

ACCESSION NO.....
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Development of Quantum Mechanics

1.1. Introduction

Newton's laws of motion are the basis of the most elementary principles of classical mechanics. Equations based on these laws are the simplest and they are suitable for solution of simple dynamical problems, such as the motion of macroscopic bodies. Lagrange's equations, Hamilton's equations and Hamilton's principle are also fundamental principles of classical mechanics, because they are consistent with each other and with Newton's laws of motion. Lagrange's and Hamilton's equations are useful for solution of complicated dynamical problems.

In principle, the properties of bulk matter must be deducible from the properties of electrons and atomic nuclei of which it is composed. However, it is found that the observed properties of matter cannot be explained on the assumption that the particles obey the laws of classical mechanics. Therefore, new concepts had to be developed. These concepts led to a new mechanics called Quantum Mechanics.

The development of Quantum Mechanics took place in two stages. The first stage began with Max Planck's presentation at a meeting of the German Physical Society on December 14, 1900, of his hypothesis that radiation is emitted or absorbed by matter in discrete packets or quanta each of energy $h\nu$, where ν is the frequency of radiation and h is Planck's constant ($h = 6.6256 \times 10^{-34} \text{ Js}$). The theory based on this hypothesis consisted of a mixture of classical and non-classical concepts, and was not completely satisfactory.

The second stage, *i.e.* Quantum Mechanics began from two different viewpoints in 1925. A particular form of this mechanics is called Matrix Mechanics introduced by Werner Heisenberg in 1925. In this mechanics unobserved quantities such as positions, velocities etc. in electronic orbits are omitted and only observed quantities such as frequencies and intensities of spectral lines are taken into account. Another form of Quantum Mechanics is called Wave

Mechanics. The mathematical theory of this mechanics was developed by Erwin Schrodinger in 1926. In this mechanics earlier ideas of classical wave theory are combined with Louis de Broglie's wave-particle relationship. The mathematical theories of Wave Mechanics and Matrix Mechanics appear to be different, but in fact they are equivalent. Numerous problems of atomic physics have been solved by the application of Quantum Mechanics. However, it has certain limitations. A more complete theory of particles called Quantum Field Theory has been accepted since 1947. To understand the development of Wave Mechanics, we begin with a brief account of black body radiation which could not be explained by classical mechanics. This is followed by description of some phenomena like the photo-electric effect, the Compton effect etc. Explanations of these phenomena are based on Planck's quantum hypothesis.

1.2. Black Body Radiation

A body which completely absorbs radiation of all wavelengths incident on it is called a perfectly black body. Since a good absorber of radiation is also a good emitter of radiation, a perfectly black body is the best possible emitter at any given temperature. The radiation emitted by such a body is called *black body radiation*, or *full radiation*, or *temperature radiation*.

A perfectly black body is an ideal conception. There is no known surface which can be regarded as perfectly black. Lamp black or platinum black is nearest approach to a perfectly black body. Lamp black can absorb about 96% of the radiant energy incident on it, and platinum black absorbs about 98%. In practice an almost perfectly black body consists of a double-walled hollow metal sphere (Fig. 1.1). The sphere has a small hole O. There is a conical projection P opposite to the hole. The inner surface of the sphere is coated with lamp black. The space between the walls is evacuated to prevent loss of heat by conduction or convection. When any radiant energy enters the sphere through the hole, it suffers multiple reflections as shown in the figure. At each reflection about 96% of the incident radiant energy is absorbed. Hence after a few reflections all the radiant energy is absorbed by the sphere. The function of the conical projection is to prevent direct reflection of the radiant energy from the surface opposite to the hole. The hole O in the sphere thus acts as a perfectly black body because it absorbs all the radiant energy incident on it. When the sphere is heated black body radiation is emitted

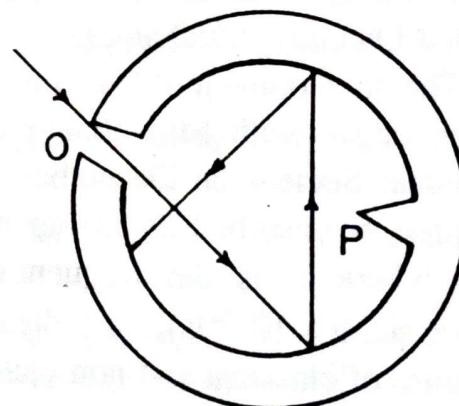


Fig. 1.1: Perfectly black body

wavelengths, at constant temperature, the sphere is heated to and maintained at that temperature. By means of an infrared spectrometer, and a bolometer (an instrument for measurement of the intensity of radiation) the intensities of the radiation of different wavelengths are measured.

The experimental results as obtained by Lummer and Pringsheim (1899) are shown in Fig. 1.2. The curves are for temperatures of the black body, E_λ and the abscissa wavelengths.

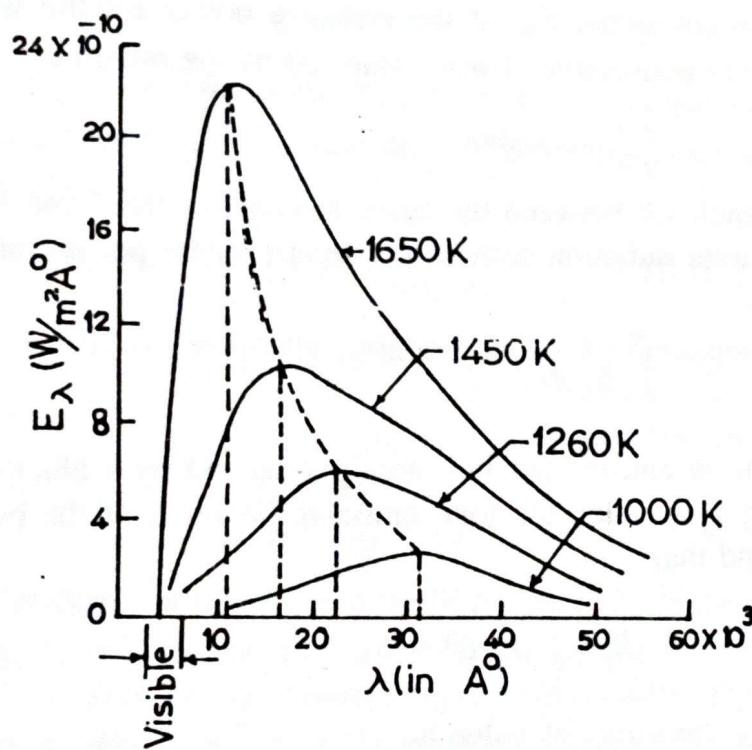


Fig. 1.2

The emissive power E_λ is defined in such a way that the quantity $E_\lambda d\lambda$ is the energy radiated per unit area per second for wavelength in the range between λ and $\lambda + d\lambda$.

Thus

$$E_\lambda = \frac{\text{energy radiated per unit area per sec. in the range } \lambda \text{ to } \lambda + d\lambda}{\text{wavelength difference } d\lambda}$$

Unit of E_λ is 1 watt per square metre per Angstrom unit, and the SI unit is 1 watt per square metre per nanometre (10^{-9} m).

From these curves the following conclusions are drawn:

- (1) As the temperature increases, E_λ for every wavelength increases.
- (2) At constant temperature as λ increases E_λ increases till it becomes maximum at a certain wavelength λ_m and then with further increase of λ , E_λ decreases. At a higher temperature the wavelength λ_m at which E_λ is maximum

shifts towards a shorter wavelength. The wavelength λ_m and the absolute temperature T are connected by the relation

$$\lambda_m T = \text{constant} \quad \dots(1)$$

This equation is known as *Wien's displacement law*. The value of the constant in Eq. (1) is $2.898 \times 10^7 \text{ A}^\circ\text{K}$, or $2.898 \times 10^{-3} \text{ m K}$. By measuring the wavelength λ_m spectroscopically the temperature of a black-body can be determined using Eq. (1). This method has been used extensively in determining temperatures of stars. In Fig. 1.2 the dotted curve is the locus of the peaks of the distribution curves for different temperatures.

(3) The maximum value, E_m , of the emissive power for the wavelength λ_m and the absolute temperature T are connected by the relation

$$\frac{E_m}{T^5} = \text{constant} \quad \dots(2)$$

(4) The area enclosed between the curve at temperature T and the axis of λ represents the total radiation emitted per square metre per second over all wavelengths,

$$\int_0^{\infty} E_{\lambda} d\lambda.$$

The total radiation emitted per unit area per second by a black-body at a given temperature T is called the total emissive power E of the body. For a black-body it found that

$$E = \int_0^{\infty} E_{\lambda} d\lambda = \sigma T^4 \quad \dots(3)$$

where σ is *Stefan's constant*. Its value is

$$\sigma = 5.6697 \times 10^{-8} \text{ W/m}^2\text{K}^4$$

Eq. (3) is called Stefan's law for the total radiation from a black-body.

1.3. Theoretical Laws of Black Body Radiation

Late in the nineteenth century a number of attempts were made to explain the spectral distribution of the intensity of radiation from a black body on the basis of classical mechanics and the electromagnetic theory. A summary of many important classical developments in the radiation theory is given below

1. Wien's Displacement Law in Terms of E_{λ} and T

In 1893 Wien showed that the energy $E_{\lambda} d\lambda$ radiated per unit area per second within the wavelength range λ and $\lambda + d\lambda$ of electromagnetic radiation by a black-body at temperature T is given by

$$E_{\lambda} d\lambda = \frac{A}{\lambda^5} f(\lambda T) d\lambda \quad \dots(1)$$

and

$$E_{\lambda} d\lambda = AT^5 F(\lambda T) d\lambda \quad \dots(1)$$

where A is a constant and $f(\lambda T)$ and $F(\lambda T)$ are functions of the product λT . From Eqs. (1) and (2) it is evident that

$$T^5 F(\lambda T) = \frac{1}{\lambda^5} f(\lambda T)$$

or

$$F(\lambda T) = (\lambda T)^{-5} f(\lambda T) \quad \dots(3)$$

Wien obtained Eqs. (1) and (2) by considering the radiation field having thermodynamic properties such as temperature, pressure, entropy etc. Eq. (2) shows that for any black body

$$\frac{E_\lambda}{T^5} = AF(\lambda T)$$

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

$$\lambda_1 T_1 = \lambda_2 T_2 = \dots, \text{ then we have}$$

$$\frac{E_{\lambda_1}}{T_1^5} = \frac{E_{\lambda_2}}{T_2^5} = \frac{E_{\lambda_3}}{T_3^5} = \dots = \text{constant.}$$

Thus the emissive power E_λ of a perfectly black body for wavelength λ is directly proportional to the 5th 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 .

2. Wien's Radiation Formula

In 1896 Wien derived the following formula for radiation from a black body

$$E_\lambda d\lambda = \frac{C_1}{\lambda^5} e^{-C_2/\lambda T} d\lambda \quad \dots(5)$$

where C_1 and C_2 are constants.

For obtaining the formula the following arbitrary assumptions were made:

- (1) The radiation inside a hollow enclosure is produced by 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. Rayleigh-Jeans Law

In 1900 Lord Rayleigh applied the principle of equipartition of energy to the electromagnetic vibrations. Then with a contribution from J.H. Jeans this attempt 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, $U_\nu d\nu$, i.e. the amount of energy per unit volume of the enclosure in the frequency range from ν to $\nu + d\nu$ is given by

$$U_\nu d\nu = \frac{8\pi\nu^2 kT}{c^3} d\nu \quad \dots(6)$$

where U_ν is the energy per unit volume per unit frequency range at frequency ν , 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 the wavelength λ by using the relation

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

and

$$d\nu = -\frac{c}{\lambda^2} d\lambda$$

The energy $U_\nu d\nu$ contained in a frequency interval between ν and $\nu + d\nu$ is equal to that contained in a corresponding wavelength interval between λ and $\lambda + d\lambda$, and an increase in frequency corresponds to a decrease in wavelength.

$$\therefore U_\lambda d\lambda = -U_\nu d\nu$$

$$\begin{aligned} &= -\frac{8\pi}{c^3} \left(\frac{c}{\lambda}\right)^2 kT \left(-\frac{c}{\lambda^2}\right) d\lambda \\ &= \frac{8\pi kT}{\lambda^4} d\lambda \end{aligned} \quad \dots(7)$$

This equation is another form of the Rayleigh-Jeans law. 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 U_λ will continuously increase, and as λ tends to zero, U_λ approaches infinity (Fig. 1.3). This is contrary 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

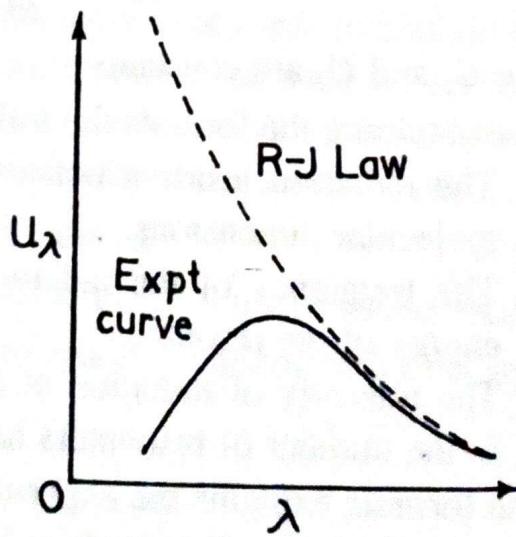


Fig. 1.3

$$U = \int_0^{\infty} U_{\lambda} d\lambda = \int_0^{\infty} \frac{8\pi kT}{\lambda^4} d\lambda \\ = 8\pi kT \left[-\frac{1}{3\lambda^3} \right]_0^{\infty} = \infty$$

This result shows that for a given quantity of radiant energy all the 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 $U_{\lambda} d\lambda \rightarrow 0$ 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 in any amount.

1.4. Planck's Quantum Hypothesis

In order to explain the distribution of energy in the spectrum of a black body, Max Planck in 1900, put forward the quantum theory of radiation. He assumed that the atoms in the walls of a black-body behave like simple harmonic oscillators, and each has a characteristic frequency of oscillation. In his theory he made the following two radical assumptions about the atomic oscillators.

(1) A simple harmonic oscillator cannot have any arbitrary values of energy but only those values of the total energy E that are given by the relation

$$E = nh\nu \quad \dots(1)$$

where $n = 0, 1, 2, 3, \dots$; n is called the quantum number, ν is the frequency of oscillation, and h is a universal constant called Planck's constant ($h = 6.625 \times 10^{-34}$ Js). In this relation $h\nu$ is the basic unit of energy and it is called a *quantum of energy*. Thus the relation shows that the total energy of an oscillator is quantized.

(2) As long as the oscillator has energy equal to one of the allowed values given by the relation $E = nh\nu$, it cannot emit or absorb energy. Therefore the oscillator is said to be in a stationary state or a quantum state of energy. *The emission or absorption of energy occurs only when the oscillator jumps from one energy state to another.* If the oscillator jumps down from a higher energy state of quantum number n_2 to a lower energy state of quantum number n_1 , the energy emitted is given by

$$E_2 - E_1 = (n_2 - n_1) h\nu$$

If $n_2 - n_1 = \text{one unit, then}$

$$E_2 - E_1 = h\nu$$

Similarly an oscillator absorbs a quantum $h\nu$ of energy when it jumps up to its next higher energy state.

According to Planck the quantum theory is applicable only to the process of emission and absorption of radiant energy.

In 1905 Einstein extended Planck's quantum theory by assuming that a monochromatic radiation of frequency ν consists of a stream of photons each of energy $h\nu$ and the photons travel through space with the speed of light.

Planck's Radiation Law

On the basis of the quantum theory, Planck obtained the formula for an average energy of an oscillator:

$$E = \frac{h\nu}{e^{h\nu/kT} - 1} \dots (2)$$

It can be shown that the number of oscillations or degrees of freedom per unit volume in the frequency range ν and $\nu + d\nu$ is given by

$$N(\nu) d\nu = \frac{8\pi\nu^2}{c^3} d\nu \dots (3)$$

where c is the speed of light in vacuum.

Then assuming that the average value of the energies of the various modes of oscillation in black-body radiation is given by Eq. (2), Planck obtained the equation

$$U_\nu d\nu = \frac{8\pi h\nu^3}{c^3} \frac{1}{e^{h\nu/kT} - 1} d\nu \dots (4)$$

where $U_\nu d\nu$ is the energy per unit volume in the frequency range ν and $\nu + d\nu$ and U_ν is the energy per unit volume per unit frequency range at frequency ν . In terms of the wavelength of the radiation this equation is:

$$U_\lambda d\lambda = \frac{8\pi hc}{\lambda^5} \cdot \frac{1}{e^{hc/\lambda kT} - 1} d\lambda \dots (5)$$

Eqs. (4) and (5) are two forms of Planck's radiation law.

When the values of U_λ as obtained from Eq. (5) for different values of λ , are plotted against the corresponding values of λ we get curves as shown in Fig. 1.4. These curves agree very well with the experimental results over the whole range of wavelengths.

From Planck's law in the form of Eq. (5) the Rayleigh-Jeans law, Wien's law and the Stefan-Boltzmann formula are obtained as mathematical consequences:

(1) **Rayleigh-Jeans law.** For small values of $hc/\lambda kT$, i.e. in the region of long wavelengths, the exponential term in Eq. (5) can be expanded and retaining only the first term, we get

$$U_\lambda d\lambda = \frac{8\pi hc}{\lambda^5} \cdot \frac{1}{hc/\lambda kT} d\lambda = \frac{8\pi kT}{\lambda^4} d\lambda \dots (6)$$

This is the Rayleigh-Jeans law.

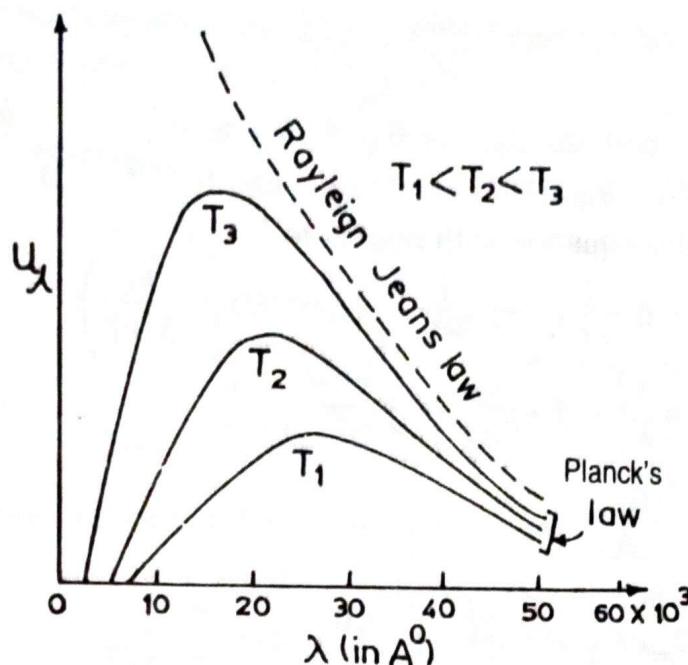


Fig. 1.4

(2) **Wien's radiation formula.** In the region of low wavelengths $hc/\lambda kT$ becomes large. Hence 1 in the denominator on the right hand side of Eq. (5) can be neglected in comparison with the exponential term. Therefore, we get

$$\begin{aligned} U_\lambda d\lambda &= \frac{8\pi hc}{\lambda^5} \cdot \frac{1}{e^{hc/\lambda kT}} d\lambda \\ &= \frac{8\pi hc}{\lambda^5} e^{-hc/\lambda kT} d\lambda \end{aligned}$$

It can be shown that for any black-body E_λ is related to U_λ at the same temperature by the equation

$$E_\lambda = \frac{c U_\lambda}{4}, \quad \text{or} \quad U_\lambda = \frac{4 E_\lambda}{c}$$

Now substituting for U_λ in the above equation we get

$$\begin{aligned} E_\lambda d\lambda &= \frac{2\pi hc^2}{\lambda^5} e^{-hc/\lambda kT} d\lambda \\ &= \frac{C_1}{\lambda^5} e^{-C_2/\lambda T} d\lambda \end{aligned} \quad \dots(7)$$

where $C_1 = 2\pi hc^2$ and $C_2 = hc/k$

Eq. (7) is Wien's radiation law.

From Planck's radiation law, we have

$$U_\lambda = \frac{8\pi hc}{\lambda^5} \cdot \frac{1}{e^{hc/\lambda kT} - 1} \quad \dots(8)$$

At constant temperature T of a black-body, the wavelength λ_m at which the energy density is maximum is given by

Taking logarithm of both the sides of Eq. (8), we have

$$\log_e U_\lambda = \log_e (8\pi hc) - 5\log \lambda - \log_e (e^{hc/\lambda kT} - 1)$$

Differentiating this equation with respect to λ

$$\begin{aligned}\frac{1}{U_\lambda} \cdot \frac{dU_\lambda}{d\lambda} &= 0 - \frac{5}{\lambda} - \left[\frac{1}{e^{hc/\lambda kT} - 1} \right] (e^{hc/\lambda kT}) \left(-\frac{hc}{\lambda^2 kT} \right) \\ &= \frac{1}{\lambda} \left[-5 + \frac{hc}{\lambda kT} \left\{ \frac{e^{hc/\lambda kT}}{e^{hc/\lambda kT} - 1} \right\} \right]\end{aligned}$$

$$\text{At } \lambda = \lambda_m, \quad \frac{dU_\lambda}{d\lambda} = 0$$

$$\therefore -5 + \frac{hc}{\lambda_m kT} \left\{ \frac{e^{hc/\lambda_m kT}}{e^{hc/\lambda_m kT} - 1} \right\} = 0$$

Let

$$\frac{hc}{\lambda_m kT} = x,$$

then

$$-5 + \frac{xe^x}{e^x - 1} = 0$$

or

$$\frac{xe^x}{e^x - 1} = 5$$

On solving this equation by trial and error method, we will get

$$x = 4.9651$$

i.e.

$$\frac{hc}{\lambda_m kT} = 4.9651$$

\therefore

$$\lambda_m T = \frac{hc}{4.9651 \times k}$$

$$\begin{aligned}&= \frac{6.62 \times 10^{-34} \times 3 \times 10^8}{4.9651 \times 1.38 \times 10^{-23}} = \frac{6.62 \times 3 \times 10^{-3}}{4.9651 \times 1.38} \\ &= 2.898 \times 10^{-3} \text{ m K}\end{aligned}$$

4. Stefan-Boltzmann Law

On the basis of the experimental data of Tyndall and of Dulong and Petit, J. Stefan in 1879 deduced empirically that the total radiant energy of all wavelengths emitted per unit area per second by a heated body is proportional to the fourth power of its absolute temperature. In 1884 Boltzmann derived the fourth power law by considering the black-body radiation as the working substance for the ideal Carnot Cycle. He showed that the law is strictly applicable to the radiation from a black-body. The law is, therefore, generally called the Stefan-Boltzmann Law. The law can be obtained directly from Planck's radiation formula. The derivation is as follows.

The energy density of the total radiation of all wavelengths in a black body enclosure at temperature T is given by

$$U = \int_0^\infty U_\lambda d\lambda = \int_0^\infty \frac{8\pi hc}{\lambda^5} \cdot \frac{1}{e^{hc/\lambda kT} - 1} d\lambda$$

Let

$$\begin{aligned}x &= \frac{hc}{\lambda kT} \\ \lambda &= \frac{hc}{kTx}\end{aligned}$$

and

$$d\lambda = -\frac{hc}{kTx^2} dx$$

when $\lambda = 0, x = \infty$, and when $\lambda = \infty, x = 0$

Hence,

$$\begin{aligned}U &= \int_0^\infty \frac{8\pi hc}{\lambda^5} \left(\frac{kTx}{hc} \right)^5 \frac{1}{e^x - 1} \left(-\frac{hc}{kTx^2} dx \right) \\ &= - \int_0^\infty \left(\frac{8\pi k^4 T^4}{h^3 c^3} \right) \frac{x^5}{e^x - 1} dx\end{aligned}$$

$$= \frac{8\pi k^4 T^4}{h^3 c^3} \int_0^\infty \frac{x^5}{e^x - 1} dx$$

The value of the integral is $\frac{\pi^4}{15}$

$$U = \frac{8\pi k^4 T^4}{h^3 c^3} \cdot \frac{\pi^4}{15} = \frac{4}{c} \left(\frac{2}{15} \frac{\pi^5 k^4}{h^3 c^2} \right) T^4 \quad \dots(8)$$

It can be shown that for any black body the total radiation of all wavelengths emitted per unit area per second at a given temperature, i.e. the total emissive power E is related to U at the same temperature by the equation

$$E = \frac{cU}{4}, \quad \text{or} \quad U = \frac{4E}{c} \quad \dots(9)$$

Substituting for U in Eq. (8), we get

$$E = \left(\frac{2\pi^5 k^4}{15 h^3 c^2} \right) T^4 \quad \dots(10)$$

or

$$E = \sigma T^4 \quad \dots(11)$$

where

$$\sigma = \frac{2\pi^5 k^4}{15 h^3 c^2} \quad \dots(12)$$

Eq. (11) is the Stefan-Boltzmann law of radiation. The constant σ is called Stefan's constant. The experimental value of this constant is

$$\sigma = 5.67 \times 10^{-8} \text{ W/m}^2 \text{K}^4$$

When the values $\sigma = 5.79 \times 10^{-8} \text{ W/m}^2\text{K}^4$ (this was the value known at that time), $k = 1.38 \times 10^{-23} \text{ J/K}$, $c = 3 \times 10^8 \text{ m/s}$ are substituted in Eq. (12), the value of h is found to be $6.57 \times 10^{-34} \text{ Js}$. This was the first calculated value of h . The recent recommended value of h which is now widely used is

$$6.6256 \times 10^{-34} \text{ Js}$$

this value of h is substituted in Eq. (5) for obtaining the values of U_h , it is found that the theoretical distribution curves agree excellently with the experimental curves over the whole range of wavelengths.

The success of Planck's hypothesis in explaining the distribution of energy in the spectrum of black body was the beginning of quantum mechanics. We now describe some more important phenomena which are explained by this hypothesis.

1.5. Photoelectric Effect

When an electromagnetic radiation of sufficiently high frequency, such as ultraviolet light and X-rays is incident on a clean metal surface electrons are emitted from it. This phenomenon is known as the *photoelectric effect*, and the emitted electrons are called *photoelectrons*. The whole range of electromagnetic radiation from γ -rays and X-rays to the ultraviolet, the visible and the infrared rays produce this effect. Most metals give this effect when exposed to ultraviolet rays or X-rays. Sodium gives this effect when exposed to all radiations of wavelengths smaller than 5455 Å. Caesium produces this effect when exposed to all radiations of wavelengths smaller than 6438 Å.

The photoelectric effect was discovered by Heinrich Hertz in 1887. Further experimental study was undertaken by Hallwachs in 1888. Then in 1899 Lenard showed that the carriers of electricity emitted from a metal surface, under the action of ultraviolet light, were electrons.

Experimental Study of the Photo-electronic Effect

The type of the apparatus that was used for the experimental study of the photoelectric effect is shown in Fig. 1.5. A photo-sensitive metal plate **A** is mounted opposite to a metal plate **B** in a highly evacuated glass tube **C**. The plates **A** and **B** form two electrodes to which a variable potential difference (p.d.) can be applied. The glass tube is fitted with a quartz window **D**. Ultraviolet light from the source **S** is transmitted by **D** and falls on the surface **A**. When the applied *P.D.* between **A** and **B** is such that **A** is at negative potential with respect to **B**, the photo-electrons emitted from **A** are accelerated towards **B**. The resulting photoelectric current *I* flowing in the circuit is measured by the micro-ammeter μA and the accelerating *P.D.* is measured by the vacuum tube voltmeter **V**.

If the *P.D.* is reversed so that now **B** is at negative potential with respect to **A**, the photoelectrons are repelled towards **A** by the retarding *P.D.* Conse-

quently the photoelectric current *I* is reduced. The photoelectric current is found to depend on the following factors:

- (1) the frequency of the incident radiation,
- (2) the intensity of the incident radiation,
- (3) the potential difference between the electrodes,
- (4) the nature of the emitting surface.

1. Effect of the Intensity of the Incident Light

The surface of the metal plate **A** is illuminated by monochromatic ultraviolet light. The accelerating *P.D.* between **A** and **B** is increased till the photo-electric current as shown by the microammeter is maximum. The current is due to the flow of all the photoelectrons emitted per second from the surface. The experiment is repeated for different known intensities of the incident light. The variation of the current with the intensity is shown in Fig. 1.6. The straight line graph shows that the number of photoelectrons emitted per second by the surface is directly proportional to the intensity of the incident radiation.

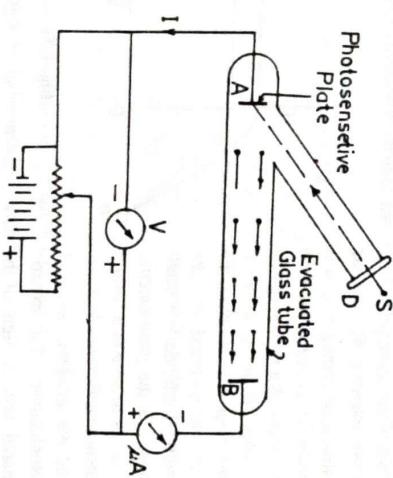


Fig. 1.5

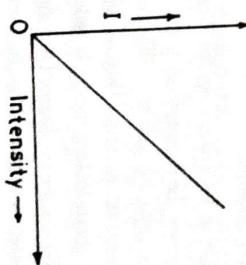


Fig. 1.6

2. Effect of Retarding Potential on the Photoelectric Current

The surface of the metal plate A is illuminated by monochromatic ultraviolet light of known intensity X_1 . Starting from a suitable accelerating P.D., it is gradually reduced to zero and then reversed by means of a reversing key so that the plate B is at negative potential with respect to A. Now the magnitude of the reversed, i.e. the retarding potential difference is gradually increased till the photoelectric current is reduced to zero at a certain retarding potential difference $-V_0$. This P.D. is called the stopping potential for the photoelectrons. The experiment is repeated with the light of the same frequency but of higher intensity X_2 . The variation of the photoelectric current with the P.D. for the intensities X_1 and X_2 is shown Fig. 1.7. The curves show that for a given metal the stopping potential V_0 is independent of the intensity of incident radiation of fixed frequency.

This fact is explained by assuming that photoelectrons with kinetic energy ranging from zero to a certain maximum value are emitted from the surface. The stopping potential V_0 just stops the photoelectrons having the maximum kinetic energy from reaching the collecting electrode B.

$$\frac{1}{2}mv_{\max}^2 = eV_0 \quad \dots(1)$$

where m is the mass of the electron, e the electronic charge and v_{\max} is the maximum velocity of emission. Those electrons which are emitted with kinetic energies less than the maximum value are stopped by smaller values of the retarding potential.

3. Effect of Frequency on the Stopping potential

To study the dependence of the stopping potential on the frequency of the incident light the surface is illuminated by light of known frequency ν_1 and an appropriate intensity. Then the magnitude of the retarding P.D. is increased till the photoelectric current is reduced to zero at the stopping potential V_0 . The experiment is repeated for light of the same intensity but of higher frequencies ν_2 and ν_3 . The observations are shown by the curves in Fig. 1.8. It is seen that as the frequency of the incident light is increased the stopping potential for a given metal surface increases.

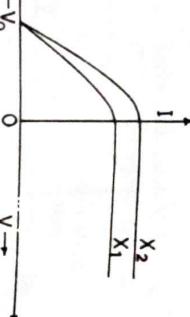


Fig. 1.7

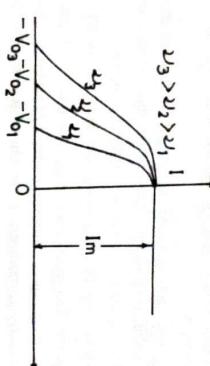


Fig. 1.8

Threshold Frequency and Planck's constant

The results of the experiment on variation of the stopping potential with the frequency of the incident radiation show that the maximum kinetic energy $(1/2)mv_{\max}^2 = eV_0$ of the photoelectrons emitted from a given surface increases linearly with the frequency of the incident radiation. Fig. 1.9 shows the graph of eV_0 against the frequency ν for three different metals. The slope of the three straight lines is the same equal

to Planck's constant, but their intercepts on the frequency axis are different. If ν_0 is the intercept of a straight line AB, it is represented by the equation $eV_0 = h\nu - h\nu_0$ $\dots(2)$

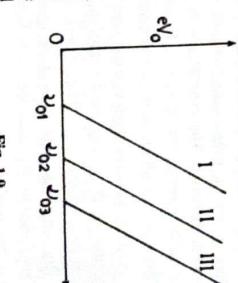


Fig. 1.9

The frequency ν_0 is the minimum frequency that can cause the emission of a photoelectron with zero kinetic energy from the surface. This frequency is called the threshold frequency for the surface. Its value is different for different surfaces. Thus the threshold frequency for a metal surface may be defined as follows:

If there is a certain minimum frequency of incident radiation that can cause the emission of photoelectrons with zero kinetic energy from the surface and below which no emission occurs.

Milikan in 1916 determined the value of h from the slope of the straight line graph of eV_0 against ν . The value was found to be $h = 6.57 \times 10^{-34}$ Js.

Characteristics of Photo-Electric Effect

From the experimental facts we state the following characteristics of the photo-electric effect:

- (1) For a given photo-sensitive surface, there is a certain minimum frequency ν_0 of incident radiation, below which there is no emission of photo-electrons. This frequency is called the threshold frequency for the surface. The value of ν_0 depends on the material and the nature of the emitting surface.

(2) For a given frequency ν ($\nu > \nu_0$) the number of the photoelectrons emitted per sec. from a given surface, under a constant accelerating potential difference, is directly proportional to the intensity of the incident radiation.

(3) When radiation of a given frequency ν ($\nu > \nu_0$) is incident on a given surface, photo-electrons with kinetic energies ranging from zero to a certain maximum value, are emitted from the surface. The stopping potential for the photo-electrons and hence the maximum kinetic energy is independent of the intensity of the radiation.

(4) The maximum kinetic energy [$(1/2)mv_{\max}^2 = eV_0]$] of the photoelectrons emitted from a given surface increases linearly with the frequency of the incident radiation. The straight line for the given surface meets the frequency axis at the threshold frequency ν_0 for the surface. The slope of the straight line is the same for all emitting surfaces and is equal to Planck's constant h .

(5) The emission of photo-electrons is an instantaneous process. As soon as radiation of frequency greater than the threshold frequency is incident on a given photo-sensitive surface, there is emission of photo-electrons.

The following three main characteristics of the photoelectric effect cannot be explained by the wave theory of light.

(1) The maximum kinetic energy of the photoelectrons is independent of the intensity of the incident light (According to the wave theory the kinetic energy should increase with an increase in the intensity of light).

(2) For each surface there is a minimum frequency (threshold frequency) below which no emission of photoelectrons occurs. (According to the wave theory the emission of the photoelectrons should occur for any frequency of the incident light, provided the intensity is sufficient).

(3) There is no time lag between the irradiation of a surface and the start of the emission. (According to the wave theory the energy of the incident light is spread over the wave front and since the energy incident on any one electron would be very small, some time will be required by an electron to absorb enough energy to escape from the surface).

Einstein's Photoelectric Equation

To derive the photo-electric equation, Einstein in 1905 applied Planck's quantum theory and made the following two assumptions.

(1) A radiation of frequency ν consists of a stream of discrete quanta each of energy $h\nu$, where h is Planck's constant. These quanta are called photons. The photons move through space with the speed of light.

(2) When a photon of energy $h\nu$ is incident on a metal surface, the entire energy of the photon is absorbed by a single electron without any time lag. The probability of its absorbing two or more photons at the same time is negligible.

Thus when radiation of frequency ν is incident on the surface of a metal in vacuum the entire energy $h\nu$ of a photon is absorbed by an electron of the metal. The incident radiation penetrates several atomic diameters into the metal and electrons at different depths absorb this amount of energy from the incident photon.

For photoelectric emission of an electron from the metal $h\nu \geq W_0$, where W_0 is the photoelectric work function of the metal. When an electron at the metal surface absorbs the energy $h\nu$, a certain minimum part of this energy is used up by the electron to do work equal to W_0 to overcome the attractive forces of the positive ions of the metal. The remaining maximum energy $(h\nu - W_0)$ is in the form of maximum kinetic energy $(1/2)mv_{\max}^2$ of the electron emitted from the surface.

$$\therefore \frac{1}{2}mv_{\max}^2 = h\nu - W_0 \quad \dots(3)$$

where m is the mass of the electron and v_{\max} is the maximum speed of the emitted electron. An electron emitted from below the surface will lose some part of the energy $h\nu$ in internal collisions with other electrons. Consequently, it will be emitted with a smaller energy. Eq. (3) is known as Einstein's photo-electric equation.

The three main characteristics of the photoelectric effect: (1) the non-dependence of the maximum energy on the intensity of the incident radiation, (2) the existence of the threshold frequency, and (3) the absence of time lag, which cannot be explained by the wave theory, are in perfect agreement with Einstein's photon theory as explained below.

According to this theory the intensity of a beam of radiation of frequency ν is proportional to the number of photons each of energy $h\nu$ passing normally through unit area of cross-section of the beam per second, and the energy of a photon is independent of the intensity. Therefore, if the intensity of the radiation is increased, the number of photons in the beam will increase in proportion to the intensity. Hence the number of photoelectrons emitted per unit area per second will increase in proportion to the intensity. But the maximum kinetic energy will be the same as before. Thus the maximum kinetic energy of the emitted photoelectrons is independent of the intensity, but the photoelectric current is proportional to the intensity.

According to this theory the threshold frequency ν_0 for a metal surface is the frequency of a photon which has just sufficient energy to liberate an electron from the surface with zero kinetic energy. From Eq. (3) this frequency is given by

$$O = h\nu_0 - W_0$$

or

$$\nu_0 = \frac{W_0}{h} \quad \dots(4)$$

The energy of a photon is not distributed over an area, as in the wave theory. It is in the form of a concentrated bundle. So when a photon is incident on an electron all its energy is absorbed by the electron without any time lag. We have seen that the photoelectric effect is explained by Einstein's photon theory according to which an electromagnetic radiation of frequency ν consists of photons each of energy $h\nu$, and a photon gives up all its energy to an electron in a metal when the radiation is incident on the metal surface. Thus this effect shows that electromagnetic radiation also has particle properties. In the next section we describe the Compton effect which is explained by considering the photon as a particle with both momentum and energy. This effect, therefore, gives one of the most conclusive indications of the particle properties of electromagnetic radiation.

1.6. The Compton Effect

When a beam of monochromatic X-rays of wavelength λ is scattered by a light element like carbon, it is observed that the scattered X-rays have maximum intensities at two wavelengths; one of them at the same wavelength λ and the other at slightly longer wavelength λ' . This effect was discovered by A.H. Compton in 1922 and its explanation was given by him in 1923. For this reason it is called the Compton effect.

Experimental Study of the Compton Effect

The experimental arrangement of Compton's apparatus is shown in Fig. 1.10.

In the figure, C is a small graphite block, and T is the molybdenum target of an X-ray tube (not shown in the figure) kept inside a lead box L . A monochromatic beam of X-rays from the target is made parallel when it passes through the slits S_1 . When the beam is incident on C , it is scattered in all directions. The beam scattered in the direction CA emerges from the box L . The angle between the directions of the incident beam and the scattered beam is the angle of scattering ϕ (Fig. 1.10). The scattered beam is allowed to fall on the analysing crystal B of a Bragg spectrometer. The reflected beam from the crystal B enters the ionisation chamber I . The ionisation current produced by the X-ray beam is measured by the microammeter μA . The angle of incidence at the crystal is varied by rotating the crystal and for each setting of the

crystal, the ionisation current is recorded. This procedure is repeated for different angles of scattering.

The experimental results obtained by Compton using a graphite block and molybdenum K_α line ($\lambda = 0.0707 \text{ \AA}$) are shown in Fig. 1.11 for the angles of scattering of 45° , 90° , and 135° .

The results showed that the wavelength separation between the two intensity peaks in the scattered radiation is given by

$$\lambda' - \lambda = \Delta\lambda = 0.024(1 - \cos \phi) \text{ \AA}$$

where ϕ is the angle of scattering.

The effect cannot be explained on the basis of the electro-magnetic theory of radiation. According to this theory the electric intensity of an incident radiation of frequency ν will cause the atomic electrons of the element to oscillate with the same frequency. These oscillating electrons will subsequently radiate electro-magnetic waves with the same frequency in different directions. Thus according to this theory the scattered X-rays should have the same wavelength as that of the incident X-rays.

Theory of the Compton Effect

To explain the effect, Compton applied Einstein's quantum theory of light with the assumption that the incident photons possess momentum. The postulates on which the theory is based are as follows.

(1) A beam of monochromatic radiation of frequency ν consists of a stream of photons, each of energy $h\nu$, travelling in the direction of the beam with the speed of light. Each photon has energy,

$$E = h\nu = \frac{hc}{\lambda}$$

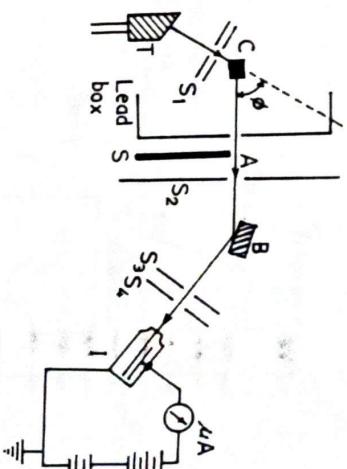


Fig. 1.10

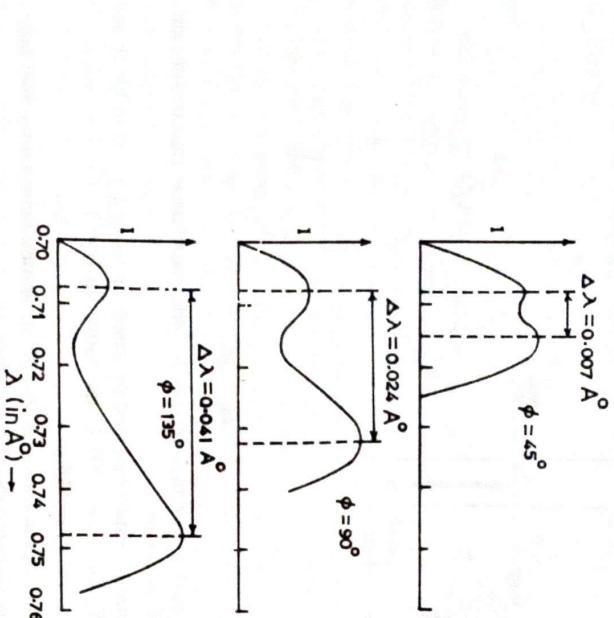


Fig. 1.11

and momentum, $p = \frac{h\nu}{c} = \frac{h}{\lambda}$

where h is Planck's constant and c is the speed of light.

(2) The scattering of X-rays by atoms of an element is the result of elastic collisions between photons and atomic electrons. (In an elastic collision, there is conservation of kinetic energy and conservation of momentum, i.e. in such a collision there is no loss of kinetic energy).

Let a beam of monochromatic X-rays of frequency ν and of wavelength λ be incident on a target O which is an element of low atomic number such as a graphite block. Suppose an incident photon makes a perfectly elastic collision with an electron initially at rest.

Suppose the photon is scattered through an angle ϕ and the electron moves in a direction θ (Fig. 1.12). Let ν' be the frequency of the scattered photon, p the momentum of the recoil electron and m_0 its rest mass. We now have:

the energy of the incident photon = $h\nu$, and its momentum = $h\nu/c$,

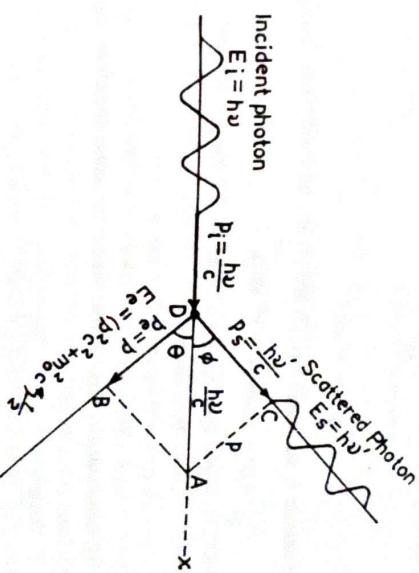


Fig. 1.12

From the principle of conservation of energy, we have
total final energy = total initial energy
i.e. $h\nu' + (p^2 c^2 + m_0^2 c^4)^{1/2} = h\nu + m_0 c^2$
 $\therefore (p^2 c^2 + m_0^2 c^4)^{1/2} = h(\nu - \nu') + m_0 c^2$

Squaring this equation, we get

$$p^2 c^2 + m_0^2 c^4 = h^2 (\nu - \nu')^2 + 2h(\nu - \nu') m_0^2 c^2 + m_0^2 c^4$$

$$\text{or } \frac{p^2 c^2}{h^2} = (\nu - \nu')^2 + \frac{2m_0 c^2}{h} (\nu - \nu') \quad \dots(1)$$

Momentum is a vector quantity and in collision between two bodies it is conserved in each of two mutually perpendicular directions. In the present case resolving the momenta along and at right angles to the direction of the incident photon, we get: (i) in the direction of the incident photon

$$p \cos \theta + \frac{h\nu'}{c} \cos \phi = \frac{h\nu}{c} \quad \dots(2)$$

or

$$\frac{pc}{h} \cos \theta = \nu - \nu' \cos \phi$$

and (ii) in the direction at right angles to the direction of the incident photon

$$p \sin \theta = \frac{h\nu'}{c} \sin \phi$$

or

$$\frac{pc}{h} \sin \theta = \nu' \sin \phi \quad \dots(3)$$

To eliminate θ , we square Eqs. (2) and (3) and then add them. This gives

$$\begin{aligned} \frac{p^2 c^2}{h^2} &= (\nu - \nu' \cos \phi)^2 + \nu'^2 \sin^2 \phi \\ &= \nu^2 - 2\nu\nu' \cos \phi + \nu'^2 \cos^2 \phi + \nu'^2 \sin^2 \phi \\ &= \nu^2 - 2\nu\nu' \cos \phi + \nu'^2 \\ &= (\nu - \nu')^2 + 2\nu\nu' - 2\nu\nu' \cos \phi \\ &= (\nu - \nu')^2 + 2\nu\nu' (1 - \cos \phi) \end{aligned} \quad \dots(4)$$

The left hand sides of Eqs. (1) and (4) are the same, therefore, equating their right hand sides, we get

$$\frac{2m_0c^2}{h} (\nu - \nu') = 2\nu\nu' (1 - \cos \phi)$$

or

$$\frac{\nu - \nu'}{\nu\nu'} = \frac{h}{m_0c^2} (1 - \cos \phi)$$

or

$$\frac{1}{\nu'} - \frac{1}{\nu} = \frac{h}{m_0c^2} (1 - \cos \phi) \quad \dots(5)$$

To express this equation in terms of the wavelengths λ and λ' , we substitute

$$\nu' = \frac{c}{\lambda'} \quad , \quad \text{and} \quad \nu = \frac{c}{\lambda} \quad ,$$

where c is the speed of light in free space, and then we get

$$\frac{\lambda'}{c} - \frac{\lambda}{c} = \frac{h}{m_0c^2} (1 - \cos \phi)$$

or

$$\lambda' - \lambda = \Delta\lambda = \frac{h}{m_0c} (1 - \cos \phi) \quad \dots(6)$$

or

$$\Delta\lambda = \frac{2h}{m_0c} \sin^2 \frac{\phi}{2} \quad \dots(7)$$

Eq. (6) or (7) is the expression for the *Compton shift* in the wavelength of the X-rays, scattered by electrons in a *light element*. The numerical value of the quantity h/m_0c in Eq. (6) is

$$\begin{aligned} \frac{h}{m_0c} &= \frac{6.626 \times 10^{-34}}{9.11 \times 10^{-31} \times 2.998 \times 10^8} = 0.2426 \times 10^{-11} \text{ m} \\ &= \frac{0.2426 \times 10^{-11}}{10^{-10}} = 0.02426 \text{ Å} \end{aligned}$$

$$\therefore \Delta\lambda = 0.02426 (1 - \cos \phi) \text{ Å}$$

Thus, this theoretical expression derived by Compton is in excellent agreement with his experimental results.

The quantity h/m_0c is called the Compton wavelength of the electron and is denoted by λ_e . Thus

$$\lambda_e = \frac{h}{m_0c} = 0.02426 \text{ Å}$$

The energy of a photon which has this wavelength is

$$E = h\nu = \frac{hc}{\lambda_e} = \frac{hc}{h/m_0c} = m_0c^2$$

Thus the Compton wavelength of the electron is the wavelength of radiation whose photon has energy equal to the rest energy m_0c^2 of the scattering electron.

The expression $\Delta\lambda$ leads to the following conclusions:

- (1) The wavelength of the radiation scattered at any angle ϕ is always greater than the wavelength of the incident radiation.
- (2) The wavelength shift $\Delta\lambda$ is independent of the wavelength of the incident X-rays, and at a fixed angle of scattering it is the same for all substances containing unbound electrons at rest.
- (3) The wavelength shift increases with the angle of scattering ϕ , and it has maximum value equal to $2h/m_0c$ when $\phi = 180^\circ$.

The derivation of the Compton shift of the wavelength of the scattered X-rays is based on the assumption that the scattering electron is free and at rest. In fact electrons are not free, they are bound to their parent atoms. In light elements such as beryllium (Be), carbon (C), and aluminium (Al), the outer electrons are loosely bound. In such elements the energy required to remove an outer electron of an atom is of the order of a few electron-volt while the photons in the X-ray region have energy of several kilo-electron volt. Therefore, for X-rays loosely bound electrons can be considered as free electrons at rest.

Limitations of Compton's Theory

(1) The Compton theory does not explain the presence of X-rays of the same wavelength in the scattered radiation, as the incident rays. An explanation for this unmodified scattered radiation is as follows: The incident X-ray photons collide with loosely bound outer electrons and also with tightly bound inner electrons of the atom. During a collision of a photon with a tightly bound electron, the electron is not detached from the atom. Consequently the entire atom recoils. In such a collision the Compton shift of the wavelength is given by replacing m_0 by the mass of the atom in Eq. (7). Calculations show that this shift is so small that it cannot be detected, because the mass of an atom is usually several thousand times greater than the mass of the electron at rest.

For example, for graphite scatterer the mass M of the atom is

$$M = 12 \times 1840 \times m_0$$

∴ the maximum value of the Compton shift due to the collisions of photons with bound electrons of graphite atoms is

$$\begin{aligned}\Delta\lambda &= \frac{2h}{Mc} \sin^2 \frac{\phi}{2} \\ &= \frac{2}{12 \times 1840} \left(\frac{h}{m_0 c} \right) \sin^2 \left(\frac{180^\circ}{2} \right) \\ &= 9.058 \times 10^{-5} \times 0.02426 \text{ Å} \\ &= 2.197 \times 10^{-6} \text{ Å}\end{aligned}$$

Thus $\Delta\lambda$ is negligible.

(2) It has been observed that the intensity of the modified X-rays is greater than that of unmodified X-rays for light elements. But for heavier elements the reverse observation has been obtained. These results are not explained by the Compton theory.

Compton Recoil Electron

To study the direction θ of ejection of the recoil electron and its energy we derive the following expressions:

Relationship Between θ and ϕ

From the Compton theory, we have

$$\frac{1}{\nu'} - \frac{1}{\nu} = \frac{h}{m_0 c^2} (1 - \cos \phi) \quad \dots(5)$$

$$\therefore \frac{\nu}{\nu'} - 1 = \frac{h\nu}{m_0 c^2} (1 - \cos \phi)$$

$$\text{or } \frac{\nu}{\nu'} = 1 + \alpha (1 - \cos \phi) \quad \dots(5a)$$

$$\text{where } \alpha = \frac{h\nu}{m_0 c^2}$$

We also have

$$\frac{pc}{h} \cos \theta = \nu - \nu' \cos \phi \quad \dots(2)$$

$$\frac{pc}{h} \sin \theta = \nu' \sin \phi \quad \dots(3)$$

Dividing Eq. (2) by Eq. (3)

$$\begin{aligned}\cot \theta &= \frac{\nu - \nu' \cos \phi}{\nu' \sin \phi} \\ &= \frac{1}{\sin \phi} \left(\frac{\nu}{\nu'} - \cos \phi \right)\end{aligned}$$

Now using Eq. (5a), we get

$$\cot \theta = \frac{1}{\sin \phi} [1 + \alpha (1 - \cos \phi) - \cos \phi]$$

$$\begin{aligned}&= \frac{(1 + \alpha)(1 - \cos \phi)}{\sin \phi} \\ &= \frac{(1 + \alpha) 2 \sin^2 \phi / 2}{2 \sin \phi / 2 \cdot \cos \phi / 2} \\ &= (1 + \alpha) \tan \frac{\phi}{2} \quad \dots(8)\end{aligned}$$

This equation shows that the maximum value of $\theta = 90^\circ$, when $\phi = 0^\circ$. Therefore, the recoil electrons are ejected at angles θ less than 90° .

Kinetic Energy of the Recoil Electron

The kinetic energy of the incident photon = $h\nu$, and the kinetic energy of the scattered photon = $h\nu'$.

∴ the kinetic energy of the recoil electron is given by

$$E = h\nu - h\nu'$$

From the Compton theory the frequency ν' of the scattered photon is given by

$$\frac{1}{\nu'} - \frac{1}{\nu} = \frac{h}{m_0 c^2} (1 - \cos \phi)$$

$$\therefore \nu' = \frac{\nu}{1 + \alpha (1 - \cos \phi)}, \quad \text{where } \alpha = \frac{h\nu}{m_0 c^2}$$

Hence

$$\begin{aligned}E &= h\nu - \frac{h\nu}{1 + \alpha (1 - \cos \phi)} \\ &= h\nu \frac{\alpha (1 - \cos \phi)}{1 + \alpha (1 - \cos \phi)} \quad \dots(9)\end{aligned}$$

The right hand side of this equation can be expressed in terms of θ .

$$\begin{aligned}E &= h\nu \frac{\alpha \times 2 \sin^2 \phi / 2}{1 + \alpha \times 2 \sin^2 \phi / 2} \\ &= h\nu \frac{2\alpha}{\cosec^2 \phi / 2 + 2\alpha} \quad \dots(9a)\end{aligned}$$

Now we have

$$\cot \phi / 2 = (1 + \alpha) \tan \theta$$

Squaring this equation

$$\cot^2 \phi / 2 = (1 + \alpha)^2 \tan^2 \theta$$

$$\begin{aligned}\text{or } \cosec^2 \phi / 2 - 1 &= (1 + \alpha)^2 (\sec^2 \theta - 1) \\ &= (1 + \alpha)^2 \sec^2 \theta - (1 + \alpha)^2 \\ &= (1 + \alpha)^2 \sec^2 \theta - 1 - 2\alpha - \alpha^2\end{aligned}$$

$$\therefore \cosec^2 \phi / 2 + 2\alpha = (1 + \alpha)^2 \sec^2 \theta - \alpha^2$$

Hence Eq. (9a) is written as

$$E = h\nu \frac{2\alpha}{(1 + \alpha)^2 \sec^2 \theta - \alpha^2}$$

or

$$E = h\nu \frac{2\alpha \cos^2 \theta}{(1 + \alpha)^2 - \alpha^2 \cos^2 \theta} \quad \dots(10)$$

The experimental values of E of the recoil electrons determined by Compton and Simon in 1925 and by Bless in 1927 agreed well with the theoretical values.

