1 Chemical Bonding in Solids

Solid-state physics is the physics of that state of matter in which a large number of atoms are chemically bound to produce a dense solid aggregate. The emphasis in this statement is placed on the large number of atoms involved, since that number is of the order of $10^{23}\,\mathrm{cm}^{-3}$. At first sight it would seem to be a hopeless task to try to apply traditional scientific methods for the description of such a vast number of atoms. However, it is exactly the large number of atoms involved that in fact makes a quantitative description possible by means of new models, applicable specifically to solids. A prerequisite, though, for the success of these models, is that the participating atoms are not simply chosen at random from the periodic table of elements; the solid must be composed of a limited number of different elements whose atoms are arranged in space with a certain order. Thus, for the solid state physicist, the showpieces are the "elementary" crystals, i.e., three-dimensional periodic arrangements of atoms of one type, or chemical compounds of two elements. An understanding of solids and of their characteristic properties thus requires that we first achieve a fundamental understanding of two particular phenomena: the first is that of the forces that hold together the atoms of a solid, in other words, the chemical bonding between atoms. The second important aspect is the structural ordering of the atoms within the solid. A consideration of these two basic questions forms the content of the first two chapters. In both cases it will only be possible to give a short introduction and for a more detailed discussion of these phenomena the reader is referred to textbooks on quantum chemistry and crystallography.

1.1 The Periodic Table of the Elements

By way of introduction to the topic of chemical bonding, we will take a brief look at the construction of the periodic table of the elements.

The electronic states of an atom are classified according to the one-electron states of the radially symmetric potential. Thus we have $1s$, $2s$, $2p$, $3s$, $3p$, $3d$, $4s$, $4p$, $4d$, $4f, \ldots$ states where the numbers give the principal quantum number, n, and the letters s, p, d, f correspond to the values of the electron's orbital angular momentum ($l = 0, 1, 2, 3, \ldots$). This classification stems from the picture in which the potential for each electron includes the effect of all other electrons by representing them as a continuous fixed charge distribution

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Table 1.1. The build-up of the periodic table by successive filling of the electronic energy shells. Indicated on the left of each column is the outer electron level that is being progressively filled, and in brackets is its maximum allowed occupation number. See also cover page

1*s* (2) H, He	4*s* (2) K, Ca	5*p* (6) In → Xe
2*s* (2) Li, Be	3*d* (10) Transition metals Sc → Zn	6*s* (2) Cs, Ba
2*p* (6) B → Ne	4*p* (6) Ga → Kr	4*f* (14) Rare earths Ce → Lu
3*s* (2) Na, Mg	5*s* (2) Rb, Sr	5*d* (10) Transition metals La → Hg
3*p* (6) Al → Ar	4*d* (10) Transition metals Y → Cd	6*p* (6) Tl → Rn

which, to a greater or lesser extent, screens the potential of the bare nucleus. In addition to the principal quantum number n and the orbital angular momentum quantum number l, there is also a magnetic quantum number m which can take $(2l+1)$ different values (ranging from $-l$ to $+l$). According to the Pauli exclusion principle, each state can be occupied by at most two electrons of opposite spin. As a function of increasing nuclear charge this then leads to the periodic tables whose structure is outlined in Table 1.1. From the order of the energy levels of the hydrogen atom, one would expect that after the 3*p*-states are filled, the next states to be occupied would be the 3*d*. But in fact, as can be seen from Table 1.1, this is not the case; following the 3*p*-levels those next occupied are the 4*s*. The subsequent filling of the 3*d*-states gives rise to the first series of transition metals (the 3*d*-metals). Similarly, one also finds 4*d*- and 5*d* transition metals. The same effect for the *f*-states leads to the so-called rare earths. The reason for this anomaly is that the electrons in *s*-states have a nonvanishing probability of being located at the nucleus thereby reducing for them the screening effect of the other electrons. Hence the *s*-electrons possess lower energy.

If one considers a thought experiment in which several initially isolated atoms are gradually brought closer together, their interaction with one another will lead to a splitting of each of their energy levels. If a very large number of atoms are involved, as in the case of a real solid, then the energy levels will lie on a quasi-continuous scale and one therefore speaks of energy bands (Fig. 1.1). The width of the band (i.e., the broadening) depends on the overlap of the wavefunctions concerned. Thus for the deep lying levels the broadening is small, and these "core levels" retain their atomic shell-like character even in the solid. For the highest occupied levels, on the other hand, the broadening is so large that the *s*-, *p*- and where present, *d*-levels merge into a single band. It is the electrons in this uppermost band that are responsible for the chemical bonding between atoms, and hence one speaks of the valence band. The ultimate source of the chemical bonding is the reduction in electronic energy which results from the level broadening. This, despite the increase in repulsion between the nuclei, leads to a decrease in the total energy as a function of atomic separation until the point where the equilibrium separation is reached – i.e., the point of minimum total energy.

The type of bonding in a solid is determined essentially by the degree of overlap between the electronic wavefunctions of the atoms involved. At the

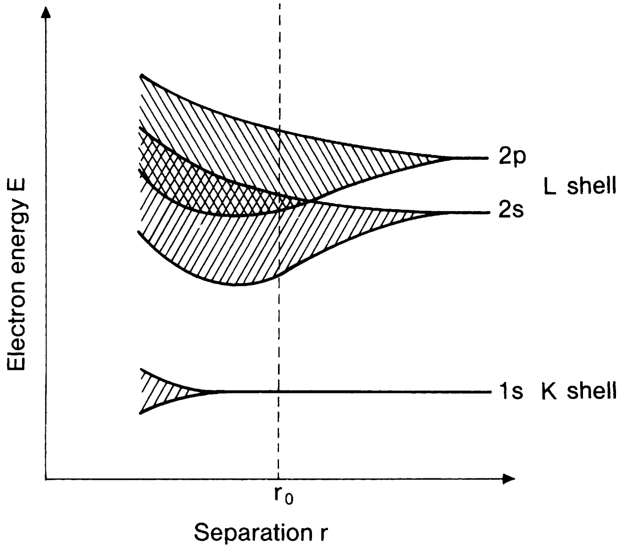

Fig. 1.1. Broadening of the energy levels as a large number of identical atoms from the first row of the periodic table approach one another (schematic). The separation r_0 corresponds to the approximate equilibrium separation of chemically bound atoms. Due to the overlap of the $2s$ and $2p$ bands, elements such as Be with two outer electrons also become metallic. Deep-lying atomic levels are only slightly broadened and thus, to a large extent, they retain their atomic character

one extreme, this overlap may be limited to neighboring atoms; in other cases the wavefunctions may be spread over many atoms. In the former case, the degree of overlap, and thus the strength of the bonding, is dependent not only on the separation of neighboring atoms, but also on the bond angles. This is referred to as directional bonding or *covalent* bonding.

