23

Uncertainty Principle and Quantum Mechanics

23.1 INTRODUCTION

In classical mechanics, we can simultaneously determine the position and the momentum of a particle. However, this is not the case in quantum mechanics. From de Broglie hypothesis of matter waves, we know that a moving particle may be considered as a group of waves and the particle may be positioned anywhere within the wave packet. This indicates that the position of the particle is uncertain within the limits of a wave packet. This uncertainty is only for microscopic particles; it has no importance for macroscopic particles. In atomic systems, the classical mechanics fails to explain the microscopic system of particles due to the above said reasons. The uncertainty principle states that the position and the momentum of a microscopic particle cannot be simultaneously measured accurately. The measurement of one quantity introduces a measure of uncertainty into the other. Hence, the classical mechanics, for which position and momentum have definite values at all instants, is not valid for atomic systems.

From the concept of de Broglie, we know that a wave is associated with a material particle. Clearly, a mathematical wave equation is required to deal with such waves. Since classical equations (mathematical formulations) were not valid at microscopic level, new equations known as *wave mechanics* or *quantum mechanics* were developed by Schrödinger in 1926. In his wave mechanics, Schrödinger assumed wave function $\psi(x, y, z, t)$ as the amplitude of matter waves. Wave function $\psi(x, y, z, t)$ is a complex quantity and is the function of position and time. It gives the idea for the probability of finding a particle in a particular region of space.

In this chapter, we will discuss uncertainty principle and Schrödinger wave equations with their applications.

23.2 BASIS FOR UNCERTAINTY PRINCIPLE

Although in the beginning scientists were reluctant to accept this principle, but the strong evidences forced them to accept the uncertainty principle. The following are some important observations about the uncertainty principle:

(i) The material particle exhibits particle nature as well as exhibits wave nature, but it does not simultaneously possess both the natures.

(ii) Instead of being contradictory, the wave and particle natures are complementary.

(iii) Bohr's principle of complementarity is the consequence of de Broglie hypothesis.

(iv) Under the de Broglie hypothesis, particles may be represented as wave packets. The particle may be anywhere inside the wave packet. Hence, there will be uncertainty in the measurement of position of the particle.

23.3 HEISENBERG'S UNCERTAINTY PRINCIPLE

Due to the dual nature of material particles, it is very difficult to locate the exact position and the momentum of the particle simultaneously. This uncertainty was explained by Werner Heisenberg in 1927 through his *uncertainty principle*. To understand the uncertainty in the measurement of position and momentum of microscopic particles, let us take the examples of narrow and wide wave packets.

In a narrow wave packet [Fig. 23.1(a)], the position of the particle can be precisely determined, but not the wavelength. As a result, the particle's momentum cannot be measured accurately as there are not enough waves to exactly measure the wavelength ($\lambda = h/m\upsilon$). On the other hand, in a wider wave packet

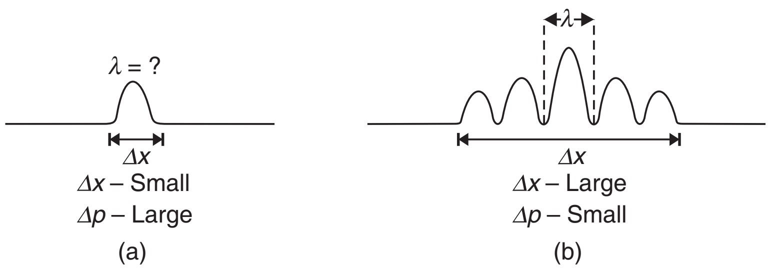

Fig. 23.1 Uncertainty in position and time

[Fig. 23.1(b)], the wavelength can be determined exactly but the position of the particle will be uncertain due to the large width of the wave packet. Hence, it can be concluded that it is impossible to simultaneously determine the exact position and the exact momentum of a particle.

23.3.1 Statement of the Uncertainty Principle

The Heisenberg's uncertainty principle states that it is not possible to simultaneously measure the position and the momentum of a particle to any desired degree of accuracy. In other words, the product of uncertainty in the measurement of position (Δx) and uncertainty in the measurement of momentum (Δp) is always constant, and it is at least equal to Planck's constant (h), i.e.,

$$\Delta p \cdot \Delta x = h \tag{23.1}$$

Equation (23.1) implies that if uncertainty in the measurement of position (Δx) increases, then uncertainty in the measurement of momentum (Δp) will decrease and vice versa.

Similar to Eq. (23.1), we can write

$$\Delta E \cdot \Delta t = h \tag{23.2}$$

and

$$\Delta J \cdot \Delta \theta = h \tag{23.3}$$

where ΔE and Δt are the uncertainties in determining energy and time, respectively. Similarly, ΔJ and $\Delta\theta$ are the uncertainties in the measurement of angular momentum and angle, respectively.

It has been experimentally observed that the product of uncertainties in position and momentum is equal to or greater than $h/4\pi$, i.e.,

$$\Delta p \cdot \Delta x \geq \frac{h}{4\pi} \tag{23.4}$$

where h is Planck's constant.

23.4 DERIVATION OF UNCERTAINTY PRINCIPLE

Uncertainty principle is the direct consequence of the dual nature of the material particle. The principle of dual nature holds that a moving particle is associated with group(s) of waves and these waves travel with the velocity equal to that of the particle.

Let us consider two simple harmonic plane waves of same amplitude A having nearly equal frequencies ω_1 and ω_2 with propagation vectors k_1 and k_2, respectively. These plane waves can be written as

$$y_1 = A \sin(\omega_1 t - k_1 x) \tag{23.5}$$

$$y_2 = A \sin(\omega_2 t - k_2 x) \tag{23.6}$$

where y_1 and y_2 are the displacements of these plane waves. Due to superposition of these waves, we will get the wave group as shown below:

$$\begin{aligned} y &= y_1 + y_2 \\ &= A \sin(\omega_1 t - k_1 x) + A \sin(\omega_2 t - k_2 x) \\ &= 2A \sin\left[\left(\frac{\omega_1 + \omega_2}{2}\right)t - \left(\frac{k_1 + k_2}{2}\right)x\right] \cos\left[\left(\frac{\omega_1 - \omega_2}{2}\right)t - \left(\frac{k_1 - k_2}{2}\right)x\right] \\ &= 2A \sin(\omega t - kx) \cos\left(\frac{\Delta\omega}{2}t - \frac{\Delta k}{2}x\right) \end{aligned} \tag{23.7}$$

where $\omega = \dfrac{\omega_1 + \omega_2}{2}$, $k = \dfrac{k_1 + k_2}{2}$, $\Delta\omega = \omega_1 - \omega_2$, and $\Delta k = k_1 - k_2$.

Equation (23.7) represents the wave group, which is the result of Eqs. (23.5) and (23.6). In Eq. (23.7), the second term is responsible for the modulation and forms a wave packet as shown in Fig. 23.2.

Fig. 23.2 Group of waves

In wave packets, the position of the particle remains uncertain between successive nodes (or extreme points of loop). From Eq. (23.7), the condition for node formation is given as:

$$\cos\left(\frac{\Delta\omega}{2}t - \frac{\Delta k}{2}x\right) = 0$$

or $$\left(\frac{\Delta\omega}{2}t - \frac{\Delta k}{2}x\right) = \frac{(2n+1)\pi}{2} \tag{23.8}$$

where $n = 0, 1, 2$, and so on.

If x_n and x_{n+1} are positions of nth and $(n + 1)$th nodes, then from Eq. (23.8), we get

$$\frac{\Delta\omega}{2}t - \frac{\Delta k}{2}x_n = \frac{(2n+1)\pi}{2} \tag{23.9}$$

and $$\frac{\Delta\omega}{2}t - \frac{\Delta k}{2}x_{n+1} = \frac{(2n+3)\pi}{2} \tag{23.10}$$

On subtracting Eq. (23.9) from Eq. (23.10), we get

$$\frac{\Delta k}{2}(x_{n+1} - x_n) = \pi$$

Now, $$X_{n+1} - X_n = \Delta x = \frac{2\pi}{\Delta k} \tag{23.11}$$

From the definition of propagation vector, we know that

$$k = \frac{2\pi}{\lambda}$$

$$= \frac{2\pi}{h/p}$$

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

or $$\Delta k = \frac{2\pi\Delta p}{h}$$

or $$\Delta p = \frac{\Delta k \cdot h}{2\pi} \tag{23.12}$$

Now, from Eqs. (23.11) and (23.12), we get

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

$$\Delta x \cdot \Delta p = h \tag{23.13}$$

Equation (23.13) represents the original statement of the uncertainty principle of Heisenberg.

23.5 TIME–ENERGY UNCERTAINTY PRINCIPLE

We can derive the expression for time–energy uncertainty with the help of position and momentum uncertainties. Let us consider a particle of rest mass m_0 moving with velocity υ_x in the X-direction. The kinetic energy of the particle can be given as

$$E = \frac{1}{2} m_0 \upsilon_x^2 = \frac{p_x^2}{2m_0} \tag{23.14}$$

Differential form of Eq. (23.14) can be written as

$$\Delta E = \frac{2 p_x \cdot \Delta p_x}{2m_0}$$

If ΔE and Δp_x are the uncertainties in energy and momentum, respectively, then

$$p_x \cdot \Delta p_x = m_0 \, \Delta E$$

or
$$\Delta p_x = \frac{m_0}{p_x} \cdot \Delta E = \frac{1}{\upsilon_x} \cdot \Delta E \tag{23.15}$$

Let the uncertainty in measuring the time interval at point x be Δt. Then, uncertainty in position Δx can be given as

$$\Delta = \upsilon_x \cdot \Delta t \tag{23.16}$$

From Eqs. (23.15) and (23.16), we get

$$\Delta p_x \cdot \Delta x = \frac{1}{\upsilon_x} \, \Delta E \cdot \upsilon_x \cdot \Delta t$$
$$= \Delta E \cdot \Delta t$$

or
$$\Delta E \cdot \Delta t = h \qquad [(\text{from Eq. (23.1)}, \Delta x \cdot \Delta p_x = h)]$$

or
$$\Delta E \cdot \Delta t \geq h/4\pi \tag{23.17}$$

Note: For calculations, the uncertainty principle expressions $\Delta x \cdot \Delta p \geq \hbar$ and $\Delta x \cdot \Delta p \geq \hbar/2$ are equally good. One can use any one of them for the solution of numerical problems. It is equally applicable for other uncertainty equations.

23.6 EXPERIMENTAL EXAMPLES OF UNCERTAINTY PRINCIPLE

There are many examples confirming the uncertainty principle. Some of them are given below.

23.6.1 Determination of the Position of a Particle by γ-ray Microscope

To measure the exact position and the momentum of an electron along the X-axis in the field of view of an ideally high resolving power microscope, let us consider a photon being incident on an electron in the field of view of microscope as shown in Fig. 23.3.

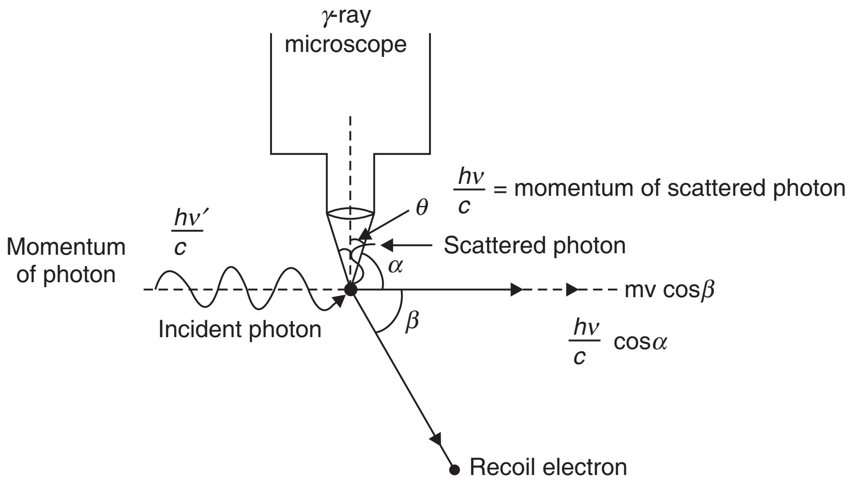

Fig. 23.3 Determination of position and momentum of electron by γ-ray microscope

The resolving power of a microscope can be given as

$$\Delta x = \frac{\lambda}{2\sin\theta} \tag{23.18}$$

where Δx is the minimum distance in the field of view that can just be resolved by the microscope (i.e., uncertainty in the measurement of the position of the electron), λ is the wavelength of the photon received at microscope after scattering, and θ is the semi-vertical angle of the cone of the light rays entering the objective lens of the microscope.

If α and β are the angles made by the scattered photon and the recoiled electron from the +ve X-axis, respectively, the law of conservation of momentum along the X-axis can be given as

$$\frac{h\nu'}{c} = \frac{h\nu}{c}\cos\alpha + m\upsilon\cos\beta \tag{23.19}$$

where $m\upsilon \cos\beta$ is the component of momentum of the recoiled electron along the +ve X-axis and α is the scattering angle of photon.

Now, from Eq. (23.19), we can write

$$m\upsilon\cos\beta = p_x = \frac{h\nu'}{c} - \frac{h\nu}{c}\cos\alpha$$

Here, α may vary from $(90 - \theta)$ to $(90 + \theta)$. Hence, we get

$$\frac{h}{c}(\nu' - \nu\cos(90° - \theta)) \le p_x \le \frac{h}{c}(\nu' - \nu\cos(90° + \theta))$$

or
$$\Delta p_x = \frac{h}{c}\,[\nu' - \nu\cos(90° + \theta) - \nu' + \nu\cos(90° - \theta)]$$

$$= \frac{h}{c}\,(\nu\sin\theta + \nu\sin\theta)$$

$$= \frac{2h\nu}{c}\sin\theta$$

$$\Delta p_x = \frac{2h\sin\theta}{\lambda} \tag{23.20}$$

From Eqs. (23.18) and (23.20), we get

$$\Delta x \cdot \Delta p_x = h \tag{23.21}$$

From Eq. (23.21), it is clear that the product of uncertainties in determining the position and the momentum is constant. This suggests that any attempt to increase the accuracy of the measurement of position of the electron will increase the inaccuracy (uncertainty) of the measurement of momentum of the electron.

Regarding uncertainty measurements, it has been observed that the product of uncertainties in the measurements of position and momentum is equal to $h/4\pi$. Hence, the exact statement of uncertainty principle can be mathematically expressed as

$$\Delta x \cdot \Delta p \ge h/4\pi \tag{23.22}$$

23.6.2 Diffraction of a Beam of Electrons by a Slit

Let a beam of electrons is transmitted through a slit of width Δy (comparable with λ) and received on a photographic plate *P*, kept at some distance from the slit (shown in Fig. 23.4).

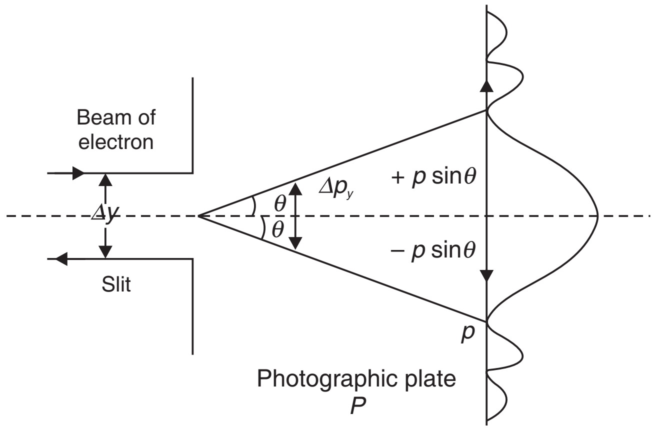

Fig. 23.4 Diffraction of an electron beam

For the electrons of the beam, we can only say that these are passing through the slit, but we cannot specify their exact location in the slit. Hence, the position of any electron recorded on the photographic plate is uncertain by the amount equal to the width of the slit (Δy). Let λ be the wavelength of the wave associated with electrons and θ be the angle of deviation corresponding to the first minimum. In Fraunhofer's diffraction at a single slit, the direction of the first minimum is given by $d \sin \theta = \lambda$, where d is the *width of the slit*. Thus, according to Fig. 23.4,

$$\Delta y \sin \theta = \lambda$$

or
$$\Delta y = \frac{\lambda}{\sin\theta} \tag{23.23}$$

Equation (23.23) gives the uncertainty in determining the position of electrons along the *Y*-axis.

Initially, the electrons are moving along the *X*-axis and therefore, they have no component of momentum along the *Y*-axis. As the electrons are deviated at the slit from their initial path to form the pattern, they acquire an additional component of momentum along the *Y*-axis. If p is the momentum of an electron after emerging from the slit, the component of momentum of the electron along the *Y*-axis is $p \sin \theta$. As the electron may be anywhere between $-p \sin \theta$ and $+p \sin \theta$, the uncertainty in its *Y*-component of momentum can be given as

$$\Delta p_y = 2p \sin \theta = \frac{2h}{\lambda} \sin \theta$$

$$\Delta y \cdot \Delta p_y \geq \frac{\lambda}{\sin\theta} \cdot \frac{2h}{\lambda} \sin \theta = 2h$$

$$\Delta y \cdot \Delta p_y \geq h \tag{23.24}$$

Equation (23.24) shows the uncertainty principle, which states that the product of uncertainties in the measurements of position and momentum is of the order of Planck's constant.

