

CHAPTER

7

Quantum Mechanics

7.1 INTRODUCTION

In the book *Basic Engineering Physics*, the old quantum theory has been discussed. This theory was a collection of the results of researches in this field between the years 1900 and 1925, which predated the modern quantum mechanics. The theory was never complete or self-consistent, but was a collection of heuristic prescriptions, which are now understood to be the first quantum corrections to classical mechanics.

The motions of particles which are subjected to external forces are discussed in newtonian (or classical) mechanics. And in newtonian mechanics it is also taken for granted that one can measure correctly the properties of particles like mass, position, velocity, acceleration, etc. Of course, this idea is valid in our common sense which we acquire through the experiences of our daily life. Classical mechanics is able to explain correctly the dynamical behavior of the material bodies in terms of the values it predicts for observable quantities and the values of the same quantities which are measured experimentally.

On the other hand, quantum mechanics also deals with the values of observable quantities related to dynamical systems but in this case, the term 'observable quantity' bears different significance in the light of the uncertainty principle in the atomic realm. The uncertainty principle plays an important role in quantum mechanics. According to quantum mechanics, simultaneous measurement of the position and momentum of a moving particle with precision is impossible while according to classical mechanics, both the position and momentum of a moving particle can be ascertained accurately at every instant of time. And for this reason, classical mechanics is considered to be deterministic, whereas quantum mechanics is considered to be probabilistic. For example, according to classical mechanics, the radius of the electronic orbit in the ground state of hydrogen atom is exactly 5.3×10^{-11} m while according to quantum mechanics, this is most probable value of the said radius.

Classical mechanics is a special case of quantum mechanics; in other words, it is an approximate version of quantum mechanics. The certainties which one comes across in classical mechanics are only apparent. The agreement which is observed between the predicted value and the experimental value of an object is due to the fact that the macroscopic material bodies consist of a large number of individual atoms and the departure of the collective behavior of the atoms from their individual behavior is unnoticeable. Thus, unlike classical mechanics, quantum mechanics includes two sets of physical principles; one for the macroscopic world and the other one for the microscopic world.

Quantum mechanics was not developed uniquely through a single formulation like classical mechanics. Rather initially it was developed through two different formulations by two renowned physicists, namely, Werner Heisenberg and Erwin Schrödinger. In 1925, on one hand, Heisenberg formulated the quantum theory in terms of observable quantities alone (like intensity and frequencies of spectral lines) to replace position, momentum and other dynamical variables of classical mechanics by matrices, while keeping the form of the equations of motion superficially the same as in classical mechanics. This formulation of quantum mechanics is known as *matrix mechanics*. On the other hand, in 1926, Schrödinger formulated the quantum theory on the basis of de Broglie hypothesis of matter waves even before it was experimentally verified by Davison and Germer in 1927. Schrödinger's quantum theory is known as wave mechanics. He proposed that the wave function Ψ describing the matter waves satisfies a partial differential equation, and gave the prescription to write down the equation for any particular system of particles. Despite the vastly different appearance of the two aforesaid theories, it was very soon recognised that they are completely equivalent. Schrödinger's equation is applicable only to non-relativistic particles. So, a new wave equation, which meets the requirements of the theory of relativity, was formulated by Paul Adrien Maurice Dirac in 1928 which is known as relativistic wave mechanics. Out of the two alternative forms of quantum mechanics — wave mechanics and matrix mechanics — it is the former one which lends itself more easily to the solution of wide variety of practical problems. For this reason, we will be dealing with Schrödinger's version of quantum mechanics, i.e., wave mechanics in this chapter. It was again Dirac who ultimately set up a general formalism of quantum mechanics in the year 1930 to unify the two formulations of Heisenberg and Schrödinger.

7.2 WAVE FUNCTION, PROBABILITY AND PROBABILITY DENSITY

We now know well that nature is strikingly symmetrical in many ways. Our observable universe is entirely composed of matter and energy. Light is one of the various forms of energy. We have learnt through Compton and photoelectric effects that light has dual, wave as well as particle nature. So, one can expect from the concept of symmetry of nature that matter also may have dual, wave as well as particle nature (i.e., character). The particle nature of matter is well known to every one. Louis de Broglie proposed the wave nature of matter in 1924 in his hypothesis which was later named after him and Davison and Germer confirmed this experimentally in case of electrons in the year 1927. When light propagates through free space, its motion in space and time can be represented by the electromagnetic wave equation as given below:

$$\nabla^2 \bar{\xi} = \frac{1}{c^2} \frac{\partial^2 \bar{\xi}}{\partial t^2} \quad \dots(7.1)$$

where c is the velocity of light in the vacuum and $\bar{\xi}$ is either the electric vector $\bar{E}(\bar{r}, t)$ or the magnetic vector $\bar{B}(\bar{r}, t)$ of the light wave. So, again from the concept of symmetry of nature one can expect a similar equation to represent the motion of a wave-particle in space and time. This is what was done by Erwin Schrödinger in 1926. The idea that the stationary states of an electron in an atom corresponding to the standing matter waves was taken up and used by him as the foundation of wave mechanics. He developed an equation, now known as Schrödinger's equation, to represent the motion of the matter-wave (in space and time) related to a free particle which is given below:

$$-\frac{\hbar^2}{2m} \nabla^2 \Psi(\bar{r}, t) = i \hbar \frac{\partial \Psi}{\partial t}(\bar{r}, t) \quad \dots(7.2)$$

where \hbar is Planck's constant and $\hbar = h/(2\pi)$ and $\Psi(\bar{r}, t)$ is a function of space and time which satisfies the Eq. (7.2). The function $\Psi(\bar{r}, t)$ is known as Schrödinger's wave function (i.e., the function which represents Schrödinger's matter wave in space and time).

7.2.1 Probability and Probability Density

When the double-slit experiment is carried out with light, such as the Young's double-slit experiment, one considers the superposition of the secondary waves arising from the two slits on the screen of recording of the interference pattern. The light intensity on this screen is determined by the square of the amplitude of the wave, which is formed as a result of superposition of the two secondary waves coming from the two slits. The intensity of light on the screen is also proportional to the number of photons reaching the screen per unit area. The probability (or chance) of finding a photon at a given point on the screen depends on the intensity of light wave at the point. This intensity (as stated above) is proportional to the square of the resultant amplitude of the waves (i.e., the electric field) at the point. Hence, the probability of finding a photon on a given point is proportional to the square of the resultant electric field at the point. Now comparing the duality (i.e., dual behavior) of photon with that of a material particle (e.g., an electron) one can arrange a similar double-slit experiment with monoenergetic material particles (i.e., electrons) as shown in Fig. 7.1.

By putting forward similar arguments in case of electron double-slit experiment as we have done in case of the double-slit experiment of photon (i.e., Young's double-slit experiment), we can conclude that the probability of finding an electron per unit area of the screen S of Figure 7.1 is proportional to the square of the wave function (or state function) Ψ for the electron.

If one compares Eqs (7.1) and (7.2), the logic which has been put forward above will be more clear. The wave function ξ (and hence the electric field vector \vec{E}) represents wave behavior of the photon while Schrödinger's wave function Ψ represents the wave behavior of the electron. So, if $|\vec{E}|^2$ gives the probability of finding the photon on the screen of Young's double-slit experiment, then $|\Psi|^2$ will give the probability of finding the electron on the screen of the electron double-slit experiment [Fig. 7.1].

Therefore in general, we can state that if $\Psi(\vec{r}, t)$ represents the wave function of a material particle, then $|\Psi(\vec{r}, t)|^2$ will represent the probability of finding that particle at point (x, y, z) at time t (since $\vec{r} = \hat{i}x + \hat{j}y + \hat{k}z$). The wave function $\Psi(\vec{r}, t)$ plays the role of probability amplitude. This function is generally a complex quantity. Since probabilities are real positive numbers (varying from $+0$ to $+1$), the probability of finding a particle, at a given position (x, y, z) at a given time (t) , is expected to be proportional to $|\Psi|^2$. And it will be equal to $|\Psi|^2$ when the wave function Ψ is a normalized one.

Probability density of a particle

It is the probability of finding the concerned particle in unit volume of a given space at a given instant of time.

It is usually expressed as the square of the absolute value of the wave function when it is normalized. If the normalized wave function Ψ_n is complex, then

$$|\Psi_n|^2 = (\Psi_n)(\Psi_n^*)$$

where Ψ_n^* is the complex conjugate of Ψ_n .

So, the probability density P can be expressed as follows:

$$P = \Psi_n^*(\vec{r}, t) \Psi_n(\vec{r}, t) = |\Psi_n(\vec{r}, t)|^2 \quad \dots(7.3)$$

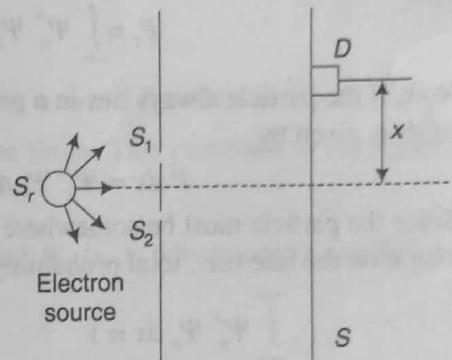


Fig. 7.1 Electron double-slit set-up for interference of electron waves. S_r : source of electrons, S_1, S_2 ; double slits, S : the screen and D : the detector.

Therefore, the probability of finding a particle having normalized wave function Ψ_n in a volume element dV at the point (x, y, z) at time t is given by

$$P_V = \Psi_n^* \Psi_n dV$$

Since at a given point of time, the particle must be somewhere in the space, the total probability P_t to find the particle in space must be equal to unity.

$$P_t = \int_{-\infty}^{+\infty} \Psi_n^* \Psi_n dV = 1 \quad \dots(7.4)$$

Now, if the particle always lies in a point of a straight line, then the probability of finding it within a distance dx is given by

$$P dx = \Psi_n^* \Psi_n dx$$

Since the particle must be somewhere on the straight line (in this case the x axis), the total probability of finding it on the line (i.e., total probability for one-dimensional motion) is given by

$$\int_{-\infty}^{+\infty} \Psi_n^* \Psi_n dx = 1 \quad \dots(7.5)$$

7.3 NORMALIZATION OF WAVE FUNCTION AND ORTHOGONALITY OF WAVE FUNCTIONS

One should note that the wave function $\Psi(x, t)$ which describes the complete space-time behavior of a particle in one-dimensional motion has an appreciable amplitude in a region where the particle is likely to be found with a greater probability. One can assume that the quantity $|\Psi(x, t)|^2 dx = \Psi^*(x, t) \Psi(x, t) dx$ is proportional to the probability of finding the particle in the interval between x and $x + dx$ at the time t where $\Psi^*(x, t)$ is the complex conjugate of $\Psi(x, t)$. The total probability of finding the particle anywhere in the one-dimensional space is given by

$$P_t = \int_{-\infty}^{+\infty} |\Psi(x, t)|^2 dx$$

Let us define the position probability density (or simply probability density) as

$$P(x, t) = |\Psi(x, t)|^2 \left[\int_{-\infty}^{+\infty} |\Psi(x, t)|^2 dx \right] \quad \dots(7.6)$$

Hence, the total probability will be

$$\begin{aligned} P_t &= \int_{-\infty}^{+\infty} P(x, t) dx \\ &= \int_{-\infty}^{+\infty} |\Psi(x, t)|^2 dx \left[\int_{-\infty}^{+\infty} |\Psi(x, t)|^2 dx \right] \\ &= 1 \end{aligned} \quad \dots(7.7)$$

This is what should be, since the total probability P_t must be always equal to unity.

Since $|\Psi(x, t)|^2$ is necessarily positive, Eq. (7.6) indicates that the probability density $P(x, t)$ is always positive. This is consistent with the expected behavior and definition of probability,

If $\Psi(x, t)$ is multiplied by one complex constant quantity N so that

$$\Psi_n(x, t) = N \Psi(x, t) \quad \text{where } \Psi_n(x, t) \text{ satisfies the following relation}$$

$$\int_{-\infty}^{+\infty} |\Psi_n(x, t)|^2 dx = |N|^2 \int_{-\infty}^{+\infty} |\Psi(x, t)|^2 dx = 1 \quad \dots(7.8)$$

Then $\Psi_n(x, t)$ is said to be the normalized wave function and N is called the norm of the unnormalized wave function $\Psi(x, t)$ required to normalize it.

From Eq. (7.8), one can have

$$|N|^2 = 1 \left/ \int_{-\infty}^{+\infty} |\Psi(x, t)|^2 dx \right. \quad \dots(7.9)$$

N is also called the normalization constant. And obviously for a wave function to be normalizable $\int |\Psi(x, t)|^2 dx$ or in general $\int |\Psi(\vec{r}, t)|^2 dV$ over all space must be finite. This condition is known as the square-integrability of the wave function.

Orthogonality Let us consider two wave functions $\Psi_m(x, t)$ and $\Psi_n(x, t)$ which satisfy Schrödinger's Eq. (7.2) with $y = z = 0$.

In case of this pair of wave functions one can show that

$$\int_{-\infty}^{+\infty} \Psi_m(x, t) \Psi_n(x, t) dx = 0 \quad \dots(7.10)$$

where $m \neq n$.

This property of two wave functions is called **orthogonality** of these functions. To be physically meaningful, both the wave functions must satisfy the condition of normalization.

$$\text{i.e., } \int_{-\infty}^{+\infty} |\Psi_m(x, t)|^2 dx = \int_{-\infty}^{+\infty} \Psi_m^*(x, t) \Psi_m(x, t) dx = 1$$

$$\text{and } \int_{-\infty}^{+\infty} |\Psi_n(x, t)|^2 dx = \int_{-\infty}^{+\infty} \Psi_n^*(x, t) \Psi_n(x, t) dx = 1$$

7.4 PHYSICAL SIGNIFICANCE AND INTERPRETATION OF WAVE FUNCTION

As the wave function of a material particle represents the physical behavior of the particle while it is in motion, it must have some physical significance, otherwise it will not be able to represent the dynamical behavior of the particle. Some important physical significances of the wave function are listed below:

- (a) Wave function gives information regarding the space-time behavior of the concerned particle.
- (b) The square of the wave function gives the measure of the probability of finding the particle about a position.
- (c) The magnitude of the wave function is large in regions where the probability of finding the particle is high and small in the region where the probability of finding the particle is low.
- (d) The wave function representing a moving particle must be continuous and single valued at each point of space. Also its value at each point of space must be finite.

Interpretation of wave function One can give a physical interpretation of the wave function as follows: During the propagation of any wave some physical quantities vary with respect to space and time. As for example, when a light wave propagates, the electric and the magnetic fields of it vary in space and time and when a sound wave propagates the pressure in the medium of propagation varies in space and time. Similarly, when a particle moves the matter wave related to it (i.e., the de Broglie wave) also propagates. And during

the time of propagation of this wave, some physical quantities also keep on varying in space and time. All the information about these varying physical quantities are carried by the wave function Ψ of the matter wave. Ψ is generally a complex quantity and is a function of position coordinates (x, y, z) as well as time (t) . In case of a moving body, the value of Ψ is related to the probability (i.e., chance) of finding the particle at a particular point in space (x, y, z) at a given time t . The wave function Ψ can also give information regarding the future behavior of the particle. The wave function Ψ actually contains all the information which the uncertainty principle allows one to know about the related particle but this wave function cannot be measured directly. As stated earlier, the probability of any event must be a real positive quantity whose value lies within the range between 0 and 1. Since wave function is generally a complex quantity which can have both positive and negative values, the probability related to the existence of the particle at a point in space and time can be expressed by $|\Psi|^2$. This is because for any allowed value of Ψ , $|\Psi|^2$ will always be positive. In order to understand this, one can express Ψ as follows:

$$\Psi = a + ib$$

where i represents the square root of (-1) , i.e., $i = \sqrt{-1}$ and a and b are two real quantities which can be expressed as the function of position coordinates (x, y, z) and time t . Now, the complex conjugate of Ψ (denoted by Ψ^*) is given by

$$\Psi^* = a - ib$$

So, the square of the modulus of Ψ can be written as

$$\begin{aligned} |\Psi|^2 &= (\Psi^*)(\Psi) = (a - ib)(a + ib) \\ &= a^2 + b^2 \end{aligned}$$

The value of $a^2 + b^2$ is always real and positive. Thus, $|\Psi|^2$ is always a positive real quantity. If Ψ_n be normalized value of Ψ , then $|\Psi_n|^2$ represents the probability density of the particle. For a particle that is represented by the wave function Ψ (or the normalized wave function Ψ_n), the probability of experimentally observing it at the position (x, y, z) at time t is given by $|\Psi_n|^2$. At any point in space where $|\Psi_n| > 0$, there is a definite probability of detecting it. It was Max Born who first gave this statistical interpretation of the wave function in 1926.

Let us now consider an ensemble of a large number of identical particles where each of them is described by the same normalized wave function Ψ_n . Then the actual density of particles at position (x, y, z) at a given time t is equal to $|\Psi_n|^2$.

If one assumes that a particle is moving along the x axis, then its wave function is a function of x and t only. If this function is normalized and denoted by $\Psi_n(x, t)$, then the probability density $P(x, t)$ is taken to be $|\Psi_n(x, t)|^2$. And the probability of finding the particle at a particular time t in a region between x and $x + dx$ is equal to $|\Psi_n|^2 dx$. This can be expressed as follows:

$$\begin{aligned} p(x, t) dx &= \Psi_n^*(x, t) \Psi_n(x, t) dx \\ &= |\Psi_n(x, t)|^2 dx \end{aligned} \quad \dots(7.11)$$

where the probability density $p(x, t)$ is defined as the probability per unit length (along the x axis for finding the particle around the point $(x, 0, 0)$ at the time t).

The probability for finding the particle in the region between the points $(x_1, 0, 0)$ and $(x_2, 0, 0)$ is given by

$$\begin{aligned} p(x_1, x_2, t) &= \int_{x_1}^{x_2} p(x, t) dx \\ &= \int_{x_1}^{x_2} \Psi_n^*(x, t) \Psi_n(x, t) dx \end{aligned}$$

or.

$$p(x_1, x_2, t) = \int_{x_1}^{x_2} |\Psi_n(x, t)|^2 dx \quad \dots(7.12)$$

In a three-dimensional case, the probability of finding the particle in a small volume dV around the point (x, y, z) at time t is given by

$$p(x, y, z, t) = \int_V \underbrace{|\Psi_n(x, y, z, t)|^2 dV}_{\text{...}} \quad \dots(7.13)$$

7.5 OPERATORS IN QUANTUM MECHANICS

The word 'operation' means action, so an operator is an actor which can change a physical quantity having taken some action on it. Basically **an operator is a mathematical rule that can change a given function into a new function**.

If α be an operator, then it is mathematically expressed as $\hat{\alpha}$. As an example, if $\hat{\alpha}$ be the differential operator $\left(\frac{d}{dx}\right)$, then when it operates on the function $f(x) = 2x^2 + 3x + 1$ one gets the following result:

$$\frac{d}{dx} f(x) = \frac{d}{dx} (2x^2 + 3x + 1) = 4x + 3 = f_1(x) \text{ (say)}$$

An operator can be either linear or complex in nature. If $\hat{\alpha}$ be a linear operator then it exhibits the following properties:

$$\hat{\alpha}(cf) = c\hat{\alpha}(f)$$

and

$$\hat{\alpha}(f+g) = \hat{\alpha}f + \hat{\alpha}g$$

where c is a constant and f and g are two functions.

An operator can generate a new function by operating on a given function. In the example given above, the operator $\hat{\alpha} = \frac{d}{dx}$ has generated the new function $f_1(x)$ by operating on the function $f(x)$.

In quantum mechanics, each dynamical variable is represented by an operator and the former provides a link with the latter (i.e., the operator) through the correspondence principle. Usually if α be a dynamical variable then the corresponding operator is denoted by $\hat{\alpha}$ where the symbol (^) is known as caret. The operators used in quantum mechanics are linear operators. The linear operators obey distributive law. Thus, if $f(x)$ and $g(x)$ are two functions of x and $\hat{\alpha}$ is a linear operator, then one gets

$$\hat{\alpha} \{f(x) + g(x)\} = \hat{\alpha}f(x) + \hat{\alpha}g(x)$$

The linear operators also obey associative laws. Sums and products of two linear operators are also linear operators. And the sum of two linear operators is commutative, i.e., $(\hat{\alpha} + \hat{\beta})f(x) = (\hat{\beta} + \hat{\alpha})f(x)$. But the product of two linear operators may or may not be commutative. For example, the product of the two linear operators $\hat{\alpha} = \frac{d}{dx}$ and $\hat{\beta} = \frac{d^2}{dx^2}$ is commutative while the product of the two linear operators $\hat{\alpha}_1 = x$ and $\hat{\beta}_1 = \frac{d}{dx}$ is not commutative.

