2

Quantum Mechanics

2.1 INTRODUCTION

The motion of particles which can be observed directly or through microscope can be explained by classical mechanics. But when the phenomena like photoelectric effect, X-rays, ultraviolet catastrophe, superconductivity were discovered, classical physics failed to explain such phenomena. The microworld of atoms obeys different laws. The new laws applicable for microparticles constitute quantum mechanics. The revision of classical concepts began with the seminal hypothesis of Planck and many distinguished physicists such as Einstein, Bohr, de Broglie, Schrödinger, Born, Pauli, Heisenberg, Dirac and others contributed to the development of quantum mechanics.

Quantum Mechanics is a branch of physics dealing with the behaviour of matter and energy on the microscope scale of atoms and subatomic particles. Quantum mechanics is fundamental to our understanding of all the fundamental forces of nature except gravity.

It provides the foundation to several branches of physics, including Electromagnetism, Particle Physics, Condensed Matter Physics, and some parts of Cosmology. Quantum Mechanics is essential to understand the theory of chemical bonding (and hence, the entire subject of chemistry), structural biology, and technologies such as electronics, information technology (IT), and nanotechnology. Hundreds of experiments and commendable work in applied sciences have proved quantum mechanics a successful and practical science.

2.2 WAVE AND PARTICLE DUALITY OF RADIATION

The concept of a particle is easy to grasp. It has mass, it is located at some definite point, it can move from one place to another, it gives energy when slowed down or stopped. Thus, the particle is specified by: (i) mass, m; (ii) velocity, v; (iii) momentum, p; and (iv) energy, E.

The concept of a wave is a bit more difficult than that of a particle. A wave is spread out over a relatively large region of space, it cannot be said to be located just here and there, it is hard to think of mass being associated with a wave. Actually, a wave is nothing but a spread out disturbance. A wave is specified by its: (i) frequency, (ii) wavelength, (iii) phase or wave velocity, (iv) amplitude, and (v) intensity.

waves. His suggestion was based on the fact: if radiation like light can act like wave sometime and like a particle at other times, then the material particles (e.g., electron, neutron, etc.) should also act as wave at some other times. According to de Broglie's hypothesis, a moving particle is associated with a wave which is known as de Broglie wave. The wavelength of the matter wave is given by

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

where m is the mass of the material particle, v its velocity and p is its momentum.

Fig. 2.1 Diagrammatic representation of a particle and a wave. A particle is localized at a point in space whereas a wave spreads over a large volume.

de Broglie wavelength. The expression of the wavelength associated with a material particle can be derived on the analogy of radiation as follows:

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

$$E = h\gamma = \frac{hc}{\lambda} \quad \text{... (1)}$$

where c is the velocity of light in vacuum and λ is its wavelength.

According to Einstein energy mass relation

$$E = mc^2 \quad \text{... (2)}$$

From equations (1) and (2), we get

$$mc^2 = \frac{hc}{\lambda} \text{ or } \lambda = \frac{hc}{mc^2} \text{ or } \lambda = \frac{h}{mc} \quad \text{... (3)}$$

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

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

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

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

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

or
$$p = \sqrt{2mE}$$

$\therefore$ de Broglie wavelength

$$\lambda = \frac{h}{\sqrt{2mE}} \quad \text{... (5)}$$

de Broglie's wavelength associated with electrons. Let us consider the case of an electron at rest mass m, and charge e which is accelerated by a potential V volts from rest to velocity v, then

$$\frac{1}{2} m_0 v^2 = eV \quad \text{or} \quad v = \sqrt{\frac{2eV}{m_0}}$$

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

or

$$\lambda = \frac{6.625 \times 10^{-34}}{\sqrt{\left(2 \times 1.632 \times 10^{-19} V \times 9.1 \times 10^{-31}\right)}}$$

$$= \frac{12.26}{\sqrt{V}} \text{ Å}$$

If $V = 100$ volts, then

$$\lambda = 1.226 \text{ Å}. \qquad \text{... (6)}$$

Equation (6) shows that the wavelength associated with an electron accelerated to 100 volts is 1.226 Å.

Wave Velocity of de Broglie Wave

The wave velocity u is given by the following expression:

$$u = \gamma \lambda$$

where γ is the frequency of matter waves. According to Planck's theory,

$$E = h\gamma$$

and from Einstein's relation,

$$E = mc^2$$

$$\therefore \quad h\gamma = mc^2 \quad \text{or} \quad \gamma = \frac{mc^2}{h} \qquad \text{...(1)}$$

For matter waves, $\lambda = \dfrac{h}{mv}$ ...(2)

Substituting these values, we get

$$u = \frac{mc^2}{h} \times \frac{h}{mv} = \frac{c^2}{v} \qquad \text{...(3)}$$

where v is the speed of material particle which is less than the speed of light c.

The wave velocity can also be expressed in terms of wavelength, we know that

$$\gamma = \frac{E}{h} = \frac{\frac{1}{2} mv^2}{h} = \frac{eV}{h} \left[\because \frac{1}{2} mv^2 = eV\right] \qquad \text{... (4)}$$

Multiplying and dividing the right-hand side of equation (4) by $h/2\,m$, we have

$$\gamma \frac{h}{2m} \times \frac{2meV}{h^2} = \frac{h}{2m} \times \frac{1}{\lambda^2} \quad \text{where} \quad \lambda = \frac{h}{\sqrt{2meV}}$$

$$\therefore \qquad u = \gamma\lambda = \frac{h}{2\,m} \times \frac{1}{\lambda^2} \times \lambda = \frac{h}{2\,m\lambda} \qquad \text{... (5)}$$

Equations (3) and (5) are the different forms of the wave velocity of de Broglie wave.

2.4 EXPERIMENTAL VERIFICATION OF DE BROGLIE'S THEORY OF MATTER WAVES: DIFFRACTION OF MATERIAL PARTICLES

(i) Davisson and Germer Experiment on Electron Diffraction

If a material particle has a wave character, it is expected to show phenomena like interference and diffraction. In 1927, Davisson and Germer demonstrated that a beam of electrons does suffer diffraction. Their apparatus is shown in Fig. 2.2. Electrons from a heated filament are accelerated through a variable potential V and emerge from the 'electron gun' G. This electron beam falls normally on a nickel crystal C. The electrons are diffracted from the crystal in all directions. The intensity of the diffracted beam in different directions is measured by a Faraday cylinder F (connected to a galvanometer), which can be moved along a circular scale S. The crystal can be turned about an axis parallel to the incident beam. Thus, any azimuth of the crystal can be presented to the plane defined by the incident beam and the beam entering the Faraday cylinder.

First of all, the accelerating potential V is given a low value, and the crystal is turned at any arbitrary azimuth. The Faraday cylinder is moved to various positions

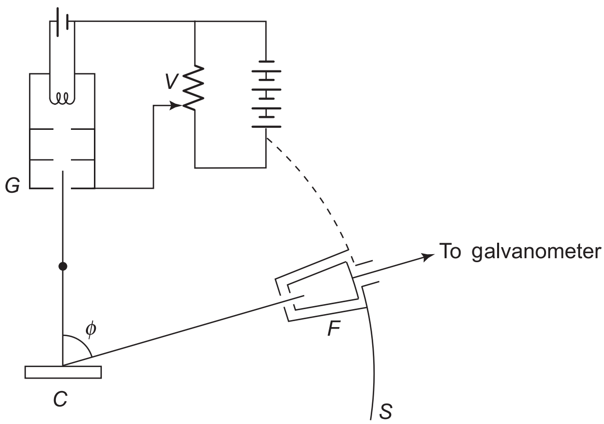

Fig. 2.2 Davisson Germer experiment setup.

on the scale *S* and the galvanometer current at each position is noted. The current, which is a measure of the intensity of the diffracted beam, is plotted against the angle ϕ between the incident beam, and the beam entering the cylinder. The observations are repeated for different accelerating potentials and the corresponding curves are drawn as shown in Fig. 2.3.

