

# Quantum Mechanics

Wave - A wave can be simply defined as spreading out the disturbance in a medium in all directions uniformly. It can not be confined to a part or region.

i.e., It is not possible to say that the wave is present here or there.

The characteristics of wave are wavelength, frequency, wave velocity, amplitude, phase and intensity etc.

Particle - A particle is defined as it is a definite mass and occupies a particular point is known as particle.

The characteristics of particle are mass, velocity, energy, momentum etc...

## de-Broglie Hypothesis

A/c to de-Broglie hypothesis when particles are accelerated then those will be spread like a wave with a certain wavelength.

Mathematically according to plank's theory the energy of photon whose frequency can be expressed as

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

where,  $h$  = plank's constant.

A/c to Einstein mass energy relation  $E = mc^2 \rightarrow (2)$

where,  $m$  = mass of the photon.

$C$  = Velocity of light.

from eq (1) & (2),  $h\nu = mc^2$

$$h\left(\frac{c}{\lambda}\right) = mc^2$$

$$\lambda = \frac{h}{mc} \quad \text{or} \quad \lambda = \frac{h}{p} \rightarrow (3)$$

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

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



This is called de-Broglie equation and the associated wavelength is called de-Broglie wavelength.

de-Broglie wavelength in terms of KE

Wkt, the KE of an moving particle

$$KE = \frac{1}{2}mv^2 \Rightarrow E = \frac{1}{2}mv^2 \left(\frac{m}{m}\right)$$

$$E = \frac{1}{2} \frac{(mv)^2}{m} \Rightarrow E = \frac{1}{2m} p^2$$



$$p^2 = 2mE \Rightarrow p = \sqrt{2mE} \quad \downarrow KE = E$$

Substituting the above value in eq (4) we get

$$\therefore \lambda = \frac{h}{p} \Rightarrow \lambda = \frac{h}{\sqrt{2mE}}$$

de-Broglie wave length of  $e^-$

Let us consider that an  $e^-$  of mass 'm' and charge 'e' is accelerated through a potential difference of 'V'. The energy acquired by the  $e^-$  is  $E = eV$ .

and its KE is  $E = \frac{1}{2}mv^2$

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

$$\therefore \frac{1}{2}mv^2 \times \frac{m}{m} = eV$$

$$\frac{(mv)^2}{2m} = eV \Rightarrow \frac{p^2}{2m} = eV$$

$$p^2 = 2meV$$

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

Substituting p value in eq (4) we get

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

$$\lambda = \frac{12.26}{\sqrt{V}} \text{ \AA}$$

where,  $h = 6.625 \times 10^{-34}$  Joules / sec

$e = -1.6 \times 10^{-19}$  Coulomb

$m = 9.1 \times 10^{-31}$  kg.

wave number,  $\bar{\nu} = \frac{1}{\lambda} = \frac{\sqrt{V}}{12.26}$

### Properties of ~~Matter~~ Matter waves (or de-Broglie waves)

wkt, de-Broglie wavelength  $\lambda = \frac{h}{mv}$

- (i) Smaller the mass of the particle, greater is the wavelength associated with it.
- (ii) Smaller the velocity of the particle, greater is the wavelength associated with it.
- (iii) When the velocity of the particle,  $v = 0$  then the wavelength  $\lambda = \infty$ , and if  $v = \infty$  then  $\lambda = 0$ . This shows that matter waves are generated by motion of the particles.
- (iv) Matter waves are produced when the particles in motion are charged (or) un-charged.
- (v) Matter waves are not electromagnetic waves, they are pilot waves guiding the particle.
- (vi) Matter waves travel faster than velocity of light.
- (vii) While position of a particle is confined to a particular location at any time, the matter wave associated with it has some spread as it is a wave.



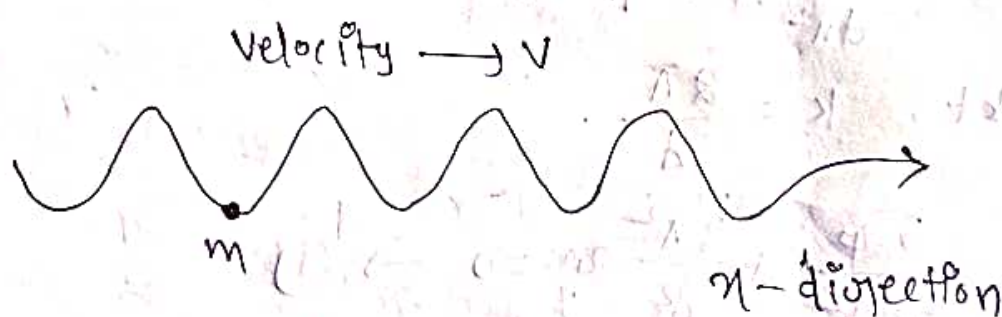
Thus the wave nature of matter introduces an uncertainty in the location of the position of the particle.

