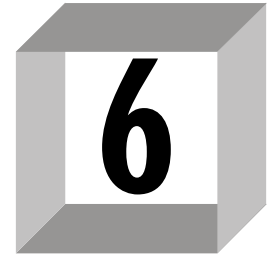# FREE ELECTRON THEORY 6

Classical theory (Free electron gas model): In 1900, Drude and Lorentz explained the properties of metals on the basis of free electron model. For free electron model, the following assumptions were made:

(a) A metal consists of positive ions core and valence electrons. The valence electrons move freely among these ion cores.

(b) Electrons and ions are bound by electrostatic attraction.

(c) The potential of these ion cores is assumed to be constant throughout the metal.

(d) The mutual repulsion between electrons is ignored.

(e) The behaviour of free electrons inside the metals is considered to be similar to that of atoms or molecules in perfect gas. These free electrons are also considered as free electron gas. There are some differences in the molecules of a perfect gas and electrons of free electron gas. The concentration of electrons in the gas is quite large as compared to the concentration of molecules in an ordinary gas. The free electrons are negatively charged while molecules are neutral. The valence electrons are also known as conduction electrons and they follow Pauli's exclusion principle. These electrons are responsible for conduction of electricity.

(f) Since, these electrons move in constant electrostatic field of ion cores, there potential energy remains constant and can be taken as zero. Thus, we can ignore the existence of ion cores. Hence, the total energy of free electrons is their kinetic energy. Also, since the movement of conduction electrons is restricted to within the crystal only, the potential energy of a stationary electron inside a metal is less than the potential energy of an identical electron just outside it.

(g) This difference of potential energies serves as a potential barrier and stops the inner electrons from leaving the surface of the metal. Thus, the movement of free electrons in a metal is equivalent to movement of a particle in a potential energy box.

Successes of classical free electron theory:

The free electron model was successful in explaining the following properties:

(1) Ohm's Law: It was successful in explaining Ohm's law. As free electrons move in random directions and do not constitute current until an electric field is applied across the metal. The electric field accelerates these electrons. During their motion, electrons suffer elastic collisions with the ions which slow down the speed of electrons. This collision gives rise to a steady state current. The magnitude of current is proportional to the voltage applied provided the temperature remains constant. This leads to Ohm's law.

(2) Wiedemann-Franz Law: As free electrons have the ability to move easily inside the metal, the metals exhibit high electrical and thermal conductivity. According to Wiedemann-Franz Law, the electronic contribution for electric to thermal conductivity of a metal is proportional to the temperature.

$\dfrac{\kappa}{\sigma} = LT$; (where L is Lorentz number $= 2.44 \times 10^{-8}$ WΩ K^{-2}

i.e., the ratio of electrical and thermal conductivities is constant for all metals at a constant temperature.

If σ be electrical conductivity and K be the thermal conductivity, then $\boxed{\dfrac{\sigma}{K} = \text{Constant}}$

(3) Free electron theory also explains the high lustre and complete opacity of metals. The opacity is due to the complete absorption of all the incident electromagnetic radiations by free electrons which are then set into forced oscillations.

Failures of classical free electron theory:

(1) The temperature dependence of resistivity could not be explained. Classical free electron theory predicted that the resistivity varies as $\sqrt{T}$ whereas actually it is found to vary linearly with temperature.

(2) This theory also failed to explain the heat capacity of solids.

(3) This theory also failed to explain paramagnetic susceptibility of the conduction electrons.

Sommerfeld's quantum theory:

In classical theory, Drude and Lorentz assumed classical Maxwell-Boltzmann statistics which allows all the free electrons to gain energy. This gives rise to a much higher value of heat capacity and paramagnetic susceptibility.

In 1927, Sommerfeld tried to solve the problem quantum mechanically using the Fermi-Dirac statistics. The possible electronic states in the potential energy box and the distribution of electrons in these states are then determined using quantum mechanics.