23.6.3 Consequences of Uncertainty Principle

The most important consequence of uncertainty principle is the dual nature of matter. In the dual nature, it is not possible to determine the wave and particle properties exactly at the same time. The complementarity principle states that the wave and particle aspects of matter are complementary, instead of being contradictory. This principle suggests that the consideration of particle and light natures is necessary to have a complete picture of the same system.

23.7 APPLICATIONS OF UNCERTAINTY PRINCIPLE

Uncertainty principle is used for explaining many facts of quantum mechanics, which cannot be explained by classical mechanics. Some of the applications of uncertainty principle are as follows.

23.7.1 Non-Existence of Electrons in the Nucleus

To prove the non-existence of an electron in the nucleus, let us first assume that the electron is present in nucleus. Since the diameter of nucleus is of the order of 10^{-14} m, the maximum uncertainty in the measurement of position of the electron in the nucleus will be of the order of $\Delta x = 10^{-14}$ m. Using Heisenberg's uncertainty relation, the uncertainty in the measurement of moment of the electron is given as

$$\Delta p_x \geq \frac{h}{4\pi \cdot \Delta x}$$

$$= \frac{6.63 \times 10^{-34}\ \text{Js}}{4 \times 3.14 \times (10^{-14}\ \text{m})} \quad (\Delta x \simeq 10^{-14}\ \text{m})$$

$$= 0.527 \times 10^{-20}\ \text{kgm/s}$$

or $$\Delta p_x \geq 0.527 \times 10^{-20}\ \text{kgm/s}$$

If uncertainty in momentum of the electron is of the order of 0.527×10^{-20} kgm/s, then the momentum of the electron must be at least of the same order. Since the mass of the electron is 9.1×10^{-31} kg, the electron in nucleus should have a velocity comparable to that of light. Using the relativistic formula for energy E of the electron, we have

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

Since the rest mass energy (m_0c^2) is negligible (0.511 MeV) in comparison to p^2c^2, the expression of energy can be given as

$$E^2 = p^2c^2$$

or $$E = pc$$

$$\simeq (0.527 \times 10^{-20}) \times (3 \times 10^8)$$

$$= \frac{0.527 \times 10^{-20} \times 3 \times 10^8}{1.6 \times 10^{-19}}\ \text{eV}$$

$$E = 9.88\ \text{MeV}$$

The above calculation shows that an electron can exist in the nucleus if its energy is of the order of 9.88 MeV. But we know that the electrons emitted by radioactive nuclei during β-decay have energies of the order of 3 MeV to 4 MeV only. Hence, electrons cannot exist in the nucleus.

23.7.2 Existence of Protons, Neutrons, and α-particles in the Nucleus

To prove the existence of protons, neutrons, and α-particles in the nucleus, let us start with the maximum uncertainty in the measurements of positions of these particles in the nucleus. This uncertainty will be equal to the order of the diameter of nucleus, i.e., $\Delta x \simeq 10^{-14}$ m. Using the uncertainty principle, the uncertainty in the momentum of above said particles can be given as

$$\Delta p_x \geq \frac{h}{4\pi \cdot \Delta x}$$

$$= \frac{6.63 \times 10^{-34}\ \text{Js}}{4 \times 3.14 \times (10^{-14}\ \text{m})} \qquad (\Delta x = 10^{-14}\ \text{m})$$

$$= 0.527 \times 10^{-20}\ \text{kgm/s}$$

For protons and neutrons, $m_0 \simeq 1.67 \times 10^{-27}$ kg. This is a non-relativisitic problem as for these particles, $\upsilon = p/m_0 \simeq 3 \times 10^6$ m/s^{-1}. The kinetic energy in this case can be given as

$$E_k = \frac{p^2}{2m} = \frac{(0.527 \times 10^{-20})^2}{2 \times 1.67 \times 10^{-27}}\ \text{J}$$

$$= \frac{(0.527 \times 10^{-20})^2}{2 \times 1.67 \times 10^{-27} \times 1.6 \times 10^{-19}}\ \text{eV} = E_k = 52\ \text{keV}$$

This value of this kinetic energy is smaller than the energies of the particles emitted by the nucleus. Hence, the particles such as protons and neutrons, or the particles heavier than these, can exist inside the nucleus.

23.7.3 Binding Energy of an Electron in an Atom

The electrons in an atom revolve in different orbits under the influence of electrostatic attraction of positively charged nucleus. If an electron is revolving in an orbit of radius R, then the maximum uncertainty in the measurement of the position of the electron will be equal to the diameter of that orbit, i.e., $2R$. Now, using the uncertainty principle, the uncertainty in the momentum can be given as

$$\Delta p_x \geq \frac{h}{4\pi \cdot 2R}$$

The above expression suggests that the momentum of an electron in an atomic orbit should be at least of the order of Δp_x. For $R = 10^{-10}$ m, the momentum of an electron can be given as

$$p_x \geq \frac{h}{4\pi \cdot 2R} = 0.527 \times 10^{-24}\ \text{kgm/s}$$

This shows that p_x is non-relativistic. Now, the kinetic energy of an electron is given as

$$E_k = \frac{p^2}{2m_0}$$

$$= \left(\frac{h}{4\pi R}\right)^2 \cdot \frac{1}{2m_0}$$

$$= \frac{h^2}{32\pi^2 m_0 R^2}$$

The electrostatic potential energy of an electron under the influence of a nucleus of atomic number Z is given as

$$V = \frac{-Ze^2}{4\pi^2 \in_0 R}$$

Now, the total energy of an electron in its orbit is

$$E = E_k + V$$

$$= \frac{h^2}{32\pi^2 m_0 R^2} - \frac{Ze^2}{4\pi^2 \in_0 R}$$

$$= \frac{(1.055 \times 10^{-34})^2}{8 \times 9.1 \times 10^{-31} \times R^2} - \frac{Z(1.6 \times 10^{-19})^2}{4 \times 3.14 \times 8.85 \times 10^{-12} \times R}$$

$$= \left(\frac{10^{-20}}{R^2} - \frac{15 \times 10^{-19} Z}{R}\right) \text{eV}$$

For $R = 10^{-10}$ m, we have

$$E = (1 - 15\, Z) \text{ eV}$$

Since first term in the bracket of the above expression is negligible compared to the second, we can write

$$E \simeq (-15\, Z) \text{ eV}$$

It is well known that the binding energies of outermost electrons in H ($Z = 1$) and He ($Z = 2$) are –13.6 eV and – 24.6 eV, respectively. From the above calculation, it is clear that the calculated value of the binding energy is comparable with the known magnitudes. Hence, the binding energy of an electron in an atom can be calculated.

23.7.4 Zero-Point Energy of a Harmonic Oscillator

From quantum mechanics, we know that the lowest energy of a simple harmonic oscillator is not zero; instead it is equal to $1/2\, \hbar\, \omega$ (where $\hbar = h/2\pi$) and is known as *zero-point energy*. This zero-point energy of the oscillator can be obtained with the help of uncertainty principle.

Let Δx and Δp_x be the uncertainties in the simultaneous measurements of the position and the momentum of a particle of mass m executing simple harmonic motion along the X-axis. Now, from the uncertainty principle, we can write

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

or

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

Total energy of the particle of mass m can be given as

$$E = E_K + V$$

$$= \frac{(\Delta p_x)^2}{2m} + \frac{1}{2}k(\Delta x)^2$$

where k is the force constant.

Now, putting the value of Δp_x in the above equation, we get

$$E = \frac{(\hbar/2\Delta x)^2}{2m} + \frac{1}{2}k(\Delta x)^2$$

$$= \frac{\hbar}{8m(\Delta x)^2} + \frac{1}{2}k(\Delta x)^2$$

Using the condition of minima, i.e., $\frac{dE}{d(\Delta x)} = 0$, we get

$$\Delta x = \left(\frac{\hbar^2}{4mk}\right)^{1/4}$$

Using this value of Δx in the total energy expression, we get

$$E_{\min} = \frac{\hbar^2}{8m}\left(\frac{4mk}{\hbar^2}\right)^{1/2} + \frac{1}{2}k\left(\frac{\hbar^2}{4mk}\right)^{1/2}$$

$$= \frac{\hbar}{4m}\left(\frac{k}{m}\right)^{1/2} + \frac{\hbar}{4}\left(\frac{k}{m}\right)^{1/2}$$

$$= \frac{\hbar}{2}\left(\frac{k}{m}\right)^{1/2}$$

Since $\left(\frac{k}{m}\right)^{1/2} = \omega$ (angular velocity), the $E_{\min}$ of the harmonic oscillator can be given as

$$E_{\min} = E_0 = \frac{1}{2}\hbar\omega \tag{23.25}$$

This relation is called the zero-point energy of a simple harmonic oscillator.

23.7.5 Radiation of Light from an Excited Atom

Since an atom takes an average time period of 10^{-8} s to come back to its ground state from the excited state, the uncertainty in the photon energy can be given as

$$\Delta E \geq \frac{h}{4\pi \cdot \Delta t} = \frac{6.6 \times 10^{-34}}{4 \times 3.14 \times 10^{-8}}$$

$$\simeq 0.525 \times 10^{-26} \text{ J}$$

Thus, the uncertainty in the frequency of the light is

$$\Delta \nu \geq \frac{\Delta E}{\hbar/4\pi} = \frac{0.525 \times 10^{-26} \times 4 \times 3.14}{6.6 \times 10^{-34}} = 0.999 \times 10^{8} \text{ Hz}$$

$$\simeq 10^{8} \text{ Hz}$$

The above value of $\Delta \nu$ gives the maximum limit of accuracy with which one can determine the frequency of the radiation emitted by an atom.

Solved Examples

Example 23.1

An electron microscope is used to locate an electron in an atom within a distance of 0.2 Å. What is the uncertainty in the momentum of the electron located in this way?

Solution

From the Heisenberg's uncertainty principle, we have

$$\Delta x \cdot \Delta p \geq \hbar/2$$

or $$\Delta p = \frac{\hbar}{2\Delta x}$$

where Δp and Δx are the uncertainties in momentum and position, respectively.

Given that $\Delta x = 0.2$ Å $= 0.2 \times 10^{-10}$ m

and $h = 6.63 \times 10^{-34}$ Js

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

$$= \frac{6.63 \times 10^{-34}}{2 \times 3.14 \times 2 \times 0.2 \times 10^{-10}}$$

$$= 2.64 \times 10^{-24} \text{ kgm/s}$$

Example 23.2

Calculate the smallest possible uncertainty in the momentum of an electron for which the uncertainty in its position is 4×10^{-10} m.

Solution

We know that

$$\Delta x \cdot \Delta p_x \simeq \hbar/2$$

$$\therefore \quad \Delta p_x = \frac{h}{2\pi \times 2 \times \Delta x}$$

$$= \frac{6.63 \times 10^{-34}}{2 \times 3.14 \times 2 \times 4 \times 10^{-10}}$$

$$= 1.32 \times 10^{-23} \text{ kgm/s}$$

Example 23.3

Calculate the smallest possible uncertainty in the position of an electron moving with a velocity of 3 $\times 10^7$ m/s.

Solution

From the principle of uncertainty, we have

$$\Delta x \cdot \Delta p \geq \hbar/2$$

or $$\Delta x = \frac{h}{4\pi \times \Delta p} \tag{1}$$

Given that $\upsilon = 3 \times 10^7$ m/s

Now, $$\Delta p \simeq p = m\upsilon = \frac{m_0 \upsilon}{\sqrt{1-\left(\upsilon^2/c^2\right)}}$$

Using the value of Δp in Eq. (1), we get

$$\Delta x = \frac{0.528 \times 10^{-34} \times \sqrt{1-\frac{\upsilon^2}{c^2}}}{m_0 \upsilon}$$

Here $\upsilon = 3 \times 10^7$ m/s, $c = 3 \times 10^8$ m/s, and $m_0 = 9 \times 10^{-31}$ kg. Using these values in the above equation, we get

$$\Delta x = \frac{0.528 \times 10^{-34} \times \sqrt{1-\left(\frac{3 \times 10^7}{3 \times 10^8}\right)^2}}{9 \times 10^{-31} \times 3 \times 10^7}$$

$$= \frac{0.528 \times 10^{-34} \times 0.995}{27 \times 10^{-24}}$$

$$= \frac{0.01945 \times 10^{-34}}{10^{-24}}$$

$$= 1.94 \times 10^{-12} \text{ m}$$

$$= 0.0194 \text{ Å}$$

Example 23.4

If the uncertainty in the location of a particle is equal to its de Broglie wavelength, then find out the uncertainty in its velocity.

Solution

From the uncertainty principle, we have

$$\Delta x \cdot \Delta p \simeq \hbar/2$$

or
$$\Delta p \simeq \frac{\hbar}{2 \cdot \Delta x}$$

Given that $\Delta x = \lambda = \frac{h}{p}$ (de Broglie wavelength). Using this value of Δx in the above expression, we get

$$\Delta p = \frac{\hbar p}{2h}$$

$$\simeq \frac{hp}{2\pi \cdot 2h}$$

$$\simeq \frac{p}{4\pi}$$

or
$$\Delta(m\upsilon) \simeq \frac{m\upsilon}{4\pi}$$

or
$$\Delta\upsilon = \frac{\upsilon}{4\pi}$$

Since $\upsilon >> 4\pi$, we get

$$\Delta\upsilon \simeq \upsilon$$

Example 23.5

An electron has a speed of 1.05×10^4 m/s with an accuracy of 0.02%. Calculate the uncertainty in the position of the electron.

Solution

From the uncertainty principle, we have

$$\Delta x \cdot \Delta p = \hbar$$

$$p = m\upsilon = 9 \times 10^{-31} \times 1.05 \times 10^4$$

$$= 9.45 \times 10^{-27} \text{ kgm/s}$$

From the given problem, we have

$$\Delta p = \frac{0.02}{100} \times 9.45 \times 10^{-27}$$

$$= 18.9 \times 10^{-31}$$

$$= 1.89 \times 10^{-30}$$

Since, $$\Delta x = \frac{\hbar}{\Delta p}$$

$$\Rightarrow \quad \Delta x = \frac{6.63 \times 10^{-34}}{2 \times 3.14 \times 1.89 \times 10^{-30}}$$
$$= 0.558 \times 10^{-4} \text{ m}$$
$$= 5.58 \times 10^{-3} \text{ m}$$

Example 23.6

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

Solution

Uncertainty in the velocity can be given as

$$\Delta \upsilon = 600 \times \frac{0.005}{100}$$
$$= 0.030 \text{ m/s}$$

Now, uncertainty in momentum can be given as

$$\Delta p_x = (9.1 \times 10^{-31}) \times 0.030$$
$$= 2.73 \times 10^{-32} \text{ kgm/s}$$

From the uncertainty principle, we have

$$\Delta x = \frac{\hbar}{\Delta p_x} = \frac{6.63 \times 10^{-34}}{2 \times 3.14 \times 2.73 \times 10^{-32}}$$
$$= 0.39 \times 10^{-2} \text{ m}$$

Example 23.7

Compare the uncertainties in the velocities of an electron and a proton confined in a box of equal dimensions. Their masses are 9.1×10^{-31} kg and 1.67×10^{-27} kg, respectively.

Solution

Since the electron and the proton are confined in a box of equal dimensions, the uncertainties in the positions of these particles will be the same. Let this uncertainty be Δx, i.e.,

$$\Delta x = \hbar / \Delta p_e \tag{1}$$

and $$\Delta x = \hbar / \Delta p_p \tag{2}$$

where Δp_e and Δp_p are the uncertainties in the momentum of the electron and the proton, respectively.

On equating Eqs. (1) and (2), we get

$$\frac{\hbar}{\Delta p_e} = \frac{\hbar}{\Delta p_p}$$

Now,

$$\frac{\Delta p_p}{\Delta p_e} = \frac{1}{1}$$

or $$\frac{\Delta \upsilon_p}{\Delta \upsilon_e} = \frac{m_e}{m_p} = \frac{9.1 \times 10^{-31}}{1.67 \times 10^{-27}}$$

or $$\frac{m_p}{m_e} = \frac{\Delta \upsilon_e}{\Delta \upsilon_p} = \frac{1.67 \times 10^{-27}}{9.1 \times 10^{-31}}$$

or $$\frac{\Delta \upsilon_e}{\Delta \upsilon_p} = 1835$$

Example 23.8

A hydrogen atom, say, has a radius of 0.5 Å. Calculate the kinetic energy needed by an electron to be confined in the atom.

Solution

Since the radius of the hydrogen atom is 0.5 Å, the uncertainty in the position of the electron will be 1 Å (diameter), i.e.,

$$\Delta x = 1 \text{ Å} = 10^{-10} \text{ m}$$

From the uncertainty principle, we have

$$\Delta x \cdot \Delta p_x \geq \hbar/2$$

or $$\Delta p_x \geq \frac{h}{4\pi \cdot \Delta x}$$

$$= \frac{6.63 \times 10^{-34}}{4 \times 3.14 \times 10^{-10}}$$

$$= 0.5278 \times 10^{-24}$$

$$= 5.278 \times 10^{-25} \text{ kgm/s}$$

Since the magnitude of the momentum cannot be less than its uncertainty, the momentum will be at least equal to Δp_x. Hence, we get

$$p = 5.278 \times 10^{-25} \text{ kgm/s}$$

Now, the kinetic energy can be given as

$$E_k = \frac{p^2}{2m} = \frac{(5.278 \times 10^{-25})^2}{2 \times 9.1 \times 10^{-31}}$$

$$= \frac{27.857 \times 10^{-50}}{18.2 \times 10^{-31}}$$

$$= 1.53 \times 10^{-19} \text{ J}$$

$$= \frac{1.53 \times 10^{-19}}{1.6 \times 10^{-19}}$$

$$= 0.96 \text{ eV}$$

Example 23.9

The speed of an electron is measured to be 5.00×10^3 m/s to an accuracy of 0.003%. Find the uncertainty in the position of this electron.

