} \end{aligned}$ | $\begin{aligned} & \overline{\mathrm{O}} \\ & \text { ì } \end{aligned}$ | तो ¢ ì |  |
| 次 | $\stackrel{\curvearrowleft}{\stackrel{\infty}{\infty}}$ |  | $\begin{aligned} & \vec{N} \\ & \stackrel{y}{6} \\ & \underset{\sim}{n} \\ & \end{aligned}$ |  |  |  |  | $\stackrel{\otimes}{\text { ® }}$ |  |  | $\begin{aligned} & \overline{\text { In }} \\ & \underset{\text { in }}{2} \end{aligned}$ |  |  | $\stackrel{\text { ¢ }}{\substack{\text { a } \\ \text { i }}}$ | $\begin{aligned} & \text { 氐 } \\ & \frac{\mathrm{N}}{2} \end{aligned}$ | $\stackrel{\text { ¢ }}{\substack{\text { a }}}$ |  |  |
| $\begin{aligned} & 4 \\ & 0 \\ & 0 \\ & 0 \\ & 0 \\ & 0 \\ & 0 \\ & 0 \end{aligned}$ | 公公 |  | $\begin{aligned} & U_{0}^{0} \\ & \mathbf{U}^{\circ} \\ & \mathrm{v} \end{aligned}$ | $\begin{aligned} & \text { 霜 } \\ & v_{0} \end{aligned}$ |  | $\begin{aligned} & \tilde{n}_{0} \\ & \frac{1}{v} \end{aligned}$ | V | $\left\lvert\, \begin{aligned} & 0 \\ & \frac{0}{2} \\ & \frac{2}{x} \\ & \frac{1}{2} \\ & \frac{2}{2} \\ & 0 \end{aligned}\right.$ | $\begin{aligned} & U_{0}^{0} \\ & \mathcal{U}_{0}^{0} \\ & \text { 俍 } \end{aligned}$ | $\begin{aligned} & Z_{0} \\ & 0_{0} \\ & \stackrel{y}{c} \end{aligned}$ |  | V | V | $\begin{array}{lll} 0_{0}^{0} & 0 \\ 0 & 0 \\ 0 & 0 \\ 0 & 0 \\ 1 & .0 \end{array}$ |  | $\left\lvert\, \begin{array}{ll} 1 & 0 \\ 0 & 0 \\ 0_{0} & 0 \\ \text { v} & 0 \\ 0 \end{array}\right.$ | $\begin{aligned} & 0_{0}^{0} \\ & 0 \\ & 0.0 \\ & 0_{0}^{0} \\ & \mathrm{v} \end{aligned}$ | Co |

## SILICON OXIDES, SILICIC ACIDS, SILANOLS, SILOXANES AND DISILOXANES

The silicon oxides, silicic acids, silanols, siloxanes, and disiloxanes each comprise at least one $\mathrm{Si}-\mathrm{O}$ group, and this group in disiloxanes is part of the $\mathrm{Si}-\mathrm{O}-\mathrm{Si}$ moiety. Silicic acids may have up to three $\mathrm{Si}-\mathrm{H}$ bonds corresponding to the $\mathrm{SiH}_{n=1,2,3}$ functional groups of alkyl silanes, and silicic acids and silanols further comprise at least one $O H$ group equivalent to that of alcohols. In addition to the $\mathrm{SiH}_{n=1,2,3}$ group of alkyl silanes, silanols, siloxanes, and disiloxanes may comprise the functional groups of organic molecules as well as the $C-S i$ group of alkyl silanes. The alkyl portion of the alkyl silanol, siloxane, or disiloxane may comprise at least one terminal methyl group $\left(\mathrm{CH}_{3}\right)$ the end of each alkyl chain, and may comprise methylene $\left(\mathrm{CH}_{2}\right)$, 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 $\mathrm{C}-\mathrm{C}$ bond is the same as that of straight-chain alkanes. In addition, the $\mathrm{C}-\mathrm{C}$ bonds within isopropyl $\left(\left(\mathrm{CH}_{3}\right)_{2} \mathrm{CH}\right)$ and tbutyl $\left(\left(\mathrm{CH}_{3}\right)_{3} \mathrm{C}\right)$ groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $\mathrm{C}-\mathrm{C}$ bonds comprise functional groups. The branched-chain-alkane groups in silanols, siloxanes, and disiloxanes are equivalent to those in branchedchain alkanes. The alkene groups when present such as the $C=C$ group are equivalent to those of the corresponding alkene. Siloxanes further 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 as given for ethers.

The distinguishing aspect of silicon oxides, silicic acids, silanols, siloxanes, and disiloxane is the nature of the corresponding $\mathrm{Si}-\mathrm{O}$ functional group. In general, the sharing of electrons between a $\mathrm{Si} 3 s p^{3} \mathrm{HO}$ and an O 2 p AO to form a $\mathrm{Si}-\mathrm{O}$-bond MO permits each participating orbital to decrease in size and energy. Consider the case wherein the Si3sp ${ }^{3}$ HO donates an excess of $50 \%$ of its electron density to the $\mathrm{Si}-\mathrm{O}$-bond MO to form an energy minimum while further satisfying the potential, kinetic, and orbital energy relationships. By considering this electron redistribution in the molecule comprising a $\mathrm{Si}-\mathrm{O}$ bond as well as the fact that the central field decreases by an integer for each successive electron of the shell, the radius $r_{S i-O 3 s p^{3}}$ of the $S i 3 s p^{3}$ shell may be calculated from the Coulombic energy using Eq. (15.18).

$$
\begin{equation*}
r_{S i-O 3 s p^{3}}=\left(\sum_{n=10}^{13}(Z-n)-0.5\right) \frac{e^{2}}{8 \pi \varepsilon_{0}(e 105.23554 \mathrm{eV})}=\frac{9.5 e^{2}}{8 \pi \varepsilon_{0}(\mathrm{e} 105.23554 \mathrm{eV})}=1.22825 a_{0} \tag{20.38}
\end{equation*}
$$

Using Eqs. (15.19) and (20.38), the Coulombic energy $E_{\text {Coulomb }}\left(S i_{S i-O}, 3 s p^{3}\right)$ of the outer electron of the $S i 3 s p^{3}$ shell is:

$$
\begin{equation*}
E_{\text {Coulomb }}\left(S i_{S i-O}, 3 s p^{3}\right)=\frac{-e^{2}}{8 \pi \varepsilon_{0} r_{S i-O 3 s p^{3}}}=\frac{-e^{2}}{8 \pi \varepsilon_{0} 1.22825 a_{0}}=-11.07743 \mathrm{eV} \tag{20.39}
\end{equation*}
$$

During hybridization, the spin-paired $3 s$ electrons are promoted to the $S i 3 s p^{3}$ shell as unpaired electrons. The energy for the promotion is the magnetic energy given by Eq. (20.6). Using Eqs. (20.6) and (20.39), the energy $E\left(S i_{S i-O}, 3 s p^{3}\right)$ of the outer electron of the $S i 3 s p^{3}$ shell is:

$$
\begin{equation*}
E\left(S i_{S i-O}, 3 s p^{3}\right)=\frac{-e^{2}}{8 \pi \varepsilon_{0} r_{\text {silane } 3 s p^{3}}}+\frac{2 \pi \mu_{0} e^{2} \hbar^{2}}{m_{e}^{2}\left(r_{12}\right)^{3}}=-11.07743 \mathrm{eV}+0.05836 \mathrm{eV}=-11.01906 \mathrm{eV} \tag{20.40}
\end{equation*}
$$

Thus, $E_{T}\left(S i-O, 3 s p^{3}\right)$, the energy change of each $S i 3 s p^{3}$ shell with the formation of the $S i-O$-bond MO is given by the difference between Eq. (20.40) and Eq. (20.7):

$$
\begin{equation*}
E_{T}\left(S i-O, 3 s p^{3}\right)=E\left(S i_{s i-O}, 3 s p^{3}\right)-E\left(S i, 3 s p^{3}\right)=-11.01906 \mathrm{eV}-(-10.25487 \mathrm{eV})=-0.76419 \mathrm{eV} \tag{20.41}
\end{equation*}
$$

Using Eq. (15.28), to meet the energy matching condition in silanols and siloxanes for all $\sigma$ MOs at the Si3sp ${ }^{3} \mathrm{HO}$ and $O 2 p \mathrm{AO}$ of each $\mathrm{Si}-\mathrm{O}$-bond MO as well as with the $C 2 s p^{3} \mathrm{HOs}$ of the molecule, the energy $E\left(S i_{R S i-O R^{\prime}}, 3 s p^{3}\right)\left(R, R^{\prime}\right.$ are alkyl or $H$ ) of the outer electron of the $S i 3 s p^{3}$ shell of the silicon atom must be the average of $E\left(S i_{\text {silane }}, 3 s p^{3}\right)$ (Eq. (20.11)) and $E_{T}\left(S i-O, 3 s p^{3}\right)$ (Eq. (20.40)).

$$
\begin{equation*}
E\left(S i_{R S i-O R^{\prime}}, 3 s p^{3}\right)=\frac{E\left(S i_{\text {silane }}, 3 s p^{3}\right)+E\left(S i_{S i-O}, 3 s p^{3}\right)}{2}=\frac{(-10.73503 \mathrm{eV})+(-11.01906 \mathrm{eV})}{2}=-10.87705 \mathrm{eV} \tag{20.42}
\end{equation*}
$$

Using Eq. (15.29), $E_{T_{\text {silumol silisame }}}\left(S i-O, 3 s p^{3}\right)$, the energy change of each $S i 3 s p^{3}$ shell with the formation of each $R S i-O R^{\prime}$-bond MO, must be the average of $E_{T}\left(S i-S i, 3 s p^{3}\right)$ (Eq. (20.12)) and $E_{T}\left(S i-O, 3 s p^{3}\right)$ (Eq. (20.41)).

$$
\begin{equation*}
E_{T_{\text {sllanol, Ilioxane }}}\left(S i-O, 3 s p^{3}\right)=\frac{E_{T}\left(S i-S i, 3 s p^{3}\right)+E_{T}\left(S i-O, 3 s p^{3}\right)}{2}=\frac{(-0.48015 \mathrm{eV})+(-0.76419 \mathrm{eV})}{2}=-0.62217 \mathrm{eV} \tag{20.43}
\end{equation*}
$$

To meet the energy matching condition in silicic acids for all $\sigma$ MOs at the $\mathrm{Si} 3 \mathrm{sp}{ }^{3} \mathrm{HO}$ and O 2 p AO of each $\mathrm{Si}-\mathrm{O}$ bond MO as well as all $H$ AOs, the energy $E\left(S i_{H_{n} S i-(O H)_{4-n}}, 3 s p^{3}\right)$ of the outer electron of the $S i 3 s p^{3}$ shell of the silicon atom must be the average of $E\left(S i_{\text {silane }}, 3 s p^{3}\right)$ (Eq. (20.15)) and $E_{T}\left(S i-O, 3 s p^{3}\right)$ (Eq. (20.40)).

$$
\begin{equation*}
E\left(S i_{H_{n} S i-(O H)_{4-n}}, 3 s p^{3}\right)=\frac{E\left(S i_{\text {silane }}, 3 s p^{3}\right)+E\left(S i_{S i-O}, 3 s p^{3}\right)}{2}=\frac{(-11.37682 \mathrm{eV})+(-11.01906 \mathrm{eV})}{2}=-11.16876 \mathrm{eV} \tag{20.44}
\end{equation*}
$$

Using Eq. (15.29), $E_{T_{\text {silicic acid }}}\left(S i-O, 3 s p^{3}\right)$, the energy change of each $S i 3 s p^{3}$ shell with the formation of each $R S i-O R^{\prime}$-bond MO, must be the average of $E_{T}\left(S i-H, 3 s p^{3}\right)$ (Eq. (20.16)) and $E_{T}\left(S i-O, 3 s p^{3}\right)$ (Eq. (20.41)).

$$
\begin{equation*}
E_{T_{\text {sllicic acid }}}\left(S i-O, 3 s p^{3}\right)=\frac{E_{T}\left(S i-H, 3 s p^{3}\right)+E_{T}\left(S i-O, 3 s p^{3}\right)}{2}=\frac{(-1.06358 \mathrm{eV})+(-0.76419 \mathrm{eV})}{2}=-0.91389 \mathrm{eV} \tag{20.45}
\end{equation*}
$$

Using Eqs. (20.22-22.26), the general force balance equation for the $\sigma$-MO of the silicon to oxygen $\mathrm{Si}-\mathrm{O}$-bond MO in terms of $n_{e}$ and $\left|L_{i}\right|$ corresponding to the angular momentum terms of the $3 s p^{3} \mathrm{HO}$ shell is:

$$
\begin{equation*}
\frac{\hbar^{2}}{m_{e} a^{2} b^{2}} D=\frac{e^{2}}{8 \pi \varepsilon_{0} a b^{2}} D+\frac{\hbar^{2}}{2 m_{e} a^{2} b^{2}} D-\left(\frac{n_{e}}{2}+\sum_{i} \frac{\left|L_{i}\right|}{Z}\right) \frac{\hbar^{2}}{2 m_{e} a^{2} b^{2}} D \tag{20.46}
\end{equation*}
$$

Having a solution for the semimajor axis $a$ of:

$$
\begin{equation*}
a=\left(1+\frac{n_{e}}{2}+\sum_{i} \frac{\left|L_{i}\right|}{Z}\right) a_{0} \tag{20.47}
\end{equation*}
$$

In terms of the angular momentum $L$, the semimajor axis $a$ is:

$$
\begin{equation*}
a=\left(1+\frac{n_{e}}{2}+\frac{L}{Z}\right) a_{0} \tag{20.48}
\end{equation*}
$$

Using the semimajor axis, 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 the Organic Molecular Functional Groups and Molecules section. The semimajor axis $a$ solutions given by Eq. (20.48) of the force balance equation, Eq. (20.46), for the $\sigma$-MO of the $\mathrm{Si}-\mathrm{O}$-bond MO of each functional group of silicon oxide, silicon dioxide, silicic acids, silanols, siloxanes, and disiloxanes are given in Table 20.15 with the force-equation parameters $Z=14, n_{e}$, and $L$ corresponding to the angular momentum of the $S i 3 s p^{3} \mathrm{HO}$ shell.

For the $\mathrm{Si}-\mathrm{O}$ functional groups, hybridization of the $3 s$ and $3 p$ AOs of Si to form a single $3 s p^{3}$ shell forms an energy minimum, and the sharing of electrons between the $S i 3 s p^{3} \mathrm{HO}$ and the $O$ AO to form a MO permits each participating orbital to decrease in radius and energy. The $O$ AO has an energy of $E(O)=-13.61805 \mathrm{eV}$, and the Si3sp ${ }^{3}$ HO has an energy of $E\left(S i, 3 s p^{3}\right)=-10.25487 \mathrm{eV}$ (Eq. (20.7)). To meet the equipotential condition of the union of the $\mathrm{Si}-\mathrm{O} \mathrm{H}_{2}$-type-ellipsoidalMO with these orbitals, the corresponding hybridization factors $c_{2}$ and $C_{2}$ of Eq. (15.61) for silicic acids, silanols, siloxanes, and disiloxanes and the hybridization factor $C_{2}$ of silicon oxide and silicon dioxide given by Eq. (15.77) are:

$$
\begin{equation*}
c_{2}\left(O \text { to Si3sp }{ }^{3} \mathrm{HO}\right)=C_{2}\left(O \text { to Si3sp }{ }^{3} \mathrm{HO}\right)=\frac{E\left(S i, 3 s p^{3}\right)}{E(O)}=\frac{-10.25487 \mathrm{eV}}{-13.61805 \mathrm{eV}}=0.75304 \tag{20.49}
\end{equation*}
$$

Each bond of silicon oxide and silicon dioxide is a double bond such that $c_{1}=2$ and $C_{1}=0.75$ in the geometry relationships (Eqs. (15.2-15.5)) and the energy equation (Eq. (15.61)). Each $\mathrm{Si}-\mathrm{O}$ bond in silicic acids, silanols, siloxanes, and disiloxanes is a single bond corresponding to $c_{1}=1$ and $C_{1}=0.5$ as in the case of alkanes (Eq. (14.152)).

Since the energy of the MO is matched to that of the $\operatorname{Si3sp}{ }^{3} \mathrm{HO}, E(A O / H O)$ in Eq. (15.61) is $E\left(S i, 3 s p^{3}\right)$ given by Eq. (20.7) and twice this value for double bonds. $E_{T}\left(\right.$ atom-atom, $\left.m s p^{3} . A O\right)$ of the $S i-O$-bond MO of each functional group is determined by energy matching in the molecule while achieving an energy minimum. For silicon oxide and silicon dioxide, $E_{T}\left(\right.$ atom-atom, $\left.m s p^{3} . A O\right)$ is three and two times -1.37960 eV given by Eq. (20.20), respectively. $E_{T}\left(\right.$ atom-atom, $\left.\mathrm{msp}^{3} . \mathrm{AO}\right)$ of silicic acids is two times -0.91389 eV given by Eq. (20.45). $E_{T}\left(\right.$ atom-atom, $\left.m s p^{3} . A O\right)$ of silanols, siloxanes, and disiloxanes is two times -0.62217 eV given by Eq. (20.43).

The symbols of the functional groups of silicon oxides, silicic acids, silanols, siloxanes, and disiloxanes are given in Table 20.14. The geometrical (Eqs. (15.1-15.5), (20.1-20.21), (20.29), (20.32-20.33), (20.37), and (20.46-20.49)) and intercept (Eqs. (15.80-15.87) and (20.21)) parameters are given in Tables 20.15 and 20.16, respectively. The energy (Eqs. (15.61), (20.120.20), (20.33-20.35), (20.37-45), and (20.49)) parameters are given in Table 20.17. The total energy of each silicon oxide, silicic acid, silanol, siloxane, or disiloxane given in Table 20.18 was calculated as the sum over the integer multiple of each $E_{D}$ (Group) of Table 20.17 corresponding to functional-group composition of the molecule. The bond angle parameters determined
using Eqs. (15.88-15.117) are given in Table 20.19. The charge-densities of exemplary siloxane, $\left(\left(\mathrm{CH}_{3}\right)_{2} \mathrm{SiO}\right)_{3}$ and disiloxane, hexamethyldisiloxane 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 are shown in Figures 20.4A and B, respectively.

Figure 20.4. (A) Color scale, translucent view of the charge-density of $\left(\left(\mathrm{CH}_{3}\right)_{2} \mathrm{SiO}\right)_{3}$ showing the orbitals of the $\mathrm{Si}, \mathrm{O}$, and $C$ 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 atoms participating in each bond, and the nuclei (red, not to scale). (B) Color scale, translucent view of the charge-density of $\left(\mathrm{CH}_{3}\right)_{3} \mathrm{SiOSi}\left(\mathrm{CH}_{3}\right)_{3}$ showing the orbitals of the $\mathrm{Si}, \mathrm{O}$, and C atoms at their radii, the ellipsoidal surface of each H or $\mathrm{H}_{2}$-type ellipsoidal MO that transitions to the corresponding outer shell of the atoms participating in each bond, and the nuclei (red, not to scale).


Table 20.14. The symbols of functional groups of silicon oxides, silicic acids, silanols, siloxanes and disiloxanes.

| Functional Group | Group Symbol |
| :---: | :---: |
| SiO bond (silicon oxide) | $\mathrm{Si}-\mathrm{O}$ (i) |
| SiO bond (silicon dioxide) | $\mathrm{Si}-\mathrm{O}$ (ii) |
| SiO bond (silicic acid) | $\mathrm{Si}-\mathrm{O}$ (iii) |
| SiO bond (silanol and siloxane) | $\mathrm{Si}-\mathrm{O}$ (iv) |
| Si -OSi bond (disiloxane) | $\mathrm{Si}-\mathrm{O}$ (v) |
| SiH group of $\mathrm{SiH}_{n=1,2,3}$ | Si-H |
| CSi bond | C-Si (i) |
| OH group | OH |
| $\mathrm{CO}\left(\mathrm{CH}_{3}-\mathrm{O}-\right.$ and $\left.\left(\mathrm{CH}_{3}\right)_{3} \mathrm{C}-\mathrm{O}-\right)$ | C-O (i) |
| CO (alkyl) | $C-O$ (ii) |
| $\mathrm{CH}_{3}$ group | $\mathrm{C}-\mathrm{H}\left(\mathrm{CH}_{3}\right)$ |
| $\mathrm{CH}_{2}$ group | $\mathrm{C}-\mathrm{H}\left(\mathrm{CH}_{2}\right)$ |
| CH | C-H |
| $C C$ bond (n-C) | $C-C$ (a) |
| $C C$ bond (iso-C) | $C-C$ (b) |
| $C C$ bond (tert-C) | $C-C$ (c) |
| CC (iso to iso-C) | $C-C$ (d) |
| $C C$ ( $t$ to $t-C$ ) | $C-C$ (e) |
| $C C$ ( $t$ to iso-C) | $C-C$ (f) |

Table 20.15. The geometrical bond parameters silicon oxides, silicic acids, silanols, siloxanes, disiloxanes and experimental values.

| Parameter | $\begin{gathered} \text { Si-O (i) } \\ \text { Group } \end{gathered}$ | $\begin{gathered} \text { Si-O (ii) } \\ \text { Group } \end{gathered}$ | $\begin{aligned} & \text { Si-O (iii) } \\ & \text { Group } \end{aligned}$ | $\begin{aligned} & \mathrm{Si}-\mathrm{O} \text { (iv) } \\ & \text { Group } \end{aligned}$ | $\begin{gathered} \text { Si-O (v) } \\ \text { Group } \end{gathered}$ | $\begin{aligned} & \mathrm{Si}-\mathrm{H} \\ & \text { Group } \end{aligned}$ | $\begin{gathered} C-S i \text { (i) } \\ \text { Group } \end{gathered}$ | $\begin{gathered} \mathrm{OH} \\ \text { Group } \end{gathered}$ | $\begin{gathered} C-O(\mathrm{i}) \\ \text { Group } \end{gathered}$ | $\begin{gathered} C-O \text { (ii) } \\ \text { Group } \end{gathered}$ | $\begin{gathered} \mathrm{C}-\mathrm{H}\left(\mathrm{CH}_{3}\right) \\ \text { Group } \end{gathered}$ | $\begin{gathered} \mathrm{C}-\mathrm{H}\left(\mathrm{CH}_{2}\right) \\ \text { Group } \end{gathered}$ | $\begin{aligned} & \mathrm{C}-\mathrm{H} \\ & \text { Group } \end{aligned}$ | $\begin{gathered} C-C \text { (a) } \\ \text { Group } \end{gathered}$ | $\begin{aligned} & C=C \\ & \text { Group } \end{aligned}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $n_{\text {e }}$ | 2 | 2 | 2 | 2 | 2 |  |  |  |  |  |  |  |  |  |  |
| $L$ | $4 \sqrt{\frac{3}{4}}$ | $6 \sqrt{\frac{3}{4}}$ | 0 | 0 | 0 |  |  |  |  |  |  |  |  |  |  |
| $a\left(a_{0}\right)$ | 2.24744 | 2.37115 | 2.00000 | 2.00000 | 2.00000 | 2.24744 | 2.20339 | 1.26430 | 1.80717 | 1.79473 | 1.64920 | 1.67122 | 1.67465 | 2.12499 | 1.47228 |
| $c^{\prime}\left(a_{0}\right)$ | 1.41056 | 1.44886 | 1.62970 | 1.62970 | 1.62970 | 1.40593 | 1.77327 | 0.91808 | 1.34431 | 1.33968 | 1.04856 | 1.05553 | 1.05661 | 1.45744 | 1.26661 |
| $\begin{gathered} \text { Bond } \\ \text { Length } \\ 2 c^{\prime}(A) \end{gathered}$ | 1.49287 | 1.53341 | 1.72480 | 1.72480 | 1.72480 | 1.48797 | 1.87675 | 0.971651 | 1.42276 | 1.41785 | 1.10974 | 1.11713 | 1.11827 | 1.54280 | 1.34052 |
| Exp. Bond Length (A) | $\begin{gathered} 1.509 \\ \text { (silicon oxide) } \\ {[18]} \end{gathered}$ | $\begin{gathered} 1.55 \\ \text { (silicon dioxide) } \\ {[19]} \end{gathered}$ | $\begin{gathered} 1.703 \\ {[20]} \end{gathered}$ | $\begin{aligned} & 1.703 \\ & {[20]} \end{aligned}$ | $\begin{gathered} 1.668 \\ {[20]} \end{gathered}$ | 1.485 (methylsilane) $18]$ 1.492 $\left(S i_{2} H_{6}[8]\right.$ 1.489 (trimethyl silane) $[9]$ | 1.867 <br> (methysilane) <br> $[8]$ <br> 1.875 <br> (tetramethyl <br> silane) $[8]$ <br> 1.877 <br> (methylsilane) <br> $[1.871$ <br> 1.871 <br> (dimethylsilane) <br> $19]$ <br> 1.878 <br> (trimethyl <br> silane) $[9]$ | $\begin{gathered} 0.971 \\ \begin{array}{c} \text { (ethanol) } \\ 0.9451 \\ \text { (methanol) } \end{array} \text { [8] } \end{gathered}$ | $\begin{gathered} 1.416 \\ \text { (dimethyl ether) } \\ {[8]} \end{gathered}$ | $\begin{gathered} 1.418 \\ \begin{array}{c} \text { (ethyl methyl } \\ \text { ether (avg.)) } \end{array} \text { [8] } \end{gathered}$ | 1.093 (methylsilane) $[8]$ 1.115 (tetramethyl silane) $[8]$ 1.107 $(C-H$ propane) $[8]$ 1.117 $(C-H$ butane) $[8]$ | $\begin{gathered} 1.107 \\ (C-H \\ \text { propane })[8] \\ 1.117 \\ (C-H \text { butane }) \\ {[8]} \end{gathered}$ | $\begin{gathered} 1.122 \\ \text { (isobutane) [8] } \end{gathered}$ | $\begin{gathered} 1.532 \\ \text { (propane) }[8] \\ 1.531 \\ \text { (butane) }[8] \end{gathered}$ | 1.342 (2-methylpropene) [8] 1.346 (2-butene) [8] 1.349 (1,3-butadiene) [8] |
| $b, c\left(a_{0}\right)$ | 1.74966 | 1.87701 | 1.15935 | 1.15935 | 1.15935 | 1.75338 | 1.30783 | 0.86925 | 1.20776 | 1.19429 | 1.27295 | 1.29569 | 1.29924 | 1.54616 | 0.75055 |
| $e$ | 0.62763 | 0.61104 | 0.81485 | 0.81485 | 0.81485 | 0.62557 | 0.80479 | 0.72615 | 0.74388 | 0.74645 | 0.63580 | 0.63159 | 0.63095 | 0.68600 | 0.86030 |

Table 20.16. The MO to HO intercept geometrical bond parameters of silicon oxides, silicic acids, silanols, siloxanes and disiloxanes. $R, R^{\prime}, R^{\prime \prime}$ are $H$ or alkyl groups. $E_{T}$ is $E_{T}\left(\right.$ atom - atom $\left.m s p^{3} \cdot A O\right)$.

| Bond | Atom | $\begin{gathered} E_{T} \\ (\mathrm{eV}) \\ \text { Bond } 1 \end{gathered}$ | $\begin{gathered} E_{T} \\ (\mathrm{eV}) \\ \text { Bond } 2 \end{gathered}$ | $E_{T}$ (eV) Bond 3 | $\begin{gathered} E_{T} \\ (\mathrm{eV}) \\ \text { Bond } 4 \end{gathered}$ | Final Total <br> Energy <br> $S i 3 s p^{3}$ <br> $C 2 s p^{3}$ <br> $(\mathrm{eV})$ | $\begin{aligned} & r_{\text {mulual }} \\ & \left(a_{0}\right) \end{aligned}$ | $\begin{aligned} & r_{\text {fral }} \\ & \left(a_{0}\right) \end{aligned}$ | $\begin{gathered} E_{\text {Conlombl }}\left(C 2 s p^{3}\right) \\ (\mathrm{eV}) \\ \text { Final } \end{gathered}$ | $\begin{gathered} E\left(S i 3 s p^{3}\right) \\ E\left(C 2 s p^{3}\right) \\ (\mathrm{eV}) \\ \text { Final } \end{gathered}$ | $\begin{aligned} & \theta^{\prime} \\ & \left({ }^{\circ}\right) \end{aligned}$ | $\begin{aligned} & \theta_{1} \\ & \left({ }^{\circ}\right) \end{aligned}$ | $\begin{aligned} & \theta_{2} \\ & \left({ }^{\circ}\right) \end{aligned}$ | $\begin{gathered} d_{1} \\ \left(a_{0}\right) \end{gathered}$ | $\begin{gathered} d_{2} \\ \left(a_{0}\right) \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\begin{aligned} & \hline \mathrm{Si}=O(\mathrm{SiO}) \\ & (\mathrm{Si}-\mathrm{O} \quad \text { (i) }) \\ & \hline \end{aligned}$ | Si | -2.06940 | 0 | 0 | 0 |  | 1.31926 | 1.09878 | -12.38264 | -12.32428 | 67.55 | 112.45 | 35.48 | 1.83015 | 0.41959 |
| $\begin{aligned} & \mathrm{Si}=O(\mathrm{SiO}) \\ & (\mathrm{Si}-\mathrm{O} \\ & \hline \end{aligned}$ | O | -2.06940 | 0 | 0 | 0 |  | 1.00000 | 0.86730 | -15.68745 |  | 24.63 | 155.37 | 11.92 | 2.19896 | 0.78840 |
| $\begin{aligned} & \mathrm{O}=\mathrm{Si}=\mathrm{O}\left(\mathrm{SiO}_{2}\right) \\ & (\mathrm{Si}-\mathrm{O} \text { (ii)) } \end{aligned}$ | Si | -1.37960 | $-1.37960$ | 0 | 0 |  | 1.31926 | 1.04080 | -13.07244 | -13.01408 | 45.59 | 134.41 | 23.33 | 2.17721 | 0.72835 |
| $\begin{aligned} & \mathrm{O}=\mathrm{Si}=\mathrm{O}\left(\mathrm{SiO}_{2}\right) \\ & (\mathrm{Si}-\mathrm{O} \\ & \text { (ii) }) \end{aligned}$ | $o$ | -1.37960 | 0 | 0 | 0 |  | 1.00000 | 0.90720 | -14.99765 |  |  |  |  |  |  |
| $(\mathrm{HO})_{3} \mathrm{SiO}-\mathrm{H}$ | $o$ | -0.91389 | 0 | 0 | 0 |  | 1.00000 | 0.93627 | -14.53194 |  | 119.87 | 60.13 | 69.07 | 0.45174 | 0.46634 |
| $\mathrm{R}_{3} \mathrm{SiO}-\mathrm{H}$ | $o$ | -0.62217 | 0 | 0 | 0 |  | 1.00000 | 0.95545 | -14.24022 |  | 121.05 | 58.95 | 70.34 | 0.42532 | 0.49275 |
| $\begin{aligned} & (\mathrm{HO})_{3} \mathrm{Si}-\mathrm{OH} \\ & (\mathrm{Si}-\mathrm{O} \text { (iii)) } \end{aligned}$ | Si | -0.91389 | -0.91389 | -0.91389 | -0.91389 |  | 1.31926 | 0.97402 | -13.96878 | -13.91042 | 112.36 | 67.64 | 50.98 | 1.25911 | 0.37059 |
| $\begin{aligned} & (\mathrm{HO})_{3} \mathrm{Si}-\mathrm{OH} \\ & (\mathrm{Si}-\mathrm{O} \text { (iii) }) \end{aligned}$ | O | -0.91389 | 0 | 0 | 0 |  | 1.00000 | 0.93627 | -14.53194 |  | 110.26 | 69.74 | 49.25 | 1.30543 | 0.32427 |
| $\begin{aligned} & \left(\mathrm{CH}_{3}\right)_{3} \mathrm{Si}-\mathrm{OH} \\ & (\mathrm{Si}-\mathrm{O} \text { (iv)) } \\ & \hline \end{aligned}$ | Si | -0.62217 | -0.60236 | -0.60236 | -0.60236 |  | 1.31926 | 1.06775 | -12.74250 | -12.68414 | 117.05 | 62.95 | 55.11 | 1.14408 | 0.48562 |
| $\begin{aligned} & \left(\mathrm{CH}_{3}\right)_{3} \mathrm{Si}-\mathrm{OH} \\ & (\mathrm{Si}-\mathrm{O} \text { (iv) }) \\ & \hline \end{aligned}$ | O | -0.62217 | 0 | 0 | 0 |  | 1.00000 | 0.95545 | -14.24022 |  | 111.35 | 68.65 | 50.14 | 1.28189 | 0.34780 |
| $\mathrm{C}-\mathrm{H}\left(\mathrm{OCH}_{3}\right)$ | 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 |
| $\begin{aligned} & \mathrm{SiO}-\mathrm{CH}_{3} \\ & \mathrm{SiO}-\mathrm{C}\left(\mathrm{CH}_{3}\right)_{3} \\ & \mathrm{C}-\mathrm{O}(\mathrm{i})) \\ & \hline \end{aligned}$ | 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 |
| $\begin{aligned} & \mathrm{SiO}-\mathrm{CH}_{3} \\ & \mathrm{SiO}-\mathrm{C}\left(\mathrm{CH}_{3}\right)_{3} \\ & (\mathrm{C}-\mathrm{O}(\mathrm{i})) \\ & \mathrm{Si}-\mathrm{O} \text { (iv) }) \\ & \hline \end{aligned}$ | $o$ | -0.72457 | -0.62217 | 0 | 0 |  | 1.00000 | 0.84129 | -16.17250 |  | 93.13 | 86.87 | 44.07 | 1.29844 | 0.04587 |
| $\begin{aligned} & -\mathrm{H}_{2} \mathrm{C}_{a}-\mathrm{OSi} \\ & (\mathrm{C}-\mathrm{O} \text { (ii)) } \end{aligned}$ | $C_{a}$ | -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 |
| $\begin{aligned} & -\mathrm{H}_{2} \mathrm{C}_{a}-\mathrm{OC}_{b}\left(\mathrm{CH}_{3}\right)_{3} \\ & -\mathrm{H}_{2} \mathrm{C}_{a}-\mathrm{OC}_{b} \mathrm{H}_{3} \\ & (\mathrm{C}-\mathrm{O} \text { (ii)) } \\ & (\mathrm{Si}-\mathrm{O} \text { (iv)) }) \\ & \hline \end{aligned}$ | O | -0.82688 | -0.62217 | 0 | 0 |  | 1.00000 | 0.83600 | -16.27480 |  | 93.79 | 86.21 | 44.30 | 1.28438 | 0.05529 |
| $\begin{aligned} & \left(\mathrm{CH}_{3} \mathrm{O}\right)_{3} \mathrm{Si}_{\mathrm{i}-\mathrm{OCH}_{3}} \\ & (\mathrm{Si}-\mathrm{O} \text { (iv) }) \end{aligned}$ | Si | -0.62217 | -0.62217 | -0.62217 | -0.62217 |  | 1.31926 | 1.06279 | -12.80192 | -12.74356 | 116.82 | 63.18 | 54.89 | 1.15016 | 0.47954 |
| $\begin{aligned} & \left(\mathrm{CH}_{3} \mathrm{O}\right)_{3} \mathrm{Si}-\mathrm{OCH}_{3} \\ & (\mathrm{Si}-\mathrm{O} \text { (iv)) } \end{aligned}$ | O | -0.62217 | -0.72457 | 0 | 0 |  | 1.00000 | 0.90919 | -14.96480 |  | 108.67 | 71.33 | 47.98 | 1.33867 | 0.29103 |
| $\begin{aligned} & \left(\mathrm{CH}_{3}\right)_{3} \mathrm{Si}-\mathrm{OSi}\left(\mathrm{CH}_{3}\right)_{3} \\ & (\mathrm{Si}-\mathrm{O}(\mathrm{v})) \end{aligned}$ | Si | -0.48015 | -0.60236 | -0.60236 | -0.60236 |  | 1.31926 | 1.07978 | -12.60048 | -12.54212 | 117.61 | 62.39 | 55.62 | 1.12931 | 0.50039 |

Table 20.16 cont' d. The MO to HO intercept geometrical bond parameters of silicon oxides, silicic acids, silanols, siloxanes and disiloxanes. $R, R^{\prime}, R^{\prime \prime}$ are $H$ or alkyl groups. $E_{T}$ is $E_{T}$ (atom-atom $\mathrm{msp}^{3} \cdot A O$ ).

| Bond | Atom | $E_{T}$ (eV) Bond 1 <br> Bond 1 | $\begin{gathered} E_{T} \\ (\mathrm{eV}) \\ \text { Bond } 2 \end{gathered}$ | $\begin{gathered} E_{T} \\ (\mathrm{eV}) \\ \text { Bond } 3 \end{gathered}$ | $\begin{gathered} E_{T} \\ (\mathrm{eV}) \\ \text { Bond } 4 \end{gathered}$ | Final Total Energy Si3sp $C 2 s p^{3}$ $(\mathrm{eV})$ | $\begin{aligned} & r_{\text {mutral }} \\ & \left(a_{0}\right) \end{aligned}$ | $\begin{aligned} & r_{\text {pmal }} \\ & \left(a_{0}\right) \end{aligned}$ | $\begin{gathered} E_{\text {Coutombomb }}\left(C 2 s p^{3}\right) \\ (\mathrm{eV}) \\ \text { Final } \end{gathered}$ | $\begin{gathered} E\left(S i 3 s p^{3}\right) \\ E\left(C 2 s p^{3}\right) \\ (\mathrm{eV}) \\ \text { Final } \end{gathered}$ | $\begin{aligned} & \theta^{\prime} \\ & \left({ }^{\circ}\right) \end{aligned}$ | $\begin{gathered} \theta_{1} \\ \left({ }^{\circ}\right) \end{gathered}$ | $\begin{aligned} & \theta_{2} \\ & \left({ }^{\circ}\right) \end{aligned}$ | $\begin{gathered} d_{1} \\ \left(a_{0}\right) \end{gathered}$ | $\begin{gathered} d_{2} \\ \left(a_{0}\right) \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\begin{aligned} & \left(\mathrm{CH}_{3}\right)_{3} \mathrm{Si}-\mathrm{OSi}\left(\mathrm{CH}_{3}\right)_{3} \\ & (\mathrm{Si}-\mathrm{O}(\mathrm{v})) \end{aligned}$ | $o$ | -0.48015 | -0.48015 | 0 | 0 |  | 1.00000 | 0.93329 | -14.57836 |  | 110.09 | 69.91 | 49.11 | 1.30909 | 0.32061 |
| $\begin{aligned} & \mathrm{H}_{3} \mathrm{Si} i_{a}-\mathrm{C}_{a} \mathrm{H}_{2}- \\ & (\mathrm{C}-\mathrm{Si}(\mathrm{i})) \end{aligned}$ | $S i_{a}$ | -0.60236 | -1.06358 | $-1.06358$ | -1.06358 |  | 1.31926 | 0.73075 | -18.61886 | -18.56050 | 85.56 | 94.44 | 33.85 | 1.82982 | 0.05655 |
| $\begin{aligned} & \mathrm{H}_{2} S i_{a}-\left(C_{a} H_{2}-\right)_{2} \\ & (C-S i \text { (i)) } \end{aligned}$ | $S i_{a}$ | -0.60236 | $-0.60236$ | $-1.06358$ | $-1.06358$ |  | 1.31926 | 0.74932 | -18.15764 | -18.09928 | 87.44 | 92.56 | 34.92 | 1.80676 | 0.03349 |
| $\begin{aligned} & H S i_{a}-\left(C_{a} H_{2}-\right)_{3} \\ & (C-S i \text { (i)) } \end{aligned}$ | $S i_{a}$ | $-0.60236$ | $-0.60236$ | -0.60236 | $-1.06358$ |  | 1.31926 | 0.76884 | -17.69642 | -17.63806 | 89.31 | 90.69 | 36.00 | 1.78249 | 0.00922 |
| $\begin{aligned} & S_{i}-\left(C_{a} H_{2}-\right)_{4} \\ & (C-S i(\mathrm{i})) \\ & \hline \end{aligned}$ | $S i_{a}$ | $-0.60236$ | $-0.60236$ | $-0.60236$ | -0.60236 |  | 1.31926 | 0.78942 | -17.23521 | -17.17685 | 91.19 | 88.81 | 37.12 | 1.75693 | 0.01634 |
| $\begin{aligned} & -\mathrm{Si}_{a} \mathrm{H}_{2}-\mathrm{CH}_{3} \\ & (\mathrm{C}-\mathrm{Si} \text { (i)) } \\ & \hline \end{aligned}$ | C | -0.60236 | 0 | 0 | 0 | -152.21805 | 0.91771 | 0.88188 | -15.42812 | -15.23725 | 98.56 | 81.44 | 41.82 | 1.64204 | 0.13123 |
| $\begin{aligned} & -\mathrm{Si}_{a} \mathrm{H}_{2}-\mathrm{C}_{a} \mathrm{H}_{2} \mathrm{CH}_{2}- \\ & (\mathrm{C}-\mathrm{Si} \text { (i)) } \\ & \hline \end{aligned}$ | $C_{a}$ | -0.60236 | $-0.92918$ | 0 | 0 | -153.14724 | 0.91771 | 0.83179 | -16.35730 | -16.16643 | 94.76 | 85.24 | 39.33 | 1.70428 | 0.06899 |
| $\mathrm{C}-\mathrm{H}\left(\mathrm{CH}_{3}\right)$ | 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 |
| $\mathrm{C}-\mathrm{H}\left(\mathrm{CH}_{2}\right)$ | 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 |
| $\mathrm{C-H}(\mathrm{CH})$ | 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 |
| $\begin{aligned} & \mathrm{H}_{3} \mathrm{C}_{a} \mathrm{C}_{b} \mathrm{H}_{2} \mathrm{CH}_{2}- \\ & (\mathrm{C}-\mathrm{C}(\mathrm{a})) \\ & \hline \end{aligned}$ | $C_{a}$ | -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 |
| $\begin{aligned} & \mathrm{H}_{3} \mathrm{C}_{a} \mathrm{C}_{b} \mathrm{H}_{2} \mathrm{CH}_{2}- \\ & (\mathrm{C}-\mathrm{C} \text { (a)) } \\ & \hline \end{aligned}$ | $C_{b}$ | -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 |
| $\begin{aligned} & R-H_{2} C_{a} C_{b}\left(H_{2} C_{c}-R^{\prime}\right) H C H_{2}- \\ & (C-C(b)) \end{aligned}$ | $C_{b}$ | -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 |
| $\begin{aligned} & R-H_{2} C_{a}\left(R^{\prime}-H_{2} C_{d}\right) C_{b}\left(R^{\prime \prime}-H_{2} C_{c}\right) C H_{2}- \\ & (C-C(c)) \end{aligned}$ | $C_{b}$ | -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 |
| $\begin{aligned} & \text { iso } C_{a} C_{b}\left(H_{2} C_{c}-R^{\prime}\right) H C H_{2}- \\ & (C-C \text { (d) }) \end{aligned}$ | $C_{b}$ | -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 |
| $\begin{aligned} & {\operatorname{tert} C_{a}\left(R^{\prime}-H_{2} C_{d}\right) C_{b}\left(R^{\prime \prime}-H_{2} C_{c}\right) \mathrm{CH}_{2}-}^{(\mathrm{C}-\mathrm{C}(\mathrm{e}))} \end{aligned}$ | $C_{b}$ | -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 |
| $\begin{aligned} & {\text { tert } C_{a} C_{b}}\left(\mathrm{H}_{2} \mathrm{C}_{c}-\mathrm{R}^{\prime}\right) \mathrm{HCH}_{2}- \\ & (\mathrm{C}-\mathrm{C}(\mathrm{f})) \end{aligned}$ | $C_{b}$ | -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 |
| $\begin{aligned} & \text { iso } C_{a}\left(R^{\prime}-H_{2} C_{d}\right) C_{b}\left(R^{n}-H_{2} C_{c}\right) \mathrm{CH}_{2}- \\ & (\mathrm{C}-\mathrm{C}(\mathrm{f})) \end{aligned}$ | $C_{b}$ | -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 20．17．The energy parameters $(\mathrm{eV})$ of functional groups of silicon oxides，silicic acids，silanols，siloxanes and disiloxanes．

|  | $N$ |  | $\sim \sim\|c\| c \mid c$ | $-\frac{\vec{E}}{\frac{E}{C}}$ |  |  | 0 \％ | $\stackrel{\text { E }}{\stackrel{1}{2}}$ |  |  |  |  | － | － | \＆ |  |  |  |  | $0$ |  |  | $\dot{f}$ |  |  | $\stackrel{ \pm}{\square}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | － |  | $3-$ | $-\frac{\vec{E}}{2}$ |  |  | \％ | － |  |  |  | $\begin{aligned} & \text { 首 } \\ & \end{aligned}$ | － |  | en | $\begin{gathered} \infty \\ \stackrel{\infty}{\infty} \\ \underset{\infty}{\sim} \end{gathered}$ | $\begin{gathered} \underset{N}{n} \\ \substack{2 \\ \hline} \end{gathered}$ | $$ |  |  |  |  |  | $\dot{+}$ |  | f |
|  | －－ |  | $\left\lvert\, \begin{gathered} \mathrm{n} \\ 0 \end{gathered}\right.$ | $-\frac{\vec{E}}{\hat{E}}$ | $-$ |  | No | $-$ |  |  |  |  | － |  | $\hat{}$ | $\bigcirc$ |  | $\stackrel{a}{c}$ |  |  |  |  |  | 悊 |  | － |
| 気 䛌 | $\sim-$ |  |  | $-\frac{\underset{E}{E}}{\partial}$ | － | － | $\sim$ | － |  |  |  | $\begin{gathered} \hat{y} \\ \substack{n \\ n \\ \\ \hline} \end{gathered}$ | － |  | . | － |  | $\begin{aligned} & \vec{n} \\ & \underset{\sim}{4} \\ & \underset{\sim}{2} \end{aligned}$ |  |  |  | $\frac{\stackrel{c}{\circ}}{\frac{\vdots}{c}}$ |  | 势 | $\begin{aligned} & \stackrel{\rightharpoonup}{*} \\ & \stackrel{\rightharpoonup}{n} \end{aligned}$ | $\stackrel{\circ}{0}$ |
| 気 㺃 | $\cdots$ |  | $\stackrel{\sim}{0}$ | $-\frac{\vec{A}}{\underset{O}{E}}$ | － | － | － | $-$ |  |  |  | $\begin{aligned} & \hat{C} \\ & \substack{6 \\ \\ \\ \hline} \end{aligned}$ | － |  |  | － |  | $\begin{gathered} \circ \\ \underset{\sim}{\circ} \\ \underset{\sim}{4} \end{gathered}$ |  |  |  |  |  | $\begin{aligned} & \mathbf{\alpha} \\ & \stackrel{\rightharpoonup}{c} \\ & \text { chat } \end{aligned}$ |  | $\frac{8}{\square}$ |
| $\left\lvert\, \begin{gathered} \text { En } \\ 0 \\ 0 \\ 0 \\ 0 \end{gathered}\right.$ | － |  | I | $-\begin{gathered} \infty \\ \\ \infty \\ \infty \\ 0 \end{gathered}$ |  |  | \％ | － |  | $\begin{array}{l\|l} 20 \\ 0 \\ 0 & 0 \\ 0 & 0 \\ 0 & 0 \end{array}$ | $\hat{N}_{\substack{n}}^{\substack{0 \\ 0 \\ \\ \hline}}$ | $\begin{gathered} o \\ \stackrel{\rightharpoonup}{6} \\ \mathbf{~} \\ \hline \end{gathered}$ | $\begin{aligned} & \stackrel{0}{2} \\ & \stackrel{0}{6} \\ & \vdots \end{aligned}$ | $\begin{aligned} & \stackrel{n}{\underset{2}{2}} \\ & \underset{\sim}{2} \end{aligned}$ | $\begin{gathered} \text { 寺 } \\ \widehat{6} \\ \stackrel{y}{2} \end{gathered}$ | $\begin{aligned} & \stackrel{\circ}{0} \\ & \stackrel{\overparen{O}}{6} \end{aligned}$ | $\begin{aligned} & \underset{\sim}{2} \\ & \underset{\sim}{\alpha} \\ & \underset{\sim}{2} \end{aligned}$ | $\begin{aligned} & \mathscr{\infty} \\ & \stackrel{2}{2} \\ & \underset{\sim}{2} \end{aligned}$ |  |  | $\underset{\substack{0 \\ i \\ i \\ i \\ i \\ i}}{\substack{2 \\ 0}}$ | $\frac{\stackrel{O}{\circ}}{\underset{\sim}{\circ}}$ |  |  |  | － |
| $\left\lvert\, \begin{array}{ll} a & 0 \\ 0 & \vdots \\ 0 & \vdots \\ 0 & \vdots \\ 0 \end{array}\right.$ | $-0$ |  | $n_{0} \mid-$ | $-2 \begin{gathered}\sim \\ \\ 0 \\ 0 \\ 0\end{gathered}$ | $\bigcirc$ |  | $\stackrel{n}{8}$ |  |  |  |  | $\begin{gathered} \stackrel{\rightharpoonup}{2} \\ \underset{6}{6} \end{gathered}$ |  | $\begin{gathered} \underset{\sim}{t} \\ \stackrel{\infty}{\omega} \\ \underset{\sim}{c} \end{gathered}$ |  | $\begin{gathered} n \\ \frac{n}{j} \\ \vdots \\ \vdots \end{gathered}$ | $\begin{gathered} \underset{y}{c} \\ \underset{y}{\infty} \\ \underset{\sim}{c} \\ \underset{\sim}{c} \end{gathered}$ | $\begin{aligned} & \text { a్ले } \\ & \text { di } \end{aligned}$ |  |  |  |  |  |  |  | N |
| İ | －－ | 0 | $\underset{\substack{n \\ 0}}{ }$ |  |  |  | 20 | － |  |  |  | $\left\|\begin{array}{c} \bar{\infty} \\ \frac{1}{c} \\ \stackrel{y}{2} \end{array}\right\|$ | － | $\begin{gathered} \stackrel{\rightharpoonup}{\infty} \\ \stackrel{\rightharpoonup}{j} \\ \stackrel{\oplus}{1} \end{gathered}$ | $\begin{gathered} \text { 解 } \\ \stackrel{\rightharpoonup}{c} \end{gathered}$ | $\bigcirc$ | $\begin{aligned} & \hat{N} \\ & \stackrel{n}{6} \\ & \stackrel{y}{c} \end{aligned}$ |  |  | $\underset{\sim}{\substack{~}} \underset{\sim}{\sim}$ |  | $\underset{\sim}{\underset{\sim}{F}}$ |  | $\begin{gathered} \frac{0}{c} \\ \stackrel{y}{4} \end{gathered}$ |  | \％ |
| $\left\lvert\, \begin{gathered} a \\ 0 \\ i \\ i \\ 0 \\ 0 \end{gathered}\right.$ | － | 0 | $\because \sim$ |  |  |  | 0 \％ | － |  |  |  |  | $\begin{gathered} \text { n } \\ \substack{c\\ } \end{gathered}$ | $\begin{aligned} & \stackrel{\rightharpoonup}{4} \\ & \stackrel{0}{6} \\ & \stackrel{i}{i} \end{aligned}$ | $\begin{aligned} & \infty \\ & \stackrel{\infty}{n} \\ & \stackrel{n}{0} \\ & \stackrel{\sim}{c} \end{aligned}$ | $\begin{gathered} \underset{\sim}{c} \\ \underset{\sim}{c} \\ \hline \end{gathered}$ |  | $\begin{gathered} \infty \\ \stackrel{\infty}{\infty} \\ \stackrel{\rightharpoonup}{\sim} \\ \end{gathered}$ |  |  | 응 | $\begin{gathered} \substack{0 \\ 0 \\ 0 \\ 0 \\ 0} \end{gathered}$ |  | ＋ |  | $\stackrel{\infty}{\frac{\infty}{6}}$ |
|  | － |  |  |  |  |  | - n | （1） |  |  |  |  | $\bigcirc$ |  | $\begin{gathered} \infty \\ \underset{\infty}{\infty} \\ \underset{\sim}{\infty} \\ \vdots \end{gathered}$ | $\begin{aligned} & \infty \\ & \stackrel{\infty}{6} \\ & \stackrel{C}{6} \end{aligned}$ | 僉 |  |  |  |  | $0$ | － | － | き 俞 cin | － |
|  | － | $\bigcirc$ |  | $-\begin{gathered} \begin{array}{c} \mathrm{O} \\ \\ \end{array} \\ \hline \end{gathered}$ | － |  | \％ | t |  | $\begin{gathered} 8 \\ \hline \end{gathered}$ |  | $\left\lvert\, \begin{gathered} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{gathered}\right.$ | $\bigcirc$ |  | $\stackrel{\stackrel{\rightharpoonup}{3}}{\substack{\text { ¢̇ }}}$ | $\begin{aligned} & \bar{\circ} \\ & \text { O} \\ & \text { 人े } \end{aligned}$ | $\begin{gathered} \hat{t} \\ \underset{\substack{2}}{\substack{c}} \mid \end{gathered}$ | $\begin{aligned} & \circ \\ & \stackrel{\circ}{6} \\ & \dot{\circ} \\ & \hline \infty \end{aligned}$ |  |  | $\cdots \xlongequal[\substack{\tilde{n} \\ i \\ 0 \\ i \\ i}]{ }$ | $\begin{array}{\|c} \mathscr{8} \\ 0 \\ 0 \\ 0 \\ \hline \end{array}$ |  | － | $\left\lvert\, \begin{aligned} & \circ \\ & 0 \\ & 0 \\ & 0 \end{aligned}\right.$ | $\frac{0}{6}$ |
|  | － | 0 | $\sim$ | $-\begin{gathered} \begin{array}{c} \mathrm{O} \\ \\ \hat{0} \end{array} \\ \hline \end{gathered}$ | － | － | n | 管 |  | $\stackrel{\circ}{\circ}$ |  |  | － |  | N |  | $\begin{array}{\|c} \underset{\sim}{n} \\ \underset{o}{0} \\ \underset{o}{\infty} \\ \underset{c}{2} \end{array}$ | $\stackrel{\circ}{\infty}$ |  |  |  | $\begin{gathered} \infty \\ 0 \\ 0 \\ 0 \\ \hline 0 \end{gathered}$ |  |  | $\begin{aligned} & \text { n } \\ & 0 \\ & 0 \\ & 0 \\ & \end{aligned}$ | ＋ |
|  | $-0$ | － | $\mathfrak{n}$ | $-\begin{gathered} \begin{array}{c} \text { 訁 } \\ \\ \\ 0 \end{array} \end{gathered}$ | $0$ |  | $-2$ | 荗 |  | $\begin{gathered} 8 \\ \infty \\ \infty \\ \infty \end{gathered}$ |  |  | － |  | त |  |  | $\begin{gathered} \circ \\ \stackrel{\circ}{6} \\ 0 . \\ \infty \end{gathered}$ |  |  |  | $\left\lvert\, \begin{gathered} 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{gathered}\right.$ |  | ¢ | \| | 砍 |
|  | $\sim$ |  | $\underset{\sim}{\sim}$ | －－ | － |  | $\sim 12$ | Co |  | $\begin{gathered} \infty \\ \infty \\ \infty \\ \infty \\ \infty \end{gathered}$ |  |  | － |  | $\stackrel{+}{9}$ | $\begin{aligned} & \overline{\text { I}} \\ & \text { 人} \\ & \text { in } \end{aligned}$ | ¢ |  |  |  |  | $\begin{aligned} & \infty \\ & 0 \\ & 0 \\ & 0 \\ & 0 \end{aligned}$ |  | $\begin{aligned} & 0.8 \\ & \substack{a \\ \hline} \end{aligned}$ | $\begin{aligned} & 0 \\ & 0 \\ & 0 \\ & 0 \\ & \underset{0}{2} \\ & \hline 1 \end{aligned}$ | $\xrightarrow{\substack { \text { ¢ } \\ \begin{subarray}{c}{\text { ¢ }{ \text { ¢ } \\ \begin{subarray} { c } { \text { ¢ } } } \\{\hline}\end{subarray}}$ |
| $\left\lvert\, \begin{array}{cc} a \\ 0 & 0 \\ 0 & \frac{訁}{2} \\ i=0 & 0 \end{array}\right.$ | $\cdots$ |  | $\underset{\sim}{\wedge}$ | $--$ | － |  | $\sim{ }^{\text {ch }}$ | 苓 |  |  |  | $\begin{array}{\|c} n \\ \\ \\ \end{array}$ | － | $\begin{gathered} i n \\ \stackrel{n}{n} \\ \stackrel{n}{n} \\ \end{gathered}$ | $\stackrel{\square}{6}$ | $\begin{aligned} & \stackrel{\rightharpoonup}{\circ} \\ & \stackrel{\circ}{\dot{r}} \end{aligned}$ | 产 | $\begin{gathered} \text { ön } \\ \underset{\sim}{2} \end{gathered}$ |  | en |  | $\begin{aligned} & \infty \\ & 0 \\ & 0 \\ & 0 \\ & 0 \end{aligned}$ | \％ | $\infty$ |  | ¢ |
|  |  |  |  | v | 5 |  |  |  | ¢ | $\begin{aligned} & 5 \\ & \Delta x \\ & y y y \end{aligned}$ | $\underbrace{s}_{i}$ | $\begin{array}{\|c} \frac{5}{e} \\ \hline \frac{0}{2} \\ \frac{0}{2} \\ \frac{2}{4} \end{array}$ |  | $\stackrel{5}{e}$ |  | $\begin{gathered} \text { en } \\ \frac{5}{e} \\ \hline \end{gathered}$ | 5 |  |  |  | es |  |  | $\frac{5}{3}$ |  |  |

Table 20.18. The total bond energies of silicon oxides, silicic acids, silanols, siloxanes, and disiloxanes calculated using the functional group composition and the energies of Table 20.17 compared to the experimental values.

| Formula | Name or Structure | $\begin{aligned} & S_{i-O(i)}^{(i)} \\ & \text { Group } \end{aligned}$ | $\begin{aligned} & \text { Si-O (ii) } \\ & \text { Group } \end{aligned}$ | $\begin{aligned} & \text { Si-O (iii) } \\ & \text { Group } \end{aligned}$ | $\begin{aligned} & \text { Si-O (iv) } \\ & \text { Group } \end{aligned}$ | $\begin{aligned} & \text { Si-O(v) } \\ & \text { Group } \end{aligned}$ | $\begin{aligned} & \text { Si-H } \\ & \text { Group } \end{aligned}$ | $\begin{gathered} C-S i(i) \\ \text { Group } \end{gathered}$ | $\begin{gathered} \text { OH } \\ \text { Group } \end{gathered}$ | $\begin{gathered} \mathrm{C-O}(\mathrm{I}) \\ \text { Group } \end{gathered}$ | $\begin{aligned} & C-O(\text { ii }) \\ & \text { Group } \end{aligned}$ | $\mathrm{CH}_{3}$ | $\mathrm{CH}_{2}$ | CH | $C-C$ (a) | $C=C$ | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| SiO | Silicon oxide | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 8.30876 | 8.29905 [18] | -0.00117 |
| $\mathrm{SiO}_{2}$ | Silicon dioxide | 1 | 1 | 0 | 0 | 0 |  | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 12.94190 | 12.98073 [19] | 0.00299 |
| $\mathrm{SiH}_{4} \mathrm{O}$ | $\mathrm{H}_{3} \mathrm{SiOH}$ | 0 | 0 | 1 | 0 | 0 | 3 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 18.67184 | 19.007018 ${ }^{\text {[27] }}$ | 0.01763 |
| $\mathrm{SiH}_{4} \mathrm{O}_{2}$ | $\mathrm{H}_{2} \mathrm{Si}(\mathrm{OH})_{2}$ | 0 | 0 | 2 | 0 | 0 |  | 0 | 2 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 25.04264 | $25.04264^{\text {a }}$ [27] | 0.00563 |
| $\mathrm{SiH}_{4} \mathrm{O}_{3}$ | $\mathrm{HSi}(\mathrm{OH})_{3}$ | 0 | 0 | 3 | 0 | 0 | 1 | 0 | 3 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 31.41344 | $31.47012^{\text {a }}$ [27] | 0.00180 |
| $\mathrm{SiH}_{4} \mathrm{O}_{4}$ | $\mathrm{Si}(\mathrm{OH})_{4}$ | 0 | 0 | 4 | 0 | 0 | 0 | 0 | 4 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 37.78423 | 38.03638 [28] | 0.00663 |
| $\mathrm{C}_{3} \mathrm{H}_{12 \mathrm{SiO}}$ | Trimethylsilanol | 0 | 0 | 0 | 1 |  |  | 3 | 1 | 0 | 0 | 3 | 0 | 0 | 0 | 0 | 57.31895 | 57.30073 [29] | -0.00032 |
| $\mathrm{C}_{2} \mathrm{H}_{6} \mathrm{SiO}$ | Vinylsilanol | 0 | 0 | 0 | 1 | 0 | 2 | 1 | 1 | 0 | 0 | 0 | 1 | 1 | 0 | 1 | 37.33784 |  |  |
| $\mathrm{CH}_{6} \mathrm{SiO}_{4}$ | (HO) $\mathrm{SiOCH}_{3}$ | 0 | 0 | 0 | 4 | 0 | 0 | 0 | 3 | 1 | 0 | 1 | 0 | 0 | 0 | 0 | 47.45144 | 49.28171a [30] | 0.03714 |
| $\mathrm{C}_{4} \mathrm{H}_{12} \mathrm{SiO}_{4}$ | Tetramethoxysilioxane | 0 | 0 | 0 | 4 | 0 |  | 0 | 0 | 4 | 0 | 4 | 0 | 0 | 0 | 0 | 83.48783 | 84.04681 [31] | 0.00665 |
| $\mathrm{C}_{6} \mathrm{H}_{1} \mathrm{SSO}_{5} \mathrm{O}_{3}$ | Triethoxysilioxane | 0 | 0 | 0 | 3 | 0 | 1 | 0 | 0 | 0 | 3 | 3 | 3 | 0 | 3 | 0 | 102.74755 | 102.57961 [31] | -0.00164 |
| $\mathrm{C}_{8} \mathrm{H}_{2} \mathrm{SSO}_{4}$ | Tetraethoxysilioxane | 0 | 0 | 0 | 4 | 0 | 0 | 0 | 0 | 0 | 4 | 4 | 4 | 0 | 4 | 0 | 132.89639 | 133.23177 [31] | 0.00252 |
| $\mathrm{C}_{6} \mathrm{H}_{12} \mathrm{Si}_{3} \mathrm{O}_{3}$ | ((CH3)2SiO) ${ }_{3}$ | 0 | 0 | 0 | 6 | 0 | 0 | 6 | 0 | 0 | 0 | 6 | 0 | 0 | 0 | 0 | 123.61510 | 123.22485 [31] | -0.00317 |
| $\mathrm{C}_{8} \mathrm{H}_{2} \mathrm{SS}_{5} \mathrm{O}_{4}$ | $\left(\left(\mathrm{CH}_{3}\right)_{2} \mathrm{SiO}\right)_{4}$ | 0 | 0 | 0 | 8 | 0 | 0 | 8 | 0 | 0 | 0 | 8 | 0 | 0 | 0 | 0 | 164.82014 | 164.79037 [31] | -0.00018 |
| $\mathrm{C}_{10} \mathrm{H}_{30} \mathrm{Si}_{5} \mathrm{O}_{5}$ | $\left(\left(\mathrm{CH}_{3}\right)_{2} \mathrm{SiO}\right)^{3}$ | 0 | 0 | 0 | 10 | 0 | 0 | 10 | 0 | 0 | 0 | 10 | 0 | 0 | 0 | 0 | 206.02517 | 206.35589 [31] | 0.00160 |
| $\mathrm{C}_{6} \mathrm{H}_{12} \mathrm{Si}_{2} \mathrm{O}$ | Hexamethyldisiloxane | 0 | 0 | 0 | 0 | 2 | 0 | 6 | 0 | 0 | 0 | 6 | 0 | 0 | 0 | 0 | 105.24639 | 105.20196 [31] | -0.00042 |

Table 20．19．The bond angle parameters of silicon oxides，silicic acids，silanols，siloxanes，disiloxanes and experimental values．In the calculation of $\theta_{v}$ ，the parameters from the preceding angle were used．$E_{T}$ is $E_{T}$（atom－atom $m s p^{3} . A O$ ）．

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
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| $\underset{\mathrm{j}}{\stackrel{\rightharpoonup}{\mathrm{j}}}$ | $\begin{aligned} & \overline{\mathrm{g}} \\ & \stackrel{0}{0} \end{aligned}$ | $\begin{aligned} & \stackrel{\rightharpoonup}{\dot{+}} \\ & \underset{O}{2} \end{aligned}$ | $\begin{aligned} & \stackrel{\text { O}}{\stackrel{0}{0}} \end{aligned}$ | $\begin{aligned} & \hline \underset{\sim}{t} \\ & \text { ó } \end{aligned}$ | $\begin{aligned} & \stackrel{\circ}{\circ} \\ & \stackrel{\otimes}{\infty} \end{aligned}$ | $\begin{aligned} & \infty \\ & \stackrel{\infty}{0} \\ & \stackrel{1}{2} \end{aligned}$ | $\begin{aligned} & \hat{2} \\ & \underset{\sim}{0} \end{aligned}$ |  | $\begin{aligned} & 7 \\ & 0 \\ & 0 \\ & 0 \end{aligned}$ | $\begin{aligned} & \text { 首 } \\ & \dot{Q} \end{aligned}$ |  | $\stackrel{\stackrel{G}{\bullet}}{\stackrel{\rightharpoonup}{0}}$ | $\begin{aligned} & \stackrel{\rightharpoonup}{6} \\ & \stackrel{1}{6} \end{aligned}$ | $\begin{aligned} & \stackrel{8}{n} \\ & \stackrel{0}{0} \end{aligned}$ |  | $\begin{aligned} & \stackrel{\rightharpoonup}{\bullet} \\ & = \end{aligned}$ | $\stackrel{\circ}{\circ}$ | $\stackrel{\widehat{c}}{\Xi}$ | $\stackrel{\widehat{0}}{\Xi}$ | － |
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| 0 O |  |  |  |  |  |  | $\stackrel{\stackrel{5}{+}}{\underset{\sim}{2}}$ |  | $\begin{aligned} & \circ \\ & \stackrel{n}{n} \\ & \stackrel{y}{2} \end{aligned}$ | $\stackrel{\stackrel{n}{\circ}}{\stackrel{2}{\circ}}$ |  | $\overline{5}$ | $\begin{aligned} & \overline{5} \\ & 0 \end{aligned}$ |  |  |  |  |  |  | ה |
| 山岩 |  | $\begin{aligned} & \stackrel{0}{\hat{6}} \\ & \underset{\substack{1}}{2} \end{aligned}$ | $\begin{aligned} & \stackrel{0}{\hat{6}} \\ & \stackrel{6}{\top} \end{aligned}$ | $\begin{aligned} & \circ \\ & \stackrel{\circ}{\otimes} \\ & \stackrel{\infty}{\infty} \end{aligned}$ |  | $\begin{aligned} & \circ \\ & \stackrel{\circ}{\infty} \\ & \stackrel{\infty}{\infty} \\ & \underset{~}{2} \end{aligned}$ |  | － |  |  | － |  |  | － |  |  | － | － | $\begin{aligned} & \text { 厄⿱丷天心. } \\ & \stackrel{\infty}{\infty} \\ & \underset{\sim}{2} \end{aligned}$ |  |
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| v | $\stackrel{\text { ® }}{\text { ¢ }}$ | － | － | － | － | － |  | in |  |  |  |  |  | Noidosor |  | － | ¢ | $\stackrel{\text { ® }}{\circ}$ | － |  |
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| $\because \overline{\bar{Z}}$ |  |  | $\begin{aligned} & \frac{E}{A} \\ & \stackrel{O}{O} \end{aligned}$ |  |  | $\begin{aligned} & \stackrel{\circ}{2} \\ & \stackrel{y y}{\infty} \\ & \stackrel{y y y}{\infty} \end{aligned}$ |  | $\begin{aligned} & \text { ơ } \\ & \text { öo } \\ & \stackrel{0}{0} \end{aligned}$ |  |  |  |  |  |  |  | $\begin{aligned} & \frac{8}{8} \\ & \stackrel{y}{2} \\ & \stackrel{y}{\infty} \end{aligned}$ | $\begin{aligned} & \ddot{+} \\ & \stackrel{y}{+} \\ & \stackrel{\infty}{\infty} \end{aligned}$ |  | $\begin{aligned} & \stackrel{8}{8} \\ & \stackrel{\rightharpoonup}{2} \\ & \stackrel{y}{\infty} \\ & \hline \end{aligned}$ |  |
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| 步等 | $\pm$ |  |  |  | $\begin{aligned} & \text { 总 } \\ & \text { an } \\ & \stackrel{1}{1} \end{aligned}$ | $\begin{aligned} & \text { 啇 } \\ & \stackrel{n}{n} \end{aligned}$ |  | $\pm$ |  |  | $\pm$ |  |  | $\pm$ |  | 喤 |  | ¢ | 弪 |  |
|  |  |  |  | $\underset{\substack{\mathrm{C}}}{\substack{\mathrm{C}}}$ |  | $\underset{\substack{\mathrm{C}}}{\substack{\text { n }}}$ |  | $\stackrel{\substack{c\\}}{\mathrm{n}}$ |  |  |  |  |  | $\left\lvert\, \begin{gathered} \vec{~} \\ -\stackrel{e}{n} \\ \stackrel{n}{2} \end{gathered}\right.$ |  | $\stackrel{\sim}{c}$ |  | $\underset{\sim}{\substack{~}}$ | cock |  |
|  |  |  | $$ |  | $\begin{aligned} & \text { 密 } \\ & \text { dus } \\ & \vdots \\ & \hline 1 \end{aligned}$ | $\begin{aligned} & \text { 侖 } \\ & \stackrel{y}{n} \\ & \stackrel{y}{1} \end{aligned}$ |  | $\begin{aligned} & \substack{8 \\ \stackrel{y}{c} \\ \stackrel{y}{n}\\ } \end{aligned}$ |  |  |  |  |  | 等 <br> $\stackrel{y}{6}$ <br> $\substack{4 \\ \hline}$ |  |  | 器 | 第 |  |  |
|  | $\begin{gathered} \bar{\alpha} \\ \underset{\sim}{\mathrm{o}} \end{gathered}$ | $\begin{gathered} \text { ⿳⿵人一⿲丶丶㇒一⿱口⿵冂卄 } \end{gathered}$ | $\begin{aligned} & \text { 答 } \\ & \text { in } \end{aligned}$ | $\begin{aligned} & \overline{\mathrm{G}} \\ & \stackrel{\rightharpoonup}{n} \end{aligned}$ | O | $\stackrel{\circ}{\stackrel{\circ}{\infty}}$ |  |  |  |  | $\begin{aligned} & \underset{\sim}{\tilde{N}} \\ & \underset{\sim}{c} \end{aligned}$ |  |  | N |  | $\begin{aligned} & \infty \\ & \stackrel{\infty}{\alpha} \\ & \underset{子}{2} \end{aligned}$ | $\frac{\stackrel{e}{6}}{子}$ | $\stackrel{\substack{6 \\ \hdashline \\ \hdashline \\ \hline}}{ }$ |  |  |
|  | $\begin{aligned} & \circ \\ & \stackrel{\circ}{\circ} \\ & \substack{0 \\ \hline} \end{aligned}$ | $\begin{gathered} \text { ̣ì } \\ \text { and } \end{gathered}$ | $\begin{gathered} \text { 염 } \\ \text { an } \end{gathered}$ | $\begin{gathered} \text { 苟 } \\ \substack{6} \end{gathered}$ | $\stackrel{i}{t}$ àn |  |  | $\begin{aligned} & \text { F } \\ & \text { O} \\ & \text { in } \end{aligned}$ |  |  | $\stackrel{\otimes}{\#}$ |  |  | E |  | $\begin{aligned} & \text { f } \\ & \stackrel{y}{2} \\ & \text { in } \end{aligned}$ | $\begin{aligned} & \underset{N}{N} \\ & \stackrel{y}{i} \end{aligned}$ | E | त |  |
| 抎䓂 |  |  | 营 <br> 0 <br>  |  | $\begin{gathered} \text { qi } \\ \substack{\text { on }} \end{gathered}$ |  |  | $\begin{aligned} & \text { F } \\ & \text { di } \end{aligned}$ |  |  | $\stackrel{\otimes}{\square}$ |  |  | E |  | ci | － | － | त |  |
|  | 苞 | $\begin{aligned} & 0 \\ & \stackrel{y}{8} \\ & \text { vin } \end{aligned}$ | $\begin{aligned} & \circ \\ & \stackrel{0}{6} \\ & \hline \end{aligned}$ | $\begin{aligned} & 0_{0}^{0} \\ & \mathrm{~S}_{0} \end{aligned}$ | 令 | $\begin{aligned} & 0_{0}^{0} \\ & \mathrm{~S}_{0} \end{aligned}$ | $\begin{aligned} & \widetilde{N} \\ & \underbrace{5}_{0} \\ & \underbrace{}_{0} \end{aligned}$ | $\begin{aligned} & \text { 导等 } \\ & \frac{1}{2} \end{aligned}$ | $\left\{\begin{array}{l} \dot{2} \\ 0 \\ 0 \end{array}\right.$ | $\begin{aligned} & 0 \\ & 0 \\ & 0 \\ & 0 \\ & 0 \\ & 0 \\ & 0 \\ & 0 \end{aligned} \frac{2}{2} \frac{2}{2}$ |  | $\begin{aligned} & \mathcal{U}_{0}^{0} \\ & \mathrm{~S}_{0} \end{aligned}$ | $\begin{aligned} & \text { İ } \\ & \text { 心 } \\ & \text { vis } \end{aligned}$ |  | $\begin{gathered} 0_{0}^{0} \\ 0_{0}^{0} \\ v_{0} \end{gathered}$ | co | $\begin{array}{ll} y_{0} & 0 \\ 0_{0}^{0} \\ 0 & 0 \\ 0 & 0 \end{array}$ | $\begin{array}{ll} x & 0 \\ 0 & 0 \\ 0 & 0 \\ 0 & 0 \end{array}$ |  | （c） |

## SUMMARY TABLES OF SILICON 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 20.20.1. Summary results of silanes.

| Formula | Name | Calculated <br> Total Bond <br> Energy (eV) | Experimental <br> Total Bond <br> Energy (eV) | Relative <br> Error |
| :--- | :--- | :---: | :---: | :---: |
| SiH | silylidyne | 3.07526 | $3.02008[6]$ | -0.01827 |
| $\mathrm{SiH}_{2}$ | silylene | 6.15052 | $6.35523[7]$ | 0.03221 |
| $\mathrm{SiH}_{3}$ | silyl | 9.22578 | $9.36494[7]$ | 0.01486 |
| $\mathrm{SiH}_{4}$ | silane | 13.57257 | $13.34577[6]$ | -0.01699 |
| $\mathrm{Si}_{2} \mathrm{H}_{6}$ | disilane | 21.76713 | $22.05572[7]$ | 0.01308 |
| $\mathrm{Si}_{3} \mathrm{H}_{8}$ | trisilane | 31.23322 | $30.81334[7]$ | -0.01363 |

Table 20.20.2. Summary results of alkyl silanes and disilanes.

| Formula | Name | Calculated <br> Total Bond <br> Energy (eV) | Experimental <br> Total Bond <br> Energy (eV) | Relative <br> Error |
| :--- | :--- | :---: | :---: | :---: |
| $\mathrm{CH}_{6} \mathrm{Si}$ | methylsilane | 25.37882 | $25.99491[9]$ | 0.02370 |
| $\mathrm{C}_{2} \mathrm{H}_{8} \mathrm{Si}$ | dimethylsilane | 38.45660 | $38.64819[9]$ | 0.00496 |
| $\mathrm{C}_{3} \mathrm{H}_{10} \mathrm{Si}$ | trimethylsilane | 51.53438 | $51.33567[9]$ | -0.00387 |
| $\mathrm{C}_{4} \mathrm{H}_{12} \mathrm{Si}$ | tetramethylsilane | 64.61216 | $64.22319[14]$ | -0.00606 |
| $\mathrm{C}_{4} \mathrm{H}_{12} \mathrm{Si}$ | diethylsilane | 62.77200 | $63.37771[15]$ | 0.00956 |
| $\mathrm{C}_{6} \mathrm{H}_{16} \mathrm{Si}$ | triethylsilane | 88.00748 | $87.46141[15]$ | -0.00624 |
| $\mathrm{C}_{8} \mathrm{H}_{20} \mathrm{Si}^{2}$ | tetraethylsilane | 113.24296 | $112.06547[15]$ | -0.01051 |
| $\mathrm{CH}_{8} \mathrm{Si}_{2}$ | methyldisilane | 34.56739 | $34.73920[16]$ | 0.00495 |
| $\mathrm{C}_{2} \mathrm{H}_{10} \mathrm{Si}_{2}$ | 1,1-dimethyldisilane | 47.36764 | $47.42283[16]$ | 0.00116 |
| $\mathrm{C}_{2} \mathrm{H}_{10} \mathrm{Si}_{2}$ | 1,2-dimethyldisilane | 47.36764 | $47.42283[16]$ | 0.00116 |
| $\mathrm{C}_{3} \mathrm{H}_{12} \mathrm{Si}_{2}$ | $1,1,1$-trimethyldisilane | 60.16789 | $60.10646[16]$ | -0.00102 |
| $\mathrm{C}_{3} \mathrm{H}_{12} \mathrm{Si}_{2}$ | $1,1,2$-trimethyldisilane | 60.16789 | $60.10646[16]$ | -0.00102 |
| $\mathrm{C}_{4} \mathrm{H}_{14} \mathrm{Si}_{2}$ | $1,1,1,2$-tetramethyldisilane | 72.96815 | $72.79442[16]$ | -0.00239 |
| $\mathrm{C}_{4} \mathrm{H}_{14} \mathrm{Si}_{2}$ | $1,1,2,2$-tetramethyldisilane | 72.96815 | $72.79442[16]$ | -0.00239 |
| $\mathrm{C}_{5} \mathrm{H}_{16} \mathrm{Si}_{2}$ | $1,1,1,2,2$-pentamethyldisilane | 85.76840 | $85.47805[16]$ | -0.00340 |
| $\mathrm{C}_{6} \mathrm{H}_{18} \mathrm{Si}_{2}$ | hexamethyldisilane | 98.56865 | $98.32646[16]$ | -0.00246 |

Table 20.20.3. Summary results of silicon oxides, silicic acids, silanols, siloxanes, and disiloxanes.

| Formula | Name | Calculated <br> Total Bond <br> Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
| :---: | :---: | :---: | :---: | :---: |
| SiO | silicon oxide | 8.30876 | 8.29905 [18] | -0.00117 |
| $\mathrm{SiO}_{2}$ | silicon dioxide | 12.94190 | 12.98073 [19] | 0.00299 |
| $\mathrm{SiH}_{4} \mathrm{O}$ | $\mathrm{H}_{3} \mathrm{SiOH}$ | 18.67184 | $19.00701^{\text {a }}$ [27] | 0.01763 |
| $\mathrm{SiH}_{4} \mathrm{O}_{2}$ | $\mathrm{H}_{2} \mathrm{Si}(\mathrm{OH})_{2}$ | 25.04264 | $25.04264^{\text {a }}$ [27] | 0.00563 |
| $\mathrm{SiH}_{4} \mathrm{O}_{3}$ | $\mathrm{HSi}(\mathrm{OH})_{3}$ | 31.41344 | $31.47012^{\text {a }}$ [27] | 0.00180 |
| $\mathrm{SiH}_{4} \mathrm{O}_{4}$ | $\mathrm{Si}(\mathrm{OH})_{4}$ | 37.78423 | 38.03638 [28] | 0.00663 |
| $\mathrm{C}_{3} \mathrm{H}_{10} \mathrm{SiO}$ | trimethylsilanol | 57.31895 | 57.30073 [29] | -0.00032 |
| $\mathrm{C}_{2} \mathrm{H}_{6} \mathrm{SiO}$ | vinylsilanol | 37.33784 |  |  |
| $\mathrm{CH}_{6} \mathrm{SiO}_{4}$ | $(\mathrm{HO})_{3} \mathrm{SiOCH}_{3}$ | 47.45144 | $49.28171^{\text {a }}$ [30] | 0.03714 |
| $\mathrm{C}_{4} \mathrm{H}_{12} \mathrm{SiO}_{4}$ | tetramethoxysilioxane | 83.48783 | 84.04681 [31] | 0.00665 |
| $\mathrm{C}_{6} \mathrm{H}_{16} \mathrm{SiO}_{3}$ | triethoxysilioxane | 102.74755 | 102.57961 [31] | -0.00164 |
| $\mathrm{C}_{8} \mathrm{H}_{20} \mathrm{SiO}_{4}$ | tetraethoxysilioxane | 132.89639 | 133.23177 [31] | 0.00252 |
| $\mathrm{C}_{6} \mathrm{H}_{18} \mathrm{Si}_{3} \mathrm{O}_{3}$ | $\left(\left(\mathrm{CH}_{3}\right)_{2} \mathrm{SiO}\right)_{3}$ | 123.61510 | 123.22485 [31] | -0.00317 |
| $\mathrm{C}_{8} \mathrm{H}_{24} \mathrm{Si}_{4} \mathrm{O}_{4}$ | $\left(\left(\mathrm{CH}_{3}\right)_{2} \mathrm{SiO}\right)_{4}$ | 164.82014 | 164.79037 [31] | -0.00018 |
| $\mathrm{C}_{10} \mathrm{H}_{30} \mathrm{Si}_{5} \mathrm{O}_{5}$ | $\left(\left(\mathrm{CH}_{3}\right)_{2} \mathrm{SiO}\right)_{5}$ | 206.02517 | 206.35589 [31] | 0.00160 |
| $\mathrm{C}_{6} \mathrm{H}_{18} \mathrm{Si}_{2} \mathrm{O}$ | hexamethyldisiloxane | 105.24639 | 105.20196 [31] | -0.00042 |

[^2]
## REFERENCES

1. D. R. Lide, CRC Handbook of Chemistry and Physics, 86th Edition, CRC Press, Taylor \& Francis, Boca Raton, (2005-6), pp. 10-202 to 10-204.
2. D. R. Lide, CRC Handbook of Chemistry and Physics, 86th Edition, CRC Press, Taylor \& Francis, Boca Raton, (2005-6), p. 9-26.
3. D. R. Lide, CRC Handbook of Chemistry and Physics, 86th Edition, CRC Press, Taylor \& Francis, Boca Raton, (2005-6), p. 9-86.
4. D. R. Lide, CRC Handbook of Chemistry and Physics, 86th Edition, CRC Press, Taylor \& Francis, Boca Raton, (2005-6), p. 9-57.
5. D. R. Lide, CRC Handbook of Chemistry and Physics, 86th Edition, CRC Press, Taylor \& Francis, Boca Raton, (2005-6), p. 9-71.
6. B. H. Boo, P. B. Armentrout, "Reaction of silicon ion $\left({ }^{2} \mathrm{P}\right)$ with silane ( $\left.\mathrm{SiH}_{4}, \mathrm{SiD}_{4}\right)$. Heats of formation of $\mathrm{SiH}_{n}, \mathrm{SiH}_{n}{ }^{+}(n=1$, $2,3)$, and $\mathrm{Si}_{2} \mathrm{H}_{\mathrm{n}}{ }^{+}(n=0,1,2,3)$. Remarkable isotope exchange reaction involving four hydrogen shifts," J. Am. Chem. Soc., (1987), Vol. 109, pp. 3549-3559.
7. G. Katzer, M. C. Ernst, A. F. Sax, J. Kalcher, "Computational thermochemistry of medium-sized silicon hydrides," J. Phys. Chem. A, (1997), Vol. 101, pp. 3942-3958.
8. D. R. Lide, CRC Handbook of Chemistry and Physics, 86th Edition, CRC Press, Taylor \& Francis, Boca Raton, (2005-6), pp. 9-19 to 9-45.
9. M. R. Frierson, M. R. Imam, V. B. Zalkow, N. L. Allinger, "The MM2 force field for silanes and polysilanes," J. Org. Chem., Vol. 53, (1988), pp. 5248-5258.
10. D. Lin-Vien. N. B. Colthup, W. G. Fateley, J. G. Grasselli, The Handbook of Infrared and Raman Frequencies of Organic Molecules, Academic Press, Inc., Harcourt Brace Jovanovich, Boston, (1991), p. 256.
11. G. Herzberg, Molecular Spectra and Molecular Structure II. Infrared and Raman Spectra of Polyatomic Molecules, Van Nostrand Reinhold Company, New York, New York, (1945), p. 344.
12. R. J. Fessenden, J. S. Fessenden, Organic Chemistry, Willard Grant Press. Boston, Massachusetts, (1979), p. 320.
13. "Cyclohexane," NIST Chemistry Handbook. http://webbook.nist.gov/.
14. D. R. Lide, CRC Handbook of Chemistry and Physics, $86^{\text {th }}$ Ed., CRC Press, Taylor \& Francis, Boca Raton, (2005-6), p. 5-28.
15. M. J. S. Dewar, C. Jie, "AM 1 calculations for compounds containing silicon," Organometallics, Vol. 6, (1987), pp. 14861490.
16. R. Walsh, "Certainties and uncertainties in the heats of formation of the methylsilylenes," Organometallics, Vol. 8, (1989), .pp. 1973-1978.
17. R. W. Kilb, L. Pierce, "Microwave spectrum, structure, and internal barrier of methyl silane," J. Chem. Phys., Vol. 27, No. 1, (1957), pp. 108-112.
18. M. W. Chase, Jr., C. A. Davies, J. R. Downey, Jr., D. J. Frurip, R. A. McDonald, A. N. Syverud, JANAF Thermochemical Tables, Third Edition, Part II, Cr-Zr, J. Phys. Chem. Ref. Data, Vol. 14, Suppl. 1, (1985), p. 1728.
19. M. W. Chase, Jr., C. A. Davies, J. R. Downey, Jr., D. J. Frurip, R. A. McDonald, A. N. Syverud, JANAF Thermochemical Tables, Third Edition, Part II, Cr-Zr, J. Phys. Chem. Ref. Data, Vol. 14, Suppl. 1, (1985), p. 1756.
20. D. Nyfeler, T. Armbruster, "Silanol groups in minerals and inorganic compounds," American Mineralogist, Vol. 83, (1998), pp. 119-125.
21. K. P. Huber, G. Herzberg, Molecular Spectra and Molecular Structure, IV. Constants of Diatomic Molecules, Van Nostrand Reinhold Company, New York, (1979).
22. J. Crovisier, Molecular Database-Constants for molecules of astrophysical interest in the gas phase: photodissociation, microwave and infrared spectra, Ver. 4.2, Observatoire de Paris, Section de Meudon, Meudon, France, May 2002, pp. 34-37, available at http://wwwusr.obspm.fr/~crovisie/.
23. "Dimethyl ether," NIST Chemistry Handbook. http://webbook.nist.gov/.
24. R. J. Fessenden, J. S. Fessenden, Organic Chemistry, Willard Grant Press. Boston, Massachusetts, (1979), p. 320.
25. "Fluoroethane," NIST Chemistry Handbook. http://webbook.nist.gov/.
26. G. Herzberg, Molecular Spectra and Molecular Structure II. Infrared and Raman Spectra of Polyatomic Molecules, Van Nostrand Reinhold Company, New York, New York, (1945), p. 326.
27. M. D. Allendorf, C. F. Melius, P. Ho, M. R. Zachariah, "Theoretical study of the thermochemistry of molecules in the Si-OH system," J. Phys. Chem., Vol. 99, (1995), pp. 15285-15293.
28. N. S. Jacobson, E. J. Opila, D. L. Myers, E. H. Copeland, "Thermodynamics of gas phase species in the Si-O-H system," J. Chem. Thermodynamics, Vol. 37, (2005), pp. 1130-1137.
29. J. D. Cox, G. Pilcher, Thermochemistry of Organometallic Compounds, Academic Press, New York, (1970), pp. 468-469.
30. J. C. S. Chu, R. Soller, M. C. Lin, C. F. Melius, "Thermal decomposition of tetramethyl orthoscilicate in the gas phase: An experimental and theoretical study of the initiation process," J. Phys. Chem, Vol. 99, (1995), pp. 663-672.
31. R. Becerra, R. Walsh, In The Chemistry of Organic Silicon Compounds; Z. Rappaport, Y. Apeloig, Eds.; Thermochemistry, Vol. 2; Wiley, New York, (1998), Chp. 4.
32. C. L. Darling, H. B. Schlegel, "Heats of formation of $\mathrm{SiH}_{\mathrm{n}} \mathrm{O}$ and $\mathrm{SiH}_{\mathrm{n}} \mathrm{O}_{2}$ calculated by ab initio molecular orbital methods at the G-2 level of theory," J. Phys. Chem. Vol. 97, (1993), 8207-8211.
33. A. C. M. Kuo, In Polymer Data Handbook; Poly(dimethylsiloxane); Oxford University Press, (1999), p 419.

# Chapter 21 

# THE NATURE OF THE SEMICONDUCTOR BOND OF SILICON 

## GENERALIZATION OF THE NATURE OF THE SEMICONDUCTOR BOND

Semiconductors are solids that have properties intermediate between insulators and metals. For an insulator to conduct, high energy and power are required to excite electrons into a conducting state in sufficient numbers. Application of high energy to cause electron ionization to the continuum level or to cause electrons to transition to conducing molecular orbitals (MOs) will give rise to conduction when the power is adequate to maintain a high population density of such states. Only high temperatures or extremely high-strength electric fields will provide enough energy and power to achieve an excited state population permissive of conduction. In contrast, metals are highly conductive at essentially any field strength and power. Diamond and alkali metals given in the corresponding sections are representative of insulator and metal classes of solids at opposite extremes of conductivity. It is apparent from the bonding of diamond comprising a network of highly stable MOs that it is an insulator, and the planar free-electron membranes in metals give rise to their high conductivity.

Column IV elements silicon, germanium, and $\alpha$-gray tin all have the diamond structure and are insulators under standard conditions. However, the electrons of these materials can be excited into a conducting excited state with modest amounts of energy compared to a pure insulator. As opposed to the 5.2 eV excitation energy for carbon, silicon, germanium, and $\alpha$-gray tin have excitation energies for conduction of only $1.1 \mathrm{eV}, 0.61 \mathrm{eV}$, and 0.078 eV , respectively. Thus, a semiconductor can carry a current by providing the relatively small amount of energy required to excite electrons to conducting excited states. As in the case of insulators, excitation can occur thermally by a temperature increase. Since the number of excited electrons increases with temperature, a concomitant increase in conductance is observed. This behavior is the opposite of that of metals. Alternatively, the absorption of photons of light causes the electrons in the ground state to be excited to a conducting state that is the basis of conversion of solar power into electricity in solar cells and detection and reception in photodetectors and fiber optic communications, respectively. In certain semiconductors, rather than decay by internal conversion to phonons, the energy of excited-state electrons is emitted as light as the electrons transition from the excited conducting state to the ground state. This photon emission process is the basis of light emitting diodes (LEDs) and semiconductor lasers which have broad application in industry.

In addition to elemental materials such as silicon and germanium, semiconductors may be compound materials such as gallium arsenide and indium phosphide, or alloys such as silicon germanium or aluminum arsenide. Conduction in materials such as silicon and germanium crystals can be enhanced by adding small amounts (e.g. 1-10 parts per million) of dopants such as boron or phosphorus as the crystals are grown. Phosphorous with five valence electrons has a free electron even after contributing four electrons to four single bond-MOs of the diamond structure of silicon. Since this fifth electron can be ionized from a phosphorous atom with only 0.011 eV provided by an applied electric field, phosphorous as an electron donor makes silicon a conductor.

In an opposite manner to that of the free electrons of the dopant carrying electricity, an electron acceptor may also transform silicon to a conductor. Atomic boron has only three valence electrons rather than the four needed to replace a silicon atom in the diamond structure of silicon. Consequently, a neighboring silicon atom has an unpaired electron per boron atom. These electrons can be ionized to carry electricity as well. Alternatively, a valence electron of a silicon atom neighboring a boron atom can be excited to ionize and bind to the boron. The resulting negative boron ion can remain stationary as the corresponding positive center on silicon migrates from atom to atom in response to an applied electric field. This occurs as an electron transfers from a silicon atom with four electrons to one with three to fill the vacant silicon orbital. Concomitantly, the positive center is transferred in the opposite direction. Thus, inter-atomic electron transfer can carry current in a cascade effect as the propagation of a "hole" in the opposite direction as the sequentially transferring electrons.

The ability of the conductivity of semiconductors to transition from that of insulators to that of metals with the application of sufficient excitation energy implies a transition of the excited electrons from covalent to metallic-bond electrons. The bonding in diamond shown in the Nature of the Molecular Bond of Diamond section is a network of covalent bonds.

Semiconductors comprise covalent bonds wherein the electrons are of sufficiently high energy that excitation creates an ion and a free electron. The free electron forms a membrane as in the case of metals given in the Nature of the Metallic Bond of Alkali Metals section. This membrane has the same planar structure throughout the crystal. This feature accounts for the high conductivity of semiconductors when the electrons are excited by the application of external fields or electromagnetic energy that causes ion-pair ( $M^{+}-e^{-}$) formation.

It was demonstrated in the Nature of the Metallic Bond of Alkali Metals section that the solutions of the external point charge at an infinite planar conductor are also those of the metal ions and free electrons of metals based on the uniqueness of solutions of Maxwell's equations and the constraint that the individual electrons in a metal conserve the classical physical laws of the macro-scale conductor. The nature of the metal bond is a lattice of metal ions with field lines that end on the corresponding lattice of electrons comprising two-dimensional charge density $\sigma$ given by Eq. (19.6) where each is equivalent electrostatically to an image point charge at twice the distance from the point charge of $+e$ due to $M^{+}$. Thus, the metallic bond is equivalent to the ionic bond given in the Alkali-Hydride Crystal Structures section with a Madelung constant of one with each negative ion at a position of one half the distance between the corresponding positive ions, but electrostatically equivalent to being positioned at twice this distance, the $M^{+}-M^{+}$-separation distance. Then, the properties of semiconductors can be understood as due to the excitation of a bound electron from a covalent state such as that of the diamond structure to a metallic state such as that of an alkali metal. The equations are the same as those of the corresponding insulators and metals.

## NATURE OF THE INSULATOR-TYPE SEMICONDUCTOR BOND

As given in the Nature of the Solid Molecular Bond of Diamond section, diamond $C-C$ bonds are all equivalent, and each $C$ - $C$ bond can be considered bound to a t-butyl group at the corresponding vertex carbon. Thus, the parameters of the diamond $C$ - $C$ functional group are equivalent to those of the t-butyl $C-C$ group of branched alkanes given in the Branched Alkanes section. Silicon also has the diamond structure. The diamond Si-Si bonds are all equivalent, and each Si-Si bond can be considered bound to three other Si-Si bonds at the corresponding vertex silicon. Thus, the parameters of the crystalline silicon $\mathrm{Si}-\mathrm{Si}$ functional group are equivalent to those of the $\mathrm{Si}-\mathrm{Si}$ group of silanes given in the Silanes $\left(\mathrm{Si}_{n} \mathrm{H}_{2 n+2}\right)$ section except for the $E_{T}\left(\right.$ atom-atom, $\left.m s p^{3} . A O\right)$ term of Eq. (15.61). Since bonds in pure crystalline silicon are only between Si3sp ${ }^{3}$ HOs having energy less than the Coulombic energy between the electron and proton of $H$ given by Eq. (1.264) $E_{T}\left(\right.$ atom-atom, $\left.m s p^{3} \cdot A O\right)=0$. Also, as in the case of the $C-C$ functional group of diamond, the Si3sp ${ }^{3}$ HO magnetic energy $E_{\text {mag }}$ is subtracted due to a set of unpaired electrons being created by bond breakage such that $c_{3}$ of Eq. (15.65) is one, and $E_{\text {mag }}$ is given by Eqs. (15.15) and (20.3).

$$
\begin{equation*}
E_{\text {mag }}\left(S i 3 s p^{3}\right)=c_{3} \frac{8 \pi \mu_{0} \mu_{B}^{2}}{r^{3}}=c_{3} \frac{8 \pi \mu_{0} \mu_{B}^{2}}{\left(1.31926 a_{0}\right)^{3}}=c_{3} 0.04983 \mathrm{eV} \tag{21.1}
\end{equation*}
$$

The symbols of the functional group of crystalline silicon is given in Table 21.1. The geometrical (Eqs. (15.1-15.5), (20.3-20.7), (20.29), and (20.33)) parameters of crystalline silicon are given in Table 21.2. Using the internuclear distance $2 c^{\prime}$, the lattice parameter $a$ of crystalline silicon is given by Eq. (17.3). The intercept (Eqs. (15.80-15.87), (20.3), and (20.21)) and energy (Eqs. (15.61), (20.3-20.7), and (20.33)) parameters of crystalline silicon are given in Tables 21.2, 21.3, and 21.4, respectively. The total energy of crystalline silicon given in Table 21.5 was calculated as the sum over the integer multiple of each $E_{D}$ (Group) of Table 21.4 corresponding to functional-group composition of the solid. The bond angle parameters of crystalline silicon determined using Eqs. (15.88-15.117), (20.4), (20.33), and (21.1) are given in Table 21.6. The diamond structure of silicon in the insulator state is shown in Figure 21.1. The predicted structure matches the experimental images of silicon determined using STM [1] as shown in Figure 21.2.
Figure 21.1. The diamond structure of silicon in the insulator state. Axes indicate positions of additional bonds of the repeating structure. (A) Twenty six $C-C$-bond MOs. (B) Fifty one $C-C$-bond MOs.

(B)


Figure 21.2. (A)-(B) STM topographs of the clean $\operatorname{Si}(111)-(7 X 7)$ surface. Reprinted with permission from Ref. [1]. Copyright 1995 American Chemical Society.

(A)

(B)

Table 21.1. The symbols of the functional group of crystalline silicon.

| Functional Group | Group Symbol |
| :---: | :---: |
| SiSi bond (diamond-type-Si) | $\mathrm{Si}-\mathrm{Si}$ |

Table 21.2. The geometrical bond parameters of crystalline silicon and experimental values.

| Parameter | $S i-S i$ <br> Group |
| :---: | :---: |
| $a\left(a_{0}\right)$ | 2.74744 |
| $c^{\prime}\left(a_{0}\right)$ | 2.19835 |
| Bond Length $2 c^{\prime}(\AA)$ | 2.32664 |
| Exp. Bond Length $(\AA)$ | $2.35[2]$ |
| $b, c\left(a_{0}\right)$ | 1.64792 |
| $e$ | 0.80015 |
| Lattice Parameter $a_{l}(\AA)$ | 5.37409 |
| Exp. Lattice Parameter $a_{l}(\AA)$ | $5.4306[3]$ |


| Bond | Atom | $\begin{gathered} E_{T} \\ (\mathrm{eV}) \\ \text { Bond } 1 \end{gathered}$ | $\begin{gathered} E_{T} \\ (e V) \\ \text { Bond } 2 \end{gathered}$ | $E_{T}$ <br> (eV) <br> Bond 3 |  | Final Total Energy Si3sp ${ }^{3}$ (eV) | $\left.\begin{array}{rl} r_{\text {initial }} \\ \left(a_{0}\right. \end{array}\right)$ | $\begin{aligned} & r_{\text {final }} \\ & \left(a_{0}\right) \end{aligned}$ | $\begin{gathered} E_{\text {Coulomb } b}\left(C 2 s p^{3}\right) \\ (e V) \\ \text { Final } \end{gathered}$ | $\begin{gathered} E\left(C 2 s p^{3}\right) \\ (e V) \\ \text { Final } \end{gathered}$ | $\begin{aligned} & \theta^{\prime} \\ & \left({ }^{\circ}\right) \end{aligned}$ | $\begin{aligned} & \theta_{1} \\ & \left({ }^{\circ}\right) \end{aligned}$ | $\begin{aligned} & \theta_{2} \\ & \left({ }^{\circ}\right) \end{aligned}$ | $\begin{gathered} d_{1} \\ \left(a_{0}\right) \end{gathered}$ | $\begin{gathered} d_{2} \\ \left(a_{0}\right) \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Si-Si | Si | 0 | 0 | 0 | 0 | -105.23554 | 1.31926 | 1.31926 | -10.31324 | -10.25487 | 108.26 | 71.74 | 49.48 | 1.78489 | 0.41346 |

Table 21.4. The energy parameters (eV) of the functional group of crystalline silicon.

| Parameters | $\begin{aligned} & \hline S i-S i \\ & \text { Group } \end{aligned}$ |
| :---: | :---: |
| $n_{1}$ | 1 |
| $n_{2}$ | 0 |
| $n_{3}$ | 0 |
| $C_{1}$ | 0.37500 |
| $\mathrm{C}_{2}$ | 0.75800 |
| $c_{1}$ | 1 |
| $c_{2}$ | 0.75800 |
| $c_{3}$ | 0 |
| $c_{4}$ | 2 |
| $c_{5}$ | 0 |
| $C_{10}$ | 0.37500 |
| $\mathrm{C}_{2}$ 。 | 0.75800 |
| $V_{e}(e \mathrm{~V})$ | -20.62357 |
| $V_{p}(\mathrm{eV})$ | 6.18908 |
| $T(e V)$ | 3.75324 |
| $V_{m}(\mathrm{eV})$ | -1.87662 |
| $E$ (Ао/но) $(\mathrm{eV})$ | -10.25487 |
| $\Delta E_{\mathrm{H}_{2} \mathrm{MO}}(\mathrm{AO} / \mathrm{HO})(\mathrm{eV})$ | 0 |
| $E_{T}($ Ао/ $/ \mathrm{Ho})(\mathrm{eV})$ | -10.25487 |
| $E_{T}\left(\mathrm{H}_{2} \mathrm{MO}\right)(\mathrm{eV})$ | -22.81274 |
| $E_{T}\left(\right.$ atom - atom, $\left.\mathrm{msp}^{3} \cdot \mathrm{AO}\right)(\mathrm{eV})$ | 0 |
| $E_{T}($ мо $)(\mathrm{eV})$ | -22.81274 |
| $\omega\left(10^{15} \mathrm{rad} / \mathrm{s}\right)$ | 4.83999 |
| $E_{K}(\mathrm{eV})$ | 3.18577 |
| $\bar{E}_{D}(\mathrm{eV})$ | -0.08055 |
| $\bar{E}_{\text {Kvib }}(\mathrm{eV})$ | $\begin{gathered} 0.06335 \\ {[4]} \\ \hline \end{gathered}$ |
| $\bar{E}_{\text {osc }}(\mathrm{eV})$ | -0.04888 |
| $E_{\text {mag }}(\mathrm{eV})$ | 0.04983 |
| $E_{T}($ Group $)(e V)$ | -22.86162 |
| $E_{\text {initial }}\left(\mathrm{c}_{4}\right.$ AO/ $/$ но) $)(\mathrm{eV})$ | -10.25487 |
| $E_{\text {initial }}\left(c_{5}\right.$ АО $/$ но) $)(\mathrm{eV})$ | 0 |
| $E_{D}($ Group $)(e V)$ | 2.30204 |

Table 21.5. The total bond energy of crystalline silicon calculated using the functional group composition and the energy of Table 21.4 compared to the experimental value [5].

| Formula | Name | $S i-S i$ | Calculated <br> Total Bond <br> Energy (eV) | Experimental <br> Total Bond <br> Energy (eV) | Relative Error |
| :--- | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{Si}_{\mathrm{n}}$ | Crystalline silicon | 1 | 2.30204 | 2.3095 | 0.003 |

Table 21.6. The bond angle parameters of crystalline silicon and experimental values [2]. In the calculation of $\theta_{v,}$ the parameters from the preceding angle were used. $E_{T}$

| $\begin{aligned} & \text { Atoms of } \\ & \text { Angle } \end{aligned}$ | $2 c^{\prime}$ Bond 1 $\left(a_{0}\right)$ | $2 c^{\prime}$ Bond 2 $\left(a_{0}\right)$ | $2 c^{\prime}$ Termina 1 Atoms $\left(a_{0}\right)$ | $\begin{aligned} & E_{\text {Coulombic }} \\ & \text { Atom } 1 \end{aligned}$ | Atom 1 Hybridization Designation (Table 20.1) | $\begin{aligned} & E_{\text {Coulombic }} \\ & \text { Atom } 2 \end{aligned}$ | Atom 2 Hybridization Designation (Table 20.1) | $\begin{gathered} c_{2} \\ \text { Atom } 1 \end{gathered}$ | $c_{2}$ <br> Atom 2 | $C_{1}$ | $C_{2}$ | $c_{1}$ | $c_{2}^{\prime}$ | $\begin{gathered} E_{T} \\ (\mathrm{eV}) \end{gathered}$ | $\begin{gathered} \theta_{v} \\ \left({ }^{\circ}\right) \end{gathered}$ | $\begin{gathered} \theta_{1} \\ \left({ }^{\circ}\right) \end{gathered}$ | $\begin{aligned} & \theta_{2} \\ & \left({ }^{\circ}\right) \end{aligned}$ | Cal. $\theta$ $\left({ }^{\circ}\right)$ | Exp. $\theta$ <br> ${ }^{\circ}$ ) |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\angle S i_{b} S i_{a} S i_{c}$ | 4.39671 | 4.39671 | 7.1668 | $\begin{gathered} -10.31324 \\ S i_{b} \\ \hline \end{gathered}$ | 1 | $\begin{gathered} -10.31324 \\ S i_{c} \\ \hline \end{gathered}$ | 1 | 1 | 1 | 0.75 | $\begin{gathered} 0.75800 \\ \text { Eq. } \\ (20.33) \\ \hline \end{gathered}$ | 1 | 1 | $\begin{gathered} -0.04983 \\ (\text { Eq. }(21.1)) \end{gathered}$ |  |  |  | 109.18 | 109.5 |
| $\angle S i_{b} S S_{a} S i_{d}$ |  |  |  |  |  |  |  |  |  |  |  |  |  |  | 70.24 |  |  | 109.76 | 109.5 |

## NATURE OF THE CONDUCTOR-TYPE SEMICONDUCTOR BOND

With the application of excitation energy equivalent to at least the band gap in the form of photons for example, electrons in silicon transition to conducting states. The nature of these states are equivalent to those of the electrons of metals with the appropriate lattice parameters and boundary conditions of silicon. Since the planar electron membranes are in contact throughout the crystalline matrix, the Maxwellian boundary condition that an equipotential must exist between contacted perfect conductors maintains that all of the planar electrons are at the energy of the highest energy state electron. This condition with the availability of a multitude of states with different ion separation distances and corresponding energies coupled with a near continuum of phonon states and corresponding energies gives rise to a continuum energy band or conduction band in the excitation spectrum. Thus, the conducting state of silicon comprises a background covalent diamond structure with free metaltype electrons and an equal number of silicon cations dispersed in the covalent lattice wherein excitation has occurred. The band gap can be calculated from the difference between the energy of the free electrons at the minimum electron-ion separation distance (the parameter $d$ given in the Nature of the Metallic Bond of Alkali Metals section) and the energy of the covalent-type electrons of the diamond-type bonds given in the Nature of the Insulator-Type Semiconductor Bond section.

The band gap is the lowest energy possible to form free electrons and corresponding $\mathrm{Si}^{+}$ions. Since the gap is the energy difference between the total energy of the free electrons and the MO electrons, a minimum gap corresponds to the lowest energy state of the free electrons. With the ionization of silicon atoms, planar electron membranes form with the corresponding ions at initial positions of the corresponding bond in the silicon lattice. The potential energy between the electrons and ions is a maximum if the electron membrane comprises the superposition of the two electrons ionized from a corresponding $\mathrm{Si}-\mathrm{Si}$ bond, and the orientation of the membrane is the transverse bisector of the former bond axis such that the magnitude of the potential is four times that of a single $\mathrm{Si}^{+}-e^{-}$pair. In this case, the potential is given by two times Eq. (19.21). Furthermore, all of the field lines of the silicon ions end on the intervening electrons. Thus, the repulsion energy between $\mathrm{Si}^{+}$ions is zero and the energy of the ionized state is a minimum. Using the parameters from Tables 21.1 and 21.6 , the $\mathrm{Si}^{+}$- $e^{-}$distance of $c^{\prime}=1.16332 \AA$, and the calculated $S i^{+}$ionic radius of $r_{S i^{+} 3 s p^{3}}=1.16360 a_{0}=0.61575 \AA$ (Eq. 20.17), the lattice structure of crystalline silicon in a conducting state is shown in Figure 21.3.

Figure 21.3. (A), (B), and (C) The conducting state of crystalline silicon showing the covalent diamond-structure network of the unit cell with two electrons ionized from a MO shown as a planar two-dimensional membrane of zero thickness that is the perpendicular bisector of the former $\mathrm{Si}-\mathrm{Si}$ bond axis. The corresponding two $\mathrm{Si}^{+}$ions (smaller radii) are centered at the positions of the atoms that contributed the ionized $S i 3 s p^{3}-\mathrm{HO}$ electrons. The electron equipotential energy surface may superimpose with multiple planar electron membranes. The surface charge density of each electron gives rise to an electric field equivalent to that of an image point charge for each corresponding positive ion of the lattice.


The optimal $\mathrm{Si}^{+}$ion-electron separation distance parameter $d$ is given by:

$$
\begin{equation*}
d=c^{\prime}=2.19835 a_{0}=1.16332 \times 10^{-10} \mathrm{~m} \tag{21.2}
\end{equation*}
$$

The band gap is given by the difference in the energy of the free electrons at the optimal $\mathrm{Si}^{+}$-electron separation distance parameter $d$ given by Eq. (21.2) and the energy of the electrons in the initial state of the $\mathrm{Si}-\mathrm{Si}$-bond MO. The total energy of electrons of a covalent $\operatorname{Si}-\operatorname{Si}$-bond MO $E_{T}\left(S i_{S i \text {-Simo }}\right)$ given by Eq. (15.65) and Table 21.4 is:

$$
\begin{equation*}
E_{T}\left(S i_{\text {Si-SiMo }}\right)=E_{T}(M O)+\bar{E}_{\text {osc }}-E_{\text {mag }}=-22.81274 \mathrm{eV}+0.04888-0.04983 \mathrm{eV}=-22.81369 \mathrm{eV} \tag{21.3}
\end{equation*}
$$

The minimum energy of a free-conducting electron in silicon for the determination of the band gap $E_{T(b a n d ~ g a p)}\left(\right.$ free $e^{-}$in $\left.S i\right)$ is given by the sum of twice the potential energy and the kinetic energy given by Eqs. (19.21) and (19.24), respectively:

$$
\begin{equation*}
E_{T(\text { band gap })}\left(\text { free } e^{-} \text {in } S i\right)=V+T=\frac{-2 e^{2}}{4 \pi \varepsilon_{0} d}+\frac{4}{3}\left(\frac{1}{2} \frac{\hbar^{2}}{m_{e} d^{2}}\right) \tag{21.4}
\end{equation*}
$$

In addition, the ionization of the MO electrons increases the charge on the two corresponding Si3sp ${ }^{3} \mathrm{HO}$ with a corresponding energy decrease, $E_{T}\left(\right.$ atom-atom, $\left.m s p^{3} . A O\right)$ given by one half that of Eq. (20.20). With $d$ given by Eq. (21.2), $E_{T(\text { band gap) }}\left(\right.$ free $e^{-}$in $\left.S i\right)$ is:

$$
\begin{align*}
E_{T(\text { band gap })}\left(\text { free } e^{-} \text {in Si }\right) & =\left(\begin{array}{l}
\frac{-2 e^{2}}{4 \pi \varepsilon_{0}\left(1.16332 \times 10^{-10} \mathrm{~m}\right)} \\
+\frac{4}{3}\left(\frac{1}{2} \frac{\hbar^{2}}{m_{e}\left(1.16332 \times 10^{-10} \mathrm{~m}\right)^{2}}\right) \\
+E_{T}\left(\text { atom }- \text { atom, } \mathrm{msp}^{3} \cdot \mathrm{AO}\right)
\end{array}\right) \\
& =-24.75614 \mathrm{eV}+3.75374 \mathrm{eV}-\frac{1.37960}{2} \mathrm{eV}  \tag{21.5}\\
& =-21.69220 \mathrm{eV}
\end{align*}
$$

The band gap in silicon $E_{g}$ given by the difference between $E_{T(b a n d ~ g a p)}\left(f r e e ~ e^{-}\right.$in $\left.S i\right)$ (Eq. (21.5)) and $E_{T}\left(S i_{S i-S i M O}\right)$ (Eq. (21.3)) is:

$$
\begin{align*}
E_{g} & =E_{T(\text { band gap) }}\left(\text { free } e^{-} \text {in } S i\right)-E_{T}\left(S i_{\text {Si-SiMO }}\right) \\
& =-21.69220 \mathrm{eV}-(-22.81179 \mathrm{eV})  \tag{21.6}\\
& =1.120 \mathrm{eV}
\end{align*}
$$

The experimental band gap for silicon [6] is:

$$
\begin{equation*}
E_{g}=1.12 \mathrm{eV} \tag{21.7}
\end{equation*}
$$

The calculated band gap is in excellent agreement with the experimentally measured value. This result along with the prediction of the correct lattice parameters, cohesive energy, and bond angles given in Tables 21.2, 21.5, and 21.6, respectively, confirms that conductivity in silicon is due to the creation of discrete ions, $\mathrm{Si}^{+}$and $e^{-}$, with the excitation of electrons from covalent bonds. The current carriers are free metal-type electrons that exist as planar membranes with current propagation along these structures shown in Figure 21.3. Since the conducting electrons are equivalent to those of metals, the resulting kinetic energy distribution over the population of electrons can be modeled using the statistics of electrons in metals, Fermi Dirac statistics given in the Fermi-Dirac section and the Physical Implications of Free Electrons in Metals section.

## REFERENCES

1. H. N. Waltenburg, J. T. Yates, "Surface chemistry of silicon," Chem. Rev., Vol. 95, (1995), pp. 1589-1673.
2. D. W. Palmer, www.semiconductors.co.uk, (2006), September.
3. D. R. Lide, CRC Handbook of Chemistry and Physics, 86th Edition, CRC Press, Taylor \& Francis, Boca Raton, (2005-6), p. 12-18.
4. D. R. Lide, CRC Handbook of Chemistry and Physics, 86th Edition, CRC Press, Taylor \& Francis, Boca Raton, (2005-6), p. 9-86.
5. B. Farid, R. W. Godby, "Cohesive energies of crystals," Physical Review B, Vol. 43 (17), (1991), pp. 14248-14250.
6. D. R. Lide, CRC Handbook of Chemistry and Physics, 86th Edition, CRC Press, Taylor \& Francis, Boca Raton, (2005-6), p. 12-82.

## Chapter 22

## BORON MOLECULAR FUNCTIONAL GROUPS AND MOLECULES

## GENERAL CONSIDERATIONS OF THE BORON MOLECULAR BOND

Boron molecules comprising an arbitrary number of atoms can be solved using similar principles and procedures as those used to solve organic molecules of arbitrary length and complexity. Boron molecules can be considered to be comprised of functional groups such as $B-B, B-C, B-H, B-O, B-N, B-X$ ( $X$ is a halogen atom), and the alkyl functional groups of organic molecules. The solutions of these functional groups or any others corresponding to the particular boron molecule can be conveniently obtained by using generalized forms of the force balance equation given in the Force Balance of the $\sigma$ MO of the Carbon Nitride Radical section for molecules comprised of boron and hydrogen only and the geometrical and energy equations given in the Derivation of the General Geometrical and Energy Equations of Organic Chemistry section for boron molecules further comprised of heteroatoms such as carbon. The appropriate functional groups with their geometrical parameters and energies can be added as a linear sum to give the solution of any molecule containing boron..

## BORANES $\left(B_{x} H_{y}\right)$

As in the case of carbon, silicon, and aluminum, the bonding in the boron atom involves four $s p^{3}$ hybridized orbitals formed from the $2 p$ and $2 s$ electrons of the outer shells except that only three HOs are filled. Bonds form between the B2sp ${ }^{3}$ HOs of two boron atoms and between a $B 2 s p^{3} \mathrm{HO}$ and a $H 1 s \mathrm{AO}$ to yield boranes. The geometrical parameters of each $B-H$ and $B-B$ functional group is solved from the force balance equation of the electrons of the corresponding $\sigma-\mathrm{MO}$ and the relationships between the prolate spheroidal axes. Then, the sum of the energies of the $H_{2}$-type ellipsoidal MOs is matched to that of the $B 2 s p^{3}$ shell as in the case of the corresponding carbon molecules. As in the case of ethane ( $C-C$ functional group given in the Ethane Molecule section) and silane ( $S i-S i$ functional group given in the Silanes section), the energy of the $B-B$ functional group is determined for the effect of the donation of $25 \%$ electron density from each participating $B 2 s p^{3} \mathrm{HO}$ to the $B-B$-bond MO.

The energy of boron 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 $(O H)$ section with the donation of $25 \%$ electron density from each participating $B 2 s p^{3} \mathrm{HO}$ to each $B-H$ and $B$ - $B$-bond MO. As in the case of acetylene given in the Acetylene Molecule section, the energies of the $B-H$ and $B-B$ functional groups are determined for the effect of the charge donation.

The $2 s p^{3}$ hybridized orbital arrangement is:

where the quantum numbers $\left(\ell, m_{\ell}\right)$ are below each electron. The total energy of the state is given by the sum over the four electrons. The sum $E_{T}\left(B, 2 s p^{3}\right)$ of experimental energies [1] of $B, B^{+}$, and $B^{2+}$ is:

$$
\begin{equation*}
E_{T}\left(B, 2 s p^{3}\right)=37.93064 \mathrm{eV}+25.1548 \mathrm{eV}+8.29802 \mathrm{eV}=71.38346 \mathrm{eV} \tag{22.2}
\end{equation*}
$$

By considering that the central field decreases by an integer for each successive electron of the shell, the radius $r_{2 s p^{3}}$ of the $B 2 s p^{3}$ shell may be calculated from the Coulombic energy using Eq. (15.13).

$$
\begin{equation*}
r_{2 s p^{3}}=\sum_{n=2}^{4} \frac{(Z-n) e^{2}}{8 \pi \varepsilon_{0}(e 71.38346 \mathrm{eV})}=\frac{6 e^{2}}{8 \pi \varepsilon_{0}(e 71.38346 \mathrm{eV})}=1.14361 a_{0} \tag{22.3}
\end{equation*}
$$

where $Z=5$ for boron. Using Eq. (15.14), the Coulombic energy $E_{\text {Coulomb }}\left(B, 2 s p^{3}\right)$ of the outer electron of the $B 2 s p^{3}$ shell is:

$$
\begin{equation*}
E_{\text {Coulomb }}\left(B, 2 s p^{3}\right)=\frac{-e^{2}}{8 \pi \varepsilon_{0} r_{2 s p^{3}}}=\frac{-e^{2}}{8 \pi \varepsilon_{0} 1.14361 a_{0}}=-11.89724 \mathrm{eV} \tag{22.4}
\end{equation*}
$$

During hybridization, one of the spin-paired $2 s$ electrons is promoted to the $B 2 s p^{3}$ shell as an unpaired electron. The energy for the promotion is the magnetic energy given by Eq. (15.15) at the initial radius of the $2 s$ electrons. From Eq. (10.62) with $Z=5$, the radius $r_{3}$ of $B 2 s$ shell is

$$
\begin{equation*}
r_{3}=1.07930 a_{0} \tag{22.5}
\end{equation*}
$$

Using Eqs. (15.15) and (22.5), the unpairing energy is:

$$
\begin{equation*}
E(\text { magnetic })=\frac{2 \pi \mu_{0} e^{2} \hbar^{2}}{m_{e}^{2}\left(r_{3}\right)^{3}}=\frac{8 \pi \mu_{0} \mu_{B}^{2}}{\left(1.07930 a_{0}\right)^{3}}=0.09100 \mathrm{eV} \tag{22.6}
\end{equation*}
$$

Using Eqs. (24.4) and (22.6), the energy $E\left(B, 2 s p^{3}\right)$ of the outer electron of the $B 2 s p^{3}$ shell is:

$$
\begin{equation*}
E\left(B, 2 s p^{3}\right)=\frac{-e^{2}}{8 \pi \varepsilon_{0} r_{2 s p^{3}}}+\frac{2 \pi \mu_{0} e^{2} \hbar^{2}}{m_{e}^{2}\left(r_{3}\right)^{3}}=-11.89724 \mathrm{eV}+0.09100 \mathrm{eV}=-11.80624 \mathrm{eV} \tag{22.7}
\end{equation*}
$$

Next, consider the formation of the $B-H$ and $B-B$-bond MOs of boranes wherein each boron atom has a $B 2 s p^{3}$ electron with an energy given by Eq. (22.7). The total energy of the state of each boron atom is given by the sum over the three electrons. The sum $E_{T}\left(B_{\text {borane }}, 2 s p^{3}\right)$ of energies of $B 2 s p^{3}$ (Eq. (22.7)), $B^{+}$, and $B^{2+}$ is:

$$
\begin{align*}
E_{T}\left(B_{\text {borane }}, 2 s p^{3}\right) & =-\left(37.93064 \mathrm{eV}+25.1548 \mathrm{eV}+E\left(B, 2 s p^{3}\right)\right)  \tag{22.8}\\
& =-(37.93064 \mathrm{eV}+25.1548 \mathrm{eV}+11.80624 \mathrm{eV})=-74.89168 \mathrm{eV}
\end{align*}
$$

where $E\left(B, 2 s p^{3}\right)$ is the sum of the energy of $B,-8.29802 \mathrm{eV}$, and the hybridization energy.
Each C-H-bond MO forms with the sharing of electrons between each B2sp ${ }^{3} \mathrm{HO}$ and each H1s AO. As in the case of $C-H$, the $H_{2}$-type ellipsoidal MO comprises $75 \%$ of the $B-H$-bond MO according to Eq. (13.429) and Eq. (13.59). Similarly to the case of $C-C$, the $B-B H_{2}$-type ellipsoidal MO comprises $50 \%$ contribution from the participating $B 2 s p^{3}$ HOs according to Eq. (14.152). The sharing of electrons between a $B 2 s p^{3} \mathrm{HO}$ and one or more $H 1$ s AOs to form $B-H$-bond MOs or between two $B 2 s p^{3}$ HOs to form a $B-B$-bond MO permits each participating orbital to decrease in size and energy. As shown below, the boron HOs have spin and orbital angular momentum terms in the force balance which determines the geometrical parameters of each $\sigma$ MO. The angular momentum term requires that each $\sigma$ MO be treated independently in terms of the charge donation. In order to further satisfy the potential, kinetic, and orbital energy relationships, each $B 2 s p^{3} \mathrm{HO}$ donates an excess of $25 \%$ of its electron density to the $B-H$ or $B-B$-bond MO to form an energy minimum. By considering this electron redistribution in the borane molecule as well as the fact that the central field decreases by an integer for each successive electron of the shell, the radius $r_{\text {borane2sp }}$ of the $B 2 s p^{3}$ shell may be calculated from the Coulombic energy using Eq. (15.18).

$$
\begin{equation*}
r_{\text {borane } 2 p^{3}}=\left(\sum_{n=2}^{4}(Z-n)-0.25\right) \frac{e^{2}}{8 \pi \varepsilon_{0}(e 74.89168 \mathrm{eV})}=\frac{5.75 e^{2}}{8 \pi \varepsilon_{0}(e 74.89168 \mathrm{eV})}=1.04462 a_{0} \tag{22.9}
\end{equation*}
$$

Using Eqs. (15.19) and (22.9), the Coulombic energy $E_{\text {Coulomb }}\left(B_{\text {borane }}, 2 s p^{3}\right)$ of the outer electron of the $B 2 s p^{3}$ shell is:

$$
\begin{equation*}
E_{\text {Coulomb }}\left(B_{\text {borane }}, 2 s p^{3}\right)=\frac{-e^{2}}{8 \pi \varepsilon_{0} r_{\text {borane2sp }}{ }^{3}}=\frac{-e^{2}}{8 \pi \varepsilon_{0} 1.04462 a_{0}}=-13.02464 \mathrm{eV} \tag{22.10}
\end{equation*}
$$

During hybridization, one of the spin-paired $2 s$ electrons are promoted to the $B 2 s p^{3}$ shell as an unpaired electron. The energy for the promotion is the magnetic energy given by Eq. (22.6). Using Eqs. (22.6) and (22.10), the energy $E\left(B_{\text {borane }}, 2 s p^{3}\right)$ of the outer electron of the $B 2 s p^{3}$ shell is:

$$
\begin{equation*}
E\left(B_{\text {borane }}, 2 s p^{3}\right)=\frac{-e^{2}}{8 \pi \varepsilon_{0} r_{\text {borane } 2 s p^{3}}}+\frac{2 \pi \mu_{0} e^{2} \hbar^{2}}{m_{e}^{2}\left(r_{3}\right)^{3}}=-13.02464 \mathrm{eV}+0.09100 \mathrm{eV}=-12.93364 \mathrm{eV} \tag{22.11}
\end{equation*}
$$

Thus, $E_{T}\left(B-H, 2 s p^{3}\right)$ and $E_{T}\left(B-B, 2 s p^{3}\right)$, the energy change of each $B 2 s p^{3}$ shell with the formation of the $B-H$ and $B-B$-bond MO, respectively, is given by the difference between Eq. (22.11) and Eq. (22.7):

$$
\begin{align*}
E_{T}\left(B-H, 2 s p^{3}\right) & =E_{T}\left(B-B, 2 s p^{3}\right)=E\left(B_{\text {borane }}, 2 s p^{3}\right)-E\left(B, 2 s p^{3}\right)  \tag{22.12}\\
& =-12.93364 \mathrm{eV}-(-11.80624 \mathrm{eV})=-1.12740 \mathrm{eV}
\end{align*}
$$

Next, consider the case that each $B 2 s p^{3} \mathrm{HO}$ donates an excess of $50 \%$ of its electron density to the $\sigma \mathrm{MO}$ to form an energy minimum. By considering this electron redistribution in the borane molecule as well as the fact that the central field decreases by an integer for each successive electron of the shell, the radius $r_{\text {borane } 2 s p^{3}}$ of the $B 2 s p^{3}$ shell may be calculated from the Coulombic energy using Eq. (15.18).

$$
\begin{equation*}
r_{\text {borane } 2 \mathrm{sp}^{3}}=\left(\sum_{n=2}^{4}(Z-n)-0.5\right) \frac{e^{2}}{8 \pi \varepsilon_{0}(e 74.89168 \mathrm{eV})}=\frac{5.5 e^{2}}{8 \pi \varepsilon_{0}(e 74.89168 \mathrm{eV})}=0.99920 a_{0} \tag{22.13}
\end{equation*}
$$

Using Eqs. (15.19) and (22.13), the Coulombic energy $E_{\text {Coulomb }}\left(B_{\text {borane }}, 2 s p^{3}\right)$ of the outer electron of the $B 2 s p^{3}$ shell is:

$$
\begin{equation*}
E_{\text {Coulomb }}\left(B_{\text {borane }}, 2 s p^{3}\right)=\frac{-e^{2}}{8 \pi \varepsilon_{0} r_{\text {borane2sp }}}=\frac{-e^{2}}{8 \pi \varepsilon_{0} 0.99920 a_{0}}=-13.61667 \mathrm{eV} \tag{22.14}
\end{equation*}
$$

During hybridization, one of the spin-paired $2 s$ electrons is promoted to the $B 2 s p^{3}$ shell as an unpaired electron. The energy for the promotion is the magnetic energy given by Eq. (22.6). Using Eqs. (22.6) and (22.14), the energy $E\left(B_{\text {borane }}, 2 s p^{3}\right)$ of the outer electron of the $B 2 s p^{3}$ shell is:

$$
\begin{equation*}
E\left(B_{\text {borane }}, 2 s p^{3}\right)=\frac{-e^{2}}{8 \pi \varepsilon_{0} r_{\text {borane } 2 s p^{3}}}+\frac{2 \pi \mu_{0} e^{2} \hbar^{2}}{m_{e}^{2}\left(r_{3}\right)^{3}}=-13.61667 \mathrm{eV}+0.09100 \mathrm{eV}=-13.52567 \mathrm{eV} \tag{22.15}
\end{equation*}
$$

Thus, $E_{T}\left(B\right.$-atom, $\left.2 s p^{3}\right)$, the energy change of each $B 2 s p^{3}$ shell with the formation of the $B$-atom-bond MO is given by the difference between Eq. (22.15) and Eq. (22.7):

$$
\begin{equation*}
E_{T}\left(B-\text { atom, } 2 s p^{3}\right)=E\left(B_{\text {borane }}, 2 s p^{3}\right)-E\left(B, 2 s p^{3}\right)=-13.52567 \mathrm{eV}-(-11.80624 \mathrm{eV})=-1.71943 \mathrm{eV} \tag{22.16}
\end{equation*}
$$

Consider next the radius of the HO due to the contribution of charge to more than one bond. The energy contribution due to the charge donation at each boron atom superimposes linearly. In general, the radius $r_{\text {mol } 2 s p^{3}}$ of the $B 2 s p^{3} \mathrm{HO}$ of a boron atom of a given borane molecule is calculated after Eq. (15.32) by considering $\sum E_{T_{m o l}}\left(M O, 2 s p^{3}\right)$, the total energy donation to all bonds with which it participates in bonding. The general equation for the radius is given by:

$$
\begin{equation*}
r_{\text {mol } 35 p^{3}}=\frac{-e^{2}}{8 \pi \varepsilon_{0}\left(E_{\text {Coulomb }}\left(B, 2 s p^{3}\right)+\sum E_{T_{\text {mol }}}\left(M O, 2 s p^{3}\right)\right)}=\frac{e^{2}}{8 \pi \varepsilon_{0}\left(e 11.89724 e V+\sum\left|E_{T_{\text {mol }}}\left(M O, 2 s p^{3}\right)\right|\right)} \tag{22.17}
\end{equation*}
$$

where $E_{\text {Coulomb }}\left(B, 2 s p^{3}\right)$ is given by Eq. (22.4). The Coulombic energy $E_{\text {Coulomb }}\left(B, 2 s p^{3}\right)$ of the outer electron of the $B 2 s p^{3}$ shell considering the charge donation to all participating bonds is given by Eq. (15.14) with Eq. (22.4). The energy $E\left(B, 2 s p^{3}\right)$ of the outer electron of the $B 2 s p^{3}$ shell is given by the sum of $E_{\text {Coulomb }}\left(B, 2 s p^{3}\right)$ and $E$ (magnetic) (Eq. (22.6)). The final values of the radius of the $B 2 s p^{3} \mathrm{HO}, r_{2 s p^{3}}, E_{\text {Coulomb }}\left(B, 2 s p^{3}\right)$, and $E\left(B_{\text {borane }} 2 s p^{3}\right)$ calculated using $\sum E_{T_{m o l}}\left(M O, 2 s p^{3}\right)$, the total energy donation to each bond with which an atom participates in bonding are given in Table 22.1. These hybridization parameters are used in Eqs. $(15.88-15.117)$ for the determination of bond angles given in Table 22.7.

Table 22.1. Atom hybridization designation (\# first column) and hybridization parameters of atoms for determination of bond angles with final values of $r_{2 s p^{3}}, E_{\text {Coulomb }}\left(B, 2 s p^{3}\right)$ (designated as $E_{\text {Coulomb }}$ ), and $E\left(B_{\text {borane }} 2 s p^{3}\right)$ (designated as $E$ ) calculated using the appropriate values of $\sum E_{T_{m o l}}\left(M O, 2 s p^{3}\right)$ (designated as $E_{T}$ ) for each corresponding terminal bond spanning each angle.

| $\#$ | $E_{T}$ | $E_{T}$ | $E_{T}$ | $E_{T}$ | $E_{T}$ | $r_{3 \text { sp }}{ }^{3}$ <br> Final | $E_{\text {Coulomb }}$ <br> $(\mathrm{eV})$ <br> Final | $E$ <br> $(\mathrm{eV})$ <br> Final |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 0 | 0 | 0 | 0 | 0 | 1.14361 | 11.89724 | 11.80624 |
| 2 | -1.71943 | 0 | 0 | 0 | 0 | 0.99920 | -13.61667 | -13.52567 |
| 3 | -1.18392 | -1.18392 | 0 | 0 | 0 | 0.95378 | -14.26508 | -14.17408 |
| 4 | -1.12740 | -1.12740 | -0.56370 | 0 | 0 | 0.92458 | -14.71574 | -14.62474 |

The MO semimajor axes of the $B-H$ and $B-B$ functional groups of boranes are determined from the force balance equation of the centrifugal, Coulombic, and magnetic forces as given in the Polyatomic Molecular Ions and Molecules section and the More Polyatomic Molecules and Hydrocarbons section. In each case, the distance from the origin of the $H_{2}$-type-ellipsoidal-MO to each focus $c^{\prime}$, the internuclear distance $2 c^{\prime}$, and the length of the semiminor axis of the prolate spheroidal
$H_{2}$-type MO $b=c$ are solved from the semimajor axis $a$. Then, the geometric and energy parameters of each MO are calculated using Eqs. (15.1-15.117).

The force balance of the centrifugal force equated to the Coulombic and magnetic forces is solved for the length of the semimajor axis. The Coulombic force on the pairing electron of the MO is:

$$
\begin{equation*}
\mathbf{F}_{\text {Coulomb }}=\frac{e^{2}}{8 \pi \varepsilon_{0} a b^{2}} D \mathbf{i}_{\xi} \tag{22.18}
\end{equation*}
$$

The spin-pairing force is:

$$
\begin{equation*}
\mathbf{F}_{\text {spin-pairing }}=\frac{\hbar^{2}}{2 m_{e} a^{2} b^{2}} D \mathbf{i}_{\xi} \tag{22.19}
\end{equation*}
$$

The diamagnetic force is:

$$
\begin{equation*}
\mathbf{F}_{\text {diamagneticMO1 }}=-\frac{n_{e} \hbar^{2}}{4 m_{e} a^{2} b^{2}} D \mathbf{i}_{\xi} \tag{22.20}
\end{equation*}
$$

where $n_{e}$ is the total number of electrons that interact with the binding $\sigma$-MO electron. The diamagnetic force $\mathbf{F}_{\text {diamagneticмо2 }}$ on the pairing electron of the $\sigma \mathrm{MO}$ is given by the sum of the contributions over the components of angular momentum:

$$
\begin{equation*}
\mathbf{F}_{\text {diamagneticMO } 2}=-\sum_{i, j} \frac{\left|L_{i}\right| \hbar}{Z_{j} 2 m_{e} a^{2} b^{2}} D \mathbf{i}_{\xi} \tag{22.21}
\end{equation*}
$$

where $|L|$ is the magnitude of the angular momentum of each atom at a focus that is the source of the diamagnetism at the $\sigma$ MO. The centrifugal force is:
$\mathbf{F}_{\text {centrifugalMO }}=-\frac{\hbar^{2}}{m_{e} a^{2} b^{2}} D \mathbf{i}_{\xi}$
The force balance equation for the $\sigma-\mathrm{MO}$ of the two-center $B-H$-bond MO is the given by centrifugal force given by Eq. (22.22) equated to the sum of the Coulombic (Eq. (22.18)), spin-pairing (Eq. (22.19)), and $\mathbf{F}_{\text {diamagneticмо2 }}$ (Eq. (22.21)) with $|L|=4 \sqrt{\frac{3}{4}} \hbar$ corresponding to the four $B 2 s p^{3}$ HOs:

$$
\begin{align*}
& \frac{\hbar^{2}}{m_{e} a^{2} b^{2}} D=\frac{e^{2}}{8 \pi \varepsilon_{0} a b^{2}} D+\frac{\hbar^{2}}{2 m_{e} a^{2} b^{2}} D-\frac{4 \sqrt{\frac{3}{4}}}{Z} \frac{\hbar^{2}}{2 m_{e} a^{2} b^{2}} D  \tag{22.23}\\
& a=\left(1+\frac{4 \sqrt{\frac{3}{4}}}{Z}\right) a_{0} \tag{22.24}
\end{align*}
$$

With $Z=5$, the semimajor axis of the $B-H$-bond MO is:

$$
\begin{equation*}
a=1.69282 a_{0} \tag{22.25}
\end{equation*}
$$

The force balance equation for each $\sigma$-MO of the $B-B$-bond MO with $n_{e}=2$ and $|L|=3 \sqrt{\frac{3}{4}} \hbar$ corresponding to three electrons of the $B 2 s p^{3}$ shell is:

$$
\begin{align*}
& \frac{\hbar^{2}}{m_{e} a^{2} b^{2}} D=\frac{e^{2}}{8 \pi \varepsilon_{0} a b^{2}} D+\frac{\hbar^{2}}{2 m_{e} a^{2} b^{2}} D-\left(1+\frac{3 \sqrt{\frac{3}{4}}}{Z}\right) \frac{\hbar^{2}}{2 m_{e} a^{2} b^{2}} D  \tag{22.26}\\
& a=\left(2+\frac{3 \sqrt{\frac{3}{4}}}{Z}\right) a_{0} \tag{22.27}
\end{align*}
$$

With $Z=5$, the semimajor axis of the $B-B$-bond MO is:

$$
\begin{equation*}
a=2.51962 a_{0} \tag{22.28}
\end{equation*}
$$

Using the semimajor axis, the geometric and energy parameters of the MO are calculated using Eqs. (15.1-15.127) in the same manner as the organic functional groups given in the Organic Molecular Functional Groups and Molecules section. For the $B-H$ functional group, $c_{1}$ is one and $C_{1}=0.75$ based on the MO orbital composition as in the case of the $C-H$-bond MO. In boranes, the energy of boron is less than the Coulombic energy between the electron and proton of $H$ given by Eq. (1.264). Thus, the energy matching condition is determined by the $c_{2}$ and $C_{2}$ parameters in Eqs. (15.51) and (15.61). Then, the hybridization factor for the $B-H$-bond MO given by the ratio of 11.89724 eV , the magnitude of $E_{\text {Coulomb }}\left(B_{\text {borane }}, 2 s p^{3}\right)$ (Eq. (22.4)), and 13.605804 eV , the magnitude of the Coulombic energy between the electron and proton of $H$ (Eq. (1.264)):

$$
\begin{equation*}
c_{2}=C_{2}\left(\text { borane } 2 \mathrm{sp}^{3} \mathrm{HO}\right)=\frac{11.89724 \mathrm{eV}}{13.605804 \mathrm{eV}}=0.87442 \tag{22.29}
\end{equation*}
$$

Since the energy of the MO is matched to that of the $B 2 s p^{3} \mathrm{HO}, E(A O / H O)$ in Eqs. (15.51) and (15.61) is $E\left(B, 2 s p^{3}\right)$ given by Eq. (22.7), and $E_{T}\left(\right.$ atom - atom, $\left.m s p^{3} . A O\right)$ is one half of -1.12740 eV corresponding to the independent single-bond charge contribution (Eq. (22.12)) of one center.

For the $B-B$ functional group, $c_{1}$ is one and $C_{1}=0.5$ based on the MO orbital composition as in the case of the $C-C-$ bond MO. The energy matching condition is determined by the $c_{2}$ and $C_{2}$ parameters in Eqs. (15.51) and (15.61), and the hybridization factor for the $B-B$-bond MO given is by Eq. (22.29). Since the energy of the MO is matched to that of the $B 2 s p^{3}$ HO, $E(A O / H O)$ in Eqs. (15.51) and (15.61) is $E\left(B, 2 s p^{3}\right)$ given by Eq. (22.7), and $E_{T}\left(\right.$ atom - atom, $\left.m s p^{3} . A O\right)$ is two times 1.12740 eV corresponding to the independent single-bond charge contributions (Eq. (22.12)) from each of the two B2sp ${ }^{3}$ HOs.

BRIDGING BONDS OF BORANES ( $B-H-B$ AND $B-B-B$ )
As in the case of the $A l 3 s p^{3}$ HOs given in the Organoaluminum Hydrides ( $A l-H-A l$ and $A l-C-A l$ ) section, the $B 2 s p^{3}$ 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 $B 2 s p^{3}$ HOs and a $H 1 s$ AO is $B-H-B$, and the designation for a three-center bond involving three $B 2 s p^{3} \mathrm{HOs}$ is $B-B-B$.

The parameters of the force balance equation for the $\sigma-\mathrm{MO}$ of the $B-H-B$-bond MO are $n_{e}=2$ and $|L|=0$ due to the cancellation of the angular momentum between borons:

$$
\begin{equation*}
\frac{\hbar^{2}}{m_{e} a^{2} b^{2}} D=\frac{e^{2}}{8 \pi \varepsilon_{0} a b^{2}} D+\frac{\hbar^{2}}{2 m_{e} a^{2} b^{2}} D-\frac{\hbar^{2}}{2 m_{e} a^{2} b^{2}} D \tag{22.30}
\end{equation*}
$$

From Eq. (22.30), the semimajor axis of the $B-H-B$-bond MO is

$$
\begin{equation*}
a=2 a_{0} \tag{22.31}
\end{equation*}
$$

The parameters in Eqs. (15.51) and (15.61) are the same as those of the $B-H-B$ functional group except that $E_{T}\left(\right.$ atom-atom, $\left.m s p^{3} . A O\right)$ is two times -1.12740 eV corresponding to the independent single-bond charge contributions (Eq. (22.12)) from each of the two $B 2 s p^{3}$ HOs.

The force balance equation and the semimajor axis for the $\sigma-\mathrm{MO}$ of the $B-B-B$-bond MO are the same as those of the $B-B$-bond MO given by Eqs. (22.30) and (22.31), respectively. The parameters in Eqs. (15.51) and (15.61) are the same as those of the $B-B$ functional group except that $E_{T}\left(\right.$ atom-atom, $\left.m s p^{3} . A O\right)$ is three times -1.12740 eV corresponding to the independent single-bond charge contributions (Eq. (22.12)) from each of the three B2sp ${ }^{3}$ HOs.

The $H_{2}$-type ellipsoidal MOs of the $B-H-B$ three-center bond intersect and form a continuous single surface. However, in the case of the $B-B-B$-bond MO the current of each $B-B$ MO forms a bisector current described in the Methane Molecule $\left(\mathrm{CH}_{4}\right)$ section that is continuous with the center $B 2 s p^{3}$-HO shell (Eqs. (15.36-15.44)). Based on symmetry, the polar angle $\phi$ at which the $\mathrm{B}-\mathrm{H}-\mathrm{B} \quad \mathrm{H}_{2}$-type ellipsoidal MOs intersect is given by the bisector of the external angle between the $B-H$ bonds:

$$
\begin{equation*}
\phi=\frac{360^{\circ}-\theta_{\angle B H B}}{2}=\frac{360^{\circ}-85.4^{\circ}}{2}=137.3^{\circ} \tag{22.32}
\end{equation*}
$$

where [2]

$$
\begin{equation*}
\theta_{\angle B H B}=85.4^{\circ} \tag{22.33}
\end{equation*}
$$

The polar radius $r_{i}$ at this angle is given by Eqs. (13.84-13.85).

$$
\begin{equation*}
r_{i}=\left(a-c^{\prime}\right) \frac{1+\frac{c^{\prime}}{a}}{1+\frac{c^{\prime}}{a} \cos \phi^{\prime}} \tag{22.34}
\end{equation*}
$$

Substitution of the parameters of Table 22.2 into Eq. (22.34) gives:

$$
\begin{equation*}
r_{i}=2.26561 a_{0}=1.19891 \times 10^{-10} \mathrm{~m} \tag{22.35}
\end{equation*}
$$

The polar angle $\phi$ at which the $B-B-B \quad H_{2}$-type ellipsoidal MOs intersect is given by the bisector of the external angle between the $B-B$ bonds:

$$
\begin{equation*}
\phi=\frac{360^{\circ}-\theta_{\angle B B B}}{2}=\frac{360^{\circ}-58.9^{\circ}}{2}=150.6^{\circ} \tag{22.36}
\end{equation*}
$$

where [3]

$$
\begin{equation*}
\theta_{\angle \text { BHB }}=58.9^{\circ} \tag{22.37}
\end{equation*}
$$

The polar radius $r_{i}$ at this angle is given by Eqs. (13.84-13.85):

$$
\begin{equation*}
r_{i}=\left(a-c^{\prime}\right) \frac{1+\frac{c^{\prime}}{a}}{1+\frac{c^{\prime}}{a} \cos \phi^{\prime}} \tag{22.38}
\end{equation*}
$$

Substitution of the parameters of Table 22.2 into Eq. (22.38) gives:

$$
\begin{equation*}
r_{i}=3.32895 a_{0}=1.76160 \times 10^{-10} \mathrm{~m} \tag{22.39}
\end{equation*}
$$

The symbols of the functional groups of boranes are given in Table 22.2. The geometrical (Eqs. (15.1-15.5) and (22.23$22.39)$ ), intercept (Eqs. (15.80-15.87) and (22.17)), and energy (Eq. (15.61), (22.4), (22.7), (22.12), and (22.29)) parameters of boranes are given in Tables 22.3, 22.4, and 22.5, respectively. In the case that the MO does not intercept the B HO due to the reduction of the radius from the donation of $B s p^{3} \mathrm{HO}$ charge to additional MOs, the energy of each MO is energy matched as a linear sum to the $B \mathrm{HO}$ by contacting it through the bisector current of the intersecting MOs as described in the Methane Molecule $\left(\mathrm{CH}_{4}\right)$ section. The total energy of each borane given in Table 22.6 was calculated as the sum over the integer multiple of each $E_{D}$ (Group) of Table 22.5 corresponding to functional-group composition of the molecule. $E_{\text {mag }}$ of Table 22.5 is given by Eqs. (15.15) and (22.3). The bond angle parameters of boranes determined using Eqs. (15.88-15.117) and (20.36) with $B 2 s p^{3}$ replacing $S i 3 s p^{3}$ are given in Table 22.7. The charge-density in diborane is shown in Figure 22.1.

Figure 22.1. Diborane. Color scale, opaque view of the charge-density of $B_{2} H_{6}$ comprising the linear combination of two sets of two $B-H$-bond MOs and two $B-H-B$-bond MOs. For each $B-H$ and $B-H-B$ bond, the ellipsoidal surface of the $H_{2}$-type ellipsoidal MO transitions to the $B 2 s p^{3} \mathrm{HO}$ shell with radius $0.89047 a_{0}$ (Eq. (22.17)). The inner B1s radius is $0.20670 a_{0}$ (Eq. (10.51)).


