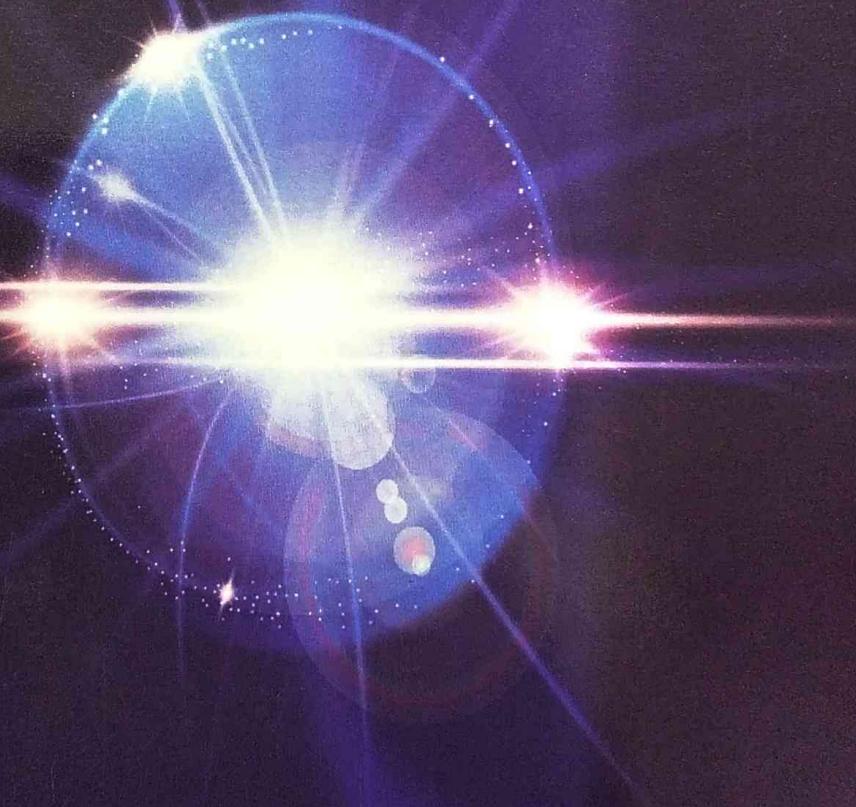


As per revised GGSIPU Syllabus

Physics for Engineers



Vol.2

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GGSIPU REVISED SYLLABUS

B. Tech. II Semester Applied Physics – II

Unit I

Quantum Mechanics: Introduction: Wave particle duality, de Broglie waves, the experiment of Davisson and Germer, electron diffraction, physical interpretation of the wave function, properties, the wave packet, group and phase velocity, the uncertainty principle. The Schrödinger wave equation (1D), Eigen values and Eigen functions, expectation values, simple Eigen value problems – solutions of the Schrödinger's equations for the free particle, the infinite well, the finite well, tunnelling effect, the scanning electron microscope, the quantum simple harmonic oscillator (qualitative), zero-point energy.

Unit II

Quantum Statistics: The need for statistics , statistical distributions: Maxwell Boltzmann, Bose-Einstein and Fermi-Dirac statistics, their comparisons, Fermions and Bosons, Applications of quantum statistics: 1. Molecular speed and energies in an ideal gas; 2. The Black body spectrum, the failure of classical statistics to give the correct explanations – Bose-Einstein statistics applied to the Black Body radiation spectrum; Fermi-Dirac distribution, free electron theory, electronic specific heats, Fermi energy and average energy; Dying stars.

Unit III

Crystal Structure: Types of solids, Unit cell, Types of crystals, Translation vectors, Lattice planes, Miller indices, Simple crystal structures, Interplanar spacing, Crystal structure analysis: Bragg's law, Laue method, Point defects: Schottky and Frankel defects.

Unit IV

Band Theory of Solids: Origin of energy bands in solids, motion of electrons in a periodic potential – the Kronig–Penny model (Qualitative). Brillouin zones, effective mass, metals, semi-conductors and insulators and their energy band structures. Extrinsic and Intrinsic semiconductors, doping – Fermi energy for doped and undoped semiconductors, the p-n junction (energy band diagrams with Fermi energy), the unbiased diode, forward and reverse biased diodes – tunnel diodes, Zener diode, photo diode its characteristics, LED

Chapter

1

Wave Particle Duality

Introduction

We have studied that the phenomenon of interference and diffraction shown by light, prove the wave nature of radiations. The transverse character of light is shown by the phenomena of polarization and the electromagnetic wave nature and the transverse character of light waves is well established by James Clerk Maxwell.

However, the black body radiation, photoelectric effect and Compton Effect could only be explained on the basis of discrete particle (the photons) nature of radiations (wave). Also, there are other physical phenomenon which prove that the radiations show wave as well as particle nature. Now, it is well proved that radiation has a dual character. In one situation it behaves like a wave whereas in other situation it is supposed to behave like a particle (matter).

In 1924, French theoretical physicist, Prince Louis de Broglie, suggested that if wave can behave like matter, so matter should also possess wave character because nature loves symmetry. Later, wave character of electron was experimentally verified by C.J. Davisson and L.H. Germer in 1927, and also by G.P. Thomson in the same year.

The hypothesis, proposed by Prince Louis de Broglie about the wave character of matter, is known as wave particle duality.

1.1 de Broglie's Hypothesis of Matter Waves

Prince Louis de Broglie put forward the following arguments which were enough to defend his hypothesis of matter wave:

- The whole energy in the universe is only in two forms: either matter or radiations.
 - Nature loves symmetry. So, the dual character of matter should also exist as in the case of radiation.
- On the basis of the above arguments, he gave the following hypothesis, called as de Broglie hypothesis of matter wave.

According to this, a moving particle has a wave associated with it and the wavelength of this matter wave, is given by;

$$\lambda = \frac{h}{mv} \quad (1)$$

Here, m and v are the mass and velocity of the particle respectively. h is Planck's constant.

The relation (1) was derived by taking analogy with radiation, but de Broglie could not provide conclusive experimental evidence for the wave nature of matter. Later Davisson and Germer gave the evidential proof about the wave nature of electron which could be considered as the first experimental proof of matter wave.

1.2 Wavelength and Velocity of de Broglie's Matter Wave

We have the equation of photonic energy of radiations as;

$$E = hv = pc = mc^2 \quad (2)$$

So,

$$hv = pc$$

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Or $p = \frac{hv}{c}$

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

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

(3)

(Here symbols used have their usual meanings)

If p , which is used as the momentum of the photon, is considered the momentum of a material particle, then the de Broglie wave length of matter wave should be given as;

$$\lambda = \frac{h}{p} \quad (4)$$

$$= \frac{h}{mv_p} \quad (5)$$

Here, $p = mv_p$ is the momentum of the particle and v_p is the particle velocity of the material particle. For the relativistic case, the wavelength is given as;

$$\boxed{\lambda = \frac{h}{mv_p} = \frac{h\sqrt{1 - \frac{v^2}{c^2}}}{m_0 v_p}}$$

Now if v_w is the wave velocity of the matter wave associated with the particle, then using the well-known relation for wave velocity, we have;

$$v_w = v\lambda \quad (6)$$

But using relation (2) and analogy of total relativistic energy of the de Broglie particle $mc^2 = hv$, we have;

$$v = \frac{mc^2}{h} \quad (7)$$

Using (5), (6) and (7), we have;

$$v_w = \frac{mc^2}{h} \frac{h}{mv_p}$$

Or

$$\boxed{v_w = \frac{c^2}{v_p}} \quad (8)$$

The Eq. (8) gives the wave velocity of de Broglie's matter wave. Here, it can be observed that the wave velocity v_w of a wave associated with a moving particle is always greater than c i.e., velocity of light, as the particle velocity v_p is always less than c . So, the relation (8) contradicts Einstein's postulate about velocity of light i.e., velocity of light cannot be attained. To justify the relation (8), the concept of wave-packet came into picture which was predicted by Schrodinger. According to him, a single wave associated with a moving de Broglie particle has no physical significance and there is always a group of waves called wave-packet associated with a moving particle. So, the wave velocity or phase velocity v_w , associated with a particle does not have any meaning and it does not matter whether it is greater than c or not.

Later, we will show that the velocity of wave-packet called group velocity is equal to the particle velocity and can be considered as the velocity of matter wave of the moving particle.

1.3 Predicted Wavelength of a Moving Electron

The theoretically predicted value of the wavelength of a moving electron can be calculated in the following manner.

Let an electron of mass m and charge e is accelerated by a potential difference V . If v_p be the velocity acquired by the electron, then the kinetic energy of the electron is given by;

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$$K.E = \frac{1}{2}mv_p^2 = eV$$

So, the de' Broglie wavelength of moving electron will be given as;

$$\lambda = \frac{h}{mv_p} = \frac{h}{m\sqrt{\frac{2eV}{m}}}$$

Or

$$\boxed{\lambda = \frac{h}{\sqrt{2meV}}} \quad (9)$$

This formula can also be used to calculate the theoretical value of wavelength of any charged particle. Particularly for electrons, it comes out to be;

Putting $h = 6.6203 \times 10^{-34} \text{ Js}$, $m = 9.1 \times 10^{-31} \text{ Kg}$ and $e = 1.6 \times 10^{-19} \text{ C}$, we get:

$$\lambda = \frac{6.6203 \times 10^{-34}}{\sqrt{2 \times 9.1 \times 10^{-31} \times 1.6 \times 10^{-19} V}}$$

Or

$$\boxed{\lambda = \frac{12.27}{\sqrt{V}} \text{ Å}} \quad (10)$$

Using Eq. (10), we can calculate the wavelength of a moving electron different accelerating potentials. For example, at 100V, the wavelength of an electron would be;

$$\lambda = \frac{12.27}{\sqrt{100}} = 1.227 \text{ Å}$$

However, this wavelength is in the range of wavelength of X-Rays, but these waves are quite different from electromagnetic waves as well as mechanical waves.

1.4 Relativistic de Broglie Wavelength

As we know, the mass is a variable quantity according to Einstein's theory of relativity, so for the particle moving with relativistic velocity, the mass of the moving particle will be taken as;

$$\boxed{m = \frac{m_0}{\sqrt{1 - \frac{v^2}{c^2}}}} \quad (11)$$

where m_0 is the rest mass of the particle, v is its velocity and c is the velocity of light.

Applying relativistic equation for kinetic energy K , viz.

$$K = (m - m_0)c^2$$

Also, $(m - m_0)c^2 = eV$

Or $(m - m_0) = \frac{eV}{c^2}$

Or $m = m_0 + \frac{eV}{c^2} = m_0(1 + \frac{eV}{m_0 c^2})$

Or $\boxed{m^{1/2} = m_0^{1/2}(1 + \frac{eV}{m_0 c^2})^{1/2}}$

Substituting the value of $m^{1/2}$ in Eq. (9) above, we get the velocity of the relativistic electron:

$$\lambda = \frac{h}{\sqrt{2Vem_0}} \left(1 + \frac{eV}{m_0 c^2}\right)^{-1/2} \quad (12)$$

Putting $\lambda = \frac{h}{\sqrt{2Vem_0}} = \frac{12.27}{\sqrt{V}} \text{ Å}$ in (12) we have the expression for the wavelength of an electron in relativistic form as;

$$\boxed{\lambda = \frac{12.28}{\sqrt{V}} \left(1 + \frac{eV}{m_0 c^2}\right)^{-1/2} \text{ Å}} \quad (13)$$

1.5 Experimental Wavelength of a Moving Electron

Davisson and Germer performed an experiment and calculated the wavelength of the wave of moving electrons which was very close enough to the wavelength predicted by de Broglie. At that time, it was considered the first experimental verification of matter wave.

1.5.1 Davisson and Germer's Experiment: Verification of de Broglie Hypothesis

Apparatus. The Davisson and Germer apparatus is shown in Fig.1.1. F is a tungsten filament which emits electrons when it is heated by passing a current from a low-tension battery B. P is a metal plate having a narrow hole, S_1 . It is maintained at a positive voltage V with respect to F so that the electrons are accelerated by the potential difference and emerge as a well collimated beam through the hole S_1 . C is a nickel crystal with its (1 1 1) face normal to the beam of electrons. When the electron beam is incident on the crystal, electrons are scattered in all directions by the atoms in the crystal.

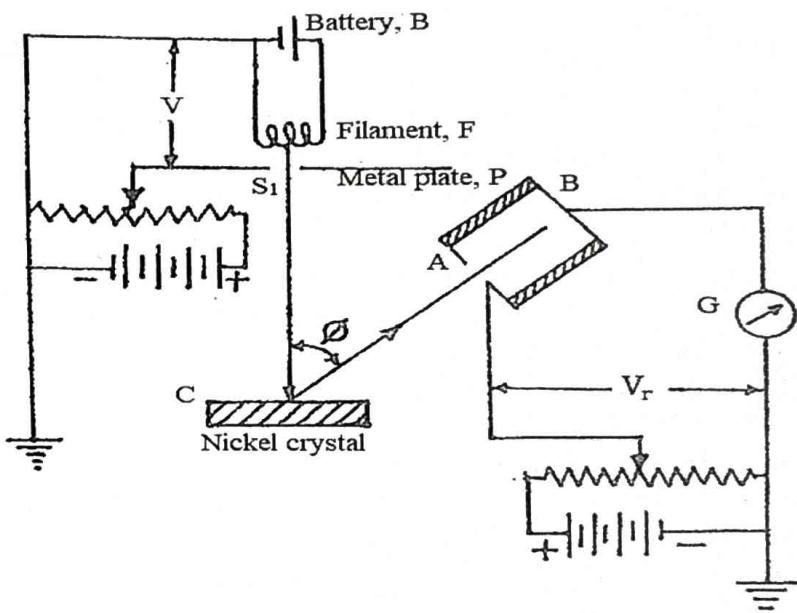


Fig. 1.1. Davisson and Germer experimental set-up

AB is the chamber called Faraday Cylinder, in which the electron beam scattered in a given direction from the nickel crystal is received. The chamber can be rotated about an axis in the face of C passing through the point of incidence of the electron beam. The electron current is measured by means of a sensitive galvanometer G. The front and back walls of the chamber are insulated from one another and a retarding potential V_r is applied between them so that only those electrons which have energy eV can enter the chamber. The apparatus is enclosed in an evacuated chamber.

Method: A known potential difference is applied between the filament F and the metal plate P. The chamber AB is set at different angles, and for each setting of the chamber, the current is noted. The current is directly proportional to the number of scattered electrons entering the chamber in 1 sec. Thus, the intensity of the scattered beam is measured as a function of the angle of scattering. The crystal is held in a fixed position throughout the measurements. This observation is repeated for different known potential differences. For each potential difference, the intensity of the current is plotted against the angle of scattering as shown in Fig.1.2.

Observation and Calculations

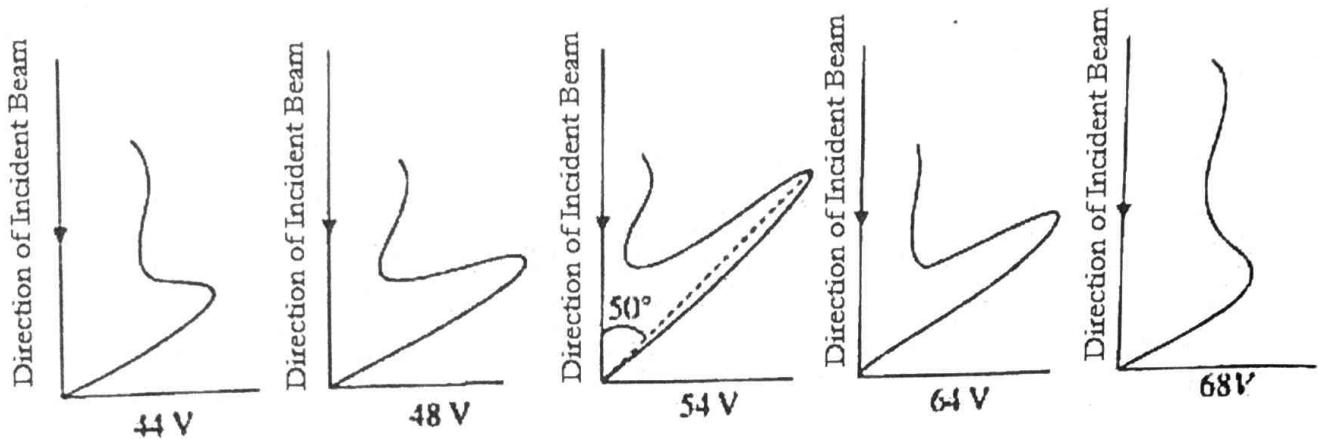


Fig.1.2.

It is seen that the intensity of the scattered beam is maximum at $\phi = 50^\circ$ when the accelerating voltage $V = 54$ volts. The plotted curve of the intensity of the current due to scattered electrons resembles with the diffraction pattern. Later, it was found that the intensity curve of scattered electrons is due to Bragg's diffraction like phenomena of waves of electrons through the crystal as in Fig.1.3. If it is so, then applying Bragg's well-known formula for diffraction, the experimental value for the wavelength of the electron can be calculated as;

$$2d \sin \theta = n\lambda \quad (14)$$

where θ is the angle at which the electrons are incident to the interatomic planes and d is the perpendicular distance between two adjacent rows of atoms in (1 1 1) planes of the nickel crystal. In this case it is 0.91\AA .

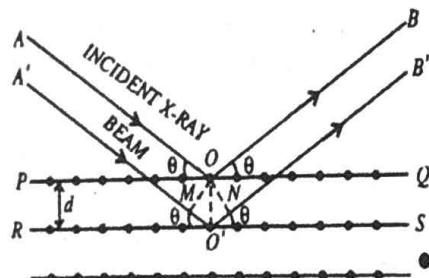


Fig.1.3. Bragg's diffraction for X-Rays

From the geometry of the crystal as in Fig. 1.4 and using Fig.1.3, we have:

$$\theta = \frac{1}{2}(180 - \phi) = \frac{1}{2}(180 - 50) = 65^\circ$$

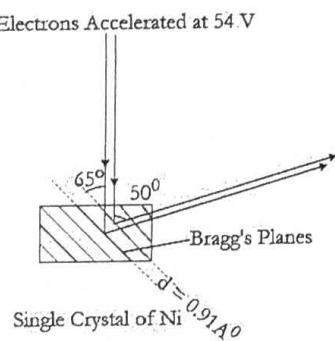


Fig. 1.4.

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Using Bragg's diffraction equation for first order for the electron waves, we have;

$$\begin{aligned}\lambda &= 2 \times 0.91\text{\AA} \sin 65^\circ \\ &= 1.65 \text{\AA}\end{aligned}\quad (15)$$

The theoretical value of wavelength of electron, accelerated by 54V potential difference, can be calculated by the Eq. (9) which comes out to be;

$$\lambda = \frac{12.28}{\sqrt{V}} = \frac{12.28}{\sqrt{54}} = \frac{12.28}{7.348} = 1.67 \text{\AA} \quad (16)$$

From (15) and (16) we can see that theoretically calculated value of wavelength as postulated by de Broglie is nearly equal to the experimentally calculated value of wavelength. As all the experimental calculations to find the wavelength, are done according to the Bragg's Diffraction equation and also the diffraction is a property of wave so from here the wave nature of moving electrons is verified. Ultimately, we can say that the de Broglie's hypothesis for waves of moving material particle is experimentally verified from this Davisson and Germer experiment.

1.6 Concept of a wave-packet

Now it has been proved experimentally that the matter can behave like a wave. But as we look at the Eq. (8), it seems that wave velocity (phase velocity) of the wave associated with the particle exceeds the velocity of light, so this wave leaves the particle, far behind from the wave as the particle velocity is very less than this wave velocity of the particle. Both these statements are not acceptable because, according to the Einstein's postulate, the velocity of light cannot be reached and the wave should be an integral part of the particle i.e. the wave should be intact with the particles and in any case, wave should not leave the particle. So, relation (8) cannot be justified in any way, as such. To justify this relation, Schrodinger gave a hypothesis. According to that, there are a number of waves associated with the de Broglie particle rather than single waves. All the waves have slightly different velocities/wavelengths from each other. They all always interfere constructively in a small region of space where the particle exists and destructively where the particle does not exist. Wherever the amplitude of the constructive interfering region is higher, the probability of particle to be there is higher. This implies that a group of waves making a region of constructive interference are always around the particle. This group of waves which confines the particle within it, is called a wave-packet (Fig.1.5). In nutshell, according to Schrödinger, it may be concluded that there is a wave-packet associated with a moving de Broglie particle rather than a single wave. Later, it will be proved that the velocity of this wave-packet called group velocity was found to be equal to the velocity of the particle and is always less than the velocity of light. It means the concept of a single wave associated with the de Broglie particle has no physical significance and so the wave velocity (phase velocity) of individual wave does not have any meaning. So, the relation (8) can be justified in a way such that the velocity of this single wave given by the relation (8), does not have any physical meaning. So, it does not contradict Einstein's Postulate about the velocity of light.

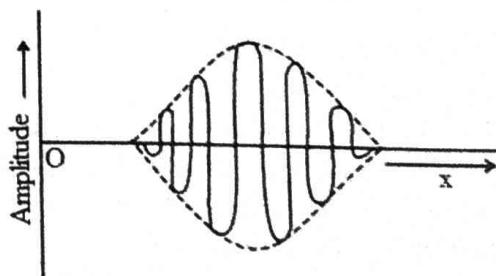


Fig.1.5. Wave packet of a de Broglie particle

1.7 Velocity of Matter Wave: Group Velocity

As it has been shown that a single wave associated with a moving particle has no physical significance and there are a group of waves associated with the particle, the velocity of wave of a particle will always mean the velocity of the group of waves. This velocity is called group velocity. It will also be shown here that this group velocity is always equal to the velocity of the particle which is confined in the wave-packet of this group of waves.

1.8 Superposition of a number of waves

To explain the concept of wave packet, let us look at the superposition of a number of waves. For simplicity, let us take only two waves of slightly different velocity and different frequencies, given as follows.

Two plane simple harmonic waves of the same amplitude but of slightly different wavelengths and frequencies, travelling simultaneously in the positive x-direction in a dispersive medium can be represented by:

$$y_1 = A \sin(\omega t - kx) \quad (17)$$

$$y_2 = A \sin[\omega' t - k' x] \quad (18)$$

Here $\omega' \sim \omega$ and $k' \sim k$

The resultant displacement y at time t and at position x is given by

$$\begin{aligned} y &= y_1 + y_2 \\ &= A \sin(\omega t - kx) + A \sin[\omega' t - k' x] \end{aligned}$$

On simplification we have,

$$y = 2A \cos\left[\left(\frac{\omega' - \omega}{2}\right)t - \left(\frac{k' - k}{2}\right)x\right] \cdot \sin\left[\left(\frac{\omega' + \omega}{2}\right)t - \left(\frac{k' + k}{2}\right)x\right] \quad (19)$$

The above Eq. (19) represents a wave equation whose angular frequency is $\frac{\omega' + \omega}{2}$, propagation constant is $\frac{k' + k}{2}$, wavelength $\lambda = \frac{2\pi}{k' + k}$ and the amplitude is $2A \cos\left[\left(\frac{\omega' - \omega}{2}\right)t - \left(\frac{k' - k}{2}\right)x\right]$.

So, the velocity of the phase which is known as wave velocity will be;

$$v_w = \frac{\frac{\omega' + \omega}{2}}{\frac{k' + k}{2}} = \frac{\omega' + \omega}{k' + k}, \quad (\text{As the wave velocity } = \frac{\omega}{k}) \quad (20)$$

Here, it should be noted from Eq. (19) that the amplitude of the resultant of two waves having slightly different frequencies and velocities, is not constant but varies as sinusoidal in nature, given as;

$$R = 2A \cos\left[\left(\frac{\omega' - \omega}{2}\right)t - \left(\frac{k' - k}{2}\right)x\right] \quad (21)$$

The Eq. (21) gives the variable amplitude which again represents an equation of a progressive wave in which $2A$ is the amplitude, $\frac{\omega' - \omega}{2}$ is angular frequency, $\frac{k' - k}{2}$ is the propagation constant and whose velocity can be given as:

$$v_g = \frac{\frac{\omega' - \omega}{2}}{\frac{k' - k}{2}} = \frac{\omega' - \omega}{k' - k}. \quad (22)$$

From the above treatment, we can say that Eq. (19) represents a beat kind of wave in which the amplitude of the wave is also propagating as a sinusoidal wave with a velocity as given by Eq. (22), different from the phase velocity given by Eq. (20). As it has already been mentioned that the particle is intact with this variable amplitude and maximum amplitude indicates the higher probability of the particle's presence. So, the velocity of this amplitude wave given by the relation (22) will be same as that

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of the particle. Later, it will be proved mathematically. In the similar way, we can find the superposition of the number of waves which are associated with the de Broglie particle. There we can justify that the amplitude of constructive interference region is moving with the velocity given by Eq. (22) and as according to Schrödinger, the particle is located in the region of the constructive interference, so the particle is also moving with the velocity given by (22), called as the group velocity of the wave-packet. So, for a wave-packet, associated with a de Broglie particle, the group velocity or the particle velocity can be written as;

$$v_g = \lim_{k' \rightarrow k} \frac{\omega' - \omega}{k' - k} = \frac{\delta\omega}{\delta k} \quad (23)$$

And the phase velocity will be given as;

$$v_w = \lim_{k' \rightarrow k} \frac{\omega' + \omega}{k' + k} = \frac{\omega}{k} \quad (24)$$

From (23) and (24) it is clear that group velocity and the phase velocity of the matter wave is entirely different.

1.9 Relation between the Group Velocity (v_g) and the Particle Velocity (v_p)

We have the well-known energy relation;

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

where E is the total energy, V is the potential energy and $\frac{1}{2}mv_p^2$ is the kinetic energy of the particle. So,

$$v_p = \sqrt{\frac{2(E-V)}{m}}$$

And the de' Broglie wavelength of the moving particle is given as;

$$\lambda = \frac{h}{mv_p} = \frac{h}{m\sqrt{\frac{2(E-V)}{m}}}$$

Now, as the group velocity is given as;

$$\begin{aligned} v_g &= \frac{d\omega}{dk} = \frac{d(2\pi v)}{d(\frac{2\pi}{\lambda})} = \frac{dv}{d(\frac{1}{\lambda})} \\ \frac{1}{v_g} &= \frac{d(\frac{1}{\lambda})}{dv} = \frac{d}{dv}\left\{\frac{m}{h}\sqrt{\frac{2(E-V)}{m}}\right\} \\ &= \frac{1}{h} \frac{d}{dv}(\sqrt{2m(hv - V)}) \\ &= \frac{1}{h} \cdot \frac{1}{2} \{2m(hv - V)\}^{-\frac{1}{2}} (2mh) \\ &= \frac{m}{\sqrt{2m(E-V)}} = \frac{1}{v_p} \end{aligned}$$

$$\text{Or } \frac{1}{v_g} = \frac{1}{v_p} \quad \text{Or,} \quad v_g = v_p$$

Or group velocity of the wave-packet is equal to the particle velocity.

1.10 Relation between the Group Velocity (v_g) and the Phase Velocity (v_w)

We have the propagation constant

$$k = \frac{2\pi}{\lambda} \quad \text{Or} \quad \lambda = \frac{2\pi}{k} \quad (25)$$

$$\text{Phase velocity } v_w = \frac{\omega}{k} \quad \text{Or} \quad \omega = v_w k \quad (26)$$

And the group velocity $v_g = \frac{d\omega}{dk}$

$$\begin{aligned} &= \frac{d}{dk}(v_w k) = v_w + k \frac{dv_w}{dk} \\ &= v_w + k \frac{dv_w}{d\lambda} \cdot \frac{d\lambda}{dk} \end{aligned} \quad (27)$$

But $\frac{d\lambda}{dk} = \frac{d}{dk}\left(\frac{2\pi}{k}\right) = -\frac{2\pi}{k^2}$

Hence $v_g = v_w + k \frac{dv_w}{d\lambda} \left(-\frac{2\pi}{k^2}\right)$

$$\begin{aligned} &= v_w - \frac{2\pi}{k} \frac{dv_w}{d\lambda} \\ &v_g = v_w - \lambda \frac{dv_w}{d\lambda} \end{aligned} \quad (28)$$

This Eq. (28) shows that the group velocity v_g is less than wave velocity (phase velocity) v_w , when the medium is dispersive. When the medium is non-dispersive, $\frac{dv_w}{d\lambda} = 0$, then $v_g = v_w$. Here, it should be noted that the relation (28) is a general relation between the group velocity of a group of waves and the phase velocity of a single wave. The relation gives that for a non-dispersive medium, group velocity is equal to the phase velocity. But here it should be noted that no medium, even the free space also is a non-dispersive medium for matter waves. So, group velocity which is equal to the particle velocity, will never be equal to the wave velocity or phase velocity. This can also be shown as follows.

1.11 Relation between the Phase Velocity and the Wavelength of de Broglie Wave

The phase velocity of the de Broglie wave associated with a particle in motion is given by

$$v_w = \frac{E}{p}$$

Substituting the expression for the total relativistic energy E , we get

$$\begin{aligned} v_w &= \frac{\sqrt{p^2 c^2 + m_0^2 c^4}}{p} \\ &= \frac{pc}{p} \sqrt{1 + \frac{m_0^2 c^2}{p^2}} \\ &= c \sqrt{1 + \frac{m_0^2 c^2}{p^2}} \end{aligned}$$

Now, substituting $p = h/\lambda$ in this equation we get;

$$v_w = c \sqrt{1 + \left(\frac{m_0^2 c^2}{h^2}\right) \lambda^2} \quad (29)$$

This equation shows that for a particle in motion, the phase velocity of the associated wave is always greater than c , and even in free space it is a function of the wavelength. In other words, we can say no medium is non-dispersive for the matter waves. So, velocity of matter waves is always less than the velocity of light.

Now we have understood that according to de Broglie, a moving particle is equivalent to a group of waves called a wave-packet, whose velocity is equal to the group velocity of the wave-packet. And according to Schrodinger, the position of the particle within the wave-packet is uncertain and the probability of finding the particle is higher at the position where the amplitude of the constructive superposition is higher in the wave-packet. It means at the quantum level where a particle can be 34the Heisenberg's uncertainty principle should be applied to find the uncertainty in the position as well as in the momentum of the particle to estimate the other physical parameters of a particle.

1.12 Heisenberg's Uncertainty Principle

As discussed in the previous section a wave packet is of finite width. So, specifying the position of an electron is uncertain within the wave-packet. Also at the same time, the spectral distribution of the amplitude of a wave-packet covers a range of wavelengths which by the de Broglie relationship means that the momentum of an electron will also be uncertain. Thus, we can say that the position and the momentum of an electron in general cannot be determined exactly and simultaneously. The principle states that for a particle of atomic magnitude in motion it is impossible to determine both the position and the momentum simultaneously with perfect accuracy. If the momentum of electron is accurately known then by the de' Broglie relation, the wavelength of the associated wave has a unique value, i.e. the associated wave is mono-chromatic. In such a case, the wave-packet has infinite length and hence the position of the electron may be anywhere between minus infinity and plus infinity.