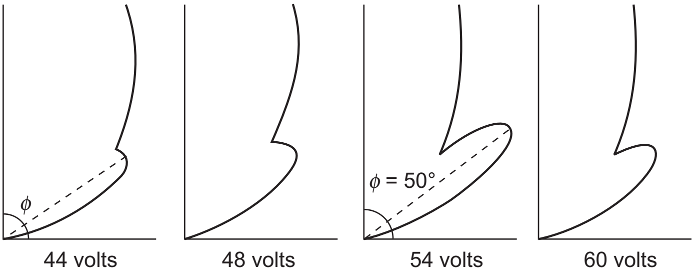

Fig. 2.3 Variation of intensity with angle ϕ

It is seen that a 'bump' begins to appear in the curve for 44-volt electrons. With increasing potential, the bump moves upwards and becomes most prominent in the curve for 54 volt electrons at $\phi = 50°$. At higher potentials the bump gradually disappears.

The bump in its most prominent state verifies the existence of electron waves. For, according to de Broglie, the wavelength associated with an electron accelerated through V volts is

$$\lambda = \frac{12.26}{\sqrt{V}} \text{ Å},$$

Hence, the wavelength associated with a 54-volt electron is

$$\lambda = \frac{12.26}{\sqrt{(54)}} = 1.67 \text{ Å}.$$

Now, it is known from X-ray analysis that the nickel crystal acts as a plane diffraction grating with grating space = d = 0.91 Å (Fig. 2.4). According to experiment, we have a diffracted electron beam at $\phi = 50°$. This arises from wave-like diffraction from the family of Bragg atomic planes. The corresponding angle of incidence relative to the family of Bragg planes is $\theta = 65° \left(= \frac{180° - 50°}{2}\right)$. Hence, using the Bragg's equation (taking the order $n = 1$), we get

$$\lambda = 2\, d \sin \theta$$
$$= 2\,(0.91 \text{ Å}) \sin 65° = 1.65 \text{ Å}.$$

This being in excellent agreement with the wavelength computed from de Broglie hypothesis, shows that electrons are wave-like in some circumstances. Other fundamental particles like neutrons also show wave-like properties. The Davisson-Germer experiment thus provides direct verification of de Broglie hypothesis of the wave nature of moving particles.

The diffraction patterns produced by electron beams were strikingly similar to the X-ray diffraction patterns obtained from powder samples. Thus, the experiment of G.P. Thomson and Kikuchi provided irrefutable proof to the existence of de Broglie waves.

2.5 PROPERTIES OF MATTER WAVES

Following are the properties of matter waves:

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

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

(3) When $v = 0$ then $\lambda = \infty$, i.e., wave becomes indeterminate and if $v = \infty$ then $\lambda = 0$. This shows that matter waves are generated by the motion of particles. These waves are produced whether the particles are charged particles or they are uncharged ($\lambda = \dfrac{h}{mv}$ is independent of charge). This fact reveals that these waves are not electromagnetic waves but they are a new kind of waves (electromagnetic waves are produced only by motion of charged particles).

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

(5) The velocity of matter waves is greater than the velocity of light. This can be proved as under:

We know that $E = h\gamma$ and and $E = mc^2$

$$\therefore \qquad h\gamma = mc^2 \qquad \text{or} \qquad v = \frac{mc^2}{h}$$

The wave velocity (v_p) is given by

$$v_p = \gamma \times \lambda = \frac{mc^2}{h} \times \frac{h}{mv} \qquad \therefore \lambda = \frac{h}{mv}$$

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

As particle velocity v cannot exceed c (velocity of light), hence v_p is greater than the velocity of light.

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

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

Wavelength of Macroscopic Bodies

For an electron having an energy 100 eV, the de Brogile wavelength is 1.33 Å which is more than the size of the electron. Whereas the wavelength of macroscopic bodies is insignificant in comparison to the size of the bodies themselves even at very low velocities, e.g., if we consider a cricket ball of mass 500 gm flying with velocity 20 km/hr, its wavelength comes to

$$\lambda = \frac{6.62\times 10^{-34}\,\text{Js}}{0.5\,\text{kg}\times 13.9\,\text{m/s}} = .95\times 10^{-34} = 10^{-34}\text{ m} = 10^{-24}\text{ Å}$$

which is insignificant in comparison to the size of the ball.

2.6 WAVE PACKET, PHASE VELOCITY AND GROUP VELOCITY

Wave velocity is also called phase velocity. Wave motion is a form of disturbance which travels through a medium due to repeated periodic motion of the particles of the medium about their mean positions, the motion being handed over from one particle to the next. The individual oscillators which make up the medium only execute simple harmonic motion about their mean positions and do not themselves travel through the medium with the wave. Every particle begins its vibration a little later than its predecessor and there is a progressive change of phase as we travel from one particle to the next. It is the phase relationship of these particles that we observe as a wave and **the velocity with which the plane of equal phase travels through the medium is known as phase velocity or wave velocity.**

Let us assume that a particle like an electron can be described mathematically by a sine wave $\psi = A\sin(\omega t - kx)$.

This wave has no beginning and no end. It is of infinite extent and completely nonlocalised. But particle (electron) is confined to a very small volume. Therefore, a monofrequency wave cannot represent a particle. It implies that the de Broglie waves are not harmonic waves but could be a combination of several waves. A superposition of several waves of slightly different frequencies gives rise to a **wave packet**. Such a wave packet possesses both wave and particle properties. The regular separation between successive maxima in a wave packet is the characteristic of a wave and at the same time it has a particle-like localization in space.

A wave packet can be described in terms of a superposition of individual harmonic waves of slightly different frequencies centred on a frequency, v_0. Let a superposition of two waves be

$$\psi_1 = A\sin(k_1x - \omega_1 t)$$
$$\psi_2 = A\sin(k_2x - \omega_2 t)$$

$$\therefore \quad \psi = \psi_1 + \psi_2$$
$$= A\sin(k_1x - \omega_1 t) + A\sin(k_2x - \omega_2 t)$$

$$= 2A\sin\left[\frac{1}{2}(k_1+k_2)x - \frac{1}{2}(\omega_1+\omega_2)t\right]\ \cos\left[\frac{1}{2}(k_1+k_2)x - \frac{1}{2}(\omega_1+\omega_2)t\right]$$

the group and phase velocities are the same, i.e., in case of electromagnetic waves in vacuum.

Relation between Particle Velocity and Group Velocity

Consider a particle of rest mass m_0 and moving with velocity v. Let ω be the angular frequency and k be the wave number of de Broglie waves associated with a particle.

$$\omega = 2\pi\gamma = 2\pi\left(\frac{mc^2}{h}\right) = \frac{2\pi m_0}{\sqrt{1-\frac{v^2}{c^2}}} \times \frac{c^2}{h}$$

$$k = \frac{2\pi}{\lambda} = 2\pi\,\frac{mv}{h} = \frac{2\pi}{h}\frac{m_0}{\sqrt{1-\frac{v^2}{c^2}}}.v$$

$$\text{wave velocity } v_p = \frac{\omega}{k} = \frac{c^2}{v}$$

As $v < c$, **the phase velocity of the associated wave is always greater than c, the velocity of light.**

The group velocity $v_g = \dfrac{d\omega}{dk} = \dfrac{d\omega/dv}{dk/dv}$.

$$\frac{d\omega}{dv} = \frac{2\pi m_0 c^2}{h}\left(-\frac{1}{2}\right)\left(1-\frac{v^2}{c^2}\right)^{-3/2} \times \frac{-2v}{c^2} = \frac{2\pi m_0 v}{h\left(1-\frac{v^2}{c^2}\right)^{3/2}}$$

$$\frac{dk}{dv} = \frac{2\pi m_0}{h}\left(1-\frac{v^2}{c^2}\right)^{-1/2} + \frac{2\pi m_0 v}{h}\left[\left(\frac{-1}{2}\right)\left(1-\frac{v^2}{c^2}\right)^{-3/2}.\left(\frac{-2v}{c^2}\right)\right]$$

$$\frac{dk}{dv} = \frac{2\pi m_0}{h}\left(1-\frac{v^2}{c^2}\right)^{-3/2}\left[1-\frac{v^2}{c^2}+\frac{v^2}{c^2}\right]$$

$$= \frac{2\pi m_0}{h}\left(1-\frac{v^2}{c^2}\right)^{-3/2}$$

$$\therefore \quad v_g = \frac{dw/dv}{dk/dv} = \frac{2\pi m_0 v}{h[1-v^2/c^2]^{3/2}} \times \frac{h(1-v^2/c^2)^{3/2}}{2\pi m_0} = v$$

$$\therefore \quad v_g = v$$

Thus, **the de Broglie wave group travels with the same velocity as that of the particle.**

2.7 WAVE FUNCTION

Waves represent the propagation of a disturbance in a medium. Light waves are represented by electromagnetic field variations and sound waves are represented by pressure variations. The de Broglie wave associated with a moving particle cannot be specified in a similar manner, since electrons have wave properties, it may be assumed that a quantity ψ represents a de Broglie wave just as the electric vector represents a light wave. The quantity ψ is called the wave function. $\psi(x, y, z, t)$ is function of space and time coordinates and it represents position of particle at some time t. However, it is not possible to locate a particle precisely at position x, y, z, there is only a probability of the particle being at the specific point (x, y, z). ψ is usually a complex quantity.

