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Efthimios Kaxiras , John D. Joannopoulos
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1 From Atoms to Solids

Materials exhibit an extremely wide range of properties, which is what makes them so useful and indispensable to humankind. The extremely wide range of the properties of materials is surprising, because most of them are made up from a relatively small subset of the elements in the Periodic Table: about 20 or 30 elements, out of more than 100 total, are encountered in most common materials. Moreover, most materials contain only very few of these elements, from one to half a dozen or so. Despite this relative simplicity in composition, materials exhibit a huge variety of properties over ranges that differ by many orders of magnitude. It is quite extraordinary that even among materials composed of single elements, physical properties can differ by many orders of magnitude.

One example is the ability of materials to conduct electricity. What is actually measured in experiments is the resistivity, that is, the difficulty with which electrical current passes through a material. Some typical single-element metallic solids (like Ag, Cu, Al) have room-temperature resistivities of 1–5 μΩ·cm, while some metallic alloys (like nichrome) have resistivities of 10^2 μΩ·cm. All these materials are considered good conductors of electrical current. Certain single-element solids (like Si and Ge) have room-temperature resistivities much higher than good conductors, for instance, 2.3×10^{11} μΩ·cm for Si, and they are considered semiconductors. Finally, certain common materials like wood (with a rather complex structure and chemical composition) or quartz (with a rather simple structure and composed of two elements, Si and O) have room-temperature resistivities of 10^{16}–10^{19} μΩ·cm (for wood) to 10^{25} μΩ·cm (for quartz). These solids are considered insulators. The range of electrical resistivities covers an impressive 25 orders of magnitude. Even for two materials that are composed of the same element, carbon, their resistivity can differ by many orders of magnitude: graphitic carbon has resistivity 3.5×10^3 μΩ·cm and is considered a semimetal, while in the diamond form, carbon has a much higher resistivity of $\sim 10^{22}$ μΩ·cm, the difference being entirely due to the different crystal structure of the two forms, as shown in Fig. 1.1.

Another example has to do with the mechanical properties of materials. Solids are classified as ductile when they yield plastically when stressed, or brittle when they do not yield easily, but instead break when stressed. A useful measure of this behavior is the yield stress σ_Y, which is the stress up to which the solid behaves as a linear elastic medium when stressed, that is, it returns to its original state when the external stress is removed. Yield stresses in materials, measured in units of MPa, range from 40 in Al, a rather soft and ductile metal, to 5×10^4 in diamond, the hardest material, a brittle insulator. The yield stresses of common steels range from 200 to 2000 MPa. Again we see an impressive range of more than three orders of magnitude in how a material responds to an external agent, in this case a mechanical stress.

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Fig. 1.1 Different forms of carbon-based solids. **Left**: A diamond in raw form, in the shape of an ideal octahedron. The structure of the diamond crystal offers many equivalent planes along which it can be cleaved, exposing a shape of very high symmetry in polished ("cut") form. **Right**: Graphite [*source:* Rob Lavinsky, iRocks.com CC-BY-SA-3.0, via Wikimedia Commons].

Naively, one might expect that the origin of these widely different properties is related to great differences in the concentration of atoms, and correspondingly that of electrons. This is far from the truth. Concentrations of atoms in a solid range from 10^{22} cm^{-3} in Cs, a representative alkali metal, to 17×10^{22} cm^{-3} in C, a representative covalently bonded solid. Anywhere from one to a dozen electrons per atom participate actively in determining the properties of solids. These considerations give a range of atomic concentrations of roughly 20, and of available electron concentrations[1] of roughly 100. These ranges are nowhere close to the ranges of yield stresses and electrical resistivities mentioned above. Rather, the variation of the properties of solids has to do with the specific ways in which the available electrons of the constituent atoms interact when these atoms are brought together at distances of a few angstroms ($1\ \text{Å} = 10^{-10}\ \text{m} = 10^{-1}\ \text{nm}$). Typical distances between nearest-neighbor atoms in solids range from 1.5 to 3 Å. The way in which the available electrons interact determines the atomic structure, and this in turn determines all the other properties of the solid, including mechanical, electrical, optical, thermal, and magnetic properties.

