Unit-4: QUANTUM MECHANICSAND FREE ELECTRON THEORY

Introduction

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 ohm'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 arised.

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 arised again to explain this phenomenon (Band theory of solids).

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

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 and energy.

A wave is nothing but spreading of disturbance in a medium. Thus the characteristics of waves are amplitude, time period, frequency, wavelength, phase and 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. 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)

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

Introducing $\vartheta = c / \lambda$, we get $hc / \lambda = mc^2$

$$\implies \lambda = h / mc = h / p \text{ where p is momentum of particle}$$

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

$$\lambda = h / mv = h / p$$

The above eqn represents de Broglie wave eqn.

de Broglie wavelength in terms of KE

The KE of a moving particle $E = (1/2) mv^2$

$$= \frac{1}{2m} m^2 v^2 = \frac{p^2}{2m} \quad < \because p = mv >$$

$$P = \sqrt{2mE}$$

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

de Broglie wavelength of Electrons

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.,

$$(½) mv^2 = eV \quad \text{or} \quad mv^2 = 2eV$$

$$m^2 v^2 = 2meV$$

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

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

Substituting the values of h, m, and e in the above eqn, we get

$$\lambda = \frac{12.26}{\sqrt{V}} \ \overset{\circ}{A}$$

Properties of de Broglie waves

Since λ = h / m v

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, λ = ∞. 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.

Heisenberg Uncertainty Principle

According to classical mechanics, a moving particle at any instant has a fixed position in space and a definite momentum which can be determined simultaneously with any desired accuracy. The classical point of view represents an approximation which is adequate for the objects of appreciable size, but not for the particles of atomic dimensions.

Since a moving particle has to be regarded as a de Broglie group, there is a limit to the accuracy with which we can measure the particle properties. The particle may be found anywhere within the wave group, moving with the group velocity. If the group is narrow, it is easy to locate its position but the uncertainty in calculating its velocity or momentum increases. On the other hand, if the group is wide, its momentum can be estimated satisfactorily, but the uncertainty in finding the location of the particle is great. Heisenberg stated that the simultaneous determination of exact position and momentum of a moving particle is impossible.

If Δx is Error in the measurement of position of the particle along X-axis

Δp is Error in the measurement of momentum

Then Δx. Δp = h ---------- (1) where h is Plank's constant

The above relation represents the uncertainty involved in measurement of both the position and momentum of the particle.

To optimize the above error, lower limit is applied to the eqn. (1)

Then $(\Delta x)(\Delta p) \geq \hbar / 2$ where $\hbar = h / 2\pi$

A particle can be exactly located ($\Delta x \to 0$) only at the expense of an infinite momentum ($\Delta p \to \infty$).

There are uncertainty relations between position and momentum, energy and time, and angular momentum and angle.

If the time during which a system occupies a certain state is not greater than Δt, then the energy of the state cannot be known within ΔE,

i.e., $(\Delta E)(\Delta t) \geq \hbar / 2$.

Applications

1) Using uncertainty principle, non-existence of electron in the nucleus can be proved.
2) Existence of protons, neutrons, and α particles in the nucleons is conformed by the uncertainty principle.
3) Binding energy of an electron in an atom can be calculated from this uncertainty principle.
4) Emission of radiation of light from an excited atom is also conformed by this principle.

Schrödinger's One-dimensional 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.

Since the wave function depends upon the *x* coordinate of the moving particle and time 't', it is given by the complex form

$$\Psi(x,\ t) = A e^{i(kx - \omega t)} \qquad \text{------------} \rightarrow (1)$$

where A is amplitude

diff eqn(1) w.r.t, x we get

$$\frac{d\Psi}{dx} = ik\ A e^{i(kx - \omega t)}$$

Again diff , we have

$$\frac{d^2\Psi}{dx^2} = i^2 k^2 A e^{i(kx - \omega t)}$$

$$= i^2 k^2 \Psi$$

$$\frac{d^2\Psi}{dx^2} = -k^2\ \Psi$$

Since $k = \dfrac{2\pi}{\lambda}$, we get

$$\frac{d^2\Psi}{dx^2} = \frac{-4\pi^2}{\lambda^2}\ \Psi \qquad \text{-------------} \rightarrow (2)$$

de Broglie wavelength associated with the particle is

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

$$\frac{1}{\lambda^2} = \frac{m^2 v^2}{h^2} = \frac{2m\left(\frac{1}{2}mv^2\right)}{h^2} \qquad \text{------------} \rightarrow (3)$$

Let E be the total energy of the particle and V be the potential energy of the particle. Then

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

Using the above value in eqn(3), we get

$$\frac{1}{\lambda^2} = \frac{2m}{h^2}(E - V)$$

Using the above value in eqn(2), we get

$$\frac{d^2\Psi}{dx^2} = \frac{-8\pi^2 m}{h^2}(E - V)\Psi$$

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

$$\frac{d^2\Psi}{dx^2} + \frac{2m}{\hbar^2}(E-V)\Psi = 0 \; (\because \; \hbar = \frac{h}{2\pi})$$

The above equation represents Schrödinger's one-Dimensional time independent wave equation. For three dimensional motion of the particle the above equation becomes

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

Where $\quad \nabla^2 = \dfrac{d^2}{dx^2} + \dfrac{d^2}{dy^2} + \dfrac{d^2}{dz^2}$

Schrödinger's One-dimensional Time Dependent Wave Equation

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

$$\Psi(x, t) = Ae^{i(kx-\omega t)}$$

Diff the above eqn w.r.t, 't', we get

$$\frac{d\Psi}{dt} = -i\omega \, Ae^{i(kx-\omega t)}$$

$$= -i \, (2\pi\vartheta) \, Ae^{i(kx-\omega t)}$$

$$= -2\pi i\vartheta \; \Psi$$

Since $\quad$ E = hϑ , $\vartheta = \dfrac{E}{h}$

$$\frac{d\Psi}{dt} = -\frac{2\pi i E}{h}\Psi$$

$$= -\frac{2\pi i E}{2\pi\hbar}\Psi \quad \text{(since h = 2}\pi\hbar\text{)}$$

$$\frac{d\Psi}{dt} = \frac{E\Psi}{i\hbar}$$

$$E\Psi = i\hbar\,\frac{d\Psi}{dt}$$

using the value of $E\Psi$ in the eqn

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

We get
$$\frac{d^2\Psi}{dx^2} + \frac{2m}{\hbar^2}\left[i\hbar\frac{d\Psi}{dt} - V\Psi\right] = 0$$

