Introduction to the Semiconductor Physics

Objectives

- Develop the concept of allowed and forbidden electron energy bands in a single-crystal material, and describe conduction and valence energy bands in a semiconductor material.

- Discuss the concept of negatively charged electrons and positively charged holes as two distinct charge carriers in a semiconductor material.

- Develop electron energy versus momentum curves in a single-crystal material, which yields the concept of direct and indirect band gap semiconductor materials.

- Discuss the concept of effective mass of an electron and a hole.

- Derive the density of quantum states in the allowed energy bands.

- Develop the Fermi-Dirac probability function, which describes the statistical distribution of electrons among the allowed energy levels, and define the Fermi energy level.
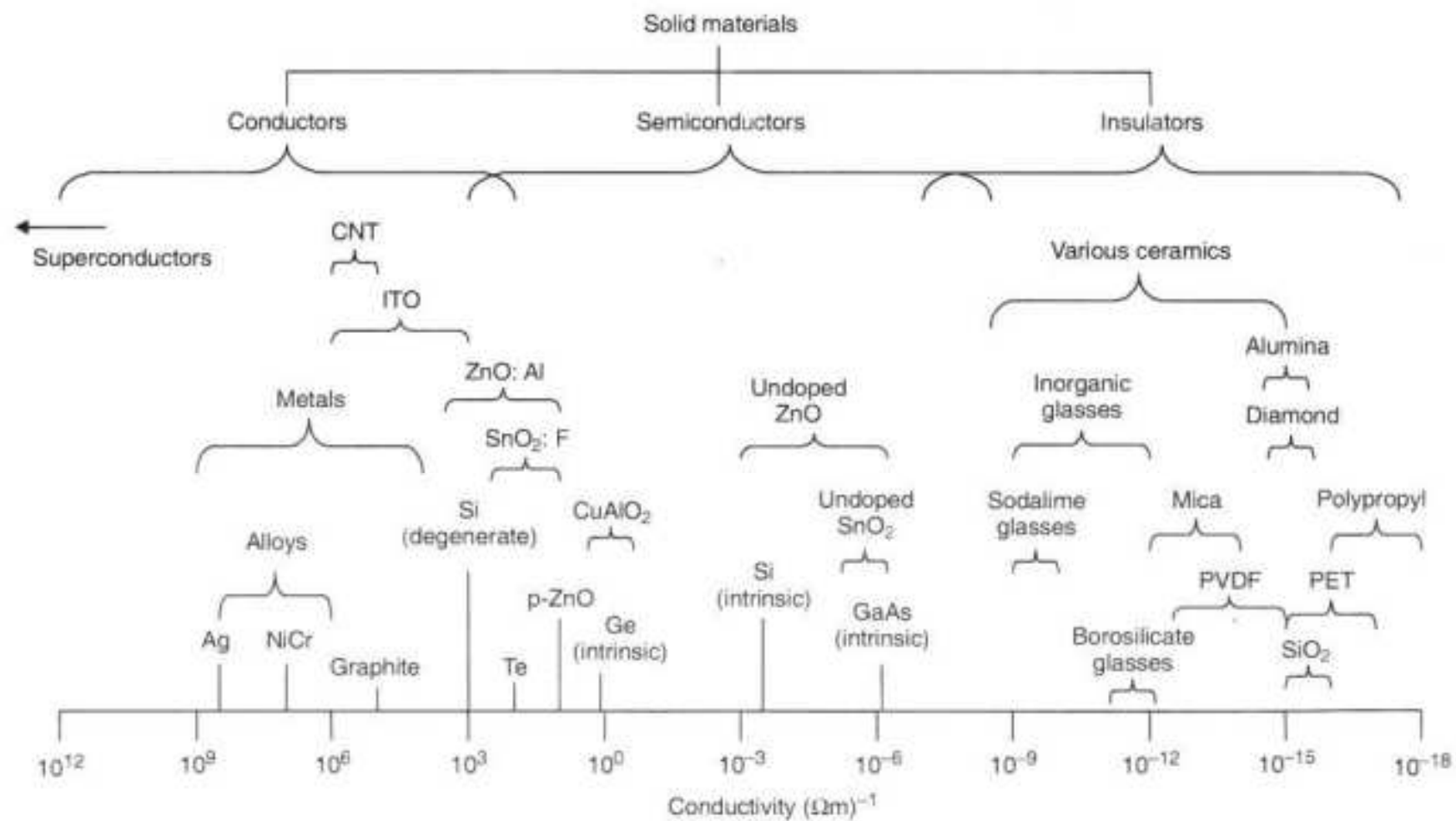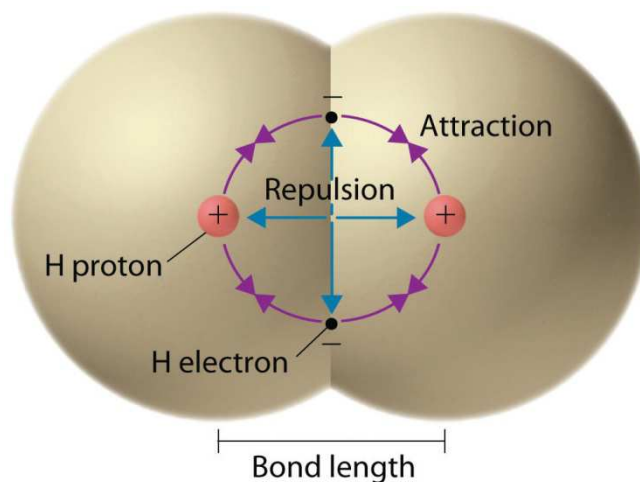
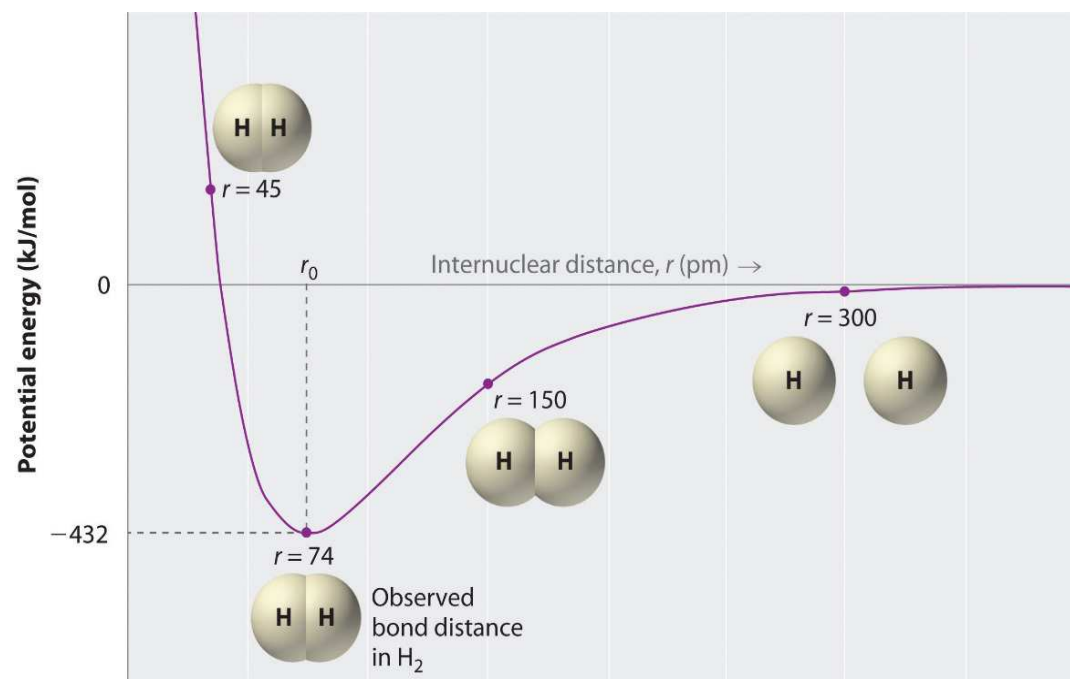**Fig. 3.1** Conductivity ranges of various materials (after Ref. [1]).

Energy of a system of two atoms


Covalent bonding

Attractive and repulsive interactions between electrons and nuclei in the hydrogen molecule : Electron–electron and proton–proton interactions are repulsive; electron–proton interactions are attractive. At the observed bond distance, the repulsive and attractive interactions are balanced.

