

# Band theory of Solids

- **Failures of quantum free electron theory:**

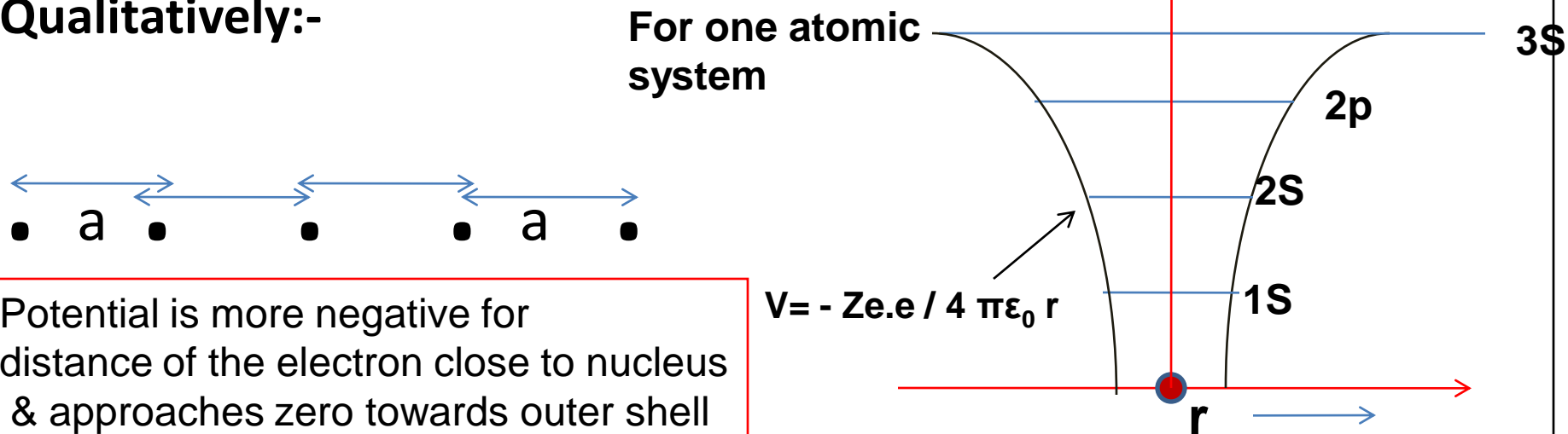
1. It could not explain the negative temperature co-efficient of resistivity for certain solids
2. It could not classify a solid on the basis of their conductivity property
3. It failed to explain the sign of Hall co-efficient.

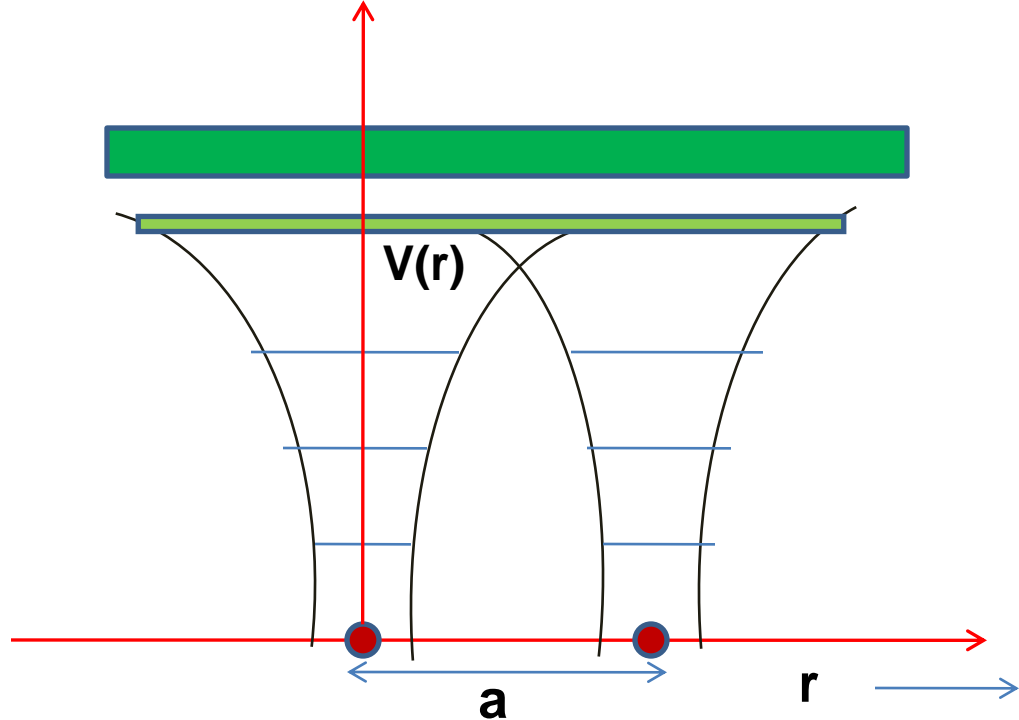
## Band theory

- Although the assumption that free electrons in a metal move in a field of zero potential seems drastic, it could be able to explain many properties of metals quite successfully
- But in non-metals, this assumption can not be applied, as no. of free electrons are less.
- To have a generalized approach we can consider that electrons inside a solid material experience a potential due to the positive ions, which are arranged in a regular and periodic manner

- $V = -Ze.e / 4 \pi \epsilon_0 r$
- They may also experience an interaction with other electrons inside the solid which is a constant when averaged over all electrons.
- In the band theory the potential experienced by the electrons due to the periodically arranged ions, was considered.
- The periodic potential experienced by the electrons is given as
- $V(x) = V(x + na)$ , 'a' being the periodicity of the lattice or the lattice parameter.

**Qualitatively:-**





For two atomic system

- The allowed energy levels for an atom are discrete (2 electrons with opposite spin can occupy a state)
- When atoms are brought into close contact, these energy levels split
- If there are a large number of atoms, the discrete energy levels form a “continuous” band.
- Hence, at equilibrium interatomic spacing, energy bands are formed in a solid.
- Due to the discrete nature of energy, there are forbidden gaps in between the allowed bands.

