

Introduction to Quantum mechanics :Failure of classical mechanics:-

Classical mechanics successfully explained the motion of the objects which are either observable directly or can be made observable by instruments like microscope. When the classical concepts were applied to the particles of atomic dimensions like electrons, they failed to describe the actual behaviour. Thus classical concepts cannot be applied to atomic phenomenon. Like motion of an electron in an atom.

We know that an atom consists of heavy positive nucleus with like negative electrons which revolve round the nucleus in circular orbits. According to classical picture the negatively charged electron experiences attractive electrostatic force due to positively charged nucleus. Thus they should come closer to each other. Secondly if we consider the case of electron moving round the nucleus, it will experience a centripetal acceleration. It is a well known fact that an accelerated charge particle radiates energy in the form of electromagnetic waves.

Therefore the energy of the electron should decrease continuously and it should come closer and closer until it collapses with nucleus. This shows the instability of the atom. The statement is contradictory to the absorbed fact of the stability of atom. Thus classical mechanics failed to explain the stability of the atom.

Drawbacks of classical mechanics:

1. The non-relativistic motion of atoms, electrons, protons etc.
2. stability of atoms.
3. Origin of discrete spectra of atoms.
4. The spectrum of black body radiation.
5. Failure to explain photo-electric effect, Compton effect, Raman effect, Zeeman effect etc.

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Wave & particle duality of Radiation:

The concept of particle is easy to grasp. It has mass, it is located at some definite point, it can move from one place to another, it gives energy when slowed down or stopped. Thus the particle is specified by,

(i) Mass (m) (ii) Velocity (v) (iii) Momentum (p) & (iv) energy (E)

The concept of wave is a bit more difficult than that of a particle. A wave is spread out over a relatively large region of space, it cannot be said to be located just here and there, it is hard

to think of mass being associated with a wave.

Actually a wave is nothing but rather a spread out disturbance. A wave is specified by its (i) frequency (ii), wave length (iii), phase of wave velocity (iv) Amplitude and (v) Intensity.

Considering the above facts, it appears difficult to accept the conflicting ideas that radiation has a dual nature. i.e., radiation is a wave which is spread out over space and also a particle which is localised at a point in space. However this acceptance is essential because radiation sometimes behaves as a wave and at other ~~other~~ times as a particle as explained below:

(i) Radiations including visible light, infra-red, ultra-violet, x-rays, etc. behave as waves in experiments based on interference, diffraction etc. This is due to the fact that these phenomena require the presence of two waves at the same position at the same time. Obviously, it is difficult for the two particles to occupy the same position at the same time. Thus we conclude that radiations behave like wave.

(ii) Planck's quantum theory was successful in explaining black body radiation, the photoelectric effect, the Compton effect etc. and had clearly established that the radiant energy, in its interaction with matter behaves as though it consists of corpuscles. Here radiation interacts with matter

in the form of photons or quanta. Thus we conclude that radiations behave like particle.

Radiations, thus, sometimes behave as a wave and at some other time as a particle, i.e., it has a wave particle dualism. Here it should be remembered that radiation cannot exhibit its particle and wave properties simultaneously.

DE-BROGLIE'S CONCEPT OF MATTER WAVES

In Newton time, matter and radiation both were assumed to consist of particles. With the discovery of phenomena like interference, diffraction and polarisation it was established that light is a kind of a wave motion. In the beginning of 20th century, some new phenomena (photo electric effect, Compton effect, etc) were discovered which could not be explained on the basis of ~~quantum~~^{wave} theory, in which light quanta or photon. These phenomena were explained on the basis of quantum theory in which light quanta or photon are endowed with corpuscular properties— mass ($h\nu/c^2$), Velocity c , and momentum $h\nu/c$. But when the photon theory was applied to phenomena such as interference, diffraction etc. it proved helpless to explain them. Thus light has a dual nature, i.e., it possesses both particle and wave properties. In some phenomena corpuscular nature predominate while in others wave nature predominate. The manifestation of properties depends upon the conditions under which the particular phenomena occurs. It is

$$p = mv$$
$$m = \frac{p}{c}$$

worthy to note that wave and particle, never expected to appear together.

Louis de-Broglie in 1924 extended the wave particle parallelism of optics to all the fundamental entities of physics such as electrons, protons, neutrons, atoms and molecules, etc. de-broglie put a bold suggestion that the correspondance between wave and particle should not be confined only to electromagnetic radiation, but it should also be valid for material particles i.e, like radiation, matter also has a dual, (i.e, particle like and wave like) characteristic. In his thesis he wrote that there was an intimate connection between waves and corpuscles not only in the case of radiation but also in the case of matter. A moving particle has always got a wave associated with it and the particle is controlled by the wave in a manner similar to that in which a photon is controlled by waves. His suggestion was based on the fact that nature loves symmetry, if radiation, like light can act like wave sometime and like a particle at other times. then the material particles (e.g: electron, neutron etc) should act as wave at some other times.

According to de-Broglie's hypothesis, a moving particle, is associated with a wave which is known as de-Broglie wave. The wave length of the matter wave is given by

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

where m is the mass of the material particle, v is its velocity and p is its momentum, h is the plank's constant.

$p = mv$
 $m = \frac{p}{v}$

Expression for the de-Broglie wavelength:

The Expression of the wavelength associated with a material particle be derived on the analogy of radiation as follows:

Considering the planck's theory of radiation the energy of a photon (quantum) is given by

$$E = h\nu = \frac{hc}{\lambda} \longrightarrow (1)$$

Where 'c' is the velocity of light in vacuum and λ is its wave length

According to Einstein energy-mass relation

$$E = mc^2 \longrightarrow (2)$$

From eqn (1) & (2), we get

$$mc^2 = \frac{hc}{\lambda} \quad (\text{or}) \quad \lambda = \frac{hc}{mc^2}$$

$$\therefore \boxed{\lambda = \frac{h}{mc}}$$

Where $mc = p$ (momentum associated with photon).

If we consider the case of a material particle of mass m and moving with a velocity v i.e., momentum mv ; then the wave length associated with this particle is given by

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

Case

a) If E is the kinetic energy of the material particle, then

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

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

∴ de Broglie wavelength.

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

Case

b) When a charged particle carrying a charge q is accelerated by a potential difference V Volts, then its K.E., E is given by

$$E = qV$$

Hence, the de-Broglie wavelength associated with this particle is given by

$$\lambda = \frac{h}{\sqrt{2mqV}}$$

Case c) When a material particle is in thermal equilibrium at a temperature T , then

$$E = \frac{3}{2}kT$$

Where k = Boltzmann's constant = $1.38 \times 10^{-23} \text{ J/K}$.

So, the de-Broglie wavelength of the material particle at temperature T is given by

$$\lambda = \frac{h}{\sqrt{2m \left(\frac{3}{2}kT \right)}}$$

(or)

$$\lambda = \frac{h}{\sqrt{3mKT}}$$

De-Broglie wavelength associated with electrons:

Let us consider the case of an electron of rest mass m_0 and charge e which is accelerated by a potential V volts from rest to velocity v , then

$$\frac{1}{2}m_0v^2 = eV \quad \text{(or)} \quad v = \sqrt{\left(\frac{2eV}{m_0} \right)}$$

$$\text{Now, } \lambda = \frac{h}{m_0 v} = \frac{h \sqrt{m_0}}{m_0 \sqrt{2eV}} = \frac{h \sqrt{m_0}}{\sqrt{2eV m_0} \cdot \sqrt{m_0}} = \frac{h}{\sqrt{2eV m_0}}$$

$$\lambda = \frac{h}{\sqrt{2eV m_0}}$$

$$\text{(or) } \lambda = \frac{6.625 \times 10^{-34}}{\sqrt{(2 \times 1.6 \times 10^{-19} \times V \times 9.1 \times 10^{-31})}}$$

$$\lambda = \frac{6.625 \times 10^{-34}}{\sqrt{29.1564 \times 10^{-50} \times V}}$$

$$\lambda = \frac{6.625 \times 10^{-25} \times 10^{-34}}{\sqrt{29.1564 \times V}}$$

$$\lambda = \frac{6.625 \times 10^{-9}}{5.399 \sqrt{V}}$$

$$= 1.226 \times 10^{-9}$$

$$\lambda = \frac{12.26 \times 10^{-10} \text{ m}}{\sqrt{V}}$$

$$\lambda = \frac{12.26 \text{ \AA}}{\sqrt{V}}$$

If $V = 100$ volts, then

$$\lambda = \frac{12.26 \text{ \AA}}{\sqrt{100}} = \frac{12.26 \text{ \AA}}{10}$$

$$\lambda = 1.226 \text{ \AA}$$

The above equation shows that the wavelength associated with an electron accelerated with to 100 volts is 1.226 \AA.

Properties of Matter waves:

Following are the properties of matter waves:

1) Lighter is the particle, greater is the wavelength associated with it.

2) Smaller is the velocity of the particle, greater is the wavelength associated with it.

3) When $v = 0$ then $\lambda = \infty$ i.e., wave becomes indeterminate and if $v = \infty$ then $\lambda = 0$. This shows that matter waves are generated

by the motion of particles. These waves are produced whether the particles are charged particles or they are uncharged

($\lambda = h/mv$ is independent of charge). This fact reveals that

these waves are not electromagnetic waves but they are a ^{new} kind of waves (electromagnetic waves are produced only by motion of charged particles).

4. The velocity of matter wave depends on the velocity of matter particle i.e., it is not a constant while the velocity of electromagnetic wave is constant.

5. The velocity of matter wave is greater than the velocity of light. The velocity of matter wave (de-Broglie wave velocity) is greater than the velocity of light.

A particle in motion with associated matter wave has two different velocities, one referring to the mechanical motion of the particle represented by v , and second related to the propagation of the wave represented by w .

We know that, $E = h\nu$ and $E = mc^2$.

$$h\nu = mc^2 \text{ (or) } \nu = \frac{mc^2}{h}$$

The wave velocity (w) is given by

$$w = \nu \times \lambda = \frac{mc^2}{h} \times \frac{h}{mv} \quad \therefore \lambda = \frac{h}{mv}$$

$$w = \frac{c^2}{v}$$

As particle velocity v cannot exceed c (velocity of light) hence w is greater than velocity of light. We can understand this unexpected result by considering the wave velocity also known as phase velocity and the group velocity.

(6) The wave and particle aspects of moving bodies can never appear together in the same experiment. What we can say is that waves have particle like properties and particles have wave like properties and the concepts are separately linked. Matter wave representation is only a symbolic representation.

7. The wave nature of matter introduces an uncertainty in the location of the position of the particle because a wave cannot be said exactly at this point or exactly at this point or exactly at that point. However, where the wave is large (strong) there is a good chance of finding the particle while, where the wave is small (weak) there is very small chance of finding the particle.

HEISENBERG'S UNCERTAINTY PRINCIPLE

In 1927, Heisenberg proposed a very interesting principle, which is a direct consequence of the dual nature of matter, known as uncertainty principle. In classical mechanics, moving particle at any instant has a fixed position in space and a definite momentum which can be determined if the initial values are known. However, in wave mechanics the particle is described in terms of a wavepacket. According to Born's probability interpretation, the particle may be found anywhere within the wavepacket. When the wavepacket is small, the position of the particle may be fixed but the particle will spread rapidly and hence the velocity becomes indeterminate. On the other hand, when the wavepacket is large, the velocity can be fixed but there is large indefiniteness in position. In this way the certainty in position involves uncertainty in momentum or velocity and certainty of momentum involves the uncertainty in position. This shows that it is impossible to know where within the wavepacket the particle is and what is its exact ~~pos~~ momentum. Hence we can measure either the position or the momentum of a particle with any desired degree of accuracy.

According to Heisenberg uncertainty principle, "it is impossible to measure both the position and momentum of a particle simultaneously to any desired degree of accuracy. In general this principle states that "It is impossible to specify precisely and simultaneously the values of both members of particular pairs of physical variables that describe the behaviour of an atomic system".

Qualitatively this principle states that, "the order of magnitude of the uncertainties in the knowledge of two variables must be at least planck's constant h ".

Considering the pair of physical variables as position and momentum, we have

$$\Delta p \cdot \Delta x \approx h \longrightarrow (1)$$

Where Δp is the uncertainty in determining the momentum and Δx is the uncertainty in determining the position of the particle. Similarly, we have

$$\Delta E \cdot \Delta t \approx h \longrightarrow (2)$$

$$\Delta J \cdot \Delta \theta \approx h \longrightarrow (3)$$

Where ΔE and Δt are uncertainties in determining the energy and time while ΔJ and $\Delta \theta$ are uncertainties in determining the angular momentum and angle.

the exact statement of uncertainty principle is as follows:

The product of uncertainties in determining the position and momentum of the particle can never be small than the order

or $\frac{h}{4\pi}$. So we have

$$\Delta p \Delta x \geq \frac{h}{4\pi}, \Delta E \Delta t \geq \frac{h}{4\pi}, \Delta J \Delta \theta \geq \frac{h}{4\pi}$$

Also we can written as

$$\Delta p \Delta x \geq \frac{h}{2}, \quad \hbar = \frac{h}{2\pi}$$

Schrodinger Wave Mechanics:

Bohr's theory of hydrogen atom was successful in explaining the hydrogen like spectrum but it has a number of short comings. For ex: it doesn't explain the fine structure of spectral lines and intensity variation in them. Moreover, its use is limited to simplest hydrogen & hydrogen-like atoms; it is incapable to explain the spectra of complex atoms. Finally, it doesn't explain satisfactorily the distribution of electrons in atoms, interaction of electrons with atoms to give the observed properties of matter.

The above mentioned short coming are due to the application of Newtonian classical mechanics to explain the properties of the systems. According to classical mechanics, it is possible to determine exactly the quantities like position, velocity, momentum, acceleration etc. which characterize the state of the system at any instant. The equations of motion then enable us to determine those quantities (and hence the state of the system) at all later instants.

Thus classical mechanics provides the correct explanation for the behaviour of macroscopic system.

In atomic systems, the classical mechanics fails to explain the macroscopic system of particles due to uncertainty principle. According to uncertainty principle, the position and momentum of a particle cannot be measured accurately at the same time, the measurement of one quantity introduces an uncertainty into the other. Therefore, classical mechanics, which assumes both to have definite values at all instants, is not valid for atomic systems. Thus, Bohr's model (just a classical atomic model) failed to give a complete explanation of the behaviour of the atomic system. Further according to De-Broglie theory, a material particle is associated with a wave. So a mathematical reformation using a wave function associated with matter waves is needed. Such a ~~mechanical~~ mathematical formation - known as wave mechanics or quantum mechanics - was developed in 1926 by Schrodinger. Schrodinger described the amplitude of matter waves by a complex quantity $\psi(x, y, z, t)$ known as wave function or the state of the system. It describes the particular dynamical system under observation.

Equation of Motion of Matter Waves.

a) schrodinger time independent wave equation:

According to de-Broglie theory, a particle of mass m , is always associated with a wave whose wavelength is given by $\lambda = h/mv$.