2.8 PHYSICAL INTERPRETATION OF WAVE FUNCTION

The first and the simple interpretation of ψ was given by Schrödinger himself in terms of charge density. We know that in any electromagnetic wave system if A is the amplitude of the wave, then the energy density, i.e., energy per unit volume is equal to A^2, so that the number of photons per unit volume, i.e., photon density is equal to $A^2/h\gamma$ or the photon density is proportional to A^2 as $h\gamma$ is constant. If ψ is the amplitude of matter waves at any point in space, then the particle density at that point may be taken as proportional to ψ^2. Thus, ψ^2 is a measure of particle density. When this is multiplied by the charge of the particle, the charge density is obtained. In this way, ψ^2 is a measure of charge density. It is observed that in some cases, ψ is appreciably different from zero within some finite region known as wave packet. It is natural to ask, "where is the particle in relation to wave packet?" To explain it, Max Born suggested a new idea about the physical significance of ψ which is generally accepted nowadays. According to Max Born **$\psi\psi^* = |\psi|^2$ gives the probability of finding the particle in the state ψ, i.e., ψ^2 is a measure of probability density.** The probability of finding a particle in volume $d\tau = dx\,dy\,dz$ is given by $|\psi|^2\,dx\,dy\,dz$. For the total probability of finding the particle somewhere is, of course, unit, i.e., the particle is certainly to be found somewhere in space.

$$\iiint |\psi|^2\,dx\,dy\,dz = 1$$

ψ satisfying above requirement is said to be normalized.

Normalization Condition

If at all the particle exists, the particle is certainly somewhere in the universe therefore, the probability of finding the particle somewhere in the universe must be unity. Since the probability of its being located in an elemental volume is proportional to $|\psi|^2\,dx\,dy\,dz$, it is convenient to choose the constant of proportionality such that the sum of the probabilities over all values of x, y, z must be unity. Thus,

$$\iiint_{-\infty}^{\infty} \psi\psi^* \, dx \, dy \, dz = 1$$

This is called the normalization condition. A wave function satisfying the above condition is said to be normalized.

Requirement of an Acceptable Wave Function

Besides being normalizable, an acceptable wave function must fulfil the following requirements:

1. ψ must be finite everywhere. If, for instance Ψ is infinite, it would mean an infinitely large probability of finding the particle at that point. This would violate the uncertainty principle $\therefore$ ψ must have a finite or zero value at any point.
2. ψ must be single valued. If ψ has more than one value at any point, it would mean more than one value of probability of finding the particle at that point which is obviously ridiculous.
3. It must be continuous and have a continuous first derivative everywhere. This is necessary from Schrödinger equation itself which shows that $d^2\psi/dx^2$ must be finite everywhere. This can be so only if $d\Psi/dx$ has no discontinuity at any boundary. Furthermore, the existence of $d\psi/dx$ as a continuous function implies ψ too is continuous across the boundary.

These requirements which must be fulfilled by an acceptable wave function carry great significance when the Schrödinger's steady state equation for a given system is solved to obtain a wave function which fulfils these requirements, then we find that the equation can be solved only for the value of energy of the system. Thus, energy quantization appears in wave mechanics as a natural feature of the solution of the wave function. **The values of energy for which Schrödinger equation can be solved are called eigenvalues and the corresponding (acceptable) wave functions are called eigenfunctions.**

2.9 HEISENBERG'S UNCERTAINTY PRINCIPLE

A monochromatic wave is infinite in extent so instead of associating a single monochromatic de Broglie wave with a moving particle, we associate a wave packet consisting of a group of waves of nearly equal amplitude centred around de Broglie $\lambda = h/p$ of the particle. The wave packet has the dimensions of the localized particle and travels with the same velocity as the particle.

The association of a group of waves with a moving particle that the position of the particle at any instant of time cannot be specified with any desired degree of accuracy. The particle can be somewhere within the group of waves, i.e., within a small region Δx of space (Δx is linear spread of the wave packet) Fig. 2.7.

The probability of finding the particle is maximum at the centre of the wave packet and falls to zero at its ends. Therefore, there is an uncertainty Δx in the position of the particle. A wave packet is formed by waves having a range of wavelength.

2.10 ELECTRON DIFFRACTION EXPERIMENT

Let us consider a stream of electrons moving along x direction passes through a narrow slit of width d ($= \Delta y$). If Δy is comparable to the wavelength of the electron beam, then the electrons are diffracted. According to single slit diffraction pattern a central maxima and two secondary minima are formed as shown in Fig. 2.4. According to diffraction theory,

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

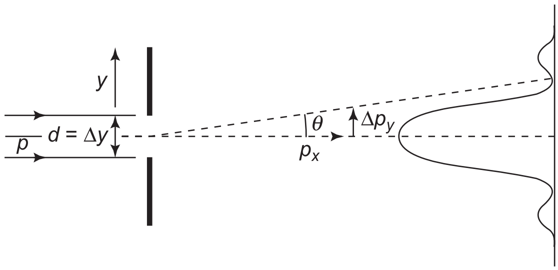

Fig. 2.8 Electron diffraction experiment.

or $$\Delta y = \frac{\lambda}{\sin \theta} \quad (1)$$

$\because$ $d = \Delta y$ = uncertainty in position of electron before being diffracted.

Before diffraction a slit electron has momentum p_x only along x direction and zero in y direction. Therefore, uncertainty in y component of momentum of $\Delta p_y = 0$. Because of the diffraction effect at the slit, the particle acquires a small component of momentum p_y in y direction. The original momentum of the particle in the X direction p_x decreases so that the resultant momentum p remains constant. The original momentum of the particle in the y direction was accurately known to be zero. Therefore, Δp_y is the uncertainty introduced in the y component of the momentum.

$\therefore$ Δp_y is the uncertainty produced in y component of momentum.

Particles that strike the screen at a point A, the first minima must have left the slit at an angle θ, given by

$$\tan \theta = \theta = \frac{\Delta p_y}{p_x} \quad (2)$$

Equating (1) and (2)

$$\frac{\Delta p_y}{p_x} = \frac{\lambda}{\Delta y}$$

$$\therefore \quad \Delta y \cdot \Delta p_y = \lambda \cdot p_x$$

$$\therefore \quad \Delta y \cdot \Delta p_y = h \qquad \because \lambda = \frac{h}{p_x}$$

which is the uncertainty principle, i.e., if we try to improve the accuracy in y, we have to reduce to Δy using a finer slit which results in turn in a wider pattern. It leads to a larger Δp_y.

2.11 γ-RAY MICROSCOPE EXPERIMENT

Consider an experiment for measurement of the position of an electron at rest using microscope. Since the size of electron is very small, light wave cannot be used for measurement as it would be 10^4 to 10^5 times smaller than the size of electrons. To illuminate an electron γ rays can be used. To determine the location of the electron, one photon must bounce off the electron, and pass through the microscope into our eyes. A γ-photon carries a very large momentum. When the photon strikes the electron, part of the momentum and energy are transferred to the electron due to the Compton scattering. Thus, when the scattered photon is registered by the microscope, only the earlier position of the electron can be deduced but the momentum of the electron is altered.