Many atomic system—a solid

$V(x)$

3p

3s

2p

2s

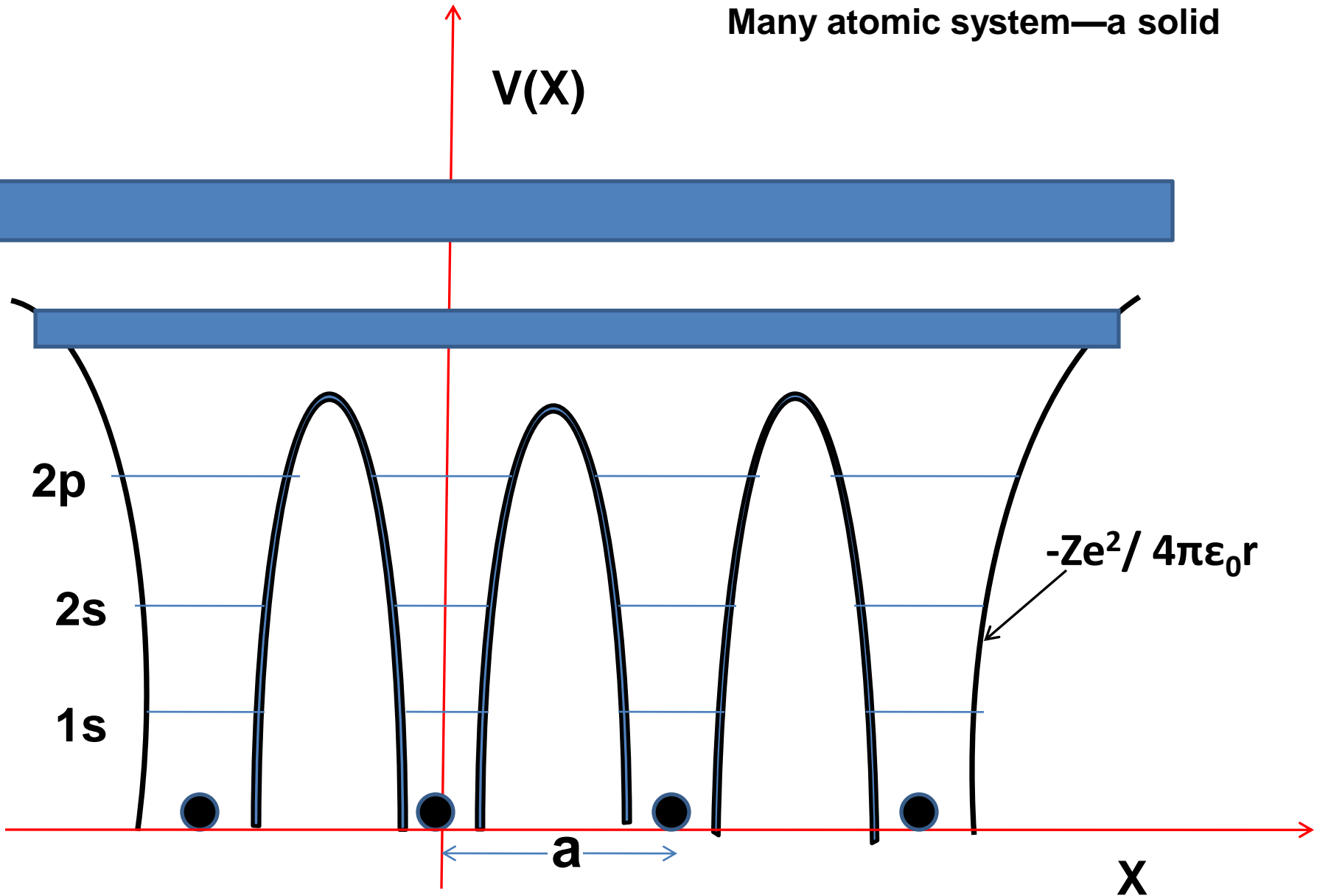
1s

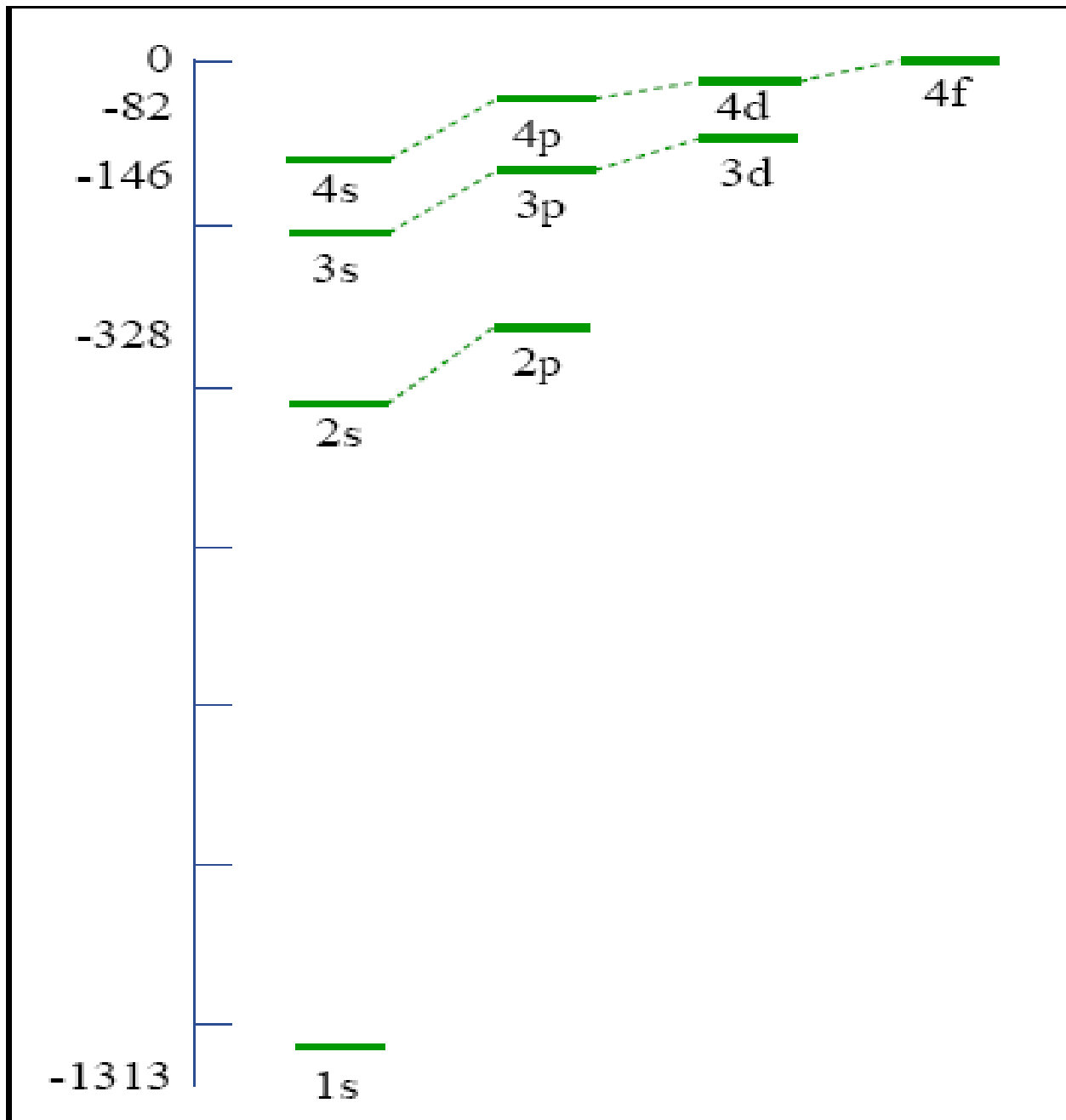
$-Ze^2 / 4\pi\epsilon_0 r$

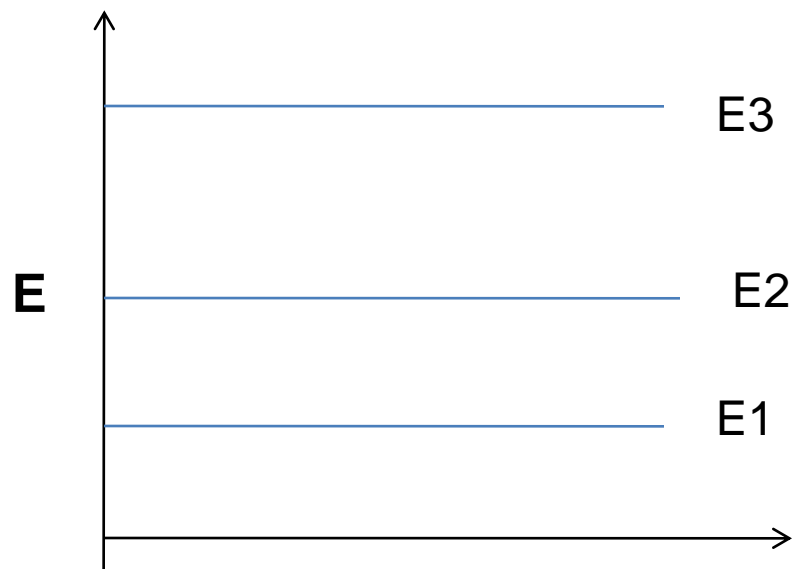
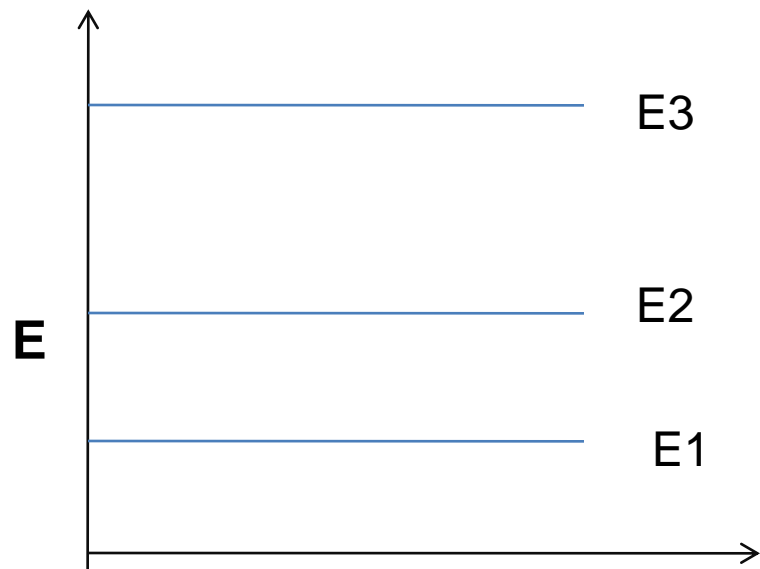
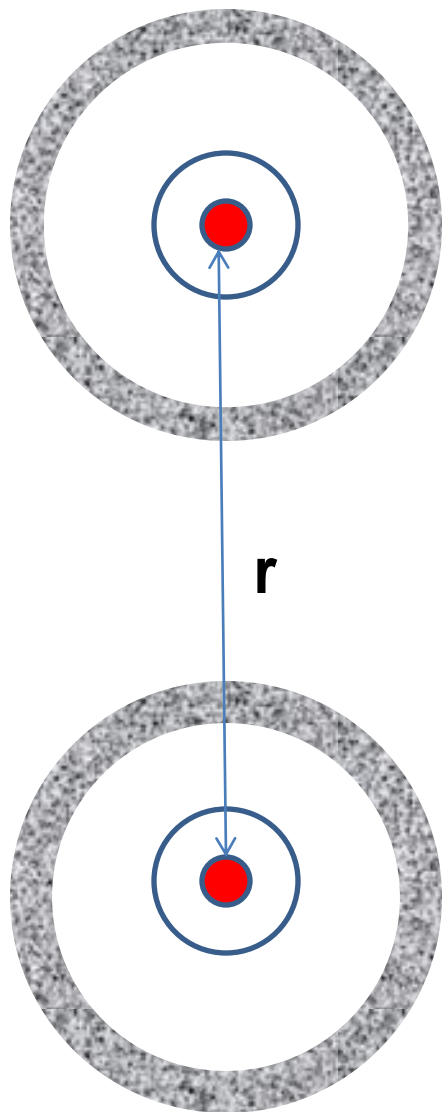
$a$

