Semiconductor Physics (BTPH104-18)

Study Material prepared by Dr. Arvind Sharma

Course Objectives: The aim and objective of the course on **Semiconductor Physics** is to introduce the students of B. Tech. class to the formal structure of semiconductor physics so that they can use these in Engineering as per their requirement.

Course Outcomes: At the end of the course, the student will be able to

CO1: Understand and explain the fundamental principles and properties of electronic materials and semiconductors.

CO2: Understand and describe the interaction of light with semiconductors in terms of fermi golden rule.

CO3: Understand and describe the impact of solid-state device capabilities and limitations on electronic circuit performance.

CO4: Understand the design, fabrication, and characterization techniques of engineered semiconductor materials.

CO5: Develop the basic tools with which they can study and test the newly developed devices and other semiconductor applications.

Detailed Syllabus

PART-A

UNIT 1: Electronic materials *(10 lectures)*

Free electron theory of metals, Density of states in 1D, 2D, and 3D, Bloch's theorem for particles in a periodic potential, Energy band diagrams, Kronig-Penny model (to introduce origin of band gap), Energy bands in solids, E-k diagram, Direct and indirect band gaps, Types of electronic materials: metals, semiconductors, and insulators, Occupation probability, Fermi level, Effective mass.

UNIT II: Semiconductors *(10 lectures)*

Intrinsic and extrinsic semiconductors, Dependence of Fermi level on carrier-concentration and

temperature (equilibrium carrier statistics), Carrier generation and recombination, Carrier transport: diffusion and drift, p-n junction, Metal-semiconductor junction (Ohmic and Schottky), Semiconductor materials of interest for optoelectronic devices.

PART-B

UNIT III: Light-semiconductor interaction *(10 lectures)*

Optical transitions in bulk semiconductors: absorption, spontaneous emission, and stimulated emission; Einstein coefficients, Population inversion, application in semiconductor Lasers; Joint density of states, Density of states for phonons, Transition rates (Fermi's golden rule), Optical loss and gain; Photovoltaic effect, Exciton, Drude model.

UNIT IV: Measurement Techniques *(10 lectures)*

Measurement for divergence and wavelength using a semiconductor laser, Measurements for carrier density, resistivity, hall mobility using Four-point probe and vander Pauw method, Hot-point probe measurement, capacitance-voltage measurements, parameter extraction from diode I-V characteristics.

Reference books and suggested reading:

1. J. Singh: Semiconductor Optoelectronics: Physics and Technology, McGraw-Hill Inc. (1995).
2. B. E. A. Saleh and M. C. Teich: Fundamentals of Photonics, John Wiley & Sons, Inc., (2007).
3. S. M. Sze: Semiconductor Devices: Physics and Technology, Wiley (2008).
4. A. Yariv and P. Yeh, Photonics: Optical Electronics in Modern Communications, Oxford University Press, New York (2007).
5. P. Bhattacharya: Semiconductor Optoelectronic Devices, Prentice Hall of India (1997).
6. Ben G. Streetman: Solid State Electronics Devices, Pearson Prentice Hall.

UNIT I - ELECTRONIC MATERIALS

Introduction

➢ Each element exists as either a solid, or a liquid, or a gas at ambient temperature and pressure.

➢ Among them, we are most interested in solids, which are often divided into metals, semiconductors and insulators. Thus, materials can be broadly classified into three types based on conductivity. They are,

o Conductors (Example: metals),

o Semi – conductors (Example: germanium, silicon) and

o Insulators (Example: wood, mica, glass).

➢ Roughly speaking, a metal represents a material which can conduct electricity well, whereas an insulator is a material which cannot convey a measurable electric current. At this stage, a semiconductor may be simply classified as a material possessing an intermediate character in electrical conduction. So, on the basis of the relative values of electrical conductivity (s) or resistivity ($\rho = 1/\sigma$), the solids are broadly classified as:

(i) *Metals:* They possess very low resistivity (or high conductivity).

$$\rho \sim 10^{-2} - 10^{-8} \ \Omega \ m$$
$$\sigma \sim 10^{2} - 10^{8} \ S \ m^{-1}$$

(ii) *Semiconductors:* They have resistivity or conductivity intermediate to metals and insulators.

$$\rho \sim 10^{-5} - 10^{6} \ \Omega \ m$$
$$\sigma \sim 10^{5} - 10^{-6} \ S \ m^{-1}$$

(iii) *Insulators:* They have high resistivity (or low conductivity).

$$\rho \sim 10^{11} - 10^{19} \ \Omega \ m$$
$$\sigma \sim 10^{-11} - 10^{-19} \ S \ m^{-1}$$

The values of ρ and σ given above are indicative of magnitude and could well go outside the ranges as well. Relative values of the resistivity are not the only criteria for distinguishing metals, insulators and

semiconductors from each other. There are some other differences, which will become clear as we go along in this chapter.

What is & Why: The Electron Theory of Metals

➢ A solid is formed as a result of bonding among huge number of atoms.

➢ The entities responsible for the bonding are the electrons.

➢ The physical and chemical properties of a given solid are decided by how the constituent atoms are bonded through the interaction of their electrons among themselves and with the potentials of the ions.

➢ The electron theory of metals covers properties of electrons responsible for the bonding of solids and electron transport properties manifested in the presence of external fields or a temperature gradient.

➢ Studies of the electron theory of metals are also important from the point of view of application-oriented research and play a vital role in the development of new functional materials.

➢ Recent progress in semiconducting devices like the IC (Integrated Circuit) or LSI (Large Scale Integrated circuit), as well as developments in magnetic and superconducting materials, certainly owe much to the successful application of the electron theory of metals.

➢ As another unique example, we may refer to amorphous metals and semiconductors, having no long-range order in their atomic arrangement. Amorphous Si is now widely used as a solar-operated battery for small calculators.

Some Basic Terminologies

Free electrons:

Electrons which move freely or randomly in all directions in the absence of an external field are known as free electrons.

Bound Electrons:

All the electrons other than valence electrons, in an isolated atom, that are bound to their parent nuclei are called as bound electrons.

Electric Field (E):

The electric field E of a conductor having uniform cross section is defined as the potential drop (V) per unit length (L) *i.e.*

$$E = V/L \ \text{V/m}$$

Current density (J):

It is defined as the current (I) per unit area of cross section (A) of an imaginary plane normal to the direction of the flow of current in a current carrying conductor *i.e.*

$$J = I/A \ \text{Am}^{-2}$$

Electron Theory of Metals

The electron theory of metals explains the following concepts:

o Structural, electrical and thermal properties of materials.

o Elasticity, cohesive force and binding in solids.

o Behavior of conductors, semiconductors, insulators etc.

So far **three electron theories** have been proposed.

1. Classical Free electron theory:

- It is a macroscopic theory.
- Proposed by Drude and Loretz in 1900.
- It explains the free electrons in lattice.
- It obeys the laws of classical mechanics.

2. Quantum Free electron theory:

- It is a microscopic theory.
- Proposed by Sommerfeld in 1928.
- It explains that the electrons move in a constant potential.
- It obeys the Quantum laws.

3. Brillouin Zone theory or Band theory:

- Proposed by Bloch in 1928.
- It explains that the electrons move in a periodic potential.
- It also explains the mechanism of semi-conductivity, based on bands and hence called band theory.

Classical Free Electron Theory

Assumptions of Free Electron Theory:

1. A metal contains a large number of free electrons which are free to move about in entire volume of the metal like the molecules of a gas in a container.
2. The free electrons move in random directions and collide with either positive ions fixed in the lattice or other free electrons. All the electrons are elastic and there is no loss of energy.
3. The velocity and the energy distribution of free electrons obey the classical Maxwell Boltzmann statistics.
4. The free electrons are moving in a completely uniform potential field due to the ions fixed in the lattice.
5. In the absence of electric field the random motion of free electrons is equally probable in all directions so that the current density vector is zero.
6. When the external electric field is applied across the ends of a metal, the electrons drift slowly with some average velocity known as drift velocity in the direction opposite to that of electric field. This drift velocity is superimposed over the random velocity. This drift velocity is responsible for the flow of electric current in a metal.

Some Important Definitions

Drift velocity

If no electric field is applied on a conductor, the free electrons move in random directions. They collide with each other and also with the positive ions. Since the motion is completely random, average velocity in any direction is zero. If a constant electric field is established inside a conductor, the electrons experience a force $F = -eE$ due to which they move in the direction opposite to direction of the field. These electrons undergo frequent collisions with positive ions. In each such collision, direction of motion of electrons undergoes random changes. As a result, in addition to the random motion, the electrons are subjected to a very slow directional motion. This motion is called drift and the average velocity of this motion is called **drift velocity v_d.**

Hence, the average velocity of the free electrons with which they move towards the positive terminal under the influence of the electrical field.

Mobility

It is defined as the drift velocity of the charge carrier per unit applied electric field.

Collision time

The average time taken by a free electron between two successive collisions is called collision time.

Mean free path

The average distance travelled by a free electron between two successive collisions is called mean free path.

Relaxation time

It is defined as the time taken by a free electron to reach its equilibrium position from the disturbed position in the presence of an electric field.

Merits of Classical Free Electron Theory

• It explains the Ohm's law.
• It explains the electrical and thermal conductivities of metals.
• It derives Wiedemann–Franz law.
• It explains the optical properties of metals.

Verification of Ohm's Law

We know that the current density,

$$J = \frac{I}{A} \quad \text{or} \quad I = JA \tag{1}$$

Here I is the current flowing per unit cross-sectional area A of the conductor. As, the microscopic form of Ohm's law is given by

$$J \propto E \quad \text{or} \quad J = \sigma E \tag{2}$$

Here, σ is known as electrical conductivity of material. Putting (2) in (1), we get

$$I = \sigma EA = \sigma\left(\frac{V}{l}\right)A \qquad\qquad \left(\text{as } E = \frac{V}{l}\right)$$

or $$I = \left(\frac{\sigma A}{l}\right)V = \left(\frac{A}{\rho L}\right)V$$

or $$I = \frac{V}{R} \qquad\qquad \left(\text{as } R = \frac{\rho l}{A}\right)$$

Here, 'R' is the resistance of metal piece with length 'l' and area 'A' and ρ is the 'resistivity' of the metal and it defines the properties of metal. Now, from above expression we can write,

$$V = IR$$

Hence, Ohm's Law is verified.

Electrical conductivity

Electrical conductivity is defined as the rate of charge flow across unit area in a conductor per unit potential (voltage) gradient.

$$\sigma = \frac{J}{E}$$ Its unit is $\Omega^{-1}m^{-1}$ or Sm^{-1}.

Expression for the Electrical Conductivity

When an electrical field (E) is applied to an electron of charge 'e' of a metallic rod, the electron moves in opposite direction to the applied field with a velocity v_d. This velocity is known as drift velocity.

Lorentz force acting on the electron $F = eE$ \hfill (1)

This force is known as the driving force of the electron.
Due to this force, the electron gains acceleration 'a'.
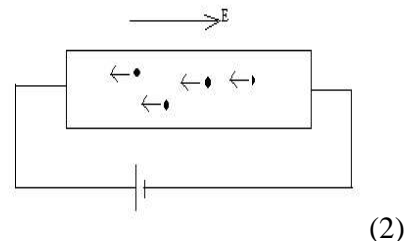From Newton's second law of motion,

$$F = ma \qquad (2)$$

From the equation (1) and (2),
$$ma = eE$$

or $$a = \frac{eE}{m} \qquad (3)$$

Acceleration in terms of drift velocity is defined as,

$$Acceleration, a = \frac{drift\,velocity, v_d}{relaxation\,time, \tau}$$

i.e. $\qquad\qquad v_d = a\tau$ $\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ (4)

Putting (3) in (4), $\quad v_d = \left(\frac{e\tau}{m}\right)E$ $\qquad\qquad\qquad\qquad\qquad\qquad$ (5)

Ohm's Law states that the current density (J) is expressed as

$$J = \sigma E \text{ or } \sigma = \frac{J}{E} \qquad\qquad\qquad\qquad\qquad\qquad (6)$$

where σ is the electrical conductivity of the electron.

But, the current density in terms of drift velocity is given as

$$J = nev_d \qquad\qquad\qquad\qquad\qquad\qquad (7)$$

Substituting equation (5) in equation (7), we have

$$J = ne\left(\frac{e\tau}{m}\right)E$$

or $\qquad\qquad \dfrac{J}{E} = \dfrac{ne^2\tau}{m}$ $\qquad\qquad\qquad\qquad\qquad\qquad$ (8)

On comparing the equation (6) and (8) , we have

$$\sigma = \frac{ne^2\tau}{m} \qquad\qquad\qquad\qquad\qquad\qquad (9)$$

This is the required expression for electric conductivity.

Mobility of Electrons

The mobility of electrons is defined as the magnitude of drift velocity acquired by the electron in a unit field.

$$\mu = \frac{v_d}{E}$$

We know $\qquad\qquad \sigma = \dfrac{J}{E} = \dfrac{I}{AE} = \dfrac{neAv_d}{AE}$ $\qquad\qquad\qquad\qquad (\because I = neAv_d)$

$$\sigma = \frac{nev_d}{E} = ne\mu$$

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

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

Thermal conductivity

Thermal conductivity K is defined as the amount of heat flowing per unit time through the material having unit area of cross-section per unit temperature gradient,

$$K = \frac{Q}{\left(\dfrac{dT}{dx}\right)}$$

Expression for Thermal Conductivity of a Metal

Consider two cross-sections A and B in a uniform metallic rod AB separated by a distance λ. Let A at a high temperature (T) and B at low temperature (T-dT). Now heat conduction takes place from A and B by the electrons. The conduction electron per unit volume is n and average velocity of these electrons is v. During the movement of electrons in the rod, collision takes place. Hence, the electrons near A lose their kinetic energy while electrons near B gain kinetic energy.
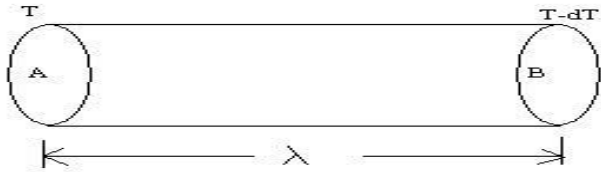
At A, average kinetic energy of an electron, $E_1 = \dfrac{3}{2}kT$ (1)

At B, average kinetic energy of the electron, $E_2 = \dfrac{3}{2}k(T - dT)$ (2)

Here, k is the Boltzmann constant.

The excess of kinetic energy carried by the electron from A to B is, E_1-$E_2 = \dfrac{3}{2}kT - \dfrac{3}{2}k(T - dT)$

$$= \frac{3}{2}kdT \qquad (3)$$

Let the electrons move in all 6 directions with equal probability. If n is the free electron density and v is the thermal velocity then,

Number of electrons crossing per unit area per time from A and B $= \frac{1}{6}nv$.

The excess of energy carried form (A to B) per unit area in unit time is,

$$E = \frac{1}{6}nv \times \frac{3}{2}kdT = \frac{1}{4}nvkdT \qquad (4)$$

Similarly, the deficient of energy carried from B to A per unit area per unit time is,

$$E' = -\frac{1}{4}nvkdT \qquad (5)$$

Hence, the net amount of energy transferred from A to B per unit area per unit time is,

$$Q = \frac{1}{2}nvkdT \qquad (6)$$

But from the basic definition of thermal conductivity, the amount of heat conducted per unit area per unit time is,

$$K = \frac{Q}{\left(\dfrac{dT}{dx}\right)} \quad \text{i.e.} \quad Q = K\left(\frac{dT}{dx}\right)$$

If we take $dx = \lambda$, the mean free path of electrons, the we can write,

$$Q = K\left(\frac{dT}{\lambda}\right) \qquad (7)$$

Putting the value of Q from (6) into (7), we get

$$\frac{1}{2}nvkdT = K\left(\frac{dT}{\lambda}\right)$$

Hence, $\qquad K = \frac{1}{2}nvk\lambda \qquad (8)$

We know that for the metals i.e. $\tau = \tau_c = \dfrac{\lambda}{v}$ or $\tau v = \lambda \qquad (9)$

Substituting the equation (8) in equation (7), we have

$$K = \frac{1}{2}nv^2k\tau \qquad (10)$$

This is the required expression for thermal conductivity. As seen, thermal conductivity of a metal is directly proportional to the concentration of free electrons and mean free path of electrons.

