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Atoms and Bonding

- What is an atomic term symbol?
- How are ionic radii determined?
- What are energy bands?

1.1 The Electron Structure of Atoms

An atom is made up of a small massive *nucleus*, in which almost all of the mass resides, surrounded by an *electron cloud*. Each element is differentiated from all others by the amount of positive charge on the nucleus, called the *proton number* or *atomic number*, Z. In a neutral atom, the nuclear charge is exactly balanced by Z electrons in the outer electron cloud, each of which carries one unit of negative charge. Variants of atoms that have slightly more or less electrons than are required for charge neutrality are called *ions*; those that have lost electrons have an overall positive charge and are called *cations*, while those that have gained electrons have an overall negative charge and are called *anions*. Many of the physical and chemical properties of solids described in later chapters are controlled by the outer electron structure of the component atoms.

1.1.1 Hydrogen

Hydrogen is the simplest atom and consists of a nucleus consisting of a single proton carrying one unit of positive charge together with a single bound electron carrying one unit of negative charge. The quantum mechanics of the hydrogen atom allows the probability of the location of the electron and its energy, defined in terms of *wavefunctions*, to be completely specified. The region of space defining the most probable location of the electron is termed an *orbital*. The wavefunctions are described by three *quantum numbers*: n, the *principal quantum number*; l, the *orbital angular momentum quantum number*; and m_l, the *magnetic quantum number*. The principal quantum number, n, defines the energy of the electron. It can take integral values 1, 2, 3, … to infinity. The energy of the electron is lowest for $n = 1$ and this represents the most stable or *ground state* of the hydrogen atom. The next lowest energy is given by $n = 2$, then by $n = 3$, and so on.

The energy of each state is given by the formula:

$$E = -A/n^2$$

where A is a constant equal to 2.179×10^{-18} J (13.6 eV)[1] and E is the energy of the level with principal quantum number n. The negative sign in the equation indicates that the energy of the electron is chosen as zero when n is infinite, that is to say, when the electron is no longer bound to the nucleus.

There is only one wavefunction and orbital associated with the lowest energy, $n = 1$, state. The states of higher energy each have n^2 different wavefunctions, corresponding to n^2

1 The unit of energy *electron volt*, eV, is frequently used for atomic processes. $1\,\text{eV} = 1.602 \times 10^{-19}$ J.

Understanding Solids: The Science of Materials, Third Edition. Richard J. D. Tilley.

Companion Website: www.wiley.com/go/tilley/understandingsolids3e

different orbitals, all of which have the same energy. There are four different wavefunctions and orbitals corresponding to $n = 2$, nine different wavefunctions and orbitals for $n = 3$, and so on. These are differentiated from each other by different values of the quantum numbers l and m_l, as explained in the following text. Wavefunctions with the same energy are said to be *degenerate*.

It is often convenient to represent the energy associated with each value of the principal quantum number, n, as a series of steps or *energy levels* (Figure 1.1). When an electron gains energy, it jumps from an energy level with a lower value of n to a level with a higher value of n. When an electron loses energy, it drops from an energy level with a higher value of n to an energy level with a lower value. The discrete packets of energy given out or taken up in this way are *photons* of electromagnetic radiation. The energy of a photon needed to excite an electron from energy E_1, corresponding to an energy level n_1 to energy E_2, corresponding to an energy level n_2 is given by:

$$\begin{aligned} E &= E_1 - E_2 = -2.179 \\ &\quad \times 10^{-18}[1/{n_1}^2 - 1/{n_2}^2]\,\text{J} \\ &= -13.6\,[\,1/{n_1}^2 - 1/{n_2}^2]\,\text{eV} \end{aligned}$$

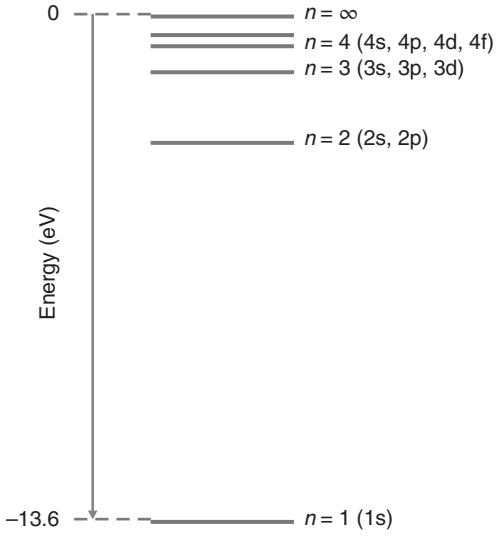

Figure 1.1 Electron energy levels of the H atom.

The energy of the photon emitted when the electron falls back from E_2 to E_1 is the same as that required for the excitation. The frequency ν (or the equivalent wavelength, λ) of the photons that are either emitted or absorbed during these energy changes is given by the equation:

$$E = E_1 - E_2 = h\nu = h\,c/\lambda$$

where h is the Planck constant. (Note that this equation applies to the transition between any two energy levels on any atom, not just between energy levels on hydrogen.) The energy needed to free the electron completely from the proton, which is called the *ionisation energy* of the hydrogen atom, is given by putting $n_1 = 1$ and $n_2 = \infty$ in the equation. The ionisation energy is 13.6 eV (2.179×10^{-18} J).

In the case of a single electron attracted to a nucleus of charge $+Ze$, the energy levels are given by:

$$E = -AZ^2/n^2$$

This shows that the energy levels are much lower in energy than in hydrogen, and that the ionisation energy of such atoms is considerably higher.

1.1.2 Many Electron Atoms

The simplest description of an atom with a nuclear charge of $+Z$ surrounded by Z electrons, called the *orbital approximation*, supposes that a single electron moves in a potential due to the nucleus and the average field of all the other electrons present in the atom, that is, it mirrors the hydrogen atom. The electron experiences an *effective nuclear charge*, Z_{eff}, which is considered to be located as a point charge at the nucleus of the atom. The energy levels of all of the orbitals drop sharply as Z_{eff} increases. When one reaches lithium, $Z = 3$, the 1s orbital energy has already decreased so much that it forms a chemically unreactive shell. This is translated into the concept of an atom as consisting of unreactive *core electrons*, surrounded by a small number of outermost *valence electrons*, which are of chemical and

physical significance. Moreover, the change of energy as Z increases justifies the approximation that the valence electrons of all atoms are at similar energies.

The orbitals are specified by two interdependent quantum numbers, l and m_l, where:

l takes values of 0, 1, 2, …, $(n-1)$
m_l takes values of 0, ±1, ±2, …, ±l

Each set of quantum numbers defines the *state* of the system. For a value of $n = 1$, there is only one state, corresponding to $n = 1$, $l = 0$, and $m_l = 0$. For $n = 2$, l can take values of 0 and 1, and m_l can then take values of 0, associated with $l = 0$, and −1, 0, and +1, associated with $l = 1$. For $n = 3$, l can take values of 0, 1, and 2, and m_l then can take values of 0, associated with $l = 0$, −1, 0, and +1, associated with $l = 1$ and −2, −1, 0, +1, +2, associated with $l = 2$. The same procedure applies to higher values of n. The various orbitals are given letter symbols. Orbitals with $l = 0$ are called *s orbitals*, those with $l = 1$ are called *p orbitals*, those with $l = 2$ are called *d orbitals*, those with $l = 3$ are called *f orbitals*, and those with $l = 4$ are called *g orbitals* (Table 1.1).

The set of orbitals derived from a single value of the principal quantum number form a *shell*. The lowest energy shell is called the K shell, and corresponds to $n = 1$. The other shells are labelled alphabetically (Table 1.1). There is only one s orbital in any shell, labelled 1s, 2s, and so on. There are three p orbitals in all shells from $n = 2$ upwards, collectively called 3p, 4p, and so on. There are five d orbitals in the shells from $n = 3$ upwards, collectively called 3d, 4d, 5d, and so on. There are seven f orbitals in the shells from $n = 4$ upwards, collectively called 4f, 5f, and so on. There are 9g orbitals added in the shells from $n = 5$ upwards and

Table 1.1 Orbitals of hydrogen-like atoms.

n	l	m_l	Orbital	Number of electrons	Shell	Capacity
1	0	0	1s (1)	2	K	2
2	0	0	2s (1)	2	L	8
	1	0, ±1	2p (3)	6		
3	0	0	3s (1)	2	M	18
	1	0, ±1	3p (3)	6		
	2	0, ±1, ±2	3d (5)	10		
4	0	0	4s (1)	2	N	32
	1	0, ±1	4p (3)	6		
	2	0, ±1, ±2	4d (5)	10		
	3	0, ±1, ±2, ±3	4f (7)	14		
5	0	0	5s (1)	2	O	50
	1	0, ±1	5p (3)	6		
	2	0, ±1, ±2	5d (5)	10		
	3	0, ±1, ±2, ±3	5f (7)	14		
	4	0, ±1, ±2, ±3, ±4	5g (9)	18		
6	0	0	6s (1)	2	P	72
	1	0, ±1	6p (3)	6		
	2	0, ±1, ±2	6d (5)	10		
	3	0, ±1, ±2, ±3	6f (7)	14		
	4	0, ±1, ±2, ±3, ±4	6g (9)	18		
	5	0, ±1, ±2, ±3, ±4, ±5	6h (11)	22		

22 h orbitals added in the shells from $n = 6$ upwards.

The extension of the various orbitals increases as the effective nuclear charge increases. This corresponds to the idea that heavy atoms are larger than light atoms. In addition, a different effective nuclear charge is experienced by electrons in differing orbitals. This has the effect of separating the energy of the *n*s, *n*p, *n*d, *n*f, and *n*g orbitals that are identical in hydrogen. It is found that for any value of *n*, the s orbitals have lowest energy, the three p orbitals have equal and slightly higher energy, the five d orbitals have equal and slightly higher energy again, and the seven f orbitals have equal and slightly higher energy again (Figure 1.2). However, the energy differences between the higher energy orbitals are very small and the energy of orbitals in different shells overlap so that the *n*d orbitals falls below that of the $(n+1)$p orbitals (3d below 4p, 4d below 5p, and 5d below 6p) and the *n*f orbitals falls below that of the $(n+2)$p orbitals (4f below 6p and 5f below 7p). The outer electron configuration of the elements is given in Appendix A, the Periodic Table. Note that in the case of the heavier elements the outer electron configurations are not as clearly defined as those of the lighter elements, and in these cases, especially with some of the lanthanoids and Period 7 elements, the quoted electron configuration must be treated with caution.

1.1.3 Orbital Shapes

The shapes of the electron orbitals, or more properly, the probability of encountering an electron in a certain small volume of space surrounding the nucleus, is of importance as it controls many of the properties exhibited in solids, such as the colour and magnetic properties of the 3d transition metal compounds. The probability of encountering an electron in an s orbital does not depend upon direction but does vary with distance from the nucleus (Figure 1.3). For hydrogen, this probability peaks at a radial distance of 0.052 92 nm for a 1s orbital; equal to the distance calculated by Bohr as the minimum allowed radius of an orbiting 'planetary' electron around a proton, and is called the *Bohr radius*. As the electron is promoted to the 2s, 3s, and 4s orbitals, the maximum probability peaks further and further from the nucleus. Generally, s orbitals are drawn as spherical *boundary surfaces* that enclose an arbitrary volume in which there is

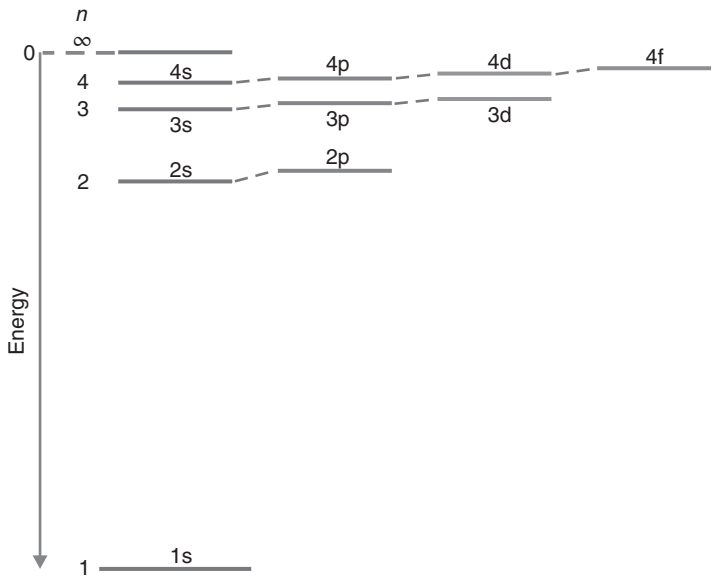

Figure 1.2 Schematic energy level diagram for a light, hydrogen-like atom.

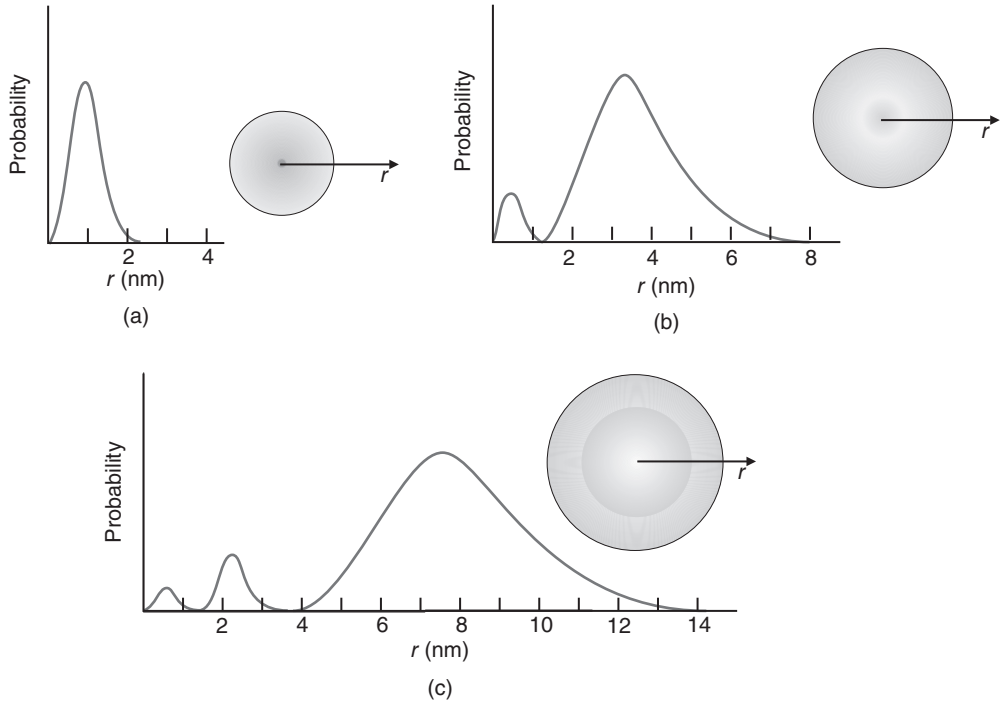

Figure 1.3 The probability of finding an s electron at a distance *r* from the nucleus: (a) 1s; (b) 2s; (c) 3s.

a high probability, say, 95%, that the electron will be found (Figure 1.3a,b).

