

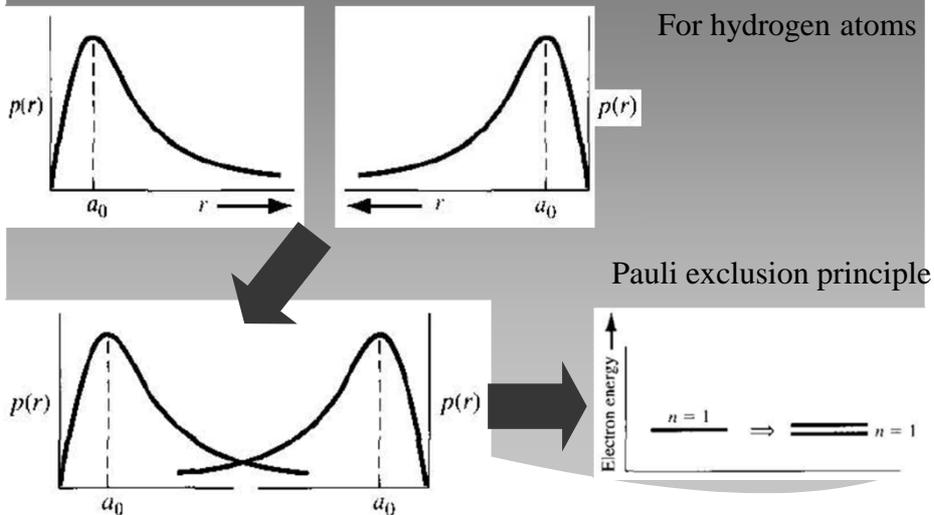
Introduction to the Quantum Theory of Solids

Outline:

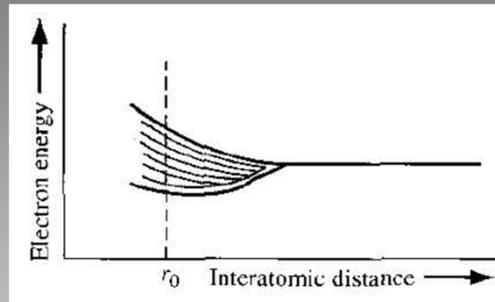
- Allowed and Forbidden Energy Bands
- Electrical Conduction in Solids
- Extension to Three Dimensions
- Density of States Function
- Statistical Mechanics

Formation of Energy Bands

For hydrogen atoms

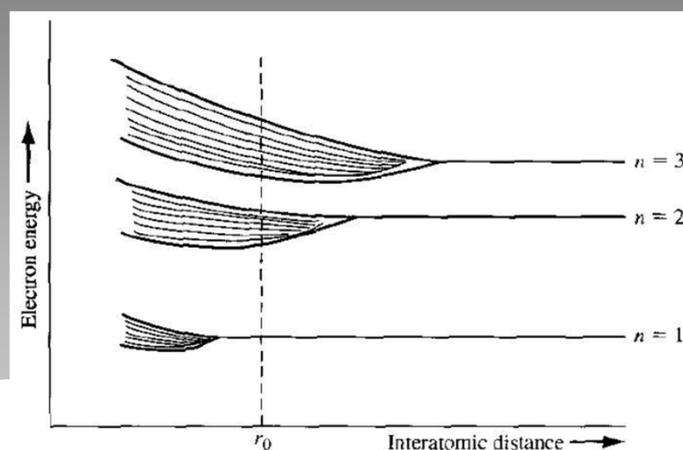


a regular periodic arrangement of hydrogen-type atoms

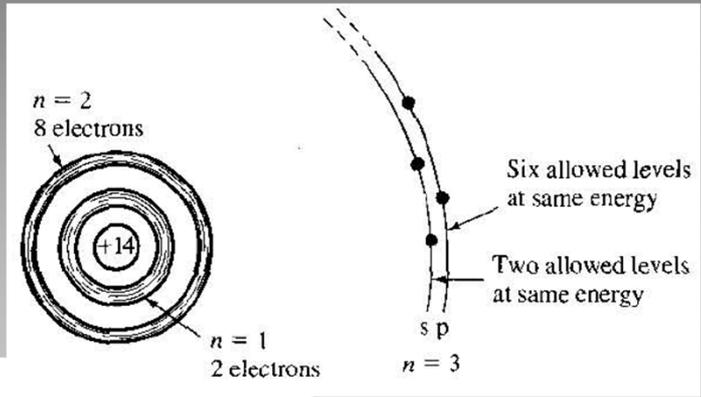


- This energy difference is extremely small, so that for all practical purposes, we have a quasi-continuous energy distribution through the allowed energy band.
- atomic thermal vibration (chapter 2 energy level diagram)