Wiedemann – Franz Law

The law states that the ratio of thermal conductivity to electrical conductivity of the metal is directly proportional to the absolute temperature of the metal.

$$\frac{K}{\sigma}\,\alpha T \quad \text{i.e.} \quad \frac{K}{\sigma} = LT,$$

Where L is the constant of proportionality and is known as Lorentz number.

We Know that, $$\sigma = \frac{ne^2\tau}{m} \tag{1}$$

And $$K = \frac{1}{2}nv^2k\tau \tag{2}$$

$$\frac{ThermalConductivity}{ElectricConductivity} = \frac{K}{\sigma} = \frac{\frac{1}{2}nv^2k\tau}{\frac{ne^2\tau}{m}} = \frac{1}{2}\frac{mv^2k}{e^2} \tag{3}$$

We know that the kinetic energy of an electron,

$$\frac{1}{2}mv^2 = \frac{3}{2}kT \tag{4}$$

Substituting equation (4) in the equation (3), we obtain

$$\frac{K}{\sigma} = \frac{1}{2}\frac{mv^2k^2}{e^2} = \frac{3}{2}\frac{kT\times k}{e^2} = \frac{3}{2}\frac{k^2T}{e^2}$$

i.e. $$\frac{K}{\sigma} = \frac{3}{2}\left(\frac{k}{e}\right)^2 T \tag{5}$$

or $$\frac{K}{\sigma} = LT, \tag{6}$$

where $$L = \frac{3}{2}\left(\frac{k}{e}\right)^2 \tag{7}$$

is a constant and is known Lorentz constant. Hence, it is proved that the ratio of thermal conductivity of a metal is directly proportional to the absolute temperature of the metal and the value of Lorentz constant, *L* can be calculated.

Substitution for the values for *k* and *e* into Eq. (7) gives L = 1.12 × 10–8 W.ohm.K^{-2}. On the other hand, for copper at 20°C, K = 386 Wm–1 K–1 and $\sigma = 5.81 \times 107$ ohm^{-1}. m^{-1}. Then, Eq. (6) gives a value of L = 2.266 × 10–8 W.ohm.K^{-2}. That is, the value of L predicted by classical free electron theory disagrees with its experimental value. To overcome this discrepancy, the quantum free electron theory assumes that only few free electrons in the vicinity of Fermi level conduct heat.

Drawbacks of Classical Free Electron Theory

1. It fails to explain the photoelectric effect, Compton effect, black body radiation, etc.
2. It gives a value of *4.5R* for the specific heat of metals. But, the experimental value is only 3R.
3. It gives a value of (*3/2*)R for the electronic specific heat. But, the experimental value is only 0.01R.

4. It does not explain the electrical conductivity of semiconductors and insulators.

5. It gives $\dfrac{K}{\sigma T} = $ constant for all temperatures. But, it is so only at low temperatures.

6. It does not explain the ferromagnetism.

7. The long mean free paths (more than one cm) of the free electrons at low temperatures cannot be explained on the basis of the classical theory.

8. This theory predicted that resistivity varies as $\sqrt{T}$, whereas actually it is found to vary linearly with temperature.

9. Experimental results show that para magnetism of metals is independent of temperature which deviates from classical result that paramagnetic susceptibility is inversely proportional to the temperature.

10. The resistivity of metals increases with increasing impurity concentration. On the other hand, in semiconductors even a very small amount of impurity causes a drastic decrease in their resistivity. The above feature cannot be explained by the classical theory.

Quantum Free Electron Theory of Metals

The drawbacks of the classical free electron theory were removed by Sommerfeld in 1928. He applied the Schrodinger's wave equation and de Broglie's concept of matter waves to obtain the expression for electron energies. Sommerfeld treated the problem quantum mechanically using the Fermi–Dirac statistics rather than the classical Maxwell–Boltzmann statistics. The important assumptions made by Sommerfeld are given below:

1) The free electrons move in a constant potential inside the metal and are confined within defined boundaries.

2) The eigen values of the conduction electron are quantized.

3) The electrons are considered to posses' wave nature.

4) In the various allowed energy levels, distribution of electrons takes place according to Pauli's exclusion principle.

5) Mutual attraction between electrons and lattice ions and the repulsion between individual electrons may be ignored.

The Salient Features of Quantum Free Electron Theory

- ✓ *Sommerfeld* proposed this theory in 1928 retaining the concept of free electrons moving in a uniform potential within the metal as in the classical theory, but treated the electrons as obeying the laws of quantum mechanics.

- ✓ Based on the *de-Broglie wave concept*, he assumed that a moving electron behaves as if it were a system of waves. (called matter waves i.e. the waves associated with a moving particle).

- ✓ According to quantum mechanics, the energy of an electron in a metal is quantized. The electrons are filled in a given energy level according to Pauli's exclusion principle. (i.e. no two electrons will have the same set of four quantum numbers).

- ✓ Each Energy level can provide only two states namely; one with spin up and other with spin down and hence only two electrons can be occupied in a given energy level.

- ✓ So, it is assumed that the permissible energy levels of a free electron are determined.

- ✓ It is assumed that the valance electrons travel in constant potential inside the metal but they are prevented from escaping the crystal by very high potential barriers at the ends of the crystal.

- ✓ In this theory, though the energy levels of the electrons are discrete, the spacing between consecutive energy levels is very less and thus the distribution of energy levels seems to be continuous.

Assumptions of Quantum Free Electron Theory along with those which are applicable from Classical Free Electron Theory also

Similarities between the two theories:

- ⭕ The valence electrons are treated as though they constitute an ideal gas.
- ⭕ Valence electrons can move freely throughout the body of the solid.
- ⭕ The mutual collisions between the electrons and the force of attraction between the electrons and ions are considered insignificant.

Difference between the two theories:

According to classical free electron theory:

- ⭕ The free electrons which constitute the electron gas can have continuous energy values.
- ⭕ It is possible that many electrons possess same energy.
- ⭕ The pattern of distribution of energy among the free electron obeys Maxwell-Boltzmann statistics.

According to quantum free electron theory:

○ The energy values of the free electrons are discontinuous because of which their energy values are discrete.

○ The free electrons obey the Pauli's exclusion principle. Hence no two electrons can possess same energy.

○ The distribution of energy among the free electrons is according to Fermi- Dirac statistics, which imposes a severe restriction on the possible ways in which the electrons absorb energy from an external source.

Basics of Quantum Theory

de-Broglie Wave Concepts

▪ The universe is made of Radiation (light) and matter (Particles).The light exhibits the dual nature i.e. it can behave both as a wave and as a particle. The phenomena of diffraction and interference can only be explained with the concept that light travels in the form of waves. The phenomena of photoelectric effect, Compton effect and black body radiation can only be explained with the concept of quantum theory of light. It means to say that light possesses particle nature. Hence, it is concluded that light exhibits the dual nature namely wave nature and particle nature.

▪ Since the nature loves symmetry was suggested by Louis deBroglie. de Broglie suggested that an electron or any other material particle must exhibit wave like properties in addition to particle nature. *The waves associated with a moving material particle are called matter waves, pilot waves or de Broglie waves.*

De-Broglie Wavelength

○ de-Broglie formulated an equation relating the momentum (p) of the electron and the wavelength (λ) associated with it, called de-Broglie wave equation.

○ $\lambda = $ **h/mv=h / p** where h - is the planck's constant.

Relation between de-Broglie Wavelength and Energy

Consider an electron with charge *e*, mass *m* and velocity *v* is under the influence of an electric potential **V**. The energy acquired by electron is given by,

$$E = eV = \frac{1}{2}mv^2 = \frac{p^2}{2m} \qquad (1)$$

Here p is the momentum of the electron. From (1), we can write

$$p = \sqrt{2meV} = \sqrt{2mE} \qquad (2)$$

The expression for de-Broglie wavelength is given by,

$$\lambda = \frac{h}{mv} = \frac{h}{p} = \frac{h}{\sqrt{2meV}} = \frac{h}{\sqrt{2mE}} \qquad (3)$$

Wave Function

- ❖ A variable quantity which characterizes de-Broglie waves is known as Wave function and is denoted by the symbol ψ.
- ❖ The value of the wave function associated with a moving particle at a point (x, y, z) and at a time 't' gives the probability of finding the particle at that time and at that point.

Physical significance of ψ

- ➢ The wave function ψ enables all possible information about the particle. ψ is a complex quantity and has no direct physical meaning. It is only a mathematical tool in order to represent the variable physical quantities in quantum mechanics.
- ➢ Born suggested that, the value of wave function associated with a moving particle at the position co-ordinates (x,y,z) in space, and at the time instant 't' is related in finding the particle at certain location and certain period of time 't'.
- ➢ If ψ represents the probability of finding the particle, then it can have two cases.

  Case 1: certainty of its Presence: +ve probability

  Case 2: certainty of its absence: - ve probability, but –ve probability is meaningless.

  Hence the wave function ψ is complex number and is of the form $a+ib$
- ➢ Even though ψ has no physical meaning, the square of its absolute magnitude $|\psi|^2$ gives a definite meaning and is obtained by multiplying the complex number with its complex conjugate then $|\psi|^2$ represents the probability density 'P' of locating the particle at a place at a given instant of time. And has real and positive solutions.

  $\boldsymbol{\psi\,(x,y,z,t)=a+ib}$

  $\boldsymbol{\psi*(x,y,z,t)=a-ib}$

  $\boldsymbol{P=\psi\psi*=|\psi|^2=a^2+b^2\ as\ i^2=-1}$

  where 'P' is called the probability density of the wave function.
- ➢ If the particle is moving in a volume 'V', then the probability of finding the particle in a

volume element *dv*, surrounding the point *x,y,z* and at instant '*t*' is *Pdv*

$\int|\psi|^2 dv = 1$ *if particle is present*

$\int|\psi 2|dv = 0$ if particle does not exist

This is called normalization condition.

Schrödinger Wave Equations

○ Schrödinger describes the wave nature of a particle in mathematical form and is known as Schrödinger wave equation. Schrödinger wave equation plays the role of Newton's laws and conservation of energy in classical mechanics i.e. it predicts the future behavior of a dynamic system. It is a wave equation in terms of wave function which predicts analytically and preciously the probability of events or outcomes. Schrödinger wave equation are of two types:

1. Time dependent wave equation and
2. Time independent wave equation.

To obtain these two equations, Schrödinger connected the expression of de-Broglie wavelength into classical wave equation for a moving particle. The obtained equations are applicable for both microscopic and macroscopic particles.

Schrödinger Time Dependent Wave Equation

To explain the wave function, let us consider a particle of mass m moving along the positive x-direction having accurately known momentum p and total energy E. The position of the particle is completely undetermined.

Let wave associated with such a particle be a plane, continuous harmonic wave travelling in the positive x-direction. The wavelength of the wave is

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

$$\therefore p = \frac{h}{\lambda} = \frac{h}{2\pi}.\frac{2\pi}{\lambda} = \hbar k$$

where

$$\hbar = \frac{h}{2\pi}, k = \frac{2\pi}{\lambda}$$

Now,

$$E = h\upsilon = \frac{h}{2\pi}.2\pi\upsilon = \hbar\omega, \qquad\qquad where \, \omega = 2\pi\upsilon$$

or

$$\omega = \frac{E}{\hbar}$$

Let the plane wave be represented by a complex variable quantity **ψ** called the wave function of the particle and is given by

$$\Psi = Ae^{i(kx-\omega t)} \tag{1}$$

Putting $\qquad\qquad \omega = 2\pi\upsilon \,$ and $\, k = \dfrac{2\pi}{\lambda}$

$$\psi = Ae^{i(\frac{2\pi x}{\lambda} - 2\pi\upsilon t)} = Ae^{-2\pi i(\upsilon t - \frac{x}{\lambda})} \tag{2}$$

As $\qquad\qquad E = h\upsilon = 2\pi\hbar\upsilon \,$ and $\, \lambda = \dfrac{h}{p} = \dfrac{2\pi\hbar}{p}$

or $\qquad\qquad \dfrac{E}{\hbar} = 2\pi\upsilon$

Therefore, for a free particle wave equation becomes

$$\Psi = Ae^{\frac{-i}{\hbar}(Et-px)} \tag{3}$$

Differentiate equation (3) w.r.t. **t**, we get

$$\frac{\partial\psi}{\partial t} = -\frac{i}{\hbar}EAe^{\frac{-i}{\hbar}(Et-px)}$$

$$EAe^{\frac{-i}{\hbar}(Et-px)} = -\frac{\hbar}{i}\frac{\partial\psi}{\partial t}$$

$$\Rightarrow E\psi = i\hbar\frac{\partial\psi}{\partial t} \tag{4}$$

Differentiate equation (3) w.r.t. **x**, we get

$$\frac{\partial\psi}{\partial x} = \frac{i}{\hbar}pAe^{\frac{-i}{\hbar}(Et-px)}$$

$$pAe^{\frac{-i}{\hbar}(Et-px)} = \frac{\hbar}{i}\frac{\partial\psi}{\partial x}$$

$$\Rightarrow p\psi = \frac{\hbar}{i}\frac{\partial\psi}{\partial x} \tag{5}$$

As total energy, E= Kinetic energy (K) +Potential energy (V)

Now, Kinetic Energy $= \dfrac{p^2}{2m}$

Equation (5) in terms of wave function $\boldsymbol{\psi}$ can be written as,

$$E\psi = \left(\frac{p^2}{2m}\right)\psi + V\psi \tag{6}$$

Putting the values of $E\psi$ and $p\psi$ from (4) and (5), we have

$$i\hbar \frac{\partial \psi}{\partial t} = \left(\frac{\hbar}{i}\frac{\partial}{\partial x}\right)^2 \frac{1}{2m}\psi + V\psi$$

$$i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2 \psi}{\partial x^2} + V\psi \tag{7}$$

Equation (7) is called Schrödinger time dependent wave equation in one-dimension. The Schrödinger time dependent wave equation in three-dimensional form is written as,

$$i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m}\left[\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2}\right] + V\psi \tag{8}$$

or $$i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2 \psi + V\psi \tag{9}$$

$$\left[\because \vec{\nabla} = \hat{i}\frac{\partial}{\partial x} + \hat{j}\frac{\partial}{\partial y} + \hat{k}\frac{\partial}{\partial z}\right] \quad \text{and} \quad \left[\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right]$$

or $$\left(-\frac{\hbar^2}{2m}\nabla^2 + V\right)\psi = i\hbar \frac{\partial \psi}{\partial t} \tag{10}$$

Equation (10) contains time and hence is called time dependent Schrödinger wave equation.

The operator $\left(-\dfrac{\hbar^2}{2m}\nabla^2 + V\right)$ is called *Hamiltonian* and is represented by **H**.