In its purest form, covalent bonding is realized between a few elements of equal "valence", i.e. elements with the same outer electronic configuration. However, an equal electronic configuration is neither a necessary nor a sufficient condition for covalent bonding. What is important is simply the relative extent of the wavefunctions in comparison to the interatomic separation. If the extent of the wavefunctions is large compared to the nearest-neighbor distance, then the exact position of the nearest neighbors plays an insignificant role in producing the greatest possible overlap with many atoms. In this case, the packing density is more important than the position of the next neighbors. Here one speaks of non-directional bonding. This regime in which the wavefunctions spread over a distance that is large in comparison to the atomic separation is characteristic of *metallic* bonding.

However, there is a further type of non-directional bonding with extremely small overlap of wavefunctions; this is the *ionic* bond. It occurs in cases where the transfer of an electron from one atom to another is sufficiently energetically favorable. A prerequisite for ionic bonding is thus a dissimilarity of the atoms involved.

In the following sections we will explore the various types of bonding in greater detail.

1.2 Covalent Bonding

We have characterized covalent bonding in solids as a bonding for which the interaction between nearest neighbor atoms is of prime importance. It is therefore possible to derive many of the essential properties of covalent solids using the quantum chemistry of molecules. For our discussion we shall refer to the simplest model for bonding, namely of a diatomic molecule with a single bonding electron.

The Hamiltonian for this molecule contains the kinetic energy of the electron and the Coulomb interaction between all partners (Fig. 1.2 a).

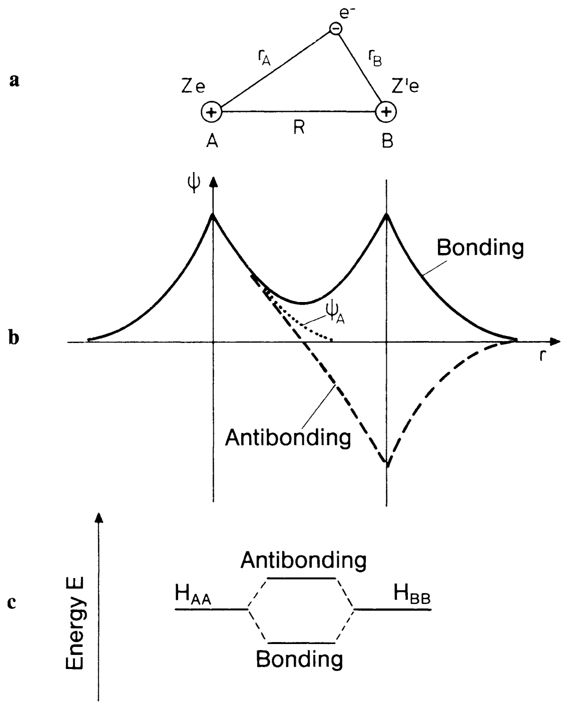

Fig. 1.2a–c. The simplest model of a covalent bond (the H_2^+ molecule). (**a**) Definition of the symbols in (1.1). (**b**) Bonding and antibonding combinations of atomic orbitals. The bonding combination leads to an accumulation of charge between the nuclei which in turn gives rise to a reduction in the Coulomb energy. (**c**) The splitting of the atomic energy level into the bonding and antibonding states. The greatest gain in energy is achieved when the bonding state is fully occupied – i.e., contains two electrons – and the antibonding state is empty (covalent bonding)

$$\mathscr{H} = -\frac{\hbar^2}{2m}\Delta - \frac{Ze^2}{4\pi\varepsilon_0 r_A} - \frac{Z'e^2}{4\pi\varepsilon_0 r_B} + \frac{ZZ'e^2}{4\pi\varepsilon_0 R} \ . \tag{1.1}$$

The appropriate molecular orbital ψ_{mo} for the electron would be the solution to the Schrödinger equation

$$\mathscr{H}\psi_{\mathrm{mo}} = E\psi_{\mathrm{mo}} \ . \tag{1.2}$$

However, even in this simple case, it is necessary to rely on approximate solutions. The expectation value of the ground-state energy may be calculated using such an approximate solution, according to

$$E' = \frac{\int \psi^* \mathscr{H} \psi d\boldsymbol{r}}{\int \psi^* \psi \, d\boldsymbol{r}} \ . \tag{1.3}$$

The approximate solution ψ may be set equal to a linear combination of states of the two separate atoms:

$$\psi = c_A \psi_A + c_B \psi_B \ . \tag{1.4}$$

Here the wavefunctions and their coefficients are real.

It is possible to show that any trial function such as ψ always leads to an energy E' that lies above the true value E (see Problem 1.8). The best values for the coefficients c_A and c_B are those which lead to a minimum value of E'.