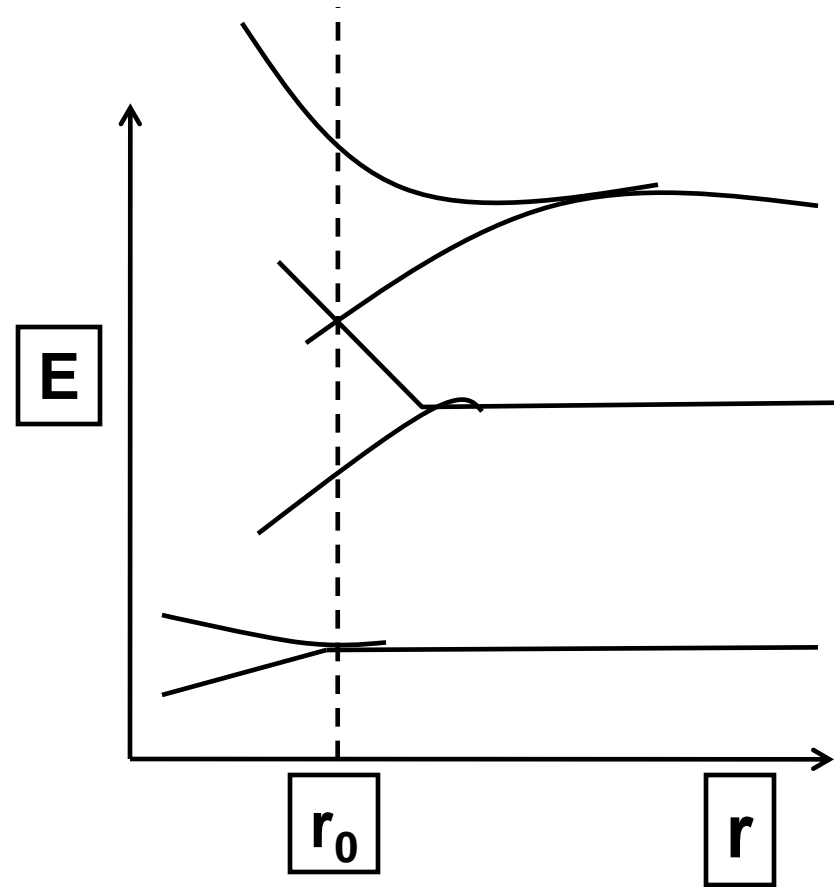
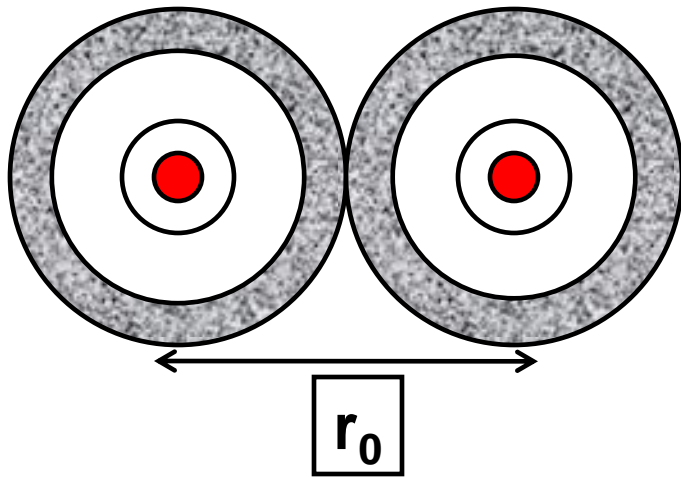
$x$