Solution

The uncertainty in speed is 0.003%, i.e.,

$$\Delta \upsilon = \frac{0.003}{100} \times 5 \times 10^3 \text{ m/s}$$

Now, the uncertainty in the momentum of the electron can be given as

$$\Delta p = m\Delta \upsilon = \frac{0.003}{100} \times 5 \times 10^3 \times 9.1 \times 10^{-31}$$

$$\Delta = 1.365 \times 10^{-31} \text{ kgm/s}$$

From the uncertainty principle, we have

$$\Delta x \cdot \Delta p = \hbar/2$$

or

$$\Delta x \geq \frac{\hbar}{2 \cdot \Delta p}$$

$$= \frac{6.63 \times 10^{-34}}{2 \times 2\pi \times 1.365 \times 10^{-31}}$$

$$= \frac{6.63 \times 10^{-34}}{2 \times 2 \times 3.14 \times 1.365 \times 10^{-31}}$$

$$= 3.867 \times 10^{-4} \text{ m}$$

Example 23.10

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

Solution

Uncertainty in the position of the electron is equal to the diameter of the hydrogen atom, i.e.,

$$\Delta x = 2 \times 0.53 \text{ Å}$$

$$\Delta x = 1.06 \times 10^{-10} \text{ m}$$

From the uncertainty principle, we have

$$\Delta x \cdot \Delta p \geq \hbar/2$$

$$\Delta p \geq \frac{6.63 \times 10^{-34}}{2 \times 2 \times 3.14 \times 1.06 \times 10^{-10}}$$

$$= 4.98 \times 10^{-25} \text{ kgm/s}$$

Now, the kinetic energy of electron is

$$E_k \geq \frac{p^2}{2m}$$

$$\geq \frac{(4.98 \times 10^{-25})^2}{2 \times 9.1 \times 10^{-31}}$$

$$\geq 1.363 \times 10^{-19} \text{ J}$$

$$\geq \frac{1.363 \times 10^{-19}}{1.6 \times 10^{-19}}$$

$$\geq 0.852 \text{ eV}$$

Note: When this problem is solved by using the uncertainty principle $\Delta x \cdot \Delta p_x = \hbar$, the minimum value of kinetic energy will come out to be 13.5 eV.

Example 23.11

If an excited state of hydrogen atom has a lifetime of 2.5×10^{-14} μs, what is the minimum error with which the energy of this state can be measured?

Solution

From the uncertainty principle, we have

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

where Δt is the uncertainty measured in time and is equal to the lifetime of the excited atom, and ΔE is the uncertainty in the measurement of energy. Since

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

$$\Rightarrow \qquad \Delta E \geq \hbar/\Delta t$$

Given that $\Delta t = 2.5 \times 10^{-14}$ s = 2.5×10^{-20} s.

Now, $$\Delta E = \frac{6.63 \times 10^{-34}}{2 \times 3.14 \times 2.5 \times 10^{-20}}$$

$$= 4.22 \times 10^{-15} \text{ J}$$

$$= \frac{4.22 \times 10^{-15}}{1.6 \times 10^{-19}} \text{ eV}$$

$$= 2.64 \times 10^{4} \text{ eV}$$

Example 23.12

The position and the momentum of 0.5 keV electrons are simultaneously determined. If the position is located within 0.4 nm, what is the percentage of uncertainty in its momentum?

Solution

We have

$$E = 0.5 \times 10^{3} \text{ eV}$$

$$= 0.5 \times 10^3 \times 1.6 \times 10^{-19}\ \text{J}$$
$$= 8 \times 10^{-17}\ \text{J}$$

Since it is a non-relativisitic case, the momentum of the electron can be given as

$$p = \sqrt{2mE}$$
$$= (2 \times 9 \times 10^{-31} \times 8 \times 10^{-17})^{1/2}$$
$$= 1.2 \times 10^{-23}\ \text{kgm/s}$$

Uncertainty in the position can be given as

$$\Delta x = 0.4 \times 10^{-9}\ \text{m}$$
$$= 4\ \text{Å}$$

From the uncertainty principle, we have

$$\Delta p = \frac{\hbar}{2 \cdot \Delta x}$$
$$= \frac{6.63 \times 10^{-34}}{2 \times 2 \times 3.14 \times 4 \times 10^{-10}}$$
$$\Delta p = 1.3 \times 10^{-25}\ \text{kgm/s}$$

The percentage uncertainty in momentum can be given as

$$\frac{\Delta p}{p} \times 100 = \frac{1.3 \times 10^{-25}}{1.2 \times 10^{-23}} \times 100$$
$$= 1.08\%$$

Example 23.13

An electron is confined to a box of length 2×10^{-9} m. Calculate the minimum uncertainty in the measurement of its velocity.

Solution

From Heisenberg's uncertainty principle, we have

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

where Δx is maximum and Δp_x is minimum. Therefore,

$$(\Delta x)_{max} (\Delta p_x)_{min} \geq \frac{\hbar}{2}$$

Since $\quad (\Delta x)_{max} = 2 \times 10^{-9}\ \text{m}$

$$\Rightarrow \quad (\Delta p_x)_{min} = \frac{\hbar}{2 \times 2\pi \times 2 \times 10^{-9}}$$

or $\quad (\Delta \upsilon_x)_{min} = \dfrac{6.63 \times 10^{-34}}{2 \times 2 \times 3.14 \times 2 \times 10^{-9} \times 9.1 \times 10^{-31}}$

$$= 0.029 \times 10^6\ \text{m/s}$$
$$= 2.9 \times 10^4\ \text{m/s}$$

Example 23.14

Using uncertainty principle, show that the simultaneous measurements of position and momentum of a particle with absolute accuracy is impossible.

Solution

From the uncertainty principle, we have

$$\Delta x \cdot \Delta p \geq \frac{h}{4\pi}$$

Case I: When position is measured with absolute accuracy, then $\Delta x = 0$. Hence,

$$\Delta p = \frac{h}{4\pi(0)}$$
$$= \infty$$

This means that uncertainty in measuring the momentum (Δp) will be infinity, i.e., the velocity of the particle cannot be determined.

Case II: When momentum is measured with absolute accuracy, then $\Delta p = 0$. Hence,

$$\Delta x = \frac{h}{4\pi(0)}$$
$$= \infty$$

This means that the position of the particle cannot be determined.

Thus, both the momentum and the position of the particle cannot be determined simultaneously with absolute accuracy.

Example 23.15

A baseball of mass 200 g is moving with a velocity of 6 m/s. If we can locate the baseball with an error equal to the magnitude of the wavelength of light used (5000 Å), then compare the uncertainty in the momentum with the total momentum of the baseball.

Solution

Step I: *Calculation of uncertainty in the momentum of the baseball.*

From the uncertainty principle, we have

$$\Delta x \cdot \Delta p \geq \frac{h}{4\pi}$$

or

$$\Delta p = \frac{h}{4\pi \times \Delta x} \tag{1}$$

Given that $\Delta x = 5000 \times 10^{-10}$ m $= 5 \times 10^{-7}$ m, $\pi = 3.14$, and $h = 6.63 \times 10^{-34}$ kgm/s.

Now, putting these values in Eq. (1), we get

$$\Delta p = \frac{6.63 \times 10^{-34}}{4 \times 3.14 \times 5 \times 10^{-7}}$$
$$= 1.055 \times 10^{-28} \text{ kgm/s}$$

Step II: *Calculation of* Δp

We know that

$$p = m\upsilon$$
$$= 200 \times 10^{-3} \times 6$$
$$= 1200 \times 10^{-3} \text{ kgm/s}$$

Now,
$$\frac{\Delta p}{p} = \frac{1.055 \times 10^{-28}}{1200 \times 10^{-3}}$$
$$= 8.79 \times 10^{-27}$$

Example 23.16

A proton is accelerated to one-tenth of the velocity of light. If the velocity can be measured with a precision of ±1%, what will be the uncertainty in its position? ($m_p = 1.675 \times 10^{-27}$ kg)

Solution

From the uncertainty principle, we have

$$\Delta x \cdot \Delta p \geq \hbar/2$$

or
$$\Delta x \cdot m(\Delta\upsilon) \geq \frac{\hbar}{2}$$

or
$$\Delta x = \frac{h}{4\pi \times m \times \Delta\upsilon}$$

Given that
$$\Delta\upsilon = \frac{1}{10} \times 3 \times 10^8 \times \frac{1}{100}$$
$$= 3 \times 10^5 \text{ m/s}$$
$$m = 1.675 \times 10^{-27} \text{ kg}$$

and
$$h = 6.63 \times 10^{-34} \text{ kgm}^2/\text{s}$$

Now,
$$\Delta x = \frac{6.63 \times 10^{-34}}{4 \times 3.14 \times 1.675 \times 10^{-27} \times 3 \times 10^5}$$
$$= \frac{6.63 \times 10^{-34}}{63.1743 \times 10^{-22}}$$
$$= 1.04 \times 10^{-13} \text{ m}$$

Example 23.17

A cricket ball weighing 200 g is to be located within 1×10^{-9} m. What is the uncertainty in its velocity? Comment on your result.

Solution

From the uncertainty principle, we have

$$\Delta x \cdot \Delta p \geq \hbar/2$$

Given that $\Delta x = 1 \times 10^{-9}$ m and mass of cricket ball = 200 g = 0.2 kg.

We know that

$$\Delta p = m \cdot \Delta \upsilon$$

Using uncertainty principle, we get

$$\Delta \upsilon \geq \frac{h}{2 \times 2\pi \times 1 \times 10^{-9} \times 0.2}$$

$$\geq \frac{6.63 \times 10^{-34}}{2 \times 2 \times 3.14 \times 1 \times 10^{-9} \times 0.2}$$

$$= 2.64 \times 10^{-25} \text{ m/s}$$

The value of uncertainty in the velocity of ball is negligible in comparison to the velocity of ball. This shows that the uncertainty principle has no meaning at macroscopic level.

Example 23.18

The lifetime of an excited state of a nucleus is 2×10^{-12} s. What is the uncertainty in the energy of γ-rays photon emitted?

Solution

From the uncertainty principle, we have

$$\Delta E \cdot \Delta t \geq \frac{h}{4\pi}$$

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

Now,

$$\Delta E \geq \frac{h}{4\pi \cdot \Delta t}$$

$$= \frac{0.527 \times 10^{-34}}{2 \times 10^{-12}} = 0.2635 \times 10^{-22} \text{ J}$$

$$= \frac{0.2635 \times 10^{-22}}{1.6 \times 10^{-19}} \text{ eV}$$

$$= 1.65 \times 10^{-4} \text{ eV}$$

Example 23.19

An excited atom has an average lifetime of 10^{-8} s. Calculate the minimum uncertainty in the frequency of this photon.

Solution

From the uncertainty principle, we have

$$\Delta E \cdot \Delta t \geq \hbar/2$$

Since the energy of the photon is given at $E = h\nu$, the uncertainty principle can be written as

$$h \cdot \Delta\nu \cdot \Delta t \geq \frac{\hbar}{2}$$

or $$\Delta\nu \cdot \Delta t \geq \frac{1}{4\pi}$$

or $$\Delta\nu \geq \frac{1}{4 \times 3.14 \times 10^{-8}}$$
$$= 8 \times 10^{6}/\text{s}$$

23.8 WAVE FUNCTION (ψ)

From the analysis of electromagnetic waves, sound waves, and other such waves, it has been observed that waves are characterised by certain definite properties. In case of electromagnetic waves, the electric and magnetic fields vary periodically, whereas in sound waves, pressure varies periodically. Similarly, in water waves the height of water surface varies periodically. Now, one can ask what varies in matter waves. In matter waves, a quantity called *wave function*, denoted by ψ, varies. Schrödinger described the amplitude of matter waves in terms of wave function ψ. Wave function $\psi(x, y, z)$ is a complex quantity, which gives the idea of the probability of finding the particle (to which it is concerned) in a particular region of space.

The wave function $\psi(r, t)$ gives the complete knowledge of behaviour of the particle, and $\psi(r)$ gives the stationary state, which is independent of time. This wave function must be well-behaved, i.e., it must be finite, single valued, and continuous over the complete range of variables, which must extend up to infinity. If ψ^* is the complex conjugate of wave function (ψ), then it requires that $\int \psi\psi^* \, d\tau$ (where $d\tau$ is the elemental volume, i.e., $d\tau = dx\,dy\,dz$) should be finite. We know that because of the uncertainty principle, the knowledge of any property of a particle is not completely definite. Due to this reason the knowledge of a particle during its motion is expressed in terms of the probability which is expressed as

$$P(r) = \int \psi\psi^* \, d\tau \tag{23.26}$$

23.9 PHYSICAL SIGNIFICANCE OF WAVE FUNCTION (ψ)

For the physical interpretation of the wave function ψ, it was initially considered as an important observable property of the system. In the beginning, it was considered that the wave function ψ is merely an auxiliary mathematical quantity employed to facilitate computations relative to the experimental results. But very soon, it was realised that it is not reasonable, because the introduction of an isolated mathematical function without enquiring into its physical significance is not justified.

The simple effort was made by Schrödinger himself for the physical interpretation of ψ in terms of charge density. It is well known that in any electromagnetic wave system, if A is the amplitude of the wave, then the energy density, i.e., the 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 $A^2/h\nu$ or the photon density is proportional to A^2 as $h\nu$ is constant. Similar to the above interpretation, if ψ is the amplitude of the matter waves at any point in space, then the particle density (material particle per unit volume) at that point will be proportional to

ψ^2. If q is the electric charge on a particle, then its charge density is equal to the product of charge and particle density. Thus, the quantity ψ^2 is the measure of charge density. Since ψ is a complex quantity, therefore, it is usually written as $\psi^* \psi$ instead of ψ^2, where ψ^* is the complex conjugate of ψ.

Although the physical interpretation of wave function ψ given by Schrödinger is satisfactory in most of the cases, the difficulty arises when we wish to follow the flight of a single electron or any material particle. It has been observed that in some cases, ψ is appreciably different from zero in some finite region known as *wave packet*. Now, the natural question arises "Where is the particle in relation to the wave packet?" To answer this question, Max Born in 1926 and then Bohr, Dirac, and Heisenberg suggested a new idea about the physical significance of ψ, which is generally accepted till today. According to this idea, $\psi\psi^* = |\psi|^2$ 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 a volume $d\tau = dx \cdot dy \cdot dz$ at any point r (x, y, z) at time t is expressed as

$$P(r, t)\, d\tau = \int |\psi(r,t)|^2\, d\tau \tag{23.27}$$

Since the total probability of finding the particle in the selected region of space is unity, i.e., particle is certain to be found somewhere in that space, thus the above expression can be given as

$$\iiint |\psi|^2\, dx\, dy\, dz = 1 \tag{23.28}$$

ψ satisfying the above requirement is said to be normalized.

23.10 PROBABILITY CURRENT DENSITY

According to the physical interpretation of wave function, it gives the idea for the probability of finding a particle in a particular region of space. It means that the motion of the particle is definitely associated with the motion of the wave function. This general idea may be made quantitative by the introduction of probability current density.

The probability $P(r)$ of finding the particle in a region of space of volume V bounded by the surface A is given by following expression:

$$P = \int_V \psi\psi^* d\tau \tag{23.29}$$

where $d\tau$ is the volume element, i.e., $d\tau = dx \cdot dy \cdot dz$.

Using the above expression, we can discuss the flow of probability by knowing the changes in the probability with time within the surface area A.