$$\frac{d^2\Psi}{dx^2} = -\frac{2m}{\hbar^2}\left[i\hbar\frac{d\Psi}{dt} - V\Psi\right]$$

$$\frac{-\hbar^2}{2m}\frac{d^2\Psi}{dx^2} + V\Psi = i\hbar\frac{d\Psi}{dt}$$

The above equation represents time dependent Schrödinger's one-dimensional wave equation. For three dimensional motions, the above equation becomes

$$\frac{-\hbar^2}{2m}\nabla^2\Psi + V\Psi = i\hbar\frac{d\Psi}{dt}$$

Physical significance of wave function Ψ

Max Born in 1926 gave a satisfactory interpretation of the wave function Ψ associated with a moving particle. He postulated that the square of the magnitude of the wave function $|\Psi|^2$ (or ΨΨ* it 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. Energy acceptable wave function must be normalizable besides being normalizable; an acceptable wave function should fulfill the following requirements (limitations)

1. It must be finite everywhere.

2. It must be single valued.

3. It must be continuous and have a continuous first derivative everywhere.

Particle in a one dimensional infinite potential well

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.
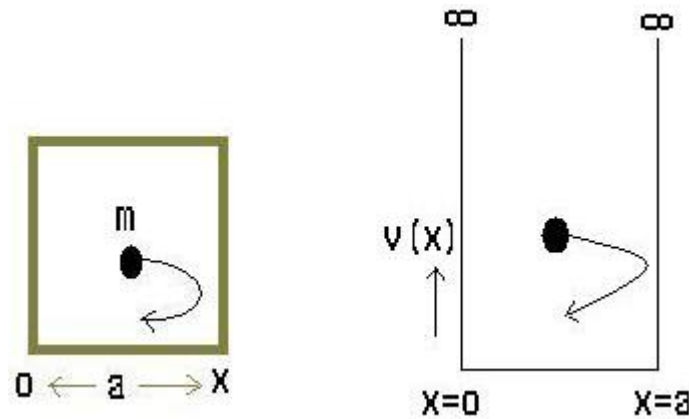
Thus, it does not lose energy when it collides the walls and its total remains constant. This box can be represented by a potential box of width a with potential walls of infinite height at x = 0 and x = a so that the potential energy, V of the particle is infinitely high on both sides of the box and inside it, Frequency is uniform. Let us assume that V = 0 inside the box,

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

V(x) = ∞,   for x ≤ 0 and x ≥ a.

Then the wave function Ψ(x) of the particle in the region 0 < x < a where V = 0 is described by the Schrödinger's equation

$$\frac{d^2\Psi}{dx^2} + \left(\frac{2m}{\hbar^2}\right)E\Psi = 0$$

$$\frac{d^2\Psi}{dx^2} + k^2\Psi = 0 \quad \text{Where } k = \sqrt{\frac{2mE}{\hbar^2}}$$

The solution of the above equation is given by

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

Where A and B are arbitrary constants.

Applying the first boundary condition, i.e., at x = 0, $\Psi(x) = 0$, we get

B = 0

Applying the second boundary condition, we have at x = a, $\Psi(x) = \Psi(a) = 0$

$$\Psi(a) = A\sin Ka = 0$$

A ≠ 0 since there will not be any solution. Hence we have

$$\sin Ka = 0$$

$$Ka = n\pi$$

$$k = \frac{n\pi}{a} \qquad \text{Where n = 1,2,3,…….}$$

We cannot take n =0 because for n = 0, K = 0, E = 0 and hence $\Psi(x) = 0$ everywhere in the box. Thus a particle with zero energy cannot be present in the box. The wave function for the motion of the particle in the region 0 < x < a are given by

$$\Psi_n(x) = A \sin Kx$$

$$\Psi_n(x) = A \sin\frac{n\pi x}{a}$$

Eigen values of Energy

We know that $K^2 = \frac{2mE}{\hbar^2}$

$$E = \frac{K^2\hbar^2}{2m}$$

Using the values of K, we get

$$E = \left[\frac{n^2\pi^2}{a^2}\right]\frac{\hbar^2}{2m}$$

$$= \frac{n^2\pi^2}{a^2}\left[\frac{h^2}{8\pi^2 m}\right]$$

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

From the above eqn, it is clear that

1. The lowest energy of the particle is obtained by putting n = 1

$$E_1 = \frac{h^2}{8ma^2} \text{ and } E_n = n^2 E_1$$

This is known as zero point energy of the system.

2. For n = 1,2,3, we get discrete energy values of the particle in the box.
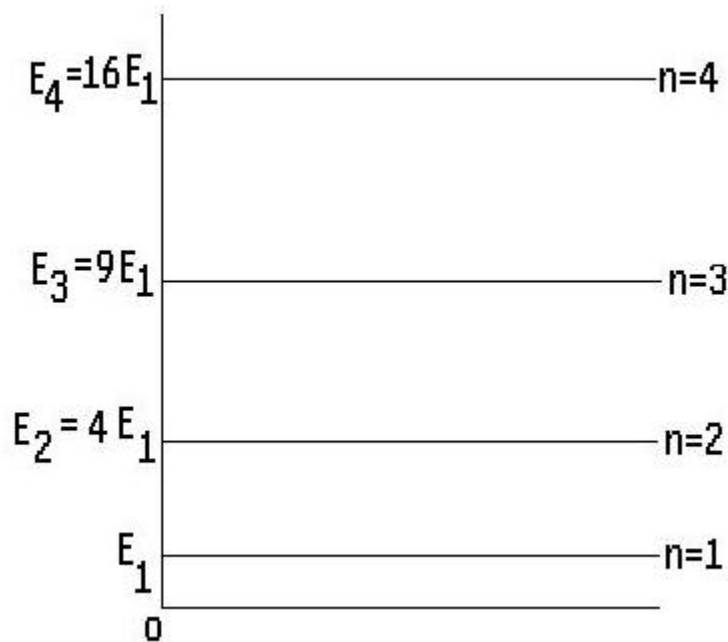
$$E_1 = \frac{h^2}{8ma^2}$$

$$E_2 = 2^2\frac{h^2}{8ma^2} = 4E_1$$

$$E_3 = 3^2 \frac{h^2}{8ma^2} = 9E_1$$

3. The spacing between the nth energy level and the next higher level increases as

$$(n+1)^2 E_1 - n^2 E_1 = (2n+1)E_1$$

4. These values of E_n are known as Eigen values of energy and the corresponding wave function Ψ_n as Eigen functions of the particle. Fig shows the energy level diagram for the particle.