Potential energy (kJ/mol)

0

−432

r_0

Internuclear distance, r (pm) →

$r = 45$

H H

$r = 300$

H   H

$r = 150$

H H

$r = 74$

H H

Observed
bond distance
in H_2

A plot of potential energy versus internuclear distance for the interaction between two gaseous hydrogen atoms : At long distances, both attractive and repulsive interactions are small. As the distance between the atoms decreases, the attractive electron–proton interactions dominate, and the energy of the system decreases. At the observed bond distance, the repulsive electron–electron and proton–proton interactions just balance the attractive interactions, preventing a further decrease in the internuclear distance. At very short internuclear distances, the repulsive interactions dominate, making the system less stable than the isolated atoms.

Ionic bonding
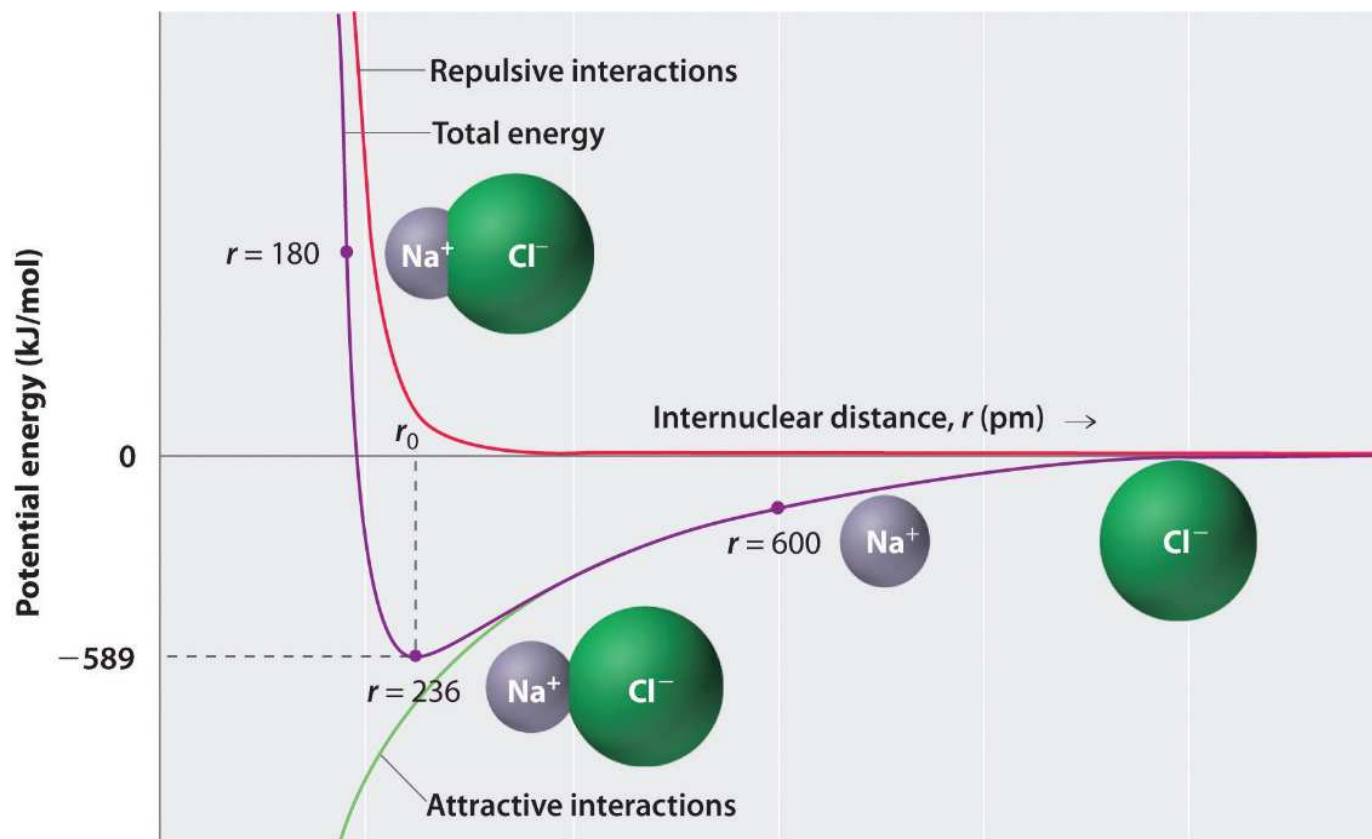
A plot of potential energy versus internuclear distance for the interaction between a gaseous Na^+ ion and a gaseous Cl^- ion: The energy of the system reaches a minimum at a particular distance (r_0) when the attractive and repulsive interactions are balanced.

http://2012books.lardbucket.org/books/principles-of-general-chemistry-v1.0m/section_12/95236acc5635a15c238054d04d2d320e.jpg

Lennard-Jones potential

3.1 | ALLOWED AND FORBIDDEN ENERGY BANDS

3.1.1   Formation of Energy Bands

- The wave functions of the electrons of the two atoms overlap, which means that the two electrons will interact.
- This interaction or perturbation results in the discrete quantized energy level **splitting** into two discrete energy levels,
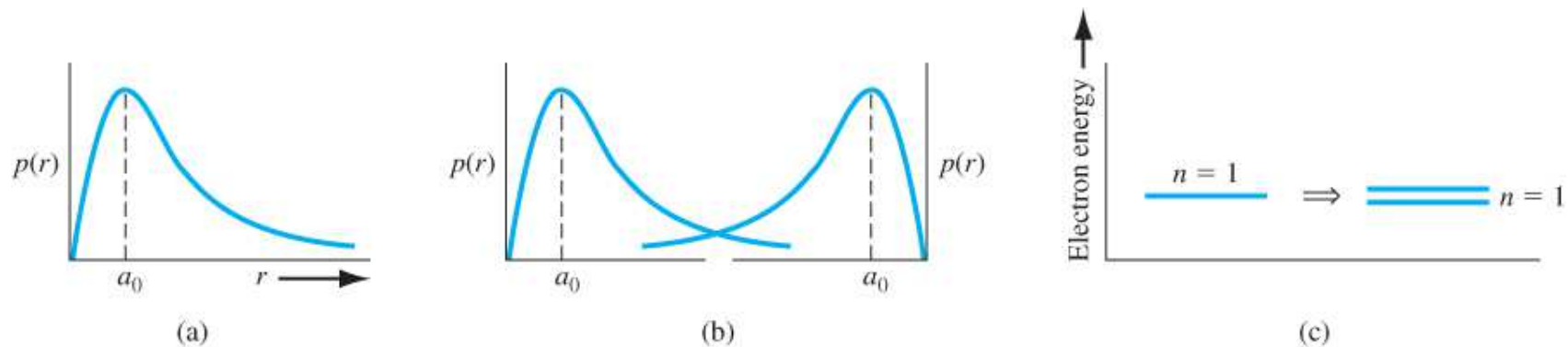
Figure 3.1 | (a) Probability density function of an isolated hydrogen atom. (b) Overlapping probability density functions of two adjacent hydrogen atoms. (c) The splitting of the $n = 1$ state.

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- pushing the atoms together, the initial quantized energy level will **split into a band** of discrete energy levels.
  This energy difference is extremely small, so that for all practical purposes, we have a quasi-continuous energy distribution through the allowed energy band.
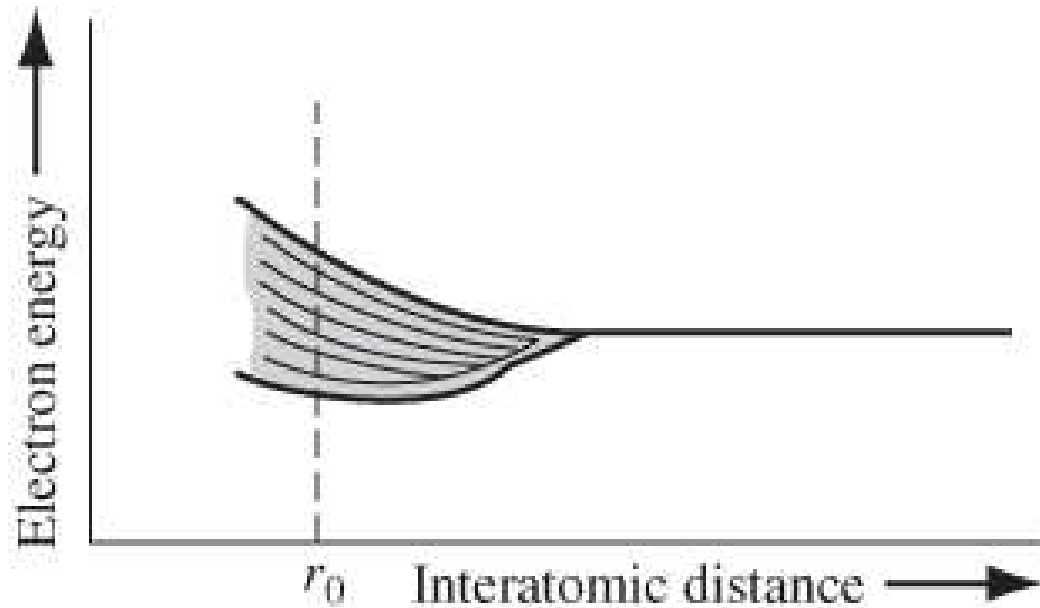
Figure 3.2 | The splitting of an energy state into a band of allowed energies.