Schrödinger Time Independent Wave Equation

Again consider equation (3), the we have

$$\Psi = Ae^{\frac{-i}{\hbar}(Et-px)} = Ae^{\frac{-i}{\hbar}Et}e^{\frac{i}{\hbar}px}$$

or $$\Psi = \psi_0 e^{\frac{-i}{\hbar}Et} \tag{11}$$

Where $\psi_0 = Ae^{\frac{i}{\hbar}px}$

Differentiate (11) partially w.r.t. t, we get

$$\frac{\partial \psi}{\partial t} = -\frac{iE}{\hbar}\psi_0 e^{\frac{-i}{\hbar}Et} \tag{12}$$

Differentiate (11) partially w.r.t. x twice, we get

$$\frac{\partial^2 \psi}{\partial x^2} = \frac{\partial^2 \psi_0}{\partial x^2} e^{-\frac{i}{\hbar}Et} \tag{13}$$

Putting equations (11), (12) and (13) in equation (7) $i\hbar \dfrac{\partial \psi}{\partial t} = -\dfrac{\hbar^2}{2m}\dfrac{\partial^2 \psi}{\partial x^2} + V\psi$, we get

$$i\hbar\left(-\frac{iE}{\hbar}\right)\psi_0 e^{-\frac{i}{\hbar}Et} = -\frac{\hbar^2}{2m}\frac{\partial^2 \psi_0}{\partial x^2} e^{-\frac{i}{\hbar}Et} + V\psi_0 e^{-\frac{i}{\hbar}Et}$$

or $$E\psi_0 = -\frac{\hbar^2}{2m}\frac{\partial^2 \psi_0}{\partial x^2} + V\psi_0$$

or $$\frac{\partial^2 \psi_0}{\partial x^2} + \frac{2m}{\hbar^2}(E-V)\psi_0 = 0 \tag{14}$$

This is time independent Schrödinger wave equation in one-dimension.

In three-dimensional, it will be of the form as

$$\nabla^2 \psi_0 + \frac{2m}{\hbar^2}(E-V)\psi_0 = 0 \tag{15}$$

where, $\left[\nabla^2 = \dfrac{\partial^2}{\partial x^2} + \dfrac{\partial^2}{\partial y^2} + \dfrac{\partial^2}{\partial z^2}\right]$ is called the Laplacian operator.

Particle in one dimensional Box

➢ The wave nature of a moving particle leads to some remarkable consequences when the particle is restricted to a certain region of space instead of being able to move freely *i.e.* when a particle bounces back and forth between the walls of a box.

➢ The Schrodinger wave equation will be applied to study the motion of a particle in 1-D box to show how quantum numbers, discrete values of energy and zero point energy arise.

➢ From wave point of view, a particle trapped in a box is like a standing wave in a string stretched between the box's walls.

➢ Consider a particle of mass 'm' moving freely along x- axis and is confined between $x=0$ and $x= L$ by infinitely two hard walls, so that the particle has no chance of penetrating them and bouncing back and forth between the walls of a 1-D box.

➢ If the particle does not lose energy when it collides with such walls, then the total energy remains constant.
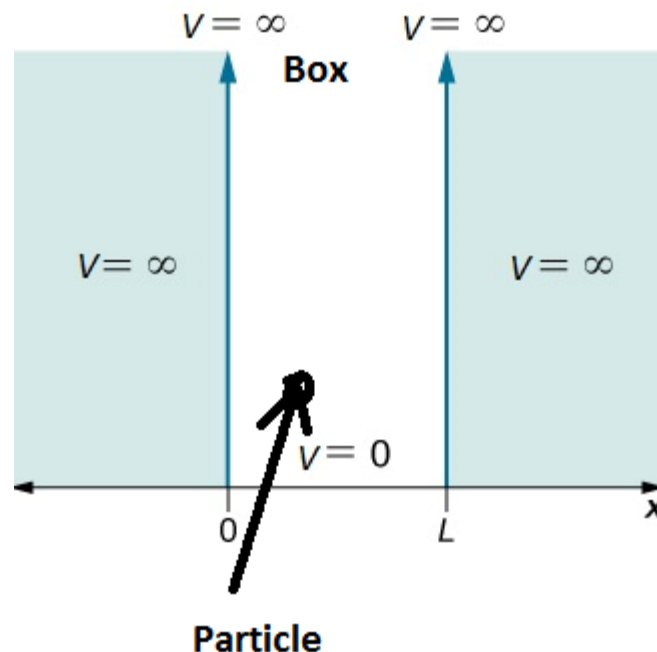
➢ This box can be represented by a potential well of width '*L*', where *V* is uniform inside the box throughout the length '*L*' i.e V= 0 inside the box or convenience and with potential walls of infinite height at x=0 and x=*L*, so that the P.E. '*V*' of a particle is infinitely high V=∞ on both sides of the box.

Boundary Conditions

The boundary conditions are

$$V(x)=0 , \psi(x)=1 \qquad \text{when } 0<x<L \tag{1}$$

$$V(x)=\infty , \psi(x)=0 \qquad \text{when } 0\geq x\geq L \tag{2}$$

Where $\psi(x)$ is the wave function and it gives the probability of finding the particle inside the box.

The Schrodinger wave equation for the particle in the potential well can be written as

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

$$\hbar = \frac{h}{2\pi}$$

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{8\pi^2 m}{h^2}(E-V)\psi = 0$$

As *V=0* for a free particle, above equation reduces to,

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{8\pi^2 m}{h^2}E\psi = 0 \tag{3}$$

In the simplest form equation (3) can be written as

$$\frac{\partial^2 \psi}{\partial x^2} + k^2\psi = 0 \tag{4}$$

Where *k* is the propagation constant and is give by

$$k = \sqrt{\frac{8\pi^2 mE}{h^2}} \tag{5}$$

The general solution of equation (4) is

$$\psi(x) = A\sin kx + B\cos kx \tag{6}$$

Where A and B are arbitrary constants and value of these constants can be obtained by applying the boundary conditions. Substituting equation (1) in (6), we get

$$0 = A\sin k(0) + B\cos k(0) \Rightarrow B = 0$$

Putting B=0 in (6)

$$\psi(x) = A\sin kx \tag{7}$$

Substituting equation (2) in (7), we get

$$0 = A\sin k(L)$$

$$\Rightarrow A = 0 \, or \sin kL = 0$$

But

$$A \neq 0$$

As already B=0, and if A=0, there is no solution at all. Therefore,

$$\sin kL = 0$$

$$i.e. kL = n\pi$$

$$\boxed{k = \frac{n\pi}{L}} \tag{8}$$

where n= 1, 2, 3, 4,…….. . and so on.

But

$$n \neq 0$$

Because if n=0, k=0, E=0 everywhere inside the box and moving particle can not have zero energy.

From (8)

$$k^2 = \left(\frac{n\pi}{L}\right)^2$$

From (5)

$$\left(\frac{n\pi}{L}\right)^2 = \frac{8\pi^2 mE}{h^2}$$

$$\boxed{E = \frac{n^2 h^2}{8mL^2}} \tag{9}$$

Zero point energy

The lowest energy of the particle is given by putting n= 1 in equation (9) *i.e.*

$$E_1 = \frac{h^2}{8mL^2} \tag{10}$$

$E_0 = 0$ is not allowed. The particle can never be at rest. The lowest energy is E_1. This is the minimum energy that the particle will be having in its lowest state or ground state. This is also called Ground state energy or Zero point energy of the system. Other levels are called excited states.

We can write

$$E_n = n^2 E_1$$

E_n

$\dfrac{9\pi^2\hbar^2}{2mL^2}$ ———— $n = 3$ ————

$\dfrac{4\pi^2\hbar^2}{2mL^2}$ ———— $n = 2$ ————

$\dfrac{\pi^2\hbar^2}{2mL^2}$ ———— $n = 1$ ————

Energy

n= 5 ———————— $25\,E_1$

n= 4 ———————— $16\,E_1$

n= 3 ———————— $9\,E_1$
n= 2 ———————— $4\,E_1$
n= 1 ———————— E_1
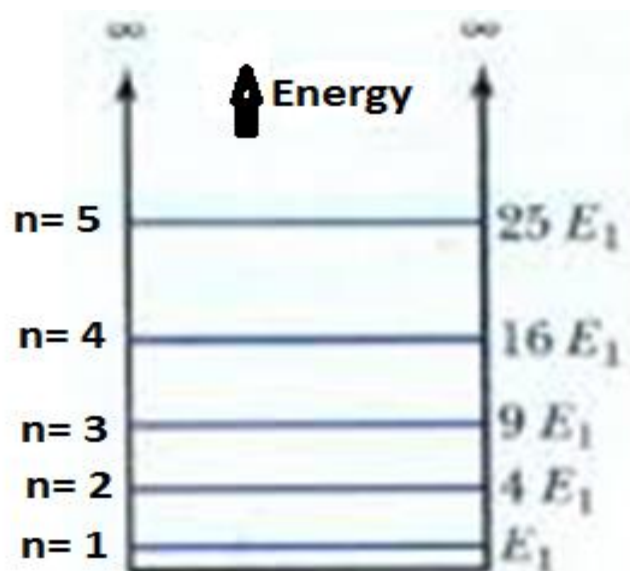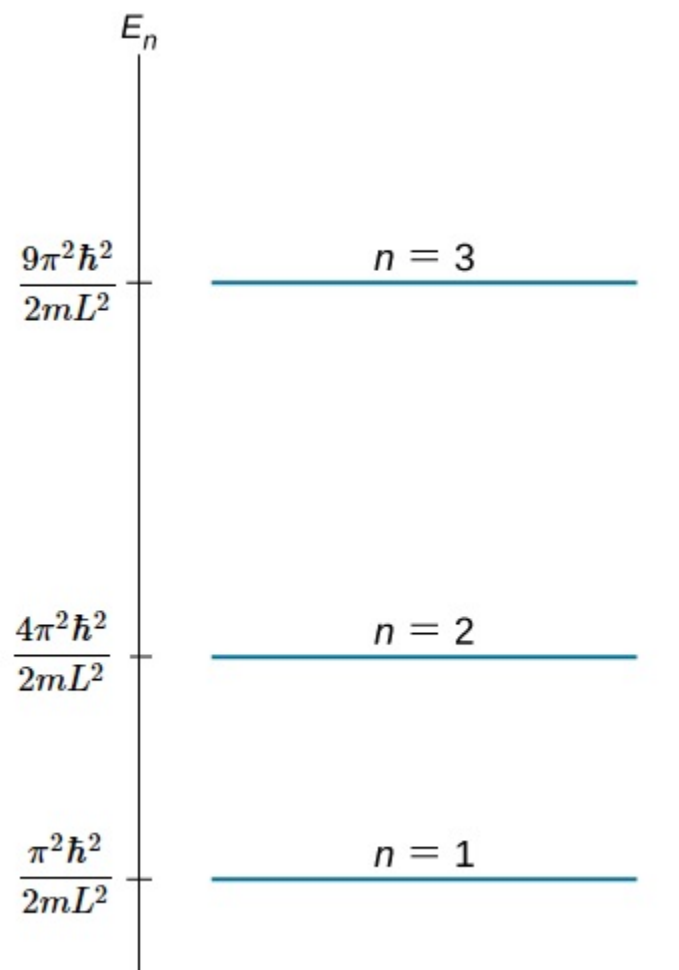
Wave Functions

The wave functions ψ_n corresponding to E_n are called Eigen functions of the particle. The integer 'n' corresponding to energy E_n are quantum number of the energy level E_n. Putting (8) in (7),

$$\psi_n = A\sin\frac{n\pi x}{L} \tag{11}$$

Normalization of Wave function

According to the normalization condition, the total probability of finding the particle somewhere inside the box must be unity.

$$\int_0^L p_x dx = \int_0^L |\psi_n|^2 \, dx = 1 \tag{12}$$

From (11) and (12),

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

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

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

The second term of the integrand expression becomes zero at both the limits. So,

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

$$A^2 = \frac{2}{L}$$

$$A = \sqrt{\frac{2}{L}} \tag{13}$$

Hence, the normalized wave function is

$$\psi_n = \sqrt{\frac{2}{L}}\sin\frac{n\pi x}{L} \tag{14}$$

The plots below show ψ_n versus x and $|\psi_n|^2$ versus x for n=1, 2, and 3etc. Note that although ψ_n can be positive or negative, $|\psi_n|^2$ is always positive.

$|\psi_n|^2$ is zero at the boundaries, satisfying our boundary conditions. In addition, $|\psi_n|^2$ is zero at other points. The number of zero points depends on the quantum number n. Only certain wavelengths for particle are allowed.
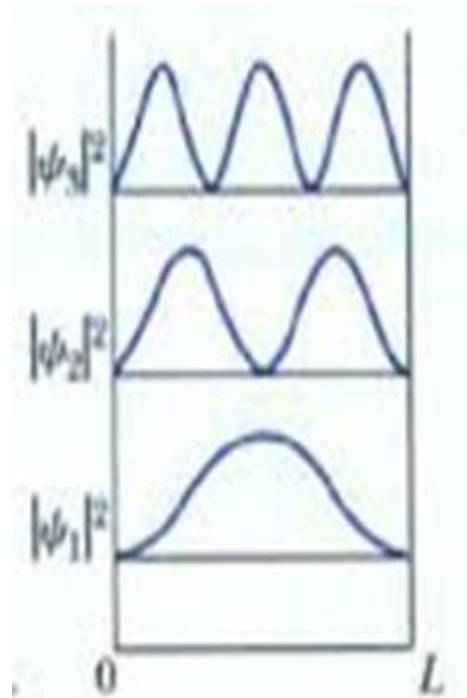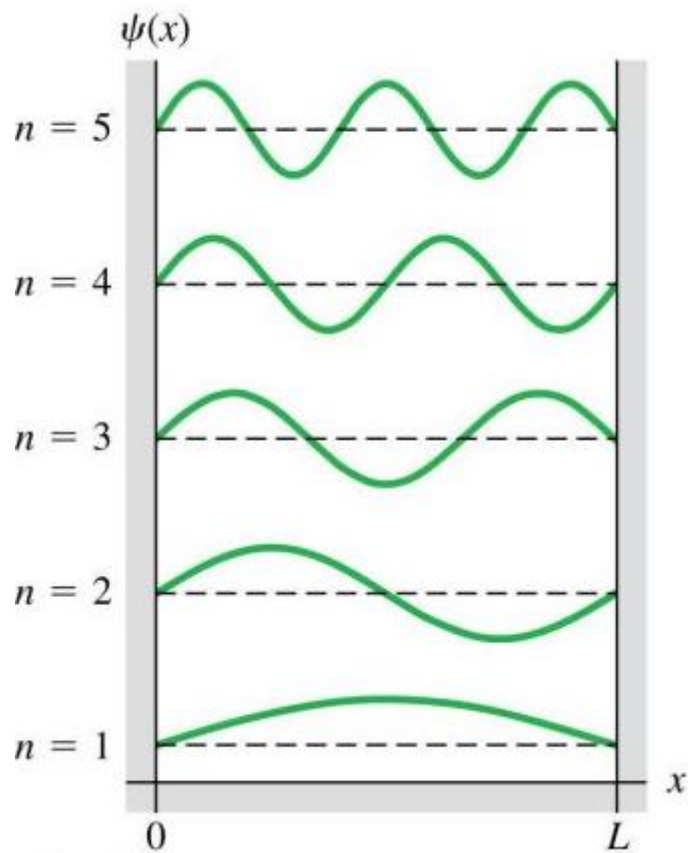
Merits of Quantum Free Electron Theory

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

    ii.   It explains the thermionic phenomenon.

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

    iv.   It can explain the specific heat of metals.

    v.   It explains magnetic susceptibility of metals.

Drawbacks of Quantum Free Electron Theory

❖ It is incapable of explaining why some crystals have metallic properties and others do not have.

❖ It fails to explain why the atomic arrays in crystals including metals should prefer certain structures and not others.

Fermi Level

For a metal containing 'N' number of free electrons, there will be 'N' number of allowed energy levels. According to the Pauli's exclusion principle, no two particles with same spin can occupy same energy state or each energy level can accommodate a maximum of two electrons, one with spin up and other with spin down, as shown in the figure below.

