

Bonding in Solids

W2.1 Atomic, Hybrid, and Molecular Orbitals Involved in Bonding in Solid-State Materials

When isolated atoms come together to form a solid, the atomic orbitals of the valence electrons are often modified as bonding between the atoms occurs. In this section the orbitals for electrons in isolated atoms (i.e., the atomic orbitals) are described first. The hybrid orbitals resulting from combinations of atomic orbitals on the same atom are described next, followed by a description of the molecular orbitals that result when atomic or hybrid orbitals on different atoms combine with each other as the atoms form bonds. It should be emphasized at the outset that the atomic, hybrid, and molecular orbitals described here are just useful approximations to the actual solutions of the Schrödinger equation for atoms and molecules. The derivations of mathematical expressions for these orbitals are not given here since it is outside the scope of this material to present in detail the physics and chemistry of atoms and molecules.

Atomic Orbitals. The *atomic orbitals* of the electrons in an atom correspond to the solutions of the Schrödinger equation for the wavefunctions ψ which are labeled with the three *quantum numbers* n , l , and m_l [i.e., $\psi(nlm_l)$]. (The magnetic quantum number m_s is discussed later.) The energies and spatial extents of the electrons in the atomic orbitals are determined by the *principal quantum number* n , which has allowed values $n = 1, 2, 3, \dots, \infty$. For example, the binding energies of the $\psi(nlm_l)$ atomic orbitals in atomic hydrogen decrease as $1/n^2$ while their radii increase as n^2 . The *orbital angular momentum quantum number* l specifies the angular momentum of the electron and can take on the values $l = 0, 1, 2, \dots, n - 1$. For example, for $n = 4$, the allowed values of l are 0 (for *s* states), 1 (for *p* states), 2 (for *d* states), and 3 (for *f* states). The *quantum number* m_l determines the *orientation* of the orbital in space and can have the $(2l + 1)$ integral values lying between $-l$ and $+l$. For *d* states with $l = 2$ the five allowed values of m_l are $-2, -1, 0, +1, \text{ and } +2$.

The probability of finding the electron at a point in space is proportional to the value of $|\psi(nlm_l)|^2$ at that point. The charge density associated with the electron in this orbital is given by $-e|\psi|^2$. The *electronic charge densities* for one-electron or hydrogenic atoms and ions are shown schematically in Fig. W2.1 for the single *s*, three *p* (p_x , p_y , and p_z), and five *d* ($d_{x^2-y^2}$, d_{z^2} , d_{xy} , d_{yz} , and d_{xz}) atomic orbitals. The shapes of these orbitals as shown are only schematic (e.g., the orbitals do not actually have the sharp boundaries indicated in the figure).

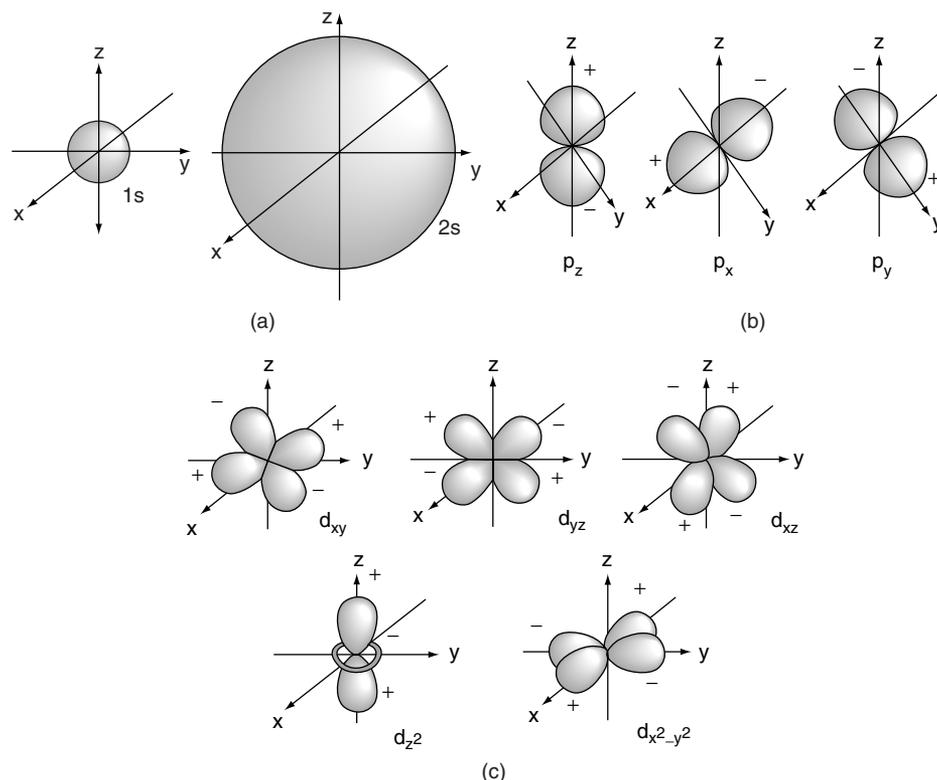


Figure W2.1. Electronic charge distribution in hydrogenlike s , p , and d atomic orbitals. The relative phases of the different lobes of the p and d orbitals are indicated with plus and minus signs. (Adapted from A. L. Companion, *Chemical Bonding*, 2nd ed., McGraw-Hill, 1979.)

It can be seen from Fig. W2.1 that the s orbital is spherically symmetric, whereas the p and d orbitals have preferred directions in space. In particular, the p_x , p_y , and p_z orbitals have two symmetric regions of high probability called *lobes* which are directed along the x , y , and z axes, respectively. The five d orbitals are more complicated. The d_{z^2} orbital has a shape that is similar to the p_z orbital but is much more extended in one direction in space. The four other d orbitals are similar to each other in shape, with four lobes as shown. It should be remembered that each orbital can accommodate no more than two electrons, no matter how many lobes it has. It is important to note that the phase of the wavefunction alternates between being positive in one lobe and negative in the adjacent lobes. The significance of this will become apparent when lobes of orbitals on different atoms overlap. Although rigorously correct in principle only for one-electron atoms and ions, these atomic orbitals are also used for multielectron atoms.

Some of the atomic orbitals that are important for bonding in solid-state materials are listed in Table W2.1. The spin of the electron is $s = \frac{1}{2}$, and in this table the allowed values $+\frac{1}{2}$ and $-\frac{1}{2}$ of the *magnetic quantum number* m_s which correspond to spin-up and spin-down electrons, respectively, are also given. A complete specification of the atomic orbital is therefore given by $\psi(nlm_l m_s)$. The maximum allowed occupancy of an atomic orbital is given by $2(2l + 1)$. A fully occupied or filled orbital or shell

TABLE W2.1 Important Atomic Orbitals for Bonding in Solids

Atomic Orbital	n	l	m_l	m_s	Maximum Occupancy
$1s$	1	0	0	$\pm\frac{1}{2}$	2 ($1s^2$)
$2s$	2	0	0	$\pm\frac{1}{2}$	2 ($2s^2$)
$2p_x, 2p_y, 2p_z$	2	1	0, ± 1	$\pm\frac{1}{2}$	6 ($2p^6$)
$3s$	3	0	0	$\pm\frac{1}{2}$	2 ($3s^2$)
$3p_x, 3p_y, 3p_z$	3	1	0, ± 1	$\pm\frac{1}{2}$	6 ($3p^6$)
$3d_{z^2}, 3d_{x^2-y^2},$ $3d_{xy}, 3d_{yz}, 3d_{xz}$	3	2	0, $\pm 1, \pm 2$	$\pm\frac{1}{2}$	10 ($3d^{10}$)

therefore contains $2(2l + 1)$ electrons. For example, a filled $3d^{10}$ shell corresponds to 10 electrons occupying all of the $n = 3, l = 2$ d orbitals of the atom. The fact that only 10 electrons can occupy an $l = 2$ orbital follows from the *Pauli exclusion principle* (PEP), which states that in a quantum system such as an atom, molecule, or solid, each electron must have a set of quantum numbers which is distinct from that of any other electron in the system.