splitting of three energy states into allowed bands of energies

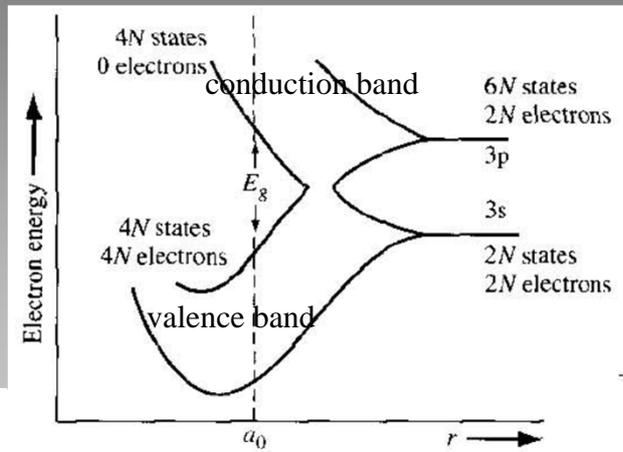


an isolated silicon atom

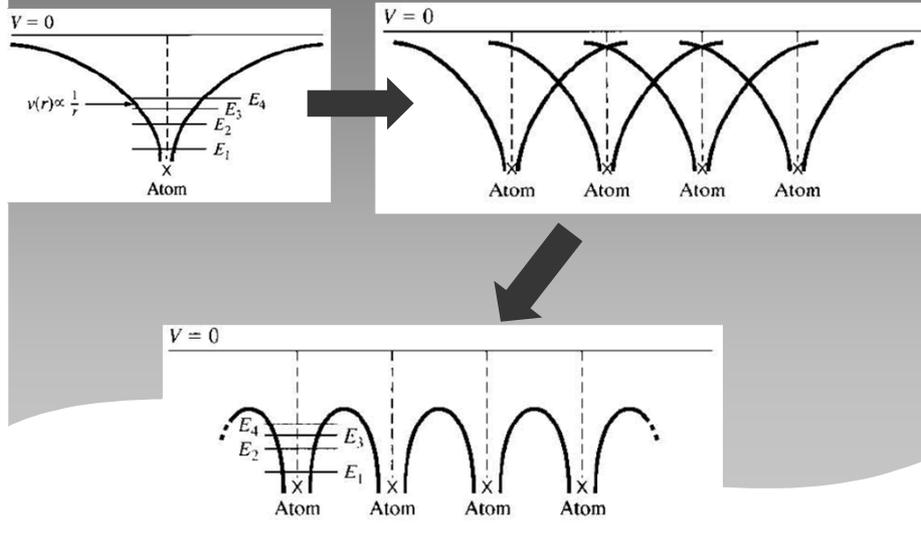


splitting of the 3s and 3p states of silicon

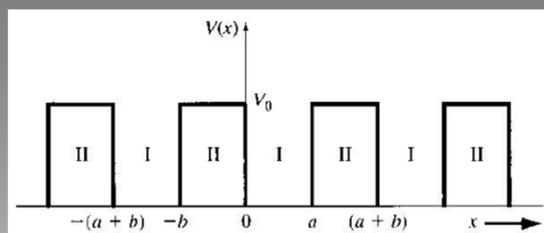
at 0K



potential function of a 1D single crystal



Kronig-Penney Model



Bloch theorem: all one-electron wave functions, for problems involving periodically varying potential energy functions, must be of the form

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

where k is called a constant of motion. \leftarrow wave number
 $u(x)$ is a periodic function with period $(a+b)$.