Table 22.2. The symbols of the functional groups of boranes.

| Functional Group | Group Symbol |
| :--- | :--- |
| $B H$ group | $B-H$ |
| $B H B$ (bridged $H$ ) | $B-H-B$ |
| $B B$ bond | $B-B$ |
| $B B B$ (bridged $B$ ) | $B-B-B$ |

Table 22.3. The geometrical bond parameters of boranes and experimental values.

| Parameter | $B-H$ <br> Group | $B-H-B$ <br> Group | $B-B$ <br> and <br> $B-B-B$ <br> Groups |
| :---: | :---: | :---: | :---: |
| $a\left(a_{0}\right)$ | 1.69282 | 2.00000 | 2.51962 |
| $c^{\prime}\left(a_{0}\right)$ | 1.13605 | 1.23483 | 1.69749 |
| Bond Length <br> $2 c^{\prime}(\AA)$ | 1.20235 | 1.30689 | 1.79654 |
| Exp. Bond <br> Length <br> $(\AA)$ | $1.19[4]$ <br> (diborane) | $1.32[4]$ <br> (diborane) | $1.798[3]$ <br> $\left(B_{13} H_{19}\right)$ |
| $b, c\left(a_{0}\right)$ | 1.25500 | 1.57327 | 1.86199 |
| $e$ | 0.67110 | 0.61742 | 0.67371 |

Table 22.4. The MO to HO intercept geometrical bond parameters of boranes. $H_{t}$ is a terminal or two-center $H . H_{b}$ is a bridge or three-center $H$. $B_{b}$ is a bridge or threecenter $B$. $E_{T}$ is $E_{T}\left(\right.$ atom - atom $\left.m s p^{3} . A O\right)$.

| Bond | Atom | $\begin{gathered} E_{T} \\ (\mathrm{eV}) \end{gathered}$ $\text { Bond } 1$ | E <br> (eV) <br> Bond 2 | Bond 3 $\begin{gathered} E_{T} \\ (\mathrm{eV}) \\ \text { Bond 3 } \end{gathered}$ | $\begin{gathered} E_{T} \\ (\mathrm{eV}) \end{gathered}$ <br> Bond 4 |  | $\begin{aligned} & r_{\text {mpualal }} \\ & \left(a_{0}\right) \end{aligned}$ | $\begin{aligned} & \hline r_{\text {frial }} \\ & \left(a_{0}\right) \end{aligned}$ | $\begin{gathered} E_{\text {Counamesem }}\left(B 2 s p^{3}\right) \\ (\mathrm{eV}) \\ \text { Final } \end{gathered}$ | $\begin{gathered} E\left(B 2 s p^{3}\right) \\ (\mathrm{eV}) \\ \text { Final } \end{gathered}$ | $\begin{aligned} & \hline \theta^{\prime} \\ & \left(^{\circ}\right) \end{aligned}$ | $\begin{aligned} & \hline \theta_{1} \\ & \left({ }^{\circ}\right) \end{aligned}$ | $\begin{aligned} & \theta_{2} \\ & \left(^{\circ}\right) \end{aligned}$ | $\begin{gathered} d_{1} \\ \left(a_{0}\right) \end{gathered}$ | $\begin{gathered} d_{2} \\ \left(a_{0}\right) \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $B-H_{i}\left(H_{12} B B-\right)$ | B | -0.56370 | -0.56370 | -1.12740 | 0 | -77.14647 | 1.14361 | 0.96140 | -14.15203 | -14.06103 | 92.75 | 87.25 | 49.92 | 1.08988 | 0.04618 |
| $B-H_{t}\left(H_{t 2} B H_{b 2}-\right)$ | $B$ | -0.56370 | -0.56370 | -1.12740 | -1.12740 | -78.27387 | 1.14361 | 0.89047 | -15.27943 | -15.18843 | 86.17 | 93.83 | 45.07 | 1.19558 | 0.05953 |
| $B-H_{t}\left(H_{t} H_{b 2} B B_{b}-\right)$ | $B$ | -0.56370 | -1.12740 | -1.12740 | -1.69110 | -79.40127 | 1.14361 | 0.82928 | -16.40683 | -16.31583 | 79.53 | 100.47 | 40.52 | 1.28676 | 0.15070 |
| $B-H_{t}\left(H_{t} H_{b} B B B_{b}-\right)$ | $B$ | -0.56370 | -1.12740 | -1.12740 | -1.69110 | -79.40127 | 1.14361 | 0.82928 | -16.40683 | -16.31583 | 79.53 | 100.47 | 40.52 | 1.28676 | 0.15070 |
| $B-H_{t}\left(H_{t} H_{b} B B_{b 2}-\right)$ | B | -0.56370 | -1.12740 | -1.69110 | -1.69110 | -79.96497 | 1.14361 | 0.80173 | -16.97053 | -16.87953 | 76.16 | 103.84 | 38.34 | 1.32780 | 0.19175 |
| $B-H_{b}\left(H_{t 2} B H_{b 2}-\right)$ | B | -1.12740 | -1.12740 | -0.56370 | -0.56370 | -78.27387 | 1.14361 | 0.89047 | -15.27943 | -15.18843 | 50.85 | 129.15 | 26.03 | 1.79706 | 0.56223 |
| $B-B\left(H_{12} B B-\right)$ | B | -1.12740 | -0.56370 | -0.56370 | 0 | -77.14647 | 1.14361 | 0.96140 | -14.15203 | -14.06103 | 50.20 | 129.80 | 23.37 | 2.31289 | 0.61540 |
| $B-B\left(H_{b 2} H_{t} B B-\right)$ | $B$ | -1.12740 | -1.12740 | -1.12740 | -0.56370 | -78.83757 | 1.14361 | 0.85878 | -15.84313 | -15.75213 | 26.62 | 153.38 | 11.93 | 2.46521 | 0.76773 |
| $B-B\left(H_{b 2} H_{t} B B-\right)$ | B | -1.12740 | -0.56370 | -1.69110 | -1.12740 | -79.40127 | 1.14361 | 0.82928 | -16.40683 | -16.31583 | 11.88 | 168.12 | 5.26 | 2.50901 | 0.81152 |
| $B-B_{b}\left(H_{b 2} H_{t} B B_{b}-\right)$ | $B$ | -1.69110 | -0.56370 | -1.12740 | -1.12740 | -79.40127 | 1.14361 | 0.82928 | -16.40683 | -16.31583 | 11.88 | 168.12 | 5.26 | 2.50901 | 0.81152 |
| $B-B_{b}\left(H_{b} H_{t} B B B_{b}-\right)$ | $B$ | -1.69110 | -0.56370 | -1.12740 | -1.12740 | -79.40127 | 1.14361 | 0.82928 | -16.40683 | -16.31583 | 11.88 | 168.12 | 5.26 | 2.50901 | 0.81152 |
| $B-B_{b}\left(H_{b} H_{t} B_{b} B B_{b}-\right)$ | B | -1.69110 | -1.69110 | -0.56370 | -1.12740 | -79.96497 | 1.14361 | 0.80173 | -16.97053 | -16.87953 |  |  |  |  |  |

Table 22.5. The energy parameters $(\mathrm{eV})$ of functional groups of boranes.

| Parameters | $\begin{aligned} & B-H \\ & \text { Group } \end{aligned}$ | $\begin{gathered} B-H-B \\ \text { Group } \\ \hline \end{gathered}$ | $\begin{gathered} B-B \\ \text { Group } \end{gathered}$ | $\begin{gathered} B-B-B \\ \text { Group } \\ \hline \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: |
| $n_{1}$ | 1 | 1 | 1 | 1 |
| $n_{2}$ | 0 | 0 | 0 | 0 |
| $n_{3}$ | 0 | 0 | 0 | 0 |
| $C_{1}$ | 0.75 | 0.75 | 0.5 | 0.5 |
| $C_{2}$ | 0.87442 | 0.87442 | 0.87442 | 0.87442 |
| $c_{1}$ | 1 | 1 | 1 | 1 |
| $c_{2}$ | 0.87442 | 0.87442 | 0.87442 | 0.87442 |
| $c_{3}$ | 0 | 0 | 0 | 0 |
| $c_{4}$ | 1 | 1 | 2 | 2 |
| $c_{5}$ | 1 | 1 | 0 | 0 |
| $C_{1 o}$ | 0.75 | 0.75 | 0.5 | 0.5 |
| $C_{2 o}$ | 0.87442 | 0.87442 | 0.87442 | 0.87442 |
| $V_{e}(\mathrm{eV})$ | -34.04561 | -27.77951 | -22.91867 | -22.91867 |
| $V_{p}(e \mathrm{~V})$ | 11.97638 | 11.01833 | 8.01527 | 8.01527 |
| $T(e V)$ | 10.05589 | 6.94488 | 4.54805 | 4.54805 |
| $V_{m}(\mathrm{eV})$ | -5.02794 | -3.47244 | -2.27402 | -2.27402 |
| $E\left({ }_{\text {AO/ }}\right.$ ( $)(\mathrm{eV})$ | -11.80624 | -11.80624 | -11.80624 | -11.80624 |
| $\Delta E_{\mathrm{H}_{2} \mathrm{MO}}(\mathrm{AO} / \mathrm{HO})(\mathrm{eV})$ | 0 | 0 | 0 | 0 |
| $E_{T}($ АО/ $/ \mathrm{H})(\mathrm{eV})$ | -11.80624 | -11.80624 | -11.80624 | -11.80624 |
| $E_{T}\left(\mathrm{H}_{2} \mathrm{MO}\right)(\mathrm{eV})$ | -28.84754 | -25.09498 | -24.43561 | -24.43561 |
| $E_{T}\left(\right.$ atom-atom, $\left.\mathrm{msp}^{3} . \mathrm{AO}\right)(\mathrm{eV})$ | -0.56370 | -2.25479 | -2.25479 | -3.38219 |
| $E_{T}(\mathrm{mo})(\mathrm{eV})$ | -29.41123 | -29.60457 | -26.69041 | -27.81781 |
| $\omega\left(10^{15} \mathrm{rad} / \mathrm{s}\right)$ | 15.2006 | 23.9931 | 6.83486 | 6.83486 |
| $E_{K}(\mathrm{eV})$ | 10.00529 | 15.79265 | 4.49882 | 4.49882 |
| $\bar{E}_{D}(\mathrm{eV})$ | -0.18405 | -0.23275 | -0.11200 | -0.11673 |
| $\bar{E}_{\text {Kvib }}(\mathrm{eV})$ | $\begin{gathered} 0.29346 \\ {[5]} \\ \hline \end{gathered}$ | $\begin{gathered} \hline 0.09844 \\ {[6]} \\ \hline \end{gathered}$ | $\begin{gathered} 0.13035 \\ {[5]} \\ \hline \end{gathered}$ | $\begin{gathered} 0.13035 \\ {[5]} \\ \hline \end{gathered}$ |
| $\bar{E}_{\text {osc }}(\mathrm{eV})$ | -0.03732 | -0.18353 | -0.04682 | -0.05156 |
| $E_{\text {mag }}(\mathrm{eV})$ | 0.07650 | 0.07650 | 0.07650 | 0.07650 |
| $E_{T}($ Group $)(\mathrm{eV})$ | -29.44855 | -29.78809 | -26.73723 | -27.86936 |
| $E_{\text {tritial }}\left(c_{+}\right.$AO/HO) $(\mathrm{eV})$ | -11.80624 | -11.80624 | -11.80624 | -11.80624 |
| $E_{\text {initial }}\left(\mathrm{c}_{5}\right.$ АО/ HO$)(\mathrm{eV})$ | -13.59844 | -13.59844 | 0 | 0 |
| $E_{D}($ Group $)(e V)$ | 4.04387 | 4.38341 | 3.12475 | 4.25687 |

Table 22.6. The total bond energies of boranes calculated using the functional group composition and the energies of Table 22.5 compared to the experimental values [7]. The structures are given in Refs. [8-9].

| Formula | Name | $\begin{aligned} & B-H \\ & \text { Group } \end{aligned}$ | $\begin{gathered} B-H-B \\ \text { Group } \end{gathered}$ | $\begin{gathered} B-B \\ \text { Group } \end{gathered}$ | $\begin{gathered} B-B-B \\ \text { Group } \end{gathered}$ | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| BB | Diboron | 0 | 0 | 1 | 0 | 3.12475 | 3.10405 | -0.00667 |
| $\mathrm{B}_{2} \mathrm{H}_{6}$ | Diborane | 4 | 2 | 0 | 0 | 24.94229 | 24.89030 | -0.00209 |
| $\mathrm{B}_{4} \mathrm{H}_{10}$ | Tetraborane(10) | 6 | 4 | 1 | 0 | 44.92160 | 45.33134 | 0.00904 |
| $\mathrm{B}_{5} \mathrm{H}_{9}$ | Pentaborane(9) | 5 | 4 | 2 | 1 | 48.25462 | 48.85411 | 0.01227 |
| $\mathrm{B}_{5} \mathrm{H}_{11}$ | Pentaborane(11) | 8 | 3 | 0 | 2 | 54.00546 | 53.06086 | -0.01780 |
| $\mathrm{B}_{6} \mathrm{H}_{10}$ | Hexaborane(10) | 6 | 4 | 2 | 2 | 56.55063 | 56.74739 | 0.00347 |
| $\mathrm{B}_{9} \mathrm{H}_{15}$ | Nonaborane(15) | 10 | 5 | 2 | 4 | 85.61380 | 84.95008 | -0.00781 |
| $\mathrm{B}_{10} \mathrm{H}_{14}$ | Decaborane(14) | 10 | 4 | 2 | 6 | 89.73467 | 89.69790 | -0.00041 |

Table 22.7. The bond angle parameters of boranes and experimental values. $H_{t}$ is a terminal or two-center $H$. $H_{b}$ is a bridge or three-center $H$. $E_{T}$ is $E_{T}$ (atom - atom $m s p^{3} . A O$ ).

| $\begin{gathered} \text { Atoms of } \\ \text { Angle } \end{gathered}$ | $\begin{array}{\|c\|} \hline 2 c^{\prime} \\ \text { Bond } 1\left(a_{0}\right) \end{array}$ | $\begin{array}{\|c\|} \hline 2 c^{\prime} \\ \text { Bond } 2\left(a_{0}\right) \end{array}$ | $\begin{gathered} 2 c^{\prime} \\ \text { Terminal } \\ \text { Atoms }\left(a_{0}\right) \end{gathered}$ | $\begin{aligned} & E_{\text {Chatabone }} \\ & \text { Atom } \end{aligned}$ | Atom 1 Hybridization Designation (Table) | $\begin{aligned} & \hline E_{\text {Calombic }} \\ & \text { Atom } 2 \end{aligned}$ | Atom 2 <br> $\begin{array}{c}\text { Hybridization } \\ \text { Designation } \\ \text { (Table) }\end{array}$ | $\begin{gathered} c_{2} \\ \text { Atom } 1 \end{gathered}$ | $\begin{gathered} c_{2} \\ \text { Atom 2 } \end{gathered}$ | $C_{1}$ | $C_{2}$ | ${ }^{1}$ | $c_{2}^{\prime}$ | $\begin{gathered} E_{V_{r}} \\ (\mathrm{eV}) \end{gathered}$ | $\begin{aligned} & \theta_{\theta_{0}} \\ & \left({ }^{\circ}\right) \end{aligned}$ | $\begin{gathered} \theta_{1} \\ \left({ }^{\circ}\right) \end{gathered}$ | $\begin{aligned} & \theta_{2} \\ & \left({ }^{\circ}\right) \end{aligned}$ | $\begin{gathered} \hline \text { Cal. } \theta \\ \left({ }^{\circ}\right) \end{gathered}$ | $\begin{gathered} \hline \text { Exp. } \theta \\ (\circ) \\ (\circ) \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\angle H_{1} B H_{1}$ | 2.27211 | 2.27211 | ${ }^{3.9623}$ | -13.61667 | $\stackrel{(22.1)}{2}$ | H | H | 0.99920 | 1 | 1 | 1 | 0.75 | 1.00080 | ${ }^{-1.71943}$ |  |  |  | 121.37 | $\begin{aligned} & 122[10] \\ & \text { (diborane) } \end{aligned}$ |
| $\angle H_{t} B H_{b}$ | 2.27211 | 2.46967 | 3.8210 | -14.71574 | $\begin{aligned} & (22.1) \\ & \hline \end{aligned}$ | H | H | 0.92458 | 1 | 1 | 1 | 0.75 | 1.08158 | -1.12740 |  |  |  | 107.30 | $\begin{aligned} & 108.9[2] \\ & \left(B_{4} H_{10}\right) \end{aligned}$ |
| $\angle H_{b} B H_{b}$ | 2.46967 | 2.46967 | 3.6606 | -14.26508 | $\begin{gathered} \hline 3 \\ (22.1) \end{gathered}$ | H | H | 0.95378 | 1 | 1 | 1 | 0.75 | 1.04846 | ${ }^{-1.12740}$ |  |  |  | 95.65 | $\stackrel{95.0[2]}{(B, H)}$ |
| $\angle B H_{b} B$ | 2.46967 | 2.46967 | 3.4358 | $\begin{array}{\|c\|} \hline-11.89724 \\ B_{s} \\ \hline \end{array}$ | $\begin{gathered} (22.1) \end{gathered}$ | $\begin{gathered} -11.89724 \\ B_{b} \\ \hline \end{gathered}$ | $\begin{gathered} 1 \\ (22.1) \end{gathered}$ | 1 | 1 | 1 | 1.14361 | 1 | 1 | 0 |  |  |  | 88.15 | $\begin{aligned} & 87.7[2] \\ & \left(B_{4} H_{10}\right) \end{aligned}$ |

## ALKYL BORANES ( $R_{x} B_{y} H_{z} ; R=$ alkyl $)$

The alkyl boranes may comprise at least a terminal methyl group $\left(\mathrm{CH}_{3}\right)$ and at least one $B$ bound by a carbon-boron single bond comprising a $C-B$ group, and may comprise methylene $\left(\mathrm{CH}_{2}\right)$, methylyne ( CH ), $\mathrm{C}-\mathrm{C}, \mathrm{B}-\mathrm{H}, \mathrm{B}-\mathrm{B}, \mathrm{B}-\mathrm{H}-\mathrm{B}$, and $B-B-B$ functional groups. 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 $\mathrm{C}-\mathrm{C}$ bonds within isopropyl $\left(\left(\mathrm{CH}_{3}\right)_{2} \mathrm{CH}\right)$ and t-butyl $\left(\left(\mathrm{CH}_{3}\right)_{3} \mathrm{C}\right)$ groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups. Additional groups include aromatics such as phenyl. These groups in alkyl boranes are equivalent to those in branched-chain alkanes and aromatics, and the $B-H, B-B, B-H-B$, and $B-B-B$ functional groups of alkyl boranes are equivalent to those in boranes.

For the $C-B$ functional group, hybridization of the $2 s$ and $2 p$ AOs of each $C$ and $B$ to form single $2 s p^{3}$ shells forms an energy minimum, and the sharing of electrons between the $C 2 s p^{3}$ and $B 2 s p^{3}$ HOs to form a MO permits each participating orbital to decrease in radius and energy. In alkyl boranes, the energy of boron is less than the Coulombic energy between the electron and proton of $H$ given by Eq. (1.264). Thus, $c_{1}$ in Eq. (15.61) is one, and the energy matching condition is determined by the $c_{2}$ and $C_{2}$ parameters. Then, the $C 2 s p^{3} \mathrm{HO}$ has an energy of $E\left(C, 2 s p^{3}\right)=-14.63489 \mathrm{eV}$ (Eq. (15.25)), and the B2sp ${ }^{3}$ HOs have an energy of $E\left(B, 2 s p^{3}\right)=-11.80624 \mathrm{eV}$ (Eq. (22.7)). To meet the equipotential condition of the union of the $C-B$ $H_{2}$-type-ellipsoidal-MO with these orbitals, the hybridization factors $C_{2}$ and $C_{2}$ of Eq. (15.61) for the $C-B$-bond MO given by Eq. (15.77) is:

$$
\begin{equation*}
c_{2}\left(C 2 s p^{3} \mathrm{HO} \text { to } \mathrm{B} 2 \mathrm{sp}{ }^{3} \mathrm{HO}\right)=C_{2}\left(C 2 s p^{3} \mathrm{HO} \text { to } \mathrm{B} 2 \mathrm{sp}{ }^{3} \mathrm{HO}\right)=\frac{E\left(B, 2 s p^{3}\right)}{E\left(C, 2 s p^{3}\right)}=\frac{-11.80624 \mathrm{eV}}{-14.63489 \mathrm{eV}}=0.80672 \tag{22.40}
\end{equation*}
$$

$E_{T}\left(\right.$ atom-atom, $\left.m s p^{3} . A O\right)$ of the $C-B$-bond MO is -1.44915 eV corresponding to the single-bond contributions of carbon and boron of -0.72457 eV given by Eq. (14.151). The energy of the $C-B$-bond MO is the sum of the component energies of the $H_{2}$-type ellipsoidal MO given in Eq. (15.51) with $E(A O / H O)=E\left(B, 2 s p^{3}\right)$ given by Eq. (22.7) and $\Delta E_{\mathrm{H}_{2} M O}(A O / H O)=E_{T}\left(\right.$ atom - atom, $\left.m s p^{3} . A O\right)$ in order to match the energies of the carbon and boron HOs.

Consider next the radius of the HO due to the contribution of charge to more than one bond. The energy contribution due to the charge donation at each boron atom and carbon atom superimposes linearly. In general, since the energy of the $B 2 s p^{3} \mathrm{HO}$ is matched to that of the $C 2 s p^{3} \mathrm{HO}$, the radius $r_{\text {mol } 2 s p^{3}}$ of the $B 2 s p^{3} \mathrm{HO}$ of a boron atom and the $C 2 s p^{3} \mathrm{HO}$ of a carbon atom of a given alkyl borane molecule is calculated after Eq. (15.32) by considering $\sum E_{T_{m o l}}\left(M O, 2 s p^{3}\right)$, the total energy donation to all bonds with which it participates in bonding. The Coulombic energy $E_{\text {Coulomb }}\left(\right.$ atom, $\left.2 s p^{3}\right)$ of the outer electron of the atom $2 s p^{3}$ shell considering the charge donation to all participating bonds is given by Eq. (15.14). The hybridization parameters used in Eqs. (15.88-15.117) for the determination of bond angles of alkyl boranes are given in Table 22.8.

Table 22.8. Atom hybridization designation (\# first column) and hybridization parameters of atoms for determination of bond angles with final values of $r_{2 s p^{3}}, E_{\text {Coulomb }}\left(\right.$ atom, $2 s p^{3}$ ) (designated as $E_{\text {Coulomb }}$ ), and $E_{\text {Coulomb }}\left(\right.$ atomalkylborane $2 s p^{3}$ ) (designated as $E)$ calculated using the appropriate values of $\sum E_{T_{m o l}}\left(M O, 2 s p^{3}\right)$ (designated as $E_{T}$ ) for each corresponding terminal bond spanning each angle.

| $\#$ | $E_{T}$ | $E_{T}$ | $E_{T}$ | $E_{T}$ | $E_{T}$ | $r_{3 s p^{3}}$ <br> $\left(a_{0}\right)$ <br> Final | $E_{\text {Coulomb }}$ <br> $(\mathrm{eV})$ <br> Final | $E$ <br> $(\mathrm{eV})$ <br> Final |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  |  |  |  |  |  |  |
| 1 | -0.36229 | -0.92918 | 0 | 0 | 0 | 0.84418 | -16.11722 | -15.92636 |

The symbols of the functional groups of alkyl boranes are given in Table 22.9. The geometrical (Eqs. (15.1-15.5) and (22.23-22.40)), intercept (Eqs. (15.32) and (15.80-15.87)), and energy (Eq. (15.61), (22.4), (22.7), (22.12), (22.29), and (22.40)) parameters of alkyl boranes are given in Tables 22.10, 22.11, and 22.12, respectively. In the case that the MO does not intercept the $B \mathrm{HO}$ due to the reduction of the radius from the donation of $B 2 s p^{3} \mathrm{HO}$ charge to additional MOs, the energy of each MO is energy matched as a linear sum to the $B \mathrm{HO}$ by contacting it through the bisector current of the intersecting MOs as described in the Methane Molecule $\left(\mathrm{CH}_{4}\right)$ section. The total energy of each alkyl borane given in Table 22.13 was calculated as the sum over the integer multiple of each $E_{D}($ Group $)$ of Table 22.12 corresponding to functional-group composition of the molecule. $E_{\text {mag }}$ of Table 22.13 is given by Eqs. (15.15) and (22.3) for $B-H$. The bond angle parameters of alkyl boranes determined using

Eqs. (15.88-15.117) are given in Table 22.14. The charge-densities of exemplary alkyl boranes, trimethylborane, tetramethyldiborane, and methyldecaborane comprising the concentric shells of atoms with the outer shell bridged by one or more $\mathrm{H}_{2}$-type ellipsoidal MOs or joined with one or more hydrogen MOs are shown in Figures 22.2A-B and 22.3A-B, respectively.

Figure 22.2. A. Trimethylborane. Color scale, translucent views of the charge-density of $\left(\mathrm{H}_{3} \mathrm{C}\right)_{3} B$ showing the orbitals of the $B$ and $C$ 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 atoms participating in each bond, and the hydrogen nuclei (red, not to scale). B. Tetramethyldiborane. Color scale, opaque view of the charge-density of $\left(\mathrm{CH}_{3}\right)_{2} \mathrm{BH}_{2} \mathrm{~B}\left(\mathrm{CH}_{3}\right)_{2}$ showing the orbitals of the $B$ and $C$ 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 atoms participating in each bond, and the hydrogen nuclei (red, not to scale).


Figure 22.3. A-B. Methyldecaborane. Color scale, translucent view of the charge-density of methyldecaborane showing the orbitals of the $B$ and $C$ 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 atoms participating in each bond, and the hydrogen nuclei (red, not to scale).


Table 22.9. The symbols of the functional groups of alkyl boranes.

| Functional Group | Group Symbol |
| :--- | :--- |
| $C-B$ bond | $C-B$ |
| $B H$ bond | $B-H$ |
| $B H B$ (bridged $H)$ | $B-H-B$ |
| $B B$ bond | $B-B$ |
| $B B B$ (bridged $B)$ | $B-B-B$ |
| $C C$ (aromatic bond) | $C=C$ |
| $C H$ (aromatic) | $C H$ (i) |
| $C H_{3}$ group | $C-H\left(\mathrm{CH}_{3}\right)$ |
| $C H_{2}$ group | $C-H\left(\mathrm{CH}_{2}\right)$ |
| $C H$ | $C-H$ (ii) |
| $C C$ bond (n- $C)$ | $C-C$ (a) |
| $C C$ bond (iso- $C)$ | $C-C$ (b) |
| $C C$ bond (tert- $C)$ | $C-C$ (c) |
| $C C$ (iso to iso- $C)$ | $C-C$ (d) |
| $C C$ ( $t$ to $t-C)$ | $C-C$ (e) |
| $C C$ ( $t$ to iso- $C)$ | $C-C$ (f) |

Table 22.10. The geometrical bond parameters of alkyl boranes and experimental values. The experimental alkyl distances from Ref. [10].

| Parameter | $\begin{aligned} & C-B \\ & \text { Group } \end{aligned}$ | $\begin{aligned} & B-H \\ & \text { Group } \end{aligned}$ | $\begin{gathered} B-H-B \\ \text { Group } \end{gathered}$ | $\begin{gathered} B-B \\ \text { and } \\ B-B-B \\ \text { Groups } \end{gathered}$ | $\begin{aligned} & C=\frac{3 t}{C} C \\ & \text { Group } \end{aligned}$ | $\begin{aligned} & \mathrm{CH} \text { (i) } \\ & \text { Group } \end{aligned}$ | $\begin{gathered} \mathrm{C}-\mathrm{H}\left(\mathrm{CH}_{3}\right) \\ \text { Group } \end{gathered}$ | $\begin{gathered} \mathrm{C}-\mathrm{H}\left(\mathrm{CH}_{2}\right) \\ \text { Group } \end{gathered}$ | $\begin{gathered} C-H \text { (ii) } \\ \text { Group } \end{gathered}$ | $\begin{gathered} C-C(\text { a) } \\ \text { Group } \end{gathered}$ | $\begin{gathered} C-C \text { (b) } \\ \text { Group } \end{gathered}$ | $\underset{\text { Group }}{C-C(\mathrm{c})}$ | $\begin{gathered} C-C(\mathrm{~d}) \\ \text { Group } \end{gathered}$ | $\begin{gathered} C-C(\mathrm{e}) \\ \text { Group } \end{gathered}$ | $\begin{gathered} C-C(f) \\ \text { Group } \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $a\left(a_{0}\right)$ | 1.78528 | 1.69282 | 2.00000 | 2.51962 | 1.47348 | 1.60061 | 1.64920 | 1.67122 | 1.67465 | 2.12499 | 2.12499 | 2.10725 | 2.12499 | 2.10725 | 2.10725 |
| $c^{\prime}\left(a_{0}\right)$ | 1.48762 | 1.13605 | 1.23483 | 1.69749 | 1.31468 | 1.03299 | 1.04856 | 1.05553 | 1.05661 | 1.45744 | 1.45744 | 1.45164 | 1.45744 | 1.45164 | 1.45164 |
| $\begin{aligned} & \text { Bond } \\ & \text { Length } \\ & c^{\prime}(A) \end{aligned}$ | 1.57443 | 1.20235 | 1.30689 | 1.79654 | 1.39140 | 1.09327 | 1.10974 | 1.11713 | 1.11827 | 1.54280 | 1.54280 | 1.53635 | 1.54280 | 1.53635 | 1.53635 |
| Exp. Bond Length (A) | $\begin{gathered} 1.578[10] \\ \text { (trimethylborane) } \\ 1.580[10] \\ (1,2- \\ \text { dimethyldiborane) } \end{gathered}$ | $\begin{gathered} 1.19[4] \\ \text { (diborane) } \end{gathered}$ | $\begin{gathered} 1.32[4] \\ \text { (diborane) } \end{gathered}$ | $\begin{aligned} & 1.798[3] \\ & \left(B_{13} H_{19}\right) \end{aligned}$ | $\begin{gathered} 1.399 \\ \text { (benzene) } \end{gathered}$ | $\begin{gathered} 1.101 \\ \text { (benzene) } \end{gathered}$ | 1.114 <br> $(C-H$ <br> (rimethylborane) <br> 1.107 <br> $(C-H$ propane $)$ <br> 1.117 <br> $(C-H$ butane $)$ | $\begin{gathered} 1.107 \\ (C-H \text { propane }) \\ 1.117 \\ (C-H \quad \text { butane }) \end{gathered}$ | $\begin{gathered} 1.122 \\ \text { (isobutane) } \end{gathered}$ | $\begin{gathered} 1.532 \\ \text { (propane) } \\ 1.531 \\ \text { (butane) } \end{gathered}$ | $\begin{gathered} 1.532 \\ \text { (propane) } \\ 1.531 \\ \text { (butane) } \end{gathered}$ | $\begin{gathered} 1.532 \\ \text { (propane) } \\ \text { 1.531 } \\ \text { (butane) } \end{gathered}$ | $\begin{gathered} 1.532 \\ \text { (propane) } \\ 1.531 \\ \text { (butane) } \end{gathered}$ | $\begin{gathered} 1.532 \\ \text { (propane) } \\ 1.531 \\ \text { (butane) } \end{gathered}$ | $\begin{gathered} 1.532 \\ \text { (propane) } \\ 1.531 \\ \text { (butane) } \end{gathered}$ |
| $b, c\left(a_{0}\right)$ | 0.98702 | 1.25500 | 1.57327 | 1.86199 | 0.66540 | 1.22265 | 1.27295 | 1.29569 | 1.29924 | 1.54616 | 1.54616 | 1.52750 | 1.54616 | 1.52750 | 1.52750 |
| $e$ | 0.83327 | 0.67110 | 0.61742 | 0.67371 | 0.89223 | 0.64537 | 0.63580 | 0.63159 | 0.63095 | 0.68600 | 0.68600 | 0.68888 | 0.68600 | 0.68888 | 0.68888 |



| － | $\begin{array}{\|c} \infty \\ c \\ 0 \\ 0 \\ 0 \end{array}$ | $\begin{aligned} & \text { d } \\ & \stackrel{8}{8} \\ & \hline 8 \end{aligned}$ | $\begin{array}{cc} 8 & 8 \\ \frac{8}{6} & \frac{8}{8} \\ \hline \end{array}$ | $\frac{6}{9}$ |  | $\begin{gathered} 9 \\ \frac{9}{6} \\ 0 \\ 8 \end{gathered}$ | $\begin{array}{\|c} \underset{\sim}{8} \\ \stackrel{c}{8} \end{array}$ | $\frac{r_{2}}{=} \frac{r_{1}^{\prime}}{x}$ | $\frac{12}{\frac{1}{5}}$ |  | $\begin{aligned} & \frac{5}{8} \\ & \frac{6}{6} \\ & \frac{\pi}{6} \\ & \hline \end{aligned}$ | $\frac{12}{\frac{1}{y}}$ |  |  |  |  |  |  |  |  | $\begin{array}{\|l\|l\|} \hline \frac{\mathrm{g}}{\mathrm{f}} \\ \stackrel{y}{2} \end{array}$ |  |  | 喿 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $=8$ | $\begin{aligned} & \text { 䜤 } \\ & \text { 荧 } \\ & \hline \end{aligned}$ | $\begin{aligned} & \text { 总 } \\ & \stackrel{y}{=} \end{aligned}$ |  | $\begin{aligned} & \stackrel{\rightharpoonup}{C} \\ & \stackrel{y}{c} \\ & \underset{\sim}{c} \end{aligned}$ | $\begin{array}{\|l} \stackrel{\circ}{\circ} \\ \stackrel{\rightharpoonup}{\circ} \\ \hline \end{array}$ | $\left\lvert\, \begin{gathered} \substack{2 \\ \underset{N}{n} \\ \underset{\sim}{n} \\ \hline} \end{gathered}\right.$ | $\begin{array}{\|c} \bar{y} \\ 0 \\ y \\ 0 \\ s \end{array}$ |  |  |  |  | $\begin{aligned} & \hat{3} \\ & \stackrel{3}{2} \\ & \hline \end{aligned}$ |  |  |  |  |  |  |  | $\begin{aligned} & \stackrel{9}{6} \\ & \underline{6} \\ & = \end{aligned}$ | $\begin{aligned} & \bar{\infty} \\ & \underset{ニ}{-} \end{aligned}$ | $\begin{aligned} & \stackrel{8}{3} \\ & \stackrel{\infty}{\omega} \end{aligned}$ |  | $\xrightarrow{\text { ⿳亠丷厂犬}}$ |
| $8$ $\circ 2$ | $\begin{aligned} & \stackrel{y}{s} \\ & \underset{\sim}{\underset{\sim}{2}} \\ & \underset{\sim}{\sim} \\ & \underset{\sim}{2} \end{aligned}$ |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  | $\begin{aligned} & 2 \\ & \substack{6 \\ 6 \\ \hline} \end{aligned}$ |  | \％ |
| $\begin{aligned} & 6= \\ & \frac{8}{2} \\ & \frac{2}{4} \\ & \frac{5}{6} \end{aligned}$ |  |  |  |  |  |  |  |  |  |  |  |  | $\begin{aligned} & \underset{8}{8} \\ & \underset{G}{c} \\ & \underset{\sim}{c} \end{aligned}$ |  | $\begin{aligned} & \text { 总 } \\ & \text { 空 } \\ & \stackrel{r}{\mathrm{r}} \end{aligned}$ |  |  | $\begin{aligned} & \stackrel{y}{g} \\ & \stackrel{y}{8} \\ & \underset{\sim}{\sigma} \end{aligned}$ |  |  |  |  |  | \％ |
| ${ }_{20}^{2}$ | $\begin{aligned} & \stackrel{m}{\vec{M}} \\ & \underset{\sim}{\leftrightarrows} \\ & \underset{\sim}{\prime} \end{aligned}$ |  |  |  | $$ |  | $\left.\begin{array}{\|c} \frac{m}{m} \\ \cdots \\ w \\ \cdots \\ \cdots \end{array} \right\rvert\,$ |  |  |  |  |  |  | $\begin{aligned} & 0 \\ & 0 \\ & 0 \\ & 0 \\ & 0 \\ & 0 \\ & 0 \end{aligned}$ | $\begin{aligned} & \text { g } \\ & \underset{寸}{寸} \\ & \underset{\sim}{g} \end{aligned}$ |  |  |  |  |  |  |  |  | cran |
| 5 | $\begin{aligned} & \stackrel{9}{ } \\ & \stackrel{\circ}{\circ} \\ & \stackrel{9}{6} \end{aligned}$ | $\begin{array}{\|l\|l} \text { 管 } \\ \infty \\ 8 \end{array}$ | $\begin{aligned} & \infty \\ & c_{1}^{\infty} \\ & \infty \\ & \infty \\ & \infty \end{aligned}$ |  | $\begin{array}{\|l} \text { 答 } \\ \text { 心 } \end{array}$ | $\begin{array}{\|c} \substack{9 \\ 0 \\ o \\ 0 \\ 0} \end{array}$ |  | $\begin{array}{ll} \infty & \infty \\ 0 & 0 \\ 0 & 7 \\ 0 & 8 \\ 0 & 0 \\ 0 \end{array}$ | $\begin{array}{\|l} \infty \\ \underset{y y}{2} \\ \infty \\ 0 \end{array}$ |  |  | $\begin{aligned} & \frac{2}{2} \\ & \substack{\infty \\ \vdots \\ \hline} \end{aligned}$ | $\left\lvert\,\right.$ | $\begin{gathered} \stackrel{y}{c} \\ \substack{c \\ 0} \end{gathered}$ | $\begin{aligned} & \frac{m}{2} \\ & \stackrel{y}{8} \\ & \stackrel{y}{5} \end{aligned}$ |  | $\begin{aligned} & 0 \\ & 0 \\ & 0 \\ & 0 \\ & 0 \end{aligned}$ | $\begin{aligned} & 8 \\ & \stackrel{8}{6} \\ & \stackrel{0}{8} \end{aligned}$ |  | $\begin{aligned} & \overline{5} \\ & \frac{5}{0} \\ & 8 \end{aligned}$ | $\begin{aligned} & \overline{\bar{\circ}} \\ & \substack{\infty \\ 0 \\ 0} \end{aligned}$ | $\begin{array}{\|c} \text { 花 } \\ 0 \\ 0 \\ 0 \end{array}$ |  | $\stackrel{\text { cid }}{\substack{\text { a } \\=\\ \hline}}$ |
| $3$ | $\begin{aligned} & \overline{\substack{c}} \\ & \stackrel{\text { m}}{\vdots} \end{aligned}$ | $\begin{aligned} & \overline{\bar{m}} \\ & \underset{寸}{\prime} \end{aligned}$ |  |  | $\begin{aligned} & \stackrel{\rightharpoonup}{c} \\ & \text { 等 } \end{aligned}$ | $\begin{aligned} & \stackrel{\rightharpoonup}{0} \\ & \underset{寸}{7} \end{aligned}$ | $\left\lvert\, \begin{gathered} \bar{\sim} \\ \underset{\sim}{\underset{\sim}{c}} \end{gathered}\right.$ | $\begin{aligned} & \stackrel{3}{3} \\ & \text { 等 } \\ & \hline \end{aligned}$ | $\begin{aligned} & \stackrel{\rightharpoonup}{9} \\ & \stackrel{?}{寸} \\ & \underset{\rightrightarrows}{2} \end{aligned}$ | $\begin{aligned} & \bar{c} \\ & \underset{寸}{\prime} \\ & \hline \end{aligned}$ |  | $\begin{aligned} & \bar{c} \\ & \text { 寽 } \\ & \underset{\rightrightarrows}{2} \end{aligned}$ | $\begin{aligned} & \stackrel{\rightharpoonup}{巳} \\ & \stackrel{y}{寸} \\ & \underset{\sim}{2} \end{aligned}$ | $\begin{aligned} & \stackrel{\rightharpoonup}{W_{寸}^{\prime}} \\ & \underset{\sim}{3} \end{aligned}$ | $\begin{aligned} & \stackrel{\rightharpoonup}{\circ} \\ & \underset{寸}{\rightrightarrows} \end{aligned}$ | $\begin{aligned} & \text { 票 } \\ & \text { 等 } \end{aligned}$ | $\begin{aligned} & \stackrel{\rightharpoonup}{\circ} \\ & \stackrel{\Im}{寸} \\ & \hline \end{aligned}$ |  |  | $\begin{aligned} & \bar{c} \\ & \stackrel{y}{寸} \\ & \underset{\sim}{2} \end{aligned}$ | $\begin{aligned} & \bar{o} \\ & \underset{寸}{\prime} \end{aligned}$ | $\begin{aligned} & \text { 姩 } \\ & \text { 等 } \end{aligned}$ |  | $\stackrel{\bar{c}}{\stackrel{\rightharpoonup}{4}}$ |
|  |  |  |  |  |  |  | $\begin{array}{\|c} 2 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{array}$ |  |  |  |  | － |  |  | $0$ | $\begin{aligned} & = \\ & 0 \\ & 0 \\ & 0 \end{aligned}$ | $\begin{aligned} & 9 \\ & 9 \\ & 9 \\ & 9 \end{aligned}$ | $\underset{\underset{y}{\underset{y}{c}}}{\underset{1}{2}}$ |  | － | － | $\bigcirc$ | $\circ \stackrel{\text { 월 }}{\underset{1}{7}}$ | $\stackrel{\stackrel{c}{c}}{\substack{\text { ¢ }}}$ |
| 要言 | $\begin{gathered} \stackrel{\rightharpoonup}{i} \\ \underset{i}{c} \end{gathered}$ |  | $\begin{aligned} & \text { 导 } \\ & \stackrel{y}{\mathrm{G}} \\ & \vdots \\ & \vdots \end{aligned}$ | $\begin{aligned} & \stackrel{\Xi}{=} \\ & \stackrel{C}{C} \\ & \vdots \end{aligned}$ | $$ |  | $\frac{\underset{y}{j}}{\substack{9 \\ 7}}$ |  | $\begin{gathered} \underset{f}{e} \\ \underset{i}{c} \\ \hdashline \end{gathered}$ |  |  | $\begin{aligned} & \stackrel{r}{\mathrm{~g}} \\ & \stackrel{N}{\mathrm{~N}} \\ & \stackrel{1}{2} \end{aligned}$ |  |  |  |  |  | $\begin{aligned} & \frac{e}{c} \\ & \frac{c}{c} \\ & \frac{1}{i} \end{aligned}$ |  |  |  | $\begin{aligned} & \stackrel{\rightharpoonup}{\mathrm{c}} \\ & \stackrel{\rightharpoonup}{\mathrm{~N}} \\ & \stackrel{\rightharpoonup}{\mathrm{~N}} \end{aligned}$ | $\begin{aligned} & \text { 导 } \\ & \text { 学 } \\ & \vdots \\ & \hline \end{aligned}$ | $\stackrel{8}{\text { 20，}}$ |
| －${ }^{\text {an }}$ |  |  |  | $\begin{aligned} & \underset{\underset{N}{\tilde{N}}}{\underset{\sim}{\top}} \end{aligned}$ | $$ |  | $\frac{\stackrel{i}{\underset{y}{N}}}{\underset{7}{7}}$ |  | $\begin{aligned} & 0 \\ & 0 \\ & 0 \\ & 0 \\ & 0 \\ & 0 \end{aligned}$ | $\begin{aligned} & \stackrel{\varrho}{\bar{c}} \\ & \underset{-1}{c} \end{aligned}$ |  |  | $\begin{aligned} & \stackrel{8}{\underset{\sim}{i}} \\ & \underset{\sim}{1} \end{aligned}$ | $\begin{aligned} & \stackrel{0}{4} \\ & \underset{y}{c} \\ & \hdashline \end{aligned}$ | $\begin{aligned} & \stackrel{\rightharpoonup}{\hat{3}} \\ & \text { B } \\ & \stackrel{8}{8} \end{aligned}$ |  |  | $\stackrel{i}{4}$ | $$ |  | $\begin{aligned} & \text { 学 } \\ & \stackrel{N}{N} \\ & \stackrel{N}{0} \end{aligned}$ |  | $\begin{array}{ll} 8 & 8 \\ 8 & 8 \\ 80 \\ 8 \\ 0 & 6 \\ \hline \end{array}$ | $\stackrel{\sim}{2}$ |
| - 孚高 |  | $\begin{aligned} & \text { E } \\ & \stackrel{e}{c} \\ & \stackrel{y}{c} \end{aligned}$ |  | $\begin{aligned} & \stackrel{\rightharpoonup}{c} \\ & \stackrel{y}{c} \\ & \stackrel{c}{c} \end{aligned}$ |  |  | $\underset{\underset{\sim}{i}}{\underset{\sim}{i}}$ |  | $\begin{aligned} & \stackrel{\ominus}{8} \\ & \stackrel{\rightharpoonup}{6} \end{aligned}$ | $\begin{aligned} & \stackrel{C}{\bar{O}} \\ & = \\ & \hline \end{aligned}$ |  | $\begin{aligned} & \text { 우 } \\ & \stackrel{y}{6} \\ & \stackrel{O}{0} \end{aligned}$ | $\begin{aligned} & \text { 肙 } \\ & \underset{\sim}{\square} \end{aligned}$ | $\begin{aligned} & \text { 导 } \\ & \hdashline \\ & \hdashline \end{aligned}$ | $\begin{aligned} & \text { 寻 } \\ & \underset{i}{i} \\ & \hdashline \end{aligned}$ |  | $\underset{\sim}{\text { 导 }}$ |  | $\begin{array}{ll} \frac{0}{2} \\ \frac{9}{6} & \frac{3}{6} \\ \hdashline \end{array}$ |  |  | $\begin{aligned} & \text { 学 } \\ & \text { 合 } \\ & \vdots \end{aligned}$ |  | ¢ |
| 免 | 20 | $\approx$ | $\infty \sim$ | $\infty$ | 0 | $\sim$ | $\approx$ | $\sim \approx$ | 20 | $\approx$ | $\infty 8$ | $\infty$ | $\sim$ | $\pm$ | $\Rightarrow$ | $\therefore \infty$ | $\cdots$ | $\approx$ | $\leftrightarrow \sim$ | $\sim$ | $\approx$ | $\infty$ | se $\sim$ | $s$ |
| 号 |  |  |  | $\begin{aligned} & T \\ & T_{3} \\ & E \\ & E \\ & \approx \\ & \approx \end{aligned}$ |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  | $=$ <br>  <br>  <br>  |  |  |  | － |

Table 22.11 cont' d. The MO to HO intercept geometrical bond parameters of alkyl boranes. $H_{t}$ is a terminal or two-center $H$. $H_{b}$ is a bridge or three-center $H$. $B_{b}$ is a bridge or three-center $B . E_{T}$ is $E_{T}$ (atom - atom $m s p^{3} . A O$ )

| Bond | Atom | $\begin{gathered} E_{y} \\ (\mathrm{eV}) \\ \text { Bond } 1 \end{gathered}$ | $\begin{gathered} k_{y} \\ (\mathrm{eV}) \\ \text { Bond } 2 \end{gathered}$ | $\begin{gathered} F_{r} \\ (\mathrm{eV}) \\ \text { Bond } 3 \end{gathered}$ |  | Final Total <br> Energy <br> $B 2 s p^{\prime}$ <br> $(\mathrm{eV})$ | $\begin{aligned} & r_{\text {ininal }} \\ & \left(a_{\mathrm{o}}\right) \end{aligned}$ | $\begin{aligned} & r_{\text {finat }} \\ & \left(a_{0}\right) \end{aligned}$ | $\begin{array}{\|c\|} f_{\text {ciant }}\left(B 2 s p^{\prime}\right) \\ (\mathrm{eV}) \\ \text { Final } \end{array}$ | $\begin{gathered} C\left(B 2 s p^{1}\right) \\ (\mathrm{eV}) \\ \text { Final } \\ \hline \end{gathered}$ | $\begin{aligned} & \theta^{\prime} \\ & \left({ }^{\circ}\right) \end{aligned}$ | $\begin{gathered} \theta_{1} \\ \left({ }^{\circ}\right) \end{gathered}$ | $\begin{aligned} & \theta_{2} \\ & \left({ }^{\circ}\right) \end{aligned}$ | $\begin{gathered} d_{1} \\ \left(a_{0}\right) \end{gathered}$ | $\begin{gathered} d_{2} \\ \left(a_{0}\right) \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $C-B\left(R_{2} B B\right)$ | B | -0.72457 | -0.72457 | $-1.12740$ | 0 |  | 1.14361 | 0.78184 | -17.40230 | -17.31130 | 111.25 | 68.75 | 47.58 | 1.20422 | 0.28340 |
| $C-B\left(R B B H_{n 2}\right)$ | B | -1.12740 | -0.72457 | -1.12740 | -1.12740 |  | 1.14361 | 0.71865 | -18.93252 | -18.84152 | 106.79 | 73.21 | 44.19 | 1.28006 | 0.20756 |
| $C-B\left(H_{s} B_{5} R B B\right)$ | $B$ | -0.72457 | -1.12740 | $-1.12740$ | $-1.69110$ |  | 1.14361 | 0.69787 | -19.49622 | -19.40522 | 105.17 | 74.83 | 43.03 | 1.30499 | 0.18263 |
| $C-B\left(H_{3} R B H_{b 2}\right)$ | B | -0.72457 | -1.69110 | -1.12740 | -1.12740 |  | 1.14361 | 0.69787 | -19.49622 | -19.40522 | 105.17 | 74.83 | 43.03 | 1.30499 | 0.18263 |
| $C-B\left(H_{b} R B B_{b 2}\right)$ | B | -0.72457 | -1.12740 | $-1,69110$ | -1.69110 |  | 1.14361 | 0.67826 | -20.05991 | -19.96891 | 103.57 | 76.43 | 41.91 | 1.32853 | 0.15909 |
| $\mathrm{C}-\mathrm{H}\left(\mathrm{BCH}_{3}\right)$ | 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 |
| $\mathrm{C}-\mathrm{H}\left(\mathrm{BCH}_{2}-\right)$ | C | -0.72457 | -0.92918 | 0 | 0 | -153.26945 | 0.91771 | 0.82562 | -16.47951 | -16.28865 | 69.93 | 110.07 | 36.76 | 1.33883 | 0.28330 |
| $\mathrm{C}-\mathrm{H}(\mathrm{BCH}-)$ | $c$ | -0.72457 | -0.92918 | -0.92918 | 0 | -154.19863 | 0.91771 | 0.78155 | -17.40869 | -17.21783 | 62.67 | 117.33 | 32.30 | 1.41549 | 0.35888 |
| $C-B\left(-B-C H_{3}\right)$ | C | -0.72457 | 0 | 0 | 0 | -152.34026 | 0.91771 | 0.87495 | -15.55033 | -15.35946 | 116.85 | 63.15 | 52.27 | 1.09248 | 0.39514 |
| $C-B\left(-B-C_{2} H_{2} R\right)$ | $C_{a}$ | -0.72457 | -0.92918 | 0 | 0 | -153.26945 | 0.91771 | 0.82562 | -16.47951 | -16.28864 | 114.01 | 65.99 | 49.83 | 1.15168 | 0.33594 |
| $\mathrm{C}-\mathrm{H}\left(\mathrm{CH}_{3}\right)$ | 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 |
| $\mathrm{C}-\mathrm{H}\left(\mathrm{CH}_{2}\right)$ | 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 |
| $\mathrm{C}-\mathrm{H}(\mathrm{CH})$ | $c$ | -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 |
| $\mathrm{H}_{3} \mathrm{C}_{6} \mathrm{C}_{0} \mathrm{H}_{2} \mathrm{CH}_{2}-(\mathrm{C}-\mathrm{C}(\mathrm{a})$ ) | $C_{a}$ | -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 |
| $\mathrm{H}_{3} \mathrm{C}_{2} \mathrm{C}_{6} \mathrm{H}_{2} \mathrm{CH}_{2}-(\mathrm{C}-\mathrm{C}(\mathrm{C}$ (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 |
| $\begin{aligned} & \mathrm{R}-\mathrm{H}_{2} \mathrm{C}_{\mathrm{C}} \mathrm{C}_{\mathrm{s}}\left(\mathrm{H}_{2} \mathrm{C}_{\mathrm{c}}-\mathrm{R}^{\prime}\right) \mathrm{HCH}_{2}- \\ & (\mathrm{C}-\mathrm{C}(\mathrm{~b})) \end{aligned}$ | $C_{b}$ | -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 |
| $\begin{aligned} & R-H_{2} C_{6}\left(R^{\prime}-H_{2} C_{t}\right) C_{b}\left(R^{*}-H_{2} C_{t}\right) \mathrm{CH}_{2}- \\ & (\mathrm{C}-\mathrm{C}(\mathrm{c})) \end{aligned}$ | $C_{b}$ | -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 |
| $\begin{aligned} & \text { isoC } \mathrm{C}_{2}\left(\mathrm{H}_{2} \mathrm{C}_{2}-\mathrm{R}^{\prime}\right) \mathrm{HCH}_{2}- \\ & \text { (C-C (d) } \end{aligned}$ | $c_{B}$ | -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 |
| $\begin{aligned} & \text { terl }_{6}\left(R^{\prime}-\mathrm{H}_{2} \mathrm{C}_{j}\right) \mathrm{C}_{6}\left(\mathrm{R}^{*}-\mathrm{H}_{2} \mathrm{C}_{6}\right) \mathrm{CH}_{2}- \\ & (\mathrm{CC}-\mathrm{C}(\mathrm{e})) \end{aligned}$ | $C_{b}$ | -0.72457 | -0.72457 | -0.72457 | -0.72457 | -154.51399 | 0.91771 | 0.76765 | -17.72417 | -17.73779 | 50.04 | 129.96 | 22.66 | 1.94462 | 0.49298 |
| $\begin{aligned} & \mathrm{HerlC}_{2} \mathrm{C}_{2}\left(\mathrm{H}_{2} \mathrm{C}_{-}-\mathrm{R}^{\prime}\right) \mathrm{HCH}_{2}- \\ & (\mathrm{C}-\mathrm{C}(\mathrm{f})) \end{aligned}$ | $C_{b}$ | -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 |
| $\begin{aligned} & i s \mathrm{soC}_{n}\left(\mathrm{R}^{\prime}-\mathrm{H}_{2} \mathrm{C}_{\mathrm{j}}\right) \mathrm{C}_{\mathrm{h}}\left(\mathrm{R}^{\prime \prime}-\mathrm{H}_{2} \mathrm{C}_{\mathrm{t}}\right) \mathrm{CH}_{2}- \\ & (\mathrm{C}-\mathrm{C}(\mathrm{f})) \end{aligned}$ | $c b$ | -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 22．12．The energy parameters $(\mathrm{eV})$ of functional groups of alkyl boranes．

|  |  | － | $0 \%$ | － |  | $\stackrel{\mathrm{S}}{2}$ | － | － | $\cdots$ | － |  |  | $\left\|\begin{array}{c} 8 \\ 0 \\ 0 \\ 6 \\ 0 \end{array}\right\|$ |  | $\begin{aligned} & 0 \\ & \stackrel{0}{0} \\ & \underset{n}{n} \\ & \end{aligned}$ |  | $\begin{aligned} & \stackrel{0}{1} \\ & \stackrel{y}{2} \\ & \stackrel{1}{6} \\ & \end{aligned}$ | $\begin{aligned} & \frac{n}{2} \\ & \frac{0}{6} \\ & \frac{1}{9} \end{aligned}$ | $\begin{gathered} \frac{n}{2} \\ \frac{2}{7} \end{gathered}$ |  |  |  | － | $\stackrel{N}{\underset{\sim}{0}} \stackrel{\text { N }}{=}$ | $\left\|\begin{array}{c} 0.0 \\ 0.0 \\ 0 \\ 0 \\ \hline 0 \end{array}\right\|$ |  |  | Fol |  | $\stackrel{+}{\sim}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | － | － | ＇ | － |  | $\frac{\vec{A}}{\mathrm{~A}}$ | － | － | in | － | 9 | $\frac{\mathrm{N}}{\mathrm{~N}}$ | $\left\|\begin{array}{c} 8 \\ 0.0 \\ 0.0 \\ 0 \\ 0 \end{array}\right\|$ | $\begin{gathered} 0 \\ 0 \\ \tilde{n} \\ \\ \underset{i}{2} \end{gathered}$ | $\begin{aligned} & 0 \\ & 0 \\ & 0 \\ & \\ & \end{aligned}$ | － |  | 令 |  | $\begin{aligned} & 20 \\ & 0.0 \end{aligned}$ |  | त్ర్రి\| | $\begin{gathered} \frac{\rightharpoonup}{0} \\ \hline \mathbf{C} \\ \hline \end{gathered}$ | $\stackrel{\stackrel{N}{त}}{\stackrel{1}{0}} \stackrel{\text { m }}{=}$ |  | $\stackrel{+}{8}$ |  | Coc |  | － |
| \| | － | － | $\mathrm{m}_{8}$ | － |  | $\stackrel{\text { E }}{\stackrel{1}{2}}$ | － | － | $\cdots$ | － | $\begin{gathered} \substack{1 \\ \infty \\ \dot{d} \\ \hline} \end{gathered}$ | $\begin{aligned} & \text { N} \\ & \text { N } \\ & \text { NQ } \end{aligned}$ | $\left\lvert\, \begin{array}{\|c} \substack{0 \\ A \\ \\ \hline} \end{array}\right.$ | $\begin{gathered} \tilde{n} \\ \infty \\ \infty \\ n \\ \hline \end{gathered}$ |  | － | $\begin{array}{\|c} \hat{e} \\ \stackrel{\rightharpoonup}{2} \\ \\ \end{array}$ | 会 |  | $\begin{aligned} & \stackrel{\alpha}{2} \\ & \stackrel{\rightharpoonup}{2} \\ & \stackrel{\rightharpoonup}{2} \end{aligned}$ |  |  | $\stackrel{3}{6}$ | $\stackrel{\stackrel{N}{त}}{\underset{\sim}{3}} \stackrel{\text { m }}{=}$ | $\begin{aligned} & \stackrel{\circ}{n} \\ & \stackrel{3}{6} \\ & 0 \end{aligned}$ | ${ }_{4}$ |  | Cob |  | 7 |
| $\left\|\begin{array}{cc} 0 & \\ 0 & 2 \\ 0 & \frac{1}{2} \\ 0 & \text { b } \\ 0 \end{array}\right\|$ |  | － | \％ | － |  | $\frac{\vec{E}}{\frac{E}{O}}$ | － | － | $\cdots$ | － | O | $\frac{N}{N}$ |  | $\left(\begin{array}{c} 0 \\ 0 \\ 0 \\ \sim \\ ? \\ ? \end{array}\right.$ | $\begin{aligned} & \stackrel{0}{0} \\ & \stackrel{\rightharpoonup}{n} \\ & \stackrel{n}{6} \end{aligned}$ | － | $\left\lvert\, \begin{gathered} \stackrel{0}{6} \\ \stackrel{y}{2} \\ \stackrel{3}{3} \end{gathered}\right.$ | ． | $\begin{aligned} & \frac{n}{\frac{n}{9}} \\ & \vdots \end{aligned}$ | $\begin{aligned} & \underset{\sim}{\tilde{2}} \\ & \stackrel{\rightharpoonup}{\circ} \\ & \stackrel{\rightharpoonup}{d} \end{aligned}$ |  |  |  |  |  |  | 2 |  |  | co |
|  |  | － 0 | \％ | － | $-2$ | $\stackrel{\text { E }}{\text { E }}$ | － | － | $\cdots$ | － | $\stackrel{\sim}{\alpha}$ | $\begin{aligned} & \text { N} \\ & \text { Nু } \\ & \underset{\sim}{2} \end{aligned}$ | $\left\|\right\|$ | $\begin{gathered} \substack{N \\ \infty \\ \infty \\ 0} \\ 0 \end{gathered}$ | $\begin{aligned} & \stackrel{\rightharpoonup}{\hat{C}} \\ & \stackrel{\rightharpoonup}{n} \\ & \stackrel{n}{n} \end{aligned}$ | － | $\begin{array}{\|c} \hat{e} \\ \stackrel{\rightharpoonup}{2} \\ \stackrel{y}{n} \\ \end{array}$ | 令 |  | $\begin{gathered} \kappa \\ \underset{\alpha}{\alpha} \end{gathered}$ |  |  | $\overline{6}$ | $\stackrel{\infty}{5} \pm$ |  |  |  |  |  | ¢ |
| a | － | － 0 | ？ | － | $-\frac{2}{\text { ® }}$ | $\stackrel{\text { E }}{\text { E }}$ | － | － | in | － | $\stackrel{1}{6}$ | $\begin{aligned} & \text { N} \\ & \text { Nু } \\ & \text { Non } \end{aligned}$ |  | $\mathfrak{c}$ |  | － | $\begin{aligned} & 20 \\ & \stackrel{y}{0} \\ & \stackrel{n}{n} \\ & \end{aligned}$ | 会 |  | $\hat{\widehat{q}}$ |  |  | $\begin{aligned} & \overline{\hat{6}} \\ & \hline \mathbf{C} \\ & \hline \end{aligned}$ | $\frac{\mathrm{N}}{\stackrel{1}{3}} \underset{=}{3}$ |  |  |  | Cot |  | － |
| $\left\|\begin{array}{ll} E & \\ 0 & 2 \\ 0 & \frac{訁}{0} \\ 0 & 0 \end{array}\right\|$ | － | － | 会 | － | $-$ | E | － | － | in | － |  |  |  |  |  | － | $\left\lvert\, \begin{aligned} & \stackrel{\rightharpoonup}{2} \\ & \stackrel{\rightharpoonup}{6} \\ & \underset{\substack{2}}{ } \end{aligned}\right.$ |  | － | $\begin{gathered} n 6 \\ 0 \\ 0 \end{gathered}$ | $\underset{\sim}{\underset{\sim}{*}}$ | $\begin{aligned} & \frac{9}{2} \\ & \stackrel{\rightharpoonup}{2} \end{aligned}$ | － |  | $$ | $\stackrel{\text { }}{\stackrel{\circ}{\circ}}$ |  |  | $\begin{aligned} & \text { 志 } \\ & \hline \end{aligned}$ | － |
| ※゙枵 |  | $\sim$ | 会 | － | $-\frac{\square}{\text { E }}$ | $\frac{\mathrm{E}}{\mathrm{~A}}$ | － | $\sim$ | N－0 | － | $\begin{gathered} \underset{8}{2} \\ \frac{1}{2} \\ \hline \end{gathered}$ |  | $\left\|\begin{array}{c} n \\ \stackrel{n}{0} \\ \dot{\rightharpoonup} \\ \dot{n} \end{array}\right\|$ | $\begin{aligned} & \hat{n} \\ & \\ & \\ & \end{aligned}$ | $\begin{aligned} & \hat{y} \\ & \stackrel{y}{n} \\ & \\ & \end{aligned}$ | － | $\begin{array}{\|c} \hat{y} \\ \stackrel{\rightharpoonup}{n} \\ \stackrel{n}{n} \\ \end{array}$ | \％ | － | $\begin{gathered} \text { 聴 } \\ \hline \end{gathered}$ | ત | $\begin{aligned} & \bar{x} \\ & \underset{\alpha}{2} \\ & \stackrel{n}{2} \end{aligned}$ | ， |  |  | ${ }^{\circ}$ | 唴 |  |  | $\stackrel{\circ}{\circ}$ |
|  |  | $\cdots \mathrm{N}$ | － |  | $-2$ |  | － | $\infty$ | 会 | － | $\left\lvert\, \begin{gathered} \infty \\ \stackrel{0}{\lambda} \\ \\ \stackrel{\rightharpoonup}{2} \\ \cdots \end{gathered}\right.$ | $\begin{array}{\|l\|l} \infty \\ \underset{\sim}{\infty} \\ \infty \\ \infty \end{array}$ | $\left\|\begin{array}{c} \frac{7}{2} \\ \frac{2}{2} \\ \stackrel{n}{2} \end{array}\right\|$ |  | $\begin{aligned} & \hat{e} \\ & \stackrel{0}{6} \\ & \\ & \end{aligned}$ | － | $\begin{array}{\|c} \hat{e} \\ \stackrel{\rightharpoonup}{n} \\ \stackrel{n}{n} \\ \end{array}$ | ¢ | － | \％ | $\underset{~+~}{~}$ | $\begin{aligned} & 0 \\ & 0 \\ & 0 \\ & \vdots \\ & \stackrel{0}{0} \end{aligned}$ | － |  | $\begin{array}{\|c} \text { n } \\ \text { a } \\ \text { on } \end{array}$ | ${ }^{\circ}$ | （ |  | $\stackrel{\text { J }}{\substack{\text { ¢ }}}$ | $\xrightarrow{\circ}$ |
| $\begin{aligned} & \text { E } \\ & \text { y } \overline{0} \\ & 0 \end{aligned}$ | － | － 0 | － | － | $-$ | $\frac{1}{2}$ | － | － | n | － |  | $\frac{\tilde{N}}{\underset{\sim}{c}}$ | $\left\|\begin{array}{c} \overline{a_{2}^{2}} \\ \stackrel{2}{2} \\ =1 \end{array}\right\|$ |  |  | $\begin{aligned} & \stackrel{\rightharpoonup}{\mathrm{N}} \\ & \stackrel{\rightharpoonup}{7} \end{aligned}$ | $\begin{aligned} & 0 \\ & \\ & \\ & \end{aligned}$ |  |  | $\begin{gathered} \text { du} \\ \text { तु̀ } \end{gathered}$ | તી | $\begin{gathered} \stackrel{\sim}{9} \\ \stackrel{7}{7} \\ \stackrel{1}{2} \end{gathered}$ | ＋ |  | $\left\|\begin{array}{c} \mathbf{t} \\ 0 \\ 0 \\ 0 \\ 0 \\ \hline \end{array}\right\|$ |  | cid |  | $\begin{aligned} & \underset{\sim}{\infty} \\ & \stackrel{\rightharpoonup}{n} \\ & \underset{7}{2} \end{aligned}$ | 筞 |
| *u | $\stackrel{N}{\circ}$ | $\sim$ | 3 | $\therefore \stackrel{N}{\tilde{N}}$ |  | $\begin{array}{\|c\|c\|c\|} \substack{\infty \\ 0} \end{array}$ | － | － | 3 | $\left\|\begin{array}{c} N \\ \tilde{n} \\ \infty \\ 0 \\ 0 \end{array}\right\|$ | $\left\|\begin{array}{c} \hat{6} \\ \vdots \\ \vdots \\ \vdots \\ \hline 1 \end{array}\right\|$ |  | $\left\|\begin{array}{c} \underset{n}{2} \\ \stackrel{n}{n} \\ \substack{7 \\ \underset{\sim}{2}} \end{array}\right\|$ | $\mathfrak{c}$ | － | － | － | $\begin{aligned} & \text { n } \\ & \stackrel{\rightharpoonup}{\hat{c}} \\ & \text { y } \\ & \text { O} \end{aligned}$ |  | $\begin{aligned} & \widehat{2} \\ & \underset{\sim}{2} \\ & \hat{6} \end{aligned}$ |  | $\begin{gathered} \underset{\sim}{N} \\ \underset{\sim}{\mu} \end{gathered}$ | － | $\stackrel{\text { ƠO }}{\stackrel{\rightharpoonup}{O}}$ |  | $\frac{\stackrel{\rightharpoonup}{4}}{\substack{0}}$ |  |  |  | ¢ |
| $\begin{aligned} & \infty \\ & 1 \\ & 0 \\ & 0 \\ & 0 \\ & 0 \\ & 0 \end{aligned}$ | － | －－ | \％ |  | － | $\left.\begin{array}{c} \frac{1}{4} \\ \infty \\ \infty \\ 0 \end{array}\right)$ | － | － | $\cdots$ | $\left\|\begin{array}{c} \tilde{y} \\ \underset{y}{2} \\ 0 \\ 0 \end{array}\right\|$ | $\begin{aligned} & \stackrel{\rightharpoonup}{\circ} \\ & \stackrel{\rightharpoonup}{\dot{j}} \\ & \underset{i}{2} \end{aligned}$ | $\begin{aligned} & \text { in } \\ & 0 \\ & 0 \\ & \infty \end{aligned}$ |  | $\begin{aligned} & \text { In } \\ & \text { In } \\ & \text { and } \end{aligned}$ |  | － |  |  | $\begin{aligned} & \stackrel{\rightharpoonup}{\infty} \\ & \underset{\sim}{\infty} \\ & \underset{\sim}{2} \end{aligned}$ | $\stackrel{\stackrel{\rightharpoonup}{\infty}}{\stackrel{\rightharpoonup}{\infty}}$ | $\underset{\infty}{\infty}$ |  | $\stackrel{-}{1}$ | $\begin{aligned} & \text { 筑 } \\ & \frac{m}{0} \end{aligned}$ | $$ | $\bigcirc$ |  | $\stackrel{+}{+}$ |  | ¢ |
| $\begin{aligned} & \infty \\ & \infty \\ & 1 \\ & \infty \\ & \infty \end{aligned}$ | － | － 0 | ？ |  | $-$ | $\left.\begin{array}{\|c} 9 \\ \frac{y}{2} \\ \infty \\ 0 \end{array} \right\rvert\,$ | － | － | \％ | $\left\|\begin{array}{c} \frac{g}{寸} \\ \stackrel{y}{\infty} \\ \stackrel{\infty}{0} \end{array}\right\|$ | $\left.\begin{gathered} \stackrel{\rightharpoonup}{\circ} \\ \frac{\rightharpoonup}{2} \\ \stackrel{\rightharpoonup}{\mathrm{i}} \end{gathered} \right\rvert\,$ | $\begin{aligned} & \stackrel{y}{n} \\ & \stackrel{n}{0} \\ & \dot{\infty} \end{aligned}$ |  | $\mathfrak{c}$ |  | － |  |  |  |  | $\underset{\substack{\infty \\ \hline \\ \hline}}{ }$ | $\begin{aligned} & \infty \\ & \infty \\ & \underset{\sim}{\circ} \\ & \underset{子}{2} \end{aligned}$ | $\stackrel{\rightharpoonup}{i}$ | $\begin{aligned} & \text { 咨 } \\ & \frac{m}{6} \end{aligned}$ | $\begin{aligned} & \tilde{O} \\ & 0 \\ & 0 \\ & 0 \\ & 0 \\ & \hline \end{aligned}$ | $\begin{aligned} & \circ \\ & \hline 0 . \\ & \hline-1 \end{aligned}$ | $\begin{gathered} \underset{A}{A} \\ \hat{\sim} \\ \stackrel{\uparrow}{1} \end{gathered}$ | $\stackrel{\square}{\square}$ |  |  |
| $\left\lvert\, \begin{aligned} & \infty \\ & 1 \\ & 1 \\ & 0 \\ & 1 \\ & 0 \\ & 0 \\ & 0 \end{aligned}\right.$ | －－ | － | － |  | $-$ | $\begin{gathered} \frac{1}{y} \\ \substack{\infty \\ 0 \\ 0} \end{gathered}$ | － | － | n | $\left\|\begin{array}{c} \text { 堼 } \\ \infty \\ 0 \end{array}\right\|$ | $\begin{array}{\|c} \overline{2} \\ \stackrel{\rightharpoonup}{\wedge} \\ \underset{\sim}{1} \end{array}$ | $\stackrel{\substack{\infty \\ \infty \\ \vdots \\ \vdots \\ \hline}}{ }$ | $\left\lvert\, \begin{gathered} \infty \\ \frac{2}{2} \\ 0 \\ 0 \\ 0 \end{gathered}\right.$ |  |  | － |  |  |  | $\begin{gathered} \text { さ̛̣ } \\ \stackrel{\rightharpoonup}{4} \\ \hline 1 \end{gathered}$ | $\stackrel{\rightharpoonup}{\dot{\sim}}$ | $\begin{aligned} & \text { ひ̈ } \\ & \stackrel{0}{2} \\ & \stackrel{i}{n} \end{aligned}$ | － | $\begin{aligned} & \text { 喜 } \\ & \stackrel{0}{\circ}-\underline{0} \end{aligned}$ |  | $\begin{aligned} & 0.0 \\ & 0 . \\ & \hline 1 \end{aligned}$ | ¢ |  | $\stackrel{\text { ¢ }}{\substack{6 \\ \hline}}$ | 帝 |
| $\begin{array}{ll} \text { F } \\ 1 \\ 0 & 0 \\ 0 \end{array}$ | － | －－ | n |  | $-$ | $\begin{gathered} \frac{1}{y} \\ \substack{2 \\ 0 \\ 0} \end{gathered}$ | － | － | $\overbrace{0}^{2}$ | $\left\|\begin{array}{c} \frac{1}{z} \\ \infty \\ \infty \end{array}\right\|$ | $\begin{gathered} \stackrel{\rightharpoonup}{6} \\ \stackrel{\rightharpoonup}{2} \\ \dot{9} \\ \stackrel{\rightharpoonup}{9} \end{gathered}$ | $\begin{aligned} & \stackrel{\infty}{\circ} \\ & \stackrel{\rightharpoonup}{6} \\ & \stackrel{2}{=} \\ & \hline \end{aligned}$ | $\left\|\begin{array}{c} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ \dot{\theta} \end{array}\right\|$ | Sol |  | － |  |  | $\begin{array}{\|l\|l} \substack{r \\ \\ \\ \\ \hline} \end{array}$ | $\stackrel{7}{7}$ | $\begin{aligned} & \stackrel{\circ}{4} \\ & \stackrel{n}{6} \end{aligned}$ | $\begin{aligned} & \stackrel{\rightharpoonup}{2} \\ & \stackrel{0}{6} \\ & 0.6 \end{aligned}$ |  |  | $\begin{gathered} \tilde{N} \\ \\ \end{gathered}$ | 会 | $\begin{aligned} & n \\ & \stackrel{n}{2} \\ & \frac{1}{4} \\ & \stackrel{\rightharpoonup}{c} \end{aligned}$ | － | \％ | 倞 |
| $\begin{array}{ll} \infty & 0 \\ 1 \\ 0 \\ 0 & 0 \\ 0 \end{array}$ | － | － | －${ }^{\circ}$ | $\because \left\lvert\, \begin{gathered} \substack{0 \\ 0 \\ \infty \\ 0} \\ 0 \end{gathered}\right.$ | $-$ | $\begin{array}{\|c} \text { N} \\ \substack{0 \\ 0 \\ 0} \end{array}$ | － | $\cdots$ | $\bigcirc$ | N | cion | $\begin{gathered} \frac{2}{0} \\ \vdots \\ \vdots \end{gathered}$ | $\left\|\begin{array}{c} 0 \\ 0 \\ 2 \\ 2 \\ 0 \end{array}\right\|$ |  |  | $\begin{aligned} & \stackrel{n}{9} \\ & \stackrel{\rightharpoonup}{f} \\ & \vdots \end{aligned}$ | $\begin{array}{\|c} 0 \\ \\ \\ \end{array}$ |  | $\begin{aligned} & \frac{2 n}{2} \\ & \stackrel{y}{寸} \\ & \vdots \end{aligned}$ | $\begin{aligned} & \stackrel{\rightharpoonup}{\stackrel{\rightharpoonup}{0}} \\ & \stackrel{\rightharpoonup}{\mathbf{N}} \end{aligned}$ | － | $\begin{gathered} \underset{\sim}{2} \\ \stackrel{\substack{0}}{ } \end{gathered}$ | $\stackrel{\infty}{\sim}$ | $\frac{\bar{\infty}}{\cdots} \Xi$ | $\begin{array}{\|l} \infty \\ \stackrel{\infty}{n} \\ \vdots \\ \vdots \end{array}$ | － | cr | ＋ | － | ＋ |
|  |  |  | ご ${ }^{\circ}$ | $0^{\circ} \mathrm{O}$ |  |  |  |  | $\mathrm{U}^{\circ}$ |  | S | $\underset{\sim}{e}$ | $\begin{aligned} & 5 \\ & e \\ & i \end{aligned}$ | © | $\begin{array}{\|c} \frac{1}{e} \\ \frac{2}{e} \\ \frac{2}{2} \\ \frac{2}{2} \\ \frac{2}{4} \end{array}$ |  |  |  |  | $\frac{5}{2}$ | $\begin{aligned} & \frac{\pi}{2} \\ & \frac{2}{8} \\ & 3 \end{aligned}$ | $5$ |  |  |  |  |  |  |  | ¢ |

Table 22.13. The total bond energies of alkyl boranes calculated using the functional group composition and the energies of Table 22.12 compared to the experimental

| Formula | Name | $\begin{aligned} & C-B \\ & \text { Group } \end{aligned}$ | $\begin{aligned} & B-H \\ & \text { Group } \end{aligned}$ | $\begin{gathered} B-H-B \\ \text { Group } \end{gathered}$ | $\begin{aligned} & B-B \\ & \text { Group } \end{aligned}$ | $\begin{gathered} B-B-B \\ \text { Group } \end{gathered}$ | $\begin{aligned} & C^{3}=c \\ & \text { Group } \end{aligned}$ | $\begin{aligned} & \mathrm{CH} \text { (i) } \\ & \text { Group } \end{aligned}$ | $\mathrm{CH}_{3}$ | $\mathrm{CH}_{2}$ | CH (ii) | $C-C$ (a) | $C-C$ (b) | $C-C$ (c) | $\overline{C-C}$ (d) | $C-C(e)$ | $C-C$ (f) | Calculated Total Bond Energy (cV) | Experimental <br> Total Bond <br> Energy (eV) | $\begin{gathered} \text { Relative } \\ \text { Error } \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{CH}_{3} \mathrm{~B}$ | methylborane | 1 | 2 | 0 | 0 | 0 | 0 | 0 | , | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 24.60991 | 24.49350 [16] | $\bullet 0.00475$ |
| $\mathrm{C}_{2} \mathrm{H}_{7} \mathrm{~B}$ | dimethylborane | 2 | 1 | 0 | 0 | 0 | 0 | 0 | 2 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 37.08821 | 37.17713 [16] | 0.00239 |
| $\mathrm{B}_{2} \mathrm{CH}_{8}$ | methyldiborane | 1 | 3 | 2 | 0 | 0 | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 0 |  | 0 | 0 | 37.42060 | 37.58259 [16] | 0.00431 |
| $\mathrm{B}_{2} \mathrm{C}_{2} \mathrm{H}_{10}$ | ethyldiborane | 1 | 3 | 2 | 0 | 0 | 0 | 0 | , | 1 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 49.57830 | 49.50736 [16] | $-0.00143$ |
| $\mathrm{C}_{3} \mathrm{H}_{9} \mathrm{~B}$ | trimethylboron | 3 | 0 | 0 | 0 | 0 | 0 | 0 | 3 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 49.56652 | 49.76102 [17] | 0.00391 |
| $\mathrm{B}_{2} \mathrm{C}_{2} \mathrm{H}_{10}$ | 1,1-dimethyldiborane | 2 | 2 | 2 | 0 | 0 | 0 | 0 | 2 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 49.89890 | 50.20118 [16] | 0.00602 |
| $\mathrm{B}_{2} \mathrm{C}_{2} \mathrm{H}_{4} 0$ | 1,2-dimethyldiborane | 2 | 2 | 2 | 0 | 0 | 0 | 0 | 2 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 49.89890 | 50.20118 [16] | 0.00602 |
| $\mathrm{B}_{4} \mathrm{CH}_{12}$ | methyltetraborane | 1 | 5 | 4 | 1 | 0 | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 57.39990 | 57.74604 [16] | 0.00599 |
| $\mathrm{Br}_{3} \mathrm{CH}_{11}$ | methylpentaborane | 1 | 4 | 4 | 2 | 1 | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 60.73292 | 61.51585 [16] | 0.01273 |
| $\mathrm{B}_{2} \mathrm{C}_{3} \mathrm{H}_{12}$ | trimethyldiborane | 3 | 1 | 2 | 0 | 0 | 0 | 0 | 3 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 62.37721 | 62.88481 [16] | 0.00807 |
| $\mathrm{B}_{4} \mathrm{C}_{2} \mathrm{H}_{14}$ | ethyltetraborane | 1 | 5 | 4 | 1 | 0 | 0 | 0 | 1 | 1 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 69.55760 | 69.99603 [16] | 0.00626 |
| $\mathrm{Br}_{5} \mathrm{C}_{2} \mathrm{H}_{13}$ | ethylpentaborane | 1 | 4 | 4 | 2 | 1 | 0 | 0 | 1 | 1 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 72.89062 | 73.76585 [16] | 0.01186 |
| $\mathrm{B}_{2} \mathrm{C}_{4} \mathrm{H}_{44}$ | 1,1-diethyldiborane | 2 | 2 | 2 | 0 | 0 | 0 | 0 | 2 | 2 | 0 | 2 | 0 | 0 | 0 | 0 | 0 | 74.21430 | 74.34420 [16] | 0.00175 |
| $\mathrm{B}_{2} \mathrm{C}_{4} \mathrm{H}_{14}$ | tetramethyldiborane | 4 | 0 | 2 | 0 | 0 | 0 | 0 | 4 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 74.85551 | 75.48171 [16] | 0.00830 |
| $\mathrm{B}_{5} \mathrm{C}_{3} \mathrm{H}_{15}$ | propylpentaboranc | 1 | 4 | 4 | 2 | 1 | 0 | 0 | 1 | 2 | 0 | 2 | 0 | 0 | 0 | 0 | 0 | 85.04832 | 85.84239 [16] | 0.00925 |
| $\mathrm{C}_{6} \mathrm{H}_{4} \mathrm{SB}^{\text {B }}$ | triethylboron | 3 | 0 | 0 | 0 | 0 | 0 | 0 | 3 | 3 | 0 | 3 | 0 | 0 | 0 | 0 | 0 | 86.03962 | 86.12941 [18] | 0.00104 |
| $\mathrm{B}_{2} \mathrm{C}_{6} \mathrm{H}_{18}$ | triethyldiborane | 3 | 1 | 2 | 0 | 0 | 0 | 0 | 3 | 3 | 0 | 3 | 0 | 0 | 0 | 0 | 0 | 98.85031 | 98.59407 [16] | $-0.00260$ |
| $\mathrm{B}_{10} \mathrm{CH}_{16}$ | methyldecaborane | 1 | 9 | 4 | 2 |  | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 102.21298 | 101.91775 [16] | -0.00290 |
| $\mathrm{C}_{8} \mathrm{H}_{1} 7 \mathrm{~B}$ | n -butylboracyclopentane | 3 | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 7 | 0 | 6 | 0 | 0 | 0 | 0 | 0 | 105.35916 | 105.69874] [18] | 0.00321 |
| $\mathrm{B}_{10} \mathrm{C}_{2} \mathrm{H}_{18}$ | ethyldecaboranc | 1 | 9 | 4 | 2 | 6 | 0 | 0 | 1 | 1 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 114.37068 | 113.56066 [16] | $-0.00713$ |
| $\mathrm{C}_{9} \mathrm{H}_{2} \mathrm{~B}$ | tripropylboron | 3 | 0 | 0 | 0 | 0 | 0 | 0 | 3 | 6 | 0 | 6 | 0 | 0 | 0 | 0 | 0 | 122.51272 | 122.59753 [18] | 0.00069 |
| $\mathrm{C}_{9} \mathrm{H}_{2} \mathrm{~B}$ | tri-isopropylboron | 3 | 0 | 0 | 0 | 0 | 0 | 0 | 6 | 0 | 3 | 0 | 6 | 0 | 0 | 0 | 0 | 122.81539 | 122.75798 [18] | -0.00047 |
| $\mathrm{B}_{2} \mathrm{C}_{3} \mathrm{H}_{22}$ | tetraethyldiborane | 4 | 0 | 2 | 0 | 0 | 0 | 0 | 4 | 4 | 0 | 4 | 0 | 0 | 0 | 0 | 0 | 123.48631 | 123.74017 [16] | 0.00205 |
| $\mathrm{Bl}_{10} \mathrm{CH}_{3} \mathrm{H}_{2}$ | propyldecaborane | 1 | 9 | 4 | 2 | 6 | 0 | 0 | 1 | 2 | 0 | 2 | 0 | 0 | 0 | 0 | 0 | 126.52838 | 125.94075 [16] | $-0.00467$ |
| $\mathrm{C}_{12} \mathrm{H}_{2} \mathrm{~B}^{\text {B }}$ | tri-s-butylboron | 3 | 0 | 0 | 0 | 0 | 0 | 0 | 6 | 3 | 3 | 3 | 6 | 0 | 0 | 0 | 0 | 159.28849 | 158.50627 [18] | $-0.00493$ |
| $\mathrm{C}_{12} \mathrm{H}_{27} \mathrm{~B}$ | tributylboron | 3 | 0 | 0 | 0 | 0 | 0 | 0 | 3 | 9 | 0 | 9 | 0 | 0 | 0 | 0 | 0 | 158.98582 | 159.03530 [16] | 0.00031 |
| $\mathrm{C}_{12 \mathrm{H} 27 \mathrm{~B}}$ | tri-isobutylboron | 3 | 0 | 0 | 0 | 0 | 0 | 0 | 6 | 3 | 3 | 0 | 9 | 0 | 0 | 0 | 0 | 159.20350 | 159.34318 [16] | 0.00088 |
| $\mathrm{C}_{18} \mathrm{H}_{1} \mathrm{~B}$ | triphenylboron | 3 | 0 | 0 | 0 | 0 | 18 | 15 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 172.15755 | 172.09681 [18] | -0.00035 |
| $\mathrm{C}_{15} \mathrm{H}_{33} \mathrm{~B}$ | tri-3-methylbutylboron | 3 | 0 | 0 | 0 | 0 | 0 | 0 | 6 | 6 | 3 | 3 | 9 | 0 | 0 | 0 | 0 | 195.67660 | 195.78095 [18] | 0.00053 |
| $\mathrm{C}_{18} \mathrm{H}_{33} \mathrm{~B}$ | tricyclohexylboron | 3 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 15 | 3 | 12 | 6 | 0 | 0 | 0 | 0 | 217.24711 | 218.23763 [18] | 0.00454 |
| $\mathrm{C}_{18} \mathrm{H}_{39} \mathrm{~B}$ | tri-n-hexylboron | 3 | 0 | 0 | 0 | 0 | 0 | 0 | 3 | 15 | 0 | 15 | 0 | 0 | 0 | 0 | 0 | 231.93202 | 231.76340 [18] | $-0.00073$ |
| $\mathrm{C}_{21} \mathrm{H}_{4} \mathrm{~B}$ | tri-n-heptylboron | 3 | 0 | 0 | 0 |  | 0 | 0 | 3 | 18 | 0 | 18 | 0 | 0 | 0 | 0 | 0 | 268.40512 | 268.22285 [18] | $-0.00068$ |
| $\mathrm{C}_{2} \mathrm{H}_{51} \mathrm{~B}$ | tri-s-octylboron | 3 | 0 | 0 | 0 | 0 | 0 | 0 | 6 | 15 | 3 | 15 | 6 | 0 | 0 | 0 | 0 | 305.18089 | 304.61292 [18] | $-0.00186$ |
| $\mathrm{C}_{2} \mathrm{H}_{51} \mathrm{~B}^{\text {B }}$ | tri-n-octylboron | 3 | 0 | 0 | 0 | 0 | 0 | 0 | 3 | 21 | 0 | 21 | 0 | 0 | 0 | 0 | 0 | 304.87822 | 304.68230 [18] | -0.00064 |

Table 22.14. The bond angle parameters of alkyl boranes and experimental values. $H_{t}$ is a terminal or two-center $H_{\text {. }} H_{b}$ is a bridge or three-center $H$. In the
calculation of $\theta_{v}$, the parameters from the preceding angle were used. The experimental alkyl angle from Ref. [10]. $E_{T}$ is $E_{T}$ (atom - atom msp ${ }^{3} . A O$ ).


## ALKOXY BORANES ( $(R O)_{x} B_{y} H_{z} ; R=$ alkyl) AND ALKYL BORINIC ACIDS $\left((R O)_{q} B_{r} H_{s}(H O)_{t}\right)$

The alkoxy boranes and borinic acids each comprise a $B-O$ functional group, at least one boron-alkyl-ether moiety or one or more hydroxyl groups, respectively, and in some cases one or more alkyl groups and borane moieties. Each alkoxy moiety, $C_{n} H_{2 n+1} O$, of alkoxy boranes comprises one of two types of $C-O$ functional groups that are equivalent to those given in the Ethers $\left(C_{n} H_{2 n+2} O_{m}, n=2,3,4,5 \ldots \infty\right)$ section. One is for methyl or t-butyl groups, and the other is for general alkyl groups. Each hydroxyl functional group of borinic acids and alkyl borinic acids is equivalent to that given in the Alcohols $\left(C_{n} H_{2 n+2} O_{m}, \quad n=1,2,3,4,5 \ldots \infty\right)$ section. The alkyl portion may be part of the alkoxy moiety, or an alkyl group may be bound to the central boron atom by a carbon-boron single bond comprising the $C-B$ group of the Alkyl Boranes ( $R_{x} B_{y} H_{z} ; R=$ alkyl $)$ section. Each alkyl portion may comprise at least a terminal methyl group $\left(\mathrm{CH}_{3}\right)$ and methylene ( $\mathrm{CH}_{2}$ ), methylyne ( CH ), and $C-C$ functional groups. 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 $\mathrm{C}-\mathrm{C}$ bonds within isopropyl $\left(\left(\mathrm{CH}_{3}\right)_{2} \mathrm{CH}\right)$ and t-butyl $\left(\left(\mathrm{CH}_{3}\right)_{3} \mathrm{C}\right)$ groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups. Additional $R$ groups include aromatics such as phenyl. These groups in alkoxy boranes and alkyl borinic acids are equivalent to those in branched-chain alkanes and aromatics given in the corresponding sections. Furthermore, $B-H, B-B, B-H-B$, and $B-B-B$ groups may be present that are equivalent to those in boranes as given in the Boranes $\left(B_{x} H_{y}\right)$ section.

The MO semimajor axes of the $B-O$ functional groups of alkoxy alkanes and borinic acids are determined from the force balance equation of the centrifugal, Coulombic, and magnetic forces as given in the Boranes ( $B_{x} H_{y}$ ) section. In each case, the distance from the origin of the $H_{2}$-type-ellipsoidal-MO to each focus $c^{\prime}$, the internuclear distance $2 c^{\prime}$, and the length of the semiminor axis of the prolate spheroidal $H_{2}$-type MO $b=c$ are solved from the semimajor axis $a$. Then, the geometric and energy parameters of each MO are calculated using Eqs. (15.1-15.117).

The parameters of the force balance equation for the $\sigma$-MO of the $B-O$-bond MO in Eqs. (22.18-22.22) are $n_{e}=2$ and $|L|=0:$

$$
\begin{equation*}
\frac{\hbar^{2}}{m_{e} a^{2} b^{2}} D=\frac{e^{2}}{8 \pi \varepsilon_{0} a b^{2}} D+\frac{\hbar^{2}}{2 m_{e} a^{2} b^{2}} D-\frac{\hbar^{2}}{2 m_{e} a^{2} b^{2}} D \tag{22.41}
\end{equation*}
$$

From Eq. (22.41), the semimajor axis of the $B-O$-bond MO is:

$$
\begin{equation*}
a=2 a_{0} \tag{22.42}
\end{equation*}
$$

For the $B-O$ functional groups, hybridization of the $2 s$ and $2 p$ AOs of each $C$ and $B$ to form single $2 s p^{3}$ shells forms an energy minimum, and the sharing of electrons between the $C 2 s p^{3}$ and $B 2 s p^{3}$ HOs to form a MO permits each participating orbital to decrease in radius and energy. The energy of boron is less than the Coulombic energy between the electron and proton of $H$ given by Eq. (1.264). Thus, in $c_{1}$ and $c_{2}$ in Eq. (15.61) is one, and the energy matching condition is determined by the $C_{2}$ parameter. The approach to the hybridization factor of $O$ to $B$ in boric acids is similar to that of the $O$ to $S$ bonding in the SO group of sulfoxides. The $O$ AO has an energy of $E(O)=-13.61805 \mathrm{eV}$, and the B2sp HOs has an energy of $E\left(B, 2 s p^{3}\right)=-11.80624 \mathrm{eV}$ (Eq. (22.7)). To meet the equipotential condition of the union of the $\mathrm{B}-\mathrm{O} \mathrm{H}_{2}$-type-ellipsoidal-MO with these orbitals in borinic acids and to energy match the OH group, the hybridization factor $C_{2}$ of Eq. (15.61) for the $B-O$-bond MO given by Eq. (15.77) is:

$$
\begin{equation*}
C_{2}\left(O A O \text { to } B 2 s p^{3} \mathrm{HO}\right)=\frac{E(O A O)}{E\left(B, 2 s p^{3}\right)}=\frac{-13.61805 \mathrm{eV}}{-11.80624 \mathrm{eV}}=1.15346 \tag{22.43}
\end{equation*}
$$

Since the energy of the MO is matched to that of the $B 2 s p^{3} \mathrm{HO}, E(A O / H O)$ in Eqs. (15.51) and (15.61) is $E\left(B, 2 s p^{3}\right)$ given by Eq. (22.7), and $E_{T}\left(\right.$ atom-atom, $\left.m s p^{3} . A O\right)$ is -1.12740 eV corresponding to the independent single-bond charge contribution (Eq. (22.12)) of one center.

The parameters of the $B-O$ functional group of alkoxy boranes are the same as those of borinic acids except for $C_{1}$ and $C_{2}$. Rather than being bound to an $H$, the oxygen is bound to a $C 2 s p^{3} \mathrm{HO}$, and consequently, the hybridization of the $C-O$ given by Eq. (15.133) includes the $C 2 s p^{3} \mathrm{HO}$ hybridization factor of 0.91771 (Eq. (13.430)). To meet the equipotential condition of the union of the $\mathrm{B}-\mathrm{O} \quad \mathrm{H}_{2}$-type-ellipsoidal-MO with the $B 2 s p^{3}$ HOs having an energy of $E\left(B, 2 s p^{3}\right)=-11.80624 \mathrm{eV}$ (Eq. (22.7)) and the $O$ AO having an energy of $E(O)=-13.61805 \mathrm{eV}$ such that the hybridization
matches that of the $C-O$-bond MO, the hybridization factor $C_{2}$ of Eq. (15.61) for the $B-O$-bond MO given by Eqs. (15.77) and (15.79) is:

$$
\begin{equation*}
C_{2}\left(B 2 s p^{3} \mathrm{HO} \text { to } \mathrm{O}\right)=\frac{E\left(B, 2 s p^{3}\right)}{E(O)} c_{2}\left(C 2 s p^{3} \mathrm{HO}\right)=\frac{-11.80624 \mathrm{eV}}{-13.61805 \mathrm{eV}}(0.91771)=0.79562 \tag{22.44}
\end{equation*}
$$

Furthermore, in order to form an energy minimum in the $B-O$-bond MO, oxygen acts as an $H$ in bonding with $B$ since the $2 p$ shell of $O$ is at the Coulomb energy between an electron and a proton (Eq. (10.163)). In this case, $k^{\prime}$ is 0.75 as given by Eq. (13.59) such that $C_{1}=0.75$ in Eq. (15.61).

Consider next the radius of the HO due to the contribution of charge to more than one bond. The energy contribution due to the charge donation at each boron atom and oxygen atom superimposes linearly. In general, since the energy of the $B 2 s p^{3}$ HO and O AO is matched to that of the $C 2 s p^{3} \mathrm{HO}$ when the molecule contains a $C-B$-bond MO and a $C-O$-bond MO, respectively, the corresponding radius $r_{\text {mol2sp }}$ of the $B 2 s p^{3} \mathrm{HO}$ of a boron atom, the $C 2 s p^{3} \mathrm{HO}$ of a carbon atom, and the $O$ AO of a given alkoxy borane or borinic acid molecule is calculated after Eq. (15.32) by considering $\sum E_{T_{m o l}}\left(M O, 2 s p^{3}\right)$, the total energy donation to all bonds with which it participates in bonding. The Coulombic energy $E_{\text {Coulomb }}\left(\right.$ atom, $\left.2 s p^{3}\right)$ of the outer electron of the atom $2 s p^{3}$ shell considering the charge donation to all participating bonds is given by Eq. (15.14). In the case that the boron or oxygen atom is not bound to a $C 2 s p^{3} \mathrm{HO}, r_{\text {mol2 } 2 p^{3}}$ is calculated using Eq. (15.31) where $E_{\text {Coulomb }}\left(\right.$ atom, $\left.m s p^{3}\right)$ is $E_{\text {Coulomb }}\left(B 2 s p^{3}\right)=-11.89724 \mathrm{eV}$ and $E(O)=-13.61805 \mathrm{eV}$, respectively.

The symbols of the functional groups of alkoxy boranes and borinic acids are given in Table 22.15. The geometrical (Eqs. (15.1-15.5) and (22.42-22.44)), intercept (Eqs. (15.31-15.32) and (15.80-15.87)), and energy (Eq. (15.61), (22.4), (22.7), (22.12), (22.29), and (22.43-22.44)) parameters of alkoxy boranes and borinic acids are given in Tables 22.16, 22.17, and 22.18, respectively. In the case that the MO does not intercept the $B \mathrm{HO}$ due to the reduction of the radius from the donation of $B 2 s p^{3} \mathrm{HO}$ charge to additional MO's, the energy of each MO is energy matched as a linear sum to the $B$ HO by contacting it through the bisector current of the intersecting MOs as described in the Methane Molecule $\left(\mathrm{CH}_{4}\right)$ section. The total energy of each alkyl borane given in Table 22.19 was calculated as the sum over the integer multiple of each $E_{D}$ (Group) of Table 22.18 corresponding to functional-group composition of the molecule. $E_{\text {mag }}$ of Table 22.18 is given by Eqs. (15.15) and (22.3) for the $B-O$ groups and the $B-H, B-B, B-H-B$, and $B-B-B$ groups. $E_{\text {mag }}$ of Table 22.18 is given by Eqs. (15.15) and (10.162) for the $O H$ group. The bond angle parameters of alkoxy boranes and borinic acids determined using Eqs. (15.8815.117) are given in Table 22.20. The charge-densities of exemplary alkoxy borane, trimethoxyborane, boric acid, and phenylborinic 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 are shown in Figures 22.4, 22.5, and 22.6, respectively.

Figure 22.4. Trimethoxyborane. Color scale, translucent views of the charge-density of $\left(\mathrm{H}_{3} \mathrm{CO}\right)_{3} B$ showing the orbitals of the $B, O$, and $C$ 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 atoms participating in each bond, and the hydrogen nuclei (red, not to scale).


0


Figure 22.5. Boric Acid. Color scale, translucent view of the charge-density of $(\mathrm{HO})_{3} B$ showing the orbitals of the $B$ and O atoms at their radii, the ellipsoidal surface of each H or $\mathrm{H}_{2}$-type ellipsoidal MO that transitions to the corresponding outer shell of the atoms participating in each bond, and the hydrogen nuclei (red, not to scale).


Figure 22.6. Phenylborinic Anhydride. Color scale, translucent view of the charge-density of phenylborinic anhydride showing the orbitals of the $B$ and $O$ 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 atoms participating in each bond, and the hydrogen nuclei (red, not to scale).

$0 \square 1 \mathrm{e} / \AA^{2}$

Table 22.15. The symbols of the functional groups of alkoxy boranes and borinic acids.

| Functional Group | Group Symbol |
| :---: | :---: |
| $B-O$ bond (borinic acid) | $B-O$ (i) |
| $B-O$ bond (alkoxy borane) | $B-O$ (ii) |
| OH group | OH |
| $\mathrm{C}-\mathrm{O}\left(\mathrm{CH}_{3}-\mathrm{O}-\mathrm{and}\left(\mathrm{CH}_{3}\right)_{3} \mathrm{C}-\mathrm{O}-\right)$ | $\mathrm{C}-\mathrm{O}$ (i) |
| C-O (alkyl) | $C-O$ (ii) |
| $C-B$ bond | $C-B$ |
| $B H$ bond | B-H |
| $B H B$ (bridged $H$ ) | $B-H-B$ |
| $B B$ bond | $B-B$ |
| $B B B$ (bridged B) | $B-B-B$ |
| $C C$ (aromatic bond) | $C \stackrel{3 e}{=} C$ |
| CH (aromatic) | CH (i) |
| $\mathrm{CH}_{3}$ group | $\mathrm{C}-\mathrm{H}\left(\mathrm{CH}_{3}\right)$ |
| $\mathrm{CH}_{2}$ group | $\mathrm{C}-\mathrm{H}\left(\mathrm{CH}_{2}\right)$ |
| CH | C-H (ii) |
| $C C$ bond ( $n-C$ ) | $C-C$ (a) |
| $\underline{C C}$ bond (iso-C) | $C-C$ (b) |

Table 22.16. The geometrical bond parameters of alkoxy boranes and borinic acids and experimental values. The experimental alkyl distances from Ref. [10].

| Parameter | $\begin{gathered} B-O(\mathrm{i}) \\ \text { Group } \end{gathered}$ | $\begin{gathered} B-O \text { (ii) } \\ \text { Group } \end{gathered}$ | $\begin{gathered} \mathrm{OH} \\ \text { Group } \end{gathered}$ | $\begin{gathered} C-O(\mathrm{i}) \\ \text { Group } \end{gathered}$ | $\begin{gathered} C-O \text { (ii) } \\ \text { Group } \end{gathered}$ | $\begin{aligned} & C-B \\ & \text { Group } \end{aligned}$ | $\begin{aligned} & B-H \\ & \text { Group } \end{aligned}$ | $\begin{gathered} B-H-B \\ \text { Group } \end{gathered}$ | $\begin{gathered} B-B \\ \text { and } \\ B-B-B \\ \text { Groups } \end{gathered}$ | $\begin{aligned} & C^{3 e}=C \\ & \text { Group } \end{aligned}$ | $\begin{aligned} & \mathrm{CH} \text { (i) } \\ & \text { Group } \end{aligned}$ | $\begin{gathered} \mathrm{C}-\mathrm{H}\left(\mathrm{CH}_{3}\right) \\ \text { Group } \end{gathered}$ | $\begin{gathered} \mathrm{C}-\mathrm{H}\left(\mathrm{CH}_{2}\right) \\ \text { Group } \end{gathered}$ | $\begin{aligned} & C-H \text { (ii) } \\ & \text { Group } \end{aligned}$ | $\begin{gathered} C-C \text { (a) } \\ \text { Group } \end{gathered}$ | $\begin{gathered} C-C \text { (b) } \\ \text { Group } \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $a\left(a_{0}\right)$ | 2.00000 | 2.00000 | 1.26430 | 1.80717 | 1.79473 | 1.78528 | 1.69282 | 2.00000 | 2.51962 | 1.47348 | 1.60061 | 1.64920 | 1.67122 | 1.67465 | 2.12499 | 2.12499 |
| $c^{\prime}\left(a_{0}\right)$ | 1.31678 | 1.29455 | 0.91808 | 1.34431 | 1.33968 | 1.48762 | 1.13605 | 1.23483 | 1.69749 | 1.31468 | 1.03299 | 1.04856 | 1.05553 | 1.05661 | 1.45744 | 1.45744 |
| $\begin{aligned} & \text { Bond Length } \\ & 2 c^{\prime}(A) \end{aligned}$ | 1.39362 | 1.37009 | 0.971651 | 1.42276 | 1.41785 | 1.57443 | 1.20235 | 1.30689 | 1.79654 | 1.39140 | 1.09327 | 1.10974 | 1.11713 | 1.11827 | 1.54280 | 1.54280 |
| Exp. Bond Length (A) | $\begin{aligned} & 1.376[17] \\ & \left(B(\mathrm{OH})_{3}\right) \end{aligned}$ | $\left.\begin{array}{c} 1.367[17] \\ \left(B\left(\mathrm{OCH}_{3}\right)_{3}\right) \end{array}\right)$ | $\left\lvert\, \begin{aligned} & 0.971[10] \\ & \text { (ethanol) } \\ & 0.9451[10] \\ & \text { (methanol) } \end{aligned}\right.$ | $\begin{gathered} 1.424[17] \\ \left(\mathrm{B}\left(\mathrm{OCH}_{3}\right)_{3}\right) \\ 1.416[10] \\ \text { (dimethyl } \\ \text { ether) } \end{gathered}$ |  | $\begin{gathered} 1.578[10] \\ \text { (trimethylborane) } \\ 1.580[10] \\ (1,2- \\ \text { dimethyldiborane) } \end{gathered}$ | $\begin{gathered} 1.19[4] \\ \text { (diborane) } \end{gathered}$ | $\begin{gathered} 1.32[4] \\ \text { (diborane) } \end{gathered}$ | $\begin{aligned} & 1.798[3] \\ & \left(B_{13} H_{19}\right) \end{aligned}$ | $\begin{aligned} & 1.39[10] \\ & \text { (benzene) } \end{aligned}$ | 1.101 [10] (benzene) | 1.114 $(C-H$ trimethylborane $)$ 1.107 $(C-H$ propane $)$ 1.117 $(C-H$ butane $)$ | $\begin{gathered} 1.107 \\ (C-H \\ \text { propane }) \\ 1.117 \\ (C-H \\ \text { butane }) \end{gathered}$ | $\begin{gathered} 1.122 \\ \text { (isobutane) } \end{gathered}$ | $\begin{gathered} 1.532 \\ \text { (propane) } \\ 1.531 \\ \text { (butane) } \end{gathered}$ | $\begin{gathered} 1.532 \\ \text { (propane) } \\ 1.531 \\ \text { (butane) } \end{gathered}$ |
| $b, c\left(a_{0}\right)$ | 1.50535 | 1.52452 | 0.86925 | 1.20776 | 1.19429 | 0.98702 | 1.25500 | 1.57327 | 1.86199 | 0.66540 | 1.22265 | 1.27295 | 1.29569 | 1.29924 | 1.54616 | 1.54616 |
| $e$ | 0.65839 | 0.64727 | 0.72615 | 0.74388 | 0.74645 | 0.83327 | 0.67110 | 0.61742 | 0.67371 | 0.89223 | 0.64537 | 0.63580 | 0.63159 | 0.63095 | 0.68600 | 0.68600 |

Table 22.17. The MO to HO intercept geometrical bond parame

 three-center $H . B_{b}$ is a bridge or three-center $B . E_{T}$ is $E_{T}\left(\right.$ atom-atom $\left.\mathrm{msp}^{3} . A O\right)$.

| Boad | Atem | $\begin{gathered} E_{y} \\ (\mathrm{eV}) \\ \text { Bond } 1 \end{gathered}$ | $\begin{gathered} E_{2} \\ (\mathrm{eV}) \end{gathered}$ $\text { Bonc } 2$ | $E_{j}$ <br> (eV) <br> Bonc. 3 | $\begin{gathered} E_{i} \\ (e v) \\ \text { (ever } 4 \end{gathered}$ | Pizel'Tetal Energy B2se (eV) | $\begin{aligned} & r_{\text {sunn }} \\ & \left(a_{0}\right) \end{aligned}$ | $\begin{aligned} & r_{\text {fenci }} \\ & \left(a_{3}\right) \end{aligned}$ | $\begin{gathered} L_{\text {Comosy }}\left(B 2 \times p^{3}\right) \\ \text { (eV) } \\ \text { Final } \end{gathered}$ | $\begin{gathered} \dot{E}\left(B 2 \cdot p^{*}\right) \\ \text { (eV) } \\ \text { Final } \end{gathered}$ | $\left({ }^{\circ}\right)$ | $\begin{aligned} & \theta \\ & \left({ }^{\circ}\right) \end{aligned}$ | $\begin{aligned} & \theta_{2} \\ & \left({ }^{\circ}\right) \end{aligned}$ | $\begin{gathered} a_{i} \\ \left(a_{i}\right) \end{gathered}$ | $\begin{gathered} d_{i} \\ \left(a_{0}\right) \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\begin{aligned} & H_{r 2} \text { BOR } \\ & (B-O \text { (ii) }) \end{aligned}$ | B | -0.56i70 | -1. 56.870 | -0.56.77 | f | -76.58278 | 1.14361 | 1.90129 | -17.588?4 | - 3.49734 | 75.64 | 104.36 | 39.51 | 1.54296 | 0.24R<1 |
| $\begin{aligned} & H_{1} B(O R)_{i} \\ & (B-O(\text { iii }) \end{aligned}$ | B | -0.56370 | -0.66370 | ${ }^{-0.56370}$ | 0 | .76.58278 | 1.14361 | 1.00129 | -13.58834 | $\because 3.49734$ | 75.64 | 104.36 | 39.51 | 1.54296 | 0.24841 |
| $\begin{aligned} & B(O R)_{2} \\ & (B-O \text { (ii) }) \end{aligned}$ | $B$ | -0.56\%70 | -0.56370 | $-0.56370$ | 0 | -76.58278 | 1.14361 | 1.00129 | $-13.58834$ | -. 3.49734 | 75.64 | 104.36 | 39.51 | 1.542\% | 0.24841 |
| $\begin{aligned} & \left.\begin{array}{l} H_{1} P B O R \\ (B-O \\ \hline \end{array}\right) \text { (ii) } \\ & \hline \end{aligned}$ | $B$ | -0.66370 | -1. 58.370 | -0.72457 | f |  | 1.14361 | 0.81581 | -16.67772 | - 6.58672 | 49.92 | 130.98 | 23.83 | 1.82951 | 0.53497 |
| $\begin{aligned} & R_{i} B O R \\ & (B-O \text { (iii) }) \\ & \hline \end{aligned}$ | $B$ | -0.56370 | -1.7245? | -0.72457 | f |  | 1.14361 | 0.80801 | -16.83860 | -6.7476:7 | 47.39 | 132.61 | 22.96 | 1.84155 | 0.54701 |
| $\begin{aligned} & R B(O R)_{2} \\ & (B-O(\text { iii }) \end{aligned}$ | $B$ | -0.56370 | -0.66370 | -0.72457 | 5 |  | 1.14361 | 0.81581 | -16.67772 | $\because 6.58672$ | 49.02 | 130.98 | 23.83 | 1.82951 | 0.53497 |
| $\begin{aligned} & -B-O C H \\ & (B-O(i) ;(C-O(\mathrm{i})) \end{aligned}$ | 0 | -0.56370 | -0.72457 | 0 | 0 |  | 1.00000 | 0.84435 | :6.11402 |  | 54.45 | 125.55 | 26.78 | 1.78542 | 0.49088 |
| $\left.\begin{array}{ll} -B-O C H_{2}- \\ & \\ B & O \text { (ii); }(\mathrm{C} \end{array}\right)$ | O | -0.56370 | -0. 82688 | 0 | 2 |  | 1.00000 | 0.83902 | :6.21633 |  | 53.50 | 126.50 | 26.26 | 1.79365 | 0.49911 |
| $\mathrm{C}-\mathrm{H}\left(\mathrm{OC}_{c} \mathrm{H}_{3}\right)$ | $C_{n}$ | -0.7245? | 0 | 0 | 6 | -152.34026 | 0.91771 | 0,87495 | -15.550:3 | $\therefore .5 .25945$ | 7885 | 101.15 | 42,40 | 1.21777 | 0.16921 |
| $\begin{aligned} & \mathrm{BO}-\mathrm{C}_{\mathrm{C}} \mathrm{H}_{3} \\ & \mathrm{BO}-\mathrm{C}_{5}(\mathrm{CH})_{3} \\ & (\mathrm{C} \quad \mathrm{O}(\mathrm{i})) \end{aligned}$ | $c_{0}$ | -0.72457 | i) | 0 | f | -152.74626 | 0.91771 | $0.8749^{*}$ | -15550:3 | - '5.3594 | 95.98 | 84,02 | 46.10 | 1.25319 | 0.109112 |
| $\begin{aligned} & \mathrm{BO}-\mathrm{C}_{0} \mathrm{H}_{3} \\ & \mathrm{BO}-\mathrm{C},(\mathrm{CHI})_{3}, \\ & (\mathrm{C}-\mathrm{O}(\mathrm{ij}) \\ & \hline \end{aligned}$ | 0 | -0.72457 | -1. 5 . 6.370 | 0 | f: |  | 1.00000 | 0.9.94435 | -16.11402 |  | 93.39 | 86.61 | 44.26 | 1.29433 | 0.04998 |
| $\begin{aligned} & -\mathrm{H}_{2} \mathrm{C}_{\mathrm{n}}-O B \\ & (\mathrm{C}-\mathrm{O} \text { (iii) } \\ & \hline \end{aligned}$ | $C^{\prime}$ | -0.82688 | -0.92918 | 0 | 5 | -153.37175 | 0.91771 | 0.82053 | -16.5818: | $\therefore 6.39095$ | 92.41 | 87.59 | 43.35 | 1.30512 | 0.03456 |
| $\begin{array}{\|l\|l\|} \hline-I I_{3} C_{n}-O B \\ (C & O \\ (\mathrm{Ciii}) \end{array}$ | 0 | -0.82688 | -0.56370 | 0 | 0 |  | 1.00000 | 0.83902 | -16.21633 |  | 94.06 | 85.94 | 44.49 | $1.2803<$ | 0.05933 |
| $\mathrm{C}-\mathrm{H}\left(\mathrm{CH}_{3}\right)$ | c | -0.92918 | $1)$ | 0 | 8 | -152.54<87 | 0.91771 | 0.86359 | -1575493 | - 5.56407 | 77.49 | 102.51 | 4.48 | 1.2356 | 0.18708 |
| C-H ( $\left.\mathrm{CH}_{3}\right)$ | c | -0.92918 | -0.02918 | 1 | 6 | $-153.47<06$ | 0.91771 | 0.81549 | -16.68412 | $\therefore 6.49325$ | 5847 | 111.53 | 35.84 | 1.35486 | 0.29933 |
| C-iI ( CII ) | c | -0.02918 | -0.92918 | -0.92918 | 8 | -154.40524 | 0.91771 | 0.77247 | -17.613:0 | - 7.42244 | 61.16 | 118.90 | 3.37 | 1.42988 | 0.37326 |
| $\begin{aligned} & \hline \mathrm{H}_{2} \mathrm{C}_{2} \mathrm{C}_{2} \mathrm{H}_{2} \mathrm{CH}_{2} \\ & (\mathrm{C}-\mathrm{C}(\mathrm{a})) \\ & \hline \end{aligned}$ | $\cdots$ | -0.92918 | 0 | 0 | 0 | -152.54/87 | 0.91771 | 0.86359 | -15.75493 | $\therefore .5 .56407$ | 63.82 | 116.18 | 30.08 | 1.83879 | 0.38106 |
| $\begin{aligned} & \mathrm{H}_{3} \mathrm{C}_{2} \mathrm{C}_{3} \mathrm{H}_{2} \mathrm{CH}_{3} \\ & (\mathrm{C}-\mathrm{C}(\mathrm{a})) \end{aligned}$ | $\cdots$ | -0.92918 | -0.92918 | 0 | 0 | -153.47 406 | 0.91771 | 0.81549 | -16.68412 | $\therefore 6.49325$ | 56.41 | 123.59 | 26.06 | 1.90890 | 0.45117 |
| $\begin{aligned} & R-H_{2} C_{C}^{\prime} C_{2}^{\prime}\left(H_{2} C_{3}^{\prime}-R^{\prime}\right) H \cdot H_{2}- \\ & (C-C \text { (b) }) \end{aligned}$ | $c$ | -0.92918 | -1.92918 | -0.92918 | 6 | -154.40524 | 0.91771 | ${ }^{3} .3 .77247$ | -17.61330 | $\therefore 7.42244$ | 48.36 | 131.70 | 2..90 | 1.97162 | 0.51388 |

Table 22．18．The energy parameters $(\mathrm{eV})$ of functional groups of alkoxy boranes and borinic acids．

| 运 | － |  | － | $0 \%$ | － |  | － | $\sim$ | $0 \cdots$ | － | $\xrightarrow{ \pm}$ | $\begin{aligned} & \text { N} \\ & \text { N } \\ & \text { Nু } \end{aligned}$ | $\left\|\begin{array}{c} \mathbf{d} \\ \underset{\sim}{A} \\ \dot{A} \end{array}\right\|$ |  |  | － | $\left\|\begin{array}{c} \hat{e} \\ \stackrel{\rightharpoonup}{\hat{h}} \\ \stackrel{n}{n} \\ \end{array}\right\|$ |  | $\begin{aligned} & \infty \\ & \stackrel{\infty}{\infty} \\ & \infty \\ & \underset{\sim}{\infty} \end{aligned}$ | $\begin{aligned} & \tilde{\varkappa} \\ & \underset{\gamma}{\alpha} \\ & \underset{\sim}{2} \end{aligned}$ | $$ | $\stackrel{\substack{n\\}}{ }$ | $\left\lvert\, \begin{aligned} & \frac{n}{6} \\ & \frac{2}{9} \\ & \hline \end{aligned}\right.$ | $\stackrel{\infty}{\circ} \pm$ | $\left\lvert\, \begin{gathered} 0 \\ \tilde{N} \\ 0 \\ 0 \\ \hline \end{gathered}\right.$ |  | $\left\lvert\, \begin{gathered} \tilde{0} \\ 0 \\ \underset{\sim}{2} \\ \underset{r}{2} \end{gathered}\right.$ |  |  | － |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| a | － | － | － | $0{ }^{\circ}$ | － | － | － | $\sim$ | －${ }^{\text {n }}$ | － |  | $\begin{array}{\|c} \tilde{N} \\ \hat{N} \\ \underset{\sim}{2} \end{array}$ | $\left.\begin{array}{\|c} 4 \\ 0 \\ \\ \hline \end{array} \right\rvert\,$ |  | $\left\|\begin{array}{c} \hat{y} \\ \stackrel{\rightharpoonup}{n} \\ \\ \end{array}\right\|$ | $0$ | $\left\|\begin{array}{c} \hat{0} \\ \stackrel{\rightharpoonup}{2} \\ \stackrel{2}{n} \\ \end{array}\right\|$ | $\begin{aligned} & \hat{N} \\ & \stackrel{N}{\hat{6}} \\ & \bar{\gamma} \end{aligned}$ | $\begin{gathered} \stackrel{\infty}{\infty} \\ \substack{\infty \\ \infty \\ \\ \hline} \end{gathered}$ | $\begin{gathered} \tilde{N} \\ \tilde{\gamma} \\ \underset{\gamma}{\gamma} \end{gathered}$ |  | $\stackrel{\substack{n}}{\underset{c}{5}}$ | $\begin{array}{\|c} \frac{n}{n} \\ \frac{6}{6} \\ \hline i \end{array}$ | $\frac{\mathrm{N}}{\stackrel{\mathrm{~N}}{\mathrm{O}}} \stackrel{\mathrm{~m}}{=}$ | $\begin{gathered} o \\ 0 \\ \stackrel{0}{0} \\ \vdots \end{gathered}$ |  | $\left\lvert\, \begin{gathered} \tilde{\tilde{N}} \\ \stackrel{\rightharpoonup}{n} \\ \stackrel{\rightharpoonup}{n} \end{gathered}\right.$ | $\left\lvert\, \begin{gathered} \stackrel{\rightharpoonup}{c} \\ \stackrel{\rightharpoonup}{6} \\ \substack{1} \\ \hline \end{gathered}\right.$ | － | 苍 |
|  | － | － | － | 2 | － | － | － | － | $-\frac{n}{0}$ |  | $\begin{gathered} n \\ \frac{n}{c} \\ \frac{2}{n} \\ \end{gathered}$ |  | $\left\lvert\, \begin{gathered} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{gathered}\right.$ |  |  | － |  |  | $\bigcirc$ |  | $\underset{\sim}{\stackrel{\rightharpoonup}{7}}$ | $\left\lvert\, \begin{gathered} \stackrel{2}{\mathrm{c}} \\ \frac{2}{9} \\ \stackrel{n}{2} \end{gathered}\right.$ | $\left\lvert\, \begin{gathered} \circ \\ 0 \\ \substack{c \\ C \\ C} \\ \hline \end{gathered}\right.$ |  | $\underbrace{2}_{0}$ | $\left\lvert\, \begin{aligned} & \text { ơ } \\ & \frac{\underset{\sim}{4}}{0} \end{aligned}\right.$ | $\left\|\begin{array}{c} \hat{N} \\ \frac{\hat{2}}{2} \\ \bar{r} \end{array}\right\|$ | $\begin{aligned} & \stackrel{2}{2} \\ & \neq 0 \\ & 0 \\ & \underset{\sim}{1} \end{aligned}$ |  | 馬 |
| ご产 | － | N | － | \％ | － | $-$ | － | － | $\sim$ | － |  |  |  |  | $\left\|\begin{array}{c} \hat{0} \\ \hat{0} \\ \vdots \\ \\ \end{array}\right\|$ | － | $\left\|\begin{array}{c} \hat{0} \\ \stackrel{\rightharpoonup}{6} \\ \stackrel{2}{2} \\ \underset{\sim}{2} \end{array}\right\|$ |  | － |  | $\begin{gathered} \bar{n} \\ \underset{\sim}{7} \end{gathered}$ | $\left\|\begin{array}{c} \bar{x} \\ \underset{2}{2} \\ \underset{\sim}{n} \end{array}\right\|$ |  |  |  |  |  | $\left\lvert\, \begin{gathered} \stackrel{\rightharpoonup}{\hat{c}} \\ \stackrel{\rightharpoonup}{6} \\ \underset{\substack{2}}{ } \end{gathered}\right.$ | $\begin{gathered} \text { 劵 } \\ \stackrel{c}{\omega} \\ \stackrel{\omega}{c} \end{gathered}$ | $\stackrel{\circ}{\circ}$ |
| ぎ | － | m | $\sim$ | 0 亿 | － | － | O | － | $\cdots$ n ${ }_{\text {同 }}$ | － |  | $\begin{aligned} & \infty \\ & \underset{A}{1} \\ & \underset{\sim}{\infty} \\ & \infty \end{aligned}$ |  |  |  | － | $\left\|\begin{array}{c} \hat{6} \\ \stackrel{\rightharpoonup}{0} \\ \stackrel{\rightharpoonup}{n} \\ \underset{\sim}{2} \end{array}\right\|$ | $\left\|\begin{array}{l} \overline{5} \\ \stackrel{\rightharpoonup}{6} \\ \stackrel{\rightharpoonup}{6} \end{array}\right\|$ | $\bigcirc$ |  | $\begin{aligned} & \stackrel{0}{0} \\ & \underset{1}{c} \\ & \underset{\sim}{c} \end{aligned}$ | $\left\lvert\, \begin{gathered} 0 \\ 0 \\ 0 \\ \vdots \\ \vdots \\ 0 \end{gathered}\right.$ | $\left\lvert\, \begin{gathered} \tilde{\sim} \\ \tilde{n} \\ \tilde{i} \\ \underset{O}{2} \end{gathered}\right.$ |  |  |  | $\left\lvert\, \begin{gathered} \hat{a} \\ \text { a } \\ \stackrel{\rightharpoonup}{0} \\ \hline \end{gathered}\right.$ |  |  | $\xrightarrow{\circ}$ |
| $\begin{aligned} & e \\ & 0 \\ & \hline \end{aligned}$ | － | － | － | in | － | － | E－ | － | -2 合 | － |  | $\frac{\underset{\sim}{\lambda}}{\underset{\sim}{\Omega}}$ |  |  |  | $\begin{aligned} & \stackrel{\rightharpoonup}{n} \\ & \stackrel{N}{i} \end{aligned}$ | $\left\lvert\, \begin{aligned} & 0 \\ & 0 \\ & 0 \\ & \underset{n}{n} \\ & \hline \end{aligned}\right.$ |  | $\begin{aligned} & \text { o} \\ & 0 \\ & 0 \\ & 0 \\ & 0 \\ & 0 \end{aligned}$ |  |  | $\begin{aligned} & \tilde{\mu} \\ & \underset{\sim}{\sim} \\ & \underset{\sim}{\tau} \end{aligned}$ | $\begin{gathered} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ \end{gathered}$ | Nor | $\begin{array}{\|c} \substack{0 \\ 0 \\ 0 \\ 0 \\ \vdots \\ \vdots} \end{array}$ |  | $\left\lvert\, \begin{gathered} \stackrel{\rightharpoonup}{0} \\ 0 \\ \underset{\sim}{2} \\ \underset{\sim}{2} \end{gathered}\right.$ | $\begin{gathered} \hat{2} \\ \mathbf{o} \\ \text { Sob } \\ \dot{f} \end{gathered}$ |  | 等 |
| $\div \pi$ | $\left\lvert\, \begin{gathered} 2 \\ 0 \end{gathered}\right.$ | $\sim$ | － | $\bigcirc{ }^{\circ}$ | $\begin{gathered} \tilde{N} \\ \\ \end{gathered}$ | - | － | m | $\bigcirc$－ | $\left.\begin{aligned} & \underset{\sim}{2} \\ & \end{aligned} \right\rvert\,$ | $\left\lvert\, \begin{gathered} \hat{0} \\ \frac{9}{1} \\ \vdots \\ \vdots \end{gathered}\right.$ |  | $\left\lvert\, \begin{gathered} \frac{2}{2} \\ \frac{2}{?} \\ \underset{\sim}{2} \end{gathered}\right.$ | $2$ | － | － | － | $\begin{aligned} & \text { n } \\ & 0 \\ & 0 \\ & 0 \\ & 0 \\ & \text { on } \end{aligned}$ |  |  | $\begin{gathered} \text { N } \\ \underset{\sim}{\mathrm{G}} \end{gathered}$ | $\left\lvert\, \begin{gathered} \underset{\sim}{n} \\ \frac{N}{i} \\ \underset{\sim}{n} \end{gathered}\right.$ | $\left\|\begin{array}{c} 0 \\ 0 \\ 0 \\ \hat{R} \\ \underset{\sim}{2} \end{array}\right\|$ | $\begin{aligned} & \stackrel{9}{o} \\ & \stackrel{\rightharpoonup}{\circ} \\ & \hline \end{aligned}$ | $\begin{array}{\|c} \tilde{0} \\ \vdots \\ \underset{\sim}{1} \\ \end{array}$ |  |  |  | － | － |
| $\left\lvert\, \begin{gathered} \infty \\ 1 \\ \infty \\ \\ \\ \hline \end{gathered}\right.$ | － | － | － | $\bigcirc{ }^{3}$ |  |  | － | － | 0 ＇s | $\underset{\substack{\text { y } \\ \infty \\ \hline \\ \hline}}{ }$ |  | $\begin{aligned} & \text { 등 } \\ & \stackrel{n}{c} \\ & \infty \end{aligned}$ | $\left\|\begin{array}{c} n \\ 0 \\ 0 \\ \substack{1 \\ \hdashline 子 \\ 子} \end{array}\right\|$ |  | $\mathfrak{c}$ | － | $\left\|\begin{array}{c} \underset{\substack{0}}{\substack{0}} \\ \underset{\sim}{7} \end{array}\right\|$ |  | $\begin{gathered} \stackrel{\rightharpoonup}{\infty} \\ \underset{\sim}{2} \\ \underset{i}{2} \end{gathered}$ | $\left\|\begin{array}{c} \bar{\infty} \\ \stackrel{\rightharpoonup}{\infty} \\ \stackrel{\rightharpoonup}{c} \end{array}\right\|$ | $\begin{array}{\|c} \infty \\ \substack{\infty \\ \infty \\ 0 \\ 0} \end{array}$ | $\left\lvert\, \begin{gathered} \tilde{\infty} \\ 0 \\ q \\ q \\ 子 \end{gathered}\right.$ |  | 侖 | $\begin{aligned} & \circ \\ & \stackrel{8}{0} \\ & \stackrel{y}{0} \\ & \vdots \end{aligned}$ | $\begin{array}{\|l\|l} \hline 0 \\ 0 \\ 0 \\ 0 \\ \hline 0 \end{array}$ | $\left\lvert\, \begin{array}{\|c} 0 \\ 0 \\ 0 \\ \underset{\sim}{0} \\ \underset{\sim}{2} \end{array}\right.$ |  |  | ¢ |
| $\begin{aligned} & \infty \\ & 1 \\ & \infty \end{aligned}$ | － | － | － | － 3 |  | － | － | $\sim$ | 0 ＇s． | $\underset{\substack { \text { a } \\ \begin{subarray}{c}{\text { a }{ \text { a } \\ \begin{subarray} { c } { \text { a } } } \\ {\hline}\end{subarray}}{ }$ |  | $\begin{aligned} & \hat{y} \\ & \stackrel{y}{c} \\ & \infty \\ & \infty \end{aligned}$ |  |  |  | － | $\left\lvert\, \begin{gathered} \underset{G}{C} \\ \underset{\substack{0}}{\underset{\sim}{2}} \end{gathered}\right.$ |  |  | $\begin{array}{\|c\|c\|c\|c\|c\|c\|c\|c\|c\|c\|c\|c\|c\|c\|} \substack{c} \end{array}$ | $\begin{array}{\|c} \stackrel{\circ}{\circ} \\ \stackrel{\infty}{\infty} \\ \substack{\infty} \end{array}$ |  | $\left\|\begin{array}{c} 8 \\ \underset{7}{7} \\ \vdots \end{array}\right\|$ |  |  | $\begin{aligned} & 0.0 \\ & 0.0 \\ & 0.0 \\ & 0.0 \end{aligned}$ | $\left\lvert\,\right.$ | $\left\lvert\, \begin{gathered} \underset{\substack{C}}{\substack{0}} \\ \underset{\rightarrow}{2} \end{gathered}\right.$ | － | ¢ |
| $\left\lvert\, \begin{aligned} & \infty \\ & 1 \\ & 1 \\ & 0 \\ & 1 \\ & 1 \\ & \infty \end{aligned}\right.$ | － | － | － | 会 | $\underset{\substack{\text { 寺 } \\ \infty \\ \hline \infty \\ \hline}}{ }$ | － | － | － | $-\underset{0}{\text { 亿 }}$ | $\underset{\substack{\text { 符 } \\ \infty}}{ }$ |  | $\begin{aligned} & \infty \\ & \infty \\ & \infty \\ & \\ & \hline \end{aligned}$ | $\left\|\begin{array}{c} \infty \\ 0 \\ \vdots \\ \substack{0 \\ 0} \end{array}\right\|$ | $\begin{gathered} J_{2}^{2} \\ \underset{\sim}{c} \end{gathered}$ |  | － |  |  | $\begin{aligned} & \text { 㞧 } \\ & \text { ત̛ } \end{aligned}$ | $\begin{gathered} \stackrel{\rightharpoonup}{n} \\ \stackrel{\rightharpoonup}{0} \\ \stackrel{\rightharpoonup}{c} \\ \vdots \end{gathered}$ | $\begin{aligned} & \bar{N} \\ & \underset{\sim}{\dot{N}} \end{aligned}$ | $\left\lvert\, \begin{gathered} \tilde{0} \\ 0 \\ \vdots \\ \end{gathered}\right.$ |  | $\begin{aligned} & \text { 喜 } \\ & \hline 0 \\ & \hline \end{aligned}$ |  | $\begin{aligned} & 0.0 \\ & 0 \\ & 0.0 \\ & 0.0 \end{aligned}$ | $\left\|\begin{array}{c} \stackrel{\rightharpoonup}{8} \\ \stackrel{\infty}{\infty} \\ \stackrel{\rightharpoonup}{\grave{c}} \end{array}\right\|$ | $\left\lvert\, \begin{gathered} \underset{G}{{\underset{C}{0}}_{0}^{0}} \\ \underset{\substack{2}}{ } \end{gathered}\right.$ | $\begin{gathered} \underset{\sim}{Z} \\ \underset{\sim}{2} \\ \underset{\sim}{c} \end{gathered}$ |  |
| $\begin{aligned} & \pi \\ & 1 \\ & \infty \end{aligned}$ | － |  | － | － | $\begin{array}{\|c} \frac{y}{2} \\ \infty \\ \infty \end{array}$ | － |  | － | － | $\underset{\substack{\text { 管 } \\ \hline 0}}{ }$ |  |  | $\left\lvert\, \begin{aligned} & 2 \\ & 2 \\ & 0 \\ & 0 \\ & \vdots \\ & \vdots \end{aligned}\right.$ |  |  | － |  |  |  | $\begin{aligned} & \underset{\partial}{7} \\ & \underset{\sim}{7} \\ & \hline \end{aligned}$ | $\begin{aligned} & \text { O} \\ & 0 \\ & \\ & \end{aligned}$ | $\left\|\begin{array}{c} \text { ci} \\ 0 \\ 0 \\ 0 \\ 0 \end{array}\right\|$ | $\left\lvert\, \begin{gathered} n \\ 0 \\ 0 \\ 0 \\ \hline 0 \end{gathered}\right.$ |  | $\begin{gathered} \underset{\sim}{c} \\ \stackrel{e}{0} \\ \stackrel{1}{2} \end{gathered}$ |  |  |  |  | － |
|  | － |  | － | － 3 | $\left\lvert\, \begin{gathered} \tilde{0} \\ \substack{0 \\ 0 \\ 0} \end{gathered}\right.$ | － | － | a | $\bigcirc$＇s． | $\begin{array}{\|c} \tilde{0} \\ \stackrel{0}{0} \\ 0 \\ 0 \end{array}$ |  | $\begin{array}{\|l\|l\|} \frac{0}{6} \\ \frac{6}{9} \end{array}$ | $\left\|\begin{array}{c} \infty \\ \infty \\ 0 \\ 0 \\ \alpha, ~ \end{array}\right\|$ |  | $\left\|\begin{array}{c} \underset{\substack{0 \\ 0}}{\substack{0}} \mid \\ \hdashline ד \end{array}\right\|$ | $\frac{\text { in }}{\substack{\text { 年 }}}$ | $\left\|\begin{array}{c} \stackrel{0}{2} \\ \hat{N} \\ \stackrel{n}{1} \end{array}\right\|$ |  | $\begin{aligned} & \frac{n}{2} \\ & \frac{\rightharpoonup}{f} \\ & \vdots \end{aligned}$ | $\left\lvert\, \begin{aligned} & \tilde{\sim} \\ & \tilde{\sim} \\ & \underset{\sim}{Q} \\ & \underset{\sim}{2} \\ & \underset{\sim}{2} \end{aligned}\right.$ |  | $\left\lvert\, \begin{gathered} \text { ñ } \\ \underset{6}{c} \\ \stackrel{y}{3} \end{gathered}\right.$ |  | $\stackrel{\underset{0}{\Phi}}{\underset{0}{\infty}} \Xi$ | $\begin{array}{\|c} \infty \\ \stackrel{n}{n} \\ \stackrel{1}{3} \\ \vdots \end{array}$ | $\begin{aligned} & 0 \\ & \frac{2}{2} \\ & \frac{1}{6} \end{aligned}$ | $\left\|\begin{array}{c} \stackrel{\rightharpoonup}{0} \\ 0 \\ 0 \\ \underset{?}{2} \end{array}\right\|$ |  | － | － |
|  |  | － | － | $0 \%$ | － | － | $\underbrace{0}_{0}$ | $\sim$ | $0{ }^{\circ}$ | － | 䓂 | $\begin{array}{\|l\|l} \hline 2 \\ 0.0 \\ 0 \\ 0 \\ 0 \end{array}$ | $\left\|\begin{array}{c} \hat{2} \\ \hat{2} \\ \underset{\alpha}{2} \end{array}\right\|$ |  |  |  | $\begin{gathered} \frac{m}{z} \\ \underset{\sim}{d} \\ \underset{i}{2} \end{gathered}$ |  | $\begin{array}{\|l} \hline \stackrel{\circ}{0} \\ \stackrel{6}{6} \\ \hline 1 \end{array}$ | $\begin{array}{\|c\|c\|c\|c\|c\|} \hline \alpha \\ \underset{\sim}{2} \\ \underset{\sim}{2} \end{array}$ |  | $\left\lvert\, \begin{gathered} \hat{O} \\ \underset{\infty}{\mathrm{o}} \\ \end{gathered}\right.$ |  | $\frac{\infty}{\frac{\infty}{0}} \ddagger$ | $\left.\begin{array}{\|c} \tilde{y} \\ \stackrel{y}{3} \\ \vdots \end{array} \right\rvert\,$ |  | 帝 | － |  | － |
|  | － | － | － | 0 \％ | － | － | $\stackrel{\sim}{0}$ | $\sim$ | $\bigcirc \%$ | － |  | $\frac{\frac{8}{2}}{\frac{9}{9}}$ | $\left\|\begin{array}{c} \infty \\ \frac{2}{0} \\ \frac{c}{a} \end{array}\right\|$ |  | $\begin{array}{ll} 6 \\ \hline \end{array}$ | $\begin{aligned} & \frac{n}{\vdots} \\ & \vdots \\ & \hdashline \end{aligned}$ |  |  | $\begin{aligned} & \stackrel{n}{2} \\ & \frac{9}{9} \\ & \vdots \end{aligned}$ | $\begin{array}{\|c\|} \hline \tilde{\sim} \\ \underset{\sim}{\infty} \\ \underset{\sim}{c} \\ \underset{\sim}{2} \end{array}$ |  | $\begin{gathered} \infty \\ 0 \\ \text { à } \\ \end{gathered}$ | $\left\lvert\, \begin{gathered} \mathbf{q} \\ \mathbf{\infty} \\ 0 \\ \hline \end{gathered}\right.$ |  | $\begin{aligned} & \stackrel{\rightharpoonup}{2} \\ & \stackrel{n}{1} \\ & \stackrel{y}{c} \end{aligned}$ | $\begin{aligned} & \text { ơ } \\ & \frac{\underset{\sim}{t}}{0} \end{aligned}$ | 容 | － | － | ®্ర̆ |
| 〕言 | － |  | － | 会 | － | 風 | －－ | － | $-\underset{\sim}{0}$ | － | － | $\begin{aligned} & \stackrel{\infty}{\otimes} \\ & \stackrel{\otimes}{\infty} \\ & \underset{寸}{+} \end{aligned}$ | $\left\|\begin{array}{c} \hat{0} \\ 0 \\ \dot{0} \\ \stackrel{\rightharpoonup}{\dot{0}} \end{array}\right\|$ |  |  | － |  | $\begin{aligned} & \text { A } \\ & \underset{\sim}{6} \\ & \underset{\sim}{?} \end{aligned}$ | － | $\begin{gathered} \hat{N} \\ \hat{0} \\ \underset{\sim}{n} \\ \hline \end{gathered}$ | $\stackrel{\rightharpoonup}{\stackrel{D}{\Xi}}$ | $\left\|\begin{array}{c} \frac{7}{2} \\ \stackrel{\rightharpoonup}{0} \\ \vdots \\ \vdots \end{array}\right\|$ | $\begin{gathered} \underset{2}{2} \\ \substack{2 \\ \underset{i}{2}} \end{gathered}$ |  | $\begin{aligned} & 2 \\ & 0 \\ & 0 \\ & \vdots \\ & \vdots \end{aligned}$ | $\frac{\mathrm{F}}{\mathbf{j}}$ |  | $\begin{array}{\|l\|} \frac{\bar{\infty}}{\mathbf{c}} \\ \frac{\dot{\alpha}}{} \end{array}$ |  | 冎 |
|  | － |  | － |  | $\begin{array}{\|c} \substack{\circ \\ \\ \\ \hline} \end{array}$ | － | －－ | － | － | $$ |  | $\begin{aligned} & \stackrel{\circ}{0} \\ & \stackrel{\circ}{n} \\ & \stackrel{2}{\circ} \end{aligned}$ | $\left\lvert\, \begin{gathered} 2 \\ 0 \\ 0 \\ 0 \\ \dot{\infty} \end{gathered}\right.$ | $\mathbf{c}_{6}^{9}$ | $\left\lvert\, \begin{gathered} \underset{C}{C} \\ \underset{\substack{0}}{\substack{2}} \mid \end{gathered}\right.$ | － |  |  | $\underset{\substack{\text { O} \\ \hdashline \\ \hline}}{ }$ | $\left\lvert\, \begin{gathered} \infty \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{gathered}\right.$ |  | $\left\|\begin{array}{c} n \\ 0 \\ \\ \end{array}\right\|$ |  | $\stackrel{\circ}{\mathrm{N}} \mathrm{\sim}$ |  | $\begin{array}{\|c} 0 \\ 0 \\ 0 \\ 0.0 \\ 0.0 \end{array}$ | $\left\lvert\, \begin{gathered} \bar{h} \\ \infty \\ \infty \\ 0 \\ \stackrel{\rightharpoonup}{r} \end{gathered}\right.$ |  | $\begin{aligned} & \bar{\infty} \\ & \stackrel{\rightharpoonup}{c} \\ & \stackrel{\rightharpoonup}{7} \end{aligned}$ | 攻 |
| $\left\lvert\, \begin{array}{ll} 0 & 0 \\ 0 & \text { 总 } \\ 1 & 0 \\ \infty \end{array}\right.$ | － |  | － | －${ }^{\circ}$ | $\stackrel{\circ}{\substack{0 \\ n \\ \hdashline}}$ | － | － 0 | － | －＇${ }^{\circ}$ | $\stackrel{\circ}{6}$ | $\xrightarrow{\text { c }}$ |  | $\left\|\begin{array}{c} \frac{7}{\mathbf{d}} \\ \frac{G}{\infty} \\ \hline \end{array}\right\|$ |  |  | － |  | con | $\begin{aligned} & \text { 导 } \\ & \underset{~}{7} \end{aligned}$ | $\left\lvert\, \begin{gathered} \hat{n} \\ \frac{0}{6} \\ \frac{\square}{9} \end{gathered}\right.$ |  | $\begin{array}{\|c} \substack{0 \\ 0\\ \\ } \end{array}$ | $\left\lvert\, \begin{gathered} 0 \\ \hline 0 \\ \hline 6 \\ \hline 9 \end{gathered}\right.$ |  | $\begin{array}{\|c} \infty \\ 0 \\ 0 \\ 0 \\ \vdots \\ \hline \end{array}$ |  | $\left\|\begin{array}{c} \bar{o} \\ \frac{9}{9} \\ \overline{9} \end{array}\right\|$ |  | $\begin{aligned} & \bar{\infty} \\ & \stackrel{6}{\grave{j}} \\ & \stackrel{\rightharpoonup}{2} \end{aligned}$ | 皆 |
|  |  | $=$ | $=$ | $=\mathrm{v}$ | U | v－ | v） $0^{\circ}$ | $0^{\circ}$ | ט゙U | $\mathrm{v}^{2}$ | e | $\therefore$ | $=1 \begin{gathered} 0 \\ =0 \\ i \end{gathered}$ |  |  | 左 |  |  |  | $2$ | $\begin{aligned} & 5 \\ & 3 \\ & 3 \\ & 3 \\ & 0 \\ & 0 \end{aligned}$ | $\underset{c}{5}$ |  | $\underbrace{s}_{0}$ | 部 |  |  | $\begin{gathered} \text { e } \\ \substack{c \\ 0 \\ 0 \\ 0 \\ 0 \\ 0} \end{gathered}$ | $\begin{aligned} & 2 \\ & 0 \\ & 0 \\ & 0 \end{aligned}$ |  |

Table 22.19. The total bond energies of alkoxy boranes and borinic acids calculated using the functional group composition and the energies of Table 22.18 compared to the experimental values.

Table 22.20. The bond angle parameters of alkoxy boranes and borinic acids and experimental values. $H_{t}$ is a terminal or two-center $H . H_{b}$ is a bridge or three-center $H$. In the calculation of $\theta_{v}$, the parameters from the preceding angle were used. The experimental alkyl angle from Ref. [10]. $E_{T}$ is $E_{T}$ (atom - atom msp ${ }^{3}$.AO).


## TERTIARY AND QUATERNARY AMINOBORANES AND BORANE AMINES ( $R_{q} B_{r} N_{s} R_{t} ; R=H ;$ alkyl)

The tertiary and quaternary amino boranes and borane amines each comprise at least one $B$ bound by a boron-nitrogen single bond comprising a $B-N$ group, and may comprise at least a terminal methyl group $\left(\mathrm{CH}_{3}\right)$, as well other alkyl and borane groups such as methylene $\left(\mathrm{CH}_{2}\right)$, methylyne $(\mathrm{CH}), C-C, B-H, B-C, B-H, B-B, B-H-B$, and $B-B-B$ functional groups. 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 $\left(\left(\mathrm{CH}_{3}\right)_{2} \mathrm{CH}\right)$ and t-butyl $\left(\left(\mathrm{CH}_{3}\right)_{3} \mathrm{C}\right)$ groups and the isopropyl to isopropyl, isopropyl to t-butyl, and tbutyl to t-butyl $C-C$ bonds comprise functional groups. These groups in tertiary and quaternary amino boranes and borane amines are equivalent to those in branched-chain alkanes, the $B-C$ group is equivalent to that of alkyl boranes, and the $B-H$, $B-B, B-H-B$, and $B-B-B$ functional groups are equivalent to those in boranes.

In tertiary amino boranes and borane amines, the nitrogen atom of each $B-N$ bond is bound to two other atoms such that there are a total of three bounds per atom. The amino or amine moiety may comprise $N H_{2}, N(H) R$, and $N R_{2}$. The corresponding functional group for the $\mathrm{NH}_{2}$ moiety is the $\mathrm{NH}_{2}$ functional group given in the Primary Amines $\left(C_{n} H_{2 n+2+m} N_{m}, n=1,2,3,4,5 \ldots \infty\right)$ section. The $N(H) R$ moiety comprises the $N H$ functional group of the Secondary Amines $\left(C_{n} H_{2 n+2+m} N_{m}, n=2,3,4,5 \ldots \infty\right)$ section and the $C-N$ functional group of the Primary Amines $\left(C_{n} H_{2 n+2+m} N_{m}, n=1,2,3,4,5 \ldots \infty\right)$ section. The $N R_{2}$ moiety comprises 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 given in the Secondary Amines $\left(C_{n} H_{2 n+2+m} N_{m}, n=2,3,4,5 \ldots \infty\right)$ section.

In quaternary amino boranes and borane amines, the nitrogen atom of each $B-N$ bond is bound to three other atoms such that there are a total of four bonds per atom. The amino or amine moiety may comprise $N H_{3}, N\left(H_{2}\right) R, N(H) R_{2}$, and $N R_{3}$. The corresponding functional group for the $\mathrm{NH}_{3}$ moiety is ammonia given in the Ammonia $\left(\mathrm{NH}_{3}\right)$ section. The $N\left(\mathrm{H}_{2}\right) R$ moiety comprises the $\mathrm{NH}_{2}$ and the $\mathrm{C}-\mathrm{N}$ functional groups given in the Primary Amines $\left(C_{n} H_{2 n+2+m} N_{m}, n=1,2,3,4,5 \ldots \infty\right)$ section. The $N(H) R_{2}$ moiety comprises the $N H$ 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 given in the Secondary Amines $\left(C_{n} H_{2 n+2+m} N_{m}, n=2,3,4,5 \ldots \infty\right)$ section. The $N R_{3}$ moiety comprises the $C-N$ functional group of tertiary amines given in the Tertiary Amines ( $\left.C_{n} H_{2 n+3} N, n=3,4,5 \ldots \infty\right)$ section.

The bonding in the $B-N$ functional groups of tertiary and quaternary amino boranes and borane amines is similar to that of the $B-O$ groups of alkoxy boranes and borinic acids given in the corresponding section. The MO semimajor axes of the $B-N$ functional groups are determined from the force balance equation of the centrifugal, Coulombic, and magnetic forces as given in the Boranes $\left(B_{x} H_{y}\right)$ section. In each case, the distance from the origin of the $H_{2}$-type-ellipsoidal-MO to each focus $c^{\prime}$, the internuclear distance $2 c^{\prime}$, and the length of the semiminor axis of the prolate spheroidal $H_{2}$-type MO $b=c$ are solved from the semimajor axis $a$. Then, the geometric and energy parameters of each MO are calculated using Eqs. (15.1-15.117).

As in the case of the $B-O$-bond MOs, the $\sigma$-MOs of the tertiary and quaternary $B-N$-bond MOs is energy matched to the $B 2 s p^{3} \mathrm{HO}$ which determines that the parameters of the force balance equation based on electron angular momentum are determined by those of the boron atom. Thus, the parameters of the force balance equation for the $\sigma-\mathrm{MO}$ of the $B-N$-bond MOs in Eqs. (22.18-22.22) are $n_{e}=1$ and $|L|=\frac{3 \sqrt{\frac{3}{4}}}{Z}$ corresponding to the three electrons of the boron atom:

$$
\begin{align*}
& \frac{\hbar^{2}}{m_{e} a^{2} b^{2}} D=\frac{e^{2}}{8 \pi \varepsilon_{0} a b^{2}} D+\frac{\hbar^{2}}{2 m_{e} a^{2} b^{2}} D-\left(\frac{1}{2}+\frac{3 \sqrt{\frac{3}{4}}}{Z}\right) \frac{\hbar^{2}}{2 m_{e} a^{2} b^{2}} D  \tag{22.45}\\
& a=\left(\frac{3}{2}+\frac{3 \sqrt{\frac{3}{4}}}{Z}\right) a_{0} \tag{22.46}
\end{align*}
$$

With $Z=5$, the semimajor axis of the tertiary $B-N$-bond MO is:
$a=2.01962 a_{0}$
For the $B-N$ functional groups, hybridization of the $2 s$ and $2 p$ AOs of $B$ to form single $2 s p^{3}$ shells forms an energy minimum, and the sharing of electrons between the $B 2 s p^{3} \mathrm{HO}$ and $N$ AO to form a MO permits each participating orbital to decrease in radius and energy. The energy of boron is less than the Coulombic energy between the electron and proton of $H$ given by Eq. (1.264). Thus, in $c_{1}$ and $c_{2}$ in Eq. (15.61) is one, and the energy matching condition is determined by the $C_{1}$ and
$C_{2}$ parameters. The $N$ AO has an energy of $E(N)=-14.53414 \mathrm{eV}$, and the $B 2 s p^{3}$ HOs have an energy of $E\left(B, 2 s p^{3}\right)=-11.80624 \mathrm{eV}$ (Eq. (22.7)). To meet the equipotential condition of the union of the $B-N H_{2}$-type-ellipsoidalMO with these orbitals, the hybridization factor $C_{2}$ of Eq. (15.61) for the $B-N$-bond MO given by Eq. (15.77) is:

$$
\begin{equation*}
C_{2}\left(N A O \text { to } B 2 s p^{3} H O\right)=\frac{E\left(B, 2 s p^{3}\right)}{E(N A O)}=\frac{-11.80624 \mathrm{eV}}{-14.53414 \mathrm{eV}}=0.81231 \tag{22.48}
\end{equation*}
$$

Since the energy of the MO is matched to that of the $B 2 s p^{3} \mathrm{HO}, E(A O / H O)$ in Eqs. (15.51) and (15.61) is $E\left(B, 2 s p^{3}\right)$ given by Eq. (22.7), and $E_{T}\left(\right.$ atom-atom, $\left.m s p^{3} . A O\right)$ for ternary $B-N$ is -1.12740 eV corresponding to the independent single-bond charge contribution (Eq. (22.12)) of one center as in the case of the alkoxy borane $B-O$ functional group. Furthermore, $k^{\prime}$ is 0.75 as given by Eq. (13.59) such that $C_{1}=0.75$ in Eq. (15.61) which is also equivalent to $C_{1}$ of the $B-O$ alkoxy borane group.
$E_{T}\left(\right.$ atom-atom, $\left.m s p^{3} . A O\right)$ of the quaternary $B-N$-bond MO is determined by considering that the bond involves an electron transfer from the nitrogen atom to the boron atom to form zwitterions such as $R_{3} N^{+}-B^{-} R_{3}^{\prime}$. By considering the electron redistribution in the quaternary amino borane and borane amine molecule as well as the fact that the central field decreases by an integer for each successive electron of the shell, the radius $r_{B-N b o r a n e 2 s p^{3}}$ of the $B 2 s p^{3}$ shell may be calculated from the Coulombic energy using Eq. (15.18) , except that the sign of the charge donation is positive:

$$
\begin{equation*}
r_{B-\text { Sborane } 2 s p^{3}}=\left(\sum_{n=2}^{4}(Z-n)+1\right) \frac{e^{2}}{8 \pi \varepsilon_{0}(e 74.89168 e V)}=\frac{7 e^{2}}{8 \pi \varepsilon_{0}(e 74.89168 e V)}=1.27171 a_{0} \tag{22.49}
\end{equation*}
$$

Using Eqs. (15.19) and (22.49), the Coulombic energy $E_{\text {Coulomb }}\left(B_{B-N b o r a n e}, 2 s p^{3}\right)$ of the outer electron of the $B 2 s p^{3}$ shell is:

$$
\begin{equation*}
E_{\text {Coulomb }}\left(B_{B-\text { Nborane }}, 2 s p^{3}\right)=\frac{-e^{2}}{8 \pi \varepsilon_{0} r_{B-\text { Nborane } 2 s p^{3}}}=\frac{-e^{2}}{8 \pi \varepsilon_{0} 1.27171 a_{0}}=-10.69881 \mathrm{eV} \tag{22.50}
\end{equation*}
$$

During hybridization, one of the spin-paired $2 s$ electrons is promoted to the $B 2 s p^{3}$ shell as an unpaired electron. The energy for the promotion is the magnetic energy given by Eq. (22.6). Using Eqs. (22.6) and (22.50), the energy $E\left(B_{B-N b o r a n e}, 2 s p^{3}\right)$ of the outer electron of the $B 2 s p^{3}$ shell is:

$$
\begin{equation*}
E\left(B_{B-\text { Nborane }}, 2 s p^{3}\right)=\frac{-e^{2}}{8 \pi \varepsilon_{0} r_{B-\text { Nborane } 2 \text { sp }}{ }^{3}}+\frac{2 \pi \mu_{0} e^{2} \hbar^{2}}{m_{e}^{2}\left(r_{3}\right)^{3}}=-10.69881 \mathrm{eV}+0.09100 \mathrm{eV}=-10.60781 \mathrm{eV} \tag{22.51}
\end{equation*}
$$

Thus, $E_{T}\left(B-N, 2 s p^{3}\right)$, the energy change of each $B 2 s p^{3}$ shell with the formation of the $B-N$-bond MO is given by the difference between Eq. (22.51) and Eq. (22.7).

$$
\begin{equation*}
E_{T}\left(B-N, 2 s p^{3}\right)=E\left(B_{B-N b o r a n e}, 2 s p^{3}\right)-E\left(B, 2 s p^{3}\right)=-10.60781 \mathrm{eV}-(-11.80624 \mathrm{eV})=1.19843 \mathrm{eV} \tag{22.52}
\end{equation*}
$$

Thus, $E_{T}\left(\right.$ atom -atom, $\left.m s p^{3} . A O\right)$ of the quaternary $B-N$-bond MO is 1.19843 eV .
Consider next the radius of the HO due to the contribution of charge to more than one bond. The energy contribution due to the charge donation at each boron atom and nitrogen atom superimposes linearly. In general, since the energy of the $B 2 s p^{3}$ HO and $N \mathrm{AO}$ is matched to that of the $C 2 s p^{3} \mathrm{HO}$ when a molecule contains a $C-B$-bond MO and a $C-N$-bond MO, respectively, the corresponding radius $r_{m o l 2 s p^{3}}$ of the $B 2 s p^{3} \mathrm{HO}$ of a boron atom, the $C 2 s p^{3} \mathrm{HO}$ of a carbon atom, and the $N$ AO of a given $B-N$-containing borane molecule is calculated after Eq. (15.32) by considering $\sum E_{T_{m o l}}\left(M O, 2 s p^{3}\right)$, the total energy donation to all bonds with which it participates in bonding. The Coulombic energy $E_{\text {Coulomb }}\left(\right.$ atom, $2 s p^{3}$ ) of the outer electron of the atom $2 s p^{3}$ shell considering the charge donation to all participating bonds is given by Eq. (15.14). In the case that the boron or nitrogen atom is not bound to a $C 2 s p^{3} \mathrm{HO}, r_{\text {mol2sp }}{ }^{3}$ is calculated using Eq. (15.31) where $E_{\text {Coulomb }}\left(\right.$ atom, $\left.m s p^{3}\right)$ is $E_{\text {Coulomb }}\left(B 2 s p^{3}\right)=-11.89724 \mathrm{eV}$ and $E(N)=-14.53414 \mathrm{eV}$, respectively. The hybridization parameters used in Eqs. (15.88-15.117) for the determination of bond angles of tertiary and quaternary amino boranes and borane amines are given in Table 22.21.