It should be noted that p and d orbitals are actually linear combinations of wavefunctions with different values of m_l (except for p_z or d_{z^2} , which correspond to $m_l = 0$). The outer or valence electron configurations of neutral atoms in their ground states are presented in Table W2.2.

Two important aspects of the bonding of electrons in neutral atoms are illustrated in Fig. W2.2, where the energies of electrons are shown schematically as a function of the atomic number Z . Starting with the energy levels of the H atom on the left, it can be seen that:

1. Electrons are more tightly bound (i.e., their energies are more negative) as the charge $+Ze$ of the nucleus increases.
2. Electrons in the same shell [i.e., in the $n = 2$ shell ($2s$ and $2p$) or the $n = 3$ shell ($3s, 3p$, and, for high enough Z , $3d$)] have similar energies which are usually quite different from the energies of electrons in other shells.

It is also clear from Fig. W2.2 that electrons outside closed shells (e.g., the single $3s$ electron of the Na atom with $Z = 11$), are much less strongly bound than those in filled shells. These less strongly bound electrons are the atomic valence electrons, which can participate readily in the hybrid or molecular orbitals described next.

Hybrid Orbitals. As atoms bond to each other in molecules and solids via covalent bonding (i.e., the sharing of electrons), it is often useful to think of the valence electron atomic orbitals having similar energies on a given atom (such as $2s$ and $2p$ or $3s, 3p$, and $3d$) combining with each other to form *hybrid orbitals*. The bonding between the atoms can then involve the hybrid orbitals in addition to the atomic orbitals. An example of this type of bonding in the CH_4 molecule is discussed later.

TABLE W2.2 Outer or Valence Electron Configurations of Neutral Atoms in Their Ground State

1	H	1s ¹	2	He	1s ²
3	Li	2s ¹	4	Be	2s ²
11	Na	3s ¹	12	Mg	3s ²
19	K	4s ¹	20	Ca	4s ²
37	Rb	5s ¹	38	Sr	5s ²
55	Cs	6s ¹	56	Ba	6s ²
87	Fr	7s ¹	88	Ra	7s ²
21	Sc	3d ¹ 4s ²	22	Ti	3d ² 4s ²
23	V	3d ³ 4s ²	24	Cr	3d ⁵ 4s ¹
25	Mn	3d ⁵ 4s ²	26	Fe	3d ⁶ 4s ²
27	Co	3d ⁷ 4s ²	28	Ni	3d ⁸ 4s ²
29	Cu	3d ¹⁰ 4s ¹	30	Zn	3d ¹⁰ 4s ²
39	Y	4d ¹ 5s ²	40	Zr	4d ² 5s ²
41	Nb	4d ⁴ 5s ¹	42	Mo	4d ⁵ 5s ¹
43	Tc	4d ⁵ 5s ²	44	Ru	4d ⁷ 5s ¹
45	Rh	4d ⁸ 5s ¹	46	Pd	4d ¹⁰
47	Cd	4d ¹⁰	48	In	5s ² 5p ¹
49	Sn	5s ² 5p ²	50	Sb	5s ² 5p ³
51	Te	5s ² 5p ⁴	52	Se	4s ² 4p ⁴
53	I	5s ² 5p ⁵	54	Xe	4s ² 4p ⁶
81	Hg	6s ² 6p ¹	82	Pb	6s ² 6p ²
83	Bi	6s ² 6p ³	84	Po	6s ² 6p ⁴
85	At	6s ² 6p ⁵	86	Rn	6s ² 6p ⁶
61	Pm	4f ⁵ 6s ²	62	Sm	4f ⁶ 6s ²
63	Eu	4f ⁷ 6s ²	64	Gd	4f ⁷ 5d ¹ 6s ²
65	Tb	4f ⁹ 6s ²	66	Dy	4f ¹⁰ 6s ²
67	Ho	4f ¹¹ 6s ²	68	Er	4f ¹² 6s ²
69	Tm	4f ¹³ 6s ²	70	Yb	4f ¹⁴ 6s ²
71	Lu	4f ¹⁴ 5d ¹ 6s ²	72	Hf	5d ² 6s ²
73	Ta	5d ³ 6s ²	74	W	5d ⁴ 6s ²
75	Re	5d ⁵ 6s ²	76	Os	5d ⁶ 6s ²
77	Ir	5d ⁷ 6s ²	78	Pt	5d ⁹ 6s ¹
79	Au	5d ¹⁰ 6s ¹	80	Hg	5d ¹⁰ 6s ²
81	Tl	6s ² 6p ¹	82	Pb	6s ² 6p ²
83	Bi	6s ² 6p ³	84	Po	6s ² 6p ⁴
85	At	6s ² 6p ⁵	86	Rn	6s ² 6p ⁶
91	Pa	5f ² 6d ¹ 7s ²	92	U	5f ³ 6d ¹ 7s ²
93	Np	5f ⁴ 6d ¹ 7s ²	94	Pu	5f ⁶ 7s ²
95	Am	5f ⁷ 7s ²	96	Cm	5f ⁷ 7s ²
97	Bk	5f ⁹ 7s ²	98	Cf	5f ¹⁰ 7s ²
99	Es	5f ¹¹ 7s ²	100	Fm	5f ¹² 7s ²
101	Md	5f ¹³ 7s ²	102	No	5f ¹⁴ 7s ²
103	Lr	5d ¹ 7s ²	104	Rf	5d ² 7s ²

† Some compilations list ⁴³Tc as having a 4d⁶5s¹ configuration and ⁵⁸Ce as having a 4f²6s² configuration.

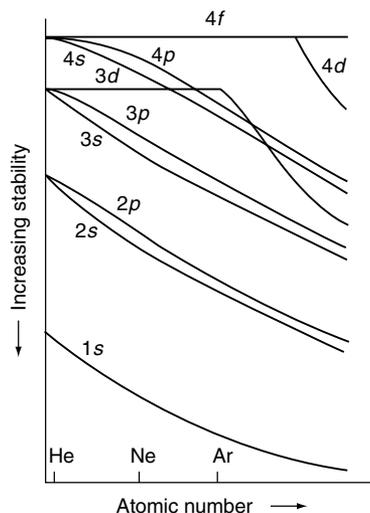


Figure W2.2. Dependence of the energies of electrons in atomic orbitals as a function of the atomic number Z . (Adapted from A. L. Companion, *Chemical Bonding*, 2nd ed., McGraw-Hill, 1979.)

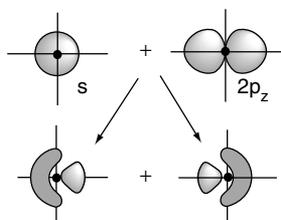


Figure W2.3. Formation of sp hybrid orbitals from s and p atomic orbitals on the same atom. (Adapted from A. L. Companion, *Chemical Bonding*, 2nd ed., McGraw-Hill, 1979.)

