

## Chapter: Theory of Metals

### **Elementary Quantum Mechanical Ideas:**

Various processes and phenomena that take place within a material in a microscopic level can't be explained by classical mechanics. To explain those phenomena, a generalized form of mechanics called Quantum mechanics is successfully applicable.

### **Wave Particle Duality: De Broglie's equation:**

Experiments showed that particles like electrons, protons and neutrons exhibit an equivalent wave length given by,  $\lambda = \frac{h}{p}$   $\Leftrightarrow$  De Broglie equation

Where,  $h = 6.624 \times 10^{-34} \text{ Js}$ , Planck's Universal constant &  $P$  = momentum of the particle.

Since,  $\hbar = h/2\pi$  and  $k = 2\pi/\lambda$  (wave number), the de Broglie eq<sup>n</sup> can also be written as,  $p = \frac{\hbar}{2\pi} \frac{2\pi}{\lambda}$

i.e.  $p = \hbar k$

Also, EM radiation energy contains packets known as photons given by Planck's equation,  $E = hf$

$\Leftrightarrow E = \hbar\omega$  (as  $\hbar = h/2\pi$  and  $\omega = 2\pi f$ )

**Two basic experiments which conformed the need of quantum mechanics rather than classical mechanics (Wave - Particle duality) :-**

**Expt.1:** It was observed that beams of particles such as electrons were diffracted from a crystal in a same manner as X-rays (EM waves) diffraction.

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

i.e.  $P = (2mE)^{1/2}$  .....(i)

**Expt.2:** When EM radiation interacts with electrons in a solid or gas, a certain max<sup>m</sup> wavelength of radiation is required to eject electrons from the surface of the material. By bombarding the material with photons of different energies it is found that for each material, a characteristic energy is required to remove the electrons from the surface of the material. The min<sup>m</sup> frequency (hence the max<sup>m</sup> wavelength) of this EM radiation was found to be  $f = \phi/h$ .....(ii), where,  $\phi$  is the characteristic energy called work function of the material.

Comparing eq<sup>ns</sup> (i) & (ii), we conclude that the EM radiation behaves like particle with packets of energy, when it collides with particles like electrons in materials. It is the wave- particle duality discussed in quantum mechanics.

## Wave function:

The suitable func<sup>n</sup> to represent wave function for matter wave is,

$$\Psi(x,t) = Ae^{-i(\omega t - kx)} \dots \dots \dots (i)$$

Where, A is normalizing constant.

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

$$\text{And, } p = \hbar k \Leftrightarrow k = p/\hbar$$

Eq<sup>n</sup> (i) can be written as,

$$\Psi(x,t) = Ae^{-i/\hbar(Et - px)} \dots \dots \dots \text{(ii)}$$

Required expression for Wave function.

### Significances of the wave function:

→ The probability that a particle will be found at a given place in space at a given instant of time is characterized by the func<sup>n</sup>  $\psi(x,y,z,t)$ . It is called the wave function. This function is either real or complex.

→ The only quantity having a physical meaning is the square of its magnitude  $P = \Psi^* \Psi = |\Psi|^2$ . Where,  $\Psi^*$  is the complex conjugate of  $\Psi$ . The quantity  $P$  is the probability density.

→ The probability of finding a particle in a volume  $dxdydz$  is,  $|\psi|^2 dxdydz$ .

→ Since total probability is unity,  $\iiint |\psi|^2 dx dy dz = 1$  — (1)

$\rightarrow$  Since, total probability is  $1.0000000000000002$ .  
**Eqn ①**  
 It is the normalizing condition and the wave func<sup>n</sup> is called normalized wave func<sup>n</sup>.

### Properties of wave function:

→ Two wave functions  $\psi_1$  &  $\psi_2$  are said to be orthogonal in the interval  $(a,b)$  if  $\int_a^b \psi_2^* \cdot \psi_1 dx = 0$

→ It must be single valued and continuous everywhere.

→ If  $\psi_1, \psi_2, \dots, \psi_n$  are sol<sup>ns</sup> of Schrodinger's wave eq<sup>n</sup>, then the linear comb<sup>n</sup>,

$\Psi = a_1 \Psi_1 + a_2 \Psi_2 + \dots + a_n \Psi_n$  must also be the sol<sup>n</sup> of Schrodinger's wave eq<sup>n</sup>.

→ The wave func<sup>n</sup>  $\Psi \rightarrow 0$  as  $x \rightarrow \pm\infty$

### Schrodinger's time independent eq<sup>n</sup>:

The SWE describes the motion of quantum mechanical particle as Newton's 2<sup>nd</sup> law equation does in classical mechanics.

The wave func<sup>n</sup> for q.m. particle is,

$$\Psi(x,t) = Ae^{-i/\hbar(Et - px)} \dots \dots \dots (i)$$

Differentiating (i) w.r.t. x, we get,

$$\frac{d\psi}{dx} = \left(\frac{ip}{\hbar}\right) A e^{-\frac{i(Et - px)}{\hbar}}$$

$$\text{Or, } \frac{d\psi}{dx} = \left(\frac{ip}{\hbar}\right) \psi \dots \dots \dots \text{(ii)}$$

$\hat{p}\psi = (\hbar/i) d\psi/dx \Rightarrow P = -i\hbar \frac{d}{dx}$  is momentum operator.

Again differentiating (ii) w.r.t. x, we get,

$$\frac{d^2\psi}{dx^2} = A(ip/\hbar)^2 \psi \Rightarrow p^2\psi = -\hbar^2 \frac{d^2\psi}{dx^2} \dots\dots(iii)$$

Consider a particle of mass 'm' and potential energy 'V' moving with velocity 'v', then total energy,

$$E = \frac{1}{2}mv^2 + V$$

$$Or, E = \frac{p^2}{2m} + V$$

Multiplying with  $\psi$  both sides,  $E\psi = \left(\frac{p^2}{2m} + V\right)\psi$

$$or, E\psi = \frac{p^2\psi}{2m} + V\psi$$

$$\text{or, } (E - V)\psi = \frac{-\hbar^2}{2m} \frac{d^2\psi}{dx^2} \quad (\text{using eqn (iii)})$$

$$\Leftrightarrow \frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2} (E-V)\psi = 0 \Leftrightarrow \text{Required time independent SWE}$$

$$\text{In 3-D, } \nabla^2 \Psi + \frac{2m}{\hbar^2} (E - V) \Psi = 0$$

Where,  $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$  is Laplacian Operator

## Time dependent SWE:

The wave func<sup>n</sup> for q.m. particle is.

$$\psi(x,t) = Ae^{-i/\hbar(Et-px)} \dots \dots \dots (i)$$

Differentiating w.r.t. 't' we get,

$$\frac{d\psi}{dt} = \left(\frac{-iE}{\hbar}\right) A e^{-i(Et-px)/\hbar}$$

$$or, \frac{d\psi}{dt} = \left(-\frac{ip}{\hbar}\right) A\psi$$

$$\Rightarrow E\psi = i\hbar \frac{d\psi}{dx} \dots \dots (i)$$

Consider a particle of mass 'm' and P.E. 'V' moving with velocity 'v'.