Free electron gas in one-dimensional box:

Let us consider an electron of mass m moving in a potential box of length L. This electron is bound to move within this box under the potential energy given by

$$\begin{cases} V(x) = 0, & \text{for } 0 < x < L \\ V(x) = \infty, & \text{for } x \leq 0 \text{ and } x \geq L \end{cases}$$
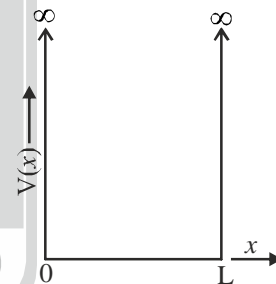
A one dimensional potential box

Let the wave function ψ_n be the eigen function of nth state. The energy eigenvalues E_n are given by Schrodinger equation

$$\frac{d^2\psi_n}{dx^2} + \frac{2m}{\hbar^2}(E_n - V)\psi_n = 0 \qquad \qquad \dots (1)$$

For the potential box, $V = 0$

Therefore, equation (1) becomes

$$\frac{d^2\psi_n}{dx^2} + \frac{2m}{\hbar^2} E_n \psi_n = 0 \qquad \qquad \dots (2)$$

Let us take $k^2 = \dfrac{2mE_n}{\hbar^2}$, thus equation (2) becomes

$$\frac{d^2\psi_n}{dx^2} + k^2 \psi_n = 0 \qquad \qquad \dots (3)$$

The general solution of the above equation is

$$\psi_n(x) = A\sin kx + B\cos kx \qquad \qquad \text{... (4)}$$

where A and B are constants.

The boundary conditions are

$$\left.\begin{array}{l} \text{at } x = 0, \quad \psi_n(0) = 0 \\ \text{at } x = L, \quad \psi_n(L) = 0 \end{array}\right\} \qquad \qquad \text{... (5)}$$

Using $x = 0$, $\psi_n(0) = 0$ equation (4) $\Rightarrow B = 0$ ... (6)

and using $x = L$, $\psi_n(L) = 0$, equation (4) $\Rightarrow \psi_n(L) = A\sin kL = 0$

$\Rightarrow \sin kL = \sin n\pi$

$\Rightarrow kL = n\pi \Rightarrow \boxed{k = \dfrac{n\pi}{L}} \qquad \text{where, } n = 1, 2, 3..... \qquad \text{... (7)}$

Thus the allowed wavefunctions are $\psi_n = A\sin\left(\dfrac{n\pi}{L}\right)x \qquad \qquad \text{... (8)}$

The allowed energy values are $E_n = \dfrac{\hbar^2 k^2}{2m} = \dfrac{\hbar^2}{2m}\left(\dfrac{n\pi}{L}\right)^2$ [using equation (7)]

$\Rightarrow E_n = \dfrac{n^2\hbar^2\pi^2}{2mL^2} = \dfrac{n^2 h^2}{8mL^2} \qquad \qquad \text{... (9)}$

Thus, $\boxed{E_n \propto n^2}$

From equation (9), it is clear that the allowed wavefunction $\psi_n(x)$ and the allowed energy values E_n exist only for integral values of n. This number n is called principal quantum number.

Thus the energy spectrum consists of discrete energy levels and the spacing of energy levels can be determined by n and L. The spacing between energy levels decreases with increasing L and it increases with increasing n. The plot of E_n vs. n is shown in the adjacent figure.
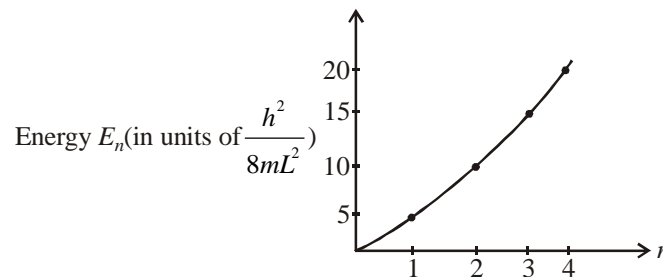
The constant A in equation (8) can be determined by using the orthonormality condition as follows