The study of the Compton effect leads to the conclusion that radiant energy in its interaction with matter behaves as a stream of discrete particles (photons) each of energy $h\nu$ and momentum $h\nu/c$. In other words, radiant energy is quantized. Therefore the Compton effect is considered as a decisive phenomenon in support of quantization of energy.

1.7. Quantum States of Energy

The idea that all matter is made up of atoms was proposed in 1803 by John Dalton and this atomic theory of matter was firmly established during the nineteenth century. But the structure of the atoms remained unknown. Without any knowledge about the atomic structure it was impossible to apply Planck's quantum theory to atomic phenomena such as the emission of spectra. Therefore, their origin remained unexplained for a long time. The first attempt for correct explanation of the structure of the atoms was made by Lord Rutherford in 1911 when he proposed the nuclear model of the atom on the basis of the scattering of α -particles from metallic foils. However, classical theories failed to explain the stability of the atom on the basis of such a model. The first step in introducing the concept of quantum states of energy was made by Niels Bohr in 1913. In order to explain the origin of the optical spectrum of hydrogen and the stability of the atom he adopted the Rutherford model and applied Planck's quantum theory to it. In his theory of the hydrogen atom he made the following three assumptions.

- (1) The electron in the hydrogen atom revolves round the nucleus only in certain allowed circular orbits. From these orbits no electromagnetic radiation is emitted in spite of the accelerated motion of the electron. Corresponding to these orbits the atom is said to be in discrete stationary states of energy or discrete energy levels. These energy states are known as quantum states of energy of the atom.
- (2) The angular momentum of the electron in motion in allowed circular orbits round the nucleus of the hydrogen atom is an integral multiple of $h/2\pi$, i.e. the angular momentum = $nh/2\pi$, where $n = 0, 1, 2, \dots$
- (3) When a quantum state of higher energy E_{n_2} changes to another quantum state of lower energy E_{n_1} the frequency ν of the radiation emitted by the atom is given by

$$\nu = \frac{E_{n_2} - E_{n_1}}{h}$$

Based on these assumptions Bohr's theory explains quite successfully the spectrum of hydrogen and hydrogen-like ions such as singly ionised helium and doubly ionised lithium. But the theory does not explain the experimental fact that each line of the spectrum of the hydrogen atom extends over a finite wave-length range, consisting of a small number of lines close together. In order to explain this *fine structure* of the spectral lines W. Wilson in 1915 and A. Sommerfeld in 1916 considered the motion of an electron in an elliptical orbit round the nucleus, and they independently stated a *general quantisation rule* in the case of an allowed elliptical orbit.

1.8. Drawbacks of the Old Quantum Theory

Planck's quantum hypothesis with its application and extension to explain the black body radiation, the photo-electric effect, the Compton effect, the variation of specific heat of solids with temperature and the spectrum of hydrogen is now called the Old Quantum Theory. Though these phenomena are successfully explained by the theory, there are numerous drawbacks of the theory. A few of them are as follows:

1. Bohr's quantization rules are arbitrary. The theory does not provide physical explanation for the assumptions.
2. The old quantum theory cannot be applied to explain the spectra of helium and of more complex atoms.
3. It can provide only a qualitative and incomplete explanation of the intensities of the spectral lines.
4. It cannot explain the dispersion of light.
5. The theory cannot be applied to explain non-harmonic vibrations of systems.

1.9. Dual Character of Light

We know that interference and diffraction of light are produced by the superposition of beams of light. Thus, these phenomena are the result of *interaction of light with light*. From experimental observations on interference, diffraction and some other phenomena such as reflection, refraction and polarisation and their interpretations it is concluded that light is a transverse wave motion. Therefore these phenomena are completely explained by the wave theory and the electromagnetic theory of radiation.

However, there is another class of phenomena: black body radiation, the photo-electric effect and the Compton effect which are produced by *interaction of radiation with matter*, and these cannot be explained by the wave theory or the electromagnetic theory of radiation. We have seen that in order to explain these phenomena, radiant energy is considered as a stream of small packets of energy. These packets of energy are known as light quanta or *photons*. The amount of energy assigned to each photon is given by

$$E = h\nu$$

In interaction of radiant energy with matter, any one of the photons can transfer all its energy to an electron of the matter.

The frequency ν is determined from the measurement of the wavelength λ of radiation, using the equation

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

The frequency or wavelength is a concept relevant to a wave, and quantum having the isolated energy $h\nu$ is the concept of a particle. Therefore, we conclude that radiation possesses dual character, and it never exhibits both characteristics in any one experiment.

SOLVED EXAMPLES

Example 1.1. Find the average number of photons per cubic metre in a monochromatic beam of radiation of frequency 10 kHz and of intensity 10^4 W/m^2 .

Solution:

The intensity of a beam of radiation is the total energy of the number of photons passing normally through unit area of the cross-section of beam per second.

Let n be the number of photons per unit volume each having energy $h\nu$. Let us consider a length l of the beam having cross-section area A .

In the volume Al the total photon-energy = $nAlh\nu$. The time taken by this energy to pass through the length l is given by

$$t = \frac{l}{c}$$

where c is the speed of light in free space.

∴ the intensity I of the beam is given by

$$I = \frac{nAlh\nu}{At} = \frac{nlh\nu}{l/c} = nh\nu c$$

Hence

$$n = \frac{I}{h\nu c}$$

Substituting the numerical values

$$n = \frac{10^4}{6.63 \times 10^{-34} \times 10^4 \times 3 \times 10^8} \\ = \frac{10^{26}}{19.89} = 5.03 \times 10^{24} \text{ photons/m}^3$$

Example 1.2. Prove that in the photo-electric effect from a metal surface, the maximum velocity of the photo-electrons is related to stopping potential by the equation

$$v_{\max} = 5.923 \times 10^5 \times \sqrt{V_0}$$

where v_{\max} is in m/sec. and V_0 is in volts.

Solution:

We have $m = 9.11 \times 10^{-31} \text{ kg}$, $e = 1.6 \times 10^{-19} \text{ C}$

The maximum kinetic energy is related to the stopping potential by the equation.

$$\frac{1}{2}mv_{\max}^2 = eV_0 \\ \therefore v_{\max} = \sqrt{\frac{2eV_0}{m}} = \sqrt{\frac{2 \times 1.6 \times 10^{-19}}{9.11 \times 10^{-31}}} \times \sqrt{V_0} \\ = 10^5 \sqrt{\frac{20 \times 16}{9.11}} \times \sqrt{V_0} \\ = 10^5 \times 5.927 \sqrt{V_0} \\ = 5.927 \times 10^5 \sqrt{V_0} \text{ m/sec.}$$

Example 1.3. The photo-electric threshold wavelength of silver is 2762 Å. Calculate

(a) the maximum kinetic energy of the ejected electrons, (b) the maximum velocity of

the electrons, and (c) the stopping potential in volts for the electrons, when the silver surface is illuminated with ultraviolet light of wavelength 2000 Å.

Solution:

$$\begin{aligned} \text{We have } \lambda &= 2000 \times 10^{-10} \text{ m} = 2 \times 10^{-7} \text{ m} \\ \text{and } \lambda_0 &= 2762 \times 10^{-10} \text{ m} = 2.762 \times 10^{-7} \text{ m} \\ (a) \quad E_{\max} &= h(\nu - \nu_0) \\ &= hc \left(\frac{1}{\lambda} - \frac{1}{\lambda_0} \right) \\ &= 6.63 \times 10^{-34} \times 3 \times 10^8 \left(\frac{10^7}{2} - \frac{10^7}{2.762} \right) \\ &= 6.63 \times 3 \times 10^{-19} \left(\frac{1}{2} - \frac{1}{2.762} \right) \\ &= 6.63 \times 3 \times 10^{-19} \times 0.138 \\ &= 2.745 \times 10^{-19} \text{ J} \end{aligned}$$

(b) The maximum velocity is given by

$$\begin{aligned} \frac{1}{2}mv_{\max}^2 &= E_{\max} \\ \therefore v_{\max} &= \sqrt{\frac{2 \times E_{\max}}{m}} \\ &= \sqrt{\frac{2 \times 2.745 \times 10^{-19}}{9.11 \times 10^{-31}}} = 10^5 \sqrt{\frac{2 \times 274.5}{9.11}} \\ &= 7.76 \times 10^5 \text{ m/sec.} \end{aligned}$$

$$\begin{aligned} (c) \quad eV_0 &= E_{\max} \\ \therefore V_0 &= \frac{E_{\max}}{e} = \frac{2.745 \times 10^{-19}}{1.6 \times 10^{-19}} \\ &= 1.715 \text{ Volts.} \end{aligned}$$

Example 1.4. A metallic surface, when illuminated with light of wavelength λ_1 , emits electrons with energies upto a maximum value E_1 , and when illuminated with light of wavelength λ_2 , where $\lambda_2 < \lambda_1$, it emits electrons with energies upto a maximum value E_2 . Prove that Planck's constant h and the work-function W_0 of the metal are given by

$$\begin{aligned} h &= \frac{(E_2 - E_1) \lambda_1 \lambda_2}{c (\lambda_1 - \lambda_2)} \\ W_0 &= \frac{E_2 \lambda_2 - E_1 \lambda_1}{\lambda_1 - \lambda_2} \end{aligned}$$

Solution:

The maximum kinetic energy E_1 is given by

$$E_1 = h\nu_1 - W_0$$

or

$$E_1 = \frac{hc}{\lambda_1} - W_0 \quad \dots(1)$$

Similarly the maximum kinetic energy E_2 is given by

$$E_2 = \frac{hc}{\lambda_2} - W_0 \quad \dots(2)$$

Subtracting Eq. (1) from Eq. (2), we get,

$$\begin{aligned} E_2 - E_1 &= hc \left(\frac{1}{\lambda_2} - \frac{1}{\lambda_1} \right) = hc \left(\frac{\lambda_1 - \lambda_2}{\lambda_1 \lambda_2} \right) \\ h &= \frac{(E_2 - E_1) \lambda_1 \lambda_2}{c (\lambda_1 - \lambda_2)} \end{aligned} \quad \dots(3)$$

Now to obtain the expression for W_0 , from Eq. (1) and (2) we have,

$$E_1 \lambda_1 = hc - W_0 \lambda_1 \quad \dots(4)$$

$$E_2 \lambda_2 = hc - W_0 \lambda_2 \quad \dots(5)$$

Subtracting Eq. (4) from Eq. (5), we get,

$$\begin{aligned} E_2 \lambda_2 - E_1 \lambda_1 &= W_0 (\lambda_1 - \lambda_2) \\ \therefore W_0 &= \frac{E_2 \lambda_2 - E_1 \lambda_1}{\lambda_1 - \lambda_2} \end{aligned} \quad \dots(6)$$

Example 1.5. A metallic surface, when illuminated with light of wavelength 3333 Å, emits electrons with energies upto 0.6 eV, and when illuminated with light of wavelength 2400 Å, it emits electrons with energies upto 2.04 eV. Calculate Planck's constant and the work-function of the metal.

Solution:

$$\begin{aligned} \text{We have } \lambda_1 &= 3333 \times 10^{-10} \text{ m} = 3.000 \times 10^{-7} \text{ m} \\ \lambda_2 &= 2400 \times 10^{-10} \text{ m} = 2.4 \times 10^{-7} \text{ m} \end{aligned}$$

$$\text{Max. energy } E_1 = 0.6 \times 1.6 \times 10^{-19} \text{ J}$$

$$\text{Max. energy } E_2 = 2.04 \times 1.6 \times 10^{-19} \text{ J}$$

(i) **Planck's constant:** Proceed as in Ex. 4 and obtain

$$\begin{aligned} h &= \frac{(E_2 - E_1) \lambda_1 \lambda_2}{c (\lambda_1 - \lambda_2)} \\ h &= \frac{(2.04 - 0.6) \times 1.6 \times 10^{-19} \times 3.333 \times 10^{-7} \times 2.4 \times 10^{-7}}{3 \times 10^8 (3.333 - 2.4) \times 10^{-7}} \\ &= \frac{1.44 \times 1.6 \times 3.333 \times 2.4 \times 10^{-34}}{3 \times 0.933} \\ &= 6.58 \times 10^{-34} \text{ Js.} \end{aligned}$$

(ii) **Work function:** Proceed as in Ex. 4 and obtain

$$\begin{aligned} W_0 &= \frac{E_2 \lambda_2 - E_1 \lambda_1}{\lambda_1 - \lambda_2} \\ \therefore W_0 &= \frac{(2.04 \times 2.4 - 0.6 \times 3.333) \times 10^{-7}}{(3.333 - 2.4) \times 10^{-7}} \text{ eV} \\ &= \frac{4.896 - 1.9998}{0.933} \\ &= \frac{2.896}{0.933} = 3.1 \text{ eV.} \end{aligned}$$

Example 1.6. An X-ray photon of wavelength 0.3 \AA is scattered through an angle 45° by a loosely bound electron. Find the wavelength of the scattered photon.

Solution:

$$\text{We have, } \lambda = 0.3 \text{ \AA}, \quad h = 6.63 \times 10^{-34} \text{ Js}, \quad m_0 = 9.11 \times 10^{-31} \text{ kg}$$

$$c = 3 \times 10^8 \text{ m/sec.}$$

The wavelength of the scattered photon is given by

$$\lambda' = \lambda + \frac{h}{m_0 c} (1 - \cos \phi) \quad \dots(1)$$

$$\text{Now, } \frac{h}{m_0 c} = \frac{6.63 \times 10^{-34}}{9.11 \times 10^{-31} \times 3 \times 10^8} = \frac{6.63 \times 10^{-11}}{9.11 \times 3} \text{ m}$$

$$= \frac{2.21 \times 10^{-11}}{9.11} = 0.2426 \times 10^{-11} \text{ m} = 0.02426 \text{ \AA.}$$

\therefore from Eq. (1)

$$\begin{aligned} \lambda' &= 0.3 + 0.02426 (1 - \cos 45^\circ) \\ &= 0.3 + 0.02426 (1 - 0.7071) \\ &= 0.3 + 0.02426 \times 0.2929 \\ &= 0.3 + 0.007106 \\ &= 0.3071 \text{ \AA} \end{aligned}$$

Example 1.7. An X-ray photon of frequency $3 \times 10^{19} \text{ Hz}$ collides with an electron and is scattered through 90° . Find the frequency of the scattered photon. Given: the Compton wavelength of the electron, $\lambda_e = 0.02426 \text{ \AA}$.

Solution:

We have

$$\lambda_e = 0.02426 \times 10^{-10} \text{ m}, \quad \phi = 90^\circ, \quad c = 10^8 \text{ m/sec.}$$

The frequency of the scattered photon is given by

$$\begin{aligned} \nu' &= \frac{\nu}{1 + \frac{h\nu}{m_0 c^2} (1 - \cos \phi)} \\ &= \frac{\nu}{1 + \frac{h\nu}{m_0 c^2}}, \quad \because \cos 90^\circ = 0 \end{aligned}$$

Now,

$$\begin{aligned} \frac{h\nu}{m_0 c^2} &= \left(\frac{h}{m_0 c} \right) \nu = \frac{\lambda_e \nu}{c} \\ &= \frac{0.02426 \times 10^{-10} \times 3 \times 10^{19}}{3 \times 10^8} \\ &= 0.2426 \end{aligned}$$

Substituting this value in the above equation

$$\begin{aligned} \nu' &= \frac{\nu}{1 + 0.2426} = \frac{3 \times 10^{19}}{1.2426} \\ &= 2.414 \times 10^{19} \text{ Hz} \end{aligned}$$

Example 1.8. Show that the maximum recoil energy of a free electron of rest mass m_0 , when struck by a photon of frequency ν , is given by

$$E_{\max} = \frac{(h\nu)^2}{h\nu + \frac{1}{2} m_0 c^2}$$

Solution:

The kinetic energy of the recoil electron is given by
 $E = h\nu - h\nu' = h(\nu - \nu')$

E will be maximum when ν' is minimum.

$$\therefore E_{\max} = h(\nu - \nu'_{\min}) \quad \dots(1)$$

$$\text{Now} \quad \nu' = \frac{\nu}{1 + \frac{h\nu}{m_0 c^2} (1 - \cos \phi)}$$

This equation shows that ν' is minimum when the denominator is maximum. The maximum value of the denominator occurs when

$$\phi = 180^\circ, \text{ i.e. when } \cos \phi = -1$$

$$\therefore \nu'_{\min} = \frac{\nu}{1 + \frac{2h\nu}{m_0 c^2 + 2h\nu}} = \frac{m_0 \nu c^2}{m_0 c^2 + 2h\nu}$$

Substituting this value of ν'_{\min} in Eq. (1),

$$\begin{aligned} E_{\max} &= h \left[\nu - \frac{m_0 \nu c^2}{m_0 c^2 + 2h\nu} \right] \\ &= \frac{2h^2 \nu^2}{2h\nu + m_0 c^2} \\ &= \frac{(h\nu)^2}{h\nu + \frac{1}{2} m_0 c^2} \end{aligned}$$

Example 1.9. Show that the maximum recoil energy of a free electron of rest mass m_0 , when struck by a photon of wavelength λ , is given by

$$E_{\max} = \frac{2m_0 c^2 \lambda_e^2}{\lambda^2 + 2\lambda_e \lambda}$$

where λ_e is the Compton wavelength of the electron.

Solution:

The kinetic energy of the recoil electron is given by

$$E = h(\nu - \nu') = hc \left(\frac{1}{\lambda} - \frac{1}{\lambda'_{\max}} \right)$$

E will be maximum when λ' is maximum.

$$\therefore E_{\max} = hc \left[\frac{1}{\lambda} - \frac{1}{\lambda'_{\max}} \right] \quad \dots(1)$$

$$\text{Now} \quad \lambda' = \lambda + \frac{h}{m_0 c} (1 - \cos \phi)$$

$$= \lambda + \lambda_e (1 - \cos \phi)$$

It is evident that the maximum value of λ' occurs when $\phi = 180^\circ$, i.e. when $\cos \phi = -1$

$$\lambda'_{\max} = \lambda + 2\lambda_e$$

Substituting this value of λ'_{\max} in Eq. (1),

$$\begin{aligned} E_{\max} &= hc \left[\frac{1}{\lambda} - \frac{1}{\lambda + 2\lambda_e} \right] \\ &= \frac{2hc\lambda_e}{\lambda(\lambda + 2\lambda_e)} \end{aligned}$$

Since

$$\lambda_e = \frac{h}{m_0 c}$$

$$h = m_0 c \lambda_e$$

Substituting for h in the above equation

$$\begin{aligned} E_{\max} &= \frac{2m_0 c \lambda_e \times c \lambda_e}{\lambda^2 + 2\lambda_e \lambda} \\ &= \frac{2m_0 c^2 \lambda_e^2}{\lambda^2 + 2\lambda_e \lambda} \end{aligned}$$

Example 1.10. An X-ray photon of frequency 3×10^{19} Hz collides with a free electron at rest and is scattered at 60° . Find the direction in which the electron will move. Given $h/m_0 c = 0.02426 \text{ \AA}$.

Solution:

$$\text{We have } \nu = 3 \times 10^{19} \text{ Hz}, \quad \phi = 60^\circ, \quad h = 6.63 \times 10^{-3} \text{ Js}$$

The angle θ which the direction of motion of the electron makes with the direction of the incident photon is given by

$$\cot \theta = (1 + \alpha) \tan \frac{\phi}{2}$$

The value of α is

$$\begin{aligned} \alpha &= \frac{h\nu}{m_0 c^2} = \left(\frac{h}{m_0 c} \right) \nu \\ &= 0.02426 \times 10^{-10} \times \frac{3 \times 10^{19}}{3 \times 10^8} \\ &= 0.2426 \end{aligned}$$

Substituting the values of α and ϕ in the above equation

$$\begin{aligned} \cot \theta &= (1 + 0.2426) \tan 30^\circ \\ &= 1.2426 \times \frac{1}{\sqrt{3}} = \frac{1.2426}{1.7320} \end{aligned}$$

$$\tan \theta = \frac{1.7320}{1.2426} = 1.3938$$

$$\theta = 54.34^\circ$$

Example 1.11. A photon of frequency ν is scattered by an electron of rest mass m_0 . The scattered photon of frequency ν' leaves in a direction at 90° to the incident photon. Show that the momentum acquired by the electron is given by

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$$p = \frac{h}{c} (\nu^2 + \nu'^2)^{1/2}$$

Solution: (See Fig. 1.13).

From the figure we have

$$p^2 = \left(\frac{h\nu}{c} \right)^2 + \left(\frac{h\nu'}{c} \right)^2$$

$$p = \frac{h}{c} (\nu^2 + \nu'^2)^{1/2}$$

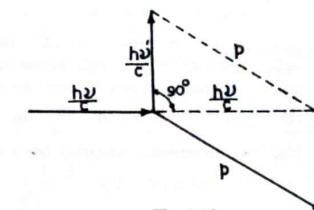


Fig. 1.13

QUESTIONS AND PROBLEMS

- Find the average number of photons per cubic metre in a monochromatic beam of γ -rays of wavelength 0.003 \AA and of intensity 10^4 W/m^2 .
(Ans. $5.03 \times 10^{17}/\text{m}^3$)
- What was Planck's hypothesis to explain the spectral distribution of the intensity of radiation from a black body? Derive Planck's radiation law.
- (a) Explain the photo-electric effect.
(b) Outline the basic facts of the photo-electric effect.
(c) Discuss the inadequacy of the wave theory of light to explain the effect.
(d) Establish Einstein's equation for the photo-electric effect.
- (a) Define the terms: (i) threshold frequency, (ii) photo-electric work function, (iii) stopping potential.
(b) Deduce Einstein's photo-electric equation.
- (a) In what way does the wave theory fail to explain the photo-electric effect.
(b) Show that Einstein's equation gives adequate explanation of all the facts about the photo-electric effect.
- (a) Explain the photo-electric effect.
(b) In the photo-electric effect, why does the existence of a cut-off frequency speak in favour of photon theory and against wave theory?
(c) A photon of energy 12 eV falls on molybdenum whose work-function is 4.15 eV. Find the stopping potential.
(Ans. 7.85 V)
- Find the maximum energy of the photo-electrons in electron-volts when light of frequency $1.5 \times 10^9 \text{ MHz}$ falls on a metal surface for which the threshold frequency is $1.2 \times 10^9 \text{ MHz}$.
(Ans. 1.24 eV)
- A photon of energy 10 eV falls on molybdenum whose work-function is 4.15 eV. Find the stopping potential.
(Ans. 5.85 Volts)
- The threshold wave-length for a metal is $3800 \times 10^{-10} \text{ m}$. Calculate the maximum kinetic energy of the photo-electrons ejected when ultra-violet light of wavelength $2500 \times 10^{-10} \text{ m}$ falls on it.
(Ans. $2.725 \times 10^{-19} \text{ J}$ i.e. 1.7 eV)

10. A certain photo-tube requires 1 volt to serve as the stopping potential for light of wavelength 5000 Å. If the light has the wavelength of 3750 Å the stopping potential is 1.82 volts. Calculate $\frac{h}{e}$ from this data.

[Hint: $eV_1 = \frac{hc}{\lambda_1} - W_0$ and $eV_2 = \frac{hc}{\lambda_2} - W_0$

Eliminate W_0 between these equations and obtain

$$e(V_2 - V_1) = \frac{hc(\lambda_1 - \lambda_2)}{\lambda_1 \lambda_2}$$

$$\frac{h}{e} = \frac{[V_2 - V_1] \lambda_1 \lambda_2}{c [\lambda_1 - \lambda_2]} \quad (\text{Ans. } 4.1 \times 10^{-15} \text{ Volt.sec})$$

11. The photo-electric threshold wavelength of tungsten is 2300 Å. The tungsten surface is illuminated with ultraviolet light of wavelength 1800 Å. Calculate

- (a) the maximum kinetic energy of the ejected electrons, (b) the maximum velocity of the ejected electrons and (c) the stopping potential, in volts, for the electrons.

(Ans. (a) 2.387×10^{-19} J, i.e. 1.49 eV (b) 7.239×10^5 m/sec. (c) 1.49 V)

12. Potassium has a work-function of 2 eV and is illuminated by mono-chromatic light of wavelength 3600 Å. Find

- (a) the maximum kinetic energy of the ejected electrons, (b) the maximum velocity of the ejected electrons, and (c) the stopping potential in volts for the electrons.

(Ans. (a) 2.325×10^{-19} J, (b) 7.14×10^5 m/sec., (c) 1.45 Volts)

13. An X-ray photon of frequency ν is scattered through an angle ϕ by an electron which is at rest. (a) Write the relativistic equations for the conservation of energy and momentum. (b) From these equations obtain an expression for the frequency of the scattered photon, and show that if the angle of scattering is 90° , the frequency of the scattered photon is given by:

$$\nu' = \frac{\nu mc^2}{h\nu + mc^2}$$

14. (a) What is the Compton effect?

- (b) Explain why this effect cannot be explained on the basis of electromagnetic theory of radiation.

- (c) Give the explanation of this effect with the help of quantum theory and find an expression of the Compton shift $\Delta\lambda$.

15. (a) What is the Compton effect?

- (b) Show that the change in the wavelength of X-ray photon on scattering from a free electron is independent of the wavelength of the incident radiation.

- (c) A beam of X-rays is scattered by loosely bound electrons at 45° from the direction of the beam. The wavelength of the scattered X-rays is 0.22 Å. What is the wavelength of X-rays in the direct beam.

[Hint: $\lambda = \lambda' - \frac{h}{mc} [1 - \cos \phi] = 0.22 - 0.002426 \left(1 - \frac{1}{\sqrt{2}}\right)$

(Ans. 0.2129 Å)

16. (a) What is the Compton effect? Give its significance.

- (b) Considering the Compton scattering of X-rays derive expressions for (i) the Compton shift and (ii) the kinetic energy of the recoil electron.

- (c) X-rays with $\lambda = 2.00 \text{ \AA}$ are scattered from a carbon block and the scattered radiation is viewed at 90° to the incident beam. Find the Compton shift.

(N.U. 1978) (Ans. 0.02426 Å)

17. An X-ray photon of frequency 1.5×10^{19} Hz is scattered by a free electron and the frequency of the scattered photon is 1.2×10^{19} Hz.

(Ans. 1.989×10^{-15} J)

18. X-rays of wavelength 0.5×10^{-10} m are scattered by free electrons in a block of carbon, through 90° . Find the momentum of (a) incident photons, (b) scattered photons, (c) recoil electrons, and (d) the energy of the recoil electrons.

(Ans. (a) $1.326 \times 10^{-23} \text{ kg.m/sec.}$, (b) $1.265 \times 10^{-23} \text{ kg.m/sec.}$,

(c) $1.832 \times 10^{-23} \text{ kg.m/sec.}$, (d) 1.79×10^{-16} J)

19. Show that the wavelength of X-radiation which is able to produce recoil electrons in the direction of the incident X-radiation is given by

$$\lambda = \lambda_i \left[\sqrt{1 + \frac{2mc^2}{K_{\max}}} - 1 \right]$$

where λ_i is the Compton wavelength of the electron and K_{\max} is the maximum recoil energy of an electron.

[Hint: See solved example 7]

20. Find the wavelength of X-radiation which is able to produce recoil electrons with maximum recoil energy of 5 KeV. (Given: the Compton wavelength of the electron = 0.02426 \AA .

$$\begin{aligned} [\text{Hint: } \lambda &= \lambda_i \left[\sqrt{1 + \frac{2mc^2}{K_{\max}}} - 1 \right]] \\ &= 0.02426 \left[\sqrt{1 + \frac{2 \times 9.11 \times 10^{-31} \times 9 \times 10^6}{5 \times 10^3 \times 1.6 \times 10^{-19}}} - 1 \right] \\ &= 0.02426 (\sqrt{1 + 205} - 1) = 0.02426 \times 13.35 = 0.32 \text{ \AA} \end{aligned}$$

2

Wave Properties of Matter

2.1 Introduction

In the previous chapter we have seen that radiation possesses dual character. It is a wave motion since it exhibits well known interference and diffraction phenomena which are caused by the interaction of radiation with radiation. It also behaves as a set of discrete particles (the photons) in some phenomena, such as black body radiation, photo-electric effect, and the Compton effect, which are caused by the interaction between radiation and matter. Matter evidently has particle properties. Therefore, by analogy with radiation, matter should also have wave properties under suitable conditions. This was first predicted by the French theoretical physicist Prince Louis De Broglie in 1924, and was verified experimentally by C.J. Davison and L.H. Germer in 1927, and also by G.P. Thomson in the same year. Wave properties of matter can be reconciled with particle properties by combining waves of different wavelengths to form group of waves (wave packets). Since the effect of a particle in motion at any instant of time is confined to a small region in space, a wave packet can be used to represent a particle in motion.

2.2 Phase Velocity and Group Velocity

A plane simple harmonic wave travelling in the positive x -direction is represented by the well known equation

$$y = A \sin \omega \left(t - \frac{x}{v} \right) \quad \dots (1)$$

where A is the amplitude, v the velocity of propagation of the wave in the positive x -direction, and ω the angular frequency which is related to the frequency ν of the wave by the formula

$$\omega = 2\pi\nu$$

The wave velocity is also called the phase velocity. The reason for this is as follows. In Eq. (1) the phase ϕ of the wave at position x and at time t is

$$\phi(x, t) = \omega \left(t - \frac{x}{v} \right)$$

Differentiating this equation with respect to t , we get

$$\frac{\partial \phi}{\partial t} = \omega \left(1 - \frac{1}{v} \frac{dx}{dt} \right)$$

For a point of constant phase, $\frac{\partial \phi}{\partial t} = 0$

$$\therefore 1 - \frac{1}{v} \left(\frac{\partial x}{\partial t} \right)_p = 0$$

or

$$\left(\frac{\partial x}{\partial t} \right)_p = v$$

$\left(\frac{\partial x}{\partial t} \right)_p$ is the velocity with which a displacement of a given phase moves forward. Therefore, this quantity is called the phase velocity, and it is usually denoted by v_p or v_ϕ . Thus the velocity of propagation or the velocity of a wave is the velocity with which a displacement of a given phase moves forward. We now rewrite Eq. (1) replacing v by v_p .

$$y = A \sin \omega \left(t - \frac{x}{v_p} \right) = A \sin \left(\omega t - \frac{\omega}{v_p} x \right)$$

where

$$v_p = \frac{\omega}{k}$$

$$= A \sin (\omega t - kx) \quad \dots (2)$$

The quantity k is called the propagation constant, or the phase constant, or the propagation number of the wave. It can be expressed in terms of the wavelength λ :

$$k = \frac{\omega}{v_p} = \frac{2\pi\nu}{\lambda} = \frac{2\pi}{\lambda} \quad \dots (3)$$

In terms of ω and k the phase velocity is given by

$$v_p = \frac{\omega}{k}$$

If the wave travels in an arbitrary direction, the displacement $\Psi(x, y, z, t)$ at distance r from the origin of the coordinate-axes is given by the wave equation

$$\Psi(x, y, z, t) = A \sin (\omega t - k_x x - k_y y - k_z z) \quad \dots (4)$$

where \vec{k} is the propagation vector, and \vec{r} the position vector of the point from the origin.

Dispersive and Nondispersive Waves

The phase velocity of a wave is independent of its amplitude but depends on the properties and state of the medium. For a wave passing through a material medium the properties involved are density and elasticity, and the state may be the pressure of a gas or the tension of a string. For light waves

in a medium such as glass, the phase velocity depends on the refractive index of the medium. If the properties, or the state depend on frequency of a wave passing through the medium, the phase velocity in the medium will not be constant, but will vary with frequency. This phenomenon is called dispersion and the medium in which the phase velocity varies with wavelength or frequency is called a dispersive medium. In such a medium waves of different wavelengths travel with different phase velocities, i.e., the waves are dispersive. Thus dispersive waves in a medium are those for which the phase velocity $v_p = \omega/k$ varies with the wavelength.

Examples of dispersive waves are: Light waves in glass, waves on water surface. A medium in which the phase velocity of a wave is independent of wavelength or frequency is called a nondispersive medium. In such a medium waves of different wavelengths travel with the same phase velocity, i.e., the waves are nondispersive. Thus nondispersive waves in a medium are those for which the phase velocity $v_p = \omega/k$ is independent of the wavelength. Examples of nondispersive waves are: Electromagnetic waves in vacuum, audible sound waves in a gas, transverse waves on a continuous stretched string.

Group Velocity

When plane waves of different wavelengths travel simultaneously in the same direction along a straight line, through a dispersive medium, i.e., a medium in which the phase velocity $v_p = \omega/k$ of a wave depends on its wavelength successive groups of the waves are produced (Fig. 2.1). These wave-groups are also called wave-packets. Each wave-group travels with a velocity v_g called the group velocity. The group velocity is different from the phase velocity of a wave.

2.3 Analytical Expression for a Group of Waves

An analytical expression for a group of waves was first obtained by Stokes. He assumed that a group of waves is formed by the superposition of two infinite trains of waves of the same amplitude but of slight different wavelengths, which travel simultaneously in the same direction along the same straight line. On the basis of this assumption, Lord Rayleigh treated the problem in the following way and he first pointed out the importance of a group of waves in the interpretation of optical phenomena and experiments.

Let two plane simple harmonic waves of the same amplitude but of slightly different wavelengths travelling simultaneously in the positive x -direction in a dispersive medium be represented by

$$y_1 = A \sin(\omega t - kx) \quad \dots(1)$$

$$y_2 = A \sin[(\omega + \delta\omega)t - (k + \delta k)x] \quad \dots(2)$$

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

$$y = y_1 + y_2$$

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$$= A \sin(\omega t - kx) + A \sin[(\omega + \delta\omega)t - (k + \delta k)x]$$

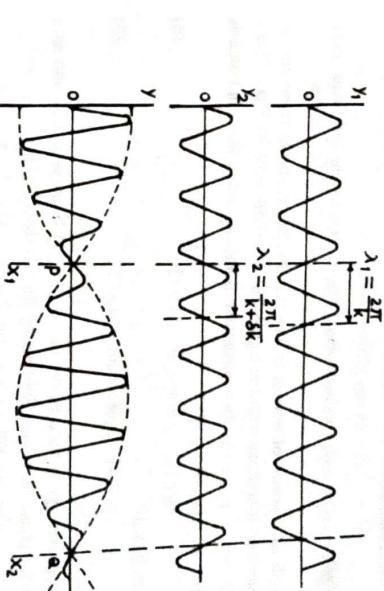


Fig. 2.1

The trigonometric equation for sum of the sines of two angles is

$$\sin C + \sin D = 2 \sin \left(\frac{C+D}{2} \right) \cos \left(\frac{C-D}{2} \right)$$

Making use of this equation, we get

$$y = 2A \cos \left(-\frac{\delta\omega}{2}t + \frac{\delta k}{2}x \right) \sin \left[\left(\frac{2\omega + \delta\omega}{2} \right)t - \left(\frac{2k + \delta k}{2} \right)x \right]$$

or $y = 2A \cos \frac{1}{2}(\delta\omega - x\delta k) \sin \left[\left(\frac{2\omega + \delta\omega}{2} \right)t - \left(\frac{2k + \delta k}{2} \right)x \right] \quad \dots(3)$

Since $\delta\omega$ and δk are small compared with ω and k respectively, in the sine term $\delta\omega$ and δk are neglected.

\therefore we get

$$y = 2A \cos \frac{1}{2}(\delta\omega - x\delta k) \sin (\omega t - kx) \quad \dots(4)$$

This is the analytical expression for the group of waves, i.e., the wave-packet formed by the two waves. From this equation we note the following points:

- The sine factor represents a carrier wave which travels with the phase velocity

$$v_p = \frac{\omega}{k}$$

(ii) The amplitude of the resultant waves is

$$R = 2A \cos \frac{1}{2}(t\delta\omega - x\delta k) \quad \dots(5)$$

For the group of waves we now obtain expressions for the following quantities:

Length of a group of waves: In Fig. 2.1 the dotted curves represent the variation of the amplitude with x at a given time t . At this time let $P(x_1, 0)$ and $Q(x_2, 0)$, where $x_2 > x_1$, be two successive points at which the amplitude is zero. Then at $P(x_1, 0)$ we have

$$\frac{1}{2}(t\delta\omega - x_1\delta k) = (2n+1)\pi/2 \quad \dots(6)$$

And at $Q(x_2, 0)$

$$\frac{1}{2}(t\delta\omega - x_2\delta k) = (n-1)\pi/2 \quad \dots(7)$$

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

The negative sign is used in the factor $(2n-1)$ because $x_2 > x_1$ and as x increases the phase decreases. Subtracting Eq. (7) from Eq. (6)

$$\frac{1}{2}(x_2 - x_1)\delta k = (2n+1)\pi/2 - (2n-1)\pi/2 = \pi$$

$$\therefore x_2 - x_1 = 2\pi/\delta k \quad \dots(8)$$

This equation gives the length of the group of waves, or the wave packet. In terms of the wavelength, the expression is

$$\frac{2\pi}{x_2 - x_1} = \frac{1}{\delta(2\pi/\lambda)} = \frac{1}{\delta(1/\lambda)} = -\lambda^2/\delta\lambda \quad \dots(9)$$

Group velocity: The group velocity v_g is the velocity with which the maximum amplitude moves. At $x=0$, and $t=0$, the maximum amplitude, as given by Eq. (5), is

$$R_{\max} = 2A$$

Suppose, at $x=x'$ and $t=t'$, the amplitude is again maximum. Then from Eqn. (5), we get

$$\frac{1}{2}(t'\delta\omega - x'\delta k) = 0$$

or,

$$x'\delta k = t'\delta\omega$$

\therefore

$$\frac{x'}{t'} = \frac{\delta\omega}{\delta k}$$

$$\text{In the limit as } \delta k \rightarrow 0, \quad \frac{x'}{t'} = \frac{d\omega}{dk}$$

Thus the maximum amplitude, i.e. the centre of a wave packet moves with velocity $\frac{d\omega}{dk}$, and this is the group velocity v_g .

Hence,

$$v_g = \frac{d\omega}{dk} \quad \dots(10)$$

Relation Between the Group Velocity (v_g) and the Phase Velocity (v_p)

We have

the propagation constant

$$k = \frac{2\pi}{\lambda} \quad \therefore \lambda = \frac{2\pi}{k} \quad \dots(11)$$

the phase velocity

$$v_p = \frac{\omega}{k} \quad \therefore \omega = v_p k \quad \dots(12)$$

and the group velocity

$$\begin{aligned} v_g &= \frac{d\omega}{dk} \\ &= \frac{d}{dk}(v_p k) = v_p + k \frac{dv_p}{dk} \\ &= v_p + k \frac{dv_p}{d\lambda} \cdot \frac{d\lambda}{dk} \end{aligned} \quad \dots(13)$$

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

$$\text{Hence} \quad v_g = v_p + k \frac{dv_p}{d\lambda} \left(-\frac{2\pi}{k^2}\right)$$

$$= v_p - \frac{2\pi}{k} \frac{dv_p}{d\lambda}$$

$$= v_p - \lambda \frac{dv_p}{d\lambda} \quad \dots(14)$$

This equation shows that v_g is less than v_p when the medium is dispersive, i.e., when v_p is a function of λ . In a medium in which there is no dispersion, i.e., in which waves of all wavelengths travel with the same speed $dv_p/d\lambda = 0$. Therefore in such a medium $v_g = v_p$. This result is true for electromagnetic waves in vacuum and elastic waves in a homogeneous medium.

The analysis given above is only an approximate one, because only two components have been considered for the formation of the group of waves.

2.4 Wave Packet formed by Superposition of a Number of Plane Waves

A plane wave travelling in the positive x -direction may be represented by

$$\psi(x, t) = A e^{i(kx - \omega t)}$$

or

$$\psi(x, t) = A e^{-i(kx - \omega t)}$$

The wave has frequency $\nu = \omega/2\pi$, wavelength $\lambda = 2\pi/k$, and velocity $v = \omega/k$. In our further discussion we choose the first form of the wave equation so that the momentum and energy operators have particular forms (See Sec. 4.7).

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If a number of plane waves of propagation number slightly different from the average value k_0 travel simultaneously along the same line in the positive x -direction in a dispersive medium, a wave packet of small extension Δx is formed [Fig. 2.2(a)]. The wave packet can be expressed, by Fourier's theorem, in the form

$$\Psi(x, t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} A(k) e^{i(kx - \omega k)} dk \quad \dots(1)$$

where $A(k)$ is a function of k . This function is called the Fourier transform of $\Psi(x, t)$ and it is given by

$$A(k) e^{-i\omega k} = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \Psi(x, t) e^{-ikx} dx \quad \dots(2)$$

$$\text{or } A(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \Psi(x, t) e^{-i(kx - \omega k)} dx \quad \dots(3)$$

Time t appears explicitly in the right-hand side of Eq. (3). But $A(k)$ does not depend on t , provided the wave packet given by Eq. (1) is a superposition of plane waves. Therefore

$$\frac{\partial A(k)}{\partial t} = 0 \quad \dots(4)$$

Fig. 2.2(b) shows the variation of $A(k)$ with the propagation number k . It can be shown that $\Delta k \approx \frac{1}{\Delta x}$, where Δk is the approximate spread in the propagation number associated with the wave packet.

Quantum Mechanics

k_0 , the angular frequency ω varies slowly with k , so that $\omega(k)$ can be expanded in a power series by Taylor's theorem:

$$\omega(k) = \omega(k_0 + (k - k_0)) = \omega(k_0) + (k - k_0) \left(\frac{d\omega}{dk} \right)_{k_0} + \frac{(k - k_0)^2}{2!} \left(\frac{d^2\omega}{dk^2} \right)_{k_0} + \dots$$

The second and higher order terms in the expansion can be neglected.

$$\omega(k) = \omega_0 + (k - k_0) \left(\frac{d\omega}{dk} \right)_{k_0} \quad \dots(5a)$$

where $\omega_0 = \omega(k_0)$

$$\text{or } \omega = \omega_0 + (k - k_0) \frac{d\omega}{dk} \quad \dots(5b)$$

Now substituting this value of ω in the expression $(kx - \omega t)$, we get

$$\begin{aligned} kx - \omega t &= kx - \left\{ \omega_0 + (k - k_0) \frac{d\omega}{dk} \right\} t \\ &= -\omega_0 t + kx - (k - k_0) \frac{d\omega}{dk} t \\ &= k_0 x - \omega_0 t + kx - k_0 x - (k - k_0) \frac{d\omega}{dk} t \\ &= (k_0 x - \omega_0 t) + (k - k_0) x - (k - k_0) \frac{d\omega}{dk} t \\ &= (k_0 x - \omega_0 t) + (k - k_0) \left[x - \left(\frac{d\omega}{dk} \right) t \right] \end{aligned}$$

Substituting for $(kx - \omega t)$ in Eq. (1) and simplifying we get

$$\Psi(x, t) = e^{i(k_0 x - \omega_0 t)} \cdot \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} A(k) e^{i(k - k_0)(x - d\omega/dk)t} dk \quad \dots(6)$$

This equation represents a wave of wavelength $\lambda_0 = 2\pi/k_0$, and frequency $\omega_0/2\pi$, which is modulated by the integral appearing as a multiplying factor. The value of the integral depends on x and t only in the expression:

$$x - \frac{d\omega}{dk} t$$

Thus the integral represents a wave packet which moves with the group velocity

$$v_g = \frac{dx}{dt} = \frac{d\omega}{dk} \quad \dots(7)$$

The phase velocity of the wave packet is the velocity of the plane wave represented by $e^{i(k_0 x - \omega_0 t)}$

Thus the phase velocity $v_p = \frac{\omega_0}{k_0}$

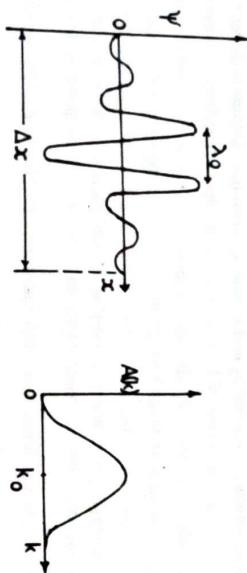


Fig. 2.2 (a)

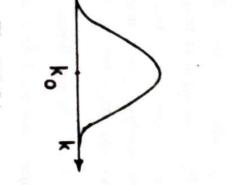


Fig. 2.2 (b)

Eq. (1) will represent a wave packet of small extension Δx , if $A(k)$ is finite only for a small range of values of k between $k_0 - \frac{\Delta k}{2}$ and $k_0 + \frac{\Delta k}{2}$ about the particular value k_0 . It is assumed that for a small range of values of k about

Wave Packet in Three Dimensions

The wave packet in three dimensions is represented by

$$\Psi(x, y, z, t) = \frac{1}{(2\pi)^3} \int_{-\infty}^{\infty} A(k_x, k_y, k_z) e^{i(k_x x + k_y y + k_z z - \omega t)} dk_x dk_y dk_z$$

This equation may be written as

$$\Psi(\vec{r}, t) = \frac{1}{(2\pi)^3} \int_{-\infty}^{\infty} A(\vec{k}) e^{i(\vec{k} \cdot \vec{r} - \omega t)} d^3 k$$

where $d^3 k$ denotes the volume element $dk_x dk_y dk_z$ in \vec{k} -space.

The Fourier transform of $\Psi(\vec{r}, t)$ in three dimensions is represented by

$$A(\vec{k}) = \frac{1}{(2\pi)^3} \int_{-\infty}^{\infty} \Psi(\vec{r}, t) e^{-i(\vec{k} \cdot \vec{r} - \omega t)} d^3 r$$

where $d^3 r$ denotes the volume element $dr dx dy dz$ in position coordinate space.

2.5 De Broglie's Hypothesis (by Analogy with the Photon)

The relationship between the energy E of a photon and the frequency ν of the associated electromagnetic wave is given by the Planck-Einstein equation

$$E = h\nu$$

According to the theory of relativity, the relation between the total relativistic energy E and the relativistic momentum p of a particle of rest mass m_0 is given by

$$E^2 = p^2 c^2 + m_0^2 c^4 \quad \dots(2)$$

Since photons have zero rest mass, the momentum of a photon from Eq. (2) is

$$p = \frac{E}{c} \quad \dots(3)$$

From Eqs. (1) and (3), we have

$$pc = h\nu$$

or

$$pc = \frac{hc}{\lambda} \quad \dots(4)$$

or

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

This equation represents the wave-particle relation for photons. In this equation λ is the wavelength of the wave associated with photons of momentum p .

In 1924 Louis De Broglie extended the wave-particle relationship for photons to all particles in motion (i.e., electrons, protons, neutrons, atoms, molecules etc.) and put forth the following hypothesis:

All particles in motion have properties characteristic of waves. The wavelength λ and the frequency ν of the wave associated with a particle in motion, are given by

$$\lambda = \frac{h}{p} = \frac{h}{mv} \quad \dots(5)$$

$$\nu = \frac{E}{h} \quad \dots(6)$$

where, h is Planck's constant = 6.6256×10^{-34} Js

v is the particle velocity,
 E is the kinetic energy, and m is the relativistic mass given by the relation

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

Eq. (5) is the De Broglie expression for the wavelength associated with a particle moving with velocity v .

We rewrite Eq. (5) and (6) in the following convenient forms:

$$p = \frac{h}{\lambda} = \frac{h}{2\pi} \cdot \frac{2\pi}{\lambda} = \hbar k \quad \dots(7)$$

where $\hbar = h/2\pi$, and $k = 2\pi/\lambda$.

$$E = h\nu = \frac{h}{2\pi} \cdot 2\pi\nu = \hbar\omega \quad \dots(8)$$

2.6 Nature of De Broglie Waves

The De Broglie expression for the wavelength associated with a particle of known momentum has been verified by the experiments of Davisson and Germer, Thomson, and Stern. These experiments show that a stream of electrons, when accelerated by a potential difference of several thousand volts, can be diffracted and the diffraction pattern is similar to that produced by X-rays. From these experiments we conclude that a stream of electrons is associated with a wave. All other particles in motion are found to have a wave nature. Before we describe these experiments we consider the physical nature of the waves to be associated with particles in motion.

Regarding the physical nature of wave to be associated with a particle in motion no definite conclusion was given by De Broglie.

A monochromatic progressive wave is of infinite extent. The phase velocity of monochromatic De Broglie's wave is greater than the velocity of light. This shows that a particle in motion cannot be represented by a monochromatic wave. At any given instant of time, the effect of particle in motion is localized over a very small region. Therefore, the particle must be represented by a wave packet. The wave packet is supposed to be formed in the following way. Let λ be the wavelength of the De Broglie wave associated with a particle moving with velocity v . Then the superposition of a number of plane waves of wavelengths slightly different from λ travelling along the same straight line gives rise to groups of waves or wave-packets. The amplitude of a wave packet varies from zero to a certain maximum value over a certain small region of

space having the dimensions of the particle. Such a wave-packet is associated with the particle.

It should be remembered that a material particle in motion cannot be supposed to be just a wave-packet. In optics it is easy to consider light as a transverse wave motion. But if we retain this concept as the basic nature of light, it is very difficult to consider a beam of light a stream of photons. In all its properties, a particle such as an electron or a proton retains its particle nature, its mass and charge are never divided in any diffraction experiment. Therefore, the De Broglie waves and De Broglie wave-packets are only theoretical devices which we employ for the purpose of explaining experimental observations.

2.7 Derivation of the De Broglie Relation

The derivation is based on the following assumptions:

- (1) The frequency ν of the wave associated with a particle in motion and the total relativistic energy E of the particle are related by the equation $\hbar\nu = E$... (1)

(This assumption was made by De Broglie.)

- (2) The particle in motion is considered as a wave-packet of small extension formed by the superposition of a large number of waves of wavelengths slightly different from the associated wavelength λ and centred about it.
 \therefore the particle velocity = the group velocity of the waves

i.e.,

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

We rewrite Eq. (1) in the following form

$$\frac{\hbar}{2\pi} 2\pi\nu = E = mc^2$$

$$\hbar\omega = \sqrt{p^2c^2 + m_0^2c^4} \quad \dots (3)$$

where $\hbar = h/2\pi$, ω is the angular frequency of the wave, m_0 the rest mass of the particle, m the relativistic mass, p the momentum mv and c the speed of light in free space.

Differentiating this equation with respect to k , we get

$$\hbar \frac{d\omega}{dk} = \frac{1}{2} \cdot \frac{1}{\sqrt{p^2c^2 + m_0^2c^4}} \left(2pc^2 \frac{dp}{dk} \right)$$

$$= \frac{pc^2}{mc^2} \frac{dp}{dk} = \frac{p}{m} \frac{dp}{dk}$$

But

$$\frac{d\omega}{dk} = \nu, \text{ and } \frac{p}{m} = v$$

\therefore

$$\hbar\nu = v \frac{dp}{dk}$$

or

$$dp = \hbar dk$$

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Integrating this equation

$$p = \hbar k + C$$

The constant C of integration is assumed to be zero.

$$\therefore p = \hbar k \quad \dots (4)$$

$$\text{or } p = \frac{2\pi}{\lambda} \cdot \frac{h}{2\pi} = \frac{h}{\lambda}$$

$$\text{or } \lambda = \frac{h}{p} \quad \dots (5)$$

This is the De Broglie expression for the wavelength associated with a particle in motion with momentum p . Wavelengths given by Eq. (5) are known as De Broglie wavelengths.

2.8 Phase Velocity of De Broglie Waves

If k is the propagation constant of the De Broglie wave and ω is its angular frequency, then the phase velocity v_p of this wave is given by the usual relation

$$v_p = \frac{\omega}{k} \quad \dots (1)$$

The momentum p of the particle is given by the De Broglie relation

$$k\hbar = p \quad \dots (2)$$

and according to De Broglie's assumption the angular frequency ω is related to the total relativistic energy by the equation

$$\hbar\omega = E \quad \dots (3)$$

Dividing Eq. (3) by Eq. (2)

$$\frac{\omega}{k} = \frac{E}{p}$$

$$\text{or } v_p = \frac{E}{p} \quad \dots (4)$$

If m is the relativistic mass of the particle and v is its velocity, then

$$E = mc^2 \text{ and } p = mv$$

$$\therefore v_p = \frac{mc^2}{mv} = \frac{c^2}{v} \quad \dots (5)$$

Since the velocity v of a particle is always less than the velocity c of light in free space, the phase velocity v_p of the De Broglie wave is always greater than c . But a velocity larger than c cannot be measured, because according to the postulate of the theory of relativity no signal or energy can be transmitted with a speed greater than the speed of light in free space. Therefore, the phase velocity has no physical meaning.

2.9 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

$$v_p = \frac{E}{p} \quad [\text{See, Eq. (4), Sec. 2.8}]$$

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

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

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

$$v_p = c \sqrt{1 + \frac{(m_0 c^2)^2}{h^2}} \lambda^2 \quad \dots(1)$$

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.

De Broglie Wavelength associated with a Particle of Mass m and Kinetic Energy K

The kinetic energy K of the particle is related to its total relativistic energy by the equation

$$E = K + m_0 c^2$$

$$\sqrt{p^2 c^2 + m_0^2 c^4} = K + m_0 c^2$$

Squaring both the sides of this equation

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

$$p^2 c^2 = K^2 + 2K m_0 c^2$$

\therefore

$$p = \frac{\sqrt{K(K + 2m_0 c^2)}}{c}$$

Hence

$$\lambda = \frac{h}{p} = \frac{hc}{\sqrt{K(K + 2m_0 c^2)}}$$

or

$$\lambda = \frac{h}{\sqrt{2m_0 K(1 + K/2m_0 c^2)}} \quad \dots(2)$$

Using this equation the De Broglie wavelength can be calculated for any particle, such as an electron, a proton, a helium atom, or even a large body.

2.10 Davisson and Germer's Experiment on Electron Diffraction and Verification of the De Broglie Relation

Theoretical formula: If a narrow beam of electrons is accelerated by a potential difference of V volts, the kinetic energy K acquired by each electron in the beam is given by

$$K = Ve, \text{ where } e \text{ is the electronic charge.}$$

The De Broglie wavelength is given by

$$\lambda = \frac{h}{\sqrt{2m_0 K(1 + K/2m_0 c^2)}}$$

If $K \ll 2m_0 c^2$, then $E_K/2m_0 c^2$ is negligible

$$\frac{h}{\sqrt{2m_0 K}} = \frac{h}{\sqrt{2m_0 Ve}} \quad \dots(1)$$

Substituting the numerical values of h , m_0 and e , we get

$$\begin{aligned} \lambda &= \frac{6.63 \times 10^{-34}}{\sqrt{2 \times 9.11 \times 10^{-31} \times 1.6 \times 10^{-19} V}} = \frac{6.63 \times 10^{-34}}{\sqrt{29.15 V}} \\ &= \frac{6.63 \times 10^{-34}}{5.399 \sqrt{V}} = \frac{1.228 \times 10^{-34}}{\sqrt{V}} = 12.28 \times \frac{10^{-10}}{\sqrt{V}} \text{ m} \end{aligned}$$

or

$$\lambda = \frac{12.28}{\sqrt{V}} \text{ Å} \quad \dots(2)$$

If $V = 100$ volts, then $\lambda = 1.228 \text{ Å}$

This is the theoretical value of λ for the known P.D. in volts.