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 energy band.

the outermost electrons in the n = 3 energy shell will begin to interact initially,
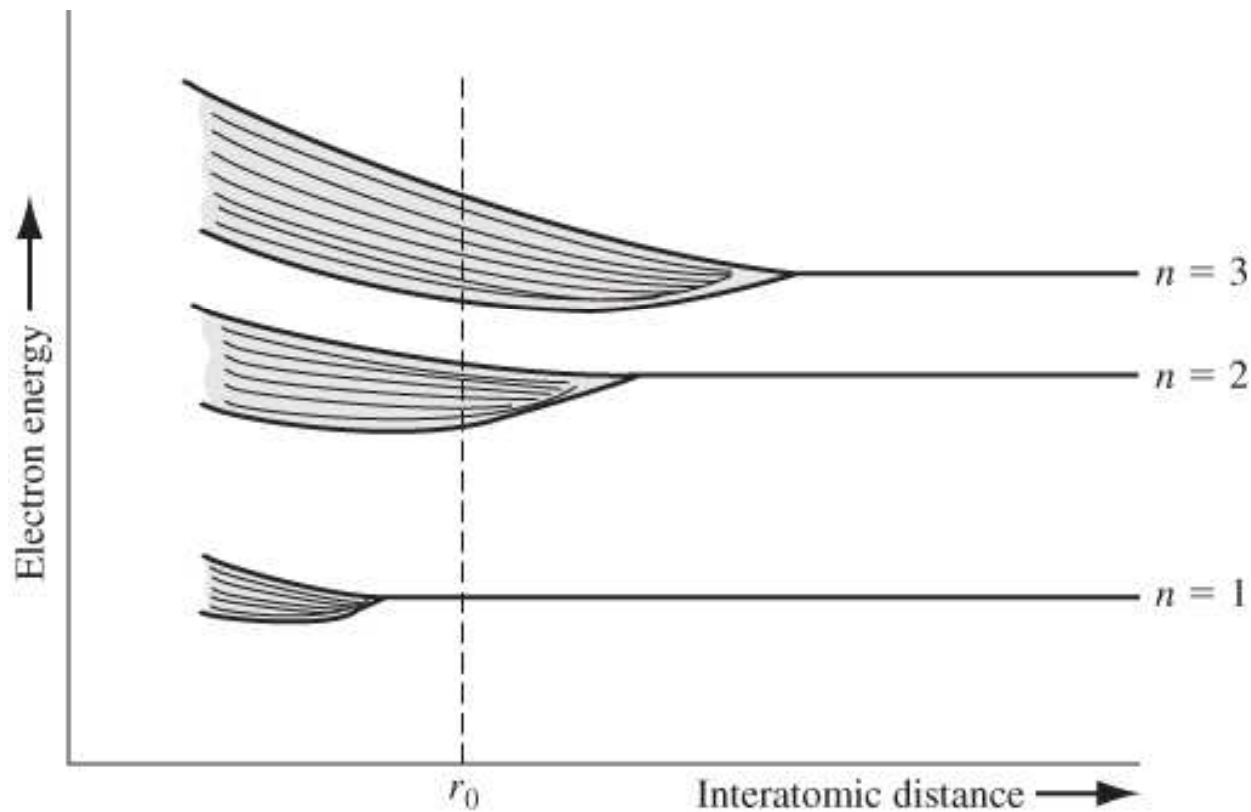
Figure 3.3 | Schematic showing the splitting of three energy states into allowed bands of energies.

- 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.
- **The bandgap energy Eg** between the top of the valence band and the bottom of the conduction band is the width of the forbidden energy band.
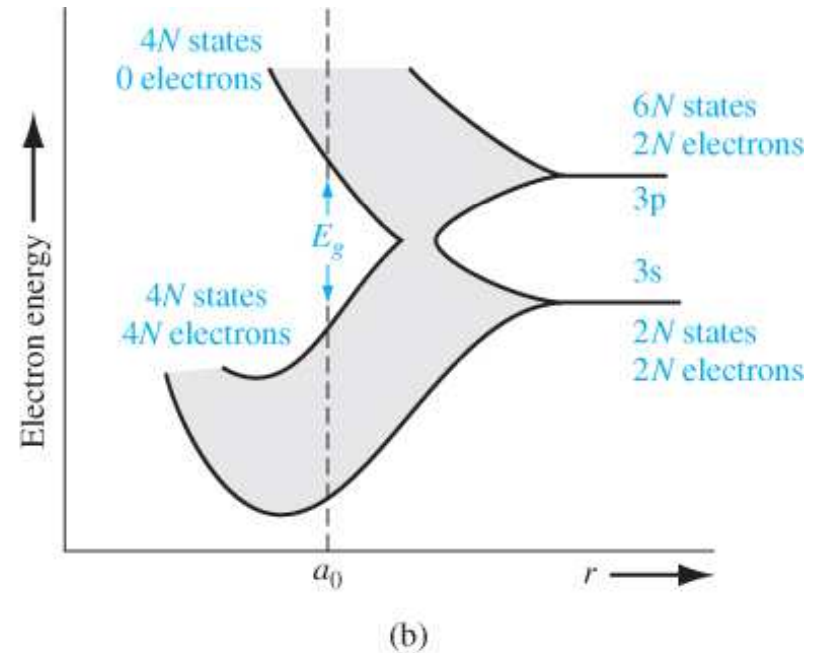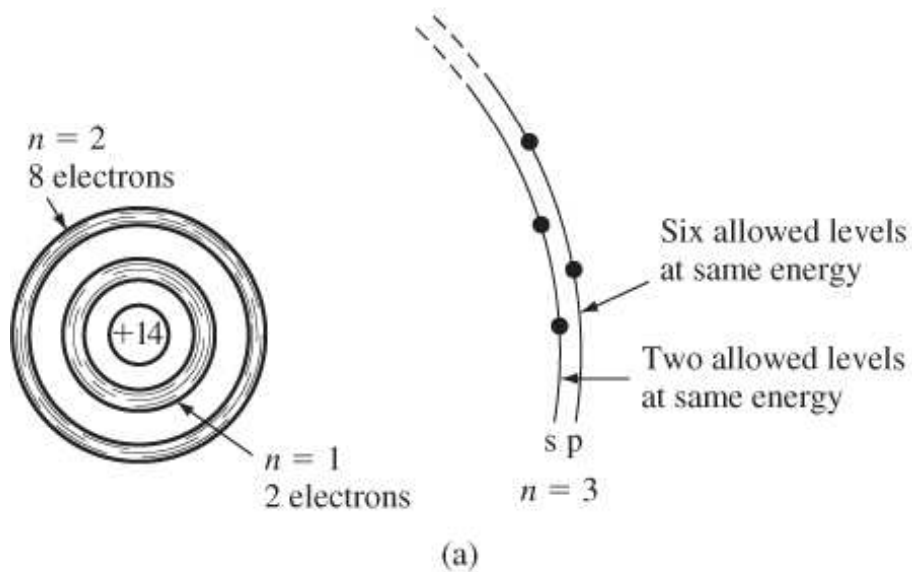
Figure 3.4 | (a) Schematic of an isolated silicon atom. (b) The splitting of the 3s and 3p states of silicon into the allowed and forbidden energy bands. (*From Shockley [6].*)

Silicon

Silicon is the primary semiconductor used in VLSI systems

Si has 14 Electrons

Energy Bands
(Shells)

Nucleus

Valence Band

At T=0K, the highest energy band occupied by an electron is called the valence band.

Silicon has 4 outer shell / valence electrons

Relative spacing of atoms →

Relative energy of electrons ↑

4N States
0 Electrons

6N States
2N Electrons

6N States
2N Electrons

Band gap $= E_g$

4N States
4N Electrons

2N States
2N Electrons

2N States
2N Electrons

8N States
4N Electrons

Actual spacing

s	m	l	n	
$\pm(\uparrow)$	+2			
$\pm(\uparrow)$	+1			
$\pm(\uparrow)$	0	2		
$\pm(\uparrow)$	−1			
$\pm(\uparrow)$	−2			
$\pm(\uparrow)$	+1			
$\pm(\uparrow)$	0	1	3	Outer shell
$\pm(\uparrow)$	−1			
$\pm(\uparrow)$	0	0		
$\pm(\uparrow)$	+1			
$\pm(\uparrow)$	0	1	2	
$\pm(\uparrow)$	−1			
$\pm(\uparrow)$	0	0		Middle shell
$\pm(\uparrow)$	0	0	1	Inner shell

Bloch's Theorem and Bloch Wavefunctions

This theorem is one of the most important formal results in all of solid state physics because it tells us the mathematical form of an electron wavefunction in the presence of a periodic potential energy.

