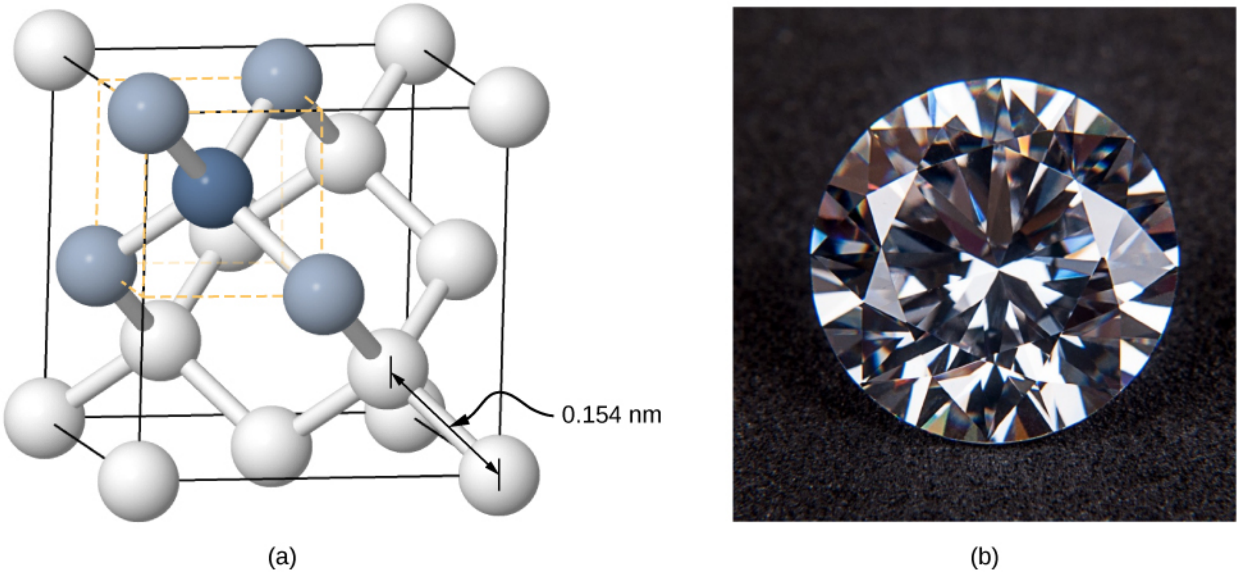

Figure 9.11 Structure of the diamond crystal. (a) The single carbon atom represented by the dark blue sphere is covalently bonded to the four carbon atoms represented by the light blue spheres. (b) Gem-quality diamonds can be cleaved along smooth planes, which gives a large number of angles that cause total internal reflection of incident light, and thus gives diamonds their prized brilliance.

Covalently bonded crystals are not as uniform as ionic crystals but are reasonably hard, difficult to melt, and are insoluble in water. For example, diamond has an extremely high melting temperature (4000 K) and is transparent to visible light. In comparison, covalently bonded tin (also known as alpha-tin, which is nonmetallic) is relatively soft, melts at 600 K, and reflects visible light. Two other important examples of covalently bonded crystals are silicon and germanium. Both of these solids are used extensively in the manufacture of diodes, transistors, and integrated circuits. We will return to these materials later in our discussion of semiconductors.

Metallic Bonding in Solids

As the name implies, metallic bonding is responsible for the formation of metallic crystals. The valence electrons are essentially free of the atoms and are able to move relatively easily throughout the metallic crystal. Bonding is due to the attractive forces between the positive ions and the conduction electrons. Metallic bonds are weaker than ionic or covalent bonds, with dissociation energies in the range $1 - 3\,\mathrm{eV}$.