1.1 Electronic Structure of Atoms

We invoked above, on several occasions, the term "available electrons" for specific types of atoms. This is not a very precise term, but was intended to convey the message that not all of the electrons of an atom are necessarily involved in determining the properties of a solid in which this atom exists. Some electrons eagerly participate in the formation of the solid, by being shared among several atoms and thus serving as the "glue" that holds those atoms together, while other electrons are very tightly bound to the nuclei of the constituent

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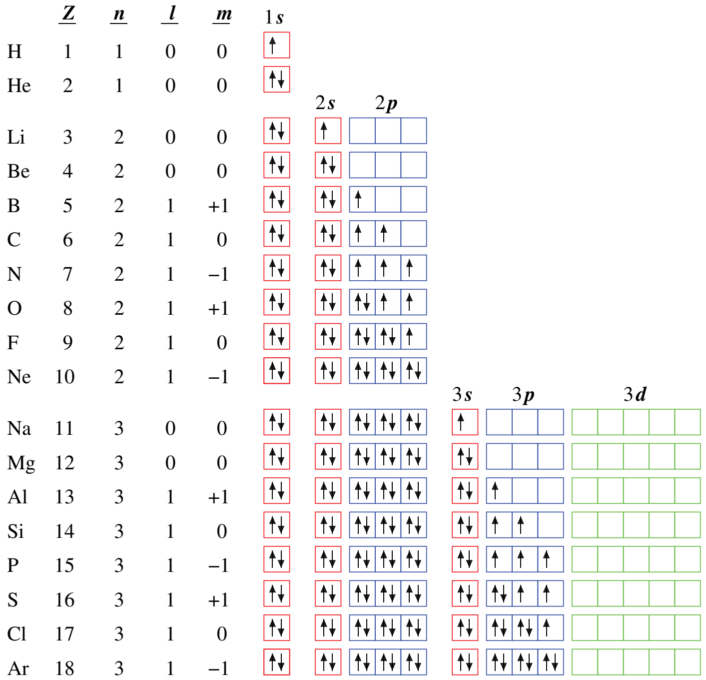
[1] The highest concentration of atoms does not correspond to the highest number of available electrons per atom.



	Z	n	l	m
H	1	1	0	0
He	2	1	0	0
Li	3	2	0	0
Be	4	2	0	0
B	5	2	1	+1
C	6	2	1	0
N	7	2	1	−1
O	8	2	1	+1
F	9	2	1	0
Ne	10	2	1	−1
Na	11	3	0	0
Mg	12	3	0	0
Al	13	3	1	+1
Si	14	3	1	0
P	15	3	1	−1
S	16	3	1	+1
Cl	17	3	1	0
Ar	18	3	1	−1

Fig. 1.2 Filling of electronic shells for the elements in the Periodic Table with atomic numbers $Z = 1$–18: s shells ($l = 0, m = 0$) are represented by one red box, p shells ($l = 1, m = 0, \pm 1$) by three blue boxes, and d shells ($l = 2, m = 0, \pm 1, \pm 2$) by five green boxes. Each box can contain up to two electrons of opposite spin (up and down arrows). For each element, we show the values of the principal (n) and angular momentum (l) quantum numbers, as well as the value of the magnetic (m) quantum number of the last electron.

atoms, almost in exactly the same way as if the atoms were in complete isolation from each other; the latter electrons play essentially no role in determining the properties of the solid. This is an important distinction, which deserves further discussion.