In order to verify the above statements let us consider the function $f(x)$ and perform the following operations:

$$(a) \quad \hat{\alpha} \hat{\beta} f(x) = \left(\frac{d}{dx} \right) \left(\frac{d^2}{dx^2} \right) f(x) = \frac{d^3}{dx^3} f(x)$$

$$\text{and} \quad \hat{\beta} \hat{\alpha} f(x) = \left(\frac{d^2}{dx^2} \right) \left(\frac{d}{dx} \right) f(x) = \frac{d^3}{dx^3} f(x)$$

Hence $(\hat{\alpha} \hat{\beta} - \hat{\beta} \hat{\alpha}) f(x)$

$$\begin{aligned} &= \left(\frac{d}{dx} \frac{d^2}{dx^2} - \frac{d^2}{dx^2} \frac{d}{dx} \right) f(x) \\ &= \frac{d}{dx} \frac{d^2}{dx^2} f(x) - \frac{d^2}{dx^2} \frac{df(x)}{dx} \\ &= \frac{d^3}{dx^3} f(x) - \frac{d^3}{dx^3} f(x) = 0 \end{aligned}$$

$$\text{i.e.,} \quad [\hat{\alpha}, \hat{\beta}] = \left[\frac{d}{dx}, \frac{d^2}{dx^2} \right] = \left(\frac{d}{dx} \frac{d^2}{dx^2} - \frac{d^2}{dx^2} \frac{d}{dx} \right) = 0$$

So, the operators $\frac{d}{dx}$ and $\frac{d^2}{dx^2}$ commute.

(b) Let $\hat{\alpha}_1 = x$ and $\hat{\beta}_1 = \frac{d}{dx}$ and let $f(x)$ be a function. Then one can write

$$\hat{\alpha}_1 \hat{\beta}_1 f(x) = x \frac{d}{dx} f(x) = x \cdot \frac{df(x)}{dx}$$

$$\begin{aligned} \text{and} \quad \hat{\beta}_1 \hat{\alpha}_1 f(x) &= \frac{d}{dx} (x) f(x) = \frac{d}{dx} \{ x(f(x) \} \\ &= x \frac{df(x)}{dx} + f(x) \end{aligned}$$

$$\text{Hence } (\hat{\alpha}_1 \hat{\beta}_1 - \hat{\beta}_1 \hat{\alpha}_1) f(x) = \left(x \frac{d}{dx} - \frac{d}{dx} x \right) f(x)$$

$$= x \frac{d}{dx} f(x) - x \frac{d}{dx} f(x) - f(x)$$

$$= -1 \cdot f(x)$$

As $f(x)$ is an arbitrary function, one can remove it from both sides and get the following expression:

$$\left[x, \frac{d}{dx} \right] = x \frac{d}{dx} - \frac{d}{dx} x = -1$$

So, the operators x and $\frac{d}{dx}$ are not commutative. In order to get a function operated upon by an operator, the function is placed at the right side of the operator.

7.5.1 Commutator

If $\hat{\alpha}$ and $\hat{\beta}$ be two operators, the commutator of this pair of operators is denoted by $[\hat{\alpha}, \hat{\beta}]$ and it is defined as
 $[\hat{\alpha}, \hat{\beta}] = \hat{\alpha}\hat{\beta} - \hat{\beta}\hat{\alpha}$.

If $[\hat{\alpha}, \hat{\beta}] = 0$, i.e., $\hat{\alpha}\hat{\beta} = \hat{\beta}\hat{\alpha}$, then the pair of operators is known as commutative.

If $[\hat{\alpha}, \hat{\beta}] \neq 0$, i.e., $\hat{\alpha}\hat{\beta} \neq \hat{\beta}\hat{\alpha}$, then the pair of operators is known as non-commutative. As for example, the pair of operators \hat{x} and \hat{p}_x is non-commutative, i.e., $[\hat{x}, \hat{p}_x] \neq 0$, actually $[\hat{x}, \hat{p}_x] = i\hbar$. This implies that the simultaneous measurement of these variables (i.e., x and p_x) with absolute precision is not possible. One should note that this incompatibility is valid for position and momentum in the same direction. When the operators are in different direction, they commute.

7.5.2 Some Quantum Mechanical Operators

Before discussing the quantum mechanical operators, let us consider two wave equations given below:

$$y = a \sin(kx - wt)$$

and

$$\Psi = Ae^{i(kx - wt)}$$

The first equation represents a wave of a simple harmonic oscillator while the second one represents the de Broglie wave of a particle and both the waves propagate along the x axis. The second equation contains a complex expression because a wave representing a moving particle can be complex.

Now, in order to understand the role of operators in wave mechanics, let us differentiate the wave function $\Psi(x, t)$ for a free particle given by

$$\Psi(x, t) = Ae^{i(kx - wt)} \text{ with respect to } x \text{ and } t.$$

$$\text{So, we get } \frac{\partial}{\partial x} \Psi(x, t) = A \frac{\partial}{\partial x} \{Ae^{i(kx - wt)}\}$$

$$\frac{\partial}{\partial t} \Psi(x, t) = A \frac{\partial}{\partial t} \{Ae^{i(kx - wt)}\}$$

Now, multiplying the first equation by $-i\hbar$

$$-i\hbar \frac{\partial}{\partial x} \Psi(x, t) = A(-i\hbar)(ik) Ae^{i(kx - wt)}$$

$$\text{or, } -i\hbar \frac{\partial}{\partial x} \Psi(x, t) = (\hbar k) \Psi(x, t)$$

$$\text{or, } -i\hbar \frac{\partial}{\partial x} \Psi(x, t) = p_x \Psi(x, t)$$

... (7.14)

$$[\because p = p_x = \hbar k]$$

Again, multiplying the second equation by $i\hbar$, we get

$$i\hbar \frac{\partial}{\partial t} \Psi(x, t) = A(i\hbar)(-iw) Ae^{i(kx - wt)}$$

$$\text{or, } i\hbar \frac{\partial}{\partial t} \Psi(x, t) = \hbar w \Psi(x, t)$$

$$\text{or, } i\hbar \frac{\partial}{\partial t} \Psi(x, t) = E \Psi(x, t)$$

... (7.15)

$$[\because E = \hbar w]$$

As the wave function $\Psi(x, t)$ in Eqs (7.14) and (7.15) is arbitrary, by dropping $\Psi(x, t)$ from both sides of the said equations, we get

$$-i\hbar \frac{\partial}{\partial x} = p_x \quad \text{and} \quad i\hbar \frac{\partial}{\partial t} = E$$

So, the momentum and energy operators can be written as

$$\hat{p}_x \equiv -i\hbar \frac{\partial}{\partial x} \quad \dots(7.16)$$

$$\hat{E} \equiv +i\hbar \frac{\partial}{\partial t} \quad \dots(7.17)$$

These two operators are mathematical operators for representing the dynamical variables of momentum and the energy of a particle.

In addition, since the coordinate x is a multiplying operator, we can express it in operator form as follows:

$$\hat{x} = x \quad \dots(7.18)$$

The operator representation of Eqs. (7.16) and (7.18) is called Schrödinger representation or coordinate representation.

The operators corresponding to the other dynamical variables that are functions of the coordinate x and momentum p_x are obtained by substituting them (i.e., x and p_x) in classical expressions by \hat{x} ($= x$) and \hat{p}_x ($= -i\hbar \frac{\partial}{\partial x}$) respectively.

Thus, if $\alpha(\hat{x}, \hat{p}_x)$ is a dynamical variable, and function of x and p_x , then the operator representation of α can be found as follows:

$$\hat{\alpha}(\hat{x}, p_x) = \alpha(\hat{x}, \hat{p}_x) = \alpha\left(\hat{x}, -i\hbar \frac{\partial}{\partial x}\right) \quad \dots(7.19)$$

As for example, by applying the above rule (i.e., Eq. 7.19) we can find operators for kinetic energy (E_k) and angular momentum about the x axis (L_x) as follows:

(i) Operator representation of kinetic energy

$$E_k = E_k(p_x) = \frac{p_x^2}{2m}$$

Now, $\hat{p}_x = -i\hbar \frac{\partial}{\partial x}$, putting this for p_x

$$\text{we get } \hat{E}_k = \frac{\left(-i\hbar \frac{\partial}{\partial x}\right)^2}{2m}$$

$$\text{or, } \hat{E}_k = \frac{-\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \quad \dots(7.20)$$

(ii) Operator representation of L_x

$$L_x = y p_z - z p_y \quad [\because \bar{L} = \bar{r} \times \bar{p}, \bar{r} = \hat{i}x + \hat{j}y + \hat{k}z \text{ and } \bar{p} = \hat{i}p_x + \hat{j}p_y + \hat{k}p_z]$$

$$\hat{L}_x = \hat{y} \hat{p}_z - \hat{z} \hat{p}_y$$

or,

$$\hat{L}_x = y \left(-i\hbar \frac{\partial}{\partial z} \right) - z \left(-i\hbar \frac{\partial}{\partial y} \right)$$

or,

$$\hat{L}_x = -i\hbar \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right)$$

Similarly we can find the operator representation of L_y and L_z as

$$\hat{L}_y = -i\hbar \left(z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right) \quad \dots(7.22)$$

and

$$\hat{L}_z = -i\hbar \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right) \quad \dots(7.23)$$

7.5.3 Operator Representation of Three-Dimensional Variables

One-dimensional operators like $\hat{x} = x$ and $\hat{p}_x = -i\hbar \frac{\partial}{\partial x}$ lead us to write the three-dimensional position and momentum operators as follows:

$$\hat{r} = \bar{r} \quad \text{and} \quad \hat{p} = -i\hbar \bar{\nabla} \quad \dots(7.24)$$

where $\bar{r} = \hat{i}x + \hat{j}y + \hat{k}z$ and $\nabla = \hat{i} \frac{\partial}{\partial x} + \hat{j} \frac{\partial}{\partial y} + \hat{k} \frac{\partial}{\partial z}$

As we have seen in a one-dimensional case, the operator representation of a three-dimensional dynamical variable $\alpha(\bar{r}, \bar{p})$ which is a function of position and momentum can be obtained by using the operator forms of \bar{r} and \bar{p} in the expression of $\alpha(\bar{r}, \bar{p})$ by using the operators \hat{r} and \hat{p} as given in Eq. (7.24):

$$\hat{\alpha}(\bar{r}, \bar{p}) = \alpha(\hat{r}, \hat{p}) = \alpha(\hat{r}, -i\hbar \bar{\nabla}) \quad \dots(7.25)$$

As an example, the hamiltonian operator \hat{H} for three-dimensional motion can be obtained by using the classical expression of hamiltonian function

$$H = \frac{p^2}{2m} + V(r)$$

Hence,

$$\hat{H} = \frac{(\hat{p})^2}{2m} + V(r)$$

or,

$$\hat{H} = -\frac{\hbar^2}{2m} \nabla^2 + V(r) \quad \dots(7.26)$$

7.5.4 Measurement of Observables

Observables are dynamical quantities like position, linear momentum, angular momentum, kinetic energy, total energy, etc., which can be measured by conducting experiments on a physical system. There is an operator corresponding to each observable in quantum mechanics which operates upon the wave function to produce a new function. And the wave function contains every information regarding the system it represents. By using the operators one can extract information regarding the observables from the wave function. And also one can theoretically predict the average value (or expectation value) of the experimental observations regarding a physical quantity by using these operators.

7.5.5 Eigen Functions and Eigen Values: Definition of Eigen Function and Eigen Value

If an operator operates (i.e., acts) on a wave function and as a result of operation produces the same wave function multiplied by a constant factor, then the wave function is called an *eigen function* and the constant multiplier is called the *eigen value* of the operator.

Let the operator \hat{A} act on the wave function Ψ and returns the same function Ψ multiplied by α , i.e.,

$$\hat{A} \Psi = \alpha \Psi \quad \dots(7.27)$$

So, according to the definition given above Ψ is the eigen function of the operator \hat{A} and α the corresponding eigen value. If the operator \hat{A} represents an observable A , the measurement of this observable will yield the value α when the state of the particle is represented by the wave function Ψ which is an eigen function of the operator \hat{A} . And in this case, the wave function Ψ represents a state of the system which is called the eigen state of the observable A . One observable may have several eigen states. The system is found to be in any one of the eigen states of it with a characteristic eigen value whenever one performs an experiment to measure the observable.

Equation (7.27), i.e., $\hat{A} \Psi = \alpha \Psi$ is called the eigen value equation. As for an example, the function $f(x) = \sin(wx + \phi)$ is an eigen function of the operator $\hat{D} = \frac{d^2}{dx^2}$ with an eigen value $(-w^2)$, because

$$\begin{aligned}\hat{D} f(x) &= \frac{d^2}{dx^2} \{\sin(wx + \phi)\} \\ &= (-w^2) \sin(wx + \phi)\end{aligned}$$

or, $\hat{D} f(x) = (-w^2) f(x)$

So, $(-w^2)$ is the eigen value of \hat{D} .

The time-independent Schrödinger's equation, i.e., the equation

$$\hat{H} u(x) = Eu(x) \quad \dots(7.28)$$

with $\left[\hat{H} = -\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}) \right]$ is also an eigen value equation where $u(x)$ is an eigen function of the operator \hat{H}

(known as hamiltonian operator) corresponding to an energy eigen value E . Since the hamiltonian function H represents the total energy of the system, the function $u(x)$ represents one energy eigen state of the system having the value of the energy equal to E . The hamiltonian operator \hat{H} may have many eigen functions representing energy eigen states with characteristic energy eigen values when there are several eigen states with the same eigen value, the states, in that case, are called the **degenerate states**.

Let us consider the wave function $\Psi = u(x) e^{-i(Et/\hbar)}$ and let \hat{H} operate on it.

So, $\hat{H} \Psi = \hat{H} [u(x) e^{-i(Et/\hbar)}]$

or, $\hat{H} \Psi = e^{-i(Et/\hbar)} \hat{H} u(x)$

or, $\hat{H} \Psi = e^{-i(Et/\hbar)} Eu(x) \text{ [by Eq. (7.28)]}$

or, $\hat{H} \Psi = E[u(x) e^{-i(Et/\hbar)}]$

or, $\hat{H} \Psi = E\Psi$

The above equation [i.e., Eq. (7.29)] shows that a stationary state wave function Ψ is an eigen function of the hamiltonian operator \hat{H} corresponding to an eigen value E .

7.5.6 Expectation Value (or Expected Average)

As stated earlier, wave function related to an observable is the solution of Schrödinger's equation. An operator is used to extract information about the corresponding observable by operating on the wave function. In order to measure an observable one can conduct one single experiment on a large number of identical systems or one can measure the same (i.e., single) observable independently a large number of times. The arithmetic average of all the experimental results so obtained in either case can be theoretically predicted by making use of the wave function that is expected to contain all information about the identical systems in the former case or the system concerned in the earlier case. The average, thus, obtained is called the expected average or the expectation value or mathematical expectation of the concerned observable.

If one wants to determine the expected value of the momentum (p_x) of a particle (moving along the x axis) at a time t , one can perform an experiment with a large number of so moving identical particles. Let the number of so moving particles (which are described by the same wave function Ψ) be n . Let n_i be the number of particles lying on the position denoted by x ; at time t . So, the average momentum can be expressed as follows:

$$p_{x(av)} = \frac{\sum_i n_i p_{xi}}{\sum_i n_i} = \frac{\sum_i n_i p_{xi}}{n}$$

$$p_{x(av)} = \sum_i \left(\frac{n_i}{n} \right) p_{xi} \quad \dots(7.30)$$

The average of Eq. (7.30) is the weighted average and the weight in this case is $\left(\frac{n_i}{n} \right)$. This weight (or ratio) can be regarded as the probability (P_i) of finding a particle with momentum p_{xi} .

Hence the expression for the average value can be written as follows:

$$p_{x(av)} = \sum_i P_i p_{xi} \quad \dots(7.31)$$

The above expression of Eq. (7.31) is true for discrete distribution of particles. If the distribution of particles be continuous, then one can replace the summation symbol by the integration symbol in the expression of Eq. (7.31). And in such case, the average value $p_{x(av)}$ of momentum can be calculated if the probability density function $p(x, t)$ be such that the probability of finding a particle in the region between x and $x + dx$ is $p(x, t) dx$ at a time t . Then the average momentum of a particle can be expressed by the following equation:

$$p_{x(av)} = \int_{-\infty}^{+\infty} p_x p(x, t) dx \quad \dots(7.32)$$

Now, if the wave function is known one can easily calculate the probability density. The probability density is given by the following expression:

$$p(x, t) = |\Psi_n(x, t)|^2 = \Psi_n^*(x, t) \Psi_n(x, t)$$

where $\Psi_n(x, t)$ is the normalized value of the $\Psi(x, t)$. On substitution of this value of $p(x, t)$ in Eq. (7.32), one can obtain

$$p_{x(av)} = \int_{-\infty}^{+\infty} p_x \Psi_n^*(x, t) \Psi_n(x, t) dx$$

This theoretically calculated average is called the *expected average* or *expectation value* of the observable which is denoted by the symbol $\langle p_x \rangle$. Then the expression for the expected average can be written as

$$\langle p_x \rangle = \int_{-\infty}^{+\infty} \Psi_n^*(x, t) p_x \Psi_n(x, t) dx$$

or,

$$\langle p_x \rangle = \int_{-\infty}^{+\infty} \Psi_n^*(x, t) p_x \Psi_n(x, t) dx \quad \dots(7.33)$$

Similarly one can calculate the expectation value of the position of a particle which is given by the following expression:

$$\langle x \rangle = \int_{-\infty}^{+\infty} \Psi_n^*(x, t) \hat{x} \Psi_n(x, t) dx \quad \dots(7.34)$$

In general, for any physical quantity $f(x, p_x, t)$ which is a function of x, p_x and t , the expected value is given by

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

or,

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

or,

$$\langle f(x, p_x, t) \rangle = \int_{-\infty}^{+\infty} \Psi_n^*(x, t) f\left(x, -i\hbar \frac{\partial}{\partial x}, t\right) \Psi_n(x, t) dx \quad \dots(7.35)$$

where $\hat{f}(x, p_x, t) = f(\hat{x}, \hat{p}_x, t) = f\left(x, -i\hbar \frac{\partial}{\partial x}, t\right)$. \dots(7.36)

For the matter of a particle in three-dimensional space, the wave function $\Psi_n(\vec{r}, t)$ of the particle is a function of the position vector \vec{r} and time t and the physical quantities are generally functions of position vector \vec{r} , momentum \vec{p} and time t .

The expected average of one such physical variable (quantity) $g(\vec{r}, \vec{p}, t)$ is given by

$$\langle g \rangle = \int_{-\infty}^{+\infty} \Psi_n^*(\vec{r}, t) \hat{g}(\vec{r}, \vec{p}, t) \Psi_n^*(\vec{r}, t) dV \quad \checkmark \quad \dots(7.37)$$

where dV is a differential volume element.

For calculation of the mathematical expectation or expectation value or expected average one can follow the rule given below:

In order to calculate the expected average, place the operator representing the dynamical variable to operate on the normalized wave function $\Psi_n(\vec{r})$ and multiply the result by $\Psi_n^*(\vec{r})$ and then integrate over the spatial coordinates.

7.5.7 Correspondence Principle or Ehrenfest Theorem-Operator Correspondence

The notion of the expectation values (or mathematical expectations) of dynamical variables [as has been given in Eqs. (7.33), (7.34) and (7.35)] can be used to check the validity of the correspondence principle which is one of the basic postulates of quantum mechanics and known as postulate of operator-variable correspondence or simply operator correspondence. In fact this postulate states about the correspondence

Postulate 2 of Quantum Mechanics

The classical dynamical variables relating to the motion of a particle are represented by mathematical operators in quantum mechanics.

of dynamical variables of classical mechanics to the operators related to the expected averages of quantum mechanics.

According to the principle of correspondence, one can expect that the relationships of classical mechanics between various dynamical variables (e.g., coordinate and momentum) of a particle will also hold good between the expected averages of these quantities for the quantum mechanical wave packet associated with the particle. **This is known as Ehrenfest theorem.**

The measure of the positional uncertainty (Δx) of a particle is given by the width of the wave packet. Since the momentum of the particle is given by $p = \hbar k$, the range of variation of the wave number (Δk) gives the measure of uncertainty in case of the momentum of the particle. For a classical particle (where large distance and momenta are involved) one can ignore the uncertainty principle in the measurement of position and momentum. It was shown by Ehrenfest that the motion of a wave packet agrees with the motion of a particle in classical mechanics if the position and momentum vectors are considered as the expected averages of these quantities.

One can show that the time rate of change of the expected average of the position coordinate x of a particle corresponds to the expected average of the velocity of the same. It can be expressed as follows:

$$\frac{d}{dt} \langle x \rangle = \frac{1}{m} \langle p_x \rangle \quad \dots(7.38)$$

One can also show that the time rate of change of the expected average of p_x corresponds to the x component of the expected average of the force acting on the particle. It can be expressed as follows:

$$\frac{d}{dt} \langle p_x \rangle = - \left\langle \frac{\partial V}{\partial x} \right\rangle = \langle F_x \rangle \quad \dots(7.39)$$

Equation (7.39) confirms the wave packet description of a moving particle for which the time rate of change of the momentum equals to the negative of the expected average of the gradient of potential, that is equal to the impressed force acting on the particle. It can be seen from this equation the wave packet description reproduces Newton's second law of motion. In fact, the Eqs. (7.38) and (7.39) together express the Ehrenfest theorem and it presents a correspondence between the wave packet formalism and the classical dynamics describing the motion of a particle.