The calculation shows that the wavelength of the waves associated with the beam of electrons is of the same order as that of X-rays. Therefore, if such a beam of electrons is reflected from a crystal, the reflected beam will show the same diffraction and interference phenomena as for X-rays of the same wavelength. This consideration was the basis of Davisson and Germer's experiments. In one set of experiments, the (1 1 1) face of the nickel crystal was arranged perpendicular the incident beam of electrons.

Experiment

Apparatus. The Davisson and Germer apparatus is shown in Fig. 2.3. F is a tungsten filament which emits electrons when it is heated by passing a current from a low tension battery B_1 . 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.

AB is the chamber 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

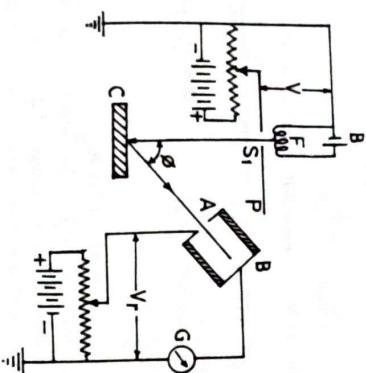


Fig. 2.3

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 is plotted against the angle of scattering.

Fig. 2.4 shows the intensity curve at constant potential difference of 54 volts.

Observations and Calculations

It is seen that the intensity of the scattered beam is maximum at $\phi = 50^\circ$ when the accelerating voltage $V = 54$ volts.
 \therefore the theoretical value of λ is given by

$$\lambda = \frac{12.28}{\sqrt{V}} = \frac{12.28}{\sqrt{54}} = \frac{12.28}{7.348} = 1.67 \text{ \AA}$$

Fig. 2.4

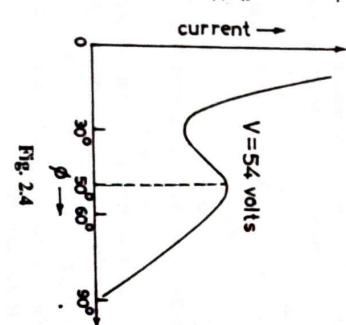
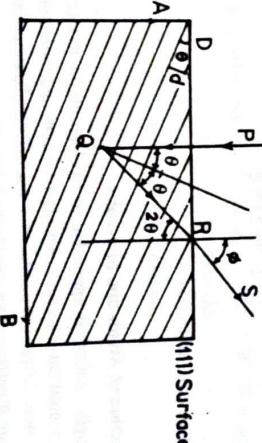


Fig. 2.5



These equations show that $\lambda > \lambda'$
 Inside the crystal, the beam of wavelength λ' is reflected from regularly spaced (331) planes containing rows of atoms in successive (111) planes (Fig. 2.5).

Wave Properties of Matter

The experimental value of λ is calculated using the formula

$$n\lambda = D \sin \phi \quad \dots (3)$$

where ϕ is the angle of scattering and D is the perpendicular distance between two adjacent rows of atoms in (111) planes of the nickel crystal. The distance D can be calculated from the knowledge of the length of the edge ($a = 3.52 \text{ \AA}$) of the unit cube of the crystal. The value of D is 2.15 \AA .

\therefore for the first order constructive interference of the electron waves

$$\lambda = 2.15 \sin 50^\circ = 2.15 \times 0.7660 \\ = 1.65 \text{ \AA}$$

This value is nearly equal to that calculated from the De Broglie relation.

Derivation of the relation $n\lambda = D \sin \phi$

The electron beam PQ when accelerated by the potential difference V in vacuum has kinetic energy $K = eV$. Therefore, the De Broglie wavelength of the beam, in vacuum, is given by

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

The beam falls normally on the (111) face of the crystal. Therefore, it enters the crystal without deviation. Due to the electrostatic fields of force between positive ion cores, an electron entering the crystal with the initial kinetic energy K gains an amount of kinetic energy V_i , where V_i is the potential energy inside. Therefore, inside the crystal, the De Broglie wavelength λ' of the electron beam is given by

$$\lambda' = \frac{h}{\sqrt{2m_0 (K + V_i)}}$$

Let θ be the angle between these planes and the (111) face of the crystal, d the interplanar spacing of these planes, QR the reflected beam from the plane AB

ϕ the angle of refraction in vacuum

D the perpendicular distance between two adjacent rows of atoms in the (111) face of the crystal.

The glancing angle of the beam PQ at $AB = 90^\circ - \theta$. Inside the crystal the reflected beams, giving maximum intensity, satisfy Bragg's equation

$$2d \sin (90^\circ - \theta) = n\lambda'$$

where $n = 1, 2, 3$,

$$n\lambda' = 2d \cos \theta \quad \dots(1)$$

The refractive index μ of the crystal for the electron beam is given by

$$\mu = \frac{\text{phase velocity in vacuum}}{\text{phase velocity in the crystal}} = \frac{\sin \phi}{\sin 2\theta}$$

or

$$\mu = \frac{v}{v'} = \frac{\sin \phi}{\sin 2\theta}$$

or

$$\mu = \frac{\gamma \lambda}{\gamma \lambda'} = \frac{\sin \phi}{\sin 2\theta}$$

or

$$\mu = \frac{\lambda}{\lambda'} = \frac{\sin \phi}{\sin 2\theta}$$

or

$$\lambda' = \frac{\lambda \sin 2\theta}{\sin \phi} = \frac{2 \lambda \sin \theta \cos \theta}{\sin \phi} \quad \dots(2)$$

Substituting this value of λ' in Eqn. (1), we get

$$n \frac{2 \lambda \sin \theta \cos \theta}{\sin \phi} = 2 d \cos \theta$$

or

$$n\lambda = \frac{d \sin \phi}{\sin \theta}$$

But from the figure

$$d = D \sin \theta$$

$$n\lambda = \frac{D \sin \theta \sin \phi}{\sin \theta} \quad \dots(3)$$

For the first order reflection $n = 1$

$$\lambda = D \sin \phi \quad \dots(4)$$

2.11 Diffraction of Atoms and Molecules

The De Broglie relation is applicable to any particle in motion. Therefore, heavier and neutral particles such as neutrons, atoms and molecules in motion, should also show diffraction and interference effects. To demonstrate diffraction of a beam of particles by crystals, the following two conditions should be satisfied:

(i) The particles in the beam should have a uniform velocity so that the wavelength of the associated wave has a fairly definite value.

(ii) The diffracted beam should be detected by means of a detector.

In diffraction experiments with a beam of electrons these conditions are easily achieved. The neutral particles from a source come out with velocities distributed over a wide range, according to Maxwell's law of distribution of velocities and it is not easy to detect neutral particles. Therefore, for neutral particles, a velocity selector is necessary to select a group of the particles with a narrow range of velocities. The beam of the particles diffracted from a crystal is detected by means of the process of ionisation by collision.

The diffraction of helium atoms was first demonstrated by Esterman, Frisch and Stern in 1931.

Diffraction of Neutrons

Thermal Neutrons

In a nuclear reactor, high-energy neutrons are generated as a result of the fission of Uranium 235. They are then slowed down to thermal equilibrium with the 'moderator' substance, such as graphite or heavy water. Such neutrons are called thermal neutrons. In the thermal equilibrium, at temperature T , their velocities are distributed over a wide range, according to Maxwell's law of distribution of velocities. Their most probable velocity v is given by

$$v = \sqrt{\frac{2kT}{m}} \quad \dots(1)$$

where k is Boltzmann's constant, T is the absolute temperature and m is the mass of a neutron. If the equilibrium temperature is 300 K (27°C), the most probable velocity for thermal neutrons is

$$v = \sqrt{\frac{2 \times 1.38 \times 10^{-23} \times 300}{1.676 \times 10^{-27}}} = 2.22 \times 10^3 \text{ m/sec.}$$

and the most probable energy of thermal neutrons at 300 K is given by

$$E = \frac{1}{2} mv^2 = \frac{1}{2} m \frac{2kT}{m} = kT \quad \dots(2)$$

For the first order reflection $n = 1$

$$\begin{aligned} \lambda &= D \sin \phi \\ &= 4.14 \times 10^{-21} \text{ J} \\ &= \frac{4.14 \times 10^{-21}}{1.6 \times 10^{-19}} = 2.6 \times 10^{-2} \text{ eV.} \end{aligned}$$

De Broglie Wavelength of Thermal Neutrons

The De Broglie wavelength of thermal neutrons moving with the most probable velocity at temperature T is given by

$$\lambda = \frac{h}{mv} = \frac{h}{m\sqrt{2kT}} \\ = \frac{h}{\sqrt{2mkT}} \quad \dots(3)$$

Substituting the values of h , m and k , we get

$$\lambda = \frac{6.63 \times 10^{-34}}{\sqrt{2 \times 1.676 \times 10^{-27} \times 1.38 \times 10^{-23} \times T}} \\ = \frac{6.63 \times 10^{-9}}{\sqrt{2 \times 1.676 \times 1.38 \times T}} \text{ m} \\ = \frac{66.3 \times 10^{-10}}{2.15\sqrt{T}} = \frac{30.8 \times 10^{-10}}{\sqrt{T}} \text{ m} \\ = \frac{30.8}{\sqrt{T}} \text{ Å} \quad \dots(4)$$

At 300°K, the value of λ is given by

$$\lambda = \frac{30.8}{\sqrt{300}} = \frac{30.8}{17.32} = 1.778 \text{ Å} \quad \dots(5)$$

This wavelength is of the same order as the distance between atoms in a crystal. Therefore, if such a beam of neutrons is reflected from a crystal, the reflected beam will show the same diffraction and interference phenomena as for X-rays of the same wavelength. Diffraction of neutrons from a crystal was suggested by Elsasser in 1936 and the phenomenon was first demonstrated by Halban and Preiswerk in 1937.

Practical Applications of Neutron Diffraction

(1) Neutron diffraction technique is used for determining the crystal lattice spacing and the position of atoms in a crystal. This technique is much superior to X-ray crystallography method. X-rays are scattered primarily by the extra-nuclear electrons. Therefore, the amplitude of scattered X-rays is proportional to the atomic number and it decreases with increasing angle of scattering. For this reason, X-rays are not useful in determining the positions of light atoms such as hydrogen. On the other hand (since the neutron is a neutral particle and is of mass much larger than extra-nuclear electrons) a beam of neutrons incident on a non-magnetic solid is scattered only by the nuclei. Therefore, the amplitudes of the beams of scattered neutrons from light and heavy atoms do not differ much and the amplitude does not depend on the scattering angle. For this reason, neutron diffraction technique is very useful in determining the positions of light atoms in crystals.

(2) The neutron has a magnetic moment. Therefore, when a beam of neutrons is incident on a magnetic substance, the scattered beam gives rise to the diffraction pattern characteristic of that substance. From the study of the neutron diffraction pattern, the distribution of the magnetic moments in the

substance can be determined. This method of determining the magnetic structure of a magnetic material is the most important contribution of neutron-diffraction technique.

Neutron Spectrometer for the Determination of Crystal Lattice Spacing

An outline of the spectrometer used in modern technique is shown in Fig. 2.6.

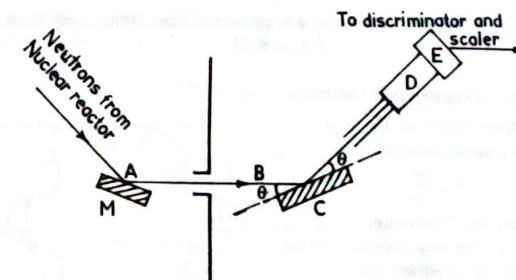
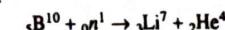


Fig. 2.6

A nuclear reactor (not shown in the figure) is used as a source of thermal neutrons. A well collimated beam of the neutrons is obtained by means of slits. The velocities in the beam are distributed according to Maxwell's law of distribution of velocities with the most probable velocity of 2.22×10^3 m/sec., at 300°K and with the corresponding wavelength 1.778 Å. A beam with narrow region of velocities around 2.22×10^3 m/sec is selected by means of a mechanical velocity selector or a crystal mono-chromator M. By this method nearly a monochromatic beam AB with associated wavelength 1.778 Å at 300°K is obtained. Lithium fluoride, sodium chloride and calcium fluoride crystals are used as crystal mono-chromators. The beam is then allowed to be incident on the crystal C whose structure is to be determined.

D is a proportional counter for detecting the diffracted beam of neutrons. It is filled with boron-trifluoride (BF_3).

The diffracted neutrons entering the proportional counter produce the following nuclear reaction



Then the positively charged α -particles (${}^4\text{He}^4$) are counted with the help of the pre-amplifier circuit, discriminator and scaler.

Method: The experimental crystal C is set at a known glancing angle θ and the intensity of the diffracted beam is measured. This procedure is repeated for

different angles. Then the intensity curve against the glancing angle is plotted. From the curve, the glancing angle θ for which the intensity is maximum is determined. This is the glancing angle corresponding to the first order diffraction.

Calculation

The value of λ is calculated from the formula

$$\lambda = \frac{30.8}{\sqrt{T}} \text{ Å}$$

Then the crystal lattice spacing d is calculated from Bragg's equation

$$2d \sin \theta = \lambda$$

2.12 Bohr's Quantization Condition

In the Bohr theory of the hydrogen atom, the quantization condition

$$L = \frac{n\hbar}{2\pi}$$

for the angular momentum L of the electron, moving in a stationary circular orbit is only arbitrary. On the basis of De Broglie's hypothesis this condition is easily obtained. For this purpose, the following assumptions are made:

(1) The motion of the electron in stationary circular orbit is represented by a standing matter wave (Fig. 2.7) of wavelength λ given by the De Broglie relation

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

where m is the mass of the electron and v is its velocity in the orbit

(2) The circular orbit contains an integral number of wavelengths, i.e..

$$\frac{2\pi r_n}{\lambda} = n \quad \dots(2)$$

where $n = 1, 2, 3, \dots$, and r_n is the radius of the orbit.

Substituting the value of λ in Eq. (2)

$$\frac{2\pi r_n mv}{h} = n$$

or

$$mv r_n = \frac{n\hbar}{2\pi}$$

or

$$L = \frac{n\hbar}{2\pi} \quad \dots(3)$$

which is Bohr's quantization condition.

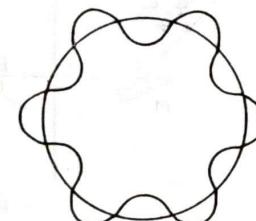


Fig. 2.7

SOLVED EXAMPLES

Example 2.1. Show that the De Broglie wavelength in A.U. of an electron in terms of the P.D. V in volts through which it is accelerated is given by

$$\lambda = \frac{12.28}{\sqrt{V}} \left(\frac{eV}{2m_0c^2} + 1 \right)^{-1/2}$$

Solution:

The De Broglie wavelength of a particle of rest mass m_0 and kinetic energy K is given by [See Eq. (2), Sec. 2.9]

$$\lambda = \frac{\hbar}{\sqrt{2m_0K}} \left(\frac{K}{2m_0c^2} + 1 \right)^{-1/2}$$

In this case $K = eV$

$$\therefore \lambda = \frac{\hbar}{\sqrt{2m_0e} \cdot \sqrt{V}} \left(\frac{eV}{2m_0c^2} + 1 \right)^{-1/2}$$

$$\text{Now } \frac{\hbar}{\sqrt{2m_0e}} = \frac{6.63 \times 10^{-34}}{\sqrt{2 \times 9.11 \times 10^{-31} \times 1.6 \times 10^{-19}}} \\ = \frac{6.63 \times 10^{-9}}{\sqrt{2 \times 9.11 \times 1.6}} = \frac{66.3 \times 10^{-10}}{5.399} = 12.28 \times 10^{-10} \text{ metre}$$

$$\therefore \lambda = \frac{12.28 \times 10^{-10}}{\sqrt{V}} \left(\frac{eV}{2m_0c^2} + 1 \right)^{-1/2} \text{ metre}$$

$$\text{or } \lambda = \frac{12.28}{\sqrt{V}} \left(\frac{eV}{2m_0c^2} + 1 \right)^{-1/2} \text{ in Å}$$

Example 2.2. The most rapidly moving valence electron in metallic sodium, at the absolute zero of temperature, has a kinetic energy 3eV. Show that its De Broglie wave-length is 7Å.

Solution:

$$K = 3 \text{ eV} = 3 \times 1.6 \times 10^{-19} \text{ J}$$

For the electron

$$m_0c^2 = 9.11 \times 10^{-31} (3 \times 10^8)^2 = 9.11 \times 9 \times 10^{-15} \text{ J} \\ = \frac{9.11 \times 9 \times 10^{-15}}{1.6 \times 10^{-19}} = \frac{9.11 \times 9}{1.6} \times 10^4 \text{ eV} \\ = 51.2 \times 10^4 \text{ eV} = 5.12 \times 10^5 \text{ eV}$$

\therefore the kinetic energy of the electron is small compared with m_0c^2 .

Hence the De Broglie wavelength is given by

$$\lambda = \frac{\hbar}{\sqrt{2m_0K}} \\ = \frac{6.63 \times 10^{-34}}{\sqrt{2 \times 9.11 \times 10^{-31} \times 3 \times 1.6 \times 10^{-19}}}$$

$$\begin{aligned} &= \frac{6.63 \times 10^{-9}}{\sqrt{2 \times 9.11 \times 3 \times 1.6}} = \frac{6.63 \times 10^{-9}}{9.35} \\ &= 0.71 \times 10^{-9} = 7.1 \times 10^{-10} \text{ m} = 7.1 \text{ Å} \end{aligned}$$

Example 2.3. Find the wavelength of the waves associated with an electron having energy equal to 1 MeV.

Solution:

We have,

$$\begin{aligned} K &= 1 \text{ MeV} = 10^6 \text{ eV} = 10^6 \times 1.6 \times 10^{-19} \text{ J} \\ &= 1.6 \times 10^{-13} \text{ J.} \end{aligned}$$

The value of $m_0 c^2$ for an electron is (see solved Ex. 2).

$$\begin{aligned} m_0 c^2 &= 5.12 \times 10^5 \text{ eV} = 5.12 \times 10^5 \times 1.6 \times 10^{-19} \text{ J} \\ &= 1.6 \times 0.512 \times 10^{-13} \text{ J.} \end{aligned}$$

Since K is comparable with $m_0 c^2$, we use the relativistic expression for λ

$$\begin{aligned} \lambda &= \frac{hc}{\sqrt{K(K + 2m_0 c^2)}} \\ &= \frac{6.63 \times 10^{-34} \times 3 \times 10^8}{\sqrt{1.6 \times 10^{-13} (1.6 \times 10^{-13} + 2 \times 1.6 \times 0.512 \times 10^{-13})}} \\ &= \frac{6.63 \times 3 \times 10^{-26}}{1.6 \times 10^{-13} \sqrt{1.024}} \\ &= \frac{6.63 \times 3 \times 10^{-13}}{1.6 \times 1.4227} = \frac{19.89 \times 10^{-13}}{2.276} = 8.739 \times 10^{-13} \\ &= 0.008739 \times 10^{-10} \text{ m} = 0.008739 \text{ Å.} \end{aligned}$$

Example 2.4. Calculate the De Broglie wavelength of an electron moving with velocity $\frac{3}{5}c$.

Solution:

We have $v = \frac{3}{5}c$ or $\frac{v}{c} = \frac{3}{5}$

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

Since v is comparable with the speed of light, m in the formula is the relativistic mass. Substituting $m = m_0 / \sqrt{1 - v^2/c^2}$ in the formula for λ , we get

$$\begin{aligned} \lambda &= \frac{h}{m_0 v} \sqrt{1 - \frac{v^2}{c^2}} \\ &= \frac{6.63 \times 10^{-34}}{9.11 \times 10^{-31} \times \frac{3}{5} c} \sqrt{1 - \frac{9}{25}} \\ &= \frac{6.63 \times 10^{-34} \times 4}{9.11 \times 10^{-31} \times 3 \times 3 \times 10^8} = \frac{6.63 \times 4 \times 10^{-11}}{9.11 \times 3 \times 3} \\ &= 0.323 \times 10^{-11} \text{ m} = 0.0323 \text{ Å.} \end{aligned}$$

Example 2.5. A particle of rest mass m_0 has a characteristic frequency ν_0 given by the relation $h\nu_0 = m_0 c^2$. The particle travels with the velocity of v relative to a stationary observer. By using special theory of the relativity prove that the observer sees a progressive wave of phase velocity c^2/v and of wavelength h/mv .

Solution:

In Fig. 2.8, S and S_0 are two frames of reference with their x -axes along the same straight line. Suppose S_0 moves in the positive x -direction with velocity v with respect

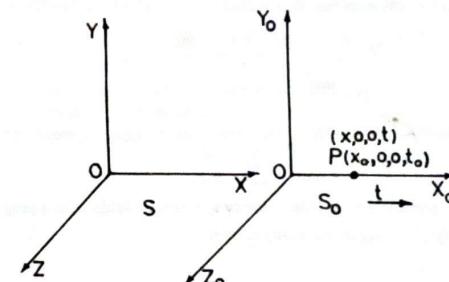


Fig. 2.8

to S which is stationary. A particle P which is stationary with respect to S_0 moves with velocity v with respect to the observer O situated in S .

Suppose the particle makes a S.H.M. represented by

$$\psi = \psi_0 \sin 2\pi\nu_0 t \quad \dots(1)$$

where ψ_0 is the amplitude of the motion, ν_0 is the frequency of oscillations in S_0 , given by

$$h\nu_0 = m_0 c^2, \quad \text{or} \quad \nu_0 = \frac{m_0 c^2}{h} \quad \dots(2)$$

and t_0 is the time recorded in S_0 .

With respect to S the coordinates for the same phenomenon are x and t . From Lorentz's transformation formula for time we have

$$t_0 = \frac{t - vx/c^2}{\sqrt{1 - v^2/c^2}} \quad \dots(3)$$

Multiplying Eq. (2) by Eq. (3), we get

$$\begin{aligned} \nu_0 t_0 &= \left(\frac{m_0 c^2}{h} \right) \frac{(t - vx/c^2)}{\sqrt{1 - v^2/c^2}} \\ &= \frac{m_0}{\sqrt{1 - v^2/c^2}} \left(\frac{c^2}{h} \right) \left(t - \frac{x}{c^2/v} \right) \\ &= \frac{mc^2}{h} \left(t - \frac{x}{c^2/v} \right) \quad \dots(4) \end{aligned}$$

Substituting this expression for $\nu_0 t_0$ in Eq. (1)

$$\psi = \psi_0 \sin 2\pi \left(\frac{mc^2}{h} \right) \left(1 - \frac{x}{c^2/v} \right) \quad \dots(5)$$

The standard equation of a simple harmonic plane progressive wave is

$$\psi = \psi_0 \sin 2\pi\nu \left(t - \frac{x}{v_p} \right) \quad \dots(6)$$

where ν is the frequency and v_p is the phase velocity.

Comparing Eq. (5) with Eq. (6) we find

$$v_p = \frac{c^2}{v} \quad \dots(7)$$

and

$$\nu = \frac{mc^2}{h} \quad \dots(8)$$

\therefore the wavelength λ is given by

$$\lambda = \frac{v_p}{\nu} = \frac{c^2}{v} \cdot \frac{h}{mc^2} = \frac{h}{mv} \quad \dots(9)$$

Thus when a particle moves with velocity v , it is associated with a progressive wave of phase velocity c^2/v and of wavelength h/mv .

QUESTIONS AND PROBLEMS

1. Discuss the nature of De Broglie wave associated with a particle in motion. Obtain an expression for the De Broglie wavelength associated with a particle of mass m moving with the velocity v .

2. Prove that the De Broglie wavelength associated with a particle having kinetic energy E_k which is not negligible compared to its rest energy $m_0 c^2$ is given by

$$\lambda = \frac{h}{\sqrt{2m_0 K}} (1 + K/2m_0 c^2)^{-1/2}$$

3. (a) Describe Davisson and Germer's experiment for the study of the diffraction of electrons.

- (b) Show that the results of this experiment are closely in agreement with the De Broglie wavelength of electrons in motion.

4. Calculate the De Broglie wavelength of an electron which has energy 12 eV.

[Hint: For the electron $m_0 c^2 = 5.12 \times 10^5$ eV

In this case 12 eV is small compared to $m_0 c^2$

\therefore use the formula $\lambda = \frac{h}{\sqrt{2m_0 K}}$ (Ans. 3.545 roman Å)

5. What is the wavelength of the wave associated with an electron having kinetic energy 100 eV? (Ans. 1.228 Å)

6. Find the De Broglie wavelength of 15 keV protons. (Rest mass of the proton = 1.67×10^{-27} kg).

[Hint: For the proton $m_0 c^2 = 9.39 \times 10^8$ eV. In this case 1.5×10^4 eV is small compared to $m_0 c^2$.
 \therefore use the formula $\lambda = h/\sqrt{2m_0 K}$] (Ans. 0.002343 Å)

7. An electron initially at rest is accelerated by a potential difference of 5000 V. Find the De Broglie wavelength. (Ans. 0.174 Å)
8. A photon of frequency ν is scattered by an electron of rest mass m_0 . The scattered photon of frequency ν' travels in direction inclined at 90° with the initial direction. Prove that the De Broglie wavelength of the recoil electron is given by

$$\lambda_r = \frac{c}{\sqrt{\nu^2 + \nu'^2}}$$

9. Explain De Broglie's concept of matter waves. Find the De Broglie wavelength of the electron in the first Bohr orbit.

[Hint: The kinetic energy of the electron in the first Bohr orbit = 13.6 eV] (Ans. 3.33 Å)

Heisenberg's Uncertainty Principle

3.1 Introduction

In the previous chapter we have seen that an electron in motion is associated with a wave whose wavelength λ is given by the De Broglie relation, and it can be considered as a wave-packet of small extension formed by the superposition of a large number of waves of wavelengths slightly different from the wavelength of the associated wave. Since a wave packet is of finite width, there will be an uncertainty in specifying the position of the electron. At the same time the spectral distribution of the amplitude of a wave-packet covers a range of wavelengths. By the De Broglie relationship this means that the momentum of the electron will also be uncertain. Therefore, in general, it is not possible to determine precisely and simultaneously, the position and the momentum of the electron. If the momentum of the 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. On the basis of these considerations, Werner Heisenberg, in 1927, enunciated the principle of *Unbestimmtheit*. This term has been translated as uncertainty, indeterminacy or indefiniteness. In this chapter we discuss the principle of uncertainty and some applications of the principle.

3.2 Uncertainty Principle

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. Quantitatively the principle is represented by Heisenberg's uncertainty relation 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 -compo-

nent of the momentum, at the same instant, is of the order of or greater than \hbar ($\hbar/2\pi = 1.054 \times 10^{-31}$ J. sec.), i.e.,

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

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

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

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

$$\Delta z \cdot \Delta p_z \gtrsim \hbar$$

Another form of the uncertainty principle is in terms of the energy E of the particle and the time t at which it is measured. The uncertainty relation for these variables is

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

where ΔE is the uncertainty in the energy and Δt the uncertainty in the time.

The uncertainty principle can also be stated in terms of the angular momentum L of the particle and its angular position ϕ in the plane perpendicular to L . The uncertainty relation for these variables is

$$\Delta L \cdot \Delta \phi \gtrsim \hbar$$

where the symbols have their usual meaning.

The pairs of variables in the above relations are *canonically conjugate* to each other (i.e., related to each other according to a general law) in accordance with Hamilton's equations of motion:

$$\frac{dp}{dt} = -\frac{\partial H(p, q)}{\partial q} \quad \dots(6)$$

$$\frac{dq}{dt} = \frac{\partial H(p, q)}{\partial p} \quad \dots(7)$$

Let us see how E and t are canonically conjugate to each other. If we substitute $H = E = P$ in Eq. (7), we get $\frac{dq}{dt} = 1$, i.e., $q = t$.

Note: In the statement of the uncertainty relation no clear definitions of Δx and Δp_x have been given. These quantities may be defined in various ways, therefore, many expressions for the product $\Delta x \cdot \Delta p_x$ are possible. If a series of measurements of x and p_x are taken on many identical systems, and if Δx and Δp_x are defined as the root mean square deviations from their mean values, it can be shown that the minimum value of the product of the uncertainties is given by

$$\Delta x \cdot \Delta p_x = \frac{\hbar}{2}$$

(For exact statement and proof see Sec. 4.16.)

In solving problems in which only one set of values are involved the minimum value of the product should be taken as

$$\Delta x \cdot \Delta p_x = \hbar$$

This expression will give better estimate of one of the uncertainties, if the other is known.

3.3 Elementary Proof of Heisenberg's Uncertainty Relation

Suppose a particle is in motion along the x -axis. The De Broglie relation between the wavelength λ of the associated wave and the momentum p_x of the particle along the x -axis is

$$\begin{aligned} \lambda &= \frac{\hbar}{p_x} \\ \therefore p_x &= \frac{\hbar}{\lambda} = \frac{\hbar}{2\pi} \cdot \frac{2\pi}{\lambda} = \hbar k \end{aligned} \quad \dots(1)$$

The particle in motion is represented by a wave-packet formed by the superposition of a number of plane waves of wavelengths different from λ . In our simple consideration we consider the wave-packet as the superposition of two simple harmonic plane waves of propagation constant k and $k + \Delta k$. The length of such a wave-packet is given by [See Eq. (8) Sec. 2.3].

$$\Delta x = \frac{2\pi}{\Delta k} \quad \dots(2)$$

Since the particle must be somewhere within the wave-packet, Δx is the uncertainty in the position of the particle, and corresponding to the uncertainty in the position, the uncertainty in the propagation constant of the associated wave is Δk .

From Eq. (1) the uncertainty Δp_x in the momentum is given by

$$\Delta p_x = \hbar \Delta k \quad \dots(3)$$

Multiplying Eq. (2) by Eq. (3), we get the product of the uncertainties as

$$\Delta x \cdot \Delta p_x = \left(\frac{2\pi}{\Delta k} \right) (\hbar \Delta k) = 2\pi\hbar = \hbar$$

If wave-packets have shapes different from that shown in Fig. 2.1 then the sign of equality is replaced by the sign \gtrsim

$$\therefore \Delta x \cdot \Delta p_x \gtrsim \hbar \quad \dots(4)$$

In obtaining this uncertainty relation we considered the wave-packet formed by the superposition of two plane waves. But superposition of two plane waves gives rise to series of wave-packets instead of a single wave-packet. A single wave-packet is formed by superposition of an infinite number of plane waves of propagation constants slightly different from one another. By Fourier analysis of a single wave-packet in one dimension, it can be shown that the width Δx of the wave-packet and the range Δk of the propagation constants of the waves, which give rise to the wave-packet are related by

$$\Delta x \gtrsim \frac{1}{\Delta k} \quad (\text{See Sec. 2.4}) \quad \dots(5)$$

Heisenberg's Uncertainty Principle

Multiplying Eq. (3) by relation (5), we get

$$\Delta x \cdot \Delta p_x \gtrsim \hbar \quad \dots(6)$$

Physical Significance of Heisenberg's Uncertainty Relation

The uncertainty relation (1) leads to the following conclusions:

(i) If the position coordinate x of a particle in motion is accurately determined at some instant, so that $\Delta x = 0$, then at the same instant the uncertainty Δp_x in the determination of the momentum becomes infinite.

(ii) If the momentum p_x of a particle is accurately determined at some instant, so that $\Delta p_x = 0$, then at the same instant the uncertainty Δx in the determination of the position coordinate becomes infinite.

Thus if an experiment is designed to measure x or p_x accurately, the other quantity will become completely uncertain. We can measure both the quantities by means of an experiment, but only within certain limits of accuracy specified by the uncertainty relation.

(iii) For a particle of mass m moving with velocity v the product of the uncertainty Δx and the uncertainty Δv in the velocity is given by

$$\Delta x \cdot \Delta v \gtrsim \frac{\hbar}{m}$$

For a heavy particle \hbar/m is very small and, therefore, the product $\Delta x \cdot \Delta v$ of the two uncertainties becomes very small. For such particles both the position x and the velocity v can be determined accurately.

For very heavy bodies, if m is such that $\frac{\hbar}{m} = 0$, the uncertainties vanish and all quantities can be determined with perfect accuracy. This is the limiting case of classical mechanics. Thus classical mechanics is true for heavy bodies, and the uncertainties are a characteristic of quantum mechanics, which is applicable to light particles, such as electrons, neutrons, protons, etc.

3.4 Elementary Proof of the Uncertainty Relation between Energy and Time

The uncertainty relation between energy and time is obtained by considering the motion of a wave-packet. A particle in motion is represented by a wave-packet. The group velocity of the wave-packet is equal to the particle velocity. Let Δx be the width of the wave-packet moving along the x -axis.

v_g the group velocity of the wave-packet, and

v_x the particle velocity along x -axis.

Suppose the wave-packet moves through Δx in time Δt .

$$\therefore \Delta t = \frac{\Delta x}{v_g} = \frac{\Delta x}{v_x} \quad \dots(1)$$

Since Δx is the uncertainty in the x -coordinate of the particle, Δt is the uncertainty in time t at which the particle passes through a point with velocity v_x . The kinetic energy of the particle is given by

$$E = \frac{p_x^2}{2m}$$

Taking differential of this equation the uncertainty ΔE in the kinetic energy is given by

$$\begin{aligned} \Delta E &= \frac{2p_x \Delta p_x}{2m} = \frac{p_x}{m} \Delta p_x = \frac{mv_x}{m} \Delta p_x \\ &= v_x \Delta p_x \end{aligned} \quad \dots(2)$$

Multiplying Eq. (1) by Eq. (2), we get

$$\Delta E \cdot \Delta t = \Delta x \cdot \Delta p_x \quad \dots(3)$$

According to the uncertainty relation between position and momentum, we have

$$\Delta x \cdot \Delta p_x \geq \hbar$$

\therefore from Eq. (3), we have

$$\Delta E \cdot \Delta t \geq \hbar \quad \dots(4)$$

This is the energy-time uncertainty relation.

Physical Significance of the Energy-time Uncertainty Relation

The physical interpretation of the energy-time uncertainty relation is quite different from that of the position-momentum uncertainty relation. If ΔE is the maximum uncertainty in the determination of the energy of a system in a particular state, then according to relation (4) the minimum time-interval for which the system remains in the state is given by

$$\Delta t = \frac{\hbar}{\Delta E}$$

And if a system remains in a particular state for a maximum time interval Δt , then the minimum uncertainty in the energy of the system in that state is given by

$$\Delta E = \frac{\hbar}{\Delta t}$$

3.5 Illustration of Heisenberg's Uncertainty Principle by Thought-Experiments

A thought experiment, or a gedanken experiment is an imaginary experiment which does not violate any fundamental law of nature, but which cannot be performed in practice. For example in a thought experiment we can imagine a man to jump over the planet Jupiter to a height and calculate the required initial velocity.

We now illustrate the principle by considering the following two thought experiments.

(1) **Diffraction of Electrons through a slit:** Suppose a mono-energetic parallel beam of electrons is moving in horizontal direction from left to right. To locate the vertical position y of a particular electron, above a fixed point O , we block the beam by a vertical screen having a slit of width Δy at distance y above O as shown in Fig. 3.1. Then a narrow beam of electrons together with the particular electron passes through the slit.

Since an electron in motion is associated with a wave, the beam passing through the slit undergoes diffraction. Therefore, a Fraunhofer diffraction pattern will be obtained on a photographic plate P placed perpendicular to the direction of the incident beam. The diffraction pattern consists of the central

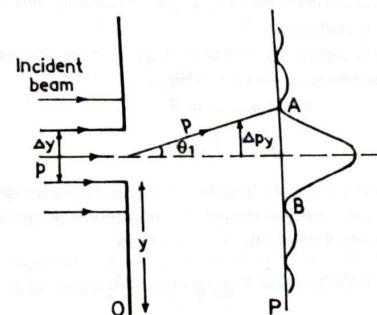


Fig. 3.1

band of maximum intensity much wider than the slit, and on both the sides of the central band there are dark and bright bands of decreasing intensity.

Let p be the momentum of an electron in the incident beam. Then the wavelength of the associated wave is given by

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

Let θ_1 be the angle of diffraction of the electrons in the beam, which form the first minimum A of the pattern. This angle is given by,

$$\sin \theta_1 = \frac{\lambda}{\Delta y} \quad \dots(2)$$

From the existence of the diffraction pattern we can conclude that

(1) Every electron deflected at the slit has passed through the slit; but the place in the slit at which the passage of an electron takes place remains quite indefinite by the amount Δy .

\therefore the uncertainty in the y coordinate of an electron which has passed through the slit = Δy .

If the electron which is deflected through θ_i in the upward or downward direction, this uncertainty, from Eqn. (2), is given by

$$\Delta y = \frac{\lambda}{\sin \theta_i} \quad \dots(3)$$

(2) At the instant when an electron is deflected at the slit, its original momentum p in the horizontal direction is decreased and it acquires component momentum Δp_y in the y -direction (the resultant momentum p remaining constant).

The original momentum of an electron in the y -direction was accurately known to be zero. Therefore, Δp_y is the uncertainty introduced in the y component of the momentum.

For the electron which is deflected through θ_i in the upward or downward direction, this uncertainty is given by (Fig. 3.1)

$$\Delta p_y = p \sin \theta_i \quad \dots(4)$$

or

$$\Delta p_y = \frac{h}{\lambda} \sin \theta_i \quad \dots(4)$$

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

$$\begin{aligned} \Delta y \cdot \Delta p_y &= \frac{\lambda}{\sin \theta_i} \cdot \frac{h}{\lambda} \sin \theta_i \\ &= h \end{aligned} \quad \dots(5)$$

The probability of an electron reaching the centre of the pattern is greatest. Therefore, Eq. (5) gives the maximum uncertainty Δp_y for a given value of Δy . Hence Eq. (5) is consistent with the uncertainty relation

$$\Delta y \cdot \Delta p_y \gtrsim h$$

In order to decrease the uncertainty in the determination of the y -coordinate, we should decrease Δy . But from, Eq. (2) we see that decrease in Δy will increase the angle θ_i and will produce a wider diffraction pattern. Then a wider diffraction pattern will give rise to a larger value of the uncertainty Δp_y .

(2) **Gamma Ray Microscope Thought Experiment:** This thought experiment was first proposed by Heisenberg. It is usually called γ -ray microscope experiment. Suppose we want to locate the position, i.e., the x -coordinate of an electron of an atom by means of a microscope. The radius of the atom is of the order of 10^{-11} m. Therefore, in order to determine the position of an electron 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 . It means

that we must illuminate the electron with γ -rays of wavelength of the order of 0.01 \AA .

Suppose initially the electron at O (Fig. 3.2) is at rest and to locate its position suppose it is illuminated by a narrow beam of monochromatic γ -rays proceeding in the x -direction.

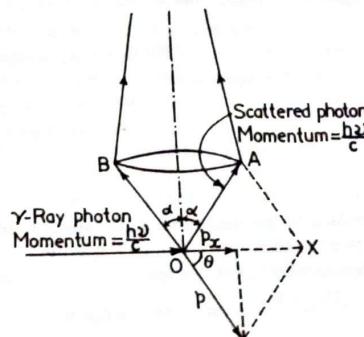


Fig. 3.2

Let ν be the frequency and λ the wavelength of the incident γ -rays. Then the momentum of an incident γ -ray photon in the x -direction

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

At least one photon should be scattered by the electron into the microscope so that the electron is visible. In this process the frequency and wavelength of the scattered photon is changed and the electron suffers a Compton recoil due to gain of momentum.

At the instant when the 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 any other direction within the cone. Suppose the photon enters the microscope along OA . Let ν' be the frequency and λ' the wavelength of the scattered photon. Then the momentum of the scattered photon along OA

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

The image of the electron formed by the microscope will be a diffraction pattern which consists of a central bright disc surrounded by alternate dark and

bright rings. Since the position of the electron may be anywhere within the central bright disc, the uncertainty in the position of the electron is the diameter of the central disc. Let Δx be the diameter of the central disc. Then the uncertainty in the position = Δx .

According to Rayleigh's criterion in optics, 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

$$R.P. = \frac{\lambda'}{2 \sin \alpha}$$

In this case

$$R.P. = \frac{\Delta x}{2}$$

$$\frac{\Delta x}{2} = \frac{\lambda'}{2 \sin \alpha}$$

or

$$\Delta x = \frac{\lambda'}{\sin \alpha} \quad \dots(1)$$

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 .

Resolving the mementa along OX , we get,

$$\frac{h\nu}{c} = \frac{h\nu'}{c} \cos(90^\circ - \alpha) + p \cos \theta$$

or

$$\frac{h}{\lambda} = \frac{h}{\lambda'} \sin \alpha + p \cos \theta$$

or

$$p \cos \theta = \frac{h}{\lambda} - \frac{h}{\lambda'} \sin \alpha \quad \dots(2)$$

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. (2) represents maximum uncertainty in p_x . Let Δp_x be this uncertainty in p_x . Then

$$\Delta p_x = \frac{h}{\lambda'} \sin \alpha \quad \dots(3)$$

Multiplying Eq. (1) by Eq. (3), we get,

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

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

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

3.6 Principle of Complementarity

In order to clarify the fundamental limitations on the accuracy of measurement of a pair of canonically conjugate variables as specified by the uncertainty

principle Bohr in 1928 introduced the *principle of complementarity*. The principle states that wave and particle properties of electromagnetic radiation and matter are merely complementary ways of regarding the same phenomenon. That is, to provide a complete explanation of the results of an experiment on an atomic phenomenon both these properties are equally essential. But because of the principle of uncertainty it is impossible to design an experiment which will reveal both these properties simultaneously. Any experiment will reveal 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. This is true even in a hypothetical experiment which can be imagined to be performed by an experimenter. Thus the complementarity principle may also be stated as follows. *By means of a physical apparatus available to an experimenter more precise measurements of a pair of complementary variables than those specified by the uncertainty principle cannot be made.*

The complementarity principle is well illustrated in the γ -ray microscope thought experiment. If the radiation, of very small wavelength is used, then

$$\Delta x = \frac{\lambda'}{\sin \alpha} \approx 0$$

\therefore the position x of the electron just after the scattering process is found with good accuracy. But Δp_x will be very large, and hence there will be no knowledge of the momentum p_x at that time. If radiation of longer wavelength is used p_x just after the scattering process will be found with good accuracy, but the position of the electron at that time will be unknown.

3.7 Application of the Uncertainty Principle

(1) Non-existence of Free Electrons in the Nucleus

We know that:

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

If the electron exists in the nucleus, it can be anywhere within the diameter of the nucleus. Therefore, the maximum uncertainty Δx in the position of the electron is the same as the diameter of the nucleus,

$$i.e., \Delta x = 2 \times 10^{-14} \text{ m} \quad \dots(1)$$

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

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

\therefore the uncertainty in the momentum p_x is

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

\therefore the minimum uncertainty in the momentum is given by

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

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

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

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.

$$\begin{aligned}\text{Then, } E_{\min} &= \sqrt{2.5 \times 10^{-24}} \\ &= 1.58 \times 10^{-12} \text{ J} \\ &= \frac{1.58 \times 10^{-12}}{1.6 \times 10^{-19}} \text{ eV} \\ &= 0.9875 \times 10^7 \\ &= 9.875 \times 10^6 \text{ eV} \\ &= 9.875 \text{ MeV.}\end{aligned}$$

Thus, if a free electron exists in the nucleus it, must have a minimum energy of about 9.0 MeV.

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.

(2) Size of Hydrogen Atom and Energy in the Ground State

(i) **Size of the Hydrogen Atom:** Suppose the electron in the hydrogen atom moves round the proton in a circular orbit of radius r . Then the maximum uncertainty in the determination of its position with respect to the proton can be taken to be equal to r , i.e., $\Delta r = r$

From the uncertainty relation, the minimum uncertainty Δp in the simultaneous determination of its momentum p in the plane of the orbit is given by

$$\Delta p = \frac{\hbar}{\Delta r} = \frac{\hbar}{r}$$

The momentum p cannot be less than the uncertainty Δp ; therefore, the minimum possible momentum is

$$p = \frac{\hbar}{r}$$

Now the kinetic energy K of the electron is given by

$$K = \frac{p^2}{2m} = \frac{\hbar^2}{2mr^2} \quad \dots(1)$$

and the electro-static potential energy is given by

$$V = -\frac{e^2}{4\pi\epsilon_0 r} \quad \dots(2)$$

\therefore the total energy of the electron in the hydrogen atom is given by

$$E = \frac{\hbar^2}{2mr^2} - \frac{e^2}{4\pi\epsilon_0 r} \quad \dots(3)$$

The ground state energy must be a minimum value of E . For a minimum or a maximum value of E

$$\frac{dE}{dr} = -\frac{\hbar^2}{mr^3} + \frac{e^2}{4\pi\epsilon_0 r^2} = 0 \quad \dots(4)$$

$$\text{i.e., } -\frac{\hbar^2}{mr^3} + \frac{e^2}{4\pi\epsilon_0 r^2} = 0$$

$$\begin{aligned}\text{or } \frac{e^2}{4\pi\epsilon_0} &= \frac{\hbar^2}{mr} \\ \therefore r &= \frac{4\pi\epsilon_0 \hbar^2}{me^2} = \frac{4\pi\epsilon_0}{me^2} \left(\frac{\hbar}{2\pi}\right)^2 \\ &= \frac{\epsilon_0 \hbar^2}{\pi me^2} \quad \dots(5)\end{aligned}$$

This is the well known expression for the radius of the first Bohr orbit. To see whether this value of r gives minimum or maximum value of E , we find

$$\begin{aligned}\frac{d^2E}{dr^2} &= +\frac{3\hbar^2}{mr^4} - \frac{e^2}{2\pi\epsilon_0 r^3} \\ &= \frac{1}{r^3} \left[\frac{3\hbar^2}{mr} - \frac{e^2}{2\pi\epsilon_0} \right]\end{aligned}$$

Substituting the value of r

$$\begin{aligned}\frac{d^2E}{dr^2} &= \frac{1}{r^3} \left[\frac{3\hbar^2}{m} \cdot \frac{me^2}{4\pi\epsilon_0 \hbar^2} - \frac{e^2}{2\pi\epsilon_0} \right] \\ &= \frac{1}{r^3} \left[\frac{3e^2}{4\pi\epsilon_0} - \frac{e^2}{2\pi\epsilon_0} \right] = \text{a positive quantity}\end{aligned}$$

\therefore when $r = \epsilon_0 h^2 / \pi m e^2$, the energy is minimum, i.e., the atom is in the ground state. Thus this value of r gives the size of the hydrogen atom. Substituting the numerical values of the constants

$$\begin{aligned} h &= 6.63 \times 10^{-34} \text{ Js}, m = 9.11 \times 10^{-31} \text{ kg} \\ e &= 1.6 \times 10^{-19} \text{ C}, \epsilon_0 = 8.85 \times 10^{-12} \text{ C}^2/\text{Nm}^2 \end{aligned}$$

in the expression for r , we get

$$r = 5.31 \times 10^{-11} \text{ m}$$

(ii) **Energy in the Ground State:** We have

$$\begin{aligned} E &= \frac{\hbar^2}{2mr^2} - \frac{e^2}{4\pi\epsilon_0 r} \\ &= \frac{1}{r} \left[\frac{\hbar^2}{2m} \cdot \frac{1}{r} - \frac{e^2}{4\pi\epsilon_0} \right] \end{aligned}$$

Substituting the value of r for the ground state, we get

$$\begin{aligned} E &= \frac{me^2}{4\pi\epsilon_0 \hbar^2} \left[\frac{\hbar^2}{2m} \cdot \frac{me^2}{4\pi\epsilon_0 \hbar^2} - \frac{e^2}{4\pi\epsilon_0} \right] \\ E &= \frac{me^2}{4\pi\epsilon_0 \hbar^2} \left[\frac{e^2}{8\pi\epsilon_0} - \frac{e^2}{4\pi\epsilon_0} \right] \\ &= -\frac{me^4}{32\pi^2\epsilon_0^2\hbar^2} = -\frac{me^4}{32\pi^2\epsilon_0^2} \cdot \left(\frac{2\pi}{\hbar} \right)^2 = -\frac{me^4}{8\epsilon_0^2\hbar^2} \end{aligned}$$

Substituting the values of the constants in this expression the energy in the ground state in electron-volt ($1 \text{ eV} = 1.6 \times 10^{-19} \text{ J}$) is

$$E = -13.6 \text{ eV}$$

This is the well known value of the ground state energy of the hydrogen atom.

(3) Ground State Energy of a Linear Harmonic Oscillator

The total energy of a linear harmonic oscillator in motion at distance x from its mean position is given by

$$\begin{aligned} E &= K.E. + P.E. \\ &= \frac{p^2}{2m} + \frac{1}{2}m\omega^2x^2 \end{aligned} \quad \dots(1)$$

where the symbols have their usual meaning. The maximum uncertainty in the determination of its position can be taken to be x , i.e., $\Delta x = x$. From the uncertainty relation the minimum uncertainty Δp in the simultaneous determination of its momentum is given by

$$\Delta p = \frac{\hbar}{\Delta x} = \frac{\hbar}{x}$$

The momentum p of the oscillator in motion cannot be less than Δp . Therefore the minimum value of the momentum is

$$p = \frac{\hbar}{x}$$

Hence the total energy E is given by

$$\begin{aligned} E &= \frac{1}{2m} \left(\frac{\hbar}{x} \right)^2 + \frac{1}{2} m\omega^2 x^2 \\ E &= \frac{\hbar^2}{2mx^2} + \frac{1}{2} m\omega^2 x^2 \end{aligned} \quad \dots(2)$$

The ground state energy must be a *minimum* value of E . Now for a minimum or a maximum value of E

$$\frac{dE}{dx} = -\frac{\hbar^2}{mx^3} + m\omega^2 x = 0$$

$$\text{i.e., } -\frac{\hbar^2}{mx^3} + m\omega^2 x = 0$$

$$\text{or } m\omega^2 x = \frac{\hbar^2}{mx^3}$$

$$\therefore x^4 = \frac{\hbar^2}{m^2\omega^2}$$

$$\therefore x^2 = \frac{\hbar}{m}\omega \quad \dots(3)$$

It can be shown that for this value of x^2 , d^2E/dx^2 is a positive quantity.

\therefore when $x^2 = \hbar/m\omega$, the energy is minimum.

Now substituting this value in Eq. (2), the ground state energy of the oscillator is given by

$$E_{\min} = \frac{\hbar^2}{2m} \cdot \frac{m\omega}{\hbar} + \frac{1}{2} m\omega^2 \cdot \frac{\hbar}{m\omega} = \hbar\omega$$

If we take the uncertainty product as

$$\Delta x \cdot \Delta p_x = \frac{\hbar}{2}, \text{ we will get}$$

$$E_{\min} = \frac{1}{2} \hbar\omega.$$

This is the zero-point of the oscillator [See Sec. 6.4, Eq. (25)].

SOLVED EXAMPLES

Example 3.1. An electron has a speed of 300 m/s accurate to 0.01%. With what fundamental accuracy can we locate the position of the electron?

Solution:

We have

$$\Delta v = 0.01\% = 300 \times \frac{0.01}{100} = 3 \times 10^{-2} \text{ m/s}$$

The uncertainty relation is

$$\Delta x \cdot \Delta p_x \gtrsim h$$

∴ For the given uncertainty in the speed, the *minimum* uncertainty in the position is given by

$$\begin{aligned}\Delta x &= \frac{\hbar}{\Delta p_x} = \frac{\hbar}{m \Delta v} = \frac{\hbar}{2\pi m \Delta v} \\ &= \frac{6.63 \times 10^{-34}}{2 \times 3.14 \times 9.11 \times 10^{-31} \times 3 \times 10^{-2}} \\ &= \frac{6.63 \times 10^{-1}}{2 \times 3.14 \times 9.11 \times 3} = \frac{663 \times 10^{-3}}{171.6} \\ &= 3.86 \times 10^{-3} \text{ m}\end{aligned}$$

Example 3.2. Find the smallest possible uncertainty in the position of an electron moving with velocity 3×10^7 m/sec.

(Given: $\hbar = 1.054 \times 10^{-34}$ Js, $m_0 = 9.11 \times 10^{-31}$ kg)

Solution:

The maximum uncertainty in the momentum is

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

From the uncertainty relation $\Delta x \cdot \Delta p_x \gtrsim h$, the minimum uncertainty in the position is given by

$$\Delta x = \frac{\hbar}{\Delta p_x} = \frac{\hbar}{m_0 v} \sqrt{1 - v^2/c^2}$$

$$\text{But } \sqrt{1 - v^2/c^2} = \sqrt{1 - (3 \times 10^7 / 3 \times 10^8)^2} = \frac{\sqrt{99}}{10} = 0.995$$

$$\begin{aligned}\Delta x &= \frac{\hbar \times 0.995}{m_0 v} = \frac{1.054 \times 10^{-34} \times 0.995}{9.11 \times 10^{-31} \times 3 \times 10^7} \\ &= \frac{1.054 \times 9.95 \times 10^{-11}}{9.11 \times 3} = 0.384 \times 10^{-11} \text{ m} \\ &= 0.0384 \times 10^{-10} \text{ m} \\ &= 0.0384 \text{ Å}\end{aligned}$$

Example 3.3. The average period that elapses between the excitation of an atom and the time it emits radiation is 10^{-8} sec. Find the uncertainty in the energy emitted

and the uncertainty in the frequency of light emitted. (Given: $\hbar = 1.054 \times 10^{-34}$ Js, $c = 6.63 \times 10^{-34}$ Js)

Solution:

The maximum uncertainty in the interval of time is

$$\Delta t = 10^{-8} \text{ s}$$

From the uncertainty relation $\Delta E \cdot \Delta t \gtrsim \hbar$, the minimum uncertainty in the energy is given by

$$\Delta E = \frac{\hbar}{\Delta t} = \frac{1.054 \times 10^{-34}}{10^{-8}} = 1.054 \times 10^{-26} \text{ J}$$

Now

$$\hbar v = E$$

∴ the uncertainty in the frequency is given by

$$\hbar \Delta v = \Delta E$$

$$\Delta v = \frac{\Delta E}{\hbar} = \frac{1.054 \times 10^{-26}}{6.63 \times 10^{-34}} = 1.59 \times 10^7 \text{ Hz}$$

QUESTIONS AND PROBLEMS

- State and explain Heisenberg's uncertainty principle. Using the following data, show that there is no existence of free electrons in the nucleus of an atom: the radius of the nucleus = 10^{-14} m, the mass of the electron = 9.11×10^{-31} kg, the maximum kinetic energy of an electron in an atom = 4 MeV, and $1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$.
- State and prove Heisenberg's uncertainty principle. Discuss its physical importance.
- Give the exact statement and proof of the uncertainty principle for a one dimensional wave packet. (See Sec. 4.16).
- State Heisenberg's uncertainty principle and illustrate it by any thought experiment.
- A microscope can locate an electron within a distance of 1 Å. Calculate the uncertainty in the measurement of its momentum. (Ans. 1.054×10^{-24} kg. m/s)
- Prove that for rotational motion of a particle the uncertainty principle can be stated in the form

$$\Delta L \cdot \Delta \phi \gtrsim \hbar$$

where ΔL is the uncertainty in the angular momentum of the particle and $\Delta \phi$ is the uncertainty in its angular position.