Schrodinger's wave equation

the motion of an electron in a single-crystal material

$$\begin{aligned}\Psi(x, t) &= \psi(x)\phi(t) = u(x)e^{jkx} \cdot e^{-j(E/\hbar)t} \\ &= u(x)e^{j(kx - (E/\hbar)t)}\end{aligned}$$

region I, $V(x)=0$

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

where $u_1(x)$ is the amplitude of the wave function in region I

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

region II, $V(x)=V_0$

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

where $u_2(x)$ is the amplitude of the wave function in region II

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

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

Solution:

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

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

If E and V(x) are finite, then

$\psi(x)$ must be finite, single-valued, and continuous.

$\partial\psi(x)/\partial x$ must be finite, single-valued, and continuous.

Apply boundary conditions

$$\begin{array}{c} \swarrow E \quad \searrow V_0 \\ \rightarrow \frac{-(\alpha^2 + \beta^2)}{2\alpha\beta} (\sin \alpha a)(\sin \beta b) + (\cos \alpha a)(\cos \beta b) = \cos k(a + b) \end{array}$$

→ numerical solution

Fix the value of bV_0

Let $b \rightarrow 0, V_0 \rightarrow \infty$

$$\begin{array}{c} P' \frac{\sin \alpha a}{\alpha a} + \cos \alpha a = \cos \underline{ka} \\ \swarrow V_0 \quad \nwarrow E \end{array}$$

where $P' = \frac{mV_0ba}{\hbar^2}$

It is not a solution of Schrodinger's wave equation but gives the conditions for which Schrodinger's wave equation will have a solution.

k-Space Diagram

For free electrons, that is $V_0=0$

$$\alpha = k$$

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

$$E = \frac{p^2}{2m} = \frac{k^2 \hbar^2}{2m}$$

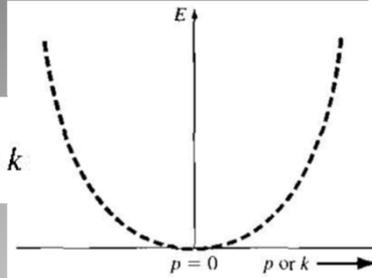
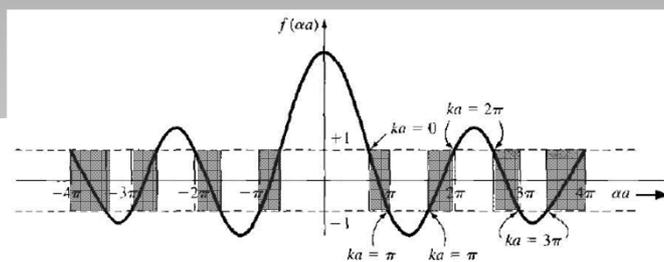
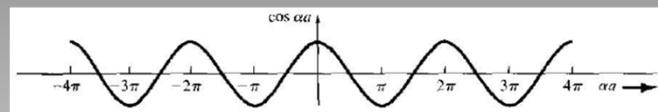
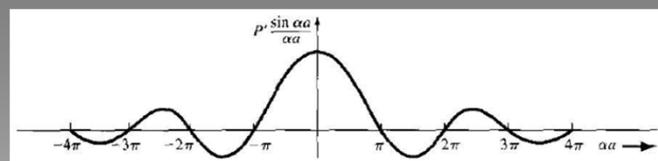


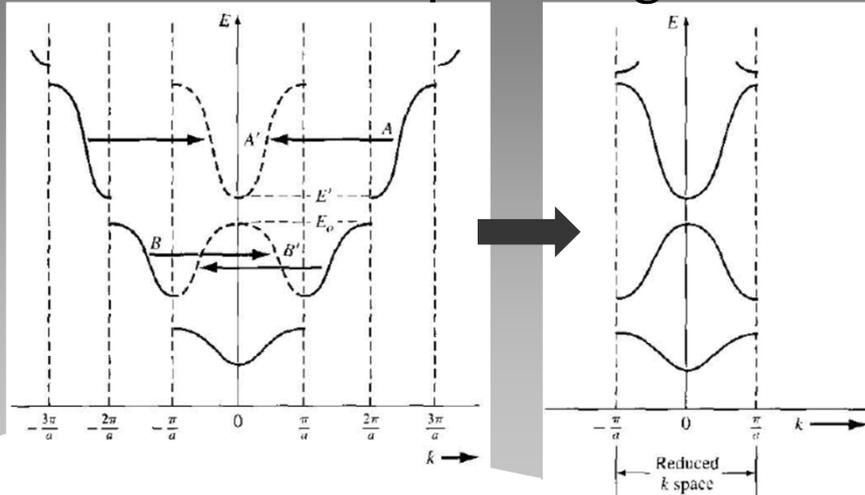
Figure 3.7 | The parabolic E versus k curve for the free electron.

