

Chapter- 7

Schrödinger's Theory and Its Applications



7.1. Transition from Deterministic Description in Classical Mechanics to Probabilistic Description in Quantum Mechanics

In classical physics, we can determine the position and the momentum simultaneously of a system (macroscopic body) with same accuracy by using Newton's laws of motion provided its initial position and momentum are known. So the *classical physics is deterministic in nature*.

In quantum mechanics, when a microparticle (electron, proton, etc.) is in motion (velocity of microparticle is comparable to velocity of light), its position can be anywhere within the wave packet. This wave packet is extending throughout a region of space. Hence, there will be an uncertainty in specifying the position of the particle. Even, we can say from Heisenberg's uncertainty principle that, if the position of the particle is exactly specified (i.e., the uncertainty $\Delta x = 0$), the momentum of the particle is completely uncertain. Similarly, the position of the microparticle is completely uncertain for the exact measurement of momentum (i.e., the uncertainty $\Delta p_x = 0$). This would make the description of the particle meaningless.

So in quantum mechanics, any physical quantity is described by probabilistic way by considering a number of allowed values with different probabilities. Thus, the explanation of natural or physical phenomenon in terms of quantum physics necessitates the transition from deterministic classical physics to a probabilistic quantum physics. *The probabilistic description of the motion of microparticle can be expressed by a function, called wave function.*

7.2. The Wave Function

In the earlier chapter, we have seen that a wave is associated with the moving quantum mechanical particles.

The space-time behaviour of each moving quantum mechanical particle can be described by a function. This function is known as wave function. It is generally denoted by $\psi(r, t)$. This measures the probability of finding a particle about a position.



Characteristics of wave function

- ① The wave function is a mathematical function that represents the space-time behaviour of each quantum mechanical particle.
 - ② The wave function is single valued, continuous and finite.
 - ③ The wave function is a square integrable function.
 - ④ The magnitude of $\psi(\vec{r}, t)$ is large in the regions where the probability of finding the particle is high and is small in the regions where the probability of finding it is low.
- Hence, the wave function $[\psi(\vec{r}, t)]$ measures the probability of the particle around a particular position.

7.3. Probability and Probability Density

We know, the wave function $[\psi(\vec{r}, t)]$ of a quantum mechanical particle gives the space-time behaviour of a particle.

Probability density *The probability density of a particle is the probability of finding the particle per unit volume of a given space at a particular time.*

It is generally expressed as the product of normalised wave function ① and its complex conjugate.

$$\text{So probability density } \rho = \psi^*(\vec{r}, t) \psi(\vec{r}, t) \quad \textcircled{2} = |\psi(\vec{r}, t)|^2 \quad \dots(7.3.1)$$

This is the relation between the wave function (ψ) of a particle in a given state and the probability per unit volume of finding the particle in the given state.

So the probability that the particle will be found in the volume element dv (at x, y, z and time t) = $\psi^* \psi dv$. Since, the particle must be somewhere in space, the total probability P , to find the particle in space should be equal to 1.

$$\therefore P = \int_{-\infty}^{+\infty} \psi^* \psi dv = 1 \quad \dots(7.3.2)$$

In one dimensional case, the probability of locating the particle within a distance dx is given by

$$P = \psi^* \psi dx$$

... (7.3.3)

① The condition of an expectable wave function is that the integral of $\psi^* \psi$ over all space (i.e., $\int_{-\infty}^{+\infty} \psi^* \psi dv$ (dv is small volume element surrounding some point)) must be finite.

$$\text{Hence, } \int_{-\infty}^{+\infty} \psi^* \psi dv = 1 \quad \text{indicates the particle must be somewhere in space at all times.}$$

A wave function that obeys the above condition is known as normalised wave function.

② If a wave function is represented by complex function then we can write, $\psi = A + iB$, whereas its complex conjugate $\psi^* = A - iB$. Then $\psi^* \psi = (A - iB)(A + iB) = A^2 + B^2$. Thus $\psi^* \psi$ is always a positive real quantity as A and B are two real quantity.

Since, the particle must be somewhere along the X -axis, the total probability for the one dimensional motion over all values of x must be 1.

$$\int_{-\infty}^{+\infty} \psi^* \psi dx = 1 \quad \dots (7.3.4)$$

So the dimension of one-dimensional wave function is $L^{-\frac{1}{2}}$.

Similarly the dimension of three-dimensional wave function is $L^{-\frac{3}{2}}$.

Normalised wave function A wave function is normalised if $\int_{-\infty}^{+\infty} |\psi|^2 dx = 1$.

7.4. Superposition Principle

We know the wave function (ψ) represents the actual state of a system. This system may have different possible allowed states. The superposition principle states that if any Schrödinger differential equation (linear) has several solutions ψ_1, ψ_2, ψ_3 , etc., then the linear combination of these solutions with different coefficients is also a solution of this Schrödinger equation. Thus,

$$\psi = a_1 \psi_1 + a_2 \psi_2 + a_3 \psi_3 + \dots = \sum_n a_n \psi_n$$

where a_n is a coefficient of the corresponding state ψ_n . This implies that the actual state of the system is a linear combination of these allowed states with different coefficients. Here, the wave functions are normalised and the functions are orthogonal to each other.

The probability of finding the system in a particular state (say ψ_1) will depend on its corresponding coefficient (a_1). Thus—the probability of finding the particle of the system in the quantum state ψ_1 is $|a_1|^2$.

Problem 1

The wave function which is in quantum states $\psi_1, \psi_2, \psi_3, \psi_4$ and ψ_5 is given by

$$\psi = \frac{1}{\sqrt{3}}\psi_1 + \frac{1}{\sqrt{3}}\psi_2 + \frac{1}{\sqrt{6}}\psi_3 + \frac{1}{\sqrt{24}}\psi_4 + \frac{1}{\sqrt{8}}\psi_5$$

What is the probability of the system being in the state given by ψ_5 and what is the total probability?

Solution The probability of finding the system in the state ψ_5 is

$$P_5 = \left(\frac{1}{\sqrt{8}} \right)^2 = \frac{1}{8}$$

The total probability of the system is given by

$$\begin{aligned} P &= \left(\frac{1}{\sqrt{3}} \right)^2 + \left(\frac{1}{\sqrt{3}} \right)^2 + \left(\frac{1}{\sqrt{6}} \right)^2 + \left(\frac{1}{\sqrt{24}} \right)^2 + \left(\frac{1}{\sqrt{8}} \right)^2 \\ &= \frac{1}{3} + \frac{1}{3} + \frac{1}{6} + \frac{1}{24} + \frac{1}{8} = \frac{8+8+4+1+3}{24} = \frac{24}{24} = 1 \end{aligned}$$

Problem 2

A superposed state of a quantum particle is given by $\psi(x) = C_1\psi_1(x) + C_2\psi_2(x)$, where $\psi_1(x)$ and $\psi_2(x)$ are orthonormal states. Show that $C_1^2 + C_2^2 = 1$. [WBUT 2012]

Solution We know the total probability, $\int_{-\infty}^{\infty} \psi^* \psi dx = 1$

$$\text{So, } \int_{-\infty}^{\infty} [C_1\psi_1(x) + C_2\psi_2(x)]^* [C_1\psi_1(x) + C_2\psi_2(x)] dx = 1$$

$$\text{or, } \int_{-\infty}^{\infty} C_1^2 \psi_1^*(x)\psi_1(x) dx + \int_{-\infty}^{\infty} C_1 C_2 \psi_1^*(x)\psi_2(x) dx$$

$$+ \int_{-\infty}^{\infty} C_2 C_1 \psi_2^*(x)\psi_1(x) dx + \int_{-\infty}^{\infty} C_2^2 \psi_2^*(x)\psi_2(x) dx = 1$$

We know from the condition of orthonormality,

$$\int_{-\infty}^{\infty} \psi_m^*(x)\psi_m(x) dx = \delta_{mn}$$

where $\delta_{mn} = 1$ for $m = n$ and $\delta_{mn} = 0$ for $m \neq n$.

So we can write from equation (1),

$$\int_{-\infty}^{\infty} C_1^2 \psi_1^*(x)\psi_1(x) dx + \int_{-\infty}^{\infty} C_2^2 \psi_2^*(x)\psi_2(x) dx = 1$$

$$\text{or, } C_1^2 \int_{-\infty}^{\infty} \psi_1^*(x)\psi_1(x) dx + C_2^2 \int_{-\infty}^{\infty} \psi_2^*(x)\psi_2(x) dx = 1$$

$$\text{or, } C_1^2 \cdot 1 + C_2^2 \cdot 1 = 1 \quad [\because \int_{-\infty}^{\infty} \psi^* \psi dx = 1]$$

$$\text{or, } C_1^2 + C_2^2 = 1$$

Problem 3

The ground state and the excited state normalised wave functions of an atom are ψ_0 and ψ_1 respectively, the corresponding energy being E_0 and E_1 . If the probability of finding the atom in the ground state is 90% and that for the excited state is 10%, then find the average energy of the atom. Also determine the normalised wave function. [WBUT 2010]

Solution Here the state of particle will be generated due to the superposition of two states ψ_0 and ψ_1 .

Suppose, the normalised and orthogonal wave function of the atom is ψ .

$$\therefore \psi = C_0\psi_0 + C_1\psi_1 \quad \dots(1)$$

where C_0 and C_1 are the coefficients of the corresponding state.

Now, we can write from normalised condition

$$\begin{aligned} \int \psi^* \psi dw &= 1 \quad \text{or, } \int (C_0^* \psi_0^* + C_1^* \psi_1^*) (C_0 \psi_0 + C_1 \psi_1) dw = 1 \\ \text{or, } C_0^* C_0 \int \psi_0^* \psi_0 dw + C_1^* C_1 \int \psi_1^* \psi_1 dw &= 1 \\ \therefore C_0^* C_0 \int \psi_0^* \psi_1 dw \text{ and } C_1^* C_1 \int \psi_1^* \psi_0 dw &\text{ are individually zero due to the orthogonality property of these wave functions.} \end{aligned}$$

$$C_0^* C_0 + C_1^* C_1 = 1 \quad [\because \int \psi^* \psi dv = 1]$$

$$\text{So, } C_0^2 + C_1^2 = 1 \quad [\because C_0 \text{ and } C_1 \text{ are two real constants}]$$

We know, the probability of finding the particle in state ψ_0 and ψ_1 are C_0^2 and C_1^2 respectively. Thus we can write from the given conditions

$$C_0^2 = 0.9 \quad \text{and} \quad C_1^2 = 0.1$$

- (i) Thus, the normalised wave function can be written from equation (1) as

$$\psi = \sqrt{0.9}\psi_0 + \sqrt{0.1}\psi_1$$

- (ii) If P_n is the probability to find an atom in the energy state E_n , the average energy of the atom is $E_{av} = \sum_n P_n E_n$

$$\text{In this case, } E_{av} = 0.9E_0 + 0.1E_1.$$

Problem 4

A particle is moving along X -axis has the wave function,

$$\psi(x) = bx \quad \text{between } x = 0 \text{ and } x = 1$$

$= 0 \quad \text{elsewhere}$

Find the probability that the particle can be found between $x = 0.30$ and $x = 0.70$.