With the abbreviations

$$S = \int \psi_A \psi_B \, d\boldsymbol{r} \quad \text{(overlap integral)} \ , \tag{1.5 a}$$

$$H_{AA} = \int \psi_A \mathscr{H} \psi_A \, d\boldsymbol{r} \ , \tag{1.5 b}$$

$$H_{AB} = \int \psi_A \mathscr{H} \psi_B \, d\boldsymbol{r} \ , \tag{1.5 c}$$

one obtains the following expression for E', which then has to be minimized

$$E' = \frac{c_A^2 H_{AA} + c_B^2 H_{BB} + 2 c_A c_B H_{AB}}{c_A^2 + c_B^2 + 2 c_A c_B S} \ . \tag{1.6}$$

For the minimum with respect to c_A and c_B we require

$$\frac{\partial E'}{\partial c_A} = \frac{\partial E'}{\partial c_B} = 0 \ , \tag{1.7}$$

which leads to the following secular equations

$$c_A (H_{AA} - E') + c_B (H_{AB} - E' S) = 0 \ , \tag{1.8 a}$$

$$c_A (H_{AB} - E' S) + c_B (H_{BB} - E') = 0 \ . \tag{1.8 b}$$

Their solution is given by the condition that the determinant vanishes, i.e.,

$$(H_{AA} - E')(H_{BB} - E') - (H_{AB} - E' S)^2 = 0 \ . \tag{1.9}$$

For simplicity, we consider a molecule with two identical nuclei (for example, H_2^+) for which we have $H_{AA} = H_{BB}$. With the single atomic eigenvalue $H_{AA} = H_{BB}$ of the individual free atoms, we then obtain two new molecular orbitals with the energies

$$E_\pm \lesssim E'_\pm = \frac{H_{AA} \pm H_{AB}}{1 \pm S} \ . \tag{1.10}$$

When the two nuclei are infinitely far apart we have $S = 0$ on account of (1.5a), whereas when the nuclear positions coincide, we have $S = 1$. From (1.10) it follows that the spatial overlap of the wavefunctions ψ_A and ψ_B leads to a splitting of the original energy level $H_{AA} = H_{BB}$ into a higher and a lower molecular energy level (Fig. 1.2c). The molecular orbital corresponding to the higher energy level is known as *antibonding*, and the other is *bonding*. In the molecule the electron occupies the lower-lying bonding orbital thereby giving rise to a reduction in the total energy. This reduction corresponds to the binding energy of the covalent bond.

From the foregoing discussion one sees that only partially occupied single-atomic orbitals, i.e., those containing less than two electrons, can participate in covalent bonding: Since the bonding molecular orbital can contain only two electrons (the Pauli principle allows two opposite spin states), any further electrons would have to occupy the higher-lying antibonding orbital, which would counteract the original gain in energy (cf. Problem 1.7).

For the diatomic molecules considered here the bonding molecular orbital consists of an additive combination of ψ_A and ψ_B, i.e. $\psi_{\mathrm{mo}} = \psi_A + \psi_B$ [in (1.4) we have $c_A = c_B$ for identical nuclei]. As shown in Fig. 1.2, this leads to an increase in the electronic charge density between the nuclei. The antibonding combination $\psi_{\mathrm{mo}} = \psi_A - \psi_B$, on the other hand, results in a decrease of this charge density.

One sees that covalent bonding is associated with a "piling-up" of charge between the atoms that form the molecule or solid concerned. It is the spatial overlap of the wavefunctions that is responsible for this bonding and which also determines the energy gain of the bonding orbitals of the molecule or solid, and thereby the binding energy. As shown in Fig. 1.3, for particular atomic orbitals (*s*, *p*, *d*, etc.) there are some orientations that favor the overlap and others that are unfavorable. This is the underlying reason for this strongly directional character of the covalent bonding, which is particularly evident in the covalently bound crystals of diamond (C), Si and Ge with their tetrahedral coordination (Fig. 1.4).

Let us take a closer look at this tetrahedral bonding for the example of diamond. From a consideration of its electronic configuration $1s^2$, $2s^2$, $2p^2$, one would expect a carbon atom to be able to participate in only two covalent bonds (corresponding to the two $2p$-orbitals each occupied by one electron). However, when these atoms form part of a crystal it is clear that a larger reduction in total energy is produced if four bonding orbitals can overlap. In a one-electron picture this may be understood in terms of the

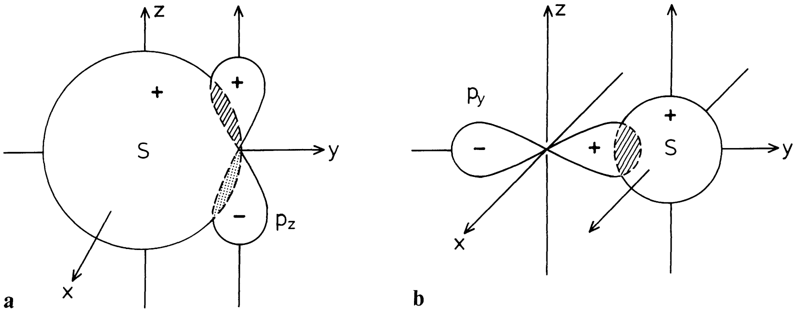

Fig. 1.3a,b. Pictorial representation of the spatial overlap between an *s*- and a *p*-wavefunction of hydrogen. The "size" of the wavefunction is illustrated by a surface of constant wavefunction amplitude. (**a**) A situation in which the overlap cancels due to sign reversal of the p_z-wavefunction. (**b**) Nonvanishing overlap between *s*- and p_x-wavefunctions

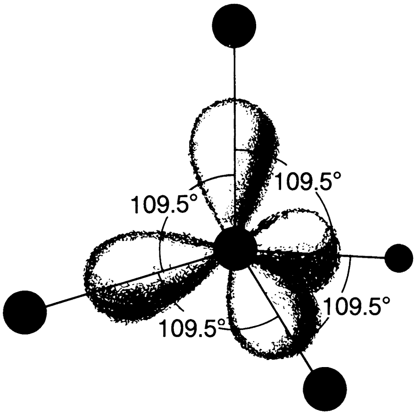

Fig. 1.4. The tetrahedral configuration of nearest neighbors in the lattice of C, Si, Ge and *α*-Sn. This structure is favored because its periodic repetition fills three-dimensional space, and because it enables the formation of sp^3 hybrid orbitals from the *s*, $p_x p_y$ and p_z states. The figure displays the orbitals of diamond (C). The orbitals of Si, Ge, and *α*-Sn possess additional nodes

following simplified description: One of the electrons from the 2*s*-orbital is excited into the empty 2*p*-orbital. Each of the 2*p*-orbitals and the single 2*s*-orbital now contains one electron and thus each of these can participate in a covalent bond. The overlap with the wavefunctions of the nearest neighbors is maximized if four new wavefunctions are formed by a linear combination of the original 2*s*, $2p_x$, $2p_y$, and $2p_z$-orbitals. These new molecular orbitals are known as sp^3 hybrids and their creation is called hybridization (Problem 1.9). The gain in energy that is produced by the overlap in the tetrahedral configuration is more than enough to compensate for the energy needed to promote the 2*s*-electron into the 2*p*-orbital.