7.6 FUNDAMENTAL POSTULATES OF QUANTUM MECHANICS

In the approach of developing the theory of wave mechanics which has been done so far, it has been tried to make plausible various new ideas on the basis of underlying physical principles involved. However, there is another alternative approach in which the formal mathematical structure of wave mechanics is founded on a number of fundamental postulates. The theory can be developed more logically on the basis of these postulates and derives justification from the success of it, in accounting for a wide variety of atomic and subatomic phenomena.

Let us enumerate and discuss briefly the fundamental postulates all of which have been introduced so far. Five fundamental postulates of wave mechanics, which are listed below, are applicable in general to any quantum mechanical system. But here we shall restrict ourselves to a single particle system for the sake of simplicity.

Postulate 1 There is a wave function associated with a particle [denoted by $\Psi(\vec{r}, t)$ or $\Psi(x, y, z, t)$] which can completely describe the space-time behavior of the particle in consistence with the uncertainty principle.

Postulate 2 In quantum mechanics, the dynamical variables related to the motion of a particle are represented by mathematical operators.

Postulate 3 For a dynamical variable α , the possible results of measurement are given only by the eigen values of the operator $\hat{\alpha}$ satisfying the following eigen value equation

$$\hat{\alpha} \Psi_e = a_e \Psi_e$$

where Ψ_e is the eigen function of the operator $\hat{\alpha}$ belonging to the eigen value a_e . The eigen functions Ψ are single-valued in space and square-integrable. And they also form a complete set of orthogonal wave functions.

Postulate 4 The probability $p dV$ of finding a particle in the volume element dV is given by the equation

$$p dV = \Psi_n^* \Psi_n dV = |\Psi_n|^2 dV$$

where Ψ_n is the normalized wave function, $p = |\Psi_n|^2$ and it is called the probability density. In a finite volume V of space, the probability of finding the particle is given by

$$\int_V p dV = \int_V |\Psi_n|^2 dV$$

And the probability of finding the particle in entire space is given by

$$P = \int_{\text{all space}} \Psi_n^* \Psi_n dV = 1$$

Postulate 5 The expected average of the results of a large number of measurements of a dynamical variable α of a particle is given by

$$\langle \alpha \rangle = \int_V \Psi_n^* \hat{\alpha} \Psi_n dV$$

where $\hat{\alpha}$ is the operator representing the variable α and Ψ_n is normalized wave function.

The operators corresponding to some observables or dynamical variables are listed in the following table:

Table 7.1 Some observables and their corresponding operators.

Observable	Operator
(a) Position	$\hat{r} = \vec{r}$ (or $\hat{x} = x, \hat{y} = y, \hat{z} = z$)
(b) Momentum	$\hat{p} = -i\hbar \vec{\nabla}$ (or, $\hat{p}_x = -i\hbar \frac{\partial}{\partial x}, \hat{p}_y = -i\hbar \frac{\partial}{\partial y}, \hat{p}_z = -i\hbar \frac{\partial}{\partial z}$)
(c) Kinetic Energy	$\hat{E}_k = \frac{-\hbar^2}{2m} \vec{\nabla}^2 = \frac{-\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right)$
(d) Potential Energy	$\hat{V}(\vec{r}) = V(\vec{r})$ or $\hat{V}(x, y, z) = V(x, y, z)$
(e) Total Energy	$\hat{E} = i\hbar \frac{\partial}{\partial t}$
(f) Hamiltonian	$\hat{H} = \frac{-\hbar^2}{2m} \vec{\nabla}^2 + V(\vec{r})$ or, $\hat{H} = \frac{-\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) + V(x, y, z)$
(g) Angular Momentum ($\vec{L} = \vec{r} \times \vec{p}$)	$\hat{L} = -i\hbar (\vec{r} \times \vec{\nabla})$

7.7 BASIC CONSIDERATIONS FOR DEVELOPING SCHRÖDINGER'S EQUATION

The laws of classical mechanics are not able to explain the origin of quantized motion in atomic or subatomic domain. The old quantum theory is also not adequate in this respect as the rules of quantization in this theory are introduced on ad hoc basis. According to Heisenberg, the failure of the old quantum theory is due to the formulation of this theory on the basis of some classical concepts which have no meaning in the context of quantized motion of particles. Thus, in order to overcome this discrepancy, the electronic orbits of atoms and the velocity of the rotating electrons in these orbits are considered. If, however, one tries to determine the position (or, the velocity) of the electron in the atomic orbits, one has to perform some experiment (e.g., gamma-ray microscopic experiment) which will disturb the system (i.e., the electron) and will introduce some uncertainties in the quantity to be measured as predicted by the principle of uncertainty.

Thus, attempts should be made to develop atomic mechanics not on the basis of unobservable classical concepts, but on the basis of some new concepts which are in fact based on observable quantities. For example, when one performs experiments to investigate an atomic structure, one measures the energies of the atomic states through measurement of wavelengths of the spectral line, intensities, etc., and not through the positions or velocities of the electrons. So the new atomic mechanics should be built on the basis of quantities like the intensities of spectral lines and the energies of the atomic states.

It was on the basis of such thinking that Schrödinger developed wave mechanics (in 1926) on the basis of de Broglie hypothesis of wave-particle duality. The concepts introduced by de Broglie to relate dynamical variables connected with the particle motion (e.g., momentum) with the characteristics of waves (e.g., wavelength) were extended by him in a more general way to a quantum system to develop a wave equation to describe the motion of atomic particles, like electrons. Schrödinger's wave equation has become the foundation of non-relativistic wave mechanics. Later (in 1928) Dirac laid the foundation of relativistic wave mechanics. And he then generalized the quantum mechanics by unifying Heisenberg's matrix mechanics and Schrödinger's wave mechanics.

7.7.1 Time-Dependent Schrödinger's Equation

According to the second postulate of quantum mechanics, the dynamical variables of classical mechanics relating to the motion of a particle can be represented by mathematical operators in quantum mechanics. If one keeps this point in view, one can easily derive Schrödinger's time-dependent equation.

Let us consider a particle of mass m , moving along the x axis with a fixed momentum p_x and total energy E in a free region. As no force is acting on the particle, it is in a region of uniform potential energy which can be assumed to be zero. Hence, in this case, the total energy will be equal to the kinetic energy. And it is $E = p_x^2/(2m)$ for non-relativistic motion. Now, keeping in view, the aforesaid second postulate, one can write the corresponding quantum mechanical expression of the classical expression $E = p_x^2/(2m)$ as follows:

$$\hat{E} = \frac{\hat{p}_x^2}{2m}$$

Now, multiplying this equation by the wave function of a free particle $\Psi(x, t)$ from right side, i.e., allowing the operators to act upon $\Psi(x, t)$, one gets the following equation:

$$\hat{E} \Psi(x, t) = \frac{\hat{p}_x^2}{2m} \Psi(x, t)$$

or,

$$i\hbar \frac{\partial}{\partial t} \Psi(x, t) = \frac{(-i\hbar \frac{\partial}{\partial x})^2}{2m} \Psi(x, t)$$

or,

$$\frac{-\hbar^2}{2m} \frac{\partial^2 \Psi(x, t)}{\partial x^2} = i\hbar \frac{\partial}{\partial t} \Psi(x, t) \quad \dots(7.40)$$

This equation is Schrödinger's one-dimensional time-dependent equation for a free particle having wave function $\Psi(x, t) = Ae^{i(kx - \omega t)}$. The wave function $\Psi(x, t)$ conveys the necessary information to locate the particle in time and space, so $\Psi(x, t)$ is a function of x and t .

Now, if the particle is not free one it will be acted upon by some external force which will be characterized by a non-zero potential energy of the particle. Let the potential energy be $V(x, t)$. So, one can write the operator equation as

$$\hat{E} = \frac{\hat{p}_x^2}{2m} + \hat{V}(x, t)$$

So, the corresponding Schrödinger's equation will be given by

$$i\hbar \frac{\partial}{\partial t} \Psi(x, t) = \frac{(-i\hbar)^2}{2m} \frac{\partial^2}{\partial x^2} \Psi(x, t) + V(x, t) \Psi(x, t)$$

or,

$$i\hbar \frac{\partial}{\partial t} \Psi(x, t) = \frac{-\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \Psi(x, t) + V(x, t) \Psi(x, t)$$

or,

$$\frac{-\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \Psi(x, t) + V(x, t) \Psi(x, t) = i\hbar \frac{\partial}{\partial t} \Psi(x, t) \quad \dots(7.41)$$

This equation [Eq. (7.41)], is Schrödinger's one-dimensional equation for one particle system.

In a three-dimensional case, Schrödinger's equation for one particle system is given by

$$\frac{-\hbar^2}{2m} \nabla^2 \Psi(\vec{r}, t) + V(\vec{r}, t) \Psi(\vec{r}, t) = i\hbar \frac{\partial}{\partial t} \Psi(\vec{r}, t) \quad \dots(7.42)$$

where $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$ is the laplacian operator named after the famous mathematician Laplace. By

using the hamiltonian operator $\hat{H} = \frac{-\hbar^2}{2m} \nabla^2 + V(\vec{r}, t)$, one can write the time-dependent Schrödinger's equation

of three dimensions as

$$\hat{H} \Psi(\vec{r}, t) = i\hbar \frac{\partial}{\partial t} \Psi(\vec{r}, t) \quad \dots(7.43)$$

//

7.7.2 Time-Independent Schrödinger's Wave Equation

In the last subsection we have seen that in case of time-dependent Schrödinger's equation, the potential energy (V) of a moving particle is a function of both time and space coordinates. But, in many physical situations the potential energy of a moving body does not depend explicitly on time. In such cases, the potential energy as well as the forces which act on the particle is a function of position (\vec{r}) only. So $V = V(\vec{r})$. In such cases, the time-dependent Schrödinger's equation of three dimensions given in Eq. (7.42) can be rewritten as follows:

$$\frac{-\hbar^2}{2m} \nabla^2 \Psi(\vec{r}, t) + V(\vec{r}) \Psi(\vec{r}, t) = i\hbar \frac{\partial \Psi(\vec{r}, t)}{\partial t} \quad \dots(7.44)$$

[since $V = V(\vec{r})$ only]

Equation (7.44) is a partial differential equation of variables which are functions of \vec{r} and t . While the potential energy V is a function of position vector \vec{r} only, the total energy E is a constant quantity. So the equation is separable into the time-dependent and time-independent parts. And because of this situation, the wave function $\Psi(\vec{r}, t)$ can be expressed as the product of two separate functions $\phi(\vec{r})$ and $f(t)$ where the former is a function of \vec{r} only and the later is a function of t only. Hence $\Psi(\vec{r}, t)$ can be written as

$$\Psi(\vec{r}, t) = \phi(\vec{r}) f(t)$$

Now, putting this value of $\Psi(\vec{r}, t)$ in Eq. (7.44), one can get

$$\frac{-\hbar^2}{2m} \nabla^2 \phi(\vec{r}) f(t) + V(\vec{r}) \phi(\vec{r}) f(t) = i\hbar \frac{\partial}{\partial t} \{ \phi(\vec{r}) f(t) \}$$

Now, dividing both sides by $\phi(\vec{r}) f(t)$, one gets,

$$\frac{-\hbar^2}{2m} \frac{1}{\phi(\vec{r})} \nabla^2 \phi(\vec{r}) + V(\vec{r}) = i\hbar \frac{1}{f(t)} \frac{\partial}{\partial t} f(t) \quad \dots(7.45)$$

The left-hand side of Eq. (7.45) is a function \vec{r} only while right-hand side is a function of t only. This is possible only when both of the sides are separately equal to a constant quantity. This constant is the total energy E of the particle. Thus, one can write two equations, when one equates the left side to E , the following equation is obtained:

$$\frac{-\hbar^2}{2m} \nabla^2 \phi(\vec{r}) + V(\vec{r}) \phi(\vec{r}) = E \phi(\vec{r})$$

$$\text{or, } \nabla^2 \phi(\vec{r}) + \frac{2m}{\hbar^2} [E - V(\vec{r})] \phi(\vec{r}) = 0 \quad \dots(7.46)$$

This is the three-dimensional time-independent Schrödinger's wave equation. From this equation, the one-dimensional time-independent Schrödinger's equation can be written as follows:

$$\frac{d^2}{dx^2} \phi(x) + \frac{2m}{\hbar^2} [E - V(x)] \phi(x) = 0 \quad \dots(7.47)$$

Equation (7.46) can be again written as follows

$$\frac{-\hbar^2}{2m} \nabla^2 \phi(\vec{r}) + V(\vec{r}) \phi(\vec{r}) = E \phi(\vec{r})$$

$$\text{or, } \hat{H} \phi(\vec{r}) = E \phi(\vec{r}) \quad \dots(7.48)$$

$$\text{where } \hat{H} = \frac{-\hbar^2}{2m} \nabla^2 + V(\vec{r})$$

Equation (7.48) is the eigen value equation where E and $\phi(r)$ are the eigen value and eigen function respectively.

Thus, when the hamiltonian operator of time-independent Schrödinger's wave equation operates on the wave function $\phi(\vec{r})$ it reproduces the same wave function $\phi(\vec{r})$ multiplied by the total energy. The eigen value E of the hamiltonian operator which is only the possible value of total energy of a quantum mechanical system.

Now, equating the right side of Eq. (7.45) to E , one can get

$$i\hbar \frac{d}{dt} f(t) = Ef(t) \quad \left[\because \text{there is only one independent variable } \frac{\partial}{\partial t} = \frac{d}{dt} \right]$$

or,

$$\frac{d}{dt} f(t) = -\frac{iE}{\hbar} f(t)$$

or,

$$\frac{df(t)}{f(t)} = \frac{iE}{\hbar} dt$$

Now, integrating both sides, one can get

$$\ln \{f(t)\} = -\frac{iE}{\hbar} t + \ln c \text{ where } c \text{ is a constant.}$$

or,

$$\ln \left\{ \frac{f(t)}{c} \right\} = -\frac{iE}{\hbar} t$$

or,

$$f(t) = ce^{-(iE/\hbar)t}$$

Thus, from the equation $\Psi(\vec{r}, t) = \phi(\vec{r}) f(t)$
one can write

$$\Psi(\vec{r}, t) = \phi(\vec{r}) ce^{-\frac{iEt}{\hbar}} \quad \dots(7.49)$$

This gives the solution of Schrödinger's equation.

Here, $\phi(\vec{r})$ and $ce^{-\frac{iEt}{\hbar}}$ are the amplitude and phase of the wave function $\Psi(\vec{r}, t)$ respectively. The time-independent form of Schrödinger's wave Eq. (7.46) is sometimes known as the amplitude equation.

Every solution of the time-independent Schrödinger's wave equation gives a definite energy value. If one writes, $\Psi = \Psi_n(\vec{r})$ as the solution for the energy value $E = E_n$, then the particular solution is given by

$$\Psi_n(\vec{r}, t) = \Psi_n(\vec{r}) ce^{iE_n t / \hbar}$$

$\Psi_n(\vec{r}, t)$ belongs to the definite energy value E_n .

One can find the probability of finding the particle with energy value E_n as follows:

$$\begin{aligned} p_n &= |\Psi_n(\vec{r}, t)|^2 = \Psi_n^*(\vec{r}, t) \Psi_n(\vec{r}, t) \\ &= \Psi_n^*(\vec{r}) c^* e^{\frac{iE_n t}{\hbar}} \Psi_n(\vec{r}) ce^{-\frac{iE_n t}{\hbar}} \end{aligned}$$

or,

$$p_n = |\Psi_n(\vec{r})|^2 = [\Psi_n(\vec{r})]^2$$

... (7.52)

Thus, the probability of finding the particle with energy E_n is independent of time t . $[\because \Psi_n^*(\vec{r}) = \Psi_n(\vec{r}) \text{ and } c^* c = 1]$

7.8 APPLICATIONS OF SCHRÖDINGER'S EQUATION

Schrödinger's equation is able to describe any system of quantum particles in space and time. As it is a differential equation, it is to be solved for finding all the information about the quantum system of particles. The solution of Schrödinger's equation is known as Schrödinger's wave function as this equation is basically a wave equation which represents the de Broglie wave of the system. In this section of the present chapter, attempts will be made to determine the wave function of a particle which remains trapped in a certain region

of space by applying the theory of Schrödinger. The possible energy values of the particles also will be calculated.

7.8.1 Particle in a Box with Infinitely Deep Potential Well

The simplest quantum-mechanical problem is that of a particle trapped in a box with infinitely hard walls. One may specify the motion of the particle along a straight line, then the problem will be one-dimensional. And when no such restriction in motion will be imposed then it will be a three-dimensional problem. The one-dimensional case will be discussed first and then it will be followed by the three-dimensional case.

(i) One-dimensional case (1D box)

Let us consider a particle of mass m capable of moving along the x axis only between two infinitely hard walls and face an infinitely deep potential as shown in Fig. 7.2.

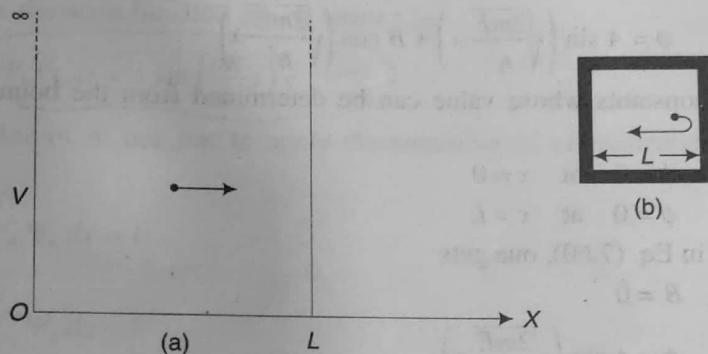


Fig. 7.2 One-dimensional infinite potential well.

The variable x can assume any value between 0 and L (i.e., $x_{\min} = 0$ and $x_{\max} = L$). The two hard walls act as infinitely high potential barriers. The particle is said to be in a one-dimensional box. The potential energy is constant within this region of length L . But it is infinite on both sides of the box. Inside the box, the potential energy can be assumed to be zero. So, one can write

$$V = 0 \quad \text{for } 0 < x < L \quad \dots(7.53)$$

$$V = \infty \quad \text{for } x \geq L \quad \text{and} \quad x \leq 0 \quad \dots(7.54)$$

The particle will need infinite amount of energy to overcome these two barriers. Since a particle cannot have infinite energy, it remains confined within the box with $0 \leq x \leq L$. It is not possible to find the particle outside the box and therefore, its wave function $\Psi(x, t)$ is zero outside. So, the wave function $\Psi(x, t)$ must satisfy the following condition:

$$\Psi(x, t) = 0 \quad \text{for } x \geq L \quad \text{and} \quad x \leq 0 \quad \dots(7.55)$$

The wave function $\Psi(x, t)$ represents a stationary wave as V is independent of time. So, it can be expressed as

$$\Psi(x, t) = \phi(x) f(t)$$

The time-dependent part of Ψ is given by the following equation:

$$f(t) = e^{-i Et/\hbar} \quad \dots(7.56)$$

Equation (7.55) implies that

$$\phi(x) = 0 \quad \text{for } x \geq L \quad \text{and} \quad x \leq 0 \quad \dots(7.57)$$

The function $\phi(x)$ can be determined having solved Schrödinger's time-independent equation. This equation is

$$-\frac{\hbar^2}{2m} \frac{d^2\phi}{dx^2} + V\phi = E\phi \quad \dots(7.58)$$

As in this case, $V = 0$, one can write,

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

or,
$$\frac{d^2\phi}{dx^2} + \frac{2mE}{\hbar^2} \phi = 0$$
 ...(7.59)

The general solution of Eq. (7.59) is given by

$$\phi = A \sin \left(\sqrt{\frac{2mE}{\hbar^2}} x \right) + B \cos \left(\sqrt{\frac{2mE}{\hbar^2}} x \right) \quad \dots(7.60)$$

where A and B are two constants whose value can be determined from the boundary conditions given below:

and
$$\phi = 0 \quad \text{at} \quad x = 0$$

$$\phi = 0 \quad \text{at} \quad x = L$$

Putting $x = 0$ and $\phi = 0$ in Eq. (7.60), one gets

$$B = 0$$

$$\therefore \phi = A \sin \left(\sqrt{\frac{2mE}{\hbar^2}} x \right) \quad \dots(7.61)$$

Now, putting $x = L$ and $\phi = 0$ and $B = 0$ in the Eq. (7.60), one can get

$$0 = A \sin \sqrt{\frac{2mE}{\hbar^2}} L + 0$$

or,
$$A \sin \sqrt{\frac{2mE}{\hbar^2}} L = 0 \quad \dots(7.62)$$

In Eq. (7.62) $A \neq 0$, because in such case $\phi(x) = 0$ for all values of x . Then one can write

$$\sin \sqrt{\frac{2mE}{\hbar^2}} L = 0$$

And hence, one can have

$$\sqrt{\frac{2mE}{\hbar^2}} \cdot L = n\pi \quad \dots(7.63)$$

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

Now, using Eqs. (7.63) and (7.61), one can write

$$\phi(x) = A \sin \left(\frac{n\pi}{L} x \right)$$

As $\phi(x)$ is dependent on n , one can write the above equation as

$$\phi_n(x) = A \sin \left(\frac{n\pi}{L} x \right) \quad \dots(7.64)$$

Squaring both sides of Eq. (7.63), one can write

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

As E is dependent on n , one can write

$$E_n = \frac{n^2 \pi^2 \hbar^2}{2mL^2} \quad \dots(7.65)$$

Here, one can regard n as a quantum number which determines the possible energy values E_n corresponding to different states represented by the function $\phi_n(x)$.

