

CHAPTER

3

Introduction to the Quantum Theory of Solids

PREVIEW

In the last chapter, we applied quantum mechanics and Schrodinger's wave equation to determine the behavior of electrons in the presence of various potential functions. We found that one important characteristic of an electron bound to an atom or bound within a finite space is that the electron can take on only discrete values of energy; that is, the energies are quantized. We also discussed the Pauli exclusion principle, which stated that only one electron is allowed to occupy any given quantum state. In this chapter, we will generalize these concepts to the electron in a crystal lattice.

One of our goals is to determine the electrical properties of a semiconductor material, which we will then use to develop the current-voltage characteristics of semiconductor devices. Toward this end, we have two tasks in this chapter: to determine the properties of electrons in a crystal lattice, and to determine the statistical characteristics of the very large number of electrons in a crystal.

To start, we will expand the concept of discrete allowed electron energies that occur in a single atom to a band of allowed electron energies in a single-crystal solid. First we will qualitatively discuss the feasibility of the allowed energy bands in a crystal and then we will develop a more rigorous mathematical derivation of this theory using Schrodinger's wave equation. This energy band theory is a basic principle of semiconductor material physics and can also be used to explain differences in electrical characteristics between metals, insulators, and semiconductors.

Since current in a solid is due to the net flow of charge, it is important to determine the response of an electron in the crystal to an applied external force, such as an electric field. The movement of an electron in a lattice is different than that of an electron in free space. We will develop a concept allowing us to relate the quantum mechanical behavior of electrons in a crystal to classical Newtonian mechanics. This

analysis leads to a parameter called the electron effective mass. As part of this development, we will find that we can define a new particle in a semiconductor called a *hole*. The motion of both electrons and holes gives rise to currents in a semiconductor.

Because the number of electrons in a semiconductor is very large, it is impossible to follow the motion of each individual particle. We will develop the statistical behavior of electrons in a crystal, noting that the Pauli exclusion principle is an important factor in determining the statistical law the electrons must follow. The resulting probability function will determine the distribution of electrons among the available energy states. The energy band theory and the probability function will be used extensively in the next chapter, when we develop the theory of the semiconductor in equilibrium. ■

3.1 | ALLOWED AND FORBIDDEN ENERGY BANDS

In the last chapter, we treated the one-electron, or hydrogen, atom. That analysis showed that the energy of the bound electron is quantized: Only discrete values of electron energy are allowed. The radial probability density for the electron was also determined. This function gives the probability of finding the electron at a particular distance from the nucleus and shows that the electron is not localized at a given radius. We can extrapolate these single-atom results to a crystal and qualitatively derive the concepts of allowed and forbidden energy bands. We can then apply quantum mechanics and Schrodinger's wave equation to the problem of an electron in a single crystal. We find that the electronic energy states occur in bands of allowed states that are separated by forbidden energy bands.

3.1.1 Formation of Energy Bands

Figure 3.1a shows the radial probability density function for the lowest electron energy state of the single, noninteracting hydrogen atom, and Figure 3.1b shows the same probability curves for two atoms that are in close proximity to each other. The wave functions of the two atom electrons overlap, which means that the two electrons

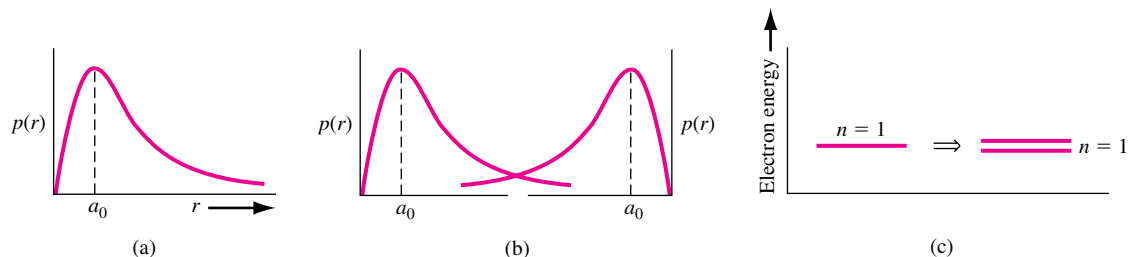


Figure 3.1 | (a) Probability density function of an isolated hydrogen atom. (b) Overlapping probability density functions of two adjacent hydrogen atoms. (c) The splitting of the $n = 1$ state.

will interact. This interaction or perturbation results in the discrete quantized energy level splitting into two discrete energy levels, schematically shown in Figure 3.1c. The splitting of the discrete state into two states is consistent with the Pauli exclusion principle.

A simple analogy of the splitting of energy levels by interacting particles is the following. Two identical race cars and drivers are far apart on a race track. There is no interaction between the cars, so they both must provide the same power to achieve a given speed. However, if one car pulls up close behind the other car, there is an interaction called *draft*. The second car will be pulled to an extent by the lead car. The lead car will therefore require more power to achieve the same speed, since it is pulling the second car and the second car will require less power since it is being pulled by the lead car. So there is a “splitting” of power (energy) of the two interacting race cars. (Keep in mind not to take analogies too literally.)

Now, if we somehow start with a regular periodic arrangement of hydrogen-type atoms that are initially very far apart, and begin pushing the atoms together, the initial quantized energy level will split into a band of discrete energy levels. This effect is shown schematically in Figure 3.2, where the parameter r_0 represents the equilibrium interatomic distance in the crystal. At the equilibrium interatomic distance, there is a band of allowed energies, but within the allowed band, the energies are at discrete levels. The Pauli exclusion principle states that the joining of atoms to form a system (crystal) does not alter the total number of quantum states regardless of size. However, since no two electrons can have the same quantum number, the discrete energy must split into a band of energies in order that each electron can occupy a distinct quantum state.

We have seen previously that, at any energy level, the number of allowed quantum states is relatively small. In order to accommodate all of the electrons in a crystal, then, we must have many energy levels within the allowed band. As an example, suppose that we have a system with 10^{19} one-electron atoms and also suppose that, at the equilibrium interatomic distance, the width of the allowed energy band is 1 eV. For simplicity, we assume that each electron in the system occupies a different energy level and, if the discrete energy states are equidistant, then the energy levels are separated by 10^{-19} eV. This energy difference is extremely small, so that for all practical purposes, we have a quasi-continuous energy distribution through the allowed

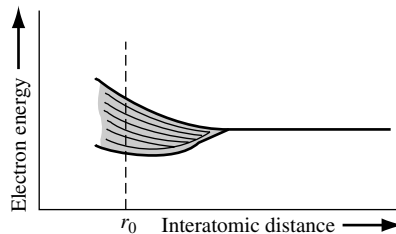


Figure 3.2 | The splitting of an energy state into a band of allowed energies.

energy band. The fact that 10^{-19} eV is a very small difference between two energy states can be seen from the following example.

Objective

EXAMPLE 3.1

To calculate the change in kinetic energy of an electron when the velocity changes by a small value.

Consider an electron traveling at a velocity of 10^7 cm/s. Assume the velocity increases by a value of 1 cm/s. The increase in kinetic energy is given by

$$\Delta E = \frac{1}{2}mv_2^2 - \frac{1}{2}mv_1^2 = \frac{1}{2}m(v_2^2 - v_1^2)$$

Let $v_2 = v_1 + \Delta v$. Then

$$v_2^2 = (v_1 + \Delta v)^2 = v_1^2 + 2v_1\Delta v + (\Delta v)^2$$

But $\Delta v \ll v_1$, so we have that

$$\Delta E \approx \frac{1}{2}m(2v_1\Delta v) = mv_1\Delta v$$

■ Solution

Substituting the number into this equation, we obtain

$$\Delta E = (9.11 \times 10^{-31})(10^5)(0.01) = 9.11 \times 10^{-28} \text{ J}$$

which may be converted to units of electron volts as

$$\Delta E = \frac{9.11 \times 10^{-28}}{1.6 \times 10^{-19}} = 5.7 \times 10^{-9} \text{ eV}$$

■ Comment

A change in velocity of 1 cm/s compared with 10^7 cm/s results in a change in energy of 5.7×10^{-9} eV, which is orders of magnitude larger than the change in energy of 10^{-19} eV between energy states in the allowed energy band. This example serves to demonstrate that a difference in adjacent energy states of 10^{-19} eV is indeed very small, so that the discrete energies within an allowed band may be treated as a quasi-continuous distribution.

Consider again a regular periodic arrangement of atoms, in which each atom now contains more than one electron. Suppose the atom in this imaginary crystal contains electrons up through the $n = 3$ energy level. If the atoms are initially very far apart, the electrons in adjacent atoms will not interact and will occupy the discrete energy levels. If these atoms are brought closer together, the outermost electrons in the $n = 3$ energy shell will begin to interact initially, so that this discrete energy level will split into a band of allowed energies. If the atoms continue to move closer together, the electrons in the $n = 2$ shell may begin to interact and will also split into a band of allowed energies. Finally, if the atoms become sufficiently close together, the innermost electrons in the $n = 1$ level may interact, so that this energy level may also split into a band of allowed energies. The splitting of these discrete energy levels is

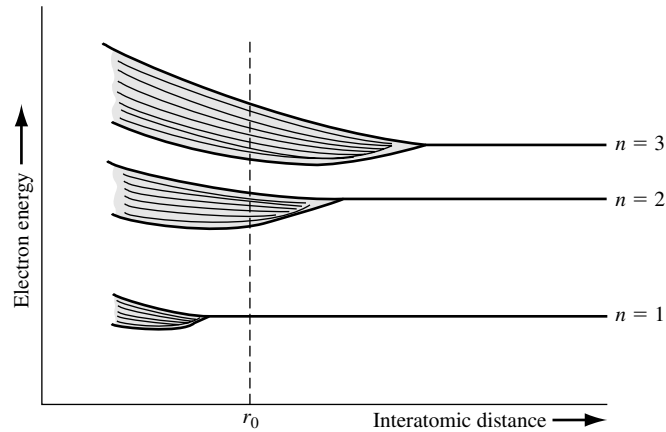


Figure 3.3 | Schematic showing the splitting of three energy states into allowed bands of energies.

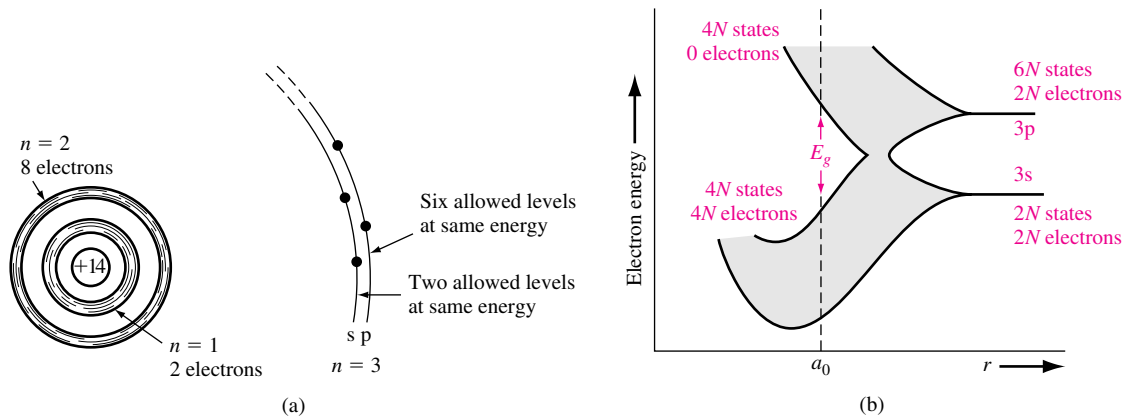


Figure 3.4 | (a) Schematic of an isolated silicon atom. (b) The splitting of the 3s and 3p states of silicon into the allowed and forbidden energy bands. (From Shockley [5].)

qualitatively shown in Figure 3.3. If the equilibrium interatomic distance is r_0 , then we have bands of allowed energies that the electrons may occupy separated by bands of forbidden energies. This energy-band splitting and the formation of allowed and forbidden bands is the energy-band theory of single-crystal materials.

The actual band splitting in a crystal is much more complicated than indicated in Figure 3.3. A schematic representation of an isolated silicon atom is shown in Figure 3.4a. Ten of the fourteen silicon atom electrons occupy deep-lying energy levels close to the nucleus. The four remaining valence electrons are relatively weakly bound and are the electrons involved in chemical reactions. Figure 3.4b shows the band splitting of silicon. We need only consider the $n = 3$ level for the valence electrons, since the first two energy shells are completely full and are tightly bound to the nucleus. The

3s state corresponds to $n = 3$ and $l = 0$ and contains two quantum states per atom. This state will contain two electrons at $T = 0$ K. The 3p state corresponds to $n = 3$ and $l = 1$ and contains six quantum states per atom. This state will contain the remaining two electrons in the individual silicon atom.

As the interatomic distance decreases, the 3s and 3p states interact and overlap. At the equilibrium interatomic distance, the bands have again split, but now four quantum states per atom are in the lower band and four quantum states per atom are in the upper band. At absolute zero degrees, electrons are in the lowest energy state, so that all states in the lower band (the valence band) will be full and all states in the upper band (the conduction band) will be empty. The bandgap energy E_g between the top of the valence band and the bottom of the conduction band is the width of the forbidden energy band.

We have discussed qualitatively how and why bands of allowed and forbidden energies are formed in a crystal. The formation of these energy bands is directly related to the electrical characteristics of the crystal, as we will see later in our discussion.

*3.1.2 The Kronig–Penney Model

In the previous section, we discussed qualitatively the spitting of allowed electron energies as atoms are brought together to form a crystal. The concept of allowed and forbidden energy bands can be developed more rigorously by considering quantum mechanics and Schrodinger's wave equation. It may be easy for the reader to "get lost" in the following derivation, but the result forms the basis for the energy-band theory of semiconductors.

The potential function of a single, noninteracting, one-electron atom is shown in Figure 3.5a. Also indicated on the figure are the discrete energy levels allowed for the electron. Figure 3.5b shows the same type of potential function for the case when several atoms are in close proximity arranged in a one-dimensional array. The potential functions of adjacent atoms overlap, and the net potential function for this case is shown in Figure 3.5c. It is this potential function we would need to use in Schrodinger's wave equation to model a one-dimensional single-crystal material.