The solution of the Schrödinger equation for the isolated atom produces a number of states in which electrons can exist. The total number of electrons in the neutral atom, equal to the total number of protons in its nucleus, called the **atomic number** Z, determines how many of the allowed states are occupied. The occupation of the allowed states leads to a certain number of shells being completely full (the ones with the lowest energy and wavefunctions that are closest to the nucleus), while some shells can be partially filled (the ones with higher energy and wavefunctions that extend farther from the nucleus).[2] A schematic representation of the filling of electronic shells for atoms with $Z = 1$–36 is given in Figs 1.2 and 1.3, where it becomes obvious which shells are completely filled and which are partially filled by electrons for each element. A continuation of this sequence of filling of electronic shells leads to the Periodic Table, presented in the next section.

The periodic filling of the electronic shells is actually quite evident in some basic properties of atoms, like their physical size or their tendency to attract electrons, referred

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[2] A more detailed discussion is given in Appendix C.

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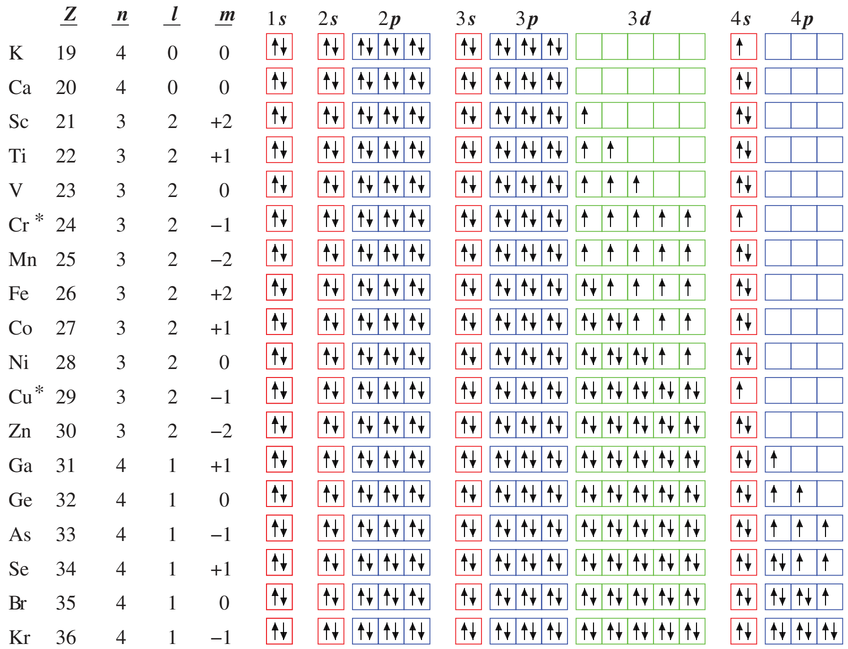

Fig. 1.3 Filling of electronic shells for elements with atomic numbers $Z = 19$–36. The notation is the same as in Fig. 1.2. Elements marked by an asterisk have electronic levels filled out of the regular order: for example, Cu has a $3d^{10}4s^1$ shell rather than a $3d^9 4s^2$ shell.

