Lecture 5

Semiconductor physics III

Introduction to Quantum Theory of Solids

- ❑ Goals
  - ➢ To determine the properties of electrons in a crystal lattice
  - ➢ To determine the statistical characteristics of the very large number of electrons in a crystal
- ❑ Energy band theory
  - ➢ A basic principle of semiconductor material physics
  - ➢ To 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
  - ➢ Using Schrodinger's wave equation
- ❑ The response of an electron in the crystal to an applied external force
  - ➢ To relate the quantum mechanical behavior of electrons in a crystal to classical Newton mechanics
- ❑ Statistical behavior of electrons in a crystal
  - ➢ The probability function will determine the distribution of electrons among the available energy states.

ALLOWED AND FORBIDDEN ENERGY BANDS （能带与禁带）

Formation of energy bands

The wave functions of the two atom electrons overlap, which means that the two electrons interact.
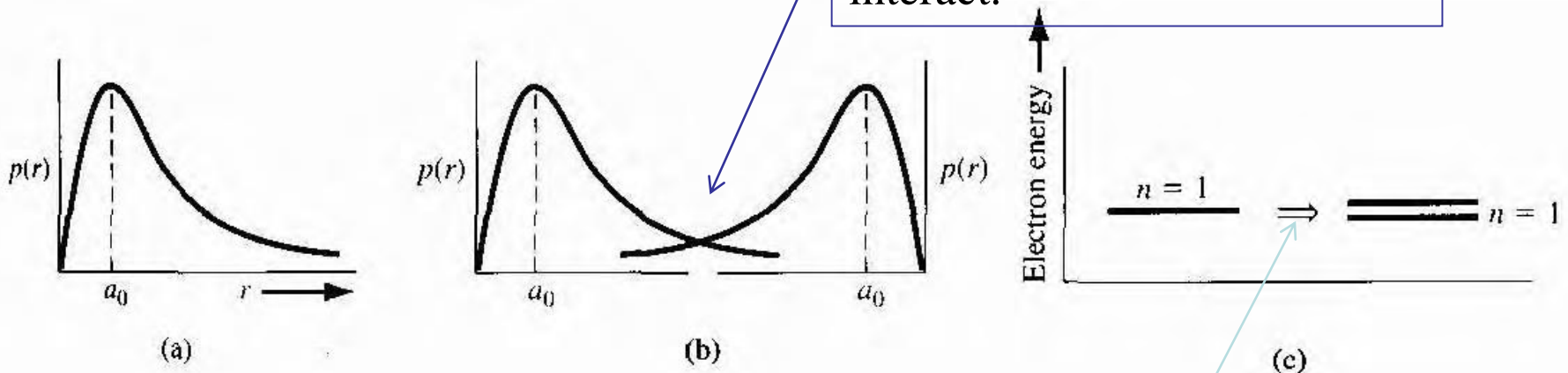

Figure (a) Probability density function of an isolated hydrogen atom.
(b) Overlapping probability density functions of two adjacent hydrogen atoms.
(c) The splitting of the $n = 1$ state.

This interaction or perturbation of the two adjacent atoms results in the discrete quantized energy level splitting into two discrete energy levels

At the equilibrium interatomic distance in the crystal, there is a band of allowed energies, but within the allowed band, the energies are at discrete levels
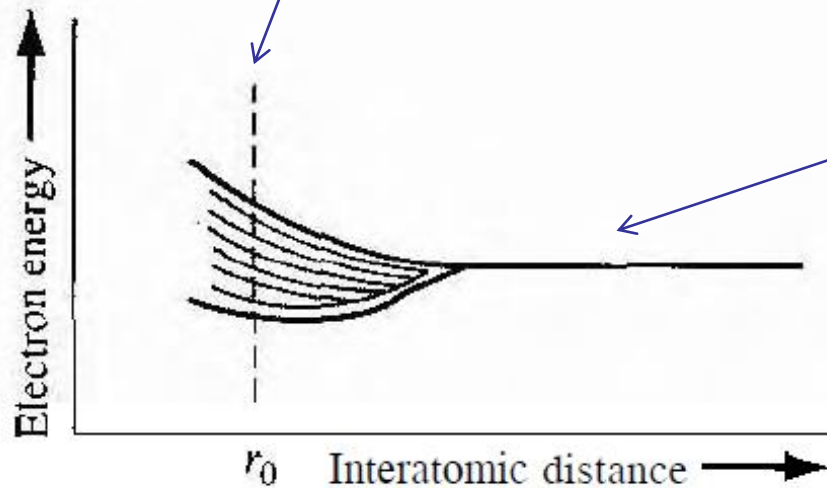
The atoms are very far apart with the initial quantized energy level.

Fig The splitting of an energy state into a band of allowed energies.

The Pauli exclusion principle （泡利不相容原理） states that the joining of atoms to form a system (crystal) does not alter the total **number of quantum** states regardless of size.

● 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**.

● 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.

Example:

Suppose that we have a system with 10^{19} one-electron atoms and at the equilibrium interatomic distance, the width of the allowed energy band is 1eV.

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 10^{-19} eV, which is a very small difference between two energy states.

Fig Schematic showing the splitting of three energy states into allowed bands of energies.
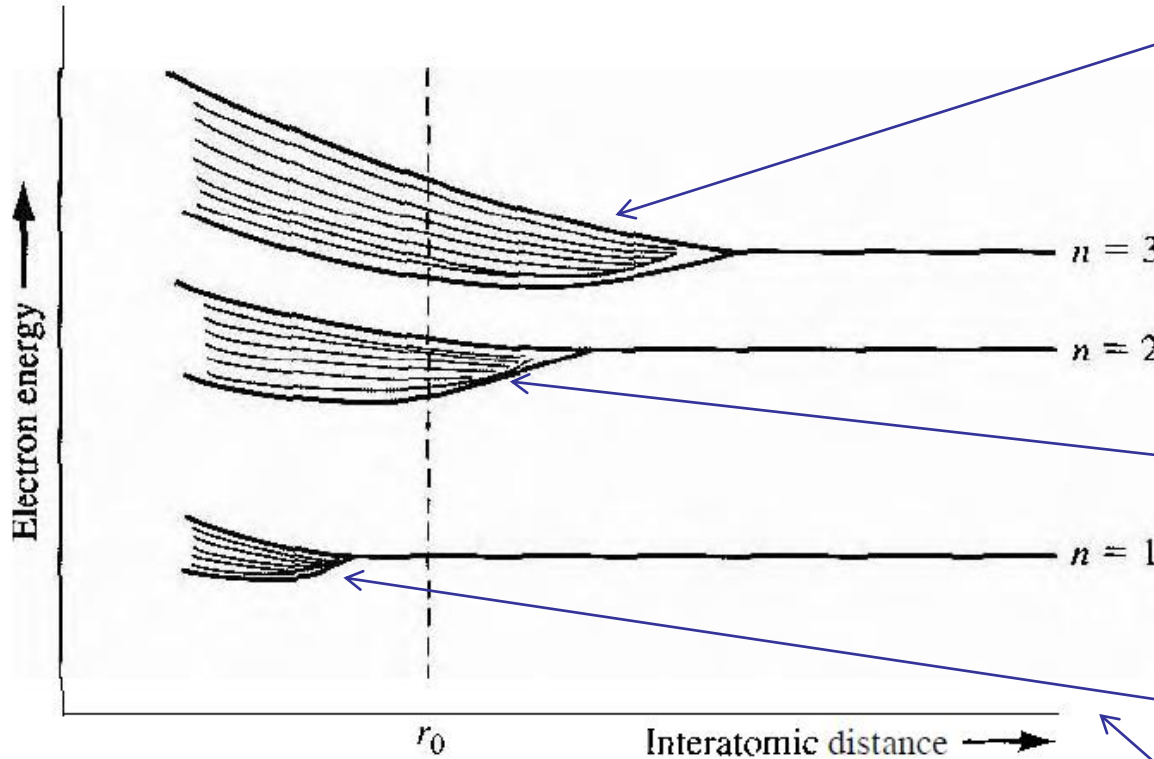
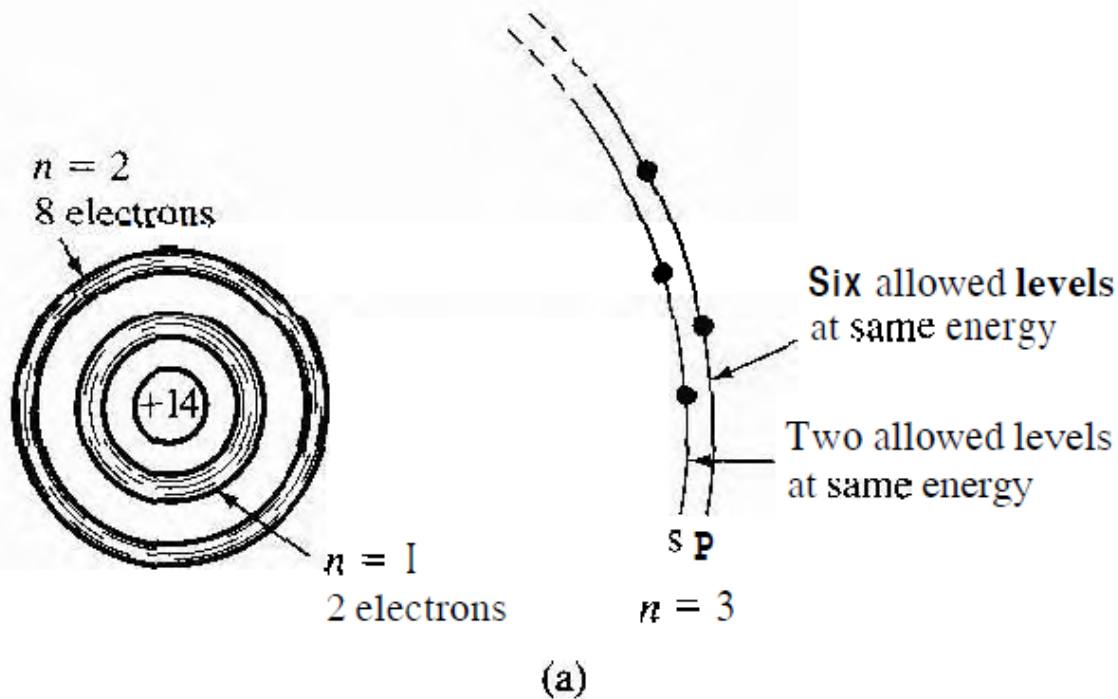If these atoms are brought closer together, the outermost electrons in the n = 3 energy shell will begin to interact

If the atoms continue to move closer, the electrons in the n=2 shell may begin to interact

n=1 shell may begin to interact

If the atoms are initially very far apart, the electrons in adjacent atoms will not interact and will occupy the discrete energy levels.

$$n = 1, 2, 3, \ldots$$
$$l = n-1, n-2, n-3, \ldots, 0$$
$$|m| = l, l-1, \ldots, 0$$

Fig (a) Schematic of an isolated silicon atom.

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.
3s state corresponds to $n = 3$, $l = 0$, $m=0$, $s=+1/2$, $-1/2$, two quantum states, two electrons at T $= 0$ K.
3p state corresponds to $n = 3$, $l = 1$, $m=0,+1,-1$, $s=+1/2$, $-1/2$, six quantum states contain the remaining two electrons

4N states
0 electrons

6N states
2N electrons

3p

E_g

4N states
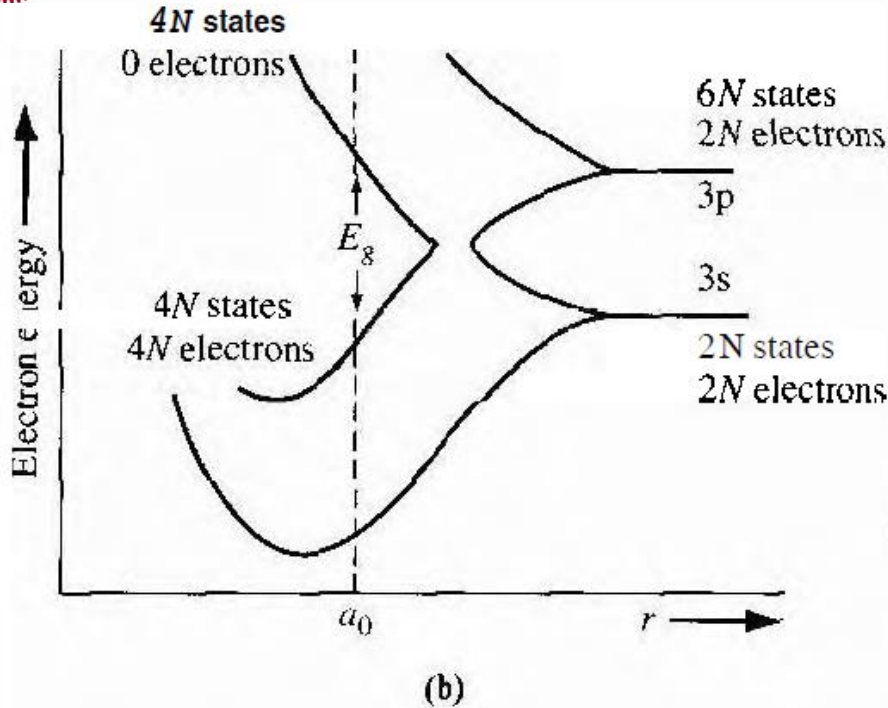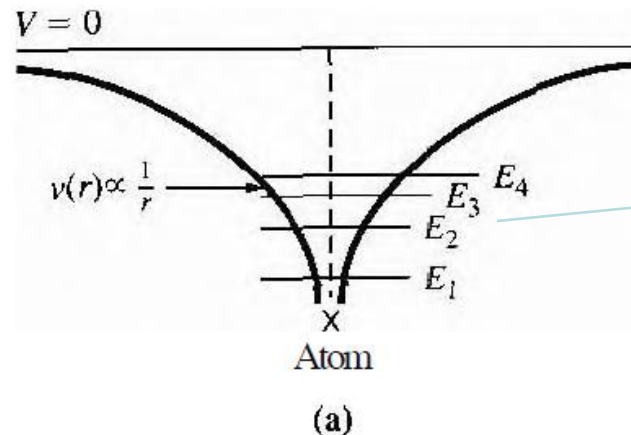4N electrons

3s

2N states
2N electrons

a_0

r

(b)

Fig (b) The splitting of the 3s and 3p states of silicon into the allowed and forbidden energy bands.

