

## 1(a). Electrical Properties of materials

### Part - A

#### 1. Define Electrical Conductivity?

The amount of electric charge (Q) conducted per unit time (t) across unit area (A) of the solid per unit applied electrical field (E).

$$\sigma = \frac{q}{tAE}$$

#### 2. What are the merits of classical free electron theory?

- (i) It is used to verify Ohm's law
- (ii) It is used to explain electrical and thermal conductivities of metals
- (iii) It is used to derive Wiedemann – Franz law
- (iv) It is used to explain the optical properties of metal.

#### 3. What are the drawbacks of the classical free electron theory?

- (i) Classical theory states that all free electrons will absorb the supplied energy. But quantum theory will absorb certain amount of supplied energy
- (ii) Electrical conductivity of semiconductors and insulators could not be explained by this theory
- (iii) The phenomenon such as photo – electric effect, Compton effect and black body radiation could not be explained by this theory

#### 4. Define Mean free path?

The average distance travelled by a free electron between any two successive collisions in the presence of an applied field is known as mean free path

$$\lambda = v_d \times \tau_c$$

#### 5. Define collision time?

The average time taken by a free electron between two successive collisions of the electrons is known as collision time

#### 6. Define relaxation time of an electron?

The average time taken by a free electron to reach its equilibrium position from the distributed position due to application of an external electric field is called relaxation time.

#### 7. Define Drift velocity?

The velocity acquired by the free electron due to the application of electric field in the direction opposite to the direction of electric field.

#### 8. Define mobility of electrons?

The magnitude of the drift velocity per unit electric field is defined as the mobility of the electrons  $\mu = \frac{V_d}{E}$

unit:  $\text{mV}^{-1} \text{S}^{-1}$

#### 9. State Wiedemann – Franz law? Give the Lorentz number and its value?

“The ratio of electrical conductivity ( $K$ ) to the thermal conductivity ( $\sigma$ ) is directly proportional to absolute temperature ( $T$ ). i.e.,  $\frac{K}{\sigma} \propto T$  (or)  $\frac{K}{\sigma} = LT$

Where  $L$  is the Lorentz number and experimentally,  $L = 2.44 \times 10^{-8} \text{ W}\Omega\text{K}^{-2}$  at  $T = 273\text{K}$

**10. What are the sources of the resistance in the metals?**

- (i) Impurities (ii) Temperature (iii) Number of free electrons

**11. Define Fermi energy and Fermi level with its importance?**

**Fermi Level** is the state at which the probability of electron occupation is 50% at any temperature above 0K and also it is the highest reference energy level of a particle at absolute 0K.

**Fermi energy** is the energy of the state at which the probability of the electron occupation is 50% at any temperature above 0K. It is also the maximum energy of the filled states at 0K.

**Importance:** Fermi level and Fermi energy determine the probability of an electron occupying a given energy level at given temperature.

**12. Define Fermi Distribution Function?**

The probability of the electron  $F(E)$  occupying at a given energy level at temperature  $T$  is known as Fermi Distribution Function. It is given by

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

Where  $E_f$  – Fermi Level;  $k$  – Boltzmann Constant;  $T$  – Temperature

**13. Define density of states. What is its use?**

It is defined as the number of available electron states per unit volume in an energy interval  $E$  and  $E+dE$ . It is denoted by  $Z(E)$

i.e.,  $Z(E) = \frac{\text{No. of available energy states between } E \text{ and } E+dE \text{ in a cubical metal piece}}{\text{Volume of that cubical metal piece}}$

**14. What are bound and free electrons?**

The electrons which are attached to the atoms and bound to the atomic lattice are called bound electrons. The valence electrons of an atoms free to move throughout the volume of metal like gas molecules of a container are called free electrons.

**15. What are the salient features of quantum theory of free electrons?**

According to sommerfield quantum theory, free electrons obey quantum law. They cannot have all possible energies but have quantized energy values. Also their distribution in different possible energy levels obeys Fermi – Dirac distribution law.

