

# SECTION -C

## Theories of Free Electrons in solids

Resistivity range in Ohm m  $\Rightarrow$  25 orders of magnitude

$$R = \rho \frac{L}{A}$$

Metallic materials

Semi-conductors

$10^{-9}$		$10^{-7}$		$10^{-5}$		$10^{-3}$		$10^{-1}$		$10^{-1}$		$10^3$	
Ag		Ni		Sb Bi		Ge		Ge				Si	
Cu Al		Pb		Graphite		(doped)							
Au													

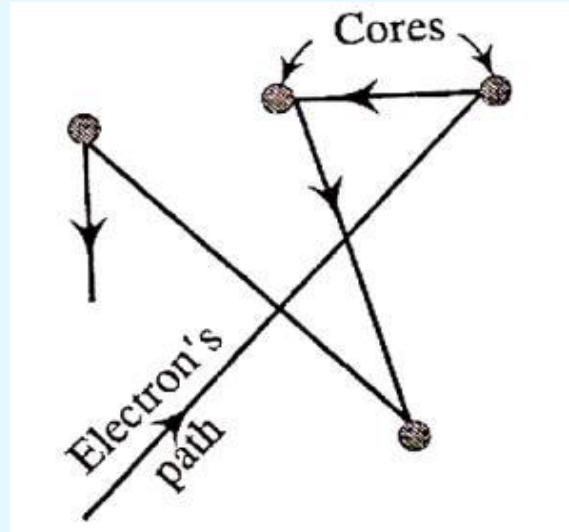
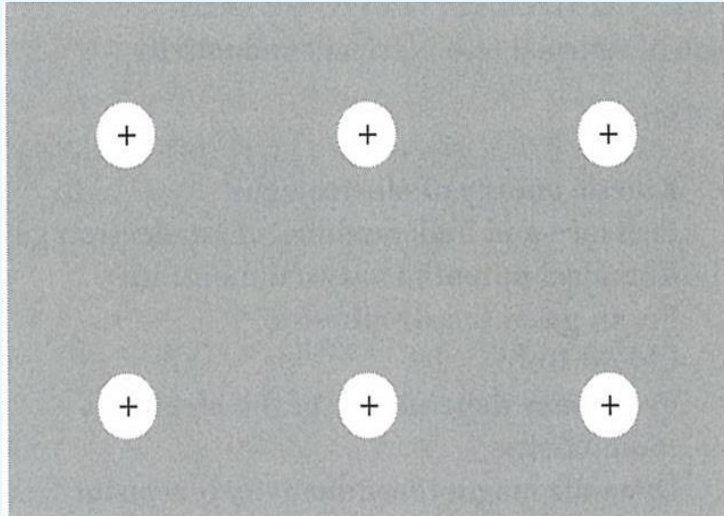
Insulators

$10^5$		$10^7$		$10^9$		$10^{11}$		$10^{13}$		$10^{15}$		$10^{17}$	
Window glass				Bakelite		Porcelain		Lucite		PVC		SiO <sub>2</sub>	
<i>Ionic conductivity</i>						Diamond		Mica				(pure)	
						Rubber							
						Polyethylene							

# Development of Free Electron Theories of Solids

- The Classical theory/Drude and Lorentz theory of free electrons (1900).
- The Quantum theory/Sommerfeld theory of free electron (1928)
- The Zone theory/Band theory/Bloch theory (1928).

# The Classical theory/Drude and Lorentz theory of free electrons (1900)



Paul Drude (1863-1906)

- It is a macroscopic theory.
- Proposed by Drude and Lorentz in 1900.
- It explains the free electrons in lattice
- It obeys the laws of classical mechanics.

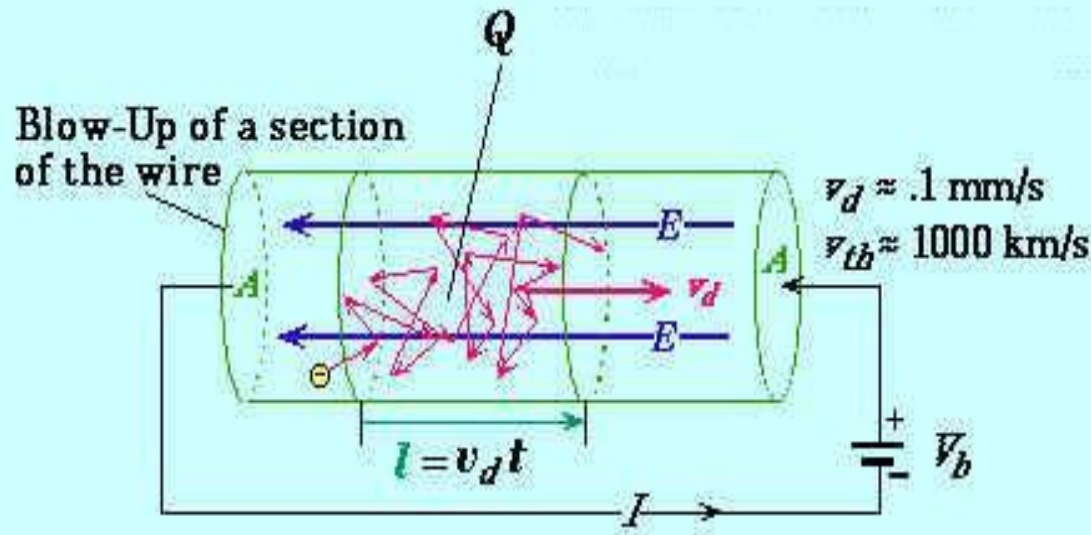


Hendrik Lorentz  
(1853-1928)

# Postulates

1. All the atoms are composed of atoms. Each atom have central nucleus around which there are revolving electrons.
2. The electrons are free to move in all possible directions about the whole volume of metals.
3. In the absence of an electric field the electrons move in random directions making collisions from time to time with positive ions which are fixed in the lattice or other free electrons. All the collisions are elastic i.e.; no loss of energy.
4. When an external field is applied the free electrons are slowly drifting towards the positive potential.
5. Since the electrons are assumed to be a perfect gas they obey classical kinetic theory of gasses.
6. Classical free electrons in the metal obey Maxwell-Boltzmann statistics.

# Ohm's Law



$$v_d = 0 + a\tau$$

$$v_d = - \left( \frac{eE}{m} \right) \tau$$

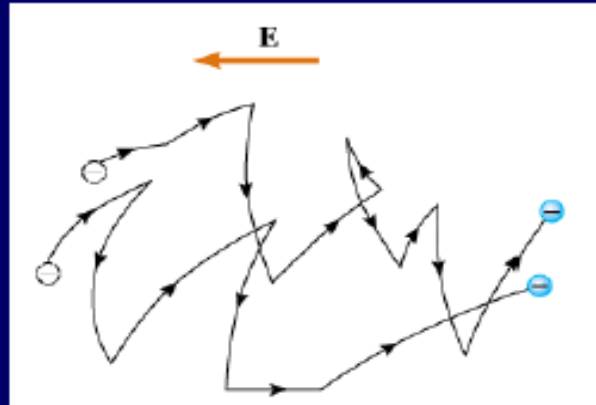
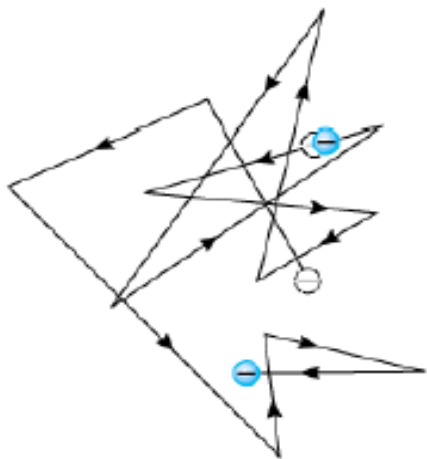
$$j = nev_d$$

$$J = \frac{ne^2\tau}{m} E$$

$$\sigma = \frac{ne^2\tau}{m}$$

$$J = \sigma E$$

Ohm's Law



# Success of Classical Free Electron Theory

1. Explains the **concept of resistance** in metals
2. Verifies **Ohm's law**
3. Explains high electrical and thermal conductivity of metals
4. Establishes relation between **electrical and thermal conductivities** of metals (Wiedemann – Franz law)

$k/\sigma = L.T$ ; wher,  $k$  is thermal conductivity,  $\sigma$  is electrical conductivity,  $L$  is Lorentz number,  $T$  is temperature (in K)

5. Explains **optical properties** of metals

# Drawbacks of Classical Free Electron Theory

✓ Classical theory failed to explain:

1. Many phenomenon observed in materials such as photoelectric effect, Compton effect and black body radiation, etc.
2. Electrical conductivity of semiconductors and insulators.
3. Specific heat capacity of solids.
4. The concept of ferromagnetism.
5. The theoretical value of paramagnetic susceptibility is greater than the experimental value.



# Sommerfeld's Quantum Mechanical Model of Electron Conduction in Metals

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



**Arnol Sommerfeld (1868–1951)**

- It is a microscopic theory.
- Proposed by Sommerfeld in 1928.
- It explains that the electrons moves in a constant potential.
- It obeys the Quantum laws.

# Quantum Free Electron Theory

- ✓ Postulates:
- Sommerfeld retained the concept of free electrons moving in a **uniform potential** within the metal.
- Treated electrons obeying **laws of quantum mechanics** instead of those of classical mechanics.
- Electron within the boundaries of the metal is considered as electron trapped in a **potential well**.
- Energy levels of electrons are explained by **distribution functions** besides the laws of quantum mechanics.
- **Fermi-Dirac statistics** was used instead of Maxwell-Boltzmann statistics.

# Energy spectrum of Electrons in Metals

- moving electrons inside a solid material can be associated with waves with a wave function  $\psi(x)$  in one dimension ( $\psi(\mathbf{r})$  in 3D)
- Hence its behaviors can be studied with the Schrödinger's equation (1D)

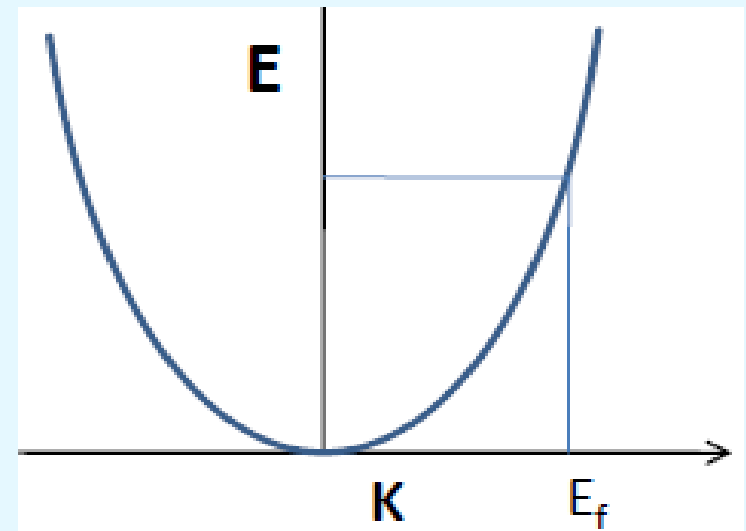
$$\frac{\partial^2 \psi(x)}{\partial x^2} + \frac{2m}{\hbar^2} (E - V) \psi(x) = 0$$

For a free particle  $V=0$ ,

$$\frac{\partial^2 \psi(x)}{\partial x^2} + k^2 \psi(x) = 0,$$

With  $k^2 = \frac{2mE}{\hbar^2}$   
 or,  $E = \frac{\hbar^2 k^2}{2m}, \hbar = \frac{h}{2\pi}$