[Proof: The kinetic energy E due to rotational motion about the axis of rotation is given by

$$E = \frac{1}{2} I \omega^2$$

$$\therefore \Delta E = \frac{1}{2} \times 2\omega \Delta I \omega = \omega \Delta L$$

or

$$\omega \Delta L = \Delta E \quad \dots(1)$$

where L is the angular momentum / ω .The angular position ϕ of the particle at time t is given by

$$\phi = \omega t$$

$$\therefore \frac{\Delta \phi}{\omega} = \Delta t \quad \dots(2)$$

Multiplying Eq. (1) by Eq. (2), we get

$$\Delta L \cdot \Delta \phi = \Delta E \cdot \Delta t$$

$$\text{But } \Delta E \cdot \Delta t \geq \hbar$$

$$\text{Hence } \Delta L \cdot \Delta \phi \geq \hbar.$$

4

Schrödinger's Wave Equation

4.1 Introduction

In classical mechanics, a wave equation is a second order differential equation in space and time. Solutions of this equation represent wave disturbances in a medium. Therefore, a wave equation is the usual basis of mathematical theory of wave motion. For example an electro-magnetic wave, travelling in the x -direction, is described by the wave equation

$$\frac{\partial^2 E_y}{\partial x^2} = \frac{1}{c^2} \frac{\partial^2 E_y}{\partial t^2}$$

where E_y is the y -component of the electric intensity.

A differential equation for the wave associated with a particle in motion cannot be derived from first principles. The equation may be developed by any one of the following procedures:

(1) The equations of motion of classical mechanics are transformed into a wave equation in accordance with wave properties of matter based on De Broglie's hypothesis.

(2) A complex variable quantity, called the wave function, is assumed to represent a plane simple harmonic wave associated with a free particle, and the classical expression for the total energy is used.

(3) A particle at a given position and at a given time is represented by a wave packet which is obtained by superposition of a group of plane waves of nearly the same wavelength, which interfere destructively everywhere except at the wave packet, and the classical expression for the total energy is used.

(4) In the classical expression for the total energy of a particle, the dynamical quantities are replaced by their corresponding operators. These operators are allowed to operate upon the wave function.

In this chapter we will follow procedure (2) to develop the Schrödinger equation.

4.2 Wave Function for a Free Particle

Let a particle of mass m be in motion along the positive x -direction with accurately known momentum p , an total energy E . The position of the particle

would be completely undetermined. The wave associated with such a particle should be a plane, continuous harmonic wave travelling in the positive x -direction. The wavelength and frequency of the wave are given by

$$\lambda = \frac{h}{p_x} \quad \text{and} \quad \nu = \frac{E}{h}$$

We rewrite these equations in terms of $\hbar = h/2\pi$ and the propagation constant $k = \frac{2\pi}{\lambda}$:

$$p_x = \frac{h}{\lambda} = \frac{h}{2\pi} \frac{2\pi}{\lambda} = \hbar k \quad \dots(1)$$

$$E = \hbar\nu = \frac{h}{2\pi} 2\pi\nu = \hbar\omega \quad \dots(2)$$

We assume that the plane wave is represented by a complex variable quantity $\psi(x, t)$. This quantity is called the wave function for the particle. (For the physical explanation of ψ , see Section 4.5). We assume that the wave function has the following form

$$\psi(x, t) = A e^{-i\omega(t - x/\nu)} \quad \dots(3a)$$

$$= A e^{-i(\omega t - \omega x/\nu)} \\ = A e^{-i(\omega t - kx)} \quad (\because \omega/\nu = k) \quad \dots(3b)$$

where A is a constant and $i = \sqrt{-1}$

Now substituting the expressions for k and ω as given by Eqs. (1) and (2), we get

$$\psi(x, t) = A e^{-i(Et/\hbar - p_x x/\hbar)} \\ = A e^{i/\hbar(p_x x - Et)} \quad \dots(4)$$

This equation represents a plane continuous simple harmonic wave associated with a particle of accurately known momentum p_x and total energy E moving in the positive x -direction. In section 4.3 we will use this form of the wave function to derive the one-dimensional Schrödinger's wave equation.

For a plane wave travelling in an arbitrary direction, the wave function is written as

$$\psi(\vec{r}, t) = A e^{i/\hbar(\vec{p} \cdot \vec{r} - Et)} \quad \dots(5)$$

where the vector \vec{p} is the momentum and the vector \vec{r} is the position vector of the particle.

Note: In Eq. (3) we have taken the form $A e^{-i\omega(t - x/\nu)}$ for the wave function and not the form $A e^{+i\omega(t - x/\nu)}$. Actually both the forms represent a wave travelling in the positive x -direction. But the first form has been chosen so that the momentum and the energy operators should have particular forms (see Sec. 4.7).

4.3 One-Dimensional Wave Equation

Suppose a particle of mass m is in motion along the positive x -direction under the action of a force $F(x)$ which is a function of x . In such a field of force, the potential energy V of the particle does not explicitly depend on time; it is a function only of x . Such a force is called a conservative force.

Let the speed of the particle be small compared with that of light. Let p_x be the momentum of the particle along the x -direction. Then the total energy E of the particle is given by

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

Multiplying both sides of this equation by the wave function ψ which is a function of x and t

$$\frac{p_x^2 \psi}{2m} + V\psi = E\psi \quad \dots(1)$$

The wave function $\psi(x, t)$ representing the plane wave associated with the particle is given by

$$\psi(x, t) = A e^{i/\hbar(p_x x - Et)} \quad \dots(2)$$

The differential equation for $\psi(x, t)$ should be such that (i) the function $\psi(x, t)$ expressed by Eq. (2) is a solution of it and (ii) when the expression for $\psi(x, t)$ is substituted in it, we should obtain Eq. (1). For this purpose we proceed as follows:

Differentiating Eq. (2) with respect to x

$$\frac{\partial \psi}{\partial x} = A \left(\frac{i}{\hbar} \right) p_x e^{i/\hbar(p_x x - Et)} \\ = \left(\frac{i}{\hbar} \right) p_x \psi \quad \dots(3)$$

and

$$\frac{\partial^2 \psi}{\partial x^2} = \left(\frac{i}{\hbar} \right) p_x \frac{\partial \psi}{\partial x} = \left(\frac{i}{\hbar} \right) p_x \left(\frac{i}{\hbar} \right) p_x \psi \\ = -\frac{1}{\hbar^2} p_x^2 \psi$$

From this equation, we have

$$p_x^2 \psi = -\hbar^2 \frac{\partial^2 \psi}{\partial x^2} \quad \dots(4)$$

Differentiating Eq. (2) with respect to t

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

$$\therefore E\psi = i\hbar \frac{\partial \psi}{\partial t} \quad \dots(5)$$

Substituting these expressions for $p_x^2 \psi$ and $E\psi$ in Eq. (1) we get

$$-\frac{\hbar^2}{2m} \cdot \frac{\partial^2 \psi}{\partial x^2} + V\psi = i\hbar \frac{\partial \psi}{\partial t} \quad \dots(6)$$

This is the time-dependent form of the Schrödinger wave equation for the motion of a particle in one dimension under the action of a conservative force. In this equation ψ is a function of x and t , and V is a function of x .

One-dimensional Wave Equation for a Free Particle

If there are no external forces such as electro-static, gravitational and nuclear forces acting on the particle, then the particle is said to be free and for the free particle $V = 0$. Therefore, the time-dependent Schrödinger wave equation for the motion of a free particle in one dimension is

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} = i\hbar \frac{\partial \psi}{\partial t} \quad \dots(7)$$

Separation of the One-dimensional Wave equation into the Time-dependent part and Time-independent part.

Eq. (6) is a partial differential equation in two variables (x, t). The equation is separable into the time-independent part and time dependent part, if the potential energy V is not a function of time t .

Let $u(x)$ and $f(t)$ be the time-independent and time-dependent parts respectively of the wave function. Then

$$\psi(x, t) = u(x)f(t) \quad \dots(8)$$

Substituting this equation in Eq. (6), we get

$$-\frac{\hbar^2}{2m} f \frac{d^2 u}{dx^2} + Vu = i\hbar u \frac{df}{dt}$$

We have used ordinary derivatives in place of partial derivatives because each of the functions, u and f depends on only one variable.

Dividing both the sides by uf , we get

$$-\frac{\hbar^2}{2m} \frac{1}{u} \frac{d^2 u}{dx^2} + V = i\hbar \frac{1}{f} \frac{df}{dt} \quad \dots(9)$$

The right-hand side of this equation is a function only of time t , and the left-hand side is a function only of the coordinate x . Therefore, the right-hand side is the time-dependent part and the left-hand side is the time-independent part of the Schrödinger equation. Since x and t are independent, each side of this equation must be equal to a constant. This constant is the total energy E of the particle. This is evident from the following consideration.

(i) Time-dependent part: Now we make use of Eq. (5):

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

Substituting Eq. (8) in this equation, we get

$$i\hbar u \frac{df}{dt} = Eu f$$

Dividing both the sides by uf , we get,

$$i\hbar \frac{1}{f} \frac{df}{dt} = E \quad \dots(10)$$

Thus the time-dependent part of the equation is equal to the total energy E of the particle, and so also the time-independent part.

To solve this equation, we separate the variables, and we obtain

$$\frac{df}{f} = \frac{E}{i\hbar} dt$$

or

$$\frac{df}{f} = -\frac{iE}{\hbar} dt$$

Integrating, we get

$$f = Ce^{-iEt/\hbar} \quad \dots(11)$$

where C is a constant.

(ii) Time-independent part: From Eqs. (9) and (10), we have

$$-\frac{\hbar^2}{2m} \frac{1}{u} \frac{d^2 u}{dx^2} + V = E$$

Multiplying both sides by u

$$-\frac{\hbar^2}{2m} \frac{d^2 u}{dx^2} + Vu = Eu \quad \dots(12a)$$

This is the one-dimensional time-independent Schrödinger Equation for a single particle. It is also called one-dimensional steady state Schrödinger equation, and its solutions $u(x)$ are called time-independent wave functions or steady state wave functions. It is a linear equation because it contains no power of u higher than the first; it is homogeneous in u because it contains no term independent of u or its derivatives; it is of the second order because its highest differential is of the second order. A convenient form of Eq. (12-a) is

$$\frac{d^2 u}{dx^2} + \frac{2m}{\hbar^2} (E - V) u = 0 \quad \dots(12b)$$

Substituting the solution of the time-dependent equation as given by Eq. (11) into Eq. (8), we get

$$\psi(x, t) = Cu(x) e^{-iEt/\hbar} \quad \dots(13a)$$

Since

$$E = h\nu = \frac{\hbar}{2\pi} 2\pi\nu = \hbar\omega$$

Eq. 13a is also written in the following form

$$\psi(x, t) = Cu(x) e^{-i\omega t} \quad \dots(13b)$$

The constant C is usually taken as 1.

Eq. (13a) is a particular solution of Eq. (6), corresponding to a particular value of the constant energy E , and it satisfies the time-independent equation (12).

General Solution

Corresponding to various values of the constant energy E , there are various particular solutions of Eq. (6). Therefore, the general solution of the equation is the sum of all particular solutions with arbitrary coefficients. Thus the general solution is written as

$$\psi(x, t) = \sum_n C_n u_n(x) e^{-iE_n t/\hbar} \quad \dots(14)$$

where C_n are constants, and the symbol \sum_n represents the process of summation over discrete values of E_n . It should be noted that the general solution does not satisfy the time-independent equation (12).

Complex Conjugate Wave Function $\psi^*(x, t)$

In the physical interpretation of the wave function $\psi(x, t)$, and solutions of the wave equation we will make use of the quantity $\psi^*(x, t)$ which is the complex conjugate of $\psi(x, t)$.

The one-dimensional time-dependent Schrödinger wave equation for $\psi^*(x, t)$ (See Sec. 4.11) is

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \psi^*}{\partial x^2} + V\psi^* = -i\hbar \frac{\partial \psi^*}{\partial t} \quad \dots(15)$$

The general solution of this equation is

$$\psi^*(x, t) = \sum_n C_n^* u_n^*(x) e^{iE_n t/\hbar} \quad \dots(16)$$

4.4 Three-dimensional Wave Equation

Suppose a particle of mass m is in motion along any direction referred to three mutually perpendicular axes under the action of a force $F(x, y, z)$ which is a function of the space coordinates (x, y, z) . In such a field of force, the potential energy V of the particle does not explicitly depend on time; it is function of the space coordinates. Such a force is called a conservative force.

Let \vec{r} be the position vector of the particle at point (x, y, z) at time t and \vec{p} be the momentum of the particle.

If the speed of the particle is small compared with that of light, the total energy E of the particle is given by

$$\frac{\vec{p}^2}{2m} + V(\vec{r}) = E$$

Since $p^2 = \vec{p}^2$, $\vec{p}^2 = p_x^2 + p_y^2 + p_z^2$, we have

$$\frac{1}{2m} (p_x^2 + p_y^2 + p_z^2) + V(\vec{r}) = E$$

Multiplying both sides of this equation by the wave function which is a function of \vec{r} and t

$$\frac{1}{2m} (p_x^2 + p_y^2 + p_z^2) \psi + V\psi = E\psi \quad \dots(1)$$

Now $\psi(\vec{r}, t) = A e^{i/\hbar (\vec{p} \cdot \vec{r} - Et)}$

Since $\vec{p} \cdot \vec{r} = p_x x + p_y y + p_z z$, we have

$$\psi(\vec{r}, t) = A e^{i/\hbar (p_x x + p_y y + p_z z - Et)} \quad \dots(2)$$

Differentiating Eq. (2) with respect to x

$$\begin{aligned} \frac{\partial \psi}{\partial x} &= A \left(\frac{i}{\hbar} \right) p_x e^{i/\hbar (p_x x + p_y y + p_z z - Et)} \\ &= \left(\frac{i}{\hbar} \right) p_x \psi \end{aligned} \quad \dots(3)$$

and

$$\begin{aligned} \frac{d\psi}{dx^2} &= \left(\frac{i}{\hbar} \right) p_x \frac{\partial \psi}{\partial x} = \left(\frac{i}{\hbar} \right) p_x \left(\frac{i}{\hbar} \right) p_x \psi \\ &= -\frac{1}{\hbar^2} p_x^2 \psi \end{aligned}$$

From this equation we have

$$p_x^2 \psi = -\frac{\hbar^2}{\partial x^2} \frac{\partial^2 \psi}{\partial x^2} \quad \dots(4a)$$

Similarly, we get

$$p_y^2 \psi = -\frac{\hbar^2}{\partial y^2} \frac{\partial^2 \psi}{\partial y^2} \quad \dots(4b)$$

$$p_z^2 \psi = -\frac{\hbar^2}{\partial z^2} \frac{\partial^2 \psi}{\partial z^2} \quad \dots(4c)$$

Differentiating Eq. (2) with respect to t

$$\begin{aligned} \frac{\partial \psi}{\partial t} &= A \left(\frac{i}{\hbar} \right) (-E) e^{i/\hbar (p_x x + p_y y + p_z z - Et)} \\ &= -\frac{i}{\hbar} E\psi \end{aligned}$$

Therefore,

$$E\psi = -\frac{\hbar}{i} \frac{\partial \psi}{\partial t} = i\hbar \frac{\partial \psi}{\partial t} \quad \dots(5)$$

Substituting these expressions for $p_x^2 \psi$, $p_y^2 \psi$, $p_z^2 \psi$, and $E\psi$ in Eq. (1), we get

$$-\frac{\hbar^2}{2m} \left(\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} \right) + V\psi = i\hbar \frac{\partial \psi}{\partial t} \quad \dots(6)$$

$$-\frac{\hbar^2}{2m} \nabla^2 \psi + V\psi = i\hbar \frac{\partial \psi}{\partial t} \quad \dots(7)$$

This is the three-dimensional time-dependent Schrödinger wave equation for the motion of a single particle. The wave equation in the form of Eq. (7) was derived by Schrödinger in 1926. The equation is of second order in space coordinates but only of first order in time. The wave equations which we deal in classical physics, such as the equations for sound waves or for electro-magnetic waves are of second order in space coordinates and time.

Separation of the Three-dimensional Wave Equation into Time-dependent part and Time-independent Part.

Eq. (6) is a partial differential equation in four variables (x, y, z, t). The equation is separable into the time-dependent part and time-independent part, if the potential energy V is not a function of time.

Let $u(\vec{r})$ and $f(t)$ be the time-independent and time-dependent parts respectively of the wave function.

Then

$$\psi(\vec{r}, t) = u(\vec{r})f(t) \quad \dots(8)$$

Substituting this equation in Eq. (6), we get

$$-\frac{\hbar^2}{2m} \left[\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} + \frac{\partial^2 u}{\partial z^2} \right] + Vu = i\hbar u \frac{df}{dt}$$

Dividing both the sides by uf , we get,

$$-\frac{\hbar^2}{2m} \cdot \frac{1}{u} \left[\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} + \frac{\partial^2 u}{\partial z^2} \right] + V = i\hbar \frac{1}{f} \frac{df}{dt} \quad \dots(9)$$

(i) **Time-dependent part:** The time-dependent part is obtained exactly in the same way as explained in Sec. 4.3. Thus the time-dependent part of the equation is

$$i\hbar \frac{1}{f} \frac{df}{dt} = E \quad \dots(10)$$

The solution of this equation is

$$f = Ce^{-iEt/\hbar} \quad \dots(11)$$

where C is a constant.

(ii) **Time-independent part:** From Eqs. (9) and (10), we get

$$-\frac{\hbar^2}{2m} \cdot \frac{1}{u} \left[\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} + \frac{\partial^2 u}{\partial z^2} \right] + V = E$$

$$-\frac{\hbar^2}{2m} \left[\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} + \frac{\partial^2 u}{\partial z^2} \right] + Vu = Eu \quad \dots(12a)$$

or

$$-\frac{\hbar^2}{2m} \left[\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right] u + Vu = Eu$$

or

$$-\frac{\hbar^2}{2m} \nabla^2 u + Vu = Eu$$

or $\left[-\frac{\hbar^2}{2m} \nabla^2 + V \right] u = Eu \quad \dots(12b)$

where ∇^2 is the Laplacian operator in Cartesian coordinates; it is defined by

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

A convenient form of Eq. (12a) is

$$\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} + \frac{\partial^2 u}{\partial z^2} + \frac{2m}{\hbar^2} (E - V) u = 0 \quad \dots(12c)$$

Eqs. (12a) or (12b) or (12c) is the three-dimensional time-independent Schrödinger wave equation for the single particle. It is also called three-dimensional steady state Schrödinger equation, and its solutions are called time-independent or steady state wave-functions.

Three-Dimensional Time-dependent Wave Function

Substituting the solution of the time-dependent equation, as given by Eq. (11) into Eq. (8), we get,

$$\psi(\vec{r}, t) = Cu(\vec{r}) e^{-iEt/\hbar} \quad \dots(13a)$$

Since $E = \hbar\nu = \frac{\hbar}{2\pi} 2\pi\nu = \hbar\omega$, we get

$$\psi(\vec{r}, t) = Cu(\vec{r}) e^{-i\omega t} \quad \dots(13b)$$

The constant C is usually taken as 1. Eq. (13a) is a particular solution of Eq. (7), corresponding to a particular value of the constant energy E , and it satisfies the time-independent equation (12). The wave function as given by this equation represents a monochromatic standing wave. The amplitude $u(\vec{r})$ of the standing wave is a function of \vec{r} .

4.5 Physical Interpretation of the Wave Function ψ

We have assumed that the wave associated with a particle in motion is represented by a complex variable quantity $\psi(x, y, z, t)$ called the wave function. Therefore, it cannot have a direct physical meaning. Since it is a complex quantity, it may be expressed in the form

$$\psi(x, y, z, t) = a + ib \quad \dots(1)$$

where a and b are real functions of the variables (x, y, z, t) , and $i = \sqrt{-1}$.

The complex conjugate of ψ , which is denoted by ψ^* is obtained by changing i to $-i$. Therefore, we have

$$\psi^*(x, y, z, t) = a - ib \quad \dots(2)$$

Multiplying Eq. (1) by Eq. (2)

$$\psi(x, y, z, t) \psi^*(x, y, z, t) = a^2 + b^2 \quad \dots(3)$$

On the left-hand side of this equation the product is denoted by

$$P = |\psi(x, y, z, t)|^2$$

$$\therefore |\psi(x, y, z, t)|^2 = a^2 + b^2 \quad \dots(4)$$

Thus the product of ψ and ψ^* is real and positive if $\psi \neq 0$. Its positive square root is denoted by $|\psi(x, y, z, t)|$ and it is called the modulus of ψ .

The quantity $|\psi(x, y, z, t)|^2$ is called the *probability density*.

The fact expressed by Eq. (4) has been used by Max Born to give the interpretation of $\psi(x, y, z, t)$, which is as follow:

For the motion of a particle, the quantity

$$Pdt = \psi(x, y, z, t) \psi^*(x, y, z, t) dt = |\psi(x, y, z, t)|^2 dt$$

is the probability that the particle will be found in a volume element $dt = dx dy dz$ surrounding the point at position (x, y, z) , at time t

For the motion of a particle in one dimension the quantity

$$Pdx = \psi(x, t) \psi^*(x, t) dx = |\psi(x, t)|^2 dx$$

is the probability that the particle will be found over a small distance dx at position x , at time t . In this case $|\psi(x, t)|^2$ is called the probability per unit distance.

Since $\psi(x, y, z, t) = u(x, y, z) e^{-i\omega t}$

and $\psi^*(x, y, z, t) = u^*(x, y, z) e^{+i\omega t}$

for a particular value of the constant energy E , we get

$$Pdt = u(x, y, z) u^*(x, y, z) dt = |u(x, y, z)|^2 dt$$

Thus for the wave function satisfying the time-independent Schrödinger equation, the probability is always independent of time.

Limitations on ψ

Because of the above interpretation of $|\psi|^2$ as a probability density, the solutions that can be allowed for ψ from the Schrödinger equation are subjected to certain limitations. The most important limitations are:

(i) ψ must be finite for all values of x, y, z .

(ii) ψ must be single-valued, i.e., for each set of values of x, y, 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 $\partial\psi/\partial x, \partial\psi/\partial y, \partial\psi/\partial z$ must be continuous everywhere. A wave function which satisfies these conditions is called a well-behaved function.

Normalization of Wave Function

Since $|\psi(x, y, z, t)|^2 dt$ is the probability that the particle will be found in a volume element dt 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

$$\int_{-\infty}^{\infty} |\psi(x, y, z, t)|^2 dt = 1 \quad \dots(5a)$$

where the integration is to be taken over all space. Eq. (5a) may also be written as

$$\int_{-\infty}^{\infty} \psi^*(x, y, z, t) \psi(x, y, z, t) dt = 1 \quad \dots(5b)$$

A wave function which satisfies the above condition is said to be *normalized* to unity, (or simply normalized). The normalization condition for the wave function for the motion of a particle in one dimension is

$$\int_{-\infty}^{\infty} \psi^*(x, t) \psi(x, t) dx = 1 \quad \dots(6)$$

For any wave function that is a solution of the time-dependent Schrödinger equation (7) (Sec. 4.4), the integral

$$\int_{-\infty}^{\infty} \psi^*(x, y, z, t) \psi(x, y, z, t) dt$$

is independent of time.

$$\therefore \int_{-\infty}^{\infty} \psi^*(x, y, z, t) \psi(x, y, z, t) dt = \int_{-\infty}^{\infty} \psi^*(x, y, z) \psi(x, y, z) dt$$

Hence the normalization condition becomes

$$\int_{-\infty}^{\infty} \psi^*(x, y, z) \psi(x, y, z) dt = 1 \quad \dots(7)$$

and for one dimensional motion the condition is

$$\int_{-\infty}^{\infty} \psi^*(x) \psi(x) dx = 1 \quad \dots(8)$$

Normalization of Wave Function

$$\psi(x, t) = \sum_n C_n \psi_n(x, t)$$

The wave function is written as

$$\begin{aligned} \psi(x, t) &= \sum_n C_n \psi_n(x) e^{-iE_n t/h} \\ &= C_1 \psi_1(x) e^{-iE_1 t/h} + C_2 \psi_2(x) e^{-iE_2 t/h} + \dots \end{aligned}$$

and its complex conjugate is

$$\psi^*(x, t) = C_1^* \psi_1^*(x) e^{-iE_1 t/h} + C_2^* \psi_2^*(x) e^{iE_2 t/h} + \dots$$

$$\begin{aligned} \text{On multiplying these series together, we get} \\ \psi^*(x, t) \psi(x, t) &= C_1^* C_1 \psi_1^*(x) \psi_1(x) + C_2^* C_2 \psi_2^*(x) \psi_2(x) + \dots \\ &\quad + C_1^* \psi_1^*(x) e^{iE_1 t/h} [C_2 \psi_2(x) e^{-iE_2 t/h} + C_3 \psi_3(x) e^{-iE_3 t/h} + \dots] \\ &\quad + C_2^* \psi_2^*(x) e^{iE_2 t/h} [C_1 \psi_1(x) e^{-iE_1 t/h} + C_3 \psi_3(x) e^{-iE_3 t/h} + \dots] \\ &\quad + C_3^* \psi_3^*(x) e^{iE_3 t/h} [C_1 \psi_1(x) e^{-iE_1 t/h} + C_2 \psi_2(x) e^{-iE_2 t/h} + \dots] \\ &\quad + \dots \end{aligned}$$

or

$$\begin{aligned}
 \psi^*(x, t) \psi(x, t) &= \sum_n C_n^* C_n \psi_n^*(x) \psi(x) \\
 &\quad + C_1^* \psi_1^*(x) e^{iE_1 t/\hbar} \sum' C_n \psi_n(x) e^{-iE_n t/\hbar} \\
 &\quad + C_2^* \psi_2^*(x) e^{iE_2 t/\hbar} \sum' C_n \psi_n(x) e^{-iE_n t/\hbar} \\
 &\quad + \dots \\
 &= \sum_n C_n^* C_n \psi_n^*(x) \psi_n(x) \\
 &\quad + [C_1^* \psi_1^*(x) e^{iE_1 t/\hbar} + C_2^* \psi_2^*(x) e^{iE_2 t/\hbar} + \dots] [\sum' C_n \psi_n(x) e^{-iE_n t/\hbar}] \\
 &= \sum_n C_n^* C_n \psi_n^*(x) \psi_n(x) + \left[\sum_m C_m^* \psi_m^*(x) e^{iE_m t/\hbar} \right] \left[\sum' C_n \psi_n(x) e^{-iE_n t/\hbar} \right] \\
 &= \sum_n C_n^* C_n \psi_n^*(x) \psi_n(x) \\
 &\quad + \sum_m \sum' C_m^* C_n \psi_m^*(x) \psi_n(x) e^{i(E_m - E_n)t/\hbar} \quad \dots(9)
 \end{aligned}$$

The summation \sum' shows that only those terms with $m \neq n$ are included.

The normalization condition for the wave function $\psi(x, t)$ is

$$\begin{aligned}
 \int_{-\infty}^{\infty} \psi^*(x, t) \psi(x, t) dx &= 1 \\
 \text{i.e.,} \quad \sum_n C_n^* C_n \int_{-\infty}^{\infty} \psi_n^*(x) \psi_n(x) dx \\
 &\quad + \sum_m \sum' C_m^* C_n e^{i(E_m - E_n)t/\hbar} \int_{-\infty}^{\infty} \psi_m^*(x) \psi(x) dx = 1 \quad \dots(10)
 \end{aligned}$$

But

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

and when $n \neq m$, the wave-functions are mutually orthogonal

$$\int_{-\infty}^{\infty} \psi_m^*(x) \psi_n(x) dx = 0, \text{ when } m \neq n$$

Hence the normalization condition becomes

$$\sum_n C_n^* C_n = 1 \quad \dots(11)$$

Thus a wave function $\psi(x, t) = \sum_n C_n \psi_n(x, t)$ satisfying Schrödinger's wave equation is normalized when the coefficients satisfy the relation given by Eq. (11).

4.6 Stationary States

In Sec. 4.3 we have seen that the corresponding to various values of the constant energy E of a particle, the general solution of the one-dimensional time-dependent Schrödinger equation is given by

$$\psi(x, t) = \sum_n C_n \psi_n(x) e^{-iE_n t/\hbar} \quad \dots(1)$$

The probability density $P(x, t)$ for the one dimensional motion is given by [See Eq. (9) Sec. 4.5]

$$\begin{aligned}
 P(x, t) &= \psi^*(x, t) \psi(x, t) \\
 &= \sum_n C_n^* C_n \psi_n^*(x) \psi_n(x) \\
 &\quad + \sum_m \sum' C_m^* C_n \psi_m^*(x) \psi_n(x) e^{i(E_m - E_n)t/\hbar}
 \end{aligned}$$

This equation shows that $P(x, t)$ depends on the time t . But if the coefficients C_n are zero for all values of energy except for one value E_k , then for this value the wave function is

$$\psi(x, t) = C_k \psi_k(x) e^{-iE_k t/\hbar}$$

Hence for this energy state the probability density is

$$P(x, t) = \psi^*(x, t) \psi(x, t) = C_k^* C_k \psi_k^*(x) \psi_k(x).$$

This is independent of time, and hence the state is called a *stationary state*.

4.7 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, e.g.

$$\begin{aligned}
 f(x) &= x^n \\
 \text{then} \quad \frac{df}{dx} &= nx^{n-1}
 \end{aligned}$$

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

$$Af(x) = af(x) \quad \dots(1)$$

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

where a is 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 $f(x)$, and

(iii) the equation, such as Eq. (1) 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.

Operator for Momentum

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

$$\psi(x, t) = A e^{i/\hbar(p_x x - Et)} \quad \dots(2)$$

Differentiating this equation with respect to x , we get

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

or

$$\frac{\hbar}{i} \frac{\partial \psi}{\partial x} = p_x \psi \quad \dots(3)$$

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

$$\hat{p}_x = \frac{\hbar}{i} \frac{\partial}{\partial x} \quad \dots(4)$$

[The symbol $\hat{}$ ('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

$$\hat{p}_y = \frac{\hbar}{i} \frac{\partial}{\partial y} \quad \dots(5)$$

$$\hat{p}_z = \frac{\hbar}{i} \frac{\partial}{\partial z} \quad \dots(6a)$$

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

$$\vec{p} = \frac{\hbar}{i} \vec{\nabla} \quad \dots(6b)$$

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,

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

\therefore

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

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

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

Dividing this equation by $2m$

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} = \frac{p_x^2}{2m} \psi \quad \dots(7)$$

$$\text{or} \quad -\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} = K \psi \quad \dots(8)$$

where,

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

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,

$$\hat{K} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \quad \dots(9a)$$

In three dimensions the operator for K is

$$\hat{K} = -\frac{\hbar^2}{2m} \nabla^2 \quad \dots(9b)$$

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 $\frac{p_x^2}{2m}$, as given by this equation, in Eq. (7), we get,

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

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

$$\text{or} \quad \left[-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V \right] \psi = E \psi \quad \dots(10)$$

This is the eigen value equation for the total energy E of the particle moving along the x -direction. The equation shows that (i) $-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V$ is the operator, (ii) $\psi(x, t)$ is the eigen function of the operator, and (iii) 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

$$\hat{H} = -\frac{\hbar^2}{2m} \nabla^2 + V \quad \dots(11)$$

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).

Importance of the Hamiltonian Operator

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

$$-\frac{\hbar^2}{2m} \nabla^2 u + Vu = Eu$$

or

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V \right] u = Eu \quad \dots(12)$$

or

$$\hat{H}u = Eu$$

In Eq. (12) we find:

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

- (ii) On the right-side, Eu is the product of the total energy E and the wave function u .

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 Schrödinger 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.

Operator for the Total Energy in terms of the Differential with respect to Time

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

$$\begin{aligned} \frac{d\Psi}{dt} &= A \left(\frac{i}{\hbar} \right) (-E) e^{i/\hbar(p_x t - Et)} \\ &= -\frac{i}{\hbar} E\Psi = \frac{1}{i\hbar} E\Psi \\ \text{or } i\hbar \frac{d\Psi}{dt} &= E\Psi \end{aligned} \quad \dots(13)$$

This equation shows that the total energy operator is

$$i\hbar \frac{d}{dt}$$

This operator is denoted by E

$$E = i\hbar \frac{d}{dt} \quad \dots(14)$$

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

Operators for a Angular Momentum

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

$$\vec{L} = \vec{r} \times \vec{p} \quad \dots(15)$$

where \vec{r} is the position vector of the particle relative to some arbitrary origin and \vec{p} is its linear momentum. From Eq. (15) the components L_x , L_y and L_z of \vec{L} along x , y and z axes, are respectively given by

$$\begin{aligned} L_x &= y p_z - z p_y \\ L_y &= z p_x - x p_z \\ L_z &= x p_y - y p_x \end{aligned} \quad \dots(16)$$

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

$$\hat{L}_x = \frac{\hbar}{i} \left[y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right]$$

$$\hat{L}_x = \frac{\hbar}{i} \left[z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right] \quad \dots(17)$$

$$\hat{L}_y = \frac{\hbar}{i} \left[x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right]$$

These operators can be transformed into spherical polar coordinates (r, θ, ϕ) . We do not give the details of the mathematical transformation, we state only the following expressions for the operators:

$$\hat{L}_x = \frac{\hbar}{i} \left[-\sin \phi \frac{\partial}{\partial \theta} - \cot \theta \cos \phi \frac{\partial}{\partial \phi} \right] \quad \dots(18)$$

$$\hat{L}_y = \frac{\hbar}{i} \left[\cos \phi \frac{\partial}{\partial \theta} - \cot \theta \sin \phi \frac{\partial}{\partial \phi} \right]$$

$$\hat{L}_z = \frac{\hbar}{i} \frac{\partial}{\partial \phi}$$

The operator for the square of the total angular momentum can be obtained from the above expressions as

$$\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$$

$$= -\hbar^2 \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] \quad \dots(19)$$

4.8 Expectation Values

The expression for the wave function $\psi(x, y, z, t)$, which we get as a solution of Schrödinger's wave equation for a particle under given conditions contains all the information about the variables of the particle subject to the uncertainty principle. Except for those variables for which the solution gives quantized values, the information is in the form of probabilities and not definite values. The interpretation of $\psi^*(x, t) \cdot \psi(x, t) dx$ as the probability that the particle will be found over a small distance dx at position x , at time t makes it possible to find the average or the expectation value $\langle x \rangle$ of the position of the particle along the x -axis. First we define the expectation value of a dynamical quantity.

The expectation value of a dynamical quantity is the mathematical expectation for the result of a single measurement. Or it is defined as the average of the results of a large number of measurements on independent identical systems, i.e., the systems represented by identical wave functions.

As an example let us find the expectation value $\langle x \rangle$ at time t of the position of an electron along the x -axis in an experimental arrangement such as the electron-diffraction experiment. Suppose we study the positions of a large number of electrons, N , all of which are described by the same wave function $\psi(x, t)$. Suppose at time t , for each electron, we make an observation for the electron's position and find the number of electrons with positions between x

Schrödinger's Wave Equation

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 $\psi^*(x, t) \cdot \psi(x, t) dx$, where $\psi(x, t)$ is normalized.

$$\therefore \text{the number of electrons in the positions between } x \text{ and } x + dx \\ = N \psi^*(x, t) \psi(x, t) dx$$

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

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

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

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

$$\therefore \langle x \rangle = \int_{-\infty}^{\infty} \psi^*(x, t) x \psi(x, t) dx \quad \dots(1)$$

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

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

$$\langle f(x) \rangle = \int_{-\infty}^{\infty} \psi^*(x, t) f(x) \psi(x, t) dx \quad \dots(2)$$

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

$$\langle V \rangle = \int_{-\infty}^{\infty} \psi^*(x, t) V(x) \psi(x, t) dx \quad \dots(3)$$

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. (3) is replaced by the operator \hat{p}_x . Thus

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

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

$$\therefore \langle p_x \rangle = \int_{-\infty}^{\infty} \psi^*(x, t) \frac{\hbar}{i} \frac{\partial}{\partial x} \psi(x, t) dx \quad \dots(4)$$

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

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

$$= \int_{-\infty}^{\infty} \psi^*(x, t) \left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \right) \psi(x, t) dx \quad \dots(5)$$

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

$$\int_{-\infty}^{\infty} \psi^* \psi dx = 1, \text{ the function } \psi^* \text{ is zero at } x = \pm \infty$$

Hence

$$\langle K \rangle = \frac{\hbar^2}{2m} \int_{-\infty}^{\infty} \frac{\partial \psi^*}{\partial x} \cdot \frac{\partial \psi}{\partial x} dx \quad \dots(6a)$$

$$= \frac{\hbar^2}{2m} \int_{-\infty}^{\infty} \left| \frac{\partial \psi}{\partial x} \right|^2 dx \quad \dots(6b)$$

4.9 Postulates of Quantum Mechanics

We have seen that in Schrödinger's formulation of quantum mechanics, 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. Based on our discussion in the earlier sections now we give five postulates which are sufficient to describe a single-particle system.

(1) For a system consisting of a particle moving in a field of conservative force, there is an associated complex wave function $\psi(x, y, z, t)$, where x, y, z are the space coordinates and t is the time. This function enables us to obtain a description of the behaviour of the system, consistent with the principle of uncertainty.

(2) With every observable dynamical quantity there is an operator. The operators corresponding to the pertinent dynamical quantities are:

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

Dynamical variable	Symbol	Quantum Mechanical Operator
	p_z	$\frac{\hbar}{i} \frac{\partial}{\partial z}$
	\vec{p}	$\frac{\hbar}{i} \vec{\nabla}$
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	$V(x, y, z)$	$V(x, y, z)$

All the operators have eigen-functions and eigen-values. The method of forming the Schrödinger wave equations is explained below.

(i) To obtain the three-dimensional time-dependent Schrödinger 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 we multiply the identity $\psi(x, y, z, t) = \psi(x, y, z, t)$ by the above equation and we get,

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

This is the required equation.

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

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V \right] u = Eu$$

This is the required equation.

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

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 $\psi^* dV$ is interpreted as the probability that the particle will be found in the volume element dV 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

$$\int \psi \psi^* dt = 1$$

The integral is taken over all space.

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

$$\langle \alpha \rangle = \int \psi^* \hat{\alpha} \psi dt, \text{ where } \psi \text{ is normalized,}$$

the integral being taken over all space.

4.10 Orthogonality of Energy Eigen Functions

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 functions is zero.

Thus

$$\int \psi_m \psi_n^* dt = \int \psi_m^* \psi_n dt = 0, \quad \text{if } m \neq n \quad \dots(1)$$

Since the wave functions are normalized, it follows that

$$\int \psi_m^* \psi_n dt = 1, \quad \text{if } m = n \quad \dots(2)$$

where $dt = dx dy dz$ is the volume element

Proof for One Dimensional Case

Let $\psi_m(x)$ and $\psi_n(x)$ be any two normalized non-degenerate eigen functions of the one-dimensional Schrödinger time-independent equation for a bound particle with corresponding eigen values E_m and E_n of energy.

The one-dimensional Schrödinger equations for ψ_m and ψ_n are

$$-\frac{\hbar^2}{2m} \frac{d^2\psi_m}{dx^2} + V\psi_m = E_m \psi_m \quad \dots(3)$$

$$-\frac{\hbar^2}{2m} \frac{d^2\psi_n}{dx^2} + V\psi_n = E_n \psi_n \quad \dots(4)$$

The Schrödinger equation for ψ_m^* which is the complex conjugate of ψ_m is the same as that for ψ_m , so long as the potential energy is real; therefore,

$$-\frac{\hbar^2}{2m} \frac{d\psi_m^*}{dx} + V\psi_m^* = E_m \psi_m^* \quad \dots(5)$$

Multiplying Eq. (4) by ψ_m^* and Eq. (5) by ψ_n , we get

$$-\frac{\hbar^2}{2m} \psi_m^* \frac{d^2\psi_n}{dx^2} + V\psi_m^* \psi_n = E_n \psi_m^* \psi_n \quad \dots(6)$$

$$-\frac{\hbar^2}{2m} \psi_n \frac{d^2\psi_m^*}{dx^2} + V\psi_n^* \psi_n = E_n \psi_m^* \psi_n \quad \dots(7)$$

Now subtracting Eq. (6) from Eq. (7)

$$\frac{\hbar^2}{2m} \left[\psi_m^* \frac{d^2\psi_n}{dx^2} - \psi_n \frac{d^2\psi_m^*}{dx^2} \right] = (E_m - E_n) \psi_m^* \psi_n$$

$$\text{or} \quad \psi_m^* \frac{d^2\psi_n}{dx^2} - \psi_n \frac{d^2\psi_m^*}{dx^2} = \frac{2m}{\hbar^2} (E_m - E_n) \psi_m^* \psi_n$$

$$\text{or} \quad \left[\psi_m^* \frac{d}{dx} \left(\frac{d\psi_n}{dx} \right) + \frac{d\psi_n}{dx} \cdot \frac{d\psi_m^*}{dx} \right] - \left[\psi_n \frac{d}{dx} \left(\frac{d\psi_m^*}{dx} \right) + \frac{d\psi_n}{dx} \cdot \frac{d\psi_m^*}{dx} \right] = \frac{2m}{\hbar^2} (E_m - E_n) \psi_m^* \psi_n$$

$$\text{or} \quad \frac{d}{dx} \left(\psi_m^* \frac{d\psi_n}{dx} \right) - \frac{d}{dx} \left(\psi_n \frac{d\psi_m^*}{dx} \right) = \frac{2m}{\hbar^2} (E_m - E_n) \psi_m^* \psi_n$$

$$\text{or} \quad \frac{d}{dx} \left(\psi_m^* \frac{d\psi_n}{dx} - \psi_n \frac{d\psi_m^*}{dx} \right) = \frac{2m}{\hbar^2} (E_m - E_n) \psi_m^* \psi_n$$

Integrating both sides from $x = -\infty$ to $x = +\infty$

$$\int_{-\infty}^{+\infty} \frac{d}{dx} \left(\psi_m^* \frac{d\psi_n}{dx} - \psi_n \frac{d\psi_m^*}{dx} \right) dx = \frac{2m}{\hbar^2} (E_m - E_n) \int_{-\infty}^{+\infty} \psi_m^* \psi_n dx$$

$$\text{or} \quad \left[\psi_m^* \frac{d\psi_n}{dx} - \psi_n \frac{d\psi_m^*}{dx} \right]_{-\infty}^{+\infty} = \frac{2m}{\hbar^2} (E_m - E_n) \int_{-\infty}^{+\infty} \psi_m^* \psi_n dx \quad \dots(8)$$

For well behaved wave functions, ψ and $\frac{d\psi}{dx}$ approach zero as $x \rightarrow \pm \infty$;

therefore the left hand side of Eq. (8) vanishes at both end points. Thus

$$\frac{2m}{\hbar^2} (E_m - E_n) \int_{-\infty}^{+\infty} \psi_m^* \psi_n dx = 0 \quad \dots(9)$$

If the wave functions belong to two distinct energy levels so that $E_m \neq E_n$, then

$$\int_{-\infty}^{+\infty} \psi_m^* \psi_n dx = 0 \quad (\text{for } m \neq n) \quad \dots(10)$$

For $m = n$, the factor $E_m - E_n = 0$. In this case according to the physical interpretation of wave functions we must have

$$\int_{-\infty}^{+\infty} \psi_m^* \psi_n dx = 1 \quad (\text{for } m = n) \quad \dots(11)$$

The wave functions, thus, show the property of orthogonality.

When two or more linearly independent wave functions $\psi_1, \psi_2, \psi_3, \dots$ correspond to the same eigen value of energy E , then the energy is said to be *degenerate*. Such wave functions are not necessarily orthogonal. But it is possible to find orthogonal linear combinations of degenerate wave functions in many different ways. For example, a linear combination of ψ_1 and ψ_2 is the wave function given by

$$\psi_a = a_1 \psi_1 + a_2 \psi_2$$

ψ_a can be made orthogonal to ψ_1 by choosing the constant coefficients a_1 and a_2 such that

$$\int \psi_1^* \psi_a dx = 0$$

or

$$\int \psi_1^* (a_1 \psi_1 + a_2 \psi_2) dx = 0$$

or

$$a_1 \int \psi_1^* \psi_1 dx + a_2 \int \psi_1^* \psi_2 dx = 0$$

or

$$\frac{a_1}{a_2} = - \frac{\int \psi_1^* \psi_2 dx}{\int \psi_1^* \psi_1 dx}$$

4.11 Schrödinger's Equation for the Complex Conjugate Wave Function $\psi^*(x, y, z, t)$

The time-dependent Schrödinger equation for the wave function $\psi(x, y, z, t)$ is

$$-\frac{\hbar^2}{2m} \nabla^2 \psi + V\psi = i\hbar \frac{\partial \psi}{\partial t} \quad \dots(1)$$

Since ψ is complex

$$\psi = \psi_1 + i\psi_2 \quad \dots(2)$$

where ψ_1 and ψ_2 are real functions of x, y, z, t . Substituting this form for ψ in Eq. (1), we get

$$-\frac{\hbar^2}{2m} \nabla^2 (\psi_1 + i\psi_2) + V(\psi_1 + i\psi_2) = i\hbar \frac{\partial}{\partial t} (\psi_1 + i\psi_2)$$

Equating real and imaginary parts on either side of this equation, we obtain the following two equations:

$$-\frac{\hbar^2}{2m} \nabla^2 \psi_1 + V\psi_1 = -\hbar \frac{\partial \psi_2}{\partial t} \quad \dots(3)$$

$$-\frac{\hbar^2}{2m} \nabla^2 \psi_2 + V\psi_2 = \hbar \frac{\partial \psi_1}{\partial t} \quad \dots(4)$$

Multiplying Eq. (4) by $-i$ and adding it to Eq. (3), we get

$$-\frac{\hbar^2}{2m} \nabla^2 (\psi_1 - i\psi_2) + V(\psi_1 - i\psi_2) = -i\hbar \frac{\partial}{\partial t} \left(\psi_1 + \frac{\psi_2}{i} \right) = -i\hbar \frac{\partial}{\partial t} (\psi_1 - i\psi_2)$$

The complex conjugate ψ^* of ψ is

Therefore,

$$-\frac{\hbar^2}{2m} \nabla^2 \psi^* + V\psi^* = -i\hbar \frac{\partial \psi^*}{\partial t} \quad \dots(6)$$

This is the equation for ψ^* .

4.12 Probability Current Density

Let a particle of mass m be moving in the positive x -direction in a region from x_1 to x_2 . (Fig. 4.1)

For the one-dimensional motion of the particle, the wave function is $\psi(x, t)$. Let dA be the area of cross-section of the region.

The probability of finding the particle in the region is

$$\int_{x_1}^{x_2} P dx dA = \int_{x_1}^{x_2} \psi(x, t) \psi^*(x, t) dx dA \quad \dots(1)$$

and the probability density of finding the particle in the region is

$$P = \psi(x, t) \psi^*(x, t) \quad \dots(2)$$

If the probability of finding the particle in the region decreases with time, the *rate of decrease* of the probability that the particle is in the region from x_1 to x_2 per unit area is called the probability current density out of the region. Therefore, the probability current density $S_2 - S_1$ out of the region in the positive x -direction is given by

$$S_2 - S_1 = - \frac{1}{dA} \left[- \frac{d}{dt} \int_{x_1}^{x_2} P dx dA \right] = - \frac{\partial}{\partial t} \int_{x_1}^{x_2} P dx$$

$$\text{or } S_2 - S_1 = - \frac{\partial}{\partial t} \int_{x_1}^{x_2} \psi \psi^* dx \quad \dots(3)$$

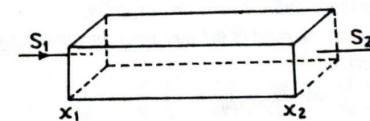


Fig. 4.1

And the probability current density at position x is

$$S = - \frac{\partial}{\partial t} \int \psi \psi^* dx \quad \dots(4)$$

Now we will show that

$$S = - \frac{i\hbar}{2m} \left[\psi^* \frac{\partial \psi}{\partial x} - \psi \frac{\partial \psi^*}{\partial x} \right]$$

The Schrödinger equations for $\psi(x, t)$ and $\psi^*(x, t)$ are

$$i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + V\psi \quad \dots(5)$$

$$-i\hbar \frac{\partial \psi^*}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi^*}{\partial x^2} + V\psi^* \quad \dots(6)$$

Multiplying Eq. (5) by ψ^* and Eq. (6) by ψ , we get

$$i\hbar \psi^* \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m} \psi^* \frac{\partial^2 \psi}{\partial x^2} + \psi^* V\psi \quad \dots(7)$$

$$-i\hbar \psi \frac{\partial \psi^*}{\partial t} = -\frac{\hbar^2}{2m} \psi \frac{\partial^2 \psi^*}{\partial x^2} + \psi V\psi^* \quad \dots(8)$$

Subtracting Eq. (8) from Eq. (7), we get

$$i\hbar \left(\psi^* \frac{\partial \psi}{\partial t} + \psi \frac{\partial \psi^*}{\partial t} \right) = -\frac{\hbar^2}{2m} \left[\psi^* \frac{\partial^2 \psi}{\partial x^2} - \psi \frac{\partial^2 \psi^*}{\partial x^2} \right]$$

$$\text{or} \quad i\hbar \frac{\partial}{\partial t} (\psi\psi^*) = -\frac{\hbar^2}{2m} \frac{\partial}{\partial x} \left[\psi^* \frac{\partial \psi}{\partial x} - \psi \frac{\partial \psi^*}{\partial x} \right]$$

$$\text{or} \quad \frac{\partial}{\partial t} (\psi\psi^*) = \frac{i\hbar}{2m} \frac{\partial}{\partial x} \left[\psi^* \frac{\partial \psi}{\partial x} - \psi \frac{\partial \psi^*}{\partial x} \right] \quad \dots(9)$$

Substituting this equation into Eq. (4), we get

$$\begin{aligned} S &= -\frac{i\hbar}{2m} \int \frac{\partial}{\partial x} \left[\psi^* \frac{\partial \psi}{\partial x} - \psi \frac{\partial \psi^*}{\partial x} \right] dx \\ &= -\frac{i\hbar}{2m} \left[\psi^* \frac{\partial \psi}{\partial x} - \psi \frac{\partial \psi^*}{\partial x} \right] \end{aligned} \quad \dots(10)$$

To show that the probability current density for a free particle is equal to the product of its probability density and its speed.

For a free particle moving in the positive x -direction the momentum p_x at position x is given by

$$\begin{aligned} \frac{\hbar}{i} \frac{\partial \psi}{\partial x} &= p_x \psi \\ \frac{\partial \psi}{\partial x} &= \frac{i}{\hbar} p_x \psi \end{aligned} \quad \dots(11)$$

and

$$-\frac{\hbar}{i} \frac{\partial \psi^*}{\partial x} = p_x \psi^* \quad \dots(12)$$

or

$$\frac{\partial \psi^*}{\partial x} = -\frac{i}{\hbar} p_x \psi^* \quad \dots(12)$$

Substituting Eqs. (11) and (12) in Eq. (10), we get

$$S = -\frac{i\hbar}{2m} \left[\psi^* \frac{i}{\hbar} p_x \psi + \psi \frac{i}{\hbar} p_x \psi^* \right]$$

$$= \frac{1}{m} (\psi\psi^* p_x) = (\psi\psi^*) \frac{p_x}{m}$$

$$\text{or} \quad S = (\psi\psi^*) \frac{mv_x}{m} = (\psi\psi^*) v_x \quad \dots(13a)$$

$$\text{also} \quad S = (\psi\psi^*) \frac{\hbar k}{m} \quad (\because p_x = \hbar k) \quad \dots(13b)$$

4.13 Ehrenfest's Theorem

The theorem states that quantum mechanics gives the same results as classical mechanics for a particle for which the average or expectation values of dynamical quantities are involved.

We prove the theorem for one-dimensional motion of a particle by showing that

$$(a) \frac{d \langle x \rangle}{dt} = \frac{\langle p_x \rangle}{m}, \text{ and } (b) \frac{d \langle p_x \rangle}{dt} = \langle F_x \rangle$$

$$(a) \text{ To show that } \frac{d \langle x \rangle}{dt} = \frac{\langle p_x \rangle}{m}$$

Let x be the position coordinate of a particle of mass m , at time t .

The expectation value of x is given by

$$\langle x \rangle = \int_{-\infty}^{\infty} \psi^* (x, t) \cdot x \psi (x, t) dx \quad \dots(1)$$

Differentiating this equation with respect to t ,

$$\frac{d \langle x \rangle}{dt} = \int_{-\infty}^{\infty} x \frac{\partial (\psi\psi^*)}{\partial t} dx \quad \dots(2)$$

Now we have [See Eq. (9), Sec. 4.12]

$$\frac{\partial (\psi\psi^*)}{\partial t} = \frac{i\hbar}{2m} \frac{\partial}{\partial x} \left[\psi^* \frac{\partial \psi}{\partial x} - \psi \frac{\partial \psi^*}{\partial x} \right] \quad \dots(3)$$

Substituting this expression for $\frac{\partial (\psi\psi^*)}{\partial t}$ in Eq. (2),

$$\frac{d \langle x \rangle}{dt} = \frac{i\hbar}{2m} \int_{-\infty}^{\infty} x \frac{\partial}{\partial x} \left[\psi^* \frac{\partial \psi}{\partial x} - \psi \frac{\partial \psi^*}{\partial x} \right] dx$$

Integrating the right hand side by parts, we get

$$\begin{aligned} \frac{d \langle x \rangle}{dt} &= \frac{i\hbar}{2m} \left[x \left(\psi^* \frac{\partial \psi}{\partial x} - \psi \frac{\partial \psi^*}{\partial x} \right) \right]_{-\infty}^{\infty} \\ &\quad - \frac{i\hbar}{2m} \int_{-\infty}^{\infty} \left(\psi^* \frac{\partial \psi}{\partial x} - \psi \frac{\partial \psi^*}{\partial x} \right) dx \end{aligned}$$

As x approaches either ∞ or $-\infty$, ψ and $\frac{\partial \psi}{\partial x}$ approach zero, and therefore the first term becomes zero.