Solution The probability of finding a particle corresponding to wave function $\psi(x)$ is located in the length dx is $\psi^*(x)\psi(x) dx = |\psi(x)|^2 dx$.

Hence, the probability within the range $0.30 < x < 0.70$ is given by

$$P = \int_{0.30}^{0.70} |\psi(x)|^2 dx = b^2 \int_{0.30}^{0.70} x^2 dx = \frac{b^2}{3} [x^3]_{0.30}^{0.70} = \frac{b^2}{3} [0.343 - 0.027] = 0.105b^2$$

Problem 5

The wave function for certain particle is given as $\psi = \cos^2 x$ for $-\frac{\pi}{2} \leq x \leq \frac{\pi}{2}$. Normalise the wave function in the given range.

Solution A function ψ is said to be normalised if it satisfies

$$\int_{-\infty}^{\infty} |\psi|^2 dv = 1 \quad \dots(1)$$

Now if $\psi(x) = A \cos^2 x$, then to make it normalise within the range $-\frac{\pi}{2}$ to $\frac{\pi}{2}$, we can write from equation (1) as,

$$\int_{-\frac{\pi}{2}}^{\frac{\pi}{2}} |\psi|^2 dx = 1 \quad \text{or,} \quad A^2 \int_{-\frac{\pi}{2}}^{\frac{\pi}{2}} \cos^4 x dx = 1 \quad \text{or,} \quad A^2 \frac{3\pi}{8} = 1 \quad \text{or,} \quad A = \sqrt{\frac{8}{3\pi}}$$

By putting $A = \sqrt{\frac{8}{3\pi}}$ in $\psi(x) = A \cos^2 x$, we get the normalised wave function as

$$\psi(x) = \sqrt{\frac{8}{3\pi}} \cos^2 x$$

Problem 6

The normalised wave function for certain particle is $\psi(x) = \frac{\sqrt{3}}{\pi} \cos x$, $0 \leq x \leq \frac{\pi}{2}$. Calculate the probability of finding the particle between $0 < x < \frac{\pi}{4}$.

Solution The probability of finding a particle corresponding to wave function $\psi(x)$ is located in the length dx is $\psi^*(x)\psi(x)dx = |\psi(x)|^2 dx$. Hence, the probability within the range $0 < x < \frac{\pi}{4}$ is given by

$$\begin{aligned} P &= \int_0^{\frac{\pi}{4}} |\psi(x)|^2 dx = \int_0^{\frac{\pi}{4}} \left[\frac{\sqrt{3}}{\pi} \cos x \right]^2 dx = \frac{3}{\pi} \int_0^{\frac{\pi}{4}} \cos^2 x dx \\ &= \frac{3}{\pi} \times \frac{1}{2} \int_0^{\frac{\pi}{4}} (1 + \cos 2x) dx \\ &= \frac{3}{2\pi} \times \left[\int_0^{\frac{\pi}{4}} dx + \int_0^{\frac{\pi}{4}} \cos 2x dx \right] \\ &= \frac{3}{2\pi} [x]_0^{\frac{\pi}{4}} + \frac{3}{2\pi} \left[\frac{\sin 2x}{2} \right]_0^{\frac{\pi}{4}} = \frac{3}{8} + \frac{3}{4\pi} [1] = 0.613 \end{aligned}$$

7.5. Observables

Observables are quantities associated with a physical system that can be measured or observed.

* **Examples:** position, momentum or energy of a particle.

In quantum mechanics every observable quantity (like position, momentum) is associated with an operator. With the help of this operator, we can find out the observable.

7.6. Operators in Quantum Mechanics

An operator is a mathematical rule that changes a given function into a new function.

If A is an operator, it is generally represented by \hat{A} .

* **Example:** If \hat{A} is an operator and stands for the operator $\frac{\partial}{\partial x}$ (say), then when it operates on a function x^2 it gives,

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

In quantum mechanics, each dynamical variable such as position, momentum, energy, etc. is represented by linear operator. They commute with a constant (or with the sum of the two linear operators but their product may or may not be commutative).

- (i) **Linear operator:** If \hat{a} is a linear operator, it satisfies (i) $\hat{a}(cf) = c\hat{a}f$, c is a constant and (ii) $\hat{a}(f+g) = \hat{a}f + \hat{a}g$, where f and g are two functions.

Commutator Commutator of two operators $\hat{\alpha}$ and $\hat{\beta}$ is represented by $[\hat{\alpha}, \hat{\beta}]$ and is defined as

$$[\hat{\alpha}, \hat{\beta}] = \hat{\alpha}\hat{\beta} - \hat{\beta}\hat{\alpha}$$

If $[\hat{\alpha}, \hat{\beta}] = 0$, i.e., $\hat{\alpha}\hat{\beta} = \hat{\beta}\hat{\alpha}$, the two operators are called **commutative**.

If $[\hat{\alpha}, \hat{\beta}] \neq 0$, i.e., $\hat{\alpha}\hat{\beta} \neq \hat{\beta}\hat{\alpha}$, the two operators are called **non-commutative**.

Problem 1

Find the value of $[\hat{x}, \frac{\partial}{\partial x}]$.

Solution Let $f(x)$ be a function on which these two operators operate.

Thus, $[\hat{x}, \frac{\partial}{\partial x}]f(x) = [x \frac{\partial}{\partial x} - \frac{\partial}{\partial x}x]f(x)$

$$\begin{aligned} &= x \frac{\partial}{\partial x}f(x) - \frac{\partial}{\partial x}\{xf(x)\} \\ &= x \frac{\partial}{\partial x}f(x) - x \frac{\partial}{\partial x}f(x) - f(x) = -f(x) \end{aligned}$$

Hence, $[\hat{x}, \frac{\partial}{\partial x}]f(x) = -f(x)$

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

So,

Again, since $[\hat{x}, \frac{\partial}{\partial x}] \neq 0$, the operators \hat{x} and $\frac{\partial}{\partial x}$ are not commutative to each other.

Problem 2

Show that the operators $\frac{\partial}{\partial x}$ and $\frac{\partial^2}{\partial x^2}$ are commutative.

Solution Let $f(x)$ be a function on which these two operators operate.

$$\begin{aligned} &[\frac{\partial}{\partial x}, \frac{\partial^2}{\partial x^2}]f(x) = \left[\frac{\partial}{\partial x} \frac{\partial^2}{\partial x^2} - \frac{\partial^2}{\partial x^2} \frac{\partial}{\partial x} \right]f(x) = \frac{\partial}{\partial x} \frac{\partial^2}{\partial x^2}f(x) - \frac{\partial^2}{\partial x^2} \frac{\partial}{\partial x}f(x) \\ &= \frac{\partial^3}{\partial x^3}f(x) - \frac{\partial^3}{\partial x^3}f(x) = 0 \end{aligned}$$

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

Therefore, the two operators are commutative.

Problem 3

What is the value of $\left[\hat{\frac{\partial}{\partial x}}, \hat{\frac{\partial}{\partial t}} \right]^\dagger$?

Solution Let f be a continuous function of x and t on which these two operators operate.

$$\begin{aligned} \left[\hat{\frac{\partial}{\partial x}}, \hat{\frac{\partial}{\partial t}} \right] f &= \left[\frac{\partial}{\partial x}, \frac{\partial}{\partial t} - \frac{\partial}{\partial t} \frac{\partial}{\partial x} \right] f \\ &= \frac{\partial}{\partial x} \left(\frac{\partial}{\partial t} f \right) - \frac{\partial}{\partial t} \left(\frac{\partial}{\partial x} f \right) \\ &= \frac{\partial^2 f}{\partial x \partial t} - \frac{\partial^2 f}{\partial t \partial x} = 0 \quad \left[: \frac{\partial^2 f}{\partial x \partial t} = \frac{\partial^2 f}{\partial t \partial x} \right] \\ \therefore \left[\hat{\frac{\partial}{\partial x}}, \hat{\frac{\partial}{\partial t}} \right] &= 0 \end{aligned}$$

Hence, the two operators are commutative.

7.6.1. Momentum Operator

Suppose, the wave function for a free particle in the positive X -direction is

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

$$\therefore \frac{\partial \psi}{\partial x} = ik A e^{i(kx - \omega t)}, \text{ where } \psi = \psi(x, t)$$

$$\text{or, } \frac{\partial \psi}{\partial x} = ik \psi \quad \text{or, } \frac{\hbar}{i} \frac{\partial \psi}{\partial x} = \hbar k \psi$$

$$\text{or, } \frac{\hbar}{i} \frac{\partial \psi}{\partial x} = p_x \psi \quad \left[: \text{ de Broglie equation of a matter wave, } p = \frac{\hbar}{\lambda} = \frac{\hbar}{2\pi} \frac{2\pi}{\lambda} = \hbar k \right]$$

This implies, the operator p_x denoted as \hat{p}_x is given by

$$\hat{p}_x = \frac{\hbar}{i} \frac{\partial}{\partial x} \quad \dots(7.6.1.1)$$

Similarly, for the y and the z components of momentum, we can write

$$\hat{p}_y = \frac{\hbar}{i} \frac{\partial}{\partial y} \quad \dots(7.6.1.2)$$

$$\text{and } \hat{p}_z = \frac{\hbar}{i} \frac{\partial}{\partial z} \quad \dots(7.6.1.3)$$

Therefore, in three dimension, the operator for the momentum \vec{p} can be represented by

$$\hat{p} = \frac{\hbar}{i} \vec{\nabla} \quad \dots(7.6.1.4)$$

7.6.2. Energy Operator

Suppose, the wave function of a free particle in positive X -direction is

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

$$\frac{\partial \psi}{\partial t} = -i\omega \psi, \quad \text{where } \psi = \psi(x, t)$$

$$i\hbar \frac{\partial \psi}{\partial t} = \hbar \omega \psi \quad \text{or, } i\hbar \frac{\partial \psi}{\partial t} = E \psi \quad [\because E = h\nu = \hbar\omega]$$

This equation implies the energy operator E denoted by \hat{E} is given by

$$\hat{E} = i\hbar \frac{\partial}{\partial t} \quad \dots (7.6.2.1)$$

► Prove that $[\hat{x}, \hat{p}_x] = i\hbar$. Give its physical significance.

Let $f(x)$ be a function on which these two operators operate.

$$\begin{aligned} [\hat{x}, \hat{p}_x]f(x) &= [\hat{x}\hat{p}_x - \hat{p}_x\hat{x}]f(x) \\ &= x \frac{i\hbar}{i} \frac{\partial}{\partial x} f(x) - \frac{\hbar}{i} \frac{\partial}{\partial x} \{xf(x)\} \quad \left[\because \hat{p}_x = \frac{\hbar}{i} \frac{\partial}{\partial x} \right] \\ &= x \frac{\hbar}{i} \frac{\partial}{\partial x} f(x) - x \frac{\hbar}{i} \frac{\partial}{\partial x} f(x) - \frac{\hbar}{i} f(x) = \frac{\hbar}{i} f(x) = i\hbar f(x) \end{aligned} \quad \dots (7.6.2.2)$$

$$\text{So, } [\hat{x}, \hat{p}_x] = i\hbar$$

Physical significance This equation implies that any position operator and its conjugate momentum operator do not commute. Thus, it is impossible to measure position and momentum simultaneously along same direction with the same accuracy. This supports the Heisenberg's position-momentum uncertainty principle.