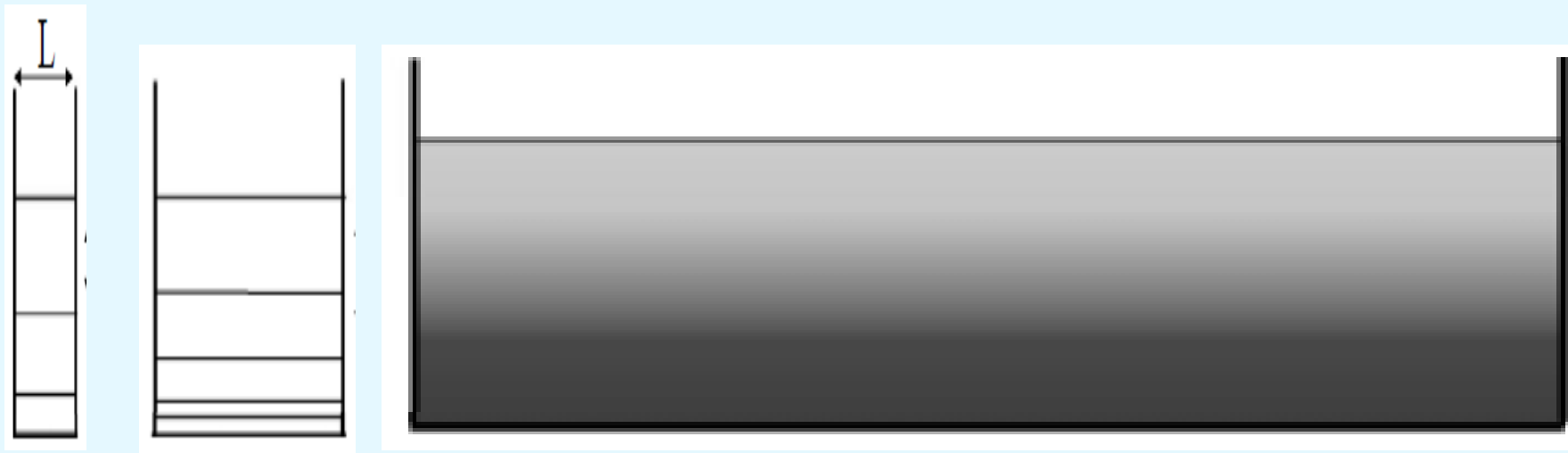
$$k = \pm n\pi / L$$



$$\psi(x) = A \sin \left( \frac{n\pi x}{L} \right)$$

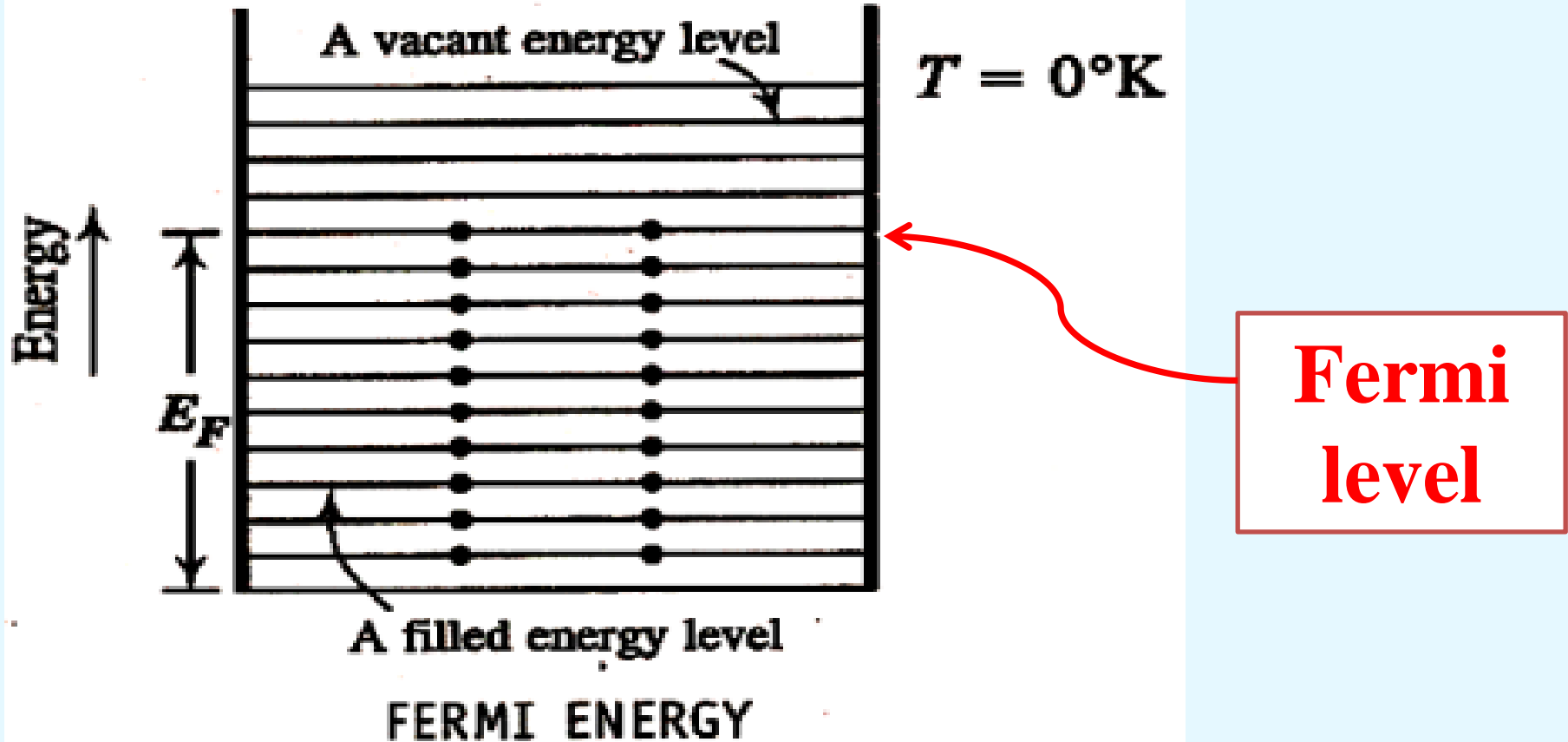
$$E_n = n^2 \frac{\pi^2 \hbar^2}{2mL^2}$$

- For a metallic conductor,  $L$  is very large
- Energy will be very small ( $\sim 10^{-19}\text{eV}$ ) and energy level spacing will also be of same order.
- Discrete energy spectrum with small level spacing
- Hence spectrum is quasi-continuous



**Variation of energy level spacing with increase in  $L$**

# Concept of Fermi level



Since electron are **Fermions** and obey **Paulli's Exclusion Principle** hence the ground state of system of free electrons is shown in above figure

# Fermi Distribution function $F(E)$

Probability that an energy level with energy  $E$ , in energy spectrum of a system, is occupied at any temperature  $T$

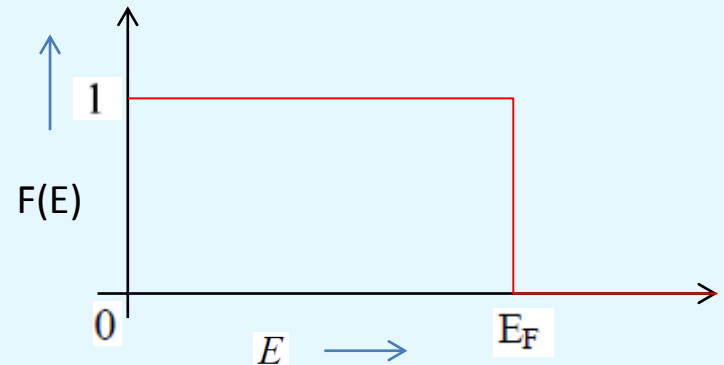
$$F(E) = \frac{1}{1 + e^{\frac{E-E_F}{k_B T}}}$$

## Effect of Temperature on Fermi—Dirac Distribution Function

### Case I - At temperature $T = 0K$

(a) For  $E < E_F$ ,  $\frac{E-E_F}{k_B T} \rightarrow -\infty$  and  $F(E) = 1$

(b) For  $E > E_F$ ,  $\frac{E-E_F}{k_B T} \rightarrow +\infty$  and  $F(E) = 0$



Thus, at absolute zero temperature  $F(E)$  is a step function. All the states with energies up to  $E_F$  are filled with electrons and the states with energies greater than  $E_F$  are empty. Thus the Fermi level may be defined as the topmost filled level at absolute temperature.

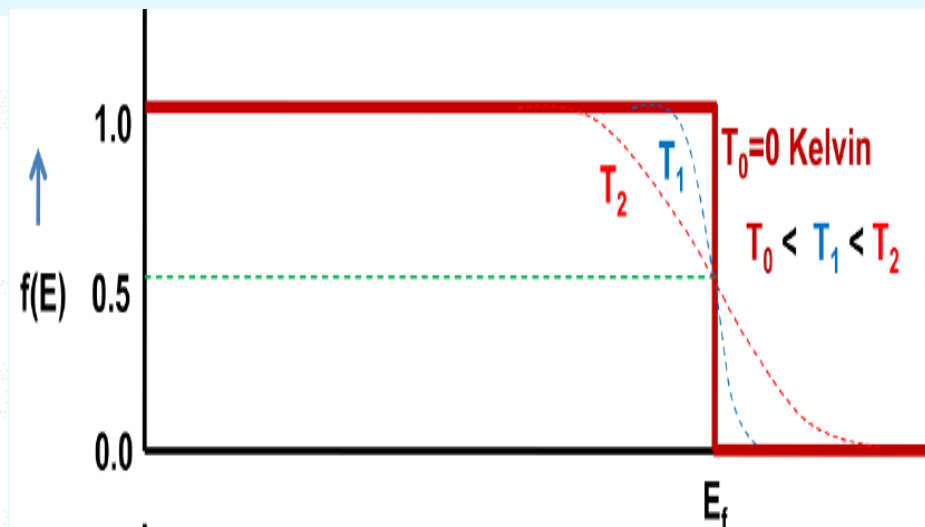
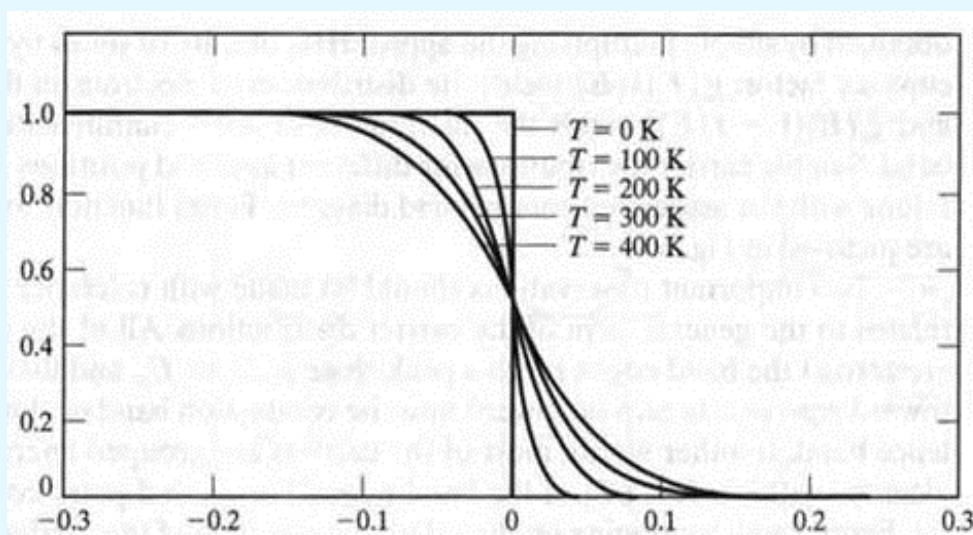
## Case II - At temperature $T > 0$ K

(a) For  $E < E_F$ ,  $\frac{E-E_F}{k_B T}$  is negative and  $F(E) \cong 1$  for  $E \ll E_F$

(b) For  $E > E_F$ ,  $\frac{E-E_F}{k_B T}$  is positive and  $F(E) \cong 0$  for  $E \gg E_F$

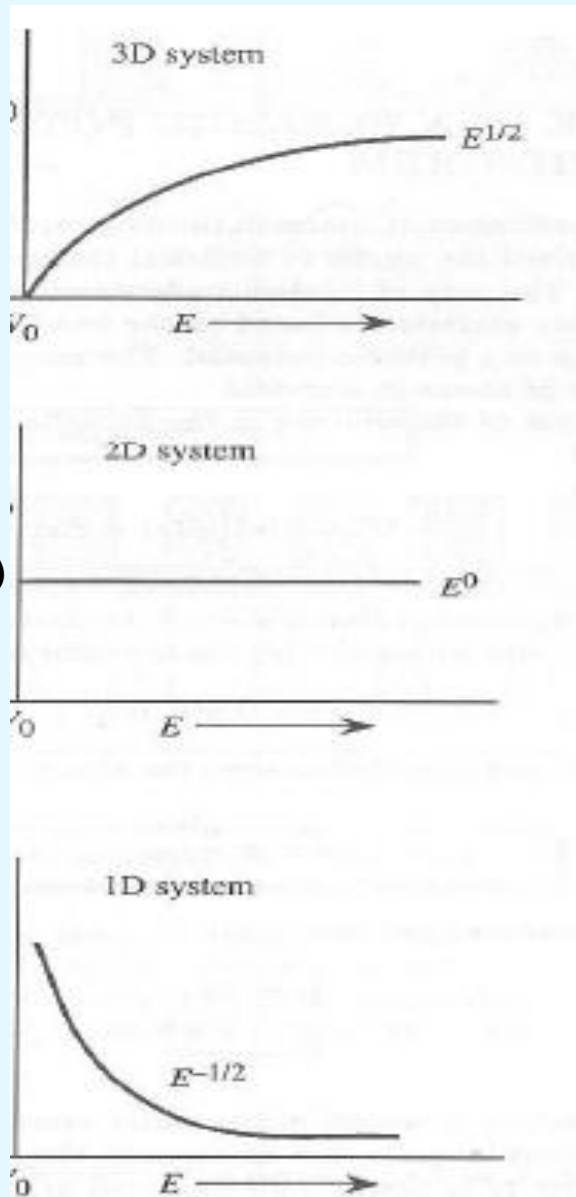
(c) For  $E = E_F$ ,  $\frac{E-E_F}{k_B T} = 0$  and  $F(E) = 1/2$

Thus, at finite temperature the probability of occupancy of the Fermi level is  $1/2$ .

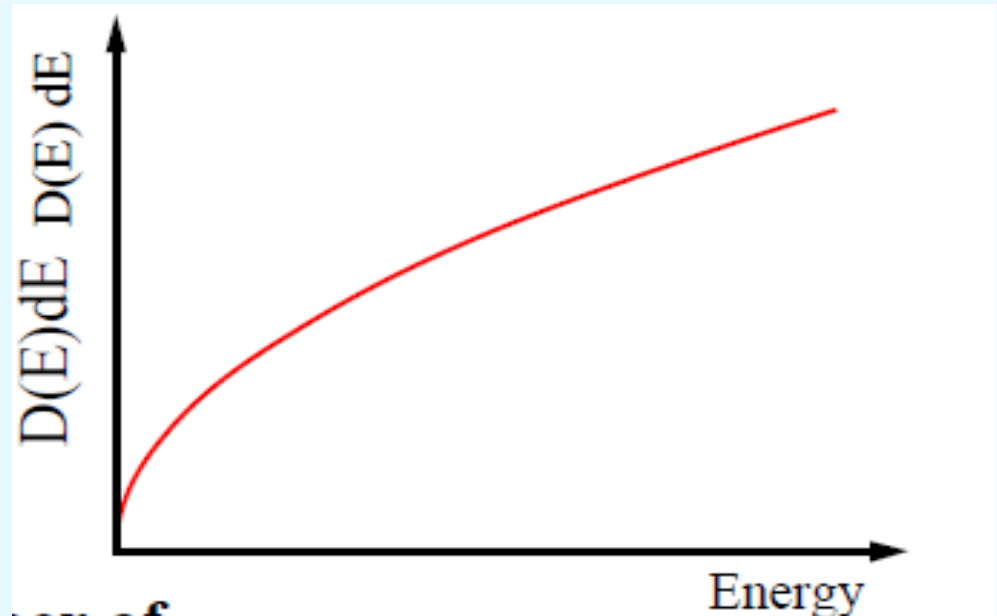


# Density of States $D(E)$

**Definition:** Number of energy states per unit energy range/volume of a quantum system



$$D(E)dE = \frac{dN}{dE} = \frac{V}{2\pi^2} \left( \frac{2m}{\hbar^2} \right)^{3/2} E^{1/2} dE$$





## Quantum free electron theory — Electrical conductivity

$$P = \hbar k$$

$$mv = \hbar k$$

$$v = \frac{\hbar k}{m}$$

Differentiating the above equation w.r.t 't' we get

$$a = \frac{dv}{dt} = \frac{\hbar}{m} \frac{dk}{dt}$$

Force on the electron in the applied field E is given by  $F = eE$

$$ma = eE$$

$$\hbar \frac{dk}{dt} = eE$$

$$dk = \frac{eE}{\hbar} dt$$

$$\frac{dk}{dt} = \frac{2\pi}{h} eE$$

On Integration gives  $k = \frac{2\pi}{h} eE \tau$

Where  $\tau$  = mean collision time

But  $J = \sigma E$

$$\begin{aligned} \Rightarrow \sigma &= \frac{J}{E} \\ &= \frac{nAeV_d}{AE} \\ &= \frac{ne}{E} \left( \frac{\hbar k}{2\pi m^*} \right) \\ &= \frac{neh}{2\pi m^* E} \left( \frac{2\pi}{h} eE \tau \right) \end{aligned}$$

$$\sigma = \frac{ne^2}{m^*} \tau$$

# Success of Quantum Free Electron Theory

1. According to classical theory, which follows Maxwell- Boltzmann statistics, all the free electrons gain energy. So it leads to much larger predicted quantities than that is actually observed.
2. But according to quantum mechanics **only one percent of the free electrons** can absorb energy. So the resulting specific heat and paramagnetic susceptibility values are in much better agreement with experimental values.
3. According to quantum free electron theory, both experimental and theoretical values of **Lorentz number** ( $L = 2.44 \times 10^{-8} \text{ W}\Omega\text{K}^{-1}$ ) are in good agreement with each other.