Total energy,  $E = k.E. + P.E.$

$$or, E = \frac{p^2}{2m} + V$$

Multiplying with  $\psi$  both sides,

$$E\psi = \frac{p^2\psi}{2m} + V\psi$$

$$or, \left(\frac{-\hbar^2}{2m} \frac{d^2}{dx^2} + V\right)\psi = E\psi \quad \Rightarrow H\psi = i\hbar \frac{d\psi}{dt} \quad \text{Required Time dependent SWE}$$

where,  $H = \frac{-\hbar^2}{2m} \frac{d^2}{dx^2} + V$  is Hamiltonian operator

**Energy well model of metal (Electron in an infinite 1-D potential well):**

Consider an electron confined in a potential well

given by,

$$V = 0 \text{ for } 0 < x < L$$

$$= \infty \text{ for } x \leq 0, x \geq L$$

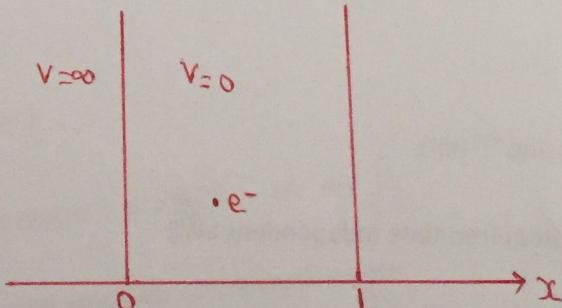


Fig. Electron in an infinite potential well

Within the box, the SWE becomes,

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2} E\psi = 0 \dots \dots \dots (i) \quad (\text{as } V=0)$$

$$\text{Let, } \frac{2mE}{\hbar^2} = K^2 \dots \dots \dots (ii)$$

$$\text{Then, } \frac{d^2\psi}{dx^2} + K^2 \psi = 0$$

The general sol<sup>n</sup> of this differential equation is,  $\psi(x) = A \sin Kx + B \cos Kx$  .....(iii)

Where, A & B are constants to be determined using boundary condition.

Since, the particle cannot have infinite energy, it cannot exist outside the well. Therefore, the wave function  $\psi$  must vanish outside and at the walls of the well. i.e. at  $x=0$  and  $x=L$

Using  $\psi = 0$  at  $x = 0$ , eq<sup>n</sup> (iii) becomes,

$$0 = 0 + B \Rightarrow B = 0$$

Using  $\psi = 0$  at  $x=L$ , eq<sup>n</sup> (iii) becomes,

$$0 = A \sin K L \Rightarrow \sin K L = 0$$

$$\Rightarrow \sin K L = \sin n\pi, \text{ with } n=0, 1, 2, \dots$$

$$\Rightarrow K L = n\pi \Rightarrow K = \frac{n\pi}{L} \quad \dots\dots\text{(iv)}$$

From eq<sup>ns</sup> (ii) & (iv),  $2mE/\hbar^2 = n^2 \pi^2/L^2$

$$\Rightarrow E = \frac{n^2 \pi^2 \hbar^2}{2mL^2}, \quad n=1, 2, 3, \dots \quad \dots\text{(v)}$$

This means the energy of particle in potential well is quantized. Each value of energy given by eq<sup>n</sup> (v) is called energy eigen value and corresponding function is called eigen function.

Now, substituting  $B=0$  and  $K = \frac{n\pi}{L}$  in eq<sup>n</sup> (iii), the allowed solutions of SWE are ,

$$\Psi_n = A \sin \frac{n\pi}{L} x$$

The coefficient A is called Normalizing constant and can be found using Normalizing condition,

$$\int_0^L \psi \psi^* dx = 1$$

$$\text{or, } A^2 \int_0^L \sin^2 \frac{n\pi}{L} x dx = 1$$

$$\text{or, } A^2 \int_0^L \left\{ 1 - \cos 2 \frac{n\pi x}{L} \right\} dx = 1$$

$$\text{or, } A^2 \left[ \int_0^L \frac{1}{2} dx - \frac{1}{2} \int_0^L \cos \frac{2n\pi}{L} x dx \right] = 1 \Rightarrow A^2 \frac{L}{2} = 1 \Rightarrow A = \sqrt{\frac{2}{L}}$$

Therefore, the normalized wave functions of the particles are

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

The first three eigen functions  $\psi_1, \psi_2, \psi_3$  together with the probability densities  $|\psi_1|^2, |\psi_2|^2, |\psi_3|^2$  are shown in fig. below.

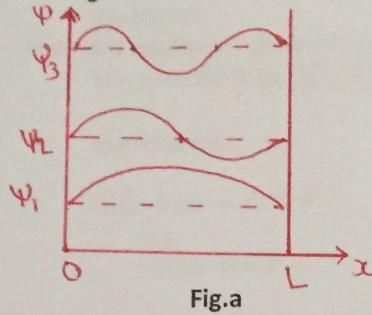


Fig.a

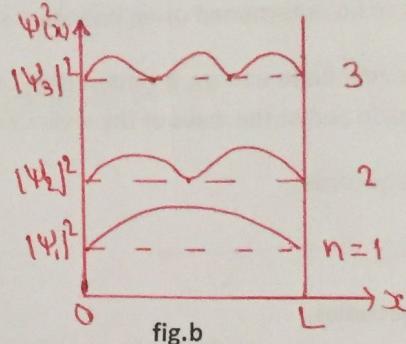


fig.b

### Heisenberg's Uncertainty Principle:

If  $\Delta x$  and  $\Delta P_x$  are the uncertainties in position and momentum of an electron during simultaneous measurement along  $x$ , then Heisenberg's uncertainty principle states that their product must be equal or greater than  $\hbar$ .

$$\text{i.e. } \Delta x \cdot \Delta P_x \geq \hbar$$

$$\text{Similarly, } \Delta E \cdot \Delta t \geq \hbar \quad \& \Delta L \cdot \Delta \theta \geq \hbar$$

Here,  $E$  is energy, 't' time, 'L' the angular momentum and ' $\theta$ ' the angular displacement

These pairs, that follow Uncertainty Principle, are called Canonical conjugate pairs.