7.7. Eigen (or Proper or Characteristic) Function and Eigen Value

Eigen function If an operator acting (operating) on a function will always produce the same function multiplied by a constant factor, the function is called an eigen function and the constant is known as eigen value of the given operator.

Thus, if \hat{A} is an operator that operates on a given function $f(x)$ then,

$$\hat{A}f(x) = cf(x) \quad \dots (7.7.1)$$

where c is a constant.

This equation is called eigen value equation. Here the constant c is known as eigen value and the function $f(x)$ is called eigen function of the corresponding operator \hat{A} .

► Special Note :

In quantum mechanics, each variable is associated with an operator which acts on a function (i.e., wave function ψ) to give a new function (i.e., wave function). The operator method is valid for a free particle as well as for a bound particle. Hence, all operators in quantum mechanics have eigen functions and eigen values.

Problem 1

Why $\sin^2 x$ is not an eigen function of the operator $\hat{A} \left(= \frac{d^2}{dx^2} \right)$?

Solution If $\hat{A} f(x) = a f(x)$, where $a = \text{constant}$, then $f(x)$ is an eigen function and its eigen value is a .

$$\text{Here, } \hat{A} f(x) = \frac{d^2}{dx^2} (\sin^2 x) = -2 \sin^2 x + 2 \cos^2 x = 2 - 4 \sin^2 x$$

So, $\sin^2 x$ is not an eigen function.

Problem 2

Which one of the following functions are eigen functions of the operator $\frac{d^2}{dx^2}$? Calculate also the eigen value where appropriate.

- i $\cos x$, ii e^{ix} , iii $\sin^2 x$, iv e^{4x} .

Solution

i $\hat{A} f(x) = \frac{d^2}{dx^2} (\cos x) = -\cos x = -f(x)$

So, $\cos x$ is an eigen function and its corresponding eigen value = -1 .

ii $\hat{A} f(x) = \frac{d^2}{dx^2} (e^{ix}) = -e^{ix} = -f(x)$

So, e^{ix} is an eigen function and its corresponding eigen value = -1 .

iii $\hat{A} f(x) = \frac{d^2}{dx^2} (\sin^2 x) = 2 - 4 \sin^2 x$

So, $\sin^2 x$ is not an eigen function.

iv $\hat{A} f(x) = \frac{d^2}{dx^2} (e^{4x}) = 16e^{4x} = 16 f(x)$

Hence, e^{4x} is an eigen function and its eigen value is 16.

7.8. Expectation Values of Dynamical Variables

The quantity that depends upon the coordinates (x, y, z, t) of a particle is called dynamical variable.

- Examples: Position, momentum, energy, etc.

The expectation value (or average value) of a dynamical quantity is the mathematical expectation (in the sense of probability theory) of the result of a single measurement. In other words, it is an average of the results of a large number of measurements on independent identical system.



Examples : The average or expectation value of any function (or any observable) $f(x)$ is given by

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

subjected to the normalisation condition $\int_{-\infty}^{+\infty} \psi^*(x, t) \psi(x, t) dx = 1$ (i.e., the function $\psi(x, t)$ is normalised).

Now, we want to find the expectation value of momentum and energy.

Expectation value of momentum If we consider $\hat{p}_x = -i\hbar \frac{\partial}{\partial x}$, the expectation value of the momentum p_x can be written by replacing $f(x)$ in equation (7.8.1) by the operator $\hat{p}_x = -i\hbar \frac{\partial}{\partial x}$.

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

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

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

... (7.8.2)

or,

$$\langle E \rangle = \int_{-\infty}^{+\infty} \psi^* \left(i\hbar \frac{\partial}{\partial t} \right) \psi dx$$

... (7.8.3)

Expectation value of energy

Similarly, the expectation value of the energy can be written as

$$\langle E \rangle = \int_{-\infty}^{+\infty} \psi^* \left(i\hbar \frac{\partial}{\partial t} \right) \psi dx \quad [\because \hat{E} = i\hbar \frac{\partial}{\partial t}]$$

$$\langle E \rangle = i\hbar \int_{-\infty}^{+\infty} \psi^* \left(\frac{\partial}{\partial t} \right) \psi dx$$

... (7.8.3)

Problem 1

A particle moving along the X-axis has the wave function,

$$\begin{aligned} \psi(x) &= bx \text{ between } x = 0 \text{ and } x = 1 \\ &= 0 \text{ elsewhere} \end{aligned}$$

Find the expectation value of position of the particle.

Solution If $\psi(x)$ is the wave function of a moving particle, expectation value of the particle's position (average value) is

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

So in this case $\langle x \rangle = \int_0^1 x |\psi(x)|^2 dx$ [$\because \psi(x)$ is real, $\psi^*(x) = \psi(x)$]

$$\begin{aligned} &= \int_0^1 x |bx|^2 dx = b^2 \int_0^1 x^3 dx = \frac{b^2}{4} \end{aligned}$$

**Problem 2**

Find expectation value of position for the wave function given by $\psi(x) = ax$ for $0 \leq x \leq 1$. [WBUT 2014]

Solution The wave function is $\psi(x) = ax$.

Applying the normalisation condition, i.e., the total probability to find the particle within the specified region is equal to 1, we can write

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

So in this case,

$$\int_0^1 (ax)(ax)dx = 1 \quad \text{or, } a^2 \int_0^1 x^2 dx = 1 \quad \text{or, } a^2 \times \frac{1}{3} = 1 \quad \text{or, } a = \sqrt{3}$$

∴ The expectation value of position of the particle

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

So in this case,

$$\begin{aligned} \langle x \rangle &= \int_0^1 (ax)x(ax)dx \\ &= a^2 \int_0^1 x^3 dx \\ &= a^2 \left[\frac{x^4}{4} \right]_0^1 = \frac{a^2}{4} \\ &= \frac{(\sqrt{3})^2}{4} = \frac{3}{4} \end{aligned}$$

Problem 3

Find the expectation value of x for the wave function given by $\phi(x) = Ae^{-bx}$.

[WBUT 2013]

Solution $\langle x \rangle = \int_{-\infty}^{\infty} \psi^*(x) \hat{x} \psi(x) dx$

$$\begin{aligned} &= \int_{-\infty}^{\infty} x A^2 e^{-2bx} dx = A^2 \int_{-\infty}^{\infty} x e^{-2bx} dx \\ &= 0 \end{aligned}$$

Problem 4

The normalised wave function of certain particle is $\psi(x) = \sqrt{\frac{3}{\pi}} \cos x$ where $-\frac{\pi}{2} \leq x \leq \frac{\pi}{2}$. Derive an expression for the expectation value of particle's momentum.

Solution If $\psi(x)$ is the wave function of a particle, expectation value of the particle's momentum

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

our problem, we can write

$$\begin{aligned}
 \langle p \rangle &= \int_{-\frac{\pi}{2}}^{\frac{\pi}{2}} \psi^* \left(-i\hbar \frac{\partial}{\partial x} \right) \psi dx = \int_{-\frac{\pi}{2}}^{\frac{\pi}{2}} \sqrt{\frac{3}{\pi}} \cos x \left(-i\hbar \frac{\partial}{\partial x} \right) \sqrt{\frac{3}{\pi}} \cos x dx \\
 &\geq \frac{3i\hbar}{\pi} \int_{-\frac{\pi}{2}}^{\frac{\pi}{2}} \cos x \sin x dx \\
 &= \frac{3i\hbar}{\pi} \int_{-\frac{\pi}{2}}^{\frac{\pi}{2}} \sin 2x dx \\
 &= \frac{3i\hbar}{2\pi} \int_{-\frac{\pi}{2}}^{\frac{\pi}{2}} \sin 2x dx
 \end{aligned} \quad \dots (1)$$

$$\text{let } y = 2x, \text{ so, } dx = \frac{dy}{2}$$

$$\text{let } y \rightarrow \frac{\pi}{2}, y \rightarrow \pi \text{ and when } x \rightarrow -\frac{\pi}{2}, y \rightarrow -\pi$$

Again when $x \rightarrow \frac{\pi}{2}$, $y \rightarrow \pi$ and when $x \rightarrow -\frac{\pi}{2}$, $y \rightarrow -\pi$

Again when we get from equation (1),

$$\text{Thus, we get from equation (1),} \quad \langle p \rangle = \frac{3i\hbar}{4\pi} \int_{-\pi}^{\pi} \sin y dy = -\frac{3i\hbar}{4\pi} [\cos y]_{-\pi}^{\pi} = 0$$

$\langle p \rangle = \frac{3i\hbar}{4\pi} \int_{-\pi}^{\pi} \sin y dy = -\frac{3i\hbar}{4\pi} [\cos y]_{-\pi}^{\pi} = 0$; it is expected that p_n should be non-zero. The \pm sign indicates that the particle is trapped in such a potential so that it will move back and forth. As a result its average momentum, $p_{av} = \frac{\sqrt{2mE} + (-\sqrt{2mE})}{2} = 0$

This is what we have evaluated as $\langle p \rangle = 0$.

Problem 5 The normalised wave function given by $\psi = \frac{1}{\sqrt{a\sqrt{\pi}}} \exp\left(-\frac{x^2}{2a^2} + iKx\right)$ describes a free particle in one dimension. In what region of space the particle is most likely found?

Solution If $\psi(x)$ is the wave function of a moving particle, expectation value of particle's position

$$\begin{aligned}
 \langle x \rangle &= \int_{-\infty}^{\infty} \psi^* x \psi dx = \int_{-\infty}^{\infty} \frac{1}{\sqrt{a\sqrt{\pi}}} \exp\left(-\frac{x^2}{2a^2} - iKx\right) x \frac{1}{\sqrt{a\sqrt{\pi}}} \exp\left(-\frac{x^2}{2a^2} + iKx\right) dx \\
 &= \frac{1}{a\sqrt{\pi}} \int_{-\infty}^{\infty} x e^{-\frac{x^2}{a^2}} dx \\
 &= 0
 \end{aligned}$$

\therefore The particle is most likely found on either side of origin $x = 0$.

7.9. Basic Postulates of Quantum (or Wave) Mechanics

On the basis of the wave nature of a moving particle, we can develop the wave equation for the particle. There are several ways to develop the wave equation by applying quantum concepts to various classical equations of mechanics. With the help of the following basic postulates, we can develop quantum mechanics.