•As the interatomic distance decreases, the 3s and 3p states interact and overlap.
•At the equilibrium interatomic distance, the bands split:
  a) four quantum states are in the lower band - **the valence band** （价带）
  b) four quantum states are in the upper band- **the conduction band** （导带）
• At T=0K, eight electrons are in valence band. The conduction band is empty.
• The **forbidden energy band** （禁带）is the bandgap energy E, between the top of the valence band and the bottom of the conduction band
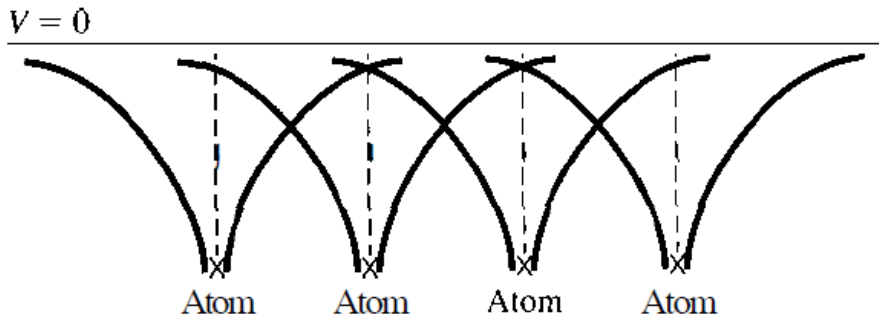
The Kronig-Penney Model

The concept of allowed and forbidden energy bands can be developed more rigorously by considering quantum mechanics and Schrodinger's wave equation.
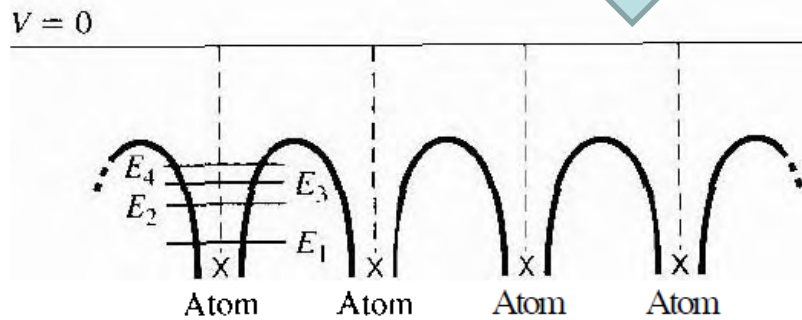

$E<0$, electrons are bound in the atom.

(a)

Fig (a) Potential function of a single isolated atom.
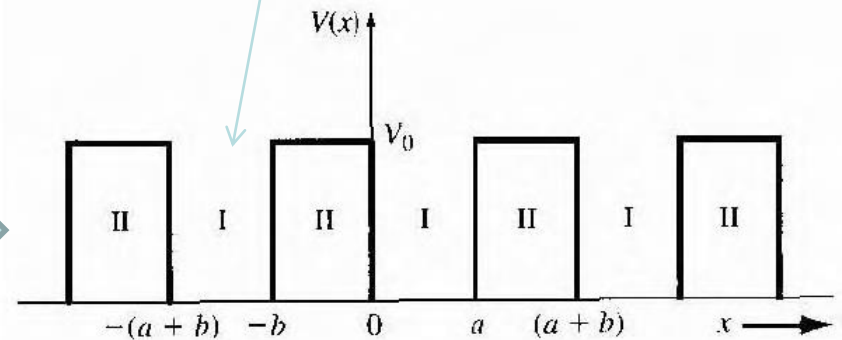• the discrete energy levels allowed for the electrons
• the energy increases with r

Fig (b) Overlapping potential functions of adjacent atoms. (c) Net potential function of a one-dimensional single crystal.

$E<V_0$, a particle is bound within the crystal.

Fig The one-dimensional periodic potential function of the Kronig-Penney model.

For simplification, the one-dimensional Kronig-Penncy model of the periodic potential function is used to represent a one-dimensional single-crystal 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, for problems involving periodically varying potential energy functions, must be of the form $\psi(x) = u(x)e^{jkx}$

k is called a constant of motion;
$u(x)$ is a periodic function with period of $a+b$

The total solution to the wave equation is the product of the time-independent solution and the time-dependent solution

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

In region I (In the atom $0 < x < a$) , $V(x) = 0$,

Substitute this result into the time-independent Schrodinger's wave equation

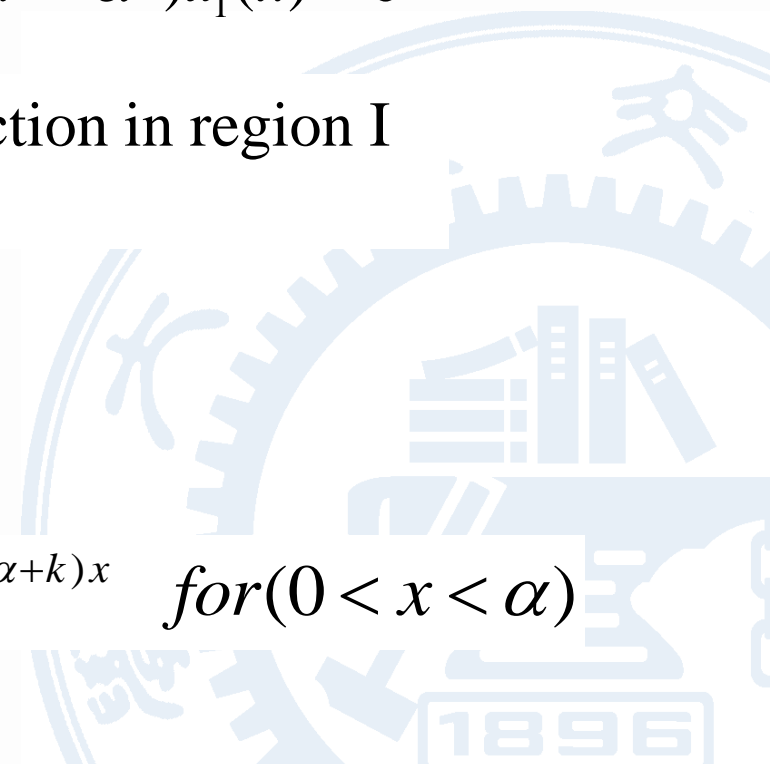$$\frac{\partial^2 \psi(x)}{\partial x^2} + \frac{2m}{\hbar^2}(E - V(x))\Psi(x) = 0$$

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

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

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

The solution is

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

In region II (between two adjacent atoms $-b < x < 0$), $V(x) = V_0$

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

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

If $E > V_0$, the parameter β is real, whereas if $E < V_0$, then β is imaginary.

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

The solution is

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

Boundary conditions

Since the potential function is everywhere finite, both the wave function and its first derivative must be continuous.
=> the wave amplitude function and its first derivative must also be continuous.

At $x = 0$ $\quad u_1(0) = u_2(0)$ $\implies$ $A + B - C - D = 0$

$$\frac{du_1}{dx}\Big|_{x=0} = \frac{du_2}{dx}\Big|_{x=0} \implies (\alpha - k)A - (\alpha + k)B - (\beta - k)C + (\beta + k)D = 0$$

As for periodicity

$$u_1(a) = u_2(-b) \implies Ae^{j(\alpha-k)\alpha} + Be^{-j(\alpha+k)\alpha} - Ce^{j(\beta-k)b} - De^{-j(\beta+k)b} = 0$$

$$\frac{du_1}{dx}\Big|_{x=a} = \frac{du_2}{dx}\Big|_{x=-b} \implies (\alpha - k)Ae^{j(\alpha-k)a} + Be^{-j(\alpha+k)a} - (\beta - k)Ce^{-j(\beta-k)b}$$
$$+(\beta + k)De^{j(\beta+k)b} = 0$$

The solution is

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

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

relates the parameter k to the total energy E and the potential function V_0

For $E < V_0$, the electron is bounded within the crystal

$$\beta = j\gamma \qquad \text{an imaginary quantity}$$

The solution is written as

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

It must be solved using numerical or graphical techniques

The solution of E will result in a band of allowed energies.

Let the potential barrier width b -> 0 and the barrier height V_0 ->∞, but the product bV_0 remains finite.

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

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

$$P^{'}\frac{\sin\alpha a}{\alpha a} + \cos\alpha a = \cos ka$$

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

The k-Space Diagram

☐ Consider a free particle (there are no potential barriers), so $V_0=0$

$$P' \frac{\sin \alpha a}{\alpha a} + \cos \alpha a = \cos ka \qquad \Longrightarrow \qquad \cos \alpha a = \cos ka$$

the total energy E is equal to the kinetic energy since $V_0=0$

$$\alpha = \sqrt{\frac{2mE}{\hbar^2}} = \sqrt{\frac{2m(\frac{1}{2}mv^2)}{\hbar^2}} = \frac{p}{h} = k \qquad p \text{ is the particle momentum}$$

The constant of the motion parameter k is called a wave number,

Relate the energy and momentum as

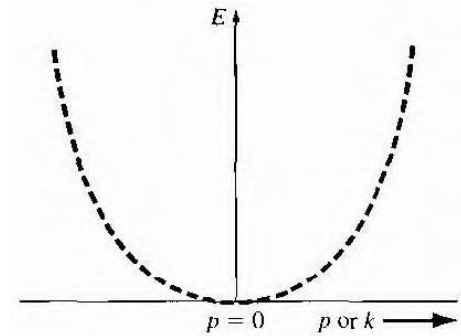$$E = \frac{p^2}{2m} = \frac{k^2 \hbar^2}{2m}$$

Fig The parabolic E versus k curve for the free electron

□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.

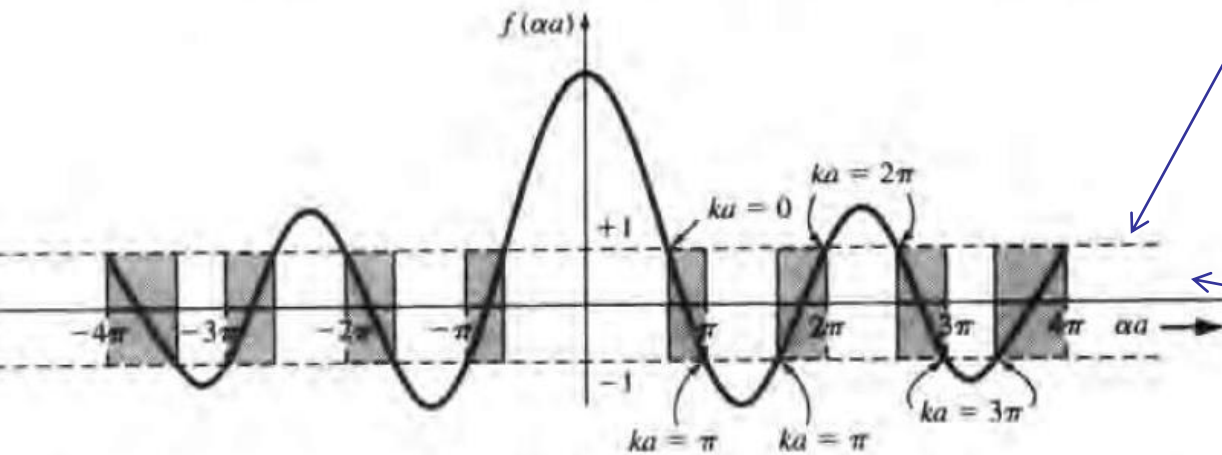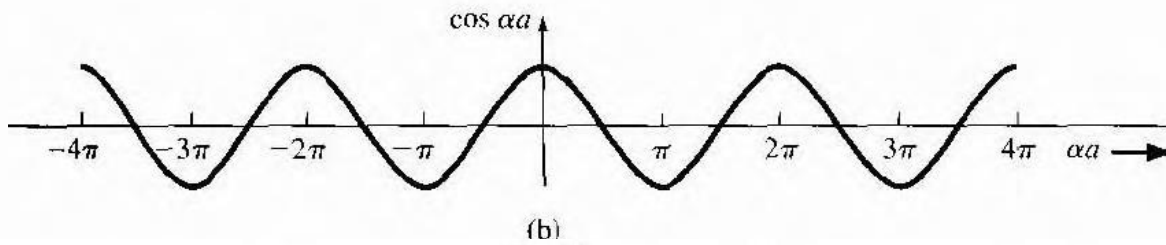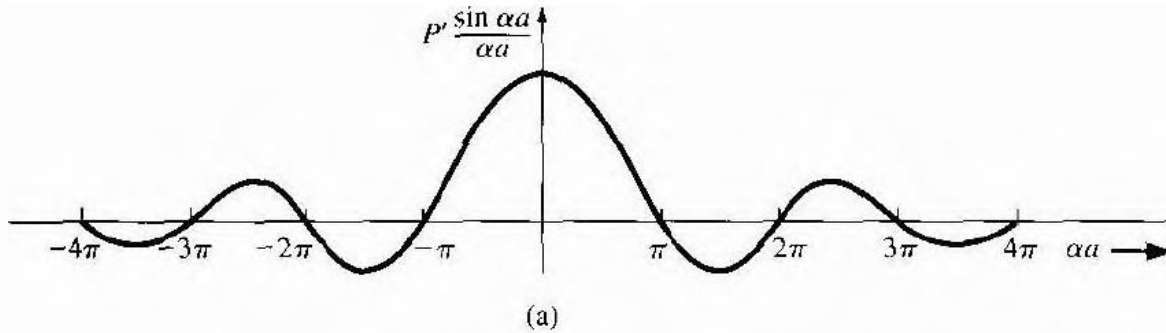$$P' = \frac{mV_0 ba}{\hbar^2}$$

For the equation

$$P' \frac{\sin \alpha a}{\alpha a} + \cos \alpha a = \cos ka$$

Define

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

The relations between the wave number k, the energy E (through α) , and the potential barrier bV_0 (through P').