9.4 | Free Electron Model of Metals

Learning Objectives

By the end of this section, you will be able to:

- Describe the classical free electron model of metals in terms of the concept electron number density
- Explain the quantum free-electron model of metals in terms of Pauli’s exclusion principle
- Calculate the energy levels and energy-level spacing of a free electron in a metal

Metals, such as copper and aluminum, are held together by bonds that are very different from those of molecules. Rather than sharing and exchanging electrons, a metal is essentially held together by a system of free electrons that wander throughout the solid. The simplest model of a metal is the **free electron model**. This model views electrons as a gas. We first consider the simple one-dimensional case in which electrons move freely along a line, such as through a very thin metal rod. The potential function $U(x)$ for this case is a one-dimensional infinite square well where the walls of the well correspond to the edges of the rod. This model ignores the interactions between the electrons but respects the exclusion principle. For the special case of $T = 0\,\mathrm{K}$, N electrons fill up the energy levels, from lowest to highest, two at a time (spin up and spin down), until the highest energy level is filled. The highest energy filled is called the **Fermi energy**.

The one-dimensional free electron model can be improved by considering the three-dimensional case: electrons moving freely in a three-dimensional metal block. This system is modeled by a three-dimensional infinite square well. Determining the allowed energy states requires us to solve the time-independent Schrödinger equation

$$-\frac{h^2}{2m_e}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\psi(x,\ y,\ z)=E\,\psi(x,\ y,\ z), \tag{9.26}$$

where we assume that the potential energy inside the box is zero and infinity otherwise. The allowed wave functions describing the electron's quantum states can be written as

$$\psi(x,\ y,\ z)=\left(\sqrt{\frac{2}{L_x}}\sin\frac{n_x\pi x}{L_x}\right)\left(\sqrt{\frac{2}{L_y}}\sin\frac{n_y\pi y}{L_y}\right)\left(\sqrt{\frac{2}{L_z}}\sin\frac{n_z\pi z}{L_z}\right), \tag{9.27}$$

where $n_x, n_y,$ and n_z are positive integers representing quantum numbers corresponding to the motion in the *x*-, *y*-, and *z*-directions, respectively, and $L_x, L_y,$ and L_z are the dimensions of the box in those directions. **Equation 9.27** is simply the product of three one-dimensional wave functions. The allowed energies of an electron in a cube $(L = L_x = L_y = L_z)$ are

$$E=\frac{\pi^2\hbar^2}{2mL^2}\left(n_1^2+n_2^2+n_3^2\right). \tag{9.28}$$

Associated with each set of quantum numbers (n_x, n_y, n_z) are two quantum states, spin up and spin down. In a real material, the number of filled states is enormous. For example, in a cubic centimeter of metal, this number is on the order of 10^{22}. Counting how many particles are in which state is difficult work, which often requires the help of a powerful computer. The effort is worthwhile, however, because this information is often an effective way to check the model.

Example 9.4

Energy of a Metal Cube

Consider a solid metal cube of edge length 2.0 cm. (a) What is the lowest energy level for an electron within the metal? (b) What is the spacing between this level and the next energy level?

Strategy

An electron in a metal can be modeled as a wave. The lowest energy corresponds to the largest wavelength and smallest quantum number: $n_x, n_y, n_z = (1,\ 1,\ 1)$. **Equation 9.28** supplies this "ground state" energy value.

Since the energy of the electron increases with the quantum number, the next highest level involves the smallest increase in the quantum numbers, or $(n_x, n_y, n_z) = (2,\ 1,\ 1), (1,\ 2,\ 1),$ or $(1, 1, 2)$.

Solution

The lowest energy level corresponds to the quantum numbers $n_x = n_y = n_z = 1$. From **Equation 9.28**, the energy of this level is

$$\begin{aligned}E(1,\ 1,\ 1) &= \frac{\pi^2 h^2}{2m_e L^2}\left(1^2+1^2+1^2\right)\\ &= \frac{3\pi^2\ (1.05\times 10-34\ \text{J}\cdot\text{s})^2}{2\,(9.11\times 10^{-31}\ \text{kg})\,(2.00\times 10^{-2}\ \text{m})^2}\\ &= 4.48\times 10^{-34}\ \text{J} = 2.80\times 10^{-15}\ \text{eV}.\end{aligned}$$

The next-higher energy level is reached by increasing any one of the three quantum numbers by 1. Hence, there are actually three quantum states with the same energy. Suppose we increase n_x by 1. Then the energy becomes

$$\begin{aligned} E(2,\ 1,\ 1) &= \frac{\pi^2 h^2}{2m_e L^2}(2^2+1^2+1^2) \\ &= \frac{6\pi^2(1.05\times 10-34\ \text{J}\cdot\text{s})^2}{2(9.11\times 10^{-31}\ \text{kg})(2.00\times 10^{-2}\ \text{m})^2} \\ &= 8.96\times 10^{-34}\ \text{J} = 5.60\times 10^{-15}\ \text{eV}. \end{aligned}$$