Now, multiplying $\phi_n(x)$ by the time-dependent part of the wave function, one can write

$$\Psi_n(x, t) = \phi_n(x) e^{-iE_n t/\hbar}$$

So, in general form, the wave function can be written as

$$\Psi_n(x, t) = A \sin\left(\frac{n\pi}{L}x\right) e^{-iE_n t/\hbar} \quad \dots(7.66)$$

To find out the value of A , one has to apply the condition of normalization of the wave function as follows:

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

$$\text{or, } \int_0^L \Psi_n^* \Psi_n dx = 1$$

Now using Eq. (7.66), one gets

$$\int_0^L A^2 \sin^2\left(\frac{n\pi}{L}x\right) dx = 1$$

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

$$\text{or, } A = \sqrt{\frac{2}{L}} \quad \dots(7.67)$$

Putting this value of A in Eq. (7.66)

$$\Psi_n(x, t) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L}x\right) e^{-iE_n t/\hbar} \quad \dots(7.68)$$

This wave function represents a stationary state where the total energy of the particle is E_n , given by Eq. (7.65).

Since $E_n = \frac{n^2 \pi^2 \hbar^2}{2mL^2}$ and $n = 1, 2, 3, \dots$, the energy of the particle cannot be continuously distributed; the possible energy values (E_n) are discrete. The lowest energy corresponds to $n = 1$.
 \therefore the lowest energy is given by

$$E_1 = \frac{\pi^2 \hbar^2}{2mL^2} \quad \dots(7.69)$$

One can express E_n in terms of E_1 as

$$E_n = \frac{n^2 \pi^2 \hbar^2}{2mL^2} = n^2 E_1 \quad \dots(7.70)$$

i.e.,

and

$$E_n = n^2 E_1 \quad \dots(7.71)$$

$$E_{n+1} = (n+1)^2 E_1 \quad \dots(7.72)$$

Now, subtracting Eq. (7.70) from Eq. (7.71), one obtains

$$E_{n+1} - E_n = (2n+1) E_1 \quad \dots(7.73)$$

or,

$$E_{n+1} - E_n = (2n+1) \cdot \frac{\pi^2 \hbar^2}{2mL^2} \quad \dots(7.74)$$

Now, in case of a macroscopic body, mL^2 is very large and the difference between two successive energy levels becomes extremely small. Hence, the possible levels (in such case) seem to have a continuous distribution. So, in a macroscopic world, the energy distribution seems to be continuous.

The probability density p_n of the particle is given by the following equation:

$$p_n = |\Psi_n(x, t)|^2 = \Psi_n^*(x, t) \Psi_n(x, t)$$

or,

$$p_n = \left(\frac{2}{L}\right) \sin^2\left(\frac{n\pi}{L}x\right) \quad \dots(7.74)$$

[by Eq. (7.68)]

When $\sin^2\left(\frac{n\pi x}{L}\right) = 1$, i.e., when $\frac{n\pi x}{L} = (2q+1)\frac{\pi}{2}$ and $q = 1, 2, 3, \dots$, the probability density p_n becomes maximum.

In other words, when $x = (2q+1)\frac{L}{2\pi}$ for $q = 1, 2, 3, 4, \dots$, the probability density p_n becomes maximum.

Figure (7.3) shows the variation of Ψ_n and $|\Psi_n|^2$ with respect to x for $n = 1, n = 2$ and $n = 3$.

As the value of n increases, the probable positions increase, which means that as the energy of a particle increases the peak number in the probability density curve also increases. According to classical theory, the particle should be found everywhere in the box with the same probability. But according to the quantum theory, the probability of existence of the particle is maximum at the antinodes and it is minimum at the nodes.

Expected average of the position

The expected average of position of the particle is given by

$$\langle x \rangle = \int_{-\infty}^{+\infty} \Psi_n^* \hat{x} \Psi_n dx = \int_0^L |\Psi_n|^2 x dx$$

or,

$$\langle x \rangle = \frac{2}{L} \int_0^L x \sin^2\left(\frac{n\pi x}{L}\right) dx$$

or,

$$\langle x \rangle = \frac{2}{L} \left[\frac{x^2}{4} - \frac{x \sin(2x\pi/L)}{4n\pi/L} - \frac{\cos(2x\pi/L)}{8(n\pi/L)^2} \right]_0^L$$

or,

$$\langle x \rangle = \frac{2}{L} \left(\frac{L^2}{4} \right)$$

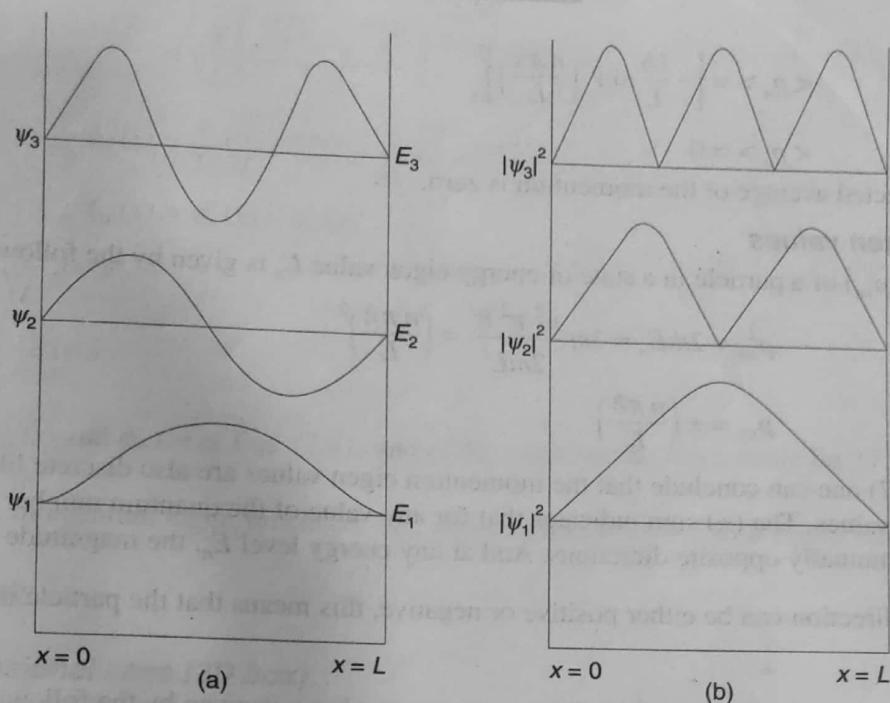


Fig. 7.3 (a) The energy band corresponding to normalized wave functions in case of ground, first excited and second excited states in one-dimensional box. (b) Probability densities of $|\Psi_1|^2$, $|\Psi_2|^2$ and $|\Psi_3|^2$.

or,

$$\langle x \rangle = \frac{L}{2}$$

So, for any value of n , the expected average of the position (x) of the particle is always $L/2$ for a box of linear dimension or length L .

It is clear from this fact that the average position of the particle is the middle point of the box in all quantum states of the particle.

Expected average of the momentum

The expected average or the mathematical expectation of the momentum of the particle is given by

$$\langle p_x \rangle = \int_{-\infty}^{+\infty} \Psi_n^* p_x \Psi_n dx = \int_0^L \Psi_n^* p_x \Psi_n dx$$

$$\text{or, } \langle p_x \rangle = \int_0^L \Psi_n^* \left(-i\hbar \frac{\partial}{\partial x} \right) \Psi_n dx \quad \dots(7.75)$$

$$\text{where } \Psi_n(x, t) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) e^{-\frac{iEnt}{\hbar}}$$

Substituting the values of Ψ_n and Ψ_n^* in Eq. (7.75), one obtains

$$\langle p_x \rangle = -\frac{2i\hbar n\pi}{L^2} \int_0^L \sin\left(\frac{n\pi x}{L}\right) \cos\left(\frac{n\pi x}{L}\right) dx$$

or,

$$\langle p_x \rangle = \left[-\frac{i\hbar}{L} \sin^2 \left(\frac{n\pi x}{L} \right) \right]_0^L$$

or,

$$\langle p_x \rangle = 0$$

Thus, the expected average of the momentum is zero.

...(7.76)

Momentum eigen values

The momentum (p_{xn}) of a particle in a state of energy eigen value E_n is given by the following equation:

$$p_{xn}^2 = 2mE_n = 2m \frac{n^2 \pi^2 \hbar^2}{2mL^2} = \left(\frac{n\pi\hbar}{L} \right)^2$$

or,

$$p_{xn} = \pm \left(\frac{n\pi\hbar}{L} \right)$$

...(7.77)

From Eq. (7.77) one can conclude that the momentum eigen values are also discrete like the corresponding energy eigen values. The (\pm) sign indicates that for any value of the quantum number n , the particle has momenta in two mutually opposite directions. And at any energy level E_n , the magnitude of the momentum is $\left(\frac{n\pi\hbar}{L} \right)$ but its direction can be either positive or negative, this means that the particle moves to and fro in the box.

The average momentum for any value of the quantum number n is given by the following equation:

$$p_{xn(av)} = \frac{1}{2} \left[\left(+\frac{n\pi\hbar}{L} \right) + \left(-\frac{n\pi\hbar}{L} \right) \right]$$

or,

$$p_{xn(av)} = 0$$

...(7.78)

This is consistent with the expected average of p_x , i.e., $\langle p_x \rangle$ as can be seen in Eq. (7.76).

Eigen function of the momentum

The eigen function Ψ'_n for an operator $\hat{\alpha}$ is given by

$$\hat{\alpha} \Psi'_n = \alpha \Psi'_n$$

where α is the eigen value of $\hat{\alpha}$. So for the momentum operator \hat{p}_x the corresponding eigen value p_{xn} with respect to the eigen function Ψ'_n is given by

$$\hat{p}_x \Psi'_n = p_{xn} \Psi'_n$$

...(7.79)

where the momentum operator \hat{p}_n is given by $\hat{p}_x = -i\hbar \frac{\partial}{\partial x}$.

The energy eigen function is given by the following expression:

$$\Psi_n = \phi_n(x) e^{-i E_n t / \hbar}$$

or,

$$\Psi_n = \sqrt{\frac{2}{L}} \sin \left(\frac{n\pi x}{L} \right) e^{-i E_n t / \hbar}$$

This energy eigen function does not satisfy Eq. (7.79). So, the energy eigen function Ψ_n is different from the momentum eigen function Ψ'_n .

One can write $\sin \theta = \frac{e^{i\theta} - e^{-i\theta}}{2i}$, so the wave function $\phi_n(x)$ can be written as

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

$$= \sqrt{\frac{2}{L}} \left(\frac{e^{\frac{in\pi x}{L}} - e^{-\frac{in\pi x}{L}}}{2i} \right)$$

or,

$$\phi_n(x) = \frac{1}{2i} \sqrt{\frac{2}{L}} e^{in\pi x/L} - \frac{1}{2i} \sqrt{\frac{2}{L}} e^{-in\pi x/L}$$

or,

$$\phi_n(x) = \phi_n^+(x) - \phi_n^-(x) \quad \dots(7.80)$$

$$\text{where } \phi_n^+(x) = \frac{1}{2i} \sqrt{\frac{2}{L}} e^{in\pi x/L}$$

$$\dots(7.81)$$

$$\text{and } \phi_n^-(x) = \frac{1}{2i} \sqrt{\frac{2}{L}} e^{-in\pi x/L} \quad \dots(7.82)$$

Now, each of $\phi_n^+(x)$ and $\phi_n^-(x)$ of Eqs. (7.81) and (7.82), satisfies the eigen value Eq. (7.79). Hence $\phi_n^+(x)$

and $\phi_n^-(x)$ are the momentum eigen functions, i.e., eigen functions of \hat{p}_x , with eigen values $\left(+\frac{n\pi\hbar}{L}\right)$ and $\left(-\frac{n\pi\hbar}{L}\right)$ respectively.

(ii) Three-dimensional case (3D box)

Let us suppose that a particle of mass m is confined in a rectangular box $ABCDHGFE$ with its edges parallel to the three axes (i.e., x axis, y axis and z axis) as has been shown in the diagram of Fig. 7.4.

Let the three sides of the said box be x_1 , y_1 , and z_1 respectively. The particle can move freely inside the box having ranges $0 < x < x_1$, $0 < y < y_1$ and $0 < z < z_1$ where the potential is zero (i.e., $V = 0$). The potential function $V(\vec{r}) = V(x, y, z)$ is having a constant value $V = 0$ in the regions given below:

$$V(x, y, z) = 0 \text{ for } 0 < x < x_1,$$

$$V(x, y, z) = 0 \text{ for } 0 < y < y_1 \text{ and}$$

$$V(x, y, z) = 0 \text{ for } 0 < z < z_1.$$

And the potential outside the box (also on the walls of it) is always infinite,

i.e.,

$$V(x, y, z) = \infty \quad \text{for } 0 \geq x \geq x_1,$$

$$V(x, y, z) = \infty \quad \text{for } 0 \geq y \geq y_1 \text{ and}$$

$$V(x, y, z) = \infty \quad \text{for } 0 \geq z \geq z_1$$

The time-independent Schrödinger's wave equation for the particle inside the box is given by the following equation:

$$\nabla^2 \Psi + \frac{2mE}{\hbar^2} \Psi = 0 \quad [\because V = 0] \quad \dots(7.83)$$

or,

$$\frac{\partial^2 \Psi}{\partial x^2} + \frac{\partial^2 \Psi}{\partial y^2} + \frac{\partial^2 \Psi}{\partial z^2} + \frac{2mE \Psi}{\hbar^2} = 0 \quad \dots(7.83)$$

Equation (7.83) can be solved by using the method of separation of variables. Let us assume that the function Ψ can be expressed as the product of three variables X , Y and Z where $X = X(x)$, $Y = Y(y)$ and $Z = Z(z)$. So, each of the three functions X , Y and Z depends only on one coordinate.

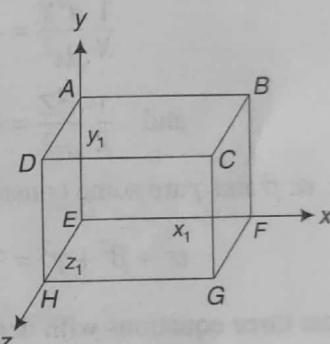


Fig. 7.4 Particle in a three-dimensional rectangular box $ABCDHGFE$ with length of edges x_1 , y_1 , and z_1 respectively.

$$\Psi(x, y, z) = X(x) Y(y) Z(z)$$

Hence,

$$\frac{\partial^2 \Psi}{\partial x^2} = YZ \frac{d^2}{dx^2} X, \quad \dots(7.84)$$

$$\frac{\partial^2 \Psi}{\partial y^2} = ZX \frac{d^2}{dy^2} Y \quad \text{and} \quad \frac{\partial^2 \Psi}{\partial z^2} = XY \frac{d^2}{dz^2} Z$$

Now, substituting these in Eq. (7.82) and then dividing by (XYZ) , one gets

$$\frac{1}{X} \frac{d^2}{dx^2} X + \frac{1}{Y} \frac{d^2}{dy^2} Y + \frac{1}{Z} \frac{d^2}{dz^2} Z + \frac{2mE}{\hbar^2} = 0 \quad \dots(7.85)$$

Now, it is to be noted that each of the terms of this equation [i.e., Eq. (7.85)] depends on a different variable and the three variables are independent of each other. And the last term of the Eq. (7.85) is a constant. The only way for this equation to be valid for all the variables of x, y and z in the intervals $(0, x_1), (0, y_1)$ and $(0, z_1)$ respectively is to be a constant.

That is each differential term in the equation will be separately constant.

Thus, one can express them as

$$\frac{1}{X} \frac{d^2X}{dx^2} = -\alpha^2, \quad \frac{1}{Y} \frac{d^2Y}{dy^2} = -\beta^2$$

and $\frac{1}{Z} \frac{d^2Z}{dz^2} = -\gamma^2$

where, α, β and γ are some constants.

$$\therefore \alpha^2 + \beta^2 + \gamma^2 = \frac{2mE}{\hbar^2}$$

These three equations with dependent variables X, Y and Z can be rewritten as follows:

$$\frac{d^2X}{dx^2} + \alpha^2 X = 0 \quad \dots(7.86)$$

$$\frac{d^2Y}{dy^2} + \beta^2 Y = 0 \quad \dots(7.87)$$

$$\frac{d^2Z}{dz^2} + \gamma^2 Z = 0 \quad \dots(7.88)$$

The general solutions of Eqs (7.86), (7.87) and (7.88) are given below:

$$X = A_1 \sin \alpha x + B_1 \cos \alpha x,$$

$$Y = A_2 \sin \beta y + B_2 \cos \beta y \text{ and}$$

$$Z = A_3 \sin \gamma z + B_3 \cos \gamma z$$

The values of the constants A_1, A_2, A_3, B_1, B_2 and B_3 can be obtained by applying the boundary condition. The boundary conditions require that the wave function vanishes at the box walls where the potential is infinite (as stated earlier).

So,

$$\Psi(0, y, z) = \Psi(x, 0, z) = \Psi(x, y, 0) = 0 \quad \dots(7.89)$$

and

$$\Psi(x_1, y, z) = \Psi(x, y_1, z) = \Psi(x, y, z_1) = 0 \quad \dots(7.90)$$

Now, by applying the boundary conditions of relations (6.89) to the above equations of X , Y and Z , one gets,

$$B_1 = B_2 = B_3 = 0$$

Again by applying the boundary conditions of relations (7.90) to the above equations of X , Y and Z , one gets,

$$\begin{aligned} \sin(\alpha x_1) &= 0 \Rightarrow \alpha x_1 = n_x \pi \text{ or } \alpha = n_x \pi / x_1, \\ \sin(\beta y_1) &= 0 \Rightarrow \beta y_1 = n_y \pi \text{ or } \beta = n_y \pi / y_1, \\ \text{and } \sin(\gamma z_1) &= 0 \Rightarrow \gamma z_1 = n_z \pi \text{ or } \gamma = n_z \pi / z_1 \end{aligned}$$

where n_x , n_y and n_z are integers and none is equal to zero.

Hence,

$$X = A_1 \sin \frac{n_x \pi x}{x_1} \quad \dots(7.91)$$

$$Y = A_2 \sin \frac{n_y \pi y}{y_1} \quad \dots(7.92)$$

and

$$Z = A_3 \sin \frac{n_z \pi z}{z_1} \quad \dots(7.93)$$

Now, substituting these values of X , Y and Z in Eq. (7.84), one gets

$$\Psi(x, y, z) = A_1 A_2 A_3 \sin \frac{n_x \pi x}{x_1} \sin \frac{n_y \pi y}{y_1} \sin \frac{n_z \pi z}{z_1}$$

or,

$$\Psi(x, y, z) = A \sin \frac{n_x \pi x}{x_1} \sin \frac{n_y \pi y}{y_1} \sin \frac{n_z \pi z}{z_1}$$

where $A = A_1 A_2 A_3$ and A is the normalization constant.