FERMI ENERGY
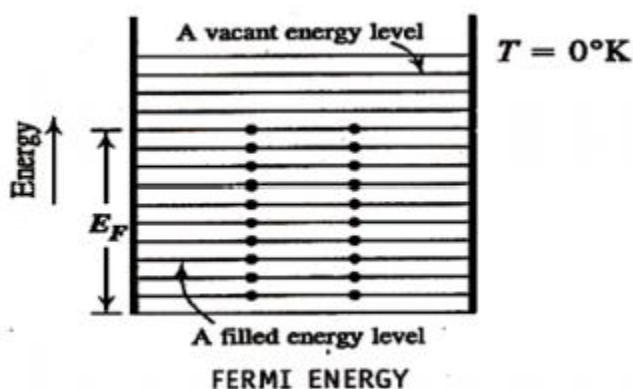
First of all, one pair of electron will occupies the lowest energy level then the next pair of electrons will occupies the next higher energy level, and so on, till all the electrons in the metal are accommodated.

Still number of allowed energy levels, are left vacant. This is the picture when there is no external energy supply for the electrons. The energy of the highest occupied level at absolute zero temperature (0 K) is called the Fermi energy and the energy level is called Fermi level. It is denoted by 'E_F'.

The electrons in the energy levels for below Fermi level cannot absorb the energy above absolute zero temperature. At ordinary temperature because there are no vacant energy levels above Fermi level into which electrons could get into after absorbing the thermal energy. Though the excitations are random, the distributions of electrons in various energy levels will be systematically governed by a statistical function at the steady state.

Therefore, as 'N' is the total number of electrons in the linear metal lattice (*i.e.*1-D) of length 'L', then in this case, we have,

$$N = 2n_F$$

Where, n_F is the principle quantum number of Fermi level which means, from total 'N' energy levels, n_F number of levels are completely occupied.

As, the energy of nth level is represented by the expression (derived from particle in 1-D box),

$$E_n = \frac{n^2 h^2}{8\, m\, L^2}$$

For, $n = n_F$,

The expression for Fermi energy is represented as,

$$E_F = \frac{n_F^2 h^2}{8\, m\, L^2} = \frac{N^2 h^2}{32\, m\, L^2}$$

Thus, the value of Fermi energy depends on the length (for 1-D) or size of the box and the number of electrons in it.

Fermi energy and its importance

Fermi level is the maximum energy level up to which the electrons can be filled at *0 K*. it is the energy of a state which the probability of electron occupation is half at any temperature above *0 K*. The important features of Fermi energy level are:

1. Fermi level acts as a reference level that separates the vacant and filled states at *0 K*.

2. At absolute zero, all the quantum states below E_F are occupied while all the quantum states having energies greater than E_F are unoccupied.

3. When the temperature is increased, few electrons gain the thermal energy and jump to the higher energy levels.

4. Fermi energy denotes the maximum kinetic energy that electrons can possess at *0 K*.

5. Fermi energy levels are used to explain the flow of electrons when two metals are brought into contact.

Total energy

The total energy 'E_o' of all the '*N*' number of electrons is calculated by adding up the energies of the individual electrons. For '*N*' electrons, the number of filled energy levels is '*N/2*' because each level can be occupied by two electrons with opposite spins. So, we can write,

$$E_o = 2 \sum_{n=1}^{n=N/2} E_n$$

Here, a factor '2' appears because each level contains 2 electrons with equal energy. Therefore using,

$$E_n = \frac{h^2}{8m} \left(\frac{n}{L}\right)^2, \text{ we get,}$$

$$E_o = 2 \frac{h}{8m} \left(\frac{1}{L}\right)^2 \sum_{n=1}^{n=N/2} n^2$$

Since, $\sum_{n=1}^{n=x} n^2 = \dfrac{1}{6}x(2x^2 + 3x + 1) \approx \dfrac{1}{3}x^3$ for, $x \gg 1$, therefore,

$$\sum_{n=1}^{n=N/2} n^2 \approx \frac{1}{3}\left(\frac{N}{2}\right)^3$$

Hence, the expression of total energy becomes,

$$E_o = 2\frac{h^2}{8m}\left(\frac{1}{L}\right)^2\frac{1}{3}\left(\frac{N}{2}\right)^3 = \frac{1}{3}\frac{h^2 N^2}{32mL^2}N$$

Therefore,

$$E_o = \frac{1}{3} N E_F$$

Therefore, the average kinetic energy ($\bar{E}$) of all the electrons at T = 0 K (for 1-D metal lattice), will be

$$\bar{E} = \frac{E_o}{N} = \frac{1}{3}E_F$$

Fermi – Dirac Distribution Function (or Occupational Probability)

In Fermi Dirac distribution all the particles in the system are indistinguishable and it obeys Pauli's exclusive principle (i.e., not more than two electrons can occupy the same energy level) on filling the particles in the energy levels. This is mainly applicable for fermions (Fermions are the particles with odd half integral spins $(0,1/2,3/2,5/2,.....)$. It means that the distribution statistics obeyed by quantum particles like electrons is called the Fermi–Dirac statistics. The Fermi–Dirac distribution function f(E) is an expression for the distribution of electrons among the energy levels as a function of temperature and gives the probability of finding an electron in a particular energy state of energy E as

$$f(E) = \frac{1}{1 + \exp\left(\dfrac{E - E_F}{kT}\right)}$$

Where E_F - Fermi energy (highest energy level of an electron)

k - Boltzmann's constant

T - Absolute temperature

Because Fermi–Dirac distribution function gives, the probability of finding (occupying) an electron in a particular energy state of energy E, that is why it is also known as occupational probability.

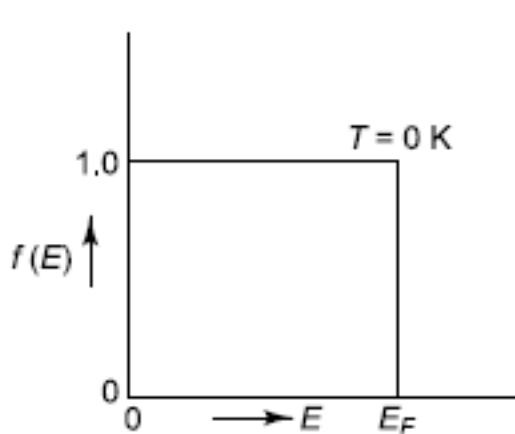## *Variation of Fermi function with Temperature*

The Fermi function varies with temperatures is discussed below:

(I)   At T=0K and E< E_F

$$f(E) = \frac{1}{1+\exp(-\infty)} = \frac{1}{1+0} = 1 \qquad \because \left(e^{-\infty} = \frac{1}{e^{\infty}} = \frac{1}{\infty} = 0 \right)$$

$f(E)=1=100\%$

It means that there is 100% probability for the electrons to occupy the energy level below the Fermi energy level.
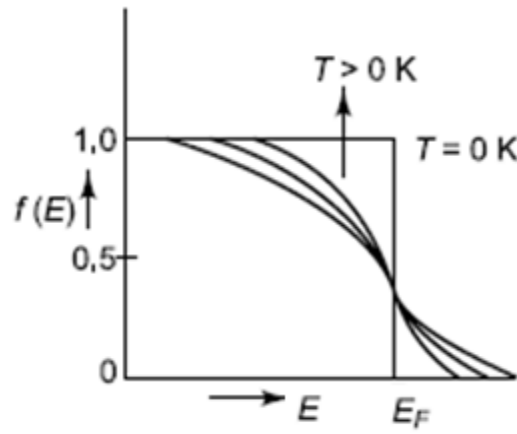
(II)   At T=0 K and E> E_F

$$f(E) = \frac{1}{1+\exp(\infty)} = \frac{1}{1+\infty} = \frac{1}{\infty} = 0 \qquad \because \left(e^{\infty} == \infty \right)$$

$f(E)=0=0\%$

It means that there is 0% probability for the electrons to occupy the energy level above the Fermi energy level.

(III)   At T>0 K and E=E_F

$$f(E) = \frac{1}{1+\exp(0)} = \frac{1}{1+1} = \frac{1}{2} \qquad \qquad \because \left(e^0 == 1\right)$$

$$f(E) = 0.5 = 50\%$$

It means that 50% probability for the electrons to occupy the Fermi energy level. That is the energy levels above Fermi level are empty and below Fermi level are filled.

Fermi level, Fermi Energy and their importance

Fermi energy level is defined as the highest reference level of a particle at absolute *0 K*.

Importance: It is the reference energy level which separates the filled energy levels and vacant energy levels.

Fermi energy (E_F) : The Fermi energy is the maximum energy of the quantum state corresponding to Fermi energy level at absolute zero

Importance: Fermi energy determines the energy of the particle at any temperature.

Properties of Fermi Function

1. It is applicable for all metals, semiconductors and insulators.
2. In semiconductors the probability of **electron** occupying an energy level E_i is

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

3. In semiconductors the probability of **hole** occupying an energy level E_i is

$$f_h(E_i) = 1 - f_e(E_i) = 1 - \frac{1}{1+\exp\left(\dfrac{E_i - E_F}{kT}\right)}$$

i.e.
$$f_h(E_i) = \frac{1+\exp\left(\dfrac{E_i - E_F}{kT}\right) - 1}{1+\exp\left(\dfrac{E_i - E_F}{kT}\right)} = \frac{1}{\exp\left(\dfrac{E_F - E_i}{kT}\right) + 1}$$

4. *At T=0 K , if E< E_F , f(E)=1=100%*
5. *At T=0 K , if E> E_F , f(E)=0=0%*
6. *At T>0 K , if E= E_F , f(E)=0.5=50% .*

Density of States

The Fermi function gives us only the probability of occupation of a quantum energy state by a single electron. The ability of a metal to conduct electricity depends on how many quantum energy states are available to for electrons and what are the energies of those states. In physics, a quantum state is characterized by a set of quantum numbers and represented by an Eigen function. It is not an easy task to list the energies of so many states individually, instead of this; we find the number of states in a unit volume of the sample having energies in the range E and E+dE. We write this number as D(E)dE, where D(E) is called the density of states at energy E. The unit of D(E) is states per cubic meter per electron volt ($m^{-3}eV^{-1}$).

We know that the permitted energy levels for electrons in a solid material will be in terms of bands. Let the energy band be spread in an energy interval between E_1 and E_2 in the material. Consider an infinitesimal small increment dE at arbitrary energy value E in the band. Since dE is an infinitesimally small increment in E, we can assume that D(E) remains constant between E and E+dE.

The density of states is defined as the number of energy states present in a unit energy interval. It is denoted by *D(E)* and given by,

$$D(E) = \frac{dN}{dE}$$

Where, *dN* represents the number of energy states present in the energy interval *E* and *E+dE*. Since each energy level can accommodate 2 electrons, the actual density of states will be twice the above value, i.e.

$$D(E) = 2 \frac{dN}{dE}$$

Density of States in 1-D

The density of states is defined as the number of energy states present in a unit energy interval. It is denoted by *D(E)* and given by,

$$D(E) = \frac{dN}{dE}$$

Where, *dN* represents the number of energy states present in the energy interval E and $E+dE$. Since each energy level can accommodate 2 electrons, the actual density of states will be twice the above value, i.e.

$$D(E) = 2\,\frac{dN}{dE}$$

As we know, $E = \frac{h^2}{8m}\left(\frac{N}{L}\right)^2$, therefore, $\frac{1}{N} = \left(\frac{h^2}{8mL^2E}\right)^{1/2}$

So,

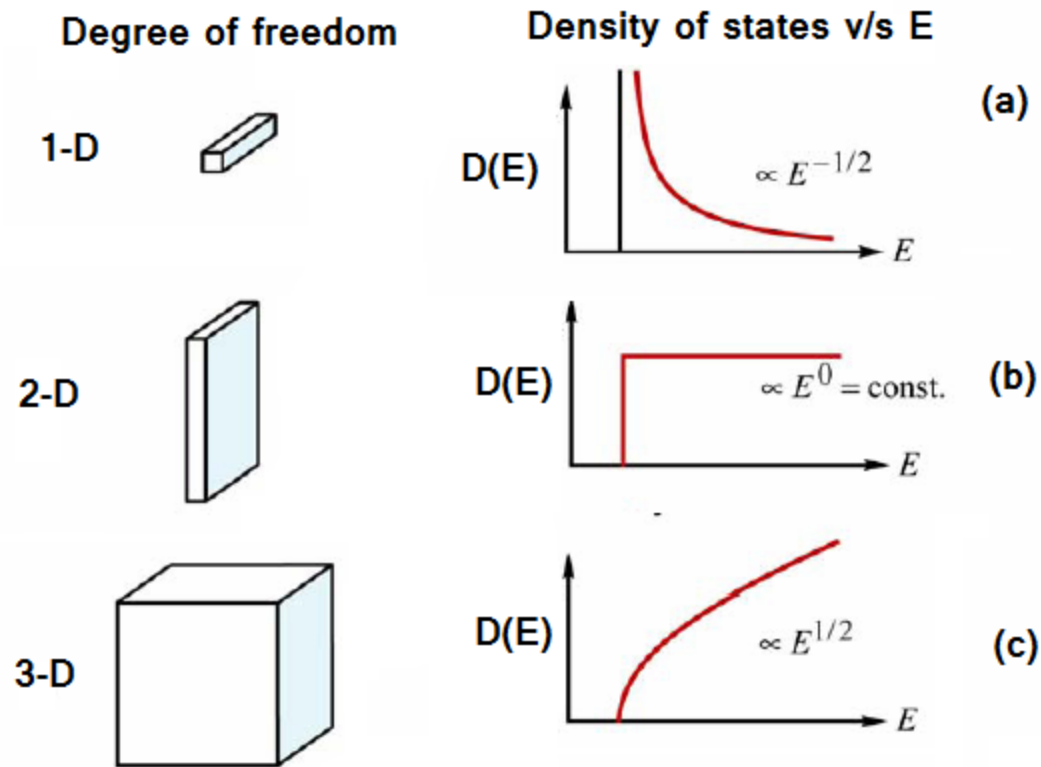$$\frac{dE}{dN} = \frac{h^2\,N}{4\,m\,L^2}$$

Therefore,

$$D(E) = 2\frac{dN}{dE} = 2\frac{1}{\frac{dE}{dN}} = \frac{8\,m\,L}{h^2\,N}$$

Substituting the expression of (1/N) in above equation, we get,

$$D(E) = \frac{4\,L}{h}\left(\frac{m}{2\,E}\right)^{1/2}$$

The plot of *D(E)* versus E is shown in fig (a). All energy levels below E_F are completely filled and all those above is are totally empty at *0 K* temperature. Thus, at *0 K*, the Fermi energy level divides or separates the filled energy levels from unfilled energy levels.

