

## UNIT-3

### QUANTUM MECHANICS

#### INTRODUCTION

##### WAVE AND PARTICLE:-

To understand the concept of dual nature one should have the knowledge of characteristics of particle and wave. It is difficult to understand the concept of a wave, since it is a physical quantity and physically it can't be seen. **"a wave can be simply defined as spreading out the disturbance in a medium, in all directions uniformly.** It can't be confined to a part (or) region i.e, it is not possible to say that the wave is present here or there.

It is easy to understand the concept of a particle, since it is a physical quantity and physically it can be seen. **"A particle is a difinet mass and occupies a particular point".**

The characteristics of wave are **wavelength,frequency,wave velocity,amplitude,phase and intensity** etc. and the particle characteristics are **mass,velocity,momentum,energy** etc.

##### DE-BROGLIE'S HYPONTHESIS:-

In 1924 de-Broglie extended dual nature to material particles like electrons, protons & neutrons etc."**According to his hypothesis when particles are accelerated then those will be spread like a wave with a certain wavelength"**

He gave simple mathematical form support his hypothesis as follows.

According to Plank's and Einstein's theory,

the energy of a photon whose frequency can be expressed as

$$E=h\nu \dots\dots\dots (1)$$

Where h=plank's constant

According to Einstein mass energy relation,

$$E=mc^2\dots\dots\dots (2)$$

Where m= mass of the photon.

C= velocity of light.

From(1) and (2) we get

$$h\nu = mc^2$$

$$h \frac{c}{\lambda} = mc^2$$

$$\lambda = \frac{h}{mc}$$

$$\lambda = \frac{h}{p} \dots\dots\dots (3)$$

In the same way, According to de-Broglie's hypothesis if an electron mass 'm' is moving with a velocity 'v' in the presence of potential 'V' then the wavelength associated with that electron can be expressed as

$$\lambda = \frac{h}{mv} = \frac{h}{p} \dots \dots \dots (4)$$

This is called de-Broglie's equation and energy of electron in terms of potential.

The energy of the electron in terms of potential is  $E=eV$

Kinetic energy of the electron  $E=\frac{1}{2} mv^2$

Above two equations given energy of electron, Hence

$$eV = \frac{1}{2} mv^2$$

Multiplying by 'm' on both sides

$$meV = \frac{1}{2} m^2 v^2 = \frac{p^2}{2m}$$

$$p = \sqrt{2meV}$$

Substituting the 'p' value in the equation (4) then

$$\lambda = \frac{h}{\sqrt{2meV}}$$

The above equation shows wavelength associated with an electron in presence of potential difference 'V'.

### **PROPERTIES OF MATTER WAVES**

1. Smaller the mass of the particle, greater is the wavelength associated with it.
2. Smaller the velocity of the particle greater is the wavelength associated with it.
3. When the velocity of the particle  $v=0$ , then the wave length  $\lambda=\infty$  so the wave becomes indeterminate and if  $v=\infty$  then  $\lambda=0$ , shows that the matter waves are generated by the motion of particles.
4. The matter waves are produced where the particles are charged or uncharged. Due to this reason these are not electromagnetic waves because electromagnetic waves are produced only the motion of charged particles.
5. The velocity of matter depends on the velocity of material particle, i.e., it is not constant while the velocity of electromagnetic wave is constant which is equal to velocity of light.
6. The velocity of matter waves is greater than the velocity of light.

## WAVE FUNCTION ' $\psi$ ' AND ITS PHYSICAL SIGNIFICANCE

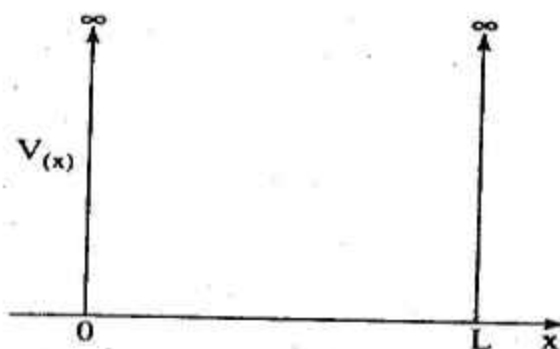
The Wave function ' $\psi$ ' of a quantum mechanical physical system is a mathematical function which gives all relevant information about the state of system at position ' $r$ ' and instant ' $t$ '.

In quantum mechanics the result of an observation of a physical system can be known only if the wave function ' $\psi$ ' of the system is known.

### Then ' $\psi$ ' have following properties

1. ' $\psi$ ' must be finite everywhere:- If ' $\psi$ ' is infinite at a particular point, then it would mean an infinity large probability of finding the particle at that point. This is not possible. Hence ' $\psi$ ' must have a finite or Zero value at any point.
2. ' $\psi$ ' must be single valued:- Let us consider ' $\psi$ ' must more than one value at any point. i.e more than one value of probability of finding the particle at that point. So ' $\psi$ ' must be single valued.
3. ' $\psi$ ' must be continuous.
4. ' $\psi$ ' must be normalized. i.e  $\int_{-\infty}^{+\infty} |\psi|^2 dv = 1$ .
5. ' $\psi$ ' must vanish at all boundaries.
6.  $\int_{-\infty}^{+\infty} |\psi|^2 dv = 0, \infty, -ve$  (or) complexes are not possible.