Table 22.21. Atom hybridization designation (\# first column) and hybridization parameters of atoms for determination of bond angles with final values of $r_{2 s p^{3}}, E_{\text {Coulomb }}\left(\right.$ atom, $\left.2 s p^{3}\right)$ (designated as $\left.E_{\text {Coulomb }}\right)$, and $E\left(\right.$ atom b-Nborane $\left.2 s p^{3}\right)$ (designated as $E$ )
calculated using the appropriate values of $\sum E_{T_{m o l}}\left(M O, 2 s p^{3}\right)$ (designated as $E_{T}$ ) for each corresponding terminal bond spanning each angle.

| $\#$ | $E_{T}$ | $E_{T}$ | $E_{T}$ | $E_{T}$ | $E_{T}$ | $r_{3 p^{3}}$ <br> Final | $E_{\text {Coulomb }}$ <br> $(\mathrm{eV})$ <br> Final | $E$ <br> $(\mathrm{eV})$ <br> Final |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | -0.46459 | 0 | 0 | 0 | 0 | 0.88983 <br> (Eq.(15.32)) | -15.29034 | -15.09948 |
| 2 | -0.56370 | -0.56370 | -0.56370 | 0 | 0 | 0.82343 <br> (Eq. (15.32)) | -16.52324 |  |

The symbols of the functional groups of tertiary and quaternary amino boranes and borane amines are given in Table 22.22. The geometrical (Eqs. (15.1-15.5) and (22.47)), intercept (Eqs. (15.31-15.32) and (15.80-15.87)), and energy (Eq. (15.61), (22.4), (22.7), (22.12), (22.48), and (22.52)) parameters of tertiary and quaternary amino boranes and borane amines are given in Tables $22.23,22.24$, and 22.25 , respectively. In the case that the MO does not intercept the $B H O$ due to the reduction of the radius from the donation of $B 2 s p^{3} \mathrm{HO}$ charge to additional MOs, the energy of each MO is energy matched as a linear sum to the $B$ HO by contacting it through the bisector current of the intersecting MOs as described in the Methane Molecule $\left(\mathrm{CH}_{4}\right)$ section. The total energy of each tertiary and quaternary amino borane or borane amine given in Table 22.26 was calculated as the sum over the integer multiple of each $E_{D}$ (Group) of Table 22.25 corresponding to functional-group composition of the molecule. $E_{\text {mag }}$ of Table 22.26 is given by Eqs. (15.15) and (22.3) for the $B-N$ groups and the $B-H, B-B$, $B-H-B$, and $B-B-B$ groups. $E_{m a g}$ of Table 22.26 is given by Eqs. (15.15) and (10.142) for $N H_{3}$. The bond angle parameters of tertiary and quaternary amino boranes and borane amines determined using Eqs. (15.88-15.117) are given in Table 22.27. The charge-densities of exemplary tertiary amino borane, tris(dimethylamino)borane and quaternary amino borane, trimethylaminotrimethylborane 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 are shown in Figures 22.7 and 22.8, respectively.

Figure 22.7. Trisdimethylaminoborane. Color scale, opaque views of the charge-density of $\left(\left(\mathrm{H}_{3} \mathrm{C}\right)_{2} \mathrm{~N}\right)_{3} B$ showing the orbitals of the $B, N$, and $C$ 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 atoms participating in each bond, and the hydrogen nuclei (red, not to scale).


Figure 22.8. Trimethylaminotrimethylborane. Color scale, opaque view of the charge-density of $\left(\mathrm{CH}_{3}\right)_{3} \mathrm{BN}\left(\mathrm{CH}_{3}\right)_{3}$ showing the orbitals of the $B, N$, and $C$ 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 atoms participating in each bond, and the hydrogen nuclei (red, not to scale).


Table 22.22. The symbols of the functional groups of tertiary and quaternary amino boranes and borane amines.

| Functional Group | Group Symbol |
| :---: | :---: |
| $B-N$ bond $3^{\circ}$ | $B-N$ (i) |
| $B-N$ bond $4^{\circ}$ | $B-N$ (ii) |
| $C-N$ bond $1^{\circ}$ amine | $C-N$ (i) |
| $C-N$ bond $2^{\circ}$ amine (methyl) | $C-N$ (ii) |
| $C-N$ bond $2^{\circ}$ amine (alkyl) | $C-N$ (iii) |
| $C-N$ bond $3^{\circ}$ amine | $C-N$ (iv) |
| $\mathrm{NH}_{3}$ group | $\mathrm{NH}_{3}$ |
| $\mathrm{NH}_{2}$ group | $\mathrm{NH}_{2}$ |
| NH group | NH |
| $C-B$ bond | $C-B$ |
| $B H$ bond | B-H |
| BHB (bridged $H$ ) | $B-H-B$ |
| $B B$ bond | $B-B$ |
| $\mathrm{CH}_{3}$ group | $\mathrm{C}-\mathrm{H}\left(\mathrm{CH}_{3}\right)$ |
| $\mathrm{CH}_{2}$ group | $\mathrm{C}-\mathrm{H}\left(\mathrm{CH}_{2}\right)$ |
| CH | $\mathrm{C}-\mathrm{H}$ (i) |
| $C C$ bond ( $n-C$ ) | $C-C$ (a) |

Table 22.23. The geometrical bond parameters of tertiary and quaternary amino boranes and borane amines and experimental values.

| Parameter | $\begin{gathered} B-N(\mathrm{i}) \\ \text { Group } \end{gathered}$ | $\begin{gathered} B-N \text { (ii) } \\ \text { Group } \end{gathered}$ | $\underset{\text { Group }}{C-N(i)}$ | $\begin{gathered} C-N \text { (ii) } \\ \text { Group } \end{gathered}$ | $\begin{gathered} C-N \text { (iii) } \\ \text { Group } \end{gathered}$ | $\begin{gathered} C-N \text { (iv) } \\ \text { Group } \end{gathered}$ | $\begin{gathered} \mathrm{NH}_{3} \\ \text { Group } \end{gathered}$ | $\mathrm{NH}_{2}$ <br> Group | $\begin{gathered} \mathrm{NH} \\ \text { Group } \end{gathered}$ | $\begin{aligned} & C-B \\ & \text { Group } \end{aligned}$ | $\begin{aligned} & B-H \\ & \text { Group } \end{aligned}$ | $\begin{gathered} B-H-B \\ \text { Group } \end{gathered}$ |  | $\begin{gathered} \mathrm{C}-\mathrm{H}\left(\mathrm{CH}_{3}\right) \\ \text { Group } \end{gathered}$ | $\begin{gathered} \mathrm{C}-\mathrm{H}\left(\mathrm{CH}_{2}\right) \\ \text { Group } \end{gathered}$ | $\begin{gathered} \mathrm{C}-\mathrm{H} \text { (i) } \\ \text { Group } \end{gathered}$ | $\begin{gathered} C-C(a) \\ \text { Group } \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $a\left(a_{0}\right)$ | 2.01962 | 2.01962 | 1.92682 | 1.94862 | 1.94862 | 1.96313 | 1.34750 | 1.28083 | 1.26224 | 1.78528 | 1.69282 | 2.00000 | 2.51962 | 1.64920 | 1.67122 | 1.67465 | 2.12499 |
| $c^{\prime}\left(a_{0}\right)$ | 1.28744 | 1.57679 | 1.38810 | 1.39593 | 1.39593 | 1.40112 | 0.97961 | 0.95506 | 0.94811 | 1.48762 | 1.13605 | 1.23483 | 1.69749 | 1.04856 | 1.05553 | 1.05661 | 1.45744 |
| $\begin{aligned} & \text { Bond } \\ & \text { Length } \\ & 2 c^{\prime}(A) \end{aligned}$ | 1.36257 | 1.66880 | 1.46910 | 1.47739 | 1.47739 | 1.48288 | 1.03677 | 1.0108 | 1.00343 | 1.57443 | 1.20235 | 1.30689 | 1.79654 | 1.10974 | 1.11713 | 1.11827 | 1.54280 |
| Exp. <br> Bond <br> Length <br> (A) | $\underset{(B N)}{1.281[5]}$ | $\begin{gathered} 1.638[17] \\ \left(\left(\mathrm{CH}_{3}\right)_{3} \mathrm{NBH}_{3}\right) \end{gathered}$ | $\begin{gathered} 1.471[10] \\ \text { (methylamine) } \end{gathered}$ | $\begin{gathered} 1.455[10] \\ \text { (dimethy amine) } \end{gathered}$ |  | $\begin{gathered} 1.458[10] \\ \text { (trimethylamine) } \end{gathered}$ | $\underset{(\text { ammonia) }}{1.0120[10]}$ | $\begin{gathered} 1.010[10] \\ \text { (methylamine) } \end{gathered}$ | $\begin{gathered} 1.00[10] \\ \text { (dimethylamine) } \end{gathered}$ | $\begin{gathered} 1.578[10] \\ \text { (rimethylorane) } \\ 1.50[1.10] \\ \text { (1.2. } \\ \text { dinethyldiborane) } \end{gathered}$ | $\underset{\substack{1.19[4] \\ \text { (diborane) }}}{ }$ | $\begin{aligned} & 1.32[4] \\ & \text { diborane } \end{aligned}$ (diborane) | $\begin{aligned} & 1.798[3] \\ & \left(B_{13} H_{19}\right) \end{aligned}$ | $1.114[10]$ <br> $(C-H$ <br> trimethylborane $)$ <br> $1.107[10]$ <br> $(C-H$ <br> propane $)$ <br> $1.117[10]$ <br> $(C-H$ <br> butane $)$ | $\begin{gathered} 1.107[10] \\ (C-H \\ \text { propane }) \\ 1.117[10] \\ (C-H \\ \text { butane }) \end{gathered}$ | $\underset{\text { (isobutane) }}{1.122[10]}$ | $\begin{aligned} & 1.532[10] \\ & \text { (propane) } \\ & 1.53[1] 0] \\ & \text { (butane) } \end{aligned}$ |
| $b, c\left(a_{0}\right)$ | 1.55607 | 1.26198 | 1.33634 | 1.35960 | 1.35960 | 1.37505 | 0.92527 | 0.85345 | 0.83327 | 0.98702 | 1.25500 | 1.57327 | 1.86199 | 1.27295 | 1.29569 | 1.29924 | 1.54616 |
| $e$ | 0.63747 | 0.78074 | 0.72041 | 0.71637 | 0.71637 | 0.71372 | 0.72698 | 0.74566 | 0.75113 | 0.83327 | 0.67110 | 0.61742 | 0.67371 | 0.63580 | 0.63159 | 0.63095 | 0.68600 |

Table 22．24．The MO to HO intercept geometrical bond parameters of tertiary and quaternary amino boranes and borane amines．$H_{t}$ is a terminal or two－center $H_{\text {．}} H_{b}$ is a bridge or three－center $H . B_{b}$ is a bridge or three－center $B$ ．$E_{T}$ is $E_{T}$（atom－atom msp ${ }^{3} . A O$ ）．

| が E® | $\begin{aligned} & \overline{\widetilde{2}} \\ & \text { 管 } \end{aligned}$ | $\begin{aligned} & \stackrel{\circ}{\bar{o}} \\ & \stackrel{\rightharpoonup}{0} \end{aligned}$ | $\frac{\stackrel{\infty}{+}}{\stackrel{+}{\circ}}$ |  |  | $\begin{aligned} & \text { n } \\ & \cline { 1 - 1 } \end{aligned}$ |  | त̈ O 0 | $\begin{aligned} & \text { K } \\ & \frac{0}{6} \\ & \hline 0 \end{aligned}$ | $\frac{\mathrm{O}}{\frac{0}{2}}$ | $\begin{aligned} & \bar{\circ} \mathrm{O} \\ & \text { దे } \end{aligned}$ | $\begin{aligned} & \text { IT } \\ & \stackrel{N}{6} \\ & \stackrel{0}{0} \end{aligned}$ | $\begin{aligned} & \text { İ } \\ & \stackrel{\text { n}}{0} \end{aligned}$ | $\begin{aligned} & \text { İ } \\ & \stackrel{N}{6} \\ & \hline \end{aligned}$ | $\begin{aligned} & \overline{\breve{o}} \\ & \text { Non } \end{aligned}$ | $\begin{aligned} & \stackrel{\circ}{\circ} \\ & \text { ¢ } \\ & \stackrel{6}{6} \end{aligned}$ | $\circ$ <br> $\stackrel{\circ}{\circ}$ <br> $\stackrel{\leftrightarrow}{6}$ |  | $\circ$ $\stackrel{\circ}{\circ}$ $\stackrel{\leftrightarrow}{6}$ | $\frac{\bar{\sigma}}{\stackrel{\rightharpoonup}{\sigma}}$ | $\begin{aligned} & \mathscr{o g} \\ & \text { on } \\ & \hline 0 \end{aligned}$ | $\begin{aligned} & \text { İㅡ́ } \\ & \text { Bin } \end{aligned}$ | $\begin{gathered} \bar{a} \\ \substack{0 \\ 0} \end{gathered}$ | $\begin{aligned} & \text { O} \\ & \text { 管 } \end{aligned}$ | $\underset{\substack{\infty \\ \hline 0 \\ \hline \\ \hline}}{ }$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\bigcirc$ | $\begin{aligned} & \text { n } \\ & \stackrel{y}{0} \\ & 0 \end{aligned}$ | $\begin{aligned} & \text { no } \\ & \text { 管 } \end{aligned}$ | $\begin{aligned} & \text { N్ర } \\ & \stackrel{0}{0} \end{aligned}$ | $$ | $\begin{aligned} & \text { © } \\ & \stackrel{0}{4} \\ & \stackrel{N}{2} \end{aligned}$ | $\begin{gathered} \text { ob } \\ \stackrel{0}{n} \\ \underset{\sim}{2} \end{gathered}$ |  | $\begin{gathered} \text { Nön } \\ \stackrel{0}{4} \end{gathered}$ | $\begin{aligned} & \text { 骨 } \\ & \stackrel{0}{n} \end{aligned}$ | $\begin{aligned} & \text { 品 } \\ & \text { 号 } \end{aligned}$ | $\begin{gathered} \text { 笑 } \\ \end{gathered}$ | $\begin{aligned} & \text { ho⿳亠口冋口} \\ & . \end{aligned}$ | $$ |  |  | $\begin{aligned} & \text { 을 } \\ & \underset{i}{2} \end{aligned}$ | $\begin{aligned} & \text { O} \\ & \underset{\sim}{\underset{~}{n}} \end{aligned}$ | $\begin{aligned} & \text { On } \\ & \underset{A}{\underset{\sim}{2}} \end{aligned}$ | $\stackrel{\text { Bn }}{\stackrel{n}{i}}$ | $\stackrel{\bar{\infty}}{\stackrel{\rightharpoonup}{\underset{~}{-}}}$ | $\begin{aligned} & \stackrel{\circ}{6} \\ & \stackrel{2}{2} \end{aligned}$ | $$ | $\frac{\text { g }}{\substack{2 \\ i n}}$ | $\begin{aligned} & \text { O} \\ & \text { nin } \end{aligned}$ | $$ |
| －○ | 風 | $$ | $\stackrel{\circ}{\infty}$ | $\stackrel{\substack{\mathrm{c} \\ \hline}}{ }$ | $\stackrel{\circ}{i}$ | ત్రి |  | $\begin{gathered} \stackrel{o}{\hat{q}} \\ \end{gathered}$ | ి্ণী | $\underset{\sim}{\text { N }}$ | $\stackrel{?}{\underset{\sim}{n}}$ | $\stackrel{\circ}{9}$ | $\stackrel{\circ}{\stackrel{\circ}{-}}$ | $\stackrel{\circ}{\circ}$ |  | $\underset{\underset{\sim}{\infty}}{\underset{\sim}{x}}$ | $\underset{\substack{\infty \\ \underset{\sim}{x}}}{\text { N }}$ | $\underset{\sim}{\infty}$ | $\underset{\sim}{\infty}$ | $\stackrel{\substack{\infty}}{\stackrel{\alpha}{c}}$ | $\underset{\substack{\stackrel{\rightharpoonup}{c} \\ \hline}}{ }$ | ®ợ | $\underset{\text { だ }}{\text { t. }}$ |  | F |
| ®○ | $\begin{aligned} & \text { J. } \\ & \text { 合 } \end{aligned}$ | $$ | $\underset{\substack{2 \\ \stackrel{\alpha}{2} \\ \hline}}{ }$ | $\underset{\text { I }}{\text { I }}$ | $\begin{aligned} & \stackrel{\otimes}{\circ} \\ & \stackrel{\circ}{\circ} \end{aligned}$ | $\begin{aligned} & \text { הָ } \\ & \underset{\sim}{\mathrm{Z}} \end{aligned}$ |  | $\begin{aligned} & \stackrel{\circ}{\circ} \\ & \stackrel{1}{6} \end{aligned}$ | $\begin{aligned} & \bar{\ominus} \\ & \stackrel{\rightharpoonup}{\circ} \end{aligned}$ | $\begin{aligned} & \stackrel{t}{\mathrm{o}} \\ & \stackrel{\text { d }}{0} \end{aligned}$ | $\begin{aligned} & \hat{6} \\ & \underset{\sim}{6} \end{aligned}$ | $\stackrel{\hat{a}}{2}$ | $\begin{aligned} & \hat{m} \\ & \text { Non } \end{aligned}$ | $\hat{}$ | $\frac{\underset{\sim}{9}}{\stackrel{1}{2}}$ | $\begin{aligned} & \overline{\mathrm{d}} \\ & \text { in } \end{aligned}$ | $\begin{aligned} & \overline{\text { d}} \end{aligned}$ | $\begin{aligned} & \overline{\text { du}} \end{aligned}$ | $\begin{aligned} & \overline{\mathrm{d}} \end{aligned}$ | $\begin{aligned} & \text { O} \\ & \text { 合 } \end{aligned}$ | $\begin{gathered} \infty \\ \underset{\alpha}{\circ} \end{gathered}$ | $\frac{n}{\underset{\sim}{c}}$ | $\stackrel{\sim}{0}$ | $\begin{gathered} \text { R} \\ \text { in } \end{gathered}$ | $\begin{aligned} & \stackrel{\circ}{6} \\ & \stackrel{⿴ 囗}{\circ} \end{aligned}$ |
| －© | $\begin{aligned} & \stackrel{\circ}{9} \\ & \stackrel{1}{2} \end{aligned}$ | $\stackrel{\stackrel{\text { t }}{\stackrel{~}{~}}}{ }$ | $\underset{\infty}{\bar{\infty}}$ | $\underset{\sim}{\infty}$ | $\begin{gathered} \text { ત్ర } \\ \stackrel{\infty}{\circ} \end{gathered}$ | $\stackrel{\text { n }}{\underset{\sim}{\wedge}}$ | E | $\underset{\underset{\infty}{ \pm}}{\stackrel{J}{ \pm}}$ | $\stackrel{\otimes}{\stackrel{\infty}{\propto}}$ | $\stackrel{\leftrightarrow}{\gtrless}$ | $\begin{gathered} \text { n } \\ \underset{寸}{7} \end{gathered}$ | $\begin{gathered} \text { Co } \\ \stackrel{子}{6} \end{gathered}$ |  |  | $\begin{aligned} & \stackrel{\circ}{\circ} \\ & \stackrel{\text { ¢ }}{6} \end{aligned}$ | $\stackrel{\text { ot }}{\stackrel{1}{i}}$ | $\stackrel{8}{\mathrm{i}}$ | $\begin{aligned} & \text { ò } \\ & \text { in } \end{aligned}$ | $\begin{aligned} & \text { ì } \\ & \stackrel{i}{n} \end{aligned}$ | $\begin{aligned} & \text { N. } \\ & \underset{\sim}{1} \end{aligned}$ | $\stackrel{\nearrow}{\infty}$ | $\begin{aligned} & \infty \\ & \stackrel{\infty}{8} \end{aligned}$ | $\begin{aligned} & \underset{\sim}{\infty} \\ & \stackrel{\infty}{=} \end{aligned}$ | $\begin{aligned} & \text { ö̀ } \\ & \text { di } \end{aligned}$ | $\stackrel{\widetilde{e}}{\underset{\infty}{+}}$ |
| 以它歌 |  |  |  |  |  |  |  | $\begin{aligned} & \infty \\ & \stackrel{y}{4} \\ & \end{aligned}$ | $\begin{aligned} & \text { o} \\ & \stackrel{0}{6} \\ & \stackrel{6}{1} \end{aligned}$ |  |  | $\begin{aligned} & \text { B } \\ & \text { 荷 } \\ & \underline{6} \end{aligned}$ |  | $$ |  |  |  |  |  | $$ | $\begin{aligned} & \stackrel{( }{\mathbb{Q}} \\ & \stackrel{\infty}{\bullet} \\ & \stackrel{i}{1} \end{aligned}$ |  |  |  |  |
| 发事要 |  |  |  | $\begin{aligned} & \text { N} \\ & \hat{0} \\ & \\ & \end{aligned}$ | $\begin{aligned} & \bar{\alpha} \\ & \stackrel{\alpha}{4} \\ & \stackrel{1}{6} \end{aligned}$ | $\begin{aligned} & \text { Z } \\ & \text { ה̃ } \\ & \text { ón } \end{aligned}$ |  | $\begin{aligned} & \text { à } \\ & \stackrel{\rightharpoonup}{a} \\ & \stackrel{n}{1} \end{aligned}$ | $\begin{aligned} & \mathscr{\infty} \\ & \stackrel{\infty}{1} \\ & \underset{\sim}{6} \end{aligned}$ | $\begin{aligned} & \text { ty } \\ & \stackrel{\rightharpoonup}{\infty} \\ & \stackrel{\leftrightarrow}{6} \end{aligned}$ |  |  |  | $\begin{aligned} & \stackrel{\circ}{\circ} \\ & \infty \\ & \infty \\ & \underset{\infty}{\circ} \end{aligned}$ |  | $\begin{aligned} & \text { Wy } \\ & \stackrel{y}{7} \\ & \end{aligned}$ |  |  | $\begin{aligned} & \text { Z } \\ & \text { त̂ } \\ & \text { ón } \end{aligned}$ |  |  |  |  |  |  |
| 塞 | $\begin{gathered} \infty \\ \stackrel{\infty}{3} \end{gathered}$ | $\begin{gathered} \text { n } \\ \stackrel{y}{*} \\ \substack{0} \end{gathered}$ | $\begin{gathered} \text { n } \\ \substack{⿱ 乛 亅 心 \\ 0} \end{gathered}$ | $\begin{gathered} \text { N } \\ \substack{+\infty \\ \infty \\ \hline} \end{gathered}$ | $\begin{gathered} \text { ön } \\ \text { © } \\ \text {. } \end{gathered}$ |  |  | $\begin{aligned} & \text { I } \\ & \underset{\mathscr{L}}{\infty} \\ & \text { O} \end{aligned}$ | $\begin{aligned} & \text { b } \\ & \text { N } \\ & 0 \\ & 0 \end{aligned}$ | $\stackrel{\text { Ì }}{8}$ |  | $\begin{aligned} & \overline{\hat{0}} \\ & \text { 区. } \\ & \text { on } \end{aligned}$ | $\stackrel{\infty}{\bar{\sigma}}$ | $\begin{aligned} & \overline{0} \\ & \text { o心. } \\ & \text { ód } \end{aligned}$ | $\begin{gathered} \text { n } \\ \stackrel{y}{*} \\ \underset{\sim}{\circ} \end{gathered}$ | $\begin{aligned} & \text { 呂 } \\ & \text { O. } \end{aligned}$ | $\begin{aligned} & \infty \\ & \stackrel{\infty}{7} \\ & \hline \end{aligned}$ |  |  | $\overline{\hat{\circ}}$ $\stackrel{\circ}{\circ}$ $\stackrel{\circ}{\circ}$ |  | $\begin{aligned} & \text { Co } \\ & \text { O. } \end{aligned}$ | $\begin{aligned} & \infty \\ & \text { B } \\ & \stackrel{\rightharpoonup}{6} \\ & \hline \end{aligned}$ | $\begin{aligned} & \infty \\ & \stackrel{\infty}{\infty} \\ & \stackrel{\infty}{\infty} \\ & 0 \end{aligned}$ | $\begin{aligned} & \infty \\ & \stackrel{\infty}{\infty} \\ & \stackrel{\infty}{\infty} \end{aligned}$ |
| 㳓 |  | さ <br> ö <br> ö | さ <br> ※ <br> ö | $\frac{\bar{i}}{9}$ | $\frac{\bar{i}}{9}$ | $\stackrel{\rightharpoonup}{\circ}$ $\stackrel{\text { or }}{\circ}$ |  | $\frac{\stackrel{N}{a}}{\partial}$ | $\frac{\bar{i}}{\partial}$ | $\begin{aligned} & \bar{\circ} \\ & \underset{寸}{\rightrightarrows} \end{aligned}$ |  | $\begin{aligned} & \bar{\circ} \\ & \underset{寸}{寸} \end{aligned}$ |  | $\begin{aligned} & \bar{\square} \\ & \underset{寸}{4} \end{aligned}$ | さ <br> © <br> ö | $\begin{aligned} & \bar{o} \\ & \underset{寸}{\rightrightarrows} \end{aligned}$ | $\begin{aligned} & \text { D } \\ & \stackrel{\circ}{\circ} \\ & \stackrel{0}{0} \end{aligned}$ | $\begin{aligned} & \bar{o} \\ & \underset{寸}{3} \end{aligned}$ |  |  | $\begin{aligned} & \bar{o} \\ & \underset{寸}{\rightrightarrows} \end{aligned}$ | $\begin{aligned} & \bar{\circ} \\ & \underset{子}{\rightrightarrows} \end{aligned}$ | さ <br> ö <br> ö | O ö ö | さ ※̈ ö |
|  |  |  |  |  | $\begin{aligned} & \text { 第 } \\ & \text { N } \end{aligned}$ |  |  |  | $\begin{aligned} & E \\ & = \\ & \end{aligned}$ |  |  | $\begin{gathered} \text { 合 } \\ \stackrel{y}{\circ} \\ \stackrel{0}{0} \end{gathered}$ |  | $\begin{gathered} \text { N } \\ \stackrel{y}{6} \\ \stackrel{0}{0} \end{gathered}$ |  |  |  |  |  |  |  |  |  |  |  |
| 成事商 | － | － | － | － | － | － | 。 | － | － | － | － | － | － | － | － | $\underset{\substack{\text { 운 } \\ \hline}}{ }$ | － | $\stackrel{\substack{4 \\ ⿻ 丷 木 \\ \hdashline \\ \hline}}{ }$ | － | － | $\begin{aligned} & \stackrel{\circ}{3} \\ & \text { en } \\ & \\ & \hline 1 \end{aligned}$ | $\begin{aligned} & \stackrel{\rightharpoonup}{0} \\ & \text { Con } \\ & \stackrel{0}{n} \end{aligned}$ | － | － | － |
| $\therefore \text { S }$ | － | － | － | $\bigcirc$ | － |  |  | － | － |  | $\begin{gathered} \text { 啇 } \\ \text { 㐌 } \end{gathered}$ | $\begin{aligned} & \text { 容 } \\ & \stackrel{1}{\wedge} \\ & \hline \end{aligned}$ | － |  | $\bigcirc$ | $\begin{aligned} & \text { 은 } \\ & \vdots \end{aligned}$ | － |  | $\begin{aligned} & \text { O} \\ & \text { 商 } \\ & \text { ni } \end{aligned}$ |  |  |  | － | ¢ 管 | 析 |
| स⿵人一口心会 | － | $\begin{aligned} & \text { 若 } \\ & \text { N } \end{aligned}$ |  | － | $\begin{gathered} \infty \\ \stackrel{\text { àn }}{\hat{\alpha}} \end{gathered}$ |  |  | － |  |  | $\begin{gathered} \text { 啇 } \\ \text { " } \\ \hline \end{gathered}$ | $\begin{aligned} & \text { K } \\ & \text { N } \\ & \text { N } \end{aligned}$ | － | $\begin{aligned} & \text { 萑 } \\ & \underset{\sim}{N} \end{aligned}$ |  |  | － |  | $\begin{aligned} & \text { O} \\ & \stackrel{0}{6} \\ & \stackrel{i}{i} \end{aligned}$ | $\begin{aligned} & \text { 花 } \\ & \text { in } \end{aligned}$ | $\underset{\substack{\text { a } \\ \vdots}}{1}$ | $\begin{aligned} & \text { it } \\ & \underset{\vdots}{7} \end{aligned}$ | － | 8 0 0 0 0 |  |
|  |  |  |  | $$ | $\begin{aligned} & \text { 花 } \\ & \text { N } \end{aligned}$ | $\begin{aligned} & \text { O. } \\ & \text { 商 } \\ & \text { ni } \end{aligned}$ |  | $\begin{gathered} \text { 啇 } \\ \text { 品 } \end{gathered}$ | $\begin{aligned} & \text { 啇 } \\ & \text { 品 } \end{aligned}$ |  |  | $\begin{aligned} & \stackrel{R}{0} \\ & \hat{0} \\ & 0 \\ & 0 \\ & \hline \end{aligned}$ |  | $\begin{aligned} & \stackrel{\circ}{\hat{3}} \\ & \stackrel{0}{6} \\ & \stackrel{\rightharpoonup}{6} \end{aligned}$ |  | $\begin{aligned} & \stackrel{\circ}{0} \\ & \stackrel{0}{6} \\ & \stackrel{\rightharpoonup}{6} \end{aligned}$ |  |  |  | $\stackrel{\text { ¢ }}{\substack{\text { N } \\ \text { ¢ }}}$ | $\begin{aligned} & \stackrel{\rightharpoonup}{3} \\ & \text { B } \\ & \\ & \hline 1 \end{aligned}$ | $\stackrel{\substack { \text { ¢ } \\ \begin{subarray}{c}{4 \\ \hdashline{ \text { ¢ } \\ \begin{subarray} { c } { 4 \\ \hdashline } } \\{\hline}\end{subarray}}{ }$ |  |  |  |
| 㕆 | $\geq$ | ＜ | $\geq$ | $0^{\circ}$ | $0^{\circ}$ | 2 | ？ | $0^{\circ}$ | $0^{\circ}$ | $\sim$ | $z$ | $\infty$ | $z$ | $\infty$ | $\geq$ | $\propto$ | $z$ | $\infty$ | $z$ | $\bullet$ | $\infty$ | $\infty$ | $\geq$ | ＞ | z |
| 号 |  |  |  |  | $\left\{\begin{array}{c} 1 \\ 1 \end{array}\right.$ |  |  |  | $\left\{\begin{array}{l} \text { O} \\ \hat{T} \\ 2 \\ y_{0} \\ 0 \\ 0 \\ 1 \\ 1 \\ 1 \\ 2 \end{array}\right.$ |  |  | $\begin{array}{\|c} a \\ z_{2} \\ 0 \\ 0 \end{array}$ |  |  |  |  |  |  |  |  |  |  |  |  |  |

Table 22．24 Cont＇d．The MO to HO intercept geometrical bond parameters of tertiary and quaternary amino boranes and borane amines．$H_{t}$ is a terminal or two－ center $H$ ．$H_{b}$ is a bridge or three－center $H . B_{b}$ is a bridge or three－center $B$ ．$E_{T}$ is $E_{T}$（atom－atom msp ${ }^{3}$ ．AO）．

| がき | 髟 | $\begin{aligned} & \text { 弇 } \\ & \frac{0}{0} \end{aligned}$ |  | $\frac{\overline{y y}}{\frac{5}{0}}$ |  | $\begin{aligned} & \text { 劵 } \\ & \hline \end{aligned}$ | $\begin{aligned} & \frac{\text { 喜 }}{\substack{8}} \end{aligned}$ | $\begin{array}{\|l\|l\|} \hline \text { 采 } \\ \hline \end{array}$ | $\begin{aligned} & \text { 吕 } \\ & \frac{8}{0} \end{aligned}$ |  | $\frac{\tilde{d}}{\underline{d}}$ | $\begin{aligned} & \text { 免 } \\ & \text { Bo } \end{aligned}$ | $\begin{aligned} & \text { 吕 } \\ & \frac{0}{0} \end{aligned}$ | 管 | $\frac{\text { 答 }}{}$ |  |  |  |  |  |  |  |  | 骨堮 |  |  |  | $\begin{aligned} & \text { 㬊 } \end{aligned}$ | 产 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\bigcirc$ ® |  | $\begin{aligned} & \text { 吕 } \\ & \stackrel{y}{b} \end{aligned}$ | 蒿 | $\begin{aligned} & \text { 哭 } \\ & \text { 品 } \end{aligned}$ | 若 | 高鬲 | $\begin{aligned} & \text { 总 } \\ & \substack{0 \\ \hline} \end{aligned}$ | $$ | 号 | $\begin{gathered} \frac{2}{9} \\ \stackrel{y}{9} \end{gathered}$ | 䳋 | $\begin{aligned} & \bar{y} \\ & \text { ⿹勹巳y } \end{aligned}$ | 号 |  | $\frac{\mathrm{O}}{\circ}$ |  |  |  |  |  |  | 気 |  |  | $\stackrel{8}{8}$ | － |  | 㗊 | $\stackrel{\text { ar }}{\text { a }}$ |
| o゙e | 等 | \％ | \％\％ | 京 | $\stackrel{\text { ¢ }}{\text { ¢ }}$ | $\stackrel{8}{7}$ | ¢ | \％ | 永 | 尔 | 守 | $\stackrel{8}{7}$ | 葹 | 8 | \％ |  |  |  |  |  |  |  | \％ | 叞云 | 尔 |  |  | $\stackrel{\circ}{\circ}$ | \％ |
| $\sigma$－ | \％ | $\overline{\underline{\underline{i}}}$ | \％ | \％ | $\stackrel{\otimes}{\stackrel{\circ}{\partial}}$ | ¢ |  | $\overline{\text { \％}}$ | \％ | $\bar{y}$ | $\stackrel{2}{\infty}$ | 僉 | \％ | \％ | $\stackrel{\text { F }}{\substack{\text { ¢ }}}$ |  |  |  |  |  |  | 运 | $\stackrel{\square}{\text { b }}$ | ${ }^{\circ}$ | \％ | ＝ |  | $\stackrel{\text { ¢ }}{\text { en }}$ | \％ |
| － | $\stackrel{ \pm}{ \pm}$ | $\stackrel{\text { ® }}{\text { ® }}$ | $\stackrel{\frac{3}{*}}{\frac{1}{*}}$ | \％ | \％ | \％ |  | \％ | ¢ ¢ | \％ | $\stackrel{\text { ¢ }}{\text { ax }}$ | 8 | ¢ ¢ | $\stackrel{a}{2}$ | \％ |  |  |  |  |  |  |  | \％ | $\stackrel{\circ}{6}$ | $\pm$ | $\overbrace{6}$ |  | 号 | 硻 |
| 4 ${ }^{\text {c }}$ |  | $\begin{aligned} & \text { 亳 } \\ & \stackrel{y}{6} \end{aligned}$ |  | $\stackrel{\circ}{⿳ 亠 丷 厂 犬}$ $\stackrel{y}{6}$ $\stackrel{y}{6}$ |  |  |  | $\begin{aligned} & \stackrel{8}{8} \\ & \stackrel{6}{6} \\ & \stackrel{1}{4} \end{aligned}$ |  |  |  |  |  | $\begin{aligned} & \text { ⿳亠口冋几} \\ & \stackrel{\rightharpoonup}{6} \\ & \hline \end{aligned}$ |  |  |  |  |  |  |  |  |  |  |  |  |  | $\begin{aligned} & \text { 高 } \\ & \text { 亳 } \\ & \hline \end{aligned}$ | － |
| 5 |  | $\begin{aligned} & \frac{2}{6} \\ & \frac{6}{6} \\ & \stackrel{1}{2} \end{aligned}$ | $\begin{aligned} & \text { 嗎 } \\ & \stackrel{6}{6} \end{aligned}$ | $\begin{aligned} & \stackrel{⿳ 士 口 䒑 口 十}{0} \\ & \stackrel{6}{9} \end{aligned}$ |  | $\begin{gathered} \text { 吡 } \\ \stackrel{i}{6} \\ \hline \end{gathered}$ | $\begin{aligned} & \stackrel{\rightharpoonup}{\mathrm{g}} \\ & \stackrel{7}{4} \end{aligned}$ | $\begin{aligned} & \frac{8}{6} \\ & \frac{8}{5} \\ & \hline \end{aligned}$ |  | $\begin{aligned} & \frac{8}{8} \\ & \frac{8}{9} \end{aligned}$ |  | $\begin{aligned} & \text { 皆 } \\ & \stackrel{\rightharpoonup}{4} \end{aligned}$ |  | $\begin{gathered} \text { !ig } \\ \stackrel{\rightharpoonup}{6} \\ \stackrel{\rightharpoonup}{6} \end{gathered}$ |  |  | No |  | $x_{0}^{2}$ |  |  | $5$ |  | $\stackrel{8}{x}$ |  | $\frac{61}{2}$ |  | $\begin{aligned} & \text { 合 } \\ & \substack{n \\ \vdots} \end{aligned}$ | － |
| 3 |  | $\begin{aligned} & \text { 龷 } \\ & \text { R } \end{aligned}$ | 䧺 | 器 |  | $\begin{aligned} & \text { 気 } \\ & \text { gio } \end{aligned}$ | 偘 | $\begin{aligned} & \text { 辜 } \\ & \hline \end{aligned}$ | $\stackrel{\text { 倉 }}{\substack{0}}$ | $\begin{aligned} & \text { 怘 } \\ & \end{aligned}$ | $\begin{aligned} & \text { 僉 } \\ & \text { on } \end{aligned}$ | $\begin{aligned} & \text { 䦈 } \\ & \hline \end{aligned}$ |  | 啇 |  | 気范 | Box ex ex ex |  | ex |  |  | $0$ |  |  |  | 舍 |  | $\begin{aligned} & \text { 龠 } \\ & 0 \end{aligned}$ | 喜 |
| 18 | $\frac{E}{a}$ | $\frac{\bar{G}}{\partial}$ | $\begin{aligned} & \text { 稁 } \\ & \frac{2}{8} \end{aligned}$ | $\frac{E}{\partial}$ | $\frac{\bar{E}}{\partial}$ | $\begin{aligned} & \text { 豆 } \\ & \underset{\sim}{2} \end{aligned}$ | $\begin{aligned} & \text { 喜 } \\ & \hline ⿳ 亠 二 口 又 寸 \end{aligned}$ | $\begin{aligned} & \underline{⿱ ⿱ 乛 冖 丁 口 阝} \\ & \hline \end{aligned}$ | 喜 | $\begin{aligned} & \text { 豆 } \\ & = \\ & \hline \end{aligned}$ |  | $\begin{aligned} & \text { 畐 } \\ & \hline \end{aligned}$ |  | 槀 | $\begin{aligned} & \text { 畐 } \\ & = \end{aligned}$ |  | 㝻鬲 |  |  | 畐畐 |  | Be | $\frac{E}{a}$ | E | $\frac{E}{a}$ | E |  | $\bar{E}$ | E |
|  |  | $\begin{aligned} & E \\ & \hline \end{aligned}$ |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  | （ |  |  |  | $\begin{aligned} & \text { 筑 } \\ & \end{aligned}$ | － |
| 㜢 | － | － | 長 | － | － |  | － | $\begin{aligned} & \text { 膏 } \\ & \text { 品 } \end{aligned}$ | $\begin{aligned} & \text { 稁 } \\ & \text { 毫 } \end{aligned}$ | $\begin{aligned} & \stackrel{\circ}{b_{0}^{2}} \\ & \stackrel{y}{c} \end{aligned}$ | － | $\begin{aligned} & \text { 管 } \\ & \text { en } \end{aligned}$ |  |  | 登 |  |  | －and <br> ar | 令 |  |  |  |  |  |  |  |  | 。 |  |
| 景 | － | － |  | － | － | $\begin{array}{r} \text { 管 } \\ \hline \end{array}$ | － | $\begin{aligned} & \text { 誊 } \\ & \text { 品 } \end{aligned}$ |  | $\begin{aligned} & \text { 誊 } \\ & \text { 品 } \end{aligned}$ |  | $\begin{aligned} & \text { 草 } \\ & \text { 草 } \end{aligned}$ | $\begin{array}{\|c} \substack{\text { 啍 } \\ \vdots \\ \hline} \end{array}$ | $$ | $\begin{aligned} & \text { 曷 } \\ & \stackrel{8}{8} \end{aligned}$ |  | 第 |  |  | $7$ | and |  | - |  |  |  |  | － |  |
|  | － |  | 喜 | － | $\frac{\infty}{\frac{\infty}{\approx}}$ |  | － | $\begin{aligned} & \text { 膏 } \\ & \text { 品 } \end{aligned}$ | $\begin{gathered} \text { 稁 } \\ \text { 亭 } \end{gathered}$ |  |  | $\begin{aligned} & \text { 管 } \\ & \end{aligned}$ | $\begin{aligned} & \text { 喿 } \\ & \text { 亳 } \end{aligned}$ | $\begin{aligned} & \text { 年 } \\ & \hline \end{aligned}$ | $\begin{aligned} & \text { 苞 } \\ & \text { B } \end{aligned}$ |  |  |  |  | 筥采 |  | Bo |  |  |  | 边 |  | － | $\frac{\square}{\frac{\infty}{z}}$ |
| 成氛彦 | $\begin{aligned} & \text { 譗 } \\ & \hline \end{aligned}$ | 㞗 | $\begin{aligned} & \text { 喜 } \\ & \text { 亭 } \end{aligned}$ | $\begin{aligned} & \text { 喜 } \\ & \text { 亭 } \end{aligned}$ |  | 薃 | 䯉 | $\begin{aligned} & \text { I్ } \\ & \text { 镸 } \end{aligned}$ | 登 | 产 | 产 | $\begin{aligned} & \text { I్ } \\ & \text { 髟 } \end{aligned}$ | $\begin{array}{\|l\|l\|} \hline \text { In } \\ \hline \end{array}$ | $\begin{aligned} & \text { 管 } \\ & \text { en } \end{aligned}$ |  | $2$ | $2$ | $\stackrel{9}{9}$ | ? |  |  | $8$ |  |  |  |  |  |  | \％ |
| 莀 | 0 | $0^{\circ}$ | z | $0^{\circ}$ | $0^{\circ}$ | $\sim$ | $z$ | $\infty$ | $z$ | $\sim$ | $z$ | $\cdots$ | $z$ | $\infty$ | $\infty$ | $\propto$ |  |  |  |  |  | 00 |  |  |  |  | $\checkmark$ | 0 | 0 |
| 笓 |  |  |  |  |  | $0$ | 泼 |  |  |  |  |  |  |  |  |  |  |  |  | $\begin{array}{ll} \Xi & 3 \\ 0 \end{array}$ | T |  | R10 | a | $\begin{gathered} 0 \\ 0 \end{gathered}$ |  |  | $$ |  |

Table 22.25. The energy parameters $(e V)$ of functional groups of tertiary and quaternary amino boranes and borane amines.

Table 22.26. The total bond energies of tertiary and quaternary amino boranes and borane amines calculated using the functional group composition and the energies

| Formula | Name | $\begin{gathered} B-N \\ \text { (i) } \\ \text { Group } \end{gathered}$ | $\begin{aligned} & B-N \\ & \text { (ii) } \\ & \text { Group } \end{aligned}$ | $\begin{gathered} C-N \\ \text { (i) } \\ \text { Group } \end{gathered}$ | $\begin{gathered} C-N \\ \text { (iii) } \\ \text { Giroup } \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{B}_{2} \mathrm{H}_{2} \mathrm{~N}$ | aminodiborane | 1 | 0 | 0 | 0 |
| ${ }^{\mathrm{B}_{2} \mathrm{C}_{2} \mathrm{H}_{1} \mathrm{~N}}$ | n-dimethylaminodiborane | 1 | 0 | 0 | 2 |
| $\mathrm{C}_{6} \mathrm{H}_{3} \mathrm{~N}_{3} \mathrm{~B}$ | tris(dimethylaminobborane | 3 | 0 | 0 | 6 |
| $\mathrm{C}_{8} \mathrm{H}_{22} \mathrm{NB}$ | di-n-butylboronamine | 1 | 0 | 0 | 0 |
| $\mathrm{C}_{12} \mathrm{H}_{2} \mathrm{NB}$ | di-n-butylboron-n-butylamine | 1 | 0 | 1 | 0 |
| $\mathrm{C}_{2} \mathrm{H}_{0} \mathrm{NB}^{\text {a }}$ | dimethylaminoborane | 0 | 1 | 0 | 2 |
| ${ }^{8 C_{3} H_{2} \mathrm{~N}}$ | trimethylaminoborane | 0 | 1 | 0 | 0 |
| $\mathrm{BC}_{3} \mathrm{H}_{2} \mathrm{~N}$ | ammonia-trimethylborane | 0 | 1 | 0 | 0 |
| $\mathrm{C}_{6} \mathrm{H}_{4} \mathrm{SNB}^{\text {N }}$ | triethylaminoborane | 0 | 1 | 0 | 0 |
| ${ }^{\text {BCa }}$ | trimethylaminotrimethylborane | 0 | 1 | 0 | 0 |

Table 22.27. The bond angle parameters of tertiary and quaternary amino boranes and borane amines and experimental values. $H_{t}$ is a terminal or two-center $H$. $H_{b}$ is a bridge or three-center $H$. In the calculation of $\theta_{v}$, the parameters from the preceding angle were used. $E_{T}$ is $E_{T}$ (atom-atom msp ${ }^{3} . A O$ ).


## HALIDOBORANES

The halidoboranes each comprise at least one $B$ bound by a boron-halogen single bond comprising a $B-X$ group where $X=F, C l, B r, I$, and may further comprise one or more alkyl groups and borane moieties. The latter comprise alkyl and aryl moieties and $B-C, B-H, B-B, B-H-B$, and $B-B-B$ functional groups wherein the $B-C$ group is equivalent to that of alkyl boranes, and the $B-H, B-B, B-H-B$, and $B-B-B$ functional groups are equivalent to those in boranes given in the corresponding sections. Alkoxy boranes and borinic acids moieties given in the Alkoxy Boranes and Alkyl Borinic Acids $\left((R O)_{q} B_{r} H_{s}(H O)_{t}\right)$ section may be bound to the $B-X$ group by a $B-O$ functional group. The former further comprise at least one boron-alkyl-ether moiety, and the latter comprise one or more hydroxyl groups, respectively. Each alkoxy moiety, $C_{n} H_{2 n+1} \mathrm{O}$, comprises one of two types of $\mathrm{C}-\mathrm{O}$ functional groups that are equivalent to those given in the Ethers $\left(C_{n} H_{2 n+2} O_{m}, n=2,3,4,5 \ldots \infty\right)$ section. One is for methyl or t-butyl groups, and the other is for general alkyl groups. Each borinic acid hydroxyl functional group is equivalent to that given in the Alcohols ( $\left.C_{n} H_{2 n+2} O_{m}, n=1,2,3,4,5 \ldots \infty\right)$ section.

Tertiary amino-borane and borane-amine moieties given in the Tertiary and Quaternary Aminoboranes and Borane Amines $\left(R_{q} B_{r} N_{s} R_{t} ; R=H ;\right.$ alkyl $)$ section can be bound to the $B-X$ group by a $B-N$ functional group. The nitrogen atom of each $B-N$ functional group is bound to two other atoms such that there are a total of three bonds per atom. The amino or amine moiety may comprise $\mathrm{NH}_{2}, \mathrm{~N}(\mathrm{H}) \mathrm{R}$, and $\mathrm{NR}_{2}$. The corresponding functional group for the $\mathrm{NH}_{2}$ moiety is the $\mathrm{NH}_{2}$ functional group given in the Primary Amines $\left(C_{n} H_{2 n+2+m} N_{m}, n=1,2,3,4,5 \ldots \infty\right)$ section. The $N(H) R$ moiety comprises the $N H$ functional group of the Secondary Amines $\left(C_{n} H_{2 n+2+m} N_{m}, n=2,3,4,5 \ldots \infty\right)$ section and the $C-N$ functional group of the Primary Amines $\left(C_{n} H_{2 n+2+m} N_{m}, \quad n=1,2,3,4,5 \ldots \infty\right)$ section. The $N R_{2}$ moiety comprises 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 given in the Secondary Amines ( $\left.C_{n} H_{2 n+2+m} N_{m}, \quad n=2,3,4,5 \ldots \infty\right)$ section.

Quaternary amino-borane and boraneamine moieties given in the Tertiary and Quaternary Aminoboranes and Borane Amines $\left(R_{q} B_{r} N_{s} R_{t} ; R=H ;\right.$ alkyl $)$ section can be bound to the $B-X$ group by a $B-N$ functional group. The nitrogen atom of each $B-N$ bond is bound to three other atoms such that there are a total of four bonds per atom. The amino or amine moiety may comprise $\mathrm{NH}_{3}, \mathrm{~N}\left(\mathrm{H}_{2}\right) \mathrm{R}, \mathrm{N}(\mathrm{H}) \mathrm{R}_{2}$, and $\mathrm{NR}_{3}$. The corresponding functional group for the $\mathrm{NH}_{3}$ moiety is ammonia given in the Ammonia $\left(\mathrm{NH}_{3}\right)$ section. The $\mathrm{N}\left(\mathrm{H}_{2}\right) \mathrm{R}$ moiety comprises the $\mathrm{NH}_{2}$ and the $\mathrm{C}-\mathrm{N}$ functional groups given in the Primary Amines $\left(C_{n} H_{2 n+2+m} N_{m}, n=1,2,3,4,5 \ldots \infty\right)$ section. The $N(H) R_{2}$ moiety comprises the $N H$ 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 given in the Secondary Amines $\left(C_{n} H_{2 n+2+m} N_{m}, n=2,3,4,5 \ldots \infty\right)$ section. The $N R_{3}$ moiety comprises the $C-N$ functional group of tertiary amines given in the Tertiary Amines ( $\left.C_{n} H_{2 n+3} N, n=3,4,5 \ldots \infty\right)$ section.

The alkyl portion may be part of the alkoxy moiety, amino or amine moiety, or an alkyl group, or it may be bound to the central boron atom by a carbon-boron single bond comprising the $C-B$ group of the Alkyl Boranes $\left(R_{x} B_{y} H_{z} ; R=\right.$ alkyl $)$ section. Each alkyl portion may comprise at least a terminal methyl group ( $\mathrm{CH}_{3}$ ) and methylene ( $\mathrm{CH}_{2}$ ), methylyne ( CH ), and $C-C$ functional groups. 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 $\mathrm{C}-\mathrm{C}$ bonds within isopropyl $\left(\left(\mathrm{CH}_{3}\right)_{2} \mathrm{CH}\right)$ and t-butyl $\left(\left(\mathrm{CH}_{3}\right)_{3} \mathrm{C}\right)$ groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups. Additional $R$ groups include aromatics such as phenyl and $-\mathrm{HC}=\mathrm{CH}_{2}$. These groups in halidobroanes are equivalent to those in branched-chain alkanes, aromatics, and alkenes given in the corresponding sections.

The bonding in the $B-X$ functional groups of halidoboranes is similar to that of the $B-O$ and $B-N$ groups of alkoxy boranes and borinic acids and tertiary and quaternary amino boranes and borane amines given in the corresponding sections. The MO semimajor axes of the $B-X$ functional groups are determined from the force balance equation of the centrifugal, Coulombic, and magnetic forces as given in the Boranes $\left(B_{x} H_{y}\right)$ section. In each case, the distance from the origin of the $H_{2}-$ type-ellipsoidal-MO to each focus $c^{\prime}$, the internuclear distance $2 c^{\prime}$, and the length of the semiminor axis of the prolate spheroidal $H_{2}$-type MO $b=c$ are solved from the semimajor axis $a$. Then, the geometric and energy parameters of each MO are calculated using Eqs. (15.1-15.117).

As in the case of the $B-O$ - and $B-N$-bond MOs, the $\sigma$-MOs of the $B-X$-bond MOs are energy matched to the $B 2 s p^{3} \mathrm{HO}$ which determines that the parameters of the force balance equation based on electron angular momentum are determined by those of the boron atom. The parameters of the force balance equation for the $\sigma-\mathrm{MO}$ of the $B-F$-bond MO in Eqs. (22.18-22.22) are $n_{e}=1$ and $|L|=0$ :

$$
\begin{equation*}
\frac{\hbar^{2}}{m_{e} a^{2} b^{2}} D=\frac{e^{2}}{8 \pi \varepsilon_{0} a b^{2}} D+\frac{\hbar^{2}}{2 m_{e} a^{2} b^{2}} D-\left(\frac{1}{2}\right) \frac{\hbar^{2}}{2 m_{e} a^{2} b^{2}} D \tag{22.53}
\end{equation*}
$$

From Eq. (22.53), the semimajor axis of the tertiary $B-F$-bond MO is

$$
\begin{equation*}
a=1.5 a_{0} \tag{22.54}
\end{equation*}
$$

The force balance equation for each $\sigma-\mathrm{MO}$ of the $B-C l$ is equivalent to that of the $B-B$-bond MO with $n_{e}=2$ and $|L|=3 \sqrt{\frac{3}{4}} \hbar$ corresponding to three electrons of the $B 2 s p^{3}$ shell is:

$$
\begin{align*}
& \frac{\hbar^{2}}{m_{e} a^{2} b^{2}} D=\frac{e^{2}}{8 \pi \varepsilon_{0} a b^{2}} D+\frac{\hbar^{2}}{2 m_{e} a^{2} b^{2}} D-\left(1+\frac{3 \sqrt{\frac{3}{4}}}{Z}\right) \frac{\hbar^{2}}{2 m_{e} a^{2} b^{2}} D  \tag{22.55}\\
& a=\left(2+\frac{3 \sqrt{\frac{3}{4}}}{Z}\right) a_{0} \tag{22.56}
\end{align*}
$$

With $Z=5$, the semimajor axis of the $B-C l$-bond MO is:

$$
\begin{equation*}
a=2.51962 a_{0} \tag{22.57}
\end{equation*}
$$

The hybridization of the bonding in the $B-X$ functional groups of halidoboranes is similar to that of the $C-X$ groups of alkyl halides given in the corresponding sections. For the $B-X$ functional groups, hybridization of the $2 s$ and $2 p$ AOs of $B$ to form single $2 s p^{3}$ shells forms an energy minimum, and the sharing of electrons between the $B 2 s p^{3} \mathrm{HO}$ and $X \mathrm{AO}$ to form a MO permits each participating orbital to decrease in radius and energy. The $F$ AO has an energy of $E(F)=-17.42282 \mathrm{eV}$, and the $B 2 s p^{3}$ HOs have an energy of $E\left(B, 2 s p^{3}\right)=-11.80624 \mathrm{eV}$ (Eq. (22.7)). To meet the equipotential condition of the union of the $B-F \quad H_{2}$-type-ellipsoidal-MO with these orbitals, the hybridization factor $c_{2}$ of Eq. (15.61) for the $B-F$-bond MO given by Eq. (15.77) is:

$$
\begin{equation*}
c_{2}\left(F A O \text { to } B 2 s p^{3} H O\right)=\frac{E\left(B, 2 s p^{3}\right)}{E(F A O)}=\frac{-11.80624 \mathrm{eV}}{-17.42282 \mathrm{eV}}=0.68285 \tag{22.58}
\end{equation*}
$$

Since the energy of the MO is matched to that of the $B 2 s p^{3} \mathrm{HO}, E(A O / H O)$ in Eqs. (15.51) and (15.61) is $E\left(B, 2 s p^{3}\right)$ given by Eq. (22.7).
$E_{T}\left(\right.$ atom-atom, $\left.m s p^{3} . A O\right)$ of the $B-F$-bond MO is determined by considering that the bond involves an electron transfer from the boron atom to the fluorine atom to form zwitterions such as $H_{2} B^{+}-F^{-}$. By considering the electron redistribution in the fluoroborane as well as the fact that the central field decreases by an integer for each successive electron of the shell, the radius $r_{B-F b o r a n e 2 s p^{3}}$ of the $B 2 s p^{3}$ shell may be calculated from the Coulombic energy using Eq. (15.18).

$$
\begin{equation*}
r_{B-\text { Fborane } 2 p^{3}}=\left(\sum_{n=2}^{4}(Z-n)-1\right) \frac{e^{2}}{8 \pi \varepsilon_{0}(e 74.89168 e V)}=\frac{5 e^{2}}{8 \pi \varepsilon_{0}(e 74.89168 e V)}=0.90837 a_{0} \tag{22.59}
\end{equation*}
$$

Using Eqs. (15.19) and (22.13), the Coulombic energy $E_{\text {Coulomb }}\left(B_{B-\text { Fborane }}, 2 s p^{3}\right)$ of the outer electron of the $B 2 s p^{3}$ shell is:

$$
\begin{equation*}
E_{\text {Coulomb }}\left(B_{B-F b o r a n e}, 2 s p^{3}\right)=\frac{-e^{2}}{8 \pi \varepsilon_{0} r_{B-F b o r a n e 2 s p^{3}}}=\frac{-e^{2}}{8 \pi \varepsilon_{0} 0.90837 a_{0}}=-14.97834 \mathrm{eV} \tag{22.60}
\end{equation*}
$$

During hybridization, one of the spin-paired $2 s$ electrons is promoted to the $B 2 s p^{3}$ shell as an unpaired electron. The energy for the promotion is the magnetic energy given by Eq. (22.6). Using Eqs. (22.6) and (22.60), the energy $E\left(B_{B-X b o r a n e}, 2 s p^{3}\right)$ of the outer electron of the $B 2 s p^{3}$ shell is:

$$
\begin{equation*}
E\left(B_{B-F b o r a n e}, 2 s p^{3}\right)=\frac{-e^{2}}{8 \pi \varepsilon_{0} r_{B-F b o r a n e 2 s p^{3}}}+\frac{2 \pi \mu_{0} e^{2} \hbar^{2}}{m_{e}^{2}\left(r_{3}\right)^{3}}=-14.97834 \mathrm{eV}+0.09100 \mathrm{eV}=-14.88734 \mathrm{eV} \tag{22.61}
\end{equation*}
$$

Thus, $E_{T}\left(B-F, 2 s p^{3}\right)$, the energy change of each $B 2 s p^{3}$ shell with the formation of the $B-F$-bond MO is given by the difference between Eq. (22.15) and Eq. (22.7).

$$
\begin{equation*}
E_{T}\left(B-F, 2 s p^{3}\right)=E\left(B_{B-F b o r a n e}, 2 s p^{3}\right)-E\left(B, 2 s p^{3}\right)=-14.88734 \mathrm{eV}-(-11.80624 \mathrm{eV})=-3.08109 \mathrm{eV} \tag{22.62}
\end{equation*}
$$

Thus, $E_{T}\left(\right.$ atom-atom, $\left.m s p^{3} . A O\right)$ for ternary $B-F$ is -6.16219 eV corresponding to the maximum charge contribution of an electron given by two times Eq. (22.62).

In chloroboranes, the energies of chlorine and boron are less than the Coulombic energy between the electron and proton of $H$ given by Eq. (1.264). Thus, $c_{1}$ and $c_{2}$ in Eq. (15.61) are one, and the energy matching condition is determined by the $C_{2}$ parameter. The $C l$ AO has an energy of $E(C l)=-12.96764 \mathrm{eV}$, and the $B 2 s p^{3} \mathrm{HOs}$ have an energy of $E\left(B, 2 s p^{3}\right)=-11.80624 \mathrm{eV}$ (Eq. (22.7)). To meet the equipotential condition of the union of the $\mathrm{B}-\mathrm{Cl} \mathrm{H}_{2}$-type-ellipsoidal-MO with these orbitals, the hybridization factor $c_{2}$ of Eq. (15.61) for the $B-C l$-bond MO given by Eq. (15.77) is:

$$
\begin{equation*}
C_{2}\left(C l A O \text { to } B 2 s p^{3} \mathrm{HO}\right)=\frac{E\left(B, 2 s p^{3}\right)}{E(C l A O)}=\frac{-11.80624 \mathrm{eV}}{-12.96764 \mathrm{eV}}=0.91044 \tag{22.63}
\end{equation*}
$$

Since the energy of the MO is matched to that of the $B 2 s p^{3} \mathrm{HO}, E(A O / H O)$ in Eqs. (15.51) and (15.61) is $E\left(B, 2 s p^{3}\right)$ given by Eq. (22.7), and $E_{T}\left(\right.$ atom - atom, $\left.m s p^{3} . A O\right)$ is given by two times Eq. (22.12) corresponding to the two centers.

Consider next the radius of the HO due to the contribution of charge to more than one bond. The energy contribution due to the charge donation at each boron atom and halogen atom superimposes linearly. In general, since the energy of the $B 2 s p^{3}$ HO and $X \mathrm{AO}$ is matched to that of the $C 2 s p^{3} \mathrm{HO}$ when a molecule contains a $C-B$-bond MO and a $C-X$-bond MO, respectively, the corresponding radius $r_{\text {mol } 2 s p^{3}}$ of the $B 2 s p^{3} \mathrm{HO}$ of a boron atom, the $C 2 s p^{3} \mathrm{HO}$ of a carbon atom, and the $X$ AO of a given halidoborane molecule is calculated after Eq. (15.32) by considering $\sum E_{T_{m o l}}\left(M O, 2 s p^{3}\right)$, the total energy donation to all bonds with which it participates in bonding. The Coulombic energy $E_{\text {Coulomb }}\left(\right.$ atom, $2 s p^{3}$ ) of the outer electron of the atom $2 s p^{3}$ shell considering the charge donation to all participating bonds is given by Eq. (15.14). In the case that the boron or halogen atom is not bound to a $C 2 s p^{3} \mathrm{HO}, r_{\text {mol } 2 s p^{3}}$ is calculated using Eq. (15.31) where $E_{\text {Coulomb }}\left(\right.$ atom, $\left.m s p^{3}\right)$ is $E_{\text {Coulomb }}\left(B 2 s p^{3}\right)=-11.89724 \mathrm{eV}, E(F)=-17.42282 \mathrm{eV}$, or $E(C l)=-12.96764 \mathrm{eV}$. The hybridization parameters used in Eqs. (15.88-15.117) for the determination of bond angles of halidoboranes are given in Table 22.28.

Table 22.28. Atom hybridization designation (\# first column) and hybridization parameters of atoms for determination of bond angles with final values of $r_{2 s p^{3}}, E_{\text {Coulomb }}\left(\right.$ atom, $\left.2 s p^{3}\right)$ (designated as $\left.E_{\text {Coulomb }}\right)$, and $E\left(\right.$ atom $\left._{B-\text { Xborane }} 2 s p^{3}\right)$ (designated as $E$ ) calculated using the appropriate values of $\sum E_{T_{m o l}}\left(M O, 2 s p^{3}\right)$ (designated as $E_{T}$ ) for each corresponding terminal bond spanning each angle.

| $\#$ | $E_{T}$ | $E_{T}$ | $E_{T}$ | $E_{T}$ | $E_{T}$ | $r_{3 s p^{3}}$ | $E_{\text {Coulomb }}$ <br> $(\mathrm{eV})$ <br> Final | $E$ <br> (eV) <br> Final |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | -0.56370 | 0 | 0 | 0 | 0 | 0.95939 <br> (Eq.(15.31)) | -14.18175 |  |
| 2 | -3.08109 | -3.08109 | 0 | 0 | 0 | 0.75339 <br> (Eq.(15.31)) | -18.05943 | -17.96843 |
| 3 | -3.08109 | 0 | 0 |  | 0 | 0.66357 <br> $($ (Eq. (15.31)) | -20.50391 | -20.26346 |

The symbols of the functional groups of halidoboranes are given in Table 22.29. The geometrical (Eqs. (15.1-15.5) and (22.47)), intercept (Eqs. (15.31-15.32) and (15.80-15.87)), and energy (Eq. (15.61), (22.4), (22.7), (22.12), (22.48), and (22.52)) parameters of halidoboranes are given in Tables 22.30, 22.31, and 22.32, respectively. In the case that the MO does not intercept the $B \mathrm{HO}$ due to the reduction of the radius from the donation of $B 2 s p^{3} \mathrm{HO}$ charge to additional MOs, the energy of each MO is energy matched as a linear sum to the $B$ HO by contacting it through the bisector current of the intersecting MOs as described in the Methane Molecule $\left(\mathrm{CH}_{4}\right)$ section. The total energy of each halidoborane given in Table 22.33 was calculated as the sum over the integer multiple of each $E_{D}($ Group $)$ of Table 22.32 corresponding to functional-group composition of the molecule. $E_{\text {mag }}$ of Table 22.33 is given by Eqs. (15.15) and (22.3) for the $B-X$ groups and the $B-O, B-N, B-H, B-B, B-H-B$, and $B-B-B$ groups. $E_{\text {mag }}$ of Table 22.33 is given by Eqs. (15.15) and (10.162) for the $O H$ group. The bond angle parameters of halidoboranes determined using Eqs. (15.88-15.117) are given in Table 22.34. The charge-densities of exemplary fluoroborane, boron trifluoride and choloroborane, boron trichloride comprising the concentric shells of atoms with the outer shell bridged by one or more $\mathrm{H}_{2}$-type ellipsoidal MOs or joined with one or more hydrogen MOs are shown in Figures 22.9 and 22.10, respectively.

Figure 22.10. (A) Boron Trifluoride. Color scale, translucent view of the charge-density of $B F_{3}$ showing the orbitals of the $B$ and $F$ atoms at their radii, and the ellipsoidal surface of each $H_{2}$-type ellipsoidal MO that transitions to the corresponding outer shell of the atoms participating in each bond. (B) Boron Trichloride. Color scale, translucent views of the charge-density of $\mathrm{BCl}_{3}$ showing the orbitals of the B and Cl atoms at their radii, and the ellipsoidal surface of each $\mathrm{H}_{2}$-type ellipsoidal MO that transitions to the corresponding outer shell of the atoms participating in each bond.


Table 22.29. The symbols of the functional groups of halidoboranes.

| Functional Group | Group Symbol |
| :---: | :---: |
| $B-F$ bond | $B-F$ |
| $B-\mathrm{Cl}$ bond | $B-C l$ |
| $B-N$ bond $3^{\circ}$ | $B-N$ (i) |
| $B-N$ bond $4^{\circ}$ | $B-N$ (ii) |
| $C-N$ bond $1^{\circ}$ amine | $C-N$ (i) |
| $C-N$ bond $2^{\circ}$ amine (methyl) | $C-N$ (ii) |
| $C-N$ bond $2^{\circ}$ amine (alkyl) | $C-N$ (iii) |
| $C-N$ bond $3^{\circ}$ amine | $C-N$ (iv) |
| $\mathrm{NH}_{3}$ group | $\mathrm{NH}_{3}$ |
| $\mathrm{NH}_{2}$ group | $\mathrm{NH}_{2}$ |
| NH group | NH |
| $B-O$ bond (borinic acid) | $B-O$ (i) |
| $B-O$ bond (alkoxy borane) | $B-O$ (ii) |
| OH group | OH |
| $\mathrm{C}-\mathrm{O}\left(\mathrm{CH}_{3}-\mathrm{O}-\mathrm{and}\left(\mathrm{CH}_{3}\right)_{3} \mathrm{C}-\mathrm{O}-\right)$ | $\mathrm{C}-\mathrm{O}$ (i) |
| C-O (alkyl) | $C-O$ (ii) |
| $C-B$ bond | $C-B$ |
| $B H$ bond | B-H |
| BHB (bridged $H$ ) | $B-H-B$ |
| $B B$ bond | $B-B$ |
| $B B B$ (bridged B) | $B-B-B$ |
| $C C$ (aromatic bond) | $C \stackrel{3 e}{=} C$ |
| CH (aromatic) | CH (i) |
| $\mathrm{CH}_{3}$ group | $\mathrm{C}-\mathrm{H}\left(\mathrm{CH}_{3}\right)$ |
| $\mathrm{CH}_{2}$ alkyl group | $\mathrm{C}-\mathrm{H}\left(\mathrm{CH}_{2}\right)$ (i) |
| CH | $C-H$ (ii) |
| $C C$ bond ( $n-C$ ) | $C-C$ (a) |
| CC bond (iso-C) | $C-C$ (b) |
| $\mathrm{HC}=\mathrm{CH}_{2} \mathrm{HC}$ (ethylene bond) | $C=C$ |
| $\underline{\mathrm{CH}_{2} \text { alkenyl group }}$ | $\mathrm{CH}_{2}$ (ii) |

Table 22.30 A . The geometrical bond parameters of halidoboranes and experimental values.

| Parameter | $\begin{aligned} & B-F \\ & \text { Group } \end{aligned}$ | $\begin{aligned} & B-C l \\ & \text { Group } \end{aligned}$ | $\begin{gathered} B-N(\text { (i) } \\ \text { Group } \end{gathered}$ | $\begin{gathered} B-N \text { (ii) } \\ \text { Group } \end{gathered}$ | $\begin{gathered} C-N(i) \\ \text { Group } \end{gathered}$ | $\begin{gathered} C-N \text { (ii) } \\ \hline \text { Group } \end{gathered}$ | $\begin{gathered} C-N \text { (iii) } \\ \text { Group } \end{gathered}$ | $\begin{aligned} & C-N(\text { (iv) } \\ & \text { Group } \end{aligned}$ | $\underset{\text { Croun }}{\substack{3}}$ | $\underset{\mathrm{Crou}}{\mathrm{Cr}}$ | $\begin{gathered} N H \\ \text { Group } \end{gathered}$ | $\begin{gathered} B-O(i) \\ \text { Group } \end{gathered}$ | $\underset{\substack{B-O \\ \text { Group }}}{ }$ | $\begin{gathered} \text { Group } \\ \text { Grou } \end{gathered}$ | $\begin{gathered} C-O(\mathrm{i}) \\ \text { Group } \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $a\left(a_{0}\right)$ | 1.5 | 2.51962 | 2.01962 | 2.01962 | 1.92682 | 1.94862 | 1.94862 | 1.96313 | 1.34750 | 1.28083 | 1.26224 | 2.00000 | 2.00000 | 1.26430 | 1.80717 |
| $c^{\prime}\left(a_{0}\right)$ | 1.22474 | 1.66357 | 1.28744 | 1.57679 | 1.38810 | 1.39593 | 1.39593 | 1.40112 | 0.97961 | 0.95506 | 0.94811 | 1.31678 | 1.29455 | 0.91808 | 1.34431 |
| $\begin{aligned} & \text { Bond } \\ & \text { Lengh } \\ & \text { Len } \\ & \hline c^{\prime}(A) \\ & \hline \end{aligned}$ | 1.29621 | 1.76065 | 1.36257 | 1.66880 | 1.46910 | 1.47739 | 1.47739 | 1.48288 | 1.03677 | 1.0108 | 1.00343 | 1.39362 | 1.37009 | 0.971651 | 1.42276 |
| Exp. Bond Length (A) | $\begin{gathered} 1.313[10] \\ \left(B F_{3}\right) \end{gathered}$ | $\begin{aligned} & 1.761[17] \\ & \left(\text { PhBCl }_{2}\right) \end{aligned}$ | $\underset{(B N)}{1.281[5]}$ | $\begin{gathered} 1.638[17] \\ \left.\left(\mathrm{CH}_{3}\right)_{3} N B H_{3}\right) \end{gathered}$ | $\begin{gathered} 1.471[10] \\ \text { (methylamine) } \end{gathered}$ | $\begin{gathered} 1.455[10] \\ \text { (dimethylamine) } \end{gathered}$ |  | $\begin{gathered} 1.458[10] \\ \text { (trimethylamine) } \end{gathered}$ | $\underset{\substack{1.0120[10] \\ \text { (ammonia) }}}{1}$ | $\begin{gathered} 1.010[10] \\ \text { (methylamine) } \end{gathered}$ | $\begin{gathered} 1.00[10] \\ \text { (dimethylamine) } \end{gathered}$ | $\begin{aligned} & 1.376[17] \\ & \left(\mathrm{B}(\mathrm{OH})_{3}\right) \end{aligned}$ | $\begin{gathered} 1.367[17] \\ \left(B\left(\mathrm{OCH}_{3}\right)_{3}\right) \end{gathered}$ | $\begin{gathered} 0.971[10] \\ \text { (ethanol) } \\ \text { (e.945 } 1[10] \\ \text { (methanol) } \end{gathered}$ | $\begin{gathered} 1.424[17] \\ \left(B\left(14 C H_{3}\right)\right. \\ 1.410[10] \\ (\text { dimethy lether) }) \end{gathered}$ |
| $b, c\left(a_{0}\right)$ | 0.86603 | 1.89235 | 1.55607 | 1.26198 | 1.33634 | ${ }^{1.35960} 0$ | 1.35960 | 1.37505 0.71372 | 0.92527 | 0.85345 | ${ }_{0}^{0.83327} 0$ | 1.50535 | 1.52452 | 0.86925 | 1.20776 |

Table 22.30B. The geometrical bond parameters of halidoboranes and experimental values.

| Parameter | $\begin{gathered} C-O \text { (ii) } \\ \text { Group } \end{gathered}$ | $\begin{gathered} C-B \\ \text { Group } \end{gathered}$ | $\begin{aligned} & B-H \\ & \text { Group } \end{aligned}$ | $\begin{gathered} B-H-B \\ \text { Group } \end{gathered}$ | $\begin{gathered} B-B \\ \text { and } \\ B-B-B \\ \text { Groups } \end{gathered}$ | $\begin{gathered} C^{3 . C} C \\ \text { Group } \end{gathered}$ | $\begin{gathered} \mathrm{CH} \text { (i) } \\ \text { Group } \end{gathered}$ | $\underset{\text { Group }}{\mathrm{C}-\mathrm{H}\left(\mathrm{CH}_{3}\right)}$ | $\underset{\text { Group }}{\mathrm{C-H}\left(\mathrm{CH}_{2}\right)}$ | $\begin{gathered} C-H \text { (ii) } \\ \text { Group } \end{gathered}$ | $\underset{\substack{C-C(\text { a) } \\ \text { Group }}}{ }$ | $\begin{gathered} C-C(b) \\ \text { Group } \end{gathered}$ | $\begin{aligned} & C=C \\ & \text { Group } \end{aligned}$ | $\begin{aligned} & \mathrm{CH}_{2} \text { (ii) } \\ & \text { Group } \end{aligned}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $a\left(a_{0}\right)$ | 1.79473 | 1.78528 | 1.6982 | 2.00000 | 2.51962 | 1.47348 | 1.60061 | 1.64920 | 1.67122 | 1.67465 | 2.12499 | 2.12499 | 1.47228 | . 64010 |
| $c^{\prime}\left(a_{c}\right)$ | 1.33968 | 1.48762 | 1.136 | 234 | 1.6 | 1.314 | 1329 | 1.048 | 1.055 | 1.05661 | 1.4574 | 1.4574 | 1.266 | 1.045 |
| $\begin{aligned} & \text { Bond } \\ & \text { Lengh } \\ & 2 c^{\prime}(A) \end{aligned}$ | 1.41785 | 1.57443 | 1.20235 | 1.30689 | 1.79654 | 1.39140 | 1.09327 | 1.10974 | 1.11713 | 1.11827 | 1.54280 | 1.54280 | 1.34052 | 1.10668 |
| $\begin{gathered} \text { Exp. } \\ \text { Bond } \\ \text { Bength } \end{gathered}$ $(A)$ | $\begin{gathered} 1.418[10] \\ \text { (ethyl methyl ether } \\ \text { (avg.)) } \end{gathered}$ | $\begin{gathered} 1.578[10] \\ \text { (rimethylobare) } \\ 1.58(1010] \\ \text { di.2. } \\ \text { dimethydiborane) } \end{gathered}$ | $\begin{gathered} 1.19[4] \\ \text { (diborane) } \end{gathered}$ | $\begin{gathered} 1.32[4] \\ \text { (diborane) } \end{gathered}$ | $\begin{aligned} & 1.798[3] \\ & \left(B_{11} H_{19}\right) \end{aligned}$ | $\begin{gathered} 1.39[10] \\ \text { (benzene) } \end{gathered}$ | $\begin{aligned} & 1.101[10] \\ & (\text { benzene } \end{aligned}$ | $1.114[10]$ $(C-H$ trimethyliborane $)$ $1.107[10]$ $(C-H$ propane $)$ 1.117 [10] $(C-H$ butane $)$ | $\begin{gathered} 1.107 \text { [10] } \\ \left(\begin{array}{c} \text { ( }-1.110 p a n e) ~ \\ 1010] \\ (C-H \text { butane }) \end{array}\right. \end{gathered}$ | $\begin{gathered} 1.122[10] \\ (\text { (isobuane) } \end{gathered}$ |  |  |  |  |
| $b, c\left(a_{5}\right)$ | 1.19429 | 0.98702 | 1.25500 | 1.57327 | 1.86199 | 0.66540 | 1.22265 | 1.27295 | 1.29569 | 1.29924 | 1.54416 | 1.54616 | 0.75055 | 1.26354 |
| - | 0.74645 | 0.83327 | 0.67110 | 0.61742 | 0.67371 | 0.89223 | 0.64537 | 0.63580 | 0.63159 | 0.63095 | 0.68600 | 0.68800 | 0.86030 | 0.63756 |

Table 22.31. The MO to HO intercept geometrical bond parameters of exemplary halidoboranes $\mathrm{F}_{2} \mathrm{BOH}, \mathrm{BF} 3_{3}, \mathrm{~F}_{2} \mathrm{BCH} \mathrm{H}_{3},\left(\mathrm{CH}_{3} \mathrm{O}\right)_{2} \mathrm{BCl}$, and BCl . $E_{T}$ is $E_{T}($ atom - atom $\left.m s p^{3} . A O\right)$.

| Bond | Atom | $\begin{gathered} E_{T} \\ (\mathrm{eV}) \\ \text { Bond } 1 \end{gathered}$ | $\begin{gathered} E_{T} \\ (\mathrm{eV}) \\ \text { Bond } 2 \end{gathered}$ $\text { Bond } 2$ | $\begin{gathered} E_{T} \\ (\mathrm{eV}) \\ \text { Bond } 3 \end{gathered}$ |  | Final Total Energy $B 2 s p^{3}$ <br> (eV) | $\begin{aligned} & r_{\text {metrad }} \\ & \left(a_{0}\right) \end{aligned}$ | $\begin{aligned} & r_{\text {final }} \\ & \left(a_{0}\right) \end{aligned}$ | $\begin{gathered} E_{\text {Coulombl }}\left(B 2 s p^{3}\right)(\mathrm{eV}) \\ \text { Final } \end{gathered}$ | $\begin{gathered} E\left(B 2 s p^{3}\right) \\ (\mathrm{eV}) \\ \text { Final } \\ \hline \end{gathered}$ | $\begin{aligned} & \hline \theta^{\prime} \\ & \left({ }^{\circ}\right) \end{aligned}$ | $\begin{aligned} & \theta_{1} \\ & \left({ }^{\circ}\right) \end{aligned}$ | $\begin{gathered} \theta_{2} \\ \left({ }^{\circ}\right) \end{gathered}$ | $\begin{gathered} d_{1} \\ \left(a_{0}\right) \end{gathered}$ | $\begin{gathered} d_{2} \\ \left(a_{0}\right) \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| BO-H ( $\mathrm{F}_{2} \mathrm{BOH}$ ) | O | -0.56370 | 0 | 0 | 0 |  | 1.00000 | 0.95939 | -14.18175 |  | 121.28 | 58.72 | 70.60 | 0.41990 | 0.49818 |
| $\begin{aligned} & -\mathrm{B-OH}\left(\mathrm{~F}_{2} \mathrm{BOH}\right) \\ & (\mathrm{B-O}(\mathrm{i})) \end{aligned}$ | O | $-0.56370$ | 0 | 0 | 0 |  | 1.00000 | 0.95939 | -14.18175 |  | 74.04 | 105.96 | 37.79 | 1.58054 | 0.26376 |
| $\begin{aligned} & -\mathrm{B-OH}\left(\mathrm{~F}_{2} \mathrm{BOH}\right) \\ & (\mathrm{B-O} \text { (i)) } \end{aligned}$ | B | $-0.56370$ | -3.08109 | -3.08109 | 0 | -81.61757 | 1.14361 | 0.73059 | -18.62313 | -18.53213 | 33.21 | 146.79 | 15.41 | 1.92806 | 0.61128 |
| $B-F\left(F_{2} \mathrm{BOH}\right)$ | B | -3.08109 | -3.08109 | -0.56370 | 0 |  | 1.14361 | 0.73059 | -18.62313 | -18.53213 | 112.74 | 67.26 | 51.08 | 0.94234 | 0.28241 |
| $B-F\left(F_{2} \mathrm{BOH}\right)$ | F | -3.08109 | 0 | 0 | 0 |  | 0.78069 | 0.66357 | -20.50391 | -20.26346 | 107.57 | 72.43 | 46.93 | 1.02441 | 0.20033 |
| $B-F\left(B F_{3}\right)$ | B | -3.08109 | -3.08109 | -3.08109 | 0 |  | 1.14361 | 0.64359 | -21.14052 | -21.04952 | 105.86 | 74.14 | 45.63 | 1.04889 | 0.17586 |
| $B-F\left(B F_{3}\right)$ | $F$ | -3.08109 | 0 | 0 | 0 |  | 0.78069 | 0.66357 | -20.50391 | -20.26346 | 107.57 | 72.43 | 46.93 | 1.02441 | 0.20033 |
| $\mathrm{C}-\mathrm{H}\left(\mathrm{BCH}_{3}\right)$ | 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 |
| C-B (-B-CH3) | C | -0.72457 | 0 | 0 | 0 | -152.34026 | 0.91771 | 0.87495 | -15.55033 | -15.35946 | 116.85 | 63.15 | 52.27 | 1.09248 | 0.39514 |
| $\mathrm{C}-\mathrm{B}\left(-\mathrm{B}-\mathrm{CH}_{3}\right)$ | B | -0.72457 | -3.08109 | -3.08109 | 0 |  | 1.14361 | 0.62663 | -21.71251 | -21.62151 | 98.92 | 81.08 | 38.84 | 1.39048 | 0.09714 |
| $B-F\left(F_{2} B^{\prime} H_{3}\right)$ | B | -3.08109 | -3.08109 | -0.72457 | 0 |  | 1.14361 | 0.62663 | -21.71251 | -21.62151 | 104.33 | 75.67 | 44.51 | 1.06965 | 0.15509 |
| $B-F\left(F_{2} B^{\prime} H_{3}\right)$ | $F$ | -3.08109 | 0 | 0 | 0 |  | 0.78069 | 0.66357 | -20.50391 | -20.26346 | 107.52 | 72.43 | 46.93 | 1.02441 | 0.20033 |
| $\mathrm{C}-\mathrm{H}\left(\mathrm{OC}_{a} \mathrm{H}_{3}\right)$ | $C_{a}$ | -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 |
| $\begin{aligned} & \mathrm{BO}-\mathrm{C}_{a} \mathrm{H}_{3} \\ & \mathrm{BO}-\mathrm{C}_{a}\left(\mathrm{CH}_{3}\right)_{3} \\ & (\mathrm{C}-\mathrm{O}(\mathrm{i})) \end{aligned}$ | $C_{a}$ | -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 |
| $\begin{aligned} & \mathrm{BO}-\mathrm{C}_{a} \mathrm{H}_{3} \\ & \mathrm{BO}-\mathrm{C}_{a}\left(\mathrm{CH}_{3}\right)_{3} \\ & (\mathrm{C}-\mathrm{O}(\mathrm{i})) \end{aligned}$ | O | -0.72457 | -0.56370 | 0 | 0 |  | 1.00000 | 0.84435 | -16.11402 |  | 93.39 | 86.61 | 44.26 | 1.29433 | 0.04998 |
| $\begin{aligned} & \left.\mathrm{ClB-(OCH}_{3}\right)_{2} \\ & (\mathrm{~B}-\mathrm{O}(\mathrm{iii}) \end{aligned}$ | B | -0.56370 | $-0.56370$ | -1.12740 | 0 | -77.14647 | 1.14361 | 0.96140 | -14.15204 | -14.06104 | 71.19 | 108.81 | 36.65 | 1.60458 | 0.31003 |
| $\begin{aligned} & \left.\mathrm{ClB-(OCH}_{3}\right)_{2} \\ & (\mathrm{B-O}(\mathrm{Oi}) ;(\mathrm{C}-\mathrm{O}(\mathrm{i})) \end{aligned}$ | O | -0.56370 | $-0.72457$ | 0 | 0 |  | 1.00000 | 0.84435 | -16.11402 |  | 54.45 | 125.55 | 26.78 | 1.78542 | 0.49088 |
| $\mathrm{B-Cl}\left(\mathrm{ClB}\left(\mathrm{OCH}_{3}\right)_{2}\right)$ | B | -1.12740 | -0.56370 | -0.56370 | 0 |  | 1.14361 | 0.96140 | -14.15203 | -14.06103 | 43.58 | 136.42 | 20.50 | 2.36004 | 0.69647 |
| $\mathrm{B-Cl}\left(\mathrm{ClB}\left(\mathrm{OCH}_{3}\right)_{2}\right)$ | Cl | -1.12740 | 0 | 0 | 0 |  | 1.05158 | 0.96529 | -14.09504 | -13.99665 | 44.32 | 135.68 | 20.88 | 2.35415 | 0.69058 |
| $\mathrm{B-Cl}\left(\mathrm{BCl}_{3}\right)$ | B | -1.12740 | -1.12740 | -1.12740 | 0 |  | 1.14361 | 0.89047 | -15.27943 | -15.18843 |  |  |  |  |  |
| $\mathrm{B-Cl}\left(\mathrm{BCl}_{3}\right)$ | Cl | -1.12740 | 0 | 0 | 0 |  | 1.05158 | 0.96529 | -14.09504 | -13.99665 | 44.32 | 135.68 | 20.88 | 2.35415 | 0.69058 |

Table 22.32A. The energy parameters $(\mathrm{eV})$ of functional groups of halidoboranes.

| Parameters | $\begin{aligned} & B-F \\ & \text { Group } \end{aligned}$ | $\begin{aligned} & \mathrm{B-Cl} \\ & \text { Group } \end{aligned}$ | $\begin{gathered} B-N(\mathrm{i}) \\ \text { Group } \end{gathered}$ | $\begin{gathered} B-N \text { (ii) } \\ \text { Group } \end{gathered}$ | $\begin{gathered} C-N \text { (i) } \\ \text { Group } \\ \hline \end{gathered}$ | $\begin{gathered} C-N \text { (ii) } \\ \text { Group } \\ \hline \end{gathered}$ | $\begin{aligned} & C-N \text { (iii) } \\ & \text { Group } \\ & \hline \end{aligned}$ | $\begin{aligned} & C-N \text { (iv) } \\ & \text { Group } \\ & \hline \end{aligned}$ | $\mathrm{NH}_{3}$ Group | $\begin{gathered} \mathrm{NH}_{2} \\ \text { Group } \end{gathered}$ | $\begin{gathered} \mathrm{NH} \\ \text { Group } \end{gathered}$ | $\begin{gathered} B-O \text { (i) } \\ \text { Group } \\ \hline \end{gathered}$ | $\begin{gathered} B-O \text { (ii) } \\ \text { Group } \end{gathered}$ | $\begin{gathered} \mathrm{OH} \\ \text { Group } \\ \hline \end{gathered}$ | $\begin{gathered} C-O \text { (i) } \\ \text { Group } \\ \hline \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $n_{1}$ | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 3 | 2 | 1 | 1 | 1 | 1 | 1 |
| $n_{2}$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 |
| $n_{3}$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 1 | 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 | 0.75 | 0.5 | 0.75 | 0.75 | 0.5 |
| $\mathrm{C}_{2}$ | 1 | 0.91044 | 0.81231 | 0.81231 | 1 | 1 | 1 | 1 | 0.93613 | 0.93613 | 0.93613 | 1.15346 | 0.79562 | 1 | 1 |
| $c_{1}$ | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 0.75 | 0.75 | 0.75 | 1 | 1 | 0.75 | 1 |
| $c_{2}$ | 0.68285 | 1 | 1 | 0.81231 | 0.91140 | 0.91140 | 0.91140 | 0.91140 | 1 | 0.94627 | 0.93383 | 1 | 1 | 1 | 0.85395 |
| $c_{3}$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 0 | 0 | 1 | 0 |
| $c_{4}$ | 1 | 1 | 1 | 1 | 2 | 2 | 2 | 2 | 1 | 1 | 1 | 1 | 1 | 1 | 2 |
| $c_{5}$ | 1 | 1 | 1 | 1 | 0 | 0 | 0 | 0 | 3 | 2 | 1 | 1 | 1 | 1 | 0 |
| $C_{10}$ | 0.5 | 0.5 | 0.75 | 0.5 | 0.5 | 1 | 1 | 0.5 | 1 | 1.5 | 0.75 | 0.5 | 0.75 | 0.75 | 0.5 |
| $C_{20}$ | 1 | 0.91044 | 0.81231 | 0.81231 | 1 | 1 | 1 | 1 | 1.5 | 1 | 1 | 1.15346 | 0.79562 | 1 | 1 |
| $V_{e}(\mathrm{eV})$ | -34.78026 | -25.95105 | -31.86906 | -29.36199 | -32.46339 | -31.98456 | -31.98456 | -31.67393 | -115.28799 | -77.89897 | -39.21967 | -32.64974 | -32.39594 | -40.92709 | -33.15757 |
| $V_{p}(\mathrm{eV})$ | 11.10909 | 8.17867 | 10.56810 | 8.62881 | 9.80175 | 9.74677 | 9.74677 | 9.71067 | 41.66718 | 28.49191 | 14.35050 | 10.33263 | 10.51010 | 14.81988 | 10.12103 |
| $T(e \mathrm{~V})$ | 11.59342 | 5.14980 | 7.88989 | 7.26921 | 8.42409 | 8.20698 | 8.20698 | 8.06719 | 42.77848 | 30.40957 | 15.53581 | 8.16244 | 8.09899 | 16.18567 | 9.17389 |
| $V_{m}(\mathrm{eV})$ | -5.79671 | -2.57490 | -3.94494 | -3.63460 | -4.21204 | -4.10349 | -4.10349 | -4.03359 | -21.38924 | -15.20478 | -7.76790 | -4.08122 | -4.04949 | -8.09284 | -4.58695 |
| $E$ (Аоно) (eV) | -11.80624 | -11.80624 | -11.80624 | -11.80624 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.53414 | -14.53414 | -14.53414 | -11.80624 | -11.80624 | -13.6181 | -14.63489 |
| $\Delta E_{\mathrm{H}_{2} \mathrm{MO}}$ (10/ (\%O) ( eV ) | 0 | 0 | 0 | 0 | -1.44915 | -1.13379 | -1.13379 | -0.92918 | 0 | 0 | 0 | 0 | 0 | 0 | -1.44915 |
| $E_{T}$ (1оОНо) (eV) | -11.80624 | -11.80624 | -11.80624 | -11.80624 | -13.18574 | -13.50110 | -13.50110 | -13.70571 | -14.53414 | -14.53414 | -14.53414 | -11.80624 | -11.80624 | -13.6181 | -13.18574 |
| $E(\mathrm{n}$, ,O/HO) (eV) | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | -14.53414 | -14.53414 | 0 | 0 | 0 | 0 | 0 |
| $E_{T}\left(\mathrm{H}_{2} \mathrm{MO}\right)(\mathrm{eV})$ | -29.68070 | -27.00372 | -29.16227 | -28.90482 | -31.63534 | -31.63540 | -31.63540 | -31.63537 | -66.76571 | -48.73642 | -31.63541 | -30.04213 | -29.64258 | -31.63247 | -31.63533 |
| $E_{T}\left(\right.$ atom -atom, msp $\left.{ }^{3} . \mathrm{AO}\right)(\mathrm{eV})$ | -6.16219 | -2.25479 | -1.12740 | 1.19843 | -1.44915 | -1.13379 | -1.13379 | -0.92918 | 0 | 0 | 0 | -1.12740 | -1.12740 | 0 | -1.44915 |
| $E_{T}(\mathrm{not})(\mathrm{eV})$ | -35.84289 | -29.25852 | -30.28967 | -27.70639 | -33.08452 | -32.76916 | -32.76916 | -32.56455 | -66.76616 | -48.73660 | -31.63537 | -31.16953 | -30.76998 | -31.63537 | -33.08452 |
| $\omega\left(10^{15} \mathrm{rad} / \mathrm{s}\right)$ | 15.9123 | 10.7150 | 16.6240 | 9.17969 | 18.9231 | 15.1983 | 26.0778 | 18.1298 | 56.8887 | 64.2189 | 47.0696 | 11.1001 | 16.9656 | 44.1776 | 12.0329 |
| $E_{K}(\mathrm{eV})$ | 10.47375 | 7.05282 | 10.94219 | 6.04223 | 12.45552 | 10.00377 | 17.16484 | 11.93333 | 37.44514 | 42.27003 | 30.98202 | 7.30627 | 11.16705 | 29.07844 | 7.92028 |
| $\bar{E}_{D}(\mathrm{eV})$ | -0.22949 | -0.15372 | -0.19822 | -0.13474 | -0.23100 | -0.20505 | -0.26859 | -0.22255 | -0.38298 | -0.40690 | -0.34836 | -0.16668 | -0.20342 | -0.33749 | -0.18420 |
| $\bar{E}_{\text {Kwb }}(\mathrm{eV})$ | $\begin{gathered} 0.17384 \\ {[5]} \end{gathered}$ | $\begin{gathered} 0.10418 \\ {[5]} \end{gathered}$ | $\begin{gathered} 0.18779 \\ {[5]} \\ \hline \end{gathered}$ | $\begin{gathered} 0.18779 \\ {[5]} \end{gathered}$ | $\begin{gathered} 0.12944 \\ {[25]} \end{gathered}$ | $\begin{gathered} 0.12944 \\ {[25]} \\ \hline \end{gathered}$ | $\begin{gathered} 0.11159 \\ {[26]} \\ \hline \end{gathered}$ | $\begin{gathered} 0.12944 \\ {[25]} \end{gathered}$ | $\begin{gathered} 0.42695 \\ {[26]} \end{gathered}$ | $\begin{gathered} 0.40929 \\ {[28]} \\ \hline \end{gathered}$ | $\begin{gathered} 0.40696 \\ {[29]} \\ \hline \end{gathered}$ | $\begin{gathered} 0.23380 \\ {[5]} \\ \hline \end{gathered}$ | $\begin{gathered} 0.23380 \\ {[5]} \\ \hline \end{gathered}$ | $\begin{aligned} & 0.46311 \\ & {[22-23]} \end{aligned}$ | $\begin{gathered} 0.13663 \\ {[24]} \\ \hline \end{gathered}$ |
| $\bar{E}_{\text {acc }}(\mathrm{eV})$ | -0.14257 | -0.10163 | -0.10433 | -0.04084 | -0.16628 | -0.14033 | -0.21280 | -0.15783 | -0.16950 | -0.20226 | -0.14488 | -0.04978 | -0.08652 | -0.10594 | -0.11589 |
| $E_{\text {mag }}(\mathrm{eV})$ | 0.07650 | 0.07650 | 0.07650 | 0.07650 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14185 | 0.14803 | 0.14803 | 0.07650 | 0.07650 | 0.11441 | 0.14803 |
| $E_{T}$ ( (imup) $(\mathrm{eV})$ | -35.98546 | -29.36015 | -30.39399 | -27.74723 | -33.25079 | -32.90949 | -32.98196 | -32.72238 | -67.27466 | -49.14112 | -31.78025 | -31.21931 | -30.85651 | -31.74130 | -33.20040 |
|  | -11.80624 | -11.80624 | -11.80624 | -11.80624 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.53414 | -14.53414 | -14.53414 | -11.80624 | -11.80624 | -13.6181 | -14.63489 |
|  | -17.42282 | -12.96764 | -14.53414 | -14.53414 | 0 | 0 | 0 | 0 | -13.59844 | -13.59844 | -13.59844 | -13.6181 | -13.6181 | -13.59844 | 0 |
| $E_{D}($ Group $)(\mathrm{eV})$ | 6.75639 | 4.58626 | 4.05361 | 1.40685 | 3.98101 | 3.63971 | 3.71218 | 3.45260 | 11.94520 | 7.41010 | 3.50582 | 5.79502 | 5.43221 | 4.41035 | 3.93062 |

Table 22．32B．The energy parameters $(\mathrm{eV})$ of functional groups of halidoboranes．

| $\left\lvert\, \begin{aligned} & \text { En } \\ & \text { y } \\ & 0 \end{aligned}\right.$ | － | $\cdots-$ | － | － | － | － | － | $\sim$ | ก |  |  | － | $\begin{aligned} & 2 \\ & \alpha \\ & \vdots \\ & \vdots \\ & \vdots \end{aligned}$ |  | － |  | $\begin{aligned} & \widehat{e} \\ & \text { 合 } \\ & \dot{寸} \end{aligned}$ | － | $\stackrel{G}{6}$ | $\underset{\substack{\hat{N} \\ \\ \hline}}{ }$ |  |  |  | $\begin{aligned} & \hat{N} \\ & \hat{E} \\ & \stackrel{1}{2} \end{aligned}$ |  |  | $\begin{aligned} & \substack{\begin{subarray}{c}{c} }} \\ {\hline} \\ {\hline} \\ & \hline \end{aligned}$ | $\begin{aligned} & Z_{0}^{2} \\ & \stackrel{\rightharpoonup}{n} \end{aligned}$ | $\stackrel{\circ}{\circ}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\begin{array}{ll} \text { U } \\ \text { Ü } \\ \text { U } \\ 0 \end{array}$ | － | － | $\cdots$ |  | － | O | － | － |  |  | $\begin{gathered} \stackrel{\infty}{\infty} \\ \stackrel{\infty}{\infty} \\ \stackrel{1}{\dot{\sim}} \end{gathered}$ | Co | $\stackrel{\substack{n \\ \\ \underset{\sim}{\sim} \\ \hline}}{ }$ | － | － | － | $\begin{aligned} & \text { n} \\ & \text { N} \\ & \text { NO} \end{aligned}$ | $\begin{gathered} \substack{\hat{n} \\ 0 \\ 0 \\ \text { ch } \\ \hline} \end{gathered}$ |  | $\begin{aligned} & \stackrel{\rightharpoonup}{*} \\ & \stackrel{\rightharpoonup}{\dot{j}} \\ & \stackrel{y}{2} \end{aligned}$ |  |  | $\stackrel{\stackrel{\rightharpoonup}{\circ}}{\stackrel{\Delta}{0}}$ | $\begin{gathered} 0 \\ 0 \\ 0 \\ \tilde{n} \\ 0 \\ i \end{gathered}$ | $\left\lvert\, \begin{aligned} & 0.0 \\ & \substack{\square \\ \hline} \end{aligned}\right.$ |  |  |  | $\stackrel{ \pm}{\square}$ |
| $\begin{aligned} & 2 \\ & x_{0}^{2} \\ & 0 \\ & 0 \\ & 0 \\ & 0 \end{aligned}$ | － | － | $\bigcirc$ | － | － | 0 | $\bigcirc \sim$ | － | \％ |  |  | $\begin{aligned} & \text { y } \\ & \hline \end{aligned}$ | $\begin{gathered} \sim \\ \tilde{N}^{\infty} \\ \cdots \\ \cdots \end{gathered}$ | $\begin{gathered} \hat{0} \\ \substack{n \\ n \\ n \\ n} \end{gathered}$ | $\bigcirc$ | $\begin{aligned} & \hat{0} \\ & \stackrel{\rightharpoonup}{n} \\ & \end{aligned}$ |  | $\begin{aligned} & \mathscr{0} \\ & \infty \\ & \infty \\ & \underset{\sim}{\infty} \\ & \hdashline \end{aligned}$ |  |  |  |  | $\stackrel{\infty}{\stackrel{\infty}{3}} \pm$ | $\begin{gathered} 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{gathered}$ |  |  | $\stackrel{\otimes}{\mathrm{q}}$ |  | ন |
|  | － | － | $0 \%$ | \％－ | － | － | 。 | － | \％ |  | $\underset{\sim}{\sim}$ | $\begin{aligned} & \text { to } \\ & \hline 1 \end{aligned}$ | $\mathfrak{c}$ | $\begin{gathered} \hat{0} \\ \substack{\hat{n} \\ n \\ n \\ \hline} \end{gathered}$ | － | 啇 | $\begin{aligned} & \hat{N} \\ & \stackrel{\hat{O}}{6} \\ & \underset{\sim}{n} \end{aligned}$ | $\begin{gathered} \infty \\ \infty \\ \infty \\ \underset{\sim}{\infty} \end{gathered}$ |  | $\begin{aligned} & \stackrel{\rightharpoonup}{6} \\ & \underset{\text { }}{2} \end{aligned}$ |  |  | $\stackrel{\pi}{9}$ | $\begin{aligned} & \hat{\imath} \\ & \stackrel{\rightharpoonup}{3} \\ & \vdots \\ & i \end{aligned}$ | $\left\lvert\, \begin{aligned} & 0 \\ & \substack{c \\ \hline} \\ & \hline 0 \end{aligned}\right.$ |  | $\stackrel{\circ}{\circ}$ |  | $\xrightarrow{+}$ |
|  | － | － | － | § | － | － | － | － |  | $-\frac{\begin{array}{c} n \\ \tilde{c} \\ \\ \end{array}}{}$ |  | $\begin{aligned} & \stackrel{O}{\circ} \\ & \stackrel{\circ}{\circ} \\ & \underset{\sim}{2} \end{aligned}$ | $\underset{\text { ন্ণ }}{\text { ন্}}$ |  | － |  |  | $\bigcirc$ | ف | $\frac{o}{c}$ |  |  |  | $: \begin{aligned} & 8 \\ & \vdots \\ & \vdots \\ & \vdots \end{aligned}$ | $\left\lvert\,\right.$ |  | $\begin{gathered} \stackrel{\rightharpoonup}{2} \\ \underset{C}{6} \\ \underset{\substack{1}}{ } \end{gathered}$ |  | － |
| $\begin{aligned} & \text { © } \\ & \text { 気 } \\ & 0 \end{aligned}$ | － | N－ | $0 \stackrel{n}{2}$ | $\stackrel{n}{6}$ | － | － | － | N | $\left\|\begin{array}{c} n \\ \underset{o}{n} \end{array}\right\|$ | $-\begin{gathered} \frac{2}{\partial} \\ \frac{\partial}{7} \\ \underset{i}{0} \\ 1 \end{gathered}$ |  |  | $\begin{gathered} n \\ \cdots \\ \cdots \\ \cdots \\ \end{gathered}$ | $\begin{gathered} \hat{0} \\ 0 \\ \substack{n \\ n \\ \\ \hline} \end{gathered}$ | － | $\begin{aligned} & \hat{C} \\ & \stackrel{0}{6} \\ & \stackrel{y}{n} \\ & \end{aligned}$ |  | － | ＋ | $\begin{gathered} \bar{n} \\ \underset{\sim}{c} \\ \underset{\sim}{n} \end{gathered}$ | $\dot{\sim}$ |  |  |  | $\begin{aligned} & \frac{2}{0} \\ & \stackrel{\square}{6} \end{aligned}$ |  |  |  | $\stackrel{\circ}{\circ}$ |
|  | － | $\sim$ | － | $\underset{\substack{n \\ 0}}{ }-$ |  | － | － | $m$ |  | $-\begin{array}{r} \infty \\ - \\ - \\ \\ \\ \\ \end{array}$ | $\begin{gathered} \infty \\ \underset{A}{\lambda} \\ \underset{\sim}{\infty} \end{gathered}$ |  | $\begin{aligned} & \text { n } \\ & 0 \\ & 0 \\ & \end{aligned}$ | $\begin{gathered} \hat{y} \\ 0 \\ \substack{n \\ n \\ \\ \hline} \end{gathered}$ | $\bigcirc$ | $\begin{aligned} & \text { 荷 } \\ & \stackrel{y}{6} \end{aligned}$ |  | － | ＋ | $\begin{gathered} \infty \\ \underset{1}{\circ} \\ \underset{\sim}{c} \end{gathered}$ |  |  |  | $\begin{aligned} & n \\ & \substack{n \\ d \\ 0} \end{aligned}$ |  |  |  |  | $\stackrel{\circ}{\square}$ |
| $\begin{aligned} & \text { EO } \\ & 0 \\ & 0.0 \\ & 0 \end{aligned}$ | － | － | $\bigcirc$ | $\bigcirc$ |  | － | － | － |  |  | $\left\lvert\, \begin{aligned} & \stackrel{\beth}{\beth} \\ & \underset{\sim}{\leftrightharpoons} \end{aligned}\right.$ |  | $\frac{8}{2}$ |  | $\begin{gathered} \stackrel{2}{2} \\ \underset{\sim}{7} \end{gathered}$ | $\underset{n}{0}$ | $\begin{gathered} \stackrel{\rightharpoonup}{\hat{N}} \\ \hat{\widehat{N}} \\ \stackrel{1}{2} \end{gathered}$ |  | － |  | $\begin{aligned} & \stackrel{N}{N} \\ & \stackrel{y}{f} \\ & \stackrel{y}{c} \end{aligned}$ | － |  | $\begin{gathered} \mathbf{t} \\ \mathbf{o} \\ 0 \\ 0 \\ \vdots \end{gathered}$ |  |  |  | $\underset{\sim}{*}$ | 容 |
|  |  | 10 | $0 \sim$ | $\because \underset{\sim}{\tilde{N}}$ | － | $0$ | － | － | \％ |  |  |  | $\underset{\sim}{\underset{\sim}{n}}$ | － | － | － | $\begin{aligned} & \text { ir } \\ & \vdots \\ & \\ & \text { Sin } \end{aligned}$ | $\begin{gathered} 0 \\ 0 \\ 0 \\ 0 \\ i \end{gathered}$ |  | $\begin{gathered} \underset{\sim}{N} \\ \underset{\sim}{2} \end{gathered}$ | $\begin{gathered} \underset{\sim}{\underset{\sim}{c}} \\ \underset{\sim}{c} \end{gathered}$ | $\stackrel{\text { ¢ }}{\text { ¢ }}$ | $\frac{\stackrel{G}{\circ}}{\stackrel{\circ}{\circ}}$ | $\begin{gathered} \mathscr{O} \\ 0 \\ \\ \vdots \end{gathered}$ |  |  |  |  | ¢ |
| $\begin{aligned} & \infty \\ & 1 \\ & \infty \\ & \infty \\ & \infty \\ & \infty \end{aligned}$ | － | － | $0 \%$ | $\because \stackrel{c}{\frac{1}{4}} \underset{\substack{\text { an }}}{\infty}$ |  | $\underset{\substack{\mathrm{y} \\ \underset{\infty}{\infty} \\ \stackrel{y}{\infty}}}{ }$ | － | － | \％ |  | $\begin{aligned} & \stackrel{\rightharpoonup}{n} \\ & \stackrel{y}{0} \\ & \vdots \end{aligned}$ |  |  | $\xrightarrow[\substack{\overbrace{0} \\ \infty \\ \\ \\ \hline}]{ }$ | － |  |  | $\begin{array}{\|c} \stackrel{\rightharpoonup}{\infty} \\ \underset{\sim}{\infty} \\ \stackrel{i}{2} \end{array}$ | $\stackrel{\substack{\infty \\ \underset{\sim}{c}}}{ }$ | $\begin{gathered} \circ \\ \stackrel{\circ}{\alpha} \\ \substack{6 \\ \hline} \end{gathered}$ | $\begin{aligned} & \underset{\infty}{\infty} \\ & \stackrel{\circ}{q} \\ & \dot{f} \end{aligned}$ | $\begin{aligned} & \hat{6} \\ & \hline \\ & \hline \end{aligned}$ | $\begin{aligned} & \text { nin } \\ & \stackrel{e}{m} \\ & \hline \end{aligned}$ | $\begin{aligned} & 0 \\ & \frac{n}{n} \\ & 0 \\ & i \end{aligned}$ | $\begin{aligned} & 0 \\ & 0 \\ & 0 \\ & 0 \\ & 0 \\ & 0 \end{aligned}$ |  |  |  | ¢ |
| $\begin{array}{ll} \infty & 0 \\ 1 \\ 0 \\ 0 & \frac{訁}{0} \end{array}$ | － | 0 | 0 ＇s | $\therefore \underset{\sim}{c}$ |  | $\underset{\substack { \text { y } \\ \underset{\infty}{\infty} \\ \begin{subarray}{c}{\infty{ \text { y } \\ \underset { \infty } { \infty } \\ \begin{subarray} { c } { \infty } }\end{subarray}}{ }$ | $0 \sim$ | 0 | ＇ 6 |  | $\begin{aligned} & \text { İ } \\ & \stackrel{y}{c} \\ & \dot{\infty} \end{aligned}$ | $\begin{gathered} n \\ \stackrel{\leftrightarrow}{6} \\ \stackrel{\leftrightarrow}{\sim} \\ \underset{\sim}{2} \end{gathered}$ |  |  | － |  |  | $$ | \|ọ| | $\begin{aligned} & \infty \\ & \substack { \infty \\ \begin{subarray}{c}{\infty \\ 0{ \infty \\ \begin{subarray} { c } { \infty \\ 0 } } \\ {\hline} \end{aligned}$ | $\begin{aligned} & \infty \\ & \otimes \\ & \underset{\sim}{\circ} \\ & \dot{\sim} \end{aligned}$ | $\begin{gathered} 0 \\ \hline \\ \hline \end{gathered}$ | $\stackrel{n}{0} \sqrt{0}$ | $\begin{array}{\|c\|} 0 \\ 0 \\ \vdots \\ 0 \\ 0 \\ \vdots \end{array}$ | $\begin{aligned} & 0 \\ & \stackrel{y}{0} \\ & \stackrel{0}{0} \\ & \hline \end{aligned}$ |  |  |  | $\xrightarrow{n}$ |
| $\begin{array}{ll} \infty & 0 \\ 1 & \tilde{2} \\ 0 & \overline{0} \\ 1 & 0 \end{array}$ | － | － 0 | － | $\underset{\substack{\infty}}{\substack{1 \\ y \\ \hline \\ 0}}$ |  | $\left\|\begin{array}{c} \frac{y}{f} \\ \infty \\ 0 \\ 0 \end{array}\right\| 0$ | － | － | ¢ |  | $\stackrel{\infty}{\infty}$ |  | $\begin{gathered} \text { 寺 } \\ \text { 年 } \end{gathered}$ | $\mathfrak{c}$ | － |  | $\begin{gathered} \infty \\ 0 \\ 0 \\ 0 \\ \\ \end{gathered}$ | $$ |  | $\stackrel{\rightharpoonup}{\text { ®. }}$ | $\begin{aligned} & \underset{0}{0} \\ & \stackrel{2}{\lambda} \\ & \stackrel{y}{3} \end{aligned}$ | $\begin{aligned} & \text { cin } \\ & \text { స్ } \\ & \text { ch } \end{aligned}$ |  | $\begin{array}{\|c} \hat{\kappa} \\ \frac{\infty}{0} \\ \hline \end{array}$ | $\begin{aligned} & 0 \\ & 0 \\ & 0 \\ & 0 \\ & 0 \end{aligned}$ |  |  |  | $\xrightarrow{\text { F }}$ |
|  | － | － |  |  |  | $\underset{\substack { \text { 等 } \\ \begin{subarray}{c}{\infty{ \text { 等 } \\ \begin{subarray} { c } { \infty } }\end{subarray}}{ }$ | － | － |  |  | $\begin{aligned} & \infty \\ & \stackrel{\infty}{5} \\ & \stackrel{\rightharpoonup}{=} \\ & \stackrel{y}{=} \end{aligned}$ |  | $\begin{aligned} & 2 \\ & y \\ & \text { d } \\ & \text { d } \end{aligned}$ |  | $0$ |  |  |  |  | $\begin{aligned} & \text { O} \\ & \stackrel{\text { n}}{2} \end{aligned}$ | $\begin{aligned} & \mathbf{N}_{\substack{0}}^{0} \\ & 0.0 \end{aligned}$ | $\begin{gathered} n \\ 0 \\ 0 \\ 0 \\ \hline \end{gathered}$ |  | $\begin{aligned} & \tilde{\sim} \\ & \\ & \underset{0}{6} \end{aligned}$ | $\begin{aligned} & 0 \\ & \substack{0 \\ 0 \\ 0 \\ \hline} \end{aligned}$ |  |  | $\underset{\infty}{ \pm}$ | － |
| $\begin{aligned} & \infty \\ & 0 \\ & 0 \\ & 0 \end{aligned}$ | － | － | －${ }^{2}$ | $\because\left\|\begin{array}{c} N \\ \hat{0} \\ 0 \\ 0 \\ 0 \end{array}\right\|$ |  | $\left\|\begin{array}{c} n \\ 0 \\ 0 \\ 0 \\ 0 \end{array}\right\| 0$ | － | － |  | N｜c｜c | $\frac{\underset{Z}{0}}{\substack{2}}$ |  | $\begin{gathered} \text { 子 } \\ \underset{\sim}{2} \\ \underset{子}{2} \end{gathered}$ |  | $\begin{gathered} \frac{n}{2} \\ \frac{2}{2} \end{gathered}$ |  |  | $\begin{aligned} & n \\ & \frac{n}{2} \\ & -1 \end{aligned}$ | $\begin{gathered} \frac{a}{2} \\ \stackrel{c}{c} \\ c \substack{2} \end{gathered}$ |  |  | $\begin{gathered} \infty \\ \stackrel{\infty}{A} \\ \underset{1}{2} \end{gathered}$ | $\stackrel{\underset{\Phi}{\infty}}{\stackrel{\Phi}{0}} \Xi$ | $\begin{gathered} \infty \\ n \\ n \\ \\ \hline \end{gathered}$ |  |  |  |  | － |
| 艮 | － | － 0 | n | n－ | － |  | － | 0 | \％ |  | 合 | N |  | － |  | $\begin{aligned} & \underset{\sim}{\infty} \\ & \underset{\sim}{\underset{j}{2}} \end{aligned}$ | $\begin{aligned} & \stackrel{7}{N_{2}} \\ & \substack{6 \\ \hdashline \\ \hline} \end{aligned}$ |  | $\underset{\substack{\underset{\sim}{c} \\ \\ \hline}}{2}$ | $\begin{gathered} \infty \\ \stackrel{\infty}{2} \\ \underset{\sim}{2} \end{gathered}$ | $\begin{aligned} & \text { N} \\ & \text { O} \\ & \text { on } \end{aligned}$ | $\begin{gathered} \overline{6} \\ \stackrel{0}{6} \\ \stackrel{\rightharpoonup}{i} \end{gathered}$ | $\frac{\infty}{\vdots} \Xi$ | $\begin{aligned} & \pi \\ & \vdots \\ & 0 \\ & 0 \\ & i \end{aligned}$ |  |  |  |  | － |
|  |  | $=2$ | $\approx$ | 5 v | S 5 | $\sim$ |  | \％ |  | ST0 | s | － | $\approx$ |  |  | $\frac{5}{0}$ |  |  |  |  | $\hat{*}_{*}^{*}$ |  | $\underbrace{\frac{s}{e}}_{c}$ | $\sqrt{v}$ |  |  | $\stackrel{s}{s}$ |  |  |

Table 22.33 .

Table 22.34. The bond angle parameters of halidoboranes and experimental values. $H_{t}$ is a terminal or two-center $H$. $H_{b}$ is a bridge or three-center $H$. In the calculation of $\theta_{v}$, the parameters from the preceding angle were used. $E_{T}$ is $E_{T}$ (atom - atom $m s p^{3} . A O$ ).

| Atoms of Angle | $\begin{gathered} 2 c^{\prime} \\ \text { Bond 1 } \\ \left(a_{0}\right) \end{gathered}$ | $\begin{gathered} 2 c^{\prime} \\ \text { Bond } 2 \\ \left(a_{0}\right) \end{gathered}$ | $2 c^{\prime}$ Terminal Atoms $\left(a_{0}\right)$ | $\begin{aligned} & E_{\text {Conlombic }} \\ & \text { Atom } 1 \end{aligned}$ | Atom 1 Hybridization Designation (Table) | $E_{\text {Coulombic }}$ | Atom 2 Hybridization Designation (Table) | $\begin{gathered} c_{2} \\ \text { Atom } 1 \end{gathered}$ | $\begin{gathered} c_{2} \\ \text { Atom } 2 \end{gathered}$ | $C_{1}$ | $C_{2}$ | $c_{1}$ | $c_{2}^{\prime}$ | $\begin{gathered} E_{T} \\ (\mathrm{eV}) \end{gathered}$ | $\begin{aligned} & \theta_{v} \\ & \left({ }^{\circ}\right) \end{aligned}$ | $\begin{aligned} & \theta_{1} \\ & \left({ }^{\circ}\right) \end{aligned}$ | $\begin{aligned} & \theta_{2} \\ & \left({ }^{\circ}\right) \end{aligned}$ | Cal. $\theta$ <br> $\left(^{\circ}\right)$ | $\begin{gathered} \text { Exp. } \theta \\ \left({ }^{\circ}\right) \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\angle H B F$ | 2.27211 | 2.44949 | 4.0988 | $\begin{array}{\|c\|} -18.05943 \\ B \end{array}$ | $\stackrel{2}{2}$ | $\begin{gathered} -17.42282 \\ F \end{gathered}$ | F | 0.75339 | $\begin{gathered} 0.78092 \\ \text { (Eq. 15.74) } \end{gathered}$ | 0.75 | 1 | 1 | 1.03654 | 0 |  |  |  | 120.43 | $\begin{gathered} 118.3[17] \\ \left(H B F_{2}\right) \end{gathered}$ |
| $\angle F B F$ | 2.44949 | 2.44949 | 4.2426 | $\begin{gathered} -17.42282 \\ F \end{gathered}$ | F | $\begin{gathered} -17.42282 \\ F \end{gathered}$ | F | $\begin{gathered} 0.78092 \\ \text { (Eq. 15.74) } \end{gathered}$ | $\begin{gathered} 0.78092 \\ \text { (Eq. 15.74) } \end{gathered}$ | 1 | 1 | 1 | $\begin{gathered} 0.78092 \\ \text { (Eq. 15.74) } \end{gathered}$ | -1.71943 |  |  |  | 120.00 | $118[10]$ $\left(H O B F_{2}\right)$ $118.3[10]$ $\left(H B F_{2}\right)$ |
| $\angle F B O$ | 2.44949 | 2.63356 | 4.4721 | -20.50391 | $\begin{gathered} 3 \\ (22.28) \end{gathered}$ | -14.18175 | $\begin{gathered} 1 \\ (22.28) \end{gathered}$ | 0.66357 | 0.95939 | 1 | 1 | 1 | 0.81148 | -1.71943 |  |  |  | 123.20 | $\begin{aligned} & 123[10] \\ & \left(\mathrm{HOBF}_{2}\right) \end{aligned}$ |
| $\angle C B C l$ | 2.97524 | 3.32714 | 5.4371 | -14.82575 | $\begin{gathered} 1 \\ (15.3 \mathrm{~A}) \end{gathered}$ | $\begin{gathered} -12.96764 \\ C l \end{gathered}$ | Cl | 0.91771 | $\begin{gathered} 0.91044 \\ \text { (Eq. (22.63)) } \end{gathered}$ | 1 | $\begin{gathered} 0.83552 \\ \text { (Eqs. (15.77), } \\ (22.63), \\ (13.430) \text { ) } \\ 0.01041 \end{gathered}$ | 1 | $\begin{gathered} 0.81317 \\ (\text { (Eq. } \\ (15.130)) \end{gathered}$ | -1.44915 |  |  |  | 119.14 |  |
| $\angle \mathrm{ClBCl}$ | 3.32714 | 3.32714 | 5.7594 | $\begin{array}{\|c\|} \hline-12.96764 \\ C l \\ \hline \end{array}$ | Cl | $\begin{gathered} -12.96764 \\ C l \\ \hline \end{gathered}$ | Cl | 1 | 1 | 1 | $\begin{gathered} 0.91044 \\ \text { (Eq. }(22.63)) \\ \hline \end{gathered}$ | 1 | 1 | -1.12740 |  |  |  | 119.88 |  |
| $\begin{gathered} \angle N B N \\ (B-N(i) \\ \& C-N(i i)) \end{gathered}$ | 2.57488 | 2.57488 | 4.4721 | -16.52324 | $\stackrel{2}{(22.21)}$ | -16.52324 | $\stackrel{2}{(22.21)}$ | 0.82343 | 0.82343 | 1 | 1 | 1 | 0.82343 | -1.65376 |  |  |  | 120.55 |  |
| $\begin{gathered} \angle C N B \\ (B-N(\text { (ii) } \\ \& C-N(\text { (iv })) \end{gathered}$ | 2.80224 | 3.15357 | 4.8531 | -15.29034 | $\begin{gathered} 1 \\ (22.21) \\ \hline \end{gathered}$ |  |  | 0.88983 | $\begin{gathered} 0.81231 \\ \text { (Eq. }(22.48) \text { ) } \end{gathered}$ | 1 | $\begin{gathered} 0.80672 \\ \text { (Eq. }(22.40)) \end{gathered}$ | 1 | 0.81508 | -0.72457 |  |  |  | 109.00 | $\begin{gathered} 109.9[17] \\ \left(\left(\mathrm{CH}_{3}\right)_{3} \mathrm{NBH}_{3}\right) \end{gathered}$ |
| $\begin{gathered} \angle H B N \\ (B-N(\text { (ii) } \\ \& C-N(\text { (iv })) \end{gathered}$ | 2.27211 | 3.15357 | 4.2895 | -11.89724 | B | -14.53414 | N | $\begin{gathered} 0.87442 \\ \text { (Eq. }(22.29) \text { ) } \end{gathered}$ | 0.93613 | 0.75 | 1 | 0.75 | 1.07056 | 0 |  |  |  | 103.28 | $\begin{gathered} 105.3[17] \\ \left(\left(\mathrm{CH}_{3}\right)_{3} \mathrm{NBH}_{3}\right) \end{gathered}$ |
| $\begin{gathered} \angle H N B \\ (B-N \text { (ii) } \end{gathered}$ | 1.95921 | 3.15357 | 4.2776 | -14.53414 | N | -11.89724 | B | 0.93613 | $\begin{gathered} 0.87442 \\ \text { (Eq. }(22.29) \text { ) } \\ \hline \end{gathered}$ | 0.75 | $\begin{gathered} 0.87442 \\ \text { (Eq. } 22.29) \text { ) } \\ \hline \end{gathered}$ | 0.75 | 0.93409 | 0 |  |  |  | 111.43 | $\begin{aligned} & 110.3[17] \\ & \left(\mathrm{H}_{3} \mathrm{NBH}_{3}\right) \end{aligned}$ |
| $\angle H N H$ | 1.91013 | 1.91013 | 3.0984 | -14.53414 | N | H | H | $\begin{array}{\|c\|} \hline 0.94627 \\ \text { Eq. }(15.134)) \\ \hline \end{array}$ | 1 | 1 | 1 | 0.75 | 1.05679 | 0 |  |  |  | 108.40 | $\begin{gathered} 107.1[10] \\ \text { (methylamine) } \end{gathered}$ |
| $\begin{gathered} \angle H N C_{a} \\ (C-N(\text { i) }) \end{gathered}$ | 1.91013 | 2.77620 | 3.8816 | -14.53414 | N | -15.35946 | $\begin{gathered} 5 \\ (15.3 \mathrm{~A}) \\ \hline \end{gathered}$ | $\begin{gathered} 0.91140 \\ \text { (Eq. }(15.135) \text { ) } \\ \hline \end{gathered}$ | 0.88583 | 0.75 | 1 | 0.75 | 0.97194 | 0 |  |  |  | 110.48 | $\begin{gathered} 110.3[10] \\ \text { (methylamine) } \end{gathered}$ |
| $\begin{gathered} \angle H C N \\ (C-N(\text { i) } \\ \&(\text { iii }) \end{gathered}$ | 2.09711 | 2.79186 | 4.0661 | -14.82575 | $\begin{gathered} 1 \\ (15.3 \mathrm{~A}) \end{gathered}$ | -14.53414 | N | 0.91771 | $\begin{gathered} 0.93383 \\ \text { (Eq. (15.136)) } \end{gathered}$ | 0.75 | 1 | 0.75 | 1.01756 | 0 |  |  |  | 111.76 | $112[10]$ (dimethylamine) |
| $\begin{gathered} \angle H N C_{a} \\ (C-N(\text { ii) } \end{gathered}$ $\&(\text { iii) })$ | 1.89621 | 2.79186 | 3.8123 | -14.53414 | N | $\begin{array}{\|c\|} \hline-15.56407 \\ \text { (Eq. } \\ (15.136)) \\ \hline \end{array}$ | $\begin{gathered} 7 \\ (15.3 \mathrm{~A}) \end{gathered}$ | $\begin{gathered} 0.91140 \\ \text { (Eq. (15.135)) } \end{gathered}$ | 0.87418 | 0.75 | 1 | 0.75 | 0.95917 | 0 |  |  |  | 107.27 | $107[10]$ (dimethylamine) |
| $\begin{gathered} \angle C N C \\ (C-N(\text { ii) } \\ \&(\text { (iii) }) \end{gathered}$ | 2.79186 | 2.79186 | 4.6260 | -17.04640 | $\begin{gathered} 33 \\ (15.3 \mathrm{~A}) \end{gathered}$ | -17.04640 | $\begin{gathered} 331 \\ (15.3 \mathrm{~A}) \end{gathered}$ | 0.79816 | 0.79816 | 1 | 1 | 1 | 0.79816 | -1.85836 |  |  |  | 111.89 | $\begin{gathered} 111.8[10] \\ \text { (dimethylamine) } \end{gathered}$ |
| $\begin{gathered} \angle B O H \\ (B-O(\mathrm{i})) \end{gathered}$ | 2.63356 | 1.83616 | 3.7771 | -11.80624 |  | -13.61805 |  | 1 | $\begin{gathered} 0.87442 \\ \text { (Eq. }(22.29) \text { ) } \\ \hline \end{gathered}$ | 0.75 | 1 | 0.75 | 0.87442 | $\begin{gathered} -0.56370 \\ \text { (Eq. }(22.12) \text { ) } \\ \hline \end{gathered}$ |  |  |  | 114.17 | $\begin{aligned} & 114.1[10] \\ & \left(F_{2} \mathrm{BOH}\right) \\ & \hline \end{aligned}$ |
| $\begin{gathered} \angle O_{a} B O_{b} \\ (B-O(\mathrm{i})) \end{gathered}$ | 2.63356 | 2.63356 | 4.5277 | $\begin{array}{\|c\|} \hline-15.75493 \\ O_{a} \\ \hline \end{array}$ | $\begin{gathered} 7 \\ (15.3 \mathrm{~A}) \end{gathered}$ | $\begin{array}{\|c\|} \hline-15.75493 \\ O_{b} \\ \hline \end{array}$ | $\begin{gathered} 7 \\ (15.3 \mathrm{~A}) \\ \hline \end{gathered}$ | 0.86359 | 0.86359 | 1 | 1 | 1 | 0.86359 | -1.44915 |  |  |  | 118.55 | $\begin{aligned} & 120[10] \\ & \left(B_{3} \mathrm{H}_{3} \mathrm{O}_{3}\right) \end{aligned}$ |
| $\begin{gathered} \angle O_{a} B O_{b} \\ (B-O \text { (ii) }) \end{gathered}$ | 2.58909 | 2.58909 | 4.4944 | $\begin{gathered} -15.75493 \\ O_{a} \\ \hline \end{gathered}$ | $\begin{gathered} 7 \\ (15.3 \mathrm{~A}) \\ \hline \end{gathered}$ | $\begin{array}{\|c\|} \hline-15.75493 \\ O_{b} \\ \hline \end{array}$ | $\begin{gathered} 7 \\ (15.3 \mathrm{~A}) \\ \hline \end{gathered}$ | 0.86359 | 0.86359 | 1 | 1 | 1 | 0.86359 | -1.44915 |  |  |  | 120.44 | $\begin{aligned} & 120[10] \\ & \left(B_{3} \mathrm{H}_{3} \mathrm{O}_{3}\right) \\ & \hline \end{aligned}$ |
| $\begin{gathered} \angle \mathrm{CBC} \\ \left(\mathrm{CH}_{3}\right)_{3} B \end{gathered}$ | 2.97524 | 2.97524 | 5.1769 | 16.11722 | $\begin{gathered} 1 \\ (22.8) \\ \hline \end{gathered}$ | 16.11722 | $\begin{gathered} 1 \\ (22.8) \\ \hline \end{gathered}$ | 0.84418 | 0.84418 | 1 | 1 | 1 | 0.84418 | -1.85836 |  |  |  | 120.92 | $120.0[10]$ (trimethylborane) |
| Methyl $\angle \mathrm{HCH}$ | 2.09711 | 2.09711 | 3.4252 | -15.75493 | $\begin{gathered} 7 \\ (15.3 \mathrm{~A}) \end{gathered}$ | H | H | 0.86359 | 1 | 1 | 1 | 0.75 | 1.15796 | 0 |  |  |  | 109.50 |  |
| $\angle B C H$ |  |  |  |  |  |  |  |  |  |  |  |  |  |  | 70.56 |  |  | 109.44 | $\begin{gathered} 112.5[10] \\ \text { (trimethylborane) } \end{gathered}$ |
| $\angle C B H_{t}$ | 2.97524 | 2.27211 | 4.5607 | -15.55033 | $\begin{gathered} 5 \\ (15.3 \mathrm{~A}) \end{gathered}$ | H | H | 0.87495 | 1 | 0.75 | 1 | 0.75 | 1.14292 | 0 |  |  |  | 120.12 |  |
| $\angle C B H_{b}$ | 2.97524 | 2.46967 | 4.6904 | -15.55033 | $\begin{gathered} 5 \\ (15.3 \mathrm{~A}) \end{gathered}$ | H | H | 0.87495 | 1 | 0.75 | 1 | 0.75 | 1.14292 | 0 |  |  |  | 118.66 |  |
| $\angle B B C$ |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  | 120.12 | 118.66 | 121.22 | $122.6[10]$ $(1,2-$ dimethyldiborane $)$ |
| $\angle H_{t} B H_{t}$ | 2.27211 | 2.27211 | 3.9623 | -13.61667 | $\begin{gathered} 2 \\ (22.1) \end{gathered}$ | H | H | 0.99920 | 1 | 1 | 1 | 0.75 | 1.00080 | -1.71943 |  |  |  | 121.37 | $122[10]$ (diborane) |

Table 22.34 cont＇d．The bond angle parameters of halidoboranes and experimental values．$H_{t}$ is a terminal or two－center $H$ ．$H_{b}$ is a bridge or three－center $H$ ．In the calculation of $\theta_{v}$ ，the parameters from the preceding angle were used．$E_{T}$ is $E_{T}$（atom－atom $\mathrm{msp}^{3} \cdot A O$ ）．

| $\underset{\substack{0 \\ \dot{x} \\ \dot{x} \\ \hline}}{ }$ |  |  |  |  |  |  | $\begin{aligned} & \text { 昌 } \\ & \vdots \\ & \hline \end{aligned}$ |  |  |
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| 部 | $\begin{aligned} & \stackrel{o}{0} \\ & \stackrel{0}{0} \end{aligned}$ | $\begin{aligned} & 6 \\ & \stackrel{\circ}{6} \end{aligned}$ | $\begin{aligned} & n \\ & \underset{\infty}{\infty} \\ & \hline \infty \end{aligned}$ | $\begin{aligned} & \text { 柰 } \\ & \stackrel{\circ}{0} \end{aligned}$ | $\begin{aligned} & \stackrel{\rightharpoonup}{\bullet} \\ & \stackrel{y}{\mid} \end{aligned}$ | $\begin{aligned} & \stackrel{+}{\bullet} \\ & \stackrel{y}{0} \end{aligned}$ |  |  |  |
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| 部会 | $\begin{aligned} & \text { 둔 } \\ & \hdashline-1 \end{aligned}$ | $\begin{aligned} & \substack{\text { O} \\ \vdots \\ \hline} \end{aligned}$ | － | － |  |  | － |  |  |
| $\sim$ | $\begin{aligned} & \stackrel{\infty}{\infty} \\ & \stackrel{\infty}{\infty} \end{aligned}$ | $\begin{aligned} & \text { 虽 } \\ & \text { d } \\ & \hline \end{aligned}$ | － | $\begin{aligned} & \stackrel{\circ}{n} \\ & \stackrel{n}{7} \end{aligned}$ |  |  | $\circ$ $\stackrel{\circ}{2}$ $\stackrel{n}{=}$ |  |  |
| $v$ | － | $\stackrel{\text { n }}{0}$ | － | ¢ |  |  | － |  |  |
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| u | － | － | － | － |  |  | － |  |  |
| $\backsim \frac{N}{\frac{\pi}{c}}$ | － | － | － | － |  |  | － |  |  |
| － | $\begin{aligned} & \text { 年 } \\ & \underset{\circ}{\circ} \end{aligned}$ | $\begin{aligned} & \infty \\ & \vdots \\ & \hat{N} \\ & 0 \end{aligned}$ | － |  |  |  |  |  |  |
|  | ＝ | ＝ | $-\underset{\text { İd }}{ }$ | $\pm$ |  |  | $\pm$ |  |  |
| 亮 | $\pm$ | $\pm$ |  | ＝ |  |  | $\pm$ |  |  |
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|  | $\underset{\substack{\mathrm{\infty}}}{\stackrel{\circ}{\mathrm{j}}}$ |  |  | $\begin{gathered} \tilde{\sim} \\ \underset{\sim}{\tilde{N}} \end{gathered}$ |  |  | ¢ |  |  |
| 抎長 |  |  |  | $\stackrel{\otimes}{\#}$ |  |  |  |  |  |
| 吵 | त्तु |  | $\begin{aligned} & \hline \text { bu } \\ & \text { dic } \\ & \hline \end{aligned}$ | $\stackrel{\circ}{\square}$ |  |  | $\underset{\text { a }}{\substack{\text { a }}}$ |  |  |
|  |  | $\begin{aligned} & \stackrel{N}{\mathrm{~N}} \\ & \stackrel{y}{\mathrm{~N}} \end{aligned}$ | $\begin{aligned} & \text { No } \\ & \text { ベっ } \end{aligned}$ |  | Us | N |  | Cos |  |

## SUMMARY TABLES OF BORON 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 22.35.1. Summary results of boranes.

| Formula | Name | Calculated <br> Total Bond <br> Energy (eV) | Experimental <br> Total Bond <br> Energy (eV) | Relative <br> Error |
| :--- | :--- | :---: | :---: | :---: |
| BB | diboron | 3.12475 | 3.10405 | -0.00667 |
| $\mathrm{~B}_{2} \mathrm{H}_{6}$ | diborane | 24.94229 | 24.89030 | -0.00209 |
| $\mathrm{~B}_{4} \mathrm{H}_{10}$ | tetraborane(10) | 44.92160 | 45.33134 | 0.00904 |
| $\mathrm{~B}_{5} \mathrm{H}_{9}$ | pentaborane(9) | 48.25462 | 48.85411 | 0.01227 |
| $\mathrm{~B}_{5} \mathrm{H}_{11}$ | pentaborane(11) | 54.00546 | 53.06086 | -0.01780 |
| $\mathrm{~B}_{6} \mathrm{H}_{10}$ | hexaborane(10) | 56.55063 | 56.74739 | 0.00347 |
| $\mathrm{~B}_{9} \mathrm{H}_{15}$ | nonaborane(15) | 85.61380 | 84.95008 | -0.00781 |
| $\mathrm{~B}_{10} \mathrm{H}_{14}$ | decaborane(14) | 89.73467 | 89.69790 | -0.00041 |

Table 22.35.2. Summary results of alkyl boranes.

| Formula | Name | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
| :---: | :---: | :---: | :---: | :---: |
| $\mathrm{CH}_{5} \mathrm{~B}$ | methylborane | 24.60991 | 24.49350 [16] | -0.00475 |
| $\mathrm{C}_{2} \mathrm{H}_{7} \mathrm{~B}$ | dimethylborane | 37.08821 | 37.17713 [16] | 0.00239 |
| $\mathrm{B}_{2} \mathrm{CH}_{8}$ | methyldiborane | 37.42060 | 37.58259 [16] | 0.00431 |
| $\mathrm{B}_{2} \mathrm{C}_{2} \mathrm{H}_{10}$ | ethyldiborane | 49.57830 | 49.50736 [16] | -0.00143 |
| $\mathrm{C}_{3} \mathrm{H}_{9} \mathrm{~B}$ | trimethylboron | 49.56652 | 49.76102 [17] | 0.00391 |
| $\mathrm{B}_{2} \mathrm{C}_{2} \mathrm{H}_{10}$ | 1,1-dimethyldiborane | 49.89890 | 50.20118 [16] | 0.00602 |
| $\mathrm{B}_{2} \mathrm{C}_{2} \mathrm{H}_{10}$ | 1,2-dimethyldiborane | 49.89890 | 50.20118 [16] | 0.00602 |
| $\mathrm{B}_{4} \mathrm{CH}_{12}$ | methyltetraborane | 57.39990 | 57.74604 [16] | 0.00599 |
| $\mathrm{B}_{5} \mathrm{CH}_{11}$ | methylpentaborane | 60.73292 | 61.51585 [16] | 0.01273 |
| $\mathrm{B}_{2} \mathrm{C}_{3} \mathrm{H}_{12}$ | trimethyldiborane | 62.37721 | 62.88481 [16] | 0.00807 |
| $\mathrm{B}_{4} \mathrm{C}_{2} \mathrm{H}_{14}$ | ethyltetraborane | 69.55760 | 69.99603 [16] | 0.00626 |
| $\mathrm{B}_{5} \mathrm{C}_{2} \mathrm{H}_{13}$ | ethylpentaborane | 72.89062 | 73.76585 [16] | 0.01186 |
| $\mathrm{B}_{2} \mathrm{C}_{4} \mathrm{H}_{14}$ | 1,1-diethyldiborane | 74.21430 | 74.34420 [16] | 0.00175 |
| $\mathrm{B}_{2} \mathrm{C}_{4} \mathrm{H}_{14}$ | tetramethyldiborane | 74.85551 | 75.48171 [16] | 0.00830 |
| $\mathrm{B}_{5} \mathrm{C}_{3} \mathrm{H}_{15}$ | propylpentaborane | 85.04832 | 85.84239 [16] | 0.00925 |
| $\mathrm{C}_{6} \mathrm{H}_{15} \mathrm{~B}$ | triethylboron | 86.03962 | 86.12941 [18] | 0.00104 |
| $\mathrm{B}_{2} \mathrm{C}_{6} \mathrm{H}_{18}$ | triethyldiborane | 98.85031 | 98.59407 [16] | -0.00260 |
| $\mathrm{B}_{10} \mathrm{CH}_{16}$ | methyldecaborane | 102.21298 | 101.91775 [16] | -0.00290 |
| $\mathrm{C}_{8} \mathrm{H}_{17} \mathrm{~B}$ | n-butylboracyclopentane | 105.35916 | $105.69874{ }^{\text {a }}$ [18] | 0.00321 |
| $\mathrm{B}_{10} \mathrm{C}_{2} \mathrm{H}_{18}$ | ethyldecaborane | 114.37068 | 113.56066 [16] | -0.00713 |
| $\mathrm{C}_{9} \mathrm{H}_{21} \mathrm{~B}$ | tripropylboron | 122.51272 | 122.59753 [18] | 0.00069 |
| $\mathrm{C}_{9} \mathrm{H}_{21} \mathrm{~B}$ | tri-isopropylboron | 122.81539 | 122.75798 [18] | -0.00047 |
| $\mathrm{B}_{2} \mathrm{C}_{8} \mathrm{H}_{22}$ | tetraethyldiborane | 123.48631 | 123.74017 [16] | 0.00205 |
| $\mathrm{B}_{10} \mathrm{C}_{3} \mathrm{H}_{20}$ | propyldecaborane | 126.52838 | 125.94075 [16] | -0.00467 |
| $\mathrm{C}_{12} \mathrm{H}_{27} \mathrm{~B}$ | tri-s-butylboron | 159.28849 | 158.50627 [18] | -0.00493 |
| $\mathrm{C}_{12} \mathrm{H}_{27} \mathrm{~B}$ | tributylboron | 158.98582 | 159.03530 [16] | 0.00031 |
| $\mathrm{C}_{12} \mathrm{H}_{27} \mathrm{~B}$ | tri-isobutylboron | 159.20350 | 159.34318 [16] | 0.00088 |
| $\mathrm{C}_{18} \mathrm{H}_{15} \mathrm{~B}$ | triphenylboron | 172.15755 | 172.09681 [18] | -0.00035 |
| $\mathrm{C}_{15} \mathrm{H}_{33} \mathrm{~B}$ | tri-3-methylbutylboron | 195.67660 | 195.78095 [18] | 0.00053 |
| $\mathrm{C}_{18} \mathrm{H}_{33} \mathrm{~B}$ | tricyclohexylboron | 217.24711 | 218.23763 [18] | 0.00454 |
| $\mathrm{C}_{18} \mathrm{H}_{39} \mathrm{~B}$ | tri-n-hexylboron | 231.93202 | 231.76340 [18] | -0.00073 |
| $\mathrm{C}_{21} \mathrm{H}_{45} \mathrm{~B}$ | tri-n-heptylboron | 268.40512 | 268.22285 [18] | -0.00068 |
| $\mathrm{C}_{24} \mathrm{H}_{51} \mathrm{~B}$ | tri-s-octylboron | 305.18089 | 304.61292 [18] | -0.00186 |
| $\mathrm{C}_{24} \mathrm{H}_{51} \mathrm{~B}$ | tri-n-octylboron | 304.87822 | 304.68230 [18] | -0.00064 |

${ }^{\text {a }}$ Crystal.

Table 22.35.3. Summary results of alkoxy boranes and borinic acids.

| Formula | Name | Calculated <br> Total Bond <br> Energy $(\mathrm{eV})$ | Experimental <br> Total Bond <br> Energy $(\mathrm{eV})$ | Relative <br> Error |
| :--- | :--- | :---: | :---: | :---: |
| $\mathrm{BH}_{3} \mathrm{O}$ | hydroxyborane | 18.29311 | $18.22572[17]$ | -0.00370 |
| $\mathrm{BH}_{3} \mathrm{O}_{2}$ | dihydroxyborane | 24.45460 | $24.43777[17]$ | -0.00069 |
| $\mathrm{BH}_{3} \mathrm{O}_{3}$ | boric acid | 30.61610 | $30.68431[7]$ | 0.00222 |
| $\mathrm{BC}_{2} \mathrm{H}_{7} \mathrm{O}_{2}$ | dimethoxyborane | 47.75325 | $47.72358[16]$ | -0.00062 |
| $\mathrm{BC}_{3} \mathrm{H}_{9} \mathrm{O}_{3}$ | trimethyl borate | 65.56408 | $65.53950[17]$ | -0.00037 |
| $\mathrm{C}_{5} \mathrm{H}_{11} \mathrm{OB}$ | methoxyboracyclopentane | 74.21858 | $74.47566^{\mathrm{a}}[18]$ | 0.00345 |
| $\mathrm{C}_{6} \mathrm{H}_{7} \mathrm{O}_{2} \mathrm{~B}$ | phenylborinic acid | 77.79659 | $78.86121^{\mathrm{a}}[18]$ | 0.01350 |
| $\mathrm{C}_{6} \mathrm{H}_{15} \mathrm{O}_{2} \mathrm{~B}$ | di-isoproxyborane | 96.97471 | $97.41737^{2}[18]$ | 0.00454 |
| $\mathrm{BC}_{6} \mathrm{H}_{15} \mathrm{O}_{3}$ | triethyl borate | 102.62050 | $102.50197[16]$ | -0.00116 |
| $\mathrm{C}_{8} \mathrm{H}_{19} \mathrm{OB}$ | di-n-butylborinic acid | 116.19591 | $116.45117[18]$ | 0.00219 |
| $\mathrm{BC}_{9} \mathrm{H}_{21} \mathrm{O}_{3}$ | tri-n-propyl borate | 139.09360 | $139.11319[16]$ | 0.00014 |
| $\mathrm{C}_{12} \mathrm{H}_{27} \mathrm{OB}^{2}$ | n-butyl di-n-butylborinate | 164.51278 | $165.29504 \mathrm{a}^{\mathrm{a}}[18]$ | 0.00473 |
| $\mathrm{C}_{12} \mathrm{H}_{27} \mathrm{O}_{2} \mathrm{~B}$ | di-n-butyl n-butylboronate | 170.03974 | $170.86964^{\mathrm{a}}[18]$ | 0.00486 |
| $\mathrm{BC}_{12} \mathrm{H}_{27} \mathrm{O}_{3}$ | tri-n-butyl borate | 175.56670 | $175.62901[18]$ | 0.00035 |
| $\mathrm{C}_{18} \mathrm{H}_{15} \mathrm{O}_{3} \mathrm{~B}_{3}$ | phenylborinic anhydride | 204.75082 | $205.96548^{\mathrm{a}}[18]$ | 0.00590 |
| $\mathrm{C}_{16 \mathrm{H}_{36} \mathrm{OB}_{2}}$ | di-n-butylborinic anhydride | 222.84551 | $223.70232^{\mathrm{a}}[18]$ | 0.00383 |
| $\mathrm{C}_{24} \mathrm{H}_{20} \mathrm{OB}_{2}$ | diphenylborinic anhydride | 240.40782 | $241.38941^{\mathrm{a}}[18]$ | 0.00407 |

Table 22.35.4. Summary results of tertiary and quaternary amino boranes and borane amines.

| Formula | Name | Calculated <br> Total Bond <br> Energy $(\mathrm{eV})$ | Experimental <br> Total Bond <br> Energy $(\mathrm{eV})$ | Relative <br> Error |
| :--- | :--- | :---: | :---: | :---: |
| $\mathrm{B}_{2} \mathrm{H}_{7} \mathrm{~N}$ | aminodiborane | 32.36213 | $31.99218[16]$ | -0.01156 |
| $\mathrm{~B}_{2} \mathrm{C}_{2} \mathrm{H}_{11} \mathrm{~N}$ | n-dimethylaminodiborane | 57.21517 | $57.52855[17]$ | 0.00545 |
| $\mathrm{C}_{6} \mathrm{H}_{18} \mathrm{~N}_{3} \mathrm{~B}$ | tris(dimethylamino)borane | 108.95023 | $108.64490[18]$ | -0.00281 |
| $\mathrm{C}_{8} \mathrm{H}_{2} \mathrm{NB}$ | di-n-butylboronamine | 117.45425 | $119.49184 \mathrm{a}[18]$ | 0.01705 |
| $\mathrm{C}_{12} \mathrm{H}_{28} \mathrm{NB}$ | di-n-butylboron-n-butylamine | 166.49595 | $167.83269 \mathrm{a}[18]$ | 0.00796 |
| $\mathrm{C}_{2} \mathrm{H}_{10} \mathrm{NB}$ | dimethylaminoborane | 49.30740 | $49.52189[18]$ | 0.00433 |
| $\mathrm{BC}_{3} \mathrm{H}_{12} \mathrm{~N}$ | trimethylaminoborane | 61.37183 | $61.05205[16]$ | -0.00524 |
| $\mathrm{BC}_{3} \mathrm{H}_{12} \mathrm{~N}$ | ammonia-trimethylborane | 62.91857 | $62.52207[16]$ | -0.00634 |
| $\mathrm{C}_{6} \mathrm{H}_{18} \mathrm{NB}$ | triethylaminoborane | 97.84493 | $97.42044[18]$ | -0.00436 |
| $\mathrm{BC}_{6} \mathrm{H}_{18} \mathrm{~N}$ | trimethylaminotrimethylborane | 98.80674 | $98.27036[17]$ | -0.00546 |

${ }^{\text {a }}$ Crystal.
Table 22.35.5. Summary results of halidoboranes.

| Formula | Name | Calculated <br> Total Bond <br> Energy (eV) | Experimental <br> Total Bond <br> Energy (eV) | Relative <br> Error |
| :--- | :--- | :---: | :---: | :---: |
| $\mathrm{HBF}_{2}$ | difluoroboron | 17.55666 | $17.41845[17]$ | -0.00793 |
| $\mathrm{BF}_{3}$ | boron trifluoride | 20.26918 | $20.09744[7]$ | -0.00855 |
| $\mathrm{BF}_{2} \mathrm{HO}$ | difluoroborinic acid | 23.71816 | $23.64784[17]$ | -0.00297 |
| $\mathrm{BFH}_{2} \mathrm{O}_{2}$ | fluoroboronic acid | 27.16713 | $27.18135[17]$ | 0.00052 |
| $\mathrm{BCH}_{3} \mathrm{~F}_{2}$ | difluoro-methyl-borane | 30.03496 | $30.33624[17]$ | 0.00993 |
| $\mathrm{BC}_{2} \mathrm{H}_{3} \mathrm{~F}_{2}$ | vinyldifluoroborane | 36.21893 | $36.54981[17]$ | 0.00905 |
| $\mathrm{BC}_{3} \mathrm{H}_{9} \mathrm{NF}_{3}$ | trimethylamine-trifluoroborane | 69.50941 | $69.11368[16]$ | -0.00573 |
| $\mathrm{HBCl}_{2}$ | dichloroboron | 13.21640 | $13.25291[17]$ | 0.00276 |
| $\mathrm{BCl}_{3}$ | boron trichloride | 13.75879 | $13.80748[17]$ | 0.00353 |
| $\mathrm{BCl}_{2} \mathrm{~F}$ | dichlorofluoroborane | 15.92892 | $15.87507[17]$ | -0.00339 |
| $\mathrm{BClF}_{2}$ | chlorodifluoroborane | 18.09905 | $17.98169[17]$ | -0.00653 |
| $\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{OCl}_{2} \mathrm{~B}$ | ethoxydichloroborane | 43.37936 | $43.55732[18]$ | 0.00409 |
| $\mathrm{C}_{2} \mathrm{H}_{4} \mathrm{O}_{2} \mathrm{ClB}$ | 2-chloro-1,3,2-dioxaborolan | 43.68867 | $43.99361 \mathrm{a}[18]$ | 0.00693 |
| $\mathrm{C}_{2} \mathrm{H}_{6} \mathrm{NCI}_{2} \mathrm{~B}$ | dimethylaminodichloroborane | 45.48927 | $45.73940[16]$ | 0.00547 |
| $\mathrm{BC}_{2} \mathrm{ClH}_{6} \mathrm{Cl}_{2}$ | dimethoxychloroborane | 48.29565 | $48.40390[17]$ | 0.00224 |
| $\mathrm{C}_{3} \mathrm{H}_{6} \mathrm{O}_{2} \mathrm{ClB}^{2}$ | 4-methyl-2-chloro-1,3,2-dioxaborolan | 55.94726 | $56.39537 \mathrm{a}[18]$ | 0.00795 |
| $\mathrm{BC}_{6} \mathrm{H}_{5} \mathrm{Cl}_{2}$ | phenylboron dichloride | 66.55838 | $66.97820[17]$ | 0.00627 |
| $\mathrm{C}_{4} \mathrm{H}_{8} \mathrm{O}_{2} \mathrm{ClB}^{2}$ | 4,5-dimethyl-2-chloro-1,3,2-dioxaborolan | 68.23418 | $68.72342^{\mathrm{a}}[18]$ | 0.00712 |
| $\mathrm{C}_{4} \mathrm{H}_{10} \mathrm{O}_{2} \mathrm{ClB}$ | diethoxychloroborane | 72.99993 | $73.07735[18]$ | 0.00106 |
| $\mathrm{C}_{4} \mathrm{H}_{12} \mathrm{~N}_{2} \mathrm{ClB}$ | bis(dimethlamino) chloroborane | 77.21975 | $77.38078[18]$ | 0.00208 |


| Formula | Name | Calculated <br> Total Bond <br> Energy $(\mathrm{eV})$ | Experimental <br> Total Bond <br> Energy $(\mathrm{eV})$ | Relative <br> Error |
| :--- | :--- | :---: | :---: | :---: |
| $\mathrm{C}_{8} \mathrm{H}_{18} \mathrm{ClB}$ | di-n-butylchloroborane | 110.57681 | $110.99317[18]$ | 0.00375 |
| $\mathrm{C}_{12} \mathrm{H}_{10} \mathrm{ClB}$ | diphenylchloroborane | 119.35796 | $119.79335[18]$ | 0.00363 |

${ }^{\text {a }}$ Crystal.