If one now considers carbon atoms arranged in the diamond structure, in which each atom is surrounded by four other atoms positioned at the corners of a tetrahedron (Fig. 2.12), one finds that in the sp^3 hybridized state all the available electrons can be shared with the neighbors such that only the bonding orbitals are occupied. This leads to a fully occupied valence band that is separated from the next highest (antibonding) band by an energy gap. Energy can only be supplied in large quanta that are sufficient to promote an electron across this band gap. At low temperature such covalently bonded solids are therefore nonconducting. If the bandgap is not too large, however, electrons can be promoted by thermal excitation leading to a measurable conductivity. In this case one speaks of semiconductors. A more precise definition of these will be given in Chaps. 9 and 12.

Instead of the sp^3 hybrid orbital carbon can also form a planar hybrid orbital from one $2s$ and two $2p$ functions (Problem 1.10). These orbitals yield a planar 120° star called sp^2. An additional p_z orbital containing one electron lies perpendicular to the plane of the star. The overlap between p_z orbitals of neighboring C atoms leads to a further bonding, the so-called π bonding. This type of bonding is found within the layers of the graphite structure of carbon. The bonding between the covalently bound layers of graphite is of the van der Waals type (Sect. 1.6) and is thus relatively weak.

An interesting spatial structure involving sp^2 orbitals is that of the fullerenes, whose most prominent member is C_{60} (Fig. 1.5). Their structure includes pentagons. For topological reasons, 12 pentagons are necessary to produce a closed structure. In addition to the 12 pentagons, the C_{60} cluster also contains 20 hexagons. Even larger molecules can be produced by the inclusion of more hexagons. C_{60} clusters can also form the basis of three-dimensional crystal structures, for example when other atoms such as alkali or alkaline earth metals are included.

A complete saturation of the covalent bonding is possible for the group IV elements C, Si, Ge and α-Sn in the three-dimensional space-filling tetrahedral configuration. The group V elements P, As, Sb, demand a three-fold coordination for saturation; they form planar layer structures. Correspondingly, the group IV elements Te and Se occur in a chain-like structure with two-fold coordination.

Covalently bonded solids can, of course, also be produced from combinations of different elements. As an example, we consider boron nitride. The two elements involved have the electronic structure: $B(2s^2,2p^1)$;

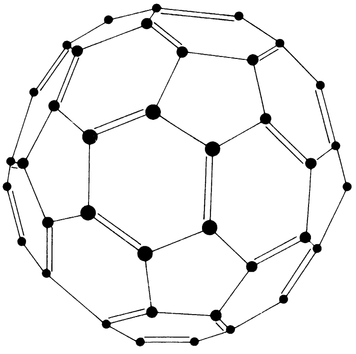

Fig. 1.5. The structure of C_{60}

$N(2s^2,2p^3)$. These elements can also bind in the diamond structure with tetrahedral coordination. Each boron atom is thereby surrounded by four nitrogen atoms and vice versa. The shared bonding electrons are comprised of five electrons from the nitrogen atom and three from boron. The total number of electrons per atom is thus the same as in the case of the carbon diamond structure. However, because two different elements are involved, the bonding has an ionic character. This will be discussed in the next section.

Typical examples of binding energy for purely covalently bonded crystals are:

C (diamond):	7.30 eV per atom (712 kJ/mol);
Si:	4.64 eV per atom (448 kJ/mol);
Ge:	3.87 eV per atom (374 kJ/mol).

1.3 Ionic Bonding

To understand ionic bonding one needs to consider the ionization energies and electron affinities of atoms. The *ionization energy* I is defined as the energy that must be supplied in order to remove an electron from a neutral atom. The *electron affinity* A is the energy that is gained when an additional electron is added to a neutral atom. Ionic bonding is produced whenever an element with a relatively low ionization energy is combined with an element with a high electron affinity. As an example we consider the combination of sodium and chlorine. The ionization energy of sodium is 5.14 eV, and the electron affinity of chlorine 3.71 eV. Thus in order to transfer one electron from a sodium atom to a chlorine atom requires an energy expenditure of 1.43 eV. The electrostatic attraction between the two ions leads to an energy gain that increases as they approach closer to one another, with a minimum separation that is determined by the sum of their two ionic radii. This electrostatic attraction contributes an energy gain of 4.51 eV thus giving an overall gain in energy of 3.08 eV. It is therefore possible for sodium and chlorine to form a diatomic molecule with a strongly ionic character. Three-dimensional crystals can also be produced in this way. In the structure so formed, each chlorine atom is surrounded by sodium neighbors, and vice versa. The exact structure is determined by the optimal use of space for the given ionic radii, and by the condition that the Coulomb attraction between oppositely charged ions should be greater than the repulsion between ions of the same sign. Figure 1.6 shows two structures that are typical for two-ion crystals; the sodium-chloride and the cesium-chloride structures.