Quantitatively the principle is represented by Heisenberg's uncertainty relation explained first by Werner Heisenberg, in 1927. This term has been translated as uncertainty, indeterminacy or indefiniteness which is as follows:

The product of the uncertainty Δx (or possible error) in the x-coordinate of a particle in motion at some instant, and the uncertainty Δp_x in the x-component of the momentum at the same instant is of the order of or greater than \hbar .

$$\Delta x \cdot \Delta p_x \gtrsim \hbar$$

The symbol \geq stands for "is of the order of, or greater than." In three dimensions, the uncertainty relations are

$$\Delta x \cdot \Delta p_x \gtrsim \hbar \quad (30)$$

$$\Delta y \cdot \Delta p_y \gtrsim \hbar \quad (31)$$

$$\Delta z \cdot \Delta p_z \gtrsim \hbar \quad (31)$$

The uncertainty principle can also be expressed in terms of the energy E of the particle and the time t at which it is measured as

$$\Delta E \cdot \Delta t \gtrsim \hbar \quad (32)$$

Where ΔE and Δt represents uncertainty in the energy and the uncertainty in the time respectively.

1.13 Heisenberg's Uncertainty Principle by Thought-Experiments

Any imaginary experiment not violating the fundamental laws of nature but cannot be performed practically is a thought experiment.

The Heisenberg's Uncertainty Principle can be explained by considering the following two thought experiments.

1.13.1 Diffraction of Electrons through a slit

Let us consider a parallel beam of electrons which is moving from left to right in a horizontal direction. For a particular electron, we can locate its vertical position y above a fixed point. We block the beam by a vertical screen having a slit of width Δy comparable to the calculated de Broglie wavelength of an electron as shown in Fig. 1.6. Then a narrow beam of electron together with the particular electron passes through the slit.

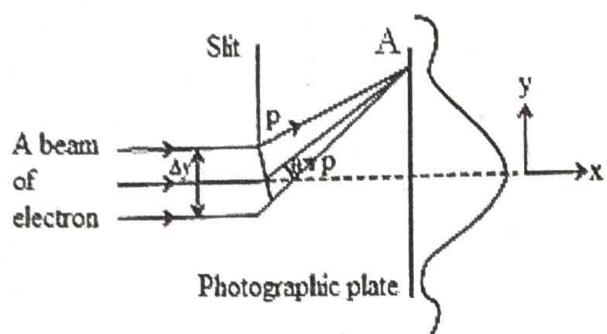


Fig. 1.6.

It can be seen that the beam that passes through the slit undergoes diffraction as a moving electron, is always associated with a wave. A Fraunhofer diffraction pattern consisting of central wide band with maximum intensity followed by dark and bright bands of decreasing intensity on both the sides is observed on the photographic plate P placed perpendicular to the direction of the incident beam. For an electron in the incident beam, if p be the momentum of an electron, then the wavelength of the associated wave is given by

$$\lambda = \frac{h}{p} \quad (33)$$

If the first minima is formed at A such that θ be the angle of diffraction of the electrons in the beam, then

$$\sin \theta = \frac{\lambda}{\Delta y} \quad (34)$$

The diffraction pattern observed concludes that:

1. While passing across the slit each electron gets deflected at the slit but the place in the slit at which the passage of an electron takes place remains quite indefinite by the amount Δy .

Thus, the uncertainty in the y coordinates of an electron which has passed through the slit = Δy .

This uncertainty for an electron, which is deflected through θ in the upward or downward direction keeping in view of Eq. (34) can be given as

$$\Delta y = \frac{\lambda}{\sin \theta} \quad (35)$$

2. The original momentum for an electron p decreases in the horizontal direction when an electron is deflected at the slit, thereby acquiring momentum Δp_y in the y -direction (the resultant momentum p remaining constant).

The original momentum of an electron however was accurately known to be zero in the y -direction. Δp_y is thus the uncertainty along the y component of the momentum.

This uncertainty for the electron which is deflected through θ in the upward or downward direction, is given by (Fig. 1.6)

$$\Delta p_y = p \sin \theta$$

$$\text{or } \Delta p_y = \frac{h}{\lambda} \sin \theta \quad (36)$$

Hence, the product of the uncertainties in the simultaneous determination of the y coordinate and y -component of the momentum of the electron at the instant when it passes through the slit is given by

$$\Delta y \cdot \Delta p_y = \frac{\lambda}{\sin \theta} \cdot \frac{h}{\lambda} \sin \theta = h \quad (37)$$

The probability of an electron reaching the centre of the pattern is greatest. Therefore, Eq. (37) gives the maximum uncertainty Δp_y for a given value of Δy . Hence, Eq. (37) is consistent with the uncertainty relation i.e.

$$\Delta y \cdot \Delta p_y \gtrsim \hbar$$

By decreasing Δy , we decrease the uncertainty in the determination of the y -coordinate but from Eq. (34) this leads to an increase in the angle θ producing a wider diffraction pattern. A wider diffraction pattern implies larger value of the uncertainty Δp_y .

1.13.2 Gamma Ray Microscope- Thought Experiment

Usually called γ -ray microscope experiment, this thought experiment was first proposed by Heisenberg. We know that, the atomic radius of an atom is of the order of 10^{-11} m. If suppose we want to locate the position i.e. the x -coordinate of an electron of an atom by means of a microscope with an uncertainty of about 10% of the radius of the atom we must employ radiation of wavelength of the order of 10^{-12} m i.e. 0.01 \AA . This means that the electron can be illuminated with γ -rays of wavelength of the order of 0.01 \AA .

Consider an electron at O (Fig. 1.7) is at rest and we want to locate its position for which we illuminate on it a narrow beam of monochromatic γ -rays proceeding in the x -direction.

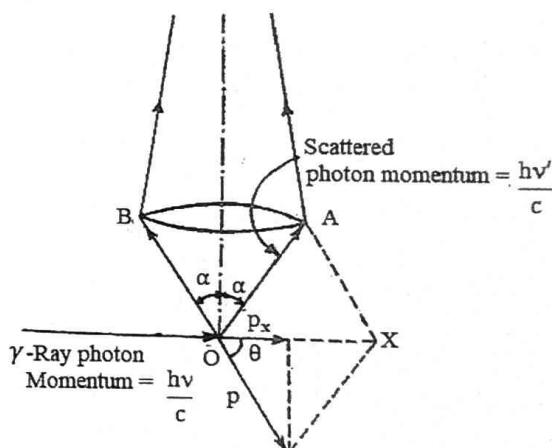


Fig. 1.7

If v be the frequency and λ the wavelength of the γ -rays. Then the momentum of an incident γ -ray photon in the x -direction is:

$$\frac{hv}{c} = \frac{h}{\lambda}$$

The electron can now be visible only when a photon gets scattered by the electron into the microscope. This causes change in the frequency and wavelength of the scattered photon resulting in Compton recoil of an electron due to gain in its momentum.

When an electron is observed in the microscope, let 2α be the angle subtended at the electron by the diameter AB of the instrument's aperture. The scattered photon may enter the microscope along the surface of the cone whose semi-vertical angle is α , or along the surface of the cone. Suppose, the photon enters the microscope along OA. Let v' be the frequency and λ' the wavelength of the scattered photon, the momentum of the scattered photon along OA is

$$\frac{hv'}{c} = \frac{h}{\lambda'}$$

The image of the electron formed by the microscope will be a diffraction pattern which consists of a central bright disc flanked on both sides by alternate dark and bright rings. The position of the electron can be anywhere within the central bright disc, the diameter of this disc thus gives the uncertainty in the position of the electron. If Δx be the diameter of the central disc and so will be the uncertainty in the position.

According to Rayleigh's criterion of resolution, the resolving power of an optical instrument is the distance between the peak intensity and the first minimum of the diffraction pattern, and its expression is

$$\begin{aligned} \text{R. P.} &= \frac{\lambda'}{2 \sin \alpha} \\ \text{R. P.} &= \frac{\Delta x}{2} \\ \therefore \quad \frac{\Delta x}{2} &= \frac{\lambda'}{2 \sin \alpha} \\ \text{or} \quad \Delta x &= \frac{\lambda'}{\sin \alpha} \end{aligned} \quad (38)$$

This is the expression for the uncertainty in the position.

Let p be the gain of momentum by the electron in the direction of recoil θ .

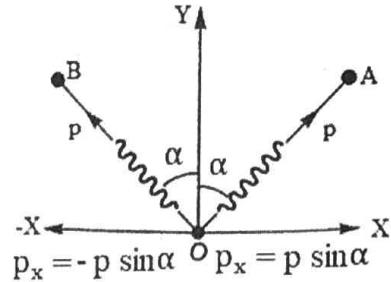
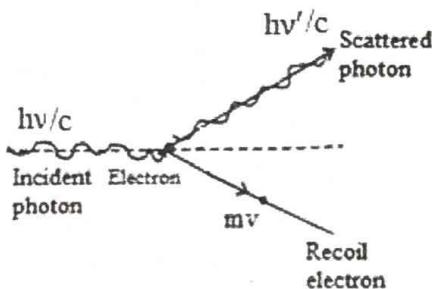


Fig. 1.8.

Resolving the momenta along OX (Fig. 1.7), we get;

$$\begin{aligned} \frac{h}{c} &= \frac{h}{c} \cos(90^\circ - \alpha) + p \cos \theta \\ \text{or} \quad \frac{h}{\lambda} &= \frac{h}{\lambda'} \sin \alpha + p \cos \theta \\ \text{Or} \quad p \cos \theta &= \frac{h}{\lambda} - \frac{h}{\lambda'} \sin \alpha \end{aligned} \quad (39)$$

In this equation, $p \cos \theta$ is the x-component p_x of the momentum p .

Since, the term h/λ on the right-hand side of this equation is accurately known and since the scattered photon can enter the microscope along any other direction making angle less than α with the axis of the microscope, the second term on the right-hand side of Eq. (38) represents maximum uncertainty in p_x . Thus,

$$\Delta p_x = \frac{h}{\lambda'} \sin \alpha \quad (40)$$

Multiplying Eq. (38) by Eq. (40), we get,

$$\Delta x \cdot \Delta p_x = h$$

Since in this equation the value of Δp_x is the maximum, equation is consistent with the uncertainty relation

$$\Delta x \cdot \Delta p_x \gtrsim \hbar \quad (41)$$

1.14 Principle of Complementarity

In 1928, Bohr introduced the principle of complementarity, according to which wave and particle properties of electromagnetic radiation and matter are merely complementary ways of regarding the same phenomenon. Both the properties are important for providing a complete explanation of the results of an experiment on an atomic phenomenon. But because of the principle of uncertainty, it is impossible to design an experiment which reveals the details of either the wave or the particle property. If we try to improve the accuracy of measurement so that both the properties should be revealed simultaneously, there is an unavoidable interaction between the measuring apparatus and the quantity to be measured.

For example, the complementarity principle for particle and wave characteristics can be very well understood with the two slit diffraction experiment of electron. If we try to define the exact trajectory (position) on the screen, the interference pattern disappears.

1.15 Applications of the Uncertainty Principle

1.15.1 Non-existence of Free Electrons in the Nucleus

We know that:

- (i) Emission of an electron from radio-active nuclei is at about 4 MeV and is the maximum possible kinetic energy of an electron.
- (ii) The rest mass of the electron, $m_0 = 9.11 \times 10^{-31} \text{ kg}$, and
- (iii) The diameter of the nucleus is $\approx 2 \times 10^{-14} \text{ m}$.

This means that if an electron exists within the diameter of the nucleus, the maximum uncertainty Δx in the position of the electron is the same as the diameter of the nucleus,

$$\text{i.e. } \Delta x = 2 \times 10^{-14} \text{ m}$$

(42)

According to Heisenberg's uncertainty relation, the product of the uncertainty Δx in the position of the electron and the uncertainty Δp_x in the x-component of its momentum is given by

$$\Delta x \cdot \Delta p_x \gtrsim \hbar$$

\therefore The uncertainty in the momentum p_x is

$$\Delta p_x \gtrsim \frac{\hbar}{\Delta x}$$

So, the minimum uncertainty in the momentum is given by

$$\begin{aligned} \Delta p_x &= \frac{\hbar}{\Delta x} \\ &= \frac{6.63 \times 10^{-34}}{2\pi \times 2 \times 10^{-14}} = \frac{6.63 \times 10^{-20}}{4\pi} \\ &= 5.278 \times 10^{-21} \text{ kg. m/sec.} \end{aligned} \quad (43)$$

It means that if an electron exists in the nucleus, its minimum momentum must be

$$p_{\min} = 5.278 \times 10^{-21} \text{ kg. m/sec.}$$

Now the total relativistic energy E of a particle is given by

$$E^2 = p^2 c^2 + m_0^2 c^4$$

For the electron of the minimum momentum, the minimum energy is given by

$$\begin{aligned} E_{\min}^2 &= p_{\min}^2 c^2 + m_0^2 c^4 \\ &= (5.278 \times 10^{-21} \times 3 \times 10^8)^2 + (9.11 \times 10^{-31})^2 (3 \times 10^8)^4 \\ &= 5.28^2 \times 9 \times 10^{-26} + 9.11^2 \times 81 \times 10^{-30} \\ &= 2.5 \times 10^{-24} + 6.72 \times 10^{-27} \text{ J}^2 \end{aligned}$$

The second term is much smaller than the first. Therefore, it can be neglected.

Thus,

$$\begin{aligned} E_{\min} &= \sqrt{2.5 \times 10^{-24}} \\ &= 1.58 \times 10^{-12} \text{ J} \\ &= \frac{1.58 \times 10^{-12}}{1.6 \times 10^{-19}} \text{ eV} \\ &= 0.9875 \times 10^7 \\ &= 9.875 \text{ MeV.} \end{aligned}$$

Thus, if a free electron exists inside the nucleus, it must have a minimum energy of about 9.0 MeV. But the maximum kinetic energy which a β^- particle emitted from radioactive nuclei can have is 4 MeV. Therefore, free electrons cannot be present within nuclei.

1.15.2 Energy of a Particle in a One-Dimensional Box

We can find out the kinetic energy of a particle trapped in one dimensional box of length l . The maximum uncertainty in the position of the particle can be given as;

$$(\Delta x)_{\max} = l$$

According to the Heisenberg's uncertainty principle, we have;

$$\Delta x \cdot \Delta p \approx \hbar \Rightarrow \Delta p \approx \frac{\hbar}{\Delta x}$$

Now as $(\Delta x)_{\max} = l$, so the minimum momentum of the particle should be;

$$\Delta p = \frac{\hbar}{l},$$

So the kinetic energy of a particle in a box will be

$$T = \frac{p^2}{2m} = \frac{\hbar^2}{2ml^2},$$

Or energy of the particle in box will be

$$E = \frac{\hbar^2}{8\pi^2 ml^2} \quad (44)$$

The Eq. (44) can also be derived with the help Schrodinger equation for a particle in a box.

1.15.3 Finite width of an Energy Band

Theoretically, it is proved that each energy level can be treated as a spectral line without any band width considering each energy level having single value of energy. But in practicality each energy band has few numbers of energy levels in its band thereby giving a finite width to a spectral line. This can be proved very easily using Heisenberg's Uncertainty principle. According to it, we have;

$$\Delta E \cdot \Delta t \gtrsim \hbar,$$

We know that the mean life time of an electron in the excited state is of the order of $\approx 10^{-8}$ sec, therefore the minimum uncertainty in the energy in any energy level should be;

$$\Delta E \approx \frac{\hbar}{\Delta t},$$

$$\text{Or} \quad \Delta E \approx \frac{6.623 \times 10^{-34}}{10^{-8}}$$

$$\approx 6.623 \times 10^{-26} \text{ Joules}$$

This is a finite value thus defining a finite band width of the excited energy levels indicating an impossibility to produce purely monochromatic radiation. In other words, each electromagnetic radiation produced has its own finite band rather than being fully monochromatic.

*****Solved Examples*******Based on de Broglie**

Ex.1. A ball of mass 10g has velocity 1m/s. Calculate the wavelength associated with it. Why does their wave nature not apparent in our daily observations. Given $h = 6 \cdot 62 \times 10^{-34}$ joule-sec.

Sol. The de-Broglie wavelength λ is given by

$$\lambda = \frac{h}{mv} = \frac{6 \cdot 62 \times 10^{-34} \text{ Js}}{(10 \times 10^{-3}) \text{ kg} \cdot (1 \text{ m/s})} = 6 \cdot 62 \times 10^{-32} \text{ m.}$$

The wavelength is much smaller than the dimensions of the ball; therefore, in such cases wave-like properties of matter cannot be observed in our daily observations.

Ex.2. (a) Find the de-Broglie wavelength in angstroms for an electron of energy V electron volts.

(b) Calculate the wavelength associated with an electron subjected to a potential difference of 1.25 kV.

Sol. (a) The de-Broglie wavelength is given by

$$\lambda = \frac{h}{mv} = \frac{h}{\sqrt{2mE}} \quad [\text{Since } E = \frac{1}{2}mv^2, \text{ so that } mv = \sqrt{2mE}]$$

Given

$$E = V \text{ electron-volt} = 1 \cdot 6 \times 10^{-19} \text{ V joule}$$

$$\text{mass of the electron } m = 9 \cdot 1 \times 10^{-31} \text{ kg}$$

$$\text{and Planck's constant } h = 6 \cdot 62 \times 10^{-34} \text{ joule-sec.}$$

$$\begin{aligned} \lambda &= \frac{6 \cdot 62 \times 10^{-34}}{\sqrt{2 \times 9 \cdot 1 \times 10^{-31} \times 1 \cdot 6 \times 10^{-19} V}} \text{ m} \\ &= \frac{12 \cdot 28 \times 10^{-10}}{\sqrt{V}} \text{ m} = \frac{12 \cdot 28}{\sqrt{V}} \text{ angstroms.} \end{aligned}$$

(b) The de-Broglie wavelength λ is given by

$$\lambda = \frac{12 \cdot 28}{\sqrt{V}} \text{ Å}$$

Here

$$V = 1 \cdot 25 \text{ kV} = 1 \cdot 25 \times 10^3 \text{ V}$$

$$\lambda = \frac{12 \cdot 28}{\sqrt{1 \cdot 25 \times 10^3}} \text{ Å} = 0 \cdot 34 \text{ Å.}$$

Ex.3. Calculate the de-Broglie wavelength associated with a proton moving with a velocity equal to $1/20^{\text{th}}$ of the velocity of light.

Sol. Velocity of proton

$$v = \frac{\text{velocity of light}}{20} = \frac{3 \times 10^8 \text{ m/s}}{20} = 1 \cdot 5 \times 10^7 \text{ m/s}$$

$$\text{and mass of the proton, } m = 1 \cdot 67 \times 10^{-27} \text{ kg.}$$

$$\text{Planck's constant } h = 6 \cdot 6 \times 10^{-34} \text{ joule-sec.}$$

$$\begin{aligned} \text{de Broglie wavelength, } \lambda &= \frac{h}{mv} = \frac{6 \cdot 6 \times 10^{-34}}{1 \cdot 67 \times 10^{-27} \times 1 \cdot 5 \times 10^7} \\ &= 2 \cdot 634 \times 10^{-14} \text{ m.} \end{aligned}$$

Ex.4. Find the energy of the neutron in units of electron-volt whose de-Broglie wavelength is 1 Å. Given mass of the neutron = $1 \cdot 674 \times 10^{-27}$ kg, Planck's constant, $h = 6 \cdot 60 \times 10^{-34}$ joule-sec.

Sol. The de Broglie wavelength λ associated with a neutron of mass m and energy E is given by

$$\lambda = \frac{h}{\sqrt{2mE}} \text{ or } \lambda^2 = \frac{h^2}{2mE}$$

$$E = \frac{h^2}{2m\lambda^2}.$$

Here $h = 6.60 \times 10^{-34}$ joule-sec, $m = 1.674 \times 10^{-27}$ kg, and $\lambda = 1\text{\AA} = 10^{-10}$ m.

$$\begin{aligned} E &= \frac{(6.60 \times 10^{-34})^2}{2 \times 1.674 \times 10^{-27} \times (10^{-10})^2} = \frac{6.6 \times 6.6}{2 \times 1.674} \times 10^{-21} \\ &= 13.01 \times 10^{-21} \text{ joules} = \frac{13.01 \times 10^{-21}}{1.6 \times 10^{-19}} \text{ eV} \\ &= 8.13 \times 10^{-2} \text{ eV} = 0.0813 \text{ eV}. \end{aligned}$$

Ex. 5 A proton and a deuteron have the same kinetic energy. Which of the two has longer de Broglie wavelength?

Sol. Let m be the mass of the proton. Then the mass of deuteron is $2m$. We have

$$\lambda_{\text{proton}} = \frac{h}{\sqrt{2mK}}$$

$$\text{and } \lambda_{\text{deuteron}} = \frac{h}{\sqrt{2(2m)K}}$$

$$\text{Dividing, } \frac{\lambda_{\text{proton}}}{\lambda_{\text{deuteron}}} = \sqrt{2} \text{ i.e. proton has longer wavelength}$$

Ex.6 Calculate the phase and group velocities of the de Broglie waves of an electron whose speed is $0.900c$.

Sol. Particle velocity $v_p = 0.900c$ = group velocity v_g

$$\begin{aligned} \text{Phase velocity, } v_w &= \frac{c^2}{v_p} = \frac{c^2}{0.900c} \\ &= \frac{c}{0.900c} = \frac{3 \times 10^8}{0.900} = 3.33 \times 10^8 \text{ m/s} \end{aligned}$$

Based on uncertainty principle

Ex.7 Calculate the uncertainty in the momentum of a proton confined in a nucleus of diameter 10^{-14} m. From this result, estimate the kinetic energy of the proton.

Sol. If the proton is confined within a diameter of radius r_0 , then the uncertainty in the momentum is given by

$$\Delta p \approx \frac{\hbar}{r_0} = \frac{(1.054 \times 10^{-34})^2}{10^{-14}} = 1.054 \times 10^{-20} \text{ kgm/s}$$

Taking the momentum p to be of the order Δp , the kinetic energy of the proton is

$$E = \frac{p^2}{2m} \approx \frac{\hbar^2}{2mr_0^2}$$

where m is the mass of the proton. Substituting the values,

$$\begin{aligned} E &= \frac{(1.054 \times 10^{-34})^2}{2 \times 1.67 \times 10^{-27} \times (10^{-14})^2} = 0.3326 \times 10^{-13} \text{ J} = \frac{0.3326 \times 10^{-13}}{1.6 \times 10^{-13}} \\ &= 0.21 \text{ MeV} \end{aligned}$$

Ex.8 The speed of bullet of mass 50g is measured to be 300 m/s with an accuracy of 0.01% with what accuracy can we locate the position of the bullet?

Sol. $\Delta p = \Delta(mv) = m(\Delta v)$

$$\begin{aligned} &= \frac{50}{1000} \times \frac{300 \times 0.01}{100} \\ &= 1.5 \times 10^{-3} \end{aligned}$$

Wave Particle Duality

$$\Delta x \approx \frac{\hbar}{\Delta p} = \frac{1.054 \times 10^{-34}}{1.5 \times 10^{-3}} = 7 \times 10^{-32} \text{ m}$$

Ex.9 A nucleon (neutron or proton) is confined to a nucleus of radius $5 \times 10^{-15} \text{ m}$. Calculate the minimum possible values of the momentum and the kinetic energy of the nucleon.

Sol. The maximum uncertainty in the position of the nucleon is

$$\Delta x_{\max} = 2 \times 5 \times 10^{-15} = 10^{-14} \text{ m}$$

According to the uncertainty principle, the minimum uncertainty in the momentum of the particle is

$$\begin{aligned}\Delta p_{\min} &\approx \frac{\hbar}{\Delta x_{\max}} = \frac{1.054 \times 10^{-34}}{10^{-14}} \\ &= 1.05 \times 10^{-20} \text{ kg.m/s}\end{aligned}$$

The momentum cannot be less than this value. Thus,

$$p_{\min} = \Delta p_{\min} = 1.05 \times 10^{-20} \text{ kgm/s}$$

The minimum kinetic energy is, therefore,

$$K_{\min} = \frac{p_{\min}^2}{2m} = \frac{(1.054 \times 10^{-20})^2}{2 \times 1.67 \times 10^{-27} \times 1.6 \times 10^{-19}} \text{ MeV} = 0.2 \text{ MeV}$$

Ex.10 Find the smallest uncertainty in the position of an electron moving with velocity $3 \times 10^7 \text{ m/s}$.

Given $\hbar = 6.63 \times 10^{-34} \text{ Js}$, $m_0 = 9.1 \times 10^{-31} \text{ kg}$

Sol. According to the uncertainty principle,

$$\Delta x_{\min} \approx \frac{\hbar}{\Delta p_{\max}}$$

$\Delta p_{\max} \approx p$, the momentum of the electron

$$= mv = \frac{m_0 v}{\sqrt{1 - \frac{v^2}{c^2}}}$$

$$\begin{aligned}\text{Therefore, } \Delta x_{\min} &= \frac{\hbar \sqrt{1 - \frac{v^2}{c^2}}}{m_0 v} = \frac{1.054 \times 10^{-34}}{9.1 \times 10^{-31} \times 3 \times 10^7} \left[1 - \left(\frac{3 \times 10^7}{3 \times 10^8} \right)^2 \right]^{1/2} \\ &= 3.8 \times 10^{-12} \text{ m} = 0.038 \text{ Å}\end{aligned}$$

Review Questions

Based on de Broglie

- What is de-Broglie hypothesis of matter waves? Who gave an experimental verification for this hypothesis?
- de Broglie matter waves travel with a phase velocity greater than the velocity of light. Does this violate Einstein's special theory of relativity? Justify your answer.
- State de Broglie's hypothesis. Derive the expression for the de Broglie wavelength of a particle in terms of a) its kinetic energy b) accelerating potential, both for the relativistic and non-relativistic cases.
- What do you understand by a wave packet? Discuss the representation of a material particle by a wave packet.
- Distinguish between group velocity and phase velocity.
- Describe the Davisson – Germer experiment for establishing the wave nature of electrons.
- Explain in brief the phase velocity of a quantum particle. Is it a measurable quantity?
- Discuss the main findings of the Davisson-Germer experiment.

Wave Particle Duality

9. Find the velocity of an electron if its de Broglie wavelength is 1.2 \AA . [Ans. $6.0 \times 10^6 \text{ m/s}$]
 10. A nonrelativistic electron has wavelength 2\AA . What is its energy? [Ans. 37.5 eV]
 11. Calculate the de Broglie wavelength of a neutron having kinetic energy 28.8 eV . Mass of neutron = $1.67 \times 10^{-27} \text{ Kg}$, $h = 6.62 \times 10^{-34} \text{ Js}$. [Ans. 4.2 \AA]

Based on Heisenberg Uncertainty Principle

12. Is the uncertainty relation $\Delta x \Delta p_y = 0$ correct or incorrect? Justify.
 13. Explain energy-time uncertainty relation.
 14. State Heisenberg's uncertainty principle for position and momentum. Illustrate the principle by Heisenberg's gamma ray microscope.
 15. Describe how the single-slit experiment using an electron beam illustrates the uncertainty principle.
 16. State Heisenberg's uncertainty principle and use it to prove the non-existence of an electron inside the nucleus.
 17. How does Heisenberg's uncertainty principle help us to decide whether an electron exist inside the nucleus or not?
 18. Give the uncertainty relation among energy and time. Name one phenomenon/experiment to prove this relation.
 19. An electron is confined to a box of length 10^{-8} m . Estimate the uncertainty in the measurement of its speed. Mass of electron = $9 \times 10^{-31} \text{ Kg}$. [Ans. $1.17 \times 10^4 \text{ m/s}$]
 20. A bullet of mass 0.03 Kg is moving with a speed of 500 m/s . The speed is measured with an accuracy of 0.02% using the uncertainty principle, estimate the uncertainty in the measurement of its position. [Ans. $2.2 \times 10^{-31} \text{ m}$]

Chapter 2

Quantum Mechanics

Introduction

So far, we have come across that the position, momentum, energy etc. of a moving de Broglie particle follows the Heisenberg's Uncertainty Principle. In order to study the dynamics of such particles which are actually represented by matter waves, we need to develop certain equations of these waves which can be used to find the various physical parameters of the de Broglie particles. As any particle behave as a wave at the quantum level, so the equation of matter waves developed by Schrödinger are called the Schrödinger wave equations. These are known as the fundamental equations of quantum mechanics. In order to find the various physical parameters of a matter wave, the known equations of classical mechanics may not be appropriate for quantum mechanical system, as it is. But we can start with some general wave equation for the development of appropriate equations for quantum mechanics.

As the nature of the wave of the particle, is undefined, so let us start with the general wave equation as;

$$\frac{\partial^2 u}{\partial x^2} = \frac{1}{v^2} \frac{\partial^2 u}{\partial t^2} \quad (\text{General wave equation for one dimensional case})$$

where u is the wave variable which varies with space, x and time, t and v is the velocity of the wave. The wave variable u can be replaced by ψ which is to be considered as the wave variable for matter wave, called, the wave function of the de Broglie wave. The physical significance of this wave function ψ and the necessary postulates of quantum mechanics which are must for the development of theory and formulations for quantum mechanics, will be discussed later in this chapter.
Let us first derive the Schrödinger wave equations of quantum mechanics.

2.1 Matter Wave Equation- Free Particle

Let a particle of mass m be in motion in space, with momentum p and total energy E . The position and the momentum of the particle cannot be determined simultaneously as per Heisenberg's Uncertainty Principle.

Let us consider that the wave associated with de Broglie particle is a plane, continuous harmonic wave travelling in the positive x -direction. The general wave equation for the matter wave can be considered as:

$$\frac{\partial^2 \psi}{\partial x^2} = \frac{1}{v^2} \frac{\partial^2 \psi}{\partial t^2} \quad (1)$$

Where ψ , the wave variable, known as wave function and v is the velocity of the matter wave.