### Schrodinger's 1-D time independent wave equation

According to de-Broglie hypothesis, the particle in motion is always associated with a wave.

To describe the motion of the particle in terms of its associated waves Schrodinger derived a wave equation is called Schrodinger wave equation.

Consider a particle of mass 'm', moving with velocity 'v' along the x-direction as shown in figure. It is associated with a wave. The displacement of the wave is given by the wave function  $\psi$ .



Since, the wave function depends upon the x-coordinate of the moving particle and time 't', it is given by the complex form

$$\psi = \psi(x, t) = A e^{i(kx - \omega t)} \rightarrow \text{①}$$

where,  $A$  = Amplitude.

$$k = \text{Propagation Vector} = \frac{2\pi}{\lambda}$$

$$\omega = \text{angular velocity} = 2\pi\nu$$

Differentiating eq ① w.r.t 'x' we get.

$$\frac{d}{dx}(\psi) = A \cdot i k \cdot e^{i(kx - \omega t)}$$

$$\frac{d\psi}{dx} = i k A e^{i(kx - \omega t)} \rightarrow \textcircled{2}$$

again differentiating the above eq<sup>②</sup> w.r.t x.

$$\frac{d^2\psi}{dx^2} = i^2 k^2 A e^{i(kx - \omega t)}$$

$$\frac{d^2\psi}{dx^2} = -k^2 \psi \quad \downarrow \quad i^2 = -1, \psi = A e^{i(kx - \omega t)}$$

$$\frac{d^2\psi}{dx^2} + k^2 \psi = 0$$

wkt,  $k = \frac{2\pi}{\lambda}$

$$\frac{d^2\psi}{dx^2} + \frac{4\pi^2}{\lambda^2} \psi = 0 \rightarrow \textcircled{4}$$

de-Broglie wavelength associated with particle is given by

$$\lambda = \frac{h}{mv} \Rightarrow \frac{1}{\lambda} = \frac{mv}{h}$$

$$\frac{1}{\lambda^2} = \frac{m^2 v^2}{h^2}$$

$$\frac{1}{\lambda^2} = \frac{2m \left( \frac{1}{2} mv^2 \right)}{h^2} \rightarrow \textcircled{5}$$

Let E be the total energy of the particle and 'V' be the potential energy of the particle then



$$\text{Total Energy} = PE + KE$$

$$E = KE + PE$$

$$\downarrow KE = \frac{1}{2}mv^2$$

$$KE = E - PE \Rightarrow KE = E - V$$

eq ⑤ becomes

$$\frac{1}{\lambda^2} = \frac{2m(E - V)}{h^2} \rightarrow \textcircled{6}$$

eq ④ becomes,

$$\frac{d^2\psi}{dx^2} + 4\pi^2 \times \frac{2m(E - V)}{h^2} \psi = 0$$

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

$$\text{wkt, } \hbar = \frac{h}{2\pi} \Rightarrow h = \hbar 2\pi$$

where,  $\hbar = \hbar$  cut.

$$\frac{d^2\psi}{dx^2} + \frac{2\pi^2 m(E - V)}{\hbar^2} \psi = 0$$

$$\frac{d^2\psi}{dx^2} + \frac{2m(E - V)}{\hbar^2} \psi = 0 \rightarrow \textcircled{7}$$

The above eq's represents schrodinger 1-D time independent wave equation.

For 3-D motion of the particle the above eq's becomes

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

where,  $\nabla^2 = \frac{d^2}{dx^2} + \frac{d^2}{dy^2} + \frac{d^2}{dz^2}$

Here,  $\nabla = \text{Del}$

$$E\psi = i\hbar \frac{d\psi}{dt}$$

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

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

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2} \left[ i\hbar \frac{d\psi}{dt} - V\psi \right] = 0$$

$$\frac{d^2\psi}{dx^2} = - \frac{2m}{\hbar^2} \left[ i\hbar \frac{d\psi}{dt} - V\psi \right]$$

$$- \frac{\hbar^2}{2m} \cdot \frac{d^2\psi}{dx^2} = i\hbar \frac{d\psi}{dt} - V\psi$$

$$E\psi = \left[ - \frac{\hbar^2}{2m} \Delta^2 \psi + V\psi = i\hbar \frac{d\psi}{dt} \right]$$

This is Schrodinger's time dependent wave equation.