**16. Arrive the microscopic form of Ohm’s law? Whether it is true for all temperature?**

According to macroscopic theory, Ohm’s law is  $V = IR$

We know that resistivity is given by  $\rho = \frac{RA}{l}$  where  $R$  – resistance;  $A$  – area of cross section and  $l$  is the length of the specimen

$$\therefore V = I \frac{\rho l}{A}$$

$$\text{(or) } \frac{V}{l} = J\rho$$

$$\text{(or) } \mathbf{J} = \sigma \mathbf{E} \left[ \because E = \frac{V}{l} ; J = \frac{I}{A} \text{ \& } \rho = \frac{1}{\sigma} \right]$$

This is the microscopic form of ohms law and it is not true for all the temperatures.

### 17. How does electrical resistivity of the metal varies with temperature?

When the temperature is increased, due to increase in thermal vibrations of atoms, the electrons make frequent collisions resulting in reduction of mean free path ( $\lambda$ ) and hence resistivity increases.

#### Part – B

### 1. What are the assumptions of classical free electron theory? On the basis of free electron theory, derive an expression for electrical conductivity and thermal conductivity of the metal and hence obtain Wiedemann – Franz law? What are the shortfall and outcomes?

#### Assumptions

- (1) All the metals are composed of atoms. Each atom has central nucleus surrounded by number of electrons in the permissible orbits
- (2) The electrons in the metal are free to move in all possible directions about the whole volume of metal like molecules of a perfect gas in a container.

#### **Absence of Electric field**

- (3) All the electrons are move in random direction and collide with each other elastically without any loss of energy
- (4) The force between the conduction electron and ion core is neglected and the total energy of the electron is assumed to be Kinetic energy (Potential energy is zero)

#### **Presence of electric field**

- (5) The free electrons moves in a direction opposite to the direction of the applied field(drifted towards positive potential)
- (6) Since free electrons are assumed to be a perfect gas, they obey classical kinetic theory of gases and the free electron velocities in the metal obey Maxwell – Boltzmann statistics.

#### Electrical conductivity

When an electric field (E) is applied between the extreme ends of a metallic rod, the electrons will move in opposite direction to the direction of applied field with a drift velocity  $V_d$ .

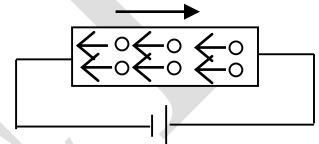
If 'E' is the electric field applied on an electron of charge 'e', then

$$\text{Lorentz Force acting on the electron, } F = eE \quad (1)$$

This force accelerates the electrons and this accelerated electron collide with positive ion core and other free electrons elastically. After collision the electron loses its kinetic energy and velocity. Due to the driving force the electron will be accelerated once again before its next collision.

$$\text{Here, Acceleration (a)} = \frac{V_d}{\tau} \quad (2)$$

Where  $V_d$  – drift velocity;  $\tau$  – Relaxation Time



$$\text{From Newton II law of motion, Force on the electron, } F = \text{mass (m) } \times \text{ acceleration (a)} \quad (3)$$

$$\text{Sub. (1) in (3), we get } F = \frac{mV_d}{\tau} \quad (4)$$

$$\text{From equations (2) \& (4) } eE = \frac{mV_d}{\tau} \quad (\text{or}) \quad V_d = \left( \frac{e\tau}{m} \right) E \quad (5)$$

From ohm's law, the current density (J) is expressed in terms of electrical conductivity ( $\sigma$ ) as

$$J = \sigma E \quad (6)$$

$$\text{Also, the current density in terms of drift velocity can be written as } J = n e V_d \quad (7)$$

$$\text{Sub. (5) in (7), we get } J = ne \left( \frac{e\tau}{m} \right) E \quad (\text{or}) \quad J = \frac{ne^2\tau}{m} E \quad (8)$$