All other wavefunctions are specified by three quantum numbers and can be divided into two parts, a radial part, with similar probability shapes to those shown in Figure 1.3, multiplied by an angular part. The maximum probability of finding the electron depends on both the radial and angular parts of the wavefunction and the resulting boundary surfaces have complex shapes. For many purposes, however, it is sufficient to describe only the angular part of the wavefunction.

The boundary surfaces of the angular parts of the three p orbitals are approximately dumbbell shaped, each consisting of two lobes. These lie along three mutually perpendicular directions, which it is natural to equate to *x*-, *y*-, and *z*-axes (Figure 1.4). The corresponding orbitals are labelled np_x, np_y, and np_z, for example, $2p_x$, $2p_y$, and $2p_z$. Note that the electron occupies both lobes of the p orbital. The probability of encountering a p electron on the perpendicular plane that separates the two halves of the dumbbell is zero, and this plane is called a *nodal plane*. The sign of the wavefunction is of importance when orbitals overlap to form bonds. The two lobes of each p orbital are labelled as + and −, and the sign changes as a nodal plane is crossed. The radial probability of encountering an electron in a p orbital is zero at the nucleus, and increases with distance from the nucleus. The maximum probability is further from the nucleus for an electron in a 3p orbital than a 2p orbital, and so on, so that 3p orbitals have a greater extension in space than 2p orbitals.

Of the five d orbitals, three of which have lobes lying between pairs of axes, d_{xy}, between the *x*- and *y*-axes, d_{xz}, between the *x*- and *z*-axes, and d_{yz}, between the *y*- and *z*-axes. The other two orbitals have lobes along the axes, $d_{x^2-y^2}$ pointing along *x*- and *y*-, and d_{z^2} pointing along the *z*-axis (Figure 1.5). Except for the d_{z^2} orbital, two perpendicular planar nodal planes separate the lobes and intersect

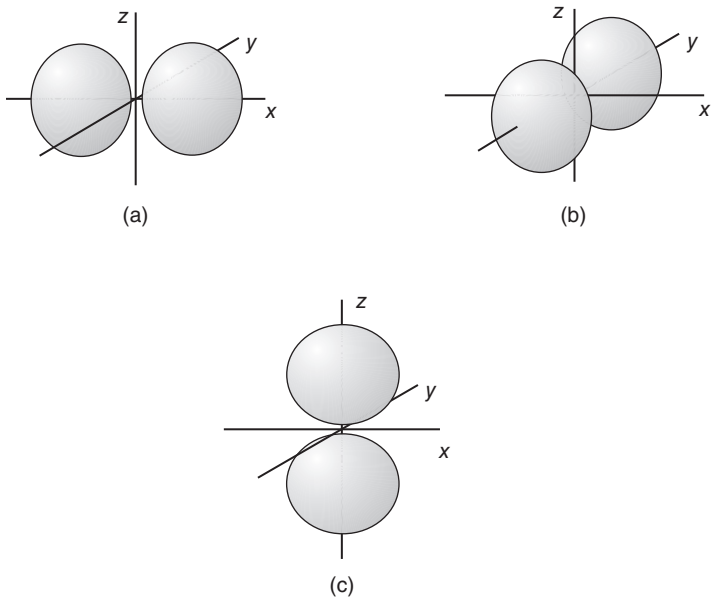

Figure 1.4 The boundary surfaces of the p orbitals: (a) p_x; (b) p_y; (c) p_z.

at the nucleus. In the d_{z^2} orbital, the nodes are conical surfaces.

1.1.4 Electron Spin and Electron Configuration

In order to account for other atomic properties, especially optical and magnetic properties, the electrons are allocated a fourth quantum number called the *spin quantum number*, *s*. The spin quantum number has a value of ½. The spin of an electron on an atom can adopt one of two different directions, represented by a quantum number, m_s, which takes values of + ½ or −½. These two spin directions are frequently represented by ↑, *spin up*, or α, and ↓, *spin down*, or β.

The *electron configuration* of an atom is the description of the number of electrons in each orbital, based upon the orbital approximation. This is usually given for the lowest energy possible, called the *ground state*. To obtain the electron configuration of an atom, the electrons are fed into the orbitals, starting with the lowest energy orbital, 1s, and then continuing to the higher energy orbitals so as fill them up systematically from the bottom up. This is called the *aufbau* (or *building up*) *principle*. Each orbital can hold a maximum of two electrons, which must have opposite values of m_s, +½ and −½. Two electrons in a single orbital are said to be *spin paired*. Thus, the s orbitals can hold 2 electrons, the three p orbitals can hold a total of 6 electrons, the five d orbitals can hold a total of 10 electrons, and the seven f orbitals a total of 14 electrons. When electrons are allocated to the p, d, and f orbitals, the lowest energy situation is that in which the electrons go into an unoccupied orbital if possible. This situation is expressed in *Hund's First Rule*: when electrons have a choice of several orbitals of equal energy, the lowest energy, or ground state, configuration corresponds to the occupation of separate orbitals with parallel spins rather than fewer orbitals with paired spins. For the heavier atoms the electron configuration does not always follow a strictly repetitive sequence, as the difference in energy between the various configurations is often miniscule. In particular, half-filled d and f orbitals are favoured when possible.

This simple approach is able to account for the overall variation in properties of the elements across the Periodic Table (Appendix A). The alkali metals, typified by Na, all have an

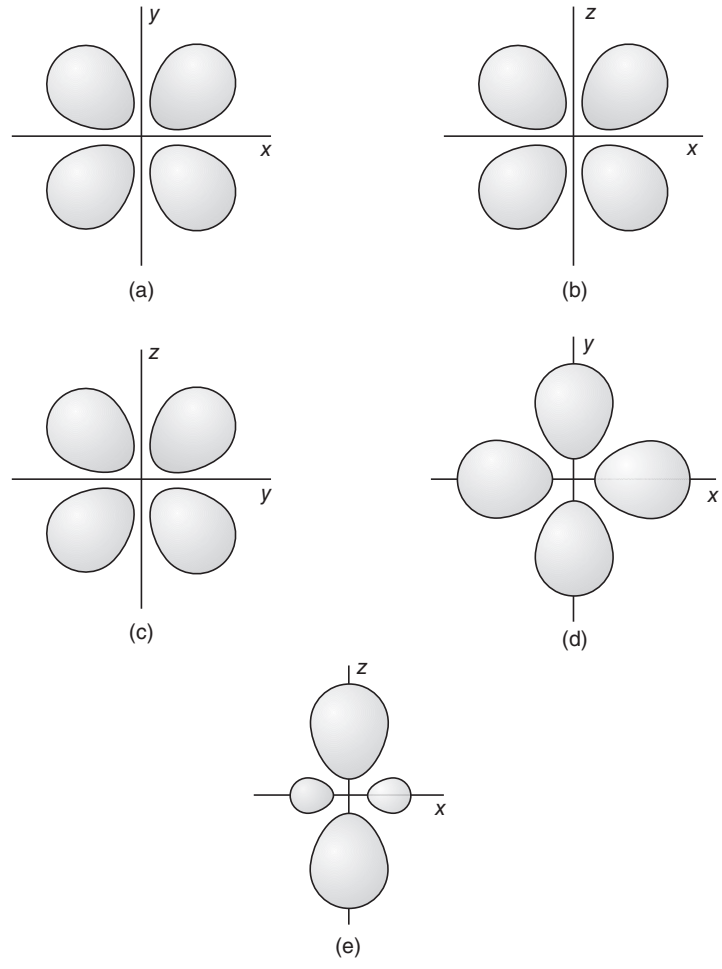

Figure 1.5 The boundary surfaces of the d orbitals: (a) d_{xy}; (b) d_{xz}; (c) d_{yz}; (d) $d_{x^2-y^2}$; (e) d_{z^2}.

outer electron configuration of ns^1, the alkaline earth elements, typified by Mg, a configuration of ns^2, the transition metals, typically Fe, have partly filled *n*d orbitals, the lanthanoids, partly filled 4f orbitals, and the inert gases such as Ne have a completely filled shell configurations.

1.1.5 Atomic Energy Levels

The spectra of atoms are a record of transitions that the outer electrons make between the available electron energy levels. The frequency ν (or the equivalent wavelength, λ) of the spectral line is related to the energy separation of the two energy levels, ΔE, by:

$$\Delta E = h\nu = h\,c/\lambda$$

where h is the Planck constant and c is the velocity of a plane light wave in a vacuum. The electron energy level scheme described earlier (Figure 1.2) applies to a one electron 'hydrogen-like' atom that has a single electron moving under the combined electrostatic field of the nucleus and all of the other electrons. While this is useful chemically, it is unable to account for the spectrum of an atom or provide any information on the possible energy levels appropriate to the electron configuration. There are a number of ways of obtaining these *many-electron* energy levels of an atom, which are described by *many electron* quantum numbers. The approach most frequently encountered, called the *Russell–Saunders coupling*, makes the approximation that the

electrostatic repulsion between electrons is the most important energy term. To obtain revised atomic configurations, all of the individual s values of the electrons are summed to yield a total spin angular momentum quantum number S. Similarly, all of the individual l values for the electrons present are summed to give a total orbital angular momentum quantum number L. (Note that one-electron quantum numbers are written in lower case while many electron quantum numbers are written in upper case.) The value of S is not used directly, but is replaced by the *spin multiplicity*, $2S + 1$. Similarly, the total angular momentum quantum number L, is replaced by a letter symbol similar to that used for the single electron quantum number l. The correspondence is

L	0	1	2	3	4	5	6
Letter	S	P	D	F	G	H	I

After $L = 3$, F, the sequence of letters is alphabetic, omitting J. Be aware that the symbol S has two interpretations, as the value of L (S Roman) and as the value of total spin (S *italic*). The compatible combinations of S and L are written in the form ^{2S+1}L, called a *term symbol*, which represents the energy level, called a *term* in spectroscopic parlance. States with a multiplicity of 1 are called *singlet* states, states with a multiplicity of 2 are called *doublet* states, with multiplicity of three, *triplets*, with multiplicity 4, *quartets*, and so on. Hence, ^{1}S is called singlet S, and ^{3}P is called triplet P.

To give an example, for a $3d^2$ transition metal cation such as Ti^{2+} or V^{3+} (which has a single energy level in Figure 1.2), the allowed Russell–Saunders terms are ^{3}F, ^{3}P, ^{1}G, ^{1}D, and ^{1}S. Although the derivation of terms is straightforward (see Appendix B), it is difficult to calculate the energies of these states. The lowest energy, ground state term, is, however, readily found using *Hund's first and second rules*: the term with the lowest energy has the highest multiplicity and for terms with the same multiplicity the term with the highest value of L is lowest in energy. The lowest energy term for a $3d^2$ ion is thus ^{3}F (Figure 1.6).

The term symbol does not account for the total complexity of an atomic spectrum and additional factors must be taken into account. The most important of these is the interaction between the electron orbital angular momentum and the electron spin angular momentum (*spin–orbit coupling* or *j–j* coupling). To include this, a new quantum number, J, is needed, given by combining L and S values (Appendix B). The new quantum number is incorporated as a subscript to the term, now written $^{2S+1}L_J$ and this is no longer called a term, but a *level*. Each value of J represents a different energy level. It is found that a singlet term always gives one level, a doublet, two, a triplet three, and so on. Thus, ground state term ^{3}P is composed of three levels $^3P_0$, ^{3}P, and $^3P_2$ (Figure 1.6). The magnitude of the energy difference between these levels depends upon the strength of the interaction between L and S. In order to find which of these states is the lowest energy, use can be made of *Hund's third rule*: the level with the lowest energy is that with the lowest J value if the valence shell is up to half full and that with the highest J value if the valence shell is more than half full.

Additionally, the spectrum of an atom in a magnetic field has more lines present than the same atom in the absence of the magnetic field, a feature called the *Zeeman effect*. In a magnetic field, each of the $^{2S+1}L_J$ levels splits into $(2J + 1)$ separated energy levels. The spacing between the levels is given by $g_J \mu_B \mathbf{B}$, where g_J is the Landé g-value,

$$g_J = 1 + \{[J(J+1) - L(L+1) + S(S+1)]\}/[2J(J+1)]$$

μ_B is a fundamental physical constant, the Bohr magneton, and $\mathbf{B}$ is the magnetic induction (Figure 1.6). A similar change, called the *Stark effect*, arises in the presence of a strong electric field.