$E_4 = 16E_1$ ──────────────── n=4

$E_3 = 9E_1$ ──────────────── n=3

$E_2 = 4E_1$ ──────────────── n=2

E_1 ──────────────── n=1

0

<u>Eigen Wave Function</u>

The eigenwave function for the motion of the particle are

$$\Psi_n(x) = A \sin\frac{n\pi x}{a} \qquad \text{in the region 0<x<a}$$

$$\Psi_n(x) = 0 \qquad \text{in the region } x \leq 0 \text{ and } x \geq a$$

The total probability that the particle is somewhere in the box must be unity.

$$\int_0^a P_x dx = \int_0^a |\Psi_n|^2 dx = 1$$

$$\int_0^a A^2 sin^2\frac{n\pi x}{a} dx = 1$$

$$\frac{A^2}{2}\int_0^a [1 - \cos\frac{2n\pi x}{a}]dx = 1$$

$$\frac{A^2}{2}\left[x - \frac{a}{2\pi n}\sin\frac{2\pi nx}{a}\right]_0^a = 1$$
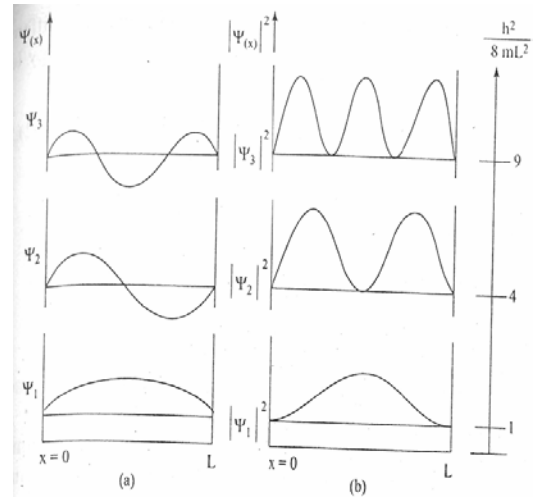
The second term becomes zero at both the limits

$$\frac{A^2 a}{2} = 1$$

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

The normalized wave function is

$$\Psi_n(x) = \sqrt{\frac{2}{a}}\sin\frac{n\pi x}{a}$$

The wave functions are shown in fig.

The wave function Ψ_1 has two nodes at x = 0 and x = a.

Ψ_2 has three nodes at x = 0, x = a/2 and x = a.

Thus Ψ_n has (n+1) nodes.

Free Electron Theory

Introduction:

In solids, electrons in outer most orbits of atoms determine its electrical properties. Electron theory explains the electrical, thermal and magnetic properties of solids, particularly metals.The electron theory of solids aredeveloped in three main stages.

1. Classical free electron theory.
2. Quantum Free Electron Theory.
3. Zone Theory/Band Theory.

Classical free electron theory: It was developed by Drude and Lorentz in 1900. According to this theory, metal contains free electrons which are responsible for the electrical conductivity. These free electrons obey the laws of classical mechanics.

Postulates (or) Salient features in classical free electron theory

- ❖ The valence electrons of metallic atoms are free to move about the whole volume of the metals like the molecules of a gas in a container. The collection of valence electrons from all the atoms in a given piece of metal forms electron gas. It is free to move throughout the volume of the metal.
- ❖ These free electrons move in random directions and make collisions with either positive ions fixed in the lattice or other free electrons. All the collisions are elastic i.e., there is no loss of energy.
- ❖ The movements of free electrons obey the laws of the classical kinetic theory of gases.
- ❖ The velocities of free electrons in a metal obey the classical Maxwell-Boltzmann law of distribution of velocities.
- ❖ The free electrons move in a completely uniform potential field due to ions fixed in the lattice.
- ❖ When an electric field is applied to the metal, the free electrons are accelerated in the direction opposite to the direction of applied electric field (towards positive terminal of the source). The average velocity acquired by an electron in the presence of electric field is known as 'drift velocity (v_d).
- ❖ In the absence of the electric field, the distance traveled between two successive collisions is called mean free path (λ) and the time taken by an electron between two successive collisions is known as relaxation time (τ). The average velocity of free electrons is called 'root mean square velocity, (v_{rms}) or thermal velocity of electrons.

Success of classical free electron theory: It was only able to explain the properties of **metals** such as

- ❖ Electrical conductivity.
- ❖ Ohm's law.
- ❖ Thermal conductivity.
- ❖ Wiedemann-Franz law.
- ❖ Complete opacity of metals and their high luster.

Failure of classical free electron theory

- ❖ It could not explained the difference between conductors, insulators and semiconductors.

❖ Even though the theory states that the conductivity is proportional to the free electron concentration, itis found that divalent and trivalent metals are not good conductors. However, monovalent metals Cu, Ag, Au, etc are good conductors.
❖ Some of the metals exhibit positive Hall coefficients, while the free electron theory predicts negative hall coefficients for all the metals.
❖ The phenomenon like photo electric effect, Compton effect and black body radiation
❖ could not be explained by classical free electron theory.
❖ It fails to explain temperature dependence of paramagnetic susceptibility andferromagnetism.

Quantum Free Electron Theory:

Quantum free electron theory was proposed by Sommerfeld in 1928. It overcomes many of the drawbacks of classical theory. Sommerfeld explained the electrical properties of solidsbased on Fermi-Dirac statistics instead of Maxwell-Boltzmann statistics. He developed this theory by applying the principles of quantum mechanics.

Postulates (or) Salient features of Quantum Free Electron Theory
- Valence electrons move freely in a constant potential within the boundaries of metaland is prevented from escaping the metal at the boundaries (high potential). Hence theelectron is trapped in a potential well.
- The distribution of electrons in various allowed energy levels occurs as per Pauli Exclusion Principle.
- The attraction between the free electrons and lattice ions and the repulsion between electrons themselves are ignored.
- The distribution of energy among the free electrons is according to Fermi-Dirac statistics.
- The energy values of free electrons are quantized.
- To find the possible energy values of electron Schrodinger time independent wave equation is applied. The problem is similar to that of particle present in a potential box.