By comparing (6) and (8)

$$\text{Electrical conductivity } \sigma = \frac{ne^2\tau}{m} \quad (9)$$

Thus, the amount of electrical charges (Q) conducted per unit time (t) per unit area (A) of a solid along unit applied electrical field (E) is called electrical conductivity

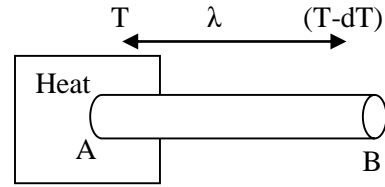
$$\sigma = \frac{q}{tAE}$$

### Thermal Conductivity

“It is defined as the amount of heat (Q) flowing per unit time through the material having unit area of cross section and maintaining at unit temperature gradient (dT/dx)”

Consider  $A = 1\text{m}^2$  &  $t = 1$  sec,

$$\text{i.e., } Q = K \frac{dT}{dx} \text{ (or) } K = \frac{Q}{\frac{dT}{dx}} \quad (10)$$



Consider two cross sections 'A' at high temperature (T) & 'B' at low temperature (T-dT) in a uniform metallic rod 'AB'. Two cross sections 'A' and 'B' are separated by a distance ' $\lambda$ '. The conduction of heat takes place from 'A' to 'B' through electrons. During collision, electrons near 'A' lose their kinetic energy while electrons near 'B' gain the energy

Let the density of conduction electron be ' $n$ ' and velocity of electron be ' $v$ '.

$$\text{At 'A' average kinetic energy of the electron} = \frac{3}{2}kT \quad \therefore K.E = \left[ \frac{1}{2}mv^2 = \frac{3}{2}kT \right] \quad (11)$$

Where  $k$  – Boltzmann Constant and  $T$  – absolute temperature

$$\text{At 'B' average kinetic energy of the electron} = \frac{3}{2}k(T-dT) \quad (12)$$

$$\therefore \text{Excess Kinetic energy from A to B of an electron} = \frac{3}{2}kT - \frac{3}{2}k(T-dT) = \frac{3}{2}kdT \quad (13)$$

$$\text{Number of electrons crossing unit area per unit time from 'A' to 'B'} = \frac{1}{6}nv \quad (14)$$

$$\text{Excess energy carried from 'A' to 'B' for unit area in unit time} = \frac{1}{6}nv \times \frac{3}{2}kdT = \frac{1}{4}nvkdT \quad (15)$$

$$\text{Similarly, Deficient energy carried from 'B' to 'A' for unit area in unit time} = -\frac{1}{4}nvkdT \quad (16)$$

$$\begin{aligned} \text{Net amount energy transferred from 'A' to 'B'} \quad Q &= \frac{1}{4}nvkdT - \left(-\frac{1}{4}nvkdT\right) \\ \text{(or) } Q &= \frac{1}{2}nvkdT \end{aligned} \quad (17)$$

$$\text{But, by definition } Q = K \frac{dT}{dx} \text{ (or) } Q = K \frac{dT}{\lambda}$$

$$\therefore K = \frac{1}{2}nvk\lambda \quad (18)$$

W.K.T for metals, relaxation time ( $\tau$ ) = Collision time ( $\tau_c$ ).

$$\text{i.e., } \tau = \tau_c = \frac{\lambda}{v} \text{ (or) } \tau v = \lambda \quad (19)$$

Sub. Eqn (19) in (18), we get  $\therefore K = \frac{1}{2}nv^2k\tau$  (20)

This is the Expression for Thermal Conductivity

### Wiedemann – Franz Law

Dividing equation (20) by (9), we get,  $\frac{\text{Thermal Conductivity}}{\text{Electrical Conductivity}} = \frac{K}{\sigma} = \frac{\frac{1}{2}nv^2k\tau}{\frac{ne^2\tau}{m}}$

(or)  $\frac{K}{\sigma} = \frac{1}{2} \frac{mv^2k}{e^2}$  (21)