An alternative approach to the Russell–Saunders coupling is to assume that the

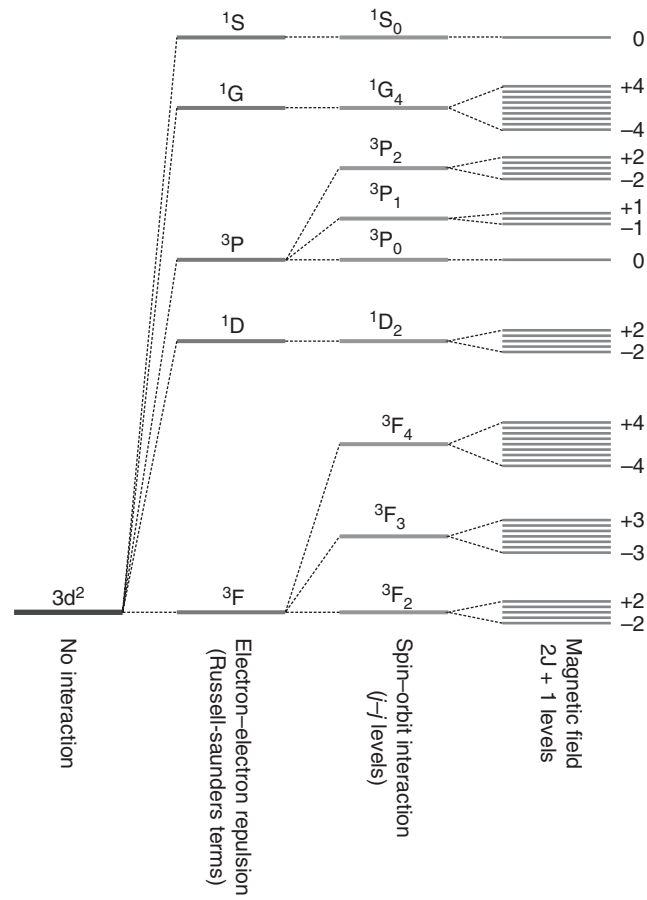

Figure 1.6 The evolution of the electron energy levels of an atom with a $3d^2$ configuration.

interaction between the orbital angular momentum and the spin angular momentum, i.e. the spin–orbit coupling, is the most important. In this case, the s and l quantum numbers for an individual electron are added to give a total angular momentum number j for a single electron. These values of j are then added to give the total angular momentum quantum number J, for the whole atom. The technique of adding j values to obtain energy levels is called the *j–j coupling*.

Note that in a heavy atom it might be preferable to go from the electron configuration to levels derived by *j–j* coupling and then add on a smaller effect due to electron–electron repulsion (Russell–Saunders coupling) before finally including the magnetic field splitting. In real atoms, the energy levels determined experimentally are often best described by an intermediate model between the two extremes of Russell–Saunders and *j–j* coupling.

1.2 Ionic Bonding

1.2.1 Ionic Size and Bonding

Ions are charged species that form when the number of electrons surrounding a nucleus varies slightly from that required for electric neutrality. Metallic elements, which have few electrons outside a closed noble gas core, tend to lose electrons and form positively charged cations; the charge written as a superscript. Non-metals tend to gain electrons and form negatively charged anions; the charge written as a superscript. Groups of atoms can also form anions, for example, carbonate, CO_3^{2-}, and nitrate, NO_3^-. Ions are called *monovalent*

if they carry a charge of ±1, *divalent* if they carry a charge of ±2, *trivalent* if they carry a charge of ±3, and so on. This does not depend upon the number of atoms in an ion. Thus, both Sr^{2+} and CO_3^{2-} are regarded as divalent ions.

Positive and negative ions attract each other electrostatically to form an *ionic bond*. Electrostatic interactions are *long range* and *non-directional* and these features typify ionic bonding. Ionic bonding has the advantage that it readily accounts for the formula of a solid. This follows directly from the idea that cations and anions have integer charges and ionic compounds are neutral overall. Thus, a cation with a charge $+a$ can combine with an anion of charge $-a$ to give neutral compounds MX. When the cations and anions have different charges, they combine in numbers to render the compound electrically neutral; for example, Al^{3+} and O^{2-} combine to give neutral Al_2O_3, while Sr^{2+} and Ti^{4+} combine with O^{2-} to give neutral perovskite, $SrTiO_3$.

The concept of allocating a fixed size to each ion is an attractive one and has been extensively utilised. Ionic radii are generally derived from X-ray crystallographic structure determinations, which give a precise knowledge of the distances between the ions. To derive ionic radii, it is assumed that the individual ions are spherical and in contact. The radius of one commonly occurring ion, such as O^{2-}, is taken as a standard. Other consistent radii can then be derived by subtracting the standard radius from measured inter-ionic distances (Figure 1.7).

The fact that the ionic radius depends upon the standard ion by which the radii were determined has led to a number of different tables of ionic radii. Although these are all internally self-consistent, radii from different sources should not be mixed. Additionally, cation radii are sensitive to the immediate surroundings. A cation surrounded by six oxygen ions in octahedral coordination has a different radius when surrounded by four oxygen ions in tetrahedral coordination or six sulfur ions in octahedral coordination. Ideally, tables of cationic radii should apply to a specific anion and coordination geometry.

The principal size characteristics of ions are the following:

+1	+2	+3	+4 (+3)	+5 (+4) [3+]	+6 (+4) [3+]	+6 (+4) [3+] {2+}	+4 (+3) [2+]	+4 (+3) [2+]	+4 (+2)	+2 (+1)	+2	+3	+4 (2+)	+5 (3+)	–2 (6+)	–1
Li 0.088	Be 0.041(t)											B 0.026 (t)	C	N	O 0.126	F 0.119
Na 0.116	Mg 0.086											Al 0.067	Si 0.040 (t)	P	S 0.170	Cl 0.167
K 0.1521	Ca 0.114	Sc 0.0885	Ti 0.0745 (0.081)	V 0.068 (0.073) [0.078]	Cr [0.0755]	Mn (0.068) [0.079*] {0.097*}	Fe (0.079*) [0.092*]	Co (0.075*) [0.089*]	Ni (0.083)	Cu 0.087 (0.108)	Zn 0.089	Ga 0.076	Ge 0.068	As 0.064	Se (0.043 t)	Br 0.182
Rb 0.163	Sr 0.1217	Y 0.104	Zr 0.086	Nb 0.078	Mo 0.074	Tc (0.078)	Ru 0.076	Rh 0.0755	Pd (0.100)	Ag (0.129)	Cd 0.109	In 0.094	Sn 0.083 (0.105)	Sb 0.075	Te (0.068)	I 0.206
Cs 0.184	Ba 0.150	La 0.1185	Hf 0.085	Ta 0.078	W 0.074 (0.079)	Re 0.066	Os 0.077	Ir 0.077	Pt 0.077 (0.092)	Au	Hg 0.116	Tl 0.1025	Pb 0.0915 (0.132)	Bi 0.086 (0.116)	Po	At

* High spin configuration

Figure 1.7 Ionic radii, nm. Cation radii apply to ions octahedrally coordinated to O^{2-} unless marked (t), tetrahedral coordination. (For high spin configuration, see Section 10.2.2.)

(i) Cations are usually smaller than anions. The reason for this is that removal of electrons to form cations leads to a contraction of the electron orbitals due to the relative increase in nuclear charge while addition of electrons to form anions leads to an expansion of the charge clouds due to a relative decrease in the nuclear charge.
(ii) The radius of an ion increases with atomic number.
(iii) Cation radius decreases rapidly with increase of positive charge for a series of isoelectronic ions such as Na^+, Mg^{2+}, and Al^{3+}, all of which have the electronic configuration [Ne].
(iv) Anion radius is largely unaffected by an increase in negative charge. For example, F^- is similar in size to O^{2-} and Cl^- is similar in size to S^{2-}.
(v) Successive valence increases decrease cation radius. For example, Fe^{3+} is smaller than Fe^{2+}.
(vi) The radius of transition metal cations, and to a lesser extent lanthanoid and actinoid cations, depends upon whether the electron spins on the cation are paired, giving a low spin state, or largely unpaired, giving a high spin state.

While the majority of the ions of elements can be considered to be spherical, cations with a lone pair of electrons in the outer orbitals, In^+, Tl^+, Sn^{2+}, Pb^{2+}, Sb^{3+}, and Bi^{3+} are definitely not so. Similarly, ions, such as CO_3^{2-}, NO_3^-, are not spherical, although at high temperatures, rotation often makes them appear so.

1.2.2 Lattice Energies

An advantage of the ionic bonding model is that ionic interaction energies can be fairly easily assessed. The electrostatic potential energy (often called the *Coulomb interaction* or *Coulomb potential*) between a pair of oppositely charged monovalent ions E_e is given by:

$$E_e = (+e)(-e)/4\pi\,\varepsilon_0 r = -e^2/4\pi\,\varepsilon_0 r$$

where the point charges on the interacting species are $\pm e$, and the distance separating the charges is r. A negative overall energy implies stability. The electrostatic energy of an ionic crystal, called the *Madelung energy*, has a form identical to this multiplied by a constant that arises from the geometry of the structure, a term representing the charges on the ions and a term giving the number of ions present.

$$E_e = [-e^2/4\pi\varepsilon_0 r] \times [\text{geometry}] \times [\text{ionic charges}] \times [\text{amount}]$$

For a crystal composed of ions of charge $\pm Ze$:

$$E_e = N_A[-e^2/4\pi\varepsilon_0 r]\,[\alpha]\,[Z^2]$$

where N_A is Avogadro's constant and r is the equilibrium distance between neighbouring oppositely charged ions in the crystal. The term reflecting the geometry of the structure, α, is called the *Madelung constant*. The Madelung constant for each structure is different and is determined by summing all of the ionic interactions over the whole of the structure.

When the formula of the compound is M_mX_n, the charges on the cations and anions differ and as a result two alternative Madelung constants, usually designated A or M, may be quoted. They differ from each other in the molecular unit chosen for evaluation, M_mX_n or $MX_{n/m}$, and whether the ionic charges are included in the constant. In such cases it is simplest to separate out the charge contribution and stoichiometry to give a r*educed Madelung constant*, which is a purely geometric term. The reduced Madelung constant of a compound M_mX_n is defined by:

$$E_e = -N_A \frac{e^2}{4\pi\varepsilon_0 r}\alpha(Z_M Z_X)\frac{m+n}{2}$$

where, to maintain charge neutrality, $mZ_M = nZ_X$. Surprisingly, the reduced Madelung constant is very similar for a wide range of structures, equal to 1.68 ± 0.08 (Table 1.2). This means that the approximate electrostatic energy of any crystal structure can be

Table 1.2 Reduced Madelung constants, α.

Structure	Formula	Example	α
Halite	M^+X^-	NaCl	1.748
Caesium chloride	M^+X^-	CsCl	1.763
Sphalerite	$M^{2+}X^{2-}$	ZnS	1.638
Wurtzite	$M^{2+}X^{2-}$	ZnO	1.641
Fluorite	$M^{2+}X_2^-$	CaF_2	1.680
Rutile	$M^{4+}X_2^{2-}$	TiO_2	1.605
β-Quartz	$M^{4+}X_2^{2-}$	SiO_2	1.480
Corundum	$M_2^{3+}X_3^{2-}$	Al_2O_3	1.669

estimated as long as the chemical formula is available. To convert between literature values of the Madelung constant A or M, and the reduced Madelung constant α, for a compound of formula M_mX_n, use:

$$\alpha Z_M Z_X (m+n)/2 = A$$
$$\alpha (m+n)/2 = M$$

In general, the electrostatic attraction between cations and anions will increase as they approach until, at some interionic distance, the electron clouds of the ions begin to overlap, leading to repulsion. Ultimately the two opposing energies will balance and the ions will adopt an equilibrium separation. The *repulsive potential energy*, E_r, can be formulated in a number of ways, typically:

$$E_r = B/r^n$$

where B and n are empirical constants.

The *potential energy*, U, per mole of an ionic crystal may be represented as the sum of the electrostatic and repulsive energy terms:

$$U = E_e + E_r = [-N_A \alpha Z^2 e^2/4\pi\varepsilon_0 r] + N_A B/r^n$$

per mole. The energy is a function of the distance between the ions, r, and at equilibrium this energy must pass through a minimum (Figure 1.8). Thus, we can write:

$$dU/dr = [N_A \alpha Z^2 e^2/4\pi\varepsilon_0 r^2] - nN_A B/r^{n+1} = 0$$

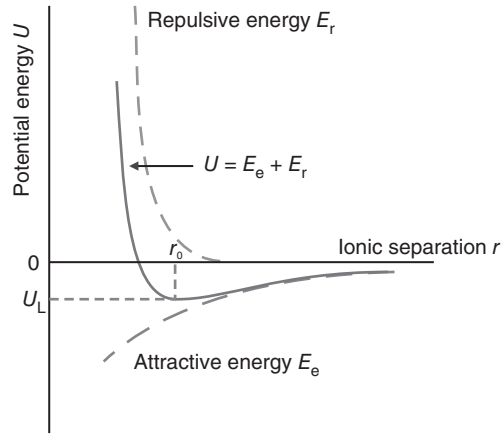

Figure 1.8 The total potential energy between two monovalent ions as a function of the ionic separation. The lattice energy U_L corresponds to the minimum, at an interatomic separation r_0.

This allows the constant B to be eliminated, to give:

$$U_L = [-N_A \alpha Z^2 e^2/4\pi\varepsilon_0 r_0][1 - 1/n]$$

where U_L is the *lattice energy* and r_0 is the equilibrium value of the interionic separation.

Using:

$$E_r = +N_A B \exp(-r/r^*)$$

where B and r^* are constants that are structure sensitive and eliminating the constant B, as earlier, gives the *Born–Mayer equation* for the lattice energy:

$$U_L = [N_A \alpha Z^2 e^2/4\pi\varepsilon_0 r_0][1 - (r^*/r_0)]$$

1.2.3 Atomistic Simulation

The analysis in Section 1.2.2 forms the basis for the computer evaluation of crystal structure information using the technique of *atomistic simulation*. In this technique interactions between pairs of atoms, written as *pair potentials*, are derived using experimental data or theoretical calculations. These can be listed as Coulombic (electrostatic) and non-Coulombic (mainly repulsive). Coulombic forces are of the form:

$$E_e = (q_i q_j)/4\pi\varepsilon_0 r_{ij}$$

where q_i and q_j are the charges on the ions and r_{ij} is the separation of the ions. The non-Coulombic potential, which is attractive at large interatomic spacing and repulsive at short interatomic spacing, is frequently given by one of three equations:

(a) *The Lennard-Jones potential*:
$V_{LJ} = Ar^{-12} - Br^{-6}$
where A and B are empirical constants and r is the interatomic distance. This equation is found to fit the behaviour of rare gas and molecular interactions well.