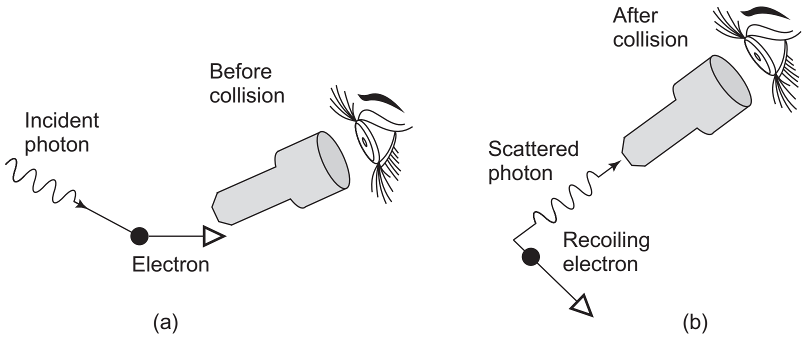

Fig. 2.9 An experiment where an attempt is made to locate electron by illuminating it with γ-rays. The γ-rays cause recoil of electron thus frustrating our efforts to know the electron position.

Let the incoming photon momentum be h/λ. The uncertainty in the electron momentum after the scattering be Δp. This Δp can have maximum values as the momentum of incident photon, i.e., h/λ

$$\therefore \qquad \Delta p = \frac{h}{\lambda}$$

The position of the electron can be determined within one wavelength of photon. The uncertainty in position is $\Delta x = \lambda$.

$$\therefore \qquad \Delta x \cdot \Delta p = \lambda \cdot \frac{h}{\lambda} = h$$

which is the uncertainty principle.

2.12 APPLICATIONS OF UNCERTAINTY PRINCIPLE

(i) Non-existence of electrons and existence of protons and neutrons in the nucleus: The radius of nucleus of any atom is of the order of 10^{-14} m. If an electron is confined inside the nucleus, then the uncertainty in the position Δx of the electron is equal to the diameter of the nucleus, i.e., $\Delta x = 2 \times 10^{-14}$ m.

(ii) ***Binding energy of an electron in atom:*** In an atom, the electron is under the influence of electrostatic potential of positively charged nucleus. It is confined to the linear dimensions equal to the diameter of electronic orbit. The uncertainty in the position Δx of an electron is of the order of $2R$ where R is the radius of the orbit and the corresponding uncertainty in the momentum component Δp_x is given by

$$\Delta p_x \geq \frac{h}{2\pi \cdot \Delta x}$$

$$\Delta p_x \geq \frac{h}{2\pi \cdot 2R}$$

which shows the momentum of electron in an orbit is at least

$$p \sim \Delta p_x \sim \frac{h}{2\pi \cdot 2R}, \; R \approx 10^{-10} \text{ m}$$

$$\text{K.E. of electron} = \frac{p^2}{2m} = \left(\frac{h}{4\pi R}\right)^2 \times \frac{1}{2m_0} = \frac{h^2}{32\pi^2 m_0 R^2}$$

The potential energy of an electron in the field of nucleus with atomic number z is given by

$$V = \frac{-ze^2}{4\pi \epsilon_0 R}$$

The total energy = K.E + P.E.

$$= \frac{h^2}{32\pi^2 m_0 R^2} - \frac{ze^2}{4\pi \epsilon_0 R} = \frac{(h/2\pi)^2}{8 m_0 R^2} - \frac{ze^2}{4\pi \epsilon_0 R}$$

$$= \left[\frac{(1.055 \times 10^{-34})^2 \div 1.6 \times 10^{-19}}{8 \times 9.1 \times 10^{-31} R^2} - \frac{z(1.6 \times 10^{-19})^2}{4 \times 3.14 \times 8.85 \times 10^{-12} \times R} \div 1.6 \times 10^{-19}\right] \text{eV}$$

where, $\dfrac{h}{2\pi} = 1.055 \times 10^{-34}$

$$E = \left[\frac{10^{-20}}{R^2} - \frac{15 \times 10^{-10}}{R} z\right] \text{eV}$$

Taking $R = 10^{-10}$ m, we have $E = (1 - 15z)$eV

Now, the binding energies of the outermost electrons in H and He are – 13.6 eV and – 24.6 eV respectively. So, the value of binding energy derived on the basis of uncertainty principle is acceptable as these are comparable in magnitudes.

(iii) ***Finite width of spectral lines:*** From Heisenberg's principle of energy and time relation, we have

$$\Delta E \cdot \Delta t \geq \hbar$$

Since the lifetime of electron in an excited orbit is finite (10^{-8} sec), so the energy levels of an atom given by $\Delta E = \dfrac{\hbar}{\Delta t}$ must have a finite width which means that the excited levels must have a finite energy spread, i.e., radiation given out when an electron jumps must be truly monochromatic, i.e., the spectral lines can never be sharp but must have a natural spectral width.

(iv) ***Strength of nuclear force:*** If we assume the nuclear radius is of the order $r_0 = 1.2 \times 10^{-13}$ cm.

From uncertainty principle, momentum will be of the order $p = \dfrac{\hbar}{r_0}$

∴ K.E. will be of the order

$$\text{K.E.} = \frac{p^2}{2m} = \frac{\hbar}{2mr_0^2} = 10 \text{ MeV}$$

where M corresponds to the mass of a nucleus (photon or neutron). Since the nucleus is bound, so that B.E. should be greater than K.E. with –ve sign so the B.E. of a nucleus is of the order of 10 MeV.

2.13 ONE-DIMENSIONAL TIME-DEPENDENT SCHRÖDINGER EQUATION

In 1926, Erwin Schrödinger formulated the wave equation for matter waves which is known as Schrödinger's equation. It plays the same role in quantum mechanics as Newton's second law does in classical mechanics. The motion of an atomic particle can be determined using Schrödinger's wave equation.

Let us consider a microparticle. Let ψ be the wave function associated with the motion of this microparticle ψ function represents the wavefield of the particle. It is smaller than *E* & *B* used to describe the electromagnetic waves and to transverse displacement for waves on a string.

For one-dimensional case, the classical wave equation has the following form

$$\frac{\partial^2 \xi}{\partial x^2} = \frac{1}{v^2}\frac{\partial^2 \xi}{\partial t^2} \tag{1}$$

A solution of the above equation is the familiar plane wave

$$\xi(x_1\ t) = Ae^{i(kx-\omega t)} \tag{2}$$

where $w = vk$ and v is phase velocity.

For microparticle, ω and *k* may be replaced with *E* & *P* using Einstein & de Broglie relations.

$$\left.\begin{aligned} \omega &= \frac{E}{h} \\ \&\qquad k &= \frac{2\pi}{\lambda} \end{aligned}\right\} \quad \begin{aligned} \omega &= 2\pi v = \frac{2\pi E}{h} = \frac{E}{\hbar} \\ k &= \frac{2\pi}{\lambda} = \frac{2\pi P}{h} = \frac{P}{\hbar} \end{aligned} \tag{3}$$

Substituting equation (3) in (2) & replacing ξ (*x*, *t*) with wave function ψ (*x*, *t*)

$$\psi(x, t) = Ae^{-i(Et - px)/\hbar} \tag{4}$$

Differentiating with respect to *t*

$$\frac{\partial \psi}{\partial t} = -\frac{i}{\hbar}E\psi \tag{5}$$

The right-hand side of equation (10) is a function of t only and the left-hand side a function of x only. Therefore, equation (10) must be valid for any x and t, it can be so only if the two sides of equation (10) are equal to a constant. Setting this constant equal to energy E, we get

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

$$\therefore \qquad \boxed{\frac{-\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} + V\psi = E\psi} \tag{12}$$

This is time independent Schrödinger equation.

In three dimensions, the time independent Schrödinger equation, is written as

$$\frac{-\hbar^2}{2m}\nabla^2\psi + V(r)\psi = E\psi \tag{13}$$

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

Equation (12) is frequently written in the form $H\psi = E\psi$.
where H is Hamiltonian operator

$$H = \frac{-\hbar^2}{2m}\nabla^2 + V \tag{14}$$

2.15 MOTION OF A FREE PARTICLE

Consider an electron moving freely in space along the positive x direction and not acted upon by any force. Since no force is acting on the electron and its potential energy is zero.