In the independent-electron approximation, the time-independent Schrodinger equation for an electron in a periodic potential is:

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + U(\vec{r}) \right]\psi = E\psi$$

where the potential energy is invariant under a lattice translation vector $\vec{T}$:

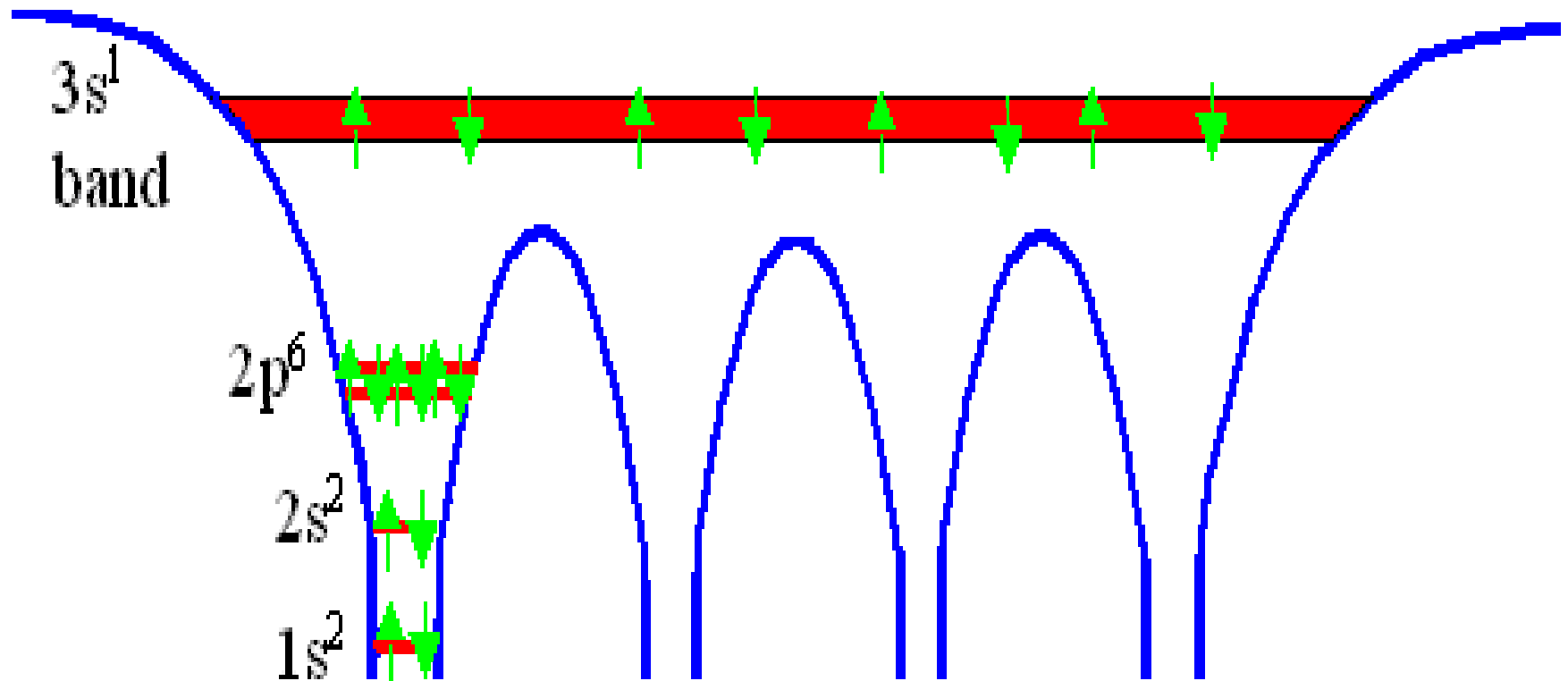$$U(\vec{r} + \vec{T}) = U(\vec{r})$$ **and** $$\vec{T} = u\vec{a} + v\vec{b} + w\vec{c}$$

Bloch showed that the solutions to the SE are the product of a plane wave and a function with the periodicity of the lattice:

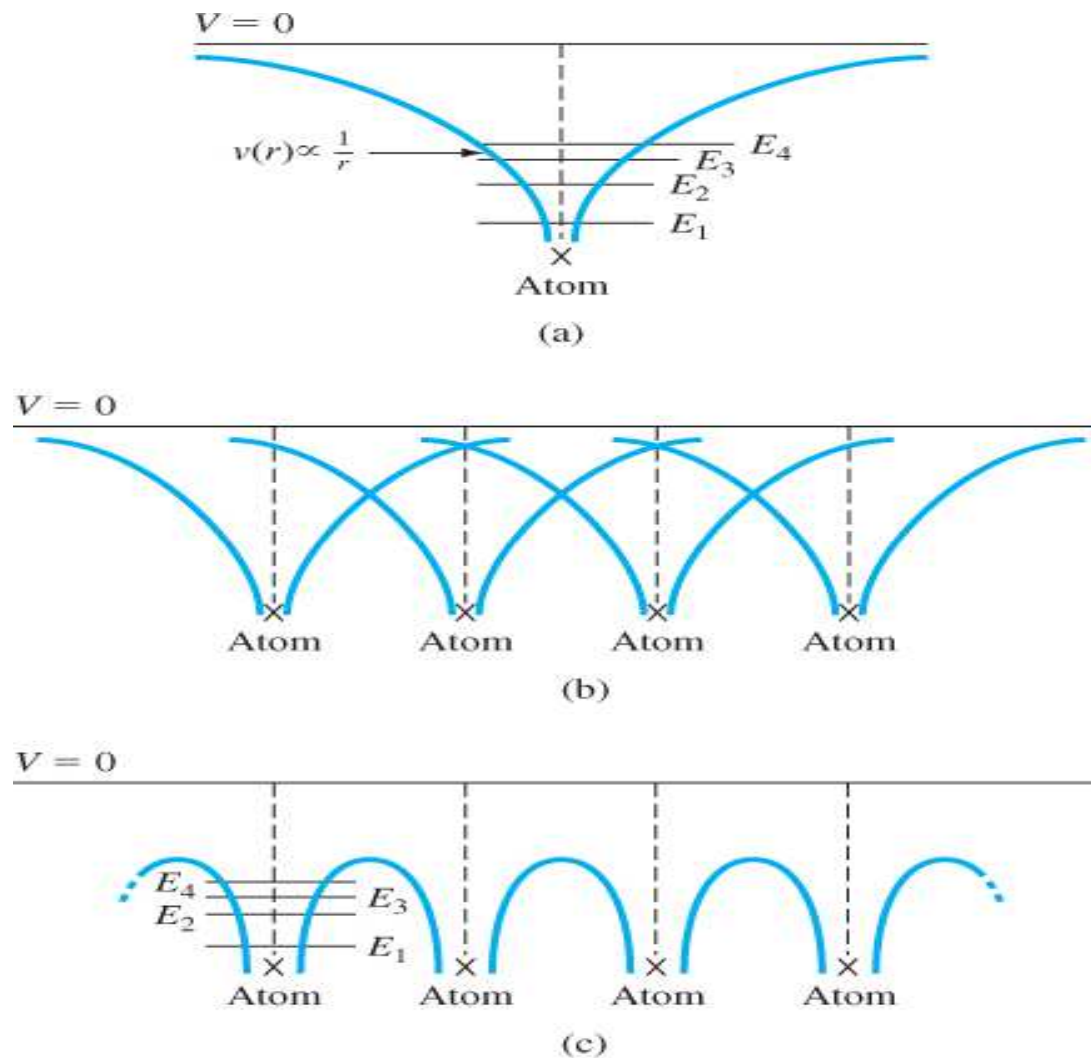$$\psi_{\vec{k}}(\vec{r}) = u_{\vec{k}}(\vec{r})e^{i\vec{k}\cdot\vec{r}}$$