Consider now the linear combination of s and p atomic orbitals on the same atom, leading to the formation of two new, equivalent hybrid sp orbitals. This process is shown schematically in Fig. W2.3, where it can be seen that the resulting sp orbitals have the directional properties of the p orbital but are asymmetric. In addition, sp orbitals can also be formed from two s orbitals on the same atom if one of the electrons in an s orbital is first excited or promoted to a higher-lying p orbital. This p orbital then combines with the remaining s orbital to form two sp hybrid orbitals. The energy initially expended to excite the electron from the s to the p orbital can be recovered when the sp hybrid participates in a bond with another atom. This process of the *hybridization* of atomic orbitals can occur in principle because it leads to the formation of strong bonds between atoms and a lowering of the energy of the system.

The directionality of hybridized sp orbitals is due to the interference between the s and p orbitals. For example, the p_z orbital might have a phase corresponding to $\psi_p > 0$ if $z > 0$ and $\psi_p < 0$ if $z < 0$. If the phase of ψ_s is > 0 , then $\psi_s + \psi_p$ will be larger (on average) for $z > 0$ than for $z < 0$. On the other hand, $\psi_s - \psi_p$ will be larger for $z < 0$ than for $z > 0$.

The hybrid sp^2 or sp^3 orbitals can be formed similarly when two s and one or two p atomic orbitals, respectively, combine on the same atom. The resulting three equivalent sp^2 hybrid orbitals have *trigonal planar* symmetry, while the four equivalent sp^3 hybrid orbitals have *tetrahedral* symmetry, as shown in Fig. W2.4. The sp^3 orbitals can be written approximately as linear combinations of the s , p_x , p_y , and p_z atomic orbitals (Borg and Dienes, 1992, p. 209). Note that the symmetric arrangements of these sp , sp^2 , and sp^3 orbitals in space result from the mutual repulsion of the electrons occupying the orbitals.

Electrons in d atomic orbitals can also participate in the formation of hybrid orbitals. Two important examples are shown in Fig. W2.5. The four dsp^2 hybrid orbitals result from the linear combination of the $d_{x^2-y^2}$, s , p_x , and p_y atomic orbitals on an atom. These dsp^2 hybrids appear similar in shape and symmetry (*square planar*) to the $d_{x^2-y^2}$ orbital but can accommodate four times as many electrons. The six d^2sp^3 hybrid orbitals that result from the linear combination of the $d_{x^2-y^2}$, d_{z^2} , s , p_x , p_y , and p_z atomic orbitals have the symmetry of an *octahedron*, also shown in Fig. W2.5. Additional hybrids involving d orbitals are the three sd^2 orbitals with *trigonal planar* symmetry, the four sd^3 orbitals with *tetrahedral* symmetry, the five dsp^3 orbitals with

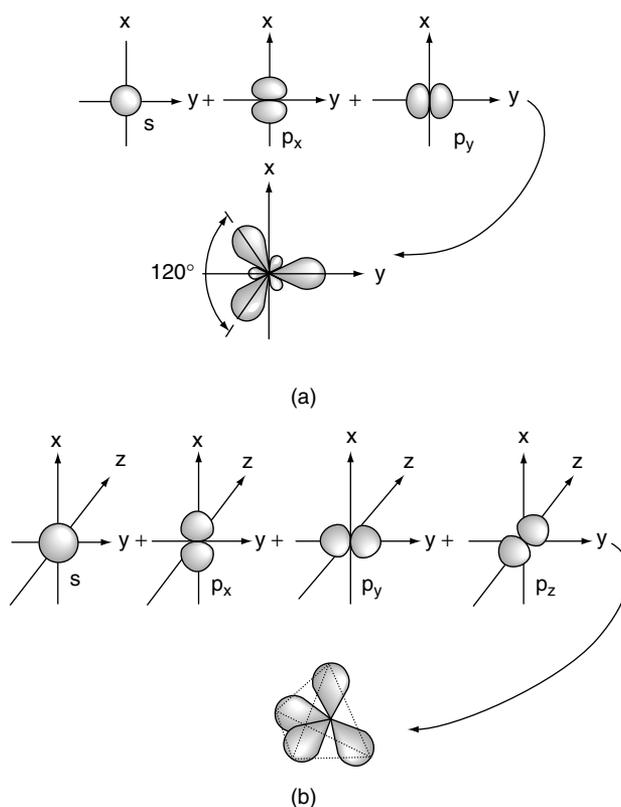


Figure W2.4. Formation of trigonal planar sp^2 and of tetrahedral sp^3 hybrid orbitals from s and p atomic orbitals on the same atom. (Adapted from A. L. Companion, *Chemical Bonding*, 2nd ed., McGraw-Hill, 1979.)

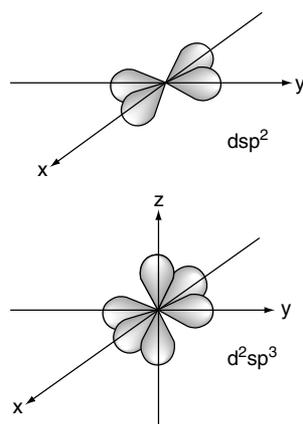


Figure W2.5. Square-planar dsp^2 and octahedral d^2sp^3 hybrid orbitals formed from s , p , and d atomic orbitals on the same atom. (Adapted from A. L. Companion, *Chemical Bonding*, 2nd ed., McGraw-Hill, 1979.)

TABLE W2.3 Important Hybrid Orbitals Involved in Bonding in Solids

Hybrid Orbital	Symmetry	Coordination Number CN (Number of Bonds)	Examples
sp	Linear	2	Cu_2O
sp^2	Trigonal planar	3	C (graphite)
sp^3	Tetrahedral	4	C (diamond)
dsp^2	Square planar	4	CuCl , CuO
d^2sp^3	Octahedral	6	FeS_2
sp^3d^3f	Cubic	8	

the symmetry of a *trigonal bipyramid*, the six d^4sp orbitals with the symmetry of a *trigonal prism*, and the eight sp^3d^3f orbitals with the symmetry of the vertices of a *cube*. The sd^3 orbitals are involved in the bonding of the Cr^{4+} ion (substituting for Si^{4+}) in tetrahedral coordination with four oxygen ions in crystals such as Mg_2SiO_4 , forsterite.

Some of the hybrid orbitals that are important for bonding in solid-state materials are listed in Table W2.3. Also listed are the symmetries of the orbitals, the *coordination number* CN or number of bonds that can be formed by an atom using these orbitals and examples of crystals in which the hybrid orbitals are involved in the bonding. The formation of these hybrid orbitals is only a transitional step in the bonding process, since these orbitals are eigenstates of neither the isolated atom nor the resulting molecule or solid.

Molecular Orbitals and Chemical Bonds. The electrons involved in the chemical bonds between atoms in a molecule no longer occupy specific atomic or hybrid orbitals but rather, occupy *molecular orbitals* (MOs) that are associated with two or more

atoms. The wavefunctions of these MOs can be calculated in principle by solving the Schrödinger equation for the molecule. This is very difficult to do in practice since the potential experienced by the electrons due to the nuclei and the other electrons is not known a priori. As a result, the solutions for the MOs must be obtained in a self-consistent manner.

As an example, consider the simplest *chemical bond*, the bond between two H atoms in the H_2 molecule. In the formation of this molecule, the $1s$ atomic orbitals of each H atom begin to overlap in space as the atoms approach each other. If the phases of the two $1s$ orbitals are the same, *constructive interference* results and a *bonding molecular orbital (BMO)* is produced. If the phases are opposite, *destructive interference* occurs and an *antibonding state* results. In an occupied bonding orbital there is an excess electron density between the nuclei. In an occupied antibonding state there is a diminished electron density between the nuclei.