Now, A can be obtained by using the normalization condition as given below.

$$\int_{0}^{x_1} \int_{0}^{y_1} \int_{0}^{z_1} \Psi^* \Psi dx dy dz = 1$$

$$\text{or, } A^2 \int_{0}^{x_1} \int_{0}^{y_1} \int_{0}^{z_1} \sin^2 \left(\frac{n_x \pi x}{x_1} \right) \sin^2 \left(\frac{n_y \pi y}{y_1} \right) \sin^2 \left(\frac{n_z \pi z}{z_1} \right) dx dy dz = 1$$

$$\text{or, } A^2 \cdot \left(\frac{x_1}{2} \right) \left(\frac{y_1}{2} \right) \left(\frac{z_1}{2} \right) = 1$$

$$\text{or, } A = \frac{2\sqrt{2}}{\sqrt{(x_1 y_1 z_1)}}$$

So, the normalized wave function $\Psi_n(x, y, z)$ is given by the following expression:

$$\Psi_n(x, y, z) = \frac{2\sqrt{2}}{\sqrt{(x_1 y_1 z_1)}} \sin \left(\frac{n_x \pi x}{x_1} \right) \sin \left(\frac{n_y \pi y}{y_1} \right) \sin \left(\frac{n_z \pi z}{z_1} \right) \quad \dots(7.94)$$

Now, one has

$$\alpha^2 + \beta^2 + \gamma^2 = \frac{2mE}{\hbar^2}$$

$$\text{or, } \frac{n_x^2 \pi^2}{x_1^2} + \frac{n_y^2 \pi^2}{y_1^2} + \frac{n_z^2 \pi^2}{z_1^2} = \frac{2mE}{\hbar^2}$$

or,

$$E = \frac{\hbar^2 \pi^2}{2m} \left[\frac{n_x^2}{x_1^2} + \frac{n_y^2}{y_1^2} + \frac{n_z^2}{z_1^2} \right] \quad \dots(7.95)$$

Now, it is clear from the above equation [i.e., Eq. (7.95)] that E is dependent on n_x , n_y and n_z , so one can make use of the suffixes with E and rewrite Eq. (7.93) as follows:

$$E_{n_x n_y n_z} = \frac{\hbar^2}{8m} \left[\left(\frac{n_x}{x_1} \right)^2 + \left(\frac{n_y}{y_1} \right)^2 + \left(\frac{n_z}{z_1} \right)^2 \right] \quad \dots(7.96)$$

It can be stated from the above discussion that $\Psi_n(x, y, z)$ represents the state of the particle with total energy $E_{n_x n_y n_z}$ as given in Eq. (7.96). The three integers n_x , n_y and n_z are called the quantum numbers and are required to specify each energy state completely. For each set of values of the constants n_x , n_y and n_z , one gets a new wave function $\Psi_n(x, y, z)$ which can be represented by $\Psi_{n(n_x n_y n_z)}(x, y, z)$. And since $\Psi_n(x, y, z)$ cannot be zero within the box, no quantum number of the set (n_x, n_y, n_z) can be zero. So, the ground state energy is given by

$$E_g = E_{111} = \frac{\hbar^2}{8m} \left(\frac{1}{x_1^2} + \frac{1}{y_1^2} + \frac{1}{z_1^2} \right) \quad \dots(7.97)$$

The corresponding wave function of energy E_{111} is given by

$$\Psi_{n(111)} = \left(\sqrt{\frac{8}{x_1 y_1 z_1}} \right) \sin \left(\frac{\pi x}{x_1} \right) \sin \left(\frac{\pi y}{y_1} \right) \sin \left(\frac{\pi z}{z_1} \right) \quad \dots(7.98)$$

The momentum of the particle in a state is given by

$$p_{n_x n_y n_z} = \sqrt{2m E_{n_x n_y n_z}}$$

or,

$$p_{n_x n_y n_z} = \sqrt{\frac{\hbar^2}{4} \left(\frac{n_x^2}{x_1^2} + \frac{n_y^2}{y_1^2} + \frac{n_z^2}{z_1^2} \right)}$$

or,

$$p_{n_x n_y n_z} = \frac{\hbar}{2} \sqrt{\left(\frac{n_x}{x_1} \right)^2 + \left(\frac{n_y}{y_1} \right)^2 + \left(\frac{n_z}{z_1} \right)^2}$$

Degeneracy of the energy states

If one considers a cubical box, then $x_1 = y_1 = z_1$. Let $x_1 = y_1 = z_1 = L$

Then the wave function of the time-independent Schrödinger's equation and its corresponding energy value are given by the following two equations respectively:

$$\Psi_{n(n_x n_y n_z)}(x, y, z) = \sqrt{\frac{8}{L^3}} \sin \left(\frac{n_x \pi x}{L} \right) \sin \left(\frac{n_y \pi y}{L} \right) \sin \left(\frac{n_z \pi z}{L} \right) \quad \dots(7.99)$$

and

$$E_{n_x n_y n_z} = \frac{\hbar^2}{8mL^2} (n_x^2 + n_y^2 + n_z^2) \quad \dots(7.100)$$

As can be seen from Eq. (7.100), in a cubical box, the total energy $E_{n_x n_y n_z} \propto (n_x^2 + n_y^2 + n_z^2)$, i.e. the total energy is proportional to the sum of squares of the three quantum numbers n_x , n_y and n_z . And the particle in such a cube can have the same value of energy for more than one set of values of the quantum numbers (n_x, n_y, n_z) . This means that more than one wave functions can have the same energy value. The state represented by such a set of wave functions, is known as degenerate state.

Let us take help of an example to understand the concept of degeneration more clearly. Let us consider the following three sets of values of n_x , n_y and n_z .

Table 7.2 Some quantum numbers, energy levels and their wavefunctions.

n_x	n_y	n_z	$n_x^2 + n_y^2 + n_z^2$	E	Ψ_n
1	1	2	6	E_{112}	$\Psi_{n(112)}$
1	2	1	6	E_{121}	$\Psi_{n(121)}$
2	1	1	6	E_{211}	$\Psi_{n(211)}$

For the aforementioned three different states, the particle has the same energy $\frac{3h^2}{4mL^2}$. So, one can write

$$E_{112} = E_{121} = E_{211} = \frac{3h^2}{4mL^2} \quad \dots(7.101)$$

For these three sets of quantum numbers (i.e., values of n_x , n_y and n_z) the wave functions are quite different. And hence one can write the following inequation

$$\Psi_{n(112)} \neq \Psi_{n(121)} \neq \Psi_{n(211)}$$

Such energy states like $\Psi_{n(112)}$, $\Psi_{n(121)}$ and $\Psi_{n(211)}$ related to the same value of energy are called degenerate states. Since in these cases the wave functions are different, the probability densities in these three states are different from each other. The states having the energy equal to $\frac{3h^2}{4mL^2}$ are considered to have a degeneracy of three fold. The number of the independent wave functions (and hence the number of independent states) corresponding to the same value of energy is called the degeneracy of the energy states.

In case of a one-dimensional box, the degeneracy of energy states is not observed. For a particle in a cubical box, the degree of degeneracy for few energy states (i.e., energy levels) are presented in the Table 7.3 which follows:

Table 7.3 Some energy levels with their degenerate quantum number sets.

Energy Levels	Energy Values	Quantum Numbers	Degree of Degeneracy
E_{111}	$\frac{3h^2}{8mL^2}$	(1, 1, 1)	No degeneracy
$E_{112}, E_{121}, E_{122}$	$\frac{6h^2}{8mL^2}$	(1, 1, 2), (1, 2, 1), (2, 1, 1)	Three-fold degeneracy
$E_{221}, E_{212}, E_{122}$	$\frac{9h^2}{8mL^2}$	(2, 2, 1), (2, 1, 2), (1, 2, 2)	Three-fold degeneracy
$E_{311}, E_{131}, E_{113}$	$\frac{11h^2}{8mL^2}$	(3, 1, 1), (1, 3, 1), (1, 1, 3)	Three-fold degeneracy
E_{222}	$\frac{12h^2}{8mL^2}$	(2, 2, 2)	No degeneracy
$E_{123}, E_{132}, E_{231}$	$\frac{14h^2}{8mL^2}$	(1, 2, 3), (1, 3, 2), (2, 3, 1), (2, 1, 3), (3, 1, 2), (3, 2, 1)	Six-fold degeneracy
$E_{213}, E_{312}, E_{321}$			

The stationary wave function (or states) $\Psi_{n(112)}$, $\Psi_{n(121)}$ and $\Psi_{n(211)}$ for the particle in a cubical box of dimension L^3 are degenerate. The linear combination of them $\Psi_n = C_1 \Psi_{n(112)} + C_2 \Psi_{n(121)} + C_3 \Psi_{n(211)}$ is also an eigen function related to the same energy value $\left(\frac{3\hbar^2}{4mL^2}\right)$.

Worked Out Problems

Wave Function and Probability

Example 7.1 A particle which is moving along the y axis has the wave function $\Psi(y)$ as given below:

$$\Psi(y) = cy \quad \text{for } 0 \leq y \leq 1$$

$$\Psi(y) = 0 \quad \text{for } 0 \geq y \geq 1$$

Find the probability that the particle lies between $y = 0.35$ and $y = 0.75$.

Sol. The probability of finding a particle represented by the wave function $\Psi(y)$ in the length dy between y and $y + dy$ is given by

$$\Psi^*(y) \Psi(y) dy = |\Psi(y)|^2 dy$$

Hence, the probability within the range $0.35 \leq y \leq 0.75$ is given by

$$\begin{aligned} P &= \int_{0.35}^{0.75} |\Psi(y)|^2 dy = c^2 \int_{0.35}^{0.75} y^2 dy \\ &= \frac{c^2}{3} [y^3]_{0.35}^{0.75} = \frac{c^2}{3} [0.422 - 0.043] \end{aligned}$$

$$\therefore P = 0.126 c^2$$

Example 7.2 Consider the wave function $\Psi = Ae^{\alpha x + i\beta t}$ where A , α and β are real positive quantities. Could it represent the wave nature of a particle?

Sol. Ψ to be an acceptable wave function, it must satisfy the normalization condition, i.e., we must get

$$\int_{-\infty}^{+\infty} |\Psi(x, t)|^2 dx = 1 \quad \dots(1)$$

In the present case, we get

$$\begin{aligned} \int_{-\infty}^{+\infty} |\Psi|^2 dx &= \int_{-\infty}^{+\infty} \Psi^* \Psi dx = \int_{-\infty}^{+\infty} A^2 e^{2\alpha x} dx \\ &= \frac{A^2}{2\alpha} [e^{2\alpha x}]_{-\infty}^{+\infty} = \infty \end{aligned}$$

By comparing the result with Eq. (1), we realize that the function Ψ is not a normalizable wave function as $\int_{-\infty}^{+\infty} |\Psi|^2 dx = \infty$. So, the given function cannot represent the wave nature of any particle.

Example 7.3 (i) Show that $\Psi = Ax + B$ where A and B are constants, is a solution to Schrödinger's equation for $E = 0$ energy level of a particle in a box. (ii) Show, however, that the probability of finding a particle with this wave function is zero.

Sol. (i) Schrödinger's equation for a particle in a box is given by

$$\frac{d^2 \Psi}{dx^2} + \frac{2m}{\hbar^2} E \Psi = 0 \quad \dots(1)$$

Now, differentiating $\Psi = Ax + B$ twice with respect to x gives $\frac{d^2 \Psi}{dx^2} = 0$ for the left-hand side

of the Schrödinger's equation. Also by putting $E = 0$ in Eq. (1), we get the same equation. So $\Psi = Ax + B$ is a solution to this Schrödinger's equation for $E = 0$.

(ii) The wave function Ψ equals to zero outside the box ($x < 0$ and $x > L$). In order that $\Psi = Ax + B$ may be continuous at $x = 0$, it must be true that $\Psi = 0$ at $x = 0$. So $A \cdot 0 + B = 0$ or $B = 0$. Similarly, in order that Ψ may be continuous at $x = L$, it must be true that $\Psi = 0$ for $L = 0$. So, $A \cdot L + 0 = 0$ or $A = 0$. With both A and B equal to zero, $\Psi = Ax + B = 0$. Thus, the wave function is equal to zero inside the box as well as outside the box and probability of finding the particle anywhere with this wave function is zero.

Example 7.4 A particle is represented by the wave function $\Psi(x) = e^{-|x|} \sin \alpha x$. What is the probability that its position to the right of the point $x = 1$ (i.e., the point $(1, 0, 0)$)?

Sol. Given $\Psi(x) = e^{-|x|} \sin \alpha x$

Let, $\Psi_1(x) = e^x \sin(\alpha x)$ for $x < 0$

and $\Psi_2(x) = e^{-x} \sin(\alpha x)$ for $x > 0$

$$\therefore \int_{-\infty}^{+\infty} |\Psi(x)|^2 dx = \frac{1}{c^2}, \quad \text{where } c \text{ is the normalization constant.}$$

$$\text{or, } \int_{-\infty}^0 |\Psi_1(x)|^2 dx + \int_0^{+\infty} |\Psi_2(x)|^2 dx = \frac{1}{c^2}$$

$$\text{or, } \int_{-\infty}^0 e^{2x} \sin^2 \alpha x dx + \int_0^{+\infty} e^{-2x} \sin^2 \alpha x dx = \frac{1}{c^2}$$

$$\begin{aligned} \therefore \text{L.H.S} &= \int_{-\infty}^0 e^{2x} \left[\frac{1 - \cos 2\alpha x}{2} \right] dx + \int_0^{+\infty} e^{-2x} \left[\frac{1 - \cos 2\alpha x}{2} \right] dx \\ &= \frac{1}{2} - \frac{1}{2} \int_0^{+\infty} e^{2x} \cos 2\alpha x dx - \frac{1}{2} \int_0^{+\infty} e^{-2x} \cos 2\alpha x dx \\ &= \frac{1}{2} - \frac{1}{4(1+\alpha^2)} - \frac{1}{4(1+\alpha^2)} \end{aligned}$$

$$\therefore \frac{1}{2} - \frac{2}{4(1+\alpha^2)} = \frac{1}{c^2}$$

$$\text{or, } \frac{1 + \alpha^2 - 1}{2(1 + \alpha^2)} = \frac{1}{c^2}$$

$$\therefore c = \sqrt{\frac{2(1+\alpha^2)}{\alpha^2}}$$

So, the normalized wave function is given by

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

The required probability is given by

$$\begin{aligned} P &= \int_1^\infty |\Psi|^2 dx = \frac{1}{c^2} \int_1^\infty e^{-2x} \sin^2 \alpha x dx \\ &= \frac{e^{-2}}{4(1+\alpha^2)} [1 + \alpha^2 - \cos 2\alpha + \alpha \sin 2\alpha] \end{aligned}$$

Normalization and Orthogonality

Example 7.5 A particle is in a cubic box with infinitely hard walls whose edges are L units long. The wave function of the particle is given by

$$\Psi = A \sin\left(\frac{n_x \pi x}{L}\right) \sin\left(\frac{n_y \pi y}{L}\right) \sin\left(\frac{n_z \pi z}{L}\right)$$

Find the value of the normalization constant A .

Sol. The condition for normalization is that the value of the normalization constant should satisfy the following condition:

$$\int_{-\infty}^{+\infty} \Psi(x, y, z) \Psi(x, y, z) dV = 1$$

i.e., the total probability in the entire space must be 1.

$$\int_{-\infty}^{+\infty} \Psi(x, y, t) \Psi(x, y, z) dx dy dz = 1 \quad \text{where } dV = dx dy dz$$

$$\text{or, } \int_{-\infty}^{+\infty} A^2 \sin^2\left(\frac{n_x \pi x}{L}\right) \sin^2\left(\frac{n_y \pi y}{L}\right) \sin^2\left(\frac{n_z \pi z}{L}\right) dx dy dz = 1$$

$$\text{or, } A^2 \int_{-\infty}^{+\infty} \sin^2\left(\frac{n_x \pi x}{L}\right) dx \int_{-\infty}^{+\infty} \sin^2\left(\frac{n_y \pi y}{L}\right) dy \int_{-\infty}^{+\infty} \sin^2\left(\frac{n_z \pi z}{L}\right) dz = 1$$

Since the wave function is zero outside the box, we can write

$$A^2 \int_0^L \sin^2\left(\frac{n_x \pi x}{L}\right) dx \int_0^L \sin^2\left(\frac{n_y \pi y}{L}\right) dy \int_0^L \sin^2\left(\frac{n_z \pi z}{L}\right) dz = 1$$

$$\text{or, } A^2 \left(\frac{L}{2}\right) \left(\frac{L}{2}\right) \left(\frac{L}{2}\right) = 1$$

$$\text{or, } A^2 = \frac{8}{L^3}$$

$$\therefore A = \sqrt{\frac{8}{L^3}}$$

Example 7.6

Two wave functions $\Psi_m(x) = A \sin\left(\frac{m\pi x}{2}\right)$ and $\Psi_n(x) = B \sin\left(\frac{n\pi x}{2}\right)$ represent the motion of a particle confined in a one-dimensional box with perfectly hard walls. A and B are normalization constants. Show that if m and n are two integers and $m \neq n$, then the two given wave functions are orthogonal to each other.

Sol. Let

$$I = \int_{-\infty}^{+\infty} \Psi_m^*(x) \Psi_n(x) dx$$

or,

$$I = \int_{-\infty}^{+\infty} A \sin\left(\frac{m\pi x}{2}\right) B \sin\left(\frac{n\pi x}{L}\right) dx$$

or,

$$I = AB \int_0^L \sin\left(\frac{m\pi x}{L}\right) \sin\left(\frac{n\pi x}{L}\right) dx$$

[\because the wave functions must be zero outside the box]

or,

$$I = \frac{AB}{2} \int_0^L 2 \sin\left(\frac{m\pi x}{L}\right) \sin\left(\frac{n\pi x}{L}\right) dx$$

or,

$$I = \frac{AB}{2} \int_0^L \left[\cos \frac{\pi}{L} (m-n)x - \cos \frac{\pi}{L} (m+n)x \right] dx$$

or,

$$I = \frac{AB}{2} \left[\frac{L}{\pi(m-n)} \sin \frac{\pi}{L} (m-n)x - \frac{L}{\pi(m+n)} \sin \pi \frac{(m+n)}{L} x \right]_0^L$$

or,

$$I = \frac{AB}{2} \times 0$$

\therefore

$$I = 0$$

i.e., $\int_{-\infty}^{+\infty} \Psi_m^*(x) \Psi_n(x) dx = 0$

Hence, $\Psi_m(x)$ and $\Psi_n(x)$ are orthogonal to each other.

Quantum Mechanical Operators

Example 7.7

Determine the expression for the following two operators:

(a) $\left(\frac{d}{dx} + x \right)^2$

(b) $\left(\frac{d}{dx} (\cos x) \right)$

Sol. Let Ψ be the corresponding wave function.

(a) $\left(\frac{d}{dx} + x \right)^2 \Psi = \left(\frac{d}{dx} + x \right) \left(\frac{d}{dx} + x \right) \Psi$

$$= \left(\frac{d}{dx} + x \right) \left(\frac{d\Psi}{dx} + x\Psi \right)$$

$$= \frac{d^2\Psi}{dx^2} + x \frac{d\Psi}{dx} + \Psi + x \frac{d\Psi}{dx} + x^2 \Psi$$

$$\text{or, } \left(\frac{d}{dx} + x \right)^2 \Psi = \left\{ \frac{d^2}{dx^2} + 2x \frac{d}{dx} + (x^2 + 1) \right\} \Psi$$

$$\therefore \left(\frac{d}{dx} + x \right)^2 = \frac{d^2}{dx^2} + 2x \frac{d}{dx} + (x^2 + 1)$$

$$\begin{aligned} \text{(b)} \quad \left(\frac{d}{dx} \cos x \right) \Psi(x) &= \frac{d}{dx} (\cos x \Psi(x)) \\ &= \cos x \frac{d}{dx} \Psi + \Psi \frac{d}{dx} (\cos x) \\ &= \cos x \frac{d}{dx} \Psi - \Psi \sin x \end{aligned}$$

$$\text{or, } \left(\frac{d}{dx} \cos x \right) \Psi = \left(\cos x \frac{d}{dx} - \sin x \right) \Psi$$

$$\text{Hence } \left(\frac{d}{dx} \cos x \right) = \cos x \frac{d}{dx} - \sin x$$

Example 7.8 Obtain the expression for the eigen function of the momentum operator $\hat{p}_x = -i\hbar \frac{d}{dx}$ corresponding to an eigen value p_x .

Sol. The operator equation for calculation of the eigen function is given by

$$\hat{p}_x \Psi = p_x \Psi.$$

where Ψ is an wave function satisfying the corresponding Schrödinger's equation.

$$\therefore -i\hbar \frac{d}{dx} \Psi = p_x \Psi$$

$$\text{or, } -i\hbar \frac{d\Psi}{\Psi} = p_x dx$$

$$\text{or, } -i\hbar \int \frac{d\Psi}{dx} = p_x x + c \quad \text{where } c \text{ is the constant of integration}$$

$$\text{or, } \ln \Psi = -\frac{p_x x}{i\hbar} - \frac{c}{i\hbar}$$

$$\text{or, } \ln \Psi = -\frac{p_x}{i\hbar} x + \ln \alpha \quad \left[\text{where } \ln \alpha = -\frac{c}{i\hbar} \right]$$

$$\text{or, } \Psi = \alpha e^{(ip_x x)/\hbar}$$

This is the eigen function of \hat{p}_x .

Example 7.9 If $\hat{A} = \cos x$ and $\hat{B} = \frac{d}{dx}$, then show that \hat{A} and \hat{B} do not commute.

Sol. Let Ψ be a wave function.

$$\begin{aligned} \text{So, } [\hat{A}, \hat{B}] \Psi &= \left[\cos x, \frac{d}{dx} \right] \Psi \\ &= \left[\cos x \frac{d}{dx} - \frac{d}{dx} \cos x \right] \Psi \end{aligned}$$

$$\begin{aligned}
 &= \cos x \frac{d\Psi}{dx} - \frac{d}{dx}(\Psi \cos x) \\
 &= \cos x \frac{d\Psi}{dx} - \Psi \frac{d\cos x}{dx} - \cos x \frac{d\Psi}{dx} \\
 &= +\Psi \sin x
 \end{aligned}$$

(in general)

∴ $[\hat{A}, \hat{B}] = \sin x$
 ∴ $[\hat{A}, \hat{B}] \neq 0$ (in general)
 ∴ \hat{A} and \hat{B} do not commute.

Example 7.10 Prove that $[\hat{A}, \hat{B}] = -[\hat{B}, \hat{A}]$ where \hat{A} and \hat{B} are two operators.