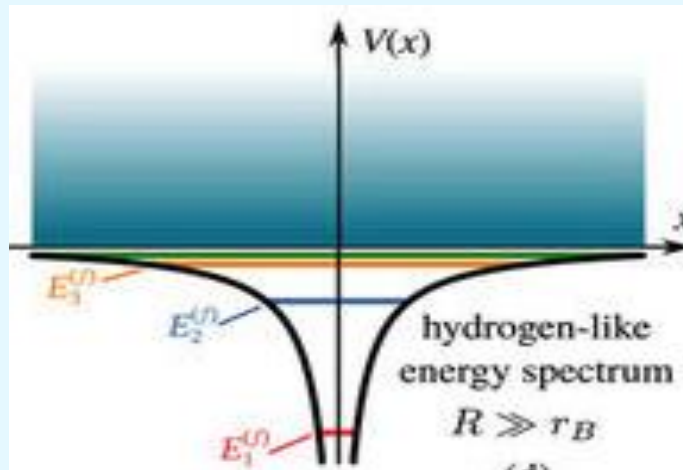


# Energy Band Theory of Solids

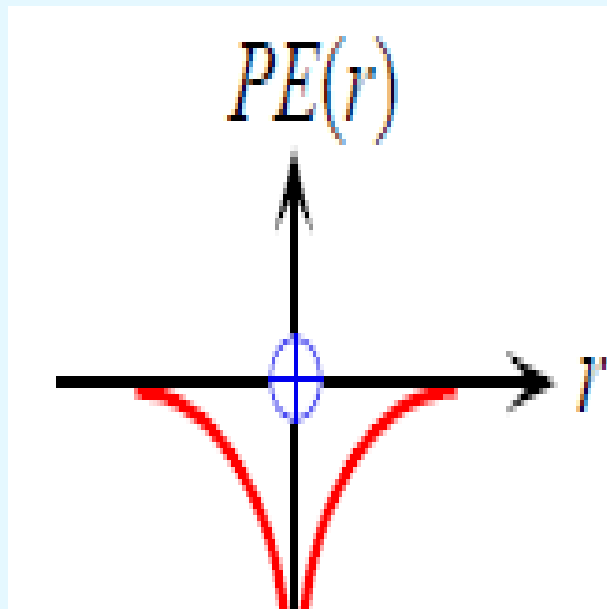
Or

# Zone Theory

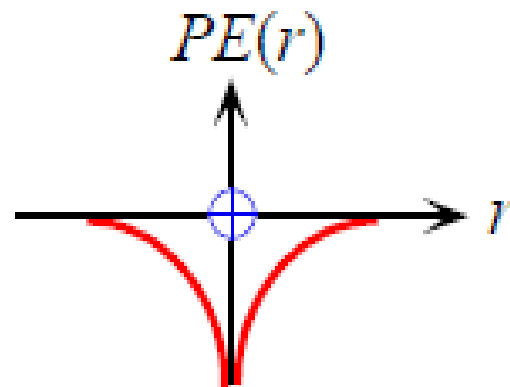
# Remember for the Hydrogen atom



$$V(x) = -\frac{1}{4\pi\epsilon_0} \frac{e^2}{r}$$

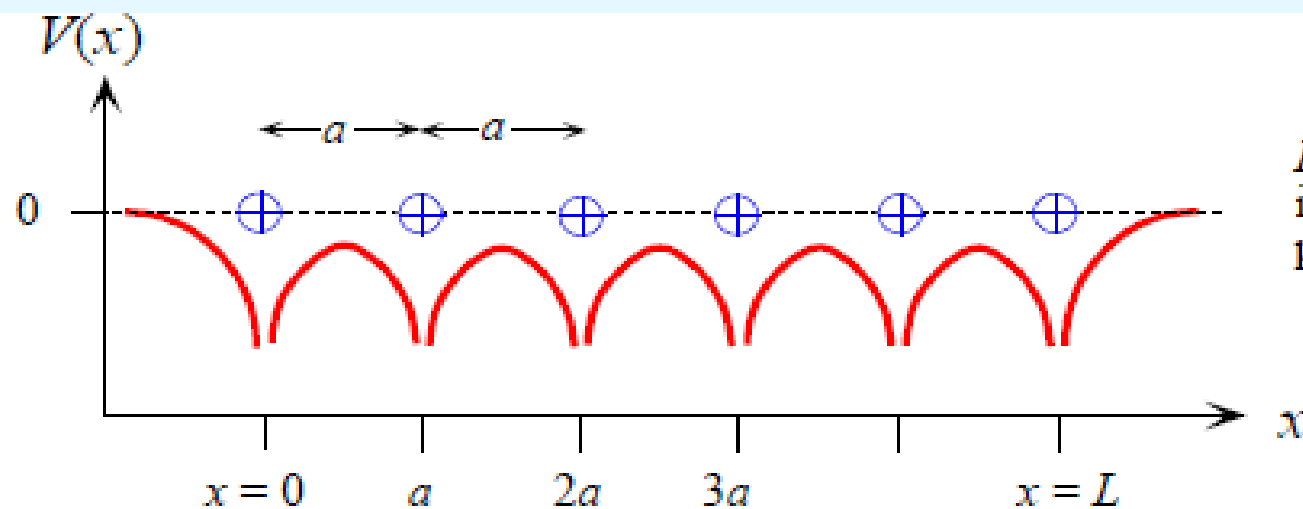
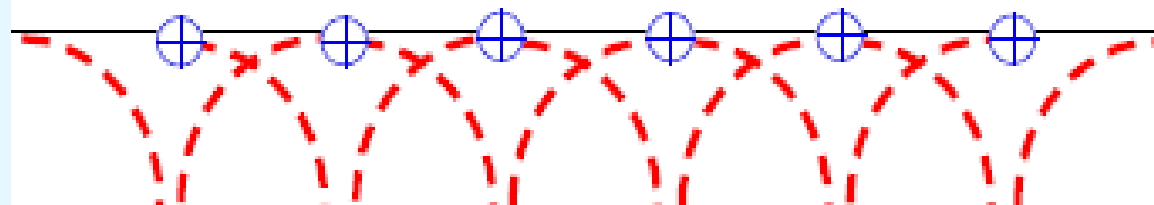


$PE$  of the electron around  
an isolated atom



$PE$  of the electron around an isolated atom

When  $N$  atoms are arranged to form the crystal then there is an overlap of individual electron  $PE$  functions.



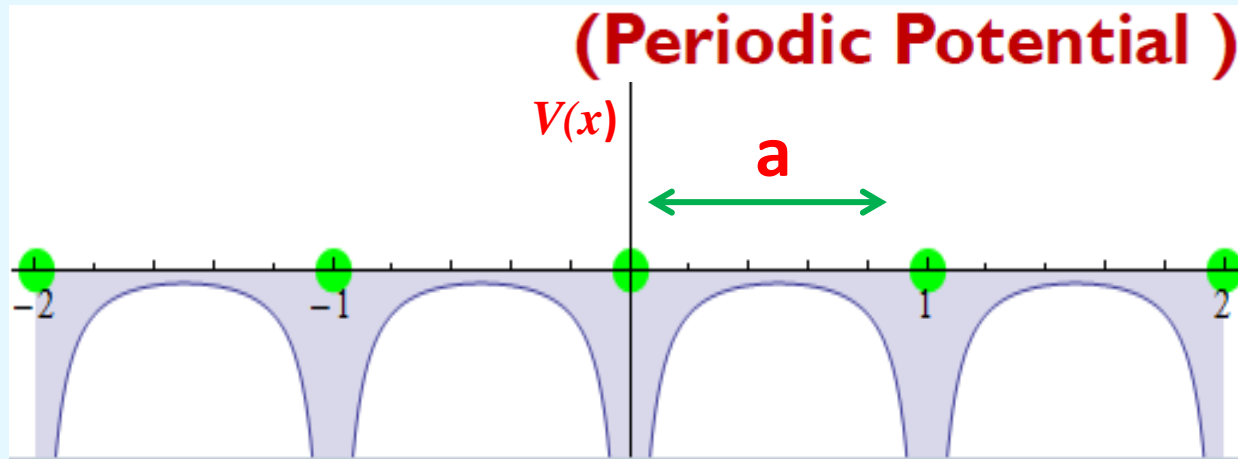
$PE$  of the electron,  $V(x)$ , inside the crystal is periodic with a period  $a$ .

Surface

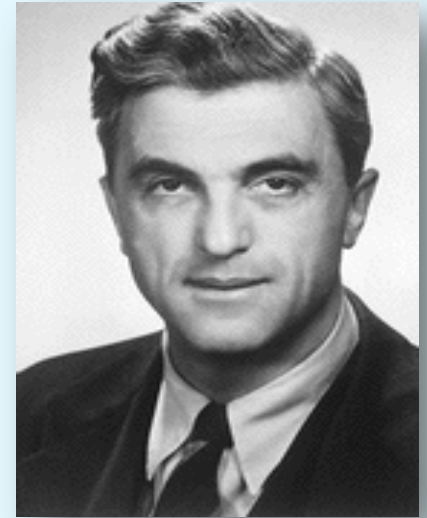
Crystal

Surface

# Concept of Periodic Potential



$$V(x) = V(x + a) = V(x + n a)$$



*Felix Bloch*  
*1905-1983*

## ■ Block Theorem

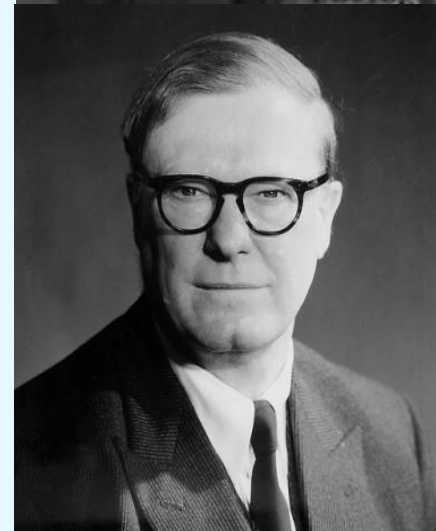
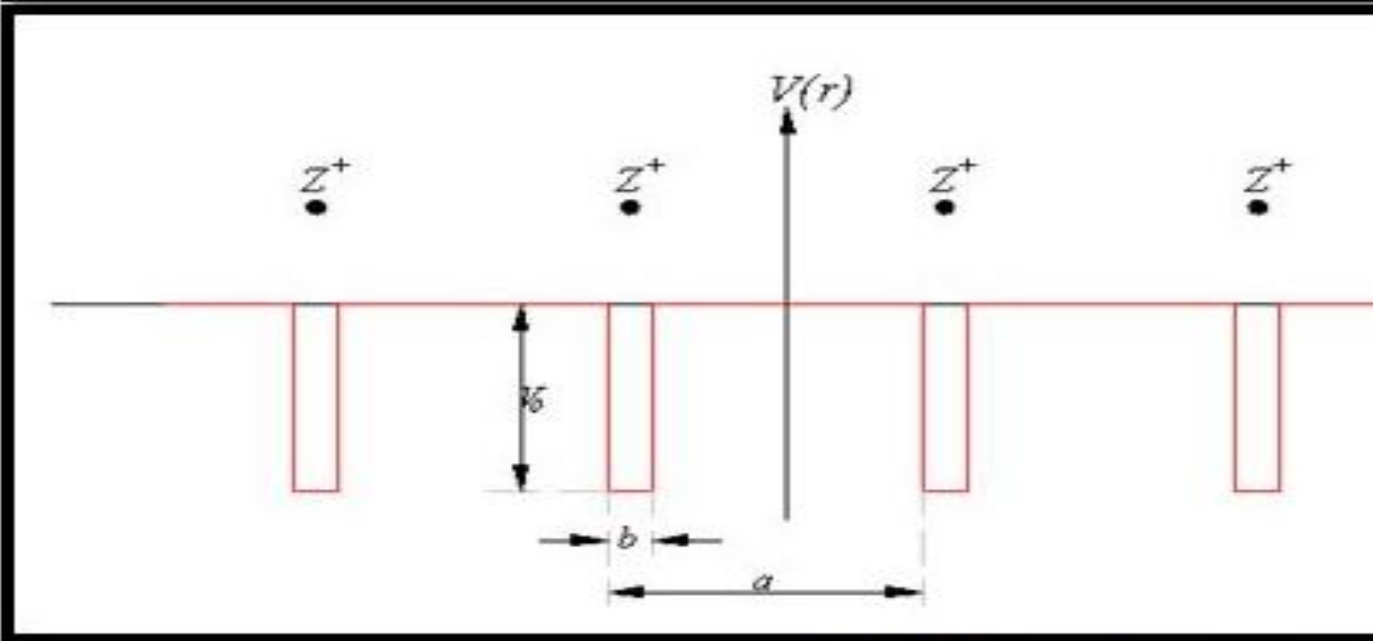
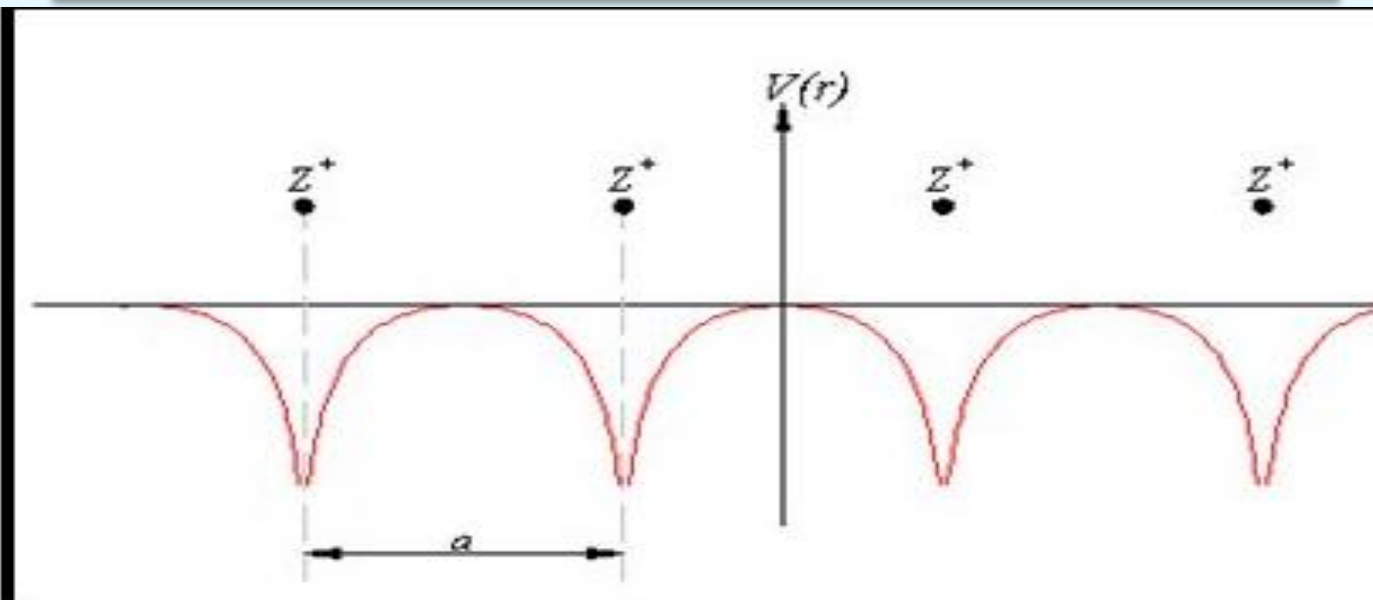
The **wave function** for an electron moving in **periodic potential** is a product of **plane wave** and a **periodic function** having periodicity same as the lattice parameter