W.K.T the kinetic energy of an electron is  $\frac{1}{2}mv^2 = \frac{3}{2}kT$

Then, equation (21) becomes  $\frac{K}{\sigma} = \frac{3}{2} \times \frac{kT \times k}{e^2} = \frac{3}{2} \left( \frac{k^2}{e^2} \right) T$

(or)  $\boxed{\frac{K}{\sigma} = LT}$

Where  $L = \frac{3}{2} \left( \frac{k^2}{e^2} \right)$  is a constant called Lorentz number. By substituting the value of

$k = 1.38 \times 10^{-23} \text{JK}^{-1}$ ,  $e = 1.6 \times 10^{-19} \text{Coloumb}$ ,  $L = 1.12 \times 10^{-8} \text{W}\Omega\text{K}^{-2}$ .

$\boxed{\frac{K}{\sigma} \propto T}$

Thus “The ratio of Thermal Conductivity to Electrical Conductivity of a metal is directly proportional to absolute temperature of the metal”

### **Success of classical free electron theory**

- i. It is used to verify Ohm’s law
- ii. It is used to explain electrical and thermal conductivities of metals
- iii. It is used to derive Wiedemann – Franz law

iv. It is used to explain the optical properties of metal

**Failure of classical free electron theory**

- i. Classical theory states that all free electrons will absorb the supplied energy. But quantum theory will absorb certain amount of supplied energy
- ii. Electrical conductivity of semiconductors and insulators could not be explained by this theory
- iii. The phenomenon such as photo – electric effect, Compton effect and black body radiation could not be explained by this theory
- iv. The theoretical and experimental values of electronic specific heat and specific heat are not matched
- v. The ratio of thermal to electrical conductivity is not constant at all temperature
- vi. The experimental and theoretical values of Lorentz number are not matched.

**2. Write the Fermi - Dirac distribution function. Explain how Fermi - function varies with temperature?**

‘The Probability  $F(E)$  of an electron occupying a given energy level at absolute temperature is called Fermi - Dirac distribution function

i.e., 
$$F(E) = \frac{1}{1 + e^{\frac{E-E_f}{kT}}}$$
 where  $E$  – energy of the level whose electron occupancy is being considered;  $E_f$  – Fermi energy;  $k$  – Boltzmann constant;  $T$  – absolute temperature

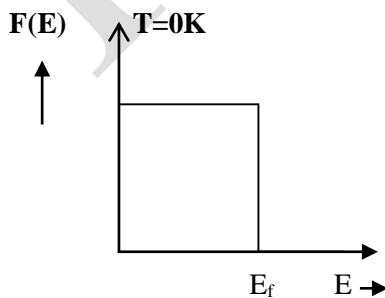
**Effect of temperature on Fermi function**

**Case 1:** at  $T = 0$  K for  $E < E_f$ , 
$$F(E) = \frac{1}{1 + e^{\frac{(Some - Ve Value)}{0}}} = \frac{1}{1 + e^{-\alpha}} = \frac{1}{1} = 1$$

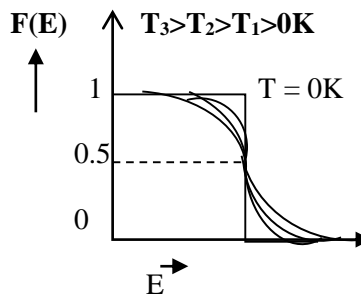
∴  $F(E) = 1$  Thus, there is a 100% chance of electron occupy below the Fermi energy of the energy level

**Case 2:** at  $T = 0$  K for  $E > E_f$ , 
$$F(E) = \frac{1}{1 + e^{\frac{(Some + Ve Value)}{0}}} = \frac{1}{1 + e^{\alpha}} = \frac{1}{1 + \alpha} = \frac{1}{\alpha} = 0$$

∴  $F(E) = 0$  Thus, there is a no chance of electron occupy above the Fermi energy of the energy level



Fig(1)



Fig(2)

**Case 3:** At any temperature other than 0K and  $E = E_f$ ,  $F(E) = \frac{1}{1 + e^0} = \frac{1}{1 + 1} = \frac{1}{2} = 0.5$

There is a 50% chance for the electron to occupy Fermi energy level

With increase in Temperature, i.e.,  $T > 0K$ , Fermi function  $F(E)$  varies with 'E' as shown in figure (2)

At very high temperature when (thermal energy)  $kT \gg E_f$  (or)  $T \rightarrow \infty$ , electron lose their quantum mechanical behavior and the Fermi distribution function reduces to classical Boltzmann distribution.