The energy of electron is

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

Where n=1, 2, 3,…

Merits of quantum free electron theory
- It explains temperature dependence of conductivity of metals. It can explain the specific heat of metals. It explains magnetic susceptibility of metals.
- It can explain photo electric effect, Compton Effect and block body radiation etc.
- It gives the correct mathematical expression for the thermal conductivity of metals.

Demerits of quantum free electron theory
- This theory fails to distinguish between metal, semiconductor and Insulator.
- It also fails to explain the positive value of Hall Co-efficient.
- According to this theory, only two electrons are present in the Fermi level and they are responsible for conduction which is not true.

Equation for electrical conductivity based on quantum free electron theory

When an electric field E is applied, the force on the elctrons is –eE. We know that force is also rate of change of momentum dp/dt.

Therefore $-eE = \dfrac{dp}{dt}$ -----------(1)

Since $p = h/\lambda = (h/2\pi)(2\pi/\lambda) = \hbar k$. Where $k = 2\pi/\lambda$.

$\Rightarrow \dfrac{dp}{dt} = \hbar \dfrac{dk}{dt}$ -------------(2)

$\Rightarrow$ Substituting (2) in (1), we have

$\Rightarrow -eE = \hbar \dfrac{dk}{dt}$

$\Rightarrow dk = -eE \dfrac{dt}{\hbar}$

$\Rightarrow$ Origin of k space moves through a distance dk in time dt. The displacement in the average collision time τ is $\Delta k = -\dfrac{eE\tau}{\hbar}$.

Since $p = mv = \hbar k \rightarrow m\Delta v = \hbar\Delta k$

$\Rightarrow \Delta k = \dfrac{m\Delta v}{\hbar}$

$\Rightarrow \dfrac{m\Delta v}{\hbar} = -\dfrac{eE\tau}{\hbar}$

$\Rightarrow \Delta v = -\dfrac{eE\tau}{m}$

Expression for current density is $J = -ne\Delta v$

Substituting Δv in the above equation, we have

$J = -ne[-\dfrac{eE\tau}{m}]$

$$J = \dfrac{ne^2 E\tau}{m}.$$

Also we have J=σE. Comparing these two equations we have $\sigma E - \dfrac{ne^2 E\tau}{m}$

Therefore the expression for electrical conductivity is given by

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

Fermi-Dirac distribution

The Fermi-Dirac distribution function, also called Fermi function. It provides the probability of occupancy of energy levels by electrons /Fermions. Fermions are half-integer spin particles, which obey the Pauli exclusion principle.

A metal piece contains very large number of electrons. Each electron possesses quantized energy states and obeys Pauli's exclusion principle. Hence, electrons satisfy Fermi- Dirac statistics. The Fermi function $F(E_i)$ provides the probability of electron occupied an energy level at energy, E_i in thermal equilibrium. The system is characterized by its temperature T and its Fermi energy E_F.

The probability $F(E_i)$ of an electron occupying energy level E_i is given by

$$F(E_i) = \frac{1}{\exp\left(\dfrac{E_i - E_f}{kT}\right) + 1}$$

Where $F(E_i)$ is called Fermi function. E_f is Fermi energy, E_i is energy of ith state and k is Boltzmann constant.

Temperature dependence of Fermi function

(a) T = 0   (b) T > 0   VARIATION OF f(E) WITH E
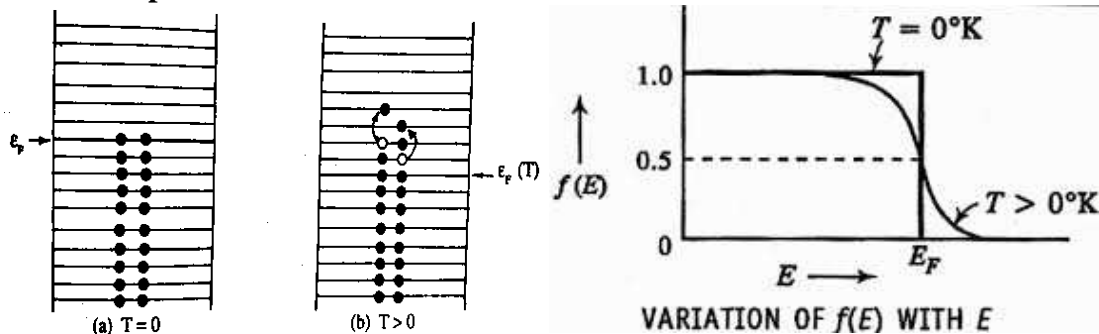
At **T=OK,** the Fermi Dirac distribution of electrons can be understood mathematically from the following two cases.

Case -1: If E>E_F,

$$e^{\frac{(E_i - E_F)}{kT}} = \infty$$

Therefore, $F(E_i)= 1/\infty$ then $F(E_i)=0$. It indicates that energy levels above Fermi level are empty.

Case -2: If E<E_F,

$$e^{\frac{(E_i - E_F)}{kT}} = 0$$

then $F(E_i)=1$.

Which means that energy levels below Fermi levels are full of electrons. The Fermi level is a boundary energy level which separates the filled energy state and empty states at 0k. The energy of the highest filled state at 0K is called Fermi Energy 'E_F' and the energy level is known as Fermi Level.

Case-3: At T>0K,

If, $E_i=E_F$

Then,

$$F(E_i)=1/2.$$

Therefore Fermi level is the energylevel for which the probability of filled states is 50% at any temperature.

If T_F is theFermi temperature and V_F is Fermi velocity corresponding to Fermi energy E_F

Then,$E_F=kT_F=>T_F= E_F/k$

And

$$V_F =\sqrt{(2E_F/m)}$$

The electrons in the levels above E_F are responsible for conduction. If the temperature is raised further, the resistance of the metals increases due to decrease of mobility.

According to classical theory, all the free electrons below E_F gain energy when temperature is increased, which is deviates from the experimental observations. However, according to quantum theory only few electrons below E_F gain energy from external source and thus theoretical values are closer to the experimental observations.

Density of states

The number of electronic states per unit energy range is called density of states of g(E). Let us consider a spherical system of radius n and it represents a vector to a

point n_x, n_y and n_z $\left(n^2 =n_x^2 +n_y^2 +n_z^2\right)$ in 3-dimensional space.