The basic postulates are—

- (1) The space-time behaviour of a particle in physical system can be described by an associated wave function $\psi(x, y, z, t)$. This function and its space derivative $\left(\frac{\partial \psi}{\partial x} + \frac{\partial \psi}{\partial y} + \frac{\partial \psi}{\partial z}\right)$ are continuous, single valued and finite.
- (2) Dynamical variables (or observables) are the physically measurable properties of the particle. In quantum mechanics, each observable (physical parameter) is associated with quantum mechanical operator. The table given below shows some quantum mechanical operators.

	Variables	Symbol (Classical)	Quantum mechanical operator
(i)	Position	x, y, z	$\hat{x}, \hat{y}, \hat{z}$
(ii)	Momentum	p_x, p_y, p_z	$-i\hbar \frac{\partial}{\partial x}, -i\hbar \frac{\partial}{\partial y}, -i\hbar \frac{\partial}{\partial z}$
(iii)	Energy	E	$i\hbar \frac{\partial}{\partial t}$

- (3) The probability that the particle (with wave function ψ) will be found in the volume element dv (i.e., $(dx dy dz)$) is $\psi^* \psi dv$. Since the total probability (P) of finding the particle somewhere in the space must be equal to 1, then probability,

$$P = \int_{-\infty}^{+\infty} \psi^* \psi dv = 1$$

- (4) The expectation value of any dynamical quantity (or function) α corresponding to its operator $\hat{\alpha}$ is given by

$$\langle \alpha \rangle = \int_{-\infty}^{+\infty} \psi^* \hat{\alpha} \psi dv \quad (4)$$

- (5) The only possible value of measurement of a dynamical variable A whose operator is \hat{A} , is given by the equation

$$\hat{A} \psi = c_n \psi_n \quad (5)$$

This equation is called *eigen value equation*. Here, c_n and ψ_n are eigen values and eigen functions of quantum state n .

- (1) The expectation value for the momentum vector \vec{p} is given by

$$\langle \vec{p} \rangle = \int_{-\infty}^{+\infty} \psi^* \hat{p} \psi dv = \int_{-\infty}^{+\infty} \psi^* (-i\hbar \vec{\nabla}) \psi dv \quad [\because \hat{p} = -i\hbar \vec{\nabla}]$$

- (2) If a particle is moving in space, then its total momentum operator $\hat{p} = -i\hbar \vec{\nabla}$. So the corresponding eigen value equation is $(-i\hbar \vec{\nabla}) \psi = p_n \psi_n$, where p_n and ψ_n are eigen values and eigen functions of quantum state n .

7.10. Schrödinger's Wave Equation

Schrödinger, in 1926, considered that if a particle has wave properties (matter waves), there should be some sort of wave equation which can describe the space-time behaviour of the quantum mechanical particle (e.g., an electron).

Therefore, Schrödinger's wave equation describes the behaviour of wave function (i.e., quantum mechanical particle) associated with matter waves under different physical situations.

This wave equation can be developed both for time dependent and time independent states.

Time dependent wave equation Here the potential energy depends on time. So the wave equation describes the change of position of the particle with time.

Time independent wave equation For time independent state, the potential energy V of a particle does not depend on time explicitly. So the potential energy V or the forces $\vec{F} = -\vec{\nabla}V$ acting on this particle varies only with the position of the particle. Thus, the wave equation that can describe only the position of a particle is called time independent Schrödinger's wave equation.

7.10.1. Time Dependent Schrödinger Wave Equation

Let us consider a plane monochromatic wave ① moving along X -direction and is represented by

$$\psi(x, t) = A e^{i(kx - \omega t)} \quad \dots (7.10.1.1)$$

where angular frequency $\omega = 2\pi\nu$, (ν = frequency of the wave) and the propagation constant $k = \frac{2\pi}{\lambda}$ (λ = wavelength of the wave).

According to quantum theory,

$$\text{energy } E = h\nu = \frac{h}{2\pi} 2\pi\nu = \hbar\omega \quad \dots (7.10.1.2)$$

$$\text{and momentum, } p = \frac{h}{\lambda} = \frac{h}{2\pi} \frac{2\pi}{\lambda} = \hbar k \quad \dots (7.10.1.3)$$

Now, we want to develop time dependent Schrödinger wave equation for (i) free particle and for (ii) particle under an external force field.

For free particle If external force is not acting on a particle, the particle is called free particle. Thus, free particle has no potential energy (i.e., $V = 0$) but it has a constant momentum p (as $F = 0$ implies $\frac{dp}{dt} = 0$ i.e., $p = \text{constant}$). The total energy of a non-relativistic free particle of mass m moving along X -direction,

$$E = \frac{p^2}{2m} \quad (\text{only kinetic energy}) \quad \dots (7.10.1.4)$$

① The Schrödinger equation takes the analogy from classical wave equation $\frac{\partial^2 y}{\partial x^2} = \frac{1}{v^2} \frac{\partial^2 y}{\partial t^2}$, whose solution is $y = A e^{-i(\frac{\omega x}{v} - \omega t)}$, where v is the velocity of the wave.

Again, we know from equation (7.10.1.1), $\psi(x, t) = A e^{i(kx - \omega t)}$

$$\text{So, } \frac{\partial \psi}{\partial t} = -i\omega \psi, \text{ where } \psi = \psi(x, t)$$

$$\text{or, } i\hbar \frac{\partial \psi}{\partial t} = \hbar \omega \psi$$

$$\text{or, } i\hbar \frac{\partial \psi}{\partial t} = E \psi \quad [\because E = \hbar \omega]$$

Again, differentiating equation (7.10.1.1) twice w.r.t. x , we get

$$\frac{\partial \psi}{\partial x} = +ik\psi \quad \text{and} \quad \frac{\partial^2 \psi}{\partial x^2} = -k^2\psi$$

$$\therefore -\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} = \frac{\hbar^2 k^2}{2m} \psi$$

$$\text{or, } -\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} = \frac{p_x^2}{2m} \psi \quad [\because p_x = \hbar k] \quad \dots(7.10.1.6)$$

$$\text{or, } -\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} = E \psi \quad \left[\because E = \frac{p_x^2}{2m} \right] \quad \dots(7.10.1.7)$$

Comparing equation (7.10.1.5) and equation (7.10.1.7), we can write

$$i\hbar \frac{\partial \psi(x, t)}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2}(x, t) \quad \dots(7.10.1.8)$$

This is one dimensional time dependent Schrödinger wave equation for a free particle of mass m .

For three dimensional motion,

$\psi(\vec{r}, t) = A e^{i(\vec{k} \cdot \vec{r} - \omega t)}$; where \vec{r} = position vector of the particle. Proceeding similarly as in the above, we get 3-dimensional Schrödinger wave equation for a free particle as

$$i\hbar \frac{\partial \psi(\vec{r}, t)}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \psi(\vec{r}, t) \quad \dots(7.10.1.9)$$

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

■ Particle under an external force field

When a particle is moving along X -axis with smaller velocity compared to that of light under an external force field F , its total energy (E) is the sum of its kinetic energy and potential energy, i.e.,

$$E = \frac{p_x^2}{2m} + V(x, t) \quad \dots(7.10.1.10)$$

Multiplying both sides of equation (7.10.1.10) by the wave function $\psi(x, t)$, we get

$$\frac{p_x^2 \psi(x, t)}{2m} + V \psi(x, t) = E \psi(x, t) \quad \dots(7.10.1.11)$$

Now, after substituting the value of

$$E \psi(x, t) = i\hbar \frac{\partial}{\partial t} \psi(x, t), \text{ [from equation (7.10.1.5)]}$$

$$\text{and } \frac{p_x^2 \psi(x, t)}{2m} = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2}(x, t), \text{ [from equation (7.10.1.6)]}$$

From equation (7.10.1.11), we get

$$\frac{\hbar^2}{2m} \frac{\partial^2 \psi(x, t)}{\partial x^2} + V(x, t) = i\hbar \frac{\partial}{\partial t} \psi(x, t) \quad \dots(7.10.1.12)$$

This is the one dimensional time dependent Schrödinger's wave equation.

For a three dimensional system, we get,

$$i\hbar \frac{\partial}{\partial t} \vec{\psi}(r, t) = -\frac{\hbar^2}{2m} \left(\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} \right) + V(r, t) \vec{\psi}(r, t) \quad \dots(7.10.1.13)$$

$$i\hbar \frac{\partial}{\partial t} \vec{\psi}(r, t) = -\frac{\hbar^2}{2m} \nabla^2 \vec{\psi}(r, t) + V(r, t) \vec{\psi}(r, t) \quad \dots(7.10.1.14)$$

$$i\hbar \frac{\partial}{\partial t} \vec{\psi}(r, t) = \hat{H} \vec{\psi}(r, t)$$

where, \hat{H} = Hamiltonian operator for three dimensional motion.

$$= -\frac{\hbar^2}{2m} \nabla^2 + V(r, t)$$

The equation (7.10.1.13) or equation (7.10.1.14) is known as three dimensional time dependent Schrödinger wave equation of a moving particle in a potential field. This equation is called time dependent equation because it involves time.

Problem 1

Prove that the wave function $\psi(x, t) = A \cos(kx - \omega t)$ does not satisfy the time dependent Schrödinger wave equation for a free particle.

Solution For a free particle, the time dependent Schrödinger equation is

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} = i\hbar \frac{\partial \psi}{\partial t} \quad \dots(1)$$

Here, $\psi(x, t) = A \cos(kx - \omega t)$

$$\therefore \frac{\partial \psi}{\partial x} = -Ak \sin(kx - \omega t) \quad \text{and} \quad \frac{\partial^2 \psi}{\partial x^2} = -Ak^2 \cos(kx - \omega t) \quad \dots(2)$$

$$\therefore -\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} = \frac{\hbar^2 Ak^2}{2m} \cos(kx - \omega t)$$

Now again,

$$\psi(x, t) = A \cos(kx - \omega t)$$

$$\therefore \frac{\partial \psi}{\partial t} = A\omega \sin(kx - \omega t) \quad \dots(3)$$

$$\therefore i\hbar \frac{\partial \psi}{\partial t} = i\hbar A\omega \sin(kx - \omega t)$$

So, we have seen from equation (2) and equation (3)

$$i\hbar \frac{\partial \psi}{\partial t} \neq -\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2}$$

So, $\psi(x, t) = A \cos(kx - \omega t)$ does not satisfy the time dependent Schrödinger wave equation for a free particle.

**Problem 2**

If a system has two eigen states ψ_1 and ψ_2 with eigen values E_1 and E_2 , under what condition will linear combination ($\psi = a\psi_1 + b\psi_2$) be also an eigen state.

[WBUT 2013]

Solution We can write from the property of Hamiltonian operator,

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

where, E is the eigen value of the state ψ .

$$\text{or, } \hat{H}(a\psi_1 + b\psi_2) = E(a\psi_1 + b\psi_2) \quad \dots(1)$$

where, $\psi = a\psi_1 + b\psi_2$

$$\begin{aligned} \text{Now, } \hat{H}(a\psi_1 + b\psi_2) &= a\hat{H}\psi_1 + b\hat{H}\psi_2 \\ &= aE_1\psi_1 + bE_2\psi_2 \end{aligned} \quad \dots(2)$$

If $E_1 = E_2 = E$, we can write equation (2) as

$$\begin{aligned} \hat{H}(a\psi_1 + b\psi_2) &= aE_1\psi_1 + bE_2\psi_2 \\ &= aE\psi_1 + bE\psi_2 \\ &= E(a\psi_1 + b\psi_2) \\ &= E\psi \quad [\because \psi = a\psi_1 + b\psi_2] \end{aligned}$$

Now equation (1) and (2) will satisfy only when $E_1 = E_2 = E$, which is required condition.

