Chapter 2

Concept of Wave Function

2.1 Introduction :

There is always a quantity asscociated with any type of waves, which varies periodically with space and time. In water waves, the quantity that varies periodically is the height of the water surface and in light waves, electric field and magnetic field vary with space and time. For De-broglie waves or matter waves asscociated with a moving particle, the quantity that vary with space and time, is called wave function of the particle.

The temporal and spatial evolution of a quantum mechanical particle is described by a wave function $\psi(x,t)$ for 1-D motion and $\psi(\vec{r},t)$ for 3-D motion. . It contains all possible information about the state of the system. These are known as configuration space wave function.

Condition for a physically accepted, well behaved, realistic wave function :

(i) $\psi(x,t)$ should be finite, single-valued and continuous everywhere in space.

(ii) $\frac{d\psi}{dx}$ should be continuous everywhere in space. But, $\frac{d\psi}{dx}$ may be discontinuous in some cases as follows:

(a) If the potential under which the particle is moving, has an infinite amount of discontinuity at some points,

(b) If the potential under which the particle is moving, is of dirac delta nature.

(iii) $\psi(x,t)$ should be square integrable i.e. $\int_{-\infty}^{\infty} |\psi(x,t)|^2 dx$ = finite quantity

Example 1: Which of the following wave function is acceptable as the solution of the Schrodinger equation for all values of x?

(a) $\psi(x) = A\sec x$ (b) $\psi(x) = A\tan x$ (c) $\psi(x) = Ae^{x^2}$ (d) $\psi(x) = Ae^{-x^2}$

Soln. $\psi(x) = A\sec x$ and $\psi(x) = A\tan x$ is not finite at $x = \frac{\pi}{2}$.

$\psi(x) = Ae^{x^2}$ is not finite at $x = \pm\infty$; $\psi(x) = Ae^{-x^2}$ is finite everywhere in space.

Correct option is (d)

Example 2: A ball bounces back off earth. You are asked to solve this quantum mechanically assuming the earth is an infinitely hard sphere. Consider surface of earth as the origin implying $V(0) = \infty$ and a linear potential eleswhere (i.e. $V(x) = -mgx \ \ for \ x > 0$). Which of the following wave function is physically admissible for this problem (with $k > 0$):

(a) $\psi(x) = \frac{e^{-kx}}{x}$ (b) $\psi(x) = Ae^{-kx^2}$ (c) $\psi(x) = -Axe^{kx}$ (d) $\psi(x) = Axe^{-kx^2}$

Soln. Since the earth has been taken as infinitely hard sphere, therefore the wave function of the ball will be zero for $x < 0$, non-zero for $x > 0$ and zero at infinity.

Since $\psi(x)$ should be continous everywhere, the wavefunction of the ball will be zero at x = 0.

Correct option is (d).

2.2 Physical significance of wave function :

Generally, $\psi(x,t)$ is a complex quantity. It can be multipliedd by any complex number without affecting its physical significance. In general, $\psi(x,t)$ has no direct physical significance. But the quantity $\psi^*(x,t)\psi(x,t) = |\psi(x,t)|^2$ is real, physically significant and is defined as position probability density i.e. probability of finding the particle per unit length at time '*t*'. Therefore, for 1-D motion the probability of finding the particle between x to $x + dx$ at time '*t*' is given by

$$\psi^*(x,t)\psi(x,t)dx = |\psi(x,t)|^2 dx$$

and for 3-D motion the probability of finding the particle within the volume element $d\tau$ located between $\vec{r}$ and $\vec{r} + d\vec{r}$ at time 't' is given by

$$\psi^*(\vec{r},t)\psi(\vec{r},t)d\tau = |\psi(\vec{r},t)|^2 d\tau$$

Now, $\psi(x,t)$ or $\psi(\vec{r},t)$ should be chosen such that total probability of finding the particle in the entire space should be equal to unity i.e.

$$\int_{-\infty}^{\infty} \psi^*(x,t)\psi(\vec{r},t)d\tau = \int_{-\infty}^{\infty} |\psi(x,t)|^2 d\tau = 1 \text{ (for 1-D motion)}$$

$$\int_{\substack{all\\space}} \psi^*(\vec{r},t)\psi(\vec{r},t)d\tau = \int_{\substack{all\\space}} |\psi(\vec{r},t)|^2 d\tau = 1 \text{ (for 3-D motion)}$$

This is called the normalization condition of the wave function.