Hence we get

$$\frac{d\langle p_x \rangle}{dt} = -\frac{i\hbar}{2m} \int_{-\infty}^{+\infty} \left(\psi^* \frac{\partial \psi}{\partial x} - \psi \frac{\partial \psi^*}{\partial x} \right) dx \quad \dots(4)$$

The expectation value of p_x is given by

$$\begin{aligned} \langle p_x \rangle &= \int_{-\infty}^{+\infty} \psi^* \frac{\hbar}{i} \frac{\partial \psi}{\partial x} dx \\ \therefore \int_{-\infty}^{+\infty} \psi^* \frac{\partial \psi}{\partial x} dx &= \frac{i}{\hbar} \langle p_x \rangle \end{aligned} \quad \dots(5)$$

Similarly

$$\int_{-\infty}^{+\infty} \psi \frac{\partial \psi^*}{\partial x} dx = -\frac{i}{\hbar} \langle p_x \rangle \quad \dots(6)$$

Substituting the values of these integrals in Eq. (4),

$$\begin{aligned} \frac{d\langle p_x \rangle}{dt} &= -\frac{i\hbar}{2m} \left[\frac{i}{\hbar} \langle p_x \rangle + \frac{i}{\hbar} \langle p_x \rangle \right] \\ &= \frac{\langle p_x \rangle}{m} \end{aligned} \quad \dots(7)$$

(b) To show that $\frac{d\langle p_x \rangle}{dt} = \langle F_x \rangle$

The expectation value of the momentum p_x is given by

$$\langle p_x \rangle = \int_{-\infty}^{+\infty} \psi^* (x, t) \frac{\hbar}{i} \frac{\partial}{\partial x} \psi (x, t) dx \quad \dots(8)$$

$$= \frac{\hbar}{i} \int_{-\infty}^{+\infty} \psi^* \frac{\partial \psi}{\partial x} dx \quad \dots(9)$$

Differentiating Eq. (9) with respect to t , we get

$$\frac{d\langle p_x \rangle}{dt} = \frac{\hbar}{i} \int_{-\infty}^{+\infty} \left[\frac{\partial \psi^*}{\partial t} \frac{\partial \psi}{\partial x} + \psi^* \frac{\partial^2 \psi}{\partial x \partial t} \right] dx \quad \dots(10)$$

Now the time-dependent Schrödinger equations for ψ and ψ^* are

$$i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + V\psi \quad \dots(11)$$

$$-i\hbar \frac{\partial \psi^*}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi^*}{\partial x^2} + V\psi^* \quad \dots(12)$$

Differentiating Eq. (11) with respect to x

$$i\hbar \frac{\partial^2 \psi}{\partial x \partial t} = -\frac{\hbar^2}{2m} \frac{\partial^3 \psi}{\partial x^3} + \frac{\partial (V\psi)}{\partial x} \quad \dots(13)$$

We write Eq. (10) in the form

$$\frac{d\langle p_x \rangle}{dt} = \int_{-\infty}^{+\infty} \left(-i\hbar \frac{\partial \psi^* \partial \psi}{\partial t \partial x} - \psi^* i\hbar \frac{\partial^2 \psi}{\partial x \partial t} \right) dx$$

Substituting the expressions for $-i\hbar \frac{\partial \psi^*}{\partial t}$ and $i\hbar \frac{\partial^2 \psi}{\partial x \partial t}$ in this equation, we obtain

$$\begin{aligned} \frac{d\langle p_x \rangle}{dt} &= \int_{-\infty}^{+\infty} \left[\left(-\frac{\hbar^2}{2m} \frac{\partial^3 \psi^*}{\partial x^3} + V\psi^* \right) \frac{\partial \psi}{\partial x} \right. \\ &\quad \left. - \psi^* \left(-\frac{\hbar^2}{2m} \frac{\partial^3 \psi}{\partial x^3} + \frac{\partial (V\psi)}{\partial x} \right) \right] dx \\ &= -\frac{\hbar^2}{2m} \int_{-\infty}^{+\infty} \left[\frac{\partial^2 \psi^*}{\partial x^2} \frac{\partial \psi}{\partial x} - \psi^* \frac{\partial^2 \psi}{\partial x^3} \right] dx \\ &\quad + \int_{-\infty}^{+\infty} \left[V\psi^* \frac{\partial \psi}{\partial x} - \psi^* \frac{\partial}{\partial x} (V\psi) \right] dx \\ &= -\frac{\hbar^2}{2m} \int_{-\infty}^{+\infty} \left[\frac{\partial}{\partial x} \left(\frac{\partial \psi}{\partial x} \frac{\partial \psi^*}{\partial x} - \psi^* \frac{\partial^2 \psi}{\partial x^2} \right) \right] dx \\ &\quad + \int_{-\infty}^{+\infty} V\psi^* \frac{\partial \psi}{\partial x} - \psi^* \left(\psi \frac{\partial V}{\partial x} + V \frac{\partial \psi}{\partial x} \right) dx \\ &= -\frac{\hbar^2}{2m} \left[\frac{\partial \psi}{\partial x} \frac{\partial \psi^*}{\partial x} - \psi^* \frac{\partial^2 \psi}{\partial x^2} \right] - \int_{-\infty}^{+\infty} \psi^* \frac{\partial V}{\partial x} \psi dx \quad \dots(14) \end{aligned}$$

As x approaches either ∞ or $-\infty$, ψ and $\frac{\partial \psi}{\partial x}$ approach zero. Therefore, the first term on the right hand side of Eq. (14) is zero. The second term represents the expectation value of the differential coefficient of the potential energy V with respect to x , i.e.,

$$\begin{aligned} \frac{\partial V}{\partial x} &= \int_{-\infty}^{+\infty} \psi^* \frac{\partial V}{\partial x} \psi dx \\ \therefore \frac{d\langle p_x \rangle}{dt} &= -\langle \frac{\partial V}{\partial x} \rangle \end{aligned}$$

But $-\frac{\partial V}{\partial x}$ is the classical force F_x .

$$\frac{d\langle p_x \rangle}{dt} = \langle F_x \rangle \quad \dots(15)$$

This equation represents Newton's second law of motion. Thus if the expectation values of dynamical quantities for a particle are considered, quantum mechanics gives the equations of classical mechanics.

4.14 Momentum Wave Function for a Free Particle

A non-relativistic free particle of mass m moving in the positive x -direction with speed v_x has kinetic energy

$$E = \frac{1}{2} m v_x^2 \text{ and momentum } p_x = mv_x.$$

It is associated with a wave of wavelength λ and frequency ν given by

$$\lambda = \frac{\hbar}{p_x}, \quad \nu = \frac{E}{\hbar}$$

The propagation constant k_x of the wave is

$$k_x = \frac{2\pi}{\lambda} = \frac{2\pi}{h/p_x} = \frac{p_x}{h/2\pi} = \frac{p_x}{\hbar}$$

and the angular frequency ω is

$$\omega = 2\pi\nu = \frac{2\pi E}{\hbar} = \frac{E}{\hbar}$$

A plane wave travelling in the positive x -direction may be represented by

$$\begin{aligned} \psi(x, t) &= Ae^{-i(k_x x - \omega t)} \\ &= Ae^{i(p_x/\hbar)x - (E/\hbar)t} \\ &= Ae^{i/\hbar(p_x x - Et)} \end{aligned}$$

The superposition of a number of such waves of propagation number slightly different from an average value travelling simultaneously along the same line in the positive x -direction forms a wave packet of small extension. By Fourier's theorem the wave packet may be expressed by

$$\psi(x, t) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} A(p_x) e^{i/\hbar(p_x x - Et)} dp_x \quad \dots(1)$$

The function $\psi(x, t)$ is called the momentum wave function for the motion of the free particle in one dimension.

The amplitude $A(p_x)$ of the x -component of the momentum is given by the Fourier transform

$$A(p) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} \psi(x, t) e^{-i/\hbar(p_x x - Et)} dx \quad \dots(2)$$

In three dimensions the wave function is represented by

$$\psi(\vec{r}, t) = \frac{1}{(2\pi\hbar)^{3/2}} \int_{-\infty}^{\infty} A(\vec{p}) e^{i/\hbar(\vec{p} \cdot \vec{r} - Et)} d^3 \vec{p} \quad \dots(3)$$

where $d^3 \vec{p} = dp_x dp_y dp_z$ is the volume element in the momentum space. In Eqs. (1), (2) and (3) $1/\sqrt{2\pi\hbar}$ and $1/(2\pi\hbar)^{3/2}$ are normalization constants.

4.15 Momentum Eigen-Functions

The eigen-value equations for the components p_x, p_y, p_z of the momentum \vec{p} of a particle in motion are

$$\frac{\hbar}{i} \frac{\partial}{\partial x} \psi_p(x, y, z) = p_x \psi_p(x, y, z) \quad \dots(1)$$

$$\frac{\hbar}{i} \frac{\partial}{\partial y} \psi_p(x, y, z) = p_y \psi_p(x, y, z) \quad \dots(2)$$

$$\frac{\hbar}{i} \frac{\partial}{\partial z} \psi_p(x, y, z) = p_z \psi_p(x, y, z) \quad \dots(3)$$

where $\psi_p(x, y, z)$ is the momentum eigen function for momentum \vec{p} .

The solutions of the three eigen-value equations are the momentum eigen-functions for the components of the momentum.

Solution of equations (1), (2), (3)

Let us solve Eq. (1).

We assume that the function $\psi_p(x, y, z)$ is the product of three functions $\psi(x), \psi(y)$ and $\psi(z)$.

$$\therefore \psi_p(x, y, z) = \psi_{p_x}(x) \psi_{p_y}(y) \psi_{p_z}(z) \quad \dots(4)$$

Substituting this equation in Eq. (1), we get

$$\frac{\hbar}{i} \psi(y) \psi(z) \frac{d\psi(x)}{dx} = p_x \psi(x) \psi(y) \psi(z)$$

Dividing this equation by $\psi(x) \psi(y) \psi(z)$, we get

$$\begin{aligned} \frac{\hbar}{i} \frac{1}{\psi(x)} \frac{d\psi(x)}{dx} &= p_x \\ \text{or} \quad \frac{1}{\psi(x)} \frac{d\psi(x)}{dx} &= \frac{i}{\hbar} p_x \end{aligned} \quad \dots(5)$$

The solution of this equation is

$$\psi_{p_x}(x) = C_1 e^{i(\hbar/p_x)x} \quad \dots(6)$$

where C_1 is a normalization constant.

Similarly the solutions of Eqs. (2) and (3) are

$$\psi_{p_y}(y) = C_2 e^{i(\hbar/p_y)y} \quad \dots(7)$$

$$\psi_{p_z}(z) = C_3 e^{i(\hbar/p_z)z} \quad \dots(8)$$

Substituting these expressions in Eq. (4), we get the momentum eigen-function for the resultant momentum \vec{p} as

$$\psi_p(x, y, z) = C e^{i(\hbar/p_x)x + i(\hbar/p_y)y + i(\hbar/p_z)z} \quad \dots(9)$$

$$\text{or} \quad \psi_p(\vec{r}) = C e^{i(\hbar/\vec{p}) \cdot \vec{r}} \quad \dots(10)$$

where C is a normalization constant. Since $\vec{p} = \hbar \vec{k}$, where \vec{k} is the propagation vector, the momentum eigen-function $\psi_p(r)$ in terms of \vec{k} is given by

$$\psi_k(\vec{r}) = C e^{i(\hbar/\vec{k}) \cdot \vec{r}} \quad \dots(11)$$

4.16 Exact Statement and Proof of Uncertainty Principle for One-Dimensional Wave Packet

In quantum theory complementary observable quantities cannot be simultaneously measured with perfect accuracy. In the previous chapter we have seen that the product of the uncertainties in the simultaneous measurements of a pair of such quantities is of the order of Planck's constant \hbar or \hbar^2 . This conclusion is based on rather qualitative considerations.

In a mathematical proof of the uncertainty principle, an exact definition of uncertainty must be given.

The uncertainty Δx in the position of a particle is defined as the square root of the mean square deviation in the position. Similarly the uncertainty Δp_x in the x -component of the momentum of a particle is defined as the square root of the mean square deviation in the momentum. Based on these definitions an exact statement of the uncertainty principle is as follows:

The product of the square root of the mean square deviation in the x -coordinate of a particle in motion, at some instant, and the square root of the mean square deviation in the conjugate momentum is equal to or greater than $\hbar/2$.

Thus

$$\Delta x \cdot \Delta p_x \geq \frac{\hbar}{2}$$

Proof:

Let $x_1, x_2, x_3, \dots, x_N$ be the N individual observations of the position of the wave-packet representing a particle in motion along the positive direction of x .

The mean value \bar{x} of these observations is given by

$$\bar{x} = \frac{x_1 + x_2 + x_3 + \dots + x_N}{N}$$

The deviations of the individual values from the mean value are

$$(x_1 - \bar{x}), (x_2 - \bar{x}), \dots, (x_N - \bar{x})$$

The mean square deviation is denoted by $\overline{(x - \bar{x})^2}$ and it is given by

$$\begin{aligned} \overline{(x - \bar{x})^2} &= \frac{(x_1 - \bar{x})^2 + (x_2 - \bar{x})^2 + \dots + (x_N - \bar{x})^2}{N} \\ &= \frac{(x_1^2 + x_2^2 + \dots + x_N^2) - 2(x_1 + x_2 + \dots + x_N)\bar{x}}{N} + \frac{\bar{x}^2 + \bar{x}^2 + \dots}{N} \\ &= \frac{x_1^2 + x_2^2 + \dots + x_N^2}{N} - \frac{2(x_1 + x_2 + \dots + x_N)\bar{x}}{N} + \frac{N\bar{x}^2}{N} \\ &= \bar{x}^2 - 2\bar{x} \cdot \bar{x} + \bar{x}^2 \\ &= \bar{x}^2 - 2\bar{x}^2 + \bar{x}^2 = \bar{x}^2 \pm \bar{x}^2 \end{aligned}$$

From the definition of the uncertainty Δx in the position, the mean square deviation is the square of the uncertainty.

$$\therefore (\Delta x)^2 = \bar{x}^2 - \bar{x}^2$$

By similar consideration the uncertainty Δp in the conjugate momentum of the particle is given by

$$(\Delta p)^2 = \bar{p}^2 - \bar{p}^2$$

We choose the origin of the coordinates such that $\bar{x} = 0$. Similarly we choose the origin in the momentum space such that $\bar{p} = 0$

$$\therefore (\Delta x)^2 = \bar{x}^2$$

$$\text{and } (\Delta p)^2 = \bar{p}^2$$

The product of these equations is

$$(\Delta x)^2 (\Delta p)^2 = \bar{x}^2 \bar{p}^2$$

We take the wavefunction normalized to unity so that

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

The average or expectation values of x^2 and p^2 are given by

$$\bar{x}^2 = \int \psi^* x^2 \psi dx \quad \dots(2)$$

$$\bar{p}^2 = \int \psi^* \left(\frac{\hbar}{i} \frac{d}{dx} \right)^2 \psi dx \quad \dots(3)$$

The R.H.S. of Eq. (3) is simplified as follows

$$\begin{aligned} \bar{p}^2 &= \int \psi^* \left(\frac{\hbar}{i} \frac{d^2 \psi}{dx^2} \right) dx \\ &= -\hbar^2 \int \psi^* \frac{d^2 \psi}{dx^2} dx \end{aligned}$$

Integrating the R.H.S by parts

$$\bar{p}^2 = -\hbar^2 \left[\psi^* \frac{d\psi}{dx} \right]_{-\infty}^{+\infty} + \hbar^2 \int \frac{d\psi^*}{dx} \frac{d\psi}{dx} dx$$

The first term on the R.H.S. is zero, because the wavefunction is zero at $-\infty$ and $+\infty$.

$$\therefore \bar{p}^2 = \hbar^2 \int \frac{d\psi^*}{dx} \frac{d\psi}{dx} dx \quad \dots(4)$$

Now substituting for \bar{x}^2 and \bar{p}^2 in Eq. (1)

$$(\Delta x)^2 (\Delta p)^2 = \hbar^2 \int \psi^* x^2 \psi dx \cdot \int \frac{d\psi^*}{dx} \frac{d\psi}{dx} dx$$

$$\text{or } \left(\int \psi^* x^2 \psi dx \right) \left(\int \frac{d\psi^*}{dx} \frac{d\psi}{dx} dx \right) = \frac{(\Delta x)^2 (\Delta p)^2}{\hbar^2} \quad \dots(5)$$

Let us consider the integral

$$\int \frac{d\psi^*}{dx} x \psi dx$$

Integrating by parts

$$\begin{aligned} \int \frac{d\psi^*}{dx} x \psi dx &= \int x \psi \frac{d\psi^*}{dx} dx \\ &= \left[x \psi \cdot \psi^* \right]_{-\infty}^{+\infty} - \int \frac{d}{dx} (x \psi) \psi^* dx \\ &= 0 - \int \left(\psi + x \frac{d\psi}{dx} \right) \psi^* dx \\ &= - \int \psi \psi^* dx - \int \frac{d\psi}{dx} x \psi^* dx \end{aligned}$$

$$\therefore \int \frac{d\psi^*}{dx} x \psi dx + \int \frac{d\psi}{dx} x \psi^* dx = - \int \psi \psi^* dx \quad \dots(6)$$

The value of the integral on the R.H.S. is 1, and the second integral on the L.H.S. is complex conjugate of the first. Let

$$\int \frac{d\psi^*}{dx} x \psi dx = A + iB,$$

$$\text{then } \int \frac{d\psi}{dx} x \psi^* dx = A - iB$$

\therefore from Eq. (6), we have

$$A + iB + A - iB = -1 \\ 2A = -1$$

Squaring this equation

$$A^2 = \frac{1}{4} \quad \dots(7)$$

The magnitude of $A + iB$ is $\sqrt{A^2 + B^2}$

$$\text{i.e. } |A + iB| = \sqrt{A^2 + B^2}$$

$$\therefore |A + iB|^2 = A^2 + B^2$$

This equation shows that

$$|A + iB|^2 \geq A^2$$

$$\therefore \left| \int \frac{d\psi^*}{dx} x \psi dx \right|^2 \geq \frac{1}{4} \quad \dots(8)$$

We now apply the Schwarz inequality (see Appendix 2)

$$\left(\int f^* f dx \right) \left(\int \phi^* \phi dx \right) \geq \left| \int f^* \phi dx \right|^2 \quad \dots(9)$$

This inequality is true for any two functions f and ϕ . Taking

$$f = \frac{d\psi}{dx}, \text{ so that } f^* = \frac{d\psi^*}{dx}$$

and

$$\phi = x\psi, \text{ so that } \phi^* = x\psi^*, \text{ we get}$$

$$\int \frac{d\psi^*}{dx} \frac{d\psi}{dx} dx \cdot \int x^2 \psi \psi^* dx \geq \left| \int \frac{d\psi^*}{dx} x \psi dx \right|^2$$

Now using Eq. (5) and inequality (8), we get

$$\frac{(\Delta x)^2 (\Delta p)^2}{\hbar^2} \geq \frac{1}{4}$$

Taking the square root, we get

$$\Delta x \Delta p \geq \frac{\hbar}{2} \quad \dots(10)$$

This is the Heisenberg uncertainty relation.

SOLVED EXAMPLES

Example 4.1. A particle moving along the positive direction of the x -axis in a region of potential energy $V(x)$ is represented by a wave-packet given by

$$\psi(x, t) = \frac{1}{\sqrt{2\pi\hbar}} \int A(p) e^{i/\hbar(p_x x - Et)} dp$$

Using the expression for non-relativistic total energy obtain the one-dimensional time-dependent Schrödinger wave equation.

Solution:

The total energy E of the particle is given by

$$\frac{p_x^2}{2m} + V(x) = E \quad \dots(1)$$

Now we have

$$\psi(x, t) = \frac{1}{\sqrt{2\pi\hbar}} \int A(p) e^{i/\hbar(p_x x - Et)} dp \quad \dots(2)$$

Differentiating this equation partially w.r.t. to x

$$\frac{\partial \psi}{\partial x} = \frac{1}{\sqrt{2\pi\hbar}} \int A(p) \left(\frac{i}{\hbar} p_x \right) e^{i/\hbar(p_x x - Et)} dp$$

$$\text{And } \frac{\partial^2 \psi}{\partial x^2} = \frac{1}{\sqrt{2\pi\hbar}} \int A(p) \left(\frac{i}{\hbar} \right)^2 p_x^2 e^{i/\hbar(p_x x - Et)} dp$$

$$\therefore -\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} = \frac{1}{\sqrt{2\pi\hbar}} \int \frac{p_x^2}{2m} A(p) e^{i/\hbar(p_x x - Et)} dp \quad \dots(3)$$

Differentiating Eq. (2) partially w.r.t. to t

$$\frac{\partial \psi}{\partial t} = \frac{1}{\sqrt{2\pi\hbar}} \int A(p) \left(\frac{i}{\hbar} \right) (-E) e^{i/\hbar(p_x x - Et)} dp$$

$$\therefore i\hbar \frac{\partial \psi}{\partial t} = \frac{1}{\sqrt{2\pi\hbar}} \int E A(p) e^{i/\hbar(p_x x - Et)} dp \quad \dots(4)$$

Subtracting Eq. (4) from (3)

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} - i\hbar \frac{\partial \psi}{\partial t} = \frac{1}{\sqrt{2\pi\hbar}} \int \left(\frac{p_x^2}{2m} - E \right) A(p) e^{i/\hbar(p_x x - Et)} dp$$

Now using Eq. (1),

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

$$\text{or } -\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + V\psi = i\hbar \frac{\partial \psi}{\partial t} \quad \dots(5)$$

This is the one-dimensional time-dependent Schrödinger wave equation.

Example 4.2. A particle is in motion along a line between $x = 0$ and $x = a$ with zero potential energy, and at points for which $x < 0$ and $x > a$ the potential energy is infinite. The wave function for the particle in the n th state is given by

$$\psi_n = A \sin \frac{n\pi x}{a}$$

Find the expression for the normalized wave function.

Solution:

For the n th state the probability that the particle will be between x and $x + dx$ is

$$\begin{aligned} P_n dx &= |\psi_n(x)|^2 dx \\ &= A^2 \sin^2 \frac{n\pi x}{a} dx \end{aligned}$$

There is only one particle in the region from $x = 0$ to $x = a$ and at all times it is some where in this region.

Therefore,

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

or

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

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

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

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

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

so

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

\therefore the normalized wave function is

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

QUESTIONS AND PROBLEMS

1. Deduce the time-independent Schrödinger equation. Give the significance of the wave function.
2. (a) Derive the time-independent Schrödinger wave equation for a particle.
(b) Give the physical meaning of the wave function. What do you understand by normalized wave function?
3. (a) Obtain the time-dependent Schrödinger wave equation for a particle.
(b) Separate the wave function into time-dependent and time-independent parts and obtain the steady state Schrödinger equation.
4. Prove that if there are two solutions of the one-dimensional time-independent Schrödinger wave equation for different values of energy E_m and E_n , then

$$\int_{-\infty}^{\infty} \psi_m^* \psi_n dx = 0$$

5. A particle moving along the positive direction of the x -axis in a region of potential energy $V(x)$ is represented by a wave-packet given by

$$\psi(x, t) = \frac{1}{\sqrt{2\pi\hbar}} \int A(p) e^{i\hbar(px - Et)} dp$$

by differentiating this equation and using the expression for non-relativistic total energy obtain the one-dimensional time-dependent Schrödinger wave equation.

6. If $\psi_1(x, t)$ and $\psi_2(x, t)$ are both solutions of the time-dependent Schrödinger equation for the motion of a particle with potential energy $V(x)$, prove that the linear combination,

$$\psi(x, t) = A_1 \psi_1(x, t) + A_2 \psi_2(x, t),$$

where A_1 and A_2 are constants, is also a solution.

7. For one-dimensional motion of a particle of mass m prove that the expectation value of its kinetic energy is given by

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

8. Show that

$$\frac{d}{dt} \langle p_x \rangle = - \langle \frac{dV}{dx} \rangle$$

State and prove Ehrenfest's theorem.

9. Using the operator representation of the x -component of the momentum of a particle prove that

$$(xp_x - p_x x) \psi = i\hbar \psi$$

where ψ is an arbitrary function.

Solution:

$$\begin{aligned} (xp_x - p_x x) \psi &= \left[x \frac{\hbar}{i} \frac{\partial \psi}{\partial x} - \frac{\hbar}{i} \frac{\partial (x\psi)}{\partial x} \right] \\ &= \frac{\hbar}{i} \left[x \frac{\partial \psi}{\partial x} - x \frac{\partial \psi}{\partial x} - \psi \right] \\ &= -\frac{\hbar}{i} \psi = i\hbar \psi \end{aligned}$$

Free States

5.1 Introduction

When a particle is not subjected to any external force, so that it moves in a region in which its potential energy is constant, it is said to be a *free particle*. Such a particle has definite value of total energy and definite value of momentum. But the position of the particle is completely unknown. In this chapter we consider application of the Schrödinger equation to two simple cases: (i) one dimensional motion of a particle under no forces, and (ii) one dimensional motion of a stream of particles, and the effect of a rectangular potential barrier on the motion.

5.2 The Free Particle

Suppose a particle of mass m is in motion along the x -axis. Suppose no force is acting on the particle, so that the potential energy of the particle is constant. For convenience, the constant potential energy is taken to be zero. Therefore, the time-independent Schrödinger equation for the free particle is

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} = E\psi \quad \dots(1)$$

Since the particle is moving freely with zero potential energy, its total energy E is the kinetic energy given by

$$E = \frac{p_x^2}{2m} \quad \dots(2)$$

where p is the momentum of the particle.

From Eq. (1), we have

$$\frac{d^2\psi}{dx^2} + \frac{2mE}{\hbar^2} \cdot \psi = 0$$

or

$$\frac{d^2\psi}{dx^2} + k^2 \psi = 0 \quad \dots(3)$$

where

$$k = \sqrt{\frac{2mE}{\hbar^2}} \quad \dots(4)$$

so that

$$E = \frac{k^2 \hbar^2}{2m} \quad \dots(5)$$

The solution of Eq. (3) is

$$\psi(x) = Ae^{ikx} + Be^{-ikx} \quad \dots(6)$$

where A and B are constants.

Eq. (6) gives the time-independent part of the wave function. The complete wave function for particle is given by

$$\begin{aligned} \psi(x, t) &= \psi(x) e^{-i\omega t} \\ &= (Ae^{ikx} + Be^{-ikx}) e^{-i\omega t} \\ &= Ae^{-i(\omega t - kx)} + Be^{-i(\omega t + kx)} \end{aligned} \quad \dots(7)$$

where

$$\omega = \frac{E}{\hbar} = \frac{k^2 \hbar^2}{2m} \cdot \frac{1}{\hbar} = \frac{\hbar k^2}{2m} \quad \dots(8)$$

Eq. (7) represents a continuous plane simple harmonic wave. The first term on the right side of Eq. (7) represents the wave travelling in the positive x -direction, and the second term represents the wave travelling in the negative x -direction. Therefore, for the motion of the particle in the positive x -direction, we have

$$\psi(x) = Ae^{ikx} \quad \dots(9)$$

or

$$\psi(x, t) = Ae^{-i(\omega t - kx)} \quad \dots(10)$$

The momentum operator, $\frac{\hbar}{i} \frac{\partial}{\partial x}$, operating on the wave function $\psi(x, t)$

gives

$$\begin{aligned} \frac{\hbar}{i} \frac{\partial \psi}{\partial x} &= \frac{\hbar}{i} [A (ik) e^{-i(\omega t - kx)}] \\ &= \hbar k A e^{-i(\omega t - kx)} \\ &= \hbar k \psi \end{aligned}$$

But from Eqs. (2) and (5)

$$p_x = \hbar k \quad \dots(11)$$

$$\frac{\hbar}{i} \frac{\partial \psi}{\partial x} = p_x \psi \quad \dots(12)$$

This equation shows that the wave function $\psi(x, t)$ for the particle is an eigen function of the liner momentum operator, and the momentum p_x is the eigen value of the operator. Hence the momentum remains sharp with the value p_x .

The probability of finding the particle between x and $x + dx$ is given by

$$\begin{aligned} P dx &= \psi(x, t) \psi^*(x, t) dx \\ &= A^2 dx \end{aligned} \quad \dots(13)$$

\therefore the probability density P for the position of the the particle with the definite value of momentum is constant over the x -axis, i.e., all positions of

the particle are equally probable. This conclusion is also obtained from the principle of uncertainty.

According to the interpretation of the wave function, the probability of finding the particle somewhere in space must be equal to 1, i.e.

$$\int_{-\infty}^{\infty} \psi(x, t) \psi^*(x, t) dx = 1 \quad \dots(14)$$

In this case $\psi(x, t) \psi^*(x, t) = \text{constant} = A^2$.

Therefore, the integral on the left side of Eq. (14) is infinite. Hence the wave function for the particle cannot be normalized and A must remain arbitrary. The difficulty arises because we are dealing with an ideal case. In practice, we cannot have an absolutely free particle. The particle will always be confined within an enclosure in the laboratory, and hence its position can be determined. This means that its momentum cannot be determined with absolute accuracy.

5.3 Potential Step

One dimensional step potential barrier for a particle is shown in Fig. 5.1. The meaning of the figure is that in region (I) to the left of the origin O the potential energy of a particle is zero, and in region (II) to the right of O it is constant equal to V_0 . Such a potential barrier does not exist in nature, but it is approximately similar to the instantaneous potential difference between the dees of a cyclotron or to the surface potential barrier of a metal.

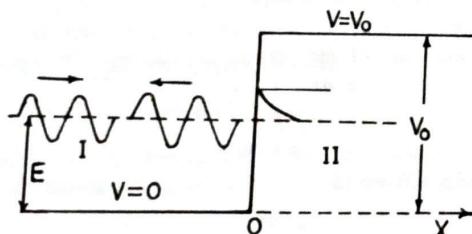


Fig. 5.1

Suppose a uniform beam of particles each of mass m and having kinetic energy E is travelling parallel to the x -axis from left to right in region (I), and is incident on the potential step. In region (I) the energy E of a particle is wholly kinetic, and in region (II) it is partly kinetic and partly potential. If $E < V_0$, then according to classical mechanics, no particle can enter region (II). However according to quantum mechanics although the wave function for an incident particle has a finite value in region (II) there is no steady transmission of the particles in that region, all the particles are reflected back from the potential

step ($V_0 > E$). In the following discussion we investigate this behaviour of the particles.

Let $\psi_1(x)$ and $\psi_2(x)$ be the wave functions for the motion of a particle in the beam in regions (I) and (II) respectively.

In region (I): $-\infty \leq x < 0$, the time-independent Schrödinger wave equation is

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

$$\text{or} \quad \frac{d^2\psi_1}{dx^2} + \frac{2mE}{\hbar^2} \psi_1 = 0$$

$$\text{or} \quad \frac{d^2\psi_1}{dx^2} + k_1^2 \psi_1 = 0 \quad \dots(1)$$

$$\text{where} \quad k_1 = \sqrt{\frac{2mE}{\hbar^2}}$$

Case 1. When $E < V_0$

In region (II): $0 \leq x \leq +\infty$ (Fig. 5.1)
if $V_0 > E$, then the equation is

$$\frac{d^2\psi_2}{dx^2} + \frac{2m}{\hbar^2} (E - V_0) \psi_2 = 0$$

$$\text{or} \quad \frac{d^2\psi_2}{dx^2} - \frac{2m}{\hbar^2} (V_0 - E) \psi_2 = 0$$

$$\text{or} \quad \frac{d^2\psi_2}{dx^2} - \beta^2 \psi_2 = 0 \quad \dots(2)$$

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

The general solutions of Eqs (1) and (2) are

$$\psi_1 = A e^{ik_1 x} + B e^{-ik_1 x} \quad \dots(3)$$

$$\psi_2 = C e^{-\beta x} + D e^{\beta x} \quad \dots(4)$$

In Eq. (3) the term $A e^{ik_1 x}$ represents a wave of amplitude A travelling in the positive x -direction and the term $B e^{-ik_1 x}$ is the wave of amplitude B reflected from the potential step in the negative x -direction. In Eq. (4) the term $C e^{-\beta x}$ is an exponentially decreasing wave function representing a non-oscillatory disturbance which penetrates the potential barrier for some finite distance in the positive x -direction (Fig. 5.1); and the term $D e^{\beta x}$ is an exponentially increasing wave function in the positive x -direction. According to the physical interpretation, ψ must remain finite when x approaches ∞ . From this condition it follows that $D = 0$. Hence in region (II), the valid solution of the wave equation is

$$\psi_2 = C e^{-\beta x} \quad \dots(5)$$

Expressions for the amplitudes B and C in terms of the amplitude A(i) At $x = 0$, we have

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

∴ from Eqns. (3) and (5), we have

$$A + B = C \quad \dots(6)$$

(ii) We also have

$$\begin{aligned} \left(\frac{d\psi_1}{dx}\right)_{x=0} &= \left(\frac{d\psi_2}{dx}\right)_{x=0} \\ Aik_1 - Bik_1 &= -C \beta \\ A - B &= -\frac{\beta}{ik_1} C = \frac{i\beta}{k_1} C \end{aligned} \quad \dots(7)$$

Adding Eqs. (6) and (7)

$$\begin{aligned} 2A &= \left(1 + \frac{i\beta}{k_1}\right)C = \left(\frac{k_1 + i\beta}{k_1}\right)C \\ C &= \left(\frac{2k_1}{k_1 + i\beta}\right)A \end{aligned} \quad \dots(8)$$

Subtracting Eq. (7) from Eq. (6)

$$\begin{aligned} 2B &= \left(1 - \frac{i\beta}{k_1}\right)C = \left(\frac{k_1 - i\beta}{k_1}\right)C \\ &= \left(\frac{k_1 - i\beta}{k_1}\right)\left(\frac{2k_1}{k_1 + i\beta}\right)A \\ B &= \left(\frac{k_1 - i\beta}{k_1 + i\beta}\right)A \end{aligned} \quad \dots(9)$$

Eqs. (9) and (8) can be expressed in polar form.

Let $k_1 = r \cos \delta$ and $\beta = r \sin \delta$.Then $r = \sqrt{k_1^2 + \beta^2}$, and $\tan \delta = \beta/k$ Substituting for k_1 and β in Eq. (9)

$$B = \frac{re^{-i\delta}}{re^{i\delta}} A = e^{-2i\delta} A \quad \dots(10)$$

Now Eq. (8) is

$$\begin{aligned} C &= \left(\frac{2k_1}{k_1 + i\beta}\right)A = \left(\frac{2k_1}{k_1 + i\beta} - 1 + 1\right)A \\ &= \left(\frac{k_1 - i\beta}{k_1 + i\beta} + 1\right)A = (e^{-2i\delta} + 1)A \\ &= (1 + e^{-2i\delta})A \end{aligned} \quad \dots(11)$$

Expressions for the wave functions in regions (I) and (II):In region (I): $x < 0$

$$\begin{aligned} \psi_1 &= Ae^{ik_1 x} + Be^{-ik_1 x} \\ &= Ae^{ik_1 x} + e^{-2i\delta} Ae^{-ik_1 x} \\ &= Ae^{-i\delta} (e^{i\delta} e^{ik_1 x} + e^{-i\delta} e^{-ik_1 x}) \\ &= 2Ae^{-i\delta} \left[\frac{e^{i(k_1 x + \delta)} + e^{-i(k_1 x + \delta)}}{2} \right] \\ &= 2Ae^{-i\delta} \cos(k_1 x + \delta) \end{aligned} \quad \dots(12)$$

In region (II): $x > 0$

$$\begin{aligned} \psi_2 &= Ce^{-\beta x} \\ &= (1 + e^{-2i\delta}) Ae^{-\beta x} \\ &= Ae^{-i\delta} (e^{i\delta} + e^{-i\delta}) e^{-\beta x} \\ &= 2Ae^{-i\delta} \left(\frac{e^{i\delta} + e^{-i\delta}}{2} \right) e^{-\beta x} \\ \psi_2 &= (2Ae^{-i\delta} \cos \delta) e^{-\beta x} \end{aligned} \quad \dots(13)$$

This shows that the wave function in region (II) is exponentially damped.

Expressions for the probability current densities

(i) In region (I):

The probability current density S_i for the incident beam of particles is given by

$$\begin{aligned} S_i &= (Ae^{ik_1 x})(Ae^{ik_1 x})^* \frac{\hbar k_1}{m} \quad [\text{See Sec. 4.12, Eq. (13)}] \\ &= (AA^* e^{ik_1 x} e^{-ik_1 x}) \frac{\hbar k_1}{m} \\ &= \frac{\hbar k_1}{m} |A|^2 \end{aligned} \quad \dots(14)$$

The probability current density S_r for the reflected beam of particles is given by

$$\begin{aligned} S_r &= (Be^{-ik_1 x})(Be^{-ik_1 x})^* \frac{\hbar k_1}{m} \\ &= \frac{\hbar k_1}{m} |B|^2 \end{aligned} \quad \dots(15)$$

Hence the net probability current density in region (I) is given by

$$S = S_i - S_r = \frac{\hbar k_1}{m} (|A|^2 - |B|^2) \quad \dots(16)$$

Now from Eq. (9) we have

$$B = \left(\frac{k_1 - i\beta}{k_1 + i\beta} \right) A$$

The complex conjugate of this equation is

$$B^* = \left(\frac{k_1 + i\beta}{k_1 - i\beta} \right) A^*$$

$$BB^* = AA^*$$

$$|B|^2 = |A|^2$$

...(17)

Hence the net probability current in region (I) to the left of the origin O is zero.

The equation $|B|^2 = |A|^2$ shows that the intensity of the reflected wave is equal to that of the incident wave, or the number of particles per second passing normally through unit area of the incident beam is equal to the number of particles per second passing normally through unit area of the reflected beam. Consequently, the incident and reflected probability currents cancel one another.

(ii) In region (II):

From the relation $|B|^2 = |A|^2$ we infer that the probability current density in region (II) to the right of the origin should be zero. However we can prove this conclusion using the wave function

$$\psi_2 = Ce^{-\beta x}$$

and its complex conjugate

$$\psi_2^* = C^* e^{-\beta x}$$

The proof is as follows:

The probability current density in region (II) is given by [See Sec. 4.12, Eq. (10)]

$$S = -\frac{i\hbar}{2m} \left[\psi_2^* \frac{\partial \psi_2}{\partial x} - \psi_2 \frac{\partial \psi_2^*}{\partial x} \right]$$

Substituting for ψ_2^* and ψ_2 in this equation

$$\begin{aligned} S &= -\frac{i\hbar}{2m} [C^* e^{-\beta x} \cdot (-i\beta) e^{-\beta x} - Ce^{-\beta x} \cdot C^* (-\beta) e^{-\beta x}] \\ &= \frac{i\hbar}{2m} CC^* \beta [e^{-2\beta x} - e^{-2\beta x}] \\ &= 0 \end{aligned} \quad \dots(18)$$

Reflection and transmission coefficients:

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

$$\begin{aligned} R &= \frac{S_r}{S_i} = \frac{(Be^{-ik_1 x})(Be^{-ik_1 x})^* \frac{\hbar k_1}{m}}{(Ae^{ik_1 x})(Ae^{ik_1 x})^* \frac{\hbar k_1}{m}} \\ &= \frac{BB^*}{AA^*} = \frac{|B|^2}{|A|^2} \end{aligned} \quad \dots(19)$$

In this case ($V_0 > E$), $|B|^2 = |A|^2$

$$R = 1$$

This shows that the reflection of the incident beam, at the potential step is total.

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

$$T = \frac{S_t}{S_i} \quad \dots(21)$$

In this case the probability current density in region (II) is zero, i.e., $S_t = 0$. Hence $T = 0$.

Conclusions: From the foregoing discussion we draw the following inferences:

- (1) The reflection of the incident beam of particles, at the potential step is total.
- (2) There is no probability current anywhere. To the left of the potential step the incident and the reflected probability currents cancel one another, and to the right of the step it is zero.
- (3) To the right of the step the wave function is not zero, but it is exponentially damped. Therefore there is a finite probability of finding the particle in region (II).

If $V_0 \rightarrow \infty$ and E is finite, then

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

In this case the wave function in region (II) is $\psi_2 = Ce^{-\beta x} \rightarrow 0$

Since $B = \left(\frac{k_1 - i\beta}{k_1 + i\beta} \right) A$, and $C = \left(\frac{2k_1}{k_1 + i\beta} \right) A$

$$\therefore \lim_{\beta \rightarrow \infty} \frac{B}{A} = \frac{\frac{k_1}{2} - i}{\frac{k_1}{2} + i} = -1$$

or

$$\frac{B}{A} = -1 \text{ or } A + B = 0 \quad \dots(22)$$

And

$$\lim_{\beta \rightarrow -} \frac{C}{A} = \frac{2k_1}{k_1 + i\beta} = 0$$

$$C = 0 \quad \dots(23)$$

or

Hence the wave function

$$\psi_1 = Ae^{ik_1 x} + Be^{-ik_1 x}$$

at $x = 0$ is

$$\psi_1(0) = A + B = 0 \quad \dots(24)$$

And the wave function $\psi_2 = Ce^{-\beta x}$ at $x = 0$ is $\psi_2 = C = 0$ The slope of ψ_1 at $x = 0$ is

$$\left(\frac{d\psi_1}{dx} \right)_{x=0} = ik_1(A - B) = 2ik_1A \quad \dots(25)$$

Thus at a point where the potential suddenly increases from zero to an infinite value the wave function ψ_1 becomes zero and its slope suddenly falls from a finite value $2ik_1A$ to zero.

Case 2. When $E > V_0$

In region (II), $0 \leq x \leq +\infty$ (Fig. 5.2)

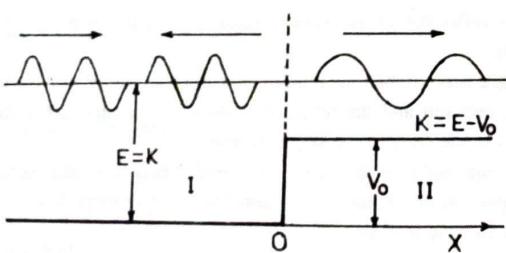


Fig. 5.2

If $E > V_0$, then the time-independent Schrödinger wave equation is

$$\frac{d^2\psi_2}{dx^2} + \frac{2m}{\hbar^2}(E - V_0)\psi_2 = 0$$

or

$$\frac{d^2\psi_2}{dx^2} + k_2^2\psi_2 = 0 \quad \dots(26)$$

where

$$k_2 = \sqrt{\frac{2m(E - V_0)}{\hbar^2}}$$

The general solution of Eq. (26) is

$$\psi_2 = Ge^{ik_2 x} + He^{-ik_2 x} \quad \dots(27)$$

In this equation the term $Ge^{ik_2 x}$ represents a wave travelling from the potential step in the positive x -direction, and the term $He^{-ik_2 x}$ a wave travelling in the negative x -direction towards the potential step. Since the particles are incident only from the left of the potential step, H must be zero. Hence in region (II) the valid solution of the wave equation is

$$\psi_2 = Ge^{ik_2 x} \quad \dots(28)$$

Expressions for the amplitudes B and G in terms of the amplitude A

From the condition that the wave function is continuous at $x = 0$, we have

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

\therefore from Eqs. (3) and (28), we have

$$A + B = G \quad \dots(29)$$

And from the condition that the derivative of the wave function is continuous at $x = 0$, we have

$$\begin{aligned} \left(\frac{d\psi_1}{dx} \right)_{x=0} &= \left(\frac{d\psi_2}{dx} \right)_{x=0} \\ Aik_1 - bik_1 &= Gik_2 \\ \therefore A - B &= \frac{k_2}{k_1}G \end{aligned} \quad \dots(30)$$

Adding Eqs. (29) and (30), we get

$$\begin{aligned} 2A &= \left(\frac{k_1 + k_2}{k_1} \right)G \\ G &= \left(\frac{2k_1}{k_1 + k_2} \right)A \end{aligned} \quad \dots(31)$$

Subtracting Eq. (30) from Eq. (29)

$$\begin{aligned} 2B &= \left(\frac{k_1 - k_2}{k_1} \right)G \\ &= \left(\frac{k_1 - k_2}{k_1} \right) \left(\frac{2k_1}{k_1 + k_2} \right)A \\ B &= \left(\frac{k_1 - k_2}{k_1 + k_2} \right)A \end{aligned} \quad \dots(32)$$

Expressions for the wave functions in regions (I) and (II)

In region (I): $x < 0$

$$\begin{aligned} \psi_1 &= Ae^{ik_1 x} + Be^{-ik_1 x} \\ &= A \left[e^{ik_1 x} + \left(\frac{k_1 - k_2}{k_1 + k_2} \right) e^{-ik_1 x} \right] \end{aligned} \quad \dots(33)$$

In region (II): $x > 0$

$$\begin{aligned}\Psi_2 &= Ge^{ik_2 x} \\ &= \left(\frac{2k_1}{k_1 + k_2} \right) Ae^{ik_2 x} \quad \dots(34)\end{aligned}$$

Expressions for the probability current densities

(i) In region (I):

The probability current density S_i for the *incident beam of particles* is given by

$$\begin{aligned}S_i &= (Ae^{ik_1 x}) (Ae^{-ik_1 x}) \cdot \frac{\hbar k_1}{m} \\ &= (AA^*) e^{ik_1 x} e^{-ik_1 x} \cdot \frac{\hbar k_1}{m} \\ &= \frac{\hbar k_1}{m} |A|^2 \quad \dots(35)\end{aligned}$$

The probability current density for the *reflected beam of particles* is given by

$$\begin{aligned}S_r &= (Be^{-ik_1 x}) (Be^{-ik_1 x}) \cdot \frac{\hbar k_1}{m} \\ &= \frac{\hbar k_1}{m} |B|^2 \quad \dots(36)\end{aligned}$$

Hence the net probability current density in the direction from left to right in region (I) is given by

$$S = S_i - S_r = \frac{\hbar k_1}{m} (|A|^2 - |B|^2)$$

From Eq. (32), we have

$$\begin{aligned}|B|^2 &= \frac{(k_1 - k_2)^2}{(k_1 + k_2)^2} |A|^2 \\ \therefore S &= \frac{\hbar k_1}{m} |A|^2 \left[1 - \frac{(k_1 - k_2)^2}{(k_1 + k_2)^2} \right] \\ &= \frac{\hbar k_1}{m} |A|^2 \left[\frac{4k_1 k_2}{(k_1 + k_2)^2} \right] \\ &= \frac{4k_1 k_2}{(k_1 + k_2)^2} \cdot \frac{\hbar k_1}{m} |A|^2 \quad \dots(37)\end{aligned}$$

(ii) In region (II):

The probability current density S_t for the *transmitted beam of particles* in region (II) is given by

$$\begin{aligned}S_t &= (Ge^{ik_2 x}) (Ge^{ik_2 x}) \cdot \frac{\hbar k_2}{m} \\ &= \frac{\hbar k_2}{m} |G|^2\end{aligned}$$

From Eq. (31), we have

$$\begin{aligned}|G|^2 &= \left(\frac{2k_1}{k_1 + k_2} \right)^2 |A|^2 = \frac{4k_1^2}{(k_1 + k_2)^2} |A|^2 \\ \therefore S_t &= \frac{\hbar k_2}{m} \cdot \frac{4k_1^2}{(k_1 + k_2)^2} |A|^2 \\ &= \frac{4k_1^2}{(k_1 + k_2)^2} \cdot \frac{\hbar k_2}{m} |A|^2 \quad \dots(38)\end{aligned}$$

Eqns. (37) and (38) show that $S = S_p$, i.e., the net probability density in the direction from left to right in region (I) is equal to the probability current density in region (II).

Reflection and transmission coefficients

The reflection coefficient R is the ratio of the probability current density for the reflected beam of particles to the probability current density for the incident beam. Thus

$$R = \frac{S_r}{S_i} = \frac{\frac{\hbar k_1}{m} \cdot |B|^2}{\frac{\hbar k_1}{m} \cdot |A|^2} = \frac{|B|^2}{|A|^2}$$

Now using Eq. (32) we get

$$R = \frac{(k_1 - k_2)^2}{(k_1 + k_2)^2} \quad \dots(39)$$

The transmission coefficient T is the ratio of the probability current density for the transmitted beam of particles to the probability current density for the incident beam. Thus

$$T = \frac{S_t}{S_i} = \frac{\frac{\hbar k_2}{m} |G|^2}{\frac{\hbar k_1}{m} |A|^2} = \frac{k_2 |G|^2}{k_1 |A|^2}$$

Now using Eq. (31), we get

$$T = \frac{k_2}{k_1} \left(\frac{2k_1}{k_1 + k_2} \right)^2 = \frac{4k_1 k_2}{(k_1 + k_2)^2} \quad \dots(40)$$

Adding Eqns. (39) and (40) it is easily verified that

$$R + T = 1 \quad \dots(41)$$

5.4 The Rectangular Potential Barrier: The Tunnel Effect

A rectangular potential barrier of height V_0 and width a for a particle is shown in Fig. 5.3. 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 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.

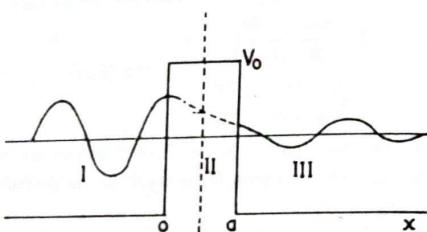


Fig. 5.3

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 (III), the energy E of a 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, the transmission probability has a small but definite value. This behaviour is called the *tunnel effect*.

Let $\psi_1(x)$, $\psi_2(x)$ and $\psi_3(x)$ be the wave functions for the motion of particle in regions (I), (II) and (III) respectively.

In region (I): $-\infty < x < 0$, the time-independent Schrödinger wave equation is

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

$$\text{or } \frac{d^2\psi_1}{dx^2} + \frac{2mE}{\hbar^2} \psi_1 = 0$$

$$\text{or } \frac{d^2\psi_1}{dx^2} + k^2\psi_1 = 0 \quad \dots(1)$$

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

Case 1. When $E < V_0$

In region (II): $0 \leq x \leq a$

If $E < V_0$, then the equation is

$$\frac{d^2\psi_2}{dx^2} + \frac{2m}{\hbar^2} (E - V_0) \psi_2 = 0$$

or

$$\frac{d^2\psi_2}{dx^2} - \frac{2m}{\hbar^2} (V_0 - E) \psi_2 = 0$$

or

$$\frac{d^2\psi_2}{dx^2} - \beta^2\psi_2 = 0 \quad \dots(2)$$

where

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

In region (III): $a \leq x < \infty$

$$\frac{d^2\psi_3}{dx^2} + \frac{2mE}{\hbar^2} \psi_3 = 0$$

or

$$\frac{d^2\psi_3}{dx^2} + k^2\psi_3 = 0 \quad \dots(3)$$

The general solutions of Eqs. (1), (2) and (3) are

$$\psi_1 = Ae^{ikx} + Be^{-ikx} \quad \dots(4)$$

$$\psi_2 = Ce^{\beta x} + De^{-\beta x} \quad \dots(5)$$

$$\psi_3 = Ge^{ikx} + He^{-ikx} \quad \dots(6)$$

Since there is no particle coming from left in the region (III), we must have $H = 0$. Therefore,

$$\psi_3 = Ge^{ikx} \quad \dots(6)$$

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

In Eq. (4) 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. (5), 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; it is an exponentially decreasing wave function. Eq. (6) represents the transmitted wave in the region (III). This wave travels in the positive x -direction.

Expression for the amplitudes A and B in terms of the amplitude G.

(i) At $x = 0$, from the condition of continuity of the wave function, we have $\psi_1(0) = \psi_2(0)$

\therefore from Eqs. (4) and (5), we get

$$A + B = C + D \quad \dots(7)$$

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

$$\begin{aligned} \left(\frac{d\psi_1}{dx} \right)_{x=0} &= \left(\frac{d\psi_2}{dx} \right)_{x=0} \\ Aik - Bik &= C\beta - D\beta \\ A - B &= \frac{\beta}{ik} (C - D) \end{aligned} \quad \dots(8)$$

∴
or

From Eqs. (7) and (8), we get

$$2A = \left(1 + \frac{\beta}{ik} \right) C + \left(1 + \frac{\beta}{ik} \right) D \quad \dots(9)$$

and

$$2B = \left(1 - \frac{\beta}{ik} \right) C + \left(1 + \frac{\beta}{ik} \right) D \quad \dots(10)$$

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

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

∴ from Eqs. (5) and (6), we get

$$Ce^{\beta a} + De^{-\beta a} = Ge^{ika} \quad \dots(11)$$

We also have

$$\begin{aligned} \left(\frac{d\psi_2}{dx} \right)_{x=a} &= \left(\frac{d\psi_3}{dx} \right)_{x=a} \\ C\beta e^{\beta a} - D\beta e^{-\beta a} &= Gi k e^{ika} \\ Ce^{\beta a} - De^{-\beta a} &= \frac{ik}{\beta} Ge^{ika} \end{aligned} \quad \dots(12)$$

∴
or

Now from Eqs. (11) and (12), we get

$$C = \frac{1}{2} \left(1 + \frac{ik}{\beta} \right) e^{-\beta a} Ge^{ika} \quad \dots(13)$$

$$D = \frac{1}{2} \left(1 - \frac{ik}{\beta} \right) e^{\beta a} Ge^{ika} \quad \dots(14)$$

Substituting the values of C and D in Eq. (9) 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:

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

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

and

Free States

we obtain

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

$$\text{or } A = \left[\cosh \beta a + \frac{i}{2} \left(\frac{\beta}{k} - \frac{k}{\beta} \right) \sinh \beta a \right] Ge^{ika} \quad \dots(15)$$

Similarly substituting the value of C and D in Eq. (10)

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

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

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

$$\text{or } B = -\frac{i}{2} \left(\frac{\beta}{k} + \frac{k}{\beta} \right) \sinh \beta a Ge^{ika} \quad \dots(16)$$

Expression for the amplitude B in terms of A

Dividing Eqs. (16) by (15), we get

$$\frac{B}{A} = \frac{-\frac{i}{2} \left(\frac{\beta}{k} + \frac{k}{\beta} \right) \sinh \beta a}{\cosh \beta - \frac{i}{2} \left(\frac{\beta}{k} - \frac{k}{\beta} \right) \sinh \beta a} \quad \dots(17)$$

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

$$\begin{aligned} R &= \frac{S_r}{S_i} = \frac{(Be^{-ika}) (Be^{-ika})^* \frac{\hbar k}{m}}{(Ae^{ika}) (Ae^{ika})^* \frac{\hbar k}{m}} \quad [\text{See Sec. 4.12, Eq. (13)}] \\ &= \frac{BB^*}{AA^*} = \left(\frac{B}{A} \right) \left(\frac{B}{A} \right)^* = \frac{|B|^2}{|A|^2} \end{aligned} \quad \dots(18)$$

where $(B/A)^*$ is the complex conjugate of B/A . From Eq. (17) the complex conjugate of B/A is

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

Hence

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

Using the trigonometrical relation

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

and simplifying the denominator, we get

$$R = \frac{\frac{1}{4} \left(\frac{\beta}{k} + \frac{k}{\beta}\right)^2 \sinh^2 \beta a}{1 + \frac{1}{4} \left(\frac{\beta}{k} + \frac{k}{\beta}\right)^2 \sinh^2 \beta a} \quad \dots(19)$$

Since

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

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

Substituting these values in Eq. (19), we get

$$\begin{aligned} R &= \frac{\frac{1}{4} \left(\sqrt{\frac{V_0 - E}{E}} + \sqrt{\frac{E}{V_0 - E}}\right)^2 \sinh^2 \beta a}{1 + \frac{1}{4} \left(\sqrt{\frac{V_0 - E}{E}} + \sqrt{\frac{E}{V_0 - E}}\right)^2 \sinh^2 \beta a} \\ &= \frac{\frac{V_0^2}{4E(V_0 - E)} \cdot \sinh^2 \beta a}{1 + \frac{V_0^2}{4E(V_0 - E)} \cdot \sinh^2 \beta a} \quad \dots(20) \end{aligned}$$

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

$$\begin{aligned} T &= \frac{S_t}{S_i} = \frac{(Ge^{ikx})(Ge^{ikx})^* \frac{\hbar k}{m}}{(Ae^{ikx})(Ae^{ikx})^* \frac{\hbar k}{m}} \quad [\text{See Sec. 4.12 Eq. (13)}] \\ &= \frac{GG^*}{AA^*} = \left(\frac{G}{A}\right) \left(\frac{G}{A}\right)^* \quad \dots(21) \end{aligned}$$

where $(G/A)^*$ is the complex conjugate of G/A .