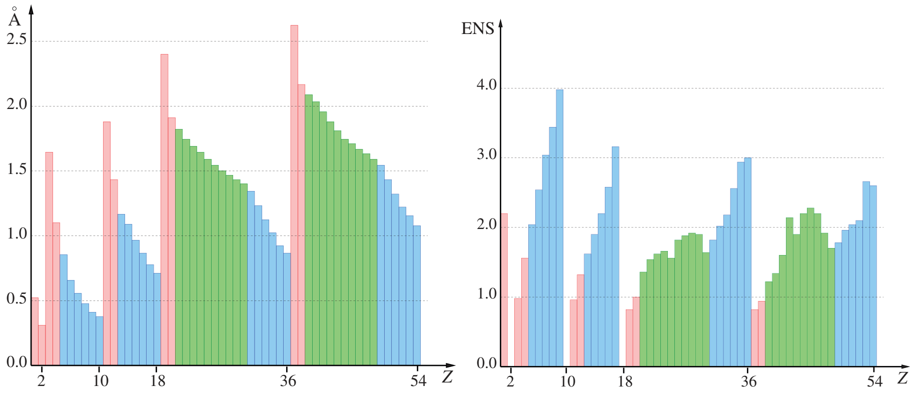

Fig. 1.4 Periodic behavior of the properties of the elements: atomic radii (Å) and electronegativity scale (ENS), for elements with atomic numbers Z from 1 to 54. The values corresponding to closed electronic shells, $Z = 2, 10, 18, 36, 54$, that is, the elements He, Ne, Ar, Kr, Xe, are indicated. The color coding corresponds to the different types of electronic shells that are being gradually filled: red for the s shells, blue for the p shells, and green for the d shells.

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to as the "electronegativity scale" (ENS), as shown in Fig. 1.4. Interestingly, as the number of protons in the nucleus increases (Z increases), the electron wavefunctions become more compact and the atom shrinks in size, while the levels for a particular (n, l) set are being gradually filled by electrons. After a shell is full, as is the case for the elements He ($Z = 2$), Ne ($Z = 10$), Ar ($Z = 18$), and Kr ($Z = 36$), the so-called noble gases, the size is a local minimum; there is an abrupt increase in size for the elements with one more proton, when the next electronic shell starts being filled. Similarly, the ENS exhibits a regular pattern, that is, with steadily increasing values within each partially filled shell and the highest value corresponding to those elements that are just one electron short of having a completely filled electronic shell, like F ($Z = 9$), Cl ($Z = 17$), Br ($Z = 35$).

1.2 Forming Bonds Between Atoms

The electrons in the outermost, partially filled shells of the isolated atom are the ones that interact strongly with similar electrons in neighboring atoms in the solid; these are called **valence electrons**, while the remaining electrons in the completely filled shells of the atom are called **core electrons**. This is shown schematically in Fig. 1.5. Core electrons are essentially unaffected when the atom is surrounded by its neighbors in the solid. For most practical purposes it is quite reasonable to neglect the presence of the core electrons as far as the solid is concerned, and consider how the valence electrons behave. The core electrons and the nucleus form the **ion**, which has a positive net charge equal in magnitude to the number of valence electrons. The description of the solid can then be based on the behavior of ions and the accompanying valence electrons.

The classification of electrons in the atom into core and valence is very useful when we address the issue of how atoms come together to form a solid. This is illustrated next in two representative and very broad cases. The first concerns the type of bonding found in metallic solids, the second the type of bonding common in insulating or semiconducting materials, called covalent bonding.

Fig. 1.5 Schematic representation of the core and valence electrons in an atom, shown as the red and blue clouds, respectively.

1.2.1 The Essence of Metallic Bonding: The Free-Electron Model

The simplest possible arrangement of the valence electrons is to have them stripped apart from the ions and distributed uniformly through the solid. This is illustrated in Fig. 1.6. The bonding comes from the fact that the electrons are now shared by all the ions and act as a glue between them. The total energy E_{tot} of the system is then lower than the energy of isolated, neutral ions. The difference is defined as the "binding energy," E_b, of the solid. This quantity is characteristic of the stability of the solid. To make it a number independent of the size of the solid, we define it as the energy per atom gained by putting all the atoms together so they can share their valence electrons. For a system composed of N atoms, each with energy E_0 when isolated from all the others, we have:

$$E_b = \frac{1}{N}(E_{\text{tot}} - NE_0) \tag{1.1}$$

The general behavior of the binding energy is shown in Fig. 1.6: when the atoms are far apart, the binding energy is zero. The valence electrons are bound to the ions, occupying states with energy lower than zero; in the simple example shown in Fig. 1.6, this energy is labeled ϵ_0 for the case of the isolated atoms. When the atoms are brought together, the attractive potential due to the presence of many ions leads to lower values for the energy of the bound valence electrons (blue line). However, there is also a Coulomb repulsion E_c between the positive ions (green line). The competition between the two terms leads to a binding energy per atom E_b that is negative, that is, overall the system gains energy by having all the electrons shared among all the ions. When the distance between the

