QUANTUM MECHANICS AND FREE ELECTRON THEORY

Introduction

The Classical Theory

➤ The **classical theory** was developed by *Drude* and *Lorentz* in 1900.
➤ According to this theory, the metals containing free electrons obey the laws of classical mechanics such as *electron can roam anywhere in the metal*, they obey *kinetic theory of gases* and *treated as free electron gas*.
➤ This theory explained successfully, *the motion of macroscopic particles* which can be observed either directly or through microscopes.
➤ This theory also explained successfully the phenomena such as o*hm's law, electrical & thermal conductivities* and *optical properties*
➤ But failed in explaining the phenomena such as *Photoelectric Effect, Compton Effect* and *Black body radiation.* Then the necessity of development of new theory (quantum theory) was arisen.

The Quantum Theory

➤ The **quantum theory** was developed by *Max Plank* in the early of 20th century.
➤ In 1928, Summerfield explained the quantum free electron theory with the help of laws of quantum mechanics such as *electrons move only in the stationary orbital* and *their motion is conditional.*
➤ As per this theory Einstein could be explained the *phenomenon of Photoelectric Effect* and proved that *light exhibits dual nature.*
➤ Hence it is proved that light exhibits dual nature and which motivated towards the existence of **matter waves**.
➤ Though quantum theory explained several phenomena, it is failed in explaining the classification of *solid into metals, semiconductors* and *insulators.*
➤ Therefore, the necessity of new theory was arisen again to explain this phenomenon (Band theory of solids).

The Band Theory

➤ The **band theory** of solids was developed by *Bloch* in 1928.
➤ According to this theory, *the free electrons move in a periodic potential* proved by the crystal lattice.
➤ This theory successfully explained the *phenomenon of classification of metals, semiconductors and insulators.*

Matter Waves

Particle: - If a certain amount of quantity occupies a certain space then it becomes a particle. The particle has mass. As it is occupying a certain space, its position can be identified. When its position changes then it has velocity. Due to its mass and velocity, the particle has momentum and energy.

From all these items it is clear that the *characteristic of a particle* are:

- Mass
- Velocity
- Momentum
- Energy.

Wave: - A wave is nothing but spreading of disturbance in a medium.

Thus the *characteristics of waves* are:

- Amplitude
- Time period
- Frequency
- Wavelength
- Phase
- Intensity.

To explain the phenomenon which involves both particle and wave nature, we use Plank's quantum theory.

According to the quantum theory, *the emission of radiation will be in the form of photons.*

Photon: - A photon has a velocity of light and mass in motion.

Thus, it has momentum and energy. That means a photon behaves as a particle. The energy of a photon is given by:-

$$E = h\vartheta$$

Where, ϑ is the frequency of radiation.

Along with frequency, other parameters attribute a wave nature to photon. This concept of dual nature of radiation prompted de Broglie to suggest the idea of matter waves.

de-Broglie Hypothesis

The dual nature of light possessing both wave and particle properties was explained by combining Plank's expression for the energy of a photon $E = h\vartheta$ with Einstein's mass energy relation $E = mc^2$.

Where c is velocity of light

      h is Plank's constant

      m is mass of particle

$$\Rightarrow h\vartheta = mc^2$$

$$\Rightarrow \frac{hc}{\lambda} = mc^2 \quad (Since, \vartheta = c / \lambda)$$

$$\Rightarrow \lambda = \frac{h}{mc} = \frac{h}{p} \quad \text{(where } p \text{ is the momentum of particle)}$$

λ *is de-Broglie wavelength associated with a photon.*

de Broglie proposed the concept of matter waves, according to which a material particle of mass 'm' moving with velocity 'v' should be associated with de Broglie wavelength λ' given by

$$\left\| \lambda = \frac{h}{mv} = \frac{h}{p} \right\| \cdots\cdots \text{①}$$

The above equation represents de Broglie wave equation.