Where $u_{\vec{k}}(\vec{r}) =$ Periodic function
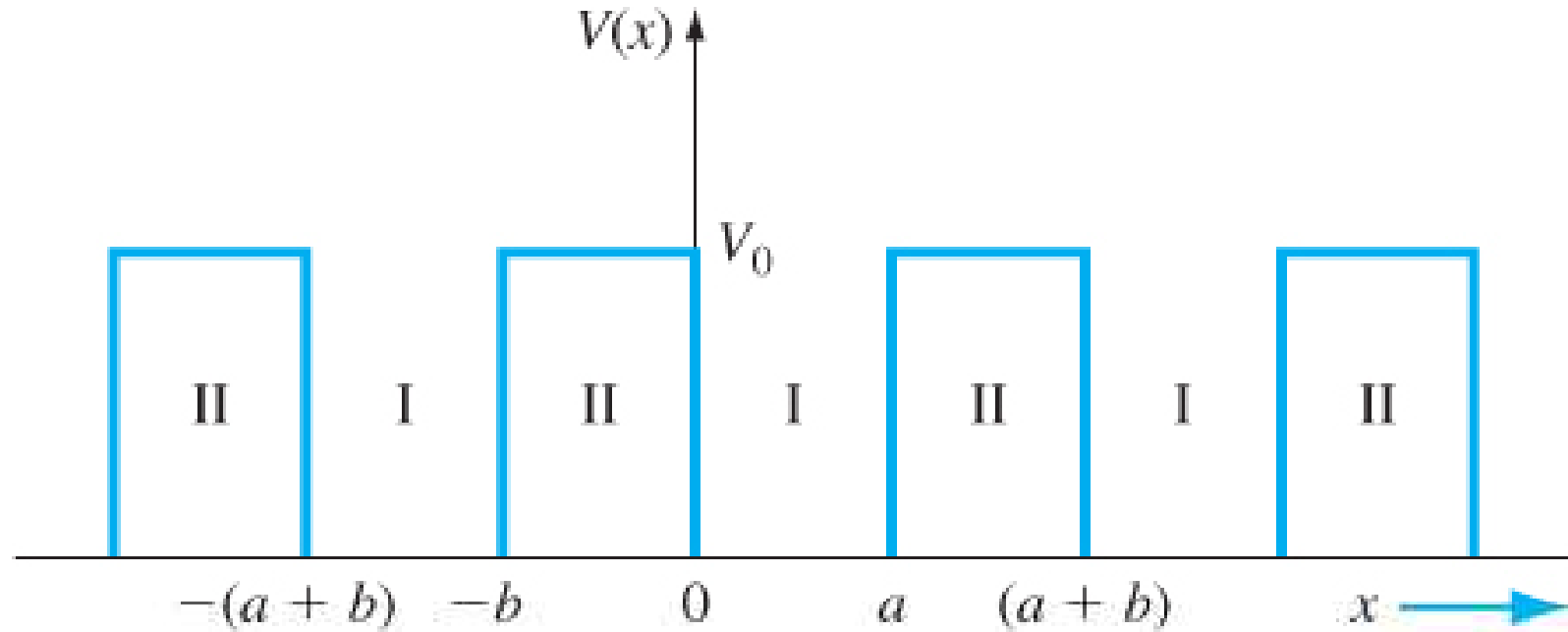
"Bloch functions"

e.g. for a **Na** crystal including some energy states, is periodic and looks more like this

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3.1.2 The Kronig–Penney Model

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.

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

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

Total solution to the wave equation is the product of the time-independent solution and the time-dependent solution, or

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

which may be written as

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

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

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

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

$$\alpha^2 = \frac{2mE}{\hbar^2} \tag{3.5}$$

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

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

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

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

so that Equation (3.6) may be written as

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

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

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

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

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

Here we are skipping some mathematical calculations and directly writing the solution of both equation 3.4 and 3.8 by assuming the potential barrier width $b \to 0$ and the barrier height $V_0 \to infinity$, but such that the product bV_0 remains finite.

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

We may define a parameter P' as

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

Then, finally, we have the relation

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

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 that 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

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

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

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

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

$p = 0 \qquad p \text{ or } k \longrightarrow$
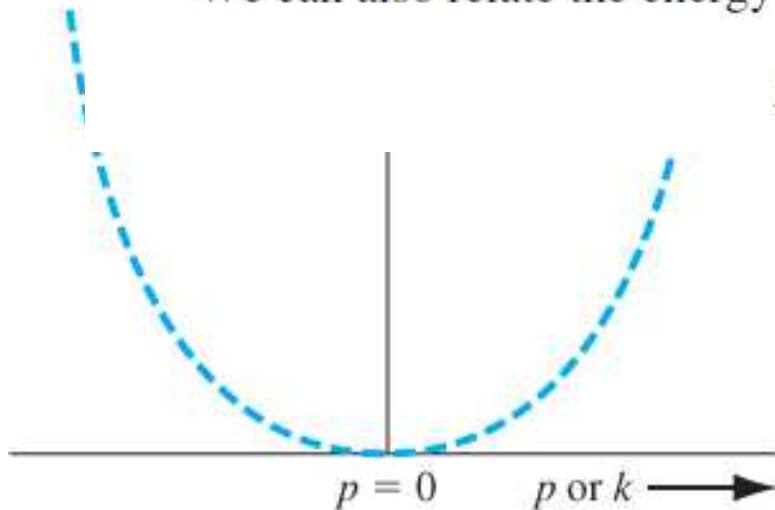
Figure 3.7 | The parabolic E versus k curve for the free electron.

consider the relation between E and k from Equation (3.24) for **the particle in the single-crystal lattice**.

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

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

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

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

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 $f(\alpha a)$.

Figure 3.9 shows the concept of allowed energy bands for the particle propagating in the crystal lattice.


