DEPARTMENT OF PHYSICS AND NANOTECHNOLOGY
SRM INSTITUTE OF SCIENCE AND TECHNOLOGY

Introduction to Classical Free Electron Theory & Quantum Free Electron Theory

Free Electron Theory

- The electron theory of materials is to explain the structure and properties of solids through their electronic structure.

- It also gives information about bonding in solids, energy levels in metals and cohesive & repulsive forces in metals.

Development of Free Electron Theory

- **The Classical free electron theory** [Drude and Lorentz]

It is a macroscopic theory, through which free electrons move in lattice and it obeys the laws of classical mechanics.

Classical Free Electron Theory of Metals

- **The Quantum free electron theory** [Sommerfeld Theory]

It is a microscopic theory, according to this theory the electrons in lattice moves in a constant potential and it obeys law of quantum mechanics.

- **Brillouin Zone Theory [Band Theory]**

Bloch developed this theory in which the electrons move in a periodic potential provided by periodicity of crystal lattice. It explains the mechanisms of conductivity, semiconductivity on the basis of **energy bands** and hence band theory.

The Classical Free Electron Theory

According to kinetic theory of gases in a metal, Drude assumed **free electrons are as a gas of electrons**.

Drude Theory

This theory initially proposed by Drude in 1900,and it's the first theory to explain the electrical conduction in conducting materials and reveals that free electrons are responsible for the electrical conduction.

Free electrons

In certain metals especially in Cu, Ag and Al valence electrons are so weakly attached to the nuclei they can be easily removed or detached such electrons are called as free electrons.

But all the valence electrons in the metals are not free electrons.

Classical Free Electron Theory of Metals

Concept of Classical Free electron Theory

- According to this theory, metals consists of positive ions fixed in lattice and negative ions wander freely within the boundaries of the metal.
- As they are responsible for conductivity called as **Conduction electrons**
- **This cloud of free electrons are called as electron gas**
- They differ from ordinary gas in two aspects

1. Free electron gas is charged while molecules of ordinary gases are neutral
2. Concentration of electron is > ordinary gas concentration

Classical Free Electron Theory of Metals

Lorentz in 1900, suggested that free electrons are treated as perfect gas. He used Maxwell-Boltzmann statistics to the electron gas with following assumptions:

1. Mutual repulsion between the **negatively charged electrons** are neglected
2. Potential field due to **positive ions** within the crystal is assumed to be constant everywhere.

Electrons motion in the absence of electric field:

1. Possess elastic collision
2. Net displacement in any direction is zero
3. The neglect of electron–electron interaction between collisions is known as the "*independent electron approximation*

Classical Free Electron Theory of Metals

Electrons motion in presence of electric field:

1. In presence of electric field the equilibrium condition disturbed and the free electrons acquire some energy from electric field.
2. The electrons cannot be accelerated indefinitely due to the collisions of electrons with lattice ions.
3. **Drift:**

The net movement of electrons due to an applied electric field is called drift.

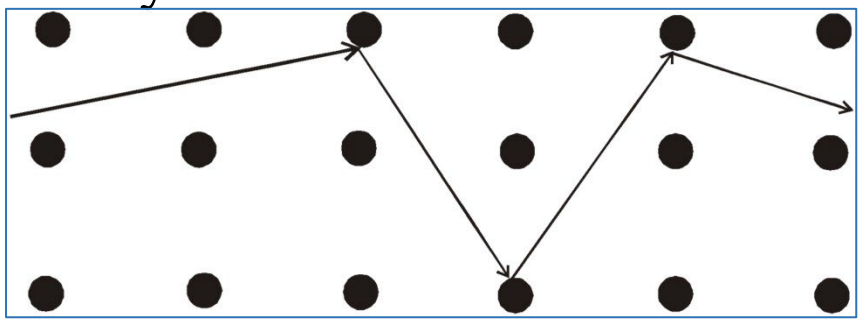
4. **Drift velocity**

In the presence of externally applied electromagnetic fields, the electrons acquire some amount of energy from the field and are directed to move towards higher potential. As a result, the electrons acquire a constant velocity known as *Drift velocity* V_d.

Classical Free Electron Theory of Metals

The time 'τ' is known as the relaxation time and it is defined as the time taken by an electron between two successive collisions. That relaxation time is also called *mean free time* [or] *collision time.*

Electrons are assumed to achieve **thermal equilibrium with their surroundings only through collision**. These collisions are assumed to maintain local thermodynamic equilibrium in a particularly simple way.



Trajectory of a conduction electron

Classical Free Electron Theory of Metals

Success of classical free electron theory:

(1) It verifies Ohm's law.

(2) It explains the electrical and thermal conductivities of metals.

(3)It derives Wiedemann – Franz law. (i.e., the relation between electrical conductivity and thermal conductivity)

(4) It explains optical properties of metals.

Classical Free Electron Theory of Metals

Drawbacks of classical free electron theory:

- The phenomena such a photoelectric effect, Compton effect and the black body radiation couldn't be explained by classical free electron theory.
- Cannot explain the electrical conductivity of semiconductors and Insulators.
- Ferromagnetism cannot be explained by theory.

QUANTUM FREE ELECTRON THEORY

Classical free electron theory could not explain many physical properties.

In 1928, Sommerfield developed a new theory applying quantum mechanical concepts and Fermi-Dirac statistics to the free electrons in the metal. This theory is called **quantum free electron theory.**

Classical free electron theory permits all electrons to gain energy. **But quantum free electron theory permits only a fraction of electrons to gain energy**.