The ionic radii are the essential factor in determining the minimum separation because, if the ions were to approach still closer, a strong overlap between the ionic electron clouds would occur. For fully occupied electron shells such as these (Sect. 1.2), the Pauli principle would then require that

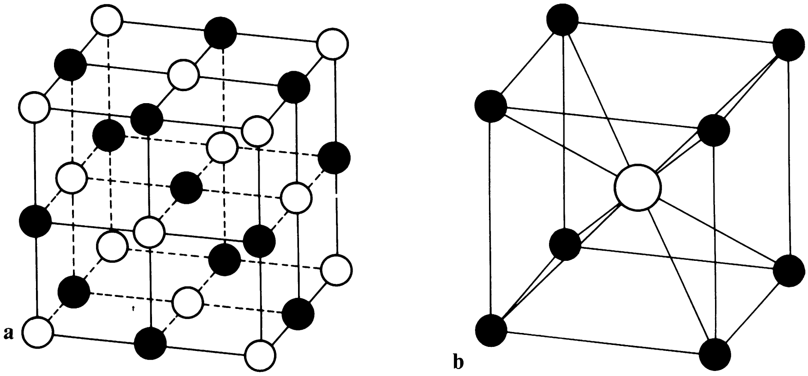

Fig. 1.6. The two structures typical for ionic bonding in solids: (**a**) NaCl structure; (**b**) CsCl structure

higher lying antibonding orbitals should become occupied. This should lead to a steep increase in the energy and therefore a strong repulsion.

Whereas this repulsive contribution to the total energy, like the covalent bond, can only be derived from a quantum mechanical calculation, the attractive Coulomb contribution to the ionic bond can be described simply as a sum over the Coulomb potentials ion sites. For the potential energy between two singly charged ions i and j at a separation r_{ij} one writes

$$\varphi_{ij} = \pm \frac{e^2}{4\pi\varepsilon_0 r_{ij}} + \frac{B}{r_{ij}^n} ; \tag{1.11}$$

the second term describes the repulsion between the two electron clouds. It is an heuristic term containing two free parameters n and B. It should, of course, be possible to determine these parameters from an exact quantum mechanical treatment of the problem. However, a commonly used approach is to derive the values of these parameters from a fit to measured experimental quantities (ionic separation, compressibility, etc.); this yields values of n mainly in the range 6 to 10.

The form of a typical potential energy curve is depicted in Fig. 1.7. The total potential energy due to all other ions j at the site of ion i is given by the summation

$$\varphi_i = \sum_{i \neq j} \varphi_{ij} . \tag{1.12}$$

If r is the separation of nearest neighbors one can write

$$r_{ij} = r p_{ij} , \tag{1.13}$$

where the p_{ij} depend on the particular crystal structure. If the crystal contains N ion pairs, then its total potential energy is given by

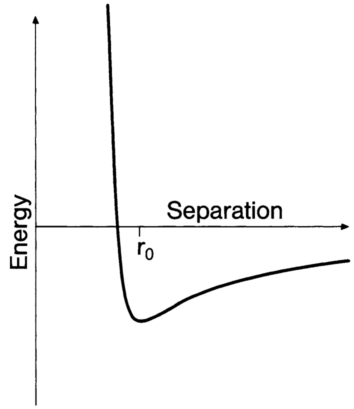

Fig. 1.7. Potential energy as a function of the separation of two ions

$$\Phi = N\varphi_i = N\left(-\frac{e^2}{4\pi\varepsilon_0 r}\sum_{i\neq j}\frac{\pm 1}{p_{ij}} + \frac{B}{r^n}\sum_{i\neq j}\frac{1}{p_{ij}^n}\right). \tag{1.14}$$

For each possible structure one has the characteristic quantity

$$A = \sum_{i\neq j}\frac{\pm 1}{p_{ij}} \tag{1.15}$$

which is known as the *Madelung constant*. For the sodium-chloride structure $A = 1.748$ and for the cesium-chloride structure $A = 1.763$.

Some typical binding energies are

NaCl:	7.95 eV per ion pair (764 kJ/mol);
NaI:	7.10 eV per ion pair (683 kJ/mol);
KrBr:	6.92 eV per ion pair (663 kJ/mol).

In ionic crystals, it is not possible for the electrons to move about freely between ions unless a large amount of energy (~10 eV) is supplied. Solids with ionic bonding are therefore nonconducting. However, the presence of

Table 1.2. The electronegativity of selected elements [1.1]

H 2.1						
Li 1.0	Be 1.5	B 2.0	C 2.5	N 3.0	O 3.5	F 4.0
Na 0.9	Mg 1.2	Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0
K 0.8	Ca 1.0	Sc 1.3	Ge 1.8	As 2.0	Se 2.4	Br 2.8
Rb 0.8	Sr 1.0	Y 1.3	Sn 1.8	Sb 1.9	Te 2.1	I 2.5