Schrödinger's time independent equation is,

$$\frac{-\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V\psi = E\psi \tag{1}$$

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2 m}{h^2}E\psi = 0 \tag{2}$$

$$\because \qquad \hbar = \frac{h}{2\pi} \ \& \ V = 0$$

If
$$K^2 = \frac{8\pi^2 mE}{h^2} \tag{3}$$

the above equation reduces to

$$\frac{d^2\psi}{dx^2} + K^2\psi = 0 \tag{4}$$

The general solution to the above equation is

$$\psi(x) = Ae^{iKx} + Be^{-iKx} \tag{5}$$

where A and B are constants. As it is assumed that the waves propagating only in the positive x direction, we can write

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

Since the electron is moving freely, there are no boundary conditions and hence no restriction on K. **All values of the energy are allowed.** The allowed values of energy form a continuum and are given by

$$E = \frac{h^2}{8\pi^2 m} K^2$$

A freely moving electron therefore possesses a continuous energy spectrum as shown in Fig. 2.10.

$$K = \sqrt{\frac{2mE}{\hbar^2}} = \frac{P}{\hbar} = \frac{2\pi}{\lambda}$$

The K vector describes the wave properties of the electrons.

As $E \propto K^2$ the graph between E & K is a parabola as shown in Fig. 2.10. The momentum is well defined in this case. Therefore, according to the uncertainty principle, it is difficult to assign a position to the electron, i.e., the electron position is indeterminate.

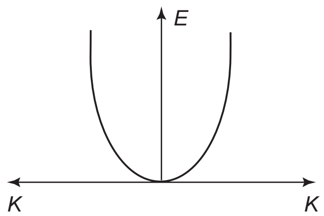

Fig. 2.10 Parabolic relationship between E & K in case of free electron.

2.16 PARTICLE TRAPPED IN ONE-DIMENSIONAL INFINITE POTENTIAL WELL

Consider the motions of electrons in one-dimensional deep potential well bounded by high potential barriers. Electrons can propagate along X-axis and can get reflected from the walls at $x = 0$ and $x = L$ as shown in Fig. 2.11 and thus it can propagate both in positive and negative x directions within the well the potential energy is zero and at the boundaries, i.e., $x = 0$ and $x = L$, potential is very high almost ∞. Therefore, the probability of finding the electron outside the well must be zero, i.e., $\psi = 0$ at $x \leq 0$ and $x \geq L$.

The Schrödinger equation is

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

$$\therefore \qquad \boxed{L = \frac{n\pi}{K}} \qquad (8)$$

This equation (6) implies that the wave equation has solutions only when the electron wavelength is restricted to discrete values such that only a whole number of half wavelength formed over the length L, i.e., the electron form standing wave pattern within the potential well.

Substitute (7) in (2)

$$K^2 = \frac{n^2\pi^2}{L^2} = \frac{8\pi^2 mE}{h^2}$$

$$\therefore \qquad E_n = \frac{h^2}{8ml^2}.n^2 \;\; (n = 1, 2, 3,\ldots.) \qquad (9)$$

The above equation shows only those values of energy are which are possible for n to be an integer.

So $$E_1 = \frac{h^2}{8mL^2},\; E_2 = \frac{h^2}{2mL^2},\; E_3 = \frac{9h^2}{8mL^2} \text{ ... etc.}$$

are allowed energy states. It is shown in Fig. 2.12.

Energy of particle in a box can take only discrete values, i.e., it is quantized. The value of energy E_1 for $n = 1$ is called zero point energy, which signifies that there must be some movement of particles (atoms, molecules, etc.) at the absolute zero temperature.

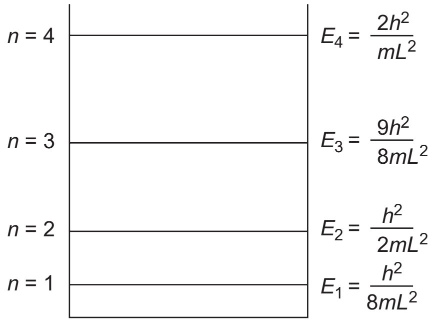

Fig. 2.12 Energy level diagram for an electron confined to a one-dimensional potential well. Note that the electron cannot have zero energy. The lowest allowed energy is E_1.

The wave functions corresponding to the above allowed discrete energy levels can be obtained as follows:

$$\psi = 2Ai \sin Kx$$

Applying normalized condition.

$$\int_0^L |\psi(x)|^2\, dx = 1 \text{ we get, } \int_0^L |2iA|^2 \sin^2 Kx dx = 1$$

$$\sin^2 Kx = \frac{1-\cos 2Kx}{2}$$

$$\int_0^L |2iA|^2 \left(\frac{1}{2} - \frac{\cos 2Kx}{2}\right) dx = 1$$

$$\therefore \qquad |2iA|^2 \left\{ \left(\frac{-\sin 2Kx}{2}\right)_0^L + \left(\frac{1}{2}x\right)_0^L \right\}$$

$$|2iA|^2 \left\{ \left(\frac{-\sin 2KL}{2} - 0\right) + \frac{L}{2} \right\} = 1$$

$$|2iA|^2 \left\{ \frac{-\sin n\pi}{2} + \frac{L}{2} \right\} = 1 \quad \because K = \frac{n\pi}{L}$$

$$|2iA|^2 \left(\frac{L}{2}\right) = 1$$

$$|2iA| = \sqrt{\frac{2}{L}}$$

Inserting the value of $|2iA|$ into equation, we get

$$\psi(x) = \sqrt{\frac{2}{L}} \sin \frac{n\pi}{L} x$$

$$|\psi(x)|^2 = \frac{2}{L} \sin^2 \frac{n\pi}{L} x$$

Analysis of the above result shows

1. While ψ_n may be negative, $|\psi_n|^2$ is always positive $|\psi_n|^2$ gives the probability of finding the electron at certain place within the well. Wave function and $|\psi_n|^2$ can be plotted as shown in Fig. 2.13. For $n = 1$, the probability of finding a particle is largest in the middle of the box for most of time.

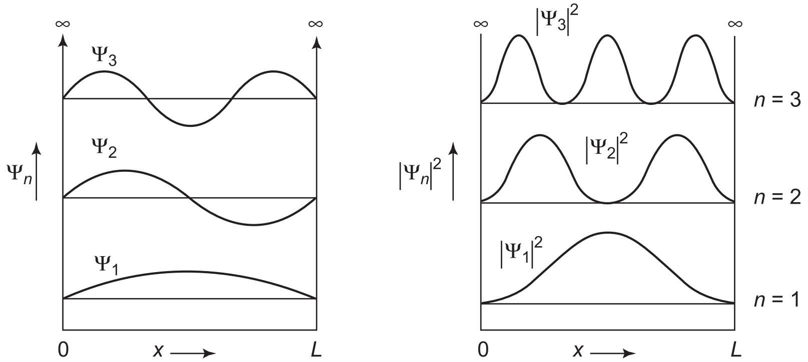

Fig. 2.13 The allowed wave functions and the corresponding probability distributions for an electron trapped in a one-dimensional potential well.