Degree of freedom		Density of states v/s E	

1-D

$D(E)$ $\propto E^{-1/2}$ **(a)**

2-D

$D(E)$ $\propto E^0 = \text{const.}$ **(b)**

3-D

$D(E)$ $\propto E^{1/2}$ **(c)**

Density of States in 2-D

In case of two dimensions, every point in the N-space will have fixed values of (N_x, N_y) and hence, energy in N-space will be,

$$E = \frac{h^2}{8\,m\,L^2}(N_x^2 + N_y^2)$$

Or,

$$N_x^2 + N_y^2 = \left(\sqrt{\frac{8\,m\,L^2 E}{h^2}}\right)^2$$

The above equation represents the equation of a circle: $x^2 + y^2 = r^2$ with radius, $r = \sqrt{\frac{8\,m\,L^2 E}{h^2}}$ in a two dimensional N-space with axis N_x and N_y as shown in the figure below:
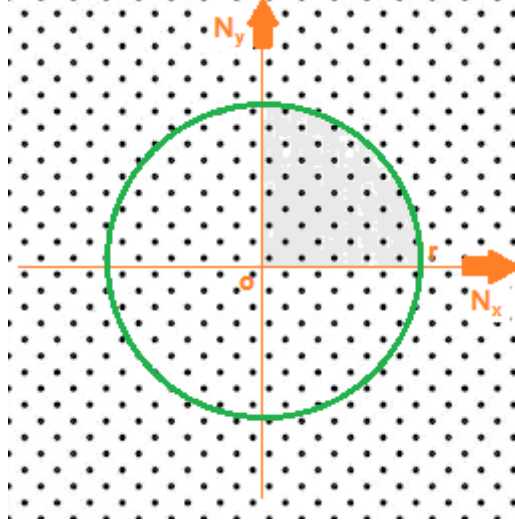
In this case, the total number of states N is the defined as the area of circle with radius 'r' in N-space with axis N_x and $\mathbf{N_y}$. However, number states cannot have negative value. Therefore, the valid states are represented by the shaded portion (grey) i.e. first quadrant which is one fourth of the area of circle. Hence, N will be,

$$N = \frac{1}{4}\pi r^2$$

$$N = \frac{1}{4}\pi \frac{8\,m\,L^2 E}{h^2}$$

Considering the unit area of the solid material, i.e. area $= L^2 = 1$, we get,

$$N = 2\pi \frac{mE}{h^2}$$

Now,

$$\frac{dN}{dE} = 2\pi \frac{m}{h^2}$$

Now, as per definition, density of states is given by,

$$D(E) = 2\frac{dN}{dE} = 4\pi\frac{m}{h^2}$$

The above equation concludes that, the density of states in 2-D, does not depend upon the energy as shown in fig (b). As the top of the energy gap is reached, there are a significant number of available states. Taking into account the other energy levels in the quantum well, the density of states becomes the stair case like function, as shown in figure below:
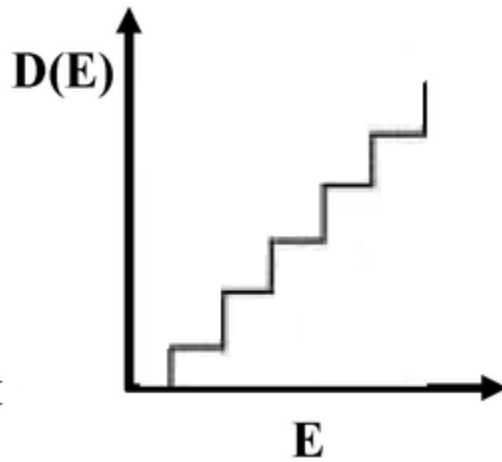
Density of states in 3-D:

The Fermi function gives us only the probability of occupation of a quantum energy state by a single electron. The ability of a metal to conduct electricity depends on how many quantum energy states are available to for electrons and what are the energies of those states. In physics, a quantum state is characterized by a set of quantum numbers and represented by an Eigen function. It is not an easy task to list the energies of so many states individually, instead of this; we find the number of states in a unit volume of the sample having energies in the range E and E+dE. We write this number as D(E)dE, where D(E) is called the density of states at energy E. The unit of D(E) is states per cubic meter per electron volt ($m^{-3}eV^{-1}$).

We know that the permitted energy levels for electrons in a solid material will be in terms of bands. Let the energy band be spread in an energy interval between E_1 and E_2 in the material. Consider an

infinitesimal small increment dEat arbitrary energy value E in the band. Since dE is an infinitesimally small increment in E, we can assume that D(E) remains constant between E and E+dE.

Mathematically, density of states is represented by D(E), where,

$$D(E) = 2\frac{dN}{dE}$$

The equation (2), $E = \frac{h^2}{8\,m\,L^2}(N_x^2 + N_y^2 + N_z^2)$, can be re-written as,

$$(N_x^2 + N_y^2 + N_z^2) = \left(\sqrt{\frac{8\,m\,L^2}{h^2}\,E}\right)^2 \qquad (3)$$

The above expression (3) represents the equation of a sphere with radius $R = \sqrt{\frac{8\,m\,L^2}{h^2}\,E}$, in 3-D N-space with perpendicular axis N_x, N_y and N_z. Therefore, the number of states in sphere = numerical value of the volume expressed in units of cubes of lattice parameters. Note that every point in the N-space will have a fixed value of (N_x, N_y, $N_{z)}$and hence the different points in the N-space will represent different energy state of the electron inside the metal. Furthermore, as the quantum number N_x, N_y and N_z can only have positive integral values, so the points corresponding to the allowed energy states for the electron inside the metal can exist only in the positive octant of the sphere in N-space, i.e. the number of energy states must be equal to the $1/8^{th}$ of the volume of sphere with radius R or volume of the positive octant of the sphere with radius R in N-space. i.e.
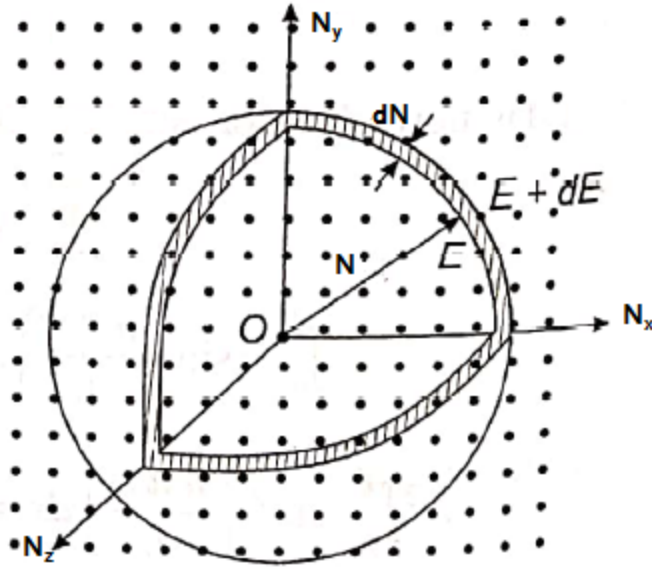
$$N = \frac{1}{8} \text{ volume of sphere with radius } R = \frac{1}{8} \times \frac{4}{3}\pi R^3$$

$$N = \frac{1}{8} \times \frac{4}{3}\pi \left(\sqrt{\frac{8 \, m \, L^2}{h^2}} \, E \right)^3$$

$$N = \frac{\pi}{6} \times L^3 \left(\frac{8 \, m}{h^2} \right)^{3/2} E^{3/2}$$

For cubical metal lattice with unit volume, Volume of lattice $= L^3 = V$

$$N = \frac{\pi}{6} V \left(\frac{8 \, m}{h^2} \right)^{3/2} E^{3/2}$$

On differentiating above equation, we get,

$$dN = \frac{8 \, \pi}{6h^3} V(2 \, m)^{3/2} \frac{3}{2} E^{1/2} dE$$

$$\frac{dN}{dE} = \frac{2 \, \pi}{h^3} V(2 \, m)^{3/2} E^{1/2}$$

Now, as per definition, $D(E) = 2\frac{dN}{dE}$

$$D(E) = 2 \times \frac{2\pi}{h^3}V(2\ m)^{3/2}E^{1/2}$$

Therefore,

$$D(E) = \frac{4\pi}{h^3}V(2\ m)^{3/2}E^{1/2} = 4\pi V\left(\frac{2\ m}{h^2}\right)^{3/2}E^{1/2}$$

In $\hbar$, form (i.e. $\hbar = h/2\pi$)

$$D(E) = \frac{V}{2\pi^2}\left(\frac{2\ m}{\hbar^2}\right)^{3/2}E^{1/2}$$

The above express can be written as,

$$D(E)\ dE = \frac{V}{2\pi^2}\left(\frac{2\ m}{\hbar^2}\right)^{3/2}E^{1/2}\ dE$$

The above equation shows that the density of states D(E) is a parabolic function of energy E as shown in the figure below,
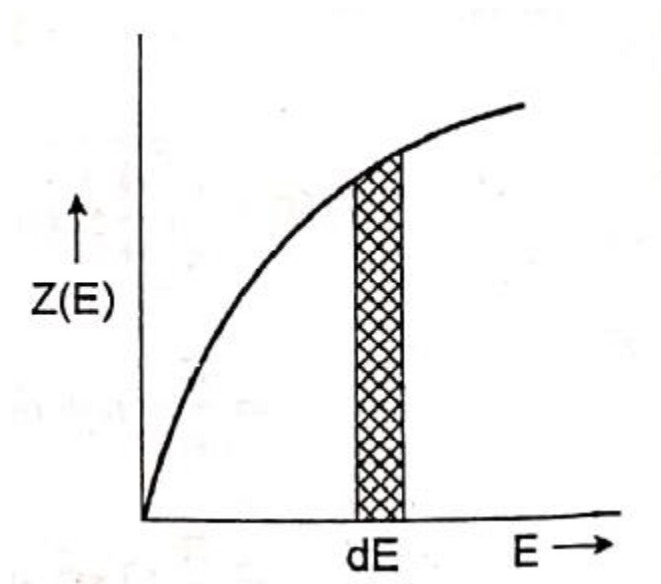
It is obvious that D(E) increases with increase in crystal's volume. The number of energy states present in unit volume having energy values lying between E and E+dE (called energy density of energy states) can be obtained by putting $V = L^3 = 1$ in equation (7),

$$D(E) \, dE = \frac{1}{2\pi^2}\left(\frac{2\,m}{\hbar^2}\right)^{3/2} E^{1/2} \, dE = 4\,\pi\left(\frac{2\,m}{h^2}\right)^{3/2} E^{1/2} dE$$

Fermi energy in 3-D and Density of electrons:

Let us consider, the occupancy probability of allowed energy states at absolute zero temeperature i.e. T=0 K. To add one electron to the allowed energy states, first, ground state is to be filled then the higher energy states (i.e. excited states). Similarily, until the last electron in the metal is added at a level above which all the other states are unoccupied. This level is defined as the Fermi level and is denoted by $E_{F(0)}$ at $T = 0$ K i.e. Fermi level is the top most energy level filled with electrons at 0 K temeperature. In other words, the Fermi level $E_{F(0)}$ divides or seperates the filled and empty energy states at zero kelvin. The energy of the Fermi level is called Fermi energy. To find out the expression of Fermi energy in 3-D, the expression for the total number of electrons inside the metal is to be formulated.

The total number of energy states in the metal wih energy $\leq$ E, is given by

$$N = \frac{\pi}{6}V\left(\frac{8\,m}{h^2}\right)^{3/2} E^{3/2}$$

Since, every energy level can occupy two electrons, so total number of electrons in the energy states lying between $E = 0$ to $E = E_{F(0)}$ at 0 K, will be,

$$N_e = 2N = 2 \times \frac{\pi}{6}V\left(\frac{8\,m}{h^2}\right)^{3/2} E_{F(0)}{}^{3/2}$$

$$N_e = \frac{\pi}{3}V\left(\frac{8\,m}{h^2}\right)^{3/2} E_{F(0)}{}^{3/2}$$

Therefore, the numberdensity of electron per unit volume is,

$$n = \frac{N_e}{V} = \frac{\pi}{3}\left(\frac{8\,m}{h^2}\right)^{3/2} E_{F(0)}{}^{3/2}$$

Hence, Fermi energy can be expressed as,

$$E_{F(0)}{}^{3/2} = \frac{3n}{\pi}\left(\frac{h^2}{8\,m}\right)^{3/2}$$

$$E_{F(0)}{}^{3/2} = \frac{3n}{\pi}\left(\frac{h^2}{8\,m}\right)^{3/2}$$

$$E_{F(0)} = \left(\frac{3n}{\pi}\right)^{2/3}\left(\frac{h^2}{8\,m}\right) = (3\,n\,\pi^2)^{2/3}\left(\frac{\hbar^2}{2\,m}\right)$$

So, the Fermi energy may be calculated simply by knowing the electron concentration 'n'. The calculated value of $E_{F(0)}$ is the order of 5 eV. This is a special feature of quantum mechanics. According to classical theory, the elctrons have zero energy at absolute zero.

Variation of Fermi energy with temperature:

Fermi energy decreases with increase in temperature. An approximate relationship between Fermi energy at a temperature 'T' and Fermi energy at T = 0, represented by $E_{F(T)}$ and $E_{F(0)}$ respectively is given by.

$$E_{F(T)} = E_{F(0)}\left[1 - \frac{\pi^2}{12}\left(\frac{k\,T}{E_{F(0)}}\right)^2\right]$$

At room temerature, i.e. T = 300 K, for $E_{F(0)}$ = 1.7 eV (i.e. metals) the value of the ratio:

$$\frac{k\,T}{E_{F(0)}} = 0.015$$

Therefore, it follows that the temperature dependency of Fermi energy is very slight and for all practical puposes (at room temeperature), we can assume at T> 0 K, Fermi level no longer represents the top-most filled energy.

Average Kinetic energy at zero kelvin:

The average kinetic energy of an electron at a temeprature T, is given by,

$$\overline{E} = \frac{1}{N_e} \int_0^\infty E.D(E).F(E)dE$$

However, at T = 0 K, the maximum energy of electron is $E_{F(0)}$ and F(E) = 1, therefore,

$$\overline{E} = \frac{1}{N_e} \int_0^{E_{F(0)}} E.D(E)\,dE$$

Substituting the expression of D(E), we get,

$$\overline{E} = \frac{1}{N_e} \int_0^{E_{F(0)}} E\,\frac{V}{2\pi^2}\left(\frac{2\,m}{\hbar^2}\right)^{3/2} E^{1/2}\,dE$$

$$\overline{E} = \frac{1}{N_e}\frac{V}{2\pi^2}\left(\frac{2\,m}{\hbar^2}\right)^{3/2} \int_0^{E_{F(0)}} E^{3/2}\,dE = \frac{1}{N_e}\frac{V}{2\pi^2}\left(\frac{2\,m}{\hbar^2}\right)^{3/2}\frac{2}{5}E_{F(0)}^{5/2}$$

Now, substituting, $N_e = \frac{V}{3\,\pi^2}\left(\frac{2\,m}{\hbar^2}\right)^{3/2} E_{F(0)}^{3/2}$ in above equation, we get,

$$\overline{E} = \frac{\dfrac{V}{2\pi^2}\left(\dfrac{2\,m}{\hbar^2}\right)^{3/2}\dfrac{2}{5}E_{F(0)}^{5/2}}{\dfrac{V}{3\,\pi^2}\left(\dfrac{2\,m}{\hbar^2}\right)^{3/2}E_{F(0)}^{3/2}} = \frac{3}{5}E_{F(0)}$$

$$\overline{E} = \frac{3}{5}E_{F(0)}$$

Electrons in a Periodic Potential - Bloch Theorem

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.
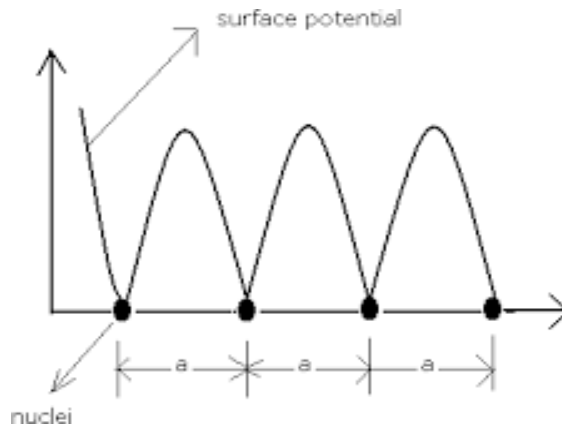
The potential is minimum at the positive ion sites and maximum between the two ions. The one-dimensional Schrödinger equation corresponding to this can be written as

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

$$\hbar = \frac{h}{2\pi}$$

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{8\pi^2 m}{h^2}(E - V)\psi = 0$$

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

$$V(x) = V(x + a) ---- (2)$$

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

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

In the above equation $U_k(x)$ is called "modulating function" or Bloch fonction. Because free electron wave is modulated by $U_k(x)$ is periodic with the periodicity at the crystal lattice. Let us now consider a linear chain of atoms in one-dimensional case. Then

$$U_k(x) = U_k(x+a) ----------------------(4)$$

Where 'a' is lattice distance.