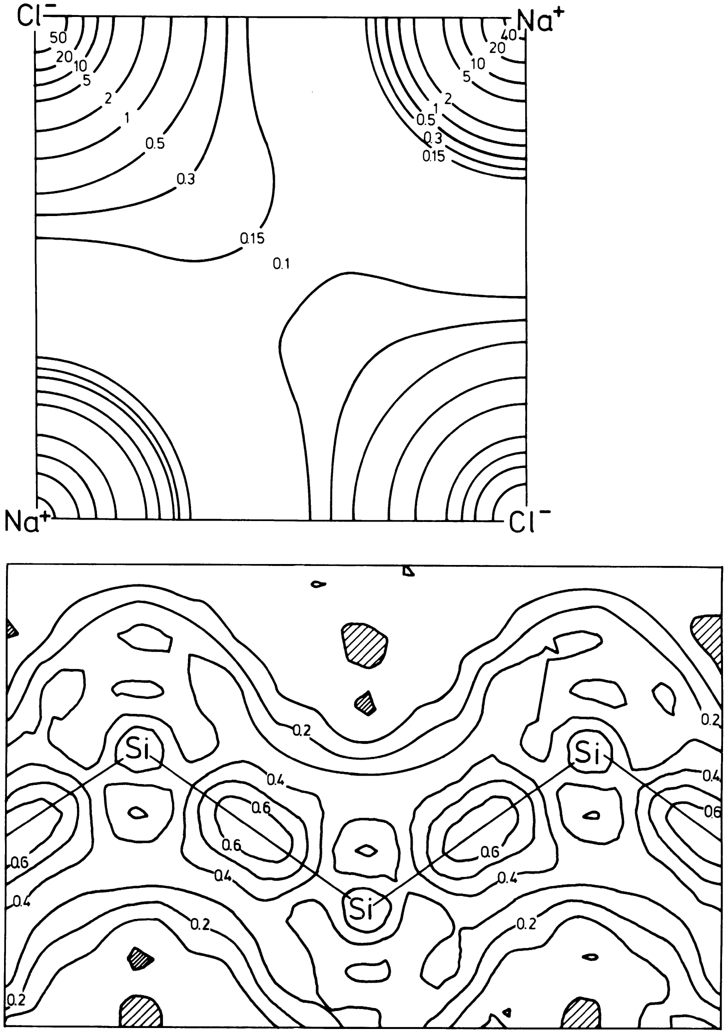

Fig. 1.8. Density of valence electrons in a typical ionic crystal (NaCl) and in a typical covalently bound crystal (Si) [1.2, 3]. One clearly sees the concentration of charge along the bond between Si atoms, whereas in the ionic bonding, the electrons are almost spherically distributed around the ions

defects means that at high temperatures the ions themselves can move around, giving rise to ionic conduction.

Ionic bonding and covalent bonding are two limiting cases, of which only the latter can exist in solids composed of a single type of atom. In the majority of cases the bonding is of an intermediate nature representing a mixture of the two extremes. A qualitative measure of the ionicity of a bond is made possible by the electronegativity scale. This scale was first developed by Pauling as a result of observations of bond energies. Subsequently Millikan made use of the physical quantities ionization energy, I, and electron affinity, A, to derive the following definition of the electronegativity of an element:

$$X = 0.184\,(I + A)\ . \tag{1.16}$$

If the ionization energy and electron affinity are expressed in electron volts one obtains the Pauling electronegativity scale of Table 1.2. The higher the ionization energy and electron affinity of an atom, the greater is its tendency to draw the electrons of a bond towards itself. In a bond between two atoms it is therefore always the atom with the higher electronegativity that is the anion. The difference in the electronegativity of the two atoms is a measure of the ionicity of the bond.

The difference between ionic bonding and covalent bonding, in particular the different electron density distributions, is illustrated in Fig. 1.8. This shows contours of constant electron density which may be deduced for example from X-ray diffraction studies. For ionic bonding (NaCl) the electrons are concentrated around the atoms, whereas for covalent bonding (Si) there is an accumulation of electrons between the atoms.

1.4 Metallic Bonding

It is possible to regard metallic bonding as an extreme case of bonding in which the electrons are accumulated between the ion cores. However, in contrast to covalent bonding, the electrons now have wavefunctions that are very extended in comparison to the separation between atoms. As an example, Fig. 1.9 shows the radial part of the $3d$ and $4s$ wavefunction of nickel in the metallic state. The $4s$ wavefunction still has significant amplitude even at a distance half way to the third nearest neighbors; thus many neighbors are involved in the bonding. This leads to a strong screening of the positive ion core, and to a bonding that has certain similarities to covalent bonding. However, due to the strong "smearing out" of the valence electrons over the whole crystal, the bonding is not directional as in the case of covalent crystals. The crystal structure of metals is thus determined, to a large extent, by the desire for optimum filling of space (Sect. 2.5).

Unlike the *s*-electrons, the *d*-electrons of transition metals are localized, and the overlap is correspondingly smaller. The *d*-electrons form a kind of covalent framework in transition metals and produce the main contribution to the binding energy.

The valence band of metals, comprising the outer *s*-, *p*- and sometimes *d*-electrons, is not fully occupied (Table 1.1). As a consequence of the quasi-continuous distribution of states on the energy scale for a large number of

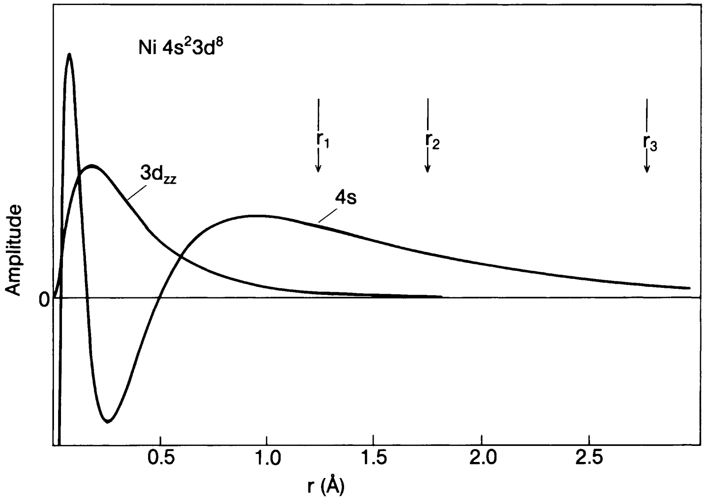

Fig. 1.9. The amplitude of the $3d_{zz}$-wavefunction and the $4s$-wavefunction of Ni [1.4]. The half-distances to the first, second and third nearest neighbors (r_1, r_2 and r_3) are shown for comparison

atoms, one can supply energy to the electrons in infinitesimally small portions; in particular, they can be accelerated by an externally applied electric field. A particular feature of metals is thus their high electrical conductivity, which is related to their similarly high thermal conductivity. In this sense, the metallic bond is a feature that is peculiar to solids, i.e., to aggregates of many atoms.

A glance at Table 1.1 indicates that the partially filled valence band of metals can arise in various ways. The alkali metals (Li, Na, K, Rb, Cs) clearly have the necessary prerequisite since the outer atomic *s*-state is only singly occupied. For the alkaline earth metals (Be, Mg, Ca, Sr, Ba) one might initially expect a full valence band formed from the doubly occupied atomic *s*-states. However, because of the overlap in energy with the bands stemming from the (empty) atomic *p*-states of the same shell, the net result is a partially occupied joint *sp*-band. The transition metals represent a special case. Here the *s*- and *p*-states again form a broad common band. As mentioned previously, the *d*-electrons have a relatively small spatial extent (Fig. 1.9) and, due to the correspondingly small overlap with the neighboring atoms, the *d*-band of the transition metals has a smaller energy width than the *sp*-band.