For $V_0 \neq 0$,

$$p' \frac{\sin \alpha a}{\alpha a} + \cos \alpha a = \cos ka \quad -1 < \cos(ka) < +1$$



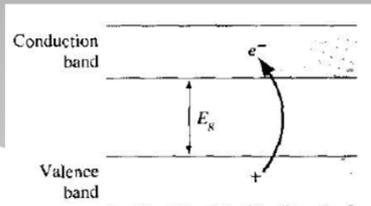
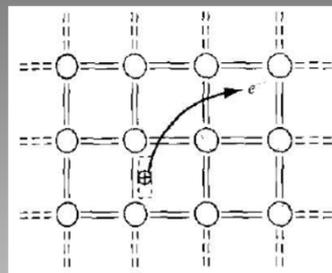
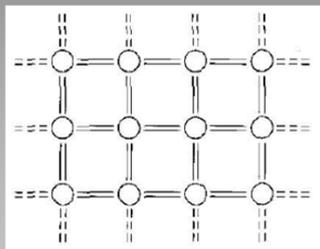
reduced k-space diagram



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

Energy Band and Bond Model

At 0K
Above 0K



No external force,

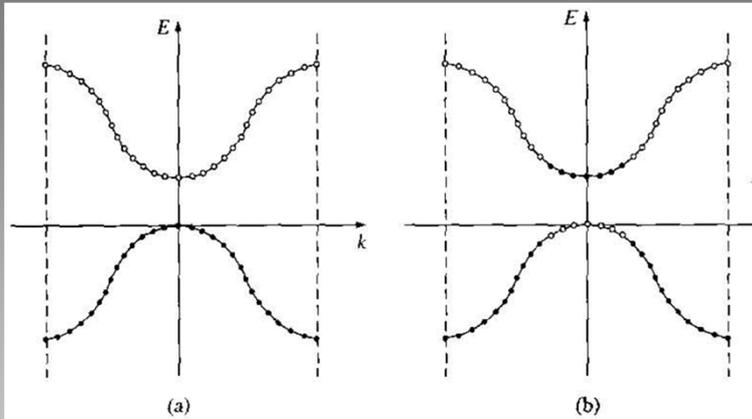
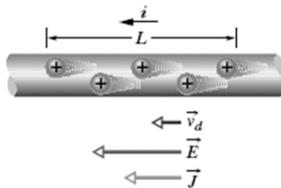


Figure 3.14 | The E versus k diagram of the conduction and valence bands of a semiconductor at (a) $T = 0$ K and (b) $T > 0$ K.



Drift Current

When a conductor does not have a current through it, its conduction electrons move randomly, with no net motion in any direction. When the conductor does have a current through it, these electrons actually still move randomly, but now they tend to *drift* with a **drift speed** v_d in the direction opposite that of the applied electric field that causes the current. The drift speed is tiny compared with the speeds in the random motion. For example, in the copper conductors of household wiring, electron drift speeds are perhaps 10^{-5} or 10^{-4} m/s, whereas the random-motion speeds are around 10^6 m/s.