Problem 3

Which of the following wave function is the solution of Schrödinger equation ?

- i A sec x, ii A tan x, iii Ae^{-x^2} , iv Ae^{x^2}

[WBUT 2007]

Solution $\psi(x)$ will be a wave function, when $\psi(x) = 0$ for $x \rightarrow \pm \infty$ (i.e., ψ must vanish at infinity).

In the above problem, $\psi(x) = Ae^{-x^2}$ is the only wave function which satisfy the above condition.

7.10.2. Time Independent Schrödinger Wave Equation; Its Solution for Eigen Value Equation

► Time independent Schrödinger wave equation

In case of time dependent Schrödinger wave equation, the potential energy (V) of a moving particle is a function of both time as well as position. But, in many cases, the potential energy of a moving particle does not depend explicitly on time.

In this case, the potential energy (or the forces that act on the particle) is a function of position \vec{r} only, i.e., $V = V(\vec{r})$.
The three dimensional time dependent Schrödinger wave equation is given by

$$\vec{i}\hbar \frac{\partial \psi(\vec{r}, t)}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \psi(\vec{r}, t) + V(\vec{r}) \psi(\vec{r}, t) \quad \dots(7.10.2.1)$$

This equation is a partial differential equation of two variables (\vec{r}, t) . When the potential energy V is a function of \vec{r} (position) only and the total energy E is constant, the equation is separable into the time independent part and time dependent part. In this case, the wave function $\psi(\vec{r}, t)$ can be written as the product of two separate functions— $\psi(\vec{r})$, a function of \vec{r} only and $f(t)$, a function of t only. Hence, we can write

$$\vec{\psi}(\vec{r}, t) = \vec{\psi}(\vec{r}) f(t) \quad \dots(7.10.2.2)$$

Substituting this in Schrödinger's wave equation (equation 7.10.1.13) we can write

$$i\hbar \vec{\psi}(\vec{r}) \frac{\partial}{\partial t} f(t) = -\frac{\hbar^2}{2m} f(t) \nabla^2 \vec{\psi}(\vec{r}) + V(\vec{r}) \vec{\psi}(\vec{r}) f(t) \quad \dots(7.10.2.3)$$

$$\text{or, } i\hbar \frac{1}{f(t)} \frac{\partial}{\partial t} f(t) = -\frac{\hbar^2}{2m} \frac{1}{\vec{\psi}(\vec{r})} \nabla^2 \vec{\psi}(\vec{r}) + V(\vec{r}) \quad \text{[dividing both sides by } \vec{\psi}(\vec{r}) f(t) \text{]}$$

The left hand side of this equation is a function of time (t) only and right hand side is a function of position (\vec{r}) only. This is only possible when they are separately equal to a constant and it is equal to E (separation constant).

Thus, we can write the right hand side of equation (7.10.2.3) as

$$-\frac{\hbar^2}{2m} \frac{1}{\vec{\psi}(\vec{r})} \nabla^2 \vec{\psi}(\vec{r}) + V(\vec{r}) = E \quad \dots(7.10.2.4)$$

$$-\frac{\hbar^2}{2m} \nabla^2 \vec{\psi}(\vec{r}) + V(\vec{r}) \vec{\psi}(\vec{r}) = E \vec{\psi}(\vec{r}) \quad \dots(7.10.2.5)$$

$$\text{or, } \nabla^2 \vec{\psi}(\vec{r}) + \frac{2m}{\hbar^2} [E - V(\vec{r})] \vec{\psi}(\vec{r}) = 0 \quad \dots(7.10.2.6)$$

This is the 3-dimensional time independent Schrödinger's wave equation.

Thus, we can write the one dimensional time independent Schrödinger's wave equation using equation (7.10.2.6) as

$$\frac{d^2 \psi(x)}{dx^2} + \frac{2m}{\hbar^2} [E - V(x)] \psi(x) = 0 \quad \dots(7.10.2.7)$$

• In that case, probability density of the particle is independent of time and the state is called stationary state.

► Solution for eigen value equation

We can get from left hand side of equation (7.10.2.3),

$$ih \frac{1}{f(t)} \frac{d}{dt} f(t) = E \quad \text{or,} \quad ih \frac{d}{dt} f(t) = E f(t)$$

$$\text{or,} \quad \frac{d}{dt} f(t) = -\frac{iE}{h} f(t) \quad \text{or,} \quad \frac{d}{f(t)} f(t) = -\frac{iE}{h} dt$$

Integrating both sides, we have

$$\ln f(t) = -\frac{iEt}{\hbar} + \ln C \quad [\text{where } C \text{ is a constant}]$$

$$\text{or,} \quad \ln \frac{f(t)}{C} = -\frac{iEt}{\hbar}$$

$$\text{or,} \quad f(t) = C e^{-\frac{iEt}{\hbar}}$$

... (7.10.2.4)

► Special Note :

The equation (7.10.2.5) can be written in the form of Hamiltonian operator (\hat{H}),

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

$$\text{or,} \quad \hat{H} \psi(\vec{r}) = E \psi(\vec{r}) \quad \text{where } \hat{H} = -\frac{\hbar^2}{2m} \vec{\nabla}^2 + V(\vec{r}) \quad \dots (1)$$

This is the eigen value equation where $\psi(\vec{r})$ and E are the eigen function and eigen value respectively.

Importance of Hamiltonian operator—

From equation (1), we see that the Hamiltonian operator of time independent Schrödinger wave equation operating on the wave function ψ produces the same function ψ multiplied by the total energy E . The eigen value E of the Hamiltonian operator is the only possible value of total energy of a quantum mechanical system.

Thus, we get from equation (7.10.2.2)

$$\therefore \psi(\vec{r}, t) = \psi(\vec{r}) C e^{-\frac{iEt}{\hbar}} \quad \dots (7.10.2.9)$$

This gives the solution of eigen value equation.

Here, $\psi(\vec{r})$ and $C e^{-\frac{iEt}{\hbar}}$ are the amplitude and phase of the wave function $\psi(\vec{r}, t)$ respectively. So the time independent form of wave equation (7.10.2.6) is sometimes known as the amplitude equation. Each solution of time independent Schrödinger equation corresponds to a definite energy. If we write, $\psi = \psi_n(\vec{r})$ as the solution for $E = E_n$, the particular solution is

$$\psi_n(\vec{r}, t) = \psi_n(\vec{r}) C e^{-\frac{iE_n t}{\hbar}} \quad \dots (7.10.2.10)$$

and it belongs to a definite energy E_n .

the probability of finding a particle

$$|\overset{\rightarrow}{\psi}_n(r, t)|^2 = \overset{\rightarrow}{\psi}_n^*(r, t) \overset{\rightarrow}{\psi}_n(r, t) = C \overset{\rightarrow}{\psi}_n(r) e^{-\frac{iE_n t}{\hbar}} C^* \overset{\rightarrow}{\psi}_n^*(r) e^{\frac{iE_n t}{\hbar}} \\ [\because \overset{\rightarrow}{\psi}_n(r) = \overset{\rightarrow}{\psi}_n^*(r) \text{ and } CC^* = 1]$$

$$|\overset{\rightarrow}{\psi}_n(r, t)|^2 = \left\{ \overset{\rightarrow}{\psi}_n(r) \right\}^2$$

or,

Hence, the probability of finding a particle does not depend upon time.

► Special Note :

Time independent Schrödinger wave equation for a particle of mass m and momentum p : For a particle of mass m moving with a velocity v, the total energy (non-relativistic) of the particle

$$E = \frac{1}{2} mv^2 + V, \text{ where } V = \text{potential energy of the particle and kinetic energy}$$

$$= \frac{1}{2} mv^2$$

or, $E = \frac{p^2}{2m} + V$, where p = momentum of the particle

$$\text{or, } E - V = \frac{p^2}{2m}$$

For a free particle $V = 0$ and in that case $E = \frac{p^2}{2m}$.

We know, time independent Schrödinger wave equation from equation (7.10.2.5)

$$\nabla^2 \overset{\rightarrow}{\psi}(r) + \frac{2m}{\hbar^2} [E - V(r)] \overset{\rightarrow}{\psi}(r) = 0$$

$$\text{or, } \nabla^2 \overset{\rightarrow}{\psi}(r) + \frac{2m}{\hbar^2} \frac{p^2}{2m} \overset{\rightarrow}{\psi}(r) = 0 \quad \left[\because \frac{p^2}{2m} = E - V \right]$$

$$\text{or, } \nabla^2 \overset{\rightarrow}{\psi}(r) + \frac{p^2}{\hbar^2} \overset{\rightarrow}{\psi}(r) = 0$$

This is Schrödinger wave equation in terms of momentum.

7.11. Physical Significance of Wave Function (ψ)

The important significances of wave function are as follows:

- ① The wave function $\psi(x, y, z, t)$ gives the space-time behaviour of each quantum mechanical particle.
- ② It measures the probability of finding a particle about a position. The quantity $|\psi|^2$ gives the probability of finding a particle per unit volume in the space (i.e., probability density in the space). Thus, the probability of finding the particle between x_1 and x_2 is $P = \int_{x_1}^{x_2} |\psi|^2 dx$.
- ③ Its magnitude is large in regions where the probability of finding the particle is high and is small in regions where the probability of finding the particle is low.
- ④ The wave function and its space derivative $\left(\frac{\partial \psi}{\partial x} + \frac{\partial \psi}{\partial y} + \frac{\partial \psi}{\partial z} \right)$ should be continuous, single valued and finite everywhere.



7.11.1. Conditions of Wave Function for a Meaningful Solution of Schrödinger Equation

The conditions (or limitations) of wave functions are—

- ① It should be the function of space and time i.e., $\psi = \psi(x, y, z, t)$
- ② The wave function ψ and its space derivatives $\frac{\partial \psi}{\partial x}, \frac{\partial \psi}{\partial y}, \frac{\partial \psi}{\partial z}$ must be continuous, single valued and finite everywhere (i.e., for all values of x, y, z).
- ③ The wave function ψ must be continuous in all regions except those regions where potential energy $V(x, y, z) = \infty$,

7.11.2. Dimension of Wave Function $\psi(x, y, z, t)$

We know, the square of the amplitude of a wave function ψ at a point gives probability density of the particle at that point.

$$\therefore |\psi(x, y, z, t)|^2 = \frac{\text{probability}}{\text{volume}}$$

$$\therefore |\psi(x, y, z, t)| = (\text{probability})^{\frac{1}{2}} (\text{volume})^{-\frac{1}{2}}$$

Since, the dimension of volume = L^3 and probability density is dimensionless.