Solution exist/Allowed band
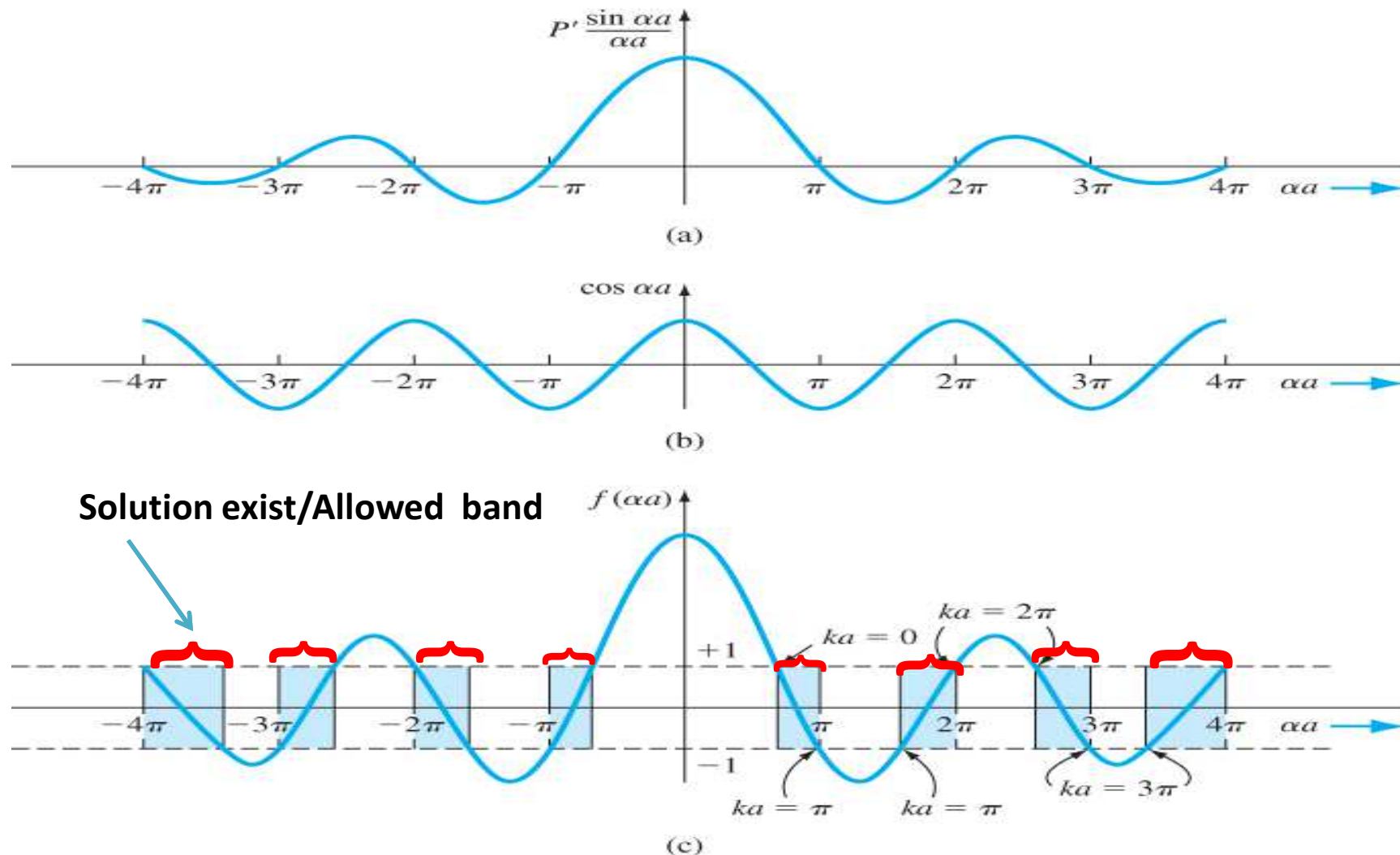
Figure 3.8 | A plot of (a) the first term in Equation (3.29), (b) the second term in Equation (3.29), and (c) the entire $f(\alpha a)$ function. The shaded areas show the allowed values of (αa) corresponding to real values of k.
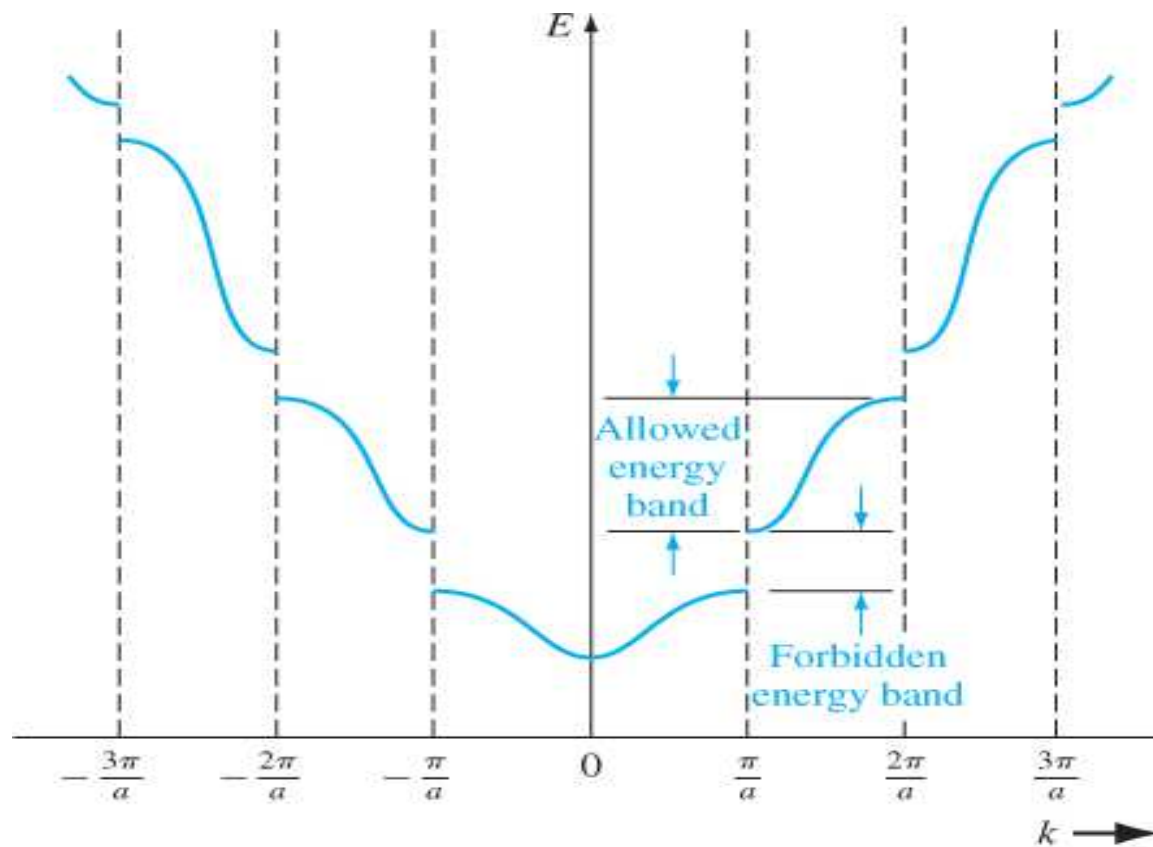
Figure 3.9 | The E versus k diagram generated from Figure 3.8. The allowed energy bands and forbidden energy bandgaps are indicated.

This plot is referred to as a reduced k-space diagram, or a **reduced-zone** representation.
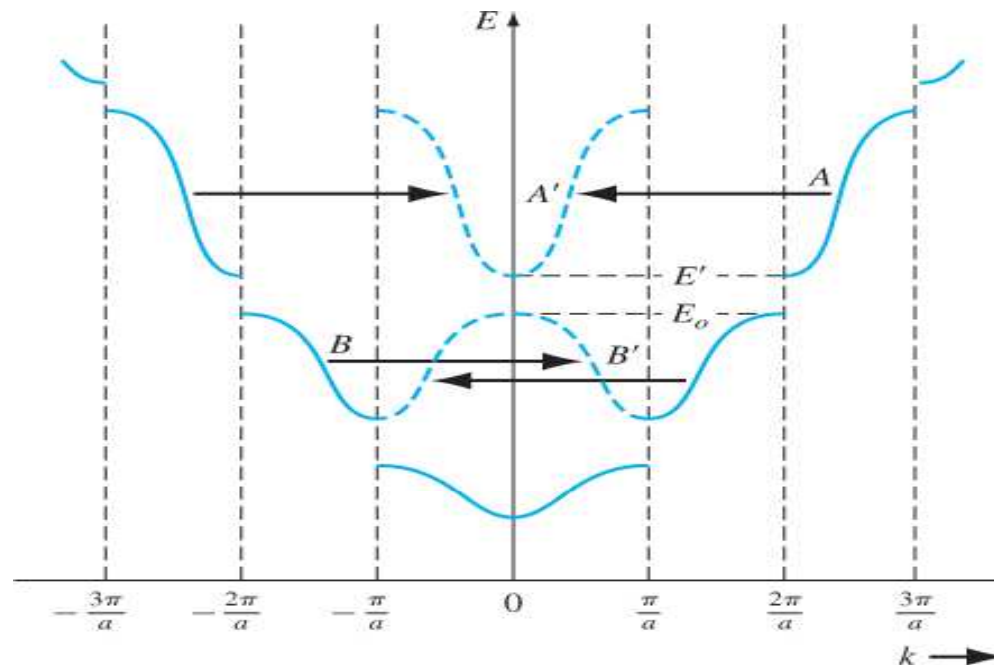
Figure 3.10 | The E versus k diagram showing 2π displacements of several sections of allowed energy bands.