When the interaction is completed and the H_2 molecule is formed, the two $1s$ orbitals have combined into a single BMO known as a σ_{1s} MO, in which the two electrons are bound equally to both nuclei. In this doubly occupied σ_{1s}^2 MO, shown schematically in Fig. W2.6a, the electron charge density midway between the two nuclei is larger than the sum of the original charge densities in the two $1s$ atomic orbitals. When a σ MO is doubly occupied, the two electrons are required by the PEP to have their spins pointing in opposite directions, corresponding to a singlet state.

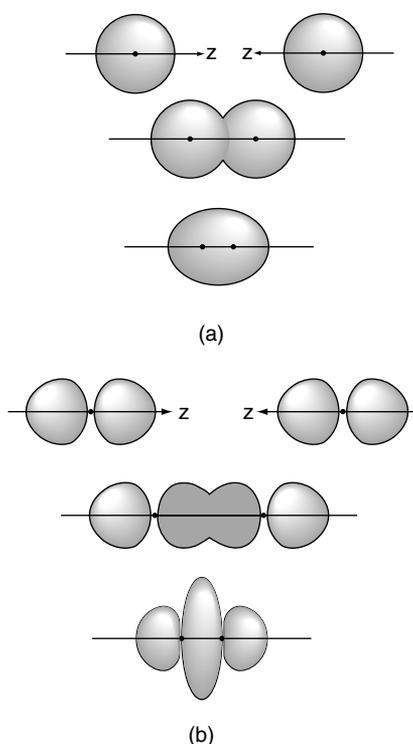


Figure W2.6. Formation of sigma molecular orbitals (σ MOs): (a) from two s atomic orbitals on different atoms; (b) from two p_z atomic orbitals on different atoms. (Adapted from A. L. Companion, *Chemical Bonding*, 2nd ed., McGraw-Hill, 1979.)

Stable molecules have lower energies than the initially isolated atoms. For example, the H_2 molecule is lower in energy than the two isolated H atoms by 4.52 eV (see Fig. 2.1 in the textbook[†]). This energy can be associated with the energy of the covalent H–H σ bond [i.e., $E(\text{H–H}) = 4.52$ eV]. The σ bonds correspond to the buildup of charge between the two atoms involved and are the strongest covalent bonds. Other σ MOs similar to the one shown in Fig. W2.6a can also be formed from any of the other atomic ($2s$, $2p$, $3s$, $3p$, $3d$, ...) or hybrid (sp , sp^2 , sp^3 , dsp^2 , d^2sp^3 , ...) orbitals. For example, when two $2p_z$ atomic orbitals (see Fig. W2.1) on different atoms overlap head-on and in phase, the σ_{2p} MO shown in Fig. W2.6b is formed.

Another important type of molecular orbital is the π MO formed from p or d atomic orbitals. For example, consider again the interaction of two $2p_z$ orbitals on different, identical atoms which are now aligned side by side with their phases synchronized, as shown schematically in Fig. W2.7. Their linear combination is known as a π MO and contains two equivalent regions of high probability, placed symmetrically with respect to the xy plane. When occupied by two electrons, the π MO corresponds to a covalent π bond. The π bonds are in general weaker than σ bonds because their charge distributions are more spread out.

The last type of MO to be discussed here is the δ MO formed from the head-on overlap of two $3d$ orbitals on different, identical atoms. An example is shown in Fig. W2.8, where two $3d_{x^2-y^2}$ orbitals overlap along the z axis. Four equivalent regions of high probability are formed symmetrically with respect to the z axis. When the δ MO contains its two allowed electrons, a covalent δ bond is formed. The δ bonds are in general weaker than σ or π bonds.

The methane molecule, CH_4 , provides a simple example of σ bonding. Here four identical σ bonds are formed from the four electrons in the $1s$ H orbitals and the four electrons in each of the sp^3 hybrid orbitals on the C atom. The resulting tetrahedral σ

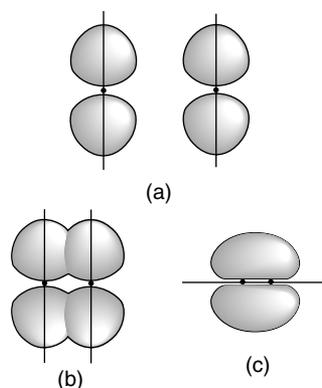


Figure W2.7. Formation of a π molecular orbital (π MO) from two p_z atomic orbitals on different atoms. (Adapted from A. L. Companion, *Chemical Bonding*, 2nd ed., McGraw-Hill, 1979.)

[†] The material on this home page is supplemental to *The Physics and Chemistry of Materials* by Joel I. Gersten and Frederick W. Smith. Cross-references to material herein are prefixed by a “W”; cross-references to material in the textbook appear without the “W.”

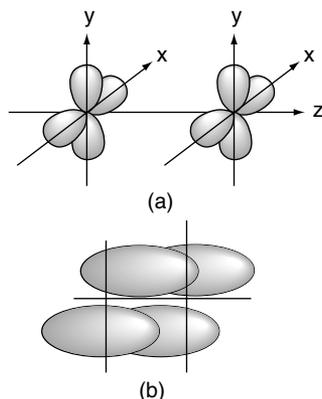


Figure W2.8. Formation of a δ molecular orbital (δ MO) from two $3d_{x^2-y^2}$ atomic orbitals on different atoms. (Adapted from A. L. Companion, *Chemical Bonding*, 2nd ed., McGraw-Hill, 1979.)

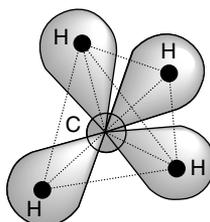


Figure W2.9. Model of the sp^3 tetrahedral σ bonding in the CH_4 (methane) molecule. (Adapted from A. L. Companion, *Chemical Bonding*, 2nd ed., McGraw-Hill, 1979.)

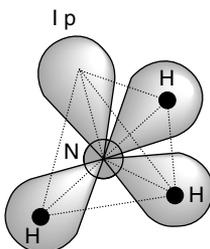


Figure W2.10. Model of the “ sp^3 tetrahedral” σ bonding in the NH_3 (ammonia) molecule. (Adapted from A. L. Companion, *Chemical Bonding*, 2nd ed., McGraw-Hill, 1979.)

bonding in CH_4 is shown schematically in Fig. W2.9, where the angles between the σ bonds have the ideal value of 109.47° .

Examination of the bonding in the ammonia molecule, NH_3 , illustrates the formation of nonbonding molecular orbitals (NBMOs). In NH_3 three σ bonds are formed between the H atoms and the N atom, as shown in Fig. W2.10. Since N has a valence of 5, the two remaining valence electrons form a *nonbonding*, or *lone pair* (*lp*), *orbital*, also shown in the figure. The NH_3 molecule does not have perfect tetrahedral symmetry since the three σ bonds and the nonbonding orbital are not equivalent. The reality

of the nonbonding orbital can be inferred from its transformation to a σ bond in the ammonium ion, NH_4^+ . Here a proton H^+ bonds to the N atom through its attraction to the electrons in the NBMO, thereby converting this orbital into the fourth σ bond in the tetrahedral NH_4^+ ion. Non-bonding orbitals can also play important roles in the bonding of solids. NBMOs participate in hydrogen bonding (see Section 2.7), which helps to stabilize the structures of solid H_2O and DNA.