If $\psi(x,t)$ or $\psi(\vec{r},t)$ is normalized at some time it remains normalized forever. This can be understood as a conservation of probability or conservation of normalization.

Method of Normalization:

Consider $\varphi(x,t)$ is an unnormalized wave function. We can construct a normalized wave function as $\psi(x,t) = N\varphi(x,t)$ where N is the normalization constant. Therefore,

$$\int_{-\infty}^{\infty} \psi^*(x,t)\psi(x,t)dx = |N^2| \int_{-\infty}^{\infty} \varphi^*(x,t)\varphi(x,t)dx = 1$$

$$\Rightarrow N = \frac{1}{\sqrt{\int_{-\infty}^{\infty} \varphi^*(x,t)\varphi(x,t)dx}}$$

Example 3: Normalize the wave function given by

$$\psi(x) = Ne^{-\alpha x} \quad (x > 0)$$
$$= Ne^{\alpha x} \quad (x < 0)$$

Soln. Normalization condition is

$$\int_{-\infty}^{\infty} \psi^* \psi dx = 1 \Rightarrow |N|^2 \left[\int_{-\infty}^{0} e^{2\alpha x} dx + \int_{0}^{\infty} e^{-2\alpha x} dx \right] = 1$$

$$\Rightarrow |N|^2 \left[\frac{1}{2\alpha} + \frac{1}{2\alpha} \right] = 1 \quad \Rightarrow N = \sqrt{\alpha}$$

Orthogonality condition of wave functions :

Two wavefunctions $\psi_m(x)$ and $\psi_n(x)$ are said to be orthogonal to each other, if

$$\int_{-\infty}^{\infty} \psi_m^*(x) \psi_n(x) dx = 0 \, (m \neq n)$$

i.e. if a particle is in the state $\psi_m(x)$, then the particle cannot be in the state $\psi_n(x)$ simultaneously together.

Orthonormality condition of wave functions :

Two wavefunctions $\psi_m(x)$ and $\psi_n(x)$ are said to be orthonormal to each other, if

$$\int_{-\infty}^{\infty} \psi_m^*(x) \psi_n(x) dx = 0 \, (m \neq n)$$

2.3 Hilbert Space :

In a vector space , the set of unit vectors $\hat{e}_1, \hat{e}_2, \hat{e}_3$...... form the orthonormal basis i.e. we can express any vector in this vector space as a linear combination of $\hat{e}_1, \hat{e}_2, \hat{e}_3$...... Similarly, a space can be defined in which a set of functions $\phi_1(x), \phi_2(x), \phi_3(x)$........ form the orthonormal basis of the coordinate system. The corresponding infinite dimensional linear vector space is called Hilbert space.

Properties of Hilbert Space:

(i) The inner product or scalar product of two functions $\psi_i(x)$ and $\psi_j(x)$ defined in the interval $a \leq x \leq b$ is defined as

$$\langle \psi_i | \psi_j \rangle = \int_a^b \psi_i^*(x) \psi_j(x) dx$$

(ii) Two functions $\psi_i(x)$ and $\psi_j(x)$ are said to be orthogonal if their inner product is zero i.e.

$$\langle \psi_i | \psi_j \rangle = \int_a^b \psi_i^*(x) \psi_j(x) dx = 0$$

This is known as orthogonality condition of two wave functions.

(iii) The norm of a function $\psi_i(x)$ is defined as

$$N = \sqrt{\langle \psi_i | \psi_i \rangle} = \left[\int_a^b \psi_i^*(x) \psi_i(x) dx \right]^{1/2}$$

(iv) A function is said to be normalized if the norm of the function is unity i.e.

$$N = \sqrt{\langle \psi_i | \psi_i \rangle} = \left[\int_a^b \psi_i^*(x) \psi_i(x) dx \right]^{1/2} = 1$$

This is known as normalization condition of a particular wave functions.