### PARTICLE IN A BOX/POTENTIAL WELL:



Consider a free particle in an infinitely deep one-dimensional potential box.

Let us consider wave equation for a particle moving along x-axis inside the box

$$\frac{d^2\psi(x)}{dx^2} + \frac{8\pi^2m}{h^2}(E - V)\psi(x) = 0 \text{----- (1)}$$

As the particle is moving inside the box  $V(x) = 0$

Thus the equation (1) becomes

$$\frac{d^2\psi(x)}{dx^2} + \frac{8\pi^2m}{h^2} E\psi(x) = 0 \text{----- (2)}$$

$$\text{Let } K^2 = \frac{8\pi^2m}{h^2} E$$

$$\Rightarrow E = \frac{K^2 h^2}{8\pi^2 m} \text{----- (3)}$$

i.e. The equation (2) becomes

$$\frac{d^2\psi(x)}{dx^2} + K^2\psi(x) = 0 \text{---- (4)}$$

The general solution for the above equation is given by

$$\psi(x) = A \sin Kx + B \cos Kx \text{---- (5)}$$

Since the particle cannot penetrate through the box (barrier)

$$(i) \quad \psi(x) = 0 \text{ at } x = 0 \text{ and}$$

$$(ii) \quad \psi(x) = 0 \text{ at } x = L$$

From the above condition (i) i.e.  $\psi(x) = 0$  at  $x = 0$

$$\psi(x) = A \sin Kx + B \cos Kx \text{ Becomes}$$

$$0 = A.0 + B.1$$

$$\Rightarrow B = 0$$

Then the equation (5) becomes

$$\psi(x) = A \sin Kx \text{----- (6)}$$

Using the second condition i.e.  $\psi(x) = 0$  at  $x = L$  the equation (6) can be written as

$$0 = A \sin KL$$

As  $A$  cannot be zero

$$\sin KL = 0$$

$$K = \frac{n\pi}{L} \text{ Where } n = 1, 2, 3, \dots$$

$\Rightarrow$  The equation (3) can be written as

$$\Rightarrow E = \frac{K^2 h^2}{8\pi^2 m} = \frac{n^2 \pi^2 h^2}{8\pi^2 mL^2} = \frac{n^2 h^2}{8mL^2}$$

$$\Rightarrow \boxed{E_n = \frac{n^2 h^2}{8mL^2}} \text{----- (7)}$$

$$E_1 = \frac{h^2}{8mL^2} \text{ For } n=1$$

$$E_2 = \frac{4h^2}{8mL^2} \text{ For } n=2$$

$$E_3 = \frac{9h^2}{8mL^2} \text{ For } n=3$$

Thus for each value of  $n$  the possible energy can be given by equation (7). From this we can conclude that the total energy is quantized and the  $n$  is known as the principal quantum number.

The value of the constant  $A$  can be obtained from the equation (6).i.e.  $\psi(x) = A \sin Kx$

As the particle is inside the box(barrier) the probability that the particle is found inside the box is unity

$$\text{i.e. } \int_0^L |\psi(x)|^2 dx = 1$$

$$\Rightarrow \int_0^L A^2 \sin^2 Kx dx = 1$$

$$\Rightarrow A^2 \int_0^L \frac{1 - \cos 2Kx}{2} dx = 1$$

$$\Rightarrow \frac{A^2}{2} \left[ \int_0^L dx - \int_0^L \cos 2Kx dx \right] = 1$$

$$\Rightarrow \frac{A^2}{2} \left[ x - \frac{1}{2K} \sin 2Kx \right]_0^L = 1$$

$$\Rightarrow \frac{A^2}{2} \left[ x - \frac{L}{2n\pi} \sin \frac{2n\pi x}{L} \right]_0^L = 1 \text{ since } K = \frac{n\pi}{L}$$

$$\Rightarrow \frac{A^2}{2} L = 1$$

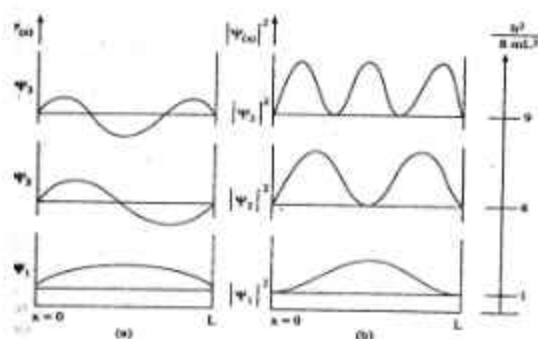
$$\Rightarrow A = \sqrt{\frac{2}{L}}$$

Therefore the normalized wave function can be written as

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L}$$

The wave function  $\psi_n(x)$  and the corresponding energies  $E_n$  which are often called as Eigen functions and Eigen values respectively describe the quantum states of the particle.