Now differentiating Eq. (23.29) with respect to time, we get

$$\begin{aligned}\frac{dP}{dt} &= \frac{d}{dt}\int_V \psi\psi^* d\tau \\ &= \int_V \left(\psi \frac{d\psi^*}{dt} + \frac{d\psi}{dt}\psi^*\right) d\tau \end{aligned} \tag{23.30}$$

From time-dependent Schrödinger wave equation, we know that

$$\frac{\hbar^2}{2m}\nabla^2\psi + V\psi = i\hbar\frac{\partial\psi}{\partial t} \tag{23.31}$$

The complex conjugate of Eq. (23.31) is given as

$$\frac{-\hbar^2}{2m}\nabla^2\psi^* + V\psi^* = -i\hbar\frac{\partial\psi^*}{\partial t} \tag{23.32}$$

Multiplying Eq. (23.31) by ψ^* and Eq. (23.32) by ψ, we get

$$\frac{-\hbar^2}{2m}\psi^*\nabla^2\psi + V\psi\psi^* = -\frac{\hbar}{i}\frac{\partial\psi}{\partial t}\psi^* \tag{23.33}$$

and

$$\frac{-\hbar^2}{2m}\psi\nabla^2\psi^* + V\psi\psi^* = \frac{\hbar}{i}\psi\frac{\partial\psi^*}{\partial t} \tag{23.34}$$

Now, subtracting Eq. (23.34) from Eq. (23.33), we get

$$-\frac{\hbar^2}{2m}\left[\psi^*\nabla^2\psi - \psi\nabla^2\psi^*\right] = -\frac{\hbar}{i}\left[\psi^*\frac{\partial\psi}{\partial t} + \psi\frac{\partial\psi^*}{\partial t}\right]$$

or

$$\frac{\hbar^2}{2m}\left[\psi^*\nabla^2\psi - \psi\nabla^2\psi^*\right] = \frac{\hbar}{i}\left[\psi^*\frac{\partial\psi}{\partial t} + \psi\frac{\partial\psi^*}{\partial t}\right]$$

or

$$-\frac{\hbar}{2mi}\left[\psi^*\nabla^2\psi - \psi\nabla^2\psi^*\right] = \left[\psi^*\frac{\partial\psi}{\partial t} + \psi\frac{\partial\psi^*}{\partial t}\right] \tag{23.35}$$

Now, using Eq. (23.30) in Eq. (23.35), we get

$$\frac{dP}{dt} = -\frac{\hbar}{2mi}\int_V\left[\psi^*\nabla^2\psi - \psi\nabla^2\psi^*\right]d\tau \tag{23.36}$$

Using Green's theorem, we can convert the above volume integral to the surface integral, i.e.,

$$\frac{dP}{dt} = -\frac{\hbar}{2mi}\int_A(\psi^*\nabla\psi - \psi\nabla\psi^*)dA \tag{23.37}$$

Let us now define a vector $S\,(r, t)$ such that

$$S\,(r, t) = \frac{\hbar}{2im}(\psi^*\nabla\psi - \psi\nabla\psi^*) \tag{23.38}$$

Now, using Eq. (23.38) in Eq. (23.39), we get

$$\begin{aligned}\frac{dP}{dt} &= -\int S\cdot dA \\ &= -\operatorname{div} S\end{aligned}$$

$$\frac{dP}{dt} + \operatorname{div} S = 0 \tag{23.39}$$

Equation (23.39) has been found to be analogous to the well-known equation of continuity in hydrodynamics, which is as follows:

$$\left(\frac{\partial\rho}{\partial t} + \operatorname{div} j\right) = 0 \tag{23.40}$$

where ρ is the fluid density and j is the current density. From Eq. (23.40), it is clear that the changes in fluid density are due to the unbalanced flow of current density across the boundaries. Thus, it becomes reasonable to interpret the vector $S(r, t)$ as a probability current density. Equation (23.40) also reveals the fact that the change in the probability is due to the flow of probability current(s). Hence, the interpretation of quantity $\psi\psi^*$ as probability density gives rise to the concept of probability density.

23.11 NORMALIZATION OF WAVE FUNCTION

From the physical interpretation of wave function (ψ), we know that $\psi\psi^*$ gives the probability of finding the particle in a particular region of space. A particle which exist in a particular region must be found somewhere in that region, i.e., the probability of finding the particle in that region will be 100%, i.e., unity. This may be written as

$$\int |\psi(r,t)|^2 \, d\tau = 1 \tag{23.41}$$

where $d\tau$ is the elemental volume of the above said region and integration extends all over the space. Equation (23.41) may be written as

$$\int \psi^*(r,t)\psi(r,t)d\tau = 1 \tag{23.42}$$

A wave function, which satisfies the above equation is said to be normalized to unity or simply normalized.

Generally, ψ is not a normalized wave function. If ψ is the solution of a wave equation, then ($N\psi$) will also be the solution of the same wave equation, where N is a constant quantity. Now, the next problem arises to select the proper value of N, such that the new wave function is a normalized function. For the normalization of this new wave function, it must satisfy the following requirement:

$$\int (N\psi)^*(N\psi)dx\,dy\,dz = 1 \tag{23.43}$$

where $dt = dx\ dy\ dz$

or $|N|^2 \int \psi\psi^* dx\,dy\,dz = 1$

$$|N|^2 = \frac{1}{\int \psi\psi^* dx\,dy\,dz} \tag{23.44}$$

where $|N|$ is termed as the normalization constant and $N\psi$ is known as the normalized wave function.

Condition of Orthogonality: If ψ_i and ψ_j are two different wave functions, both being satisfactory solutions of wave equation for a given system, then these functions will be normalized if

$$\int \psi_i^* \psi_i \, d\tau = 1 \text{ and } \int \psi_j^* \psi_j \, d\tau = 1$$

If the two wave functions ψ_i and ψ_j are such that the integral $\int \psi_i^* \psi_j \, d\tau$ or $\int \psi_j^* \psi_i \, d\tau$ vanishes over the entire space, i.e.,

$$\int \psi_i^* \psi_j \, d\tau = 0 \text{ or } \int \psi_j^* \psi_i \, d\tau = 0 \tag{23.45}$$

where $i \neq j$

then the wave functions are said to be mutually orthogonal.

23.12 SCHRÖDINGER WAVE EQUATION

The de Broglie hypothesis states that a wave is associated with a material particle during its motion. It should be very clear that what type of wave is associated with the motion of the particle and what type of mechanics is required for the formulation of such waves. Schrödinger worked extensively on wave mechanics, used to deal with the matter waves. He suggested two important equations for the motion of matter waves, which we will discuss now.

23.13 TIME-INDEPENDENT SCHRÖDINGER WAVE EQUATION

From the theory of matter waves, we know that a material particle is equivalent to a wave packet. For locating the position of the particle within a wave packet, Schrödinger derived a wave equation known as *time-independent Schrödinger wave equation*.

To establish the time-independent Schrödinger wave equation, let us consider a system of stationary waves associated with a particle. Let $\psi(x, y, z)$ be the wave displacement for the matter wave at any time t. ψ is the wave function, which is a finite, single-valued, and periodic function. The classical differential equation of a wave motion is

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

or

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} = \frac{1}{\upsilon^2}\frac{\partial^2\psi}{\partial t^2} \tag{23.46}$$

where υ is the wave velocity.

The solution of Eq. (23.46) is given by

$$\psi(r, t) = \psi_0 e^{-2\pi i\left(\nu t - \frac{x}{\lambda}\right)}$$

$$= \psi_0 e^{-i\left(2\pi\nu t + \frac{2\pi}{\lambda}x\right)}$$

$$\psi(r, t) = \psi_0(r)\, e^{-i(\omega t + kx)} \tag{23.47}$$

where ψ_0 is the amplitude of the wave at the considered point and is the function of position only [i.e., (x, y, z)].

On differentiating Eq. (23.47) twice with respect to t, we get

$$\frac{\partial^2\psi}{\partial t^2} = -\omega^2\,\psi_0(r)e^{-i(\omega t + kx)}$$

$$\frac{\partial^2\psi}{\partial t^2} = -\omega^2\,\psi(r, t) \tag{23.48}$$

On substituting the value of $\frac{\partial^2\psi}{\partial t^2}$ in Eq. (23.46), we get

$$\nabla^2\psi = \frac{-\omega^2}{\upsilon^2}\psi(r,t) \tag{23.49}$$

We know that

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

$$= \frac{2\pi\upsilon}{\lambda} \qquad \text{(because } \upsilon = \nu\lambda\text{)}$$

or

$$\frac{\omega}{\upsilon} = \frac{2\pi}{\lambda}$$

Using the value of ω/υ in Eq. (23.49), we get

$$\nabla^2\psi = \frac{4\pi^2}{\lambda^2}\psi(r, t)$$

or

$$\nabla^2\psi + \frac{4\pi^2}{\lambda^2}\psi(r, t) = 0 \qquad (23.50)$$

In order to introduce the concept of wave mechanics, let us use the concept of de Broglie hypothesis. From de Broglie hypothesis, we have

$$\lambda = \frac{h}{m\upsilon} \qquad (23.51)$$

Now, using the value of λ in Eq. (23.50), we get

$$\nabla^2\psi + \frac{4\pi^2 m^2 \upsilon^2}{h^2}\psi = 0 \qquad (23.52)$$

If E and V are the total energy and the potential energy of the particle, respectively, then its kinetic energy is given as

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

or

$$m^2\upsilon^2 = 2m(E - V)$$

Substituting this value of $m^2\upsilon^2$ in Eq. (23.52), we get

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

or

$$\nabla^2\psi + \frac{2m}{\hbar^2}(E - V)\psi = 0 \qquad (23.53)$$

Equation (23.53) is the Schrödinger time-independent wave equation.

For free particle, potential energy, i.e., V is zero. Therefore, the time-independent Schrödinger wave equation for free particle can be given as

$$\nabla^2\psi + \frac{2mE}{h^2}\psi = 0 \qquad (23.54)$$

23.14 TIME-DEPENDENT SCHRÖDINGER WAVE EQUATION

Time-dependent Schrödinger equation may be obtained by eliminating E from Eq. (23.53).

From Eq. (23.47), we have

$$\psi(r,t) = \psi_0 e^{-2\pi i(\nu t - x/\lambda)}$$
$$= \psi_0 e^{-i2\pi\nu t + \frac{2\pi}{\lambda}x}$$
$$= \psi_0 e^{-i(\omega t + kx)}$$

Differentiating the above equation with respect to t, we get

$$\frac{\partial\psi}{\partial t} = -i\omega\psi_0(r)\, e^{-i(\omega t + kx)}$$
$$= -i(2\pi\nu)\,\psi_0(r)\, e^{-i(\omega t + kx)} \qquad (\omega = 2\pi\nu)$$
$$= -2\pi i\nu\,\psi$$
$$= -\frac{2\pi iE}{h}\psi \qquad (E = h\nu)$$
$$= -\frac{iE}{\hbar}\psi \qquad (\hbar = \frac{h}{2\pi})$$
$$= \frac{E\psi}{i\hbar}$$
$$E\psi = i\hbar\frac{\partial\psi}{\partial t} \tag{23.55}$$

Substituting the value of $E\psi$ in Eq. (23.53), we get

$$\nabla^2\psi + \frac{2m}{\hbar^2}\left[i\hbar\frac{\partial\psi}{\partial t} - V\psi\right] = 0$$
$$\nabla^2\psi = -\frac{2m}{\hbar^2}\left[i\hbar\frac{\partial\psi}{\partial t} - V\psi\right]$$

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

or
$$\left[\left(-\hbar^2/2m\right)\nabla^2 + V\right]\psi = i\hbar\frac{\partial\psi}{\partial t} \tag{23.56}$$

Equation (23.56) is the time-dependent Schrödinger wave equation. In this equation, operator $\left[\left(-\hbar^2/2m\right)\nabla^2 + V\right]$ is called *Hamiltonian* and is represented by H, while the operator $i\hbar\,\partial/\partial t$, operated on ψ, gives the eigenvalue of energy (E). Now, from Eqs. (23.55) and (23.56), we can write

$$H\psi = E\psi \tag{23.57}$$

Equation (23.57) is the Schrödinger's equation describing the motion of an H relativisitic material particle.

23.15 EIGENVALUES AND EIGENFUNCTIONS

The Schrödinger equation may have many solutions. Out of these solutions, some are imaginary, which have no significance. The solutions have significance only for certain values called the eigenvalues of the total energy E. In an atom, these (eigenvalues) correspond to the energy values associated with different orbitals in the atom. Thus, we can conclude that Bohr's postulate, according to which the various energy levels exist in an atom, is the direct consequence of the wave mechanical concept. The solution of the wave equation for these definite values of E gives the corresponding values of the wave function ψ, known as eigenfunctions.

Only those eigenfunctions have physical significance, which satisfy certain conditions listed as follows:

(i) They must be single-valued functions.
(ii) They should be finite.
(iii) They should be continuous throughout the entire space under consideration. In other words, we can say that they should be continuous for all possible values of coordinates (x, y, z), including infinity.

For further illustration of eigenfunctions and eigenvalues, let us take the following example of Hamiltonian operator.

Example: The Hamiltonian Operator

A wave function can describe the state of a physical system, which contains all the informations about the system. The wave function depends on time and its temporal development is given by Eq. (23.56).

$$H\psi(x, t) = i\hbar\frac{\partial\psi}{\partial t}(x, t) \tag{23.58}$$

H is the Hamiltonian operator, which plays a central role in the quantum mechanics. In the above equation, H is operated on the wave function $\psi(x, t)$. For a single particle in a potential V, the Hamiltonian operator can be given as

$$H = \frac{p_{op}^2}{2m} + V(x) \tag{23.59}$$

If $V(x)$ does not depend explicitly on time, then the solution of Eq. (23.58) is given as

$$\psi(r, t) = \psi_E(x)\, e^{-iEt/\hbar} \tag{23.60}$$

where

$$H\,\psi_E(x) = E\,\psi_E(x) \tag{23.61}$$

The solutions of this equation $\psi_E(x)$ are called the eigenfunctions of the Hamiltonian, and E are the eigenvalues. Usually, the eigenfunctions corresponding to different eigenvalues (i.e., different values of constant E) are orthogonal.

23.16 APPLICATIONS OF SCHRÖDINGER WAVE EQUATION

There are many applications of the Schrödinger wave equation. Out of these, a simple problem of a particle in a box is discussed below.

23.16.1 Particle in a One-Dimensional Box

Let us consider a particle such as a gas molecule or an electron confined in a one-dimensional potential box as shown in Fig. 23.5. The box possesses the particle of mass m, moving along the X-axis only between the two rigid walls A and B at $x = 0$ and $x = L$. The particle is free to move between the walls. Suppose that the particle does not lose energy when it bounces back from the walls of the box, i.e., the walls of the box are infinitely hard. Let us also consider that the potential energy V of the particle is zero inside the box, but becomes infinite at the walls and outside. The potential energy of the box may be defined as

$$V = 0 \text{ for } 0 \le x \le L$$

$$V = \infty \text{ for } x < 0 \text{ and } x > L \tag{23.62}$$

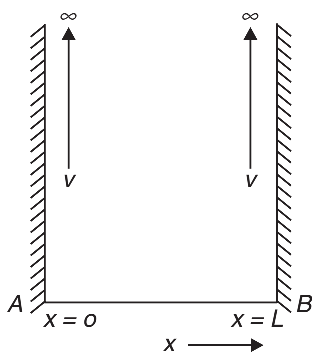

Fig. 23.5 One-dimensional square well potential

The Schrödinger wave equation for the particle is given by

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

Inside the box, $V = 0$, therefore the above equation takes the form

$$\frac{d^2\psi}{dx^2} + \frac{2mE}{\hbar^2}\psi = 0 \tag{23.63}$$

Let $2mE/\hbar^2 = k^2$, then Eq. (23.63) takes the form

$$\frac{d^2\psi}{dx^2} + k^2\psi = 0 \tag{23.64}$$

The general solution of Eq. (23.64) can be given as

$$\psi(x) = A \sin kx + B \cos kx \tag{23.65}$$

where A and B are constants. The values of A and B can be determined by applying the boundary conditions. Since this particle cannot penetrate the walls and cannot exist outside the box, the probability of finding the particle (i.e., ψ) will be zero outside the box. Hence,

$$\psi = 0 \text{ at } x = 0 \text{ and } \psi = 0 \text{ at } x = L$$

Applying these boundary conditions to Eq. (23.65), we get

$$0 = A \sin 0 + B \cos 0 \qquad \text{(because at } x = 0,\ \psi = 0)$$

or $\quad B = 0$

Now, Eq. (23.65) takes the form

$$\psi = A \sin kx$$

Using the boundary condition, $\psi = 0$ at $x = L$, we get

$$A \sin kL = 0$$

In the above equation, either A is zero or $\sin kL$ is zero. Since A is the amplitude of the wave, $A \neq 0$. Hence, we get

$$\sin kL = 0$$

or

$$kL = n\pi \qquad (n = 0, 1, 2, 3, ...)$$

or

$$k = \frac{n\pi}{L} \tag{23.66}$$

Now, the wave function ψ can be given as

$$\psi(x) = A \sin \frac{n\pi x}{L} \tag{23.67}$$

We have assumed that

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

Again, from Eq. (23.66), we have

$$k^2 = \frac{n^2\pi^2}{L^2} = \frac{2mE}{\hbar^2}$$

or

$$E_n = \frac{n^2h^2}{8mL^2} \qquad \text{(using } E_n \text{ for } E \text{ in general and } \hbar = h / 2\pi\text{)}$$

$$= \frac{h^2}{8m}\left[\frac{n^2}{L^2}\right] \tag{23.68}$$

where $n = 1, 2, 3.$

Equation (23.68) gives the value of energy of a particle inside an infinitely deep potential well. It is clear from this expression that the particle has only discrete sets of values of energy, i.e., the energy of the particle is quantised. The discrete energy values are given by

$$E_1 = \frac{h^2}{8mL^2} \text{ for } n = 1$$

$$E_2 = \frac{4 \cdot h^2}{8mL^2} = 4E_1 \text{ for } n = 2$$

$$E_3 = 9\frac{h^2}{8mL^2} = 9E_1 \text{ for } n = 3$$

$$E_4 = 16\frac{h^2}{8mL^2} = 16E_1 \text{ for } n = 4$$

$$\vdots \quad \vdots$$

The discrete energy levels of the particle in deep potential box have been shown in Fig. 23.6.