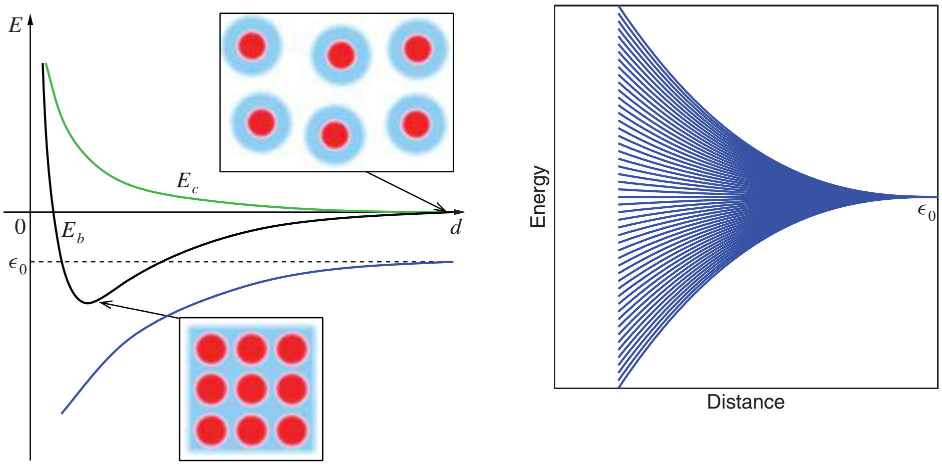

Fig. 1.6 Illustration of metallic bonding between many atoms. **Left**: The binding energy E_b of the solid as a function of the distance between the ions; E_c is the Coulomb repulsion between the ions and ϵ_0 is the energy of the valence electrons in the isolated neutral atom. The insets indicate schematically the charge distribution, with red circles representing the ions and blue clouds representing the valence electrons which end up being uniformly distributed between the ions in the solid. **Right**: The corresponding energy-level diagram. The original N degenerate levels of the isolated individual atoms (at large distances) form a distribution of states in the solid that span a wide energy range, as the distance between atoms decreases.

ions becomes too small, the Coulomb repulsion between ions becomes too strong and the binding energy rises and eventually becomes positive, at which point the solid is not stable any longer. There is an optimal distance between the ions at which the binding energy attains its lowest value, which corresponds to the optimal structure of the solid.

An interesting issue is the behavior of the electron energy levels as the distance between the ions decreases. As shown in the right panel of Fig. 1.6, these energy levels are degenerate in the case of isolated atoms. Because electrons are fermions, they cannot all reside on the same energy level when the atoms are very close to each other. As a result, when the atoms get closer together the electron energy levels break the degeneracy and form a distribution over a range of values. The closer the distance between ions, the wider this energy range is, as the distance between ions approaches that of interatomic distances in the solid. In the limit of a very large number of atoms (as is the case for typical solids), the difference between consecutive energy values becomes infinitesimally small and the electron energy levels form a continuum distribution.

To put these notions on a more quantitative basis, we will use a very simple model in which the ionic potential is a uniformly distributed positive background. This frees us from needing to consider the detailed behavior of the ions. Moreover, we will neglect any kind of interaction between the electrons (coming from their Coulomb repulsion or from exchange and correlation effects). This is referred to as the "free-electron" or "jellium" model. Although evidently oversimplified, this model is quite useful in describing many of the properties of metallic solids, at least in a qualitative way.