For three-dimensional case we can write;

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

As this is a second order differential equation, the general solution for the one-dimensional case is written as;

$$\begin{aligned} \psi(r, t) &= \psi_0 e^{-i\omega(t-x/v)} \\ &= \psi_0 e^{-i(\omega t - \omega x/v)} \end{aligned}$$

$$\text{Or, } \psi(r, t) = \psi_0 e^{-i(\omega t - kx)} \quad (2)$$

Putting $k = \frac{p}{\hbar}$, and $\omega = \frac{E}{\hbar}$, in the Eq. (2), we have:

$$\psi(r, t) = \psi_0 e^{-i(Et/\hbar - px/\hbar)} \quad (3)$$

The Eq. (3) describes the wave equivalent equation of a free particle having total energy E and momentum p moving along the positive x direction, as the energy and momentum are such physical parameters which can be defined for wave as well as for a particle. The expression (3) is correct for a freely moving particle. This may be considered as an ideal case as in most of the cases, the quantum dynamics of any particle is possible only under a lot of restrictions. So, for practical purpose, the free particle equation should be modified under some restriction imposed on the motion of the particle, for example, motion of an electron bound to an atom, etc.

2.1.1 Time independent wave equation

In most of the situations, one of the restrictions is the independency of the potential energy of the particle. Although the motion of the particle is constrained under some forces and the potential energy vary with the position of the particle only. For this case, the Schrödinger equation can be modified by removing the time varying function.

The wave-function given by the Eq. (2) can be re-written as

$$\psi(x, t) = \psi_x \cdot \psi_t$$

where, $\psi_x = \psi_0 e^{i(kx)}$ and $\psi_t = \psi_0 e^{-i\omega t}$

If the function $\psi_t = \psi_0 e^{-i\omega t}$ does not vary with time then the wave function (2) can be treated as independent of time i.e.

$$\psi(x, t) = \psi(x) = \psi_0 e^{i(kx)}$$

The Schrödinger equation thus can be said as time independent equation. It can also be done in the following way:

Differentiating Eq. (2) with respect to t, we have

$$\begin{aligned} \frac{\partial \psi}{\partial t} &= -i\omega \psi_0 e^{-i(\omega t - kx)} \\ \frac{\partial^2 \psi}{\partial t^2} &= -\omega^2 \psi_0 e^{-i(\omega t - kx)} \end{aligned}$$

Or

$$\frac{\partial^2 \psi}{\partial t^2} = -\omega^2 \psi$$

On substitution, the Eq. (1) becomes

$$\frac{\partial^2 \psi}{\partial x^2} = -\frac{\omega^2}{v^2} \psi$$

Or

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{4\pi^2}{\lambda^2} \psi = 0, \quad (\text{as } \frac{\omega}{v} = \frac{2\pi}{\lambda})$$

Now according to de Broglie Hypothesis, $\lambda = \frac{h}{p} = \frac{h}{mv}$,

$$\text{So, } \frac{\partial^2 \psi}{\partial x^2} + \frac{4\pi^2 m^2 v^2}{h^2} \psi = 0 \quad (4)$$

The kinetic energy of a particle can be written as:

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

So, the Eq. (4) can be written as

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

For three-dimensional case, it will be written as;

$$\nabla^2 \psi + \frac{2m}{\hbar^2} (E - V) \psi = 0 \quad (5)$$

Here, it should be noted that in Eq. (4), the potential energy V does not vary with time and so the wave function ψ may be treated as time independent.

This is called Schrodinger's time independent wave equation.

2.1.2 Time Dependent Wave Equation

If the restrictions imposed on the particle are such that the potential energy becomes time dependent then, for finding various physical parameters of quantum dynamics of the particle we need time dependent Schrödinger wave equation.

Differentiating Eq. (3) with respect to t

$$\begin{aligned} \frac{\partial \psi}{\partial t} &= \psi_0 \left(\frac{i}{\hbar} \right) (-E) e^{i/\hbar(p_x x - Et)} \\ \frac{\partial \psi}{\partial t} &= -\frac{i}{\hbar} E \psi = \frac{E \psi}{i\hbar} \end{aligned} \quad (6)$$

Or

$$E \psi = i\hbar \frac{\partial \psi}{\partial t} \quad (7)$$

We have,

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

Or

$$\left(-\frac{\hbar^2}{2m} \nabla^2 + V \right) \psi = E \psi$$

Putting (7) in the above equation, we have:

$$\left(-\frac{\hbar^2}{2m} \nabla^2 + V \right) \psi = i\hbar \frac{\partial \psi}{\partial t} \quad (8)$$

Or

$$\hat{H} \psi = E \psi$$

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

The Eq. (8) is the time-dependent form of the Schrodinger wave equation for the motion of a particle. In this equation, ψ is a function of x and t and V is a function of x and t .

2.2 Physical Significance of the Wave-function ψ

The matter-wave variable ψ , called wave-function, undergoes periodic changes and is the only physical quantity that gives information about the particle within the wave-packet and further can be used to find other physical parameters like position, energy, momentum etc., of the quantum particle. Schrodinger suggested that the different values of amplitudes in the wave-packet give the probability of particle to be there in the wave-packet. Large value of amplitude corresponds to a larger probability for finding the particle. Initially it was thought that ψ should be related to the amplitude in the wave-packet so as to find the probability of finding the particle within the wave-packet. Taking the analogy of electromagnetic waves, if A is the amplitude than $|A|^2$ is the photon density. In the same manner, ψ should directly give the probability of the particle at that position within the wave-packet. As the amplitude may be negative but the probability is never be negative. It means ψ cannot signify the probability directly and ψ does have any physical significance other than the wave variable.

To remove this discrepancy, in 1926 Max-Born suggested a quantity called "probability density", which was later developed by Bohr, Dirac, Heisenberg and others and is widely accepted till date. According

to them, the quantity $|\psi|^2$ removes the difficulty of the negative sign of the amplitude and may be represented as the probability density of the particle in the state ψ . The probability of finding the particle in a volume element $d\tau$ about any point r at time t can be expressed as:

$$p(r) d\tau = |\psi(r, t)|^2 d\tau$$

The function ψ , sometimes may be called as probability amplitude of the particle. The postulate suggested by Born shows that the quantum mechanical laws and the results of their measurements can be interpreted on the basis of the probability considerations.

According to this interpretation, since the particle always exists in this universe, so probability of finding the particle somewhere in the universe would be:

$$p(r) d\tau = \int_{-\infty}^{\infty} |\psi(r, t)|^2 d\tau = 1$$

This expression is also known as the condition for normalization of any wave-function.

2.3 Properties of well-defined "Wave-function ψ "

The physical parameters of a quantum particle can be given by ψ i.e. a wave-function when it is operated by a suitable operator. Such kind of quantum particles can be quantized and bounded under some conditions. All the wave-functions are not suitable for a quantum mechanical system and so we have to consider various properties that can be satisfied for a well-defined wave-function.

- (i) ψ must be finite everywhere for all values of x, y, z and t .
- (ii) ψ must be single-valued, i.e., for each set of values of x, y and z ; ψ , must have one value only.
- (iii) ψ must be continuous in all regions except in those regions where the potential energy, $V(x, y, z) = \infty$.
- (iv) The partial derivatives $\partial\psi/\partial x, \partial\psi/\partial y, \partial\psi/\partial z$ also must be continuous everywhere.

A wave function satisfying the above conditions is called a well-defined wave-function.

2.4 Normalization of wave function

Since $|\psi\psi^*| d\tau$ or $|\psi|^2$ is the probability that the particle will be found in a volume element $d\tau$ surrounding the point at the position (x, y, z) at the time t , the total probability that the particle will be somewhere in space at the time t must be equal to 1. Thus, we have

$$\int_{-\infty}^{\infty} |\psi\psi^*| d\tau = \int_{-\infty}^{\infty} |\psi(x, y, z, t)|^2 d\tau = 1$$

where the integration is to be taken over all space.

Any wave-function satisfying the above relation is called a normalized wave-function.

2.5 Orthogonality of Wave Function

Any two normalized wave functions $\psi_m(x, y, z)$ and $\psi_n(x, y, z)$ corresponding to two different eigen values E_m and E_n of energies are orthogonal, that is the integral of the product of one of them and the complex conjugate of the other over the common domain of the function is zero.

Thus,

$$\int \psi_m \psi_n^* d\tau = \int \psi_m^* \psi_n d\tau = 0, \text{ if } m \neq n$$

Since the wave functions are normalized, it follows that

$$\int \psi_m^* \psi_m d\tau = 1, \quad \text{if } m = n$$

where $d\tau = dx dy dz$ is the volume element

2.6 Operators in Quantum Mechanics, Eigen Function, Eigen Value and Eigen Value Equation

An operator is a rule which changes a function into another function. For example, the operator $\frac{d}{dx}$ represents differentiation with respect to x . When it operates on a function then e.g. we have;

$$f(x) = x^n$$

then $\frac{df}{dx} = nx^{n-1}$

If a function $f(x)$ is such that an operator A which operates on $f(x)$ gives

$$Af(x) = af(x) \quad (9)$$

or $\frac{1}{f(x)} |Af(x)| = a$

where a is a constant, then

- (i) $f(x)$ is called eigen-function of the operator (the German word eigen means proper or characteristic).
- (ii) the constant a is called the eigen-value of the operator belonging to the eigen-function $f(x)$,
- (iii) the equation, such as Eq.(9) is called the eigen-value equation.

Thus, an eigen value equation states that an operator, acting on a function, reproduces the same function multiplied by a constant factor.

Now, we derive some operators of quantum mechanics for a free particle. The operators will also be valid for a bound particle. All operators of quantum mechanics have eigen-functions and eigen values.

2.6.1 Operator for Momentum

The wave function for a free particle moving along the positive x -direction is

$$\psi(x, t) = \psi_0 e^{\frac{i}{\hbar}(p_x x - Et)} \quad (10)$$

Differentiating this equation with respect to x , we get

$$\begin{aligned} \frac{\partial \psi}{\partial x} &= \psi_0 \left(\frac{i}{\hbar} \right) p_x e^{\frac{i}{\hbar}(p_x x - Et)} = \frac{i}{\hbar} p_x \psi \\ \text{or } \frac{\hbar}{i} \frac{\partial \psi}{\partial x} &= p_x \psi \end{aligned} \quad (11)$$

This is the eigen value equation for the x -component of the momentum. The equation shows that:

- (i) $\frac{\hbar}{i} \frac{\partial}{\partial x}$ is the operator, (ii) $\psi(x, t)$ is the eigen function of the operator, and (iii) p_x is the eigen value of the operator.

Hence, $\frac{\hbar}{i} \frac{\partial}{\partial x}$ is the momentum operator for the x -component of the momentum. The operator is denoted by \hat{p}_x . Thus

$$\hat{p}_x = \frac{\hbar}{i} \frac{\partial}{\partial x} \quad (12)$$

[The symbol '^'('hat') is used above the quantity to distinguish the operator from the physical quantity.] Similarly, for the y and z -components of the momentum, the operators are

$$\hat{p}_y = \frac{\hbar}{i} \frac{\partial}{\partial y} \quad (13)$$

$$\hat{p}_z = \frac{\hbar}{i} \frac{\partial}{\partial z} \quad (14)$$

The momentum operator is defined as the operator which, operating on the wave function, reproduces the wave-function multiplied by the momentum.

In three dimensions, the operator for the momentum \vec{p} is

$$\hat{p} = \frac{\hbar}{i} \vec{\nabla} \quad (15)$$

2.6.2 Operator for Kinetic Energy

From the momentum operator, we have

$$\frac{\hbar}{i} \frac{\partial \psi}{\partial x} = p_x \psi$$

Differentiating this equation with respect to x,

$$\frac{\hbar}{i} \frac{\partial^2 \psi}{\partial x^2} = p_x \frac{\partial \psi}{\partial x}$$

But,

$$\frac{\partial \psi}{\partial x} = \frac{i}{\hbar} p_x \psi$$

∴

$$\frac{\hbar}{i} \frac{\partial^2 \psi}{\partial x^2} = p_x \frac{i}{\hbar} p_x \psi$$

or

$$\frac{\hbar^2}{i^2} \frac{\partial^2 \psi}{\partial x^2} = p_x^2 \psi$$

or

$$-\hbar^2 \frac{\partial^2 \psi}{\partial x^2} = p_x^2 \psi$$

Dividing this equation by $2m$

$$\frac{-\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} = \frac{p_x^2}{2m} \psi \quad (16)$$

or

$$\frac{-\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} = K \psi \quad (17)$$

where, $K = \frac{p_x^2}{2m}$ is the kinetic energy of the particle.

This is the eigen value equation for the kinetic energy of the particle moving along the x-direction. The equation shows that:

(i) $\frac{-\hbar^2}{2m} \frac{\partial^2}{\partial x^2}$ is the operator, (ii) $\psi(x, t)$ is the eigen function of the operator, and (iii) $K = \frac{p_x^2}{2m}$ is the eigen value of the operator.

Hence $\frac{-\hbar^2}{2m} \frac{\partial^2}{\partial x^2}$ is the kinetic energy operator for the motion of the particle along the x-direction. The operator is denoted by \hat{K} . Thus,

$$\hat{K} = \frac{-\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \quad (18)$$

In three dimensions, the operator for K is

$$\hat{K} = \frac{-\hbar^2}{2m} \nabla^2 \quad (19)$$

2.6.3 Operator for Total Energy

The total energy of the particle moving along the x-axis is given by

$$E = \frac{p_x^2}{2m} + V(x)$$

Where $V(x)$ is the potential energy.

Substituting the value of $\frac{p_x^2}{2m}$, from the above Equation in Eqn. (16), we get,

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

or

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

or

$$\left[\frac{-\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + V \right] \psi = E\psi \quad (20)$$

This is the eigen value equation for the total energy E of the particle moving along the x -direction. The equation shows that $-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V$ is the operator, $\psi(x, t)$ is the eigen function of the operator and E is the eigen value of the operator. Hence $\frac{-\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V$ is the total energy operator for the motion of the particle along the x -direction. This operator is denoted by \hat{H}_x and is called the Hamiltonian operator for the one-dimensional motion. Thus,

$$\hat{H}_x = \frac{-\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V$$

For the three-dimensional motion, the total energy operator will be

$$\frac{-\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) + V$$

or

$$\frac{-\hbar^2}{2m} \nabla^2 + V$$

Where, $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$.

The total energy operator is denoted by \hat{H} and is called the Hamiltonian operator. Thus,

$$\hat{H} = \frac{-\hbar^2}{2m} \nabla^2 + V \quad (21)$$

Thus, the Hamiltonian operator \hat{H} is the differential operator which, operating on the wave function, reproduces the same wave function multiplied by the total energy. (For the total energy operator, we write \hat{H} and not \hat{E} because the total energy is assumed to be expressed in terms of the momentum, similar to the Hamiltonian function H , which stands for the total energy in terms of the position and momentum coordinates).

2.6.4 Importance of the Hamiltonian Operator

Let $\psi(x, y, z)$ be the wave function associated with a particle in motion. The three-dimensional time-independent Schrodinger equation is

$$\frac{-\hbar^2}{2m} \nabla^2 \psi + V\psi = E\psi$$

or

$$\left[\frac{-\hbar^2}{2m} \nabla^2 + V \right] \psi = E\psi \quad (22)$$

or

$$\hat{H}\psi = E\psi$$

In Eq. (22) we find:

(i) On the left-side, the operator is the Hamiltonian operator which operates on the wave function $\psi(x, y, z)$.

(ii) On the right-side, $E\psi$ is the product of the total energy E and the wave function ψ .

Thus, the Hamiltonian operator operating on the wave function reproduces the same function multiplied by the total energy E .

Therefore, the solutions of the time-independent Schrodinger equation are the eigen-functions of the Hamiltonian operator, and the eigen-values E , of the operator are the only possible values of the total energy that a quantum mechanical system may possess.

2.6.5 Operator for the Total Energy in terms of the differential with respect to time
 Differentiating Eq. (2) with respect to t , we get

$$\frac{\partial \psi}{\partial t} = \psi_0 \left(\frac{i}{\hbar} \right) (-E) e^{i/\hbar(p_x x - Et)}$$

Or,

$$-\frac{i}{\hbar} E \psi = \frac{1}{i\hbar} E \psi$$

or

$$i\hbar \frac{\partial \psi}{\partial t} = E \psi \quad (23)$$

This equation shows that the total energy operator is $i\hbar \frac{\partial}{\partial t}$.

This operator is denoted by \hat{E}

$$\therefore \hat{E} = i\hbar \frac{\partial}{\partial t} \quad (24)$$

The total energy operator is defined as the operator which, operating on the wave function reproduces the wave function multiplied by the total energy.

2.6.6 Operators for Angular Momentum

In classical mechanics the angular momentum \vec{L} of a particle is defined by

$$\vec{L} = \vec{r} \times \vec{p} \quad (25)$$

Where \vec{r} is the position vector of the particle relative to some arbitrary origin and \vec{p} is its linear momentum. From Eq. (25) the components L_x , L_y and L_z of \vec{L} along x , y and z axes, are respectively given by

$$\begin{aligned} L_x &= y p_z - z p_y \\ L_y &= z p_x - x p_z \\ L_z &= x p_y - y p_x \end{aligned} \quad (26)$$

Now using the expression for the linear momentum operators, the operators for L_x , L_y and L_z are given by

$$\begin{aligned} \hat{L}_x &= \frac{\hbar}{i} \left[y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right] \\ \hat{L}_y &= \frac{\hbar}{i} \left[z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right] \\ \hat{L}_z &= \frac{\hbar}{i} \left[x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right] \end{aligned} \quad (27)$$

List of Some of the Operators with Their Symbols

Dynamical variable	Symbol	Quantum Operator	Mechanical
Position	x	x	
	y	y	
	z	z	
Momentum	p_x	$\frac{\hbar}{i} \frac{\partial}{\partial x}$	
	p_y	$\frac{\hbar}{i} \frac{\partial}{\partial y}$	
	p_z	$\frac{\hbar}{i} \frac{\partial}{\partial z}$	

	\vec{p}	$\frac{\hbar}{i} \frac{\partial}{\partial z}$ $\frac{\hbar}{i} \vec{\nabla}$
Total energy	E	$i\hbar \frac{\partial}{\partial t}$
Total energy	E	$-\frac{\hbar^2}{2m} \nabla^2 + V$
Kinetic energy	K	$\frac{\hbar^2}{2m} \nabla^2$
Potential energy	$V(x, y, z)$	$V(x, y, z)$

2.7 Expectation Values

Keeping in view the uncertainty principle, solution of Schrodinger's wave equation for a particle is given by wave function $\psi(x, y, z, t)$, which contains all the information about the variables of the particle. This information is in the form of probabilities and not the definite values except for those variables for which the solution gives quantized values. It is possible to find the average or the expectation value of a dynamical quantity by knowing the quantity $\psi^*(x, t)\psi(x, t)dx$ which is the probability that the particle will be found over a small distance dx at position x , at time t . The expectation value of a dynamical quantity may be defined as the mathematical expectation for the result of a single measurement. In other words, it is the average of the results of a large number of measurements on independent identical systems, i.e., the systems represented by identical wave functions.

Let us take an example wherein we can find the expectation value $\langle x \rangle$ at time t of the position of an electron along the x -axis in an electron-diffraction experimental arrangement. If we want to study the positions of a large number of electrons say N , each of them is described by the same wave function $\psi(x, t)$. Also, if we want to find the electron position at time 't' and find the number of electrons with positions between x and $x + dx$ then the probability that an electron will be in the position between x and $x + dx$

$$= \frac{\text{number of electrons in the positions between } x \text{ and } x+dx}{N}$$

But according to the interpretation of the wave function, this probability is $\psi^*(x, t)\psi(x, t)dx$, where $\psi(x, t)$ is normalized.

∴ The number of electrons in the positions between x and $x + dx$

$$= N\psi^*(x, t)\psi(x, t)dx$$

Hence, the sum of all the measured values $x_1, x_2, x_3, \dots, x_N$ for all the N electrons is given by

$$x_1, x_2, x_3 + \dots + x_N = \int_{-\infty}^{\infty} \hat{x} N \psi^*(x, t)\psi(x, t)dx$$

$$\therefore \frac{x_1, x_2, x_3 + \dots + x_N}{N} = \int_{-\infty}^{\infty} \psi^*(x, t) \hat{x} \psi(x, t)dx$$

The left-hand side of this equation is the expectation value $\langle x \rangle$.

$$\therefore \langle x \rangle = \int_{-\infty}^{\infty} \psi^*(x, t) \hat{x} \psi(x, t)dx \quad (28)$$

where the function $\psi(x, t)$ is normalized.

In a similar way, the expectation value of any function $f(x)$ is given by

$$\langle f(x) \rangle = \frac{\int_{-\infty}^{\infty} \psi^*(x, t) \hat{f}(x) \psi(x, t) dx}{\int_{-\infty}^{\infty} \psi^*(x, t) \psi(x, t) dx}$$

As the function $\psi(x, t)$ is normalized then the expectation value can be written as

$$\langle f(x) \rangle = \int_{-\infty}^{\infty} \psi^*(x, t) \hat{f}(x) \psi(x, t) dx \quad (29)$$

If the wave-function is not normalized within some limits, then the expectation value is written as

$$\langle f(x) \rangle = \frac{\int \psi^*(x, t) \hat{f}(x) \psi(x, t) dx}{\int \psi^*(x, t) \psi(x, t) dx}$$

Where $\hat{f}(x)$ is the operator for the function $f(x)$

Thus, if the potential energy is a function of x , i.e. $V(x)$, its expectation value is given by

$$\langle V \rangle = \int_{-\infty}^{\infty} \psi^*(x, t) \hat{V}(x) \psi(x, t) dx \quad (30)$$

To obtain the expectation value of the momentum p_x , we should express p_x in terms of x but we cannot find p_x and x exactly and simultaneously. Therefore, to find $\langle p_x \rangle$, the function $f(x)$ in Eq. (30) is replaced by the operator \hat{p}_x . Thus

$$\langle p_x \rangle = \int_{-\infty}^{\infty} \psi^*(x, t) \hat{p}_x \psi(x, t) dx$$

$$\text{Since, } \hat{p}_x = \frac{\hbar}{i} \frac{\partial}{\partial x}$$

$$\therefore \langle p_x \rangle = \int_{-\infty}^{\infty} \psi^*(x, t) \frac{\hbar}{i} \frac{\partial}{\partial x} \psi(x, t) dx \quad (31)$$

In the same way, the expectation value $\langle K \rangle$ of the kinetic energy is given by

$$\begin{aligned} \langle K \rangle &= \int_{-\infty}^{\infty} \psi^*(x, t) \hat{K} \psi(x, t) dx \\ &= \int_{-\infty}^{\infty} \psi^*(x, t) \left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \right) \psi(x, t) dx \end{aligned} \quad (32)$$

This equation can be expressed in a simple form:

$$\langle K \rangle = -\frac{\hbar^2}{2m} \int_{-\infty}^{\infty} \psi^* \frac{\partial}{\partial x} \left(\frac{\partial \psi}{\partial x} \right) dx$$

Integrating by parts

$$\langle K \rangle = -\frac{\hbar^2}{2m} \left[\left\{ \psi^* \frac{\partial \psi}{\partial x} \right\}_{-\infty}^{+\infty} - \int_{-\infty}^{\infty} \frac{\partial \psi^*}{\partial x} \cdot \frac{\partial \psi}{\partial x} dx \right]$$

The first term on the right hand is zero, because according to the normalization condition

$$\int_{-\infty}^{\infty} \psi^* \psi dx = 1$$

$$\text{Hence, } \langle K \rangle = \frac{\hbar^2}{2m} \int_{-\infty}^{\infty} \frac{\partial \psi^*}{\partial x} \cdot \frac{\partial \psi}{\partial x} dx \quad (33)$$

$$= \frac{\hbar^2}{2m} \int_{-\infty}^{\infty} \left| \frac{\partial \psi}{\partial x} \right|^2 dx \quad (34)$$

2.8 Postulates of Quantum Mechanics

Quantum mechanics is based on the Schrodinger wave equation in which a complex variable quantity $\psi(x, y, z, t)$ called the wave-function is introduced to represent the wave associated with a particle in

motion. On the basis of prior discussion, we are now able to give five postulates so as to describe a single-particle system.

- (1) There is always a complex wave function $\psi(x, y, z, t)$ associated with a system consisting of a particle moving in a conservative field, where x, y, z are the space coordinates and t is the time. This function describes the behaviour of the system, in accordance with the principle of uncertainty.
- (2) With every observable dynamical quantity there is an operator. All the operators have eigenfunctions and eigen-values. The method of forming the Schrodinger wave equations is explained below.
- (i) To obtain the three-dimensional time-dependent Schrodinger wave equation, we equate the two operators for the total energy E ;

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

Now operate on the wave-function $\psi(x, y, z, t)$, we get:

$$-\frac{\hbar^2}{2m} \nabla^2 \psi + V\psi = i\hbar \frac{\partial \psi}{\partial t} \quad (35)$$

This is the required equation.

- (ii) To obtain the three-dimensional time-independent Schrodinger equation, we assume $\psi(x, y, z)$ to be the eigen-function of the total energy operator $\left[-\frac{\hbar^2}{2m} \nabla^2 + V\right]$. Therefore, we get

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V\right] \psi = E\psi \quad (36)$$

This is the required equation.

- (iii) To obtain the time-dependent part of the Schrodinger equation, we assume $f(t)$ to be the eigen-function of the total energy operator $\hbar \frac{\partial}{\partial t}$. Therefore, we get, $i\hbar \frac{\partial \psi}{\partial t} = E\psi$

This is the required equation.

- (3) The wave function $\psi(x, y, z, t)$ and its partial derivatives $\frac{\partial \psi}{\partial x}, \frac{\partial \psi}{\partial y}, \frac{\partial \psi}{\partial z}$ must be finite, continuous and single valued for all values of x, y, z and t .
- (4) The product $\psi(x, y, z, t)\psi^*(x, y, z, t)$, where ψ^* is the complex conjugate of ψ , is always a real quantity. The product is called the probability density and $\psi\psi^*dV$ is interpreted as the probability that the particle will be found in the volume element $d\tau$, at x, y, z and time t . Since the total probability that the particle will be somewhere in space must be equal to 1, we have

$$\int_{-\infty}^{\infty} \psi\psi^* d\tau = 1$$

The integral is taken over all space.

- (5) The average or expectation value of a physical observable α with which an operator $\hat{\alpha}$ is associated is defined by

$$\langle \alpha \rangle = \int_{-\infty}^{\infty} \psi^* \hat{\alpha} \psi d\tau$$
, where ψ is a normalized wave-function. The integral being taken over all space.

2.9 Applications of Schrodinger Equation

2.9.1 Free particle

A particle does not experience any external force and is thus said to be free particle. Such kind of particle has definite total energy and definite momentum. But the exact position of particle is completely unknown.

Suppose, the motion of the particle of mass m is along the x -axis. Let no force be acting on the particle such that the potential energy of the particle is zero i.e., $V(x) = 0$, so the time-independent Schrodinger wave equation for such kind of particle will be;

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} = E\psi \quad (\text{for } V(x) = 0)$$

where E is the total energy of the particle.

$$\text{or} \quad \frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2} E\psi = 0 \quad (37)$$

$$\text{or} \quad \frac{d^2\psi}{dx^2} + \frac{8\pi^2 m}{\hbar^2} E\psi = 0$$

$$\text{or} \quad \frac{d^2\psi}{dx^2} + k^2\psi = 0$$

$$\text{where, } k = \sqrt{\frac{8\pi^2 m}{\hbar^2}} E$$

$$\text{or} \quad E = \frac{k^2 \hbar^2}{8\pi^2 m} \quad (38)$$

As the particle may be anywhere in the space and does not bound within the limits so the Eq. (37) cannot be solved using the general solution of the differential equation, with boundary conditions. That's why the energy given by Eq. (38) of a free particle is not quantized as it is not bound within a system.

2.9.2 Particle in a box

When the motion of a particle is confined to a limited region such that the particle moves back and forth in the region, the particle is said to be in a bound state. If one-dimensional motion of a particle is assumed to take place with zero potential energy over a fixed distance and if the potential energy is assumed to become infinite at the extremities of the distance, it is described as a particle in a one-dimensional box. This is the simplest example of all motions in bound states. But in practice such a motion is not possible. However, the Schrodinger equation will first be applied to study the motion of a particle in a one-dimensional box because the study will show how quantum numbers, discrete values of energy and zero-point energy arise.

Particle in a one-Dimensional Box or Particle in an Infinitely Deep One-Dimensional Potential Well

We 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 at one corner of the box and the x -axis be perpendicular to the parallel opposite wall. Let a be the distance between the walls so that the motion along the x axis confined between $x = 0$ and $x = a$ as in Fig. 2.1

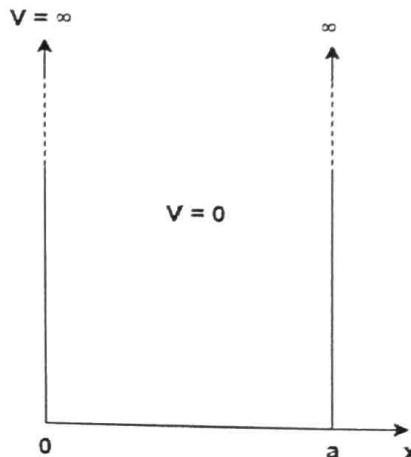


Fig. 2.1 One dimensional infinite square well

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 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, the wave-function $\psi(x) = 0$ outside the box. The potential energy variation for the particle is shown in Fig. 2.1. Because of its appearance it is called a square well potential of infinite depth.

Since the probability of particle to be within the box is 100%. So, the wave-function $\psi \rightarrow 0$ outside the box. And the potential energy of the particle is zero and time independent. So inside the box, the time-independent Schrodinger wave equation for the particle is written as;

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} = E\psi$$

where E is the total energy of the particle.

$$\text{or} \quad \frac{d^2\psi}{dx^2} + \frac{2mE}{\hbar^2} \psi = 0 \quad (39)$$

$$\text{or} \quad \frac{d^2\psi}{dx^2} + k^2\psi = 0 \quad (40)$$

$$\text{Where, } k = \sqrt{\frac{2mE}{\hbar^2}} \quad (41)$$

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

The general solution of Eq. (40) is:

$$\psi(x) = A \sin kx + B \cos kx \quad (42)$$

where, A and B are constants of integration. We have the boundary conditions;

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

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

From the first condition, we get

$$B = 0$$

Therefore, from Eq. (42) we have

$$\psi(x) = A \sin kx \quad (43)$$

Now using the second condition, we have

$$\psi(a) = A \sin ka = 0 \quad (44)$$

We cannot take $A = 0$, because there will then be no solution. Hence, Eq. (44) is satisfied only when

$$\begin{aligned} ka &= n\pi \\ \text{or} \quad k &= \frac{n\pi}{a} \end{aligned} \quad (45)$$

where, $n = 1, 2, 3, \dots$

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 in the box. That is, a particle in the box cannot have zero energy. Hence, the wave-functions for a particle in the region $0 < x < a$ are given by

$$\psi_n(x) = A \sin \frac{n\pi x}{a} \quad (46)$$

Eigen Values of Energy for a Particle in a Box

Substituting the value of k in Eq. (45), we get

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

From this equation, we get

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

$$\text{Or, } E_n = \frac{n^2 \pi^2 \hbar^2}{2ma^2}$$

This equation shows that the eigen-values of the energy are discrete (not continuous). These values are called the energy-levels of the particle.