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

$u(x)$  : periodic function with period  $a$   
 $e^{jkx}$   $\therefore$  traveling wave

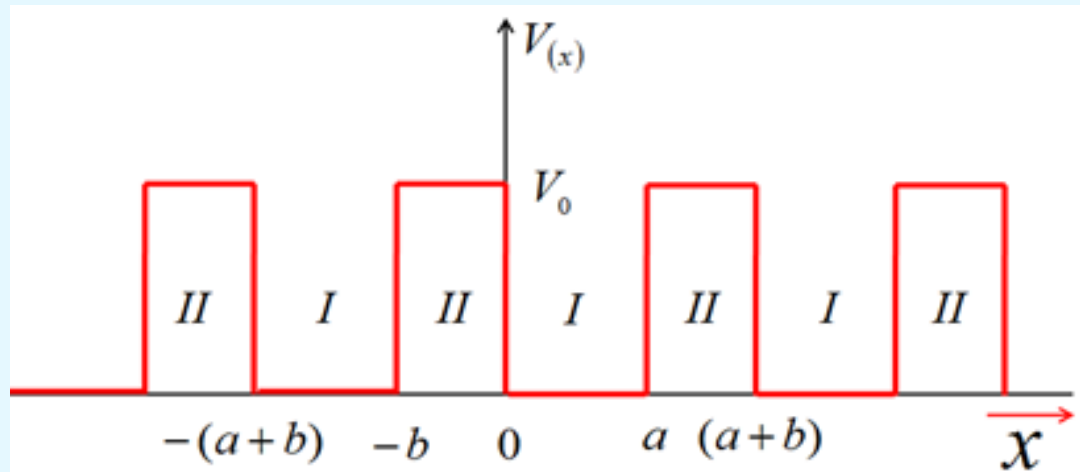
$$u(x) = u(x + a) = u(x + n a)$$

# Kronig-Penny Model





$$V(x) = \begin{cases} 0 & 0 < x < a \\ V_0 & -b < x < 0 \end{cases}$$

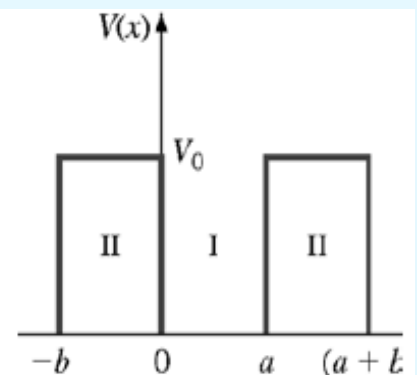


Time-independent Schrodinger wave equation

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

Region I:  $\frac{\partial^2 \psi(x)}{\partial x^2} + \frac{2mE}{\hbar^2} \psi(x) = 0 \quad (0 \leq x \leq a)$

Region II:  $\frac{\partial^2 \psi(x)}{\partial x^2} + \frac{2m(E - V_0)}{\hbar^2} \psi(x) = 0 \quad (-b \leq x \leq 0)$



■ Block Theorem

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

## Region I

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

## Region II :

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

$$\beta = \sqrt{\frac{2m(E - V_o)}{\hbar^2}} = j\gamma \quad \text{if } V_o > E$$

When **Boundary Conditions** are applied, then it is found that only those solutions are applicable for which

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

$$\alpha = \sqrt{\frac{2mE}{\hbar^2}} \quad \beta = j\gamma = j\sqrt{\frac{2m(V_o - E)}{\hbar^2}}, \quad \gamma > 0$$

### Case 1: Free particle:

$bV_o$  is finite value, and  
 $b \rightarrow 0$

$$V_o = 0$$

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

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

$$\boxed{\cos \alpha a = \cos ka \text{ (free particle)}} \Rightarrow \boxed{\alpha = k}$$

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

$$\Rightarrow \begin{cases} p = \hbar k \\ E = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m} \end{cases}$$

### Case 2: bound electrons in crystal:

$bV_o$  is finite value, but

$$b \rightarrow 0$$

$$V_o \rightarrow \infty \Rightarrow E \ll V_o$$

} Periodic  $\delta$ function potential barrier

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



$$b \rightarrow 0 \Rightarrow \sinh \gamma b \approx \gamma b \text{ \& \; } \cosh \gamma b \rightarrow 1$$

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

E - k equation  $P' \frac{\sin \alpha a}{\alpha a} + (\cos \alpha a) = \cos ka$

$$P' = \frac{mV_o b a}{\hbar^2}$$

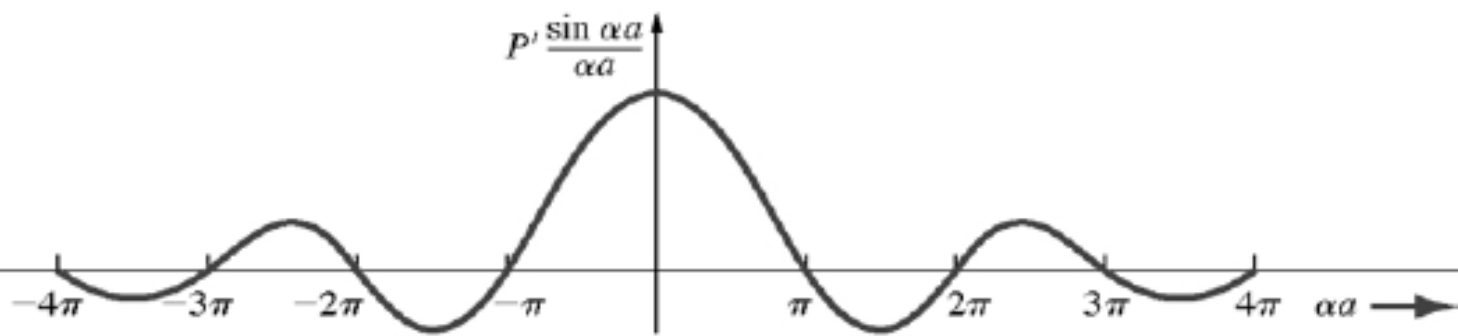
$$\alpha = \sqrt{\frac{2mE}{\hbar^2}}$$

energy term      momentum term

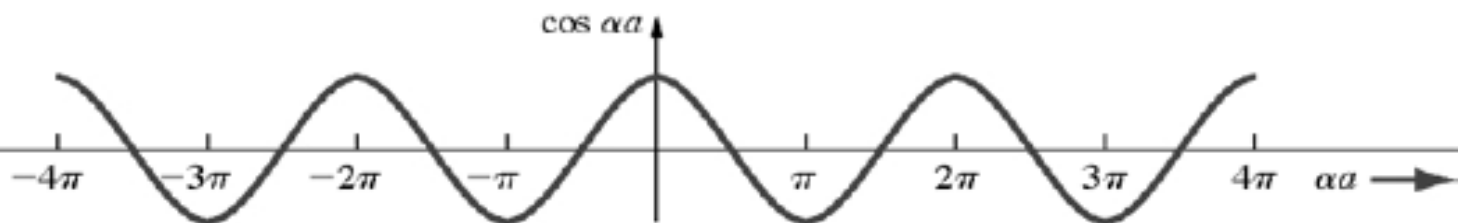
$$f(\alpha a) = P' \frac{\sin \alpha a}{\alpha a} + (\cos \alpha a)$$

$$-1 \leq f(\alpha a) = \cos ka \leq +1$$

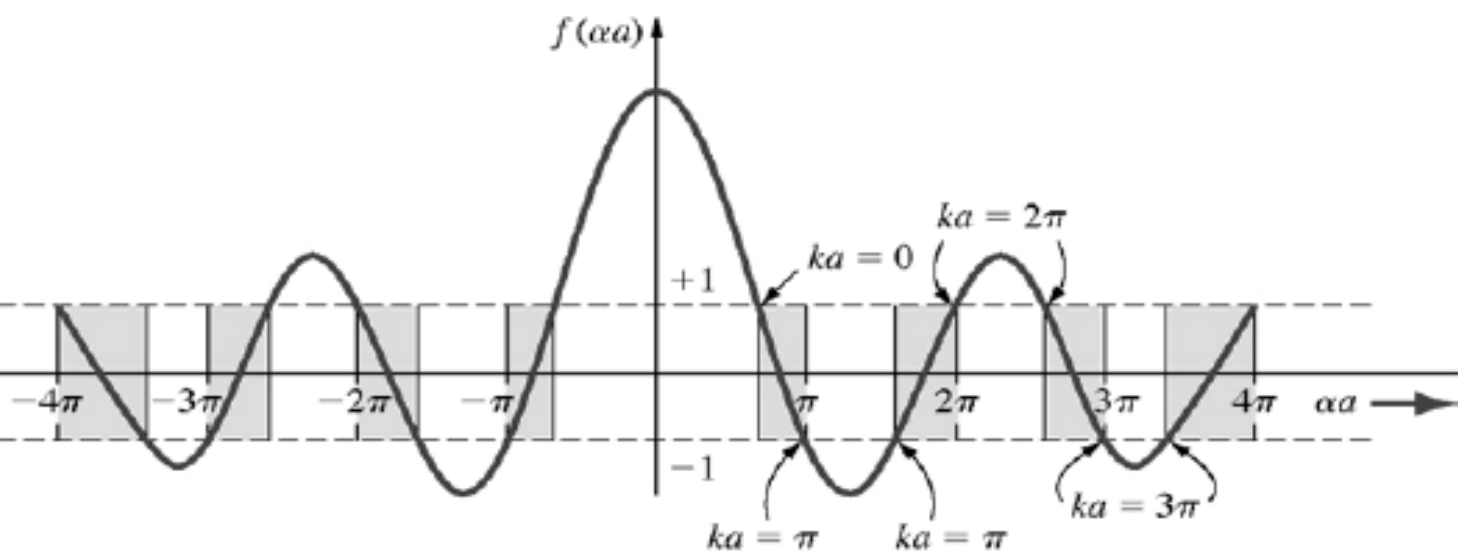
The above eq does not lend itself to an analytical solution, but must be solved using **numerical** or **graphical techniques** to obtain the relation between  $k$ ,  $E$



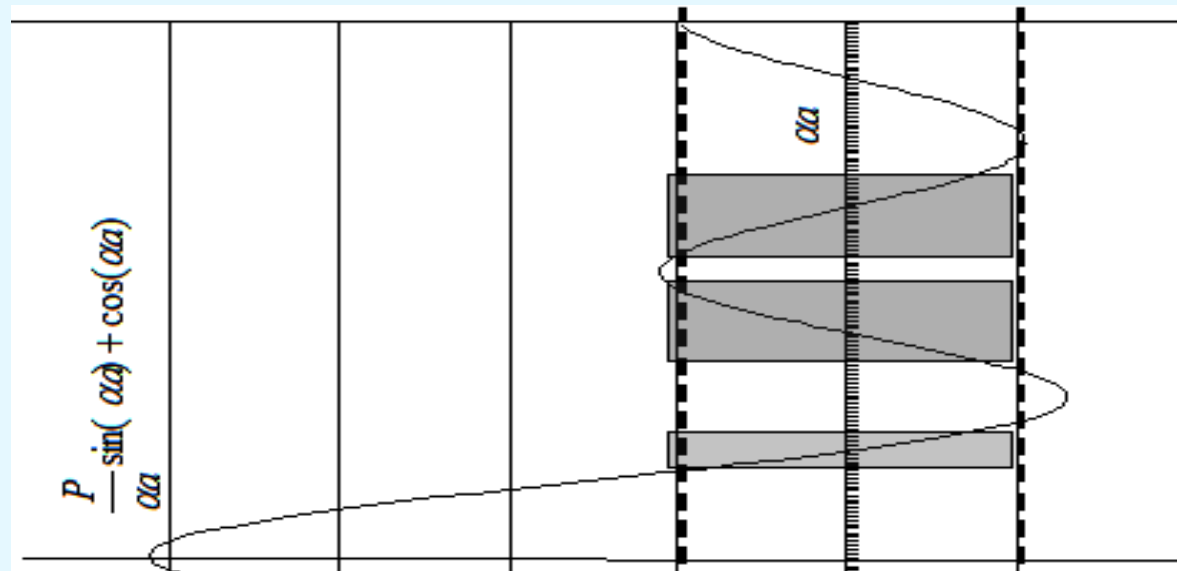
(a)



(b)

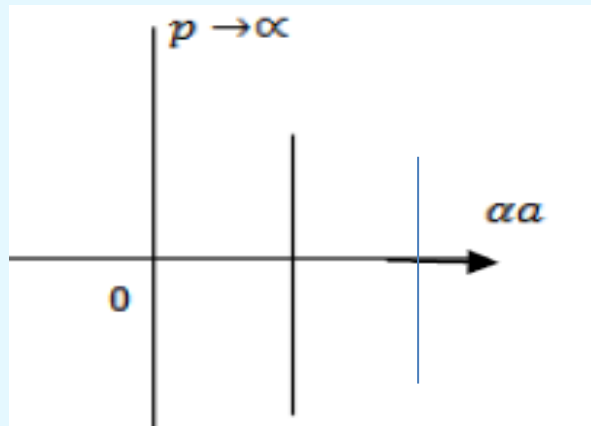


The parameter  $\alpha$  is related to the total energy  $E$  of the particle



- Electrons in solids are permitted to be in allowed energy bands separated by forbidden energy gaps.
- The allowed energy band width increases with  $\alpha a$ .