From equation (3) and (4), $(x+a) = e^{ik(x+a)} . U_k(x+a)$

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

$$\psi(x+a) = \psi(x). \ e^{ika}$$

This is referred to as Bloch condition.

Kronig-Penney Model

According to quantum free electron theory of metals, a conduction electron in a metal experiences constant (or zero) potential and free to move inside the crystal but will not come out of the metal because an infinite potential exists at the surface. This theory successfully explains electrical conductivity, specific heat, thermionic emission and paramagnetism. This theory is fails to explain

many other physical properties, for example: (i) it fails to explain the difference between conductors, insulators and semiconductors, (ii) positive Hall coefficient of metals and (iii) lower conductivity of divalent metals than monovalent metals. To overcome the above problems, the periodic potentials due to the positive ions in a metal have been considered. shown in Fig. (a), if an electron moves through these ions, it experiences varying potentials. The potential of an electron at the positive ion site is zero and is maximum in between two ions. The potential experienced by an electron, when it passes along a line through the positive ions is as shown in Fig.(b).

(a)

(b)

(c)
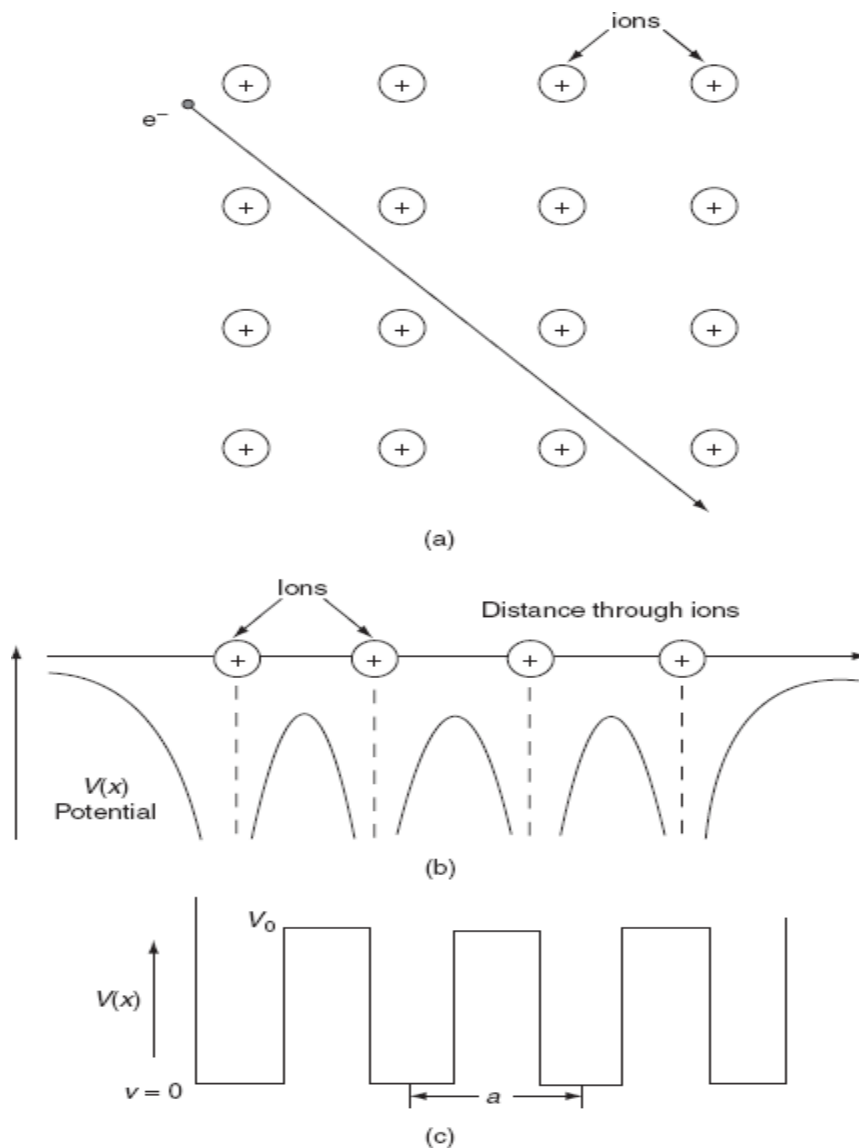
It is not easy to solve Schrödinger's equation with these potentials. So, Kronig and Penney approximated these potentials inside the crystal to the shape of rectangular steps as shown in Fig. (c). This model is called Kronig-Penney model of potentials.
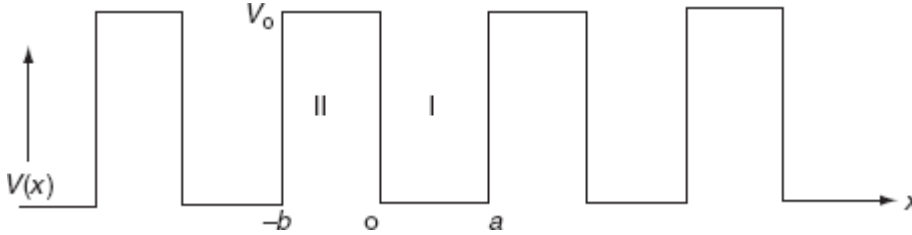
The energies of electrons can be known by solving Schrödinger's wave equation in such a lattice. The Schrödinger time-independent wave equation for the motion of an electron along X-direction is given by:

$$\frac{d^2\psi_1(x)}{dx^2} + \frac{2m}{\hbar^2} E\,\psi_1(x) = 0 \qquad\qquad \text{for } 0<x<a \tag{1}$$

$$\frac{d^2\psi_2(x)}{dx^2} + \frac{2m}{\hbar^2}(E - V_o)\,\psi_2(x) = 0 \qquad\qquad \text{for } -b<x<0 \tag{2}$$

We define two real quantities (say) α and β such that:

$$\alpha^2 = \frac{2mE}{\hbar^2} \tag{3}$$

and,

$$\beta^2 = \frac{2m}{\hbar^2}(V_o - E) \tag{4}$$

Therefore, the equation (1) and (2) becomes,

$$\frac{d^2\psi_1(x)}{dx^2} + \alpha^2\psi_1(x) = 0 \qquad\qquad \text{for } 0<x<a \tag{5}$$

$$\frac{d^2\psi_2(x)}{dx^2} - \beta^2\psi_2(x) = 0 \qquad\qquad \text{for } -b<x<0 \tag{6}$$

According to Bloch's theorem, the wave function solution of the Schrödinger equation when the potential is periodic and to make sure the function $\psi(x)$ is also continuous and smooth, can be written in the following form:

$\psi(x)=e^{ikx}u_k(x)$

where $u_k(x)$ is the periodic with periodicity of lattice i.e.

$$u_k(x) = u_k(x+a) \tag{7}$$

Boundary Conditions

a) First boundary conditions:

  i) $\quad u_1|_{x=0} = u_2|_{x=0}$

  ii) $\quad \dfrac{du_1}{dx}\bigg|_{x=0} = \dfrac{du_2}{dx}\bigg|_{x=0}$ $\tag{8}$

b) Second boundary conditions:

  iii) $\quad u_1|_{x=a} = u_2|_{x=-b}$

  iv) $\quad \dfrac{du_1}{dx}\bigg|_{x=a} = \dfrac{du_2}{dx}\bigg|_{x=-b}$ $\tag{9}$

Using the above boundary conditions of Eq.(8) and Eq (9), and then solving for constants keeping in mind the continuity and periodicity of wave function, one obtains the equation

$$P\frac{\sin(\alpha a)}{\alpha a} + \cos(\alpha a) = \cos(ka) \tag{10}$$

where, $P = \dfrac{mV_o}{\hbar^2}ab$, and $\alpha^2 = \dfrac{2mE}{\hbar^2}$, therefore, $E = \dfrac{\alpha^2 \hbar^2}{2m}$ and $k = \dfrac{2\pi}{\lambda}$

Equation (10) is a condition of existence of a solution for the electron wave function.

The physical significance of P is that as it increases the area of potential barrier increases i.e the electron is bound more strongly to a particular potential well. When $P \to 0$, the potential barrier becomes very weak i.e. electron becomes free.

There are only two variables in equation (10) namely α and k. This equation (10) shows the relation between the energy (through α) and the wave-vector, k, and as you can see, since the left hand side of the equation can only range from -1 to 1 then there are some limits on the values that α (and thus, the energy) can take. At some ranges of values of the energy, there is no solution according to these equation and thus, the system will not have those energies. These are the so-called band-gaps, which can be shown to exist in *any* shape of periodic potential (not just delta or square barriers). This has been plotted in Fig. below:

(a)

(b)

(c)
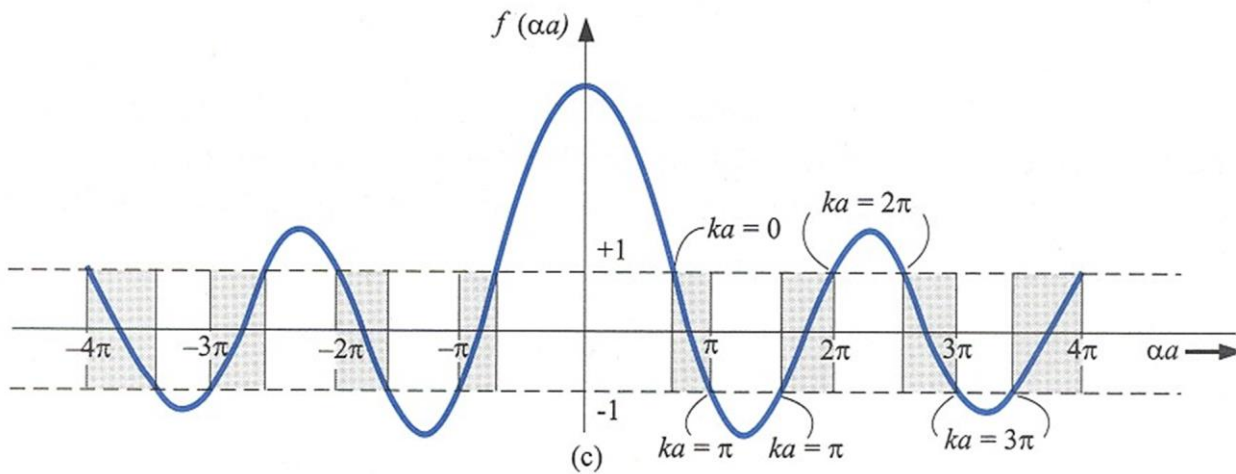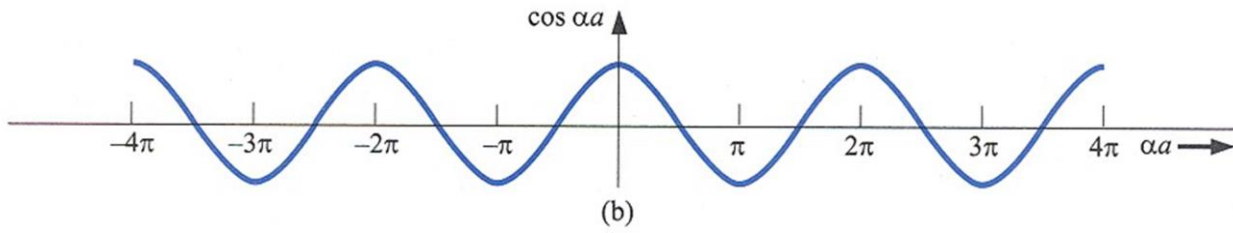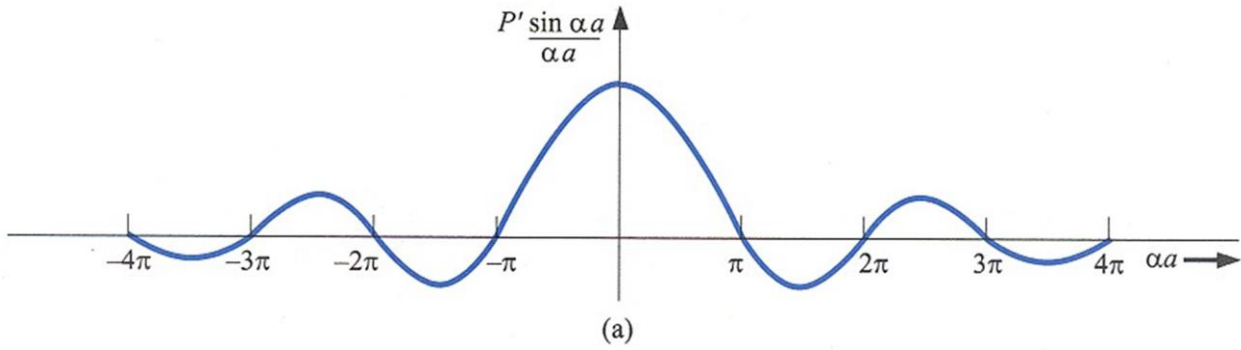
Graph of right hand side of eqn. (10) as a function of P for $P=2$.

1. The permissible limit of the term $P\frac{\sin(\alpha a)}{\alpha a} + \cos(\alpha a)$ lies between +1 to -1. By varying αa, a wave mechanical nature could be plotted as shown in Fig, the shaded portion of the wave shows the bands of allowed energy with the forbidden region as unshaded portion.

This means that the energy spectrum of the electron consist of alternate regions of allowed and forbidden energy bands.
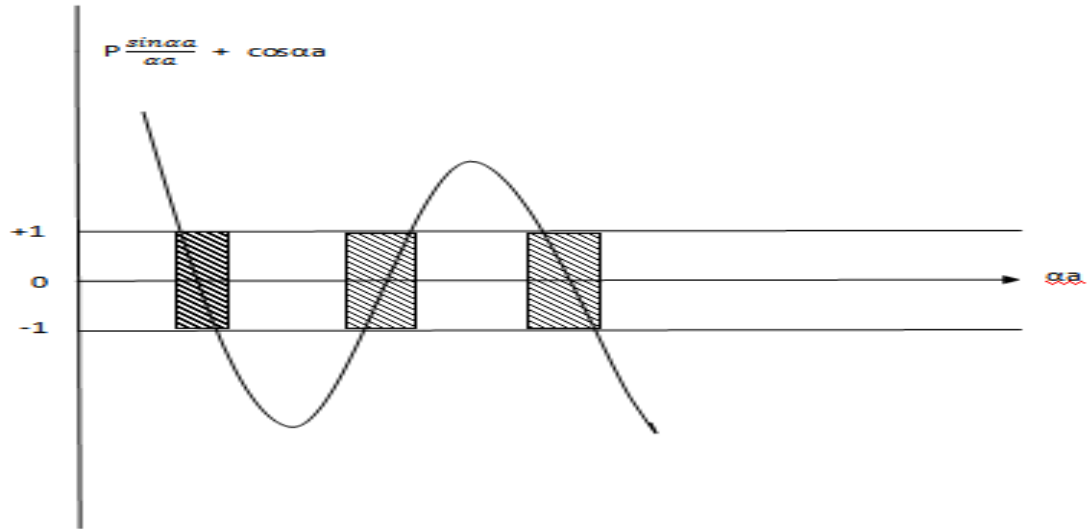
2. With increase of **αa**, the allowed energy states for a electron increases there by the width of the allowed bands increases and width of forbidden bands decreases i.e., the strength of the potential barrier diminishes. This is a consequence of the fact that the first term of equation (10) decreases on the average with increaseing **αa**

3. Let us now consider the effect of varying P. As P is a measure of potential barrier strength, so if V_{ob} is large i.e .if P is large, the function described by the L.H.S of equation (10) crosses +1 and -1 at stepper angle. Thus, allowed energy region becomes narrower and forbidden regions are wider as can be seen in diagram given below:
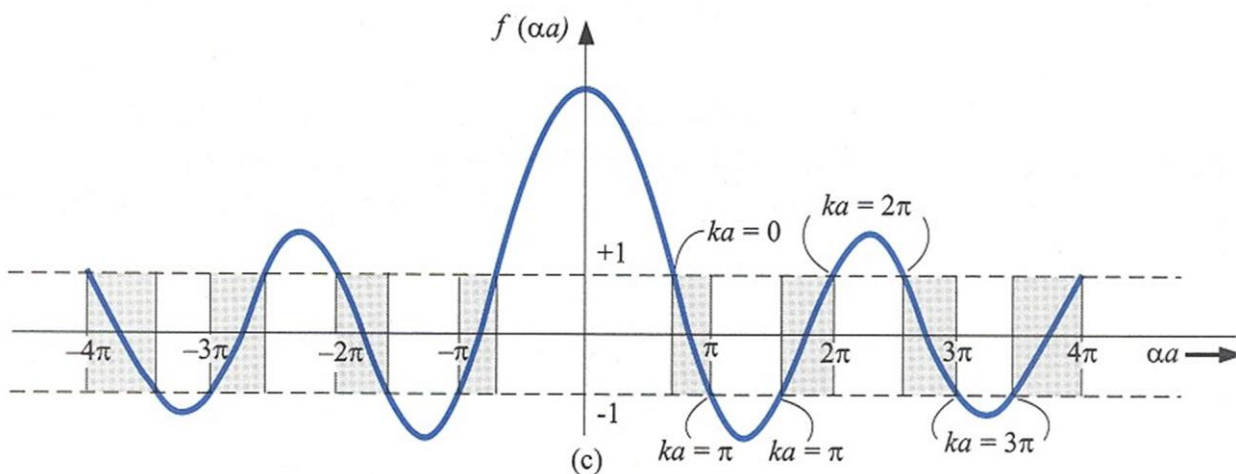
As $\alpha a = \pm n\pi$

$\cos \alpha a = \cos ka$

$\therefore ka = \pm n\pi, \quad k = \pm \dfrac{n\pi}{a}$

These values of **k** are points of discontinuity in E-k curve for electrons in the crystal.

