

FREE ELECTRON MODEL OF METALS -2

Sommerfeld, in 1928 modified the free electron model on the basis of quantum statistics. The assumptions of sommerfeld model are:

1. The metal contains a large number of conduction electrons which are not completely free but partially so, and bound to the metal as a whole.
2. The forces between conduction electrons and the ion cores are neglected in the free - electron approximation, so that the electron within the metal is treated as free.
3. Due to their light mass and dense packing the electrons in metals may be considered as a gas under very high compression and hence thought of a degenerate gas or free electron gas.
4. The electrons are assumed to obey Pauli's exclusion principle and hence they obey Fermi-Dirac statistics. The important characteristics of Fermi-Dirac statistics are the dependence of distribution on temperature and the occurrence of zero point energy which is the consequence of Pauli's exclusion principle.

Assuming free electrons within a metal ($V_0=0$) and recalling schroedinger equation for this case we get allowed energy values of electrons within metal are

$$E_n = n^2 \pi^2 \hbar^2 / 2mL^2 \text{ and}$$

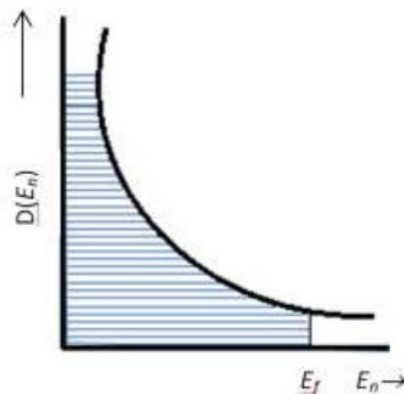
$$\text{Eigen function is } \Psi_n = (2/L)^{1/2} \sin(n\pi x/L)$$

As the electron can occupy two spin states there are two quantum states for a single electron and therefore the density of states for this case is

$$D(E_n) = dn/dE_n = 2 \cdot (L/\pi\hbar)(m/2E_n)^{1/2}$$

This result is depicted as

We may observe that the states are filled upto E_f called for me energy level



FREE ELECTRON MODEL OF METALS -1

The characteristics of metals are

1. They have electrical and thermal conductivities
2. Metals obey ohms law which states that current density J in steady state is proportional to electric field E implies $J = \sigma E$ where σ is electrical conductivity
3. The conductivity of metals decreases with increase in temperature
4. Metals obey Wiedemann-Franz law which states that 'the ratio of thermal and electrical conductivities at a given temperature is small for all metals and is proportional to temperature T '.

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

To explain the observed features of metals Drude in 1900 proposed the idea of free electrons in metals, later it was modified by Lorentz and then Drude and Lorentz put forward a theory to explain the observed properties of the metals on the basis of free electron theory of metals.

The assumptions are

- Each metal contains large number of free electrons which behave like the molecules of a perfect gas and are free to move throughout the whole volume of the metal.
- These free electrons collide with imperfections of lattice and among themselves.
- The collisions of electrons among themselves have no contribution to conductivities.
- The thermal and electrical conductivities are solely due to free electrons.
- In thermal equilibrium the free electrons obey classical statistics (Maxwell Boltzmann)
- This free electron model of metals leads to semi quantitative agreement with WF law

The shortcomings of Lorentz and Drude free electron theory are

- The electronic contribution to specific heats has serious disagreement with experimental results.
- The experimental fact that Paramagnetism of metals is nearly independent of temperature could not be explained by the theory
- The occurrence of long electronic mean free paths could not be explained.

These difficulties were resolved by Sommerfeld using Fermi-Dirac statistics rather than classical statistics.

BLOCH'S THEOREM

INTRODUCTION

The free electron model of metals assumes the conduction electrons within a metal move in a region of constant potential and so completely free to move about the crystal, restrained only by the surface of the crystal and the electrons obey Fermi-Dirac statistics.

This theory explained several electronic properties of metals eg., specific heat, Paramagnetism etc.,

There are several **limitations** to this theory as:

- It could not explain other properties of solids
- It could not distinguish between a metal and an insulator, the resistivity of a good conductor at low temperatures may be of the order of 10^{-10} ohm-meter and that of a good insulator may be as high as 10^{20} ohm-meter.
- It could not explain the behaviour of semiconductors.