The energy spacing between the lowest energy state and the next-highest energy state is therefore

$$\text{E}(2,\ 1,\ 1) - \text{E}(1,\ 1,\ 1) = 2.80\times 10^{-15}\ \text{eV}.$$

Significance

This is a very small energy difference. Compare this value to the average kinetic energy of a particle, $k_\text{B}T$, where k_B is Boltzmann's constant and T is the temperature. The product $k_\text{B}T$ is about 1000 times greater than the energy spacing.

9.4 Check Your Understanding What happens to the ground state energy of an electron if the dimensions of the solid increase?

Often, we are not interested in the total number of particles in all states, but rather the number of particles dN with energies in a narrow energy interval. This value can be expressed by

$$dN = n(E)dE = g(E)dE\cdot F$$

where $n(E)$ is the **electron number density**, or the number of electrons per unit volume; $g(E)$ is the **density of states**, or the number of allowed quantum states per unit energy; dE is the size of the energy interval; and F is the **Fermi factor**. The Fermi factor is the probability that the state will be filled. For example, if $g(E)dE$ is 100 available states, but F is only 5%, then the number of particles in this narrow energy interval is only five. Finding $g(E)$ requires solving Schrödinger's equation (in three dimensions) for the allowed energy levels. The calculation is involved even for a crude model, but the result is simple:

$$g(E) = \frac{\pi V}{2}\left(\frac{8m_e}{h^2}\right)^{3/2} E^{1/2}, \qquad \textbf{(9.29)}$$

where V is the volume of the solid, m_e is the mass of the electron, and E is the energy of the state. Notice that the density of states increases with the square root of the energy. More states are available at high energy than at low energy. This expression does *not* provide information of the density of the electrons in physical space, but rather the density of energy levels in "energy space." For example, in our study of the atomic structure, we learned that the energy levels of a hydrogen atom are much more widely spaced for small energy values (near than ground state) than for larger values.

This equation tells us how many electron states are available in a three-dimensional metallic solid. However, it does not tell us how likely these states will be filled. Thus, we need to determine the Fermi factor, F. Consider the simple case of $T = 0\,\text{K}$. From classical physics, we expect that all the electrons $(\sim 10^{22}/\text{cm}^3)$ would simply go into the ground state to achieve the lowest possible energy. However, this violates Pauli's exclusion principle, which states that no two electrons can be in the same quantum state. Hence, when we begin filling the states with electrons, the states with lowest energy become occupied first, then states with progressively higher energies. The *last electron* we put in has the highest energy. This energy is the Fermi energy E_F of the free electron gas. A state with energy $E < E_\text{F}$ is occupied by a single electron, and a state with energy $E > E_\text{F}$ is unoccupied. To describe this in terms of a probability $F(E)$ that a state of energy E is occupied, we write for $T = 0\,\text{K}$:

$$\begin{aligned} F(E) &= 1 \quad (E < E_\text{F}) \\ F(E) &= 0 \quad (E > E_\text{F}). \end{aligned} \qquad \textbf{(9.30)}$$

The density of states, Fermi factor, and electron number density are plotted against energy in **Figure 9.12**.

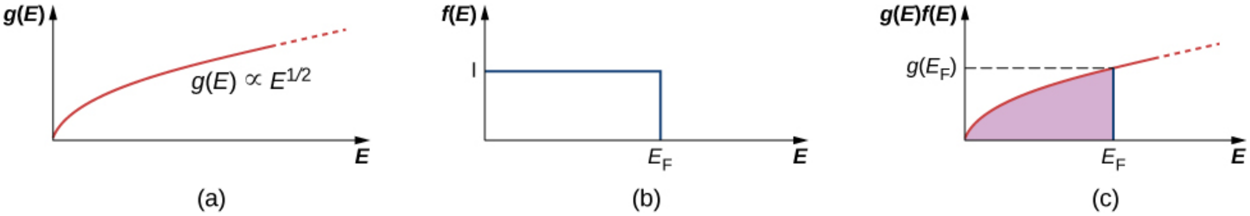

Figure 9.12 (a) Density of states for a free electron gas; (b) probability that a state is occupied at $T = 0\,\text{K}$; (c) density of occupied states at $T = 0\,\text{K}$.