For convenience, Fig. 26-5 shows the equivalent drift of *positive* charge carriers in the direction of the applied electric field \vec{E} . Let us assume that these charge carriers all move with the same drift speed v_d and that the current density J is uniform across the wire's cross-sectional area A . The number of charge carriers in a length L of the wire is nAL , where n is the number of carriers per unit volume. The total charge of the carriers in the length L , each with charge e , is then

$$q = (nAL)e.$$

Because the carriers all move along the wire with speed v_d , this total charge moves through any cross section of the wire in the time interval

$$t = \frac{L}{v_d}.$$

Equation 26-1 tells us that the current i is the time rate of transfer of charge across a cross section, so here we have

$$i = \frac{q}{t} = \frac{nALe}{L/v_d} = nAev_d. \quad (26-6)$$

Solving for v_d and recalling Eq. 26-5 ($J = i/A$), we obtain

$$v_d = \frac{i}{nAe} = \frac{J}{ne}$$

or, extended to vector form,

$$\vec{J} = (ne)\vec{v}_d. \quad (26-7)$$

Here the product ne , whose SI unit is the coulomb per cubic meter (C/m^3), is the *carrier charge density*. For positive carriers, ne is positive and Eq. 26-7 predicts that \vec{J} and \vec{v}_d have the same direction. For negative carriers, ne is negative and \vec{J} and \vec{v}_d have opposite directions.

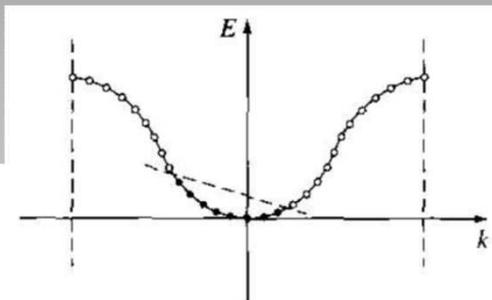
$$J = qNv_d$$

$$J = q \sum_{i=1}^N v_i$$

If external force $\neq 0$, electrons can gain energy and a net momentum.

For electrons,
$$J = -e \sum_{i=1}^n v_i$$

n is the number of electrons per unit volume in the conduction band.



Electron Effective Mass

the motion of electrons in the lattice:

- externally applied force,
- internal forces in the crystal due to positively charged ions or protons and negatively charged electrons

$$F_{\text{total}} = F_{\text{ext}} + F_{\text{int}} = ma$$

$$F_{\text{ext}} = m^*a$$

where m : rest mass, m^* : effective mass

For free electrons

from $E = p^2/2m = \hbar^2k^2/2m$ and $p = \hbar k$

$$\frac{dE}{dk} = \frac{\hbar^2 k}{m} = \frac{\hbar p}{m} \quad \rightarrow \quad \frac{1}{\hbar} \frac{dE}{dk} = \frac{p}{m} = v$$

$$\frac{d^2E}{dk^2} = \frac{\hbar^2}{m} \quad \rightarrow \quad \frac{1}{\hbar^2} \frac{d^2E}{dk^2} = \frac{1}{m}$$

in an electric field,

$$F = ma = -eE \quad a = \frac{-eE}{m}$$

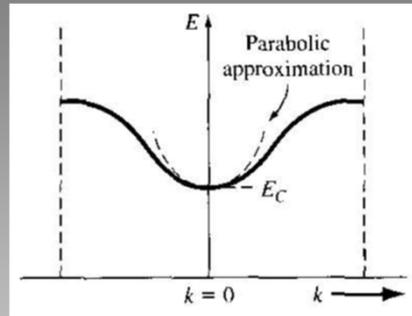
near the bottom of conduction band

Parabolic approximation

$$E - E_c = C_1(k)^2$$

$$\frac{d^2 E}{dk^2} \approx 2C_1$$

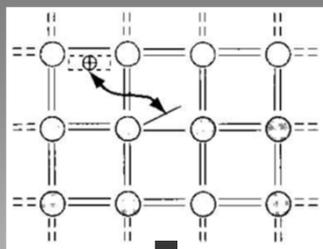
$$\frac{1}{\hbar^2} \frac{d^2 E}{dk^2} = \frac{2C_1}{\hbar^2} = \frac{1}{m^*}$$



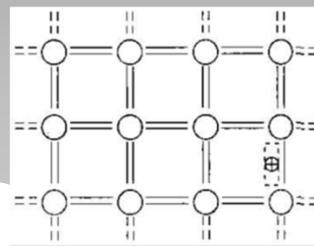
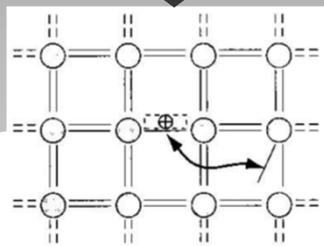
If we apply an electric field to the electron in the bottom of the allowed energy band,

$$a = \frac{-eE}{m_n^*}$$

Concept of the Hole



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.