(v) Functions which are orthogonal and normalized are called orthonormal functions and they will satisfy the condition:

$$\langle \psi_i | \psi_j \rangle = \int_a^b \psi_i^*(x)\psi_j(x)\,dx = \delta_{ij}$$

(vi) A set of functions $\psi_1(x), \psi_2(x), \psi_3(x)$........ is linearly independent if there exist a relation like $c_1\psi_1(x) + c_2\psi_2(x) + c_3\psi_3(x) + ... = 0$, where all c_1, c_2, c_3.......... are zero. Otherwise, they are said to be linearly dependent. A set of linearly independent functions is complete.

2.4 Operator formalism :

An operator is a mathematical rule (or procedure) which operating on one function transforms it into another function i.e. $\hat{A}\psi(x) = \phi(x)$. Every dynamical variable in Quantum mechanics represented by a operator.

Operations	Symbol	Result of the operation
Taking the square root	$\sqrt{\ }$	$\sqrt{x^m} = x^{m/2}$
Differentiation w.r.t. x	$\frac{d}{dx}$	$\frac{d}{dx}(x^m) = mx^{m-1}$

Position Operator : $\hat{x}, \hat{y}, \hat{z}$

Momentum Operator : $\hat{p}_x = -i\hbar\frac{\partial}{\partial x},\ \hat{p}_y = -i\hbar\frac{\partial}{\partial y},\ \hat{p}_z = -i\hbar\frac{\partial}{\partial z} \Rightarrow \hat{p} = -i\hbar\vec{\nabla}$

Potential energy Operator : $\hat{V}$

Kinetic energy Operator : $\hat{K} = \frac{\hat{p}^2}{2m} = -\frac{\hbar^2}{2m}\vec{\nabla}^2$

Commutator Bracket:

The commutator bracket of two operators $\hat{A}$ and $\hat{B}$ is defined as $[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}$.

Example:

(1) $\left[\hat{x}, \frac{d}{dx}\right]\psi = \hat{x}\frac{d\psi}{dx} - \frac{d}{dx}(\hat{x}\psi) = x\frac{d\psi}{dx} - x\frac{d\psi}{dx} - \psi = -\psi \Rightarrow \left[\hat{x}, \frac{d}{dx}\right] = -1$

(2) $[\hat{x}, \hat{p}_x]\psi = \hat{x}\hat{p}_x\psi - \hat{p}_x\hat{x}\psi = -i\hbar x\frac{\partial\psi}{\partial x} + i\hbar\frac{\partial}{\partial x}(x\psi) = i\hbar\psi \Rightarrow [\hat{x}, \hat{p}_x] = i\hbar$

Similarly, $[\hat{y}, \hat{p}_y] = i\hbar$ and $[\hat{z}, \hat{p}_z] = i\hbar$

Linear Operator:

If an operator $\hat{A}$ is said to be a linear if

(i) $\hat{A}[c\psi(x)] = c\hat{A}\psi(x)$ and (ii) $\hat{A}[\psi_1(x) + \psi_2(x)] = \hat{A}\psi_1(x) + \hat{A}\psi_2(x)$

All Quantum mechanical Operators are linear in nature.

Properties of the commutator bracket:

1. $[\hat{A}, \hat{B}] = -[\hat{B}, \hat{A}]$
2. $[\hat{A}, \hat{B} + \hat{C} + \hat{D} + ...] = [\hat{A}, \hat{B}] + [\hat{A}, \hat{C}] + ...$

3. $\left[\hat{A},\hat{B}\right]^{\dagger}=\left[\hat{B}^{\dagger},\hat{A}^{\dagger}\right]$

4. $\left[\hat{A},\hat{B}\hat{C}\right]=\left[\hat{A},\hat{B}\right]\hat{C}+\hat{B}\left[\hat{A},\hat{C}\right]$

5. $\left[\hat{A},\left[\hat{B}\hat{C}\right]\right]+\left[\hat{B},\left[\hat{C},\hat{A}\right]\right]+\left[\hat{C},\left[\hat{A},\hat{B}\right]\right]=0$