Therefore the free electron theory must be modified

The free electron theory is modified by taking into account the periodic potential with the periodicity of the lattice. In one electron model of a solid, the periodic potential may be thought of as arising due to periodic charge distribution associated with ion cores situated on the lattice sites plus the constant contribution due to all other free electrons of the crystal. The latter contribution to the potential accounts, in an average sense, the interaction effects of a single electron with all others.

A one dimensional representation of a periodic potential with a period of lattice constant ' a ' is depicted as

Fig

The potential at the surface is interrupted; this is because the lattice spacing is not quite uniform at the surface.

In order to study the motion of an electron in a crystalline solid, we have to write the Schrödinger equation for the electron motion and find its solution under periodic boundary conditions. The solution of the Schrödinger equation was simplified by F. Bloch who realised the symmetry properties of the potential in which the electron in a crystalline solid moves. The main point of Bloch's analysis is that the boundary condition satisfied by the wave function in a periodic potential is different from the boundary condition for obtaining a bound state.

Bloch's Theorem: Statement

⇒ If an electron in a linear lattice of lattice constant 'a' characterised by potential function $V(x) = V(x+a)$ satisfies the Schrodinger equation

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

then the wavefunction $\psi(x)$ of electron with energy E obtained as a solution of Schrodinger equation are of the form:

$$\psi(x) = u_k(x) e^{\pm i k x}$$

with $u_k(x) = u_k(x+a)$

Proof:

The Schrodinger equation is

$$\frac{d^2\psi(x)}{dx^2} + \frac{2m}{\hbar^2} [E - V(x)] \psi(x) = 0 \quad \text{--- (1)}$$

Replacing 'x' by 'x+a' we get

$$\frac{d^2\psi(x+a)}{d(x+a)^2} + \frac{2m}{\hbar^2} [E - V(x+a)] \psi(x+a) = 0 \quad \text{--- (2)}$$

As $\frac{d}{d(x+a)} = \frac{d}{dx}$ & $V(x+a) = V(x)$

eq (2) can be written as

$$\frac{d^2 \psi(x+a)}{dx^2} + \frac{2m}{\hbar^2} [E - V(x)] \psi(x+a) = 0 \quad - (3)$$

This equation states that $\psi(x+a)$ is also a solution of Schrodinger equation with the same energy E . This suggests that

$\psi(x)$ and $\psi(x+a)$ are related as

$$\psi(x+a) = A \psi(x) \quad - (4) \quad \text{where } A \text{ is a complex number.}$$

Replacing 'a' by $x+a$ in eq (4) we get

$$\psi(x+2a) = A^2 \psi(x) \quad \text{Similarly by the process of induction}$$

$$\vdots$$

$$\psi(x+Na) = A^N \psi(x) \quad - (5)$$

If we impose the boundary condition $\psi(x+Na) = \psi(x)$, we get

$$A^N = 1 = e^{i2\pi p} \quad \text{with } p = 0, \pm 1, \pm 2, \pm 3, \dots$$

$$\therefore A = e^{i2\pi p/N} \quad - (6)$$

i.e., 'A' can assume 'N' different values $e^0, e^{2\pi i/N}, e^{4\pi i/N}, \dots, e^{2\pi i(N-1)/N}$

The next possible value of A with $p=N$ is same as first one with $p=0$. Thus only 'N' successive values of p are to be considered

$$\therefore \psi(x+a) = e^{i2\pi p/N} \psi(x) \quad - (7) \quad \left[\text{Substg in eq (4)} \right]$$

where p takes only integral values from 0 to N-1

(3)