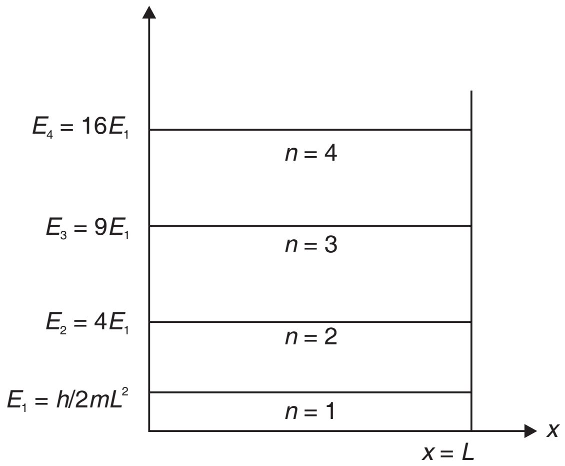

Fig. 23.6 Discrete energy levels of a particle in a deep potential well

In Eq. (23.64), we still require the exact value of constant A. To find the value of constant A, we apply normalization condition, i.e.,

$$\int_{-\infty}^{\infty} |\psi_n(x)|^2 \, dx = 1$$

Using the boundary conditions of our problem, we can write

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

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

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

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

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

or $$\frac{A^2}{2} L = 1$$

or $$A = \sqrt{\frac{2}{L}}$$

By putting the value of A in Eq. (23.67), we get

$$\psi(x) = \sqrt{\left(\frac{2}{L}\right)} \sin \frac{n\pi x}{L} \tag{23.69}$$

Equation (23.69) gives the wave functions of a particle enclosed in an infinitely deep potential well.

The first three normalized wave functions ψ_1, ψ_2, and ψ_3 along with their corresponding probability densities $|\psi_1|^2$, $|\psi_2|^2$, and $|\psi_3|^3$ are shown in Figs. 23.7 (a) and (b).

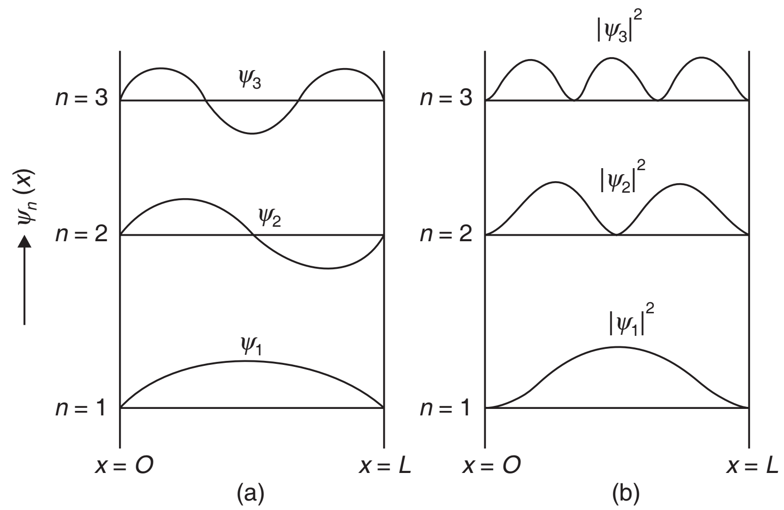

Fig. 23.7 Wave function and probability density of a particle inside an infinite potential well

23.16.2 Physical Interpretation of Probability Density Distribution

For physical interpretation of probability density distribution, let us consider three conditions corresponding to $n = 1$, 2, and 3, respectively.

Condition I: When $n = 1$

This is the condition of ground state where particle is normally found.

$$E_1 = \frac{h^2}{8mL^2} = E_0$$

For this state, ψ (eigenfunction) is expressed as

$$\psi_1 = \sqrt{\left(\frac{2}{L}\right)} \sin\left(\frac{\pi x}{L}\right)$$

At $x = 0$ and $x = L$, $\psi_1 = 0$. But at $x = L/2$, ψ_1 has the maximum value.

A plot of ψ_1 versus x is shown in Fig. 23.8(a) and the plot of $|\psi_1|^2$ versus x is shown in Fig. 23.8(b).

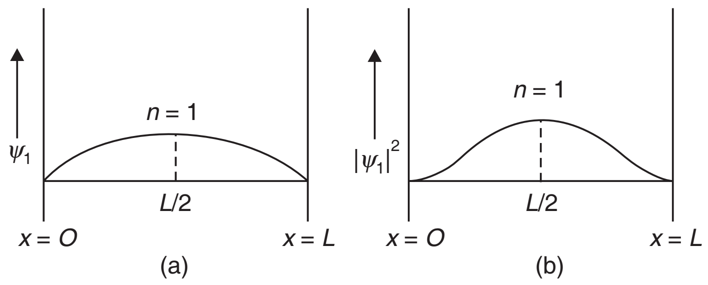

Fig. 23.8 Plot showing the variation in ψ_1 and $|\psi_1|^2$ against x

From Fig. 23.8(b), it is clear that the probability of finding the particle inside the box is maximum at $x = L/2$, while it is zero at $x = 0$ and $x = L$. We can conclude that in ground state, the probability of finding the particle is maximum at central region, while it is minimum at the walls of the box.

Condition II: When $n = 2$

This condition is known as *first excited state*. In this case, the energy of the particle can be given as

$$E_2 = \frac{4h^2}{8mL^2} = 4E_0$$

In this condition, wave function ψ^2 can be given as

$$\psi^2 = \sqrt{\left(\frac{2}{L}\right)}\sin\left(\frac{2\pi x}{L}\right)$$

From the above expression, it is clear that ψ^2 is zero for $x = 0$, $L/2$, and L. But it is maximum at $x = L/4$ and $x = 3L/4$.

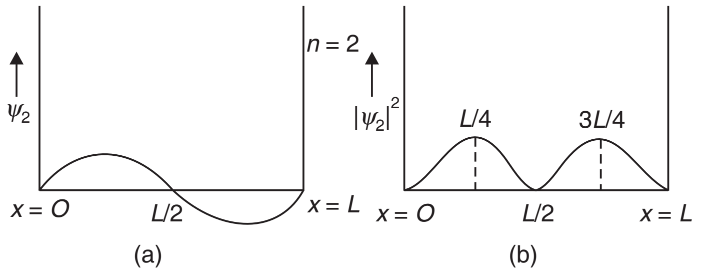

Fig. 23.9 Variation in ψ_2 and $|\psi_2|^2$ against x

The variation in ψ_2 and probability density $|\psi_2|^2$ with x is shown in Fig. 23.9. It is clear from this figure that particle is observed neither at the walls nor at the centre of the box. The maximum probability of finding the particle is either at $x = L/4$ or $3L/4$.

Condition III: When $n = 3$

Similar to above conditions, we can obtain the expression of energy for the *second excited state* which can be given as

$$E_3 = \frac{9h^2}{8mL^2} = 9E_0$$

and corresponding eigenfunction in this state can be given as

$$\psi_3 = \sqrt{\left(\frac{2}{L}\right)}\sin\left(\frac{3\pi x}{L}\right)$$

$$\psi_3 = 0 \text{ for } x = 0, \frac{L}{3}, \frac{2L}{3}, \text{ and } L$$

ψ_3 has maximum values for $x = L/6, L/2,$ and $5L/6$. The variation in ψ_3 and $|\psi_3|^2$ versus x is shown in Fig. 23.10

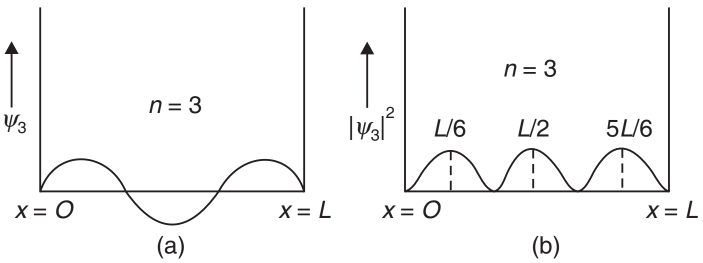

Fig. 23.10 Variation in eigenfunction and probability density versus *x*

It is clear from Fig. 23.10 that the particle is most likely to be found at the locations $x = L/6, L/2,$ or $5L/6$. This means that particle is found neither at the walls nor at the centre of the box.

23.17 ENERGY EIGENVALUES OF A PARTICLE IN A POTENTAL WELL OF INFINITE DEPTH

For a particle which is in a potential well of infinite depth, the potential energy is expressed as

$$V(x) \begin{array}{lll} = \infty & \text{for} & x < 0 \\ = 0 & \text{for} & 0x < l \\ = \infty & \text{for} & l < x \end{array} \Bigg] \tag{23.70}$$

If $\psi(x)$ is the solution of Schrödinger's wave equation for the above problem, then it is expressed in terms of probability for finding the particle in the different regions as expressed in Eq. (23.70). For different conditions of Eq. (23.70), $\psi(x)$ is expressed as

$$\psi(x) \begin{array}{ll} = 0 & x < 0 \\ = 0 & x > 0 \end{array} \Bigg] \tag{23.71}$$

and inside the box where $V(x) = 0$, the Schrödinger wave equation takes the form

$$\frac{d^2\,\psi(x)}{dx^2} + \frac{2\,mE}{\hbar^2}\;\psi(x) = 0 \tag{23.72}$$

or $$\frac{d^2\,\psi(x)}{dx^2} + k^2\,\psi(x) = 0 \tag{23.73}$$

where $$k^2 = \frac{2\,mE}{\hbar^2} \tag{23.74}$$

The most general solution of Eq. (23.73) is of the form A sin kx + B cos kx, which can be expressed as Eq. (23.78). Using the suitable boundary conditions (see Section 23.16),

$$\psi(x) = A\sin kx \tag{23.75}$$

The condition $u(l) = 0$ implies that

$$ka = n\pi \quad \text{where} \quad n = 1, 2, 3, \ldots$$

Thus, the energy eigenvalues are

$$E_n = \frac{\hbar^2\,k^2}{2\,m} = \frac{\hbar^2\,\pi^2\,n^2}{2\,ml^2}, \quad \text{where} \quad n = 1, 2, 3, \ldots \tag{23.76}$$

Now, it is easy to check that the solutions are normalized if $A = \sqrt{2/l}$, so that

$$\psi_n(x) = \sqrt{\frac{2}{l}}\sin\frac{n\pi x}{l} \tag{23.77}$$

The solutions have the property that

$$\begin{aligned}\int_0^l \psi_n^*(x)\,\psi_m(x)\,dx &= \int_0^l \frac{2}{l}\sin\frac{n\pi x}{L}\sin\frac{m\pi x}{L}\,dx \\ &= \frac{1}{a}\int_0^l\left\{\cos\frac{(n-m)\pi x}{l} - \cos\frac{(n+m)\pi x}{l}\right]dx \\ &= \frac{\sin(n-m)\pi}{(n-m)\pi} - \frac{\sin(n+m)\pi}{(n+m)\pi} \\ &= 0 \quad \text{if} \quad n \neq m \\ &= 1 \quad \text{if} \quad n = m\end{aligned} \tag{23.78}$$

The conclusion of the above can be given by the following expression:

$$\int_0^l \psi_n^*(x)\,\psi_m(x) = \delta_{mn} \tag{23.79}$$

It implies that eigenfunctions corresponding to different eigenvalues are orthogonal.

We can draw the following important physical information from the eigensolutions:

(i) The ground state energy, i.e., the state of lowest energy can be described by $\upsilon_1(x)$ and it is given as

$$E_1 = \frac{\pi^2\hbar^2}{2ml^2} \tag{23.80}$$

Classically, the lowest energy of the particle, i.e., the sum of kinetic and potental energies would be zero. But, according to the quantum mechanical treatment, we see the presence of a minimum energy.

(ii) Inside the well, $p^2 = 2\ mE$ and hence, we have

$$<p^2> = 2\ m\ E_n = \frac{\hbar^2 \pi^2 n^2}{l^2} \tag{23.81}$$

for the eigenfunction $\psi_n(x)$.

(iii) The number of nodes in a solution increases with the energy of nodes as shown in Fig. 23.11. This is understandable, since the kinetic energy grows with the curvature of the solutions. The expectation value of the kinetic energy is given as

$$<K> = \frac{\hbar^2}{2m} \int dx \left| \frac{d\psi(x)}{dx} \right|^2 \tag{23.82}$$

From the above expression, it is clear that $<K>$ will be large if $\psi(x)$ varies a lot.

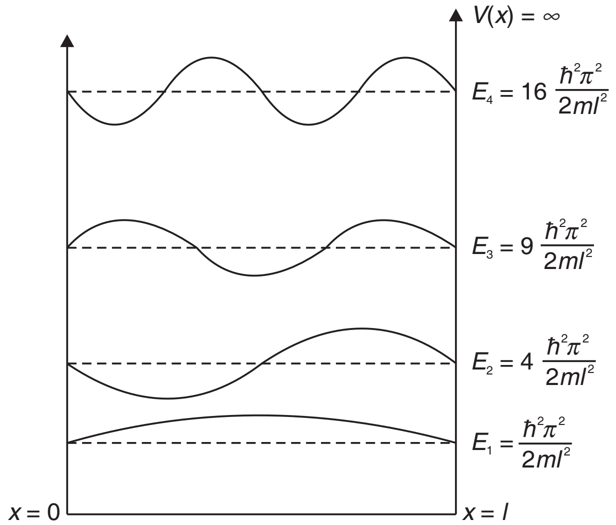

Fig. 23.11 Eigensolution for a particle in a potential well of infinite depth

23.18 ENERGY EIGENVALUES FOR A FREE PARTICLE

The Schrödinger wave equation for a particle of mass m, total energy E, and potential energy V is given as

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

For a free particle, $V = 0$ and the above equation can be given as

$$\nabla^2\psi + \frac{2m}{\hbar^2} E\psi = 0 \tag{23.83}$$

or

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} + \frac{2m}{\hbar^2}E\psi = 0 \tag{23.84}$$

Since Eq. (23.84) is a partial differential equation in three independent variables x, y, and z, so it can be solved by the method of separation of variables imposing the suitable boundry conditions for ψ. Now, the solution of Eq. (23.81) can be written as

$$\psi(x, y, z) = X(x)\, Y(y)\, Z(z) \tag{23.85}$$

Using the method of separation of variables, the differential equations for x, y, and z can be given as

$$\frac{\partial^2 X}{\partial x^2} + \frac{2m}{\hbar^2} E_x\; X = 0 \tag{23.86}$$

$$\frac{\partial^2 Y}{\partial y^2} + \frac{2m}{\hbar^2} E_y\; Y = 0 \tag{23.87}$$

$$\frac{\partial^2 Z}{\partial z^2} + \frac{2m}{\hbar^2} E_z\; Z = 0 \tag{23.88}$$

The general solution of Eqs. (23.86), (23.87), and (23.88) can be given as Eqs. (23.89), (23.90), and (23.91), respectively.

$$X(x) = N_x \sin \left\{ \frac{\sqrt{2mE_x}}{\hbar} (x - x_0) \right] \tag{23.89}$$

$$Y(y) = N_y \sin \left\{ \frac{\sqrt{2mE_y}}{\hbar} (y - y_0) \right] \tag{23.90}$$

$$Z(x) = N_z \sin \left\{ \frac{\sqrt{2mE_z}}{\hbar} (z - z_0) \right] \tag{23.91}$$

where N_x, N_y, N_z, x_0, y_0, and z_0 are arbitrary constants.

From Eqs. (23.86), (23.87), and (23.88), we can write

$$E_x + E_y + E_z = E \tag{23.92}$$

As any sine function is single-valued, finite, and continuous for real values of its argument, therefore, for finite values of x, y, and z, the values of E_x, E_y, E_z and hence, E must be positive. Thus, the eigenfunction and eigenvalues of the free particle will be given as

$$\begin{aligned} \psi &= X \cdot Y \cdot Z \\ &= N \sin \left\{ \frac{\sqrt{2mE_x}}{\hbar} (x - x_0) \right] \sin \left\{ \frac{\sqrt{2mE_y}}{\hbar} (y - y_0) \right] \sin \left\{ \frac{\sqrt{2mE_z}}{\hbar} (z - z_0) \right] \end{aligned} \tag{23.93}$$

where $N = N_x N_y N_z$ is known as normalization constant

and $$E = E_x + E_y + E_z \tag{23.94}$$

where E_x, E_y, and E_z are positive. It is clear from the above equation that a free particle has a continuous set of energy levels.

23.19 POTENTIAL STEP

In the case of a potential step the potential function undergoes only one discontinuous change as shown in Fig. 23.12 and hence the potential function of a potential step may be represented as

$$V(x) = \begin{Bmatrix} 0 \text{ for } x < 0 \\ V_0 \text{ for } x > 0 \end{Bmatrix} \quad 23.95$$

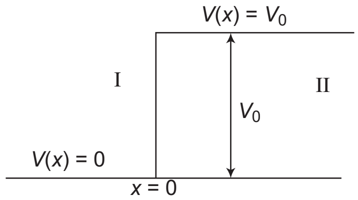

Fig. 23.12 Potential step as defined in equation

As defined in equation (23.95) we have considered V_0 as the height of the potential barrier. Let us consider electron having energy E moving from left to right i.e. along the positive x-direction. The energy of the electron may be greater than V_0 or less than V_0.

According to classical mechanics if energy of electron is more than V_0 then it will penetrate in the region II, but if it will less than electron will be reflected back at $x = 0$.