Example: Consider an electron confined in a 1-D infinite potential well of width extending from  $x=0$  to  $x=L$ . So the uncertainty in position is equal to width  $L$  of the well. The momentum is

$$P_x = \hbar K \text{ in +ve } X\text{- dir}^n \text{ and } P_x = -\hbar K \text{ in -ve } X\text{- dir}^n. \text{ Uncertainty in momentum,}$$

$$\Delta P_x = \hbar K - (-\hbar K) = 2\hbar K$$

When the electron is in ground state,  $n=1$  and  $K \frac{L}{\hbar} = \pi$ .

$$\text{Therefore } \Delta P_x = 2 \hbar \pi / L$$

Product of uncertainties,

$$\Delta x \cdot \Delta P_x = L \cdot 2 \hbar \pi / L = \hbar$$

### Uses of uncertainty principle:

- ◊ The existence of protons and neutrons and non-existence of electrons in nucleus of an atom.
- ◊ To find the binding energy of electrons in nucleus of an atom.
- ◊ To find the radius of Bohr's first orbit as well as the finite width of the spectral lines.

### Finite potential Barrier (Tunneling effect):

Consider a barrier of potential  $V$  having width ' $L$ '.

A moving particle of energy  $E < V$  be incident on the barrier.

The potential function for the barrier can be expressed as,

$$V(x) = 0 \text{ for } x < 0, x > L \\ = V \text{ for } 0 < x < L$$

The SWE and their solutions for these regions are as follows:

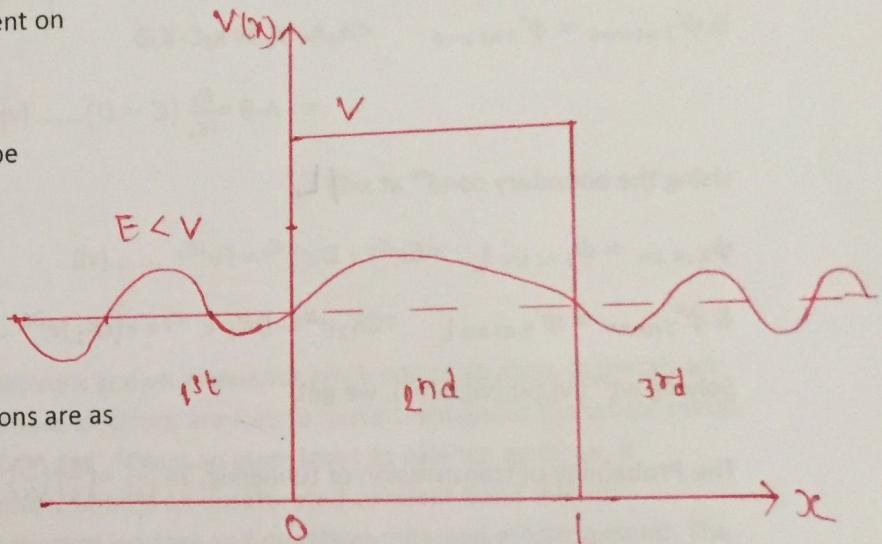


Fig. Potential Barrier

For 1<sup>st</sup> region,

$$\frac{d^2\psi_1}{dx^2} + \frac{2m}{\hbar^2} E \psi_1 = 0$$

$$\text{or, } \frac{d^2\psi_1}{dx^2} + K_1^2 \psi_1 = 0 \text{ Where, } K_1^2 = \frac{2m}{\hbar^2} E$$

It's general solution is,  $\psi_1 = A e^{ik_1 x} + B e^{-ik_1 x} \dots\dots (i)$

For 2<sup>nd</sup> region,

$$\frac{d^2\psi_2}{dx^2} + \frac{2m}{\hbar^2} (E-V) \psi_2 = 0$$

$$\text{or, } \frac{d^2\psi_2}{dx^2} - \frac{2m}{\hbar^2} (V-E) \psi_2 = 0 \text{ (as } E < V)$$

$$\text{or, } \frac{d^2\psi_2}{dx^2} - K_2^2 \psi_2 = 0 \text{ Where, } K_2^2 = \frac{2m}{\hbar^2} (V-E)$$

It's general solution is,  $\psi_2 = C e^{k_2 x} + D e^{-k_2 x} \dots\dots (ii)$

For 3<sup>rd</sup> region,

$$\frac{d^2\psi_3}{dx^2} + \frac{2m}{\hbar^2} E \psi_3 = 0$$

$$\text{or, } \frac{d^2\psi_3}{dx^2} + K_1^2 \psi_3 = 0 \text{ Where, } K_1^2 = \frac{2m}{\hbar^2} E$$

It's general solution is,  $\psi_3 = Fe^{ik_1 x} + Ge^{-ik_1 x}$

Since there is no reflected wave in 3<sup>rd</sup> region,  $\psi_3 = Fe^{ik_1 x} \dots \text{(iii)}$

Using the boundary cond<sup>ns</sup> at  $x = 0$

$$\psi_1 \text{ at } x=0 = \psi_2 \text{ at } x=0 \quad \Leftrightarrow A+B=C+D \dots \text{(iv)}$$

$$\& \psi'_1 \text{ at } x=0 = \psi'_2 \text{ at } x=0 \quad \Leftrightarrow ik_1A - iK_1B = k_2C - K_2D$$

$$\Leftrightarrow A-B = \frac{K_2}{iK_1} (C-D) \dots \text{(v)}$$

Using the boundary cond<sup>ns</sup> at  $x=L$

$$\psi_2 \text{ at } x=L = \psi_3 \text{ at } x=L \quad \Leftrightarrow Ce^{K_2 L} + D e^{-K_2 L} = Fe^{iK_1 L} \dots \text{(vi)}$$

$$\& \psi'_2 \text{ at } x=L = \psi'_3 \text{ at } x=L \quad \Leftrightarrow CK_2 e^{K_2 L} - DK_2 e^{-K_2 L} = F(iK_1)e^{iK_1 L} \dots \text{(vii)}$$