Since

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

So, the quantised energy values inside the box are given by;

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

From Eq. (47), we come to the following conclusions:

(i) The lowest energy of the particle is obtained by putting $n = 1$ in Eq. (47) and it is

$$E_1 = \frac{\pi^2 \hbar^2}{2ma^2} \quad (48)$$

It is called the ground state energy-level of the particle. The values of E_n in terms of E_1 , are given by

$$E_n = n^2 E_1 \quad (49)$$

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

(ii) The spacing between the n^{th} energy-level and the next higher-level, increases as;

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

The wave-functions ψ_n corresponding to E_n are called Eigen-functions of the particle. The integer n corresponding to the energy E_n is called the quantum number of the energy-level E_n . Fig. 2.2 shows the energy-level diagram for the particle.

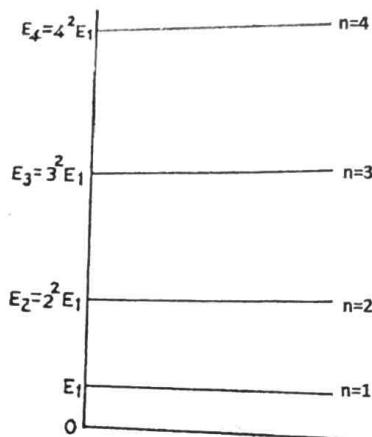


Fig. 2.2 Energy levels of a particle

Eigen Values of Energy for a Particle in a Box

The exact eigen function for a particle in box of infinite hard wall can be found using the normalisation characteristics of a well-defined wave-function.

Now we have the wave-function for the motion of the particle inside a box;

$$\psi_n(x) = A \sin \frac{n\pi x}{a} \quad (\text{in the region } 0 < x < a) \quad (50)$$

and

$$\psi_n(x) = 0, \quad (\text{in the region } x < 0; x > a)$$

As the particle must exist somewhere inside the box, the total probability that the particle is somewhere in the box must be unity. Therefore, using normalisation condition, we have

$$\int_0^a |\psi_n(x)|^2 dx = 1 \quad (51)$$

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

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

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

The second term of the integrated expression becomes zero at both limits. Therefore,

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

or

$$A = \sqrt{\frac{2}{a}} \quad (52)$$

Hence, the exact wave function for a particle in one-dimensional box will be given as;

$$\psi_n(x) = \sqrt{\frac{2}{a}} \sin \frac{n\pi x}{a} \quad (53)$$

The wave-functions for the first three values of n are shown in Fig. 2.3. It is evident that the wave-function ψ_1 has two nodes at $x = 0$ and at $x = a$. The wave function ψ_2 has three nodes at $x = 0$, $x = a/2$ and at $x = a$. The wave function ψ_3 has four nodes at $x = 0$, $x = \frac{a}{3}$, $x = \frac{2a}{3}$ and at $x = a$. Thus, the wave-function ψ_n will have $(n+1)$ nodes.

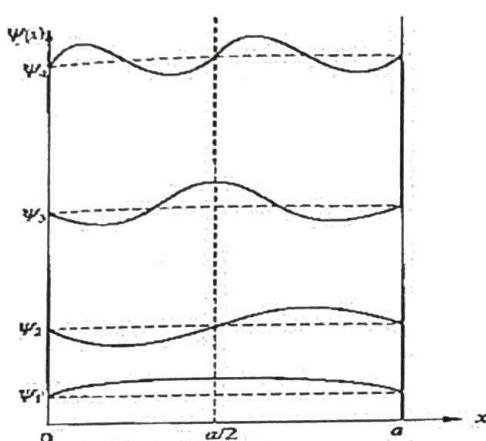


Fig. 2.3. Wave functions

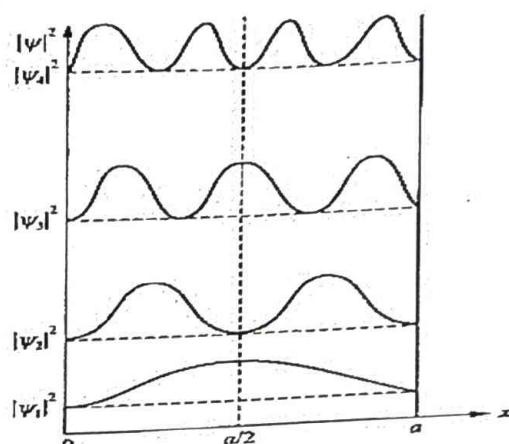


Fig. 2.4 Probability densities

2.9.3 Particle in a Finite Well

Potential energies are never infinite in the real world but potential wells with barriers of finite height certainly do exist. A physical example of this quantum mechanical problem can be thought as the α particle trying to escape out the Coulomb barrier.

Let us suppose a particle of mass m is bound in a square well (Fig. 2.5) which is V_0 high and width is ' a ' and contains a particle having energy E less than V_0 . According to classical mechanics, this particle can strike and can bounce back or reflect back from the two walls without entering regions I and III but from the quantum mechanics viewpoint it can bounce back and forth and has the probability of entering into the regions I and III even when E is less than V_0 ($E < V_0$)

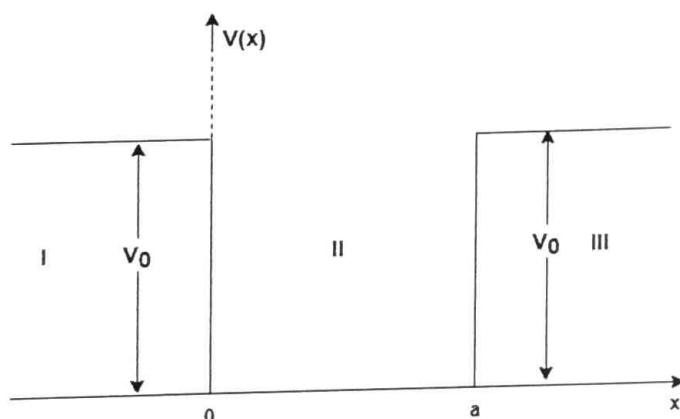


Fig. 2.5. A square well with finite barriers.

So let us say, $V = V_0$ be the potential energy in region (I): $x < 0$

$V = 0$ the potential energy in region (II): $0 \leq x \leq a$

$V = V_0$ the potential energy in region (III): $x > a$

The total energy E of the particle is less than V_0 .

The time independent Schrodinger wave equations for the three regions can be written as :

For Region(I):

$$-\frac{\hbar^2}{2m} \frac{d^2\psi_1}{dx^2} + V_0 \psi_1 = E \psi_1$$

$$\text{Or } \frac{d^2\psi_1}{dx^2} - \frac{2m}{\hbar^2} (V_0 - E)\psi_1 = 0$$

$$\text{Or } \frac{d^2\psi_1}{dx^2} - \beta^2\psi_1 = 0 \quad (54)$$

Where $\beta = \sqrt{\frac{2m(V_0-E)}{\hbar^2}}$

Region (II):

$$-\frac{\hbar^2}{2m} \frac{d^2\psi_2}{dx^2} = E\psi_2$$

$$\text{Or } \frac{d^2\psi_2}{dx^2} + \frac{2mE}{\hbar^2}\psi_2 = 0$$

$$\text{Or } \frac{d^2\psi_2}{dx^2} + k^2\psi_2 = 0 \quad (55)$$

Where $k = \sqrt{\frac{2mE}{\hbar^2}}$

Region (III):

$$\frac{d^2\psi_3}{dx^2} - \beta^2\psi_3 = 0 \quad (56)$$

The general solutions of these equations are of the form:

$$\psi_1 = Ae^{\beta x} + Be^{-\beta x} \quad (57)$$

$$\psi_2 = C \sin kx + D \cos kx \quad (58)$$

$$\psi_3 = Ge^{\beta x} + He^{-\beta x} \quad (59)$$

The solutions to Eq. (57) and (59) are real exponentials and both ψ_1 and ψ_3 must be finite everywhere. As $e^{-\beta x} \rightarrow \infty$ as $x \rightarrow -\infty$ and $e^{\beta x} \rightarrow \infty$ as $x \rightarrow \infty$, so the coefficients B and G must be zero. Therefore, the allowed wave functions in regions (I) and (III) are:

$$\psi_1 = Ae^{\beta x} \quad (60)$$

$$\psi_3 = He^{-\beta x} \quad (61)$$

Now we have to find out probable energies of the particle inside the well, as in this case the particle also has the probability to be outside the well. Although it decreases exponentially on both the sides, outside the well, as shown by the eigen functions given by Eq. (60) and (61).

From the continuity condition of the wave function and its derivative, we have:

$$(i) \quad \text{At } x = 0$$

$$\psi_1(0) = \psi_2(0)$$

Thus $A = D$

$$\text{And } \left(\frac{d\psi_1}{dx}\right)_{x=0} = \left(\frac{d\psi_2}{dx}\right)_{x=0} \quad (62)$$

$$A[\beta e^{\beta x}]_{x=0} = [Ck \cos kx - Dk \sin kx]_{x=0}$$

$$(ii) \quad \beta A = kC \quad (63)$$

$$\psi_2(a) = \psi_3(a)$$

$$C \sin ka + D \cos ka = He^{-\beta a} \quad (64)$$

$$\text{And } \left(\frac{d\psi_2}{dx} \right)_{x=a} = \left(\frac{d\psi_3}{dx} \right)_{x=a}$$

Thus,

$$\begin{aligned} [Ck \cos kx - Dk \sin kx]_{x=a} &= [-H\beta e^{-\beta x}]_{x=a} \\ kC \cos ka - kD \sin ka &= -\beta H e^{-\beta a} \end{aligned} \quad (65)$$

Dividing (65) by (64), we get

$$\frac{kC \cos ka - kD \sin ka}{C \sin ka + D \cos ka} = -\beta$$

Substituting $D = A$ and $C = \frac{\beta}{k}A$, we get

$$\frac{\beta A \cos ka - kA \sin ka}{\frac{\beta}{k}A \sin ka + A \cos ka} = -\beta$$

Or

$$\frac{k\beta \cos ka - k^2 \sin ka}{\beta \sin ka + k \cos ka} = -\beta$$

Or cross-multiplying we get

$$k\beta \cos ka - k^2 \sin ka = -\beta^2 \sin ka - k\beta \cos ka$$

Simplifying we get,

$$2k\beta \cos ka = (k^2 - \beta^2) \sin ka$$

$$\text{Or } \tan ka = \frac{2k\beta}{k^2 - \beta^2} \quad (66)$$

For convenience we take the width of the potential well as $2b$ i.e., $a = 2b$

$$\text{Thus, } \tan 2kb = \frac{2k\beta}{k^2 - \beta^2} \quad (67)$$

$$\frac{2\tan kb}{1 - \tan^2 kb} = \frac{2k\beta}{k^2 - \beta^2}$$

Simplifying the equation we get,

$$\begin{aligned} (k^2 - \beta^2) \tan kb &= k\beta(1 - \tan^2 kb) \\ k^2 \tan kb - k\beta - \beta^2 \tan kb + k\beta \tan^2 kb &= 0 \\ k(k \tan kb - \beta) + \beta \tan kb(k \tan kb - \beta) &= 0 \\ (k \tan kb - \beta)(\beta \tan kb + k) &= 0 \end{aligned}$$

This equation gives:

$$\text{Either } k \tan kb = \beta \quad (68)$$

$$\text{Or } k \cot kb = -\beta \quad (69)$$

These equations cannot be valid simultaneously because if we eliminate β between them, we get $\tan^2 kb = -1$. This makes k imaginary and β negative. One or the other of these equations will be satisfied for a certain set of values of β which may be represented as $\beta_1, \beta_2, \beta_3, \dots, \dots$. A set of energy eigen values E_n is given by

$$\beta = \sqrt{\frac{2m(V_0 - E)}{\hbar^2}}$$

$$\text{Or } E_n = V_0 - \frac{\hbar^2 \beta_n^2}{2m} \quad (70)$$

For the solution (68) these energy levels can be determined by a simple graphical method: Multiplying Eq. (68) by the half width b of the potential well we get

$$kb \tan kb = \beta b$$

Putting $kb = \xi$ and $\beta b = \eta$, we get

$$\xi \tan \xi = \eta \text{ or } \eta = \xi \tan \xi \quad (71)$$

Since,

$$\beta = \sqrt{\frac{2m(V_0-E)}{\hbar^2}} \text{ and } k = \sqrt{\frac{2mE}{\hbar^2}}$$

$$\text{Therefore, } k^2 + \beta^2 = \frac{2mV_0}{\hbar^2}$$

$$\text{Or } (kb)^2 + (\beta b)^2 = \frac{2mV_0b^2}{\hbar^2}$$

$$\text{Or } \xi^2 + \eta^2 = \frac{2mV_0b^2}{\hbar^2} = \gamma^2 \quad (72)$$

$$\text{Where } \gamma = \left(\frac{2mV_0b^2}{\hbar^2}\right)^{1/2}$$

This equation represents a circle of known radius $(\frac{2mV_0b^2}{\hbar^2})^{1/2}$ in the $\xi - \eta$ plane. The first quadrant of the circle of known radius is drawn in Fig. (2.6). Then the coordinates (ξ, η) of the point of intersection of the curve $\eta = \xi \tan \xi$ with the circle are found. Knowing the value of η , the value of β can be found and hence the energy level E can be determined using Eq. (70). In this way energy levels for different values of V_0b^2 can be determined.

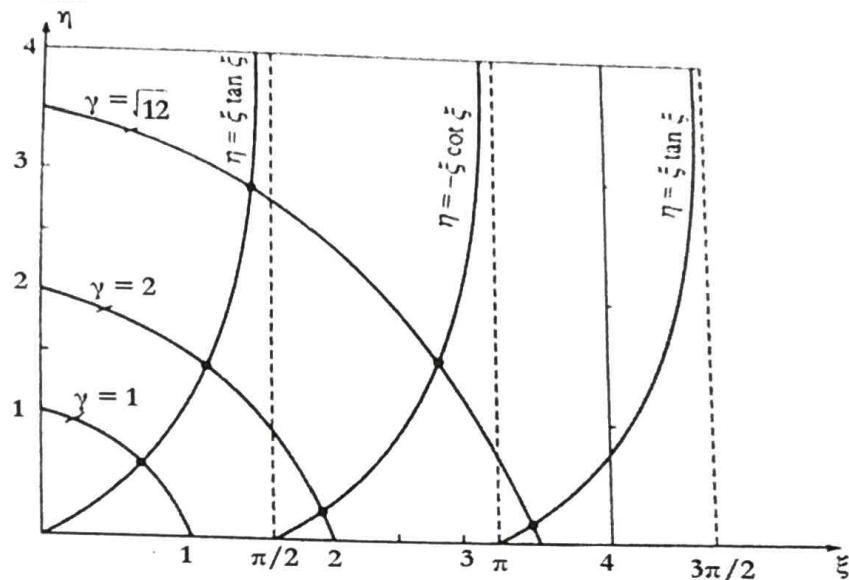


Fig. 2.6. Graphical determination of the energy levels for a square well potential.

By similar method we can determine the energy levels of the solution of Eq. (69). In this case the coordinates of the point of intersection of the curve $\eta = -\xi \cot \xi$ with the same circle in the first quadrant are found.

Special case:

- (i) When $V_0 \rightarrow \infty$, then the solution of Eq. (68)

$$k \tan kb = \beta = \infty$$

$$\text{Or } \tan kb = \infty$$

$$\begin{aligned} \text{Thus, } kb &= (2n+1) \frac{\pi}{2} \\ \text{Or } b \sqrt{\frac{2mE_n}{\hbar^2}} &= (2n+1) \frac{\pi}{2} \\ E_n &= \frac{(2n+1)^2 \pi^2 \hbar^2}{8mb^2} \dots \text{ Energy for even eigen function} \end{aligned} \quad (73)$$

(ii) When $V_0 \rightarrow \infty$, then for the solution of Eq. (68)

$$\tan kb = -\frac{k}{\beta} = -\frac{k}{\infty} = 0$$

Thus, $kb = n\pi$

$$\text{Or } b \sqrt{\frac{2mE_n}{\hbar^2}} = n\pi$$

$$\text{Or } E_n = \frac{(2n)^2 \pi^2 \hbar^2}{8mb^2} \quad (\text{energy for odd eigen function}) \quad (74)$$

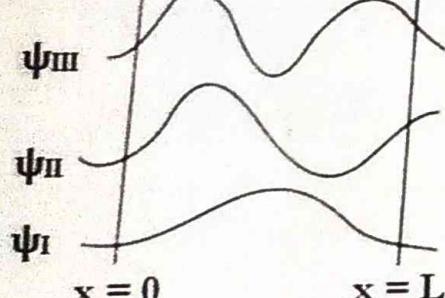
For the most generalise case i.e., for a particle trapped in a one-dimensional box of infinite potentially hard wall, we can have as When $V_0 \rightarrow \infty$, then from Eqns. (68) and (69);

$$kb = n \frac{\pi}{2}, \text{ where } n=1,2,3\dots\dots$$

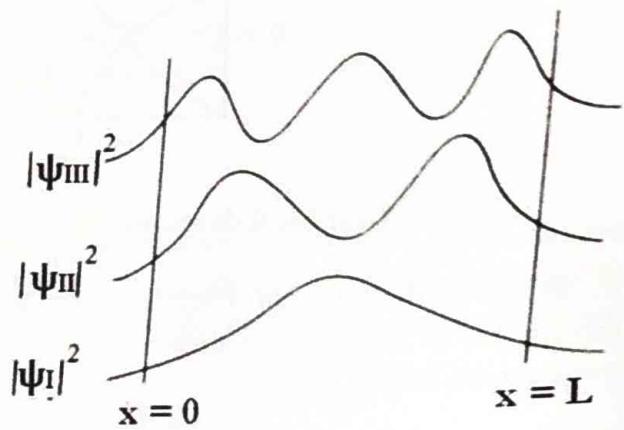
$$E_n = \frac{n^2 \pi^2 \hbar^2}{8mb^2} = \frac{n^2 \pi^2 \hbar^2}{2ma^2}$$

Which already have been discussed for the case of particle in a one-dimensional box with infinite potential wall.

The plots for wave functions and probability densities for a particle in a finite potential well will be similar as in the case of infinite well, except exponentially decaying wavefunctions and probability densities outside well on each side of the well Fig. 2.7 (a), (b). It shows that the particle has a certain probability of being found outside the wall of the well.



(a)



(b)

Fig.2.7 (a) Wave functions (b) Probability densities of a particle in a finite potential well. The particle has certain probability outside the well.

Also, the wavelengths that fit into the well are longer than for an infinite well of the same width, the corresponding particle momenta are lower as $\lambda = \frac{h}{p}$. Hence, the energy levels in the above quantum mechanical problem are lower for each n than they are for a particle in an infinite well because some energy may transmit outside the well.

2.9.4 Particle at a Potential Barrier -The Tunnel Effect

Consider a particle that strikes a potential barrier of height V_0 such that $E < V_0$ but the barrier has a finite width. The particle shows certain probability not necessarily great but not zero either of passing through the barrier and emerging on the other side. The particle lacks the energy to go over the top of the barrier but it can nevertheless tunnel through it. The higher the barrier and wider it is, lesser would be the chances that the particle can get through.

An example to this quantum mechanical problem is the alpha particles emitted by radioactive nuclei. It is seen that an alpha particle whose kinetic energy is only a few MeV is able to escape from a nucleus whose potential wall is 25MeV high. The probability of escape is so small that an alpha particle has to strike the wall around 10^{38} or more times before it emerges but sooner or later it gets out. Tunnelling also takes place in certain semiconductor diodes in which electrons pass through potential barriers even though their kinetic energies are smaller than the barrier heights.

A rectangular potential barrier of height V_0 and width a for a particle is shown in Fig. 2.8. It extends over the region (II) from $x = 0$ to $x = a$ in which the potential energy, V of the particle will be constant equal to V_0 on both the sides of the barrier in regions (I) and (III), $V = 0$; this means that when the particle is in these regions, no forces act on it.

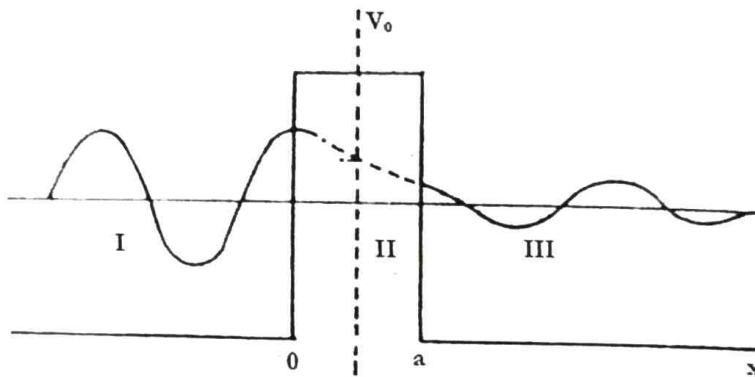


Fig. 2.8. Tunnel Effect

Suppose a beam of particles travelling parallel to the x axis from left to right is incident on the potential barrier. In the regions (I) and (II), the energy E of the particle is wholly kinetic and, in the region, (II) it is partly kinetic and partly potential. If $E < V_0$ then according to classical mechanics, the probability of any particle reaching the region (III) after crossing the region (II) is zero. However, according to quantum mechanics, a particle may tunnel through a potential barrier even having energy less than the potential barrier. This behaviour of a quantum mechanical particle is termed as tunnel effect.

Now let us find out the tunnelling probability of a quantum mechanical particle.

Let $\psi_1(x)$, $\psi_2(x)$ and $\psi_3(x)$ be the wavefunctions for the motion of particle in regions (I), (II) and (III) respectively. The time independent Schrodinger wave equations for three can be written as;

$$\begin{aligned}
 -\frac{\hbar^2}{2m} \frac{d^2\psi_1}{dx^2} &= E\psi_1 & -\infty < x < 0, & \text{Region (I)} \\
 \text{Or } \frac{d^2\psi_1}{dx^2} + \frac{2mE}{\hbar^2} \psi_1 &= 0 \\
 \text{Or } \frac{d^2\psi_1}{dx^2} + k^2 \psi_1 &= 0 \dots \text{where } k = \sqrt{\frac{2mE}{\hbar^2}}
 \end{aligned} \tag{75}$$

Case I: when $E < V_0$

$$\begin{aligned}
 \frac{d^2\psi_2}{dx^2} + \frac{2m(E-V_0)}{\hbar^2} \psi_2 &= 0 & 0 < x < a & \text{Region (II)} \\
 \frac{d^2\psi_2}{dx^2} - \frac{2m(V_0-E)}{\hbar^2} \psi_2 &= 0 & \text{for } E < V_0 \\
 \text{Or} \\
 \frac{d^2\psi_2}{dx^2} - \beta^2 \psi_2 &= 0 & & \tag{76} \\
 \text{Where } \beta &= \sqrt{\frac{2m(V_0-E)}{\hbar^2}} \\
 \frac{d^2\psi_3}{dx^2} + \frac{2mE}{\hbar^2} \psi_3 &= 0 & a < x < \infty & \text{Region (III)} \\
 \text{Or} \\
 \frac{d^2\psi_3}{dx^2} + k^2 \psi_3 &= 0 & & \tag{77}
 \end{aligned}$$

The general solutions of Eqns. (75), (76) and (77) are

$$\psi_1 = Ae^{ikx} + Be^{-ikx} \tag{78}$$

$$\psi_2 = Ce^{\beta x} + De^{-\beta x} \tag{79}$$

$$\psi_3 = Ge^{ikx} + He^{-ikx} \tag{80}$$

Since there is no reflection of the particle, in the region (III), so we must have $H = 0$. Therefore,

$$\psi_3 = Ge^{ikx}$$

The interpretation of the terms in the above solutions is as follows:

In Eq. (78), the term Ae^{ikx} is a wave of amplitude A travelling in the positive x direction and the term Be^{-ikx} is the wave of amplitude B reflected in the negative x-direction from the potential barrier, when the incident wave falls on the barrier. In Eq. (79), the term $De^{-\beta x}$ is an exponentially decreasing wave function representing a non-oscillatory disturbance which moves through the barrier in the positive x direction and the term $Ce^{\beta x}$ is the reflected disturbance within the barrier and it is an exponentially decreasing wave function. Eq. (80) represents the transmitted wave in the region (III). This wave travels in the positive x direction.

Now we have to find out the reflection and transmission through the barrier. For this the values of arbitrary constants A, B, C, D and G have to be calculated, using various boundary conditions.

- (i) At $x = 0$, from the condition of continuity of the wave function, we have $\psi_1(0) = \psi_2(0)$
Thus, from Eq. (78) and (79), we get
$$A + B = C + D \tag{81}$$

From the condition that $\frac{d\psi}{dx}$ is continuous at $x=0$, we have

$$\left(\frac{d\psi_1}{dx} \right)_{x=0} = \left(\frac{d\psi_2}{dx} \right)_{x=0}$$

Thus, $Aik - Bik = C\beta - D\beta$

$$\text{Or } A - B = \frac{\beta}{ik} (C - D) \quad (82)$$

From Eqns. (81) and (82), we get

$$2A = \left(1 + \frac{\beta}{ik}\right)C + \left(1 - \frac{\beta}{ik}\right)D$$

And

$$2B = \left(1 - \frac{\beta}{ik}\right)C + \left(1 + \frac{\beta}{ik}\right)D \quad (83)$$

(ii) At $x = a$, we have

$$\psi_2(a) = \psi_3(a)$$

So from Eqns. (77) and (78), we get

$$Ce^{\beta a} + De^{-\beta a} = Ge^{ika} \quad (84)$$

We also have .

$$\left(\frac{d\psi_2}{dx} \right)_{x=a} = \left(\frac{d\psi_3}{dx} \right)_{x=a}$$

Therefore,

$$C\beta e^{\beta a} - D\beta e^{-\beta a} = Ge^{ika}$$

Or

$$Ce^{\beta a} - De^{-\beta a} = \frac{ik}{\beta} Ge^{ika} \quad (85)$$

From Eqns. (84) and (85), we get

$$C = \frac{1}{2} \left(1 + \frac{ik}{\beta}\right) e^{-\beta a} Ge^{ika} \quad (86)$$

$$D = \frac{1}{2} \left(1 - \frac{ik}{\beta}\right) e^{\beta a} Ge^{ika} \quad (87)$$

Substituting the values of C and D in Eq. (82) we get,

$$2A = \left[\left(1 + \frac{\beta}{ik}\right) \frac{1}{2} \left(1 + \frac{ik}{\beta}\right) e^{-\beta a} + \left(1 - \frac{\beta}{ik}\right) \frac{1}{2} \left(1 - \frac{ik}{\beta}\right) e^{\beta a} \right] \times Ge^{ika}$$

Simplifying this equation, we get

$$A = \left[\left(\frac{e^{\beta a} + e^{-\beta a}}{2} \right) - \frac{1}{2} \left(\frac{\beta}{ik} + \frac{ik}{\beta} \right) \left(\frac{e^{\beta a} - e^{-\beta a}}{2} \right) \right] Ge^{ika}$$

Using the trigonometric relations:

$$\frac{e^{\beta a} + e^{-\beta a}}{2} = \cosh \beta a$$

And

$$\frac{e^{\beta a} - e^{-\beta a}}{2} = \sinh \beta a$$

We obtain

Quantum Mechanics

$$A = [\cosh \beta a + \frac{i}{2} \left(\frac{\beta}{k} - \frac{k}{\beta} \right) \sinh \beta a] Ge^{ika} \quad (88)$$

Similarly substituting the value of C and D in Eq. (83)

$$\begin{aligned} 2B &= \left[\left(1 - \frac{\beta}{ik} \right) \frac{1}{2} \left(1 + \frac{ik}{\beta} \right) e^{-\beta a} + \left(1 + \frac{\beta}{ik} \right) \frac{1}{2} \left(1 - \frac{ik}{\beta} \right) e^{\beta a} \right] Ge^{ika} \\ &= \left[-\frac{1}{2} \left(\frac{\beta}{ik} - \frac{ik}{\beta} \right) e^{-\beta a} + \frac{1}{2} \left(\frac{\beta}{ik} - \frac{ik}{\beta} \right) e^{\beta a} \right] Ge^{ika} \\ &= \left[\left(\frac{\beta}{ik} - \frac{ik}{\beta} \right) \left(\frac{e^{\beta a} - e^{-\beta a}}{2} \right) \right] Ge^{ika} \end{aligned}$$

$$\text{Or } B = -\frac{i}{2} \left(\frac{\beta}{k} + \frac{k}{\beta} \right) (\sinh \beta a) Ge^{ika} \quad (89)$$

Expression for the amplitude B in terms of A

Dividing Eqns. (89) by (88), we get

$$\frac{B}{A} = \frac{-\frac{i}{2} \left(\frac{\beta}{k} + \frac{k}{\beta} \right) \sinh \beta a}{\cosh \beta a + \frac{i}{2} \left(\frac{\beta}{k} - \frac{k}{\beta} \right) \sinh \beta a} \quad (90)$$

Reflection Coefficient

The reflection coefficient R is defined as the ratio of the probability current density S_r for the reflected beam of particles from the potential barrier to the probability current density S_i for the incident beam of particles. Thus, it is given by

$$\begin{aligned} R &= \frac{S_r}{S_i} = \frac{(Be^{-ikx})(Be^{-ikx})^* \frac{\hbar k}{m}}{(Ae^{ikx})(Ae^{ikx})^* \frac{\hbar k}{m}} \\ &= \frac{BB^*}{AA^*} = \left(\frac{B}{A} \right) \left(\frac{B}{A} \right)^* = \frac{|B|^2}{|A|^2} \end{aligned} \quad (91)$$

Where $\left(\frac{B}{A} \right)^*$ is the complex conjugate of $\left(\frac{B}{A} \right)$. From Eq. (90) the complex conjugate of $\frac{B}{A}$ is

$$\left(\frac{B}{A} \right)^* = \frac{\left(\frac{i}{2} \left(\frac{\beta}{k} + \frac{k}{\beta} \right) \sinh \beta a \right)}{\cosh \beta a - \frac{i}{2} \left(\frac{\beta}{k} - \frac{k}{\beta} \right) \sinh \beta a}$$

$$\begin{aligned} \text{Hence, } R &= \left(\frac{B}{A} \right) \left(\frac{B}{A} \right)^* = \frac{|B|^2}{|A|^2} \\ &= \frac{\frac{1}{4} \left(\frac{\beta}{k} + \frac{k}{\beta} \right)^2 \sinh^2 \beta a}{\cosh^2 \beta a + \frac{1}{4} \left(\frac{\beta}{k} - \frac{k}{\beta} \right)^2 \sinh^2 \beta a} \end{aligned}$$