## REFERENCES

1. D. R. Lide, CRC Handbook of Chemistry and Physics, 86th Edition, CRC Press, Taylor \& Francis, Boca Raton, (2005-6), pp. 10-202 to 10-204.
2. V. Ramakrishna, B. J. Duke, "Can the bis(diboranyl) structure of $[B(4) H(10)]$ be observed? The story continues," Inorg. Chem., Vol. 43, No. 25, (2004), pp. 8176-8184.
3. J. C. Huffman, D. C. Moody, R. Schaeffer, "Studies of boranes. XLV. Crystal structure, improved synthesis, and reactions of tridecaborane(19)," Inorg. Chem., Vol. 15, No. 1. (1976), pp. 227-232.
4. K. Kuchitsu, "Comparison of molecular structures determined by electron diffraction and spectroscopy. Ethane and diborane," J. Chem. Phys., Vol. 49, No. 10, (1968), pp. 4456-4462.
5. D. R. Lide, CRC Handbook of Chemistry and Physics, $86^{\text {th }}$ Ed., CRC Press, Taylor \& Francis, Boca Raton, (2005-6), p. 9-82.
6. diborane $\left({ }^{11} B_{2} H_{6}\right)$ at http://webbook.nist.gov/.
7. D. R. Lide, CRC Handbook of Chemistry and Physics, 86th Edition, CRC Press, Taylor \& Francis, Boca Raton, (2005-6), pp. 9-63; 5-4 to 5-42.
8. W. N. Lipscomb, "The boranes and their relatives," Nobel Lecture, December 11, 1976.
9. A. B. Burg, R. Kratzer, "The synthesis of nonaborane, $B_{9} H_{11}$," Inorg. Chem., Vol. 1, No. 4, (1962), pp. 725-730.
10. D. R. Lide, CRC Handbook of Chemistry and Physics, 86th Edition, CRC Press, Taylor \& Francis, Boca Raton, (2005-6), p. 9-19 to 9-45.
11. BCCB at http://webbook.nist.gov/.
12. G. Herzberg, Molecular Spectra and Molecular Structure II. Infrared and Raman Spectra of Polyatomic Molecules, Van Nostrand Reinhold Company, New York, New York, (1945), pp. 362-369.
13. G. Herzberg, Molecular Spectra and Molecular Structure II. Infrared and Raman Spectra of Polyatomic Molecules, Van Nostrand Reinhold Company, New York, New York, (1945), p. 344.
14. R. J. Fessenden, J. S. Fessenden, Organic Chemistry, Willard Grant Press. Boston, Massachusetts, (1979), p. 320.
15. cyclohexane at http://webbook.nist.gov/.
16. R. L. Hughes, I. C. Smith,, E. W. Lawless, Production of the Boranes and Related Research, Ed. R. T. Holzmann, Academic Press, New York, (1967), pp. 390-396.
17. M. J. S. Dewar, C. Jie, E. G. Zoebisch, "AM1 calculations for compounds containing boron," Organometallics, Vol. 7, (1988), pp. 513-521.
18. J. D. Cox, G. Pilcher, Thermochemistry of Organometallic Compounds, Academic Press, New York, (1970), pp. 454-465.
19. W. I. F. David, R. M. Ibberson, G. A. Jeffrey, J. R. Ruble, "The structure analysis of deuterated benzene and deuterated nitromethane by pulsed-neutron powder diffraction: a comparison with single crystal neutron analysis," Physica B (1992), $180 \& 181$, pp. 597-600.
20. G. A. Jeffrey, J. R. Ruble, R. K. McMullan, J. A. Pople, "The crystal structure of deuterated benzene," Proceedings of the Royal Society of London. Series A, Mathematical and Physical Sciences, Vol. 414, No. 1846, (Nov. 9, 1987), pp. 47-57.
21. H. B. Burgi, S. C. Capelli, "Getting more out of crystal-structure analyses," Helvet. Chim Acta, Vol. 86, (2003), pp. 16251640.
22. K. P. Huber, G. Herzberg, Molecular Spectra and Molecular Structure, IV. Constants of Diatomic Molecules, Van Nostrand Reinhold Company, New York, (1979).
23. J. Crovisier, Molecular Database-Constants for molecules of astrophysical interest in the gas phase: photodissociation, microwave and infrared spectra, Ver. 4.2, Observatoire de Paris, Section de Meudon, Meudon, France, May 2002, pp. 34-37, available at http://wwwusr.obspm.fr/~crovisie/.
24. dimethyl ether at http://webbook.nist.gov/.
25. methylamine at http://webbook.nist.gov/.
26. D. Lin-Vien. N. B. Colthup, W. G. Fateley, J. G. Grasselli, The Handbook of Infrared and Raman Frequencies of Organic Molecules, Academic Press, Inc., Harcourt Brace Jovanovich, Boston, (1991), p. 482.
27. W. S. Benedict, E. K. Plyler, "Vibration-rotation bands of ammonia," Can. J. Phys., Vol. 35, (1957), pp. 1235-1241.
28. T. Amano, P. F. Bernath, R. W. McKellar, "Direct observation of the $v_{1}$ and $v_{3}$ fundamental bands of $\mathrm{NH}_{2}$ by difference frequency laser spectroscopy," J. Mol. Spectrosc., Vol. 94, (1982), pp. 100-113.
29. D. R. Lide, CRC Handbook of Chemistry and Physics, $79^{\text {th }}$ Ed., CRC Press, Boca Raton, Florida, (1998-9), pp. 9-80 to 9-85.
30. D. R. Lide, CRC Handbook of Chemistry and Physics, $86^{\text {th }}$ Ed., CRC Press, Taylor \& Francis, Boca Raton, (2005-6), p. 9-55.
31. G. Herzberg, Molecular Spectra and Molecular Structure II. Infrared and raman spectra of polyatomic molecules, Van Nostrand Reinhold Company, New York, NY, (1945), p. 326.

## Chapter 23

## ORGANOMETALLIC AND COORDINATE FUNCTIONAL GROUPS AND MOLECULES

## GENERAL CONSIDERATIONS OF THE ORGANOMETALLIC AND COORDINATE BOND

Organometallic and coordinate compounds comprising an arbitrary number of atoms can be solved using similar principles and procedures as those used to solve organic molecules of arbitrary length and complexity. Organometallic and coordinate compounds can be considered to be comprised of functional groups such as $M-C, M-H, M-X(X=F, C l, B r, I)$, $M-O H, M-O R$, and the alkyl functional groups of organic molecules. The solutions of these functional groups or any others corresponding to the particular organometallic or coordinate compound can be conveniently obtained by using generalized forms of the force balance equation given in the Force Balance of the $\sigma$ MO of the Carbon Nitride Radical section for molecules comprised of metal and atoms other than carbon and the geometrical and energy equations given in the Derivation of the General Geometrical and Energy Equations of Organic Chemistry section for organometallic and coordinate compounds comprised of carbon. The appropriate functional groups with their geometrical parameters and energies can be added as a linear sum to give the solution of any organometallic or coordinate compound.

## ALKYL ALUMINUM HYDRIDES ( $R_{n} A l H_{3-n}$ )

Similar to the case of carbon and silicon, the bonding in the aluminum atom involves four $s p^{3}$ hybridized orbitals formed from the outer $3 p$ and $3 s$ shells except that only three HOs are filled. In organoaluminum compounds, bonds form between a $A l 3 s p^{3} \mathrm{HO}$ and at least one $C 2 s p^{3} \mathrm{HO}$ and one or more $H 1 s$ AOs. The geometrical parameters of each AlH functional group is solved from the force balance equation of the electrons of the corresponding $\sigma-\mathrm{MO}$ and the relationships between the prolate spheroidal axes. Then, the sum of the energies of the $H_{2}$-type ellipsoidal MOs is matched to that of the $A l 3 s p^{3}$ shell as in the case of the corresponding carbon and silicon molecules. As in the case of alkyl silanes given in the corresponding section, the sum of the energies of the $H_{2}$-type ellipsoidal MO of the $\mathrm{Al}-\mathrm{C}$ functional group is matched to that of the $A l 3 s p^{3}$ shell, and Eq. (15.51) is solved for the semimajor axis with $n_{1}=1$ in Eq. (15.50).

The energy of aluminum 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 the donation of $25 \%$ electron density from the participating $A l 3 s p^{3} \mathrm{HO}$ to each $\mathrm{Al}-\mathrm{H}$-bond MO.

The $3 s p^{3}$ hybridized orbital arrangement after Eq. (13.422) is

where the quantum numbers $\left(\ell, m_{\ell}\right)$ are below each electron. The total energy of the state is given by the sum over the three electrons. The sum $E_{T}\left(A l, 3 s p^{3}\right)$ of experimental energies [1] of $A l, A l^{+}$, and $A l^{2+}$ is

$$
\begin{equation*}
E_{T}\left(A l, 3 s p^{3}\right)=-(28.44765 \mathrm{eV}+18.82856 \mathrm{eV}+5.98577 \mathrm{eV})=-53.26198 \mathrm{eV} \tag{23.2}
\end{equation*}
$$

By considering that the central field decreases by an integer for each successive electron of the shell, the radius $r_{3 s p^{3}}$ of the
$A l 3 s p^{3}$ shell may be calculated from the Coulombic energy using Eq. (15.13):

$$
\begin{equation*}
r_{3 s p^{3}}=\sum_{n=10}^{12} \frac{(Z-n) e^{2}}{8 \pi \varepsilon_{0}(e 53.26198 \mathrm{eV})}=\frac{6 e^{2}}{8 \pi \varepsilon_{0}(e 53.26198 \mathrm{eV})}=1.53270 a_{0} \tag{23.3}
\end{equation*}
$$

where $Z=13$ for aluminum. Using Eq. (15.14), the Coulombic energy $E_{\text {Coulomb }}\left(A l, 3 s p^{3}\right)$ of the outer electron of the $A l 3 s p^{3}$ shell is:

$$
\begin{equation*}
E_{\text {Coulomb }}\left(A l, 3 s p^{3}\right)=\frac{-e^{2}}{8 \pi \varepsilon_{0} r_{3 s p^{3}}}=\frac{-e^{2}}{8 \pi \varepsilon_{0} 1.53270 a_{0}}=-8.87700 \mathrm{eV} \tag{23.4}
\end{equation*}
$$

During hybridization, the spin-paired $3 s$ electrons are promoted to the $A l 3 s p^{3}$ shell as unpaired electrons. The energy for the promotion is the magnetic energy given by Eq. (15.15) at the initial radius of the $3 s$ electrons. From Eq. (10.255) with $Z=13$, the radius $r_{12}$ of the Al3s shell is:

$$
\begin{equation*}
r_{12}=1.41133 a_{0} \tag{23.5}
\end{equation*}
$$

Using Eqs. (15.15) and (23.5), the unpairing energy is:

$$
\begin{equation*}
E(\text { magnetic })=\frac{2 \pi \mu_{0} e^{2} \hbar^{2}}{m_{e}^{2}\left(r_{12}\right)^{3}}=\frac{8 \pi \mu_{o} \mu_{B}^{2}}{\left(1.41133 a_{0}\right)^{3}}=0.04070 \mathrm{eV} \tag{23.6}
\end{equation*}
$$

Using Eqs. (23.4) and (23.6), the energy $E\left(A l, 3 s p^{3}\right)$ of the outer electron of the $A l 3 s p^{3}$ shell is:

$$
\begin{equation*}
E\left(A l, 3 s p^{3}\right)=\frac{-e^{2}}{8 \pi \varepsilon_{0} r_{3 s p^{3}}}+\frac{2 \pi \mu_{0} e^{2} \hbar^{2}}{m_{e}^{2}\left(r_{12}\right)^{3}}=-8.87700 \mathrm{eV}+0.04070 \mathrm{eV}=-8.83630 \mathrm{eV} \tag{23.7}
\end{equation*}
$$

Next, consider the formation of the $A l-H$-bond MO of organoaluminum hydrides wherein each aluminum atom has an $A l 3 s p^{3}$ electron with an energy given by Eq. (23.7). The total energy of the state of each aluminum atom is given by the sum over the three electrons. The sum $E_{T}\left(A l_{\text {organoall }} 3 s p^{3}\right)$ of energies of $A l 3 s p^{3}$ (Eq. (23.7)), $A l^{+}$, and $A l^{2+}$ is:

$$
\begin{align*}
E_{T}\left(A l_{\text {organoAl }} 3 s p^{3}\right) & =-\left(28.44765 \mathrm{eV}+18.82856 \mathrm{eV}+E\left(A l, 3 s p^{3}\right)\right)  \tag{23.8}\\
& =-(28.44765 \mathrm{eV}+18.82856 \mathrm{eV}+8.83630 \mathrm{eV})=-56.11251 \mathrm{eV}
\end{align*}
$$

where $E\left(A l, 3 s p^{3}\right)$ is the sum of the energy of $A l,-5.98577 \mathrm{eV}$, and the hybridization energy.
Each $A l-H$-bond MO of each functional group $A l H_{n=1,2,3}$ forms with the sharing of electrons between each $A l 3 s p^{3} \mathrm{HO}$ and each $H 1 s$ AO. As in the case of $C-H$, the $H_{2}$-type ellipsoidal MO comprises $75 \%$ of the $A l-H$-bond MO according to Eq. (13.429). Furthermore, the donation of electron density from each $A l 3 s p^{3} \mathrm{HO}$ to each $A l-H$-bond MO permits the participating orbital to decrease in size and energy. As shown below, the aluminum HOs have spin and orbital angular momentum terms in the force balance which determines the geometrical parameters of the $\sigma$ MO. The angular momentum term requires that each $\mathrm{Al}-\mathrm{H}$-bond MO be treated independently in terms of the charge donation. In order to further satisfy the potential, kinetic, and orbital energy relationships, each $A l 3 s p^{3} \mathrm{HO}$ donates an excess of $25 \%$ of its electron density to each $A l-H$-bond MO to form an energy minimum. By considering this electron redistribution in the organoaluminum hydride molecule as well as the fact that the central field decreases by an integer for each successive electron of the shell, the radius $r_{\text {organoAlH } 3 s p^{3}}$ of the $A l 3 s p^{3}$ shell may be calculated from the Coulombic energy using Eq. (15.18).

$$
\begin{equation*}
r_{\text {organoAlH } 3 s p^{3}}=\left(\sum_{n=10}^{12}(Z-n)-0.25\right) \frac{e^{2}}{8 \pi \varepsilon_{0}(e 56.11251 \mathrm{eV})}=\frac{5.75 e^{2}}{8 \pi \varepsilon_{0}(e 56.11251 \mathrm{eV})}=1.39422 a_{0} \tag{23.9}
\end{equation*}
$$

Using Eqs. (15.19) and (23.9), the Coulombic energy $E_{\text {Coulomb }}\left(A l_{\text {organoAlH }}, 3 s p^{3}\right)$ of the outer electron of the $A l 3 s p^{3}$ shell is:

$$
\begin{equation*}
E_{\text {Coulomb }}\left(A l_{\text {organoAlH }}, 3 s p^{3}\right)=\frac{-e^{2}}{8 \pi \varepsilon_{0} r_{\text {organoAlH } 3 s p^{3}}}=\frac{-e^{2}}{8 \pi \varepsilon_{0} 1.39422 a_{0}}=-9.75870 \mathrm{eV} \tag{23.10}
\end{equation*}
$$

During hybridization, the spin-paired $3 s$ electrons are promoted to the $A l 3 s p^{3}$ shell as unpaired electrons. The energy for the promotion is the magnetic energy given by Eq. (23.6). Using Eqs. (23.6) and (23.10), the energy $E\left(A l_{\text {organoAlH }}, 3 s p^{3}\right)$ of the outer electron of the $A l 3 s p^{3}$ shell is:

$$
\begin{equation*}
E\left(A l_{\text {organoallH }}, 3 s p^{3}\right)=\frac{-e^{2}}{8 \pi \varepsilon_{0} r_{3 s p^{3}}}+\frac{2 \pi \mu_{0} e^{2} \hbar^{2}}{m_{e}^{2}\left(r_{12}\right)^{3}}=-9.75870 \mathrm{eV}+0.04070 \mathrm{eV}=-9.71800 \mathrm{eV} \tag{23.11}
\end{equation*}
$$

Thus, $E_{T}\left(A l-H, 3 s p^{3}\right)$, the energy change of each $A l 3 s p^{3}$ shell with the formation of the $A l-H$-bond MO is given by the difference between Eq. (23.11) and Eq. (23.7):

$$
\begin{equation*}
E_{T}\left(A l-H, 3 s p^{3}\right)=E\left(A l_{\text {organoAlH }}, 3 s p^{3}\right)-E\left(A l, 3 s p^{3}\right)=-9.71800 \mathrm{eV}-(-8.83630 \mathrm{eV})=-0.88170 \mathrm{eV} \tag{23.12}
\end{equation*}
$$

The MO semimajor axis of the $A l-H$ functional group of organoaluminum hydrides is determined from the force balance equation of the centrifugal, Coulombic, and magnetic forces as given in the Polyatomic Molecular Ions and Molecules section and the More Polyatomic Molecules and Hydrocarbons section. The distance from the origin of the $H_{2}$-type-ellipsoidalMO to each focus $c^{\prime}$, the internuclear distance $2 c^{\prime}$, and the length of the semiminor axis of the prolate spheroidal $H_{2}$-type MO $b=c$ are solved from the semimajor axis $a$. Then, the geometric and energy parameters of the MO are calculated using Eqs. (15.1-15.117).

The force balance of the centrifugal force equated to the Coulombic and magnetic forces is solved for the length of the semimajor axis. The Coulombic force on the pairing electron of the MO is:

$$
\begin{equation*}
\mathbf{F}_{\text {Coulomb }}=\frac{e^{2}}{8 \pi \varepsilon_{0} a b^{2}} D \mathbf{i}_{\xi} \tag{23.13}
\end{equation*}
$$

The spin pairing force is

$$
\begin{equation*}
\mathbf{F}_{\text {spin-pairing }}=\frac{\hbar^{2}}{2 m_{e} a^{2} b^{2}} D \mathbf{i}_{\xi} \tag{23.14}
\end{equation*}
$$

The diamagnetic force is:

$$
\begin{equation*}
\mathbf{F}_{\text {diamagneticMO1 }}=-\frac{n_{e} \hbar^{2}}{4 m_{e} a^{2} b^{2}} D \mathbf{i}_{\xi} \tag{23.15}
\end{equation*}
$$

where $n_{e}$ is the total number of electrons that interact with the binding $\sigma$-MO electron. The diamagnetic force $\mathbf{F}_{\text {diamagneticMO2 }}$ on the pairing electron of the $\sigma \mathrm{MO}$ is given by the sum of the contributions over the components of angular momentum:

$$
\begin{equation*}
\mathbf{F}_{\text {diamagneticMO2 }}=-\sum_{i, j} \frac{\left|L_{i}\right| \hbar}{Z_{j} 2 m_{e} a^{2} b^{2}} D \mathbf{i}_{\xi} \tag{23.16}
\end{equation*}
$$

where $|L|$ is the magnitude of the angular momentum of each atom at a focus that is the source of the diamagnetism at the $\sigma$ MO. The centrifugal force is:

$$
\begin{equation*}
\mathbf{F}_{\text {centrifugalMO }}=-\frac{\hbar^{2}}{m_{e} a^{2} b^{2}} D \mathbf{i}_{\xi} \tag{23.17}
\end{equation*}
$$

The force balance equation for the $\sigma-\mathrm{MO}$ of the $A l-H$-bond MO is the same as that of the $S i-H$ except that $Z=13$ and there are three spin-unpaired electron in occupied orbitals rather than four, and the orbital with $\ell, m_{\ell}$ angular momentum quantum numbers of (1,1) is unoccupied. With $n_{e}=2$ and $|L|=3 \sqrt{\frac{3}{4}} \hbar$ and $|L|=3 \sqrt{\frac{3}{4}} \hbar$ corresponding to the spin and orbital angular momentum of the three occupied HOs of the $A l 3 s p^{3}$ shell, the force balance equation is:

$$
\begin{align*}
& \frac{\hbar^{2}}{m_{e} a^{2} b^{2}} D=\frac{e^{2}}{8 \pi \varepsilon_{0} a b^{2}} D+\frac{\hbar^{2}}{2 m_{e} a^{2} b^{2}} D-\left(1+\frac{6 \sqrt{\frac{3}{4}}}{Z}\right) \frac{\hbar^{2}}{2 m_{e} a^{2} b^{2}} D  \tag{23.18}\\
& a=\left(2+\frac{6 \sqrt{\frac{3}{4}}}{Z}\right) a_{0} \tag{23.19}
\end{align*}
$$

With $Z=13$, the semimajor axis of the $A l-H$-bond MO is:

$$
\begin{equation*}
a=2.39970 a_{0} \tag{23.20}
\end{equation*}
$$

Using the semimajor axis, the geometric and energy parameters of the MO are calculated using Eqs. (15.1-15.127) in the same manner as the organic functional groups given in the Organic Molecular Functional Groups and Molecules section. For the $\mathrm{Al}-\mathrm{H}$ functional group, $c_{1}$ is one and $C_{1}=0.75$ based on the orbital composition as in the case of the $C-H$-bond MO. In organoaluminum hydrides, the energy of aluminum is less than the Coulombic energy between the electron and proton of $H$ given by Eq. (1.264). Thus, $c_{2}$ in Eqs. (15.51) and (15.61) is also one, and the energy matching condition is determined by the $C_{2}$ parameter. Then, the hybridization factor for the $\mathrm{Al}-\mathrm{H}$-bond MO is given by the ratio of 8.87700 eV , the magnitude of $E_{\text {Coulomb }}\left(A l_{\text {organoAlH }}, 3 s p^{3}\right)$ (Eq. (23.4)), and 13.605804 eV , the magnitude of the Coulombic energy between the electron and proton of $H$ (Eq. (1.264)):

$$
\begin{equation*}
C_{2}\left(\text { organo } \mathrm{AlH} 3 \mathrm{sp}^{3} \mathrm{HO}\right)=\frac{8.87700 \mathrm{eV}}{13.605804 \mathrm{eV}}=0.65244 \tag{23.21}
\end{equation*}
$$

Since the energy of the MO is matched to that of the $A l 3 s p^{3} \mathrm{HO}, E(A O / H O)$ in Eqs. (15.51) and (15.61) is $E\left(A l, 3 s p^{3}\right)$ given by Eq. (23.7), and $E_{T}\left(\right.$ atom-atom, $\left.m s p^{3} . A O\right)$ is -0.88170 eV corresponding to the independent single-bond charge
contribution (Eq. (23.12)). The energies $E_{D}\left(A l H_{n=1,2}\right)$ of the functional groups $A l H_{n=1,2}$ of organoaluminum hydride molecules are each given by the corresponding integer $n$ times that of $\mathrm{Al}-\mathrm{H}$ :

$$
\begin{equation*}
E_{D}\left(A l H_{n=1,2}\right)=n E_{D}(A l H) \tag{23.22}
\end{equation*}
$$

The branched-chain organoaluminum hydrides, $R_{n} \mathrm{AlH}_{3-n}$, comprise at least a terminal methyl group $\left(\mathrm{CH}_{3}\right)$ and at least one Al bound by a carbon-aluminum single bond comprising a $\mathrm{C}-\mathrm{Al}$ group, and may comprise methylene ( $\mathrm{CH}_{2}$ ), methylyne ( CH ), $\mathrm{C}-\mathrm{C}$, and $A l H_{n=1,2}$ functional groups. The methyl and methylene functional groups are equivalent to those of straightchain 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 $\mathrm{C}-\mathrm{C}$ bonds within isopropyl $\left(\left(\mathrm{CH}_{3}\right)_{2} \mathrm{CH}\right)$ and t-butyl $\left(\left(\mathrm{CH}_{3}\right)_{3} \mathrm{C}\right)$ groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups. These groups in branched-chain organoaluminum hydrides are equivalent to those in branched-chain alkanes.

For the $C-A l$ functional group, hybridization of the $2 s$ and $2 p$ AOs of each $C$ and the $3 s$ and $3 p$ AOs of $A l$ to form single $2 s p^{3}$ and $3 s p^{3}$ shells, respectively, forms an energy minimum, and the sharing of electrons between the $C 2 s p^{3}$ and $A l 3 s p^{3}$ HOs to form a MO permits each participating orbital to decrease in radius and energy. Furthermore, the energy of aluminum is less than the Coulombic energy between the electron and proton of $H$ given by Eq. (1.264). Thus, in organoaluminum hydrides, the $C 2 s p^{3} \mathrm{HO}$ has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of $E\left(C, 2 s p^{3}\right)=-14.63489 \mathrm{eV}$ (Eq. (15.25)), and the Al HO has an energy of $E\left(A l, 3 s p^{3}\right)=-8.83630 \mathrm{eV}$. To meet the equipotential, minimum-energy condition of the union of the $A l 3 s p^{3}$ and $C 2 s p^{3} \mathrm{HOs}, c_{2}$ and $C_{2}$ of Eqs. (15.2-15.5), (15.51), and (15.61) for the $\mathrm{Al}-\mathrm{C}$-bond MO given by Eqs. (15.77) and (15.79) is:

$$
\begin{align*}
C_{2}\left(C 2 s p^{3} \mathrm{HO} \text { to } \mathrm{Al} 3 \mathrm{sp}{ }^{3} \mathrm{HO}\right) & =c_{2}\left(C 2 s p^{3} \mathrm{HO} \text { to } \mathrm{Al} 3 \mathrm{sp}{ }^{3} \mathrm{HO}\right) \\
& =\frac{E\left(A l, 3 s p^{3}\right)}{E\left(C, 2 s p^{3}\right)} c_{2}\left(C 2 s p^{3} \mathrm{HO}\right)=\frac{-8.83630 \mathrm{eV}}{-14.63489 \mathrm{eV}}(0.91771)=0.55410 \tag{23.23}
\end{align*}
$$

The energy of the $C-A l$-bond MO is the sum of the component energies of the $H_{2}$-type ellipsoidal MO given in Eq. (15.51). Since the energy of the MO is matched to that of the $A l 3 s p^{3} \mathrm{HO}, E(A O / H O)$ in Eqs. (15.51) and (15.61) is $E\left(A l, 3 s p^{3}\right)$ given by Eq. (23.7). Since the $C 2 s p^{3}$ HOs have four electrons with a corresponding total field of ten in Eq. (15.13); whereas, the $A l 3 s p^{3}$ HOs have three electrons with a corresponding total field of six, $E_{T}\left(\right.$ atom-atom, $\left.m s p^{3} . A O\right)$ is -0.72457 eV corresponding to the single-bond contributions of carbon (Eq. (14.151)). $\Delta E_{H_{2} M O}(A O / H O)=E_{T}\left(\right.$ atom - atom, $\left.m s p^{3} . A O\right)$ in order to match the energies of the carbon and aluminum HOs.

## BRIDGING BONDS OF ORGANOALUMINUM HYDRIDES ( $A l-H-A l$ AND $A l-C-A l$ )

As given in the Nature of the Chemical Bond of Hydrogen-Type Molecules and Molecular Ions section, the Organic Molecular Functional Groups and Molecules section, and other sections on bonding in neutral molecules, the molecular chemical bond typically comprises an integer number of paired electrons. One exception 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, adenine, fullerene, and graphite is that the paired electrons are distributed over a linear combination of bonds such that the bonding between two atoms involves less than an integer multiple of two electrons. 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.

The $A l 3 s p^{3}$ HOs comprise four orbitals containing three electrons as given by Eq. (23.1). These three occupied orbitals can form three single bonds with other atoms wherein each $A l 3 s p^{3} \mathrm{HO}$ and each orbital from the bonding atom contribute one electron each to the pair of the corresponding bond. However, an alternative bonding is possible that further lowers the energy of the resulting molecule wherein the remaining unoccupied orbital participates in bonding. (Actually an unoccupied orbital has no physical basis. It is only a convenient concept for the bonding electrons in this case additionally having the electron angular momentum state with $\ell, m_{\ell}$ quantum numbers of $(1,1)$ ). In this case the set of two paired electrons are distributed over three atoms and belong to two bonds. Such an electron deficient bonding involving two paired electrons centered on three atoms is called a three-center bond as opposed to the typical single bond called a two-center bond. The designation for a three-center bond involving two $A l 3 s p^{3} \mathrm{HOs}$ and a $H 1 s \mathrm{AO}$ is $A l-H-A l$, and the designation for a three-center bond involving two $A l 3 s p^{3} \mathrm{HOs}$ and a $C 2 s p^{3} \mathrm{HO}$ is $\mathrm{Al}-\mathrm{C}-\mathrm{Al}$.

Each $A l-H-A l$-bond MO and $A l-C-A l$-bond MO comprises the corresponding single bond and forms with further sharing of electrons between each $A l 3 s p^{3} \mathrm{HO}$ and each $H 1 s$ AO and $C 2 s p^{3} \mathrm{HO}$, 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 $A l 3 s p^{3}$ HO to each $A l-H-A l$-bond MO and $A l-C-A l$-bond MO permits the participating orbital to decrease in size and energy. In order to further satisfy the potential, kinetic, and orbital energy relationships, the $A l 3 s p^{3} \mathrm{HO}$ donates an additional excess of $25 \%$ of its electron density to form the bridge (three-center-bond MO) to decrease the energy in the multimer. By considering this electron redistribution in the organoaluminum hydride molecule as well as the fact that the central field decreases by an integer for each successive electron of the shell, the radius $r_{\text {organoAlH } 3 s p^{3}}$ of the $A l 3 s p^{3}$ shell calculated from the Coulombic energy, the Coulombic energy $E_{\text {Coulomb }}\left(A l_{\text {organoall }}, 3 s p^{3}\right)$ of the outer electron of the $A l 3 s p^{3}$ shell, and the energy $E\left(A l_{\text {organoalH }}, 3 s p^{3}\right)$ of the outer electron of the $A l 3 s p^{3}$ shell are given by Eqs. (23.9), (23.10), and (23.11), respectively. Thus, $E_{T}\left(A l-H-A l, 3 s p^{3}\right)$ and $E_{T}\left(A l-C-A l, 3 s p^{3}\right)$, the energy change with the formation of the three-center-bond MO from the corresponding two-centerbond MO and the unoccupied $A l 3 s p^{3} \mathrm{HO}$ is given by Eq. (23.12):

$$
\begin{equation*}
E_{T}\left(A l-H-A l, 3 s p^{3}\right)=E_{T}\left(A l-C-A l, 3 s p^{3}\right)=-0.88170 \mathrm{eV} \tag{23.24}
\end{equation*}
$$

The upper range of the experimental association enthalpy per bridge for both of the reactions.

$$
\begin{equation*}
2 \mathrm{AlH}\left(\mathrm{CH}_{3}\right)_{2} \rightarrow\left[\mathrm{AlH}\left(\mathrm{CH}_{3}\right)_{2}\right]_{2} \tag{23.25}
\end{equation*}
$$

and

$$
\begin{equation*}
2 \mathrm{Al}\left(\mathrm{CH}_{3}\right)_{3} \rightarrow\left[\mathrm{Al}\left(\mathrm{CH}_{3}\right)_{3}\right]_{2} \tag{23.26}
\end{equation*}
$$

is [2]

$$
\begin{equation*}
E_{T}\left(A l-H-A l, 3 s p^{3}\right)=E_{T}\left(A l-C-A l, 3 s p^{3}\right)=-0.867 \mathrm{eV} \tag{23.27}
\end{equation*}
$$

which agrees with Eq. (23.24) very well.
The symbols of the functional groups of alkyl organoaluminum hydrides are given in Table 23.1. The geometrical (Eqs. (15.1-15.5), (23.20), and (23.23)) and intercept (Eqs. (15.80-15.87)) parameters of alkyl organoaluminum hydrides are given in Tables 23.2 and 23.3, respectively. Since the energy of the $A l 3 s p^{3} \mathrm{HO}$ is matched to that of the $C 2 s p^{3} \mathrm{HO}$, the radius $r_{\text {mol } 2 s p^{3}}$ of the $A l 3 s p^{3} \mathrm{HO}$ of the aluminum atom and the $C 2 s p^{3} \mathrm{HO}$ of the carbon atom of a given $C-A l$-bond MO are calculated after Eq. (15.32) by considering $\sum E_{T_{m o l}}\left(M O, 2 s p^{3}\right)$, the total energy donation to all bonds with which each atom participates in bonding. In the case that the MO does not intercept the Al HO due to the reduction of the radius from the donation of $\mathrm{Al} 3 s p^{3}$ HO charge to additional MO's, the energy of each MO is energy matched as a linear sum to the Al HO by contacting it through the bisector current of the intersecting MOs as described in the Methane Molecule ( $\mathrm{CH}_{4}$ ) section. The energy (Eq. (15.61), (23.4), (23.7), and (23.21-23.23)) parameters of alkyl organoaluminum hydrides are given in Table 23.5. The total energy of each alkyl aluminum hydride given in Table 23.5 was calculated as the sum over the integer multiple of each $E_{D}$ (Group) of Table 23.4 corresponding to functional-group composition of the molecule. $E_{\text {mag }}$ of Table 23.4 is given by Eqs. (15.15) and (23.3). The bond angle parameters of organoaluminum hydrides determined using Eqs. (15.88-15.117) are given in Table 23.6. The charge-density in trimethyl aluminum is shown in Figure 23.1.

Figure 23.1. Trimethylaluminum. Color scale, translucent view of the charge-density of $\left(\mathrm{H}_{3} \mathrm{C}\right)_{3} \mathrm{Al}$ comprising the linear combination of three sets of three $C-H$-bond MOs and three $C-A l$-bond MOs with the $A l_{\text {ogranoal }} 3 s p^{3}$ HOs and $C 2 s p^{3}$ HOs shown transparently. Each $C-A l$-bond MO comprises a $H_{2}$-type ellipsoidal MO bridging $C 2 s p^{3}$ and $A l 3 s p^{3}$ HOs. For each $C-H$ and $C-A l$ bond, the ellipsoidal surface of the $H_{2}$-type ellipsoidal MO that transitions to the $C 2 s p^{3}$ HO shell with radius $0.89582 a_{0}$ (Eq. (15.32)) or $A l 3 s p^{3} \mathrm{HO}$, the $A l 3 s p^{3} \mathrm{HO}$ shell with radius $0.85503 a_{0}$ (Eq. (15.32)), inner Alls, Al2s, and $A l 2 p$ shells with radii of $A l 1 s=0.07778 a_{0}$ (Eq. (10.51)), $A l 2 s=0.33923 a_{0}$ (Eq. (10.62)), and $A l 2 p=0.45620 a_{0}$ (Eq. (10.212)), respectively, and the nuclei (red, not to scale), are shown.


Table 23.1. The symbols of the functional groups of organoaluminum hydrides.

| Functional Group | Group Symbol |
| :---: | :---: |
| AlH group of $A l H_{n=1,2}$ | Al-H |
| AlHAl (bridged H) | $A l-H-A l$ |
| CAl bond | $C-A l$ |
| AlCAl (bridged C) | $A l-C-A l$ |
| $\mathrm{CH}_{3}$ group | $\mathrm{C}-\mathrm{H}\left(\mathrm{CH}_{3}\right)$ |
| $\mathrm{CH}_{2}$ group | $\mathrm{C}-\mathrm{H}\left(\mathrm{CH}_{2}\right)$ |
| CH | C-H |
| $C C$ bond ( $n-C$ ) | $C-C$ (a) |
| $C C$ bond (iso-C) | $C-C$ (b) |
| $C C$ bond (tert-C) | $C-C$ (c) |
| $C C$ (iso to iso-C) | $C-C$ (d) |
| $C C$ ( $t$ to $t-C$ ) | $C-C$ (e) |
| $\underline{C C}(t$ to iso- $C$ ) | $C-C$ (f) |

Table 23.2. The geometrical bond parameters of organoaluminum hydrides and experimental values [3].

| Parameter | $\begin{gathered} C-A l \\ \text { and } \\ A l-C-A l \\ \text { Groups } \end{gathered}$ | $A l-H$ and $A l-H-A l$ Groups | $\begin{gathered} \mathrm{C}-\mathrm{H}\left(\mathrm{CH}_{3}\right) \\ \text { Group } \end{gathered}$ | $\begin{gathered} \mathrm{C}-\mathrm{H}\left(\mathrm{CH}_{2}\right) \\ \quad \text { Group } \end{gathered}$ | $\begin{aligned} & C-H \\ & \text { Group } \end{aligned}$ | $\begin{gathered} C-C \text { (a) } \\ \text { Group } \end{gathered}$ | $\begin{gathered} C-C \text { (b) } \\ \text { Group } \end{gathered}$ | $\begin{gathered} C-C(c) \\ \text { Group } \end{gathered}$ | $\begin{gathered} C-C(\mathrm{~d}) \\ \text { Group } \end{gathered}$ | $\begin{gathered} C-C(e) \\ \text { Group } \end{gathered}$ | $\begin{gathered} C-C(\mathrm{f}) \\ \text { Group } \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $a\left(a_{0}\right)$ | 1.89887 | 2.39970 | 1.64920 | 1.67122 | 1.67465 | 2.12499 | 2.12499 | 2.10725 | 2.12499 | 2.10725 | 2.10725 |
| $c^{\prime}\left(a_{0}\right)$ | 1.85120 | 1.56589 | 1.04856 | 1.05553 | 1.05661 | 1.45744 | 1.45744 | 1.45164 | 1.45744 | 1.45164 | 1.45164 |
| $\begin{aligned} & \text { Bond Length } \\ & 2 c^{\prime}(A) \end{aligned}$ | 1.95923 | 1.65727 | 1.10974 | 1.11713 | 1.11827 | 1.54280 | 1.54280 | 1.53635 | 1.54280 | 1.53635 | 1.53635 |
| Exp. Bond Length (A) | $\begin{gathered} 1.957 \\ \text { (trimethylaluminum) } \end{gathered}$ | $\begin{gathered} 1.6482 \mathrm{E}-10 \\ (\text { AlH }) \end{gathered}$ | 1.113 <br> (trimethylaluminum) <br> 1.107 <br> $(\mathrm{C}-H$ propane $)$ <br> 1.117 <br> $(\mathrm{C}-\mathrm{H}$ butane $)$ | $\begin{gathered} 1.107 \\ (C-H \text { propane }) \\ 1.117 \\ (C-H \text { butane }) \end{gathered}$ | $\begin{gathered} 1.122 \\ \text { (isobutane) } \end{gathered}$ | $\begin{gathered} 1.532 \\ \text { (propane) } \\ 1.531 \\ \text { (butane) } \end{gathered}$ |  |  | $\begin{gathered} 1.532 \\ \text { (propane) } \\ 1.531 \\ \text { (butane) } \end{gathered}$ |  |  |
| $b, c\left(a_{0}\right)$ | 0.42282 | 1.81839 | 1.27295 | 1.29569 | 1.29924 | 1.54616 | 1.54616 | 1.52750 | 1.54616 | 1.52750 | 1.52750 |
| $e$ | 0.97489 | 0.65254 | 0.63580 | 0.63159 | 0.63095 | 0.68600 | 0.68600 | 0.68888 | 0.68600 | 0.68888 | 0.68888 |

Table 23.3. The MO to HO intercept geometrical bond parameters of organoaluminum hydrides. $R, R^{\prime}, R^{\prime \prime}$ are $H$ or alkyl groups. $E_{T}$ is $E_{T}\left(\right.$ atom-atom,msp $\left.{ }^{3} . A O\right)$.

| Bond | Atom |  | $\begin{gathered} E_{r} \\ (\mathrm{eV}) \\ \text { Bond } 2 \end{gathered}$ | $\begin{gathered} E_{T} \\ (\mathrm{eV}) \end{gathered}$ $\text { Bond } 3$ | $\begin{gathered} E_{T} \\ (\mathrm{eV}) \\ \text { Bond } 4 \end{gathered}$ | Final Total <br> Energy <br> Al3sp $p^{3}$ <br> $C 2 s p^{3}$ <br> $(\mathrm{eV})$ | $\begin{aligned} & r_{\text {mintal }} \\ & \left(a_{0}\right) \end{aligned}$ | $\begin{aligned} & r_{\text {fral }} \\ & \left(a_{0}\right) \end{aligned}$ | $\begin{gathered} E_{\text {Coulomb }}\left(A l 3 s p^{3}\right) \\ E_{\text {Coulomb }}\left(C 2 s p^{3}\right) \\ \text { (eV) } \\ \text { Final } \end{gathered}$ | $\begin{gathered} E\left(A l 3 s p^{3}\right) \\ E\left(C 2 s p^{3}\right) \\ (\mathrm{eV}) \\ \text { Final } \end{gathered}$ | $\begin{aligned} & \theta^{\prime} \\ & \left({ }^{\circ}\right) \end{aligned}$ | $\begin{gathered} \theta_{1} \\ \left({ }^{\circ}\right) \end{gathered}$ | $\begin{aligned} & \theta_{2} \\ & \left({ }^{\circ}\right) \end{aligned}$ | $\begin{gathered} d_{1} \\ \left(a_{0}\right) \end{gathered}$ | $\begin{gathered} d_{2} \\ \left(a_{0}\right) \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Al-H ( AlH ) | Al | -0.88170 | 0 | 0 | 0 | -56.99421 | 1.53270 | 1.39422 | -9.75870 | -9.71800 | 91.03 | 88.97 | 50.05 | 1.54088 | 0.02501 |
| $\mathrm{Al}-\mathrm{H}\left(\mathrm{RAlH}_{2}\right)$ | Al | -0.88170 | $-0.88170$ | -0.36229 | 0 |  | 1.53270 | 0.80263 | -16.95144 | -16.91074 |  |  |  |  |  |
| $\mathrm{Al}-\mathrm{H}\left(\mathrm{R}_{2} \mathrm{AlH}\right)$ | Al | -0.88170 | -0.36229 | -0.36229 | 0 |  | 1.53270 | 0.82801 | -16.43203 | -16.39133 |  |  |  |  |  |
| $\begin{array}{\|l} \hline A l-H\left(R_{2} A l\left(H_{b}\right)_{2}\right) \\ \left(H_{b}=\text { bridge } \mathrm{H}\right) \\ \hline \end{array}$ | Al | -1.32255 | -1.32255 | -0.36229 | -0.36229 |  | 1.53270 | 0.74776 | -18.19543 | -18.15473 |  |  |  |  |  |
| $\mathrm{H}_{2} \mathrm{Al}-\mathrm{Ca}_{a} \mathrm{H}_{2}-$ | Al | -0.36229 | $-0.88170$ | -0.88170 | 0 | -56.47480 | 1.53270 | 0.80263 | -16.95144 | -16.91074 | 154.88 | 25.12 | 53.69 | 1.12447 | 0.72673 |
| Hal-( $\left.\mathrm{C}_{a} \mathrm{H}_{2}-\right)_{2}$ | Al | -0.36229 | $-0.36229$ | -0.88170 | 0 | -55.95538 | 1.53270 | 0.82801 | -16.43203 | -16.39133 | 155.38 | 24.62 | 54.66 | 1.09845 | 0.75276 |
| $\mathrm{Al}-\left(\mathrm{Ca}_{a} \mathrm{H}_{2}-\right)_{3}$ | Al | -0.36229 | -0.36229 | -0.36229 | 0 | -56.47480 | 1.53270 | 0.85503 | -15.91261 | -15.87191 | 155.90 | 24.10 | 55.68 | 1.07072 | 0.78048 |
| $\begin{aligned} & \left(-C_{a} H_{2}\right)_{2} A l-\left(C_{b}\right)_{2} \\ & \left(C_{b}=\text { bridge } \mathrm{C}\right) \end{aligned}$ | Al | $-0.36229$ | -0.36229 | -0.36229 | $-0.80314$ | -57.27793 | 1.53270 | 0.81395 | -16.71575 | -16.67505 | 155.11 | 24.89 | 54.12 | 1.11286 | 0.73834 |
| $\mathrm{Al}^{-\mathrm{CH}_{3}}$ | C | -0.36229 | 0 | 0 | 0 | -151.97798 | 0.91771 | 0.89582 | -15.18804 | -14.99717 | 156.63 | 23.37 | 57.19 | 1.02888 | 0.82232 |
| Al- $\mathrm{Ca}_{a} \mathrm{H}_{2} \mathrm{CH}_{2}-$ | $C_{a}$ | -0.36229 | -0.92918 | 0 | 0 | -152.90716 | 0.91771 | 0.84418 | -16.11722 | -15.92636 | 155.69 | 24.31 | 55.27 | 1.08186 | 0.76935 |
| $\begin{aligned} & \left(-C_{a} H_{2}\right)_{2}\left(C_{b}\right) A l-C_{b}-A l \\ & \left(C_{b}=\text { bridge } \mathrm{C}\right) \\ & \hline \end{aligned}$ | $C_{b}$ | -0.80314 | -0.80314 | 0 | 0 | -153.22196 | 0.91771 | 0.82801 | -16.43203 | -16.24116 | 155.38 | 24.62 | 54.66 | 1.09845 | 0.75276 |
| $\mathrm{C}-\mathrm{H}\left(\mathrm{CH}_{3}\right)$ | 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 |
| $\mathrm{C}-\mathrm{H}\left(\mathrm{CH}_{2}\right)$ | 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 |
| $\mathrm{C}-\mathrm{H}(\mathrm{CH})$ | 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 |
| $\begin{aligned} & \mathrm{H}_{3} \mathrm{C}_{\mathrm{G}} \mathrm{C}_{b} \mathrm{H}_{2} \mathrm{CH}_{2}- \\ & (\mathrm{C}-\mathrm{C}(\mathrm{a})) \end{aligned}$ | $C_{a}$ | -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 |
| $\begin{aligned} & \mathrm{H}_{3} \mathrm{C}_{a} \mathrm{C}_{b} \mathrm{H}_{2} \mathrm{CH}_{2}- \\ & (\mathrm{C}-\mathrm{C}(\mathrm{a})) \\ & \hline \end{aligned}$ | $C_{b}$ | -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 |
| $\begin{aligned} & R-H_{2} C_{a} C_{b}\left(H_{2} C_{c}-R^{\prime}\right) H C H_{2}- \\ & (\mathrm{C}-\mathrm{C}(\mathrm{~b})) \end{aligned}$ | $C_{b}$ | -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 |
| $\begin{aligned} & R-H_{2} C_{a}\left(R^{\prime}-H_{2} C_{d}\right) C_{b}\left(R^{\prime \prime}-H_{2} C_{c}\right) C H_{2}- \\ & (C-C(c)) \end{aligned}$ | $C_{b}$ | -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 |
| $\begin{aligned} & \text { isoC } C_{a} C_{b}\left(H_{2} C_{c}-R^{\prime}\right) H C H_{2}- \\ & (C-C \text { (d) }) \\ & \hline \end{aligned}$ | $C_{b}$ | -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 |
| $\begin{aligned} & {\text { tert } \mathrm{C}_{a}\left(\mathrm{R}^{\prime}-\mathrm{H}_{2} \mathrm{C}_{d}\right) C_{b}\left(R^{\prime \prime}-\mathrm{H}_{2} \mathrm{C}_{c}\right) \mathrm{CH}_{2}-}^{(\mathrm{C}-\mathrm{C}(\mathrm{e}))} \end{aligned}$ | $C_{b}$ | $-0.72457$ | -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 |
| $\begin{aligned} & \text { tert } C_{a} C_{b}\left(H_{2} C_{c}-R^{\prime}\right) \mathrm{HCH}_{2}- \\ & (\mathrm{C}-\mathrm{C}(\mathrm{f})) \\ & \hline \end{aligned}$ | $C_{b}$ | -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 |
| $\begin{aligned} & i s O_{a}\left(R^{\prime}-\mathrm{H}_{2} C_{d}\right) C_{b}\left(R^{\prime \prime}-\mathrm{H}_{2} C_{c}\right) \mathrm{CH}_{2}- \\ & (\mathrm{C}-\mathrm{C}(\mathrm{f})) \end{aligned}$ | $C_{b}$ | $-0.72457$ | -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 23.4. The energy parameters $(\mathrm{eV})$ of functional groups of organoaluminum hydrides.

| Parameters | $\begin{gathered} C-A l \\ \text { and } \\ A l-C-A l \text { a } \\ \text { Groups } \\ \hline \end{gathered}$ | $\begin{gathered} A l-H \\ \text { and } \\ A l-H-A l \mathrm{a} \\ \text { Groups } \\ \hline \end{gathered}$ | $\mathrm{CH}_{3}$ <br> Group | $\mathrm{CH}_{2}$ <br> Group | $\begin{aligned} & C-H \\ & \text { Group } \end{aligned}$ | $\begin{gathered} C-C \text { (a) } \\ \text { Group } \end{gathered}$ | $\begin{gathered} C-C \text { (b) } \\ \text { Group } \end{gathered}$ | $\begin{gathered} C-C(\mathrm{c}) \\ \text { Group } \end{gathered}$ | $\begin{gathered} C-C(\mathrm{~d}) \\ \text { Group } \end{gathered}$ | $\begin{gathered} C-C(\mathrm{e}) \\ \text { Group } \end{gathered}$ | $\begin{gathered} C-C(f) \\ \text { Group } \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $n_{1}$ | 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 | 0.75 | 0.75 | 0.75 | 0.75 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| $C_{2}$ | 0.55410 | 0.65244 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $c_{1}$ | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $c_{2}$ | 0.55410 | 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 | 1 | 1 | 1 | 1 | 2 | 2 | 2 | 2 | 2 | 2 |
| $c_{5}$ | 0 | 1 | 3 | 2 | 1 | 0 | 0 | 0 | 0 | 0 | 0 |
| $C_{10}$ | 0.5 | 0.75 | 0.75 | 0.75 | 0.75 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| $C_{20}$ | 0.55410 | 0.65244 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $V_{e}(\mathrm{eV})$ | -35.55430 | -27.09887 | -107.32728 | -70.41425 | -35.12015 | -28.79214 | -28.79214 | -29.10112 | -28.79214 | -29.10112 | -29.10112 |
| $V_{p}(\mathrm{eV})$ | 7.34971 | 8.68884 | 38.92728 | 25.78002 | 12.87680 | 9.33352 | 9.33352 | 9.37273 | 9.33352 | 9.37273 | 9.37273 |
| $T(\mathrm{eV})$ | 9.36194 | 5.64629 | 32.53914 | 21.06675 | 10.48582 | 6.77464 | 6.77464 | 6.90500 | 6.77464 | 6.90500 | 6.90500 |
| $V_{m}(\mathrm{eV})$ | -4.68097 | -2.82315 | -16.26957 | -10.53337 | -5.24291 | -3.38732 | -3.38732 | -3.45250 | -3.38732 | -3.45250 | -3.45250 |
| E(лоно) (eV) | -8.83630 | -8.83630 | -15.56407 | -15.56407 | -14.63489 | -15.56407 | -15.56407 | -15.35946 | -15.56407 | -15.35946 | -15.35946 |
| $\Delta E_{H_{2} \text { HO }}$ (АОІНО) $(\mathrm{eV})$ | -0.72457 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $E_{T}$ ( (1/ $/ \mathrm{Ho}$ ) ( eV ) | -8.11172 | -8.83630 | -15.56407 | -15.56407 | -14.63489 | -15.56407 | -15.56407 | -15.35946 | -15.56407 | -15.35946 | -15.35946 |
| $E_{T}\left(H_{2}, \mathrm{MO}\right)(\mathrm{eV})$ | -31.63534 | -24.42317 | -67.69451 | -49.66493 | -31.63533 | -31.63537 | -31.63537 | -31.63535 | -31.63537 | -31.63535 | -31.63535 |
| $E_{T}\left(\right.$ atom-atom, msp $\left.{ }^{3} \cdot \mathrm{AO}\right)(\mathrm{eV})$ | -0.72457 | -0.88170 | 0 | 0 | 0 | -1.85836 | -1.85836 | -1.44915 | -1.85836 | -1.44915 | -1.44915 |
| $E_{T}($ (мо) $(\mathrm{eV})$ | -32.35994 | -25.30487 | -67.69450 | -49.66493 | -31.63537 | -33.49373 | -33.49373 | -33.08452 | -33.49373 | -33.08452 | -33.08452 |
| $\omega$ o ( $10^{15} \mathrm{rad} / \mathrm{s}$ ) | 8.31610 | 11.7938 | 24.9286 | 24.2751 | 24.1759 | 9.43699 | 9.43699 | 15.4846 | 9.43699 | 9.55643 | 9.55643 |
| $E_{K}(\mathrm{eV})$ | 5.47380 | 7.76290 | 16.40846 | 15.97831 | 15.91299 | 6.21159 | 6.21159 | 10.19220 | 6.21159 | 6.29021 | 6.29021 |
| $\bar{E}_{D}(\mathrm{eV})$ | -0.14978 | -0.13948 | -0.25352 | -0.25017 | -0.24966 | -0.16515 | -0.16515 | -0.20896 | -0.16515 | -0.16416 | -0.16416 |
| $\bar{E}_{\text {Kuvb }}(\mathrm{eV})$ | $\begin{gathered} 0.05721 \\ {[4]} \\ \hline \end{gathered}$ | $\begin{gathered} 0.20861 \\ {[5]} \\ \hline \end{gathered}$ | $\begin{gathered} 0.35532 \\ \text { (Eq. }(13.458)) \end{gathered}$ | $\begin{gathered} 0.35532 \\ \text { (Eq. }(13.458)) \end{gathered}$ | $\begin{gathered} 0.35532 \\ \text { (Eq. }(13.458)) \end{gathered}$ | $\begin{gathered} 0.12312 \\ {[6]} \end{gathered}$ | $\begin{gathered} 0.17978 \\ {[7]} \\ \hline \end{gathered}$ | $\begin{gathered} 0.09944 \\ {[8]} \\ \hline \end{gathered}$ | $\begin{gathered} 0.12312 \\ {[6]} \end{gathered}$ | $\begin{gathered} 0.12312 \\ {[6]} \end{gathered}$ | $\begin{gathered} 0.12312 \\ {[6]} \\ \hline \end{gathered}$ |
| $\bar{E}_{\text {occ }}(\mathrm{eV})$ | -0.12118 | -0.03518 | -0.22757 | -0.14502 | -0.07200 | -0.10359 | -0.07526 | -0.15924 | -0.10359 | -0.10260 | -0.10260 |
| $E_{\text {mag }}(\mathrm{eV})$ | 0.14803 | 0.03178 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 |
| $E_{T}($ Group $)(\mathrm{eV})$ | -32.48112 | -25.34005 | -67.92207 | -49.80996 | -31.70737 | -33.59732 | -33.49373 | -33.24376 | -33.59732 | -33.18712 | -33.18712 |
| $E_{\text {irrual }}\left(\mathrm{c}_{4}\right.$ AOIHO) $(\mathrm{eV})$ | -14.63489 | -8.83630 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 |
|  | 0 | -13.59844 | -13.59844 | -13.59844 | -13.59844 | 0 | 0 | 0 | 0 | 0 | 0 |
| $E_{D}($ Group $)(\mathrm{eV})$ | 3.21134 | 2.90531 | 12.49186 | 7.83016 | 3.32601 | 4.32754 | 4.29921 | 3.97398 | 4.17951 | 3.62128 | 3.91734 |
| Exp. $E_{D}($ (Group) $(\mathrm{eV})$ |  | $\begin{gathered} 2.98 \\ (\text { AlH [9]) } \\ \hline \end{gathered}$ |  |  |  |  |  |  |  |  |  |

Table 23．5．The total bond energies of gaseous－state organoaluminum hydrides calculated using the functional group composition and the energies of Table 23.4 compared to the gaseous－state experimental values［10］except where indicated．

| Formula | Name | $\begin{aligned} & A l-H \\ & \text { Group } \end{aligned}$ | $\begin{aligned} & C-A l \\ & \text { Group } \end{aligned}$ | $\mathrm{CH}_{3}$ | $\mathrm{CH}_{2}$ | CH | $C-C$（a） | $C-C$（b） | $C-C$（c） | $C-C$（d） | $C-C$（e） | C－C（f） | Calculated <br> Total Bond <br> Energy（eV） | Experimental Total Bond Energy（eV） | Relative Error |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{C}_{2} \mathrm{H}_{7} \mathrm{Al}$ | Dimethylaluminum hydride | 1 | 2 | 2 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 34.31171 | 34.37797 a ［11］ | 0.00193 |
| $\mathrm{C}_{3} \mathrm{H}_{9} \mathrm{Al}$ | Trimethyl aluminum | 0 | 3 | 3 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 47.10960 | 46.95319 | －0．00333 |
| $\mathrm{C}_{4} \mathrm{H}_{11} \mathrm{Al}$ | Diethylaluminum hydride | 1 | 2 | 2 | 2 | 0 | 2 | 0 | 0 | 0 | 0 | 0 | 58.62711 | $60.10948^{\text {b }}$ | 0.02466 |
| $\mathrm{C}_{6} \mathrm{H}_{15} \mathrm{Al}$ | Triethylaluminum hydride | 0 | 3 | 3 | 3 | 0 | 3 | 0 | 0 | 0 | 0 | 0 | 83.58270 | 83.58176 | －0．00001 |
| $\mathrm{C}_{6} \mathrm{H}_{15} \mathrm{Al}$ | Di－n－propylaluminum hydride | 1 | 2 | 2 | 4 | 0 | 4 | 0 | 0 | 0 | 0 | 0 | 82.94251 | $84.40566^{\text {b }}$ | 0.01733 |
| $\mathrm{C}_{9} \mathrm{H}_{21} \mathrm{Al}$ | Tri－n－propyl aluminum | 0 | 3 | 3 | 6 | 0 | 6 | 0 | 0 | 0 | 0 | 0 | 120.05580 | $121.06458{ }^{\text {b }}$ | 0.00833 |
| $\mathrm{C}_{8} \mathrm{H}_{19} \mathrm{Al}$ | Di－n－butylaluminum hydride | 1 | 2 | 2 | 6 | 0 | 6 | 0 | 0 | 0 | 0 | 0 | 107.25791 | $108.71051^{\text {b }}$ | 0.01336 |
| $\mathrm{C}_{8} \mathrm{H}_{19} \mathrm{Al}$ | Di－isobutylaluminum hydride | 1 | 2 | 4 | 2 | 2 | 0 | 6 | 0 | 0 | 0 | 0 | 107.40303 | $108.77556^{\text {b }}$ | 0.01262 |
| $\mathrm{C}_{12} \mathrm{H}_{27} \mathrm{Al}$ | Tri－n－butyl aluminum | 0 | 3 | 3 | 9 | 0 | 9 | 0 | 0 | 0 | 0 | 0 | 156.52890 | $157.42429{ }^{\text {b }}$ | 0.00569 |
| $\mathrm{C}_{12} \mathrm{H}_{27} \mathrm{Al}$ | Tri－isobutyl aluminum | 0 | 3 | 6 | 3 | 3 | 0 | 9 | 0 | 0 | 0 | 0 | 156.74658 | $157.58908^{\text {b }}$ | 0.00535 |

Table 23．6．The bond angle parameters of organoaluminum hydrides and experimental values［3］．In the calculation of $\theta_{v}$ ，the parameters from the preceding angle were used．$E_{T}$ is $E_{T}$（atom－atom，$m s p^{3} . A O$ ）．

| $\begin{aligned} & 0 \\ & \dot{x} \times 0 \\ & i \end{aligned}$ |  |  |  |  |  |  |  |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\underset{\sim}{\circ}$ |  | $\begin{aligned} & \text { in } \\ & \stackrel{2}{2} \end{aligned}$ | $\begin{aligned} & \text { 寸 } \\ & \text { 寸 } \end{aligned}$ | $\begin{aligned} & \text { I } \\ & \stackrel{O}{0} \end{aligned}$ | $\begin{aligned} & \ddagger \\ & \stackrel{\infty}{\infty} \end{aligned}$ | $\begin{aligned} & \stackrel{+}{\dot{O}} \\ & \hline \end{aligned}$ |  | $\begin{aligned} & q \\ & \dot{\theta} \\ & \underset{\sim}{2} \end{aligned}$ | $\begin{aligned} & \stackrel{\rightharpoonup}{\bullet} \\ & = \end{aligned}$ | $\begin{aligned} & \stackrel{0}{0} \\ & \stackrel{y}{0} \end{aligned}$ | $\stackrel{\text { Ỳ }}{\Xi}$ | $\stackrel{\sqrt{3}}{\vdots}$ | $\xrightarrow{0}$ |
| $0^{\circ}$ O |  |  |  |  |  |  |  |  |  |  |  |  |  |
| 0 O |  |  |  |  |  |  |  |  |  |  |  |  |  |
| 0 O |  |  | $\begin{aligned} & 0 \\ & \stackrel{n}{2} \\ & \end{aligned}$ | $\begin{aligned} & \stackrel{\circ}{2} \\ & \stackrel{2}{2} \end{aligned}$ |  | n | n | $\left\lvert\, \begin{gathered} 0 \\ \stackrel{n}{2} \\ \stackrel{2}{2} \end{gathered}\right.$ |  |  |  |  | ¢ |
| से | $\begin{aligned} & \stackrel{\circ}{\infty} \\ & \stackrel{\infty}{\infty} \\ & \underset{\sim}{1} \end{aligned}$ | $\bigcirc$ |  |  | $\bigcirc$ |  |  |  | $\begin{gathered} \stackrel{\infty}{\infty} \\ \stackrel{\infty}{\infty} \\ \underset{\sim}{+} \end{gathered}$ | $\bigcirc$ | $\bigcirc$ | $\begin{gathered} \stackrel{\infty}{\infty} \\ \stackrel{\infty}{\infty} \\ \end{gathered}$ |  |
| $\sim$ | $\begin{aligned} & \text { ה. } \\ & \text { 合. } \end{aligned}$ | $\begin{aligned} & \stackrel{\circ}{n} \\ & \stackrel{i}{~} \\ & = \end{aligned}$ |  |  | $\begin{aligned} & \circ \\ & \stackrel{\circ}{n} \\ & \stackrel{1}{3} \end{aligned}$ |  |  |  | $\begin{gathered} \stackrel{\rightharpoonup}{6} \\ \stackrel{\sim}{\infty} \\ \underset{\sim}{\circ} \end{gathered}$ |  | $\begin{aligned} & \stackrel{\rightharpoonup}{\infty} \\ & \stackrel{+}{O} \\ & \hline \end{aligned}$ | $\begin{gathered} \underset{\sim}{i} \\ \stackrel{N}{\infty} \\ \underset{\sim}{0} \end{gathered}$ |  |
| $v$ | － | $\cong$ |  |  | $\stackrel{\overbrace{}}{\circ}$ |  |  |  | － | $\stackrel{n}{\circ}$ | $\stackrel{n}{\circ}$ | － |  |
| $\checkmark$ | － | － |  |  | － |  |  |  | － | － | － | － |  |
| v | $\square$ | $\checkmark$ |  |  | $\square$ |  |  |  | － | $\stackrel{\cong}{0}$ | $\stackrel{\varkappa}{\circ}$ | $\square$ |  |
| $\text { vi } \frac{\pi}{4}$ | $\begin{aligned} & \underset{\sim}{\infty} \\ & \stackrel{\infty}{\infty} \\ & \underset{\infty}{\circ} \end{aligned}$ | － |  |  | － |  |  |  | $\begin{aligned} & \stackrel{\rightharpoonup}{2} \\ & \frac{0}{\infty} \\ & 0 \end{aligned}$ |  | $\frac{\underset{i}{\lambda}}{\underset{O}{2}}$ | $\begin{aligned} & \stackrel{\rightharpoonup}{2} \\ & \substack{\infty \\ 0} \end{aligned}$ |  |
| $0^{\circ} \frac{\bar{Z}}{4}$ | $\frac{E}{2}$ | $\begin{aligned} & \text { O} \\ & \text { O} \\ & \text { O } \end{aligned}$ |  |  | $\begin{aligned} & \text { O} \\ & \text { O} \\ & \infty \\ & 0 \end{aligned}$ |  |  |  | $\begin{aligned} & \stackrel{\rightharpoonup}{6} \\ & \stackrel{y}{\infty} \\ & 0 \end{aligned}$ | $\stackrel{\curvearrowleft}{\underset{\AA}{\infty}}$ | $\stackrel{\cong}{\underset{\sim}{\infty}}$ | $\begin{aligned} & \stackrel{\rightharpoonup}{n} \\ & \stackrel{y}{\infty} \\ & \underset{\sim}{\infty} \end{aligned}$ |  |
|  | $\sim$ | Ј |  |  | $\pm$ |  |  |  | $\stackrel{\sim}{\sim}$ | － | － | $\stackrel{\sim}{\sim}$ |  |
|  |  | エ |  |  | $\pm$ |  |  |  | $\begin{aligned} & \stackrel{y}{\square} \\ & \underset{\substack{0}}{0} \\ & \underset{-}{\circ} \end{aligned}$ |  |  |  |  |
|  | － | $\wedge$ |  |  | $\wedge$ |  |  |  | ¢ | in | in | $\stackrel{\sim}{\sim}$ |  |
| 喑 |  | $\begin{gathered} \underset{\sim}{q} \\ \underset{\sim}{n} \\ \underset{\sim}{n} \end{gathered}$ |  |  | $\begin{gathered} \underset{\sim}{4} \\ \stackrel{4}{6} \\ \stackrel{y}{6} \end{gathered}$ |  |  |  | $\begin{aligned} & \underset{7}{\circ} \\ & \stackrel{0}{0} \\ & \underset{-1}{1} \end{aligned}$ | $\begin{aligned} & \underset{\sim}{\hat{n}} \\ & \stackrel{n}{n} \\ & \stackrel{n}{1} \\ & \hline \end{aligned}$ |  | $\begin{aligned} & \frac{1}{7} \\ & \mathbf{O}_{6}^{0} \\ & \underset{-1}{6} \end{aligned}$ |  |
|  |  | $\begin{aligned} & \text { N} \\ & \underset{\sim}{\sim} \end{aligned}$ |  |  | $\begin{gathered} \text { N } \\ \underset{\sim}{\sim} \end{gathered}$ |  |  |  | $\begin{aligned} & \stackrel{\infty}{\stackrel{ }{\circ}} \underset{\underset{\sim}{2}}{ } \end{aligned}$ | $\frac{\overparen{6}}{7}$ | $\frac{\widehat{6}}{7}$ | $\stackrel{\infty}{\stackrel{\infty}{\circ}}$ |  |
|  | $\underset{\substack{\text { ờ } \\ \text { on }}}{ }$ | $\begin{aligned} & \text { 창 } \\ & \text { O} \end{aligned}$ |  |  |  |  |  |  | $\begin{aligned} & \text { fy } \\ & \stackrel{y}{2} \end{aligned}$ | $\begin{aligned} & \text { ๙} \\ & \underset{\sim}{\mathrm{N}} \end{aligned}$ | $\begin{aligned} & \text { 층 } \\ & \text { ì } \end{aligned}$ | $\begin{aligned} & \text { N} \\ & \text { 厄̀ } \\ & \text { ה } \end{aligned}$ |  |
|  | $\begin{gathered} \text { O} \\ \text { d } \\ \text { N } \end{gathered}$ | $\begin{aligned} & \text { 충 } \\ & \text { ה̀ } \end{aligned}$ |  |  | $\stackrel{\text { ® }}{\text { ® }}$ |  |  |  | ¢ $\stackrel{y}{2}$ i | $\begin{aligned} & \hat{\mathrm{H}} \\ & \stackrel{y}{\mathrm{i}} \end{aligned}$ | $\begin{aligned} & \hat{\text { f}} \\ & \stackrel{\rightharpoonup}{\mathrm{N}} \end{aligned}$ | त्⿵人 |  |
|  | $\begin{aligned} & U_{0} \\ & U_{0} \\ & V \end{aligned}$ |  | $=\begin{aligned} & z \\ & y \\ & y \end{aligned}$ |  | $\left\lvert\, \begin{aligned} & 0 \\ & \frac{0}{2} \\ & \frac{2}{2} \\ & \frac{y}{0} \\ & \frac{0}{2} \\ & \frac{1}{v} \end{aligned}\right.$ | O． | $\begin{aligned} & z \\ & v_{0}^{0} \\ & v_{0} \end{aligned}$ | $\left\lvert\, \begin{aligned} & z \\ & 0_{0}^{0} \\ & 0_{0} \end{aligned}\right.$ | $\begin{aligned} & 0_{0}^{0} \\ & 0_{0}^{\circ} \\ & 0_{0} \\ & 0 \\ & 0 \end{aligned}$ | $\begin{array}{ll} x_{1} & 0 \\ 0 & 0 \\ 0 & 0 \\ 0 & .0 \end{array}$ | $\begin{array}{ll} 1 & v_{0} \\ 0 & 0^{0} \\ 0 & 0_{0} \\ 0 & 0 \end{array}$ | $\begin{aligned} & e_{0}^{0} \\ & 0_{0} \\ & e_{0}^{0} \\ & \mathrm{v} \\ & \hline 0 \end{aligned}$ | U－ |

## TRANSITION METAL ORGANOMETALLIC AND COORDINATE BOND

The transition-metal atoms fill the $3 d$ orbitals in the series $S c$ to $Z n$. The $4 s$ orbitals are filled except in the cases of $C r$ and $C u$ wherein one $4 s$ electron occupies a $3 d$ orbital to achieve a half-filled and filled $3 d$ shell, respectively. Experimentally the transition-metal elements ionize successively from the $4 s$ shell to the $3 d$ shell [12]. Thus, bonding in the transition metals involves the hybridization of the $3 d$ and $4 s$ electrons to form the corresponding number of $3 d 4 s$ HOs except for Cu and Zn which each have a filled inner $3 d$ shell and one and two outer $4 s$ electrons, respectively. $C u$ may form a single bond involving the $4 s$ electron or the $3 d$ and $4 s$ shells may hybridize to form multiple bonds with one or more ligands. The $4 s$ shell of Zn hybridizes to form two $4 s \mathrm{HOs}$ that provide for two possible bonds, typically two metal-alkyl bonds.

For organometallic and coordinate compounds comprised of carbon, the geometrical and energy equations are given in the Derivation of the General Geometrical and Energy Equations of Organic Chemistry section. For metal-ligand bonds other than to carbon, the force balance equation is that developed in the Force Balance of the $\sigma$ MO of the Carbon Nitride Radical section wherein the diamagnetic force terms include orbital and spin angular momentum contributions. The electrons of the $3 d 4 s$ HOs may pair such that the binding energy of the HO is increased. The hybridization factor accordingly changes which effects the bond distances and energies. The diamagnetic terms of the force balance equations of the electrons of the MOs formed between the $3 d 4 s$ HOs and the AOs of the ligands also changes depending on whether the nonbonding HOs are occupied by paired or unpaired electrons. The orbital and spin angular momentum of the HOs and MOs is then determined by the state that achieves a minimum energy including that corresponding to the donation of electron charge from the HOs and AOs to the MOs. Historically, according to crystal field theory and molecular orbital theory [13] the possibility of a bonding metal atom achieving a so called "high-spin" or "low-spin" state having unpaired electrons occupying higher-energy orbitals versus paired electrons occupying lower-energy orbitals was due to the strength of the ligand crystal field or the interaction between metal orbitals and the ligands, respectively. Excited-state spectral data recorded on transition-metal organometallic and coordinate compounds has been misinterpreted. Excitation of an unpaired electron in a $3 d 4 s \mathrm{HO}$ to a $3 d 4 s$ paired state is equivalent to an excitation of the molecule to a higher energy MO since the MOs change energy due to the corresponding change in the hybridization factor and diamagnetic force balance terms. But, levels misidentified as crystal field levels do not exist in the absence of excitation by a photon.

The parameters of the $3 d 4 s$ HOs are determined using Eqs. (15.12-15.21). For transition metal atoms with electron configuration $3 d^{n} 4 s^{2}$, the spin-paired $4 s$ electrons are promoted to the $3 d 4 s$ shell during hybridization as unpaired electrons. Also, for $n>5$ the electrons of the $3 d$ shell are spin-paired and these electrons are promoted to the $3 d 4 s$ shell during hybridization as unpaired electrons. The energy for each promotion is the magnetic energy given by Eq. (15.15) at the initial radius of the $4 s$ electrons and the paired $3 d$ electrons determined using Eq. (10.102) with the corresponding nuclear charge $Z$ of the metal atom and the number of electrons, $n$, of the corresponding ion with the filled outer shell from which the pairing energy is determined. Typically, the electrons from the $4 s$ and $3 d$ shells successively fill unoccupied HOs until the HO shell is filled with unpaired electrons, then the electrons pair per HO. The magnetic energy of pairing given by Eqs. (15.13) and (15.15) is added to $E_{\text {Coulomb }}($ atom, $3 d 4 s)$ the for each pair. Thus, after Eq. (15.16), the energy $E($ atom, $3 d 4 s)$ of the outer electron of the atom $3 d 4 s$ shell is given by the sum of $E_{\text {Coulomb }}($ atom, $3 d 4 s)$ and $E$ (magnetic):

$$
\begin{equation*}
E(\text { atom }, 3 d 4 s)=\frac{-e^{2}}{8 \pi \varepsilon_{0} r_{3 d 4 s}}+\frac{2 \pi \mu_{0} e^{2} \hbar^{2}}{m_{e}^{2} r_{4 s}^{3}}+\sum_{3 d \text { pairs }} \frac{2 \pi \mu_{0} e^{2} \hbar^{2}}{m_{e}^{2} r_{3 d}^{3}}-\sum_{H O \text { pairs }} \frac{2 \pi \mu_{0} e^{2} \hbar^{2}}{m_{e}^{2} r_{3 d 4 s}^{3}} \tag{23.28}
\end{equation*}
$$

The sharing of electrons between the metal $3 d 4 s$ HOs and the ligand AOs or HOs to form a $M-L$-bond MO ( $L$ not $C$ ) permits each participating hybridized or atomic orbital to decrease in radius and energy. Due to the low binding energy of the metal atom and the high electronegativity of the ligand, an energy minimum is achieved while further satisfying the potential, kinetic, and orbital energy relationships, each metal $3 d 4 s$ HO donates an excess of an electron per bond of its electron density to the $M-L$-bond MO. 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. After Eq. (15.17), the total energy $E_{T}$ (mol.atom, $3 d 4 s$ ) of the HO electrons is given by the sum of energies of successive ions of the atom over the $n$ electrons comprising the total electrons of the initial AO shell and the hybridization energy:

$$
\begin{equation*}
E_{T}(\text { mol.atom }, 3 d 4 s)=E(\text { atom }, 3 d 4 s)-\sum_{m=2}^{n} I P_{m} \tag{23.29}
\end{equation*}
$$

where $I P_{m}$ is the $m$ th ionization energy (positive) of the atom and the sum of $-I P_{1}$ plus the hybridization energy is $E($ atom, $3 d 4 s)$. Thus, the radius $r_{3 d 4 s}$ of the hybridized shell due to its donation of a total charge $-Q e$ to the corresponding MO is given by:

$$
\begin{equation*}
r_{3 d 4 s}=\left(\sum_{q=Z-n}^{Z-1}(Z-q)-Q\right) \frac{-e^{2}}{8 \pi \varepsilon_{0} E_{T}(\text { mol.atom }, 3 d 4 s)}=\left(\sum_{q=Z-n}^{Z-1}(Z-q)-s(0.25)\right) \frac{-e^{2}}{8 \pi \varepsilon_{0} E_{T}(\text { mol.atom }, 3 d 4 s)} \tag{23.30}
\end{equation*}
$$

where $-e$ is the fundamental electron charge, $s=1,2,3$ for a single, double, and triple bond, respectively, and $s=4$ for typical coordinate and organometallic compounds wherein $L$ is not carbon. The Coulombic energy $E_{\text {Coulomb }}$ (mol.atom, $3 d 4 s$ ) of the outer electron of the atom $3 d 4 s$ shell is given by

$$
\begin{equation*}
E_{\text {Coulomb }}(\text { mol.atom, } 3 d 4 s)=\frac{-e^{2}}{8 \pi \varepsilon_{0} r_{3 d 4 s}} \tag{23.31}
\end{equation*}
$$

In the case that during hybridization the metal spin-paired $4 s \mathrm{AO}$ electrons are unpaired to contribute electrons to the $3 d 4 s \mathrm{HO}$, 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). In addition in the case that the $3 d 4 s$ HO electrons are paired, the corresponding magnetic energy is added. Then, the energy $E$ (mol.atom, $3 d 4 s$ ) of the outer electron of the atom $3 d 4 s$ shell is given by the sum of $E_{\text {Coulomb }}($ mol.atom, $3 d 4 s)$ and $E$ (magnetic) :

$$
\begin{equation*}
E(\text { mol.atom }, 3 d 4 s)=\frac{-e^{2}}{8 \pi \varepsilon_{0} r_{3 d 4 s}}+\frac{2 \pi \mu_{0} e^{2} \hbar^{2}}{m_{e}^{2} r_{4 s}^{3}}-\sum_{H O \text { pairs }} \frac{2 \pi \mu_{0} e^{2} \hbar^{2}}{m_{e}^{2} r_{3 d 4 s}^{3}} \tag{23.32}
\end{equation*}
$$

$E_{T}($ atom-atom, $3 d 4 s)$, the energy change of each atom $m s p^{3}$ shell with the formation of the atom-atom-bond MO is given by the difference between $E$ (mol.atom, $3 d 4 s$ ) and $E($ atom, $3 d 4 s)$ :

$$
\begin{equation*}
E_{T}(\text { atom }- \text { atom }, 3 d 4 s)=E(\text { mol.atom }, 3 d 4 s)-E(\text { atom }, 3 d 4 s) \tag{23.33}
\end{equation*}
$$

Any unpaired electrons of ligands typically pair with unpaired HO electrons of the metal. In the case that no such electrons of the metal are available, the ligand electrons pair and form a bond with an unpaired metal HO when available. An unoccupied HO may form by the pairing of the corresponding HO electrons to form an energy minimum due to the effect on the bond parameters such as the diamagnetic force term, hybridization factor, and the $E_{T}\left(\right.$ atom-atom, $\left.m s p^{3} . A O\right)$ term. In the case of carbonyls, the two unpaired $C s p^{3}$ HO electrons on each carbonyl pair with any unpaired electrons of the metal HOs. Any excess carbonyl electrons pair in the formation of the corresponding MO and any remaining metal HO electrons pair where possible. In the latter case, the energy of the HO for the determination of the hybridization factor and other bonding parameters in Eqs. (15.51) and (15.65) is given by the Coulombic energy plus the pairing energy.

The force balance of the centrifugal force equated to the Coulombic and magnetic forces is solved for the length of the semimajor axis. The Coulombic force on the pairing electron of the MO is:

$$
\begin{equation*}
\mathbf{F}_{\text {Coulomb }}=\frac{e^{2}}{8 \pi \varepsilon_{0} a b^{2}} D \mathbf{i}_{\xi} \tag{23.34}
\end{equation*}
$$

The spin pairing force is

$$
\begin{equation*}
\mathbf{F}_{\text {spin-pairing }}=\frac{\hbar^{2}}{2 m_{e} a^{2} b^{2}} D \mathbf{i}_{\xi} \tag{23.35}
\end{equation*}
$$

The diamagnetic force is:

$$
\begin{equation*}
\mathbf{F}_{\text {diamagneticMO1 }}=-\frac{n_{e} \hbar^{2}}{4 m_{e} a^{2} b^{2}} D \mathbf{i}_{\xi} \tag{23.36}
\end{equation*}
$$

where $n_{e}$ is the total number of electrons that interact with the binding $\sigma$-MO electron. The diamagnetic force $\mathbf{F}_{\text {diamagneticMO2 }}$ on the pairing electron of the $\sigma \mathrm{MO}$ is given by the sum of the contributions over the components of angular momentum:

$$
\begin{equation*}
\mathbf{F}_{\text {diamagneticMO2 }}=-\sum_{i} \frac{\left|L_{i}\right| \hbar^{2}}{Z 2 m_{e} a^{2} b^{2}} D \mathbf{i}_{\xi} \tag{23.37}
\end{equation*}
$$

where $\left|L_{i}\right|$ is the magnitude of the angular momentum component of the metal atom at a focus that is the source of the diamagnetism at the $\sigma$-MO. The centrifugal force is:

$$
\begin{equation*}
\mathbf{F}_{\text {centrifugalMO }}=-\frac{\hbar^{2}}{m_{e} a^{2} b^{2}} D \mathbf{i}_{\xi} \tag{23.38}
\end{equation*}
$$

The general force balance equation for the $\sigma-\mathrm{MO}$ of the metal (M) to ligand (L) M-L -bond MO in terms of $n_{e}$ and $\left|L_{i}\right|$ corresponding to the orbital and spin angular momentum terms of the $3 d 4 s \mathrm{HO}$ shell is:

$$
\begin{equation*}
\frac{\hbar^{2}}{m_{e} a^{2} b^{2}} D=\frac{e^{2}}{8 \pi \varepsilon_{0} a b^{2}} D+\frac{\hbar^{2}}{2 m_{e} a^{2} b^{2}} D-\left(\frac{n_{e}}{2}+\sum_{i} \frac{\left|L_{i}\right|}{Z}\right) \frac{\hbar^{2}}{2 m_{e} a^{2} b^{2}} D \tag{23.39}
\end{equation*}
$$

Having a solution for the semimajor axis $a$ of:

$$
\begin{equation*}
a=\left(1+\frac{n_{e}}{2}+\sum_{i} \frac{\left|L_{i}\right|}{Z}\right) a_{0} \tag{23.40}
\end{equation*}
$$

In term of the total angular momentum $L$, the semimajor axis $a$ is:

$$
\begin{equation*}
a=\left(1+\frac{n_{e}}{2}+\frac{L}{Z}\right) a_{0} \tag{23.41}
\end{equation*}
$$

Using the semimajor axis, 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 the Organic Molecular Functional Groups and Molecules section.

Bond angles in organometallic and coordinate compounds are determined using the standard Eqs. (15.70-15.79) and (15.88-15.117) with the appropriate $E_{T}\left(\right.$ atom-atom, $\left.m s p^{3} . A O\right)$ for energy matching with the $B-C$ terminal bond of the corresponding angle $\angle B A C$. For bond angles in general, if the groups can be maximally displaced in terms of steric interactions and magnitude of the residual $E_{T}$ term is less that the steric energy, then the geometry that minimizes the steric interactions is the lowest energy. Steric-energy minimizing geometries include tetrahedral $\left(T_{d}\right)$ and octahedral symmetry $\left(O_{h}\right)$.

## SCANDIUM FUNCTIONAL GROUPS AND MOLECULES

The electron configuration of scandium is $[A r] 4 s^{2} 3 d$ having the corresponding term ${ }^{2} D_{3 / 2}$. The total energy of the state is given by the sum over the three electrons. The sum $E_{T}(S c, 3 d 4 s)$ of experimental energies [1] of $S c, S c^{+}$, and $S c^{2+}$ is:

$$
\begin{equation*}
E_{T}(S c, 3 d 4 s)=-(24.75666 \mathrm{eV}+12.79977 \mathrm{eV}+6.56149 \mathrm{eV})=-44.11792 \mathrm{eV} \tag{23.42}
\end{equation*}
$$

By considering that the central field decreases by an integer for each successive electron of the shell, the radius $r_{3 d 4 s}$ of the $S c 3 d 4 s$ shell may be calculated from the Coulombic energy using Eq. (15.13).

$$
\begin{equation*}
r_{3 d 4 s}=\sum_{n=18}^{20} \frac{(Z-n) e^{2}}{8 \pi \varepsilon_{0}(e 44.11792 \mathrm{eV})}=\frac{6 e^{2}}{8 \pi \varepsilon_{0}(e 44.11792 \mathrm{eV})}=1.85038 a_{0} \tag{23.43}
\end{equation*}
$$

where $Z=21$ for scandium. Using Eq. (15.14), the Coulombic energy $E_{\text {Coulomb }}(S c, 3 d 4 s)$ of the outer electron of the $S c 3 d 4 s$ shell is:

$$
\begin{equation*}
E_{\text {Coulomb }}(S c, 3 d 4 s)=\frac{-e^{2}}{8 \pi \varepsilon_{0} r_{3 d 4 s}}=\frac{-e^{2}}{8 \pi \varepsilon_{0} 1.85038 a_{0}}=-7.35299 \mathrm{eV} \tag{23.44}
\end{equation*}
$$

During hybridization, the spin-paired $4 s$ electrons are promoted to the $S c 3 d 4 s$ shell as unpaired electrons. The energy for the promotion is the magnetic energy given by Eq. (15.15) at the initial radius of the $4 s$ electrons. From Eq. (10.102) with $Z=21$ and $n=21$, the radius $r_{21}$ of the $S c 4 s$ shell is:

$$
\begin{equation*}
r_{21}=2.07358 a_{0} \tag{23.45}
\end{equation*}
$$

Using Eqs. (15.15) and (23.45), the unpairing energy is:

$$
\begin{equation*}
E(\text { magnetic })=\frac{2 \pi \mu_{0} e^{2} \hbar^{2}}{m_{e}^{2}\left(r_{21}\right)^{3}}=\frac{8 \pi \mu_{0} \mu_{B}^{2}}{\left(2.07358 a_{0}\right)^{3}}=0.01283 \mathrm{eV} \tag{23.46}
\end{equation*}
$$

Using Eqs. (23.44) and (23.46), the energy $E(S c, 3 d 4 s)$ of the outer electron of the $S c 3 d 4 s$ shell is:

$$
\begin{equation*}
E(S c, 3 d 4 s)=\frac{-e^{2}}{8 \pi \varepsilon_{0} r_{3 d 4 s}}+\frac{2 \pi \mu_{0} e^{2} \hbar^{2}}{m_{e}^{2}\left(r_{21}\right)^{3}}=-7.352987 \mathrm{eV}+0.01283 \mathrm{eV}=-7.34015 \mathrm{eV} \tag{23.47}
\end{equation*}
$$

Next, consider the formation of the $S c-L$-bond MO wherein each scandium atom has an $S c 3 d 4 s$ electron with an energy given by Eq. (23.47). The total energy of the state of each scandium atom is given by the sum over the three electrons. The sum $E_{T}\left(S c_{S c-L} 3 d 4 s\right)$ of energies of $S c 3 d 4 s$ (Eq. (23.47)), $S c^{+}$, and $S c^{2+}$ is:

$$
\begin{align*}
E_{T}\left(S c_{S c-L} 3 d 4 s\right) & =-(24.75666 \mathrm{eV}+12.79977 \mathrm{eV}+E(S c, 3 d 4 s))  \tag{23.48}\\
& =-(24.75666 \mathrm{eV}+12.79977 \mathrm{eV}+7.34015 \mathrm{eV})=-44.89658 \mathrm{eV}
\end{align*}
$$

where $E(S c, 3 d 4 s)$ is the sum of the energy of $S c,-6.56149 \mathrm{eV}$, and the hybridization energy.
The scandium HO donates an electron to each MO. Using Eq. (23.30), the radius $r_{3 d 4 s}$ of the $S c 3 d 4 s$ shell calculated from the Coulombic energy is:

$$
\begin{equation*}
r_{S c-L 3 d 4 s}=\left(\sum_{n=18}^{20}(Z-n)-1\right) \frac{e^{2}}{8 \pi \varepsilon_{0}(e 44.89658 \mathrm{eV})}=\frac{5 e^{2}}{8 \pi \varepsilon_{0}(e 44.89658 \mathrm{eV})}=1.51524 a_{0} \tag{23.49}
\end{equation*}
$$

Using Eqs. (15.19) and (23.49), the Coulombic energy $E_{\text {Coulomb }}\left(S c_{S c-L}, 3 d 4 s\right)$ of the outer electron of the $S c 3 d 4 s$ shell is:

$$
\begin{equation*}
E_{\text {Coulomb }}\left(S c_{\text {Sc-L }}, 3 d 4 s\right)=\frac{-e^{2}}{8 \pi \varepsilon_{0} r_{S c-L 3 d 4 s}}=\frac{-e^{2}}{8 \pi \varepsilon_{0} 1.51524 a_{0}}=-8.97932 \mathrm{eV} \tag{23.50}
\end{equation*}
$$

The only magnetic energy term is that for the unpairing of the $4 s$ electrons given by Eq. (23.46). Using Eqs. (23.32), (23.46), and (23.50), the energy $E\left(S c_{S c-L}, 3 d 4 s\right)$ of the outer electron of the $S c 3 d 4 s$ shell is:

$$
\begin{equation*}
E\left(S c_{S c-L}, 3 d 4 s\right)=\frac{-e^{2}}{8 \pi \varepsilon_{0} r_{S c-L 3 d 4 s}}+\frac{2 \pi \mu_{0} e^{2} \hbar^{2}}{m_{e}^{2}\left(r_{21}\right)^{3}}=-8.97932 \mathrm{eV}+0.01283 \mathrm{eV}=-8.96648 \mathrm{eV} \tag{23.51}
\end{equation*}
$$

Thus, $E_{T}(S c-L, 3 d 4 s)$, the energy change of each $S c 3 d 4 s$ shell with the formation of the $S c-L$-bond MO is given by the difference between Eq. (23.51) and Eq. (23.47).

$$
\begin{equation*}
E_{T}(S c-L, 3 d 4 s)=E\left(S c_{S c-L}, 3 d 4 s\right)-E(S c, 3 d 4 s)=-8.96648 \mathrm{eV}-(-7.34015 \mathrm{eV})=-1.62633 \mathrm{eV} \tag{23.52}
\end{equation*}
$$

The semimajor axis $a$ solution given by Eq. (23.41) of the force balance equation, Eq. (23.39), for the $\sigma$-MO of the $S c-L$-bond MO of $S c L_{n}$ is given in Table 23.8 with the force-equation parameters $Z=21, n_{e}$, and $L$ corresponding to the orbital and spin angular momentum terms of the $3 d 4 s$ HO shell.

For the $S c-L$ functional groups, hybridization of the $4 s$ and $3 d$ AOs of $S c$ to form a single $3 d 4 s$ shell forms an energy minimum, and the sharing of electrons between the $S c 3 d 4 s \mathrm{HO}$ and $L \mathrm{AO}$ to form a MO permits each participating orbital to decrease in radius and energy. The $F$ AO has an energy of $E(F)=-17.42282 \mathrm{eV}$, the Cl AO has an energy of $E(C l)=-12.96764 \mathrm{eV}$, the $O$ AO has an energy of $E(O)=-13.61805 \mathrm{eV}$, and the $S c 3 d 4 \mathrm{~s}$ HOs have an energy of $E(S c, 3 d 4 s)=-7.34015 \mathrm{eV}$ (Eq. (23.47)). To meet the equipotential condition of the union of the $S c-L H_{2}$-type-ellipsoidalMO with these orbitals, the hybridization factor(s), at least one of $c_{2}$ and $C_{2}$ of Eq. (15.61) for the $S c-L$-bond MO given by Eq. (15.77) is:

$$
\begin{align*}
& c_{2}(\text { FAO to Sc3d } 4 \mathrm{sHO})=C_{2}(\text { FAO to Sc } 3 d 4 s H O)=\frac{E(S c, 3 d 4 s)}{E(F A O)}=\frac{-7.34015 \mathrm{eV}}{-17.42282 \mathrm{eV}}=0.42130  \tag{23.53}\\
& c_{2}(\mathrm{ClAO} \text { to } S c 3 d 4 \mathrm{sHO})=C_{2}(C l A O \text { to } S c 3 d 4 \mathrm{sHO})=\frac{E(S c, 3 d 4 s)}{E(C l A O)}=\frac{-7.34015 \mathrm{eV}}{-12.96764 \mathrm{eV}}=0.56604  \tag{23.54}\\
& c_{2}(O \text { to } S c 3 d 4 \mathrm{sHO})=\frac{E(S c, 3 d 4 s)}{E(O)}=\frac{-7.34015 \mathrm{eV}}{-13.61805 \mathrm{eV}}=0.53900 \tag{23.55}
\end{align*}
$$

Since the energy of the MO is matched to that of the $S c 3 d 4 s \mathrm{HO}, E(A O / H O)$ in Eq. (15.61) is $E(S c, 3 d 4 s)$ given by Eq. (23.47) and twice this value for double bonds. $E_{T}$ (atom-atom, $m s p^{3} . A O$ ) of the $S c-L$-bond MO is determined by considering that the bond involves an electron transfer from the scandium atom to the ligand atom to form partial ionic character in the bond as in the case of the zwitterions such as $\mathrm{H}_{2} \mathrm{~B}^{+}-\mathrm{F}^{-}$given in the Halido Boranes section. $E_{T}\left(\right.$ atom - atom, msp $\left.{ }^{3} . A O\right)$ is -3.25266 eV , two times the energy of Eq. (23.52) for single bonds, and -6.50532 eV , four times the energy of Eq. (23.52) for double bonds.

The symbols of the functional groups of scandium coordinate compounds are given in Table 23.7. The geometrical (Eqs. (15.1-15.5) and (23.41)), intercept (Eqs. (15.31-15.32) and (15.80-15.87)), and energy (Eqs. (15.61) and (23.28-23.33)) parameters of scandium coordinate compounds are given in Tables 23.8, 23.9, and 23.10, respectively. The total energy of each scandium coordinate compound given in Table 23.11 was calculated as the sum over the integer multiple of each $E_{D}$ (Group) of Table 23.10 corresponding to functional-group composition of the compound. The charge-densities of exemplary scandium coordinate compound, scandium trifluoride comprising the concentric shells of atoms with the outer shell bridged by one or more $\mathrm{H}_{2}$-type ellipsoidal MOs or joined with one or more hydrogen MOs is shown in Figure 23.2.

Figure 23.2. Scandium Trifluoride. Color scale, translucent view of the charge-density of $S c F_{3}$ showing the orbitals of the $S c$ and $F$ atoms at their radii, the ellipsoidal surface of each $H_{2}$-type ellipsoidal MO that transitions to the corresponding outer shell of the atoms participating in each bond, and the nuclei (red, not to scale).


Table 23.7. The symbols of the functional groups of scandium coordinate compounds.

| Functional Group | Group Symbol |
| :--- | :--- |
| $S c F$ group of $S c F$ | $S c-F$ (a) |
| $S c F$ group of $S c F_{2}$ | $S c-F$ (b) |
| $S c F$ group of $S c F_{3}$ | $S c-F$ (c) |
| $S c C l$ group of $S c C l$ | $S c-C l$ |
| $S c O$ group of $S c O$ | $S c-O$ |

Table 23.8. The geometrical bond parameters of scandium coordinate compounds and experimental values.

| Parameter | $S c-F$ (a) <br> Group | $S c-F(b)$ <br> Groups | $S c-F$ (c) <br> Group | $S c-C l$ <br> Group | $S c-O$ <br> Group |
| :---: | :---: | :---: | :---: | :---: | :---: |
| $n_{e}$ | 1 2 | 2 | 2 | 1 |  |
| $L$ | $2+\sqrt{\frac{3}{4}}$ | $4 \sqrt{\frac{3}{4}}$ | $2+\sqrt{\frac{3}{4}}$ | $1+3 \sqrt{\frac{3}{4}}$ | $3+2 \sqrt{\frac{3}{4}}$ |
| $a\left(a_{0}\right)$ | 1.63648 | 2.16496 | 2.13648 | 2.17134 | 1.72534 |
| $c^{\prime}\left(a_{0}\right)$ | 1.60922 | 1.60294 | 1.59236 | 1.95858 | 1.51672 |
| Bond <br> Length <br> $2 c^{\prime}(A)$ | 1.70313 | 1.69647 | 1.68528 | 2.07287 | 1.60523 |
| Exp. <br> Bond <br> Length <br> $(A)$ | $1.788[14]$ <br> (scandium <br> fluoride) | $1.788[14]$ <br> (scandium <br> fluoride) | $1.788[41]$ <br> (scandium <br> fluoride) | $2.229[15]$ <br> (scandium <br> chloride) | $1.668[15]$ <br> (scandium <br> oxide) |
| $b, c\left(a_{0}\right)$ | 0.29743 | 1.45521 | 1.45521 | 0.93737 | 0.82240 |
| $e$ | 0.98335 | 0.74040 | 0.74040 | 0.90202 | 0.87909 |

Table 23.9. The MO to $H O$ intercept geometrical bond parameters of scandium coordinate compounds. $E_{T}$ is $E_{T}$ (atom-atom,msp ${ }^{3} . A O$ ).

| Bond | Atom | $\begin{gathered} E_{T} \\ \text { (eV) } \\ \text { Bond } 1 \end{gathered}$ | $\begin{gathered} E_{T} \\ (\mathrm{eV}) \end{gathered}$ $\text { Bond } 2$ |  | $\begin{gathered} E_{T} \\ (\mathrm{eV}) \end{gathered}$ $\text { Bond } 4$ | Final Total Energy Sc3d4s (eV) | $\begin{aligned} & r_{\text {mpital }} \\ & \left(a_{0}\right) \end{aligned}$ | $\begin{aligned} & r_{\text {ftnal }} \\ & \left(a_{0}\right) \end{aligned}$ | $\begin{gathered} E_{\text {Contomomb }}(S c 3 d 4 s) \\ (\mathrm{eV}) \\ \text { Final } \end{gathered}$ | $\begin{gathered} E(S c 3 d 4 s) \\ (\mathrm{eV}) \\ \text { Final } \end{gathered}$ | $\begin{aligned} & \theta^{\prime} \\ & \left({ }^{\circ}\right) \end{aligned}$ | $\begin{gathered} \theta_{1} \\ \left({ }^{\circ}\right) \end{gathered}$ | $\begin{aligned} & \theta_{2} \\ & \left({ }^{\circ}\right) \end{aligned}$ | $\begin{gathered} d_{1} \\ \left(a_{0}\right) \end{gathered}$ | $\begin{gathered} d_{2} \\ \left(a_{0}\right) \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Sc-F (ScF) | Sc | -1.62633 | 0 | 0 | 0 |  | 1.85038 | 1.51524 | -8.97932 |  | 168.71 | 11.29 | 85.68 | 0.12329 | 1.48593 |
| Sc-F (ScF) | F | -1.62633 | 0 | 0 | 0 |  | 0.78069 | 0.71425 | -19.04915 |  | 160.05 | 19.95 | 55.03 | 0.93785 | 0.67137 |
| Sc-F (ScF2) | Sc | -1.62633 | -1.62633 | 0 | 0 |  | 1.85038 | 1.28288 | -10.60565 |  | 108.71 | 71.29 | 56.61 | 1.19135 | 0.41159 |
| Sc-F (ScF2) | F | -1.62633 | 0 | 0 | 0 |  | 0.78069 | 0.71425 | -19,04915 |  | 60.07 | 119.93 | 25.17 | 1.95936 | 0.35642 |
| $\mathrm{Sc}-\mathrm{F}\left(\mathrm{ScF}_{3}\right)$ | Sc | -1.62633 | -1.62633 | -1.62633 | 0 |  | 1.85038 | 1.11231 | -12.23198 |  | 101.31 | 78.69 | 49.97 | 1.37413 | 0.21823 |
| $\mathrm{Sc}-\mathrm{F}\left(\mathrm{ScF}_{3}\right)$ | F | -1.62633 | 0 | 0 | 0 |  | 0.78069 | 0.71425 | -19.04915 |  | 63.75 | 116.25 | 26.73 | 1.90822 | 0.31586 |
| $\mathrm{Sc}-\mathrm{Cl}(\mathrm{ScCl})$ | Sc | -1.62633 | 0 | 0 | 0 |  | 1.85038 | 1.51524 | -8.97932 |  | 144.35 | 35.65 | 70.43 | 0.72737 | 1.23121 |
| $\mathrm{Sc}-\mathrm{Cl}(\mathrm{ScCl})$ | Cl | -1.62633 | 0 | 0 | 0 |  | 1.05158 | 0.93229 | -14.59397 |  | 128.86 | 51.14 | 50.76 | 1.37364 | 0.58494 |
| $\mathrm{Sc}-\mathrm{O}(\mathrm{ScO})$ | Sc | -3.25266 | 0 | 0 | 0 |  | 1.85038 | 1.28288 | -10.60565 |  | 142.18 | 37.82 | 73.04 | 0.50331 | 1.01341 |
| $\mathrm{Sc}-\mathrm{O}(\mathrm{ScO})$ | $o$ | -3.25266 | 0 | 0 | 0 |  | 1.00000 | 0.80647 | -16.87072 |  | 125.78 | 54.22 | 52.71 | 1.04524 | 0.47148 |

Table 23.10. The energy parameters ( eV ) of functional groups of scandium coordinate compounds.

| Parameters | $S c-F(\mathrm{a})$ <br> Groups | $S c-F(b)$ Groups | $\begin{gathered} S c-F(c) \\ \text { Group } \end{gathered}$ | $S c-C l$ Group | $\begin{aligned} & \begin{array}{l} S c-O \\ \text { Group } \end{array} \end{aligned}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| $n_{1}$ | 1 | 1 | 1 | 1 | 2 |
| $n_{2}$ | 0 | 0 | 0 | 0 | 0 |
| $n_{3}$ | 0 | 0 | 0 | 0 | 0 |
| $C_{1}$ | 0.75 | 1 | 1 | 0.5 | 0.375 |
| $C_{2}$ | 0.42130 | 0.42130 | 0.42130 | 0.56604 | 1 |
| $c_{1}$ | 1 | 1 | 1 | 1 | 1 |
| $c_{2}$ | 0.42130 | 1 | 1 | 0.56604 | 0.53900 |
| $c_{3}$ | 0 | 0 | 0 | 0 | 0 |
| $c_{4}$ | 1 | 1 | 1 | 1 | 2 |
| $c_{5}$ | 1 | 1 | 1 | 1 | 2 |
| $C_{10}$ | 0.75 | 1 | 1 | 0.5 | 0.375 |
| $\mathrm{C}_{2}$ | 0.42130 | 0.42130 | 0.42130 | 0.56604 | 1 |
| $V_{e}(\mathrm{eV})$ | -34.05166 | -32.30098 | -32.89066 | -23.32429 | -53.06036 |
| $V_{p}(\mathrm{eV})$ | 8.45489 | 8.48805 | 8.54444 | 6.94677 | 17.94106 |
| $T(e V)$ | 10.40395 | 7.45996 | 7.69741 | 5.37095 | 15.37682 |
| $V_{m}(\mathrm{eV})$ | -5.20198 | -3.72998 | -3.84870 | -2.68548 | -7.68841 |
| $E($ AO/HO) (eV) | -7.34015 | -7.34015 | -7.34015 | -7.34015 | -14.68031 |
| $\Delta E_{\mathrm{H}_{2} \mathrm{MO}}(\mathrm{AO} / \mathrm{HO})(\mathrm{eV})$ | 0 | 0 | 0 | 0 | 0 |
| $E_{T}(\mathrm{AO/HO})(\mathrm{eV})$ | -7.34015 | -7.34015 | -7.34015 | -7.34015 | -14.68031 |
| $E_{T}\left(\mathrm{H}_{2} \mathrm{MO}\right)(\mathrm{eV})$ | -27.73495 | -27.42310 | -27.83768 | -21.03220 | -42.11120 |
| $E_{T}\left(\right.$ atom - atom, msp $\left.{ }^{3} \cdot \mathrm{AO}\right)(\mathrm{eV})$ | -3.25266 | -3.25266 | -3.25266 | -3.25266 | -6.50532 |
| $E_{T}(\mathrm{MO})(\mathrm{eV})$ | -30.98761 | -30.67576 | -31.09034 | -24.28486 | -48.61652 |
| $\omega\left(10^{15} \mathrm{rad} / \mathrm{s}\right)$ | 11.1005 | 15.2859 | 8.59272 | 6.87387 | 33.9452 |
| $E_{K}(\mathrm{eV})$ | 7.30656 | 10.06142 | 5.65588 | 4.52450 | 22.34334 |
| $\bar{E}_{D}(\mathrm{eV})$ | -0.16571 | -0.19250 | -0.14628 | -0.10219 | -0.22732 |
| $\bar{E}_{\text {Kvib }}(\mathrm{eV})$ | $\begin{gathered} 0.09120 \\ {[14]} \end{gathered}$ | $\begin{gathered} 0.09120 \\ {[14]} \end{gathered}$ | $\begin{gathered} 0.09120 \\ {[14]} \end{gathered}$ | $\begin{gathered} 0.04823 \\ {[16]} \end{gathered}$ | $\begin{gathered} 0.12046 \\ {[17]} \end{gathered}$ |
| $\bar{E}_{\text {osc }}(\mathrm{eV})$ | -0.12011 | -0.14690 | -0.10068 | -0.07808 | -0.16709 |
| $E_{T}($ Group $)(e \mathrm{~V})$ | -31.10771 | -30.82266 | -31.19102 | -24.36294 | -48.95069 |
| $E_{\text {initial }}\left(c_{4} A O / H O\right)(e V)$ | -7.34015 | -7.34015 | -7.34015 | -7.34015 | -7.34015 |
| $E_{\text {initial }}\left(c_{5} A O / H O\right)(\mathrm{eV})$ | -17.42282 | -17.42282 | -17.42282 | -12.96764 | -13.61806 |
| $E_{D}($ Group $)(e V)$ | 6.34474 | 6.05969 | 6.42804 | 4.05515 | 7.03426 |

Table 23.11. The total bond energies of gaseous-state scandium coordinate compounds calculated using the functional group composition and the energies of Table 23.10 compared to the gaseous-state experimental values [15].

| Formula | Name | $\begin{gathered} S c-F(a) \\ \text { Groups } \end{gathered}$ | $\begin{aligned} & S c-F \text { (b) } \\ & \text { Groups } \end{aligned}$ | $\begin{gathered} S c-F(\mathrm{c}) \\ \text { Group } \end{gathered}$ | $\begin{gathered} S c-C l \\ \text { Group } \end{gathered}$ | $S c-O$ <br> Group | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| ScF | Scandium fluoride | 1 | 0 | 0 | 0 | 0 | 6.34474 | 6.16925 | -0.02845 |
| $\mathrm{ScF}_{2}$ | Scandium difluoride | 0 | 2 | 0 | 0 | 0 | 12.11937 | 12.19556 | 0.00625 |
| $\mathrm{ScF}_{3}$ | Scandium trifluoride | 0 | 0 | 3 | 0 | 0 | 19.28412 | 19.27994 | -0.00022 |
| ScCl | Scandium chloride | 0 | 0 | 0 | 1 | 0 | 4.05515 | 4.00192 | -0.01330 |
| ScO | Scandium oxide | 0 | 0 | 0 | 0 | 1 | 7.03426 | 7.08349 | 0.00695 |

## TITANIUM FUNCTIONAL GROUPS AND MOLECULES

The electron configuration of titanium is $[A r] 4 s^{2} 3 d^{2}$ having the corresponding term ${ }^{3} F_{2}$. The total energy of the state is given by the sum over the four electrons. The sum $E_{T}(T i, 3 d 4 s)$ of experimental energies [1] of $T i, T i^{+}, T i^{2+}$, and $T i^{3+}$ is

$$
\begin{equation*}
E_{T}(T i, 3 d 4 s)=-(43.2672 \mathrm{eV}+27.4917 \mathrm{eV}+13.5755 \mathrm{eV}+6.82812 \mathrm{eV})=-91.16252 \mathrm{eV} \tag{23.56}
\end{equation*}
$$

By considering that the central field decreases by an integer for each successive electron of the shell, the radius $r_{3 d 4 s}$ of the $T i 3 d 4 s$ shell may be calculated from the Coulombic energy using Eq. (15.13):

$$
\begin{equation*}
r_{3 d 4 s}=\sum_{n=18}^{21} \frac{(Z-n) e^{2}}{8 \pi \varepsilon_{0}(e 91.16252 \mathrm{eV})}=\frac{10 e^{2}}{8 \pi \varepsilon_{0}(e 91.16252 \mathrm{eV})}=1.49248 a_{0} \tag{23.57}
\end{equation*}
$$

where $Z=22$ for titanium. Using Eq. (15.14), the Coulombic energy $E_{\text {Coulomb }}(T i, 3 d 4 s)$ of the outer electron of the Ti3d $4 s$ shell is:

$$
\begin{equation*}
E_{\text {Coulomb }}(T i, 3 d 4 s)=\frac{-e^{2}}{8 \pi \varepsilon_{0} r_{3 d 4 s}}=\frac{-e^{2}}{8 \pi \varepsilon_{0} 1.49248 a_{0}}=-9.11625 \mathrm{eV} \tag{23.58}
\end{equation*}
$$

During hybridization, the spin-paired $4 s$ electrons are promoted to the Ti3d $4 s$ shell as unpaired electrons. The energy for the promotion is the magnetic energy given by Eq. (15.15) at the initial radius of the $4 s$ electrons. From Eq. (10.102) with $Z=22$ and $n=22$, the radius $r_{22}$ of the Ti4s shell is:

$$
\begin{equation*}
r_{22}=1.99261 a_{0} \tag{23.59}
\end{equation*}
$$

Using Eqs. (15.15) and (23.59), the unpairing energy is:

$$
\begin{equation*}
E(\text { magnetic })=\frac{2 \pi \mu_{0} e^{2} \hbar^{2}}{m_{e}^{2}\left(r_{22}\right)^{3}}=\frac{8 \pi \mu_{0} \mu_{B}^{2}}{\left(1.99261 a_{0}\right)^{3}}=0.01446 \mathrm{eV} \tag{23.60}
\end{equation*}
$$

Using Eqs. (23.58) and (23.60), the energy $E(T i, 3 d 4 s)$ of the outer electron of the $T i 3 d 4 s$ shell is:

$$
\begin{equation*}
E(T i, 3 d 4 s)=\frac{-e^{2}}{8 \pi \varepsilon_{0} r_{3 d 4 s}}+\frac{2 \pi \mu_{0} e^{2} \hbar^{2}}{m_{e}^{2}\left(r_{22}\right)^{3}}=-9.11625 \mathrm{eV}+0.01446 \mathrm{eV}=-9.10179 \mathrm{eV} \tag{23.61}
\end{equation*}
$$

Next, consider the formation of the $T i-L$-bond MO wherein each titanium atom has a Ti3d $4 s$ electron with an energy given by Eq. (23.61). The total energy of the state of each titanium atom is given by the sum over the four electrons. The sum $E_{T}\left(T i_{T i-L} 3 d 4 s\right)$ of energies of $T i 3 d 4 s$ (Eq. (23.61)), $T i^{+}, T i^{2+}$, and $T i^{3+}$ is:

$$
\begin{align*}
E_{T}\left(T i_{T i-L} 3 d 4 s\right) & =-(43.2672 \mathrm{eV}+27.4917 \mathrm{eV}+13.5755 \mathrm{eV}+E(T i, 3 \mathrm{~d} 4 \mathrm{~s})) \\
& =-(43.2672 \mathrm{eV}+27.4917 \mathrm{eV}+13.5755 \mathrm{eV}+9.10179 \mathrm{eV})  \tag{23.62}\\
& =-93.43619 \mathrm{eV}
\end{align*}
$$

where $E(T i, 3 d 4 s)$ is the sum of the energy of $T i,-6.82812 \mathrm{eV}$, and the hybridization energy.
The titanium HO donates an electron to each MO. Using Eq. (23.30), the radius $r_{3 d 4 s}$ of the Ti3d $4 s$ shell calculated from the Coulombic energy is:

$$
\begin{equation*}
r_{T i-L 3 d 4 s}=\left(\sum_{n=18}^{21}(Z-n)-1\right) \frac{e^{2}}{8 \pi \varepsilon_{0}(e 93.43619 e V)}=\frac{9 e^{2}}{8 \pi \varepsilon_{0}(e 93.43619 \mathrm{eV})}=1.31054 a_{0} \tag{23.63}
\end{equation*}
$$

Using Eqs. (15.19) and (23.63), the Coulombic energy $E_{\text {Coulomb }}\left(T i_{T i-L}, 3 d 4 s\right)$ of the outer electron of the $T i 3 d 4 s$ shell is:

$$
\begin{equation*}
E_{\text {Coulomb }}\left(T i_{T i-L}, 3 d 4 s\right)=\frac{-e^{2}}{8 \pi \varepsilon_{0} r_{T i-L 3 d 4 s}}=\frac{-e^{2}}{8 \pi \varepsilon_{0} 1.31054 a_{0}}=-10.38180 \mathrm{eV} \tag{23.64}
\end{equation*}
$$

The only magnetic energy term is that for the unpairing of the $4 s$ electrons given by Eq. (23.60). Using Eqs. (23.32), (23.60), and (23.64), the energy $E\left(T i_{T i-L}, 3 d 4 s\right)$ of the outer electron of the $T i 3 d 4 s$ shell is:

$$
\begin{equation*}
E\left(T i_{T i-L}, 3 d 4 s\right)=\frac{-e^{2}}{8 \pi \varepsilon_{0} r_{T i-L 3 d 4 s}}+\frac{2 \pi \mu_{0} e^{2} \hbar^{2}}{m_{e}^{2}\left(r_{22}\right)^{3}}=-10.38180 \mathrm{eV}+0.01446 \mathrm{eV}=-10.36734 \mathrm{eV} \tag{23.65}
\end{equation*}
$$

Thus, $E_{T}(T i-L, 3 d 4 s)$, the energy change of each $T i 3 d 4 s$ shell with the formation of the $T i-L$-bond MO is given by the difference between Eq. (23.65) and Eq. (23.61).

$$
\begin{equation*}
E_{T}(T i-L, 3 d 4 s)=E\left(T i_{T i-L}, 3 d 4 s\right)-E(T i, 3 d 4 s)=-10.36734 \mathrm{eV}-(-9.10179 \mathrm{eV})=-1.26555 \mathrm{eV} \tag{23.66}
\end{equation*}
$$

The semimajor axis $a$ solution given by Eq. (23.41) of the force balance equation, Eq. (23.39), for the $\sigma$-MO of the $T i-L$-bond MO of $T i L_{n}$ is given in Table 23.13 with the force-equation parameters $Z=22, n_{e}$, and $L$ corresponding to the orbital and spin angular momentum terms of the $3 d 4 s \mathrm{HO}$ shell.

For the $T i-L$ functional groups, hybridization of the $4 s$ and $3 d$ AOs of $T i$ to form a single $3 d 4 s$ shell forms an energy minimum, and the sharing of electrons between the $T i 3 d 4 s \mathrm{HO}$ and $L \mathrm{AO}$ to form a MO permits each participating orbital to
decrease in radius and energy. The $F \mathrm{AO}$ has an energy of $E(F)=-17.42282 \mathrm{eV}$, the Cl AO has an energy of $E(C l)=-12.96764 \mathrm{eV}$, the Br AO has an energy of $E(B r)=-11.8138 \mathrm{eV}$, the $I \mathrm{AO}$ has an energy of $E(I)=-10.45126 \mathrm{eV}$, the $O \mathrm{AO}$ has an energy of $E(O)=-13.61805 \mathrm{eV}$, and the Ti3d4s HOs have an energy of $E(T i, 3 d 4 s)=-9.10179 \mathrm{eV}$ (Eq. (23.61)). To meet the equipotential condition of the union of the $T i-L H_{2}$-type-ellipsoidalMO with these orbitals, the hybridization factor(s), at least one of $c_{2}$ and $C_{2}$ of Eq. (15.61) for the $T i-L$-bond MO given by Eq. (15.77) is:

$$
\begin{align*}
& C_{2}(\text { FAO to Ti3d } 4 \mathrm{sHO})=\frac{E(T i, 3 d 4 s)}{E(F A O)}=\frac{-9.10179 \mathrm{eV}}{-17.42282 \mathrm{eV}}=0.52241  \tag{23.67}\\
& C_{2}(\mathrm{ClAO} \text { to Ti3d } 4 \mathrm{sHO})=\frac{E(T i, 3 d 4 \mathrm{~s})}{E(C l A O)}=\frac{-9.10179 \mathrm{eV}}{-12.96764 \mathrm{eV}}=0.70188  \tag{23.68}\\
& c_{2}(\mathrm{BrAO} \text { to Ti3d } 4 \mathrm{sHO})=C_{2}(\mathrm{BrAO} \text { to } T i 3 d 4 \mathrm{sHO})=\frac{E(T i, 3 d 4 \mathrm{~s})}{E(B r A O)}=\frac{-9.10179 \mathrm{eV}}{-11.8138 \mathrm{eV}}=0.77044  \tag{23.69}\\
& c_{2}(\mathrm{IAO} \text { to Ti3d } 4 \mathrm{sHO})=C_{2}(I A O \text { to } T i 3 d 4 \mathrm{sHO})=\frac{E(T i, 3 d 4 \mathrm{~s})}{E(I A O)}=\frac{-9.10179 \mathrm{eV}}{-10.45126 \mathrm{eV}}=0.87088  \tag{23.70}\\
& c_{2}(O \text { to Ti3d } 4 \mathrm{sHO})=\frac{E(T i, 3 d 4 \mathrm{~s})}{E(O)}=\frac{-9.10179 \mathrm{eV}}{-13.61805 \mathrm{eV}}=0.66836 \tag{23.71}
\end{align*}
$$

Since the energy of the MO is matched to that of the $\operatorname{Ti3d} d 4 \mathrm{HO}, E(A O / H O)$ in Eq. (15.61) is $E(T i, 3 d 4 s)$ given by Eq. (23.61) and twice this value for double bonds. $E_{T}\left(\right.$ atom-atom, $\left.m s p^{3} . A O\right)$ of the $T i-L$-bond MO is determined by considering that the bond involves an electron transfer from the titanium atom to the ligand atom to form partial ionic character in the bond as in the case of the zwitterions such as $H_{2} B^{+}-F^{-}$given in the Halido Boranes section. $E_{T}\left(\right.$ atom - atom, msp ${ }^{3}$. AO) is -2.53109 eV , two times the energy of Eq. (23.66).

The symbols of the functional groups of titanium coordinate compounds are given in Table 23.12. The geometrical (Eqs. (15.1-15.5) and (23.41)), intercept (Eqs. (15.31-15.32) and (15.80-15.87)), and energy (Eqs. (15.61) and (23.28-23.33)) parameters of titanium coordinate compound are given in Tables 23.13, 23.14, and 23.15, respectively. The total energy of each titanium coordinate compounds given in Table 23.16 was calculated as the sum over the integer multiple of each $E_{D}$ (Group) of Table 23.15 corresponding to functional-group composition of the compound. The bond angle parameters of titanium coordinate compounds determined using Eqs. (15.88-15.117) are given in Table 23.17. The $E_{T}\left(\right.$ atom-atom, $\left.\mathrm{msp}{ }^{3} . \mathrm{AO}\right)$ term for $\mathrm{TiOCl}_{2}$ was calculated using Eqs. (23.30-23.33) as a linear combination of $s=1$ and $s=2$ for the energies of $E(T i, 3 d 4 s)$ given by Eqs. (23.63-23.66) corresponding to a $\mathrm{Ti}-\mathrm{Cl}$ single bond and a $\mathrm{Ti}=O$ double bond. The charge-densities of exemplary titanium coordinate compound, titanium tetrafluoride comprising the concentric shells of atoms with the outer shell bridged by one or more $\mathrm{H}_{2}$-type ellipsoidal MOs or joined with one or more hydrogen MOs is shown in Figure 23.3.

Figure 23.3. Titanium Tetrafluoride. Color scale, translucent view of the charge-density of $\mathrm{TiF}_{4}$ showing the orbitals of the Ti and $F$ atoms at their radii, the ellipsoidal surface of each $H_{2}$-type ellipsoidal MO that transitions to the corresponding outer shell of the atoms participating in each bond, and the nuclei (red, not to scale).

$0 \square 1 \mathrm{e} / \AA^{2}$

Table 23.12. The symbols of the functional groups of titanium coordinate compounds.

| Functional Group | Group Symbol |
| :---: | :---: |
| TiF group of TiF | Ti-F (a) |
| TiF group of $T i F_{2}$ | Ti-F (b) |
| TiF group of $\mathrm{TiF}_{3}$ | Ti-F (c) |
| TiF group of $\mathrm{TiF}_{4}$ | Ti-F (d) |
| TiCl group of TiCl | $\mathrm{Ti}-\mathrm{Cl}$ (a) |
| TiCl group of $\mathrm{TiCl}_{2}$ | $\mathrm{Ti}-\mathrm{Cl}$ (b) |
| TiCl group of $\mathrm{TiCl}_{3}$ | $\mathrm{Ti}-\mathrm{Cl}$ (c) |
| TiCl group of $\mathrm{TiCl}_{4}$ | $\mathrm{Ti}-\mathrm{Cl}$ (d) |
| TiBr group of TiBr | Ti-Br (a) |
| TiBr group of $\mathrm{TiBr}_{2}$ | Ti-Br (b) |
| TiBr group of $\mathrm{TiBr}_{3}$ | Ti-Br (c) |
| TiBr group of $\mathrm{TiBr}_{4}$ | $\mathrm{Ti}-\mathrm{Br}$ (d) |
| TiI group of TiI | Ti-I (a) |
| TiI group of $\mathrm{TiI}_{2}$ | Ti-I (b) |
| TiI group of $\mathrm{TiI}_{3}$ | Ti-I (c) |
| TiI group of $\mathrm{TiI}_{4}$ | Ti-I (d) |
| TiO group of TiO | Ti-O (a) |
| TiO group of $\mathrm{TiO}_{2}$ | $\mathrm{Ti}-\mathrm{O}$ (b) |

Table 23.13. The geometrical bond parameters of titanium coordinate compounds and experimental values.

| Parameter | $\begin{gathered} T i-F(a) \\ \text { Group } \end{gathered}$ | $\begin{gathered} \hline T i-F(b) \\ \text { Group } \\ \hline \end{gathered}$ | $\begin{gathered} T i-F(\mathrm{c}) \\ \text { Group } \end{gathered}$ | $\begin{gathered} T i-F(\mathrm{~d}) \\ \text { Group } \\ \hline \end{gathered}$ | $\begin{gathered} \mathrm{Ti}-\mathrm{Cl} \text { (a) } \\ \text { Group } \\ \hline \end{gathered}$ | $\begin{gathered} \mathrm{Ti}-\mathrm{Cl}(\mathrm{~b}) \\ \text { Group } \\ \hline \end{gathered}$ | $\begin{gathered} \mathrm{Ti}-\mathrm{Cl} \text { (c) } \\ \text { Group } \\ \hline \end{gathered}$ | $\begin{gathered} \mathrm{Ti}-\mathrm{Cl}(\mathrm{~d}) \\ \text { Group } \\ \hline \end{gathered}$ | $\begin{gathered} \mathrm{Ti}-\mathrm{Br} \text { (a) } \\ \text { Group } \end{gathered}$ | $\begin{gathered} \mathrm{Ti}-\mathrm{Br}(\mathrm{~b}) \\ \text { Group } \\ \hline \end{gathered}$ | $\begin{gathered} \mathrm{Ti-Br}(\mathrm{c}) \\ \text { Group } \\ \hline \end{gathered}$ | $\begin{gathered} \hline T i-\mathrm{Br}(\mathrm{~d}) \\ \text { Group } \end{gathered}$ | $\begin{gathered} \hline T i-I \text { (a) } \\ \text { Groups } \end{gathered}$ | $\begin{gathered} T i-I \text { (b) } \\ \text { Group } \end{gathered}$ | $\begin{gathered} \hline T i-I(\mathrm{c}) \\ \text { Group } \\ \hline \end{gathered}$ | $\begin{gathered} \hline T i-I(\mathrm{~d}) \\ \text { Group } \\ \hline \end{gathered}$ | $\begin{gathered} \text { Ti-O (a) } \\ \text { Group } \\ \hline \end{gathered}$ | $\begin{gathered} \text { Ti-O (b) } \\ \text { Group } \\ \hline \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $n_{e}$ | 2 | 2 | 2 | 2 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 4 | 4 | 4 | 4 | 2 | -2 |
| L | $1+\sqrt{\frac{3}{4}}$ | 3 | $4 \sqrt{\frac{3}{4}}$ | 4 | $9 \sqrt{\frac{3}{4}}$ | $4+3 \sqrt{\frac{3}{4}}$ | $3+5 \sqrt{\frac{3}{4}}$ | 8 | $2+3 \sqrt{\frac{3}{4}}$ | 3 | 4 | $3+2 \sqrt{\frac{3}{4}}$ | 3 | 1 | $3 \sqrt{\frac{3}{4}}$ | $4 \sqrt{\frac{3}{4}}$ | $9 \sqrt{\frac{3}{4}}$ | $3+6 \sqrt{\frac{3}{4}}$ |
| $a\left(a_{0}\right)$ | 2.16355 | 2.13636 | 2.15746 | 2.18182 | 2.85428 | 2.79991 | 2.83319 | 2.86364 | 2.70900 | 2.63636 | 2.68182 | 2.71509 | 3.13636 | 3.04545 | 3.11809 | 3.15746 | 2.35428 | 2.37255 |
| $c^{\prime}\left(a_{0}\right)$ | 1.66163 | 1.65115 | 1.65929 | 1.66863 | 2.01658 | 1.99728 | 2.00911 | 2.01988 | 2.16524 | 2.13601 | 2.15435 | 2.16767 | 2.19131 | 2.15932 | 2.18492 | 2.19867 | 1.53242 | 1.53835 |
| Bond Length $2 c^{\prime}(A)$ | 1.75859 | 1.74751 | 1.75611 | 1.76600 | 2.13426 | 2.11383 | 2.12635 | 2.13775 | 2.29159 | 2.26066 | 2.28006 | 2.29416 | 2.31918 | 2.28532 | 2.31242 | 2.32697 | 1.62184 | 1.62812 |
| Exp. Bond Length <br> (A) | $\begin{gathered} 1.745[15] \\ \left(T i F_{4}\right) \end{gathered}$ | $\begin{gathered} 1.745[15] \\ \left(T i F_{4}\right) \end{gathered}$ | $\begin{gathered} 1.745[15] \\ \left(T i F_{4}\right) \end{gathered}$ | $\begin{gathered} 1.745[15] \\ \left(\text { TiF }_{4}\right) \end{gathered}$ | $\begin{gathered} 2.170[18] \\ \left(\mathrm{TiCl}_{4}\right) \end{gathered}$ | $\begin{gathered} 2.170[18] \\ \left(\text { TiCl }_{4}\right) \end{gathered}$ | $\begin{gathered} 2.170[81] \\ \left(\text { TiCl }_{4}\right) \end{gathered}$ | $\begin{gathered} 2.170[18] \\ \left(\mathrm{TiCl}_{4}\right) \end{gathered}$ | $\begin{gathered} 2.31[19] \\ \left(\text { TiBr }_{4}\right) \end{gathered}$ | $\begin{gathered} 2.31[19] \\ \left(\text { TiBr }_{4}\right) \end{gathered}$ | $\begin{gathered} 2.31[19] \\ \left(T i B r_{4}\right) \end{gathered}$ | $\begin{gathered} 2.31[19] \\ \left(\text { TiBr }_{4}\right) \end{gathered}$ | $\begin{gathered} 2.5[20] \\ \left(\text { TiI }_{4}\right) \end{gathered}$ | $\begin{gathered} 2.5[20] \\ \left(T i I_{4}\right) \end{gathered}$ | $\begin{gathered} 2.5[20] \\ \left(T I_{4}\right) \end{gathered}$ | $\begin{gathered} 2.5[20] \\ \left(T i i_{4}\right) \end{gathered}$ | $\begin{gathered} 1.623[15] \\ (\mathrm{TiO}) \end{gathered}$ | $\begin{aligned} & 1.62[15] \\ & \left(\mathrm{TiO}_{2}\right) \end{aligned}$ |
| $b, c\left(a_{0}\right)$ | 1.38562 | 1.35563 | 1.37891 | 1.40571 | 2.01998 | 1.96224 | 1.99760 | 2.02990 | 1.62802 | 1.54527 | 1.59717 | 1.63491 | 2.24387 | 2.14759 | 2.22456 | 2.26615 | 1.78727 | 1.80623 |
| $e$ | 0.76801 | 0.77288 | 0.76909 | 0.76479 | 0.70651 | 0.71334 | 0.70914 | 0.70536 | 0.79927 | 0.81021 | 0.80332 | 0.79838 | 0.69868 | 0.70903 | 0.70072 | 0.69634 | 0.65091 | 0.64840 |


Table 23.15. The energy parameters ( eV ) of functional groups of titanium coordinate compounds.

| Parameters | $\begin{aligned} & \hline T i-F \text { (a) } \\ & \text { Group } \end{aligned}$ | $\begin{gathered} T i-F(\mathrm{~b}) \\ \text { Group } \end{gathered}$ | $\begin{gathered} T i-F \text { (c) } \\ \text { Group } \end{gathered}$ | $\begin{gathered} T i-F(\mathrm{~d}) \\ \text { Group } \end{gathered}$ | $\begin{gathered} \mathrm{Ti}-\mathrm{Cl} \text { (a) } \\ \text { Group } \\ \hline \end{gathered}$ | $\begin{gathered} \mathrm{Ti}-\mathrm{Cl} \text { (b) } \\ \text { Group } \end{gathered}$ | $\begin{gathered} \mathrm{Ti}-\mathrm{Cl}(\mathrm{c}) \\ \text { Group } \\ \hline \end{gathered}$ | $\begin{gathered} \mathrm{Ti}-\mathrm{Cl}(\mathrm{~d}) \\ \text { Group } \\ \hline \end{gathered}$ | $\begin{gathered} \mathrm{Ti-Br}(\mathrm{a}) \\ \text { Group } \end{gathered}$ | $\begin{array}{\|c} \hline T i-B r \text { (b) } \\ \text { Group } \end{array}$ | $\begin{gathered} T i-B r \text { (c) } \\ \text { Group } \end{gathered}$ | $\begin{gathered} T i-B r(\mathrm{~d}) \\ \text { Group } \end{gathered}$ | $\begin{array}{c\|} \hline T i-I \text { (a) } \\ \text { Groups } \\ \hline \end{array}$ | $\begin{aligned} & T i-I \text { (b) } \\ & \text { Group } \end{aligned}$ | $\begin{gathered} T i-I(\mathrm{c}) \\ \text { Group } \end{gathered}$ | $\begin{gathered} \hline T i-I(\mathrm{~d}) \\ \text { Group } \\ \hline \end{gathered}$ | $\begin{array}{\|c\|} \hline T i-O \text { (a) } \\ \text { Group } \end{array}$ | $\begin{array}{\|c\|} \hline T i-O(b) \\ \text { Group } \end{array}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $n_{1}$ | , | 1 | , | , | , | , | 1 | , | 1 | , | , | 1 | 1 | 1 | 1 | 1 |  | 2 |
| $n_{2}$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 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 | 0 | 0 |
| $C_{1}$ | 0.75 | 0.75 | 0.75 | 0.75 | 0.5 | 0.5 | 0.5 | 0.5 | 0.375 | 0.375 | 0.375 | 0.375 | 0.375 | 0.375 | 0.375 | 0.375 | 0.75 | 0.75 |
| $C_{2}$ | 0.52241 | 0.52241 | 0.52241 | 0.52241 | 0.70188 | 0.70188 | 0.70188 | 0.70188 | 0.77044 | 0.77044 | 0.77044 | 0.77044 | 0.87088 | 0.87088 | 0.87088 | 0.87088 | 0.66836 | 0.66836 |
| $c_{1}$ | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $c_{2}$ | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 0.77044 | 0.77044 | 0.77044 | 0.77044 | 0.87088 | 0.87088 | 0.87088 | 0.87088 | 1 | 1 |
| $c_{3}$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $c_{4}$ | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 2 | 2 |
| $c_{5}$ | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 2 | 2 |
| $C_{10}$ | 0.75 | 0.75 | 0.75 | 0.75 | 0.5 | 0.5 | 0.5 | 0.5 | 0.375 | 0.375 | 0.375 | 0.375 | 0.375 | 0.375 | 0.375 | 0.375 | 0.75 | 0.75 |
| $C_{20}$ | 0.52241 | 0.52241 | 0.52241 | 0.52241 | 0.70188 | 0.70188 | 0.70188 | 0.70188 | 0.77044 | 0.77044 | 0.77044 | 0.77044 | 0.87088 | 0.87088 | 0.87088 | 0.87088 | 0.66836 | 0.66836 |
| $V_{e}(\mathrm{eV})$ | -33.25925 | -33.86525 | -33.39295 | -32.86502 | -23.75423 | -24.35881 | -23.98503 | -23.65338 | -21.23559 | -22.13551 | -21.56268 | -21.16382 | -18.70299 | -19.43040 | -18.84456 | -18.54225 | -55.18049 | -54.66023 |
| $V_{p}(\mathrm{eV})$ | 8.18824 | 8.24018 | 8.19979 | 8.15389 | 6.74697 | 6.81216 | 6.77204 | 6.73594 | 6.28375 | 6.36973 | 6.31552 | 6.27670 | 6.20899 | 6.30098 | 6.22715 | 6.18821 | 17.75727 | 17.68877 |
| $T(\mathrm{eV})$ | 7.68627 | 7.92591 | 7.73895 | 7.53157 | 4.16116 | 4.34992 | 4.23287 | 4.12996 | 3.91945 | 4.19811 | 4.02016 | 3.89744 | 2.98164 | 3.19007 | 3.02181 | 2.93626 | 11.71917 | 11.51929 |
| $V_{m}(\mathrm{eV})$ | -3.84314 | -3.96296 | -3.86948 | -3.76578 | -2.08058 | -2.17496 | -2.11643 | -2.06498 | -1.95972 | -2.09906 | -2.01008 | -1.94872 | -1.49082 | -1.59503 | -1.51090 | -1.46813 | -5.85959 | -5.75964 |
| $E$ (лоно) (eV) | -9.10179 | -9.10179 | -9.10179 | -9.10179 | -9.10179 | -9.10179 | -9.10179 | -9.10179 | -9.10179 | -9.10179 | -9.10179 | -9.10179 | -9.10179 | -9.10179 | -9.10179 | -9.10179 | -18.20358 | -18.20358 |
| $\Delta E_{H_{2} \mathrm{NO}_{\mathrm{O}}}$ ( (оіно) $(\mathrm{eV})$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $E_{T}$ (Аонно) (eV) | -9.10179 | -9.10179 | -9.10179 | -9.10179 | -9.10179 | -9.10179 | -9.10179 | -9.10179 | -9.10179 | -9.10179 | -9.10179 | -9.10179 | -9.10179 | -9.10179 | -9.10179 | -9.10179 | -18.20358 | -18.20358 |
| $E_{T}\left(H_{2} \mu \mathrm{O}\right)(\mathrm{eV})$ | -30.32966 | -30.76391 | -30.42547 | -30.04713 | -24.02848 | -24.47348 | -24.19834 | -23.95426 | -22.09391 | -22.76852 | -22.33888 | -22.04019 | -20.10497 | -20.63618 | -20.20830 | -19.98770 | -49.76721 | -49.41539 |
| $\begin{aligned} & E_{T}\left(\text { atom-atom }, m s p^{3} \cdot A O\right) \\ & (\mathrm{eV}) \end{aligned}$ | -2.53109 | -2.53109 | -2.53109 | -2.53109 | -2.53109 | -2.53109 | -2.53109 | -2.53109 | -2.53109 | -2.53109 | -2.53109 | -2.53109 | -2.53109 | -2.53109 | -2.53109 | -2.53109 | -2.53109 | -2.53109 |
| $E_{T}(\mathrm{mc})(\mathrm{eV})$ | -32.86076 | -33.29501 | -32.95657 | -32.57823 | -26.55957 | -27.00457 | -26.72944 | -26.48535 | -24.62500 | -25.29961 | -24.86997 | -24.57129 | -22.63607 | -23.16728 | -22.73939 | -22.51880 | -52.29830 | -51.94648 |
| © ( ) $10^{15} \mathrm{rad} / \mathrm{s}$ ) | 8.13148 | 8.28718 | 8.16593 | 8.02956 | 5.07876 | 5.22741 | 8.67440 | 5.05389 | 4.98373 | 5.19112 | 5.05970 | 4.96698 | 7.02884 | 4.44530 | 4.29087 | 4.21088 | 12.2500 | 8.00936 |
| $E_{K}(\mathrm{eV})$ | 5.35228 | 5.45477 | 5.37496 | 5.28520 | 3.34292 | 3.44077 | 5.70964 | 3.32656 | 3.28038 | 3.41689 | 3.33039 | 3.26935 | 4.62650 | 2.92598 | 2.82433 | 2.77168 | 8.06316 | 5.27190 |
| $\bar{E}_{D}(\mathrm{eV})$ | -0.15040 | -0.15384 | -0.15116 | -0.14817 | -0.09607 | -0.09910 | -0.12636 | -0.09557 | -0.08824 | -0.09252 | -0.08979 | -0.08789 | -0.09632 | -0.07840 | -0.07560 | -0.07417 | -0.14690 | -0.11798 |
| $\bar{E}_{\text {Kvw }}(\mathrm{eV})$ | $\begin{gathered} 0.07315 \\ {[21]} \end{gathered}$ | $\begin{gathered} 0.07315 \\ {[21]} \end{gathered}$ | ${ }_{[21]}^{0.07315}$ | $\begin{gathered} 0.07315 \\ {[21]} \end{gathered}$ | $\begin{gathered} 0.04823 \\ {[16]} \end{gathered}$ | $\begin{gathered} 0.04823 \\ {[16]} \end{gathered}$ | $\begin{gathered} 0.04823 \\ {[16]} \end{gathered}$ | $\begin{gathered} 0.04823 \\ {[16]} \end{gathered}$ | $\begin{gathered} 0.03658 \\ {[19]} \end{gathered}$ | $\begin{gathered} 0.03658 \\ {[19]} \end{gathered}$ | $\begin{gathered} 0.03658 \\ {[19]} \end{gathered}$ | $\begin{gathered} 0.03658 \\ {[19]} \end{gathered}$ | ${ }_{[20]}^{0.02976}$ | $\begin{gathered} 0.02976 \\ {[20]} \end{gathered}$ | ${ }_{[20]}^{0.02976}$ | $\begin{gathered} 0.02976 \\ {[20]} \end{gathered}$ | $\begin{gathered} 0.12510 \\ {[14]} \end{gathered}$ | $\begin{gathered} 0.12510 \\ {[14]} \end{gathered}$ |
| $\bar{E}_{\text {occ }}(\mathrm{eV})$ | -0.11383 | -0.11726 | -0.11458 | -0.11159 | -0.07195 | -0.07498 | -0.10224 | $-0.07145$ | -0.06995 | -0.07423 | -0.07150 | -0.06961 | -0.08144 | -0.06352 | -0.06072 | -0.05929 | -0.08435 | -0.05543 |
| $E_{T}$ (Grap) (eV) | -32.97458 | -33.41227 | -33.07115 | -32.68982 | -26.63152 | -27.07955 | -26.83168 | -26.55680 | -24.69495 | -25.37384 | -24.94147 | -24.64090 | -22.71751 | -23.23080 | -22.80011 | -22.57809 | -52.46699 | -52.05734 |
| $E_{\text {intual }}\left(\mathrm{c}_{4}\right.$ АОІНо) $(\mathrm{eV})$ | -9.10179 | -9.10179 | -9.10179 | -9.10179 | -9.10179 | -9.10179 | -9.10179 | -9.10179 | -9.10179 | -9.10179 | -9.10179 | -9.10179 | -9.10179 | -9.10179 | -9.10179 | -9.10179 | -9.10179 | -9.10179 |
|  | -17.42282 | -17.42282 | -17.42282 | -17.42282 | -12.96764 | -12.96764 | -12.96764 | -12.96764 | -11.8138 | -11.8138 | -11.8138 | -11.8138 | -10.45126 | -10.45126 | -10.45126 | -10.45126 | -13.61806 | -13.61806 |
| $E_{D}$ (Gruap) (eV) | 6.44997 | 6.88766 | 6.54654 | 6.16521 | 4.56209 | 5.01012 | 4.76225 | 4.48737 | 3.77936 | 4.45825 | 4.02588 | 3.72530 | 3.16446 | 3.67775 | 3.24706 | 3.02504 | 7.02729 | 6.61764 |

 compared to the gaseous-state experimental values.

| Formula | Name | $\begin{gathered} T i-F \\ \text { (a) } \\ \text { Group } \end{gathered}$ | $T i-F$ <br> (b) <br> Group | $T i-F$ <br> (c) <br> Group | $T i-F$ <br> (d) <br> Group | $\mathrm{Ti}-\mathrm{Cl}$ <br> (a) <br> Group | $\begin{aligned} & \mathrm{Ti-Cl} \\ & \text { (b) } \\ & \text { Group } \end{aligned}$ | $\begin{aligned} & \text { Ti-Cl } \\ & \text { (c) } \\ & \text { Group } \\ & \hline \end{aligned}$ | $\begin{aligned} & \mathrm{Ti-Cl} \\ & \text { (d) } \\ & \text { Group } \end{aligned}$ | $\begin{aligned} & T i-B r \\ & \text { (a) } \\ & \text { Group } \end{aligned}$ | $T i-B r$ <br> (b) <br> Group | $\begin{aligned} & \text { Ti-Br } \\ & \text { (c) } \\ & \text { Group } \\ & \hline \end{aligned}$ | $\mathrm{Ti}-\mathrm{Br}$ <br> (d) <br> Group | $T i-1$ <br> (a) <br> Groups | $T i-I$ <br> (b) Group | $T i-I$ <br> (c) Group | $T i-I$ <br> (d) <br> Group | Ti-O <br> (a) Group | $\begin{gathered} \text { Ti-O } \\ \text { (b) } \\ \text { Group } \end{gathered}$ | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| TiF | Titanium fluoride | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | , | 0 | 0 | 0 | 6.44997 | 6.41871 [21] | -0.00487 |
| TiF ${ }_{2}$ | Titanium difluoride | 0 | 2 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 13.77532 | 13.66390 [21] | -0.00815 |
| $\mathrm{TiF}_{3}$ | Titanium trifluoride | 0 | 0 | 3 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 19.63961 | 19.64671 [21] | 0.00036 |
| $\mathrm{TiF}_{4}$ | Titanium tetrafluoride | 0 | 0 | 0 | 4 | 0 | 0 |  | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 24.66085 | 24.23470 [21] | -0.01758 |
| TiCl | Titanium chloride | 0 | 0 | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 4.56209 | 4.56198 [22] | -0.00003 |
| $\mathrm{TiCl}_{2}$ | Titanium dichoride | 0 | 0 | 0 | 0 | 0 | 2 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 10.02025 | 9.87408 [22] | -0.01517 |
| $\mathrm{TiCl}_{3}$ | Titanium trichloride | 0 | 0 | 0 | 0 | 0 | 0 | 3 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 14.28674 | 14.22984 [22] | -0.00400 |
| $\mathrm{TiCl}_{4}$ | Titanium tetrachloride | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 4 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 17.94949 | 17.82402 [22] | -0.00704 |
| TiBr | Titanium bromide | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 3.77936 | 3.78466 [19] | 0.00140 |
| $\mathrm{TiBr}_{2}$ | Titanium dibromide | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 2 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 8.91650 | 8.93012 [19] | 0.00153 |
| $\mathrm{TiBr}_{3}$ | Titanium tribromide | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 3 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 12.07765 | 12.02246 [19] | -0.00459 |
| $\mathrm{TiBr}_{4}$ | Titanium tetrabromide | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 4 | 0 | 0 | 0 | 0 | 0 | 0 | 14.90122 | 14.93239 [19] | 0.00209 |
| TiI | Titanium iodide | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 3.16446 | 3.15504 [20] | -0.00299 |
| $\mathrm{TiI}_{2}$ | Titanium diiodide | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 2 | 0 | 0 | 0 | 0 | 7.35550 | 7.29291 [20] | -0.00858 |
| $\mathrm{TiI}_{3}$ | Titanium triiodide | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 3 | 0 | 0 | 0 | 9.74119 | 9.71935 [20] | -0.00225 |
| $\mathrm{TiI}_{4}$ | Titanium tetraiodide | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 4 | 0 | 0 | 12.10014 | 12.14569 [20] | 0.00375 |
| TiO | Titanium oxide | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 0 | 7.02729 | 7.00341 [23] | -0.00341 |
| $\mathrm{TiO}_{2}$ | Titanium dioxide | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 2 | 13.23528 | 13.21050 [23] | -0.00188 |
| TiOF | Titanium fluoride oxide | 0 | 0 | 0 | 1 | 0 |  | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 12.78285 | 12.77353 [23] | -0.00073 |
| $\mathrm{TiOF}_{2}$ | Titanium difluoride oxide | 0 | 0 | 0 | 2 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 18.94807 | 18.66983 [23] | -0.01490 |
| TiOCl | Titanium chloride oxide | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 11.10501 | 11.25669 [23] | 0.01347 |
| $\mathrm{TiOCl}_{2}$ | Titanium dichloride oxide | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 2 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 15.59238 | 15.54295 [23] | -0.00318 |


| Atoms of Angle | $\begin{gathered} 2 c^{\prime} \\ \text { Bond } 1\left(a_{0}\right) \end{gathered}$ | $\begin{gathered} 2 c^{\prime} \\ \text { Bond } 2\left(a_{0}\right) \end{gathered}$ | $2 c^{\prime}$ Terminal Atoms $\left(a_{0}\right)$ | $\begin{aligned} & E_{\text {Contambic }} \\ & \text { Atom } 1 \end{aligned}$ | Atom 1 Hybridization Designation <br> (Table 15.3A) | $\begin{aligned} & E_{\text {Contambic }} \\ & \text { Atom } 2 \end{aligned}$ | Atom 2 Hybridization Designation (Table 15.3A) | $\begin{gathered} c_{2} \\ \text { Atom } 1 \end{gathered}$ | $\begin{gathered} c_{2} \\ \text { Atom } 2 \end{gathered}$ | $C_{1}$ | $C_{2}$ | $c_{1}$ | $c_{2}^{\prime}$ | $\begin{gathered} E_{T} \\ (\mathrm{eV}) \end{gathered}$ | $\begin{aligned} & \theta_{v} \\ & \left({ }^{\circ}\right) \end{aligned}$ | $\begin{gathered} \theta_{1} \\ \left({ }^{\circ}\right) \end{gathered}$ | $\begin{aligned} & \theta_{2} \\ & \left({ }^{\circ}\right) \end{aligned}$ | $\begin{gathered} \text { Cal. } \theta \\ \left({ }^{\circ}\right) \end{gathered}$ | Exp. $\theta$ <br> $\left({ }^{\circ}\right)$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\angle \mathrm{OTICl}$ | 3.07671 | 4.03976 | 6.2075 | $\begin{gathered} -13.61806 \\ O \end{gathered}$ | O | $\begin{gathered} -12.96764 \\ C l \end{gathered}$ | Cl | $\begin{gathered} 0.66836 \\ (\text { (Eq. } \\ (23.71)) \end{gathered}$ | $\begin{gathered} 0.70188 \\ (\text { Eq. } \\ (23.68)) \end{gathered}$ | 0.75 | 0.68512 | 1 | 0.68512 | -0.59304 |  |  |  | 120.85 | $\begin{gathered} 120 \\ \left(\text { TiOCl }_{2}\right) \end{gathered}$ |

## VANADIUM FUNCTIONAL GROUPS AND MOLECULES

The electron configuration of vanadium is $[A r] 4 s^{2} 3 d^{3}$ having the corresponding term ${ }^{4} F_{3 / 2}$. The total energy of the state is given by the sum over the five electrons. The sum $E_{T}(V, 3 d 4 s)$ of experimental energies [1] of $V, V^{+}, V^{2+}, V^{3+}$, and $V^{4+}$ is

$$
\begin{equation*}
E_{T}(V, 3 d 4 s)=-(65.2817 \mathrm{eV}+46.709 \mathrm{eV}+29.311 \mathrm{eV}+14.618 \mathrm{eV}+6.74619 \mathrm{eV})=-162.66589 \mathrm{eV} \tag{23.72}
\end{equation*}
$$

By considering that the central field decreases by an integer for each successive electron of the shell, the radius $r_{3 d 4 s}$ of the $V 3 d 4 s$ shell may be calculated from the Coulombic energy using Eq. (15.13).

$$
\begin{equation*}
r_{3 d 4 s}=\sum_{n=18}^{22} \frac{(Z-n) e^{2}}{8 \pi \varepsilon_{0}(e 162.66589 \mathrm{eV})}=\frac{15 e^{2}}{8 \pi \varepsilon_{0}(e 162.66589 \mathrm{eV})}=1.25464 a_{0} \tag{23.73}
\end{equation*}
$$

where $Z=23$ for vanadium. Using Eq. (15.14), the Coulombic energy $E_{\text {Coulomb }}(V, 3 d 4 s)$ of the outer electron of the $V 3 d 4 s$ shell is:

$$
\begin{equation*}
E_{\text {Coulomb }}(V, 3 d 4 s)=\frac{-e^{2}}{8 \pi \varepsilon_{0} r_{3 d 4 s}}=\frac{-e^{2}}{8 \pi \varepsilon_{0} 1.25464 a_{0}}=-10.844393 \mathrm{eV} \tag{23.74}
\end{equation*}
$$

During hybridization, the spin-paired $4 s$ electrons are promoted to the $V 3 d 4 s$ shell as unpaired electrons. The energy for the promotion is the magnetic energy given by Eq. (15.15) at the initial radius of the $4 s$ electrons. From Eq. (10.102) with $Z=23$ and $n=23$, the radius $r_{23}$ of the $V 4 s$ shell is:

$$
\begin{equation*}
r_{23}=2.01681 a_{0} \tag{23.75}
\end{equation*}
$$

Using Eqs. (15.15) and (23.74), the unpairing energy is:

$$
\begin{equation*}
E(\text { magnetic })=\frac{2 \pi \mu_{0} e^{2} \hbar^{2}}{m_{e}^{2}\left(r_{23}\right)^{3}}=\frac{8 \pi \mu_{0} \mu_{B}^{2}}{\left(2.01681 a_{0}\right)^{3}}=0.01395 \mathrm{eV} \tag{23.76}
\end{equation*}
$$

Using Eqs. (23.73) and (23.75), the energy $E(V, 3 d 4 s)$ of the outer electron of the $V 3 d 4 s$ shell is:

$$
\begin{equation*}
E(V, 3 d 4 s)=\frac{-e^{2}}{8 \pi \varepsilon_{0} r_{3 d 4 s}}+\frac{2 \pi \mu_{0} e^{2} \hbar^{2}}{m_{e}^{2}\left(r_{23}\right)^{3}}=-10.844393 \mathrm{eV}+0.01395 \mathrm{eV}=-10.83045 \mathrm{eV} \tag{23.77}
\end{equation*}
$$

Next, consider the formation of the $V-L$-bond MO wherein each vanadium atom has a $V 3 d 4 s$ electron with an energy given by Eq. (23.76). The total energy of the state of each vanadium atom is given by the sum over the five electrons. The sum $E_{T}\left(V_{V-L} 3 d 4 s\right)$ of energies of $V 3 d 4 s$ (Eq. (23.76)), $V^{+}, V^{2+}, V^{3+}$, and $V^{4+}$ is:

$$
\begin{align*}
E_{T}\left(V_{V-L} 3 d 4 s\right) & =-\binom{65.2817 \mathrm{eV}+46.709 \mathrm{eV}+29.311 \mathrm{eV}}{+14.618 \mathrm{eV}+E(V, 3 \mathrm{~d} 4 \mathrm{~s})}=-\binom{65.2817 \mathrm{eV}+46.709 \mathrm{eV}+29.311 \mathrm{eV}}{+14.618 \mathrm{eV}+10.83045}  \tag{23.78}\\
& =-166.75015 \mathrm{eV}
\end{align*}
$$

where $E(V, 3 d 4 s)$ is the sum of the energy of $V,-6.74619 \mathrm{eV}$, and the hybridization energy.
The vanadium HO donates an electron to each MO. Using Eq. (23.30), the radius $r_{3 d 4 s}$ of the $V 3 d 4 s$ shell calculated from the Coulombic energy is:

$$
\begin{equation*}
r_{V-L 3 d 4 s}=\left(\sum_{n=18}^{22}(Z-n)-1\right) \frac{e^{2}}{8 \pi \varepsilon_{0}(e 166.75015 \mathrm{eV})}=\frac{14 e^{2}}{8 \pi \varepsilon_{0}(e 166.75015 \mathrm{eV})}=1.14232 a_{0} \tag{23.79}
\end{equation*}
$$

Using Eqs. (15.19) and (23.78), the Coulombic energy $E_{\text {Coulomb }}\left(V_{V-L}, 3 d 4 s\right)$ of the outer electron of the $V 3 d 4 s$ shell is

$$
\begin{equation*}
E_{\text {Coulomb }}\left(V_{V-L}, 3 d 4 s\right)=\frac{-e^{2}}{8 \pi \varepsilon_{0} r_{V-L 3 d 4 s}}=\frac{-e^{2}}{8 \pi \varepsilon_{0} 1.14232 a_{0}}=-11.91072 \mathrm{eV} \tag{23.80}
\end{equation*}
$$

The only magnetic energy term is that for the unpairing of the $4 s$ electrons given by Eq. (23.75). Using Eqs. (23.32), (23.73), and (23.79), the energy $E\left(V_{V-L}, 3 d 4 s\right)$ of the outer electron of the $V 3 d 4 s$ shell is:

$$
\begin{equation*}
E\left(V_{V-L}, 3 d 4 s\right)=\frac{-e^{2}}{8 \pi \varepsilon_{0} r_{V-L 3 d 4 s}}+\frac{2 \pi \mu_{0} e^{2} \hbar^{2}}{m_{e}^{2}\left(r_{23}\right)^{3}}=-11.91072 \mathrm{eV}+0.01446 \mathrm{eV}=-11.89678 \mathrm{eV} \tag{23.81}
\end{equation*}
$$

Thus, $E_{T}(V-L, 3 d 4 s)$, the energy change of each $V 3 d 4 s$ shell with the formation of the $V-L$-bond MO is given by the difference between Eq. (23.80) and Eq. (23.76):

$$
\begin{equation*}
E_{T}(V-L, 3 d 4 s)=E\left(V_{V-L}, 3 d 4 s\right)-E(V, 3 d 4 s)=-11.89678 \mathrm{eV}-(-10.83045 \mathrm{eV})=-1.06633 \mathrm{eV} \tag{23.82}
\end{equation*}
$$

The semimajor axis $a$ solution given by Eq. (23.41) of the force balance equation, Eq. (23.39), for the $\sigma$-MO of the $V-L$-bond MO of $V L_{n}$ is given in Table 23.19 with the force-equation parameters $Z=23, n_{e}$, and $L$ corresponding to the orbital and spin angular momentum terms of the $3 d 4 s$ HO shell. The semimajor axis $a$ of carbonyl and organometallic compounds are solved using Eq. (15.51).