The interaction of two atomic or hybrid orbitals on different atoms can also lead to the formation of a less stable, *antibonding* MO (ABMO) lying higher in energy than the more stable BMO. In the case of the H_2 molecule the spins of the two electrons in the σ_{1s} BMO are antiparallel, corresponding to a singlet spin state, while in the σ_{1s} ABMO the spins are parallel, corresponding to a triplet spin state. The energy of the σ_{1s} ABMO state lies well above that of the σ_{1s} BMO in H_2 , as shown in Fig. 2.1. The triplet state of this molecule is therefore unstable. Examples of stable molecules in which ABMOs are actually occupied by electrons are O_2 and NO.

W2.2 Absence of Covalent Bonding in White Sn (β -Sn) and Pb

The absence of covalent bonding and the existence instead of metallic bonding in the group IV elements white Sn (β -Sn) of row 5 and Pb of row 6 can be attributed to the increased separation between the s and p energy levels in these atoms. This results from the fact that the $5s$ and $6s$ electrons are relatively more strongly bound to the nuclei. It is therefore no longer energetically favorable for the $5s^2p^2$ and $6s^2p^2$ atomic electrons to undergo the hybridizations to $5sp^3$ and $6sp^3$ orbitals, respectively, which are necessary for covalent bonding to occur. Another specific indication of the relatively stronger binding of the $6s$ electrons is that Pb ($6s^26p^2$) often has a valence equal to 2 in solids (e.g., PbO and PbS), indicating that the more strongly bound $6s^2$ electrons do not participate in the bonding.

W2.3 Madelung Energy of Ionic Crystals

A general expression for the electrostatic energy (i.e., the *Madelung energy*) of an ionic crystal is obtained by adding together all the Coulomb interaction energies of the ions. Let $z_i e$ denote the charge of the basis ion at position \mathbf{s}_i . Neutrality requires that $\sum_{i=1}^n z_i = 0$, where n is the number of ions in a unit cell. The Madelung energy is

$$U = \frac{e^2}{4\pi\epsilon_0} \left(\frac{N}{2} \sum_{i,j}^n \frac{z_i z_j}{|\mathbf{s}_i - \mathbf{s}_j|} + \frac{N}{2} \sum_{\mathbf{R}} \sum_{i,j}^n \frac{z_i z_j}{|\mathbf{R} + \mathbf{s}_i - \mathbf{s}_j|} \right), \quad (\text{W2.1})$$

where \mathbf{R} is a Bravais lattice vector and N is the number of unit cells in the crystal (assumed to be large). Note that $\mathbf{R} = 0$ is excluded from the sum. In the first sum the term $i = j$ is omitted. The evaluation of this sum is carried out by summing over “shells” of ions of given charge at a given distance from the central ion. The interactions involving the cell at $\mathbf{R} = 0$ are illustrated in Fig. W2.11.

This contribution of the electrostatic interaction to the cohesive energy of an ionic crystal containing $2N$ ions is usually expressed as $U = -NAe^2/4\pi\epsilon_0 d$, where $A > 0$ is the *Madelung constant* and the energy of interaction for a NN cation–anion pair separated by a distance d is $-e^2/4\pi\epsilon_0 d$. For the CsCl, NaCl, and cubic ZnS crystal structures, the values of A are 1.7627, 1.7476, and 1.6381, respectively. On this basis

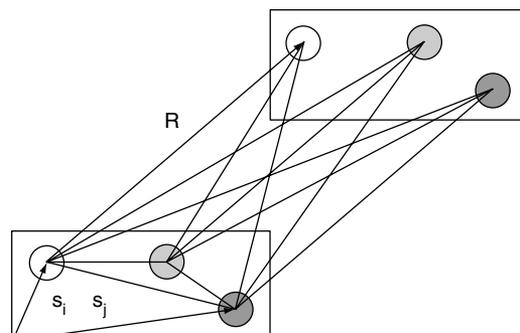


Figure W2.11. The lines within the box correspond to the intrabasis Coulomb interactions (within a given unit cell), while the lines joining the boxes denote the intercell interactions.

the CsCl crystal structure is expected to be slightly more stable than the NaCl crystal structure. Other effects not included here, where ions have been treated as point charges, such as overlap of charge clouds, make the very small calculated difference between the CsCl and NaCl crystal structures rather meaningless. The actual ion–ion interaction is more realistically modeled as the sum of a short-range repulsive potential and the long-range Coulomb interaction,

$$V(r) = \frac{B}{r^m} - \frac{z_c z_d e^2}{4\pi\epsilon_0 r}, \quad (\text{W2.2})$$

where B and m are empirical parameters. Ionic bonding and the Madelung energy are described in more detail in Chapter 13.

W2.4 Hydrogen Bonding in Ice (Solid H₂O)

An example of a crystal in which hydrogen bonding plays an essential role is solid H₂O or ice, where the hydrogen-bonding unit can be written as O–H···O. Each oxygen atom in ice is bonded by strong O–H σ bonds with the two H atoms in the H₂O molecule and by weaker H···O hydrogen bonds to two H atoms in neighboring H₂O molecules. The arrangement of a central O atom with the four H atoms is tetrahedral (Fig. W2.12). The O–H distance in the O–H bond is about 0.10 nm and is about 0.175 nm in the weaker H···O hydrogen bond. Ice has several stable crystal structures which share this tetrahedral orientation of each O atom with respect to the four H atoms surrounding it and also with respect to its four next-NN O atoms. At any given instant, two of the four H atoms in each of these tetrahedral O-centered units in ice are bonded to the central O atom by strong O–H bonds. The other two H atoms are bonded to the central O atom via the weaker H···O bonds. Neutron diffraction studies of solid D₂O have shown, however, that the four D (or H) atoms associated with each O atom are constantly changing their positions so that each D (or H) atom spends half of its time in strong σ bonds to the central O atom and the other half in strong σ bonds with a neighboring O atom. These results are consistent with thermodynamic studies of the high residual entropy found in ice crystals, which reflects the “disorder” present in ice even at very low temperatures. Thus while H₂O molecules retain their identity in crystals of ice, it is not possible to say which two of the four H atoms are bonded via strong O–H σ bonds with the central O atom at any instant.

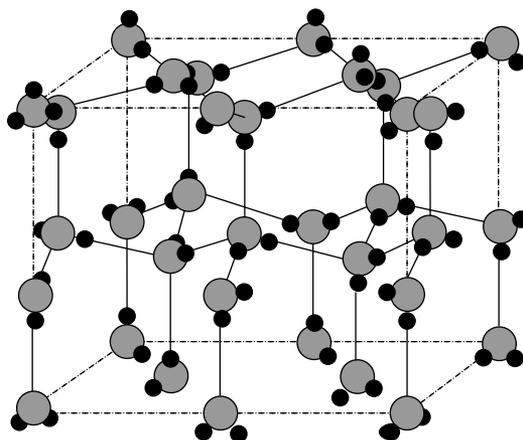
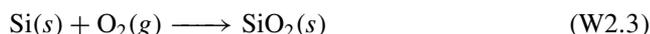


Figure W2.12. Crystal structure of ice (solid H_2O) illustrating hydrogen bonding and showing the disorder in the positions of the protons (H atoms). (From N. H. Fletcher, *The Chemical Physics of Ice*, Cambridge University Press, Cambridge, 1970. Reprinted with the permission of Cambridge University Press.)

The strengths of the two bonds in $\text{O}-\text{H}\cdots\text{O}$ bonding units are quite different, with the much stronger $\text{O}-\text{H}$ σ bond having an energy $E(\text{O}-\text{H}) \approx 4.8$ eV, while the much weaker $\text{H}\cdots\text{O}$ hydrogen bond has an energy $E(\text{H}\cdots\text{O})$ of only about 0.4 eV. Thus the melting of ice (which involves the weakening of the $\text{H}\cdots\text{O}$ hydrogen bonds between H_2O molecules) and the boiling of water (which involves the breaking of the hydrogen bonds) occur at relatively low temperatures. The processes of melting and boiling leave the much stronger $\text{O}-\text{H}$ σ bonds within each H_2O molecule intact.