Using the trigonometric relation

$$\cosh^2 \beta a = 1 + \sinh^2 \beta a$$

And simplifying the denominator, we get

$$R = \frac{\frac{1}{4} \left(\frac{\beta}{k} + \frac{k}{\beta} \right)^2 \sinh^2 \beta a}{1 + \frac{1}{4} \left(\frac{\beta}{k} + \frac{k}{\beta} \right)^2 \sinh^2 \beta a} \quad (92)$$

$$\text{Since, } k = \sqrt{\frac{2mE}{\hbar^2}} \text{ and } \beta = \sqrt{\frac{2m(V_0 - E)}{\hbar^2}}$$

$$\text{Thus, } \frac{\beta}{k} = \sqrt{\frac{V_0 - E}{E}} \quad \text{and} \quad \frac{k}{\beta} = \sqrt{\frac{E}{V_0 - E}}$$

Substituting these values in Eq. (92) we get

$$\begin{aligned} R &= \frac{\frac{1}{4} \left(\sqrt{\frac{V_0 - E}{E}} + \sqrt{\frac{E}{V_0 - E}} \right)^2 \sinh^2 \beta a}{1 + \frac{1}{4} \left(\sqrt{\frac{V_0 - E}{E}} + \sqrt{\frac{E}{V_0 - E}} \right)^2 \sinh^2 \beta a} \\ &= \frac{\frac{V_0^2}{4E(V_0 - E)} \cdot \sinh^2 \beta a}{1 + \frac{V_0^2}{4E(V_0 - E)} \cdot \sinh^2 \beta a} \end{aligned} \quad (93)$$

This is the expression for the reflection coefficient when $E < V_0$

Transmission coefficient

The transmission coefficient T is defined as the ratio of the probability current density S_t for the transmitted beam of particles through the potential barrier to the probability current density S_i for the incident beam. Thus, it is given by

$$\begin{aligned} T &= \frac{S_t}{S_i} = \frac{(Ge^{ikx})(Ge^{ikx})^* \frac{\hbar k}{m}}{(Ae^{ikx})(Ae^{ikx})^* \frac{\hbar k}{m}} \\ &= \frac{GG^*}{AA^*} = \left(\frac{G}{A}\right)\left(\frac{G}{A}\right)^* \end{aligned} \quad (94)$$

Where $\left(\frac{G}{A}\right)^*$ is the complex conjugate of $\left(\frac{G}{A}\right)$

From Eq. (89), we have

$$\frac{A}{G} = [\cosh \beta a + \frac{i}{2} \left(\frac{\beta}{k} - \frac{k}{\beta} \right) \sinh \beta a] e^{ika}$$

Thus,

$$\left(\frac{A}{G}\right)^* = [\cosh \beta a - \frac{i}{2} \left(\frac{\beta}{k} - \frac{k}{\beta} \right) \sinh \beta a] e^{-ika}$$

$$\text{Hence, } \left(\frac{A}{G}\right)\left(\frac{A}{G}\right)^* = \cosh^2 \beta a + \frac{1}{4} \left(\frac{\beta}{k} - \frac{k}{\beta} \right)^2 \sinh^2 \beta a$$

$$\text{Or } \frac{1}{T} = \left| \frac{A}{G} \right|^2 = \cosh^2 \beta a + \frac{1}{4} \left(\frac{\beta}{k} - \frac{k}{\beta} \right)^2 \sinh^2 \beta a$$

Using the trigonometric relation

$$\cosh^2 \beta a = 1 + \sinh^2 \beta a$$

And simplifying we get

$$\text{Or } \frac{1}{T} = 1 + \frac{1}{4} \left(\frac{\beta}{k} - \frac{k}{\beta} \right)^2 \sinh^2 \beta a \quad (95)$$

Substituting

$$\frac{\beta}{k} = \sqrt{\frac{V_0 - E}{E}} \quad \text{and} \quad \frac{k}{\beta} = \sqrt{\frac{E}{V_0 - E}} \quad \text{in Eq. (95), we get}$$

$$\frac{1}{T} = 1 + \frac{V_0^2}{4E(V_0 - E)} \sinh^2 \beta a \quad (96)$$

$$T = \frac{1}{1 + \frac{V_0^2}{4E(V_0 - E)} \sinh^2 \beta a} \quad (97)$$

When $\beta a \gg 1$ then $\sinh^2 \beta a \gg 1$, therefore Eq. (97) can be written as

$$T = \frac{4E(V_0 - E)}{V_0^2 \sinh^2 \beta a} \quad (98)$$

And we also have

$$\begin{aligned} \sinh \beta a &= \frac{e^{\beta a} - e^{-\beta a}}{2} = \frac{e^{-\beta a}}{2} (e^{2\beta a} - 1) \approx \frac{e^{-\beta a} e^{2\beta a}}{2} \\ &= \frac{e^{\beta a}}{2} \end{aligned}$$

So from Eq. (98) we have

$$T = \frac{4E(V_0 - E)}{V_0^2 \frac{e^{2\beta a}}{4}}$$

Or

$$T = \frac{16E(V_0 - E) e^{-2\beta a}}{V_0^2}$$

Generally, the term $\frac{16E(V_0 - E)}{V_0^2}$, always is of the order 1. So, the approximate probability for tunnelling for a quantum mechanical particle having energy $E < V_0$, can be find out with the expression given as;

$$T = e^{-2\beta a}$$

Where a is the width of the barrier and $\beta = \sqrt{\frac{2m(V_0 - E)}{\hbar^2}}$

This is the expression for the transmission coefficient in the case when $E < V_0$

Besides the explanation of the emission of α from the nucleus, the tunnel effect also provides explanations for the following phenomenon:

- a) The field emission of electrons from a cold metallic surface
- b) The electrical breakdown of insulators
- c) The reverse breakdown of semi-conductor diodes
- d) The switching action of a tunnel diode
- e) The emission of α particles from a radio-active element.

2.10 Harmonic oscillator

A harmonic motion takes place when a system of some kind vibrates about a equilibrium position. In classical mechanics, consider a particle of mass 'm' executing S.H.M along x axis about its mean position such that the displacement from the mean position be x . Then, according to the condition of to perform S.H.M, restoring force F will act on the particle to oppose its motion, i.e. proportional to the displacement and will be directed opposite to this. Therefore,

$$F \propto -x \text{ or } F = -kx \dots \dots \dots \quad (99)$$

Here, k is the constant of proportionality and is known as force constant or force per unit displacement. Now, according to the Newton second law of motion, "the acceleration produced, is defined as the force applied per unit mass of a moving object, i.e.

$$\frac{d^2x}{dt^2} = \frac{F}{m}$$

Or we can write, Force = mass x acceleration i.e.

$$F = m \frac{d^2x}{dt^2} \quad (100)$$

From (99) and (100)

$$m \frac{d^2x}{dt^2} = -kx \quad \text{or} \quad \frac{d^2x}{dt^2} = -\frac{k}{m} x$$

or

We have

$$\frac{d^2x}{dt^2} + \frac{k}{m} x = 0 \quad (101)$$

This is the classical second order differential equation of SHM.

The potential energy function $V(x)$ that corresponds to Hooke's law force can be obtained by calculating the work needed to bring a particle from $x = 0$ to $x = x$ against such a force such that

$$V(x) = - \int_0^x F(x) dx = k \int_0^x x dx = \frac{1}{2} kx^2$$

that is plotted below

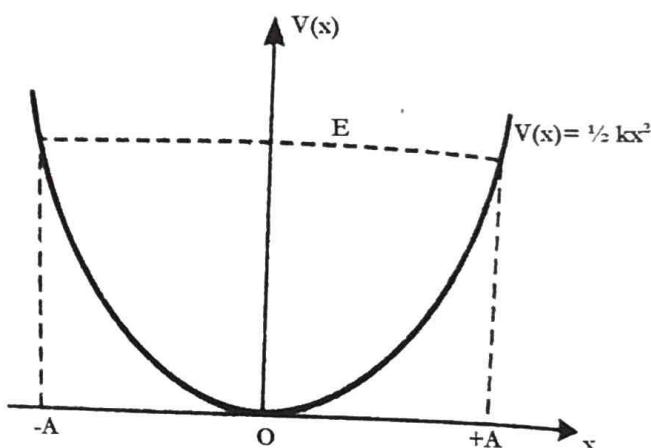


Fig. 2.9 Potential Energy of a harmonic oscillator is proportional to x^2 where x is the displacement from mean position

The curve $V(x)$ vs x is a parabola. If the energy of the oscillator is E , the particle vibrates back and forth between $x = -A$ and $x = A$ where E and A are related by $E = \frac{1}{2} kA^2$

Let us solve the problem quantum mechanically,

The time independent Schrödinger wave equation for the linear motion of a particle along the x axis is

$$\frac{-\hbar^2}{2m} \frac{d^2\psi}{dx^2} + V\psi = E\psi \quad (102)$$

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

$$\text{Or } \frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2} (E - \frac{1}{2} kx^2) \psi = 0 \quad (103)$$

Where E is the total energy of the particle, V the potential energy and ψ the wave function of the particle which is function of x alone.

Substitute $\frac{2m}{\hbar^2} E = \alpha$ and $\sqrt{\frac{mk}{\hbar^2}} = \beta$ in Eq. (103), we get

$$\frac{d^2\psi}{dx^2} + (\alpha - \beta^2 x^2) \psi = 0 \quad (104)$$

Let us introduce a dimensionless independent variable ξ such that

$$\xi = \sqrt{\beta} x$$

$$\text{Now, } \frac{d^2}{dx^2} = \beta \frac{d^2}{d\xi^2}$$

Substituting in Eq. (104) we get

$$\beta \frac{d^2\psi}{d\xi^2} + (\alpha - \beta^2 \frac{\xi^2}{\beta})\psi = 0$$

Or

$$\frac{d^2\psi}{d\xi^2} + (\frac{\alpha}{\beta} - \xi^2)\psi = 0 \quad (105)$$

The general solution of Eq. (105) is given by:

$$\psi(\xi) = CU(\xi)e^{-\frac{\xi^2}{2}} \quad (106)$$

Eq. (105) then takes the form as

$$\frac{d^2U}{d\xi^2} - 2\xi \frac{dU}{d\xi} + (\frac{\alpha}{\beta} - 1)U = 0$$

If we replace $(\frac{\alpha}{\beta} - 1)$ by $2n$ the above equation becomes the Hermite differential equation. The

function $U(\xi)$ may be replaced with Hermite polynomial H . Thus,

$$\frac{d^2H}{d\xi^2} - 2\xi \frac{dH}{d\xi} + 2nH = 0 \quad (107)$$

Thus, the solution of Eq. (105) is obtained by replacing U by Hermite polynomial H in Eq. (107). We

get,

$$\psi(\xi) = CH(\xi)e^{-\frac{\xi^2}{2}}$$

In general,

$$\psi_n(\xi) = CH_n(\xi)e^{-\frac{\xi^2}{2}}$$

The solution is acceptable only for $n = 0, 1, 2$

Eigen values of Energy

$$\text{Since } \frac{\alpha}{\beta} - 1 = 2n$$

$$\text{Thus, } \frac{\alpha}{\beta} = 2n + 1$$

$$\text{Or } \alpha = (2n + 1)\beta$$

$$\Rightarrow \frac{8\pi^2 m E}{h^2} = (2n + 1) \sqrt{\frac{4\pi^2 m k}{h^2}}$$

The restriction gives a corresponding restriction on E i.e.

$$E = (n + \frac{1}{2}) \frac{h}{2\pi} \sqrt{\frac{k}{m}}$$

But $\frac{1}{2\pi} \sqrt{\frac{k}{m}} = \nu$ is the frequency of oscillations. The energy can thus be written as:

$$E = \left(n + \frac{1}{2}\right) h\nu$$

Or

$$E = \left(n + \frac{1}{2}\right) \hbar (2\pi\nu) = \left(n + \frac{1}{2}\right) \hbar \omega \quad (108)$$

Where $n = 0, 1, 2, \dots$

Eq. (108) represents that a harmonic oscillator can take only certain discrete energies separated by intervals $\hbar\nu$, where ν is the frequency of the classical oscillator and \hbar is Planck's constant.

Conclusions drawn:

1. According to quantum mechanics, the energy levels are equally spaced and quantized as shown in Fig. 2.10
2. The energy levels are non-degenerate
3. For $n = 0$, $E_0 = \frac{1}{2} \hbar\nu$ i.e. minimum energy is not zero. This energy is called zero-point energy. A harmonic oscillator thus in equilibrium with its surroundings can approach to an energy $E = E_0$ and not $E = 0$ as temperature approaches 0.

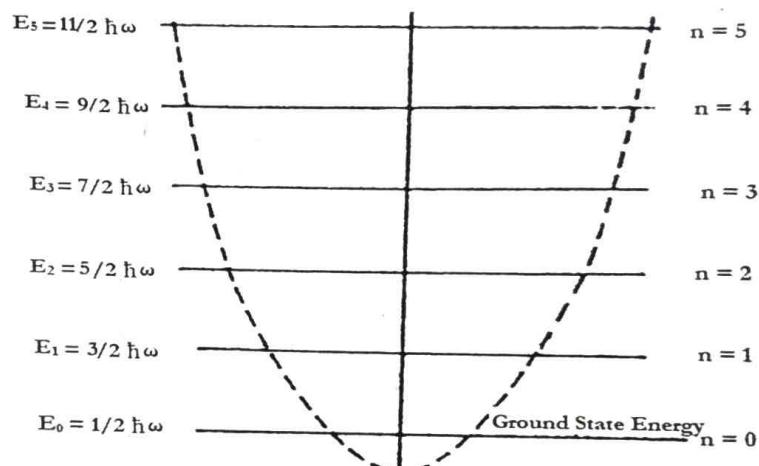


Fig. 2.10 Energy levels of a linear harmonic oscillator

Fig. 2.10 shows the probability density curve for the lowest energy state $n = 0$. The classical probability is shown below in Fig. 2.11

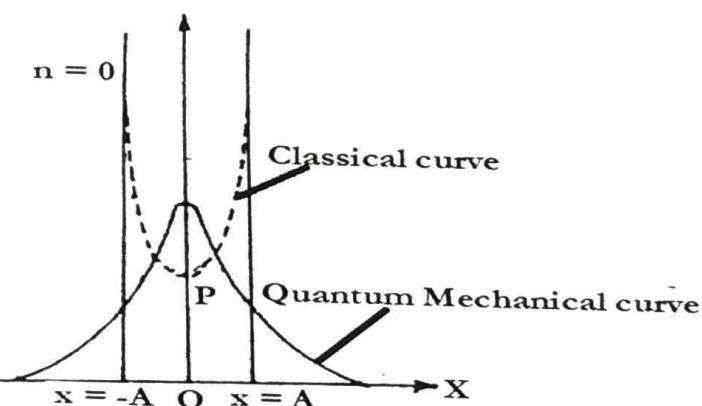


Fig. 2.11 Probability density curve for the lowest state

Classically the particle is found at the ends of the path. The particle is least likely found at the middle. Quantum mechanically, the probability density is maximum at the middle ($x = 0$) and drops off at either end. Therefore, quantum mechanically there is small probability outside the classical region. This feature is a characteristic of quantum mechanics and is closely related to Heisenberg's uncertainty relation.

As n increases, there is general agreement between classical and quantum mechanical curves as shown in Fig. 2.12 for $n = 10$

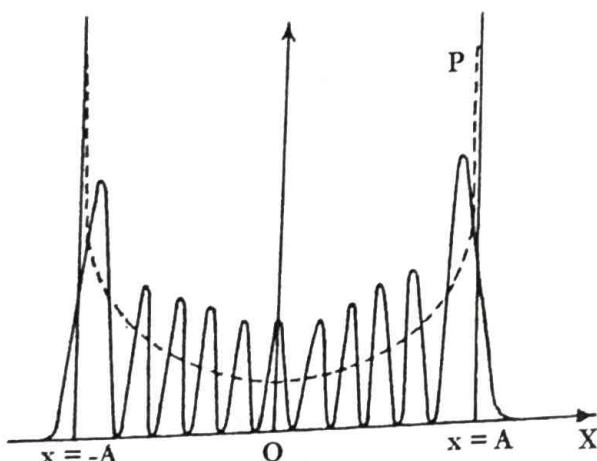


Fig. 2.12 Probability density for harmonic oscillator in state $n = 10$. The dotted curve shows the classical probability distribution

Thus, the results of quantum mechanics differ from those of classical mechanics in the following respect.

- (i) The particle executing simple harmonic motion can have discrete energies i.e., $\frac{1}{2}\hbar\omega, \frac{3}{2}\hbar\omega, \frac{5}{2}\hbar\omega$.
- (ii) The minimum energy is not zero but this is $\frac{1}{2}\hbar\omega$ known as zero-point energy.
- (iii) The quantum mechanical harmonic oscillator has some probability outside the classical region. This probability is 17%.

2.11 Electron Microscope

The magnified images of an object can be produced with the help of an instrument called microscope and can be readily used to study the objects that are too small and not visible by normal eyes. Electron microscopes have the highest magnifying powers amongst all the microscopes available that can enlarge objects up to one million times. In comparison to regular optical microscopes where the objects to be magnified is illuminated with visible light in case of electron microscopes a beam of electrons is used instead of conventional light.

In 1932 Ernst Rusk and Max Knoll designed the first electron microscope and were awarded with the Nobel Prize in 1986. The principle of electron microscope lies on two facts:

- a. As per the experimental verification by Davisson and Germer experiment, the electrons have wave nature that can be treated in the similar manner as light and is in accordance with the de Broglie hypothesis that all the particles possess a wave like character.
- b. The magnetic field affects the motion of electrons that is utilised to focus electrons, as optical lenses do to light.

Resolving power and magnification

The resolving power of a microscope depends on the wavelength of the source, the illumination of the object and also on the numerical aperture of the microscope. Smaller is the numerical aperture smaller is the resolving power, but smaller is the wavelength greater is the resolving power of the microscope. The wavelength of electrons moving with velocity 'v' is given by de Broglie's wavelength $\lambda = h/mv$ where h is the Planck's constant and m is the mass of the electron. Fast electrons have very short wavelengths in comparison to the wavelength of light and thus fast-moving electrons can be used in place of light that leads to a very high resolving power of the electron microscopes. The numerical aperture of electrons is usually smaller in comparison to the optical microscopes.

Further, the magnification of electron microscopes is very high because the focal length of the magnetic lenses can be varied by simply varying magnetic field and it can be made very small. Magnetic lenses of very short focal length lead, to very high magnifying power. The first electron microscope designed by Ruska and Knoll was capable of achieving magnifications to the order of 400 times. With continuously improved techniques, till now magnification over 1,00,000 has been achieved by electron microscopes.

Types of electron microscopes

Electron microscopes can be divided in two categories:

1. Scanning Electron Microscope (SEM)
2. Transmission Electron Microscope (TEM)

Although both the electron microscopes work on the principle of using electron beam as a source of illumination, they differ in the type of signal used for the formation of image. A scanning electron microscope uses electron reflected from the surface of specimen, which are magnified for the formation of a 3-dimensional image whereas a transmission electron microscope (TEM) uses electrons transmitted through the specimen for the formation of 2-D image. The magnification achieved in case of SEM is limited to around 3,00,000 times whereas magnification as high as 20,00,000 times has been achieved in modern TEM.

Construction

It consists of an electron gun to produce electrons and a slide for placing the sample that is to be magnified (Fig. 2.13). To focus the electrons there are three sets of magnets that are acting as magnetic lenses. These are: condenser magnetic lenses, objective lenses and projective magnetic lens. A fluorescent screen is placed to make the magnified image of the sample on it. This arrangement is enclosed in a rigid metal frame in which high level vacuum is maintained. The slide for placing the object and the fluorescent screen can be inserted from outside, as compared to the optical microscopes, the whole instrument stands very high.

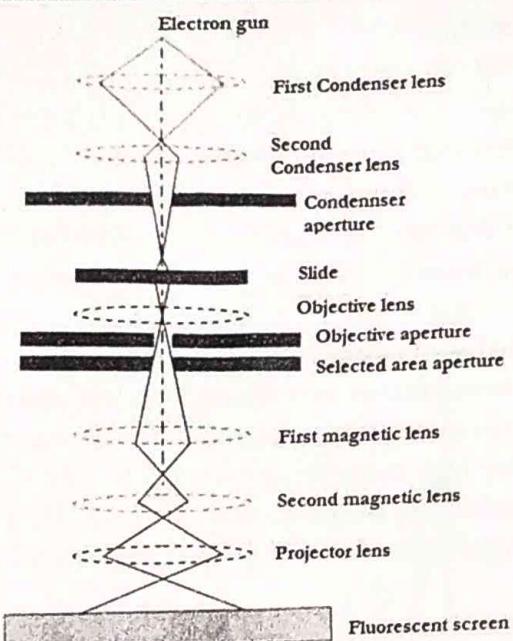


Fig. 2.13 Electron Microscope

Working Principle

In electron microscopes, firstly electrons are generated from the electron gun, which consists of a thin wire like tungsten filament. When high voltage is applied on the filament, due to the thermionic emission electrons are emitted from the filament and are accelerated by the negative potential in the electron gun. As the electrons emitted by the electron gun are unstable, a high-level vacuum is maintained. These electrons pass through the first set of magnetic lenses which acts as a condenser and focusses the electrons on the object that is to be magnified. This lens is therefore called condensive magnetic lens. The object or the sample must be very thin to avoid energy losses of the incident electrons. The electrons transmitted through the object are then passed through the second magnetic lenses which acts as objective and is called objective magnetic lenses. The electrons are further passed through the third set of magnetic lenses called projective magnetic lens which finally projects the electrons on a fluorescent screen on which the image is produced.

Applications

Unlike optical microscopes, we cannot see objects in colour, using an electron microscope. Also, we can only place inanimate objects in the electron microscope, i.e., if we want to look at the bug in the electron microscope, it must be dead. But because of high resolving power, the electron microscopes are very useful to view very tiny dimensions that cannot be viewed even by the optical microscopes. This makes it very important in scientific researches.

As per the syllabus our focus will be more on detailed discussion on SEM.

2.11.1 Scanning Electron Microscope (SEM)

Scanning Electron microscope is a microscope that uses a light beam of highly energetic electrons to examine very small objects. This examination can yield information on morphology, topography and crystallography of the material. Morphology refers to the shape, size of the particles making up the object. Topography on the other hand is the surface features of an object on how it looks including its

texture or hardness. Crystallography describes how the atoms are arranged in the object. They may be ordered, in a regular lattice thereby producing a crystal or they may be randomly organized as in the case of amorphous. The way in which they are arranged can affect the properties of material, such as conductivity, electrical properties and strength. The first SEM was available commercially in 1965. Electron microscopes were developed because light microscopes are limited by the physics of light to 500 x 1000X magnification and a resolution of 0.2 micrometres.

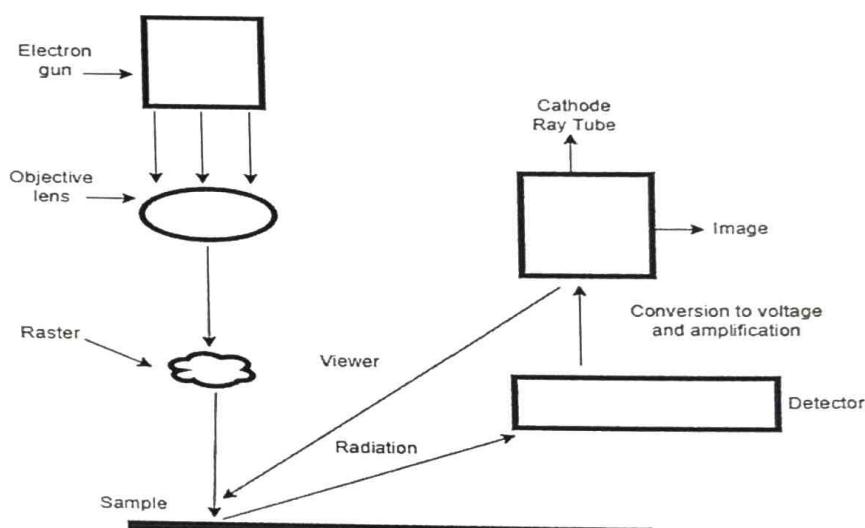


Fig. 2.14 Scanning Electron Microscope (SEM)

Principle

SEM (Fig. 2.14) uses a highly focused beam of high energy electrons to generate a variety of signals at the surface of solid specimens. The electron specimen interactions can cater a large information about morphology, topography and crystallography of the material making the sample.

Components

Essential components include an electron source(gun), electron lenses, sample stage, detectors, display output devices

Working

In SEM, an electron gun emits a beam of electrons which passes through a condenser lens and is refined into a thin stream. From there, the objective lens focusses the electron beam onto the specimen. This objective lens contains a set of coils which are energized with varying voltages. The coils create an electromagnetic field that exerts a force upon the electrons in the electron beam, which in turn directs the electrons to scan the specimen in a controlled pattern called a raster. The electromagnetic field of the coils also causes a spot of light on a cathode ray tube to move along at the same rate as the scanning electron beam. When the electrons from the beam hit the specimen, a series of interaction deflect secondary particles to a detector which then converts the signal to voltage and amplifies it. This voltage is then applied to a cathode ray tube and converted to an image. The intensity of the image or brightness is determined by the number of secondary particles that hit the cathode ray tube, which is dependent upon the angle the electrons bounce off the specimen. Thus, the image of the specimen depends on its topography.

When an electron from the beam encounters a nucleus in the specimen, the resultant attraction produces a deflection in the electrons path known as Rutherford scattering. A few of these electrons will be completely backscattered, re-emerging from the surface of the sample. Since the scattering angle is strongly dependent on the atomic number of the nucleus involved, the primary electrons arriving at

a given detector position can be used to yield images containing information on both topology and atomic composition. Some of the beams of electrons can also interact with the electrons in the sample. The amount of energy given to the secondary electrons as a result of the interactions is small, and so they have a limited range in the sample of a few nanometres and often do not escape. The electrons that are at very short distances from the surface are able to escape and are able to be observed by the detector. The images of these secondary particles contain a lot of detailed information.

Advantages:

1. SEM can produce images of greater clarity and three-dimensional quality and requires less sample preparation.
2. It has got a rather larger depth of field that is more of the image being magnified is in focus.
3. SEM has got extremely wide range of magnification, producing images in the range of 10 to 100,000 times their normal size.
4. It produces three-dimensional view of a specimen and is very helpful in analysing its shape and structure.

Solved examples

Based on normalization, expectation value, probability of particle

Ex.1 The wave function of a particle is $\psi = A \cos^2 x$ for interval $-\pi/2$ to $\pi/2$. Find the value of A.

Sol. $\psi = A \cos^2 x$ $-\pi/2$ to $\pi/2$

Then $\int_{-\pi/2}^{\pi/2} |\psi|^2 dx = 1$

Or $\int_{-\pi/2}^{\pi/2} A^2 \cos^4 x dx = 1$

Or $2A^2 \int_0^{\pi/2} \cos^4 x dx = 1$ (an even function)

Or $2A^2 \left(\frac{3\pi}{16}\right) = 1$

Hence $A = \sqrt{\frac{8}{3\pi}}$

Ex.2 A particle limited to the x-axis has the wave function $\psi = ax$ between $x = 0$ and $x = 1$, $\psi = 0$ elsewhere. Find (a) the probability that particle x can be found between $x = 0.45$ and $x = 0.55$ (b) the expectation value $\langle x \rangle$ of the particle's position.

Sol. (a) The probability is

$$\int_{x_1}^{x_2} |\psi|^2 dx = a^2 \int_{0.45}^{0.55} x^2 dx = a^2 \left[\frac{x^3}{3} \right]_{0.45}^{0.55} = 0.0251a^2$$

(b) The expectation value is

$$\langle x \rangle = \int_0^1 x |\psi|^2 dx = a^2 \int_0^1 x^3 dx = a^2 \left[\frac{x^4}{4} \right]_0^1 = \frac{a^2}{4}$$

Ex.3 The wave function of a particle is given by

$\psi(x) = Ce^{-\alpha^2 x^2}$, $-\infty < x < +\infty$, where C and α are some constants. Calculate the probability of finding the particle in the region $0 < x < \infty$.

Sol. $P = \int_0^\infty |\psi(x)|^2 dx = \int_0^\infty C^2 e^{-2\alpha^2 x^2} dx$

[Also, from standard integral $\int_0^\infty e^{-ax^2} dx = \frac{1}{2} \sqrt{\frac{\pi}{2}}]$ to confirm

We get, $P = C^2 \int_0^\infty e^{-2a^2x^2} dx = \frac{1}{2} C^2 \sqrt{\frac{\pi}{2a^2}}$

Applying normalizing condition i.e.,

$$\int_{-\infty}^{\infty} |\psi(x)|^2 dx = \int_{-\infty}^{\infty} C^2 e^{-2a^2x^2} dx = 1$$

$$\Rightarrow C^2 \sqrt{\frac{\pi}{2a^2}} = 1$$

$$\text{which gives } C^2 = \sqrt{\frac{2a^2}{\pi}}$$

$$\therefore P = \sqrt{\frac{2a^2}{\pi}} \frac{1}{2} \sqrt{\frac{\pi}{2a^2}} = \frac{1}{2}$$

Ex. 4 Normalize the wave function $\phi(x) = e^{-|x|} \sin \alpha x$.