The solution to Schrodinger's wave equation, for this one-dimensional single-crystal lattice, is made more tractable by considering a simpler potential function. Figure 3.6 is the one-dimensional Kronig–Penney model of the periodic potential function, which is used to represent a one-dimensional single-crystal lattice. We need to solve Schrodinger's wave equation in each region. As with previous quantum mechanical problems, the more interesting solution occurs for the case when $E < V_0$, which corresponds to a particle being bound within the crystal. The electrons are contained in the potential wells, but we have the possibility of tunneling between wells. The Kronig–Penney model is an idealized periodic potential representing a one-dimensional single crystal, but the results will illustrate many of the important features of the quantum behavior of electrons in a periodic lattice.

To obtain the solution to Schrodinger's wave equation, we make use of a mathematical theorem by Bloch. The theorem states that all one-electron wave functions,

*Indicates sections that can be skipped without loss of continuity.

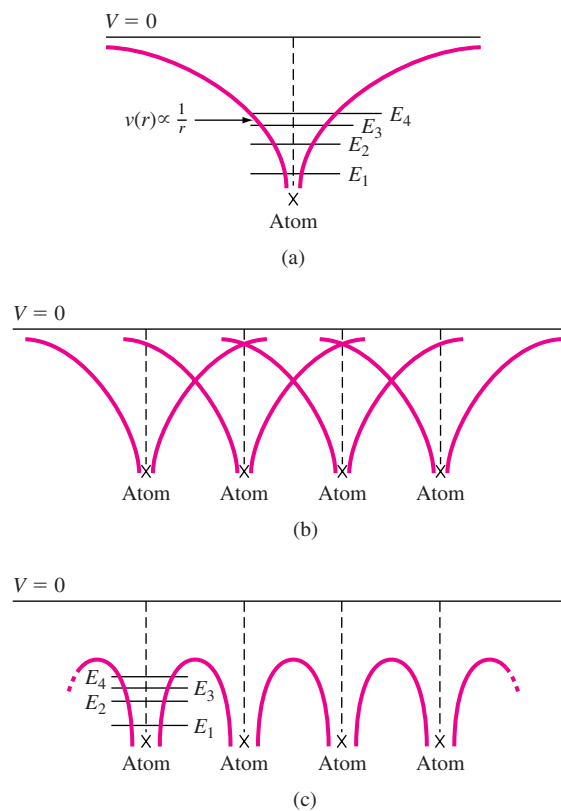


Figure 3.5 | (a) Potential function of a single isolated atom. (b) Overlapping potential functions of adjacent atoms. (c) Net potential function of a one-dimensional single crystal.

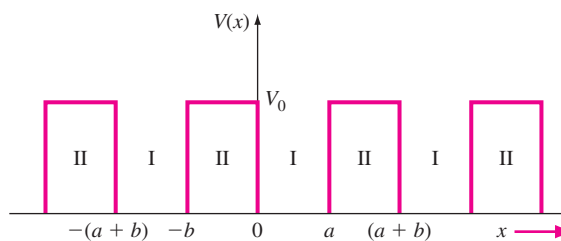


Figure 3.6 | The one-dimensional periodic potential function of the Kronig-Penney model.

for problems involving periodically varying potential energy functions, must be of the form

$$\psi(x) = u(x)e^{jkx} \quad (3.1)$$

The parameter k is called a constant of motion and will be considered in more detail as we develop the theory. The function $u(x)$ is a periodic function with period $(a + b)$.

We stated in Chapter 2 that the total solution to the wave equation is the product of the time-independent solution and the time-dependent solution, or

$$\Psi(x, t) = \psi(x)\phi(t) = u(x)e^{jkx} \cdot e^{-j(E/\hbar)t} \quad (3.2)$$

which may be written as

$$\Psi(x, t) = u(x)e^{j(kx - (E/\hbar)t)} \quad (3.3)$$

This traveling-wave solution represents the motion of an electron in a single-crystal material. The amplitude of the traveling wave is a periodic function and the parameter k is also referred to as a wave number.

We can now begin to determine a relation between the parameter k , the total energy E , and the potential V_0 . If we consider region I in Figure 3.6 ($0 < x < a$) in which $V(x) = 0$, take the second derivative of Equation (3.1), and substitute this result into the time-independent Schrodinger's wave equation given by Equation (2.13), we obtain the relation

$$\frac{d^2u_1(x)}{dx^2} + 2jk\frac{du_1(x)}{dx} - (k^2 - \alpha^2)u_1(x) = 0 \quad (3.4)$$

The function $u_1(x)$ is the amplitude of the wave function in region I and the parameter α is defined as

$$\alpha^2 = \frac{2mE}{\hbar^2} \quad (3.5)$$

Consider now a specific region II, $-b < x < 0$, in which $V(x) = V_0$, and apply Schrodinger's wave equation. We obtain the relation

$$\frac{d^2u_2(x)}{dx^2} + 2jk\frac{du_2(x)}{dx} - \left(k^2 - \alpha^2 + \frac{2mV_0}{\hbar^2}\right)u_2(x) = 0 \quad (3.6)$$

where $u_2(x)$ is the amplitude of the wave function in region II. We may define

$$\frac{2m}{\hbar^2}(E - V_0) = \alpha^2 - \frac{2mV_0}{\hbar^2} = \beta^2 \quad (3.7)$$

so that Equation (3.6) may be written as

$$\frac{d^2u_2(x)}{dx^2} + 2jk\frac{du_2(x)}{dx} - (k^2 - \beta^2)u_2(x) = 0 \quad (3.8)$$

Note that from Equation (3.7), if $E > V_0$, the parameter β is real, whereas if $E < V_0$, then β is imaginary.

The solution to Equation (3.4), for region I, is of the form

$$u_1(x) = Ae^{j(\alpha-k)x} + Be^{-j(\alpha+k)x} \quad \text{for } (0 < x < a) \quad (3.9)$$

and the solution to Equation (3.8), for region II, is of the form

$$u_2(x) = Ce^{j(\beta-k)x} + De^{-j(\beta+k)x} \quad \text{for } (-b < x < 0) \quad (3.10)$$

Since the potential function $V(x)$ is everywhere finite, both the wave function $\psi(x)$ and its first derivative $\partial\psi(x)/\partial x$ must be continuous. This continuity condition implies that the wave amplitude function $u(x)$ and its first derivative $\partial u(x)/\partial x$ must also be continuous.

If we consider the boundary at $x = 0$ and apply the continuity condition to the wave amplitude, we have

$$u_1(0) = u_2(0) \quad (3.11)$$

Substituting Equations (3.9) and (3.10) into Equation (3.11), we obtain

$$A + B - C - D = 0 \quad (3.12)$$

Now applying the condition that

$$\left. \frac{du_1}{dx} \right|_{x=0} = \left. \frac{du_2}{dx} \right|_{x=0} \quad (3.13)$$

we obtain

$$(\alpha - k)A - (\alpha + k)B - (\beta - k)C + (\beta + k)D = 0 \quad (3.14)$$

We have considered region I as $0 < x < a$ and region II as $-b < x < 0$. The periodicity and the continuity condition mean that the function u_1 , as $x \rightarrow a$, is equal to the function u_2 , as $x \rightarrow -b$. This condition may be written as

$$u_1(a) = u_2(-b) \quad (3.15)$$

Applying the solutions for $u_1(x)$ and $u_2(x)$ to the boundary condition in Equation (3.15) yields

$$Ae^{j(\alpha-k)a} + Be^{-j(\alpha+k)a} - Ce^{-j(\beta-k)b} - De^{j(\beta+k)b} = 0 \quad (3.16)$$

The last boundary condition is

$$\left. \frac{du_1}{dx} \right|_{x=a} = \left. \frac{du_2}{dx} \right|_{x=-b} \quad (3.17)$$

which gives

$$\begin{aligned} (\alpha - k)Ae^{j(\alpha-k)a} - (\alpha + k)Be^{-j(\alpha+k)a} - (\beta - k)Ce^{-j(\beta-k)b} \\ + (\beta + k)De^{j(\beta+k)b} = 0 \end{aligned} \quad (3.18)$$

We now have four homogeneous equations, Equations (3.12), (3.14), (3.16), and (3.18), with four unknowns as a result of applying the four boundary conditions. In a set of simultaneous, linear, homogeneous equations, there is a nontrivial solution if,

and only if, the determinant of the coefficients is zero. In our case, the coefficients in question are the coefficients of the parameters A , B , C , and D .

The evaluation of this determinant is extremely laborious and will not be considered in detail. The result is

$$\frac{-(\alpha^2 + \beta^2)}{2\alpha\beta}(\sin \alpha a)(\sin \beta b) + (\cos \alpha a)(\cos \beta b) = \cos k(a + b) \quad (3.19)$$

Equation (3.19) relates the parameter k to the total energy E (through the parameter α) and the potential function V_0 (through the parameter β).

As we mentioned, the more interesting solutions occur for $E < V_0$, which applies to the electron bound within the crystal. From Equation (3.7), the parameter β is then an imaginary quantity. We may define

$$\beta = j\gamma \quad (3.20)$$

where γ is a real quantity. Equation (3.19) can be written in terms of γ as

$$\frac{\gamma^2 - \alpha^2}{2\alpha\gamma}(\sin \alpha a)(\sinh \gamma b) + (\cos \alpha a)(\cosh \gamma b) = \cos k(a + b) \quad (3.21)$$

Equation (3.21) does not lend itself to an analytical solution, but must be solved using numerical or graphical techniques to obtain the relation between k , E , and V_0 . The solution of Schrodinger's wave equation for a single bound particle resulted in discrete allowed energies. The solution of Equation (3.21) will result in a band of allowed energies.

To obtain an equation that is more susceptible to a graphical solution and thus will illustrate the nature of the results, let the potential barrier width $b \rightarrow 0$ and the barrier height $V_0 \rightarrow \infty$, but such that the product bV_0 remains finite. Equation (3.21) then reduces to

$$\left(\frac{mV_0ba}{\hbar^2}\right) \frac{\sin \alpha a}{\alpha a} + \cos \alpha a = \cos ka \quad (3.22)$$

We may define a parameter P' as

$$P' = \frac{mV_0ba}{\hbar^2} \quad (3.23)$$

Then, finally, we have the relation

$$P' \frac{\sin \alpha a}{\alpha a} + \cos \alpha a = \cos ka \quad (3.24)$$

Equation (3.24) again gives the relation between the parameter k , total energy E (through the parameter α), and the potential barrier bV_0 . We may note that Equation (3.24) is not a solution of Schrodinger's wave equation but gives the conditions for which Schrodinger's wave equation will have a solution. If we assume the crystal is infinitely large, then k in Equation (3.24) can assume a continuum of values and must be real.

3.1.3 The k -Space Diagram

To begin to understand the nature of the solution, initially consider the special case for which $V_0 = 0$. In this case $P' = 0$, which corresponds to a free particle since there are no potential barriers. From Equation (3.24), we have that

$$\cos \alpha a = \cos ka \quad (3.25)$$

or

$$\alpha = k \quad (3.26)$$

Since the potential is equal to zero, the total energy E is equal to the kinetic energy, so that, from Equation (3.5), Equation (3.26) may be written as

$$\alpha = \sqrt{\frac{2mE}{\hbar^2}} = \sqrt{\frac{2m(\frac{1}{2}mv^2)}{\hbar^2}} = \frac{p}{\hbar} = k \quad (3.27)$$

where p is the particle momentum. The constant of the motion parameter k is related to the particle momentum for the free electron. The parameter k is also referred to as a wave number.

We can also relate the energy and momentum as

$$E = \frac{p^2}{2m} = \frac{k^2 \hbar^2}{2m} \quad (3.28)$$

Figure 3.7 shows the parabolic relation of Equation (3.28) between the energy E and momentum p for the free particle. Since the momentum and wave number are linearly related, Figure 3.7 is also the E versus k curve for the free particle.

We now want to consider the relation between E and k from Equation (3.24) for the particle in the single-crystal lattice. As the parameter P' increases, the particle becomes more tightly bound to the potential well or atom. We may define the left side of Equation (3.24) to be a function $f(\alpha a)$, so that

$$f(\alpha a) = P' \frac{\sin \alpha a}{\alpha a} + \cos \alpha a \quad (3.29)$$

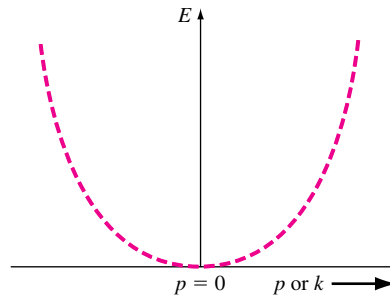


Figure 3.7 | The parabolic E versus k curve for the free electron.

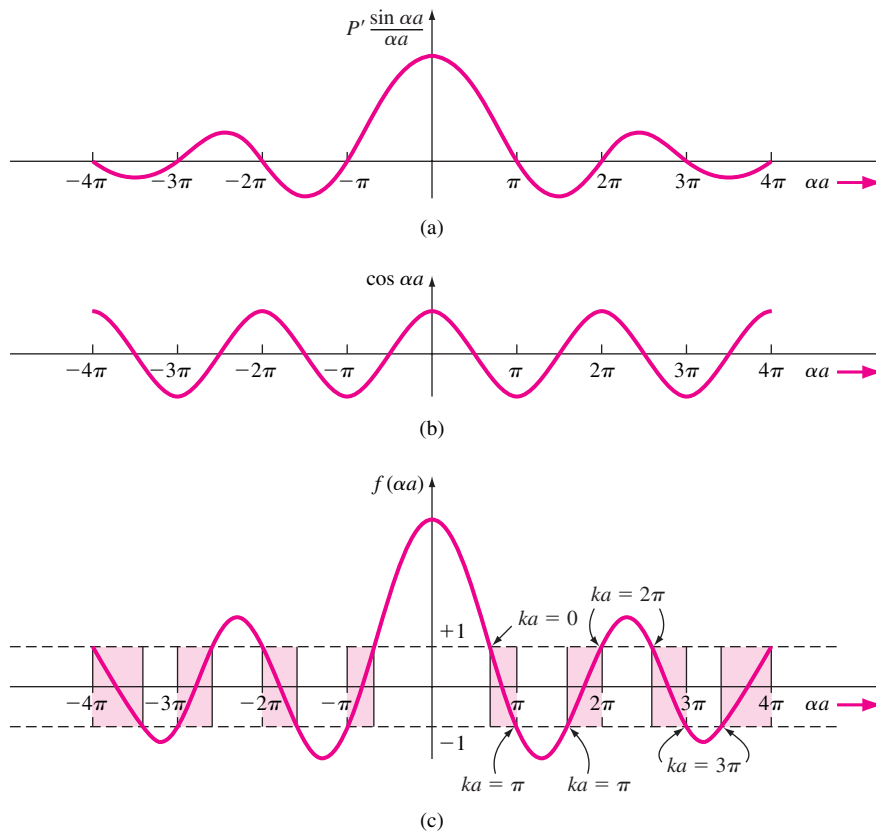


Figure 3.8 | A plot of (a) the first term in Equation (3.29), (b) the second term in Equation (3.29), and (c) the entire $f(\alpha a)$ function. The shaded areas show the allowed values of (αa) corresponding to real values of k .

