

ELECTRICAL PROPERTIES OF MATERIALS

**2.3 Quantum Free Electron Theory**

The drawbacks of classical free electron theories were removed by **Sommerfeld in 1928**. Quantum concepts are used in classical theory and hence it is known as quantum free electron theory.

He applied Schrodinger's wave equation and De-Broglie's concept of matter waves to obtain the expression for electron energies. He substituted the quantum statistics of Fermi-Dirac in place of the classical statistics and hence, it is known as the quantum free electron theory.

**Basic assumptions of Quantum free electron theory**

- The electrons are considered as free electron gas.
- The electrons possess wave nature.
- Free electrons obey Fermi-Dirac statistics and Pauli's exclusion principle.
- The free electron is fully responsible for electrical conduction.
- The allowed energy levels of an electron are quantized.
- The correct values of electrical conductivity, thermal conductivity, specific heat, optical absorption, ferromagnetic susceptibility are determined by quantum free electron theory of solids.

**Merits of Quantum theory**

- ❖ In this theory, the electrons are treated quantum mechanically rather than classically.
- ❖ Quantum theory successfully explains the ohm's law.
- ❖ It explains the electrical conductivity, thermal conductivity, photoelectric effect, Compton effect and specific heat capacity of metals.

**Demerits of Quantum theory**

- ❖ It fails to explain the classification between metals, semiconductors and insulators.
- ❖ It fails to give the reason for positive value of Hall coefficient.
- ❖ It can't be able to explain the transport properties of metals.

**2.3.1. Particle in a Three dimension box:**

The solution of one dimension potential well is extended for a three dimensional potential box.

In a three dimensional potential box the particle can move in any direction .so we use three quantum numbers  $n_x, n_y$  and  $n_z$  to the three coordinate axes namely x,y and z respectively.

If a,b,c are the lengths of the box along x,y and z axes then,

$$E_{n_x, n_y, n_z} = \frac{n_x^2 h^2}{8m a^2}$$

If a= b = c as for a cubical box then

$$E_{n_x, n_y, n_z} = \frac{h^2}{8ma^2} [ n_x^2 + n_y^2 + n_z^2 ] \text{-----(1)}$$

The corresponding normalized wave function is

$$\begin{aligned} \Psi_{n_x, n_y, n_z} &= \sqrt{\left(\frac{2}{a}\right)}\sqrt{\left(\frac{2}{a}\right)}\sqrt{\left(\frac{2}{a}\right)} \sin \frac{n_x \pi x}{a} \sin \frac{n_y \pi y}{a} \sin \frac{n_z \pi z}{a} \\ &= \sqrt{\left(\frac{8}{a^3}\right)} \sin \frac{n_x \pi x}{a} \sin \frac{n_y \pi y}{a} \sin \frac{n_z \pi z}{a} \text{-----(2)} \end{aligned}$$

From the equations (1), (2) we understand that several combinations of the three quantum numbers( $n_x, n_y, n_z$ ) lead to different energy eigen values and eigen function.

**2.3.2. Degenerate states:**

For several combinations of quantum numbers, we have the same energy eigen value but different eigen function. Such a state of energy levels is called degenerate state.

The three combinations of quantum numbers (1,1,2), (1,2,1) and (2,1,1) which give the same Eigen value but different Eigen functions are called 3- fold degenerate state.

**Example:**

If  $(n_x, n_y, n_z)$  is (1,1,2), (1,2,1) and (2,1,1)

Then

$$E_{112} = \frac{h^2}{8ma^2} ( 1^2 + 1^2 + 2^2 ) = \frac{6h^2}{8ma^2}$$

$$E_{121} = \frac{6h^2}{8ma^2}$$

$$E_{211} = \frac{6h^2}{8ma^2}$$

The corresponding wave functions are

$$\Psi_{112} = \sqrt{\left(\frac{8}{a^3}\right)} \sin \frac{\pi x}{a} \sin \frac{\pi y}{a} \sin \frac{2\pi z}{a} \dots$$

$$\Psi_{121} = \sqrt{\left(\frac{8}{a^3}\right)} \sin \frac{\pi x}{a} \sin \frac{2\pi y}{a} \sin \frac{\pi z}{a} \dots$$

$$\Psi_{211} = \sqrt{\left(\frac{8}{a^3}\right)} \sin \frac{2\pi x}{a} \sin \frac{\pi y}{a} \sin \frac{\pi z}{a} \dots$$