W2.5 Standard Enthalpies of Formation

Cohesive energies ΔH_c must in general be distinguished from the *standard enthalpies of formation* $\Delta_f H^\circ$ of crystals, which are the changes in enthalpy involved in the formation of a crystal from the constituent elements in their standard states. For example, the standard enthalpy of formation at $T = 0$ K of $\alpha\text{-SiO}_2(\text{s})$ (i.e., α -quartz), according to the reaction



is equal to the *standard enthalpy change* $\Delta_r H^\circ$ for this reaction. Thus

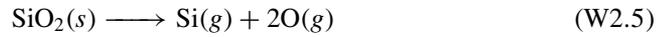
$$\begin{aligned} \Delta_r H^\circ[\text{SiO}_2(\text{s})] &= \Delta_f H^\circ[\text{SiO}_2(\text{s})] - \Delta_f H^\circ[\text{Si}(\text{s})] - \Delta_f H^\circ[\text{O}_2(\text{g})] \\ &= -905.978 - 0 - 0 = -905.978 \text{ kJ/mol.} \end{aligned} \quad (\text{W2.4})$$

Solid $\text{Si}(\text{s})$ and molecular $\text{O}_2(\text{g})$ in Eq. (W2.3) are in their standard states with standard enthalpies of formation $\Delta_f H^\circ$, which by definition are equal to zero.[†] The negative

[†] Unless otherwise specified, the standard enthalpies of formation $\Delta_f H^\circ$ used in this section are from the NBS Tables of Chemical Thermodynamic Properties, *J. Phys. Chem. Ref. Data*, **11**, Suppl. 2 (1982).

value for $\Delta_f H^\circ[\text{SiO}_2(s)]$ indicates that energy is released when $\text{SiO}_2(s)$ is formed from $\text{Si}(s)$ and $\text{O}_2(g)$ (i.e., the reaction is exothermic).

The cohesive energy of $\alpha\text{-SiO}_2$ at $T = 0$ K according to the reaction



is given by

$$\begin{aligned} \Delta H_c[(\text{SiO}_2(s))] &= \Delta_f H^\circ[\text{Si}(g)] + 2\Delta_f H^\circ[\text{O}(g)] - \Delta_f H^\circ[\text{SiO}_2(s)] \\ &= 451.29 + 2(246.785) - (-905.978) \\ &= +1850.84 \text{ kJ/mol.} \end{aligned} \quad (\text{W2.6})$$

Here $\Delta_f H^\circ[\text{Si}(g)]$ and $\Delta_f H^\circ[\text{O}(g)]$ are the standard enthalpies of formation of gas-phase Si and O atoms from solid $\text{Si}(s)$ and $\text{O}_2(g)$ at $T = 0$ K, respectively.

W2.6 Bond Energies

The cohesive energy $\Delta H_c[\text{SiO}_2(s)]$ was shown in Eq. (W2.6) to be equal to 1850.84 kJ/mol. If this energy is assumed to be shared by the $4N_A$ Si–O bonds per mole of $\text{SiO}_2(s)$ (N_A is Avogadro's number), the Si–O bond energy is then

$$E(\text{Si–O}) = 4.80 \text{ eV.} \quad (\text{W2.7})$$

The bond energies for single bonds listed in Table W2.4 have been obtained from cohesive energies using this procedure. The crystals whose cohesive energies are used are also listed. The close connection between bond energies and the electronegativity scale is discussed in Section 2.8.

W2.7 Ionization Energies and Electron Affinities

It is clear from the discussions presented in Chapter 2 that the valence electrons play a critical role in the bonding of atoms in solids. Certain important properties and parameters pertaining to atoms (or ions) include ionization energy, electron affinity, valence,

TABLE W2.4 Bond Energies

Bond X–Y	$E(X\text{--}Y)$ (eV)	Source
Si–Si	2.34	Si(<i>s</i>)
Si–C	3.21	$\beta\text{-SiC}(s, \text{cubic})$
Si–Ge	2.14	Average of Si(<i>s</i>) and Ge(<i>s</i>)
Si–N	3.45	$\text{Si}_3\text{N}_4(s)$
Si–O	4.80	$\alpha\text{-SiO}_2(s)$
C–C	3.70	C(<i>s</i> , diamond)
Ge–Ge	1.95	Ge(<i>s</i>)
Ge–O	3.66	$\text{GeO}_2(s)$
B–N	3.32	$\beta\text{-BN}(s, \text{cubic})$
Al–N	2.90	AlN(<i>s</i>)
Al–O	5.33	$\text{Al}_2\text{O}_3(s)$

and atomic or ionic radius. Of these important quantities, only the ionization energies and electron affinities are obtained directly from experiment. The other parameters (i.e., valence, electronegativity, and atomic radii), can only be inferred from the measured properties of atoms.

The first *ionization energy* $IE(1)$ of an atom is the energy required to remove an electron from the neutral atom. $IE(1)$ is also known as the *ionization potential*. Conversely, the *electron affinity* EA of an atom is the energy released when an additional electron is bound to a neutral atom, leading to the formation of a negative ion with charge $-e$. The quantity $IE(1)$ is thus a measure of the ease with which atoms give up electrons (i.e., of their ability to become cations), while EA is the corresponding quantity for the formation of anions.

The reactivity of an atom (i.e., its tendency to combine with other atoms to form a solid), will be greater for atoms with low values of $IE(1)$, such as Li and Na, or with high values of EA , such as F and Cl. Conversely, atoms with high values of $IE(1)$ and low values of EA , such as He and Ne, will tend to be unreactive. Strongly ionic crystals with high ionicities will be formed from pairs of atoms in which one atom has a low $IE(1)$ and the other atom has a high EA . The classic example is NaCl, where the Na atom has $IE(1) = 5.15$ eV, the Cl atom has $EA = 3.62$ eV, and the resulting ionicity (see Table 2.6) is $f_i = 0.94$.

Values of $IE(1)$ and $IE(2)$ for the elements are presented in Table 2.9, with $IE(1)$ also shown graphically in Fig. 2.7a as a function of atomic number Z . It can be seen that $IE(1)$ generally increases in a given row of the periodic table from left to right as Z , the resulting nuclear charge $+Ze$, and the attractive electrostatic potential felt by the electrons all increase. For example, at the beginning of the second row $IE(1) = 5.39$ eV for Li with $Z = 3$, while at the end of the same row $IE(1) = 21.56$ eV for Ne with $Z = 10$. Even though Z and the nuclear charge of atoms also increase down a given group, $IE(1)$ generally decreases in this direction because of the increase in atomic size and the screening of the nuclear charge by electrons in filled inner shells.

The two atoms with the highest first ionization energies, He with $IE(1) = 24.59$ eV and Ne with $IE(1) = 21.56$ eV, both have filled outer-electron shells. These two elements, along with the other inert-gas elements in group VIII, are therefore quite stable and unreactive. Only at low temperatures are these elements able to form close-packed crystals in which the neutral atoms are bonded by the weak van der Waals interaction.

Atomic excitation energies can also play a role in chemical bonding, particularly in the formation of hybrid orbitals (see Section W2.1). For example, while $IE(1) = 9.32$ eV for Be is relatively high due to its $1s^2 2s^2$ filled-shell electron configuration, Be is nevertheless reactive due to the low first excitation energy of about 2.7 eV, which is required to excite a $2s$ electron to a $2p$ atomic level. The $2s$ and the $2p$ electrons of the excited Be atom can then form a pair of sp hybrid orbitals. Under these conditions, the Be atom can be considered to have a valence of 2. These sp orbitals can form bonds with other atoms, such as O in solid BeO, which has the wurtzite (i.e., hexagonal ZnS) crystal structure.