Solving eq<sup>ns</sup> (iv), (v), (vi), & (vii), we get,

$$\text{The Probability of transmission or tunneling, } T = \left| \frac{F}{A} \right|^2 = \left( \frac{F}{A} \right) \left( \frac{F}{A} \right)^*$$

$$\text{or, } T = \frac{4E(V-E)}{4E(V-E) + V^2 \sinh^2 K_2 L} \dots \text{(viii)}$$

If the width and height of the potential are very large, the term  $4E(V - E)$  in the denominator of eq<sup>n</sup> (viii) can be neglected in comparing to  $V^2 \sinh^2 K_2 L$ .

$$\text{Also, } \sinh K_2 L = \frac{e^{K_2 L} - e^{-K_2 L}}{2} = \frac{e^{K_2 L}}{2} \text{ for large } L$$

$$\text{Therefore, eq<sup>n</sup> (viii) can be written as, } T = \frac{4E(V-E)}{V^2 \left( \frac{e^{K_2 L}}{2} \right)^2}$$

$$\text{Hence, } T = \frac{16E(V-E)}{V^2} e^{-2K_2 L} \dots \text{(viii)}$$

Eq<sup>n</sup> (viii) gives the probability of tunneling of the particle through potential barrier of width 'L' and height 'V'.

$$\text{The reflection coefficient is given by, } R = \left| \frac{B}{A} \right|^2 = 1-T$$

This is the surprising result of Q.M., which shows that there is finite probability of emission of electron ( $\beta$ - emission) from the nucleus of an atom even though the electron has lower energy than the energy by which it is bounded.

#### Pauli Exclusion Principle:

It states that no two electrons within a given system may have all four identical quantum numbers  $n, l, m_l$  and  $m_s$ . Each set of values for  $n, l, m_l$  and  $m_s$  represent a possible electronic state and correspondingly a wave function  $\Psi n, l, m_l, m_s$ .

Where,  $n$  is principle q.n.

$l$  = Orbital angular q.n.

$m_l$  = magnetic orbital q.n.

and  $m_s$  = spin magnetic q.n.

#### Free electron theory of metal:

According to this theory, the outer most electrons known as valence electrons of an atom in metals are very loosely attached to the parent atom. These electrons are free to move throughout the whole metal. These freely roaming electrons form "Electron gas". When an atom loses its valence electron, it becomes positively charged ion. So, the metallic bond is an unsaturated covalent bond due to electrostatic attraction between positively charged ion core and negatively charged electron cloud. The metallic bond is weaker than saturated bonds (i.e. ionic and covalent bonds).

In free electron theory, it is assumed that the potential due to the ion cores is uniform throughout the metal. Although, the P.E. of an electron due to electrostatic attraction in the metal has a finite negative value, we assume it to be zero because we are concerned with change in P.E. rather than just P.E.

So, if the electron has K.E. only as  $E = \frac{1}{2}mv^2$  .....(i)

But,  $\lambda = h/p = h/mv$ ,  $K = 2\pi/\lambda$  and  $v = \hbar K/m$

$$\text{Eq}^n \text{ (i) becomes, } E = \frac{m \frac{\hbar^2 K^2}{m^2}}{2} \Leftrightarrow E = \frac{\hbar^2 K^2}{2m} \text{ .....(ii)}$$

Eq<sup>n</sup> (ii) represents K.E. of the free electron within the metal. The relationship bet<sup>n</sup> E and K is parabolic in nature.

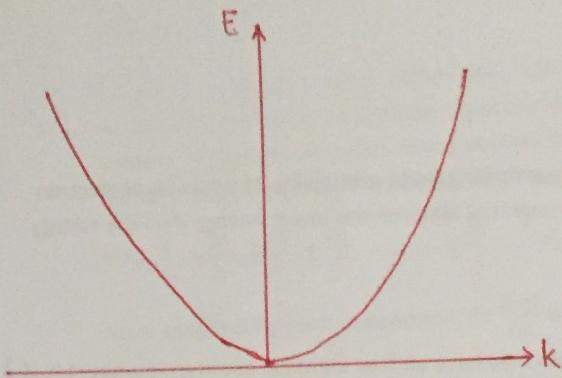


Fig. E-K diagram of free electron in metal

Electron in a linear solid(metal):

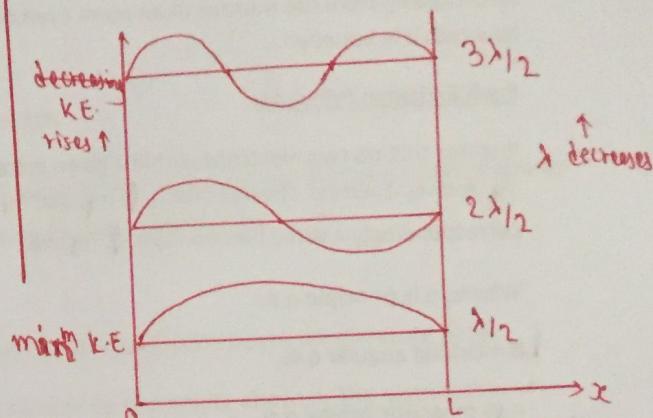


Fig. Relationship bet<sup>n</sup> K.E. & wavelength in linear wire.

Consider a copper wire of length  $L$ . There are many free electrons within the linear solid. The wavelength exhibited by electrons in the wire will depend upon their K.E.