(b) *The Morse potential*:
$V_M = D\{1 - \exp[-\beta(r - r_e)]\}^2$
where D, β, and r_e are empirical constants. This form works well for covalently bonded solids (Section 1.3).

(c) *The Buckingham potential*:
$V_B = B\exp(-r/\rho) - C/r^6$
which is of most value for ionic and semi-ionic solids. In this equation B, C, and ρ are empirical parameters, which vary from one ion pair to another.

Many ions are polarizable and this must be taken into account if reasonable answers are to be obtained. It is estimated by using the *shell model*, in which the polarizability is imagined to deform the electron cloud surrounding an atom as if the electron cloud were a shell attached to the nucleus by a spring. The simplest form for the polarizability α is:

$$\alpha = Y^2/k$$

where Y is the charge on the (massless) shell and k is the empirically determined *spring constant*. The potential energy stored in the spring is given by:

$$E_p = \frac{1}{2}k\,\delta r^2$$

or, if this approximation is not sufficiently accurate, by:

$$E_p = \frac{1}{2}k_2\,\delta r^2 + \left(\frac{1}{24}\right)k_4\,\delta r^4$$

where δr is the amount by which the spring between the shell and the core is stretched.

Computer routines sum all of these interactions over as many atoms as is reasonable and use techniques that effectively allow the finite answer to be extended to a crystal of any size. Pair potentials are somewhat limited and these are gradually being replaced, where the computational requirements allow it, with *many-body potentials*. These are more sophisticated than pair potentials and are able to more faithfully model processes at an atomic level.

There are two broad genres of computation. In *static lattice* simulations the atoms in the crystal, positioned at r_1, r_2, r_3, and so on. A first approximation energy is derived and further iterations are then made by changing the ionic positions until a minimum energy is reached. The final set of atomic coordinates give the crystal structure and unit cell dimensions of the atom array, which are then easily compared to those obtained via X-ray diffraction. By applying virtual forces or electric fields to the optimal structure other properties, such as crystal stability under high pressure, elastic constants and dielectric behaviour can be assessed. By removing or adding ions the energy of formation of point defects can be determined.

The other broad area of atomistic simulation concerns dynamic properties. Here the atoms are given a position and a velocity. Successive configurations of the structure are allowed to evolve with time, either the atomic trajectories following Newton's laws of motion (*molecular* or *lattice dynamics*) or else determined using probability theory (*Monte Carlo* methods). Using these approaches, defect formation and migration, diffusion, the annealing of materials, fracture, grain growth and sintering, nanoscale materials, and damage from radiation emitted by radioactive atoms can be simulated. Molecular dynamics simulations have been used, for example, to study the enormously complex problem of protein folding.

1.3 Covalent Bonding

1.3.1 Bond Geometry

Ionic bonding is unable to explain the properties of most molecules, particularly organic

molecules, which have definite shapes. Methane, CH_4, has the central carbon atom surrounded by hydrogen atoms to form a tetrahedral molecule; benzene C_6H_6, consists of six carbon atoms linked in a hexagonal ring, with one H atom linked to each C atom. The links between the atoms in such molecules are described as *covalent bonds*. A covalent bond is formed by the overlap of partly-filled orbitals. The *direction* of the bond will be such as to make the overlap as great as possible and the *strongest* bonds are formed when the overlapping of the orbitals is at a maximum.

The simplest covalent bond is, perhaps, the single bond between two hydrogen atoms that make up the hydrogen (H_2) molecule. An isolated hydrogen atom has a single electron in a spherical 1s orbital. As distance between two H atoms is reduced, two different kinds of interaction are possible, depending on whether the spins of the electrons in the s orbitals of the two atoms are parallel or opposed. If the spins are opposed, covalent bonding occurs and the nuclei are pulled together. It is found that the electron density, which was originally spherically distributed around each atom is now concentrated between the nuclei (Figure 1.9a,b). If the spins of the two electrons are parallel, the electron clouds repel and bonding does not occur, even if the atoms approach closely (Figure 1.9c,d). The resulting orbitals that encompass both atoms are called *molecular orbitals*.

Any partly filled orbitals can overlap to form bonds in this way. A bond formed by two s orbitals, two end-on p orbitals, or by a single s and a single p orbital has rotational symmetry about the bond axis (Figure 1.10a,b) and is termed σ *bond*. Two p orbitals, linked sideways, cause an increase of the electron density on either side of a nodal plane on which the two nuclei are situated. Such bonds are termed π *bonds* (Figure 1.10c,d). It is important to note that the designation of a bond as σ or π does not depend on the type of orbital forming the bond, only the geometry of overlap of the orbitals.

Although covalent bonds due to simple orbital overlap accounts for a large number of molecular structures, it does not explain the geometry of many other simple molecules such as methane, CH_4, ammonia, NH_3, and water, H_2O. In these cases, the simple atomic orbitals are rearranged in such a way that they can make stronger bonds (with greater overlap) than the unaltered orbitals. This can be illustrated by the tetrahedral geometry of many bonds in organic compounds. The outer electron configuration of carbon is $2s^2\ 2p^2$. If one electron is promoted from the filled $2s^2$ orbital into the empty p orbital, the four singly occupied orbitals rearrange into *sp^3-hybrid* orbitals. The resulting four orbitals point

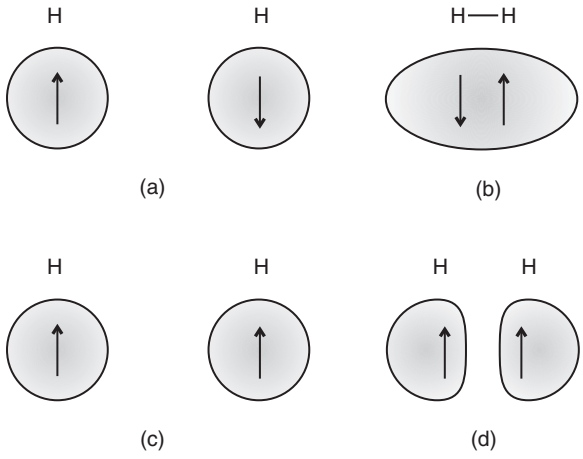

Figure 1.9 Covalent bond formation: (a) two H atoms with opposed electron spins form an H_2 molecule (b); (c) two H atoms with parallel electron spins do not bond (d).

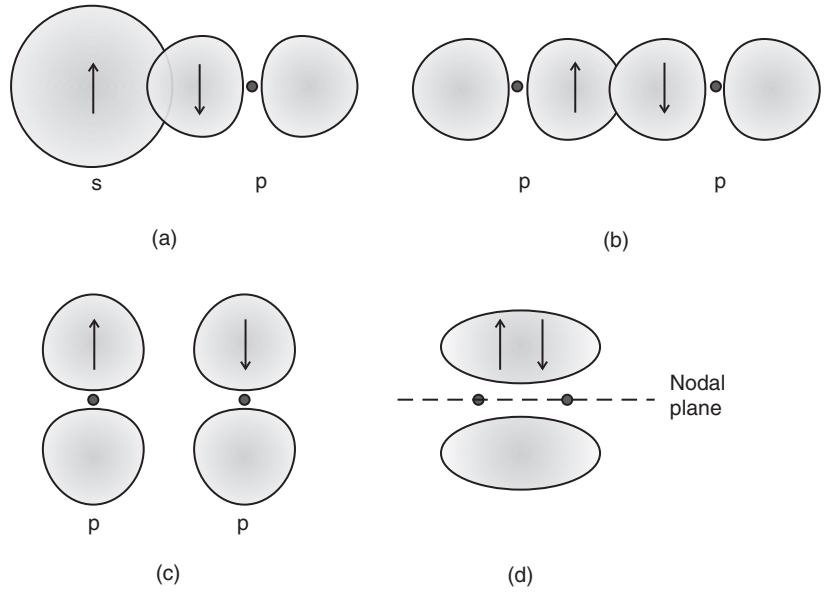

Figure 1.10 Covalent bonding: (a) σ bonding via overlap of s and p orbitals; (b) σ bonding via overlap of two p orbitals; (c) sideways on approach of two p orbitals leading to (d) π bond formation.

towards the corners of a tetrahedron, at angles of 109.5° to each other (Figure 1.11). These orbitals have an overlapping power of twice the overlapping power of s orbitals so that the bonds are extremely strong. The C—C bond energy in diamond, the hardest of all solids, is 245 kJ mol^{-1}.

It is a general rule of hybrid bond formation that the same number of hybrid orbitals form and can be used for bonding as the number of atomic orbitals used in the initial combination. Thus, one s and one p orbital yield two sp-hybrid orbitals resulting in linear molecules. One s orbital and two p orbitals yield three new sp^2-hybrid orbitals for bond formation. For maximum overlap these orbitals point as far away from each other as possible, forming bonds at angles of 120° yielding triangular molecules. This type of bonding is commonly encountered in borosilicate glasses, where the boron atoms are linked to three oxygen atoms at the corners of an equilateral triangle. The geometry of some hybrid orbitals is given in Table 1.3.

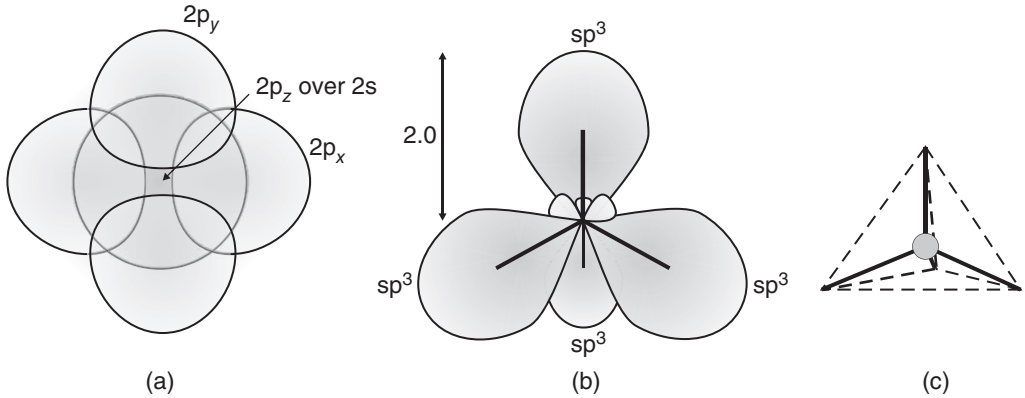

Figure 1.11 (a) The 2s and 2p orbitals on C; (b) four sp^3 hybrid orbitals; (c) tetrahedral geometry of the sp^3 orbitals.

Table 1.3 The geometry of some hybrid orbitals.

Orbital configuration	Coordination number	Geometry	Example
sp	2	Linear	$HgCl_2$
sp^2	3	Trigonal	BCl_3
sp^3	4	Tetrahedral	CH_4
dsp^3	5	Trigonal bipyramidal	PCl_5
d^2sp^3	6	Octahedral	SF_6

One of the characteristic features of covalent compounds is the presence of multiple bonds between atoms. Single bonds, described earlier, are *always* σ bonds. Multiple bonds result when atoms link via σ and π bonds at the same time. A double bond between two atoms then consists of σ and one π bond, while a triple bond consists of one σ and two π bonds.

1.3.2 Bond Energies

As atoms come together to form a covalent molecule, the atomic orbitals interact and spread over all of the nuclei to give molecular orbitals that extend over the whole molecule. Each pair of atomic orbitals gives rise to two molecular orbitals, one of which has a higher energy than the original pair and one with a lower energy than the original pair. The molecular orbital of lower energy than the parent atomic orbitals has the greatest concentration of electron density between the nuclei, and is a *bonding orbital*. The molecular orbital of higher energy than the parent atomic orbitals, the *antibonding orbital*, has the electron density concentrated in the region outside of the line joining the nuclei. If they have cylindrical symmetry, they are called σ orbitals, the lower energy orbital is labelled σ and upper antibonding one labelled σ*. If the molecular orbitals are derived from sideways on overlap of p orbitals, they lack this symmetry and are called π orbitals, the lower bonding orbital labelled π and the upper antibonding orbital labelled π*. The available electrons are fed into the molecular orbitals, using the Pauli principle and Hund's rules (the aufbau principle), to arrive at a molecular electron configuration. For a stable molecule to form, the total energy of the electrons in the molecular orbitals that are occupied must be less than the energy total when the electrons occupy separate atomic orbitals.

The principle can be illustrated by describing the ground state electron configuration and bond energy for homonuclear diatomic molecules. For H_2 the two 1s orbitals of the isolated atoms combine to give two molecular orbitals, σ1s (bonding) and, σ*1s (antibonding) (Figure 1.12). Both electrons will occupy the bonding, σ, orbital provided that they have opposed spins. This will be the lowest energy configuration, or *ground state*, of the pair, and a covalently bonded hydrogen molecule, H_2, will form. The bond energy will be $2E_{bond}$.

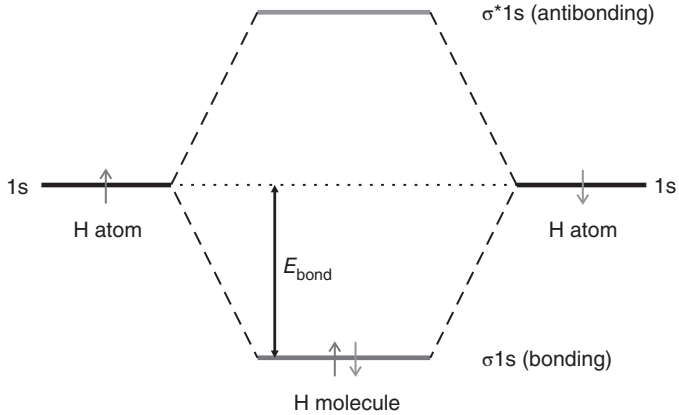

Figure 1.12 The formation of molecular orbitals in an H_2 molecule.

When two helium atoms interact, there are four electrons to be placed in the orbitals and so both the σ1s and σ*1s orbitals will be filled. The effect of the filled antibonding orbital completely negates the effect of the filled bonding orbital. No energy is gained by the system and so He_2 does not form.