Periodic Potential:  $V(x) = V(x + n a)$

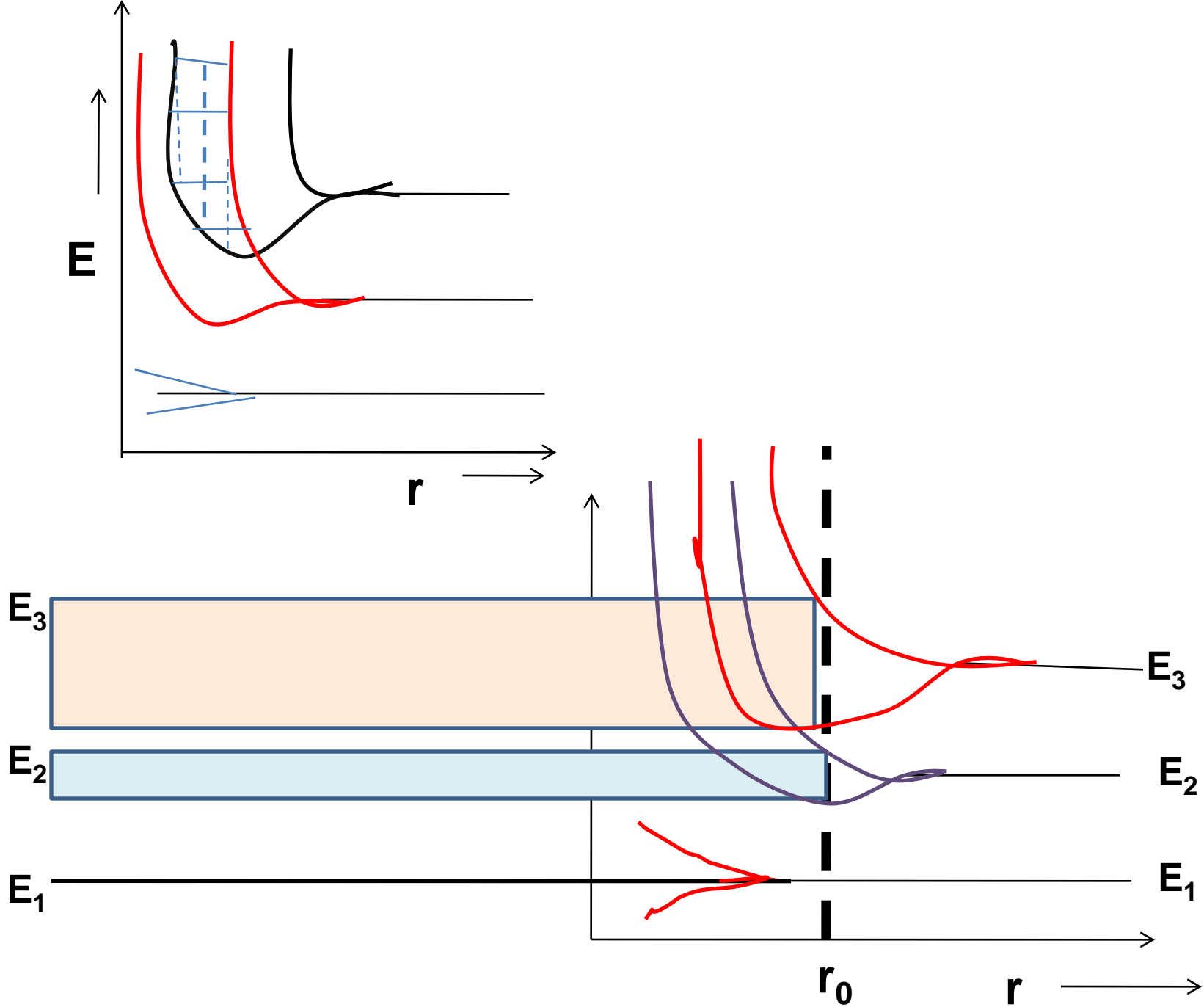






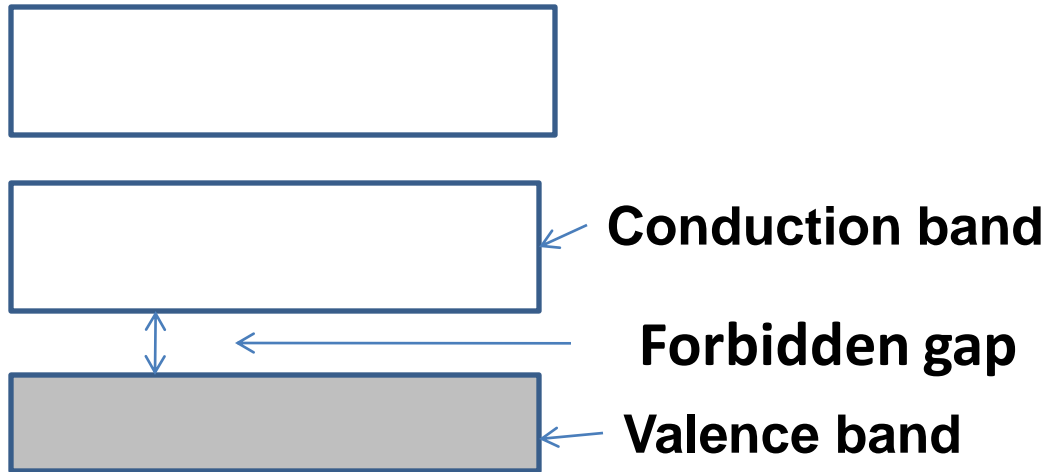


- This also leads to lowering of total energy.
- but the energy levels of inner electrons remain sharp
- **The width of the bands depend on inter atomic spacing**





- Higher bands are wider and forbidden gap decreases towards higher state
- When no. of free electrons are more, splitting is more, so, overlapping of bands occur
- Depending on the no. of electrons in a solid, some bands are completely filled, some partially filled and some are empty
- Highest filled band is called valence band and lowest empty band is called conduction band.
- Most of the properties can be understood by considering the VB, CB and the FG between them.
- These are... the occupation state of VB, width of FG, density of state in the VB and the impurities present which introduces allowed states in the FG



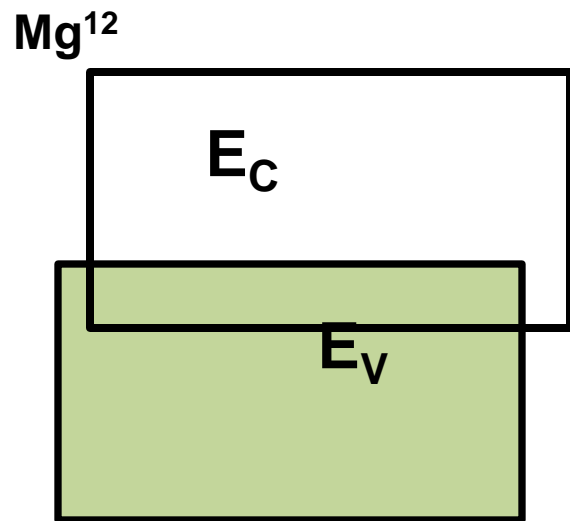
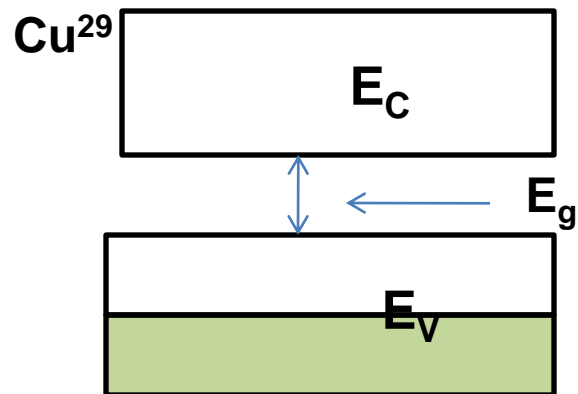
Band structure in a solid

- Valence band may be partially filled, half filled or completely filled
- Forbidden gap may be narrow, wide or totally absent

# Classification in a solid

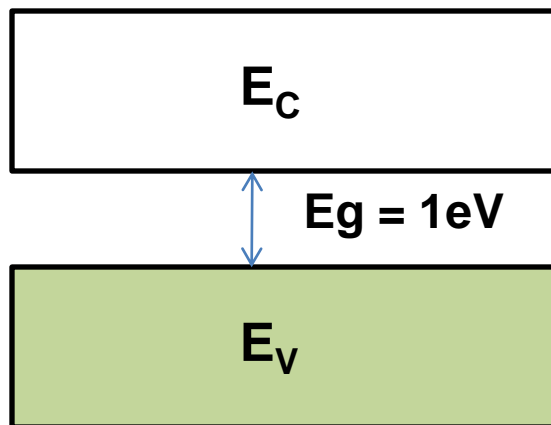
## Conductors

$$\rho = 10^{-4} - 10^{-6} \Omega\text{m}$$



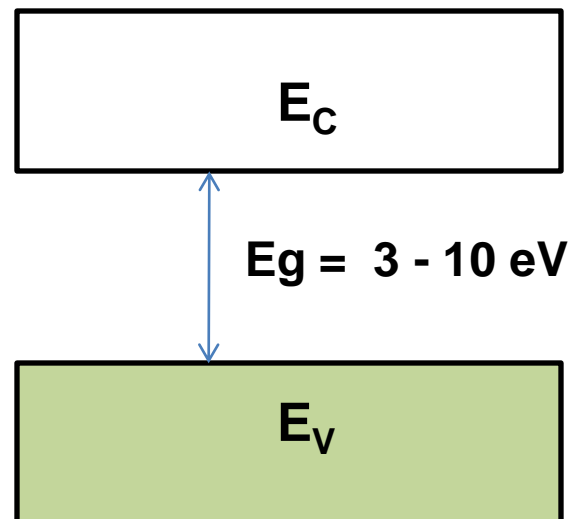
## semiconductors

$$\rho = 10^2 - 10^9 \Omega\text{m}$$



## Insulators

$$\rho = 10^{11} - 10^{22} \Omega\text{m}$$



**Conductors:** These solids have either half filled valence band like Cu, so that, no. of free electrons available is exactly equal to the no. of allowed states available in the same band, a very small amount of externally supplied energy can enable the electrons to move raise the conductivity

Or, some have overlapping of valence band and conduction band, such that there is no distinguished barriers for the electrons to overcome. On the other hand, plenty of allowed states are available for the electrons, due to the merging of two bands.

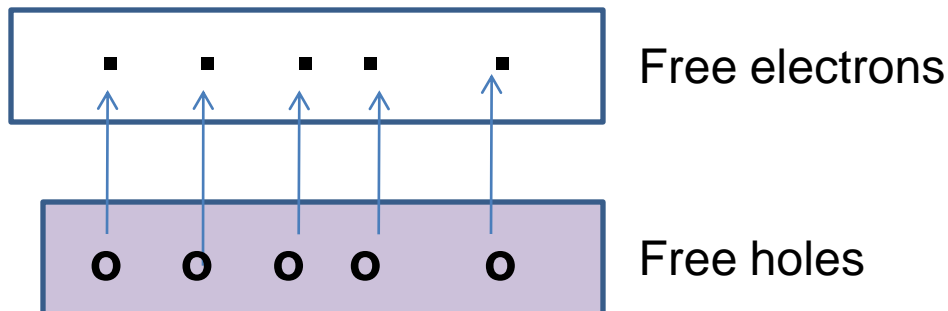
Ex:- Mg

### **Insulators:**

- Valence band completely filled, conduction band empty and forbidden gap very wide (3—7 eV),
- Normally electrons can not acquire this large energy to overcome the forbidden gap and remain immobile.

# Semiconductors:

- Filled valence band
- Empty conduction band
- Narrow forbidden gap (1 eV)
- Electrons in the valence band can easily acquire this energy, ( at  $T > 0$  or ext. electric field ) free themselves from the valence band and move in the conduction band, behaving as free carriers.
- When the electrons leave the valence band, a vacant space— "hole" is created in the valence band which are equivalent to positive charge carriers and contribute to the conductivity.