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

(a)

(b)

$$f(\alpha a) = P' \frac{\sin \alpha a}{\alpha a} + \cos \alpha a = \cos ka \implies f(\alpha a) \text{ is limited between 1 and -1}$$

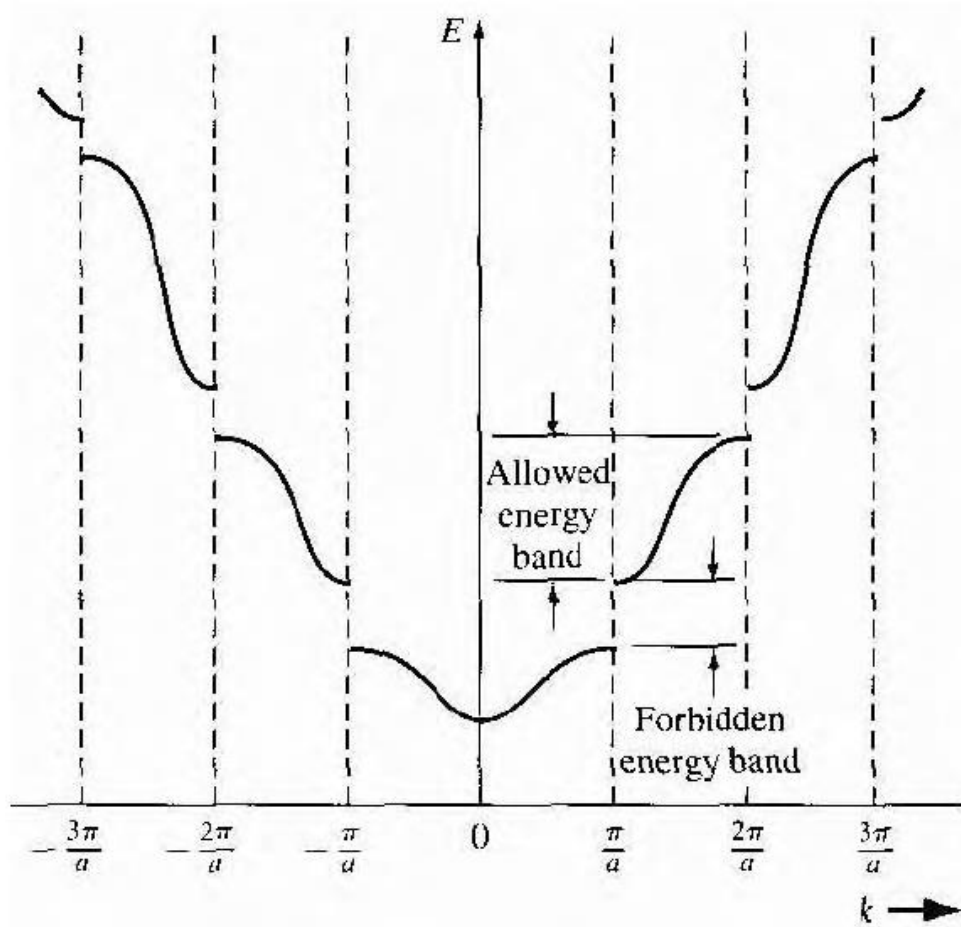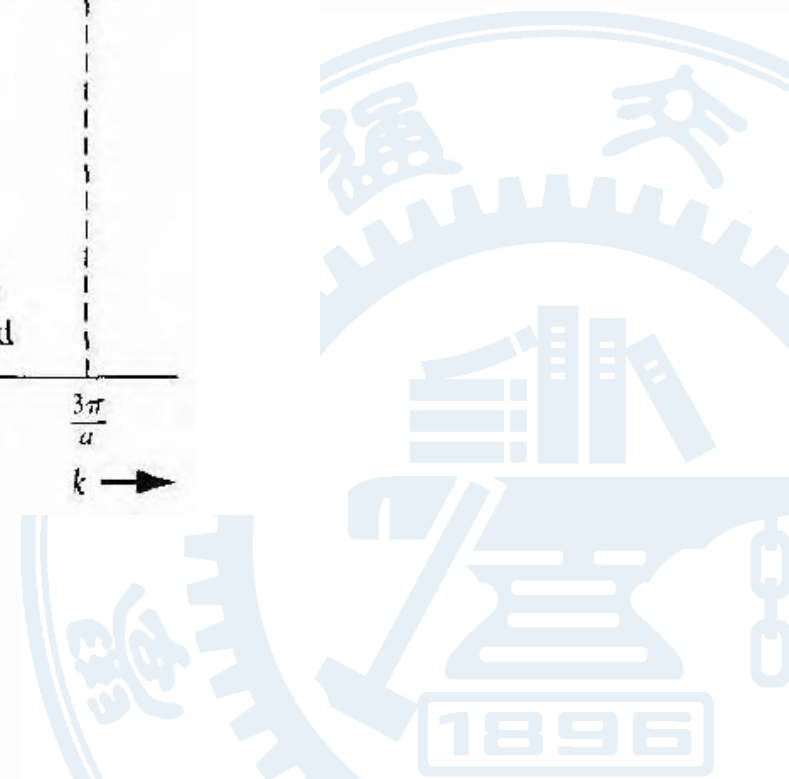The energy E of the particle is a function of the wave number k

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Fig The *E* versus *k* diagram
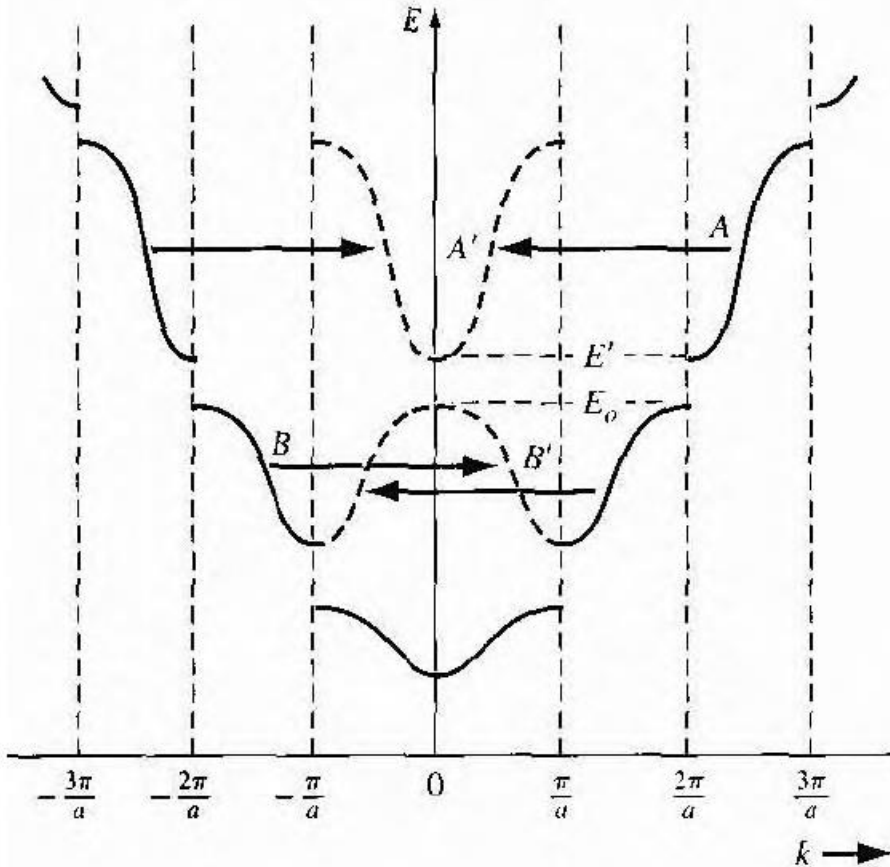
$$\cos ka = \cos(ka + 2n\pi) = \cos(ka - 2n\pi)$$

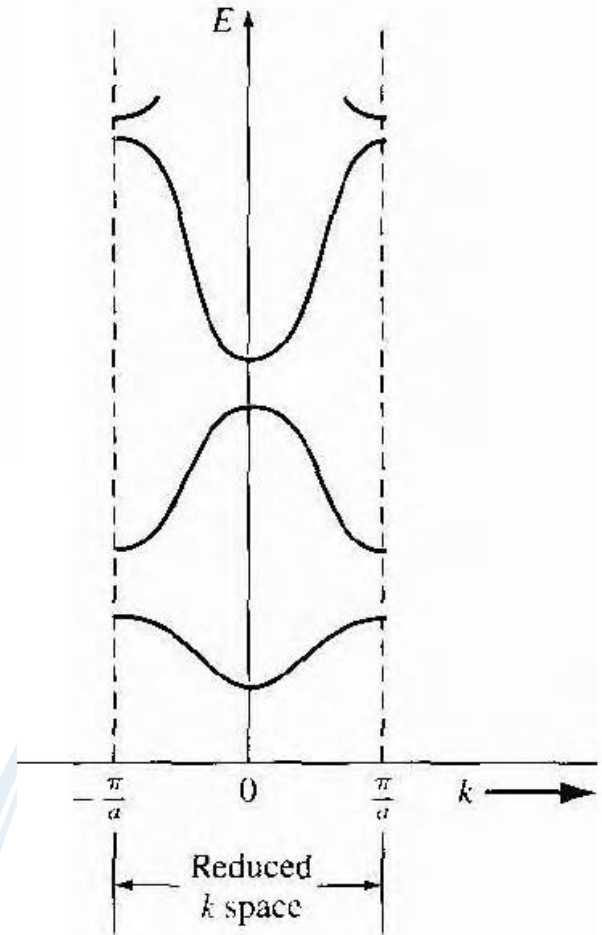Fig E versus k diagram showing 2π displacements of several sections of allowed energy bands.

Fig The *E* **versus** *k* **diagram** in the reduced-zone representation

Example:

To determine the lowest allowed energy bandwidth.

Assume that the coefficient *P′ = 10* and that the potential width *a = 5A*

Solution:

To find the lowest allowed energy bandwidth. we need to find the difference in αa values as ka changes from 0 to π

$$P'\frac{\sin \alpha a}{\alpha a} + \cos \alpha a = \cos ka \qquad\qquad \alpha^2 = \frac{2mE}{\hbar^2}$$

For $ka = 0$ $\qquad 1 = 10\frac{\sin \alpha a}{\alpha a} + \cos \alpha a \qquad\qquad\Longrightarrow\qquad \alpha a = 2.268 rad$

$$E_1 = 1.68 \times 10^{-19} J = 1.053 eV$$

For $ka = \pi, \alpha a = \pi.$

$$\alpha^2 = \frac{2mE}{\hbar^2} \qquad\qquad\Longrightarrow\qquad \sqrt{\frac{2mE}{\hbar^2}} \bullet a = \pi$$

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

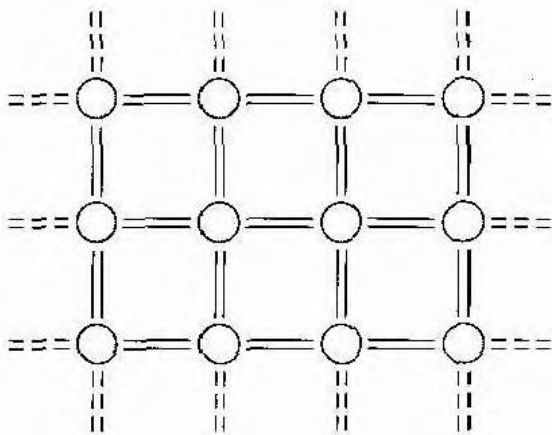The allowed energy bandwidth $\qquad AE = E_2 - E_1 = 1.50 - 1.053 = 0.447 eV$

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Electrical Conduction in solids

□ The motion of electrons in the various allowed energy bands ->determining the current-voltage characteristics of semiconductor devices

■ **The Energy Band and the Bond Model**

T=0K

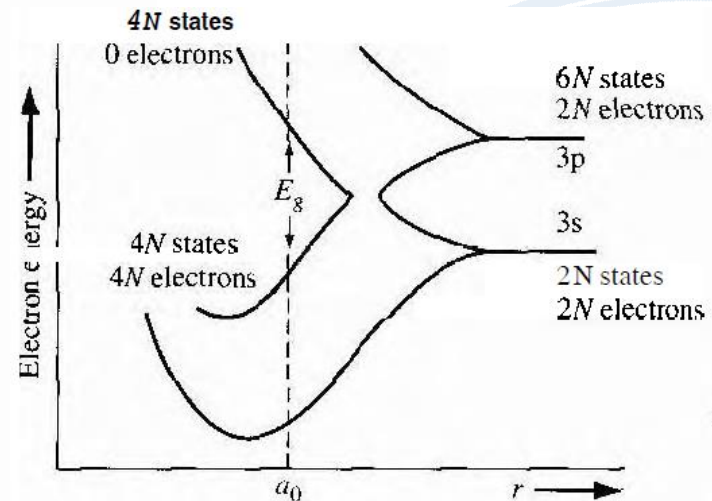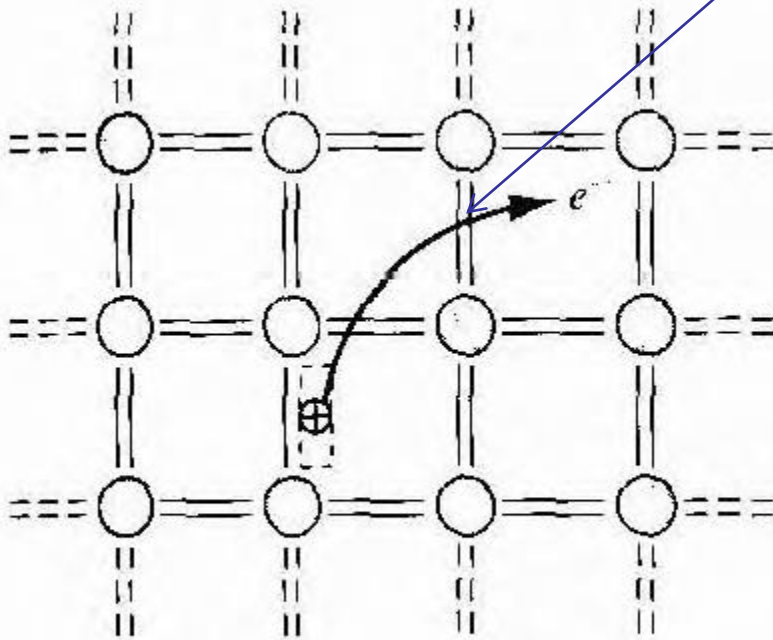Fig Two-dimensional representation of the covalent bonding in a semiconductor at $T = 0$ K

Fig Energy band of silicon

T>0K
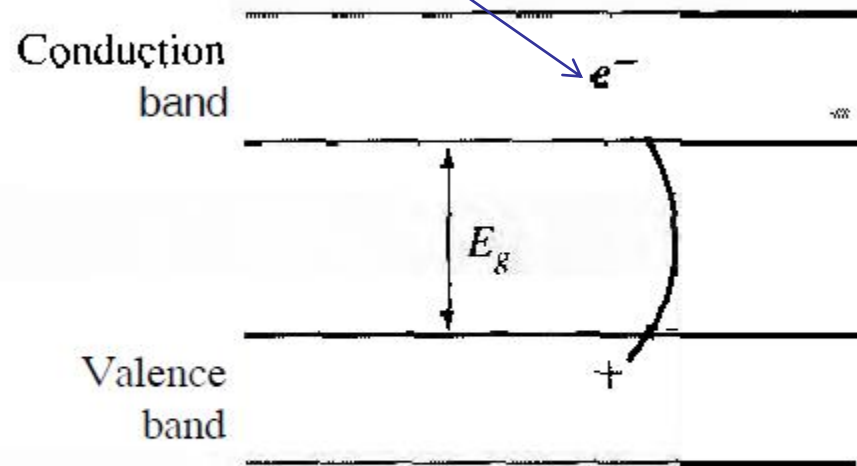
Some electrons have gained enough energy to jump to the conduction band and have left empty states in the valence band.