For min<sup>m</sup> K.E., the wavelength of electron will be greatest and will progressively go down as the K.E. increases. So, for min<sup>m</sup> K.E. we have,  $\lambda = \lambda/2 \Rightarrow \lambda = 2L/1$

And for higher values of K.E<sup>s</sup>, the rel<sup>n</sup>ship become,

$$\lambda = 2L/2 \Rightarrow \lambda = 2L/2$$

$$\lambda = 3L/2 \quad \lambda = 2L/3$$

$$\lambda = nL/2 \Rightarrow \lambda = 2L/n$$

Now, arranging for wavelength in terms of length of the wire, we will get,

$$\lambda = 2L/1, 2L/2, 2L/3, \dots, 2L/n \dots \text{(i)}$$

Wave length and wave number are related as  $K = 2\pi/\lambda \dots \text{(ii)}$

Substituting the value of  $\lambda$  from eq<sup>n</sup> (i) in (ii), we get,

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

$$K = \frac{2\pi}{2L_1}, \frac{2\pi}{2L_2}, \frac{2\pi}{2L_3}, \dots, \frac{2\pi}{2L_n}$$

$$K = \frac{\pi}{L}, \frac{2\pi}{L}, \frac{3\pi}{L}, \frac{4\pi}{L}, \dots, \frac{n\pi}{L}$$

In normal condition, a solid is electrically neutral with no net flow of electrons in any direction. This means a free electron have a velocity in one direction must be matched by similar electron having same velocity in opposite direction. Since velocity is related to momentum, which in turn is related to wave number must have both the positive and negative values.

$$K = \pm \frac{\pi}{L}, \pm \frac{2\pi}{L}, \pm \frac{3\pi}{L}, \pm \frac{4\pi}{L}, \dots, \pm \frac{n\pi}{L} \dots \text{(ii)}$$

Now, substituting for K in equation,  $E = \frac{\hbar^2 K^2}{2m}$  we get,

$E = \frac{n^2 \hbar^2 \pi^2}{2m L^2}$  This shows that a free electron in a metal does not possess any arbitrary value of energy rather its energy is quantized by virtue of E being function of principle q.n. 'n'.

### Fermi energy:

Fermi energy is defined as the highest filled energy level at absolute zero temperature (0 K).

All the energy levels upto the Fermi level are filled at 0K and empty above it. The distribution of electrons among various levels is in accordance with Pauli's Exclusion Principle.

If N is the total no. of electrons to be accommodated on the line, then for even N, we have  $N = 2n_f$ . Where  $n_f$  is principle q.n. of Fermi level.

We have,

$$\text{Energy, } E = \frac{n^2 \hbar^2 \pi^2}{2m L^2}$$

$$\text{For } n = n_f, \text{ Fermi energy, } E_f = \frac{\hbar^2}{2m} \left( \frac{\pi n_f}{L} \right)^2 \dots \text{(i)}$$

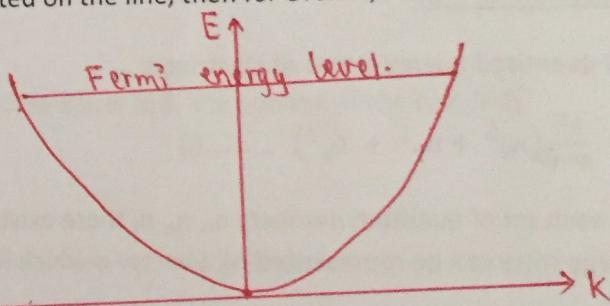


Fig. The Highest filled energy level at 0K

Thus the Fermi energy depends upon the length of the box and the no. of electrons in the box.

$$E_f = \frac{\hbar^2}{2m} \left( \frac{\pi N}{2} \right)^2 \quad (\because N = 2n_f)$$

$$E_f = \frac{\hbar^2}{2m} K_f^2 \dots \text{(ii)}$$

Where,  $K_f$  is the Fermi Wave vector and the sphere of radius  $K_f$  in E-K space is called Fermi sphere.

### Degenerate State:

In a single dimensional solid, the energy of the electron is expressed as,

$$\text{In 3-D, } n^2 = n_x^2 + n_y^2 + n_z^2$$

Where,  $n_x, n_y, n_z$  be 1, 2, 3, .....

$n_x, n_y, n_z$

When different combinations of principle quantum number represent same energy, these are called

### 'degenerate states'.

For example,  $n(1,1,2)$ ,  $n(1,2,1)$ , and  $n(2,1,1)$  represent same electron energy. These all three electronic states are degenerate states.

### Density of state function:

The density of state function  $Z(E)$  is defined as the number of energy states per unit energy in an energy interval of  $dE$ .

Density of state function,  $Z(E) = \frac{dN}{dE}$

### Derivation for $Z(F)$ :

The quantized energy states of electron is .

$$E_n = \frac{h^2}{8\pi m} (n_x^2 + n_y^2 + n_z^2) \quad \dots \dots \dots (i)$$

For each set of quantum numbers  $n_x$ ,  $n_y$ ,  $n_z$  there exists a specific energy level called energy state. Each energy state can be represented by a vector  $n$  which is the radius from origin to a point  $(n_x, n_y, n_z)$ .

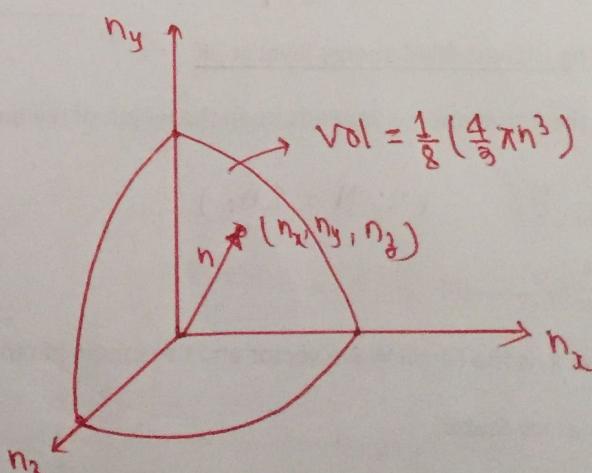
The no. of energy states in any volume

is proportional to that volume.