Under quantum mechanical consideration electron can be treated as wave and while moving from left to right it faces a sudden shift in potential at $x = 0$. This is analogous to the propagation of light wave when it strikes a glass plate and faces a change in refractive index. Similar to light wave the electron will be partly reflected and partly transmitted at $x = 0$ i.e. at discontinuity. According to the energy of electron we can take us this problem in two cases: as discussed below:

Case I: When $E > V_0$

Now we apply schrodinger wave equation to region I and II in the region I, the schrodiger wave equation can be given as.

$$\frac{d^2\psi_1}{dx^2} + \frac{2m}{\hbar^2} - K_1^2$$

or
$$\frac{d^2\psi_1}{dx^2} + K_1^2\ \psi_1 = 0 \text{ where } \frac{2ME}{\hbar^2}\ K_1^2 \quad (23.96)$$

In the region II, Schroding wave equation can be written as

$$\frac{d^2\psi_2}{dx^2} + \frac{2ME}{\hbar^2}(E - V_0)\ \psi_0 = 0$$

or
$$\frac{d^2\psi_2}{dx^2} + K_2^2\ 4_2 = 0 \text{ where } K_2^2 = \frac{2m(E - V_0)}{\hbar^2} \quad (23.97)$$

The general solution of equation (10.96) and (10.97) have the form

$$\psi_1 = A\, e^{ik_1 x} + B\, e^{-ik_1 x}\ \{x < 0) \quad (10.98)$$

$$\psi_2 = C\, e^{ik_2 x} + D\, e^{-ik_2 x} \ \{x > 0\} \tag{10.99}$$

where A, B, C and D are the constants and their value can be determined by using boundary conditions.

In equation (10.98) first term represents incident wave and second term corresponds to reflected wave. Since there is discontinuity at $x = 0$ in region I so equation (10.98) represents the solution of schrodinger's wave equation in region I.

Similar to above, equation (10.99) also have two terms in which first term represent incident wave and second term corresponds to reflected wave. Since there is no discontinuity in region II so, no part of electron wave will reflect back. Thus in equation (10.99) $D = 0$ and equation (23.99) can be given as.

$$\psi_2 = C\, e^{ik_2 x} \tag{23.100}$$

In this way equation (23.98) and equation (23.100) will be the solution of Schrodinger's wave equation in I and II region respectively.

From probability of wave function, ψ must to finite, i.e., it must be continuous. So we will have the following boundary conditions.

$$(\psi_1)_{x=0} (\psi_2)_{x=0} \tag{23.101}$$

and
$$\left(\frac{\partial \psi_1}{\partial x}\right)_{x=0} = \left(\frac{\partial \psi_2}{\partial x}\right)_{x=0} \tag{23.102}$$

Using these boundary conditions to equation (23.98) and (23.100) we get

$$A + B = C \tag{23.103}$$

and
$$K_1 A - K_1 B = K_2 C \tag{23.104}$$

Putting the value of C in equation (23.104) we get.

$$K_1 A - K_1 B = K_2 (A + B)$$

$$(K_1 - K_2)\, A = (K_1 + K_2) B$$

or
$$B = \left(\frac{K_1 - K_2}{K_1 + K_2}\right) A \tag{23.105}$$

Using the value of B in equation (10.103) we get.

$$A + \left(\frac{K_1 - K_2}{K_1 + K_2}\right) A = C$$

or
$$C = \left(\frac{2\, K_1}{K_1 + K_2}\right) A$$

In this case B and C represent the amplitudes of reflected and transmitted beam respectively in terms of amplitude of incident wave.

If $\psi\psi^*$ represents the probability density and v is the velocity of the stream of particles then $\psi\psi^* v$ represents the current density i.e. number of particles crossing unit area placed perpendicular to the direction of motion.

Not incident flux *Ni* can be given as.

$$Ni = |A\psi\psi^*|^2\, v = |A|^2\, v = |A|^2\, \frac{K_1 \hbar}{m} \tag{23.107}$$

Since $$K_1 = \sqrt{\frac{2mE}{\hbar^2}} = \sqrt{\frac{2m\left(\frac{1}{2}\right)mv^2}{\hbar^2}} = \frac{mv}{\hbar} \quad \therefore\ v = \frac{K_1 \hbar}{m}$$

Similarly the reflected flux Nr can be given as

$$N_r = |B|^2\, v = \left|\left(\frac{K_1 - K_2'}{K_1 + K_2}\right)\right|^2 |A|^2\, \frac{k_1 \hbar}{m} \tag{23.108}$$

and the transmitted flux N_t can be given as

$$N_t = \frac{4\,K_1^2}{(K_1 + K_2)^2}\, \frac{K_2 \hbar}{m} |A|^2$$

$$\left[\text{Since }\ K_2 = \sqrt{\frac{2m(E - V_0)}{\hbar^2}}\right] = \sqrt{\frac{2m\left(\frac{1}{2}\right)mv_1^2}{\hbar^2}} = \frac{mv_1}{\hbar} \qquad \left\{\therefore\ v_1 = \frac{k_0 \hbar}{m}\right.$$

or $$N_t = \frac{4\,K_1^2\,K_2}{(k_1 + k_2)^2}\, \frac{\hbar}{m} |A|^2$$

or $$N_t = \frac{4\,K_1^2\,K_2}{(k_1 + k_2)^2} |A|^2\, \frac{k_1 \hbar}{m} \tag{23.109}$$

From equation (23.107), (23.108) and (23.109) we can write.

$$N_i = N_t + N_r$$

According to the quantum mechanics there will be some probability of reflection and some probability of transmission. The reflection (R) transmission (T) coefficients can be defined as

$$\text{Reflection coefficient } R = \frac{\text{Magnitude of reflected flux}}{\text{Magnitude of incident flux}} = \frac{N_r}{N_i}$$

or $$R = \frac{(K_1 - K_2)^2}{(K_1 + K_2)^2} \tag{23.110}$$

$$\text{Transmission coefficient } (T) = \frac{\text{Magnitude of transmitted flow}}{\text{Magnitude of incident flux}} = \frac{N_t}{N_i}$$

or $$T = \frac{4\,K_1\,K_2}{(K_1 + K_2)^2} \tag{23.111}$$

From equation (23.110) and (23.111) we get

$$T + R = \frac{4\,K_1\,K_2}{(K_1 + K_2)^2} + \frac{(K_1 - K_2)^2}{(K_1 + K_2)^2} = 1$$

Case II: When $E < V_0$

The Schrodinger wave equation in region I is the same and is given as.

$$\psi = A\,e^{ik_1 x} + B\,e^{-ik_1 x} \tag{9.112}$$

For region II, the schrodinger wave equation is given as

$$\frac{d^2\psi_2}{dx^2} - \frac{2m}{\hbar^2}(V_0 - E)\,\psi_2 = 0$$

or $$\frac{d^2\psi_2}{dx^2} + K_3^2\,\psi_2 = 0 \text{ where } K_3^2 = \frac{2m}{\hbar^2}(V_0 - E) \tag{23.113}$$

The general solution of this equation can be given as

and $$\psi_2 = C\,e^{k_3 x} + D\,e^{-k_3 x}$$

Since no particle goes to region II so. $e^{-k_3 x} = 0$

and $$\psi_2 = D\,e^{-k_3 x} \tag{23.114}$$

Using the earlier boundary condition we get

$$A + B = D \tag{23.115}$$

$$ik_1\,A - ik_2\,B = -k_2 D \tag{23.116}$$

After solving equation (23.115) and (23.116) we get

$$B = \left(\frac{(ik_1 + k_3)}{(ik_1 - k_3)}\right)A \tag{23.117}$$

and $$D = \left[\frac{2i\,K_1}{(ik - k_3)}\right]A \tag{23.118}$$

Now incident flux $N_i = v\,|A|^2$ (23.119)

and reflected flux

$$N_r = v\,|B|^2 = v\left|\left(\frac{ik_1 + k_3}{ik_1 - k_3}\right)\right|^2 |A|^2$$

$$= -v|A|^2 = N_i \tag{23.120}$$

It means all the particles are reflected at the barrier.

Transmitted flux can be given as

$$N_t = \frac{4k_1^2}{k_1^2 + k_3^2} |A|^2 \tag{23.121}$$

From equation (23.121) it is clear that N_t is not zero until K_1. It means if $N_i \neq 0$ there is some probability of particles going to the region II. It shows that even if the energy of the particles is less than the height of potential barrier, there is some probability of its penetration.

10.20 RECTANGULAR POTENTIAL BARRIER

Let us consider a beam of particles of kinetic energy E incident from the left on a potential barrier of height V and width $OA = L$ (Fig. 23.13). Here $V > E$ and on both sides of the barrier, $V = 0$, $2t$ means that no forces act upon the particles there.

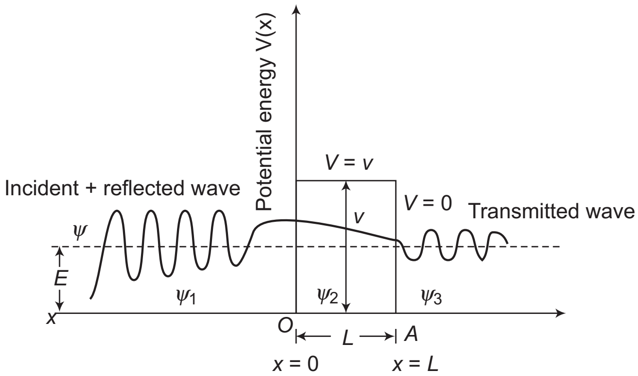

Fig. 23.13 Potential barrier of height V and with L and tunneling of electron beam

This potential is described by.

$$\left.\begin{array}{ll} V = 0 & \text{for } x < 0 \text{ (region I)} \\ V = 0 & \text{for } 0 < x < L \text{ (region II)} \\ V = 0 & \text{for } x > L \text{ (region III)} \end{array}\right] \tag{23.122}$$

Let us consider ψ_1, ψ_2 and ψ_2 be the respective wave functions in the regions I, II and III as shown in Fig. (23.23).

Now the schrodinger wave equation for different regions can be given as

Region I $$\frac{d^2 \psi_1}{dx^2} + \frac{8\pi^2 m E}{\hbar^2} \psi_1 = 0 \tag{23.123}$$

Region II $$\frac{d^2 \psi_2}{dx^2} + \frac{8\pi^2 m E}{\hbar^2} \psi_1 = 0 \tag{23.124}$$

Region III $$\frac{d^2 \psi_3}{dx^2} + \frac{8\pi^2 m E}{\hbar^2} \psi_2 = 0 \tag{23.125}$$

Let us assume $\alpha^2 = \dfrac{8\pi^2\, m\, E}{\hbar^2}$ and $\beta^2 = \dfrac{8\pi^2 m\,(V-E)}{\hbar^2}$

Using these values in above equations we get

Region I $$\frac{d^2\,\psi_1}{dx^2} + \alpha^2\,\psi_1 = 0 \tag{23.126}$$

Region II $$\frac{d^2\,\psi_2}{dx^2} + \beta^2\,\psi_2 = 0 \tag{23.127}$$

Region III $$\frac{d^2\,\psi_3}{dx^2} + \alpha^2\,\psi_3 = 0 \tag{23.128}$$

The solution of these equation can be given as

Region I $$\psi_1 = A\,e^{i\alpha x} + B\,e^{-i\alpha x} \tag{23.129}$$

Region II $$\psi_2 = F\,e^{-\beta x} + G\,e^{\beta x} \tag{23.130}$$

Region III $$\psi_3 = C\,e^{i\alpha x} + D\,e^{-i\alpha x} \tag{23.131}$$

where A, B, C, D, F and G are the constants which represents the corresponding components of each wave. These can be defined as

A = Amplitude of incidenting wave on the barrier from the left.

B = Amplitude of reflected wave in region I

F = Amplitude of the wave, penetrating the barrier in the region II.

G = Amplitude of reflected wave (from the surface at A) in region II

C = Amplitude of transmitted wave, in the region III

D = Amplitude of a (non existent) reflected wave, in region III.

It should be noted that we have drawn the wave function through all three regions in Fig. (9.13) so that it is continuous and single valued everywhere along the x-axis.

We know that the probability density associated with the wave function is proportional to the square of the amplitude of that function. Thus the barrier transmission coefficient can be defined as.

$$T = \frac{|C|^2}{|A|^2} \tag{23.132}$$

and the reflection coefficient for the barrier surface at $x = 0$ as

$$R = \frac{|B|^2}{|A|^2} \tag{23.133}$$

If the barrier is high, compared to the total energy of the particle, or is thick compared to the wave-length of the wave function, then the transmission coefficient can be given as.

$$T = 16\frac{E}{V}\left(1-\frac{E}{V}\right)\exp\left[-\frac{2L}{(h/2\pi)}\sqrt{2m\,(V-E)}\right] \tag{23.134}$$

where L is the physical thickness of the barrier. The ratio $\frac{|C|^2}{|A|^2}$ is also called the "Penetrability" of the barrier.

23.20.1 Tunneling

The property of the barrier penetration is entirely due to the wave nature of matter and is very similar to the total internal reflection of light waves. If two plates of glass are placed closed to each other with a layer of air as a medium between them, the light will be transmitted from one plate to another, even though the angle of incidence is greater than critical angle. However the intensity of transmitted wave will decrease exponentially with thickness of the layer of air. The wave function has the form more or less as shown in Fig. (23.13).

From the equation (23.134) it is clear that there is some probability that the incident particles on the barrier from one side will appear on the other side. Such probability is zero classically. But a finite quantity in quantum mechanics. We thus conclude that if a particle with energy E is incident on a thin energy barrier of height greater than E, there is a finite probability of particle, penetrating the barrier this phenomena is known as tunnel effect. This effect was used by George Gamow in 1928 to explain the process of α-decay exhibited by radioactive nuclei. It also used in the explanation of thermionic and field emission.

Example 23.20

Find the energy of an electron moving in one-dimension in an infinitely high potential box of width 1 Å. (Mass of the electron is 9.1×10^{-31} kg and $h = 6.63 \times 10^{-34}$ Js.)

Solution

From the expression of energy of a particle in a deep potential box of width L, we have

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

where $n = 1, 2, 3, ...$

Particle is generally found in the ground state, which occurs corresponding to $n = 1$.

Hence,

$$\begin{aligned} E &= \frac{h^2}{8mL^2} \\ &= \frac{(6.63\times10^{-34})^2}{8\times9.1\times10^{-31}\times(1\times10^{-10})^2} \\ &= \frac{43.96\times10^{-68}}{72.8\times10^{-51}} \\ &= 6.038\times10^{-18}\text{ J} \end{aligned}$$

$$= \frac{6.038 \times 10^{-18}}{1.6 \times 10^{-19}} \text{ eV}$$

$$= 37.74 \text{ eV}$$

Example 23.21

A particle is in motion along a line between $x = 0$ and $x = a$ with zero potential energy. At points for which $x < 0$ and $x > a$, the potential energy is infinite. The wave function for the particle in the nth state is given by

$$\psi_n = A \sin \frac{n\pi x}{a}$$

Find the expression for the normalized wave function.

Solution

The wave function of a particle in deep potential box is given as

$$\psi_n = A \sin \frac{n\pi x}{a}$$

where n represents the nth order and a is the length of the line along which the particle is moving.

To find the value of A, we will use the condition of normalization as given below.

$$\int_{-\infty}^{+\infty} |\psi(x)|^2 \, dx = 1$$

When we use this condition, we get

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

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

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

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

or
$$A = \sqrt{\frac{a}{2}}$$

Using this value of A in wave function, the normalized wave function of the particle is given as

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

Example 23.22

A particle of mass m is represented by the wave function $\psi_n = A_n \sin \dfrac{n\pi x}{a}$ in the range $0 \le x \le a$ and $\psi = 0$ elsewhere. Find the normalized form of the wave function.

Solution

Solution of this problem is same as the solution of Example 23.21.

Example 23.23

An electron is bound in one-dimensional potential box which has the width 2.5×10^{-10} m. Assuming the height of the box to be infinite, calculate the two lowest permitted energy values of the electron.

Solution

The energy of a particle of mass m moving in one-dimensional potential box of infinite height and of width L is given as

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

where $n = 1, 2, 3, ...$

The first lowest energy of the electron is obtained by putting $n = 1$ and the second lowest energy level corresponds to $n = 2$. Hence,

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

and
$$E_2 = 4 \cdot \frac{h^2}{8mL^2} = 4E_1$$

Now,
$$E_1 = \frac{(6.63 \times 10^{-34})^2}{8 \times 9.1 \times 10^{-31} \times (2.5 \times 10^{-10})^2}$$

$$= \frac{43.956 \times 10^{-68}}{455 \times 10^{-51}}$$

$$= 9.66 \times 10^{-19} \text{ J}$$

$$= \frac{9.66 \times 10^{-19}}{1.6 \times 10^{-19}} \text{ eV}$$

$$= 6.04 \text{ eV}$$

Since $E_2 = 4E_1$

$\Rightarrow$ $E_2 = 4 \times 6.04 \text{ eV} = 24.16 \text{ eV}$

Hence, the first two lowest energy levels of the electron are 6.04 eV and 24.16 eV, respectively.

Example 23.24

A particle confined to move along the X-axis has the wave function $\psi = ax$ between $x = 0$ and $x = 1.0$, and $\psi = 0$ elsewhere. Find the probability that the particle can be found between $x = 0.35$ to $x = 0.45$. Also, find the expectation value $<x>$ of particle's position.

Solution

The probability of finding the particle between x_1 and x_2 in nth state can be given as

$$P = \int_{x_1}^{x_2} |\psi_n|^2 \, dx$$

Given that $\psi_n = ax$ between $x = 0$ and $x = 1$, and $x_1 = 0.35$ and $x_2 = 0.45$.