$$\text{conductivity} := \sigma = ne\mu_e + pe\mu_h$$

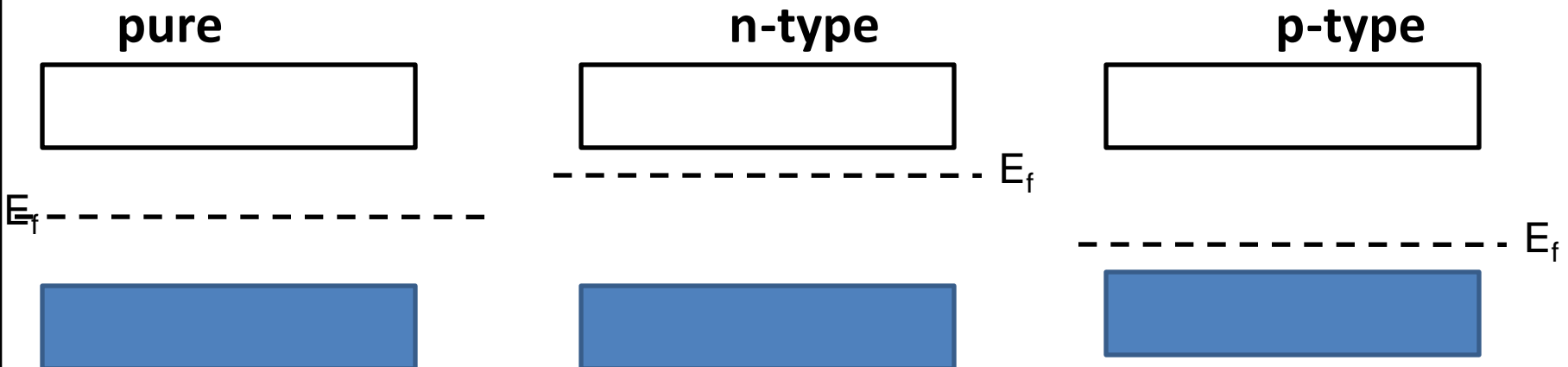
# Intrinsic and extrinsic semiconductor

- conductivity of pure semiconductors is poor
- doping improves the conductivity

pentavalent impurity added to pure SC results in n-type SC, where, majority carriers are electrons and minority are holes, conductivity is  $\sigma = ne\mu_e$

whereas trivalent impurity addition results in the p-type SC, majority carrier holes and minority are electrons  
conductivity  $\sigma = pe\mu_h$

## Fermi level



- If donor atoms are doped at the rate of one part in  $10^6$ :

i.e., to  $10^6$  intrinsic atoms one impurity atoms/dopant are added

If 'N' is the intrinsic atom concentration

**Then the concentration of donor atoms  $N_d$  is:-**

$$N_d = N / 10^6$$

# Carrier Concentration:

- In intrinsic semiconductor:**

No. of electrons in the conduction band

$$n_e = 2 \left[ \frac{2\pi m_e^* k_\beta T}{h^2} \right]^{\frac{3}{2}} e^{\frac{(E_F - E_C)}{k_\beta T}}$$

No. of holes in the valence band

$$n_h = 2 \left[ \frac{2\pi m_h^* k_\beta T}{h^2} \right]^{\frac{3}{2}} e^{\frac{(E_V - E_F)}{k_\beta T}}$$

As  $n_e = n_h = n_i$  and  $E_C - E_V = E_g$

So,

$$n_i = 2 \left[ \frac{2\pi k_\beta T}{h^2} \right]^{\frac{3}{2}} (m_e^* m_h^*)^{\frac{3}{4}} e^{-\frac{E_g}{2k_\beta T}}$$



# Carrier Concentration:

- In extrinsic semiconductor:

i) **N-type**; majority carriers 
$$n_e = \left[ \frac{2\pi m_e^* k_\beta T}{h^2} N_d \right]^{\frac{1}{2}} e^{-\frac{E_d}{k_\beta T}}$$

Where,  $N_d$  is the donor conc. ,  $E_d$  is the ionisation energy of the donors

ii) **P-type**; majority carriers 
$$n_h = \left[ \frac{2\pi m_h^* k_\beta T}{h^2} N_a \right]^{\frac{1}{2}} e^{-\frac{E_a}{k_\beta T}}$$

With  $N_a$  ,the acceptor conc. and  $E_a$ , the ionisation energy of the acceptors

# Kronig-Penny model :

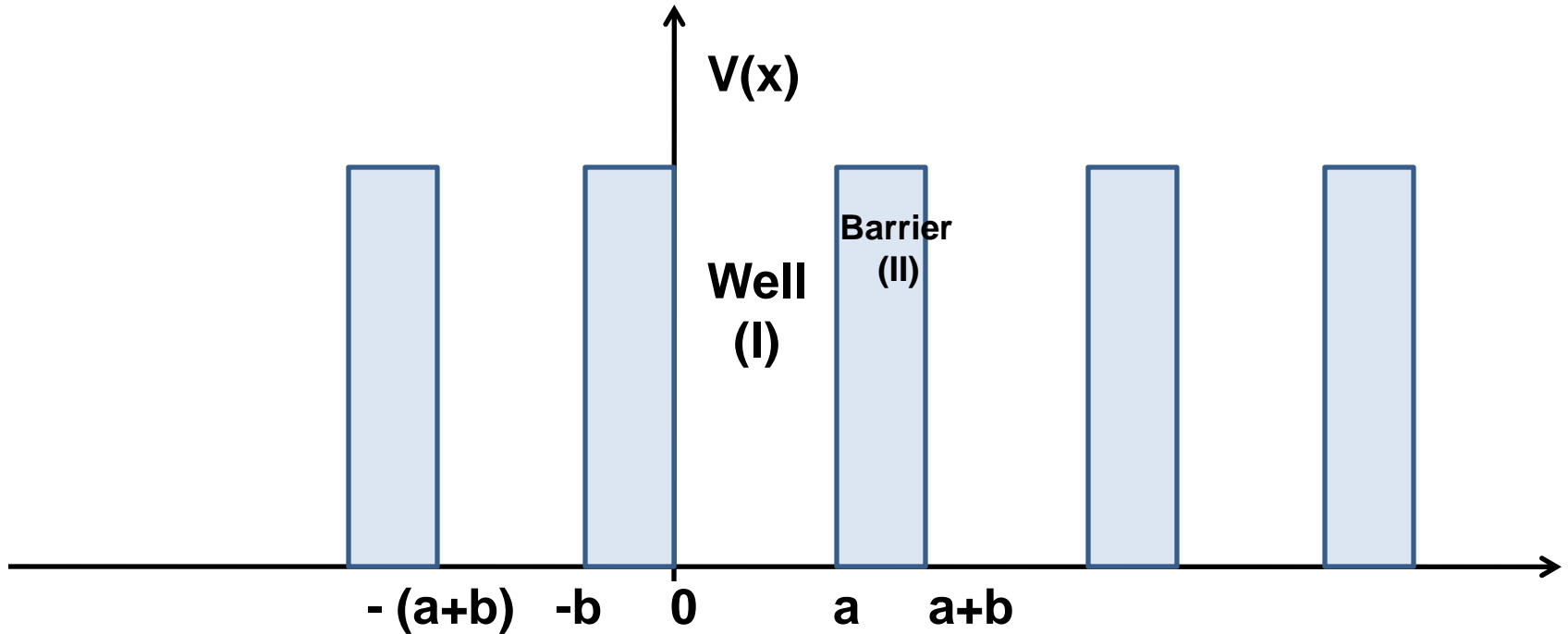
- Electrons moving inside the solid material experience a periodic potential
- $V(x) = V(x + na)$
- The Schrödinger's equation for the electrons is

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

- Solution of the equation is obtained by using Bloch's theorem

$$\psi_k(x) = u_k(x) e^{ikx}$$

- Where,  $u_k(x) = u_k(x + na)$
- Is called the Bloch's function having the same periodicity "a"
- Solution for Schrödinger's equation for Kronig Penny model is possible for energies that satisfy the following conditions