Conduction band

E_g

Valence band

(a)

(b)

Fig (a) Two-dimensional representation of the breakdown 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
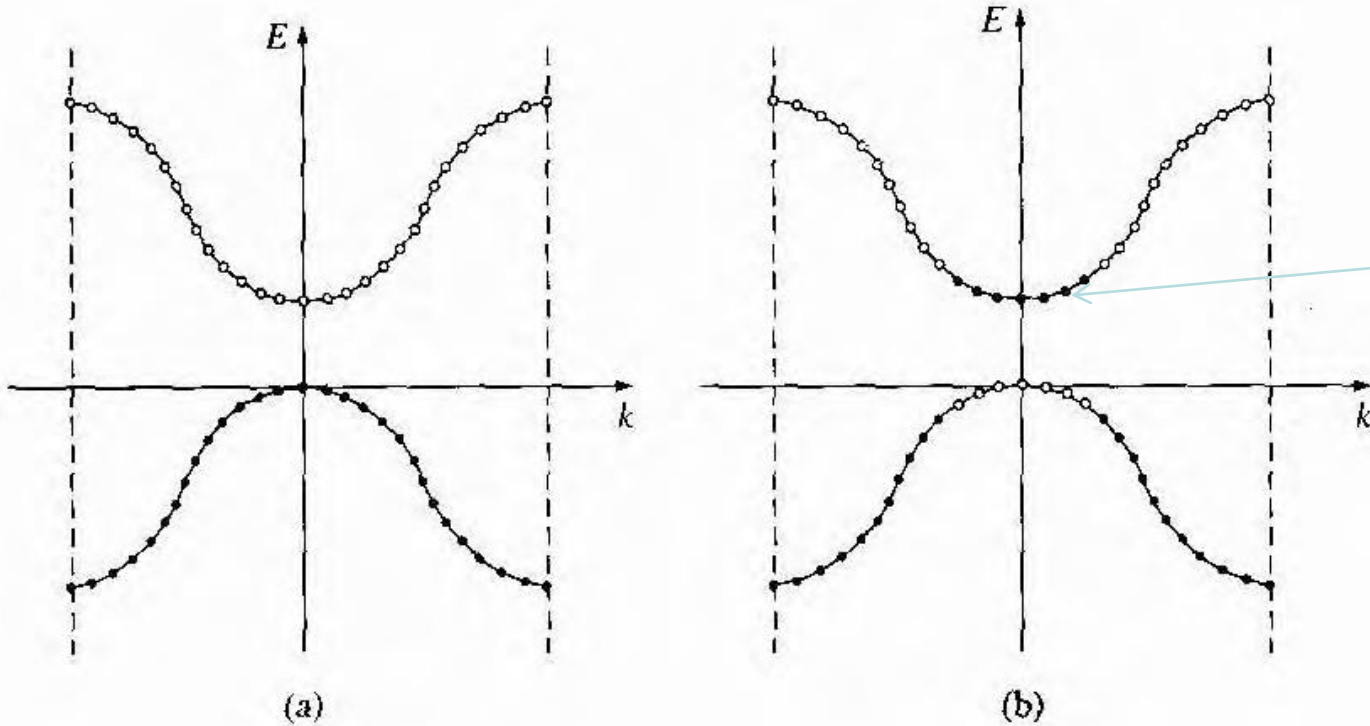
Symmetric distribution <--- no external force

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

With the temperature increasing, more covalent bonds are broken and more electrons jump into conduction band.

□Drift current

Current is due to the net flow of charge.

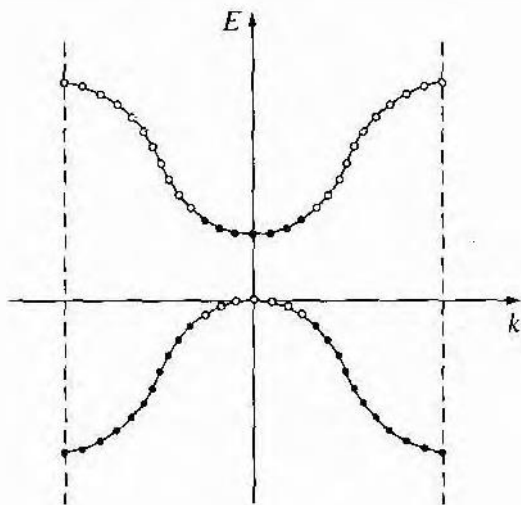For a collection of positively charged ions with a volume density N (cm^{-3}) and an average drift velocity v_d (cm/s), the drift current density is

$$J = qNv_d \qquad A/cm^2$$

Considering the individual ion velocities, v_i is the velocity of the *ith* ion

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

• The electron distribution in the conduction band is an even function of **k** **when no external force is applied**

• **k** for a free electron is related to momentum
  k=p/h

=>the number of electrons with a + |k| value
   = that of electrons with a - |k| value

=>**the net drift current density due to these electrons is zero.**

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If a **force** is applied to a particle and the particle moves, it must gain energy

$$dE = Fdx = Fvdt$$

If an external force is applied to the electrons in the conduction band, there are empty energy states into which the electrons can move.

=> electrons can gain energy and a net momentum because of the external force. --- in agreement with Law of conservation of energy
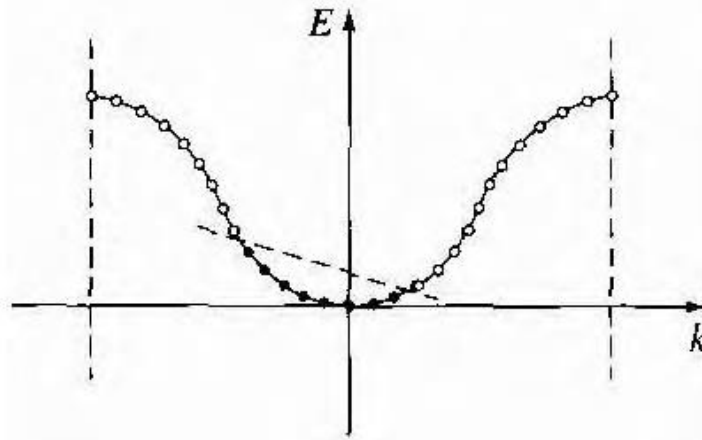
The drift current density due to the motion of electrons

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

Fig The asymmetric distribution of electros in the E versus k diagram when an external force is applied.

❑Electron Effective Mass

The movement of an electron in a lattice will, in general, be different from that of an electron in free space.

The total force:

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

The internal forces in the crystal are due to positively charged ions or protons and negatively charged electrons. a is the acceleration rate 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

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

a is now directly related to the external force.

m^* is called **the effective mass**, takes into account the particle mass and also takes into account the effect of the internal forces.
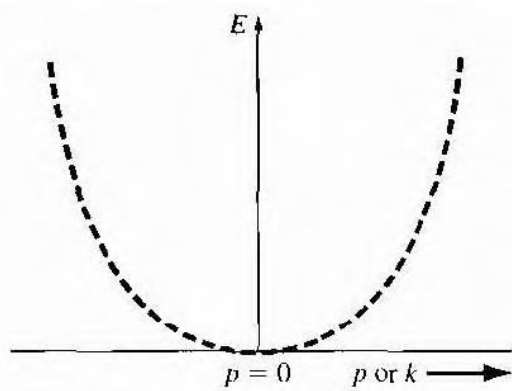
- ## Mass of a free electron

Fig The parabolic E versus k curve for the free electron.

E-k relationship

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

Take the first derivative of E with respect to k,

$$\frac{dE}{dk} = \frac{\hbar^2 k}{m} = \frac{\hbar p}{m} \qquad k = p/\hbar$$

Relating momentum to velocity

$$\frac{1}{\hbar}\frac{dE}{dk} = \frac{p}{m} = v$$

Take the second derivative of E with respect to k,

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

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

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

For the case of a free electron, the mass is a constant (nonrelativistic effect), so the second derivative function of energy is a constant.

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

$$F = ma = -eE$$

where a is the acceleration, E is the applied electric field, and e is the electronic charge.

$$a = \frac{-eE}{m}$$

The motion of the free electron is in the opposite direction to the applied electric field because of the negative charge.
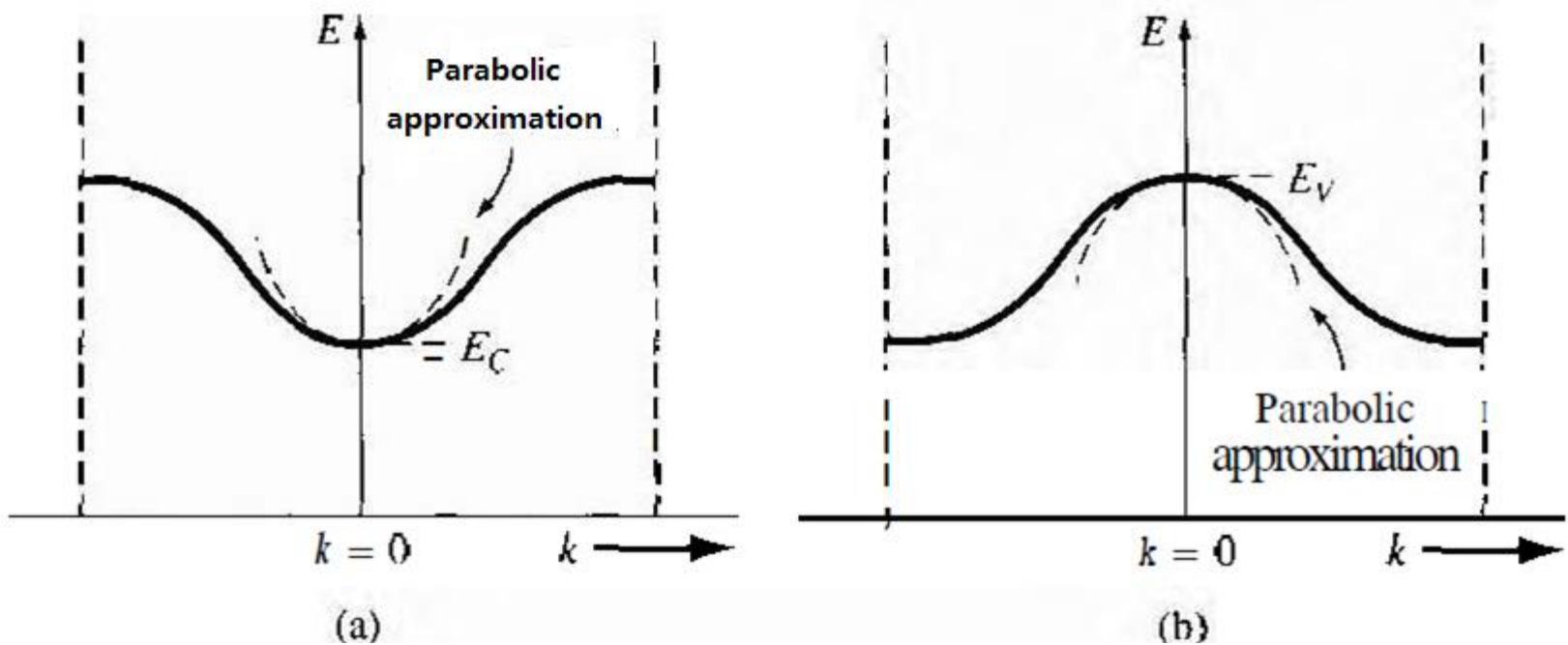
- Mass of an electron in the energy band

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

Consider the electron in the bottom of an allowed conduction energy band

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

C_1 is a positive quantity

Taking the second derivative of E with respect to k

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

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**.

➢Since the internal forces and quantum mechanical properties are taken into account through the effective mass, **the electron in the bottom of the conduction band can be thought of as a classical particle whose motion can be modeled by Newton mechanics**.

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

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

m_n^* is the effective mass of the electron, a constant

Concept of the Hole

For $T > 0$ K, valence electrons may gain thermal energy and 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.
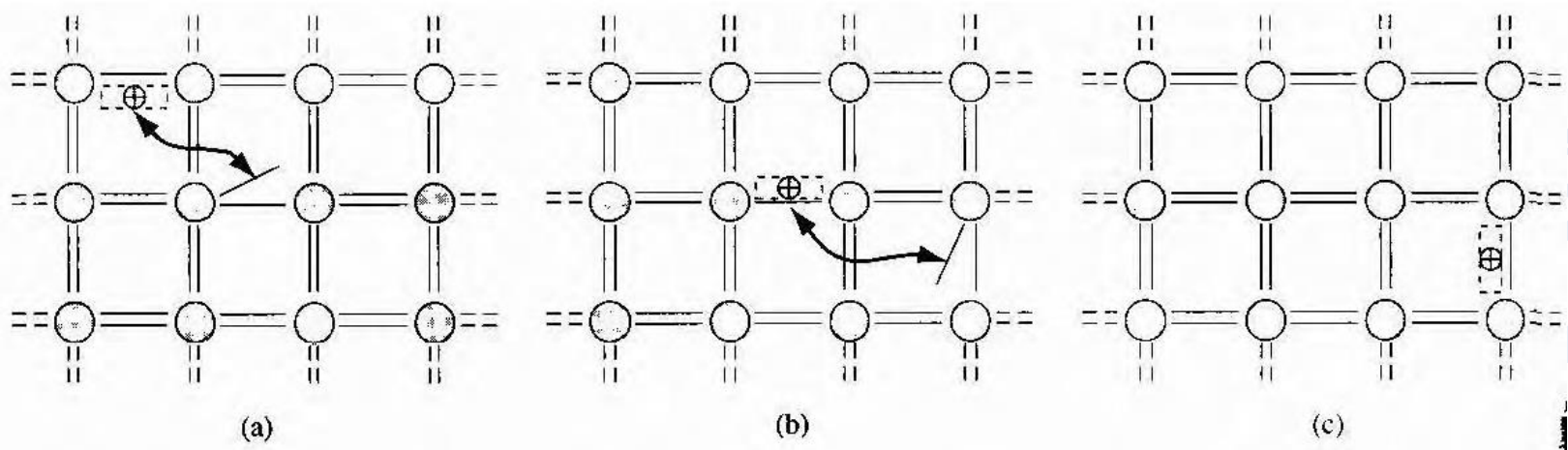

(a)　　　　　　　　　(b)　　　　　　　　　(c)

Fig Visualization of the movement of a hole in a semiconductor. the movement of valence electrons alternately filling one empty state and creating a new empty state.

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 can be modeled using Newton mechanics.

The drift current density due to electrons in the valence band is

$$J = -e \sum_{i(filled)} v_i$$ the summation extends over all filled states

Total energy band= filled energy band+ empty energy band

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

If a band is totally full

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

The band is symmetric in k space and each state is occupied
$\Rightarrow$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.

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

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The drift current density due to electrons in the valence band is written as: $J = +e \sum_{i(empty)} v_i$

The summation of v_i

$$v(E) = \left(\frac{1}{\hbar}\right)\left(\frac{dE}{dk}\right)$$ associated with the empty state
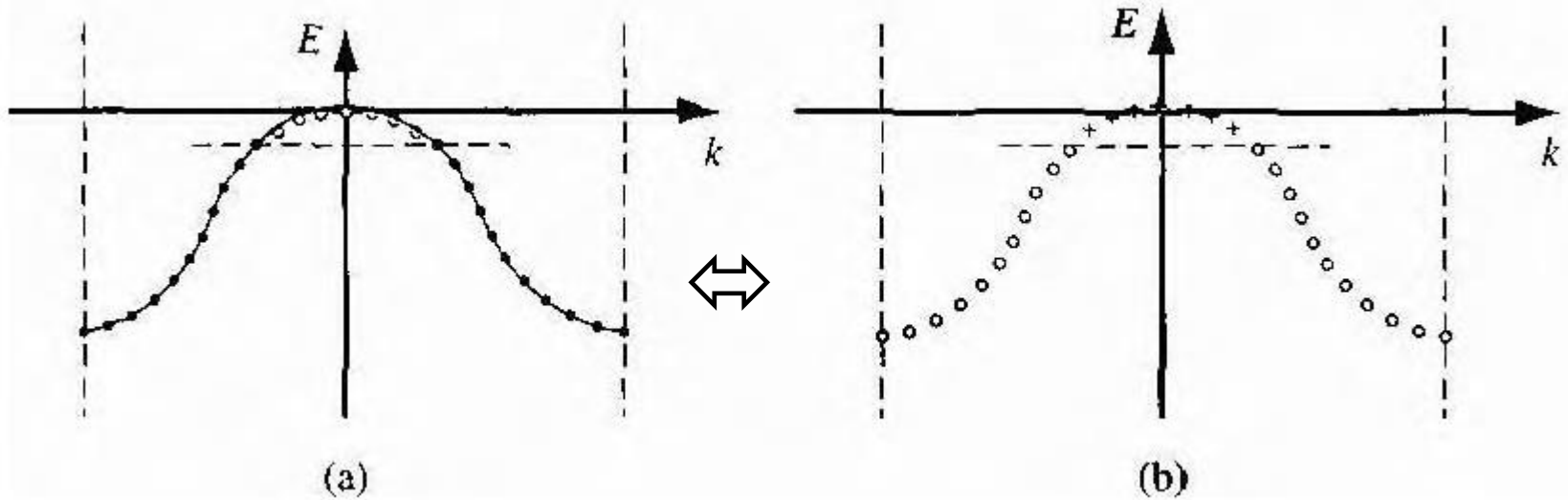

Fig (a) Valence band with conventional electron-filled states and empty states.
(b) Concept of positive charges occupying the original empty states.