Sol. Let Ψ be a wave function corresponding to both of the operators.

$$\therefore [\hat{A}, \hat{B}] \Psi = (\hat{A}\hat{B} - \hat{B}\hat{A}) \Psi = \hat{A}\hat{B} \Psi - \hat{B}\hat{A} \Psi \quad \dots(1)$$

$$\begin{aligned}
 \text{Again } [\hat{B}, \hat{A}] \Psi &= (\hat{B}\hat{A} - \hat{A}\hat{B}) \Psi = \hat{B}\hat{A} \Psi - \hat{A}\hat{B} \Psi \\
 &= -(\hat{A}\hat{B} - \hat{B}\hat{A}) \Psi \\
 &= -[\hat{A}, \hat{B}] \Psi \quad [\text{by Eq. (1)}]
 \end{aligned}$$

$$\text{Hence } [\hat{A}, \hat{B}] = -[\hat{B}, \hat{A}]$$

Example 7.11 If $[\hat{z}, \hat{p}_z] = i\hbar$, then prove that (a) $[\hat{L}_x, \hat{z}] = -i\hbar \hat{y}$ and (b) $[\hat{L}_x, \hat{p}_z] = -i\hbar \hat{p}_y$.

Sol. We know that $\hat{L}_x = \hat{y}\hat{p}_z - \hat{z}\hat{p}_y$

Now,

$$\begin{aligned}
 \text{(a) } [\hat{L}_x, \hat{z}] &= [\hat{y}\hat{p}_z - \hat{z}\hat{p}_y, \hat{z}] \\
 &= [\hat{y}\hat{p}_z, \hat{z}] - [\hat{z}\hat{p}_y, \hat{z}] \\
 &= \hat{y}\hat{p}_z \hat{z} - \hat{z}\hat{y}\hat{p}_z - \hat{z}\hat{p}_y \hat{z} + \hat{z}\hat{z}\hat{p}_y \\
 &= \hat{y}\hat{p}_z \hat{z} - \hat{y}\hat{z}\hat{p}_z + \hat{y}\hat{z}\hat{p}_z - \hat{z}\hat{y}\hat{p}_z - \hat{z}\hat{p}_y \hat{z} + \hat{z}\hat{z}\hat{p}_y \\
 &= \hat{y}(\hat{p}_z \hat{z} - \hat{z}\hat{p}_z) + (\hat{y}\hat{z} - \hat{z}\hat{y})\hat{p}_z - \hat{z}(\hat{p}_y \hat{z} - \hat{z}\hat{p}_y) \\
 &= \hat{y}[\hat{p}_z, \hat{z}] + [\hat{y}, \hat{z}]\hat{p}_z - \hat{z}[\hat{p}_y, \hat{z}] \\
 &= -\hat{y}[\hat{z}, \hat{p}_z] + 0 - 0 \\
 &= -i\hbar \hat{y}
 \end{aligned}$$

$$\begin{aligned}
 \text{(b) } \hat{L}_x &= \hat{y}\hat{p}_z - \hat{z}\hat{p}_y \\
 \therefore [\hat{L}_x, \hat{p}_z] &= [\hat{y}\hat{p}_z - \hat{z}\hat{p}_y, \hat{p}_z] \\
 &= [\hat{y}\hat{p}_z, \hat{p}_z] - [\hat{z}\hat{p}_y, \hat{p}_z] \\
 &= \hat{y}\hat{p}_z \hat{p}_z - \hat{p}_z \hat{y}\hat{p}_z - \hat{z}\hat{p}_y \hat{p}_z + \hat{p}_z \hat{z}\hat{p}_y \\
 &= (\hat{y}\hat{p}_z - \hat{p}_y)\hat{p}_z - \hat{z}\hat{p}_y \hat{p}_z + \hat{p}_z \hat{z}\hat{p}_y \\
 &= [\hat{y}, \hat{p}_z]\hat{p}_z - \hat{z}\hat{p}_y \hat{p}_z + \hat{z}\hat{p}_z \hat{p}_y - \hat{z}\hat{p}_z \hat{p}_y + \hat{p}_z \hat{z}\hat{p}_y
 \end{aligned}$$

$$\begin{aligned}
 \text{or, } [\hat{L}_x, \hat{p}_z] &= [\hat{y}, \hat{p}_z]\hat{p}_z - \hat{z}(\hat{p}_y \hat{p}_z - \hat{p}_z \hat{p}_y) - (\hat{z}\hat{p}_z - \hat{p}_z \hat{z})\hat{p}_y \\
 &= [\hat{y}, \hat{p}_z]\hat{p}_z - \hat{z}[\hat{p}_y, \hat{p}_z] - [\hat{z}, \hat{p}_z]\hat{p}_y \\
 &= 0 + 0 - [\hat{z}, \hat{p}_z]\hat{p}_y \\
 &= -(i\hbar)\hat{p}_y
 \end{aligned}$$

$$\therefore [\hat{L}_x, \hat{p}_z] = -i\hbar \hat{p}_y$$

Example 7.12 Show that (a) $[\hat{L}_x, \hat{x}] = 0$; (b) $[\hat{L}_x, \hat{p}_x] = 0$; (c) $[\hat{L}_x, \hat{L}_y] = -i\hbar \hat{L}_z$.

Sol. (a)

$$\hat{L}_x = \hat{y} \hat{p}_z - \hat{z} \hat{p}_y$$

Now

$$[\hat{L}_x, \hat{x}] = \hat{L}_x \hat{x} - \hat{x} \hat{L}_x$$

or,

$$[\hat{L}_x, \hat{x}] = (\hat{y} \hat{p}_z - \hat{z} \hat{p}_y) \hat{x} - \hat{x} (\hat{y} \hat{p}_z - \hat{z} \hat{p}_y)$$

or,

$$[\hat{L}_x, \hat{x}] = -i\hbar \left[\left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) x - x \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) \right]$$

Now,

$$[\hat{L}_x, \hat{x}] \Psi = -i\hbar \left[\left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) x - x \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) \right] \Psi$$

$$= -i\hbar \left[\left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) x \Psi - x \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) \Psi \right]$$

$$= -i\hbar \left[xy \frac{\partial}{\partial z} \Psi - zx \frac{\partial \Psi}{\partial y} - xy \frac{\partial \Psi}{\partial z} + zx \frac{\partial \Psi}{\partial y} \right]$$

$$= 0$$

or,

$$[\hat{L}_x, \hat{x}] \Psi = 0$$

Hence

$$[\hat{L}_x, \hat{x}] = 0.$$

(b)

$$\hat{L}_x = \hat{y} \hat{p}_z - \hat{z} \hat{p}_y$$

Now

$$[\hat{L}_x, \hat{p}_x] = \hat{L}_x \hat{p}_x - \hat{p}_x \hat{L}_x$$

or,

$$[\hat{L}_x, \hat{p}_x] = (\hat{y} \hat{p}_z - \hat{z} \hat{p}_y) \hat{p}_x - \hat{p}_x (\hat{y} \hat{p}_z - \hat{z} \hat{p}_y)$$

or,

$$[\hat{L}_x, \hat{p}_x] = -\hbar^2 \left[\left(y \frac{\partial^2}{\partial z \partial x} - z \frac{\partial^2}{\partial y \partial x} \right) - \frac{\partial}{\partial x} \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) \right]$$

Now

$$[\hat{L}_x, \hat{p}_x] \Psi = -\hbar^2 \left[\left(y \frac{\partial^2}{\partial z \partial x} - z \frac{\partial^2}{\partial y \partial x} \right) \Psi - \frac{\partial}{\partial x} \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) \Psi \right]$$

$$= -\hbar^2 \left[y \frac{d^2 \Psi}{\partial z \partial x} - z \frac{d^2 \Psi}{\partial y \partial x} - \frac{\partial}{\partial x} \left(y \frac{\partial \Psi}{\partial z} + z \frac{\partial \Psi}{\partial y} \right) \right]$$

$$= -\hbar^2 \left[y \frac{\partial^2 \Psi}{\partial z \partial x} - z \frac{\partial^2 \Psi}{\partial y \partial x} - y \frac{\partial^2 \Psi}{\partial x \partial z} + z \frac{\partial^2 \Psi}{\partial x \partial y} \right]$$

$$= 0$$

or,

$$[\hat{L}_x, \hat{p}_x] \Psi = 0$$

Hence

$$[\hat{L}_x, \hat{p}_x] = 0.$$

(c)

$$[\hat{L}_x, \hat{L}_y] \Psi = (\hat{L}_x \hat{L}_y - \hat{L}_y \hat{L}_x) \Psi$$

or,

$$[\hat{L}_x, \hat{L}_y] \Psi = (\hat{y} \hat{p}_z - \hat{z} \hat{p}_y) (\hat{z} \hat{p}_x - \hat{z} \hat{p}_z) \Psi - (\hat{z} \hat{p}_x - \hat{x} \hat{p}_z) (\hat{y} \hat{p}_z - \hat{z} \hat{p}_y) \Psi$$

or,

$$[\hat{L}_x, \hat{L}_y] \Psi = -\hbar^2 \left[\left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) \left(z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right) \Psi - \left(z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right) \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) \Psi \right]$$

or,

$$[\hat{L}_x, \hat{L}_y] \Psi = -\hbar^2 y \frac{\partial}{\partial z} \left(z \frac{\partial \Psi}{\partial x} - x \frac{\partial \Psi}{\partial z} \right) - z \frac{\partial}{\partial y} \left(z \frac{\partial \Psi}{\partial x} - x \frac{\partial \Psi}{\partial z} \right) \\ - z \frac{\partial}{\partial x} \left(y \frac{\partial \Psi}{\partial z} - z \frac{\partial \Psi}{\partial y} \right) + x \frac{\partial}{\partial z} \left(y \frac{\partial \Psi}{\partial z} - z \frac{\partial \Psi}{\partial y} \right)$$

or,

$$[\hat{L}_x, \hat{L}_y] \Psi = -\hbar^2 y \frac{\partial \Psi}{\partial x} + yz \frac{\partial^2 \Psi}{\partial z \partial x} - 0 - xy \frac{\partial^2 \Psi}{\partial z^2} - 0 - z^2 \frac{\partial^2 \Psi}{\partial y \partial x} + 0 + zx \frac{\partial^2 \Psi}{\partial y \partial z} - 0 \\ - yz \frac{\partial^2 \Psi}{\partial x \partial z} + 0 + z^2 \frac{\partial^2 \Psi}{\partial x \partial y} + 0 + xy \frac{\partial^2 \Psi}{\partial z^2} - x \frac{\partial \Psi}{\partial y} - zx \frac{\partial^2 \Psi}{\partial y \partial z}$$

or,

$$[\hat{L}_x, \hat{L}_y] \Psi = -\hbar^2 \left[y \frac{\partial \Psi}{\partial x} - x \frac{\partial \Psi}{\partial y} \right]$$

or,

$$[\hat{L}_x, \hat{L}_y] \Psi = (-i\hbar) \left[y(-i\hbar) \frac{\partial \Psi}{\partial x} - x(-i\hbar) \frac{\partial \Psi}{\partial y} \right]$$

or,

$$[\hat{L}_x, \hat{L}_y] \Psi = (-i\hbar) [\hat{y}\hat{p}_x - \hat{x}\hat{p}_y]$$

or,

$$[\hat{L}_x, \hat{L}_y] \Psi = -i\hbar \hat{L}_z \quad [:\hat{L}_z = yp_x - xp_y] \quad \Psi = \Psi \begin{bmatrix} 0 & 1 \\ 0 & 0 \end{bmatrix}$$

Example 7.13

Evaluate the following operators which are combinations of \hat{x} and $\frac{\partial}{\partial x}$, or $\frac{\partial}{\partial t}$ and t :

(a) $\left[\hat{x}, \frac{\partial}{\partial x} \right]$

(b) $\left[(\hat{x})^2, \frac{\partial^2}{\partial x^2} \right]$

(c) $\left[(\hat{x})^3, \frac{\partial^2}{\partial x^2} \right]$

(d) $\left[t, \frac{\partial}{\partial t} \right]$

Sol. (a) $\left[\hat{x}, \frac{\partial}{\partial x} \right] \Psi = \left(\hat{x} \frac{\partial}{\partial x} - \frac{\partial}{\partial x} \hat{x} \right) \Psi = x \frac{\partial \Psi}{\partial x} - \frac{\partial}{\partial x} (x\Psi) = x \frac{\partial \Psi}{\partial x} - x \frac{\partial \Psi}{\partial x} - \Psi = -\Psi$

or, $\left[\hat{x}, \frac{\partial}{\partial x} \right] \Psi = -\Psi = (-1)\Psi$

or, $\left[\hat{x}, \frac{\partial}{\partial x} \right] \Psi = \hat{u}_n \Psi$, where $u_n = -1$

$\therefore \left[\hat{x}, \frac{\partial}{\partial x} \right] = \hat{u}_n$ (= unit negative operator)

(b) $\left[\hat{x}, \frac{\partial^2}{\partial x^2} \right] \Psi = \left(\hat{x} \frac{\partial^2}{\partial x^2} - \frac{\partial^2}{\partial x^2} \hat{x} \right) \Psi$

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

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

$$= 0$$

$\therefore \left[\hat{x}, \frac{\partial^2}{\partial x^2} \right] = 0$

$$(c) \quad \left[(\hat{x})^3, \frac{\partial^2}{\partial x^2} \right] \Psi = \left\{ (\hat{x})^3 \frac{\partial^2}{\partial x^2} - \frac{\partial^2}{\partial x^2} (\hat{x})^3 \right\} \Psi \\ = x^3 \frac{\partial^2}{\partial x^2} \Psi - \frac{\partial^2}{\partial x^2} (x^3 \Psi) \\ = x^3 \frac{\partial^2}{\partial x^2} \Psi - x^3 \frac{\partial^2 \Psi}{\partial x^2} - \Psi \frac{\partial^2}{\partial x^2} (x^3) \\ = -6x \Psi$$

$$\therefore \quad \left[(\hat{x})^3, \frac{\partial^2}{\partial x^2} \right] = -6\hat{x}$$

$$(d) \quad \left[t, \frac{\partial}{\partial t} \right] \Psi = \left(t \frac{\partial}{\partial t} - \frac{\partial}{\partial t} t \right) \Psi \\ = t \frac{\partial \Psi}{\partial t} - t \frac{\partial \Psi}{\partial t} - \Psi$$

$$\text{or,} \quad \left[t, \frac{\partial}{\partial t} \right] \Psi = -\Psi = \hat{u}_n \Psi$$

where $u_n = -1$ and \hat{u}_n is unit negative operator

$$\therefore \quad \left[t, \frac{\partial}{\partial t} \right] = \hat{u}$$

Eigen Functions and Eigen Values

By the principle of eigen values and eigen functions, we get $\hat{\alpha} \Psi = \alpha \Psi$ where $\hat{\alpha}$ is the operator and α is its numerical eigen value.

Example 7.14 Find the eigen function and eigen value of the momentum operator.

Sol. The momentum operator is given by

$$\hat{p}_x = -i\hbar \frac{\partial}{\partial x}$$

Let p_x be the eigen value of \hat{p}_x .

$$\therefore \quad -i\hbar \frac{\partial}{\partial x} \Psi = p_x \Psi(x)$$

$$\text{or,} \quad -i\hbar \frac{d\Psi(x)}{\Psi(x)} = p_x dx \quad [\text{Since there is no mention of other independent variables}]$$

$$\text{or,} \quad -i\hbar \int \frac{d\Psi(x)}{\Psi(x)} = p_x \int dx$$

$$\text{or,} \quad -i\hbar \ln \Psi(x) = p_x x + c_1, \quad \text{where } c_1 \text{ is the constant of integration}$$

$$\text{or,} \quad \ln \Psi(x) = \frac{i}{\hbar} p_x x + \frac{i}{\hbar} c_1$$

$$\text{or,} \quad \ln \Psi(x) = \frac{i}{\hbar} p_x x + c_2 \quad \text{where } c_2 = \frac{i}{\hbar} c_1$$

or, $\Psi(x) = ce \left(\frac{ip_x x}{\hbar} \right)$ where $c_2 = \ln c$

which is the required eigen function.

The eigen value p_x can be any number. On putting the boundary conditions such that $\Psi(x)$ be a periodic function in some distance L (periodic potential).

$$e^{(ip_x x/\hbar)} = e^{ip_x (x+L)/\hbar}$$

Putting $x = 0$, we get

$$1 = e^{ip_x L/\hbar}$$

or, $1 = \cos \left(\frac{p_x L}{\hbar} \right) + i \sin \left(\frac{p_x L}{\hbar} \right)$

or, $\cos \left(\frac{p_x L}{\hbar} \right) + i \sin \left(\frac{p_x L}{\hbar} \right) = 1 + i 0$

Hence $\cos \left(\frac{p_x L}{\hbar} \right) = 1$

or, $\cos \left(\frac{p_x L}{\hbar} \right) = \cos (2n \pi)$

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

or, $p_x = \frac{2n\pi\hbar}{L}$

The eigen function is now given by

$$\Psi(x) = ce^{(ip_x x/\hbar)} = ce^{i(2\pi n x/L)}$$

So, the eigen functions are discrete and real.

Example 7.15 Show that the function $\Psi(x) = cx e^{-\frac{1}{2}x^2}$ is an eigen function of the operator $\left(x^2 - \frac{d^2}{dx^2} \right)$. Find the eigen value.

Sol. By the definition of eigen function and eigen value, one gets

$$\hat{\alpha} \Psi(x) = \alpha \Psi(x)$$

where α is eigen value of $\hat{\alpha}$,

i.e., the operator returns the same function multiplied by the eigen value.

$$\begin{aligned} \text{Now, } & \left(x^2 - \frac{d^2}{dx^2} \right) \left\{ cx e^{-\frac{1}{2}x^2} \right\} \\ &= cx^3 e^{-\frac{1}{2}x^2} - c \frac{d^2}{dx^2} \left\{ xe^{-\frac{1}{2}x^2} \right\} \\ &= cx^3 e^{-\frac{1}{2}x^2} - c \frac{d}{dx} \left\{ e^{-\frac{1}{2}x^2} - x^2 e^{-\frac{1}{2}x^2} \right\} \\ &= cx^3 e^{-\frac{1}{2}x^2} + cx e^{-\frac{1}{2}x^2} + 2 cx e^{-\frac{1}{2}x^2} - cx^3 e^{-\frac{1}{2}x^2} \\ &= 3 cx e^{-\frac{1}{2}x^2} \\ &= (3) \Psi(x) \quad \text{where } \Psi(x) = cx e^{-\frac{1}{2}x^2} \end{aligned}$$

$$\text{or, } \left(x^2 - \frac{d^2}{dx^2} \right) \Psi(x) = (3) \Psi(x)$$

\therefore the eigen value of the eigen function $\Psi(x) = cx e^{-\frac{1}{2}x^2}$ is 3.

Hence, $cx e^{-\frac{1}{2}x^2}$ is an eigen function of the operator $\left(x^2 - \frac{d^2}{dx^2} \right)$.

Expected Averages

Example 7.16 The wave function of a particle in a one-dimensional box of length L is given by

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

Find the expected average or expectation value of x and x^2 .

Sol. The expected average of x is given by

$$\langle x \rangle = \int_0^L \Psi_n^*(x) \hat{x} \Psi_n(x) dx$$

$$\text{or, } \langle x \rangle = \frac{2}{L} \int_0^L x \sin^2 \frac{n\pi x}{L} dx$$

$$\text{or, } \langle x \rangle = \frac{L}{2}$$

The expected average of x^2 is given by

$$\langle x^2 \rangle = \int_0^L \Psi_n^*(x) (\hat{x})^2 \Psi_n(x) dx$$

$$\text{or, } \langle x^2 \rangle = \frac{2}{L} \int_0^L x^2 \sin^2 \frac{n\pi x}{L} dx$$

$$= \frac{L^2}{3} - \frac{L^2}{2x^2\pi^2}$$

$$\therefore \langle x^2 \rangle = L^2 \left(\frac{1}{3} - \frac{1}{2x^2\pi^2} \right)$$

Example 7.17 $\Psi(x) = \left[\frac{2(1+\alpha^2)}{\alpha^2} \right]^{\frac{1}{2}} e^{-|x|} \sin \alpha x$ is the wave function for a particle. Calculate the expected

average of position x and square of the momentum p_x .

Sol. We have,

$$\Psi(x) = \left[\frac{2(1+\alpha^2)}{\alpha^2} \right]^{\frac{1}{2}} e^x \sin \alpha x, \quad \text{for } x < 0$$

$$\text{and } \Psi(x) = \left[\frac{2(1+\alpha^2)}{\alpha^2} \right]^{\frac{1}{2}} e^{-x} \sin \alpha x, \quad \text{for } x > 0$$

Now $\langle x \rangle = \int_{-\infty}^{+\infty} \Psi^*(x) \hat{x} \Psi(x) dx$

or, $\langle x \rangle = \frac{2(1+\alpha^2)}{\alpha^2} \left[\int_{-\infty}^0 x e^{2x} \sin^2 \alpha x dx + \int_0^{+\infty} x e^{-2x} \sin^2 \alpha x dx \right] = 0$

$\therefore \langle x \rangle = 0$

Also, $\langle (p_x)^2 \rangle = -\hbar^2 \int_{-\infty}^{+\infty} \Psi^*(x) \frac{d^2}{dx^2} \Psi(x) dx$

or, $\langle (p_x)^2 \rangle = -\hbar^2 \left[\int_{-\infty}^0 e^x \sin \alpha x \frac{d^2}{dx^2} (e^x \sin \alpha x) dx + \int_0^{+\infty} e^{-x} \sin \alpha x \frac{d^2}{dx^2} (e^{-x} \sin \alpha x) dx \right]$

$\therefore \langle (p_x)^2 \rangle = \hbar^2(1 + \alpha^2)$

Example 7.18 For the one-dimensional motion of a particle with normalized wave function is $\Psi_n = A \sin \alpha x$. Calculate the expected average of the kinetic energy for this particle which is confined in a region between $x = 0$ and $x = 10$.