de-Broglie wavelength in terms of Kinetic Energy

The Kinetic Energy of a moving particle:

$$E = \frac{1}{2}mv^2$$

$$E = \frac{1}{2m}m^2v^2$$

$$E = \frac{p^2}{2m} \qquad (Since, p = mv)$$

$$\Rightarrow p = \sqrt{2mE}$$

$$\therefore \lambda = \frac{h}{\sqrt{2mE}}$$

The kinetic energy gain by the electron

Let us consider that an electron of mass m and charge e is accelerated through a potential difference of Frequency volts. The energy acquired by the electron is eV and is related to ½ mv^2, i.e. $E = \frac{p^2}{2m}$

$p = \sqrt{2mE} = \sqrt{2mVe}$ (Since, *E=Ve* where *V* is the velocity & *e* is the charge of an electron)

$$\therefore \lambda = \frac{h}{\sqrt{2mVe}} \text{ (From Equation ①)}$$

OR

$\Rightarrow$ ½ $mv^2 = eV$ (Since, *E=Ve* where *V* is the velocity & *e* is the charge of an electron)

$\Rightarrow mv^2 = 2eV \Rightarrow m^2 v^2 = 2meV$ (Multiplying both sides with *m*)

$\Rightarrow mv = \sqrt{2meV} \Rightarrow p = \sqrt{2meV}$

$\therefore \lambda = \frac{h}{\sqrt{2meV}}$ (From Equation ①)

Substituting the values of: $h = 6.625 \times 10^{-34}, m = 9 \times 10^{-31}$ and $e = 1.6 \times 10^{-19}$ in the above equation we get,

$$\Rightarrow \lambda = \frac{6.625 \times 10^{-34}}{\sqrt{2 \times 9 \times 10^{-31} \times V \times 1.6 \times 10^{-19}}} = \frac{12.26}{\sqrt{V}} \text{Å}$$

$$\therefore \lambda = \frac{1.226}{\sqrt{V}} nm$$

Properties of de Broglie waves

Since, $\lambda = \frac{h}{mv}$

1. Lighter the particle, greater is the wavelength associated with it.
2. Lesser the velocity of the particle, longer the wavelength associated with it.
3. For v = 0, $\lambda = \infty$. This means that only with moving particle, matter waves is associated.
4. Whether the particle is changed or not, matter waves is associated with it.
5. It can be proved that matter waves travel faster than light.
6. No single phenomena exhibit both particle nature and wave nature simultaneously.
7. The wave nature of matter introduces an uncertainty in the location of the particle & the momentum of the particle exists when both are determined simultaneously.

Wave Function

➢ Max Born in 1926 gave a satisfactory interpretation of the wave function Ψ associated with a moving particle.

➢ The quantity which varies periodically in the case of matter waves is called **wave function** (Ψ). The wave function gives the information about state of the system at a position 'r' and instant 't'.

➢ If the amplitude of the wave is large then probability of locations of the particle is large. If amplitude is *zero* then probability of finding the particle is *zero*.

Let, $\Psi = a + ib$

$\Rightarrow \Psi^* = a - ib$

$\Rightarrow \Psi\Psi^* = (a + ib)(a - ib) = a^2 + b^2$ (a & b are real functions)

Physical Significance and Limitations of wave functions

Max postulated that the square of the magnitude of the wave function $|\Psi|^2$ (or $\Psi\Psi^*$ if Ψ is complex), evaluated at a particular point represents the probability of finding the particle at the point. $|\Psi|^2$ is called the probability density and Ψ is the probability amplitude. Thus the probability of the particle within an element volume dt is $|\Psi|^2 d\tau$. Since the particle is certainly somewhere, the integral at $|\Psi|^2 d\tau$ over all space must be unity i.e.

$$\int_{-\infty}^{\infty} |\Psi|^2 d\tau = 1$$

A wave function that obeys the above equations is said to be normalized. An acceptable wave function should fulfill the following requirements (limitations)

i.   It must be finite everywhere.
ii. It must be single valued.
iii. It must be continuous and have a continuous first derivative everywhere.