The electron wave function  $\psi_n(x)$  and the corresponding probability density functions  $|\psi_n(x)|^2$  for the ground and first two excited states of an electron in a potential well are shown in the fig. below.



### Important Questions

1. a. Derive time independent Schrödinger wave equation for a free particle?  
b. Explain physical significance of wave function?
2. a. Show that energies of a particle in a potential box are quantized?

An electron is confined to a one dimensional potential box of length 2A.U. Calculate energies corresponding to the second and fourth quantum states in eV. ?

3. a. Derive an expression for time dependent Schrödinger wave equation?
4. What are the properties of matter waves?

## Free Electron theory of metals

Classical free electron theory is based on the following postulates:

1. A solid metal is composed of atoms and the atoms have nucleus, around which there are revolving electrons.
2. In a metal the valance electrons of atoms are free to move throughout the volume of the metal like gas molecules of a perfect gas in a container
3. The free electrons move in a random directions and collide with either positive ions fixed to the lattice or other free electrons and collisions are elastic in nature i.e. there is no loss of energy.
4. The movement of free electrons obeys the classical kinetic theory of gasses. The mean K.E. of a free electron is equal to that of gas molecule  $\left(\frac{3}{2}KT\right)$ .
5. The electron velocities in a metal obey Maxwell-Boltzman distribution of velocities.
6. The free electrons move in a uniform potential field due to ions fixed in the lattice
7. When an electric field is applied to the metal the free electrons are accelerated. The accelerated electrons move in opposite direction of the applied.
8. The electric conduction is due to the free electrons only.

### ROOT MEAN SQUARE (R.M.S.) VELOCITY:

Let  $\bar{C}$  be the r.m.s velocity of the free electron. then the

$$\text{Kinetic energy} = \frac{1}{2}m\bar{C}^2$$

But according to the classical free electron theory the mean

$$\text{Kinetic Energy} = \left(\frac{3}{2}KT\right).$$

$$\therefore \frac{1}{2}m\bar{C}^2 = \frac{3}{2}KT$$

$$\Rightarrow \bar{C} = \sqrt{\frac{3KT}{m}} \quad \text{where } \bar{C} = \text{root mean square velocity}$$

### MEAN FREE PATH ( $\lambda$ ) AND MEAN COLLISION TIME ( $\tau_c$ )

The average distance travelled by an electron between two successive collisions in the presence of applied field is known as 'Mean free path ( $\lambda$ )'.

The time taken by an electron between two successive collisions is known as "Mean Collision Time ( $\tau_c$ )" of the electron

$$\tau_c = \frac{\lambda}{\bar{C}} = \lambda \sqrt{\frac{m}{3KT}}$$

### DRIFT VELOCITY ( $v_d$ ):

It is the average velocity acquired by the free electrons of a metal in a particular direction during the application of the electric field.

### ELECTRICAL CONDUCTIVITY IN METALS:



Let us consider a conductor of length  $l$  and area of cross section  $A$

The volume of the conductor  $= Al$

If there are  $n$  number of electrons per unit volume of the metal

then the total number of electrons in the metal  $= Aln$

If  $e$  is the charge of the electron then the total charge  $q$  due to all electrons in the conductor is given by  $q = Aln.e$

Let  $t$  be the time taken by the electron to move from one end to other end then

$$\text{Current } (I) = \frac{\text{charge}}{\text{time}} = \frac{q}{t} = \frac{Aln.e}{t}$$

$$\text{But } \frac{l}{t} = v_d$$

$$\therefore I = Anev_d$$

$$\Rightarrow v_d = \frac{I}{Ane} = \frac{J}{ne}$$

$$\text{Where } J = \text{current density} = \frac{I}{A}$$

In a metal the current density  $J$  is given by the equation

$$J = nev_d \text{ -----(1)}$$

Where  $n$  = number of electrons per Unit volume,  $e$  = electron charge and  $v_d$  = drift velocity

If  $E$  is the applied electric field then the electric force acting on a free electron is given by

$$F = eE \text{ -----(2)}$$

$$\text{From Newton's II nd law } F = ma \text{ -----(3)}$$



From (2) and (3)  $ma = eE$

i.e.  $a = \frac{eE}{m}$

but  $a = \text{drift velocity/collision time} = \frac{v_d}{\tau_c}$

$$v_d = a\tau_c = \frac{eE}{m}\tau_c$$

$$\therefore J = ne \cdot \frac{eE}{m}\tau_c = \frac{ne^2E}{m}\tau_c \dots\dots\dots(4)$$

But from microscopic form of ohms law

$$J = \sigma E \dots\dots\dots(5)$$

On comparing Eq(4)&(5)

$$\therefore \text{Conductivity } \sigma = \frac{ne^2}{m}\tau_c \text{ or Resistivity } \rho = \frac{m}{ne^2\tau_c}$$

Conductivity may also be expressed in terms of mobility ( $\mu$ ) which is defined as drift velocity per unit electric field

$$\mu = \frac{v_d}{E} = \frac{e}{m}\tau_c$$

From (4)  $\boxed{\sigma = ne\mu}$

### RELAXATION TIME( $\tau_r$ )

Under the influence of an external electric field free electrons attain a directional velocity of motion. If the field is switched off the velocity starts decreasing exponentially. Such a process that tends to restore equilibrium is called relaxation process.