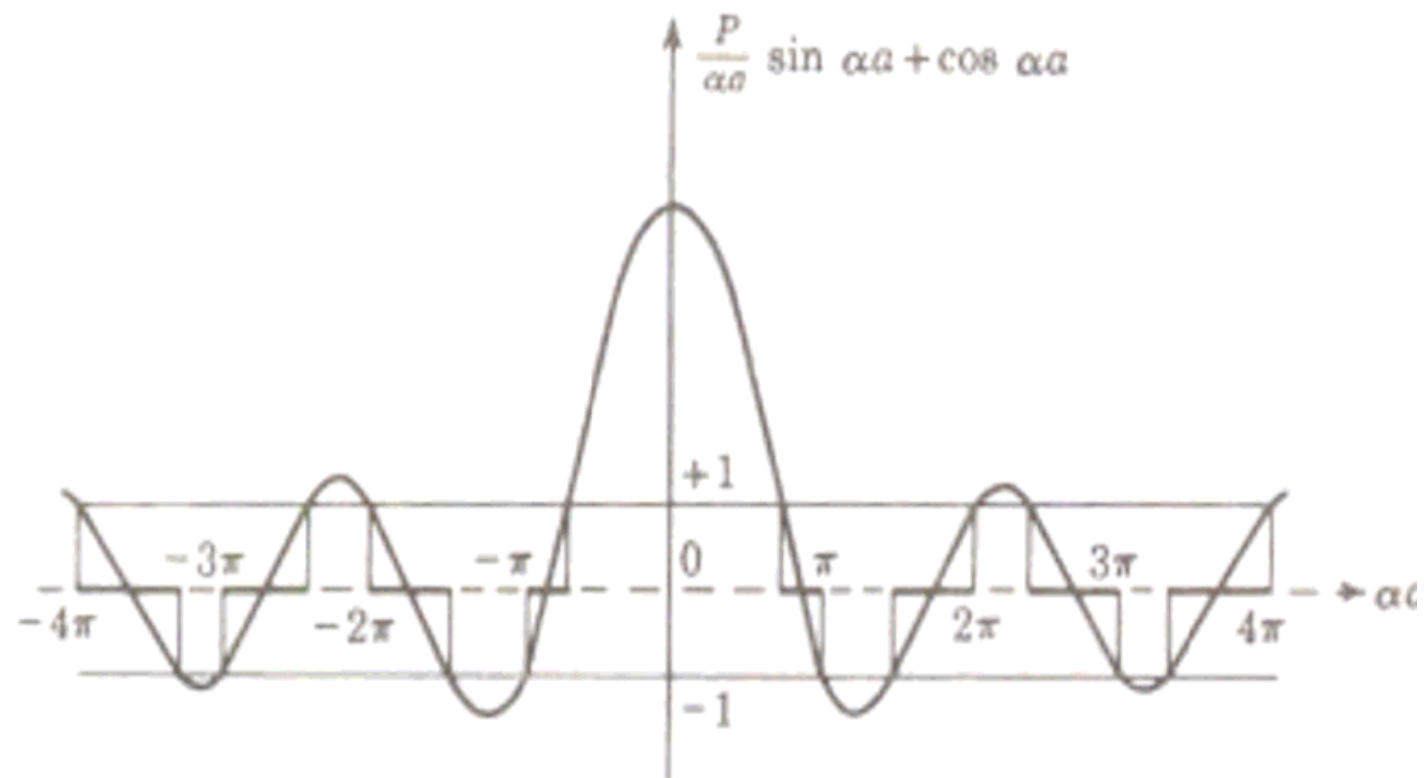


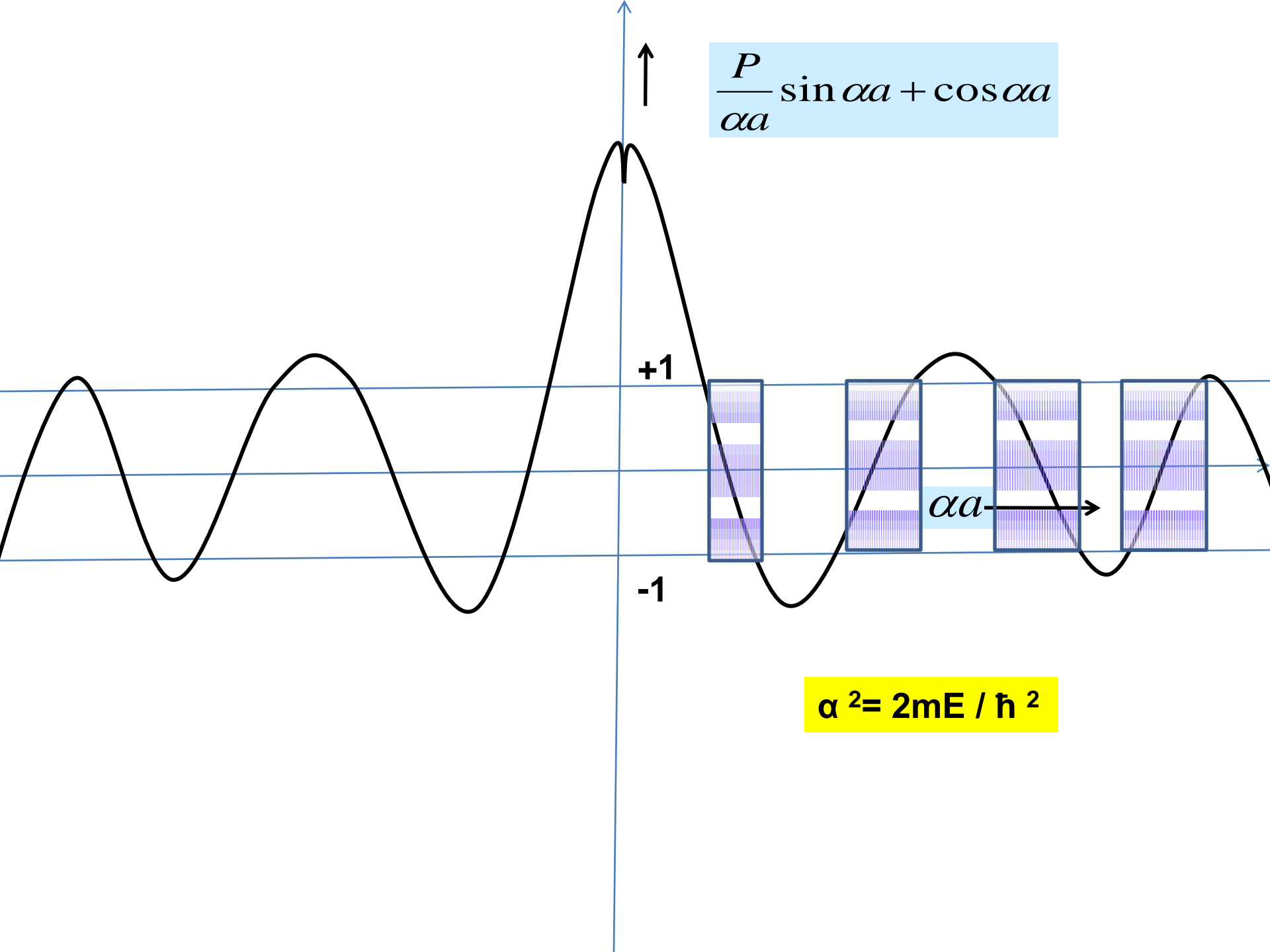
$$\frac{P}{\alpha a} \sin \alpha a + \cos \alpha a = \cos ka$$

Where,  $P = \beta^2 ab / 2$  ,  $\beta^2 = 2m(V_0 - E) / \hbar^2$  ,  $\alpha^2 = 2mE / \hbar^2$

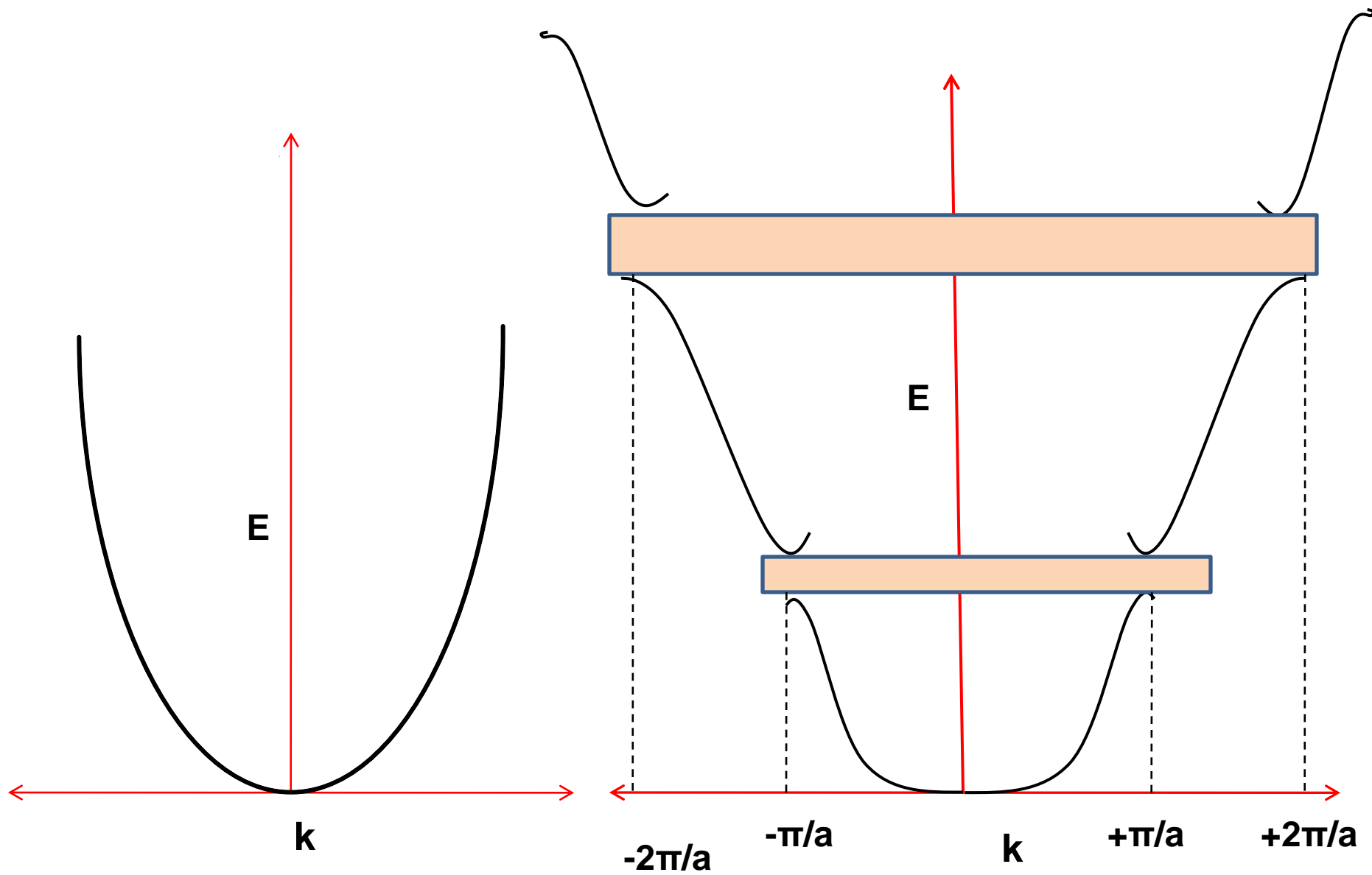
Or,  $P = V_0 mab / 2 = \text{barrier strength}$