1) It must be continuous and single value function.
2) The total probability of finding the particle is unity(Normalized).

$$\iiint_{-\infty}^{\infty} |\Psi|^2 dxdydz = 1$$

3) Ψ must be finite for all values of x,y,z.
4) Ψ must be single valued that is for each set of values x,y,z the wave function must have only one value.
5) Ψ must be continuous in all regions except where potential energy is infinite.
6) Ψ must be analytical. It possess continuous first order derivative.
7) Ψ vanishes at the boundaries.
8) A wave function satisfying the following condition is said to be *"orthogonal wave function"*.

$$\int_{-\infty}^{\infty} \Psi_i^* \Psi_j dx = 0$$

Schrodinger time independent and time dependent wave equations

Schrödinger's *Time Independent* Wave Equation

According to de-Broglie hypothesis, the particle in motion is always associated with a wave. To describe the motion of a particle in terms of its associated wave, Schrödinger derived a wave equation which is termed as *Schrödinger's wave equation*.

Consider a particle of mass *'m'* moving with velocity *'v'* along the x direction. It is associated with a wave. The displacement of a wave is given by the wave function Ψ.

Let Ψ(r,t) be the wave displacement for the de-Broglie waves at any location *'r'* at time *'t'*.

The differential equation of the wave motion in three dimensions is given by:

$$\nabla^2 \Psi = \frac{1}{v^2}\frac{\partial^2 \Psi}{\partial t^2} \quad \dots ①$$

where $\nabla^2 = \frac{d^2}{dx^2} + \frac{d^2}{dy^2} + \frac{d^2}{dz^2}$

The solution of the above equation is:

$$\Psi(r, t) = \Psi_0(r) e^{-i\omega t}$$

Differentiating twice with respect to 't', we get

$$\frac{\partial^2 \Psi}{\partial t^2} = -\omega^2 \Psi_0(r) e^{-i\omega t}$$

$$\frac{\partial^2 \Psi}{\partial t^2} = -\omega^2 \Psi(r, t)$$

Substituting in equation ①, we get

$$\nabla^2 \Psi = \frac{-\omega^2}{v^2} \Psi \ldots ②$$

We know that,

$$\omega = 2\pi\vartheta = \frac{2\pi v}{\lambda} \Rightarrow \frac{\omega}{v} = \frac{2\pi}{\lambda} \ldots ③$$

From equations ② & ③, we get

$$\nabla^2 \Psi = \frac{-4\pi^2}{\lambda^2} \Psi \qquad \Rightarrow \nabla^2 \Psi + \frac{4\pi^2}{\lambda^2} \Psi = 0$$

But $\lambda = \frac{h}{mv}$

$$\nabla^2 \Psi + \frac{4\pi^2 m^2 v^2}{h^2} \Psi = 0 \ldots ④$$

Let E and V are the total energy and potential energy then,

$$\frac{1}{2} mv^2 = E - V$$

$$m^2 v^2 = 2m(E - V)$$

Substituting m^2v^2 in equation ④, we get

$$\nabla^2 \Psi + \frac{8\pi^2 m}{h^2} (E - V)\Psi = 0$$

$$\boxed{\nabla^2 \boldsymbol{\Psi} + \frac{2m}{\hbar^2} (\boldsymbol{E} - \boldsymbol{V})\boldsymbol{\Psi} = 0} \qquad (\because \hbar = \frac{h}{2\pi})$$

Schrödinger's *Time Dependent* Wave Equation

Let us eliminate the total energy E from time independent wave equation. The wave function is given by:

$$\Psi(r, t) = \Psi_0(r)e^{-i\omega t}$$

Differentiating with respect to 't', we get

$$\frac{\partial \Psi}{\partial t} = -i\omega \Psi_0(r)e^{-i\omega t}$$

$$\frac{\partial \Psi}{\partial t} = -i(2\pi\vartheta)\Psi_0(r)e^{-i\omega t} \qquad (\because \omega = 2\pi\vartheta)$$

$$\frac{\partial \Psi}{\partial t} = -2\pi i\vartheta\Psi(r, t) \qquad (\because \Psi(r, t) = \Psi_0(r)e^{-i\omega t})$$

$$\frac{\partial \Psi}{\partial t} = \frac{-2\pi iE}{h}\Psi \Rightarrow \frac{\partial \Psi}{\partial t} = \frac{-iE}{\hbar}\Psi$$

$$E\Psi = \frac{-\hbar}{i}\frac{\partial \Psi}{\partial t} = \frac{-i\hbar\partial\Psi}{\partial t}$$