The large spreading of the wavefunction of valence electrons in metals makes it particularly difficult to theoretically predict their binding energy. On the other hand, the valence electrons are free to move between the atoms. This simplifies the description of the electrical conductivity and the specific heat of the electrons, as will become clear in Chap. 6.

1.5 The Hydrogen Bond

One speaks of a hydrogen bond when a hydrogen atom is bound to two other atoms. At first sight, it is surprising that such a bond can exist since hydrogen has only one electron. However, one can imagine the hydrogen bond as follows: when hydrogen takes part in a covalent bond with a strongly electronegative atom, for example, oxygen, its single electron is almost completely transferred to the partner atom. The proton which remains can then exert an attractive force on a second negatively charged atom. Because of the extended electron cloud of the electronegative atom and the extremely small size of the proton with its strongly reduced electron screening, it is not possible for a third atom to be bound. The hydrogen atom is thus always doubly coordinated in a hydrogen bond. Such bonds are most common between strongly electronegative atoms, but are not limited to this case alone. They can be of a symmetric A–H–A type or of an asymmetric A–H…B type. A criterion for the existence of a hydrogen bond is that the observed separation of the atoms A and B is smaller than it would be if only van der Waals bonding (Sect. 1.6) were present. A further indication of the presence of hydrogen bonds may be obtained from infrared spectroscopy, in which the band corresponding to hydrogen vibrations shows a strong shift, and is often broadened, too. Generally, speaking, the phenomena associated with hydrogen bonding are quite diverse, and this type of bonding is harder to characterize than most other types. The binding energies of hydrogen bonds are of the order of 0.1 eV per bond.

It is hydrogen bonds that are responsible for linking the two chains of the double helix in the DNA molecule and, as such, these bonds play a crucial role in the mechanism of genetic reproduction. The best-known example from the realm of inorganic chemistry is water, in particular when it is in the form of ice. Each oxygen atom in ice is surrounded by four further oxygen atoms in a tetrahedral configuration and the bonding is provided by hydrogen atoms. Hydrogen bonds are also present in the liquid form of water, which leads, for example, to the anomaly in the expansion coefficient: water has its highest density at 4 °C. The reason for this is that the liquid form of water also contains complexes of H_2O molecules that are held together by hydrogen bonds. In comparison to H_2O molecules without hydrogen bonds, the former occupy a larger volume. As the temperature increases the hydrogen-bonded aggregates melt, leading to an increase in the density. Above 4°C one finds the usual thermal expansion, i.e., the density decreases with further increasing temperature.

1.6 The van der Waals Bond

This is an additional type of bond that, in principle, is always present. However, the van der Waals bond is only significant in cases where other types of bonding are not possible, for example, between atoms with closed electron shells, or between saturated molecules. The physical source of this bonding is charge fluctuations in the atoms due to zero-point motion. The dipole moments which thereby arise cause an additional attractive force. Van der Waals forces are responsible for the bonding in molcular crystals. The bonding energy is dependent on the polarizability of the atoms involved and is mostly of the order of 0.1 eV. Typical atomic bonding radii for van der Waals bonding are considerably larger than for chemical bonding. The attractive part of the potential between atoms that interact only via van der Waals forces varies as r^{-6}, where r is the separation of the atoms (or molecules). This can be readily understood as a consequence of the dipole interaction. A dipole moment p_1 resulting from a momentary charge fluctuation gives rise to an electric field at distance r of strength $\mathscr{E} \sim p_1/r^3$. A second atom of polarizability α situated at distance r is polarized by this electric field and acquires an induced dipole moment of $p_2 \sim \alpha p_1/r^3$. Since the potential of this dipole in the field is proportional to $\mathscr{E}$ and to p_2, it follows that the attractive part of the van der Waals interaction varies as r^{-6} (Problem 1.11).

Problems

1.1 a) Calculate the Madelung constant A for a linear ionic chain.

b) Make approximate numerical calculations of the Madelung constant ($A = 1.7476$) for the NaCl lattice. Use two different approaches: First, a cubic geometry where $2ma$ is the length of a side of the cube and a the separation of nearest neighbors, and, second, a spherical geometry where ma is the radius of the sphere. In both cases the reference ion is located at the center. Carry out the calculation for m-values of $m = 97$, 98, and 99 and compare the results. What is the cause of the discrepancy?

1.2 Determine the isothermal bulk modulus

$$\kappa = V\left(\frac{\partial p}{\partial V}\right)_T$$

and the lattice energy per ion pair for NaCl using the expression for the lattice energy of N ion pairs:

$$U(r) = N\left(-\frac{e^2}{4\pi\varepsilon_0 r}A + \frac{B}{r^n}\sum_{i\neq j}\frac{1}{p_{ij}^n}\right) .$$

Using the value $n = 9$, calculate B from the condition that $U(\boldsymbol{r})$ is a minimum at the equilibrium separation.

1.3 It is well known that common salt (NaCl) is easily dissolved in water. In the solution Na and Cl atoms are present as positive and negative ("solvated") ions. Show that, due to the high dielectric constant of water and the resulting screening of the Coulomb potential, the binding energy of a NaCl crystal in water is smaller than the mean thermal energy of the free ions. Calculate the equilibrium separation of the ions of a hypothetical NaCl crystal in water and show that this separation is larger than the van der Waals radius of a water molecule, thereby justifying the approximate approach used here to discuss the solubility of NaCl.

1.4 Discuss the ionicity of alkali halides with the help of Table 1.2.

1.5 Take the CsCl structure and assume that the cation radius becomes smaller while the anion radius remains constant. What happens to the binding energy? Show that for small cations the NaCl lattice becomes the preferred structure. For an even smaller cation radius the ZnS lattice has the largest binding energy (Madelung constant $A = 1.638$). Give examples.