$$\int_0^L \psi_n^*(x)\psi_n(x)\, dx = 1 \qquad \qquad \text{... (10)}$$

The above condition states that the probability of finding an electron somewhere in the box (1-D) is unity.
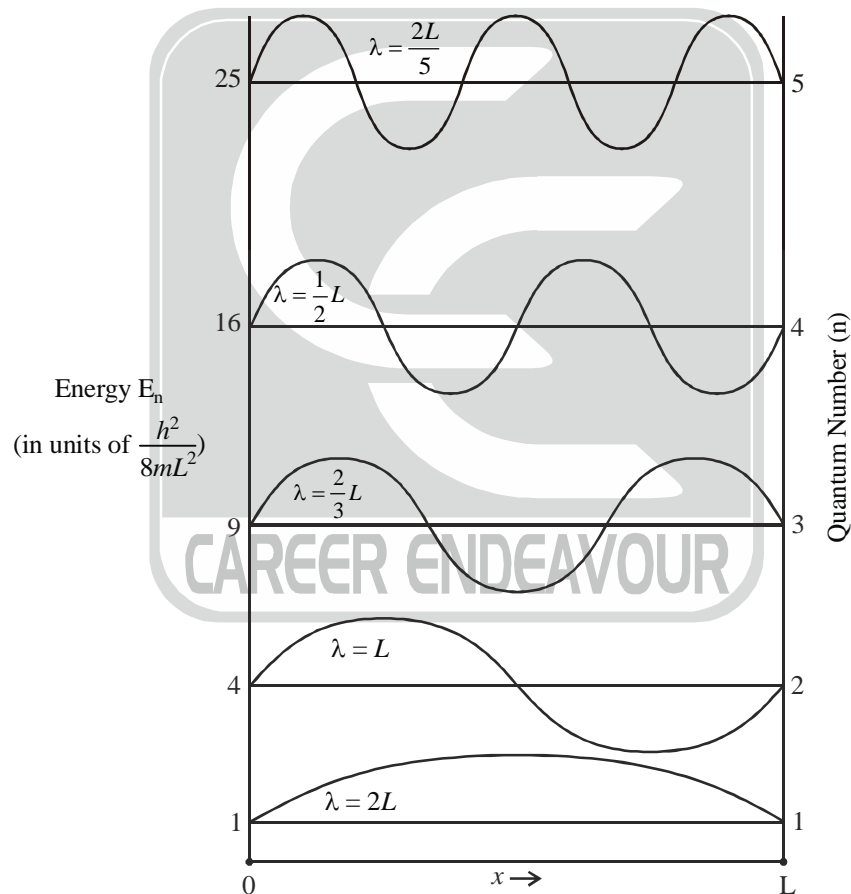
Thus,

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

$$\Rightarrow \frac{|A|^2}{2} \int_0^L \left\{ 1 - \cos \left(\frac{2n\pi}{L} x \right) \right\} dx = 1 \Rightarrow \frac{|A|^2}{2} \int_0^L dx = 1 \Rightarrow \frac{|A|^2}{2} [x]_0^L = 1 \Rightarrow \frac{|A|^2}{2} \cdot L = 1$$

$$\Rightarrow A = \sqrt{\frac{2}{L}} \qquad\qquad\qquad\qquad\qquad\qquad\qquad ... (11)$$

Thus equation (8) $\Rightarrow \psi_n(x) = \sqrt{\frac{2}{L}} \sin \left(\frac{n\pi}{L} x \right)$ $\qquad\qquad\qquad ... (12)$

The wave functions corresponding to $n = 1, 2, 3, 4$ and 5 are shown in the figure below.

In further sections, we will determine the Fermi energy and density of states.

Fermi energy:

The distribution of electrons among the various possible energy levels is governed by Pauli's exclusion principle which states that "no two electrons can have all their quantum numbers identical". Thus, each orbital or state can be occupied by at the most one electron. In a solid, an electron in a conduction electronic state has the quantum numbers n and m_s where n is the principal quantum number and m_s is the magnetic spin quantum number. Each set of values of n and m_s define a quantum state. For each value of n, m_s can take values, +1/2 and –1/2. This means that each energy level defined by the quantum number