6. $\left[\hat{A},f\left(\hat{A}\right)\right]=0$

7. $\left[f\left(\hat{A}\right),G\left(\hat{A}\right)\right]=0$

8. $\left[f\left(\hat{A}\right),G\left(\hat{B}\right)\right]=0$ only if $\left[\hat{A},\hat{B}\right]=0$

9. $\left[\hat{A},\hat{B}^{n}\right]=n\hat{B}^{n-1}\left[\hat{A},\hat{B}\right]$

10. $\left[\hat{A}^{n},\hat{B}\right]=n\hat{A}^{n-1}\left[\hat{A},\hat{B}\right]$

Example 4: Find the commutator bracket $\left[\left[\hat{A},\hat{B}\right],\left[\hat{B},\hat{A}\right]\right]$

Soln: $\left[\left[\hat{A},\hat{B}\right],\left[\hat{B},\hat{A}\right]\right]=\left[\hat{A},\hat{B}\right]\left[\hat{B},\hat{A}\right]-\left[\hat{B},\hat{A}\right]\left[\hat{A},\hat{B}\right]$

$$=\left(\hat{A}\hat{B}-\hat{B}\hat{A}\right)\left(\hat{B}\hat{A}-\hat{A}\hat{B}\right)-\left(\hat{B}\hat{A}-\hat{A}\hat{B}\right)\left(\hat{A}\hat{B}-\hat{B}\hat{A}\right)$$

$$=\hat{A}\hat{B}\hat{B}\hat{A}-\hat{A}\hat{B}\hat{A}\hat{B}-\hat{B}\hat{A}\hat{B}\hat{A}+\hat{B}\hat{A}\hat{A}\hat{B}-\hat{B}\hat{A}\hat{A}\hat{B}+\hat{A}\hat{B}\hat{A}\hat{B}+\hat{B}\hat{A}\hat{B}\hat{A}-\hat{A}\hat{B}\hat{B}\hat{A}=0$$

Example 5: Find the commutator bracket $\left[x^{2},p^{2}\right]$.

Soln: $\left[x^{2},p^{2}\right]=\left[x^{2},pp\right]=\left[x^{2},p\right]p+p\left[x^{2},p\right]=2x[x,p](p)+(p)2x[x,p]=2i\hbar(xp+px)$

Example 6: If $\hat{H}=\frac{p^{2}}{2m}+V(x)$, then calculate $\left[x,\left[x,\hat{H}\right]\right]$.

Soln: $\left[x,\hat{H}\right]=\left[x,\frac{p^{2}}{2m}\right]+\left[x,V(x)\right]=\frac{1}{2m}\left[x,p^{2}\right]+0=\frac{1}{2m}2p[x,p]=\frac{i\hbar}{m}p$

$$\left[x,\left[x,\hat{H}\right]\right]=\left[x,\frac{i\hbar}{m}p\right]=\frac{i\hbar}{m}[x,p]=-\frac{\hbar^{2}}{m}$$

Eigenvalues and Eigenfunctions:

If an operator $\hat{A}$ operating on a function $\psi_{n}(x)$ gives $\hat{A}\psi_{n}(x)=\lambda\psi_{n}(x)$, then $\psi_{n}(x)$ is called the eigenfunction of $\hat{A}$ corresponding to eigenvalue λ and the above equation is known as eigenvalue equation of operator $\hat{A}$.

Example: $\hat{A}=\frac{d^{2}}{dx^{2}}$ and $\psi_{n}(x)=ae^{-2x}\Rightarrow\hat{A}\psi_{n}(x)=\frac{d^{2}}{dx^{2}}\left(ae^{-2x}\right)=4ae^{-2x}=4\psi_{n}(x)$

$\psi_{n}(x)$ is an eigenfunction of $\hat{A}$ corresponding to eigenvalue 4.

If the commutator bracket of two operators $\hat{A}$ and $\hat{B}$ is equal to zero i.e. $\left[\hat{A},\hat{B}\right]=0$, then the physical observables corresponding to these operators are simultaneously accurately measurable and they have a complete set of simultaneous eigenfunctions.

Example 7: The operator $\left(x+\frac{d}{dx}\right)$ has the eigenvalue α. Determine the corresponding wavefunction.