- Plot of the LHS with ' $\alpha a$ ' gives an oscillating curve having both positive & negative values
- Amplitude of the curve decreases as ' $\alpha a$ ' increases
- RHS, which is a cosine function, can have values only between -1 to +1
- So, values of ' $\alpha$ ' =  $2mE / \hbar^2$  , or ' $E$ ' for which the portion of the curve lies between these values are allowed and other values are forbidden
- Hence, in a solid there are allowed energy bands separated by forbidden gaps
- As we move towards the higher state allowed band width increases and forbidden band width decreases
- Forbidden gaps appear at values of  $k = \pm n\pi / a$  , which defines the Brillouin zones
- Ex,  $k = +\pi / a$  to  $k = -\pi / a$  is 1<sup>st</sup> Brillouin zone and from  $+2\pi / a$  to  $-2\pi / a$  minus 1<sup>st</sup> zone is 2<sup>nd</sup> Brillouin zone



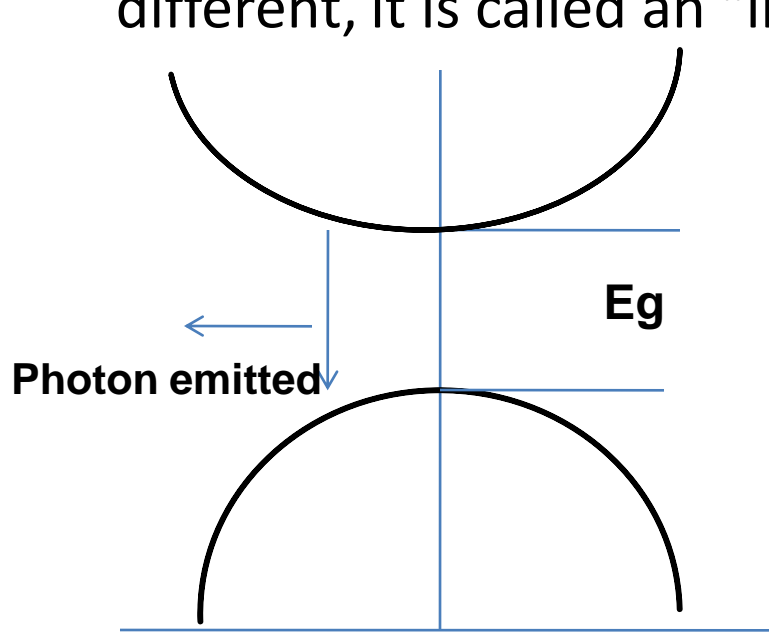


# band gap

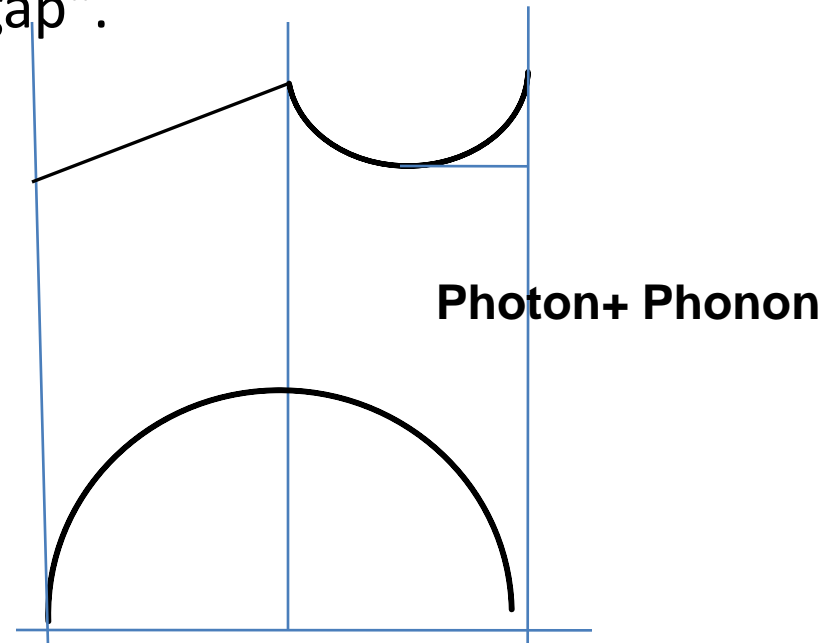


- **Direct and indirect band gap semiconductors:**

The minimal-energy state in the [conduction band](#), and the maximal-energy state in the [valence band](#), are each characterized by a certain [k-vector](#) in the [Brillouin zone](#). If the k-vectors are the same, it is called a "direct gap". If they are different, it is called an "indirect gap".