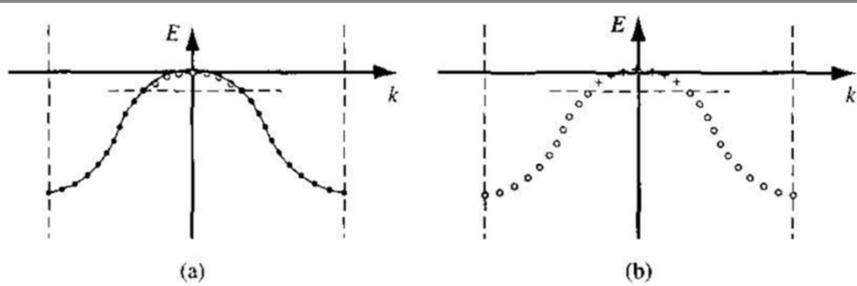


Figure 3.18 (a) Valence band with conventional electron-filled states and empty states. (b) Concept of positive charges occupying the original empty states.

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

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 $-|v|$.

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

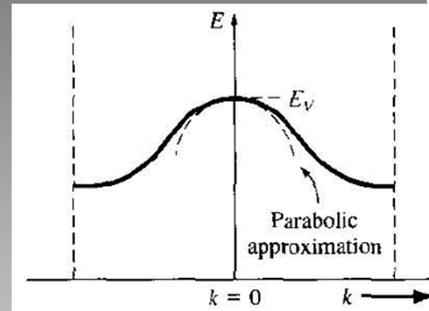
$$J = +e \sum_{i(\text{empty})} v_i \quad \text{where} \quad v(E) = \left(\frac{1}{\hbar} \right) \left(\frac{dE}{dk} \right)$$

Near the top of valence band

Parabolic approximation

$$(E - E_v) = -C_2(k)^2$$

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



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.

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,

$$F = m^* a = -eE$$

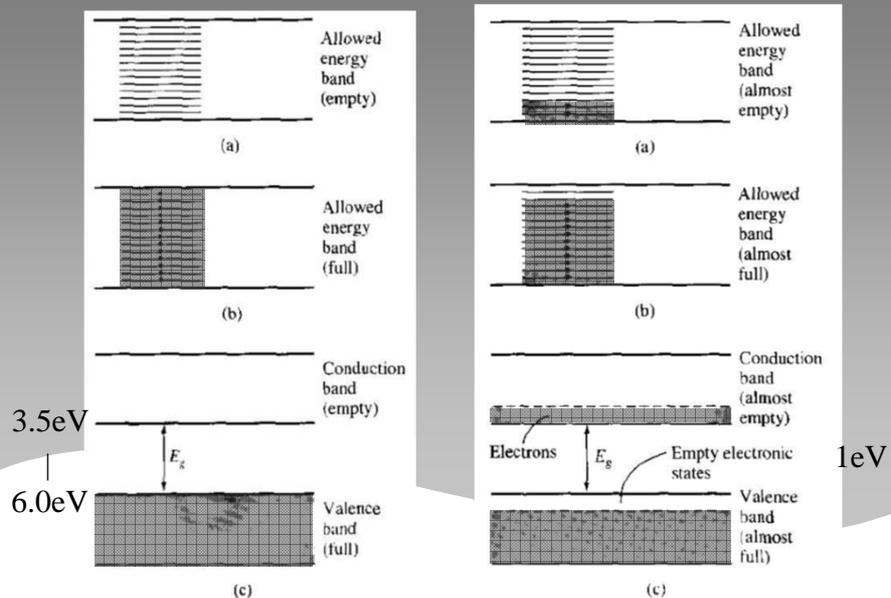
m^* is now a negative quantity,

$$a = \frac{-eE}{-|m^*|} = \frac{+eE}{|m^*|}$$

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

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.