Consider an electron near the top of the allowed energy band

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

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
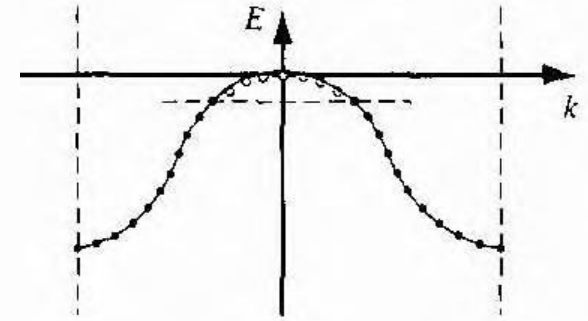
Fig The allowed energy band

Taking the second derivative of E with respect to k

$$\frac{d^2 E}{dk^2} = -2C_2$$

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

An electron moving near the top of an allowed valence energy band behaves as if it has a negative mass.

✓ **The effective mass may be negative**

The effective mass parameter relating quantum mechanics and classical mechanics leads to this strange result.

✓ **The energy is quantized.**

Solutions to Schrodinger's wave equation also led to results that contradicted classical mechanics.

For an applied electric field into an electron near the top of an allowed valence energy band
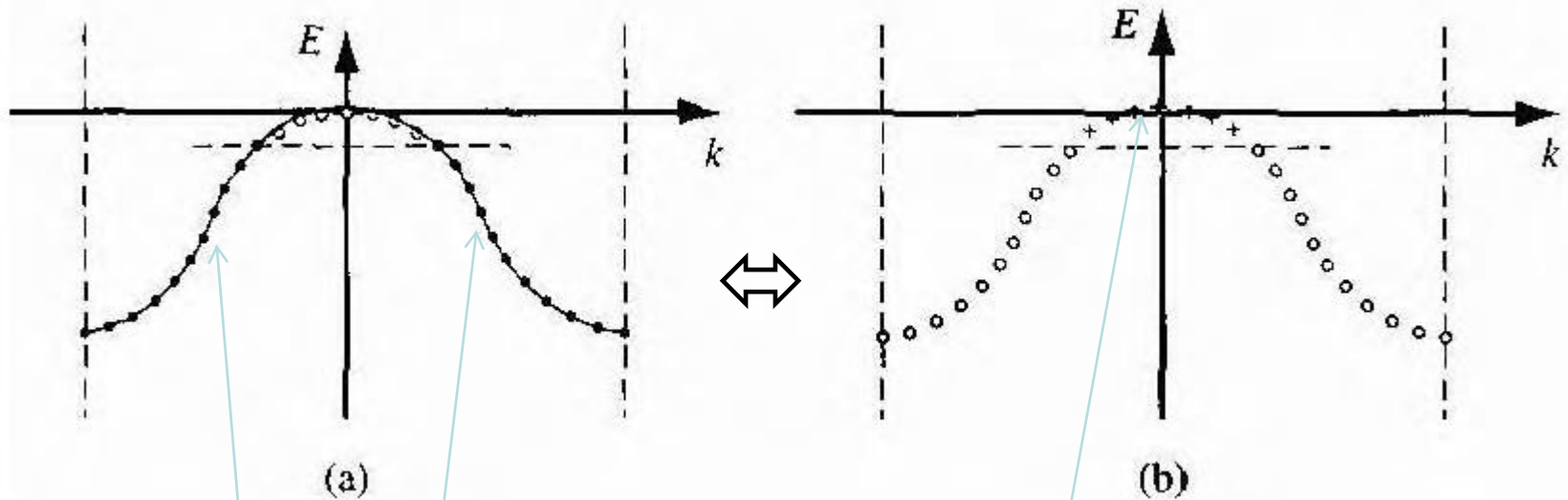
$$F = m^* a = -eE$$

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

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

The net motion of electrons in a nearly full band can he described by considering just the empty states.

(a) ⇔ (b)

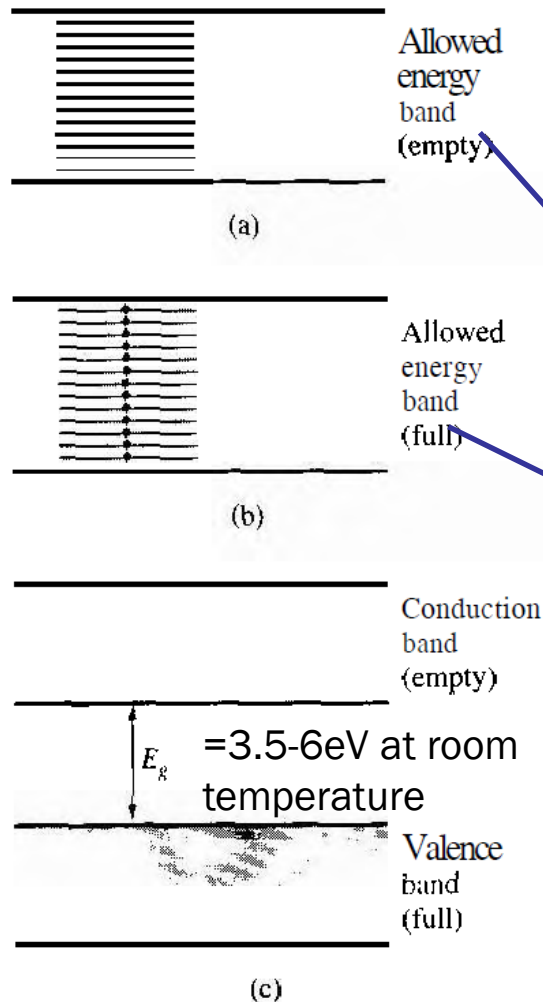This band has particles (**electrons**) with a negative electronic charge and a negative effective mass. ⇔ This band has particles (**holes**) with a positive electronic charge and a positive effective mass.

●**Metals, Insulators, and Semiconductors**

Each crystal has its own energy-band structure.=> resulting in difference in electrical characteristics for solids
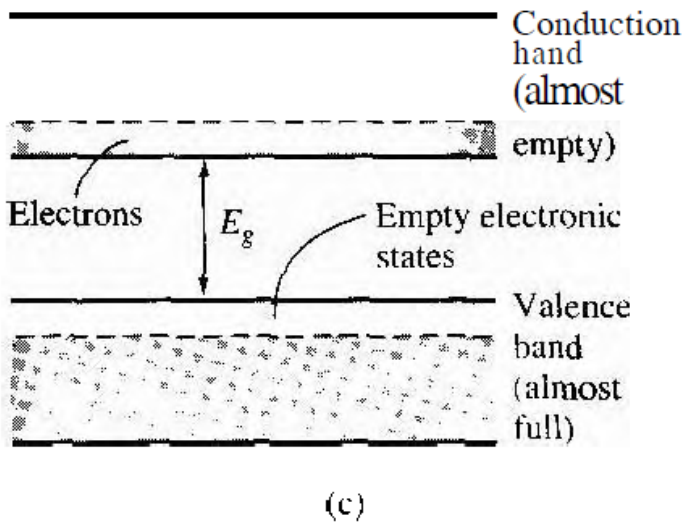
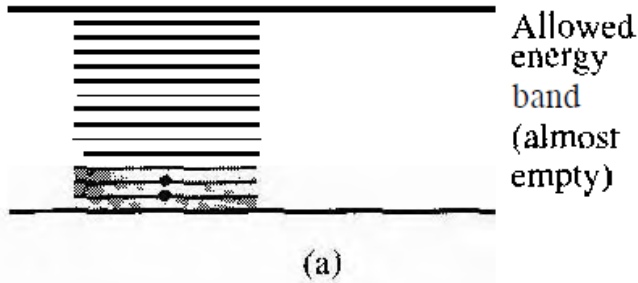**Insulators** : A material that has energy bands either completely empty or completely full.

No particle can move with an applied electric field.

A completely full energy band will also not give rise to a current.

E_g =3.5-6eV at room temperature

Fig The energy band of insulators
(a) An empty conduction band
(b) A completely full valence band
(c) The band gap energy between the two allowed bands

Semiconductors

(a)

Allowed energy band (almost empty)

(b)

Allowed energy band (almost full)

(c)

Conduction band (almost empty)

Electrons — E_g — Empty electronic states

Valence band (almost full)

E_g=1ev at room temperature

An energy band with relatively few electrons near the bottom of the band.
=> If an electric field is applied, the electrons can gain energy, move to higher energy states, and move through the crystal.

An allowed energy band is almost full of electrons. =>holes in this band to form current under E.

Semiconductors : A material that has energy bands almost empty or full. The resistivity of a semiconductor can be controlled and varied over many orders of magnitude.

Fig The energy band of semiconductors
(a) An almost empty conduction band
(b) A almost full valence band
(c) The band gap energy between the two allowed bands

The characteristics of a metal include a very low resistivity.

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.

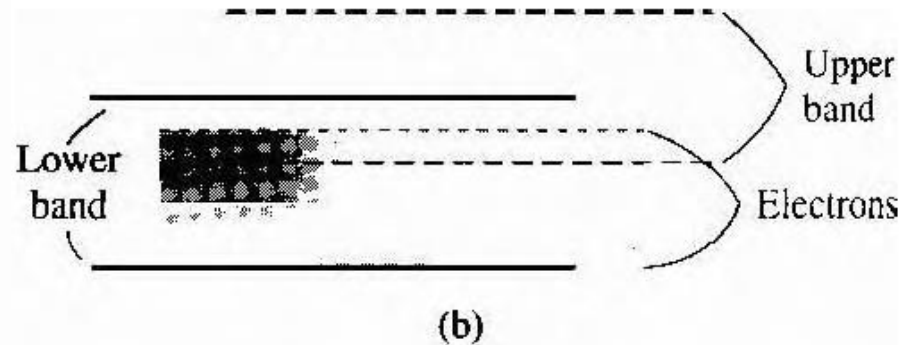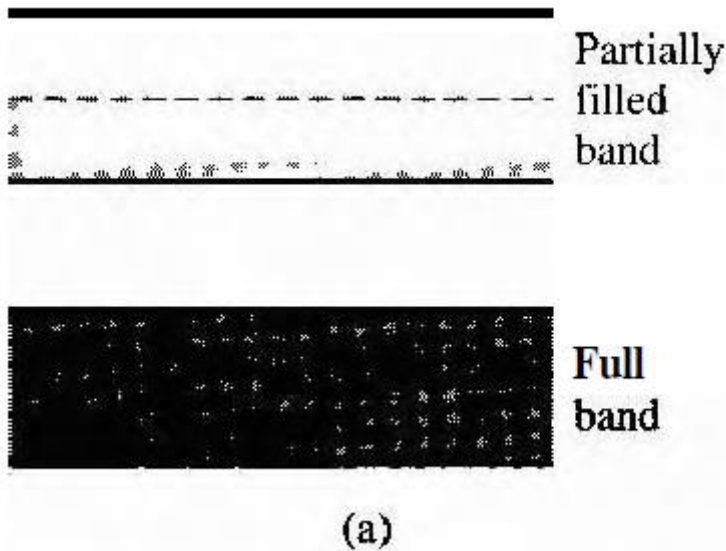The energy-band diagram for a metal may be in one of two forms.

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

Extension to three dimensions

■ **To extend the basic concept of allowed and forbidden energy bands and the basic concept of effective mass to 3D and to real crystals.**

■ **The potential function to a 3D crystal is different since the distance between atoms varies as the direction through the crystal changes.**
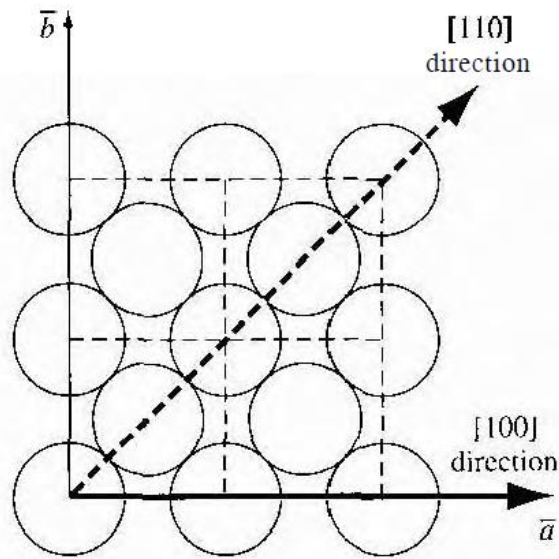

• Electrons traveling in different directions encounter different potential patterns and therefore different *k*-space boundaries.

• The *E* versus *k* diagrams are in general a function of the *k*-space direction in a crystal.

Fig The (100) plane of a face-centered cubic crystal showing the [100] and [110] directions

• The k-Space Diagrams of GaAs
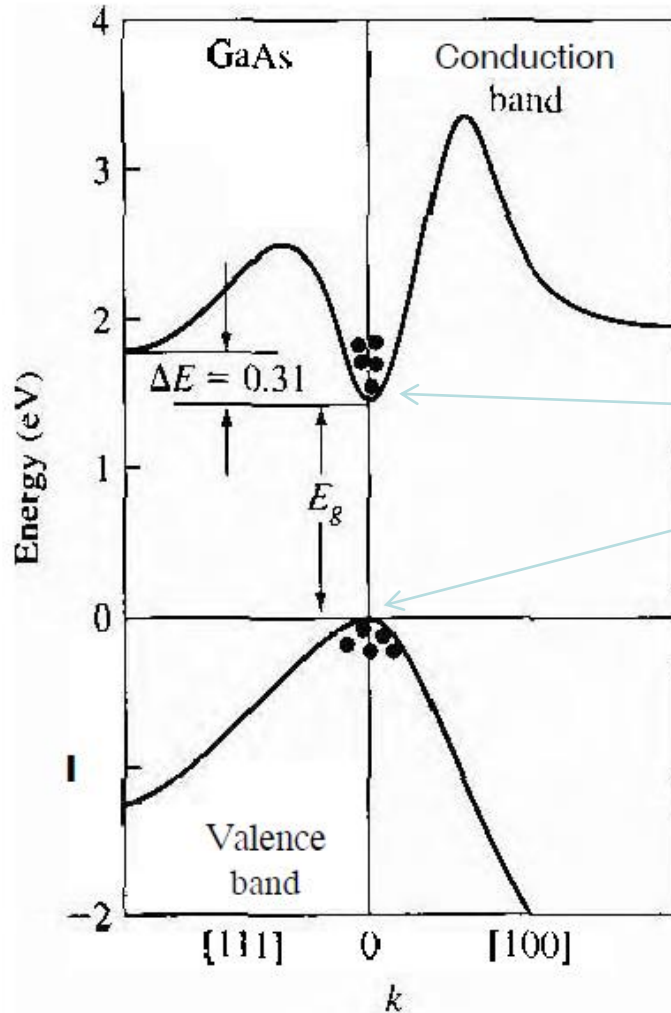
The [100] direction is along the normal $+k$ axis and [111] is along the $-k$ axis due to symmetric *E-K* diagram for 1D model.