The electron affinities EA for the elements up to $Z = 87$ are presented in Table 2.10 and Fig. 2.7b. It can be seen that EA is much smaller than $IE(1)$ for a given atom. Also, EA increases irregularly from left to right across each row of the periodic table, reaching its maximum value for the group VII elements, which require just one additional electron to achieve a filled-shell configuration. All the elements in group II (and

He) with filled s^2 shells and in group VIII with filled s^2 and p^6 shells have negative values of EA. These atoms are therefore unstable as negative ions.

W2.8 Valence

The *valence* z of an atom is usually defined either as the number of electrons it can share with other atoms in covalent bonds or as the number of electrons it can gain or lose in the formation of ionic bonds. These two definitions are often equivalent. For example, the H atom can share its single $1s$ electron in a covalent bond with another H atom or can give it up to a F atom during the formation of an ionic HF molecule. In either case the valence of the H atom is 1.

On the basis of this definition, the most common valences for atoms are given by the number of outer-shell s and p electrons and so can readily be predicted from their locations in the periodic table. For example, atoms from group I (H, Li, Na, ...) and VII (F, Cl, Br, ...) have valence 1, atoms from group II (Be, Mg, Ca, ...) and VI (O, S, Se, ...) have valence 2, atoms from group III (B, Al, Ga, ...) and V (N, P, As, ...) have valence 3, atoms from group IV (C, Si, Ge, ...) have valence 4, while atoms from group VIII (He, Ne, Ar, ...) have valence 0.

As with many such simple definitions, there are a large number of instructive exceptions. For the transition metals and the noble metals Cu, Ag, and Au, for example, there exist unfilled or just filled $3d$, $4d$, or $5d$ shells lying in energy just below the $4s$, $5s$, and $6s$ valence electrons. As a result, the d electrons may participate in bonding and thereby act as valence electrons. Oxides of the $3d$, $4d$, and $5d$ transition metals and of the noble metals illustrate this point since the valences for the metal cations can vary from oxide to oxide, depending on the crystal structure. Some examples are shown in Table W2.5. Note that in Fe_3O_4 , magnetite, and Mn_3O_4 , hausmannite, the Fe and Mn cations are observed to have two different valence states, +2 and +3, within the same oxide. Also included in the table are oxides of Pb, a metal with a $6s^2 6p^2$

TABLE W2.5 Valence, Bonding, and Crystal Structures of Some Oxide Crystals

Chemical Formula	Valence z of Metal Ion	Local Atomic Bonding Units	Crystal Structure
Cu_2O	+1	$\text{Cu}-\text{O}_2$, $\text{O}-\text{Cu}_4$	Cuprite (BCC)
CuO	+2	$\text{Cu}-\text{O}_4$, $\text{O}-\text{Cu}_4$	Tenorite (monoclinic)
MnO	+2	$\text{Mn}-\text{O}_6$, $\text{O}-\text{Mn}_6$	NaCl
Mn_2O_3	+3	$\text{Mn}-\text{O}_6$, $\text{O}-\text{Mn}_4$	Distorted fluorite
Mn_3O_4	+2 (1) +3 (2)	$\text{Mn}-\text{O}_4$, $\text{O}-\text{Mn}^{2+}\text{Mn}_3^{3+}$ $\text{Mn}-\text{O}_6$	Hausmannite (tetragonal)
$\beta\text{-MnO}_2$	+4	$\approx \text{Mn}-\text{O}_6$, $\text{O}-\text{Mn}_3$	Rutile (tetragonal)
FeO	+2	$\text{Fe}-\text{O}_6$, $\text{O}-\text{Fe}_6$	NaCl
Fe_3O_4	+2 (1) +3 (1) +3 (1)	$\text{Fe}-\text{O}_6$, $\text{O}-\text{Fe}^{2+}\text{Fe}_3^{3+}$ $\text{Fe}-\text{O}_6$ $\text{Fe}-\text{O}_4$, $\text{O}-\text{Fe}_2^{2+}\text{Fe}_2^{3+}$	Magnetite (inverse spinel)
Fe_2O_3	+3	$\approx \text{Fe}-\text{O}_6$, $\text{O}-\text{Fe}_4$	Corundum (hexagonal)
Pb_2O	+1	$\text{Pb}-\text{O}_2$, $\text{O}-\text{Pb}_4$	Cuprite (BCC)
PbO	+2	$\text{Pb}-\text{O}_4$, $\text{O}-\text{Pb}_4$	Tetragonal
PbO_2	+4	$\text{Pb}-\text{O}_6$, $\text{O}-\text{Pb}_3$	Rutile (tetragonal)

electron configuration. The valence of Pb can vary due to the relatively large energy separation between the $6s^2$ and $6p^2$ atomic energy levels.

The overall electrical neutrality of these oxide crystals requires that the total positive charge of the metal cations be balanced by the total negative charge of the oxygen anions. This balance is clearly reflected in the chemical formulas, assuming a valence of oxygen equal to 2, and also in the local atomic bonding units, $M-O_m$ and $O-M_n$, where m and n are the integral numbers of NNs of the metal M cations and of the O anions, respectively. The following relationship involving the numbers of NNs and the valences of the metal cation, $z(M)$, and oxygen, $z(O)$, is found to be satisfied for all the oxides listed in the table:

$$mz(O) = nz(M). \quad (\text{W2.8})$$

W2.9 Electronegativity

As an example of the use of Eq. (2.12), that is,

$$E(A-B) = \frac{E(A-A) + E(B-B)}{2} + k(X_A - X_B)^2, \quad (2.12)$$

consider quartz, SiO_2 . The single-bond energies $E(\text{Si-Si}) = 2.34$ eV and $E(\text{Si-O}) = 4.80$ eV are derived from thermochemical data (see Table W2.4). Using the single-bond energy $E(\text{O-O}) \approx 1.48$ eV derived from similar data on H_2O and H_2O_2 , Eq. (2.12) yields $(X_{\text{Si}} - X_{\text{O}})^2 = 2.89$. It follows that $(X_{\text{Si}} - X_{\text{O}}) = -1.70$ since it is known that $X_{\text{Si}} < X_{\text{O}}$. To obtain an absolute scale for electronegativity, Pauling assigned the value $X = 4.0$ to F, the most electronegative atom. In this way, the values of electronegativity presented in Table 2.11 have been obtained from Eq. (2.12). From Table 2.11 it can be seen that $(X_{\text{Si}} - X_{\text{O}}) = 1.8 - 3.5 = -1.7$, as found above. These values of electronegativity reproduce fairly well the measured single-bond energies $E(A-B)$ in a wide range of materials. It should be noted that electronegativities have not been assigned to the elements in group VIII of the periodic table, since these atoms with filled outer-electron shells do not ordinarily form bonds with other atoms.

It can be seen from Tables 2.9, 2.10, and 2.11 that the atoms with the highest electronegativities [i.e., F (4.0), O (3.5), N (3.0), and Cl (3.0)] are also the atoms with some of the highest first ionization energies IE(1) and highest electron affinities EA. This observation is the basis of an alternative electronegativity scale proposed by Mulliken[†] in which these strictly atomic properties have been used to define X , as follows:

$$X = \frac{\text{IE}(1) + \text{EA}}{5.42}. \quad (\text{W2.9})$$

Here IE(1) and EA are expressed in electron volts. When applied to Si and O using the data presented in Tables 2.9 and 2.10, the values $X_{\text{Si}} = 1.76$ and $X_{\text{O}} = 2.78$ are obtained from Eq. (W2.9), compared with Pauling's values of 1.8 and 3.5. Mulliken's scale of electronegativity is thus only reasonably consistent with that of Pauling.