Consider a sphere of radius n and another sphere of radius $(n+dn)$ in which energy values are E and E+dE respectively. as shown in fig.
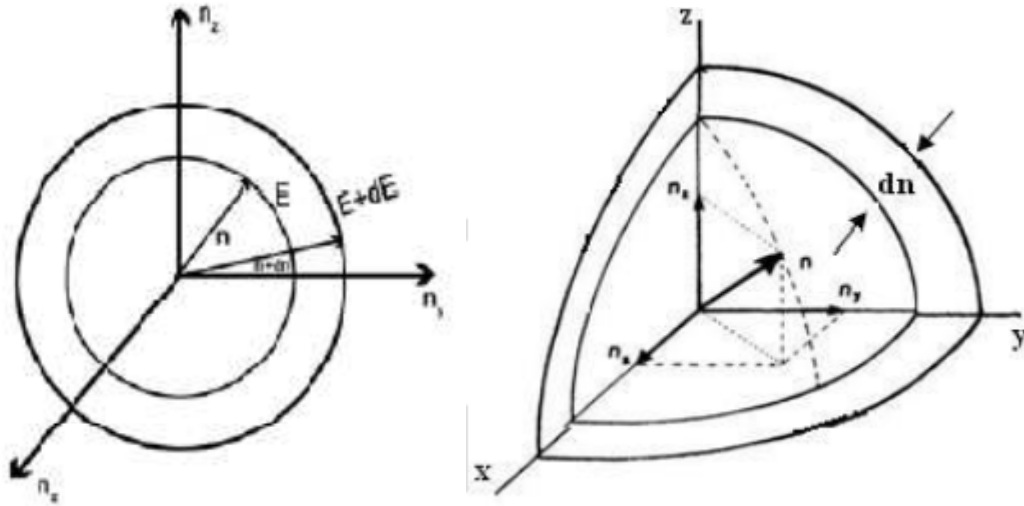
Number of energy states available in sphere of radius n is $\dfrac{1}{8}\left(\dfrac{4}{3}\pi n^3\right)$ ------------(1)

Number of energy states in sphere of radius (n+dn) is $\dfrac{1}{8}\left(\dfrac{4}{3}\pi(n+dn)^3\right)$ -----------(2)

E and dE are energy values of above two regions respectively from eq (1) & (2) we can write number of energy states available in dn or dE region as

$$g^1(E)dE = \dfrac{1}{8}\left[\dfrac{4}{3}\pi(n+dn)^3\right] - \dfrac{1}{8}\left[\dfrac{4}{3}\pi n^3\right]$$

$$= \dfrac{\pi}{6}\left[(n+dn)^3 - n^3\right]$$

$$= \dfrac{\pi}{6}\left[n^3 + dn^3 + 3n^2dn + 3ndn^2 - n^3\right]$$

Neglecting higher order terms, we get

$$g^1(E)dE = \dfrac{\pi}{6}\left(3n^2dn\right)$$

$$= \dfrac{\pi}{2}\left(n(ndn)\right) ---------(3)$$

The expression for nth energy level can be written as,

$$E = \frac{n^2 h^2}{8ma^2}$$

$$n^2 = \left[\frac{8ma^2}{h^2}\right]E \quad\text{------(4)}$$

$$n = \left[\frac{8ma^2}{h^2}E\right]^{\frac{1}{2}} \quad\text{-----(5)}$$

Differentiating Eq (4) by taking n and E as variable, we get

$$2ndm = \frac{8ma^2}{h^2}dE$$

$$ndn = \frac{1}{2}\left(\frac{8ma^2}{h^2}\right)dE \quad\text{-------(6)}$$

Substituting Eq (5) and (6) in Eq (3) we get,

$$g'(E)dE = \frac{\pi}{2}\left(\frac{8ma^2}{h^2}\right)^{\frac{1}{2}}E^{\frac{1}{2}}\frac{1}{2}\left(\frac{8ma^2}{h^2}\right)dE$$

$$= \frac{\pi}{4}\left(\frac{8ma^2}{h^2}\right)^{\frac{3}{2}}E^{\frac{1}{2}}dE$$

According to Pauli exclusion principle, each energy level contains two electrons i.e each energy level will have two sub energy levels so above equation should be multiplied by 2

$$g'(E)dE = 2\frac{\pi}{4}\left(\frac{8ma^2}{h^2}\right)^{\frac{3}{2}}E^{\frac{1}{2}}dE$$

$$= \frac{\pi}{2}\left(\frac{8ma^2}{h^2}\right)^{\frac{3}{2}}E^{\frac{1}{2}}dE$$

$$= \frac{\pi}{2}\left(\frac{8m}{h^2}\right)^{\frac{3}{2}}a^3 E^{\frac{1}{2}}dE$$

Density of states $g(E)dE = \frac{g'(E)}{V}dE$ If length of energy level is a then its volume

V= a³, therefore, the density of states can be written as

$$\boxed{g(E)dE = \frac{\pi}{2}\left(\frac{8m}{h^2}\right)^{\frac{3}{2}}E^{\frac{1}{2}}dE}$$

Band theory of Solids

Bloch theorem:

Bloch's theorem (1928) applies to wave functions of electrons inside a crystal and rests in the fact that the Coulomb potential in a crystalline solid is periodic.

Statement: Bloch's theorem establishes that the wave function $\psi_{\vec{k}}(\vec{r})$ in a crystal, obtained from Schrödinger's can be expressed as the product of a plane wave and a function $u_{\vec{k}}(\vec{r})$ which has the same periodicity as the lattice

A crystalline solid consists of a lattice, which is composed of a large number of ion cores at regular intervals, and the conduction electrons that can move freely throughout the lattice. The conduction electrons move inside periodic positive ion cores. Hence, instead of considering uniform constant potential as we have done in the electron theory, we have to consider the variation of potential inside the metallic crystal with the periodicity of the lattice as shown fig.
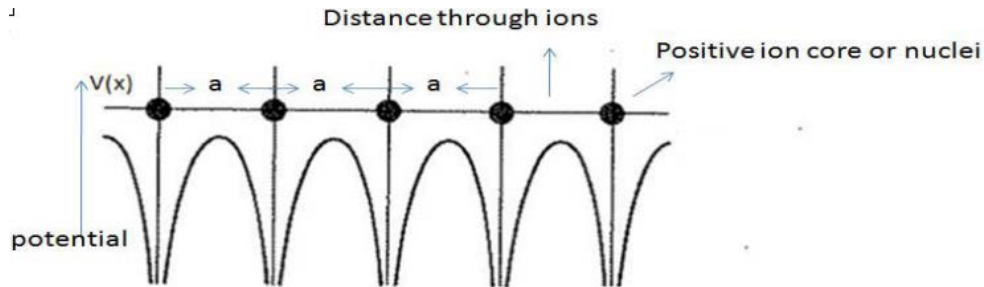
The potential is minimum at the positive ion sites and maximum between the two ions. The one-dimensional Schrödinger equation corresponding to this can be written as