If the particle has wave properties, it is expected that there should be some sort of wave equation which describes the behaviour of the particle. Consider a system of stationary waves associated with a particle. Let x, y, z be the coordinates of the particle and ψ , the wave displacement for the de-Broglie at any time t , ψ is called as wave function. It is assumed that ψ is finite, single valued and periodic function. The classical differential equation of a wave motion is given by

$$\frac{\partial^2 \psi}{\partial t^2} = v^2 \left(\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} \right)$$
$$= v^2 \left[\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right] \psi$$

$$\frac{\partial^2 \psi}{\partial t^2} = v^2 \nabla^2 \psi \longrightarrow (1)$$

Where, $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$ [∇^2 being Laplacian operator]

and v is the wave velocity.

The solution of eqn(1) is given by

$$\psi = \psi_0 \sin \omega t = \psi_0 \sin 2\pi \nu t \longrightarrow (2)$$

when ν is the frequency of the stationary wave associated with the particle.

Differentiating eqn(2), twice we get

$$\frac{\partial \psi}{\partial t} = \frac{\partial}{\partial t} (\psi_0 \sin 2\pi \nu t)$$

$$\frac{\partial \psi}{\partial t} = \psi_0 (2\pi \nu) \cos 2\pi \nu t$$

$$\text{and } \frac{\partial^2 \psi}{\partial t^2} = \frac{\partial}{\partial t} \left[\psi_0 (2\pi \nu) \cos 2\pi \nu t \right]$$

$$= -\psi_0 (2\pi \nu)^2 \sin 2\pi \nu t$$

$$\frac{\partial^2 \psi}{\partial t^2} = -4\pi^2 \nu^2 \psi \quad (\because \psi = \psi_0 \sin 2\pi \nu t)$$

$$\frac{\partial^2 \psi}{\partial t^2} = -4\pi^2 \frac{\nu^2}{\lambda^2} \psi \quad (\because \nu = \frac{v}{\lambda} \Rightarrow \nu = \frac{v}{\lambda})$$

$$\boxed{\frac{\partial^2 \psi}{\partial t^2} = -\frac{4\pi^2 \nu^2}{\lambda^2} \psi} \quad \text{--- (3)}$$

Substituting the value of $\left(\frac{\partial^2 \psi}{\partial t^2}\right)$ from eq'n (3) in eq'n (1) we get

$$v^2 \nabla^2 \psi = -\frac{4\pi^2 \nu^2}{\lambda^2} \psi$$

$$\frac{v^2 \nabla^2 \psi}{v^2} = -\frac{4\pi^2 \nu^2}{\lambda^2} \psi$$

$$\nabla^2 \psi = -\frac{4\pi^2 \nu^2}{\lambda^2} \psi$$

$$\therefore \nabla^2 \psi + \frac{4\pi^2 \nu^2}{\lambda^2} \psi = 0 \quad \text{--- (4)}$$

Now from de-Broglie relation,

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

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

--- (5)

$$\left[\begin{aligned} \lambda &= \frac{h}{mv} \\ \lambda^2 &= \frac{h^2}{m^2 v^2} \\ \frac{1}{\lambda^2} &= \frac{m^2 v^2}{h^2} \end{aligned} \right]$$

If E and V be the potential energies of the particle respectively, then its kinetic energy $\frac{1}{2}mv^2$ is given by

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

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

$$\frac{m^2 v^2}{2} = m(E - V)$$

$$m^2 v^2 = 2m(E - V) \longrightarrow (6)$$

From eqns (5) & (6) we have,

$$\nabla^2 \psi + \frac{4\pi^2}{h^2} \times 2m(E - V) \psi = 0.$$

$$\nabla^2 \psi + \frac{8\pi^2 m}{h^2} (E - V) \psi = 0. \longrightarrow (7)$$

Eqn (7) is known as Schrodinger time independent wave equation.

Substituting $\hbar = \frac{h}{2\pi}$ in eqn (7) the Schrodinger wave equation

can be written as

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

$$\nabla^2 \psi + \frac{2m}{\hbar^2} (E - V) \psi = 0. \longrightarrow (8)$$

For a free particle $V=0$, hence the Schrodinger wave equation for a free particle can be expressed as

$$\nabla^2 \psi + \frac{2mE}{\hbar^2} \psi = 0 \longrightarrow (9)$$

Calculate the de-Broglie wavelength associated with the following:

i) A golf ball of 50 grams moving with a velocity of 20 m/s.

ii) A proton moving with a velocity of 2200 m/s

iii) An electron moving with a kinetic energy 10 eV.

iv) If an electron beam in a TV picture tube is accelerated by 10,000 V.

Sol:- a) Given data,

$$\text{mass, } m = 50 \text{ g} = 50 \times 10^{-3} \text{ kg}$$

$$\text{Velocity, } V = 20 \text{ m/sec.}$$

$$\text{Wave length, } \lambda = \frac{h}{mv} = \frac{6.625 \times 10^{-34}}{(50 \times 10^{-3})(20)} = \frac{6.625 \times 10^{-34}}{1000 \times 10^{-3}}$$

$$\therefore \lambda_a = 6.625 \times 10^{-34} \text{ m.}$$

b) Given data,

$$\text{mass of proton} = 1.627 \times 10^{-27} \text{ kg}$$

$$\text{Velocity, } V = 2200 \text{ m/sec.}$$

$$\lambda = \frac{h}{mv} = \frac{6.625 \times 10^{-34}}{1.627 \times 10^{-27} \times 2200} = 1.85 \times 10^{-10} = 1.85 \text{ \AA}$$

Given

$$\text{c) Mass of electron, } = 9.1 \times 10^{-31} \text{ kg.}$$

$$\text{Kinetic energy} = 10 \text{ eV}$$

$$\text{We know, } 1 \text{ eV} = 1.602 \times 10^{-19} \text{ J.}$$

$$10 \text{ eV} = 10 \times 1.602 \times 10^{-19} \text{ J}$$

$$= 1.602 \times 10^{-18} \text{ J}$$

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

$$\lambda = \frac{6.625 \times 10^{-34}}{\sqrt{2 \times 9.1 \times 10^{-31} \times 1.602 \times 10^{-18}}}$$

$$\lambda = \frac{6.625 \times 10^{-34}}{\sqrt{9.1 \times 3.204 \times 10^{-13}}}$$

$$\lambda = 3.88 \times 10^{-10} \text{ m}$$

$$\lambda = 3.88 \text{ \AA}$$

d) Given data

Electron potential = 10,000 V.

$$\lambda = \frac{12.26}{\sqrt{V}} \text{ \AA} = \frac{12.155 \times 10^{-10}}{\sqrt{10,000}} = \frac{12.155 \times 10^{-10}}{100}$$

$$\lambda = 0.12155 \times 10^{-10} \text{ m (or) } 0.12155 \text{ \AA}$$

Wave function and its probability interpretation:-

Wave-function (ψ):

It is an essential element of a quantum mechanical system by using it we can get any meaningful information about the system. It is denoted by $\psi(x, t)$.

Probability density:-

The wave function itself is a complex valued function.

$$\text{i.e. } \psi = A + iB$$

The complex conjugate of ψ is $\psi^* = A - iB$

$$|\psi|^2 = \psi \psi^* = (A + iB)(A - iB) = A^2 + B^2 \rightarrow \text{It is a real quantity}$$

$|\psi|^2$ is known as probability density.

The probability of finding a particle at any point at a given time is proportional to $|\psi|^2 = \psi\psi^*$

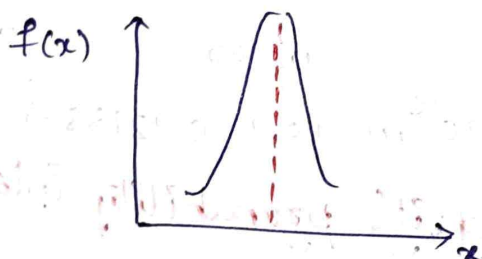
A large value of $|\psi|^2$ means strong possibility of finding the particle at that point at any given time.

properties of wave-function:

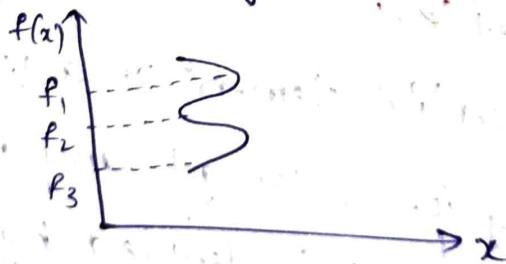
$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}(E - V)\psi = 0.$$

A wave function has many possible solutions, but every solution is not acceptable only those solutions are acceptable which has following properties.

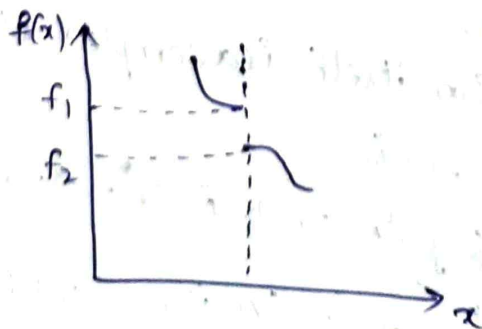
- 1) $\psi(x)$ and $\frac{d\psi}{dx}$ must be finite everywhere.



- 2) $\psi(x)$ and $\frac{d\psi}{dx}$ must be single valued.



- 3) $\psi(x)$ and $\frac{d\psi}{dx}$ must be continuous.



It is discontinuous at point x .

- 4) $\psi(x)$ must vanish at infinity for bound states.

Postulates of Wave Mechanics :-

The postulates of the quantum mechanics may be stated as follows:

Postulate 1: Wave-function to describe physical system.

There is an associated wave function ψ with the system & any state of the system is described as fully as possible by this wave function. This is the state function of the system.

For a wave function ψ to describe any physical system, the following boundary conditions must be satisfied:

(i) $\psi(x)$ as well as $d\psi(x)$ must be finite for all values of x .

Let $\psi(x)$ is infinite at that point i.e., $|\psi(x)|^2$ is infinite.

This shows that the particle is completely localised. This is in contradiction with the wave property of the system.

Moreover, when physical quantities are evaluated they lead to infinite values for infinite $\psi(x)$ and $d\psi(x)/dx$. This is physically unacceptable as physical quantities seldom behave unreasonably.

(ii) $\psi(x)$ as well as $d\psi(x)/dx$ must be continuous for all values of x in the region except where the ~~region~~ ~~except~~ potential $V(x, y, z)$ is infinite.

For $d\psi(x)/dx$ to be infinite, $\psi(x)$ must be continuous because derivative of a discontinuous function is always infinite. The discontinuous value of the function i.e., the infinite value of $d\psi(x)/dx$ will lead to the infinite value of the system which is not possible.

(iii) $\psi(x)$ as well as $d\psi(x)/dx$ must be single valued all x in the region.

Let $\psi(x)$ has a multi-valued at some point. Then the probability of finding the system between x and $x+dx$ is $|\psi(x)|^2 dx$ and will be multi-valued. In this way there will be more than one answer of a question (probability of a particle between x and $x+dx$) which is not obviously correct.

(iv) In addition to the above conditions, the wave-function $\psi(x)$ must satisfy the Born conditions. According to Born condition, the probability of finding a particle in volume element $dx dy dz$ is given by $|\psi(x)|^2 dx dy dz$ or $\psi \psi^* dx dy dz$. If the particle is somewhere in the space, then the probability be equal to unity i.e.,

$$\int_{\text{All space}} \psi \psi^* dx dy dz = 1$$

This is called normalization condition.

When there are n -particles in the space, then

$$\int_{\text{All space}} \psi \psi^* dx dy dz = n$$

where ψ is now unnormalized wave function. The normalized wave function will be $\psi/\sqrt{n}$. The quantity $(1/\sqrt{n}) = C$ is called the normalization constant.

Postulate 2: operators for observable quantities:

With every dynamical variable, there is associated an operator.

The quantities which are obtained by the process of observable quantities. As observable quantities are the result of measurement, these quantities are real. Some of the observable quantities like position coordinates, components of velocity, components of linear momentum, components of angular momentum etc. have the physical meaning in quantum mechanics as in classical mechanics.

There are certain observable quantities like spin, symmetry under interchange of identical particles etc. In quantum mechanics which do not have any equivalence in classical mechanics. Time is not an observed quantity but it is a universal parameter.

Every observable quantity in classical mechanics can be expressed by an operator in quantum mechanics. An operator is anything which is capable of doing something to a function or any mathematical operation as multiplication $\times$, differentiation d/dr , integration $\int$ can be expressed by certain symbols known as operator. When any operator say $\hat{O}$ operates on a wave function ψ and the result is expressed as $\hat{O}\psi = a\psi$,

Then the observable quantity a is known as eigen value of the operator $\hat{O}$ for the function ψ known as eigen function.

Quantum mechanical operators.

classical quantity	Quantum mechanical operator
Cartesian components of position x, y, z	$\hat{x}, \hat{y}, \hat{z}$
position vector $\vec{r}$	$\hat{\vec{r}}$
momentum $\vec{p}$	$(-i\hbar \vec{\nabla})$
cartesian components of linear momentum P_x, P_y, P_z	$(-i\hbar \frac{\partial}{\partial x}, -i\hbar \frac{\partial}{\partial y}, -i\hbar \frac{\partial}{\partial z})$
Total Energy E	$(-\hbar \frac{\partial}{\partial t})$

Postulate 3: Expected value of dynamical quantity

The expected or average value of a dynamical quantity is the mathematical expectation for the result of a single measurement. It may also be defined as the average of the result of a large number of measurements on independent systems.