If  $v_o$  is the velocity at  $t = 0$  at which the field is switched off.

The velocity at any time is given by

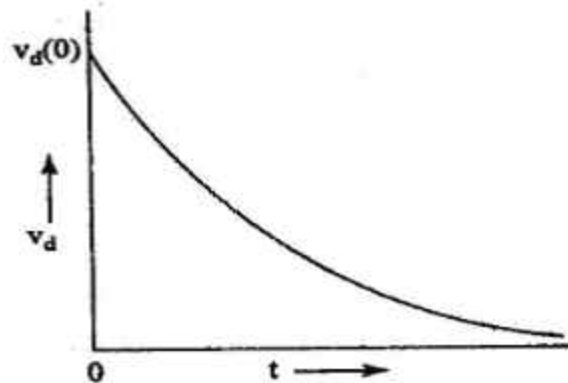
$$v = v_o e^{-\frac{t}{\tau_r}}$$

In the above expression  $\tau_r$  = relaxation time

If  $t = \tau_r$

$$v = v_o e^{-\frac{t}{\tau_r}} = v_o e^{-1} = \frac{v_o}{e}$$

∴ Relaxation time  $\tau_r$  is defined as the time required for the electron to reduce its velocity to  $\frac{1}{e}$  of its initial value. (OR) time taken for the drift velocity to decay  $\frac{1}{e}$  of its initial value.



### Failure of classical free electron theory:

1. The phenomena such as photo electric effect, Compton Effect and black body radiation could not be explained by classical free electron theory.
2. According to classical theory the value of specific heat of metals is given by  $4.5R$  ( $R$  = Universal gas constant) where as the experimental value is nearly  $3R$  (Dulong Petit law)
3. Electrical conductivity of semiconductor or insulator could not be explained by using this model.
4. According to classical free electron model  $\frac{K}{\sigma T}$  is constant. (Wiedemann-Franz law) as this not constant at low temperatures.
5. Ferromagnetism could not be explained by this theory
6. According to classical free electron theory, Resistivity

$$\rho = \frac{m}{ne^2\tau_c} = \frac{m}{ne^2} \sqrt{\frac{3KT}{m}} \frac{1}{\lambda} = \frac{\sqrt{3KTm}}{ne^2\lambda}$$

$$\rho = \sqrt{T}$$

But according to experiments  $\rho \propto T$

### QUANTUM FREE ELECTRON THEORY:

Sommerfeld applied quantum mechanics to explain conductivity phenomenon in metals. He has improved the Drude- Lorentz theory by quantizing the free electron energy and retaining the classical concept of force motion of electrons at random.

#### **ASSUMPTIONS**

1. The electrons are free to move within the metal like gaseous molecules. They are confined to the metal due to surface potential.
2. The velocities of electrons obey Fermi-Dirac distribution because electrons are spin – half particles.
3. The electrons would go into different energy levels and obey Pauli's exclusion principle.

4. The motion of the electron is associated with a wave called matter wave, according to the deBroglie hypothesis.
5. The electrons can not have all energies but will have discrete energies according to the equation  $E_n = \frac{n^2 h^2}{8ma^2}$  where  $a$  is the dimension of the metals.

**Derive an expression for electrical conductivity by using quantum free electron theory**

According to Quantum theory

$$p = mv = \hbar K \text{ ---(1)}$$

$$\text{Where } \hbar = \frac{h}{2\pi}, K = \frac{2\pi}{\lambda}$$

Differentiating equation (1) w.r.t to  $t$

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

At equilibrium the Lorentz force  $F = -eE$  acting on the electron is equal and opposite to the product of mass and acceleration of the electron  
i.e.

$$\begin{aligned} eE &= ma \\ \Rightarrow m \frac{\hbar}{m} \frac{dK}{dt} &= eE \end{aligned}$$

$$\Rightarrow dK = \frac{eE}{\hbar} dt \text{ ---(2)}$$

Integrating (2) between the limits 0 and  $t$

$$\begin{aligned} \int_0^t dK &= \int_0^t \frac{eE}{\hbar} dt \\ K(t) - K(0) &= \frac{eE}{\hbar} t \end{aligned}$$

$$\Delta K = \frac{eE}{\hbar} t_c \text{ where } t_c = \text{mean collision time.}$$

$$\text{But } J = ne\Delta v \text{ and } \Delta v = \hbar \frac{\Delta K}{m}$$

$$\Delta v = \hbar \frac{\Delta K}{m} = \frac{\hbar}{m} \frac{eE}{\hbar} t = \frac{eEt}{m}$$

$$\therefore J = \frac{ne^2 Et}{m^*}$$

From microscopic form of Ohm's law

$$J = \sigma E$$

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

This is the expression for the electrical conductivity.