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}(E - V)\psi = 0 \quad \text{where } \hbar = h/2\Pi$$

$$\frac{d^2\psi}{dx^2} + \frac{8\Pi^2 m}{h^2}(E - V(x))\psi = 0 \text{ ------(1)}$$

The periodic potential V(x) may be defined by means of the lattice constant 'a' as

$$V(x) = V(x + a) \text{ --------- (2)}$$

Bloch has shown that the one-dimensional solution of the Schrödinger equation is of the form.

$$\psi(x) = e^{ikx} . U_k(x) \text{ ----------(3)}$$

In the above equation $U_k(x)$ is called "modulating function". Because free electron wave is modulated by $U_k(x)$ is periodic with the periodicity at the crystal lattice.

Case study

Consider a linear chain of atoms of length L in one-dimensional case with "N" number of atoms in the chain. Then,

$$U_k(x) = U_k(x+Na) \text{ ------------------ (4)}$$

Where 'a' is lattice distance
From equation (3) and (4),

$$\psi(x+Na) = e^{ik(x+Na)} . U_k(x+Na)$$

$$= e^{ikNa} . U_k(x) e^{ikx}$$

$$\boxed{\psi(x+Na) = \psi(x). e^{ikNa} \text{ ------------------ (5)}}$$

This is referred to as Bloch condition.
Similarly, the complex conjugate of eq.(5) can be written as

$$\boxed{\psi^*(x+Na) = \psi^*(x). e^{-ikNa} \text{ -------------(6)}}$$

From eq(5) and eq(6)

$$\psi(x+Na) . \psi^*(x+Na) = \psi(x). \psi^*(x)$$

$$\boxed{|\psi(x+Na)|^2 = |\psi(x)|^2 \text{ --------(7)}}$$

From this equation, it is clear that the electron is not localized around ones particular atom and the probability of finding the electron is same throughout the crystal.
Therefore, in eq(5),

$$e^{ikNa} = 1$$

$$kNa = 2\Pi n \text{, where n is an integer}$$

$$k = (2\Pi n)/Na$$

$$\boxed{k = (2\Pi n)/L}$$

Where L is the length of the chain of atoms and n= ±1, ±2, ±3, ±4, ………
When n=N/2, we have k=Π/a. This is the edge of first Brillouin zone.

Kronig-Penney model

Kronig-penny approximated the potentials of an electrons inside the crystal in terms of the shapes of rectangular steps as shown, which is known as Kronig Penny model. The periodic potential is taken in the form of rectangular one dimensional array of square well potentials and it is the best suited to solve Schrodinger wave equation.
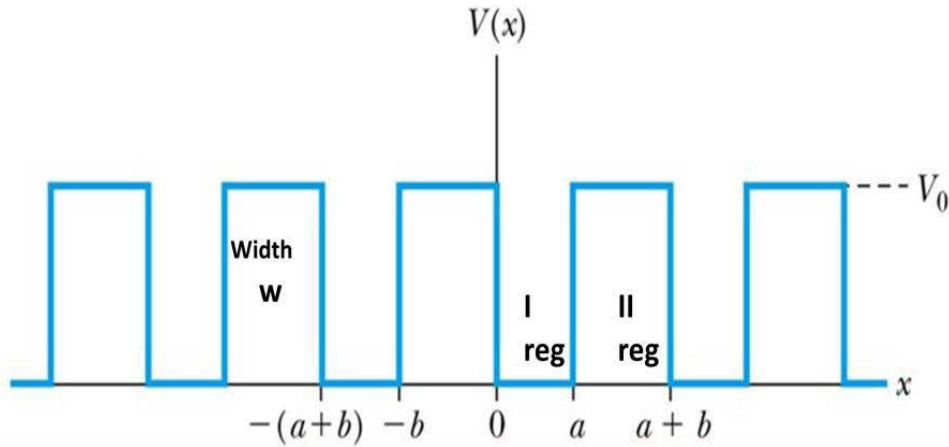
It is assumed that the potential energy is zero $V(x) = 0$ in the I-region and potential energy is $V(x) = 1$, in the II-region.

i.e the Boundary conditions are

$V(x) = 0$, where x lies between o< x< a in region -I

$V(x) = 1$, where x lies between -b < x< 0 in region -II

This model explains many of the characteristic features of the behavior of electrons in a periodic lattice.

The wave function related to this model can be obtained by solving Schrodinger equations for the two regions,

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}\, E\psi = 0, \text{for } 0 < x < a \ \ with \ V(x) = 0 \ \ldots\ldots\ldots\ldots\ (1)$$

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}\, (E - V_0)\psi = 0, \text{for } -b < x < 0 \ \ with \ V(x) = V_0 \ \ldots\ldots\ldots\ (2)$$

Again,

$$\frac{d^2\psi}{dx^2} + \alpha^2\,\psi = 0 \ \ldots\ldots\ldots\ (3)$$

where $\alpha^2 = \dfrac{2mE}{\hbar^2}$ and $\alpha = \dfrac{2\Pi}{h}\sqrt{2mE}$

$$\frac{d^2\psi}{dx^2} - \beta^2\,\psi = 0 \ \ldots\ldots\ldots\ (4)$$

where $\beta^2 = \dfrac{2m}{\hbar^2}(V_0 - E)$

The solution of these equations from Bloch theorem,

$$\psi_k(x) = u_k(x)exp(ikx)$$

From figure, square well potentials, if V_o increases, the width of barrier 'w' decreases, if V_o decreases the width of barrier w increases. But the (product) barrier strength $V_o$wremainsconstant.