The average value of the expectation value of an observable quantity corresponding to operator $\hat{O}$ of a physical system in the state $\psi(x, y, z)$ is given by

$$\langle \hat{O} \rangle = \frac{\int \psi^* \hat{O} \psi \, dx \, dy \, dz}{\int \psi^* \psi \, dx \, dy \, dz}$$

If the wave function is normalized to unity, then the denominator is equal to unity, hence

$$\langle \hat{O} \rangle = \int \psi^* \hat{O} \psi \, dx \, dy \, dz$$

for ex:- $\langle P_x \rangle = -i\hbar \int \psi^* \frac{\partial \psi}{\partial x} \, dx \, dy \, dz$

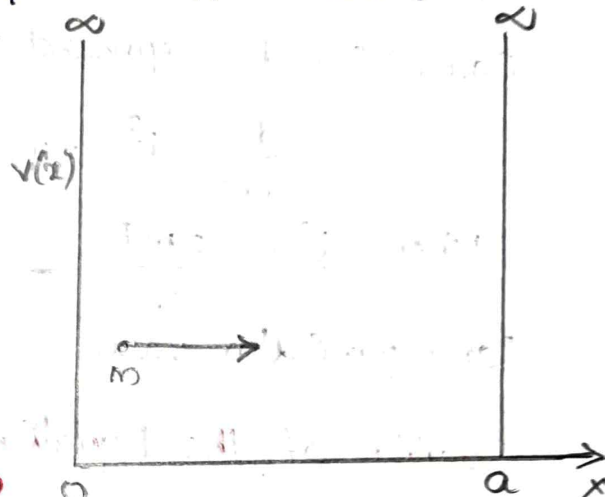
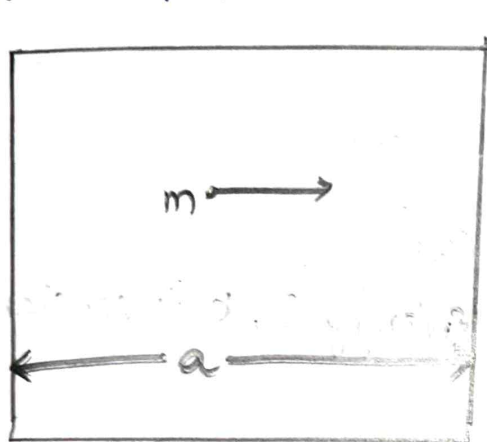
$$\langle P_y \rangle = -i\hbar \int \psi^* \frac{\partial \psi}{\partial y} \, dx \, dy \, dz$$

$$\langle P_z \rangle = -i\hbar \int \psi^* \frac{\partial \psi}{\partial z} \, dx \, dy \, dz$$

$$\langle E \rangle = i\hbar \int \psi \psi^* \frac{\partial \psi}{\partial t} \, dx \, dy \, dz$$

Particle in one dimensional box:

(particle in an infinitely deep one dimensional potential well). Let us consider the one dimensional motion along x -axis of a particle of mass m in a hollow rectangular box having perfectly rigid walls. Let the origin be one corner of the box and the x -axis be perpendicular to the parallel opposite walls.



one dimensional motion of a particle in a hollow rectangular box.

Square well potential of infinite depth.

Let a be the distance between the walls so that the motion along the x -axis is confined between $x = 0$ and $x = a$. Suppose inside the box, i.e. in the region $0 < x < a$, there is no force acting on the particle so that in this region, i.e. inside the box, the potential energy $V(x)$ is zero. When the particle collides with the perfectly rigid walls there is no loss of energy so that the total energy E of the particle remains constant. In order to leave the region, the particle will have to do an infinite amount of work. Since this is not possible, it cannot exist outside the box. Hence for $x \geq 0$ and $x \leq a$, i.e. outside the box, the wave function

$$\psi(x) = 0.$$

The potential energy curve for such a particle as shown in above figure. Because of its appearance it is called a Square well potential of infinite depth.

Wave Equation for a particle:

For the motion of the particle along the x-axis inside the box where $V(x) = 0$, the time independent Schrodinger wave equation is

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2} E\psi = 0 \quad [\because V(x) = 0] \quad \text{Eq'n (1)}$$

where E is the total energy of the particle.

Eq'n (1) can be expressed as

$$\frac{d^2\psi}{dx^2} + k^2\psi = 0 \quad \longrightarrow (2)$$

$$\text{Where } k^2 = \frac{2mE}{\hbar^2} \quad \longrightarrow (2a)$$

For a particular value of the energy E , k is constant.

Solution of the Equation :-

The general solution of Eq'n (2) is

$$\psi(x) = A \sin kx + B \cos kx \quad \longrightarrow (3)$$

Where A and B are constants of integration. We have the boundary conditions as:

(i) At $x = 0$, $\psi(x) = 0$

(ii) At $x = a$, $\psi(x) = 0$

From the first condition, one obtains $B = 0$.

$\therefore$ From Eq'n (3) one obtains $\psi(x) = A \sin kx = 0 \quad \longrightarrow (4)$

Using second boundary condition, one obtains

$$\psi(a) = A \sin ka = 0 \quad \longrightarrow (5)$$

We cannot take $A = 0$ because there will be no solution.

Hence Eq'n (4) is satisfied only when $ka = n\pi$

$$k = \frac{n\pi}{a} \quad \longrightarrow (6)$$

Where $n = 1, 2, 3, 4, \dots$ i.e., n is an integer.

We cannot take $n=0$ because for $n=0, k=0, E=0$ and hence $\psi(x)=0$ everywhere in the box. This means that a particle with zero energy cannot be present inside the box, i.e., a particle in the box cannot have zero energy. Hence, the wave functions for the motion of particle in the region $0 < x < a$ are given by

$$\psi_n(x) = A \sin \frac{n\pi x}{a} \quad [\text{where } n \text{ is even}]$$

→ (7)

Eigenvalues of Energy:

Substituting the value of k from Eq. (2a) in Eq. (6) one obtains

$$\text{i.e., } k^2 = \frac{2mE}{\hbar^2} \Rightarrow k = \sqrt{\frac{2mE}{\hbar^2}} \quad \therefore k = \frac{n\pi}{a}$$

$$\therefore k = \sqrt{\frac{2mE}{\hbar^2}} = \frac{n\pi}{a}$$

$$\frac{2mE}{\hbar^2} = \frac{n^2\pi^2}{a^2} \Rightarrow E = \frac{n^2\pi^2\hbar^2}{2ma^2}$$

$$\therefore E_n = \frac{n^2\pi^2\hbar^2}{2ma^2} \longrightarrow (8)$$

Eq. (8) represents the eigen values of the energy. These values are called the energy levels of the particle. Using $\hbar = \frac{h}{2\pi}$, Eq. (8) becomes as

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

$$\therefore \frac{n^2 \pi^2 \hbar^2}{2ma^2} = \frac{n^2 h^2}{8ma^2}$$

From Eq. (8) we can draw the following conclusions:

i) The lowest energy of the particle is obtained by putting $n=1$ in Eq. (8) one obtains for $n=1$ as

$$E_1 = \frac{\pi^2 \hbar^2}{2ma^2} \longrightarrow (9)$$

It is called the ground state energy level of the particle.

The value of E_n in terms of E_1 are given by

$$E_n = n^2 E_1 \longrightarrow (10)$$

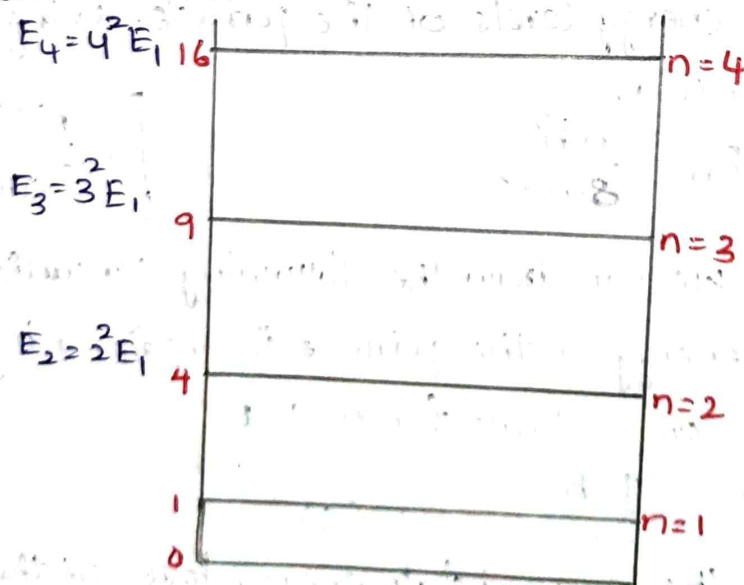
The 'n' numbers are called quantum numbers while the 'E' values are called Energy levels. The quantum states with higher values of $n = (2, 3, 4 \dots \text{etc})$ are termed as Excited States.

According to quantum mechanics, the kinetic energy is not equal to zero in ground state.

(ii) The possible values of energy of the particle in the potential box are discrete corresponding to $n = 1, 2, 3 \dots$

The classical mechanics doesn't need any such requirement of discrete energy levels for bound systems. The quantization of energy conclusion is universal, i.e., whenever a particle is confined to move in a limited space, its energy is quantized. For example, the energies of electrons bound to atoms and molecules are quantized.

(iii) The energy levels: The quantization of energy is shown graphically in below figure. The allowed energy levels are shown as horizontal lines.



Energy levels

That these lines are straight emphasizes the fact that energy (E) is the same irrespective of the position (x) of the particle.

since for a particular value of n , the Energy (E) doesn't change with ~~position~~ x , the latter is often termed "constant of motion". Further, since H or E is independent of time (t) the system under consideration is a good and simple example of conservative system.

The lowest value of E is not zero but $\pi^2 \hbar^2 / 2ma^2$ (for $n=1$). Evidently, the particle in a box will continue to move to and fro in the region 0 to L even at the temperature of absolute zero, for this reason it is called the "Zero point energy".

The dependence of E on n^2 results in the increased spacing between energy levels as n increases.

$$\Delta E = E_{n+1} - E_n = [(n+1)^2 - n^2] E_1 = [n^2 + 1 + 2n - n^2] E_1 \\ = (2n+1) E_1 \longrightarrow (11)$$

Since the Energy E_1 is proportional to $1/a^2$, smaller the box greater are the energy spacing (ΔE) i.e. the quantization is more pronounced. Alternatively, as the box is made wider, ΔE decreases and in the limited case of $L \rightarrow \infty$ (free particle) the quantization vanishes.

The wave functions ψ_n corresponding to E_n are called Eigen functions.

Normalization of the wave Functions:

The wave functions for the motion of the particle are

$$\psi_n(x) = A \sin \frac{n\pi x}{a} \longrightarrow (12)$$

in the region $0 < x < a$ and $\psi_n = 0$ in the region $x < 0, x > a$. This wave function is still incomplete as much as the constant 'A' is not determined. A can be determined by making use of the fact that the total probability of the particle

Somewhere in the box must be unity, i.e.,

$$\int_0^a |\psi_n(x)|^2 dx = 1$$

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

$$\text{(or)} A^2 \int_0^a \frac{1}{2} (1 - \cos \frac{2n\pi x}{a}) dx = 1$$

$$\begin{aligned} \because \cos 2\theta &= 1 - 2\sin^2 \theta \\ 2\sin^2 \theta &= 1 - \cos 2\theta \\ \sin^2 \theta &= \frac{1 - \cos 2\theta}{2} \end{aligned}$$

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

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

$$\Rightarrow \frac{A^2}{2} [a - 0] = \frac{A^2}{2} a = 1$$

$$\Rightarrow \boxed{A = \sqrt{\frac{2}{a}}} \longrightarrow (13)$$

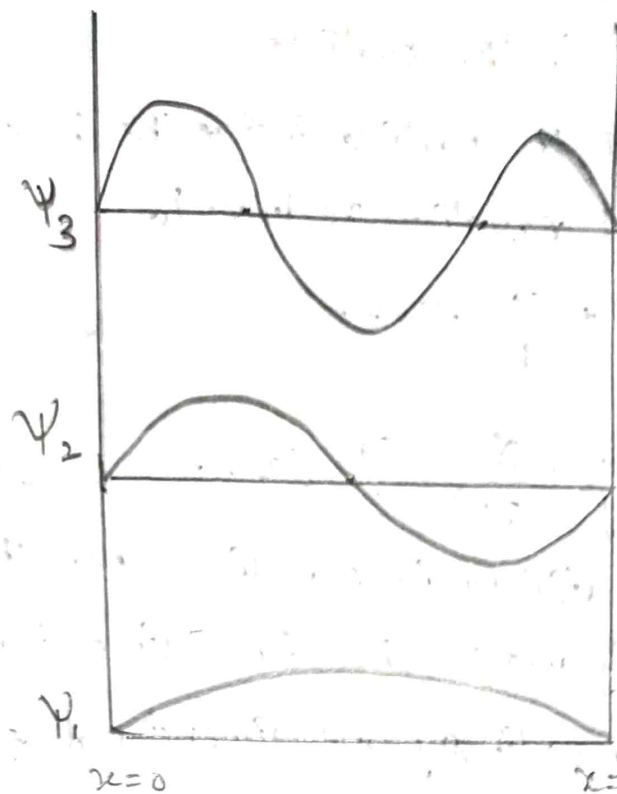
The normalized wave function is thus:

$$\boxed{\psi_n = \sqrt{\frac{2}{a}} \sin \frac{n\pi x}{a}} \longrightarrow (14)$$

Note: Actually $\psi = \pm \sqrt{2/a} \sin \frac{n\pi x}{a}$. However, since probability is given by $|\psi|^2$ and not by ψ , it is immaterial whether positive or negative A is chosen. Customarily, we select positive series of normalized ψ functions.

Form of the Wave function:

The expression for the real form of the wave function can be used conveniently to draw its graphical representation. The wave functions for the first three values of n as shown in adjacent figure.



It is evident that the wave function ψ_1 has two nodes at $x=0$, $x=a$. The wave function ψ_2 has three nodes at $x=0$, $x=a/2$ and $x=a$. The wave function ψ_3 has four nodes at $x=0$, $x=a/3$, $x=2a/3$, and $x=a$. Thus the wave function ψ_n will have $(n+1)$ nodes. Obviously, the increasing number of nodes is ~~considering~~ consistent with increasing energy of the system.

Particle in a Rectangular three dimensional box:

Let a particle of mass m be in motion in a rectangular potential box as shown in figure. With sides of length a, b, c to be parallel to the x, y and z axes respectively, suppose there is no force acting on the particle inside the box, so that in the region $0 < x < a$, $0 < y < b$ and $0 < z < c$, the potential energy $V(x, y, z) = 0$ and outside the box $V(x, y, z) = \infty$.

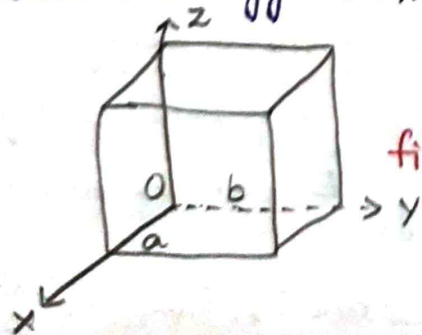


fig: Particle in a three dimensional rectangular box.

Wave Equation for the particle

For the motion of the particle inside the box, the Schrodinger time independent equation reduces to

$$\nabla^2 \psi + \frac{2m}{\hbar^2} E \psi = 0 \longrightarrow (1)$$

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{2m}{\hbar^2} E \psi = 0 \longrightarrow (2)$$

This is a partial differential equation where the wave function ψ is a function of x, y and z . The three dimensional Equation (2) can be reduced to ordinary one dimensional equation by the method of separation of variables. We assume that the wave function $\psi(x, y, z)$ is equal to the product of three functions x, y and z each of which is a function of one variable only. Thus we have

$$\psi(x, y, z) = X(x) Y(y) Z(z) \longrightarrow (3)$$

Substituting (3) in Eq. (2), one obtains

$$YZ \frac{d^2 X}{dx^2} + ZX \frac{d^2 Y}{dy^2} + XY \frac{d^2 Z}{dz^2} + \frac{2mE}{\hbar^2} XYZ = 0 \longrightarrow (4)$$

dividing Eq. (4) with XYZ , we get

$$\frac{1}{X} \frac{d^2 X}{dx^2} + \frac{1}{Y} \frac{d^2 Y}{dy^2} + \frac{1}{Z} \frac{d^2 Z}{dz^2} + \frac{2mE}{\hbar^2} = 0 \longrightarrow (5)$$

In Eq. (5), $\frac{2mE}{\hbar^2}$ is constant for a particular value of kinetic energy since the velocity of the particle, being a vector quantity, can be resolved into three components along the coordinate axes, the kinetic energy E can be expressed as the sum of the corresponding terms E_x, E_y & E_z . Hence

$$E = E_x + E_y + E_z \longrightarrow (6)$$

From (5) & (6) we have following three ordinary differential equations, each comprising a single variable.

$$\frac{1}{x} \frac{d^2 x}{dx^2} + \frac{2mE_x}{\hbar^2} = 0 \longrightarrow (7)$$

$$\frac{1}{y} \frac{d^2 y}{dy^2} + \frac{2mE_y}{\hbar^2} = 0 \longrightarrow (8)$$

$$\frac{1}{z} \frac{d^2 z}{dz^2} + \frac{2mE_z}{\hbar^2} = 0 \longrightarrow (9)$$

Each of these equations has a form similar to the schrodinger eq'n $\frac{d^2 \psi}{dx^2} + k^2 \psi = 0$ for a particle in one dimensional box with similar boundary conditions. The problem of the particle in three dimensional box is reduced to one of three particles in three separate one dimensional boxes of lengths a, b and c .