For the $V-L$ functional groups, hybridization of the $4 s$ and $3 d$ AOs of $V$ to form a single $3 d 4 s$ shell forms an energy
minimum, and the sharing of electrons between the $V 3 d 4 s \mathrm{HO}$ and $L$ AO to form a MO permits each participating orbital to decrease in radius and energy. The $F \mathrm{AO}$ has an energy of $E(F)=-17.42282 \mathrm{eV}$, the Cl AO has an energy of $E(C l)=-12.96764 \mathrm{eV}$, the $C_{\text {aryl }} 2 s p^{3} \mathrm{HO}$ has an energy of $E\left(C_{\text {aryl }}, 2 s p^{3}\right)=-15.76868 \mathrm{eV}$ (Eq. (14.246)), the $C 2 s p^{3} \mathrm{HO}$ has an energy of $E\left(C, 2 s p^{3}\right)=-14.63489 \mathrm{eV}$ (Eq. (15.25)), the $N$ AO has an energy of $E(N)=-14.53414 \mathrm{eV}$, the $O$ AO has an energy of $E(O)=-13.61805 \mathrm{eV}$, and the $V 3 d 4 \mathrm{~s}$ HO has an energy of $E_{\text {Coulomb }}(V, 3 d 4 s)=-10.84439 \mathrm{eV}$ (Eq. (23.75)) and $E(V, 3 d 4 s)=-10.83045 \mathrm{eV}$ (Eq. (23.76)). To meet the equipotential condition of the union of the $V-L H_{2}$-type-ellipsoidalMO with these orbitals, the hybridization factor(s), at least one of $c_{2}$ and $C_{2}$ of Eq. (15.61) for the $V-L$-bond MO given by Eq. (15.77) is:

$$
\begin{align*}
& C_{2}(F A O \text { to } V 3 d 4 s H O)=\frac{E(V, 3 d 4 s)}{E(F A O)}=\frac{-10.83045 \mathrm{eV}}{-17.42282 \mathrm{eV}}=0.62162  \tag{23.83}\\
& C_{2}(C l A O \text { to } V 3 d 4 s H O)=\frac{E(V, 3 d 4 s)}{E(C l A O)}=\frac{-10.83045 \mathrm{eV}}{-12.96764 \mathrm{eV}}=0.83519  \tag{23.84}\\
& C_{2}\left(C 2 s p^{3} \mathrm{HO} \text { to } \mathrm{V} 3 d 4 \mathrm{sHO}\right)=\frac{E_{\text {Coulomb }}(V, 3 d 4 s)}{E\left(C, 2 s p^{3}\right)} c_{2}\left(C 2 s p^{3} \mathrm{HO}\right)=\frac{-10.84439 \mathrm{eV}}{-14.63489 \mathrm{eV}}(0.91771)=0.68002  \tag{23.85}\\
& c_{2}\left(C_{\text {aryl }} 2 s p^{3} \mathrm{HO} \text { to } \mathrm{V} 3 d 4 \mathrm{sHO}\right)=C_{2}\left(C_{\text {aryl }} 2 s p^{3} \mathrm{HO} \text { to } \mathrm{V} 3 \mathrm{~d} 4 \mathrm{sHO}\right)=\frac{E_{\text {Coulomb }}(\mathrm{V}, 3 \mathrm{~d} 4 \mathrm{~s})}{E\left(C_{\text {aryl }}, 2 s p^{3}\right)}=\frac{-10.84439 \mathrm{eV}}{-15.76868 \mathrm{eV}}=0.68772  \tag{23.86}\\
& c_{2}(\mathrm{NAO} \text { to } \mathrm{V} 3 d 4 \mathrm{sHO})=C_{2}(\mathrm{NAO} \text { to } \mathrm{V} 3 \mathrm{~d} 4 \mathrm{sHO})=\frac{E(V, 3 d 4 s)}{E(N A O)}=\frac{-10.83045 \mathrm{eV}}{-14.53414 \mathrm{eV}}=0.74517  \tag{23.87}\\
& c_{2}(\mathrm{O} \text { to } \mathrm{V} 3 d 4 \mathrm{sHO})=\frac{E(V, 3 d 4 s)}{E(O)}=\frac{-10.83045 \mathrm{eV}}{-13.61805 \mathrm{eV}}=0.79530 \tag{23.88}
\end{align*}
$$

where Eqs. (15.76), (15.79), and (13.430) were used in Eq. (23.84). Since the energy of the MO is matched to that of the $V 3 d 4 s$ HO of coordinate compounds, $E(A O / H O)$ in Eq. (15.61) is $E(V, 3 d 4 s)$ given by Eq. (23.76) and twice this value for double bonds. For carbonyls and organometallics, the energy of the MO is matched to that of the Coulomb energy of the $V 3 d 4 s \mathrm{HO}$ such that $E(A O / H O)$ in Eq. $(15.61)$ is $E_{\text {Coulomb }}(V, 3 d 4 s)$ given by Eq. (23.73). $E_{T}\left(\right.$ atom-atom, $\left.m s p^{3} . A O\right)$ of the $V-L$-bond MO is determined by considering that the bond involves an electron transfer from the vanadium atom to the ligand atom to form partial ionic character in the bond as in the case of the zwitterions such as $\mathrm{H}_{2} \mathrm{~B}^{+}-\mathrm{F}^{-}$given in the Halido Boranes section. For coordinate compounds, $E_{T}\left(\right.$ atom-atom, $\left.m s p^{3} . A O\right)$ is -2.53109 eV , two times the energy of Eq. (23.81). For carbonyl and organometallic compounds, $E_{T}\left(\right.$ atom - atom, $\left.m s p^{3} . A O\right)$ is -1.65376 eV and -2.26759 eV , respectively. The former is based on the energy match between the $V 3 d 4 s \mathrm{HO}$ and the $C 2 s p^{3} \mathrm{HO}$ of a carbonyl group and is given by the linear combination of -0.72457 eV (Eq. (14.151)) and -0.92918 eV (Eq. (14.513)), respectively. The latter is equivalent to that of ethylene and the aryl group, -2.26759 eV , given by Eq. (14.247). The $C=O$ functional group of carbonyls is equivalent to that of formic acid given in the Carboxylic Acids section except that $\bar{E}_{\text {Kvib }}$ corresponds to that of a metal carbonyl and $E_{T}(A O / H O)$ of Eq. (15.47) is:

$$
\begin{equation*}
E_{T}(A O / H O)=-\Delta E_{H_{2} M O}(A O / H O)=-(-14.63489 \mathrm{eV}-3.58557 \mathrm{eV})=18.22046 \mathrm{eV} \tag{23.89}
\end{equation*}
$$

wherein the additional $E(A O / H O)=-14.63489 \mathrm{eV}$ (Eq. (15.25)) component corresponds to the donation of both unpaired electrons of the $C 2 s p^{3} \mathrm{HO}$ of the carbonyl group to the metal-carbonyl bond. The benzene groups of organometallic, $V\left(C_{6} H_{6}\right)_{2}$ are equivalent to those given in the Aromatic and Heterocyclic Compounds section.

The symbols of the functional groups of vanadium coordinate compounds are given in Table 23.18. The geometrical (Eqs. (15.1-15.5) and (23.41)), intercept (Eqs. (15.31-15.32) and (15.80-15.87)), and energy (Eqs. (15.61) and (23.28-23.33)) parameters of vanadium coordinate compounds are given in Tables 23.19, 23.20, and 23.21, respectively. The total energy of each vanadium coordinate compound given in Table 23.22 was calculated as the sum over the integer multiple of each $E_{D}$ (Group) of Table 23.21 corresponding to functional-group composition of the compound. The bond angle parameters of vanadium coordinate compounds determined using Eqs. (15.88-15.117) are given in Table 23.23. The $E_{T}\left(\right.$ atom - atom, $\left.m s p^{3} . A O\right)$ term for $\mathrm{VOCl}_{3}$ was calculated using Eqs. (23.30-23.33) with $s=1$ for the energies of $E(V, 3 d 4 s)$ given by Eqs. (23.78-23.81). The charge-densities of exemplary vanadium carbonyl and organometallic compounds, vanadium hexacarbonyl $\left(V(C O)_{6}\right)$ and dibenzene vanadium $\left(V\left(C_{6} H_{6}\right)_{2}\right)$, respectively, 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 are shown in Figures 23.4A and B.

Figure 23.4. (A) Vanadium Hexacarbonyl. Color scale, translucent view of the charge-density of $V(C O)_{6}$ showing the orbitals of the $V, C$, and $O$ atoms at their radii, the ellipsoidal surface of each $H_{2}$-type ellipsoidal MO that transitions to the corresponding outer shell of the atoms participating in each bond, and the nuclei (red, not to scale). (B) Dibenzene Vanadium. Color scale, translucent view of the charge-density of $V\left(C_{6} H_{6}\right)_{2}$ showing the orbitals of the $V$ and $C$ 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 atoms participating in each bond, and the hydrogen nuclei (red, not to scale).


Table 23.18. The symbols of the functional groups of vanadium coordinate compounds.

| Functional Group | Group Symbol |
| :--- | :--- |
| $V F$ group of $V F_{5}$ | $V-F$ |
| $V C l$ group of $V \mathrm{VCl}_{4}$ | $\mathrm{~V}-\mathrm{Cl}$ |
| VN group of VN | $\mathrm{V}-\mathrm{N}$ |
| VO group of VO and $\mathrm{VO}_{2}$ | $\mathrm{~V}-\mathrm{O}$ |
| VCO group of $\mathrm{V}(\mathrm{CO})_{6}$ | $\mathrm{~V}-\mathrm{CO}$ |
| $\mathrm{C}=\mathrm{O}$ | $\mathrm{C}=\mathrm{O}$ |
| $V C_{\text {aryl group of } V\left(\mathrm{C}_{6} \mathrm{H}_{6}\right)_{2}} \quad \mathrm{~V}-\mathrm{C}_{6} \mathrm{H}_{6}$ |  |
| CC (aromatic bond) | $\mathrm{C}=\mathrm{C}$ |
| CH (aromatic) | CH |

Table 23.19. The geometrical bond parameters of vanadium coordinate compounds and experimental values.

| Parameter | $\begin{aligned} & V-F \\ & \text { Group } \end{aligned}$ | $\begin{aligned} & V-C l \\ & \text { Group } \end{aligned}$ | $\begin{aligned} & V-N \\ & \text { Group } \end{aligned}$ | $\begin{aligned} & V-O \\ & \text { Group } \end{aligned}$ | $\mathrm{V}-\mathrm{CO}$ <br> Group | $\begin{aligned} & C=O \\ & \text { Group } \end{aligned}$ | $V-C_{6} H_{6}$ <br> Group | $C=C$ <br> Group | CH <br> Group |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $n_{e}$ | 2 | 3 | 1 | 2 |  |  |  |  |  |
| $L$ | $2 \sqrt{\frac{3}{4}}$ | 2 | $4+8 \sqrt{\frac{3}{4}}$ | $3 \sqrt{\frac{3}{4}}$ |  |  |  |  |  |
| $a\left(a_{0}\right)$ | 2.07531 | 2.58696 | 1.97514 | 2.11296 | 2.34957 | 1.184842 | 2.21181 | 1.47348 | 1.60061 |
| $c^{\prime}\left(a_{0}\right)$ | 1.49187 | 2.03222 | 1.62806 | 1.62997 | 1.85880 | 1.08850 | 2.07080 | 1.31468 | 1.03299 |
| Bond Length $2 c^{\prime}(A)$ | 1.57893 | 2.15081 | 1.72306 | 1.72509 | 1.96727 | 1.15202 | 2.19164 | 1.39140 | 1.09327 |
| Exp. Bond Length ( $A$ ) | $\begin{gathered} 1.71[18] \\ \left(V F_{5}\right) \end{gathered}$ | $\begin{gathered} 2.138[18] \\ \left(\mathrm{VCl}_{4}\right) \end{gathered}$ | $\begin{gathered} 1.612[24] \\ (V N) \end{gathered}$ | $\begin{gathered} 1.890[25] \\ 1.5893[18] \\ (V O) \\ \hline \end{gathered}$ | $\begin{aligned} & 2.015[18] \\ & \left(V(\mathrm{CO})_{6}\right) \end{aligned}$ | $\begin{gathered} 1.138[18] \\ \left(V(\mathrm{CO})_{6}\right) \end{gathered}$ | $\begin{gathered} 2.17[26] \\ \left(V\left(C_{6} H_{6}\right)_{2}\right) \end{gathered}$ | $\begin{aligned} & 1.399[3] \\ & \text { (benzene) } \end{aligned}$ | $1.101[3]$ (benzene) |
| $b, c\left(a_{0}\right)$ | 1.44264 | 1.60075 | 1.11830 | 1.34454 | 1.43713 | 0.46798 | 0.77710 | 0.66540 | 1.22265 |
|  | 0.71887 | 0.78556 | 0.82428 | 0.77142 | 0.79112 | 0.91869 | 0.93625 | 0.89223 | 0.64537 |

Table 23．20．The MO to HO intercept geometrical bond parameters of vanadium coordinate compounds．$E_{T}$ is $E_{T}$（atom－atom，HO．AO）．

| が急 | $\left\|\begin{array}{c} o \\ \substack{a \\ d \\ d} \end{array}\right\|$ | $\left\lvert\, \begin{gathered} \hat{n} \\ \\ 0 \end{gathered}\right.$ | $\left\|\begin{array}{c} o \\ \vdots \\ \hdashline \\ \hdashline \end{array}\right\|$ |  | 碇 | $\stackrel{\underset{\sim}{6}}{\stackrel{\rightharpoonup}{c}}$ | N |  |  |  | Cobe | Bo | $\begin{array}{\|c} \circ \\ \underset{\sim}{2} \\ \underset{\sim}{2} \end{array}$ | $\begin{array}{\|c} \text { त } \\ \text { त्वn } \end{array}$ |  | $\stackrel{n}{2}$ | 运 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| －Ed | $\left\lvert\, \begin{gathered} \stackrel{\circ}{8} \\ \underset{\sim}{\underset{~}{2}} \end{gathered}\right.$ |  | $\left\|\begin{array}{c} \stackrel{a}{e} \\ \frac{\alpha}{i} \\ \frac{1}{i} \end{array}\right\|$ | $\begin{gathered} \infty \\ \stackrel{\infty}{\circ} \\ \stackrel{\rightharpoonup}{\circ} \\ \dot{c} \end{gathered}$ |  | $\underset{\underset{e}{\circ}}{\stackrel{t}{\mathrm{o}}} \mid$ |  | $\left.\begin{array}{\|c} \stackrel{\circ}{2} \\ \stackrel{i}{2} \end{array} \right\rvert\,$ |  |  | $02 e_{0}^{2}$ | : | $\begin{array}{\|c} 0 \\ \vdots \\ \vdots \\ \vdots \\ \end{array}$ | $$ |  | in | $\xrightarrow{4}$ |
| ®。 | $\begin{gathered} \infty \\ \underset{\sim}{f} \\ \hline \end{gathered}$ | $\xrightarrow[\substack{\text { con }}]{\substack{0}}$ | ¢ | $\underset{\sim}{\underset{\sim}{c}}$ | $\underset{\sim}{c}$ | $\stackrel{m}{\substack{n \\ \underset{y}{c} \\ \hline}}$ | $\underset{\sim}{2} \underset{\sim}{f}$ | $\left\|\begin{array}{c} \underset{\sim}{c} \\ \underset{\sim}{c} \end{array}\right\|$ |  |  | $\dot{\sim}$ | $\dot{b l}$ |  | $\stackrel{\circ}{\stackrel{\circ}{\infty}} \underset{\substack{0}}{ }$ | $\begin{aligned} & \stackrel{\rightharpoonup}{*} \\ & \stackrel{y}{\infty} \end{aligned}$ | $\infty$ | 解 |
| $\sigma$ 〇 | $\begin{aligned} & \underset{\sim}{n} \\ & \stackrel{\theta}{\theta} \end{aligned}$ | $\begin{aligned} & \overline{\mathrm{a}} \\ & \mathrm{a} \end{aligned}$ | $\left\|\begin{array}{c} \overline{\mathrm{n}} \\ \stackrel{n}{2} \end{array}\right\|$ | $\stackrel{\infty}{\infty} \stackrel{n}{2}$ | $\stackrel{\infty}{2} \underset{\sim}{n}$ | $\begin{aligned} & \infty \\ & \stackrel{n}{6} \\ & \vdots \end{aligned}$ | $\stackrel{\infty}{n} \underset{\sim}{i} \underset{\sim}{\underset{\sim}{2}}$ | $\left\|\begin{array}{l} 0 \\ \vdots \\ \vdots \end{array}\right\|$ |  |  | $x_{\infty}^{\infty}$ | $\mathfrak{b}$ | $\begin{aligned} & \stackrel{8}{9} \\ & \stackrel{1}{9} \end{aligned}$ | $\begin{aligned} & \infty \\ & \stackrel{\infty}{6} \\ & \stackrel{\circ}{0} \end{aligned}$ |  |  | \％ |
| － | $\left\lvert\,\right.$ | $\stackrel{\rightharpoonup}{\dot{\circ}}$ | $\mid \underset{\infty}{\dot{\infty}}$ | $\underset{\infty}{\underset{\sim}{\circ}}$ | $\underset{\substack{A \\ A}}{\substack{\underset{A}{d} \\ \hline}}$ | $\begin{aligned} & \underset{\sim}{9} \\ & \stackrel{y}{\circ} \end{aligned}$ |  | $\left\lvert\, \begin{gathered} p \\ \dot{\alpha} \\ \hline \end{gathered}\right.$ | $\stackrel{\partial}{\partial}$ |  |  | $0$ | $\begin{aligned} & 9 \\ & 9 \\ & 0 \end{aligned}$ | $\begin{aligned} & \tilde{A} \\ & \tilde{i} \end{aligned}$ | $\begin{aligned} & \bar{\infty} \\ & \stackrel{\sim}{\hat{2}} \end{aligned}$ | $\begin{aligned} & \stackrel{i}{f} \\ & \stackrel{9}{2} \end{aligned}$ | $\xrightarrow{7}$ |
|  |  |  |  |  |  |  |  |  |  |  | 等 | － |  |  |  |  | $\xrightarrow{\frac{7}{8}}$ |
|  | $\left\lvert\, \begin{gathered} n \\ 0 \\ 0 \\ 0 \\ \hdashline \end{gathered}\right.$ | $\begin{aligned} & \frac{n}{2} \\ & \dot{\alpha} \\ & \dot{c} \\ & \underset{\sim}{n} \end{aligned}$ |  | $\begin{aligned} & \stackrel{\rightharpoonup}{\tilde{o}} \\ & \underset{\sim}{4} \end{aligned}$ |  | $\begin{gathered} \text { 㚃 } \\ \text { che } \end{gathered}$ |  |  | $\begin{gathered} \stackrel{n}{6} \\ \vdots \\ \vdots \end{gathered}$ |  |  |  | $\begin{aligned} & \stackrel{I}{0} \\ & \stackrel{\infty}{\circ} \\ & \underset{\sim}{\circ} \end{aligned}$ | $\begin{aligned} & 0 \\ & 0 \\ & \underset{\sim}{0} \\ & \underset{\sim}{2} \end{aligned}$ | $\begin{aligned} & \overline{\widetilde{N}} \\ & \underset{\sim}{0} \\ & \underset{\sim}{2} \end{aligned}$ |  |  |
| E | $\left\|\begin{array}{c} 7 \\ \underset{0}{0} \\ 0 \end{array}\right\|$ | $\left(\begin{array}{c} \infty \\ 0 \\ 0 \\ 0 \\ 0 \end{array}\right.$ | 商 |  |  |  |  |  | $\begin{gathered} \hat{4} \\ \substack{0 \\ \hline} \\ \hline \end{gathered}$ |  |  | $\begin{gathered} \overline{2} \\ \\ \\ \hline 0 \end{gathered}$ | $\begin{aligned} & \text { bo } \\ & \stackrel{0}{0} \\ & \stackrel{0}{0} \end{aligned}$ | $\begin{aligned} & \text { A} \\ & \\ & \stackrel{0}{\circ} \end{aligned}$ | $\begin{aligned} & \text { त्仓 } \\ & \stackrel{y}{\circ} \end{aligned}$ | $\begin{gathered} \stackrel{6}{2} \\ \substack{0 \\ \hline} \end{gathered}$ | N |
| 通 | $\left\lvert\, \begin{gathered} \text { d } \\ \substack{a \\ G} \end{gathered}\right.$ |  |  |  |  |  | $\stackrel{\rightharpoonup}{\circ} \mathrm{Cos}$ | $$ |  |  |  | $\bar{A}$ |  | $\frac{\mathrm{E}}{\mathrm{E}}$ | $\frac{\bar{E}}{\stackrel{\rightharpoonup}{\partial}}$ |  | ： |
|  |  |  |  |  |  |  |  |  |  |  | （ |  |  | 硞 | （1） |  |  |
| स家蓆 | － | － | － |  |  |  | － |  | － |  | － | － |  | － | － | － | － |
|  |  | － |  |  |  |  | 0 － |  | － |  | 000 |  |  | － | － | － | － |
| 世家 |  | － | $\left\lvert\, \begin{gathered} 0 \\ \stackrel{\rightharpoonup}{6} \\ \underset{\vdots}{2} \end{gathered}\right.$ |  |  |  |  |  | － |  |  | － | $\begin{aligned} & \infty \\ & \stackrel{\infty}{0} \\ & \stackrel{\omega}{0} \\ & \stackrel{1}{c} \end{aligned}$ |  |  |  | － |
| 心家商 | $\left\|\begin{array}{c} \hat{6} \\ \stackrel{\rightharpoonup}{6} \\ \vdots \end{array}\right\|$ | － | － |  | －－ |  | －－ |  | － |  | 0.0 | － |  | $\begin{aligned} & \text { 呂 } \\ & \stackrel{\rightharpoonup}{6} \\ & \stackrel{y}{2} \end{aligned}$ | $\begin{aligned} & \text { O} \\ & \text { Oit } \\ & 0 \end{aligned}$ |  | － |
|  | $\left\|\begin{array}{c} \hat{6} \\ \stackrel{\rightharpoonup}{6} \\ \hdashline \end{array}\right\|$ | － |  |  | － 0 |  | － 0 |  |  |  |  |  |  | $\begin{gathered} \stackrel{0}{6} \\ \stackrel{0}{00} \\ \stackrel{1}{2} \end{gathered}$ | $\begin{aligned} & \stackrel{0}{0} \\ & \stackrel{0}{0} \\ & \stackrel{0}{0} \end{aligned}$ |  |  |
| \& | $\left\|\begin{array}{c} \hat{0} \\ 0 \\ \hdashline \\ \hdashline \end{array}\right\|$ | $\begin{gathered} 0 \\ 0 \\ 0 \\ \hdashline \end{gathered}$ | $\left\lvert\, \begin{gathered} \underset{\substack{\circ \\ \hdashline \\ \vdots}}{ } \mid \end{gathered}\right.$ |  |  | 骨 <br>  |  |  |  |  | nol |  |  |  | $\begin{gathered} \text { no } \\ \substack{0 \\ 0 \\ 0} \end{gathered}$ | $\stackrel{\stackrel{2}{n}}{\substack{7 \\ 7}}$ | － |
| 宕 | $\rightarrow$ | 12 | － | J | $0 \rightarrow$ |  | ＜$\rightarrow$ |  | $0 \rightarrow$ | － | － | $\checkmark$ | － | $\cup$ | $0^{3}$ | － | － |
| 号 | $\begin{gathered} \substack{n \\ 5 \\ 4 \\ 1 \\ \vdots \\ \hline} \end{gathered}$ |  | $\begin{array}{\|c} 0 \\ 0 \\ 0 \\ 0 \\ 1 \\ 0 \end{array}$ | $\begin{array}{l\|l\|l} 0 & 0 \\ 0 & = \\ 1 & 1 \\ 1 & 1 \\ -1 \end{array}$ |  |  |  | $\begin{aligned} & 8 \\ & 0 \\ & 0 \\ & 1 \\ & \Delta \end{aligned}$ | $\begin{array}{ll} 8 & 0 \\ 8 & 8 \\ 0 & 0 \\ 1 & 1 \\ -1 \end{array}$ | $\begin{aligned} & 8 \\ & 0 \\ & 0 \\ & 0 \\ & 1 \\ & 1 \end{aligned}$ |  | $\begin{gathered} 20 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 1 \end{gathered}$ | 2 0 3 3 0 1 1 |  |  | $-1$ | 起 |

Table 23.21. The energy parameters ( eV ) of functional groups of vanadium coordinate compounds.

| Parameters | $\begin{aligned} & V-F \\ & \text { Group } \end{aligned}$ | $\begin{aligned} & V-\mathrm{Cl} \\ & \text { Group } \end{aligned}$ | $\begin{aligned} & V-N \\ & \text { Group } \end{aligned}$ | $\begin{aligned} & V-O \\ & \text { Group } \end{aligned}$ | $\begin{gathered} V-C O \\ \text { Group } \end{gathered}$ | $\begin{aligned} & C=O \\ & \text { Group } \end{aligned}$ | $\begin{gathered} V-\mathrm{C}_{6} \mathrm{H}_{6} \\ \text { Group } \end{gathered}$ | $\begin{aligned} & C=C \\ & C=C \\ & \text { Group } \end{aligned}$ | CH Group |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $f_{1}$ | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 0.75 | 1 |
| $n_{1}$ | 1 | 1 | 1 | 2 | 1 | 2 | 1 | 2 | 1 |
| $n_{2}$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $n_{3}$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $C_{1}$ | 0.75 | 0.375 | 0.5 | 0.5 | 0.5 | 0.5 | 0.375 | 0.5 | 0.75 |
| $\mathrm{C}_{2}$ | 0.62162 | 0.83519 | 0.74517 | 0.79530 | 0.68002 | 1 | 0.68772 | 0.85252 | 1 |
| $c_{1}$ | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $c_{2}$ | 1 | 0.83519 | 0.74517 | 0.79530 | 1 | 0.85395 | 0.68772 | 0.85252 | 0.91771 |
| $c_{3}$ | 0 | 0 | 0 | 0 | 0 | 2 | 0 | 0 | 1 |
| $c_{4}$ | 1 | 1 | 1 | 2 | 2 | 4 | 2 | 3 | 1 |
| $c_{5}$ | 1 | 1 | 1 | 2 | 0 | 0 | 0 | 0 | 1 |
| $C_{10}$ | 0.75 | 0.375 | 0.5 | 0.5 | 0.5 | 0.5 | 0.375 | 0.5 | 0.75 |
| $C_{20}$ | 0.62162 | 0.83519 | 0.74517 | 0.79530 | 0.68002 | 1 | 0.68772 | 0.85252 | 1 |
| $V_{e}(e \mathrm{~V})$ | -33.02514 | -23.70273 | -29.14480 | -54.37349 | -31.45782 | -134.96850 | -30.84785 | -101.12679 | -37.10024 |
| $V_{p}(\mathrm{eV})$ | 9.11995 | 6.69504 | 8.35707 | 16.69453 | 7.31967 | 24.99908 | 6.57031 | 20.69825 | 13.17125 |
| $T(\mathrm{eV})$ | 7.95669 | 4.58120 | 7.37791 | 12.86667 | 6.69438 | 56.95634 | 6.97344 | 34.31559 | 11.58941 |
| $V_{m}(\mathrm{eV})$ | -3.97835 | -2.29060 | -3.68896 | -6.43333 | -3.34719 | -28.47817 | -3.48672 | -17.15779 | -5.79470 |
| $E$ (Ао/но) $(\mathrm{eV})$ | -10.83045 | -10.83045 | -10.83045 | -21.66089 | -10.84439 | 0 | -10.84439 | 0 | -14.63489 |
| $\Delta E_{\mathrm{H}_{2} \mathrm{MO}}(\mathrm{AO} / \mathrm{HO})(\mathrm{eV})$ | 0 | 0 | 0 | 0 | 0 | -18.22046 | 0 | 0 | -1.13379 |
| $E_{T}($ AO/ $/ \mathrm{HO})(\mathrm{eV})$ | -10.83045 | -10.83045 | -10.83045 | -21.66089 | -10.84439 | 18.22046 | -10.84439 | 0 | -13.50110 |
| $E_{T}\left(\mathrm{H}_{2} \mathrm{MO}\right)(\mathrm{eV})$ | -30.75729 | -25.54754 | -27.92923 | -52.90652 | -31.63535 | -63.27080 | -31.63521 | -63.27075 | -31.63539 |
| $E_{T}\left(\right.$ atom - atom, $\left.\mathrm{msp}^{3} . \mathrm{AO}\right)(\mathrm{eV})$ | -2.13266 | -2.13266 | -2.13266 | -2.13266 | -1.65376 | -3.58557 | -2.26759 | -2.26759 | -0.56690 |
| $E_{T}(\mathrm{mo})(\mathrm{eV})$ | -32.88995 | -27.68020 | -30.06189 | -55.03919 | -33.28913 | -66.85630 | -33.90295 | -65.53833 | -32.20226 |
| $\omega\left(10^{15} \mathrm{rad} / \mathrm{s}\right)$ | 16.2908 | 5.56044 | 21.3383 | 16.7215 | 13.9922 | 22.6662 | 30.6471 | 49.7272 | 26.4826 |
| $E_{K}(\mathrm{eV})$ | 10.72287 | 3.65998 | 14.04526 | 11.00636 | 9.20994 | 14.91930 | 20.17243 | 32.73133 | 17.43132 |
| $\bar{E}_{D}(\mathrm{eV})$ | -0.21307 | -0.10476 | -0.22289 | -0.18062 | -0.19986 | -0.25544 | -0.30124 | -0.35806 | -0.26130 |
| $\bar{E}_{\text {Kvib }}(\mathrm{eV})$ | $\begin{gathered} 0.07538 \\ {[27]} \end{gathered}$ | $\begin{gathered} 0.05059 \\ {[28]} \end{gathered}$ | $\begin{gathered} 0.12708 \\ {[24]} \end{gathered}$ | $\begin{gathered} 0.12539 \\ {[14]} \end{gathered}$ | $\begin{gathered} 0.04749 \\ {[29]} \end{gathered}$ | $\begin{gathered} 0.24962 \\ {[29]} \end{gathered}$ | $\begin{gathered} 0.04749 \\ {[29]} \end{gathered}$ | $\begin{gathered} 0.19649 \\ {[30]} \end{gathered}$ | $\begin{gathered} 0.35532 \\ \text { Eq. }(13.458) \end{gathered}$ |
| $\bar{E}_{\text {osc }}(\mathrm{eV})$ | -0.17538 | -0.07947 | -0.15934 | -0.11793 | -0.17612 | -0.13063 | -0.27750 | -0.25982 | -0.08364 |
| $E_{\text {mag }}(\mathrm{eV})$ | 0.05793 | 0.05793 | 0.05793 | 0.05793 | 0.05793 | 0.11441 | 0.05793 | 0.14803 | 0.14803 |
| $E_{T}($ Group $)(\mathrm{eV})$ | -33.06533 | -27.75967 | -30.22123 | -55.27504 | -33.46525 | -67.11757 | -34.18046 | -49.54347 | -32.28590 |
| $E_{\text {initial }}\left(c_{s}\right.$ АО/но) $(\mathrm{eV})$ | -10.83045 | -10.83045 | -10.83045 | -10.83045 | -14.63489 | -14.63489 | -15.76868 | -14.63489 | -14.63489 |
| $E_{\text {initial }}\left(c_{s}\right.$ AO/HO) $(\mathrm{eV})$ | -17.42282 | -12.96764 | -14.53414 | -13.61806 | 0 | 0 | 0 | 0 | -13.59844 |
| $E_{D}($ Group $)(\mathrm{eV})$ | 4.81206 | 3.96159 | 4.85665 | 6.37803 | 4.19547 | 8.34918 | 2.64309 | 5.63881 | 3.90454 |
| Exp. $E_{D}($ Group $)(e V)$ |  |  |  | $\begin{gathered} 6.4(\mathrm{VO} \\ [25]) \end{gathered}$ |  |  |  |  |  |

Table 23.22. The total bond energies of gaseous-state vanadium coordinate compounds calculated using the functional group composition and the energies of Table

| Formula | Name | $\begin{aligned} & V-F \\ & \text { Group } \end{aligned}$ | $\begin{aligned} & V-C l \\ & \text { Group } \end{aligned}$ | $\begin{aligned} & V-N \\ & \text { Group } \end{aligned}$ | $\begin{aligned} & V-O \\ & \text { Group } \end{aligned}$ | $\begin{gathered} V-C O \\ \text { Group } \end{gathered}$ | $\begin{aligned} & C=O \\ & \text { Group } \end{aligned}$ | $\begin{gathered} V-C_{6} H_{6} \\ \text { Group } \end{gathered}$ | $\begin{aligned} & C^{3 e}=C \\ & \text { Group } \end{aligned}$ | $\begin{gathered} \mathrm{CH} \\ \text { Group } \end{gathered}$ | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy $(\mathrm{eV})$ | Relative Error |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{VF}_{5}$ | Vanadium pentafluoride | 5 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 24.06031 | 24.24139 [15] | 0.00747 |
| $\mathrm{VCl}_{4}$ | Vanadium tetrachloride | 0 | 4 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 15.84635 | 15.80570 [15] | -0.00257 |
| VN | Vanadium nitride | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 4.85655 | 4.81931 [24] | -0.00775 |
| Vo | Vanadium oxide | 0 | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 6.37803 | 6.60264 [15] | 0.03402 |
| $\mathrm{VO}_{2}$ | Vanadium dioxide | 0 | 0 | 0 | 2 | 0 | 0 | 0 | 0 | 0 | 12.75606 | 12.89729 [34] | 0.01095 |
| $\mathrm{VOCl}_{3}$ | Vanadium trichloride oxide | 0 | 3 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 18.26279 | 18.87469 [15] | 0.03242 |
| $\mathrm{V}(\mathrm{CO})_{6}$ | Vanadium hexacarbonyl | 0 | 0 | 0 | 0 | 6 | 6 | 0 | 0 | 0 | 75.26791 | 75.63369 [32] | 0.00484 |
| $\left.\mathrm{V}\left(\mathrm{C}_{6} \mathrm{H}_{6}\right)\right)_{2}$ | Dibenzene vanadium | 0 | 0 | 0 | 0 | 0 | 0 | 2 | 12 | 12 | 119.80633 | $121.20193{ }^{\text {a }}$ [33] | 0.01151 |

Table 23.23. The bond angle parameters of vanadium coordinate compounds and experimental values. $E_{T}$ is $E_{T}$ (atom-atom,HO.AO).

| Atoms of Angle | $\begin{gathered} 2 c^{\prime} \\ \text { Bond } 1 \end{gathered}$ $\left(a_{0}\right)$ | $\begin{gathered} 2 c^{\prime} \\ \text { Bond } 2 \end{gathered}$ $\left(a_{0}\right)$ | $2 c^{\prime}$ Terminal Atoms $\left(a_{0}\right)$ | $\begin{aligned} & E_{\text {Coulombic }} \text { ic } \\ & \text { Atom } \end{aligned}$ | Atom 1 <br> Hybridization Designation <br> (Table 15.3A) | $\begin{aligned} & E_{\text {Conlombic }} \text { a } \\ & \text { Atom } 2 \end{aligned}$ | Atom 2 <br> Hybridization Designation <br> (Table 15.3A) | $\begin{gathered} c_{2} \\ \text { Atom } 1 \end{gathered}$ | $\begin{gathered} c_{2} \\ \text { Atom } 2 \end{gathered}$ | $C_{1}$ | $C_{2}$ | $c_{1}$ | $c_{2}^{\prime}$ | $\begin{gathered} E_{T} \\ (\mathrm{eV}) \end{gathered}$ | $\begin{aligned} & \theta_{v} \\ & \left({ }^{\circ}\right) \end{aligned}$ | $\begin{gathered} \theta_{1} \\ \left({ }^{\circ}\right) \end{gathered}$ | $\begin{gathered} \theta_{2} \\ \left({ }^{\circ}\right) \end{gathered}$ | Cal. $\theta$ <br> $\left(^{\circ}\right)$ | $\begin{gathered} \text { Exp. } \theta \\ \left({ }^{\circ}\right) \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\angle O V C l$ | 2.88926 | 4.06444 | 5.9161 | $\begin{gathered} -13.61806 \\ O \end{gathered}$ | O | $\begin{gathered} -12.96764 \\ C l \end{gathered}$ | Cl | $\begin{gathered} 0.79530 \\ (\text { Eq. } \\ (23.87)) \end{gathered}$ | $\begin{gathered} 0.83519 \\ (\text { Eq. } \\ (23.83)) \end{gathered}$ | 0.75 | 0.81525 | 1 | 0.81525 | -0.46070 |  |  |  | 115.56 | 111.3 [15] ( $\mathrm{KOCl}_{3}$ ) |
| $\angle \mathrm{ClVCl}$ | 4.06444 | 4.06444 | 6.7231 | $\begin{gathered} -12.96764 \\ C l \end{gathered}$ | Cl | $\begin{gathered} -12.96764 \\ \mathrm{Cl} \\ \hline \end{gathered}$ | Cl | $\begin{gathered} 0.83519 \\ (\mathrm{Eq.} \\ (23.83)) \end{gathered}$ | $\begin{gathered} 0.83519 \\ (\mathrm{Eq} . \\ (23.83)) \end{gathered}$ | 1 | 0.5 | 1 | 0.83519 |  |  |  |  | 111.60 | 111.3 [18] $\left(\mathrm{VOCl}_{3}\right)$ |
| $\begin{gathered} \angle C C C \\ \text { (aromatic) } \end{gathered}$ | 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 | $\begin{gathered} 120[34-36] \\ \text { (benzene) } \end{gathered}$ |
| $\begin{gathered} \angle C C H \\ \text { (aromatic) } \end{gathered}$ |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  | 120.19 |  | 119.91 | $\begin{gathered} 120[34-36] \\ \text { (benzene) } \end{gathered}$ |

## CHROMIUM FUNCTIONAL GROUPS AND MOLECULES

The electron configuration of chromium is $[A r] 4 s^{1} 3 d^{5}$ having the corresponding term ${ }^{7} S_{3}$. The total energy of the state is given by the sum over the six electrons. The sum $E_{T}(\mathrm{Cr}, 3 d 4 s)$ of experimental energies [1] of $\mathrm{Cr}, \mathrm{Cr}^{+}, \mathrm{Cr}^{2+}, \mathrm{Cr}^{3+}, \mathrm{Cr}^{4+}$, and $\mathrm{Cr}^{5+}$ is

$$
\begin{equation*}
E_{T}(C r, 3 d 4 s)=-\binom{90.6349 \mathrm{eV}+69.46 \mathrm{eV}+49.16 \mathrm{eV}}{+30.96 \mathrm{eV}+16.4857 \mathrm{eV}+6.76651 \mathrm{eV}}=-263.46711 \mathrm{eV} \tag{23.90}
\end{equation*}
$$

By considering that the central field decreases by an integer for each successive electron of the shell, the radius $r_{3 d 4 s}$ of the $C r 3 d 4 s$ shell may be calculated from the Coulombic energy using Eq. (15.13).

$$
\begin{equation*}
r_{3 d 4 s}=\sum_{n=18}^{23} \frac{(Z-n) e^{2}}{8 \pi \varepsilon_{0}(e 263.46711 \mathrm{eV})}=\frac{21 e^{2}}{8 \pi \varepsilon_{0}(e 263.46711 \mathrm{eV})}=1.08447 a_{0} \tag{23.91}
\end{equation*}
$$

where $Z=24$ for chromium. Using Eq. (15.14), the Coulombic energy $E_{\text {Coulomb }}(C r, 3 d 4 s)$ of the outer electron of the $C r 3 d 4 s$ shell is:

$$
\begin{equation*}
E_{\text {Coulomb }}(C r, 3 d 4 s)=\frac{-e^{2}}{8 \pi \varepsilon_{0} r_{3 d 4 s}}=\frac{-e^{2}}{8 \pi \varepsilon_{0} 1.08447 a_{0}}=-12.546053 \mathrm{eV} \tag{23.92}
\end{equation*}
$$

Next, consider the formation of the $C r-L$-bond MO wherein each chromium atom has a $C r 3 d 4 s$ electron with an energy given by Eq. (23.91). The total energy of the state of each chromium atom is given by the sum over the six electrons. The sum $E_{T}\left(\mathrm{Cr}_{C r-L} 3 d 4 s\right)$ of energies of $\mathrm{Cr} 3 d 4 s$ (Eq. (23.91)), $\mathrm{Cr}^{+}, \mathrm{Cr}^{2+}, \mathrm{Cr}^{3+}, \mathrm{Cr}^{4+}$, and $\mathrm{Cr}^{5+}$ is:

$$
\begin{align*}
E_{T}\left(C r_{C r-L} 3 d 4 s\right) & =-\binom{90.6349 \mathrm{eV}+69.46 \mathrm{eV}+49.16 \mathrm{eV}}{+30.96 \mathrm{eV}+16.4857 \mathrm{eV}+E_{\text {Coulomb }}(C r, 3 \mathrm{~d} 4 \mathrm{~s})}  \tag{23.93}\\
& =-\binom{90.6349 \mathrm{eV}+69.46 \mathrm{eV}+49.16 \mathrm{eV}}{+30.96 \mathrm{eV}+16.4857 \mathrm{eV}+12.546053 \mathrm{eV}}=-269.24665 \mathrm{eV}
\end{align*}
$$

where $E(C r, 3 d 4 s)$ is the sum of the energy of $\mathrm{Cr},-6.76651 \mathrm{eV}$, and the hybridization energy.
The chromium HO donates an electron to each MO. Using Eq. (23.30), the radius $r_{3 d 4 s}$ of the $C r 3 d 4 s$ shell calculated from the Coulombic energy is:

$$
\begin{equation*}
r_{C r-L 3 d 4 s}=\left(\sum_{n=18}^{23}(Z-n)-1\right) \frac{e^{2}}{8 \pi \varepsilon_{0}(e 269.24665 \mathrm{eV})}=\frac{20 e^{2}}{8 \pi \varepsilon_{0}(e 269.24665 \mathrm{eV})}=1.01066 a_{0} \tag{23.94}
\end{equation*}
$$

Using Eqs. (15.19) and (23.93), the Coulombic energy $E_{\text {Coulomb }}\left(C r_{C r-L}, 3 d 4 s\right)$ of the outer electron of the $C r 3 d 4 s$ shell is

$$
\begin{equation*}
E_{\text {Coulomb }}\left(C r_{C r-L}, 3 d 4 s\right)=\frac{-e^{2}}{8 \pi \varepsilon_{0} r_{C r-L 3 d 4 s}}=\frac{-e^{2}}{8 \pi \varepsilon_{0} 1.01066 a_{0}}=-13.46233 \mathrm{eV} \tag{23.95}
\end{equation*}
$$

Thus, $E_{T}(C r-L, 3 d 4 s)$, the energy change of each $C r 3 d 4 s$ shell with the formation of the $C r-L$-bond MO is given by the difference between Eq. (23.94) and Eq. (23.91):

$$
\begin{equation*}
E_{T}(C r-L, 3 d 4 s)=E\left(C r_{C r-L}, 3 d 4 s\right)-E(C r, 3 d 4 s)=-13.46233 \mathrm{eV}-(-12.546053 \mathrm{eV})=-0.91628 \mathrm{eV} \tag{23.96}
\end{equation*}
$$

The semimajor axis $a$ solution given by Eq. (23.41) of the force balance equation, Eq. (23.39), for the $\sigma$-MO of the $C r-L$-bond MO of $C r L_{n}$ is given in Table 23.25 with the force-equation parameters $Z=24, n_{e}$, and $L$ corresponding to the orbital and spin angular momentum terms of the $3 d 4 s \mathrm{HO}$ shell. The semimajor axis $a$ of carbonyl and organometallic compounds are solved using Eq. (15.51).

For the $C r-L$ functional groups, hybridization of the $4 s$ and $3 d$ AOs of $C r$ to form a single $3 d 4 s$ shell forms an energy minimum, and the sharing of electrons between the $C r 3 d 4 s$ HO and $L$ AO to form a MO permits each participating orbital to decrease in radius and energy. The $F \mathrm{AO}$ has an energy of $E(F)=-17.42282 \mathrm{eV}$, the Cl AO has an energy of $E(C l)=-12.96764 \mathrm{eV}$, the $C_{\text {aryl }} 2 s p^{3} \mathrm{HO}$ has an energy of $E\left(C_{\text {aryl }}, 2 s p^{3}\right)=-15.76868 \mathrm{eV}$ (Eq. (14.246)), the $C 2 s p^{3} \mathrm{HO}$ has an energy of $E\left(C, 2 s p^{3}\right)=-14.63489 \mathrm{eV}$ (Eq. (15.25)), the $O$ AO has an energy of $E(O)=-13.61805 \mathrm{eV}$, and the Cr 3 d 4 s HO has an energy of $E_{\text {Coulomb }}(C r, 3 d 4 s)=-12.54605 \mathrm{eV}$ (Eq. (23.91)). To meet the equipotential condition of the union of the $\mathrm{Cr}-\mathrm{L} \quad \mathrm{H}_{2}$-type-ellipsoidal-MO with these orbitals, the hybridization factor(s), at least one of $c_{2}$ and $C_{2}$ of Eq. (15.61) for the $\mathrm{Cr}-L$-bond MO given by Eq. (15.77) is:

$$
\begin{align*}
& c_{2}(\text { FAO to Cr } 3 d 4 s \mathrm{HO})=C_{2}(\text { FAO to } \mathrm{Cr} 3 d 4 s H O)=\frac{E_{\text {Coulomb }}(C r, 3 d 4 s)}{E(F A O)}=\frac{-12.54605 \mathrm{eV}}{-17.42282 \mathrm{eV}}=0.72009  \tag{23.97}\\
& c_{2}(\text { ClAO to Cr } 3 d 4 \mathrm{sHO})=C_{2}(\text { ClAO to } \mathrm{Cr} 3 d 4 \mathrm{sHO})=\frac{E_{\text {Coulomb }}(\mathrm{Cr}, 3 d 4 \mathrm{~s})}{E(C l A O)}=\frac{-12.54605 \mathrm{eV}}{-12.96764 \mathrm{eV}}=0.96749 \tag{23.98}
\end{align*}
$$

$$
\begin{align*}
& c_{2}\left(\mathrm{C} 2 \mathrm{sp}{ }^{3} \mathrm{HO} \text { to } \mathrm{Cr} 3 \mathrm{~d} 4 \mathrm{sHO}\right)=\mathrm{C}_{2}\left(\mathrm{C} 2 \mathrm{sp}{ }^{3} \mathrm{HO} \text { to } \mathrm{Cr} 3 d 4 \mathrm{sHO}\right)=\frac{E_{\text {Coulomb }}(\mathrm{Cr}, 3 \mathrm{~d} 4 \mathrm{~s})}{E\left(C, 2 s p^{3}\right)}=\frac{-12.54605 \mathrm{eV}}{-14.63489 \mathrm{eV}}=0.85727  \tag{23.99}\\
& C_{2}\left(C_{\text {aryl }} 2 s p^{3} \mathrm{HO} \text { to } \mathrm{Cr} 3 d 4 \mathrm{sHO}\right)=\frac{E_{\text {Coulomb }}(C r, 3 d 4 s)}{E\left(C_{\text {aryl }}, 2 s p^{3}\right)}=\frac{-12.54605 \mathrm{eV}}{-15.76868 \mathrm{eV}}=0.79563  \tag{23.100}\\
& c_{2}(O \text { to } \mathrm{Cr} 3 d 4 s \mathrm{HO})=C_{2}(\text { O to } \mathrm{Cr} 3 d 4 s \mathrm{HO})=\frac{E_{\text {Coulomb }}(\mathrm{Cr}, 3 d 4 \mathrm{~s})}{E(O)}=\frac{-12.54605 \mathrm{eV}}{-13.61805 \mathrm{eV}}=0.92128 \tag{23.101}
\end{align*}
$$

Since the energy of the MO is matched to that of the $C r_{\text {Coulomb }} 3 d 4 s \mathrm{HO}, E(A O / H O)$ in Eq. (15.61) is $E_{\text {Coulomb }}(C r, 3 d 4 s)$ given by Eq. (23.91) and twice this value for double bonds. $E_{T}\left(\right.$ atom-atom, $\left.m s p^{3} . A O\right)$ of the $C r-L$-bond MO is determined by considering that the bond involves an electron transfer from the chromium atom to the ligand atom to form partial ionic character in the bond as in the case of the zwitterions such as $\mathrm{H}_{2} \mathrm{~B}^{+}-\mathrm{F}^{-}$given in the Halido Boranes section. For coordinate compounds, $E_{T}\left(\right.$ atom-atom, $\left.m s p^{3} . A O\right)$ is -1.83256 eV , two times the energy of Eq. (23.95). For carbonyl and organometallic compounds, $E_{T}\left(\right.$ atom-atom, $\left.\mathrm{msp}^{3} . A O\right)$ is -1.44915 eV (Eq. (14.151)), and the $C=O$ functional group of carbonyls is equivalent to that of vanadium carbonyls. The benzene and substituted benzene groups of organometallics are equivalent to those given in the Aromatic and Heterocyclic Compounds section.

The symbols of the functional groups of chromium coordinate compounds are given in Table 23.24. The corresponding designation of the structure of the $\left(\mathrm{CH}_{3}\right)_{3} \mathrm{C}_{6} \mathrm{H}_{3}$ group of $\mathrm{Cr}\left(\left(\mathrm{CH}_{3}\right)_{3} \mathrm{C}_{6} \mathrm{H}_{3}\right)_{2}$ is equivalent to that of toluene shown in Figure 23.5B. The geometrical (Eqs. (15.1-15.5) and (23.41)), intercept (Eqs. (15.31-15.32) and (15.80-15.87)), and energy (Eqs. (15.61) and (23.28-23.33)) parameters of chromium coordinate compounds are given in Tables 23.25, 23.26, and 23.27, respectively. The total energy of each chromium coordinate compound given in Table 23.28 was calculated as the sum over the integer multiple of each $E_{D}($ Group $)$ of Table 23.27 corresponding to functional-group composition of the compound. The bond angle parameters of chromium coordinate compounds determined using Eqs. (15.88-15.117) are given in Table 23.29. The $E_{T}\left(\right.$ atom-atom, $\left.\mathrm{msp}^{3} . \mathrm{AO}\right)$ term for $\mathrm{CrOCl}_{3}$ was calculated using Eqs. (23.30-23.33) with $s=1$ for the energies of $E_{\text {Coulomb }}(C r, 3 d 4 s)$ given by Eqs. (23.93-23.95). The charge-densities of exemplary chromium carbonyl and organometallic compounds, chromium hexacarbonyl $\left(\mathrm{Cr}(\mathrm{CO})_{6}\right)$ and di-(1,2,4-trimethylbenzene) chromium $\left(\mathrm{Cr}\left(\left(\mathrm{CH}_{3}\right)_{3} \mathrm{C}_{6} \mathrm{H}_{3}\right)_{2}\right)$, respectively, 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 are shown in Figures 23.5A and C.

Figure 23.5. (A) Chromium Hexacarbonyl. Color scale, translucent view of the charge-density of $\mathrm{Cr}(\mathrm{CO})_{6}$ showing the orbitals of the $\mathrm{Cr}, \mathrm{C}$, and O atoms at their radii, the ellipsoidal surface of each $\mathrm{H}_{2}$-type ellipsoidal MO that transitions to the corresponding outer shell of the atoms participating in each bond, and the nuclei (red, not to scale). (B) Toluene. (C) Di-(1,2,4trimethylbenzene) Chromium. Color scale, opaque view of the charge-density of $\mathrm{Cr}\left(\left(\mathrm{CH}_{3}\right)_{3} \mathrm{C}_{6} \mathrm{H}_{3}\right)_{2}$ showing the orbitals of the Cr and C 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 atoms participating in each bond.


Table 23.24. The symbols of the functional groups of chromium coordinate compounds.

| Functional Group | Group Symbol |
| :--- | :--- |
| CrF group of $\mathrm{CrF}_{2}$ | $\mathrm{Cr}-\mathrm{F}$ |
| CrCl group of $\mathrm{CrCl}_{2}$ | $\mathrm{Cr}-\mathrm{Cl}$ |
| CrO group of CrO | $\mathrm{Cr}-\mathrm{O}$ (a) |
| CrO group of $\mathrm{CrO}_{2}$ | $\mathrm{Cr}-\mathrm{O}$ (b) |
| CrO group of $\mathrm{CrO}_{3}$ | $\mathrm{Cr}-\mathrm{O}$ (c) |
| CrCO group of $\mathrm{Cr}(\mathrm{CO})_{6}$ | $\mathrm{Cr}-\mathrm{CO}$ |
| $\mathrm{C=O}$ | $\mathrm{C}=\mathrm{O}$ |
| CrCaryl group of $\mathrm{Cr}\left(\mathrm{C}_{6} \mathrm{H}_{6}\right)_{2}$ and | $\mathrm{Cr}-\mathrm{C}_{6} \mathrm{H}_{6}$ |
| $\mathrm{Cr}\left(\left(\mathrm{CH}_{3}\right)_{3} \mathrm{C}_{6} \mathrm{H}_{3}\right)_{2}$ | Ce |
| CC (aromatic bond) | CH |
| CH (aromatic) | $\mathrm{C}-\mathrm{C}$ |
| $\mathrm{C}_{a}-\mathrm{C}_{b}\left(\mathrm{CH}_{3}\right.$ to aromatic bond) | $\mathrm{C}-\mathrm{H}\left(\mathrm{CH}_{3}\right)$ |
| $\mathrm{CH}_{3}$ group |  |

Table 23.25. The geometrical bond parameters of chromium coordinate compounds and experimental values.

| Parameter | $\begin{aligned} & C r-F \\ & \text { Group } \end{aligned}$ | $\begin{aligned} & \mathrm{Cr}-\mathrm{Cl} \\ & \text { Group } \end{aligned}$ | $\mathrm{Cr}-\mathrm{O} \text { (a) }$ <br> Group | $\mathrm{Cr}-\mathrm{O} \text { (b) }$ <br> Group | $\begin{aligned} & \mathrm{Cr}-\mathrm{O}(\mathrm{c}) \\ & \text { Group } \end{aligned}$ | $\mathrm{Cr}-\mathrm{CO}$ <br> Group | $\begin{aligned} & C=O \\ & \text { Group } \end{aligned}$ | $\mathrm{Cr}-\mathrm{C}_{6} \mathrm{H}_{6}$ <br> Group | $\begin{aligned} & C \stackrel{3 e}{C} C \\ & \text { Group } \end{aligned}$ | CH <br> Group | $C-C$ <br> Group | $\mathrm{C}-\mathrm{H}\left(\mathrm{CH}_{3}\right)$ <br> Group |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $n_{e}$ | 1 | 3 | 2 | 2 | 2 |  |  |  |  |  |  |  |
| $L$ | $8 \sqrt{\frac{3}{4}}$ | $6 \sqrt{\frac{3}{4}}$ | $9 \sqrt{\frac{3}{4}}$ | $4+4 \sqrt{\frac{3}{4}}$ | $4+4 \sqrt{\frac{3}{4}}$ |  |  |  |  |  |  |  |
| $a\left(a_{0}\right)$ | 1.78868 | 2.71651 | 2.32476 | 2.31100 | 2.31100 | 2.17050 | 1.184842 | 2.52782 | 1.47348 | 1.60061 | 2.06004 | 1.64920 |
| $c^{\prime}\left(a_{0}\right)$ | 1.57606 | 1.93487 | 1.58852 | 1.58381 | 1.58381 | 1.83734 | 1.08850 | 2.05820 | 1.31468 | 1.03299 | 1.43528 | 1.04856 |
| Bond Length $2 c^{\prime}(\AA)$ | 1.66802 | 2.04778 | 1.68122 | 1.67624 | 1.67624 | 1.94456 | 1.15202 | 2.17830 | 1.39140 | 1.09327 | 1.51904 | 1.10974 |
| Exp. Bond Length (A) | $\begin{aligned} & 1.720[15] \\ & \left(\mathrm{CrO}_{2} \mathrm{~F}_{2}\right) \end{aligned}$ | $\begin{aligned} & 2.126[15] \\ & \left(\mathrm{CrO}_{2} \mathrm{Cl}_{2}\right) \end{aligned}$ | $\begin{gathered} 1.627[37] \\ \left(\mathrm{CrO}_{n} n=1,2,3\right) \end{gathered}$ | $\begin{gathered} 1.627[37] \\ \left(\mathrm{CrO}_{n} n=1,2,3\right) \end{gathered}$ | $\begin{gathered} 1.627[37] \\ \left(\mathrm{CrO}_{n} n=1,2,3\right) \end{gathered}$ | $\begin{gathered} 1.92[3] \\ \left(\mathrm{Cr}(\mathrm{CO})_{6}\right) \end{gathered}$ | $\begin{gathered} 1.16[3] \\ 1.141[38] \\ \left(\mathrm{Cr}(\mathrm{CO})_{6}\right) \end{gathered}$ | $\begin{gathered} 2.125[39] \\ \left(\mathrm{Cr}\left(\mathrm{C}_{6} \mathrm{H}_{6}\right)_{2}\right) \end{gathered}$ | $\begin{aligned} & 1.399[3] \\ & \text { (benzene) } \end{aligned}$ | $1.101 \text { [3] }$ <br> (benzene) | $\begin{aligned} & 1.524 \text { [3] } \\ & \text { (toluene) } \end{aligned}$ | $\begin{aligned} & 1.11 \text { (avg.) [3] } \\ & \text { (toluene) } \end{aligned}$ |
| $b, c\left(a_{0}\right)$ | 0.84582 | 1.90675 | 1.69738 | 1.68294 | 1.68294 | 1.15552 | 0.46798 | 1.46755 | 0.66540 | 1.22265 | 1.47774 | 1.27295 |
| $e$ | 0.88113 | 0.71226 | 0.68331 | 0.68534 | 0.68534 | 0.84651 | 0.91869 | 0.81422 | 0.89223 | 0.64537 | 0.69673 | 0.63580 |

Table 23.26. The MO to HO intercept geometrical bond parameters of chromium coordinate compounds. $E_{T}$ is $E_{T}$ (atom-atom,HO.AO).

Table 23.27. The energy parameters $(\mathrm{eV})$ of functional groups of chromium coordinate compounds.

| Parameters | $\begin{aligned} & C r-F \\ & \text { Group } \end{aligned}$ | $\begin{aligned} & \mathrm{Cr}-\mathrm{Cl} \\ & \text { Group } \end{aligned}$ | $\begin{gathered} \mathrm{Cr}-\mathrm{O} \text { (a) } \\ \text { Group } \end{gathered}$ | $\begin{gathered} C r-O(b) \\ \text { Group } \end{gathered}$ | $\begin{gathered} \mathrm{Cr}-\mathrm{O} \text { (c) } \\ \text { Group } \end{gathered}$ | $\begin{gathered} \mathrm{Cr}-\mathrm{CO} \\ \text { Group } \end{gathered}$ | $\begin{gathered} C=O \\ \text { Group } \end{gathered}$ | $\mathrm{Cr}-\mathrm{C}_{6} \mathrm{H}_{6}$ <br> Group | $\begin{gathered} C \stackrel{3 e}{C=} C \\ \text { Group } \end{gathered}$ | $\begin{gathered} \mathrm{CH} \\ \text { Group } \end{gathered}$ | $\begin{gathered} C-C \\ \text { Group } \end{gathered}$ | $\mathrm{CH}_{3}$ <br> Group |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $f_{1}$ | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 0.75 | 1 |  |  |
| $n_{1}$ | 1 | 1 | 2 | 2 | 2 | 1 | 2 | 1 | 2 | 1 | 1 | 3 |
| $n_{2}$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 2 |
| $n_{3}$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $C_{1}$ | 0.5 | 0.375 | 0.5 | 0.5 | 0.5 | 0.375 | 0.5 | 0.375 | 0.5 | 0.75 | 0.5 | 0.75 |
| $\mathrm{C}_{2}$ | 0.72009 | 0.96749 | 0.92128 | 0.92128 | 0.92128 | 0.85727 | 1 | 0.79563 | 0.85252 | 1 | 1 | 1 |
| $c_{1}$ | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $c_{2}$ | 0.72009 | 0.96749 | 0.92128 | 0.92128 | 0.92128 | 0.85727 | 0.85395 | 1 | 0.85252 | 0.91771 | 0.91771 | 0.91771 |
| $c_{3}$ | 0 | 0 | 0 | 0 | 0 | 0 | 2 | 0 | 0 | 1 | 0 | 0 |
| $c_{4}$ | 1 | 1 | 2 | 2 | 2 | 2 | 4 | 2 | 3 | 1 | 2 | 1 |
| $c_{5}$ | 1 | 1 | 2 | 2 | 2 | 0 | 0 | 0 | 0 | 1 | 0 | 3 |
| $C_{10}$ | 0.5 | 0.375 | 0.5 | 0.5 | 0.5 | 0.375 | 0.5 | 0.375 | 0.5 | 0.75 | 0.5 | 0.75 |
| $C_{20}$ | 0.72009 | 0.96749 | 0.92128 | 0.92128 | 0.92128 | 0.85727 | 1 | 0.79563 | 0.85252 | 1 | 1 | 1 |
| $V_{e}(\mathrm{eV})$ | -34.33458 | -24.26770 | -52.72902 | -53.12750 | -53.12750 | -31.58105 | -134.96850 | -30.12868 | -101.12679 | -37.10024 | -29.95792 | -107.32728 |
| $V_{p}(e \mathrm{~V})$ | 8.63282 | 7.03190 | 17.13015 | 17.18105 | 17.18105 | 7.40515 | 24.99908 | 6.61055 | 20.69825 | 13.17125 | 9.47952 | 38.92728 |
| $T(\mathrm{eV})$ | 9.59777 | 4.46671 | 11.34075 | 11.49446 | 11.49446 | 7.27506 | 56.95634 | 5.95942 | 34.31559 | 11.58941 | 7.27120 | 32.53914 |
| $V_{m}(\mathrm{eV})$ | -4.79888 | -2.23336 | -5.67037 | -5.74723 | -5.74723 | -3.63753 | -28.47817 | -2.97971 | -17.15779 | -5.79470 | -3.63560 | -16.26957 |
| $E$ (АоІно) ( eV ) | -12.54605 | -12.54605 | -25.09211 | -25.09211 | -25.09211 | -12.54605 | 0 | -12.54605 | 0 | -14.63489 | -15.35946 | -15.56407 |
| $\Delta E_{\mathrm{H}_{2} \text { NO }}($ Ао/но) $(\mathrm{eV})$ | 0 | 0 | 0 | 0 | 0 | -1.44915 | -18.22046 | -1.44915 | 0 | -1.13379 | -0.56690 | 0 |
| $E_{T}($ AO/Ho) $(\mathrm{eV})$ | -12.54605 | -12.54605 | -25.09211 | -25.09211 | -25.09211 | -11.09690 | 18.22046 | -11.09690 | 0 | -13.50110 | -14.79257 | -15.56407 |
| $E_{T}\left(H_{2} M O\right)(\mathrm{eV})$ | -33.44892 | -27.54850 | -55.02060 | -55.29133 | -55.29133 | -31.63528 | -63.27080 | -31.63533 | -63.27075 | -31.63539 | -31.63537 | -67.69451 |
| $E_{T}\left(\right.$ atom - atom, $\left.\mathrm{msp}{ }^{3} . \mathrm{AO}\right)(\mathrm{eV})$ | -1.83256 | -1.83256 | -1.83256 | -1.83256 | -1.83256 | -1.44915 | -3.58557 | -1.44915 | -2.26759 | -0.56690 | -1.13379 | 0 |
| $E_{T}($ мо $)(\mathrm{eV})$ | -35.28148 | -29.38106 | -56.85316 | -57.12389 | -57.12389 | -33.08452 | -66.85630 | -33.08452 | -65.53833 | -32.20226 | -32.76916 | -67.69450 |
| $\omega\left(10^{15} \mathrm{rad} / \mathrm{s}\right)$ | 10.3697 | 9.45766 | 12.6881 | 12.8518 | 7.98665 | 18.8708 | 22.6662 | 12.7018 | 49.7272 | 26.4826 | 16.2731 | 24.9286 |
| $E_{K}(\mathrm{eV})$ | 6.82553 | 6.22520 | 8.35152 | 8.45929 | 5.25695 | 12.42109 | 14.91930 | 8.36057 | 32.73133 | 17.43132 | 10.71127 | 16.40846 |
| $\bar{E}_{D}(e \mathrm{~V})$ | -0.18236 | -0.14503 | -0.16252 | -0.16435 | -0.12956 | -0.23068 | -0.25544 | -0.18925 | -0.35806 | -0.26130 | -0.21217 | -0.25352 |
| $\bar{E}_{\text {Kuw }}(\mathrm{eV})$ | $\begin{gathered} 0.07005 \\ {[40]} \end{gathered}$ | $\begin{gathered} 0.04030 \\ {[40]} \end{gathered}$ | $\begin{gathered} 0.11144 \\ {[37]} \end{gathered}$ | $\begin{gathered} 0.11144 \\ {[37]} \end{gathered}$ | $\begin{gathered} 0.11144 \\ {[37]} \end{gathered}$ | $\begin{gathered} 0.04724 \\ {[41]} \end{gathered}$ | $\begin{gathered} 0.24962 \\ {[29]} \end{gathered}$ | $\begin{gathered} 0.05951 \\ {[42]} \end{gathered}$ | $\begin{gathered} 0.19649 \\ {[30]} \end{gathered}$ | $\begin{gathered} 0.35532 \\ \text { Eq. } \\ (13.458) \end{gathered}$ | $\begin{gathered} 0.14940 \\ {[43]} \end{gathered}$ | $\begin{gathered} 0.35532 \\ (\text { Eq. } \\ (13.458)) \end{gathered}$ |
| $\bar{E}_{\text {osc }}(\mathrm{eV})$ | -0.14733 | -0.12488 | -0.10680 | -0.10863 | -0.07384 | -0.20706 | -0.13063 | -0.15950 | -0.25982 | -0.08364 | -0.13747 | -0.22757 |
| $E_{\text {mag }}(\mathrm{eV})$ | 0.08971 | 0.08971 | 0.08971 | 0.08971 | 0.08971 | 0.14803 | 0.11441 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 |
| $E_{T}($ Group) $)(\mathrm{eV})$ | -35.42881 | -29.50594 | -57.06677 | -57.34114 | -57.27156 | -33.29158 | -67.11757 | -33.24401 | -49.54347 | -32.28590 | -32.90663 | -67.92207 |
| $E_{\text {iprual }}\left(\mathrm{c}_{4}\right.$ AO/ Ho) $(\mathrm{eV})$ | -12.54605 | -12.54605 | -12.54605 | -12.54605 | -12.54605 | -14.63489 | -14.63489 | -15.76868 | -14.63489 | -14.63489 | -14.63489 | -14.63489 |
|  | -17.42282 | -12.96764 | -13.61806 | -13.61806 | -13.61806 | 0 | 0 | 0 | 0 | -13.59844 | 0 | -13.59844 |
| $E_{D}($ Gmup $)(e V)$ | 5.45994 | 3.99224 | 4.73854 | 5.01291 | 4.94333 | 4.02180 | 8.34918 | 1.70665 | 5.63881 | 3.90454 | 3.63685 | 12.49186 |

Table 23.28. The total bond energies of gaseous-state chromium coordinate compounds calculated using the functional group composition and the energies of Table 23.27 compared to the gaseous-state experimental values except where indicated.

| Formula | Name | $\begin{aligned} & C r-F \\ & \text { Group } \end{aligned}$ | $\begin{gathered} \mathrm{Cr}-\mathrm{Cl} \\ \text { Group } \end{gathered}$ | $\begin{gathered} \mathrm{Cr}-\mathrm{O} \\ \text { (a) } \\ \text { Group } \end{gathered}$ | $\begin{aligned} & \text { Cr-O } \\ & \text { (b) } \\ & \text { Group } \end{aligned}$ | $\begin{aligned} & \mathrm{Cr}-\mathrm{O} \\ & \text { (c) } \\ & \text { Group } \end{aligned}$ | $\begin{gathered} C r-C O \\ \text { Group } \end{gathered}$ | $\begin{aligned} & C=O \\ & \text { Group } \end{aligned}$ | $\underset{\substack{\mathrm{Cr}-\mathrm{C}_{6} H_{6} \\ \text { Group }}}{\text { and }}$ | $\begin{aligned} & C^{3 e}=C \\ & \text { Group } \end{aligned}$ | $\begin{gathered} C H \\ \text { Group } \end{gathered}$ | $\begin{aligned} & C-C \\ & \text { Group } \end{aligned}$ | $\underset{\substack{\mathrm{CH}_{3} \\ \text { Group }}}{ }$ | $\begin{aligned} & \text { Calculated } \\ & \text { Total Bond } \\ & \text { Energy (eV) } \end{aligned}$ | $\begin{aligned} & \text { Experimental } \\ & \text { Total Bond } \\ & \text { Energy (eV) } \end{aligned}$ | $\begin{aligned} & \text { Relative } \\ & \text { Error } \end{aligned}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{CrF}_{2}$ | Chromium difluoride | 2 | ${ }^{0}$ | , | , | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 10.91988 | 10.92685 [15] | 0.00064 |
| $\mathrm{CrCl}_{2}$ | Chromium dichloride | 0 | 2 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |  | 7.98449 | 7.96513 [15] | -0.00243 |
| CrO | Chromium oxide | 0 | 0 | 1 | 2 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 4.73854 | 4.75515 [37] | 0.00349 |
| $\mathrm{CrO}_{2}$ | Chromium dioxide | 0 | 0 | 0 | 0 | 3 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 10.02583 | 10.04924 [37] | 0.00233 |
| $\mathrm{CrO}_{3}$ | Chromium trioxide | 0 | , | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 14.83000 | 14.85404 [37] | 0.00162 |
| $\mathrm{CrO}_{2} \mathrm{Cl}_{2}$ | Chromium dichloride dioxide | 0 | 2 | 2 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 17.46158 | 17.30608 [15] | -0.00899 |
| $\mathrm{Cr}(\mathrm{CO})_{6}$ | Chromium hexacarbonyl | 0 | 0 | 0 | 0 | 0 | 6 | 6 | 0 | 0 |  | 0 | 0 | 74.22588 | 74.61872 [44] | 0.00526 |
| $\mathrm{Cr}\left(\mathrm{C}_{6} \mathrm{H}_{6}\right)_{2}$ | Dibenzene chromium | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 2 | 12 | 12 | 0 |  | 117.93345 | 117.97971 [44] | 0.00039 |
| $\mathrm{Cr}\left(\left(\mathrm{CH}_{3}\right)_{3} \mathrm{C}_{6} \mathrm{H}_{3}\right)_{2}$ | Di-(1,2,4-trimethylbenzene) chromium | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 2 | 12 | 6 | 6 | 6 | 191.27849 | $192.42933^{\text {a }}[44]$ | 0.00598 |

Table 23.29. The bond angle parameters of chromium coordinate compounds and experimental values. $E_{T}$ is $E_{T}$ (atom-atom,HO.AO).

| Atoms of Angle | $\begin{gathered} 2 c^{\prime} \\ \text { Bond } 1\left(a_{0}\right) \end{gathered}$ | $\begin{gathered} 2 c^{\prime} \\ \text { Bond } 2\left(a_{0}\right) \end{gathered}$ | $\begin{gathered} 2 c^{\prime} \\ \text { Terminal } \\ \text { Atoms }\left(a_{0}\right) \end{gathered}$ | $\begin{aligned} & E_{\text {Coulombic }} \\ & \text { Atom } 1 \end{aligned}$ | Atom 1 Hybridization Designation (Table 15.3A) | $\begin{aligned} & E_{\text {Conlombic }} \\ & \text { Atom } 2 \end{aligned}$ | Atom 2 Hybridization Designation (Table 15.3A) | Atom 1 | $\begin{gathered} c_{2} \\ \text { Atom } 2 \end{gathered}$ | $C_{1}$ | $C_{2}$ | $c_{1}$ | $c_{2}^{\prime}$ | $\begin{gathered} E_{T} \\ (\mathrm{eV}) \end{gathered}$ | $\begin{gathered} \theta_{v} \\ \left({ }^{\circ}\right) \end{gathered}$ | $\begin{gathered} \theta_{1} \\ \left({ }^{\circ}\right) \end{gathered}$ | $\begin{aligned} & \theta_{2} \\ & \left({ }^{\circ}\right) \end{aligned}$ | $\begin{gathered} \text { Cal. } \theta \\ \left({ }^{\circ}\right) \end{gathered}$ | $\begin{gathered} \text { Exp. } \theta \\ \left({ }^{\circ}\right) \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\angle \mathrm{OCrO}$ | 3.17704 | 3.17704 | 5.1463 | $\begin{gathered} -13.61806 \\ O \end{gathered}$ | O | $\stackrel{-13.61806}{O}$ | O | 1 | 1 | 1 | $\begin{gathered} 0.92128 \\ (\text { Eq. } \\ (23.100)) \end{gathered}$ | 1 | 1 | -0.85938 |  |  |  | 108.18 | $\begin{aligned} & 108.7[15] \\ & \left(\mathrm{CrO}_{2} \mathrm{Cl}_{2}\right) \end{aligned}$ |
| $\angle \mathrm{ClCrCl}$ | 3.86974 | 3.86974 | 6.4704 | $\begin{array}{\|c\|} \hline-12.96764 \\ C l \end{array}$ | Cl | $\begin{gathered} -12.96764 \\ C l \end{gathered}$ | Cl | $\begin{gathered} 0.96749 \\ (\text { Eq. } \\ (23.97)) \end{gathered}$ | $\begin{gathered} 0.96749 \\ (\text { Eq. } \\ (23.97)) \end{gathered}$ | 1 | 0.75 | 1 | 0.96749 | -0.85938 |  |  |  | 113.45 | $\begin{aligned} & 113.0[15] \\ & \left(\mathrm{CrO}_{2} \mathrm{Cl}_{2}\right) \end{aligned}$ |
| $\begin{gathered} \angle C C C \\ \text { (aromatic) } \end{gathered}$ | 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 | $\begin{aligned} & 120[34-36] \\ & \text { (benzene) } \end{aligned}$ |
| $\begin{gathered} \angle C C H \\ \text { (aromatic) } \end{gathered}$ |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  | 120.19 |  | 119.91 | $\begin{aligned} & 120[34-36] \\ & \text { (benzene) } \end{aligned}$ |

## MANGANESE FUNCTIONAL GROUPS AND MOLECULES

The electron configuration of manganese is $[A r] 4 s^{2} 3 d^{5}$ having the corresponding term ${ }^{6} S_{5 / 2}$. The total energy of the state is given by the sum over the seven electrons. The sum $E_{T}(M n, 3 d 4 s)$ of experimental energies [1] of $\mathrm{Mn}, \mathrm{Mn}^{+}, \mathrm{Mn}^{2+}, \mathrm{Mn}^{3+}$, $\mathrm{Mn}^{4+}, \mathrm{Mn}^{5+}$, and $\mathrm{Mn}^{6+}$ is:

$$
\begin{equation*}
E_{T}(M n, 3 d 4 s)=-\binom{119.203 \mathrm{eV}+95.6 \mathrm{eV}+72.4 \mathrm{eV}+51.2 \mathrm{eV}}{+33.668 \mathrm{eV}+15.6400 \mathrm{eV}+14.22133 \mathrm{eV}}=-401.93233 \mathrm{eV} \tag{23.102}
\end{equation*}
$$

By considering that the central field decreases by an integer for each successive electron of the shell, the radius $r_{3 d 4 s}$ of the Mn3d $4 s$ shell may be calculated from the Coulombic energy using Eq. (15.13).

$$
\begin{equation*}
r_{3 d 4 s}=\sum_{n=18}^{24} \frac{(Z-n) e^{2}}{8 \pi \varepsilon_{0}(e 395.14502 \mathrm{eV})}=\frac{28 e^{2}}{8 \pi \varepsilon_{0}(e 395.14502 \mathrm{eV})}=0.96411 a_{0} \tag{23.103}
\end{equation*}
$$

where $Z=25$ for manganese. Using Eq. (15.14), the Coulombic energy $E_{\text {Coulomb }}(M n, 3 d 4 s)$ of the outer electron of the $\operatorname{Mn} 3 d 4 s$ shell is:

$$
\begin{equation*}
E_{\text {Coulomb }}(M n, 3 d 4 s)=\frac{-e^{2}}{8 \pi \varepsilon_{0} r_{3 d 4 s}}=\frac{-e^{2}}{8 \pi \varepsilon_{0} 0.96411 a_{0}}=-14.112322 \mathrm{eV} \tag{23.104}
\end{equation*}
$$

During hybridization, the spin-paired $4 s$ electrons are promoted to the $M n 3 d 4 s$ shell as unpaired electrons. The energy for the promotion is the magnetic energy given by Eq. (15.15) at the initial radius of the $4 s$ electrons. From Eq. (10.102) with $Z=25$ and $n=25$, the radius $r_{25}$ of the $M n 4 s$ shell is:

$$
\begin{equation*}
r_{25}=1.83021 a_{0} \tag{23.105}
\end{equation*}
$$

Using Eqs. (15.15) and (23.104), the unpairing energy is:

$$
\begin{equation*}
E_{4 s}(\text { magnetic })=\frac{2 \pi \mu_{0} e^{2} \hbar^{2}}{m_{e}^{2}\left(r_{25}\right)^{3}}=\frac{8 \pi \mu_{0} \mu_{B}^{2}}{\left(1.83021 a_{0}\right)^{3}}=0.01866 \mathrm{eV} \tag{23.106}
\end{equation*}
$$

The electrons from the $4 s$ and $3 d$ shells successively fill unoccupied HOs until the HO shell is filled with unpaired electrons, then the electrons pair per HO. In the case of the $M n 3 d 4 s$ shell having seven electrons and six orbitals, one set of electrons is paired. Using Eqs. (15.15) and (23.102), the pairing energy is given by:

$$
\begin{equation*}
E_{3 d 4 s}(\text { magnetic })=-\frac{2 \pi \mu_{0} e^{2} \hbar^{2}}{m_{e}^{2}\left(r_{3 d 4 s}\right)^{3}}=-\frac{8 \pi \mu_{0} \mu_{B}^{2}}{\left(0.96411 a_{0}\right)^{3}}=-0.12767 \mathrm{eV} \tag{23.107}
\end{equation*}
$$

Thus, after Eq. (23.28), the energy $E(M n, 3 d 4 s)$ of the outer electron of the $M n 3 d 4 s$ shell is given by adding the magnetic energy of unpairing the $4 s$ electrons (Eq. (23.105)) and pairing of one set of Mn3d4s electrons (Eq. (23.106)) to $E_{\text {Coulomb }}(M n, 3 d 4 s)$ (Eq. (23.103)).

$$
\begin{align*}
E(M n, 3 d 4 s) & =\frac{-e^{2}}{8 \pi \varepsilon_{0} r_{3 d 4 s}}+\frac{2 \pi \mu_{0} e^{2} \hbar^{2}}{m_{e}^{2} r_{4 s}^{3}}+\sum_{3 d \text { pairs }} \frac{2 \pi \mu_{0} e^{2} \hbar^{2}}{m_{e}^{2} r_{3 d}^{3}}-\sum_{H O \text { pairs }} \frac{2 \pi \mu_{0} e^{2} \hbar^{2}}{m_{e}^{2} r_{3 d 4 s}^{3}}  \tag{23.108}\\
& =-14.112322 \mathrm{eV}+0.01866 \mathrm{eV}-0.12767 \mathrm{eV}=-14.22133 \mathrm{eV}
\end{align*}
$$

Next, consider the formation of the $M n-L$-bond MO wherein each manganese atom has a $M n 3 d 4 s$ electron with an energy given by Eq. (23.107). The total energy of the state of each manganese atom is given by the sum over the seven electrons. The sum $E_{T}\left(M n_{M n-L} 3 d 4 s\right)$ of energies of $M n 3 d 4 s$ (Eq. (23.107)), $M n^{+}, M n^{2+}, M n^{3+}, M n^{4+}, M n^{5+}$, and $M n^{6+}$ is:

$$
\begin{align*}
E_{T}\left(M n_{M n-L} 3 d 4 s\right) & =-\binom{119.203 \mathrm{eV}+95.6 \mathrm{eV}+72.4 \mathrm{eV}+51.2 \mathrm{eV}}{+33.668 \mathrm{eV}+15.6400 \mathrm{eV}+E(M n, 3 \mathrm{~d} 4 \mathrm{~s})} \\
& =-\binom{119.203 \mathrm{eV}+95.6 \mathrm{eV}+72.4 \mathrm{eV}+51.2 \mathrm{eV}}{+33.668 \mathrm{eV}+15.6400 \mathrm{eV}+14.22133 \mathrm{eV}}  \tag{23.109}\\
& =-401.93233 \mathrm{eV}
\end{align*}
$$

where $E(M n, 3 d 4 s)$ is the sum of the energy of $M n,-7.43402 \mathrm{eV}$, and the hybridization energy.
The manganese HO donates an electron to each MO. Using Eq. (23.30), the radius $r_{3 d 4 s}$ of the Mn3d4s shell calculated from the Coulombic energy is:

$$
\begin{equation*}
r_{M n-L 3 d 4 s}=\left(\sum_{n=18}^{24}(Z-n)-1\right) \frac{e^{2}}{8 \pi \varepsilon_{0}(e 401.93233 \mathrm{eV})}=\frac{27 e^{2}}{8 \pi \varepsilon_{0}(e 401.93233 \mathrm{eV})}=0.91398 a_{0} \tag{23.110}
\end{equation*}
$$

Using Eqs. (15.19) and (23.109), the Coulombic energy $E_{\text {Coulomb }}\left(M n_{M n-L}, 3 d 4 s\right)$ of the outer electron of the $M n 3 d 4 s$ shell is:

$$
\begin{equation*}
E_{\text {Coulomb }}\left(M n_{M n-L}, 3 d 4 s\right)=\frac{-e^{2}}{8 \pi \varepsilon_{0} r_{M n-L 3 d 4 s}}=\frac{-e^{2}}{8 \pi \varepsilon_{0} 0.91398 a_{0}}=-14.88638 \mathrm{eV} \tag{23.111}
\end{equation*}
$$

The magnetic energy terms are those for the unpairing of the $4 s$ electrons (Eq. (23.105)) and pairing one set of Mn3d4s electrons (Eq. (23.106)). Using Eqs. (23.32), (23.105), (23.106), and (23.110), the energy $E\left(M n_{M n-L}, 3 d 4 s\right)$ of the outer electron of the $\operatorname{Mn} 3 d 4 s$ shell is:

$$
\begin{align*}
E\left(M n_{M n-L}, 3 d 4 s\right) & =\frac{-e^{2}}{8 \pi \varepsilon_{0} r_{M n-L 3 d 4 s}}+\frac{2 \pi \mu_{0} e^{2} \hbar^{2}}{m_{e}^{2}\left(r_{25}\right)^{3}}-\frac{2 \pi \mu_{0} e^{2} \hbar^{2}}{m_{e}^{2}\left(r_{3 d 4 s}\right)^{3}}  \tag{23.112}\\
& =-14.88638 \mathrm{eV}+0.01866 \mathrm{eV}-0.12767 \mathrm{eV}=-14.99539 \mathrm{eV}
\end{align*}
$$

Thus, $E_{T}(M n-L, 3 d 4 s)$, the energy change of each $M n 3 d 4 s$ shell with the formation of the $M n-L$-bond MO is given by the difference between Eq. (23.111) and Eq. (23.107):

$$
\begin{align*}
E_{T}(M n-L, 3 d 4 s) & =E\left(M n_{M n-L}, 3 d 4 s\right)-E(M n, 3 d 4 s) \\
& =-14.99539 \mathrm{eV}-(-14.22133 \mathrm{eV})=-0.77406 \mathrm{eV} \tag{23.113}
\end{align*}
$$

The semimajor axis $a$ solution given by Eq. (23.41) of the force balance equation, Eq. (23.39), for the $\sigma$-MO of the $M n-L$-bond MO of $M n L_{n}$ is given in Table 23.31 with the force-equation parameters $Z=25, n_{e}$, and $L$ corresponding to the orbital and spin angular momentum terms of the $3 d 4 s$ HO shell. The semimajor axis $a$ of carbonyl and organometallic compounds are solved using Eq. (15.51).

For the $M n-L$ functional groups, hybridization of the $4 s$ and $3 d$ AOs of $M n$ to form a single $3 d 4 s$ shell forms an energy minimum, and the sharing of electrons between the $M n 3 d 4 s \mathrm{HO}$ and $L$ AO to form a MO permits each participating orbital to decrease in radius and energy. The $F \mathrm{AO}$ has an energy of $E(F)=-17.42282 \mathrm{eV}$, the Cl AO has an energy of $E(C l)=-12.96764 \mathrm{eV}$, the $C 2 s p^{3} \mathrm{HO}$ has an energy of $E\left(C, 2 s p^{3}\right)=-14.63489 \mathrm{eV}$ (Eq. (15.25)), the Coulomb energy of $\operatorname{Mn} 3 d 4 s \quad \mathrm{HO}$ is $\quad E_{\text {Coulomb }}(M n, 3 d 4 s)=-14.11232 \mathrm{eV} \quad$ (Eq. (23.103)), the $M n 3 d 4 s \quad \mathrm{HO}$ has an energy of $E(M n, 3 d 4 s)=-14.22133 \mathrm{eV}$ (Eq. (23.107)), and 13.605804 eV is the magnitude of the Coulombic energy between the electron and proton of $H$ (Eq. (1.264)). To meet the equipotential condition of the union of the $M n-L H_{2}$-type-ellipsoidalMO with these orbitals, the hybridization factor(s), at least one of $c_{2}$ and $C_{2}$ of Eq. (15.61) for the $M n-L$-bond MO given by Eq. (15.77) is:

$$
\begin{align*}
& C_{2}(F A O \text { to Mn } 3 d 4 s H O)=\frac{E(M n, 3 d 4 s)}{E(F A O)}=\frac{-14.22133 \mathrm{eV}}{-17.42282 \mathrm{eV}}=0.81625  \tag{23.114}\\
& C_{2}(C l A O \text { to Mn } 3 d 4 s H O)=\frac{E(C l A O)}{E(M n, 3 d 4 s)}=\frac{-12.96764 \mathrm{eV}}{-14.22133 \mathrm{eV}}=0.91184  \tag{23.115}\\
& c_{2}\left(C 2 s p^{3} \mathrm{HO} \text { to Mn3d } 4 s H O\right)=\frac{E_{\text {Coulomb }}(M n, 3 d 4 s)}{E\left(C, 2 s p^{3}\right)} c_{2}\left(C 2 s p^{3} \mathrm{HO}\right)=\frac{-14.11232 \mathrm{eV}}{-14.63489 \mathrm{eV}}(0.91771)=0.88495  \tag{23.116}\\
& C_{2}(\mathrm{Mn} 3 d 4 \mathrm{sHO} \text { to Mn3d } 4 s H O)=\frac{E(H)}{E_{\text {Coulomb }}(M n, 3 d 4 s)}=\frac{-13.605804 \mathrm{eV}}{-14.11232 \mathrm{eV}}=0.96411 \tag{23.117}
\end{align*}
$$

where Eqs. (15.76), (15.79), and (13.430) were used in Eq. (23.115) and Eq. (15.71) was used in Eq. (23.116). Since the energy of the MO is matched to that of the $M n 3 d 4 s \mathrm{HO}$ in coordinate compounds, $E(A O / H O)$ in Eq. (15.61) is $E(M n, 3 d 4 s)$ given by Eq. (23.107) and $E(A O / H O)$ in Eq. (15.61) of carbonyl compounds is $E_{\text {Coulomb }}(M n, 3 d 4 s)$ given by Eq. (23.103). $E_{T}\left(\right.$ atom-atom, $\left.m s p^{3} . A O\right)$ of the $M n-L$-bond MO is determined by considering that the bond involves an electron transfer from the manganese atom to the ligand atom to form partial ionic character in the bond as in the case of the zwitterions such as $H_{2} B^{+}-F^{-}$given in the Halido Boranes section. For the coordinate compounds, $E_{T}\left(\right.$ atom-atom, $\left.m s p^{3} . A O\right)$ is -1.54812 eV , two times the energy of Eq. (23.112). For the $M n-C O$ bonds of carbonyl compounds, $E_{T}\left(\right.$ atom-atom, $\left.m s p^{3} . A O\right)$ is -1.44915 eV (Eq. (14.151)), and the $C=O$ functional group of carbonyls is equivalent to that of vanadium carbonyls.

The symbols of the functional groups of manganese coordinate compounds are given in Table 23.30. The geometrical (Eqs. (15.1-15.5) and (23.41)), intercept (Eqs. (15.31-15.32) and (15.80-15.87)), and energy (Eqs. (15.61) and (23.28-23.33)) parameters of manganese coordinate compounds are given in Tables 23.31, 23.32, and 23.33, respectively. The total energy of each manganese coordinate compound given in Table 23.34 was calculated as the sum over the integer multiple of each $E_{D}$ (Group) of Table 23.33 corresponding to functional-group composition of the compound. The charge-densities of exemplary manganese carbonyl compound, dimanganese decacarbonyl $\left(\mathrm{Mn}_{2}(\mathrm{CO})_{10}\right)$ 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 23.6.

Figure 23.6. Diamanganese decacarbonyl. Color scale, opaque view of the charge-density of $\mathrm{Mn}_{2}(\mathrm{CO})_{10}$ showing the orbitals of the $M n, C$, and $O$ atoms at their radii and the ellipsoidal surface of each $H_{2}$-type ellipsoidal MO that transitions to the corresponding outer shell of the atoms participating in each bond.

$0 \square 1 \mathrm{e} / \AA^{2}$

Table 23.30. The symbols of the functional groups of manganese coordinate compounds.

| Functional Group | Group Symbol |
| :--- | :--- |
| MnF group of MnF | $\mathrm{Mn}-\mathrm{F}$ |
| MnCl group of MnCl | $\mathrm{Mn}-\mathrm{Cl}$ |
| MnCO group of $\mathrm{Mn}_{2}(\mathrm{CO})_{10}$ | $\mathrm{Mn}-\mathrm{CO}$ |
| MnMn group of $\mathrm{Mn}_{2}(\mathrm{CO})_{10}$ | $\mathrm{Mn}-\mathrm{Mn}$ |
| $\mathrm{C}=\mathrm{O}$ | $\mathrm{C}=\mathrm{O}$ |

Table 23.31. The geometrical bond parameters of manganese coordinate compounds and experimental values.

| Parameter | $M n-F$ <br> Group | $M n-C l$ <br> Group | $M n-C O$ <br> Group | $M n-M n$ <br> Group | $C=O$ <br> Group |
| :---: | :---: | :---: | :---: | :---: | :---: |
| $n_{e}$ | 2 | 3 |  | 5 |  |
| $L$ | $2+4 \sqrt{\frac{3}{4}}$ | $4+6 \sqrt{\frac{3}{4}}$ |  | $3 \sqrt{\frac{3}{4}}$ |  |
| $a\left(a_{0}\right)$ | 2.21856 | 2.86785 | 2.23676 | 3.60392 | 1.184842 |
| $c^{\prime}\left(a_{0}\right)$ | 1.64864 | 2.04780 | 1.72695 | 2.73426 | 1.08850 |
| Bond Length $2 c^{\prime}(\AA)$ | 1.74484 | 2.16729 | 1.82772 | 2.89382 | 1.15202 |
| Exp. Bond Length <br> $(A)$ | $1.729[45]$ <br> $\left(M n F_{2}\right)$ | $2.202[15]$ <br> $\left(M n C l_{2}\right)$ | $1.830[46]$ | $2.923[46]$ | $1.151[29,46]$ |
| $\left(M n_{2}(C O)_{10}\right)$ | $\left(M n_{2}(C O)_{10}\right)$ | $\left(M n_{2}(C O)_{10}\right)$ |  |  |  |
| $b, c\left(a_{0}\right)$ | 1.48459 | 2.00775 | 1.42153 | 2.34778 | 0.46798 |
| $e$ | 0.74311 | 0.71405 | 0.77208 | 0.75869 | 0.91869 |

Table 23.32. The MO to HO intercept geometrical bond parameters of manganese coordinate compounds. $E_{T}$ is $E_{T}$ (atom-atom,HO.AO).

| Bond | Atom | $\begin{gathered} E_{T} \\ (\mathrm{eV}) \\ \text { Bond } 1 \end{gathered}$ | $\begin{gathered} E_{T} \\ (\mathrm{eV}) \\ \text { Bond 2 } \end{gathered}$ | $\begin{gathered} E_{T} \\ (\mathrm{eV}) \\ \text { Bond 3 } \end{gathered}$ | $\begin{gathered} E_{T} \\ (\mathrm{eV}) \\ \text { Bond } 4 \end{gathered}$ | $\begin{gathered} E_{T} \\ (\mathrm{eV}) \\ \text { Bond } 5 \end{gathered}$ | $\begin{gathered} E_{T} \\ (\mathrm{eV}) \\ \text { Bond } 6 \end{gathered}$ | $\begin{gathered} \text { Final Total } \\ \text { Energy } \\ \text { Mnsid4s } \\ \text { (eV) } \end{gathered}$ | $\begin{aligned} & r_{\text {manal }} \\ & \left(a_{0}\right) \end{aligned}$ | $\begin{aligned} & r_{\text {mad }} \\ & \left(a_{0}\right) \end{aligned}$ | $\begin{gathered} E_{\text {Catamanem }}(M n 334 s) \\ (\text { eV) } \\ \text { Final } \end{gathered}$ | $\begin{gathered} E(M n 3 d 4 s) \\ \text { (eV) } \\ \text { Final } \end{gathered}$ | $\begin{aligned} & \hline \theta^{\prime} \\ & \left({ }^{\circ}\right) \end{aligned}$ | $\begin{aligned} & \theta_{1} \\ & \left({ }^{\circ}\right) \end{aligned}$ | $\begin{aligned} & \theta_{2} \\ & \left({ }^{\circ}\right) \end{aligned}$ | $\begin{gathered} d_{1} \\ \left(a_{0}\right) \end{gathered}$ | $\begin{gathered} d_{2} \\ \left(a_{0}\right) \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Mn-F (MnF) | Mn | -0.77406 | 0 | 0 | 0 | 0 | 0 |  | 0.96411 | 0.91398 | -14.88638 |  | 83.28 | 96.72 | 37.69 | 1.75558 | 0.10694 |
| Mn-F (MnF) | F | $-0.77406$ | 0 | 0 | 0 | 0 | 0 |  | 0.78069 | 0.74770 | -18.19688 |  | 63.75 | 116.25 | 26.85 | 1.97934 | 0.33070 |
| $\mathrm{Mn}-\mathrm{Cl}$ ( MnCl$)$ | Mn | $-0.77406$ | 0 | 0 | 0 | 0 | 0 |  | 0.96411 | 0.91398 | -14.88638 |  | 41.12 | 138.88 | 17.42 | 2.73630 | 0.68851 |
| $\mathrm{Mn}-\mathrm{Cl}$ ( MnCl$)$ | Cl | $-0.77406$ | 0 | 0 | 0 | 0 | 0 |  | 1.05158 | 0.99011 | -13.74170 |  | 54.01 | 125.99 | 23.52 | 2.62968 | 0.58189 |
| $\mathrm{MnC}=0$ | $o$ | -1.79278 | 0 | 0 | 0 | 0 | 0 |  | 1.00000 | 0.81871 | -16.61853 |  | 147.43 | 32.57 | 70.34 | 0.39853 | 0.68997 |
| $\mathrm{MnC}=0$ | C | -1.79278 | $-0.72457$ | 0 | 0 | 0 | 0 | -154.13305 | 0.91771 | 0.78451 | -17.34311 | -17.15225 | 146.31 | 33.69 | 68.42 | 0.43577 | 0.65274 |
| Mn-CO ((CO) $\left.)_{s} \mathrm{MnMn}(\mathrm{CO})_{s}\right)$ | C | $-0.72457$ | $-1.79278$ | 0 | 0 | 0 | 0 |  | 0.91771 | 0.78451 | -17.34311 | -17.15225 | 78.68 | 101.32 | 32.76 | 1.88097 | 0.15402 |
| $\mathrm{Mn}-\mathrm{CO}\left((\mathrm{CO})_{s} \mathrm{MnMn}(\mathrm{CO})_{s}\right)$ | Mn | -0.72457 | -0.72457 | -0.72457 | -0.72457 | -0.72457 | -0.77002 |  | 0.96411 | 0.70795 | -19.21864 |  | 69.05 | 110.95 | 27.72 | 1.98013 | 0.25319 |
| $\mathrm{Mn}-\mathrm{Mn}\left((\mathrm{CO})_{s} \mathrm{Mn}-\mathrm{Mn}(\mathrm{CO})_{s}\right)$ | Mn | -0.72457 | -0.72457 | $-0.72457$ | $-0.72457$ | -0.72457 | -0.77002 |  | 0.96411 | 0.73524 | -18.50521 |  |  |  |  |  |  |

Table 23.33. The energy parameters ( eV ) of functional groups of manganese coordinate compounds.

| Parameters | $\begin{aligned} & M n-F \\ & \text { Group } \end{aligned}$ | $\mathrm{Mn}-\mathrm{Cl}$ <br> Group | $\mathrm{Mn}-\mathrm{CO}$ Group | $M n-M n$ Group | $\begin{aligned} & C=O \\ & \text { Group } \end{aligned}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| $f_{1}$ | 1 | 1 | 1 | 1 | 1 |
| $n_{1}$ | 1 | 1 | 1 | 1 | 2 |
| $n_{2}$ | 0 | 0 | 0 | 0 | 0 |
| $n_{3}$ | 0 | 0 | 0 | 0 | 0 |
| $C_{1}$ | 0.5 | 0.375 | 0.375 | 0.25 | 0.5 |
| $C_{2}$ | 0.81625 | 0.91184 | 1 | 0.96411 | 1 |
| $c_{1}$ | 1 | 1 | 1 | 1 | 1 |
| $c_{2}$ | 1 | 1 | 0.88495 | 1 | 0.85395 |
| $c_{3}$ | 0 | 0 | 0 | 0 | 2 |
| $c_{4}$ | 1 | 1 | 2 | 2 | 4 |
| $c_{5}$ | 1 | 1 | 0 | 0 | 0 |
| $C_{10}$ | 0.5 | 0.375 | 0.375 | 0.25 | 0.5 |
| $\mathrm{C}_{2}$ o | 0.81625 | 0.91184 | 1 | 0.96411 | 1 |
| $V_{e}(\mathrm{eV})$ | -31.60440 | -23.79675 | -28.59791 | -19.76726 | -134.96850 |
| $V_{p}(e \mathrm{~V})$ | 8.25276 | 6.64412 | 7.87853 | 4.97605 | 24.99908 |
| $T(e V)$ | 7.12272 | 4.14889 | 6.39271 | 2.74246 | 56.95634 |
| $V_{m}(\mathrm{eV})$ | -3.56136 | -2.07445 | -3.19636 | -1.37123 | -28.47817 |
| $E($ Ао/но) (eV) | -14.22133 | -14.22133 | -14.11232 | -14.11232 | 0 |
| $\Delta E_{\mathrm{H}_{2} \mathrm{MO}}($ AO/ HO$)(\mathrm{eV})$ | 0 | 0 | 0 | 0 | -18.22046 |
| $E_{T}($ Ао/но) $)(\mathrm{eV})$ | -14.22133 | -14.22133 | -14.11232 | -14.11232 | 18.22046 |
| $E_{T}\left(\mathrm{H}_{2} \mathrm{MO}\right)(\mathrm{eV})$ | -34.01162 | -29.29952 | -31.63535 | -27.53231 | -63.27080 |
| $E_{T}\left(\right.$ atom-atom, $\left.\mathrm{msp}^{3} . \mathrm{AO}\right)(\mathrm{eV})$ | -1.54812 | -1.54812 | -1.44915 | -1.54005 | -3.58557 |
| $E_{T}($ мо $)(\mathrm{eV})$ | -35.55974 | -30.84764 | -33.08452 | -29.07235 | -66.85630 |
| $\omega\left(10^{15} \mathrm{rad} / \mathrm{s}\right)$ | 7.99232 | 4.97768 | 7.56783 | 2.96657 | 22.6662 |
| $E_{K}(\mathrm{eV})$ | 5.26068 | 3.27640 | 4.98128 | 1.95265 | 14.91930 |
| $\bar{E}_{D}(\mathrm{eV})$ | -0.16136 | -0.11046 | -0.14608 | -0.08037 | -0.25544 |
| $\bar{E}_{\text {Kvib }}(\mathrm{eV})$ | ${ }_{[47]}^{0.07672}$ | $\begin{gathered} 0.04772 \\ {[47]} \end{gathered}$ | $\begin{gathered} 0.04749 \\ {[29]} \end{gathered}$ | $\begin{gathered} 0.01537 \\ {[48]} \end{gathered}$ | $\begin{gathered} 0.24962 \\ {[29]} \end{gathered}$ |
| $\bar{E}_{\text {osc }}(\mathrm{eV})$ | -0.12299 | -0.08660 | -0.12234 | -0.07268 | -0.13063 |
| $E_{\text {mag }}(e V)$ | 0.12767 | 0.12767 | 0.14803 | 0.12767 | 0.11441 |
| $E_{T}($ Group $)(\mathrm{eV})$ | -35.68273 | -30.93425 | -33.20686 | -29.14504 | -67.11757 |
| $E_{\text {initial }}\left(\mathrm{c}_{+}\right.$Ао/но) $(\mathrm{eV})$ | -14.22133 | -14.22133 | -14.63489 | -14.11232 | -14.63489 |
| $E_{\text {initial }}\left(\mathrm{c}_{\text {s }}\right.$, Ао/но) $(\mathrm{eV})$ | -17.42282 | -12.96764 | 0 | 0 | 0 |
| $E_{D}($ Group $)(\mathrm{eV})$ | 4.03858 | 3.74528 | 3.93708 | 0.92039 | 8.34918 |

Table 23.34. The total bond energies of gaseous-state manganese coordinate compounds calculated using the functional group composition and the energies of Table 23.33 compared to the gaseous-state experimental values.

| Formula | Name | $M n-F$ <br> Group | $M n-C l$ <br> Group | $M n-C O$ <br> Group | $M n-M n$ <br> Group | $C=O$ <br> Group | Calculated <br> Total Bond <br> Energy (eV) | Experimental <br> Total Bond <br> Energy (eV) |  |
| :--- | :--- | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| MnF | Mangancse fluoridc | 1 | 0 | 0 | 0 | 0 | 4.03858 | $3.97567[15]$ |  |
| MnCl | Manganese chloride | 0 | 1 | 0 | 0 | 0 | -0.01582 |  |  |
| $\mathrm{Mn}_{2}(\mathrm{CO})_{10}$ | Dimanganese decacarbonyl | 0 | 0 | 10 | 1 | 0 | 3.74528 | $3.73801[15]$ | -0.00194 |
| Error |  |  |  |  |  |  |  |  |  |

## IRON FUNCTIONAL GROUPS AND MOLECULES

The electron configuration of iron is $[A r] 4 s^{2} 3 d^{6}$ having the corresponding term ${ }^{5} D_{4}$. The total energy of the state is given by the sum over the eight electrons. The sum $E_{T}(\mathrm{Fe}, 3 \mathrm{~d} 4 \mathrm{~s})$ of experimental energies [1] of $\mathrm{Fe}, \mathrm{Fe}^{+}, \mathrm{Fe}^{2+}, \mathrm{Fe}^{3+}, \mathrm{Fe}^{4+}, \mathrm{Fe}^{5+}$, $F e^{6+}$, and $F e^{7+}$ is:

$$
\begin{equation*}
E_{T}(F e, 3 d 4 s)=-\binom{151.06 \mathrm{eV}+124.98 \mathrm{eV}+99.1 \mathrm{eV}+75.0 \mathrm{eV}}{+54.8 \mathrm{eV}+30.652 \mathrm{eV}+16.1877 \mathrm{eV}+7.9024 \mathrm{eV}}=-559.68210 \mathrm{eV} \tag{23.118}
\end{equation*}
$$

By considering that the central field decreases by an integer for each successive electron of the shell, the radius $r_{3 d 4 s}$ of the $F e 3 d 4 s$ shell may be calculated from the Coulombic energy using Eq. (15.13).

$$
\begin{equation*}
r_{3 d 4 s}=\sum_{n=18}^{25} \frac{(Z-n) e^{2}}{8 \pi \varepsilon_{0}(e 559.68210 \mathrm{eV})}=\frac{36 e^{2}}{8 \pi \varepsilon_{0}(e 559.68210 \mathrm{eV})}=0.87516 a_{0} \tag{23.119}
\end{equation*}
$$

where $Z=26$ for iron. Using Eq. (15.14), the Coulombic energy $E_{\text {Coulomb }}(F e, 3 d 4 s)$ of the outer electron of the Fe3d4s shell is

$$
\begin{equation*}
E_{\text {Coulomb }}(F e, 3 d 4 s)=\frac{-e^{2}}{8 \pi \varepsilon_{0} r_{3 d 4 s}}=\frac{-e^{2}}{8 \pi \varepsilon_{0} 0.87516 a_{0}}=-15.546725 \mathrm{eV} \tag{23.120}
\end{equation*}
$$

During hybridization, the spin-paired $4 s$ electrons and the one. set of paired $3 d$ electrons are promoted to the $F e 3 d 4 s$ shell as initially unpaired electrons. The energies for the promotions are given by Eq. (15.15) at the initial radii of the $4 s$ and $3 d$ electrons. From Eq. (10.102) with $Z=26$ and $n=26$, the radius $r_{26}$ of the $F e 4 s$ shell is

$$
\begin{equation*}
r_{26}=1.72173 a_{0} \tag{23.121}
\end{equation*}
$$

and with $Z=26$ and $n=24$, the radius $r_{24}$ of the $F e 3 d$ shell is:

$$
\begin{equation*}
r_{24}=1.33164 a_{0} \tag{23.122}
\end{equation*}
$$

Using Eqs. (15.15), (23.120), and (23.121), the unpairing energies are:

$$
\begin{align*}
& E_{4 s}(\text { magnetic })=\frac{2 \pi \mu_{0} e^{2} \hbar^{2}}{m_{e}^{2}\left(r_{26}\right)^{3}}=\frac{8 \pi \mu_{0} \mu_{B}^{2}}{\left(1.72173 a_{0}\right)^{3}}=0.02242 \mathrm{eV}  \tag{23.123}\\
& E_{3 d}(\text { magnetic })=\frac{2 \pi \mu_{0} e^{2} \hbar^{2}}{m_{e}^{2}\left(r_{24}\right)^{3}}=\frac{8 \pi \mu_{0} \mu_{B}^{2}}{\left(1.33164 a_{0}\right)^{3}}=0.04845 \mathrm{eV} \tag{23.124}
\end{align*}
$$

The electrons from the $4 s$ and $3 d$ shells successively fill unoccupied HOs until the HO shell is filled with unpaired electrons, then the electrons pair per HO. In the case of the $F e 3 d 4 s$ shell having eight electrons and six orbitals, two sets of electrons are paired. Using Eqs. (15.15) and (23.118), the pairing energy is given by:

$$
\begin{equation*}
E_{3 d 4 s}(\text { magnetic })=-\frac{2 \pi \mu_{0} e^{2} \hbar^{2}}{m_{e}^{2}\left(r_{3 d 4 s}\right)^{3}}=-\frac{8 \pi \mu_{0} \mu_{B}^{2}}{\left(0.87516 a_{0}\right)^{3}}=-0.17069 \mathrm{eV} \tag{23.125}
\end{equation*}
$$

Thus, after Eq. (23.28), the energy $E(F e, 3 d 4 s)$ of the outer electron of the $F e 3 d 4 s$ shell is given by adding the magnetic energies of unpairing the $4 s$ (Eq. (23.122)) and $3 d$ electrons (Eq. (23.123)) and pairing of two sets of Fe3d $4 s$ electrons (Eq. (23.124)) to $E_{\text {Coulomb }}(F e, 3 d 4 s)$ (Eq. (23.119)).

$$
\begin{align*}
E(F e, 3 d 4 s) & =\frac{-e^{2}}{8 \pi \varepsilon_{0} r_{3 d 4 s}}+\frac{2 \pi \mu_{0} e^{2} \hbar^{2}}{m_{e}^{2} r_{4 s}^{3}}+\sum_{3 d \text { pairs }} \frac{2 \pi \mu_{0} e^{2} \hbar^{2}}{m_{e}^{2} r_{3 d}^{3}}-\sum_{H O \text { pairs }} \frac{2 \pi \mu_{0} e^{2} \hbar^{2}}{m_{e}^{2} r_{3 d 4 s}^{3}}  \tag{23.126}\\
& =-15.546725 \mathrm{eV}+0.02242 \mathrm{eV}+0.04845 \mathrm{eV}-2(0.17069 \mathrm{eV})=-15.81724 \mathrm{eV}
\end{align*}
$$

Next, consider the formation of the $\mathrm{Fe}-L$-bond MO wherein each iron atom has an Fe 3 d 4 s electron with an energy given by Eq. (23.125). The total energy of the state of each iron atom is given by the sum over the eight electrons. The sum $E_{T}\left(F e_{F e-L} 3 d 4 s\right)$ of energies of $F e 3 d 4 s$ (Eq. (23.125)), $F e^{+}, \mathrm{Fe}^{2+}, \mathrm{Fe}^{3+}, \mathrm{Fe}^{4+}, \mathrm{Fe}^{5+}, \mathrm{Fe}^{6+}$, and $\mathrm{Fe}^{7+}$ is:

$$
\begin{align*}
E_{T}\left(F e_{F e-L} 3 d 4 s\right) & =-\binom{151.06 \mathrm{eV}+124.98 \mathrm{eV}+99.1 \mathrm{eV}+75.0 \mathrm{eV}}{+54.8 \mathrm{eV}+30.652 \mathrm{eV}+16.1877 \mathrm{eV}+E(F e, 3 \mathrm{~d} 4 \mathrm{~s})}  \tag{23.127}\\
& =-\binom{151.06 \mathrm{eV}+124.98 \mathrm{eV}+99.1 \mathrm{eV}+75.0 \mathrm{eV}}{+54.8 \mathrm{eV}+30.652 \mathrm{eV}+16.1877 \mathrm{eV}+15.81724 \mathrm{eV}}=-567.59694 \mathrm{eV}
\end{align*}
$$

where $E(F e, 3 d 4 s)$ is the sum of the energy of $F e,-7.9024 \mathrm{eV}$, and the hybridization energy.
The iron HO donates an electron to each MO. Using Eq. (23.30), the radius $r_{3 d 4 s}$ of the $F e 3 d 4 s$ shell calculated from the Coulombic energy is:

$$
\begin{equation*}
r_{F e-L 3 d 4 s}=\left(\sum_{n=18}^{25}(Z-n)-1\right) \frac{e^{2}}{8 \pi \varepsilon_{0}(e 567.59694 \mathrm{eV})}=\frac{35 e^{2}}{8 \pi \varepsilon_{0}(e 567.59694 \mathrm{eV})}=0.83898 a_{0} \tag{23.128}
\end{equation*}
$$

Using Eqs. (15.19) and (23.127), the Coulombic energy $E_{\text {Coulomb }}\left(F e_{F e-L}, 3 d 4 s\right)$ of the outer electron of the $F e 3 d 4 s$ shell is

$$
\begin{equation*}
E_{\text {Coulomb }}\left(F e_{F e-L}, 3 d 4 s\right)=\frac{-e^{2}}{8 \pi \varepsilon_{0} r_{F e-L 3 d 4 s}}=\frac{-e^{2}}{8 \pi \varepsilon_{0} 0.83898 a_{0}}=-16.21706 \mathrm{eV} \tag{23.129}
\end{equation*}
$$

The magnetic energy terms are those for the unpairing of the $4 s$ and $3 d$ electrons (Eqs. (23.122) and (23.123), respectively) and paring two sets of Fe3d4s electrons (Eq. (23.124)). Using Eqs. (23.32), (23.128) and (23.122-23.124), the energy $E\left(F e_{F e-L}, 3 d 4 s\right)$ of the outer electron of the $F e 3 d 4 s$ shell is:

$$
\begin{align*}
E\left(F e_{F e-L}, 3 d 4 s\right) & =\frac{-e^{2}}{8 \pi \varepsilon_{0} r_{F e-L 3 d 4 s}}+\frac{2 \pi \mu_{0} e^{2} \hbar^{2}}{m_{e}^{2}\left(r_{26}\right)^{3}}+\frac{2 \pi \mu_{0} e^{2} \hbar^{2}}{m_{e}^{2}\left(r_{24}\right)^{3}}-2 \frac{2 \pi \mu_{0} e^{2} \hbar^{2}}{m_{e}^{2}\left(r_{3 d 4 s}\right)^{3}}  \tag{23.130}\\
& =-16.21706 \mathrm{eV}+0.02242 \mathrm{eV}+0.04845 \mathrm{eV}-2(0.17069 \mathrm{eV})=-16.48757 \mathrm{eV}
\end{align*}
$$

Thus, $E_{T}(\mathrm{Fe}-L, 3 d 4 s)$, the energy change of each Fe 3 d 4 s shell with the formation of the $\mathrm{Fe}-L$-bond MO is given by the difference between Eq. (23.129) and Eq. (23.125):

$$
\begin{equation*}
E_{T}(F e-L, 3 d 4 s)=E\left(F e_{F e-L}, 3 d 4 s\right)-E(F e, 3 d 4 s)=-16.48757 \mathrm{eV}-(-15.81724 \mathrm{eV})=-0.67033 \mathrm{eV} \tag{23.131}
\end{equation*}
$$

The semimajor axis $a$ solution given by Eq. (23.41) of the force balance equation, Eq. (23.39), for the $\sigma$-MO of the $\mathrm{Fe}-L$-bond MO of $\mathrm{Fe}_{n}$ is given in Table 23.36 with the force-equation parameters $Z=26, n_{e}$, and $L$ corresponding to the orbital and spin angular momentum terms of the $3 d 4 s$ HO shell. The semimajor axis $a$ of carbonyl and organometallic compounds are solved using Eq. (15.51).

For the $\mathrm{Fe}-L$ functional groups, hybridization of the $4 s$ and $3 d \mathrm{AOs}$ of Fe to form a single $3 d 4 s$ shell forms an energy minimum, and the sharing of electrons between the Fe3d4s HO and L AO to form a MO permits each participating orbital to decrease in radius and energy. The $F \mathrm{AO}$ has an energy of $E(F)=-17.42282 \mathrm{eV}$, the Cl AO has an energy of $E(C l)=-12.96764 \mathrm{eV}$, the $C_{\text {aryl }} 2 s p^{3} \mathrm{HO}$ has an energy of $E\left(C_{\text {aryl }}, 2 s p^{3}\right)=-15.76868 \mathrm{eV}$ (Eq. (14.246)), the C2sp ${ }^{3} \mathrm{HO}$ has an energy of $E\left(C, 2 s p^{3}\right)=-14.63489 \mathrm{eV}$ (Eq. (15.25)), the $O$ AO has an energy of $E(O)=-13.61805 \mathrm{eV}$, the Coulomb energy of Fe 3 d 4 s HO is $E_{\text {Coulomb }}(F e, 3 d 4 s)=-15.546725 \mathrm{eV}$ (Eq. (23.119)), and the Fe3d4s HO has an energy of $E(F e, 3 d 4 s)=-15.81724 \mathrm{eV}$ (Eq. (23.125)). To meet the equipotential condition of the union of the $\mathrm{Fe}-L \mathrm{H}_{2}$-type-ellipsoidal-MO with these orbitals, the hybridization factor(s), at least one of $c_{2}$ and $C_{2}$ of Eq. (15.61) for the Fe-L-bond MO given by Eq. (15.77) is:

$$
\begin{align*}
& c_{2}(F A O \text { to } F e 3 d 4 s H O)=C_{2}(F A O \text { to } F e 3 d 4 s H O)=\frac{E(F e, 3 d 4 s)}{E(F A O)}=\frac{-15.81724 \mathrm{eV}}{-17.42282 \mathrm{eV}}=0.90785  \tag{23.132}\\
& c_{2}(\mathrm{ClAO} \text { to } \mathrm{Fe} 3 \mathrm{~d} 4 \mathrm{sHO})=C_{2}(\mathrm{ClAO} \text { to } \mathrm{Fe} 3 \mathrm{~d} 4 \mathrm{sHO})=\frac{E(\mathrm{ClAO})}{E(F e, 3 d 4 \mathrm{~s})}=\frac{-12.96764 \mathrm{eV}}{-15.81724 \mathrm{eV}}=0.81984  \tag{23.133}\\
& c_{2}\left(C 2 s p^{3} \mathrm{HO} \text { to } \mathrm{Fe} 3 \mathrm{~d} 4 \mathrm{sHO}\right)=\frac{E\left(C, 2 s p^{3}\right)}{E_{\text {Coulomb }}(F e, 3 d 4 s)} c_{2}\left(C 2 s p^{3} \mathrm{HO}\right)=\frac{-14.63489 \mathrm{eV}}{-15.54673 \mathrm{eV}}(0.91771)=0.86389  \tag{23.134}\\
& c_{2}\left(C_{\text {aryl }} 2 s p^{3} \mathrm{HO} \text { to Fe3d } 4 \mathrm{sHO}\right)=\mathrm{C}_{2}\left(C_{\text {aryl }} 2 s p^{3} \mathrm{HO} \text { to } \mathrm{Fe} 3 \mathrm{~d} 4 \mathrm{sHO}\right) \\
& =\frac{E\left(C, 2 s p^{3}\right)}{E_{\text {Coulomb }}(F e, 3 d 4 s)} c_{2}\left(C_{\text {aryl }} 2 s p^{3} \mathrm{HO}\right)=\frac{-14.63489 \mathrm{eV}}{-15.54673 \mathrm{eV}}(0.85252)=0.80252  \tag{23.135}\\
& c_{2}(O \text { to } \mathrm{Fe} 3 d 4 \mathrm{sHO})=C_{2}(O \text { to } \mathrm{Fe} 3 d 4 \mathrm{sHO})=\frac{E(O)}{E(F e, 3 d 4 \mathrm{~s})}=\frac{-13.61805 \mathrm{eV}}{-15.81724 \mathrm{eV}}=0.86096 \tag{23.136}
\end{align*}
$$

where Eqs. (15.76), (15.79), and (13.430) were used in Eq. (23.133) and Eqs. (15.76), (15.79), and (14.417) were used in Eq. (23.134). Since the energy of the MO is matched to that of the Fe3d4s HO in coordinate compounds, $\mathrm{E}(\mathrm{AO} / \mathrm{HO})$ in Eq. (15.61) is $E(F e, 3 d 4 s)$ given by Eq. (23.125) and $E(A O / H O)$ in Eq. (15.61) of carbonyl and organometallic compounds is $E_{\text {Coulomb }}(F e, 3 d 4 s)$ given by Eq. (23.119). $\quad E_{T}\left(\right.$ atom-atom, $\left.m s p^{3} . A O\right)$ of the $\mathrm{Fe}-L$-bond MO is determined by considering that the bond involves an electron transfer from the iron atom to the ligand atom to form partial ionic character in the bond as in the case of the zwitterions such as $\mathrm{H}_{2} \mathrm{~B}^{+}-F^{-}$given in the Halido Boranes section. For the coordinate compounds, $E_{T}\left(\right.$ atom-atom, $\left.\mathrm{msp}^{3} . \mathrm{AO}\right)$ is -1.34066 eV , two times the energy of Eq. (23.130). For the $\mathrm{Fe}-\mathrm{C}$ bonds of carbonyl and organometallic compounds, $E_{T}\left(\right.$ atom-atom, $\left.m s p^{3} . A O\right)$ is -1.44915 eV (Eq. (14.151)), and the $C=O$ functional group of carbonyls is equivalent to that of vanadium carbonyls. The aromatic cyclopentadienyl moieties of organometallic $\mathrm{Fe}\left(\mathrm{C}_{5} \mathrm{H}_{5}\right)_{2}$ comprise $C \stackrel{3 e}{=} C$ and $C H$ functional groups that are equivalent to those given in the Aromatic and Heterocyclic Compounds section.

The symbols of the functional groups of iron coordinate compounds are given in Table 23.35. The geometrical (Eqs. (15.1-15.5) and (23.41)), intercept (Eqs. (15.31-15.32) and (15.80-15.87)), and energy (Eqs. (15.61) and (23.28-23.33)) parameters of iron coordinate compounds are given in Tables 23.36, 23.37, and 23.38, respectively. The total energy of each iron coordinate compound given in Table 23.39 was calculated as the sum over the integer multiple of each $E_{D}$ (Group) of Table 23.38 corresponding to functional-group composition of the compound. The charge-densities of exemplary iron carbonyl and organometallic compounds, iron pentacarbonyl $\left(\mathrm{Fe}(\mathrm{CO})_{5}\right)$ and bis-cylopentadienyl iron or ferrocene ( $\mathrm{Fe}\left(\mathrm{C}_{5} \mathrm{H}_{5}\right)_{2}$ ) comprising the concentric shells of atoms with the outer shell bridged by one or more $\mathrm{H}_{2}$-type ellipsoidal MOs or joined with one or more hydrogen MOs are shown in Figures 23.7 and 23.8, respectively.

Figure 23.7. Iron Pentacarbonyl. Color scale, translucent view of the charge-density of $\mathrm{Fe}(\mathrm{CO})_{5}$ showing the orbitals of the $\mathrm{Fe}, \mathrm{C}$, and O atoms at their radii, the ellipsoidal surface of each $\mathrm{H}_{2}$-type ellipsoidal MO that transitions to the corresponding outer shell of the atoms participating in each bond, and the nuclei (red, not to scale).


0

Figure 23.8. Bis-cylopentadienyl Iron. Color scale, opaque view of the charge-density of $\mathrm{Fe}\left(\mathrm{C}_{5} \mathrm{H}_{5}\right)_{2}$ showing the orbitals of the Fe and C atoms at their radii and the ellipsoidal surface of each H or $\mathrm{H}_{2}$-type ellipsoidal MO that transitions to the corresponding outer shell of the atoms participating in each bond.


Table 23.35. The symbols of the functional groups of iron coordinate compounds.

| Functional Group | Group Symbol |
| :---: | :---: |
| FeF group of FeF | $F e-F$ (a) |
| $\mathrm{FeF}_{2}$ group of $\mathrm{FeF}_{2}$ | $F e-F(b)$ |
| $\mathrm{FeF}_{3}$ group of $\mathrm{FeF}_{3}$ | $F e-F$ (c) |
| FeCl group of FeCl | $\mathrm{Fe}-\mathrm{Cl}$ (a) |
| $\mathrm{FeCl}_{2}$ group of $\mathrm{FeCl}_{2}$ | $\mathrm{Fe}-\mathrm{Cl}$ (b) |
| $\mathrm{FeCl}_{3}$ group of $\mathrm{FeCl}_{3}$ | $\mathrm{Fe}-\mathrm{Cl}$ (c) |
| FeO group of FeO | $\mathrm{Fe}-\mathrm{O}$ |
| FeCO group of $\mathrm{Fe}(\mathrm{CO})_{5}$ | $\mathrm{Fe}-\mathrm{CO}$ |
| $C=O$ | $C=O$ |
| FeCaryl group of $\mathrm{Fe}\left(\mathrm{C}_{5} \mathrm{H}_{5}\right)_{2}$ | $\mathrm{Fe}-\mathrm{C}_{5} \mathrm{H}_{5}$ |
| CC (aromatic bond) | $C \stackrel{3 e}{=} C$ |
| CH (aromatic) | CH |

Table 23.36. The geometrical bond parameters of iron coordinate compounds and experimental values.

| Parameter | $\begin{gathered} F e-F(\text { a }) \\ \text { Group } \end{gathered}$ | $\begin{gathered} F e-F \text { (b) } \\ \text { Group } \end{gathered}$ | $\begin{gathered} F e-F(c) \\ \text { Group } \end{gathered}$ | $\begin{gathered} \mathrm{Fe}-\mathrm{Cl}(\mathrm{a}) \\ \text { Group } \end{gathered}$ | $\begin{gathered} \mathrm{Fe}-\mathrm{Cl}(\mathrm{~b}) \\ \text { Group } \end{gathered}$ | $\begin{gathered} \mathrm{Fe}-\mathrm{Cl}(\mathrm{c}) \\ \text { Group } \end{gathered}$ | $\begin{aligned} & \mathrm{Fe}-\mathrm{O} \\ & \text { Group } \end{aligned}$ | $\begin{gathered} \mathrm{Fe}-\mathrm{CO} \\ \text { Group } \end{gathered}$ | $\begin{aligned} & C=O \\ & \text { Group } \end{aligned}$ | $\begin{gathered} \mathrm{Fe}-\mathrm{C}_{5} \mathrm{H}_{5} \\ \text { Group } \end{gathered}$ | $\begin{aligned} & C^{3 e}=C \\ & \text { Group } \end{aligned}$ | $\begin{gathered} \mathrm{CH} \\ \text { Group } \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $n_{\text {e }}$ | 2 | 2 | 2 | 3 | 3 | 3 | 2 |  |  |  |  |  |
| $L$ | $4+\sqrt{\frac{3}{4}}$ | $5 \sqrt{\frac{3}{4}}$ | $5 \sqrt{\frac{3}{4}}$ | $\sqrt[3]{\frac{3}{4}}$ | 0 | $\sqrt{\frac{3}{4}}$ | $4 \sqrt{\frac{3}{4}}$ |  |  |  |  |  |
| $a\left(a_{0}\right)$ | 2.18715 | 2.16654 | 2.16654 | 2.59993 | 2.50000 | 2.53331 | 2.13323 | 2.18970 | 1.184842 | 2.33324 | 1.47348 | 1.60061 |
| $c^{\prime}\left(a_{0}\right)$ | 1.79227 | 1.78380 | 1.78380 | 2.05629 | 2.01639 | 2.02978 | 1.57408 | 1.70868 | 1.08850 | 1.96889 | 1.31468 | 1.03299 |
| $\begin{aligned} & \text { Bond Length } \\ & 2 c^{\prime}(A) \\ & \hline \end{aligned}$ | 1.89685 | 1.88790 | 1.88790 | 2.17628 | 2.13405 | 2.14822 | 1.66594 | 1.80839 | 1.15202 | 2.08379 | 1.39140 | 1.09327 |
| Exp. Bond Length (A) | $\begin{gathered} 1.80[15] \\ \left(F e F_{n} n=1,2,3\right) \end{gathered}$ | $\begin{gathered} 1.80[15] \\ \left(F e F_{n} n=1,2,3\right) \end{gathered}$ | $\begin{gathered} 1.80[15] \\ \left(F e F_{n} n=1,2,3\right) \end{gathered}$ | ${ }_{(\mathrm{FeCl})}^{2.09[15]}$ | $\begin{gathered} 2.09[15] \\ (\mathrm{FeCl}) \\ 2.17[50] \\ \left(\mathrm{FCl}_{n} n=2,3\right) \end{gathered}$ | $2.09[15]$ $(\mathrm{FeCl})$ $2.17[50]$ $\left(F C l_{n} \quad n=2,3\right)$ | $\begin{gathered} 1.619[15] \\ (\mathrm{FeO}) \end{gathered}$ | $1.806[29]$ $\left(\mathrm{Fe}(\mathrm{CO})_{5} \mathrm{Fe}-\mathrm{CO}\right.$ equatorial $)$ $1.833[29]$ $\left(\mathrm{Fe}(\mathrm{CO})_{5} \mathrm{Fe}-\mathrm{CO}\right.$ axial $)$ $1.82[9-22]$ $\left(\mathrm{Fe}(\mathrm{CO})_{5} \mathrm{Fe}-\mathrm{CO}\right.$ avg. $)$ $0.020[3]$ $\left(\mathrm{Fe}(\mathrm{CO})_{5}\right.$ $(\mathrm{Fe}-\mathrm{CO}$ equatorial-Fe-CO axial $)$ | $\begin{gathered} 1.145[29] \\ \left(\mathrm{Fe}(\mathrm{CO})_{s}\right) \end{gathered}$ | $\begin{gathered} 2.064[3] \\ \left(\mathrm{Fe}\left(\mathrm{C}_{5} H_{5}\right)_{2}\right) \end{gathered}$ | $\begin{aligned} & 1.399[3] \\ & \text { (benzene) } \end{aligned}$ | $\begin{aligned} & 1.101 \text { [3] } \\ & \text { (benzene) } \end{aligned}$ |
| $b, c\left(a_{0}\right)$ | 1.25356 | 1.22962 | 1.22962 | 1.59100 | 1.47790 | 1.51580 | 1.43978 | 1.36937 | 0.46798 | 1.25199 | 0.66540 | 1.22265 |
| $e$ | 0.81945 | 0.82334 | 0.82334 | 0.79090 | 0.80656 | 0.80124 | 0.73788 | 0.78033 | 0.91869 | 0.84384 | 0.89223 | 0.64537 |

Table 23.37. The MO to HO intercept geometrical bond parameters of iron coordinate compounds. $E_{T}$ is $E_{T}$ (atom-atom,HO.AO).

Table 23.38. The energy parameters $(\mathrm{eV})$ of functional groups of iron coordinate compounds.

Table 23.39. The total bond energies of gaseous-state iron coordinate compounds calculated using the functional group composition and the energies of Table 23.38 compared to the gaseous-state experimental values.

$$
4-1+1+0
$$

## COBALT FUNCTIONAL GROUPS AND MOLECULES

The electron configuration of cobalt is $[A r] 4 s^{2} 3 d^{7}$ having the corresponding term ${ }^{4} F_{9 / 2}$. The total energy of the state is given by the sum over the nine electrons. The sum $E_{T}(\mathrm{Co}, 3 \mathrm{~d} 4 \mathrm{~s})$ of experimental energies $[1]$ of $\mathrm{Co}, \mathrm{Co}^{+}, \mathrm{Co}^{2+}, \mathrm{Co}^{3+}, \mathrm{Co}^{4+}, \mathrm{Co}^{5+}$, $\mathrm{Co}^{6+}, \mathrm{Co}^{7+}$, and $\mathrm{Co}^{8+}$ is:

$$
\begin{equation*}
E_{T}(C o, 3 d 4 s)=-\binom{186.13 \mathrm{eV}+157.8 \mathrm{eV}+128.9 \mathrm{eV}+102.0 \mathrm{eV}+79.5 \mathrm{eV}}{+51.3 \mathrm{eV}+33.50 \mathrm{eV}+17.084 \mathrm{eV}+7.88101 \mathrm{eV}}=-764.09501 \mathrm{eV} \tag{23.137}
\end{equation*}
$$

By considering that the central field decreases by an integer for each successive electron of the shell, the radius $r_{3 d 4 s}$ of the Co3d4s shell may be calculated from the Coulombic energy using Eq. (15.13).

$$
\begin{equation*}
r_{3 d 4 s}=\sum_{n=18}^{26} \frac{(Z-n) e^{2}}{8 \pi \varepsilon_{0}(e 764.09501 \mathrm{eV})}=\frac{45 e^{2}}{8 \pi \varepsilon_{0}(e 764.09501 \mathrm{eV})}=0.80129 a_{0} \tag{23.138}
\end{equation*}
$$

where $Z=27$ for cobalt. Using Eq. (15.14), the Coulombic energy $E_{\text {Coulomb }}(C o, 3 d 4 s)$ of the outer electron of the Co3d $4 s$ shell is

$$
\begin{equation*}
E_{\text {Coulomb }}(\text { Co }, 3 d 4 \mathrm{~s})=\frac{-e^{2}}{8 \pi \varepsilon_{0} r_{3 d 4 \mathrm{~s}}}=\frac{-e^{2}}{8 \pi \varepsilon_{0} 0.80129 a_{0}}=-16.979889 \mathrm{eV} \tag{23.139}
\end{equation*}
$$

During hybridization, the spin-paired $4 s$ electrons and the two sets of paired $3 d$ electrons are promoted to the Co3d4s shell as initially unpaired electrons. The energies for the promotions are given by Eq. (15.15) at the initial radii of the $4 s$ and $3 d$ electrons. From Eq. (10.102) with $Z=27$ and $n=27$, the radius $r_{27}$ of the Co4s shell is:

$$
\begin{equation*}
r_{27}=1.72640 a_{0} \tag{23.140}
\end{equation*}
$$

and with $Z=27$ and $n=25$, the radius $r_{25}$ of the Co3d shell is:

$$
\begin{equation*}
r_{25}=1.21843 a_{0} \tag{23.141}
\end{equation*}
$$

Using Eqs. (15.15), (23.139), and (23.140), the unpairing energies are:

$$
\begin{align*}
& E_{4 \mathrm{~s}}(\text { magnetic })=\frac{2 \pi \mu_{0} e^{2} \hbar^{2}}{m_{e}^{2}\left(r_{27}\right)^{3}}=\frac{8 \pi \mu_{0} \mu_{B}^{2}}{\left(1.72640 a_{0}\right)^{3}}=0.02224 \mathrm{eV}  \tag{23.142}\\
& E_{3 d}(\text { magnetic })=\frac{2 \pi \mu_{0} e^{2} \hbar^{2}}{m_{e}^{2}\left(r_{25}\right)^{3}}=\frac{8 \pi \mu_{0} \mu_{B}^{2}}{\left(1.21843 a_{0}\right)^{3}}=0.06325 \mathrm{eV} \tag{23.143}
\end{align*}
$$

The electrons from the $4 s$ and $3 d$ shells successively fill unoccupied HOs until the HO shell is filled with unpaired electrons, then the electrons pair per HO. In the case of the Co3d $4 s$ shell having nine electrons and six orbitals, three sets of electrons are paired. Using Eqs. (15.15) and (23.137), the pairing energy is given by:

$$
\begin{equation*}
E_{3 d 4 s}(\text { magnetic })=-\frac{2 \pi \mu_{0} e^{2} \hbar^{2}}{m_{e}^{2}\left(r_{3 d 4 s}\right)^{3}}=-\frac{8 \pi \mu_{0} \mu_{B}^{2}}{\left(0.80129 a_{0}\right)^{3}}=-0.22238 \mathrm{eV} \tag{23.144}
\end{equation*}
$$

Thus, after Eq. (23.28), the energy $E(C o, 3 d 4 s)$ of the outer electron of the $C o 3 d 4 s$ shell is given by adding the magnetic energies of unpairing the $4 s$ (Eq. (23.141)) and 3d electrons (Eq. (23.142)) and pairing of three sets of Co3d4s electrons (Eq. (23.143)) to $E_{\text {Coulomb }}(C o, 3 d 4 s)$ (Eq. (23.138)).

$$
\begin{align*}
E(C o, 3 d 4 s) & =\frac{-e^{2}}{8 \pi \varepsilon_{0} r_{3 d 4 s}}+\frac{2 \pi \mu_{0} e^{2} \hbar^{2}}{m_{e}^{2} r_{4 s}^{3}}+\sum_{3 d \text { pairs }} \frac{2 \pi \mu_{0} e^{2} \hbar^{2}}{m_{e}^{2} r_{3 d}^{3}}-\sum_{\text {HO pairs }} \frac{2 \pi \mu_{0} e^{2} \hbar^{2}}{m_{e}^{2} r_{3 d 4 s}^{3}}  \tag{23.145}\\
& =-16.979889 \mathrm{eV}+0.02224 \mathrm{eV}+2(0.06325 \mathrm{eV})-3(0.22238 \mathrm{eV})=-17.49830 \mathrm{eV}
\end{align*}
$$

Next, consider the formation of the $C o-L$-bond MO wherein each cobalt atom has an Co3d4s electron with an energy given by Eq. (23.144). The total energy of the state of each cobalt atom is given by the sum over the nine electrons. The sum $E_{T}\left(\mathrm{Co}_{\mathrm{Co-L}} 3 \mathrm{~d} 4 \mathrm{~s}\right)$ of energies of $\mathrm{Co3d} 4 \mathrm{~s}$ (Eq. (23.144)), $\mathrm{Co}^{+}, \mathrm{Co}^{2+}, \mathrm{Co}^{3+}, \mathrm{Co}^{4+}, \mathrm{Co}^{5+}, \mathrm{Co}^{6+}, \mathrm{Co}^{7+}$, and $\mathrm{Co}^{8+}$ is:

$$
\begin{align*}
E_{T}\left(C o_{C o-L} 3 d 4 s\right) & =-\binom{186.13 \mathrm{eV}+157.8 \mathrm{eV}+128.9 \mathrm{eV}+102.0 \mathrm{eV}+79.5 \mathrm{eV}}{+51.3 \mathrm{eV}+33.50 \mathrm{eV}+17.084 \mathrm{eV}+E(C o, 3 d 4 s)}  \tag{23.146}\\
& =-\binom{186.13 \mathrm{eV}+157.8 \mathrm{eV}+128.9 \mathrm{eV}+102.0 \mathrm{eV}+79.5 \mathrm{eV}}{+51.3 \mathrm{eV}+33.50 \mathrm{eV}+17.084 \mathrm{eV}+17.49830 \mathrm{eV}}=-773.71230 \mathrm{eV}
\end{align*}
$$

where $E(C o, 3 d 4 s)$ is the sum of the energy of $C o,-7.88101 \mathrm{eV}$, and the hybridization energy.
The cobalt HO donates an electron to each MO. Using Eq. (23.30), the radius $r_{3 d 4 s}$ of the Co3d $4 s$ shell calculated from the Coulombic energy is:

$$
\begin{equation*}
r_{C o-L 3 d 4 s}=\left(\sum_{n=18}^{26}(Z-n)-1\right) \frac{e^{2}}{8 \pi \varepsilon_{0}(e 773.71230 e V)}=\frac{44 e^{2}}{8 \pi \varepsilon_{0}(e 773.71230 e V)}=0.77374 a_{0} \tag{23.147}
\end{equation*}
$$

Using Eqs. (15.19) and (23.146), the Coulombic energy $E_{\text {Coulomb }}\left(C o_{C o-L}, 3 d 4 s\right)$ of the outer electron of the Co3d $4 s$ shell is:

$$
\begin{equation*}
E_{\text {Coulomb }}\left(\text { Co }_{\text {Co-L }}, 3 d 4 s\right)=\frac{-e^{2}}{8 \pi \varepsilon_{0} r_{C o-L 3 d 4 s}}=\frac{-e^{2}}{8 \pi \varepsilon_{0} 0.77374 a_{0}}=-17.58437 \mathrm{eV} \tag{23.148}
\end{equation*}
$$

The magnetic energy terms are those for the unpairing of the $4 s$ and $3 d$ electrons (Eqs. (23.141) and (23.142), respectively) and paring three sets of Co3d4s electrons (Eq. (23.143)). Using Eqs. (23.32), (23.148) and (23.141-23.143), the energy $E\left(C o_{C o-L}, 3 d 4 s\right)$ of the outer electron of the Co3d $4 s$ shell is:

$$
\begin{align*}
E\left(C o_{C o-L}, 3 d 4 s\right) & =\frac{-e^{2}}{8 \pi \varepsilon_{0} r_{\text {Fe-L3d4s }}}+\frac{2 \pi \mu_{0} e^{2} \hbar^{2}}{m_{e}^{2}\left(r_{27}\right)^{3}}+\frac{2 \pi \mu_{0} e^{2} \hbar^{2}}{m_{e}^{2}\left(r_{25}\right)^{3}}-3 \frac{2 \pi \mu_{0} e^{2} \hbar^{2}}{m_{e}^{2}\left(r_{3 d 4 s}\right)^{3}}  \tag{23.149}\\
& =-17.58437 \mathrm{eV}+0.02224 \mathrm{eV}+2(0.06325 \mathrm{eV})-3(0.22238 \mathrm{eV})=-18.10278 \mathrm{eV}
\end{align*}
$$

Thus, $E_{T}(C o-L, 3 d 4 s)$, the energy change of each $C o 3 d 4 s$ shell with the formation of the $C o-L$-bond MO is given by the difference between Eq. (23.148) and Eq. (23.144):

$$
\begin{equation*}
E_{T}(C o-L, 3 d 4 s)=E\left(C o_{C o-L}, 3 d 4 s\right)-E(C o, 3 d 4 s)=-18.10278 \mathrm{eV}-(-17.49830 \mathrm{eV})=-0.60448 \mathrm{eV} \tag{23.150}
\end{equation*}
$$

The semimajor axis $a$ solution given by Eq. (23.41) of the force balance equation, Eq. (23.39), for the $\sigma$-MO of the $C o-L$-bond MO of $\mathrm{CoL}_{n}$ is given in Table 23.41 with the force-equation parameters $Z=27, n_{e}$, and $L$ corresponding to the orbital and spin angular momentum terms of the $3 d 4 \mathrm{~s} \mathrm{HO}$ shell. The semimajor axis $a$ of carbonyl and organometallic compounds are solved using Eq. (15.51).

For the Co-L functional groups, hybridization of the $4 s$ and $3 d$ AOs of Co to form a single $3 d 4 s$ shell forms an energy minimum, and the sharing of electrons between the Co3d4s HO and $L \mathrm{AO}$ to form a MO permits each participating orbital to decrease in radius and energy. The $F \mathrm{AO}$ has an energy of $E(F)=-17.42282 \mathrm{eV}$, the Cl AO has an energy of $E(C l)=-12.96764 \mathrm{eV}$, the $C 2 s p^{3} \mathrm{HO}$ has an energy of $E\left(C, 2 s p^{3}\right)=-14.63489 \mathrm{eV}$ (Eq. (15.25)), the Coulomb energy of Co3d4s HO is $E_{\text {Coulomb }}(C o, 3 d 4 s)=-16.979889 \mathrm{eV}$ (Eq. (23.138)), 13.605804 eV is the magnitude of the Coulombic energy between the electron and proton of $H$ (Eq. (1.264)), and the Co3d4s HO has an energy of $E(C o, 3 d 4 s)=-17.49830 \mathrm{eV}$ (Eq. (23.144)). To meet the equipotential condition of the union of the $\mathrm{Co}-\mathrm{L} \mathrm{H}_{2}$-type-ellipsoidal-MO with these orbitals, the hybridization factor(s), at least one of $c_{2}$ and $C_{2}$ of Eq. (15.61) for the Co - $L$-bond MO given by Eq. (15.77) is:

$$
\begin{align*}
& c_{2}(\text { FAO to Co3d } 4 \mathrm{sHO})=\frac{E(F A O)}{E(C o, 3 d 4 s)}=\frac{-17.42282 \mathrm{eV}}{-17.49830 \mathrm{eV}}=0.99569  \tag{23.151}\\
& C_{2}(\mathrm{ClAO} \text { to Co3d } 4 \mathrm{sHO})=\frac{E(C l A O)}{E(C o, 3 d 4 s)}=\frac{-12.96764 \mathrm{eV}}{-17.49830 \mathrm{eV}}=0.74108  \tag{23.152}\\
& c_{2}\left(\mathrm{C} 2 \mathrm{sp}{ }^{3} \mathrm{HO} \text { to Co3d } 4 \mathrm{sHO}\right)=\frac{E\left(C, 2 s p^{3}\right)}{E_{\text {Coulomb }}(\mathrm{Co}, 3 d 4 \mathrm{~s})} c_{2}\left(\mathrm{C} 2 \mathrm{sp}{ }^{3} \mathrm{HO}\right)=\frac{-14.63489 \mathrm{eV}}{-16.97989 \mathrm{eV}}(0.91771)=0.79097  \tag{23.153}\\
& c_{2}(\mathrm{HAO} \text { to Co3d } 4 \mathrm{sHO})=C_{2}(\mathrm{HAO} \text { to Co3d } 4 \mathrm{sHO})=\frac{E(\mathrm{H})}{E_{\text {Coulomb }}(\mathrm{Co}, 3 d 4 \mathrm{~s})}=\frac{-13.605804 \mathrm{eV}}{-16.97989 \mathrm{eV}}=0.80129 \tag{23.154}
\end{align*}
$$

where Eqs. (15.76), (15.79), and (13.430) were used in Eq. (23.152) and Eq. (15.71) was used in Eq. (23.153). Since the energy of the MO is matched to that of the $\mathrm{Co} 3 d 4 \mathrm{~s} \mathrm{HO}$ in coordinate compounds, $E(A O / H O)$ in Eq. (15.61) is $E(C o, 3 d 4 s)$ given by Eq. (23.144) and $E(A O / H O)$ in Eq. (15.61) of carbonyl compounds is $E_{\text {Coulomb }}(C o, 3 d 4 s)$ given by Eq. (23.138). $E_{T}\left(\right.$ atom-atom, $\left.m s p^{3} . A O\right)$ of the $C o-L$-bond MO is determined by considering that the bond involves an electron transfer from the cobalt atom to the ligand atom to form partial ionic character in the bond as in the case of the zwitterions such as $\mathrm{H}_{2} \mathrm{~B}^{+}-\mathrm{F}^{-}$given in the Halido Boranes section. For the coordinate compounds, $E_{T}\left(\right.$ atom - atom, $\left.m s p^{3} . A O\right)$ is -1.20896 eV , two times the energy of Eq. (23.149). For the $C o-C$ bonds of carbonyl compounds, $E_{T}\left(\right.$ atom-atom, msp $\left.{ }^{3} . A O\right)$ is -1.13379 eV (Eq. (14.247)), and the $C=O$ functional group of carbonyls is equivalent to that of vanadium carbonyls.