Substituting into Schrodinger's independent wave equation, we get

$$\nabla^2\Psi + \frac{2m}{\hbar^2}\left(i\hbar\frac{\partial \Psi}{\partial t} - V\Psi\right) = 0$$

$$\nabla^2\Psi = -\frac{2m}{\hbar^2}\left(i\hbar\frac{\partial \Psi}{\partial t} - V\Psi\right)$$

$$-\frac{h^2}{2m}(\nabla^2\Psi) = i\hbar\frac{\partial \Psi}{\partial t} - V\Psi$$

$$\left\|\left(-\frac{h^2}{2m}\nabla^2 + V\right)\Psi = i\hbar\frac{\partial \Psi}{\partial t}\right\|$$

Hamiltonian $\hat{H} = \left(-\frac{h^2}{2m}\nabla^2 + V\right)$

$i\hbar\frac{\partial \Psi}{\partial t}$ is called *Energy Operator* operated on Ψ

$$[\![\hat{H}\Psi = E\Psi]\!]$$

### Applications of Schrödinger's Equation:

1. **Binding Potential:**

   The potential which binds the particle to move in a particular region of a space is the Solution of a Schrodinger's equation for such a potential leads to discrete energy state of a particle. **Example:** Particle in a box

2. **Non-Binding Potential:**

   The potential which does not bind a particle to a particular region of a space, so that the particle can approach infinite distance so, discrete energy states are not obtained. **Example:** Stop Potential

Particle in a one dimensional box (wave function and allowed energy levels)

Consider a particle of mass '*m*' moving back and forth between the walls of a one dimensional box separated by a distance '*a*' as shown in fig. Let the particle travel only along the *x*-axis and is confined between $x = 0$ and $x = a$ by two infinitely hard walls so that the particle has no chance of penetrating them.
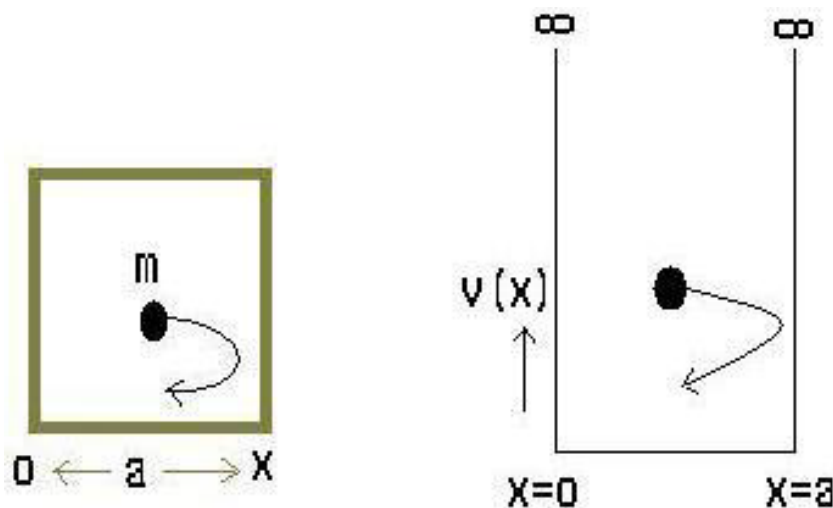
Thus, it does not lose energy when it collide the walls and its total remains constant. This box can be represented by a potential box of width '*L*' with potential walls of infinite height at $x = 0$ and $x = L$ so that the potential energy, V of the particle is infinitely high on both sides of the box and inside it, Frequency is uniform. Let us assume that V = 0 inside the box,