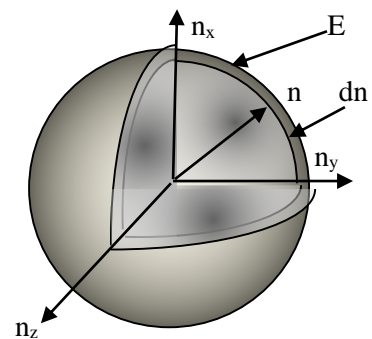
Uses:

- (i) It gives the probability of the electron occupation at the given energy state at given temperature
- (ii) It is used to calculate the number of free electrons per unit volume at given temperature
- (iii) It is used to calculate the Fermi energy of the metal

3. (i) Obtain an expression for the density of states for the metal.  
 (ii) How it is used to calculate the Fermi energy of the metals? Give its importance.  
 (iii) What happen for non-zero temperature?  
 (iv) Discuss the average energy of electrons at zero Kelvin.

**Density of States:**

It is defined as the number of available electron states per unit volume in an energy interval  $E$  and  $E+dE$ . It is denoted by  $Z(E)$



$$Z(E) = \frac{\text{Number of available energy states between } E \text{ \& } E + dE \text{ in a metal piece } (N(E) dE)}{\text{Volume of the metal piece } (a^3)}$$

Let us consider a cubical metal piece of side 'a'. The electron will behave as a wave in this metal and confined with the allowed energy levels.

The energy of the electron in three dimensional potential well is  $E = \frac{h^2}{8ma^2} (n_x^2 + n_y^2 + n_z^2)$  (1)

where the energy of an electron is determined by sum of the square of quantum numbers ( $n_x, n_y, n_z$ ). For this, A imaginary sphere is constructed with quantum numbers  $n_x, n_y, n_z$  as three coordinate axes in a three dimensional



space. A radius vector 'n' is drawn from the origin 'O' to a point  $n_x, n_y, n_z$ . it is observe that, all the points lie on the surface of this sphere will have same energy 'E'.

Thus,  $n^2 = n_x^2 + n_y^2 + n_z^2$  denotes the radius of the sphere with energy 'E'. This sphere is further divided into many shells. Each shell represents a particular combination of quantum numbers and therefore represents particular energy value

Let us consider two such energy values E and E+dE. The number of available energy states between E and E+dE can be determined by finding the number of energy states between the shells of radius n and n+dn.

$$\text{Number of energy states within a sphere of radius 'n'} = \frac{4}{3} \pi n^3 \quad (1)$$

Since the quantum number  $n_x, n_y, n_z$  have only +ve integer value, we have to take only one octant of sphere  $\left(\frac{1}{8}\right)$

$$\therefore \text{No. of available energy states within one octant of sphere of radius 'n'} \left. \begin{array}{l} \\ \text{Corresponding to energy 'E'} \end{array} \right\} = \frac{1}{8} \times \left[ \frac{4}{3} \pi n^3 \right] \quad (2)$$

$$\text{III}^{\text{rd}} \text{ly No. of available energy states within one octant of sphere of radius 'n+dn' corresponding to energy 'E+dE'} \left. \right\} = \frac{1}{8} \times \left[ \frac{4}{3} \pi (n + dn)^3 \right] \quad (3)$$

$$\begin{aligned} \text{No. of available energy states between the shell of radius 'n' \& 'n+dn'} &= \frac{1}{8} \times \left[ \frac{4}{3} \pi (n + dn)^3 \right] - \frac{4}{3} \pi n^3 \\ &= \frac{1}{8} \times \frac{4\pi}{3} \left( [n + dn]^3 - n^3 \right) \end{aligned}$$

$$\therefore N(E) = \frac{1}{8} \times \frac{4\pi}{3} (n^3 + dn^3 + 3n^2 dn + 3ndn^2 - n^3)$$