## FERMI DIRAC DISTRIBUTION:

In quantum theory different electrons occupy different energy levels at 0°K. Electrons obey Pauli's exclusion principle. As the electrons receive energy they are excited to higher levels which are unoccupied at 0 K. The occupation of electrons obeys Fermi-Dirac distribution law. The particles that obey Fermi-Dirac distribution law are called Fermions.

The Fermi-Dirac distribution function at a temperature T is given by

$$f(E) = \frac{1}{e^{(E-E_f)/KT} + 1}$$

Where  $E_f$  = Fermi energy,  $f(E)$  = the probability that a state of energy (E) is filled.

(1) At T=0 K for  $E > E_f$   $E = \frac{n^2 h^2}{8ma^2}$

$$f(E) = \frac{1}{e^{\infty} + 1} = 1$$

This means that all the energy state below  $E_f$  are filled.

For  $E > E_f$

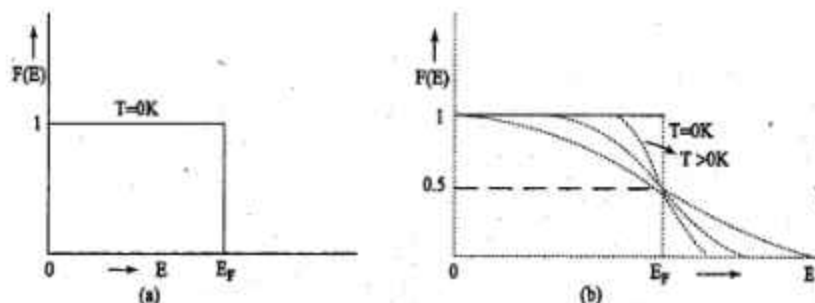
$$f(E) = \frac{1}{e^{\infty} + 1} = 0 \text{ Means that all the energy levels above } E_f \text{ are empty.}$$

From this we define Fermi level as it is the level at 0K below which all the levels are filled and above which all the levels are empty or it is the highest occupied state at 0K

(2) At T>0 and  $E = E_f$

$$f(E) = \frac{1}{1+1} = \frac{1}{2}$$

Fermi level is the state at which the probability of electron occupation is  $\frac{1}{2}$  at any temperature.



## FERMI ENERGY:

The Fermi energy is a concept in quantum mechanics referring to the energy of the highest occupied quantum state in a system of Fermions at absolute zero temperature.

For the one dimensional infinite square well the energy of the particle is given by

$$E = \frac{n^2 h^2}{8ma^2}$$

Suppose now instead of one particle in this box we have particles in the box and that particles are fermions with spin  $\frac{1}{2}$  then only two particles can have the same energy. i.e. Two particles have the same energy of

$$E_1 = \frac{h^2}{8ma^2}$$

Two particles having energy

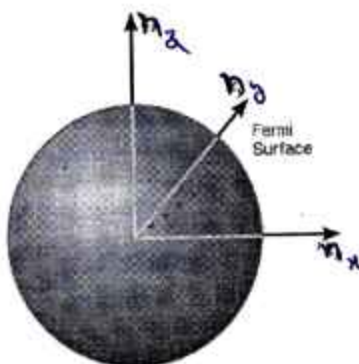
$$E_2 = \frac{4h^2}{8ma^2}$$

∴ All the energy levels up to  $n=N/2$  are occupied and all the higher levels are empty.

$$E_f = E_{N/2} = \frac{(N/2)^2 h^2}{8ma^2} = \frac{N^2 h^2}{32ma^2}$$

$$E_f = \frac{N^2 h^2}{32ma^2}$$

## DENSITY OF STATES



The number of states with energy less than  $E_f$  is equal to the number of states that lie within a sphere of radius  $|n_f|$  in a region of K-space where  $n_x$ ,  $n_y$  and  $n_z$  are positive.

$$\therefore N = 2 \times \frac{1}{8} \times \frac{4}{3} \pi n_f^3$$

$$\therefore N = 2 \times \frac{1}{8} \times \frac{4}{3} \pi n_f^3 = \frac{3N}{\pi} \Rightarrow n_f = \left( \frac{3N}{\pi} \right)^{\frac{1}{3}}$$