Figure 3.8a is a plot of the first term of Equation (3.29) versus αa . Figure 3.8b shows a plot of the $\cos \alpha a$ term and Figure 3.8c is the sum of the two terms, or $f(\alpha a)$.

Now from Equation (3.24), we also have that

$$f(\alpha a) = \cos ka \quad (3.30)$$

For Equation (3.30) to be valid, the allowed values of the $f(\alpha a)$ function must be bounded between $+1$ and -1 . Figure 3.8c shows the allowed values of $f(\alpha a)$ and the allowed values of αa in the shaded areas. Also shown on the figure are the values of ka from the right side of Equation (3.30) which correspond to the allowed values of $f(\alpha a)$.

The parameter α is related to the total energy E of the particle through Equation (3.5), which is $\alpha^2 = 2mE/\hbar^2$. A plot of the energy E of the particle as a function of the wave number k can be generated from Figure 3.8c. Figure 3.9 shows this plot and shows the concept of allowed energy bands for the particle propagating in the

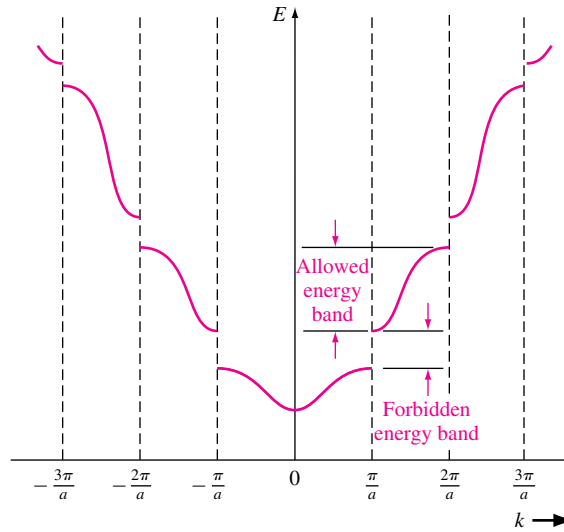


Figure 3.9 | The E versus k diagram generated from Figure 3.8. The allowed energy bands and forbidden energy bandgaps are indicated.

crystal lattice. Since the energy E has discontinuities, we also have the concept of forbidden energies for the particles in the crystal.

EXAMPLE 3.2

Objective

To determine the lowest allowed energy bandwidth.

Assume that the coefficient $P' = 10$ and that the potential width $a = 5 \text{ \AA}$.

■ Solution

To find the lowest allowed energy bandwidth, we need to find the difference in αa values as ka changes from 0 to π (see Figure 3.8c). For $ka = 0$, Equation (3.29) becomes

$$1 = 10 \frac{\sin \alpha a}{\alpha a} + \cos \alpha a$$

By trial and error, we find $\alpha a = 2.628$ rad. We see that for $ka = \pi$, $\alpha a = \pi$.

For $\alpha a = \pi$, we have

$$\sqrt{\frac{2mE_2}{\hbar^2}} \cdot a = \pi$$

or

$$E_2 = \frac{\pi^2 \hbar^2}{2ma^2} = \frac{\pi^2 (1.054 \times 10^{-34})^2}{2(9.11 \times 10^{-31})(5 \times 10^{-10})^2} = 2.407 \times 10^{-19} \text{ J} = 1.50 \text{ eV}$$

For $\alpha a = 2.628$, we find that $E_1 = 1.68 \times 10^{-19} \text{ J} = 1.053 \text{ eV}$. The allowed energy bandwidth is then

$$\Delta E = E_2 - E_1 = 1.50 - 1.053 = 0.447 \text{ eV}$$

■ Comment

We see from Figure 3.8c that, as the energy increases, the widths of the allowed bands increase from this Kronig–Penney model.

TEST YOUR UNDERSTANDING

E3.1 Using the parameters given in Example 3.2, determine the width (in eV) of the forbidden energy band that exists at $ka = \pi$ (see Figure 3.8c). ($\Lambda^{\circ} 6L^{\circ} \tau = \mathcal{E} \nabla \cdot \text{su} \nabla$)

Consider again the right side of Equation (3.24), which is the function $\cos ka$. The cosine function is periodic so that

$$\cos ka = \cos (ka + 2n\pi) = \cos (ka - 2n\pi) \quad (3.31)$$

where n is a positive integer. We may consider Figure 3.9 and displace portions of the curve by 2π . Mathematically, Equation (3.24) is still satisfied. Figure 3.10 shows how various segments of the curve can be displaced by the 2π factor. Figure 3.11 shows the case in which the entire E versus k plot is contained within $-\pi/a < k < \pi/a$. This plot is referred to as a reduced k -space diagram, or a reduced-zero representation.

We noted in Equation (3.27) that for a free electron, the particle momentum and the wave number k are related by $p = \hbar k$. Given the similarity between the free

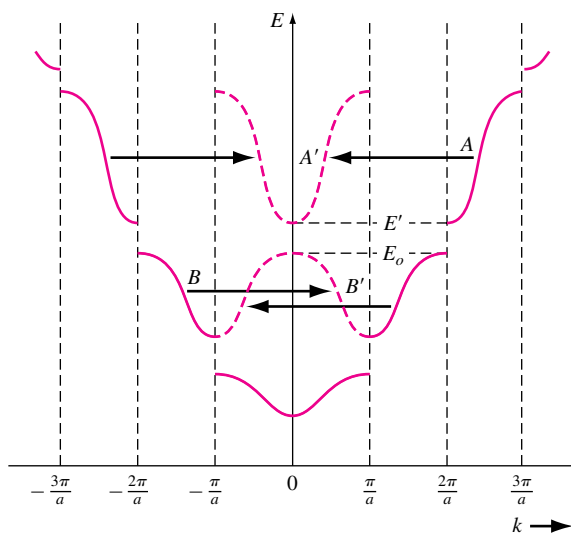


Figure 3.10 | The E versus k diagram showing 2π displacements of several sections of allowed energy bands.

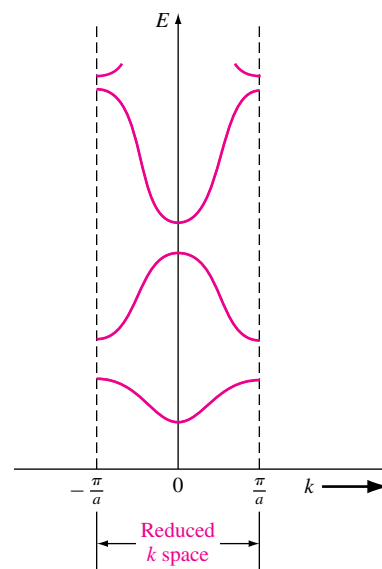


Figure 3.11 | The E versus k diagram in the reduced-zone representation.

electron solution and the results of the single crystal shown in Figure 3.9, the parameter $\hbar k$ in a single crystal is referred to as the *crystal momentum*. This parameter is not the actual momentum of the electron in the crystal, but is a constant of the motion that includes the crystal interaction.

We have been considering the Kronig–Penney model, which is a one-dimensional periodic potential function used to model a single-crystal lattice. The principle result of this analysis, so far, is that electrons in the crystal occupy certain allowed energy bands and are excluded from the forbidden energy bands. For real three-dimensional single-crystal materials, a similar energy-band theory exists. We will obtain additional electron properties from the Kronig–Penney model in the next sections.

3.2 | ELECTRICAL CONDUCTION IN SOLIDS

Again, we are eventually interested in determining the current–voltage characteristics of semiconductor devices. We will need to consider electrical conduction in solids as it relates to the band theory we have just developed. Let us begin by considering the motion of electrons in the various allowed energy bands.

3.2.1 The Energy Band and the Bond Model

In Chapter 1, we discussed the covalent bonding of silicon. Figure 3.12 shows a two-dimensional representation of the covalent bonding in a single-crystal silicon lattice. This figure represents silicon at $T = 0$ K in which each silicon atom is surrounded by eight valence electrons that are in their lowest energy state and are directly involved in the covalent bonding. Figure 3.4b represented the splitting of the discrete silicon energy states into bands of allowed energies as the silicon crystal is formed. At $T = 0$ K, the $4N$ states in the lower band, the valence band, are filled with the valence electrons. All of the valence electrons schematically shown in Figure 3.12 are in the valence band. The upper energy band, the conduction band, is completely empty at $T = 0$ K.

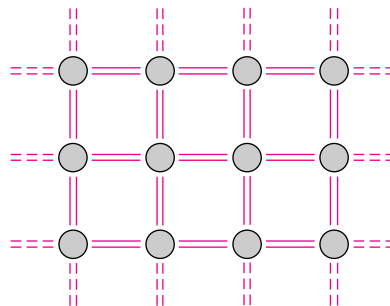


Figure 3.12 | Two-dimensional representation of the covalent bonding in a semiconductor at $T = 0$ K.

As the temperature increases above 0 K, a few valence band electrons may gain enough thermal energy to break the covalent bond and jump into the conduction band. Figure 3.13a shows a two-dimensional representation of this bond-breaking effect and Figure 3.13b, a simple line representation of the energy-band model, shows the same effect.

The semiconductor is neutrally charged. This means that, as the negatively charged electron breaks away from its covalent bonding position, a positively charged “empty state” is created in the original covalent bonding position in the valence band. As the temperature further increases, more covalent bonds are broken, more electrons jump to the conduction band, and more positive “empty states” are created in the valence band.

We can also relate this bond breaking to the E versus k energy bands. Figure 3.14a shows the E versus k diagram of the conduction and valence bands at

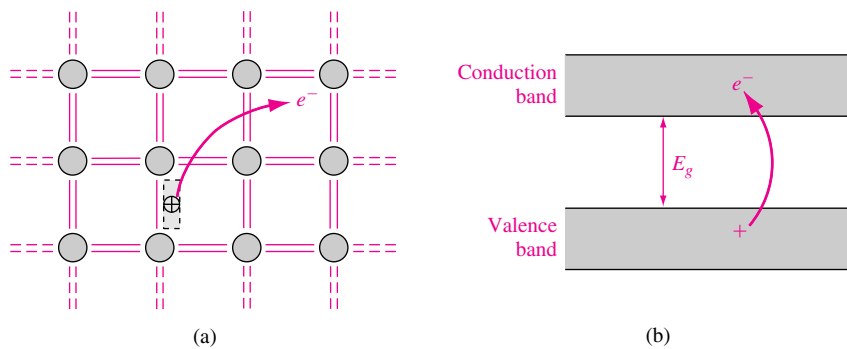


Figure 3.13 | (a) Two-dimensional representation of the breaking of a covalent bond. (b) Corresponding line representation of the energy band and the generation of a negative and positive charge with the breaking of a covalent bond.

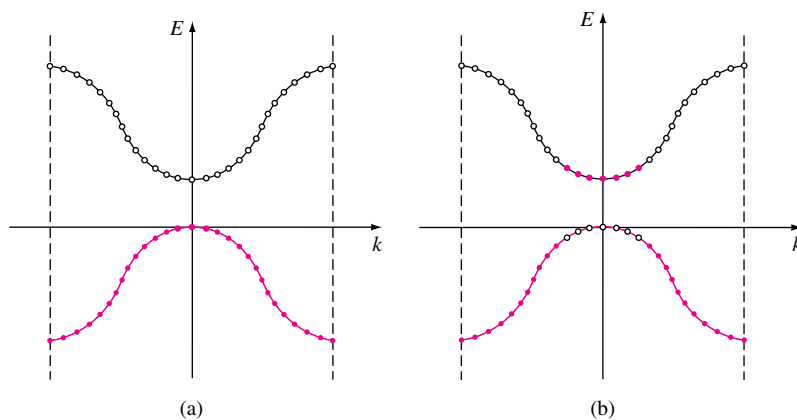


Figure 3.14 | The E versus k diagram of the conduction and valence bands of a semiconductor at (a) $T = 0$ K and (b) $T > 0$ K.

$T = 0$ K. The energy states in the valence band are completely full and the states in the conduction band are empty. Figure 3.14b shows these same bands for $T > 0$ K, in which some electrons have gained enough energy to jump to the conduction band and have left empty states in the valence band. We are assuming at this point that no external forces are applied so the electron and “empty state” distributions are symmetrical with k .

3.2.2 Drift Current

Current is due to the net flow of charge. If we had a collection of positively charged ions with a volume density N (cm^{-3}) and an average drift velocity v_d (cm/s), then the drift current density would be

$$J = qNv_d \quad \text{A/cm}^2 \quad (3.32)$$

If, instead of considering the average drift velocity, we considered the individual ion velocities, then we could write the drift current density as

$$J = q \sum_{i=1}^N v_i \quad (3.33)$$

where v_i is the velocity of the i th ion. The summation in Equation (3.33) is taken over a unit volume so that the current density J is still in units of A/cm^2 .

Since electrons are charged particles, a net drift of electrons in the conduction band will give rise to a current. The electron distribution in the conduction band, as shown in Figure 3.14b, is an even function of k when no external force is applied. Recall that k for a free electron is related to momentum so that, since there are as many electrons with a $+|k|$ value as there are with a $-|k|$ value, the net drift current density due to these electrons is zero. This result is certainly expected since there is no externally applied force.

If a force is applied to a particle and the particle moves, it must gain energy. This effect is expressed as

$$dE = F dx = Fv dt \quad (3.34)$$

where F is the applied force, dx is the differential distance the particle moves, v is the velocity, and dE is the increase in energy. If an external force is applied to the electrons in the conduction band, there are empty energy states into which the electrons can move; therefore, because of the external force, electrons can gain energy and a net momentum. The electron distribution in the conduction band may look like that shown in Figure 3.15, which implies that the electrons have gained a net momentum.