Soln: Eigenvalue equation: $\left(x+\frac{d}{dx}\right)\psi=\alpha\psi\Rightarrow\frac{d\psi}{dx}=(\alpha-x)\psi\Rightarrow\int\frac{d\psi}{\psi}=\int(\alpha-x)dx$

$$\Rightarrow \ln\psi = \left(\alpha x - \frac{x^2}{2}\right) + \ln\psi_0 \Rightarrow \psi = \psi_0 \exp\left(\alpha x - \frac{x^2}{2}\right)$$

Example 8: Find the constant B which makes e^{-ax^2} an eigenfunction of the operator $\left(\frac{d^2}{dx^2} - Bx^2\right)$.

What is the corresponding eigenvalue?

Soln: $\left(\frac{d^2}{dx^2} - Bx^2\right)e^{-ax^2} = \left(4a^2x^2 - 2a + Bx^2\right)e^{-ax^2}$

For e^{-ax^2} to be eigenfunction of the operator $\left(\frac{d^2}{dx^2} - Bx^2\right)$, then the eigenvalue

$\left(4a^2x^2 - 2a - Bx^2\right)$ must be independent of x i.e. $\left(4a^2 - B\right) = 0 \Rightarrow B = 4a^2$

Therefore, $\left(\frac{d^2}{dx^2} - Bx^2\right)e^{-ax^2} = -2ae^{-ax^2}$; Thus the eigenvalue of the operator is (-2a).

Hermitian operator:

A operator $\hat{A}$ is said to be hermitian if $\hat{A}^\dagger = \hat{A}$ and its should satisfy the following relation:

Dirac representation: $\left(\langle\phi|\hat{A}|\psi\rangle\right)^\dagger = \langle\psi|\hat{A}^\dagger|\phi\rangle = \langle\psi|\hat{A}|\phi\rangle$

Schrodinger representation: $\left(\phi, \hat{A}\psi\right) = \left(\hat{A}\phi, \psi\right) \Rightarrow \int \phi^*\hat{A}\psi\, d\tau = \int \left(\hat{A}\phi\right)^*\psi\, d\tau$

Properties:

(1) Eigenvalues of hermitian operators are real.
(2) Eigenfunctions corresponding to different eigenvalues of a hermitian operator are orthogonal.
(3) All physical observable in quantum mechanics are represented by hermitian operators.

Example: $\left(\phi, \hat{p}_x\psi\right) = \int_{-\infty}^{\infty}\phi^*\left(-i\hbar\frac{\partial}{\partial x}\right)\psi\, dx = \int_{-\infty}^{\infty}\phi^*\left(-i\hbar\frac{\partial\psi}{\partial x}\right)dx$

$$= -i\hbar\left[\phi^*\psi\right]_{-\infty}^{\infty} + i\hbar\int_{-\infty}^{\infty}\left(\frac{d\phi^*}{dx}\right)\psi\, dx \quad = -i\hbar\int_{-\infty}^{\infty}\left(\frac{d\phi^*}{dx}\right)\psi\, dx = \int_{-\infty}^{\infty}\hat{p}_x^*\phi^*\psi\, dx$$

Hence, the momentum operator $\hat{p}_x$ is hermitian in nature.

Similarly, we can see that $\frac{\partial}{\partial x}$ is anti-hermitian i.e. $\left[\frac{\partial}{\partial x}\right]^\dagger = -\frac{\partial}{\partial x}$

Projection operator:

A operator is said to be projection operator if $\hat{A}^\dagger = \hat{A}$ and $\hat{A}^2 = \hat{A}$

Properties:

(1) Eigenvalues of a projection operator is 0 and 1.