      To get this, differentiating above Schrodinger wave equations 3 & 4 w.r.to x, and by applying boundary conditions of x (w.r.to their corresponding Ψ), to known the values of constants
A, B of region -I, C,D-for reg-II,we get mathematical expression (by simplification).

$$\boxed{coska = P\,\dfrac{sin\alpha a}{\alpha a} + cos\alpha a}$$

--------(5)

Where P $= \dfrac{4\Pi^2 ma}{h^2}$ Voω and $\propto = \dfrac{2\Pi}{h}\sqrt{2mE}$

P is called scattering power of the barrier and Voω is called barrier strength.
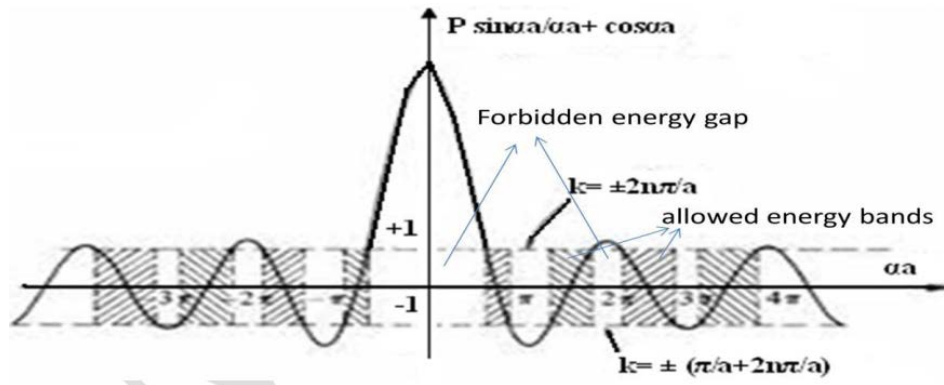
The left hand side of the equation (5) is plotted as a function of '∝a' for the value of P = 3 Π / 2 which is shown in fig, the right hand side takes values between -1 to +1 as indicated by the horizontal lines in fig. Therefore the equation (3) is satisfied only for those values of 'ka' for which left hand side between ± 1.

From the above figure, the following conclusions are drawn.

1) The energy spectrum of the electron consists of a number of allowed and forbidden energy bands.
2) As '∝a' increases the width of the allowed energy band increases and the width of forbidden band decreases.
3) With increasing potential barrier P, the width of an allowed band decreases.

4) As P→∞, the allowed energy becomes infinitely narrow and the energy spectrum is a line spectrum as shown in fig.
5) When P→0 then all the electrons are completely free to move in the crystal without any constraints. Therefore, no energy level exists that is all the energies are allowed to the

electrons as shown in fig. This case supports the classical free electrons theory.
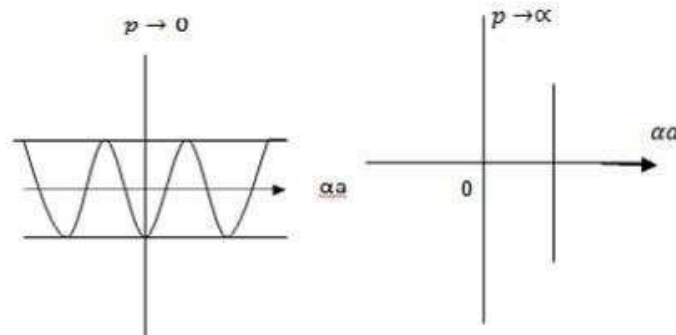
Brillouin Zone OR E-K diagram

The Brillouin zone are the boundaries that are marked by the values of wave vector k,in which electrons can have allowed energy values. These represent the allowed values of k of the electrons in 1D, 2D,&3D.

The energy of the electron in a constant potential box is,

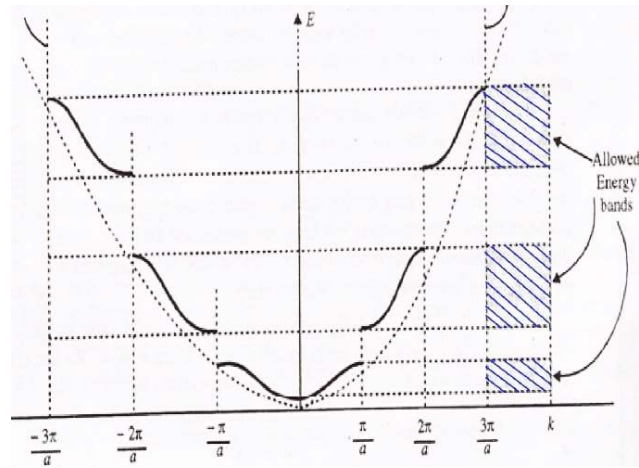$$E = \frac{n^2 h^2}{8ma^2} \dots (1) \text{where a = length of the box}$$

But,

$$k = \frac{n\pi}{a} \Rightarrow k^2 = \frac{n^2 \Pi^2}{a^2}$$

$$\frac{n^2}{a^2} = \frac{k^2}{\pi^2} \quad \dots \dots \dots (2)$$

Substitute eqn (2) in (1) ,we get $E = \frac{k^2 h^2}{8m\pi^2}$; $E \propto k^2$

It represents parabolic equation. A graph is drawn between the total energy (E) and the wave vector k for various values of k.

i.e. $k = \frac{n\pi}{a}$; $n = \pm1, \pm2, \pm3, \dots \dots$

It is the energy spectrum of an electron moving in presence of a periodic potential field and is divided into allowed energy regions (allowed zones) or forbidden energy gaps (forbidden zones).

Allowed energy values lie in the region k= $-\pi/a$ to = $+\pi/a$. This zone is called the first Brillouin zone. The break in the energy values is called forbidden energy band. The next another allowed zone spread from k=$-\pi/a$ to $-2\pi/a$ and $+\pi/a$ to $+2\pi/a$, which is called as the second Brillouin zone. Similarly, the higher Brillouin zones are formed.