Sol. Let the normalized wave function be, $\psi(x) = A \phi(x)$, where A is the normalization constant. From the normalization property, we have

$$\int_{-\infty}^{\infty} \psi \psi^* dx = 1$$

i.e.,

$$\int_{-\infty}^{\infty} A^* \phi^*(x) A \phi(x) dx = 1$$

Or

$$A A^* \int_{-\infty}^{\infty} \phi^*(x) \phi(x) dx = 1$$

$$\text{Or } |A|^2 \int_{-\infty}^{\infty} e^{-|x|} \sin \alpha x \cdot e^{-|x|} \sin \alpha x dx = 1$$

$$\text{Or } \frac{|A|^2}{2} \int_{-\infty}^{\infty} e^{-2|x|} 2 \sin^2 \alpha x dx = 1$$

$$\text{Or } \frac{|A|^2}{2} \int_{-\infty}^{\infty} e^{-2|x|} (1 - \cos 2\alpha x) dx = 1$$

$$\text{Or } \frac{|A|^2}{2} \left[\int_{-\infty}^{\infty} e^{-2|x|} dx - \int_{-\infty}^{\infty} e^{-2|x|} \cos 2\alpha x dx \right] = 1$$

$$\text{Or } \frac{|A|^2}{2} \left[0 - \left(-\frac{\alpha^2}{1+\alpha^2} \right) \right] = 1$$

$$\text{Or } \frac{|A|^2}{2} \cdot \frac{\alpha^2}{1+\alpha^2} = 1$$

So, that

$$|A| = \sqrt{\frac{2(1+\alpha^2)}{\alpha^2}}$$

So, the normalized wave function is given by

$$\psi(x) = A \phi(x) = \sqrt{\frac{2(1+\alpha^2)}{\alpha^2}} e^{-|x|} \sin \alpha x$$

Ex.5 Find the value of normalization constant A for the wave function $\psi = Axe^{-x^2/2}$. Given that

$$\left[\int_0^\infty x^2 e^{-\alpha x^2} dx = \frac{1}{4} \sqrt{\frac{\pi}{\alpha^3}} \right]$$

Sol. From the Normalization condition, $\int_{-\infty}^{\infty} |\psi|^2 dx = 1$

Here

$$\psi = Axe^{-x^2/2}$$

$$A^2 \int_{-\infty}^{\infty} x^2 e^{-x^2} dx = 1 \Rightarrow 2A^2 \int_0^{\infty} x^2 e^{-x^2} dx = 1 \text{ (due to even function)}$$

$$\text{Given that } \int_0^{\infty} x^2 e^{-\alpha x^2} dx = \frac{1}{4} \sqrt{\frac{\pi}{\alpha^3}}$$

$$\text{Here, } \alpha = 1 \quad 2A^2 \frac{1}{4} \frac{\sqrt{\pi}}{1} = 1$$

$$A^2 = \frac{2}{\sqrt{\pi}} \quad \text{or} \quad A = \frac{\sqrt{2}}{\pi^{1/4}}$$

Ex.6 The wave function of a particle is $\psi = A \cos^2 x$ for $-\frac{\pi}{2} < x < \frac{\pi}{2}$

- (i) Find the value of A (ii) Find the probability that the particle be found between $x = 0$ and $x = \frac{\pi}{4}$

$$\text{Sol. As } \psi = A \cos^2 x \quad -\frac{\pi}{2} < x < \frac{\pi}{2}$$

$$(i) \int_{-\pi/2}^{\pi/2} |\psi|^2 dx = 1$$

$$\Rightarrow 2A^2 \int_0^{\pi/2} \cos^4 x dx = 1 \quad \text{or} \quad 2A^2 \frac{3\pi}{16} = 1$$

$$\frac{3\pi}{8} A^2 = 1 \quad \therefore \quad A = \sqrt{\frac{8}{3\pi}}$$

$$(ii) P = \int_0^{\pi/4} |\psi|^2 dx = A^2 \int_0^{\pi/4} \cos^4 x dx \text{ as } A = \sqrt{\frac{8}{3\pi}}$$

$$P = \frac{8}{3\pi} \int_0^{\pi/4} \cos^4 x dx$$

$$P = 0.462$$

Ex.7 The normalized state of a free particle is represented by a wave function

$$\psi(x) = Ne^{-(x^2/2a^2)} e^{ikx}$$

(a) Find: (i) the factor N (ii) the expectation value of position and momentum.

(b) In what region of space, the particle is most likely to be found?

Sol.(a) (i) This factor N, being the normalisation constant can be found from the normalisation condition as follows:

$$\int_{-\infty}^{\infty} \psi^* \psi dx = 1$$

$$\text{Or } |N|^2 \int_{-\infty}^{\infty} (e^{-x^2/2a^2} e^{+ikx}) \cdot (e^{-x^2/2a^2} e^{-ikx}) dx = 1 \quad (\text{where } |N|^2 = NN^*)$$

$$\text{Or } |N|^2 \int_{-\infty}^{\infty} e^{-x^2/a^2} dx = 1$$

$$\text{Or } |N|^2 \cdot a \sqrt{\pi} = 1$$

$$\text{Or } |N| = \frac{1}{a^{1/2} \pi^{1/4}}$$

$$\text{Or } N = \frac{1}{a^{1/2} \pi^{1/4}} e^{i\phi}$$

here ϕ is a factor, which is arbitrary.

(ii) The expectation value of position coordinate x is given by

$$\begin{aligned} \langle x \rangle &= \int_{-\infty}^{\infty} \psi^* x \psi dx = \int_{-\infty}^{\infty} N^* e^{-\left(\frac{x^2}{2a^2}\right)} e^{-ikx} \cdot x \cdot N e^{-\left(\frac{x^2}{2a^2}\right)} e^{ikx} dx \\ &= NN^* \int_{-\infty}^{+\infty} e^{-\left(\frac{x^2}{a^2}\right)} x dx = 0 \end{aligned}$$

The expectation value of momentum coordinate p_x is given by

$$\begin{aligned}
 \langle P_x \rangle &= \int_{-\infty}^{\infty} \psi^* \hat{p}_x \psi dx \\
 &= \int_{-\infty}^{\infty} N^* e^{-\left(\frac{x^2}{2a^2}\right) - ikx} \left(\frac{\hbar}{i} \cdot \frac{\partial}{\partial x}\right) \left[N e^{-\left(\frac{x^2}{2a^2}\right) + ikx} \right] dx \\
 &= \int_{-\infty}^{\infty} N^* e^{-\left(\frac{x^2}{2a^2}\right) - ikx} \left(\frac{\hbar}{i}\right) N e^{-\left(\frac{x^2}{2a^2}\right) + ikx} \cdot \left(-\frac{2x}{2a^2} + ik\right) dx \\
 &= NN^* \frac{i\hbar}{a^2} \int_{-\infty}^{\infty} e^{-x^2/a^2} x dx + NN^* \int_{-\infty}^{\infty} \hbar k e^{-x^2/a^2} dx = 0 + \hbar k = \hbar k
 \end{aligned}$$

So, that $\langle p_x \rangle = \hbar k$ and $\langle x \rangle = 0$

(b) The probability density is given by

$$P(x) = |\psi(x)|^2 = \psi^*(x) \psi(x) = |N|^2 e^{-x^2/a^2} = \frac{1}{a\sqrt{\pi}} e^{-x^2/a^2}$$

According to this equation, the probability is maximum for $x=0$ and decreases exponentially for $|x| > a$. So, the particle is most likely to be found in a region with width a on either side of the origin $x=0$

Based on Eigen value

Ex.8 An Eigen-function of an operator $\frac{d^2}{dx^2}$, is $\psi = e^{\alpha x}$. Find the corresponding Eigen value.

Sol. Let

$$G = \frac{d^2}{dx^2}$$

$$G\psi = \frac{d^2}{dx^2}(e^{\alpha x}) = \frac{d}{dx} \left[\frac{d}{dx} e^{\alpha x} \right] = \frac{d}{dx} (\alpha e^{\alpha x}) = \alpha^2 e^{\alpha x}$$

But

$$e^{\alpha x} = \psi$$

$$\therefore G\psi = \alpha^2 \psi$$

Hence, Eigen value $G = \alpha^2$

Based on particle in one-dimensional box

Ex.9 Particle is moving in a one-dimensional box (of infinite height) of width 2.5 nm at the centre of the box when it is in its state of least energy. Find the probability to be in the region of 0.5 nm in the middle of the box.

Sol. Since we know that,

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

when the particle is in least energy state ($n=1$) the wave function becomes

$$\psi_1(x) = \sqrt{\frac{2}{a}} \sin \frac{\pi x}{a}$$

At the centre of the box, $x = \frac{a}{2}$, the probability of finding the particle at midpoint of the box is

$$|\psi_1(x)|^2 = \frac{2}{a} \sin^2 \frac{\pi x}{a}$$

Probability P' in the interval Δx is given by

$$P' = |\psi_1(x)|^2 (\Delta x) = \frac{2}{a} \Delta x, \text{ at } x = \frac{a}{2}$$

With (i) $a = 2.5 \text{ nm}$

(ii) $\Delta x = 0.5 \text{ nm}$

Thus,

$$P' = \frac{2}{2.5} \times (0.5) = 0.4$$

$$P' = 0.4$$

Ex.10 Find the least energy of an electron moving in one dimension in an infinitely high potential box of width 1 Å.

Sol. The Eigen value of energy, $E_n = \frac{n^2 h^2}{8ma^2}$

When the particle is in the least energy state ($n = 1$), the energy,

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

with $h = 6.62 \times 10^{-34} \text{ Js}$, $m = 9.1 \times 10^{-31} \text{ kg}$ and $a = 1 \times 10^{-10} \text{ m}$

$$\begin{aligned} \text{i.e., } E_1 &= \frac{(6.62 \times 10^{-34})^2}{8 \times 9.1 \times 10^{-31} \times (1 \times 10^{-10})^2} \\ &= \frac{6.62}{8 \times 9.1} \times 10^{-68} \times 10^{+51} \\ &= \frac{6.62}{72.8} \times 10^{-17} = \frac{6620}{728} \times 10^{-19} \\ &= 9.093 \times 10^{-19} \text{ J} = 5.68 \text{ eV} \end{aligned}$$

Assume that the potentials are constant in time and that are also constant for prescribed region of space.

Ex.11 Determine the expectation value of position of a particle in one-dimensional box, for ground state.

$$\text{Sol. Given : } \psi = \sqrt{\frac{2}{a}} \sin \frac{n\pi x}{a}, \quad \text{limit range} = 0 \text{ to } a$$

We know expectation value of any function x is given by

$$\langle x \rangle = \int_{-\infty}^{+\infty} x |\psi|^2 dx$$

Then for one-dimensional box

$$\begin{aligned} \langle x \rangle &= \int_0^a x \cdot \frac{2}{a} \sin^2 \frac{n\pi x}{a} dx \quad [\cos 2x = 1 - 2\sin^2 x] \\ &= \frac{1}{a} \int_0^a \left(x - x \cos 2 \frac{n\pi x}{a} \right) dx = \frac{1}{a} \left[\int_0^a x dx - \int_0^a x \cos 2 \frac{n\pi x}{a} dx \right] \\ &= \frac{1}{a} \left\{ \left[\frac{x^2}{2} \right]_{x=0}^{x=a} - \left[\frac{x \sin 2 \frac{n\pi x}{a}}{2 \frac{n\pi}{a}} \right]_{x=0}^{x=a} - \frac{1}{2 \frac{n\pi}{a}} \left[\frac{1 \cdot \cos 2 \frac{n\pi x}{a}}{(2 \frac{n\pi}{a})} \right]_{x=0}^{x=a} \right\} \\ &= \frac{1}{a} \times \frac{a^2}{2} = \frac{a}{2} \end{aligned}$$

Ex.12 Find the probability that a particle trapped in a box 'a' wide can be found between $0.30a$ and $0.65a$ for the first excited state.

Sol. Since, we know that for the particle in box

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

\therefore The probability to find the particle between x_1 and x_2 is

$$\begin{aligned} P &= \int_{x_1}^{x_2} |\psi_n(x)|^2 dx = \frac{2}{a} \int_{x_1}^{x_2} \sin^2 \frac{n\pi x}{a} dx \\ &= \left[\frac{x}{a} - \frac{1}{2n\pi} \sin \frac{2n\pi x}{a} \right]_{x_1}^{x_2} \end{aligned}$$

Given $x_1 = 0.30 a$ and $x_2 = 0.65 a$, $n = 2$ (for first excited state).

$$\begin{aligned} P &= \left[\frac{0.65a}{a} - \frac{1}{2n\pi} \sin \frac{2 \times 2 \times \pi \times 0.65a}{a} - \frac{0.30a}{a} + \frac{1}{2n\pi} \sin \frac{2 \times 2 \times \pi \times 0.30a}{a} \right] \\ &= \left[0.35 - \frac{1}{2n\pi} (\sin 2.60\pi - \sin 1.2\pi) \right] \end{aligned}$$

Ex.13 Calculate the expectation value $\langle P_x \rangle$ of the momentum of a particle trapped inside a one-dimensional box.

Sol. For one-dimensional box of length the wave function may be given as

$$\psi_n = \sqrt{\frac{2}{a}} \sin \frac{n\pi x}{a}$$

$$\text{Complex conjugate } \psi_n^* = \sqrt{\frac{2}{a}} \sin \frac{n\pi x}{a}$$

One-dimensional momentum operator $\hat{P}_x = -i\hbar \frac{\partial}{\partial x}$

$$\text{Or } \langle P_x \rangle = \int_{-\infty}^{\infty} \psi^* \left(-i\hbar \frac{\partial}{\partial x} \right) \psi dx$$

$$= \frac{2}{a} (-i\hbar) \int_0^a \sin \left(\frac{n\pi x}{a} \right) \cdot \sin \left(\frac{n\pi x}{a} \right) dx$$

As the Particle must be within the box, the limit varies from 0 to a.

$$= \frac{2}{a} (-i\hbar) \int_0^a \sin \left(\frac{n\pi x}{a} \right) \cdot \frac{n\pi}{a} \cos \left(\frac{n\pi x}{a} \right) dx$$

$$= \frac{2n\pi}{a^2} (-i\hbar) \int_0^a \sin \frac{n\pi x}{a} \cos \frac{n\pi x}{a} dx$$

This comes out to be zero.

Clearly, the expectation value (Average value) of momentum of the particle is $\langle P_x \rangle = 0$.

Ex.14 A particle of mass m is moving in an infinitesimal deep well potential well potential extending from $x = 0$ to $x = a$. Show $\langle E \rangle = \frac{n^2 h^2}{8ma^2}$.

Or

Prove that the value of energy obtained for a particle of mass m moving in a one-dimensional box can also be obtained with the help of relation used to obtain expectation value.

Sol. The normalized wave function for a particle of mass m in one-dimensional box is given by

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

$$\text{Now the energy operator } E = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2}$$

$$\text{So, that } \langle E \rangle = \int_0^a \psi_n^* \hat{E} \psi_n(x) dx$$

$$= -\frac{\hbar^2}{2m} \int_0^a \sqrt{\frac{2}{a}} \sin \frac{n\pi x}{a} \times \frac{d^2}{dx^2} \left(\sqrt{\frac{2}{a}} \sin \frac{n\pi x}{a} \right) dx$$

$$= -\frac{\hbar^2}{2m} \cdot \frac{2}{a} \int_0^a \sin \frac{n\pi x}{a} \frac{d^2}{dx^2} \left(\sin \frac{n\pi x}{a} \right) dx = \frac{n^2 \pi^2 \hbar^2}{ma^3} \int_0^a \sin^2 \frac{n\pi x}{a} dx$$

$$= \frac{n^2 \pi^2 \hbar^2}{2ma^3} \int_0^a \left[1 - \cos \frac{2n\pi x}{a} \right] dx = \frac{n^2 \pi^2 \hbar^2}{2ma^3} \times a = \frac{n^2 \hbar^2}{8ma^2}$$

Ex.15 A particle is moving in a one-dimensional potential box of infinite height. What is the probability of finding the particle in a small interval Δx at the centre of the box when it is in the energy state, next to the least energy state?

Sol. The wave function of the particle in the first excited state ($n = 2$) is

$$\psi_n = \sqrt{\frac{2}{a}} \sin \frac{2\pi x}{a}$$

At the centre of the box i.e., at $(x = \frac{a}{2})$, $\psi_2 = 0$

Hence, the probability to be at the centre $= |\psi_0(x)|^2 \Delta x = 0$
i.e. $P = 0$.

Ex.16 Suppose two identical conducting wires, lying along the x-axis are separated by an air gap of thickness $L = 1\text{nm}$ (\sim few atomic diameters). An electron is moving inside either conductor has

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potential energy zero, whereas in the gap its potential energy $V_0 > 0$. Thus, the gap is a kind of barrier discussed in the tunnel effect problem. The electron approaches the barrier from the left with energy such that $V_0 - E = 1\text{eV}$ i.e., the electron is 1eV below the top of the barrier. Find the probability of the electron emerging on the other side of the barrier? If the barrier is twice as wide, how the probability changes?

Sol. The probability is given by

$$T = e^{-2\beta a}$$

Where a is the width of the barrier and $\beta = \sqrt{\frac{2m(V_0-E)}{\hbar^2}}$

$$\beta = \frac{\sqrt{2m(V_0-E)}}{\hbar} = \frac{\sqrt{2mc^2(V_0-E)}}{\hbar c}$$

$$= \frac{\sqrt{2 \times 5 \times 10^5 \times 1}}{197} \approx 5.1 \text{ nm}^{-1}$$

Thus,

$$T = e^{-2 \times 5.1 \times 1} = e^{-10.2} = 3.7 \times 10^{-5} \approx 0.04\%$$

Thus, the probability is not very large. However, if large number of electrons approaches the barrier a few of them will tunnel through.

For $a = 2\text{nm}$, $= e^{-20.4} = 1.4 \times 10^{-9}$, much smaller than the previous one indicating the extreme sensitivity of the transmission probability to the gap width- a fact which is utilised in the scanning tunnelling microscope.

Ex.17 Electrons with energies 1.0eV and 2.0eV are incident on a barrier 10.0eV high and 0.50nm wide.

(a) Find their respective transmission probabilities (b) How are these affected if the barrier is doubled in width?

Sol. (a) For the 1.0eV electrons

$$\begin{aligned} \beta &= \frac{\sqrt{2m(V_0-E)}}{\hbar} \\ &= \frac{\sqrt{2 \times 9.1 \times 10^{-31} (10 - 1) (1.6 \times 10^{-19})}}{1.05 \times 10^{-34}} \\ &= 1.6 \times 10^{10} \text{ m}^{-1} \end{aligned}$$

Since, $a = 0.50\text{nm} = 5 \times 10^{-10}\text{m}$, $2\beta a = 2 \times 1.6 \times 10^{10} \times 5 \times 10^{-10} = 16$

And the approximate transmission probability is

$$T_1 = e^{-2\beta a} = e^{-16} = 1.1 \times 10^{-7}$$

One 1eV electron out of 8.9 million can tunnel through the 10eV barrier on the average. For the 2eV electrons a similar calculation gives $T_2 = 2.4 \times 10^{-7}$

These electrons are over twice as likely to tunnel through the barrier.

(b) If the barrier is doubled in width to 1.0 nm, the transmission probabilities become

$$T'_1 = 1.3 \times 10^{-14} \quad T'_2 = 5.1 \times 10^{-14}$$

Evidently T is more sensitive to the width of the barrier than to the particle energy here.

*****Review Questions*******Based on wave-function, expectation value**

1. Why wave functions are to be normalized?
2. What is the physical significance of the wave function?
3. What are the continuity and boundary conditions that must be satisfied for a wave function to be physically acceptable?
4. Explain what do you understand by expectation value of a dynamical variable?
5. The particle trapped in one dimensional box of length L is described by a wave function $\psi = x$. Normalise the wavefunction between a and b.

$$[\text{Ans. } \int_a^b |\psi|^2 dx = \frac{1}{3} (b^3 - a^3)]$$

Based on Schrodinger equation

6. Obtain the time-dependent Schrodinger equation for a particle of mass m moving wave function? Why should the wave function be normalized?
7. What is meant by the expectation value of a dynamical variable? How is it obtained mathematically?
8. Write the time-independent Schrodinger equation for a particle in a force field. Explain all the terms.
9. Explain what do you understand by expectation value of a dynamical variable?

Based on particle in a box

10. Write an expression for the energy eigenvalues of a particle of mass in confined in a one-dimensional box of length L. State whether the permitted energy levels are quantized or continuous?
11. Write a short note on the energy quantization for a particle in a 1D potential box.
12. The lowest possible energy for a particle entrapped in a box is 40 eV. What are the next three higher energies the particle can have? [Ans. 160eV, 360eV, 640 eV]
13. An electron is trapped in an infinite well of width 1cm. For what value of n will the electron have an energy of 1eV. [Ans. 1.5×10^7]
14. An electron of energy 342 eV is confined in a one dimensional box of length 1 Å. Calculate a) the quantum number n of the energy level of the electron b) the energy required to take the electron to the next higher level. [Ans.(a) n = 3 , (b)266eV]

Unit -II

Quantum Statistics: The need for statistics , statistical distributions: Maxwell Boltzmann, Bose-Einstein and Fermi-Dirac statistics, their comparisons, Fermions and Bosons, Applications of quantum statistics: 1. Molecular speed and energies in an ideal gas; 2. The Black body spectrum, the failure of classical statistics to give the correct explanations – Bose-Einstein statistics applied to the Black Body radiation spectrum; Fermi-Dirac distribution, free electron theory, electronic specific heats, Fermi energy and average energy; Dying stars

Chapter 3

Quantum Statistics

3.1 Introduction

In the physical world many phenomena involve systems comprising a large number of particles, say it be a system comprising a gas of many molecules or atoms, a metal with many free electrons etc. In a given system, position and momentum of all the particles defines the overall behaviour like pressure, volume, temperature and energy of a system of many particles. The properties like pressure, volume, temperature and energy of a system which shows the overall behaviour of the system are called macroscopic properties of the system. Statistical Mechanics very well depicts the relation of the overall macroscopic behaviour of a system to the microscopic properties (position or momentum) of the system. Thus, the importance of statistical mechanics lies in the overall behaviour of a system due to each and every particle of the system. This branch is not concerned with the actual motion of an individual particle rather it examines the average or the most probable properties of the system statistically, without going into the details of the characteristic of its constituents. The larger the number of particles in the physical system, the more accurate are the Statistical predictions.

In this chapter, we are going to study a system of particles as a whole consisting of classical particles like molecules of a gas and the quantum particles like photons and free electrons, as a part of Statistical Mechanics. Here, we have mentioned below some of the phenomenon which could not be explained by classical mechanics that lead to the origin of Quantum Mechanics.

The classical mechanics explains correctly the various physical properties related to the statics and dynamics of celestial bodies like planets, stars and macroscopic as well as microscopic terrestrial bodies moving with non-relativistic speeds (i.e., $v \ll c$, where c is the speed of light). But it failed to explain so many phenomena of physics. Some of the inadequacies of classical mechanics are;

- (i) It does not hold in the region of atomic dimensions i.e., it cannot explain the non-relativistic motion of atoms, electrons, protons etc.
- (ii) It could not explain the stability of atoms.
- (iii) It could not explain the observed spectrum of black body radiations.
- (iv) It could not explain the observed variation of specific heat of metals and gases.
- (v) It could not explain the origin of discrete spectra of atoms, since according to classical mechanics the energy changes are always continuous.

The classical mechanics also could not explain a large number of other observed phenomena like photoelectric effect, Compton Effect, Raman Effect, etc. This inadequacy of classical mechanics led to the development of quantum mechanics.

3.2 Basic assumptions of Statistical Mechanics

Since, we are considering a large number of constituent particles we take certain assumptions in case of Statistical Mechanics:

- (i) There are extremely large numbers of particles ($\approx 10^{23}$) in a given system.
- (ii) In a given system, the number of particles is fixed.
- (iii) The volume of the given system is fixed as there is no work done by the system or on the system.

(iv) The exchange of energy can take place between particles but simultaneously their interactions can be considered extremely weak.

This assumption allows us to treat the energy levels of the system as the sum of the energy levels of a corresponding single-particle system allowing the system to move between different microstates.

3.3 Statistical Balance

In a thermodynamically isolated system, let us consider N particles, each of mass m in which the interaction amongst particles is almost negligible. If E is the total energy of the system which is equal to the sum of the energies of the individual particles such that

$$E = E_1 + E_2 + E_3 + \dots + E_i \quad (1)$$

where E_i is energy of the i^{th} particle. The available states of energy to the particles are E_1, E_2, E_3, \dots . These energy states can be quantized or may be continuous. If at any particular instant of time, n_1 particles have energy E_1 , n_2 particles have energy E_2 and so on then the total number of particles in the system is:

$$N = n_1 + n_2 + n_3 + \dots + n_i = \sum_i n_i \quad (2)$$

where $i = 1, 2, 3, \dots$

The total energy is:

$$U = n_1 E_1 + n_2 E_2 + n_3 E_3 + \dots = \sum_i n_i E_i \quad (3)$$

Eq.(3) above represents the total energy of a system in which the particles are non-interacting.

$$\text{For an isolated system, } U = \sum_i n_i E_i = \text{Constant} \quad (4)$$

The isolated system here signifies that the volume, temperature and pressure are kept constant such that the total energy of the system remains constant for a gas having N molecules. These molecules however can collide amongst themselves and with the walls of the container such that the energy changes from one energy state to another and is sufficient to establish thermal equilibrium but not so much that their motions are strongly correlated. This implies the values of n_1, n_2, n_3, \dots etc. also continuously changes. Hence, it can be concluded that for each microscopic state of a system of particles, there is particular most favoured distribution. The system attains equilibrium or balance when this statistical equilibrium is reached. For an isolated system thus, the values of n_1, n_2, n_3, \dots etc. vary only near the values corresponding to the most probable distribution. Thus, in statistical thermodynamics, we need to focus more on the most probable distribution for a given composition of the system. This means we actually need to determine the most probable way in which a certain total amount of energy E is distributed amongst the N members of a system of particles in thermal equilibrium at the absolute temperature T .

Statistical Distribution for Different Kind of Particles

Depending upon the types of particles, in general, we have three different kinds of statistical distributions:

- (i) Maxwell-Boltzmann Distribution law
- (ii) Fermi-Dirac Distribution law
- (iii) Bose-Einstein Distribution law

(Classical distribution)

(Quantum distribution)

(Quantum distribution)

3.4 Classical and Quantum Statistics

Broadly any microscopic system can be classified in two different ways:

3.4.1 Classical Statistics

Maxwell Boltzmann Statistics

Identical particles like the molecules of a gas that are distinguishable on the basis of their energies and whose wave function do not overlap, comes under classical statistics or Maxwell-Boltzmann Statistics (M-B statistics). In Maxwell-Boltzmann distribution, it has been assumed that all the energy levels are accessible to all the particles of the system. In other words, in such kind of classical systems a continuous range of energies is available to the particles. Such kind of distribution was first explained by Maxwell. This distribution forms the basis of understanding of many properties of different materials. Various concepts arising in thermodynamics like entropy, energy, temperature etc. can be well understood by this distribution. The distribution however, is based on a number of assumptions and approximations. On changing these assumptions one can lead, to either Bose-Einstein distribution or Fermi-Dirac distribution.

3.4.2 Quantum Statistics

In Quantum systems, the particles are indistinguishable and available energies are discrete. There are certain levels prohibited to a certain group of particles. Each energy state is associated with a certain group of particles and can be well associated with a certain available wave function. The probability of a particular distribution is restricted by the available wave functions of any state. These restrictions are taken into account in quantum statistics. If the wave functions do overlap appreciably, the situation changes because the particles cannot now be distinguished, and the overlapping wave functions fall out into two categories.

There are two types of quantum statistics. In both the kinds of quantum statistics, the particles are identical and indistinguishable.

Bose-Einstein Statistics

Particles are assumed that they are not restricted by Pauli's exclusion principle and are characterised by symmetric wave functions. These particles are called bosons. It has been experimentally found that all the particles having spin zero or integral multiple of 1 are bosons. Helium nuclei and mesons are bosons. Photons also belong to this category.

Fermi-Dirac Statistics

Particles are assumed to obey Pauli's exclusion principle. They are characterised by anti-symmetric wave functions. These particles have odd half-integral spin ($\frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \dots$). The particles under this category are called fermions. Protons, neutrons and electrons are fermions.

We all know that a quantum particle also shows wave nature. We have also studied that a quantum particle is represented by a wave and the characteristic properties of the particle are determined by a variable wave-function. Different types of particles possess different wave functions in different situations, called eigen function.

3.5 Symmetric and Anti-Symmetric Wave-Functions

Since, the bosons or the fermions are the moving particles, so we have introduced a variable quantity Ψ associated with the moving particle. This is called as wave function which is extensively discussed earlier in the chapter of quantum mechanics. The wave function Ψ characterises de-Broglie waves

Quantum Statistics

associated with a particle. In order to satisfy the condition of in-distinguishability of particles in a given system, we have to construct the wave function for a system of identical particles.

Mathematically, if we interchange the particles occupying any pair of states there should be no change in the probability density of the system. For this, let us take the probability density of a two-particle wave function $\psi(r_1, r_2)$ which should be same as that for the wavefunction $\psi(r_2, r_1)$ when there is an exchange of particles such that:

$$|\psi(r_1, r_2)|^2 = |\psi(r_2, r_1)|^2 \quad (5)$$

This can be achieved in two ways;

Symmetric wave-function: $\psi(r_1, r_2) = \psi(r_2, r_1)$ (6)

Anti-symmetric wave-function: $\psi(r_1, r_2) = -\psi(r_2, r_1)$ (7)

The symmetry of the wave function for identical particles is dependent on the spin of the particles. It is seen that particles with zero or integral spin are termed as bosons (e.g. mesons, photons) and have symmetric wave function under particle interchange. The particles with half integral intrinsic spin termed as fermions have anti-symmetric wave function under particle interchange. The electrons belong to this category and no two electrons can be under same state but any number of bosons may occupy the same state.

We shall now see what happens to the probability of bosons for the two particles to be in the same state and in case of fermions for their probability in preventing the particles to be in the same state.

To understand this, let us consider a system of two particles, 1 and 2, in state a and b respectively. For the distinguishable particles, there can be either of the two possibilities as described by the wave functions given:

$$\psi_1 = \psi_a(1)\psi_b(2)$$

$$\psi_2 = \psi_a(2)\psi_b(1)$$

For indistinguishable particles, one cannot tell which of them is in which state, and since there is equal probability of these states, so the wave function can be written as a linear combination of ψ_1 and ψ_2 . If the particles are bosons, the system is described by symmetric wave function as:

Bosons: $\psi_B = \frac{1}{\sqrt{2}} [\psi_a(1)\psi_b(2) + \psi_a(2)\psi_b(1)] = \psi_S$ (Symmetric wave-function)

If the particles are fermions, the system is described by the anti-symmetric wave function as:

Fermions: $\psi_F = \frac{1}{\sqrt{2}} [\psi_a(1)\psi_b(2) - \psi_a(2)\psi_b(1)] = \psi_A$ (Anti-symmetric wave-function)

Here, $1/\sqrt{2}$ is needed, for normalization of the wave functions.

The next question that comes in our mind is that what will be the probability that both the particles are in the same state, say a.

For distinguishable particles, that follows Maxwell-Boltzmann Statistics or M-B Statistics:

$$\psi_M = \psi_a(1)\psi_a(2)$$

The probability density for distinguishable particles is given as:

$$\psi_M^* \psi_M = \psi_a^*(1)\psi_a^*(2)\psi_a(1)\psi_a(2)$$

For indistinguishable particles like bosons:

$$\psi_B = \frac{1}{\sqrt{2}} [\psi_a(1)\psi_a(2) + \psi_a(2)\psi_a(1)] = \frac{2}{\sqrt{2}} [\psi_a(1)\psi_a(2)] = \sqrt{2} [\psi_a(1)\psi_a(2)]$$

So, the probability density of bosons will be;

$$\psi_B^* \psi_B = 2[\psi_a^*(1)\psi_a^*(2)\psi_a(1)\psi_a(2)] = 2\psi_M^* \psi_M$$

Thus, the probability that both the bosons be in the same state is twice as likely to be in the same state as distinguishable particles.