Fig Energy band structure of GaAs

The maxima in the valence band energy and minima in the conduction band energy both occur at $k = 0$
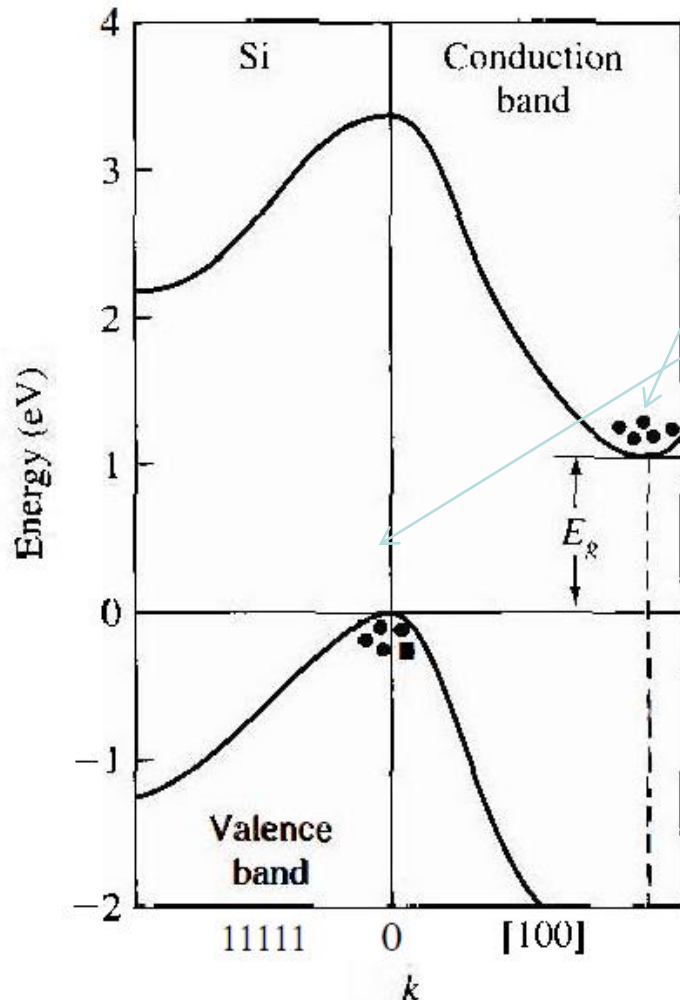
A semiconductor with this property is said to be a **direct bandgap (直接带隙) semiconductor.**
=>Transitions between the two allowed bands can take place with no change in crystal momentum.

• **The k-Space Diagrams of Si**

Fig Energy band structure of Si

The minimum in the conduction band energy occurs not at $k = 0$, but along the [100] direction.

The maximum in the valence band energy occurs at $k = 0$

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* （间接带隙）*semiconductor*

=>Momentum of electron change due to transition between valence band and conduction band.
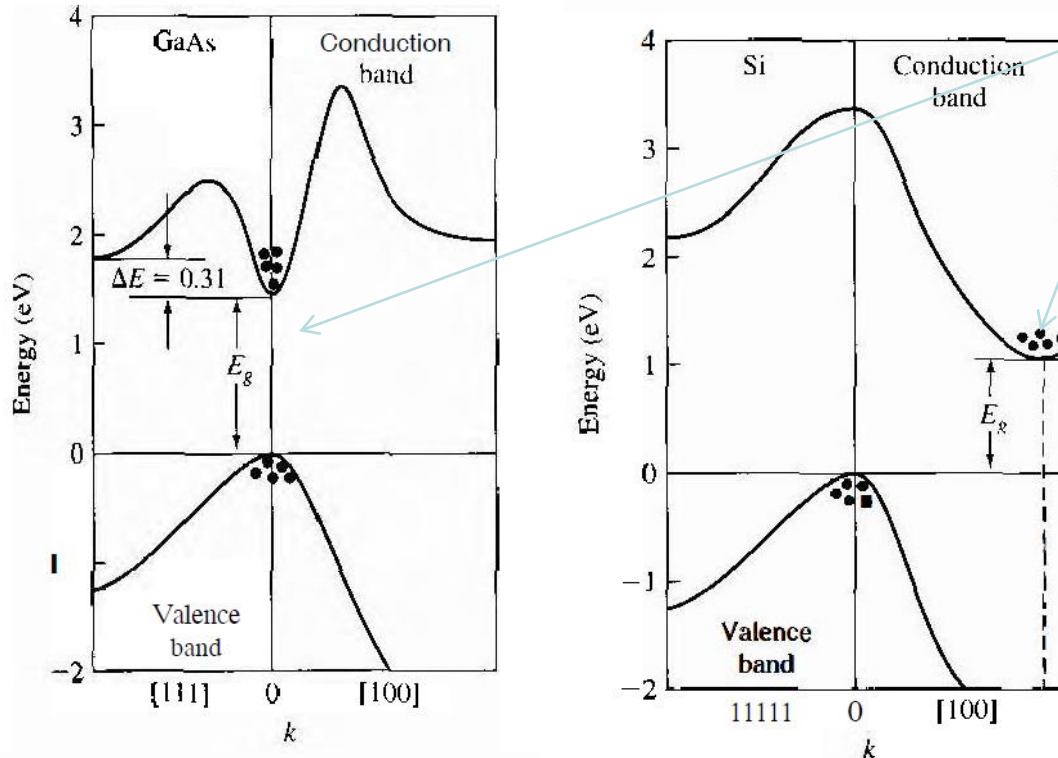=>Interaction with the crystal occur so that crystal momentum is conserved.

☐ **Additional Effective Mass Concepts**

For the one-dimensional E versus k diagram, the effective mass

$$1/m^* = 1/\hbar^2 \bullet d^2E/dk^2$$

The curvature of the E - k diagrams near the minimum of the conduction band energy is related to the effective mass of the electron.

• Question. Is the effective mass of an electron in the conduction band of GaAs smaller or larger than that in silicon?

A complication occurs in the effective mass concept in a real crystal.

• In 3D crystals, the curvature of the E versus k diagram at the conduction band minimum may not be the same in the three k directions.

• The effective mass parameters used in calculations will be a kind of **statistical average (统计平均)** that is adequate for most.
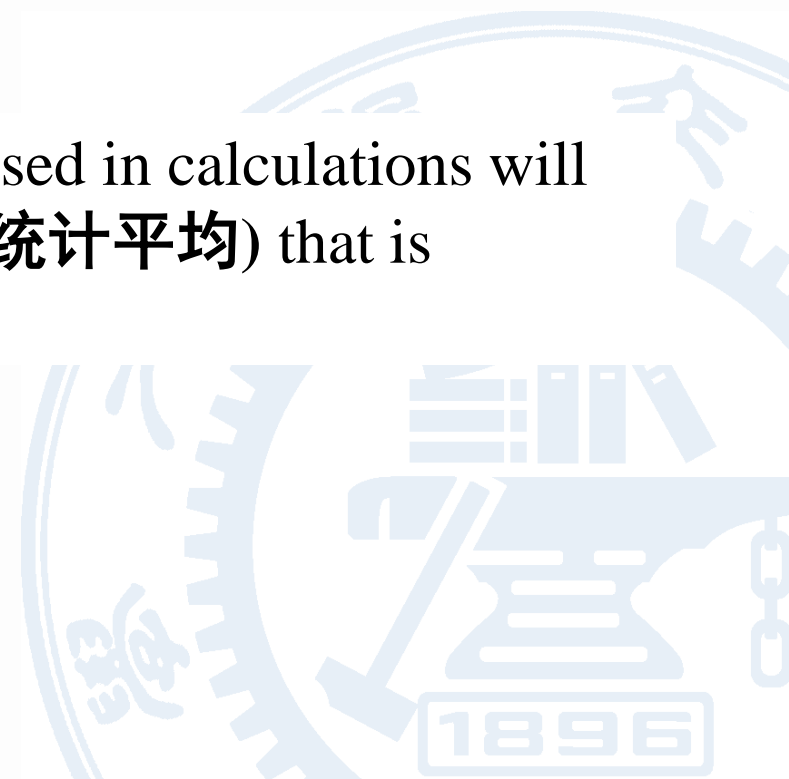
DENSITY OF STATES FUNCTION
状态密度函数

I-V curve of semiconductor

=> The number of electrons and holes available for conduction in the semiconductor

=>The number of carriers $= f$ (the number of available energy or quantum states （量子态）) ---- Pauli exclusion principle

=> Electron and hole concentrations

=> Density of states function:

   the density of these allowed energy states as a function of energy

Mathematical Derivation

➤ Electrons are allowed to move relatively freely in the conduction band of a semiconductor, but are confined to the crystal.

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

$$V(x, y, z) = 0 \quad for \quad 0 < x < a$$
$$0 < y < a$$
$$0 < z < a$$
$$V(x, y, z) = \infty \quad elsewhere$$

where the crystal is assumed to be a cube with length *a*.

The time-independent Schrodinger's wave equation in 1D

$$\frac{\partial^2 \psi(x)}{\partial x^2} + \frac{2mE}{\hbar^2} \psi(x) = 0$$
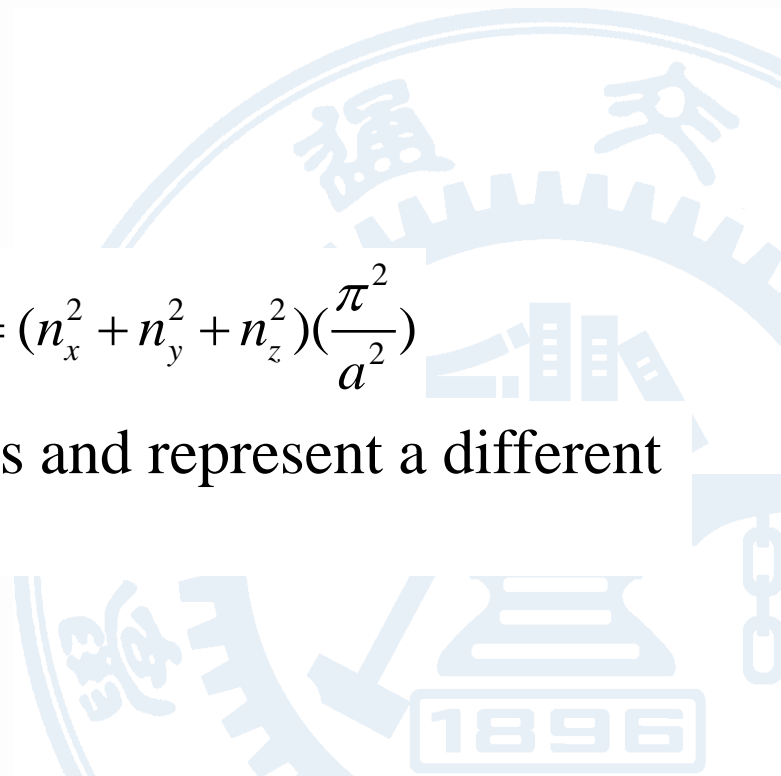
Its solution

$$\psi(x) = A_1 \cos Kx + A_2 \sin Kx$$

$$K = \sqrt{\frac{2mE}{\hbar^2}} \quad K = \frac{n\pi}{a}$$

Extending to 3D

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

where n_x, n_y, n_z are positive integers and represent a different quantum state.

Each point represents an allowed quantum state corresponding to various n_x, and n_y
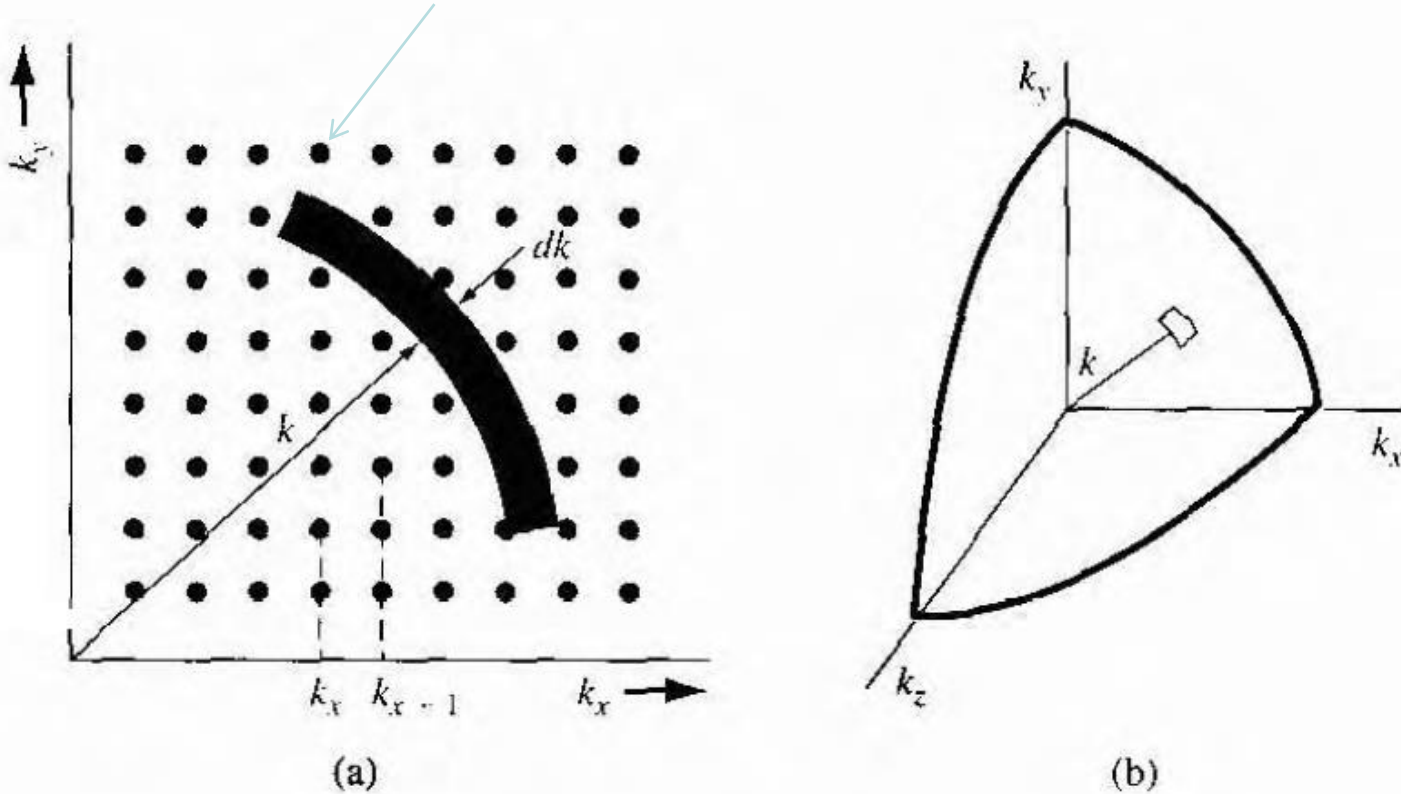
Fig (a) A two-D array of allowed quantum stales in k space.
(b) The positive one-eighth of the spherical k space

The distance between two quantum states in the k_x direction

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

So the volume V_k of a single quantum state is

$$V_k = (\frac{\pi}{a})^3$$

The differential density of quantum states in k space is

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

A differential volume in k space

$$\frac{d}{dk}\left(\frac{4}{3}\pi k^3\right)$$

"2" takes into account the two spin states allowed for each quantum state

considers only the quantum states for positive values of k_x, k_y, and k_z.

