1

Chemical Bonding in Solids

In this chapter, we discuss different mechanisms that can lead to bonding between atoms so that they form solids. We will encounter different cases such as ionic, covalent, or metallic bonding. It has to be kept in mind that these are just idealized limiting cases. Often mixed bonding types are found, for example, a combination of metallic and covalent bonding in the transition metals.

As in conventional chemistry, only a restricted number of all the electrons participate in the bonding. These so-called valence electrons are the electrons in the outermost shell(s) of an atom. The electrons in the inner shells, or core electrons, are bound so tightly to the nucleus that they do not feel the presence of other atoms in their neighborhood.

1.1

Attractive and Repulsive Forces

Two different forces must be present to establish bonding in a solid or in a molecule. An attractive force is necessary for any bonding. Different types of attractive forces are discussed below. A repulsive force, on the other hand, is required in order to keep the atoms from getting too close to each other. An expression for an interatomic potential can be written as

$$\phi(r) = \frac{A}{r^n} - \frac{B}{r^m}, \tag{1.1}$$

where $n > m$, that is, the repulsive part has to prevail for short distances (sometimes this is achieved by assuming an exponential repulsion potential). Such a potential and the resulting force are shown in Figure 1.1. The reason for the strong repulsion at short distances is the Pauli exclusion principle. For a strong overlap of the electron clouds of two atoms, the wave functions have to change in order to become orthogonal to each other, because the Pauli principle forbids having more than two electrons in the same quantum state. The orthogonalization costs much energy, hence the strong repulsion.

Solid State Physics: An Introduction. Philip Hofmann

ISBN: 978-3-527-40861-0

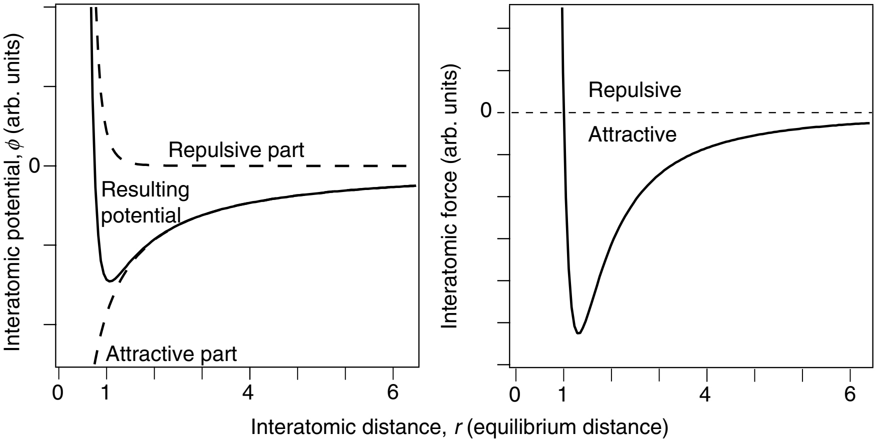

Figure 1.1 (a) Typical interatomic potential for bonding in solids according to (1.1) with $n = 6$ and $m = 1$. (b) Resulting force, that is, $-\text{grad}\phi(\mathbf{r})$.

1.2
Ionic Bonding

Ionic bonding involves the transfer of electrons from an electropositive atom to an electronegative atom. The bonding force is the Coulomb attraction between the two resulting ions. Ionizing both atoms usually costs some energy. In the case of NaCl, the ionization energy of Na is 5.1 eV but the electron affinity of Cl is only 3.6 eV. The net energy cost for creating a pair of ions is thus $5.1 - 3.6 = 1.5$ eV. The energy gain is given by the Coulomb potential. For just one Na and one Cl ion separated by a distance $a = 0.28$ nm, this is $-e^2/4\pi\varepsilon_0 a$, which amounts to 5.1 eV. Potential energies for more complicated structures are discussed below. It is important to distinguish between the different energy contributions involved: The *ionization energy* is the energy needed to turn atoms into ions, the *lattice energy* is the electrostatic energy gain by assembling a lattice, and the *cohesive energy* is the lattice energy minus the ionization energy, that is, it represents the total energy balance to form the ionic solid.

The fact that the total potential energy curve in Figure 1.1 contains a repulsive part in addition to the Coulomb potential means that the actual potential minimum for a given interatomic distance a is a bit shallower than expected from the pure Coulomb potential (10% or so). Therefore, the lattice energy can be calculated rather accurately using classical physics if the interatomic distance a is known. Predicting this distance, however, requires the inclusion of quantum effects. In any event, ionic bonding is very strong. The cohesive energy per atom is in the order of several electron volts.