Insulators, and Semiconductors



Metals

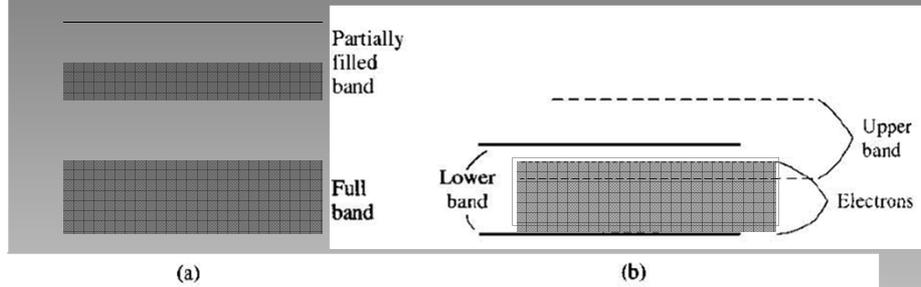
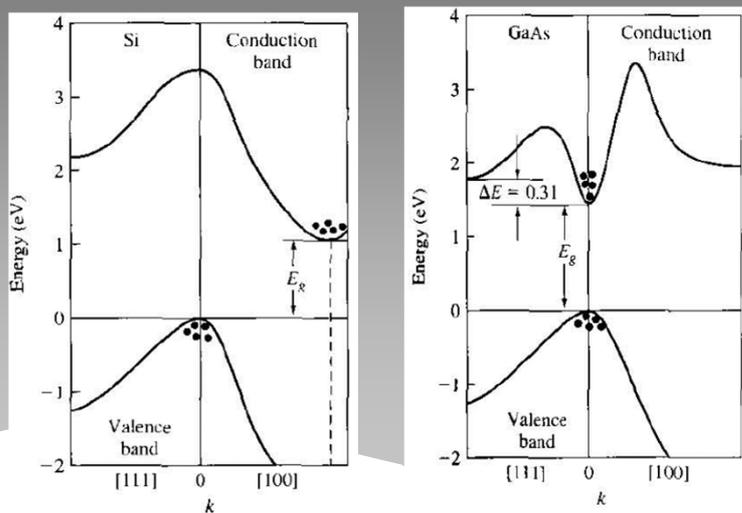


Figure 3.21 | Two possible energy bands of a metal showing (a) a partially filled band and (b) overlapping allowed energy bands.

k-space diagrams of Si and GaAs



Concentration of electrons or holes

n_0 and p_0 in conduction and valence bands, respectively

$$n_0 = \int n(E) dE \quad \leftarrow n(E) \text{ for unit vol.}$$

$$g_c(E) \times f_F(E)$$

density of quantum states per unit volume

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 .)

density of quantum states

Considering a free electron confined to a three-dimensional infinite potential well, where the potential well represents the crystal.

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

Solving the Schrodinger's eq. then we got,

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

where n_x , n_y , and n_z are positive integers.

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

↓

$$k^2 = \frac{2mE}{\hbar^2}$$

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

↓ For unit vol.