V(x) = 0, for 0 < x < L,

V(x) = ∞, for x ≤ 0 and x ≥ L

The Schrodinger's time independent wave equation can be written as

$$\frac{\partial^2 \Psi}{\partial x^2} + \frac{2m}{\hbar^2}(E - V)\Psi = 0$$

Inside the box $V=0$

So,

$$\frac{\partial^2 \Psi}{\partial x^2} + \frac{2m}{\hbar^2}E\Psi = 0$$

But $K^2 = \frac{2mE}{\hbar^2}$

$$\frac{\partial^2 \Psi}{\partial x^2} + K^2\Psi = 0$$

The general solution of above equation can be written as

$$\Psi(x) = A\sin(kx) + B\cos(kx)$$

A,B,k are constants and can be determined by boundary conditions:

i.   Where $x=0$ then the wave function $\Psi(0) = 0$
ii.   Where $x=L$ then the wave function $\Psi(L) = 0$

Applying first boundary condition

$$0 = A\sin 0 + B\cos 0$$

$$B = 0$$

$$\Psi(x) = A\sin(kx)$$

Applying second boundary condition

$$\sin kL = 0$$

$$kL = n\pi$$

$$k = \frac{n\pi}{L}$$

$$\Psi(x) = A\sin\frac{n\pi}{L}x$$

But $K^2 = \dfrac{2mE}{\hbar^2}$ $\Rightarrow$ $\dfrac{n^2\hbar^2}{L^2} = \dfrac{2mE}{\hbar^2}$

$$E_n = \frac{n^2 h^2}{8mL^2}$$

$$\|E_n \propto n^2\|$$

From normalized condition,

$$\int_0^L \left|\Psi^2\right| dx = 1$$

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

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

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

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

$$\frac{A^2}{2}[x]_0^L - \frac{A^2}{2}\left[\frac{\sin 2\left(\frac{n\pi}{L}x\right)}{\left(\frac{2n\pi}{L}\right)}\right]_0^L = 1$$

$$\frac{A^2}{2}L = 1 \qquad \Rightarrow A^2 = \frac{2}{L}$$

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

$$\left\|\Psi(x) = \sqrt{\frac{2}{L}}\sin\frac{n\pi}{L}x\right\|$$

Case 1: For $n=0$ $\Psi_0(x) = 0$, $E_0 = 0$, hence the motion at the electron is sustained.

Case 2 : For $n=1$, $\Psi_1(x) = \sqrt{\frac{2}{L}}\sin\left(\frac{\pi x}{L}\right)$, $E_1 = \frac{h^2}{8mL^2}$

For $n=2$, $\Psi_2(x) = \sqrt{\frac{2}{L}}\sin\left(\frac{2\pi x}{L}\right)$
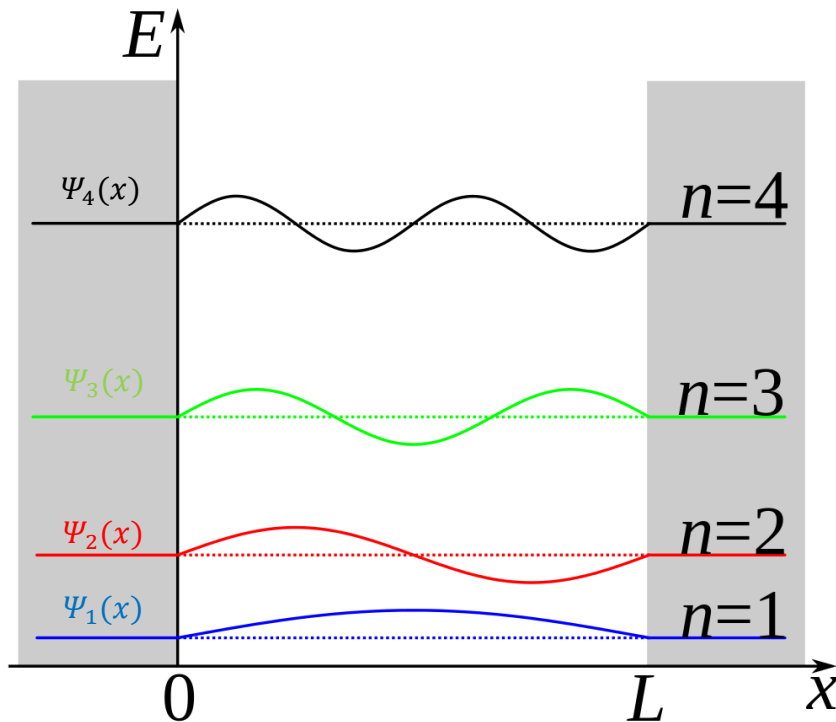
$$E_2 = \frac{4h^2}{8mL^2} = 4E_1$$

