CHAPTER – V

FREE ELECTRON THEORY OF METALS

5.1 DRUDE-LORENTZ'S CLASSICAL THEORY (FREE ELECTRON GAS MODEL)

Drude, in 1900, postulated that the metals consist of positive ion cores with the valence electrons moving freely among these cores. The electrons are, however, bound to move within the metal due to electrostatic attraction between the positive ion cores and the electrons. The potential field of these ion cores, which is responsible for such an interaction, is assumed to be constant throughout the metal and the mutual repulsion among the electrons is neglected. The behaviour of free electrons moving inside the metals is considered to be similar to that of atoms or molecules in perfect gas. These free electrons are, therefore, also referred to as *free electron gas* and the theory is accordingly named as *free electron gas model.* The free electron gas, however, differs from an ordinary gas in some respects. Firstly, the free electron gas is negatively charged whereas the molecules of an ordinary gas are mostly neutral. Secondly, the concentration of electrons in an electron gas is quite large as compared to the concentration of molecules in an ordinary gas. The valence electrons are also called the conduction electrons and obey the Pauli's exclusion principle. These electrons are responsible for conduction of electricity through metals. Since the conduction electrons move in a uniform electrostatic field of ion cores, their potential energy remains constant and is normally taken as zero, i.e., the existence of ion cores is ignored. Thus the total energy of a conduction electron is equal to its 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. This energy difference, V_o, serves as a potential barrier and stops the inner electrons from leaving the surface of the metal. Thus, in free electron gas model, the movement of free electrons in a metal is equivalent to the movement of a free electron gas inside a 'potential energy box' which, in one-dimensional case, is represented by a line as shown in Fig. 5.1.
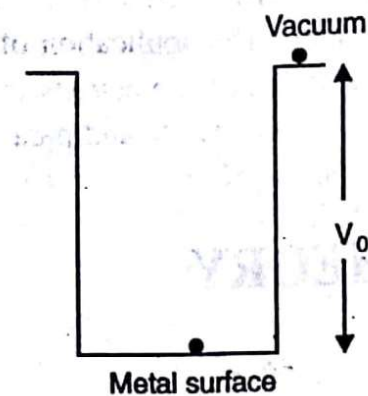
Vacuum

V_0

Metal surface

Fig. 5.1. *Metallic surface bounded by potential barrier V_0 which represents the difference in potential energy of a stationary electron present at the surface of the metal and just outside it (in vacuum).*

Based on the Drude's considerations that the electron gas behaves as a perfect gas, H.A. Lorentz postulated in 1909 that the electrons constituting the electron gas obey Maxwell-Boltzmann statistics under equilibrium conditions. The combined ideas of Drude and Lorentz constitue the *Drude-Lorentz theory*. As the theory is based on the classical ideas of Maxwell-Boltzmann statistics, it is called the classical theory.

The theory has been successfully applied to explain the various properties of metals. For example, it proves the validity of Ohm's law. The free electrons in a metal move in random directions and do not constitute a current until an electric field is applied across the metal which accelerates the electrons in a particular direction. The electrons, however, cannot be accelerated indefinitely. During their motion, the electrons suffer elastic collisions with the metal ions which slow down their speed. This gives rise to a steady state current of magnitude proportional to the voltage applied provided the temperature remains constant. This leads to Ohm's law. Also, as the free electrons can move easily, the metals exhibit high electrical and thermal conductivities. Moreover, since the electrons move freely inside the metals irrespective of the crystal structure, the ratio of the electrical conductivity, σ, to the thermal conductivity, K, should be constant for all metals at a constant temperature, i.e.,

$$\frac{\sigma}{K} = \text{constant}$$

This is called the *Wiedemann-Franz law* and has been realized in practice. The theory also explains the high lustre and complete opacity of metals. The opacity is due to absorption of all the incident electromagnetic radiations by free electrons which are then set into forced oscillations. The electrons return to their normal states by emitting the same amount of energy in all directions, thus producing metallic lustre.

Besides these successes, the theory also met with a number of failures. It correctly predicted the room temperature resistivity of various metals but the temperature dependence of resistivity could not be established accurately. The theory predicted that resistivity varies as $\sqrt{T}$ whereas actually it is found to vary linearly with temperature. The theory failed to explain the heat capacity and paramagnetic susceptibility of the conduction electrons. These

properties are based on interactions of free electrons with the external sources of energy which may be thermal or magnetic in nature. The application of Maxwell-Boltzmann statistics to this theory allows all the free electrons to gain energy which results in much higher values of heat capacity and para-magnetic susceptibility. As we shall describe later, the use of Fermi-Dirac or quantum statistics allows only a fraction of the total number of free electrons to gain energy and the values of heat capacity and paramagnetic susceptibility thus obtained match with the observed values. These are the principal achieve-ments of the Sommerfeld's theory. The classical theory is also unable to account for the occurrence of long mean free paths ($\sim 10^8$ to 10^9 interatomic spacings, or more than one centimetre) at low temperatures.

5.2 SOMMERFELD'S QUANTUM THEORY

Considering the free nature of valence electrons as assumed in the classical theory, Sommerfeld treated the problem quantum mechanically using the Fermi-Dirac statistics rather than the classical Maxwell-Boltzmann statistics. The possible electronic energy states in the potential energy box and the distribution of electrons in these states are then determined using quantum statistics. We describe the one-dimensional and three-dimensional cases separately.