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

The density of quantum states is a function of momentum related variable k

For a free electron, $\quad k^2 = \frac{2mE}{\hbar^2} \Rightarrow dk = \frac{1}{\hbar}\sqrt{\frac{m}{2E}}dE$

The density of quantum states is a function of energy E

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

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

The number of energy states between E and $E + dE$ in the crystal space volume of a^3

The density of quantum states per unit volume of the crystal

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

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. It is quantum states **per unit energy per unit volume.**

The density of quantum states is typically a large number, but an effective density of states in a semiconductor is usually less than the density of atoms in the semiconductor crystal.

Extension to Semiconductors

✓ From →the density of allowed electron quantum states using the model of a free electron with mass m bounded in a 3D infinite potential well

✓ To → the density of quantum states in the conduction band or valence band in a semiconductor.

Free electron
in 3D infinite potential well

Electron
in conduction band
of a semiconductor

Hole
in valence band
of a semiconductor

$$E = \frac{h^2 k^2}{2m}$$

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

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

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

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

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

Quantum states do not exist within the forbidden energy band.

$$g(E) = 0, \quad E_v < E < E_c$$

$g_C(E)$

E_C

E_V

$g_V(E)$

$g(E)$ ⟶
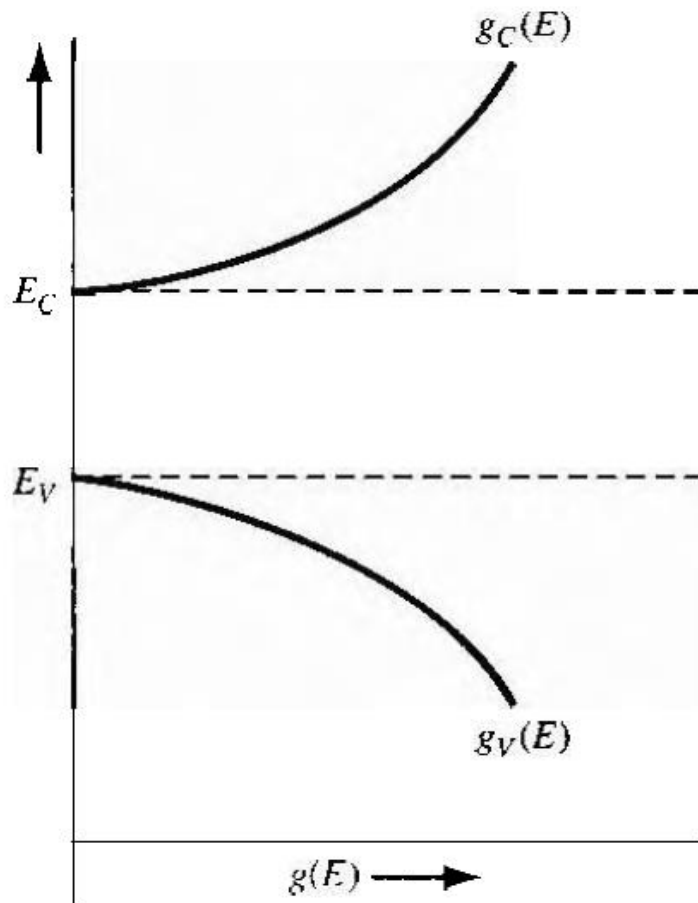
If the electron and hole effective masses were equal, then the functions $g_c(E)$ and $g_v(E)$ would be symmetrical about the energy midway.

Fig The density of energy states in the conduction band and the density of energy states in the valence band as a function of energy.
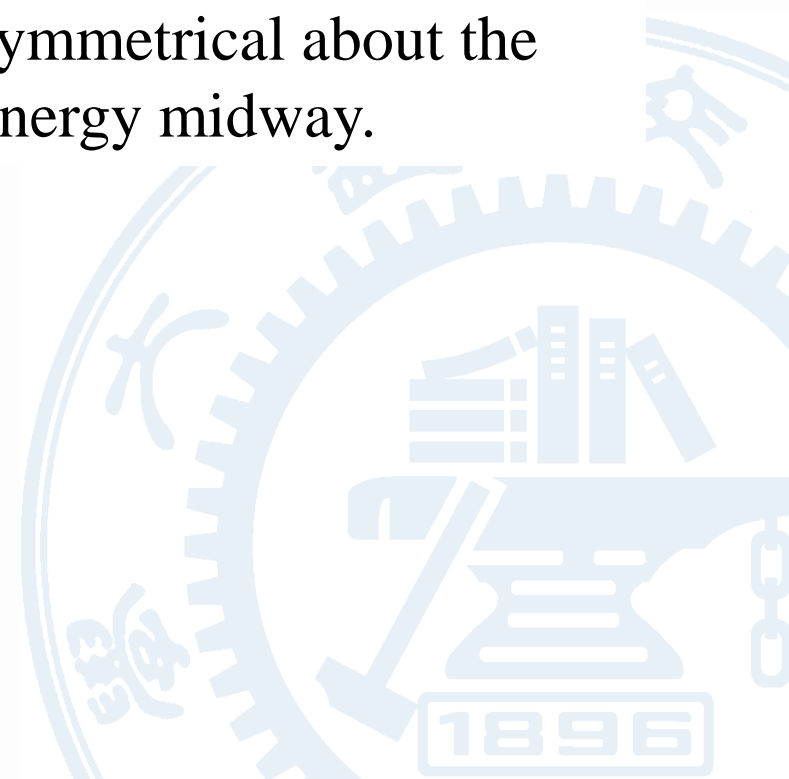
STATISTICAL MECHANICS

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.

Statistical Laws

•**Maxwell-Boltzmann probability function**

The particles are considered to be distinguishable by being numbered with no limit to the number of particles allowed in each energy state.

For example, the behavior of gas molecules in a container at fairly low pressure.
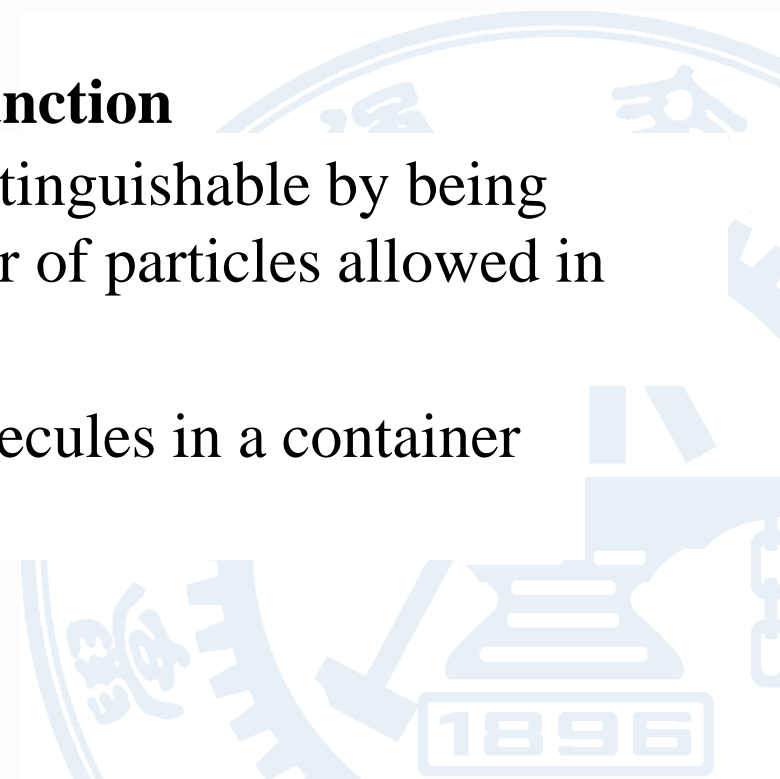
•Bose-Einstein function

Boson (波色子)

The particles in this case are indistinguishable and, again, there is no limit to the number of particles permitted in each quantum state.
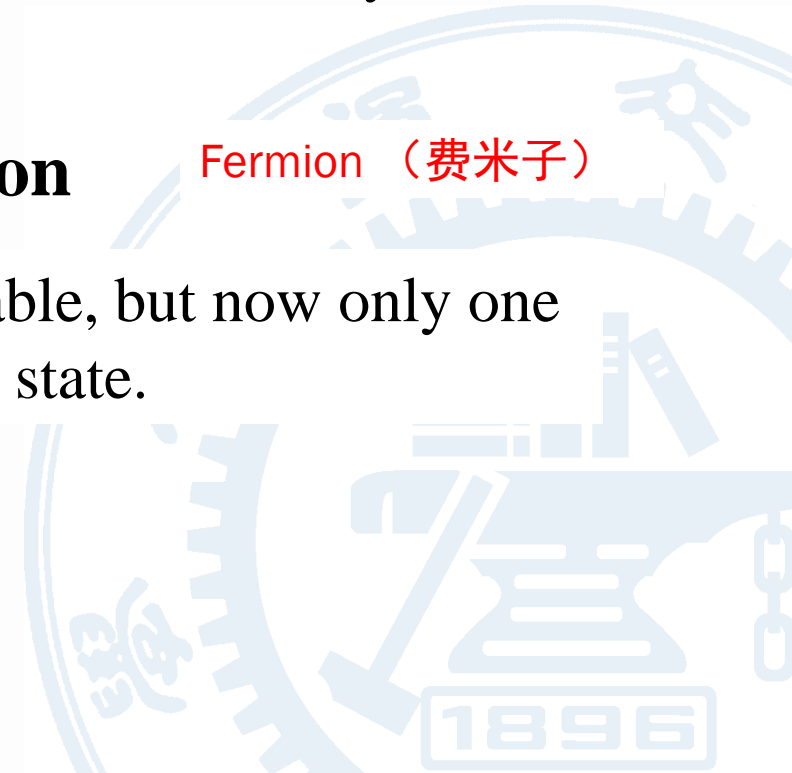
For example, the behavior of photons, or black body radiation.

•Fermi-Dirac probability function

Fermion （费米子）

The particles are again indistinguishable, but now only one particle is permitted in each quantum state.
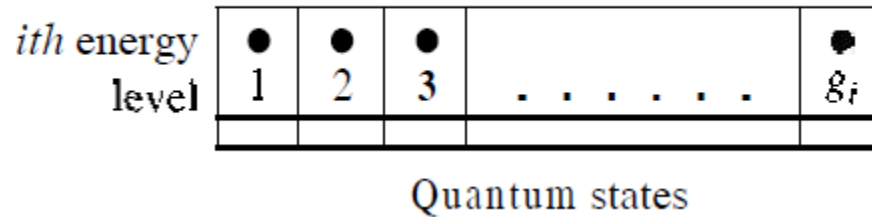
For example, electrons in a crystal

The Fermi-Dirac Probability Function

In the ith energy level, there are g_i quantum states.

Quantum states

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 ith energy level is $\quad g_i(g_i - 1) \bullet \bullet \bullet (g_i - (N_i - 1)) = \dfrac{g_i!}{(g_i - N_i)!}$

Since the particles are indistinguishable, the actual number of independent ways of realizing a distribution of N_i particles in the ith level is

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

The total number of ways of arranging (N_1, N_2, N_3, . . . , N_n) indistinguishable particles among n energy levels is the product of all distributions

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

The total number of particles $\quad N = \sum_{i=1}^{n} N_i$

The maximum W is found by varying N_i among the E_i levels

EXAMPLE

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

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

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

We may write the most probable distribution function as

$$\frac{N(E)}{g(E)} = f_F(E) = \frac{1}{1 + \exp(\dfrac{E - E_F}{kT})}$$

Fermi-Dirac distribution

$N(E)$ is the number of particles per unit volume per unit energy
$g(E)$ is the number of quantum states per unit volume per unit energy.
E_F is called the Fermi energy.

k is Boltzmann's constant $= 8.6173324 \times 10^{-5}$ eV/K

Fermi-Dirac distribution gives the probability that a quantum state at the energy E will be occupied by an electron.
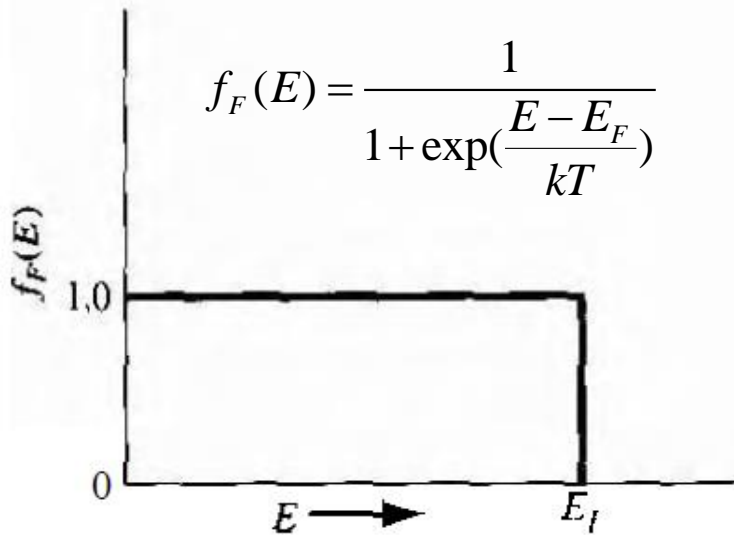
The Distribution Function and the Fermi Energy

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

Fig The Fermi probability function versus energy for $T = 0$ K.

Quantum state

Energy level

Fig Discrete energy levels and quantum states for a particular system at $T = 0$ K.