It is more convenient to write $\psi(x)$ in terms of another function $u_k(x)$ defined by the equation

$$\psi(x) = e^{ikx} u_k(x) \quad \text{--- (8)}$$

$$\text{where } k = \frac{2\pi P}{Na} = \frac{2\pi P}{L} \quad \text{--- (9)}$$

where $L = Na$ is the length of the crystal

Rewriting eq(7) using eq(8) we get

$$e^{ik(x+a)} u_k(x+a) = e^{i2\pi P/N} e^{ikx} u_k(x)$$

$$\Rightarrow e^{ikx} u_k(x+a) = e^{i2\pi P/N} u_k(x) \quad \text{--- (10) (cancelling } e^{ikx} \text{ on either side)}$$

$$\text{using } k = \frac{2\pi P}{Na} \text{ we get } \frac{2\pi P}{N} = ka$$

Substituting this in eq(10)

$$\cancel{e^{ikx}} u_k(x+a) = \cancel{e^{ikx}} u_k(x) \quad \text{(RHS)}$$

$$\Rightarrow \underline{u_k(x+a) = u_k(x)} \quad \text{--- (11)}$$

Hence proved.

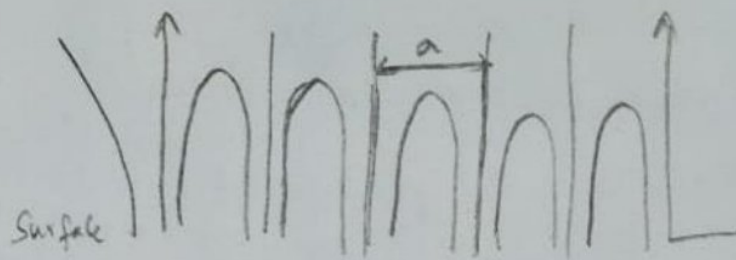
$$\psi(x) = e^{ikx} u_k(x) \quad \text{is equivalent to plane wave}$$

modulated by a function $u_k(x)$ with the periodicity of the lattice

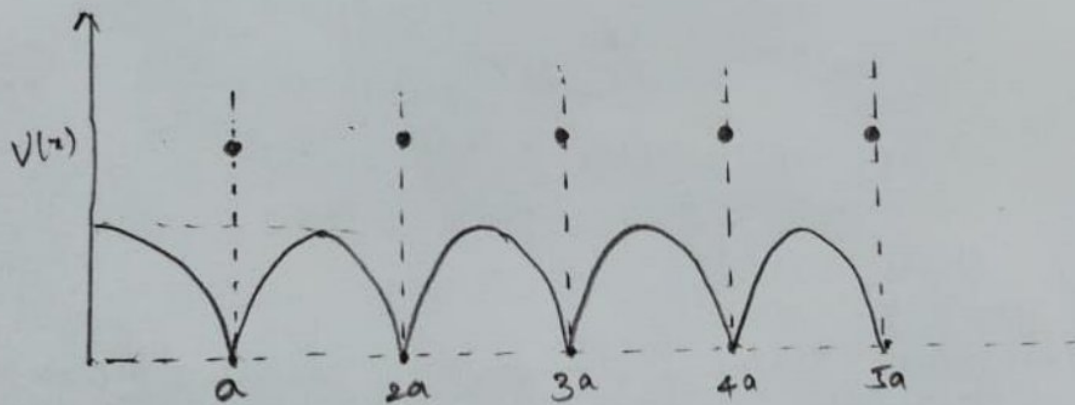
These functions are called Bloch functions & the Bloch theorem

Summary is $\psi(x)$ can be written as e^{ikx} and a periodic fn $u_k(x)$

(A)



Representation of the potential within a perfectly periodic crystal lattice of lattice constant a with surface barriers



potential in a Crystalline solid

Density of Energy States : It is given by the number of available electron states per unit volume per unit energy range at a certain energy level E .

To evaluate the density of states, first of all, we should find the no. of electron energy states occupying between E and $E + dE$.

Number of Energy States

Consider a specimen of a metal & let it be in a cube shape of side ' L '. Within the volume of the specimen, the electrons are free to move. These electrons obeying Pauli's Exclusion principle is called Fermi gas. Since the electrons are confined inside the cube, their wave properties limit the energy values.