Physical significance of Wave function ( $\psi$ ):-

Consider a particle having 3-D motion along  $x, y, z$  coordinates. The value of wave function ( $\psi$ ) associated with a moving particle of a point  $x, y, z$  is space.

Since wave function is a complex quantity it may be expressed in the form  $\psi(x, y, z) = a + ib$ , where  $a, b$  are real functions and  $i = \sqrt{-1}$ .

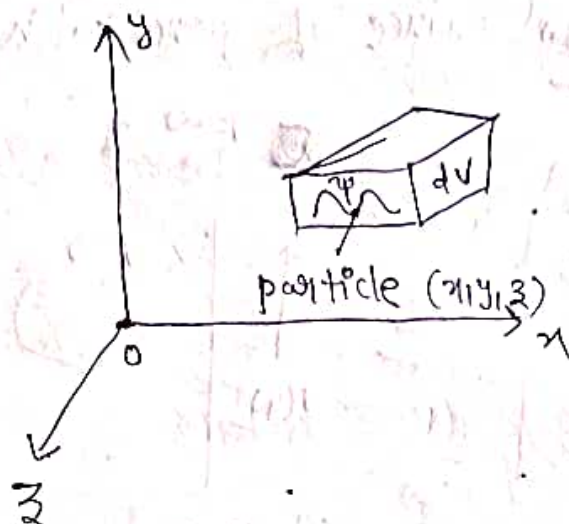


The complex conjugate of  $\psi$  is given by  $\psi^*(x, y, z) = a - ib$   
 Multiplying the above 2 equations we have

$$\psi \psi^* = (a + ib)(a - ib)$$

$$\psi \psi^* = a^2 + b^2$$

$$P = \psi \psi^* = |\psi(x, y, z)|^2 = a^2 + b^2 \rightarrow (1)$$



Thus the product of  $\psi$  and  $\psi^*$  is real and positive if  $\psi \neq 0$  and is known as probability density of the particle associated with de-Broglie wave.

When the motion of particle is confined to a volume element  $dv$  then  $P dv = \psi(x, y, z) \cdot \psi^*(x, y, z) dv$   
 $= |\psi(x, y, z)|^2 dv \rightarrow (2)$

The probability of finding the particle in  $dv$ , surrounding the point of  $(x, y, z)$  for the motion of the particle in 1-D, the probability  $P dx = \psi(x) \psi^*(x) dx = |\psi(x)|^2 dx \rightarrow (3)$  is the probability of finding the particle over a small distance  $dx$ .

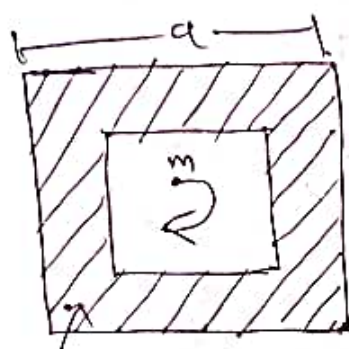
If  $\psi$  is continuous then the normalised distribution function is given by  $|\psi(x, y, z)|^2 dv = 1$ . So

$$\int_{-\infty}^{\infty} |\psi(x) \cdot \psi^*(x)|^2 dv = 1$$

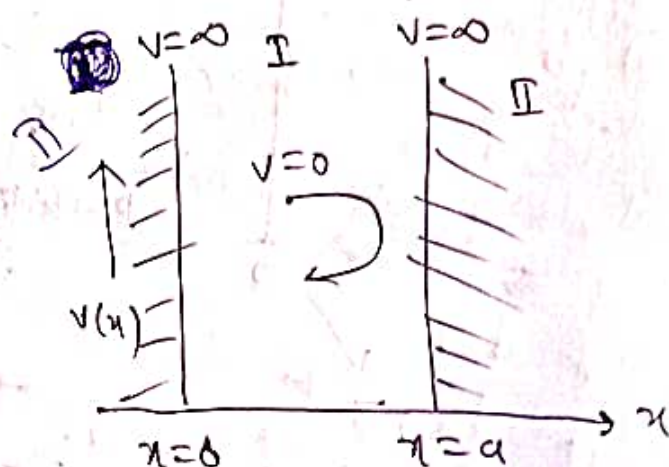
## Particle in a 1-D potential box or Infinite Square

### Well Potential:-

Consider a particle moves back and forth between the walls of 1-D box separated by width 'a' as shown in figure. Let the particle travel only along x-axis and is confined between  $x=0$  and  $x=a$  by two infinitely hard walls so that the particle has no chance of penetrating them as shown in figure.



Rigid walls



$V = \text{potential}$

Box represents by a potential walls of infinite height at  $x=0$  and  $x=a$ . So that potential energy  $V$  of the particle is infinitely high on both sides of the box and inside the box potential energy ( $V$ ) is uniform or constant. i.e.,  $V=0$  inside the box.