In this model, the electronic states must also reflect this symmetry of the potential which is uniform, so they must be plane waves:

$$\psi_i(\mathbf{r}) = \frac{1}{\sqrt{V}} e^{i\mathbf{k}_i \cdot \mathbf{r}} \tag{1.2}$$

where V is the volume of the solid and $\mathbf{k}_i$ the wave-vector which characterizes state ψ_i. Since the wave-vectors suffice to characterize the single-particle states, we will use those as the only index, that is, $\psi_i \rightarrow \psi_{\mathbf{k}}$. Plane waves are actually a very convenient and useful basis for expressing various physical quantities. In particular, they allow the use of Fourier transform techniques, which simplify the calculations. In the following we will be using relations implied by the Fourier transform method, which are discussed in Appendix A.

We identify the state of such an electron by its wave-vector $\mathbf{k}$, which takes values from 0 up to a maximum magnitude k_{F}, called the "Fermi momentum." In three-dimensional (3D) cartesian coordinates the wave-vector is written as $\mathbf{k} = k_x\hat{\mathbf{x}} + k_y\hat{\mathbf{y}} + k_z\hat{\mathbf{z}}$ and the energy of the state with wave-vector $\mathbf{k}$ is:

$$\epsilon_{\mathbf{k}} = \frac{\hbar^2 \mathbf{k}^2}{2m_e} \tag{1.3}$$

We consider that the solid is a rectangular object with sides L_x, L_y, L_z, with $V = L_xL_yL_z$ its total volume. For a typical solid, the values of L_x, L_y, L_z are very large on the scale of

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atomic units, of order 10^8–10^9 a_0, where a_0 is the Bohr radius ($a_0 = 0.529177$ Å, with 1 Å $= 10^{-10}$ m). From Fourier analysis, we can take $\mathrm{d}k_x, \mathrm{d}k_y, \mathrm{d}k_z$ to be given by:

$$\mathrm{d}k_x \mathrm{d}k_y \mathrm{d}k_z = \frac{(2\pi)^3}{L_x L_y L_z} \Longrightarrow \frac{\mathrm{d}\mathbf{k}}{(2\pi)^3} = \frac{1}{V} \Longrightarrow \lim_{L_x, L_y, L_z \to \infty} \sum_{\mathbf{k}} = V \int \frac{\mathrm{d}\mathbf{k}}{(2\pi)^3} \tag{1.4}$$

as discussed in Appendix A, Eq. (A.46). For each free-electron state characterized by **k** there is a multiplicity factor of 2 coming from the spin, which allows each electron to exist in two possible states, spin up or down, for a given value of its energy. Therefore, the total number of states available to the system is:

$$2 \sum_{|\mathbf{k}| \le k_{\mathrm{F}}} = 2V \int_0^{k_{\mathrm{F}}} \frac{\mathrm{d}\mathbf{k}}{(2\pi)^3} = \frac{k_{\mathrm{F}}^3}{3\pi^2} V = N \tag{1.5}$$

which we have set equal to the total number of electrons N in the solid. This leads to the following relation between the density $n = N/V$ and the Fermi momentum k_{F}:

$$n = \frac{k_{\mathrm{F}}^3}{3\pi^2} \tag{1.6}$$

which in turn gives for the energy of the highest occupied state ϵ_{F}, called the "Fermi energy":

$$\epsilon_{\mathrm{F}} = \frac{\hbar^2 k_{\mathrm{F}}^2}{2m_e} = \frac{\hbar^2 (3\pi^2 n)^{2/3}}{2m_e} \tag{1.7}$$

These results help us make some sense of the spectrum of energy levels in the solid: the energy of electronic states is now given by Eq. (1.3), which is a continuous set of values, from 0 up to ϵ_{F}. This is to be compared to the set of N individual atomic levels, when the atoms are isolated, as illustrated in Fig. 1.6. Moreover, if we assume that each atom has one valence electron in the atomic state, we will need only $N/2$ free-electron states to accommodate all these electrons in the solid due to spin degeneracy, as worked out above, in Eq. (1.5). The binding or cohesive energy in this case comes from the much more delocalized nature of the states in the solid as compared to those in individual isolated atoms.