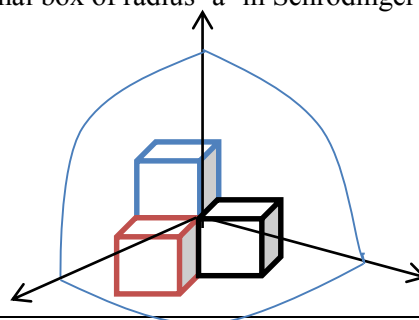
$$\text{Neglecting higher power of } dn \text{ which is very small, } N(E) dE = \frac{1}{8} \times \left[ \frac{4}{3} 3n^2 dn \right] \text{ (or)}$$

$$N(E) dE = \left[ \frac{\pi}{2} n^2 dn \right] \text{ (or) } N(E) dE = \left[ \frac{\pi}{2} n(ndn) \right] \quad (4)$$

We know that, the particle in a one dimensional box of radius 'a' in Schrödinger's wave equation is

$$E = \frac{n^2 h^2}{8ma^2} \quad (5)$$

$$\text{(or) } n^2 = \frac{8ma^2 E}{h^2} \quad (6)$$



$$(or) n = \left[ \frac{8ma^2 E}{h^2} \right]^{\frac{1}{2}} \quad (7)$$

$$\text{Differentiating eqn (6) w.r.t } n \text{ \& } E, \text{ we get } 2ndn = \frac{8ma^2}{h^2} dE \quad (8)$$

$$(or) ndn = \frac{8ma^2}{2h^2} dE \quad (9)$$

Sub the value of Eqn(4) & Eqn (7) in Eqn. (9) , we get

$$N(E) dE = \frac{\pi}{2} \times \left[ \frac{8ma^2 E}{h^2} \right]^{\frac{1}{2}} \times \left[ \frac{8ma^2}{2h^2} \right] dE$$

$$(or) N(E) dE = \frac{\pi}{2} \times \frac{1}{2} \times \left[ \frac{8ma^2}{h^2} \right]^{\frac{3}{2}} \times E^{\frac{1}{2}} dE$$

Pauli's exclusion principle states that 'two electrons of opposite spins can occupy each state'

$$\begin{aligned} \therefore N(E) dE &= 2 \times \frac{\pi}{4} \times \left[ \frac{8ma^2}{h^2} \right]^{\frac{3}{2}} \times E^{\frac{1}{2}} dE = \frac{\pi}{2} \times \left[ \frac{2 \times 2^2 m}{h^2} \right]^{\frac{3}{2}} \times a^3 \times E^{\frac{1}{2}} dE \\ \therefore N(E) dE &= \frac{4\pi}{h^3} \times (2m)^{\frac{3}{2}} \times a^3 \times E^{\frac{1}{2}} dE \end{aligned} \quad (10)$$

Density of states is number of energy states per unit volume

$$\begin{aligned} \therefore Z(E) dE &= \frac{N(E)dE}{V} = \frac{\frac{4\pi}{h^3} \times (2m)^{\frac{3}{2}} \times a^3 \times E^{\frac{1}{2}} dE}{a^3} \\ \therefore Z(E) dE &= \frac{4\pi}{h^3} \times (2m)^{\frac{3}{2}} \times E^{\frac{1}{2}} dE \end{aligned} \quad (11)$$

This is the density of charge carriers in the energy interval 'E' & 'E+dE'. It is used to calculate carrier concentration in metals and semiconductors.