A few notes are in order. First, the electron number density (last row) distribution drops off sharply at the Fermi energy. According to the theory, this energy is given by

$$E_F = \frac{h^2}{8m_e}\left(\frac{3N}{\pi V}\right)^{2/3}. \tag{9.31}$$

Fermi energies for selected materials are listed in the following table.

Element	Conduction Band Electron Density $\left(10^{28}\ \text{m}^{-3}\right)$	Free-Electron Model Fermi Energy (eV)
Al	18.1	11.7
Ba	3.15	3.64
Cu	8.47	7.00
Au	5.90	5.53
Fe	17.0	11.1
Ag	5.86	5.49

Table 9.3 Conduction Electron Densities and Fermi Energies for Some Metals

Note also that only the graph in part (c) of the figure, which answers the question, "How many particles are found in the energy range?" is checked by experiment. The **Fermi temperature** or effective "temperature" of an electron at the Fermi energy is

$$T_F = \frac{E_F}{k_B}. \tag{9.32}$$

Example 9.5

Fermi Energy of Silver

Metallic silver is an excellent conductor. It has 5.86×10^{28} conduction electrons per cubic meter. (a) Calculate its Fermi energy. (b) Compare this energy to the thermal energy $k_B T$ of the electrons at a room temperature of 300 K.

Solution

a. From **Equation 9.31**, the Fermi energy is

$$\begin{aligned} E_F &= \frac{h^2}{2m_e}(3\pi^2 n_e)^{2/3} \\ &= \frac{(1.05 \times 10^{-34}\ \text{J} \cdot \text{s})^2}{2(9.11 \times 10^{-31}\ \text{kg})} \times [(3\pi^2(5.86 \times 10^{28}\ \text{m}^{-3})]^{2/3} \\ &= 8.79 \times 10^{-19}\ \text{J} = 5.49\ \text{eV}. \end{aligned}$$

This is a typical value of the Fermi energy for metals, as can be seen from **Table 9.3**.

b. We can associate a Fermi temperature T_F with the Fermi energy by writing $k_B T_F = E_F$. We then find for the Fermi temperature

$$T_F = \frac{8.79 \times 10^{-19}\ \text{J}}{1.38 \times 10^{-23}\ \text{J/K}} = 6.37 \times 10^4\ \text{K},$$

which is much higher than room temperature and also the typical melting point $(\sim 10^3\ \text{K})$ of a metal. The ratio of the Fermi energy of silver to the room-temperature thermal energy is

$$\frac{E_F}{k_B T} = \frac{T_F}{T} \approx 210.$$

To visualize how the quantum states are filled, we might imagine pouring water slowly into a glass, such as that of **Figure 9.13**. The first drops of water (the electrons) occupy the bottom of the glass (the states with lowest energy). As the level rises, states of higher and higher energy are occupied. Furthermore, since the glass has a wide opening and a narrow stem, more water occupies the top of the glass than the bottom. This reflects the fact that the density of states $g(E)$ is proportional to $E^{1/2}$, so there is a relatively large number of higher energy electrons in a free electron gas. Finally, the level to which the glass is filled corresponds to the Fermi energy.