To derive the electron configurations of the other homonuclear X_2 molecules, formed from the elements of the second period, Li_2 to Ne_2, exactly the same procedure is followed. The interaction of the 2s outer orbitals will form σ2s and σ*2s orbitals. End-on overlap of the p orbitals produces $\sigma 2p_x$ and $\sigma^* 2p_x$ orbitals. The sideways on overlap of a pair of p orbitals forms one $\pi 2p_y$ bonding orbital, one $\pi 2p_z$ bonding orbital, one $\pi^* 2p_y$ antibonding orbital, and one $\pi^* 2p_z$ antibonding orbital. The difference in energy between the $\sigma 2p_x$ and π2p orbitals is small and gradually changes along the series, so that the $\sigma 2p_x$ orbital drops below the π2p orbitals for the last three molecules, O_2, F_2, and (hypothetical) Ne_2 (Figure 1.13). The molecular configurations of the homonuclear diatomic molecules can now be obtained (Table 1.4).

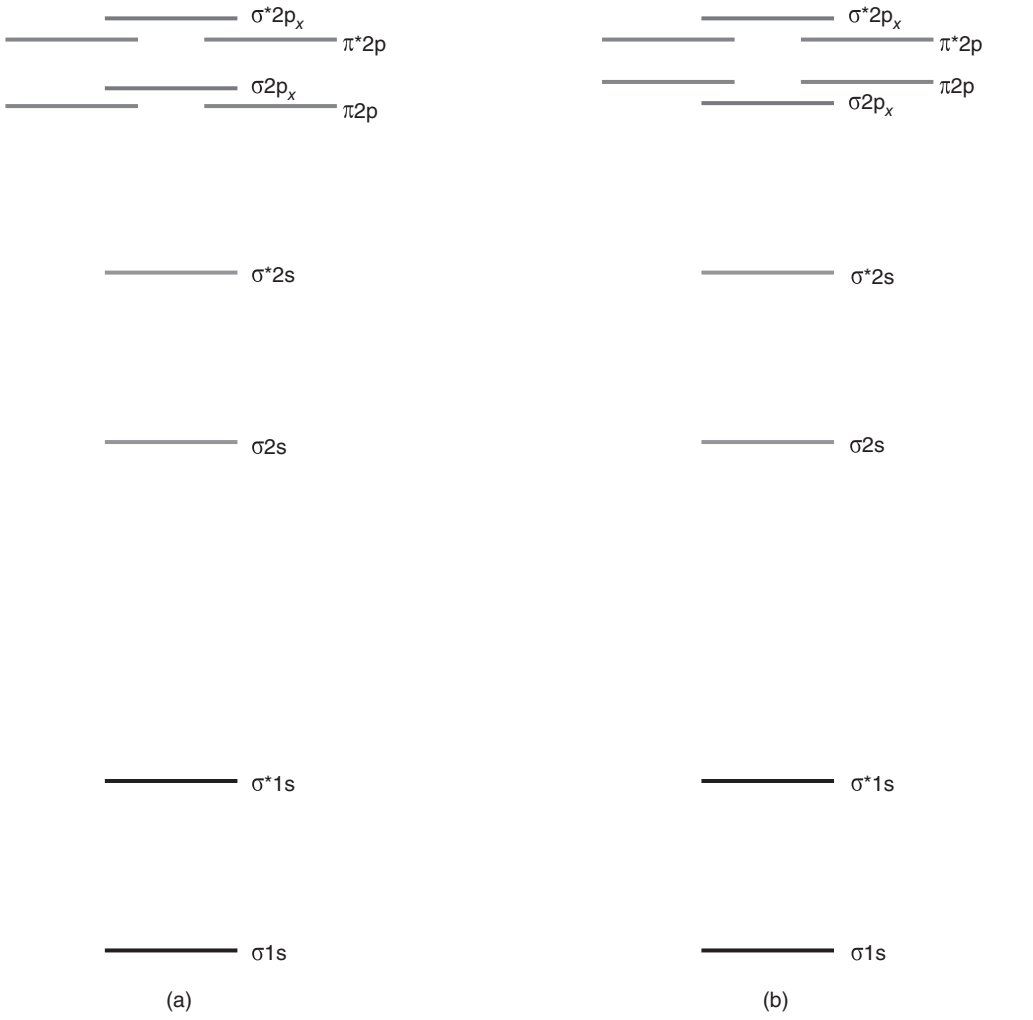

Figure 1.13 Schematic molecular orbital energy level diagram for homonuclear diatomic molecules; (a) H_2 to N_2; (b) O_2 to Ne_2.

Table 1.4 The electron configurations of some homonuclear diatomic molecules.

Molecule	Ground state configuration	Bond length (nm)	Bond energy (kJ mol^{-1})
Li_2	$[He_2]\,(\sigma 2s)^2$	0.267	101
Be_2	$[He_2](\sigma 2s)^2(\sigma^* 2s)^2$	—	—
B_2	$[Be_2](\pi 2p)^2$	0.159	289
C_2	$[Be_2](\pi 2p)^4$	0.124	599
N_2	$[Be_2](\pi 2p)^4(\sigma 2p_x)^2$	0.110	941
O_2	$[Be_2](\pi 2p)^4(\sigma 2p_x)^2\,(\pi^* 2p)^2$	0.121	494
F_2	$[Be_2](\pi 2p)^4(\sigma 2p_x)^2\,(\pi^* 2p)^4$	0.142	154
Ne_2	$[Be_2](\pi 2p)^4(\sigma 2p_x)^2(\pi^* 2p)^4(\sigma^* 2p_x)^2$	—	—

[He] is shorthand for $(\sigma 1s)^2(\sigma^* 1s)^2$.
[Be_2] is shorthand for $(\sigma 1s)^2(\sigma^* 1s)^2\,(\sigma 2s)^2(\sigma 2s^*)^2$.

When a molecular orbital is formed between atoms of two different elements, A and X, then the energy levels of the initial atomic orbitals will differ, as will their extensions in space. The difference between the atoms can be thought of in terms of *electronegativity*, which is a measure of the power to attract electrons during chemical bonding. Atoms with a low electronegativity are called *electropositive* elements. Atoms with a high electronegativity are called *electronegative* elements. Despite differences in electronegativity, the molecular orbital diagram remains similar (Figure 1.14). The bonding energy E_b is now computed with respect to the average energy of the isolated A and X atoms, $\frac{1}{2}(E_A + E_X)$. In the case where element A is more metallic (electropositive) in character than element X, it is found that the X atom contributes most to the bonding molecular orbital and the atom A more to the antibonding molecular orbital. The bonding molecular orbitals are then often said to be X-like in character and the antibonding orbitals A-like in character.

When the two nuclei are different, the symmetrical build-up of electron density found for identical atoms will become distorted and the electron density will pile up in the region of the non-metal atom and be depleted towards the metal atom. A covalent bond in which the electron pair is distributed unevenly is sometimes called a *polar covalent bond*. The bond will have one end that carries a small positive charge, written δ+, and the

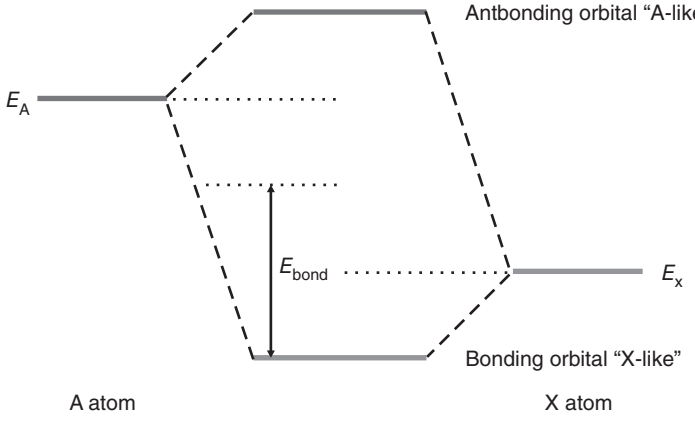

Figure 1.14 Molecular orbitals formed by a more metallic atom A and a less metallic atom X.

other end with a small negative charge, δ−. The charge separation gives rise to an *internal electric dipole* and such molecules are called *polar molecules*. For example, water is a polar molecule as the two O—H bonds form dipoles pointing from the oxygen towards the hydrogen atoms. However, not all molecules containing several internal dipoles show an overall dipole moment as, depending upon the molecular symmetry, they may sum to zero. These internal electric dipoles result in many important properties of molecules and molecular solids, including piezo- and ferroelectric behaviour (Section 9.2).

1.4 Metallic Bonding

In both ionic and covalent bonding, all electrons are immobile. The characteristic of metals and semiconductors is that at least the outer electrons are mobile and able to move freely through the solid under an applied voltage. As well as this, metallic bonds must act between both identical and different metallic atoms, as is revealed by the formation of numerous alloy structures as well as the structures of the elements. The bonds act between many atoms, as metal atoms in crystals often have 8 or 12 neighbours. The bonds are maintained in the liquid state, as liquid metals retain the distinguishing properties of crystalline metals.

The present-day understanding of metals and metallic bonding has arisen from the combination of two different approaches. In the first of these, electrons travel more or less freely through the structure, akin to gas atoms in a volume, and are not really associated with any particular atom, giving rise to the *free-electron gas* theory. A second approach, more chemical in nature, considers metallic bonds as a delocalisation of covalent bonds throughout the solid. The application of these ideas, called *band theory*, successfully explains the detailed physical properties of metals.

1.4.1 Molecular Orbitals and Energy Bands

The molecular orbital model of chemical bonding indicates that when two atoms approach, the outer atomic orbitals on each atom interact to form a pair of molecular orbitals, one of lower energy, the bonding orbital, and one of higher energy, the antibonding orbital. As further atoms are added to the pair, each new atomic orbital is transformed into a new molecular orbital. Calculation shows that the separation between the higher energy (antibonding) and lower energy (bonding) orbitals rapidly becomes constant as the number of atoms in the solid increases, and the new molecular orbitals fit into the energy space between them. When a large number of atoms are present, so many orbitals are incorporated that the energy space is essentially spanned by a continuum, and *energy bands* have been created (Figure 1.15). The upper part of the band will correspond to antibonding orbitals

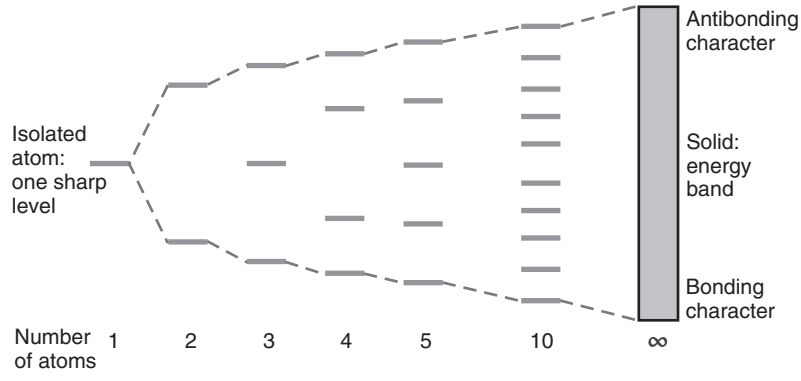

Figure 1.15 The schematic development of energy bands from delocalised molecular orbitals.

and is said to have an *antibonding character*. The lower part of the band will correspond to bonding orbitals and have a *bonding character*.

Although broadening of sharp atomic orbitals into energy bands will happen to each of the atomic orbitals on metallic atoms as they come together to form a crystal, the energy spread in an energy band is related to the extension of each orbital. The filled core electron orbitals are compact and are shielded from strong interactions with orbitals on other atoms by the valence electron orbitals. No significant overlap of these orbitals with orbitals on other atoms is possible. Thus, core electron orbitals hardly broaden and form very narrow energy bands little different from the energy levels a free atom. On the other hand, spreading of the energy bands associated with the outer orbitals is significant, more so for the heavier elements, simply because of their larger size and consequently greater interaction. Because of this, the outer orbitals on most of the heavier elements in the periodic table are transformed into rather wide bands in the solid state. Moreover, outer s and p bands are so broad that they usually overlap (Figure 1.16). Any d and f orbitals present are always shielded beneath outer s and p orbitals. They only interact weakly with orbitals on other atoms and form narrow d or f bands.

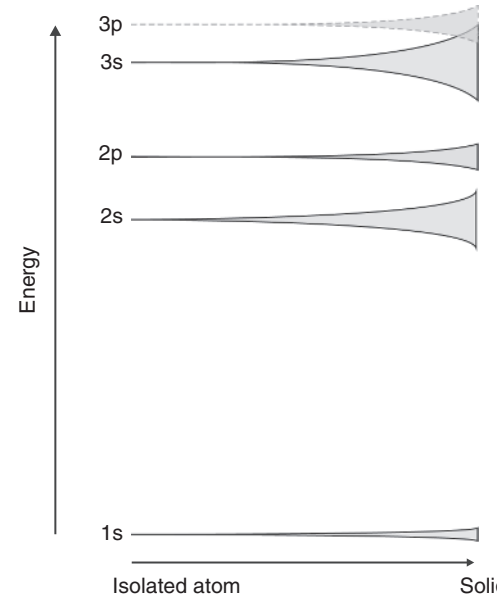

Figure 1.16 Schematic development of energy bands from atomic orbitals for magnesium metal as the atoms approach each other to form a crystal. The outermost filled 3s and empty 3p bands overlap in the metal.

1.4.2 The Free Electron Gas

The free-electron gas theory of metals started with a gross approximation: the idea that a metal contained a 'gas' of electrons, which were moving about at random in an analogous way to gas molecules in the atmosphere. The model, an adaptation of the kinetic theory of gases, was very successful. The imposition of a voltage caused the random motion to be replaced by a drift in average motion that was equated with the electric current that flowed. This simple model predicted that a metal should obey Ohm's law and that the resistivity of a metal should increase slightly with temperature. However, it could not explain some important properties. In particular, the theory was unable to account for the fact that metals had a similar specific heat to insulators. If an electron gas occurs in metals, but not in insulators, it could be proved that metals should have a molar specific heat of about $4.5R$, while insulators would have a molar specific heat of only $3R$, where R is the gas constant (Section 13.1).