From figure,

Region-I :-  $V_x = 0$  for  $0 < x < a$

Region-II :-  $V_x = \infty$  for  $x \leq 0$  and  $x \geq a$ .

Then the wave function  $\psi(x)$  of the particle in the region  $0 < x < a$  where  $V=0$  is described by Schrodinger equation.



$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2} (\epsilon - V) \psi = 0$$

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2} \epsilon \psi = 0 \quad \downarrow \quad V=0$$

$$\frac{d^2\psi}{dx^2} + k^2 \psi = 0 \rightarrow (1) \quad \text{where } k^2 = \frac{2m\epsilon}{\hbar^2}$$

The solution for the above eqn is given by

$$\psi(x) = A \sin kx + B \cos kx \rightarrow (2)$$

where A and B are arbitrary constants. Applying the first boundary condition.

i.e., At  $x=0$ ,  $\psi(x)=0$ .

$$\text{we get } A \sin k(0) + B \cos k(0) = 0$$

$$\boxed{B=0}$$

Applying the second boundary condition.

i.e., at  $x=a$ ,  $\psi(a)=0$  we get

$$\psi(a) = A \sin k(a) = 0$$

$$A \neq 0, \sin k(a) = 0$$

$$\sin ka = \sin n\pi$$

$$ka = n\pi$$

$$k = \frac{n\pi}{a} \quad \text{where, } n=1, 2, 3, \dots$$

Thus a particle with zero energy can not be present in the box and hence  $n \neq 0$ .

$\therefore$  The wave function for the motion of the particle in the

region  $0 < x < a$  are given by

$$\psi_n(x) = A \sin kx \Rightarrow \psi_n(x) = A \sin \frac{n\pi x}{a} \rightarrow (9)$$

Eigen values of Energy:-

We know that  $k^2 = \frac{2mE}{\hbar^2}$

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

substituting the value of  $k = \frac{n\pi}{a}$

$$E = \frac{n^2 \hbar^2 k^2}{2m a^2} \quad \text{or} \quad k^2 = \frac{h^2}{2\pi^2}$$

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

From the above equation it is clear that.

(i) The lowest energy of the particle is obtained by putting  $n=1$ . i.e.,  $E_1 = \frac{h^2}{8m\pi^2}$  and  $E_n = n^2 E_1$ .

(ii) For  $n=2, 3, 4, \dots$  we get discrete energy values of the particle.

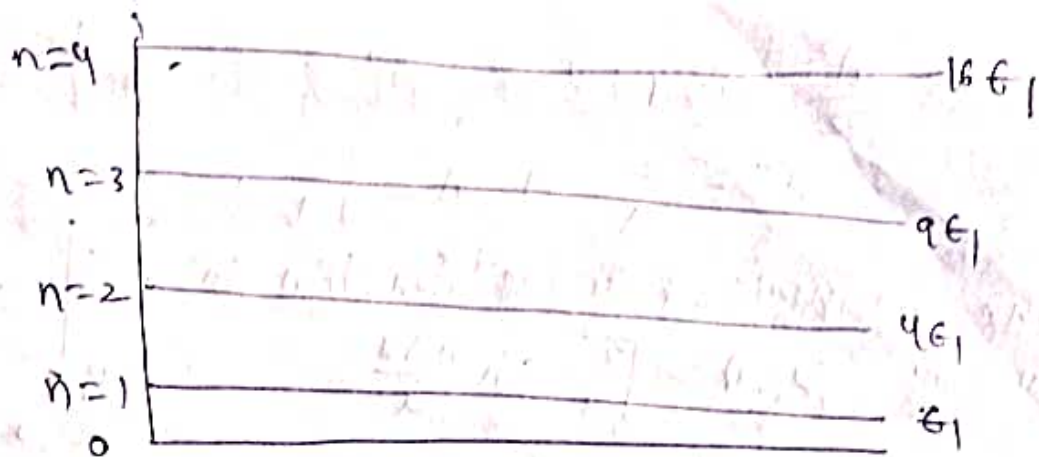
$$n=2, E_2 = 4E_1$$

$$n=3, E_3 = 9E_1$$

$$n=4, E_4 = 16E_1$$

(iii) The spacing between  $n^{\text{th}}$  energy level and the next higher energy level increases as  $(n+1)^2 E_1 - n^2 E_1$   
 $= (2n+1) E_1$ .