### Carrier Concentration

Normally all the energy states are not filled. Hence the probability of filling the electron is done by Fermi distribution function (E). The number of electrons per unit volume (or) density of electrons is called carrier concentration

$$\text{Carrier concentration of electrons in energy bands } n_c = \int Z(E).F(E)dE$$

$$(or) n_c = \frac{4\pi}{h^3} \times (2m)^{\frac{3}{2}} \times \int_{\text{energyband}} E^{\frac{1}{2}} dE.F(E) \quad (12)$$

$$(or) n_c = \frac{4\pi}{h^3} \times (2m)^{\frac{3}{2}} \times \int_{\text{energyband}} E^{\frac{1}{2}} \frac{1}{1 + e^{\frac{E-E_f}{kT}}} dE \quad (13)$$

$n_c$  is known as carrier distribution function

### Fermi energy at 0 Kelvin

We know that 0 K maximum energy levels that can be occupied by the electron is called Fermi energy level ( $E_{f_0}$ )

(i.e.,) at 0 K for  $E < E_f$  and therefore  $F(E) = 1$

∴ Integrating equation 12 within the limits 0 to  $E_{f_0}$ , then the carrier concentration is

$$n_c = \int_0^{E_{f_0}} \frac{4\pi}{h^3} \times (2m)^{\frac{3}{2}} \times E^{\frac{1}{2}} dE. = \frac{4\pi}{h^3} \times (2m)^{\frac{3}{2}} \times \int_0^{E_{f_0}} E^{\frac{1}{2}} dE.$$

$$(or) n_c = \frac{8\pi}{3h^3} (2mE_{f_0})^{\frac{3}{2}} \quad (14)$$

$$(or) E_{f_0} = \left( \frac{h^2}{2m} \right) \times \left( \frac{3n_c}{8\pi} \right)^{\frac{2}{3}} \quad (15)$$

This is the Fermi energy of electrons in solids at absolute zero. Thus, Fermi energy of a metal depends only on the density of electrons of that metal.

When the temperature increases, Fermi level (or) Fermi energy slightly decreases

$$\text{It can be shown that } E_f = E_{f_0} \left[ 1 - \frac{\pi^2}{12} \left[ \frac{kT}{E_{f_0}} \right]^2 \right]$$

### Importance:

- (i) It is the level which separates the filled valence energy level and vacant conduction energy levels
- (ii) It determines the energy of the particle at any temperature

### Average energy of electrons at 0K

$$\text{Average energy of electron } (E_{avg}) = \frac{\text{Total energy of electrons at 0K } (E_T)}{\text{Number of Energy States at 0K } (n_c)} \quad (16)$$

Here, Total Energy of electrons at 0K = Number of Energy states at 0K x Energy of the electron

$$E_T = \int_0^{E_{f_0}} Z(E) dE \cdot E$$

$$\therefore E_T = \frac{4\pi}{h^3} \times (2m)^{\frac{3}{2}} \int_0^{E_{f_0}} E^{\frac{1}{2}} \cdot E \cdot dE$$

$$(or) E_T = \frac{4\pi}{h^3} \times (2m)^{\frac{3}{2}} \times \frac{E_{F_0}^{\frac{5}{2}}}{\frac{5}{2}}$$

$$(or) E_T = \frac{8\pi}{5h^3} \times (2m)^{\frac{3}{2}} \times E_{F_0}^{\frac{5}{2}} \quad (17)$$

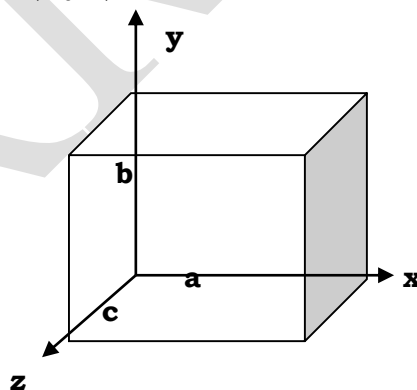
Substituting Eqn (13) & (15) in (14), we get

$$E_{Avg} = \frac{\frac{8\pi}{5h^3} \times (2m)^{\frac{3}{2}} \times E_{F_0}^{\frac{5}{2}}}{\frac{8\pi}{3h^3} (2m)^{\frac{3}{2}} \times E_{F_0}^{\frac{3}{2}}} = \frac{3}{5} E_{F_0}^{\frac{5}{2}} - E_{0F}^{\frac{3}{2}}$$