So, the no. of energy states within the sphere of radius ' $n$ ' and having energies less than  $E$ , is given by,

$$N = \frac{1}{8} \frac{4\pi n^3}{3} \dots \dots \text{(iii)}$$

(as 'n' can take integer values only, so the energy states are defined only in positive octant of the sphere made by radius vector 'n')



$$\text{But we have, } E = \frac{n^2 h^2}{8m} \Leftrightarrow n^2 = \left[ \frac{8m}{h^2} E \right]^1 \Leftrightarrow n = \left[ \frac{8m}{h^2} E \right]^{1/2} \dots\dots \text{(iv)}$$

Substitute 'n' from (iv) in (iii) we get,

$$N = \frac{1}{8} \frac{4\pi \left[ \left( \frac{8m}{h^2} E \right)^{1/2} \right]^3}{3}$$

$$\text{or, } N = \frac{1}{8} \frac{4\pi}{3} \left[ \frac{8m}{h^2} E \right]^{3/2} \Leftrightarrow N = \frac{\pi}{6} \left[ \frac{8m}{h^2} \right]^{3/2} E^{\frac{3}{2}}$$

Differentiating w.r.t. E , we get,

$$\frac{dN}{dE} = \frac{d}{dE} \left( \frac{\pi}{6} \left[ \frac{8m}{h^2} \right]^{3/2} E^{\frac{3}{2}} \right)$$

$$\text{or, } \frac{dN}{dE} = \frac{\pi}{6} \left[ \frac{8m}{h^2} \right]^{3/2} \frac{dE^{3/2}}{dE}$$

$$\text{or, } \frac{dN}{dE} = \frac{\pi}{6} \left[ \frac{8m}{h^2} \right]^{3/2} \frac{3}{2} E^{\frac{1}{2}}$$

$$\text{or, } \frac{dN}{dE} = \frac{\pi}{4} \left[ \frac{8m}{h^2} \right]^{3/2} E^{\frac{1}{2}}$$

$$\text{or, } \frac{dN}{dE} = \frac{2\pi l^3}{h^3} [2m]^{3/2} E^{\frac{1}{2}}$$

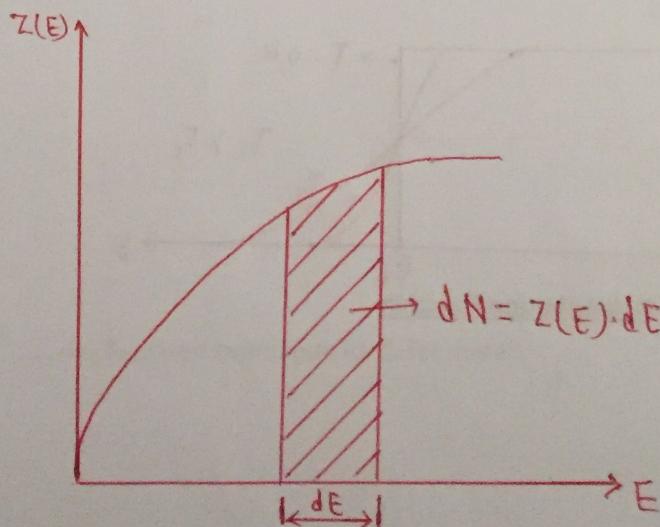
For an electron placed in 3-D potential box with all sides equal to  $l$ , the volume of the box,  $V = l^3$

Then,

$$\frac{dN}{dE} = \frac{2\pi V}{h^3} [2m]^{3/2} E^{\frac{1}{2}}$$

Hence, Density of state function,  $Z(E) = \frac{dN}{dE} = C E^{\frac{1}{2}}$  .....(v) Where,  $C = \frac{2\pi V}{h^3} [2m]^{3/2}$

The plot of  $Z(E)$  Versus  $E$  is shown below.



### Fermi - Dirac Distribution function (F-D dist<sup>n</sup>):

The F-D dist<sup>n</sup> function applies to non-interactive particles with half integer spin which must obey Pauli Exclusion Principle. Particles obeying F-D statistics are called Fermions. This function expresses the Probability of occupancy of particle in available energy levels in a given system.

$$\text{F-D dist}^n \text{ function, } F(E) = \frac{1}{1 + e^{\frac{E - E_f}{kT}}}$$

Where,

$F(E)$  is the probability of occupancy or occupation index

$E$  is the energy of electron

$E_f$  is Fermi Energy

$T$  is absolute temperature

$K$  is Boltzmann constant =  $1.38 \times 10^{-23}$  J/K

Case (i): If  $E = E_f$  at  $T=0$  K,  $F(E)$  is indeterminable

Case (ii): If  $E < E_f$  at  $T=0$  K,  $F(E) = \frac{1}{1 + e^{-\infty}} = 1$

i.e. probability of finding the electrons below Fermi level at absolute zero is certain.

Case (iii): If  $E > E_f$  at  $T \neq 0$  K,  $F(E) = \frac{1}{e^{\frac{-(E-E_f)}{kT}}} = e^{\frac{-(E-E_f)}{kT}}$  i.e. at higher temperature, the F-D dist<sup>n</sup> function approximates to Maxwell-Boltzmann Classical dist<sup>n</sup> function.

Higher the temperature, greater the probability of higher energy states being occupied.

Case (iv): If  $E = E_f$  at  $T \neq 0$  K,  $F(E) = \frac{1}{1 + e^{\frac{E-E_f}{kT}}} = \frac{1}{1 + e^0} = \frac{1}{2} = F(E) = \frac{1}{1+1} = 1/2$

i.e. For any temperature the occupation index is 0.5 if the energy of electron is equal to Fermi energy.

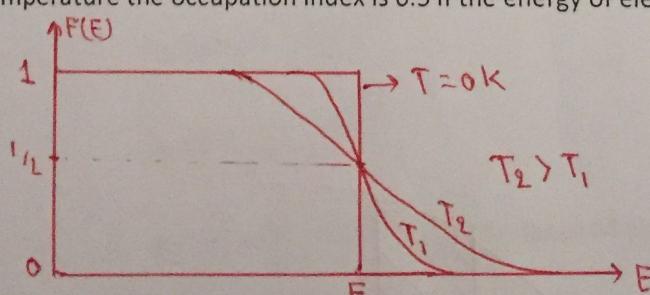


Fig. F-D distribution Function

Q. Find the population density N(E) and Fermi energy E<sub>f</sub> from F-D distribution Function

Sol"

The no. of energy states dN(E) in a small energy interval dE is given by,

$$dN(E) = Z(E) \cdot F(E)$$

where, Z(E) is density of state function

F(E) is F-D distribution function.