**Case (i)** when  $P \rightarrow \infty$ , the allowed energy states are compressed to a line spectrum.



$$\left. \begin{array}{l} bV_0 \text{ is finite value, but} \\ b \rightarrow 0 \\ V_0 \rightarrow \infty \Rightarrow E \ll V_0 \end{array} \right\}$$

**Case (ii)** when  $P \rightarrow 0$  the energy band is broadened and it is quasi continuous.

$$\left. \begin{array}{l} bV_0 \text{ is finite value, and} \\ b=0 \\ V_0=0 \end{array} \right\}$$

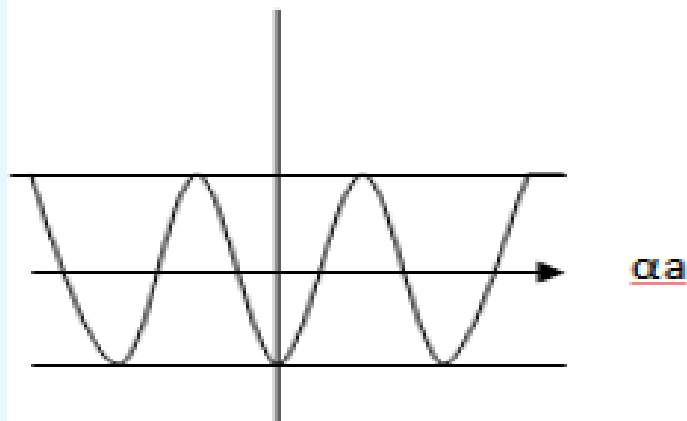
$$\cos \alpha a = \cos ka \quad (\text{free particle})$$

$$\Rightarrow$$

$$\alpha = k$$

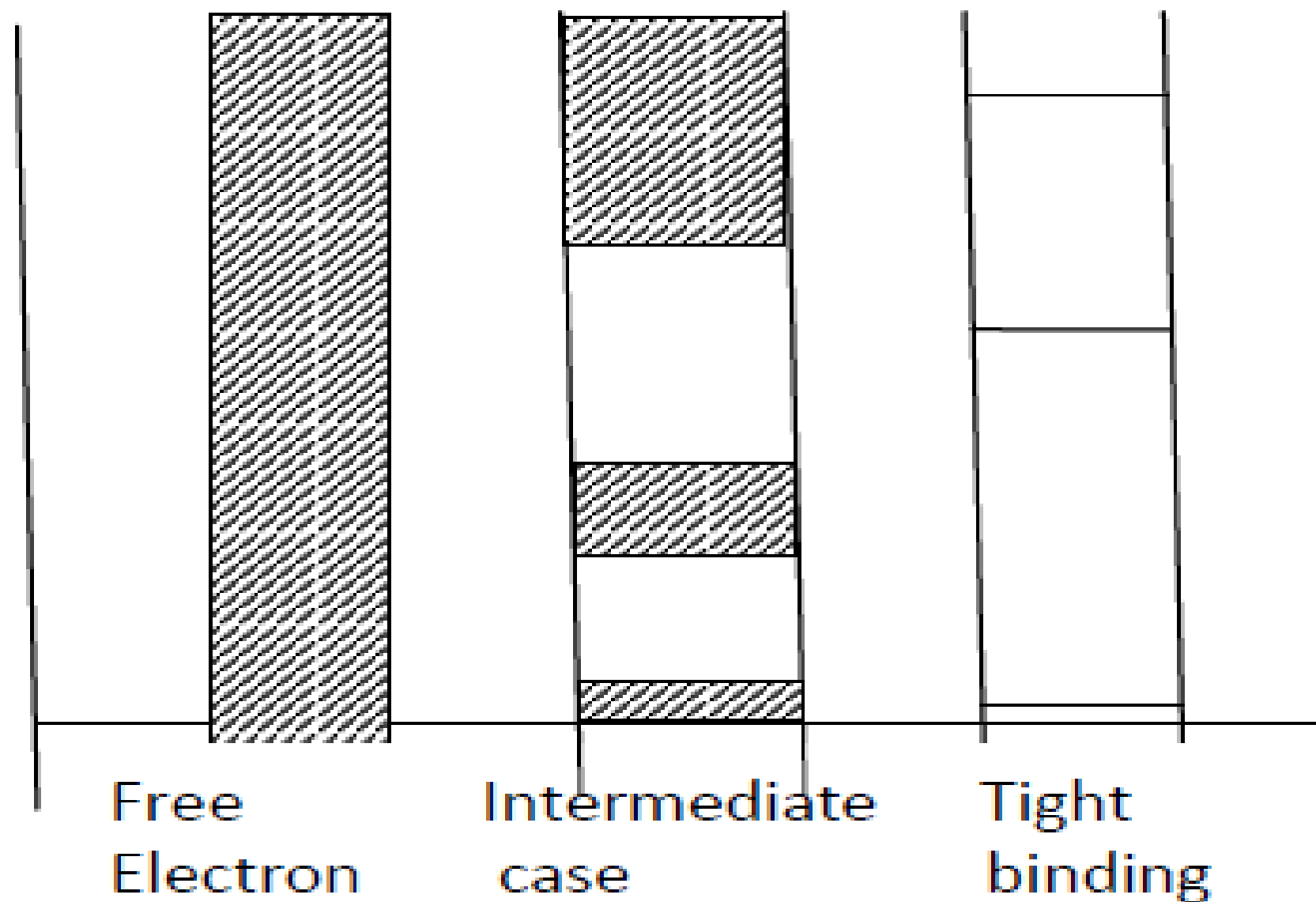
$$\beta = \alpha = \sqrt{\frac{2mE}{\hbar^2}}$$

$$p \rightarrow 0$$



$$\Rightarrow \begin{cases} p = \hbar k \\ E = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m} \end{cases}$$

E





# The $E$ - $k$ Diagrams

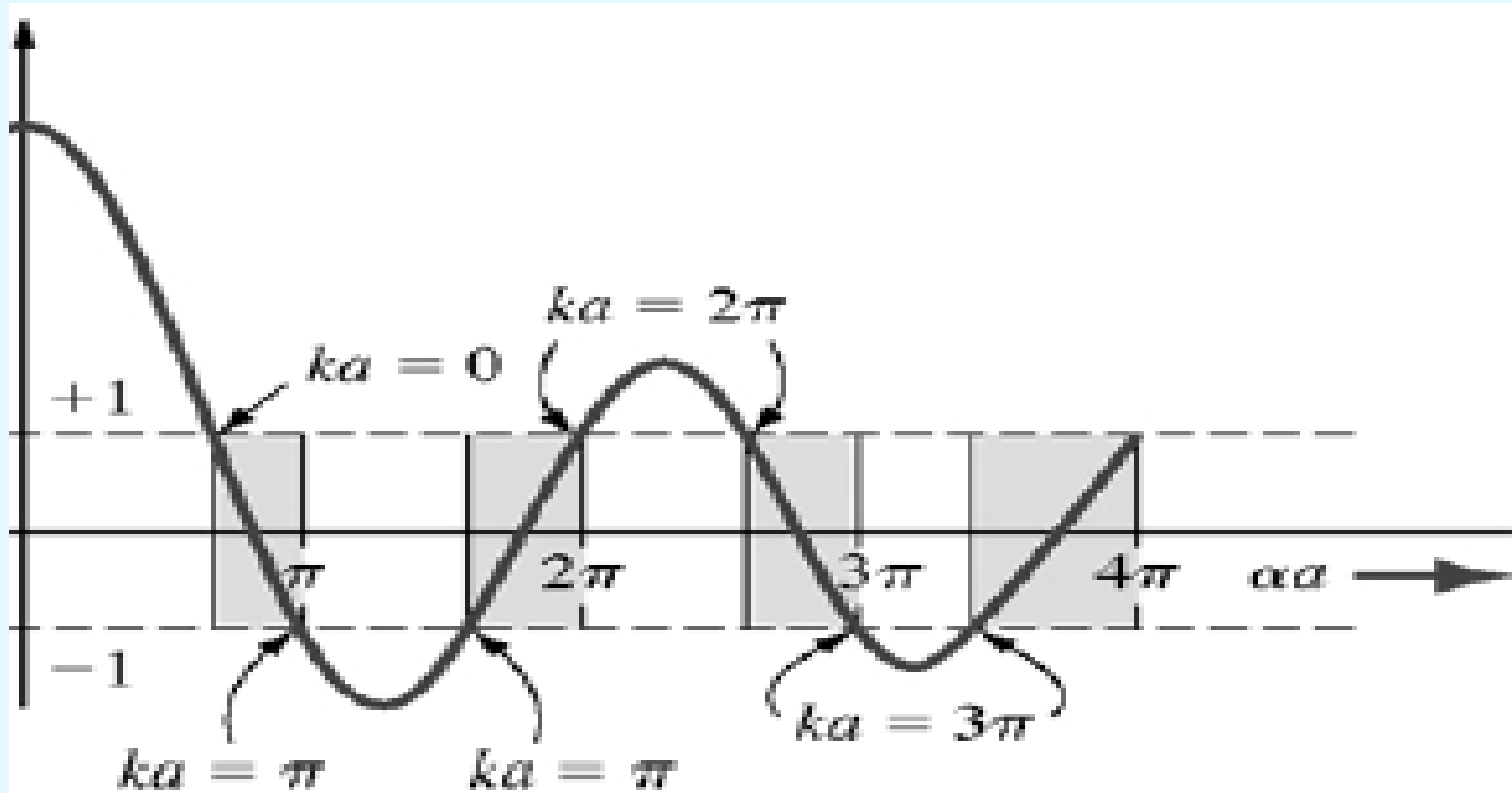
The energy discontinuities for electron moving in a periodic potential are produced whenever

$$\cos ka = \pm 1$$

i.e.