So the Fermi energy

$$E_f = \frac{\hbar^2 \pi^2 n_f^2}{2ma^2} = \frac{\hbar^2 \pi^2}{2ma^2} \left( \frac{3N}{\pi} \right)^{\frac{2}{3}}$$

$$E_f = \frac{\hbar^2 \pi^2}{2m a^2} \left( \frac{3N}{\pi} \right)^{\frac{2}{3}} = \frac{\hbar^2 \pi^{\frac{4}{3}} (3N)^{\frac{2}{3}}}{2m (a^3)^{\frac{2}{3}}} = \frac{\hbar^2}{2m} \left( \frac{3N\pi^2}{a^3} \right)^{\frac{2}{3}} = \frac{\hbar^2}{2m} \left( \frac{3N\pi^2}{V} \right)^{\frac{2}{3}}$$

$$\therefore N^{\frac{2}{3}} = \frac{2m}{\hbar^2} \left( \frac{V}{3\pi^2} \right)^{\frac{2}{3}} E_f$$

$$\Rightarrow N = \left( \frac{2m}{\hbar^2} \right)^{\frac{3}{2}} \left( \frac{V}{3\pi^2} \right) E_f^{\frac{3}{2}}$$

Therefore density of states:  $D(E) = \frac{dN}{dE} = \frac{3}{2} \left( \frac{2m}{\hbar^2} \right)^{\frac{3}{2}} \left( \frac{V}{3\pi^2} \right) E_f^{\frac{1}{2}}$

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

Therefore the total number of energy states per unit volume per unit energy range

$$Z(E) = \frac{D(E)}{V} = \frac{1}{2\pi^2} \left( \frac{2m}{\hbar^2} \right)^{\frac{3}{2}} E_f^{\frac{1}{2}} = \frac{1}{2\pi^2} \frac{(2m)^{\frac{3}{2}}}{h^3} 8\pi^3 E_f^{\frac{1}{2}}$$

$$Z(E) = \frac{4\pi}{h^3} (2m)^{\frac{3}{2}} E_f^{\frac{1}{2}}$$

Therefore the number of energy states in the energy interval  $E$  and  $E + dE$  are

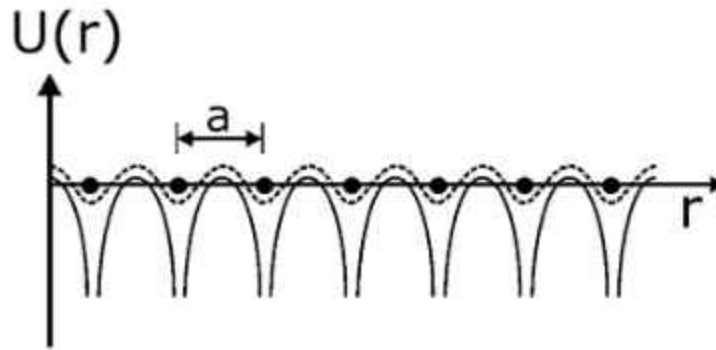
$$Z(E)dE = \frac{4\pi}{h^3} (2m)^{\frac{3}{2}} E_f^{\frac{1}{2}} dE$$

### Important questions

1. a. Explain the salient features of classical free electron theory
- b. On the basis of classical free electron theory, derive the expressions for i) drift Velocity, ii) current density iii) mobility?
- c. What are drawbacks of classical free electron theory of materials?
2. a. Explain Fermi-Dirac distribution for electrons in a metal. Discuss its variation with temperature?
- b. Explain the terms 'Mean free path' 'Relaxation time' and 'Drift velocity' of an electron in a metal?
- c. Discuss the origin of electrical resistance in metals?
3. a. Derive the expression for electrical conductivity on the basis of quantum free electron theory?
- b. Explain i) Fermi energy?
- c. Evaluate the Fermi function for an energy  $KT$  above Fermi energy?

## BAND THEORY OF SOLIDS

### BLOCH THEOREM:



Metals and alloys are crystalline in nature. When the electron move into the periodic ion core, it enters into the periodic potential i.e. potential is minimum at the positive ion sites and maximum between the two ions.

The one dimensional Schrödinger wave for this case is

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{8\pi^2 m(E - V)}{h^2} \psi = 0$$

The periodic potential  $V(x)$  may be defined as

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

Bloch has shown that the one dimensional solution of the form

$$\psi(x) = e^{ikx} u_k(x) = e^{ika} u_k(a)$$

Where  $u_k(x) = u_k(x + a)$

$$\psi(x + a) = e^{ik(x+a)} u_k(x + a)$$

$$= e^{ikx} e^{ika} u_k(x + a)$$

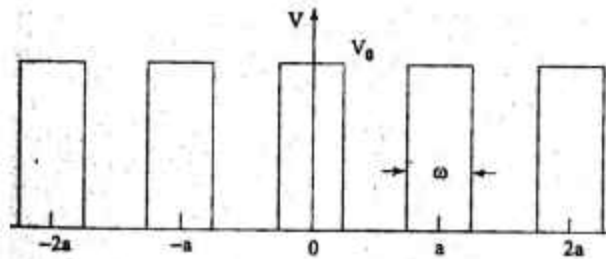
$$= e^{ika} e^{ikx} u_k(x)$$

$$\boxed{\psi(x + a) = e^{ika} \psi(x)}$$

This is referred as Bloch condition.