We may write the drift current density due to the motion of electrons as

$$J = -e \sum_{i=1}^n v_i \quad (3.35)$$

where e is the magnitude of the electronic charge and n is the number of electrons per unit volume in the conduction band. Again, the summation is taken over a unit

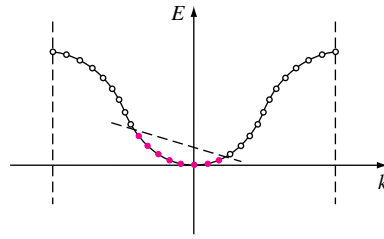


Figure 3.15 | The asymmetric distribution of electrons in the E versus k diagram when an external force is applied.

volume so the current density is A/cm^2 . We may note from Equation (3.35) that the current is directly related to the electron velocity; that is, the current is related to how well the electron can move in the crystal.

3.2.3 Electron Effective Mass

The movement of an electron in a lattice will, in general, be different from that of an electron in free space. In addition to an externally applied force, there are internal forces in the crystal due to positively charged ions or protons and negatively charged electrons, which will influence the motion of electrons in the lattice. We can write

$$F_{\text{total}} = F_{\text{ext}} + F_{\text{int}} = ma \quad (3.36)$$

where F_{total} , F_{ext} , and F_{int} are the total force, the externally applied force, and the internal forces, respectively, acting on a particle in a crystal. The parameter a is the acceleration and m is the rest mass of the particle.

Since it is difficult to take into account all of the internal forces, we will write the equation

$$F_{\text{ext}} = m^*a \quad (3.37)$$

where the acceleration a is now directly related to the external force. The parameter m^* , called the *effective mass*, takes into account the particle mass and also takes into account the effect of the internal forces.

To use an analogy for the effective mass concept, consider the difference in motion between a glass marble in a container filled with water and in a container filled with oil. In general, the marble will drop through the water at a faster rate than through the oil. The external force in this example is the gravitational force and the internal forces are related to the viscosity of the liquids. Because of the difference in motion of the marble in these two cases, the mass of the marble would appear to be different in water than in oil. (As with any analogy, we must be careful not to be too literal.)

We can also relate the effective mass of an electron in a crystal to the E versus k curves, such as was shown in Figure 3.11. In a semiconductor material, we will be dealing with allowed energy bands that are almost empty of electrons and other energy bands that are almost full of electrons.

To begin, consider the case of a free electron whose E versus k curve was shown in Figure 3.7. Recalling Equation (3.28), the energy and momentum are related by $E = p^2/2m = \hbar^2 k^2/2m$, where m is the mass of the electron. The momentum and wave number k are related by $p = \hbar k$. If we take the derivative of Equation (3.28) with respect to k , we obtain

$$\frac{dE}{dk} = \frac{\hbar^2 k}{m} = \frac{\hbar p}{m} \quad (3.38)$$

Relating momentum to velocity, Equation (3.38) can be written as

$$\frac{1}{\hbar} \frac{dE}{dk} = \frac{p}{m} = v \quad (3.39)$$

where v is the velocity of the particle. The first derivative of E with respect to k is related to the velocity of the particle.

If we now take the second derivative of E with respect to k , we have

$$\frac{d^2 E}{dk^2} = \frac{\hbar^2}{m} \quad (3.40)$$

We may rewrite Equation (3.40) as

$$\frac{1}{\hbar^2} \frac{d^2 E}{dk^2} = \frac{1}{m} \quad (3.41)$$

The second derivative of E with respect to k is inversely proportional to the mass of the particle. For the case of a free electron, the mass is a constant (nonrelativistic effect), so the second derivative function is a constant. We may also note from Figure 3.7 that $d^2 E/dk^2$ is a positive quantity, which implies that the mass of the electron is also a positive quantity.

If we apply an electric field to the free electron and use Newton's classical equation of motion, we can write

$$F = ma = -eE \quad (3.42)$$

where a is the acceleration, E is the applied electric field, and e is the magnitude of the electronic charge. Solving for the acceleration, we have

$$a = \frac{-eE}{m} \quad (3.43)$$

The motion of the free electron is in the opposite direction to the applied electric field because of the negative charge.

We may now apply the results to the electron in the bottom of an allowed energy band. Consider the allowed energy band in Figure 3.16a. The energy near the bottom of this energy band may be approximated by a parabola, just as that of a free particle. We may write

$$E - E_c = C_1(k)^2 \quad (3.44)$$

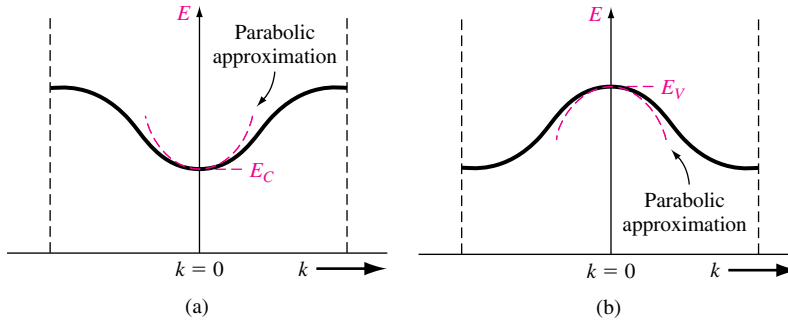


Figure 3.16 | (a) The conduction band in reduced k space, and the parabolic approximation. (b) The valence band in reduced k space, and the parabolic approximation.

The energy E_c is the energy at the bottom of the band. Since $E > E_c$, the parameter C_1 is a positive quantity.

Taking the second derivative of E with respect to k from Equation (3.44), we obtain

$$\frac{d^2 E}{dk^2} = 2C_1 \quad (3.45)$$

We may put Equation (3.45) in the form

$$\frac{1}{\hbar^2} \frac{d^2 E}{dk^2} = \frac{2C_1}{\hbar^2} \quad (3.46)$$

Comparing Equation (3.46) with Equation (3.41), we may equate $\hbar^2/2C_1$ to the mass of the particle. However, the curvature of the curve in Figure 3.16a will not, in general, be the same as the curvature of the free-particle curve. We may write

$$\frac{1}{\hbar^2} \frac{d^2 E}{dk^2} = \frac{2C_1}{\hbar^2} = \frac{1}{m^*} \quad (3.47)$$

where m^* is called the effective mass. Since $C_1 > 0$, we have that $m^* > 0$ also.

The effective mass is a parameter that relates the quantum mechanical results to the classical force equations. In most instances, the electron in the bottom of the conduction band can be thought of as a classical particle whose motion can be modeled by Newtonian mechanics, provided that the internal forces and quantum mechanical properties are taken into account through the effective mass. If we apply an electric field to the electron in the bottom of the allowed energy band, we may write the acceleration as

$$a = \frac{-eE}{m_n^*} \quad (3.48)$$

where m_n^* is the effective mass of the electron. The effective mass m_n^* of the electron near the bottom of the conduction band is a constant.

3.2.4 Concept of the Hole

In considering the two-dimensional representation of the covalent bonding shown in Figure 3.13a, a positively charged “empty state” was created when a valence electron was elevated into the conduction band. For $T > 0$ K, all valence electrons may gain thermal energy; if a valence electron gains a small amount of thermal energy, it may hop into the empty state. The movement of a valence electron into the empty state is equivalent to the movement of the positively charged empty state itself. Figure 3.17 shows the movement of valence electrons in the crystal alternately filling one empty state and creating a new empty state, a motion equivalent to a positive charge moving in the valence band. The crystal now has a second equally important charge carrier that can give rise to a current. This charge carrier is called a *hole* and, as we will see, can also be thought of as a classical particle whose motion can be modeled using Newtonian mechanics.

The drift current density due to electrons in the valence band, such as shown in Figure 3.14b, can be written as

$$J = -e \sum_{i(\text{filled})} v_i \quad (3.49)$$

where the summation extends over all filled states. This summation is inconvenient since it extends over a nearly full valence band and takes into account a very large number of states. We may rewrite Equation (3.49) in the form

$$J = -e \sum_{i(\text{total})} v_i + e \sum_{i(\text{empty})} v_i \quad (3.50)$$

If we consider a band that is totally full, all available states are occupied by electrons. The individual electrons can be thought of as moving with a velocity as given by Equation (3.39):

$$v(E) = \left(\frac{1}{\hbar} \right) \left(\frac{dE}{dk} \right) \quad (3.39)$$

The band is symmetric in k and each state is occupied so that, for every electron with a velocity $|v|$, there is a corresponding electron with a velocity $-|v|$. Since the band is full, the distribution of electrons with respect to k cannot be changed with an externally applied force. The net drift current density generated from a completely full

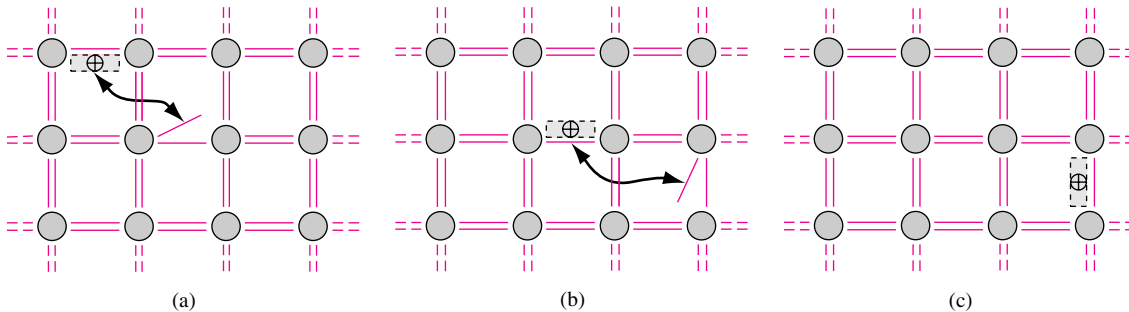


Figure 3.17 | Visualization of the movement of a hole in a semiconductor.

band, then, is zero, or

$$-e \sum_{i(\text{total})} v_i \equiv 0 \quad (3.51)$$

We can now write the drift current density from Equation (3.50) for an almost full band as

$$J = +e \sum_{i(\text{empty})} v_i \quad (3.52)$$

where the v_i in the summation is the

$$v(E) = \left(\frac{1}{\hbar} \right) \left(\frac{dE}{dk} \right)$$

associated with the empty state. Equation (3.52) is entirely equivalent to placing a positively charged particle in the empty states and assuming all other states in the band are empty, or neutrally charged. This concept is shown in Figure 3.18. Figure 3.18a shows the valence band with the conventional electron-filled states and empty states, while Figure 3.18b shows the new concept of positive charges occupying the original empty states. This concept is consistent with the discussion of the positively charged “empty state” in the valence band as shown in Figure 3.17.

The v_i in the summation of Equation (3.52) is related to how well this positively charged particle moves in the semiconductor. Now consider an electron near the top of the allowed energy band shown in Figure 3.16b. The energy near the top of the allowed energy band may again be approximated by a parabola so that we may write

$$(E - E_v) = -C_2(k)^2 \quad (3.53)$$

The energy E_v is the energy at the top of the energy band. Since $E < E_v$ for electrons in this band, then the parameter C_2 must be a positive quantity.

Taking the second derivative of E with respect to k from Equation (3.53), we obtain

$$\frac{d^2 E}{dk^2} = -2C_2 \quad (3.54)$$

We may rearrange this equation so that

$$\frac{1}{\hbar^2} \frac{d^2 E}{dk^2} = \frac{-2C_2}{\hbar^2} \quad (3.55)$$

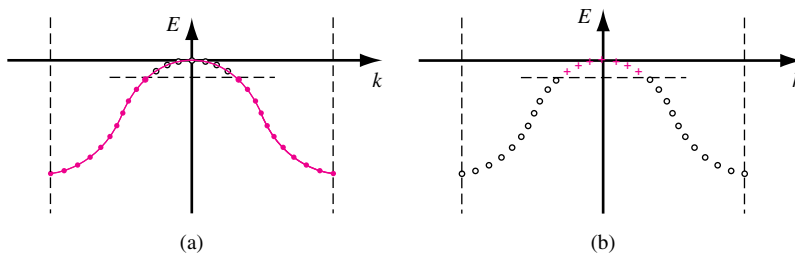


Figure 3.18 | (a) Valence band with conventional electron-filled states and empty states. (b) Concept of positive charges occupying the original empty states.

Comparing Equation (3.55) with Equation (3.41), we may write

$$\frac{1}{\hbar^2} \frac{d^2 E}{dk^2} = \frac{-2C_2}{\hbar^2} = \frac{1}{m^*} \quad (3.56)$$

where m^* is again an effective mass. We have argued that C_2 is a positive quantity, which now implies that m^* is a negative quantity. An electron moving near the top of an allowed energy band behaves as if it has a negative mass.

We must keep in mind that the effective mass parameter is used to relate quantum mechanics and classical mechanics. The attempt to relate these two theories leads to this strange result of a negative effective mass. However, we must recall that solutions to Schrodinger's wave equation also led to results that contradicted classical mechanics. The negative effective mass is another such example.

In discussing the concept of effective mass in the last section, we used an analogy of marbles moving through two liquids. Now consider placing an ice cube in the center of a container filled with water: the ice cube will move upward toward the surface in a direction opposite to the gravitational force. The ice cube appears to have a negative effective mass since its acceleration is opposite to the external force. The effective mass parameter takes into account all internal forces acting on the particle.

If we again consider an electron near the top of an allowed energy band and use Newton's force equation for an applied electric field, we will have

$$F = m^* a = -eE \quad (3.57)$$

However, m^* is now a negative quantity, so we may write

$$a = \frac{-eE}{-|m^*|} = \frac{+eE}{|m^*|} \quad (3.58)$$

An electron moving near the top of an allowed energy band moves in the same direction as the applied electric field.

The net motion of electrons in a nearly full band can be described by considering just the empty states, provided that a positive electronic charge is associated with each state and that the negative of m^* from Equation (3.56) is associated with each state. We now can model this band as having particles with a positive electronic charge and a positive effective mass. The density of these particles in the valence band is the same as the density of empty electronic energy states. This new particle is the *hole*. The hole, then, has a positive effective mass denoted by m_p^* and a positive electronic charge, so it will move in the same direction as an applied field.

3.2.5 Metals, Insulators, and Semiconductors

Each crystal has its own energy-band structure. We noted that the splitting of the energy states in silicon, for example, to form the valence and conduction bands, was complex. Complex band splitting occurs in other crystals, leading to large variations in band structures between various solids and to a wide range of electrical characteristics observed in these various materials. We can qualitatively begin to understand

some basic differences in electrical characteristics caused by variations in band structure by considering some simplified energy bands.