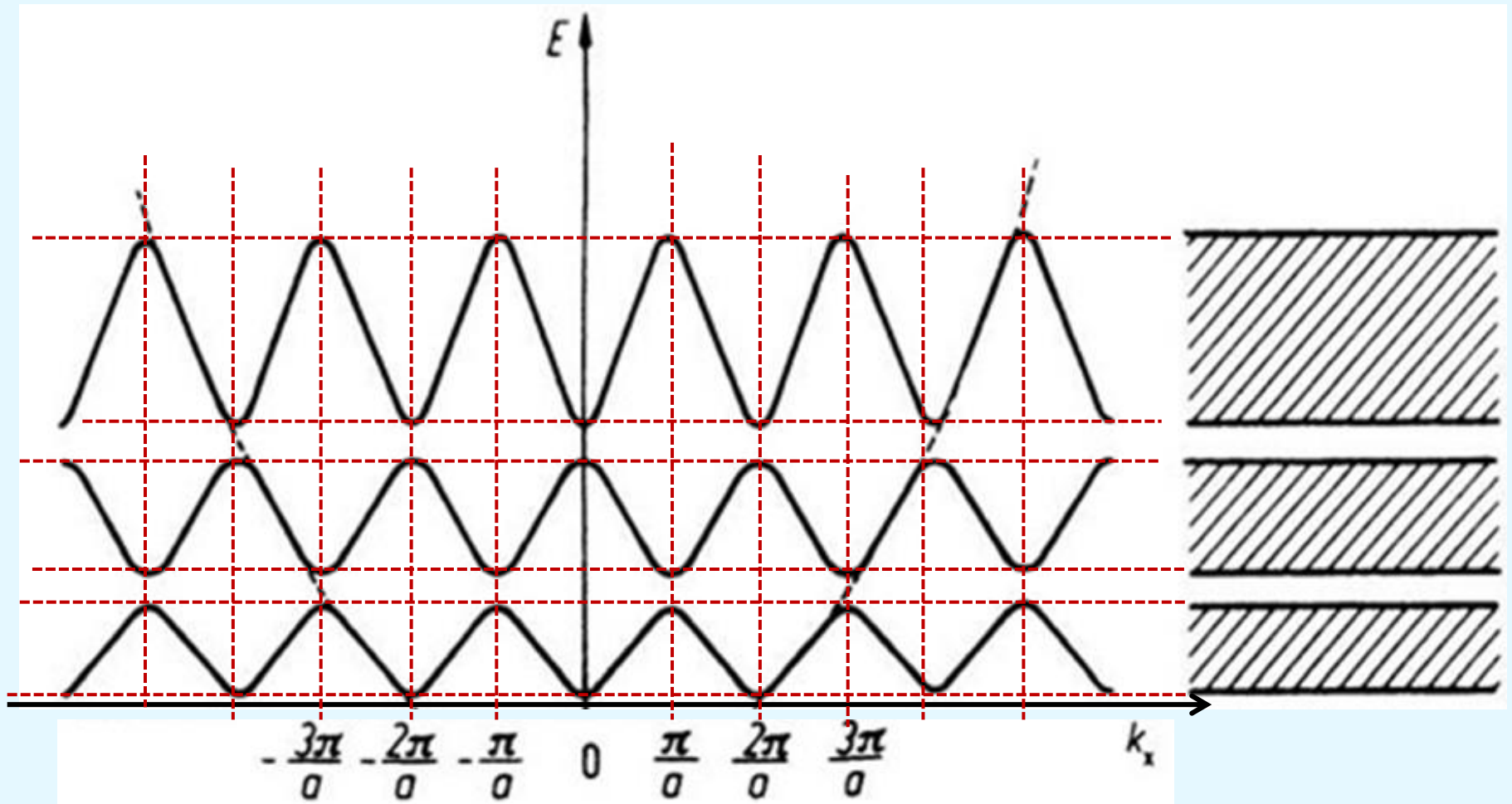
$$ka = \pm n\pi$$

$$k = \pm n \frac{\pi}{a}$$

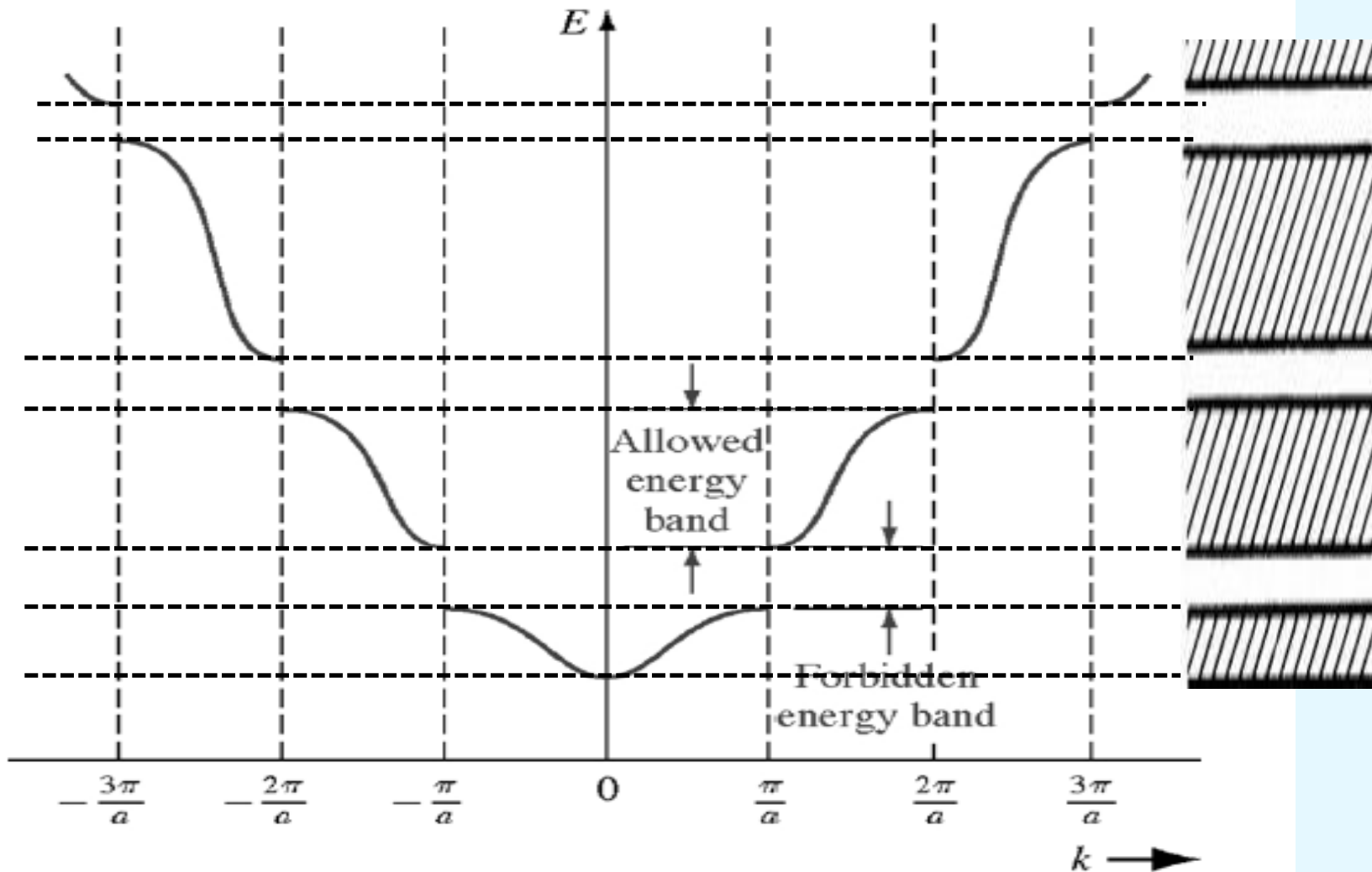


Three ways to represent the variation of **Energy ( $E$ )** with **momentum ( $k$ )** within an allowed band of energy

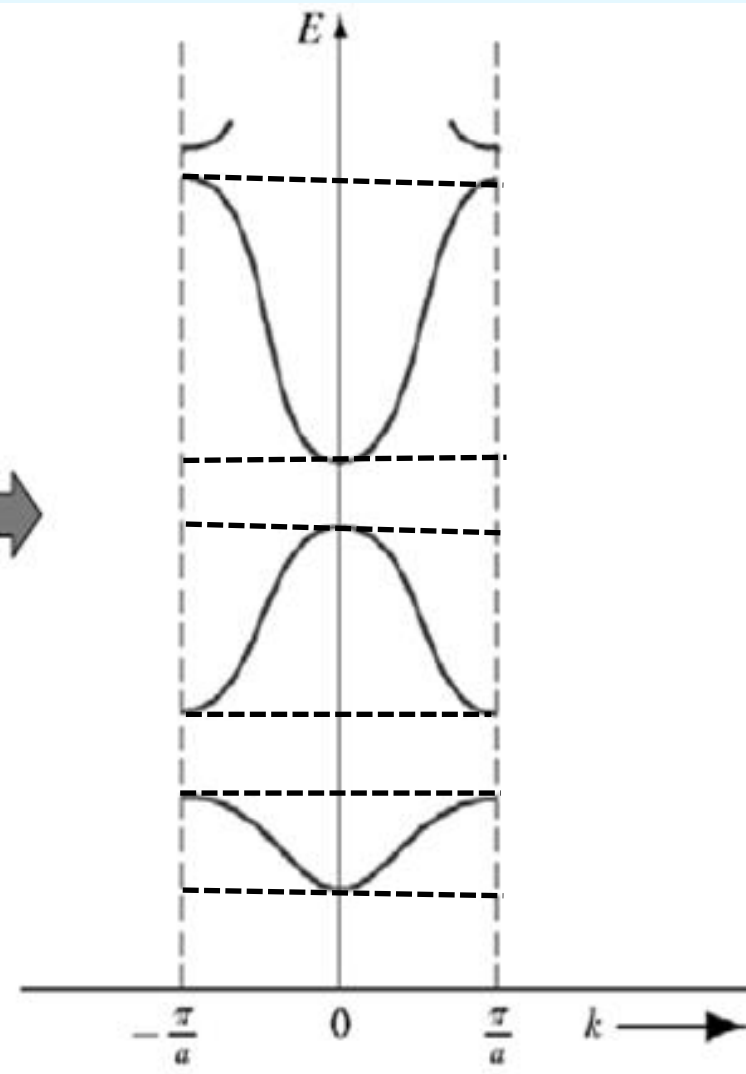
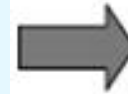
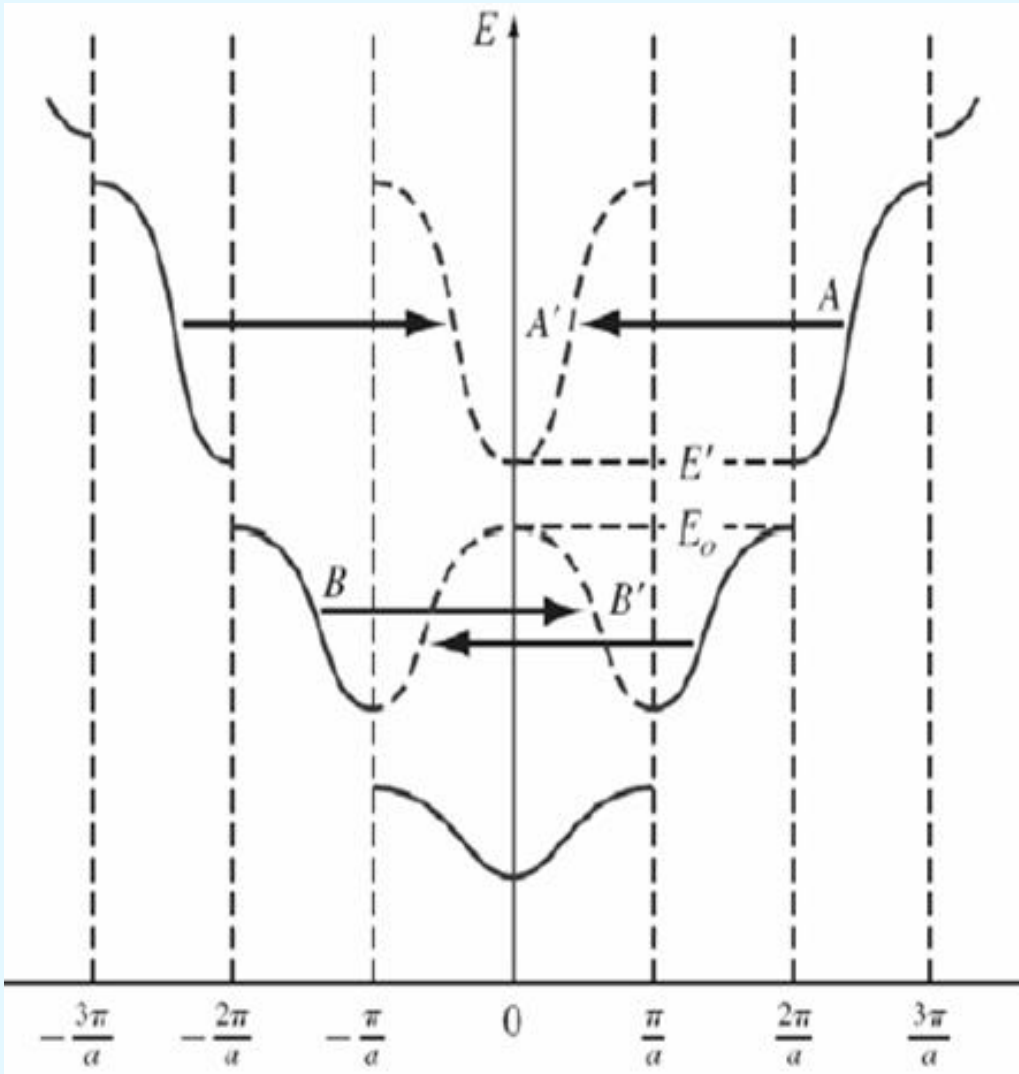
## 1. Periodic Zone Scheme



## 2. Extended Zone Scheme



### 3. Reduced Zone Scheme

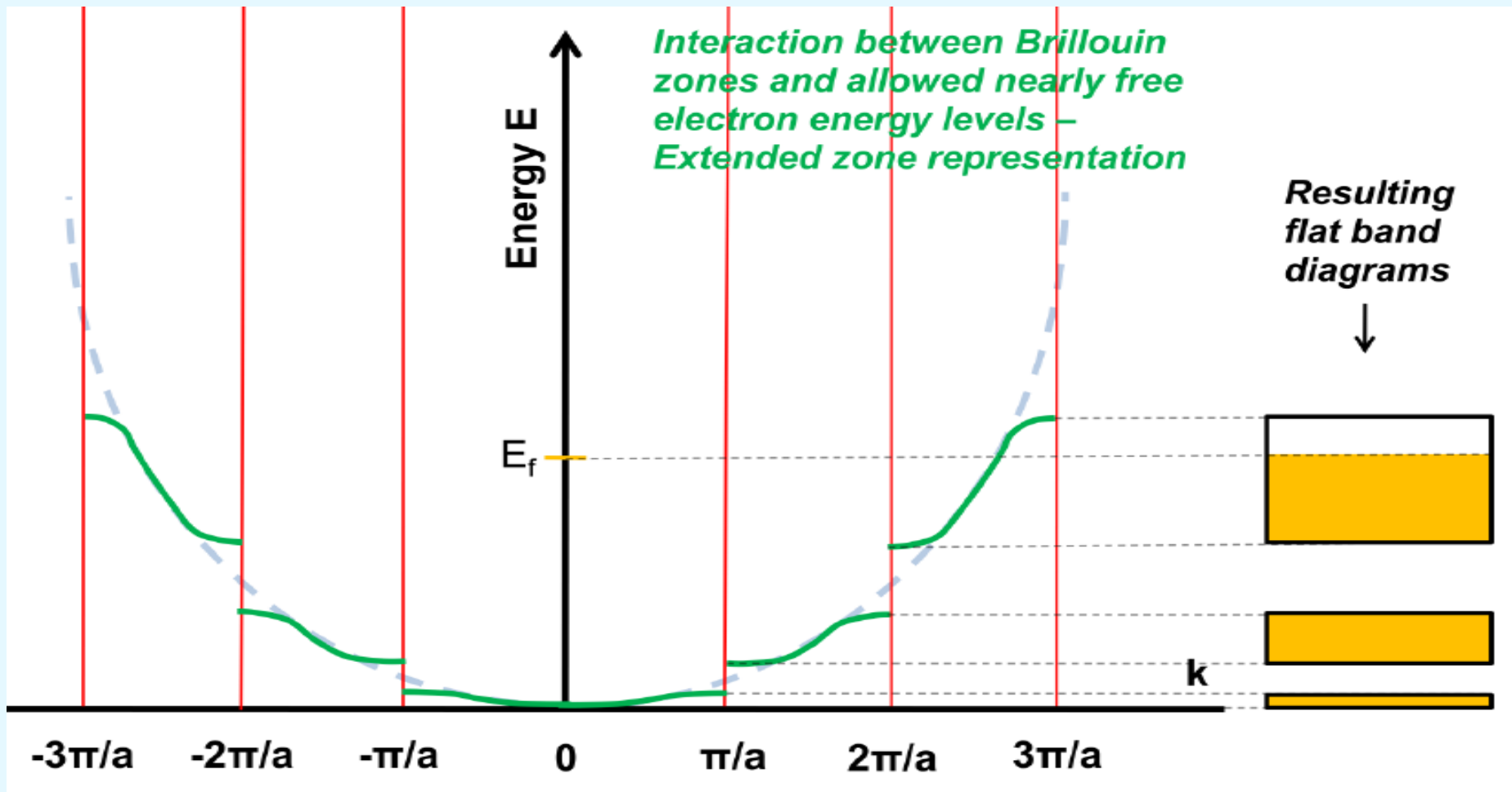


Reduced  $k$ -space

Displacement of portions of the curve in left figure by  $2\pi$

# Brillouin Zones

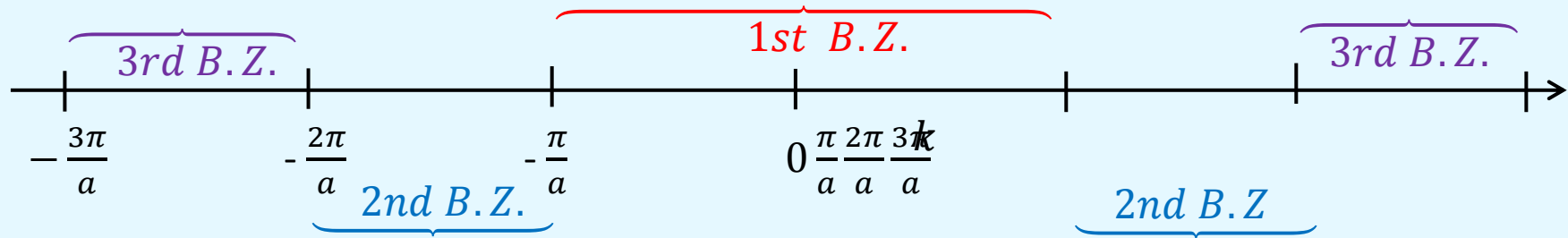
Permissive values of  $k$  within an allowed band of energy are called **Brillouin Zones**