### KRONIG-PENNEY MODEL:

The free electrons in a metal move under a periodic potential due to regularly arranged positive ions. The nature of the energies of the electron is determined by solving Schrödinger wave equation. For simplicity, the periodic potential is taken in the form of regular one-dimensional array of square well potentials.



Within the wall the electron has potential energy

$$V = 0, 0 < x < a$$

Outside the wall the electron has the PE

$$V = V_0, -b < x < 0$$

∴ the Schrödinger wave equation for the two regions are

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{8\pi^2 m E}{h^2} = 0, 0 < x < a \text{ ----- (1)}$$

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{8\pi^2 m (E - V)}{h^2} \psi = 0, -b < x < 0 \text{ ----- (2)}$$

$$\text{Let } \alpha^2 = \frac{8\pi^2 m E}{h^2}$$

$$\text{And } \beta^2 = \frac{8\pi^2 m (V_0 - E)}{h^2}$$

Then (1) and (2) becomes

$$\frac{\partial^2 \psi}{\partial x^2} + \alpha^2 \psi = 0, \text{ ----- (3)}$$

$$\frac{\partial^2 \psi}{\partial x^2} - \beta^2 \psi = 0, \text{ ----- (4)}$$

On solving equations (3) and (4) and by applying Bloch Theorem we get

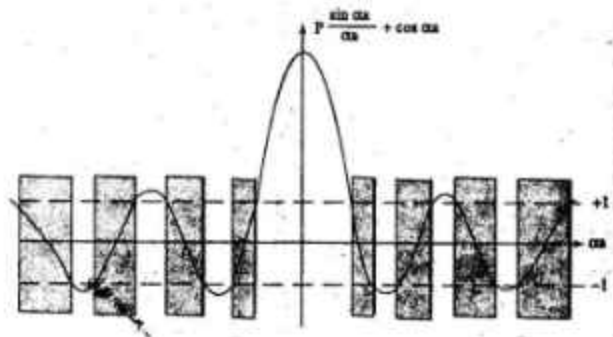
$$\boxed{P \frac{\sin \alpha a}{\alpha a} + \cos \alpha a = \cos ka} \text{ ----- (5)}$$



Where  $P = \frac{mabV_0}{\hbar^2}$

and  $\alpha^2 = \frac{8\pi^2mE}{h^2} \Rightarrow E = \frac{h^2\alpha^2}{8\pi^2m}$

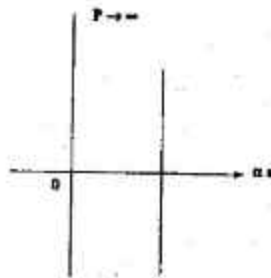
The nature of the equation is illustrated by the plot i.e. drawn between  $P \frac{\sin \alpha a}{\alpha a} + \cos \alpha a$  and  $\alpha a$  and at the same time the RHS having the value between +1 and -1



In the above graph only some of the range of  $\alpha a$  values are allowed indicating the a limiting range of energies are allowed. Allowed energy region is indicated by dark region and the forbidden region is indicated by dotted lines.

#### Special cases:

- (i) If  $P \rightarrow \infty$  the allowed band reduces to single energy level. This is the special case of electron trapped.



- (ii) If  $P \rightarrow 0$

$$\cos \alpha a = \cos ka$$

$$k = \alpha$$

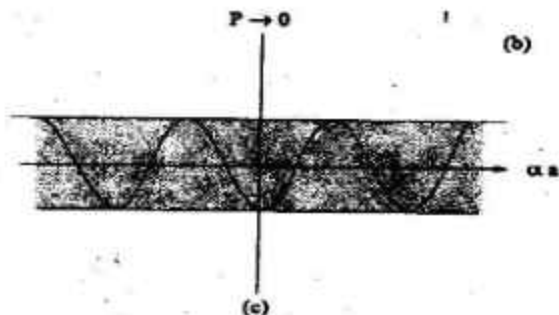
$$k^2 = \alpha^2 = \frac{8\pi^2mE}{h^2} \Rightarrow E = \frac{h^2k^2}{8\pi^2m} = \frac{h^2}{8\pi^2m} \frac{4\pi^2}{\lambda^2}$$

$$\Rightarrow E = \frac{h^2}{2m} \frac{m^2v^2}{h^2} = \frac{1}{2}mv^2$$

Therefore Total energy = KE + PE

$$\Rightarrow \text{Potential Energy } V = 0$$

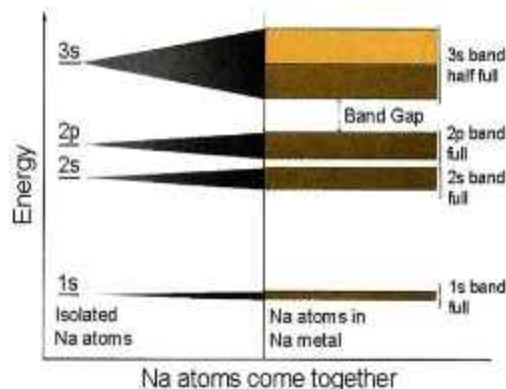
And this is the case of free electron.