There are several possible energy-band conditions to consider. Figure 3.19a shows an allowed energy band that is completely empty of electrons. If an electric field is applied, there are no particles to move, so there will be no current. Figure 3.19b shows another allowed energy band whose energy states are completely full of electrons. We argued in the previous section that a completely full energy band will also not give rise to a current. A material that has energy bands either completely empty or completely full is an insulator. The resistivity of an insulator is very large or, conversely, the conductivity of an insulator is very small. There are essentially no charged particles that can contribute to a drift current. Figure 3.19c shows a simplified energy-band diagram of an insulator. The bandgap energy E_g of an insulator is usually on the order of 3.5 to 6 eV or larger, so that at room temperature, there are essentially no electrons in the conduction band and the valence band remains completely full. There are very few thermally generated electrons and holes in an insulator.

Figure 3.20a shows an energy band with relatively few electrons near the bottom of the band. Now, if an electric field is applied, the electrons can gain energy, move to

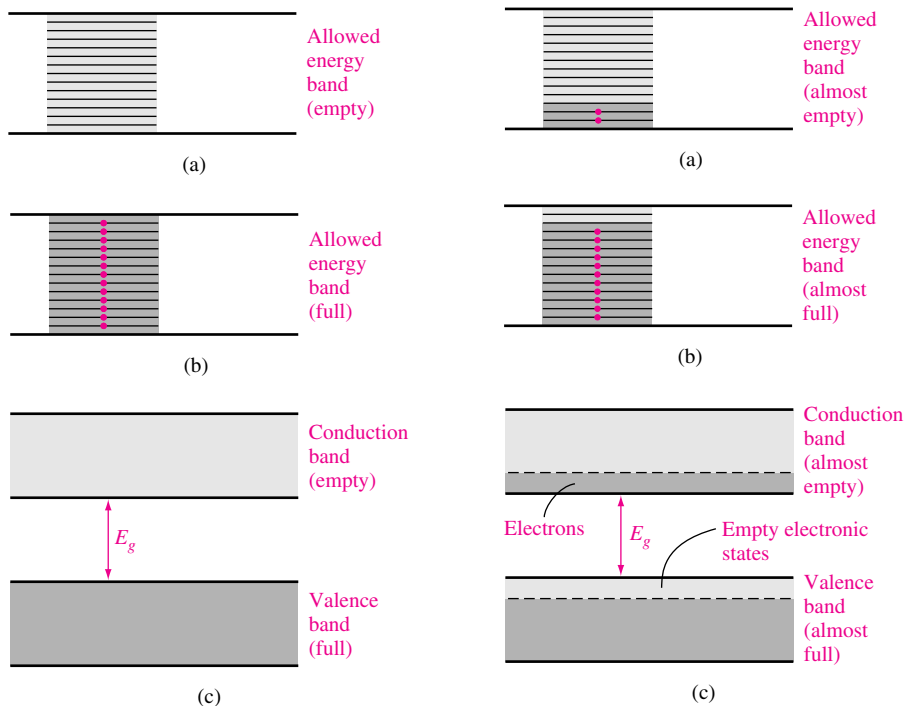


Figure 3.19 | Allowed energy bands showing (a) an empty band, (b) a completely full band, and (c) the bandgap energy between the two allowed bands.

Figure 3.20 | Allowed energy bands showing (a) an almost empty band, (b) an almost full band, and (c) the bandgap energy between the two allowed bands.

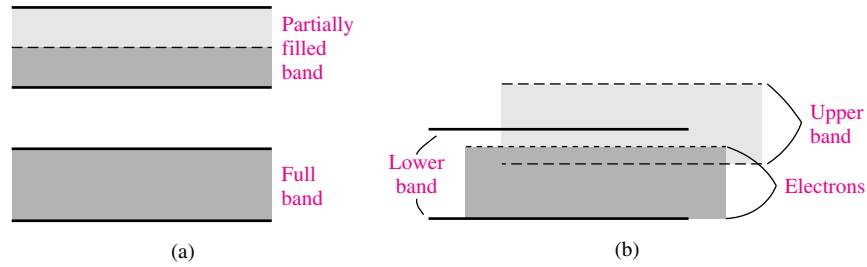


Figure 3.21 | Two possible energy bands of a metal showing (a) a partially filled band and (b) overlapping allowed energy bands.

higher energy states, and move through the crystal. The net flow of charge is a current. Figure 3.20b shows an allowed energy band that is almost full of electrons, which means that we can consider the holes in this band. If an electric field is applied, the holes can move and give rise to a current. Figure 3.20c shows the simplified energy-band diagram for this case. The bandgap energy may be on the order of 1 eV. This energy-band diagram represents a semiconductor for $T > 0$ K. The resistivity of a semiconductor, as we will see in the next chapter, can be controlled and varied over many orders of magnitude.

The characteristics of a metal include a very low resistivity. The energy-band diagram for a metal may be in one of two forms. Figure 3.21a shows the case of a partially full band in which there are many electrons available for conduction, so that the material can exhibit a large electrical conductivity. Figure 3.21b shows another possible energy-band diagram of a metal. The band splitting into allowed and forbidden energy bands is a complex phenomenon and Figure 3.21b shows a case in which the conduction and valence bands overlap at the equilibrium interatomic distance. As in the case shown in Figure 3.21a, there are large numbers of electrons as well as large numbers of empty energy states into which the electrons can move, so this material can also exhibit a very high electrical conductivity.

3.3 | EXTENSION TO THREE DIMENSIONS

The basic concept of allowed and forbidden energy bands and the basic concept of effective mass have been developed in the last sections. In this section, we will extend these concepts to three dimensions and to real crystals. We will qualitatively consider particular characteristics of the three-dimensional crystal in terms of the E versus k plots, bandgap energy, and effective mass. We must emphasize that we will only briefly touch on the basic three-dimensional concepts; therefore, many details will not be considered.

One problem encountered in extending the potential function to a three-dimensional crystal is that the distance between atoms varies as the direction through the crystal changes. Figure 3.22 shows a face-centered cubic structure with the [100] and [110] directions indicated. Electrons traveling in different directions encounter different potential patterns and therefore different k -space boundaries. The E versus k diagrams are in general a function of the k -space direction in a crystal.

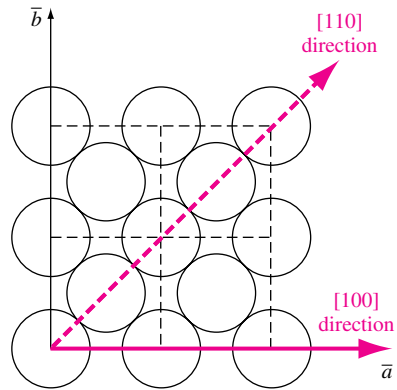


Figure 3.22 | The (100) plane of a face-centered cubic crystal showing the [100] and [110] directions.

3.3.1 The k -Space Diagrams of Si and GaAs

Figure 3.23 shows an E versus k diagram of gallium arsenide and of silicon. These simplified diagrams show the basic properties considered in this text, but do not show many of the details more appropriate for advanced-level courses.

Note that in place of the usual positive and negative k axes, we now show two different crystal directions. The E versus k diagram for the one-dimensional model

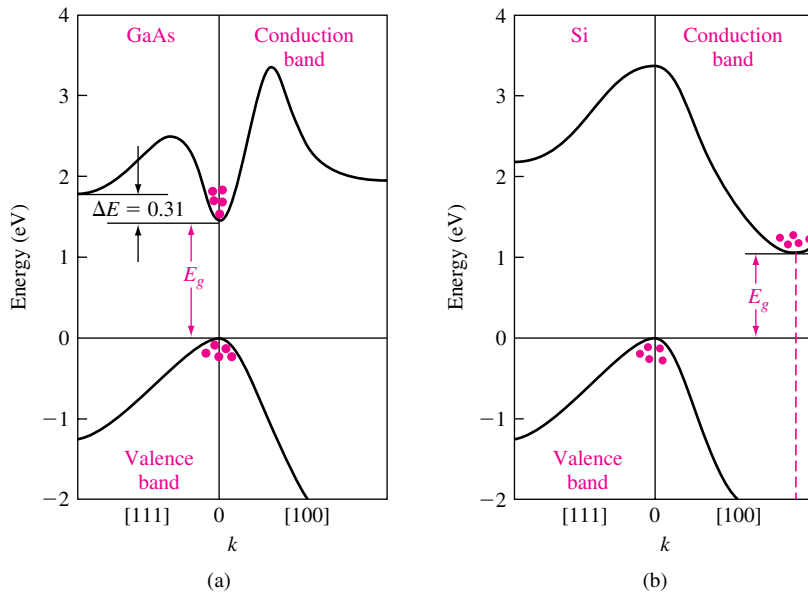


Figure 3.23 | Energy band structures of (a) GaAs and (b) Si. (From Sze [11].)

was symmetric in k so that no new information is obtained by displaying the negative axis. It is normal practice to plot the [100] direction along the normal $+k$ axis and to plot the [111] portion of the diagram so the $+k$ points to the left. In the case of diamond or zincblende lattices, the maxima in the valence band energy and minima in the conduction band energy occur at $k = 0$ or along one of these two directions.

Figure 3.23a shows the E versus k diagram for GaAs. The valence band maximum and the conduction band minimum both occur at $k = 0$. The electrons in the conduction band tend to settle at the minimum conduction band energy which is at $k = 0$. Similarly, holes in the valence band tend to congregate at the uppermost valence band energy. In GaAs, the minimum conduction band energy and maximum valence band energy occur at the same k value. A semiconductor with this property is said to be a *direct* bandgap semiconductor; transitions between the two allowed bands can take place with no change in crystal momentum. This direct nature has significant effect on the optical properties of the material. GaAs and other direct bandgap materials are ideally suited for use in semiconductor lasers and other optical devices.

The E versus k diagram for silicon is shown in Figure 3.23b. The maximum in the valence band energy occurs at $k = 0$ as before. The minimum in the conduction band energy occurs not at $k = 0$, but along the [100] direction. The difference between the minimum conduction band energy and the maximum valence band energy is still defined as the bandgap energy E_g . A semiconductor whose maximum valence band energy and minimum conduction band energy do not occur at the same k value is called an *indirect* bandgap semiconductor. When electrons make a transition between the conduction and valence bands, we must invoke the law of conservation of momentum. A transition in an indirect bandgap material must necessarily include an interaction with the crystal so that crystal momentum is conserved.

Germanium is also an indirect bandgap material, whose valence band maximum occurs at $k = 0$ and whose conduction band minimum occurs along the [111] direction. GaAs is a direct bandgap semiconductor, but other compound semiconductors, such as GaP and AlAs, have indirect bandgaps.

3.3.2 Additional Effective Mass Concepts

The curvature of the E versus k diagrams near the minimum of the conduction band energy is related to the effective mass of the electron. We may note from Figure 3.23 that the curvature of the conduction band at its minimum value for GaAs is larger than that of silicon, so the effective mass of an electron in the conduction band of GaAs will be smaller than that in silicon.

For the one-dimensional E versus k diagram, the effective mass was defined by Equation (3.41) as $1/m^* = 1/\hbar^2 \cdot d^2E/dk^2$. A complication occurs in the effective mass concept in a real crystal. A three-dimensional crystal can be described by three k vectors. The curvature of the E versus k diagram at the conduction band minimum may not be the same in the three k directions. We will not consider the details of the various effective mass parameters here. In later sections and chapters, the effective mass parameters used in calculations will be a kind of statistical average that is adequate for most device calculations.

3.4 | DENSITY OF STATES FUNCTION

As we have stated, we eventually wish to describe the current-voltage characteristics of semiconductor devices. Since current is due to the flow of charge, an important step in the process is to determine the number of electrons and holes in the semiconductor that will be available for conduction. The number of carriers that can contribute to the conduction process is a function of the number of available energy or quantum states since, by the Pauli exclusion principle, only one electron can occupy a given quantum state. When we discussed the splitting of energy levels into bands of allowed and forbidden energies, we indicated that the band of allowed energies was actually made up of discrete energy levels. We must determine the density of these allowed energy states as a function of energy in order to calculate the electron and hole concentrations.

3.4.1 Mathematical Derivation

To determine the density of allowed quantum states as a function of energy, we need to consider an appropriate mathematical model. Electrons are allowed to move relatively freely in the conduction band of a semiconductor, but are confined to the crystal. As a first step, we will consider a free electron confined to a three-dimensional infinite potential well, where the potential well represents the crystal. The potential of the infinite potential well is defined as

$$\begin{aligned}
 V(x, y, z) &= 0 && \text{for } 0 < x < a && (3.59) \\
 & && 0 < y < a && \\
 & && 0 < z < a && \\
 V(x, y, z) &= \infty && \text{elsewhere} &&
 \end{aligned}$$

where the crystal is assumed to be a cube with length a . Schrodinger's wave equation in three dimensions can be solved using the separation of variables technique. Extrapolating the results from the one-dimensional infinite potential well, we can show (see Problem 3.21) that

$$\frac{2mE}{\hbar^2} = k^2 = k_x^2 + k_y^2 + k_z^2 = (n_x^2 + n_y^2 + n_z^2) \left(\frac{\pi^2}{a^2} \right) \quad (3.60)$$

where n_x , n_y , and n_z are positive integers. (Negative values of n_x , n_y , and n_z yield the same wave function, except for the sign, as the positive integer values, resulting in the same probability function and energy, so the negative integers do not represent a different quantum state.)

We can schematically plot the allowed quantum states in k space. Figure 3.24a shows a two-dimensional plot as a function of k_x and k_y . Each point represents an allowed quantum state corresponding to various integral values of n_x and n_y . Positive and negative values of k_x , k_y , or k_z have the same energy and represent the same

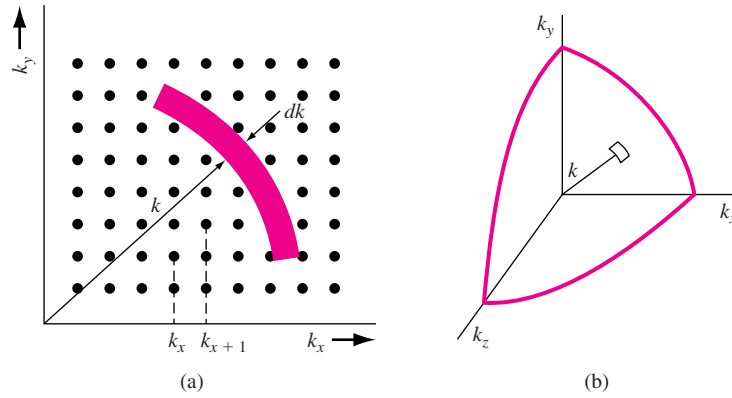


Figure 3.24 | (a) A two-dimensional array of allowed quantum states in k space. (b) The positive one-eighth of the spherical k space.

energy state. Since negative values of k_x , k_y , or k_z do not represent additional quantum states, the density of quantum states will be determined by considering only the positive one-eighth of the spherical k space as shown in Figure 3.24b.