The boundary conditions applicable to the solution is $X(0) = X(a) = 0$ so the eigenvalues of E_x are given by

$$E_x = \frac{\pi^2 \hbar^2}{2ma^2} n_x^2 \longrightarrow (10)$$

where $n = 1, 2, 3, \dots$ and the corresponding normalized eigen functions are given by

$$X(x) = \sqrt{\frac{2}{a}} \sin \frac{n_x \pi x}{a} \longrightarrow (11)$$

$$Y(y) = \sqrt{\frac{2}{b}} \sin \frac{n_y \pi y}{b} \longrightarrow (12) \quad \& \quad E_y = \frac{\pi^2 \hbar^2}{2mb^2} n_y^2 \longrightarrow (13)$$

$$Z(z) = \sqrt{\frac{2}{c}} \sin \frac{n_z \pi z}{c} \longrightarrow (14)$$

$$E_z = \frac{\pi^2 \hbar^2}{2mc^2} n_z^2 \longrightarrow (15)$$

Where n_x, n_y and n_z are now the quantum numbers for the three separate boxes.

Eigenvalues of Energy:

From Eq'ns (10), (13) & (15), Eq'n (6) becomes

$$E_{n_x, n_y, n_z} = \frac{\pi^2 \hbar^2 n_x^2}{2ma^2} + \frac{\pi^2 \hbar^2 n_y^2}{2mb^2} + \frac{\pi^2 \hbar^2 n_z^2}{2mc^2}$$

$$E_{n_x, n_y, n_z} = \frac{\pi^2 \hbar^2}{2m} \left[\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2} \right] \longrightarrow (16)$$

Where $n_x = 1, 2, 3, \dots$, $n_y = 1, 2, 3, \dots$, $n_z = 1, 2, 3, \dots$

Eq'n (16) gives the eigen values of the energy of the particle. These values are called the ~~gave~~ energy levels of the particle. The lowest (ground state) energy E_1 corresponds to $n_x = n_y = n_z = 1$.

Wave functions:

The total normalized wave functions inside the box for the stationary states are given by

$$\Psi_{n_x, n_y, n_z}(x, y, z) = X(x) Y(y) Z(z)$$

From eq'ns (11), (12) & (14)

$$= \sqrt{\frac{8}{abc}} \sin \frac{n_x \pi x}{a} \sin \frac{n_y \pi y}{b} \sin \frac{n_z \pi z}{c} \longrightarrow (17)$$

Where n_x, n_y and n_z are integers. The wave functions are zero outside the box. It may easily be proved that the wave function is normalized because

$$= \frac{8}{abc} \int_0^a \left(\sin \frac{n_x \pi x}{a} \right)^2 dx \int_0^b \left(\sin \frac{n_y \pi y}{b} \right)^2 dy \int_0^c \left(\sin \frac{n_z \pi z}{c} \right)^2 dz = 1$$

From Eq'ns (16) & (17) we have the following conclusions:

(i) Three integers n_x, n_y and n_z which are called quantum numbers are required to describe each stationary state.

If we change the sign of the quantum numbers there is no change in the energy and in the wave function except

that the minus sign appears on RHS of Eq'n (17). Obviously, all the stationary states are given by the positive integral values of n_x, n_y and n_z . No quantum number can be zero, because if any one of them is taken zero, then $\psi(x, y, z) = 0$, which would mean that the particle doesn't exist in the box.

(ii) The lowest possible energy i.e., the ground state occurs when $n_x = n_y = n_z = 1$ and it depends on the values of a, b & c .

(iii) If the particle is confined in a cubical box in which $a = b = c = L$, the eigen values of energy are given by

$$E_{n_x, n_y, n_z} = \frac{\pi^2 \hbar^2}{2mL^2} (n_x^2 + n_y^2 + n_z^2) \longrightarrow (18)$$

In this case, the energy of the particle in the ground state

is given by
$$E_{111} = \frac{3\pi^2 \hbar^2}{2mL^2} \longrightarrow (19)$$

No other state will have this energy and this energy and this state has only one wave function. Therefore, the ground state and the energy level is said to be non-degenerate.

We note that E_{111} is three times that for a particle in one dimensional box of length L .

The corresponding wave function is

$$\psi_{111} = \sqrt{\frac{8}{L^3}} \sin \frac{\pi x}{L} \sin \frac{\pi y}{L} \sin \frac{\pi z}{L} \longrightarrow (20)$$

(iv) Degeneracy: In cubical box, the energy depends on the sum of the squares of the quantum numbers. Consequently, the particle having the same energy in a excited state will have several different stationary states or different wave functions. Such states and energy levels are said to be degenerate.

For example, We consider the first excited state when only one of the quantum numbers is 2 while the others are 1 each, i.e.

n_x	n_y	n_z
2	1	1
1	2	1
1	1	2

Obviously, there are three independent states corresponding to the following three combinations of n_x, n_y and n_z : (2,1,1), (1,2,1) and (1,1,2). Each state has the same energy as

$$E_{211} = E_{121} = E_{112} = \frac{6\pi^2 \hbar^2}{2mL^2} \longrightarrow (21)$$

But a different wave function

$$\left. \begin{aligned} \psi_{211} &= \sqrt{\frac{8}{L^3}} \sin \frac{2\pi x}{L} \sin \frac{\pi y}{L} \sin \frac{\pi z}{L} \\ \psi_{121} &= \sqrt{\frac{8}{L^3}} \sin \frac{\pi x}{L} \sin \frac{2\pi y}{L} \sin \frac{\pi z}{L} \\ \psi_{112} &= \sqrt{\frac{8}{L^3}} \sin \frac{\pi x}{L} \sin \frac{\pi y}{L} \sin \frac{2\pi z}{L} \end{aligned} \right\} \longrightarrow (22)$$

Obviously, the first excited state is triply degenerate or ~~threefold~~ threefold degenerate. The first three energy levels of a particle in a cubical box are shown in figure. The degeneracy arises whenever there is an integral relation among a, b and c .

$E_{222} = \frac{12\pi^2 \hbar^2}{2mL^2}$	<u>222</u>	Non degenerate
$E_{221} = E_{212} = E_{122} = \frac{9\pi^2 \hbar^2}{2mL^2}$	<u>221</u> <u>212</u> <u>122</u>	Triply degenerate
$E_{211} = E_{121} = E_{112} = \frac{6\pi^2 \hbar^2}{2mL^2}$	<u>211</u> <u>121</u> <u>112</u>	Triply degenerate
$E_{111} = \frac{3\pi^2 \hbar^2}{2mL^2}$	<u>111</u>	Non degenerate

First three energy levels of a particle in a cubical box.

Degree Of Degeneracy :

The number of independent wave functions for the stationary states of an energy level is called the degeneracy of the level.

Energy levels, quantum numbers & degree of degeneracy for a particle in a cubical box.

Energy levels.	Quantum numbers	degree of degeneracy.
$\frac{3\pi^2\hbar^2}{2mL^2}$	(111)	Non degenerate
$\frac{6\pi^2\hbar^2}{2mL^2}$	(211), (121), (112)	Triply degerate/three fold degenerate
$\frac{9\pi^2\hbar^2}{2mL^2}$	(221), (212), (122)	Threefold degenerate
$\frac{11\pi^2\hbar^2}{2mL^2}$	(311), (131), (113)	Threefold degenerate
$\frac{12\pi^2\hbar^2}{2mL^2}$	(222)	Non degenerate
$\frac{14\pi^2\hbar^2}{2mL^2}$	(123), (132), (213), (231), (312), (321)	Six fold degenerate
$\frac{17\pi^2\hbar^2}{2mL^2}$	(322), (232), (223)	threefold degenerate
$\frac{18\pi^2\hbar^2}{2mL^2}$	(411), (144), (114)	Threefold degenerate
$\frac{19\pi^2\hbar^2}{2mL^2}$	(331), (313), (133)	Threefold degenerate
$\frac{21\pi^2\hbar^2}{2mL^2}$	(421), (412), (241), (214), (124), (142)	six fold degenerate

Physical Representation of the Wave function:

The function Ψ involves three variables x, y and z and therefore it cannot be represented by graphically. A qualitative understanding of the wave function can be achieved, however from the nature of the expression (2.11), the value of the function in the ground state ($n_x = n_y = n_z = 1$) is maximum when $x = \frac{a}{2}, y = \frac{b}{2}, z = \frac{c}{2}$.

(i.e. at the bottom centre) and is positive everywhere. In the excited states, the function changes sign and exhibits nodes in some particular regions. For example, for the state ψ_{211} , the function vanishes at $x = \frac{a}{2}$ irrespective of the values of y and z , i.e. along the YZ plane which is, therefore, the nodal plane. Similarly, the XY and XZ planes passing through $b/2$ and $\frac{c}{2}$ are nodal planes for the states ψ_{121} and ψ_{112} respectively.

BAND THEORY OF SOLIDS AND SEMICONDUCTING MATERIALS.

According to the Band theory of solids, the electrons in crystals are arranged in energy bands which are separated by energy gap regions where no wavelike electron orbitals exist. Such forbidden regions are called "energy band gaps". The formation of these bands is due to the interaction of the conduction electron waves with the ion cores of the crystal.

Basis of the Band Theory of Solids:

A study on the thermal, electrical and magnetic properties of materials suggests that the band theory of solids is due to the following reasons:

- (i) Some solids are good conductors of electricity, some are semiconductors, and others are insulators.
- (ii) There is variation in resistivity with temperature, especially in case of semiconductors.
- (iii) The potential experienced by an electron during its motion through the crystal is periodic, instead of being constant of zero.

It is clear that the motion of an electron in periodic potential needs more emphasis to establish the band theory of solids. The simplest quantum mechanical view of the potential experienced by an electron in passing through the crystal is perfectly periodic as shown in below figure.

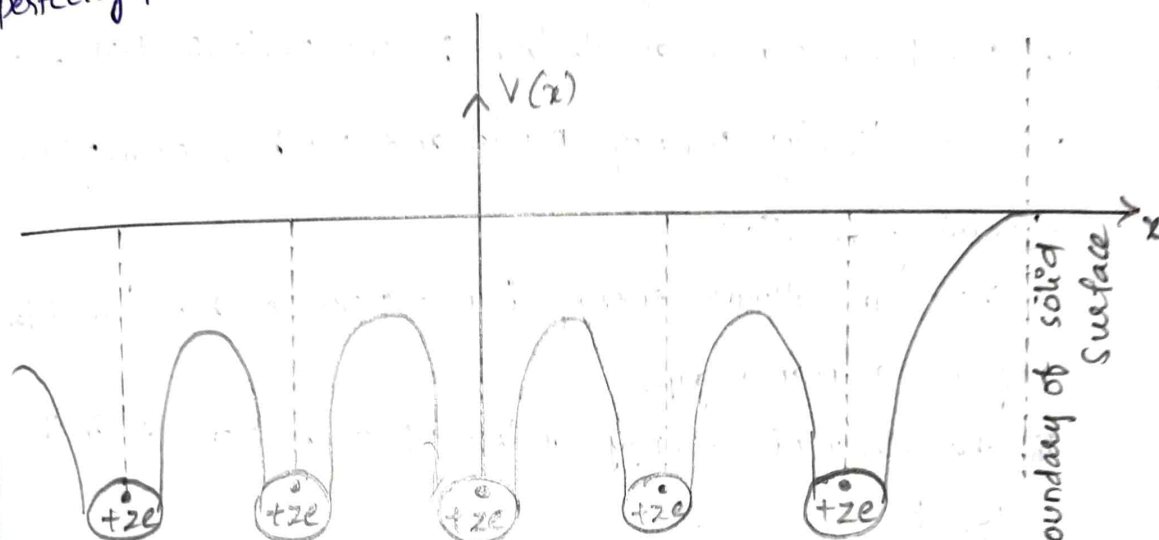


Fig: one dimensional representation of potential experienced by an electron in a perfectly periodic crystal Lattice.

The distribution of potential between the nuclei is a series of humps and increases at the boundary of the solids. The periodicity of the potential is due to the coulomb interaction between the moving electrons and the periodic charge distribution arising from the positive ions situated ~~at~~ on the lattice sites. Hence, the periodicity of the potential is equal to the periodicity of the lattice.

Electrons in a periodic potential of Ion cores:

The behaviour of an electron in periodic potential is described by constructing the electron wave functions using one-electron approximation. The total wave function for the system is obtained from the combination of wave functions, each one of which involves the coordinates of one electron. Thus, the net field experienced by an electron is assumed to be the

resultant of the field due to the ion cores and the average field due to the charge distribution of all the electrons. The motion of an electron in the ion core can be described by the Kronig-Penney model and the wave function associated with the electron is given by Bloch functions. The analysis of the behaviour of an electron in the periodic lattice in the view of Kronig-Penney model and Bloch theorem yields the following results:

- (i) There are allowed energy bands separated by forbidden regions or band gaps.
- (ii) The electronic energy functions $E(k)$ are periodic in the wave vector k .

Bloch theorem :

According to the free electron theory, an electron experiences constant potential (V_0) throughout the crystal lattice. One dimensional Schrodinger wave equation for such electron is given as

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{2m}{\hbar^2} (E - V_0) \psi = 0 \longrightarrow (1)$$

where ψ is the wave-function associated with the electron of Mass M and total energy E .