Now from Eq. (15) we have

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

Hence

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

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

Using the trigonometrical relation
 $\cosh^2 \beta a = 1 + \sinh^2 \beta a$

and simplifying, we get

$$\frac{1}{T} = 1 + \frac{1}{4} \left(\frac{\beta}{k} + \frac{k}{\beta}\right)^2 \sinh^2 \beta a \quad \dots(22)$$

Substituting $\frac{\beta}{k} = \sqrt{\frac{V_0 - E}{E}}$, and $\frac{k}{\beta} = \sqrt{\frac{E}{V_0 - E}}$ in Eq. (22), we get

$$\frac{1}{T} = 1 + \frac{V_0^2}{4E(V_0 - E)} \sinh^2 \beta a \quad \dots(23)$$

$$\therefore T = \frac{1}{1 + \frac{V_0^2}{4E(V_0 - E)} \cdot \sinh^2 \beta a} \quad \dots(24)$$

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

From Eqns. (20) and (24) it is easily seen that
 $R + T = 1$

In this case when $E < V_0$, the expression for T leads to the following conclusions.

(1) The transmission coefficient is zero if E is zero, and it has a finite value less than 1 for an incident beam of particles having initial kinetic energy. That is, there is a finite probability for a particle to tunnel through a potential barrier of height V_0 even when its initial kinetic energy is less than V_0 .

(2) If the energy E is increased, $(V_0 - E)$ decreases and $\beta = \sqrt{\frac{2m(V_0 - E)}{\hbar^2}}$ also decreases, but $\sinh^2 \beta a$ for a fixed value of the width of the potential barrier decreases more rapidly than $(V_0 - E)$. Therefore T increases steadily with E . This increase in T with E/V_0 is shown by the part OA of the curve of T against E/V_0 (Fig. 5.4).

(3) When the particle energy E approaches V_0 , then

$$\beta a = a \sqrt{\frac{2m(V_0 - E)}{\hbar^2}} \text{ will be } \ll 1$$

then

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

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

Substituting this value in Eq. (23), we get

$$\begin{aligned} \frac{1}{T} &= 1 + \frac{V_0^2}{4E(V_0 - E)} \cdot \frac{2m(V_0 - E)a^2}{\hbar^2} \\ &= 1 + \frac{2mV_0^2 a^2}{4E\hbar^2} \\ &= 1 + \frac{mV_0^2 a^2}{2E\hbar^2} \end{aligned}$$

Hence when $E \rightarrow V_0$

$$\frac{1}{T} = 1 + \frac{mV_0 a}{2\hbar^2}$$

$$\therefore T = \frac{1}{1 + \frac{mV_0 a^2}{2\hbar^2}} \quad \dots(25)$$

Thus when E increases from a low value and approaches V_0 , the transmission coefficient increases from a low value to that given by Eq. (24) which shows that at $E \rightarrow V_0$, $T < 1$.

Case 2. When $E > V_0$

In this case the reflection and transmission coefficients are most easily obtained as follows:

We have

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

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

$$\therefore \sinh \beta a = \frac{e^{i\beta a} - e^{-i\beta a}}{2} = \frac{e^{i\alpha a} - e^{-i\alpha a}}{2} - i \left(\frac{e^{i\alpha a} - e^{-i\alpha a}}{2i} \right) = i \sin \alpha a$$

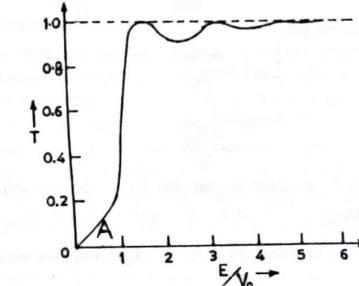


Fig. 5.4

$$\text{Hence } \sinh^2 \beta a = -\sin^2 \alpha a$$

Now substituting for $\sinh^2 \beta a$ in Eqs. (20) and (24), we get

$$R = \frac{\frac{V_0^2}{4E(E - V_0)} \cdot \sin^2 \alpha a}{1 + \frac{V_0^2}{4E(E - V_0)} \cdot \sin^2 \alpha a} \quad \dots(26)$$

$$\text{and } T = \frac{1}{1 + \frac{V_0^2}{4E(E - V_0)} \cdot \sin^2 \alpha a} \quad \dots(27)$$

From these equations, it is easily seen that
 $R + T = 1$

In this case when $E > V_0$ the expression for T leads to the following conclusions.

(1) When E approaches V_0 , then

$$\alpha a = a \sqrt{\frac{2m(E - V_0)}{\hbar^2}}, \text{ will be } \ll 1$$

$$\therefore \sin \alpha a = a \sqrt{\frac{2m(E - V_0)}{\hbar^2}}$$

and

$$\sin^2 \alpha a = \frac{2m(E - V_0)a^2}{\hbar^2}$$

Hence

$$\begin{aligned} \frac{1}{T} &= 1 + \frac{V_0^2}{4E(E - V_0)} \cdot \frac{2m(E - V_0)a^2}{\hbar^2} \\ &= 1 + \frac{2mV_0^2a^2}{4E\hbar^2} = 1 + \frac{mV_0^2a^2}{2E\hbar^2} \end{aligned}$$

Since $E \rightarrow V_0$, we get

$$\begin{aligned} \frac{1}{T} &= 1 + \frac{mV_0a^2}{2\hbar^2} \\ \therefore T &= \frac{1}{1 + \frac{mV_0a^2}{2\hbar^2}} \end{aligned}$$

This expression is the same as that obtained in the previous case ($E < V_0$).

- (2) If the energy E is increased above V_0 , $(E - V_0)$ increases and $\alpha = \sqrt{\frac{2m(E - V_0)}{\hbar^2}}$ also increases, but $(E - V_0)$ increases more rapidly than $\sin^2 \alpha a$ for a fixed value of the width of the potential barrier. Therefore T increases with E . This increase is shown by the curve beyond the point A (Fig. 5.4).

(3) For $E > V_0$, the transmission coefficient, $T = 1$ when $\alpha a = n\pi$, where $n = 1, 2, 3, \dots$.

$$\text{or, when } a = \frac{n\pi}{\alpha} = \frac{n\pi}{\sqrt{2m(E - V_0)}} = \frac{n\pi\hbar}{\sqrt{2m(E - V_0)}}$$

$$\text{or, when } a = \frac{n\hbar}{2 \times \sqrt{2m(E - V_0)}}$$

But $\frac{\hbar}{\sqrt{2m(E - V_0)}}$ is the De Broglie wavelength λ of the particle in the region of kinetic energy $(E - V_0)$. Hence $T = 1$, when

$$a = n \left(\frac{\lambda}{2} \right)$$

This shows that if the width of the barrier is an integral multiple of half wavelengths, there is perfect transmission of the incident beam of particles. Eq. (27) also shows that as E increases, T oscillates between the maximum value 1 and a value less than 1 (Fig. 5.4).

The tunnel effect provides explanations for the following phenomena:

- (1) the field emission of electrons from a cold metallic surface,
 (2) the electrical breakdown of insulators,

- (3) the reverse breakdown of semi-conductor diodes,
 (4) the switching action of a tunnel diode and
 (5) the emission of α -particles from a radio-active element.

5.5 Emission of α -particles from a Radioactive Element

On the basis of the tunnel effect we give an explanation of the emission of α -particles from a radioactive element.

Potential Energy Curve

Elements with atomic number $Z \geq 81$ are usually unstable, and consequently undergo spontaneous disintegration with the emission of α -particles, β -particles and γ -rays. (An α -particle consists of two neutrons and two protons and hence it is the nucleus of the helium atom). This phenomenon is called natural radio-activity. There is a narrow range of kinetic energies of α -particles emitted by radioactive elements. An α -particle emitted by thorium, $_{90}\text{Th}^{232}$, has lowest energy (4.007 MeV) and that emitted by thorium C , $_{84}\text{Po}^{212}$ has highest energy (8.95 MeV). Since an α -particle carries a positive charge $2e$, when it has been emitted from a nucleus of atomic number Z , its potential energy, at a large distance from the residual nucleus of atomic number $Z - 2$ is given by

$$V(r) = \frac{(Z-2)e}{4\pi\epsilon_0 r} (2e) = \frac{2(Z-2)e^2}{4\pi\epsilon_0 r}$$

where r is the distance of the α -particle from the centre of the nucleus. If the distance r is decreased, the potential energy increases till it becomes maximum equal to V_0 at a position $r = r_0$ just outside the nucleus. The maximum potential energy is equal to the work which must be done against the repulsive electro-

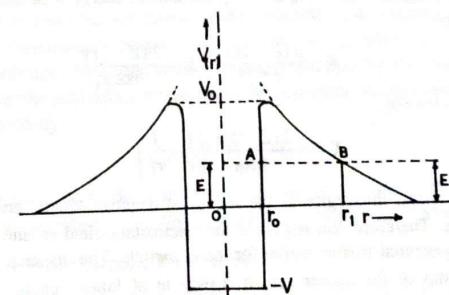


Fig. 5.5

static force to move the α -particle from $r = \infty$ to $r = r_0$. When it is inside the nucleus, it is acted upon by short range and extremely powerful attractive forces due to the nucleus. These forces are effective over a short distance r_0 from the centre of the nucleus. This distance is called, the *effective radius of the nucleus*. Due to the attractive forces the potential energy of the α -particle inside the nucleus is negative. Therefore, the graph of the potential energy $V(r)$ of an α -particle against its distance r from the centre of the nucleus is in the form of a potential well as shown in Fig. 5.5. The maximum positive potential energy of an α -particle just outside the nucleus is given by

$$V_0 = \frac{2(Z-2)e^2}{4\pi\epsilon_0 r_0}$$

For ${}_{84}\text{Po}^{210}$ which emits an α -particle with kinetic energy 5.3 MeV, if we substitute

$$Z = 84, e = 1.6 \times 10^{-19} \text{ coul}, \quad \epsilon_0 = 8.85 \times 10^{-12} \text{ coul}^2/\text{Nm}^2 \quad \text{and} \\ r_0 = 1.5 \times 10^{-15} \text{ A}^{\frac{1}{3}} = 1.5 \times 10^{-15} \times 210^{\frac{1}{3}} \text{ m}$$

we get, $V_0 = 27 \text{ MeV}$. This value is much greater than the maximum observed kinetic energy.

Failure of Classical Mechanics to explain the Emission of α -Particles

When an α -particle is emitted from a radio-active nucleus with kinetic energy E , this energy must be equal to the total energy (kinetic plus potential) of the α -particle before ejection. This energy is shown by the dashed line AB in Fig. 5.5. The energy E is equal to the potential energy of the α -particle at $r = r_1$.

$$E = \frac{2(Z-2)e^2}{4\pi\epsilon_0 r_1}$$

In the region from $r = r_0$ to $r = r_1$, the kinetic energy K of the α -particle is given by

$$K + \frac{2(Z-2)e^2}{4\pi\epsilon_0 r} = E = \frac{2(Z-2)e^2}{4\pi\epsilon_0 r_1}$$

where $r_0 < r < r_1$

$$\therefore K = -\frac{2(Z-2)e^2}{4\pi\epsilon_0} \left(\frac{1}{r} - \frac{1}{r_1} \right)$$

Since $r < r_1$, this region is the region of negative kinetic energy for the α -particle. Therefore, this region of the electrostatic field around the nucleus is called potential barrier region for the α -particle. The distance $AB = r_1 - r_0$ is the width of the barrier for an α -particle of kinetic energy E , and the maximum positive potential energy V_0 of the α -particle just outside the nucleus is the height of the potential barrier. Since for an α -particle E is much less than

V_0 , according to the laws of classical mechanics, if an α -particle is originally inside the nucleus it can never come out.

Quantum-mechanical Explanation of the Emission of α -Particles

In quantum mechanics, it is assumed that an α -particle in the nucleus is in constant to and fro motion. The motion is confined to the region surrounded by the potential barrier. Therefore, it is associated with a standing wave. The wave is propagated through the potential barrier and it emerges from the barrier as a progressive wave with a small amplitude.

The wave function $\psi(r)$ of an α -particle in the three regions is shown qualitatively in Fig. 5.6. In the nucleus, the wave function has an oscillating character, in the barrier-region the wave function is exponentially attenuated, and outside the barrier region the wave function has again an oscillating character with a small amplitude. Since $|\psi(r)|^2$ gives the probability of finding a particle at distance r , we conclude that there is a finite probability of transmission of an α -particle through the potential barrier.

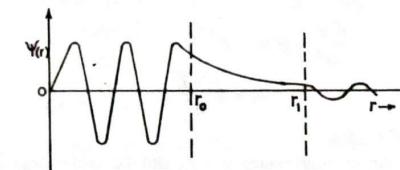


Fig. 5.6

The quantum-mechanical theory of the emission of α -particles was first given by G. Gamow, and independently by R.W. Gurney and E.U. Condon in 1928. According to the theory, an approximate expression for the transmission coefficient or the probability of passage of an α -particle through the potential barrier is given by

$$T = e^{-2/\hbar} \int_{r_0}^{r_1} \sqrt{2m(V-E)} dr$$

where m is the mass of the α -particle, V is its potential energy at distance r from the nucleus when $r > r_0$, and $(r_1 - r_0)$ is the width of the barrier.

5.6 Square Well Potential, Free States

One dimensional square well potential of depth V_0 between $x = 0$ and $x = a$ is shown in Fig. 5.7. It means that potential energy of a particle in the region $0 \leq x \leq a$ is $-V_0$. Suppose a uniform beam of particles each of mass m and

having total positive energy E is travelling from left to right parallel to the positive direction of the x -axis. Now we consider the following regions.

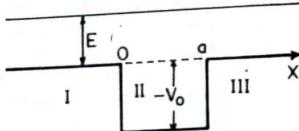


Fig. 5.7

Region (I): $-\infty \leq x \leq 0$

In this region the potential energy is zero and the total energy is E . Therefore, the time-independent Schrödinger wave equation for a particle is

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

or $\frac{d^2\psi_1}{dx^2} + \frac{2mE}{\hbar^2} \psi_1 = 0$

or $\frac{d^2\psi_1}{dx^2} + k_1^2 \psi_1 = 0 \quad \dots(1)$

where $k_1 = \sqrt{\frac{2mE}{\hbar^2}}$

Region (II): $0 \leq x \leq a$

In this region the potential energy is $-V_0$, and the total energy is the same as E . Therefore, the wave equation is

$$-\frac{\hbar^2}{2m} \cdot \frac{d^2\psi_2}{dx^2} - V_0 \psi_2 = E\psi_2$$

or $\frac{d^2\psi_2}{dx^2} + k_2^2 \psi_2 = 0 \quad \dots(2)$

where $k_2 = \sqrt{\frac{2m(E + V_0)}{\hbar^2}}$

Region (III): $a \leq x < +\infty$

In this region the potential energy is zero, and the total energy is the same as E . Therefore, the wave equation is

$$\frac{d^2\psi_3}{dx^2} + k_1^2 \psi_3 = 0 \quad \dots(3)$$

The general solutions of Eqs. (1), (2) and (3) are

$$\psi_1 = Ae^{ik_1 x} + Be^{-ik_1 x} \quad \dots(4)$$

$$\psi_2 = Ce^{ik_2 x} + De^{-ik_2 x} \quad \dots(5)$$

$$\psi_3 = Ge^{ik_1 x} + He^{-ik_1 x} \quad \dots(6)$$

Since the beam of particles is travelling from left to right and no particle from right to left in region (III), we must have $H = 0$.

$$\psi_3 = Ge^{ik_1 x} \quad \dots(7)$$

From the condition that the wave function, and its derivative with respect to x must be continuous at the boundaries $x = 0$ and $x = a$, we have

(i) at $x = 0$

$$\psi_1(0) = \psi_2(0) \\ A + B = C + D \quad \dots(8)$$

and

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

$$ik_1(A - B) = ik_2(C - D)$$

or

$$A - B = \frac{k_2}{k_1} (C - D) \quad \dots(9)$$

(ii) at $x = a$

$$\psi_2(a) = \psi_3(a) \\ Ce^{ik_2 a} + De^{-ik_2 a} = Ge^{ik_1 a} \quad \dots(10)$$

and

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

$$Ce^{ik_2 a} - De^{-ik_2 a} = \frac{k_1}{k_2} Ge^{ik_1 a} \quad \dots(11)$$

From these four equations we now derive an expression for the transmission coefficient T .

Adding Eqs. (8) and (9)

$$2A = \left(1 + \frac{k_2}{k_1} \right) C + \left(1 - \frac{k_2}{k_1} \right) D \quad \dots(12)$$

Now adding Eqs. (10) and (11), and then dividing both the sides by $2e^{ik_2 a}$, we get

$$C = \frac{1}{2} \left(1 + \frac{k_1}{k_2} \right) Ge^{i(k_1 - k_2)a} \quad \dots(13)$$

Subtracting Eq. (11) from Eq. (10), and then dividing both the sides by $2e^{-ik_2 a}$, we get

$$D = \frac{1}{2} \left(1 - \frac{k_1}{k_2} \right) Ge^{i(k_1 + k_2)a} \quad \dots(14)$$

Now substituting these values of C and D in Eq. (12), we get

$$2A = \left[\left(1 + \frac{k_2}{k_1} \right) \cdot \frac{1}{2} \left(1 + \frac{k_1}{k_2} \right) e^{-ik_2 a} + \left(1 - \frac{k_2}{k_1} \right) \cdot \frac{1}{2} \left(1 - \frac{k_1}{k_2} \right) e^{ik_2 a} \right] Ge^{ik_1 a}$$

$$\begin{aligned}
 &= \left[\frac{1}{2} \left\{ 2 + \left(\frac{k_1}{k_2} + \frac{k_2}{k_1} \right) \right\} e^{-ik_2 a} \right. \\
 &\quad \left. + \frac{1}{2} \left\{ 2 - \left(\frac{k_1}{k_2} + \frac{k_2}{k_1} \right) \right\} e^{ik_2 a} \right] G e^{ik_1 a} \\
 &= \left[e^{ik_2 a} + e^{-ik_2 a} - \frac{1}{2} \left(\frac{k_1}{k_2} + \frac{k_2}{k_1} \right) (e^{ik_2 a} - e^{-ik_2 a}) \right] G e^{ik_1 a} \\
 A &= \left[\frac{e^{ik_2 a} + e^{-ik_2 a}}{2} - \frac{i}{2} \left(\frac{k_1}{k_2} + \frac{k_2}{k_1} \right) \left(\frac{e^{ik_2 a} - e^{-ik_2 a}}{2i} \right) \right] G e^{ik_1 a} \\
 A &= \left[\cos k_2 a - \frac{i}{2} \left(\frac{k_1}{k_2} + \frac{k_2}{k_1} \right) \sin k_2 a \right] G e^{ik_1 a} \\
 \text{or } \frac{A}{G} &= \left[\cos k_2 a - \frac{i}{2} \left(\frac{k_1}{k_2} + \frac{k_2}{k_1} \right) \sin k_2 a \right] e^{ik_1 a} \quad \dots(15)
 \end{aligned}$$

∴ the complex conjugate of A/G is

$$\left(\frac{A}{G} \right)^* = \left[\cos k_2 a + \frac{i}{2} \left(\frac{k_1}{k_2} + \frac{k_2}{k_1} \right) \sin k_2 a \right] e^{-ik_1 a} \quad \dots(16)$$

Now the transmission coefficient T is given by

$$T = \frac{GG^*}{AA^*} = \left(\frac{G}{A} \right) \left(\frac{G}{A} \right)^*$$

From Eqs. (15) and (16)

$$\begin{aligned}
 \left(\frac{A}{G} \right) \left(\frac{A}{G} \right)^* &= \cos^2 k_2 a + \frac{1}{4} \left(\frac{k_1}{k_2} + \frac{k_2}{k_1} \right)^2 \sin^2 k_2 a \\
 \text{or } \frac{1}{T} &= 1 - \sin^2 k_2 a + \frac{1}{4} \left(\frac{k_1}{k_2} + \frac{k_2}{k_1} \right)^2 \sin^2 k_2 a \\
 &= 1 + \frac{1}{4} \left[\left(\frac{k_1}{k_2} + \frac{k_2}{k_1} \right)^2 - 4 \right] \sin^2 k_2 a \\
 &= 1 + \frac{1}{4} \left(\frac{k_1}{k_2} - \frac{k_2}{k_1} \right)^2 \sin^2 k_2 a \quad \dots(17)
 \end{aligned}$$

Since $k_1 = \sqrt{\frac{2mE}{\hbar^2}}$, and $k_2 = \sqrt{\frac{2m(E + V_0)}{\hbar^2}}$

$$\therefore \frac{k_1}{k_2} = \sqrt{\frac{E}{E + V_0}}, \text{ and } \frac{k_2}{k_1} = \sqrt{\frac{E + V_0}{E}}$$

Substituting these expressions in Eq. (17), we get

$$\begin{aligned}
 \frac{1}{T} &= 1 + \frac{V_0^2}{4E(E + V_0)} \sin^2 \frac{a\sqrt{2m(E + V_0)}}{\hbar} \\
 T &= \frac{1}{1 + \frac{V_0^2}{4E(E + V_0)} \cdot \sin^2 \frac{a\sqrt{2m(E + V_0)}}{\hbar}} \quad \dots(18)
 \end{aligned}$$

This equation shows that in general $T < 1$, and $T = 1$
when $\frac{a\sqrt{2m(E + V_0)}}{\hbar} = n\pi$, where $n = 1, 2, 3, \dots$

Thus as E is increased T oscillates between the maximum value 1 and a value less than 1. The energy values of the particle for $T = 1$ are given by

$$\frac{a\sqrt{2m(E + V_0)}}{\hbar} = n\pi$$

Simplifying this equation, we get

$$E = \frac{n^2\pi^2\hbar^2}{2ma^2} - V_0 \quad \dots(19)$$

On the basis of this result a qualitative explanation of Ramsauer effect discovered in 1921 can be given.

SOLVED EXAMPLES

Example 5.1. Derive an approximate expression for the transmission coefficient for a rectangular potential barrier for which $\frac{a}{\hbar} \sqrt{2m(V_0 - E)} > 1$.

(Ans. The transmission coefficient in the case $E < V_0$ is given by)

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

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

When $\beta a > 1$, $e^{\beta a}$ is large but $e^{-\beta a}$ is very small. Therefore, $e^{-\beta a}$ in the expression for $\sinh \beta a$ can be neglected compared to $e^{\beta a}$.

$$\text{Hence } \sinh^2 \beta a = \left(\frac{e^{\beta a} - e^{-\beta a}}{2} \right)^2 = \frac{1}{4} e^{2\beta a}$$

Substituting this value in Eq. (1) and neglecting 1 compared to the second term, we get

$$\frac{1}{T} = \frac{V_0^2}{4E(V_0 - E)} \frac{1}{4} e^{2\beta a}$$

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

$$= \frac{16E}{V_0} \left(1 - \frac{E}{V_0} \right) e^{-2\beta a} \quad \dots(2)$$

$$= \frac{16E}{V_0} \left(1 - \frac{E}{V_0} \right) e^{-2/\hbar \sqrt{2m(V_0 - E)} a} \quad \dots(3)$$

Example 5.2. Find the height of the potential barrier for α -particles emitted from Radon (${}_{86}\text{R}_n^{222}$) assuming that the effective nuclear radius is given by

$$r_0 = 1.5 \times 10^{-15} \text{ A}^{1/3} \text{ m}$$

Solution:

$$\begin{aligned} V_0 &= \frac{2(Z-2)e^2}{4\pi\epsilon_0 r_0} \\ &= \frac{2(86-2)(1.6 \times 10^{-19})^2}{4\pi \times 8.85 \times 10^{-12} \times 1.5 \times 10^{-15} \times (222)^{1/3}} \text{ J} \\ &= \frac{2 \times 84 \times 1.6^2 \times 10^{-11}}{4\pi \times 8.85 \times 1.5 \times 6.055} = \frac{430.08 \times 10^{-11}}{1009.57} \\ &= 0.426 \times 10^{-11} \text{ J} \end{aligned}$$

Now because

$$\begin{aligned} 1 \text{ MeV} &= 1.6 \times 10^{-12} \text{ J} \\ V_0 &= \frac{0.426 \times 10^{-11}}{1.6 \times 10^{-13}} = \frac{42.6}{1.6} = 26.62 \text{ MeV.} \end{aligned}$$

Example 5.3. Find the width of the potential barrier for an α -particle emitted with kinetic energy 5.5 MeV from ${}_{86}\text{R}_n^{222}$

Solution:

The width of the potential barrier due to the nucleus is given by

$$a = r_1 - r_0$$

where r_0 is the effective nuclear radius, and r_1 is the distance from the centre of the nucleus, at which the potential energy of the α -particle is equal to the kinetic energy of the emitted α -particle.

$$\text{Now } r_0 = 1.5 \times 10^{-15} \text{ A}^{1/3}$$

$$= 1.5 \times 10^{-15} \times 222^{1/3} = 1.5 \times 10^{-15} \times 6.055$$

$$= 9.08 \times 10^{-15} \text{ m}$$

and r_1 is given by

$$E = \frac{2(Z-2)e^2}{4\pi\epsilon_0 r_1}$$

$$\text{or } r_1 = \frac{2(Z-2)e^2}{4\pi\epsilon_0 E}$$

$$= \frac{2 \times (86-2) \times (1.6 \times 10^{-19})^2}{4\pi \times 8.85 \times 10^{-12} \times 5.5 \times 1.6 \times 10^{-13}}$$

$$= \frac{2 \times 84 \times 1.6^2 \times 10^{-13}}{4\pi \times 8.85 \times 5.5 \times 1.6}$$

$$= 0.4397 \times 10^{-13} \text{ m}$$

$$= 43.97 \times 10^{-15} \text{ m}$$

$$\therefore a = r_1 - r_0 \\ = 43.97 \times 10^{-15} - 9.08 \times 10^{-15} \\ = 34.89 \times 10^{-15} \text{ m}$$

Example 5.4. A stream of electrons, each of energy $E = 3 \text{ eV}$ is incident on a potential barrier of height $V_0 = 4 \text{ eV}$. The width of the barrier is 20 \AA . Calculate the percentage transmission of the beam through this barrier.

Solution:

$$\text{We have } E = 3 \text{ eV} = 3 \times 1.6 \times 10^{-19} \text{ J}$$

$$V_0 = 4 \text{ eV} = 4 \times 1.6 \times 10^{-19} \text{ J}$$

$$a = 20 \text{ \AA} = 20 \times 10^{-10} = 2 \times 10^{-9} \text{ m}$$

The coefficient of transmission is given by

$$T = \frac{16E}{V_0} \left(1 - \frac{E}{V_0} \right) e^{-2\beta a}$$

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

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

$$\begin{aligned}
 &= \frac{2 \times 2 \times 10^{-9}}{1.054 \times 10^{-34}} \sqrt{2 \times 9.11 \times 10^{-31} \times 1.6 \times 10^{-19}} \\
 &= \frac{2 \times 2}{1.054} \sqrt{2 \times 9.11 \times 1.6} \\
 &= \frac{4 \times 5.4}{1.054} = 20.49 \\
 T &= \frac{16 E}{V_0} \left(1 - \frac{E}{V_0}\right) e^{-2\beta a} \\
 &= \frac{16 \times 3}{4} \left(1 - \frac{3}{4}\right) \frac{1}{2.718^{20.49}} \\
 &= \frac{3}{7.9 \times 10^8} = \frac{30}{7.9} \times 10^{-9} = 3.797 \times 10^{-9}
 \end{aligned}$$

\therefore percentage transmission = $3.797 \times 10^{-7}\%$

Example 5.5. An α -particle having energy 10 MeV approaches a potential barrier of height equal to 30 MeV. Determine the width of the potential barrier if the transmission coefficient is 2×10^{-3} . Given that: mass of a α -particle = $4 \times 1.67 \times 10^{-27}$ kg.
 $\hbar = 1.054 \times 10^{-34}$ J Sec.

Solution:

$$T = \frac{16 E}{V_0} \left(1 - \frac{E}{V_0}\right) e^{-2\beta a} \quad \dots(1)$$

or

$$e^{2\beta a} = \frac{16 E}{TV_0} \left(1 - \frac{E}{V_0}\right)$$

$$\begin{aligned}
 2\beta a &= 2.303 \log_{10} \frac{16 E}{TV_0} \left(1 - \frac{E}{V_0}\right) \\
 a &= \frac{1}{2\beta} \times 2.303 \log_{10} \frac{16 E}{TV_0} \left(1 - \frac{E}{V_0}\right) \quad \dots(2)
 \end{aligned}$$

Now

$$\begin{aligned}
 \beta &= \frac{1}{\hbar} \sqrt{2m(V_0 - E)} \\
 &= \frac{1}{1.054 \times 10^{-34}} \sqrt{2 \times 4 \times 1.67 \times 10^{-27} \times (30 - 10) \times 10^6 \times 1.6 \times 10^{-19}} \\
 &= \frac{10^{14}}{1.054} \sqrt{2 \times 4 \times 1.67 \times 20 \times 1.6} = \frac{20.68 \times 10^{14}}{1.054} = 19.62 \times 10^{14}
 \end{aligned}$$

Hence

$$\begin{aligned}
 a &= \frac{10^{-14}}{2 \times 19.62} \times 2.303 \log_{10} \frac{16 \times 10}{2 \times 10^{-3} \times 30} \left(1 - \frac{10}{30}\right) \\
 &= \frac{10^{-14}}{2 \times 19.62} \times 2.303 \log_{10} \frac{16}{9} \times 10^3 = \frac{10^{-14} \times 2.303 \times 3.25}{39.24} \\
 &= 1.91 \times 10^{-15} \text{ m}
 \end{aligned}$$

QUESTIONS AND PROBLEMS

1. (a) A beam of electrons, each of energy E , is incident on a rectangular potential barrier of width a and height V_0 , where $V_0 > E$. Obtain an expression for the transmission-coefficient through the barrier.
 (b) Explain the phenomenon of α -decay of a radio-active nucleus.
2. A beam of particles each of mass m and energy E , moving in a region of zero potential energy, approaches a rectangular potential barrier of width a and height V_0 , where $V_0 > E$.

If $\beta a > 1$, where $\beta = \sqrt{\frac{2m(V_0 - E)}{\hbar^2}}$, prove that the transmission-coefficient is given by

$$T = \frac{16 E}{V_0} \left(1 - \frac{E}{V_0}\right) e^{-2\beta a}$$

3. Find the reflection and transmission coefficients for a rectangular barrier of width a and height V_0 for the case where $E > V_0$. Show that the transmission-coefficient is 1 for certain value of the energy, given by

$$E = \frac{n^2 \pi^2 \hbar^2}{2ma^2} + V_0, \text{ where } n = 1, 2, 3, \dots$$

5. Explain the problem of the leaking of a particle through a rectangular potential barrier of finite width and explain theory of α -particle decay.
6. Show that the reflection coefficient R for a step barrier for the case $E > V_0$ is given by

$$R = \left[\frac{1 - \sqrt{1 - V_0/E}}{1 + \sqrt{1 - V_0/E}} \right]^2$$

6

Bound States

6.1. Introduction

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 Schrödinger 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. Later in this chapter we will consider the motion of a particle in three-dimensional box and the motion of the harmonic oscillator.

6.2 Particle in a One-Dimensional Box

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 walls (Fig. 6.1). Let a be the distance between the walls so that the motion along the x -axis is confined between $x = 0$ and $x = a$.

Suppose inside the box, i.e., in the region

$$0 < x < a$$

there is no force acting on the particle so that in this region the potential energy $V(x)$ is zero. When the particle collides with the perfectly rigid walls, there is no loss of energy so that the total energy E of the particle remains constant. In order to leave the region, the particle will have to do an infinite amount of work. Since this is not possible, it cannot exist outside the box. Hence for $x \leq 0$ and $x \geq a$

the wave-function $\psi(x) = 0$.

Bound States

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The potential energy curve for the particle is shown in Fig. 6.2; because of its appearance it is called a *square well potential of infinite depth*.

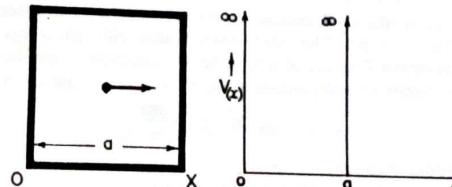


Fig. 6.1

Fig. 6.2

Wave Equation for the Particle

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

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

where E is the total energy of the particle,

$$\text{or } \frac{d^2\psi}{dx^2} + \frac{2mE}{\hbar^2} \psi = 0 \quad \dots(1)$$

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

$$\text{where, } k = \sqrt{\frac{2mE}{\hbar^2}} \quad \dots(3)$$

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

Solution of the Equation

The general solution of Eq. (2) is

$$\psi(x) = A \sin kx + B \cos kx \quad \dots(4)$$

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. (4) we have

$$\psi(x) = A \sin kx \quad \dots(5)$$

Now using the second condition, we have

$$\psi(a) = A \sin ka = 0 \quad \dots(6)$$

We cannot take $A = 0$, because there will then be no solution. Hence Eq. (6) is satisfied only when

or

$$ka = n\pi \quad k = \frac{n\pi}{a} \quad \dots(7)$$

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

We cannot take $n = 0$, because for $n = 0, k = 0, E = 0$ and hence $\psi(x) = 0$. This means that a particle with zero energy cannot be 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 the motion in the region $0 < x < a$ are given by

$$\psi_n(x) = A \sin \frac{n\pi x}{a} \quad \dots(8)$$

Eigen Values of Energy

Substituting the value of k in Eq. (7), we get

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

From this equation we get

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

or

$$E_n = \frac{n^2\pi^2\hbar^2}{2ma^2} \quad \dots(9)$$

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 $\hbar = \frac{h}{2\pi}$, we also have

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

From Eq. (9), we get the following conclusions:

(1) The lowest energy of the particle is obtained by putting $n = 1$ in Eq. (9) and it is

$$E_1 = \frac{\pi^2\hbar^2}{2ma^2} \quad \dots(10)$$

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

$$E_n = n^2E_1 \quad \dots(11)$$

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

(3) 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. 6.3 shows the energy-level diagram for the particle.

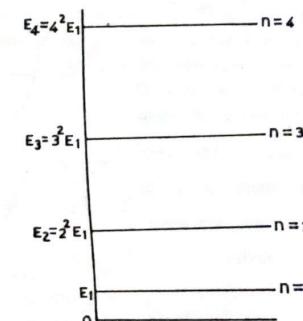


Fig. 6.3

Normalization of the Wave-Functions

The wave-functions for the motion of the particle are

$$\psi_n(x) = A \sin \frac{n\pi x}{a}, \quad \dots(8)$$

in the region $0 < x < a$

and $\psi_n(x) = 0$, in the region $x < 0; x > a$.

The total probability that the particle is somewhere in the box must be unity. Therefore, we have

$$\int_0^a |\psi_n(x)|^2 dx = 1 \quad \dots(12)$$

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

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

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

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

$$\frac{A^2 a}{2} = 1 \quad \dots(13)$$

or

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

Hence the normalized wave function is

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

The wave-functions for the first three values of n are shown in Fig. 6.4. 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 $x = 0$, $x = \frac{a}{2}$ 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.

Orthogonality of the Wave-Functions

Let $\psi_n(x)$ and $\psi_m(x)$ be the normalized wave-functions of the particle in the interval $(0, a)$ corresponding to the different energy-levels E_n and E_m respectively. These wave-functions are

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

$$\psi_m(x) = \sqrt{\frac{2}{a}} \sin \frac{m\pi x}{a}$$

where m and n are integers.

In this case the functions are real, therefore

$$\psi_n^*(x) = \psi_n(x),$$

and

$$\psi_m^*(x) = \psi_m(x)$$

Now we have, when $m \neq n$

$$\begin{aligned} \int_0^a \psi_m^* \psi_n dx &= \frac{2}{a} \int_0^a \sin \frac{m\pi x}{a} \sin \frac{n\pi x}{a} dx \\ &= \frac{1}{a} \int_0^a \left[\cos \frac{(m-n)\pi x}{a} - \cos \frac{(m+n)\pi x}{a} \right] dx \\ &= \frac{1}{2a} \left[\frac{a}{\pi(m-n)} \sin \frac{(m-n)\pi x}{a} - \frac{a}{\pi(m+n)} \sin \frac{(m+n)\pi x}{a} \right]_0^a = 0 \end{aligned}$$

\therefore both the terms are zero at $x = 0$, and at $x = a$.

Hence, the functions are mutually orthogonal in the interval $(0, a)$. These functions are also normalized in this interval. The wave-functions which, are

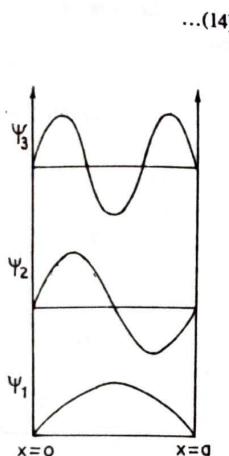


Fig. 6.4

normalized and mutually orthogonal in an interval, are said to form an orthogonal set in this interval. Since the wave-functions are zero outside the interval $(0, a)$, they are also orthogonal in the whole range of x , i.e., in the interval $(-\infty, \infty)$.

Eigen-values of the momentum: The eigen values of the momentum p_n along the x -axis are given by

$$\begin{aligned} p_n^2 &= 2mE_n \\ &= 2m \frac{n^2\pi^2\hbar^2}{2ma^2} \\ &= \frac{n^2\pi^2\hbar^2}{a^2} \end{aligned}$$

$$\therefore p_n = \pm \frac{n\pi\hbar}{a} \quad \dots(15)$$

$$\text{or} \quad p_n = \pm \frac{n\hbar}{2a} \quad \dots(16)$$

The \pm sign shows that the particle is moving back and forth in the potential box.

Eq. (15) shows that the eigen-values of the momentum of the particle are discrete, and the difference between the momenta corresponding to two consecutive energy-levels is constant equal to $\frac{\hbar}{2a}$.

Probability of Location of the Particle over a Small Range Between x and $x + dx$

According to quantum mechanics, the probability $P(x) dx$ that the particle be found over a small distance dx at the position x is given by

$$\begin{aligned} P(x) dx &= \left| \psi_n(x) \right|^2 dx \\ &= \frac{2}{a} \sin^2 \frac{n\pi x}{a} dx \end{aligned} \quad \dots(17)$$

so that the probability-density for the one dimensional motion is

$$P(x) = \frac{2}{a} \sin^2 \frac{n\pi x}{a} \quad \dots(18)$$

The probability-density is maximum when

$$\frac{n\pi x}{a} = \frac{\pi}{2}, \frac{3\pi}{2}, \frac{5\pi}{2},$$

$$\text{or} \quad x = \frac{a}{2n}, \frac{3a}{2n}, \frac{5a}{2n} \quad \dots(19)$$

Thus for the state defined by $n = 1$, the most probable position of the particle is at $x = \frac{a}{2}$. For $n = 2$, the most probable positions are at

$$x = \frac{a}{4} \text{ and } x = \frac{3a}{4}$$

For $n = 3$, the most probable positions are at

$$x = \frac{a}{6}, x = \frac{3a}{6}, x = \frac{5a}{6}$$

The variation of the probability densities with x for first three values of n are shown in Fig. 6.5.

Thus the quantum mechanical result is quite different from the classical one. According to classical mechanics, a particle in such a potential box would travel with a uniform velocity from one wall to the other, and at the walls it would be perfectly reflected. Therefore, the probability of finding the particle within a small distance dx anywhere in

the box is the same and is equal to $\frac{dx}{a}$. The probability-density $\frac{1}{a}$ is represented by a straight line at height $\frac{1}{a}$ above the x -axis as shown in Fig. 6.5.

6.3 Particle in a Rectangular Three-Dimensional Box

Let a particle of mass m be in motion in a rectangular potential box (Fig. 6.6) with sides of lengths a, b, c , parallel to the x, y and z -axes respectively. Suppose there is no force acting on the particle inside the box, so that in the region

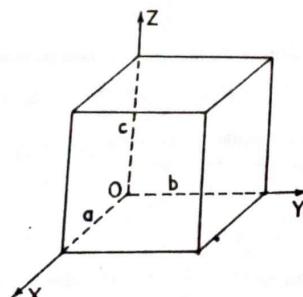


Fig. 6.6

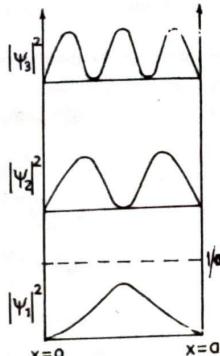


Fig. 6.5

$$\begin{aligned} 0 < x < a \\ 0 < y < b \\ 0 < z < c \end{aligned}$$

the potential energy $V(x, y, z) = 0$ and outside the box $V(x, y, z) = \infty$

Wave Equation for the Particle

For the motion of the particle inside the box, the Schrödinger time-independent wave equation is

$$-\frac{\hbar^2}{2m} \nabla^2 \psi = E\psi \quad \dots(1)$$

$$\text{or } \frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{2mE}{\hbar^2} E\psi = 0 \quad \dots(2)$$

We assume that the wave-function $\psi(x, y, z)$ is equal to the product of three functions X, Y and Z each of which is a function of one variable only.

Thus we have

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

Substituting this equation in Eq. (2), we get

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

We have used ordinary derivatives instead of partial derivatives because each of the functions X, Y and Z is a function of one variable only.

Dividing Eq. (4) by XYZ , we get

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

In this equation $2mE/\hbar^2$ is a constant for a particular value of the kinetic energy. Since the velocity of the particle, being a vector quantity, can be resolved into three components along the coordinate axes, the kinetic energy E can be expressed as the sum of the corresponding terms E_x, E_y and E_z .

Hence

$$E = E_x + E_y + E_z \quad \dots(6)$$

Therefore, from Eqs. (5) and (6), we get

$$\left[\frac{1}{X} \frac{d^2X}{dx^2} + \frac{2mE_x}{\hbar^2} \right] + \left[\frac{1}{Y} \frac{d^2Y}{dy^2} + \frac{2mE_y}{\hbar^2} \right] + \left[\frac{1}{Z} \frac{d^2Z}{dz^2} + \frac{2mE_z}{\hbar^2} \right] = 0$$

This equation gives three independent equations:

$$\frac{d^2X}{dx^2} + \frac{2mE_x}{\hbar^2} X = 0 \quad \dots(7)$$

$$\frac{d^2Y}{dy^2} + \frac{2mE_y}{\hbar^2} Y = 0 \quad \dots(8)$$

$$\frac{d^2Z}{dz^2} + \frac{2mE_z}{\hbar^2} Z = 0 \quad \dots(9)$$

Eq. (7) is the equation for the one-dimensional case discussed in Section 6.2. The boundary condition applicable to the solution is

$$X(0) = X(a) = 0$$

So the eigen values of E_x are given by

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

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

and the corresponding normalized eigen functions are given by

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

The solution for Y and Z are of the same form, therefore, we have

$$E_y = \frac{\pi^2 \hbar^2}{2mb^2} n_y^2 \quad \dots(12)$$

$$Y(y) = \sqrt{\frac{2}{b}} \sin \frac{n_y \pi y}{b} \quad \dots(13)$$

and

$$E_z = \frac{\pi^2 \hbar^2}{2mc^2} n_z^2 \quad \dots(14)$$

$$Z(z) = \sqrt{\frac{2}{c}} \sin \frac{n_z \pi z}{c} \quad \dots(15)$$

Eigen Values of Energy

Substituting the expressions for E_x , E_y and E_z in Eq. (6), we get

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

where,

$$n_x = 1, 2, 3, \dots$$

$$n_y = 1, 2, 3, \dots$$

$$n_z = 1, 2, 3, \dots$$

This equation gives the eigen values of the energy of the particle. These values are called the energy-levels of the particle.

Wave-Functions

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

$$\begin{aligned} \Psi_{n_x, n_y, n_z}(x, y, z) &= X(x) Y(y) Z(z) \\ &= \sqrt{\frac{8}{abc}} \sin \frac{n_x \pi x}{a} \cdot \sin \frac{n_y \pi y}{b} \cdot \sin \frac{n_z \pi z}{c} \end{aligned} \quad \dots(17)$$

where n_x , n_y and n_z are integers.

The wave-functions are zero outside the box. It may easily be proved that the wave-function is normalized, because

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

From Eqs. (17) and (16) we get the following conclusions:

(1) Three integers n_x , n_y , and n_z , which are called *quantum numbers*, are required to describe each stationary state. If we change the sign of the quantum numbers, there is no change in the energy and in the wave-function except that the minus sign will appear on the right hand side of Eq. (17). Therefore, all the stationary states are given by the positive integral values of n_x , n_y and n_z . No quantum number can be zero, because if any one of them is taken zero, then $\psi(x, y, z) = 0$, which would mean that the particle does not exist in the box.

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

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

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

In this case the energy of the particle in the ground state is given by

$$E_{111} = \frac{3\pi^2 \hbar^2}{2mL^2} \quad \dots(19)$$

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

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

For example for the first excited state, the values of the quantum numbers are:

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

Thus there are three different eigen functions and hence three different stationary states. Each state has the same energy $\frac{6\pi^2 \hbar^2}{2mL^2}$. Therefore the first excited state is said to be triply degenerate or three-fold degenerate.

Degree of Degeneracy: The number of independent wave-functions for the stationary states of an energy-level is called the degree of degeneracy of the level.

For a particle in a cubical box a number of energy-levels with the corresponding quantum numbers and the degree of degeneracy are given in the following table:

Energy Levels	Quanum Numbers (n_x, n_y, n_z)			Degree of Degeneracy
$\frac{3\pi^2\hbar^2}{2mL^2}$	(111)			Non-degenerate
$\frac{6\pi^2\hbar^2}{2mL^2}$	(211), (121), (112)			Three-fold degenerate
$\frac{9\pi^2\hbar^2}{2mL^2}$	(221), (212), (122)			Three-fold degenerate
$\frac{11\pi^2\hbar^2}{2mL^2}$	(311), (131), (113)			Three-fold degenerate
$\frac{12\pi^2\hbar^2}{2mL^2}$	(222)			Non-degenerate
$\frac{14\pi^2\hbar^2}{2mL^2}$	(123), (132), (213)			Six-fold degenerate
$\frac{17\pi^2\hbar^2}{2mL^2}$	(322), (232), (223)			Three-fold degenerate
$\frac{18\pi^2\hbar^2}{2mL^2}$	(411), (141), (114)			Three-fold degenerate
$\frac{19\pi^2\hbar^2}{2mL^2}$	(331), (313), (133)			Three-fold degenerate
$\frac{21\pi^2\hbar^2}{2mL^2}$	(421), (412), (241)			Six-fold degenerate
	(214), (124), (142)			

6.4 Simple Harmonic Oscillator

When a particle oscillates about its means position along a straight line under the action of a force which (i) is directed towards the mean position and (ii) is proportional to the displacement at any instant from this position, the motion of the particle is said to be simple harmonic, and the oscillating particle is called a simple harmonic oscillator, or a linear harmonic oscillator.

The harmonic oscillator is an important example of periodic motion because it serves as an exact or an approximate model for many problems in classical or quantum physics. At temperatures above 0° K, the atoms in a crystal are temporarily displaced from their normal positions in the structure, due to absorption of thermal energy. Consequently, interatomic forces obeying

Hooke's law act on the displaced atoms. Under the action of such restoring forces each atom vibrates about its normal position which is the correct position in the ideal structure. Thus the vibrations of each atom are similar to those of a simple harmonic oscillator.

One-Dimensional Simple Harmonic Oscillator in Classical Mechanics

Let the equilibrium position of a linear harmonic oscillator of mass m be the origin 0, and the straight line of its motion be the x -axis. When x is its displacement from 0, the restoring force F is given by

$$F = -kx$$

where k is a positive constant.

According to the second law of motion

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

Therefore, its Newtonian equation of motion is

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

$$\text{or } \frac{d^2x}{dt^2} = -\left(\frac{k}{m}\right)x = -\omega^2x$$

$$\text{where } \omega = \sqrt{\frac{k}{m}}$$

The general solution of this equation is

$$x = A \sin(\omega t + \theta) \quad \dots(1)$$

where A and θ are constants, which may be determined from the initial conditions. Eq. (1) shows that the particle performs simple harmonic oscillations with frequency.

$$\nu = \frac{\omega}{2\pi} = \frac{1}{2\pi} \sqrt{\frac{k}{m}} \quad \dots(2)$$

where ω is called the angular frequency of oscillations.

The potential energy $V(x)$ at the displacement x is given by

$$V = \int_0^x dV = \int_0^x \frac{dV}{dx} dx$$

$$\frac{dV}{dx} = -F = -(-kx) = kx$$

$$\therefore V = \int_0^x kx dx = \frac{1}{2} kx^2 = \frac{1}{2} m\omega^2 x^2 \quad \dots(3)$$

And the kinetic energy K at the displacement x is given by

$$\begin{aligned} K &= \frac{1}{2} m \left(\frac{dx}{dt} \right)^2 = \frac{1}{2} mA^2\omega^2 \cos^2(\omega t + \theta) \\ &= \frac{1}{2} m\omega^2 A^2 [1 - \sin^2(\omega t + \theta)] \end{aligned}$$

$$= \frac{1}{2} m\omega^2 (A^2 - x^2) \quad \dots(4)$$

Therefore, according to classical mechanics the total energy E of the oscillator is given by

$$\begin{aligned} E &= K + V \\ &= \frac{1}{2} m\omega^2 (A^2 - x^2) + \frac{1}{2} m\omega^2 x^2 \\ &= \frac{1}{2} m\omega^2 A^2 \end{aligned} \quad \dots(5)$$

Eq. (3) shows that the potential energy has a parabolic form. It means that the particle moves in a potential well of parabolic form. Eq. (5) shows that the total energy of a particle oscillating with a constant frequency $\nu = \frac{\omega}{2\pi}$ is proportional to the square of the amplitude. According to classical mechanics the particle can oscillate with any amplitude, consequently the total energy increases continuously with increase in the amplitude.

Probability of finding the Linear Simple Harmonic Oscillator within a Small Distance dx According to Classical Mechanics

The classical probability of finding the particle performing a linear simple harmonic motion within the distance between x and $x + dx$ from its equilibrium position is the ratio of the time which the particle takes to pass over the distance dx during the course of its one oscillation to the period of oscillation, $T (= 2\pi/\omega)$.

Thus if the particle passes through the distance dx in one direction in time dt , then the probability $P(x) dx$ of finding it within dx is given by

$$P(x) dx = \frac{2dt}{T} = \frac{2dt}{2\pi/\omega} = \frac{\omega dt}{\pi} \quad \dots(6)$$

But $x = A \sin(\omega t + \theta)$

$\therefore dx = A\omega \cos(\omega t + \theta) dt$

Hence $dt = \frac{dx}{A\omega \cos(\omega t + \theta)} = \frac{dx}{A\omega \sqrt{1 - x^2/A^2}}$
 $= \frac{dx}{\omega \sqrt{A^2 - \omega^2}}$

But $A^2 = \frac{2E}{m\omega^2}$ [See Eq. (5)]

$\therefore dt = \frac{dx}{\omega \sqrt{\frac{2E}{m\omega^2} - x^2}}$

Substituting this value of dt in Eq. (6), we get

$$P(x) dx = \frac{dx}{\pi \sqrt{\frac{2E}{m\omega^2} - x^2}} \quad \dots(7)$$

6.5 One-Dimensional Simple Harmonic Oscillator in Quantum Mechanics

Wave Equation for the Oscillator

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

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

or $\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2} (E - V) \psi = 0 \quad \dots(1)$

where E is the total energy of the particle, V the potential energy, and ψ the wave-function for the particle, which is a function of x alone.

For a linear oscillator along the x -axis with the angular frequency ω under a restoring force proportional to the displacement x , the potential energy is given by

$$V = \frac{1}{2} m\omega^2 x^2 \quad \dots(2)$$

Substituting the value of V in Eq. (1) we get

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2} \left(E - \frac{1}{2} m\omega^2 x^2 \right) \psi = 0 \quad \dots(3)$$

or $\frac{d^2\psi}{dx^2} + \left(\frac{2mE}{\hbar^2} - \frac{m^2\omega^2}{\hbar^2} x^2 \right) \psi = 0 \quad \dots(4)$

This is the Schrödinger wave equation for the oscillator.

Simplification of the Wave Equation

To simplify Eq. (4) we introduce a dimensionless independent variable y which is related to x by the equation:

$$y = \sqrt{\frac{m\omega}{\hbar}} x \quad \dots(5)$$

so that $x = \sqrt{\frac{\hbar}{m\omega}} y$

Now we have

$$\begin{aligned} \frac{d\psi}{dx} &= \frac{d\psi}{dy} \frac{dy}{dx} = \frac{d\psi}{dy} \sqrt{\frac{m\omega}{\hbar}} \\ \text{and, } \frac{d^2\psi}{dx^2} &= \frac{d^2\psi}{dy^2} \frac{dy}{dx} \sqrt{\frac{m\omega}{\hbar}} = \frac{d^2\psi}{dy^2} \frac{m\omega}{\hbar} \\ &= \frac{m\omega}{\hbar} \frac{d^2\psi}{dy^2} \end{aligned} \quad \dots(6)$$

Substituting the values of $\frac{d^2\psi}{dx^2}$ and x^2 in Eq. (4) we get

$$\frac{m\omega}{\hbar} \frac{d^2\psi}{dy^2} + \left(\frac{2mE}{\hbar^2} - \frac{m^2\omega^2}{\hbar^2} \cdot \frac{\hbar}{m\omega} y^2 \right) \psi = 0$$

or

$$\frac{m\omega}{\hbar} \frac{d^2\psi}{dy^2} + \left(\frac{2mE}{\hbar^2} - \frac{m\omega}{\hbar} y^2 \right) \psi = 0$$

or

$$\frac{m\omega}{\hbar} \frac{d^2\psi}{dy^2} + \frac{m\omega}{\hbar} \left(\frac{\hbar}{m\omega} \cdot \frac{2mE}{\hbar^2} - y^2 \right) \psi = 0$$

or

$$\frac{d^2\psi}{dy^2} + \left(\frac{2E}{\hbar\omega} - y^2 \right) \psi = 0 \quad \dots(7)$$

or

$$\frac{d^2\psi}{dy^2} + (\lambda - y^2) \psi = 0 \quad \text{where } \lambda = \frac{2E}{\hbar\omega} \quad \dots(8)$$

Though Eq. (7) is in a simplified form, it is not easy to solve it. For large values of y , such that $y^2 > > \lambda$, we may neglect λ . Therefore, Eq. (7) is transformed to the form

$$\frac{d^2\psi}{dy^2} - y^2\psi = 0 \quad \dots(9)$$

For large values of y , the approximate solution of this equation is

$$\psi = e^{-y^2/2} \quad \dots(10)$$

(Since $\psi \rightarrow 0$, when $y \rightarrow \infty$, we reject the form $e^{+y^2/2}$)

Differentiating Eq. (10) with respect to y , we get

$$\frac{d\psi}{dy} = e^{-y^2/2} \left(-\frac{2y}{2} \right) = -ye^{-y^2/2}$$

Again differentiating

$$\begin{aligned} \frac{d^2\psi}{dy^2} &= -[y(-ye^{-y^2/2}) + e^{-y^2/2}] \\ &= (y^2 - 1)e^{-y^2/2} = (y^2 - 1)\psi \end{aligned}$$

$$\text{or } \frac{d^2\psi}{dy^2} - (y^2 - 1)\psi = 0 \quad \dots(11)$$

For large values of y this equation is reduced to Eq. (9). This suggests that an accurate solution of Eq. (7) must be of the form

$$\psi = e^{-y^2/2} H(y) \quad \dots(12)$$

where $H(y)$ is a finite polynomial in y .