1.3
Covalent Bonding

Covalent bonding is based on the true sharing of electrons between different atoms. The simplest case is that of the hydrogen molecule that we will discuss quantitatively below. In solids, covalent bonding is often found for elements with a roughly half-filled outer shell. A prominent example is carbon that forms solids as diamond or graphite as well as complex molecules such as Buckminster Fullerene C_{60} or carbon nanotubes. The covalent bonds in diamond are constructed from a linear combination of the 2s orbital and three 2p orbitals. This results in four so-called sp^3 orbitals that stick out in a tetrahedral configuration from the carbon atoms. In graphite, the 2s orbital is combined with only two 2p orbitals, giving three sp^2 orbitals, all in one plane and separated by an angle of 120°, and one p orbital oriented perpendicular to this plane. This linear combination of orbitals already reveals an important characteristic for the covalent bonding: it is highly directional. In addition to this, it is also very stable and the bonding energies are several electron volts.

A very instructive example for covalent bonding is the hydrogen molecule H_2 for which we will sketch a solution here. We go into some detail, as much of this will be useful in later chapters. As a starting point, take two hydrogen atoms with their nuclei at $\mathbf{R}_A$ and $\mathbf{R}_B$ and we call $|\mathbf{R}_B - \mathbf{R}_A| = R$. We do, of course, know the solution of the Schrödinger equation for each of the atoms. Let these ground-state wave functions be Ψ_A and Ψ_B, respectively. The Hamilton operator for the hydrogen molecule can be written as

$$\begin{aligned} H = &-\frac{\hbar^2\nabla_1^2}{2m_e} - \frac{\hbar^2\nabla_2^2}{2m_e} + \frac{e^2}{4\pi\varepsilon_0}\left\{\frac{1}{R} + \frac{1}{|\mathbf{r}_1-\mathbf{r}_2|}\right. \\ &\left.-\frac{1}{|\mathbf{R}_A-\mathbf{r}_1|} - \frac{1}{|\mathbf{R}_B-\mathbf{r}_2|} - \frac{1}{|\mathbf{R}_A-\mathbf{r}_2|} - \frac{1}{|\mathbf{R}_B-\mathbf{r}_1|}\right\}, \end{aligned} \tag{1.2}$$

where $\mathbf{r}_1$ and $\mathbf{r}_2$ are the coordinates of the electrons belonging to the A and the B nucleus, respectively. The first two terms refer to the kinetic energy of the two electrons. The operators ∇_1^2 and ∇_2^2 act only on the coordinates $\mathbf{r}_1$ and $\mathbf{r}_2$, respectively. The electrostatic term contains the repulsion between the two nuclei and the repulsion between the two electrons as well as the attraction of each electron to each nucleus.

The solution of this problem is not simple. It would be greatly simplified by removing the electrostatic interaction between the two electrons because then the Hamiltonian could be written as the sum of two parts, one for each electron. This could then be solved by a product of the two wave functions that are solutions to the two individual Hamiltonians, that is, the two-particle wave function would look like $\Psi(\mathbf{r}_1, \mathbf{r}_2) = \Psi_A(\mathbf{r}_1)\Psi_B(\mathbf{r}_2)$. Actually, this is not quite right because such a wave function is not in accordance with the Pauli principle. Since the electrons are fermions, the total wave function must be antisymmetric with respect to particle exchange and the simple product wave function does not fulfill this requirement.

The total wave function consists of a spatial part and a spin part and therefore there are two possibilities for forming an antisymmetric wave function. We can either choose a symmetric spatial part and an antisymmetric spin part or vice versa. This is achieved by constructing the spacial wave function of the form

$$\Psi_{\uparrow\downarrow}(\mathbf{r}_1,\mathbf{r}_2) \propto \Psi_{\mathrm{A}}(\mathbf{r}_1)\Psi_{\mathrm{B}}(\mathbf{r}_2) + \Psi_{\mathrm{A}}(\mathbf{r}_2)\Psi_{\mathrm{B}}(\mathbf{r}_1), \tag{1.3}$$

$$\Psi_{\uparrow\uparrow}(\mathbf{r}_1,\mathbf{r}_2) \propto \Psi_{\mathrm{A}}(\mathbf{r}_1)\Psi_{\mathrm{B}}(\mathbf{r}_2) - \Psi_{\mathrm{A}}(\mathbf{r}_2)\Psi_{\mathrm{B}}(\mathbf{r}_1). \tag{1.4}$$

The plus sign in (1.3) returns a symmetric spatial wave function that we can take for an antisymmetric spin wave function with the total spin equal to zero (the so-called singlet state); the minus in (1.4) results in an antisymmetric spatial wave function for a symmetric spin wave function with the total spin equal to 1 (the so-called triplet state).