The solution of this equation can be given as

$$\psi(x) = e^{\pm i k x} \longrightarrow (2)$$

$$\& (E - V_0) = \frac{\hbar^2 k^2}{2m} = \frac{p^2}{2m} = E_k \longrightarrow (3)$$

Now, if we consider that the electron is moving through one-dimensional periodic potential $V(x)$, then the Schrodinger wave equation can be given as

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{2m}{\hbar^2} (E - V(x)) \psi = 0 \longrightarrow (4)$$

Since the potential is periodic with period equal to the lattice constant a , so $V(x)$ can be given as

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

The solution of Eq'n (4) can be given by the Bloch theorem or Floquet's theorem, according to which, "the solution of Eq'n (4) are the plane waves similar to Eq (2) which are modulated by the function $u_k(x)$ having the same periodicity as that of the lattice." Hence the solution of Eq'n (4) will be of the form given as

$$\Psi(x) = e^{\pm i k x} u_k(x) \longrightarrow (5)$$

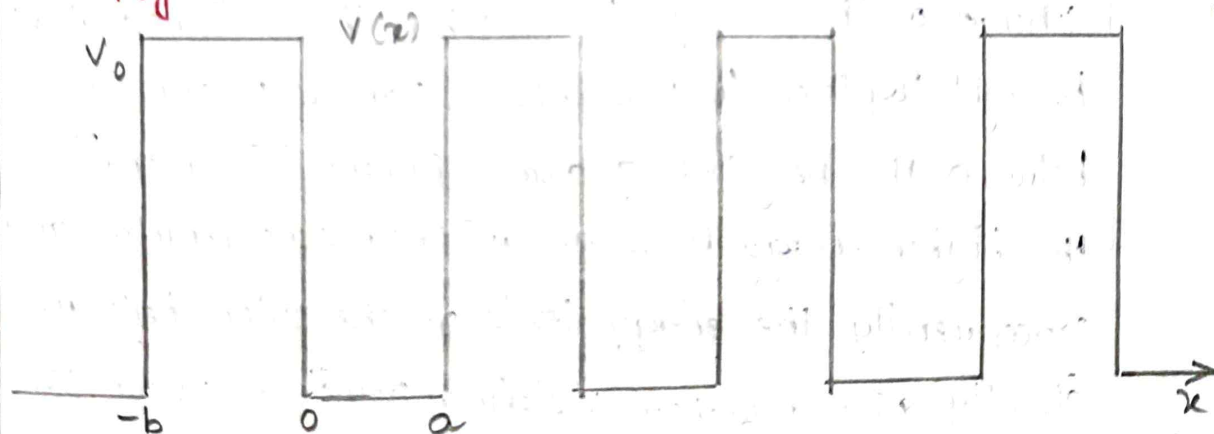
$$u_k(x) = u_k(x+a) \longrightarrow (6)$$

The type of wave functions are called the Bloch functions.

Kronig-penney Model:

Kronig-penney model illustrates the behaviour of electrons in a periodic potential, considering simply one-dimensional model of the periodic potential as shown in below figure.

Fig: one-dimensional periodic potential due to ion cores



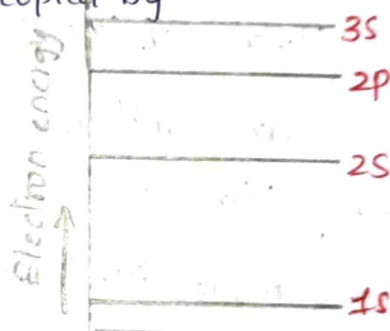
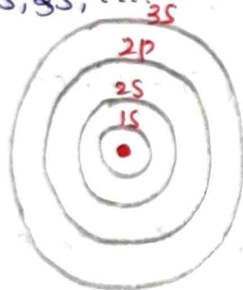
The problem is simplified by replacing the periodic potential with a square well of period $(a+b)$. At the bottom of the well, i.e., for $0 < x < a$, the electron is assumed to be very close to the nucleus, where the potential energy is zero; but outside the well, i.e., for $-b < x < 0$, the potential energy is assumed to be V_0 .

Although, this approximation does not match exactly with the potential offered by the ion cores in the lattice, yet it is able to describe the important features of an electron during its motion in the periodic lattice.

The wave functions for the electron can be obtained by solving the schrodinger wave equation for the regions $0 < x < a$ and $-b < x < 0$.

Energy bands in solids:-

In an isolated atom, there are discrete energy levels as $1s, 2s, 3s, \dots$ which are occupied by the electrons of the atom.

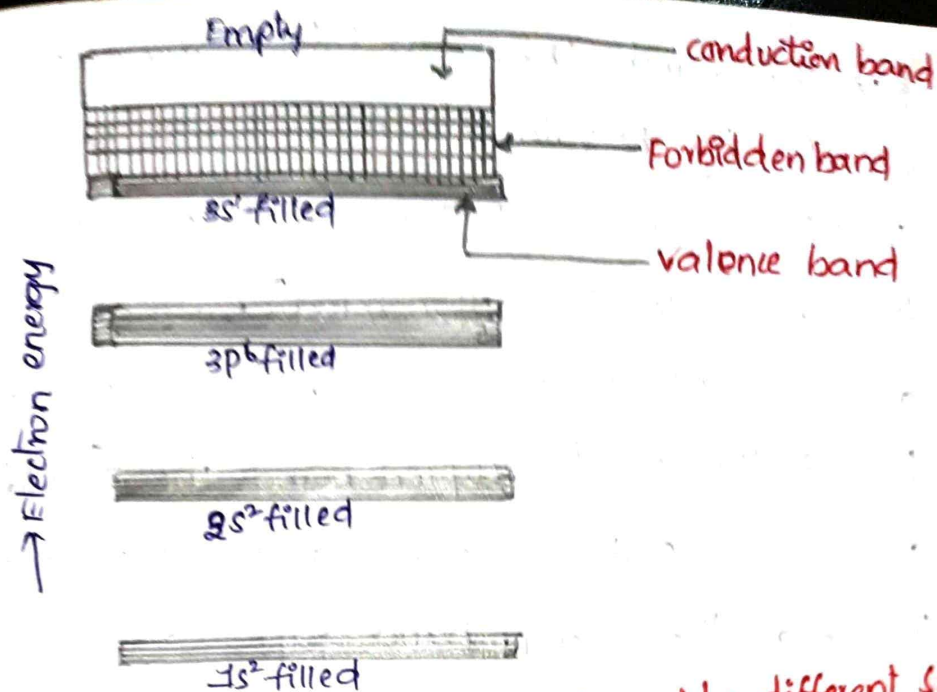


Electrons of an isolated atom in discrete energy levels

If all the atoms of a solid are assumed to be isolated from one another, then they have completely identical electronic schemes of their energy levels. When these isolated atoms are brought together to form a solid, various interactions occur between the neighboring atoms. During this interaction, the higher energy levels are affected considerably, and consequently, the energy levels of the outer shells are slightly altered without violating Pauli's exclusion principle.

Hence, the single energy levels of atoms split into large number of energy levels as shown in adjacent figure.

Since there are many atoms in a solid, so the separation between the split energy levels is very small. Hence, the split energy levels are almost continuous and are said to form an energy band.



Energy bands formed due to the interaction b/w different sodium atoms in a solid.

These are energy bands in a solid corresponding to the energy levels in an atom. An electron in a solid can have only those discrete energies that lie within these energy bands. These energy bands are known as the allowed energy bands, which are generally separated by some energy gap known as the forbidden energy bands or not allowed energy bands. Energy band occupied by the valence electrons is known as valence band, and the energy band which is empty occupied by the conduction electrons is known as the conducting band.

For ex:- Sodium crystal. Sodium crystal has many closely packed sodium atoms, which is usually referred to as crystal lattice. Each sodium atom has eleven electrons with electronic configuration $1s^2, 2s^2, 2p^6$ and $3s^1$. In this configuration, all the subshells are filled except $3s^1$. The outermost electron $3s^1$ of this atom is called the valence electron. When more no. of atoms are brought together to form a solid, then the outer energy levels are split to form an energy band (i.e. large no. of split energy levels closely spaced).

In this band, there are two regions: one region is occupied by the valence electrons known as, valence band, whereas the other region is ~~emp~~ either empty or occupied by the conduction electrons (called conduction band) valence band is also known as the highest occupied band, whereas the ~~conduction~~ conduction band is the lowest occupied band. The forbidden energy gap between the conduction band and the valence band is known as the energy band gap.

Density of states:-

Density of states can be defined as the no. of electronic states present in a unit energy range. If $D(E)$ is density of states, then

$$D(E) = \frac{dn}{dE} \longrightarrow (1)$$

Where 'dn' represents the no. of electronic quantum states present in the energy interval E and $E + dE$. For a free electron gas, since each energy level contains two electronic states, one with spin up and other with spin down, we have the actual density of states twice the values given in Eq'n (1)

Thus,

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

From eq'n

$$E_n = \frac{n^2 \pi^2 \hbar^2}{2mL^2} \longrightarrow (a)$$

$$\Rightarrow \frac{dE}{dn} = \frac{\pi^2 \hbar^2}{2mL^2} \left(\frac{d}{dn} (n^2) \right) = \frac{\hbar^2}{2m} \left(\frac{\pi}{L} \right)^2 \cdot 2n$$

$$\frac{dE}{dn} = \frac{n \pi^2 \hbar^2}{mL^2} = \frac{n \pi^2 \left(\frac{h}{2\pi} \right)^2}{mL^2}$$

$$(\because \hbar = \frac{h}{2\pi})$$

$$\frac{dE}{dn} = \frac{nh^2}{4mL^2} \rightarrow (3)$$

From (2) & (3) $\Rightarrow$

$$D(E) = 2 \left[\frac{4mL^2}{nh^2} \right] = \frac{8mL^2}{nh^2} = \frac{8mL^2}{h^2} \cdot \frac{1}{n}$$

From Eq'n (a)

$$E = \frac{n^2 \pi^2 \hbar^2}{2mL^2} = \frac{n^2 \pi^2 \left(\frac{h}{2\pi}\right)^2}{2mL^2} = \frac{n^2 h^2}{8mL^2}$$

$$\therefore \frac{1}{n^2} = \frac{h^2}{8mL^2 E}$$

$$\Rightarrow \frac{1}{n} = \left(\frac{h^2}{8mL^2 E} \right)^{1/2} \rightarrow (4)$$

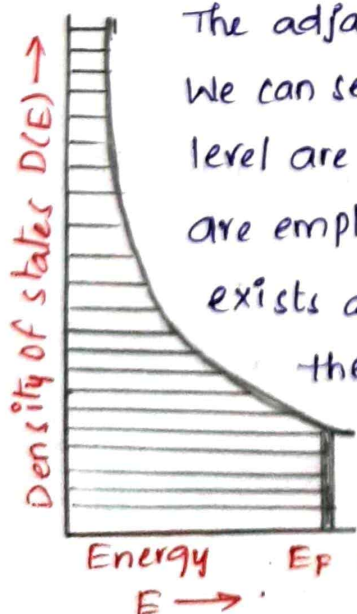
$$\therefore D(E) = \frac{8mL^2}{h^2} \cdot \left(\frac{h^2}{8mL^2 E} \right)^{1/2}$$

$$D(E) = \left(\frac{8mL^2}{h^2} \cdot \frac{8mL^2}{h^2} \cdot \frac{h^2}{8mL^2} \right)^{1/2} \cdot \frac{1}{\sqrt{E}}$$

$$D(E) = \left(\frac{8mL^2}{h^2 E} \right)^{1/2}$$

$$D(E) = \left(\frac{16mL^2}{2h^2 E} \right)^{1/2} = \frac{4L}{h} \left(\frac{m}{2E} \right)^{1/2}$$

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



The adjacent figure shows the plot of $D(E)$ versus E . We can see that the levels present below the Fermi level are filled and all those present above it are empty. However, this type of situation, in fact, exists at absolute zero. This means at 0K, the Fermi level divides the filled and unfilled levels in the metallic crystal.

Fig: Variation of electronic states

E_F density $D(E)$ with energy for one dimensional metallic

Fermi Level :-

Let us consider the occupancy of the allowed energy states at absolute zero. Let us add electrons to the allowed energy states. First we will fill the ground state and then the higher excited states will be filled, until the last electron is added at a level, above which all other states are unoccupied. This level is defined as Fermi level as shown in Figure.



Fig:- Density of states as a function of energy at absolute zero. Clearly, Fermi energy E_F is defined as the energy of the topmost filled level. We can calculate it from the total no. of free electrons N as

$$N = \int_0^{E_F} g(E) dE = \frac{V}{3\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} E_F^{3/2}$$

$$(or) E_F = \frac{\hbar^2}{2m} \left(3\pi^2 \frac{N}{V} \right)^{2/3}$$

Above eqn will lead for Fermi surface, the fermi vector as

$$E_F = \frac{\hbar^2}{2m} k_F^2$$

$$\text{where } k_F = \left(\frac{3\pi^2 N}{V} \right)^{1/3}$$

The electron velocity v_F at the fermi surface is

$$v_F = \frac{\hbar k_F}{m} = \frac{\hbar}{m} \left(\frac{3\pi^2 N}{V} \right)^{1/3}$$

Now, the Fermi temperature is defined as

$$T_F = \frac{E_F}{k_B} = \frac{\hbar^2}{2mk_B} \left(\frac{3\pi^2 N}{V} \right)^{2/3}$$

As stated above at absolute zero, all the allowed states of energy up to Fermi level will be occupied. As the temperature is raised, a variation in electron energy is provided by the energy of the crystal.

We note that this variation is quite small as compared to the electron energy itself such that the energy distribution can only change slightly at a temperature higher than 0K . It is clear that only electrons with energies near E_F will change their state on raising the temperature because thermal energy will be insufficient to excite electrons with lower energies to unoccupied states above E_F .

Effective Mass :-

When an external field is applied to a semiconductor, the charge carriers i.e. the electrons & holes, experience force due to the external applied field and also due to the internal periodic field produced by the crystal. If the external applied field is much weaker than the internal field, the effect of the latter is to modify the mass of the carriers in such a way that the carriers respond to the applied field with this modified mass obeying the laws of classical mechanics. This modified mass of the carriers is termed the "effective mass" of the carriers and usually denoted by m^* . m^* is usually different from electronic mass (m) in vacuum. The effective mass approximation avoids the quantum nature of the problem & allows us to use classical mechanics to study the effect of external fields or forces on the charge carriers, i.e. on the electrons or the holes inside the crystal. Thus, the force on e^- of mass m^* and charge $-e$ in an electric field E in terms of m^* can be written as $m^*a = -eE$ where a is the acceleration.

Recombination of Electrons and Holes

This is the process in which the free electrons in the conduction band jump into the valence band to combine with holes. In this process of recombination, the electron-hole ($e-h$) pair is destroyed. The rate of recombination is approximately proportional to the product of electron concentration and hole concentration. In this process, the minimum energy released in the form of electromagnetic radiation is equal to the band gap (E_g). We have

$$E_g = h\nu$$

where h is Planck's constant and ν is the frequency of the radiation. The wavelength of the radiation is given by

$$\lambda = \frac{c}{\nu} = \frac{ch}{E_g}$$

where c ($= 3 \times 10^8$ m/s) is the velocity of light in free space. The generation and recombination of electrons and holes are illustrated in Fig. 21.5.