Sol. The kinetic energy operator is given by

$$\hat{E}_k = \frac{\hat{p}_x^2}{2m} = \frac{1}{2m} \left(-i\hbar \frac{d}{dx} \right) \left(-i\hbar \frac{d}{dx} \right)$$

or, $\hat{E}_k = \frac{-\hbar^2}{2m} \frac{d^2}{dx^2}$

\therefore the expected average of the kinetic energy is

$$\langle E_k \rangle = \int_0^{10} \Psi_n^* \hat{E}_k \Psi_n dx$$

or, $\langle E_k \rangle = \frac{-A^2 \hbar^2}{2m} \int_0^{10} \sin \alpha x \frac{d^2}{dx^2} (\sin \alpha x) dx$

or, $\langle E_k \rangle = \frac{\alpha^2 A^2 \hbar^2}{2m} \int_0^{10} \sin^2 \alpha x dx$

or, $\langle E_k \rangle = \frac{\alpha^2 A^2 \hbar^2}{2m} \int_0^{10} \frac{1 - \cos 2\alpha x}{2} dx$

or, $\langle E_k \rangle = \frac{\alpha^2 A^2 \hbar^2}{4m} \left[x - \frac{\sin 2\alpha x}{2\alpha} \right]_0^{10}$

$\therefore \langle E_k \rangle = \frac{\alpha^2 A^2 \hbar^2}{4m} \left[10 - \frac{\sin 20\alpha}{2\alpha} \right]$

Miscellaneous Problems

Example 7.19 Compute the lowest energy of a neutron confined to the nucleus of an atom where the nucleus is considered a box with size of 10^{-14} m. ($\hbar = 6.26 \times 10^{-34}$ Js, $m = 1.6 \times 10^{-24}$ g).

Sol. Consider the nucleus as a cubical box of size 10^{-14} m.

$$\therefore x = y = z = 10^{-14} \text{ m} = 1 \text{ (say)}$$

For the neutron to be in the lowest energy state $n_x = n_y = n_z = 1$

$$\text{Now, } E = \frac{\pi^2 \hbar^2}{2m} \left[\frac{n_x^2}{l_x^2} + \frac{n_y^2}{l_y^2} + \frac{n_z^2}{l_z^2} \right] \quad [\because l_x = l_y = l_z = 1]$$

$$\text{or, } E = \frac{\pi^2 \hbar^2}{2m} \left[\frac{3}{l^2} \right]$$

$$\text{or, } E = \frac{3\hbar^2}{8ml^2} = \frac{3 \times (6.62 \times 10^{-34})^2}{8 \times 1.6 \times 10^{-27} \times 10^{-28}}$$

$$\therefore E = 10.29 \times 10^{-23} \text{ J} = 6.43 \text{ MeV}$$

Example 7.20 Show that $\Psi = \phi e^{-iwt}$ is a wave function of a stationary state.

Sol. For Ψ to be the wave function of a stationary state, the value of $|\Psi|^2$ at each point in space must be constant, i.e., independent of time.

$$\text{Now, } |\Psi|^2 = \Psi^* \Psi = (\phi e^{-iwt})^* (\phi e^{-iwt})$$

$$\text{or, } |\Psi|^2 = (\phi^*) (\phi) e^{iwt} e^{-iwt}$$

$$\text{or, } |\Psi|^2 = |\phi|^2 e^0 = |\phi|^2$$

where $|\phi|^2$ is not a function of time, so, $|\Psi|^2$ is also independent of time. Hence, $\Psi = \phi e^{-iwt}$ is a wave function of stationary state.

Example 7.21 Find the probability that a particle trapped in a box of size L (units) can be found between $0.45 L$ and $0.55 L$ for the ground and the first excited states.

Sol. The part between $0.45 L$ and $0.55 L$ of the box is one-tenth of the size of the box and is centered on the middle of the box. Classically, we could expect the particle to be in this region 10 per cent of the time. The quantum mechanics gives quite different predictions that depend on the quantum number of the particles state. The probability of finding the particle between x_1 and x_2 when it is in the n^{th} state is given by,

$$P = \int_{x_1}^{x_2} |\Psi_n|^2 dx = \frac{2}{L} \int_{x_1}^{x_2} \sin^2 \frac{n\pi x}{L} dx$$

$$\text{or, } P = \left[\frac{x}{L} - \frac{1}{2n\pi} \sin \left(\frac{2n\pi x}{L} \right) \right]_{x_1}^{x_2}$$

For the ground state $n = 1$

$$\therefore \text{we have } P = 0.198 = 19.8\%$$

For the 1st excited state $n = 2$

$$\therefore P = 0.0065 = 0.65\%$$

The low figure is consistent with the probability density $|\Psi_n|^2 = 0$ at $x = L$.

Example 7.22

A system has two energy eigen states ϵ_0 and $3\epsilon_0$. Ψ_1 and Ψ_2 are the corresponding normalized wave functions. At an instant the system is in a superposed state $\Psi = c_1 \Psi_1 + c_2 \Psi_2$ and $c_1 = \frac{1}{\sqrt{2}}$.

- Find the value of c_2 if Ψ is normalized.
- What is the probability that an energy measurement would yield a value of $3\epsilon_0$?
- Find out the expectation value of the energy. [WBUT 2007]

Sol.

$$(i) \int_{-\infty}^{+\infty} \Psi^*(x) \Psi(x) dx = 1$$

$$\text{or, } \int_{-\infty}^{+\infty} (c_1 \Psi_1 + c_2 \Psi_2)^* (c_1 \Psi_1 + c_2 \Psi_2) dx = 1$$

$$\text{or, } \int_{-\infty}^{+\infty} c_1^* c_1 \Psi_1^* \Psi_1 dx + \int_{-\infty}^{+\infty} c_2^* c_2 \Psi_2^* \Psi_2 dx + \int_{-\infty}^{+\infty} (c_1^* c_2 \Psi_1^* \Psi_2 + c_1 c_2^* \Psi_1^* \Psi_2) dx = 1$$

$$\text{or, } \int_{-\infty}^{+\infty} |c_1|^2 \Psi_1^* \Psi_1 dx + \int_{-\infty}^{+\infty} |c_2|^2 \Psi_2^* \Psi_2 dx + 0 = 1$$

$$\text{or, } c_1^2 + c_2^2 = 1$$

$$\text{or, } \frac{1}{2} + c_2^2 = 1$$

$$\text{or, } c_2^2 = \frac{1}{2}, \quad \text{Hence } c_2 = \frac{1}{\sqrt{2}}$$

- The probability of finding the energy $3\epsilon_0$ is given by

$$c_2^* c_2 = \frac{1}{\sqrt{2}} \cdot \frac{1}{\sqrt{2}} = \frac{1}{2}$$

$$\begin{aligned} (iii) \int_{-\infty}^{+\infty} (c_1 \Psi_1 + c_2 \Psi_2)^* \hat{H}(c_1 \Psi_1 + c_2 \Psi_2) dx \\ &= \int_{-\infty}^{+\infty} (c_1^* \Psi_1^* + c_2^* \Psi_2^*) (c_1 \hat{H} \Psi_1 + c_2 \hat{H} \Psi_2) dx \\ &= \int_{-\infty}^{+\infty} (c_1^* \Psi_1^* + c_2^* \Psi_2^*) (\epsilon_0 c_1 \Psi_1 + 3\epsilon_0 c_2 \Psi_2) dx \\ &= \int_{-\infty}^{+\infty} (\epsilon_0 c_1^* c_1 \Psi_1^* \Psi_1 + \epsilon_0 c_2^* c_1 \Psi_2^* \Psi_1 + 3\epsilon_0 c_1^* c_2 \Psi_1^* \Psi_2 + 3\epsilon_0 c_2^* c_2 \Psi_2^* \Psi_2) dx \\ &= \int_{-\infty}^{+\infty} (\epsilon_0 c_1^2 \Psi_1^* \Psi_1) + 0 + 0 + 3\epsilon_0 c_2^2 \Psi_2^* \Psi_2 dx \\ &= \epsilon_0 \int_{-\infty}^{+\infty} |c_1 \Psi_1|^2 dx + 3\epsilon_0 \int_{-\infty}^{+\infty} |c_2 \Psi_2|^2 dx \\ &= \epsilon_0 c_1^2 + 3\epsilon_0 c_2^2 \quad [\because \Psi_1 \text{ and } \Psi_2 \text{ are normalized}] \end{aligned}$$

$$= \epsilon_0 \cdot \frac{1}{2} + 3\epsilon_0 \cdot \frac{1}{2}$$

$$= 2\epsilon_0$$

Example 7.23 A particle of mass m is confined within the range between $x = 0$ and $x = L$.

- (i) Write down Schrödinger's equation for the particle.
- (ii) Solve the equation to find out the normalized eigen functions.
- (iii) Show that the eigen functions corresponding to two different eigen values are orthogonal.
- (iv) If p_x be the momentum, then find $\langle p_x \rangle$ as well as $\langle p_x^2 \rangle$ in the ground state. [WBUT 2008]

Sol. (i) As the particle is confined in the range between $x = 0$ and $x = L$, it may be in a deep potential well or in any potential dependent on x . In the first case $V = \text{constant}$ and in the second case $V = V(x)$. So, Schrödinger's time-independent equation for the particle is given by

$$\frac{d^2}{dx^2} \Psi(x) + \frac{2m}{\hbar^2} [E - V(x)] \Psi(x) = 0$$

- (ii) If the particle be in deep potential well, then $V = \text{constant}$ and let $V = 0$.

So, the wave equation becomes

$$\frac{d^2}{dx^2} \Psi(x) + \frac{2mE}{\hbar^2} \Psi(x) = 0$$

or,
$$\frac{d^2 \Psi(x)}{dx^2} + k^2 \Psi(x) = 0 \quad \text{where } k^2 = \frac{2mE}{\hbar^2}$$

The general solution of the equation is given by

$$\Psi(x) = A \sin(kx) + B \cos(kx)$$

Now, the boundary conditions are

at $x = 0, \Psi(x) = 0$ and

at $x = L, \Psi(x) = 0$

\therefore when $x = 0$, we get $B = 0$

So, the equation becomes

$$\Psi(x) = A \sin(kx)$$

Again, at $x = L, \Psi(x) = 0$, so we get

$$\Psi(L) = A \sin(kL)$$

or, $A \sin(kL) = 0$ or, $\sin(kL) = \sin n\pi$

or, $kL = n\pi$

$\therefore k = \frac{n\pi}{L}$ where $n = 1, 2, 3, \dots$

Hence the permissible wave function is given by

$$\Psi(x) = A \sin\left(\frac{n\pi x}{L}\right)$$

Let $\Psi_n(x)$ be the normalized wave function

$$\therefore \Psi_n(x) = \frac{1}{N} \Psi(x) \quad \text{where } N \text{ is the norm.}$$

Now $\int_{-\infty}^{+\infty} \Psi_n^*(x) \Psi_n(x) dx = 1$

or, $\frac{1}{N^2} \int_{-\infty}^{+\infty} \Psi^*(x) \Psi(x) dx = 1$

or, $\int_0^L A^2 \sin^2 \left(\frac{n\pi x}{L} \right) dx = N^2$

or, $\int_0^L \sin^2 \left(\frac{n\pi x}{L} \right) dx = \frac{N^2}{A^2}$

or, $\frac{1}{2} \int_0^L \left(1 - \cos \left(\frac{2n\pi x}{L} \right) \right) dx = \frac{N^2}{A^2}$

or, $[x]_0^L - \int_0^L \cos \left(\frac{2n\pi x}{L} \right) dx = \frac{2N^2}{A^2}$

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

or, $L - \frac{L}{2n\pi} \sin (2n\pi) = \frac{2N^2}{A^2}$

or, $L - 0 = \frac{2N^2}{A^2}$

$\therefore L = \frac{2N^2}{A^2}$

$$2N^2 = A^2 L \Rightarrow N = \sqrt{\frac{L}{2}} A$$

$\therefore \Psi_n(x) = \sqrt{\frac{2}{L}} \cdot \frac{1}{A} \sin \left(\frac{n\pi x}{L} \right)$

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

(iii) Let us consider two eigen functions $\Psi_n(x)$ and $\Psi_m(x)$ where $m \neq n$

Let $I = \int_{-\infty}^{+\infty} \Psi_m^*(x) \Psi_n(x) dx$

or, $I = \int_{-\infty}^{+\infty} \frac{2}{L} \sin \left(\frac{m\pi x}{L} \right) \sin \left(\frac{n\pi x}{L} \right) dx$

$$= \frac{1}{L} \int_0^L \left[\cos \frac{\pi}{L} (m-n)x - \cos \frac{\pi}{L} (m+n)x \right] dx$$

$$= \frac{1}{L} \left[\frac{L}{(m-n)\pi} \sin \frac{\pi}{L} (m-n)x - \frac{L}{(m+n)\pi} \sin \frac{\pi}{L} (m+n)x \right]_0^L$$

$$= \frac{1}{L} \times \frac{L}{\pi} [0 + 0 + 0 + 0]$$

or,

$$I = \int_{-\infty}^{+\infty} \Psi_m^*(x) \Psi_n(x) dx = 0$$

Hence $\Psi_m(x)$ and $\Psi_n(x)$ are orthogonal.

- (iv) The ground-state wave function is $\Psi_1(x)$.

$$\therefore \quad \Psi_1(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{\pi x}{L}\right)$$

$$\langle p_x \rangle = \int_{-\infty}^{+\infty} \Psi_1^*(x) \hat{p}_x \Psi_1(x) dx$$

or,

$$\begin{aligned} \langle p_x \rangle &= \frac{2}{L} \int_0^L \sin\left(\frac{\pi x}{L}\right) \left(-i\hbar \frac{\partial}{\partial x}\right) \sin\left(\frac{\pi x}{L}\right) dx \\ &= \left(\frac{2}{L}\right) (-i\hbar) \left(\frac{\pi}{2}\right) \int_0^L \sin\left(\frac{\pi x}{L}\right) \cos\left(\frac{\pi x}{L}\right) dx \\ &= -\frac{i\hbar\pi}{2L} \int_0^L \left(\sin\left(\frac{2\pi x}{L}\right)\right) dx \\ &= -\frac{i\hbar\pi}{2L} \left[-\frac{L}{2\pi} \cos\left(\frac{2\pi x}{L}\right)\right]_0^L \\ &= \frac{i\hbar}{4} (1 - 1) = 0 \end{aligned}$$

$$\langle p_x \rangle = 0$$

$$\begin{aligned} \langle p_x^2 \rangle &= \int_0^L \Psi_1(x) \hat{p}_x^2 \Psi_1(x) dx \\ &= \frac{2}{L} \int_0^L \sin\left(\frac{\pi x}{L}\right) \left(-\hbar^2 \frac{\partial^2}{\partial x^2}\right) \sin\left(\frac{\pi x}{L}\right) dx \\ &= \frac{2\hbar^2}{L} \int_0^L \left(\frac{\pi}{L}\right)^2 \sin^2\left(\frac{\pi x}{L}\right) dx \\ &= \frac{2\hbar^2 \pi^2}{L^3} \int_0^L \sin^2\left(\frac{\pi x}{L}\right) dx \\ &= \frac{\hbar^2 \pi^2}{L^3} \int_0^L \left[1 - \cos\left(\frac{2\pi x}{L}\right)\right] dx \\ &= \frac{\hbar^2 \pi^2}{L^3} \times L + \frac{\hbar^2 \pi^2}{L^3} \int_0^L \cos\left(\frac{2\pi x}{L}\right) dx \end{aligned}$$

$$\begin{aligned}
 &= \frac{\hbar^2 \pi^2}{L^2} + \frac{\hbar^2 \pi^2}{L^3} \times \frac{L}{2\pi} \left[\sin \left(\frac{2\pi x}{L} \right) \right]_0^L \\
 <p_x^2> &= \frac{\hbar^2 \pi^2}{L^2} \\
 <p_x^2> &= \frac{\hbar^2}{4L^2}
 \end{aligned}$$

Example 7.24 Show that $[x^n, \hat{p}_n] = +i\hbar nx^{n-1}$, n being a positive integer.

Sol. Let Ψ be the state function.

$$\begin{aligned}
 \hat{p}_x x^n \Psi(x) &= (-i\hbar) \frac{\partial}{\partial x} (x^n \Psi(x)) \\
 &= (-i\hbar) nx^{n-1} \Psi + (-i\hbar) x^n \frac{\partial \Psi}{\partial x} \\
 &= \left\{ -i\hbar \frac{\partial}{\partial x} (x^n) \right\} \Psi + x^n \left(-i\hbar \frac{\partial}{\partial x} \Psi \right) \\
 &= -\hat{p}_x x^n \Psi + x^n \hat{p}_x \Psi + 2 \hat{p}_n x^n \Psi
 \end{aligned}$$

or, $\hat{p}_x x^n \Psi = [x_n, \hat{p}_n] \Psi + 2 \hat{p}_n x^n \Psi$

or, $[x^n, \hat{p}_x] \Psi = -\hat{p}_x x^n \Psi$

or, $[x^n, \hat{p}_x] \Psi = -\left(-i\hbar \frac{\partial}{\partial x} x^n \right) \Psi$

or, $[x_n, \hat{p}_n] = (i\hbar nx^{n-1}) \Psi$

∴ $[x^n, \hat{p}_x] = i\hbar nx^{n-1}$

Example 7.25 Show that the eigen value of a hermitian operator is real.

Sol. An operator \hat{A} is hermitian if it satisfies the condition,

$$\int \Psi_1^* (\hat{A} \Psi_2) dV = \int (\hat{A} \Psi_1)^* \Psi_2 dV$$

where Ψ_1^* is the complex conjugate of Ψ_1 . Ψ_1 and Ψ_2 are two eigen functions of the operator \hat{A} . A hermitian operator is linear and has real eigen value.

Now $\hat{A} \Psi = \lambda \Psi$

$$\hat{A}^* \Psi^* = \lambda^* \Psi^*$$

$$\therefore \int \Psi^* \hat{A} \Psi dx = \int \Psi^* \lambda \Psi dx = \lambda \int \Psi^* \Psi dx$$

$$\text{and } \int \Psi \hat{A}^* \Psi^* dx = \int \Psi \lambda^* \Psi^* dx = \lambda^* \int \Psi \Psi^* dx$$

$$\therefore \lambda \int \Psi^* \Psi dx = \lambda^* \int \Psi \Psi^* dx \quad [\because \hat{A} \text{ is hermitian}]$$

or, $\lambda = \lambda^*$

∴ λ is real, i.e., if the eigen value of a hermitian operator is real.