The advent of quantum theory suggested that the electrons in the metal, although still free, should be treated like waves. If this was so, the Schrödinger equation could be used to determine the energy of an electron in a metal. The only variables to be specified were the dimensions of the solid and the potential energy experienced by the electron. As a first step, suppose that the potential energy is constant throughout the metal and a single electron is confined to a line of length a. (This is often referred to as the *particle in a box* model.) The potential energy is set as zero on the line (or in the box) and infinity at

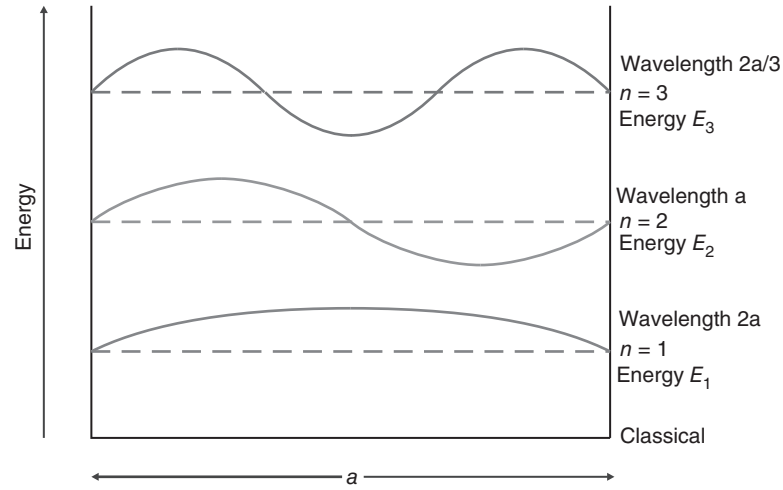

Figure 1.17 The energy levels and allowed wavelengths of an electron wave confined to a line of length *a*.

the extremities, so that the electron wave is completely trapped. The solutions in such a case show that the only allowed electron waves are standing waves with nodes at the fixed ends of the line (Figure 1.17). The allowed wavelengths, λ, are given by:

$$\lambda = 2a/n$$

where n is a quantum number that can take integer values 1, 2, 3, ... The wave equation describing this situation is:

$$\psi = \sqrt{(2/a)}\ \sin k\,x$$

where k is called the *wavenumber*. This equation represents a series of *plane waves*. It has quantised values given by:

$$k = 2\pi/\lambda = n\pi/a$$

(In three dimensions, $\boldsymbol{k}$ is a vector quantity, called the *wave vector*.)

The electron is confined not only to certain wavelengths but also to quantised energies:

$$E_n = k^2h^2/8\pi^2m$$

where E_n is the energy of the wave associated with the quantum number n and m is the mass of the electron. The form of the energy vs. k graph is parabolic (Figure 1.18). Extending this model to three dimensions shows that the energy of a single electron in a rectangular block of metal with sides a, b, and c, lying along the three axes x, y, and z, is:

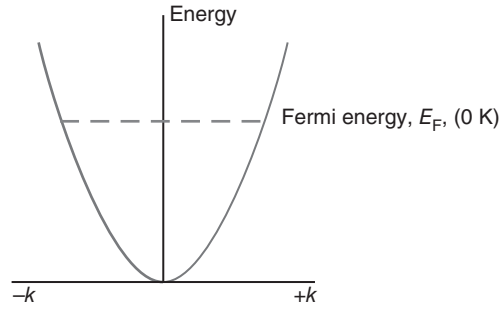

Figure 1.18 The relationship between energy, *E* and wavenumber, *k*, for an electron confined to a line. The Fermi energy, E_F, is the uppermost energy level filled at 0 K.

$$E(n_x, n_y, n_z) = [h^2/8m][n_x{}^2/a^2 + n_y{}^2/b^2 + n_z{}^2/c^2]$$

where n_x, n_y, and n_z are the quantum numbers along the x-, y-, and z-axes. For a cubic block of side a, this reduces to:

$$E(n_x, n_y, n_z) = [h^2/8ma^2\,][n_x{}^2 + n_y{}^2 + n_z{}^2]$$

Wavefunctions with the same energy are said to be *degenerate*. Thus, for a cubic container, the solutions ($n_x = 1$, $n_y = 1$, $n_z = 2$), ($n_x = 1$, $n_y = 2$, $n_z = 1$), and ($n_x = 2$, $n_y = 1$, $n_z = 1$) are degenerate. The degeneracy means that the number of energy levels within a particular

energy range is not a constant, but increases with increasing values of k. In order to solve the problem of the electron contribution to the specific heat of a metal, it is necessary to discover how many energy levels $N(E)$ occur in any particular range energy dE between the energies E and $E + \delta E$. The result for a cube of volume V is:

$$N(E) = [2\pi V][8m/h^2]^{3/2}E^{1/2}$$

This equation is called the *density of states function*. This curve, like the E vs. k curve, is also parabolic in form. The number of energy levels in a small range of energy increases sharply as the energy increases. As each energy level can accommodate two electrons, the number of electrons in an energy interval between E and $E + \delta E$ is double that of the density of states.

The simplest extension of these ideas to many electrons employs a similar strategy to the orbital approximation for atoms. The energy levels calculated earlier, derived for one electron, are populated with the additional electrons, following the Pauli exclusion principle and the aufbau principle. Each level can hold just two electrons, with differing spins. To determine the overall distribution, electrons are allocated, two at a time to the energy levels, starting with the lowest energy, up to a maximum energy governed by the number of electrons available. At absolute zero, the uppermost-occupied level is at the *Fermi energy* E_F (Figure 1.18). In three dimensions this highest filled energy level takes the form of a surface, the *Fermi surface*.

At temperatures above absolute zero, the electrons are liable to gain energy. However, it is not possible for electrons in lower levels to move into slightly more energetic levels as these are already filled. Only those electrons with the highest energies, near to the Fermi surface, can move to higher energy levels. The vast body of electrons remains untouched by the rise of temperature because no empty energy levels are available to them and so do not contribute appreciably to the specific heat. Thus, the electronic heat capacity is almost negligible.

The statistics that govern the distribution of electrons between the energy levels are called *Fermi–Dirac statistics*. Fermi–Dirac statistics applies to particles with a half-integral spin, such as electrons, protons, and neutrons. Such particles are called *fermions*. No two identical fermions can occupy a single (quantised) energy level. Fermi–Dirac statistics specify the probability, P_i, that an energy level, E_i, will be occupied is given by:

$$P_i = 1/\exp[(E_i - \mu)/k_B T] + 1$$

where μ is the chemical potential of the fermions and k_B is the Boltzmann constant. The chemical potential of electrons in a metal is equal to the Fermi energy (strictly speaking, at absolute zero), E_F, hence:

$$P_i = 1/\{\exp[(E_i - E_F)/k_B T] + 1\}$$

The distribution of electrons at temperatures other than 0 K is given by the *Fermi function*:

$$P(E) = 1/\{\exp[(E - E_F)/k_B T] + 1\}$$

where $P(E)$ is the probability than an energy level E is occupied by an electron at absolute temperature T (Figure 1.19). At $T = 0$ K, $P(E) = 1$ for $E < E_F$ and 0 for $E > E_F$ and the curve has a sharp cut off. At higher temperatures the curve changes smoothly from $P(E) = 1$ to 0. The equation also shows that at $E = E_F$, $P(E) = ½$. Thus, the Fermi level in metals above 0 K can be defined as the energy for which $P(E) = ½$.

1.4.3 Energy Bands

In the free-electron approach a single electron moves in a constant potential. In a solid the electron moves in a *periodic potential* that is representative of the crystal structure. The first solution to the way in which a periodic potential modifies the free electron model was given by Bloch in 1928. The solution of the Schrödinger equation was found to consist of the free electron waves multiplied

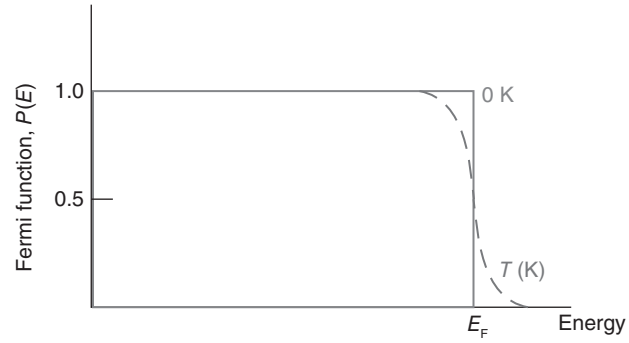

Figure 1.19 The Fermi function, $P(E)$.

by a function with the same periodicity as the crystal structure. These wave equations are called the *Bloch functions*. Two generalisations are found. Firstly, if the potential is weak the wavefunctions are similar to the free electron wavefunctions. Secondly, regardless of the potential, electron waves with a long wavelength and low energy also have wavefunctions that are almost the same as the free electron wavefunctions. In this extreme, the energy levels are closely spaced and vary with wavenumber in a parabolic fashion as described previously. The electron is 'not aware' of the atoms in the solid.

As the wavelength approaches the same dimensions as the atom spacing in the crystal, the electron waves in a solid behave in a similar way to any other waves in any medium. When a wave encounters an object of the same dimensions as the wavelength, a considerable interaction occurs and the wave is *diffracted* (Section 12.6). In the present situation, the conditions for diffraction to occur are given by Bragg's law. For an electron wave normally incident upon planes of atoms, diffraction of the wave occurs at values of the wavenumber:

$$k = \pm n\pi/a$$

where n is an integer taking values 1, 2, 3, and so on and a is the spacing of the planes of atoms. Waves with these wavenumbers will not be able to pass through the crystal and the one-dimensional E vs. k curve is broken at these values (Figure 1.20a). Propagation will occur again when the wavenumber increases slightly. Substitution of the appropriate values into the Schrödinger equation reveals that the change in wave vector is accompanied by an energy jump from a lower value to a higher one. It is not possible for an electron to have an energy value lying between the two extremes. This is described by saying that an electron can exist within a band of allowed energies. These bands are separated from each other by bands of forbidden energies (Figure 1.20b).

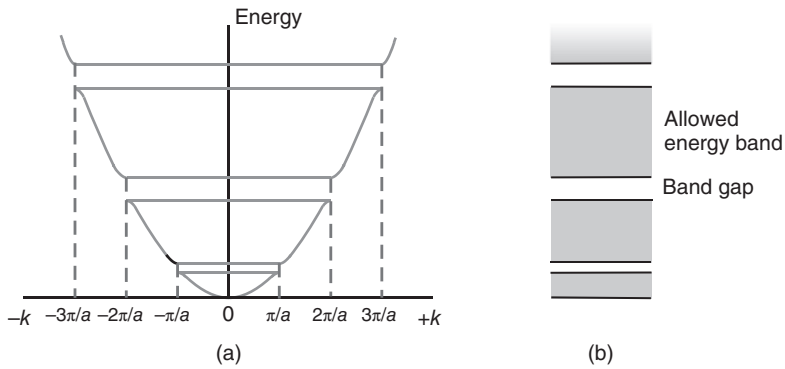

Figure 1.20 (a) The one-dimensional free-electron E vs. k curve broken into energy bands due to the periodic potential of atomic nuclei of separation a. (b) Schematic representation of energy bands.

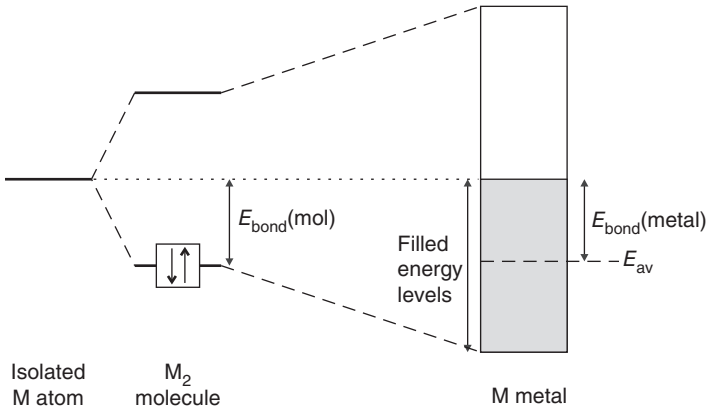

Figure 1.21 The bonding in a molecule, M_2, and a solid metal.

The discontinuities in the energy vs. k curve due to electron diffraction mark the boundaries of *Brillouin zones*. The first Brillouin zone in the one-dimensional case (Figure 1.20a) extends from k values *of* $-\pi/a$ to π/a. The second Brillouin zone lies between k values of π/a to $2\pi/a$ on the positive side of the graph and from $-\pi/a$ to $-2\pi/a$ on the negative side. The third, fourth, and so on Brillouin zones can be similarly located.

The band model accounts for the overall properties of metals. In terms of the cohesive energy of a metal, the upper energy levels of a band are antibonding in character, while the lower energy levels are bonding in character. The electrons will feed into the energy levels in a band, following the aufbau principle, with two electrons of opposing spins in each level. The core levels will be filled and be neutral in terms of bonding. Provided that the upper band is only partly filled, the lower energy bonding levels will be populated while the higher energy antibonding levels will be empty. In this case the atoms will experience an overall bonding interaction that would be expected to be roughly similar to the bonding energy of a diatomic molecule. For such a diatomic M_2 molecule, bonding is due to a filled bonding orbital combined with an empty antibonding orbital. In a solid metal, M, bonding energy is due to preferential filling of the lower bonding character part of the energy band while leaving the upper antibonding character energy band empty (Figure 1.21). Moreover, as the electrons are delocalised metallic bonds are expected to be *non-directional*.

The fact that the uppermost band is only partly occupied also accounts qualitatively for electrical conductivity. The electrons in the highest energy band are delocalised over all the atoms in a metallic solid, and the imposition of an external voltage is able to cause the electrons to move through the material provided that there are empty energy levels available.

The loss of the outer electrons has two other consequences. As the remaining core electron orbitals are of a spherical shape, the crystal structures of many metals can be considered in terms of the packing of spherical atoms. Spheres can pack most efficiently when each is surrounded by a large number, 8–12, nearest neighbours so the delocalisation concept explains the high apparent valence of metals in crystals. Delocalisation also negates the main chemical distinguishing feature of an element and individual chemical and physical variations will be suppressed so that one metallic element is similar to another and alloys would be expected to form readily.