Now,
$$\begin{aligned} P &= \int_{0.35}^{0.45} (ax)^2 \, dx \\ &= a^2 \int_{0.35}^{0.45} x^2 \, dx \\ &= \frac{a^2}{3}\left[x^3\right]_{0.35}^{0.45} \\ &= \frac{a^2}{3}\left[(0.45)^3 - (0.35)^3\right] \\ &= \frac{a^2}{3}[0.09112 - 0.04287] \\ &= 1.6083a^2 \times 10^{-2} \\ &= 0.0161a^2 \end{aligned}$$

We know that the expectation value (average value) of position can be given as

$$<x> = \int_{-\infty}^{\infty} \psi_n^* x \cdot \psi_n(x) dx$$

Since the particle is confined in a box having its limit $x = 0$ to $x = 1$ and $\psi_n = \psi_n^* = ax$,

$$\Rightarrow \quad \begin{aligned} <x> &= \int_0^1 ax \cdot x \cdot ax \, dx \\ &= a^2 \int_0^1 x^3 \, dx \\ &= \frac{a^2}{4} \\ &= 0.25a^2 \end{aligned}$$

Example 23.25

Find the probabilities of finding a particle trapped in a box of length L in the region from $0.45L$ to $0.55L$ for the ground state and the first excited state.

Solution

If a particle is trapped in a box of length L, then the wave function can be given as

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

Now, the probability of finding the particle between $0.45L$ to $0.55L$ can be given as

$$P = \int_{0.45L}^{0.55L} \left(\sqrt{\left(\frac{2}{L}\right)} \sin \frac{n\pi x}{L} \right)^2 dx$$

$$= \frac{2}{L} \int_{0.45L}^{0.55L} \sin^2 \frac{n\pi x}{L} dx$$

$$= \frac{1}{L} \int_{0.45L}^{0.55L} \left(1 - \cos \frac{2\pi n x}{L} \right) dx$$

$$= \frac{1}{L} \left[x - \frac{L}{2\pi n} \sin \frac{2\pi n x}{L} \right]_{0.45L}^{0.55L}$$

For $n = 1$, we have

$$P = \frac{1}{L} \left[\left(0.55L - \frac{L}{2\pi} \sin(1.10\pi) \right) - \left(0.45L - \frac{L}{2\pi} \sin(0.90\pi) \right) \right]$$

$$= \left[\left(0.55 - \frac{1}{2\pi} \sin 198° \right) - \left(0.45 - \frac{1}{2\pi} \sin 162° \right) \right]$$

$$= (0.55 - 0.45) - \frac{1}{2\pi} (\sin 198° - \sin 162°)$$

$$= 0.10 - \frac{1}{2\pi} (\sin 198° - \sin 162°)$$

$$= 0.10 - (-0.0984)$$

$$= 0.1984$$

$$= 19.84\%$$

Similarly, for the first excited state (for $n = 2$), the above calculation gives the value of probability as $P = 0.65\%$.

Example 23.26

Calculate the energy difference between the ground state and first excited state of an electron in a one-dimensional rigid box of length 10^{-8} cm.

Solution

The energy of a particle of mass m in a one-dimensional box of length L is given as

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

where $n = 1, 2, 3, ...$

$$E_n = \frac{n^2(6.63\times10^{-34})^2}{8\times9.1\times10^{-31}\times(10^{-10})^2} = 6.03\times10^{-18}\,n^2\text{ J}$$

$$= \frac{6.03\times10^{-18}}{1.6\times10^{-19}}n^2\text{ eV}$$

$$= 37.68\,n^2\text{ eV}$$

For ground state, $n = 1$

Hence, $E_1 = 37.68$ eV

For first excited state, $n = 2$

Hence, $E_2 = 37.68 \times 2^2 = 150.72$ eV

Difference in energy between the first excited state and the ground state can be given as

$$\Delta E = E_2 - E_1 = 150.72 - 37.68$$

$$= 113.04\text{ eV}$$

Example 23.27

An electron is confined to move between two rigid walls separated by 1 Å. Find the de Broglie wavelength representing the first three allowed energy states of the electron and their corresponding energies.

Solution

The backward and forward motions of the electron between the rigid walls of the box form a stationary wave pattern with nodes at the walls. Hence, the distance between the walls will be a whole multiple of half of the de Broglie wavelength. Hence, we get

$$L = n\left(\frac{\lambda}{2}\right)$$

where $n = 1, 2, 3, ...$

or $$\lambda = \left(\frac{2L}{n}\right)$$

Given that $L = 1\text{ Å} = 10^{-10}$ m

Thus, corresponding to $n = 1, 2, 3, ...$,

$$\lambda = \frac{2\times1\text{Å}}{n} = 2\text{ Å}, 1\text{ Å}, 0.667\text{ Å} ...$$

The energy of the electron in the box can be given as

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

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

$$= 6.04 \times 10^{-18}\, n^2 \text{ J}$$

$$= \frac{6.04 \times 10^{-18}}{1.6 \times 10^{-19}} n^2 \text{ eV}$$

$$= n^2 \cdot 37.73 \text{ eV}$$

$$E_1 = 37.73 \text{ eV (For } n = 1)$$

$$E_2 = 150.92 \text{ eV (For } n = 2)$$

$$E_3 = 339.57 \text{ eV (For } n = 3)$$

Example 23.28

Can you observe the energy states of a ball of mass 100 g moving in a box of length 1 m?

Solution

We know that the energy of a particle moving in a box is given as

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

Given that $m = 100$ g = 0.1 kg and $L = 1$ m. Therefore,

$$E_n = \frac{n^2 \times (6.63 \times 10^{-34})^2}{8 \times 0.1 \times 1} = 5.49 \times 10^{-68}\, n^2 \text{ J}$$

$$= n^2 \frac{5.49 \times 10^{-68}}{1.6 \times 10^{-19}} = 3.43 \times 10^{-49}\, n^2 \text{ eV}$$

$$\Rightarrow \quad E_1 = 3.43 \times 10^{-49} \text{ eV}$$

$$E_2 = 1.372 \times 10^{-48} \text{ eV}$$

$$E_3 = 3.087 \times 10^{-48} \text{ eV}$$

and so on.

The energy difference between different energy levels is so small that we cannot observe it.

Example 23.29

A particle is moving in a one-dimensional box of width 30 Å. Calculate the probability of finding the particle within and at interval of 2 Å at the centre of the box when it is in its state of least energy.

Solution

The wave function of a particle trapped in a deep potential box is given as

$$\psi_n(x) = \sqrt{\left(\frac{2}{L}\right)} \sin \frac{n\pi x}{L}$$

In the ground state ($n = 1$), particle will be at its lowest energy state. Therefore,

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

At the centre of the box, $x = L/2$. The probability of finding the particle in the unit interval at the centre of the box is given as

$$|\psi(x)|^2 = \left[\sqrt{\left(\frac{2}{L}\right)}\sin\frac{\pi(L/2)}{L}\right]^2$$

$$= \frac{2}{L}\sin^2\frac{\pi}{2} = \frac{2}{L}$$

The probability P in the interval Δx is given as

$$P = |\psi(x)|^2\,\Delta x$$

$$P = \frac{2}{L}\Delta x$$

Given that $L = 30$ Å and $\Delta x = 2$ Å

$$\Rightarrow \qquad P = \frac{2}{30}\times 2$$

$$= 0.16$$

$$= 16\ \%$$

Example 23.30

The wave function of a free particle in normalized state is represented by

$$\psi(x) = Ne^{-(x^2/2a^2)\,+\,jkx}$$

Calculate the normalization factor N and the maximum probability of finding the particle.

Solution

From the normalization condition, we know that

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

Putting the value of ψ and ψ^* in the above equation, we get

$$\int_{-\infty}^{\infty}Ne^{-(x^2/2a^2)-jkx}Ne^{-(x^2/2a^2)+jkx}dx = 1$$

or $$N^2\int_{-\infty}^{\infty}e^{-x^2/a^2}dx = 1$$

Since $$\int_{-\infty}^{\infty}e^{-x^2/a^2}dx = a\sqrt{\pi}$$

$$\Rightarrow \qquad N^2 a\sqrt{\pi} = 1$$

or $$N = \frac{1}{a^{1/2}\pi^{1/4}}$$

The maximum probability $P(x)$ can be given as

$$P(x) = |\,\psi^*(x)\ \psi(x)\,|$$
$$= N^2 e^{-x^2/a^2}$$
$$= \frac{1}{a\sqrt{\pi}} e^{-x^2/a^2}$$

Example 23.31

Normalize the eigenfunction $\phi(x) = e^{icx}$ within the region $-a \le x \le a$.

Solution

Given that $\phi(x) = e^{icx}$

In order to normalize the wave function $\phi(x)$, let us multiply it by k. Thus,

$$\phi(x) = ke^{icx}$$

To find out the value of c, we apply normalization condition as

$$\int_{-a}^{a} \phi(x)\phi^*(x)dx = 1$$
$$\phi(x) = ke^{icx} \text{ and } \phi^*(x) = ke^{-icx}$$

Now, using these values in the above equation, we get

$$k^2 \int_{-a}^{a} e^{icx} e^{-icx} dx = 1$$
$$k^2 \int_{-a}^{a} dx = 1$$
$$k^2 [x]_{-a}^{a} = 1$$

or $$k^2 \cdot 2a = 1$$

or $$k = \frac{1}{\sqrt{2a}}$$

Hence, the normalized wave function can be given as

$$\phi(x) = \frac{1}{\sqrt{2a}} \cdot e^{icx}$$

Example 23.32

Which of the following are eigenfunctions of the operator $\partial^2/\partial x^2$? Find out the appropriate eigenvalue for them.

(i) $\sin x$ (ii) $\sin^2 x$ (iii) e^{2x} (iv) e^{ix}
(v) $\sin nx$

Solution

(i) Given that $f(x) = \sin x$

Operating $\partial^2/\partial x^2$ on $f(x)$, we get

$$\frac{\partial^2}{\partial x^2}(\sin x) = -\sin x = -f(x)$$

Hence, $\sin x$ is an eigenfunction having eigenvalue –1.

(ii) Given that $f(x) = \sin^2 x$

Operating $\frac{\partial^2}{\partial x^2}$ on $f(x)$, we get

$$\frac{\partial^2}{\partial x^2}(\sin^2 x) = 2 - 4\sin^2 x$$

Hence, it is not an eigenfunction for $f(x) = \sin^2 x$.

(iii) Given that $f(x) = e^{2x}$

Operating $\frac{\partial^2}{\partial x^2}$ on $f(x)$, we get

$$\frac{\partial^2}{\partial x^2}(e^2 x) = 2 \times 2e^{2x} = 4 f(x)$$

Hence, e^{2x} is an eigenfunction having eigenvalue +4.

(iv) Given that $f(x) = e^{ix}$

Now, $$\frac{\partial^2}{\partial x^2} f(x) = \frac{\partial^2}{\partial x^2}(e^{ix}) = -1 f(x)$$

Thus, e^{ix} is an eigenfunction having eigenvalue –1.

(v) Given that $f(x) = \sin nx$

Now, $$\frac{\partial^2}{\partial x^2}(\sin nx) = -n^2 f(x)$$

Thus, $\sin nx$ is an eigenfunction having eigenvalue $-n^2$.

Example 23.33

Write the Hamiltonian operator of a free particle moving in one direction under the influence of zero potential energy.

Solution

According to classical mechanics, the Hamiltonian is given by the sum of kinetic energy and potential energy, i.e.,

$$H = \frac{1}{2} m\upsilon^2 + \text{PE}$$

For zero potential energy,

$$H = \frac{1}{2} m\upsilon^2 = \frac{1}{2m} p_x^2$$

where p_x is the linear momentum along the X-axis.

But for linear operator, the operator is $\frac{\hbar}{i}\frac{\partial}{\partial x}$. Therefore,

$$\widehat{H} = \frac{1}{2m}\left[\frac{\hbar}{i}\frac{\partial}{\partial x}\right]^2$$

$$= \frac{1}{2m}\left[\frac{\hbar}{i}\frac{\partial}{\partial x}\right]\left[\frac{\hbar}{i}\frac{\partial}{\partial x}\right]$$

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

23.19 FORMULAE AND HIGHLIGHTS

1. According to the principle of uncertainty, it is not impossible to simultaneously measure the position and the momentum of a particle to any desired degree of accuracy.
2. Mathematically, uncertainty principle is expressed as

   (i) $\Delta p \cdot \Delta x \geq h/4\pi$ (ii) $\Delta E \cdot \Delta t \geq h/4\pi$

   (iii) $\Delta J \cdot \Delta \theta = h/4\pi$
3. The complementarity principle states that the wave and the particle aspects of matter are complementary, instead of being contradictory.
4. The expression of zero-point energy of simple harmonic oscillator is given as

   $$E_{\min} = E_0 = \frac{1}{2}\hbar\omega$$
5. According to the uncertainty principle, the simultaneous measurement of position and momentum of a particle with absolute accuracy is impossible.
6. The uncertainty principle has no meaning at macroscopic level.
7. Schrödinger wave equations are used to deal with the matter waves.
8. Time-independent Schrödinger wave equation is given as

   $$\nabla^2\psi + \frac{2m}{\hbar^2}(E - V)\psi = 0$$
9. Schrödinger wave equation for a free particle is given as

   $$\nabla^2\psi + \frac{2mE}{h^2}\psi = 0$$
10. Time-dependent Schrödinger wave equation is given as

    $$\left(-\frac{\hbar^2}{2m}\nabla^2 + V\right)\psi = i\hbar\frac{\partial\psi}{\partial t}$$
11. Wave function ψ gives the probability of finding the particle (i.e., $\psi\psi^* = |\psi|^2$) in the state ψ, i.e., ψ^2 is a measure of probability density.
12. Condition of normalization is given as

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

13. The energy of a particle inside an infinitely deep potential well is given as

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

14. Wave function of a particle enclosed in an infinitely deep potential well is given as

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

15. Probability current density is expressed as

$$\frac{dP}{dt} + \text{div}\,S = 0$$

16. A wave function that satisfies the condition

$$\int \psi^*(r,t)\psi(r,t)d\tau = 1$$

is said to be normalized to unity.

17. Eigenfunctions must be single-valued, finite, and continuous throughout the entire space under consideration.
18. If H is the Hamiltonian operator operated on eigenfunction $\psi(x)$, then it gives E as eigenvalue, i.e.,

$$H\psi_E(x) = E\psi_E(x)$$

19. For an infinitely deep potential well, eigenfunctions corresponding to different eigenvalues are orthogonal.

Exercises

Section A
Theoretical Questions

1. What are the consequences of the de Broglie concept?
2. State and explain Heisenberg's uncertainty principle.
3. Derive uncertainty principle using the concept of wave groups.
4. State and explain Heisenberg's uncertainty principle for position and momentum.
5. State and explain Heisenberg's uncertainty principle for energy and time.
6. What is uncertainty principle? How is this principle related to the concept of de Broglie hypothesis?
7. Mention and explain any two applications of uncertainty principle.
8. Using uncertainty principle, obtain the limit of accuracy with which one can determine the frequency of the radiation emitted by an excited atom.
9. Using uncertainty principle, show that the electrons cannot exist in the nucleus.

10. Using uncertainty principle, calculate the binding energy of an electron in an atom.
11. What are the consequences of uncertainty principle?
12. What is the significance of uncertainty principle for macroscopic bodies?
13. What is the importance of Schrödinger wave equations?
14. Deduce time-independent Schrödinger wave equation?
15. Derive time-dependent and time-independent Schrödinger wave equations.
16. What is the physical significance of wave function?
17. What is the importance of wave function in quantum mechanics?
18. What is the normalization condition?
19. Solve Schrödinger's wave equation for a particle in a one-dimensional rigid box of side L and having potential energy (V) as follows:

$$V(x) = \infty \text{ for } x < 0 \text{ and } x > L$$

$$V(x) = 0 \text{ for } 0 \le x \le L$$

20. A particle of mass m is represented by the wave function $\psi_1 = A_n \sin \dfrac{n\pi x}{a}$ in the range $0 \le x \le a$ and $\psi = 0$ elsewhere. Find the normalized form of the wave function.
21. Derive an expression for the wave function and energy of a particle confined in a one-dimensional potential box using Schrödinger's wave equation.
22. What do you mean by eigenfunction and eigenvalues?
23. Discuss the problem of one-dimensional box.
24. Find the eigenfunctions and eigenvalues of a free particle.
25. Write down the Schrödinger wave equation for a particle in an infinitely deep potential well and find its eigenvalues and eigenfunctions.
26. What is the condition for the normalized wave function? Describe in detail.
27. Explain the concept of probability current density.
28. Discuss the interpretation of position probability and normalization of wave function.
29. Prove that

$$\frac{\partial P}{\partial t} + \text{div } S = 0$$

where P is the probability density and S is the current density

Section B
Numerical Problems

1. Calculate the uncertainty in the momentum of an electron which is restricted to a region of linear dimension equal to 2 Å. (*Ans*. 2.64×10^{-23} kgm/s)

$$\left[\textit{Hint}: \Delta p \cdot \Delta x = \hbar/2 \qquad \Delta p = \frac{\hbar}{4\pi \times 2 \times 10^{-10}} \right]$$

2. If the uncertainty in the position of an electron is 2×10^{-9} m, calculate the uncertainty in its momentum. (*Ans*. 2.76×10^{-26} kgm/s)
3. Calculate the minimum uncertainty in the energy state of an atom if an electron remains in the state for about 10^{-8} s. (*Ans*. 3.3×10^{-8} eV)

   $$\left[Hint: \Delta E \cdot \Delta t = \frac{\hbar}{2} \right]$$

4. The position and the momentum of 0.5 keV electrons are simultaneously determined. If the position is located within 0.2 nm, what is the percentage uncertainty in its momentum? (*Ans*. 2.2%)

   [*Hint*: At the given value of energy, the given problem is non-relativistic.