Case (i) When $P \rightarrow \infty$

The allowed energy states are compressed to a line spectrum i.e. we are back to the case of discrete energy spectrum existing in isolated atoms.
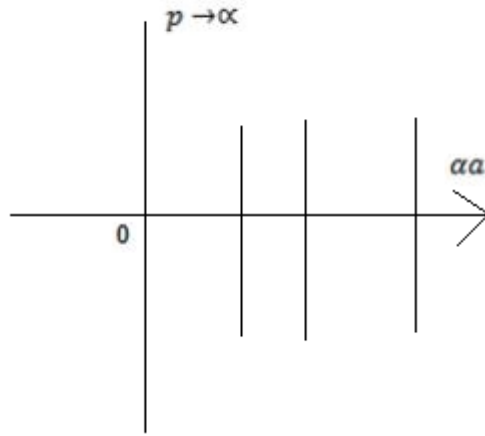
$\sin \alpha a = 0$

$\alpha a = n\pi$

$\alpha = \dfrac{n\pi}{a}$

where *n*= 1, 2, 3, 4,…….. . and so on.

$$\alpha^2 = \left(\dfrac{n\pi}{a} \right)^2$$

From (3)

$$\alpha^2 = \dfrac{2mE}{\hbar^2}$$

$$\left(\dfrac{n\pi}{a} \right)^2 = \dfrac{8\pi^2 mE}{h^2} \qquad \because \hbar = \dfrac{h}{2\pi}$$

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

Here, the energy depends on the width of the potential rather than any other parameter. The energy level of electron in the crystal lattice is discrete and is similar to the particle in a potential box with atomic dimensions. This is because with a large value of potential strength barrier the tunneling effect is explicitly improbable.

Case (ii) When $P \to 0$

The energy band is broadened and it is quasi continuous.

$$\cos \alpha a = \cos ka \Rightarrow \alpha = k$$
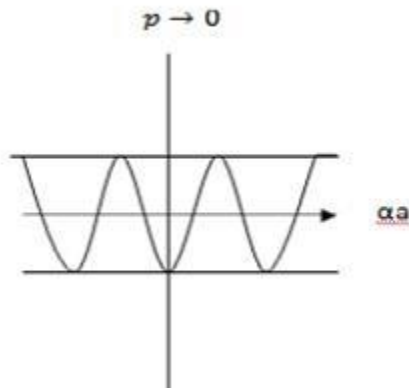
Substituting the values $k^2 = \alpha^2 = \dfrac{2mE}{\hbar^2}$

On rearranging, we get

$$E = \frac{\hbar^2 k^2}{2m} = \frac{h^2 k^2}{8\pi^2 m} = \frac{h^2}{8\pi^2 m}\left(\frac{2\pi}{\lambda}\right)^2 = \frac{h^2}{2m\lambda^2}$$

λ Here refers to wave nature of electron and is equated to the de Broglie's wavelength

$$E = \frac{h^2 p^2}{2mh^2} = \frac{p^2}{2m} = \frac{m^2 v^2}{2m} = \frac{1}{2}mv^2$$

The energy obtained above corresponds to the energy of the completely free particles. No energy levels exist in this case and all energies are allowed to the electrons.

Thus, by varying P, we cover the whole range, from completely free electron to completely bound electron and is depicted below in Fig.:
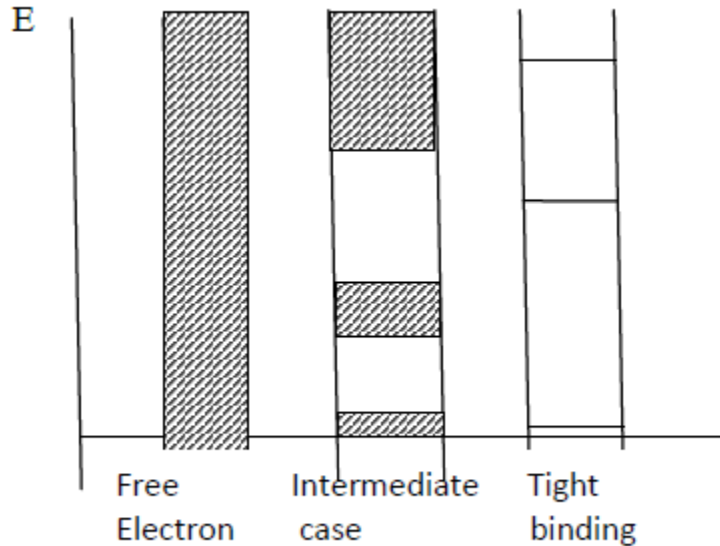
Hence, using this model a system can be analyzed from the Free State condition to the extremely bounded condition.

E-k Diagram

In KP model, it was observed that electron moving in a periodic potential has energy values only between allowed energy bands. The discontinuities in energy values arise at a point k= ±nπ/a.

The allowed eigen values are

$$E = \hbar^2 k^2/2m$$

where k is wave number (n =1,2,3………).

An E-K diagram shows the characteristics of a semiconductor material.

- ✓ The energy and wave vector (or momentum) diagram is a plot of total electron energy (potential as well as kinetic) as a function of crystal direction dependent on electron wave vector at some point in space.
- ✓ The electron wave vector k is proportional to the momentum and therefore the velocity of the electron.

The energy of electrons, $E = mv^2/2$

As $\qquad\qquad p = mv$

so $\qquad\qquad E = p^2/2m$

Also, we know according to Quantum mechanics,

$$p = \hbar k$$

i.e. p is proportional to k

Hence, $\qquad\qquad E = \hbar^2 k^2/2m.$

Therefore, E vs k curve is parabolic in nature. From the graph, it is seen that the lowest energy band which is allowed for electrons in the metal lattice has the values of k extending from $k = -\pi/a$ to $k = +\pi/a$ for (n=1). Therefore the energy of first energy band extends from $E_0 > 0$ to $E_1 = \hbar^2 k^2/2m$.

This range of allowed k values between $-\pi/a$ to $+\pi/a$ is called first Brillion Zone. After a break in the energy values called the forbidden zone, we get another allowed zone of energy values extending from $k = -\pi/a$ to $k = -2\pi/a$ and $k = +\pi/a$ to $k = +2\pi/a$. This zone is called the second Brillion zone. Hence, the origin of allowed energy bands and forbidden gap is clear from the figure which represents E-k diagram

in KP model.

First two Brillouin Zones for 1D Metal Lattice
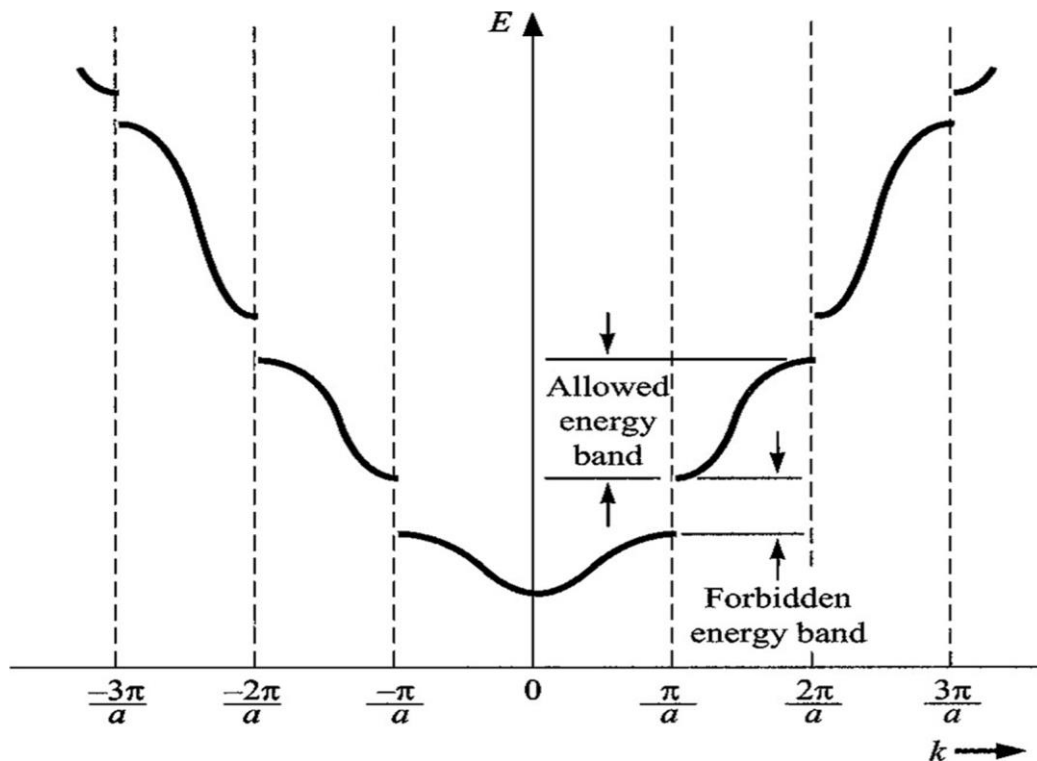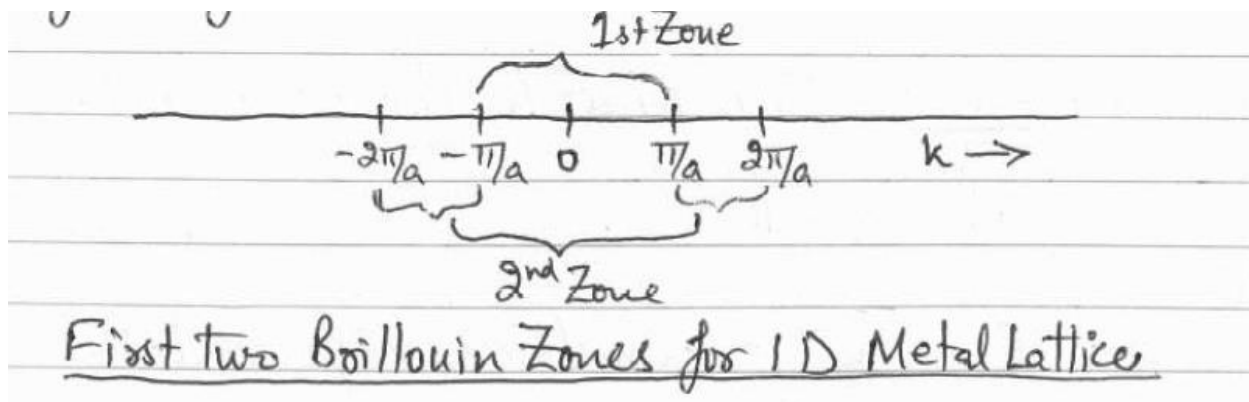
Electron Effective Mass

We know that an electron has a well defined mass 'm'. The question is that when the electron is accelerated by an electric field inside a crystal what is its mass?

➢ Actually the electron in the crystal interacts with the crystal lattice. As a result, its behavior towards external forces is different from that of a free electron.

➢ Therefore, when an electron in periodic potential of lattice is accelerated by an electric field, then the mass of the electron is called effective mass. It is represented by m*.

As we know, the total force acting on electrons in a crystal is

$$F_{Total} = F_{ext} + F_{int} = ma$$

where, F_{int} →internal forces in the crystal due to positively charged ions and negatively charged electrons

F_{ext} →externally applied electric field

m → rest mass of electron

a → acceleration.

It is difficult to account for all of the internal force. So, we define

$$F_{ext} = m^*a$$

m^* → effective mass of the electron (which takes into account internal forces)

Acceleration a → directly related only to external applied force.

According to de Broglie hypothesis, a moving electron is associated with a wave. The velocity of an electron (v) is equal to the group velocity (v_g) of the associated wave. The group velocity is given by:

$$v = v_g = \frac{dw}{dk} \qquad (1)$$

where ω is the angular frequency ($2\pi v$) and k is the propagation vector of the wave.