∴ The average energy of electron at 0K is  $E_{Avg} = \frac{3}{5} E_{f_0}$

**4. Derive an expression for particle in three dimensional box. What are degenerate and non-degenerate states?**

The Solution of one dimensional potential box can be extended for a three dimensional potential box. Here the particle can move in any direction in space. Hence instead of one quantum number 'n' three quantum numbers  $n_x, n_y, n_z$  are considered corresponding to the three coordinating axis (x,y,z)



**Three dimensional potential box.**

If a,b,c, are the length of the box as shown in figure along x,y,z axis ,then the energy of the particle  $E_n = E_x + E_y + E_z$

$$\text{i.e., } E_{n_x, n_y, n_z} = \frac{n_x^2 h^2}{8ma^2} + \frac{n_y^2 h^2}{8mb^2} + \frac{n_z^2 h^2}{8mc^2}$$

For a perfect cubic box  $a = b = c$

$$\text{Energy Eigen value is } E_{n_x, n_y, n_z} = \frac{h^2}{8m} [n_x^2 + n_y^2 + n_z^2] \quad (1)$$

The corresponding normalized wave function of an electron in a cubical box can be rewritten as

$$\psi_{n_x, n_y, n_z} = \sqrt{\frac{2}{a}} \times \sqrt{\frac{2}{a}} \times \sqrt{\frac{2}{a}} \cdot \sin \frac{n_x \pi x}{a} \cdot \sin \frac{n_y \pi y}{a} \cdot \sin \frac{n_z \pi z}{a} \quad (2)$$

### Degeneracy:

It is nothing but the quantum numbers having same Eigen value but different Eigen states. Such states and energy levels are called *Degenerate state*

Eg : if a state of quantum numbers are

$$n_x = 1 ; n_y = 2 ; \quad n_z = 1 \quad , \quad n_x = 1 ; n_y = 1 ; \quad n_z = 2 \quad \&$$

$$n_x = 2 ; n_y = 1 ; \quad n_z = 1 \quad \text{have same Eigen values as } n_x^2 + n_y^2 + n_z^2 = 6$$

$$E_{121} = E_{112} = E_{211} = \frac{6h^2}{8ma^2} \quad (3)$$

But the corresponding Eigen functions are

$$\left. \begin{aligned} \psi_{121} &= \sqrt{\frac{8}{a^3}} \cdot \sin \frac{\pi x}{a} \cdot \sin \frac{2\pi y}{a} \cdot \sin \frac{\pi z}{a} \\ \psi_{112} &= \sqrt{\frac{8}{a^3}} \cdot \sin \frac{\pi x}{a} \cdot \sin \frac{\pi y}{a} \cdot \sin \frac{2\pi z}{a} \\ \psi_{211} &= \sqrt{\frac{8}{a^3}} \cdot \sin \frac{2\pi x}{a} \cdot \sin \frac{\pi y}{a} \cdot \sin \frac{\pi z}{a} \end{aligned} \right\} \quad (4)$$

**Non – Degeneracy:**

For various combinations of quantum numbers if we have same energy Eigen value and Eigen function then each states and energy levels are called *Non – Degenerate state*

Eg: for  $n_x = 2$  ;  $n_y = 2$  ;  $n_z = 2$  we have  $E_{222} = \frac{12h^2}{8ma^2}$  &

$$\psi_{222} = \sqrt{\frac{8}{a^3}} \cdot \sin \frac{2\pi x}{a} \cdot \sin \frac{2\pi y}{a} \cdot \sin \frac{2\pi z}{a}$$