So the dimension of $|\psi(x, y, z, t)| = L^{-\frac{3}{2}}$.

Similarly, the dimension of $\psi(x, y, z, t)$ for one dimensional motion of a particle = $L^{-\frac{1}{2}}$.

7.12. The Free Particle

If external force is not acting on a particle in a specified region of space, the particle is called free particle.

For a free particle, the force

$$F = \frac{dp}{dt} = 0 \quad \text{or, } p = \text{constant}$$

As the momentum of a free particle is constant, the kinetic energy $E = \frac{1}{2}mv^2 = \frac{m^2p^2}{2m} = \frac{p^2}{2m}$ is also constant.

According to de Broglie hypothesis, any moving material particle is associated with a matter wave. The displacement of this matter wave is represented by wave function ψ . As the energy $E = h\nu = \frac{h}{2\pi}2\pi\nu = \hbar\omega$ and momentum $p = \frac{\hbar}{\lambda} = \frac{\hbar}{2\pi}\frac{2\pi}{\lambda} = \hbar k$ are constant for a free particle, the matter wave corresponding to a free particle travelling along positive X direction is given by a complex wave function,

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

7.12.1. Schrödinger Wave Equation for a Free Particle and its Solution

As no force $F = -\frac{dV}{dx}$ is acting on a free particle, its potential energy $V = \text{constant}$ (i.e., not changing with time).

If we consider the constant potential energy (V) to be zero, the time independent Schrödinger wave equation for a free particle would be [from equation (7.10.2.7)],

$$\frac{d^2\psi}{dx^2} + \frac{2mE}{\hbar^2}\psi = 0 \quad \dots(7.12.1.1)$$

equation (7.12.1.1) can be written as

$$\frac{d^2\psi}{dx^2} + k^2\psi = 0 \quad \dots(7.12.1.2)$$

$$\frac{d^2\psi}{dx^2} + \frac{2mE}{\hbar^2}\psi = 0 \quad \dots(7.12.1.3)$$

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

where k^2 is the general solution of equation (7.12.1.2) can be written as

$$\psi(x) = Ae^{ikx} + Be^{-ikx} \quad \dots(7.12.1.4)$$

The general solution of equation (7.12.1.4) represents $\psi(x) = Ae^{ikx} + Be^{-ikx}$. Here A and B are two arbitrary constants. The first term of equation (7.12.1.4) represents that the wave travels along (+ve) X -axis whereas the 2nd term represents the wave travels along (-ve) X -axis respectively. Hence, the solution ψ is a linear combination of plane waves. The values of A and B can be find out from the boundary condition.

Properties of free particle

- ① A free particle has a definite energy and momentum.
- ② It is characterised by a complex wave function of the type $\psi(x, t) = Ae^{i(kx - \omega t)}$.

Momentum and Energy of a free particle

Momentum of a free particle is,

$$p = \frac{\hbar}{\lambda} = \hbar k$$

We know from equation (7.12.1.3), $k = \frac{\sqrt{2mE}}{\hbar}$

$$\text{or, } \hbar k = \sqrt{2mE} \quad \dots(7.12.1.5)$$

$$\text{Thus, } p = \sqrt{2mE}$$

Now, the energy of the free particle in terms of Planck's constant can be given from equation (7.12.1.3) by putting $p = \hbar k$ as

$$E = \frac{\hbar^2 k^2}{2m} \quad \dots(7.12.1.6)$$

7.13. Applications of Schrödinger Wave Equation

7.13.1. Particle in a One Dimensional Box (i.e., in an Infinitely Deep One Dimensional Potential Well)

Let us consider a free particle of rest of mass m trapped in an infinitely deep potential energy well of width L [Fig. 1]. The particle is constrained to move along straight line say X -axis. The potential energy $V(x) = 0$ everywhere except at the boundaries (i.e., $x = 0$ and $x = L$) where it is infinitely large [Fig. 2].

- ⑥ The function Ae^{ikx} when multiplied by the factor $e^{-i\omega t}$ represents a plane wave going towards the right. Similarly, the function Be^{-ikx} , when multiplied by $e^{-i\omega t}$, represents a plane wave going towards left.

Mathematically, the potential well can be expressed as

$$\left. \begin{array}{l} V(x) = 0 \text{ at } 0 < x < L \\ \approx \infty \text{ at } x \leq 0 \text{ and } x \geq L \end{array} \right\} \quad \dots (7.13.1_1)$$

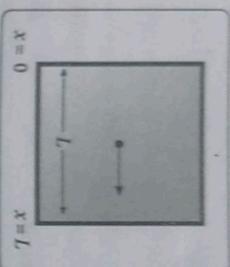


Fig. 1 ▷ One dimensional potential box

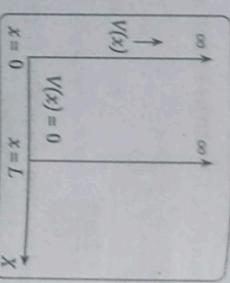


Fig. 2 ▷ The potential energy curve for the particle confined within an infinitely deep potential well with boundaries at $x = 0$ and $x = L$

► Special Note :

Here, the origin is considered at the corner of the box and the X-axis is perpendicular to the parallel opposite walls [Fig. 1] separated by a distance L . So the motion along the X-axis is confined between $x = 0$ and $x = L$. The potential energy at various points of the particle is shown in Fig. 2 and because of its appearance, it is called a rectangular or square well potential of infinite depth. Since, the motion is restricted within the range $0 < x < L$, the particle is reflected back whenever it reaches the end of the range.

As the potential well is infinitely deep, a particle cannot exist outside the well (i.e., box) and is reflected back whenever it reaches the end of the range.

Since the potential energy is independent of time, the one dimensional time independent Schrödinger's wave equation is

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

Now, the time independent Schrödinger wave equation for a free particle in the region where $V(x) = 0$ is given by

$$\frac{d^2\psi(x)}{dx^2} + \frac{2m}{\hbar^2} E \psi(x) = 0 \quad \dots (7.13.1.2)$$

$$\text{or, } \frac{d^2\psi(x)}{dx^2} + k^2 \psi(x) = 0 \quad \dots (7.13.1.3)$$

$$\text{where } k^2 = \frac{2m}{\hbar^2} E \text{ or, } E = \frac{\hbar^2 k^2}{2m}$$

The general solution of equation (7.13.1.3) is given by

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

Now from the boundary conditions

$$(I) \text{ at } x = 0, \psi(x) = 0 \text{ and (II) at } x = L, \psi(x) = 0$$

Thus, when $x = 0$, we get from equation (7.13.1.4) $A = 0$.

So the equation (7.13.1.4) becomes

$$\psi(x) = B \sin kx \quad \dots (7.13.1.5)$$



ψ vanishes at $x = L$, $\psi(x) = 0$, we have from equation (7.13.1.5)

$$\beta \sin kL = 0$$

if $\beta \neq 0$, otherwise the trial solution, $\psi(x)$ vanishes everywhere. So we can take

$$\sin kL = 0 \quad \text{or,} \quad \sin kL = \sin n\pi$$

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

...(7.13.1.7)

$\psi_n(x) = B \sin \frac{n\pi x}{L}$ Hence the permissible wave functions for this motion are given where $n = 1, 2, 3, \dots$, etc. (7.13.1.5)

$$\psi_n(x) = B \sin \frac{n\pi x}{L}$$

...(7.13.1.8)

Eigen values of energy We get the energy of the particle $E = \frac{\hbar^2 k^2}{2m}$. Now substituting $k = \frac{n\pi}{L}$ we get the corresponding energy of particle

$$E_n = \frac{\hbar^2 (n\pi)^2}{2m L^2}$$

$$E_n = \frac{n^2 \hbar^2}{8m L^2}$$

...(7.13.1.9)

Hence, energy eigen values are inversely proportional to the square of width of the potential well. It also shows, the allowed values of energy E_n depend upon the different values of n . So the particle has discrete values of energy (hence, momentum) i.e., energy is quantised. The different values of E_n are known as eigen values and the corresponding values of ψ_n are called eigen functions.

From equation (7.13.1.9) and equation (7.13.1.8), it has been seen for $n = 0$, the values of $E_0 = 0$ and $\psi_0(x) = 0$. It means that a particle cannot exist in a box if its energy is zero.

Hence, though in classical considerations, the particle can have any value of energy from zero to infinity, but quantum mechanically the particle has only discrete values of energy [Fig. 3].

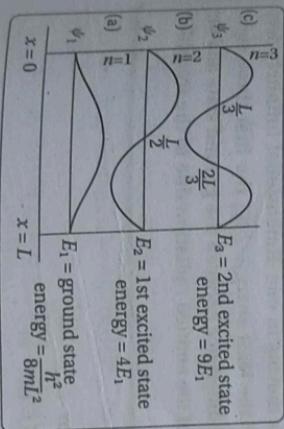


Fig. 3 ▷ The energy band corresponding to normalised wave functions for ground state and other excited state

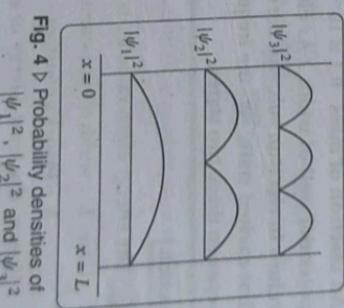


Fig. 4 ▷ Probability densities of $|\psi_1|^2$, $|\psi_2|^2$ and $|\psi_3|^2$

Q We cannot take $n = 0$ otherwise $\psi(x) = 0$ everywhere in the box for $k = 0$ even if the particle is inside the box. The negative values of n are not considered as they simply repeat the corresponding positive values of n and thus do not give the independent solutions as $|\psi_n|^2$ is always positive.



Normalised wave function (i.e., eigen function). The wave function is represented by

$$\psi_n(x) = B \sin \frac{n\pi x}{L}$$

Now, the constant B can be determined from the normalisation condition (i.e., the total probability that the particle is located somewhere in the well must be unity). Now, the probability that a particle is located in length dx is $\psi^* \psi dx$. So from normalisation condition,

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

But, $\psi_n(x) = 0$ outside the box,

$$\therefore \int_0^L \psi_n^* \psi_n(x) dx = 1 \quad \text{or, } \int_0^L B^2 \sin^2 \frac{n\pi x}{L} dx = 1 \quad [\text{as } \psi_n(x) \text{ is real, so } \psi_n^*(x) = \psi_n(x)]$$

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

$$\text{or, } \frac{B^2}{2} L = 1 \quad \left[\because \int_0^L \cos \frac{2n\pi x}{L} dx = 0\right]$$

$$\text{or, } B = \sqrt{\frac{2}{L}}$$

So the normalised wave function (or eigen function for a particle inside a well of finite width L) is

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L} \quad \dots (7.13.1.10)$$

The normalised wave functions and their corresponding probability densities are shown in [Fig 3 and 4]. From the Fig 3, it is observed that the wavefunction $\psi_n(x)$ will have $(n+1)$ nodes. In every case $|\psi_n|^2 = 0$ at $x = 0$ and $x = L$, (i.e., at the boundary of the box).