In quantum mechanics, the energy, 'E' of an electron is given by:

$$E = \hbar w \qquad (2)$$

Differentiating the equation (2) with respect to k

$$\frac{dE}{dk} = \hbar \frac{dw}{dk} \qquad (3)$$

From (1) & (3)

$$v_g = \frac{1}{\hbar}\left(\frac{dE}{dk}\right) \qquad (4)$$

Differentiating Equation (3) with respect to 't' , we get acceleration of electron as

$$a = \frac{dv_g}{dt} = \frac{1}{\hbar}\frac{d}{dt}\left(\frac{dE}{dk}\right) = \frac{1}{\hbar}\frac{d^2E}{dk^2}\left(\frac{dk}{dt}\right) \qquad (5)$$

In quantum theory, the momentum of an electron is given by:

$$p = \hbar k \qquad (6)$$

Differentiating Equation (6) with respect to 't' , we get acceleration of electron as

$$\frac{dp}{dt} = \hbar \frac{dk}{dt} \qquad (7)$$

Eqn. (5) using eqn. (7), reduces to

$$a = \frac{1}{\hbar^2}\frac{d^2E}{dk^2}\left(\frac{dp}{dt}\right) \qquad (8)$$

From Newton's second Law:

$$F = \frac{dp}{dt} = m * a$$

Hence, from (8) becomes

$$a = \frac{1}{\hbar^2}\left(\frac{d^2E}{dk^2}\right)m*a$$

or

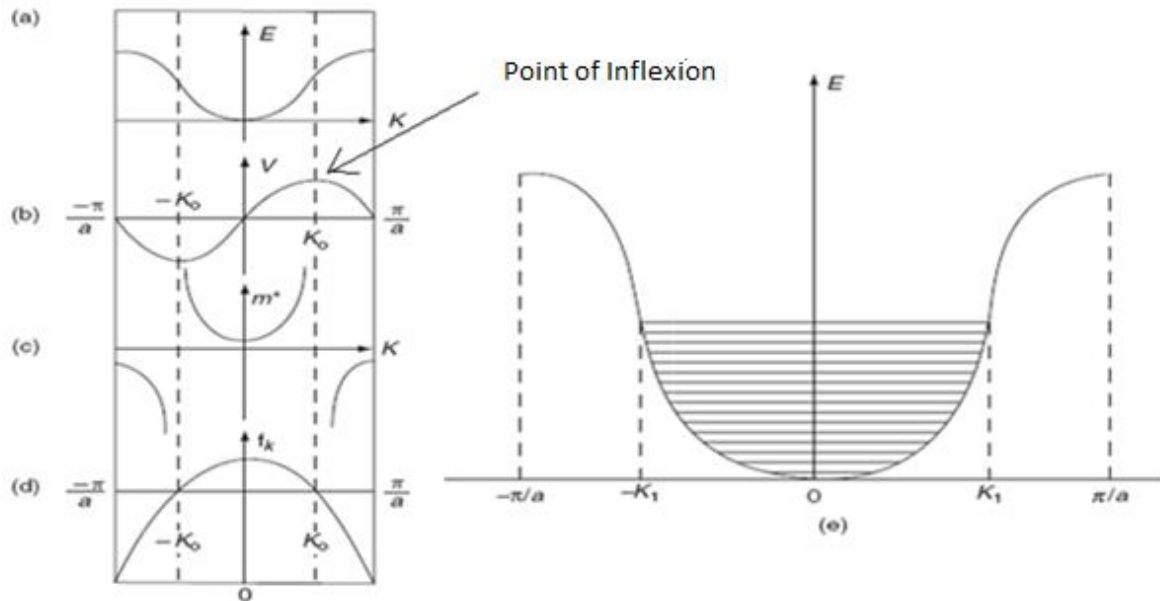$$m* = \frac{\hbar^2}{\left(\dfrac{d^2E}{dk^2}\right)} \rightarrow \text{Effective mass of electron} \tag{9}$$

and

$$E = \frac{\hbar^2 k^2}{2m*}$$

The role of $m* = \hbar^2\left(\dfrac{d^2E}{dk^2}\right)^{-1}$ is same as that of classical mass in Newtonian mechanics. This expression

(9) shows that the effective mass is determined by (d^2E/dk^2) i.e. the effective mass of electron is not constant but depends upon the value of (d^2E/dk^2) i.e. the shape of E-k diagram. Fig. below shows the variation of E with K :

(a) *E-k* diagram (b) Velocity versus K (c) Effective mass of an electron (d) Degree of freedom of an electron (e) *E-k* diagram

From the (i) variation of E with k Fig. (a), (ii) plot v versus k Fig. (b), (iii) plot m^* versus k Fig. (c) and (iv) plot f_k versus k Fig. (d), it is observed that

➢ At the bottom of the energy band, the velocity of an electron is zero and as the value of k increases, the velocity increases and attains a maximum value at $k = k_0$, known as the point of inflexion on the $E-k$ curve.

➢ Beyond this point, the velocity decreases and attains zero value at $k = \pm \dfrac{\pi}{a}$, which is the top of the band.

➢ **The effective mass** is represented as a function of k in Fig.(c). For the lower portion of E-k curve, (d^2E / dk^2) is positive so m^* is positive, and increases with increase of k. It attains a maximum value at the point of inflection k_0. For further higher values of k (ie. beyond the point of inflexion), (d^2E / dk^2) is negative, hence m^* is negative.

➢ As, $k = \pm \dfrac{\pi}{a}$ the effective mass approaches to a smaller negative value. At the point of inflexion $[(d^2E / dK^2) = 0]$, m^* becomes infinite.

➢ Physically, that in the upper half of the band, the electron behaves as having negative mass or as behaving like particles with positive charges.

➢ Until the velocity reaches its maximum value, the electron is accelerated by the field, beyond this maximum velocity the same field produces a decrease in velocity, i.e., the mass must become negative in the upper part of the band.

➢ The degree of freedom of an electron inside a metal crystal with periodic potential is defined as

$$f_k = \frac{m}{m*} = \frac{m}{\hbar^2}\left(\frac{d^2E}{dk^2}\right)$$

f$_k$ is a measure of the extend to which an electron in the state k is free.

(i)   If m* is large, f$_k$ is small i.e. m*>m and electron behaves as a heavy particle and is motion gets restricted.

(ii)   When f$_k$=1, m*=m and electron behaves as a free particle.

(iii)   When m* is small, f_k is large i.e. m*<m and electron behaves lighter than a free electron and hence moves faster.

Variation of f_k vs k is shown above in Fig. (d).

Note that $f_k>0$ (i.e. m*<m) in the lower half of the energy band and $f_k<0$ (i.e. m*>m) in the upper half of energy band i.e. an electron behaves as a positively charged particle in the upper half of the energy band (when k is close to ±π/a). Such particles are called holes.
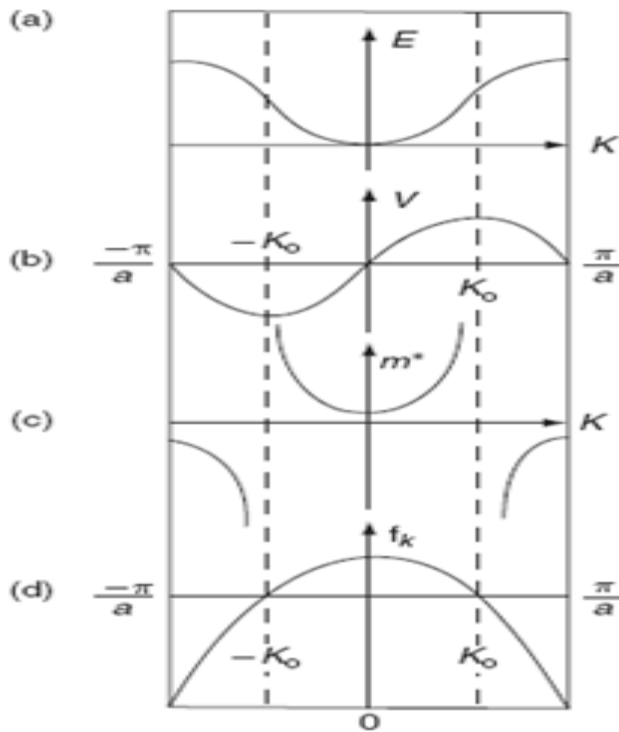

(a) *E-k* diagram (b) Velocity versus *K* (c) Effective mass of an electron

(d) Degree of freedom of an electron

Physical significance of Effective Mass & Concept of the Hole

The concept of effective mass provides a satisfactory description of the charge carriers in the crystals. In crystals such as Alkali metals, which have partially filled energy bands, the conduction takes place through electrons. However, in intrinsic semiconductor crystals for which the energy band is nearly full, the topmost electrons in the energy band have negative effective mass and hence behave as positively

charged particles that we call as holes. Alternatively, the electrons vacancies at top of energy band are also holes by nature as they have negative mass and negative charge so that the product $m^*e = +ve$.

- When valence electron goes to conduction band positively charged empty state is created.

- If a valence electron gets a small amount of energy, it can occupy this empty state.

- Movement of valence electron→movement of positively charged empty state in opposite direction.

- The charge carrier in the form of positively charged empty state is called the hole.
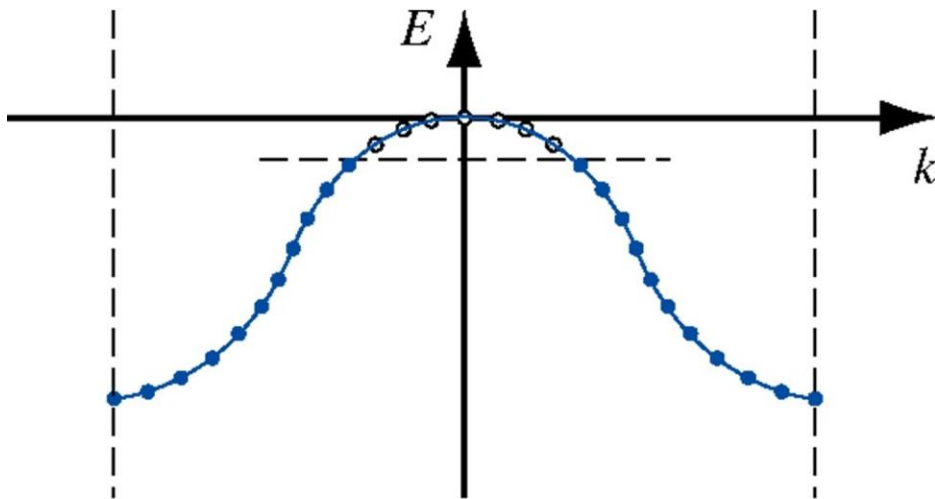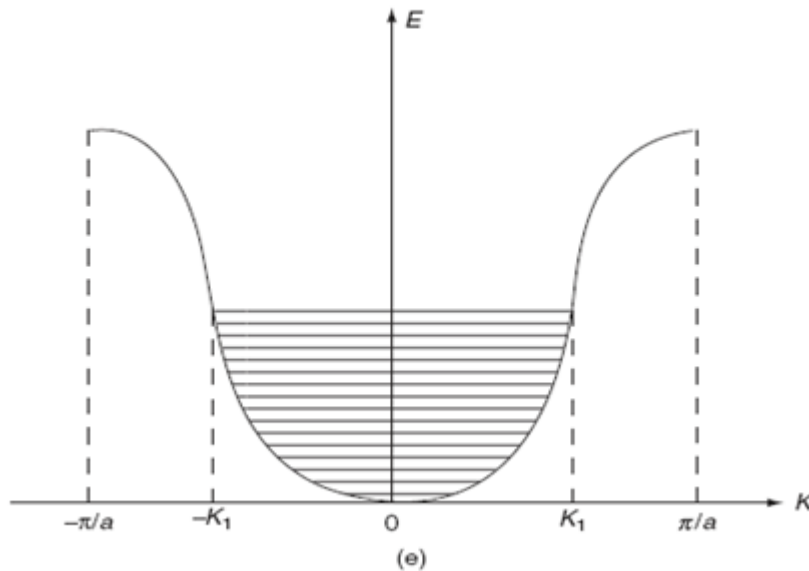

(a)

(a) Valence band with conventional electron filled states and empty states (holes)

Distinction between Metals, Semiconductors and Insulators

To distinguish between metals, semiconductors and insulators on the basis of band theory, let us consider an energy band which is filled with electrons up to a certain value k_1 ($<\pi/a$)as shown in figure below

(e)

We need to find the effective number of free electrons present in this band as this will provide information about the conductivity of band. From above E-k diagram it is clear that
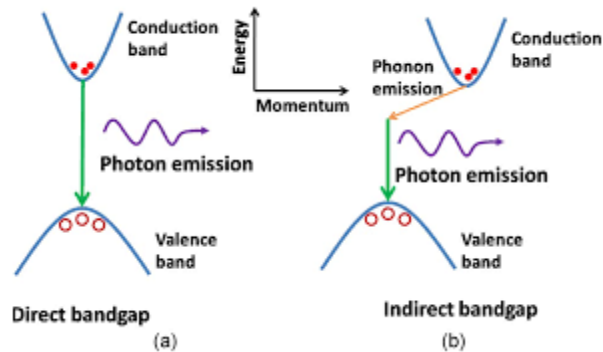
1. The effective number of free electrons in a completely filled band is zero. This is because (dE/dk)i.e slope of curve vanishes at top of the band (near k = $\pm\pi/a$)

2. The effective no. of free electrons has a maximum value when (dE/dk) becomes maximum i.e. when the band is filled upto the point of inflexion.

   ❖ It also follows that from the above discussion that in a solid having a certain number of energy bands that are completely filled and others bands that are completely empty, as shown in figure (a) below, will act as insulators.

   ❖ On the other hand, a solid having partially filled energy bands has a metallic character as shown in figure (c).

Insulator   Semiconductor   Conductor
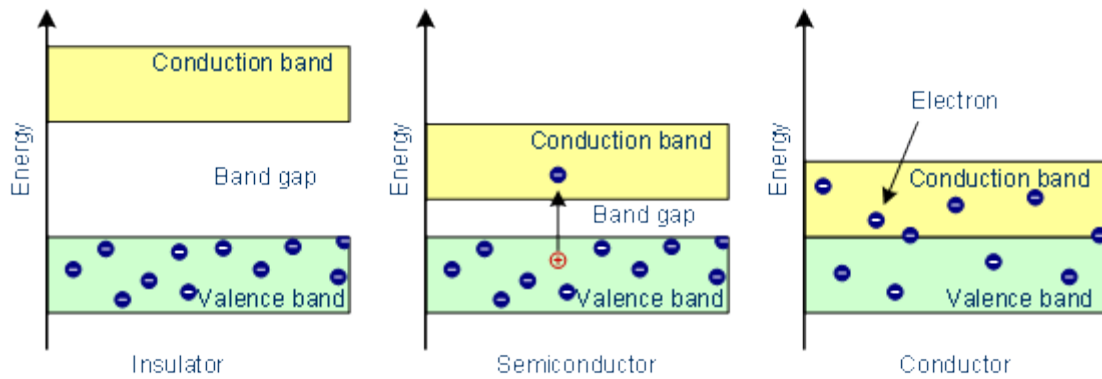
❖ Note that the situation shown in Fig (a) can strictly occur at T=0K, For T> 0K, some electrons from the topmost filled energy band (valence band) absorbs thermal energy and gets excited to next empty band (conduction band) where they participate in the conduction process.

❖ The number of such conduction electrons depends upon the value of forbidden gap between the valence band and the conduction band.

❖ The larger the band gap, the smaller the number of free electrons and hence larger the tendency of electrons to behave as insulators.

❖ If the band gap is small, the number of thermally excited electrons can be appreciable even at room temperature and the material behaves an intrinsic (pure) semiconductor.

❖ At 0K, even these materials behave as insulators because electrons from the valence band cannot be thermally excited to the conduction band.

❖ Therefore, intrinsic semiconductors behaves as insulators at 0K and all insulators may behave as semiconductors at temperatures higher than 0K.

Conductors	Insulators	Semiconductors
1. Conduction band and valence band overlap. There is no forbidden band.	1.Forbidden gap is very large. (> 5eV)	1.Forbidden gap is small
2. Large number of free electrons are available for conduction. Holes are not present.	2.Valence band is completely filled and conduction band is totally empty.	2.Valence band is partially empty and has holes. Conduction band is partially filled with free electrons.
3. Electrical conductivity is very large	3.Electrical conductivity is very small	3.Electrical properties lies between conductors and insulators

Direct and Indirect Energy Band Gap Semiconductors

Direct bandgap (a)   Indirect bandgap (b)

Direct Energy Band Gap Semiconductors	Indirect Energy Band Gap Semiconductors
1.Direct band gap semiconductor have top of valence band and bottom of conduction band lies at the same values of k 	Indirect band gap semiconductor have top of valence band and bottom of conduction band lies at the different values of k
2. In Direct band gap semiconductor electrons excite from valence band to conduction band directly. There is no involvement of intermediate state.	2. In Indirect semiconductor electrons can't directly excite from valence band to conduction band while it first gets excited to intermediate level and then to conduction band.
3. The electron transitions conserve the momentum and de-excitation leads to emission of light or photons.	3.The electron transitions do not conserve the momentum and de-excitation leads to emission of heat or phonons.
4. These materials are usually alloy based, e.g. Gallium arsenide (GaAs), Cadmium sulphide (CdS) etc.	4. These metals are pure semiconductors e.g.. Silicon, Germanium etc.

5. These are used for making opto-electronic devices like LED, Solar cells, photodiode, semiconductor lasers etc.	5. These are used for making zener diodes, transistors, rectifier diodes etc.