Change of Dependent Variable from ψ to $H(y)$ in Eq. (7)

To change the differential equation (7) into a differential equation for the dependent variable $H(y)$ we differentiate Eq. (12) with respect to y , we get

$$\frac{d\psi}{dy} = e^{-y^2/2} \frac{dH}{dy} + He^{-y^2/2} (-y)$$

$$= \left(\frac{dH}{dy} - Hy \right) e^{-y^2/2}$$

Now differentiating this equation with respect to y , we get

$$\begin{aligned} \frac{d^2\psi}{dy^2} &= \left(\frac{d^2H}{dy^2} - y \frac{dH}{dy} - H \right) e^{-y^2/2} + \left(\frac{dH}{dy} - Hy \right) e^{-y^2/2} (-y) \\ &= \left[\frac{d^2H}{dy^2} - 2y \frac{dH}{dy} - H + Hy^2 \right] e^{-y^2/2} \end{aligned}$$

Now substituting the expression for $\frac{d^2\psi}{dy^2}$ and the expression for ψ in Eq.

(7), we get

$$\left[\frac{d^2H}{dy^2} - 2y \frac{dH}{dy} - H + Hy^2 \right] e^{-y^2/2} + (\lambda - y^2) He^{-y^2/2} = 0$$

$$\text{or } \frac{d^2H}{dy^2} - 2y \frac{dH}{dy} + (\lambda - 1) H = 0 \quad \dots(13)$$

This is a well known Hermite's differential equation.

Solution of Hermite's Differential Equation

This equation is solved by the method of Frobenius, according to which the solution is a power series in positive powers of y . If the lowest power of y is zero, the solution will be of the form.

$$H(y) = A_0 + A_1 y + A_2 y^2 + A_3 y^3 + A_4 y^4 + \dots \quad \dots(14)$$

$$= \sum_{n=0}^{\infty} A_n y^n \quad \dots(15)$$

Differentiating Eq. (14) with respect to y

$$\frac{dH}{dy} = A_1 + 2A_2 y + 3A_3 y^2 + 4A_4 y^3 + \dots \quad \dots(16)$$

Multiplying this equation by $-2y$

$$\begin{aligned} -2y \frac{dH}{dy} &= -2(A_1 y + 2A_2 y^2 + 3A_3 y^3 + \dots) \\ &= \sum_{n=0}^{\infty} -2n A_n y^n \end{aligned} \quad \dots(17)$$

Differentiating Eq. (16) with respect to y

$$\begin{aligned} \frac{d^2H}{dy^2} &= 2A_2 + 3.2A_3 y + 4.3A_4 y^2 + \dots \\ &= \sum_{n=0}^{\infty} (n+2)(n+1) A_{n+2} y^n \end{aligned} \quad \dots(18)$$

Multiplying both the sides of Eq. (15) by $(\lambda - 1)$

$$(\lambda - 1) H(y) = \sum_{n=0}^{\infty} (\lambda - 1) A_n y^n \quad \dots(19)$$

Substituting Eqns. (17), (18) and (19) in Eq. (13), we get

$$\sum_{n=0}^{\infty} [(n+2)(n+1)A_{n+2} - 2nA_n + (\lambda - 1)A_n] y^n = 0$$

$$\text{or } \sum_{n=0}^{\infty} [(n+2)(n+1)A_{n+2} - (2n+1-\lambda)A_n] y^n = 0$$

This equation must be true for all value of y and, therefore, the coefficient of each power of y must vanish separately.

Hence we have

$$(n+2)(n+1)A_{n+2} - (2n+1-\lambda)A_n = 0$$

$$\text{or } A_{n+2} = \frac{2n+1-\lambda}{(n+1)(n+2)} A_n \quad \dots(20)$$

where $n = 0, 1, 2, 3, \dots$

This equation is called the recursion formula connecting the coefficients A_{n+2} and A_n .

In the solution of any second-order differential equation, there must be two arbitrary constants. So we consider A_0 and A_1 as the two arbitrary constants and we determine all other coefficients in terms of A_0 and A_1 :

Substituting $n = 0, 2, 4, 6, \dots$ successively in Eq. (20), we get

$$A_2 = \frac{(1-\lambda)}{2!} A_0$$

$$A_4 = \frac{(5-\lambda)}{3 \times 4} A_2 = \frac{(5-\lambda)(1-\lambda)}{3 \times 4 \times 2!} A_0 = \frac{(1-\lambda)(5-\lambda)}{4!} A_0$$

$$A_6 = \frac{(9-\lambda)}{5 \times 6} A_4 = \frac{(9-\lambda)(1-\lambda)(5-\lambda)}{5 \times 6 \times 4!} A_0$$

$$= \frac{(1-\lambda)(5-\lambda)(9-\lambda)}{6!} A_0$$

.....

Substituting $n = 1, 3, 5, 7, \dots$ successively in Eq. (20)

$$A_3 = \frac{(3-\lambda)}{2 \times 3} A_1 = \frac{(3-\lambda)}{3!} A_1$$

$$A_5 = \frac{(7-\lambda)}{4 \times 5} A_3 = \frac{(7-\lambda)(3-\lambda)}{4 \times 5 \times 3!} A_1 = \frac{(3-\lambda)(7-\lambda)}{5!} A_1$$

Similarly

$$A_7 = \frac{(3-\lambda)(7-\lambda)(11-\lambda)}{7!} A_1$$

.....

Substituting the values of these coefficients in Eq. (14)

$$H(y) = A_0 \left[1 + \frac{(1-\lambda)}{2!} y^2 + \frac{(1-\lambda)(5-\lambda)}{4!} y^4 + \frac{(1-\lambda)(5-\lambda)(9-\lambda)}{6!} y^6 + \dots \right]$$

$$+ A_1 \left[y + \frac{(3-\lambda)}{3!} y^3 + \frac{(3-\lambda)(7-\lambda)}{5!} y^5 + \frac{(3-\lambda)(7-\lambda)(11-\lambda)}{7!} y^7 + \dots \right] \quad \dots(21)$$

This is a solution of Eq. (13).

This equation shows that the polynomial $H(y)$ is the sum of two infinite series. This means that if $H(y)$ does not terminate for some value of n , the wave-function

$$\psi = e^{-y^2/2} H(y)$$

will become infinite as y becomes infinite. (See solved Ex. 6.5).

Conditions for Finite Value of the Wave-Function, and Eigen Values of Energy

The wave-function will have a finite value at infinity, i.e., $\psi(\infty) = 0$, if $H(y)$ terminates at some value of n . For this to happen the following two conditions must be satisfied:

(1) From some value of n , $A_{n+2} = 0$

$$\text{i.e., } \frac{2n+1-\lambda}{(n+1)(n+2)} A_n = 0 \quad \dots(22)$$

$$\text{or } 2n+1 = \lambda$$

(2) If in Eq. (22) n is an odd value, the second series in Eq. (21) will terminate at some value of n . But the first series will not terminate. Hence when n is an odd value, A_0 must be zero. For example, when $n = 5$, then $\lambda = 11$ and the second series in Eq. (21) will terminate at y^5 , but the first series will not terminate.

If n is even, the first series in Eq. (21) will terminate at some value of n . But in this case, the second series will not terminate. Hence when n is even, A_1 must be zero. For example when $n = 4$, then $\lambda = 9$ and the first series will terminate at y^4 , but the second series will not terminate.

Substituting the value of λ as given by Eq. (8) in Eq. (22) we get the eigen-values of the total energy E :

$$\frac{2E}{\hbar\omega} = (2n+1)$$

$$\text{or } E_n = \frac{1}{2} (2n+1) \hbar\omega \quad \dots(23)$$

$$E_n = (n + \frac{1}{2}) \hbar\omega$$

Substituting $\hbar = \frac{h}{2\pi}$ and $\omega = 2\pi\nu$, this expression has the form

$$E_n = (n + \frac{1}{2}) \hbar \nu \quad \dots(24)$$

where, $n = 0, 1, 2, \dots$, ω is the angular frequency and ν is the frequency of the classical harmonic oscillator, given by

$$\nu = \frac{\omega}{2\pi} = \frac{1}{2\pi} \sqrt{\frac{k}{m}}$$

From Eq. (23) we get the following conclusions:

(1) The lowest energy of the oscillator is obtained by putting $n = 0$ in Eq. (23) and it is

$$E_0 = \frac{1}{2} \hbar \omega \quad \dots(25)$$

This is called the ground state energy or the zero point vibrational energy of the harmonic oscillator. The zero-point energy is the characteristic result of quantum mechanics. The values of E_n in terms of E_0 are given by

$$E_n = (2n + 1) E_0 \quad \dots(26)$$

where $n = 0, 1, 2, 3, \dots$

(2) The eigen-values of the total energy depend only on one quantum number n . Therefore all the energy-levels of the oscillator are non-degenerate.

(3) The successive energy-levels are equally spaced; the separation between two adjacent energy-levels being $\hbar\omega$. The energy-level diagram for the harmonic oscillator is shown in Fig. 6.7.

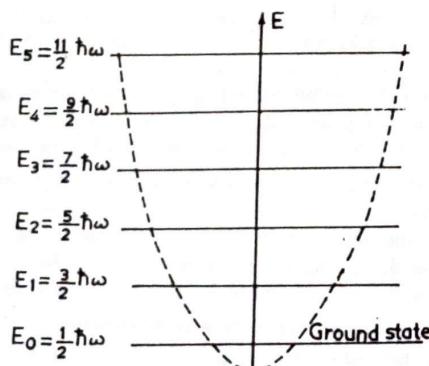


Fig. 6.7

Wave Functions of the Harmonic Oscillator

When the parameter λ is given by

$$\lambda = 2n + 1$$

$H(y)$ is a polynomial of degree n with a constant multiplier. If the multiplier is chosen such that the coefficient of y^n is 2^n , the polynomial is denoted by $H_n(y)$ and is called Hermite's Polynomial. Then the wave-function for the state E_n is given by

$$\psi_n = N_n e^{-y^2/2} H_n(y) \quad \dots(27)$$

where N_n is a normalization factor given by

$$N_n = \left(\frac{\alpha}{\pi} \right)^{1/4} (2^n n!)^{-1/2} \quad \dots(28)$$

where

$$\alpha = \frac{m\omega}{\hbar}$$

Substituting the value of N_n and $y = x \sqrt{\alpha}$ in Eq. (27) we get

$$\psi_n(x) = \left(\frac{\alpha}{\pi} \right)^{1/4} (2^n n!)^{-1/2} e^{-\alpha x^2/2} H_n(x \sqrt{\alpha}) \quad \dots(29)$$

This equation gives the general formula for the n th wave-function.

The Hermite polynomials of low degree are easily calculated from Eq. (21). For example to find $H_0(x \sqrt{\alpha})$ for the ground state we have $n = 0$, then from Eq. (22) $\lambda = 1$

Now with the even value of n , the coefficient A_1 in Eq. (21) must be zero. Therefore, from Eq. (21)

$$H_0(y) = A_0$$

$$H_0(x \sqrt{\alpha}) = 2^0 = 2^0 = 1$$

Now substituting $n = 0$ and $H_0(x \sqrt{\alpha}) = 1$ in Eq. (29), we get the wave-function for the ground state of the harmonic oscillator:

$$\psi_0(x) = \left(\frac{\alpha}{\pi} \right)^{1/4} e^{-\alpha x^2/2} \quad \dots(30)$$

The first six Hermite polynomials are given in the following table:

n	$\lambda = 2n + 1$	E_n	$H_n(y)$
0	1	$\frac{1}{2} \hbar \omega$	$H_0(y) = 1$
1	3	$\frac{3}{2} \hbar \omega$	$H_1(y) = 2y$
2	5	$\frac{5}{2} \hbar \omega$	$H_2(y) = 4y^2 - 1$
3	7	$\frac{7}{2} \hbar \omega$	$H_3(y) = 8y^3 - 12y$
4	9	$\frac{9}{2} \hbar \omega$	$H_4(y) = 16y^4 - 48y^2 + 12$
5	11	$\frac{11}{2} \hbar \omega$	$H_5(y) = 32y^5 - 160y^3 + 120y$

The first six wave functions are shown in Fig. 6.8.

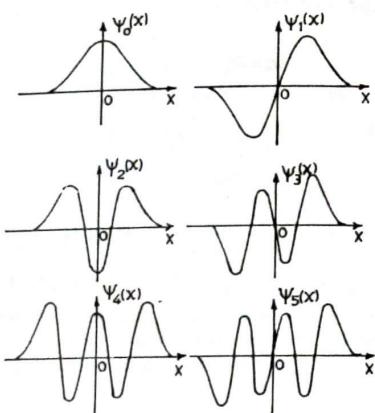


Fig. 6.8

Comparison of the Classical Probability-Density and Quantum Mechanical Probability-Density

According to classical mechanics the probability-density of a linear simple harmonic oscillator, having amplitude A and energy $E_n = (n + \frac{1}{2}) \hbar\omega$, is given by

$$P(x) = \frac{1}{\pi\sqrt{A^2 - x^2}} = \frac{1}{\pi\sqrt{\frac{2E_n}{m\omega^2} - x^2}} \quad [\text{See Sec. 6.4, Eq. (7)}]$$

This equation shows that the probability of finding the particle is maximum at $x = \pm A$, i.e., at the extremities of the path, and it is minimum at $x = 0$, i.e., at the equilibrium position. The classical probability-density for $n = 0$ and $n = 10$ is shown by dotted curves in Fig. 6.9 and Fig. 6.10.

According to quantum mechanics the probability-density of the particle in the n th energy-state is given by

$$P(x) = \Psi_n(x)\Psi^*(x)$$

Calculations show that for $n = 0$, $|\Psi_0|^2$ is maximum at $x = 0$ and decreases on either side of $x = 0$ along the continuous curve (Fig. 6.9). For

$n = 10$, $|\Psi_{10}|^2$ has 5 peaks on either side of $x = 0$ (Fig. 6.10). This means that the disagreement between two probability-densities becomes less and less when n increases.

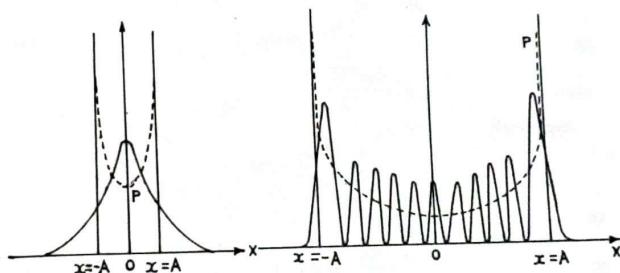


Fig. 6.9

Fig. 6.10

6.6 Particle in a One-Dimensional Square Potential Well of Finite Depth

Suppose a particle of mass m is bound in a square potential well (Fig. 6.11). Let $V = V_0$ be the potential energy in region (I): $x < 0$

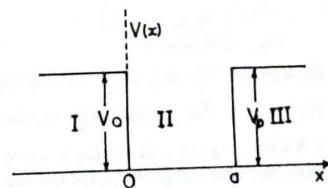


Fig. 6.11

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

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

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

The time-independent Schrödinger wave equations for the three regions are as follows:

Region (I):

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

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

$$\frac{d^2\psi_1}{dx^2} - \beta^2\psi_1 = 0 \quad \dots(1)$$

where

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

Region (II):

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

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

or

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

where

Region (III):

$$\frac{d^2\psi_3}{dx^2} - \beta^2\psi_3 = 0 \quad \dots(3)$$

The general solutions of these equations are

$$\psi_1 = Ae^{\beta x} + Be^{-\beta x} \quad \dots(4)$$

$$\psi_2 = C'e^{ikx} + D'e^{-ikx} \quad \dots(5)$$

$$= C \sin kx + D \cos kx \quad \dots(6)$$

$$\psi_3 = Ge^{\beta x} + He^{-\beta x}$$

In region (I) the term $Be^{-\beta x}$ is an exponentially increasing function as x decreases from zero to $-\infty$. The normalization condition $\int_{-\infty}^a \psi^* \psi dx = 1$ requires that $B = 0$. A similar argument shows that in region (III) $G = 0$. Therefore the allowed wave functions in regions (I) and (III) are

$$\psi_1 = Ae^{\beta x} \quad \dots(7)$$

$$\psi_3 = He^{-\beta x} \quad \dots(8)$$

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

(i) at $x = 0$

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

This equation gives

$$\therefore \begin{aligned} \left(\frac{d\psi_1}{dx} \right)_{x=0} &= \left(\frac{d\psi_2}{dx} \right)_{x=0} \\ [A\beta e^{\beta x}]_{x=0} &= [Ck \cos kx - Dk \sin kx]_{x=0} \end{aligned} \quad \dots(9)$$

$$\text{and} \quad \begin{aligned} \left(\frac{d\psi_2}{dx} \right)_{x=a} &= \left(\frac{d\psi_3}{dx} \right)_{x=a} \\ \beta A &= kC \end{aligned} \quad \dots(10)$$

$$\text{and (ii) at } x = a \quad \begin{aligned} \psi_2(a) &= \psi_3(a) \\ C \sin ka + D \cos ka &= H e^{-\beta a} \end{aligned} \quad \dots(11)$$

$$\begin{aligned} \left(\frac{d\psi_2}{dx} \right)_{x=a} &= \left(\frac{d\psi_3}{dx} \right)_{x=a} \\ [Ck \cos ka - Dk \sin ka]_{x=a} &= [-H \beta e^{-\beta a}]_{x=a} \\ kC \cos ka - kD \sin ka &= -\beta H e^{-\beta a} \end{aligned} \quad \dots(12)$$

$$\begin{aligned} \text{Dividing Eq. (12) by (11), we get} \\ \frac{kC \cos ka - kD \sin ka}{C \sin ka + D \cos ka} &= -\beta \\ \frac{B \cos ka - kA \sin ka}{B \sin ka + A \cos ka} &= -\beta \end{aligned}$$

$$\begin{aligned} \text{Substituting } D = A, \text{ and } C = \frac{\beta}{k} A, \text{ we get} \\ \frac{B \cos ka - kA \sin ka}{B \sin ka + A \cos ka} &= -\beta \\ \frac{k \beta \cos ka - k^2 \sin ka}{\beta \sin ka + k \cos ka} &= -\beta \end{aligned}$$

$$\begin{aligned} \text{Cross multiplying, we get} \\ k \beta \cos ka - k^2 \sin ka &= -\beta^2 \sin ka - k \beta \cos ka \\ \text{Simplifying we get} \\ 2k \beta \cos ka &= (k^2 - \beta^2) \sin ka \quad \dots(13) \\ \text{or} \quad \tan ka &= \frac{2k \beta}{k^2 - \beta^2} \end{aligned}$$

$$\begin{aligned} \text{For convenience we take the width of the potential well as } 2b, \text{ i.e., } a = 2b \\ \therefore \quad \tan 2kb &= \frac{2k \beta}{k^2 - \beta^2} \quad \dots(14) \end{aligned}$$

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

Simplifying this equation

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

either

$$k \tan kb = \beta \quad \dots(15)$$

or

$$k \cot kb = -\beta \quad \dots(16)$$

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 by $\beta_1, \beta_2, \beta_3, \dots$. A set of energy eigen-values E_n is then given by

$$\beta = \sqrt{\frac{2m(V_0 - E)}{\hbar^2}} \quad \dots(17)$$

or

$$E_n = V_0 - \frac{\hbar^2 \beta_n^2}{2m} \quad \dots(17)$$

For the solution (15) these energy levels can be determined by a simple graphical method:

Multiplying Eq. (15) by the half-width b of the potential well, we get

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

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

$$\frac{\xi \tan \xi}{\hbar^2} = \eta \quad \text{or} \quad \eta = \xi \tan \xi \quad \dots(18)$$

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

$$\therefore k^2 + \beta^2 = \frac{2mV_0}{\hbar^2}$$

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

$$\text{or} \quad \xi^2 + \eta^2 = \frac{2mV_0b^2}{\hbar^2} \quad \dots(19)$$

This equation represents a circle of known radius $\left(\frac{2mV_0b^2}{\hbar^2}\right)^{1/2}$ in the $\xi - \eta$ plane. The first quadrant of the circle of known radius is drawn. 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. (17). In this way energy levels for different values of V_0b^2 can be determined.

By similar method we can determine the energy levels for the solution of Eq. (16). 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 for the solution of Eq. (15)

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

or

$$\tan kb = \infty$$

$$\begin{aligned} kb &= (2n+1)\frac{\pi}{2} \\ \text{or} \quad b\sqrt{\frac{2mE_n}{\hbar^2}} &= (2n+1)\frac{\pi}{2} \\ \therefore E_n &= \frac{(2n+1)^2 \pi^2 \hbar^2}{8mb^2} \end{aligned} \quad \dots(20)$$

(ii) When $V_0 \rightarrow \infty$, then for the solution of Eq. (16)

$$\begin{aligned} \tan kb &= -\frac{k}{\beta} = -\frac{k}{\infty} = 0 \\ \therefore kb &= n\pi \\ \text{or} \quad b\sqrt{\frac{2mE_n}{\hbar^2}} &= n\pi \\ \therefore E_n &= \frac{(2n)^2 \pi^2 \hbar^2}{8mb^2} \end{aligned} \quad \dots(21)$$

SOLVED EXAMPLES

Example 6.1. Find the lowest energy of an electron confined to move in a one-dimensional potential box of length 1 Å. Given $m = 9.11 \times 10^{-31}$ kg, $\hbar = 1.054 \times 10^{-34}$ J. sec, 1 eV = 1.6×10^{-19} J

Solution:

$$\begin{aligned} \text{We have } a &= 1 \text{ Å} = 10^{-10} \text{ m} \\ E_1 &= \frac{1^2 \pi^2 \hbar^2}{2ma^2} = \frac{\pi^2 \times (1.054 \times 10^{-34})^2}{2 \times 9.11 \times 10^{-31} \times (10^{-10})^2} \\ &= \frac{1.054^2 \pi^2 \times 10^{-17}}{2 \times 9.11} = \frac{10.95 \times 10^{-17}}{18.22} = 6 \times 10^{-18} \text{ J} \\ &= \frac{6 \times 10^{-18}}{16} = \frac{600}{16} = 37.5 \text{ eV} \\ &= 1.6 \times 10^{-14} \text{ m.} \end{aligned}$$

Example 6.2. Find the lowest energy of a neutron confined to a nucleus of size 10^{-14} m. Given: mass of the neutron = 1.67×10^{-27} kg.

$$\begin{aligned} \text{We have } a &= 10^{-14} \text{ m} \\ E_1 &= \frac{1^2 \pi^2 \hbar^2}{2ma^2} = \frac{\pi^2 \times (1.054 \times 10^{-34})^2}{2 \times 1.67 \times 10^{-27} \times (10^{-14})^2} \\ &= \frac{1.054^2 \pi^2 \times 10^{-13}}{3.34} = \frac{10.95 \times 10^{-13}}{3.34} \\ &= 3.28 \times 10^{-13} \\ &= \frac{3.28 \times 10^{-13}}{16} = \frac{32.8}{16} \times 10^6 \text{ eV} = 2.05 \text{ MeV} \\ &= 1.6 \times 10^{-19} \text{ J.} \end{aligned}$$

Example 6.3. (a) Find the lowest energy of an electron confined in a cubical box of each side 1 Å.

(b) Find the temperature at which the average energy of the molecules of a perfect gas would be equal to the lowest energy of the electron. (Given $k = 1.38 \times 10^{-23}$ J/K).

Solution:

(a) We have $a = 10^{-10}$ m.

The possible energies of a particle in a cubical box of each side a are given by

$$E = \frac{\pi^2 \hbar^2}{2ma^2} (n_x^2 + n_y^2 + n_z^2)$$

For the lowest energy $n_x = n_y = n_z = 1$

$$E_1 = \frac{3\pi^2 \hbar^2}{2ma^2} = \frac{3\pi^2 \times (1.054 \times 10^{-34})^2}{2 \times 9.11 \times 10^{-31} \times (10^{-10})^2}$$

$$= \frac{3 \times 1.054^2 \pi^2 \times 10^{-17}}{2 \times 9.11} = \frac{37.85 \times 10^{-17}}{18.22} \text{ J}$$

(b) Let T K be the required temperature. Then

$$\frac{3}{2} kT = \frac{3\pi^2 \hbar^2}{2ma^2}, \text{ where } k \text{ is Boltzmann's constant}$$

$$= 18.03 \times 10^{-18} \text{ J}$$

$$\therefore T = \frac{2 \times 18.03 \times 10^{-18}}{3 \times 1.38 \times 10^{-23}}$$

$$= \frac{2 \times 18.03 \times 10^5}{3 \times 1.38} \text{ K}$$

$$= 8.71 \times 10^5 \text{ K}$$

Example 6.4. The potential energy of a simple harmonic oscillator of mass m , oscillating with angular frequency ω is

$$V(x) = \frac{1}{2} m\omega^2 x^2$$

(a) Write the time-independent Schrödinger equation for a simple harmonic oscillator.

(b) Given the eigen-function of the Hamiltonian operator for the ground state as

$$\psi_0 = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2}$$

where $\alpha = \frac{m\omega}{\hbar}$, calculate the energy eigen value in the ground state.

Solution:

(a) The Hamiltonian operator for the oscillator is

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2} m\omega^2 x^2$$

Therefore, the time-independent Schrödinger equation is

$$\left[-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2} m\omega^2 x^2 \right] \psi(x) = E\psi(x)$$

(b) For the ground state the Schrödinger equation is

$$\left[-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2} m\omega^2 x^2 \right] \psi_0 = E_0 \psi_0 \quad \dots(1)$$

$$\text{Now } \psi_0 = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2}$$

$$\begin{aligned} \therefore \frac{d\psi_0}{dx} &= \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2} (-\alpha x) = -\alpha x \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2} \\ &= -\alpha x \psi_0 \quad \dots(2) \end{aligned}$$

And

$$\begin{aligned}\frac{d^2\psi_0}{dx^2} &= -\alpha x \frac{d\psi_0}{dx} - \alpha\psi_0 = -\alpha x (-\alpha x\psi_0) - \alpha\psi_0 \\ &= \alpha^2 x^2 \psi_0 - \alpha\psi_0\end{aligned}$$

Multiplying this equation by $-\hbar^2/2m$

$$-\frac{\hbar^2}{2m} \frac{d^2\psi_0}{dx^2} = -\frac{\hbar^2}{2m} \alpha^2 x^2 \psi_0 + \frac{\hbar^2}{2m} \alpha\psi_0$$

Substituting $\alpha = m\omega/\hbar$ and simplifying we get

$$\left[-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2} m\omega^2 x^2 \right] \psi_0 = \frac{1}{2} \hbar\omega\psi_0$$

... (3)

Comparing Eqs. (1) and (3) $E_0 = V_2 \hbar\omega$.

Example 6.5. Prove that if the power series

$$\begin{aligned}H(y) &= A_0 + A_1 y + A_2 y^2 + A_3 y^3 + \dots \\ &= \sum_{n=0}^{n=\infty} A_n y^n.\end{aligned}$$

whose coefficient are connected by

$$A_{n+2} = \frac{2n+1-\lambda}{(n+1)(n+2)} A_n$$

does not terminate for some value of n , then the wave-function

$$\psi = e^{-y^2/2} H(y)$$

will be infinite as y approaches infinity.

Solution:

If n is a large number, then in the recursion formula we can neglect all constant numbers which appear in the sum or difference with n . So, for large values of n the recursion formula becomes

$$A_{n+2} = \frac{2n}{n^2} A_n = \frac{2}{n} A_n \quad \dots (1)$$

Now we have the exponential series

$$\begin{aligned}e^y &= 1 + y^2 + \frac{y^4}{2!} + \dots + \frac{y^n}{(\frac{n}{2})!} + \frac{y^{n+2}}{(\frac{n+2}{2})!} + \dots \\ &= \sum_{n=0}^{\infty} B_n y^n\end{aligned}$$

where n is even

It is evident that the coefficients B_n and B_{n+2} of y^n and y^{n+2} respectively are

$$B_n = \frac{1}{(\frac{n}{2})!}$$

$$B_{n+2} = \frac{1}{(\frac{n+2}{2})!}$$

Therefore, the recursion formula for the exponential series is

$$\frac{B_{n+2}}{B_n} = \frac{\left(\frac{n}{2}\right)!}{\left(\frac{n+2}{2}\right)!} = \frac{\left(\frac{n}{2}\right)!}{\left(\frac{n+1}{2}\right)!}$$

or

$$\frac{B_{n+2}}{B_n} = \frac{\left(\frac{n}{2}\right)!}{\left(\frac{n+1}{2}\right)\left(\frac{n}{2}\right)!} = \frac{1}{\frac{n+1}{2}}$$

∴ for large values of n

$$\frac{B_{n+2}}{B_n} = \frac{2}{n}$$

or

$$B_{n+2} = \frac{2}{n} B_n \quad \dots (2)$$

Dividing Eq. (1) by Eq. (2)

$$\frac{A_{n+2}}{B_{n+2}} = \frac{A_n}{B_n} = C$$

where C is a constant

$$A_n = CB_n$$

Thus for large values of n , we have

$$\sum A_n y^n = \sum CB_n y^n = C \sum B_n y^n = Ce^{y^2}$$

Hence

$$H(y) = f(y) + Ce^{y^2}$$

where $f(y)$ is that part of the series, which does not contain high powers of y . The complete wave-function is then

$$\begin{aligned}\psi(y) &= e^{-y^2/2} H(y) \\ &= e^{-y^2/2} [f(y) + Ce^{y^2}] \\ &= e^{-y^2/2} f(y) + Ce^{y^2/2} \quad \dots (3)\end{aligned}$$

This equation shows that as y approaches infinity, the last term on the right hand side becomes infinite. Hence the condition that $\psi(y)$ must be finite for all values of y will be satisfied, if the power series $H(y)$ terminates after a finite number of terms so that only the first term $e^{-y^2/2} f(y)$ remains in Eq. (3).

QUESTIONS AND PROBLEMS

1. A particle of mass m is confined in a field free region between impenetrable walls at $x = 0$ and $x = a$. Show that the stationary energy levels of the particle are given by

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

Obtain the corresponding wave-functions.

2. (a) Write down the time-dependent and time-independent Schrödinger wave equations for a particle.
 (b) Solve the Schrödinger wave equation for a particle moving in a rectangular potential box and obtain its energy levels. Show that the eigen-values of energy are discrete.
3. Find the energies of the six lowest energy-levels of a particle in a cubical box. Which of the levels are degenerate?
 (Ans. 3, 6, 9, 11, 12 and $14 \times \frac{\pi^2 \hbar^2}{2mL^2}$, 1st and 5th levels are non-degenerate; 2nd, 3rd and 4th are three-fold degenerate and the 6th is six-fold degenerate).
4. Determine the degree of degeneracy of the energy-level $\frac{38\pi^2 \hbar^2}{2mL^2}$ of a particle in a cubical potential box.
 (Ans. The quantum numbers (611), (161), (116), (532), (523), (352), (325), (253) and (235) give the same energy level; therefore, the level is nine-fold degenerate).
5. Write down the Schrödinger equation for a linear harmonic oscillator and obtain the eigen-values of the energy of the oscillator.
6. (a) Solve the Schrödinger equation for the linear harmonic oscillator and obtain its energy-levels.
 (b) Compare the energy-values obtained quantum mechanically with those obtained by classical mechanics and old quantum theory.
7. (a) Explain the meaning of the eigen-functions and eigen-values of an operator.
 (b) Establish the time-independent Schrödinger equation for a linear harmonic oscillator and obtain its energy-levels.
8. Calculate the probability of finding a simple harmonic oscillator within the classical limits, if the oscillator is in its normal state.
9. Show that the lowest or ground-state energy level of a particle in one dimensional potential box with rigid walls is in agreement with the uncertainty principle.
 (Ans. The ground-state energy is $E_1 = \frac{\pi^2 \hbar^2}{2ma^2}$ the maximum uncertainty in the position of the particle in the box is $\Delta x = a$, where a is the width of the box. From the uncertainty relation the uncertainty in the momentum is given by

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

\therefore the minimum uncertainty in the momentum $= \frac{\hbar}{a}$, i.e., corresponding to $\Delta x = a$, the minimum momentum is of the order of \hbar/a .

\therefore the minimum kinetic energy $= \frac{(\hbar/a)^2}{2m} = \frac{\hbar^2}{2ma^2}$. Thus the ground-state energy E_1 being greater than this minimum value is in agreement with the uncertainty principle.)

The Hydrogen Atom and The Rigid Rotator

7.1 Introduction

The hydrogen atom is a system of two particles, a proton and a single electron bound by electrostatic force of attraction. It, being the simplest atoms, forms the basis for the theoretical treatment of more complex atomic systems. Bohr's theory of the hydrogen atom marked the beginning of the old quantum theory of atomic structure. Wave mechanics had its beginning when Schrödinger in 1926 gave the solution of the wave equation for the hydrogen atom. Subsequently there was extensive development of quantum mechanical theory of the hydrogen atom by Heisenberg, Max Born, and Jordan, before the treatment was finally given by Pauli.

The quantum mechanical treatment given in this chapter is due to Sommerfeld. It differs in some minor details from that of Schrödinger.

7.2 Wave Equations for the Hydrogen Atom

In the hydrogen atom the charge of the proton is $+e$ and that of the electron $-e$. Therefore, the electrostatic potential energy of the system in the absence of external fields is (in SI units)

$$V = \frac{e(-e)}{4\pi\epsilon_0 r} = -\frac{e^2}{4\pi\epsilon_0 r} \quad \dots(1)$$

where r is the distance between the particles and ϵ_0 the permittivity of free space.

Let m_1 and m_2 be the respective masses of the proton and the electron, and $(x_1, y_1, z_1), (x_2, y_2, z_2)$ their Cartesian coordinates (Fig. 7.1). The time-independent Schrödinger wave equation for the system of the two particles is

$$\begin{aligned} & -\frac{\hbar^2}{2m_1} \left(\frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial y_1^2} + \frac{\partial^2}{\partial z_1^2} \right) \Psi_T \\ & -\frac{\hbar^2}{2m_2} \left(\frac{\partial^2}{\partial x_2^2} + \frac{\partial^2}{\partial y_2^2} + \frac{\partial^2}{\partial z_2^2} \right) \Psi_T + V \Psi_T = E_T \Psi_T \end{aligned} \quad \dots(2)$$

where Ψ_T is a function of $x_1, y_1, z_1, x_2, y_2, z_2$; the subscript T in Ψ_T and E_T means that these quantities refer to the complete system of the proton and the electron.

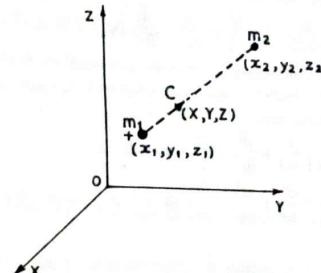


Fig. 7.1

and the potential energy V is

$$V = -\frac{e^2}{\sqrt{(x_2 - x_1)^2 + (y_2 - y_1)^2 + (z_2 - z_1)^2}}$$

To simplify Eq. (2), we define three coordinates (X, Y, Z) of the centre of mass of the system, and the three coordinates (x, y, z) of the electron relative to the proton by the following equations:

$$MX = m_1 x_1 + m_2 x_2$$

$$MY = m_1 y_1 + m_2 y_2$$

$$MZ = m_1 z_1 + m_2 z_2$$

$$x = x_2 - x_1, y = y_2 - y_1, z = z_2 - z_1$$

where $M = m_1 + m_2$ is the total mass of the system. In terms of the new coordinates Eq. (2) is transformed to the following form

$$\begin{aligned} & -\frac{\hbar^2}{2M} \left(\frac{\partial^2}{\partial X^2} + \frac{\partial^2}{\partial Y^2} + \frac{\partial^2}{\partial Z^2} \right) \Psi_T \\ & -\frac{\hbar^2}{2m_r} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \Psi_T + V(x, y, z) \Psi_T = E_T \Psi_T \end{aligned} \quad \dots(3)$$

In this equation the symbol m_r has been introduced to represent the quantity

$$m_r = \frac{m_1 m_2}{m_1 + m_2}$$

This quantity is the reduced mass of the electron. Eq. (3) can be separated into two parts by expressing Ψ_T as the product of a function of X, Y, Z and a

function of x, y, z . Thus substituting $\psi_T = \psi_c(X, Y, Z)\psi(x, y, z)$ in Eq. (3) and dividing through by $\psi_c\psi$, we get

$$\begin{aligned} -\frac{\hbar^2}{2M} \cdot \frac{1}{\psi_c} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \psi_c \\ -\frac{\hbar^2}{2m_r} \cdot \frac{1}{\psi} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \psi + V(x, y, z) = E_T \quad \dots(4) \end{aligned}$$

The first part of this equation depends only on X, Y, Z , and the other only on x, y, z . Therefore, each part must be equal to a constant. Hence we obtain the following two equations

$$-\frac{\hbar^2}{2M} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \psi_c = E_{tr} \psi_c \quad \dots(5)$$

$$-\frac{\hbar^2}{2m_r} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \psi + V(x, y, z) \psi = E \psi \quad \dots(6)$$

where $E = E_T - E_{tr}$

Eq. (5) represents the motion of a free particle of mass $M = m_1 + m_2$ with the translational energy E_{tr} . In our problem the translational motion is not important and the translational energy is not required.

Eq. (6) is the three dimensional wave equation of the electron of reduced mass m_r , having potential energy $V(x, y, z)$ and total energy E .

The wave equation may be written as

$$\left[-\frac{\hbar^2}{2m_r} \nabla^2 + V \right] \psi = E \psi \quad \dots(7)$$

where $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$ is the Laplacian of $\psi(x, y, z)$ in the Cartesian coordinates x, y, z . We write Eq. (7) in a convenient form as

$$\nabla^2 \psi + \frac{2m_r}{\hbar^2} (E - V) \psi = 0 \quad \dots(8)$$

The variables in this equation cannot be separated in the Cartesian coordinates. Therefore, the Cartesian coordinates of the electron relative to the proton are replaced by the spherical polar coordinates (r, θ, ϕ) and the Laplacian operator ∇^2 is transformed into spherical polar coordinates by using the equations (See Fig. 7.2)

$$x = r \sin \theta \cos \phi$$

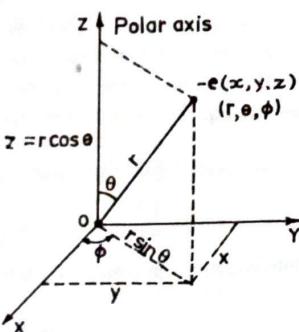


Fig. 7.2

$$\begin{aligned} y &= r \sin \theta \sin \phi \\ z &= r \cos \theta \end{aligned}$$

The Laplacian operator, in spherical polar coordinates, is

$$\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \quad \dots(9)$$

Therefore, the Schrödinger equation in spherical polar coordinates becomes

$$\begin{aligned} \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} \\ + \frac{2m_r}{\hbar^2} \left[E + \frac{e^2}{4\pi\epsilon_0 r} \right] \psi = 0 \quad \dots(10) \end{aligned}$$

In this equation the wave-function ψ is a function of (r, θ, ϕ) .

Separation of Variables

The equation in spherical polar coordinates can be easily separated into three equations, each involving a single independent variable. For this purpose we assume the wave-function $\psi(r, \theta, \phi)$ to be a product of three functions,

$$\psi(r, \theta, \phi) = R(r) Q(\theta) F(\phi) \quad \dots(11a)$$

where $R(r)$ is a function of r alone,

$Q(\theta)$ is a function of θ alone and

$F(\phi)$ is a function of ϕ alone.

(Note: we use the symbols Q and F for the functions of θ and ϕ respectively and not the symbols Θ and Φ to avoid any confusion in writing).

The function $R(r)$ will show the variation of the wave function ψ along a radius vector from the nucleus, when θ and ϕ are constant. The function $Q(\theta)$ will show the variation of ψ with zenith angle θ along a circle on a sphere with nucleus as the centre, when r and ϕ are constant. The function $F(\phi)$ will show the variation of ψ with azimuthal angle ϕ along a circle with centre on OZ , where r and θ are constant.

In a simple form Eq. (11a) is written as

$$\psi = R Q F \quad \dots(11b)$$

Substituting this equation into Eq. (10), we get

$$\begin{aligned} \frac{QF}{r^2} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{RF}{r^2 \sin \theta} \frac{d}{d\theta} \left(\sin \theta \frac{dQ}{d\theta} \right) + \frac{RQ}{r^2 \sin^2 \theta} \frac{d^2 F}{d\phi^2} \\ + \frac{2m_r}{\hbar^2} \left(E + \frac{e^2}{4\pi\epsilon_0 r} \right) R Q F = 0 \quad \dots(12) \end{aligned}$$

In this equation we have used ordinary derivatives instead of partial derivatives because each function depends on only one variable.

Now multiplying Eq. (12) by $\frac{r^2 \sin^2 \theta}{R Q F}$, we get

fur
div

$$\frac{\sin^2 \theta}{R} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{\sin \theta}{Q} \frac{d}{d\theta} \left(\sin \theta \frac{dQ}{d\theta} \right) + \frac{1}{F} \frac{d^2 F}{d\phi^2} \\ + \frac{2m_r}{\hbar^2} \left(E + \frac{e^2}{4\pi\epsilon_0 r} \right) r^2 \sin^2 \theta = 0$$

Transposing the third term to the right-hand side

$$\frac{\sin^2 \theta}{R} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{\sin \theta}{Q} \frac{d}{d\theta} \left(\sin \theta \frac{dQ}{d\theta} \right) \\ + \frac{2m_r}{\hbar^2} \left(E + \frac{e^2}{4\pi\epsilon_0 r} \right) r^2 \sin^2 \theta = -\frac{1}{F} \frac{d^2 F}{d\phi^2} \quad \dots(13)$$

Azimuthal Wave Equation, or the ϕ Equation

The left side of Eq. (13) is a function of r and θ and the right side is a function of ϕ only. Thus each side can be varied independently of the other. Therefore, the equation will be true only if both sides are equal to the same constant. This constant is denoted by m^2 , where m is called the *magnetic quantum number*. (See Sec. 7.8).

Therefore, the right side of Eq. (13) becomes

$$-\frac{1}{F} \frac{d^2 F}{d\phi^2} = m^2$$

$$\text{or} \quad \frac{d^2 F}{d\phi^2} + m^2 F = 0 \quad \dots(14)$$

This is the *first of the three differential equations*, and is called the *azimuthal wave equation*, or the ϕ equation. In the solution of Eq. (14) we will see that m must be a positive or negative integer or zero.

Radial Wave Equation

Equating the left side of Eq. (13) to m^2 and then dividing it by $\sin^2 \theta$, we get

$$\frac{1}{R} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{1}{Q \sin \theta} \frac{d}{d\theta} \left(\sin \theta \frac{dQ}{d\theta} \right) \\ + \frac{2m_r r^2}{\hbar^2} \left(E + \frac{e^2}{4\pi\epsilon_0 r} \right) = \frac{m^2}{\sin^2 \theta}$$

Transposing the second term on the left side to the right side we get

$$\frac{1}{R} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{2m_r r^2}{\hbar^2} \left(E + \frac{e^2}{4\pi\epsilon_0 r} \right) = \frac{m^2}{\sin^2 \theta} - \frac{1}{Q \sin \theta} \frac{d}{d\theta} \left(\sin \theta \frac{dQ}{d\theta} \right) \dots(15)$$

The left side of this equation is a function of r only, while the right side is a function of θ only, and hence both sides of the equation must be equal to the same constant. We denote this constant by β .

Equating the left-side of Eq. (15) to β we get

The Hydrogen Atom and The Rigid Rotator

$$\frac{1}{R} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{2m_r r^2}{\hbar^2} \left(E + \frac{e^2}{4\pi\epsilon_0 r} \right) = \beta$$

Multiplying both sides by $\frac{R}{r^2}$ and rearranging, we get

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \left[\frac{2m_r}{\hbar^2} \left(E + \frac{e^2}{4\pi\epsilon_0 r} \right) - \frac{\beta}{r^2} \right] R = 0 \quad \dots(16)$$

This is the *radial wave equation*.Polar Wave Equation, or the θ EquationEquating β to the right-side of Eq. (15), we get

$$\beta = \frac{m^2}{\sin^2 \theta} - \frac{1}{Q \sin \theta} \frac{d}{d\theta} \left(\sin \theta \frac{dQ}{d\theta} \right)$$

Multiplying both sides of this equation by Q and rearranging, we get

$$\frac{1}{\sin \theta} \frac{d}{d\theta} \left(\sin \theta \frac{dQ}{d\theta} \right) + \left[\beta - \frac{m^2}{\sin^2 \theta} \right] Q = 0 \quad \dots(17)$$

This is the *polar wave equation*, or the θ equation.

Thus, the azimuthal wave equation, radial wave equation and polar wave equation for the electron respectively are

$$\frac{d^2 F}{d\phi^2} + m^2 F = 0 \quad \dots(14)$$

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \left[\frac{2m_r}{\hbar^2} \left(E + \frac{e^2}{4\pi\epsilon_0 r} \right) - \frac{\beta}{r^2} \right] R = 0 \quad \dots(16)$$

$$\frac{1}{\sin \theta} \frac{d}{d\theta} \left(\sin \theta \frac{dQ}{d\theta} \right) + \left[\beta - \frac{m^2}{\sin^2 \theta} \right] Q = 0 \quad \dots(17)$$

The solution of the polar equation depends on the solution of the azimuthal equation and the solution of the radial equation depends on the solution of the polar equation. Hence we should solve the equations in order, F , Q , and R . The full treatment of these equations is complicated. Therefore, to begin with we consider in Sec. 7.3 the application of the radial equation to the ground state of hydrogen.

7.3 Ground State of the Hydrogen Atom

The potential energy of the electron is spherically symmetrical. Therefore, there will be a set of wave-functions which are spherically symmetrical. Such wave-functions are functions of r only, i.e.,

$$\psi = R(r) \quad \dots(1)$$

The Schrödinger wave equation for these functions is obtained by putting $\beta = 0$ in the radial wave equation (16) of Sec. 7.2. Thus we get

$$\text{or} \quad \frac{1}{r^2} \left(r^2 \frac{dR}{dr} + \frac{2m_r}{\hbar^2} \left(E + \frac{e^2}{4\pi\epsilon_0 r} \right) R \right) = 0$$

$$\text{or} \quad \frac{1}{r^2} \left(r^2 \frac{d^2R}{dr^2} + \frac{dR}{dr} 2r \right) + \frac{2m_r}{\hbar^2} \left(E + \frac{e^2}{4\pi\epsilon_0 r} \right) R = 0$$

$$\text{or} \quad \frac{d^2R}{dr^2} + \frac{2}{r} \frac{dR}{dr} + \frac{2m_r}{\hbar^2} \left(E + \frac{e^2}{4\pi\epsilon_0 r} \right) R = 0 \quad \dots(2)$$

This equation can also be obtained directly from Eq. (10) of Sec. 7.2 by substituting $\psi = R(r)$ in that equation.

The simplest solution of Eq. (2) is

$$R(r) = e^{-\alpha r} \quad \dots(3)$$

where α is a constant to be determined.

From Eq. (3) it is evident that:

- (i) R is finite for all values of r . It has a large value only near the proton.
- (ii) For each value of r , R has one value only.
- (iii) R is continuous.

From Eq. (3), we obtain

$$\frac{dR}{dr} = -\alpha e^{-\alpha r} = -\alpha R$$

and

$$\frac{d^2R}{dr^2} = -\alpha \frac{dR}{dr} = -\alpha(-\alpha R) = \alpha^2 R$$

Substituting the expressions for these differential coefficients in Eq. (2), we get

$$\alpha^2 R - \frac{2\alpha R}{r} + \frac{2m_r}{\hbar^2} \left(E + \frac{e^2}{4\pi\epsilon_0 r} \right) R = 0$$

Since $R(r)$ is not zero, we divide both sides of this equation by $R(r)$ and after rearrangement of the terms, we get

$$\left(\alpha^2 + \frac{2m_r E}{\hbar^2} \right) = \frac{1}{r} \left(2\alpha - \frac{m_r e^2}{2\pi\epsilon_0 \hbar^2} \right) \quad \dots(4)$$

The left side of Eq. (4) is independent of r , and since the equation must be true for any value of r , both sides of this equation must be zero. Thus, equating the right side of Eq. (4) to zero,

$$2\alpha - \frac{m_r r^2}{2\pi\epsilon_0 \hbar^2} = 0$$

or

$$\alpha = \frac{m_r r^2}{4\pi\epsilon_0 \hbar^2} \quad \dots(5)$$

The value of $\frac{1}{\alpha}$ is $\frac{4\pi\epsilon_0 \hbar^2}{m_r e^2}$. This quantity is the radius a_0 of the first Bohr orbit.

$$\text{Thus} \quad a_0 = \frac{4\pi\epsilon_0 \hbar^2}{m_r e^2} \quad \dots(6)$$

Similarly equating the left side of Eq. (4) to zero,

$$\alpha^2 + \frac{2m_r E}{\hbar^2} = 0$$

$$\text{or} \quad E = -\frac{\hbar^2 \alpha^2}{2m_r} \quad \dots(7)$$

Substituting the value of α in this equation,

$$E = -\frac{\hbar^2}{2m_r} \left(\frac{m_r e^2}{4\pi\epsilon_0 \hbar^2} \right)^2$$

$$= -\frac{m_r e^4}{32\pi^2 \epsilon_0^2 \hbar^2} \quad \dots(8a)$$

Substituting $\hbar = h/2\pi$, we get

$$E = -\frac{m_r e^4}{8\epsilon_0^2 h^2} \quad \dots(8b)$$

The total energy E of the electron, as given by Eq. (8a) or (8b) is the same as that derived by the Bohr theory for $n = 1$. Therefore, this is the lowest energy-level for the electron in the hydrogen atom and is called the ground state energy of the hydrogen atom. Thus the spherically symmetrical wave-function $R(r) = e^{-\alpha r}$ with the value of α given by Eq. (5) describes the ground state of the hydrogen atom.

Most Probable Position of the Electron in the Ground State

The wave-function for the electron in the ground state of the hydrogen atom is

$$R(r) = e^{-\alpha r}$$

$$\text{where} \quad \alpha = \frac{m_r e^2}{4\pi\epsilon_0 \hbar^2}$$

To obtain the probability of finding the electron between r and $r + dr$ from the nucleus, we describe two concentric spheres about the nucleus with radii r and $r + dr$. The volume of the shell between these spheres is $4\pi r^2 dr$. The probability of finding the electron within this shell is given by

$$P_r dr = |R(r)|^2 4\pi r^2 dr$$

$$= 4\pi r^2 e^{-2\alpha r} dr \quad \dots(9)$$

where P_r is called the radial probability-density.

$\therefore P_r$ is given by

$$P_r = 4\pi r^2 e^{-2\alpha r} \quad \dots(10)$$

For the most probable position of the electron, P_r will be maximum as shown in Fig. 7.3.

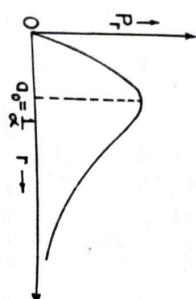


Fig. 7.3

Suppose at $r = r_1$, P_r is maximum.

Differentiating Eq. (10) with respect to r ,

$$\frac{dP_r}{dr} = 4\pi [r^2 e^{-2\alpha r} (-2\alpha) + 2r e^{-2\alpha r}]$$

$$= 8\pi r e^{-2\alpha r} [-r\alpha + 1]$$

At $r = r_1$, P_r is maximum

$$\left(\frac{dP_r}{dr} \right)_{r=r_1} = 0$$

Hence

$$r_1 = \frac{1}{\alpha} = \frac{4\pi e \hbar^2}{m_e c^2} = a_0$$

Thus the most probable position of the electron is at a distance equal to the radius of the first Bohr orbit. The wave-function $R(r) = e^{-\alpha r}$, therefore, represents an s -state with the smallest circular orbit.

7.4 Solution of the Azimuthal Wave Equation

The azimuthal wave equation

$$\frac{d^2 F}{d\phi^2} + m^2 F = 0 \quad \dots(1)$$

is a simple differential equation. The solution of this equation is

$$F(\phi) = A e^{im\phi} + B e^{-im\phi} \quad \dots(2)$$

where A and B are constants, and m is the magnetic quantum number.

Since ϕ can vary from 0 to 2π radians, Eq. (2) shows that the function $F(\phi)$ is finite, whatever the value of ϕ . Now to find the condition that $F(\phi)$ has a single value for a given value of ϕ , we note that ϕ is repetitive, i.e., the azimuthal angles ϕ and $(\phi + 2\pi)$ both represent the same meridian plane. Hence we must have

$$F(\phi) = F(\phi + 2\pi)$$

$$A e^{im\phi} + B e^{-im\phi} = A e^{im(\phi+2\pi)} + B e^{-im(\phi+2\pi)}$$

$$A e^{im\phi} - A e^{im(\phi+2\pi)} + B e^{-im\phi} - B e^{-im(\phi+2\pi)} = 0 \quad \dots(3)$$

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$$A e^{im\phi} (1 - e^{2im\phi}) + B e^{-im\phi} (1 - e^{-2im\phi}) = 0 \quad \dots(4)$$

Since the terms $A e^{im\phi}$ and $B e^{-im\phi}$ are not zero, we must have

$$1 - e^{2im\phi} = 0 \quad \dots(5)$$

$$1 - e^{-2im\phi} = 0 \quad \dots(6)$$

From these equations, we get

$$e^{2im\phi} = 1 \quad \dots(7)$$

$$\cos 2im\phi + i \sin 2im\phi = 1 \quad \dots(8)$$

Taking the real part of Eq. (7) or Eq. (8),

$$\cos 2im\phi = 1$$

$$2im\phi = 0, \pm 2\pi, \pm 4\pi, \pm 6\pi, \dots$$

$$m = 0, \pm 1, \pm 2, \pm 3, \dots \quad \dots(9)$$

Thus the condition that the azimuthal wave-function must be single valued everywhere will be satisfied only when the magnetic quantum number m is zero or a positive or negative integer.

The most useful forms of the azimuthal wave-functions are

$$F(\phi) = A e^{im\phi}$$

$$F(\phi) = B e^{-im\phi}$$

$$F(\phi) = C \cos |m| \phi$$

$$F(\phi) = D \cos |m| \phi$$

Normalization of the Azimuthal Wave-Function

We use the following form of the wave-function

$$F(\phi) = A e^{im\phi}$$

The normalization condition for the total wave-function $\Psi(r, \theta, \phi)$ is

$$\iiint \Psi \Psi^* dV = 1$$

where dV is the volume element.