# Brillouin Zones in I-D

The energy discontinuities for electron moving in a periodic potential are produced whenever

$$k = \pm n \frac{\pi}{a}$$



**First Brillouin Zone**

$$-\frac{\pi}{a} < k < \frac{\pi}{a}$$

**Second Brillouin Zone**  $-\frac{2\pi}{a} < k < -\frac{\pi}{a}$  and  $\frac{\pi}{a} < k < \frac{2\pi}{a}$

**Third Brillouin Zone**  $-\frac{3\pi}{a} < k < -\frac{2\pi}{a}$  and  $\frac{2\pi}{a} < k < \frac{3\pi}{a}$

**...and so on...**

# Brillouin Zones in 2-D

If we have a 2-D square lattice then condition for generation of energy discontinuities will be:

$$n_1 k_x + n_2 k_y = \frac{\pi}{a} (n_1^2 + n_2^2)$$

**Taken**  $n_1 = \pm 1, n_2 = 0 \Rightarrow k_x = \pm \frac{\pi}{a}$

$n_1 = 0, n_2 = \pm 1 \Rightarrow k_y = \pm \frac{\pi}{a}$

*Region enclosed by these lines gives 1st B.Z.*

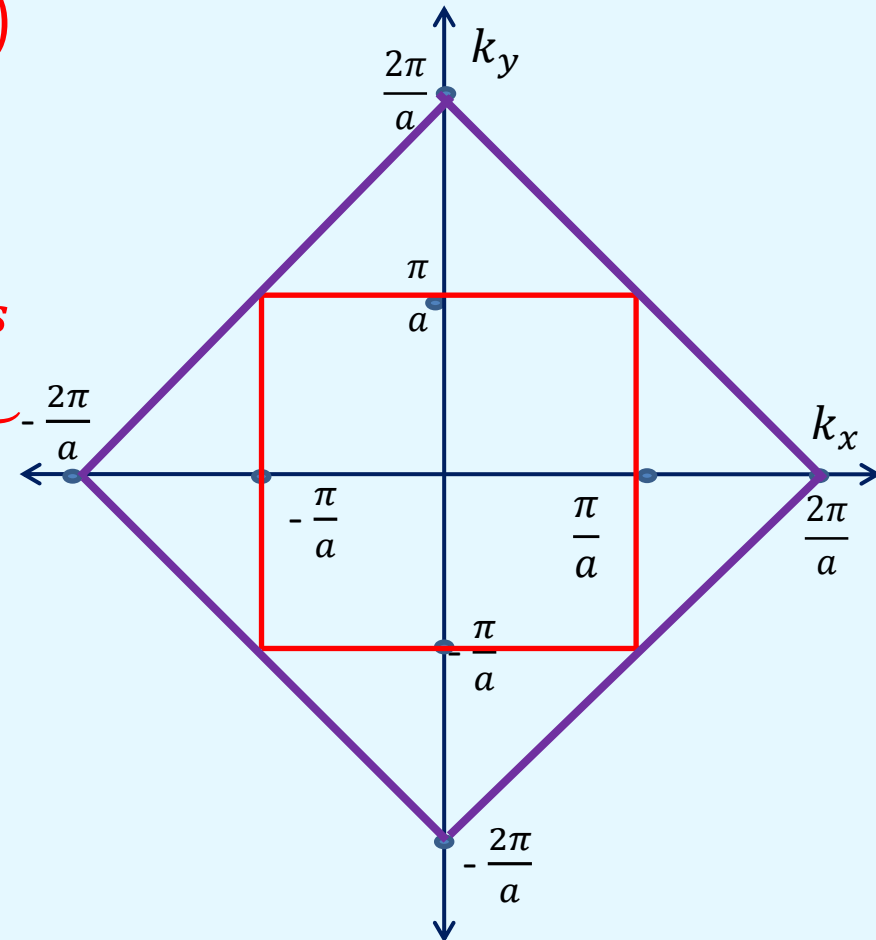
$$n_1 = +1, n_2 = +1 \Rightarrow k_x + k_y = +\frac{2\pi}{a}$$

$$n_1 = -1, n_2 = +1 \Rightarrow -k_x + k_y = +\frac{2\pi}{a}$$

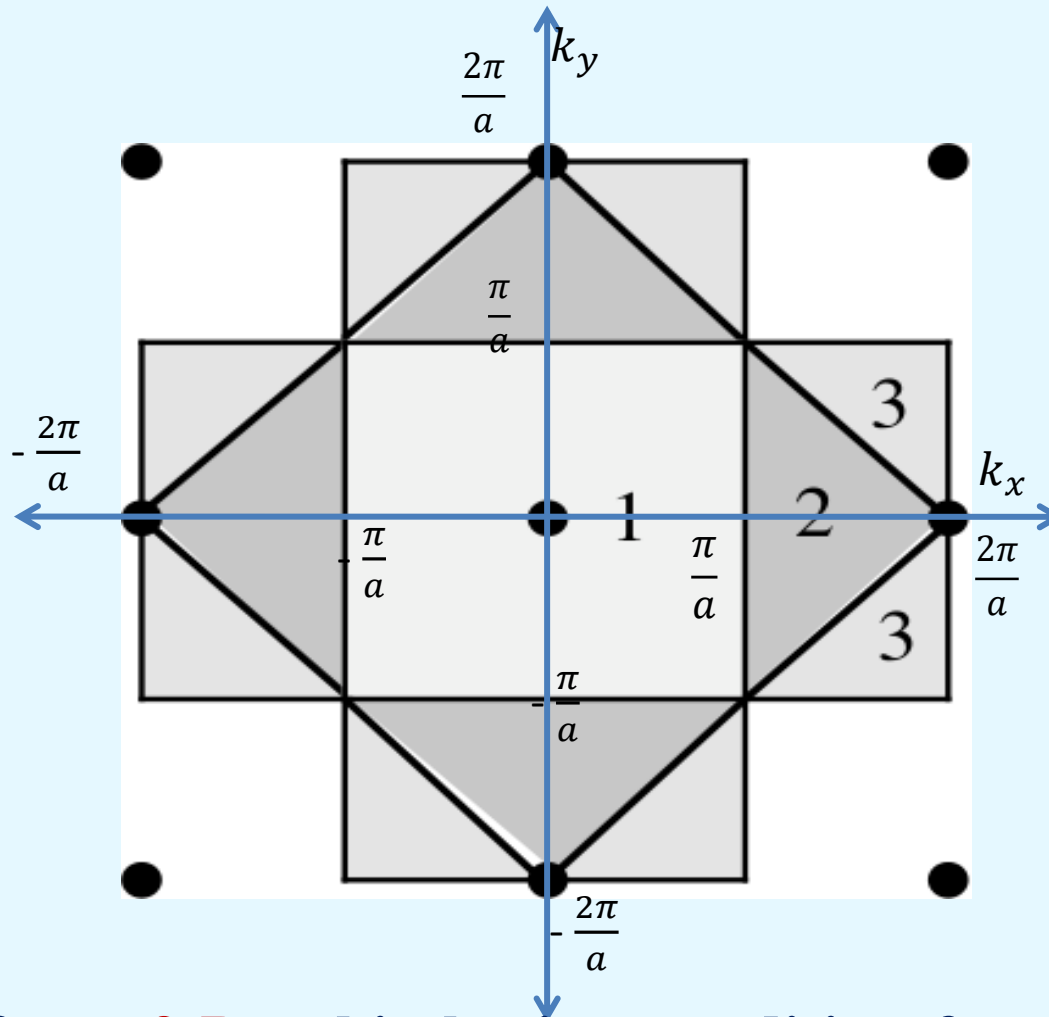
$$n_1 = +1, n_2 = -1 \Rightarrow k_x - k_y = +\frac{2\pi}{a}$$

$$n_1 = -1, n_2 = -1 \Rightarrow -k_x - k_y = +\frac{2\pi}{a}$$

*Region enclosed by these lines gives 2nd B.Z.*



# Brillouin Zones in 2-D



Similarly, for a **3-D** cubic lattice, condition for generation of energy discontinuities will be:

$$n_1 k_x + n_2 k_y + n_3 k_z = \frac{\pi}{a} (n_1^2 + n_2^2 + n_3^2)$$



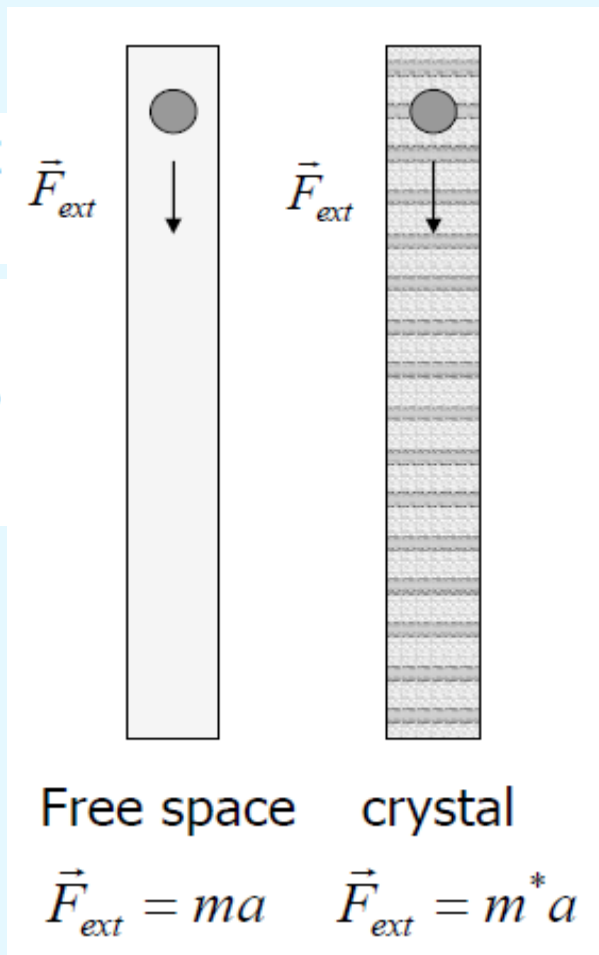
# Electron effective mass

The movement of an electron in a lattice is different from that of an electron in free space

$m^*$ : **effective mass**

Which takes into account of the particle mass and the effects of internal forces

**Definition:** The mass of the electron as experienced by external force when it moves through the crystal is called the **Effective Mass**



Group Velocity defined as the velocity of the wavefunction of the electrons (analogous to speed of sinusoidal wave ):

$$v_g = \frac{dx}{dt} = \frac{d\omega}{dk}$$

**But**

$$\omega = E / \hbar \Rightarrow$$

$$v_g = \frac{1}{\hbar} \frac{dE}{dk}$$

Acceleration:

$$v_g = \frac{1}{\hbar} \frac{dE}{dk}$$

$$a = \frac{dv_g}{dt} = \frac{d}{dt} \left[ \frac{1}{\hbar} \frac{dE}{dk} \right] = \frac{1}{\hbar} \frac{d}{dk} \left[ \frac{dE}{dt} \right] = \frac{1}{\hbar} \frac{d}{dk} \left[ \frac{dE}{dk} \frac{dk}{dt} \right]$$

$$a = \frac{1}{\hbar} \frac{d^2E}{dk^2} \frac{dk}{dt} = \frac{1}{\hbar^2} \frac{d^2E}{dk^2} \hbar \frac{dk}{dt} = \frac{1}{\hbar^2} \frac{d^2E}{dk^2} F_{ext}$$

$$F_{ext} = \hbar \frac{dk}{dt}$$

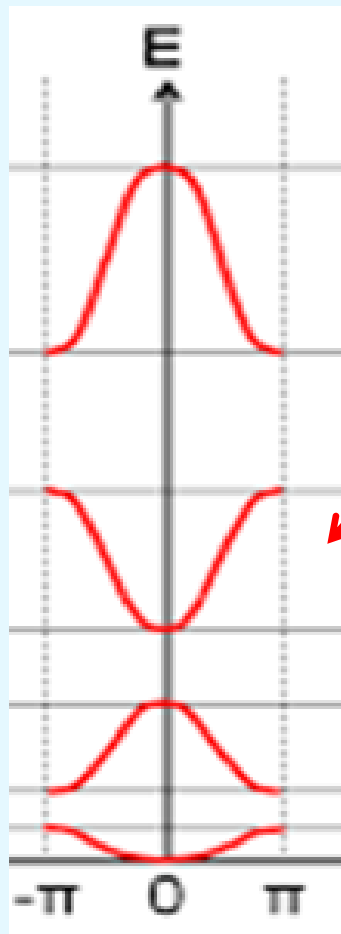
Using  $F_{ext} = m^* a$

$$m^* = \left[ \frac{1}{\hbar^2} \frac{d^2E}{dk^2} \right]^{-1} = \hbar^2 \left[ \frac{d^2E}{dk^2} \right]^{-1}$$

$$v_g = \frac{1}{\hbar} \frac{dE}{dk}$$

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

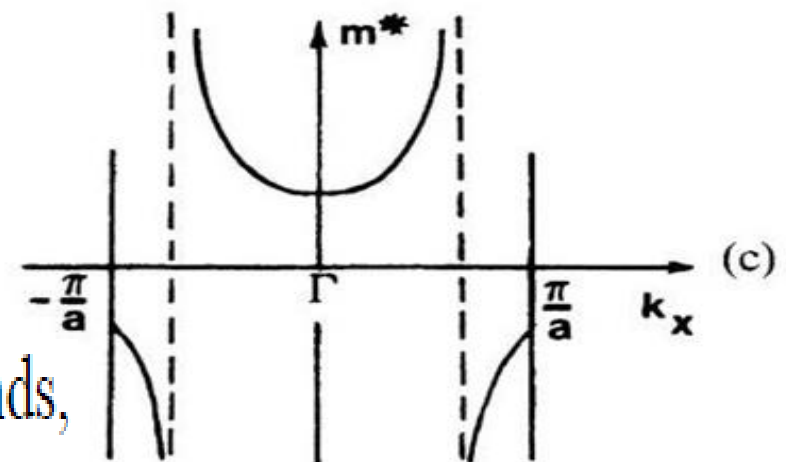
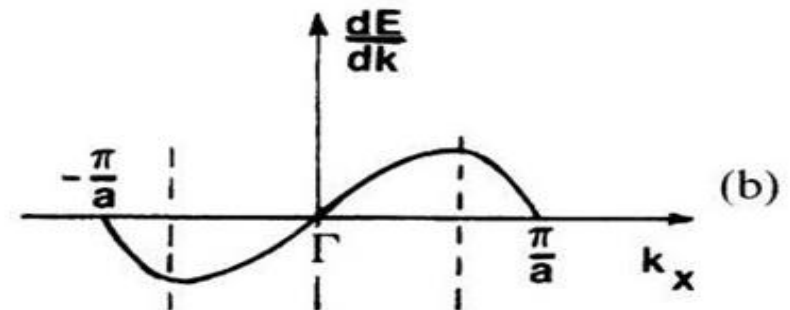
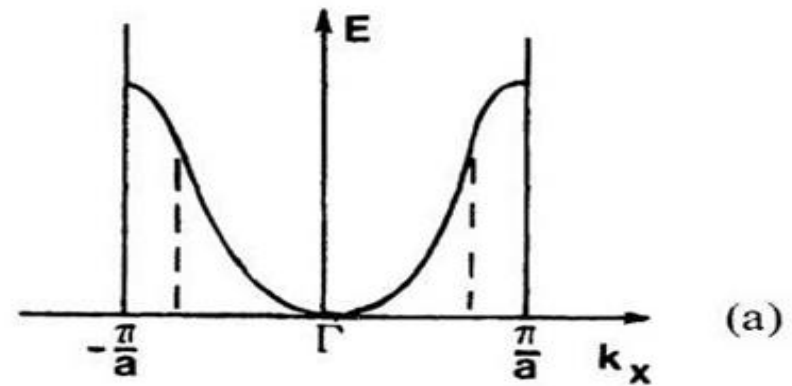
- The **first derivative** of E with k is related to the **velocity** of free particle
- The **second derivative** of E versus k is inversely proportional to the **mass** of free particle



*E-k diagram*

*Group velocity*

*Effective mass*



$m^*$  is positive near the bottoms of all bands,  
 $m^*$  is negative near the tops of all bands.