At $T = 0$ K $E < E_F, f_F(E < E_F) = 1$

$E > E_F, f_F(E > E_F) = 0$

All electrons have energies below the Femi energy at $T = 0$ K.
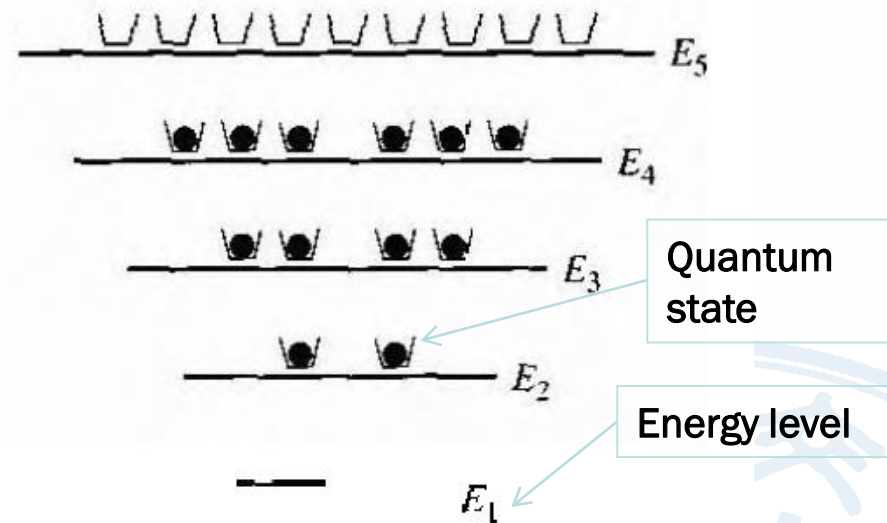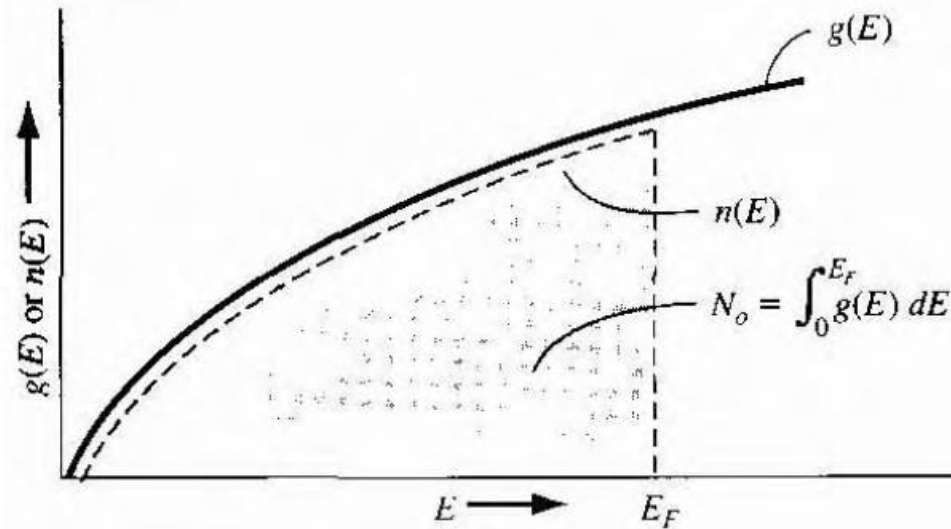
The probability of a quantum state being occupied in energy level E_5 is zero. The Fermi energy, for this case, must be above E_4 but less than E_5.

63

$$n(E) \le g(E)$$

$$N_o = \int_0^{E_F} g(E)\, dE$$

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

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.

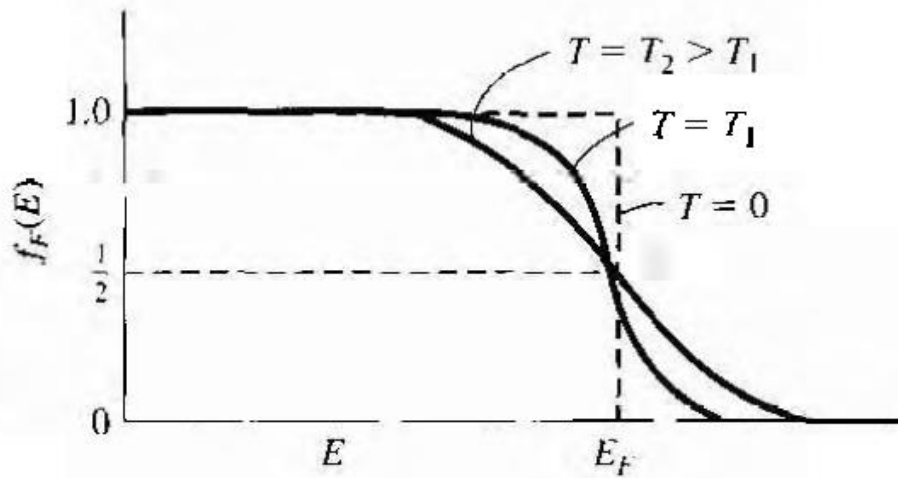If $g\,(\,E\,)$ and N_0 are known for this particular system, then the Fermi energy E_F can be determined.

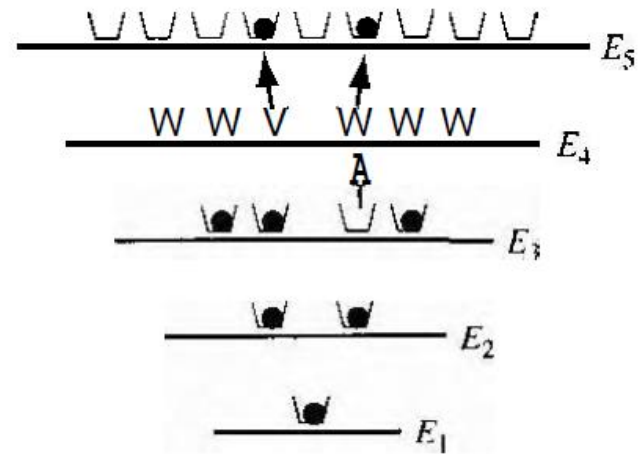Fig The Fermi probability function versus energy for different temperatures

Fig Discrete energy states and quantum states for T > 0 K.

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

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.
=>Some electrons have jumped to higher energy levels with increasing thermal energy.

Example

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

Determine the probability that an energy level $3kT$ above the Fermi energy is occupied by an electron.

Solution

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

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

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 he quite small.
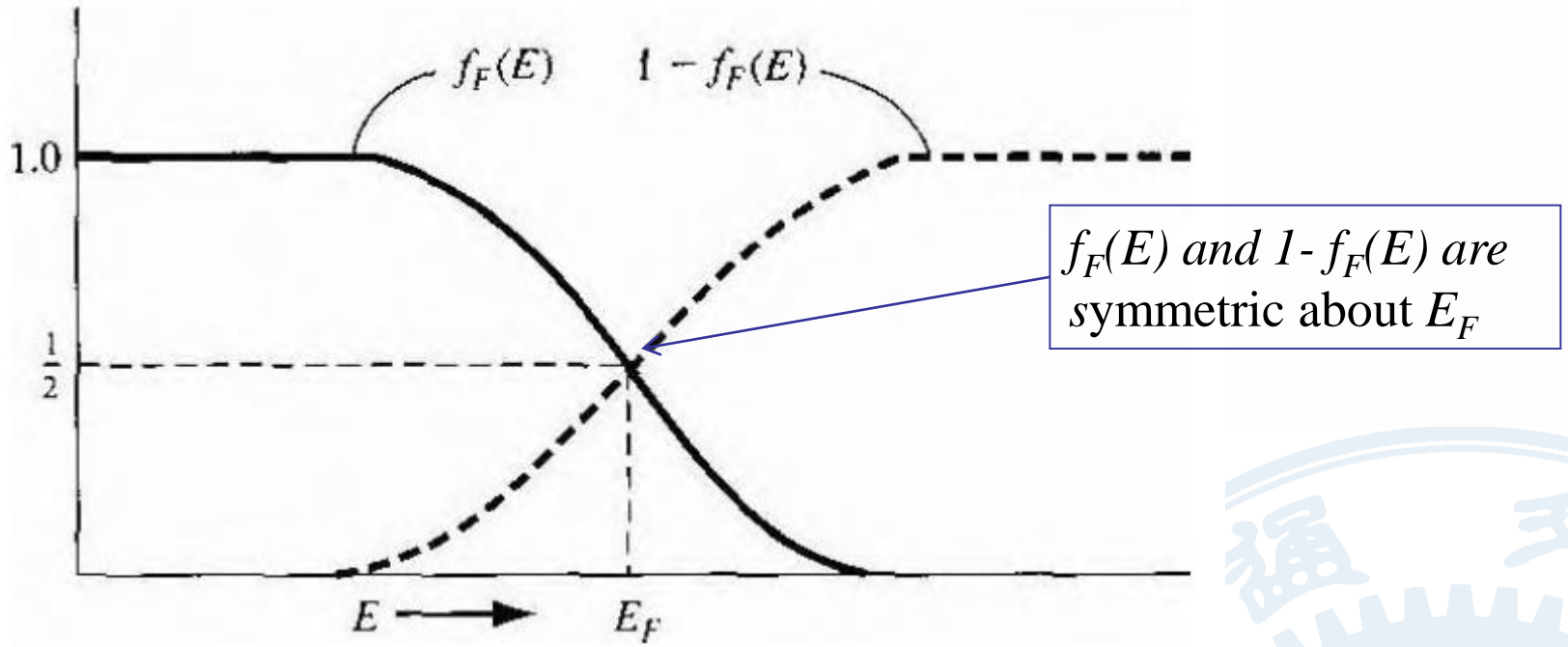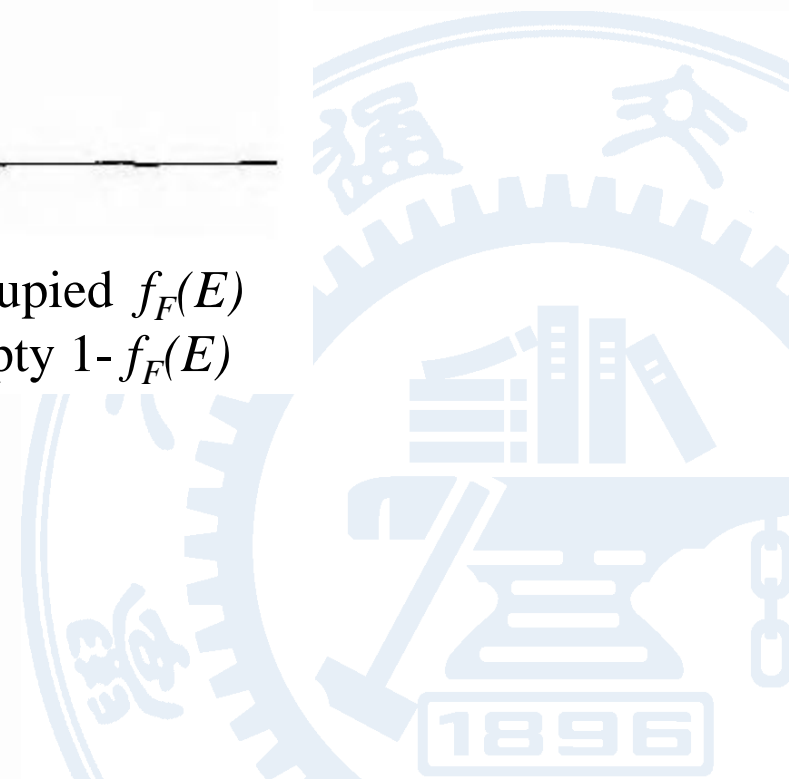
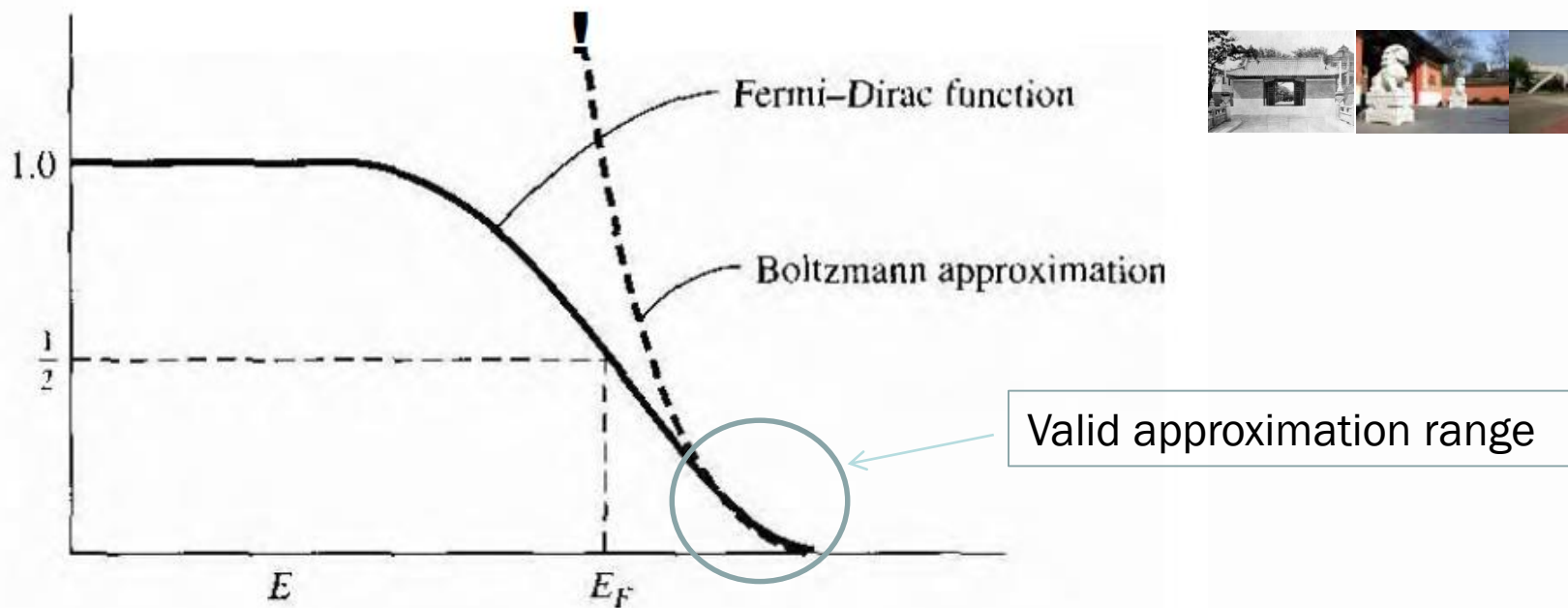Fig The probability of a state being occupied $f_F(E)$ and the probability of a state being empty $1 - f_F(E)$

Fig The Femi-Dirac probability function and the Maxwell-Boltzmann approximation.

Consider the case when $E-E_F>>kT$,

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

Fermi-Dirac distribution function

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

Maxwell-Boltzmann approximation.

Example

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

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

$$=> \exp[\frac{-(E-E_F)}{kT}] = 0.05 \qquad => (E-E_F) = kT\ln(\frac{1}{0.05}) \approx 3kT$$

The Maxwell-Boltzmann and Fermi-Dirac functions are within 5 percent of each other when $E - E_F = 3kT$

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 (conduction band). A hole is a positively charged particle with a positive effective mass existing at the top of an allowed energy band (valence band).

➢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.

Homework4

Assume the Fermi energy level is 0.03eV 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 =300K.