Since electronegativity is a parameter that is neither directly measured from experiment nor precisely defined from first principles, it is not surprising that several scales

[†] R. S. Mulliken, *J. Chem. Phys.*, **2**, 782 (1934); **3**, 573 (1935).

of electronegativity exist in addition to those of Pauling and Mulliken. Scales based on different assumptions and using different physical properties as input have been proposed by Sanderson (1976) and by Phillips (1973). The Phillips electronegativity scale for elements in tetrahedrally coordinated environments is based on dielectric properties, in particular the optical dielectric function. The difference between the Pauling and Phillips electronegativities is that Phillips includes the effects of screening of ions by the valence electrons through use of the Thomas–Fermi screening factor $\exp(-k_{TF}r)$, defined in Chapter 7. These electronegativity scales have been found to be particularly useful when applied to physical properties closely related to those used in their definition.

One of the main uses of electronegativities has been in the prediction of the fraction of ionic character of a given bond (i.e., the ionicity of the bond). Ionicities as determined by Phillips have been presented in Table 2.6. With Pauling's definition of electronegativity given in Eq. (2.12), the ionicity of the binary compound AB is defined by Pauling to be

$$f_i(\text{Pauling}) = 1 - \exp\left[-\frac{(X_A - X_B)^2}{4}\right]. \quad (\text{W2.10})$$

While the Pauling and Phillips definitions of X agree for the elements in the first row of the periodic table, there are significant discrepancies for elements in lower rows.

A serious deficiency of Pauling's and other electronegativity scales is that a single value of X is typically assigned to an atom, independent of its valence in a solid. Since, as shown in Table W2.5, the valence of an atom can vary in different crystal structures, it should be expected that its electronegativity can also vary. Some examples of the dependence of electronegativity on valence include $X_{\text{Cu}} = 1.9$ for the normal Cu valence state of 1, [i.e., Cu(1)] but $X_{\text{Cu}} = 2.0$ for Cu(2), as well as $X_{\text{Fe}} = 1.8$ for Fe(2), but $X_{\text{Fe}} = 1.9$ for Fe(3).

W2.10 Atomic Radii

For the one-electron atom H and for one-electron ions (He^+ , Li^{2+} , Be^{3+} , ...) with nuclear charge $+Ze$, the expectation value or most probable value for the radius of the electron in its ground-state orbital is given by

$$\langle r \rangle = \frac{a_1}{Z} = \frac{0.0529 \text{ nm}}{Z}, \quad (\text{W2.11})$$

where $a_1 = 4\pi\epsilon_0\hbar^2/me^2$ is the first Bohr radius. The inverse dependence of $\langle r \rangle$ on Z reflects the increased attraction of the electron as the nuclear charge $+Ze$ increases. A useful approximate expression for the radius of the outermost electron orbital with principal quantum number n in a neutral atom is

$$\langle r \rangle \approx n^2 a_1 / Z_{\text{eff}}, \quad (\text{W2.12})$$

where $+Z_{\text{eff}}e$ is the effective nuclear charge experienced by the outermost electrons. Note that Z_{eff} will be less than Z as a result of the screening of the nuclear charge by the electrons in filled inner shells.

Some general observations concerning the radii presented in Table 2.12 can be made (note that the only anions listed in the table are O^{2-} , S^{2-} , Se^{2-} , Te^{2-} , F^- , Cl^- , Br^- , and I^- ; the rest are cations):

1. The radii of atoms and ions increase as one moves down the periodic table, in qualitative agreement with the dependence on the principal quantum number n expressed in Eq. (W2.12).
2. For a given atom the radii r_{cov} and r_{met} are closer in value to each other than to the radius r_{ion} of the same atom.
3. Anions such as O^{2-} or F^- which have gained additional electrons have $r_{ion} > r_{cov}$, whereas the reverse is true for cations such as Be^{2+} and Mg^{2+} which have given up electrons.
4. In the case of Si the three radii presented in Table 2.12 are quite different (i.e., $r_{ion} = 0.040$ nm, $r_{cov} = 0.118$ nm, and $r_{met} = 0.132$ nm). These values apply, in principle, to the Si^{4+} ion in crystalline SiO_2 or in the SiF_4 molecule, to crystalline Si with the diamond crystal structure, and to metal silicides such as V_3Si in which the Si atom has 12 NNs, respectively.
5. Values of r_{ion} will depend on the valence of the ion (see Table 2.4 and also the sources listed in this table for values of r_{ion} for other valences). For example, the values of r_{ion} presented in Table 2.12 for the group V elements are appropriate for the cations N^{5+} , P^{5+} , and so on. The values of r_{ion} for the corresponding anions N^{3-} , P^{3-} , As^{3-} , and Sb^{3-} are much larger (i.e., 0.150, 0.190, 0.200, and 0.220 nm, respectively).

As an example of the use of these radii, consider again SiO_2 and the question of its ionicity. Assuming ionic bonding, the interatomic distance $d(Si-O)$ in SiO_2 is predicted to be equal to the sum of the radii r_{ion} for Si and O (i.e., 0.040 nm + 0.140 nm = 0.180 nm). For the case of covalent bonding, the corresponding sum of the radii r_{cov} is 0.118 nm + 0.066 nm = 0.184 nm. The actual Si–O interatomic distance in SiO_2 has in fact been measured to be 0.161 nm (independent of the actual crystal structure). Therefore, neither the ionic nor the covalent radii listed in Table 2.12 are in fact completely appropriate for SiO_2 . The actual situation is that the bonding in SiO_2 is of the mixed ionic–covalent type, with the ionicity of the Si–O bond close to 50%.

The van der Waals atomic radii r_{vdw} are appropriate for neutral atoms with filled outer shells which are effectively in contact with other atoms in solids but which are not bonded to them. In such cases the internuclear distance $d(A-B)$ can be set equal to the sum of the van der Waals radii of atoms A and B. Examples include atoms such as He and Ne in inert-gas crystals, nonbonded atoms in adjacent molecules in molecular crystals such as solid H_2 , Cl_2 , or solid hydrocarbons, and nonbonded atoms such as C in adjacent planes in the layered crystal graphite. Selected values of r_{vdw} are presented in Table 2.13. These values for r_{vdw} were chosen by Pauling to be essentially the same as the values of r_{ion} for the corresponding anions. This choice should not be surprising since, for example, in the Cl_2 molecule “the bonded (Cl) atom presents the same face to the outside world in directions away from its bond as the ion, Cl^- , does in all directions” (Pauling, 1960, p. 258).

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PROBLEMS

- W2.1** To see how rapidly the summation involved in the calculation of the Madelung energy U converges, use Eq. (W2.1) to calculate the contributions to the summation from the first five shells of ions surrounding a central ion in the NaCl and CsCl crystal structures.
- W2.2** Compare the electronegativity difference $|X_C - X_{Si}|$ calculated from Eq. (2.12) and the Si–Si, C–C, and Si–C bond energies listed in Table W2.4 with the Pauling electronegativities for Si and C listed in Table 2.11.
- W2.3** Calculate the Pauling ionicities f_i for SiC, GaAs, AlN, ZnS, HgS, and NaCl. Compare your results with the Phillips ionicities listed in Table 2.6 for the same compounds. Are there any systematic differences between the two scales?