5. Uncertainty principle,
   $\Delta x \,.\, \Delta p \geq \hbar$
   $\Delta E \,.\, \Delta t \geq \hbar$
   $\Delta L \,.\, \Delta \theta \geq \hbar$
6. $E_n = \dfrac{n^2 h^2}{8ma^2}$
7. $\psi(x) = \sqrt{\dfrac{2}{a}} \sin \dfrac{n\pi x}{a}$

QUESTIONS WITH ANSWERS

1. **What are the assumptions of Planck's quantum theory?**
   The assumptions of Planck's quantum theory are:
   - Atoms in the black body are assumed to be simple harmonic oscillators.
   - The harmonic oscillators do not emit energy continuously.
   - Energy is emitted in the form of quanta of magnitude *hv*.
2. **State de Broglie's hypothesis.**
   According to de Broglie's hypothesis, a particle moving with a velocity *v* and mass *m* has a wave associated with it. The wavelength of this wave is given by
   $$\lambda = \frac{h}{mv} = \frac{h}{p}$$
3. **What is the physical significance of the wave function?**
   - The wave function $\psi(x, y, z, t)$ signifies the probability of finding a particle in space at any given instant of time.
   - It relates statistically the moving particle and its matter wave.
   - It is a complex quantity.
   - $|\psi\,(x, y, z)|^2$ gives the probability density of the particle, which is a real quantity.
4. **Which experiments were carried out to verify uncertainty principle?**
   Electron diffraction experiment and γ-ray microscope experiment were used to verify uncertainty principle.
5. **What is a wave function?**
   A variable quantity which characterizes de Broglie wave is known as wave function and is denoted by the symbol ψ.
6. **Mention physical significance of the wave function.**
   - It relates the particle and wave nature of matter statistically.
   - It is a complex quantity and hence cannot be measured.
   - It must be well behaved. That is, single valued and continuous everywhere.
   - If the particle is certainly to be found somewhere in space, then the probability value is equal to one.

$$\text{i.e., } P = \iiint_V |\psi|^2 dx\, dy\, dz = 1$$

A wave function satisfying the above relation is called a normalized wave function.

7. **Write the Schrödinger time independent and dependent wave equation and explain the terms.**
   - Schrödinger's time independent wave equation is

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

   - Schrödinger's time dependent wave equation is

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

where ψ is the wave function and Ψ is a function of Cartesian coordinates.

8. **What are Hamiltonian and energy operators?**
   The Schrödinger time independent wave equation is

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

The above equation can be written as

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

or $H\psi = E\psi$

where $H\left(\frac{-\hbar^2}{2m}\nabla^2 + V\right)$ is called the Hamiltonian operator

and $E = i\hbar\frac{\partial}{\partial t}$ is called the energy operator.

9. **What is zero point energy?**
   The possible energies of a particle in a box of length a is given by

$$E = \frac{n^2h^2}{8ma^2} \quad [\text{where } n = 1, 2, 3, \ldots.]$$

If $n = 1$ then $E = \frac{h^2}{8ma^2}$

This is the energy of the ground state of the particle. Since the particle in a box cannot be at rest, its minimum energy is positive and is often called the zero point energy.

10. **What are eigenvalues and eigenfunctions?**
   The allowed values of energy for different values of n are given by

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

$$= \frac{(6.63 \times 10^{-34})^2}{1.674 \times 10^{-27} \times (10^{-10})^2}$$

$$= 2.6 \times 10^{-20} \text{ Joules}$$

$$= \frac{2.6 \times 10^{-20}}{1.6 \times 10^{-19}} \text{ eV}$$

$$E = 0.164 \text{ eV}$$

2. Compute de Broglie wavelength of 10^{11} KeV neutrons ($m_n = 1.675 \times 10^{-27}$ kg).

Solution: Given data: $E = 10^{11}$ KeV = $10^{11} \times 10^3$ eV

$$E = 1.6 \times 10^{-19} \times 10^{14} \text{ J} = 1.6 \times 10^{-5} \text{ J}$$

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

$$\lambda = \frac{6.625 \times 10^{-34}}{\sqrt{2 \times 1.675 \times 10^{-27} \times 1.6 \times 10^{-5}}}$$

$$= 2.86 \times 10^{-18} \text{ m}$$

3. An electron microscope uses 1.25 Ke V electrons. Find its ultimate resolving power on the assumption that this is equal to the wavelength of the electron, given that

$$e = 4.8 \times 10^{-10} \text{ e.s.u.}, m = 9.0 \times 10^{-28} \text{ gm}$$

$$h = 6.65 \times 10^{-27} \text{ erg-sec.}$$

Solution: Given data: $E = 1.25$ KeV $= 1.25 \times 10^3$ eV $= 1.25 \times 10^3 \times 1.6 \times 10^{-19}$ J

$$m = 9.0 \times 10^{-28} \text{ gm}$$

$$h = 6.63 \times 10^{-34} \text{ J sec.}$$

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

$$\lambda = \frac{6.63 \times 10^{-34}}{\sqrt{2 \times 9.1 \times 10^{-31} \times 1.25 \times 10^3 \times 1.6 \times 10^{-19}}}$$

$$= 3.475 \times 10^{-11} \text{ m}$$

$$= 0.348 \text{ A.U.}$$

So, the resolving power of microscope is 0.348 Å.

4. What is de Broglie wavelength of an electron which has been accelerated from rest through a potential difference of 100 V?

Solution: Given data: V = 100 V.

Formula: $$\lambda = \frac{12.26}{\sqrt{V}}\ \text{Å}$$

$$= \frac{12.26}{\sqrt{100}}$$

$$= 1.226\ \text{Å}$$

5. Estimate the amount of accelerating voltage to which electrons are to be subjected in order to associate them with de Broglie wavelength of 0.50 Å. Given that $m = 9.0 \times 10^{-28}$ gm

Solution: Given data: $\lambda = 0.50$ Å $= .5 \times 10^{-8}$ cm

$m = 9.0 \times 10^{-28}$ gm

$h = 6.62 \times 10^{-34}$ J. sec.

Formula: $$y = \frac{12.26}{\sqrt{V}}\ \text{A.U.}$$

$$\therefore \quad V = \frac{(12.26)^2}{\lambda^2}$$

$$= \frac{(12.26)^2}{(0.5)^2}$$

$$= 601.2 \text{ volts}$$

6. Calculate de Broglie wavelength associated with a proton moving with a velocity equal to $1/20$ th of the velocity of light.

Solution: Given data: $v_p = \frac{1}{20} \times 3 \times 10^8 = 1.5 \times 10^7$ m/sec

$m_p = 1.67 \times 10^{-27}$ kg

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

$$= \frac{6.62 \times 10^{-34}}{1.67 \times 10^{-27} \times 1.5 \times 10^7}$$

$$= 2.64 \times 10^{-14} \text{ m.}$$

7. Compute the de Broglie wavelength of a proton whose kinetic energy is equal to the rest energy of an electron. Mass of a proton is 1836 times that of electron.

Solution: Given data: $m_p = 1836 \times m_e$

$= 1836 \times 9.1 \times 10^{-31}$ kg

$E = m_0 c^2$

$= 9.1 \times 10^{-31} \times (3 \times 10^8)^2$

$= 8.19 \times 10^{-14}$ J

$$\therefore \qquad p = \frac{h}{\lambda} = \frac{6.62 \times 10^{-34}}{10^{-10}}$$

$$E = \frac{6.62 \times 10^{-34}}{10^{-10}} \times 3 \times 10^{8}\,\text{J}$$

$$= \frac{6.62 \times 10^{-34} \times 3 \times 10^{8}}{10^{-10} \times 1.6 \times 10^{-19}}\,\text{eV}$$

$$= 1.24 \times 10^{4}\ \text{eV}$$

11. Calculate the de Broglie wavelength of an α particle accelerated through 200 V.

$$m_\alpha = 6.576 \times 10^{-21}\ \text{kg.}$$

Solution: Given data: $m_\alpha = 6.576 \times 10^{21}$ kg

$V = 200$ V

$e_\alpha = 2 \times e$

Formula: $E = eV$

$$\lambda = \frac{h}{\sqrt{2m_\alpha E_\alpha}}$$

$$\lambda = \frac{h}{\sqrt{2m_\alpha e_\alpha V}} = \frac{6.62 \times 10^{-34}}{\sqrt{2 \times 6.576 \times 10^{-21} \times 2 \times 1.6 \times 10^{-19} \times 200}}$$

$$= 7.216 \times 10^{-16}\ \text{m}$$

12. A beam of 10 kV electrons is passed through a thin metallic sheet whose interplanar spacing is 0.55 Å. Calculate the angle of deviation of the first order diffraction maximum.