$$[\![E_2 = 4E_1]\!]$$

$\Psi_2(x)$ is maximum at quarter distance from either side of the box.

For $n=3$, $\Psi_3(x) = \sqrt{\frac{2}{L}}\sin\left(\frac{3\pi x}{L}\right)$

$$\left[\!\left[E_3 = \frac{9h^2}{8mL^2} = 9E_1\right]\!\right]$$

$\Psi_3(x)$ is maximum at exactly middle and one sixth distance from either side of the box.

Merits and demerits of classical <u>free electron theory</u>

Free Electron Theory

The physical properties of solid are governed by the valence electrons of atoms in a solid. The mobility of these valence electrons in a solid decides the electrical, thermal and magnetic properties of solid. To study these properties electron theories were proposed. These electron theories were used to explain the structure and properties of solids.

These theories are:-

i.   Classical Free electron theory
ii. Quantum Free electron theory
iii. Zone(Band) theory

According to free electron theory the free electrons available in the metal are responsible for its electrical conductivity based on classical mechanics. In order to overcome the drawbacks of classical free electron theory, Quantum free electron theory was developed based on quantum laws. Later band theory was developed to explain the various properties of metals.

Classical Free Electron Theory

➢ Classical free electron theory was proposed by Drude and Lorentz.
➢ According to this theory a metal is supposed to consists of +ve ions fixed in the lattice whose free electrons move freely and randomly in the metal like gas molecules in a vessel.
➢ When an electric field is applied the free electron experiences an electric force and gets accelerated. These accelerated electrons collide with the +ve ions losing some of their energy and acquires a constant velocity along the metal. This constant velocity of electrons is known as **drift velocity v_d**.
➢ The average distance travelled by the face electron between two successive collisions in the presence of applied fields is called **mean free path λ**.
➢ The time taken to travel mean free path λ is known as **mean free time** or **relation time** denoted by τ.

<u>Postulates of Classical Free electron theory</u>

1) In an atom electrons revolve around the nucleus
2) The valence electrons of atoms are free to move about the whole volume of the metal like molecules of perfect gas in a container and forms electron gas.
3) These free electrons moves in random directions and collide with positive ions fixed to the lattice. All collisions are elastic in nature.

4) The movement of electrons obeys laws of classical K.E. of the gas.
5) The electron velocity obeys Maxwell-Boltzmann distribution of velocities.
6) The free electrons moves in uniform potential field
7) When an electric field is applied to the metal the free electrons are accelerated in the direction opposite to the direction of applied field.

Electrical Conductivity

As shown in the Figure, let an electric field E is maintained between two ends of a metal of area of cross section A.

Force acting on the electron in electric field $F = -eE$,

where 'e' is a charge of an electron
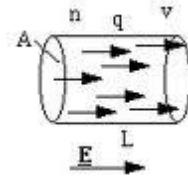
Then the acceleration of electron $a = \dfrac{Force}{mass} = \dfrac{F}{m} = -\dfrac{eE}{m}$

If the electron collide with a +ve ion then its drifting tendency decreases and random motion increases. At its next collision its velocity changes. On an average its:-

$$velocity = acceleration \times time = a\tau$$

Where 'τ' is the time between two collisions. This average velocity is the drift velocity of electron.

$$\therefore \boldsymbol{v_d = a\tau = -\left[\dfrac{eE}{m}\right]\tau}$$

Let there are n electrons per unit volume with each of change e and mass m. In a time dt, if all the electrons travels a distance l then $l = v_d dt$