### Eigen Wave Functions:-

The eigen wave function for the motion of the particle is given by  $\psi_n(x) = A \frac{\sin n\pi x}{a}$ ,  $0 < x < a$ .

$$\psi_n(x) = 0, \quad x \leq 0, x \geq a.$$

The total probability that the particle is somewhere in the box must be unity.

$$\text{i.e., } \int_0^a P dx = \int_0^a |\psi_n(x)|^2 dx = 1$$

$$\int_0^a A^2 \sin^2\left(\frac{n\pi x}{a}\right) dx = 1$$

$$A^2 \int_0^a \sin^2\left(\frac{n\pi x}{a}\right) dx = 1$$

$$A^2 \int_0^a \frac{1 - \cos 2\left(\frac{n\pi x}{a}\right)}{2} dx = 1$$

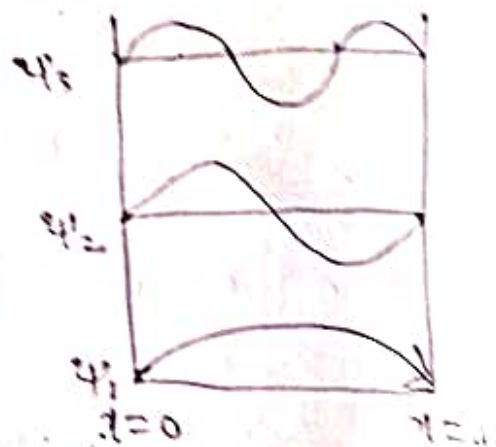
$$\frac{A^2}{2} \int_0^a \left(1 - \cos 2\left(\frac{n\pi x}{a}\right)\right) dx = 1$$

$$\frac{A^2}{2} \left[ x - \frac{a}{n\pi} \sin\left(\frac{2n\pi x}{a}\right) \right]_0^a = 1$$

$$\frac{A^2}{2} (a) = 1$$

$$A^2 = \frac{2}{a} \Rightarrow A = \sqrt{\frac{2}{a}}$$

$\therefore$  The normalised wave function is given by  $\psi_n(x) = \sqrt{\frac{2}{a}} \sin \frac{n\pi x}{a}$



From figure the wave function  $\psi_1$  has two nodes at  $x=0$  and  $x=a$ .

$\psi_2$  has three nodes at  $x=0$ ,  $x=\frac{a}{2}$ ,  $x=a$ .

$\psi_3$  has four nodes at  $x=0$ ,  $x=\frac{a}{3}$ ,  $x=\frac{2a}{3}$  and  $x=a$ .

Thus  $\psi_n$  has  $(n+1)$  nodes



# Free Electron Theory of Metals

The physical properties of solids are governed by the valence electrons of atoms in a solid. The mobility of these valence electrons in a solid decides the electrical, thermal and magnetic properties of solids.

To study these properties electron theories were proposed.

They are

- (i) Classical free electron theory.
- (ii) Quantum free electron theory.
- (iii) Zone or Band Theory.

## Classical free electron theory:-

The first theory was developed by Drude and Lorentz. According to this theory metal contains free electrons which are responsible for electrical conductivity and metals obey laws of classical mechanics.

## Quantum Free Electron Theory:-

This theory was proposed by Sommerfeld, according to this theory the free electrons move with a constant potential. This theory obeys quantum laws.

## Zone or Band Theory:-

Bloch introduced the band theory, according to this theory free electrons move in a periodic potential provided by the lattice. It gives complete informational study of electrons.



## Success (or) Advantages (or) Merits of Classical Free Electron Theory:-

- (i) It verifies ohm's law.
- (ii) It explains electrical & thermal conductivities of metals.
- (iii) It derives wide mann-frenz law.
- (iv) It explains optical properties of metals.

## Failures (or) Drawbacks (or) Disadvantages (or) Demerits of classical free electron theory:-

- (i) It fails to explain the electrical conductivity of semiconductors & insulators.
- (ii) This theory fails to explain the specific heat of metal.
- (iii) This theory cannot explain magnetic susceptibility of metals.
- (iv) This theory can not explain the thermal conductivity at low temperature.
- (v) Phenomenons like photo electric effect, compton's effect and black body radiation could not be explained by this theory.
- (vi) It fails to explain mean free path of the electrons.

## Merits of Quantum Free Electron Theory:-

- (i) It explains the specific heat of metals.
- (ii) It explains magnetic susceptibility of metals.
- (iii) It successfully explains electrical and thermal conductivity of metals.
- (iv) It can explain photoelectric effect, compton effects and body radiation.



(v) It can explain thermionic phenomenon.

### Demerits of Quantum Free Electron Theory:-

(i) It is unable to explain the metallic properties exhibited by only certain crystals.

(ii) This theory fails to distinguish between metal, semiconductor and insulator.

(iii) It also fails to explain the positive value of Hall coefficient.