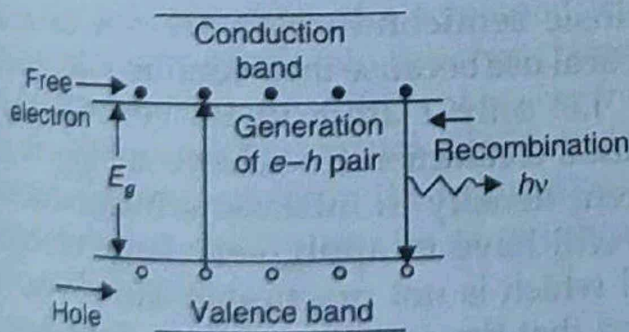


Fig. 21.5: The generation and recombination of electrons and holes in a semiconductor

While some electron-hole pairs are lost due to recombination, new $e-h$ pairs are generated due to thermal excitation. For an intrinsic semiconductor at a constant temperature, the rate of combination and the rate of generation of $e-h$ pairs are equal, and hence the electron and hole concentrations remain constant at their thermal equilibrium value. With the rise in temperature, the thermal equilibrium value of the electron and the hole concentrations also increases.

Intrinsic Conductivity

Since there are two types of charge carriers (free electrons and holes) in the intrinsic semiconductor, its specific conductance is the sum of the conductivities σ_n due to free electrons and σ_p due to holes. Thus, the electric conductivity of an intrinsic semiconductor is

$$\sigma_i = \sigma_n + \sigma_p = ne\mu_n + pe\mu_h \quad (21.1)$$

where μ_n and μ_h are electron and hole mobilities respectively. The mobility μ is defined as the drift velocity per unit electric field. The magnitude of μ_h is always less than μ_n for semiconductors. The mobilities of electrons and holes are $\mu_n = 1250$ cm²/Vs and $\mu_h = 480$ cm²/Vs. n and p are concentrations (number of charge carriers per cubic meter) of electrons and holes respectively in a semiconductor. Since for an intrinsic semiconductor

$$n = p = n_i \quad (21.2)$$

one obtains

$$\sigma_i = n_i e (\mu_n + \mu_h) \quad (21.3)$$

The mobilities depend on temperature as a modest power law, i.e. μ goes as $1/T^{3/2}$

$$\text{or} \quad \mu_n = \alpha T^{-3/2} \quad \text{and} \quad \mu_h = \beta T^{-3/2}$$

$$\text{Thus} \quad \mu_n + \mu_h = (\alpha + \beta) T^{-3/2} = \gamma T^{-3/2}$$

Equation (3) becomes

$$\sigma_i = \gamma n_i T^{-3/2} = \gamma (en_i) T^{-3/2}$$

$$\text{Now} \quad n_i = CT^{-3/2} \exp(E_g/2k_B T)$$

$$\text{with} \quad C = 2 \left(\frac{2\pi m k_B}{h^2} \right)^{3/2}$$

$$= \left[\frac{2\pi \times 9.1 \times 10^{-31} \times 1.38 \times 10^{-23}}{(6.626)^2 \times 10^{-68}} \right]^{3/2} = 4.83 \times 10^{21}$$

$$\text{Hence} \quad n_i = 4.83 \times 10^{21} T^{-3/2} \exp(-E_g/2k_B T)$$

Using this value of n_i , one obtains

$$\sigma_i = \gamma C e \exp(-E_g/2k_B T) \quad (21.4)$$

or

$$\sigma_i = B \exp(-E_g/2k_B T)$$

$$\text{or} \quad \rho_i = \frac{\exp(E_g/2k_B T)}{B} = A \exp(E_g/2k_B T) \quad (21.5)$$

Charge Carrier Densities in Extrinsic Semiconductors

We have seen that the introduction of impurities in pure semiconductors increases the density of one type or another type of charge carriers. The product of holes and electrons in a semiconductor is constant depending on the width of energy gap and temperature and hence the introduction of the impurities results in an increase in the density of one type of carrier and a decrease in the density of the other type of carrier. In an extrinsic semiconductor, the carriers introduced by the impurities are called *majority carriers* and the other type are called *minority carriers*. It is important to note that the low value for minority carrier density is due to added recombination.

Let N_d be the donor impurity density, N_a the acceptor impurity density, p the density of holes and n the density of electrons in an extrinsic semiconducting material. From the condition of charge neutrality, we have

$$N_d + p = N_a + n$$

or

$$n = (N_d - N_a) + p$$

$$= (N_d - N_a) + \frac{n_i^2}{n} \quad (\because np = n_i^2)$$

$$\text{or } n^2 - (N_d - N_a)n - n_i^2 = 0 \quad (21.7)$$

Solving the quadratic equation in n , one obtains

$$n = \frac{(N_d - N_a) \pm \sqrt{(N_d - N_a)^2 + 4n_i^2}}{2} \quad (21.8)$$

$$\text{or } n \approx (N_d - N_a) \text{ when } (N_d - N_a) \gg n_i$$

Obviously, the electron density (n) in the N-type semiconductor equals the difference in the donor and acceptor impurity densities when they are large compared to the intrinsic density, n_i . Similarly, the hole density (p) in a P-type semiconductor is given by

$$p = (N_a - N_d) \text{ when } (N_a - N_d) \gg n_i$$

Charge Densities in Extrinsic Semiconductors

The density of impurity atoms in N- and P-type materials is so low compared to the density of semiconductor atoms that the rate of thermal pair generation is not affected appreciably by the presence of impurity atoms. In the case of intrinsic semiconductors, we have seen that the concentration product was a constant at a given temperature.

$$np = n_i^2 \quad (21.14)$$

Assuming all impurity atoms in extrinsic semiconductors to be ionized at the usual operating temperatures, the free charge densities in impurity material can be based upon N_D , the donor atom density in N-material, or N_A , the acceptor atom density in P-material.

The electrical neutrality of the material demands

$$p = N_D = n + N_A \quad (21.15)$$

The LHS of Eq. (21.15) gives the total positive charge as the sum of holes in the valence bonds and the positive charge associated with the donor atoms that have given up electrons and become positive ions. The RHS of Eq. (21.15) sums the negative charge of the electron density n and the negative charge due to electrons held by the ionized acceptor atoms.

Using Eq. (21.14), one can write

$$n = \frac{n_i^2}{p} \quad \text{and} \quad p = \frac{n_i^2}{n} \quad (21.16)$$

Only donor impurities are introduced in N-type material, so $N_A = 0$. The donor density will be made much larger than the density of intrinsic holes, i.e.

$$N_D \gg p$$

and in N-type material the electron density is written from Eq. (21.15) as

$$n \cong N_D \quad (21.17)$$

On the similar reasoning for P-type material, we have $N_D = 0$ and $N_A \gg n$. One obtains density relations in P-type material as

$$n \cong \frac{n_i^2}{N_A} \quad (21.18)$$

$$p \cong N_A \quad (21.19)$$

From the above results, we can conclude that the density of majority carrier approximates the impurity atom density at usual ambient temperatures and the density of minority carriers reduces below the intrinsic level. This means that the increased electron density in N-type material raises the probability that an electron will meet and recombine with a hole and so the hole density decreases to maintain n^2 constant.

21.4 SEMICONDUCTOR DEVICES

A semiconductor device can be defined as a unit which consists, partly or wholly, of semiconducting materials and which can perform useful functions in electronic apparatus and solid state research. Examples of semiconductor devices are semiconductor diodes (P-N junction), transistors, integrated circuits (ICs), etc. Si, Ge and GaAs are most commonly used materials for the fabrication of semiconductor devices. For convenience, the properties of these semiconductors are summarized in Table 21.3.

Almost all semiconductor devices are comprised of a single crystal semiconductor incorporating two or more semiconducting regions of different impurity density. The difference in the electric fields and carrier densities associated with differently doped regions, called junctions, permit a wide range of essentially nonlinear conductivity effects in devices incorporating two, three or more distinct regions. Most semiconductor devices can be understood through the simplest of such junctions, called the P-N junction, which is a system of two semiconductors in physical contact, one with excess of electrons (N-type) and other with excess of holes (P-type) (Table 21.3).

P-N Junction

When a P-type semiconductor is brought into contact with N-type semiconductor as the process of crystallisation is taking place, the

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P-N Junction

When a P-type semiconductor is brought in contact with N-type semiconductor as the process of crystallisation is taking place,

Table 21.3: Properties of Si and Ge semiconductors

Property	Symbol	Unit	Value		GaAs
			Germanium (Ge)	Silicon (Si)	
Atomic number			32	14	
Atomic weight			72.6	28.08	144.63
Density		kg/m ³	5.32 × 10 ³	2.33 × 10 ³	5.32 × 10 ³
Atom concentration		atoms/m ³	4.4 × 10 ²⁸	5 × 10 ²⁸	2.21 × 10 ²⁸
Relative dielectric constant	ϵ_r		16	11.8	10.9
Band gap at 0 K	E_{g0}	eV	0.785	1.21	1.43
Band gap at 300 K	E_g	eV	0.72	1.1	1.32
Intrinsic carrier (generation) at 300 K	n_i	$\frac{\text{Carriers}}{\text{m}^3}$	2.5 × 10 ¹⁹	1.5 × 10 ¹⁶	9.0 × 10 ¹²
Crystal structure			Diamond	Diamond	Zinc blende
Lattice constant	a	Å	5.65748	5.43086	5.6534
Melting point		°C	936	1420	1250
Minority carrier lifetime		second (s)	~10 ⁻³	~2.5 × 10 ⁻³	~10 ⁻⁸
Breakdown field		V/m	~10 ⁷	~3 × 10 ⁷	~4 × 10 ⁵
Diffusion constant	D_n (electron) D_n (holes)	m ² /s	0.009842 0.004662	0.003367 0.001295	0.001036 0.000906
Effective density of states in the conduction band	N_c	m ⁻³	1.04 × 10 ²⁵	2.8 × 10 ²⁵	4.7 × 10 ²²
Effective density of states in the valence band	N_v	m ⁻³	6.4 × 10 ²⁴	1.02 × 10 ²⁵	7.0 × 10 ²²
Intrinsic conductivity	σ_i	S m ⁻¹	2.2428	0.4325 × 10 ⁻³	1.2832 × 10 ⁻⁶
Mobility (drift) at 300 K	μ_n (electron)	$\frac{\text{m}^2}{\text{Vs}}$	0.38	0.13	0.85
	μ_h (hole)	$\frac{\text{m}^2}{\text{Vs}}$	0.18	0.05	0.04
Work function	W	Volt (V)	4.4	4.8	4.7
Raman phonon energy		eV	0.037	0.063	0.035

resulting combination is called a P-N junction. This junction has important properties and is, in effect, the basis of modern semiconductor theory and practice. Most semiconductor devices contain one or more P-N junctions. The most important characteristic of a P-N junction is its ability to conduct current in one direction only. In the reverse direction, it offers very high resistance.

P-N Junction with No External Voltage

Figure 21.16 shows a P-N junction just immediately after it is formed. There is no

external voltage connected to the P-N junction. Since N-type material has a high concentration of free electrons while P-type material has a high concentration of holes, the following processes are initiated:

- At the junction, holes from the P-region diffuse into the N-region and free electrons from the N-region diffuse into the P-region. This process is called *diffusion*. Holes combine with the free electrons in the N-region whereas electrons combine with the holes in the P-region.

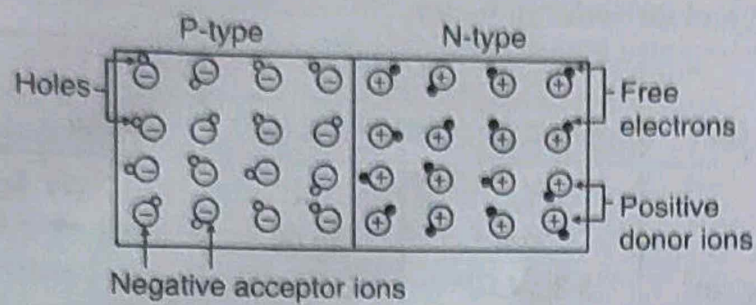


Fig. 21.16: A P-N junction when just formed

- ii. The diffusion of holes from P-region to N region and electrons from N-region to P-region across the junction takes place because they move haphazardly due to thermal energy and also because there is a difference in their concentrations (the P-region has more holes whereas N-region has more free electrons) in the two regions.
- iii. As the free electrons move across the junction from N-type to P-type, positive donor ions are uncovered, i.e. they are robbed off free electrons. Hence, a positive charge is built on the N-side of the junction. At the same time, the free electrons cross the junction and uncover the negative acceptor ions by filling in the holes. Therefore, a net negative charge is established on P-side of the junction. When a sufficient number of donor and acceptor ions are uncovered, further diffusion is stopped. It is because now, a barrier is set up against further movement of charge carriers. This is called *potential barrier* or *junction barrier*. The potential barrier is of the order of 0.1 to 0.3 volts. Figure 21.17 shows the electrostatic potential difference across the P-N junction. How this potential barrier is developed? It is because now positive charge (ions) on N-side repels holes to cross from P-type to N-type and negative charge (ions) on N-side repels free electron to enter from N type to P-type. Because of this difference in potential established between the two sections, which inhibits further electron-hole combinations at the junction, and

the Fermi level of the two sides is in the same level as shown in Fig. 21.17c.

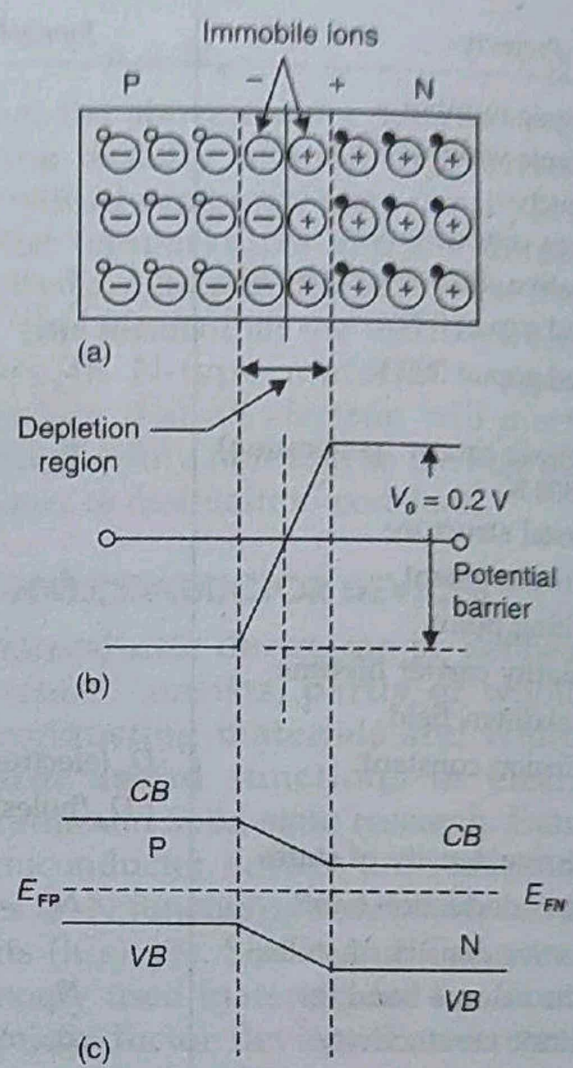


Fig. 21.17: Potential barrier across the P-N junction

- iv. The region across the P-N junction in which the potential changes from positive to negative is called the *depletion region*. The width of this region is of the order of 6×10^{-8} m. Since this region has immobile (fixed) ions which are electrically charged, it is also called as the *space-charge region*. Outside this region on each of side of the junction, material is still neutral.
- v. The potential barrier for a silicon P-N junction is about 0.7 V, whereas for a germanium P-N junction it is approximately 0.3 V.