The antisymmetric wave function (1.4) vanishes if $\mathbf{r}_1 = \mathbf{r}_2$, that is, the two electrons cannot be at the same place simultaneously. This leads to a depletion of the electron density between the nuclei and hence to an antibonding state. For the symmetric case, on the other hand, the electrons have opposite spins and can be at the same place, which leads to a charge accumulation between the nuclei and hence to a bonding state (see Figure 1.2).

An approximate way to calculate the eigenvalues of (1.2) was suggested by W. Heitler and F. London in 1927. The idea is to use the known single-particle 1*s* wave functions for atomic hydrogen for Ψ_{A} and Ψ_{B} to form a two-electron wave function

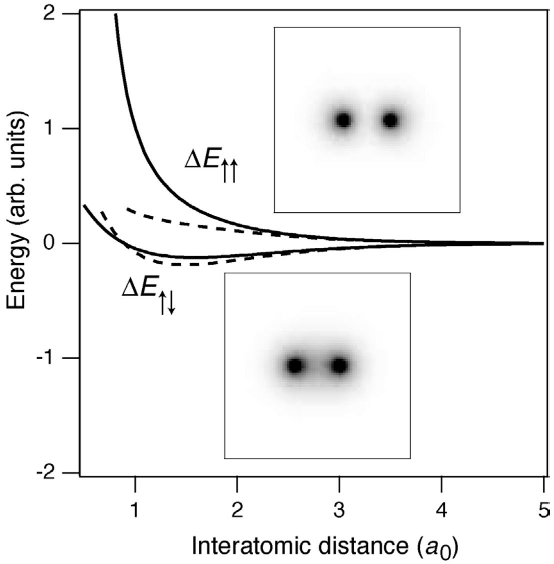

Figure 1.2 The energy changes $\Delta E_{\uparrow\uparrow}$ and $\Delta E_{\uparrow\downarrow}$ for the formation of the hydrogen molecule. The dashed lines represent the approximation for long distances. The two insets show gray scale images of the corresponding electron probability density.

Ψ ($\mathbf{r}_1$, $\mathbf{r}_2$), which is given by either (1.3) or (1.4). An upper limit for the ground-state energy eigenvalues can then be calculated by

$$E = \frac{\int \Psi(\mathbf{r}_1, \mathbf{r}_2) H \Psi(\mathbf{r}_1, \mathbf{r}_2) \mathrm{d}\mathbf{r}_1 \mathrm{d}\mathbf{r}_2}{\int \Psi(\mathbf{r}_1, \mathbf{r}_2) \Psi(\mathbf{r}_1, \mathbf{r}_2) \mathrm{d}\mathbf{r}_1 \mathrm{d}\mathbf{r}_2}. \tag{1.5}$$

The calculation is quite lengthy and shall not be given here. The resulting ground-state energies for the singlet and triplet states can be written as

$$E_{\text{singlet}} = 2E_0 + \Delta E_{\uparrow\downarrow}, \tag{1.6}$$

$$E_{\text{triplet}} = 2E_0 + \Delta E_{\uparrow\uparrow}. \tag{1.7}$$

E_0 is the ground-state energy for one hydrogen atom that appears here twice because we start with two atoms. The energies $\Delta E_{\uparrow\uparrow}$ and $\Delta E_{\uparrow\downarrow}$ are also shown in Figure 1.2. $\Delta E_{\uparrow\uparrow}$ is always larger than zero and does not lead to any chemical bonding. $\Delta E_{\uparrow\downarrow}$, however, shows a minimum below zero at approximately 1.5 times the Bohr radius. This is the binding state.

For long distances between the nuclei, (1.6) and (1.7) can further be simplified to give

$$E = 2E_0 + C \pm X, \tag{1.8}$$

that is, the energy change upon bonding has two parts, one that does depend on the relative spin orientations of the electrons ($\pm X$) and one that does not (C). The energy difference between the two states is then given by $2X$, where X is called the exchange energy. In the case of the hydrogen molecule, the exchange energy is always negative.

We will encounter similar concepts in the chapter about magnetism where the underlying principle for magnetic ordering is very similar to what we have here. The total energy of a system of electrons depends on their relative spin directions through the exchange energy, and therefore a particular ordered spin configuration is favored. For two electrons, the "magnetic" character is purely given by the sign of X. For a negative X, the coupling with two opposite spins is favorable (the antiferromagnetic case) whereas a positive X would lead to a situation where two parallel spins give the lowest energy (the ferromagnetic case).

1.4
Metallic Bonding

In metals, the outer valence electrons are removed from the ion cores, but in contrast to ionic solids, there are no electronegative ions to bind them. Therefore, they are free to migrate between the remaining ion cores. These delocalized valence electrons are involved in the conduction of electricity and are therefore often called conduction electrons. One can expect metals to form from elements for which the energy cost of removing outer electrons is not too big. Nevertheless, this removal always costs some energy that has to be more than compensated by the bonding. Explaining the energy gain from the bonding in an intuitive picture is difficult but we can at least try to make it plausible. The ultimate reason must be some sort of energy lowering.