We have been considering the Kronig–Penney model, which is a one-dimensional periodic potential function used to model a single-crystal lattice. The principal 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.
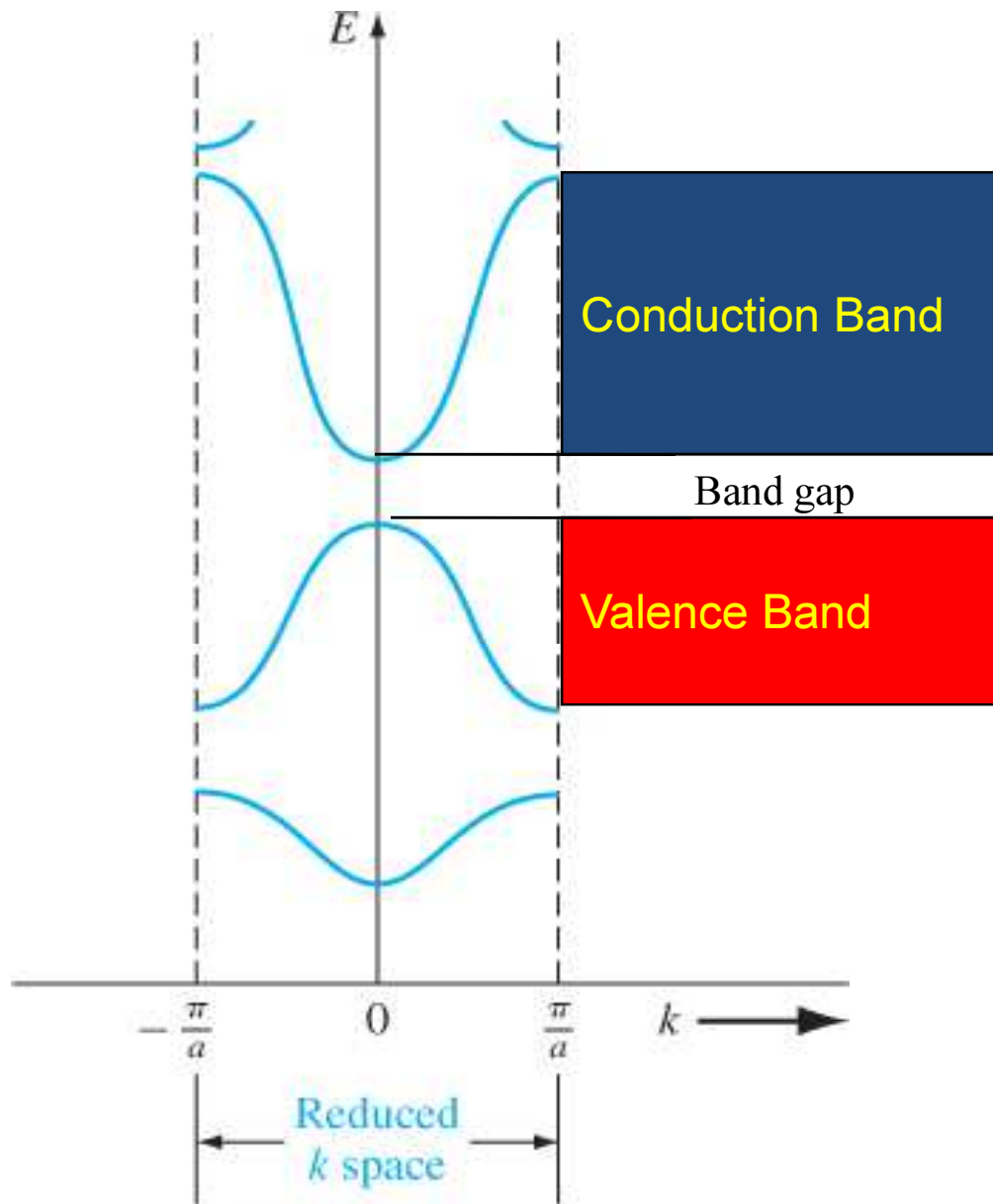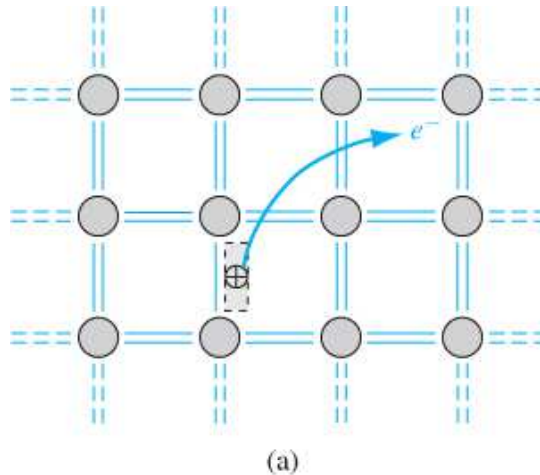
**Figure 3.11** | The E versus k diagram in the reduced-zone representation.

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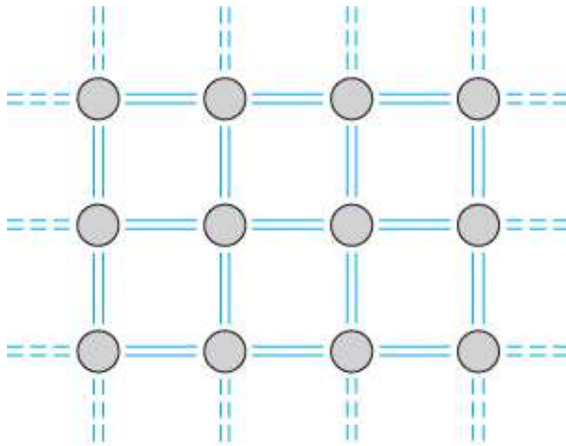
Figure 3.12 | Two-dimensional representation of the covalent bonding in a semiconductor at $T = 0$ K.

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.
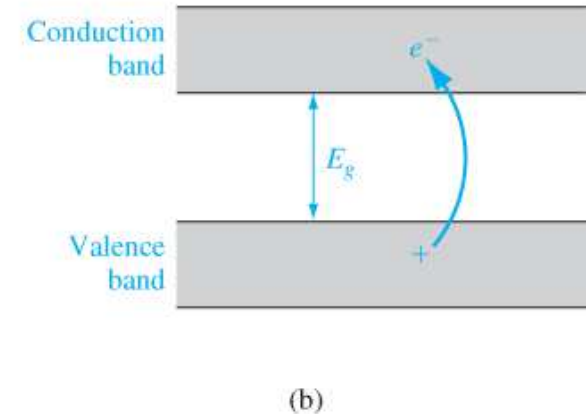
- At T = 0 K, the 4N states in the lower band, the valence band, are filled with the valence electrons.
- The semiconductor is **neutrally charged**. This means that, as the negatively charged electron breaks away from its covalent bonding position, a positively charged "empty state" is created in the original covalent bonding position in the valence band.
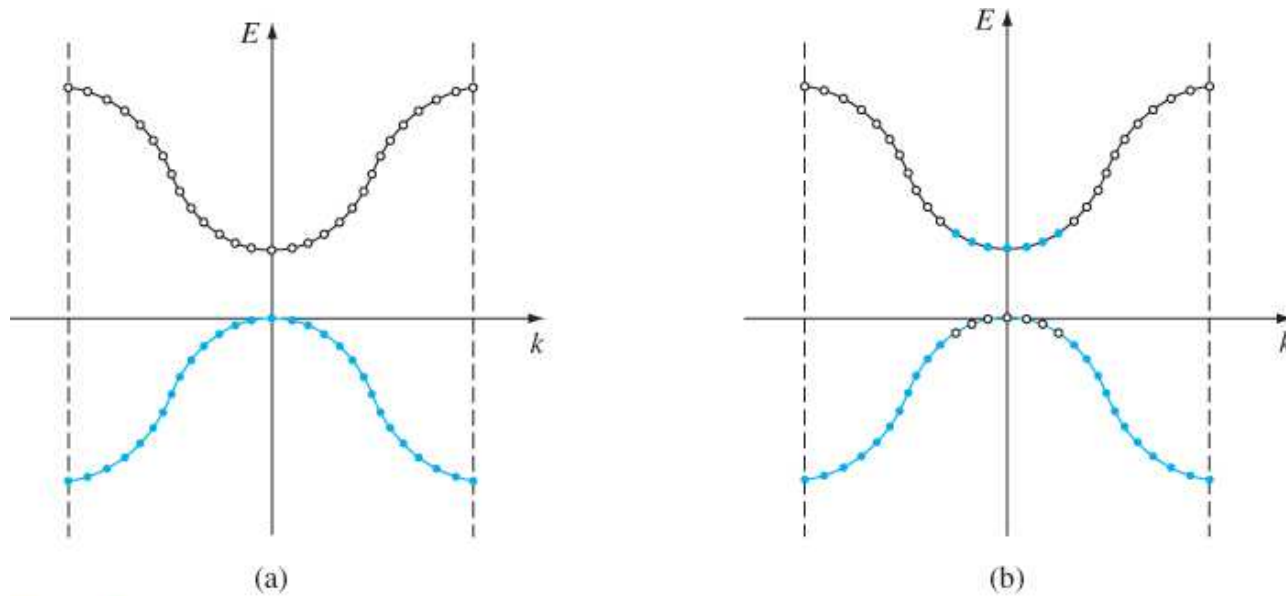
Figure 3.14 | The E versus k diagram of the conduction and valence bands of a semiconductor at (a) $T = 0$ K and (b) $T > 0$ K.

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

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

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

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

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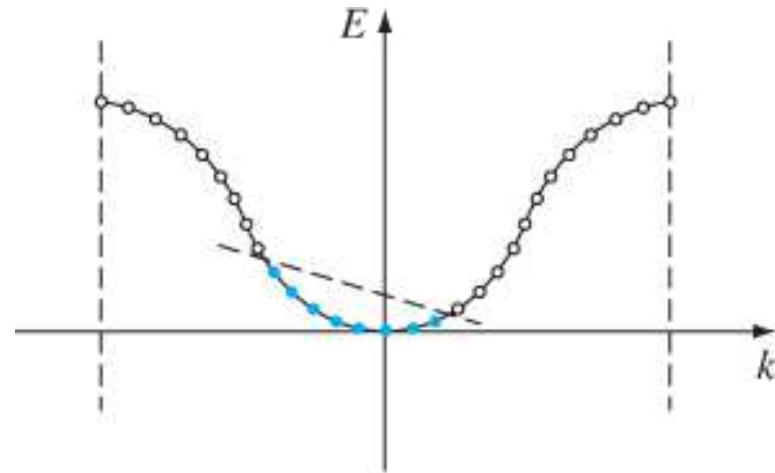
If a force is applied to a particle and the particle moves, it must gain energy. This effect is expressed as

$$dE = F\,dx = F\,v\,dt \qquad (3.34)$$

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

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

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.