The potential barrier discourages the diffusion of majority carriers across the junction. However, the potential barrier helps minority carriers (few free electrons in the

p-region and few holes in the N-region) to drift across the junction. The minority carriers are constantly generated due to thermal energy. But electric current cannot flow since no circuit has been connected to the P-N junction.

Forward and Reverse Biasing

Forward Biasing

We have seen that the natural tendency of the majority carriers (free electrons in the N-section and holes in the P-section) was to combine at the junction. This is how the depletion region and potential barrier were formed. Actually, the combination of electrons and holes at the junction allows electrons to move in the same direction in both the P- and N-sections. In the N-section, free electrons move toward the junction; in the P-section, for the holes to move toward the junction, valence electrons move away from the junction. Therefore, electron flow in both the sections is in the same direction. This, of course, would be the basis of current flow.

With the P-N junction alone, the action stops because there is no external circuit and because of the potential barrier that builds up. So, for current to flow, a battery can be connected to the diode to overcome the potential barrier. And the polarity of the battery should be such that the majority carriers in both sections are driven toward the junction. When the battery is connected in this way, it provides forward bias, causing *forward* or *high current* to flow, because it allows the majority carriers to provide the current flow.

To apply forward bias, positive terminal of the battery is connected to P-type and negative terminal to N-type as shown in Fig. 21.18a. The applied forward potential establishes an electric field which acts against the potential barrier field. Obviously, the resultant field is weakened and the barrier height is reduced at the P-N junction (Figs 21.18b and c). Since potential barrier height is very small (~ 0.2 V), hence a small forward voltage is sufficient to completely eliminate the barrier. Obviously, at some forward voltage, the potential barrier at the P-N junction can be eliminated altogether. Then the junction resistance will

become almost zero and a low resistance path is established for the entire circuit. Thus, a large current is generated in the circuit even for the small potential difference applied. Such a circuit is called *forward bias circuit* and the current is called *forward current*. The salient features of the forward bias circuit are as follows:

- At some forward voltage, the potential barrier is eliminated altogether.
- The P-N junction offers low forward resistance (r_f) to current flow.
- The magnitude of current in the circuit due to the establishment of low resistance path depends upon the applied forward voltage and it reduces as the voltage is increased thereby forward current increases. It is given by

$$I = I_0 (e^{V/\eta V_T} - 1) \quad (21.20)$$

where V = applied voltage

$$V_T = \frac{T}{11600} \text{ here } T = \text{temperature in Kelvin}$$

$\eta = 1$ for Ge and 2 for Si

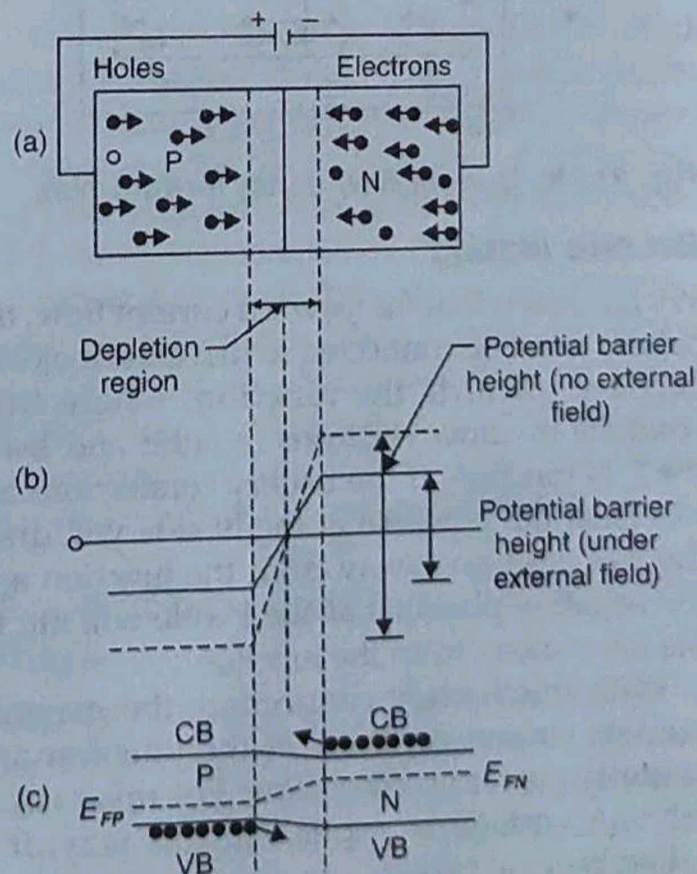


Fig. 21.18: P-N junction showing forward biasing

The mechanism of current flow in a forward biased P-N junction is as follows:

- The free electrons from the negative battery terminal continue to arrive into the N-region while the free electrons in the N-region move towards the P-N junction.
- The electrons travel through the N-region as free electrons. Obviously, current in N-region of the P-N junction is by free electrons.
- When these free electrons reach the P-N junction, they combine with holes and become valence electrons. Since a hole is in the covalent bond, and hence when a free electron combines with a hole, it becomes a valence electron.
- Current in the P-region is by holes. The electrons travel through P-region as valence electrons.
- These valence electrons after leaving the crystal flow into the positive terminal of the battery.

The current flow in a forward biased P-N junction is illustrated in Fig. 21.19.

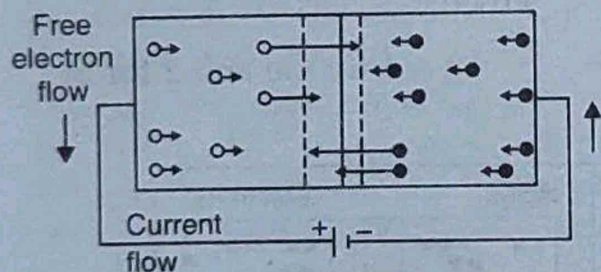


Fig. 21.19: Current flow under forward bias

Reverse Biasing

We have seen that for forward current flow, the battery must be connected to drive the majority carriers towards the junction, where they combine to allow electrons to enter and leave the P-N junction. If the battery connections are reversed, the potential at the N-side will draw the free electrons away from the junction and the negative potential at the P-side will attract the holes away from the junction.

With this battery connection, the majority carriers cannot combine at the junction and majority current cannot flow. For this reason, when a voltage is applied in this way, it is called reverse bias.

However, reverse bias can cause a *reverse current* to flow because minority carriers are present in the semiconductor sections. Remember that although the P-section is doped to have excess holes, yet some electrons are freed because of thermal agitation. Also, although the N-section is doped to have excess free electrons, some electrons are freed to produce holes in the N-section. The free electrons in the P-section and the holes in the N-section are the minority carriers. Now, with reverse bias, one can see that the battery potentials repel the minority carriers toward the junction. As a result, these minority carriers cross the P-N junction in exactly the same way that the majority carriers did with forward bias. However, since there are much fewer minority carriers than there are majority carriers, this minority current, or reverse current as it is usually called, is much less and is of the order of μA . Reverse bias P-N junction is shown in Fig. 21.20. The salient features of the reverse biased P-N junction are as follows:

- The height of the potential barrier is increased and width of depletion region also increases (Figs 21.20b and c).

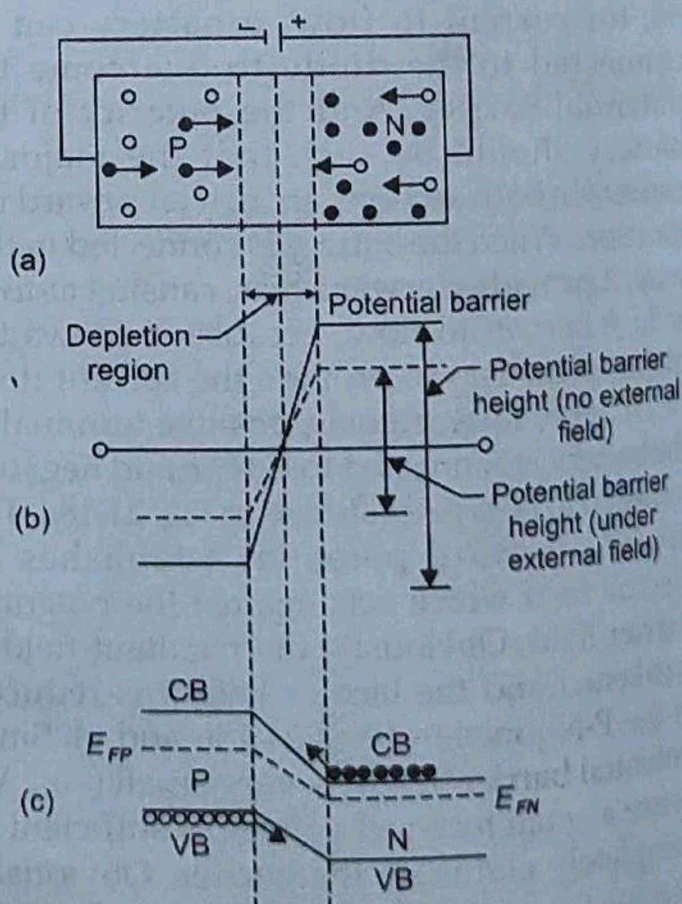


Fig. 21.20: P-N junction showing reverse biasing

- ii. The reverse bias P-N junction offers very high resistance to current flow. This resistance is called reverse resistance (R_r).
- iii. Due to the establishment of high resistance path, very small current flows in the circuit. This current is usually called as the *leakage current* or *reverse saturation current*.

The current in the above situation is given

by

$$I = I_0(e^{V/nV_T} - 1) \quad (21.21)$$

Since applied voltage V is negative, hence as it increases, the first term in RHS reduces very fast and current from Eq. (21.21) reduces to $I = (-)I_0$ which is quite low and constant.

Volt-Ampere Characteristic of P-N Junction

The P-N junction can be represented by a symbol of arrow and dash as shown in Fig. 21.21. The arrow head represents the P-section of the crystal and shows the direction of flow of holes or conventional current. Since the P-N junction diode's resistance changes according to the direction of current flow and hence it is called a *nonlinear* device. Basically, its nonlinearity is dependent on the polarity of the applied voltage.



Fig. 21.21: Symbol of the P-N junction diode

A graph between the potential difference across the P-N junction and the current through the junction is called the V - I characteristics of the P-N junction diode and is shown in Fig. 21.22.

In the forward direction, though considerably more current flows and the current for the most part increases linearly as the bias voltage is increased, in the forward direction, then, the P-N junction can be considered a linear device over a large portion of its operating curve. The small portion of the curve that is just above zero bias is nonlinear. This results because both majority and minority currents actually comprise the overall current. Since the minority carriers are low energy carriers, majority current starts

first and then as the voltage is raised, minority current joins in, causing a nonlinear rise in current. But as the voltage is increased further, minority current becomes saturated since there are only few minority carriers. The curve then follows the majority current increase which is linear.

Because of the nonlinearity of the curve, if

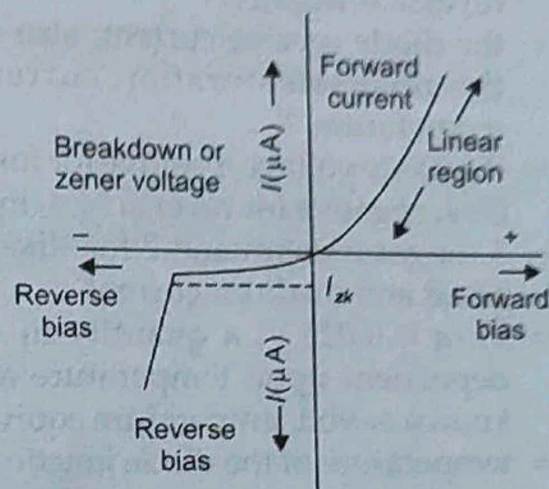


Fig. 21.22: V - I characteristics of a P-N junction diode

a very small signal voltage is applied to the diode so that it only operates around the knee, the signal will be distorted. The signals must be large enough so that they operate mostly over the linear part of the curve.

When reverse bias is applied, a slight reverse current flows. This reverse current increases only negligibly as the bias voltage is increased a lot (20 to 25 volts). At this stage, current suddenly rises in the reverse direction due to the breakdown of the crystal, i.e. covalent bonds of the crystal are broken in very large number. This breakdown reverse bias is called the *breakdown* or *zener voltage*. Diodes are also designed to produce a useful wide range of zener breakdown region and are used in special voltage-regulating circuits.

Effect of Temperature on P-N Junction Diodes

We know that temperature rise boosts the generation of electron-hole pairs in semiconductors and increases their conductivity. From the consideration of the energies of the carriers crossing the depletion region in a P-N junction diode, an involved calculation

21.7 PHOTODIODE

A photodiode is a P-N junction diode packed into a transparent plastic working under reverse biased condition.

Principle

A very small current flows through a P-N junction diode when it is reverse biased. It is because minority charge carriers take part in conduction. The number of minority carriers depend upon the working temperature. However, when photons (light) of suitable frequency are incident on the junction, the number of charge carriers increases. But this happens only when light radiations touch the junction which is not the case in ordinary diode.

Working

In a photodiode, visible light is focussed on the junction through a lens. Light on being incident produces free electrons and holes. Thus, the number of charge carriers increases and hence current increases. Generally, a photodiode is optimized for its sensitivity to light. As the light intensity increases, more and more charge carriers are generated and reverse bias current increases.

In this respect, a photodiode acts as a photo detector, a device which converts incoming light signal into electrical signal.

Applications

Some of the important applications of photodiodes are (i) photo detection (both visible and invisible) (ii) demonstration (iii) logic circuits (iv) switching (v) optical communication system.

21.8 SOLAR CELLS

Solar cells, which convert the sunlight directly into electricity, at present furnish the most important long duration power supply for satellites and space vehicles. These cells have also been successfully employed in small-scale terrestrial applications. Today, the solar cell is considered a major device for obtaining energy from the sun. It can convert sunlight directly into electricity with high conversion efficiency, provide nearly permanent power at low operating cost and is virtually free of pollution. Recently, research and pollution development of low-cost, flat panel solar cells, thin film devices, concentrator systems and many innovative concepts have increased. We can expect that in near future, the costs of small solar power modular units and solar power plants will be economically feasible for large-scale use of solar energy.

The first solar cell was developed by Chapin *et al.* in 1954 using a diffused silicon P-N junction. Subsequently, the cadmium sulphide solar cell was developed by Raynolds *et al.* in 1954. Till date, solar cells have been made of many other semiconductors, using various device configurations and employing single-crystal, polycrystal and amorphous thin film structures.