One energy contribution that is lowered is the kinetic energy of the conduction electrons. Consider the kinetic energy contribution in a Hamiltonian, $T = -\hbar^2\nabla^2/2m$. A matrix element $\langle\Psi|T|\Psi\rangle$ measures the kinetic energy of a particle. $T\Psi$ is proportional to the second spatial derivative of the wave function, that is, the curvature. For an electron that is localized to an atom, the curvature of its wave function is much higher than that for a nearly free electron in a metal and this is where the energy gain comes from.

The other contribution to the electron energy is the potential energy. One should think that the average electrostatic potential of any single electron in a solid is almost zero because there are (almost) as many other electrons as there are ions with the same amount of charge. But this turns out to be wrong. In fact, the electrons see an attractive potential. The reason is again partly due to the Pauli principle that, loosely speaking, does not allow two electrons with the same spin direction to be at the same place and therefore the electrons go "out of each others way." In addition to this, there is also a direct Coulomb interaction between the electrons, which makes them avoid each other. We will discuss this in more detail when dealing with magnetism.

Typically, metallic bonding is not as strong as covalent or ionic bonding but it amounts to a few electron volts per atom. Stronger bonding is found in transition metals, that is, metals with both s and p conduction electrons and a partially filled d shell. The explanation for this is that we have a mixed bonding. The s and p electrons turn into delocalized metallic conduction electrons, whereas the d electrons create much more localized, covalent-type bonds.

1.5
Hydrogen Bonding

Hydrogen atoms have only one electron and can form one covalent bond. If the bond is to a very electronegative atom (like F or O), the electron is mostly located close to that atom and the hydrogen nucleus represents an isolated positive (partial) charge. This can lead to a considerable charge density because of the small size and it can therefore attract negative (partial) charges in other molecules to form an electrostatic bond. This type of bonding is called hydrogen bonding. It is usually quite weak but in some cases the cohesive energy can be up to several hundred meV per atom. It is responsible for the intermolecular attraction in water ice and for the bonding of the double helix in DNA.

1.6
van der Waals Bonding

The term van der Waals bonding refers to a weak, purely quantum mechanical effect. The electron cloud around an atom or a molecule has no static charge distribution but one governed by quantum mechanical fluctuations. For a simple atom with a closed shell, this can be viewed as a fluctuating dipole moment. This dipole moment can polarize other atoms nearby and the interaction of the two neighboring dipoles reduces the total energy, that is, it can lead to bonding. This type of interaction is present in any solid but it is much weaker than ionic, covalent, or metallic bonding. Typical binding energies are in the meV range and therefore van der Waals bonding is only observable for solids that do not show other bonding behavior, for example, noble gases. Pure van der Waals crystals can only exist at very low temperatures.

1.7
Discussion and Problems

1.7.1
Discussion

1. Why is a typical interatomic potential, such as in Figure 1.1, so asymmetric?
2. Which elements are likely to form crystals through ionic bonding?
3. What kind of forces are important for ionic bonding?
4. How does the lattice energy in an ionic crystal depend on the interatomic distance?
5. Explain the difference between cohesive energy and lattice energy.
6. Which elements are likely to form metals?
7. Where does the energy gain in metallic bonding come from?
8. What is the difference between a simple metal and a transition metal (definition and typical physical properties)?
9. Why is van der Waals bonding much weaker than most other bonding types?

1.7.2
Problems

1. *Metallic bonding*: One can use some simple-minded arguments to explain why metallic bonding is stable. One argument is that allowing the wave functions to be smeared out in space reduces the momentum uncertainty Δp and thereby the highest momentum (and energy) through $\Delta p \Delta x = \hbar/2$. Estimate how much Δp would be reduced by allowing the wave function to spread from typical atomic dimensions (Bohr radius) to the typical dimensions of the lattice unit cell (a few Angstrom or 10 times the Bohr radius). If you assume that the highest p would correspond to a highest kinetic energy $E = p^2/2m_e$, how much would this reduce the kinetic energy?

2. *van der Waals force*: Show that the bonding energy due to the van der Waals force between two atoms depends on their distance r as r^{-6}. *Hint*: The van der Waals interaction is due to the mutual interaction of fluctuating dipoles. Suppose that one atom forms a dipole moment, at some time. This can be modeled as two point

charges, separated by a distance d. What is the electric field due to this dipole at some distance r that is much greater than d? Assume that a second atom at the distance r is polarized in the field such that its induced dipole moment is proportional to the field (see (9.4) in Chapter 9) and calculate how the potential energy of the system depends on r.