The distance between two quantum states in the k_x direction, for example, is given by

$$k_{x+1} - k_x = (n_x + 1) \left(\frac{\pi}{a} \right) - n_x \left(\frac{\pi}{a} \right) = \frac{\pi}{a} \quad (3.61)$$

Generalizing this result to three dimensions, the volume V_k of a single quantum state is

$$V_k = \left(\frac{\pi}{a} \right)^3 \quad (3.62)$$

We can now determine the density of quantum states in k space. A differential volume in k space is shown in Figure 3.24b and is given by $4\pi k^2 dk$, so the differential density of quantum states in k space can be written as

$$g_T(k) dk = 2 \left(\frac{1}{8} \right) \frac{4\pi k^2 dk}{\left(\frac{\pi}{a} \right)^3} \quad (3.63)$$

The first factor, 2, takes into account the two spin states allowed for each quantum state; the next factor, $\frac{1}{8}$, takes into account that we are considering only the quantum states for positive values of k_x , k_y , and k_z . The factor $4\pi k^2 dk$ is again the differential volume and the factor $(\pi/a)^3$ is the volume of one quantum state. Equation (3.63) may be simplified to

$$g_T(k) dk = \frac{\pi k^2 dk}{\pi^3} \cdot a^3 \quad (3.64)$$

Equation (3.64) gives the density of quantum states as a function of momentum, through the parameter k . We can now determine the density of quantum states as a function of energy E . For a free electron, the parameters E and k are related by

$$k^2 = \frac{2mE}{\hbar^2} \quad (3.65a)$$

or

$$k = \frac{1}{\hbar} \sqrt{2mE} \quad (3.65b)$$

The differential dk is

$$dk = \frac{1}{\hbar} \sqrt{\frac{m}{2E}} dE \quad (3.66)$$

Then, substituting the expressions for k^2 and dk into Equation (3.64), the number of energy states between E and $E + dE$ is given by

$$g_T(E) dE = \frac{\pi a^3}{\pi^3} \left(\frac{2mE}{\hbar^2} \right) \cdot \frac{1}{\hbar} \sqrt{\frac{m}{2E}} dE \quad (3.67)$$

Since $\hbar = h/2\pi$, Equation (3.67) becomes

$$g_T(E) dE = \frac{4\pi a^3}{h^3} \cdot (2m)^{3/2} \cdot \sqrt{E} dE \quad (3.68)$$

Equation (3.68) gives the total number of quantum states between the energy E and $E + dE$ in the crystal space volume of a^3 . If we divide by the volume a^3 , then we will obtain the density of quantum states per unit volume of the crystal. Equation (3.68) then becomes

$$g(E) = \frac{4\pi(2m)^{3/2}}{h^3} \sqrt{E} \quad (3.69)$$

The density of quantum states is a function of energy E . As the energy of this free electron becomes small, the number of available quantum states decreases. This density function is really a double density, in that the units are given in terms of states per unit energy per unit volume.

Objective

EXAMPLE 3.3

To calculate the density of states per unit volume over a particular energy range.

Consider the density of states for a free electron given by Equation (3.69). Calculate the density of states per unit volume with energies between 0 and 1 eV.

■ Solution

The volume density of quantum states, from Equation (3.69), is

$$N = \int_0^{1\text{eV}} g(E) dE = \frac{4\pi(2m)^{3/2}}{h^3} \cdot \int_0^{1\text{eV}} \sqrt{E} dE$$

or

$$N = \frac{4\pi(2m)^{3/2}}{h^3} \cdot \frac{2}{3} \cdot E^{3/2}$$

The density of states is now

$$N = \frac{4\pi[2(9.11 \times 10^{-31})]^{3/2}}{(6.625 \times 10^{-34})^3} \cdot \frac{2}{3} \cdot (1.6 \times 10^{-19})^{3/2} = 4.5 \times 10^{27} \text{ m}^{-3}$$

or

$$N = 4.5 \times 10^{21} \text{ states/cm}^3$$

■ Comment

The density of quantum states is typically a large number. An effective density of states in a semiconductor, as we will see in the following sections and in the next chapter, is also a large number, but is usually less than the density of atoms in the semiconductor crystal.

3.4.2 Extension to Semiconductors

In the last section, we derived a general expression for the density of allowed electron quantum states using the model of a free electron with mass m bounded in a three-dimensional infinite potential well. We can extend this same general model to a semiconductor to determine the density of quantum states in the conduction band and the density of quantum states in the valence band. Electrons and holes are confined within the semiconductor crystal so we will again use the basic model of the infinite potential well.

The parabolic relationship between energy and momentum of a free electron was given in Equation (3.28) as $E = p^2/2m = \hbar^2 k^2/2m$. Figure 3.16a showed the conduction energy band in the reduced k space. The E versus k curve near $k = 0$ at the bottom of the conduction band can be approximated as a parabola, so we may write

$$E = E_c + \frac{\hbar^2 k^2}{2m_n^*} \quad (3.70)$$

where E_c is the bottom edge of the conduction band and m_n^* is the electron effective mass. Equation (3.70) may be rewritten to give

$$E - E_c = \frac{\hbar^2 k^2}{2m_n^*} \quad (3.71)$$

The general form of the E versus k relation for an electron in the bottom of a conduction band is the same as the free electron, except the mass is replaced by the effective mass. We can then think of the electron in the bottom of the conduction band as being a “free” electron with its own particular mass. The right side of Equation (3.71) is of the same form as the right side of Equation (3.28), which was used in the derivation of the density of states function. Because of this similarity, which yields the “free” conduction electron model, we may generalize the free electron results of Equation (3.69) and write the density of allowed electronic energy states in the conduction band as

$$g_c(E) = \frac{4\pi(2m_n^*)^{3/2}}{h^3} \sqrt{E - E_c} \quad (3.72)$$

Equation (3.72) is valid for $E \geq E_c$. As the energy of the electron in the conduction band decreases, the number of available quantum states also decreases.

The density of quantum states in the valence band can be obtained by using the same infinite potential well model, since the hole is also confined in the semiconductor crystal and can be treated as a “free” particle. The effective mass of the hole is m_p^* . Figure 3.16b showed the valence energy band in the reduced k space. We may also approximate the E versus k curve near $k = 0$ by a parabola for a “free” hole, so that

$$E = E_v - \frac{\hbar^2 k^2}{2m_p^*} \quad (3.73)$$

Equation (3.73) may be rewritten to give

$$E_v - E = \frac{\hbar^2 k^2}{2m_p^*} \quad (3.74)$$

Again, the right side of Equation (3.74) is of the same form used in the general derivation of the density of states function. We may then generalize the density of states function from Equation (3.69) to apply to the valence band, so that

$$g_v(E) = \frac{4\pi(2m_p^*)^{3/2}}{h^3} \sqrt{E_v - E} \quad (3.75)$$

Equation (3.75) is valid for $E \leq E_v$.

We have argued that quantum states do not exist within the forbidden energy band, so $g(E) = 0$ for $E_v < E < E_c$. Figure 3.25 shows the plot of the density of quantum states as a function of energy. If the electron and hole effective masses were equal, then the functions $g_c(E)$ and $g_v(E)$ would be symmetrical about the energy midway between E_c and E_v , or the midgap energy, E_{midgap} .

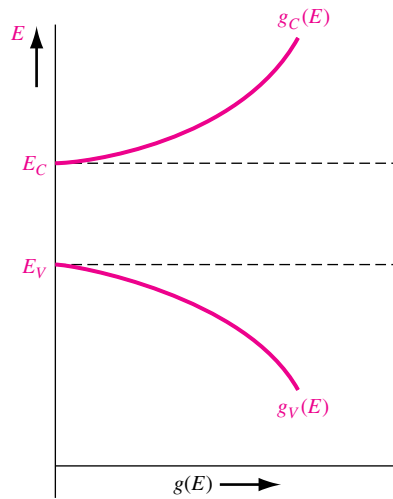


Figure 3.25 | The density of energy states in the conduction band and the density of energy states in the valence band as a function of energy.

TEST YOUR UNDERSTANDING

- E3.2** Determine the total number of energy states in silicon between E_c and $E_c + kT$ at $T = 300$ K. (Ans. 6.101×10^{17} suV)
- E3.3** Determine the total number of energy states in silicon between E_v and $E_v - kT$ at $T = 300$ K. (Ans. 8.101×10^{17} suV)

3.5 | STATISTICAL MECHANICS

In dealing with large numbers of particles, we are interested only in the statistical behavior of the group as a whole rather than in the behavior of each individual particle. For example, gas within a container will exert an average pressure on the walls of the vessel. The pressure is actually due to the collisions of the individual gas molecules with the walls, but we do not follow each individual molecule as it collides with the wall. Likewise in a crystal, the electrical characteristics will be determined by the statistical behavior of a large number of electrons.

3.5.1 Statistical Laws

In determining the statistical behavior of particles, we must consider the laws that the particles obey. There are three distribution laws determining the distribution of particles among available energy states.

One distribution law is the Maxwell–Boltzmann probability function. In this case, the particles are considered to be distinguishable by being numbered, for example, from 1 to N , with no limit to the number of particles allowed in each energy state. The behavior of gas molecules in a container at fairly low pressure is an example of this distribution.

A second distribution law is the Bose–Einstein function. The particles in this case are indistinguishable and, again, there is no limit to the number of particles permitted in each quantum state. The behavior of photons, or black body radiation, is an example of this law.

The third distribution law is the Fermi–Dirac probability function. In this case, the particles are again indistinguishable, but now only one particle is permitted in each quantum state. Electrons in a crystal obey this law. In each case, the particles are assumed to be noninteracting.

3.5.2 The Fermi–Dirac Probability Function

Figure 3.26 shows the i th energy level with g_i quantum states. A maximum of one particle is allowed in each quantum state by the Pauli exclusion principle. There are g_i ways of choosing where to place the first particle, $(g_i - 1)$ ways of choosing where to place the second particle, $(g_i - 2)$ ways of choosing where to place the third particle, and so on. Then the total number of ways of arranging N_i particles in the i th energy level (where $N_i \leq g_i$) is

$$(g_i)(g_i - 1) \cdots (g_i - (N_i - 1)) = \frac{g_i!}{(g_i - N_i)!} \quad (3.76)$$

This expression includes all permutations of the N_i particles among themselves.

However, since the particles are indistinguishable, the $N_i!$ number of permutations that the particles have among themselves in any given arrangement do not count as separate arrangements. The interchange of any two electrons, for example, does not produce a new arrangement. Therefore, the actual number of independent ways of realizing a distribution of N_i particles in the i th level is

$$W_i = \frac{g_i!}{N_i!(g_i - N_i)!} \quad (3.77)$$

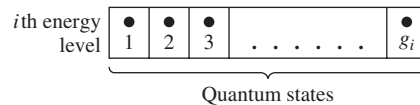
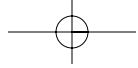


Figure 3.26 | The i th energy level with g_i quantum states.



EXAMPLE 3.4

Objective

To determine the possible number of ways of realizing a particular distribution.

Let $g_i = N_i = 10$. Then $(g_i - N_i)! = 1$.

■ Solution

Equation (3.77) becomes

$$\frac{g_i!}{N_i!(g_i - N_i)!} = \frac{10!}{10!} = 1$$

■ Comment

If we have 10 particles to be arranged in 10 quantum states, there is only one possible arrangement. Each quantum state contains one particle.

EXAMPLE 3.5

Objective

To again determine the possible number of ways of realizing a particular distribution.

Let $g_i = 10$ and $N_i = 9$. In this case $g_i - N_i = 1$ so that $(g_i - N_i)! = 1$.

■ Solution

Equation (3.77) becomes

$$\frac{g_i!}{N_i!(g_i - N_i)!} = \frac{10!}{(9!)(1)} = \frac{(10)(9!)}{9!} = 10$$

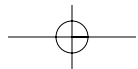
■ Comment

In this case, if we have 10 quantum states and 9 particles, there is one empty quantum state. There are 10 possible arrangements, or positions, for the one empty state.

Equation (3.77) gives the number of independent ways of realizing a distribution of N_i particles in the i th level. The total number of ways of arranging $(N_1, N_2, N_3, \dots, N_n)$ indistinguishable particles among n energy levels is the product of all distributions, or

$$W = \prod_{i=1}^n \frac{g_i!}{N_i!(g_i - N_i)!} \quad (3.78)$$

The parameter W is the total number of ways in which N electrons can be arranged in this system, where $N = \sum_{i=1}^n N_i$ is the total number of electrons in the system. We want to find the most probable distribution, which means that we want to find the maximum W . The maximum W is found by varying N_i among the E_i levels, which varies the distribution, but at the same time, we will keep the total number of particles and total energy constant.



We may write the most probable distribution function as

$$\frac{N(E)}{g(E)} = f_F(E) = \frac{1}{1 + \exp\left(\frac{E - E_F}{kT}\right)} \quad (3.79)$$

where E_F is called the Fermi energy. The number density $N(E)$ is the number of particles per unit volume per unit energy and the function $g(E)$ is the number of quantum states per unit volume per unit energy. The function $f_F(E)$ is called the Fermi–Dirac distribution or probability function and gives the probability that a quantum state at the energy E will be occupied by an electron. Another interpretation of the distribution function is that $f_F(E)$ is the ratio of filled to total quantum states at any energy E .

3.5.3 The Distribution Function and the Fermi Energy

To begin to understand the meaning of the distribution function and the Fermi energy, we can plot the distribution function versus energy. Initially, let $T = 0$ K and consider the case when $E < E_F$. The exponential term in Equation (3.79) becomes $\exp[(E - E_F)/kT] \rightarrow \exp(-\infty) = 0$. The resulting distribution function is $f_F(E < E_F) = 1$. Again let $T = 0$ K and consider the case when $E > E_F$. The exponential term in the distribution function becomes $\exp[(E - E_F)/kT] \rightarrow \exp(+\infty) \rightarrow +\infty$. The resulting Fermi–Dirac distribution function now becomes $f_F(E > E_F) = 0$.