Solution: Given data: $V = 10\ \text{kV} = 10 \times 10^{3}$ V

$d = 0.55\ \text{Å} = 0.55 \times 10^{-10}$ m

$n = 1$

Formula:

$$\lambda = \frac{12.26}{\sqrt{V}}\ \text{Å and } 2d \sin\theta = n\lambda$$

$$\lambda = \frac{12.26}{\sqrt{10 \times 10^{3}}}$$

$$= 0.1226\ \text{Å}$$

$$\theta = \sin^{-1}\left(\frac{n\lambda}{2d}\right) = \sin^{-1}\left(\frac{1 \times 0.1226 \times 10^{-10}}{2 \times 0.55 \times 10^{-10}}\right)$$

$$= \sin^{-1}(0.11145) = 6.399°$$

13. An electron and a 150 gm baseball are travelling at 220 m/s measured to an accuracy of 0.065%. Calculate and compare uncertainty in position of each of the bodies.

Solution: Given data; $v_e = 220$ m/s,

$$\text{accuracy} = 0.065\%$$
$$m = 150 \text{ gm} = 0.15 \text{ kg}$$
$$v_m = 220 \text{ m/s}$$
$$v_e = 220 \times \frac{0.065}{100} = .143 \text{ m/s}$$

Formula: $\Delta x = \frac{\hbar}{m\Delta v} = \frac{h}{2\pi m\Delta v}$

(*i*) $\Delta v_e = v_e \times 0.065\% = 220 \times \frac{0.065}{100} = 0.143$ m/s

$$\Delta x_e = \frac{6.63\times10^{-34}}{(2\times3.14\times9.1\times10^{-31})(0.143)} = 0.811 \times 10^{-3} \text{ m}$$

(*ii*) $\Delta v_m = 0.143$ m/s

$$\Delta x_m = \frac{\hbar}{m\Delta V_m} = \frac{6.63\times10^{-34}}{2\times3.14\times0.15\times0.143} = 4.92 \times 10^{-33} \text{ m}$$

The results show that the uncertainty in position of the electron is very large compared to its dimensions (= 10^{-15} m) whereas the uncertainty in position of the baseball is nearly as small as zero.

14. An electron has a speed of 500 m/s correct up to 0.01% with what minimum accuracy can you locate the position of this electron.

Solution: Given data: $v_e = 500$ m/s

$$\Delta v_e = \text{accuracy} = 0.01\% = 500 \times \frac{0.01}{100} = 0.05 \text{ m/s}$$
$$\Delta x = ?$$

Formula: $\Delta p = m\Delta v$

$$= \text{m} \cdot \Delta v$$
$$= 9.1 \times 10^{-31} \times 0.05$$
$$= 4.55 \times 10^{-32} \text{ kg m/s}$$

The uncertainty in position is given by

$$\Delta x = \frac{h}{2\pi\Delta p} = \frac{6.63\times10^{-34}}{2\times3.14\times4.55\times10^{-32}}$$

$$= 2.320 \text{ mm}$$

15. An electron has a speed of 600 m/s with an accuracy of 0.005%. Calculate the uncertainty with which we can locate the position of the electron.

Solution: Given data: $\hbar = 6.6 \times 10^{-34}$ J

$$m = 9.1 \times 10^{-31} \text{ kg}$$
$$v = 600 \text{ m/s}$$
$$\Delta v = 600 \times \frac{0.005}{100} = 0.03 \text{ m/s}$$

19. In jumping from an excited state to a stationary state, an atom takes 10^{-8} sec. What is the uncertainty in the energy of the emitted radiation?

Solution: Given data: $\Delta t = 10^{-8}$ sec

Formula: $\Delta E \,.\, \Delta t = \dfrac{h}{2\pi}$

The excited atom gives up its excess energy by emitting one or more photons of characteristic frequency. The average time gap between the excitation of an atom and the time it radiates energy is 10^{-8} sec. So, the photon energy is uncertain by an amount given by

$$\Delta E = \frac{h}{2\pi\,\Delta t} = \frac{6.63\times 10^{-34}}{10^{-8}\times 2\pi} = \frac{1.055\times 10^{-34}}{10^{-8}}$$

$$= 1.055 \times 10^{-26}\text{ J}$$

and the frequency of the light is uncertain by an amount.

$$\Delta v = \frac{\Delta E}{h} = 1.6\times 10^{7}\text{ Hz and this limit cannot be reduced.}$$

20. Using uncertainty relation, calculate the time required for the atomic system to retain rotation energy for a line of wavelength 6000 Å and width 10^{-4} Å.

Solution: Given data: $d\lambda = 10^{-4}$ Å $= 10^{-14}$ m

$\lambda = 6000$ Å $= 6 \times 10^{-7}$ m

Formula: $E = \dfrac{hc}{\lambda}$

$$\therefore \quad \Delta E = \frac{hc}{\lambda^2}\,\Delta\lambda \text{ and } \Delta E \,.\, \Delta t = \frac{h}{2\pi}$$

$$\therefore \quad \Delta t = \frac{h}{2\pi}\times\frac{1}{\Delta E}$$

$$= \frac{\hbar}{2\pi}\times\frac{\lambda^2}{\hbar c\Delta\lambda} = \frac{\lambda^2}{2\pi c.\Delta\lambda}$$

$$= \frac{(6\times 10^{-7})^2}{2\times 3.14\times 3\times 10^{8}\times 10^{-11}}$$

$$= 1.9 \times 10^{-11}\text{ sec.}$$

21. If the uncertainty in the location of a particle is equal to its de Broglie wavelength, what is the uncertainty with velocity?

Solution: Given data: $\Delta x = \lambda$

Formula $\quad \Delta x\, \Delta p = h$

$$\Delta x \,.\, m\Delta v = h$$

$$\Delta v = \frac{h}{m\lambda} = \frac{h}{m\times h/mv} = v$$

$$\therefore \quad \Delta v = v$$

22. A nucleon is confined to a nucleus of diameter 5×10^{-4} m. Calculate the minimum uncertainty in the momentum of the nucleon. Also calculate the minimum kinetic energy of the nucleon.

Solution: Given data: $(\Delta x)_{max} = 5 \times 10^{-4}$ m

Formula: $(\Delta p)_{min}\,(\Delta x)_{max} = h$

$$(\Delta p)_{min} = \frac{\hbar}{(\Delta x)_{max}} = \frac{1.055 \times 10^{-34}}{5 \times 10^{-4}}$$

$$= 2.11 \times 10^{-31} \text{ kgm sec.}$$

Now p cannot be less than $(\Delta P)_{min}$

$$p_{min} = (\Delta P)_{min}$$

$$\therefore \qquad E = \frac{P_1^2}{2m} = \frac{(2.11 \times 10^{-31})^2}{2 \times 1.67 \times 10^{-27}} \text{ J}$$

$$= \frac{1.332 \times 10^{-35}}{1.6 \times 10^{-19}} \text{ eV}$$

$$= 8.33 \times 10^{-17}$$

23. Find the energy of an electron moving in one dimension in an infinitely high potential box of width 1 Å, given mass of the electron 9.11×10^{-31} kg m and $h = 6.63 \times 10^{-34}$ Js.

Solution: Given data:

$$a = 1 \text{ Å} = 10^{-10} \text{ m}$$
$$m = 9.11 \times 10^{-31} \text{ kg}$$
$$h = 6.63 \times 10^{-34} \text{ Js}$$

Formula:

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

`

$$E = \frac{(6.63 \times 10^{-34})^2}{8 \times 9.11 \times 10^{-31} \times (10^{-10})^2} \text{ J}$$

$$= 9.1 \times 10^{-19} \text{ J}$$

$$= \frac{9.1 \times 10^{-19}}{1.602 \times 10^{-19}} \text{ eV}$$

$$= 5.68 \text{ eV}$$

24. An electron is bound by a potential which closely approaches an infinite square well of width 2.5×10^{-10} m. Calculate the lowest three permissible quantum energies the electron can have.

Solution: Given data: $a = 2.5 \times 10^{-10}$ m

Formula:

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

$$E_1 = \frac{(6.63 \times 10^{-34})}{8 \times 9.1 \times 10^{-31} \times (2.5 \times 10^{-10})^2} = 9.63 \times 10^{-19} \text{ J}$$

$$\therefore \qquad E = \frac{(6.6\times10^{-34})^2}{2\times(1.6\times10^{-27})\,(3\times10^{-10})^2}$$

$$= 1.45 \times 10^{-21} \text{ joule}$$

Further, $\quad 2\,d \sin\theta = n\,\lambda$

or $$\sin\theta = \frac{n\lambda}{2d} = \frac{1\times(3\times10^{-10})}{2\times(3.039\times10^{-10})} = 0.4936$$

$$\theta = \sin^{-1}(0.4936) = 29°\,33'$$

27. A hydrogen atom is 0.53 Å in radius. Use uncertainty principle to estimate the minimum energy an electron can have in this atom.