Problem 1

An electron of mass 9.1×10^{-31} kg is moving in one dimensional infinitely deep potential well of width 1 Å. Find **i** the least energy; **ii** the first three eigen values in electron volt; **iii** the energy difference between the ground state and the first excited state; **iv** the frequency of the emitted radiation due to the transition between these two states.

Solution

i The energy eigen value E_n is given by $E_n = \frac{n^2 h^2}{8mL^2}$

Here, L = width of the potential well = 10^{-10} m

h = Planck's constant = 6.63×10^{-34} J · s

Hence, the least energy or zero point energy (i.e., for $n = 1$) of an electron (i.e., the ground state energy)

$$E_1 = \frac{h^2}{8mL^2} = \frac{(6.63 \times 10^{-34})^2}{8 \times 9.1 \times 10^{-31} \times (10^{-10})^2} = \frac{43.95 \times 10^{-68}}{72.8 \times 10^{-51}} = \frac{0.603 \times 10^{-17}}{1.6 \times 10^{-19}} = 37.73 \text{ eV}$$

The first three eigen values of energy are :

- ① ground state energy, $E_1 = 37.73 \text{ eV}$
- ② 1st excited state energy, $E_2 = 2^2 E_1 = 150.95 \text{ eV}$
- ③ 2nd excited state energy, $E_3 = 3^2 E_1 = 339.63 \text{ eV}$

So the energy of the 1st excited state

$$E_2 = 2^2 E_1 = 150.95 \text{ eV} \text{ and that of ground state is } E_1 = 37.73 \text{ eV}$$

Thus, the energy difference between first excited state energy E_2 and the ground state energy E_1 is given by,

$$E_2 - E_1 = (150.95 - 37.73) \text{ eV} = 113.22 \text{ eV}$$

If ν is the frequency of the emitted radiation due to transition between above mentioned two states then,

$$\nu = \frac{E}{\hbar} = \frac{113.22 \text{ eV}}{6.63 \times 10^{-34} \text{ J} \cdot \text{s}} = \frac{113.22 \times 1.6 \times 10^{-19}}{6.63 \times 10^{-34}} = 27.3 \times 10^{15} \text{ Hz}$$

Problem 2

An electron is trapped completely in a one dimensional region of width 1 \AA . How much energy must be supplied to excite the electron from ground state to first excited state?

Solution The energy eigen value E_n is given by $E_n = \frac{n^2 h^2}{8mL^2}$

Here, L = width of the one dimensional region = $1 \text{ \AA} = 10^{-10} \text{ m}$

h = Planck's constant = $6.63 \times 10^{-34} \text{ J} \cdot \text{s}$

m = mass of electron = $9.1 \times 10^{-31} \text{ kg}$

Hence, the energy of the ground state ($n = 1$) is

$$E_1 = \frac{h^2}{8mL^2} = \frac{(6.63 \times 10^{-34})^2}{8 \times 9.1 \times 10^{-31} \times (10^{-10})^2} = \frac{0.603 \times 10^{-17}}{1.6 \times 10^{-19}} \text{ eV} = 37.68 \text{ eV}$$

The energy of the 1st excited state is

$$E_2 = 2^2 E_1 = 4 \times 37.68 \text{ eV} = 150.72 \text{ eV}$$

∴ The energy that must be supplied to excite the electron from ground state to first excited state is

$$E_2 - E_1 = (150.72 - 37.68) \text{ eV} = 113.04 \text{ eV}$$

Problem 3

Evaluate the expectation value of x for a one dimensional potential box of length L . [WBUT 2003]

Solution

For a one dimensional potential box, $\psi_n(x) = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L}$



So the expectation value

$$\begin{aligned} \langle x \rangle &= \int_0^L x |\psi_n(x)|^2 dx = \frac{2}{L} \int_0^L x \sin^2 \frac{n\pi x}{L} dx = \frac{2}{L} \int_0^L \left[\frac{1}{2} x^2 - \cos \frac{2n\pi x}{L} \right] dx \\ &= \frac{1}{L} \int_0^L x dx - \frac{1}{L} \int_0^L x \cos \frac{2n\pi x}{L} dx \\ &= \frac{1}{L} \cdot \frac{L^2}{2} - \frac{1}{L} \left[x \int_0^L \cos \frac{2n\pi x}{L} dx - \int_0^L \left[\int_0^L \cos \frac{2n\pi x}{L} dx \right] dx \right] \\ &\approx \frac{L}{2} - 0 + 0 \quad \left[: \int_0^L \cos \frac{2n\pi x}{L} dx \approx 0 \right] \\ &= \frac{L}{2} \end{aligned}$$

This implies that the expectation value of position of the particle is at the middle of the box in all quantum states. This value is independent of n and it does not give any information about the quantum state of the particle.

Problem 4

Find the probability that a particle in a one dimensional box of length L can be found in between $0.40L$ and $0.60L$ for the ground state.

Solution The wave function of a particle trapped inside a one dimensional box of length L is given by,

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

Hence, the probability of finding the particle within the range x_1 to x_2 is given by,

$$\begin{aligned} P &= \int_{x_1}^{x_2} |\psi_n(x)|^2 dx \quad [\because \psi_n(x) = \psi_n(x)] \\ &= \frac{2}{L} \int_{x_1}^{x_2} \sin^2 \frac{n\pi x}{L} dx = \left[\frac{x}{L} - \frac{1}{2n\pi} \sin \frac{2n\pi x}{L} \right]_{x_1}^{x_2} \end{aligned}$$

Here, $x_1 = 0.40L$ and $x_2 = 0.60L$

Now, for the ground state $n = 1$ and the corresponding probability,

$$\begin{aligned} P_G &= \left[\frac{x}{L} - \frac{1}{2\pi} \sin \frac{2\pi x}{L} \right]_{x_1}^{x_2} = \left[0.20 - \frac{1}{2\pi} \sin \frac{2\pi(0.60L)}{L} + \frac{1}{2\pi} \sin \frac{2\pi(0.40L)}{L} \right] \\ &= \left[0.20 - \frac{1}{2\pi} (\sin 2\pi(0.60) - \sin 2\pi(0.40)) \right] = 0.1966 \end{aligned}$$

Problem 5

The allowed values of energy of a quantum mechanical system are E_1, E_2, E_3 and E_4 with probabilities 0.2, 0.1, 0.4 and 0.3 respectively. Find the expectation value of energy for the system.

Solution The expectation value of energy for the system is given by,

$$E_{\text{expect}} = P_1 E_1 + P_2 E_2 + P_3 E_3 + P_4 E_4 = 0.2E_1 + 0.1E_2 + 0.4E_3 + 0.3E_4$$


7.13.2. Dimensions

Consider a free particle of rest mass m confined to a rectangular box [Fig.5] of sides a , b and c . The sides of the box are parallel to the X , y and Z -axes respectively. As the particle moves inside the box, no force act on the particle) inside the box, i.e., no force $V(x, y, z) = 0$ inside the box. Mathematically, it can be expressed as

$$V(r) = 0, \text{ at } 0 < x < a, 0 < y < b \text{ and } 0 < z < c \\ \infty, \text{ outside the box} \quad \dots(7.13.2.1)$$

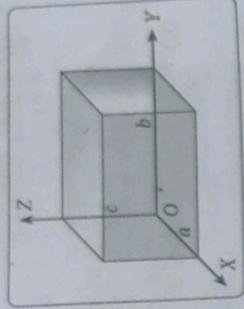


Fig. 5 ▷ Three dimensional potential box

Wave equation for the particle Since, the potential energy is independent of time, the three dimensional Schrödinger wave equation for a free particle inside the box is given by (from equation (7.10.2.6))

$$\nabla^2\psi + \frac{2m}{\hbar^2} E\psi = 0 \quad \dots(7.13.2.2)$$

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} + \frac{2mE}{\hbar^2}\psi = 0$$

Now, ψ is a function of x, y, z coordinates. So we can write

$$\psi(r) = X(x) Y(y) Z(z) = XYZ \quad (\text{say})$$

where $X(x)$, $Y(y)$ and $Z(z)$ are the function of x, y and z coordinates respectively.

Substituting this in equation (7.13.2.2), we have

$$XYZ \frac{d^2X}{dx^2} + XZ \frac{d^2Y}{dy^2} + XY \frac{d^2Z}{dz^2} + \frac{2m}{\hbar^2} EXYZ = 0 \quad \dots(7.13.2.4)$$

Here, we have used ordinary derivatives because each of the functions X , Y and Z is a function of one variable only.

Dividing equation (7.13.2.4) by XYZ we get,

$$\frac{1}{X} \frac{d^2X}{dx^2} + \frac{1}{Y} \frac{d^2Y}{dy^2} + \frac{1}{Z} \frac{d^2Z}{dz^2} + \frac{2mE}{\hbar^2} = 0 \quad \dots(7.13.2.5)$$

Since $\frac{2mE}{\hbar^2}$ is constant for a particular value of kinetic energy (as P.E. $V = 0$ inside the box) and velocity of the particle is a vector quantity, the velocity can be resolved along the three co-ordinate axes. Thus, the total energy E can be written as the sum of its three components along the three axes, i.e.,

$$E = E_x + E_y + E_z$$

So we can write equation (7.13.2.5) using equation (7.13.2.6) as

$$\left[\frac{1}{X} \frac{d^2X}{dx^2} + \frac{2mE_x}{\hbar^2} \right] + \left[\frac{1}{Y} \frac{d^2Y}{dy^2} + \frac{2mE_y}{\hbar^2} \right] + \left[\frac{1}{Z} \frac{d^2Z}{dz^2} + \frac{2mE_z}{\hbar^2} \right] = 0 \quad \dots(7.13.2.7)$$



As the three co-ordinates are independent of each other, we can separate equation (7.13.2.7) into three independent equations corresponding to each co-ordinate. Thus, the three independent equations are

$$(i) \frac{1}{X} \frac{d^2X}{dx^2} + \frac{2mE_x}{\hbar^2} = 0$$

$$\text{or, } \frac{d^2X}{dx^2} + \alpha^2 X = 0, \text{ where } \alpha^2 = \frac{2mE_x}{\hbar^2} \quad \dots (7.13.2.8)$$

$$(ii) \frac{d^2Y}{dy^2} + \beta^2 Y = 0, \text{ where } \beta^2 = \frac{2mE_y}{\hbar^2} \quad \dots (7.13.2.9)$$

$$(iii) \frac{d^2Z}{dz^2} + \gamma^2 Z = 0, \text{ where } \gamma^2 = \frac{2mE_z}{\hbar^2} \quad \dots (7.13.2.10)$$

The general solutions of equations (7.13.2.8), (7.13.2.9) and (7.13.2.10) are given by

X(x) = A_1 \cos \alpha x + B_1 \sin \alpha x \quad \dots (7.13.2.11)
$$Y(y) = A_2 \cos \beta y + B_2 \sin \beta y \quad \dots (7.13.2.12)$$

$$Z(z) = A_3 \cos \gamma z + B_3 \sin \gamma z \quad \dots (7.13.2.13)$$

where the values of constants $A_1, A_2, A_3, B_1, B_2, B_3$ can be determined from the boundary conditions.