These metallic properties are more dependent upon the close approach of the atoms than on the relative configuration of the atoms. The geometry of the nearest neighbour atoms does not change greatly in a liquid compared to a crystal. For example, the number of nearest

neighbours to any sodium atom in a crystal of sodium metal, eight, is similar to the number in the liquid state. This means that a liquid metal should have similar properties to the solid. For example, liquid mercury shows metallic conductivity because this property is determined by the delocalisation of the outer electrons. However, Brillouin zones will not occur in liquids or glasses, as they are features of crystalline arrays.

1.4.4 Bands in Ionic and Covalent Solids

In the discussion of ionic and covalent bonding, the spreading of atomic orbitals into bands has been ignored. It is reasonable to re-examine ionic and covalent solids in band terms. Consider the archetypal ionic compound, sodium chloride. When the atoms are isolated, the lowest energy corresponds to Na and Cl atoms in their respective ground states. As the interatomic separation decreases to approximately 1.0 nm, energy is gained by the transfer of an electron from sodium to chlorine to form Na^+ and Cl^- ions. The energy of the Cl^- ions now falls below that of the Na^+ ions and the ions order on a lattice. However, even at this spacing the energy levels are still similar to those on isolated ions. As the interatomic spacing decreases further, the electron orbitals overlap. Electrons with opposed spins tend to lose energy while those with parallel spins tend to gain energy. These are the familiar bonding and antibonding interactions, and cause the narrow energy levels to broaden into bands. However, the ionic electron distribution is not changed. The band that develops on the Cl^- ions, the 3p band, is full and the band that develops on the Na^+ ions, the 3s band, remains empty (Figure 1.22). Thus, the ionic model is still a good model for the bonding in NaCl.

In the case of a covalently bonded crystal such as germanium, which is composed of a tetrahedral array of germanium atoms linked by sp^3-hybrid bonding, a modification of the molecular orbital model is again needed. Isolated Ge atoms have an outer electron configuration s^2p^2, which is replaced by four degenerate sp^3 hybrid orbitals as the atoms are brought closer (Figure 1.23). Each sp^3 orbital on an atom contains one electron and overlap with adjacent orbitals causes strong bonds with a tetrahedral geometry to form.

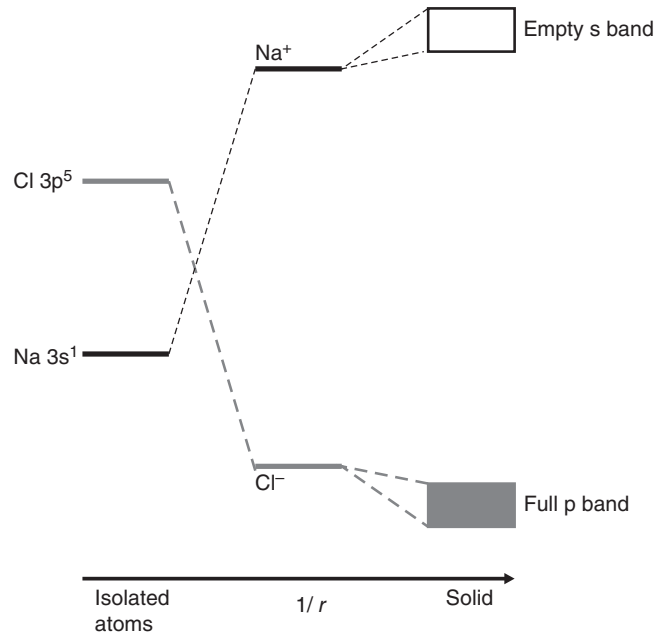

Figure 1.22 Schematic development of energy bands from isolated atoms for sodium chloride, NaCl. For clarity, the core energy levels of both atoms have been ignored and only relative energy changes are included.

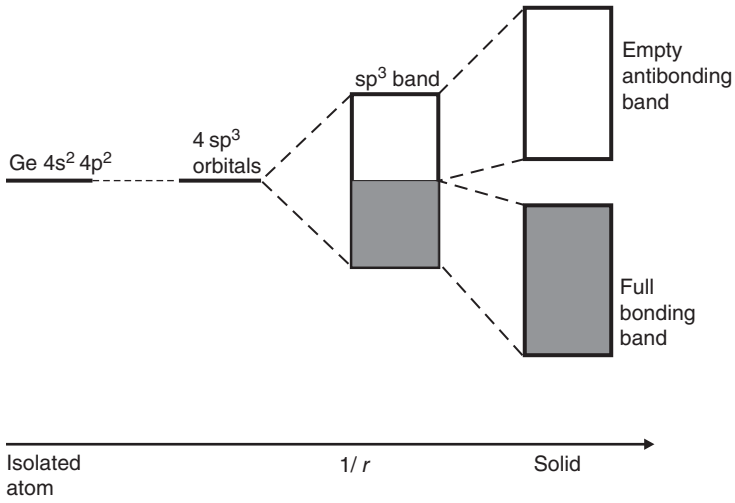

Figure 1.23 Schematic development of energy bands from isolated atoms for germanium, Ge. For clarity, the core energy levels of both atoms have been ignored and only relative energy changes are included.

As the atoms approach further, each single sp^3 energy level widens into a band, the lower half of which is bonding and the upper part antibonding. The band is able to contain a maximum of eight electrons. As each atom donates one electron per sp^3 energy level, the band is half full. Continued approach causes the antibonding part of the band to increase in energy due to the repulsion between the parallel electrons and the bonding part to decrease in energy due to the favourable interaction between the spin-paired electrons. At a critical separation, the single band is split into two bands separated by an energy gap. The lower of these bands is usually called the *bonding band* and the upper the *antibonding band* when the chemistry of the material is discussed, or the *valence band* and *conduction band* in semiconductor physics. The electrons, one in each sp^3 orbital, that combine in a covalent bond end up in the lowest bonding band, which will be completely full. The upper antibonding band will be completely empty. The cohesive energy in these crystals is, in fact, due to the appearance of the energy gap between the upper (empty) and lower (filled) bands.

The elements carbon (diamond), C, silicon, Si, germanium, Ge, and one form of tin, α-Sn, all crystallise with the same structure. The size variation of this series of atoms modifies the band formation in a predictable way. The smallest atom, carbon, C, has the smallest degree of orbital interaction and hence the narrowest bands. The energy gap is large and diamond has a very high cohesive strength. As the atoms increase in size, the orbital interactions increase, the bands widen, the energy gap narrows, and the cohesive energy falls. Unlike diamond, α-tin is a weak solid, easily crushed.

While this description is quite different than that of covalent bonding, the separation of the energy bands in the solid is similar to the separation of the bonding and antibonding molecular orbitals that would be found on a diatomic C_2, Si_2, Ge_2, or Sn_2 molecule with a similar interatomic separation to the atoms in the crystal. The covalent bond picture is, therefore, closely related to the band picture. In the covalent model, the bond energy is related to the separation of the molecular orbitals. In the solid, the cohesive energy is related to the separation of the energy bands. With this limitation in mind, the covalent bonding model is adequate for many solids.

1.5 Weak Chemical Bonds

Although the strong chemical bonds described earlier play a dominant role in determination of the overall properties of solids, weak interactions are often of vital importance,

especially in living organisms. For example, noble gas atoms experience weak interatomic forces that lead to liquefaction and, except for helium, solidification at low temperatures, while hydrogen bonding is vital in the functioning of the molecules central to life, such as proteins and DNA (Table 1.5).

The strongest of the weak bonds are *hydrogen bonds*. These form when a hydrogen atom lies between two highly electronegative atoms, either fluorine, oxygen, chlorine, or nitrogen. The bond results from the interaction of the small positive charge, δ+, found in dipolar molecules containing hydrogen with the partial charge of δ− located on the electronegative partner, especially the exposed lone pair electrons on atoms such as oxygen and nitrogen. The hydrogen atom has an ambiguous position in the bond. At low temperatures it adopts a position nearer to one or other of the electronegative atoms, while at high temperatures it is found, on average, midway between them. In general the two links making up the bond, O—H and H … O, are not in the same straight line. The angle between them commonly deviates from 180° by 10° to 20°, and sometimes by much more.

Because hydrogen bonds are comparatively weak, it follows that they are not only easily ruptured but they are also formed with equal ease. Thus, they form in all appropriate materials at normal temperatures and are important in compounds such as water, H_2O, hydrogen fluoride, HF, and potassium hydrogen fluoride, KHF_2. The existence of hydrogen bonds dramatically changes many of the properties of the material. For example, HF, H_2O, and ammonia, NH_3, are characterised by melting points, boiling points, and molar heats of vaporisation that are abnormally high in comparison with those of similar molecules unable to link in this way. The fact that water is liquid on the Earth at normal temperatures is largely due to hydrogen bonding. In living organisms, hydrogen bonding is of great importance in controlling the folded (*tertiary*) structure of proteins. The tertiary structure largely determines the biological activity of the molecule and mistakes in the folding can lead to serious illness. Hydrogen bonding also endows solids with significant physical properties, such as ferroelectric behaviour (Section 9.3).

Permanent dipoles are usually found on molecules containing two atoms with very different electronegativities. For example, a molecule of HCl has the covalent bond slightly deformed to give rise to a region of depleted electron density (enhanced positive charge, δ+), associated with the hydrogen atom, and a region of increased electron density (augmented negative charge, δ−), associated with the chlorine atom. The resultant dipole has a dipole moment of 3.60×10^{-30} C m. Water, an angular molecule, has two internal dipoles, with the δ+ region residing on each hydrogen and the δ− region on the oxygen. These

Table 1.5 Bonds between atoms, ions, and molecules.

Type of bond	Approximate energy (kJ mol^{-1})	Species involved
Covalent	350	Atoms with partly filled orbitals
Ionic	250	Cations and anions
Metallic	200	Metal atoms
Ion–dipole	15	Ions and polar molecules
Dipole–dipole	2	Stationary polar molecules
Dipole–dipole	0.3	Rotating polar molecules
Dispersion	2	All atoms and molecules
Hydrogen bond	20	N, O, or F plus H

add together so that the resultant is directed towards the oxygen atom, and is augmented by the negative charge associated with the two lone pairs of electrons to give a dipole moment, of 6.17×10^{-30} C m.

The charges making up the dipole can interact with ions to give *ion–dipole interaction energies* of about 15 kJ mol^{-1}. The hydration of cations, in both water solution and solid hydrates, is mainly due to ion–dipole effects. Permanent dipoles can also interact with other dipoles in *dipole–dipole interactions*, which vary from approximately 2 kJ mol^{-1} for fixed molecules to about one tenth of this value if the molecules are free to rotate.

The noble gases are monatomic at normal temperatures. On cooling, helium, the lightest, turns to a liquid (with very curious properties) at 4.2 K, the lowest known boiling point of an element. Helium can only be turned into a solid by applying pressure. The other members of the family can be liquefied and solidified by cooling. This condensation is due to weak interactions between the outer electrons on the atoms. Fleeting fluctuations in the electron clouds create momentary dipoles, which lead to a weak attraction and, at low temperatures, condensation. The force of attraction is called the *London* or *dispersion force* and the interaction is called the *van der Waals bonding* and occurs between all atoms and molecules. Although the bond energy is only about 2 kJ mol^{-1}, it is responsible for the liquid states of many molecular species, including H_2 and benzene. The strength of the interaction increases as the size of the molecules increase. Because of this, large molecules tend to exist as solids, smaller ones as liquids, and light molecules as gases. This trend is exemplified by the smooth increase in melting and boiling points of the alkanes, which have a series formula C_nH_{2n+2} (Figure 1.24). The lightest of these are gases at room temperature (methane, ethane, propane), while the heavier ones are liquids (octane, C_8H_{18}), and then waxy solids ($C_{18}H_{38}$ and higher).

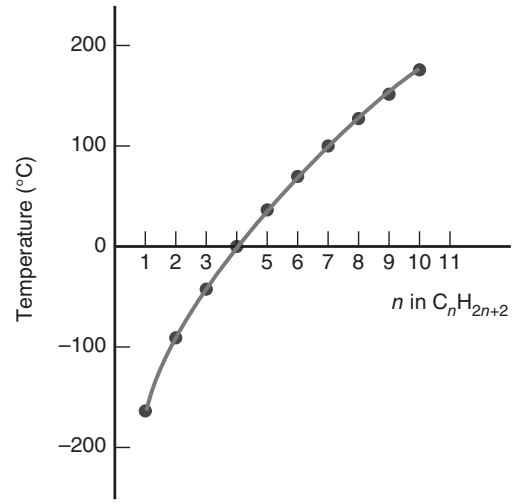

Figure 1.24 The boiling points of the alkanes, C_nH_{2n+2}, plotting against n, which is proportional to the size of the molecule.

A commonly used form of the interaction energy between a pair of atoms or molecules is the *Lennard-Jones potential*, V_{LJ}:

$$V_{LJ} = Ar^{-12} - Br^{-6}$$

where A and B are constants and r is the distance between the atoms or molecules. The first term in this equation is a repulsive energy term and the second an attractive energy. The potential energy passes through a minimum V_m at a distance r_0. Under normal circumstances, this would represent the bonding energy of a pair of atoms or molecules, at an equilibrium separation of r_0. The Lennard-Jones potential can be written in terms of V_m as:

$$V_{LJ} = 4V_m[(r(0)/r)^6 - (r(0)/r)^{12}]$$

where $r(0)$ is the value of r when V_{LJ} is zero (Figure 1.25).

Thermal energy is taken to be of the order of k_BT, where k_B is Boltzmann's constant and T is the absolute temperature. In cases where the energy of the bond, V_m, is greater than k_BT, one can expect pairs of atoms or molecules to be stable, and a liquid phase to condense. When V_m is less than k_BT, the bond would be expected to be too weak to hold the pair together, and a gas is likely.

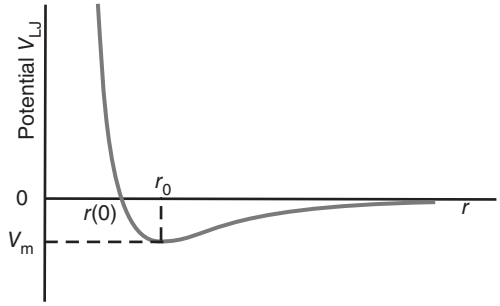

Figure 1.25 The Lennard-Jones potential between two atoms separated by a distance r.