Solution: Given $\Delta x_{max} = 0.53$ Å

Heisenberg's uncertainty principle

$$\Delta x \Delta p = \frac{h}{2\pi}$$

$$(\Delta x)_{max}(\Delta p)_{min} = \frac{h}{2\pi} \qquad \text{(i)}$$

$$\text{and } (\text{K.E.})_{min} = \frac{p^2_{min}}{2m} = \frac{(\Delta p)^2_{min}}{2m} \quad [\because p_{min} = \Delta p_{min}]$$

$$(\Delta p)_{min} = \frac{h}{2\pi}\frac{1}{\Delta x} = \frac{6.63\times10^{-34}}{2\times3.14}\frac{1}{0.53\times10^{-10}}$$

$$= 1.9919 \times 10^{-24}$$

$$= 19.919 \times 10^{-25} \text{ kg m/sec}$$

$$\text{and } (\text{K.E.})_{min} = \frac{(\Delta p)^2_{min}}{2m} = \frac{(19.919\times10^{-24})^2}{2\times9.1\times10^{-31}}$$

$$= \mathbf{2.18 \times 10^{-18}\ J}$$

28. The speed of an electron is measured to be 5.0×10^3 m/sec to an accuracy of 0.003%. Find the uncertainty in determining the position of this electron.

Solution: Given $v = 5.0 \times 10^3$ m/sec

Formula used is

$$\Delta x \Delta p = \frac{h}{2\pi}$$

$$\Delta v = v\times\frac{0.003}{100} = 5.0\times10^3\times\frac{0.003}{100} = 0.15 \text{ m/sec}$$

$$\text{and } \Delta p = m\Delta v = 9.1\times10^{-31}\times0.15 = 1.365\times10^{-31} \text{ kg m/sec}$$

$$\Delta x = \frac{6.63\times10^{-34}}{2\times3.14\times\Delta p} = \frac{6.63\times10^{-34}}{2\times3.14\times1.365\times10^{-31}}$$

$$= \mathbf{7.734 \times 10^{-4}\ m}$$

29. An electron has speed of 6.6×10^4 m/sec with an accuracy of 0.01%. Calculate the uncertainty in position of an electron. Given mass of an electron as 9.1×10^{-31} kg and Planck's constant h as 6.6×10^{-34} J sec.

Solution: Given $v = 6.6 \times 10^4$ m/sec and $\Delta v = 6.6\times10^4 \times \frac{0.01}{100}$ m/sec

$$= 6.6 \text{ m/sec.}$$

Formula used is

$$\Delta x \Delta p = \frac{h}{2\pi} \text{ or } \Delta x = \frac{h}{2\pi}\frac{1}{\Delta p}$$

$$\Delta p = m\Delta v = 9.1 \times 10^{-31} \times 6.6$$

$$\Delta x = \frac{h}{2\pi}\frac{1}{\Delta p} = \frac{6.63\times10^{-34}}{2\times3.14\times9.1\times10^{-31}\times6.6}$$

$$\Delta x = \mathbf{1.758 \times 10^{-5}\ m}$$

30. If an excited state of hydrogen atom has a lifetime of 2.5×10^{-14} sec, what is the minimum error with which the energy of this state can be measured? Given $h = 6.63 \times 10^{-34}$ J sec.

Solution: Given $\Delta t = 2.5 \times 10^{-14}$ sec.

Formula used is

$$\Delta E \Delta t == \frac{h}{2\pi}$$

$$\Delta E = \frac{h}{2\pi\ \Delta t} = \frac{6.63\times10^{-34}}{2\times3.14\times2.5\times10^{-14}} = 0.422\times10^{-20}\,\text{J}$$

$$\Delta E = \mathbf{4.22 \times 10^{-21}}\text{J}$$

31. Find the energy of an electron moving in one dimension in an infinitely high potential box of width 1.0 Å. Given $m = 9.1 \times 10^{-31}$ kg and $h = 6.62 \times 10^{-34}$ J sec.

Solution: Given $l = 1.0 \times 10^{-10}$ m, m = 9.1×10^{-31} kg and $h = 6.62 \times 10^{-34}$ J sec.

Formula used is

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

$$= \frac{n^2(6.63\times10^{-34})^2}{8\times9.1\times10^{-31}\times(1.0\times10^{-10})^2}$$

$$= 0.602 \times 10^{-17}\, n^2\text{J}$$

For $n = 1$,

$$E_1 = 6.04 \times 10^{-18}\text{J}$$

and for $n = 2$,

or $$\Delta p = \Delta(mv) = \frac{h}{2\pi}\frac{1}{\Delta x} = \frac{h}{2\pi}\frac{p}{h} = \frac{mv}{2\pi}$$

$$m\Delta v = \frac{mv}{2\pi}$$

or $$\Delta v = \frac{v}{2\pi}$$

35. The position and momentum of 0.5 KeV electron are simultaneously determined. If its position is located within 0.2 nm, what is the percentage uncertainty in its momentum?

Solution: Given $E = 0.5 \times 10^3 \times 1.6 \times 10^{-19} = 0.8 \times 10^{-16}$ J and $\Delta x = 0.2 \times 10^{-9}$ m.

Now

$$\Delta x \Delta p = \frac{h}{2\pi} \text{ and momentum } p = \sqrt{2mE}$$

so $$p = \sqrt{2 \times 9.1 \times 10^{-31} \times 0.8 \times 10^{-16}} = 12.06 \times 10^{-24}$$

or $$p = 1.21 \times 10^{-23} \text{ kg m/sec}$$

or $$\Delta p = \frac{h}{2\pi}\frac{1}{\Delta x} = \frac{\text{h}}{2\pi}\frac{1}{0.2 \times 10^{-9}}$$

$$\Delta p = \frac{6.63 \times 10^{-34}}{2 \times 3.14 \times 0.2 \times 10^{-9}} = 5.279 \times 10^{-25} \text{ kg m/sec}$$

∴ Percentage uncertainty in momentum

$$\frac{\Delta p}{p} \times 100 = \frac{5.279 \times 10^{-25}}{1.21 \times 10^{-23}} \times 100$$

$$= \frac{5.279 \times 10^{-23}}{1.21 \times 10^{-23}} = 4.36\%$$

EXERCISE

1. Explain de Broglie's concept of matter waves.
2. Write an expression for the wavelength of a particle.
3. What do you understand by a wave packet? What is the relationship between phase velocity and group velocity?
4. Distinguish between phase velocity and group velocity. Show that the de Broglie wave group associated with a moving particle travels with the same velocity as that of the particle.
5. Can a wave given by an equation $y = A \sin(\omega t - kx)$ represent a particle? Explain the concept of a wave packet? How does this concept lead to Heisenberg's uncertainty principle.

5. Compute the energy difference between the ground state and the first excited state for an electron in a one-dimensional rigid box of length 10^{-8} cm. Given $m = 9.1 \times 10^{-31}$ kg and $h = 6.626 \times 10^{-34}$ J sec.

[Ans: 114 eV]

6. Calculate the value of lowest energy of an electron in one dimensional force free region of length 4 Å.

[Ans: 3.78×10^{-19} J]

7. The lowest energy possible for a certain particle entrapped in a box is 40 eV. What are the next three higher energies the particle can have?

[Ans: 160 eV, 360 eV and 640 eV]

8. Find the energy levels of an electron in a box 1 nm wide. Mass of electron is 9.1×10^{-31} kg. Also find the energy levels of 10 gm marble in a box 10 cm wide.

[Ans: 6.02×10^{-20} J, 24.08×10^{-20} J and 54.18×10^{-20} J; and for marble 5.49×10^{-64} J, 21.96×10^{-64} J and 49.41×10^{-64} J]