According to Pauli Exclusion principle, each state is occupied by two electrons with opposite spins.

$$\text{So, } dN(E) = 2 \cdot Z(E) \cdot F(E)$$

The total no. of electrons upto Fermi level (also called population density function),

$$N(E) = \int_0^{E_f} dN(E) dE = \int_0^{E_f} 2 \cdot Z(E) \cdot F(E) dE$$

Since, the probability of occupancy of electron from ground state to Fermi level is 100% i.e. F(E)=1, so

$$N(E) = \int_0^{E_f} 2 \cdot Z(E) dE$$

$$\text{or, } N(E) = \int_0^{E_f} 2 \cdot C E^{\frac{1}{2}} dE = \frac{2CE_f^{\frac{3}{2}}}{\frac{3}{2}} = \frac{4}{3} CE_f^{\frac{3}{2}}$$

$$\text{Since, } C = \frac{2\pi V}{h^3} [2m]^{\frac{3}{2}}$$

$$N(E) = \frac{8\pi V}{3h^3} (2m)^{\frac{3}{2}} (E_f)^{\frac{3}{2}}$$

$$N(E) = \frac{8\pi V}{3h^3} (2mE_f)^{\frac{3}{2}} \dots \text{(i)} \Rightarrow \text{the required expression for Population density.}$$

Derivation for E<sub>f</sub>:

$$\text{We have, } N(E) = \frac{8\pi V}{3h^3} (2mE_f)^{\frac{3}{2}}$$

$$\text{or, } (2mE_f)^{\frac{3}{2}} = \frac{3Nh^3}{8\pi V}$$

$$\text{or, } 2mE_f = \left( \frac{3Nh^3}{8\pi V} \right)^{\frac{2}{3}}$$

$$\text{or, } E_f = \frac{1}{2m} \left( \frac{3Nh^3}{8\pi V} \right)^{\frac{2}{3}}$$

$$\text{or, } E_f = \frac{\cancel{\pi}^2}{2m} \left( \frac{3\pi^2 N}{V} \right)^{\frac{2}{3}} \dots \text{(iv) Required expression for } E_f \text{ for metal.}$$

If 'n' be the no. of electrons per unit volume i.e.  $n=N/V$  then,

$$E_f = \frac{\hbar^2}{2m} (3\pi^2 n)^{2/3}$$

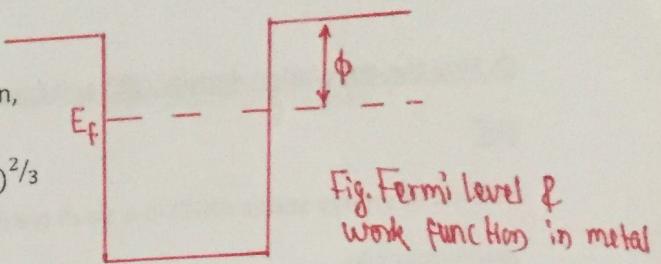


Fig. Fermi level & work function in metal

#### Thermionic emission, work Function :

When a metal is heated, the free electrons become more energetic as the F-D distribution function extends to higher temperature. Some of the electrons acquire sufficiently large energies to leave the metal and become free. This phenomenon is called Thermionic emission. (Fig. above)

This situation is self-limiting because as the electrons accumulate outside the metal, they prevent electrons from leaving the metal. Also, the emitted electrons leave a net positive charge behind, which pulls the electrons inward. Only those electrons having energy greater than  $E_f + \phi$  can leave the metal. The electrons at Fermi level must be given a threshold value of energy to leave the metal surface. This threshold value of energy is called work function ( $\phi$ ) of the metal. The no. of emitted electrons depends on the temperature (by F-D statistics).

The conduction electrons behave as if they are free within metal. So, P.E. can be considered to be zero, within metal. Total energy of free electrons is purely Kinetic.

$$\text{i.e. } E = \frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2$$

Suppose that the surface of the metal is perpendicular to the direction of emission, say along x-direction. For an electron to be emitted from the metal surface, it's K.E.  $= \frac{1}{2}mv_x^2$  must be greater than the potential barrier  $E_f + \phi$ .

$$\text{i.e. } \frac{1}{2}mv_x^2 > E_f + \phi$$

The no. of electrons per unit volume having momentum between  $P_x$  and  $P_x + dP_x$  is given by,

$$N(P_x) dP_x$$

The no. of electrons arriving at the surface of metal per unit time per unit volume

$$= \text{velocity} \times N(P_x) dP_x$$

$$= \frac{P_x}{m} \cdot N(P_x) dP_x \quad (\because \text{momentum } P_x = mv_x)$$

Let, r be the reflection coefficient i.e. probability that the electron will be reflected from the barrier into the metal.

Therefore, probability of emission (escape) =  $1-r$

$$\text{No. of escaping electrons} = (1-r) \frac{P_x}{m} \cdot N(P_x) dP_x$$

Adding contribution by the entire electrons, which have momentum greater than  $P_{x0}$  (threshold momentum), the emission current density can be written as,

$$J = e \int_{P_{x0}}^{\infty} (1 - r) \frac{P_x}{m} N(P_x) dp_x$$

$$\text{or, } J = \frac{e}{m} \int_{P_{x0}}^{\infty} (1 - r) P_x N(P_x) dp_x \dots \dots \dots \text{(i)}$$

On calculation, we get the no. of electrons in momentum range  $P_x$  &  $P_x + dP_x$  as,

$$N(P_x) dP_x = \frac{4\pi m K T}{h^3} e^{\frac{E_f}{K T}} e^{\frac{-P_x^2}{2m K T}} dP_x \dots \dots \dots \text{(ii)}$$

Solving eqn's (i) & (ii) using integral table we get,

$$J = A_0 (1 - r) T^2 e^{\frac{E_f}{K T}} \dots \dots \dots \text{(iii)} \quad \text{Richardson's Equation}$$

$$\text{Where, } A_0 = \frac{4\pi m K^2}{h^3} = 1.2 \times 10^6 \text{ Am}^{-2} \text{ K}^{-2}$$

### Schottky Effect:

When an electric field applied to a metal is increased, the work function is decreased and hence, thermionic emission from the metal surface increases. This effect is called **Schottky Effect**.