The symbols of the functional groups of cobalt coordinate compounds are given in Table 23.40. The geometrical (Eqs. (15.1-15.5) and (23.41)), intercept (Eqs. (15.31-15.32) and (15.80-15.87)), and energy (Eqs. (15.61) and (23.28-23.33)) parameters of cobalt coordinate compounds are given in Tables 23.41, 23.42, and 23.43, respectively. The total energy of each cobalt coordinate compound given in Table 23.44 was calculated as the sum over the integer multiple of each $E_{D}$ (Group) of Table 23.43 corresponding to functional-group composition of the compound. The charge-densities of exemplary cobalt carbonyl compound, cobalt tetracarbonyl hydride $\left(\mathrm{CoH}(\mathrm{CO})_{4}\right)$ comprising the concentric shells of atoms with the outer shell bridged by one or more $\mathrm{H}_{2}$-type ellipsoidal MOs or joined with one or more hydrogen MOs is shown in Figure 23.9.

Figure 23.9. Cobalt Tetracarbonyl Hydride. Color scale, translucent view of the charge-density of $\mathrm{CoH}(\mathrm{CO})_{4}$ showing the orbitals of the $\mathrm{Co}, \mathrm{C}$, and O atoms at their radii, the ellipsoidal surface of each H or $\mathrm{H}_{2}$-type ellipsoidal MO that transitions to the corresponding outer shell of the atoms participating in each bond, and the nuclei (red, not to scale).


Table 23.40. The symbols of the functional groups of cobalt coordinate compounds.

| Functional Group | Group Symbol |
| :--- | :--- |
| $\mathrm{CoF}_{2}$ group of CoF | 2 |
| CoCl group of CoCl | $\mathrm{Co}-\mathrm{F}$ |
| $\mathrm{CoCl}_{2}$ group of $\mathrm{CoCl}_{2}$ | $\mathrm{Co}-\mathrm{Cl}$ (a) |
| $\mathrm{CoCl}_{3}$ group of $\mathrm{CoCl}_{3}$ | $\mathrm{Co}-\mathrm{Cl}$ (b) |
| CoH group of $\mathrm{CoH}(\mathrm{CO})_{4}$ | $\mathrm{Co}-\mathrm{Cl} \mathrm{(c)}$ |
| CoCO group of $\mathrm{CoH}(\mathrm{CO})_{4}$ | $\mathrm{Co}-\mathrm{H}$ |
| $\mathrm{C=O}$ | $\mathrm{Co}-\mathrm{CO}$ |

Table 23.41. The geometrical bond parameters of cobalt coordinate compounds and experimental values.

| Parameter | $C o-F$ <br> Group | $C o-C l(a)$ <br> Group | $C o-C l(b)$ <br> Group | $C o-C l(c)$ <br> Group | $C o-H$ <br> Group | $C o-C O$ <br> Group | $C=O$ <br> Group |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $n_{e}$ | 2 | 3 | 3 | 3 | 1 |  |  |
| $L$ | $7 \sqrt{\frac{3}{4}}$ | $4+3 \sqrt{\frac{3}{4}}$ | $2+4 \sqrt{\frac{3}{4}}$ | $6+2 \sqrt{\frac{3}{4}}$ | $5 \sqrt{\frac{3}{4}}$ |  |  |
| $a\left(a_{0}\right)$ | 2.22453 | 2.74437 | 2.70237 | 2.78637 | 1.66038 | 2.25172 | 1.184842 |
| $c^{\prime}\left(a_{0}\right)$ | 1.72222 | 1.92437 | 1.90959 | 1.93904 | 1.43949 | 1.73271 | 1.08850 |
| Bond Length <br> $2 c^{\prime}(\AA)$ | 1.82272 | 2.03667 | 2.02102 | 2.05219 | 1.52349 | 1.83382 | 1.15202 |
| Exp. Bond <br> Length <br> $(\AA)$ | $1.72[54]$ |  |  |  |  |  |  |
| $\left(C o F_{2}\right)$ | $2.09[15]$ | $(C o C l)$ | $2.09[15]$ | $2.09[15]$ | $1.542[3]$ | $1.82[55]$ | $1.145[29]$ |
| $(C o C l)$ | $(C o C l)$ | $(C o H)$ | $\left(N i(C O)_{4}\right)$ | $\left(F e(C O)_{5}\right)$ |  |  |  |
| $b, c\left(a_{0}\right)$ | 1.40801 | 1.95662 | 1.91214 | 2.00100 | 0.82748 | 1.43804 | 0.46798 |
| $e$ | 0.77420 | 0.70121 | 0.70663 | 0.69590 | 0.86697 | 0.76951 | 0.91869 |

Table 23.42. The MO to HO intercept geometrical bond parameters of cobalt coordinate compounds. $E_{T}$ is $E_{T}$ (atom-atom,HO.AO).

| Bond | Atom | $\begin{gathered} E_{T} \\ (\mathrm{eV}) \\ \text { Bond } 1 \end{gathered}$ | $\begin{gathered} E_{T} \\ (\mathrm{eV}) \\ \text { Bond } 2 \end{gathered}$ | $\begin{gathered} E_{T} \\ (\mathrm{eV}) \\ \text { Bond 3 } \end{gathered}$ | $\begin{gathered} E_{T} \\ (\mathrm{eV}) \\ \text { Bond } 4 \end{gathered}$ | $\begin{gathered} E_{T} \\ (\mathrm{eV}) \\ \text { Bond } 5 \end{gathered}$ | Final Total Energy Co3d4s (eV) | $\begin{aligned} & r_{\text {minualal }}\left(a_{0}\right) \end{aligned}$ | $\begin{aligned} & r_{\text {final }} \\ & \left(a_{0}\right) \end{aligned}$ | $\begin{gathered} E_{\text {Coulomemb }}(\operatorname{Co3} d 4 s) \\ (\mathrm{eV}) \\ \text { Final } \end{gathered}$ | $\begin{gathered} E(\operatorname{Co3} d 4 s) \\ (\mathrm{eV}) \\ \text { Final } \end{gathered}$ | $\left(^{\circ}\right)$ | $\begin{aligned} & \theta_{1} \\ & \left({ }^{\circ}\right) \end{aligned}$ | $\begin{aligned} & \theta_{2} \\ & \left({ }^{\circ}\right) \end{aligned}$ | $\begin{gathered} d_{1} \\ \left(a_{0}\right) \end{gathered}$ | $\begin{gathered} d_{2} \\ \left(a_{0}\right) \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Co-F ( $\mathrm{CoF}_{2}$ ) | Co | -0.60448 | -0.60448 | 0 | 0 | 0 |  | 0.80129 | 0.74803 | -18.18885 |  | 75.69 | 104.31 | 30.98 | 1.90713 | 0.18492 |
| $\mathrm{Co}-\mathrm{F}\left(\mathrm{CoF}_{2}\right)$ | F | -0.60448 | 0 | 0 | 0 | 0 |  | 0.78069 | 0.75473 | -18.02730 |  | 76.49 | 103.51 | 31.41 | 1.89848 | 0.17626 |
| $\mathrm{Co}-\mathrm{Cl}(\mathrm{CoCl})$ | Co | -0.60448 | 0 | 0 | 0 | 0 |  | 0.80129 | 0.77374 | -17.58437 |  |  |  |  |  |  |
| $\mathrm{Co}-\mathrm{Cl}(\mathrm{CoCl})$ | Cl | -0.60448 | 0 | 0 | 0 | 0 |  | 1.05158 | 1.00248 | -13.57212 |  | 56.06 | 123.94 | 25.15 | 2.48414 | 0.55976 |
| $\mathrm{Co}-\mathrm{Cl}\left(\mathrm{CoCl}_{2}\right)$ | Co | -0.60448 | -0.60448 | 0 | 0 | 0 |  | 0.80129 | 0.74803 | -18.18885 |  |  |  |  |  |  |
| $\mathrm{Co}-\mathrm{Cl}\left(\mathrm{CoCl}_{2}\right)$ | Cl | -0.60448 | 0 | 0 | 0 | 0 |  | 1.05158 | 1.00248 | -13.57212 |  | 60.34 | 119.66 | 27.10 | 2.40562 | 0.49603 |
| $\mathrm{Co}-\mathrm{Cl}\left(\mathrm{CoCl}_{3}\right)$ | Co | -0.60448 | -0.60448 | -0.60448 | 0 | 0 |  | 0.80129 | 0.72397 | -18.79333 |  |  |  |  |  |  |
| $\mathrm{Co}-\mathrm{Cl}\left(\mathrm{CoCl}_{3}\right)$ | Cl | -0.60448 | 0 | 0 | 0 | 0 |  | 1.05158 | 1.00248 | -13.57212 |  | 51.48 | 128.52 | 23.08 | 2.56342 | 0.62438 |
| $\mathrm{CoC}=O$ | O | -1.79278 | 0 | 0 | 0 | 0 |  | 1.00000 | 0.81871 | -16.61853 |  | 147.43 | 32.57 | 70.34 | 0.39853 | 0.68997 |
| $\mathrm{CoC}=\mathrm{O}$ | C | -1.79278 | -0.56690 | 0 | 0 | 0 | -153.97537 | 0.91771 | 0.79171 | -17.18543 | -16.99457 | 146.55 | 33.45 | 68.83 | 0.42793 | 0.66057 |
| $\mathrm{Co}-\mathrm{CO}\left(\mathrm{CoH}(\mathrm{CO})_{4}\right)$ | C | -0.56690 | -1.79278 | 0 | 0 | 0 |  | 0.91771 | 0.79171 | -17.18543 | -16.99457 | 78.00 | 102.00 | 32.58 | 1.89734 | 0.16463 |
| $\mathrm{Co}-\mathrm{CO}\left(\mathrm{CoH}(\mathrm{CO})_{4}\right)$ | Co | -0.56690 | -0.56690 | -0.56690 | -0.56690 | 0 |  | 0.80129 | 0.79597 | -17.09334 |  | 78.47 | 101.53 | 32.84 | 1.89180 | 0.15908 |
| $\mathrm{Co}-\mathrm{H}$ | Co | 0 | -0.56690 | -0.56690 | -0.56690 | -0.56690 |  | 0.80129 | 0.70689 | -19.24748 |  | 118.72 | 61.28 | 48.52 | 1.09980 | 0.33969 |

Table 23.43. The energy parameters (eV) of functional groups of cobalt coordinate compounds.

| Parameters | $\begin{aligned} & C o-F \\ & \text { Group } \end{aligned}$ | Co-Cl <br> (a) <br> Group | $\mathrm{Co}-\mathrm{Cl}$ <br> (b) <br> Group | $\mathrm{Co}-\mathrm{Cl}$ <br> (c) <br> Group | $\begin{gathered} \hline \mathrm{Co}-\mathrm{H} \\ \text { Group } \end{gathered}$ | Co-CO <br> Group | $\begin{aligned} & C=O \\ & \text { Group } \end{aligned}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $f_{1}$ | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $n_{1}$ | 1 | 1 | 1 | 1 | 1 | 1 | 2 |
| $n_{2}$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $n_{3}$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $C_{1}$ | 0.375 | 0.5 | 0.5 | 0.5 | 0.5 | 0.375 | 0.5 |
| $\mathrm{C}_{2}$ | 1 | 0.74108 | 0.74108 | 0.74108 | 0.80129 | 1 | 1 |
| $C_{1}$ | 1 | 1 | 1 | 1 | 0.75 | 1 | 1 |
| $C_{2}$ | 0.99569 | 1 | 1 | 1 | 0.80129 | 0.79097 | 0.85395 |
| $C_{3}$ | 0 | 0 | 0 | 0 | 0 | 0 | 2 |
| $C_{4}$ | 1 | 1 | 1 | 1 | 1 | 2 | 4 |
| $C_{5}$ | 1 | 1 | 1 | 1 | 1 | 0 | 0 |
| $\mathrm{C}_{10}$ | 0.375 | 0.5 | 0.5 | 0.5 | 0.5 | 0.375 | 0.5 |
| $\mathrm{C}_{2}$ o | 1 | 0.74108 | 0.74108 | 0.74108 | 0.80129 | 1 | 1 |
| $V_{e}(e V)$ | -32.43083 | -24.59516 | -25.09218 | -24.11830 | -30.00832 | -25.31882 | -134.96850 |
| $V_{p}(e V)$ | 7.90017 | 7.07026 | 7.12499 | 7.01677 | 9.45183 | 7.85231 | 24.99908 |
| $T(e V)$ | 7.28938 | 4.48102 | 4.64262 | 4.32790 | 9.03661 | 5.62211 | 56.95634 |
| $V_{m}(e V)$ | -3.64469 | -2.24051 | -2.32131 | -2.16395 | -4.51831 | -2.81105 | -28.47817 |
| $E$ (Ао/но) (eV) | -17.49830 | -17.49830 | -17.49830 | -17.49830 | -16.97989 | -16.97989 | 0 |
| $\Delta E_{\mathrm{H}_{2} \mathrm{MO}}($ Аоо/но) $(\mathrm{eV})$ | 0 | 0 | 0 | 0 | 0 | 0 | -18.22046 |
| $E_{T}$ (Ао/но) $(\mathrm{eV})$ | -17.49830 | -17.49830 | -17.49830 | -17.49830 | -16.97989 | -16.97989 | 18.22046 |
| $E_{T}\left(\mathrm{H}_{2} \mathrm{MO}\right)(\mathrm{eV})$ | -38.38427 | -32.78269 | -33.14419 | -32.43588 | -33.01808 | -31.63534 | -63.27080 |
| $E_{T}\left(\right.$ atom-atom, $\left.\mathrm{msp}^{3} . \mathrm{AO}\right)(\mathrm{eV})$ | -1.20896 | -1.20896 | -1.20896 | -1.20896 | 0 | -1.13379 | -3.58557 |
| $E_{T}$ (мо) (eV) | -39.59324 | -33.99165 | -34.35315 | -33.64484 | -33.01808 | -32.76916 | -66.85630 |
| $\omega\left(10^{15} \mathrm{rad} / \mathrm{s}\right)$ | 15.1528 | 9.19478 | 5.66480 | 5.41058 | 12.2308 | 7.49254 | 22.6662 |
| $E_{K}(e V)$ | 9.97387 | 6.05217 | 3.72867 | 3.56134 | 8.05053 | 4.93172 | 14.91930 |
| $\bar{E}_{D}(e V)$ | -0.24738 | -0.16544 | -0.13123 | -0.12561 | -0.18534 | -0.14397 | -0.25544 |
| $\bar{E}_{\text {Kvib }}(e \mathrm{~V})$ | $\begin{gathered} 0.09448 \\ {[54]} \end{gathered}$ | $\begin{gathered} 0.05222 \\ {[56]} \end{gathered}$ | $\begin{gathered} 0.05222 \\ {[56]} \end{gathered}$ | $\begin{gathered} 0.05222 \\ {[56]} \end{gathered}$ | $\begin{gathered} 0.23887 \\ {[57]} \end{gathered}$ | $\begin{gathered} 0.07181 \\ {[58]} \end{gathered}$ | $\begin{gathered} 0.24962 \\ {[29]} \end{gathered}$ |
| $\bar{E}_{\text {osc }}(e V)$ | -0.20014 | -0.13933 | -0.10512 | -0.09950 | -0.06590 | -0.10806 | -0.13063 |
| $E_{\text {mag }}(\mathrm{eV})$ | 0.22238 | 0.22238 | 0.22238 | 0.22238 | 0.22238 | 0.14803 | 0.11441 |
| $E_{T}$ (Group) (eV) | -39.79337 | -34.13098 | -34.45827 | -33.74434 | -33.08398 | -32.87722 | -67.11757 |
| $E_{\text {initial }}\left(c_{4}\right.$ АО/Но) $(e V)$ | -17.49830 | -17.49830 | -17.49830 | -17.49830 | -16.97989 | -14.63489 | -14.63489 |
| $E_{\text {initial }}\left(c_{5}\right.$ Ао/но) $(e \mathrm{eV})$ | -17.42282 | -12.96764 | -12.96764 | -12.96764 | -13.59844 | 0 | 0 |
| $E_{D}$ (Group) (eV) | 4.87226 | 3.66504 | 3.99233 | 3.27840 | 2.50565 | 3.60744 | 8.34918 |

Table 23.44. The total bond energies of gaseous-state cobalt coordinate compounds calculated using the functional group composition and the energies of Table 23.43 compared to the gaseous-state experimental values.

| Formula | Name | $\begin{aligned} & \text { Co-F } \\ & \text { Group } \end{aligned}$ | $\begin{gathered} \mathrm{Co}-\mathrm{Cl}(\mathrm{a}) \\ \text { Group } \end{gathered}$ | $\begin{gathered} \mathrm{Co}-\mathrm{Cl} \text { (b) } \\ \text { Group } \end{gathered}$ | $\begin{gathered} \mathrm{Co}-\mathrm{Cl}(\mathrm{c}) \\ \text { Group } \end{gathered}$ | $\begin{gathered} \text { Co-H } \\ \text { Group } \end{gathered}$ | $\begin{gathered} C O-C O \\ \text { Group } \end{gathered}$ | $\begin{aligned} & C=O \\ & \text { Group } \end{aligned}$ | Calcula:ed lotal Bond Energy (eV) | Experimental Total Boad F.nergy (eV) | Relative Error |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{COF}_{2}$ | Cobalt difluoride | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 9.45115 | 9.75552 [54] | 0.03120 |
| COCl | Cobalt chloride | 0 | : | 0 | 0 | 0 | 0 | 0 | 3.66504 | 3.68049 [15] | 0.00420 |
| $\mathrm{Col}_{2}$ | Cobalt dichloride | 0 | 0 | 2 | 0 | 0 | 0 | 0 | 7.98467 | 7.92106 [15] | -0.00803 |
| $\mathrm{CoCl}_{3}$ | Cobalt trichloride | 0 | 0 | 0 | 3 | 0 |  | 0 | 9.83521 | 9.87205 [15] | 0.00373 |
| $\mathrm{COH}(\mathrm{CO})_{4}$ | Cobalt tetracarbonyl hydride | 0 | 0 | 0 | 0 | I | 4 | 4 | 50.33217 | 50.36087 [53] | 0.00057 |

## NICKEL FUNCTIONAL GROUPS AND MOLECULES

The electron configuration of nickel is $[A r] 4 s^{2} 3 d^{8}$ having the corresponding term ${ }^{3} F_{4}$. The total energy of the state is given by the sum over the ten electrons. The sum $E_{T}(\mathrm{Ni}, 3 \mathrm{~d} 4 \mathrm{~s})$ of experimental energies [1] of $\mathrm{Ni}, \mathrm{Ni}^{+}, \mathrm{Ni}^{2+}, \mathrm{Ni}^{3+}, \mathrm{Ni}^{4+}, \mathrm{Ni}^{5+}, \mathrm{Ni}^{6+}$, $\mathrm{Ni}^{7+}, \mathrm{Ni}^{8+}$, and $\mathrm{Ni}^{9+}$ is:

$$
\begin{equation*}
E_{T}(N i, 3 d 4 s)=-\binom{224.6 \mathrm{eV}+193 \mathrm{eV}+162 \mathrm{eV}+133 \mathrm{eV}+108 \mathrm{eV}+76.06 \mathrm{eV}}{+54.9 \mathrm{eV}+35.19 \mathrm{eV}+18.16884 \mathrm{eV}+7.6398 \mathrm{eV}}=-1012.55864 \mathrm{eV} \tag{23.155}
\end{equation*}
$$

By considering that the central field decreases by an integer for each successive electron of the shell, the radius $r_{3 d 4 s}$ of the Ni3d4s shell may be calculated from the Coulombic energy using Eq. (15.13).

$$
\begin{equation*}
r_{3 d 4 s}=\sum_{n=18}^{27} \frac{(Z-n) e^{2}}{8 \pi \varepsilon_{0}(e 1012.55864 \mathrm{eV})}=\frac{55 e^{2}}{8 \pi \varepsilon_{0}(e 1012.55864 \mathrm{eV})}=0.73904 a_{0} \tag{23.156}
\end{equation*}
$$

where $Z=28$ for nickel. Using Eq. (15.14), the Coulombic energy $E_{\text {Coulomb }}(N i, 3 d 4 s)$ of the outer electron of the Ni3d4s shell is:

$$
\begin{equation*}
E_{\text {Coulomb }}(N i, 3 d 4 s)=\frac{-e^{2}}{8 \pi \varepsilon_{0} r_{3 d 4 s}}=\frac{-e^{2}}{8 \pi \varepsilon_{0} 0.73904 a_{0}}=-18.410157 \mathrm{eV} \tag{23.157}
\end{equation*}
$$

During hybridization, the spin-paired $4 s$ electrons and the three sets of paired $3 d$ electrons are promoted to the $N i 3 d 4 s$ shell as initially unpaired electrons. The energies for the promotions are given by Eq. (15.15) at the initial radii of the $4 s$ and $3 d$ electrons. From Eq. (10.102) with $Z=28$ and $n=28$, the radius $r_{28}$ of the Ni4s shell is

$$
\begin{equation*}
r_{28}=1.78091 a_{0} \tag{23.158}
\end{equation*}
$$

and with $Z=28$ and $n=26$, the radius $r_{26}$ of the Ni3d shell is:

$$
\begin{equation*}
r_{26}=1.15992 a_{0} \tag{23.159}
\end{equation*}
$$

Using Eqs. (15.15), (23.157), and (23.158), the unpairing energies are:

$$
\begin{align*}
& E_{4 s}(\text { magnetic })=\frac{2 \pi \mu_{0} e^{2} \hbar^{2}}{m_{e}^{2}\left(r_{28}\right)^{3}}=\frac{8 \pi \mu_{0} \mu_{B}^{2}}{\left(1.78091 a_{0}\right)^{3}}=0.02026 \mathrm{eV}  \tag{23.160}\\
& E_{3 d}(\text { magnetic })=\frac{2 \pi \mu_{0} e^{2} \hbar^{2}}{m_{e}^{2}\left(r_{26}\right)^{3}}=\frac{8 \pi \mu_{0} \mu_{B}^{2}}{\left(1.15992 a_{0}\right)^{3}}=0.07331 \mathrm{eV} \tag{23.161}
\end{align*}
$$

The electrons from the $4 s$ and $3 d$ shells successively fill unoccupied HOs until the HO shell is filled with unpaired electrons, then the electrons pair per HO. In the case of the Ni3d4s shell having ten electrons and six orbitals, four sets of electrons are paired. Using Eqs. (15.15) and (23.155), the pairing energy is given by:

$$
\begin{equation*}
E_{3 d 4 s}(\text { magnetic })=-\frac{2 \pi \mu_{0} e^{2} \hbar^{2}}{m_{e}^{2}\left(r_{3 d 4 s}\right)^{3}}=-\frac{8 \pi \mu_{0} \mu_{B}^{2}}{\left(0.73904 a_{0}\right)^{3}}=-0.28344 \mathrm{eV} \tag{23.162}
\end{equation*}
$$

Thus, after Eq. (23.28), the energy $E(N i, 3 d 4 s)$ of the outer electron of the $N i 3 d 4 s$ shell is given by adding the magnetic energies of unpairing the $4 s$ (Eq. (23.159)) and 3d electrons (Eq. (23.160)) and pairing of four sets of Ni3d4s electrons (Eq. (23.161)) to $E_{\text {Coulomb }}(N i, 3 d 4 s)$ (Eq. (23.156)).

$$
\begin{align*}
E(N i, 3 d 4 s) & =\frac{-e^{2}}{8 \pi \varepsilon_{0} r_{3 d 4 s}}+\frac{2 \pi \mu_{0} e^{2} \hbar^{2}}{m_{e}^{2} r_{4 s}^{3}}+\sum_{3 d \text { pairs }} \frac{2 \pi \mu_{0} e^{2} \hbar^{2}}{m_{e}^{2} r_{3 d}^{3}}-\sum_{\text {HO pairs }} \frac{2 \pi \mu_{0} e^{2} \hbar^{2}}{m_{e}^{2} r_{3 d 4 s}^{3}}  \tag{23.163}\\
& =-18.410157 \mathrm{eV}+0.02026 \mathrm{eV}+3(0.07331 \mathrm{eV})-4(0.28344 \mathrm{eV})=-19.30374 \mathrm{eV}
\end{align*}
$$

Next, consider the formation of the $N i-L$-bond MO wherein each nickel atom has a Ni3d4s electron with an energy given by Eq. (23.162). The total energy of the state of each nickel atom is given by the sum over the ten electrons. The sum $E_{T}\left(N i_{N i-L} 3 d 4 s\right)$ of energies of $N i 3 d 4 s$ (Eq. (23.162)), $N i^{+}, N i^{2+}, N i^{3+}, N i^{4+}, N i^{5+}, N i^{6+}, N i^{7+}, N i^{8+}$, and $N i^{9+}$ is:

$$
\begin{align*}
E_{T}\left(N i_{N i-L} 3 d 4 s\right) & =-\binom{224.6 \mathrm{eV}+193 \mathrm{eV}+162 \mathrm{eV}+133 \mathrm{eV}+108 \mathrm{eV}+76.06 \mathrm{eV}}{+54.9 \mathrm{eV}+35.19 \mathrm{eV}+18.16884 \mathrm{eV}+E(N i, 3 d 4 \mathrm{~s})}  \tag{23.164}\\
& =-\binom{224.6 \mathrm{eV}+193 \mathrm{eV}+162 \mathrm{eV}+133 \mathrm{eV}+108 \mathrm{eV}+76.06 \mathrm{eV}}{+54.9 \mathrm{eV}+35.19 \mathrm{eV}+18.16884 \mathrm{eV}+19.30374 \mathrm{eV}}=-1024.22258 \mathrm{eV}
\end{align*}
$$

where $E(N i, 3 d 4 s)$ is the sum of the energy of $N i,-7.6398 \mathrm{eV}$, and the hybridization energy.
The nickel HO donates an electron to each MO. Using Eq. (23.30), the radius $r_{3 d 4 s}$ of the Ni3d4s shell calculated from the Coulombic energy is:

$$
\begin{equation*}
r_{N i-L 3 d 4 s}=\left(\sum_{n=18}^{27}(Z-n)-1\right) \frac{e^{2}}{8 \pi \varepsilon_{0}(e 1024.22258 e V)}=\frac{54 e^{2}}{8 \pi \varepsilon_{0}(e 1024.22258 e V)}=0.71734 a_{0} \tag{23.165}
\end{equation*}
$$

Using Eqs. (15.19) and (23.164), the Coulombic energy $E_{\text {Coulomb }}\left(N i_{N i-L}, 3 d 4 s\right)$ of the outer electron of the $N i 3 d 4 s$ shell is

$$
\begin{equation*}
E_{\text {Coulomb }}\left(N i_{N i-L}, 3 d 4 s\right)=\frac{-e^{2}}{8 \pi \varepsilon_{0} r_{N i-L 3 d 4 s}}=\frac{-e^{2}}{8 \pi \varepsilon_{0} 0.71734 a_{0}}=-18.96708 \mathrm{eV} \tag{23.166}
\end{equation*}
$$

The magnetic energy terms are those for the unpairing of the $4 s$ and $3 d$ electrons (Eqs. (23.159) and (23.160), respectively) and paring four sets of Ni3d4s electrons (Eq. (23.161)). Using Eqs. (23.32), (23.165) and (23.159-23.161), the energy $E\left(N i_{N i-L}, 3 d 4 s\right)$ of the outer electron of the $N i 3 d 4 s$ shell is:

$$
\begin{align*}
E\left(N i_{N i-L}, 3 d 4 s\right) & =\frac{-e^{2}}{8 \pi \varepsilon_{0} r_{N i-L 3 d 4 s}}+\frac{2 \pi \mu_{0} e^{2} \hbar^{2}}{m_{e}^{2}\left(r_{28}\right)^{3}}+3 \frac{2 \pi \mu_{0} e^{2} \hbar^{2}}{m_{e}^{2}\left(r_{26}\right)^{3}}-4 \frac{2 \pi \mu_{0} e^{2} \hbar^{2}}{m_{e}^{2}\left(r_{3 d 4 s}\right)^{3}}  \tag{23.167}\\
& =-18.96708 \mathrm{eV}+0.02026 \mathrm{eV}+3(0.07331 \mathrm{eV})-4(0.28344 \mathrm{eV})=-19.86066 \mathrm{eV}
\end{align*}
$$

Thus, $E_{T}(N i-L, 3 d 4 s)$, the energy change of each $N i 3 d 4 s$ shell with the formation of the $N i-L$-bond MO is given by the difference between Eq. (23.166) and Eq. (23.162):

$$
\begin{equation*}
E_{T}(N i-L, 3 d 4 s)=E\left(N i_{N i-L}, 3 d 4 s\right)-E(N i, 3 d 4 s)=-19.86066 \mathrm{eV}-(-19.30374 \mathrm{eV})=-0.55693 \mathrm{eV} \tag{23.168}
\end{equation*}
$$

The semimajor axis $a$ solution given by Eq. (23.41) of the force balance equation, Eq. (23.39), for the $\sigma$-MO of the $\mathrm{Ni}-\mathrm{L}$-bond MO of $\mathrm{NiL}_{n}$ is given in Table 23.46 with the force-equation parameters $\mathrm{Z}=28, n_{e}$, and $L$ corresponding to the orbital and spin angular momentum terms of the $3 d 4 \mathrm{~s} \mathrm{HO}$ shell. The semimajor axis $a$ of carbonyl and organometallic compounds are solved using Eq. (15.51).

For the $\mathrm{Ni}-L$ functional groups, hybridization of the $4 s$ and $3 d$ AOs of $N i$ to form a single $3 d 4 s$ shell forms an energy minimum, and the sharing of electrons between the Ni3d4s HO and L AO to form a MO permits each participating orbital to decrease in radius and energy. The Cl AO has an energy of $E(C l)=-12.96764 \mathrm{eV}$, the $C_{\text {aryl }} 2 s p^{3} \mathrm{HO}$ has an energy of $E\left(C_{\text {aryl }}, 2 s p^{3}\right)=-15.76868 \mathrm{eV}$ (Eq. (14.246)), the $C 2 s p^{3} \mathrm{HO}$ has an energy of $E\left(C, 2 s p^{3}\right)=-14.63489 \mathrm{eV}$ (Eq. (15.25)), the Coulomb energy of $N i 3 d 4 s$ HO is $E_{\text {Coulomb }}(N i, 3 d 4 s)=-18.41016 \mathrm{eV}$ (Eq. (23.156)), and the $N i 3 d 4 s$ HO has an energy of $E(N i, 3 d 4 s)=-19.30374 \mathrm{eV}$ (Eq. (23.162)). To meet the equipotential condition of the union of the $\mathrm{Ni}-\mathrm{L} \mathrm{H}_{2}$-type-ellipsoidal-MO with these orbitals, the hybridization factor(s), at least one of $c_{2}$ and $C_{2}$ of Eq. (15.61) for the $\mathrm{Ni}-\mathrm{L}$-bond MO given by Eq. (15.77) is:

$$
\begin{align*}
& C_{2}(C I A O \text { to } N i 3 d 4 s H O)=\frac{E(C l A O)}{E(N i, 3 d 4 s)}=\frac{-12.96764 \mathrm{eV}}{-19.30374 \mathrm{eV}}=0.67177  \tag{23.169}\\
& c_{2}\left(C 2 s p^{3} \mathrm{HO} \text { to } \mathrm{Ni} 3 d 4 \mathrm{sHO}\right)=\frac{E\left(C, 2 s p^{3}\right)}{E_{\text {Coulomb }}(N i, 3 d 4 s)} c_{2}\left(C 2 s p^{3} \mathrm{HO}\right)=\frac{-14.63489 \mathrm{eV}}{-18.41016 \mathrm{eV}}(0.91771)=0.72952  \tag{23.170}\\
& C_{2}\left(C_{\text {aryl }} 2 s p^{3} \mathrm{HO} \text { to } \mathrm{Ni} 3 d 4 s H O\right)=\frac{E\left(C, 2 s p^{3}\right)}{E_{\text {Coulomb }}(N i, 3 d 4 s)} c_{2}\left(C_{\text {aryl }} 2 s p^{3} \mathrm{HO}\right)=\frac{-14.63489 \mathrm{eV}}{-18.41016 \mathrm{eV}}(0.85252)=0.67770 \tag{23.171}
\end{align*}
$$

where Eqs. (15.76), (15.79), and (13.430) were used in Eq. (23.169) and Eqs. (15.76), (15.79), and (14.417) were used in Eq. (23.170). Since the energy of the MO is matched to that of the Ni3d4s HO in coordinate compounds, $E(A O / H O)$ in Eq. (15.61) is $E(N i, 3 d 4 s)$ given by Eq. (23.162) and $E(A O / H O)$ in Eq. (15.61) of carbonyl compounds and organometallics is $E_{\text {Coulomb }}(N i, 3 d 4 s)$ given by Eq. (23.156). $\quad E_{T}\left(\right.$ atom-atom, $\left.\mathrm{msp}^{3} . A O\right)$ of the $N i-L$-bond MO is determined by considering that the bond involves an electron transfer from the nickel atom to the ligand atom to form partial ionic character in the bond as in the case of the zwitterions such as $\mathrm{H}_{2} \mathrm{~B}^{+}-F^{-}$given in the Halido Boranes section. For the coordinate compounds, $E_{T}\left(\right.$ atom-atom, $\left.m s p^{3} . A O\right)$ is -1.11386 eV , two times the energy of Eq. (23.167). For the $\mathrm{Ni}-\mathrm{C}$ bonds of carbonyl compound, $\mathrm{Ni}(\mathrm{CO})_{4}$ and organometallic, nickelocene, $E_{T}\left(\right.$ atom-atom, $\left.m \mathrm{sp}^{3} . \mathrm{AO}\right)$ is -1.85837 eV (two times Eq. (14.513)) and -0.92918 eV (Eq. (14.513)), respectively. The $C=O$ functional group of $\mathrm{Ni}(\mathrm{CO})_{4}$ is equivalent to that of vanadium carbonyls. The aromatic cyclopentadienyl moieties of organometallic $\mathrm{Ni}\left(\mathrm{C}_{5} \mathrm{H}_{5}\right)_{2}$ comprise $\mathrm{C}^{3 e}=\mathrm{C}$ and CH functional groups that are equivalent to those given in the Aromatic and Heterocyclic Compounds section.

The symbols of the functional groups of nickel coordinate compounds are given in Table 23.45. The geometrical (Eqs. (15.1-15.5) and (23.41)), intercept (Eqs. (15.31-15.32) and (15.80-15.87)), and energy (Eqs. (15.61) and (23.28-23.33)) parameters of nickel coordinate compounds are given in Tables 23.46, 23.47, and 23.48, respectively. The total energy of each nickel coordinate compound given in Table 23.49 was calculated as the sum over the integer multiple of each $E_{D}(G r o u p)$ of Table
23.48 corresponding to functional-group composition of the compound. The charge-densities of exemplary nickel carbonyl and organometallic compounds, nickel tetracarbonyl $\left(\mathrm{Ni}(\mathrm{CO})_{4}\right)$ and bis-cylopentadienyl nickel or nickelocene $\left(\mathrm{Ni}\left(\mathrm{C}_{5} \mathrm{H}_{5}\right)_{2}\right)$ 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 are shown in Figure 23.10A and B, respectively.

Figure 23.10. (A) Nickel Tetracarbonyl. Color scale, translucent view of the charge-density of $\mathrm{Ni}(\mathrm{CO})_{4}$ showing the orbitals of the $\mathrm{Ni}, \mathrm{C}$, and O atoms at their radii, the ellipsoidal surface of each $\mathrm{H}_{2}$-type ellipsoidal MO that transitions to the corresponding outer shell of the atoms participating in each bond, and the nuclei (red, not to scale). (B) Nickelocene. Color scale, opaque view of the charge-density of $\mathrm{Ni}\left(\mathrm{C}_{5} \mathrm{H}_{5}\right)_{2}$ showing the orbitals of the Ni and C atoms at their radii and the ellipsoidal surface of each H or $\mathrm{H}_{2}$-type ellipsoidal MO that transitions to the corresponding outer shell of the atoms participating in each bond.


Table 23.45. The symbols of the functional groups of nickel coordinate compounds.

| Functional Group | Group Symbol |
| :--- | :--- |
| NiCl group of NiCl | $\mathrm{Ni}-\mathrm{Cl}$ (a) |
| $\mathrm{NiCl}_{2}$ group of NiCl | 2 |
| NiCO group of $\mathrm{Ni}(\mathrm{CO})_{4}$ | $\mathrm{Ni}-\mathrm{Cl}$ (b) |
| $\mathrm{C}=\mathrm{O}$ | $\mathrm{Ni}-\mathrm{CO}$ |
| NiCaryl group of $\mathrm{Ni}\left(\mathrm{C}_{5} \mathrm{H}_{5}\right)_{2}$ | $\mathrm{C}=\mathrm{O}$ |
| CC (aromatic bond) | $\mathrm{Ni}-\mathrm{C}_{5} \mathrm{H}_{5}$ |
| CH (aromatic) | $\mathrm{Ce}=\mathrm{C}$ |

Table 23.46. The geometrical bond parameters of nickel coordinate compounds and experimental values.

| Parameter | $\begin{aligned} & \mathrm{Ni}-\mathrm{Cl}(\mathrm{a}) \\ & \text { Group } \end{aligned}$ | $\begin{aligned} & \mathrm{Ni}-\mathrm{Cl}(\mathrm{~b}) \\ & \text { Group } \end{aligned}$ | $\begin{gathered} \mathrm{Ni}-\mathrm{CO} \\ \text { Group } \end{gathered}$ | $C=O$ <br> Group | $\mathrm{Ni}-\mathrm{C}_{5} \mathrm{H}_{5}$ <br> Group | $C=C$ <br> Group | $\begin{gathered} \mathrm{CH} \\ \text { Group } \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $n_{e}$ | 3 | 3 |  |  |  |  |  |
| $L$ | $5+5 \sqrt{\frac{3}{4}}$ | $4+6 \sqrt{\frac{3}{4}}$ |  |  |  |  |  |
| $a\left(a_{0}\right)$ | 2.83322 | 2.82843 | 2.22132 | 1.184842 | 3.00077 | 1.47348 | 1.60061 |
| $c^{\prime}\left(a_{0}\right)$ | 2.05367 | 2.05193 | 1.72098 | 1.08850 | 2.10426 | 1.31468 | 1.03299 |
| Bond Length $2 c^{\prime}(\AA)$ | 2.17351 | 2.17167 | 1.82140 | 1.15202 | 2.22705 | 1.39140 | 1.09327 |
| Exp. Bond Length $(\AA)$ | $\begin{gathered} 2.137[15,59] \\ (\mathrm{NiCl}) \\ 2.09[15,59] \\ \left(\mathrm{NiCl}_{2}\right) \end{gathered}$ | $\begin{gathered} 2.137[15,59] \\ (\mathrm{NiCl}) \\ 2.09[15,59] \\ \left(\mathrm{NiCl}_{2}\right) \end{gathered}$ | $\begin{gathered} 1.82[55] \\ \left(\mathrm{Ni}(\mathrm{CO})_{4}\right) \end{gathered}$ | $\begin{gathered} 1.15[55] \\ \left(\mathrm{Ni}(\mathrm{CO})_{4}\right) \end{gathered}$ | $\begin{gathered} 2.185[60] \\ \left(\mathrm{Ni}\left(\mathrm{C}_{5} \mathrm{H}_{5}\right)_{2}\right) \end{gathered}$ | $\begin{aligned} & 1.399[3] \\ & \text { (benzene) } \end{aligned}$ | $1.101 \text { [3] }$ (benzene) |
| $b, c\left(a_{0}\right)$ | 1.95181 | 1.94669 | 1.40446 | 0.46798 | 2.13933 | 0.66540 | 1.22265 |
| $e$ | 0.72485 | 0.72547 | 0.77475 | 0.91869 | 0.70124 | 0.89223 | 0.64537 |

Table 23．47．The MO to HO intercept geometrical bond parameters of nickel coordinate compounds．$E_{T}$ is $E_{T}$（atom－atom，HO．AO）．

| ＊゙ ¢® |  | $\begin{aligned} & n \\ & 0 \\ & 0 \\ & 0 \end{aligned}$ |  |  |  |  | $\stackrel{N}{\hat{N}} \underset{\substack{0}}{ }$ |  |  | $\begin{aligned} & \bar{n} \\ & 0 \\ & \text { in } \\ & 0 \end{aligned}$ |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\sigma$ ef |  | $\begin{aligned} & 0 \\ & 0 \\ & 0 \\ & \vdots \\ & i \end{aligned}$ |  |  |  |  | $\begin{aligned} & \text { n } \\ & \substack{0 \\ 0 \\ -\\ \hline} \end{aligned}$ | $\begin{aligned} & \text { t } \\ & \text { 人 } \\ & \text { S} \end{aligned}$ | $\begin{aligned} & \text { 答 } \\ & \underset{-1}{ } \end{aligned}$ | $\begin{aligned} & \underset{\sim}{t} \\ & \underset{O}{0} \end{aligned}$ |  |  |
| ®゚ |  | $\begin{aligned} & \stackrel{\circ}{\lambda} \\ & \underset{\sim}{2} \end{aligned}$ |  |  | $\underset{\sim}{c}$ |  | $\underset{\sim}{\underset{\sim}{\infty}}$ | $\underset{\sim}{8}$ | $\begin{aligned} & \mathfrak{n} \\ & \infty \\ & \infty \\ & \infty \end{aligned}$ | $\stackrel{0}{\infty} \underset{\infty}{\infty}$ |  |  |
| 0 － |  | $\begin{aligned} & \stackrel{\rightharpoonup}{\varrho} \\ & \stackrel{1}{\leftrightharpoons} \end{aligned}$ |  |  |  |  |  | $\begin{aligned} & \underset{\sim}{\underset{~}{2}} \end{aligned}$ | $\begin{aligned} & \underset{\circ}{\circ} \\ & \underset{O}{2} \end{aligned}$ | $\begin{gathered} \text { t } \\ \text { 岁 } \end{gathered}$ |  |  |
| － |  | $\begin{gathered} \text { m } \\ \underset{i}{2} \end{gathered}$ |  |  | OT | M | $\frac{9}{2}$ | $\begin{aligned} & \text { y } \\ & \underset{\text { N }}{ } \end{aligned}$ | $\begin{gathered} \hat{\infty} \\ \stackrel{\sim}{n} \end{gathered}$ | $\begin{aligned} & \stackrel{\circ}{\dot{~}} \\ & \underset{\sim}{2} \end{aligned}$ |  |  |
|  |  |  |  |  |  | － | $\begin{gathered} n \\ 0 \\ 0 \\ \\ \end{gathered}$ |  | $\begin{aligned} & \underset{2}{2} \\ & \underset{2}{2} \\ & \underset{1}{2} \end{aligned}$ | $\begin{aligned} & \stackrel{\tilde{\kappa}}{\hat{\alpha}} \\ & \stackrel{\rightharpoonup}{\circ} \\ & \vdots \end{aligned}$ |  | － |
|  | $\begin{gathered} \infty \\ \stackrel{\infty}{0} \\ 0 \\ \underset{\sim}{\infty} \\ \hline \end{gathered}$ | $\begin{aligned} & \underset{\sim}{r} \\ & \underset{\sim}{n} \\ & \underset{\sim}{2} \end{aligned}$ |  | $\begin{aligned} & \hat{n} \\ & \underset{\sim}{n} \\ & \cdots \\ & \cdots \end{aligned}$ |  |  | $\begin{gathered} \text { N } \\ \underset{\sim}{t} \\ \end{gathered}$ |  |  | $\begin{aligned} & \text { N} \\ & \underset{O}{\circ} \\ & \underset{؟}{7} \end{aligned}$ | $\left\lvert\, \begin{gathered} 2 \\ \underset{\sim}{2} \\ \underset{\sim}{2} \\ \underset{1}{n} \end{gathered}\right.$ | － |
| 成 | $\begin{aligned} & \text { さ } \\ & \underset{\sim}{\wedge} \end{aligned}$ |  | $\begin{aligned} & \infty \\ & 0 \\ & 0 \\ & 0 \\ & 0 . \\ & 0 . \end{aligned}$ | 응 |  | $\stackrel{i}{\stackrel{\infty}{\infty}}$ |  | $$ | $\begin{aligned} & \hat{0} \\ & \frac{0}{2} \\ & 0 \end{aligned}$ | $\begin{aligned} & \hat{0} \\ & \stackrel{\rightharpoonup}{\hat{O}} \\ & \hline \end{aligned}$ | $\begin{aligned} & \substack{0 \\ 0 \\ 0 \\ 0 \\ 0} \end{aligned}$ | － |
| ） |  | $\begin{aligned} & \infty \\ & \stackrel{\infty}{n} \\ & \underset{\sim}{6} \end{aligned}$ | $\begin{gathered} \text { t } \\ \text { d } \\ \text { No } \end{gathered}$ | $\begin{gathered} \infty \\ \stackrel{n}{2} \\ -8 \\ - \end{gathered}$ |  |  | $\frac{\underset{N}{\lambda}}{\hat{O}}$ | $\begin{aligned} & \text { t } \\ & \text { Non } \\ & \text { N } \end{aligned}$ | $\begin{array}{\|l\|} \frac{\Sigma}{\lambda} \\ \partial \\ \hline \end{array}$ | $\frac{\underset{\lambda}{\hat{j}}}{}$ | $\begin{aligned} & \text { t } \\ & \stackrel{\rightharpoonup}{\mathrm{N}} \\ & \hat{O} \end{aligned}$ | $\frac{\bar{E}}{\text { E }}$ |
|  |  |  |  |  |  | ¢ |  |  | $\begin{aligned} & 9 \\ & \frac{0}{2} \\ & \vdots \\ & \\ & \hdashline \end{aligned}$ |  |  |  |
| 边 | $\bigcirc$ | － | － | － | 0 | 00 | － | － | － | － | － | － |
| $\leftrightarrow S_{0}^{J}$ | － | $\bigcirc$ | － | － | － | 00 | － | $\begin{aligned} & \infty \\ & \underset{\alpha}{\grave{\alpha}} \\ & \stackrel{\rightharpoonup}{i} \end{aligned}$ | $\begin{aligned} & \text { I } \\ & \text { I } \\ & 0 \\ & \vdots \\ & \hline \end{aligned}$ | $\begin{aligned} & \text { İ } \\ & \text { Ì } \\ & \text { ò } \end{aligned}$ | － | 8 |
| \& | $\bigcirc$ | － | － | － | － 0 | － 0 | － | $\begin{gathered} \infty \\ \text { ふু } \\ \text { 人} \end{gathered}$ | $\begin{aligned} & 0 \\ & 0 \\ & 0 \\ & 0 \\ & 0 \\ & 0 \\ & i \end{aligned}$ |  | － | \％ |
| $\Leftrightarrow \frac{S}{0}$ | $\bigcirc$ | $\bigcirc$ | $\begin{aligned} & \text { O} \\ & \text { in } \\ & \text { ni } \end{aligned}$ |  |  | $\bigcirc \frac{\sim}{c}$ |  |  |  | $\begin{gathered} \text { N } \\ \stackrel{C}{0} \\ \stackrel{1}{i} \end{gathered}$ | $\begin{aligned} & 2 \\ & 20 \\ & 0 \\ & 0 \\ & 0 \\ & i \end{aligned}$ | n |
| $\leftrightarrow \underset{C}{C}$ | $\begin{aligned} & 0 \\ & 0 \\ & \text { in } \\ & 0 \\ & i \end{aligned}$ | $\begin{aligned} & \text { on } \\ & 0 \\ & \text { n } \\ & 0 \end{aligned}$ | $\begin{aligned} & \text { n } \\ & 0 \\ & 0 \\ & 0 \\ & 0 \end{aligned}$ |  |  |  | $\begin{gathered} \infty \\ \underset{c}{\alpha} \\ \vdots \end{gathered}$ | $\begin{aligned} & \infty \\ & \underset{\sim}{\alpha} \\ & \stackrel{\rightharpoonup}{i} \end{aligned}$ |  |  | $\begin{aligned} & \text { a } \\ & \text { 岂 } \\ & \vdots \\ & \vdots \end{aligned}$ | C |
|  | z | こ | 之 | 0 | © | 00 | $\cup$ | \％ | $\cup$ | 0 | \％ | $\cup$ |
| 若 | $\begin{aligned} & \tilde{y} \\ & z \\ & z \\ & \vdots \\ & 1 \\ & z \end{aligned}$ | $\left\lvert\, \begin{aligned} & \hat{0} \\ & \text { z } \\ & 0 \\ & 1 \\ & z \\ & \vdots \end{aligned}\right.$ |  |  |  |  | $\begin{aligned} & \frac{2}{0} \\ & \frac{0}{8} \\ & \frac{1}{z} \\ & \frac{1}{z} \\ & \frac{1}{z} \end{aligned}$ | $\begin{aligned} & \frac{7}{0} \\ & \frac{8}{z} \\ & 0 \\ & 0 \\ & \frac{1}{z} \end{aligned}$ | $\begin{aligned} & \underset{y}{y} \\ & y \\ & y \\ & u \end{aligned}$ | $\begin{gathered} U \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{gathered}$ | $\left\{\begin{array}{l} z_{n}^{n} \\ v^{\prime} \\ \frac{2}{2} \end{array}\right.$ | 2 |

Table 23.48. The energy parameters ( $e V$ ) of functional groups of nickel coordinate compounds.

| Parameters | $\mathrm{Ni}-\mathrm{Cl}$ <br> (a) <br> Group | $\mathrm{Ni}-\mathrm{Cl}$ <br> (b) <br> Group | $\mathrm{Ni}-\mathrm{CO}$ <br> Group | $\begin{aligned} & C=O \\ & \text { Group } \end{aligned}$ | $\begin{gathered} \mathrm{Ni}-\mathrm{C}_{5} \mathrm{H}_{5} \\ \text { Group } \end{gathered}$ | $\begin{aligned} & C^{3 e}=C \\ & \text { Group } \end{aligned}$ | $\begin{gathered} \mathrm{CH} \\ \text { Group } \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $f_{1}$ | 1 | 1 | 1 | 1 | 1 | 0.75 | 1 |
| $n_{1}$ | 1 | 1 | 1 | 2 | 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 | 0.5 | 0.375 | 0.5 | 0.5 | 0.5 | 0.75 |
| $\mathrm{C}_{2}$ | 0.67177 | 0.67177 | 1 | 1 | 0.67770 | 0.85252 | 1 |
| $C_{1}$ | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $c_{2}$ | 1 | 1 | 0.72952 | 0.85395 | 1 | 0.85252 | 0.91771 |
| $c_{3}$ | 0 | 0 | 0 | 2 | 0 | 0 | 1 |
| $C_{4}$ | 1 | 1 | 2 | 4 | 2 | 3 | 1 |
| $c_{5}$ | 1 | 1 | 0 | 0 | 0 | 0 | 1 |
| $C_{10}$ | 0.5 | 0.5 | 0.375 | 0.5 | 0.5 | 0.5 | 0.75 |
| $\mathrm{C}_{20}$ | 0.67177 | 0.67177 | 1 | 1 | 0.67770 | 0.85252 | 1 |
| $V_{e}(e V)$ | -24.32206 | -24.37691 | -23.81088 | -134.96850 | -22.49426 | -101.12679 | -37.10024 |
| $V_{p}(e V)$ | 6.62512 | 6.63072 | 7.90586 | 24.99908 | 6.46585 | 20.69825 | 13.17125 |
| $T(e V)$ | 4.29230 | 4.30926 | 5.35963 | 56.95634 | 3.74808 | 34.31559 | 11.58941 |
| $V_{m}(e V)$ | -2.14615 | -2.15463 | -2.67981 | -28.47817 | -1.87404 | -17.15779 | -5.79470 |
| $E$ (Ао/но) (eV) | -19.30374 | -19.30374 | -18.41016 | 0 | -18.41016 | 0 | -14.63489 |
| $\Delta E_{\mathrm{H}_{2} \mathrm{MO}}($ АОО HO$)(\mathrm{eV})$ | 0 | 0 | 0 | -18.22046 | -0.92918 | 0 | -1.13379 |
| $E_{T}$ (Ао/но) $(\mathrm{eV})$ | -19.30374 | -19.30374 | -18.41016 | 18.22046 | -17.48097 | 0 | -13.50110 |
| $E_{T}\left(\mathrm{H}_{2} \mathrm{MO}\right)(\mathrm{eV})$ | -34.85452 | -34.89529 | -31.63537 | -63.27080 | -31.63535 | -63.27075 | -31.63539 |
| $E_{T}\left(\right.$ atom-atom, $\left.\mathrm{msp}^{3} . \mathrm{AO}\right)(\mathrm{eV})$ | -1.11386 | -1.11386 | -1.85837 | -3.58557 | -0.92918 | -2.26759 | -0.56690 |
| $E_{T}$ (мо) (eV) | -35.96838 | -36.00914 | -33.49374 | -66.85630 | -32.56455 | -65.53833 | -32.20226 |
| $\omega\left(10^{15} \mathrm{rad} / \mathrm{s}\right)$ | 8.78663 | 8.82133 | 7.64687 | 22.6662 | 7.69080 | 49.7272 | 26.4826 |
| $E_{K}(e V)$ | 5.78351 | 5.80635 | 5.03330 | 14.91930 | 5.06222 | 32.73133 | 17.43132 |
| $\bar{E}_{D}(e V)$ | -0.17113 | -0.17166 | -0.14866 | -0.25544 | -0.14495 | -0.35806 | -0.26130 |
| $\bar{E}_{\text {Kvib }}(e \mathrm{~V})$ | $\begin{gathered} 0.05257 \\ {[59]} \end{gathered}$ | $\begin{gathered} 0.05257 \\ {[59]} \end{gathered}$ | $\begin{gathered} 0.04711 \\ {[55]} \end{gathered}$ | $\begin{gathered} 0.24962 \\ {[29]} \end{gathered}$ | $\begin{gathered} 0.04711 \\ {[55]} \end{gathered}$ | $\begin{gathered} 0.19649 \\ {[30]} \end{gathered}$ | 0.35532 Eq. $(13.458)$ |
| $\bar{E}_{\text {osc }}(\mathrm{eV})$ | -0.14484 | -0.14537 | -0.12510 | -0.13063 | -0.12139 | -0.25982 | -0.08364 |
| $E_{\text {mag }}(\mathrm{eV})$ | 0.28344 | 0.28344 | 0.14803 | 0.11441 | 0.14803 | 0.14803 | 0.14803 |
| $E_{T}($ Group $)(e V)$ | -36.11322 | -36.15452 | -33.61884 | -67.11757 | -32.68594 | -49.54347 | -32.28590 |
| $E_{\text {initial }}\left(c_{4}\right.$ Ао/но) $(e V)$ | -19.30374 | -19.30374 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 |
| $E_{\text {initial }}\left(c_{5}\right.$ АО/Но) $(\mathrm{eV})$ | -12.96764 | -12.96764 | 0 | 0 | 0 | 0 | -13.59844 |
| $E_{D}($ Group $)(e V)$ | 3.84184 | 3.88314 | 4.34906 | 8.34918 | 1.14858 | 5.63881 | 3.90454 |

Table 23.49. The total bond energies of gaseous-state nickel coordinate compounds calculated using the functional group composition and the energies of Table 23.48 compared to the gaseous-state experimental values.

| Formula | Narne | $\begin{gathered} \mathrm{Ai}-\mathrm{Cl}(\mathrm{a}) \\ \text { Group } \end{gathered}$ | $\begin{gathered} \mathrm{Ni}-\mathrm{Cl} \text { (b) } \\ \text { Group } \end{gathered}$ | $\begin{gathered} \mathrm{Ni}-\mathrm{CO} \\ \text { Group } \end{gathered}$ | $\begin{aligned} & C=O \\ & \text { Group } \end{aligned}$ | $\begin{gathered} \mathrm{Ni}-\mathrm{C}_{5} \mathrm{H}_{5} \\ \text { Group } \end{gathered}$ | $\begin{aligned} & \stackrel{S}{3 n}_{=}^{=} \\ & \text {Group } \end{aligned}$ | $\begin{gathered} C H \\ \text { Croup } \end{gathered}$ | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| NiCl | Nickel chloride | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 3.84184 | 3.82934 [59] | -0.00327 |
| $\mathrm{NiCl}_{2}$ | Nickel dichloride | 0 | 2 | 0 | 0 | 0 | 0 | 0 | 7.76628 | 7.74066 [59] | -0.00331 |
| $\mathrm{Ni}(\mathrm{CO})_{4}$ | Nickel tetracarbonyl | 0 | 0 | 4 | 0 | 0 | 0 | 0 | 50.79297 | 50.77632 [55] | -0.00033 |
| $\mathrm{Ni}\left(\mathrm{C}_{5} \mathrm{H}_{5}\right)_{2}$ | Bis-cylopentadienyl nickel (nickelocene) | 0 | 0 | 0 | 0 | 2 | 10 | 10 | 97.73062 | 97.84649 [53] | 0.00118 |

## COPPER FUNCTIONAL GROUPS AND MOLECULES

The electron configuration of copper is $[A r] 4 s^{1} 3 d^{10}$ having the corresponding term ${ }^{2} S_{1 / 2}$. The single outer $4 s$ [61] electron having an energy of -7.72638 eV [1] forms a single bond to give an electron configuration with filled $3 d$ and $4 s$ shells. Additional bonding of copper is possible involving a double bond or two single bonds by the hybridization of the $3 d$ and $4 s$ shells to form a Cu3d4s shell and the donation of an electron per bond. The total energy of the copper ${ }^{2} S_{1 / 2}$ state is given by the sum over the eleven electrons. The sum $E_{T}(\mathrm{Cu}, 3 \mathrm{~d} 4 \mathrm{~s})$ of experimental energies [1] of $\mathrm{Cu}, \mathrm{Cu}^{+}, \mathrm{Cu}^{2+}, \mathrm{Cu}^{3+}, \mathrm{Cu}^{4+}, \mathrm{Cu}^{5+}$, $\mathrm{Cu}^{6+}, \mathrm{Cu}^{7+}, \mathrm{Cu}^{8+}, \mathrm{Cu}^{9+}$, and $\mathrm{Cu}^{10+}$ is

$$
\begin{equation*}
E_{T}(C u, 3 d 4 s)=-\binom{265.3 \mathrm{eV}+232 \mathrm{eV}+199 \mathrm{eV}+166 \mathrm{eV}+139 \mathrm{eV}+103 \mathrm{eV}+79.8 \mathrm{eV}}{+57.38 \mathrm{eV}+36.841 \mathrm{eV}+20.2924 \mathrm{eV}+7.72638 \mathrm{eV}}=-1306.33978 \mathrm{eV} \tag{23.172}
\end{equation*}
$$

By considering that the central field decreases by an integer for each successive electron of the shell, the radius $r_{3 d 4 s}$ of the Cu3d4s shell may be calculated from the Coulombic energy using Eq. (15.13).

$$
\begin{equation*}
r_{3 d 4 s}=\sum_{n=18}^{28} \frac{(Z-n) e^{2}}{8 \pi \varepsilon_{0}(e 1306.33978 \mathrm{eV})}=\frac{66 e^{2}}{8 \pi \varepsilon_{0}(e 1306.33978 \mathrm{eV})}=0.68740 a_{0} \tag{23.173}
\end{equation*}
$$

where $Z=29$ for copper. Using Eq. (15.14), the Coulombic energy $E_{\text {Coulomb }}(C u, 3 d 4 s)$ of the outer electron of the Cu3d4s shell is:

$$
\begin{equation*}
E_{\text {Coulomb }}(C u, 3 d 4 s)=\frac{-e^{2}}{8 \pi \varepsilon_{0} r_{3 d 4 s}}=\frac{-e^{2}}{8 \pi \varepsilon_{0} 0.68740 a_{0}}=-19.793027 \mathrm{eV} \tag{23.174}
\end{equation*}
$$

During hybridization, the unpaired $4 s$ electron and five sets of spin-paired $3 d$ electrons are promoted to the $C u 3 d 4 s$ shell as initially unpaired electrons. The energies for the promotions of the initially paired electrons are given by Eq. (15.15) at the initial radius of the $3 d$ electrons. From Eq. (10.102) with $Z=29$ and $n=28$, the radius $r_{28}$ of the Cu3d shell is:

$$
\begin{equation*}
r_{28}=1.34098 a_{0} \tag{23.175}
\end{equation*}
$$

Using Eqs. (15.15), and (23.174), the unpairing energy is:

$$
\begin{equation*}
E_{3 d}(\text { magnetic })=\frac{2 \pi \mu_{0} e^{2} \hbar^{2}}{m_{e}^{2}\left(r_{28}\right)^{3}}=\frac{8 \pi \mu_{0} \mu_{B}^{2}}{\left(1.34098 a_{0}\right)^{3}}=0.04745 \mathrm{eV} \tag{23.176}
\end{equation*}
$$

The electrons from the $4 s$ and $3 d$ shells successively fill unoccupied HOs until the HO shell is filled with unpaired electrons, then the electrons pair per HO. In the case of the Cu3d4s shell having eleven electrons and six orbitals, five sets of electrons are paired. Using Eqs. (15.15) and (23.172), the pairing energy is given by:

$$
\begin{equation*}
E_{3 d 4 \mathrm{~s}}(\text { magnetic })=-\frac{2 \pi \mu_{0} e^{2} \hbar^{2}}{m_{e}^{2}\left(r_{3 d 45}\right)^{3}}=-\frac{8 \pi \mu_{0} \mu_{B}^{2}}{\left(0.68740 a_{0}\right)^{3}}=-0.35223 \mathrm{eV} \tag{23.177}
\end{equation*}
$$

Thus, after Eq. (23.28), the energy $E(C u, 3 d 4 s)$ of the outer electron of the $C u 3 d 4 s$ shell is given by adding the magnetic energies of unpairing five sets of $3 d$ electrons (Eq. (23.175)) and pairing of five sets of Cu3d4s electrons (Eq. (23.176)) to $E_{\text {Coulomb }}(C u, 3 d 4 s)$ (Eq. (23.173)).

$$
\begin{align*}
E(C u, 3 d 4 s) & =\frac{-e^{2}}{8 \pi \varepsilon_{0} r_{3 d 4 s}}+\frac{2 \pi \mu_{0} e^{2} \hbar^{2}}{m_{e}^{2} r_{4 s}^{3}}+\sum_{3 d \text { pairs }} \frac{2 \pi \mu_{0} e^{2} \hbar^{2}}{m_{e}^{2} r_{3 d}^{3}}-\sum_{\text {HO pairs }} \frac{2 \pi \mu_{0} e^{2} \hbar^{2}}{m_{e}^{2} r_{3 d 4 s}^{3}}  \tag{23.178}\\
& =-19.793027 \mathrm{eV}+0 \mathrm{eV}+5(0.04745 \mathrm{eV})-5(0.35223 \mathrm{eV})=-21.31697 \mathrm{eV}
\end{align*}
$$

Next, consider the formation of the $C u-L$-bond MO wherein each copper atom has a Cu3d $4 s$ electron with an energy given by Eq. (23.178). The total energy of the state of each copper atom is given by the sum over the eleven electrons. The sum $E_{T}\left(\mathrm{Cu}_{\mathrm{Cu}-\mathrm{L}} 3 d 4 \mathrm{~s}\right)$ of energies of Cu 3 d 4 s (Eq. (23.178)), $\mathrm{Cu}^{+}, \mathrm{Cu}^{2+}, \mathrm{Cu}^{3+}, \mathrm{Cu}^{4+}, \mathrm{Cu}^{5+}, \mathrm{Cu}^{6+}, \mathrm{Cu}^{7+}, \mathrm{Cu}^{8+}, \mathrm{Cu}^{9+}$, and $\mathrm{Cu}^{10+}$ is:

$$
\begin{align*}
E_{T}\left(C u_{C u-L} 3 d 4 \mathrm{~s}\right) & =-\left(\begin{array}{l}
265.3 \mathrm{eV}+232 \mathrm{eV}+199 \mathrm{eV}+166 \mathrm{eV} \\
+139 \mathrm{eV}+103 \mathrm{eV}+79.8 \mathrm{eV}+57.38 \mathrm{eV} \\
+36.841 \mathrm{eV}+20.2924 \mathrm{eV}+E(C u, 3 \mathrm{~d} 4 \mathrm{~s})
\end{array}\right)  \tag{23.179}\\
& =-\left(\begin{array}{l}
265.3 \mathrm{eV}+232 \mathrm{eV}+199 \mathrm{eV}+166 \mathrm{eV} \\
+139 \mathrm{eV}+103 \mathrm{eV}+79.8 \mathrm{eV}+57.38 \mathrm{eV} \\
+36.841 \mathrm{eV}+20.2924 \mathrm{eV}+21.31697 \mathrm{eV}
\end{array}\right)=-1319.93037 \mathrm{eV}
\end{align*}
$$

where $E(C u, 3 d 4 s)$ is the sum of the energy of $C u,-7.72638 \mathrm{eV}$, and the hybridization energy.
The copper HO donates an electron to each MO. Using Eq. (23.30), the radius $r_{3 d 4 s}$ of the Cu3d4s shell calculated from the Coulombic energy is:

$$
\begin{equation*}
r_{C u-L 344 \mathrm{~s}}=\left(\sum_{n=18}^{28}(Z-n)-1\right) \frac{e^{2}}{8 \pi \varepsilon_{0}(e 1319.93037 \mathrm{eV})}=\frac{65 e^{2}}{8 \pi \varepsilon_{0}(e 1319.93037 \mathrm{eV})}=0.67002 a_{0} \tag{23.180}
\end{equation*}
$$

Using Eqs. (15.19) and (23.179), the Coulombic energy $E_{\text {Coulomb }}\left(C u_{C u-L}, 3 d 4 s\right)$ of the outer electron of the Cu3d4s shell is:

$$
\begin{equation*}
E_{\text {Coulomb }}\left(C u_{\text {Cu-L }}, 3 d 4 s\right)=\frac{-e^{2}}{8 \pi \varepsilon_{0} r_{C u-L 3 d 4 s}}=\frac{-e^{2}}{8 \pi \varepsilon_{0} 0.67002 a_{0}}=-20.30662 \mathrm{eV} \tag{23.181}
\end{equation*}
$$

The magnetic energy terms are those for the unpairing of the five sets of $3 d$ electrons (Eq. (23.175)) and pairing of five sets of Cu3d4s electrons (Eq. (23.176)). Using Eqs. (23.32), (23.180), and (23.175-23.176), the energy $E\left(C u_{\text {Cu-L }}, 3 d 4 s\right)$ of the outer electron of the Cu3d4s shell is:

$$
\begin{align*}
E\left(C u_{C u-L}, 3 d 4 s\right) & =\frac{-e^{2}}{8 \pi \varepsilon_{0} r_{u-L 3 d 4 s}}+0 \frac{2 \pi \mu_{0} e^{2} \hbar^{2}}{m_{e}^{2}\left(r_{29}\right)^{3}}+5 \frac{2 \pi \mu_{0} e^{2} \hbar^{2}}{m_{e}^{2}\left(r_{22}\right)^{3}}-5 \frac{2 \pi \mu_{0} e^{2} \hbar^{2}}{m_{e}^{2}\left(r_{\text {d4s }}\right)^{3}}  \tag{23.182}\\
& =-20.30662 \mathrm{eV}+0 \mathrm{eV}+5(0.04745 \mathrm{eV})-5(0.35223 \mathrm{eV})=-21.83056 \mathrm{eV}
\end{align*}
$$

Thus, $E_{T}(\mathrm{Cu}-L, 3 d 4 s)$, the energy change of each Cu 3 d 4 s shell with the formation of the $\mathrm{Cu}-L$-bond MO is given by the difference between Eq. (23.181) and Eq. (23.177).

$$
\begin{equation*}
E_{T}(C u-L, 3 d 4 s)=E\left(C u_{C u-L}, 3 d 4 s\right)-E(C u, 3 d 4 s)=-21.83056 \mathrm{eV}-(-21.31697 \mathrm{eV})=-0.51359 \mathrm{eV} \tag{23.183}
\end{equation*}
$$

The semimajor axis $a$ solution given by Eq. (23.41) of the force balance equation, Eq. (23.39), for the $\sigma$-MO of the $C u-L$-bond MO of $C u L_{n}$ is given in Table 23.51 with the force-equation parameters $Z=29, n_{e}$, and $L$ corresponding to the orbital and spin angular momentum terms of the $3 d 4 \mathrm{~s} \mathrm{HO}$ shell.

For the $C u-L$ functional groups, hybridization of the $4 s$ and $3 d$ AOs of $C u$ to form a single $3 d 4 s$ shell forms an energy minimum, and the sharing of electrons between the Cu3d 4 s HO and $L \mathrm{AO}$ to form a MO permits each participating orbital to decrease in radius and energy. The $F \mathrm{AO}$ has an energy of $E(F)=-17.42282 \mathrm{eV}$, the Cl AO has an energy of $E(C l)=-12.96764 \mathrm{eV}$, the $O$ AO has an energy of $E(O)=-13.61805 \mathrm{eV}$, the Cu AO has an energy of $E(C u)=-7.72638 \mathrm{eV}$, and the Cu3d4s HO has an energy of $E(C u, 3 d 4 s)=-21.31697 \mathrm{eV}$ (Eq. (23.177)). To meet the equipotential condition of the union of the $\mathrm{Cu}-\mathrm{L} \quad \mathrm{H}_{2}$-type-ellipsoidal-MO with these orbitals, the hybridization factor(s), at least one of $c_{2}$ and $C_{2}$ of Eq. (15.61) for the $\mathrm{Cu}-L$-bond MO given by Eq. (15.77) is:

$$
\begin{align*}
& C_{2}(F A O \text { to } C u A O)=\frac{E(C u A O)}{E(F A O)}=\frac{-7.72638 \mathrm{eV}}{-17.42282 \mathrm{eV}}=0.44346  \tag{23.184}\\
& c_{2}(C l A O \text { to } C u A O)=C_{2}(C l A O \text { to } C u A O)=\frac{E(C u A O)}{E(C l A O)}=\frac{-7.72638 \mathrm{eV}}{-12.96764 \mathrm{eV}}=0.59582  \tag{23.185}\\
& C_{2}(\text { FAO to } \mathrm{Cu} 3 \mathrm{~d} 4 \mathrm{sHO})=\frac{E(F A O)}{E(C u, 3 d 4 \mathrm{~s})}=\frac{-17.42282 \mathrm{eV}}{-21.31697 \mathrm{eV}}=0.81732  \tag{23.186}\\
& C_{2}(O \text { to } C u 3 d 4 \mathrm{sHO})=\frac{E(O)}{E(C u, 3 d 4 \mathrm{~s})}=\frac{-13.61805 \mathrm{eV}}{-21.31697 \mathrm{eV}}=0.63884 \tag{23.187}
\end{align*}
$$

Since the energy of the MO is matched to that of the Cu 3 d 4 s HO in coordinate compounds, $E(A O / H O)$ in Eq. (15.61) is $E(C u, 3 d 4 s)$ given by Eq. (23.177) and twice this value for double bonds. $E_{T}\left(\right.$ atom-atom, $\left.m s p^{3} . A O\right)$ of the $C u-L$-bond MO is determined by considering that the bond involves an electron transfer from the copper atom to the ligand atom to form partial ionic character in the bond as in the case of the zwitterions such as $\mathrm{H}_{2} \mathrm{~B}^{+}-\mathrm{F}^{-}$given in the Halido Boranes section. For the twobond coordinate compounds, $E_{T}\left(\right.$ atom-atom, $\left.\mathrm{msp}^{3} . \mathrm{AO}\right)$ is -1.02719 eV , two times the energy of Eq. (23.182).

The symbols of the functional groups of copper coordinate compounds are given in Table 23.50. The geometrical (Eqs. (15.1-15.5) and (23.41)), intercept (Eqs. (15.31-15.32) and (15.80-15.87)), and energy (Eqs. (15.61) and (23.28-23.33)) parameters of copper coordinate compounds are given in Tables 23.51, 23.52, and 23.53, respectively. The total energy of each copper coordinate compound given in Table 23.54 was calculated as the sum over the integer multiple of each $E_{D}$ (Group) of Table 23.53 corresponding to functional-group composition of the compound. The charge-densities of exemplary copper coordinate compounds, copper chloride $(\mathrm{CuCl})$ and copper dichloride $\left(\mathrm{CuCl}_{2}\right)$ comprising the concentric shells of atoms with the outer shell bridged by one or more $\mathrm{H}_{2}$-type ellipsoidal MOs or joined with one or more hydrogen MOs are shown in Figures 23.11A and $B$, respectively.

Figure 23.11. (A) Copper Chloride. Color scale, translucent view of the charge-density of CuCl showing the orbitals of the Cu and Cl atoms at their radii, the ellipsoidal surface of each $\mathrm{H}_{2}$-type ellipsoidal MO that transitions to the corresponding outer shell of the atoms participating in each bond, and the nuclei (red, not to scale). (B) Copper Dichloride. Color scale, translucent view of the charge-density of $\mathrm{CuCl}_{2}$ showing the orbitals of the Cu and Cl atoms at their radii, the ellipsoidal surface of each $\mathrm{H}_{2}$-type ellipsoidal MO that transitions to the corresponding outer shell of the atoms participating in each bond, and the nuclei (red, not to scale).


Table 23.50. The symbols of the functional groups of copper coordinate compounds.

| Functional Group | Group Symbol |
| :--- | :--- |
| CuF group of CuF | $\mathrm{Cu}-\mathrm{F}$ (a) |
| $\mathrm{CuF}_{2}$ group of CuF | 2 |
| CuCl group of CuCl | $\mathrm{Cu}-\mathrm{F}$ (b) |
| CuO group of CuO | $\mathrm{Cu}-\mathrm{Cl}$ |

Table 23.51. The geometrical bond parameters of copper coordinate compounds and experimental values.
$\left.\left.\left.\begin{array}{|c|c|c|c|c|}\hline \text { Parameter } & \begin{array}{c}C u-F(a) \\ \text { Group }\end{array} & \begin{array}{c}C u-F(b) \\ \text { Group }\end{array} & \begin{array}{c}C u-C l \\ \text { Group }\end{array} & \begin{array}{c}C u-O \\ \text { Group }\end{array} \\ \hline n_{e} & 1 & 2 & 2 & 1 \\ \hline L & 10+2 \sqrt{\frac{3}{4}} & 2+4 \sqrt{\frac{3}{4}} & 0 & 3+10 \sqrt{\frac{3}{4}} \\ \hline a\left(a_{0}\right) & 1.90455 & 2.18842 & 2.00000 & 1.90208 \\ \hline c^{\prime}\left(a_{0}\right) & 1.69208 & 1.63632 & 1.83213 & 1.59251 \\ \hline \begin{array}{c}\text { Bond Length } \\ 2 c^{\prime}(\AA)\end{array} & 1.79083 & 1.73181 & 1.93905 & 1.68544 \\ \hline \begin{array}{c}\text { Exp. Bond Length } \\ (\AA)\end{array} & \begin{array}{c}1.7449[3] \\ (C u F)\end{array} & \begin{array}{c}1.7449[3] \\ (C u F)\end{array} & \begin{array}{c}2.051[15] \\ (C u C l)\end{array} & 1.724[15] \\ (C u O)\end{array}\right] \begin{array}{cccc|}\hline b, c\left(a_{0}\right) & 0.87417 & 1.45314 & 0.80205\end{array}\right] 1.04009\right]$
Table 23.52. The MO to HO intercept geometrical bond parameters of copper coordinate compounds. $E_{T}$ is $E_{T}$ (atom-atom,HO.AO).

| Bond | Atom | $\begin{gathered} E_{T} \\ (\mathrm{eV}) \\ \text { Bond } 1 \end{gathered}$ | $\begin{gathered} E_{T} \\ (\mathrm{eV}) \\ \text { Bond } 2 \end{gathered}$ | $\begin{gathered} E_{T} \\ \text { (eV) } \\ \text { Bond 3 } \end{gathered}$ |  | Final Total Energy Cu3d4s (eV) | $\begin{aligned} & r_{\text {murual }} \\ & \left(a_{0}\right) \end{aligned}$ | $\begin{aligned} & r_{\text {flnal }} \\ & \left(a_{0}\right) \end{aligned}$ | $\begin{gathered} E_{\text {Conlomoms }}(\mathrm{Cu} 3 d 4 s) \\ \text { (eV) } \\ \text { Final } \end{gathered}$ | $\begin{gathered} E(\text { Cu3d } 4 s) \\ (\mathrm{eV}) \\ \text { Final } \end{gathered}$ | $\theta^{\prime}$ | $\begin{aligned} & \theta_{1} \\ & \left({ }^{\circ}\right) \end{aligned}$ | $\begin{aligned} & \theta_{2} \\ & \left({ }^{\circ}\right) \end{aligned}$ | $\begin{gathered} d_{1} \\ \left(a_{0}\right) \end{gathered}$ | $\begin{gathered} d_{2} \\ \left(a_{0}\right) \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Cu-F (CuF) | Cu | 0 | 0 | 0 | 0 |  | 1.76095 | 1.76095 | -7.72638 |  | 150.35 | 29.65 | 85.13 | 0.16163 | 1.53045 |
| $\mathrm{Cu}-\mathrm{F}(\mathrm{CuF})$ | $F$ | 0 | 0 | 0 | 0 |  | 0.78069 | 0.78092 | -17.42282 |  | 123.18 | 56.82 | 48.39 | 1.26473 | 0.42736 |
| $\mathrm{Cu}-\mathrm{F}\left(\mathrm{CuF}_{2}\right)$ | Cu | -0.51359 | -0.51359 | 0 | 0 |  | 0.68740 | 0.65349 | -20.82022 |  | 50.41 | 129.59 | 20.28 | 2.05281 | 0.41649 |
| $\mathrm{Cu}-\mathrm{F}\left(\mathrm{CuF}_{2}\right)$ | $F$ | -0.51359 | 0 | 0 | 0 |  | 0.78069 | 0.75856 | -17.93641 |  | 68.67 | 111.33 | 29.09 | 1.91230 | 0.27597 |
| $\mathrm{Cu}-\mathrm{Cl}(\mathrm{CuCl})$ | Cu | 0 | 0 | 0 | 0 |  | 1.76095 | 1.76095 | -7.72638 |  | 153.16 | 26.84 | 82.50 | 0.26095 | 1.57119 |
| $\mathrm{Cu}-\mathrm{Cl}(\mathrm{CuCl})$ | Cl | 0 | 0 | 0 | 0 |  | 1.05158 | 1.05158 | -12.96764 |  | 139.26 | 40.74 | 58.82 | 1.03532 | 0.79682 |
| $\mathrm{Cu}-\mathrm{O}(\mathrm{CuO})$ | Cu | -0.51359 | 0 | 0 | 0 |  | 0.68740 | 0.67002 | -20.30662 |  | 100.40 | 79.60 | 39.32 | 1.47156 | 0.12096 |
| $\mathrm{Cu}-\mathrm{O}(\mathrm{CuO})$ | O | -0.51359 | 0 | 0 | 0 |  | 1.00000 | 0.96279 | -14.13165 |  | 119.26 | 60.74 | 53.86 | 1.12187 | 0.47064 |

Table 23.53. The energy parameters $(\mathrm{eV})$ of functional groups of copper coordinate compounds.

| Parameters | $C u-F(a)$ Group | $C u-F(b)$ Group | Cu-Cl <br> Group | $\begin{aligned} & \mathrm{Cu}-\mathrm{O} \\ & \text { Group } \end{aligned}$ |
| :---: | :---: | :---: | :---: | :---: |
| $n_{1}$ | 1 | 1 | 1 | 2 |
| $n_{2}$ | 0 | 0 | 0 | 0 |
| $n_{3}$ | 0 | 0 | 0 | 0 |
| $C_{1}$ | 0.75 | 0.5 | 0.5 | 0.375 |
| $\mathrm{C}_{2}$ | 0.44346 | 0.81732 | 0.59582 | 1 |
| $C_{1}$ | 0.75 | 1 | 1 | 1 |
| $c_{2}$ | 1 | 1 | 0.59582 | 0.63884 |
| $c_{3}$ | 0 | 0 | 0 | 0 |
| $C_{4}$ | 1 | 1 | 1 | 2 |
| $c_{5}$ | 1 | 1 | 1 | 2 |
| $\mathrm{C}_{10}$ | 0.75 | 0.5 | 0.5 | 0.375 |
| $C_{2}$ 。 | 0.44346 | 0.81732 | 0.59582 | 1 |
| $V_{e}(e V)$ | -34.12088 | -32.18726 | -27.68094 | -52.91628 |
| $V_{p}(e V)$ | 8.04085 | 8.31487 | 7.42620 | 17.08719 |
| $T(e V)$ | 8.95771 | 7.35401 | 6.92024 | 13.91013 |
| $V_{m}(e V)$ | -4.47886 | -3.67700 | -3.46012 | -6.95506 |
| $E$ (ао/но) (eV) | -7.72638 | -21.31697 | -7.72638 | -42.633933 |
| $\Delta E_{\mathrm{H}_{2} \mathrm{MO}}\left({ }_{\text {АО/НО }}\right)(\mathrm{eV})$ | 0 | 0 | 0 | 0 |
| $E_{T}$ (Ао/но) $(\mathrm{eV})$ | -7.72638 | -21.31697 | -7.72638 | -42.633933 |
| $E_{T}\left(\mathrm{H}_{2} \mathrm{MO}\right)(\mathrm{eV})$ | -29.32755 | -41.51235 | -24.52100 | -68.46008 |
| $E_{T}\left(\right.$ atom-atom, $\left.\mathrm{msp}^{3} . \mathrm{AO}\right)(\mathrm{eV})$ | 0 | -1.02719 | 0 | -1.02719 |
| $E_{T}$ (мо) (eV) | -29.32755 | -42.53954 | -24.52100 | -69.48726 |
| $\omega\left(10^{15} \mathrm{rad} / \mathrm{s}\right)$ | 29.1710 | 8.16340 | 7.97779 | 9.65069 |
| $E_{K}(\mathrm{eV})$ | 19.20083 | 5.37329 | 5.25112 | 6.35225 |
| $\bar{E}_{D}(e V)$ | -0.25424 | -0.19508 | -0.11116 | -0.17324 |
| $\bar{E}_{\text {Kvib }}(e \mathrm{~V})$ | $\begin{gathered} 0.07721 \\ {[62]} \end{gathered}$ | $\begin{gathered} 0.07721 \\ {[62]} \end{gathered}$ | $\begin{gathered} 0.05149 \\ {[62]} \end{gathered}$ | $\begin{gathered} 0.07937 \\ {[62]} \end{gathered}$ |
| $\bar{E}_{\text {osc }}(\mathrm{eV})$ | -0.21563 | -0.15648 | -0.08542 | -0.13355 |
| $E_{\text {mag }}(e \mathrm{~V})$ | 0 | 0.35223 | 0 | 0.35223 |
| $E_{T}($ Group $)(e V)$ | -29.54319 | -42.69602 | -24.60642 | -69.75437 |
| $E_{\text {initial }}\left(c_{4}\right.$ AO/HO) $(\mathrm{eV})$ | -7.72638 | -21.31697 | -7.72638 | -21.31697 |
| $E_{\text {initial }}\left(c_{5}\right.$ Ао/Но) $(e \mathrm{~V})$ | -17.42282 | -17.42282 | -12.96764 | -13.61806 |
| $E_{D}($ Group $)(e V)$ | 4.39399 | 3.95623 | 3.91240 | 2.93219 |

Table 23.54. The total bond energies of gaseous-state copper coordinate compounds calculated using the functional group composition and the energies of Table 23.53 compared to the gaseous-state experimental values.

| Formula | Name | $C u-F(a)$ <br> Group | $C u-F(b)$ <br> Group | $C u-C l$ <br> Group | $C u-O$ <br> Group | Calculated <br> Total Bond <br> Energy (eV) | Experimental <br> Total Bond <br> Energy (eV) | Relative <br> Error |
| :--- | :--- | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{CuF}^{\mathrm{CuF}} 2$ | Copper fluoride | Copper difluoride | 1 | 0 | 0 | 0 | 0 | 4.39399 |
| CuCl | Copper chloride | 0 | 2 | 0 | 0 | 7.91246 | $7.89020[63]$ | 0.01174 |
| CuO | Copper oxide | 0 | 0 | 1 | 0 | 3.91240 | $3.80870[63]$ | -0.00280 |

## ZINC FUNCTIONAL GROUPS AND MOLECULES

The electron configuration of zinc is $[A r] 4 s^{2} 3 d^{10}$ having the corresponding term ${ }^{1} S_{0}$. The two outer $4 s$ [61] electrons having energies of -9.394199 eV and -17.96439 eV [1] hybridize to form a single shell comprising two HOs. Each HO donates an electron to any single bond that participates in bonding with the HO such that two single bonds with ligands are possible to achieve a filled, spin-paired outer electron shell. Then, the total energy of the ${ }^{1} S_{0}$ state of the bonding zinc atom is given by the sum over the two electrons. The sum $E_{T}(\mathrm{Zn}, 4 \mathrm{sHO})$ of experimental energies [1] of Zn , and $\mathrm{Zn}^{+}$, is:

$$
\begin{equation*}
E_{T}(\mathrm{Zn}, 4 s \mathrm{HO})=-(17.96439 \mathrm{eV}+9.394199 \mathrm{eV})=-27.35859 \mathrm{eV} \tag{23.188}
\end{equation*}
$$

By considering that the central field decreases by an integer for each successive electron of the shell, the radius $r_{4 s H O}$ of the Zn4s HO shell may be calculated from the Coulombic energy using Eq. (15.13).

$$
\begin{equation*}
r_{4 \text { sHO }}=\sum_{n=28}^{29} \frac{(Z-n) e^{2}}{8 \pi \varepsilon_{0}(e 27.35859 \mathrm{eV})}=\frac{3 e^{2}}{8 \pi \varepsilon_{0}(e 27.35859 \mathrm{eV})}=1.49194 a_{0} \tag{23.189}
\end{equation*}
$$

where $Z=30$ for zinc. Using Eq. (15.14), the Coulombic energy $E_{\text {Coulomb }}(Z n, 4 s H O)$ of the outer electron of the Zn 4 s shell is

$$
\begin{equation*}
E_{\text {Coulomb }}(\mathrm{Zn}, 4 s \mathrm{HO})=\frac{-e^{2}}{8 \pi \varepsilon_{0} r_{4 \text { sHO }}}=\frac{-e^{2}}{8 \pi \varepsilon_{0} 1.49194 a_{0}}=-9.119530 \mathrm{eV} \tag{23.190}
\end{equation*}
$$

During hybridization, the spin-paired $4 s \mathrm{AO}$ electrons are promoted to the Zn 4 s HO shell as unpaired electrons. The energy for the promotion is given by Eq. (15.15) at the initial radius of the $4 s$ electrons. From Eq. (10.102) with $Z=30$ and $n=30$, the radius $r_{30}$ of the Zn 4 s AO shell is:

$$
\begin{equation*}
r_{30}=1.44832 a_{0} \tag{23.191}
\end{equation*}
$$

Using Eqs. (15.15) and (23.190), the unpairing energy is:

$$
\begin{equation*}
E_{4 s}(\text { magnetic })=\frac{2 \pi \mu_{0} e^{2} \hbar^{2}}{m_{e}^{2}\left(r_{30}\right)^{3}}=\frac{8 \pi \mu_{0} \mu_{B}^{2}}{\left(1.44832 a_{0}\right)^{3}}=0.03766 \mathrm{eV} \tag{23.192}
\end{equation*}
$$

Using Eqs. (23.189) and (23.191), the energy $E(\mathrm{Zn}, 4 \mathrm{sHO})$ of the outer electron of the Zn 4 s HO shell is:

$$
\begin{equation*}
E(\mathrm{Zn}, 4 s \mathrm{HO})=\frac{-e^{2}}{8 \pi \varepsilon_{0} r_{4 s H O}}+\frac{2 \pi \mu_{0} e^{2} \hbar^{2}}{m_{e}^{2}\left(r_{30}\right)^{3}}=-9.119530 \mathrm{eV}+0.03766 \mathrm{eV}=-9.08187 \mathrm{eV} \tag{23.193}
\end{equation*}
$$

Next, consider the formation of the $\mathrm{Zn}-L$-bond MO wherein each zinc atom has a $\mathrm{Zn} 4 s \mathrm{HO}$ electron with an energy given by Eq. (23.192). The total energy of the state of each zinc atom is given by the sum over the two electrons. The sum $E_{T}\left(\mathrm{Zn}_{\text {zn-L }} 4 s \mathrm{HO}\right)$ of energies of $\mathrm{Zn} 4 s H O$ (Eq. (23.192)) and $\mathrm{Zn}^{+}$is:

$$
\begin{equation*}
E_{T}\left(Z n_{Z n-L} 4 s H O\right)=-(17.96439 \mathrm{eV}+E(\mathrm{Zn}, 4 s H O))=-(17.96439 \mathrm{eV}+9.08187 \mathrm{eV})=-27.04626 \mathrm{eV} \tag{23.194}
\end{equation*}
$$

where $E(\mathrm{Zn}, 4 \mathrm{sHO})$ is the sum of the energy of $\mathrm{Zn},-9.394199 \mathrm{eV} \mathrm{eV}$, and the hybridization energy.
The zinc HO donates an electron to each MO. Using Eq. (23.30), the radius $r_{4 s H O}$ of the Zn 4 sHO shell calculated from the Coulombic energy is:

$$
\begin{equation*}
r_{\text {Zn-L4sHO }}=\left(\sum_{n=28}^{29}(Z-n)-1\right) \frac{e^{2}}{8 \pi \varepsilon_{0}(e 27.04626 \mathrm{eV})}=\frac{2 e^{2}}{8 \pi \varepsilon_{0}(e 27.04626 \mathrm{eV})}=1.00611 a_{0} \tag{23.195}
\end{equation*}
$$

Using Eqs. (15.19) and (23.194), the Coulombic energy $E_{\text {Coulomb }}\left(\mathrm{Zn}_{Z n-L}, 4 s \mathrm{HO}\right)$ of the outer electron of the Zn 4 sHO shell is:

$$
\begin{equation*}
E_{\text {Coulomb }}\left(Z n_{Z n-L}, 4 s H O\right)=\frac{-e^{2}}{8 \pi \varepsilon_{0} r_{Z n-L 4 s H O}}=\frac{-e^{2}}{8 \pi \varepsilon_{0} 1.00611 a_{0}}=-13.52313 \mathrm{eV} \tag{23.196}
\end{equation*}
$$

During hybridization, the spin-paired $2 s$ electrons are promoted to the Zn 4 sHO shell as unpaired electrons. The energy for the promotion is the magnetic energy given by Eq. (23.191). Using Eqs. (23.195) and (23.191), the energy $E\left(Z n_{Z n-L}, 4 s H O\right)$ of the outer electron of the Zn 4 s HO shell is:

$$
\begin{equation*}
E\left(Z n_{Z n-L}, 4 s H O\right)=\frac{-e^{2}}{8 \pi \varepsilon_{0} r_{Z n-L 4 s H O}}+\frac{2 \pi \mu_{0} e^{2} \hbar^{2}}{m_{e}^{2}\left(r_{30}\right)^{3}}=-13.52313 \mathrm{eV}+0.03766 \mathrm{eV}=-13.48547 \mathrm{eV} \tag{23.197}
\end{equation*}
$$

Thus, $E_{T}(\mathrm{Zn}-L, 4 s \mathrm{HO})$, the energy change of each $\mathrm{Zn} 4 s \mathrm{HO}$ shell with the formation of the $\mathrm{Zn}-L$-bond MO is given by the difference between Eq. (23.196) and Eq. (23.192):

$$
\begin{equation*}
E_{T}(Z n-L, 4 s H O)=E\left(Z n_{Z n-L}, 4 s H O\right)-E(Z n, 4 s H O)=-13.48547 \mathrm{eV}-(-9.08187 \mathrm{eV})=-4.40360 \mathrm{eV} \tag{23.198}
\end{equation*}
$$

The semimajor axis $a$ solution given by Eq. (23.41) of the force balance equation, Eq. (23.39), for the $\sigma$-MO of the $Z n-L$-bond MO of $Z n L_{n}$ is given in Table 23.56 with the force-equation parameters $Z=30, n_{e}$, and $L$ corresponding to the orbital and spin angular momentum terms of the 4 s HO shell. The semimajor axis $a$ of organometallic compounds are solved using Eq. (15.51).

For the $\mathrm{Zn}-L$ functional groups, hybridization of the $4 s$ AOs of $Z n$ to form a single $4 s$ HO shell forms an energy minimum, and the sharing of electrons between the Zn 4 s HO and $L \mathrm{AO}$ to form a MO permits each participating orbital to decrease in radius and energy. The Cl AO has an energy of $E(C l)=-12.96764 \mathrm{eV}$, the $C 2 s p^{3} \mathrm{HO}$ has an energy of $E\left(C, 2 s p^{3}\right)=-14.63489 \mathrm{eV}$ (Eq. (15.25)), the Coulomb energy of the Zn 4 s HO is $E_{\text {Coulomb }}(\mathrm{Zn}, 4 \mathrm{sHO})=-9.119530 \mathrm{eV}$ (Eq. (23.189)), and the Zn 4 s HO has an energy of $E(\mathrm{Zn}, 4 s \mathrm{HO})=-9.08187 \mathrm{eV}$ (Eq. (23.192)). To meet the equipotential condition of the union of the $\mathrm{Zn}-\mathrm{L}_{2} \quad \mathrm{H}_{2}$-type-ellipsoidal-MO with these orbitals, the hybridization factor(s), at least one of $c_{2}$ and $C_{2}$ of Eq. (15.61) for the $\mathrm{Zn}-L$-bond MO given by Eq. (15.77) is:

$$
\begin{align*}
& C_{2}(\text { ClAO to Zn4sHO })=\frac{E(\mathrm{Zn}, 34 \mathrm{sHO})}{E(C l A O)}=\frac{-9.08187 \mathrm{eV}}{-12.96764 \mathrm{eV}}=0.70035  \tag{23.199}\\
& \begin{aligned}
c_{2}\left(\mathrm{C} 2 \mathrm{sp}{ }^{3} \mathrm{HO} \text { to } \mathrm{Zn} 4 \mathrm{sHO}\right) & =C_{2}\left(C 2 s p^{3} \mathrm{HO} \text { to } \mathrm{Zn} 4 \mathrm{sHO}\right) \\
& =\frac{E_{\text {Coulomb }}(\mathrm{Zn}, 4 \mathrm{sHO})}{E\left(C, 2 s p^{3}\right)} c_{2}\left(C 2 s p^{3} \mathrm{HO}\right)=\frac{-9.11953 \mathrm{eV}}{-14.63489 \mathrm{eV}}(0.91771)=0.57186
\end{aligned}
\end{align*}
$$

where Eqs. (15.76), (15.79), and (13.430) were used in Eq. (23.199). Since the energy of the MO is matched to that of the Zn 4 sHO in coordinate compounds, $E(\mathrm{AO} / \mathrm{HO})$ in Eq. (15.61) is $E(\mathrm{Zn}, 4 s \mathrm{HO})$ given by Eq. (23.192) and $E(\mathrm{Zn}, 4 \mathrm{sHO})$ for organometallics is $E_{\text {Coulomb }}(\mathrm{Zn}, 4 \mathrm{sHO})$ given by Eq. (23.189). $E_{T}\left(\right.$ atom-atom,msp $\left.{ }^{3} . A O\right)$ of the Zn - $L$-bond MO is determined by considering that the bond involves an electron transfer from the zinc atom to the ligand atom to form partial ionic character in the bond as in the case of the zwitterions such as $\mathrm{H}_{2} \mathrm{~B}^{+}-F^{-}$given in the Halido Boranes section. For the coordinate compounds, $E_{T}\left(\right.$ atom-atom, $\left.m s p^{3} . A O\right)$ is -8.80720 eV , two times the energy of Eq. (23.197).

The symbols of the functional groups of zinc coordinate compounds are given in Table 23.55. The geometrical (Eqs. (15.1-15.5) and (23.41)), intercept (Eqs. (15.31-15.32) and (15.80-15.87)), and energy (Eqs. (15.61) and (23.28-23.33)) parameters of zinc coordinate compounds are given in Tables 23.56, 23.57, and 23.58, respectively. The total energy of each zinc coordinate compound given in Table 22.59 was calculated as the sum over the integer multiple of each $E_{D}$ (Group) of Table 23.58 corresponding to functional-group composition of the compound. The charge-densities of exemplary zinc coordinate and organometallic compounds, zinc chloride ( ZnCl ) and di-n-butylzinc $\left(\mathrm{Zn}\left(\mathrm{C}_{4} \mathrm{H}_{9}\right)_{2}\right)$ 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 are shown in Figures 23.12A and B, respectively.

Figure 23.12. (A) Zinc Chloride. Color scale, translucent view of the charge-density of ZnCl showing the orbitals of the Zn and Cl atoms at their radii, the ellipsoidal surface of each $\mathrm{H}_{2}$-type ellipsoidal MO that transitions to the corresponding outer shell of the atoms participating in each bond, and the nuclei (red, not to scale). (B) Di-n-butylzinc. Color scale, translucent view of the charge-density of $\mathrm{Zn}\left(\mathrm{C}_{4} \mathrm{H}_{9}\right)_{2}$ showing the orbitals of the Zn and $C$ atoms at their radii, the ellipsoidal surface of each H or $\mathrm{H}_{2}$-type ellipsoidal MO that transitions to the corresponding outer shell of the atoms participating in each bond, and the nuclei (red, not to scale).


Table 23.55. The symbols of the functional groups of zinc coordinate compounds.

| Functional Group | Group Symbol |
| :---: | :---: |
| ZnCl group of ZnCl | $\mathrm{Zn}-\mathrm{Cl}$ (a) |
| $\mathrm{ZnCl}_{2}$ group of $\mathrm{ZnCl}_{2}$ | $\mathrm{Zn}-\mathrm{Cl}$ (b) |
| ZnCalkyl group of $\mathrm{RZnR}{ }^{\prime}$ | $\mathrm{Zn}-\mathrm{C}$ |
| $\mathrm{CH}_{3}$ group | $\mathrm{C}-\mathrm{H}\left(\mathrm{CH}_{3}\right)$ |
| $\mathrm{CH}_{2}$ group | $\mathrm{C}-\mathrm{H}\left(\mathrm{CH}_{2}\right)$ |
| $C C$ bond ( $n-C$ ) | C-C |

Table 23.56. The geometrical bond parameters of zinc coordinate compounds and experimental values.

| Parameter | $\begin{aligned} & \mathrm{Zn}-\mathrm{Cl}(\mathrm{a}) \\ & \text { Group } \end{aligned}$ | $\begin{aligned} & \mathrm{Zn}-\mathrm{Cl}(\mathrm{~b}) \\ & \text { Group } \end{aligned}$ | $\begin{aligned} & \hline Z n-C \\ & \text { Group } \end{aligned}$ | $\begin{gathered} \mathrm{C}-\mathrm{H}\left(\mathrm{CH}_{3}\right) \\ \text { Group } \\ \hline \end{gathered}$ | $\begin{gathered} \mathrm{C}-\mathrm{H}\left(\mathrm{CH}_{2}\right) \\ \text { Group } \\ \hline \end{gathered}$ | $\begin{aligned} & C-C \\ & \text { Group } \end{aligned}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $n_{e}$ | 6 | 5 |  |  |  |  |
| $L$ | $4 \sqrt{\frac{3}{4}}$ | 10 |  |  |  |  |
| $a\left(a_{0}\right)$ | 4.11547 | 3.83333 | 1.87715 | 1.64920 | 1.67122 | 2.12499 |
| $c^{\prime}\left(a_{0}\right)$ | 1.97928 | 1.91023 | 1.81177 | 1.04856 | 1.05553 | 1.45744 |
| Bond Length $2 c^{\prime}(\AA)$ | 2.09478 | 2.02170 | 1.91750 | 1.10974 | 1.11713 | 1.54280 |
| Exp. Bond Length ( $\AA$ ) | $\begin{gathered} 2.05[15] \\ \left(\mathrm{ZnCl}_{2}\right) \end{gathered}$ | $\begin{gathered} 2.05[15] \\ \left(\mathrm{ZnCl}_{2}\right) \end{gathered}$ | $\begin{gathered} 1.930[15] \\ \left(\mathrm{CH}_{3} \mathrm{ZnCH}_{3}\right) \end{gathered}$ | $1.113[3]$ (trimethylaluminum) $1.107[3]$ $(C-H$ propane) $1.117[3]$ $(C-H$ butane $)$ | 1.107 [3] ( $C-H$ propane) 1.117 [3] ( $C-H$ butane) | $1.532 \text { [3] }$ <br> (propane) <br> 1.531 [3] <br> (butane) |
| $b, c\left(a_{0}\right)$ | 3.60826 | 3.32347 | 0.49108 | 1.27295 | 1.29569 | 1.54616 |
| $e$ | 0.48094 | 0.49832 | 0.96517 | 0.63580 | 0.63159 | 0.68600 |

Table 23．57．The MO to HO intercept geometrical bond parameters of zinc coordinate compounds．$E_{T}$ is $E_{T}$（atom－atom，HO．AO）．

| － |  |  |  |  | $\begin{gathered} N \\ \underset{N}{\infty} \\ \underset{O}{\circ} \end{gathered}$ | $\begin{aligned} & \underset{N}{N} \\ & \underset{\infty}{\infty} \end{aligned}$ | $\stackrel{N}{N}$ | $\begin{gathered} N \\ \underset{\infty}{\infty} \\ 0 \\ 0 \end{gathered}$ | $\begin{aligned} & \stackrel{\infty}{\infty} \\ & \underset{\sim}{\infty} \\ & \hline \end{aligned}$ |  | $\left\|\begin{array}{c} \bullet \\ \underset{\sim}{\infty} \\ 0 \\ 0 \end{array}\right\|$ | N |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| O E |  |  |  |  | $\begin{aligned} & \circ \\ & \vdots \\ & \vdots \\ & \vdots \\ & 0 \end{aligned}$ | $\begin{aligned} & \text { o } \\ & \text { d } \\ & \text { d } \end{aligned}$ |  |  | $\begin{aligned} & \text { t } \\ & \text { N } \\ & \underset{\sim}{n} \end{aligned}$ | $$ | $\begin{gathered} \underset{\sim}{\infty} \\ \infty \\ \infty \\ - \end{gathered}$ | $\begin{aligned} & \text { O} \\ & \text { ò } \\ & \underset{-}{2} \end{aligned}$ |
| 0 O |  |  |  |  | $\begin{gathered} \underset{\sim}{c} \\ \underset{\sim}{\infty} \\ \hline \end{gathered}$ | $\begin{aligned} & \text { N} \\ & \underset{\sim}{\infty} \\ & \text { in } \end{aligned}$ | $\begin{gathered} \text { ơ } \\ \underset{\sim}{\infty} \\ i \end{gathered}$ | $\begin{gathered} \underset{O}{O} \\ \underset{i}{n} \end{gathered}$ |  | $\begin{aligned} & \underset{\sim}{ \pm} \\ & \stackrel{\sim}{\infty} \end{aligned}$ | $\begin{aligned} & \infty \\ & 0 \\ & 0 \\ & 0 \\ & \hline \end{aligned}$ | $\begin{aligned} & 8 \\ & \stackrel{8}{\circ} \\ & \hline \end{aligned}$ |
| $\bigcirc$ |  |  |  |  | $\stackrel{8}{\stackrel{8}{\mathrm{~A}}}$ | $\begin{aligned} & 8 \\ & \stackrel{y}{\lambda} \end{aligned}$ | $\stackrel{8}{\stackrel{8}{\mathrm{~N}}}$ | $\underset{\sim}{\underset{\sim}{c}}$ | $\begin{aligned} & \bar{n} \\ & \text { ì } \end{aligned}$ | $\stackrel{n}{\vdots}$ | $\begin{aligned} & \frac{\infty}{3} \\ & \hdashline= \end{aligned}$ | 会 |
| $\cdots$－ |  |  |  |  | $\begin{gathered} 8 \\ \stackrel{y}{n} \\ \end{gathered}$ | $\begin{aligned} & 8 \\ & \stackrel{N}{n} \end{aligned}$ | $\begin{gathered} 8 \\ \stackrel{N}{n} \end{gathered}$ | $\begin{gathered} 8 \\ \stackrel{N}{n} \end{gathered}$ | $\stackrel{\text { g }}{\stackrel{\text { g }}{\lambda}}$ | $\underset{\substack{\text { G } \\ \mathscr{O}}}{ }$ | $\begin{aligned} & \infty \\ & \infty \\ & \dot{0} \end{aligned}$ | $\begin{aligned} & \underset{\sim}{f} \\ & \stackrel{\rightharpoonup}{n} \end{aligned}$ |
|  |  |  |  |  |  |  |  |  | $\begin{aligned} & \hat{y} \\ & \underset{0}{0} \\ & \vdots \\ & \underset{n}{1} \end{aligned}$ |  | $\begin{array}{\|c} \hat{0} \\ \hat{0} \\ \stackrel{n}{n} \\ \stackrel{n}{1} \end{array}$ |  |
|  | $\begin{aligned} & n \\ & \underset{\sim}{n} \\ & \\ & \end{aligned}$ | $\begin{aligned} & \underset{\mathrm{I}}{\mathrm{~N}} \\ & \underset{\sim}{\mathrm{I}} \end{aligned}$ | $\begin{gathered} \underset{0}{0} \\ \underset{\sim}{2} \\ \underset{\sim}{7} \end{gathered}$ | $\begin{aligned} & \underset{\sim}{\mathrm{I}} \\ & \underset{\sim}{n} \\ & \underset{\sim}{n} \end{aligned}$ | $\left\lvert\, \begin{aligned} & n \\ & \\ & \infty \\ & \underset{\sim}{1} \end{aligned}\right.$ | $\begin{aligned} & \text { n } \\ & \hat{n} \\ & \vdots \\ & \underset{寸}{1} \end{aligned}$ | $\begin{aligned} & \text { n } \\ & \\ & \infty \\ & \underset{J}{2} \end{aligned}$ | $\begin{gathered} n \\ n \\ 0 \\ \infty \\ \vdots \end{gathered}$ | $\begin{gathered} \underset{\sim}{c} \\ \stackrel{\rightharpoonup}{\sim} \\ \stackrel{i}{6} \end{gathered}$ | $\begin{aligned} & \underset{7}{7} \\ & \underset{0}{0} \\ & \underset{\sim}{6} \end{aligned}$ |  | $\begin{aligned} & \underset{\sim}{\mp} \\ & \underset{\circ}{\circ} \\ & \underset{\sim}{0} \end{aligned}$ |
| \％ | $\begin{aligned} & \overline{0} \\ & 0 \\ & \hline \end{aligned}$ | $$ | $\begin{aligned} & \hat{2} \\ & \underset{O}{\circ} \\ & \underset{O}{2} \end{aligned}$ | $$ | $\begin{aligned} & \pm \\ & \underset{\sim}{9} \\ & \underset{\sim}{2} \end{aligned}$ | $\frac{\underset{\sim}{\lambda}}{\underset{O}{\theta}}$ | $\begin{aligned} & \underset{~}{2} \\ & \underset{\sim}{g} \end{aligned}$ | $\frac{\underset{A}{A}}{\hat{O}}$ | $\begin{aligned} & \text { ô } \\ & \hat{o} \\ & 0 \\ & 0 \\ & 0 \end{aligned}$ | $\begin{aligned} & \stackrel{\rightharpoonup}{4} \\ & \stackrel{y}{\infty} \\ & \stackrel{\infty}{\infty} \end{aligned}$ | $\begin{aligned} & 2 \\ & 0 \\ & 0 \\ & 0 \\ & 0 \\ & 0 \end{aligned}$ | or |
|  | $\begin{aligned} & \pm \\ & \underset{\sim}{g} \\ & \underset{\sim}{2} \end{aligned}$ | $\begin{aligned} & \infty \\ & \stackrel{n}{n} \\ & \vdots \\ & \hline \end{aligned}$ | $\begin{aligned} & \pm \\ & \underset{\sim}{g} \\ & \underset{\sim}{2} \end{aligned}$ |  |  | $\frac{\underset{\lambda}{\lambda}}{\vdots}$ | $\begin{aligned} & \underset{\sim}{\partial} \\ & \underset{\sim}{g} \end{aligned}$ | $\frac{\underset{\lambda}{\lambda}}{\vdots}$ | $\frac{\underset{\lambda}{\lambda}}{\hat{O}}$ | $\frac{\underset{i}{\lambda}}{\underset{O}{\circ}}$ | $\frac{\underset{\lambda}{\lambda}}{\vdots}$ | $\stackrel{\text { N }}{\text { N}}$ |
|  |  |  |  |  |  |  |  |  | $\begin{gathered} \hat{\infty} \\ \vdots \\ \vdots \\ \vdots \\ \vdots \\ \vdots \end{gathered}$ |  |  | ¢ <br> $\substack{+7 \\ \dot{\sim} \\ \cdots \\ \hline}$ |
| NS 要若 | $\bigcirc$ | － | 0 | － | $\bigcirc$ | － | 0 | $\bigcirc$ | $\bigcirc$ | $\bigcirc$ | － | － |
| $\Leftrightarrow \stackrel{S}{0}$ | $\bigcirc$ | $\bigcirc$ | 0 | － | － | － | － | － | $\bigcirc$ | $\bigcirc$ | － | － |
| $\Leftrightarrow S_{C}^{C}$ | $\bigcirc$ | $\bigcirc$ | $\begin{aligned} & 8 \\ & 0 \\ & 0 \\ & \vdots \\ & 7 \\ & 7 \end{aligned}$ | － | － | － | － | － | － | $\frac{\infty}{\underset{\sim}{\alpha}}$ | － | ¢ |
| $\Leftrightarrow \underset{C}{C}$ | $\begin{aligned} & o \\ & 0 \\ & \vdots \\ & \vdots \\ & \dot{T} \end{aligned}$ |  | $\begin{aligned} & \stackrel{\circ}{\circ} \\ & \stackrel{N}{O} \\ & \dot{寸} \end{aligned}$ | $\begin{aligned} & \stackrel{\circ}{\circ} \\ & \overparen{O} \\ & \underset{寸}{\prime} \\ & \hline \end{aligned}$ | $\bigcirc$ | 0 | 0 | 0 |  | $\frac{\infty}{\underset{\alpha}{\alpha}}$ | $\begin{aligned} & \infty \\ & \frac{\infty}{2} \\ & \alpha \\ & \underset{\alpha}{1} \end{aligned}$ | ¢ |
|  | ミ | こ | ミ | E | ミ | $\cup$ | ミ | $\cup$ | U | $\checkmark$ | $0^{\circ}$ | U |
| 荷 | $\begin{aligned} & \tilde{E} \\ & \text { N } \\ & \underset{\sim}{U} \\ & 1 \\ & \tilde{N} \end{aligned}$ |  |  |  | $\begin{aligned} & \tilde{N}_{2}^{2} \\ & \frac{1}{1} \\ & \frac{1}{2} \end{aligned}$ | $\begin{aligned} & \approx \\ & \frac{2}{2} \\ & 1 \\ & \tilde{N} \end{aligned}$ |  | $\begin{aligned} & \tilde{v}_{1} \\ & \mathcal{U}^{\prime} \\ & \mathcal{N}^{\prime} \\ & \tilde{v} \\ & \Sigma \end{aligned}$ |  | $\begin{array}{\|c} \overparen{z} \\ \underline{y} \\ z \\ 1 \\ u \end{array}$ | $\left\lvert\, \begin{aligned} & 1 \\ & \mathcal{N}^{\prime} \\ & \mathbb{N}_{1} \\ & 0_{0} \\ & 0 \\ & \mathbb{Z} \end{aligned}\right.$ | $\begin{aligned} & \mathbb{N}^{\prime} \\ & z^{\prime} \\ & v_{0} \\ & 0 \end{aligned}$ |

Table 23.58. The energy parameters ( eV ) of functional groups of zinc coordinate compounds.

| Parameters | $\begin{aligned} & \mathrm{Zn}-\mathrm{Cl}(\mathrm{a}) \\ & \text { Group } \end{aligned}$ | $\begin{gathered} \mathrm{Zn}-\mathrm{Cl}(\mathrm{~b}) \\ \text { Group } \\ \hline \end{gathered}$ | $\begin{aligned} & \hline \mathrm{Zn}-\mathrm{C} \\ & \text { Group } \\ & \hline \end{aligned}$ | $\mathrm{CH}_{3}$ <br> Group | $\begin{gathered} \mathrm{CH}_{2} \\ \text { Group } \end{gathered}$ | $\begin{aligned} & C-C \\ & \text { Group } \end{aligned}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $n_{1}$ | 1 | 1 | 1 | 3 | 2 | 1 |
| $n_{2}$ | 0 | 0 | 0 | 2 | 1 | 0 |
| $n_{3}$ | 0 | 0 | 0 | 0 | 0 | 0 |
| $C_{1}$ | 0.75 | 0.75 | 0.5 | 0.75 | 0.75 | 0.5 |
| $\mathrm{C}_{2}$ | 0.70035 | 0.70035 | 0.57186 | 1 | 1 | 1 |
| $C_{1}$ | 1 | 1 | 1 | 1 | 1 | 1 |
| $c_{2}$ | 1 | 1 | 0.57186 | 0.91771 | 0.91771 | 0.91771 |
| $c_{3}$ | 0 | 0 | 2 | 0 | 1 | 0 |
| $C_{4}$ | 1 | 1 | 2 | 1 | 1 | 2 |
| $c_{5}$ | 1 | 1 | 0 | 3 | 2 | 0 |
| $C_{10}$ | 0.75 | 0.75 | 0.5 | 0.75 | 0.75 | 0.5 |
| $\mathrm{C}_{20}$ | 0.70035 | 0.70035 | 0.57186 | 1 | 1 | 1 |
| $V_{e}(e V)$ | -14.41370 | -15.58624 | -34.63883 | -107.32728 | -70.41425 | -28.79214 |
| $V_{p}(e V)$ | 6.87412 | 7.12260 | 7.50965 | 38.92728 | 25.78002 | 9.33352 |
| $T(e V)$ | 1.75116 | 2.03299 | 9.22644 | 32.53914 | 21.06675 | 6.77464 |
| $V_{m}(e V)$ | -0.87558 | -1.01649 | -4.61322 | -16.26957 | -10.53337 | -3.38732 |
| $E$ (Ао/но) (eV) | -9.08187 | -9.08187 | -9.11953 | -15.56407 | -15.56407 | -15.56407 |
| $\Delta E_{\mathrm{H}_{2} \mathrm{MO}}($ АО/НО) $(\mathrm{eV})$ | 0 | 0 | 0 | 0 | 0 | 0 |
| $E_{T}$ (Ао/но) $(\mathrm{eV})$ | -9.08187 | -9.08187 | -9.11953 | -15.56407 | -15.56407 | -15.56407 |
| $E_{T}\left(\mathrm{H}_{2} \mathrm{MO}\right)(\mathrm{eV})$ | -15.74587 | -16.52901 | -31.63548 | -67.69451 | -49.66493 | -31.63537 |
| $E_{T}\left(\right.$ atom-atom, $\left.\mathrm{msp}^{3} \cdot \mathrm{AO}\right)(\mathrm{eV})$ | -8.80720 | -8.80720 | 0 | 0 | 0 | -1.85836 |
| $E_{T}$ (мо) (eV) | -24.55307 | -25.33621 | -31.63537 | -67.69450 | -49.66493 | -33.49373 |
| $\omega\left(10^{15} \mathrm{rad} / \mathrm{s}\right)$ | 4.37145 | 3.99216 | 8.59541 | 24.9286 | 24.2751 | 9.43699 |
| $E_{K}(e V)$ | 2.87737 | 2.62771 | 5.65765 | 16.40846 | 15.97831 | 6.21159 |
| $\bar{E}_{D}(e V)$ | -0.08240 | -0.08125 | -0.14887 | -0.25352 | -0.25017 | -0.16515 |
| $\bar{E}_{\text {Kvib }}(e \mathrm{~V})$ | $\begin{gathered} 0.04842 \\ {[14]} \end{gathered}$ | $\begin{gathered} 0.04842 \\ {[14]} \end{gathered}$ | $\begin{gathered} 0.06236 \\ {[64]} \end{gathered}$ | $\begin{gathered} 0.35532 \\ (\mathrm{Eq} . \\ (13.458)) \end{gathered}$ | $\begin{gathered} 0.35532 \\ (\mathrm{Eq} . \\ (13.458)) \\ \hline \end{gathered}$ | $\begin{gathered} 0.12312 \\ {[6]} \end{gathered}$ |
| $\bar{E}_{\text {osc }}(\mathrm{eV})$ | -0.05819 | -0.05704 | -0.11768 | -0.22757 | -0.14502 | -0.10359 |
| $E_{\text {mag }}(\mathrm{eV})$ | 0.03445 | 0.03445 | 0.14803 | 0.14803 | 0.14803 | 0.14803 |
| $E_{T}($ Group $)(e V)$ | -24.61126 | -25.39325 | -31.75305 | -67.92207 | -49.80996 | -33.59732 |
| $E_{\text {initial }}\left(c_{4}\right.$ АО/но) $(\mathrm{eV})$ | -9.08187 | -9.08187 | -14.63489 | -14.63489 | -14.63489 | -14.63489 |
| $E_{\text {initial }}\left(\mathrm{c}_{5}\right.$ Ао/но) $(\mathrm{eV})$ | -12.96764 | -12.96764 | 0 | -13.59844 | -13.59844 | 0 |
| $E_{D}($ Group $)(e V)$ | 2.56175 | 3.34374 | 2.18721 | 12.49186 | 7.83016 | 4.32754 |

Table 23.59. The total bond energies of gaseous-state zinc coordinate compounds calculated using the functional group composition and the energies of Table 23.58 compared to the gaseous-state experimental values.

| Formula | Name | $\mathrm{Zn-Cl}(\mathrm{a})$ <br> Group | $\mathrm{Zn}-\mathrm{Cl}(\mathrm{b})$ <br> Group | $\mathrm{Zn}-\mathrm{C}$ <br> Group | $\mathrm{CH}_{3}$ <br> Group | $\mathrm{CH}_{2}$ <br> Group | $\mathrm{C}-\mathrm{C}$ <br> Group | Calculated <br> Total Bond <br> Energy (eV) | Experimental <br> Total Bond <br> Energy (eV) |
| :--- | :--- | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| ZnCl | Zinc chloride | 1 | 0 | 0 | 0 | 0 | 0 | 2.56175 | $2.56529[15]$ |
| Relative |  |  |  |  |  |  |  |  |  |
| Error |  |  |  |  |  |  |  |  |  |

## GERMANIUM ORGANOMETALLIC FUNCTIONAL GROUPS AND MOLECULES

The branched-chain alkyl germanium molecules, $G e C_{n} H_{2 n-2}$, comprise at least one $G e$ bound by a carbon-germanium single bond comprising a $C-G e$ group, and the digermanium molecules further comprise a $G e-G e$ functional group. Both comprise at least a terminal methyl group $\left(\mathrm{CH}_{3}\right)$ and may comprise methylene $\left(\mathrm{CH}_{2}\right)$, methylyne $(\mathrm{CH})$, and $\mathrm{C}-\mathrm{C}$ functional groups. 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 $\left(\left(\mathrm{CH}_{3}\right)_{2} \mathrm{CH}\right)$ and t-butyl $\left(\left(\mathrm{CH}_{3}\right)_{3} \mathrm{C}\right)$ groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $\mathrm{C}-\mathrm{C}$ bonds comprise functional groups.

As in the cases of carbon, silicon, and tin, the bonding in the germanium atom involves four $s p^{3}$ hybridized orbitals. For germanium, they are formed from the $4 p$ and $4 s$ electrons of the outer shells. $G e-C$ bonds form between a $G e 4 s p^{3} \mathrm{HO}$ and a $C 3 s p^{3} \mathrm{HO}$, and $G e-G e$ bonds form between between $G e 4 s p^{3}$ HOs to yield germanes and digermanes, respectively. The geometrical parameters of each $G e-C$ and $G e-G e$ functional group is solved using Eq. (15.51) and the relationships between the prolate spheroidal axes. Then, the sum of the energies of the $H_{2}$-type ellipsoidal MOs is matched to that of the Ge4sp ${ }^{3}$ shell as in the case of the corresponding carbon, silicon, and tin molecules. As in the case of the transition metals, the energy of each functional group is determined for the effect of the electron density donation from each participating $C 3 s p^{3} \mathrm{HO}$ and $G e 4 s p^{3}$ HO to the corresponding MO that maximizes the bond energy.

The $G e$ electron configuration is $[A r] 4 s^{2} 3 d^{10} 4 p^{2}$, and the orbital arrangement is:
4 p state

$$
\begin{equation*}
\frac{\uparrow}{1} \frac{\uparrow}{0} \frac{}{-1} \tag{23.201}
\end{equation*}
$$

corresponding to the ground state ${ }^{3} P_{0}$. The energy of the germanium $4 p$ shell is the negative of the ionization energy of the germanium atom [1] given by

$$
\begin{equation*}
E(\text { Ge }, 4 p \text { shell })=-E(\text { ionization } ; G e)=-7.89943 \mathrm{eV} \tag{23.202}
\end{equation*}
$$

The energy of germanium is less than the Coulombic energy between the electron and proton of $H$ given by Eq. (1.264), but the atomic orbital may hybridize in order to achieve a bond at an energy minimum. After Eq. (13.422), the Ge4s atomic orbital (AO) combines with the Ge4p AOs to form a single $G e 4 s p^{3}$ hybridized orbital (HO) with the orbital arrangement:

\[

\]

where the quantum numbers $\left(\ell, m_{\ell}\right.$ ) are below each electron. The total energy of the state is given by the sum over the four electrons. The sum $E_{T}\left(G e, 4 s p^{3}\right)$ of experimental energies [1] of $G e, G e^{+}, G e^{2+}$, and $G e^{3+}$ is:

$$
\begin{equation*}
E_{T}\left(G e, 4 s p^{3}\right)=45.7131 \mathrm{eV}+34.2241 \mathrm{eV}+15.93461 \mathrm{eV}+7.89943 \mathrm{eV}=103.77124 \mathrm{eV} \tag{23.204}
\end{equation*}
$$

By considering that the central field decreases by an integer for each successive electron of the shell, the radius $r_{4 s p^{3}}$ of the $G e 4 s p^{3}$ shell may be calculated from the Coulombic energy using Eq. (15.13).

$$
\begin{equation*}
r_{4 s p^{3}}=\sum_{n=28}^{31} \frac{(Z-n) e^{2}}{8 \pi \varepsilon_{0}(e 103.77124 \mathrm{eV})}=\frac{10 e^{2}}{8 \pi \varepsilon_{0}(e 103.77124 \mathrm{eV})}=1.31113 a_{0} \tag{23.205}
\end{equation*}
$$

where $Z=32$ for germanium. Using Eq. (15.14), the Coulombic energy $E_{\text {Coulomb }}\left(G e, 4 s p^{3}\right)$ of the outer electron of the $G e 4 s p^{3}$ shell is:

$$
\begin{equation*}
E_{\text {Coulomb }}\left(G e, 4 s p^{3}\right)=\frac{-e^{2}}{8 \pi \varepsilon_{0} r_{4 s p^{3}}}=\frac{-e^{2}}{8 \pi \varepsilon_{0} 1.31113 a_{0}}=-10.37712 \mathrm{eV} \tag{23.206}
\end{equation*}
$$

During hybridization, the spin-paired $4 s$ electrons are promoted to the $G e 4 s p^{3}$ shell as unpaired electrons. The energy for the promotion is the magnetic energy given by Eq. (15.15) at the initial radius of the $4 s$ electrons. From Eq. (10.102) with $Z=32$ and $n=30$, the radius $r_{30}$ of the Ge4s shell is:

$$
\begin{equation*}
r_{30}=1.19265 a_{0} \tag{23.207}
\end{equation*}
$$

Using Eqs. (15.15) and (23.207), the unpairing energy is:

$$
\begin{equation*}
E(\text { magnetic })=\frac{2 \pi \mu_{0} e^{2} \hbar^{2}}{m_{e}^{2}\left(r_{30}\right)^{3}}=\frac{8 \pi \mu_{o} \mu_{B}^{2}}{\left(1.19265 a_{0}\right)^{3}}=0.06744 \mathrm{eV} \tag{23.208}
\end{equation*}
$$

Using Eqs. (23.206) and (23.208), the energy $E\left(G e, 4 s p^{3}\right)$ of the outer electron of the $G e 4 s p^{3}$ shell is:

$$
\begin{equation*}
E\left(G e, 4 s p^{3}\right)=\frac{-e^{2}}{8 \pi \varepsilon_{0} r_{4 s p^{3}}}+\frac{2 \pi \mu_{0} e^{2} \hbar^{2}}{m_{e}^{2}\left(r_{30}\right)^{3}}=-10.37712 \mathrm{eV}+0.06744 \mathrm{eV}=-10.30968 \mathrm{eV} \tag{23.209}
\end{equation*}
$$

Next, consider the formation of the $G e-L$-bond MO of gernmanium compounds wherein $L$ is a ligand including germanium and carbon and each gemanium atom has a Ge4sp electron with an energy given by Eq. (23.209). The total energy of the state of each germanium atom is given by the sum over the four electrons. The sum $E_{T}\left(G e_{G e-L}, 4 s p^{3}\right)$ of energies of $G e 4 s p^{3}$ (Eq. (23.209)), $G e^{+}, G e^{2+}$, and $G e^{3+}$ is:

$$
\begin{align*}
E_{T}\left(G e_{G e-L}, 4 s p^{3}\right) & =-\left(45.7131 \mathrm{eV}+34.2241 \mathrm{eV}+15.93461 \mathrm{eV}+E\left(G e, 4 s p^{3}\right)\right) \\
& =-(45.7131 \mathrm{eV}+34.2241 \mathrm{eV}+15.93461 \mathrm{eV}+10.30968 \mathrm{eV})  \tag{23.210}\\
& =-106.18149 \mathrm{eV}
\end{align*}
$$

where $E\left(G e, 4 s p^{3}\right)$ is the sum of the energy of $G e,-7.89943 \mathrm{eV}$, and the hybridization energy.
A minimum energy is achieved while matching the potential, kinetic, and orbital energy relationships given in the Hydroxyl Radical ( $O H$ ) section with the donation of electron density from the participating $G e 4 s p^{3} \mathrm{HO}$ to each $G e-L$-bond MO. Consider the case wherein each $G e 4 s p^{3}$ HO donates an excess of $25 \%$ of its electron density to the $G e-L$-bond MO to form an energy minimum. By considering this electron redistribution in the germanium molecule as well as the fact that the central field decreases by an integer for each successive electron of the shell, in general terms, the radius $r_{G e-L 4 s p^{3}}$ of the $G e 4 s p^{3}$ shell may be calculated from the Coulombic energy using Eq. (15.18).

$$
\begin{equation*}
r_{G e-L 4 s p^{3}}=\left(\sum_{n=28}^{31}(Z-n)-0.25\right) \frac{e^{2}}{8 \pi \varepsilon_{0}(e 106.18149 \mathrm{eV})}=\frac{9.75 e^{2}}{8 \pi \varepsilon_{0}(\mathrm{e} 106.18149 \mathrm{eV})}=1.24934 a_{0} \tag{23.211}
\end{equation*}
$$

Using Eqs. (15.19) and (23.211), the Coulombic energy $E_{\text {Coulomb }}\left(G e_{G e-L}, 4 s p^{3}\right)$ of the outer electron of the $G e 4 s p^{3}$ shell is:

$$
\begin{equation*}
E_{\text {Coulomb }}\left(G e_{G e-L}, 4 s p^{3}\right)=\frac{-e^{2}}{8 \pi \varepsilon_{0} r_{G e-L s s p^{3}}}=\frac{-e^{2}}{8 \pi \varepsilon_{0} 1.24934 a_{0}}=-10.89041 \mathrm{eV} \tag{23.212}
\end{equation*}
$$

During hybridization, the spin-paired $4 s$ electrons are promoted to the $G e 4 s p^{3}$ shell as unpaired electrons. The energy for the promotion is the magnetic energy given by Eq. (23.208). Using Eqs. (23.208) and (23.212), the energy $E\left(G e_{G e-L}, 4 s p^{3}\right)$ of the outer electron of the Ge4sp ${ }^{3}$ shell is:

$$
\begin{equation*}
E\left(G e_{G e-L}, 4 s p^{3}\right)=\frac{-e^{2}}{8 \pi \varepsilon_{0} r_{G e-L 4 s p^{3}}}+\frac{2 \pi \mu_{0} e^{2} \hbar^{2}}{m_{e}^{2}\left(r_{30}\right)^{3}}=-10.89041 \mathrm{eV}+0.06744 \mathrm{eV}=-10.82297 \mathrm{eV} \tag{23.213}
\end{equation*}
$$

Thus, $E_{T}\left(G e-L, 4 s p^{3}\right)$, the energy change of each $G e 4 s p^{3}$ shell with the formation of the $G e-L$-bond MO is given by the difference between Eq. (23.213) and Eq. (23.209):

$$
\begin{equation*}
E_{T}\left(G e-L, 4 s p^{3}\right)=E\left(G e_{G e-L}, 4 s p^{3}\right)-E\left(G e, 4 s p^{3}\right)=-10.82297 \mathrm{eV}-(-10.30968 \mathrm{eV})=-0.51329 \mathrm{eV} \tag{23.214}
\end{equation*}
$$

Now, consider the formation of the $G e-L$-bond MO of gernmanium compounds wherein $L$ is a ligand including germanium and carbon. For the $G e-L$ functional groups, hybridization of the $4 p$ and $4 s$ AOs of $G e$ to form a single $G e 4 s p^{3}$ HO shell forms an energy minimum, and the sharing of electrons between the Ge4sp ${ }^{3} \mathrm{HO}$ and $L$ HO to form a MO permits each participating orbital to decrease in radius and energy. The $C 2 s p^{3} \mathrm{HO}$ has an energy of $E\left(C, 2 s p^{3}\right)=-14.63489 \mathrm{eV}$ (Eq. (15.25)) and the Ge4sp HO has an energy of $E\left(G e, 4 s p^{3}\right)=-10.30968 \mathrm{eV}$ (Eq. (23.209)). To meet the equipotential condition of the union of the $\mathrm{Ge}-\mathrm{L} \quad \mathrm{H}_{2}$-type-ellipsoidal-MO with these orbitals, the hybridization factor $C_{2}$ of Eq. (15.61) for the $G e-L$-bond MO given by Eq. (15.77) is:

$$
\begin{equation*}
C_{2}\left(G e 4 s p^{3} \mathrm{HO} \text { to } \mathrm{Ge} 4 s p^{3} \mathrm{HO}\right)=C_{2}\left(\mathrm{C} 2 s p^{3} \mathrm{HO} \text { to } \mathrm{Ge} 4 s p^{3} \mathrm{HO}\right)=\frac{E\left(G e, 4 s p^{3} \mathrm{HO}\right)}{E\left(C, 2 s p^{3}\right)}=\frac{-10.30968 \mathrm{eV}}{-14.63489 \mathrm{eV}}=0.70446 \tag{23.215}
\end{equation*}
$$

Since the energy of the MO is matched to that of the Ge4sp $\mathrm{HO}, E(A O / H O)$ in Eq. (15.61) is $E\left(G e, 4 s p^{3} \mathrm{HO}\right)$ given by Eq. (23.209). In order to match the energies of the HOs within the molecule, $E_{T}\left(\right.$ atom-atom, $\left.m s p^{3} \cdot A O\right)$ of the $G e-L$-bond MO for the ligands carbon or germanium is $\frac{-0.72457}{2}$ (Eq. (14.151)).

The symbols of the functional groups of germanium compounds are given in Table 23.60. The geometrical (Eqs. (15.1$15.5)$ ), intercept (Eqs. (15.31-15.32) and (15.80-15.87)), and energy (Eqs. (15.61) and (23.28-23.33)) parameters of germanium compounds are given in Tables 23.61, 23.62, and 23.63, respectively. The total energy of each germanium compounds given in Table 22.64 was calculated as the sum over the integer multiple of each $E_{D}$ (Group) of Table 23.63 corresponding to functionalgroup composition of the compound. The bond angle parameters of germanium compounds determined using Eqs. (15.8815.117) are given in Table 23.65. The charge-densities of exemplary germanium and digermanium compounds, tetraethylgermanium $\left(\mathrm{Ge}\left(\mathrm{CH}_{2} \mathrm{CH}_{3}\right)_{4}\right)$ and hexaethyldigermanium $\left(\left(\mathrm{C}_{2} \mathrm{H}_{5}\right)_{3} \mathrm{GeGe}\left(\mathrm{C}_{2} \mathrm{H}_{5}\right)_{3}\right)$ 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 23.13A and $B$, respectively.

Figure 23.13. (A) Color scale, charge-density of $\mathrm{Ge}\left(\mathrm{CH}_{2} \mathrm{CH}_{3}\right)_{4}$ showing the orbitals of the Ge and C 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 atoms participating in each bond, and the hydrogen nuclei. (B) Color scale, charge-density of $\left(\mathrm{C}_{2} \mathrm{H}_{5}\right)_{3} \mathrm{GeGe}\left(\mathrm{C}_{2} \mathrm{H}_{5}\right)_{3}$ showing the orbitals of the $G e$ and $C$ 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 atoms participating in each bond, and the hydrogen nuclei.


Table 23.60. The symbols of functional groups of germanium compounds.

| Functional Group | Group Symbol |
| :---: | :---: |
| GeC group | $G e-C$ |
| GeGe group | $G e-G e$ |
| $\mathrm{CH}_{3}$ group | $\mathrm{C-H}\left(\mathrm{CH}_{3}\right)$ |
| $\mathrm{CH}_{2}$ alkyl group | $\mathrm{C}-\mathrm{H}\left(\mathrm{CH}_{2}\right)$ |
| CH alkyl | C-H |
| $C C$ bond ( $n-C$ ) | $C-C$ (a) |
| $C C$ bond (iso-C) | $C-C$ (b) |
| $C C$ bond (tert-C) | $C-C$ (c) |
| $C C$ (iso to iso-C) | $C-C$ (d) |
| $C C$ ( $t$ to $t-C$ ) | $C-C$ (e) |
| $C C$ ( $t$ to iso-C) | $C-C$ (f) |

Table 23.61. The geometrical bond parameters of germanium compounds and experimental values [3].

| Parameter | $\begin{aligned} & \text { Ge-C } \\ & \text { Group } \end{aligned}$ | $\begin{gathered} G e-G e \\ \text { Group } \end{gathered}$ | $\mathrm{C}-\mathrm{H}\left(\mathrm{CH}_{3}\right)$ <br> Group | $\mathrm{C}-\mathrm{H}\left(\mathrm{CH}_{2}\right)$ <br> Group | $\begin{aligned} & C-H \\ & \text { Group } \end{aligned}$ | $\begin{gathered} C-C \text { (a) } \\ \text { Group } \end{gathered}$ | $\begin{gathered} C-C \text { (b) } \\ \text { Group } \end{gathered}$ | $\begin{gathered} C-C(c) \\ \text { Group } \end{gathered}$ | $\begin{gathered} C-C(d) \\ \text { Group } \end{gathered}$ | $\begin{gathered} C-C(e) \\ \text { Group } \end{gathered}$ | $\begin{gathered} C-C(\mathrm{f}) \\ \text { Group } \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $a\left(a_{0}\right)$ | 2.27367 | 2.27367 | 1.64920 | 1.67122 | 1.67465 | 2.12499 | 2.12499 | 2.10725 | 2.12499 | 2.10725 | 2.10725 |
| $c^{\prime}\left(a_{0}\right)$ | 1.79654 | 1.79654 | 1.04856 | 1.05553 | 1.05661 | 1.45744 | 1.45744 | 1.45164 | 1.45744 | 1.45164 | 1.45164 |
| $\begin{aligned} & \text { Bond Length } \\ & 2 c^{\prime}(A) \end{aligned}$ | 1.90137 | 1.90137 | 1.10974 | 1.11713 | 1.11827 | 1.54280 | 1.54280 | 1.53635 | 1.54280 | 1.53635 | 1.53635 |
| Exp. Bond Length (A) | 1.945 $\left(\left(\mathrm{CH}_{3}\right)_{4} \mathrm{Ge}\right)$ 1.945 $\left(\mathrm{CH}_{3} \mathrm{GeH}_{3}\right)$ 1.89 $\left(\mathrm{CH}_{3} \mathrm{GeCl}_{3}\right)$ |  | $\begin{gathered} 1.107 \\ (C-H \\ \text { propane }) \\ 1.117 \\ (C-H \\ \text { butane }) \end{gathered}$ | $\begin{gathered} 1.107 \\ (C-H \\ \text { propane }) \\ 1.117 \\ (C-H \\ \text { butane }) \end{gathered}$ | $\begin{gathered} 1.122 \\ \text { (isobutane) } \end{gathered}$ | $\begin{gathered} 1.532 \\ \text { (propane) } \\ 1.531 \\ \text { (butane) } \end{gathered}$ | 1.532 (propane) 1.531 (butane) | $\begin{gathered} 1.532 \\ \text { (propane) } \\ 1.531 \\ \text { (butane) } \end{gathered}$ | 1.532 (propane) 1.531 (bulane) | 1.532 (propane) 1.531 (butane | 1.532 (propane) 1.531 (butane) |
| $b, c\left(a_{0}\right)$ | 1.39357 | 1.39357 | 1.27295 | 1.29569 | 1.29924 | 1.54616 | 1.54616 | 1.52750 | 1.54616 | 1.52750 | 1.52750 |
| $e$ | 0.79015 | 0.79015 | 0.63580 | 0.63159 | 0.63095 | 0.68600 | 0.68600 | 0.68888 | 0.68600 | 0.68888 | 0.68888 |

Table 23.62. The MO to HO intercept geometrical bond parameters of germanium compounds. $R, R^{\prime}, R^{\prime \prime}$ are $H$ or alkyl groups. $E_{T}$ is $E_{T}$ (atom-atom,msp ${ }^{3}$. $A O$ ).

| Bond | Atom | $\begin{gathered} E_{T} \\ (\mathrm{eV}) \\ \text { Bond } 1 \end{gathered}$ | $\begin{gathered} E_{V} \\ (\mathrm{eV}) \\ \text { Bond } 2 \end{gathered}$ | $\begin{gathered} E_{T} \\ (\mathrm{eV}) \\ \text { Bond } 3 \end{gathered}$ | $\begin{gathered} E_{T} \\ (\text { (eV) } \\ \text { Bond 4 } \end{gathered}$ | Final Total Energy Ge $4 s p^{3}$ $C 2 s p^{3}$ (eV) | $\begin{aligned} & r_{\text {manad }} \\ & \left(a_{0}\right) \end{aligned}$ | $\begin{aligned} & r_{\text {malal }}\left(a_{0}\right) \\ & \left(\begin{array}{l} \text { an } \end{array}\right. \end{aligned}$ | $\begin{gathered} E_{\text {Conomomb }}\left(\mathrm{C} 2 s p^{3}\right) \\ \text { Fival } \\ \text { Final } \end{gathered}$ | $\begin{gathered} E\left(G e 4 s p^{3}\right) \\ E\left(C 2 s p^{3}\right) \\ (\text { ev) } \\ \text { Final } \end{gathered}$ | $\begin{aligned} & \theta^{\prime} \\ & \left({ }^{\prime}\right) \end{aligned}$ | $\begin{aligned} & \theta_{1} \\ & \left({ }^{\circ}\right) \end{aligned}$ | $\begin{aligned} & \theta_{2} \\ & \left({ }^{\circ}\right) \end{aligned}$ | $\begin{gathered} d_{1} \\ \left(a_{0}\right) \end{gathered}$ | $\begin{gathered} d_{2} \\ \left(a_{0}\right) \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\left.\mathrm{CH}-\mathrm{CH}_{3}\right)$ | c | $-0.18114$ | 0 | 0 | 0 | -151.79683 | 0.91771 | 0.90664 | -15.00689 | -14.81603 | 82.43 | 97.57 | 44.91 | 1.16793 | 0.11938 |
| $\left(\mathrm{CH}_{3}\right)_{3} \mathrm{Ge}-\mathrm{CH}_{3}$ | ${ }^{\text {Ge }}$ | $-0.18114$ | $-0.18114$ | $-0.18114$ | $-0.18114$ |  | 1.31113 | 0.87495 | -15.55033 |  | 91.73 | 88.27 | 38.87 | 1.77020 | 0.02634 |
| $\left(\mathrm{CH}_{3}\right)_{3} \mathrm{Ge}-\mathrm{CH}_{3}$ | C | $-0.18114$ | 0 | 0 | 0 |  | 0.91771 | 0.90664 | -15.00689 | -14.81603 | 94.20 | 85.80 | 40.45 | 1.73010 | 0.06644 |
| $\left(\mathrm{CH}_{3}\right)_{3} \mathrm{Ge}-\mathrm{Ge}\left(\mathrm{CH}_{3}\right)_{3}$ | Ge | $-0.18114$ | $-0.18114$ | $-0.18114$ | $-0.18114$ |  | 1.31113 | 0.87495 | -15.55033 |  | 91.73 | 88.27 | 38.87 | 1.77020 | 0.02634 |
| $\mathrm{C}-\mathrm{H}\left(\mathrm{CH}_{3}\right)$ | 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 |
| $\mathrm{C-H}\left(\mathrm{CH}_{2}\right)(\mathrm{i})$ | 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 |
| $\mathrm{C-H}(\mathrm{CH})(\mathrm{i})$ | 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 |
| $\begin{aligned} & \mathrm{H}_{3} \mathrm{C}_{a} \mathrm{C}_{\mathrm{C}} \mathrm{H}_{2} \mathrm{CH}_{2}- \\ & (\mathrm{C}-\mathrm{C}(\mathrm{a})) \end{aligned}$ | $C_{a}$ | -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 |
| $\begin{aligned} & \mathrm{H}_{L_{C} C_{a} \mathrm{H}_{2} C H_{2}-} \\ & (\mathrm{C}-\mathrm{C}(\mathrm{a})) \end{aligned}$ | $C_{b}$ | $-0.92918$ | -0.92918 | 0 | 0 | -153.47406 | 0.91771 | 0.81549 | -16.68412 | -16.49325 | 56.41 | 123.59 | 26.06 | 1.90890 | 0.45117 |
| $\begin{aligned} & R-H_{2} C_{a} C_{b}\left(H_{2} C_{c}-R^{\prime}\right) H C H_{2}- \\ & (C-C(b)) \end{aligned}$ | $C_{b}$ | -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 |
| $\begin{aligned} & R-H_{2} C_{( }\left(R^{\prime}-H_{2} C_{d}\right) C_{b}\left(R^{\prime \prime}-H_{2} C_{c}\right) \mathrm{CH}_{2}- \\ & (\mathrm{C}-\mathrm{C}(\mathrm{c})) \end{aligned}$ | $C_{b}$ | -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 |
| $\begin{aligned} & \text { iso } C_{a} C_{b}\left(H_{2} C_{c}-R^{\prime}\right) H C H_{2}- \\ & (C-C \text { (d)) } \end{aligned}$ | $C_{b}$ | $-0.92918$ | -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 |
| $\begin{aligned} & {\operatorname{terlC} C_{a}}^{\left(R^{\prime}-H_{2} C_{d}\right) C_{b}\left(R^{n}-H_{2} C_{c}\right) C H_{2}-} \\ & (C-C(\mathrm{e})) \end{aligned}$ | $C_{b}$ | $-0.72457$ | -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 |
| $\begin{aligned} & \text { tert } C_{a} C_{b}\left(H_{2} C_{c}-R^{\prime}\right) H C H_{2}- \\ & (C-C(\mathrm{f})) \end{aligned}$ | $C_{b}$ | $-0.72457$ | -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 |
| $\begin{aligned} & \text { iso } C_{a}\left(R^{\prime}-H_{2} C_{d}\right) C_{b}\left(R^{n}-H_{2} C_{c}\right) C H_{2}- \\ & (C-C(f)) \end{aligned}$ | $C_{b}$ | $-0.72457$ | -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 23.63. The energy parameters ( eV ) of functional groups of germanium compounds.

| Parameters | $\begin{aligned} & \text { Ge-C } \\ & \text { Group } \end{aligned}$ | $\begin{gathered} G e-G e \\ \text { Group } \end{gathered}$ | $\begin{gathered} \mathrm{CH}_{3} \\ \text { Group } \end{gathered}$ | $\begin{gathered} \mathrm{CH}_{2} \\ \text { Group } \end{gathered}$ | $\begin{gathered} \mathrm{CH} \\ \text { Group } \end{gathered}$ | $\begin{gathered} C-C \text { (a) } \\ \text { Group } \end{gathered}$ | $\begin{gathered} C-C \text { (b) } \\ \text { Group } \end{gathered}$ | $\begin{gathered} C-C(c) \\ \text { Group } \end{gathered}$ | $\begin{gathered} C-C \text { (d) } \\ \text { Group } \end{gathered}$ | $\begin{gathered} C-C(e) \\ \text { Group } \end{gathered}$ | $\begin{gathered} C-C(\mathrm{f}) \\ \text { Group } \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $n_{1}$ | 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 |
| $C_{2}$ | 0.70446 | 0.70446 | 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 |
| $C_{1}$ | 0.5 | 0.5 | 0.75 | 0.75 | 0.75 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| $C_{20}$ | 0.70446 | 0.70446 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $V_{e}(\mathrm{eV})$ | -32.46926 | -32.46926 | -107.32728 | -70.41425 | -35.12015 | -28.79214 | -28.79214 | -29.10112 | -28.79214 | -29.10112 | -29.10112 |
| $V_{p}(\mathrm{eV})$ | 7.57336 | 7.57336 | 38.92728 | 25.78002 | 12.87680 | 9.33352 | 9.33352 | 9.37273 | 9.33352 | 9.37273 | 9.37273 |
| $T(\mathrm{eV})$ | 7.14028 | 7.14028 | 32.53914 | 21.06675 | 10.48582 | 6.77464 | 6.77464 | 6.90500 | 6.77464 | 6.90500 | 6.90500 |
| $V_{m}(\mathrm{eV})$ | -3.57014 | -3.57014 | -16.26957 | -10.53337 | -5.24291 | -3.38732 | -3.38732 | -3.45250 | -3.38732 | -3.45250 | -3.45250 |
| E( (оо/но) (eV) | -10.30968 | -10.30968 | -15.56407 | -15.56407 | -14.63489 | -15.56407 | -15.56407 | -15.35946 | -15.56407 | -15.35946 | -15.35946 |
| $\Delta E_{\mathrm{H}_{2} \mathrm{MO}}($ (AOHO) $(\mathrm{eV})$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $E_{T}$ ( (\%/но) ( eV ) | -10.30968 | -10.30968 | -15.56407 | -15.56407 | -14.63489 | -15.56407 | -15.56407 | -15.35946 | -15.56407 | -15.35946 | -15.35946 |
| $E_{T}\left(\mathrm{H}_{2} \mathrm{MO}\right)(\mathrm{eV})$ | -31.63544 | -31.63544 | -67.69451 | -49.66493 | -31.63533 | -31.63537 | -31.63537 | -31.63535 | -31.63537 | -31.63535 | -31.63535 |
| $E_{T}\left(\right.$ atom-atom, msp $\left.{ }^{3} \cdot \mathrm{AO}\right)(\mathrm{eV})$ | -0.36229 | -0.36229 | 0 | 0 | 0 | -1.85836 | -1.85836 | -1.44915 | -1.85836 | -1.44915 | -1.44915 |
| $E_{T}(\mathrm{mo})(\mathrm{eV})$ | -31.99766 | -31.99766 | -67.69450 | -49.66493 | -31.63537 | -33.49373 | -33.49373 | -33.08452 | -33.49373 | -33.08452 | -33.08452 |
| $\omega\left(10^{15} \mathrm{rad} / \mathrm{s}\right)$ | 14.9144 | 14.9144 | 24.9286 | 24.2751 | 24.1759 | 9.43699 | 9.43699 | 15.4846 | 9.43699 | 9.55643 | 9.55643 |
| $E_{K}(\mathrm{eV})$ | 9.81690 | 9.81690 | 16.40846 | 15.97831 | 15.91299 | 6.21159 | 6.21159 | 10.19220 | 6.21159 | 6.29021 | 6.29021 |
| $\bar{E}_{D}(\mathrm{eV})$ | -0.19834 | -0.19834 | -0.25352 | -0.25017 | -0.24966 | -0.16515 | -0.16515 | -0.20896 | -0.16515 | -0.16416 | -0.16416 |
| $\bar{E}_{\text {Kvit }}(\mathrm{eV})$ | $\begin{gathered} 0.15312 \\ {[66]} \end{gathered}$ | $\begin{gathered} 0.06335 \\ {[14]} \end{gathered}$ | $\begin{gathered} 0.35532 \\ \text { Eq. }(13.458) \end{gathered}$ | $\begin{gathered} 0.35532 \\ \text { Eq. (13.458) } \end{gathered}$ | $\begin{gathered} 0.35532 \\ \text { Eq. (13.458) } \end{gathered}$ | $\begin{gathered} 0.12312 \\ {[6]} \end{gathered}$ | $\begin{gathered} 0.17978 \\ {[7]} \end{gathered}$ | $\begin{gathered} 0.09944 \\ {[8]} \end{gathered}$ | $\begin{gathered} 0.12312 \\ {[6]} \end{gathered}$ | $\begin{gathered} 0.12312 \\ {[6]} \end{gathered}$ | $\begin{gathered} 0.12312 \\ {[6]} \end{gathered}$ |
| $\bar{E}_{\text {osc }}(\mathrm{eV})$ | -0.12178 | -0.16666 | -0.22757 | -0.14502 | -0.07200 | -0.10359 | -0.07526 | -0.15924 | -0.10359 | -0.10260 | -0.10260 |
| $E_{\text {mag }}(\mathrm{eV})$ | 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 $)(\mathrm{eV})$ | -32.11943 | -32.16432 | -67.92207 | -49.80996 | -31.70737 | -33.59732 | -33.49373 | -33.24376 | -33.59732 | -33.18712 | -33.18712 |
| $E_{\text {intual }}\left(\mathrm{c}_{4}\right.$ AOIHO) $(\mathrm{eV})$ | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 |
|  | 0 | 0 | -13.59844 | -13.59844 | -13.59844 | 0 | 0 | 0 | 0 | 0 | 0 |
| $E_{D}($ Group $)(\mathrm{eV})$ | 2.84965 | 2.89454 | 12.49186 | 7.83016 | 3.32601 | 4.32754 | 4.29921 | 3.97398 | 4.17951 | 3.62128 | 3.91734 |

Table 23.64. The total bond energies of gaseous-state germanium compounds calculated using the functional group composition (separate functional groups designated in the first row) and the energies of Table 23.63 compared to the gaseous-state experimental values [67].
$\begin{array}{llllllll} & \text { Name } & \mathrm{Ge}-\mathrm{C} & \mathrm{Ge}-\mathrm{Ge} & \mathrm{CH}_{3} & \mathrm{CH}_{2} & \mathrm{CH} & \mathrm{C}-\mathrm{C} \text { (a) } \\ \text { Formula } & & & \text { Calculated } & \text { Experimental } & \text { Relative Error } \\ \text { Total Bond }\end{array}$
$\begin{array}{ll}\mathrm{C}_{8} \mathrm{H}_{20} \mathrm{Ge} & \text { Tetraethylgermanium } \\ \mathrm{C}_{12} \mathrm{H}_{28} \mathrm{Ge} & \text { Tetra-n-propylgermanium } \\ \mathrm{C}_{12} \mathrm{H}_{30} \mathrm{Ge}_{2} & \text { Hexaethyldigermanium }\end{array}$
Table 23.65. The bond angle parameters of germanium compounds and experimental values [3]. In the calculation of $\theta_{v}$, the parameters from the preceding angle were used. $E_{T}$ is $E_{T}$ (atom-atom, $m s p^{3} \cdot A O$ ).

| Atoms of Angle | $\begin{gathered} 2 c^{\prime} \\ \text { Bond } 1 \\ \left(a_{0}\right) \end{gathered}$ | $\begin{gathered} 2 c^{\prime} \\ \text { Bond } 2 \\ \left(a_{0}\right) \end{gathered}$ |  | $\begin{aligned} & E_{\text {Coinombic } e c} \\ & \text { Atom } 1 \end{aligned}$ | Atom 1 Hybridization Designation (Table 15.3.A) | $\begin{aligned} & E_{\text {Coulombic }} \\ & \text { Atom } \end{aligned}$ | $\begin{gathered} \text { Atom } 2 \\ \text { Hybridization } \\ \text { Designation } \\ \text { (Table 15.3.A) } \end{gathered}$ | $\begin{gathered} c_{2} \\ \text { Atom } 1 \end{gathered}$ | $\begin{gathered} c_{2} \\ \text { Atom } 2 \end{gathered}$ | $C_{1}$ | $C_{2}$ | $c_{1}$ | $c_{2}^{\prime}$ | $\begin{aligned} & E_{T} \\ & (\mathrm{eV}) \end{aligned}$ | $\begin{aligned} & \theta_{v} \\ & \left({ }^{\circ}\right) \end{aligned}$ | $\begin{aligned} & \theta_{1} \\ & \left({ }^{\circ}\right) \end{aligned}$ | $\begin{aligned} & \theta_{2} \\ & \left({ }^{\circ}\right) \end{aligned}$ | $\begin{gathered} \text { Cal. } \theta \\ \left({ }^{\circ}\right) \end{gathered}$ | $\underset{\substack{\text { Exp. } \theta \\\left({ }^{\circ}\right)}}{ }$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\begin{aligned} & \text { Methyl } \\ & \angle H C_{a} H \end{aligned}$ | 2.09711 | 2.09711 | 3.4252 | -15.75493 | 7 | H | H | 0.86359 | 1 | 1 | 1 | 0.75 | 1.15796 | 0 |  |  |  | 109.50 |  |
| $\angle H_{a} C_{a} G e$ |  |  |  |  |  |  |  |  |  |  |  |  |  |  | 70.56 |  |  | 109.44 | 108 (tetramethyl germanium) |
| $\angle C_{a} \operatorname{GeC}_{b}$ | 3.59307 | 3.59307 | 5.7446 | -15.55033 | 5 | -15.55033 | 5 | 0.87495 | 0.87495 | 1 | 1 | 1 | 0.87495 | $-1.85836$ |  |  |  | 106.14 | $\begin{gathered} 109.5 \\ \text { (tetramethyl } \\ \text { germanium) } \end{gathered}$ |
| Methylene $\angle H C_{a} H$ | 2.11106 | 2.11106 | 3.4252 | -15.75493 | 7 | H | H | 0.86359 | 1 | 1 | 1 | 0.75 | 1.15796 | 0 |  |  |  | 108.44 | $\begin{gathered} 107 \\ \text { (propane) } \end{gathered}$ |
| $\angle C_{a} C_{b} C_{c}$ |  |  |  |  |  |  |  |  |  |  |  |  |  |  | 69.51 |  |  | 110.49 | $\begin{gathered} 112 \\ \text { (propane) } \\ 113.8 \\ \text { (butane) } \\ 110.8 \\ \text { (isobutane) } \end{gathered}$ |
| $\angle C_{a} C_{b} H$ |  |  |  |  |  |  |  |  |  |  |  |  |  |  | 69.51 |  |  | 110.49 | $\begin{gathered} 111.0 \\ \text { (butane) } \\ 111.4 \\ \text { (isobutane) } \end{gathered}$ |
| $\begin{aligned} & \text { Methyl } \\ & \angle H C_{a} H \end{aligned}$ | 2.09711 | 2.09711 | 3.4252 | -15.75493 | 7 | H | H | 0.86359 | 1 | 1 | 1 | 0.75 | 1.15796 | 0 |  |  |  | 109.50 |  |
| $\angle C_{a} C_{b} C_{c}$ |  |  |  |  |  |  |  |  |  |  |  |  |  |  | 70.56 |  |  | 109.44 |  |
| $\angle C_{a} C_{b} H$ |  |  |  |  |  |  |  |  |  |  |  |  |  |  | 70.56 |  |  | 109.44 |  |
| $\begin{aligned} & \angle C_{b} C_{a} C_{C} \\ & \text { iso } C_{a} \end{aligned}$ | 2.91547 | 2.91547 | 4.7958 | $\begin{array}{\|c} \hline-16.68412 \\ C_{b} \end{array}$ | 26 | $\begin{gathered} -16.68412 \\ C_{c} \end{gathered}$ | 26 | 0.81549 | 0.81549 | 1 | 1 | 1 | 0.81549 | $-1.85836$ |  |  |  | 110.67 | $\begin{gathered} 110.8 \\ \text { (isobutane) } \end{gathered}$ |
| $\begin{gathered} \angle C_{b} C_{a} H \\ \text { iso } C_{a} \end{gathered}$ | 2.91547 | 2.11323 | 4.1633 | $\begin{gathered} -15.55033 \\ C_{a} \end{gathered}$ | 5 | $\begin{gathered} -14.82575 \\ C_{b} \end{gathered}$ | 1 | 0.87495 | 0.91771 | 0.75 | 1 | 0.75 | 1.04887 | 0 |  |  |  | 110.76 |  |
| $\begin{aligned} & \angle C_{c} C_{b} H \\ & \text { iso } H \\ & \text { iso } C_{a} \end{aligned}$ | 2.91547 | 2.09711 | 4.1633 | $\begin{array}{\|c} -15.55033 \\ C_{b} \end{array}$ | 5 | $\begin{array}{\|c} -14.82575 \\ C_{a} \end{array}$ | 1 | 0.87495 | 0.91771 | 0.75 | 1 | 0.75 | 1.04887 | 0 |  |  |  | 111.27 | $\begin{gathered} 111.4 \\ \text { (isobutane) } \end{gathered}$ |
| $\begin{aligned} & \angle C_{b} C_{a} C_{b} \\ & \text { tert } C_{a} \end{aligned}$ | 2.90327 | 2.90327 | 4.7958 | $\begin{array}{\|c} -16.68412 \\ C_{b} \end{array}$ | 26 | $\begin{array}{\|c} -16.68412 \\ C_{b} \end{array}$ | 26 | 0.81549 | 0.81549 | 1 | 1 | 1 | 0.81549 | $-1.85836$ |  |  |  | 111.37 | $\begin{gathered} 110.8 \\ \text { (isobutane) } \end{gathered}$ |
| $\angle C_{b} C_{a} C_{d}$ |  |  |  |  |  |  |  |  |  |  |  |  |  |  | 72.50 |  |  | 107.50 |  |

## TIN FUNCTIONAL GROUPS AND MOLECULES

As in the cases of carbon, silicon and germanium, the bonding in the tin atom involves four $s p^{3}$ hybridized orbitals formed from the $5 p$ and $5 s$ electrons of the outer shells. $S n-X \quad X=$ halide, oxide, $S n-H$, and $S n-S n$ bonds form between $S n 5 s p^{3}$ HOs and between a halide or oxide AO, a $H 1 s \mathrm{AO}$, and a $\operatorname{Sn} 5 s p^{3} \mathrm{HO}$, respectively to yield tin halides and oxides, stannanes, and distannanes, respectively. The geometrical parameters of each $\mathrm{Sn}-X \quad X=$ halide, oxide, $\mathrm{Sn}-H$, and $\mathrm{Sn}-\mathrm{Sn}$ functional group is solved from the force balance equation of the electrons of the corresponding $\sigma-\mathrm{MO}$ and the relationships between the prolate spheroidal axes. Then, the sum of the energies of the $H_{2}$-type ellipsoidal MOs is matched to that of the $\operatorname{Sn5sp}{ }^{3}$ shell as in the case of the corresponding carbon and tin molecules. As in the case of the transition metals, the energy of each functional group is determined for the effect of the electron density donation from each participating $S n 5 s p^{3} \mathrm{HO}$ and AO to the corresponding MO that maximizes the bond energy.