1.6 Calculate approximately the zero-point entropy of ice. In the ice structure the oxygen atoms form a wurtzite lattice which is stabilized by hydrogen bonds between the nearest neighbor oxygen atoms. The zero-point entropy results from the possible ways of distributing the two hydrogen atoms per oxygen atom over the four bonds to the nearest neighbors.

1.7 Discuss the electron configuration of the oxygen molecule. Why is the bond strength equivalent to a chemical double bond? Why is O_2 paramagnetic? Give an argument to explain why O_2^+ is a stable ion.

1.8 Prove that the estimate of the ground-state energy obtained with the help of an approximate wavefunction using the Ritz procedure,

$$E = \frac{(\psi, \mathscr{H}\psi)}{(\psi, \psi)} ;$$

is always greater than or equal to the exact eigenvalue E_0. To do this, expand the approximate function in terms of the exact eigenfunctions ψ_i (exact eigenvalue E_i).

1.9 The carbon atom in its tetrahedral bonding configuration in diamond can be approximately represented by four $2sp^3$ wavefunctions, which are linear superpositions of the four hydrogenic $2s$, $2p_x$, $2p_y$, $2p_z$ atomic wavefunctions ϕ_j:

$$\psi_i = \sum_j a_{ij}\phi_j , \quad \text{with} \quad i,j = 1,2,3,4$$

and where the possible functions ϕ_j appear in spherical coordinates as follows:

$$\phi_1 = \phi\,(2s) = c\,\mathrm{e}^{-\varrho}\,(1-\varrho)\ ,$$
$$\phi_2 = \phi\,(2p_z) = c\,\mathrm{e}^{-\varrho}\,\varrho\cos\theta\ ,$$
$$\phi_3 = \phi\,(2p_x) = c\,\mathrm{e}^{-\varrho}\varrho\sin\theta\cos\varphi\ ,$$
$$\phi_4 = \phi\,(2p_y) = c\,\mathrm{e}^{-\varrho}\,\varrho\sin\theta\sin\varphi\ , \quad \text{and}$$
$$\varrho = \frac{Zr}{2a_0} \quad (a_0\ \text{Bohr radius, Z = nuclear charge, here that of carbon}).$$

One demands of the ψ_i that, like the ϕ_j, they are orthonormal, i.e.

$$\int \psi_i\,\psi_k^*\,d\mathbf{r} = \delta_{ik}\ .$$

a) Plot the contours of ϕ (ϱ = const, θ, φ) for the $2s$ and one of the $2p$ states on a polar diagram.

b) Prove that the orthonormality requirement for the $\psi_i(2sp^3)$ wavefunctions leads to the condition

$$\sum_j a_{ij}\,a_{kj} = \delta_{ik} \quad \text{with} \quad a_{ij} = a_{ji}^*\ .$$

c) Determine four possible ψ_i functions which fulfill the orthonormality requirement with $a_{ij} = \frac{1}{2}$ or $a_{ij} = -\frac{1}{2}$.

d) Show that the maxima of $|\psi_i|^2$ are located in tetrahedral directions and draw these by means of vectors pointing to the corners of a cube whose edges are parallel to the x, y and z axes.

e) Show that the electron density $\sum_{i=1}^4 |\psi_i|^2$ has spherical symmetry.

f) Discuss possible reasons why the real valence electron density in a diamond crystal is nevertheless not spherical around a carbon atom but is concentrated in tetrahedral bonding directions.

1.10 a) In analogy to the sp^3 hybridization of carbon in the diamond lattice, discuss the possibility of the carbon atom forming sp^2 hybrid orbitals with three planar bonding directions. Plot a qualitative picture of the three bonding sp^2 orbitals and the remaining unpaired p_z orbital and give their electron occupation.

b) Assuming sp^2 hybridization for the carbon atoms explain the chemical bonding in the benzene molecule C_6H_6. What is the origin of the π bonding system parallel to the hexagonal ring skeleton of the six carbon atoms.

c) Assuming sp^2 hybridization explain the highly anisotropic properties of the planar hexagonal graphite lattice of carbon (quasi-metallic properties parallel to the carbon planes). How are these anisotropic properties exploited in every-day life?

1.11 As a simple quantum mechanical model for the van der Waals interaction consider two identical harmonic oscillators (oscillating dipoles) at a separation R. Each dipole consists of a pair of opposite charges whose separations are x_1 and x_2, respectively, for the two dipoles. A restoring force f acts between each pair of charges.

a) Write down the Hamiltonian $\mathscr{H}_0$ for the two oscillators without taking into account electrostatic interaction between the charges.

b) Determine the interaction energy $\mathscr{H}_1$ of the four charges.

c) Assuming $|x_1| \leq R$, $|x_2| \leq R$ approximate $\mathscr{H}_1$ as follows

$$\mathscr{H}_1 \approx -\frac{2\,\mathrm{e}^2 x_1 x_2}{R^3} \; .$$

d) Show that transformation to normal coordinates

$$x_\mathrm{s} = \frac{1}{\sqrt{2}}\,(x_1 + x_2) \; ,$$

$$x_\mathrm{a} = \frac{1}{\sqrt{2}}\,(x_1 - x_2)$$

decouples the total energy $\mathscr{H} = \mathscr{H}_0 + \mathscr{H}_1$ into a symmetric and an antisymmetric contribution.

e) Calculate the frequencies ω_s and ω_a of the symmetric and antisymmetric normal vibration modes. Evaluate the frequencies ω_s and ω_a as Taylor series in $2e^2/(fR^3)$ and truncate the expansions after second order terms.

f) The energy of the complete system of two interacting oscillators can be expressed as $U = -\frac{1}{2}\hbar\,(\omega_\mathrm{s} + \omega_\mathrm{a})$. Derive an expression for the energy of the isolated oscillators and show that this is decreased by an amount c/R^6 when mutual interaction (bonding) occurs.

1.12 Calculate how the van der Waals bonding of a molecule depends on its distance, d, from a solid surface. For simplicity, choose a simple cubic lattice. Show that the result does not depend on the structure of the crystal.