   Hence, $p = \sqrt{2\,mE}$

   and $\Delta p \cdot \Delta x = \frac{h}{4\pi}$]

5. The uncertainty in measuring the speed of an accelerated electron is 1.2×10^5 m/s. Calculate the uncertainty in finding its location while it is still in motion. (*Ans*. 4.72×10^{-10} m/s)

   $$\left[Hint: \Delta p \cdot \Delta x = \frac{h}{4\pi} \right.$$

   $$\text{or} \qquad m \cdot \Delta \upsilon \cdot \Delta x = \frac{h}{4\pi}$$

   $$\left. \text{or} \qquad \Delta x = \frac{h}{4\pi m \cdot \Delta \upsilon} \right]$$

6. Calculate the uncertainty in the position of a dust particle with mass equal to 1 mg if uncertainty in its velocity is 5.5×10^{-20} m/s. (*Ans*. 9.58×10^{-10} m/s)

   $$\left[Hint: \Delta p \cdot \Delta x = \frac{h}{4\pi} \right.$$

   $$\left. \text{or} \qquad m \cdot \Delta \upsilon \cdot \Delta x = \frac{h}{4\pi} \right]$$

7. A proton is accelerated to one-tenth of the velocity of light. If the velocity can be measured with a precision of ± 0.5%, what must be the uncertainty in its position? ($m_p = 1.675 \times 10^{-27}$ kg) (*Ans*. 2.1×10^{-13} m)

   $$\left[Hint: \Delta p \cdot \Delta x = \frac{\hbar}{2} \right.$$

   $$\left. m \cdot \Delta \upsilon \cdot \Delta x = \frac{h}{4\pi} \right]$$

8. An electron has a speed of 500 m/s with uncertainty of 0.02%. What is the uncertainty in locating its position? (*Ans*. 5.77×10^{-4} m)

   $$\left[Hint: \Delta \upsilon = \frac{500 \times 0.02}{100} = 1 \text{ m/s} \right.$$

and $m \cdot \Delta\upsilon \cdot \Delta x = \frac{h}{4\pi}\Big]$

9. The time period of radar vibration is 0.25 μs. What is the order of uncertainty in the energy of the photon? (*Ans*. 2.64×10^{-23} J)

   $\left[Hint: \Delta t \cdot \Delta E = \frac{h}{4\pi}\right]$

10. The lifetime of an excited state of a nucleus is 152×10^{-12} s. What is the uncertainty in the energy of the emitted γ-ray photon? (*Ans*. 1.65×10^{-4} eV)

    $\left[Hint: \Delta t \cdot \Delta E = \frac{h}{4\pi}\right]$

11. If the uncertainty in the energy of an electron is equal to $h/4\pi$, then determine the uncertainty in its time. (*Ans*. $\Delta t = 1$s)

    $\Big[Hint: \Delta t \cdot \Delta E = \frac{h}{4\pi}$

    $\Delta t = \frac{h/4\pi}{h/4\pi} = 1\Big]$

12. An electron has the velocity of 4×10^5 m/s within the accuracy of 0.01%. Calculate the uncertainty in the position of the electron. (*Ans*. 1.448×10^{-6} m)

13. Find the values of momentum of a particle in a one-dimensional box with impenetrable walls of length 2 Å for $n = 1$ and $n = 2$. (*Ans*. 3.31×10^{-24} kgm/s and 6.62×10^{-24} kgm/s)

    [*Hint*: For a particle in a one-dimensional box of length l with impenetrable walls, momentum p_n is given as

    $$p_n = n\,\frac{\hbar\pi}{l}$$

    where $n = 1, 2, \ldots$

    $$p_1 = \frac{\hbar\pi}{l} = \frac{h \cdot \pi}{2\pi \cdot l} = \frac{h}{2l}$$

    and $p_2 = \frac{2h}{2l}\Big]$

14. Calculate the values of energy of an electron in a one-dimensional box with impenetrable walls of length 1 Å for $n = 1$ and $n = 2$. (*Ans*. 37.7 eV, 150.8 eV)

    $\Big[Hint: E_n = \frac{n^2 h^2}{8\,ml^2}$

    for $n = 1, E_1 = \frac{h^2}{8\,ml^2}$

    and for $n = 2, E_2 = \frac{4\,h^2}{8\,ml^2}\Big]$

15. Calculate the lowest value of energy of an electron in a one-dimensional force-free region of length 4 Å. (*Ans*. 2.36 eV)

$$\left[Hint: E_n = \frac{n^2 h^2}{8 ml^2} \right]$$

16. The lowest possible energy for a certain particle entrapped in a box is 20 eV. What are the next three higher energies that the particle can have? (*Ans*. 80 eV, 180 eV, 320 eV)

[*Hint*: $E_n = \dfrac{n^2 h^2}{8 ml^2}$

$$E_1 = \frac{h^2}{8 ml^2} = 20 \text{ eV (Given)}$$

$E_2 = 4E_1$
$E_3 = 9E_1$
$E_4 = 16E_1$]

17. A particle is confined in a box of length L. Calculate the probability of finding the particle between $0.4L$ to $0.6L$ in the ground state. (*Ans*. 0.4)

[*Hint*: $P_n \Delta x = \psi_n \cdot \psi_n^* \Delta x$

$$= \frac{1}{2} \sin^2 \frac{n\pi}{L} x \cdot \Delta x$$

Mean position $x = \dfrac{0.4\,L + 0.6\,L}{2} = 0.5L = \dfrac{L}{2}$

$\Delta x = 0.6L - 0.4L = 0.2L$]

18. Calculate the average value of P^2 for the wave function $\psi_x = \left(\dfrac{2}{l}\right)^{1/2} \sin\left(\dfrac{\pi x}{l}\right)$ in the region $0 < x < 1$, and $\psi_x = 0$ outside the region. (*Ans*. $\langle P^2 \rangle = (\hbar\pi/l)^2$)

[*Hint*: $\langle P^2 \rangle = \int_0^l \psi^* \hat{P}^2 \psi\, dx$

$$= \int_0^l \psi^* (-i\hbar)^2 \frac{\partial^2}{\partial x^2} \psi\, dx \,]$$

19. A particle of mass 2 mg is attached to a spring of spring constant 10^{-3} N/m. Calculate its zero-point energy and classical value of amplitude of zero-point vibration. (*Ans*. 7.37×10^{-15} eV)

[*Hint*: Frequency of vibration $\nu = \dfrac{1}{2\pi}\sqrt{\dfrac{k}{m}}$ and zero-point energy $E_0 = \dfrac{1}{2} h\nu$]

20. A particle trapped in a one-dimensional box of length L is described by the wave function $\psi = x$. Normalize the wave function between a and b. (*Ans*. $\dfrac{1}{3}(b^3 - a^3)$)

[*Hint*: $\int_a^b |\psi|^2 dx = \int_a^b x^2 dx = \left[\frac{x^3}{3}\right]_a^b = \frac{1}{3}(b^3 - a^3)$]

21. Calculate the expectation values of P and P^2 for the normalized wave function

$$\psi(x) = \sqrt{\left(\frac{2}{a}\right)} \sin\left(\frac{\pi x}{a}\right)$$

in the region $0 < x < a$ and $\psi(x) = 0$ for $x > a$ and $x < 0$, where P is the momentum of the particle.

(*Ans*. $< P > = 0$, $< P^2 > = \pi\hbar^2/a^2$)

$\Big[$*Hint*: $< P > = \int \psi^* \hat{P}\psi \, dx$

$\hat{P} = -i\hbar\nabla = -i\hbar\frac{\partial}{\partial x}\Big]$

22. What is the lowest energy that a neutron of mass 1.67×10^{-27} kg can have if it is confined to move along the edge of an impenetrable box of length 2×10^{-14} m. (*Ans*. 0.5125 eV)

$\Big[$*Hint*: $E_n = \frac{n^2 h^2}{8\,mL^2}$, $n = 1, 2, \ldots$

$E_1 = \frac{h^2}{8\,mL^2}\Big]$

23. Write a Hamiltonian for a freely moving particle and hence, the corresponding Schrödinger wave equation.

[*Hint*: $H = KE + PE = \frac{Px^2}{2\,m} + 0$

$$\hat{H} = \frac{1}{2m}\left[\frac{\hbar}{i}\frac{d}{dx}\right]\left[\frac{\hbar}{i}\frac{d}{dx}\right] = \frac{-\hbar^2}{2m}\frac{d^2}{dx^2}$$

We know that $H\psi = E\psi$]

24. The state of a free particle is represented by a wave function

$$\psi(x) = Ne^{-(x^2/2a^2 + ik_0 x)}$$

Find out the value of normalization factor N. (*Ans*. $N = a^{1/2}\,\pi^{1/4}$)

25. Normalize the wave function $\phi(x) = e^{-|x|} \sin dx$

Section C
Multiple Choice Questions

1. Heisenberg uncertainty principle is the consequence of
   (a) Bohr hypothesis
   (b) de Broglie hypothesis
   (c) diffraction
   (d) interference

2. Expression of Heisenberg's uncertainty principle is given as
   (a) $\Delta E \cdot \Delta t \geq \hbar/2$ (b) $\Delta E \cdot \Delta x \geq \hbar/2$
   (c) $\Delta E \cdot \Delta P \geq \hbar/2$ (d) $\Delta P \cdot \Delta t \geq \hbar/2$
3. Which one of the following is not the uncertainty principle?
   (a) $\Delta \cdot x \cdot \Delta p \geq \hbar/2$ (b) $\Delta J \cdot \Delta\theta \geq \hbar/2$
   (c) $\Delta \cdot E \cdot \Delta t \geq \hbar/2$ (d) none of these
4. Uncertainty principle was discovered by
   (a) de Broglie (b) Bohr
   (c) Schrödinger (d) Heisenberg
5. Bohr's complementarity principle is the consequence of
   (a) Bohr's hypothesis (b) de Broglie hypothesis
   (c) Rutherford model (d) none of these
6. If the certainty in the position of a particle increases, then the certainty in the momentum of the same particle during simultaneous measurement
   (a) increases (b) decreases
   (c) is not affected (d) none of these
7. If the uncertainty in the location of a particle is equal to the de Broglie wavelength, the uncertainty in its velocity is
   (a) more than the velocity of the particle (b) less than the velocity of the particle
   (c) equal to the velocity of light (d) none of these
8. The minimum uncertainty in the frequency of a photon of lifetime 10^{-8} s will be
   (a) 15.92×10^6 /s (b) 25.08×10^5 /s
   (c) 1.585×10^7 /s (d) 3.508×10^7 /s
9. The minimum uncertainty in the velocity of an electron, which is confined in a 10 Å box is
   (a) 11.6×10^4 m/s (b) 22.6×10^6 m/s
   (c) 18.8×10^5 m/s (d) 2.5×10^6 m/s
10. Wave function ψ gives the idea for
   (a) probability of finding particle (b) energy of particle
   (c) momentum of particle (d) energy and momentum of particle
11. The equation of motion of matter waves was derived by
   (a) de Broglie (b) Heisenberg
   (c) Schrödinger (d) Bohr
12. Time-independent Schrödinger wave equation for zero-potential energy is given as
   (a) $\nabla^2\psi + \frac{2mE}{\hbar^2}\psi = 0$ (b) $\nabla^2\psi + \frac{\hbar^2}{2mE}\psi = 0$
   (c) $\nabla\psi + \frac{2mE}{\hbar^2}\psi = 0$ (d) $\nabla\psi + \frac{\hbar^2}{2mE}\psi = 0$
13. A normalized wave function should satisfy the condition
   (a) $\int_{-\infty}^{\infty} \psi^* \psi \, d\tau = 0$ (b) $\int_{-\infty}^{\infty} \psi \, d\tau = 0$

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

14. An eigenfunction should have the property of being
    (a) finite (b) single-valued
    (c) continuous (d) all of the above
15. The energy of a free particle confined in a one-dimensional box of length L is
    (a) $\dfrac{n^2\hbar^2}{8\,mL^2}$ (b) $\dfrac{n^2h^2}{8\,mL^2}$
    (c) $\dfrac{n^2\pi^2\hbar^2}{2\,mL^2}$ (d) $\dfrac{n^2h^2}{2\,m^2L}$
16. The kinetic energy of a particle in a box is proportional to the
    (a) quantum number (b) square of quantum number
    (c) length of box (d) square of the length of box
17. For a normalized wave function ψ, the value of $\int_{-\infty}^{+\infty} \psi^*\psi\, d\tau$ will be
    (a) 1 (b) 0
    (c) 2 (d) ∞
18. Time-independent Schrödinger wave equation for a free particle in a box is given as
    (a) $\nabla^2\psi + \dfrac{2\,mE}{\hbar^2}\psi = 0$ (b) $\nabla^2\psi + \dfrac{2\,mE}{\hbar^2}\psi = 1$
    (c) $\nabla\psi + \dfrac{2\,mE}{\hbar}\psi = 0$ (d) $\nabla\psi + \dfrac{2\,mE}{\hbar^2}\psi = 1$
19. The lowest kinetic energy of a particle of mass m confined in a one-dimensional box of length L is
    (a) proportional to L (b) inversely proportional to L^2
    (c) proportional to L^2 (d) none of these
20. The probability current density equation is given as
    (a) $\dfrac{ds}{dt} + \text{div}\, P = 0$ (b) $\dfrac{dP}{dt} + \text{div}\, s = 0$
    (c) $s + \text{div}\, P = 0$ (d) $\text{div}\, s + \dfrac{d^2s}{dt^2} = 0$
21. A wave function $\psi(r, t)$ is said to be normalized to unity if it satisfies the condition
    (a) $\int \psi^*(r,t)\,\psi(r,t)\,d\tau = 1$ (b) $\dfrac{d}{dx}\psi^*(r,t)\,\psi(r,t)\,d\tau = 0$
    (c) $\int \psi^*(r,t)\,\hat{x}\,\psi(r,t)\,d\tau = 1$ (d) $\int \psi^*(r,t)\,\psi(r,t)\,d\tau = 0$

22. An eigenfunction has physical significance if
    (a) it is single-valued (b) it is finite
    (c) it is continuous (d) all of the above
23. Which one of following is not the eigenfunction of the operator d^2/dx^2 ?
    (a) $\sin x$ (b) $\cos x$
    (c) $\sin^2 x$ (d) e^{2x}

Answers

1. (b)	2. (a)	3. (d)	4. (d)	5. (b)	6. (b)
7. (c)	8. (a)	9. (a)	10. (a)	11. (c)	12. (a)
13. (d)	14. (d)	15. (b)	16. (b)	17. (a)	18. (a)
19. (b)	20. (b)	21. (a)	22. (d)	23. (c)	

Section D
Fill in the Blanks

1. Uncertainty principle is the consequence of ....
2. Uncertainty principle has no significance in case of .... objects.
3. Uncertainty principle was proposed by ....
4. According to the uncertainty principle, it is impossible to .... determine the exact position and momentum of a particle.
5. The product of uncertainties in determining the position and the momentum of a particle at the same instant is ....
6. The uncertainty relation between energy and time is ....
7. Uncertainty principle has .... importance for macroscopic objects.
8. Heisenberg's uncertainty principle for momentum and position is ....
9. The quantity which varies periodically in matter waves is ....
10. An acceptable wave function ψ associated with a moving particle must be .... and ....
11. Wave function is a .... quantity.
12. Schrödinger wave equation is used to describe the behaviour of ....
13. In wave mechanics, the wave function ψ_n and the corresponding energies E_n, are often called .... and ...., respectively.
14. Normalized wave function must be .... valued.
15. $|\psi|^2$ gives the .... of finding a particle in a state ψ.
16. The kinetic energy of a free particle confined in a one-dimensional box is proportional to the ....
17. The kinetic energy of a free particle confined in a one-dimensional box is .... to the square of length of the potential box.
18. Schrödinger wave equation is not valid for ....

19. If a wave function satisfies the condition $\int \psi^*(r,t)\psi(r,t)d\tau = 1$, then ψ is said to be ....
20. An eigenfunction is single-valued, finite, and ....
21. According to the probability current density equation, the change in .... is due to the flow of probability current(s).

Answers

1. de Broglie hypothesis
2. macroscopic
3. Heisenberg
4. simultaneously
5. impossible
6. $\Delta E \cdot \Delta t \geq h/4\pi$
7. no
8. $\Delta p \cdot \Delta x \geq \hbar/2$
9. wave function
10. single-valued, finite
11. complex
12. matter waves
13. eigenfunction, eigenvalue
14. single
15. probability
16. square of quantum number
17. inversely proportional
18. relativistic particles
19. normalized
20. continuous
21. probability

Section E
True and False Statements

1. It is impossible to simultaneously determine the exact position and the momentum of a particle.
2. Uncertainty principle is significant for microscopic bodies only.
3. Uncertainty principle was discovered by de Broglie.
4. Uncertainty principle is equally valid for macroscopic as for well as microscopic particles.
5. The statement of uncertainty principle can be given as $\Delta p \cdot \Delta x \geq h/4\pi$.
6. In matter waves, pressure varies periodically.
7. In matter waves, wave function ψ varies periodically.
8. $|\psi|^2$ gives the probability of finding a particle in a state ψ.
9. Wave function (ψ) is a single-valued, finite, and continuous function.
10. The kinetic energy of a free particle in a deep one-dimensional potential box is proportional to the square of quantum number and inversely proportional to the square of length of the box.
11. The kinetic energy of a free particle confined in a one-dimensional box is proportional to the square of length of the box and inversely proportional to the square of the quantum number.

Answers

1. True
2. True
3. False
4. False
5. True
6. False
7. True
8. True
9. Tsrue
10. True
11. False