For indistinguishable particles like fermions:

$$\Psi_F = \frac{1}{\sqrt{2}}[\psi_a(1)\psi_a(2) - \psi_a(1)\psi_a(2)] = 0$$

And the probability density of fermions;

$$\psi_F^* \psi_F = 0$$

In case of fermions, it is impossible for both the particles to be in the same state, which is in agreement with Pauli's exclusion principle.

Thus, we can conclude: if a boson is present in certain quantum state the probability of finding other boson in the same state is twice and on the other hand for fermions if an electron is in a certain quantum state the probability of finding other electron in the same state would be nil.

3.6 Distribution Functions of Three kinds of Statistics

Here are the distribution formulae for the three kinds of statistics.

1. Maxwell-Boltzmann Distribution Function

The probability $f(E)$ that a gas molecule occupies a state of energy E turns out to be

$$f_{MB}(E) = \frac{1}{e^{\alpha} e^{E/kT}} \quad (8)$$

2. Bose-Einstein Distribution Function

The probability $f(E)$ that a boson occupies a state of energy E turns out to be

$$f_{BE}(E) = \frac{1}{e^{\alpha} e^{E/kT} - 1}; \quad (9)$$

3. Fermi-Dirac Distribution Function

The probability for a fermion turns out to be

$$f_{FD}(E) = \frac{1}{e^{\alpha} e^{E/kT} + 1}; \quad (10)$$

where α depends on the properties of a particular system and is a function of T . It is always positive and the value of α is calculated by $\frac{-E_f}{kT}$.

The variation of $f(E)$ with energy E is shown below in the Fig. (3.1), for three different distribution functions.

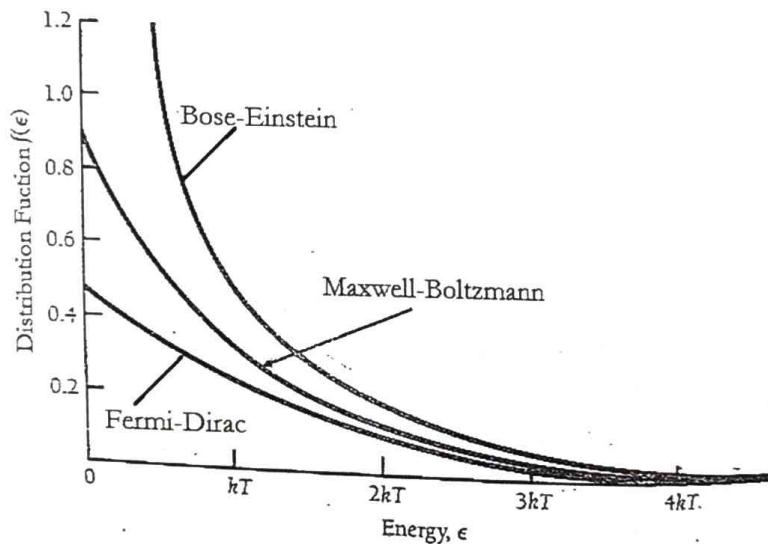


Fig. 3.1

The -1 term in the denominator of Eq. (10) expresses the increased likelihood of multiple occupancy of an energy state by bosons compared with the likelihood for distinguishable particles such as molecules of the gas. The $+1$ term in the denominator of Eq. (10) is a consequence of the uncertainty principle. No matter whatever be the values of α , E , and T are, $f(E)$ can never exceed 1. When $E \gg kT$, both the functions as given in Eqns. (9) and (10) approach to that of MB statistics as in Eq. (8). For a given ratio of E/kT , $f_{BE}(E)$ for bosons is always greater than $f_{FD}(E)$. We can also conclude that at low energies, we cannot ignore k in the denominator and we have:

$$f_{BE} > f_{MB} > f_{FD}$$

However, at high temperatures k can be ignored such that both bosons and fermions follow the classical statistics. In general, all the elementary particles found in nature are either bosons or fermions.

3.7 Comparison of the Three Statistics

Maxwell-Boltzmann	Fermi-Dirac	Bose-Einstein
1. Particles are taken distinguishable.	1. Particles are indistinguishable that obeys Pauli's exclusion principle.	1. Particles are indistinguishable that do not obey Pauli's exclusion principle.
2. Only particles are taken into consideration.	2. Only quantum states are taken into consideration.	2. Only quantum states are taken into consideration.
3. No restriction on the number of particles in a given state.	3. Restriction on the number of particles in a given quantum state.	3. Restriction on the number of particles in a given quantum state.
4. Any spin, particles far enough apart so wave functions do not overlap.	4. Spin $\frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \dots$; wave functions are anti-symmetric to interchange of particle labels.	4. Spin 1, 2, 3, ..., wave functions are symmetric to interchange of particle labels.
5. Maximum probability distribution	5. Maximum probability distribution	5. Maximum probability distribution
$\propto \frac{1}{e^{(\alpha + \beta E_i)}}$	$\propto \frac{1}{[e^{(\alpha + \beta E_i)} + 1]}$	$\propto \frac{1}{[e^{(\alpha + \beta E_i)} - 1]}$
6. -----	6. At high temperatures, Fermi-Dirac distribution approaches Maxwell-Boltzmann distribution.	6. At high temperatures, Bose-Einstein distribution approaches Maxwell-Boltzmann distribution
7. Applicable to ideal gas molecules.	7. Applicable to electrons of high concentration.	7. Applicable to photons and symmetrical particles.
8. $n_i = \frac{1}{e^{(\alpha + \beta E_i)}}$	8. $n_i = \frac{1}{[e^{(\alpha + \beta E_i)} + 1]}$	8. $n_i = \frac{1}{[e^{(\alpha + \beta E_i)} - 1]}$

3.8 Applications of Statistical Mechanics

3.8.1 Molecular speed and energies in an ideal gas

Maxwell-Boltzmann Statistics can be applied to understand the distribution of energies among the molecules of an ideal gas and is given as:

$$n_i = \frac{g_i}{e^{\alpha} e^{E_i/k_B T}}$$

If for a sample N is very large and is the total number of molecules then instead of taking discrete values of molecular energies e.g. E_1, E_2, E_3, \dots one can consider instead a continuous distribution of energies. If $n(E)dE$ is the number of molecules whose energies lies between E and $E + dE$, then the above equation can be written as:

$$n(E)dE = g(E)e^{-\alpha} e^{-\left(\frac{E}{k_B T}\right)} dE \quad (11)$$

Where $g(E)dE$ is the number of states that have energies between E and $E + dE$ and has to be calculated first. A molecule of energy E has a momentum \mathbf{p} whose magnitude p is specified by:

$$p = \sqrt{2mE} = \sqrt{p_x^2 + p_y^2 + p_z^2}$$

Each set of momentum components p_x, p_y, p_z specifies a different state of motion. Let us imagine a momentum space whose coordinate axes are p_x, p_y, p_z as in Fig. 3.2. The number of states $g(p) dp$ with momenta whose magnitudes are between p and $p+dp$ is proportional to the volume of a spherical shell in momentum space p in radius and dp thick, which is $4\pi p^2 dp$. Thus, the number of momentum states is given as:

$$g(p)dp = Bp^2 dp$$

Where B is constant and the function $g(p)$ is not same as $g(E)$. Since each momentum p corresponds to a single energy E, the number of energy states $g(E)dE$ between E and $E+dE$ is the same as number of momentum states $g(p)dp$ between p and $p+dp$ and so,

$$g(E)dE = Bp^2 dp \quad (12)$$

$$\text{Also, } p^2 = 2mE \text{ and } dp = \frac{m dE}{\sqrt{2mE}}$$

Equation (12) becomes now,

$$g(E)dE = 2m^{3/2} B \sqrt{E} dE$$

Substitute this in Eq. (11) above we get,

$$n(E)dE = e^{-\alpha} e^{-\left(\frac{E}{k_B T}\right)} 2m^{3/2} B \sqrt{E} dE$$

$$n(E)dE = e^{-\left(\frac{E}{k_B T}\right)} C \sqrt{E} dE$$

Where $C = 2m^{3/2} AB$ is a constant to be evaluated.

For finding C, we make use of normalisation condition that the total number of molecules is N, so that

$$N = \int_0^\infty n(E)dE = C \int_0^\infty \sqrt{E} e^{-\left(\frac{E}{k_B T}\right)} dE$$

From definite integrals we have,

$$\int_0^\infty \sqrt{x} e^{-ax} dx = \frac{1}{2a} \sqrt{\frac{\pi}{a}}$$

Here, $a = 1/k_B T$

$$N = \frac{C}{2} \sqrt{\pi} (kT)^{3/2}$$

$$C = \frac{2\pi N}{(\pi k_B T)^{3/2}}$$

Thus,

$$n(E) dE = \frac{2\pi N}{(\pi k_B T)^{3/2}} \sqrt{E} e^{-\left(\frac{E_i}{k_B T}\right)} dE \quad (13)$$

The above formula in Eq. (13) gives the number of molecules with energies between E and $E + dE$ in a sample of an ideal gas that contains N molecules and whose absolute temperature is T . The equation can be plotted in terms of $k_B T$.

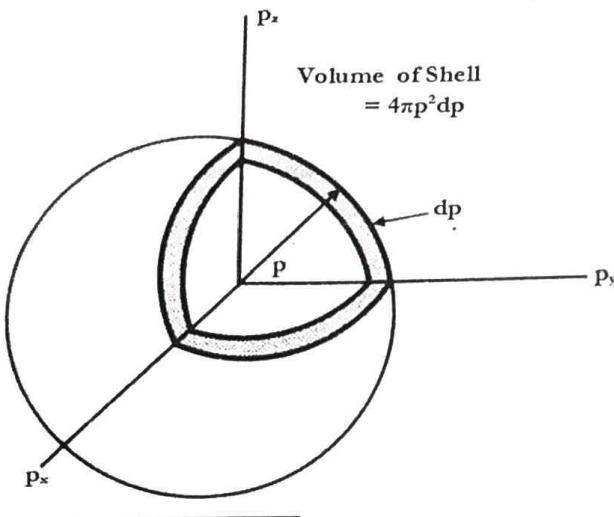


Fig. 3.2 The coordinates in momentum space are p_x , p_y and p_z . The number of momentum states available to a particle with a momentum whose magnitude is between p and $p+dp$ is proportional to the volume of a spherical shell in momentum space of radius p and thickness dp .

The curve is not symmetrical as shown in Fig. (3.2) about the most probable energy because the lower limit to E is $E = 0$ while there is in principle no upper limit.

In order to find the average or the mean energy per molecule we have to first calculate the total energy of the system. For this multiply $n(E)dE$ by the energy E and then integrate over all energies from 0 to ∞ :

$$E = \int_0^\infty E n(E) dE = \frac{2\pi N}{(\pi k_B T)^{3/2}} \int_0^\infty E^{3/2} e^{-\left(\frac{E_i}{k_B T}\right)} dE$$

Making use of the definite integral,

$$\int_0^\infty x^{3/2} e^{-ax} dx = \frac{3}{4a^2} \sqrt{\frac{\pi}{a}}$$

We have

The total energy of N gas molecules as

$$E = \frac{2\pi N}{(\pi k_B T)^{3/2}} \frac{3}{4} (k_B T)^2 \sqrt{\pi k_B T} = \frac{3}{2} N k_B T$$

The average energy of an ideal gas molecule is E/N or

Average molecular energy is

$$\bar{E} = \frac{3}{2} k_B T$$

Which is independent of the molecule's mass, a light molecule had a greater average speed at a given temperature than a heavy one.

Distribution of Molecular Speeds

The distribution of molecular speeds in an ideal gas can be found from Eq. (13) above by making the substitutions

$$E = \frac{1}{2} m v^2, \quad dE = m v \, dv$$

The result for the number of molecules with speed between v and $v + dv$ is

$$n(v)dv = 4\pi N \frac{m^{3/2}}{(2\pi k_B T)^{3/2}} v^2 e^{-mv^2/2k_B T} dv \quad (14)$$

The above Eq. (14) obtained by Maxwell in 1859, is plotted below in Fig. 3.3

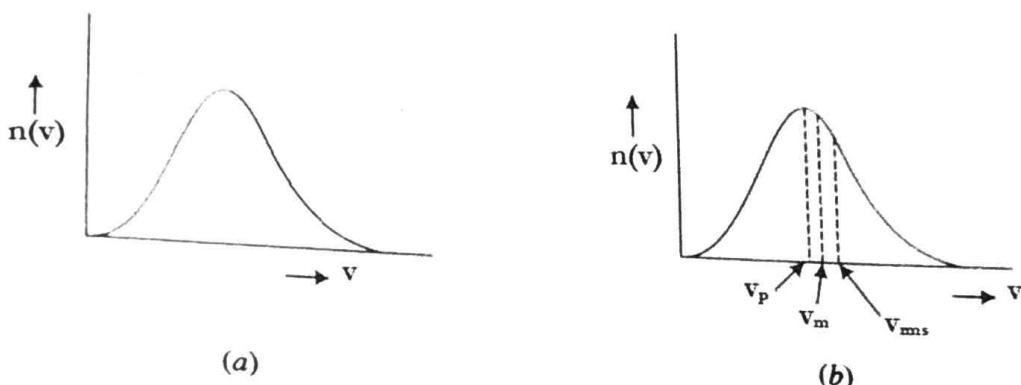


Fig. 3.3 (a) Maxwell Boltzmann speed distribution (b) most probable speed (v_p), mean speed (v_m) and rms speed (v_{rms}) marked on speed distribution curve.

The speed of a molecule with the average energy of $3/2k_B T$ is

$$v_{rms} = \sqrt{\bar{v}^2} = \sqrt{\frac{3k_B T}{m}}$$

Since, $\sqrt{1/2mv^2} = 3/2k_B T$. This speed is v_{rms} because it is the square root of the average of the squared molecular speeds – the root mean square speed – and it is not the same as the simple arithmetical average speed \bar{v} . The relationship between \bar{v} and v_{rms} depends on the distribution law that governs the molecular speeds in a particular system. For a Maxwell-Boltzmann distribution the rms speed is about 9% greater than the arithmetical average speed.

Because the speed distribution of Eq. (14) is not symmetrical, the most probable speed v_p is smaller than either \bar{v} or v_{ms} . To find v_p we set equal to zero the derivative of $n(v)$ with respect to v and solve the resulting equation for v . The result is

$$v_p = \sqrt{\frac{2k_B T}{m}}$$

3.8.2 The Black body spectrum

The failure of classical statistics to give the correct explanations for the blackbody radiation spectrum led to further explanations by S. N Bose using the Bose-Einstein Statistics. Let us first see what is blackbody radiation spectrum and how the classical statistics could not explain this very concept.

3.8.2.1 Spectral Distribution in Black-body Radiation

Lummer and Pringsheim investigated the distribution of energy for the radiation emitted by a blackbody at different temperatures. The experimental arrangement of Lummer and Pringsheim is shown in Fig 3.4. The blackbody with a small aperture is enclosed in an electrically heated chamber whose temperature was recorded by a thermocouple.

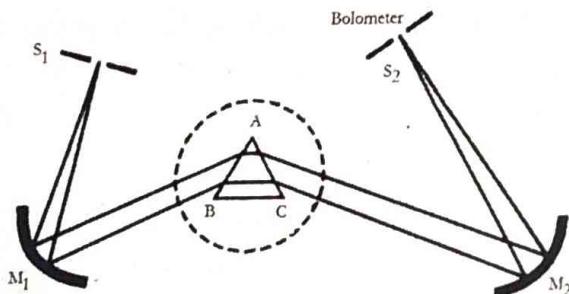


Fig. 3.4

The radiations from the black-body pass through the slit S_1 and fall on the reflector M_1 . After being reflected, the parallel beam of radiations falls on a rock-salt or parallel beam of ABC placed on the turn table of the spectrometer. The emergent light is focused by the reflector (concave mirror) M_2 on a line bolometer placed behind the slit S_2 . The bolometer is connected to a sensitive galvanometer. The turn table is rotated slowly so that different parts of the radiation spectrum successively fall on the bolometer and the corresponding deflections in the galvanometer connected in the bolometer circuit are read. The intensity of each line is proportional to the deflection in the galvanometer. A curve between intensity and the wavelength is drawn Fig. 3.5.

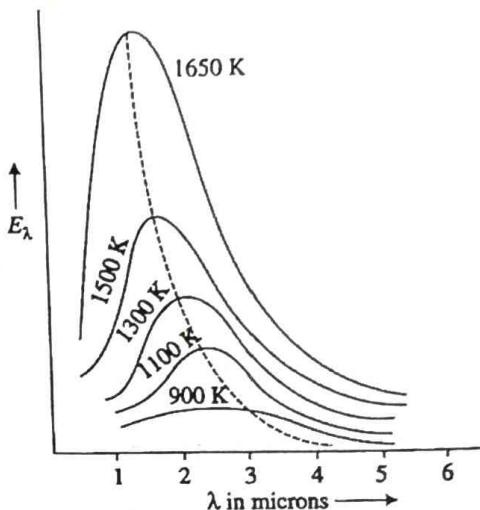


Fig. 3.5

Explanation of the curve

- The energy is not uniformly distributed in the radiation spectrum of a blackbody.
- At a given temperature, the intensity of radiation increases with increase of wavelength and becomes maximum at a particular wavelength. By further increasing the wavelength, intensity of heat radiations decreases.
- An increase in temperature causes a decrease in \$\lambda_m\$ such that \$\lambda_m T = \text{constant} = 0.2896 \text{ cm K}\$, where \$\lambda_m\$ is the wavelength for which the energy emitted is maximum. This relation is called Wien's displacement law.
- An increase in temperature causes an increase in energy emission for all wavelengths.
- The area under each curve represents the total energy emitted by the blackbody at a particular temperature, for the range of the wavelengths considered. This area increases with increase of temperature.

It is found that area is directly proportional to the fourth power of the absolute temperature i.e. \$E \propto T^4\$ which is Stefan's law.

3.8.2.2 Wien's Displacement Law in Terms of \$E_\lambda\$ and T

In 1893, Wien's showed that the energy \$E_\lambda d\lambda\$ i.e. radiation per unit area per second within the wavelength range \$\lambda\$ and \$\lambda + d\lambda\$ of electromagnetic radiation by a black-body at temperature T, is given by:

$$E_\lambda d\lambda = \frac{A}{\lambda^5} f(\lambda T) d\lambda \quad (15)$$

$$E_\lambda d\lambda = AT^5 F(\lambda T) d\lambda \quad (16)$$

where A is a constant and \$f(\lambda T)\$ and \$F(\lambda T)\$ are functions of the product \$\lambda T\$. From Eqns. (15) and (16), it is evident that:

$$\begin{aligned} T^5 F(\lambda T) &= \frac{1}{\lambda^5} f(\lambda T) \\ F(\lambda T) &= (\lambda T)^{-5} f(\lambda T) \end{aligned} \quad (17)$$

Wien obtained Eqns. (15) and (16) by considering the radiation field having thermodynamic properties such as temperature, pressure, entropy etc. Eq. (16) shows that for any black body:

$$\frac{E_\lambda}{T^5} = A F(\lambda T)$$

Thus, if $E_{\lambda_1}, E_{\lambda_2}, \dots$ are the emissive powers for the respective wavelengths $\lambda_1, \lambda_2, \dots$, and if T_1, T_2, \dots are the corresponding absolute temperatures of the black body, then

$$\frac{E_{\lambda_1}}{T_1^5} = AF(\lambda_1 T_1), \quad \frac{E_{\lambda_2}}{T_2^5} = AF(\lambda_2 T_2), \dots$$

If the wavelengths are inversely proportional to the corresponding temperatures, i.e. if

$$\lambda_1 T_1 = \lambda_2 T_2 = \dots, \text{then we have}$$

$$\frac{E_{\lambda_1}}{T_1^5} = \frac{E_{\lambda_2}}{T_2^5} = \frac{E_{\lambda_3}}{T_3^5} = \dots = \text{constant.} \quad (18)$$

Thus, the emissive power E_λ of a perfectly black body for wavelength λ is directly proportional to the fifth power of the absolute temperature, if the wavelength is inversely proportional to the absolute temperature. This conclusion is known as the Wien Displacement law in terms of E_λ and T .

3.8.2.3 Wien's Radiation Formula

In 1896, Wien derived the following formula for radiation from a black body:

$$E_\lambda d\lambda = \frac{8\pi hc}{\lambda^5} e^{-hc/\lambda kT} d\lambda \quad (19)$$

For obtaining the formula, the following arbitrary assumptions were made:

- (1) The radiation inside a hollow enclosure is produced by the resonators of molecular dimensions.
- (2) The frequency of the radiation emitted is proportional to the kinetic energy of the resonator.
- (3) The intensity of radiation of any particular wavelength is proportional to the number of resonators having required amount of energy.

The formula explains the experimental results fairly well for low values of λT but for higher values it gives values of E_λ lower than the experimental values.

3.8.2.4 Rayleigh-Jeans Law

In 1900, Lord Rayleigh applied the principle of equipartition of energy to the electromagnetic vibrations. This contribution from J.H. Jeans led to the deduction of a formula for energy per unit volume inside an enclosure with perfectly reflecting walls. This formula is called the Rayleigh-Jeans Law. According to this law, the energy density, $E_v dv$, i.e. the amount of energy per unit volume of the enclosure in the frequency range from v to $v + dv$ is given by:

$$E_v dv = \frac{8\pi v^2 kT}{c^3} dv \quad (20)$$

where E_v is the energy per unit volume per unit frequency range at frequency v , k is Boltzmann's constant and c is the speed of light in free space.

The Rayleigh-Jeans formula can be transformed in terms of wavelength λ by using the relation:

$$v = \frac{c}{\lambda} \text{ and } dv = -\frac{c}{\lambda^2} d\lambda$$

Substituting this value of dv , the formula given by Eq. (20) can be written as

$$E_\lambda d\lambda = \frac{8\pi kT}{c^3} \cdot \frac{c^2}{\lambda^2} \cdot \left(-\frac{c}{\lambda^2}\right) d\lambda$$

Considering the modulus of the energy density, we have;

$$E_\lambda d\lambda = \frac{8\pi kT}{\lambda^4} d\lambda \quad (21)$$

The Eq. (21) is another form of the Rayleigh-Jeans law, depicting variation of energy density of radiation with the wavelength. The law explains the experimental facts for very long wavelengths, but not for shorter wavelengths. According to the law as λ decreases, the energy density E_λ will continuously increase and as λ tends to zero, E_λ approaches infinity. This is contradictory to the experimental results.

The law leads to an absurd result which is as follows. The total energy of radiation per unit volume of the enclosure for all wavelengths from zero to infinity is given by

$$E = \int_0^{\infty} E_{\lambda} d\lambda = \int_0^{\infty} \frac{8\pi kT}{\lambda^4} d\lambda = 8\pi kT \left[-\frac{1}{3\lambda^3} \right] = \infty$$

This result shows that for a given quantity of radiant energy, all energy will finally be confined in vibrations of very small wavelengths. Thus, if the classical treatment is correct, on opening a shutter in the black body cavity, we would be bombarded with radiation of extremely short wavelengths. But experimental results show that $E_{\lambda} d\lambda \rightarrow 0$ as $\lambda \rightarrow 0$. This discrepancy between the theoretical conclusion and the experimental result is called "ultraviolet catastrophe". This absurd result is because of the assumption that energy can be absorbed or emitted by the atomic oscillators continuously by any amount.

3.8.2.5 Planck's Radiation Law

Planck found an empirical formula to explain the experimentally observed distribution of energy in the spectrum of a black-body. The formula may be deduced using following assumptions which may be called as Planck's hypothesis.

1. A black-body radiation chamber is filled up not only with radiations, but also with simple harmonic oscillators or resonators of molecular dimensions (called as Planck's oscillators or resonators) which can vibrate with all possible frequencies. The vibration of the resonator entails one degree of freedom only.
2. The oscillators or resonators cannot radiate or absorb energy continuously; but an oscillator of frequency v can only radiate or absorb energy in units or quanta of magnitude hv , where h is a universal constant, called the Planck's constant and its value being equal to 6.62×10^{-34} joule-sec. This assumption is the most revolutionary in character. In other words, this states that the exchange between radiation and matter cannot take place continuously, but are limited to discrete set of values $0, hv, 2hv, 3hv, \dots, nhv$, i.e., multiples of some small unit, called the quantum.

In order to derive Planck's radiations law, we shall first derive the number of resonators per unit volume; lying in the frequency range v and $v + dv$ and the average energy of Planck's resonator.

The number of modes of vibration per unit volume with frequency range v and $v + dv$ is

$$= \frac{4\pi v^2 dv}{c^3}$$

Now the black body radiation travel with velocity of light c and are transverse in character unlike sound waves in the string which are longitudinal.

As there are two possible polarization states for each transverse wave, the number of modes of vibration of wave is twice as that for longitudinal wave. Therefore, for black body radiations or electromagnetic waves, the number of modes of vibration per unit volume within frequency range v and $v + dv$ is

$$= \frac{2 \times 4\pi v^2 dv}{c^3} = \frac{8\pi v^2 dv}{c^3}$$

Average energy of Planck's Oscillator

If N is the total number of Planck's resonators and E their total energy, then energy per Planck Oscillator is given by:

$$\bar{\epsilon} = \frac{E}{N}$$

According to Maxwell's law of molecular motion, if ϵ is a certain amount of energy, the probabilities that a system will have energies $0, \epsilon, 2\epsilon, \dots, r\epsilon, \dots$ are in the ratio;

$$1:e^{-\epsilon/kT}:e^{-r\epsilon/kT}:\dots\text{etc.}$$

If N_0 is the number of resonators having energy zero, then the number of resonators N_1 having energy ε will be $N_0 e^{-\varepsilon/kT}$, the number of resonators N_2 having energy 2ε will be $N_0 e^{-2\varepsilon/kT}$ and in general, the number of resonators N_r having energy $r\varepsilon$ will be $N_0 e^{-r\varepsilon/kT}$ and so on

$$\begin{aligned} N &= N_0 + N_1 + N_2 + \dots + N_r + \dots \\ &= N_0 + N_0 e^{-\varepsilon/kT} + N_0 e^{-2\varepsilon/kT} + \dots + N_0 e^{-r\varepsilon/kT} + \dots \\ &= N_0 [1 + e^{-\varepsilon/kT} + e^{-2\varepsilon/kT} + \dots + e^{-r\varepsilon/kT} + \dots]. \end{aligned}$$

Putting $e^{-\varepsilon/kT} = y$.

$$N = N_0 [1 + y + y^2 + \dots + y^r + \dots]$$

$$N = \frac{N_0}{1-y}.$$

The total energy of Planck's resonator will be

$$\begin{aligned} E &= 0 \times N_0 + \varepsilon \times N_1 + 2\varepsilon \times N_2 + \dots + r\varepsilon \times N_r + \dots \\ &= 0 + \varepsilon N_0 e^{-\varepsilon/kT} + 2\varepsilon N_0 e^{-2\varepsilon/kT} + \dots + r\varepsilon N_0 e^{-r\varepsilon/kT} + \dots \\ &= N_0 \varepsilon [e^{-\varepsilon/kT} + 2e^{-2\varepsilon/kT} + \dots + re^{-r\varepsilon/kT} + \dots] \\ &= N_0 \varepsilon [y + 2y^2 + \dots + ry^r + \dots] \end{aligned} \tag{22}$$

Let $S = y + 2y^2 + \dots + ry^r + \dots$

$$\therefore Sy = y^2 + 2y^3 + \dots + (r-1)y^r.$$

On subtracting, $S - Sy = y + y^2 + \dots + y^r + \dots$

$$S(1-y) = \frac{y}{1-y} \Rightarrow S = \frac{y}{(1-y)^2}.$$

Also, $E = N_0 \varepsilon S$

Therefore, the average energy of a resonator will be

$$\begin{aligned} \bar{\varepsilon} &= \frac{E}{N} = \frac{N_0 \varepsilon \frac{y}{(1-y)^2}}{\frac{N_0}{1-y}} \\ &= \frac{\varepsilon y}{1-y} = \frac{\varepsilon e^{-\varepsilon/kT}}{1 - e^{-\varepsilon/kT}} \end{aligned}$$

$$\text{Or } \bar{\varepsilon} = \frac{\varepsilon}{e^{-\varepsilon/kT}}$$

According to Planck's hypothesis of quantum theory, $\varepsilon = hv$; therefore, the average of Planck's oscillator is given by

$$\bar{\varepsilon} = \frac{hv}{e^{hv/kT} - 1}. \tag{23}$$

Now, the energy density belonging to the range dv can be obtained by multiplying the average energy of a Planck's oscillator by the number of oscillators per unit volume, in the frequency range v and $v + dv$, i.e.

$$\text{or } E_v dv = \left(\frac{8\pi v^2}{c^3} dv \right) \left(\frac{hv}{e^{hv/kT} - 1} \right)$$

$$E_v dv = \frac{8\pi hv^3}{c^3} \cdot \frac{1}{e^{hv/kT} - 1} dv \quad (24)$$

Where $E_v dv$ is energy density (i.e., total energy per unit volume) belonging to the range dv . Eq. (24) is called Planck's radiation law in terms of frequency.

The energy density $E_\lambda d\lambda$ belonging to range $d\lambda$ can be obtained by using the relation $v = \frac{c}{\lambda}$ and hence,

$$|dv| = \left| -\frac{c}{\lambda^2} d\lambda \right|$$

$$\text{Thus, } E_\lambda d\lambda = \frac{8\pi h}{c^3} \left(\frac{c^3}{\lambda^3} \right) \cdot \frac{1}{e^{hc/\lambda kT} - 1} \cdot \left| -\frac{c}{\lambda^2} d\lambda \right|$$

$$E_\lambda d\lambda = \frac{8\pi hc}{\lambda^5} \cdot \frac{d\lambda}{e^{hc/\lambda kT} - 1}. \quad (25)$$

This is Planck's radiation law in terms of wavelength.

Wien's Law and Rayleigh Jeans Law from Planck's radiation Law

Planck's radiation law is

$$E_\lambda d\lambda = \frac{8\pi hc}{\lambda^5} \cdot \frac{d\lambda}{e^{hc/\lambda kT} - 1}.$$

(a) For shorter wavelengths $e^{hc/\lambda kT}$ becomes large as compared to unity and hence Planck's law reduces to

$$E_\lambda d\lambda = \frac{8\pi hc}{\lambda^5} \cdot \frac{d\lambda}{e^{hc/\lambda kT}}$$

$$E_\lambda d\lambda = \frac{8\pi hc}{\lambda^5} e^{-hc/\lambda kT} d\lambda$$

which is Wien's law.