### Expression for electrical conductivity ( $\sigma$ ) in Quantum Free Electron Theory:-

When an electric field ' $E$ ' is applied the force on the electron is  $-eE$ .

Wkt, force is also given by rate of change of momentum.

$$\text{i.e., } \frac{dp}{dt} = -eE \rightarrow (1)$$

Since, from de-Broglie wave length equation

$$p = \frac{h}{\lambda} \Rightarrow \frac{h}{\frac{2\pi}{k}} = \hbar k.$$

$$\text{where, } \hbar = \frac{h}{2\pi}, \quad k = \frac{2\pi}{\lambda}$$

$$\therefore \frac{dp}{dt} = \hbar \frac{dk}{dt} \rightarrow (2)$$

Substituting eq (2) in eq (1)

$$\text{we have } -eE = \hbar \frac{dk}{dt}$$

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

Origin of k-space moves through a distance  $dk$  in time  $dt$ . The displacement in the avg. collision time  $\tau$  is  $\Delta k = -\frac{eE\tau}{\hbar} \rightarrow (3)$

Wkt,  $p = mv = \hbar k$ .

$$m \Delta v = \hbar \Delta k$$

$$\Delta k = \frac{m \Delta v}{\hbar} \rightarrow (4)$$

eq (3) & (4) becomes,

$$\frac{m \Delta v}{\hbar} = -\frac{eE\tau}{\hbar}$$

$$\Delta v = -\frac{eE\tau}{m}$$

Expression for current density is given by

$$\bar{J} = -ne\Delta v.$$

Substituting  $\Delta v$  value in the above eq. we get

$$\bar{J} = -ne \cdot \left(-\frac{eE\tau}{m}\right)$$

$$\bar{J} = \left(\frac{ne^2\tau}{m}\right) E \rightarrow (5)$$

A/c to definition of current density  $\bar{J} = \sigma E \rightarrow$

from eq (5) & (6).

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

$\therefore$  The expression for electrical conductivity is given

by  $\sigma = \frac{ne^2\tau}{m} \rightarrow (6)$



and its resistivity  $\rho = \frac{1}{\sigma} = \frac{m}{ne^2\tau} \rightarrow (P)$

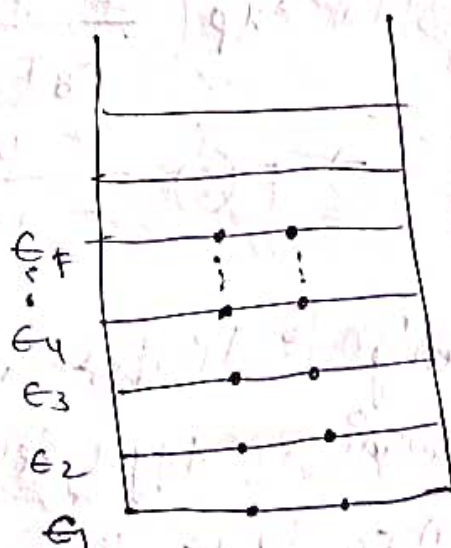
### Fermi-Dirac Distribution Function $F(E)$ :-

Consider that the assembly of electrons as electron gas, which behaves like a system of Fermi-particles (or Fermi ions).

The Fermi-ions obeying Fermi-Dirac statistics.  
i.e., Pauli's exclusion principle.

### Fermi Energy:-

It is the energy of state at which the probability of electron occupation is  $\frac{1}{2}$  at any temperature above 0 K. It separates filled energy states and unfilled energy states. The highest energy level that can be occupied by an  $e^-$  at 0 K is called "Fermi-energy" level.



At 0 K.

### Fermi Level:-

It is a level at which the  $e^-$  probability is  $\frac{1}{2}$  at any temperature above 0 K. Always it is 1/2.

(or '0' at '0'k.

∴ The probability function  $F(\epsilon)$  of an  $e^-$  occupying energy level is given by.

$$F(\epsilon) = \frac{1}{1 + \exp\left(\frac{\epsilon - \epsilon_F}{k_B T}\right)}$$

where,  $E_F$  = Fermi Energy.

$k_B$  = Boltzmann Constant.

$T$  = Absolute Temperature.

Temperature Dependent of  $F(\epsilon)$ :-

Case-i:- Probability of occupation at  $T = '0' K$ .

and  $E < E_F$  then  $F(\epsilon) = 1$ .

wkt,

$$F(\epsilon) = \frac{1}{1 + \exp\left(\frac{\epsilon - \epsilon_F}{k_B T}\right)}$$

$$F(\epsilon) = \frac{1}{1 + e^{-\infty}} \Rightarrow F(\epsilon) = \frac{1}{1 + \frac{1}{e^{\infty}}} = \frac{1}{1 + 0} = 1$$

The above eq. clearly indicates at  $T = '0' K$  the energy level below the Fermi energy level  $\epsilon_F$  is fully occupied by electrons leaving the upper level vacant.