The branched-chain alkyl stannanes and distannanes, $\mathrm{Sn}_{m} \mathrm{C}_{n} \mathrm{H}_{2(m+n)+2}$, comprise at least a terminal methyl group $\left(\mathrm{CH}_{3}\right)$ and at least one Sn bound by a carbon-tin single bond comprising a $\mathrm{C}-\mathrm{Sn}$ group, and may comprise methylene $\left(\mathrm{CH}_{2}\right)$, methylyne $(\mathrm{CH}), \mathrm{C}-\mathrm{C}, \mathrm{SnH}_{n=1,2,3}$, and $\mathrm{Sn}-\mathrm{Sn}$ functional groups. 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 $\mathrm{C}-\mathrm{C}$ bonds within isopropyl $\left(\left(\mathrm{CH}_{3}\right)_{2} \mathrm{CH}\right)$ and t-butyl $\left(\left(\mathrm{CH}_{3}\right)_{3} \mathrm{C}\right)$ groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups.

The $S n$ electron configuration is $[K r] 5 s^{2} 4 d^{10} 5 p^{2}$, and the orbital arrangement is:

\[

\]

corresponding to the ground state ${ }^{3} P_{0}$. The energy of the carbon $5 p$ shell is the negative of the ionization energy of the tin atom [1] given by:

$$
\begin{equation*}
E(\text { Sn, } 5 p \text { shell })=-E(\text { ionization } ; S n)=-7.34392 \mathrm{eV} \tag{23.217}
\end{equation*}
$$

The energy of tin is less than the Coulombic energy between the electron and proton of $H$ given by Eq. (1.264), but the atomic orbital may hybridize in order to achieve a bond at an energy minimum. After Eq. (13.422), the Sn5s atomic orbital (AO) combines with the $\operatorname{Sn5} 5$ AOs to form a single $\operatorname{Sn5sp}{ }^{3}$ hybridized orbital (HO) with the orbital arrangement is:

where the quantum numbers $\left(\ell, m_{\ell}\right)$ are below each electron. The total energy of the state is given by the sum over the four electrons. The sum $E_{T}\left(S n, 4 s p^{3}\right)$ of experimental energies [1] of $\mathrm{Sn}, \mathrm{Sn}^{+}, \mathrm{Sn}^{2+}$, and $\mathrm{Sn}^{3+}$ is:

$$
\begin{equation*}
E_{T}\left(S n, 5 s p^{3}\right)=40.73502 \mathrm{eV}+30.50260 \mathrm{eV}+14.6322 \mathrm{eV}+7.34392 \mathrm{eV}=93.21374 \mathrm{eV} \tag{23.219}
\end{equation*}
$$

By considering that the central field decreases by an integer for each successive electron of the shell, the radius $r_{5 s p^{3}}$ of the $\operatorname{Sn} 5 s p^{3}$ shell may be calculated from the Coulombic energy using Eq. (15.13).

$$
\begin{equation*}
r_{5 s p^{3}}=\sum_{n=46}^{49} \frac{(Z-n) e^{2}}{8 \pi \varepsilon_{0}(e 93.21374 \mathrm{eV})}=\frac{10 e^{2}}{8 \pi \varepsilon_{0}(e 93.21374 \mathrm{eV})}=1.45964 a_{0} \tag{23.220}
\end{equation*}
$$

where $Z=50$ for tin. Using Eq. (15.14), the Coulombic energy $E_{\text {Coulomb }}\left(S n, 5 s p^{3}\right)$ of the outer electron of the $S n 5 s p^{3}$ shell is:

$$
\begin{equation*}
E_{\text {Coulomb }}\left(S n, 5 s p^{3}\right)=\frac{-e^{2}}{8 \pi \varepsilon_{0} r_{5 s p^{3}}}=\frac{-e^{2}}{8 \pi \varepsilon_{0} 1.45964 a_{0}}=-9.321374 \mathrm{eV} \tag{23.221}
\end{equation*}
$$

During hybridization, the spin-paired $5 s$ electrons are promoted to the $\operatorname{Sn} 5 s p^{3}$ shell as unpaired electrons. The energy for the promotion is the magnetic energy given by Eq. (15.15) at the initial radius of the $5 s$ electrons. From Eq. (10.255) with $Z=50$, the radius $r_{48}$ of the $\operatorname{Sn} 5 s$ shell is:

$$
\begin{equation*}
r_{48}=1.33816 a_{0} \tag{23.222}
\end{equation*}
$$

Using Eqs. (15.15) and (23.206), the unpairing energy is:

$$
\begin{equation*}
E(\text { magnetic })=\frac{2 \pi \mu_{0} e^{2} \hbar^{2}}{m_{e}^{2}\left(r_{48}\right)^{3}}=\frac{8 \pi \mu_{0} \mu_{B}^{2}}{\left(1.33816 a_{0}\right)^{3}}=0.04775 \mathrm{eV} \tag{23.223}
\end{equation*}
$$

Using Eqs. (23.203) and (23.207), the energy $E\left(S n, 5 s p^{3}\right)$ of the outer electron of the $S n 5 s p^{3}$ shell is:

$$
\begin{equation*}
E\left(S n, 5 s p^{3}\right)=\frac{-e^{2}}{8 \pi \varepsilon_{0} r_{5 s p^{3}}}+\frac{2 \pi \mu_{0} e^{2} \hbar^{2}}{m_{e}^{2}\left(r_{48}\right)^{3}}=-9.321374 \mathrm{eV}+0.04775 \mathrm{eV}=-9.27363 \mathrm{eV} \tag{23.224}
\end{equation*}
$$

Next, consider the formation of the $S n-L$-bond MO of tin compounds wherein $L$ is a ligand including tin and each tin atom has a $S n 5 s p^{3}$ electron with an energy given by Eq. (23.224). The total energy of the state of each tin atom is given by the sum over the four electrons. The sum $E_{T}\left(S n_{S n-L}, 5 s p^{3}\right)$ of energies of $S n 5 s p^{3}$ (Eq. (23.224)), $S n^{+}, S n^{2+}$, and $S n^{3+}$ is:

$$
\begin{align*}
E_{T}\left(S n_{S n-L}, 5 s p^{3}\right) & =-\left(40.73502 \mathrm{eV}+30.50260 \mathrm{eV}+14.6322 \mathrm{eV}+E\left(S n, 5 s p^{3}\right)\right)  \tag{23.225}\\
& =-(40.73502 \mathrm{eV}+30.50260 \mathrm{eV}+14.6322 \mathrm{eV}+9.27363 \mathrm{eV})=-95.14345 \mathrm{eV}
\end{align*}
$$

where $E\left(S n, 5 s p^{3}\right)$ is the sum of the energy of $S n,-7.34392 \mathrm{eV}$, and the hybridization energy.
A minimum energy is achieved while matching the potential, kinetic, and orbital energy relationships given in the Hydroxyl Radical ( $O H$ ) section with the donation of electron density from the participating $S n 5 s p^{3} \mathrm{HO}$ to each $S n-L$-bond MO. As in the case of acetylene given in the Acetylene Molecule section, the energy of each $S n-L$ functional group is determined for the effect of the charge donation. For example, as in the case of the $\mathrm{Si}-\mathrm{Si}$-bond MO given in the Alkyl Silanes and Disilanes section, the sharing of electrons between two $S n 5 s p^{3}$ HOs to form a $S n-S n$-bond MO permits each participating orbital to decrease in size and energy. In order to further satisfy the potential, kinetic, and orbital energy relationships, each $S n 5 s p^{3}$ HO donates an excess of $25 \%$ of its electron density to the $S n-S n$-bond MO to form an energy minimum. By considering this electron redistribution in the distannane molecule as well as the fact that the central field decreases by an integer for each successive electron of the shell, in general terms, the radius $r_{S n-L 5 s p^{3}}$ of the $S n 5 s p^{3}$ shell may be calculated from the Coulombic energy using Eq. (15.18).

$$
\begin{equation*}
r_{S n-L S s p^{3}}=\left(\sum_{n=46}^{49}(Z-n)-0.25\right) \frac{e^{2}}{8 \pi \varepsilon_{0}(e 95.14345 \mathrm{eV})}=\frac{9.75 e^{2}}{8 \pi \varepsilon_{0}(e 95.14345 \mathrm{eV})}=1.39428 a_{0} \tag{23.226}
\end{equation*}
$$

Using Eqs. (15.19) and (23.210), the Coulombic energy $E_{\text {Coulomb }}\left(S n_{S n-L}, 5 s p^{3}\right)$ of the outer electron of the $S n 5 s p^{3}$ shell is:

$$
\begin{equation*}
E_{\text {Coulomb }}\left(S n_{S n-L}, 5 s p^{3}\right)=\frac{-e^{2}}{8 \pi \varepsilon_{0} r_{S n-L S s p^{3}}}=\frac{-e^{2}}{8 \pi \varepsilon_{0} 1.39428 a_{0}}=-9.75830 \mathrm{eV} \tag{23.227}
\end{equation*}
$$

During hybridization, the spin-paired $5 s$ electrons are promoted to the $\operatorname{Sn} 5 s p^{3}$ shell as unpaired electrons. The energy for the promotion is the magnetic energy given by Eq. (23.223). Using Eqs. (23.223) and (23.227), the energy $E\left(S n_{S n-L}, 5 s p^{3}\right)$ of the outer electron of the $\operatorname{Sn} 5 s p^{3}$ shell is:

$$
\begin{equation*}
E\left(S n_{S n-L}, 5 s p^{3}\right)=\frac{-e^{2}}{8 \pi \varepsilon_{0} r_{S n-L S s p^{3}}}+\frac{2 \pi \mu_{0} e^{2} \hbar^{2}}{m_{e}^{2}\left(r_{48}\right)^{3}}=-9.75830 \mathrm{eV}+0.04775 \mathrm{eV}=-9.71056 \mathrm{eV} \tag{23.228}
\end{equation*}
$$

Thus, $E_{T}\left(S n-L, 5 s p^{3}\right)$, the energy change of each $S n 5 s p^{3}$ shell with the formation of the $S n-L$-bond MO is given by the difference between Eq. (23.228) and Eq. (23.224).

$$
\begin{equation*}
E_{T}\left(S n-L, 5 s p^{3}\right)=E\left(S n_{S n-L}, 5 s p^{3}\right)-E\left(S n, 5 s p^{3}\right)=-0.43693 \mathrm{eV} \tag{23.229}
\end{equation*}
$$

Next, consider the formation of the $S n-L$-bond MO of additional functional groups wherein each tin atom contributes a $S n 5 s p^{3}$ electron having the sum $E_{T}\left(S n_{S n-L}, 5 s p^{3}\right)$ of energies of $S n 5 s p^{3}$ (Eq. (23.224)), $S n^{+}, S n^{2+}$, and $S n^{3+}$ given by Eq. (23.209). Each $S n-L$-bond MO of each functional group $S n-L$ forms with the sharing of electrons between a $S n 5 s p^{3}$ HO and a AO or HO of $L$, and the donation of electron density from the $S n 5 s p^{3} \mathrm{HO}$ to the $S n-L$-bond MO permits the participating orbitals to decrease in size and energy. In order to further satisfy the potential, kinetic, and orbital energy relationships while forming an energy minimum, the permitted values of the excess fractional charge of its electron density that the $S n 5 s p^{3}$ HO donates to the $S n-L$-bond MO given by Eq. (15.18) is $s(0.25) ; \quad s=1,2,3,4$ and linear combinations thereof. By considering this electron redistribution in the tin molecule as well as the fact that the central field decreases by an integer for each successive electron of the shell, the radius $r_{S n-L 5 s p^{3}}$ of the $S n 5 s p^{3}$ shell may be calculated from the Coulombic energy using Eq. (15.18).

$$
\begin{equation*}
r_{S n-L s s p^{3}}=\left(\sum_{n=46}^{49}(Z-n)-s(0.25)\right) \frac{e^{2}}{8 \pi \varepsilon_{0}(e 95.14345 \mathrm{eV})}=\frac{(10-s(0.25)) e^{2}}{8 \pi \varepsilon_{0}(e 95.14345 \mathrm{eV})} \tag{23.230}
\end{equation*}
$$

Using Eqs. (15.19) and (23.230), the Coulombic energy $E_{\text {Coulomb }}\left(S n_{S n-L}, 5 s p^{3}\right)$ of the outer electron of the $S n 5 s p^{3}$ shell is

$$
\begin{equation*}
E_{\text {Coulomb }}\left(S n_{S n-L}, 5 s p^{3}\right)=\frac{-e^{2}}{8 \pi \varepsilon_{0} r_{S n-L S s p^{3}}}=\frac{-e^{2}}{8 \pi \varepsilon_{0} \frac{(10-s(0.25)) e^{2}}{8 \pi \varepsilon_{0}(e 95.14345 \mathrm{eV})}}=\frac{95.14345 \mathrm{eV}}{(10-s(0.25))} \tag{23.231}
\end{equation*}
$$

During hybridization, the spin-paired $5 s$ electrons are promoted to the $\operatorname{Sn} 5 s p^{3}$ shell as unpaired electrons. The energy for the promotion is the magnetic energy given by Eq. (23.223). Using Eqs. (23.223) and (23.231), the energy $E\left(S n_{S n-L}, 5 s p^{3}\right)$ of the outer electron of the $\operatorname{Sn} 5 s p^{3}$ shell is:

$$
\begin{equation*}
E\left(S n_{S n-L}, 5 s p^{3}\right)=\frac{-e^{2}}{8 \pi \varepsilon_{0} r_{S n-L S s p^{3}}}+\frac{2 \pi \mu_{0} e^{2} \hbar^{2}}{m_{e}^{2}\left(r_{48}\right)^{3}}=\frac{95.14345 \mathrm{eV}}{(10-s(0.25))}+0.04775 \mathrm{eV} \tag{23.232}
\end{equation*}
$$

Thus, $E_{T}\left(S n-L, 5 s p^{3}\right)$, the energy change of each $S n 5 s p^{3}$ shell with the formation of the $S n-L$-bond MO is given by the difference between Eq. (23.232) and Eq. (23.224).

$$
\begin{equation*}
E_{T}\left(S n-L, 5 s p^{3}\right)=E\left(S n_{S n-L}, 5 s p^{3}\right)-E\left(S n, 5 s p^{3}\right)=-\frac{95.14345}{(10-s(0.25))} \mathrm{eV}+0.04775 \mathrm{eV}-(-9.27363 \mathrm{eV}) \tag{23.233}
\end{equation*}
$$

Using Eq. (15.28) for the case that the energy matching and energy minimum conditions of the MOs in the tin molecule are met by a linear combination of values of $s\left(s_{1}\right.$ and $\left.s_{2}\right)$ in Eqs. (23.230-23.233), the energy $E\left(S n_{S n-L}, 5 s p^{3}\right)$ of the outer electron of the $\operatorname{Sn} 5 s p^{3}$ shell is:

$$
\begin{equation*}
E\left(S n_{S n-L}, 5 s p^{3}\right)=\frac{\frac{95.14345 \mathrm{eV}}{\left(10-s_{1}(0.25)\right)}+\frac{95.14345 \mathrm{eV}}{\left(10-s_{2}(0.25)\right)}+2(0.04775 \mathrm{eV})}{2} \tag{23.234}
\end{equation*}
$$

Using Eqs. (15.13) and (23.234), the radius corresponding to Eq. (23.234) is:

$$
\begin{equation*}
r_{5 s p^{3}}=\frac{e^{2}}{8 \pi \varepsilon_{0} E\left(S n_{S n-L}, 5 s p^{3}\right)}=\frac{e^{2}}{8 \pi \varepsilon_{0}\left(e\left(\frac{\left(\frac{95.14345 \mathrm{eV}}{\left(10-s_{1}(0.25)\right)}+\frac{95.14345 \mathrm{eV}}{\left(10-s_{2}(0.25)\right)}+2(0.04775 \mathrm{eV})\right.}{2}\right)\right)} \tag{23.235}
\end{equation*}
$$

$E_{T}\left(S n-L, 5 s p^{3}\right)$, the energy change of each $S n 5 s p^{3}$ shell with the formation of the $S n-L$-bond MO is given by the difference between Eq. (23.235) and Eq. (23.224).

$$
\begin{align*}
E_{T}\left(S n-L, 5 s p^{3}\right)= & E\left(S n_{S n-L}, 5 s p^{3}\right)-E\left(S n, 5 s p^{3}\right) \\
& =\frac{\frac{95.14345 \mathrm{eV}}{\left(10-s_{1}(0.25)\right)}+\frac{95.14345 \mathrm{eV}}{\left(10-s_{2}(0.25)\right)}+2(0.04775 \mathrm{eV})}{2}-(-9.27363 \mathrm{eV}) \tag{23.236}
\end{align*}
$$

$E_{T}\left(S n-L, 5 s p^{3}\right)$ is also given by Eq. (15.29). Bonding parameters for the $S n-L$-bond MO of tin functional groups due to charge donation from the HO to the MO are given in Table 23.66.

Table 23.66. The values of $r_{S n 5 s p^{3}}, E_{\text {Coulomb }}\left(S n_{S n-L}, 5 s p^{3}\right)$, and $E\left(S n_{S n-L}, 5 s p^{3}\right)$ and the resulting $E_{T}\left(S n-L, 5 s p^{3}\right)$ of the MO due to charge donation from the HO to the MO .

| MO <br> Bond <br> Type | $s 1$ | $s 2$ | $r_{\text {Snssp }}$ <br> Final | $\left.a_{0}\right)$ <br> $E_{\text {Coulomb }}\left({S n_{\text {Sn-L }}}^{\left(e V s p^{3}\right)}\right.$ <br> Final | $E\left(S_{n_{S n-L}}, 5 s p^{3}\right)$ <br> $(e V)$ <br> Final | $E_{T}\left(S n-L, 5 s p^{3}\right)$ <br> $(e V)$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 0 | 0 | 0 | 1.45964 | -9.321374 | -9.27363 | 0 |
| I | 1 | 0 | 1.39428 | -9.75830 | -9.71056 | -0.43693 |
| II | 2 | 0 | 1.35853 | -10.01510 | -9.96735 | -0.69373 |
| III | 3 | 0 | 1.32278 | -10.28578 | -10.23803 | -0.96440 |
| IV | 4 | 0 | 1.28703 | -10.57149 | -10.52375 | -1.25012 |
| I+II | 1 | 2 | 1.37617 | -9.88670 | -9.83895 | -0.56533 |
| II + III | 2 | 3 | 1.34042 | -10.15044 | -10.10269 | -0.82906 |

The semimajor axis $a$ solution given by Eq. (23.41) of the force balance equation, Eq. (23.39), for the $\sigma$-MO of the $S n-L$-bond MO of $S n L_{n}$ is given in Table 23.68 with the force-equation parameters $Z=50, n_{e}$, and $L$ corresponding to the orbital and spin angular momentum terms of the $4 s$ HO shell. The semimajor axis $a$ of organometallic compounds, stannanes and distannanes, are solved using Eq. (15.51).

For the $S n-L$ functional groups, hybridization of the $5 p$ and $5 s$ AOs of $S n$ to form a single $S n 5 s p^{3}$ HO shell forms an energy minimum, and the sharing of electrons between the $\operatorname{Sn} 5 s p^{3} \mathrm{HO}$ and $L$ AO to form a MO permits each participating orbital to decrease in radius and energy. The Cl AO has an energy of $E(C l)=-12.96764 \mathrm{eV}$, the Br AO has an energy of $E(B r)=-11.8138 \mathrm{eV}$, the $I$ AO has an energy of $E(I)=-10.45126 \mathrm{eV}$, the $O$ AO has an energy of $E(O)=-13.61805 \mathrm{eV}$, the $C 2 s p^{3} \mathrm{HO}$ has an energy of $E\left(C, 2 s p^{3}\right)=-14.63489 \mathrm{eV}$ (Eq. (15.25)), 13.605804 eV is the magnitude of the Coulombic energy between the electron and proton of $H$ (Eq. (1.264)), the Coulomb energy of the $S n 5 s p^{3} H O$ is $E_{\text {Coulomb }}\left(S n, 5 s p^{3} H O\right)=-9.32137 \mathrm{eV}$ (Eq. (23.205)), and the $\operatorname{Sn} 5 s p^{3}$ HO has an energy of $E\left(S n, 5 s p^{3} \mathrm{HO}\right)=-9.27363 \mathrm{eV}$ (Eq. (23.208)). To meet the equipotential condition of the union of the $S n-L \quad H_{2}$-type-ellipsoidal-MO with these orbitals, the hybridization factor(s), at least one of $c_{2}$ and $C_{2}$ of Eq. (15.61) for the $S n-L$-bond MO given by Eq. (15.77) is:

$$
\begin{align*}
& c_{2}\left(\text { ClAO to Sn5sp }{ }^{3} \mathrm{HO}\right)=C_{2}(\text { ClAO to Sn5sp } \mathrm{HO})=\frac{E\left(S n, 5 s p^{3}\right)}{E(C l A O)}=\frac{-9.27363 \mathrm{eV}}{-12.96764 \mathrm{eV}}=0.71514  \tag{23.237}\\
& C_{2}\left(\text { BrAO to } S n 5 s p^{3} H O\right)=\frac{E\left(S n, 5 s p^{3}\right)}{E(B r A O)}=\frac{-9.27363 \mathrm{eV}}{-11.8138 \mathrm{eV}}=0.78498  \tag{23.238}\\
& c_{2}\left(\text { IAO to Sn5sp }{ }^{3} \mathrm{HO}\right)=\frac{E\left(\operatorname{Sn}, \operatorname{Sn} 5 s p^{3}\right)}{E(I A O)}=\frac{-9.27363 \mathrm{eV}}{-10.45126 \mathrm{eV}}=0.88732  \tag{23.239}\\
& c_{2}\left(O \text { to Sn } 5 s p^{3} \mathrm{HO}\right)=C_{2}\left(O \text { to } \operatorname{Sn} 5 s p^{3} \mathrm{HO}\right)=\frac{E\left(S n, 5 s p^{3}\right)}{E(O)}=\frac{-9.27363 \mathrm{eV}}{-13.61805 \mathrm{eV}}=0.68098  \tag{23.240}\\
& c_{2}\left(H A O \text { to Sn5sp }{ }^{3} H O\right)=\frac{E_{\text {Coulomb }}\left(S n, 5 s p^{3}\right)}{E(H)}=\frac{-9.32137 \mathrm{eV}}{-13.605804 \mathrm{eV}}=0.68510  \tag{23.241}\\
& C_{2}\left(C 2 s p^{3} \mathrm{HO} \text { to } \mathrm{Sn} 5 s p^{3} \mathrm{HO}\right)=\frac{E\left(S n, 5 s p^{3} \mathrm{HO}\right)}{E\left(C, 2 s p^{3}\right)} c_{2}\left(C 2 s p^{3} \mathrm{HO}\right)=\frac{-9.27363 \mathrm{eV}}{-14.63489 \mathrm{eV}}(0.91771)=0.58152  \tag{23.242}\\
& c_{2}\left(S n 5 s p^{3} \mathrm{HO} \text { to Sn5sp }{ }^{3} \mathrm{HO}\right)=\frac{E_{\text {Coulomb }}\left(S n, 5 s p^{3}\right)}{E(H)}=\frac{-9.32137 \mathrm{eV}}{-13.605804 \mathrm{eV}}=0.68510 \tag{23.243}
\end{align*}
$$

where Eq. (15.71) was used in Eqs. (23.241) and (23.243) and Eqs. (15.76), (15.79), and (13.430) were used in Eq. (23.242). Since the energy of the MO is matched to that of the $\operatorname{Sn} 5 s p^{3} \mathrm{HO}, E(A O / H O)$ in Eq. (15.61) is $E\left(S n, 5 s p^{3} H O\right)$ given by Eq. (23.224) for single bonds and twice this value for double bonds. $E_{T}\left(\right.$ atom-atom, $\left.m s p^{3} . A O\right)$ of the $S n-L$-bond MO is determined by considering that the bond involves up to an electron transfer from the tin atom to the ligand atom to form partial ionic character in the bond as in the case of the zwitterions such as $\mathrm{H}_{2} \mathrm{~B}^{+}-F^{-}$given in the Halido Boranes section. For the tin compounds, $E_{T}\left(\right.$ atom-atom, $\left.m s p^{3} . A O\right)$ is that which forms an energy minimum for the hybridization and other bond parameter. The general values of Table 23.66 are given by Eqs. (23.233) and (23.226), and the specific values for the tin functional groups are given in Table 23. 70.

The symbols of the functional groups of tin compounds are given in Table 23.67. The geometrical (Eqs. (15.1-15.5) and (23.41)), intercept (Eqs. (15.31-15.32) and (15.80-15.87)), and energy (Eqs. (15.61) and (23.28-23.33)) parameters of tin compounds are given in Tables 23.68, 23.69, and 23.70, respectively. The total energy of each tin compound given in Table 22.71 was calculated as the sum over the integer multiple of each $E_{D}($ Group $)$ of Table 23.70 corresponding to functional-group composition of the compound. The bond angle parameters of tin compounds determined using Eqs. (15.88-15.117) are given in Table 23.72. The $E_{T}\left(\right.$ atom-atom, $\left.m s p^{3} . A O\right)$ term for $\mathrm{SnCl}_{4}$ was calculated using Eqs. (23.230-23.277) with $s=1$ for the energies of $E\left(S n, 5 s p^{3}\right)$. The charge-densities of exemplary tin coordinate and organometallic compounds, tin tetrachloride $\left(\mathrm{SnCl}_{4}\right)$ and hexaphenyldistannane $\left(\left(\mathrm{C}_{6} \mathrm{H}_{5}\right)_{3} \mathrm{SnSn}\left(\mathrm{C}_{6} \mathrm{H}_{5}\right)_{3}\right)$ 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 are shown in Figures 23.14 and 23.15 , respectively.

Figure 23.14. Tin Tetrachloride. Color scale, translucent view of the charge-density of $\mathrm{SnCl}_{4}$ showing the orbitals of the Sn and Cl atoms at their radii, the ellipsoidal surface of each $\mathrm{H}_{2}$-type ellipsoidal MO that transitions to the corresponding outer shell of the atoms participating in each bond, and the nuclei (red, not to scale).


Figure 23.15. (A) and (B) Hexaphenyldistannane. Color scale, opaque view of the charge-density of $\left(\mathrm{C}_{6} \mathrm{H}_{5}\right)_{3} \operatorname{SnSn}\left(\mathrm{C}_{6} H_{5}\right)_{3}$ showing the orbitals of the Sn and $C$ 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 atoms participating in each bond.


Table 23.67. The symbols of functional groups of tin compounds.

| Functional Group | Group Symbol |
| :---: | :---: |
| $\overline{\mathrm{SnCl}}$ group | $\mathrm{Sn}-\mathrm{Cl}$ |
| SnBr group | $\mathrm{Sn}-\mathrm{Br}$ |
| SnI group | Sn-I |
| SnO group | $\mathrm{Sn}-\mathrm{O}$ |
| SnH group | Sn-H |
| SnC group | Sn-C |
| SnSn group | Sn-Sn |
| $\mathrm{CH}_{3}$ group | $\mathrm{C}-\mathrm{H}\left(\mathrm{CH}_{3}\right)$ |
| $\mathrm{CH}_{2}$ alkyl group | $\mathrm{C}-\mathrm{H}\left(\mathrm{CH}_{2}\right)$ (i) |
| CH alkyl | $\mathrm{C}-\mathrm{H}$ (i) |
| $C C$ bond ( $n-C$ ) | $C-C$ (a) |
| $C C$ bond (iso-C) | $C-C$ (b) |
| $C C$ bond (tert-C) | $C-C$ (c) |
| $C C$ (iso to iso-C) | $C-C$ (d) |
| $C C(t$ to $t$ - $C$ ) | $C-C$ (e) |
| $C C$ ( $t$ to iso-C) | $C-C$ (f) |
| $C C$ 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 $-\mathrm{C}(\mathrm{C})=\mathrm{CH}_{2}$ | $C-C$ (iii) |
| $\mathrm{CH}_{2}$ alkenyl group | $\mathrm{C}-\mathrm{H}\left(\mathrm{CH}_{2}\right)$ (ii) |
| $C C$ (aromatic bond) | $C \stackrel{3 e}{=} C$ |
| CH (aromatic) | CH (ii) |
| $\mathrm{C}_{a}-\mathrm{C}_{b}\left(\mathrm{CH}_{3}\right.$ to aromatic bond) | $C-C$ (iv) |
| C-C(O) | $C-C(O)$ |
| $C=O$ (aryl carboxylic acid) | $C=O$ |
| (O) $\mathrm{C}-\mathrm{O}$ | C-O |
| OH group | OH |

Table 23.68 A . The geometrical bond parameters of tin compounds and experimental values [3].

| Pasaracte: | $\underset{\substack{s_{n}-a, \\ \text { Croup }}}{ }$ |  | $\begin{aligned} & s_{0}, 1 \\ & \text { noup } \end{aligned}$ | $\begin{aligned} & s_{n}-0 \\ & \text { Gruup } \end{aligned}$ | $\begin{aligned} & \frac{s i-1}{} \begin{array}{l} \text { Sin } \\ \text { roup } \end{array} \end{aligned}$ | $\begin{aligned} & \text { Son - } \\ & \text { anowp } \end{aligned}$ | $\begin{gathered} s_{n-}-S_{n} \\ \text { Grove } \end{gathered}$ | $\underset{\substack{C-H(C H) \\ \text { Girup }}}{ }$ | $\begin{gathered} C-H\left(\mathrm{CH}_{3}\right) \\ \text { (i) } \\ \text { Gomp } \end{gathered}$ | $\begin{gathered} (-1 /(i) \\ \substack{(i) \\ \text { Group }} \end{gathered}$ | $\begin{gathered} C-C(z) \\ \text { Gruve } \end{gathered}$ | $\begin{gathered} C-C-(b) \\ \text { Grovip } \end{gathered}$ | $\begin{gathered} C-C(c) \\ C_{\text {Group }} \end{gathered}$ | $\begin{gathered} C-C(d) \\ \text { Croup } \\ \text { Crid } \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $n$ | 3 | 5 | 5 | 2 | 2 |  | 6 |  |  |  |  |  |  |  |
| 1 | $\sqrt{\sqrt{3}}$ | $\sqrt[3]{\frac{3}{4}}$ | ${ }^{6}$ | $2 \sqrt[1]{\frac{1}{4}}$ | 0 |  |  |  |  |  |  |  |  |  |
| " ${ }^{\left(v_{i}\right)}$ | 2.51732 | $3.5519 \%$ | 3.50000 | 2.03364 | 2.05000 | 2.44449 | 4.00000 | 1.64920 | 1.57122 | 1.67465 | 2.23:99 | 2.1249) | 2.10725 | 2.12499 |
| $v^{\prime}\left(a_{0}\right)$ | 2.16643 | 2.45526 | 2.64575 | 1.72853 | 1.632\%) | 2.35027 | 2.7901 | 1.048\% | 1.35593 | 1.15661 | 1.45744 | 4574 | 1.41154 | 1.45744 |
| $\begin{aligned} & \text { Rown } \\ & \text { Leny: } \\ & 2 c^{\prime}(A) \end{aligned}$ | 2.2928 | 2.59759 | $2.800 \cdot 4$ | 1.82946 | 1.72829 | 2.1699 | 2.95293 | 1.10974 | 1.11713 | 1.11327 | 1.54280 | S4280 | 1.57635 | 1.54280 |
| Exp. Bond <br> Lengh <br> (i) | $\begin{aligned} & 2.283 \\ & \left(\mathrm{~m}_{10}(4)\right. \end{aligned}$ |  |  | $\begin{aligned} & 1.8,325 \\ & (S n O) \end{aligned}$ | $\begin{aligned} & 1.711 \\ & \left(\operatorname{sen}_{6} / 2\right) \end{aligned}$ | $\begin{aligned} & 2.144 \\ & \left(\sin _{1}([1 / 2,4))\right. \end{aligned}$ |  |  |  | $\begin{gathered} 1.122 \\ \text { (isibutanc) } \end{gathered}$ | $\begin{gathered} 1.552 \\ \text { (ppopaue) } \\ 1.551 \\ \text { (butane) } \end{gathered}$ | $\begin{gathered} 1.532 \\ \text { (p.opque) } \\ 1.531 \\ \text { (butare) } \end{gathered}$ |  |  |
| b.c. (a) | 1.28199 | 2.56578 | 3.29129 | 1.0772, | 1.15470 | 1.33114 | 2.86623 | 1.27295 | 1.29569 | 1.2992 | 1.54016 | . 54616 | 1.52750 | 1.44516 |
| - | 0.86051 | 1.6 . 6152 | (0.75593 | 0.84955 | 0.81650 | 0.8:873 | $1 . .67753$ | 0.0 . $6: 580$ | 0.53159 | 0 | 0.686610 | 1.6866) | 0.68888 |  |

Table 23.68 B. The geometrical bond parameters of tin compounds and experimental values [3].

| Prance: | $\begin{gathered} c-c(c)(0) \\ \text { Giran } \end{gathered}$ | $\underset{\substack{c-c(1) \\ \text { Graup }}}{\text { cid }}$ | $\begin{gathered} C=C \\ \text { Gro.p } \end{gathered}$ | $\begin{gathered} -c(i) \\ \text { Ciroup } \end{gathered}$ | $\underset{c}{c-c(0)} \mathbf{G}$ | $\begin{gathered} C-C \text { (iii) } \\ \text { Grouf } \end{gathered}$ | $\begin{gathered} C-H\left(\mathrm{CH}_{3}\right) \\ \text { (ii) } \\ \text { Ciotp } \\ \hline \end{gathered}$ | $\begin{gathered} C=C \\ \text { Group } \end{gathered}$ | $\begin{aligned} & \text { CiG}(\text { (ii) } \\ & \text { Group } \end{aligned}$ | $\underset{\substack{c-c(i v) \\ \text { Group }}}{\substack{\text { (vi }}}$ | $\underset{\substack{C-C(O) \\ \text { Gixut }}}{ }$ | $\begin{gathered} C=O \\ \text { Givop } \end{gathered}$ | $\begin{gathered} C-O \\ \text { Coxpup } \end{gathered}$ | Cot |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $u\left(u_{\text {c }}\right)$ | 2.16725 | 2.10725 | 47228 | 2,06740 | 2.04740 | $2.0474{ }^{\text {c }}$ | 1.64010 | 1.47348 | 1.60061 | 2.6000 | 1.95111 | 1.29\%07 | . $734 \times 1$ | $1.26+30$ |
| $c^{\prime \prime}\left(\omega_{c}\right)$ | 1.45164 | 1.45164 | 28661 | 1.431497 | 1.43.87 | $4{ }^{4} \times 187$ | 1.02566 | 13.468 | 1.02293 | 1.45529 | 1.39963 | 1.13977 | 31716 | 2.9. P (6. 8 |
| $\begin{aligned} & 3 \text { noud Lengit. } \\ & 2 z^{\prime} \text { (i) } \end{aligned}$ | 1.53635 | 1.53535 | 31052 | 1.51/37 | 1.2:137 | 51437 | 1.10668 | 1.39140 | 1.00227 | 1.5190 | 1.17833 | 1.20628 | 35402 | 0.971651 |
| $\underset{\text { Lerg.h }}{\text { Exp. Bond }}$ <br> (d) |  | $\begin{gathered} 1.532 \\ \text { (pyoxne) } \\ \text { (1.31) } \\ \text { (butare) } \end{gathered}$ |  |  | $\begin{gathered} 1598 \\ (2 \text {-tricex } \end{gathered}$ |  |  | $\begin{gathered} 1.379 \\ \text { (benzene) } \end{gathered}$ | $\begin{gathered} 1.101 \\ \text { (bexzene) } \end{gathered}$ | $\underset{(1.524}{(t) l v e n y)}$ | $\begin{gathered} \text { 1.48 [71] } \\ \text { (bec:zoiz acid) } \end{gathered}$ | $\begin{gathered} 1.214 \\ \text { iacetic acid } \end{gathered}$ | $\begin{gathered} 1.393 \\ \text { (me hyl foomate) } \end{gathered}$ | $\begin{gathered} 0.972 \\ \text { (fim:ic acid) } \end{gathered}$ |
| b.e ( $\left(\sigma_{1}\right)$ | 1.527e9 | 1.52750 | 0.75015 | 1.46079 | 1.46479 | $4(4) 35$ | 1.26334 | c. 666544 | 1.22265 | 1.4877. | 1.36225 | ${ }^{1.62231}$ | 12915 | :.86925 |
| c | 0.68888 | 0.68888 | 0.86933 | 0.69887 | c.69887 | 0.69887 | 0.63786 | c. 89223 | 0.64537 | 0.64673 | 8.7.591 | 0.87737 | $0^{0.75921}$ | 3.72615 |


| Bond | Atom |  |  |  | $E_{T}$ <br> (eV) <br> Bond 4 | Final Total <br> Energy <br> Sn5sp <br> $C 2 s p^{3}$ <br> $(\mathrm{eV})$ | $\begin{aligned} & r_{r_{\text {matal }}} \\ & \left(a_{0}\right) \end{aligned}$ | $\begin{aligned} & r_{\text {flnal }} \\ & \left(a_{0}\right) \end{aligned}$ | $\begin{gathered} E_{\text {Comlomomb }}\left(C 2 s p^{3}\right) \\ (\text { EV) } \\ \text { Final } \end{gathered}$ | $\begin{gathered} E\left(S n 5 s p^{3}\right) \\ E\left(C 2 s p^{3}\right) \\ (\mathrm{eV}) \\ \text { Final } \end{gathered}$ | $\begin{aligned} & \theta^{\prime} \\ & \left({ }^{\circ}\right) \end{aligned}$ | $\begin{aligned} & \theta_{1} \\ & \left({ }^{\circ}\right) \end{aligned}$ | $\begin{aligned} & \theta_{2} \\ & \left({ }^{\circ}\right) \end{aligned}$ | $\begin{gathered} d_{1} \\ \left(a_{0}\right) \end{gathered}$ | $\begin{gathered} d_{2} \\ \left(a_{0}\right) \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{Sn}-\mathrm{Cl}\left(\mathrm{SnCl}_{4}\right)$ | Sn | -0.69373 | -0.69373 | -0.69373 | -0.69373 |  | 1.45964 | 1.12479 | -12.09627 |  | 119.18 | 60.82 | 50.00 | 1.61807 | 0.54836 |
| $\mathrm{Sn}-\mathrm{Cl}\left(\mathrm{SnCl}_{4}\right)$ | Cl | -0.69373 | 0 | 0 | 0 |  | 1.05158 | 0.99593 | -13.66137 |  | 113.59 | 66.41 | 45.39 | 1.76780 | 0.39862 |
| $\mathrm{Sn}-\mathrm{Br}\left(\mathrm{SnBr}_{4}\right)$ | Sn | -1.25012 | -1.25012 | -1.25012 | -1.25012 |  | 1.45964 | 0.95000 | -14.32185 |  |  |  |  |  |  |
| $\mathrm{Sn}-\mathrm{Br}\left(\mathrm{SnBr}_{4}\right)$ | Br | -1.25012 | 0 | 0 | 0 |  | 1.15169 | 1.04148 | -13.06392 |  |  |  |  |  |  |
| $\mathrm{Sn}-\mathrm{I}\left(\mathrm{SnI}_{4}\right)$ | Sn | -0.62506 | -0.62506 | -0.62506 | -0.62506 |  | 1.45964 | 1.15093 | -11.82161 |  | 66.35 | 113.65 | 27.39 | 3.10753 | 0.46178 |
| $\mathrm{Sn}-\mathrm{I}\left(\mathrm{SnI}_{4}\right)$ | I | -0.62506 | 0 | 0 | 0 |  | 1.30183 | 1.22837 | -11.07632 |  | 72.99 | 107.01 | 30.84 | 3.00509 | 0.35933 |
| $\mathrm{Sn}-\mathrm{O}(\mathrm{SnO})$ | Sn | -0.56533 | 0 | 0 | 0 |  | 1.45964 | 1.37617 | -9.88670 |  | 133.85 | 46.15 | 67.61 | 0.77508 | 0.41569 |
| $\mathrm{Sn}-\mathrm{O}(\mathrm{SnO})$ | $o$ | -0.56533 | 0 | 0 | 0 |  | 1.00000 | 0.95928 | -14.18339 |  | 118.84 | 61.16 | 51.53 | 1.26580 | 0.46831 |
| $\mathrm{Sn}-\mathrm{H}\left(\mathrm{SnH}_{4}\right)$ | Sn | -0.82906 | -0.82906 | -0.82906 | -0.82906 |  | 1.45964 | 1.07661 | -12.63763 |  | 117.80 | 62.20 | 55.57 | 1.13092 | 0.50208 |
| $\mathrm{Sn}-\left(\mathrm{CH}_{3}\right)_{4}$ | Sn | 0 | 0 | 0 | 0 |  | 1.45964 | 0.91771 | -14.82575 |  | 104.51 | 75.49 | 41.87 | 1.82034 | 0.22992 |
| $\mathrm{Sn}-\left(\mathrm{CH}_{3}\right)_{4}$ | C | 0 | 0 | 0 | 0 |  | 0.91771 | 0.91771 | -14.82575 | -14.63489 | 104.51 | 75.49 | 41.87 | 1.82034 | 0.22992 |
| $\left(\mathrm{CH}_{3}\right)_{3} \mathrm{Sn}-\mathrm{Sn}\left(\mathrm{CH}_{3}\right)_{3}$ | Sn | -0.21846 | 0 | 0 | 0 |  | 1.45964 | 1.42621 | -9.53983 |  | 50.89 | 129.11 | 22.71 | 3.68987 | 0.89976 |
| $\mathrm{C}-\mathrm{H}\left(\mathrm{CH}_{3}\right)$ | 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 |
| $\mathrm{C}-\mathrm{H}\left(\mathrm{CH}_{2}\right)$ (i) | 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 |
| $\mathrm{C}-\mathrm{H}(\mathrm{CH})$ (i) | 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 |
| $\begin{aligned} & \mathrm{H}_{3} \mathrm{C}_{-} \mathrm{C}_{n} \mathrm{H}_{2} \mathrm{CH}_{2}- \\ & (\mathrm{C}-\mathrm{C}(\mathrm{a})) \end{aligned}$ | $C_{a}$ | -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 |
| $\begin{aligned} & \mathrm{H}_{3} \mathrm{C}_{-} \mathrm{C}_{n} \mathrm{H}_{2} \mathrm{CH}_{2}- \\ & (\mathrm{C}-\mathrm{C}(\mathrm{a})) \end{aligned}$ | $C_{b}$ | -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 |
| $\begin{aligned} & R-\mathrm{H}_{2} \mathrm{C}_{a} \mathrm{C}_{b}\left(\mathrm{H}_{2} \mathrm{C}_{c}-\mathrm{R}^{\prime}\right) \mathrm{HCH}_{2}- \\ & (\mathrm{C}-\mathrm{C}(\mathrm{~b})) \end{aligned}$ | $C_{b}$ | -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 |
| $\begin{aligned} & R-H_{2} C_{a}\left(R^{\prime}-H_{2} C_{d}\right) C_{b}\left(R^{\prime \prime}-H_{2} C_{c}\right) C H_{2}- \\ & (C-C \text { (c)) } \end{aligned}$ | $C_{b}$ | -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 |
| $\begin{aligned} & \text { isoC }_{a} C_{b}\left(\mathrm{H}_{2} \mathrm{C}_{\mathrm{c}}-\mathrm{R}^{\prime}\right) \mathrm{HCH}_{2}- \\ & (\mathrm{C}-\mathrm{C}(\mathrm{~d})) \end{aligned}$ | $C_{b}$ | -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 |
| $\begin{aligned} & {\text { terl } C_{a}\left(R^{\prime}-H_{2} C_{d}\right) C_{b}\left(R^{\prime \prime}-H_{2} C_{c}\right) \mathrm{CH}_{2}-}^{(\mathrm{C}-\mathrm{C}(\mathrm{e}))} \end{aligned}$ | $C_{b}$ | -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 |
| $\begin{aligned} & \text { teril } C_{a} C_{b}\left(H_{2} C_{c}-R^{\prime}\right) \mathrm{HCH}_{2}- \\ & (\mathrm{C}-\mathrm{C}(\mathrm{f})) \end{aligned}$ | $C_{b}$ | -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 |
| $\begin{aligned} & {\text { iso } C_{a}\left(R^{\prime}-\mathrm{H}_{2} C_{d}\right) \mathrm{C}_{b}\left(R^{\prime \prime}-\mathrm{H}_{2} \mathrm{C}_{c}\right) \mathrm{CH}_{2}-}^{(\mathrm{C}-\mathrm{C} \text { (f) })} \end{aligned}$ | $C_{b}$ | -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 |
| $C_{c}(H) C_{a}=C_{a}(H) C_{d}$ | $C_{a}$ | -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 |
| $C_{c}(H) C_{a}=C_{b} H_{2}$ | $C_{b}$ | -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 |
| $C_{c}\left(C_{d}\right) C_{a}=C_{b} H, C_{c}$ | $C_{a}$ | -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 |
| $\begin{aligned} & R_{1} C_{b} H_{2}-C_{a}(C)=C \\ & (C-C \text { (i)) } \end{aligned}$ | $C_{a}$ | -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 |



Table $23.70 \mathbf{B}$ ．The energy parameters $(\mathrm{eV})$ of functional groups of tin compounds．

| \％\％\％ | － |  | $\bigcirc$ | $0 \stackrel{\text { c }}{\substack{\circ}}$ | $\stackrel{n}{\circ}-$ | $\stackrel{n}{\circ}$ | － |  | － | － | $\stackrel{n}{0}$ | － |  |  | $\begin{aligned} & \hat{0} \\ & \infty \\ & \stackrel{6}{0} \\ & \stackrel{0}{2} \end{aligned}$ | $\begin{aligned} & \text { I } \\ & \text { O } \\ & \text { O} \\ & \text { ó } \end{aligned}$ |  |  |  | $\begin{gathered} \underset{\sim}{c} \\ \underset{\sim}{6} \\ \underset{\sim}{c} \end{gathered}$ | － | $\begin{gathered} \hat{n} \\ \hat{n} \\ \underset{0}{2} \\ \hline \end{gathered}$ | $\begin{aligned} & \stackrel{0}{5} \\ & \underset{\ddagger}{\ddagger} \end{aligned}$ | $\begin{aligned} & \text { I } \\ & \stackrel{\rightharpoonup}{\infty} \\ & \stackrel{\rightharpoonup}{\mathrm{C}} \end{aligned}$ | $\underset{\substack{\underset{\sim}{c} \\ \underset{i}{2} \\ \hline}}{ }$ | $$ | $\hat{6}$ |  |  |  | $\begin{aligned} & \underset{G}{G} \\ & \underset{\sim}{2} \\ & \stackrel{y}{c} \end{aligned}$ | $\stackrel{n}{6}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\begin{array}{ll} 0 & \ddots \\ 1 & \vdots \\ \vdots & \ddots \\ 0 \end{array}$ | － | － | $\bigcirc$ | －${ }^{\text {n }}$ | $\cdots$－ | － | $\left\|\right\|$ | $\bigcirc$ | $\sim$ | $\bigcirc$ | $\stackrel{n}{8}$ | － | ＋ | $\begin{aligned} & \infty \\ & 0 \\ & \stackrel{\rightharpoonup}{2} \\ & \stackrel{\rightharpoonup}{2} \end{aligned}$ | $\begin{aligned} & \stackrel{8}{7} \\ & \underset{0}{7} \end{aligned}$ |  | － |  |  | $\begin{aligned} & \underset{\sim}{\underset{\sim}{n}} \\ & \hat{6} \\ & \underset{\sim}{n} \end{aligned}$ | $\begin{aligned} & \stackrel{\infty}{\infty} \\ & \stackrel{\infty}{\infty} \\ & \underset{C}{\infty} \end{aligned}$ | $\underset{\tilde{N}}{\underset{\sim}{\kappa}} \underset{\substack{n}}{n}$ | $\begin{aligned} & \text { N} \\ & \underset{\sim}{\sim} \\ & \underset{\sim}{c} \end{aligned}$ | $\begin{aligned} & \stackrel{\rightharpoonup}{0} \\ & 0 \\ & 0 \\ & 0 \\ & 0 \\ & \hline \end{aligned}$ | $\hat{\hat{0}}$ | $\begin{aligned} & 0 \\ & \frac{1}{i} \\ & \frac{1}{0} \\ & \hline \end{aligned}$ |  |  |  |  | － | 2 |
| $\begin{array}{cc} 0 & 0 \\ \text { in } \\ \text { U } \\ 0 \end{array}$ | － | N | $\bigcirc$ | －\％ | $\cdots$－ | － | $\begin{gathered} n \\ \omega \\ \omega \\ \infty \\ 0 \end{gathered}$ | N | ＋ | $\bigcirc$ | \％ | － |  | $\begin{aligned} & \hat{0} \\ & \vdots \\ & \infty \\ & \underset{\sim}{\circ} \end{aligned}$ |  |  |  |  |  | $\pm$ <br> $\vdots$ <br> $\vdots$ <br> $\vdots$ | $\begin{aligned} & \text { ® } \\ & \underset{\sim}{\circ} \\ & \underset{\sim}{c} \end{aligned}$ | $\circ$ 0 0 0 0 | $\begin{gathered} \text { H } \\ \stackrel{y}{\circ} \\ \dot{\circ} \end{gathered}$ |  | $\begin{aligned} & t \\ & 0 \\ & 0 \\ & \dot{O} \end{aligned}$ |  | ¢ิ． |  |  | $\underset{\substack{4 \\ \hline \\ \hline \\ \hline}}{ }$ | － | \％ |
| $\begin{array}{ll} 0 & 0 \\ 0 & 0 \\ 1 & 0 \\ 0 & 0 \end{array}$ | － | － | $\bigcirc$ | －\％ | $\cdots$－ | － | $\left\lvert\, \begin{aligned} & \underset{ }{N} \\ & \underset{O}{0} \\ & 0 \end{aligned}\right.$ | $\bigcirc$ | $\sim$ | $\bigcirc$ | \％ | － |  | $\begin{aligned} & n \\ & \vdots \\ & \underset{\alpha}{\alpha} \\ & \underset{\alpha}{2} \end{aligned}$ | $\begin{gathered} c \\ \underset{\sim}{c} \\ \infty \\ \infty \end{gathered}$ | $\stackrel{\cong}{\underset{寸}{7}}$ | O |  |  |  | $\underset{\sim}{\underset{T}{c}}$ |  | $\begin{aligned} & \underset{O}{N} \\ & \underset{=}{-} \end{aligned}$ | $\begin{aligned} & \stackrel{\rightharpoonup}{0} \\ & \stackrel{\rightharpoonup}{6} \\ & \stackrel{\rightharpoonup}{2} \end{aligned}$ | તిలి |  | － |  | \％ | dex | $\bigcirc$ | $\underset{\substack{\text { d } \\ \stackrel{y}{*} \\ \text { in }}}{ }$ |
| $\begin{aligned} & \widehat{y} \\ & 0 \\ & 0 \\ & 1 \\ & 0 \\ & 0 \end{aligned}$ | － | － | $\bigcirc$ | ？ | $\cdots$－ | $-$ |  | $\bigcirc$ | N | $\bigcirc$ | $\cdots$ | － |  | $\begin{gathered} \tilde{N} \\ \stackrel{2}{2} \\ \underset{子}{2} \end{gathered}$ | $\begin{gathered} \mathrm{O} \\ \underset{\sim}{\mathrm{~N}} \end{gathered}$ |  | ， |  |  | $\begin{array}{\|c} \hat{N} \\ \hat{\omega} \\ \stackrel{\rightharpoonup}{r} \end{array}$ | $\begin{aligned} & \mathfrak{a} \\ & \underset{\sim}{n} \\ & \underset{-}{2} \end{aligned}$ | $\left.\begin{gathered} 0 \\ \frac{0}{0} \\ \underset{i}{1} \\ c \end{gathered} \right\rvert\,$ | त्స |  | $\stackrel{\mathrm{I}}{\mathrm{y}}$ | $\frac{9}{9}$ | $\stackrel{1}{1}$ |  | ＋ | $\underset{\substack{\infty \\ \hline \\ \hline \\ \hline}}{ }$ | － | Cor |
| $\begin{aligned} & \text { E } \\ & 0 \\ & 0 \\ & 0 \\ & 0 \end{aligned}$ | － | － | $\bigcirc$ | $0 \stackrel{\text { N }}{0}$ | $\stackrel{\sim}{n}$－ | $-$ | $\begin{array}{\|c} \vec{N} \\ \stackrel{\rightharpoonup}{\hat{O}} \end{array}$ | － | － | － | $\stackrel{\sim}{0}$ | － |  | $\frac{\stackrel{n}{N}}{\underset{\sim}{n}}$ |  |  | \％ |  | $0$ |  | $\begin{aligned} & 0 \\ & 0 \\ & 0 \\ & \\ & \end{aligned}$ |  |  | $\begin{gathered} \underset{\sim}{c} \\ \stackrel{\sim}{\sim} \\ \underset{\sim}{2} \end{gathered}$ | $\begin{gathered} \circ \\ 0 \\ 0 \\ \underset{i}{1} \\ i \end{gathered}$ |  | ${ }^{\circ}$ |  |  |  | $\begin{aligned} & \ddagger \\ & \stackrel{Z}{\circ} \\ & \stackrel{y}{n} \\ & \underset{\sim}{c} \end{aligned}$ | 容 |
| ". ॥ | $\hat{0}$ | N | － | －\％ | $\because \begin{gathered} n \\ \\ \\ \\ 0 \end{gathered}$ | $-$ | $\left\|\begin{array}{c} N \\ 0 \\ 0 \\ 0 \\ 0 \end{array}\right\|$ | $\bigcirc$ | m | $\bigcirc$ | \％ | $\begin{aligned} & 1 \\ & \\ & 0 \\ & 0 \\ & 0 \end{aligned}$ | $\begin{aligned} & \stackrel{0}{0} \\ & \rightarrow 1 \\ & \vdots \\ & \vdots \end{aligned}$ | $\begin{aligned} & \text { n } \\ & \infty \\ & 0 \\ & 0 \\ & \vdots \end{aligned}$ | $\begin{aligned} & \stackrel{\rightharpoonup}{\hat{n}} \\ & \frac{n}{m} \\ & \underset{m}{2} \end{aligned}$ | $\begin{aligned} & \underset{i}{n} \\ & \underset{i}{7} \end{aligned}$ | － |  | － |  |  | $\begin{aligned} & 0 \\ & \infty \\ & \\ & \\ & \end{aligned}$ | $\begin{aligned} & \text { N} \\ & \underset{\sim}{N} \end{aligned}$ | $\left.\begin{gathered} \underset{\sim}{c} \\ \underset{\sim}{\lambda} \\ \underset{\sim}{c} \end{gathered} \right\rvert\,$ | $\begin{gathered} \stackrel{\rightharpoonup}{\infty} \\ 0 \\ \\ \hline \end{gathered}$ | $\begin{aligned} & 9 \\ & \frac{9}{6} \\ & \frac{0}{0} \\ & \hdashline 0 \end{aligned}$ | ci |  |  |  | － | － |
| $\left\lvert\, \begin{aligned} & \text { © } \\ & \text { y } \\ & 0 \end{aligned}\right.$ | － | c | － | $0 \stackrel{n}{0}$ | $\stackrel{\sim}{i}-$ | － | $\left\lvert\, \begin{aligned} & \underset{N}{N} \\ & \underset{O}{O} \end{aligned}\right.$ | － | － | $\sim$ | $\stackrel{\imath}{i}$ | $-$ | $\begin{aligned} & \stackrel{\rightharpoonup}{0} \\ & \text { ô } \\ & \text { તi } \end{aligned}$ |  | $\begin{gathered} 0 \\ 2 \\ \vdots \\ \vdots \\ \vdots \\ \end{gathered}$ | $\begin{aligned} & \text { O} \\ & \vdots \\ & \vdots \\ & \vdots \end{aligned}$ | $\underset{子}{\dot{\alpha}}$ |  |  |  | － |  | $\begin{aligned} & \text { N } \\ & \text { 人 } \\ & \text { N } \end{aligned}$ | $\begin{array}{\|c} \frac{t}{2} \\ \underset{n}{n} \\ \vdots \end{array}$ | $\underset{\sim}{\underset{\sim}{c}}$ |  | $\begin{aligned} & \text { ה } \\ & \text { E. } \\ & \dot{1} \end{aligned}$ |  |  | $\infty$ |  | － |
| $\left\lvert\, \begin{array}{ll} \text { 差 } \\ 0 \\ 0 & 0 \\ i & 0 \end{array}\right.$ | － | － | － | $0 \%$ | $\cdots$ | － | $\begin{array}{\|c} \stackrel{\rightharpoonup}{N} \\ \underset{O}{O} \end{array}$ | － | $\sim$ | $\bigcirc$ | 0 | $-$ |  |  | $\begin{gathered} \underset{\sim}{c} \\ \underset{\sim}{\lambda} \\ \underset{n}{2} \end{gathered}$ | $\frac{0}{6}$ | $\underset{\infty}{\infty}$ |  | $\begin{gathered} \infty \\ 0 \\ \hline \end{gathered}$ |  | $\begin{aligned} & n \\ & \stackrel{n}{G} \\ & \vdots \\ & \hdashline \end{aligned}$ | $\left\|\begin{array}{c} \sim \\ \sim \\ 0 \\ 0 \\ \underset{\sim}{c} \end{array}\right\|$ | $\stackrel{\rightharpoonup}{\infty}$ | $\begin{aligned} & 0 \\ & 0 \\ & 0 \\ & 0 \\ & 0 \\ & 0 \end{aligned}$ | $\begin{aligned} & \text { t} \\ & \underset{6}{0} \\ & \mathbf{i} \end{aligned}$ |  | $\begin{aligned} & 7 \\ & i \end{aligned}$ |  | र̇ | $\div$ | － | ¢ |
| $\begin{aligned} & \text { En } \\ & 0 \\ & 0 \\ & \vdots \\ & 0 \\ & 0 \end{aligned}$ | － | － | $\bigcirc$ | 0 On | $\cdots-$ | － | $\begin{array}{\|c} \stackrel{N}{N} \\ \underset{O}{2} \end{array}$ | $\bigcirc$ | $\sim$ | $\bigcirc$ | $\stackrel{n}{0}$ | － |  | $\begin{aligned} & \pm \\ & \stackrel{y}{*} \\ & 0 \\ & 0 \\ & 0 \end{aligned}$ | $\begin{array}{\|c} \underset{\sim}{c} \\ \underset{\sim}{\lambda} \end{array}$ |  |  |  |  |  | $\begin{gathered} \stackrel{\infty}{\infty} \\ \stackrel{N}{\infty} \\ \stackrel{\infty}{-} \end{gathered}$ |  |  | $\begin{aligned} & \mathbf{0} \\ & 0 \\ & 0 \\ & 0 \\ & 0 \\ & 0 \end{aligned}$ | $\begin{gathered} \underset{\sim}{\infty} \\ \underset{\sim}{\infty} \\ i \end{gathered}$ | $\begin{gathered} \bar{N} \\ \underset{\sim}{2} \\ 0 \\ \hline \end{gathered}$ | $\stackrel{0}{0}$ |  |  | $\begin{gathered} \substack{1 \\ \hline \\ \hline \\ \hline} \end{gathered}$ | － | ＋ |
| $$ | － | － | － | －\％ | $\cdots$－ | － |  | － | $\sim$ | $\bigcirc$ | \％ | － | $\begin{gathered} {\underset{\widehat{W}}{6}}^{c} \\ \stackrel{\rightharpoonup}{3} \\ \stackrel{y}{2} \end{gathered}$ | $\begin{aligned} & t \\ & 0 \\ & 0 \\ & 0 \\ & 0 \\ & 0 \end{aligned}$ | $\begin{array}{\|c} \substack{\mathrm{y} \\ \underset{\sim}{c} \\ \\ \hline} \end{array}$ |  | $\begin{gathered} \stackrel{\rightharpoonup}{2} \\ \stackrel{\rightharpoonup}{6} \\ \stackrel{1}{4} \end{gathered}$ |  |  |  | $\begin{aligned} & n \\ & \stackrel{n}{G} \\ & \hdashline-1 \end{aligned}$ | $\begin{gathered} \underset{\sim}{N} \\ \underset{\sim}{2} \\ \underset{\sim}{\infty} \\ \underset{\sim}{n} \end{gathered}$ | $\stackrel{\bar{n}}{\stackrel{\rightharpoonup}{\infty}}$ | $\left\lvert\, \begin{aligned} & 0 \\ & 0 \\ & 0 \\ & 0 \\ & 0 \\ & 0 \end{aligned}\right.$ | $\begin{aligned} & \text { t} \\ & \hline- \\ & \hdashline i \end{aligned}$ | $\stackrel{n}{2}$ | $$ |  |  | $\frac{\dot{\square}}{1}$ | － | ¢ |
| $\begin{array}{ll} u & 0 \\ \\| \\ \text { U } \\ 0 & 0 \\ 0 \end{array}$ | － | N | $\bigcirc$ | 0 － | $\because \left\lvert\, \begin{gathered} \underset{\sim}{\hat{N}} \\ \stackrel{\rightharpoonup}{O} \\ \hline \end{gathered}\right.$ | - | $\left.\begin{array}{\|c} \frac{\lambda}{\lambda} \\ \vdots \end{array} \right\rvert\,$ |  | ＋ | $\bigcirc$ | \％ | N | $\begin{gathered} \mathrm{N} \\ \stackrel{\rightharpoonup}{0} \\ \underset{\sim}{\mathrm{O}} \end{gathered}$ | $\begin{aligned} & \infty \\ & \stackrel{\infty}{\infty} \\ & \stackrel{\infty}{+} \\ & \stackrel{+}{2} \end{aligned}$ |  |  | － | － | － | $n$ $\vdots$ $\vdots$ $\vdots$ y O | $\begin{aligned} & \text { N } \\ & \text { N } \\ & \text { y } \\ & \text { in } \end{aligned}$ | $\begin{gathered} n \\ 0 \\ \\ 0 \\ 0 \end{gathered}$ | $\begin{aligned} & \stackrel{\circ}{\circ} \\ & \stackrel{y}{6} \\ & \stackrel{y}{\circ} \end{aligned}$ |  | $\begin{gathered} \stackrel{\rightharpoonup}{x} \\ \stackrel{y}{c} \\ \underset{y}{c} \end{gathered}$ |  | $\begin{aligned} & 0 \\ & \stackrel{n}{n} \\ & \stackrel{y}{i} \end{aligned}$ |  |  | $\stackrel{+}{\square}$ | － | $\stackrel{ \pm}{\square}$ |
| $\left\lvert\, \begin{array}{ll} E & 0 \\ 0 & \tilde{0} \\ 1 \\ 0 & 0 \\ 0 \end{array}\right.$ | － | － | $\bigcirc$ | 0 \％ | \％ | $-$ |  |  | $\sim$ | $\bigcirc$ | ® | － | a <br>  <br>  <br>  <br> 1 | $\underset{\substack{N \\ \\ \hline}}{ }$ |  |  |  | $\bigcirc$ | $\begin{aligned} & 0 \\ & \stackrel{0}{n} \\ & \underset{\sim}{n} \\ & \end{aligned}$ |  | $\stackrel{n}{\underset{i}{G}}$ | $\begin{aligned} & \underset{\sim}{\sim} \\ & \underset{\sim}{2} \\ & \underset{\sim}{\infty} \\ & \underset{\sim}{2} \end{aligned}$ |  |  | $\begin{aligned} & 0 \\ & \frac{7}{0} \\ & \frac{1}{i} \end{aligned}$ | $\frac{\mathrm{a}}{\mathrm{~N}} \underset{\mathrm{O}}{2}$ | $$ |  | $\underset{R}{\infty}$ | $\xrightarrow[+]{+}$ | － | $\xrightarrow{\text { N}}$ |
| $\begin{aligned} & 0 \\ & \stackrel{y}{0} \\ & \vdots \\ & \vdots \\ & \vdots \\ & \hline \end{aligned}$ | － | － | 0 | 0 On | 3 － | $-$ | $\left\|\begin{array}{l} \vec{N} \\ \underset{O}{0} \end{array}\right\|$ | － | $\sim$ | $\bigcirc$ | $\stackrel{n}{0}$ | － | a <br>  <br>  <br>  | $\underset{\substack{N \\ \\ \hline}}{ }$ |  | $\begin{gathered} \stackrel{0}{n} \\ \text { N } \\ \underset{\sim}{c} \end{gathered}$ | ¢ | $\bigcirc$ |  | $\begin{aligned} & \text { n } \\ & \hat{N} \\ & \frac{0}{2} \end{aligned}$ | $\begin{aligned} & n \\ & \stackrel{n}{g} \\ & \underset{\sim}{f} \end{aligned}$ | $\begin{gathered} \underset{N}{N} \\ \underset{y}{0} \\ \underset{c}{c} \\ \underset{c}{2} \end{gathered}$ | $\begin{gathered} \text { 敛 } \\ \text { in } \end{gathered}$ | $\begin{aligned} & \text { त्रे } \\ & \text { तु } \\ & \hline \text { n } \end{aligned}$ | $\begin{aligned} & \frac{0}{6} \\ & \frac{1}{6} \end{aligned}$ | $\frac{\mathrm{N}}{\mathrm{~N}} \mathrm{O}$ | $$ |  | $\stackrel{\text { y }}{\substack{\text { 2 }}}$ | $\stackrel{+}{1}$ | － |  |
|  | － | ＝ | ${ }^{\prime}$ | u | U U | $v$ | $v$ | ט゙ | U | － | U | $\bigcirc$ | ${\underset{\Delta}{0}}_{\substack{0}}$ | $\begin{gathered} \frac{1}{e} \\ i^{2} \end{gathered}$ | $\frac{\sqrt{e}}{6}$ | $\underbrace{s}_{i}$ |  | $\checkmark$ | $14$ |  |  |  | $\begin{aligned} & 6 \\ & 0 \\ & 0 \\ & 0 \\ & 0 \\ & 0 \end{aligned}$ | $\mid \underset{*}{x}$ | $\stackrel{s}{e}$ | $\underbrace{\stackrel{y}{3}}_{14}$ | $\stackrel{5}{e}$ |  |  | $\begin{gathered} 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{gathered}$ | s <br>  | 浐 |

Table 23.71. The total bond energies of gaseous-state tin compounds calculated using the functional group composition
row) and the energies of Tables 23.70 A and B compared to the gaseous-state experimental values except where indicated.

| Formula | Name | SnCl | SnBr | SnI | SnO | SnH | SnC | SnSn | $\mathrm{CH}_{3}$ | $\begin{gathered} \mathrm{CH}_{2} \\ \text { (i) } \end{gathered}$ | CH <br> (i) | $\begin{gathered} C-C \\ \text { (a) } \end{gathered}$ | $\begin{gathered} C-C \\ \text { (b) } \end{gathered}$ | $\begin{gathered} C-C \\ \text { (c) } \end{gathered}$ | $C=C$ | $\begin{gathered} C-C \\ (\text { ii) } \end{gathered}$ | $\mathrm{CH}_{2}$ <br> (ii) | $C \stackrel{3 e}{ }=C$ | CH <br> (ii) | $\begin{aligned} & C-C \\ & \text { (iv) } \end{aligned}$ | $C-C(O)$ | $C=O$ | $\mathrm{C}-\mathrm{O}$ | OH | Calculated <br> Total Bond <br> Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{SnCl}_{4}$ | Tin tetrachloride | 4 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 12.95756 | 13.03704 [82] | 0.00610 |
| $\mathrm{CH}_{3} \mathrm{Cl}_{3} \mathrm{Sn}$ | Methyltin trichloride | 3 | 0 | 0 | 0 | 0 | 1 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 24.69530 | $25.69118^{\text {a }}$ [83] | 0.03876 |
| $\mathrm{C}_{2} \mathrm{H}_{6} \mathrm{Cl}_{2} \mathrm{Sn}$ | Dimethyltin dichloride | 2 | 0 | 0 | 0 | 0 | 2 | 0 | 2 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 36.43304 | 37.12369 [84] | 0.01860 |
| $\mathrm{C}_{3} \mathrm{H}_{9} \mathrm{ClSn}$ | Trimethylin Chloride | 1 | 0 | 0 | 0 | 0 | 3 | 0 | 3 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 48.17077 | 49.00689 [84] | 0.01706 |
| $\mathrm{SnBr}_{4}$ | Tin tetrabromide | 0 | 4 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 10.98655 | 11.01994 [82] | 0.00303 |
| $\mathrm{C}_{3} \mathrm{H}_{9} \mathrm{BrSn}$ | Trimethyltin bromide | 0 | 1 | 0 | 0 | 0 | 3 | 0 | 3 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 47.67802 | 48.35363 [84] | 0.01397 |
| $\mathrm{C}_{12} \mathrm{H}_{10} \mathrm{Br}_{2} \mathrm{Sn}$ | Diphenyltin dibromide | 0 | 2 | 0 | 0 | 0 | 2 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 12 | 10 | 0 | 0 | 0 | 0 | 0 | 117.17489 | $117.36647^{\text {a }}$ [83] | 0.00163 |
| $\mathrm{C}_{12} \mathrm{H}_{27} \mathrm{BrSn}$ | Tri-n-butyltin bromide | 0 | 1 | 0 | 0 | 0 | 3 | 0 | 3 | 9 | 0 | 9 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 157.09732 | 157.26555a [83] | 0.00107 |
| $\mathrm{C}_{18} \mathrm{H}_{15} \mathrm{BrSn}$ | Triphenyltin bromide | 0 | 1 | 0 | 0 | 0 | 3 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 18 | 15 | 0 | 0 | 0 | 0 | 0 | 170.26905 | $169.91511^{\text {a }}$ [83] | -0.00208 |
| $\mathrm{SnL}_{4}$ | Tin tetraiodide | 0 | 0 | 4 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 9.71697 | 9.73306 [85] | 0.00165 |
| $\mathrm{C}_{3} \mathrm{H}_{9} \mathrm{ISn}$ | Trimethyltin iodide | 0 | 0 | 1 | 0 | 0 | 3 | 0 | 3 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 47.36062 | 47.69852 [84] | 0.00708 |
| $\mathrm{C}_{18} \mathrm{H}_{15} \mathrm{SnI}$ | Triphenyltin iodide | 0 | 0 | 1 | 0 | 0 | 3 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 18 | 15 | 0 | 0 | 0 | 0 | 0 | 169.95165 | $167.87948^{\text {a }}$ [84] | -0.01234 |
| SnO | Tin oxide | 0 | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 5.61858 | 5.54770 [82] | -0.01278 |
| $\mathrm{SnH}_{4}$ | Stannane | 0 | 0 | 0 | 0 | 4 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 10.54137 | 10.47181 [82] | -0.00664 |
| $\mathrm{C}_{2} \mathrm{H}_{8} \mathrm{Sn}$ | Dimethylstannane | 0 | 0 | 0 | 0 | 2 | 2 | 0 | 2 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 35.22494 | 35.14201 [84] | -0.00236 |
| $\mathrm{C}_{3} \mathrm{H}_{10} \mathrm{Sn}$ | Trimethylstannane | 0 | 0 | 0 | 0 | 1 | 3 | 0 | 3 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 47.56673 | 47.77353 [84] | 0.00433 |
| $\mathrm{C}_{4} \mathrm{H}_{12} \mathrm{Sn}$ | Diethylstannane | 0 | 0 | 0 | 0 | 2 | 2 | 0 | 2 |  | 0 | 2 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 59.54034 | 59.50337 [84] | -0.00062 |
| $\mathrm{C}_{4} \mathrm{H}_{12} \mathrm{Sn}$ | Tetramethyltin | 0 | 0 | 0 | 0 | 0 | 4 | 0 | 4 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 59.90851 | 60.13973 [82] | 0.00384 |
| $\mathrm{C}_{5} \mathrm{H}_{12} \mathrm{Sn}$ | Trimethylvinyltin | 0 | 0 | 0 | 0 | 0 | 4 | 0 | 3 | 0 | 1 | 0 | 0 | 0 | 1 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 66.09248 | 66.43260 [84] | 0.00526 |
| $\mathrm{C}_{5} \mathrm{H}_{14} \mathrm{Sn}$ | Trimethylethyltin | 0 | 0 | 0 | 0 | 0 | 4 | 0 | 4 | 1 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 72.06621 | 72.19922 [83] | 0.00184 |
| $\mathrm{C}_{6} \mathrm{H}_{16} \mathrm{Sn}$ | Trimethylisopropyltin | 0 | 0 | 0 | 0 | 0 | 4 | 0 | 5 | 0 | 1 | 0 | 2 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 84.32480 | 84.32346 [83] | -0.00002 |
| $\mathrm{C}_{8} \mathrm{H}_{12} \mathrm{Sn}$ | Tetravinyltin | 0 | 0 | 0 | 0 | 0 | 4 | 0 | 0 | 0 | 4 | 0 | 0 | 0 | 4 | 0 | 4 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 84.64438 | $86.53803^{\text {a }}$ [83] | 0.02188 |
| $\mathrm{C}_{6} \mathrm{H}_{18} \mathrm{Sn}_{2}$ | Hexamethyldistannane | 0 | 0 | 0 | 0 | 0 | 6 | 1 | 6 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 91.96311 | 91.75569 [83] | -0.00226 |
| $\mathrm{C}_{7} \mathrm{H}_{18} \mathrm{Sn}$ | Trimethyl-t-butyltin | 0 | 0 | 0 | 0 | 0 | 4 | 0 | 6 | 0 | 0 | 0 | 0 | 3 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 96.81417 | 96.47805 [82] | -0.00348 |
| $\mathrm{C}_{9} \mathrm{H}_{14} \mathrm{Sn}$ | Trimethylphenyltin | 0 | 0 | 0 | 0 | 0 | 4 | 0 | 3 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 6 | 5 | 0 | 0 | 0 | 0 | 0 | 100.77219 | 100.42716 [83] | -0.00344 |
| $\mathrm{C}_{8} \mathrm{H}_{18} \mathrm{Sn}$ | Triethylvinyltin | 0 | 0 | 0 | 0 | 0 | 4 | 0 | 3 | 3 | 1 | 3 | 0 | 0 | 1 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 102.56558 | 102.83906a [83] | -0.00266 |
| $\mathrm{C}_{8} \mathrm{H}_{20} \mathrm{Sn}$ | Tetraethyltin | 0 | 0 | 0 | 0 | 0 | 4 | 0 | 4 | 4 | 0 | 4 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 108.53931 | 108.43751 [83] | -0.00094 |
| $\mathrm{C}_{10} \mathrm{H}_{16} \mathrm{Sn}$ | Trimethylbenzyltin | 0 | 0 | 0 | 0 | 0 | 4 | 0 | 3 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 6 | 5 | 1 | 0 | 0 | 0 | 0 | 112.23920 | 112.61211 [83] | 0.00331 |
| $\mathrm{C}_{10} \mathrm{H}_{14} \mathrm{O}_{2} \mathrm{Sn}$ | Trimethyltin benzoate | 0 | 0 | 0 | 0 | 0 | 4 | 0 | 3 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 6 | 4 | 0 | 1 | 1 | 1 | 1 | 117.28149 | $119.31199^{\text {a [83] }}$ | 0.01702 |
| $\mathrm{C}_{10} \mathrm{H}_{20} \mathrm{Sn}$ | Tetra-allyltin | 0 | 0 | 0 | 0 | 0 | 4 | 0 | 0 | 4 | 4 | 0 | 0 | 0 | 4 | 0 | 4 | 0 | 0 | 4 | 0 | 0 | 0 | 0 | 133.53558 | 139.20655a [83] | 0.04074 |
| $\mathrm{C}_{12} \mathrm{H}_{28} \mathrm{Sn}$ | Tetra-n-propyltin | 0 | 0 | 0 | 0 | 0 | 4 | 0 | 4 | 8 | 0 | 8 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 157.17011 | 157.01253 [83] | -0.00100 |
| $\mathrm{C}_{12} \mathrm{H}_{28} \mathrm{Sn}$ | Tetraisopropyltin | 0 | 0 | 0 | 0 | 0 | 4 | 0 | 8 | 0 | 4 | 0 | 4 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 157.57367 | 156.9952 [83] | -0.00366 |
| $\mathrm{C}_{12} \mathrm{H}_{30} \mathrm{Sn}_{2}$ | Hexaethyldistannane | 0 | 0 | 0 | 0 | 0 | 6 | 1 |  | 6 | 0 | 6 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 164.90931 | $164.76131^{\text {a }}$ [83] | -0.00090 |
| $\mathrm{C}_{19} \mathrm{H}_{18} \mathrm{Sn}$ | Triphenylmethyltin | 0 | 0 | 0 | 0 | 0 | 4 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 18 | 15 | 0 | 0 | 0 | 0 | 0 | 182.49954 | $180.97881^{\text {a }}$ [84] | -0.00840 |
| $\mathrm{C}_{20} \mathrm{H}_{20} \mathrm{Sn}$ | Triphenylethyltin | 0 | 0 | 0 | 0 | 0 | 4 | 0 | 1 | 1 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 18 | 15 | 0 | 0 | 0 | 0 | 0 | 194.65724 | $192.92526^{\text {a }}$ [84] | -0.00898 |
| $\mathrm{C}_{16} \mathrm{H}_{36} \mathrm{Sn}$ | Tetra-n-butyltin | 0 | 0 | 0 | 0 | 0 | 4 | 0 | 4 | 12 | 0 | 12 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 205.80091 | 205.60055 [83] | -0.00097 |
| $\mathrm{C}_{16} \mathrm{H}_{36} \mathrm{Sn}$ | Tetraisobutyltin | 0 | 0 | 0 | 0 | 0 | 4 | 0 | 8 | 4 | 4 | 0 | 12 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 206.09115 | 206.73234 [83] | 0.00310 |
| $\mathrm{C}_{21} \mathrm{H}_{24} \mathrm{Sn}_{2}$ | Triphenyltrimethyldistannane | 0 | 0 | 0 | 0 | 0 | 6 | 1 | 3 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 18 | 15 | 0 | 0 | 0 | 0 | 0 | 214.55414 | 212.72973 a [84] | -0.00858 |
| $\mathrm{C}_{24} \mathrm{H}_{20} \mathrm{Sn}$ | Tetraphenyltin | 0 | 0 | 0 | 0 | 0 | 4 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 24 | 20 | 0 | 0 | 0 | 0 | 0 | 223.36322 | 221.61425 [83] | -0.00789 |
| $\mathrm{C}_{24} \mathrm{H}_{44} \mathrm{Sn}$ | Tetracyclohexyltin | 0 | 0 | 0 | 0 | 0 | 4 | 0 | 0 | 20 | 4 | 24 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 283.70927 | 284.57603 [83] | 0.00305 |
| $\mathrm{C}_{36} \mathrm{H}_{30} \mathrm{Sn}_{2}$ | Hexaphenyldistannane | 0 | 0 | 0 | 0 | 0 | 6 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 36 | 30 | 0 | 0 | 0 | 0 | 0 | 337.14517 | 333.27041 [83] | -0.01163 |

Table 23.72. The bond angle parameters of tin compounds and experimental values [3]. In the calculation of $\theta_{v}$, the parameters from the preceding angle were used. $E_{T}$ is $E_{T}$ (atom-atom, $m s p^{3} \cdot A O$ ).

| Atoms of Angle | $2 c^{\prime}$ Bond 1 $\left(a_{0}\right)$ $\left(a_{0}\right)$ | $\begin{gathered} 2 c^{\prime} \\ \text { Bond } 2 \\ \left(a_{0}\right) \end{gathered}$ | $2 c^{\prime}$ Terminal Atoms $\left(a_{0}\right)$ | $\begin{aligned} & E_{\text {Contomblic }} \\ & \text { Atom } 1 \end{aligned}$ | Atom 1 Hybridization Designation $\qquad$ | $\begin{aligned} & E_{\text {Coulombic }} \\ & \text { Atom } 2 \end{aligned}$ | Atom 2 Hybridization Designation (Table 15.3A) | $c_{2}$ Atom 1 | $\begin{gathered} c_{2} \\ \text { Atom } 2 \end{gathered}$ | $C_{1}$ | $C_{2}$ | $c_{1}$ | $c_{2}^{\prime}$ | $\begin{gathered} E_{T} \\ (\mathrm{eV}) \end{gathered}$ | $\begin{aligned} & \theta_{v} \\ & \left({ }^{\circ}\right) \end{aligned}$ | $\begin{gathered} \theta_{1} \\ \left({ }^{\circ}\right) \end{gathered}$ | $\begin{aligned} & \theta_{2} \\ & \left({ }^{\circ}\right) \end{aligned}$ | $\begin{gathered} \text { Cal. } \theta \\ \left({ }^{\circ}\right) \end{gathered}$ | Exp. $\theta$ $\left(^{\circ}\right)$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\angle \mathrm{ClSnCl}$ | 4.33286 | 4.33286 | 6.9892 | $\begin{gathered} -12.96764 \\ C l \\ \hline \end{gathered}$ | Cl | $\begin{array}{\|c\|} \hline-12.96764 \\ C l \\ \hline \end{array}$ | Cl | 0.71514 | 0.71514 | 0.75 | 0.71514 | 1 | 0.71514 | -0.87386 |  |  |  | 107.52 | $\begin{gathered} 109.5 \\ \text { (tin tetrachloride) } \end{gathered}$ |
| $\angle H S n H$ | 3.26599 | 3.26599 | 5.3417 | $\begin{gathered} -9.32137 \\ S n \\ \hline \end{gathered}$ | (Eq. 23.221) | H | H | 0.68510 | 1 | 0.75 | 1 | 1 | 0.68510 | $\begin{gathered} -1.65813 \\ (\text { Eq. } 23.236) \end{gathered}$ |  |  |  | 109.72 | $\begin{gathered} 109.5 \\ \text { (stannane) } \end{gathered}$ |
| $\angle C S n C$ | 4.10053 | 4.10053 | 6.7082 | -14.82575 | 1 | -14.82575 | 1 | 0.91771 | 0.91771 | 1 | 1 | 1 | 0.91771 | 0 |  |  |  | 109.76 | $\begin{gathered} 109.5 \\ \text { (tetramethyltin) } \\ \hline \end{gathered}$ |
| $\begin{aligned} & \text { Methyl } \\ & \angle H C_{a} H \end{aligned}$ | 2.09711 | 2.09711 | 3.4252 | -15.75493 | 7 | H | H | 0.86359 | 1 | 1 | 1 | 0.75 | 1.15796 | 0 |  |  |  | 109.50 |  |
| $\angle H C_{a} \mathrm{Sn}$ |  |  |  |  |  |  |  |  |  |  |  |  |  |  | 70.56 |  |  | 109.44 |  |
| $\angle C_{a} C_{b} C_{c}$ |  |  |  |  |  |  |  |  |  |  |  |  |  |  | 70.56 |  |  | 109.44 |  |
| Methylene $\angle H C_{a} H$ | 2.11106 | 2.11106 | 3.4252 | -15.75493 | 7 | H | H | 0.86359 | 1 | 1 | 1 | 0.75 | 1.15796 | 0 |  |  |  | 108.44 | $\begin{gathered} 107 \\ \text { (propane) } \end{gathered}$ |
| $\angle C_{a} C_{b} C_{c}$ |  |  |  |  |  |  |  |  |  |  |  |  |  |  | 69.51 |  |  | 110.49 | 112 (propane) 113.8 (butane) 110.8 (isobutane) |
| $\angle C_{a} C_{b} H$ |  |  |  |  |  |  |  |  |  |  |  |  |  |  | 69.51 |  |  | 110.49 | 111.0 (butane) 111.4 (isobutane) |
| $\begin{aligned} & \text { Methyl } \\ & \angle H C_{a} H \end{aligned}$ | 2.09711 | 2.09711 | 3.4252 | -15.75493 | 7 | H | H | 0.86359 | 1 | 1 | 1 | 0.75 | 1.15796 | 0 |  |  |  | 109.50 |  |
| $\angle C_{a} C_{b} C_{c}$ |  |  |  |  |  |  |  |  |  |  |  |  |  |  | 70.56 |  |  | 109.44 |  |
| $\angle C_{a} C_{b} H$ |  |  |  |  |  |  |  |  |  |  |  |  |  |  | 70.56 |  |  | 109.44 |  |
| $\begin{gathered} \angle C_{b} C_{a} C_{c} \\ \text { iso } C_{a} \end{gathered}$ | 2.91547 | 2.91547 | 4.7958 | $\begin{gathered} -16.68412 \\ C_{b} \end{gathered}$ | 26 | $\begin{array}{\|c\|} \hline-16.68412 \\ C_{c} \end{array}$ | 26 | 0.81549 | 0.81549 | 1 | 1 | 1 | 0.81549 | -1.85836 |  |  |  | 110.67 | $\begin{gathered} 110.8 \\ \text { (isobutane) } \end{gathered}$ |
| $\begin{gathered} \angle C_{b} C_{a} H \\ \text { iso } C_{a} \end{gathered}$ | 2.91547 | 2.11323 | 4.1633 | $\begin{gathered} -15.55033 \\ C_{a} \end{gathered}$ | 5 | $\begin{array}{\|c\|} \hline-14.82575 \\ C_{b} \end{array}$ | 1 | 0.87495 | 0.91771 | 0.75 | 1 | 0.75 | 1.04887 | 0 |  |  |  | 110.76 |  |
| $\begin{gathered} \angle C_{a} C_{b} H \\ \text { iso } C_{a} \end{gathered}$ | 2.91547 | 2.09711 | 4.1633 | $\begin{gathered} -15.55033 \\ C_{b} \end{gathered}$ | 5 | $\begin{array}{\|c\|} \hline-14.82575 \\ C_{a} \end{array}$ | 1 | 0.87495 | 0.91771 | 0.75 | 1 | 0.75 | 1.04887 | 0 |  |  |  | 111.27 | $\begin{gathered} 111.4 \\ \text { (isobutane) } \end{gathered}$ |
| $\begin{gathered} \angle C_{b} C_{a} C_{b} \\ \operatorname{tert} C_{a} \end{gathered}$ | 2.90327 | 2.90327 | 4.7958 | $\begin{gathered} -16.68412 \\ C_{b} \end{gathered}$ | 26 | $\begin{gathered} -16.68412 \\ C_{b} \end{gathered}$ | 26 | 0.81549 | 0.81549 | 1 | 1 | 1 | 0.81549 | -1.85836 |  |  |  | 111.37 | $\begin{gathered} 110.8 \\ \text { (isobutane) } \end{gathered}$ |
| $\angle C_{b} C_{a} C_{d}$ |  |  |  |  |  |  |  |  |  |  |  |  |  |  | 72.50 |  |  | 107.50 |  |
| $\begin{gathered} \angle H C_{a} C_{c} \\ \left(C_{c}(H) C_{a}=C_{b}\right) \end{gathered}$ | 2.11323 | 2.86175 | 4.2895 | $\begin{gathered} -15.95954 \\ C_{a} \end{gathered}$ | 10 | $\begin{array}{\|c\|} \hline-14.82575 \\ C_{c} \end{array}$ | 1 | 0.85252 | 0.91771 | 0.75 | 1 | 0.75 | 1.07647 | 0 |  |  |  | 118.36 |  |
| $\begin{gathered} \angle C_{c} C_{a} C_{c} \\ \left(C_{c}\left(C_{c}\right) C_{a}=C_{b}\right) \end{gathered}$ | 2.86175 | 2.86175 | 4.7958 | $\begin{gathered} -16.68411 \\ C_{c} \\ \hline \end{gathered}$ | 25 | $\begin{array}{\|c\|} \hline-16.68411 \\ C_{c} \end{array}$ | 25 | 0.81549 | 0.81549 | 1 | 1 | 1 | 0.81549 | -1.85836 |  |  |  | 113.84 |  |
| $\begin{gathered} \angle C_{b} C_{a} C_{c} \\ \left(C_{b}=C_{a} C_{c}\right) \end{gathered}$ | 2.53321 | 2.86175 | 4.7539 | $\begin{gathered} -16.88873 \\ C_{b} \end{gathered}$ | 30 | $\begin{gathered} -16.68411 \\ C_{c} \end{gathered}$ | 25 | 0.80561 | 0.81549 | 1 | 1 | 1 | 0.81055 | -1.85836 |  |  |  | 123.46 | 124.4 (1,3,5-hexatriene CbCcCc) 121.7 $(1,3,5$-hexatriene CaCbCc) 124.4 (1,3-butadiene CCC) 125.3 (2-butene CbCaCc) |

Table 23.72 cont' d. The bond angle parameters of tin compounds and experimental values [3]. In the calculation of $\theta_{v}$, the parameters from the preceding angle

| Atoms of Angle | $\begin{gathered} 2 c^{\prime} \\ \text { Bond } 1 \\ \left(a_{0}\right) \end{gathered}$ | $\begin{gathered} 2 c^{\prime} \\ \text { Bond } 2 \\ \left(a_{0}\right) \end{gathered}$ | $\begin{gathered} 2 c^{\prime} \\ \text { Terminal } \\ \text { Atoms } \\ \left(a_{0}\right) \end{gathered}$ | $\begin{aligned} & E_{\text {Conlemblic } C} \\ & \text { Atom 1 } \end{aligned}$ | Atom 1 <br> Hybridization <br> Designation(Table 15.3A) | $\begin{aligned} & E_{\text {Colombic }} \\ & \text { Atom } 2 \end{aligned}$ | Atom 2 $\begin{gathered}\text { Hybridization } \\ \text { Designation } \\ \text { (Table 15.3A) }\end{gathered}$ | $\begin{gathered} c_{2} \\ \text { Atom } 1 \end{gathered}$ | $\begin{gathered} c_{2} \\ \text { Atom } 2 \end{gathered}$ | $C_{1}$ | $C_{2}$ | $c_{1}$ | $c_{2}^{\prime}$ | $\begin{gathered} E_{T} \\ (\mathrm{eV}) \end{gathered}$ | $\begin{aligned} & \theta_{v} \\ & \left({ }^{\circ}\right) \end{aligned}$ | $\begin{aligned} & \theta_{1} \\ & \left({ }^{\circ}\right) \end{aligned}$ | $\begin{aligned} & \theta_{2} \\ & \left({ }^{\circ}\right) \end{aligned}$ | $\begin{array}{\|c} \hline \text { Cal. } \theta \\ \left({ }^{\circ}\right) \end{array}$ | $\begin{gathered} \text { Exp. } \theta \\ \left({ }^{\circ}\right) \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\angle H C_{a} C_{b}$ |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  | 118.36 | 123.46 | 118.19 |  |
| $\begin{gathered} \angle H C_{a} H \\ \left(H_{2} C_{a}=C_{b} C_{c}\right) \end{gathered}$ | 2.04578 | 2.04578 | 3.4756 | -15.99955 | 10 | H | H | 0.85252 | 1 | 1 | 1 | 0.75 | 1.17300 | 0 |  |  |  | 116.31 | $\begin{gathered} 118.5 \\ \text { (2-methylpropene) } \end{gathered}$ |
| $\begin{gathered} \angle C_{b} C_{a} H \\ \left(H_{2} C_{a}=C_{b} C_{c}\right) \end{gathered}$ |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  | 116.31 |  | 121.85 | $\begin{gathered} 121 \\ \text { (2-methylpropene) } \end{gathered}$ |
| $\underset{\text { (aromatic) }}{\angle C C C}$ | 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 [34-36] |
| $\begin{gathered} \angle C C H \\ \text { (aromatic) } \end{gathered}$ |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  | 120.19 |  | 119.91 | 120 [34-36] (benzene) |
| $\angle C_{a} O_{b} H$ | 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 |  |
| $\angle C_{b} C_{a} O_{a}$ | 2.82796 | 2.27954 | 4.4721 | -17.17218 | 38 | -13.61806 | 0 | 0.79232 | $\begin{gathered} 0.85395 \\ \text { (Eq. (15.133)) } \end{gathered}$ | 1 | 1 | 1 | 0.82313 | -1.65376 |  |  |  | 121.86 | $\begin{aligned} & 122[55] \\ & \text { (benzoic acid) } \end{aligned}$ |
| $\angle C_{b} C_{a} O_{n}$ | 2.82796 | 2.63431 | 4.6690 | -16.40067 | 20 | -13.61806 | o | 0.82959 | $\begin{gathered} 0.85395 \\ \text { (Eq. (15.133)) } \end{gathered}$ | 1 | 1 | 1 | 0.84177 | -1.65376 |  |  |  | 117.43 | 118 [55] (benzoic acid) |
| $\angle O_{a} C_{a} O_{b}$ | 2.27954 | 2.63431 | 4.3818 | $\begin{gathered} -16.17521 \\ O_{\mathrm{a}} \\ \hline \end{gathered}$ | 13 | $\begin{gathered} -15.75493 \\ O_{b} \end{gathered}$ | 7 | 0.84115 | 0.86359 | 1 | 1 | 1 | 0.85237 | -1.44915 |  |  |  | 126.03 | $\begin{gathered} 122[55] \\ \text { (benzoic acid) } \end{gathered}$ |

## LEAD ORGANOMETALLIC FUNCTIONAL GROUPS AND MOLECULES

The branched-chain alkyl lead molecules, $P b C_{n} H_{2 n-2}$, comprise at least one $P b$ bound by a carbon-lead single bond comprising a $\mathrm{C}-\mathrm{Pb}$ group, at least a terminal methyl group $\left(\mathrm{CH}_{3}\right)$, and may comprise methylene $\left(\mathrm{CH}_{2}\right)$, methylyne ( CH ), and $\mathrm{C}-\mathrm{C}$ functional groups. 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 $\left(\left(\mathrm{CH}_{3}\right)_{2} \mathrm{CH}\right)$ and t-butyl $\left(\left(\mathrm{CH}_{3}\right)_{3} \mathrm{C}\right)$ groups and the isopropyl to isopropyl, isopropyl to t-butyl, and tbutyl to t-butyl $\mathrm{C}-\mathrm{C}$ bonds comprise functional groups.

As in the cases of carbon, silicon, tin, and germanium, the bonding in the lead atom involves four $s p^{3}$ hybridized orbitals. For lead, they are formed from the $6 p$ and $6 s$ electrons of the outer shells. $P b-C$ bonds form between a $P b 6 s p^{3}$ HO and a $C 3 s p^{3} \mathrm{HO}$ to yield alkyl leads. The geometrical parameters of the $\mathrm{Pb}-C$ functional group are solved using Eq. (15.51) and the relationships between the prolate spheroidal axes. Then, the sum of the energies of the $H_{2}$-type ellipsoidal MOs is matched to that of the $P b 6 s p^{3}$ shell as in the case of the corresponding carbon, silicon, tin, germanium molecules. As in the case of the transition metals, the energy of each functional group is determined for the effect of the electron density donation from each participating $C 3 s p^{3} \mathrm{HO}$ and $P b 6 s p^{3} \mathrm{HO}$ to the corresponding MO that maximizes the bond energy.

The $P b$ electron configuration is $[X e] 6 s^{2} 4 f^{14} 5 d^{10} 6 p^{2}$, and the orbital arrangement is:

\[

\]

corresponding to the ground state ${ }^{3} P_{0}$. The energy of the lead $6 p$ shell is the negative of the ionization energy of the lead atom [1] given by:

$$
\begin{equation*}
E(P b, 6 p \text { shell })=-E(\text { ionization } ; P b)=-7.41663 \mathrm{eV} \tag{23.245}
\end{equation*}
$$

The energy of lead is less than the Coulombic energy between the electron and proton of $H$ given by Eq. (1.264), but the atomic orbital may hybridize in order to achieve a bond at an energy minimum. After Eq. (13.422), the Pb6s atomic orbital (AO) combines with the $P b 6 p$ AOs to form a single $P b 6 s p^{3}$ hybridized orbital (HO) with the orbital arrangement

\[

\]

where the quantum numbers $\left(\ell, m_{\ell}\right)$ are below each electron. The total energy of the state is given by the sum over the four electrons. The sum $E_{T}\left(\mathrm{~Pb}, 6 s p^{3}\right)$ of experimental energies [1] of $\mathrm{Pb}, \mathrm{Pb}^{+}, \mathrm{Pb}^{2+}$, and $\mathrm{Pb}^{3+}$ is:

$$
\begin{equation*}
E_{T}\left(P b, 6 s p^{3}\right)=42.32 \mathrm{eV}+31.9373 \mathrm{eV}+15.03248 \mathrm{eV}+7.41663 \mathrm{eV}=96.70641 \mathrm{eV} \tag{23.247}
\end{equation*}
$$

By considering that the central field decreases by an integer for each successive electron of the shell, the radius $r_{6 s p^{3}}$ of the $P b 6 s p^{3}$ shell may be calculated from the Coulombic energy using Eq. (15.13).

$$
\begin{equation*}
r_{6 s p^{3}}=\sum_{n=78}^{81} \frac{(Z-n) e^{2}}{8 \pi \varepsilon_{0}(e 96.70641 \mathrm{eV})}=\frac{10 e^{2}}{8 \pi \varepsilon_{0}(e 96.70641 \mathrm{eV})}=1.40692 a_{0} \tag{23.248}
\end{equation*}
$$

where $Z=82$ for lead. Using Eq. (15.14), the Coulombic energy $E_{\text {Coulomb }}\left(P b, 6 s p^{3}\right)$ of the outer electron of the $P b 6 s p^{3}$ shell is

$$
\begin{equation*}
E_{\text {Coulomb }}\left(P b, 6 s p^{3}\right)=\frac{-e^{2}}{8 \pi \varepsilon_{0} r_{6 s p^{3}}}=\frac{-e^{2}}{8 \pi \varepsilon_{0} 1.40692 a_{0}}=-9.67064 \mathrm{eV} \tag{23.249}
\end{equation*}
$$

During hybridization, the spin-paired $6 s$ electrons are promoted to the $P b 6 s p^{3}$ shell as unpaired electrons. The energy for the promotion is the magnetic energy given by Eq. (15.15) at the initial radius of the $6 s$ electrons. From Eq. (10.102) with $Z=82$ and $n=80$, the radius $r_{80}$ of the $P b 6 s$ shell is:

$$
\begin{equation*}
r_{80}=1.27805 a_{0} \tag{23.250}
\end{equation*}
$$

Using Eqs. (15.15) and (23.250), the unpairing energy is:

$$
\begin{equation*}
E(\text { magnetic })=\frac{2 \pi \mu_{0} e^{2} \hbar^{2}}{m_{e}^{2}\left(r_{80}\right)^{3}}=\frac{8 \pi \mu_{o} \mu_{B}^{2}}{\left(1.27805 a_{0}\right)^{3}}=0.05481 \mathrm{eV} \tag{23.251}
\end{equation*}
$$

Using Eqs. (23.249) and (23.251), the energy $E\left(P b, 6 s p^{3}\right)$ of the outer electron of the $P b 6 s p^{3}$ shell is:

$$
\begin{equation*}
E\left(P b, 6 s p^{3}\right)=\frac{-e^{2}}{8 \pi \varepsilon_{0} r_{6 s p^{3}}}+\frac{2 \pi \mu_{0} e^{2} \hbar^{2}}{m_{e}^{2}\left(r_{80}\right)^{3}}=-9.67064 \mathrm{eV}+0.05481 \mathrm{eV}=-9.61584 \mathrm{eV} \tag{23.252}
\end{equation*}
$$

Next, consider the formation of the $\mathrm{Pb}-L$-bond MO of lead compounds wherein $L$ is a ligand including carbon and each lead atom has a $P b 6 s p^{3}$ electron with an energy given by Eq. (23.252). The total energy of the state of each lead atom is given by the sum over the four electrons. The sum $E_{T}\left(P b_{P b-L}, 6 s p^{3}\right)$ of energies of $P b 6 s p^{3}$ (Eq. (23.252)), $P b^{+}, P b^{2+}$, and $P b^{3+}$ is:

$$
\begin{align*}
E_{T}\left(P b_{P b-L}, 6 s p^{3}\right) & =-\left(42.32 \mathrm{eV}+31.9373 \mathrm{eV}+15.03248 \mathrm{eV}+E\left(P b, 6 s p^{3}\right)\right)  \tag{23.253}\\
& =-(42.32 \mathrm{eV}+31.9373 \mathrm{eV}+15.03248 \mathrm{eV}+9.61584 \mathrm{eV})=-98.90562 \mathrm{eV}
\end{align*}
$$

where $E\left(P b, 6 s p^{3}\right)$ is the sum of the energy of $P b,-7.41663 \mathrm{eV}$, and the hybridization energy.
A minimum energy is achieved while matching the potential, kinetic, and orbital energy relationships given in the Hydroxyl Radical ( $O H$ ) section with the donation of electron density from the participating $P b 6 s p^{3} \mathrm{HO}$ to each $\mathrm{Pb}-L$-bond MO. Consider the case wherein each $P b 6 s p^{3} \mathrm{HO}$ donates an excess of $25 \%$ of its electron density to the $P b-L$-bond MO to form an energy minimum. By considering this electron redistribution in the lead molecule as well as the fact that the central field decreases by an integer for each successive electron of the shell, in general terms, the radius $r_{P b-L 6 s p^{3}}$ of the $P b 6 s p^{3}$ shell may be calculated from the Coulombic energy using Eq. (15.18).

$$
\begin{equation*}
r_{P b-L 6 s p^{3}}=\left(\sum_{n=78}^{81}(Z-n)-0.25\right) \frac{e^{2}}{8 \pi \varepsilon_{0}(e 98.90562 \mathrm{eV})}=\frac{9.75 e^{2}}{8 \pi \varepsilon_{0}(e 98.90562 \mathrm{eV})}=1.34124 a_{0} \tag{23.254}
\end{equation*}
$$

Using Eqs. (15.19) and (23.254), the Coulombic energy $E_{\text {Coulomb }}\left(P b_{P b-L}, 6 s p^{3}\right)$ of the outer electron of the $P b 6 s p^{3}$ shell is:

$$
\begin{equation*}
E_{\text {Coulomb }}\left(P b_{P b-L}, 6 s p^{3}\right)=\frac{-e^{2}}{8 \pi \varepsilon_{0} r_{P b-L 6 s p^{3}}}=\frac{-e^{2}}{8 \pi \varepsilon_{0} 1.34124 a_{0}}=-10.14417 \mathrm{eV} \tag{23.255}
\end{equation*}
$$

During hybridization, the spin-paired $6 s$ electrons are promoted to the $P b 6 s p^{3}$ shell as unpaired electrons. The energy for the promotion is the magnetic energy given by Eq. (23.251). Using Eqs. (23.251) and (23.255), the energy $E\left(P b_{P b-L}, 6 s p^{3}\right)$ of the outer electron of the $P b 6 s p^{3}$ shell is:

$$
\begin{equation*}
E\left(P b_{P b-L}, 6 s p^{3}\right)=\frac{-e^{2}}{8 \pi \varepsilon_{0} r_{P b-L 6 s p^{3}}}+\frac{2 \pi \mu_{0} e^{2} \hbar^{2}}{m_{e}^{2}\left(r_{80}\right)^{3}}=-10.14417 \mathrm{eV}+0.05481 \mathrm{eV}=-10.08936 \mathrm{eV} \tag{23.256}
\end{equation*}
$$

Thus, $E_{T}\left(P b-L, 6 s p^{3}\right)$, the energy change of each $P b 6 s p^{3}$ shell with the formation of the $P b-L$-bond MO is given by the difference between Eq. (23.256) and Eq. (23.252).

$$
\begin{equation*}
E_{T}\left(P b-L, 6 s p^{3}\right)=E\left(P b_{P b-L}, 6 s p^{3}\right)-E\left(P b, 6 s p^{3}\right)=-10.08936 \mathrm{eV}-(-9.61584 \mathrm{eV})=-0.47352 \mathrm{eV} \tag{23.257}
\end{equation*}
$$

Next, consider the formation of the $\mathrm{Pb}-C$-bond MO by bonding with a carbon having a $C 2 s p^{3}$ 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 $E_{T}\left(C_{\text {ethane }}, 2 s p^{3}\right)$ of calculated energies of $C 2 s p^{3}, C^{+}, C^{2+}$, and $C^{3+}$ from Eqs. (10.123), (10.113-10.114), (10.68), and (10.48), respectively, is:

$$
\begin{align*}
E_{T}\left(C_{\text {ethane }}, 2 s p^{3}\right) & =-\left(64.3921 \mathrm{eV}+48.3125 \mathrm{eV}+24.2762 \mathrm{eV}+E\left(C, 2 s p^{3}\right)\right)  \tag{23.258}\\
& =-(64.3921 \mathrm{eV}+48.3125 \mathrm{eV}+24.2762 \mathrm{eV}+14.63489 \mathrm{eV})=-151.61569 \mathrm{eV}
\end{align*}
$$

where $E\left(C, 2 s p^{3}\right)$ is the sum of the energy of $C,-11.27671 \mathrm{eV}$, and the hybridization energy.
The sharing of electrons between the $P b 6 s p^{3} \mathrm{HO}$ and $C 2 s p^{3} \mathrm{HOs}$ to form a $\mathrm{Pb}-\mathrm{C}$-bond MO permits each participating hybridized orbital to decrease in radius and energy. A minimum energy is achieved while satisfying the potential, kinetic, and orbital energy relationships, when the $P b 6 s p^{3} \mathrm{HO}$ donates, and the $C 2 s p^{3} \mathrm{HO}$ receives, excess electron density equivalent to an electron within the $\mathrm{Pb}-\mathrm{C}$-bond MO. By considering this electron redistribution in the alkyl lead molecule as well as the fact that the central field decreases by an integer for each successive electron of the shell, the radius $r_{P b-C 2 s p^{3}}$ of the $C 2 s p^{3}$ shell of the $\mathrm{Pb}-\mathrm{C}$-bond MO may be calculated from the Coulombic energy using Eqs. (15.18) and (23.258).

$$
\begin{equation*}
r_{P b-C 2 s p^{3}}=\left(\sum_{n=2}^{5}(Z-n)+1\right) \frac{e^{2}}{8 \pi \varepsilon_{0}(e 151.61569 \mathrm{eV})}=\frac{11 e^{2}}{8 \pi \varepsilon_{0}(e 151.61569 \mathrm{eV})}=0.98713 a_{0} \tag{23.259}
\end{equation*}
$$

Using Eqs. (15.19) and (23.259), the Coulombic energy $E_{\text {Coulomb }}\left(C_{P b-C}, 2 s p^{3}\right)$ of the outer electron of the $C 2 s p^{3}$ shell is

$$
\begin{equation*}
E_{\text {Coulomb }}\left(C_{P b-C}, 2 s p^{3}\right)=\frac{-e^{2}}{8 \pi \varepsilon_{0} r_{P b-C 2 s p^{3}}}=\frac{-e^{2}}{8 \pi \varepsilon_{0} 0.98713 a_{0}}=-13.78324 \mathrm{eV} \tag{23.260}
\end{equation*}
$$

During hybridization, the spin-paired $2 s$ electrons are promoted to the $C 2 s p^{3}$ shell as unpaired electrons. The energy for the promotion is the magnetic energy given by Eq. (14.145). Using Eqs. (14.145) and (23.260), the energy $E\left(C_{P b-C}, 2 s p^{3}\right)$ of the outer electron of the $C 2 s p^{3}$ shell is:

$$
\begin{equation*}
E\left(C_{P b-C}, 2 s p^{3}\right)=\frac{-e^{2}}{8 \pi \varepsilon_{0} r_{P b-C 2 s p^{3}}}+\frac{2 \pi \mu_{0} e^{2} \hbar^{2}}{m_{e}^{2}\left(r_{3}\right)^{3}}=-13.78324 \mathrm{eV}+0.19086 \mathrm{eV}=-13.59238 \mathrm{eV} \tag{23.261}
\end{equation*}
$$

Thus, $E_{T}\left(P b-C, 2 s p^{3}\right)$, the energy change of each $C 2 s p^{3}$ shell with the formation of the $P b-C$-bond MO is given by the difference between Eq. (23.261) and Eq. (14.146).

$$
\begin{equation*}
E_{T}\left(P b-C, 2 s p^{3}\right)=E\left(C_{P b-C}, 2 s p^{3}\right)-E\left(C, 2 s p^{3}\right)=-13.59238 \mathrm{eV}-(-14.63489 \mathrm{eV})=1.04251 \mathrm{eV} \tag{23.262}
\end{equation*}
$$

Now, consider the formation of the $P b-L$-bond MO of lead compounds wherein $L$ is a ligand including carbon. For the $P b-L$ functional groups, hybridization of the $6 p$ and $6 s$ AOs of $P b$ to form a single $P b 6 s p^{3}$ HO shell forms an energy minimum, and the sharing of electrons between the $P b 6 s p^{3} \mathrm{HO}$ and $L \mathrm{HO}$ to form a MO permits each participating orbital to decrease in radius and energy. The $C 2 s p^{3}$ HO has an energy of $E\left(C, 2 s p^{3}\right)=-14.63489 \mathrm{eV}$ (Eq. (15.25)) and the Pb6sp HO has an energy of $E\left(P b, 6 s p^{3}\right)=-9.61584 \mathrm{eV}$ (Eq. (23.252)). To meet the equipotential condition of the union of the $P b-L$ $H_{2}$-type-ellipsoidal-MO with these orbitals, the hybridization factors $c_{2}$ and $C_{2}$ of Eq. (15.61) for the $P b-L$-bond MO given by Eq. (15.77) are:

Since the energy of the MO is matched to that of the $\operatorname{Pb6sp^{3}} \mathrm{HO}, E(A O / H O)$ in Eq. (15.61) is $E\left(P b, 6 s p^{3} H O\right)$ given by Eq. (23.252). In order to match the energies of the carbon and lead HOs within the molecule, $E_{T}\left(\right.$ atom -atom, $\left.m s p^{3} . A O\right)$ of the $\mathrm{Pb}-L$-bond MO for the ligand carbon is one half $E_{T}\left(P b-C, 2 s p^{3}\right)$ (Eq. (23.262)).

The symbols of the functional groups of lead compounds are given in Table 23.73. The geometrical (Eqs. (15.1-15.5)), intercept (Eqs. (15.31-15.32) and (15.80-15.87)), and energy (Eqs. (15.61) and (23.28-23.33)) parameters of lead compounds are given in Tables 23.74, 23.75, and 23.76, respectively. The total energy of each lead compound given in Table 22.77 was calculated as the sum over the integer multiple of each $E_{D}$ (Group) of Table 23.76 corresponding to functional-group composition of the compound. The bond angle parameters of lead compounds determined using Eqs. (15.88-15.117) are given in Table 23.78. The charge-densities of exemplary lead compound, tetraethyl lead $\left(\mathrm{Pb}\left(\mathrm{CH}_{2} \mathrm{CH}_{3}\right)_{4}\right)$ 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 23.16.

Figure 23.16. Color scale, charge-density of $\mathrm{Pb}\left(\mathrm{CH}_{2} \mathrm{CH}_{3}\right)_{4}$ showing the orbitals of the Pb and C 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 atoms participating in each bond, and the hydrogen nuclei.


Table 23.73. The symbols of functional groups of lead compounds.

| Functional Group | Group Symbol |
| :--- | :--- |
| PbC group | $\mathrm{Pb}-\mathrm{C}$ |
| $\mathrm{CH}_{3}$ group | $\mathrm{C}-\mathrm{H}\left(\mathrm{CH}_{3}\right)$ |
| CH alkyl group | $\mathrm{C}-\mathrm{H}\left(\mathrm{CH}_{2}\right)$ |
| CH alkyl | $\mathrm{C}-\mathrm{H}$ |
| CC bond (n-C) | $\mathrm{C}-\mathrm{C}$ (a) |
| CC bond (iso- C$)$ | $\mathrm{C}-\mathrm{C}$ (b) |
| CC bond (tert- C$)$ | $\mathrm{C}-\mathrm{C}$ (c) |
| CC (iso to iso- $)$ | $\mathrm{C}-\mathrm{C}$ (d) |
| $\mathrm{CC}(t$ to $t-C)$ | $\mathrm{C}-\mathrm{C}$ (e) |
| $\mathrm{CC}(t$ to iso- $C)$ | $\mathrm{C}-\mathrm{C}$ (f) |

Table 23.74. The geometrical bond parameters of lead compounds and experimental values [3].

| Parameter | $\begin{gathered} \hline P b-C \\ \text { Group } \end{gathered}$ | $\mathrm{C}-\mathrm{H}\left(\mathrm{CH}_{3}\right)$ <br> Group | $\mathrm{C}-\mathrm{H}\left(\mathrm{CH}_{2}\right)$ <br> Group | $\begin{aligned} & \hline \mathrm{C}-\mathrm{H} \\ & \text { Group } \end{aligned}$ | $\begin{gathered} \hline C-C \text { (a) } \\ \text { Group } \end{gathered}$ | $\begin{gathered} \hline C-C \text { (b) } \\ \text { Group } \end{gathered}$ | $\begin{aligned} & \hline C-C \\ & \text { (c) } \\ & \text { Group } \end{aligned}$ | $C-C$ <br> (d) Group | $\begin{aligned} & \hline C-C \\ & \text { (e) } \\ & \text { Group } \end{aligned}$ | $\begin{gathered} C-C(\mathrm{f}) \\ \text { Group } \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $a\left(a_{0}\right)$ | 2.21873 | 1.64920 | 1.67122 | 1.67465 | 2.12499 | 2.12499 | 2.10725 | 2.12499 | 2.10725 | 2.10725 |
| $c^{\prime}\left(a_{0}\right)$ | 2.12189 | 1.04856 | 1.05553 | 1.05661 | 1.45744 | 1.45744 | 1.45164 | 1.45744 | 1.45164 | 1.45164 |
| Bond Length $2 c^{\prime}(A)$ | 2.24571 | 1.10974 | 1.11713 | 1.11827 | 1.54280 | 1.54280 | 1.53635 | 1.54280 | 1.53635 | 1.53635 |
| Exp. <br> Bond <br> Length <br> (A) | $\begin{gathered} 2.238 \\ \left(\left(\mathrm{CH}_{3}\right)_{4} \mathrm{~Pb}\right) \end{gathered}$ | $\begin{gathered} 1.107 \\ (C-H \\ \text { propane }) \\ 1.117 \\ (C-H \\ \text { butane }) \\ \hline \end{gathered}$ | $\begin{gathered} 1.107 \\ (C-H \\ \text { propane }) \\ 1.117 \\ (C-H \\ \text { butane }) \\ \hline \end{gathered}$ | $\begin{gathered} 1.122 \\ \text { (isobutane) } \end{gathered}$ | $\begin{gathered} 1.532 \\ \text { (propane) } \\ 1.531 \\ \text { (butane) } \end{gathered}$ | $\begin{gathered} 1.532 \\ \text { (propane) } \\ 1.531 \\ \text { (butane) } \end{gathered}$ | $\begin{gathered} 1.532 \\ \text { (propane) } \\ 1.531 \\ \text { (butane) } \end{gathered}$ | $\begin{gathered} 1.532 \\ \text { (propane) } \\ 1.531 \\ \text { (butane) } \end{gathered}$ | $\begin{gathered} 1.532 \\ \text { (propane) } \\ 1.531 \\ \text { (butane) } \end{gathered}$ | $\begin{gathered} 1.532 \\ \text { (propane) } \\ 1.531 \\ \text { (butane) } \end{gathered}$ |
| $b, c\left(a_{0}\right)$ | 0.64834 | 1.27295 | 1.29569 | 1.29924 | 1.54616 | 1.54616 | 1.52750 | 1.54616 | 1.52750 | 1.52750 |
| $e$ | 0.95635 | 0.63580 | 0.63159 | 0.63095 | 0.68600 | 0.68600 | 0.68888 | 0.68600 | 0.68888 | 0.68888 |

Table 23.75. The MO to HO intercept geometrical bond parameters of lead compounds. $R, R^{\prime}, R^{\prime \prime}$ are $H$ or alkyl groups. $E_{T}$ is $E_{T}$ (atom-atom,msp ${ }^{3}$. $A O$ ).

| Bond | Atom | $\begin{gathered} E_{T} \\ (\mathrm{eV}) \\ \text { Bond 1 } \end{gathered}$ | $\begin{gathered} E_{r} \\ (\mathrm{eV}) \\ \text { Bond } 2 \end{gathered}$ | $\begin{gathered} E_{T} \\ (\mathrm{eV}) \\ \text { Bond 3 } \end{gathered}$ | $\begin{gathered} E_{V} \\ (\text { (eV) } \\ \text { Bond } 4 \end{gathered}$ | Final Total Energy $P b 6 s p^{3}$ $C 2 s p^{3}$ $(\mathrm{eV})$ | $\begin{aligned} & r_{\text {mada }} \\ & \left(a_{0}\right) \end{aligned}$ | $\begin{aligned} & r_{\text {mal }} \\ & \left(a_{0}\right) \end{aligned}$ | $\begin{gathered} E_{\text {Conomomb }}\left(C 2 s p^{3}\right) \\ \text { (eV) } \\ \text { Final } \end{gathered}$ | $\begin{gathered} E\left(P b 6 s p^{3}\right) \\ E\left(C 2 s p^{3}\right) \\ (\text { eV) } \\ \text { Final } \end{gathered}$ | $\begin{aligned} & \theta^{\prime} \\ & \left({ }^{\prime}\right) \end{aligned}$ | $\begin{aligned} & \theta_{1} \\ & \left({ }^{\circ}\right) \end{aligned}$ | $\begin{aligned} & \theta_{2} \\ & \left({ }^{\circ}\right) \end{aligned}$ | $\begin{gathered} d_{1} \\ \left(a_{0}\right) \end{gathered}$ | $\begin{gathered} d_{2} \\ \left(a_{0}\right) \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{C-H}\left(\mathrm{CH}_{3}\right)$ | C | 0.26063 | 0 | 0 | 0 | -151.35506 | 0.91771 | 0.93414 | -14.56512 | -14.37426 | 85.33 | 94.67 | 47.00 | 1.12468 | 0.07613 |
| $\left(\mathrm{CH}_{3}\right)_{3} \mathrm{~Pb}-\mathrm{CH}_{3}$ | Pb | 0.26063 | 0.26063 | 0.26063 | 0.26063 |  | 1.40692 | 0.98713 | -13.78324 |  | 147.67 | 32.33 | 54.52 | 1.28781 | 0.83408 |
| $\left(\mathrm{CH}_{3}\right)_{3} \mathrm{~Pb}-\mathrm{CH}_{3}$ | C | 0.26063 | 0 | 0 | 0 |  | 0.91771 | 0.93414 | -14.56512 | -14.37426 | 146.47 | 33.53 | 52.74 | 1.34322 | 0.77867 |
| $\mathrm{C}-\mathrm{H}\left(\mathrm{CH}_{3}\right)$ | 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 |
| $\mathrm{C}-\mathrm{H}\left(\mathrm{CH}_{2}\right)(\mathrm{i})$ | 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 |
| $\mathrm{C}-\mathrm{H}(\mathrm{CH})(\mathrm{i})$ | 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 |
| $\begin{aligned} & \mathrm{H}_{3} \mathrm{C}_{a} \mathrm{C}_{\mathrm{L}} \mathrm{CH}_{2}- \\ & (\mathrm{C}-\mathrm{C}(\mathrm{a})) \end{aligned}$ | $C_{a}$ | -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 |
| $\begin{aligned} & \mathrm{H}_{3} C_{a} C_{b} \mathrm{H}_{2} \mathrm{CH}_{2}- \\ & (\mathrm{C}-\mathrm{C}(\mathrm{a})) \end{aligned}$ | $C_{b}$ | -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 |
| $\begin{aligned} & R-H_{2} C_{a} C_{b}\left(H_{2} C_{c}-R^{\prime}\right) H C H_{2}- \\ & (C-C(b)) \end{aligned}$ | $C_{b}$ | -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 |
| $\begin{aligned} & R-H_{2} C_{a}\left(R^{\prime}-H_{2} C_{d}\right) C_{b}\left(R^{\prime \prime}-H_{2} C_{c}\right) C H_{2}- \\ & (C-C(c)) \end{aligned}$ | $C_{b}$ | -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 |
| $\begin{aligned} & \text { iso }_{a} C_{b}\left(H_{2} C_{c}-R^{\prime}\right) H C H_{2}- \\ & (C-C(d)) \end{aligned}$ | $C_{b}$ | -0.92918 | -0.92918 | -0.92918 | 0 | -154.40324 | 0.91771 | 0.77247 | -17.61330 | -17.4224 | 48.30 | 131.70 | 21.90 | 1.97162 | 0.51388 |
| $\begin{aligned} & {\operatorname{tert~} G_{a}( }^{\prime}\left(R^{\prime}-\mathrm{H}_{d}\right) \mathrm{C}_{b}\left(R^{n \prime}-\mathrm{H}_{2} C_{c}\right) C H_{2}- \\ & (C-C(\mathrm{e})) \end{aligned}$ | $C_{b}$ | -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 |
| $\begin{aligned} & \operatorname{tertC}_{a} C_{b}\left(H_{2} C_{c}-R^{\prime}\right) \mathrm{HCH}_{2}- \\ & (\mathrm{C}-\mathrm{C}(\mathrm{f})) \end{aligned}$ | $C_{b}$ | -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 |
| $\begin{aligned} & \text { isoCo }\left(R ' H_{2} C_{d}\right) C_{b}\left(R^{\prime \prime}-H_{2} C_{c}\right) \mathrm{CH}_{2}- \\ & (\mathrm{C}-\mathrm{C}(\mathrm{f}) \end{aligned}$ | $C_{b}$ | -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 23.77. The total bond energies of gaseous-state lead compounds calculated using the functional group composition (separate functional groups designated in the first row) and the energies of Table 23.76 compared to the gaseous-state experimental values [86].

Table 23.78. The bond angle parameters of lead compounds and experimental values [3]. In the calculation of $\theta_{v}$, the parameters from the preceding angle were

| $\begin{aligned} & \text { Atoms of } \\ & \text { Angle } \end{aligned}$ | $\begin{gathered} 2 c^{\prime} \\ \text { Bond 1 } \\ \left(a_{0}\right) \end{gathered}$ | $\begin{gathered} 2 c^{\prime} \\ \text { Bond } 2 \\ \left(a_{6}\right) \end{gathered}$ | $\begin{gathered} 2 c^{\prime} \\ \text { Terminal } \\ \text { Atoms } \\ \left(a_{0}\right) \end{gathered}$ | $\begin{aligned} & E_{\text {Comumbic }} \\ & \text { Atom } 1 \end{aligned}$ | Atom 1 $\begin{gathered}\text { Hybridization } \\ \text { Designation } \\ \text { (Table 15.3.A) }\end{gathered}$ | $\begin{aligned} & E_{\text {Contombic }} \\ & \text { Atom } 2 \end{aligned}$ | Atom 2 Hybridization Designation (Table 15.3.A) | $\begin{gathered} c_{2} \\ \text { Atom } 1 \end{gathered}$ | $\begin{gathered} c_{2} \\ \text { Atom } 2 \end{gathered}$ | $C_{1}$ | $C_{2}$ | $c_{1}$ | $c_{2}^{\prime}$ | $\begin{gathered} E_{r} \\ (\mathrm{eV}) \end{gathered}$ | $\begin{aligned} & \theta_{y} \\ & \left({ }^{\circ}\right) \end{aligned}$ | $\begin{aligned} & \theta_{1} \\ & \left({ }^{\circ}\right) \end{aligned}$ | $\begin{aligned} & \theta_{2} \\ & \left({ }^{\circ}\right) \end{aligned}$ | $\begin{gathered} \text { Cal. } \theta \\ \left({ }^{\circ}\right) \end{gathered}$ | $\begin{gathered} \text { Exp. } \theta \\ \left({ }^{\circ}\right) \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\begin{aligned} & \text { Methyl } \\ & \angle H C_{a} H \end{aligned}$ | 2.09711 | 2.09711 | 3.4252 | -15.75493 | 7 | H | H | 0.86359 | 1 | 1 | 1 | 0.75 | 1.15796 | 0 |  |  |  | 109.50 |  |
| $\angle H_{a} C_{a} P b$ |  |  |  |  |  |  |  |  |  |  |  |  |  |  | 70.56 |  |  | 109.44 |  |
| $\angle C_{a} P C_{b}$ | 4.24378 | 4.24378 | 6.9282 | -14.82575 | 1 | -14.82575 | 1 | 0.91771 | 0.91771 | 1 | 1 | 1 | 0.91771 | -1.85836 |  |  |  | 109.43 | $\begin{gathered} 109.5 \\ \text { (tetramethyllead) } \end{gathered}$ |
| Methylene $\angle H C_{a} H$ | 2.11106 | 2.11106 | 3.4252 | -15.75493 | 7 | H | H | 0.86359 | 1 | 1 | 1 | 0.75 | 1.15796 | 0 |  |  |  | 108.44 | $\begin{gathered} 107 \\ \text { (propane) } \\ \hline \end{gathered}$ |
| $\angle C_{a} C_{b} C_{c}$ |  |  |  |  |  |  |  |  |  |  |  |  |  |  | 69.51 |  |  | 110.49 | $\begin{gathered} 112 \\ \text { (propane) } \\ 13.8 \\ \text { (butane) } \\ \text { (isobutane) } \\ \text { (is.8. } \end{gathered}$ |
| $\angle C_{a} C_{b} H$ |  |  |  |  |  |  |  |  |  |  |  |  |  |  | 69.51 |  |  | 110.49 | $\begin{gathered} 111.0 \\ \text { (butane) } \\ 111.4 \\ \text { (isobutane) } \end{gathered}$ |
| $\begin{aligned} & \text { Methyl } \\ & \angle H C_{a} H \end{aligned}$ | 2.09711 | 2.09711 | 3.4252 | -15.75493 | 7 | H | H | 0.86359 | 1 | 1 | 1 | 0.75 | 1.15796 | 0 |  |  |  | 109.50 |  |
| $\angle C_{a} C_{b} C_{c}$ |  |  |  |  |  |  |  |  |  |  |  |  |  |  | 70.56 |  |  | 109.44 |  |
| $\angle C_{a} C_{b} H$ |  |  |  |  |  |  |  |  |  |  |  |  |  |  | 70.56 |  |  | 109.44 |  |
| $\begin{aligned} & \angle C_{b} C_{a} C_{c} \\ & \text { iso } C_{a} \end{aligned}$ | 2.91547 | 2.91547 | 4.7958 | $\begin{gathered} -16.68412 \\ C_{b} \end{gathered}$ | 26 | $\begin{gathered} -16.68412 \\ C_{c} \end{gathered}$ | 26 | 0.81549 | 0.81549 | 1 | 1 | 1 | 0.81549 | -1.85836 |  |  |  | 110.67 | $\begin{gathered} 110.8 \\ \text { (isobutane) } \end{gathered}$ |
| $\begin{aligned} & \angle C_{b} C_{a} H \\ & \text { iso } C_{a} \end{aligned}$ | 2.91547 | 2.11323 | 4.1633 | $\begin{gathered} -15.55033 \\ C_{o} \\ \hline \end{gathered}$ | 5 | $\begin{gathered} -14.82575 \\ C_{b} \end{gathered}$ | 1 | 0.87495 | 0.91771 | 0.75 | 1 | 0.75 | 1.04887 | 0 |  |  |  | 110.76 |  |
| $\begin{gathered} \angle C_{a} C_{b} H \\ \text { iso } C_{a} \\ \hline \end{gathered}$ | 2.91547 | 2.09711 | 4.1633 | $\begin{gathered} -15.55033 \\ C_{h} \end{gathered}$ | 5 | $\stackrel{-14.82575}{C_{a}}$ | 1 | 0.87495 | 0.91771 | 0.75 | 1 | 0.75 | 1.04887 | 0 |  |  |  | 111.27 | $\begin{gathered} 111.4 \\ \text { (isobutane) } \end{gathered}$ |
| $\begin{aligned} & \angle C_{b} C_{a} C_{b} \\ & \text { tert } C_{a} \end{aligned}$ | 2.90327 | 2.90327 | 4.7958 | $\begin{gathered} -16.68412 \\ C_{h} \end{gathered}$ | 26 | $\begin{gathered} -16.68412 \\ C_{b} \end{gathered}$ | 26 | 0.81549 | 0.81549 | 1 | 1 | 1 | 0.81549 | -1.85836 |  |  |  | 111.37 | $\begin{gathered} 110.8 \\ \text { (isobutane) } \end{gathered}$ |
| $\angle C_{b} C_{a} C_{d}$ |  |  |  |  |  |  |  |  |  |  |  |  |  |  | 72.50 |  |  | 107.50 |  |

## ALKYL ARSINES (( $\left.\left.C_{n} H_{2 n+1}\right)_{3} A s, \quad n=1,2,3,4,5 \ldots \infty\right)$

The alkyl arsines, $\left(C_{n} H_{2 n+1}\right)_{3} A s$, comprise a $A s-C$ functional group. The alkyl portion of the alkyl arsine may comprise at least two terminal methyl groups $\left(\mathrm{CH}_{3}\right)$ at each end of each chain, and may comprise methylene $\left(\mathrm{CH}_{2}\right)$, and methylyne $(\mathrm{CH})$ 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 $\mathrm{C}-\mathrm{C}$ bonds within isopropyl $\left(\left(\mathrm{CH}_{3}\right)_{2} \mathrm{CH}\right)$ and t-butyl $\left(\left(\mathrm{CH}_{3}\right)_{3} \mathrm{C}\right)$ 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 arsines are equivalent to those in branched-chain alkanes. The $A s-C$ group may further join the $A s 4 s p^{3} \mathrm{HO}$ to an aryl HO.

As in the case of phosphorous, the bonding in the arsenic atom involves $s p^{3}$ hybridized orbitals formed, in this case, from the $4 p$ and $4 s$ electrons of the outer shells. The $A s-C$ bond forms between $A s 4 s p^{3}$ and $C 2 s p^{3}$ HOs to yield arsines. The semimajor axis $a$ of the $A s-C$ 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 the Organic Molecular Functional Groups and Molecules section.

The energy of arsenic 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 ( $O H$ ) section with hybridization of the arsenic 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 $A s 4 s p^{3}$ shell as in the case of the corresponding phosphine molecules.

The $A s$ electron configuration is $[A r] 4 s^{2} 3 d^{10} 4 p^{3}$ corresponding to the ground state ${ }^{4} S_{3 / 2}$, and the $4 s p^{3}$ hybridized orbital arrangement after Eq. (13.422) is:

\[

\]

where the quantum numbers $\left(\ell, m_{\ell}\right)$ are below each electron. The total energy of the state is given by the sum over the five electrons. The sum $E_{T}\left(A s, 4 s p^{3}\right)$ of experimental energies [1] of $A s, A s^{+}, A s^{2+}, A s^{3+}$, and $A s^{4+}$ is:

$$
\begin{equation*}
E_{T}\left(A s, 4 s p^{3}\right)=62.63 \mathrm{eV}+50.13 \mathrm{eV}+28.351 \mathrm{eV}+18.5892 \mathrm{eV}+9.7886 \mathrm{eV}=169.48880 \mathrm{eV} \tag{23.265}
\end{equation*}
$$

By considering that the central field decreases by an integer for each successive electron of the shell, the radius $r_{4 s p^{3}}$ of the $A s 4 s p^{3}$ shell may be calculated from the Coulombic energy using Eq. (15.13).

$$
\begin{equation*}
r_{4 s p^{3}}=\sum_{n=28}^{32} \frac{(Z-n) e^{2}}{8 \pi \varepsilon_{0}(e 169.48880 \mathrm{eV})}=\frac{15 e^{2}}{8 \pi \varepsilon_{0}(e 169.48880 \mathrm{eV})}=1.20413 a_{0} \tag{23.266}
\end{equation*}
$$

where $Z=33$ for arsenic. Using Eq. (15.14), the Coulombic energy $E_{\text {Coulomb }}\left(A s, 4 s p^{3}\right)$ of the outer electron of the $A s 4 s p^{3}$ shell is:

$$
\begin{equation*}
E_{\text {Coulomb }}\left(A s, 4 s p^{3}\right)=\frac{-e^{2}}{8 \pi \varepsilon_{0} r_{4 s p^{3}}}=\frac{-e^{2}}{8 \pi \varepsilon_{0} 1.20413 a_{0}}=-11.29925 \mathrm{eV} \tag{23.267}
\end{equation*}
$$

During hybridization, the spin-paired $4 s$ electrons are promoted to the $A s 4 s p^{3}$ shell as paired electrons at the radius $r_{4 s p^{3}}$ of the $A s 4 s p^{3}$ shell. The energy for the promotion is the difference in the magnetic energy given by Eq. (15.15) at the initial radius of the $4 s$ electrons and the final radius of the $A s 4 s p^{3}$ electrons. From Eq. (10.102) with $Z=33$ and $n=30$, the radius $r_{30}$ of the As $4 s$ shell is:

$$
\begin{equation*}
r_{30}=1.08564 a_{0} \tag{23.268}
\end{equation*}
$$

Using Eqs. (15.15) and (23.268), the unpairing energy is:

$$
\begin{equation*}
E(\text { magnetic })=\frac{2 \pi \mu_{0} e^{2} \hbar^{2}}{m_{e}^{2}}\left(\frac{1}{\left(r_{30}\right)^{3}}-\frac{1}{\left(r_{4 s p^{3}}\right)^{3}}\right)=8 \pi \mu_{o} \mu_{B}^{2}\left(\frac{1}{\left(1.08564 a_{0}\right)^{3}}-\frac{1}{\left(1.20413 a_{0}\right)^{3}}\right)=0.02388 \mathrm{eV} \tag{23.269}
\end{equation*}
$$

Using Eqs. (23.267) and (23.269), the energy $E\left(A s, 4 s p^{3}\right)$ of the outer electron of the $A s 4 s p^{3}$ shell is:

$$
\begin{equation*}
E\left(A s, 4 s p^{3}\right)=\frac{-e^{2}}{8 \pi \varepsilon_{0} r_{4 s p^{3}}}+\frac{2 \pi \mu_{0} e^{2} \hbar^{2}}{m_{e}^{2}}\left(\frac{1}{\left(r_{30}\right)^{3}}-\frac{1}{\left(r_{4 s p^{3}}\right)^{3}}\right)=-11.29925 \mathrm{eV}+0.02388 \mathrm{eV}=-11.27537 \mathrm{eV} \tag{23.270}
\end{equation*}
$$

For the $A s-C$ functional group, hybridization of the $2 s$ and $2 p$ AOs of each $C$ and the $4 s$ and $4 p$ AOs of each $A s$ to form single $2 s p^{3}$ and $4 s p^{3}$ shells, respectively, forms an energy minimum, and the sharing of electrons between the $C 2 s p^{3}$ and $A s 4 s p^{3}$ HOs to form a MO permits each participating orbital to decrease in radius and energy. In branched-chain alkyl arsines, the energy of arsenic 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 $C 2 s p^{3} \mathrm{HO}$ has an energy of $E\left(C, 2 s p^{3}\right)=-14.63489 \mathrm{eV}$ (Eq. (15.25)), and the $A s 4 s p^{3} \mathrm{HO}$ has an energy of $E\left(A s, 4 s p^{3}\right)=-11.27537 \mathrm{eV}$ (Eq. (23.270)). To meet the equipotential condition of the union of the $A s-C H_{2}$-type-ellipsoidal-MO with these orbitals, the hybridization factor $C_{2}$ of Eq. (15.61) for the $A s-C$-bond MO given by Eqs. (15.77), (15.79), and (13.430) is:

$$
\begin{equation*}
C_{2}\left(C 2 s p^{3} \mathrm{HO} \text { to } \mathrm{As} 4 s p^{3} \mathrm{HO}\right)=\frac{E\left(A s, 4 s p^{3}\right)}{E\left(C, 2 s p^{3}\right)} c_{2}\left(C 2 s p^{3} \mathrm{HO}\right)=\frac{-11.27537 \mathrm{eV}}{-14.63489 \mathrm{eV}}(0.91771)=0.70705 \tag{23.271}
\end{equation*}
$$

The energy of the $A s-C$-bond MO is the sum of the component energies of the $H_{2}$-type ellipsoidal MO given in Eq. (15.51) with $E(A O / H O)=E\left(A s, 4 s p^{3}\right)$ given by Eq. (23.270), and $E_{T}\left(\right.$ atom -atom, $\left.m s p^{3} . A O\right)$ is zero in order to match the energies of the carbon and arsenic HOs.

The symbols of the functional groups of branched-chain alkyl arsines are given in Table 23.79. 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 arsines are given in Tables 23.80, 23.81, and 23.82, respectively. The total energy of each alkyl arsine given in Table 23.83 was calculated as the sum over the integer multiple of each $E_{D}$ (Group) of Table 23.82 corresponding to functional-group composition of the molecule. The bond angle parameters of alkyl arsines determined using Eqs. (15.88-15.117) are given in Table 23.84. The color scale, charge-density of exemplary alkyl arsine, triphenylarsine, comprising atoms with the outer shell bridged by one or more $\mathrm{H}_{2}$-type ellipsoidal MOs or joined with one or more hydrogen MOs is shown in Figure 23.17.

Figure 23.17. Color scale, charge-density of triphenylarsine showing the orbitals of the atoms at their radii, the ellipsoidal surface of each H or $\mathrm{H}_{2}$-type ellipsoidal MO that transitions to the corresponding outer shell of the atom(s) participating in each bond, and the hydrogen nuclei.