Example 1.1 1D model of atoms in a box

To illustrate these ideas, we consider a simple example of six "atoms" in one dimension, each represented by a box of size a, as shown in Fig. 1.7. Consistent with the free-electron model, we will take the electron in such an atom to have a sinusoidal wavefunction $\psi_0(x)$ and energy ϵ_0 given by:

$$\psi_0(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{\pi x}{a}\right), \quad \epsilon_0 = \frac{\hbar^2 \pi^2}{2m_e a^2}$$

corresponding to the largest possible wavelength of $\lambda_0 = 2a$ within the box of the isolated atom. If we condense these six atoms into a one-dimensional (1D) "solid" of size $L = 6a$, the lowest energy level in the solid will have energy $\epsilon_1 = \epsilon_0/36 = 0.028\epsilon_0$. Assuming that each atom has one valence electron, all the electrons in this 1D solid can be accommodated by the three lowest states with

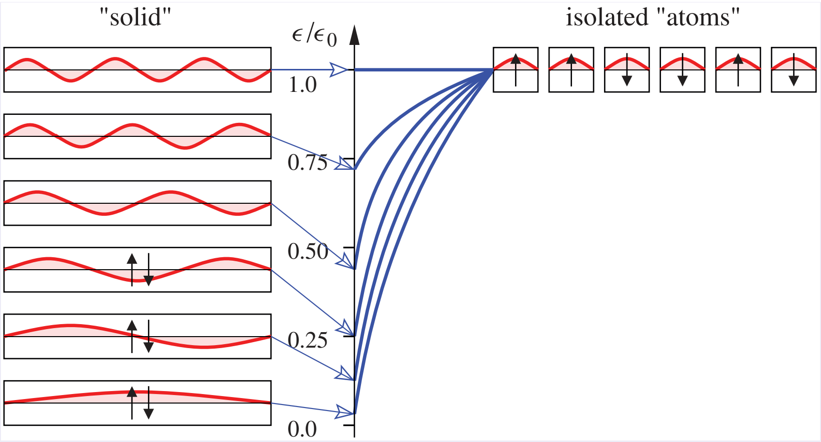

Fig. 1.7

A simple 1D model of the energy levels associated with the free-electron model for a system of six "atoms." The red sinusoidal curves represent the single-particle wavefunctions. In each atom, contained in a small box of size a, the lowest free-electron state within the box has wavelength $\lambda = 2a$ and energy $\epsilon_0 = \hbar^2\pi^2/2m_e a^2$. For six atoms forming a "solid" of size $L = 6a$, the six lowest-energy states and their corresponding energies in units of ϵ_0 are shown on the vertical axis.

energies $\epsilon_1, \epsilon_2 = 0.111\epsilon_0, \epsilon_3 = 0.25\epsilon_0$, giving a much lower total energy for the condensed system of $E_{\text{tot}} = 0.778\epsilon_0$ compared to the six isolated atoms, and a binding energy per atom of $E_b = -0.870\epsilon_0$. This component, namely the electronic kinetic energy contribution to the total energy, is the dominant component within our simple model. The actual total energy of the solid must include also the Coulomb repulsion of the electrons, as well as the electron–ion attraction, but these terms cancel each other for uniform and equal densities of the two oppositely charged sets of particles.

Generalizing this simple model, and considering only the kinetic energy of the electrons in the free-electron model, including a factor of 2 for the spin degeneracy, we find that the total energy of this system is given by:

$$E^{\text{kin}} = 2\sum_{|\mathbf{k}|\leq k_{\text{F}}} \epsilon_{\mathbf{k}} = 2V\int_0^{k_{\text{F}}} \frac{d\mathbf{k}}{(2\pi)^3}\frac{\hbar^2 k^2}{2m_e} = \frac{V}{\pi^2}\frac{\hbar^2 k_{\text{F}}^5}{10m_e} = \frac{3}{5}N\epsilon_{\text{F}} \tag{1.8}$$