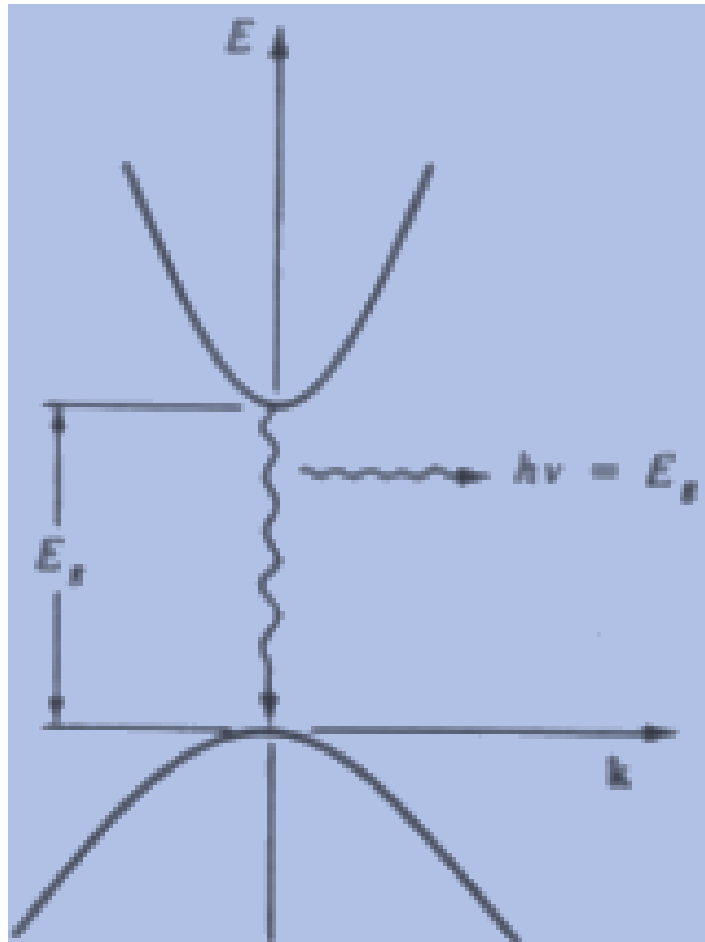


**Direct band gap**  
**Ex: GaAs**



**Indirect band gap**  
**Ex: Si, Ge**





(a) Direct



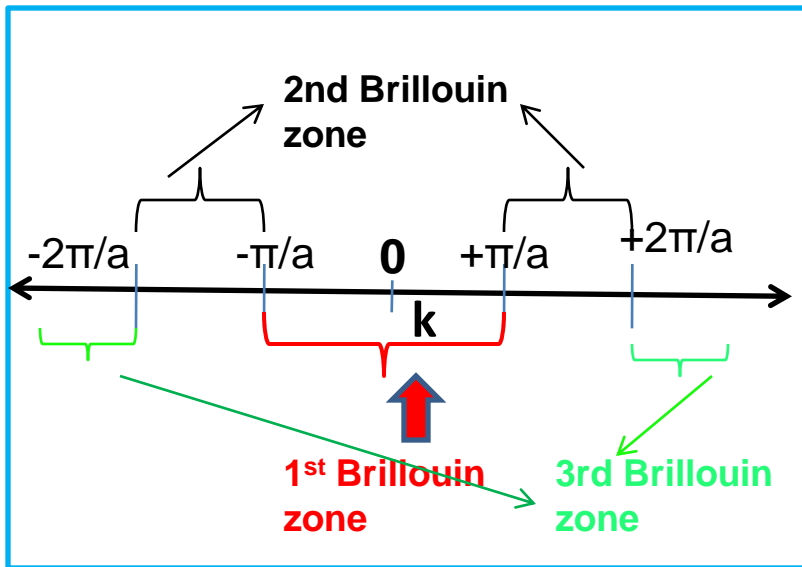
(b) Indirect

# Simple and compound semiconductors:

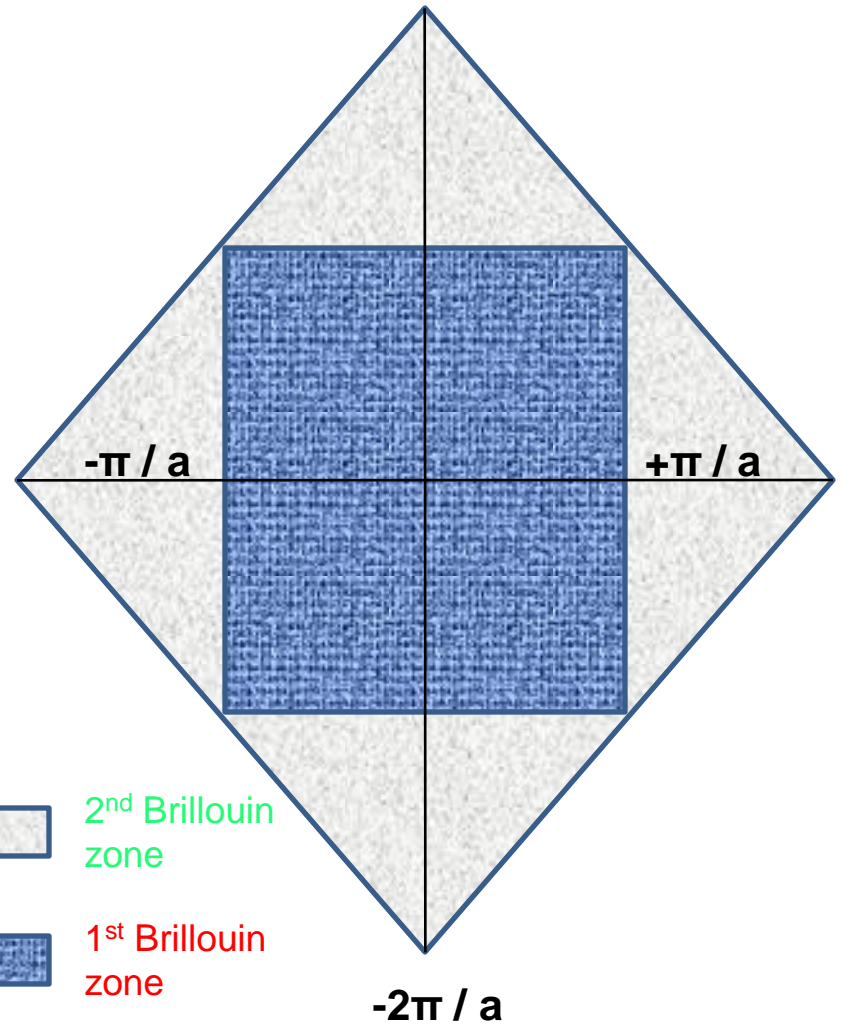
- Si and Ge belonging to gr.-IV(  $s^2 p^2$ ) are simple semiconductors and are extensively used in electronic devices : FET, diodes , bipolar transistors , LSI, VLSI, gates, solar cells etc.
- Compound semiconductors are formed by combination of gr.-II and IV, gr.-III and V , gr.-IV and VI elements to engineer the band gap for various applications. Ex; ZnO , SiC , GaAs , CdS , ZnTe, ZnSe, InAs etc.
- If they are amorphous, they are called glassy semiconductors and are used for specific applications. ex.- As- Se alloy, Se-Te alloy, As-Se-Th alloy etc. These are known as chalcogenides.

# Brillouin Zones

1D



$+2\pi / a$



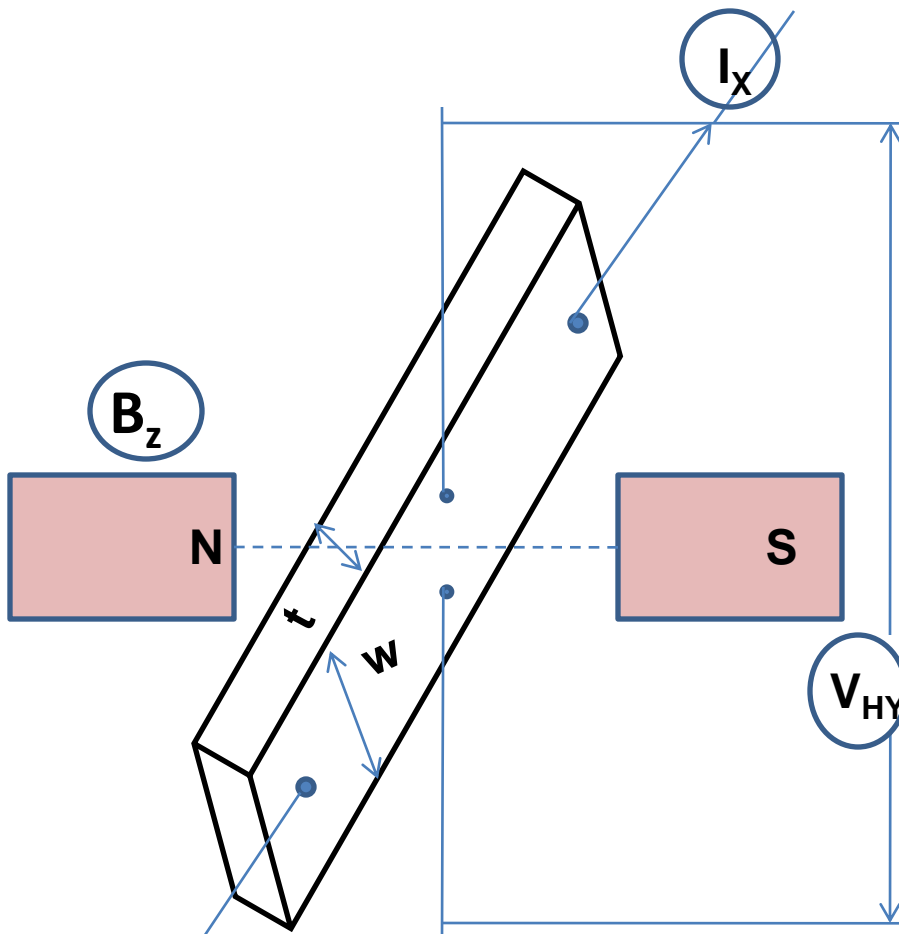
2<sup>nd</sup> Brillouin zone

1<sup>st</sup> Brillouin zone

$-2\pi / a$

2D

# Hall Effect:



Since, in a semiconductor, two types of Charge carriers are present,  $R_H$  can be positive (p-type) or negative (n-type)

$$R_H = 1 / nq = V_y w / I_x B$$

When a current carrying conductor/ semi-Conductor is placed in an ext. magnetic Field a potential difference is established in a direction perpendicular to both Current and magnetic field, known as Hall voltage

- ❖ current  $I_x$  in the material along x-axis
- ❖ magnetic field  $B_z$  along z-axis
- ❖ current density  $J_x = nq \langle v_x \rangle$
- ❖ Lorentz force on electrons due to magnetic field,

$$F = F_y = q ( v \times B ) \text{ or } F_y = q \langle v_x \rangle B_z$$

- ❖ Due to charge separation, a potential difference (electric field ) is set up

$$\text{Or, } qE_H = q \langle v_x \rangle B_z$$

$$\text{Or, } E_H = \langle v_x \rangle B_z = J_x B_z / nq$$

$$\text{As, } V_H = E_H w$$

$$\text{Hence, } (V_H)_y = I_x B_z w / nq wt$$

$$\text{Or, Hall voltage, } (V_H)_y = R_H I_x B_z / t$$

Where  $R_H = 1 / nq = E_y / J_x B_z$ , is known as Hall co-efficient