(b) For longer wavelengths $e^{hc/\lambda kT}$ may be approximated to $(1 + \frac{hc}{\lambda kT})$ and hence Planck's law reduces to

$$E_\lambda d\lambda = \frac{8\pi hc}{\lambda^5} \frac{1}{(1 + \frac{hc}{\lambda kT} - 1)} d\lambda$$

$$= \frac{8\pi hc}{\lambda^5} \cdot \frac{\lambda kT}{hc} d\lambda$$

$$E_\lambda d\lambda = \frac{8\pi kT}{\lambda^4} d\lambda$$

which is Rayleigh-Jeans law

Thus, we see that Wien's law holds for shorter wavelengths and Rayleigh-Jeans law for longer wavelengths. We can say that both the Wien's and Rayleigh-Jeans law are incorporated in the Planck's law.

3.9 Planck's Validation for Experimental Curve of blackbody radiation

The experimental curves for black body radiation were obtained by Lummer and Pringsheim in different range of temperatures. It was neither completely explained by Wein's nor Rayleigh Jeans but the Planck's radiation formula validates the same.

The actual form is the distribution curve which has been derived by Planck from theoretical considerations and represents the experimental results accurately. Planck's formula is consistent with Wien's law and hence an experimental verification of Planck's formula is the same thing as an experimental verification of Wien's law. The curve shown in Fig. 3.6 for a temperature of 1600 K, in accordance with these laws brings out clearly the close agreement between Wien's and Planck's formula and their wide deviation from that of Rayleigh-Jeans formula. The circles show the actual observation

on the energy distribution in the spectrum of a black body at 1600K. The thick full line shows the distribution predicted by Planck's formula indicating that the Planck's law is in perfect agreement with the experiments. The lower dotted line, which coincides with the thick full line upto about $\lambda = 2.2$ microns, corresponds to Wien's formula, while the upper thin solid line is from the Rayleigh-Jeans formula. It is evident that the curve obtained by Planck approximates to that of Wien's for small wavelengths and to that of Rayleigh-Jeans for long wavelengths.

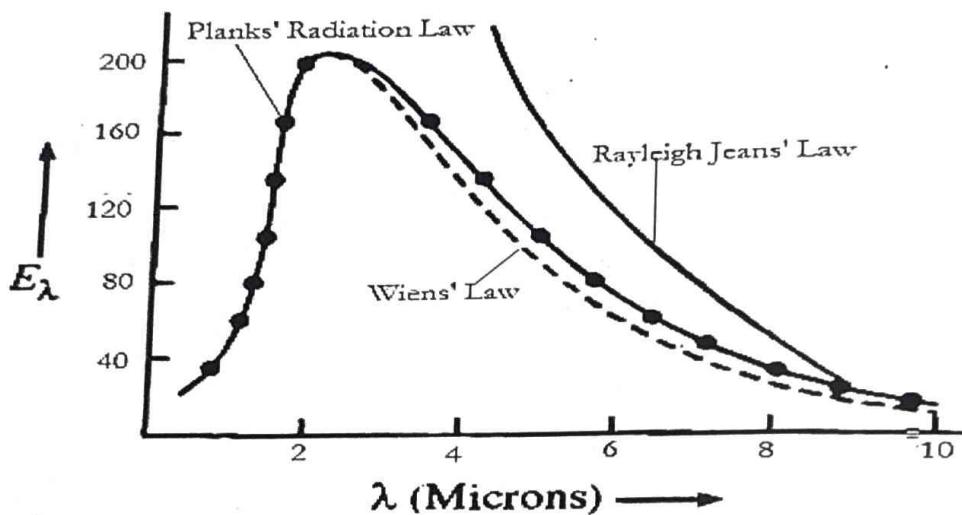


Fig. 3.6

It is desirable at this stage to have a comparison between the three radiation formulae in an analytical way. Putting $\frac{hv}{kT} = \frac{hc}{\lambda kT} = x$, the three radiation formulae may be written as:

$$\text{Rayleigh-Jeans} \quad E_\lambda d\lambda = \frac{8\pi kT}{\lambda^4} d\lambda$$

$$\text{Wien's} \quad E_\lambda d\lambda = \frac{8\pi kT}{\lambda^4} \cdot \frac{x}{e^x} d\lambda$$

$$\text{Planck's} \quad E_\lambda d\lambda = \frac{8\pi kT}{\lambda^4} \cdot \frac{x}{e^x - 1} d\lambda.$$

It can be seen that both the parts (exponential growth and exponential decay), of the black-body radiation curve which were separately explained by Wein and Rayleigh Jeans, respectively, are validated by Planck's single formula. Thus, the Wien's and Planck's formulae differ from that of Rayleigh-Jeans through the presence of the additional factors $\frac{x}{e^x}$ and $\frac{x}{e^x - 1}$ respectively. As we have already shown that both Wien's and Rayleigh-Jeans formulae are the special cases, Planck's formula which seems to be the correct formula for thermal radiation and is applicable for all wavelengths.

Bose-Einstein statistics applied to the Black Body radiation spectrum

Though Eq. (25) above explains the blackbody radiation completely. Planck got the right formula but his derivation had flaw as we know that the energies of the harmonic oscillator are given by $\varepsilon_n = (n + \frac{1}{2})hv$ with ($n = 0, 1, 2, \dots$) and not by $\varepsilon_n = nhv$. If the energies of the harmonic oscillator are taken as $\varepsilon_n = (n + \frac{1}{2})hv$, the average energy of the harmonic oscillator does not come out to be $hv(e^{\frac{hv}{kT}} - 1)$ and thus will lead to a different formula from Eq. (25). Thus, further work was carried out on the radiation formula with the point that the electromagnetic waves in a cavity can be considered

as many photons in the cavity. The photons have spin 1 (bosons) and follow the statistics (Bose-Einstein statistics) according to which the average number of photons $f(\nu)$ in each state of energy $\varepsilon = h\nu$ is given by:

$$f(\varepsilon) = \frac{1}{e^{\alpha+\varepsilon/kT} - 1} = \frac{1}{e^{\alpha+h\nu/kT} - 1}$$

The value of α depends on the number of particles in the system. As the number of photons in a cavity need not be conserved and are continuously exchanged from the surroundings $\alpha = 0$. Hence, the Bose-Einstein distribution function for photons is

$$f(\varepsilon) = \frac{1}{e^{h\nu/kT} - 1}$$

Which gives the average number of photons in each state of energy $\varepsilon = h\nu$ and so the average energy of all the photons that are in the state of energy $h\nu$ is given by,

$$h\nu(e^{\frac{h\nu}{kT}} - 1)$$

Bose found that the number of states per unit volume having energies between $h\nu$ and $h(\nu + d\nu)$ is

$$g(\nu) d\nu = \frac{8\pi\nu^2}{c^3} d\nu$$

Thus, the energy per unit volume $u(\nu) d\nu$ radiated by a black body between ν and $\nu + d\nu$ is equal to the number of states per unit volume having energies between $h\nu$ and $h(\nu + d\nu)$ multiplied by the average energy of a state i.e.

$$E_\nu d\nu = \frac{8\pi h\nu^3}{c^3} \cdot \frac{1}{e^{h\nu/kT} - 1} d\nu$$

Which is same as Planck's Radiation formula. Therefore, the Bose Einstein statistics gives proper explanation of black body radiation formula.

3.10 Fermi-Dirac Distribution Function

Fermi Dirac Statistics is obeyed by indistinguishable particles of half-internal spin that have anti-symmetric wave function and obey Pauli Exclusion Principle. The most probable distribution of n_i fermions in g_i states having energy ε_i is given by:

$$n_i = \frac{g_i}{e^{\alpha+\beta\varepsilon_i} + 1} \quad (26)$$

It can be shown thermodynamically that $\beta = 1/kT$ and $\alpha = -\varepsilon_F/kT$ where ε_F is called Fermi energy. Thus, we can write the most probable distribution of n_i fermions in g_i states as:

$$n_i = \frac{g_i}{e^{(\varepsilon_i-\varepsilon_F)/kT} + 1} \quad (27)$$

This equation is also known as Fermi-Dirac Distribution law.

The Fermi Dirac statistics is applicable to electron gas in metals and so it leads to the properties of metals like electrical and thermal conductivity, thermionic emission, photo electric effect and specific heat of metals.

3.11 Fermi-Energy

Let us consider N-non-interacting electrons contained in a box at absolute zero temperature. Using Pauli's exclusion principle on the energy distribution of condition electrons, it can be shown that all the energy levels below a certain level will be filled with electrons and all the levels above it will be empty.

Quantum Statistics

The level which divides the filled and empty levels is called the Fermi level at absolute zero and the corresponding energy of that level is called the Fermi energy and is denoted by $\varepsilon_F(0)$. We note that according to quantum theory, even at absolute zero, all the electrons are not condensed into a state of zero energy as it happens in classical theory, but they occupy states between energy values 0 and $\varepsilon_F(0)$. This is the essential feature of quantum theory.

Let N non-interacting electrons be distributed among quantum states such that there are $n_1, n_2, \dots, n_i \dots$ number of particles in quantum states possessing constant energies $\varepsilon_1, \varepsilon_2, \dots, \varepsilon_i \dots$ respectively. If g_i is statistical weight of i^{th} quantum state, then according to Fermi-Dirac distribution law, the most probable distribution is given by

$$n_i = \frac{g_i}{e^{\alpha + \beta \varepsilon_i + 1}} \text{ where } \beta = \frac{1}{kT} \quad (28a)$$

This may be expressed as

$$n_i = \frac{g_i}{\frac{1}{A} e^{\beta \varepsilon_i + 1}} \quad (28b)$$

$$A = e^{-\alpha} \quad (29)$$

Where

A as in the denominator of Eq. (28a) a positive sign appears before one, α may be positive or negative. The number of particle states lying between momentum P and $P + dP$ is given by

$$g(P) dP = g_s \cdot \frac{4\pi P^2}{h^3/V} = g_s \cdot \frac{4\pi V p^2 dP}{h^3/V} \quad (30)$$

Where g_s is the spin degeneracy factor caused by the particle spin s and given by

$$g_s = (2s + 1) = 2 \text{ for electron gas since } s = 1/2 \quad (31)$$

This means that each level can be occupied by two particles one with spin up and the other with spin down ($\uparrow \downarrow$).

Since $\varepsilon = P^2/2m$ or $dP = (m/2\varepsilon)^{1/2} d\varepsilon$, the number of states between energy ε and $\varepsilon + d\varepsilon$ given by

$$g(\varepsilon) = 2 \frac{4\pi V (2m\varepsilon) \left(\frac{m}{2\varepsilon}\right)^{1/2} d\varepsilon}{h^3} \quad (32)$$

For a gas of fermions at temperature T in a volume, the mean number of fermions in the energy range between ε and $\varepsilon + d\varepsilon$ is given by

$$dn(\varepsilon) = \frac{8\pi m V}{h^3} \sqrt{2m} \cdot \frac{\varepsilon^{1/2} d\varepsilon}{e^{\alpha + \varepsilon/kT} + 1}. \quad (33)$$

The value of ε_F is determined by the condition that the total number of particles is constant at a given temperature T .

The expression for the number of fermions with energy between ε and $\varepsilon + d\varepsilon$ is written as

$$n(\varepsilon) d\varepsilon = f(\varepsilon) g(\varepsilon) = \frac{8\pi m V}{h^3} \sqrt{2m} \frac{\varepsilon^{1/2} d\varepsilon}{e^{\varepsilon - \varepsilon_F/kT} + 1} \quad (34)$$

This expression is called Fermi-Dirac Energy Distribution law.

Thus, at absolute zero all states with $0 < \varepsilon \leq \varepsilon_F(0)$ are completely filled and states with $\varepsilon > \varepsilon_F(0)$ are empty. The value $\varepsilon_F(0)$ of ε_F at $T = 0$ K is determined by

$$\begin{aligned} n &= \int_0^{\varepsilon_F(0)} dn(\varepsilon) = \int_0^{\varepsilon_F(0)} f(\varepsilon) g(\varepsilon) d\varepsilon = \int_0^{\varepsilon_F(0)} g(\varepsilon) d\varepsilon \\ &= \int_0^{\varepsilon_F(0)} \frac{8\pi m V}{h^3} (2m)^{\frac{1}{2}} \varepsilon^{\frac{1}{2}} d\varepsilon = \frac{8\pi m V}{h^3} (2m)^{\frac{1}{2}} \cdot \frac{2}{3} [\varepsilon_F(0)]^{3/2} \\ i.e. \quad \varepsilon_F(0) &= \frac{h^3}{8m} \left(\frac{3n}{\pi V}\right)^{2/3} \end{aligned} \quad (35)$$

This represents the energy of the highest level occupied at $T = 0\text{ K}$.

3.12 Mean Energy /Average Energy of electrons

The number of electrons in an electron gas having energies between ε and $\varepsilon + d\varepsilon$ is given by

$$n(\varepsilon) d\varepsilon = \frac{8\pi m V}{h^3} \sqrt{2m} \cdot \frac{\varepsilon^{1/2} d\varepsilon}{e^{(\varepsilon - \varepsilon_F)/kT} + 1} \quad (36)$$

Where m is mass of electrons, the Fermi energy $\varepsilon_F(0)$ is

$$\begin{aligned} \varepsilon_F(0) &= \frac{h^3}{8m} \left(\frac{3N}{\pi V} \right)^{2/3} \\ \therefore \frac{V}{h^3} &= \frac{3N}{8\pi m \sqrt{2m}} [\varepsilon_F(0)]^{-3/2}. \end{aligned}$$

Substituting this in Eq. (34), we get

$$n(\varepsilon) d\varepsilon = \frac{3}{2} N [\varepsilon_F(0)]^{-3/2} \frac{\varepsilon^{1/2} d\varepsilon}{e^{(\varepsilon - \varepsilon_F)/kT} + 1}.$$

At $T = 0\text{K}$, all of the electrons have energies less than to $\varepsilon_F(0)$ (i.e. $\varepsilon \leq \varepsilon_F$), so that at $T = 0\text{K}$, we have

$$e^{(\varepsilon - \varepsilon_F)kT} = e^{-\infty} = 0.$$

\therefore at absolute zero

$$n(\varepsilon) d\varepsilon = \frac{3}{2} N [\varepsilon_F(0)]^{-3/2} \varepsilon^{1/2} d\varepsilon. \quad (37)$$

The total energy at absolute zero

$$\begin{aligned} E_0 &= \int_0^{\varepsilon_F(0)} \varepsilon n(\varepsilon) d\varepsilon \\ &= \frac{3}{2} N [\varepsilon_F(0)]^{-3/2} \int_0^{\varepsilon_F(0)} \varepsilon^{3/2} d\varepsilon = \frac{3}{5} N \varepsilon_F(0). \end{aligned}$$

\therefore Average energy $\bar{\varepsilon}_0$ at absolute zero is

$$\bar{\varepsilon}_0 = \frac{\varepsilon_0}{N} = \frac{3}{5} \varepsilon_F(0).$$

3.13 Applications

3.13.1 Fermi-Dirac function applied to free electrons at different temperature

Let us consider the situation at absolute zero temperature i.e.

At $T = 0\text{K}$;

$$(\varepsilon - \varepsilon_F)/kT \rightarrow -\infty \text{ (when } \varepsilon < \varepsilon_F\text{)}$$

$$\rightarrow +\infty \text{ (when } \varepsilon > \varepsilon_F\text{).}$$

Thus at $T = 0\text{K}$

$$\begin{aligned} \frac{\varepsilon - \varepsilon_F}{kT} &\rightarrow -\infty \text{ when } \varepsilon < \varepsilon_F \\ \frac{\varepsilon - \varepsilon_F}{kT} &\rightarrow +\infty \text{ when } \varepsilon > \varepsilon_F \end{aligned}$$

$$\begin{aligned} f(\varepsilon) &= \frac{1}{e^{-\infty} + 1} = 1 \text{ for } \varepsilon < \varepsilon_F(0) \\ &= \frac{1}{e^{\infty} + 1} = 0 \text{ for } \varepsilon > \varepsilon_F(0) \end{aligned}$$

This is shown in Fig. 3.7, by solid line

Thus, at $T = 0\text{ K}$, the probability of occupation of all the states having energies $\varepsilon < \varepsilon_F$ is one or we can say that at $T = 0\text{K}$ all the states below energy ε_F are occupied and the probability of occupation of all the states having energies $\varepsilon > \varepsilon_F$ is zero. So, we can say that at $T = 0\text{K}$ all the states above energy ε_F are unoccupied.

Thus, Fermi energy is defined as the maximum energy of a particle at $T = 0\text{K}$

At $T \neq 0K$;

$$\text{For } \varepsilon = \varepsilon_F, f(\varepsilon) = \frac{1}{e^{(\varepsilon_i - \varepsilon_F)/kT} + 1} = \frac{1}{e^0 + 1} = \frac{1}{2}$$

$$\text{For, } \varepsilon < \varepsilon_F, f(\varepsilon) = \frac{1}{e^{(\varepsilon_i - \varepsilon_F)/kT} + 1} = \frac{1}{e^{(a-ve \text{ quantity})} + 1}$$

= a quantity slightly less than one that decreases as ε increases.

$$\text{For, } \varepsilon > \varepsilon_F, f(\varepsilon) = \frac{1}{e^{(\varepsilon_i - \varepsilon_F)/kT} + 1} = \frac{1}{e^{(a+ve \text{ quantity})} + 1}$$

= a quantity slightly less than $1/2$ that decreases as ε increases.

$$\text{For, } \varepsilon = 0, f(\varepsilon) = \frac{1}{e^{(\varepsilon_i - \varepsilon_F)/kT} + 1} = \frac{1}{e^{-\varepsilon_F/kT} + 1}$$

= a quantity less than 1 that decreases as T increases.

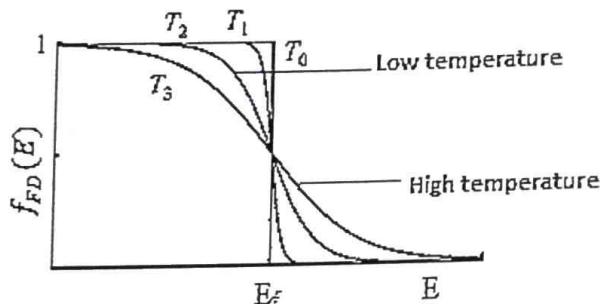


Fig. 3.7 Distribution function for fermions at different temperatures

Fig. 3.7 above shows the variation $f(E)$ at three different temperatures $T = 0K, T_1, T_2$ where $T_2 > T_1$. At $T = 0 K$, all the particles reside below the Fermi energy. At finite temperatures, the probability of occupation of higher energy states is small in comparison to the lower energy states.

2. Specific Heat Anomaly of metals and its Solution:

Experiments show that the specific heat of metals referred to 1 g-atom does not exceed a value of $3R$ even at very large temperatures.

Theoretically the specific heat of metal shall get contribution from the atoms as well as the free electrons i.e.

$$C_V (\text{metals}) = C_V (\text{atomic}) + C_V (\text{electronic}).$$

According to the law of equipartition of energy of classical statistics, the average energy associated with each quadratic term is $\frac{1}{2} kT$. Further according to the classical kinetic theory of matter, the atoms of a solid substance are at rest under the action of their mutual attractions and repulsions at the absolute zero of temperature. The energy of solids in this state is assumed to be zero. When the temperature is raised, the atoms are set into vibrations about their positions of equilibrium and the restoring force proportional to displacement is produced as long as the amplitude of vibration is not too large. Thus, the vibrations of the atoms are simple harmonic in nature.

In the case of S.H.M, the energy of atom along one co-ordinate can be represented as the sum of two quadratic terms viz

$$\frac{1}{2} mx^2 + \frac{1}{2} Kx^2$$

Where K is the force constant, x is the displacement from mean position and $x = dx/dt$. Here the first term represents the kinetic and the second term represents the potential energy.

According to law of equipartition of energy, the average energy associated with the motion of an atom along one co-ordinate

$$2 \times \frac{1}{2} kT = kT.$$

As each atom is free to vibrate along three co-ordinate axes, the total average energy of each atom $3kT$. The total energy of 1 gram atom of solid containing N (= Avogadro number) atom is given by

$$E_{\text{atomic}} = NkT = 3RT$$

Where

$$R = Nk = \text{gas constant for a gram-atom.}$$

Therefore, atomic contribution to specific heat referred to 1 gram-atom of metal is:

$$C_V(\text{atomic}) = \left[\frac{\partial E_{\text{atomic}}}{\partial T} \right]_F = \frac{\partial}{\partial T}(3RT) = 3R. \quad (38)$$

As the electrons inside the metal are assumed to be free to move along three axes, they do not possess the potential energy; but possess only the kinetic energy. According to law of equipartition of energy. The average energy associated with the motion

$$= 3 \cdot \frac{1}{2} kT = \frac{3}{2} kT.$$

Assuming one free electron per atom in the metal, the total energy of a gram-atom of solid containing N_{atom} is

$$E_{\text{Electronic}} = \frac{3}{2} NkT = \frac{3}{2} RT.$$

Therefore, the electronic contribution to specific referred to 1 gram-atom is

$$C_V(\text{electronic}) = \frac{\partial E_{\text{Electronic}}}{\partial T} = \frac{\partial}{\partial T}\left(\frac{3}{2} RT\right) = \frac{3}{2} R. \quad (39)$$

Hence classically the specific heat referred to 1 gram-atom of metals is

$$C_V = 3R + \frac{3}{2} R = \frac{9}{2} R \quad (40)$$

Which is too high as compared to the experimental value $3R$. This specific heat anomaly of metals is the chief problem which the classical statistic could not solve. This specific heat anomaly was solved by Fermi-Dirac statistics in a very elegant manner

According to Fermi-Dirac Statistics, the electronic contribution to the specific heat gram-atom of metal at low temperature is

$$C_V(\text{electronic}) = \frac{1}{2} \frac{Nk^2\pi^2}{\varepsilon_F(0)} T = \lambda T \quad (41)$$

Where

$$\lambda = \frac{1}{2} \frac{Nk^2\pi^2}{\varepsilon_F(0)} \quad (42)$$

Therefore, the heat capacity of electrons per kmol of a monovalent metal at constant volume i.e., the specific heat of electrons in metal at constant volume is given as:

$$C_V(\text{electronic}) = N \frac{\partial E_{\text{Electronic}}}{\partial T} = \frac{N_A 5\pi^2 \bar{E}_0}{6} \left(\frac{k}{\varepsilon_F} \right)^2 T = \frac{\pi^2}{2} \left(\frac{kT}{\varepsilon_F} \right) kN = \frac{\pi^2}{2} \left(\frac{kT}{\varepsilon_F} \right) R \quad (43)$$

here $kN = R$ is gas constant and N is Avogadro number.

Therefore, the specific heat of metals should be equal to the sum of the atomic and electronic specific heat. But at the room temperature or higher temperatures the value of $\frac{\pi^2}{2} \left(\frac{kT}{\varepsilon_F} \right)$ is very small (much smaller than $3/2$) and so the atomic specific heat (as given by Dulong Petit law for room temperature

or higher temperatures as $C = 3/2 R$) dominates over the electronic specific heat. Therefore, for a wide range of temperatures, specific heat of metals is almost equal to the atomic specific heat. However, at low temperatures, the contribution of electronic specific heat is proportional to T . As the temperature is increased to high values, whereas the atomic specific heat is equal to $C = 3/2R$, the electronic specific heat keeps on increasing with T . Therefore, the contribution of electronic specific heat is significant at very high temperatures also.

3.14 Dying stars

Besides metals there are many dead, decaying dying stars that contain degenerate fermion gases.

a. White Dwarfs

During the final stages of evolution, there are many stars that have original masses less than about 8 solar masses and are known as white dwarfs which constitutes around 10% of the stars in our galaxy. With its mass of two-thirds that of the sun, white dwarf is about the size of the earth; handful of its matter would weigh over a ton on the earth. After the nuclear reactions that provided it with energy run out of a fuel, such kind of stars shows high instability resulting in formation of a red giant thereby throwing off its outer layer. The left-out core then cools and gravitational contraction takes place till the atoms collapse into nuclei and electrons get closely packed together. As volume V decreases due to further contraction the Fermi energy increases as:

$$\epsilon_F = \frac{\hbar^2}{2m} \left[\frac{3N}{8\pi V} \right]^{2/3}$$

Where quantity N/V is the density of the free electrons.

As soon as ϵ_F exceeds kT , the electron starts forming a degenerate gas with their Fermi energy reaching 0.5 MeV in a typical white dwarf. With ϵ_F inversely proportional to m and the nuclei being more massive in comparison to electrons behaviour is classical in nature.

The nuclei finally cool down when the nuclear reactions inside the stars come to an end and due to gravitational influence, they come up together. However, since most of the low energy states of the electrons are already filled so they do not cool down due to which the electron gas becomes more hotter and hotter with the star shrinkage. In comparison to the star's mass even though the total electron mass is just a small fraction but it exerts sufficient pressure so as to stop the gravitational contraction. The size of the white dwarf is determined by proper balance in between the inward gravitational pull of its atomic nuclei and the pressure of its degenerate electron gas. Since in case of white dwarfs the states lower than ϵ_F are filled and only the electrons with the highest energies can radiate (as these types of electrons have empty low states to fall into), the star becomes dimmer and dimmer and ceases of to radiate in few billions of years. The energies of the electrons are since blocked below Fermi level; it turns into black dwarf which is a dead lump of matter.

It is seen that if the mass of a shrinking star increases, the electron pressure which is needed to maintain equilibrium also increases and if the mass turns out to be more than $1.4M_{\text{sun}}$, gravitational pull becomes so dominating which can then not be counteracted by an electron gas. Such type of star can never then become a stable white dwarf.

b. Neutron Stars

When a star becomes too heavy $8M_{\text{sun}}$ then due to this large mass there is a sudden collapse of the star when it runs out of fuel and tries to explode violently. As a result, the explosion explodes into space with most of the star's mass. This event called supernova is billions of times brighter than the original star. The mass which is left after explosion is greater than $1.4M_{\text{sun}}$. Due to the gravitational pull the star

contracts immensely giving rise to more and more energetic electrons. As soon as the fermi energy reaches 1.1 MeV, the average electron energy is 0.8 MeV which is actually the minimum energy required for an electron to react with proton to produce neutron. This becomes possible only when the stars density is 20 times greater than that of white dwarf. Neutrons are produced till electrons and protons vanish and as a result the neutrons (fermions) end up as a degenerate gas supporting the star further against gravitational shrinkage due to the immense pressure being produced.

c. Black holes

With the above discussion we can say that if an old star whose mass is less than $1.4M_{\text{sun}}$ it becomes a white dwarf and for those lying in between 1.4 and $\sim 3 M_{\text{sun}}$ becomes a neutron star. But if mass is much larger than $3 M_{\text{sun}}$ both degenerate electron gas and a degenerate neutron gas cannot resist the gravitational collapse. Does this mean that a star ends upto a point in space? According to uncertainty principle however beyond a certain size with enough gravitational pull even a massive old star is prevented from being collapsed. Thus, for a star with $M > 3 M_{\text{sun}}$ it ends upto a black hole. The gravitational pull is so intense to permit anything even the photons to escape past. It is seen that not only heavy stars but with time even white dwarfs and neutron stars attract more and more of cosmic dust and gases such that they add up to a lot of additional mass ending up themselves to black holes.

Solved examples

Ex.1 The density of silver is 10.5 g/cm^3 and its atomic weight is 108. If each atom contributes one electron for conduction, calculate (i) the number density of conduction electrons, (ii) Fermi energy and (iii) mean energy of the electron at 0 K.

Sol. (i) Number density of conduction electrons

$$\frac{N}{V} = \frac{\rho N_A}{M} = \frac{10.5 \times 6.02 \times 10^{23}}{108}$$

$$= 5.85 \times 10^{22} \text{ cm}^{-3} = 5.85 \times 10^{28} \text{ m}^{-3}$$

(ii) Fermi energy

$$\varepsilon_F = \frac{h^2}{8m} \left[\frac{3N}{\pi V} \right]^{2/3}$$

$$= \frac{6.626 \times 10^{-34}}{8 \times 9.1 \times 10^{-31}} \left(\frac{3}{\pi} \times 5.85 \times 10^{28} \right)^{2/3}$$

$$= 8.816 \times 10^{-19} \text{ J} = 5.51 \text{ eV}$$

(iii) Mean energy of the electron at 0K = $\frac{3}{5} E_F$

$$= \frac{3}{5} \times 5.51 \text{ eV} = 3.31 \text{ eV}$$

Ex.2 The density of the sodium is 0.97 g/cm^3 and its atomic weight is 23. If it has one free electron per atom, calculate its Fermi energy.

Sol. Electron density

$$\frac{N}{V} = \frac{\rho N_A}{M} = \frac{0.97 \times 6.02 \times 10^{23}}{23}$$

$$= 2.53 \times 10^{22} \text{ electron cm}^{-3} = 5.85 \times 10^{28} \text{ electrons m}^{-3}$$

Fermi energy

$$\begin{aligned}\varepsilon_F &= \frac{\hbar^2}{8m} \left[\frac{3N}{\pi V} \right]^{2/3} \\ &= \frac{6.626 \times 10^{-34}}{8 \times 9.1 \times 10^{-31}} \left(\frac{3}{\pi} \times 2.53 \times 10^{28} \right)^{2/3} \\ &= 5.032 \times 10^{-19} J = 3.145 \text{ eV}\end{aligned}$$

*****Review questions*****

1. What are bosons? Give two examples.
2. What are fermions? Give two examples.
3. Classify the following into bosons and fermions: photons, protons, electrons, helium atoms.
4. What are the basic postulates of Maxwell-Boltzmann statistics? Write down the distribution law for a system obeying Maxwell-Boltzmann statistics.
5. State the basic postulates of Maxwell-Boltzmann, Bose Einstein and Fermi-Dirac statistics.
6. What is Fermi energy? What is its physical significance?
7. Write down the distribution formula for Maxwell-Boltzmann, Bose Einstein and Fermi Dirac statistics. When are the three equal?
8. Explain the condition for a system to obey Maxwell-Boltzmann statistics.
9. Explain Fermi-Dirac distribution function. Plot this function (with energy) for various temperatures including 0K.
10. Compare the salient features of the three statistical distribution functions, Maxwell-Boltzmann, Fermi-Dirac and Bose-Einstein. Give one example of particles in each of these categories.
11. Show that the Pauli's exclusion principle follows directly from the distribution function for Fermi-Dirac statistics.
12. Distinguish between classical and quantum statistics.
13. Differentiate between symmetric and anti-symmetric wave functions. also
14. Make a comparison of the statistical distribution functions $f(E)$ for Bose-Einstein and Fermi Dirac systems of identical particles. Plot the $f(E)$ vs. energy at temperatures $T = 0\text{K}$ and $T > 0\text{K}$.
15. Distinguish between Maxwell-Boltzmann, Bose-Einstein and Fermi-Dirac statistics on the basis of their functions.