Case-ii:- Probability of occupation at  $T = '0' K$  and  $\epsilon > \epsilon_F$  then  $F(\epsilon) = 0$ .

wkt,

$$F(\epsilon) = \frac{1}{1 + e^{\infty}} = \frac{1}{\infty} = 0$$

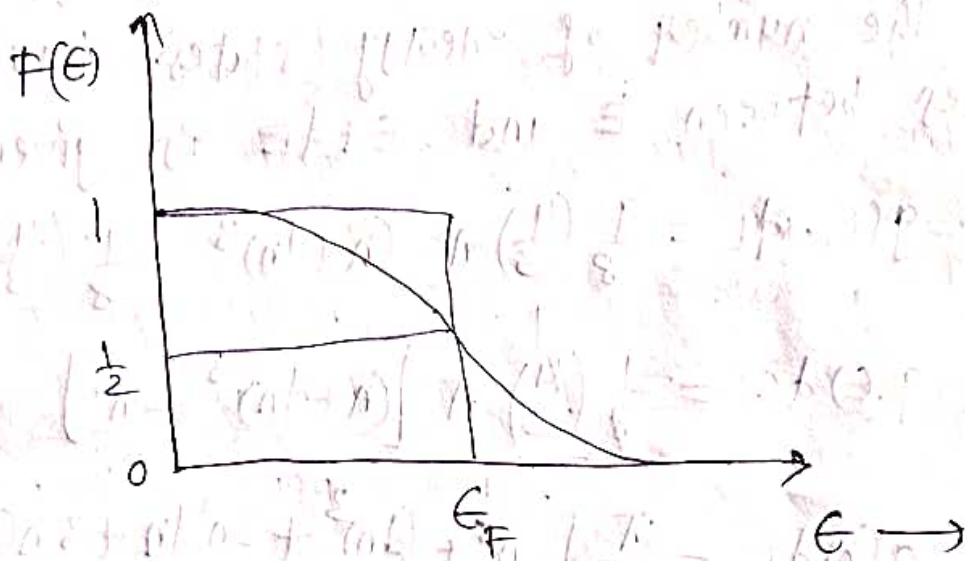


The above eq. indicates no probability to occupy the energy levels by electron and hence it is empty.

Case-ii - Probability of occupation at  $T = 0\text{K}$  and  $E = E_F$  then  $F(E) = \frac{1}{2}$ .

Wkt,  $F(E) = \frac{1}{1+e^0} \Rightarrow F(E) = \frac{1}{1+1} = \frac{1}{2}$  //

The above condition states that there is a 50% probability for the electrons to occupy Fermi energy.



Density of States (DOS) :-

The number of electrons per unit volume in an energy level at a given temperature is equal to the product of density of states  $g(E)$  and Fermi-Dirac distribution function  $f(E)$ .

i.e.,  $n_c = g(E) \cdot f(E) \cdot dE \rightarrow \text{①}$

where,  $n_c$  = concentration of electrons.

$g(E)$  = density of states.

$f(E)$  = probability of occupation of electron.

Consider a sphere of radius ' $n$ ' and another sphere of radius  $n+dn$  with the energy values are  $E$  and  $E+dE$  respectively.

∴ The number of energy states available in the sphere of radius ' $n$ ' is by considering one octant of the sphere.

The number of energy states with in a sphere of radius  $n+dn$  is given by  $\frac{1}{8} \left( \frac{4}{3} \right) \pi (n+dn)^3$ .

Thus the number of energy states having energy values between  $E$  and  $E+dE$  is given by

$$g(E) \cdot dE = \frac{1}{8} \left( \frac{4}{3} \right) \pi (n+dn)^3 - \frac{1}{8} \left( \frac{4}{3} \right) \pi n^3$$

$$g(E) dE = \frac{1}{8} \left( \frac{4}{3} \right) \pi [(n+dn)^3 - n^3]$$

$$g(E) dE = \frac{\pi}{6} [n^3 + 3n^2 dn + 3n(dn)^2 + (dn)^3 - n^3]$$

Compared to  $dn$ ,  $dn^2$  &  $dn^3$  are very small and hence neglecting the higher powers of  $dn$  we get

$$g(E) dE = \frac{\pi}{6} [3n^2 dn] = \frac{\pi}{2} n^2 dn \rightarrow (2)$$

The expression for  $n^{\text{th}}$  energy level is given by

$$E = \frac{n^2 h^2}{8m a^2} \quad \text{or} \quad n^2 = \frac{8m a^2 E}{h^2} \rightarrow (3)$$

$$n = \left( \frac{8m a^2 E}{h^2} \right)^{\frac{1}{2}} \rightarrow (4)$$



Differentiating eq(3) w.r to  $\epsilon$ . we get

$$2n dn = \frac{8ma^2}{h^2} d\epsilon$$

$$dn = \frac{1}{2n} \cdot \frac{8ma^2}{h^2} d\epsilon$$

Substitute  $n$  value in above equation.