The Fermi–Dirac distribution function for $T = 0$ K is plotted in Figure 3.27. This result shows that, for $T = 0$ K, the electrons are in their lowest possible energy states. The probability of a quantum state being occupied is unity for $E < E_F$ and the probability of a state being occupied is zero for $E > E_F$. All electrons have energies below the Fermi energy at $T = 0$ K.

Figure 3.28 shows discrete energy levels of a particular system as well as the number of available quantum states at each energy. If we assume, for this case, that

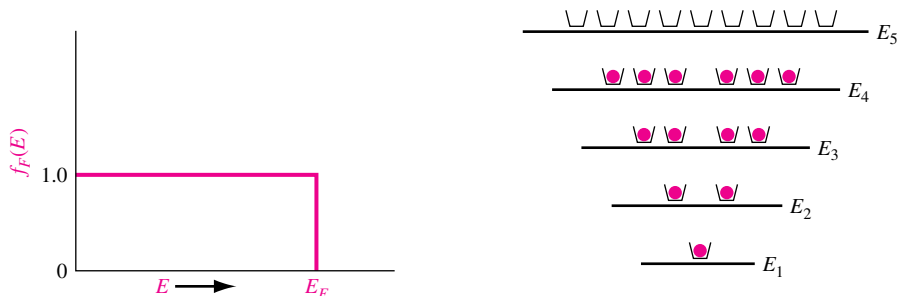


Figure 3.27 | The Fermi probability function versus energy for $T = 0$ K.

Figure 3.28 | Discrete energy states and quantum states for a particular system at $T = 0$ K.

the system contains 13 electrons, then Figure 3.28 shows how these electrons are distributed among the various quantum states at $T = 0$ K. The electrons will be in the lowest possible energy state, so the probability of a quantum state being occupied in energy levels E_1 through E_4 is unity, and the probability of a quantum state being occupied in energy level E_5 is zero. The Fermi energy, for this case, must be above E_4 but less than E_5 . The Fermi energy determines the statistical distribution of electrons and does not have to correspond to an allowed energy level.

Now consider a case in which the density of quantum states $g(E)$ is a continuous function of energy as shown in Figure 3.29. If we have N_0 electrons in this system, then the distribution of these electrons among the quantum states at $T = 0$ K is shown by the dashed line. The electrons are in the lowest possible energy state so that all states below E_F are filled and all states above E_F are empty. If $g(E)$ and N_0 are known for this particular system, then the Fermi energy E_F can be determined.

Consider the situation when the temperature increases above $T = 0$ K. Electrons gain a certain amount of thermal energy so that some electrons can jump to higher energy levels, which means that the distribution of electrons among the available energy states will change. Figure 3.30 shows the same discrete energy levels and quantum states as in Figure 3.28. The distribution of electrons among the quantum states has changed from the $T = 0$ K case. Two electrons from the E_4 level have gained enough energy to jump to E_5 , and one electron from E_3 has jumped to E_4 . As the temperature changes, the distribution of electrons versus energy changes.

The change in the electron distribution among energy levels for $T > 0$ K can be seen by plotting the Fermi–Dirac distribution function. If we let $E = E_F$ and $T > 0$ K, then Equation (3.79) becomes

$$f_F(E = E_F) = \frac{1}{1 + \exp(0)} = \frac{1}{1 + 1} = \frac{1}{2}$$

The probability of a state being occupied at $E = E_F$ is $\frac{1}{2}$. Figure 3.31 shows the Fermi–Dirac distribution function plotted for several temperatures, assuming the Fermi energy is independent of temperature.

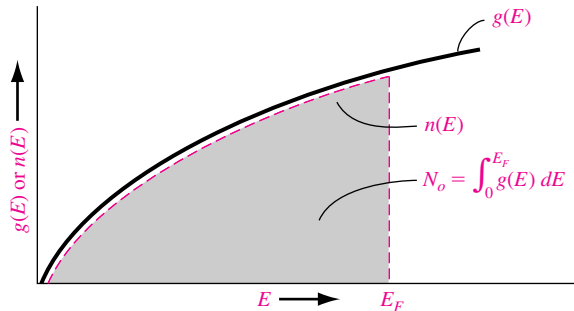


Figure 3.29 | Density of quantum states and electrons in a continuous energy system at $T = 0$ K.

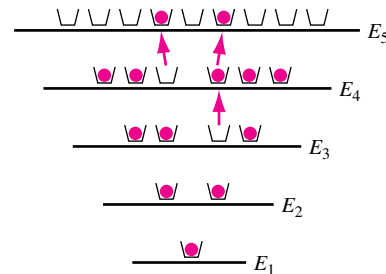


Figure 3.30 | Discrete energy states and quantum states for the same system shown in Figure 3.28 for $T > 0$ K.

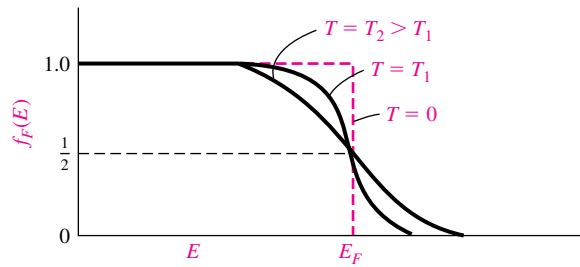


Figure 3.31 | The Fermi probability function versus energy for different temperatures.

We can see that for temperatures above absolute zero, there is a nonzero probability that some energy states above E_F will be occupied by electrons and some energy states below E_F will be empty. This result again means that some electrons have jumped to higher energy levels with increasing thermal energy.

Objective

EXAMPLE 3.6

To calculate the probability that an energy state above E_F is occupied by an electron.

Let $T = 300$ K. Determine the probability that an energy level $3kT$ above the Fermi energy is occupied by an electron.

■ Solution

From Equation (3.79), we can write

$$f_F(E) = \frac{1}{1 + \exp\left(\frac{E - E_F}{kT}\right)} = \frac{1}{1 + \exp\left(\frac{3kT}{kT}\right)}$$

which becomes

$$f_F(E) = \frac{1}{1 + 20.09} = 0.0474 = 4.74\%$$

■ Comment

At energies above E_F , the probability of a state being occupied by an electron can become significantly less than unity, or the ratio of electrons to available quantum states can be quite small.

TEST YOUR UNDERSTANDING

E3.4 Assume the Fermi energy level is 0.30 eV below the conduction band energy.

(a) Determine the probability of a state being occupied by an electron at E_c .

(b) Repeat part (a) for an energy state at $E_c + kT$. Assume $T = 300$ K.

[Answers: (a) 1.0×10^{-10} , (b) 0.0474]

- E3.5** Assume the Fermi energy level is 0.35 eV above the valence band energy.
 (a) Determine the probability of a state being empty of an electron at E_v . (b) Repeat part (a) for an energy state at $E_v - kT$. Assume $T = 300$ K.

We can see from Figure 3.31 that the probability of an energy above E_F being occupied increases as the temperature increases and the probability of a state below E_F being empty increases as the temperature increases.

EXAMPLE 3.7**Objective**

To determine the temperature at which there is a 1 percent probability that an energy state is empty.

Assume that the Fermi energy level for a particular material is 6.25 eV and that the electrons in this material follow the Fermi–Dirac distribution function. Calculate the temperature at which there is a 1 percent probability that a state 0.30 eV below the Fermi energy level will not contain an electron.

■ Solution

The probability that a state is empty is

$$1 - f_F(E) = \frac{1}{1 + \exp\left(\frac{E - E_F}{kT}\right)}$$

Then

$$0.01 = \frac{1}{1 + \exp\left(\frac{5.95 - 6.25}{kT}\right)}$$

Solving for kT , we find $kT = 0.06529$ eV, so that the temperature is $T = 756$ K.

■ Comment

The Fermi probability function is a strong function of temperature.

TEST YOUR UNDERSTANDING

- E3.6** Repeat Exercise E3.4 for $T = 400$ K.
E3.7 Repeat Exercise E3.5 for $T = 400$ K.

We may note that the probability of a state a distance dE above E_F being occupied is the same as the probability of a state a distance dE below E_F being empty. The function $f_F(E)$ is symmetrical with the function $1 - f_F(E)$ about the Fermi energy, E_F . This symmetry effect is shown in Figure 3.32 and will be used in the next chapter.

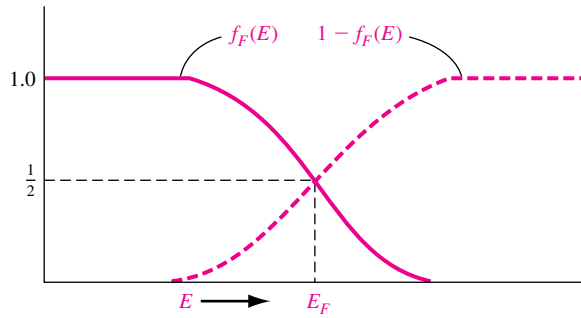


Figure 3.32 | The probability of a state being occupied, $f_F(E)$, and the probability of a state being empty, $1 - f_F(E)$.

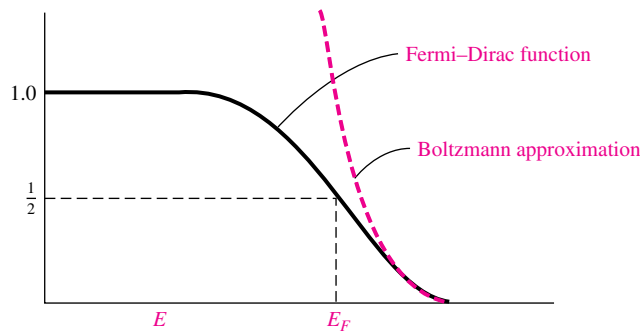


Figure 3.33 | The Fermi-Dirac probability function and the Maxwell-Boltzmann approximation.

Consider the case when $E - E_F \gg kT$, where the exponential term in the denominator of Equation (3.79) is much greater than unity. We may neglect the 1 in the denominator, so the Fermi-Dirac distribution function becomes

$$f_F(E) \approx \exp\left[\frac{-(E - E_F)}{kT}\right] \quad (3.80)$$

Equation (3.80) is known as the Maxwell-Boltzmann approximation, or simply the Boltzmann approximation, to the Fermi-Dirac distribution function. Figure 3.33 shows the Fermi-Dirac probability function and the Boltzmann approximation. This figure gives an indication of the range of energies over which the approximation is valid.

Objective

EXAMPLE 3.8

To determine the energy at which the Boltzmann approximation may be considered valid.

Calculate the energy, in terms of kT and E_F , at which the difference between the Boltzmann approximation and the Fermi-Dirac function is 5 percent of the Fermi function.

■ Solution

We can write

$$\frac{\exp\left[\frac{-(E - E_F)}{kT}\right] - \frac{1}{1 + \exp\left(\frac{E - E_F}{kT}\right)}}{\frac{1}{1 + \exp\left(\frac{E - E_F}{kT}\right)}} = 0.05$$

If we multiply both numerator and denominator by the $1 + \exp(\)$ function, we have

$$\exp\left[\frac{-(E - E_F)}{kT}\right] \cdot \left\{1 + \exp\left[\frac{E - E_F}{kT}\right]\right\} - 1 = 0.05$$

which becomes

$$\exp\left[\frac{-(E - E_F)}{kT}\right] = 0.05$$

or

$$(E - E_F) = kT \ln\left(\frac{1}{0.05}\right) \approx 3kT$$

■ Comment

As seen in this example and in Figure 3.33, the $E - E_F \gg kT$ notation is somewhat misleading. The Maxwell–Boltzmann and Fermi–Dirac functions are within 5 percent of each other when $E - E_F \approx 3kT$.

The actual Boltzmann approximation is valid when $\exp[(E - E_F)/kT] \gg 1$. However, it is still common practice to use the $E - E_F \gg kT$ notation when applying the Boltzmann approximation. We will use this Boltzmann approximation in our discussion of semiconductors in the next chapter.

3.6 | SUMMARY

- Discrete allowed electron energies split into a band of allowed energies as atoms are brought together to form a crystal.
- The concept of allowed and forbidden energy bands was developed more rigorously by considering quantum mechanics and Schrodinger's wave equation using the Kronig–Penney model representing the potential function of a single crystal material. This result forms the basis of the energy band theory of semiconductors.
- The concept of effective mass was developed. Effective mass relates the motion of a particle in a crystal to an externally applied force and takes into account the effect of the crystal lattice on the motion of the particle.
- Two charged particles exist in a semiconductor. An electron is a negatively charged particle with a positive effective mass existing at the bottom of an allowed energy band. A hole is a positively charged particle with a positive effective mass existing at the top of an allowed energy band.

- The E versus k diagram of silicon and gallium arsenide were given and the concept of direct and indirect bandgap semiconductors was discussed.
- Energies within an allowed energy band are actually at discrete levels and each contains a finite number of quantum states. The density per unit energy of quantum states was determined by using the three-dimensional infinite potential well as a model.
- In dealing with large numbers of electrons and holes, we must consider the statistical behavior of these particles. The Fermi–Dirac probability function was developed, which gives the probability of a quantum state at an energy E of being occupied by an electron. The Fermi energy was defined.

GLOSSARY OF IMPORTANT TERMS

- allowed energy band** A band or range of energy levels that an electron in a crystal is allowed to occupy based on quantum mechanics.
- density of states function** The density of available quantum states as a function of energy, given in units of number per unit energy per unit volume.
- electron effective mass** The parameter that relates the acceleration of an electron in the conduction band of a crystal to an external force; a parameter that takes into account the effect of internal forces in the crystal.
- Fermi–Dirac probability function** The function describing the statistical distribution of electrons among available energy states and the probability that an allowed energy state is occupied by an electron.
- fermi energy** In the simplest definition, the energy below which all states are filled with electrons and above which all states are empty at $T = 0$ K.
- forbidden energy band** A band or range of energy levels that an electron in a crystal is not allowed to occupy based on quantum mechanics.
- hole** The positively charged “particle” associated with an empty state in the top of the valence band.
- hole effective mass** The parameter that relates the acceleration of a hole in the valence band of a crystal to an applied external force (a positive quantity); a parameter that takes into account the effect of internal forces in a crystal.
- k -space diagram** The plot of electron energy in a crystal versus k , where k is the momentum-related constant of the motion that incorporates the crystal interaction.
- Kronig–Penney model** The mathematical model of a periodic potential function representing a one-dimensional single-crystal lattice by a series of periodic step functions.
- Maxwell–Boltzmann approximation** The condition in which the energy is several kT above the Fermi energy or several kT below the Fermi energy so that the Fermi–Dirac probability function can be approximated by a simple exponential function.
- Pauli exclusion principle** The principle which states that no two electrons can occupy the same quantum state.