Number of electrons in the volume element

$$= Volume \ \times Number \ of \ electrons \ per \ unit \ volume$$

$$= Al \times n$$

$$= Anv_d dt$$

Total change crossing in time dt = Number of electrons in the volume element × Change on the electron

$$= Anev_d dt$$

Current $I = \dfrac{Total\ charge\ crossing\ in\ time\ dt}{time, dt} = \dfrac{Anev_d dt}{dt} = Anev_d$

Current density $J = \dfrac{I}{A} = \dfrac{Anev_d}{A} = nev_d$

$$J = ne\left[\dfrac{eE}{m}\right]\tau = \dfrac{ne^2 E\tau}{m}$$

Relaxation time

If applied field is cutoff then the drift velocity of the electron reaches steady value

$$m\dfrac{dv_d}{dt} = -m\dfrac{v_d}{T}$$

$$\dfrac{dv_d}{dt} = -\dfrac{v_d}{T}$$

$$\log v_d = -\dfrac{1}{T}t + \log v_{d_0}$$

$$\log\left(\dfrac{v_d}{v_{d_0}}\right) = -\dfrac{t}{T}$$

$$v_d = v_{d_0}e^{\frac{-t}{T}}$$

If t = T then $v_d(t) = v_{d_0}e^{\frac{-t}{T}}$

Mobility of electron in a metal is defined as the steady state drift velocity per unit electric field

$$\mu = \dfrac{v_d}{E} = \dfrac{e\tau}{m}$$

Conductivity,

$$\sigma = \dfrac{J}{E} = \dfrac{ne^2 E\tau}{mE} = \dfrac{ne^2\tau}{m} = ne\mu$$

Resistivity,

$$\rho = \dfrac{1}{\sigma} = \dfrac{m}{ne^2\tau}$$

Merits

1. It explains the electrical resistivity in a metal.
2. It explains the electrical conductivity in a metal.
3. A relationship between resistively and conductivity with temperature is resistivity established.
4. A relationship between resistivity and conductivity with mean free path of electrons is established.
5. It explains thermal conductivity of metals.
6. It provides verification of Ohm's law.

Drawbacks

Classical free electron theory successfully explains electrical conductivity, Thermal conductivity and other phenomenon of metals, but could not explain number of other experimentally observed facts.

i. Specific heat of solids

When heat is supplied to the solids free electrons also absorb energy. So free electrons also contribute to the specific heat of solid which is called electronic specific heat.

The energy of electrons in one kilo mole of solid is given by:-

$$E = \frac{3}{2} N_A K_B T$$

The electronic specific heat is given by:-

$$C_V = \frac{dE}{dT} = \frac{3}{2} N_A K_B$$

$$C_V = 12.5 \frac{KJ}{Kmol.k}$$

But the experimental value of C_V is hundred times less than above value. So, classical free electron theory fails to explain the specific heat of solids.

ii. Temperature dependence of Conductivity

The electrical conductivity of conductor is given by:-

$$\sigma = \frac{ne^2 \lambda}{\sqrt{3mk_B T}}$$

$$\sigma \propto \frac{1}{\sqrt{T}}$$

But experimentally it was found that

$$\sigma \propto \frac{1}{T}$$

So, classical free electron theory fails to explain temperature dependence of electrical conductivity of metals.

iii. **Dependence of conductivity on electron concentration**

According to free electron theory of metals, the electrical conductivity of conductor is given by

$$\sigma = \frac{ne^2\lambda}{\sqrt{3mk_BT}}$$

$$\sigma \propto n$$

Experimentally there is no direct relationship between electron concentration and electrical conductivity.

iv. At low temperature $\frac{K}{\sigma T}$ is not constant, But by classical theory it is constant at all temperatures.

v. The phenomena such as photo electric effect, Compton Effect and black body radiation could not be explained by classical free electron theory.

vi. Electrical conductivity of semiconductors or insulator could not be explained by this theory.

vii. Ferromagnetism could not be explained by this theory.