3.2.3   Electron Effective Mass

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

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

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

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.

$E = p^2/2m = \hbar^2 k^2/2m$, 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

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

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

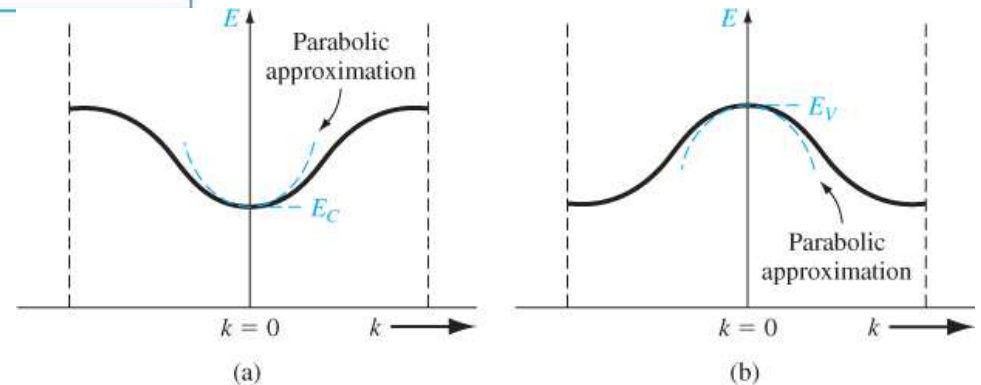$$\frac{1}{\hbar}\frac{dE}{dk} = \frac{p}{m} = v \qquad (3.39)$$

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

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

We may rewrite Equation (3.40) as

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

The energy near the bottom of this energy band may be approximated by a parabola, just as that of a free particle.

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.

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

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

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

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

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

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

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

3.2.4   Concept of the Hole

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**
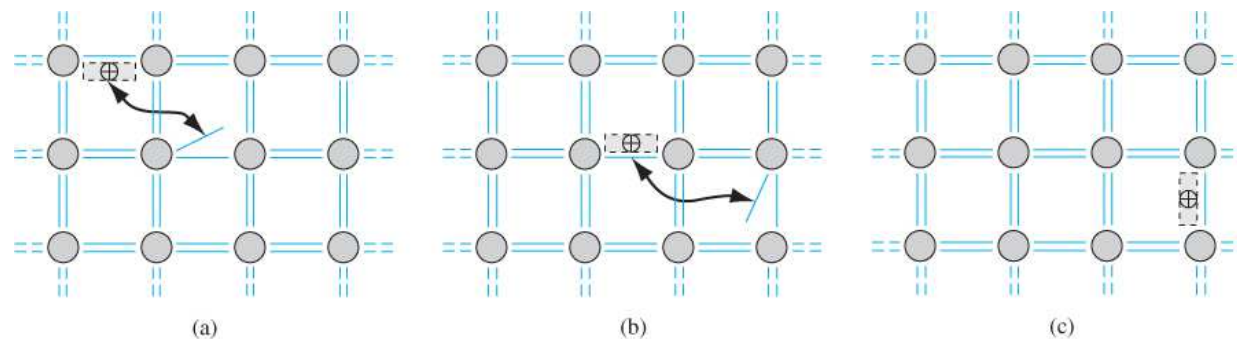

(a)   (b)   (c)

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

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

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

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

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

externally applied force. The net drift current density generated from a completely full band, then, is zero, or

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

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

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

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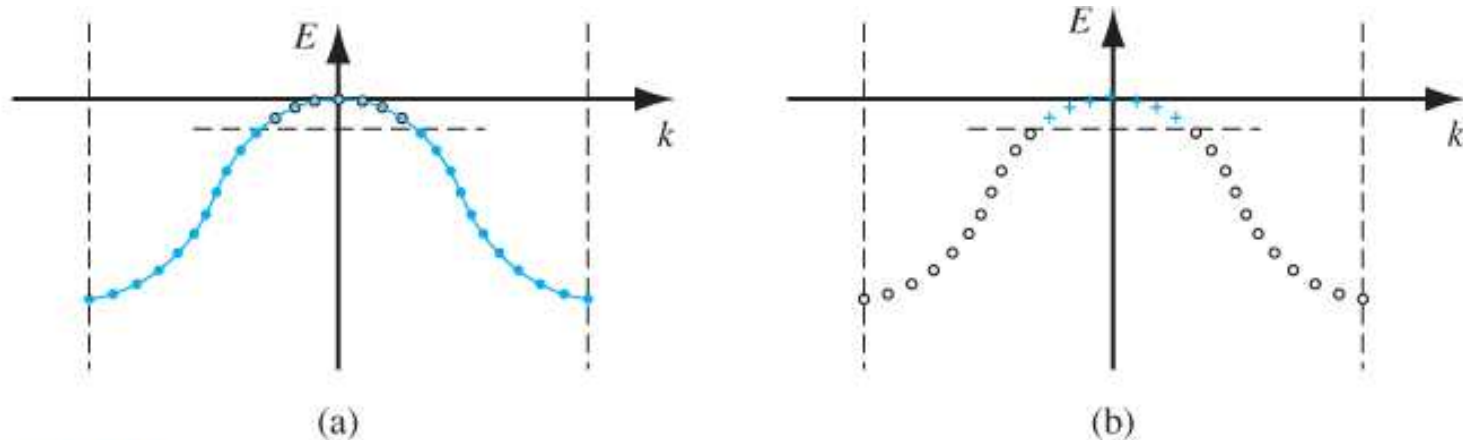
Figure 3.18 | (a) Valence band with conventional electron-filled states and empty states. (b) Concept of positive charges occupying the original empty states.

- the valence band with the conventional electron-filled states and empty states,
- 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

$$(E - E_v) = -C_2(k)^2 \tag{3.53}$$

The energy E_v is the energy at the top of the energy band. Since $E < E_v$ for electrons in this band, 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

$$\frac{d^2E}{dk^2} = -2C_2 \tag{3.54}$$
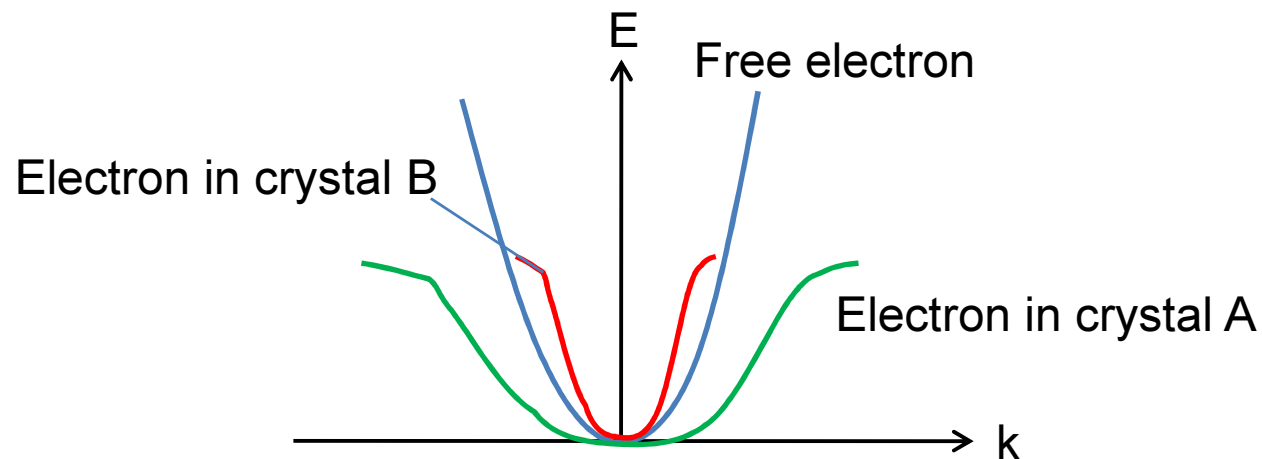
We may rearrange this equation so that

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

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

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.

E versus k curve

➢Curvature of E-k depends on the medium that electron moves in

Effective mass changes

$$m^*_A \ > \ m \ > \ m^*_B$$

Ex; $m^*_{Si} = 0.916m_0$, $m^*_{GaAs} = 0.065m_0$ m_0; in free space