5.2.1 Free Electron Gas in One-Dimensional Box

Consider an electron of mass m which is bound to move in a one-dimensional crystal of length L. The electron is prevented from leaving the crystal by the presence of a large potential energy barrier at its surfaces. Although the barriers extend over a few atomic layers near the surface, these are taken infinitely large for the sake of simplicity. The problem is identical to that of an electron moving in a one-dimensional potential box which is represented by a line and is bounded by infinite potential energy barriers as shown in Fig. 5.2. The potential energy within the crystal or box is assumed to be zero. Thus
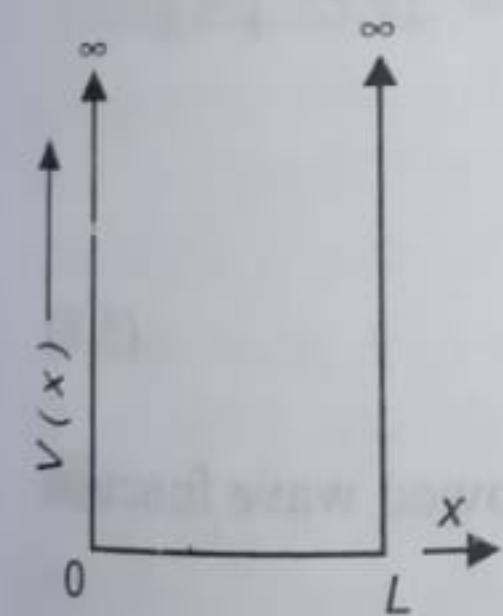
Fig. 5.2 One-dimension-al potential box bounded by infinite potential en-ergy barriers.

we have

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

$$V(x) = \infty \qquad \text{for } x \leq 0 \text{ and } x \geq L \qquad (5.1$$

The wave function ψ_n of the electron occupy-ing the nth state is determined from the solution of the Schrodinger equation, i.e.,

$$\frac{d^2 \psi_n}{dx^2} + \frac{2m}{\hbar^2}(E_n - V)\psi_n = 0 \qquad (5.$$

where E_n represents the kinetic energy of the electron in the nth state and V is its potential energy. Since $V = 0$ inside the box, Eq. (5.2) becomes

$$\frac{d^2\psi_n}{dx^2} + \frac{2m}{\hbar^2} E_n\psi_n = 0 \qquad (5.3)$$

The general solution to this equation is

$$\psi_n(x) = A \sin kx + B \cos kx \qquad (5.4)$$

where A and B are arbitrary constants to be determined from the boundary conditions and k is given by

$$k = \sqrt{\frac{2mE_n}{\hbar^2}} \qquad (5.5)$$

The boundary conditions are

$$\psi_n(0) = 0 \qquad \text{and} \qquad \psi_n(L) = 0 \qquad (5.6)$$

These conditions are based on the fact that at $x = 0$ and L, $V \to \infty$ and the product $V(x)\,\psi_n(x)$ in Eq. (5.2) also approaches infinity. Thus in order that the wave function $\psi_n(x)$ may be continuous, the kinetic energy E_n must also become infinite which is not feasible. Hence $\psi_n(x)$ must vanish for $x = 0$ and L.

For $x = 0$, Eq. (5.4) gives $B = 0$ and the solution (5.4) becomes

$$\psi_n(x) = A \sin kx \qquad (5.7)$$

Also, since $\psi_n(L) = 0$, Eq. (5.7) yields

$$\sin kL = 0$$

or

$$k = \frac{n\pi}{L} \qquad (5.8)$$

where $n = 1, 2, 3,....$ Thus the expression (5.7) for the allowed wave function becomes

$$\psi_n(x) = A \sin\left(\frac{n\pi}{L}\right)x \qquad (5.9)$$

The allowed energy values can be obtained from Eqs. (5.5) and (5.8) as

$$E_n = \frac{\hbar^2}{2m}\left(\frac{n\pi}{L}\right)^2 = \frac{n^2 h^2}{8mL^2} \qquad (5.10)$$
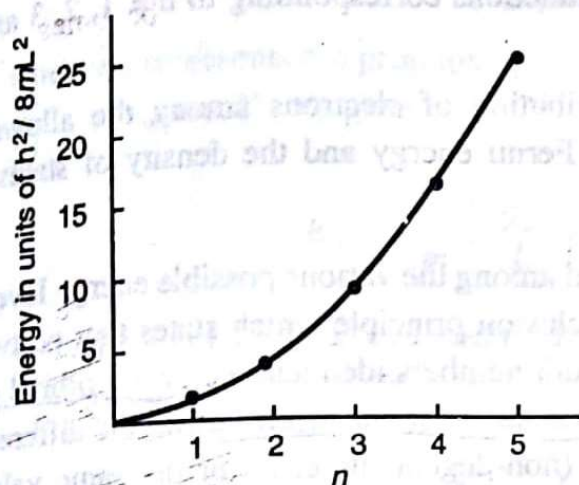
or

$$E_n \propto n^2$$

Fig. 5.3. E_n versus n for a one-dimensional crystal.

It is apparent from Eqs. (5.9) and (5.10) that the allowed wave functions $\psi_n(x)$ and the allowed energy values E_n exist only for integral values of n. The number n is called the quantum number. Hence the energy spectrum consists of discrete energy levels where the spacing between the levels is determined by the values of n and L. It decreases with increase in L. If L is of the order of a few centimetres, the energy levels form almost a continuum. But if L has atomic dimensions, the spacing between the levels becomes appreciable. The plot of E_n versus n is shown in Fig. 5.3.

The constant A in Eq. (5.9) is determined by using the condition that the probability of finding an electron somewhere on the line is unity, i.e.,

$$\int_0^L \psi_n^*(x)\psi_n(x)dx = 1$$

Using Eq. (5.9), we get

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

or

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

or

$$\frac{A^2}{2}\int_0^L dx = 1$$

or

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

Substituting it in Eq. (5.9), we get the normalized wave function as

$$\psi_n(x) = \sqrt{\frac{2}{L}}\,sin\left(\frac{n\pi}{L}x\right) \qquad (5.11)$$