Photovoltaic Effect and Solar Cells

The photovoltaic effect can be observed in nature in a variety of materials, but the materials that have shown the best performance in sunlight are the semiconductors. In photovoltaic conversion, the solar radiation falls on devices called solar cells which convert the sunlight

directly into electricity. The principal advantages associated with solar cells are that they have no moving parts, require little maintenance and work quite satisfactorily with beam or diffuse radiation.

21.9 LIGHT-EMITTING DIODE (LED)

LED is a solid state (P-N junction diode) light source which has replaced incandescent lamps in many day to day applications.

LED is just not an ordinary P-N junction diode where silicon is used. Here we use compounds having elements like gallium, arsenic and phosphorous which are semi-transparent unlike silicon which is opaque. (Gallium arsenide gives infrared radiations and gallium arsenide phosphide gives visible light either red or yellow).

The advantages of an LED are:

- i. Low voltage of operation
- ii. Long life (more than 20 years)
- iii. Fast ON-OFF switching (10^{-9} sec).

The other uses of LED are:

1. For indicating power ON/OFF (power level indicators)
2. Optical switching applications
3. Solid state video displays
4. Optical communication—Energy coupling circuits.

All natural colours are composed from three primary colours namely red, green and blue. LED in red and green have been available but the blue one has been missing. Blue light emitters have several potential applications. They can be used for full colour displays of large area. They can be used in traffic lights as replacements for ordinary bulbs resulting in huge power savings as well as cost. Use of blue lasers can also result in higher density storage of information in optical CD-ROMs. Blue light emitters have been fabricated using several materials including ZnO, ZnSe and SiC. These attempts have been reasonably successful. However, maximum success in last few years has been achieved with GaN. This material has proved to be very useful as it is also capable of operating at high power

density, high temperature and unfriendly environment. GaN having a band gap of 3.4 eV can give continuously varying band gap by combining with AlN to get up to 6.2 eV and with InN to get a band gap down to 1.9 eV. The high thermal conductivity and superior stability of this material makes it ideal for several applications over other competing materials.

Effective mass (m^*) :- of an electron (e^-)

When an electron in a periodic potential is accelerated by an electric field & magnetic field, then the mass of electron is called effective mass. It is denoted by m^* .

Let electron of charge e and mass m inside a crystal lattice of electric field E .

$$\text{Acceleration } a = \frac{eE}{m} \quad (\because F = qE \rightarrow ma = eE)$$

is not a constant in the periodic lattice in the crystal. It can be considered that its variation is caused by the variation of electron mass when it moves in the crystal lattice.

$$\therefore a = \frac{eE}{m^*}$$

$$\text{Electrical force on the electron } F = m^* a$$

$$\Rightarrow a = \frac{F}{m^*} \quad \text{--- (1)}$$

According to quantum theory an electron moving with velocity ' v ' can be treated as wave packet moves with group velocity.

$$v_g = \frac{d\omega}{dk} = \frac{d}{dk}(2\pi\nu) = 2\pi \frac{d\nu}{dk}$$

$$E = h\nu \Rightarrow \nu = \frac{E}{h}$$

$$\therefore v_g = 2\pi \frac{d(E/h)}{dk} = \frac{2\pi}{h} \frac{dE}{dk} = \frac{1}{h} \frac{dE}{dk}$$

$$\Rightarrow v_g = \frac{1}{h} \frac{dE}{dk} \quad \text{--- (2)}$$

The rate of change of velocity is known as acceleration

$$a = \frac{dv_g}{dt} = \frac{d}{dt} \left(\frac{1}{\hbar} \frac{dE}{dk} \right) = \frac{1}{\hbar} \frac{d}{dt} \left(\frac{dE}{dk} \right)$$

$$\Rightarrow a = \frac{1}{\hbar} \frac{d}{dt} \left(\frac{dE}{dk} \right) \frac{dk}{dk}$$

$$a = \frac{1}{\hbar} \frac{d^2 E}{dk^2} \frac{dk}{dt} \quad \text{--- (3)}$$

$$p = \hbar k \quad \text{--- (3)}$$

We know that

$$F = \frac{dp}{dt} = \frac{d}{dt} (\hbar k) = \hbar \frac{dk}{dt} \quad \text{--- (5)}$$

$$F = \hbar \frac{dk}{dt} \Rightarrow \frac{dk}{dt} = \frac{F}{\hbar} \quad \text{--- (6)}$$

Substituting eq'n (6) in eq'n (3), we get

$$a = \frac{1}{\hbar} \frac{d^2 E}{dk^2} \frac{F}{\hbar}$$

$$\Rightarrow a = \frac{1}{\hbar^2} \frac{d^2 E}{dk^2} F \quad \text{--- (7)}$$

From (1) and (7)

$$\frac{F}{m^*} = \frac{1}{\hbar^2} \frac{d^2 E}{dk^2} F \Rightarrow \frac{1}{m^*} = \frac{1}{\hbar^2} \frac{d^2 E}{dk^2}$$

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

$m^* \rightarrow$ effective mass of electron

$\hbar \rightarrow \frac{h}{2\pi}$, h - Planck's constant

$k \rightarrow$ wave vector



Direct and Indirect band gap of semiconductor

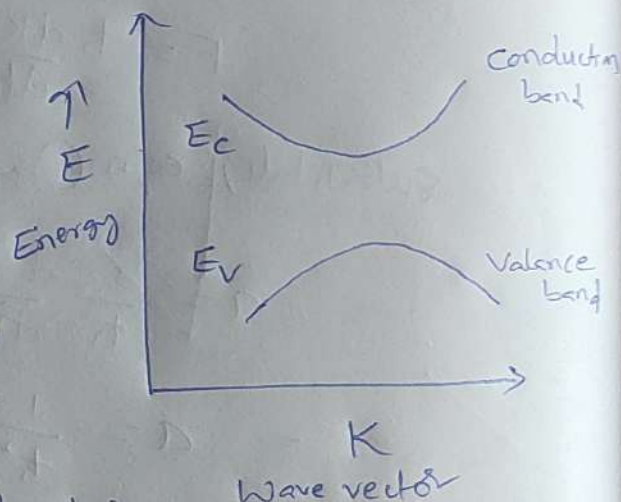
Energy versus (E) - Wave vector (K) [$E-K$] diagram shows characteristics of a particle in a semiconductor material, whether it is direct or indirect band gap semiconductor. It also shows one relationship between the energy and momentum of available quantum mechanical states for electrons in the material.

Consider a basic $E-K$ diagram as shown in figure.

$E \rightarrow$ energy of e^-

$K \rightarrow$ Wave vector / Propagation constant / momentum

In this diagram, the band gap which is the difference in energy between top of the valence band and bottom of the conduction band.



Direct band gap semiconductor:-

The material in which top of the valence band coincides with the bottom of the conduction band at the same value of K , that materials are called direct band gap.

Ex:- Ga, As

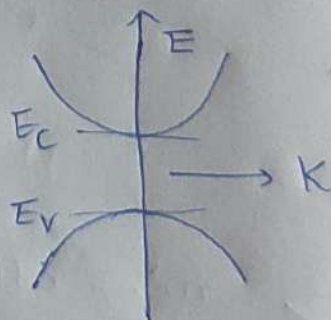


Fig Direct band gap semiconductor

Indirect band gap semiconductor:-

The materials in which top of the valence band does not coincide with the bottom of the conduction band (or) the top of the valence band and bottom of the conduction band occurs at different values of K , are known as indirect band gap semiconductors.

Ex/- Si and Ge

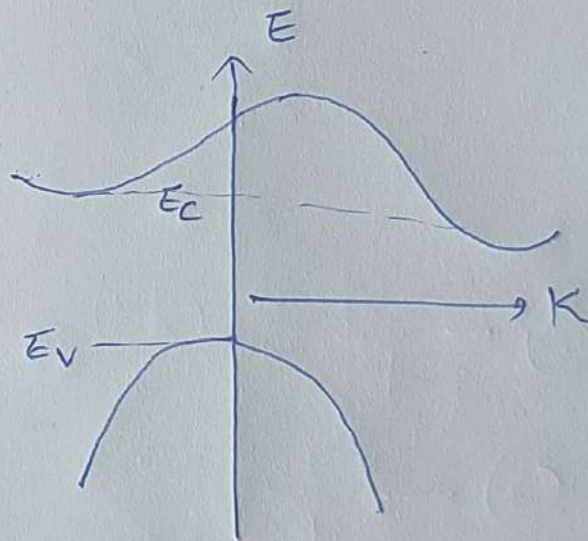


Fig. Indirect band gap semiconductor

8.15 HALL EFFECT

When a current carrying conductor (or semiconductor) is placed in a transverse magnetic field, a potential difference is developed across the conductor in the direction perpendicular to both current and magnetic field. This phenomenon is called *Hall effect*.

8.15.1 Hall Voltage and Hall Coefficient

Consider a slab of a material having length, breadth, and thickness l , b , and d , respectively. This slab of specimen material is subjected to an external electric field $\vec{E}_x$ along the x -axis and a magnetic field H_z

along the z -axis as shown in Fig. 8.24. The electric field $\vec{E}_x$ applied along the x -direction exerts a force on the charge carriers (say electrons, each of charge e), due to which electrons acquire a drift velocity v_x in the x -direction. The charge moving with drift velocity v_x experiences a magnetic force $\vec{F}_m$ perpendicular to both the velocity v_x and the magnetic field induction $\vec{B}_z$, which is given as

$$\begin{aligned}\vec{F}_m &= e(v_x \hat{i} \times B_z \hat{k}) \\ &= -e v_x B_z \hat{j}\end{aligned}\quad (8.26)$$

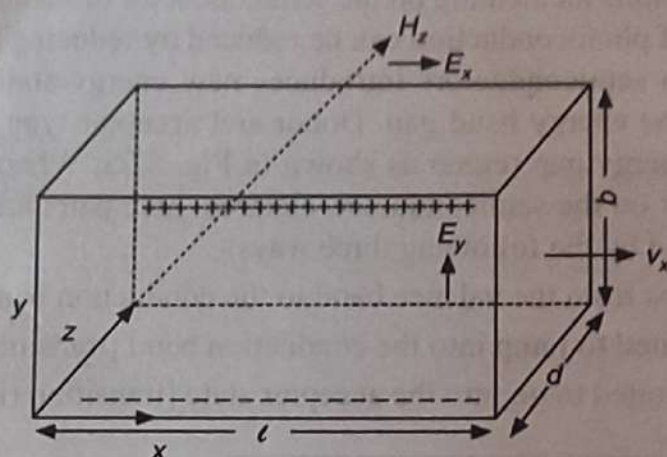


Fig. 8.24 Hall effect in a slab of specimen

This force acts along the negative y -axis. This deflecting force on the electron drifts it downwards to the lower edge of the specimen. Consequently, lower surface of the slab collects a negative charge and upper surface, a positive charge as shown in Fig. 8.24. Thus, an induced electric field called Hall electric field E_H is established which causes a Hall potential difference V_H across the positive and the negative y -axis. This Hall electric field opposes the drifting of electrons and very soon an equilibrium is reached due to the establishment of the condition of balance between the magnetic force $e(\vec{v} \times \vec{B})$ on the electron along the negative y -axis and the electric force eE_H along the positive y -axis, and consequently, drift velocity acquires a steady value. In this situation, the net force acting on the electron will be zero, i.e.,

$$e\vec{E}_H + e\vec{v}_x \times \vec{B}_z = 0$$

$$\text{or} \quad \vec{E}_H = -(\vec{v}_x \times \vec{B}_z) \quad (8.27)$$

$$\text{In terms of magnitude, } E_H = v_x B_z. \quad (8.28)$$

For the breadth b of specimen slab in the y -direction, Hall electric field is given as

$$E_H = \frac{V_H}{b} \quad \text{or} \quad V_H = bE_H \quad (8.29)$$

where V_H is known as Hall voltage.

Putting the value of E_H in Eq. (8.29), we get

$$V_H = b v_x B_z \quad (8.30)$$

If n is the number of charge carriers (electrons) per unit volume, then the relation between the current density (J_x) and the drift velocity (v_x) can be given as

$$v_x = -\frac{J_x}{ne} \quad (8.31)$$

Putting the value of v_x in Eq. (8.28), we get

$$E_H = \left(-\frac{1}{ne}\right) J_x B_z \quad (8.32)$$

The quantity $(1/ne)$ is called Hall coefficient for the material or the specimen slab and is represented as

$$R_H = -\frac{1}{ne} \quad (8.33)$$

Negative sign is due to the consideration of the electrom charge. From Eq. (8.32),

$$R_H = \frac{E_H}{J_x B_z} \quad (8.34)$$

But $J_x = \frac{I_x}{\text{Area}} = \frac{I_x}{bd}$

Hence,
$$R_H = \frac{(V_H/b)}{(I_x/bd)B_z} = \frac{V_H}{I_x} \frac{d}{B_z} \Omega\text{-m}^3/\text{Wb} \quad (8.35)$$

In the above expression, B_z is in weber/metre and d is in metre.

Hall Angle: Under the influence of applied electric field E_x and Hall electric field E_H at right angle, drift velocity (v_x) of charge carriers makes an angle with the x -direction. This angle is known as the Hall angle, which is given as

$$\phi = \frac{E_H}{E_x}$$

For specimen slab of length l , Hall angle is given as

$$\phi = \frac{E_H}{E_x} = \frac{V_H/b}{V_x/l} = \frac{V_H l}{V_x b} \text{ rad} \quad (8.36)$$

Hall Mobility: Mobility of charged carriers is defined as the drift velocity per unit applied field, which is given as

$$\mu_e = \frac{v_x}{E_x}$$

or $v_x = \mu_e E_x$

Putting this value of v_x in Eq. (8.30), we get

$$V_H = b\mu_e E_x B_z$$

or
$$E_H = \frac{V_H}{b} = \mu_e E_x B_z$$



$\mu_e = \frac{v_x}{E_x}$

Putting the value of E_H from Eq. (8.34), we get

$$R_H J_x B_z = \mu_e E_x B_z$$

or
$$\mu_e = R_H \frac{J_x}{E_x} = R_H \sigma \quad (8.37)$$

where σ is the electric conductivity of the specimen.

Substituting the value of R_H in Eq. (8.37), we get

$$\begin{aligned} \mu_e &= \left(\frac{V_H}{I_x B_z} \right) \frac{J_x}{E_x} \\ &= \frac{E_H b}{J_x b d} \frac{d}{B_z} \frac{J_x}{E_x} \\ &= \left(\frac{E_H}{E_x} \right) \frac{1}{B_z} = \frac{\phi}{B_z} \end{aligned}$$

Hence
$$\mu_e = \frac{\phi}{B_z} \text{ rad-m}^2/\text{Wb} \quad (8.38)$$

8.15.2 Applications of Hall Effect

Some important applications of Hall effect are as follows:

- (i) It is used to determine the sign of charge carriers.
- (ii) Carrier concentration can be determined using Hall effect.
- (iii) It is used to measure the mobility of charge carriers directly.
- (iv) It is used to determine whether the given material is a metal, a semiconductor, or an insulator.
- (v) It is used to measure the conductivity of a given specimen.