Review Exercises**Part 1: Multiple Choice Questions**

1. The probability of finding a particle in a distance dx around the point x is given by
 - (a) Ψ^*
 - (b) $\Psi^* \Psi dx$
 - (c) $\Psi \Psi^*$
 - (d) Ψ
2. For a stationary state, the probability density is
 - (a) function of time
 - (b) dependent on wave function
 - (c) independent of time
 - (d) independent of space coordinates
3. Schrödinger's wave equation for a moving particle contains
 - (a) second-order time derivative
 - (b) first-order time derivative
 - (c) third-order time derivative
 - (d) None of above
4. A free particle has
 - (a) definite momentum but indefinite energy
 - (b) definite energy and indefinite momentum
 - (c) definite energy and definite momentum
 - (d) energy and momentum both indefinite
5. The energy, which a particle moving in a one-dimensional box can have, is
 - (a) directly proportional to the quantum number
 - (b) inversely proportional to the quantum number
 - (c) directly proportional to the square of the quantum number
 - (d) inversely proportional to the square of the quantum number
6. For a particle trapped in a box of length l , the value of the expected average is
 - (a) $\frac{1}{l}$
 - (b) $\frac{2}{l}$
 - (c) $\frac{l}{2}$
 - (d) None of these
7. The expected average of the momentum of a particle trapped in a box of length l is
 - (a) $\frac{h}{l}$
 - (b) $\frac{h}{2l}$
 - (c) 1
 - (d) 0
8. A particle is freely moving inside a box. Which of the following is incorrect for the energy of the particle?
 - (a) The energy is directly proportional to the square of the quantum number n .
 - (b) The energy is inversely proportional to the length of the box l .
 - (c) The energy is inversely proportional to the mass of the particle.
 - (d) The energy is directly proportional to the potential of the box.
9. Which of the following functions is an eigen function of the operator $\frac{d^2}{dx^2}$?
 - (a) $\Psi = c \ln x$
 - (b) $\Psi = cx^2$
 - (c) $\Psi = \frac{c}{x}$
 - (d) $\Psi = ce^{-mx}$

10. The ground-state energy of a particle moving in a one-dimensional potential box is given in terms of length l of the box by

(a) $\frac{2\hbar^2}{8ml^2}$

(b) $\frac{\hbar^2}{8ml^2}$

(c) $\frac{\hbar}{8ml^2}$

(d) zero

11. Which one of the following is not an acceptable wave function of a quantum particle?

(a) $\Psi = e^x$

(b) $\Psi = e^{-x}$

(c) $\Psi = x^n$

(d) $\Psi = \sin x$

12. The wave function of motion of a particle in a one-dimensional box of length l is given by $\Psi_n = \frac{A \sin n\pi x}{L}$ where A is the norm for a wave function. The value of A is

(a) $\sqrt{\frac{1}{L}}$

(b) $\sqrt{\frac{2}{L}}$

(c) $\frac{1}{L}$

(d) $\frac{2}{L}$

13. The spacing between the n^{th} energy state and the next energy state in a one-dimensional potential box increases by

(a) $(2n - 1)$

(b) $(2n + 1)$

(c) $(n - 1)$

(d) $(n + 1)$

14. If E_1 be the energy of the ground state of a one-dimensional potential box of length l and E_2 be the energy of the ground state when the length of the box is halved, then

(a) $E_2 = 2E_1$

(b) $E_2 = E_1$

(c) $E_2 = 4E_1$

(d) $E_2 = 3E_1$

15. The energy of a particle which is confined in a cubic box of side l is given by

$$E = \frac{\hbar^2}{8ml^2} (n_x^2 + n_y^2 + n_z^2)$$
 If n_x, n_y, n_z may have either of the three values $-1, 2$, and 3 , then the degree of degeneracy of this energy level is given by

(a) 3

(b) 6

(c) 2

(d) 4

16. The normalized wave function for a particle in a rectangular box of dimensions a, b, c is given by

(a) $\Psi_n = \sqrt{\frac{abc}{2}} \sin \frac{n_x \pi x}{a} \sin \frac{n_y \pi x}{b} \sin \frac{n_z \pi z}{c}$

(b) $\Psi_n = \sqrt{\frac{2}{abc}} \sin \frac{n_x \pi x}{a} \sin \frac{n_y \pi x}{b} \sin \frac{n_z \pi x}{c}$

(c) $\Psi_n = \sqrt{\frac{1}{abc}} \sin \frac{n_x \pi x}{a} \sin \frac{n_y \pi x}{b} \sin \frac{n_z \pi x}{c}$

(d) $\Psi_n = \sqrt{\frac{8}{abc}} \sin \frac{n_x \pi x}{a} \sin \frac{n_y \pi x}{b} \sin \frac{n_z \pi x}{c}$

17. The waves representing a free particle in three dimensions are

(a) standing waves (b) progressive waves (c) transverse waves (d) polarized waves

18. If the quantum numbers n_x, n_y and n_z are each equal to zero for a particle trapped in a rectangular potential well, then the particle

(a) may be absent from the well (b) may be present in the well

(c) may or may not be present in the well (d) None of these

19. Schrödinger's time-independent wave equation is

(a) $\hat{H} \Psi = E \Psi^2$ (b) $\hat{H} \Psi^2 = E \Psi$ (c) $\hat{H} \Psi^3 = E \Psi^2$ (d) $\hat{H} \Psi = E \Psi$

20. For the function $e^{\beta x}$, the eigen value of the operator $\frac{d}{dx}$ is given by

(a) β

(b) β^2

(c) $\frac{\beta^2}{2}$

(d) $\frac{\beta}{2}$

21. Which of the following is a linear operator?
 (a) $\log()$ (b) $\sqrt{\quad}$ (c) $\frac{d}{dx}$ (d) $\exp()$
22. The expected average of momentum of a particle in an infinite well is
 (a) \hbar (b) $\frac{\hbar}{2}$ (c) $k\hbar$ (d) 0
23. The wave functions $\Psi_m(x)$ and $\Psi_n(x)$ are orthogonal to each other. Which of the following relations must hold for them?
 (a) $\int_{-\infty}^{+\infty} \Psi_m^* \Psi_n dx = 1$ (b) $\int_{-\infty}^{+\infty} \Psi_m \Psi_n dx = 0$ (c) $\int_{-\infty}^{+\infty} \Psi_m^* \Psi_n dx = 0$ (d) $\int_{-\infty}^{+\infty} \Psi_m \Psi_n dx = 1$
24. If $\Psi(x, t)$ be a normalized wave function we must have
 (a) $\int_{-\infty}^{+\infty} \Psi^* \Psi dx = 1$ (b) $\int_{-\infty}^{+\infty} \Psi^* \Psi dx = 0$ (c) $\int_{-\infty}^{+\infty} \Psi^* \Psi dx = \frac{1}{2}$ (d) $\int_{-\infty}^{+\infty} \Psi \Psi dx = 1$
25. Which of the following functions is an eigen function of the momentum operator?
 (a) $A \ln x$ (b) $A \sqrt{x/m}$ (c) Ax^2 (d) None of these
- [Ans. 1 (b), 2 (c), 3 (b), 4 (c), 5 (c), 6 (c), 7 (d), 8 (d), 9 (d), 10 (c), 11 (c), 12 (b), 13 (b), 14 (d), 15 (b), 16 (d), 17 (b), 18 (a), 19 (d), 20 (a), 21 (c), 22 (d), 23 (c), 24 (a), 25 (d)]

Short Questions with Answers

1. What is a wave function? Mention four points on its physical significance.

Ans. Schrödinger's equation represents the wave behavior of a particle while it moves. The solution of this differential equation is a function of space and time coordinates. As this function [usually denoted by $\Psi(\vec{r}, t)$] is related to the wave behavior of a particle it is called a wave function.

The following are the four points regarding the physical significance of the wave function $\Psi(\vec{r}, t)$:

- (a) It gives information regarding the space-time behavior of a particle.
- (b) $|\Psi(\vec{r}, t)|^2 = \Psi^*(\vec{r}, t) \Psi(\vec{r}, t)$ measures the probability of finding a particle in space and time.
- (c) The magnitude of the wave function is large where the probability of finding the particle is high.
- (d) The wave function must be continuous and single-valued at each point in space.

2. Define adjoint of an operator.

Ans. Let us consider two operators \hat{Q} and \hat{Q}^\dagger which satisfy the following relation:

$$\int \phi^* \hat{Q} \Psi dV = \int (\hat{Q}^\dagger \phi)^* \Psi dV$$

In this case \hat{Q}^\dagger is said to be the adjoint of \hat{Q} . In other words so far as the value of the integral is concerned, it does not make any difference whether \hat{Q} acts on ψ or its adjoint \hat{Q}^\dagger acts on the other function.

3. Define self-adjoint or hermitian operator.

Ans. The physical quantities are real. The eigen values of operators representing a physical quantity must be real. This condition limits the type of functions which can serve as operators for the physical quantities. An operator \hat{Q} which corresponds to a physical quantity must be in a position to satisfy the following condition:

$$\langle q \rangle = \langle q \rangle^*$$

$$\text{or, } \int \phi^* \hat{Q} \Psi dV = \int (\hat{Q} \phi)^* \Psi dV$$

where ϕ and Ψ are two arbitrary wave functions. The operators whose eigen values are real are known as **real or hermitian or self-adjoint operators**.

An operator \hat{Q} is considered to be self-adjoint or hermitian if $\hat{Q} = \hat{Q}^\dagger$.

4. Show that the expected average of hermitian operator is real.

Ans. Let \hat{Q} be a hermitian operator and Ψ_1 and Ψ_2 be two eigen functions of \hat{Q} corresponding to the eigen values q_1 and q_2 respectively. Then

$$\hat{Q} \Psi_1 = q_1 \Psi_1 \quad \text{and} \quad \hat{Q} \Psi_2 = q_2 \Psi_2$$

The condition of self-adjointness (or hermitianity) is given by

$$\int \Psi_1^* \hat{Q} \Psi_2 dV = \int (\hat{Q} \Psi_1)^* \Psi_2 dV$$

$$\text{or, } \int \Psi_1^* q_2 \Psi_2 dV = \int q_1^* \Psi_1^* \Psi_2 dV$$

$$\text{or, } (q_2 - q_1^*) \int \Psi_1^* \Psi_2 dV = 0$$

This is true for any two eigen function of \hat{Q} . So, if $q_2 = q_1$, then $q_1^* = q_2$
Hence q_1 is real.

5. Find the eigen function and eigen values of the operator $\hat{L}_z = -i\hbar \frac{d}{d\phi}$

Ans. The eigen value equation of \hat{L}_z is given by

$$\hat{L}_z \Psi(\phi) = q \Psi(\phi) \Rightarrow -i\hbar \frac{d\Psi}{d\phi} = q\Psi$$

$$\text{or, } \frac{d\Psi}{\Psi} = -\frac{q}{i\hbar} d\phi \Rightarrow \int \frac{d\Psi}{\Psi} = +\frac{iq}{\hbar} \int d\phi + \ln c$$

$$\text{or, } \Psi = ce^{\left(\frac{iq}{\hbar}\phi\right)}$$

The function Ψ is a periodic function of variable ϕ with a period of 2π , i.e., $\Psi(\phi) = \Psi(\phi + 2\pi)$. This implies that the eigen value q is an integral multiple of \hbar and Ψ as given by the above mentioned formula is the eigen function of \hat{L}_z .

6. (a) Write down Schrödinger's time-dependent equation.

[WBUT 2006]

- (b) State quantum mechanical postulates.

Ans. (a) Refer to Section 7.7.1.

(b) Refer to Section 7.6.

7. Show that a normalized wave function must have unit norm.

Ans. We know that Schrödinger's wave equation is a linear and homogeneous equation in Ψ and its derivatives (like $\frac{\partial\Psi}{\partial x}$ and $\frac{\partial\Psi}{\partial t}$) are also linear. For this reason, if any solution of this equation is multiplied by a constant quantity then the new wave function so resulted will also be a solution. So, in order to avoid this arbitrariness, it becomes necessary to impose a normalization condition.

Let us assume that $\Psi_1(\bar{r}, t)$ is a solution of Schrödinger's equation and

$$\int_{-\infty}^{+\infty} |\Psi_1(\bar{r}, t)|^2 dV = N^2 \quad \dots(1)$$

where $|\Psi_1(\bar{r}, t)|^2 = \Psi_1^*(\bar{r}, t) \Psi_1(\bar{r}, t)$ $\Psi_1(\bar{r}, t)$ is a positive real number and the value of the integral is also so, N is, therefore, a real positive number and it is called the norm (or normalization constant) of $\Psi_1(\bar{r}, t)$. Let us now consider another wave function $\Psi(\bar{r}, t)$ which is related to the present function $\Psi_1(\bar{r}, t)$ through the following equation:

$$\Psi(\bar{r}, t) = \frac{1}{N} \Psi_1(\bar{r}, t) \quad \dots(2)$$

where $\Psi(\bar{r}, t)$ is also a solution of Schrödinger's equation, as it merely differs from the present solution $\Psi_1(\bar{r}, t)$ by a factor of $(1/N)$ which is a constant.

Now, substituting this value of $\Psi_1(\bar{r}, t)$ in Eq. (1), one gets

$$\begin{aligned} & \int_{-\infty}^{+\infty} N^2 |\Psi(\bar{r}, t)|^2 dV = N^2 \\ \text{or, } & \int_{-\infty}^{+\infty} |\Psi(\bar{r}, t)|^2 dV = 1 \end{aligned} \quad \dots(3)$$

The wave function $\Psi(\bar{r}, t)$ satisfies Eq. (3) and it is called the normalized wave function.

Hence, a normalized wave function must possess a unit norm, i.e., the normalization constant of a normalized wave function is unity.

8. What do you mean by an orthogonal wave function? Discuss briefly.

Ans. Let us consider a set of wave functions where each member of the set satisfies Schrödinger's wave equation, namely, $\Psi_1(\bar{r})$, $\Psi_2(\bar{r})$, $\Psi_3(\bar{r})$, etc. Such that any two members [e.g., $\Psi_m(\bar{r})$ and $\Psi_n(\bar{r})$] of the set satisfy the condition given below:

$$\int \Psi_m^*(\bar{r}) \Psi_n(\bar{r}) dV = 0 \quad \dots(1)$$

where $m \neq n$, then

the functions in the aforesaid set are said to be orthogonal in analogy with the condition of orthogonality of two vectors.

9. Derive Schrödinger's wave equation from the fundamental postulates of quantum mechanics.

Ans. Refer to Section 7.7.1.

10. What is the need for normalizing a wave function? Write down the normalization condition of two wave functions. What will be the condition for single wave function?

Ans. As we know Schrödinger's wave function predicts the position of the related particle in space and time. The wave function must have a finite value at any point in space and time.

The square of the wave function (i.e., $|\Psi|^2$) is proportional to the probability of finding the particle in space.

But according to the definition of probability in statistics, its value can range from 0 to +1 only. For this reason, the wave function needs to be normalized so that it can satisfy the demand of probability theory.

The normalization condition of any two wave functions which are the solutions of the same Schrödinger's equation is given by,

$$\Psi_n = \frac{1}{N} \Psi \quad \text{and} \quad \int_{-\infty}^{+\infty} \Psi_n^* \Psi_n dV = 1$$

where Ψ_n is the normalized wave function and Ψ is unnormalized one. The normalization condition for a single wave function is given by

$$\int_{-\infty}^{+\infty} \Psi_n^* \Psi_n dV = 1$$

part 2: Descriptive Questions

1. (a) What is the physical interpretation of wave function?
 (b) How is wave function related to the probability of finding a particle at any point in space at a given time?
 (c) What is probability density?
 (d) Discuss the probability density of a particle represented by a wave which is generated by the superposition of two de Broglie waves.
2. (a) What do you mean by normalization of a wave function? What is the use of normalization?
 (b) How can you normalize a wave function by multiplying it with a suitable constant?
 (c) Can you normalize every wave function?
 (d) Consider two wave functions Ψ and $\Psi \exp(i\theta)$ where θ is a real quantity. What is the probability density of a particle for each of the states?
3. (a) What do you mean by stationary states? Why are they called so?
 (b) What is the condition for which the system can be represented by stationary states?
4. (a) Write down Schrödinger's time-dependent wave equation for three-dimensional and one-dimensional cases.
 (b) Obtain the time-independent form of Schrödinger's equation from its time-dependent form.
 (c) Under what condition can we obtain the time-independent form of Schrödinger's equation?
5. (a) What are the limitations of an any acceptable wave function?
 (b) Consider a particle moving along the x direction and represented by a normalized wave function Ψ_n . What is the probability of finding the particle in a region which is at infinity from the origin?
6. Write down Schrödinger's equation for one-dimensional motion of a free particle in a one-dimensional potential box. Find the eigen function and eigen energy. [WBUT 2002]
7. (a) Write down Schrödinger's equation for a particle of mass m in a rectangular box with infinitely hard walls whose edges are a, b , and c . What are the boundary conditions?
 What conditions are responsible for the quantization of energy of the particle?
 (b) The wave functions of a particle are given by

$$\Psi(x, y, z) = A \sin\left(\frac{n_x \pi x}{a}\right) \sin\left(\frac{n_y \pi y}{b}\right) \sin\left(\frac{n_z \pi z}{c}\right)$$

where n_x, n_y and n_z belong to the set $\{1, 2, 3, \dots\}$

Find the value of the normalization constant A .

8. Obtain the time-independent Schrödinger's equation. Show that the energy eigen values of a particle enclosed in a potential box is quantized. [WBUT 2003]
9. (a) Write down the time-independent Schrödinger's equation for a free particle of mass m and momentum \bar{p} .
 (b) Why in case of moving electron quantum mechanics is used while for moving cars we use newtonian mechanics? Explain. [WBUT 2004]
10. (a) Give the physical interpretation of the wave function $\Psi(x)$.
 (b) Obtain the expression for the stationary energy levels for a particle of mass m which is free to move in a region of zero potential between two rigid walls with $x = 0$ and $x = L$. Are the energy levels degenerate?
 (c) Find the corresponding wave function pertaining to part (b) of this question and normalize it. [WBUT 2005]

11. Write down Schrödinger's equation for a particle confined in a one-dimensional box. [WBUT 2006]

12. If the wave function $\Psi(x)$ of a quantum mechanical particle is given by

$$\Psi(x) = a \sin \frac{\pi x}{L}, \quad \text{for } 0 \leq x \leq L$$

$$= 0 \quad \text{for } 0 \geq x \geq L$$

Then determine the value of a . Also determine the value of x where the probability of finding the particle is maximum. [WBUT 2007]

13. A particle of mass m is confined within the space between $x = 0$ and $x = L$.
 - (i) Write down Schrödinger's equation for such a system.
 - (ii) Solve the equation to find out the normalized eigen functions.
 - (iii) Show that the eigen functions corresponding to two different eigen values are orthogonal.
 - (iv) If p_x denotes the momentum then find $\langle p_x \rangle$ as well as $\langle p_x^2 \rangle$ in the ground state.

[WBUT 2008]

14. What are the values of $[\hat{x}, \frac{\partial}{\partial x}]$, $[\hat{L}_x, \hat{x}]$ and $[\hat{p}_x, \hat{p}_y]$? [WBUT 2004]

15. Show that (i) $[\hat{p}_x, \hat{x}_n] = -i\hbar n x^{n-1}$ and (ii) $[\hat{p}_x, f(x)] = -i\hbar \frac{df}{dx}$.

16. (a) State the basic postulates of quantum mechanics.
 (b) Define degeneracy and non-degeneracy. Prove that the lowest state of a free particle in a cubical box is not degenerate.
 (c) What do you mean by orthogonal wave function? Write down the condition of orthogonality.

Part 3: Numerical Problems

1. A particle exists inside a one-dimensional potential box of length L . Calculate the probability of finding the particle in a region between $\frac{L}{4}$ and $\frac{3L}{4}$ when the particle is in the lowest energy state. [Ans. 0.818]
2. Examine whether the operator \hat{L} is linear in the following two cases:
 - (i) $\hat{L}f(x) = f(x) + \sin x$
 - (ii) $\hat{L}f(x) = f(-x)$[Ans. (i) non-linear, (ii) linear]
3. Show that $\frac{\partial}{\partial x}$ and $\frac{\partial^2}{\partial x^2}$ are commutative.
4. A particle is moving along the x axis has the wave function

$$\Psi(x) = ax \quad \text{for } 0 \leq x \leq 1$$

$$= 0 \quad \text{for } 0 \geq x \geq 1$$
Find the expected average $\langle x \rangle$ of the position of the particle. $\left[\text{Ans. } \frac{a^2}{4} \right]$
5. Prove that the wave function $\Psi(x, t) = A \cos(kx - \omega t)$ does not satisfy the time-dependent Schrödinger's equation for a free particle.
6. For an electron of mass 9.1×10^{-31} kg moving in the one-dimensional infinitely deep potential well of width 0.1 nm, find (i) the least possible energy, (ii) the first three eigen values in electron volt, (iii) the energy difference between the ground state and the first excited state, and (iv) the frequency of the emitted radiation due to the transition between the two states.
 [Ans. (i) 37.73 eV, (ii) $E_1 = 37.73$ eV, $E_2 = 150.95$ eV, $E_3 = 339.63$ eV, (iii) 113.22 eV, (iv) $v = 27.3 \times 10^{15}$ Hz]
7. Calculate the normalization constant for a wave function (at $t = 0$) given by

$$\Psi(x) = Ae^{-\sigma^2 x^2/2} \cdot e^{ikx}$$
[Ans. $(\sigma/\sqrt{\pi})^{1/2}$]
8. Determine the probability density for the wave function

$$\Psi(x) = Ae^{-\frac{\sigma^2 x^2}{2}} e^{ikx}$$
[Ans. $p = \frac{\sigma}{\sqrt{\pi}} \exp(-\sigma^2 x^2)$]
9. Consider two stationary state solutions $\Psi_1(\vec{r})$ and $\Psi_2(\vec{r})$ corresponding to energy states E_1 and E_2 respectively for time-independent Schrödinger's equation.
10. Prove that for two linear operators $\hat{\alpha}$ and $\hat{\beta}$, $[\hat{\alpha}, \hat{\beta}] + [\hat{\beta}, \hat{\alpha}] = 0$.
11. If $\hat{\alpha}$, $\hat{\beta}$ and $\hat{\gamma}$ are three linear operators, then prove that

$$[\hat{\alpha}, [\hat{\beta}, \hat{\gamma}]] + [\hat{\beta}, [\hat{\gamma}, \hat{\alpha}]] + [\hat{\gamma}, [\hat{\alpha}, \hat{\beta}]] = 0$$
12. The minimum energy possible for a particle trapped in a one-dimensional infinite potential well is 10 eV. What are the next three energy levels? [Ans. 40 eV, 90 eV, 160 eV]

13. Find the commutator $[\hat{A}, \hat{B}]$ where $\hat{A} = x^3$ and $\hat{B} = x \frac{d}{dx}$. [Ans. $-3x^3$]
14. Calculate the expected average of p_x^2 for the wave function $\Psi = \sqrt{\frac{2}{L}} \sin\left(\frac{\pi x}{L}\right)$ in the region from $x=0$ to $x=L$. [Ans. $(\hbar \pi)^2/L$]
15. Prove the following relation:

$$[\hat{A}, \hat{B} + \hat{C}] = [\hat{A}, \hat{B}] + [\hat{A}, \hat{C}]$$

$$(A - B) = (A)(B) - (B)(A)$$

$$\text{commutator} = \text{anti-commutator}$$

$$[A, B] = A(B) - B(A)$$

$$[A, B] = A(B) - B(A)$$