Table 23.79. The symbols of functional groups of alkyl arsines.

| Functional Group | Group Symbol |
| :---: | :---: |
| $A s-C$ | As-C |
| $\mathrm{CH}_{3}$ group | C-H(CH3) |
| $\mathrm{CH}_{2}$ group | $\mathrm{C}-\mathrm{H}\left(\mathrm{CH}_{2}\right)$ |
| CH | $\mathrm{C}-\mathrm{H}$ (i) |
| $C C$ bond ( $n-C$ ) | $C-C$ (a) |
| $C C$ bond (iso-C) | $C-C$ (b) |
| $C C$ bond (tert-C) | $C-C$ (c) |
| $C C$ (iso to iso-C) | $C-C$ (d) |
| $C C$ ( $t$ to $t-C$ ) | $C-C$ (e) |
| $C C$ ( $t$ to iso-C) | $C-C$ (f) |
| $C C$ (aromatic bond) | $C \stackrel{3 e}{=} C$ |
| CH (aromatic) | CH (ii) |

Table 23.80. The geometrical bond parameters of alkyl arsines and experimental values [3].

| Parameter | $\begin{aligned} & A s-C \\ & \text { Group } \end{aligned}$ | $\begin{gathered} \mathrm{C}-\mathrm{H}\left(\mathrm{CH}_{3}\right) \\ \text { Group } \end{gathered}$ | $\begin{gathered} \mathrm{C}-\mathrm{H}\left(\mathrm{CH}_{2}\right) \\ \text { Group } \end{gathered}$ | $\begin{gathered} C-H \text { (i) } \\ \text { Group } \end{gathered}$ | $\begin{gathered} C-C \text { (a) } \\ \text { Group } \end{gathered}$ | $\begin{gathered} C-C \text { (b) } \\ \text { Group } \end{gathered}$ | $\begin{gathered} C-C \text { (c) } \\ \text { Group } \end{gathered}$ | $\begin{gathered} C-C(d) \\ \text { Group } \end{gathered}$ | $\begin{gathered} C-C(e) \\ \text { Group } \end{gathered}$ | $\begin{gathered} C-C(f) \\ \text { Group } \end{gathered}$ | $C \stackrel{3 e}{=} C$ <br> Group | $\begin{gathered} C H \text { (ii) } \\ \text { Group } \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $a\left(a_{0}\right)$ | 2.33431 | 1.64920 | 1.67122 | 1.67465 | 2.12499 | 2.12499 | 2.10725 | 2.12499 | 2.10725 | 2.10725 | 1.47348 | 1.60061 |
| $c^{\prime}\left(a_{0}\right)$ | 1.81700 | 1.04856 | 1.05553 | 1.05661 | 1.45744 | 1.45744 | 1.45164 | 1.45744 | 1.45164 | 1.45164 | 1.31468 | 1.03299 |
| $\begin{aligned} & \hline \text { Bond Length } \\ & 2 c^{\prime}(A) \end{aligned}$ | 1.92303 | 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 <br> (A) | $\begin{gathered} 1.979 \\ \left(\left(\mathrm{CH}_{3}\right)_{2} \mathrm{AsCH}_{3}\right) \end{gathered}$ | $\begin{gathered} 1.107 \\ (C-H \text { propane }) \\ 1.117 \\ (C-H \text { butane }) \\ \hline \end{gathered}$ | $\begin{gathered} 1.107 \\ (C-H \text { propane }) \\ 1.117 \\ (C-H \text { butane }) \end{gathered}$ | $\begin{gathered} 1.122 \\ \text { (isobutane) } \end{gathered}$ | $\begin{gathered} 1.532 \\ \text { (propane) } \\ 1.531 \\ \text { (butane) } \\ \hline \end{gathered}$ | $\begin{gathered} 1.532 \\ \text { (propane) } \\ 1.531 \\ \text { (butane) } \\ \hline \end{gathered}$ | 1.532 (propane) 1.531 (butane) | $\begin{gathered} 1.532 \\ (\text { (propane) } \\ 1.531 \\ \text { (butane) } \end{gathered}$ | $\begin{gathered} 1.532 \\ \text { (propane) } \\ 1.531 \\ \text { (butane) } \end{gathered}$ |  | $\begin{gathered} 1.399 \\ \text { (benzene) } \end{gathered}$ | $\begin{gathered} 1.101 \\ \text { (benzene) } \end{gathered}$ |
| $b, c\left(a_{3}\right)$ | 1.46544 | 1.27295 | 1.29569 | 1.29924 | 1.54616 | 1.54616 | 1.52750 | 1.54616 | 1.52750 | 1.52750 | 0.66540 | 1.22265 |
| $e$ | 0.77839 | 0.63580 | 0.63159 | 0.63095 | 0.68600 | 0.68600 | 0.68888 | 0.68600 | 0.68888 | 0.68888 | 0.89223 | 0.64537 |


| Bond | Atom |  | $\begin{gathered} E_{T} \\ (\mathrm{eV}) \end{gathered}$ $\text { Bond } 2$ |  |  | Final Total <br> Energy <br> $C 2 s p^{3}$ <br> $(\mathrm{eV})$ | $\begin{aligned} & r_{\text {mpual }} \\ & \left(a_{0}\right) \end{aligned}$ | $\begin{aligned} & r_{\text {flnal }} \\ & \left(a_{0}\right) \end{aligned}$ | $\begin{gathered} E_{\text {Coutomb }} \text { (eV) } \\ \text { Final } \end{gathered}$ | $\begin{gathered} E\left(C 2 s p^{3}\right) \\ (\mathrm{eV}) \\ \text { Final } \end{gathered}$ | $\begin{aligned} & \theta^{\prime} \\ & \left({ }^{\circ}\right) \end{aligned}$ | $\begin{aligned} & \theta_{1} \\ & \left({ }^{\circ}\right) \end{aligned}$ | $\begin{aligned} & \theta_{2} \\ & \left({ }^{\circ}\right) \end{aligned}$ | $\begin{gathered} d_{1} \\ \left(a_{0}\right) \end{gathered}$ | $\begin{gathered} d_{2} \\ \left(a_{0}\right) \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{C}-\mathrm{H}\left(\mathrm{CH}_{3}\right)$ | C | 0 | 0 | 0 | 0 | -151.61569 | 0.91771 | 0.91771 | -14.82575 | -14.63489 | 83.62 | 96.38 | 45.76 | 1.15051 | 0.10195 |
| $\left(\mathrm{CH}_{3}\right)_{2} \mathrm{As}-\mathrm{CH}_{3}$ | C | 0 | 0 | 0 | 0 |  | 0.91771 | 0.91771 | -14.82575 | -14.63489 | 89.82 | 90.18 | 38.77 | 1.81991 | 0.00291 |
| $\left(\mathrm{CH}_{3}\right)_{2} \mathrm{As}-\mathrm{CH}_{3}$ | As | 0 | 0 | 0 | 0 |  | 0.91771 | 0.91771 | -14.82575 |  | 89.82 | 90.18 | 38.77 | 1.81991 | 0.00291 |
| $\mathrm{C}-\mathrm{H}\left(\mathrm{CH}_{3}\right)$ | 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 |
| $\mathrm{C}-\mathrm{H}\left(\mathrm{CH}_{2}\right)$ | 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 |
| $\mathrm{C}-\mathrm{H}(\mathrm{CH})$ | 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 |
| $\begin{aligned} & \mathrm{H}_{3} \mathrm{C}_{a} \mathrm{C}_{b} \mathrm{H}_{2} \mathrm{CH}_{2}- \\ & (\mathrm{C}-\mathrm{C}(\mathrm{a})) \end{aligned}$ | $C_{a}$ | -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 |
| $\begin{aligned} & \mathrm{H}_{3} \mathrm{C}_{\mathrm{a}} \mathrm{C}_{b} \mathrm{H}_{2} \mathrm{CH}_{2}- \\ & (\mathrm{C}-\mathrm{C} \text { (a)) } \end{aligned}$ | $C_{b}$ | -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 |
| $\begin{aligned} & R-H_{2} C_{a} C_{b}\left(H_{2} C_{c}-R^{\prime}\right) H C H_{2}- \\ & (C-C(b)) \end{aligned}$ | $C_{b}$ | -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 |
| $\begin{aligned} & R-H_{2} C_{a}\left(R^{\prime}-H_{2} C_{d}\right) C_{b}\left(R^{\prime \prime}-H_{2} C_{c}\right) C H_{2}- \\ & (C-C(c)) \end{aligned}$ | $C_{b}$ | -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 |
| $\begin{aligned} & \text { iso } C_{a} C_{b}\left(H_{2} C_{c}-R^{\prime}\right) H C H_{2}- \\ & (\mathrm{C}-\mathrm{C}(\mathrm{~d})) \end{aligned}$ | $C_{b}$ | -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 |
| $\begin{aligned} & {\operatorname{tert~} C_{a}\left(R^{\prime}-H_{2} C_{d}\right) C_{b}\left(R^{\prime \prime}-H_{2} C_{c}\right) \mathrm{CH}_{2}-}^{(\mathrm{C}-\mathrm{C}(\mathrm{e}))} \end{aligned}$ | $C_{b}$ | -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 |
| $\begin{aligned} & {\operatorname{tertI} C_{a} C_{b}\left(H_{2} C_{c}-R^{\prime}\right) \mathrm{HCH}_{2}-}^{(\mathrm{C}-\mathrm{C}(\mathrm{f}))} \end{aligned}$ | $C_{b}$ | -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 |
| $\begin{aligned} & \text { iso } C_{a}\left(R^{\prime}-H_{2} C_{d}\right) C_{b}\left(R^{\prime \prime}-H_{2} C_{c}\right) \mathrm{CH}_{2}- \\ & (\mathrm{C}-\mathrm{C} \text { (f)) } \end{aligned}$ | $C_{b}$ | -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 23.82. The energy parameters $(\mathrm{eV})$ of functional groups of alkyl arsines.

| Parameters | $\begin{aligned} & A s-C \\ & \text { Group } \end{aligned}$ | $\begin{gathered} \mathrm{CH}_{3} \\ \text { Group } \end{gathered}$ | $\begin{gathered} \mathrm{CH}_{2} \\ \text { Group } \end{gathered}$ | CH (i) Group | $\begin{gathered} C-C(\text { a) } \\ \text { Group } \end{gathered}$ | $\begin{gathered} C-C(b) \\ \text { Group } \end{gathered}$ | $\begin{gathered} C-C(\mathrm{c}) \\ \text { Group } \end{gathered}$ | $\begin{gathered} C-C(\mathrm{~d}) \\ \text { Group } \end{gathered}$ | $\begin{gathered} C-C(\mathrm{e}) \\ \text { Group } \end{gathered}$ | $\begin{gathered} C-C(\mathrm{f}) \\ \text { Group } \end{gathered}$ | $\begin{aligned} & C \stackrel{3 e}{=} C \\ & \text { Group } \end{aligned}$ | $\begin{gathered} \mathrm{CH} \text { (ii) } \\ \text { Group } \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $f_{1}$ | 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 |
| $C_{2}$ | 0.70705 | 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 |
| $C_{10}$ | 0.5 | 0.75 | 0.75 | 0.75 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.75 |
| $\mathrm{C}_{2}$ 。 | 0.70705 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 0.85252 | 1 |
| $V_{e}(\mathrm{eV})$ | -31.18832 | -107.32728 | -70.41425 | -35.12015 | -28.79214 | -28.79214 | -29.10112 | . 28.79214 | -29.10112 | -29.10112 | -101.12679 | -37.10024 |
| $V_{p}(\mathrm{eV})$ | 7.48806 | 38.92728 | 25.78002 | 12.87680 | 9.33352 | 9.33352 | 9.37273 | 9.33352 | 9.37273 | 9.37273 | 20.69825 | 13.17125 |
| $T(\mathrm{eV})$ | 6.68041 | 32.53914 | 21.06675 | 10.48582 | 6.77464 | 6.77464 | 6.90500 | 6.77464 | 6.90500 | 6.90500 | 34.31559 | 11.58941 |
| $V_{m}(\mathrm{eV})$ | -3.34021 | -16.26957 | -10.53337 | -5.24291 | -3.38732 | -3.38732 | -3.45250 | -3.38732 | -3.45250 | -3.45250 | -17.15779 | -5.79470 |
| $E$ (Ао/Но) (eV) | -11.27537 | -15.56407 | -15.56407 | -14.63489 | -15.56407 | -15.56407 | -15.35946 | -15.56407 | -15.35946 | -15.35946 | 0 | -14.63489 |
| $\Delta E_{\mathrm{H}_{2} \mathrm{MO}}$ (АОІ HO ) ( eV ) | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | -1.13379 |
| $E_{T}$ ( (о/rо) (eV) | -11.27537 | -15.56407 | -15.56407 | -14.63489 | -15.56407 | -15.56407 | -15.35946 | -15.56407 | -15.35946 | -15.35946 | 0 | -13.50110 |
| $E_{T}\left(\mathrm{H}_{2} \mathrm{MO}\right)(\mathrm{eV})$ | -31.63542 | -67.69451 | -49.66493 | -31.63533 | -31.63537 | -31.63537 | -31.63535 | -31.63537 | -31.63535 | -31.63535 | -63.27075 | -31.63539 |
| $E_{T}\left(\right.$ atom-atom, $\left.\mathrm{msp}{ }^{3} . \mathrm{AO}\right)(\mathrm{eV})$ | 0 | 0 | 0 | 0 | -1.85836 | -1.85836 | -1.44915 | -1.85836 | -1.44915 | -1.44915 | -2.26759 | -0.56690 |
| $E_{T}(\mathrm{mo})(\mathrm{eV})$ | -31.63537 | -67.69450 | -49.66493 | -31.63537 | -33.49373 | -33.49373 | -33.08452 | -33.49373 | -33.08452 | -33.08452 | -65.53833 | -32.20226 |
| $\omega\left(10^{15} \mathrm{rad} / \mathrm{s}\right)$ | 6.89218 | 24.9286 | 24.2751 | 24.1759 | 9.43699 | 9.43699 | 15.4846 | 9.43699 | 9.55643 | 9.55643 | 49.7272 | 26.4826 |
| $E_{K}(\mathrm{eV})$ | 4.53655 | 16.40846 | 15.97831 | 15.91299 | 6.21159 | 6.21159 | 10.19220 | 6.21159 | 6.29021 | 6.29021 | 32.73133 | 17.43132 |
| $\bar{E}_{D}(\mathrm{eV})$ | -0.13330 | -0.25352 | -0.25017 | -0.24966 | -0.16515 | -0.16515 | -0.20896 | -0.16515 | -0.16416 | -0.16416 | -0.35806 | -0.26130 |
| $\bar{E}_{\text {Kvib }}(\mathrm{eV})$ | $\begin{gathered} 0.15498 \\ {[66]} \end{gathered}$ | $\begin{gathered} 0.35532 \\ \text { (Eq. (13.458)) } \end{gathered}$ | $\begin{gathered} 0.35532 \\ \text { (Eq. }(13.458)) \\ \hline \end{gathered}$ | $\begin{gathered} 0.35532 \\ \text { (Eq. (13.458)) } \end{gathered}$ | $\begin{gathered} 0.12312 \\ {[6]} \\ \hline \end{gathered}$ | $\begin{gathered} 0.17978 \\ {[7]} \end{gathered}$ | $\begin{gathered} 0.09944 \\ {[B]} \end{gathered}$ | $\begin{gathered} 0.12312 \\ {[6]} \end{gathered}$ | $\begin{gathered} 0.12312 \\ {[6]} \end{gathered}$ | $\begin{gathered} 0.12312 \\ {[6]} \end{gathered}$ | $\begin{gathered} 0.19649 \\ {[30]} \\ \hline \end{gathered}$ | $\begin{gathered} 0.35532 \\ \text { Eq. }(13.458) \\ \hline \end{gathered}$ |
| $\bar{E}_{o c c}(\mathrm{eV})$ | -0.05581 | -0.22757 | -0.14502 | -0.07200 | -0.10359 | -0.07526 | -0.15924 | -0.10359 | -0.10260 | -0.10260 | -0.25982 | -0.08364 |
| $E_{\text {mag }}(\mathrm{eV})$ | 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) | -31.69118 | -67.92207 | -49.80996 | -31.70737 | -33.59732 | -33.49373 | -33.24376 | -33.59732 | -33.18712 | -33.18712 | -49.54347 | -32.28590 |
| $E_{\text {inutal }}\left(\mathrm{c}_{\mathrm{i}}\right.$ АО/Но) $(\mathrm{eV})$ | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 |
| $E_{\text {intral }}(\mathrm{c}$, Ао/но) $(\mathrm{eV})$ | 0 | -13.59844 | -13.59844 | -13.59844 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | -13.59844 |
| $E_{D}$ (Group) $(\mathrm{eV})$ | 2.42140 | 12.49186 | 7.83016 | 3.32601 | 4.32754 | 4.29921 | 3.97398 | 4.17951 | 3.62128 | 3.91734 | 5.63881 | 3.90454 |

[^3]
Table 23．84．The bond angle parameters of alkyl arsines and experimental values［3］．In the calculation of $\theta_{v}$ ，the parameters from the preceding angle were used．

|  |  |  |  | $\frac{0}{2}$ |  |  |  |  |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 艇: | $\begin{aligned} & \stackrel{0}{n} \\ & \stackrel{0}{2} \end{aligned}$ | $\begin{aligned} & \text { J. } \\ & \text { g } \end{aligned}$ | $\begin{aligned} & \infty \\ & \stackrel{\circ}{\circ} \\ & \underset{\alpha}{\circ} \end{aligned}$ | $\begin{aligned} & \underset{寸}{\ddagger} \\ & \stackrel{\otimes}{\infty} \end{aligned}$ | $\begin{aligned} & \stackrel{\rightharpoonup}{\bullet} \\ & \stackrel{0}{\bullet} \end{aligned}$ | $\begin{aligned} & \stackrel{\rightharpoonup}{\bullet} \\ & \stackrel{\rightharpoonup}{\circ} \end{aligned}$ | $\begin{aligned} & \stackrel{B}{n} \\ & \stackrel{y}{2} \end{aligned}$ |  |  | $\begin{aligned} & \stackrel{\rightharpoonup}{\oplus} \\ & \stackrel{1}{\circ} \end{aligned}$ | $\stackrel{\overbrace{}}{\stackrel{0}{\ominus}}$ | $\stackrel{\widehat{y}}{=}$ | $\stackrel{\widehat{e n}}{\ni}$ |  |
| がこ |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| ○。 |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| ó |  | $\stackrel{\circ}{\circ}$ |  |  | $\begin{aligned} & \overline{5} \\ & 0 \end{aligned}$ | $\begin{aligned} & \overline{5} \\ & 0 . \end{aligned}$ |  |  | － |  |  |  |  | 8 |
| 近会 | － |  |  | － |  |  | － |  |  |  | － | － | $\stackrel{\circ}{\text { ¢ }}$ |  |
| $\sim$ | $\begin{aligned} & \stackrel{\circ}{2} \\ & \stackrel{0}{7} \end{aligned}$ |  | $\begin{array}{\|l\|l} \hline 0 \\ \text { on } \\ \text { Bo } \\ 0 \end{array}$ | $\begin{aligned} & \stackrel{\circ}{0} \\ & \stackrel{n}{3} \end{aligned}$ |  |  | $\stackrel{\circ}{\bullet}$ $\stackrel{2}{3}$ |  |  |  |  |  | $\begin{gathered} \stackrel{9}{9} \\ \stackrel{y}{2} \\ \stackrel{y}{\circ} \end{gathered}$ |  |
| － | \％ |  | － | $\underset{O}{\text { Ron }}$ |  |  | \％ |  |  | － | \％ | \％ | － |  |
| v | － |  | － | － |  |  | － |  |  | － | － | － | － |  |
| v | － |  | － | － |  |  | － |  |  | － | ¢ٌ | กั่ | － |  |
| v | － |  | $\begin{gathered} \text { or } \\ \substack{0 \\ 0 \\ 0} \end{gathered}$ | － |  |  | － |  |  | $\begin{gathered} \stackrel{9}{2} \\ \stackrel{6}{0} \\ \stackrel{0}{0} \end{gathered}$ | $\frac{\mathrm{N}}{\mathrm{E}}$ | $\frac{\mathrm{E}}{\mathrm{E}}$ | $\begin{aligned} & \text { 名 } \\ & \stackrel{y}{\infty} \\ & \underset{\alpha}{\infty} \end{aligned}$ |  |
| v | $\begin{aligned} & \text { or } \\ & \text { O. } \\ & 0.0 \end{aligned}$ |  | $\begin{array}{\|l\|l} \hline 0 \\ \text { on } \\ 0.0 \\ 0 \end{array}$ |  |  |  | $\begin{aligned} & \text { or } \\ & \text { O} \\ & 0.0 \end{aligned}$ |  |  |  |  | $\begin{aligned} & \text { 华 } \\ & \substack{\infty\\ } \end{aligned}$ |  |  |
|  | $=$ |  | － | $\pm$ |  |  | $\pm$ |  |  | ¢ | － | － | ¢ |  |
|  | $\pm$ |  | $$ | $\pm$ |  |  | ェ |  |  | 铞 | 答 |  | 等 |  |
|  | － |  | $\checkmark$ | $\checkmark$ |  |  | $\sim$ |  |  | ¢ | in | in | $\stackrel{\square}{\circ}$ |  |
| $\text { 鬼 } t a y$ | $\begin{aligned} & \text { 条 } \\ & \stackrel{y}{6} \\ & \stackrel{6}{6} \end{aligned}$ |  |  | $\begin{aligned} & \substack { 8 \\ \stackrel{y}{c} \\ \begin{subarray}{c}{6{ 8 \\ \stackrel { y } { c } \\ \begin{subarray} { c } { 6 } } \\ { } \\ {\hline} \end{aligned}$ |  |  |  |  |  | 圱 | 器 | 颜 |  |  |
|  | $\begin{aligned} & \text { Ï } \\ & \text { 付 } \end{aligned}$ |  | $\begin{aligned} & \frac{0}{n} \\ & n \\ & n \end{aligned}$ |  |  |  | $\begin{gathered} \text { İ } \\ \text { 简 } \end{gathered}$ |  |  | $\begin{aligned} & \stackrel{\circ}{8} \\ & \stackrel{\circ}{+} \end{aligned}$ | $\frac{\sqrt{6}}{7}$ | $\stackrel{\substack{6 \\ 7}}{\substack{\text { a }}}$ | － |  |
| 呍 | $\begin{aligned} & \underset{\text { İ }}{\text { in }} \end{aligned}$ |  |  | $\stackrel{\circ}{\beth}$ |  |  | $\underset{\substack{\underset{\text { in }}{~} \\ \hline}}{ }$ |  |  | $\begin{aligned} & \stackrel{\rightharpoonup}{2} \\ & \frac{1}{2} \end{aligned}$ | 劄 | F | － |  |
|  | $\begin{aligned} & \text { F } \\ & \stackrel{\rightharpoonup}{i} \\ & \text { in } \end{aligned}$ |  | $\begin{array}{\|c\|c} \hline 8 \\ \stackrel{y}{d} \\ \substack{0} \end{array}$ | $\stackrel{\circ}{\bar{i}}$ |  |  | 츷 |  |  | city | $\begin{aligned} & \text { f } \\ & \stackrel{y}{2} \\ & \text { in } \end{aligned}$ |  | － |  |
|  |  | $\begin{aligned} & n \\ & 0_{0}^{\prime} \\ & \mathbb{v}^{2} \end{aligned}$ | $\begin{gathered} e_{0}^{0} \\ e_{0}^{0} \\ v^{2} \end{gathered}$ | $\begin{aligned} & \frac{0}{2} \\ & \frac{2}{2} \\ & \frac{0}{2} \\ & \frac{1}{2} \end{aligned}$ | $\begin{aligned} & \text { Us }_{0}^{0} \\ & \text { vi } \end{aligned}$ | $\begin{aligned} & z \\ & \text { z } \\ & \text { vi } \end{aligned}$ |  |  | $\begin{aligned} & z \\ & z_{0} \\ & 0_{0} \end{aligned}$ | $\begin{aligned} & 0_{0}^{0} \\ & 0 \\ & 0 \\ & 0 \\ & 0 \\ & 0 \end{aligned}$ | $\begin{array}{ll} y_{1} & 0 \\ 0_{0} & 0 \\ 0 & 0 \\ 0 & 0 \end{array}$ | $\begin{aligned} & \text { y } \\ & 0 \\ & 0 \\ & 0 \\ & 0.0 \\ & \text { vo } \end{aligned}$ | $\begin{aligned} & 0_{0} \\ & 心_{0} \\ & v_{0} \\ & \end{aligned}$ | cres |

## ALKYL STIBINES $\left(\left(C_{n} H_{2 n+1}\right)_{3} S b, n=1,2,3,4,5 \ldots \infty\right)$

The alkyl stibines, $\left(C_{n} H_{2 n+1}\right)_{3} \mathrm{Sb}$, comprise a $\mathrm{Sb}-\mathrm{C}$ functional group. The alkyl portion of the alkyl stibine may comprise at least two terminal methyl groups $\left(\mathrm{CH}_{3}\right)$ at each end of each chain, and may comprise methylene $\left(\mathrm{CH}_{2}\right)$, and methylyne $(\mathrm{CH})$ 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 $\mathrm{C}-\mathrm{C}$ bonds within isopropyl $\left(\left(\mathrm{CH}_{3}\right)_{2} \mathrm{CH}\right)$ and t-butyl $\left(\left(\mathrm{CH}_{3}\right)_{3} \mathrm{C}\right)$ 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 stibines are equivalent to those in branched-chain alkanes. The $S b-C$ group may further join the $S b 5 s p^{3} \mathrm{HO}$ to an aryl HO.

As in the case of phosphorous, the bonding in the antimony atom involves $s p^{3}$ hybridized orbitals formed, in this case, from the $5 p$ and $5 s$ electrons of the outer shells. The $S b-C$ bond forms between $S b 5 s p^{3}$ and $C 2 s p^{3}$ HOs to yield stibines. The semimajor axis $a$ of the $S b-C$ 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 the Organic Molecular Functional Groups and Molecules section.

The energy of antimony 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 ( $O H$ ) section with hybridization of the antimony 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 $S b 5 s p^{3}$ shell as in the case of the corresponding phosphine and arsine molecules.

The $S b$ electron configuration is $[K r] 5 s^{2} 4 d^{10} 5 p^{3}$ corresponding to the ground state ${ }^{4} S_{3 / 2}$, and the $5 s p^{3}$ hybridized orbital arrangement after Eq. (13.422) is:

where the quantum numbers $\left(\ell, m_{\ell}\right)$ are below each electron. The total energy of the state is given by the sum over the five electrons. The sum $E_{T}\left(S b, 5 s p^{3}\right)$ of experimental energies [1] of $S b, S b^{+}, S b^{2+}, S b^{3+}$, and $S b^{4+}$ is:

$$
\begin{equation*}
E_{T}\left(S b, 5 s p^{3}\right)=56.0 \mathrm{eV}+44.2 \mathrm{eV}+25.3 \mathrm{eV}+16.63 \mathrm{eV}+8.60839 \mathrm{eV}=150.73839 \mathrm{eV} \tag{23.273}
\end{equation*}
$$

By considering that the central field decreases by an integer for each successive electron of the shell, the radius $r_{5 s p^{3}}$ of the $S b 5 s p^{3}$ shell may be calculated from the Coulombic energy using Eq. (15.13).

$$
\begin{equation*}
r_{5 s p^{3}}=\sum_{n=46}^{50} \frac{(Z-n) e^{2}}{8 \pi \varepsilon_{0}(e 150.73839 \mathrm{eV})}=\frac{15 e^{2}}{8 \pi \varepsilon_{0}(e 150.73839 \mathrm{eV})}=1.35392 a_{0} \tag{23.274}
\end{equation*}
$$

where $Z=51$ for antimony. Using Eq. (15.14), the Coulombic energy $E_{\text {Coulomb }}\left(S b, 5 s p^{3}\right)$ of the outer electron of the $S b 5 s p^{3}$ shell is:

$$
\begin{equation*}
E_{\text {Coulomb }}\left(S b, 5 s p^{3}\right)=\frac{-e^{2}}{8 \pi \varepsilon_{0} r_{5 s p^{3}}}=\frac{-e^{2}}{8 \pi \varepsilon_{0} 1.35392 a_{0}}=-10.04923 \mathrm{eV} \tag{23.275}
\end{equation*}
$$

During hybridization, the spin-paired $5 s$ electrons are promoted to the $S b 5 s p^{3}$ shell as paired electrons at the radius $r_{5 s p^{3}}$ of the $S b 5 s p^{3}$ shell. The energy for the promotion is the difference in the magnetic energy given by Eq. (15.15) at the initial radius of the $5 s$ electrons and the final radius of the $S b 5 s p^{3}$ electrons. From Eq. (10.102) with $Z=51$ and $n=48$, the radius $r_{48}$ of the Sb5s shell is:

$$
\begin{equation*}
r_{48}=1.23129 a_{0} \tag{23.276}
\end{equation*}
$$

Using Eqs. (15.15) and (23.276), the unpairing energy is:

$$
\begin{equation*}
E(\text { magnetic })=\frac{2 \pi \mu_{0} e^{2} \hbar^{2}}{m_{e}^{2}}\left(\frac{1}{\left(r_{48}\right)^{3}}-\frac{1}{\left(r_{5 s p^{3}}\right)^{3}}\right)=8 \pi \mu_{0} \mu_{B}^{2}\left(\frac{1}{\left(1.23129 a_{0}\right)^{3}}-\frac{1}{\left(1.35392 a_{0}\right)^{3}}\right)=0.01519 \mathrm{eV} \tag{23.277}
\end{equation*}
$$

Using Eqs. (23.275) and (23.277), the energy $E\left(S b, 5 s p^{3}\right)$ of the outer electron of the $S b 5 s p^{3}$ shell is:

$$
\begin{equation*}
E\left(S b, 5 s p^{3}\right)=\frac{-e^{2}}{8 \pi \varepsilon_{0} r_{5 s p^{3}}}+\frac{2 \pi \mu_{0} e^{2} \hbar^{2}}{m_{e}^{2}}=-10.04923 \mathrm{eV}+0.01519 \mathrm{eV}=-10.03404 \mathrm{eV} \tag{23.278}
\end{equation*}
$$

For the $S b-C$ functional group, hybridization of the $2 s$ and $2 p$ AOs of each $C$ and the $5 s$ and $5 p$ AOs of each $S b$ to form single $2 s p^{3}$ and $5 s p^{3}$ shells, respectively, forms an energy minimum, and the sharing of electrons between the $C 2 s p^{3}$ and $S b 5 s p^{3}$ HOs to form a MO permits each participating orbital to decrease in radius and energy. In branched-chain alkyl stibines, the energy of antimony 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 $C 2 s p^{3}$ HO has an energy of $E\left(C, 2 s p^{3}\right)=-14.63489 \mathrm{eV}$ (Eq. (15.25)), and the $S b 5 s p^{3} \mathrm{HO}$ has an energy of $E\left(S b, 5 s p^{3}\right)=-10.03404 \mathrm{eV}$ (Eq. (23.278)). To meet the equipotential condition of the union of the $\mathrm{Sb}-\mathrm{C} \quad \mathrm{H}_{2}$-type-ellipsoidal-MO with these orbitals, the hybridization factor $C_{2}$ of Eq. (15.61) for the $S b-C$-bond MO given by Eqs. (15.77), (15.79), and (13.430) is:

$$
\begin{equation*}
C_{2}\left(C 2 s p^{3} H O \text { to } S b 5 s p^{3} H O\right)=\frac{E\left(S b, 5 s p^{3}\right)}{E\left(C, 2 s p^{3}\right)} c_{2}\left(C 2 s p^{3} H O\right)=\frac{-10.03404 \mathrm{eV}}{-14.63489 \mathrm{eV}}(0.91771)=0.62921 \tag{23.279}
\end{equation*}
$$

The energy of the $\mathrm{Sb}-\mathrm{C}$-bond MO is the sum of the component energies of the $H_{2}$-type ellipsoidal MO given in Eq. (15.51) with $E(A O / H O)=E\left(S b, 5 s p^{3}\right)$ given by Eq. (23.278), and $E_{T}\left(\right.$ atom-atom, $\left.m s p^{3} . A O\right)$ is zero in order to match the energies of the carbon and antimony HOs.

The symbols of the functional groups of branched-chain alkyl stibines are given in Table 123.85. 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 stibines are given in Tables 23.86, 23.87, and 23.88, respectively. The total energy of each alkyl stibine given in Table 23.89 was calculated as the sum over the integer multiple of each $E_{D}($ Group $)$ of Table 23.88 corresponding to functional-group composition of the molecule. The bond angle parameters of alkyl stibines determined using Eqs. (15.88-15.117) are given in Table 23.90. The color scale, charge-density of exemplary alkyl stibine, triphenylstibine, comprising atoms with the outer shell bridged by one or more $\mathrm{H}_{2}$-type ellipsoidal MOs or joined with one or more hydrogen MOs is shown in Figure 23.18.

Figure 23.18. Color scale, charge-density of triphenylstibine showing the orbitals of the atoms at their radii, the ellipsoidal surface of each H or $\mathrm{H}_{2}$-type ellipsoidal MO that transitions to the corresponding outer shell of the atom(s) participating in each bond, and the hydrogen nuclei.

$0 \square 1 \mathrm{e} / \AA^{2}$

Table 23.85. The symbols of functional groups of alkyl stibines.

| Functional Group | Group Symbol |
| :---: | :---: |
| $\overline{S b-C}$ | $\mathrm{Sb}-\mathrm{C}$ |
| $\mathrm{CH}_{3}$ group | $\mathrm{C}-\mathrm{H}\left(\mathrm{CH}_{3}\right)$ |
| $\mathrm{CH}_{2}$ group | $\mathrm{C}-\mathrm{H}\left(\mathrm{CH}_{2}\right)$ |
| CH | $\mathrm{C}-\mathrm{H}$ (i) |
| $C C$ bond ( $n-C$ ) | $C-C$ (a) |
| $C C$ bond (iso-C) | $C-C$ (b) |
| $C C$ bond (tert-C) | $C-C$ (c) |
| $C C$ (iso to iso-C) | $C-C$ (d) |
| $C C$ ( $t$ to $t-C$ ) | $C-C$ (e) |
| $C C$ ( $t$ to iso-C) | $C-C$ (f) |
| $C C$ (aromatic bond) | $C \stackrel{3 e}{=} C$ |
| CH (aromatic) | CH (ii) |

Table 23.86. The geometrical bond parameters of alkyl stibines and experimental values [3].

| Parameter | $\begin{aligned} & S b-C \\ & \text { Group } \end{aligned}$ | $\begin{gathered} \mathrm{C}-\mathrm{H}\left(\mathrm{CH}_{3}\right) \\ \text { Group } \end{gathered}$ | $\begin{gathered} \mathrm{C}-\mathrm{H}\left(\mathrm{CH}_{2}\right) \\ \text { Group } \end{gathered}$ | $\begin{gathered} C-H(\mathrm{i}) \\ \text { Group } \end{gathered}$ | $\begin{gathered} C-C(a) \\ \text { Group } \end{gathered}$ | $\begin{gathered} C-C \text { (b) } \\ \text { Group } \end{gathered}$ | $\begin{gathered} C-C(\mathrm{c}) \\ \text { Group } \end{gathered}$ | $\begin{gathered} C-C(\mathrm{~d}) \\ \text { Group } \end{gathered}$ | $\begin{gathered} C-C(\mathrm{e}) \\ \text { Group } \end{gathered}$ | $\begin{gathered} C-C(f) \\ \text { Group } \end{gathered}$ | $\begin{aligned} & C=\frac{3 e}{C=C} \\ & \text { Group } \end{aligned}$ | $\begin{aligned} & \mathrm{CH} \text { (ii) } \\ & \text { Group } \end{aligned}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $a\left(a_{0}\right)$ | 2.38997 | 1.64920 | 1.67122 | 1.67465 | 2.12499 | 2.12499 | 2.10725 | 2.12499 | 2.10725 | 2.10725 | 1.47348 | 1.60061 |
| $c^{\prime}\left(a_{0}\right)$ | 1.94894 | 1.04856 | 1.05553 | 1.05661 | 1.45744 | 1.45744 | 1.45164 | 1.45744 | 1.45164 | 1.45164 | 1.31468 | 1.03299 |
| $\begin{aligned} & \text { Bond Length } \\ & 2 c^{\prime}(A) \end{aligned}$ | 2.06267 | 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 (A) |  | $\begin{gathered} 1.107 \\ (\mathrm{C}-H \text { propane }) \\ 1.117 \\ (\mathrm{C}-\mathrm{H} \text { butane }) \\ \hline \end{gathered}$ | $\begin{gathered} 1.107 \\ (C-H \text { propane }) \\ 1.117 \\ (C-H \text { butane }) \\ \hline \end{gathered}$ | $\begin{gathered} 1.122 \\ \text { (isobutane) } \end{gathered}$ |  |  |  | 1.532 (propane) 1.531 (butane) | 1.532 (propane) 1.531 (butane) | 1.532 (propane) 1.531 (butane) | $\begin{gathered} 1.399 \\ \text { (benzene) } \end{gathered}$ | $\begin{gathered} 1.101 \\ \text { (benzene) } \end{gathered}$ |
| $b, c\left(a_{0}\right)$ | 1.38332 | 1.27295 | 1.29569 | 1.29924 | 1.54616 | 1.54616 | 1.52750 | 1.54616 | 1.52750 | 1.52750 | 0.66540 | 1.22265 |
| $e$ | 0.81547 | 0.63580 | 0.63159 | 0.63095 | 0.68600 | 0.68600 | 0.68888 | 0.68600 | 0.68888 | 0.68888 | 0.89223 | 0.64537 |

Table 23.87. The MO to HO intercept geometrical bond parameters of alkyl stibines. $R, R^{\prime}, R^{\prime \prime}$ are $H$ or alkyl groups. $E_{T}$ is $E_{T}$ (atom-atom,msp ${ }^{3} . A O$ ).

| Bond | Atom | $\begin{gathered} E_{T} \\ (\mathrm{eV}) \\ \text { Rond } \end{gathered}$ $\text { Bond } 1$ |  | $E_{T}$ $(\mathrm{eV})$ <br> Bond 3 | $E_{T}$ $(\mathrm{eV})$ <br> Bond 4 | Final Total <br> Energy <br> $C 2 s p^{3}$ <br> $(\mathrm{eV})$ | $\begin{aligned} & r_{\text {inval }} \\ & \left(a_{3}\right) \end{aligned}$ | $\begin{aligned} & r_{\text {frnal }} \\ & \left(a_{0}\right) \end{aligned}$ | $\begin{gathered} E_{\text {Coulomb }}\left(\begin{array}{l} \text { and } \\ (\mathrm{eV}) \\ \text { Final } \end{array}\right. \end{gathered}$ | $\begin{gathered} E\left(C 2 s p^{3}\right) \\ (\mathrm{eV}) \\ \text { Final } \end{gathered}$ | $\begin{aligned} & \theta^{\prime} \\ & \left({ }^{\circ}\right) \end{aligned}$ | $\begin{aligned} & \theta_{1} \\ & \left({ }^{\circ}\right) \end{aligned}$ | $\begin{aligned} & \theta_{2} \\ & \left({ }^{\circ}\right) \end{aligned}$ | $\begin{gathered} d_{1} \\ \left(a_{0}\right) \end{gathered}$ | $\begin{gathered} d_{2} \\ \left(a_{0}\right) \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{C}-\mathrm{H}\left(\mathrm{CH}_{3}\right)$ | C | 0 | 0 | 0 | 0 | -151.61569 | 0.91771 | 0.91771 | -14.82575 | -14.63489 | 83.62 | 96.38 | 45.76 | 1.15051 | 0.10195 |
| $\left(\mathrm{CH}_{3}\right)_{2} \mathrm{Sb}-\mathrm{CH}_{3}$ | C | 0 | 0 | 0 | 0 |  | 0.91771 | 0.91771 | -14.82575 | -14.63489 | 99.00 | 81.00 | 40.94 | 1.80541 | 0.14353 |
| $\left(\mathrm{CH}_{3}\right)_{2} \mathrm{Sb}-\mathrm{CH}_{3}$ | Sb | 0 | 0 | 0 | 0 |  | 1.35392 | 0.91771 | -14.82575 |  | 99.00 | 81.00 | 40.94 | 1.80541 | 0.14353 |
| $\mathrm{C}-\mathrm{H}\left(\mathrm{CH}_{3}\right)$ | 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 |
| $\mathrm{C}-\mathrm{H}\left(\mathrm{CH}_{2}\right)$ | 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 |
| $\mathrm{C}-\mathrm{H}(\mathrm{CH})$ | 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 |
| $\begin{aligned} & \mathrm{H}_{3} \mathrm{C}_{a} \mathrm{C}_{b} \mathrm{H}_{2} \mathrm{CH}_{2}- \\ & (\mathrm{C}-\mathrm{C} \text { (a)) } \end{aligned}$ | $C_{a}$ | -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 |
| $\begin{aligned} & \mathrm{H}_{3} \mathrm{C}_{\mathrm{C}} \mathrm{C}_{b} \mathrm{H}_{2} \mathrm{CH}_{2}- \\ & (\mathrm{C}-\mathrm{C}(\mathrm{a})) \end{aligned}$ | $C_{b}$ | -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 |
| $\begin{aligned} & R-\mathrm{H}_{2} C_{a} C_{b}\left(H_{2} C_{c}-R^{\prime}\right) H C H_{2}- \\ & (\mathrm{C}-\mathrm{C} \text { (b)) } \end{aligned}$ | $C_{b}$ | -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 |
| $\begin{aligned} & R-\mathrm{H}_{2} \mathrm{C}_{a}\left(R^{\prime}-\mathrm{H}_{2} \mathrm{C}_{d}\right) C_{b}\left(R^{\prime \prime}-\mathrm{H}_{2} \mathrm{C}_{c}\right) \mathrm{CH}_{2}- \\ & (\mathrm{C}-\mathrm{C}(\mathrm{c})) \end{aligned}$ | $C_{b}$ | -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 |
| $\begin{aligned} & \text { isoC }_{a} C_{b}\left(\mathrm{H}_{2} \mathrm{C}_{c}-\mathrm{R}^{\prime}\right) \mathrm{HCH}_{2}- \\ & (\mathrm{C}-\mathrm{C}(\mathrm{~d})) \end{aligned}$ | $C_{b}$ | -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 |
| $\begin{aligned} & {\operatorname{tert} C_{a}\left(R^{\prime}-H_{2} C_{d}\right) C_{b}\left(R^{\prime \prime}-H_{2} C_{c}\right) \mathrm{CH}_{2}-}_{(\mathrm{C}-\mathrm{C}(\mathrm{e}))} \end{aligned}$ | $C_{b}$ | $-0.72457$ | -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 |
| $\begin{aligned} & {\operatorname{tert} C_{a} C_{b}\left(H_{2} C_{c}-R^{\prime}\right) H C H_{2}-}_{(C-C ~(f))} \end{aligned}$ | $C_{b}$ | -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 |
| $\begin{aligned} & \text { isoC }_{a}\left(R^{\prime}-H_{2} C_{d}\right) C_{b}\left(R^{\prime \prime}-H_{2} C_{c}\right) \mathrm{CH}_{2}- \\ & (\mathrm{C}-\mathrm{C}(\mathrm{f})) \end{aligned}$ | $C_{b}$ | -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 23.88. The energy parameters ( eV ) of functional groups of alkyl stibines.

| Parameters | $S b-C$ Group | $\begin{gathered} \mathrm{CH}_{3} \\ \text { Group } \end{gathered}$ | $\begin{gathered} \mathrm{CH}_{2} \\ \text { Group } \end{gathered}$ | CH (i) Group | $\begin{aligned} & C-C \text { (a) } \\ & \text { Group } \end{aligned}$ | $C-C \text { (b) }$ <br> Group | $\begin{aligned} & C-C \text { (c) } \\ & \text { Group } \end{aligned}$ | $\begin{gathered} C-C(\mathrm{~d}) \\ \text { Group } \end{gathered}$ | $\begin{gathered} C-C \text { (e) } \\ \text { Group } \end{gathered}$ | $\begin{gathered} C-C(\mathrm{f}) \\ \text { Group } \end{gathered}$ | $\begin{aligned} & C^{3 e}=C \\ & \text { Group } \end{aligned}$ | 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 |
| $C_{2}$ | 0.62921 | 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 |
| $C_{1}$, | 0.5 | 0.75 | 0.75 | 0.75 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.75 |
| $C_{20}$ | 0.62921 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 0.85252 | 1 |
| $V_{e}(\mathrm{eV})$ | -31.92151 | -107.32728 | -70.41425 | -35.12015 | -28.79214 | -28.79214 | -29.10112 | -28.79214 | -29.10112 | -29.10112 | -101.12679 | -37.10024 |
| $V_{p}(\mathrm{eV})$ | 6.98112 | 38.92728 | 25.78002 | 12.87680 | 9.33352 | 9.33352 | 9.37273 | 9.33352 | 9.37273 | 9.37273 | 20.69825 | 13.17125 |
| $T(\mathrm{eV})$ | 6.67822 | 32.53914 | 21.06675 | 10.48582 | 6.77464 | 6.77464 | 6.90500 | 6.77464 | 6.90500 | 6.90500 | 34.31559 | 11.58941 |
| $V_{m}(\mathrm{eV})$ | -3.33911 | -16.26957 | -10.53337 | -5.24291 | -3.38732 | -3.38732 | -3.45250 | -3.38732 | -3.45250 | -3.45250 | -17.15779 | -5.79470 |
| E(Ао/но) (eV) | -10.03404 | -15.56407 | -15.56407 | -14.63489 | -15.56407 | -15.56407 | -15.35946 | -15.56407 | -15.35946 | -15.35946 | 0 | -14.63489 |
|  | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | -1.13379 |
| $E_{T}$ ( (ояно) (eV) | -10.03404 | -15.56407 | -15.56407 | -14.63489 | -15.56407 | -15.56407 | -15.35946 | -15.56407 | -15.35946 | -15.35946 | 0 | -13.50110 |
| $E_{T}\left(\mathrm{H}_{2} \mathrm{MO}\right)(\mathrm{eV})$ | -31.63532 | -67.69451 | -49.66493 | -31.63533 | -31.63537 | -31.63537 | -31.63535 | -31.63537 | -31.63535 | -31.63535 | -63.27075 | -31.63539 |
| $E_{T}\left(\right.$ atom-atom, $\left.\mathrm{msp}^{3} \cdot \mathrm{AO}\right)(\mathrm{eV})$ | 0 | 0 | 0 | 0 | -1.85836 | -1.85836 | -1.44915 | -1.85836 | -1.44915 | -1.44915 | -2.26759 | -0.56690 |
| $E_{T}($ мо) $(\mathrm{eV})$ | -31.63537 | -67.69450 | -49.66493 | -31.63537 | -33.49373 | -33.49373 | -33.08452 | -33.49373 | -33.08452 | -33.08452 | -65.53833 | -32.20226 |
| $\omega\left(10^{15} \mathrm{rad} / \mathrm{s}\right)$ | 6.27593 | 24.9286 | 24.2751 | 24.1759 | 9.43699 | 9.43699 | 15.4846 | 9.43699 | 9.55643 | 9.55643 | 49.7272 | 26.4826 |
| $E_{K}(\mathrm{eV})$ | 4.13093 | 16.40846 | 15.97831 | 15.91299 | 6.21159 | 6.21159 | 10.19220 | 6.21159 | 6.29021 | 6.29021 | 32.73133 | 17.43132 |
| $\bar{E}_{D}(e \mathrm{~V})$ | -0.12720 | -0.25352 | -0.25017 | -0.24966 | -0.16515 | -0.16515 | -0.20896 | -0.16515 | -0.16416 | -0.16416 | -0.35806 | -0.26130 |
| $\bar{E}_{\text {Kuvb }}(\mathrm{eV})$ | $\begin{gathered} 0.14878 \\ {[66]} \end{gathered}$ | $\begin{gathered} 0.35532 \\ \text { (Eq. }(13.458) \text { ) } \end{gathered}$ | $\begin{gathered} 0.35532 \\ \text { (Eq. }(13.458) \text { ) } \end{gathered}$ | $\begin{gathered} 0.35532 \\ \text { (Eq. }(13.458)) \end{gathered}$ | $\begin{gathered} 0.12312 \\ {[6]} \end{gathered}$ | $\begin{gathered} 0.17978 \\ {[7]} \end{gathered}$ | $\begin{gathered} 0.09944 \\ {[8]} \end{gathered}$ | $\begin{gathered} 0.12312 \\ {[6]} \end{gathered}$ | $\begin{gathered} 0.12312 \\ {[6]} \end{gathered}$ | $\begin{gathered} 0.12312 \\ {[6]} \end{gathered}$ | $\begin{gathered} 0.19649 \\ {[30]} \end{gathered}$ | $\begin{gathered} 0.35532 \\ \text { Eq. }(13.458) \\ \hline \end{gathered}$ |
| $\bar{E}_{\text {occ }}(\mathrm{eV})$ | -0.05281 | -0.22757 | -0.14502 | -0.07200 | -0.10359 | -0.07526 | -0.15924 | -0.10359 | -0.10260 | -0.10260 | -0.25982 | -0.08364 |
| $E_{\text {mag }}(\mathrm{eV})$ | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 | 0.14803 |
| $E_{T}\left(\right.$ Group) ${ }^{\text {a }}$ (eV) | -31.68818 | -67.92207 | -49.80996 | -31.70737 | -33.59732 | -33.49373 | -33.24376 | -33.59732 | -33.18712 | -33.18712 | -49.54347 | -32.28590 |
| $E_{\text {luriala }}\left(\mathrm{c}_{4}\right.$ АоІно) $(\mathrm{eV})$ | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 |
| $E_{\text {lintal }}(\mathrm{s}$ АоIभо) $(\mathrm{eV})$ | 0 | -13.59844 | -13.59844 | -13.59844 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | -13.59844 |
| $E_{D}($ Group) $(\mathrm{eV})$ | 2.41840 | 12.49186 | 7.83016 | 3.32601 | 4.32754 | 4.29921 | 3.97398 | 4.17951 | 3.62128 | 3.91734 | 5.63881 | 3.90454 |

Table 23.89. The total bond energies of alkyl stibines calculated using the functional group composition and the energies of Table 23.88 compared to the experimental values [88]. | $\mathrm{C}_{3} \mathrm{H}_{9} \mathrm{Sb}$ | Trimethylstibine |
| :--- | :--- |
| $\mathrm{C}_{6} \mathrm{H}_{15} \mathrm{Sb}$ | Triethylstibine |
| $\mathrm{C}_{18} \mathrm{H}_{15} \mathrm{Sb}$ | Triphenylstibine |

lative Error
0.00651 Total Bond $\begin{array}{cc}\text { nergy (eV) } & \text { Energy (eV) } \\ 44.73078 & 45.02378\end{array}$ $\begin{array}{cc}80.69402 & -0.00632 \\ 165.81583 & -0.00908 \\ & \end{array}$
Table 23.90. The bond angle parameters of alkyl stibines and experimental values [3]. In the calculation of $\theta_{v}$, the parameters from the preceding angle were used. $E_{T}$ is $E_{T}$ (atom-atom, $m s p^{3} . A O$ ).


## ALKYL BISMUTHS ( $\left.\left(C_{n} H_{2 n+1}\right)_{3} B i, n=1,2,3,4,5 \ldots \infty\right)$

The alkyl bismuths, $\left(\mathrm{C}_{n} \mathrm{H}_{2 n+1}\right)_{3} \mathrm{Bi}$, comprise a $\mathrm{Bi}-\mathrm{C}$ functional group. The alkyl portion of the alkyl bismuth may comprise at least two terminal methyl groups $\left(\mathrm{CH}_{3}\right)$ at each end of each chain, and may comprise methylene $\left(\mathrm{CH}_{2}\right)$, and methylyne $(\mathrm{CH})$ 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 $\mathrm{C}-\mathrm{C}$ bonds within isopropyl $\left(\left(\mathrm{CH}_{3}\right)_{2} \mathrm{CH}\right)$ and t-butyl $\left(\left(\mathrm{CH}_{3}\right)_{3} \mathrm{C}\right)$ 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 bismuths are equivalent to those in branched-chain alkanes. The $B i-C$ group may further join the $B i 6 s p^{3} \mathrm{HO}$ to an aryl HO .

As in the case of phosphorous, arsenic, and antimony, the bonding in the bismuth atom involves $s p^{3}$ hybridized orbitals formed, in this case, from the $6 p$ and $6 s$ electrons of the outer shells. The $B i-C$ bond forms between $B i 6 s p^{3}$ and $C 2 s p^{3}$ HOs to yield bismuths. The semimajor axis $a$ of the $B i-C$ 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 the Organic Molecular Functional Groups and Molecules section.

The energy of bismuth 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 ( $O H$ ) section with hybridization of the bismuth 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 $B i 6 s p^{3}$ shell as in the case of the corresponding phosphines, arsines, and stibines.

The $B i$ electron configuration is $[X e] 6 s^{2} 4 f^{14} 5 d^{10} 6 p^{3}$ corresponding to the ground state ${ }^{4} S_{3 / 2}$, and the $6 s p^{3}$ hybridized orbital arrangement after Eq. (13.422) is:

\[

\]

where the quantum numbers $\left(\ell, m_{\ell}\right)$ are below each electron. The total energy of the state is given by the sum over the five electrons. The sum $E_{T}\left(B i, 6 s p^{3}\right)$ of experimental energies [1] of $B i, B i^{+}, B i^{2+}, B i^{3+}$, and $B i^{4+}$ is:

$$
\begin{equation*}
E_{T}\left(B i, 6 s p^{3}\right)=56.0 \mathrm{eV}+45.3 \mathrm{eV}+25.56 \mathrm{eV}+16.703 \mathrm{eV}+7.2855 \mathrm{eV}=150.84850 \mathrm{eV} \tag{23.281}
\end{equation*}
$$

By considering that the central field decreases by an integer for each successive electron of the shell, the radius $r_{6 s p^{3}}$ of the Bi6sp ${ }^{3}$ shell may be calculated from the Coulombic energy using Eq. (15.13).

$$
\begin{equation*}
r_{6 s p^{3}}=\sum_{n=78}^{82} \frac{(Z-n) e^{2}}{8 \pi \varepsilon_{0}(e 150.84850 \mathrm{eV})}=\frac{15 e^{2}}{8 \pi \varepsilon_{0}(e 150.84850 \mathrm{eV})}=1.35293 a_{0} \tag{23.282}
\end{equation*}
$$

where $Z=83$ for bismuth. Using Eq. (15.14), the Coulombic energy $E_{\text {Coulomb }}\left(B i, 6 s p^{3}\right)$ of the outer electron of the $B i 6 s p^{3}$ shell is:

$$
\begin{equation*}
E_{\text {Coulomb }}\left(B i, 6 s p^{3}\right)=\frac{-e^{2}}{8 \pi \varepsilon_{0} r_{6 s p^{3}}}=\frac{-e^{2}}{8 \pi \varepsilon_{0} 1.35293 a_{0}}=-10.05657 \mathrm{eV} \tag{23.283}
\end{equation*}
$$

During hybridization, the spin-paired $6 s$ electrons are promoted to the $B i 6 s p^{3}$ shell as paired electrons at the radius $r_{6 s p^{3}}$ of the $B i 6 s p^{3}$ shell. The energy for the promotion is the difference in the magnetic energy given by Eq. (15.15) at the initial radius of the $6 s$ electrons and the final radius of the $B i 6 s p^{3}$ electrons. From Eq. (10.102) with $Z=83$ and $n=80$, the radius $r_{80}$ of the Bi6s shell is:

$$
\begin{equation*}
r_{80}=1.20140 a_{0} \tag{23.284}
\end{equation*}
$$

Using Eqs. (15.15) and (23.284), the unpairing energy is:

$$
\begin{equation*}
E(\text { magnetic })=\frac{2 \pi \mu_{0} e^{2} \hbar^{2}}{m_{e}^{2}}\left(\frac{1}{\left(r_{80}\right)^{3}}-\frac{1}{\left(r_{6 s p^{3}}\right)^{3}}\right)=8 \pi \mu_{o} \mu_{B}^{2}\left(\frac{1}{\left(1.20140 a_{0}\right)^{3}}-\frac{1}{\left(1.35293 a_{0}\right)^{3}}\right)=0.01978 \mathrm{eV} \tag{23.285}
\end{equation*}
$$

Using Eqs. (23.283) and (23.285), the energy $E\left(B i, 6 s p^{3}\right)$ of the outer electron of the Bi6sp ${ }^{3}$ shell is:

$$
\begin{equation*}
E\left(B i, 6 s p^{3}\right)=\frac{-e^{2}}{8 \pi \varepsilon_{0} r_{6 s p^{3}}}+\frac{2 \pi \mu_{0} e^{2} \hbar^{2}}{m_{e}^{2}}\left(\frac{1}{\left(r_{80}\right)^{3}}-\frac{1}{\left(r_{6 s p^{3}}\right)^{3}}\right)=-10.05657 \mathrm{eV}+0.01978 \mathrm{eV}=-10.03679 \mathrm{eV} \tag{23.286}
\end{equation*}
$$

Next, consider the formation of the $B i-L$-bond MO of bismuth compounds wherein $L$ is a very stable ligand and each bismuth atom has a $B i 6 s p^{3}$ electron with an energy given by Eq. (23.286). The total energy of the state of each bismuth atom is given by the sum over the five electrons. The sum $E_{T}\left(B i_{B i-L}, 6 s p^{3}\right)$ of energies of $B i 6 s p^{3}$ (Eq. (23.286)), $B i^{+}, B i^{2+}, B i^{3+}$, and $B i^{4+}$ is:

$$
\begin{align*}
E_{T}\left(B i_{B i-L}, 6 s p^{3}\right) & =-\left(56.0 \mathrm{eV}+45.3 \mathrm{eV}+25.56 \mathrm{eV}+16.703 \mathrm{eV}+E\left(B i, 6 s p^{3}\right)\right)  \tag{23.287}\\
& =-(56.0 \mathrm{eV}+45.3 \mathrm{eV}+25.56 \mathrm{eV}+16.703 \mathrm{eV}+10.03679 \mathrm{eV})=-153.59979 \mathrm{eV}
\end{align*}
$$

where $E\left(B i, 6 s p^{3}\right)$ is the sum of the energy of $B i,-7.2855 \mathrm{eV}$, and the hybridization energy.
A minimum energy is achieved while matching the potential, kinetic, and orbital energy relationships given in the Hydroxyl Radical ( OH ) section with the donation of electron density from the participating $B i 6 s p^{3} \mathrm{HO}$ to each $\mathrm{Bi}-L$-bond MO. Consider the case wherein each Bi6sp ${ }^{3}$ HO donates an excess of $25 \%$ of its electron density to the $B i-L$-bond MO to form an energy minimum. By considering this electron redistribution in the bismuth molecule as well as the fact that the central field decreases by an integer for each successive electron of the shell, in general terms, the radius $r_{B i-L 6 s p^{3}}$ of the Bi6sp ${ }^{3}$ shell may be calculated from the Coulombic energy using Eq. (15.18).

$$
\begin{equation*}
r_{B i-L 6 s p^{3}}=\left(\sum_{n=78}^{82}(Z-n)-0.25\right) \frac{e^{2}}{8 \pi \varepsilon_{0}(e 153.59979 \mathrm{eV})}=\frac{14.75 e^{2}}{8 \pi \varepsilon_{0}(e 153.59979 \mathrm{eV})}=1.30655 a_{0} \tag{23.288}
\end{equation*}
$$

Using Eqs. (15.19) and (23.288), the Coulombic energy $E_{\text {Coulomb }}\left(B i_{B i-L}, 6 s p^{3}\right)$ of the outer electron of the Bi6sp ${ }^{3}$ shell is:

$$
\begin{align*}
E_{\text {Coulomb }}\left(B i_{B i-L}, 6 s p^{3}\right) & =\frac{-e^{2}}{8 \pi \varepsilon_{0} r_{B i-L 6 s p^{3}}} \\
& =\frac{-e^{2}}{8 \pi \varepsilon_{0} 1.30655 a_{0}}  \tag{23.289}\\
& =-10.41354 \mathrm{eV}
\end{align*}
$$

During hybridization, the spin-paired $6 s$ electrons are promoted to the $B i 6 s p^{3}$ shell as paired electrons at the radius $r_{6 s p^{3}}$ of the $B i 6 s p^{3}$ shell. The energy for the promotion is the difference in the magnetic energy given by Eq. (15.15) at the initial radius of the $6 s$ electrons and the final radius of the $B i 6 s p^{3}$ electrons. Using Eqs. (23.285) and (23.289), the energy $E\left(B i_{B i-L}, 6 s p^{3}\right)$ of the outer electron of the $B i 6 s p^{3}$ shell is:

$$
\begin{equation*}
E\left(B i_{B i-L}, 6 s p^{3}\right)=\frac{-e^{2}}{8 \pi \varepsilon_{0} r_{B i-L 6 s p^{3}}}+\frac{2 \pi \mu_{0} e^{2} \hbar^{2}}{m_{e}^{2}\left(r_{80}\right)^{3}}=-10.41354 \mathrm{eV}+0.01978 \mathrm{eV}=-10.39377 \mathrm{eV} \tag{23.290}
\end{equation*}
$$

Thus, $E_{T}\left(B i-L, 6 s p^{3}\right)$, the energy change of each $B i 6 s p^{3}$ shell with the formation of the $B i-L$-bond MO is given by the difference between Eq. (23.290) and Eq. (23.286).

$$
\begin{equation*}
E_{T}\left(B i-L, 6 s p^{3}\right)=E\left(B i_{B i-L}, 6 s p^{3}\right)-E\left(B i, 6 s p^{3}\right)=-10.39377 \mathrm{eV}-(-10.03679 \mathrm{eV})=-0.35698 \mathrm{eV} \tag{23.291}
\end{equation*}
$$

Next, consider the formation of the $B i-C$-bond MO by bonding with a carbon having a $C 2 s p^{3}$ electron with an energy given by Eq. (14.146). The total energy of the state is given by the sum over the five electrons. The sum $E_{T}\left(C_{\text {ethane }}, 2 s p^{3}\right)$ of calculated energies of $C 2 s p^{3}, C^{+}, C^{2+}$, and $C^{3+}$ from Eqs. (10.123), (10.113-10.114), (10.68), and (10.48), respectively, is:

$$
\begin{align*}
E_{T}\left(C_{\text {ethane }}, 2 s p^{3}\right) & =-\left(64.3921 \mathrm{eV}+48.3125 \mathrm{eV}+24.2762 \mathrm{eV}+E\left(C, 2 s p^{3}\right)\right)  \tag{23.292}\\
& =-(64.3921 \mathrm{eV}+48.3125 \mathrm{eV}+24.2762 \mathrm{eV}+14.63489 \mathrm{eV})=-151.61569 \mathrm{eV}
\end{align*}
$$

where $E\left(C, 2 s p^{3}\right)$ is the sum of the energy of $C,-11.27671 \mathrm{eV}$, and the hybridization energy.
The sharing of electrons between the $B i 6 s p^{3} \mathrm{HO}$ and $C 2 s p^{3} \mathrm{HOs}$ to form a $B i-C$-bond MO permits each participating hybridized orbital to decrease in radius and energy. A minimum energy is achieved while satisfying the potential, kinetic, and orbital energy relationships, when the $B i 6 s p^{3} \mathrm{HO}$ donates, and the $C 2 s p^{3} \mathrm{HO}$ receives, excess electron density equivalent to an electron within the $B i-C$-bond MO. By considering this electron redistribution in the alkyl bismuth molecule as well as the fact that the central field decreases by an integer for each successive electron of the shell, the radius $r_{B i-C 2 s p^{3}}$ of the $C 2 s p^{3}$ shell of the $B i-C$-bond MO may be calculated from the Coulombic energy using Eqs. (15.18) and (23.292):

$$
\begin{equation*}
r_{B i-C 2 s p^{3}}=\left(\sum_{n=2}^{5}(Z-n)+1\right) \frac{e^{2}}{8 \pi \varepsilon_{0}(e 151.61569 \mathrm{eV})}=\frac{11 e^{2}}{8 \pi \varepsilon_{0}(e 151.61569 \mathrm{eV})}=0.98713 a_{0} \tag{23.293}
\end{equation*}
$$

Using Eqs. (15.19) and (23.293), the Coulombic energy $E_{\text {Coulomb }}\left(C_{B i-C}, 2 s p^{3}\right)$ of the outer electron of the $C 2 s p^{3}$ shell is:

$$
\begin{equation*}
E_{\text {Coulomb }}\left(C_{B i-C}, 2 s p^{3}\right)=\frac{-e^{2}}{8 \pi \varepsilon_{0} r_{B i-C 2 s p^{3}}}=\frac{-e^{2}}{8 \pi \varepsilon_{0} 0.98713 a_{0}}=-13.78324 \mathrm{eV} \tag{23.294}
\end{equation*}
$$

During hybridization, the spin-paired $2 s$ electrons are promoted to the $C 2 s p^{3}$ shell as unpaired electrons. The energy for the promotion is the magnetic energy given by Eq. (14.145). Using Eqs. (14.145) and (23.294), the energy $E\left(C_{B i-C}, 2 s p^{3}\right)$ of the outer electron of the $C 2 s p^{3}$ shell is:

$$
\begin{equation*}
E\left(C_{B i-C}, 2 s p^{3}\right)=\frac{-e^{2}}{8 \pi \varepsilon_{0} r_{B i-C 2 s p^{3}}}+\frac{2 \pi \mu_{0} e^{2} \hbar^{2}}{m_{e}^{2}\left(r_{3}\right)^{3}}=-13.78324 \mathrm{eV}+0.19086 \mathrm{eV}=-13.59238 \mathrm{eV} \tag{23.295}
\end{equation*}
$$

Thus, $E_{T}\left(B i-C, 2 s p^{3}\right)$, the energy change of each $C 2 s p^{3}$ shell with the formation of the $B i-C$-bond MO is given by the difference between Eq. (23.295) and Eq. (14.146).

$$
\begin{equation*}
E_{T}\left(B i-C, 2 s p^{3}\right)=E\left(C_{B i-C}, 2 s p^{3}\right)-E\left(C, 2 s p^{3}\right)=-13.59238 \mathrm{eV}-(-14.63489 \mathrm{eV})=1.04251 \mathrm{eV} \tag{23.296}
\end{equation*}
$$

Now, consider the formation of the $\mathrm{Bi}-L$-bond MO of bismuth compounds wherein $L$ is a ligand including carbon. For the $B i-C$ functional group, hybridization of the $2 s$ and $2 p$ AOs of each $C$ and the $6 s$ and $6 p$ AOs of each Bi to form single $2 s p^{3}$ and $6 s p^{3}$ shells, respectively, forms an energy minimum, and the sharing of electrons between the $C 2 s p^{3}$ and Bi6sp ${ }^{3}$ HOs to form a MO permits each participating orbital to decrease in radius and energy. In branched-chain alkyl bismuths, the energy of bismuth is less than the Coulombic energy between the electron and proton of $H$ given by Eq. (1.264). Thus, the energy matching condition is determined by the $c_{2}$ and $C_{2}$ parameters in Eq. (15.61). Then, the $C 2 s p^{3}$ HO has an energy of $E\left(C, 2 s p^{3}\right)=-14.63489 \mathrm{eV}$ (Eq. (15.25)), and the $B i 6 s p^{3} \mathrm{HO}$ has an energy of $E\left(B i, 6 s p^{3}\right)=-10.03679 \mathrm{eV}$ (Eq. (23.286)). To meet the equipotential condition of the union of the $B i-C \quad H_{2}$-type-ellipsoidal-MO with these orbitals, the hybridization factors $c_{2}$ and $C_{2}$ of Eq. (15.61) for the $B i-C$-bond MO given by Eqs. (15.77) are:

$$
\begin{equation*}
c_{2}\left(C 2 s p^{3} \mathrm{HO} \text { to } \mathrm{Bi} 6 s p^{3} \mathrm{HO}\right)=C_{2}\left(C 2 s p^{3} \mathrm{HO} \text { to Bi } 6 s p^{3} \mathrm{HO}\right)=\frac{E\left(\mathrm{Bi}, 6 s p^{3}\right)}{E\left(C, 2 s p^{3}\right)}=\frac{-10.03679 \mathrm{eV}}{-14.63489 \mathrm{eV}}=0.68581 \tag{23.297}
\end{equation*}
$$

The energy of the $B i-C$-bond MO is the sum of the component energies of the $H_{2}$-type ellipsoidal MO given in Eq. (15.51) with $E(A O / H O)=E\left(B i, 6 s p^{3}\right)$ given by Eq. (23.286), and $E_{T}\left(\right.$ atom-atom, $\left.m s p^{3} . A O\right)$ is $E_{T}\left(B i-C, 2 s p^{3}\right)$ (Eq. (23.296)) in order to match the energies of the carbon and bismuth HOs.

The symbols of the functional groups of branched-chain alkyl bismuths are given in Table 23.91. 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 bismuths are given in Tables 23.92, 23.93, and 23.94, respectively. The total energy of each alkyl bismuth given in Table 23.95 was calculated as the sum over the integer multiple of each $E_{D}($ Group $)$ of Table 23.94 corresponding to functional-group composition of the molecule. The bond angle parameters of alkyl bismuths determined using Eqs. (15.88-15.117) are given in Table 23.96. The color scale, charge-density of exemplary alkyl bismuth, triphenylbismuth, comprising atoms with the outer shell bridged by one or more $\mathrm{H}_{2}$-type ellipsoidal MOs or joined with one or more hydrogen MOs is shown in Figure 23.19.

Figure 23.19. Color scale, charge-density of triphenylbismuth 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 23.91. The symbols of functional groups of alkyl bismuths.

| Functional Group | Group Symbol |
| :---: | :---: |
| Bi-C | $B i-C$ |
| $\mathrm{CH}_{3}$ group | $\mathrm{C}-\mathrm{H}\left(\mathrm{CH}_{3}\right)$ |
| $\mathrm{CH}_{2}$ group | $\mathrm{C}-\mathrm{H}\left(\mathrm{CH}_{2}\right)$ |
| CH | C-H (i) |
| $C C$ bond ( $n-C$ ) | $C-C$ (a) |
| $C C$ bond (iso-C) | $C-C$ (b) |
| $C C$ bond (tert-C) | $C-C$ (c) |
| $C C$ (iso to iso-C) | $C-C$ (d) |
| $C C(t$ to $t-C)$ | $C-C$ (e) |
| $C C$ ( $t$ to iso-C) | $C-C$ (f) |
| $C C$ (aromatic bond) | $C^{3 e}=C$ |
| CH (aromatic) | CH (ii) |

Table 23．92．The geometrical bond parameters of alkyl bismuths and experimental values［3］．

| Parameter | $\begin{aligned} & B i-C \\ & \text { Group } \end{aligned}$ | $\begin{gathered} \mathrm{C}-\mathrm{H}\left(\mathrm{CH}_{3}\right) \\ \text { Group } \end{gathered}$ | $\begin{gathered} \mathrm{C}-\mathrm{H}\left(\mathrm{CH}_{2}\right) \\ \text { Group } \end{gathered}$ | $\begin{gathered} C-H \text { (i) } \\ \text { Group } \end{gathered}$ | $\begin{gathered} C-C \text { (a) } \\ \text { Group } \end{gathered}$ | $\begin{gathered} C-C \text { (b) } \\ \text { Group } \end{gathered}$ | $\begin{gathered} C-C(c) \\ \text { Group } \end{gathered}$ | $\begin{gathered} C-C(\mathrm{~d}) \\ \text { Group } \end{gathered}$ | $\begin{aligned} & C-C(\mathrm{e}) \\ & \text { Group } \end{aligned}$ | $\begin{gathered} C-C(\mathrm{f}) \\ \text { Group } \end{gathered}$ | $C \stackrel{3 e}{=} C$ <br> Group | CH（ii） Group |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $a\left(a_{0}\right)$ | 2.18901 | 1.64920 | 1.67122 | 1.67465 | 2.12499 | 2.12499 | 2.10725 | 2.12499 | 2.10725 | 2.10725 | 1.47348 | 1.60061 |
| $c^{\prime}\left(a_{0}\right)$ | 2.06296 | 1.04856 | 1.05553 | 1.05661 | 1.45744 | 1.45744 | 1.45164 | 1.45744 | 1.45164 | 1.45164 | 1.31468 | 1.03299 |
| $\begin{aligned} & \text { Bond Length } \\ & 2 c^{\prime}(A) \end{aligned}$ | 2.18334 | 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 （A） | $\begin{gathered} 2.263 \\ \left(\mathrm{Bi}\left(\mathrm{CH}_{3}\right)_{3}\right) \end{gathered}$ | $\begin{gathered} 1.107 \\ (C-H \text { propane }) \\ 1.117 \\ (C-H \text { butane }) \\ \hline \end{gathered}$ | $\begin{gathered} \hline 1.107 \\ (C-H \text { propane }) \\ 1.117 \\ (C-H \text { butane }) \\ \hline \end{gathered}$ | $\begin{gathered} 1.122 \\ \text { (isobutane) } \end{gathered}$ | $\begin{gathered} 1.532 \\ \text { (propane) } \\ 1.531 \\ \text { (butane) } \\ \hline \end{gathered}$ | 1.532 （propane） 1.531 （butane） | $\begin{gathered} 1.532 \\ \text { (propane) } \\ 1.531 \\ \text { (butane) } \\ \hline \end{gathered}$ | $\begin{gathered} 1.532 \\ \text { (propane) } \\ 1.531 \\ \text { (butane) } \\ \hline \end{gathered}$ | 1.532 （propane） 1.531 （butane） | $\begin{gathered} 1.532 \\ \text { (propane) } \\ 1.531 \\ \text { (butane) } \\ \hline \end{gathered}$ | $\begin{gathered} 1.399 \\ \text { (benzene) } \end{gathered}$ | $\begin{gathered} 1.101 \\ \text { (benzene) } \end{gathered}$ |
| $b, c\left(a_{0}\right)$ | 0.73210 | 1.27295 | 1.29569 | 1.29924 | 1.54616 | 1.54616 | 1.52750 | 1.54616 | 1.52750 | 1.52750 | 0.66540 | 1.22265 |
| $e$ | 0.94242 | 0.63580 | 0.63159 | 0.63095 | 0.68600 | 0.68600 | 0.68888 | 0.68600 | 0.68888 | 0.68888 | 0.89223 | 0.64537 |

Table 23．93．The MO to HO intercept geometrical bond parameters of alkyl bismuths．$R, R^{\prime}, R^{\prime \prime}$ are $H$ or alkyl groups．$E_{T}$ is $E_{T}$（atom－atom，msp ${ }^{3}$ ．$A O$ ）．

| で | $\begin{gathered} 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{gathered}$ | $\begin{aligned} & \text { ty } \\ & \underset{Z}{A} \end{aligned}$ | $\begin{aligned} & \bar{\infty} \\ & \infty \\ & \infty \\ & \infty \\ & \infty \end{aligned}$ | $\begin{gathered} \infty \\ \stackrel{\infty}{\infty} \\ \frac{\infty}{0} \end{gathered}$ | $\begin{gathered} \text { K్స్రి } \end{gathered}$ | $\begin{aligned} & \stackrel{\rightharpoonup}{\mathrm{N}} \\ & \underset{\sim}{n} \end{aligned}$ | $\stackrel{\circ}{\infty}$ | $$ | $\begin{aligned} & \infty \\ & \stackrel{\infty}{n} \\ & \stackrel{y}{2} \end{aligned}$ | ह हn nin | $\begin{aligned} & \infty \\ & \stackrel{\infty}{n} \\ & \stackrel{i}{2} \end{aligned}$ |  | $\stackrel{1}{N}$ $\underset{子}{4}$ | ¢ ¢ ¢ ¢ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| －E | $\begin{aligned} & \bar{\partial} \\ & \hat{O} \\ & \underset{-}{2} \end{aligned}$ | $\begin{aligned} & \underset{\sim}{g} \\ & \underset{\sim}{m} \\ & \underset{\sim}{2} \end{aligned}$ | $\begin{aligned} & n \\ & \underset{\sim}{\sim} \end{aligned}$ | $\begin{aligned} & \underset{\sim}{U} \\ & \underset{\sim}{c} \end{aligned}$ | $\begin{aligned} & \stackrel{\circ}{\circ} \\ & \stackrel{+}{\stackrel{1}{n}} \end{aligned}$ | $\begin{aligned} & \infty \\ & \text { ๙ } \\ & \underset{\sim}{4} \end{aligned}$ | $\stackrel{\stackrel{\infty}{\infty}}{\stackrel{\infty}{\infty}}$ | $\begin{aligned} & \circ \\ & 0 . \\ & \stackrel{0}{2} \end{aligned}$ |  | $\begin{aligned} & \text { t } \\ & \stackrel{N}{\hat{N}} \end{aligned}$ |  | $$ | $\begin{gathered} \text { 筑 } \end{gathered}$ | O |
| $0^{\circ} 0$ | $\begin{gathered} 0 \\ 0 \\ \infty \\ \infty \end{gathered}$ | $\begin{array}{\|c} \underset{\sim}{n} \\ \underset{i n}{2} \end{array}$ | $\begin{aligned} & \stackrel{8}{\circ} \\ & \stackrel{\rightharpoonup}{n} \end{aligned}$ | $\stackrel{\stackrel{\infty}{\dot{7}}}{\stackrel{+}{子}}$ | $\begin{aligned} & \underset{\sim}{\underset{\sim}{c}} \\ & \stackrel{y}{c} \end{aligned}$ | $\begin{gathered} \stackrel{r}{2} \\ \underset{\sim}{m} \end{gathered}$ | $\stackrel{\infty}{\stackrel{\circ}{\circ}}$ | $\begin{aligned} & \text { ®. } \\ & \stackrel{\sim}{4} \end{aligned}$ | $\stackrel{\stackrel{\rightharpoonup}{\mathrm{N}}}{2}$ | $\stackrel{\text { t }}{\stackrel{y}{\mathrm{~N}}}$ | $\stackrel{\stackrel{\rightharpoonup}{\lambda}}{\stackrel{1}{2}}$ | $\begin{aligned} & \stackrel{\text { ® }}{\text { d }} \end{aligned}$ | $\underset{\text { d }}{\underset{\sim}{\text { I }}}$ | $\begin{aligned} & \stackrel{\text { ® }}{ } \\ & \end{aligned}$ |
| $\sigma$－ | $\begin{aligned} & \text { ָ} \\ & \text { j} \end{aligned}$ | $\underset{\sim}{\dot{\infty}}$ | $\underset{\sim}{\underset{\sim}{0}}$ | $\begin{aligned} & \bar{n} \\ & \text { í } \end{aligned}$ | $\stackrel{n}{\Xi}$ | $\begin{gathered} \underset{\partial}{\underset{\infty}{\circ}} \\ \underset{\sim}{2} \end{gathered}$ | $\begin{aligned} & \stackrel{\infty}{6} \\ & \hline \end{aligned}$ | $\begin{aligned} & \text { ñ } \\ & \underset{\sim}{n} \end{aligned}$ | $\underset{\underset{\sim}{\sim}}{\stackrel{\rightharpoonup}{2}}$ | $\stackrel{\imath}{\mathrm{m}}$ | $\stackrel{\stackrel{\overbrace{}}{\mathrm{m}}}{\stackrel{1}{2}}$ | $\begin{aligned} & \stackrel{\circ}{\mathrm{Q}} \end{aligned}$ |  | $\begin{aligned} & \stackrel{\circ}{\mathrm{Q}} \\ & \text { R } \end{aligned}$ |
| －© | $\stackrel{\substack{\circ \\ \stackrel{\infty}{\infty}}}{ }$ | $\begin{gathered} \underset{\partial}{\Xi} \\ \underset{y}{2} \end{gathered}$ | $\begin{aligned} & \underset{\sim}{\infty} \\ & \dot{f} \end{aligned}$ | $\stackrel{\underset{\sim}{\underset{~}{~}} \underset{\sim}{2}}{ }$ | $\underset{\substack{f \\ \otimes \\ \hline}}{ }$ | $\frac{0}{3}$ |  |  | $\begin{gathered} \stackrel{\infty}{\infty} \\ \stackrel{+}{\infty} \end{gathered}$ | $\begin{aligned} & \bar{\sim} \\ & \underset{子}{\circ} \end{aligned}$ | $\underset{\substack{++ \\ \hline}}{ }$ | $\begin{aligned} & \text { t. } \\ & \stackrel{\rightharpoonup}{n} \end{aligned}$ | $\stackrel{\infty}{\stackrel{\infty}{i}}$ | $\begin{aligned} & \text { to } \\ & \text { in } \end{aligned}$ |
| $\frac{0}{x} \frac{0}{4}$ | $\begin{aligned} & \underset{0}{0} \\ & \underset{\sim}{7} \\ & \underset{\sim}{2} \end{aligned}$ | $\begin{aligned} & \underset{\sim}{0} \\ & \underset{\sim}{7} \\ & \underset{\sim}{2} \end{aligned}$ |  | $\begin{aligned} & \hat{o} \\ & 0 \\ & 0 \\ & \\ & \end{aligned}$ |  | $\begin{aligned} & \text { İ } \\ & \underset{y}{*} \\ & \underset{\sim}{7} \end{aligned}$ | $\begin{aligned} & \hat{o} \\ & \hat{0} \\ & \stackrel{n}{n} \\ & \end{aligned}$ | $\begin{aligned} & \text { N} \\ & \text { N} \\ & \underset{\sim}{f} \end{aligned}$ | $\begin{aligned} & \underset{\sim}{Z} \\ & \underset{\sim}{\underset{7}{2}} \end{aligned}$ | $\stackrel{\imath}{\AA}$ | $\begin{aligned} & \text { J } \\ & \text { I } \\ & \underset{\sim}{7} \end{aligned}$ |  | $\begin{aligned} & \stackrel{\infty}{\star} \\ & \stackrel{\text { N}}{\vdots} \end{aligned}$ |  |
|  | $\begin{aligned} & 0 \\ & \substack{0 \\ \vdots \\ \underset{\sim}{4} \\ \hline} \end{aligned}$ | $\begin{aligned} & \stackrel{0}{0} \\ & \stackrel{\rightharpoonup}{o} \\ & \underset{\sim}{1} \end{aligned}$ | $\begin{gathered} 2 \\ \stackrel{2}{5} \\ \underset{1}{1} \\ \end{gathered}$ | $\begin{gathered} \underset{\sim}{\underset{~}{c}} \\ \underset{\sim}{c} \\ \dot{\sim} \end{gathered}$ |  | $\begin{aligned} & 0 \\ & \stackrel{0}{2} \\ & \underset{\substack{2}}{1} \end{aligned}$ | $\begin{aligned} & \underset{\sim}{\underset{2}{2}} \\ & \stackrel{c}{\mathbf{~}} \end{aligned}$ | $\begin{aligned} & \text { I } \\ & \underset{6}{0} \\ & \underset{-1}{2} \end{aligned}$ | $\begin{aligned} & \circ \\ & \stackrel{0}{6} \\ & \stackrel{0}{9} \end{aligned}$ | $\stackrel{\circ}{\circ}$ $\stackrel{0}{\circ}$ $\stackrel{\circ}{\leftrightarrows}$ | $\begin{aligned} & \text { on } \\ & \stackrel{N}{6} \\ & \underset{~}{1} \end{aligned}$ | $\begin{aligned} & \stackrel{\circ}{0} \\ & \stackrel{0}{2} \\ & \underset{~}{7} \end{aligned}$ | $\begin{aligned} & \text { ơo } \\ & \stackrel{0}{\circ} \\ & \underset{~}{7} \end{aligned}$ |  |
| 瓦 | $\stackrel{0}{7}$ | $\stackrel{0}{\stackrel{\circ}{2}}$ | $\begin{gathered} \text { I } \\ \text { à } \\ -1 \end{gathered}$ | $\begin{gathered} \stackrel{\rightharpoonup}{0} \\ 0 \\ 0 \\ 0 \\ 0 \end{gathered}$ | $\begin{aligned} & \stackrel{\rightharpoonup}{6} \\ & \stackrel{y}{\infty} \\ & \underset{O}{0} \end{aligned}$ | $\underset{\text { A }}{\text { A }}$ |  | $\begin{aligned} & \stackrel{9}{6} \\ & \stackrel{y}{\infty} \\ & \stackrel{\circ}{\infty} \end{aligned}$ | $\underset{\text { 충 }}{\text { 충 }}$ |  | $\underset{\text { 층 }}{\text { 층 }}$ | $\begin{aligned} & \text { n} \\ & \stackrel{\rightharpoonup}{0} \\ & \stackrel{0}{0} \end{aligned}$ | $\stackrel{i n}{\stackrel{i}{\infty}} \stackrel{1}{\infty}$ | n O 0 0 0 |
| 逐 | $\frac{\stackrel{\rightharpoonup}{\lambda}}{2}$ | $\frac{\stackrel{\rightharpoonup}{A}}{\partial}$ | $\begin{aligned} & \underset{\sim}{\mathrm{N}} \\ & \underset{\sim}{2} \end{aligned}$ | $\frac{\stackrel{\rightharpoonup}{A}}{\partial}$ | $\frac{\mathrm{E}}{\mathrm{E}}$ | $\frac{\stackrel{\rightharpoonup}{\lambda}}{2}$ | $\frac{\text { 틀 }}{2}$ | $\begin{aligned} & \text { 층 } \\ & \stackrel{i}{2} \end{aligned}$ | $\frac{\underset{A}{A}}{\hat{O}}$ | $\frac{\text { 틀 }}{2}$ | $\begin{aligned} & \text { 츨 } \\ & \stackrel{i}{0} \end{aligned}$ | $\frac{\stackrel{\rightharpoonup}{A}}{\hat{o}}$ | $\begin{aligned} & \stackrel{\rightharpoonup}{\lambda} \\ & \stackrel{i}{0} \end{aligned}$ | $\frac{\Sigma}{\hat{a}}$ |
|  | $\begin{aligned} & \text { 㫭 } \\ & \text { on } \\ & \vdots \\ & \vdots \end{aligned}$ |  |  | $\begin{aligned} & \hat{\infty} \\ & \frac{8}{4} \\ & \text { N } \\ & \end{aligned}$ |  | $\pm$ $\vdots$ $\vdots$ $\vdots$ $\vdots$ |  |  | $\pm$ <br>  <br> $\vdots$ <br> $\vdots$ | $\stackrel{5}{0}$ $\underset{7}{7}$ 7 7 | $\underset{N}{Z}$ + + $\vdots$ $\vdots$ |  |  |  |
| N | $\bigcirc$ | － | $\bigcirc$ | － | － | － | $\bigcirc$ | $\bigcirc$ | $\bigcirc$ | $$ | $\bigcirc$ | $$ | $\bigcirc$ |  |
| $\Leftrightarrow \stackrel{B}{0}$ | $\bigcirc$ | － | $\begin{aligned} & \text { In } \\ & \text { N } \\ & 0 \end{aligned}$ | $\bigcirc$ | $\bigcirc$ | $\begin{gathered} \infty \\ \underset{\alpha}{\alpha} \\ \stackrel{\rightharpoonup}{i} \end{gathered}$ | － | － | $\begin{aligned} & \infty \\ & \text { तิ } \\ & \text { 人े } \end{aligned}$ | $\begin{aligned} & \text { 合 } \\ & \underset{\sim}{N} \end{aligned}$ | $\begin{aligned} & \infty \\ & \stackrel{\alpha}{\alpha} \\ & \stackrel{i}{1} \end{aligned}$ | $\begin{aligned} & \text { 花 } \\ & \underset{i}{\text { N}} \end{aligned}$ | $\begin{gathered} \infty \\ \stackrel{\alpha}{\alpha} \\ \stackrel{i}{~} \end{gathered}$ |  |
| $\Leftrightarrow \text { 合若 }$ | 0 | － | $\begin{aligned} & \text { n } \\ & \underset{\sim}{n} \\ & 0 \end{aligned}$ | － | $\begin{aligned} & \infty \\ & \text { ふ̀ } \\ & \text { ה } \end{aligned}$ | $\begin{gathered} \infty \\ \underset{\alpha}{2} \\ \vdots \end{gathered}$ | － | $\begin{aligned} & \infty \\ & \text { ふ̀ } \\ & \text { 人} \end{aligned}$ | $\begin{aligned} & \infty \\ & \text { ふ̀ } \\ & \text { 人े } \end{aligned}$ | $\underset{\substack{\text { N } \\ \multirow{2}{*}{\hline}\\ \hline}}{\text { n}}$ |  | $\underset{\substack{\text { N } \\ \multirow{2}{*}{\hline}\\ \hline}}{\text { n}}$ | $\begin{aligned} & \infty \\ & \text { ふ̀ } \\ & \text { 人̀ } \end{aligned}$ |  |
| $\leftrightarrow \stackrel{S}{0}$ | $\begin{gathered} \pi \\ \\ 0 \end{gathered}$ | $\begin{aligned} & \text { n } \\ & \text { ה } \\ & 0 \end{aligned}$ | $\begin{aligned} & \tilde{\pi} \\ & \\ & 0 \end{aligned}$ | $\frac{\infty}{\grave{\alpha}}$ | $\frac{\infty}{\grave{\alpha}}$ | $$ | $$ | $\frac{\infty}{\grave{\alpha}}$ | $\begin{aligned} & \infty \\ & \underset{\sim}{\grave{\alpha}} \end{aligned}$ | $$ | $\frac{\infty}{\grave{\alpha}}$ |  |  |  |
| $\frac{\square}{\frac{5}{4}}$ | $\cup$ | $\checkmark$ | 二 | $\cup$ | $\checkmark$ | U | $0^{\circ}$ | vo | vo | ט | U0 | 0 | 0 | ט゙ |
| 䓞 |  |  |  | $\begin{aligned} & 2 \\ & 2 \\ & z \\ & z \end{aligned}$ | $\underset{y}{\text { En }}$ | $\begin{aligned} & \mathbb{E} \\ & = \\ & i \\ & i \\ & 0 \end{aligned}$ |  | $\begin{aligned} & 1 \\ & y_{0}^{2} \\ & v_{0} \\ & 0 \\ & 0 \\ & 0 \\ & 0 \\ & \text { su } \end{aligned}$ |  |  |  | $\begin{aligned} & 1 \\ & 0 \\ & 0 \\ & 0 \\ & 0 \\ & 0 \\ & 0 \\ & 1 \\ & \vdots \\ & 0 \\ & 0 \\ & 0 \\ & 0 \\ & 0 \\ & 0 \\ & 0 \\ & 1 \\ & 0 \\ & 0 \\ & 0 \\ & 0 \\ & 0 \\ & 0 \\ & 0 \\ & 0 \\ & 0 \end{aligned}$ |  | $\begin{aligned} & 1 \\ & z^{n} \\ & 0 \\ & 0 \\ & 0 \\ & y^{1} \\ & 1 \\ & 0 \\ & 0 \\ & 0 \\ & 0 \\ & 0 \\ & 0 \\ & 0 \\ & 0 \\ & 1 \\ & 0 \\ & 0 \end{aligned}$ |

Table 23.94. The energy parameters $(\mathrm{eV})$ of functional groups of alkyl bismuths.

| Parameters | $\begin{aligned} & B i-C \\ & \text { Group } \end{aligned}$ | $\mathrm{CH}_{3}$ Group | $\begin{gathered} \mathrm{CH}_{2} \\ \text { Group } \end{gathered}$ | $\begin{aligned} & \mathrm{CH} \text { (i) } \\ & \text { Group } \end{aligned}$ | $\begin{gathered} C-C \text { (a) } \\ \text { Group } \end{gathered}$ | $\begin{aligned} & C-C \text { (b) } \\ & \text { Group } \end{aligned}$ | $\begin{aligned} & C-C(c) \\ & \text { Group } \end{aligned}$ | $\begin{aligned} & C-C(\mathrm{~d}) \\ & \text { Group } \end{aligned}$ | $\begin{gathered} C-C(e) \\ \text { Group } \end{gathered}$ | $\begin{gathered} C-C(\mathrm{f}) \\ \text { Group } \end{gathered}$ | $C \stackrel{3 e}{=} C$ <br> Group | $\begin{aligned} & \mathrm{CH} \text { (ii) } \\ & \text { Group } \end{aligned}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $f_{1}$ | 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 |
| $C_{1}$ | 0.375 | 0.75 | 0.75 | 0.75 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.75 |
| $\mathrm{C}_{2}$ | 0.68581 | 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 |
| $c_{2}$ | 0.68581 | 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 |
| $C_{10}$ | 0.375 | 0.75 | 0.75 | 0.75 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.75 |
| $C_{20}$ | 0.68581 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 0.85252 | 1 |
| $V_{e}(\mathrm{eV})$ | -31.82881 | -107.32728 | -70.41425 | -35.12015 | -28.79214 | -28.79214 | -29.10112 | -28.79214 | -29.10112 | -29.10112 | -101.12679 | -37.10024 |
| $V_{p}(\mathrm{eV})$ | 6.59529 | 38.92728 | 25.78002 | 12.87680 | 9.33352 | 9.33352 | 9.37273 | 9.33352 | 9.37273 | 9.37273 | 20.69825 | 13.17125 |
| $T(\mathrm{eV})$ | 7.27014 | 32.53914 | 21.06675 | 10.48582 | 6.77464 | 6.77464 | 6.90500 | 6.77464 | 6.90500 | 6.90500 | 34.31559 | 11.58941 |
| $V_{m}(\mathrm{eV})$ | -3.63507 | -16.26957 | -10.53337 | -5.24291 | -3.38732 | -3.38732 | -3.45250 | -3.38732 | -3.45250 | -3.45250 | -17.15779 | -5.79470 |
| E(Aоіно) (eV) | -10.03679 | -15.56407 | -15.56407 | -14.63489 | -15.56407 | -15.56407 | -15.35946 | -15.56407 | -15.35946 | -15.35946 | 0 | -14.63489 |
| $\Delta E_{H_{2} \text { МО }}$ (АоІно) $(\mathrm{eV})$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | -1.13379 |
|  | -10.03679 | -15.56407 | -15.56407 | -14.63489 | -15.56407 | -15.56407 | -15.35946 | -15.56407 | -15.35946 | -15.35946 | 0 | -13.50110 |
| $E_{T}\left(\mathrm{H}_{2} \mathrm{MO}\right)(\mathrm{eV})$ | -31.63524 | -67.69451 | -49.66493 | -31.63533 | -31.63537 | -31.63537 | -31.63535 | -31.63537 | -31.63535 | -31.63535 | -63.27075 | -31.63539 |
| $E_{T}\left(\right.$ atom-atom, $\left.\mathrm{msp}{ }^{3} \cdot \mathrm{AO}\right)(\mathrm{eV})$ | 1.04251 | 0 | 0 | 0 | -1.85836 | -1.85836 | -1.44915 | -1.85836 | -1.44915 | -1.44915 | -2.26759 | -0.56690 |
| $E_{T}($ мо) $(\mathrm{eV})$ | -30.59286 | -67.69450 | -49.66493 | -31.63537 | -33.49373 | -33.49373 | -33.08452 | -33.49373 | -33.08452 | -33.08452 | -65.53833 | -32.20226 |
| $\omega$ ( $10^{15} \mathrm{rad} / \mathrm{s}$ ) | 33.4696 | 24.9286 | 24.2751 | 24.1759 | 9.43699 | 9.43699 | 15.4846 | 9.43699 | 9.55643 | 9.55643 | 49.7272 | 26.4826 |
| $E_{K}(\mathrm{eV})$ | 22.03030 | 16.40846 | 15.97831 | 15.91299 | 6.21159 | 6.21159 | 10.19220 | 6.21159 | 6.29021 | 6.29021 | 32.73133 | 17.43132 |
| $\bar{E}_{D}(\mathrm{eV})$ | -0.28408 | -0.25352 | -0.25017 | -0.24966 | -0.16515 | -0.16515 | -0.20896 | -0.16515 | -0.16416 | -0.16416 | -0.35806 | -0.26130 |
| $\bar{E}_{\text {Kvb }}(\mathrm{eV})$ | $\begin{gathered} 0.14878 \\ {[66]} \end{gathered}$ | $\begin{gathered} 0.35532 \\ \text { (Eq. }(13.458)) \end{gathered}$ | $\begin{gathered} 0.35532 \\ \text { (Eq. }(13.458) \text { ) } \end{gathered}$ | $\begin{gathered} 0.35532 \\ \text { (Eq. (13.458)) } \end{gathered}$ | $\begin{gathered} 0.12312 \\ {[6]} \end{gathered}$ | $\begin{gathered} 0.17978 \\ {[7]} \\ \hline \end{gathered}$ | $\begin{gathered} 0.09944 \\ {[8]} \end{gathered}$ | $\begin{gathered} 0.12312 \\ {[6]} \end{gathered}$ | $\begin{gathered} 0.12312 \\ {[6]} \end{gathered}$ | $\begin{gathered} 0.12312 \\ {[6]} \end{gathered}$ | $\begin{gathered} 0.19649 \\ {[30]} \\ \hline \end{gathered}$ | $\begin{gathered} 0.35532 \\ \text { Eq. }(13.458) \\ \hline \end{gathered}$ |
| $\bar{E}_{\text {asc }}(\mathrm{eV})$ | -0.20968 | -0.22757 | -0.14502 | -0.07200 | -0.10359 | -0.07526 | -0.15924 | -0.10359 | -0.10260 | -0.10260 | -0.25982 | -0.08364 |
| $E_{\text {mag }}(\mathrm{eV})$ | 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) $(\mathrm{eV})$ | -30.80254 | -67.92207 | -49.80996 | -31.70737 | -33.59732 | -33.49373 | -33.24376 | -33.59732 | -33.18712 | -33.18712 | -49.54347 | -32.28590 |
|  | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 |
| $E_{\text {intual }}(\mathrm{cs}$, AO/ $/$ HO) $(\mathrm{eV})$ | 0 | -13.59844 | -13.59844 | -13.59844 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | -13.59844 |
| $E_{D}($ Group $)(\mathrm{eV})$ | 1.53276 | 12.49186 | 7.83016 | 3.32601 | 4.32754 | 4.29921 | 3.97398 | 4.17951 | 3.62128 | 3.91734 | 5.63881 | 3.90454 |

Table 23.95 . The total bond energies of alkyl bismuths calculated using the functional group composition and the energies of Table 23.94 compared to the

[^4]Total Bond $\quad \begin{gathered}\text { Total Bond } \\ \text { Ener } \\ \text { (eV) }\end{gathered}$

78.3918184
163.751
164.66490

| Atoms of Angle | $\begin{gathered} 2 c^{\prime} \\ \text { Bond } 1 \\ \left(a_{0}\right) \end{gathered}$ | $\begin{gathered} 2 c^{\prime} \\ \text { Bond 2 } \\ \left(a_{0}\right) \end{gathered}$ |  | $E_{\text {Coulombic }}$ or $E$ $E$ Atom 1 | Atom 1Hybridization <br> Designation(Table 15.3.A) | $\begin{aligned} & E_{\text {Conlumbile } e} \\ & \text { Atom } 2 \end{aligned}$ | $\begin{gathered} \text { Atom 2 } \\ \text { Hybridization } \\ \text { Designation } \\ \text { (Table 15.3.A) } \\ \hline \end{gathered}$ | $\begin{gathered} c_{2} \\ \text { Atom } 1 \end{gathered}$ | $\begin{gathered} c_{2} \\ \text { Atom } 2 \end{gathered}$ | $C_{1}$ | $C_{2}$ | $c_{1}$ | $c^{\prime}$ | $\begin{aligned} & E_{T} \\ & (\mathrm{eV}) \end{aligned}$ | $\begin{aligned} & \theta_{0} \\ & \left({ }^{\circ}\right) \end{aligned}$ | $\begin{gathered} \theta \\ \left.{ }^{\circ}\right) \end{gathered}$ | $\begin{aligned} & \theta_{2} \\ & \left({ }^{\circ}\right) \end{aligned}$ | Cal. $\theta$ <br> $\left({ }^{\circ}\right)$ | $\underset{\left({ }^{\circ}\right)}{\substack{\text { Exp. }}}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\begin{aligned} & \text { Methyl } \\ & \angle H C_{a} H \end{aligned}$ | 2.09711 | 2.09711 | 3.4252 | -15.75493 | 7 | H | H | 0.86359 | 1 | 1 | 1 | 0.75 | 1.15796 | 0 |  |  |  | 109.50 |  |
| $\angle H_{a} C_{a} B i$ |  |  |  |  |  |  |  |  |  |  |  |  |  |  | 70.56 |  |  | 109.44 |  |
| $\angle C_{a} B C_{b}$ | 4.12592 | 4.12592 | 6.1806 | -15.18804 | 2 | -15.18804 | 2 | 0.89582 | 0.89582 | 1 | 1 | 1 | 0.89582 | -1.85836 |  |  |  | 97.01 | $\begin{array}{\|c\|} \hline 97.1 \\ \text { (trimethylbismuth) } \end{array}$ |
| $\begin{gathered} \text { Methylene } \\ \angle H C_{a} H \\ \hline \end{gathered}$ | 2.11106 | 2.11106 | 3.4252 | -15.75493 | 7 | H | H | 0.86359 | 1 | 1 | 1 | 0.75 | 1.15796 | 0 |  |  |  | 108.44 | $\begin{gathered} 107 \\ \text { (propane) } \\ \hline \end{gathered}$ |
| $\angle C_{a} C_{b} C_{c}$ |  |  |  |  |  |  |  |  |  |  |  |  |  |  | 69.51 |  |  | 110.49 | 112 (propane) 13.8 (butane) 110.8 (isobutane) |
| $\angle C_{a} C_{b} H$ |  |  |  |  |  |  |  |  |  |  |  |  |  |  | 69.51 |  |  | 110.49 | $\begin{gathered} 111.0 \\ \text { (butane) } \\ 111.4 \\ \text { (isobutane) } \end{gathered}$ |
| $\begin{aligned} & \text { Methyl } \\ & \angle H C_{a} H \end{aligned}$ | 2.09711 | 2.09711 | 3.4252 | -15.75493 | 7 | H | H | 0.86359 | 1 | 1 | 1 | 0.75 | 1.15796 | 0 |  |  |  | 109.50 |  |
| $\angle C_{a} C_{b} C_{c}$ |  |  |  |  |  |  |  |  |  |  |  |  |  |  | 70.56 |  |  | 109.44 |  |
| $\angle C_{a} C_{b} H$ |  |  |  |  |  |  |  |  |  |  |  |  |  |  | 70.56 |  |  | 109.44 |  |
| $\begin{aligned} & \angle C_{a} C_{C} C_{a} \\ & \text { iso } C_{a} \end{aligned}$ | 2.91547 | 2.91547 | 4.7958 | $\underset{C_{b}}{-16.68412}$ | 26 | $\begin{gathered} -16.68412 \\ C_{c} \end{gathered}$ | 26 | 0.81549 | 0.81549 | 1 | 1 | 1 | 0.81549 | $-1.85836$ |  |  |  | 110.67 | $\begin{gathered} 110.8 \\ \text { (isobutane) } \end{gathered}$ |
| $\begin{gathered} \angle C_{b} C_{a} H \\ \text { iso } C_{a} \\ \hline \end{gathered}$ | 2.91547 | 2.11323 | 4.1633 | $\begin{gathered} -15.55033 \\ C_{a} \end{gathered}$ | 5 | $\begin{gathered} -14.82575 \\ C_{b} \end{gathered}$ | 1 | 0.87495 | 0.91771 | 0.75 | 1 | 0.75 | 1.04887 | 0 |  |  |  | 110.76 |  |
| $\begin{gathered} \angle C_{a} C_{b} H \\ \text { iso } C_{a} \end{gathered}$ | 2.91547 | 2.09711 | 4.1633 | $\begin{gathered} -15.55033 \\ C_{b} \end{gathered}$ | 5 | $\begin{array}{\|c} -14.82575 \\ C_{a} \end{array}$ | 1 | 0.87495 | 0.91771 | 0.75 | 1 | 0.75 | 1.04887 | 0 |  |  |  | 111.27 | $\begin{gathered} 111.4 \\ \text { (isobutane) } \end{gathered}$ |
| $\begin{aligned} & \angle C_{b} C_{a} C_{b} C_{b} \\ & \text { tert } C_{a} \\ & \hline \end{aligned}$ | 2.90327 | 2.90327 | 4.7958 | $\begin{gathered} -16.68412 \\ C_{b} \end{gathered}$ | 26 | $\begin{gathered} -16.68412 \\ C_{b} \end{gathered}$ | 26 | 0.81549 | 0.81549 | 1 | 1 | 1 | 0.81549 | -1.85836 |  |  |  | 111.37 | $\begin{gathered} 110.8 \\ \text { (isobutane) } \end{gathered}$ |
| $\angle C_{b} C_{a} C_{d}$ |  |  |  |  |  |  |  |  |  |  |  |  |  |  | 72.50 |  |  | 107.50 |  |

## SUMMARY TABLES OF ORGANOMETALLIC AND COORDINATE 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 23.97.1. Summary results of organoaluminum compounds.

| Formula | Name | Calculated <br> Total Bond <br> Energy $(\mathrm{eV})$ | Experimental <br> Total Bond <br> Energy $(\mathrm{eV})$ | Relative <br> Error |
| :--- | :--- | :---: | :---: | :---: |
| $\mathrm{C}_{2} \mathrm{H}_{7} \mathrm{Al}$ | dimethylaluminum hydride | 34.31171 | $34.37797^{\mathrm{a}}[11]$ | 0.00193 |
| $\mathrm{C}_{3} \mathrm{H}_{9} \mathrm{Al}$ | trimethyl aluminum | 47.10960 | $46.95319[10]$ | -0.00333 |
| $\mathrm{C}_{4} \mathrm{H}_{11} \mathrm{Al}$ | diethylaluminum hydride | 58.62711 | $60.10948^{\mathrm{b}}[10]$ | 0.02466 |
| $\mathrm{C}_{6} \mathrm{H}_{15} \mathrm{Al}$ | triethylaluminum hydride | 83.58270 | $83.58176[10]$ | -0.00001 |
| $\mathrm{C}_{6} \mathrm{H}_{15} \mathrm{Al}$ | di-n-propylaluminum hydride | 82.94251 | $84.40566^{\mathrm{b}}[10]$ | 0.01733 |
| $\mathrm{C}_{9} \mathrm{H}_{21} \mathrm{Al}$ | tri-n-propyl aluminum | 120.05580 | $121.06458^{\mathrm{b}}[10]$ | 0.00833 |
| $\mathrm{C}_{8} \mathrm{H}_{19} \mathrm{Al}$ | di-n-butylaluminum hydride | 107.25791 | $108.71051^{\mathrm{b}}[10]$ | 0.01336 |
| $\mathrm{C}_{8} \mathrm{H}_{19} \mathrm{Al}$ | di-isobutylaluminum hydride | 107.40303 | $108.77556^{\mathrm{b}}[10]$ | 0.01262 |
| $\mathrm{C}_{12} \mathrm{H}_{27} \mathrm{Al}$ | tri-n-butyl aluminum | 156.52890 | $157.42429^{\mathrm{b}}[10]$ | 0.00569 |
| $\mathrm{C}_{12} \mathrm{H}_{27} \mathrm{Al}$ | tri-isobutyl aluminum | 156.74658 | $157.58908^{\mathrm{b}}[10]$ | 0.00535 |

[^5]Table 23.97.2. Summary results of scandium coordinate compounds.

| Formula | Name | Calculated <br> Total Bond <br> Energy (eV) | Experimental <br> Total Bond <br> Energy (eV) | Relative Error |
| :--- | :--- | :---: | :---: | :---: |
| ScF | scandium fluoride | 6.34474 | $6.16925[15]$ | -0.02845 |
| $\mathrm{ScF}_{2}$ | scandium difluoride | 12.11937 | $12.19556[15]$ | 0.00625 |
| $\mathrm{ScF}_{3}$ | scandium trifluoride | 19.28412 | $19.27994[15]$ | -0.00022 |
| ScCl | scandium chloride | 4.05515 | $4.00192[15]$ | -0.01330 |
| ScO | scandium oxide | 7.03426 | $7.08349[15]$ | 0.00695 |

Table 23.97.3. Summary results of titanium coordinate compounds.

| Formula | Name | Calculated <br> Total Bond <br> Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
| :---: | :---: | :---: | :---: | :---: |
| TiF | titanium fluoride | 6.44997 | 6.41871 [21] | -0.00487 |
| $\mathrm{TiF}_{2}$ | titanium difluoride | 13.77532 | 13.66390 [21] | -0.00815 |
| $\mathrm{TiF}_{3}$ | titanium trifluoride | 19.63961 | 19.64671 [21] | 0.00036 |
| $\mathrm{TiF}_{4}$ | titanium tetrafluoride | 24.66085 | 24.23470 [21] | -0.01758 |
| TiCl | titanium chloride | 4.56209 | 4.56198 [22] | -0.00003 |
| $\mathrm{TiCl}_{2}$ | titanium dichloride | 10.02025 | 9.87408 [22] | -0.01517 |
| $\mathrm{TiCl}_{3}$ | titanium trichloride | 14.28674 | 14.22984 [22] | -0.00400 |
| $\mathrm{TiCl}_{4}$ | titanium tetrachloride | 17.94949 | 17.82402 [22] | -0.00704 |
| TiBr | titanium bromide | 3.77936 | 3.78466 [19] | 0.00140 |
| $\mathrm{TiBr}_{2}$ | titanium dibromide | 8.91650 | 8.93012 [19] | 0.00153 |
| $\mathrm{TiBr}_{3}$ | titanium tribromide | 12.07765 | 12.02246 [19] | -0.00459 |
| $\mathrm{TiBr}_{4}$ | titanium tetrabromide | 14.90122 | 14.93239 [19] | 0.00209 |
| TiI | titanium iodide | 3.16446 | 3.15504 [20] | -0.00299 |
| $\mathrm{TiI}_{2}$ | titanium diiodide | 7.35550 | 7.29291 [20] | -0.00858 |
| TiI3 | titanium triiodide | 9.74119 | 9.71935 [20] | -0.00225 |
| $\mathrm{TiI}_{4}$ | titanium tetraiodide | 12.10014 | 12.14569 [20] | 0.00375 |
| TiO | titanium oxide | 7.02729 | 7.00341 [23] | -0.00341 |
| $\mathrm{TiO}_{2}$ | titanium dioxide | 13.23528 | 13.21050 [23] | -0.00188 |
| TiOF | titanium fluoride oxide | 12.78285 | 12.77353 [23] | -0.00073 |
| $\mathrm{TiOF}_{2}$ | titanium difluoride oxide | 18.94807 | 18.66983 [23] | -0.01490 |
| TiOCl | titanium chloride oxide | 11.10501 | 11.25669 [23] | 0.01347 |
| $\mathrm{TiOCl}_{2}$ | titanium dichloride oxide | 15.59238 | 15.54295 [23] | -0.00318 |

Table 23.97.4. Summary results of vanadium coordinate compounds.

| Formula | Name | Calculated <br> Total Bond <br> Energy $(\mathrm{eV})$ | Experimental <br> Total Bond <br> Energy $(\mathrm{eV})$ | Relative Error |
| :--- | :--- | :---: | :---: | :---: |
| $\mathrm{VF}_{5}$ | vanadium pentafluoride | 24.06031 | $24.24139[15]$ | 0.00747 |
| $\mathrm{VCl}_{4}$ | vanadium tetrachloride | 15.84635 | $15.80570[15]$ | -0.00257 |
| VN | vanadium nitride | 4.85655 | $4.81931[24]$ | -0.00775 |
| VO | vanadium oxide | 6.37803 | $6.60264[15]$ | 0.03402 |
| $\mathrm{VO}_{2}$ | vanadium dioxide | 12.75606 | $12.89729[34]$ | 0.01095 |
| $\mathrm{VOCl}_{3}$ | vanadium trichloride oxide | 18.26279 | $18.87469[15]$ | 0.03242 |
| $\mathrm{~V}(\mathrm{CO})_{6}$ | vanadium hexacarbonyl | 75.26791 | $75.63369[32]$ | 0.00484 |
| $\mathrm{~V}(\mathrm{C} 6 \mathrm{H} 6))_{2}$ | dibenzene vanadium | 119.80633 | $121.20193 \mathrm{a}[33]$ | 0.01151 |
| ${ }^{\mathrm{a}}$ Liquid. |  |  |  |  |

Table 23.97.5. Summary results of chromium coordinate compounds.

| Formula | Name | Calculated <br> Total Bond <br> Energy (eV) | Experimental <br> Total Bond <br> Energy (eV) | Relative Error |
| :--- | :--- | :---: | :---: | :---: |
| $\mathrm{CrF}_{2}$ | chromium difluoride | 10.91988 | $10.92685[15]$ | 0.00064 |
| $\mathrm{CrCl}_{2}$ | chromium dichloride | 7.98449 | $7.96513[15]$ | -0.00243 |
| CrO | chromium oxide | 4.73854 | $4.75515[37]$ | 0.00349 |
| $\mathrm{CrO}_{2}$ | chromium dioxide | 10.02583 | $10.04924[37]$ | 0.00233 |
| $\mathrm{CrO}_{3}$ | chromium trioxide | 14.83000 | $14.85404[37]$ | 0.00162 |
| $\mathrm{CrO}_{2} \mathrm{Cl}_{2}$ | chromium dichloride dioxide | 17.46158 | $17.30608[15]$ | -0.00899 |
| $\mathrm{Cr}_{2}(\mathrm{CO})_{6}$ | chromium hexacarbonyl | 74.22588 | $74.61872[44]$ | 0.00526 |
| $\mathrm{Cr}\left(\mathrm{C}_{6} \mathrm{H}_{6}\right)_{2}$ | dibenzene chromium | 117.93345 | $117.97971[44]$ | 0.00039 |
| $\mathrm{Cr}\left(\left(\mathrm{CH}_{3}\right)_{3} \mathrm{C}_{6} \mathrm{H}_{3}\right)_{2}$ | di-(1,2,4-trimethylbenzene $)$ | 191.27849 | $192.42933 \mathrm{a}[44]$ | 0.00598 |

${ }^{\mathrm{a}}$ Liquid.
Table 23.97.6. Summary results of manganese coordinate compounds.

| Formula | Name | Calculated <br> Total Bond <br> Energy $(\mathrm{eV})$ | Experimental <br> Total Bond <br> Energy (eV) | Relative Error |
| :--- | :--- | :---: | :---: | :---: |
| MnF | manganese fluoride | 4.03858 | $3.97567[15]$ | -0.01582 |
| MnCl | manganese chloride | 3.74528 | $3.73801[15]$ | -0.00194 |
| $\mathrm{Mn}_{2}(\mathrm{CO})_{10}$ | dimanganese decacarbonyl | 123.78299 | $122.70895[49]$ | -0.00875 |

Table 23.97.7. Summary results of iron coordinate compounds.

| Formula | Name | Calculated <br> Total Bond <br> Energy (eV) | Experimental <br> Total Bond <br> Energy (eV) | Relative Error |
| :--- | :--- | :---: | :---: | :---: |
| FeF | iron fluoride | 4.65726 | $4.63464[15]$ | -0.00488 |
| $\mathrm{FeF}_{2}$ | iron difluoride | 10.03188 | $9.98015[15]$ | -0.00518 |
| $\mathrm{FeF}_{3}$ | iron trifluoride | 15.31508 | $15.25194[15]$ | -0.00414 |
| $\mathrm{FeCl}^{\mathrm{FeCl}_{2}}$ | iron chloride | 2.96772 | $2.97466[15]$ | 0.00233 |
| $\mathrm{FeCl}_{3}$ | iron dichloride | 8.07880 | $8.28632[15]$ | 0.02504 |
| FeO | iron trichloride | 10.82348 | $10.70065[50]$ | -0.01148 |
| $\mathrm{Fe}(\mathrm{CO})_{5}$ | iron oxide | 4.09983 | $4.20895[15]$ | 0.02593 |
| $\mathrm{Fe}(\mathrm{C} 5 \mathrm{C} 5)_{2}$ | iron pentacarbonyl | 61.75623 | $61.91846[29]$ | 0.00262 |
|  | (ferrocene) | 98.90760 | $98.95272[53]$ | 0.00046 |

Table 23.97.8. Summary results of cobalt coordinate compounds.

| Formula | Name | Calculated <br> Total Bond <br> Energy $(\mathrm{eV})$ | Experimental <br> Total Bond <br> Energy (eV) | Relative Error |
| :--- | :--- | :---: | :---: | :---: |
| $\mathrm{CoF}_{2}$ | cobalt difluoride | 9.45115 | $9.75552[54]$ | 0.03120 |
| CoCl | cobalt chloride | 3.66504 | $3.68049[15]$ | 0.00420 |
| $\mathrm{Col}_{2}$ | cobalt dichloride | 7.98467 | $7.92106[15]$ | -0.00803 |
| $\mathrm{CoCl}_{3}$ | cobalt trichloride | 9.83521 | $9.87205[15]$ | 0.00373 |
| $\mathrm{CoH}(\mathrm{CO})_{4}$ | cobalt tetracarbonyl hydride | 50.33217 | $50.36087[53]$ | 0.00057 |

Table 23.97.9. Summary results of nickel coordinate compounds.

| Formula | Name | Calculated <br> Total Bond <br> Energy (eV) | Experimental <br> Total Bond <br> Energy (eV) | Relative Error |
| :--- | :--- | :---: | :---: | :---: |
| NiCl | nickel chloride | 3.84184 | $3.82934[59]$ | -0.00327 |
| $\mathrm{NiCl}_{2}$ | nickel dichloride | 7.76628 | $7.74066[59]$ | -0.00331 |
| $\mathrm{Ni}(\mathrm{CO})_{4}$ | nickel tetracarbonyl | 50.79297 | $50.77632[55]$ | -0.00033 |
| $\mathrm{Ni}\left(\mathrm{C}_{5} \mathrm{H}_{5}\right)_{2}$ | bis-cyclopentadienyl nickel <br> (nickelocene) | 97.73062 | $97.84649[53]$ | 0.00118 |

Table 23.97.10. Summary results of copper coordinate compounds.

| Formula | Name | Calculated <br> Total Bond <br> Energy $(\mathrm{eV})$ | Experimental <br> Total Bond <br> Energy (eV) | Relative Error |
| :--- | :--- | :---: | :---: | :---: |
| CuF | copper fluoride | 4.39399 | $4.44620[63]$ | 0.01174 |
| $\mathrm{CuF}_{2}$ | copper difluoride | 7.91246 | $7.89040[63]$ | -0.00280 |
| $\mathrm{CuCl}_{\mathrm{CuO}}$ | copper chloride | 3.91240 | $3.80870[15]$ | -0.02723 |

Table 23.97.11. Summary results of zinc coordinate compounds.

| Formula | Name | Calculated <br> Total Bond <br> Energy (eV) | Experimental <br> Total Bond <br> Energy (eV) | Relative Error |
| :--- | :--- | :---: | :---: | :---: |
| ZnCl | zinc chloride | 2.56175 | $2.56529[15]$ | 0.00138 |
| ZnCl | zinc dichloride | 6.68749 | $6.63675[15]$ | -0.00764 |
| ${\mathrm{Zn}\left(\mathrm{CH}_{3}\right)_{2}}^{\left(\mathrm{CH}_{3} \mathrm{CH}_{2}\right)_{2} \mathrm{Zn}}$ | dimethylzinc | 29.35815 | $29.21367[15]$ | -0.00495 |
| $\left(\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CH}_{2}\right)_{2} \mathrm{Zn}$ | diethylzinc | 53.67355 | $53.00987[65]$ | -0.01252 |
| $\left(\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{CH}_{2}\right)_{2} \mathrm{Zn}$ | di-n-propylzinc | 77.98895 | $77.67464[65]$ | -0.00405 |

Table 23.97.12. Summary results of germanium compounds.

| Formula | Name | Calculated <br> Total Bond <br> Energy (eV) | Experimental <br> Total Bond <br> Energy (eV) | Relative Error |
| :--- | :--- | :---: | :---: | :---: |
| $\mathrm{C}_{8} \mathrm{H}_{20} \mathrm{Ge}$ | tetraethylgermanium | 109.99686 | $110.18166[67]$ | 0.00168 |
| $\mathrm{C}_{12} \mathrm{H}_{22} \mathrm{Ge}$ | tetra-n-propylgermanium | 158.62766 | $158.63092[67]$ | 0.00002 |
| $\mathrm{C}_{12} \mathrm{H}_{30} \mathrm{Ge}_{2}$ | hexaethyldigermanium | 167.88982 | $167.89836[67]$ | 0.00005 |

Table 23.97.13. Summary results of tin compounds.

| Formula | Name | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
| :---: | :---: | :---: | :---: | :---: |
| $\mathrm{SnCl}_{4}$ | tin tetrachloride | 12.95756 | 13.03704 [82] | 0.00610 |
| $\mathrm{CH}_{3} \mathrm{Cl}_{3} \mathrm{Sn}$ | methyltin trichloride | 24.69530 | $25.69118^{\text {a }}$ [83] | 0.03876 |
| $\mathrm{C}_{2} \mathrm{H}_{6} \mathrm{Cl}_{2} \mathrm{Sn}$ | dimethyltin dichloride | 36.43304 | 37.12369 [84] | 0.01860 |
| $\mathrm{C}_{3} \mathrm{H}_{9} \mathrm{ClSn}$ | trimethyltin chloride | 48.17077 | 49.00689 [84] | 0.01706 |
| $\mathrm{SnBr}_{4}$ | tin tetrabromide | 10.98655 | 11.01994 [82] | 0.00303 |
| $\mathrm{C}_{3} \mathrm{H}_{9} \mathrm{BrSn}$ | trimethyltin bromide | 47.67802 | 48.35363 [84] | 0.01397 |
| $\mathrm{C}_{12} \mathrm{H}_{10} \mathrm{Br}_{2} \mathrm{Sn}$ | diphenyltin dibromide | 117.17489 | $117.36647^{\text {a }}$ [83] | 0.00163 |
| $\mathrm{C}_{12} \mathrm{H}_{27} \mathrm{BrSn}$ | tri-n-butyltin bromide | 157.09732 | $157.26555^{\text {a }}$ [83] | 0.00107 |
| $\mathrm{C}_{18} \mathrm{H}_{15} \mathrm{BrSn}$ | triphenyltin bromide | 170.26905 | $169.91511^{\text {a }}$ [83] | -0.00208 |
| $\mathrm{SnI}_{4}$ | tin tetraiodide | 9.71697 | 9.73306 [85] | 0.00165 |
| $\mathrm{C}_{3} \mathrm{H}_{9} \mathrm{Sn}$ | trimethyltin iodide | 47.36062 | 47.69852 [84] | 0.00708 |
| $\mathrm{C}_{18} \mathrm{H}_{15} \mathrm{SnI}$ | triphenyltin iodide | 169.95165 | $167.87948^{\text {a }}$ [84] | -0.01234 |
| SnO | tin oxide | 5.61858 | 5.54770 [82] | -0.01278 |
| $\mathrm{SnH}_{4}$ | stannane | 10.54137 | 10.47181 [82] | -0.00664 |
| $\mathrm{C}_{2} \mathrm{H}_{8} \mathrm{Sn}$ | dimethylstannane | 35.22494 | 35.14201 [84] | -0.00236 |
| $\mathrm{C}_{3} \mathrm{H}_{10} \mathrm{Sn}$ | trimethylstannane | 47.56673 | 47.77353 [84] | 0.00433 |
| $\mathrm{C}_{4} \mathrm{H}_{12} \mathrm{Sn}$ | diethylstannane | 59.54034 | 59.50337 [84] | -0.00062 |
| $\mathrm{C}_{4} \mathrm{H}_{12} \mathrm{Sn}$ | tetramethyltin | 59.90851 | 60.13973 [82] | 0.00384 |
| $\mathrm{C}_{5} \mathrm{H}_{12} \mathrm{Sn}$ | trimethylvinyltin | 66.08296 | 66.43260 [84] | 0.00526 |
| $\mathrm{C}_{5} \mathrm{H}_{14} \mathrm{Sn}$ | trimethylethyltin | 72.06621 | 72.19922 [83] | 0.00184 |
| $\mathrm{C}_{6} \mathrm{H}_{16} \mathrm{Sn}$ | trimethylisopropyltin | 84.32480 | 84.32346 [83] | -0.00002 |
| $\mathrm{C}_{8} \mathrm{H}_{12} \mathrm{Sn}$ | tetravinyltin | 84.64438 | $86.53803{ }^{\text {a [83] }}$ | 0.02188 |
| $\mathrm{C}_{6} \mathrm{H}_{18} \mathrm{Sn}_{2}$ | hexamethyldistannane | 91.96311 | 91.75569 [83] | -0.00226 |
| $\mathrm{C}_{7} \mathrm{H}_{18} \mathrm{Sn}$ | trimethyl-t-butyltin | 96.81417 | 96.47805 [82] | -0.00348 |
| $\mathrm{C}_{9} \mathrm{H}_{14} \mathrm{Sn}$ | trimethylphenyltin | 100.77219 | 100.42716 [83] | -0.00344 |
| $\mathrm{C}_{8} \mathrm{H}_{18} \mathrm{Sn}$ | triethylvinyltin | 102.56558 | $102.83906^{\text {a }}$ [83] | 0.00266 |
| $\mathrm{C}_{8} \mathrm{H}_{20} \mathrm{Sn}$ | tetraethyltin | 108.53931 | 108.43751 [83] | -0.00094 |
| $\mathrm{C}_{10} \mathrm{H}_{16} \mathrm{Sn}$ | trimethylbenzyltin | 112.23920 | 112.61211 [83] | 0.00331 |
| $\mathrm{C}_{10} \mathrm{H}_{14} \mathrm{O}_{2} \mathrm{Sn}$ | trimethyltin benzoate | 117.28149 | $119.31199^{\text {a }}$ [83] | 0.01702 |
| $\mathrm{C}_{10} \mathrm{H}_{20} \mathrm{Sn}$ | tetra-allyltin | 133.53558 | $139.20655^{\text {a }}$ [83] | 0.04074 |
| $\mathrm{C}_{12} \mathrm{H}_{28} \mathrm{Sn}$ | tetra-n-propyltin | 157.17011 | 157.01253 [83] | -0.00100 |
| $\mathrm{C}_{12} \mathrm{H}_{28} \mathrm{Sn}$ | tetraisopropyltin | 157.57367 | 156.9952 [83] | -0.00366 |
| $\mathrm{C}_{12} \mathrm{H}_{3} \mathrm{Sn}_{2}$ | hexaethyldistannane | 164.90931 | $164.76131^{\text {a }}$ [83] | -0.00090 |
| $\mathrm{C}_{19} \mathrm{H}_{18} \mathrm{Sn}$ | triphenylmethyltin | 182.49954 | $180.97881^{\text {a }}$ [84] | -0.00840 |
| $\mathrm{C}_{20} \mathrm{H}_{20} \mathrm{Sn}$ | triphenylethyltin | 194.65724 | $192.92526^{\text {a }}$ [84] | -0.00898 |
| $\mathrm{C}_{16} \mathrm{H}_{36} \mathrm{Sn}$ | tetra-n-butyltin | 205.80091 | 205.60055 [83] | -0.00097 |
| $\mathrm{C}_{16} \mathrm{H}_{36} \mathrm{Sn}$ | tetraisobutyltin | 206.09115 | 206.73234 [83] | 0.00310 |
| $\mathrm{C}_{21} \mathrm{H}_{24} \mathrm{Sn}_{2}$ | triphenyl-trimethyldistannane | 214.55414 | $212.72973{ }^{\text {a }}$ [84] | -0.00858 |
| $\mathrm{C}_{24} \mathrm{H}_{20} \mathrm{Sn}$ | tetraphenyltin | 223.36322 | 221.61425 [83] | -0.00789 |
| $\mathrm{C}_{24} \mathrm{H}_{44} \mathrm{Sn}$ | tetracyclohexyltin | 283.70927 | 284.57603 [83] | 0.00305 |
| $\mathrm{C}_{36} \mathrm{H}_{30} \mathrm{Sn}_{2}$ | hexaphenyldistannane | 337.14517 | 333.27041 [83] | -0.01163 |

${ }^{\text {a }}$ Crystal.
Table 23.97.14. Summary results of lead compounds.

| Formula | Name | Calculated <br> Total Bond <br> Energy (eV) | Experimental <br> Total Bond <br> Energy (eV) | Relative Error |
| :--- | :--- | :---: | :---: | :---: |
| $\mathrm{C}_{4} \mathrm{H}_{12} \mathrm{~Pb}$ | tetramethyl-lead | 57.55366 | $57.43264[86]$ | -0.00211 |
| $\mathrm{C}_{8} \mathrm{H}_{20} \mathrm{~Pb}$ | tetraethyl-lead | 106.18446 | $105.49164[86]$ | -0.00657 |

Table 23.97.15. Summary results of alkyl arsines.

| Formula | Name | Calculated <br> Total Bond <br> Energy (eV) | Experimental <br> Total Bond <br> Energy (eV) | Relative Error |
| :--- | :--- | :---: | :---: | :---: |
| $\mathrm{C}_{3} \mathrm{H}_{9} \mathrm{As}$ | trimethylarsine | 44.73978 | $45.63114[87]$ | 0.01953 |
| $\mathrm{C}_{6} \mathrm{H}_{15} \mathrm{As}$ | triethylarsine | 81.21288 | $81.01084[87]$ | -0.00249 |
| $\mathrm{C}_{18} \mathrm{H}_{15} \mathrm{As}$ | triphenylarsine | 167.33081 | $166.49257[87]$ | -0.00503 |

Table 23.97.16. Summary results of alkyl stibines.

| Formula | Name | Calculated <br> Total Bond <br> Energy (eV) | Experimental <br> Total Bond <br> Energy (eV) | Relative Error |
| :--- | :--- | :---: | :---: | :---: |
| $\mathrm{C}_{3} \mathrm{H}_{9} \mathrm{Sb}$ | trimethylstibine | 44.73078 | $45.02378[88]$ | 0.00651 |
| $\mathrm{C}_{6} \mathrm{H}_{15} \mathrm{Sb}$ | triethylstibine | 81.20388 | $80.69402[88]$ | -0.00632 |
| $\mathrm{C}_{18} \mathrm{H}_{15} \mathrm{Sb}$ | triphenylstibine | 167.32181 | $165.81583[88]$ | -0.00908 |

Table 23.97.17. Summary results of alkyl bismuths.

| Formula | Name | Calculated <br> Total Bond <br> Energy (eV) | Experimental <br> Total Bond <br> Energy (eV) | Relative Error |
| :--- | :--- | :---: | :---: | :---: |
| $\mathrm{C}_{3} \mathrm{H}_{9} \mathrm{Bi}$ | trimethylbismuth | 42.07387 | $42.79068[88]$ | 0.01675 |
| $\mathrm{C}_{6} \mathrm{H}_{15} \mathrm{Bi}$ | triethylbismuth | 78.54697 | $78.39153[88]$ | -0.00198 |
| $\mathrm{C}_{18} \mathrm{H}_{15} \mathrm{Bi}$ | triphenylbismuth | 164.66490 | $163.75184[88]$ | -0.00558 |

## REFERENCES

1. D. R. Lide, CRC Handbook of Chemistry and Physics, 86th Edition, CRC Press, Taylor \& Francis, Boca Raton, (2005-6), pp. 10-202 to 10-204.
2. B. G. Willis, K. F. Jensen, "An evaluation of density functional theory and ab initio predictions for bridge-bonded aluminum compounds," J. Phys. Chem. A, Vol. 102, (1998), pp. 2613-2623.
3. D. R. Lide, CRC Handbook of Chemistry and Physics, 86th Edition, CRC Press, Taylor \& Francis, Boca Raton, (2005-6), pp. 9-19 to 9-45.
4. T. Shinzawa, F. Uesugi, I. Nishiyama, K. Sugai, S. Kishida, H. Okabayashi, "New molecular compound precursor for aluminum chemical vapor deposition," Applied Organometallic Chem., Vol. 14, (2000), pp. 14-24.
5. D. R. Lide, CRC Handbook of Chemistry and Physics, 86th Edition, CRC Press, Taylor \& Francis, Boca Raton, (2005-6), p. 9-82.
6. G. Herzberg, Molecular Spectra and Molecular Structure II. Infrared and Raman Spectra of Polyatomic Molecules, Van Nostrand Reinhold Company, New York, New York, (1945), p. 344.
7. R. J. Fessenden, J. S. Fessenden, Organic Chemistry, Willard Grant Press. Boston, Massachusetts, (1979), p. 320.
8. cyclohexane at http://webbook.nist.gov/.
9. D. R. Lide, CRC Handbook of Chemistry and Physics, 86th Ed., CRC Press, Taylor \& Francis, Boca Raton, (2005-6), p. 9-54.
10. J. D. Cox, G. Pilcher, Thermochemistry of Organic and Organometallic Compounds, Academic Press, New York, (1970).
11. M. B. J. Smith, J. Organometal. Chem., Vol. 76, (1974), pp. 171-201.
12. NIST Atomic Spectra Database, www.physics.nist.gov/cgi-bin/AtData/display.ksh.
13. J. E. Huheey, Inorganic Chemistry Principles of Structure and Reactivity, $2^{\text {nd }}$ Ed., Harper \& Row, New York, (1978), Chp. 9.
14. D. R. Lide, CRC Handbook of Chemistry and Physics, 86th Edition, CRC Press, Taylor \& Francis, Boca Raton, (2005-6), p. 9-86.
15. J. Li, P. C. de Mello, K. Jug, "Extension of SINDO1 to transition metal compounds," J. Comput. Chem., Vol. 13(1), (1992), pp. 85-92.
16. D. R. Lide, CRC Handbook of Chemistry and Physics, 86th Edition, CRC Press, Taylor \& Francis, Boca Raton, (2005-6), p. 9-81.
17. G. Herzberg, Molecular Spectra and Molecular Structure II. Infrared and Raman Spectra of Polyatomic Molecules, Van Nostrand Reinhold Company, New York, New York, (1945), p. 567.
18. D. R. Lide, CRC Handbook of Chemistry and Physics, 86th Edition, CRC Press, Taylor \& Francis, Boca Raton, (2005-6), p. 9-27.
19. M. W. Chase, Jr., C. A. Davies, J. R. Downey, Jr., D. J. Frurip, R. A. McDonald, A. N. Syverud, JANAF Thermochemical Tables, Third Edition, Part I, Al-Co, J. Phys. Chem. Ref. Data, Vol. 14, Suppl. 1, (1985), pp. 467, 509, 522, 535.
20. M. W. Chase, Jr., C. A. Davies, J. R. Downey, Jr., D. J. Frurip, R. A. McDonald, A. N. Syverud, JANAF Thermochemical Tables, Third Edition, Part II, Cr-Zr, J. Phys. Chem. Ref. Data, Vol. 14, Suppl. 1, (1985), pp. 1411, 1438, 1447, 1460.
21. M. W. Chase, Jr., C. A. Davies, J. R. Downey, Jr., D. J. Frurip, R. A. McDonald, A. N. Syverud, JANAF Thermochemical Tables, Third Edition, Part II, Cr-Zr, J. Phys. Chem. Ref. Data, Vol. 14, Suppl. 1, (1985), pp. 1096, 1153, 1174, 1192.
22. M. W. Chase, Jr., C. A. Davies, J. R. Downey, Jr., D. J. Frurip, R. A. McDonald, A. N. Syverud, JANAF Thermochemical Tables, Third Edition, Part I, Al-Co, J. Phys. Chem. Ref. Data, Vol. 14, Suppl. 1, (1985), pp. 808, 866, 887, 906.
23. M. W. Chase, Jr., C. A. Davies, J. R. Downey, Jr., D. J. Frurip, R. A. McDonald, A. N. Syverud, JANAF Thermochemical Tables, 3rd Edition, Part I, Al-Co \& Part II, Cr-Zr, J. Phys. Chem. Ref. Data, Vol. 14, Suppl. 1, (1985), pp. 796, 843, 1082, 1132, 1738, 1762.
24. M. W. Chase, Jr., C. A. Davies, J. R. Downey, Jr., D. J. Frurip, R. A. McDonald, A. N. Syverud, JANAF Thermochemical Tables, Third Edition, Part II, Cr-Zr, J. Phys. Chem. Ref. Data, Vol. 14, Suppl. 1, (1985), p. 1616.
25. G. Herzberg, Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules, Krieger Publishing Company, Malabar, FL, (1950), p. 578.
26. E. L. Muetterties, J. R. Bleeke, E. J. Wucherer, "Structural, stereochemical, and electronic features of arene-metal complexes," Chem. Rev., Vol. 82, No. 5, (1982), pp. 499-525.
27. vanadium pentafluoride at http://webbook.nist.gov/.
28. vanadium oxytrichloride at http://webbook.nist.gov/.
29. M. W. Chase, Jr., C. A. Davies, J. R. Downey, Jr., D. J. Frurip, R. A. McDonald, A. N. Syverud, JANAF Thermochemical Tables, Third Edition, Part I, Al-Co \& Part II, Cr-Zr, J. Phys. Chem. Ref. Data, Vol. 14, Suppl. 1, (1985), p. 698.
30. G. Herzberg, Molecular Spectra and Molecular Structure II. Infrared and Raman Spectra of Polyatomic Molecules, Van Nostrand Reinhold Company, New York, New York, (1945), pp. 362-369.
31. M. W. Chase, Jr., C. A. Davies, J. R. Downey, Jr., D. J. Frurip, R. A. McDonald, A. N. Syverud, JANAF Thermochemical Tables, Third Edition, Part II, Cr-Zr, J. Phys. Chem. Ref. Data, Vol. 14, Suppl. 1, (1985), p. 1763.
32. Wagman, D. D.; Evans, W. H.; Parker, V. B.; Halow, I.; Bailey, .S. .M.; Schumm, R. L.; Nuttall, R. H. The NBS Tables of Chemical. Thermodynamic Properties, J. Phys. Chem. Ref. Data, Vol. 11, Suppl. 2 (1982)Wagman, D. D.; Evans, W. H.; Parker, V. B.; Halow, I.; Bailey, .S. .M.; Schumm, R. L.; Nuttall, R. H. The NBS Tables of Chemical. Thermodynamic Properties, J. Phys. Chem. Ref. Data, Vol. 11, Suppl. 2 (1982)Wagman, D. D.; Evans, W. H.; Parker, V. B.; Halow, I.; Bailey, .S. .M.; Schumm, R. L.; Nuttall, R. H. The NBS Tables of Chemical. Thermodynamic Properties, J. Phys. Chem. Ref. Data, Vol. 11, Suppl. 2 (1982)Wagman, D. D.; Evans, W. H.; Parker, V. B.; Halow, I.; Bailey, .S. .M.; Schumm, R. L.; Nuttall, R. H. The NBS Tables of Chemical. Thermodynamic Properties, J. Phys. Chem. Ref. Data, Vol. 11, Suppl. 2 (1982).
33. J. D. Cox, G. Pilcher, Thermochemistry of Organometallic Compounds, Academic Press, New York, (1970), p. 478.
34. W. I. F. David, R. M. Ibberson, G. A. Jeffrey, J. R. Ruble, "The structure analysis of deuterated benzene and deuterated nitromethane by pulsed-neutron powder diffraction: a comparison with single crystal neutron analysis," Physica B (1992), $180 \& 181$, pp. 597-600.
35. G. A. Jeffrey, J. R. Ruble, R. K. McMullan, J. A. Pople, "The crystal structure of deuterated benzene," Proceedings of the Royal Society of London. Series A, Mathematical and Physical Sciences, Vol. 414, No. 1846, (Nov. 9, 1987), pp. 47-57.
36. H. B. Burgi, S. C. Capelli, "Getting more out of crystal-structure analyses," Helv. Chim. Acta, Vol. 86, (2003), pp. 1625-1640.
37. M. W. Chase, Jr., C. A. Davies, J. R. Downey, Jr., D. J. Frurip, R. A. McDonald, A. N. Syverud, JANAF Thermochemical Tables, Third Edition, Part II, Cr-Zr, J. Phys. Chem. Ref. Data, Vol. 14, Suppl. 1, (1985), pp. 968, 969, 970.
38. A. Jost, B. Rees, "Electronic structure of chromium hexacarbonyl at 78K. I. Neutron diffraction study, Acta. Cryst. Vol. B31 (1975), pp. 2649-2658.
39. J. A. Ibers, "The structure of dibenzene chromium," J. Phys. Chem., Vol. 40, (1964), pp.3129-3130.
40. B.B. Ebbinghaus, "Thermodynamics of gas phase chromium species: The chromium chlorides, oxychlorides, fluorides, oxyfluorides, hydroxides, oxyhydroxides, mixed oxyfluorochlorohydroxides, and volatility calculations in waste incineration processes," Combustion and Flame, Vol. 101, (1995), pp. 311-338.
41. "Hexacarbonylnickel," NIST Chemistry Handbook. http://webbook.nist.gov/.
42. "CrCC," NIST Chemistry Handbook. http://webbook.nist.gov/.
43. D. Lin-Vien. N. B. Colthup, W. G. Fateley, J. G. Grasselli, The Handbook of Infrared and Raman Frequencies of Organic Molecules, Academic Press, Inc., Harcourt Brace Jovanovich, Boston, (1991), p. 481.
44. J. D. Cox, G. Pilcher, Thermochemistry of Organometallic Compounds, Academic Press, New York, (1970), p. 489.
45. N. Vogt, "Equilibrium bond lengths, force constants and vibrational frequencies of $\mathrm{MnF}_{2}, \mathrm{FeF}_{2}, \mathrm{CoF}_{2}, \mathrm{NiF}_{2}$, and $\mathrm{ZnF} \mathrm{F}_{2}$ from least-squares analysis of gas-phase electron diffraction data," J. Molecular Structure, Vol. 570, (2001), pp. 189-195.
46. L. F. Dahl, "The structure of dimanganese decacarbonyl, $\mathrm{Mn}_{2}(\mathrm{CO})_{10}$," Acta. Cryst., Vol. 16, (1963), pp. 419-426.
47. G. Herzberg, Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules, Krieger Publishing Company, Malabar, FL, (1950), p. 550.
48. "Mn3," NIST Chemistry Handbook. http://webbook.nist.gov/.
49. J. D. Cox, G. Pilcher, Thermochemistry of Organometallic Compounds, Academic Press, New York, (1970), p. 491.
50. M. W. Chase, Jr., C. A. Davies, J. R. Downey, Jr., D. J. Frurip, R. A. McDonald, A. N. Syverud, JANAF Thermochemical Tables, Third Edition, Part I, Al-Co, J. Phys. Chem. Ref. Data, Vol. 14, Suppl. 1, (1985), pp. 822, 879.
51. M. W. Chase, Jr., C. A. Davies, J. R. Downey, Jr., D. J. Frurip, R. A. McDonald, A. N. Syverud, JANAF Thermochemical Tables, Third Edition, Part II, Cr-Zr, J. Phys. Chem. Ref. Data, Vol. 14, Suppl. 1, (1985), p. 1054.
52. M. W. Chase, Jr., C. A. Davies, J. R. Downey, Jr., D. J. Frurip, R. A. McDonald, A. N. Syverud, JANAF Thermochemical Tables, Third Edition, Part II, Cr-Zr, J. Phys. Chem. Ref. Data, Vol. 14, Suppl. 1, (1985), p. 1239.
53. J. D. Cox, G. Pilcher, Thermochemistry of Organometallic Compounds, Academic Press, New York, (1970), p. 493.
54. M. W. Chase, Jr., C. A. Davies, J. R. Downey, Jr., D. J. Frurip, R. A. McDonald, A. N. Syverud, JANAF Thermochemical Tables, Third Edition, Part II, Cr-Zr, J. Phys. Chem. Ref. Data, Vol. 14, Suppl. 1, (1985), p. 953.
55. M. W. Chase, Jr., C. A. Davies, J. R. Downey, Jr., D. J. Frurip, R. A. McDonald, A. N. Syverud, JANAF Thermochemical Tables, Third Edition, Part II, Cr-Zr, J. Phys. Chem. Ref. Data, Vol. 14, Suppl. 1, (1985), p. 695.
56. G. Herzberg, Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules, Krieger Publishing Company, Malabar, FL, (1950), p. 522.
57. D. R. Lide, CRC Handbook of Chemistry and Physics, 86th Ed., CRC Press, Taylor \& Francis, Boca Raton, (2005-6), p. 9-85.
58. "Co(CO)," NIST Chemistry Handbook. http://webbook.nist.gov/.
59. M. W. Chase, Jr., C. A. Davies, J. R. Downey, Jr., D. J. Frurip, R. A. McDonald, A. N. Syverud, JANAF Thermochemical Tables, Third Edition, Part II, Cr-Zr, J. Phys. Chem. Ref. Data, Vol. 14, Suppl. 1, (1985), pp. 794, 840.
60. P. Seiler, J. D. Dunitz, "The structure of nickelocene at room temperature and at 101 K," Acta. Cryst., Vol. B36, (1980), pp. 2255-2260.
61. NIST Atomic Spectra Database, www.physics.nist.gov/cgi-bin/AtData/display.ksh.
62. D. R. Lide, CRC Handbook of Chemistry and Physics, 86th Edition, CRC Press, Taylor \& Francis, Boca Raton, (2005-6), pp. 9-83 to 9-84.
63. M. W. Chase, Jr., C. A. Davies, J. R. Downey, Jr., D. J. Frurip, R. A. McDonald, A. N. Syverud, JANAF Thermochemical Tables, Third Edition, Part II, Cr-Zr, J. Phys. Chem. Ref. Data, Vol. 14, Suppl. 1, (1985), pp. 1013, 1017, 1020.
64. "Dimethylzinc," NIST Chemistry Handbook. http://webbook.nist.gov/.
65. J. D. Cox, G. Pilcher, Thermochemistry of Organometallic Compounds, Academic Press, New York, (1970), pp. 446-447.
66. D. Lin-Vien. N. B. Colthup, W. G. Fateley, J. G. Grasselli, The Handbook of Infrared and Raman Frequencies of Organic Molecules, Academic Press, Inc., Harcourt Brace Jovanovich, Boston, (1991), p. 13.
67. J. D. Cox, G. Pilcher, Thermochemistry of Organic and Organometallic Compounds, Academic Press, New York, (1970), pp. 470-471.
68. H. Preut, "Structure of triphenyltin bromide," Acta. Cryst., Vol. B35, (1979), pp. 744-746.
69. S. W. Ng, "Triphenyltin iodide," Acta. Cryst., Vol. C51, (1995), pp. 629-631.
70. Von H. Preut, H.-J. Haupt, F. Huber, "Die Kristall-und molekularstruktur des hexaphenyl-distannans," Zeitschrift für anorganische und allgemeine Chemie, Vol. 396, Issue 1, January, (1973), pp. 81-89.
71. G. A. Sim, J. M. Robertson, T. H. Goodwin, "The crystal and molecular structure of benzoic acid," Acta Cryst., Vol. 8, (1955), pp.157-164.
72. D. Lin-Vien. N. B. Colthup, W. G. Fateley, J. G. Grasselli, The Handbook of Infrared and Raman Frequencies of Organic Molecules, Academic Press, Inc., Harcourt Brace Jovanovich, Boston, (1991), pp 5,14.
73. J. F. Sanz, A. Marquez, "Molecular structure and vibrational analysis of distannane from ab initio second-order perturbation calculations. A theoretical approach to the tin-X bond (X=Cl, Si, Ge, Sn)," J. Phys. Chem., Vol. 93, (1989), pp. 7328-7333.
74. G. Herzberg, Molecular Spectra and Molecular Structure II. Infrared and Raman Spectra of Polyatomic Molecules, Van Nostrand Reinhold Company, New York, New York, (1945), p. 326.
75. "b1 2-methyl-1-propene," NIST Chemistry Handbook. http://webbook.nist.gov/.
76. "a1 2-methyl-1-propene," NIST Chemistry Handbook. http://webbook.nist.gov/.
77. "Acetic acid," NIST Chemistry Handbook. http://webbook.nist.gov/.
78. G. Herzberg, Molecular Spectra and Molecular Structure II. Infrared and Raman Spectra of Polyatomic Molecules, Krieger Publishing Company, Malabar, FL, (1991), p. 195.
79. D. Lin-Vien. N. B. Colthup, W. G. Fateley, J. G. Grasselli, The Handbook of Infrared and Raman Frequencies of Organic Molecules, Academic Press, Inc., Harcourt Brace Jovanovich, Boston, (1991), p. 138.
80. K. P. Huber, G. Herzberg, Molecular Spectra and Molecular Structure, IV. Constants of Diatomic Molecules, Van Nostrand Reinhold Company, New York, (1979).
81. J. Crovisier, Molecular Database-Constants for molecules of astrophysical interest in the gas phase: photodissociation, microwave and infrared spectra, Ver. 4.2, Observatoire de Paris, Section de Meudon, Meudon, France, May 2002, pp. 34-37, available at http://wwwusr.obspm.fr/~crovisie/.
82. D. R. Lide, CRC Handbook of Chemistry and Physics, 86th Edition, CRC Press, Taylor \& Francis, Boca Raton, (2005-6), pp. 5-8, 5-10, 5-14, 5-16, 5-28.
83. J. D. Cox, G. Pilcher, Thermochemistry of Organometallic Compounds, Academic Press, New York, (1970), pp. 472-477.
84. P. G. Harrison, Chemistry of Tin, Blackie, Glasgow, (1989), pp. 10-12.
85. O. Knacke, O. Kubaschewski, K. Hesselmann, Thermochemical Properties of Inorganic Substances, $2^{\text {nd }}$ Edition, Vol. II, Springer, New York (1991), pp. 1888-1889.
86. J. D. Cox, G. Pilcher, Thermochemistry of Organometallic Compounds, Academic Press, New York, (1970), pp. 476-477.
87. J. D. Cox, G. Pilcher, Thermochemistry of Organometallic Compounds, Academic Press, New York, (1970), pp. 484-485.
88. J. D. Cox, G. Pilcher, Thermochemistry of Organometallic Compounds, Academic Press, New York, (1970), pp. 486-487.

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.

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.
"Mills proposes such a basic approach to quantum theory that it deserves considerably more attention from the general scientific community than it has received so far. The new theory appears to be a realization of Einstein's vision and a fitting closure of the "Quantum Century" that started in 1900..." - Dr. Reinhart Engelmann, Professor of Electrical Engineering, Oregon Graduate Institute of Science and Technology

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[^0]:    ${ }^{1}$ The BEC is incorrectly interpreted as a single large atom having a corresponding probability wave function of quantum mechanics. Since excitation occurs in units of $\hbar$ in order of to conserve angular momentum as shown previously for electronic (Chapter 2), vibrational (Chapter 11), rotational (Chapter 12), and translational excitation (Chapter 3) and Bose-Einstein statistics arise from an underlying deterministic physics (Chapter 24), this state comprised of an ensemble of individual atoms is predicted classically using known equations [110]. As in the case of the coherent state of photons in a laser cavity (Chapter 4), the coherency of the BEC actually disproves the inherent Heisenberg Uncertainty Principle (HUP) of quantum mechanics since the atomic positions and energies are precisely determined simultaneously. Furthermore, it is possible to form a BEC comprising molecules in addition to atoms [111] wherein the molecules lack zero-order vibration in contradiction to the HUP. The classical physics underlying Bose-Einstein statistics was covered in the Statistical Mechanics section.

[^1]:    ${ }^{2}$ The hydrino molecule comprises two hydrogen isotope nuclei and two electrons in a single molecular orbital (MO). Uniquely the MO comprises a paired and unpaired electron (Parameters and Magnetic Energies Due to the Spin Magnetic Moment of $\mathrm{H}_{2}(1 / 4)$ section). To conserve spin angular momentum during the formation of a bond between two hydrino atoms, the bond energy must be released as a neutrino such as an electron neutrino of spin $1 / 2$ that serves the function of the third body of $M^{*}$ Eq. (16.216a):

    $$
    \begin{equation*}
    H(1 / p)+H(1 / p) \rightarrow H_{2}(1 / p)+v_{e} \tag{16.216b}
    \end{equation*}
    $$

[^2]:    ${ }^{\text {a }}$ theory

[^3]:     values [87].

    Experimental Relative Error
    0.01953
    

    Energy (eV)
    
    
    
    $=C$
    000
    $\begin{array}{cccc}C-C & C-C & C-C & C-C \text { (f) } \\ \text { (d) } & \text { (e) } & \end{array}$
    (c) (d)
    $\begin{array}{lll}0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0\end{array}$
    (b)

    0
    $\begin{array}{lll}\text { (e) } & \text { (!) } H \supset & { }^{2} H \nu\end{array}$

[^4]:    Calculated Experimental

[^5]:    a Estimated
    ${ }^{b}$ Crystal