Recalling, the Schrodinger equation to the electron motion in the 3-dims reveals that the electron energy is quantized. The quantized values of energy is given by

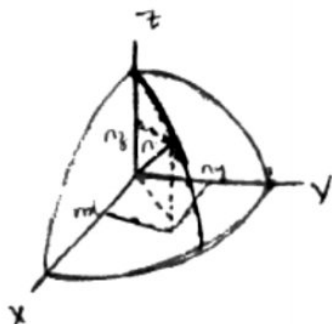
$$E = \frac{h^2}{8mL^2} (n_x^2 + n_y^2 + n_z^2) \quad \text{--- (1)}$$

The state of a free electron is determined by the four quantum numbers n_x, n_y, n_z and spin quantum number $m_s = \pm 1/2$.

From (1) it follows that the energy of an electron is determined by the sum of the squares of quantum nos. We get same value of energy for different combinations of these '3' quantum nos. Each set corresponds to a specific energy state (Energy level) E .

Density of Energy States : It is given by the number of

we therefore represent a quantum state by a point in quantum number space. Quantum number space is an imaginary state where the values of Quantum nos are denoted along the 3 axes respectively



In such a space, a radius vector 'n' may be drawn from the origin of the co-ordinate system to a point (n_x, n_y, n_z) where

$$n^2 = n_x^2 + n_y^2 + n_z^2 \quad \text{--- (2)}$$

All points on the surface of sphere of radius 'n' will have same energy. And all points within the sphere represent quantum states with energies smaller than E.

So, the number of states within a sphere of radius n = Vol. of sphere

$$= \frac{4\pi}{3} n^3$$

Since quantum nos can have only positive integer values, the n-values can only be defined in the positive octant of the sphere

→ Number of energy states within one octant of the sphere of radius n

$$= \frac{1}{8} \times \frac{4\pi}{3} n^3 \quad \text{--- (3)}$$

→ Similarly the no. of energy states within one octant of a sphere of radius $(n+dn)$ corresponding to energy $(E+dE)$

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

∴ The no. of energy states having energy values between E and $E + dE$

is given by
$$N(E)dE = \frac{1}{8} \left[\frac{4\pi}{3} (n + dn)^3 \right] - \frac{1}{8} \left[\frac{4\pi}{3} n^3 \right] \approx \frac{\pi}{6} (3n^2 dn)$$

neglecting higher powers of dn

∴ $N(E)dE = \frac{\pi}{2} n^2 dn$ — (5)

Recalling eq (1) we have

$$E = \frac{h^2}{8mL^2} (n_x^2 + n_y^2 + n_z^2) = \frac{n^2 h^2}{8mL^2}$$

$$n^2 = \frac{8mL^2}{h^2} E \quad \text{--- (6)} \quad \text{or } n = \left(\frac{8mL^2}{h^2} \right)^{1/2} E^{1/2}$$

Differentiating the eq. (6) we get

$$2n dn = \frac{4mL^2}{h^2} dE \quad \text{--- (7)}$$

$$\Rightarrow N(E)dE = \frac{\pi}{2} n^2 dn = \frac{\pi}{2} n (2n dn) = \frac{\pi}{2} \left(\frac{8mL^2}{h^2} \right)^{1/2} E^{1/2} \times \left(\frac{4mL^2}{h^2} \right) dE$$

$$\Rightarrow N(E)dE = \frac{\pi}{4} \left[\frac{8mL^2}{h^2} \right]^{3/2} E^{1/2} dE \quad \text{--- (8)}$$

Since there exist 2 spin states for an electron and as per Pauli's exclusion principle, 2 electrons of opposite spin can occupy each state. Hence, the no. of energy states available for electron to occupy is double the above value & so

$$\begin{aligned} N(E)dE &= \frac{\pi}{2} \left[\frac{8mL^2}{h^2} \right]^{3/2} E^{1/2} dE \\ &= \frac{4\pi}{h^3} (2m)^{3/2} L^3 \cdot E^{1/2} dE = \frac{4\pi}{h^3} (2m)^{3/2} V \cdot E^{1/2} dE \end{aligned}$$

where Volume $V = L^3$

Now density of states is given by

$$Z(E)dE = \frac{N(E)dE}{V} = \frac{4\pi}{h^3} (2m)^{3/2} E^{1/2} dE$$

Note: $Z(E)$ is independent of dimensions (L) of the potential box.