CHECKPOINT

After studying this chapter, the reader should have the ability to:

- Discuss the concept of allowed and forbidden energy bands in a single crystal both qualitatively and more rigorously from the results of using the Kronig–Penney model.



- Discuss the splitting of energy bands in silicon.
- State the definition of effective mass from the E versus k diagram and discuss its meaning in terms of the movement of a particle in a crystal.
- Discuss the concept of a hole.
- Qualitatively, in terms of energy bands, discuss the difference between a metal, insulator, and semiconductor.
- Discuss the effective density of states function.
- Understand the meaning of the Fermi–Dirac distribution function and the Fermi energy.

REVIEW QUESTIONS

1. What is the Kronig–Penney model?
2. State two results of using the Kronig–Penney model with Schrodinger’s wave equation.
3. What is effective mass?
4. What is a direct bandgap semiconductor? What is an indirect bandgap semiconductor?
5. What is the meaning of the density of states function?
6. What was the mathematical model used in deriving the density of states function?
7. In general, what is the relation between density of states and energy?
8. What is the meaning of the Fermi–Dirac probability function?
9. What is the Fermi energy?

PROBLEMS

Section 3.1 Allowed and Forbidden Energy Bands

- 3.1 Consider Figure 3.4b, which shows the energy-band splitting of silicon. If the equilibrium lattice spacing were to change by a small amount, discuss how you would expect the electrical properties of silicon to change. Determine at what point the material would behave like an insulator or like a metal.
- 3.2 Show that Equations (3.4) and (3.6) are derived from Schrodinger’s wave equation, using the form of solution given by Equation (3.3).
- 3.3 Show that Equations (3.9) and (3.10) are solutions of the differential equations given by Equations (3.4) and (3.8), respectively.
- 3.4 Show that Equations (3.12), (3.14), (3.16), and (3.18) result from the boundary conditions in the Kronig–Penney model.
- 3.5  Plot the function $f(\alpha a) = 9 \sin \alpha a / \alpha a + \cos \alpha a$ for $0 \leq \alpha a \leq 6\pi$. Also, given the function $f(\alpha a) = \cos ka$, indicate the allowed values of αa which will satisfy this equation.
- 3.6  Repeat Problem 3.5 for the function

$$f(\alpha a) = 6 \sin \alpha a / \alpha a + \cos \alpha a = \cos ka$$
- 3.7 Using Equation (3.24), show that $dE/dk = 0$ at $k = n\pi/a$, where $n = 0, 1, 2, \dots$
- 3.8 Using the parameters in Problem 3.5 and letting $a = 5 \text{ \AA}$, determine the width (in eV) of the forbidden energy bands that exist at (a) $ka = \pi$, (b) $ka = 2\pi$, (c) $ka = 3\pi$, and (d) $ka = 4\pi$. Refer to Figure 3.8c.

- 3.9** Using the parameters in Problem 3.5 and letting $a = 5 \text{ \AA}$, determine the width (in eV) of the allowed energy bands that exist for (a) $0 < ka < \pi$, (b) $\pi < ka < 2\pi$, (c) $2\pi < ka < 3\pi$, and (d) $3\pi < ka < 4\pi$.
- 3.10** Repeat Problem 3.8 using the parameters in Problem 3.6.
- 3.11** Repeat Problem 3.9 using the parameters in Problem 3.6.
- 3.12** The bandgap energy in a semiconductor is usually a slight function of temperature. In some cases, the bandgap energy versus temperature can be modeled by

$$E_g = E_g(0) - \frac{\alpha T^2}{\beta + T}$$

where $E_g(0)$ is the value of the bandgap energy at $T = 0 \text{ K}$. For silicon, the parameter values are $E_g(0) = 1.170 \text{ eV}$, $\alpha = 4.73 \times 10^{-4} \text{ eV/K}$ and $\beta = 636 \text{ K}$. Plot E_g versus T over the range $0 \leq T \leq 600 \text{ K}$. In particular, note the value at $T = 300 \text{ K}$.

Section 3.2 Electrical Conduction in Solids

- 3.13** Two possible conduction bands are shown in the E versus k diagram given in Figure 3.34. State which band will result in the heavier electron effective mass; state why.
- 3.14** Two possible valence bands are shown in the E versus k diagram given in Figure 3.35. State which band will result in the heavier hole effective mass; state why.
- 3.15** The E versus k diagram for a particular allowed energy band is shown in Figure 3.36. Determine (a) the sign of the effective mass and (b) the direction of velocity for a particle at each of the four positions shown.
- 3.16** Figure 3.37 shows the parabolic E versus k relationship in the conduction band for an electron in two particular semiconductor materials. Determine the effective mass (in units of the free electron mass) of the two electrons.
- 3.17** Figure 3.38 shows the parabolic E versus k relationship in the valence band for a hole in two particular semiconductor materials. Determine the effective mass (in units of the free electron mass) of the two holes.
- 3.18** The forbidden energy band of GaAs is 1.42 eV. (a) Determine the minimum frequency of an incident photon that can interact with a valence electron and elevate the electron to the conduction band. (b) What is the corresponding wavelength?
- 3.19** The E versus k diagrams for a free electron (curve A) and for an electron in a semiconductor (curve B) are shown in Figure 3.39. Sketch (a) dE/dk versus k and

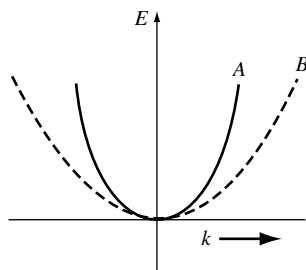


Figure 3.34 | Conduction bands for Problem 3.13.

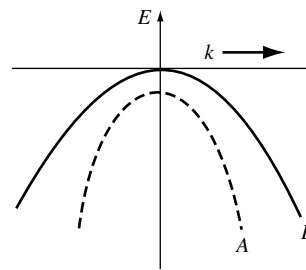


Figure 3.35 | Valence bands for Problem 3.14.

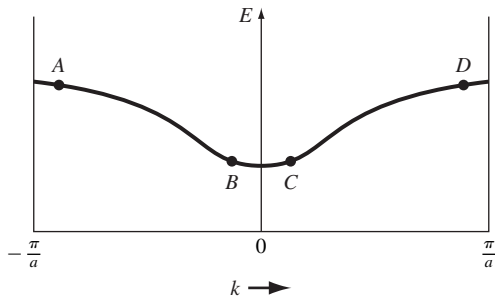


Figure 3.36 | Figure for Problem 3.15.

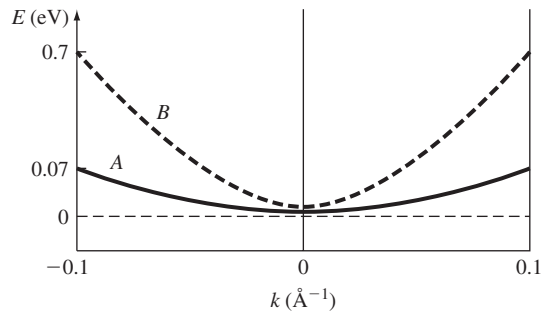


Figure 3.37 | Figure for Problem 3.16.

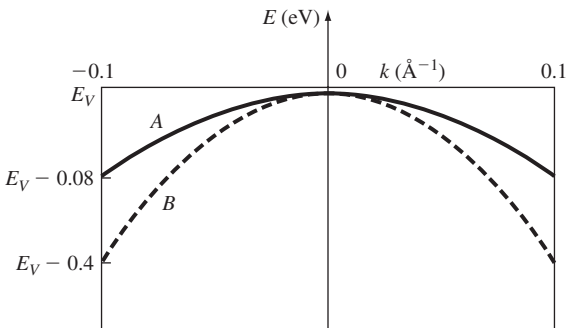


Figure 3.38 | Figure for Problem 3.17.

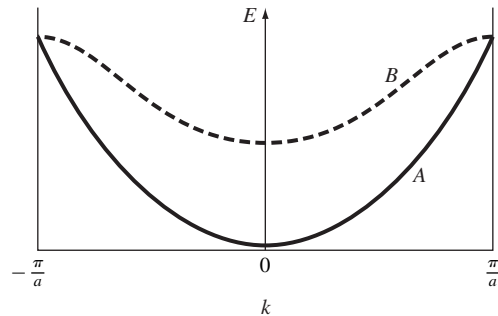


Figure 3.39 | Figure for Problem 3.19.

(b) d^2E/dk^2 versus k for each curve. (c) What conclusion can you make concerning a comparison in effective masses for the two cases?

Section 3.3 Extension to Three Dimensions

3.20 The energy band diagram for silicon is shown in Figure 3.23b. The minimum energy in the conduction band is in the [100] direction. The energy in this one-dimensional direction near the minimum value can be approximated by

$$E = E_0 - E_1 \cos \alpha(k - k_0)$$

where k_0 is the value of k at the minimum energy. Determine the effective mass of the particle at $k = k_0$ in terms of the equation parameters.

Section 3.4 Density of States Function

- 3.21** Starting with the three-dimensional infinite potential well function given by Equation (3.59) and using the separation of variables technique, derive Equation (3.60).
- 3.22** Show that Equation (3.69) can be derived from Equation (3.64).
- 3.23** Determine the total number of energy states in GaAs between E_c and $E_c + kT$ at $T = 300$ K.

- 3.24** Determine the total number of energy states in GaAs between E_v and $E_v - kT$ at $T = 300$ K.
- 3.25** (a) Plot the density of states in the conduction band for silicon over the range $E_c \leq E \leq E_c + 0.2$ eV. (b) Repeat part (a) for the density of states in the valence band over the range $E_v - 0.2$ eV $\leq E \leq E_v$.
- 3.26** Find the ratio of the effective density of states in the conduction band at $E_c + kT$ to the effective density of states in the valence band at $E_v - kT$.

Section 3.5 Statistical Mechanics

- 3.27** Plot the Fermi–Dirac probability function, given by Equation (3.79), over the range $-0.2 \leq (E - E_F) \leq 0.2$ eV for (a) $T = 200$ K, (b) $T = 300$ K, and (c) $T = 400$ K.
- 3.28** Repeat Example 3.4 for the case when $g_i = 10$ and $N_i = 8$.
- 3.29** (a) If $E_F = E_c$, find the probability of a state being occupied at $E = E_c + kT$. (b) If $E_F = E_v$, find the probability of a state being empty at $E = E_v - kT$.
- 3.30** Determine the probability that an energy level is occupied by an electron if the state is above the Fermi level by (a) kT , (b) $5kT$, and (c) $10kT$.
- 3.31** Determine the probability that an energy level is empty of an electron if the state is below the Fermi level by (a) kT , (b) $5kT$, and (c) $10kT$.
- 3.32** The Fermi energy in silicon is 0.25 eV below the conduction band energy E_c . (a) Plot the probability of a state being occupied by an electron over the range $E_c \leq E \leq E_c + 2kT$. Assume $T = 300$ K. (b) Repeat part (a) for $T = 400$ K.
- 3.33** Four electrons exist in a one-dimensional infinite potential well of width $a = 10$ Å. Assuming the free electron mass, what is the Fermi energy at $T = 0$ K.
- 3.34** (a) Five electrons exist in a three-dimensional infinite potential well with all three widths equal to $a = 10$ Å. Assuming the free electron mass, what is the Fermi energy at $T = 0$ K. (b) Repeat part (a) for 13 electrons.
- 3.35** Show that the probability of an energy state being occupied ΔE above the Fermi energy is the same as the probability of a state being empty ΔE below the Fermi level.
- 3.36** (a) Determine for what energy above E_F (in terms of kT) the Fermi–Dirac probability function is within 1 percent of the Boltzmann approximation. (b) Give the value of the probability function at this energy.
- 3.37** The Fermi energy level for a particular material at $T = 300$ K is 6.25 eV. The electrons in this material follow the Fermi–Dirac distribution function. (a) Find the probability of an energy level at 6.50 eV being occupied by an electron. (b) Repeat part (a) if the temperature is increased to $T = 950$ K. (Assume that E_F is a constant.) (c) Calculate the temperature at which there is a 1 percent probability that a state 0.30 eV below the Fermi level will be empty of an electron.
- 3.38** The Fermi energy for copper at $T = 300$ K is 7.0 eV. The electrons in copper follow the Fermi–Dirac distribution function. (a) Find the probability of an energy level at 7.15 eV being occupied by an electron. (b) Repeat part (a) for $T = 1000$ K. (Assume that E_F is a constant.) (c) Repeat part (a) for $E = 6.85$ eV and $T = 300$ K. (d) Determine the probability of the energy state at $E = E_F$ being occupied at $T = 300$ K and at $T = 1000$ K.
- 3.39** Consider the energy levels shown in Figure 3.40. Let $T = 300$ K. (a) If $E_1 - E_F = 0.30$ eV, determine the probability that an energy state at $E = E_1$ is occupied by an electron and the probability that an energy state at $E = E_2$ is empty. (b) Repeat part (a) if $E_F - E_2 = 0.40$ eV.



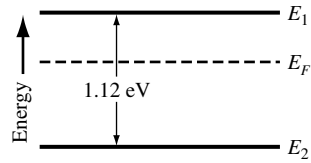


Figure 3.40 | Energy levels for Problem 3.39.

- 3.40** Repeat problem 3.39 for the case when $E_1 - E_2 = 1.42$ eV.
- 3.41** Determine the derivative with respect to energy of the Fermi–Dirac distribution function. Plot the derivative with respect to energy for (a) $T = 0$ K, (b) $T = 300$ K, and (c) $T = 500$ K.
- 3.42** Assume the Fermi energy level is exactly in the center of the bandgap energy of a semiconductor at $T = 300$ K. (a) Calculate the probability that an energy state in the bottom of the conduction band is occupied by an electron for Si, Ge, and GaAs. (b) Calculate the probability that an energy state in the top of the valence band is empty for Si, Ge, and GaAs.
- 3.43** Calculate the temperature at which there is a 10^{-6} probability that an energy state 0.55 eV above the Fermi energy level is occupied by an electron.
- 3.44** Calculate the energy range (in eV) between $f_F(E) = 0.95$ and $f_F(E) = 0.05$ for $E_F = 7.0$ eV and for (a) $T = 300$ K and (b) $T = 500$ K.

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