Quantum Free Electron Theory of Metals

According to Quantum mechanics moving particles has some sort of wave motion

Then wavelength $\lambda = h/p$ (De-Broglie wavelength)

To characterize moving particle having wave motion-(ψ)-wavefunction is introduced

According to quantum theory of free electrons energy of a free electron is given by

$E_n = n^2h^2/8mL^2$

•According to quantum theory of free electrons the electrical conductivity is given by

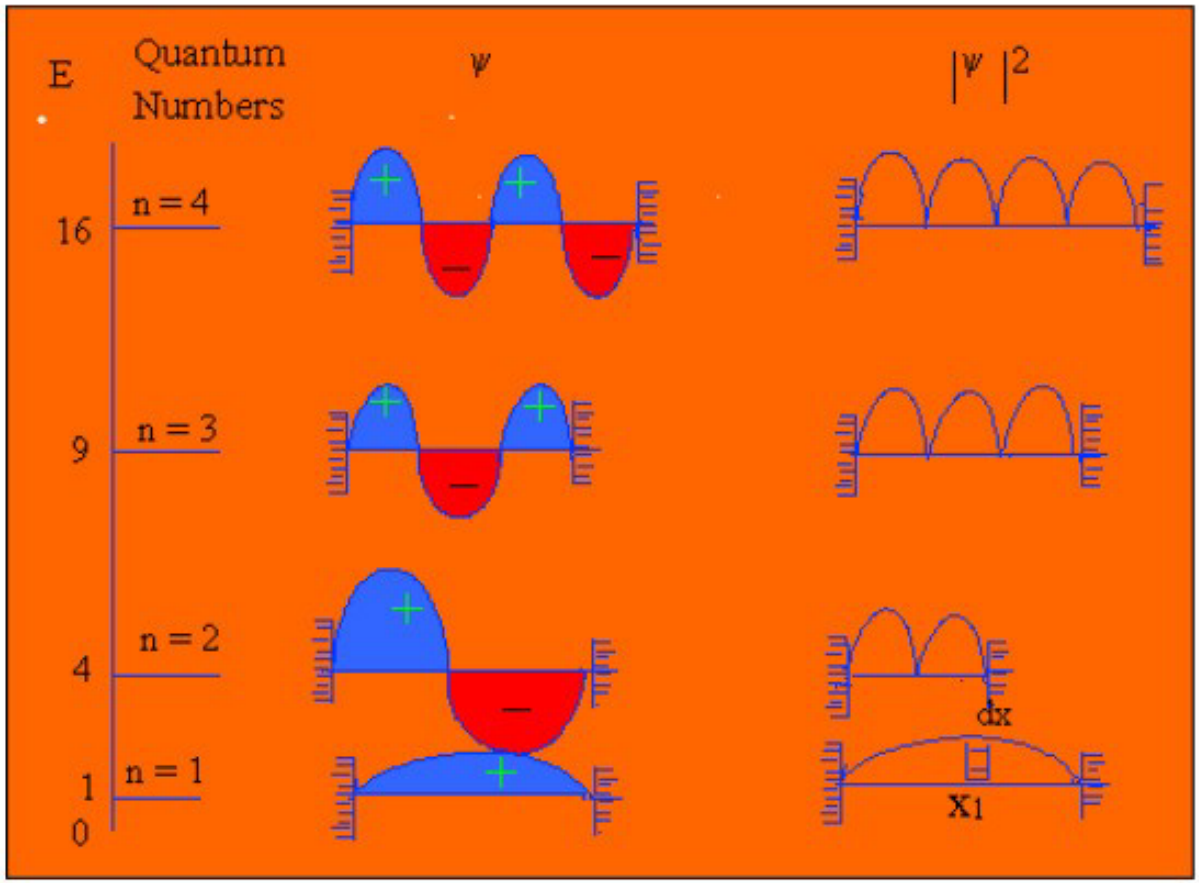
$\sigma = ne^2T/m$

Therefore,

$$E = E_n = n^2 h^2 / 8mL_x^2 \qquad (2.6)$$

where we have used the fact that $\hbar = h / 2\pi$ and associated E with a subscript n to indicate the n^{th} energy level with quantum number n.

The function $\sin (n\pi x / L_x)$ is called an eigenfunction and the energy $E_n = n^2 h^2 / 8mL_x^2$ is called an eigenvalue. The eigenvalues and the eigenfunctions for this problem for value of n = 1, 2, 3 and 4 are shown in the accompanying figure. The values of the square of the eigenfunctions (which are also the wavefunctions in this case) are also shown in the figure.



Quantum Free Electron Theory of Metals

MERITS OF QUANTUM FREE ELECTRON THEORY

1.It successfully explains the electrical and thermal conductivity of metals.

2. We can explain the Thermionic phenomenon.

3.Temperature dependence of conductivity of metals can be explained by this theory.

4. It can explain the specific heat of metals.

5. It explains magnetic susceptibility of metals.

DEMERITS OF QUANTUM FREE ELECTRON THEORY

1. It is unable to explain the metallic properties of exhibited by only certain crystals

1. Failed to give difference of metals/semiconductors/ insulators

3. It is unable to explain why the atomic arrays in metallic crystals should prefer certain structures only

Classical vs Quantum free electron theory

According to classical theory, the free electrons in a metal have random motions with equal probability in all directions.

But according to quantum theory, the free electrons occupy different energy levels, up to Fermi level at 0 K.

So, they possess different energies and hence they possess different velocities.