In thermionic emission, an electron emitted from the metal surface leave behind an equivalent positive charge (called image charge).

The electrostatic force between the real charge and image charge can be written as,

$$F = \frac{-e \cdot e}{4\pi\epsilon_0 (2x)^2} = \frac{-e^2}{16\pi\epsilon_0 x^2} \dots \dots \dots \text{(i)}$$

The P.E. can be found as,

$$V(x) = \int_x^{\infty} F(x) dx = \frac{-e^2}{16\pi\epsilon_0} \int_x^{\infty} \frac{dx}{x^2} = \frac{-e^2}{16\pi\epsilon_0} \frac{1}{x} \dots \dots \dots \text{(ii)}$$

If  $E$  is the applied electric field, then the P.E. due to this field,

$$V(x) = -eE \cdot x \dots \dots \dots \text{(iii)}$$

Now, net P.E. of the barrier will be,

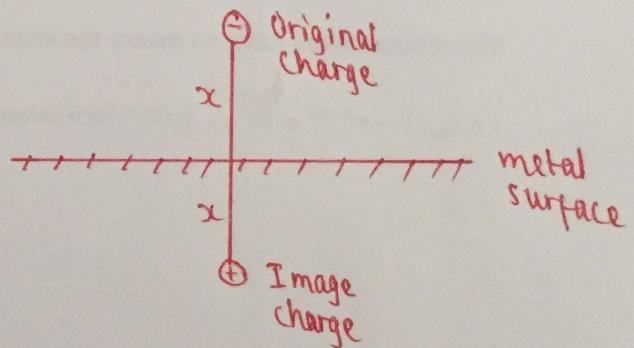


Fig. metal surface with and image charge

$$E_f + \phi - \frac{e^2}{16\pi\epsilon_0 x} \frac{1}{x} - eE \cdot x \quad \dots \dots \text{(iv)}$$

The reduction in work function (or barrier height) will be maximum if,

$$\frac{d}{dx} \left( - \frac{e^2}{16\pi\epsilon_0 x} \frac{1}{x} - eE \cdot x \right) = 0$$

$$\text{or, } \frac{e^2}{16\pi\epsilon_0 x^2} - eE = 0$$

$$\text{or, } \frac{e^2}{16\pi\epsilon_0 x^2} = eE \quad \Leftrightarrow x = \left( \frac{e}{16\pi\epsilon_0 E} \right)^{\frac{1}{2}} \dots \dots \text{(v)}$$

Hence,

$$V_{\max} = - \frac{e^2}{16\pi\epsilon_0 x} - eE \cdot x \quad \text{Using } x \text{ from (v)}$$

$$\Leftrightarrow V_{\max} = - \frac{e^2}{16\pi\epsilon_0} \left( \frac{e}{16\pi\epsilon_0 E} \right)^{\frac{-1}{2}} - eE \cdot \left( \frac{e}{16\pi\epsilon_0 E} \right)^{\frac{1}{2}}$$

$$V_{\max} = \left( \frac{e^3 E}{4\pi\epsilon_0} \right)^{\frac{1}{2}} \dots \dots \text{(vi)}$$

The effective work function can be written as,

$$\phi_{\text{eff}} = \phi + V_{\max} = \phi - \left( \frac{e^3 E}{4\pi\epsilon_0} \right)^{\frac{1}{2}} \dots \dots \text{(vii)}$$

The reduced work function means the increase in emission current density, given by

$$J = A_0 (1 - r) T^2 e^{\frac{\phi_{\text{eff}}}{kT}} \dots \dots \text{(viii)} \Leftrightarrow \text{Richardson's Equation for Schottky effect.}$$

Fermi level at equilibrium:

(Contact Potential)

## \* Fermi level at equilibrium (Contact potential) :-

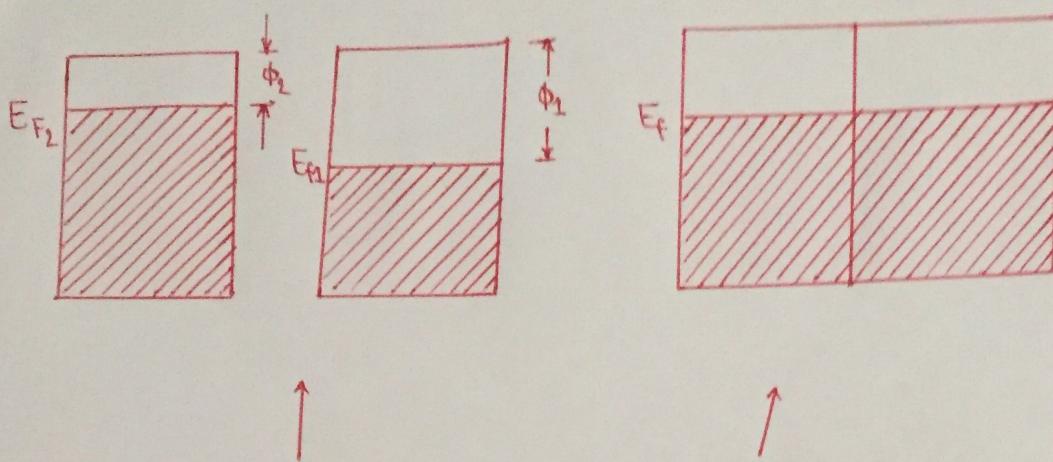


Fig. a. metals when separate

fig. b. metals in contact.

When two metals with different Fermi energy and work function are brought in contact, electrons from metal with ~~higher~~ <sup>lower</sup> Fermi level will start crossing over to metal with lower Fermi level. Metal having lost electrons becomes positively charged whereas metal having received electrons become negatively charged. Consecutively, a P.d. is developed at the junction called contact potential.

This electron transfer from one metal to another reduces the total energy of electrons in metal-metal system. This process continues till the contact potential is large enough to prevent further transfer of electrons. So, the system reaches equilibrium. At equilibrium, the Fermi levels of both metals will be same.

The contact potential ( $\Delta V$ ) is due to the difference in work functions of metals in contact.

$$\text{i.e. } e \Delta V = \phi_2 - \phi_1 \Rightarrow \Delta V = \frac{\phi_2 - \phi_1}{e}$$

seebach effect: see book

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