Finally we conclude that

- (i) Electrons in solids are permitted to be in allowed energy bands separated by forbidden energy gaps.
- (ii) Allowed energy band width increases with  $\alpha a$
- (iii)  $P \rightarrow \infty$  is the case of electron trapped and  $P \rightarrow 0$  is the case of classical free particle

### ORIGIN OF ENERGY BANDS:



In an isolated atom the electrons are tightly bound and have discrete sharp energy levels. When two identical atoms are brought close together the outermost orbit of these atoms overlaps and interacts. Then the energy levels corresponding to those atoms are split into two. If more atoms are brought together more levels are formed and for a solid of  $N$  atoms each of energy levels of an atom splits into  $N$  levels of

Depends on the degree of overlap of electrons of adjacent atoms and is largest for outermost atomic electrons.

The electrons in the inner shells are strongly bound to their nucleus while the electrons in the outer most shells are not strongly bound to the nucleus. The electrons in the outermost shell are called valence electrons. The band formed by the energy levels containing the valence electrons is known as valence band.

### Valence Band:

The band formed by the energy levels of valence electrons is called valence band. Or the band having highest occupied band energy. It may be partial or completely filled.

### Conduction band:

This is the lowest unfilled energy band. This is empty or partially filled.

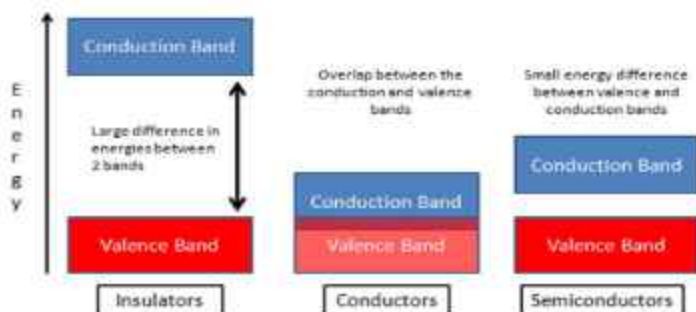
### Forbidden Energy gap:

The conduction band and valence band are separated by a region or gap known as forbidden band. In this there is no electron exist.

## CLASSIFICATION OF MATERIALS INTO CONDUCTORS, SEMICONDUCTORS AND INSULATORS:

### INSULATOR:

In case of insulators the forbidden band is wide. Due to this free electrons cannot jump from valence band to conduction band. In insulators the energy gap between Valence and conduction band is of the order of 10eV.



### CONDUCTORS:

In case of conductors there is no forbidden band the valence band and conduction band overlap each other. Here plenty of electrons are available for electronic conduction.

### SEMICONDUCTORS:

In semiconductors there is small forbidden band exist between valence band and conduction band. In semiconductors forbidden band gap is between 0.7 to 1.1 eV. For semiconductors the electrical properties lie between insulators and good conductors.

### EFFECTIVE MASS OF THE ELECTRON:

The effective mass of the electron is the mass of the electron when it is accelerated in a periodic potential and is denoted by  $m^*$ .

When an electron is placed in a periodic potential and it is accelerated with the help of electric field. Then the mass of the electron is varied. That varied mass is called effective mass  $m^*$ .

Consider the free electron as a wave packet. The group velocity  $v_g$  corresponding to particle velocity is

$$v_g = \frac{d\omega}{dK}$$

Where  $K$  is wave vector and  $\omega$  is angular velocity of the electron.

$$v_g = 2\pi \frac{dv}{dK} = \frac{2\pi}{h} \frac{dE}{dK} = \frac{1}{\hbar} \frac{dE}{dK}$$

$$\text{But acceleration } a = \frac{dv_g}{dt} = \frac{1}{\hbar} \frac{d^2E}{dK dt} = \frac{1}{\hbar} \frac{d^2E}{dK^2} \frac{dK}{dt}$$

$$\text{But } \hbar K = p \Rightarrow \frac{dp}{dt} = \hbar \frac{dK}{dt} = F$$

$$\Rightarrow \frac{dK}{dt} = \frac{F}{\hbar}$$

$$\therefore a = \frac{1}{\hbar} \frac{d^2E}{dK^2} \frac{F}{\hbar}$$

$$\Rightarrow F = \frac{\hbar^2}{\frac{d^2E}{dK^2}} a$$

But

$$m^* a = \frac{\hbar^2}{\frac{d^2E}{dK^2}} a \Rightarrow m^* = \frac{\hbar^2}{\frac{d^2E}{dK^2}}$$

**Special classes:**

(1). If  $\frac{d^2E}{dK^2}$  is positive then the effective mass is positive

(2) If  $\frac{d^2E}{dK^2}$  is negative then the effective mass is negative.

(3) If  $\frac{d^2E}{dK^2} = 0$  then the effective mass becomes  $\infty$