This quantity is evidently positive and only depends on the density of electrons in the solid, n. The attraction of electrons to the positive charge of the ions provides the bonding for the atoms in the solid, but we have eliminated these terms from the free-electron model. In thinking about the properties of metallic solids, it is often useful to express equations in terms of another quantity, called r_s, which is defined as the radius of the sphere whose volume corresponds to the average volume per electron in the solid:

$$\frac{4\pi}{3}r_s^3 = \frac{V}{N} = n^{-1} = \frac{3\pi^2}{k_{\text{F}}^3} \tag{1.9}$$

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and r_s is typically measured in atomic units. This gives the following expression for k_F:

$$k_F = \frac{(9\pi/4)^{1/3}}{r_s} \Longrightarrow k_F a_0 = \frac{(9\pi/4)^{1/3}}{(r_s/a_0)} \tag{1.10}$$

where the last expression contains the dimensionless combinations of variables $k_F a_0$ and r_s/a_0. In actual metals (r_s/a_0) varies between 2 and 6.

It is helpful to introduce here the units of energy that are typically involved in the formation of bonds in solids. The rydberg (Ry) is the natural unit for energies in atoms:

$$\frac{\hbar^2}{2m_e a_0^2} = \frac{e^2}{2a_0} = 1 \text{ Ry} \tag{1.11}$$

Another useful unit is the electron-volt (eV), the potential energy gained by an electron when it moves across a voltage difference of 1 V. The rydberg and the electron-volt are related by:

$$1 \text{ Ry} = 13.6058 \text{ eV} \tag{1.12}$$

Typical binding energies per atom, for metallic solids, are in the range of a few electron-volts.

1.2.2 The Essence of Covalent Bonding

We consider next what can happen when two atoms of the same type come together to form a diatomic molecule. For simplicity, we will assume that each atom has only one valence electron outside its core, in a state with energy ϵ_1, as indicated in Fig. 1.8; this corresponds,

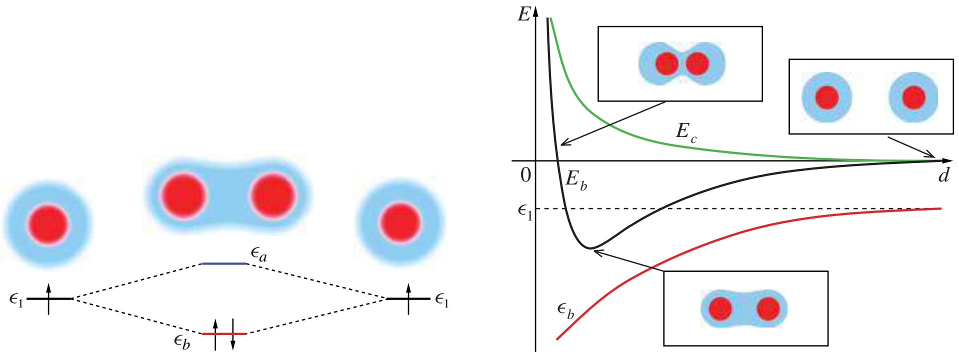

Fig. 1.8 Schematic representation of the formation of a bond between two atoms with one valence electron each. **Left**: When separated, the atoms each have a valence state of energy ϵ_1 with one electron in it; when they are brought together, new states are formed, the bonding state with energy $\epsilon_b < \epsilon_1$ and the anti-bonding state with energy $\epsilon_a > \epsilon_1$; the two available valence electrons occupy the lower-energy bonding state. **Right**: The binding energy E_b per atom (black line) of a diatomic molecule as a function of the distance d between the ions composing it. The energy of the bonding state ϵ_b is shown as a red line; for large distances it approaches the value ϵ_1 of the electron state in the isolated atom. The Coulomb repulsion between the two cores (E_c) is shown as a green line.