$$dn = \frac{1}{2} \cdot \left( \frac{h^2}{8ma^2\epsilon} \right)^{1/2} \cdot \frac{8ma^2}{h^2} d\epsilon.$$

substituting  $n^2$  and  $dn$  values in eq(3) & eq(5) we get eq(2) as.

$$g(\epsilon) \cdot d\epsilon = \frac{\pi}{2} \cdot \frac{8ma^2\epsilon}{h^2} \cdot \frac{1}{2} \cdot \left( \frac{h^2}{8ma^2} \right)^{1/2} \cdot \frac{8ma^2}{h^2} \cdot \frac{d\epsilon}{\sqrt{\epsilon}}$$

$$g(\epsilon) d\epsilon = \frac{\pi}{4} \cdot \left( \frac{8ma^2}{h^2} \right)^2 \cdot \left( \frac{h^2}{8ma^2} \right)^{1/2} (\epsilon)^{\frac{1}{2}} d\epsilon.$$

$$g(\epsilon) d\epsilon = \frac{\pi}{4} \cdot \frac{8ma^2}{h^2} \times \frac{8ma^2}{h^2} \times \frac{1}{\sqrt{8ma^2}} \epsilon^{\frac{1}{2}} d\epsilon$$

$$g(\epsilon) d\epsilon = \frac{\pi}{h^3} (2ma^2) \cdot \sqrt{8ma^2} \epsilon^{\frac{1}{2}} d\epsilon$$

$$g(\epsilon) d\epsilon = \frac{2\pi}{h^3} (2ma^2) \sqrt{2ma^2} \epsilon^{\frac{1}{2}} d\epsilon$$

$$g(\epsilon) d\epsilon = \frac{2\pi}{h^3} (2ma^2)^{3/2} \epsilon^{\frac{1}{2}} d\epsilon.$$

Here,  $a^2 = 1$ ,

$$g(\epsilon) d\epsilon = \frac{2\pi}{h^3} (2m)^{3/2} \epsilon^{\frac{1}{2}} d\epsilon \rightarrow \textcircled{7}$$

The above eq ① represents density of energy states per unit volume.

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$$g(E) = \frac{1}{V} \frac{dN}{dE}$$

where  $V$  is the volume of the system.

$$g(E) = \frac{1}{V} \left( \frac{dN}{dE} \right) \quad \text{--- (2)}$$

For a 3D free electron gas, the number of states  $N$  is given by

$$N = \frac{V}{(2\pi)^3} \int_0^k 4\pi k^2 dk$$

$$N = \frac{V}{(2\pi)^3} \cdot 4\pi \int_0^k k^2 dk = \frac{V}{(2\pi)^3} \cdot 4\pi \left[ \frac{k^3}{3} \right]_0^k = \frac{V}{(2\pi)^3} \cdot \frac{4\pi}{3} k^3$$

$$N = \frac{V}{(2\pi)^3} \cdot \frac{4\pi}{3} k^3 \quad \text{--- (3)}$$

$$\frac{dN}{dE} = \frac{V}{(2\pi)^3} \cdot 4\pi k^2 \cdot \frac{dk}{dE} \quad \text{--- (4)}$$

$$\frac{dN}{dE} = \frac{V}{(2\pi)^3} \cdot 4\pi k^2 \cdot \frac{1}{\hbar v_F} \quad \text{--- (5)}$$

$$\frac{dN}{dE} = \frac{V}{(2\pi)^3} \cdot 4\pi k^2 \cdot \frac{1}{\hbar v_F} \quad \text{--- (6)}$$

$$\frac{dN}{dE} = \frac{V}{(2\pi)^3} \cdot 4\pi k^2 \cdot \frac{1}{\hbar v_F} \quad \text{--- (7)}$$

$$g(E) = \frac{1}{V} \frac{dN}{dE}$$

$$g(E) = \frac{1}{V} \left( \frac{dN}{dE} \right) = \frac{1}{V} \left( \frac{V}{(2\pi)^3} \cdot 4\pi k^2 \cdot \frac{1}{\hbar v_F} \right)$$