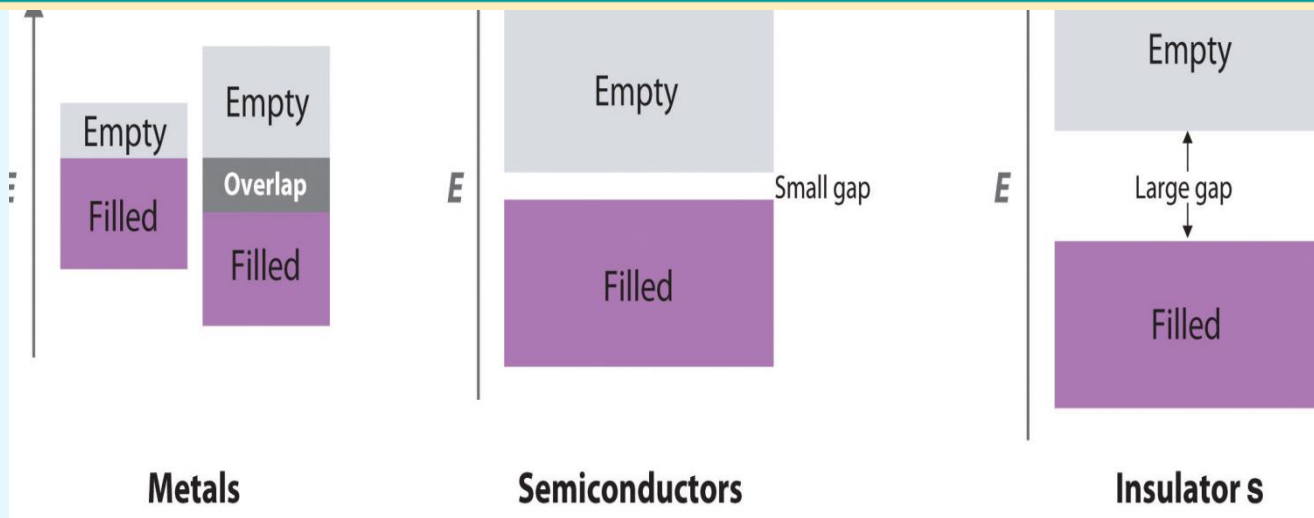
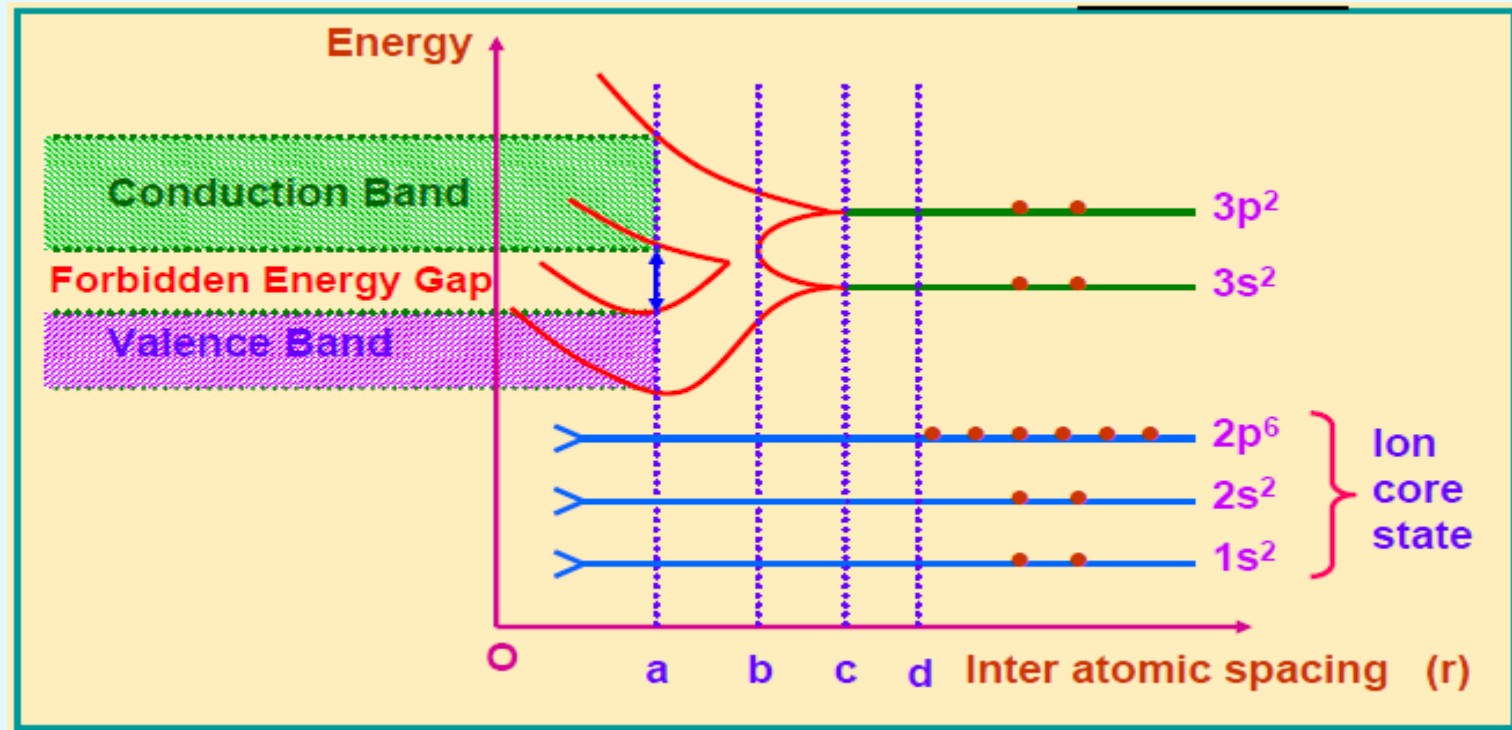
## What is the Effective Mass?

An electron in crystal may behave as if it had a mass different from the free electron mass  $m_0$ . There are crystals in which the effective mass of the carriers is much larger or much smaller than  $m_0$ . The effective mass may be anisotropic, and it may even be negative. The important point is that the electron in a periodic potential is accelerated relative to the lattice in an applied electric or magnetic field as if its mass is equal to an effective mass.

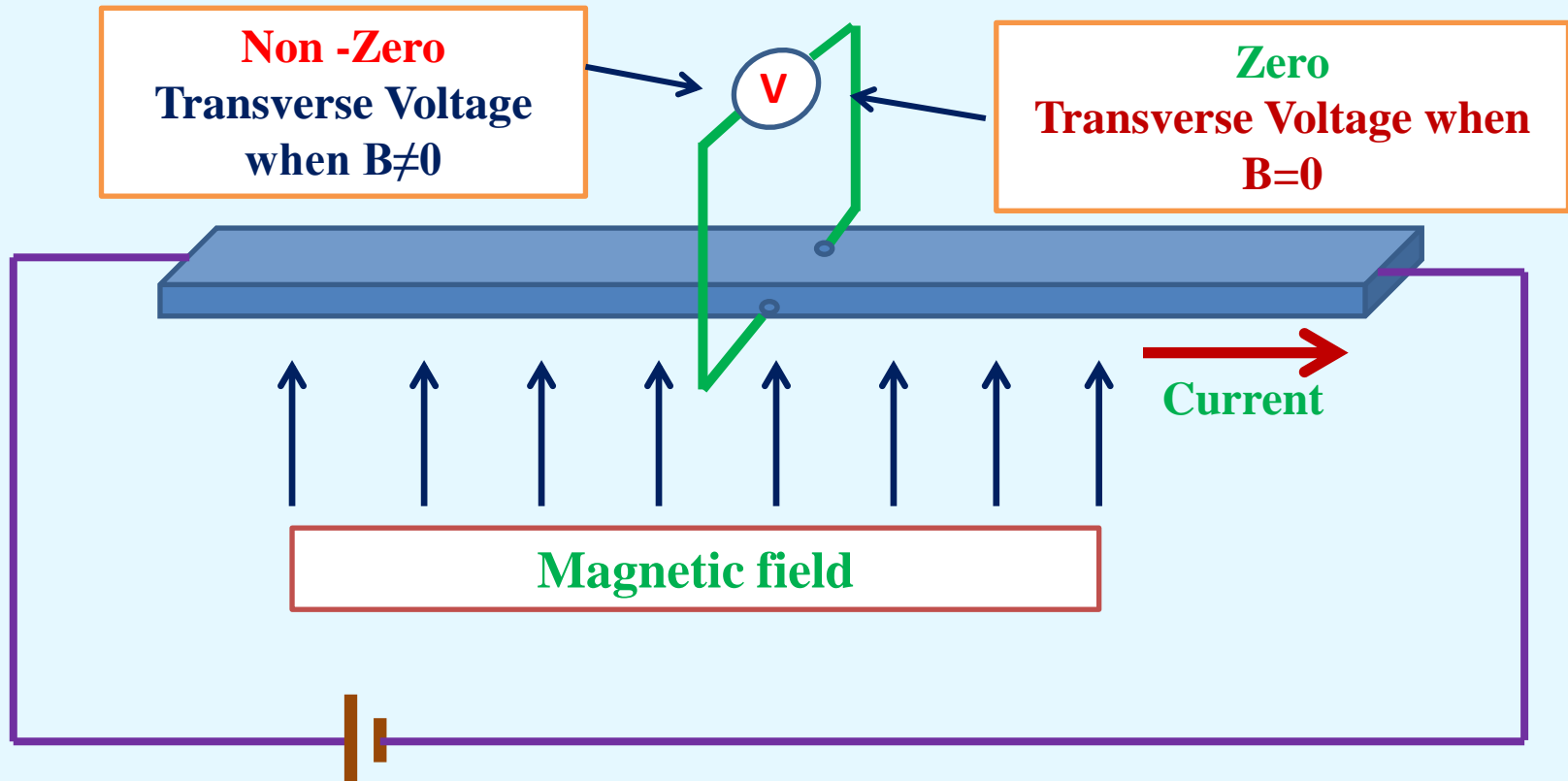
### SIGNIFICANCE of Negative Effective Mass

The **Negative Effective Mass** tells you that the electron responds to the field *opposite* to how a free electron would. Indirectly it tells you about the **formation of Holes**

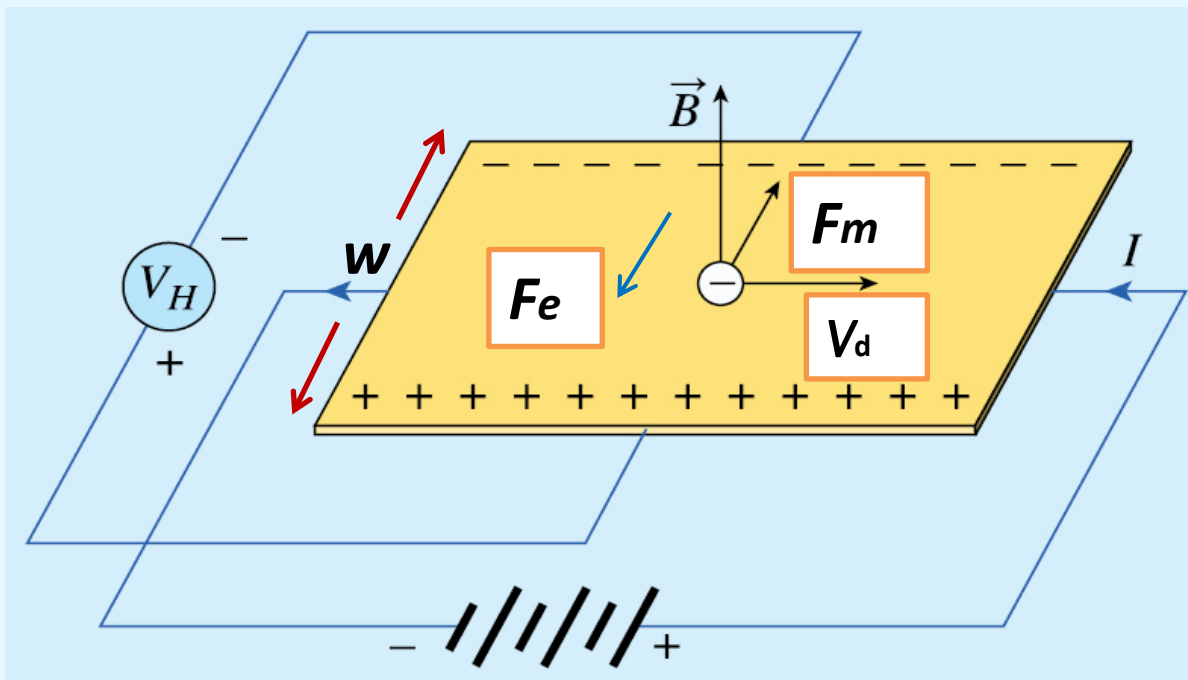
# Formation of Energy Bands in Solids:



# HALL EFFECT



Phenomena of production of **transverse voltage** called **Hall voltage** in a conductor carrying current when placed in magnetic field perpendicular to current flow



Edwin Herbert Hall

In equilibrium  $\vec{F}_e = -\vec{F}_m$

$$qE = qv_d B$$

$$E = v_d B$$

$$\frac{V_H}{w} = v_d B$$

$$V_H = w v_d B$$

$$= w \frac{I}{neA} B$$

$$V_H = \frac{I}{R_H}$$

$$R_H = \frac{neA}{wB}$$

Hall  
Resistance

# Applications of Hall Effect

- To find drift speeds of current carriers
- To find carrier concentration
- To find nature of carriers in a material
- Measurement of magnetic field
- Hall effect sensors