Applying the boundary conditions so that the wave function becomes zero at the walls of the box where the potential well is infinite, we get

$$X = 0 \text{ when } x = 0 \text{ and } x = a; \quad Y = 0 \text{ when } y = 0 \text{ and } y = b;$$

$$Z = 0 \text{ when } z = 0 \text{ and } z = c$$

Now, for $x = 0, X = 0$; for $y = 0, Y = 0$ and for $z = 0, Z = 0$

So we get from equations (7.13.2.11), (7.13.2.12) and (7.13.2.13)

$$A_1 = A_2 = A_3 = 0$$

Thus, equations (7.13.2.11), (7.13.2.12) and (7.13.2.13) become

$$X(x) = B_1 \sin \alpha x \quad \dots (7.13.2.14)$$

$$Y(y) = B_2 \sin \beta y \quad \dots (7.13.2.15)$$

$$Z(z) = B_3 \sin \gamma z \quad \dots (7.13.2.16)$$

Again at $x = a, X(x) = 0$.

Thus from equation (7.13.2.14), $B_1 \sin \alpha a = 0$

or $\sin \alpha a = 0$ [$\because B \neq 0$ otherwise the trial solution $X(x) = 0$ everywhere]

$$\text{or, } \sin n_x \pi = 0 \quad \dots (7.13.2.17)$$

$$\text{or, } \alpha = \frac{n_x \pi}{a}, \text{ where } n_x = 1, 2, 3$$



Similarly by applying the boundary conditions at $y = b$, $Y(y) = 0$ and at $z = c$, $Z(z) = 0$, we get from equations (7.13.2.15) and (7.13.2.16)

$$\beta = \frac{n_y \pi}{b}, \quad \text{where } n_y = 1, 2, 3 \quad \dots(7.13.2.18)$$

$$\gamma = \frac{n_z \pi}{c}, \quad \text{where } n_z = 1, 2, 3 \quad \dots(7.13.2.19)$$

Substituting the values of α , β and γ in equation (7.13.2.14), (7.13.2.15), (7.13.2.16), (7.13.2.17) and combining all of these, we get from equation (7.13.2.3),

$$\psi_{n_x, n_y, n_z}(\vec{r}) = B_1 B_2 B_3 \sin \frac{n_x \pi x}{a} \sin \frac{n_y \pi y}{b} \sin \frac{n_z \pi z}{c} \quad \dots(7.13.2.20)$$

$$\text{or, } \psi_{n_x, n_y, n_z}(\vec{r}) = B \sin \frac{n_x \pi x}{a} \sin \frac{n_y \pi y}{b} \sin \frac{n_z \pi z}{c} \quad \dots(7.13.2.21)$$

where $B = B_1 B_2 B_3$ is normalisation constant.

Normalised wave function To find B , we shall use the normalisation condition (i.e., the probability of finding the particle anywhere inside the box is equal to one).

$$\text{So, } \int_0^a \int_0^b \int_0^c |\psi|^2 dx dy dz = 1$$

$$\text{or, } B^2 \int_0^a \int_0^b \int_0^c \sin^2 \frac{n_x \pi x}{a} \sin^2 \frac{n_y \pi y}{b} \sin^2 \frac{n_z \pi z}{c} dx dy dz = 1$$

$$\text{or, } B^2 \frac{a}{2} \cdot \frac{b}{2} \cdot \frac{c}{2} = 1 \quad \text{or, } B = \sqrt{\frac{8}{abc}} \quad \dots(7.13.2.22)$$

Thus, we can write the normalised eigen functions from equation (7.13.2.17) as

$$\psi_{n_x, n_y, n_z}(x, y, z) = \sqrt{\frac{8}{abc}} \sin \frac{n_x \pi x}{a} \sin \frac{n_y \pi y}{b} \sin \frac{n_z \pi z}{c} \quad \dots(7.13.2.22)$$

Eigen value of energy of the particle (or energy levels of the particle)

We know from equation (7.13.2.6),

$$E_{n_x, n_y, n_z} = E_x + E_y + E_z$$

$$\text{Substituting the values of } E_x = \frac{\alpha^2 \hbar^2}{2m}, E_y = \frac{\beta^2 \hbar^2}{2m} \text{ and } E_z = \frac{\gamma^2 \hbar^2}{2m} \text{ in above equation we get,}$$

$$E_{n_x, n_y, n_z} = \frac{\alpha^2 \hbar^2}{2m} + \frac{\beta^2 \hbar^2}{2m} + \frac{\gamma^2 \hbar^2}{2m}$$

$$\text{or, } E_{n_x, n_y, n_z} = \frac{\hbar^2}{2m} \left[\frac{n_x^2 \pi^2}{a^2} + \frac{n_y^2 \pi^2}{b^2} + \frac{n_z^2 \pi^2}{c^2} \right]$$

$$\text{or, } E_{n_x, n_y, n_z} = \frac{\hbar^2}{8m} \left[\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2} \right] \quad \dots(7.13.2.23)$$

For a cubical box, $a = b = c$, the equation (7.13.2.19) is reduced to

$$E_{n_x, n_y, n_z} = \frac{\hbar^2}{8ma^2} [n_x^2 + n_y^2 + n_z^2] \quad \dots(7.13.2.24)$$



Degeneracy and non-degeneracy The property of two or more independent quantum states (with different sets of quantum numbers and different eigen functions) of a particle for the same value of energy is called degeneracy. Corresponding quantum states are called degenerate states and the number of quantum states (i.e., eigen functions) are called the degree of degeneracy of the level. If there exists only one eigen function belonging to a given energy value (i.e., eigen value), the state is called non-degenerate state.

* **Examples :** For a free particle in a cubical box of side 'a' for the three sets of quantum number n_x, n_y, n_z , the expression of the eigen value is

$$E_{n_x, n_y, n_z} = \frac{\hbar^2}{8ma^2} (n_x^2 + n_y^2 + n_z^2)$$

and eigen function is

$$\psi_{n_x, n_y, n_z}(x, y, z) = \sqrt{\frac{8}{a^3}} \sin \frac{n_x \pi x}{a} \sin \frac{n_y \pi y}{a} \sin \frac{n_z \pi z}{a}$$

① In the ground state, quantum number $n_x = n_y = n_z = 1$

$$\text{So, } E_{1,1,1} = \frac{3\hbar^2}{8ma^2}$$

and the corresponding wave function (i.e., eigen function) is

$$\psi_{1,1,1} = \sqrt{\frac{8}{a^3}} \sin \frac{\pi x}{a} \sin \frac{\pi y}{a} \sin \frac{\pi z}{a}$$

Thus, the lowest energy state of a free particle in a cubical box is non-degenerate state as there is only one eigen function.

② Now, for the first excited energy state, there are three quantum states with quantum number (2, 1, 1) or (1, 2, 1) or (1, 1, 2) for which the energy is same. So, $E_{2,1,1} = E_{1,2,1} = E_{1,1,2} = \frac{6\hbar^2}{8ma^2}$

But there are three different eigen functions $\psi_{2,1,1}; \psi_{1,2,1}; \psi_{1,1,2}$. So the first excited state has threefold degeneracy.

③ Similarly, for the 2nd excited state, there are three quantum states of quantum number (2, 2, 1) or (2, 1, 2) or (1, 2, 2). In this case, we get the same energy $E_{2,2,1} = E_{2,1,2} = E_{1,2,2} = \frac{9\hbar^2}{8ma^2}$, but there are three different eigen functions. So the 2nd excited state also has threefold degeneracy.

④ For the third excited state, $n_x = n_y = n_z = 2$. In this case,

$$E_{2,2,2} = \frac{12\hbar^2}{8ma^2}$$

But, in this case we get only one eigen function for the energy $E_{2,2,2} = \frac{12\hbar^2}{8ma^2}$. Thus, this third excited state is a non-degenerate state.



Problem 1 For a free particle in a cubical box of side a for three sets of quantum number n_x, n_y and n_z , the energy is given by
find the energy of the ground state of an electron moving in a cubical box having each side equal to 1 \AA . (mass of electron = $9.1 \times 10^{-31} \text{ kg}, h = 6.63 \times 10^{-34} \text{ Js}$) [WBUT 2014]

Solution For a free particle in a cubical box of side a for three sets of quantum number n_x, n_y and n_z , the energy is given by

$$E_{n_x, n_y, n_z} = \frac{h^2}{8ma^2}(n_x^2 + n_y^2 + n_z^2)$$

For the ground state $n_x = n_y = n_z = 1$, here $a = 1\text{ \AA} = 10^{-10} \text{ m}$

$$E_{1, 1, 1} = \frac{h^2}{8ma^2}[1^2 + 1^2 + 1^2]$$

$$\begin{aligned} &= \frac{3h^2}{8ma^2} = \frac{3 \times (6.63 \times 10^{-34})^2}{8 \times (9.1 \times 10^{-31})(10^{-10})^2} \\ &= 1.81 \times 10^{-17} = 113.2 \text{ eV} \end{aligned}$$

Problem 2

Think of the nucleus as a box with a size of 10^{-14} m across, compute the energy of a neutron confined to the nucleus. Given $h = 6.62 \times 10^{-34} \cdot \text{s}$ and mass of neutron, $m = 1.6 \times 10^{-27} \text{ kg}$.

Solution If we consider the nucleus as a cubical box with size of a m across, its corresponding eigen values of energy is given (from equation 7.13.2.24) by

$$E_{n_x, n_y, n_z} = \frac{h^2}{8ma^2} [n_x^2 + n_y^2 + n_z^2]$$

Here, $a = 10^{-14} \text{ m}$

For the lowest energy state of neutron $n_x = n_y = n_z = 1$

$$\therefore E_{1, 1, 1} = \frac{h^2}{8ma^2}(3) = \frac{3 \times (6.62 \times 10^{-34})^2}{8 \times (1.6 \times 10^{-27}) \times (10^{-14})^2} = 10.27 \times 10^{-13} = 6.41 \text{ MeV}$$

For the first excited state, the corresponding energy

$$E_{2, 1, 1} = E_{1, 2, 1} = E_{1, 1, 2} = \frac{h^2}{8ma^2} [1 + 4 + 1] = \frac{h^2}{8ma^2} (6) = 12.86 \text{ MeV}$$

The 1st excited state is three fold degenerate.

For the 2nd excited state, the corresponding energy

$$E_{2, 2, 1} = E_{2, 1, 2} = E_{1, 2, 2} = \frac{h^2}{8ma^2} [4 + 4 + 1] = \frac{h^2}{8ma^2} (9) = 19.29 \text{ MeV}$$

The 2nd excited state is also 3-fold degenerate.

For the third excited state, the energy

$$E_{2, 2, 2} = \frac{h^2}{8ma^2} [4 + 4 + 4] = \frac{h^2}{8ma^2} (12) = 25.72 \text{ MeV}$$

The third excited state is non-degenerate.