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

For semiconductors

near the bottom of conduction band

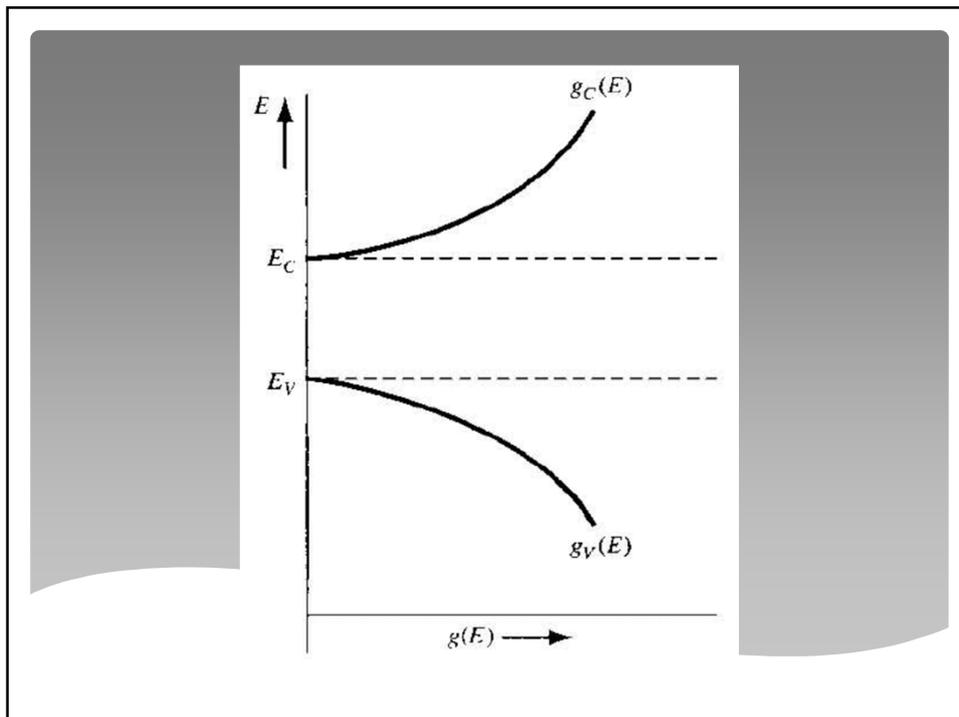
$$E - E_c = \frac{\hbar^2 k^2}{2m_n^*}$$

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

near the top of valence band

$$E_v - E = \frac{\hbar^2 k^2}{2m_p^*}$$

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



Fermi-Dirac probability function

The particles are indistinguishable, but now only one particle is permitted in each quantum state. Electrons in a crystal obey this law.

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

where E_F is called the Fermi energy.

It gives the probability that a quantum state at the energy E will be occupied by an electron.

At 0K

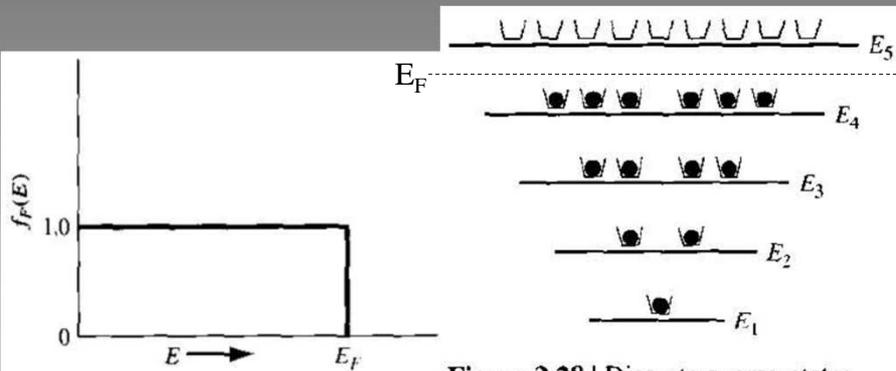


Figure 3.27 | The Fermi probability function versus energy for $T = 0$ K.

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

> 0K

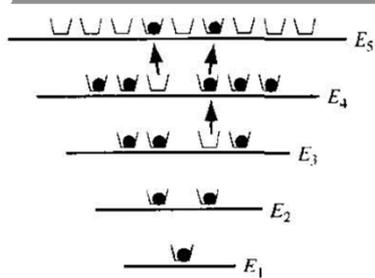


Figure 3.30 | Discrete energy states and quantum states for the same system shown in Figure 3.28 for $T > 0$ K.

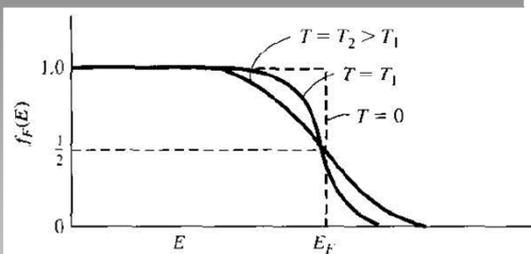


Figure 3.31 | The Fermi probability function versus energy for different temperatures.