The volume element in spherical polar coordinates is

$$dV = (r \sin \theta d\phi) (rd\theta) (dr)$$

$$= r^2 dr \sin \theta d\theta d\phi$$

$$\therefore \int_0^R \int_0^\pi \int_0^{2\pi} r^2 dr \sin \theta d\theta d\phi \int_0^{2\pi} FF^* d\phi = 1$$

Hence for the wave-function $F(\phi)$

$$\int_0^R \int_0^\pi r^2 dr \sin \theta d\theta \int_0^{2\pi} FF^* d\phi = 1$$

$$\int_0^{2\pi} (A e^{im\phi}) (A e^{im\phi}) d\phi = 1$$

$$A^2 \int_0^{2\pi} e^{im\phi} e^{-im\phi} d\phi = 1$$

$$A^2 \int_0^{2\pi} d\phi = 1$$

or

$$A^2 \times 2\pi = 1$$

Hence

$$A = \frac{1}{\sqrt{2\pi}}$$

or

Hence the azimuthal wave function which is a solution of the azimuthal wave equation for a given value of the magnetic quantum number m is given by

$$F_m(\phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi}$$

...(10)

7.5 Solution of the Polar Wave Equation

The polar wave equation is

$$\frac{1}{\sin \theta} \frac{d}{d\theta} \left(\sin \theta \frac{dQ}{d\theta} \right) + \left(\beta - \frac{m^2}{\sin^2 \theta} \right) Q = 0$$

To solve this equation, we substitute

$$\sin \theta = \cos \theta$$

$$\frac{dQ}{d\theta} = \frac{dQ}{dx} \frac{dx}{d\theta} = -\sin \theta \frac{dQ}{dx}$$

$$\frac{d}{d\theta} = -\sin \theta \frac{d}{dx}$$

$$\therefore$$

...(3)

From Eq. (2), we get

$$\sin \theta \frac{dQ}{d\theta} = -\sin^2 \theta \frac{dQ}{dx} = -(1-x^2) \frac{dQ}{dx}$$

And from Eq. (3), we have

$$\frac{1}{\sin \theta} \frac{d}{d\theta} = -\frac{d}{dx}$$

Substituting for these expressions in Eq. (1)

$$-\frac{d}{dx} \left[(1-x^2) \frac{dQ}{dx} \right] + \left(\beta - \frac{m^2}{1-x^2} \right) Q = 0$$

or

$$\frac{d}{dx} \left[(1-x^2) \frac{dQ}{dx} \right] + \left(\beta - \frac{m^2}{1-x^2} \right) Q = 0$$

This equation is known as *Legendre's equation*. The solutions of this equation satisfy the conditions of single-valuedness and continuity of the wave function Q if the constant β is of the form

$$\beta = (k+m)(k+m+1) \quad \dots(5)$$

so that

$$\beta = l(l+1)$$

...(6)

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where $l = 0, 1, 2, 3, \dots$

Thus l must be zero or a positive integer. For a given value of l , the parameter m has the values:

$$m = 0, \pm 1, \pm 2, \dots, \pm l$$

The solutions are written as

$$Q_{lm}(\theta) = N_{lm} P_l^m(\cos \theta)$$

where N_{lm} is the normalization constant given by

$$N_{lm} = \sqrt{\frac{(2l+1)(l-m)!}{2(l+m)!}} \quad \dots(7)$$

The values of the Legendre functions for some values of l and $|m|$ are

$P_0^0(\cos \theta) = 1$	$P_1^1(\cos \theta) = \sin \theta$
$P_1^0(\cos \theta) = \cos \theta$	$P_2^1(\cos \theta) = 3 \sin \theta \cos \theta$
$P_2^0(\cos \theta) = \frac{1}{2}(3 \cos^2 \theta - 1)$	$P_3^1(\cos \theta) = \frac{3}{2} \sin \theta (5 \cos^2 \theta - 1)$
and so on.	

The normalized wave functions for $l = 0, 1, 2$, and $m = 0, \pm 1, \pm 2$ are given in Table 7.1.

7.6 Solution of the Radial Wave Equation

Substituting $\beta = l(l+1)$ in Eq. (16) of Sec. 7.2, we get

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \left[\frac{2me^2}{\hbar^2} \left(E + \frac{e^2}{4\pi\epsilon_0 r} \right) - \frac{l(l+1)}{r^2} \right] R = 0$$

or

$$\frac{d^2 R}{dr^2} + \frac{2}{r} \frac{dR}{dr} + \left[\frac{2me^2}{\hbar^2} \left(E + \frac{e^2}{4\pi\epsilon_0 r} \right) - \frac{l(l+1)}{r^2} \right] R = 0 \quad \dots(1)$$

where l is the orbital quantum number and other symbols have their usual meaning. This is the differential equation for the radial motion as well as for the angular motion of the electron.

There are two sets of solutions of Eq. (1). The first set is applicable when $E < 0$ and corresponds to bound states, and the second set is applicable to unbound states. We will solve the equation only for bound states of the electron. For solution of Eq. (1) we proceed as follows.

Simplification of the Equation

$$\text{Let } \alpha = \sqrt{-\frac{8mE}{\hbar^2}} \quad \dots(2)$$

$$\lambda = \frac{e^2}{4\pi\epsilon_0\hbar} \sqrt{-\frac{m_r}{2E}} \quad \dots(3)$$

so that

$$\lambda\alpha = \frac{2m_r e^2}{4\pi\epsilon_0\hbar^2} \quad \dots(4)$$

and from Eq. (2)

$$\frac{2m_r E}{\hbar^2} = -\frac{\alpha^2}{4}$$

And let

$$\rho = \alpha r \quad \dots(5)$$

so that

$$r = \frac{\rho}{\alpha} \quad \dots(6)$$

It is easily seen that ρ is dimensionless. Now we have

$$\begin{aligned} \frac{dR}{dr} &= \frac{dR}{d\rho} \frac{d\rho}{dr} = \frac{dR}{d\rho} \alpha = \alpha \frac{dR}{d\rho} \\ \frac{d^2R}{dr^2} &= \alpha \frac{d^2R}{d\rho^2} \frac{d\rho}{dr} = \alpha^2 \frac{d^2R}{d\rho^2} \end{aligned}$$

Substituting these expression in Eq. (1)

$$\alpha^2 \frac{d^2R}{d\rho^2} + \frac{2}{r} \alpha \frac{dR}{d\rho} + \left[\frac{2m_r E}{\hbar^2} + \frac{2m_r e^2}{4\pi\epsilon_0\hbar^2} \frac{1}{r} - \frac{l(l+1)}{r^2} \right] R = 0 \quad \dots(7)$$

Now substituting $r = \frac{\rho}{\alpha}$, $\frac{2m_r E}{\hbar^2} = -\frac{\alpha^2}{4}$ and

$$\frac{2m_r e^2}{4\pi\epsilon_0\hbar^2} = \lambda\alpha \text{ in Eq. (7),}$$

$$\alpha^2 \frac{d^2R}{d\rho^2} + \frac{2}{\rho/\alpha} \alpha \frac{dR}{d\rho} + \left[-\frac{\alpha^2}{4} + \frac{\lambda\alpha}{\rho/\alpha} - \frac{l(l+1)}{(\rho/\alpha)^2} \right] R = 0$$

Dividing through by α^2 , we get

$$\frac{d^2R}{d\rho^2} + \frac{2}{\rho} \frac{dR}{d\rho} + \left[-\frac{1}{4} + \frac{\lambda}{\rho} - \frac{l(l+1)}{\rho^2} \right] R = 0$$

$$\text{or } \frac{d^2R}{d\rho^2} + \frac{2}{\rho} \frac{dR}{d\rho} + \left[\frac{\lambda}{\rho} - \frac{1}{4} - \frac{l(l+1)}{\rho^2} \right] R = 0 \quad \dots(8)$$

Though this equation is in a simplified form, it is not easy to solve it. So we examine the solution for $\rho \rightarrow \infty$. In this case from Eq. (8), we get

$$\frac{d^2R}{d\rho^2} - \frac{R}{4} = 0$$

The solution of this equation is

$$R(\rho) = B_1 e^{\rho/2} + B_2 e^{-\rho/2}$$

The first term on the right hand side shows that when $\rho \rightarrow \infty$, $R \rightarrow \infty$. Therefore, we must assume $B_1 = 0$. Thus in this case the solution is

$$R(\rho) = B_2 e^{-\rho/2}$$

This suggests that an accurate solution of Eq. (8) must be of the form

$$R(\rho) = e^{-\rho/2} F(\rho) \quad \dots(9)$$

where $F(\rho)$ is a finite polynomial in ρ .

Change of Dependent Variable from R to F in Eq. (8)

From Eq. (9), we get

$$\begin{aligned} \frac{dR}{d\rho} &= e^{-\rho/2} \frac{dF}{d\rho} + F e^{-\rho/2} \left(-\frac{1}{2} \right) \\ &= \left(\frac{dF}{d\rho} - \frac{1}{2} F \right) e^{-\rho/2} \end{aligned} \quad \dots(10)$$

$$\begin{aligned} \frac{d^2R}{d\rho^2} &= \left(\frac{d^2F}{d\rho^2} - \frac{1}{2} \frac{dF}{d\rho} \right) e^{-\rho/2} + \left(\frac{dF}{d\rho} - \frac{1}{2} F \right) e^{-\rho/2} \left(-\frac{1}{2} \right) \\ &= \left(\frac{d^2F}{d\rho^2} - \frac{dF}{d\rho} + \frac{1}{4} F \right) e^{-\rho/2} \end{aligned} \quad \dots(11)$$

Substituting Eqs. (9), (10) and (11) in Eq. (8) and dividing both sides by $e^{-\rho/2}$, we get

$$\begin{aligned} \left(\frac{d^2F}{d\rho^2} - \frac{dF}{d\rho} + \frac{1}{4} F \right) + \frac{2}{\rho} \left[\frac{dF}{d\rho} - \frac{1}{2} F \right] \\ + \left[\frac{\lambda}{\rho} - \frac{1}{4} - \frac{l(l+1)}{\rho^2} \right] F = 0 \end{aligned}$$

$$\text{or } \frac{d^2F}{d\rho^2} + \left(\frac{2}{\rho} - 1 \right) \frac{dF}{d\rho} + \left[\frac{\lambda-1}{\rho} - \frac{l(l+1)}{\rho^2} \right] F = 0 \quad \dots(12)$$

Solution of the Differential Equation for $F(\rho)$

Eq. (12) can be solved by the power-series method. For this purpose we assume that

$$\begin{aligned} F(\rho) &= \rho^s (A_0 + A_1 \rho + A_2 \rho^2 + \dots) \\ &= \sum_{k=0}^{\infty} A_k \rho^{s+k} \end{aligned} \quad \dots(13)$$

Substituting Eq. (13) into Eq. (12), we get

$$\begin{aligned} \sum_{k=0}^{\infty} (s+k)(s+k-1) A_k \rho^{s+k-2} + \left(\frac{2}{\rho} - 1 \right) \sum_{k=0}^{\infty} (s+k) A_k \rho^{s+k-1} \\ + \left[\frac{\lambda-1}{\rho} - \frac{l(l+1)}{\rho^2} \right] \sum_{k=0}^{\infty} A_k \rho^{s+k} = 0 \end{aligned}$$

Simplifying this equation we get

or

$$\sum_{k=0}^{\infty} [(s+k)(s+k-1) + 2(s+k) - l(l+1)] A_k p^{s+k-2} = 0$$

$$- \sum_{k=0}^{\infty} (s+k+1-\lambda) A_k p^{s+k-1} = 0$$

$$\sum_{k=0}^{\infty} [(s+k)(s+k+1) - l(l+1)] A_k p^{s+k-2} = 0$$

$$- \sum_{k=0}^{\infty} (s+k+1-\lambda) A_k p^{s+k-1} = 0$$

To take out the first term containing A_0 from the first summation, we write $k=0$ in the first summation, and the remaining summation is obtained by writing $k+1$ in place of k . Thus we obtain

$$[s(s+1) - l(l+1)] A_0 p^{s-2}$$

$$+ \sum_{k=0}^{\infty} [(s+k+1)(s+k+2) - l(l+1)] A_{k+1} p^{s+k-1} = 0$$

$$[s(s+1) - l(l+1)] A_0 p^{s-2}$$

$$+ \sum_{k=0}^{\infty} [(s+k+1)(s+k+2) - l(l+1)] A_{k+1} p^{s+k-1} = 0$$

$$- \sum_{k=0}^{\infty} (s+k+1-\lambda) A_k p^{s+k-1} = 0$$

$$[s(s+1) - l(l+1)] A_0 p^{s-2}$$

$$+ \sum_{k=0}^{\infty} [(s+k+1)(s+k+2) - l(l+1)] A_{k+1} p^{s+k-1} = 0$$

$$- (s+k+1-\lambda) A_k p^{s+k-1} = 0 \quad \dots(14)$$

The coefficient of each power of p must vanish separately. Therefore, we get

$$s(s+1) - l(l+1) = 0 \quad \dots(15)$$

$$\text{and } [(s+k+1)(s+k+2) - l(l+1)] A_{k+1} - (s+k+1-\lambda) A_k = 0 \quad \dots(16)$$

where $k = 0, 1, 2, \dots$

Eq. (15) is called the indicial equation and is employed to determine the value of p . Assuming that $A_0 \neq 0$, the solution of Eq. (15) gives two values of s :

$$s = l \quad \dots(17)$$

$$\text{or } s = -(l+1) \quad \dots(18)$$

For the boundary condition that $R(p)$ must be finite at $p=0$, we must choose

$$s = l$$

Now substituting this value of s in Eq. (16) we obtain the recursion relation between the coefficients of successive terms of the series:

$$A_{k+1} = \frac{l+k+1-\lambda}{(l+k+1)(l+k+2)-l(l+1)} A_k$$

$$\text{or } A_{k+1} = \frac{k+l+1-\lambda}{(k+l)(k+2l+2)} A_k \quad \dots(19)$$

where $k = 0, 1, 2, \dots$

The boundary condition that at $r = \infty, R$ must be zero, will be satisfied if the series for $F(p)$ terminates for some value of k . Suppose for some value of k

$$\lambda = k + l + 1.$$

Then A_{k+1} will be zero and the recursion relation shows that every further coefficient will be zero. Therefore the series for $F(p)$ will terminate at the term

$$p^l A_k p^k.$$

Since $k = 0, 1, 2, \dots$ and

$$l = 0, 1, 2, \dots$$

λ must be an integer n .

$$\text{i.e. } \lambda = n = k + l + 1 \quad \dots(20)$$

This equation shows that n can have the values given by

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

For a given value of n , l is given by

$$l = n - (k+1)$$

Thus the maximum value which l can have is $(n-1)$. Therefore l can have the values

$$l = 0, 1, 2, \dots, (n-1) \quad \dots(22)$$

k is called the radial quantum number and n the total quantum number or the principle quantum number.

Eigen-values of Energy

We have

$$n = \lambda$$

But λ is given by [Eq. (3)] as

$$\lambda = \frac{e^2}{4\pi\epsilon_0\hbar} \sqrt{-\frac{m_e}{2E}}$$

Therefore,

$$n = \frac{e^2}{4\pi\epsilon_0\hbar} \sqrt{-\frac{m_e}{2E}}$$

Squaring both the sides and rearranging, we get

$$E_n = -\left(\frac{m_e e^4}{32\pi^2 \epsilon_0^2 \hbar^2}\right) \frac{1}{n^2} \quad \dots(23a)$$

$$E_n = -\left(\frac{m_e e^4}{8\epsilon_0^2 \hbar^2}\right) \frac{1}{n^2} \quad \dots(23b)$$

This equation gives the eigen values of the total energy of the electron. These values of the energy are called the energy-levels of the hydrogen atom.

(1) Eq. (23a) or Eq. (23b) is identical with the expression obtained by Bohr for the energy levels of the hydrogen atom.

Radius of the First Bohr Orbit

From Eq. (2), we have

$$\begin{aligned}\alpha^2 &= -\frac{8m_r}{\hbar^2} E_n \\ &= -\frac{8m_r}{\hbar^2} \left(-\frac{m_r e^4}{32\pi^2 \epsilon_0^2 \hbar^2} \right) \frac{1}{n^2} = \left(\frac{m_r^2 e^4}{4\pi^2 \epsilon_0^2 \hbar^4} \right) \frac{1}{n^2} \\ \therefore \alpha &= \frac{m_r e^2}{2\pi \epsilon_0 \hbar^2 n} \end{aligned} \quad \dots(24)$$

From this equation, we get

$$\frac{2}{\alpha} = \frac{4\pi \epsilon_0 \hbar^2 n}{m_r e^2}$$

The value of $\frac{2}{\alpha}$ for $n = 1$, is called the radius of the first Bohr orbit and it is denoted by a_0 .

$$\therefore a_0 = \frac{4\pi \epsilon_0 \hbar^2}{m_r e^2} \quad \dots(25)$$

Radial Wave-Function and Complete Wave-Function

The solution of the radial wave equation for the radial wave-function for a given value of the principal quantum number n and the orbital quantum number l , and the derivation of an expression for the normalization constant require complicated mathematical details. So we state only the expression for normalized radial wave-function $R_{nl}(r)$ for the hydrogen atom as

$$R_{nl}(r) = - \left[\left(\frac{2}{na_0} \right)^3 \frac{(n-l-1)!}{2n(n+1)!} \right]^{1/2} \cdot e^{-\rho/2} \rho^l \cdot L_{n+l}^{2l+1}(\rho) \quad \dots(26)$$

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

$$\rho = \alpha r = \left(\frac{m_r e^2}{2\pi \epsilon_0 \hbar^2 n} \right) r \quad \dots(27)$$

The function $L_{n+l}^{2l+1}(\rho)$ are associated Laguerre functions, defined by

$$L_r^l = \frac{d^l}{dp^l} L_r(p)$$

where $L_r(p)$ are the Laguerre polynomials defined as

$$L_r(p) = e^p \frac{d^r}{dp^r} (p^r e^{-p})$$

The normalized wave-functions for the first three values of n are given in Table 7.1, and the variation of the first two radial wave-functions, $R_{10}(r)$, $R_{20}(r)$ with r/a_0 are shown in Fig. (7.4) and (7.5).

The complete wave-function for the hydrogen atom is written as

$$\Psi_{nlm}(r, \theta, \phi) = R_{nl}(r) Q_{lm}(\theta) F_m(\phi) \quad \dots(28)$$

where $n = 1, 2, 3, 4, \dots$

$l = 0, 1, 2, 3, \dots, (n-1)$

$m = 0, +1, +2, +3, \dots, +l$,

and $F_m(\phi)$, $Q_{lm}(\theta)$, and $R_{ln}(r)$ are given by Eq. (10) (Sec. 7.4), (7) (Sec. 7.5), and (26) Sec. (7.6). The complete wave-functions for the first three values of n are given in Table 7.2.

TABLE 7.1
Normalized Polar and Radial Wave Functions

n	l	m	$Q_{lm}(\theta)$	$R_{nl}(r)$
1	0	0	$\frac{1}{\sqrt{2}}$	$2 \left(\frac{1}{a_0} \right)^{3/2} e^{-r/a_0}$
2	0	0	$\frac{1}{\sqrt{2}}$	$\frac{1}{2\sqrt{2}} \left(\frac{1}{a_0} \right)^{3/2} \left(2 - \frac{r}{a_0} \right) e^{-r/2a_0}$
2	1	0	$\frac{\sqrt{6}}{2} \cos \theta$	$\frac{1}{2\sqrt{6}} \left(\frac{1}{a_0} \right)^{3/2} \frac{r}{a_0} e^{-r/2a_0}$
2	1	± 1	$\frac{\sqrt{3}}{2} \sin \theta$	$\frac{1}{2\sqrt{6}} \left(\frac{1}{a_0} \right)^{3/2} \frac{r}{a_0} e^{-r/2a_0}$
3	0	0	$\frac{1}{\sqrt{2}}$	$\frac{2}{81\sqrt{3}} \left(\frac{1}{a_0} \right)^{3/2} \left(27 - 18 \frac{r}{a_0} + 2 \frac{r^2}{a_0^2} \right) e^{-r/3a_0}$
3	1	0	$\frac{\sqrt{6}}{2} \cos \theta$	$\frac{4}{81\sqrt{6}} \left(\frac{1}{a_0} \right)^{3/2} \left(6 - \frac{r}{a_0} \right) \frac{r}{a_0} e^{-r/3a_0}$
3	1	± 1	$\frac{\sqrt{3}}{2} \sin \theta$	$\frac{4}{81\sqrt{6}} \left(\frac{1}{a_0} \right)^{3/2} \left(6 - \frac{r}{a_0} \right) \frac{r}{a_0} e^{-r/3a_0}$
3	2	0	$\frac{\sqrt{10}}{4} (3 \cos^2 \theta - 1)$	$\frac{4}{81\sqrt{30}} \left(\frac{1}{a_0} \right)^{3/2} \frac{r^2}{a_0^2} e^{-r/3a_0}$
3	2	± 1	$\frac{\sqrt{15}}{2} \sin \theta \cos \theta$	$\frac{4}{81\sqrt{30}} \left(\frac{1}{a_0} \right)^{3/2} \frac{r^2}{a_0^2} e^{-r/3a_0}$
3	2	± 2	$\frac{\sqrt{15}}{4} \sin^2 \theta$	$\frac{4}{81\sqrt{30}} \left(\frac{1}{a_0} \right)^{3/2} \frac{r^2}{a_0^2} e^{-r/3a_0}$

TABLE 7.2
Normalised Complete Wave Functions for the Hydrogen Atom

n	l	m	$\psi_{nlm}(r, \theta, \phi)$
1	0	0	$\frac{1}{\sqrt{\pi}} \left(\frac{1}{a_0}\right)^{3/2} e^{-r/a_0}$
2	0	0	$\frac{1}{4\sqrt{2\pi}} \left(\frac{1}{a_0}\right)^{3/2} \left(2 - \frac{r}{a_0}\right) e^{-r/2a_0}$
2	1	0	$\frac{1}{4\sqrt{2\pi}} \left(\frac{1}{a_0}\right)^{3/2} \frac{r}{a_0} e^{-r/2a_0} \cos \theta$
2	1	± 1	$\frac{1}{8\sqrt{\pi}} \left(\frac{1}{a_0}\right)^{3/2} \frac{r}{a_0} e^{-r/2a_0} \sin \theta e^{\pm i\phi}$
3	0	0	$\frac{1}{81\sqrt{3\pi}} \left(\frac{1}{a_0}\right)^{3/2} \left(27 - 18\frac{r}{a_0} + 2\frac{r^2}{a_0^2}\right) e^{-r/3a_0}$
3	1	0	$\frac{1}{81} \sqrt{\frac{2}{\pi}} \left(\frac{1}{a_0}\right)^{3/2} \left(6 - \frac{r}{a_0}\right) \frac{r}{a_0} e^{-r/3a_0} \cos \theta$
3	1	± 1	$\frac{1}{81\sqrt{\pi}} \left(\frac{1}{a_0}\right)^{3/2} \left(6 - \frac{r}{a_0}\right) \frac{r}{a_0} e^{-r/3a_0} \sin \theta e^{\pm i\phi}$
3	2	0	$\frac{1}{81\sqrt{6\pi}} \left(\frac{1}{a_0}\right)^{3/2} \frac{r^2}{a_0^2} e^{-r/3a_0} (3\cos^2 \theta - 1)$
3	2	± 1	$\frac{1}{81\sqrt{\pi}} \left(\frac{1}{a_0}\right)^{3/2} \frac{r^2}{a_0^2} e^{-r/3a_0} \sin \theta \cos \theta e^{\pm i\phi}$
3	2	± 2	$\frac{1}{162\sqrt{\pi}} \left(\frac{1}{a_0}\right)^{3/2} \frac{r^2}{a_0^2} e^{-r/3a_0} \sin^2 \theta e^{\pm 2i\phi}$

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{m_e e^2} = 0.53 \text{ \AA} = \text{radius of the first Bohr orbit.}$$

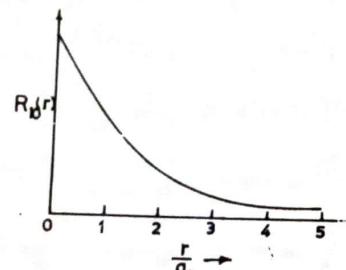


Fig. 7.4

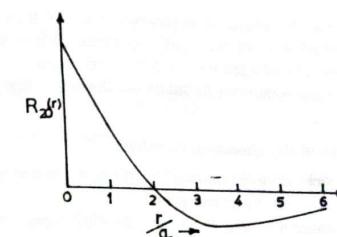


Fig. 7.5

7.7 Degeneracy of an Energy-Level of the Hydrogen Atom

The eigen-values of the energy of the hydrogen atom depend only on the principal quantum number n . For a given value of n the possible values of the orbital quantum number l are

$$l = 0, 1, 2, 3, \dots, (n-1) \quad \dots(1)$$

Thus for a given value of n , total number of values which l can have is n .

For each of the values of l , the possible values of the magnetic quantum number m are

$$m = 0, \pm 1, \pm 2, \pm 3, \dots, \pm l \quad \dots(2)$$

Thus for each value of l , the number of values which m can have is $(2l+1)$.

Therefore for the possible values of l given by Eq. (1), the total number of values of m

$$\begin{aligned} &= (2 \times 0 + 1) + (2 \times 1 + 1) + (2 \times 2 + 1) + \dots [2(n-1) + 1] \\ &= 2[1 + 2 + 3 + \dots + (n-1)] + n \\ &= 2 \left(\frac{n-1}{2}\right) [2 \times 1 + (n-1-1) \times 1] + n \\ &= (n-1)n + n \\ &= n^2 \end{aligned}$$

Thus for a given value of n which gives the energy level E_n , there are n^2 sets of values of l and m . Each set defines an independent quantum state having the same energy E_n .

This phenomenon in which there are a number of independent quantum states of a system, each belonging to the same energy level is called *degeneracy*. An energy-level which contains more than one independent quantum state is called a *degenerate* energy-level, and the total number of the independent quantum states is called the degree of degeneracy of the energy-level.

In the present case the degree of degeneracy = n^2 . All the energy-levels of the principal quantum number $n > 1$ are degenerate. For example, the first excited energy-level of hydrogen ($n = 2$) is fourfold degenerate. If the spin of the electron is also taken into consideration the degree of degeneracy is doubled.

7.8 Interpretation of the Quantum Numbers

We have seen that there are three quantum numbers n , l and m in the quantum mechanical treatment of the hydrogen atom.

The quantum number n is associated with the total energy of the electron. So it is called the *principal quantum number* or the *total quantum number*.

Now we will show that the quantum numbers l and m are related to the angular momentum of the electron.

The operator for the square of the total angular momentum is [See Sec. 4.7, Eq. (19)]

$$\hat{L}^2 = -\hbar^2 \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] \quad \dots(1)$$

It means that the operator, acting on the angular part of the wave-function, reproduces the same wave-function multiplied by the square of the total angular momentum:

$$\therefore -\hbar^2 \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] Y(\theta, \phi) = L_2 Y(\theta, \phi) \quad \dots(2)$$

$$\text{or} \quad \hat{L}^2 Y(\theta, \phi) = L_2 Y(\theta, \phi) \quad \dots(3)$$

where $Y(\theta, \phi)$ is the angular part of $\psi(r, \theta, \phi)$; and it is given by

$$Y(\theta, \phi) = Q(\theta) F(\phi) \quad \dots(4)$$

The polar equation and the azimuthal wave equation respectively are

$$\frac{1}{\sin \theta} \frac{d}{d\theta} \left(\sin \theta \frac{dQ}{d\theta} \right) + \left[l(l+1) - \frac{m^2}{\sin^2 \theta} \right] Q = 0 \quad \dots(5)$$

$$\frac{d^2 F}{d\phi^2} + m^2 F = 0 \quad \dots(6)$$

From Eq. (6)

$$m^2 = -\frac{1}{F} \frac{d^2 F}{d\phi^2} \quad \dots(7)$$

Substituting this expression for m^2 in Eq. (5)

$$\frac{1}{\sin \theta} \frac{d}{d\theta} \left(\sin \theta \frac{dQ}{d\theta} \right) + \left[l(l+1) + \frac{1}{\sin^2 \theta} \frac{d^2 F}{d\phi^2} \right] Q = 0$$

Multiplying this equation by F

$$\frac{F}{\sin \theta} \frac{d}{d\theta} \left(\sin \theta \frac{dQ}{d\theta} \right) + \left[l(l+1) F + \frac{1}{\sin^2 \theta} \frac{d^2 F}{d\phi^2} \right] Q = 0$$

$$\text{or} \quad \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial Q F}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 Q F}{\partial \phi^2} = -l(l+1) Q F$$

$$\text{or} \quad \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] Y(\theta, \phi) = -l(l+1) Y(\theta, \phi)$$

Multiplying this equation by $-\hbar^2$

$$-\hbar^2 \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] Y(\theta, \phi) = l(l+1) \hbar^2 Y(\theta, \phi) \quad \dots(8)$$

$$\text{or} \quad \hat{L}^2 Y(\theta, \phi) = l(l+1) \hbar^2 Y(\theta, \phi) \quad \dots(9)$$

This equation shows that $Y(\theta, \phi)$ is an eigen function of the operator \hat{L}^2 and the eigen value of the operator is $l(l+1) \hbar^2$.

Comparing Eqs. (3) and (9) we find that the magnitude of the total angular momentum is given by

$$L = \hbar \sqrt{l(l+1)} \quad \dots(10)$$

Thus the quantum number l determines the magnitude of the total angular momentum, and therefore, it is called the *orbital-angular momentum quantum number* or *orbital quantum number*.

The operator for the z -component of the total angular momentum is

$$\hat{L}_z = \frac{\hbar}{i} \frac{\partial}{\partial \phi}$$

$$\therefore \frac{\hbar}{i} \frac{\partial}{\partial \phi} F(\phi) = L_z F(\phi)$$

$$\text{or} \quad \hat{L}_z F(\phi) = L_z F(\phi) \quad \dots(11)$$

where L_z is the z -component of the angular momentum. A solution of the azimuthal wave equation for the hydrogen atom is

$$F(\phi) = A e^{im\phi}$$

Differentiating this equation with respect to ϕ

$$\frac{\partial F(\phi)}{\partial \phi} = A i m e^{im\phi} = im F(\phi)$$

Multiplying this equation by \hbar/i

$$\frac{\hbar}{i} \frac{\partial F(\phi)}{\partial \phi} = \frac{\hbar}{i} im F(\phi) = \hbar m F(\phi)$$

$$\hat{L}_z F(\phi) = \hbar m F(\phi) \quad \dots(12)$$

This equation shows that $F(\phi)$ is an eigen-function of the operator \hat{L}_z and the eigen-value of the operator is $\hbar m$. Comparing Eqs. (11) and (12) the z -component of the angular momentum is given by

$$L_z = \hbar m \quad \dots(13)$$

Thus the quantum number m determines the z -component of the angular momentum. When a magnetic field is applied along the z -axis, the degeneracy of the quantum states having the same values of n and l but different values

of m can be removed. Therefore, this quantum number is called the *magnetic quantum number*.

7.9 Rigid Rotator

A rigid body which can rotate about a fixed axis is called a rigid rotator. In its simplest form a rigid rotator consists of two particles at a constant distance from one another, rotating about an axis passing through their centre of mass and perpendicular to the line joining them (Fig. 7.5).

Moment of Inertia of the Rigid Rotator

Let m_1 and m_2 be respectively the masses of the two particles A and B at constant distance r from one another, and r_1 and r_2 their distances from the centre of mass, C. Their axis of rotation passes through C and perpendicular to the line AB. The moment of inertia of the particles about this axis is given by

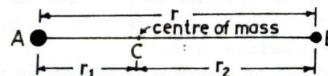


Fig. 7.6

$$I = m_1 r_1^2 + m_2 r_2^2 \quad \dots(1)$$

By the definition of the centre of mass, we have

$$m_1 r_1 = m_2 r_2$$

From this equation

$$\frac{r_1}{1/m_1} = \frac{r_2}{1/m_2} = \frac{r_1 + r_2}{1/m_1 + 1/m_2} = \frac{r}{1/m_1 + 1/m_2}$$

$$\therefore m_1 r_1 = m_2 r_2 = \left(\frac{m_1 m_2}{m_1 + m_2} \right) r$$

$$\text{Hence } r_1 = \left(\frac{m_2}{m_1 + m_2} \right) r, \text{ and } r_2 = \left(\frac{m_1}{m_1 + m_2} \right) r$$

Substituting these expressions for r_1 and r_2 in Eq. (1)

$$\begin{aligned} I &= m_1 \left(\frac{m_2}{m_1 + m_2} \right)^2 r^2 + m_2 \left(\frac{m_1}{m_1 + m_2} \right)^2 r^2 \\ &= \frac{m_1 m_2 r^2}{(m_1 + m_2)^2} [m_2 + m_1] = \left(\frac{m_1 m_2}{m_1 + m_2} \right) r^2 \quad \dots(2) \\ &= m_r r^2 \quad \dots(3) \end{aligned}$$

where $m_r = \frac{m_1 m_2}{m_1 + m_2}$ is the reduced mass of the two particles. From Eq. (3) we infer that the rotation of the two particles about the axis passing through their centre of mass and perpendicular to the line AB joining them is equivalent to the rotation, about the same axis, of a single particle of mass equal to the reduced mass m_r , located at distance r from the axis.

Wave Equation for the Rigid Rotator and its Energy Levels

The time-independent Schrödinger wave equation in spherical polar coordinates (r, θ, ϕ) for a particle of mass m_r having total energy E and potential energy V is

$$\begin{aligned} \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta} \right) \\ + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} + \frac{2m_r}{\hbar^2} (E - V) \psi = 0 \quad \dots(4) \end{aligned}$$

where ψ is a function of r, θ and ϕ . In the case of the rigid rotator, there is no potential energy and no dependence of ψ on the radial coordinate r . Therefore, Eq. (4) is simplified to the form

$$\frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} = - \frac{2m_r E}{\hbar^2} \psi$$

where the wave function ψ is a function of θ and ϕ . Multiplying both sides by r^2 , and writing $Y(\theta, \phi)$ for the function ψ

$$\left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial Y}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 Y}{\partial \phi^2} \right] Y(\theta, \phi) = - \frac{2m_r r^2 E}{\hbar^2} Y(\theta, \phi)$$

$$\text{or } -\hbar^2 \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial Y}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 Y}{\partial \phi^2} \right] Y(\theta, \phi) = 2IE Y(\theta, \phi) \quad \dots(5)$$

where I is the moment inertia $m_r r^2$. Eq. (5) is written as

$$\hat{L}^2 Y(\theta, \phi) = 2IE Y(\theta, \phi) \quad \dots(6)$$

where \hat{L}^2 is the operator for the square of the total angular momentum (See Eq. (19), Sec. 4.7).

Comparing this equation with Eq. (9), Sec. 7.8, i.e.,

$$\hat{L}^2 Y(\theta, \phi) = l(l+1)\hbar^2 Y(\theta, \phi), \text{ for the hydrogen atom, we get}$$

$$\begin{aligned} 2IE &= l(l+1)\hbar^2 \\ \therefore E_l &= \frac{l(l+1)\hbar^2}{2I} \quad \dots(7a) \end{aligned}$$

where

$$l = 0, 1, 2, \dots$$

For a rigid diatomic molecule the orbital quantum number is usually denoted by J instead of l . Thus the energy levels of a rigid diatomic molecule are given by

$$E_J = \frac{J(J+1)\hbar^2}{2I} \quad \dots(7b)$$

where $J = 0, 1, 2, \dots$

For each value of J the number of values of the magnetic quantum number M is $(2J+1)$. Therefore each energy level consists of $(2J+1)$ sub-levels each having the same energy corresponding to the value of J . Thus the energy levels are degenerate.

Rigid Rotator in a Fixed Plane

It has been pointed out that for a rigid rotator there is no potential energy and no dependence of ψ on the radial coordinate r . If the rigid rotator is confined to the $X-Y$ plane, then the polar angle, $\theta = 90^\circ$. Under these restrictions the wave Eq. (4) is simplified to the form

$$\frac{1}{r^2} \frac{d^2\psi}{d\phi^2} + \frac{2m_r}{\hbar^2} E\psi = 0 \quad \dots(8)$$

where ψ is a function of the azimuthal angle ϕ , i.e., $\psi = F(\phi)$. Multiplying both sides of Eq. (8) by r^2 and writing $F(\phi)$ for the wave function we get

$$\frac{d^2F(\phi)}{d\phi^2} + \frac{2IE}{\hbar^2} F(\phi) = 0$$

where I is the moment of inertia $m_r r^2$ of the reduced mass about the axis of rotation. Substituting m^2 for the constant $2IE/\hbar^2$, we get

$$\frac{d^2F}{d\phi^2} + m^2 F = 0 \quad \dots(9)$$

This is the time-independent Schrödinger wave equation for the rigid rotator in the $X-Y$ plane.

Wave Function for the Rotator

A solution of Eq. (9) is

$$F(\phi) = A e^{im\phi} \quad \dots(10)$$

where A is a constant and $m = 0, \pm 1, \pm 2, \dots$. To normalize the wave function, we use the condition

$$\int_0^{2\pi} FF^* d\phi = 1$$

$$\text{or } \int_0^{2\pi} (Ae^{im\phi})(Ae^{-im\phi})^* d\phi = 1$$

$$\text{or } A^2 \int_0^{2\pi} e^{im\phi} \cdot e^{-im\phi} d\phi = 1$$

$$\text{or } A^2 \times 2\pi = 1$$

$$\therefore A = \frac{1}{\sqrt{2\pi}} \quad \dots(11)$$

Hence the normalized wave function of the rotator is

$$F_m(\phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi} \quad \dots(12)$$

Energy levels

The energy levels of the rotator are given by

$$\frac{2IE}{\hbar^2} = m^2$$

or

$$E_m = \frac{m^2\hbar^2}{2I}$$

where

... (13)

$$m = 0, \pm 1, \pm 2, \dots$$

SOLVED EXAMPLES

Example 7.1. Show that for the hydrogen atom the wave function

$$Q_{20}(\theta) = \frac{\sqrt{10}}{4} (3 \cos^2 \theta - 1)$$

is a solution of the θ equation and it is normalized.

Solution:

(i) The θ equation for the hydrogen atom is

$$\frac{1}{\sin \theta} \frac{d}{d\theta} \left(\sin \theta \frac{dQ}{d\theta} \right) + \left(\beta - \frac{m^2}{\sin^2 \theta} \right) Q = 0 \quad \dots(1)$$

where $\beta = l(l+1)$.

The given wave function is for $l=2$, and $m=0$

\therefore the θ equation for $l=2$ and $m=0$ is

$$\frac{1}{\sin \theta} \frac{d}{d\theta} \left(\sin \theta \frac{dQ}{d\theta} \right) + 6Q = 0 \quad \dots(2)$$

Now the given wave function is written as

$$Q = \frac{\sqrt{10}}{4} (3 \cos^2 \theta - 1)$$

$$\therefore \frac{dQ}{d\theta} = \frac{\sqrt{10}}{4} (-3 \times 2 \cos \theta \sin \theta) = -\frac{3\sqrt{10}}{2} \cos \theta \sin \theta$$

Multiply both sides by $\sin \theta$

$$\left(\sin \theta \frac{dQ}{d\theta} = -\frac{3\sqrt{10}}{2} \cos \theta \sin^2 \theta \right)$$

$$\therefore \frac{d}{d\theta} \left(\sin \theta \frac{dQ}{d\theta} \right) = -\frac{3\sqrt{10}}{2} [\cos \theta \times 2 \sin \theta \cos \theta + \sin^2 \theta (-\sin \theta)]$$

$$\begin{aligned} \therefore \frac{1}{\sin \theta} \frac{d}{d\theta} \left(\sin \theta \frac{dQ}{d\theta} \right) &= -\frac{3\sqrt{10}}{2} [2 \cos^2 \theta - \sin^2 \theta] \\ &= -\frac{3\sqrt{10}}{2} [2 \cos^2 \theta - (1 - \cos^2 \theta)] \\ &= -\frac{3\sqrt{10}}{2} (3 \cos^2 \theta - 1) \end{aligned} \quad \dots(3)$$

$$\text{And } 6Q = \frac{6\sqrt{10}}{4} (3 \cos^2 \theta - 1) = \frac{3\sqrt{10}}{2} (3 \cos^2 \theta - 1) \quad \dots(4)$$

Adding Eq. (3) and (4)

$$\frac{1}{\sin \theta} \frac{d}{d\theta} \left(\sin \theta \frac{dQ}{d\theta} \right) + 6Q = 0$$

This equation is the same as the θ equation for $l=2$ and $m=0$. Therefore, the given wave function is a solution of the θ equation.

(ii) The normalization condition for the total wave function is

$$\iiint \psi(r, \theta, \phi) \psi^*(r, \theta, \phi) d\tau = 1 \quad \dots(1)$$

where $d\tau$ is the volume element in spherical polar coordinates,

$$d\tau = (r \sin \theta d\phi) (r d\theta) dr = (r^2 dr) (\sin \theta d\theta) (d\phi)$$

The total wave function is product of the three separate functions $R(r) Q(\theta) F(\phi)$, i.e.,

The Hydrogen Atom and The Rigid Rotator

$$\psi(r, \theta, \phi) = RQF$$

Hence the normalization condition becomes

$$\int_0^\infty RR^* r^2 dr \int_0^\pi QQ^* \sin \theta d\theta \int_0^{2\pi} FF^* d\phi = 1 \quad \dots(2)$$

\therefore for the wave function $Q(\theta)$, the normalization condition is

$$\int_0^\pi QQ^* \sin \theta d\theta = 1 \quad \dots(3)$$

The given wave function is

$$Q_{20}(\theta) = \frac{\sqrt{10}}{4} (3 \cos^2 \theta - 1) = \frac{\sqrt{10}}{4} [3(1 - \sin^2 \theta) - 1]$$

or

$$Q = \frac{\sqrt{10}}{4} (2 - 3 \sin^2 \theta)$$

Since Q is real, the complex conjugate Q^* has the same value. Now we evaluate the integral on left-side of Eq. (3)

$$\begin{aligned} \int_0^\pi QQ^* \sin \theta d\theta &= \int_0^\pi \frac{10}{16} (2 - 3 \sin^2 \theta)^2 \sin \theta d\theta \\ &= \frac{10}{16} \int_0^\pi (4 - 12 \sin^2 \theta + 9 \sin^4 \theta) \sin \theta d\theta \\ &= \frac{10}{16} \times 2 \int_0^{\pi/2} (4 \sin \theta - 12 \sin^3 \theta + 9 \sin^5 \theta) d\theta \end{aligned}$$

The values of the definite integrals are

$$\int_0^{\pi/2} \sin \theta d\theta = 1, \quad \int_0^{\pi/2} \sin^3 \theta d\theta = \frac{2}{3}$$

$$\int_0^{\pi/2} \sin^5 \theta d\theta = \frac{4}{5} \cdot \frac{2}{3} = \frac{8}{15}$$

Hence

$$\int_0^\pi QQ^* \sin \theta d\theta = \frac{10 \times 2}{16} \left[4 - 12 \times \frac{2}{3} + 9 \times \frac{8}{15} \right] = \frac{5}{4} \times \frac{4}{5} = 1$$

Hence the wave function is normalized.

Example 7.2. The wave function $\psi(r, \theta, \phi)$ of the hydrogen atom for 1s state is

$$\psi(1s) = \left(\frac{1}{\pi a_0^3} \right)^{1/2} e^{-r/a_0}$$

Show that the wave function is normalized, and find the average distance of the electron from the nucleus, in 1s orbital, given that

$$\int_0^\infty x^n e^{-ax} dx = \frac{[(n+1)!]}{a^{n+1}}$$

Solution:

(i) the normalization condition for the complete wave function in 1s state is

$$\begin{aligned} \iiint \psi(1s) \psi^*(1s) d\tau &= 1 \\ \iiint |\psi(1s)|^2 d\tau &= 1 \end{aligned} \quad \dots(1)$$

or

where $d\tau$ is the volume element.

$$d\tau = (r \sin \theta d\phi) (rd\theta) dr = (r^2 dr) (\sin \theta d\theta) (d\phi)$$

Now we evaluate the integral on left side of Eq. (1)

$$\begin{aligned} \iiint |\psi_1(1s)|^2 d\tau &= \iiint \frac{1}{\pi a_0^3} e^{-2r/a_0} (r^2 dr) (\sin \theta d\theta) (d\phi) \\ &= \frac{1}{\pi a_0^3} \int_0^\infty r^2 e^{-2r/a_0} dr \int_0^\pi \sin \theta d\theta \int_0^{2\pi} d\phi \end{aligned} \quad \dots(2)$$

The values of the integrals are

$$\int_0^\infty r^2 e^{-2r/a_0} dr = \frac{\Gamma(2+1)}{(2/a_0)^3} = 2 \times \frac{a_0^3}{8} = \frac{a_0^3}{4}$$

$$\int_0^\pi \sin \theta d\theta = 2 \int_0^{\pi/2} \sin \theta d\theta = 2, \quad \text{and} \int_0^{2\pi} d\phi = 2\pi$$

Substituting these values in Eq. (2)

$$\iiint |\psi_1(1s)|^2 d\tau = \frac{1}{\pi a_0^3} \times \frac{a_0^3}{4} \times 2 \times 2\pi = 1$$

Hence the wave function is normalized.

(ii) Expectation value of r in 1s state

$$\begin{aligned} \langle r \rangle &= \iiint \psi^*(1s) r \psi(1s) d\tau \\ &= \iiint \left(\frac{1}{\pi a_0^3} \right)^{1/2} e^{-r/a_0} \left(\frac{1}{\pi a_0^3} \right)^{1/2} e^{-r/a_0} (r^2 dr) (\sin \theta d\theta) (d\phi) \\ &= \frac{1}{\pi a_0^3} \int_0^\infty r^3 e^{-2r/a_0} dr \int_0^\pi \sin \theta d\theta \int_0^{2\pi} d\phi \end{aligned}$$

The values of the integrals are

$$\int_0^\infty r^3 e^{-2r/a_0} dr = \frac{\Gamma(3+1)}{(2/a_0)^4} = \frac{3 \times 2 \times 1}{1} \times \frac{a_0^4}{16} = \frac{3a_0^4}{8}$$

$$\int_0^\pi \sin \theta d\theta = 2, \quad \text{and} \int_0^{2\pi} d\phi = 2\pi$$

Hence

$$\langle r \rangle = \frac{1}{\pi a_0^3} \times \frac{3a_0^4}{8} \times 2 \times 2\pi = \frac{3}{2} a_0$$

Example 7.3. The normalized wave function of the hydrogen atom for 1s state is

$$\psi(1s) = \left(\frac{1}{\pi a_0^3} \right)^{1/2} e^{-r/a_0}$$

where $a_0 = \frac{4\pi\epsilon_0\hbar^2}{m_e e^2}$ is the Bohr radius. Find the expectation value of the potential energy of the electron in 1s state, given that

$$\int_0^\infty x^n e^{-ax} dx = \frac{(n+1)}{a^{n+1}}$$

Solution:

The potential energy of the electron at distance r from the nucleus is given by

$$V = -\frac{e^2}{4\pi\epsilon_0 r} \quad (\text{in SI units})$$

The expectation value of the potential energy is given by

$$\begin{aligned} \langle V \rangle &= \iiint \psi^*(1s) V \psi(1s) d\tau \\ &= \iiint \left(\frac{1}{\pi a_0^3} \right)^{1/2} e^{-r/a_0} \left(-\frac{e^2}{4\pi\epsilon_0 r} \right) \left(\frac{1}{\pi a_0^3} \right)^{1/2} e^{-r/a_0} \\ &\quad \cdot (r^2 dr) (\sin \theta d\theta) (d\phi) \\ &= -\left(\frac{e^2}{4\pi\epsilon_0} \right) \frac{1}{\pi a_0^3} \int_0^\infty r e^{-2r/a_0} dr \int_0^\pi \sin \theta d\theta \int_0^{2\pi} d\phi \end{aligned}$$

The values of the integrals are

$$\begin{aligned} \int_0^\infty r e^{-2r/a_0} dr &= \frac{\Gamma(1+1)}{(2/a_0)^2} \\ &= \frac{1}{1} \times \frac{a_0^2}{4} = \frac{a_0^2}{4} \end{aligned}$$

$$\int_0^\pi \sin \theta d\theta = 2, \quad \text{and} \int_0^{2\pi} d\phi = 2\pi$$

Hence

$$\begin{aligned} \langle V \rangle &= -\left(\frac{e^2}{4\pi\epsilon_0} \right) \frac{1}{\pi a_0^3} \times \frac{a_0^2}{4} \times 2 \times 2\pi \\ &= -\frac{e^2}{4\pi\epsilon_0 a_0} = -\frac{e^2}{4\pi\epsilon_0} \times \frac{m_e e^2}{4\pi\epsilon_0 h^2} \\ &= -\frac{m_e e^4}{(4\pi\epsilon_0)^2 h^2} \end{aligned}$$

QUESTIONS AND PROBLEMS

- (a) Write the time-independent Schrödinger wave equation for the hydrogen atom in spherical polar coordinates and separate it into three differential equations for the three parts of the total wave-function.
(b) Solve the azimuthal wave equation and show that the magnetic quantum number m must be zero or a positive or negative integer.
- (a) State the radial part of the time-independent Schrödinger wave equation for the hydrogen atom with interpretation of the wave-function.
(b) Apply this equation to find the energy of the atom in the ground state.
(Ans. $E_1 = -\frac{m_e e^4}{32\pi^2 \epsilon_0^2 \hbar^2}$)

3. Write down the radial part of the time-independent Schrödinger wave equation for the hydrogen atom and solve the equation to obtain the eigen values of the energy of the atom.

$$(\text{Ans. } E_n = -\frac{m_e e^4}{32\pi^2 \epsilon_0^2 h^2} \frac{1}{n^2})$$

4. State Schrödinger's equation for hydrogen atom in spherical polar coordinates. Explain the significance of various quantum numbers defining a state of the system. What is the order degeneracy of a certain energy state?
5. (a) Explain how the problem of the hydrogen atom can be solved quantum-mechanically. Solve the radial part of the Schrödinger equation for the hydrogen atom and obtain the eigen-values of the energy. Explain the degeneracy in the spectrum.
6. The complete wave function of the hydrogen atom for 2p state is

$$\psi_{210} = \frac{1}{4} \left(\frac{1}{2\pi a_0^3} \right)^{1/2} \frac{r}{a_0} e^{-r/2a_0} \cos \theta$$

Prove that the wave function is normalized. Given that

$$\int_0^\infty x^n e^{-ax} dx = \frac{(n+1)}{a^{n+1}}$$

7. Find the expectation value of the distance of the electron from the nucleus in the hydrogen atom in 2p state.
 (Ans. 5a₀)
8. Obtain the Schrödinger wave equation for a rigid rotator that is constrained to rotate about a fixed axis and that has a moment of inertia I about that axis. Find the normalized energy eigen-functions and eigen values of energy. Is there any degeneracy?

APPENDIX 1

Relation between Relativistic Energy E and Relativistic Momentum p for the a particle

The total relativistic energy E of a particle of rest mass m_0 moving with velocity v is given by

$$E = m c^2 \quad \dots(1)$$

$$\text{or } E = \frac{m_0 c^2}{\sqrt{1 - v^2/c^2}}$$

Squaring both the sides of this equation

$$E^2 \left(1 - \frac{v^2}{c^2} \right) = m_0^2 c^4 \quad \dots(2)$$

The relativistic momentum p of the particle is

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

Squaring both the sides of this equation

$$p^2 = \frac{E^2 v^2}{c^4}$$

$$p^2 c^2 = \frac{E^2 v^2}{c^2}$$

$$\text{or } \frac{E^2 v^2}{c^2} = p^2 c^2 \quad \dots(3)$$

Now adding Eqs. (2) and (3), we get

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

$$E = (p^2 c^2 + m_0^2 c^4)^{1/2} \quad \dots(4)$$

APPENDIX 2

Schwarz' Inequality

Let f and g be two functions of x such that the following integrals exist

$$A = \int f^* f dx, \quad B = \int f^* g dx, \quad C = \int g^* g dx$$

Let λ be a real variable independent of x . Then the following integral is always positive or zero (zero only when g is directly proportional to f), and hence has no real roots in λ .

$$\begin{aligned} & \int [\lambda f^*(x) + g^*(x)] [\lambda f(x) + g(x)] dx \\ &= \int [f^* f \lambda^2 + (f^* g + g^* f) \lambda + g^* g] dx \\ &= \lambda^2 A + \lambda \left[\int f^* g dx + \int g^* f dx \right] + \int g^* g dx \\ &= \lambda^2 A + \lambda (B + B^*) + C \\ &= A\lambda^2 + (B + B^*)\lambda + C \end{aligned}$$

The roots of

$$A\lambda^2 + (B + B^*)\lambda + C = 0 \text{ are given by}$$

$$\lambda = -\frac{B + B^*}{2A} \pm \frac{1}{2A} \sqrt{(B + B^*)^2 - 4AC}$$

For no real roots the following inequality must hold

$$4AC \geq (B + B^*)^2$$

Suppose $B = a + ib$, then $B^* = a - ib$.

$$\therefore B + B^* = 2a, \quad \text{and } BB^* = |B|^2 = a^2 + b^2$$

$$\text{Hence } 4AC \geq 4a^2$$

$$\text{or } AC \geq a^2$$

$$\text{or } AC \geq |B|^2 - b^2$$

$$\text{or } AC \geq |B|^2$$

$$\text{or } \left[\int f^* f dx \right] \left[\int g^* g dx \right] \geq \left| \int f^* g dx \right|^2$$

This is the general form of Schwarz' inequality.

APPENDIX 3

Some Physical Constants and Units

Quantity	Symbol	Value
Angstrom unit	\AA	10^{-10} m
Avogadro's number	N	$6.023 \times 10^{23} \text{ mole}^{-1}$
Bohr radius	a_0	$5.2918 \times 10^{-11} \text{ m}$
Boltzmann's constant	k	$1.3806 \times 10^{-23} \text{ J/K}$
Compton wavelength of electron	$\lambda_0 = \frac{h}{m_0 c}$	0.02426 \AA
Electron charge	e	$1.6022 \times 10^{-19} \text{ C}$
Electron rest mass	m_0	$9.1096 \times 10^{-31} \text{ kg}$
Electron volt	eV	$1.6022 \times 10^{-19} \text{ J}$
Electron rest energy	$m_0 c^2$	$5.1 \times 10^5 \text{ eV}$
Ideal gas constant	R	8.3142 J/mol K
Neutron rest mass	m_n	$1.6749 \times 10^{-27} \text{ kg}$
Permeability of free space	μ_0	$4\pi \times 10^{-7} \text{ Wh/Am (H/m)}$
Permittivity of free space	ϵ_0	$8.8542 \times 10^{-12} \text{ C}^2/\text{Nm}^2 (\text{F/m})$
Planck's constant	h	$6.6256 \times 10^{-34} \text{ Js}$
	$\hbar = \frac{h}{2\pi}$	$1.0546 \times 10^{-34} \text{ Js}$
Proton rest mass	m_p	$1.6726 \times 10^{-27} \text{ kg}$
Speed of light in free space	c	$2.9979 \times 10^8 \text{ m/s}$
Stefan's constant	σ	$5.6697 \times 10^{-8} \text{ W/m}^2 \text{K}^4$

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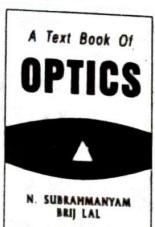
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