Classification of crystalline solids
Based on the width of forbidden band, solids are classified into conductors, semiconductors, and insulators.
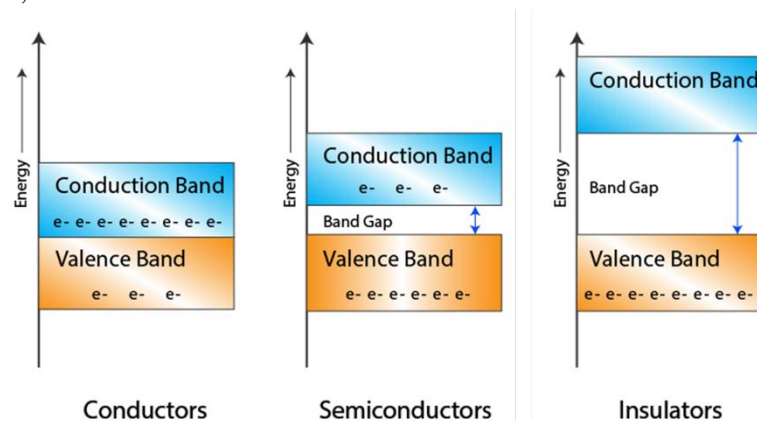
Conductors: The valence band and conduction bands are overlapped with each other and the energy gap E_g is zero. At room temperatures, free electrons already exist in huge number at conduction band. These solids are good electrical conductors as well as good thermal conductors. The electrical resistivity increases at high temperature by collisions among the free electrons.
Ex: Al, Cu, Ag, Au etc.,

Semiconductors: The valence band and conduction bands are separated with a small energy band gap $E_g \approx 1$ eV. At low temperatures (0 K), free electrons are not available in conduction band. These solids behave like insulators at low temperatures. The electrical conductivity increases at high temperatures by the transition of free electrons from valence band to conduction band. Thus, these solids behave like electrical conductors at high temperatures.

Ex: Silicon $E_g = 1.1$ ev, Germanium $E_g = 0.7$ev.

Insulators: The valance band and conduction bands are separated by a very large energy gap $E_g \geq 3$ eV. At room temperatures, conduction band is empty and valance band is full of electrons. Therefore, these solids are electrical insulators. Even at high temperature, valence electrons are unable to jump in to conduction band.

Ex: Glass, Mica, Ebonite, Rubber etc.,

Effective mass of electron

When an electron in a periodic potential of lattice is accelerated by an known electric field or magnetic field, then the mass of the electron is called effective mass and is represented by m∗.

To explain, let us consider an electron of charge 'e' and mass 'm' moving inside a crystallattice of electric field E.

The acceleration a = eE / m is not a constant in the periodic lattice of the crystal. It canbe considered that its variation is caused by the variation of electron's mass when itmoves in the crystal lattice.

Therefore, the acceleration of electron is given by
$$a = eE / m*$$
The electrical force on the electron is given by
$$F = m* \, a \text{ --------------(1)}$$
By considering the free electron as a wave packet , the group velocity V_g corresponding tothe particle's velocity can be written as

$$v_g = \frac{d\omega}{dk} = \frac{d(2\Pi v)}{dk} = 2\Pi \frac{dv}{dk} = \left(\frac{2\Pi}{h}\right)\frac{d(hv)}{dk} = \frac{1}{\hbar}\frac{dE}{dk} \text{ ---------(2)}$$

where, the energy E = hυ and $\hbar = \dfrac{h}{2\Pi}$

$$\text{Acceleration a} = \frac{dv_g}{dt} = \frac{d\left(\frac{1}{\hbar}\frac{dE}{dk}\right)}{dt} = \frac{1}{\hbar}\frac{d^2E}{dk.dt} = \frac{1}{\hbar}\left(\frac{d^2E}{dk.dk}\right)\left(\frac{dk}{dt}\right) = \frac{1}{\hbar}\left(\frac{d^2E}{dk^2}\right)\left(\frac{dk}{dt}\right)$$

$$\text{Since } \hbar k = p \text{ and } \frac{dP}{dt} = F, \qquad\qquad \frac{dk}{dt} = \frac{F}{\hbar}$$
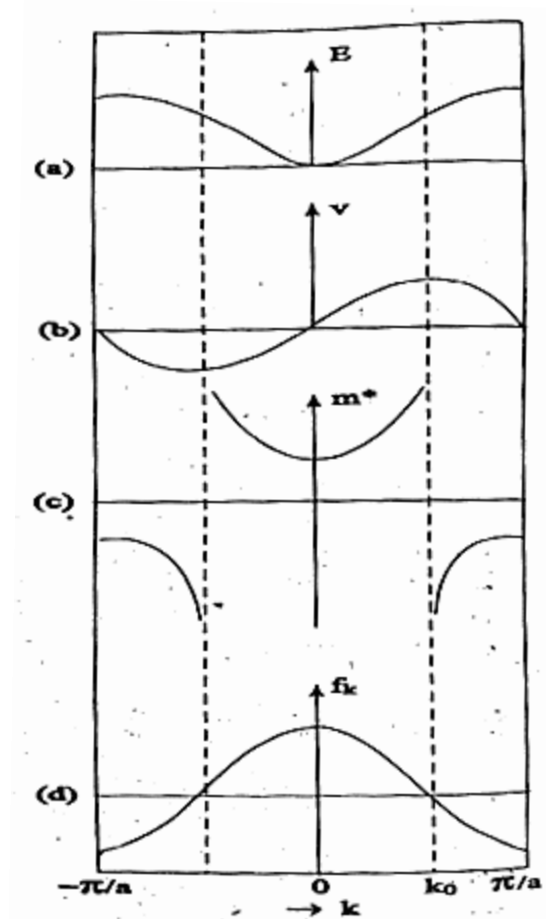
$$\therefore \ a = \frac{1}{\hbar^2}\left(\frac{d^2E}{dk^2}\right)F$$

$$F = \left[\frac{\hbar^2}{\left(\frac{d^2E}{dk^2}\right)}\right]a \ \text{----------(3)}$$

Comparing equations (1) and (3) we get,

$$m^* = \left[\frac{\hbar^2}{\left(\frac{d^2E}{dk^2}\right)}\right]\text{------------(4)}$$

This equation indicates that the effective mass is determined by $\dfrac{d^2E}{dk^2}$

1) **Variation of E with K:** Variation of E withK corresponds to first Brillouin Zone. Usingthis type of variation velocity can becalculated.

2) **Variation of V with K:** For K=0 velocity iszero and as k value increases V also increasesreaching its maximum value at $K_o$known aspoint of inflexion. Beyond $K_o$velocitydecreases and reaches to 0 at K=π/a.

3) **Variation of m* with K:** Near K=0, m*=m.As K value increases m* also increases reaching its maximum value at K_o. Above K_o,m* is negative and decreases as K tends toπ/a. Beyond $K_o$velocity decreases and henceretarding force acts on electron and itbehaves as positively **charged particle referred to as hole**.

4) **Variation of f_k:**Degree of freedom of anelectron is defined as f_k=m/m*. $f_k$ismeasureof the extent to which the electron is free in astate K. If m* is large $f_k$is small, particlebehaves as heavy particle. If f_k=1, electronbehaves as free electron.