Drift Velocity

When a metal is subjected to an electric field E along -x direction then all the electrons experiences a force along +x direction given by

$$Force = -eE$$

$$Acceleration\ of\ electrons = \frac{Force}{Mass} = \frac{eE}{m}$$

Using Newton's law of motion

$$m\frac{dV}{dt} = -Ee - \frac{mv}{\tau}$$

But under study state $\frac{dV}{dt} = 0$

$$V_d = \frac{-Ee\tau}{m}$$

In the presence of field, in addition to random velocity, there is an additional net velocity associated with electrons called *drift velocity*.
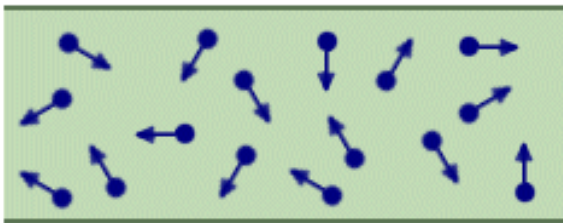
Electrical Conductivity

When an electric field is applied in the metal the electrons modify their random motion and drift slowly in the direction opposite to the opposition field.
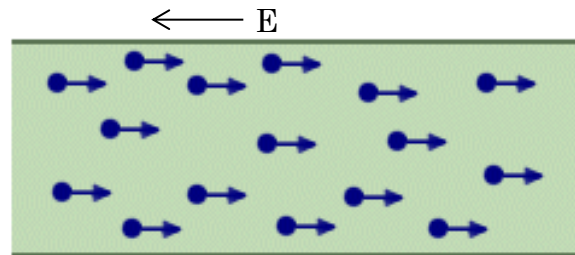
Due to applied field force experienced by the electrons is:-

$$F = -eE$$

$$a = -\frac{Ee}{m}$$

Random motion of electrons

Motion of electrons with applied field

The drift velocity of the electron is

$$V_d = a\tau = -\frac{Ee}{m}\tau$$

Current density (J) $= -V_d ne$

$$J = \frac{Ee\tau}{m}(ne) = \frac{ne^2\tau}{m}E$$

But $J = \sigma E$

$$\sigma = \frac{ne^2\tau}{m}$$

Resistivity $\rho = \frac{1}{\sigma} = \frac{m}{ne^2\tau}$

Postulates of quantum free electron theory

Classical free electron theory could not explain physical properties such as specific heat, mean free path etc. Classical free electron theory permits only fraction of electrons to gain energy.

Drawbacks of Quantum Free Electron theory

1. This theory could not explain the differences between conductors, semi-conductors and insulators.
2. On the basis of free electron theory it has been shown that the electrical conductivity is proportional to electron concentration. It is proved that divalent and trivalent metals are less conductive than monovalent metals.
3. This theory predicts negative hall coefficient but some metals like Be, Zn, Cd exhibit positive Hall coefficient.
4. Free electron modal always predicts a spherical fermi surface is often non spherical.

Success of Quantum Free electron theory

1. **<u>The Specific heat behavior of metals</u>**
    According to Quantum theory when heat energy is supplied to the solid, the electrons occupying higher energy levels occupying Fermi level absorb energy and excites to higher energy levels. But only small percentage of electrons is capable of contributions specific heat of solid.
    The energy of the electrons in one kilo mole of solid is

    $$E = \frac{1}{2} N_A K_B T \left[\frac{K_B T}{E_F} \right]$$

    $$\left[\left[E = \frac{1}{2} N_A \frac{(K_B T)^2}{E_F} \right]\right]$$

    $$C_V = \frac{dE}{dT} = N_A \, K_B{}^2 \frac{T}{E_F}$$

    For T=300K and $E_F = 5ev$ then $C_V = 0.129 \, kJ/kmol/k$ which agrees experimental results.
2. It explains electrical and terminal conductivities of metals.
3. It explains thermionic emission
4. It explains photoelectric effect, thermoelectric effect and gravitational effect of metals.
5. It explains paramagnetic susceptibility.