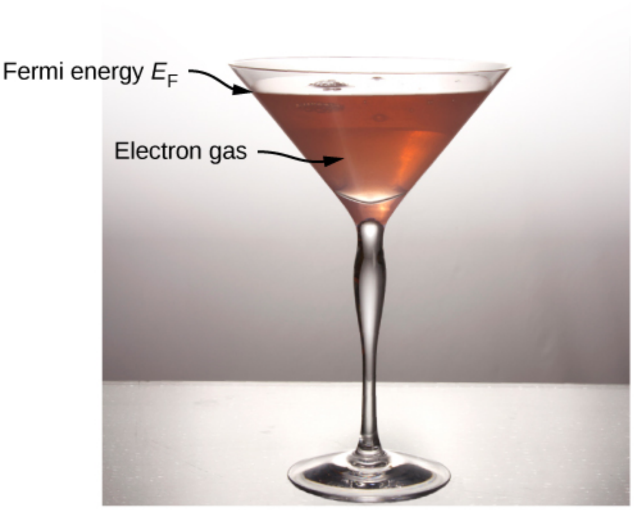

Figure 9.13 An analogy of how electrons fill energy states in a metal. As electrons fill energy states, lowest to highest, the number of available states increases. The highest energy state (corresponding to the water line) is the Fermi energy. (credit: modification of work by “Didriks”/Flickr)

Suppose that at $T = 0\ \text{K}$, the number of conduction electrons per unit volume in our sample is n_e. Since each field state has one electron, the number of filled states per unit volume is the same as the number of electrons per unit volume.

9.5 | Band Theory of Solids

Learning Objectives

By the end of this section, you will be able to:

- Describe two main approaches to determining the energy levels of an electron in a crystal
- Explain the presence of energy bands and gaps in the energy structure of a crystal
- Explain why some materials are good conductors and others are good insulators
- Differentiate between an insulator and a semiconductor

The free electron model explains many important properties of conductors but is weak in at least two areas. First, it assumes a constant potential energy within the solid. (Recall that a constant potential energy is associated with no forces.) **Figure 9.14** compares the assumption of a constant potential energy (dotted line) with the periodic Coulomb potential, which drops as $-1/r$ at each lattice point, where r is the distance from the ion core (solid line). Second, the free electron model assumes an impenetrable barrier at the surface. This assumption is not valid, because under certain conditions, electrons can escape the surface—such as in the photoelectric effect. In addition to these assumptions, the free electron model does not explain the dramatic differences in electronic properties of conductors, semiconductors, and insulators. Therefore, a more complete model is needed.

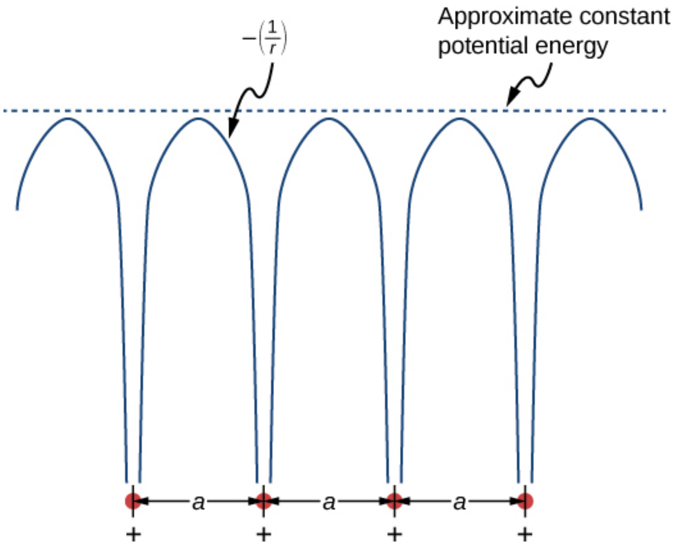

Figure 9.14 The periodic potential used to model electrons in a conductor. Each ion in the solid is the source of a Coulomb potential. Notice that the free electron model is productive because the average of this field is approximately constant.

We can produce an improved model by solving Schrödinger’s equation for the periodic potential shown in **Figure 9.14**. However, the solution requires technical mathematics far beyond our scope. We again seek a qualitative argument based on quantum mechanics to find a way forward.

We first review the argument used to explain the energy structure of a covalent bond. Consider two identical hydrogen atoms so far apart that there is no interaction whatsoever between them. Further suppose that the electron in each atom is in the same ground state: a 1s electron with an energy of $-13.6\,\text{eV}$ (ignore spin). When the hydrogen atoms are brought closer together, the individual wave functions of the electrons overlap and, by the exclusion principle, can no longer be in the same quantum state, which splits the original equivalent energy levels into two different energy levels. The energies of these levels depend on the interatomic distance, α (**Figure 9.15**).