The range over which bonding forces are significant varies widely. Covalent bonds act over a few nanometres only. Interactions that are essentially electrostatic in nature, as in ionic bonds, operate over larger distances, and are proportional to $1/r$, where r is the inter-ionic distance. Ion–dipole interactions decrease more rapidly, being proportional to $1/r^2$. Dipole–dipole interactions vary as $1/r^3$ for static dipoles and $1/r^6$ for rotating dipoles. Dispersion forces also decrease as $1/r^6$.

1.6 Computation of Material Properties

The calculation of materials properties using the bonding models described above has a long pedigree. The shortcomings of traditional bonding concepts are overcome by using the theoretical approach called *density functional theory*. (A functional is a function of a function. In this case, the energy of the wavefunction is a function of the electron density which is a function of electron position.) Density functional theory has been successfully applied to modelling the properties of a wide range of solids using an approach rather akin to that described for bonding in metals. The important feature of this theoretical advance is that the correlation energy, together with the exchange energy, called the *exchange–correlation* energy, can be expressed solely in terms of the electron density distribution in the material. Despite this superficially simple statement, it remains a central task of density functional calculations to find appropriate expressions for the exchange–correlation energy. One way is to use a model of a uniform electron gas occupying a volume with a uniform distribution of positive charge, the so-called *jellium model*, clearly similar to the electron gas model of a metal.

There still remains the problem of how one is to represent the wavefunctions of the system. For many materials a simple approach is satisfactory, that is to use plane waves similar to those derived as solutions to the wave equation for a free electron gas. In this case the many electron wavefunction is written as the sum of plane waves. A problem arises because near to atomic nuclei the number of plane waves needed increases enormously – too much for simple computation. This problem is removed by replacing the strong potential field of each nucleus with a weak *pseudopotential*, which reduces the number of plane waves needed, the plane wave basis set, to manageable proportions.

Further Reading

The Following References Expand the Material in this Chapter:

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Shannon, R.D. (1976). *Acta Crystallogr. A* 32: 751–756.

Shannon, R.D. and Prewitt, C.T. (1969). *Acta Crystallogr.* B25: 925–946; Acta Crystallogr. B, 26, 1046 (1970).

The Computation of Properties is Described in:

Lesar, R. (2013). *Introduction to Computational Materials Science*. Cambridge: MRS/Cambridge University Press.

Problems and Exercises

Quick Quiz

1.1 An orbital is:
(a) A bond between an electron and a nucleus.
(b) A region where the probability of finding an electron is high.
(c) An electron orbit around an atomic nucleus.

1.2 The configuration of an atom is:
(a) The number of electrons around the nucleus.
(b) The electron orbitals around the nucleus.
(c) The arrangement of electrons in the various orbitals.

1.3 The outer electron configuration of the noble gases is:
(a) ns^2np^6.
(b) $ns^2np^6(n+1)s^1$.
(c) ns^2np^5.

1.4 The valence electron configuration of the alkali metals is:
(a) ns^2.
(b) np^1.
(c) ns^1.

1.5 How many electrons can occupy orbitals with $n = 3, l = 2$?
(a) 6 electrons.
(b) 10 electrons.
(c) 14 electrons.

1.6 How many electrons can occupy the 4f orbitals?
(a) 14
(b) 10
(c) 7

1.7 The Russell–Saunders coupling is:
(a) A procedure to obtain the energy of many-electron atoms.
(b) A description of atomic energy levels.
(c) A procedure to obtain many-electron quantum numbers.

1.8 A term symbol is
(a) A label for a set of atomic energy levels.
(b) A label for an orbital.
(c) An electron configuration.

1.9 An atom has a term ^1S. What is the value of the spin quantum number, S?
(a) ½.
(b) 0.
(c) 1.

1.10 An atom has a term ^1S. What is the value of the orbital quantum number, L?
(a) 2.
(b) 1.
(c) 0.

1.11 An anion is:
(a) An atom that has lost a small number of electrons.

(b) An atom that has gained a small number of electrons.
(c) A charged atom stable in solutions.

1.12 Ionic bonds are formed by which process:
(a) Electron sharing.
(b) Electron transfer.
(c) Electron delocalisation.

1.13 The Madelung energy is:
(a) The bond energy of an ionic crystal.
(b) The lattice energy of an ionic crystal.
(c) The electrostatic energy of an ionic crystal.

1.14 Cations are generally:
(a) Smaller than anions.
(b) Bigger than anions.
(c) The same size as anions.

1.15 Covalent bonds are formed by which process:
(a) Electron sharing.
(b) Electron transfer.
(c) Electron delocalisation.

1.16 Covalent bonds are:
(a) Strongly directional.
(b) Completely non-directional.
(c) Variable in direction.

1.17 A σ bond is characterised by:
(a) Being formed between identical atoms.
(b) Being formed by two s orbitals.
(c) Radial symmetry about the bond axis.

1.18 Bonding molecular orbitals have:
(a) The same energy as antibonding orbitals.
(b) A lower energy than antibonding orbitals.
(c) A higher energy than antibonding orbitals.

1.19 sp^2 hybrid orbitals:
(a) Point towards the vertices of a tetrahedron.
(b) Point towards the vertices of a triangle.
(c) Point towards the vertices of a cube.

1.20 Multiple bonds between two similar atoms:
(a) Always consist of the same types of molecular orbital.
(b) Always consist of the same types of hybrid orbital.
(c) Always consist of different types of molecular orbital.

1.21 Metallic bonds are formed by which process:
(a) Electron sharing.
(b) Electron transfer.
(c) Electron delocalisation.

1.22 A metallic bond is predominantly:
(a) Strongly directional.
(b) Completely non-directional.
(c) Partly directional.

1.23 The Fermi energy is:
(a) The uppermost energy level filled.
(b) The highest energy in a band.
(c) The energy of an electron in a band.

1.24 Energy bands can form:
(a) Only in crystals.
(b) Only in metals.
(c) Only in electrical conductors.

1.25 Hydrogen bonding is found in:
(a) Solid and liquid hydrogen.
(b) Hydrocarbons.
(c) Compounds containing oxygen and hydrogen.

1.26 Van der Waal's bonds are due to:
(a) Dispersion forces.
(b) Ion–dipole forces.
(c) Dipole–dipole forces.

Calculations and Questions

1.1 What energy is required to liberate an electron in the $n = 3$ orbital of a hydrogen atom?

1.2 What is the energy change when an electron moves from the $n = 2$ orbital to the $n = 6$ orbital in a hydrogen atom?

1.3 Calculate the energy of the lowest orbital (the ground state) of the single electron hydrogen-like atoms with $Z = 2$ (He^+) and 3 (Li^{2+}).

1.4 What are the frequencies and wavelengths of the photons emitted from a hydrogen atom when an electron makes a transition from $n = 4$ to the lower levels $n = 1$, 2 and 3?

1.5 What are the frequencies and wavelengths of the photons emitted from a hydrogen atom when an electron makes a transition from $n = 5$ to the lower levels $n = 1$, 2 and 3?

1.6 What are the frequencies and wavelengths of photons emitted when an electron on a Li^{2+} ion makes a transition from $n = 3$ to the lower levels $n = 1$ and 2?

1.7 What are the frequencies and wavelengths of photons emitted when an electron on a He^+ ion makes a transition from $n = 4$ to the lower levels $n = 1$, 2 and 3?

1.8 Sodium lights emit yellow colour, with photons of wavelength 589 nm. What is the energy of these photons?

1.9 Mercury lights emit photons with a wavelength 435.8 nm. What is the energy of the photons?

1.10 What are the possible quantum numbers for an electron in a 2p orbital?

1.11 Titanium has the term symbol ^3F. What are the possible values of J? What is the ground state level?

1.12 Phosphorus has the term symbol ^4S. What are the possible values of J? What is the ground state level?

1.13 Scandium has a term symbol ^2D. What are the possible values of J? What is the ground state level?

1.14 Boron has a term symbol ^2P. What are the possible values of J? What is the ground state level?

1.15 What is the splitting g_J, for sulfur, with ground state $^3P_2$?

1.16 What is the splitting g_J, for iron, with a ground state $^5D_4$?

1.17 Draw a diagram equivalent to Figure 1.6, for the *ground state* of a chlorine atom, with a ground state $^2P_{3/2}$.

1.18 Write out the electron configuration of the ions: Cl^-, Na^+, Mg^{2+}, S^{2-}, N^{3-}, Fe^{3+}.

1.19 Write out the electron configuration of the ions: F^-, Li^+, O^{2-}, P^{3-}, Co^{2+}.

1.20 Write the symbols of the ions formed by oxygen, hydrogen, sodium, calcium, zirconium, and tungsten.

1.21 Write the symbols of the ions formed by iron, chlorine, aluminium, sulfur, lanthanum, and tantalum.

1.22 Calculate the lattice energy of the ionic oxide CaO, which has the halite (NaCl) structure. $\alpha = 1.75$, $n = 9$, $r_0 = 0.24$ nm.

1.23 Calculate the lattice energy of the ionic halides NaCl and KCl, which have the halite (NaCl) structure. $\alpha = 1.75$, $n = 9$, r_0 (NaCl) = 0.281 nm, r_0 (KCl) = 0.314 nm.

1.24 Calculate the lattice energy of the ionic halides NaBr and KBr, which have the halite (NaCl) structure. $\alpha = 1.75$, $n = 9$, r_0 (NaBr) = 0.298 nm, r_0 (KBr) = 0.329 nm.

1.25 Determine the number of free electrons in gold, assuming that each atom contributes one electron to the 'electron gas'. The molar mass of gold is 0.196 97 kg mol^{-1}, and the density is 19 281 kg m^{-3}.

1.26 Determine the number of free electrons in nickel, assuming that each atom contributes two electrons to the 'electron gas'. The molar mass of nickel is 0.058 69 kg mol^{-1}, and the density is 8907 kg m^{-3}.

1.27 Determine the number of free electrons in copper, assuming that each atom contributes one electron to the 'electron gas'. The molar mass of copper is 0.063 55 kg mol^{-1}, and the density is 8933 kg m^{-3}.

1.28 Determine the number of free electrons in magnesium, assuming that each atom contributes two electrons to the 'electron gas'. The molar mass of magnesium is 0.024 31 kg mol^{-1}, and the density is 1738 kg m^{-3}.

1.29 Determine the number of free electrons in iron, assuming that each atom contributes two electrons to the 'electron gas'. The molar mass of iron is 0.055 85 kg mol^{-1}, and the density is 7873 kg m^{-3}.

1.30 Calculate the lowest energy level of a free electron in a cube of metal 1 cm on edge and compare it with thermal energy at room temperature, given by $k_B T$, where k_B is Boltzmann's constant and T is the absolute temperature.

1.31 Estimate the Fermi energy of silver. The molar mass of silver is 0.1079 kg mol^{-1}, the density is 10 500 kg m^{-3}, and each silver atom contributes one electron to the 'electron gas'.

1.32 Estimate the Fermi energy of sodium. The molar mass of sodium is 0.022 99 kg mol^{-1}, the density is 966 kg m^{-3}, and each sodium atom contributes one electron to the 'electron gas'.

1.33 Estimate the Fermi energy of calcium. The molar mass of calcium is 0.044 08 kg mol^{-1}, the density is 1530 kg m^{-3}, and each calcium atom contributes two electrons to the 'electron gas'.

1.34 Estimate the Fermi energy of aluminium. The molar mass of aluminium is 0.026 98 kg mol^{-1}, the density is 2698 kg m^{-3}, and each aluminium atom contributes three electrons to the 'electron gas'.

1.35 Draw the wavefunctions and the probability of locating an electron at a position x for an electron trapped in a one-dimensional potential well, with internal potential 0 and external potential infinity.

1.36 Make accurate plots of the Fermi function, which expresses the probability of finding an electron at an energy E, for temperatures of 0, 300, 1000, and 5000 K.

1.37 The Lennard-Jones constants for argon are $A = 1.78 \times 10^{-134}$ J m^{12} and $B = 1.08 \times 10^{-77}$ J m^6.

(a) Plot the attractive and repulsive potential energies;
(b) Estimate the minimum potential energy of the pair, which can be considered the bonding energy of a molecule of argon;
(c) The equilibrium interatomic separation of this molecule.

1.38 By equating the thermal energy ($k_B T$, where k_B is the Boltzmann constant), with the bonding energy, estimate the temperature at which argon atoms are likely to start to form pairs, and so form a liquid, using the data in Question 1.37. Compare this to the boiling point of argon (−185.9 °C).

1.39 If the atoms in liquid argon are surrounded by 12 nearest neighbours on average, estimate the energy of evaporation of the liquid.

1.40 The Lennard-Jones constants for neon are $A = 4.39 \times 10^{-136}\,\mathrm{J\,m^{12}}$ and $B = 9.30 \times 10^{-79}\,\mathrm{J\,m^{6}}$. Calculate:
(a) The bonding energy;
(b) The equilibrium separation;
of a pair of neon atoms.

1.41 The Lennard-Jones constants for helium are $A = 4.91 \times 10^{-137}\,\mathrm{J\,m^{12}}$ and $B = 4.16 \times 10^{-80}\,\mathrm{J\,m^{6}}$ and for xenon are $A = 2.54 \times 10^{-133}\,\mathrm{J\,m^{12}}$ and $B = 5.66 \times 10^{-77}\,\mathrm{J\,m^{6}}$. Using these values and those in Questions 1.37 and 1.40, estimate the Lennard-Jones constants for krypton, Kr.

1.42 Derive the relationship

$$V_{LJ} = 4V_{min}[(r(0)/r)^6 - (r(0)/r)^{12}]$$

from $V_{LJ} = Ar^{-12} - Br^{-6}$.

1.43 The melting points and boiling points of the noble gases are given in the table. Explain these trends, and suggest why the melting and boiling points are so close.

Element	Melting point (°C)	Boiling point (°C)
Helium	—	−268.9
Neon	−248.6	−246.1
Argon	−189.4	−185.9
Krypton	−157.4	−157.4
Xenon	−111.8	−108.0
Radon	−71	−61.7