(2) Product of two projection operators is also a projection operator if $\left[\hat{p}_1, \hat{p}_2\right] = 0$

(3) Sum of two projection operator is a projection operator if $\left\{\hat{p}_1, \hat{p}_2\right\} = 0$

Unitary Operator:

An operator $\hat{A}$ is said to be unitary if $\hat{A}^\dagger = \hat{A}^{-1}$

Parity Opertor:

Parity opeartor corresponds to space reflection about the origin i.e $\hat{P}\psi(x) = \psi(-x)$

In general, $\hat{P}\psi(\vec{r}) = \psi(-\vec{r})$; where $\vec{r} = x\hat{i} + y\hat{j} + z\hat{k}$ and $-\vec{r} = -x\hat{i} - y\hat{j} - z\hat{k}$

When parity operator acts on a wavefunction, the following changes take place in various co-ordinate system:

(i) Cartesian co-ordinate system: $x \to -x,\ y \to -y,\ z \to -z$

(ii) Spherical polar co-ordinate system : $r \to r, \theta \to \pi - \theta, \phi \to \pi + \phi$

(iii) Cyllindrical co-ordiante system: $\rho \to \rho, \phi \to \pi + \phi, z \to -z$

Properties:

(1) Eigenvalues of the parity operator is 1, -1.

$\hat{P}\psi(x) = \psi(-x) = \psi(x) \to$ even parity . $\hat{P}\psi(x) = \psi(-x) = -\psi(x) \to$ odd parity

(2) Parity operator is hermitian in nature

(3) Parity operator commutes with hamiltonian operator if the potential under which particle is moving i.e. V(x) is symmetric in nature.

Example 9: Let, $N = \hat{b}^\dagger\hat{b}$ where the operator $\hat{b}$ satisfies the relation $\hat{b}\hat{b}^\dagger + \hat{b}^\dagger\hat{b} = 1$ and $\hat{b}^2 = \left(\hat{b}^\dagger\right)^2 = 0$; then eigenvalues of N are

(a) +ve and –ve integers (b) all +ve integers (c) ± 1 and 0 only (d) 0 and 1 only

Soln: $\hat{N}|\psi\rangle = \lambda|\psi\rangle \Rightarrow \hat{b}^\dagger\hat{b}|\psi\rangle = \lambda|\psi\rangle \quad \Rightarrow \left(\hat{b}^\dagger\hat{b}\right)^2|\psi\rangle = \lambda^2|\psi\rangle$

$\Rightarrow \hat{b}^\dagger\hat{b}\hat{b}^\dagger\hat{b}|\psi\rangle = \lambda^2|\psi\rangle \Rightarrow \hat{b}^\dagger\left(1 - \hat{b}^\dagger\hat{b}\right)\hat{b}|\psi\rangle = \lambda^2|\psi\rangle$

$\Rightarrow \hat{b}^\dagger\hat{b} - \hat{b}^\dagger\hat{b}^\dagger\hat{b}\hat{b}|\psi\rangle = \lambda^2|\psi\rangle \Rightarrow \hat{b}^\dagger\hat{b}|\psi\rangle = \lambda^2|\psi\rangle \Rightarrow \lambda|\psi\rangle = \lambda^2|\psi\rangle \Rightarrow \lambda = 0, 1$

Example 10: Let the wave function of a particle of mass 'm' at a given instant be $\psi(x) = Ae^{-x^2/a^2}$.

What will be the function $\vec{K}\psi(x)$ where 'K' is the kinetic energy? Is this wave function an eigenfunction of kinetic energy?

Soln. The kinetic energy operator is $K = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}$. Thus,

$$K\psi(x) = -\frac{\hbar^2}{2m}\frac{d^2}{dx}\left(Ae^{-x^2/a^2}\right) = -\frac{\hbar^2}{2m}\frac{d}{dx}\left[-\frac{2A}{a^2}xe^{-x^2/a^2}\right]$$

$$= -\frac{\hbar^2}{2m}\frac{d}{dx}\left[-\frac{2A}{a^2}xe^{-x^2/a^2}\right] = \frac{2A\hbar^2}{2ma^2}\left[x\left(\frac{-2x}{a^2}e^{-x^2/a^2}\right) + e^{-x^2/a^2}\right] = \frac{A\hbar^2}{ma^2}\left(1 - \frac{2x^2}{a^2}\right)e^{-x^2/a^2}$$

This is not an eigenfunction of kinetic energy.

Example 11: An operator A is defined as $A\psi(x) = \psi^*(x)\psi(x)$. Is this a linear operator?

Soln. For the given operator,

$$A\left[\psi_1(x) + \psi_2(x)\right] = \left[\psi_1(x) + \psi_2(x)\right]^*\left[\psi_1(x) + \psi_2(x)\right]$$

$$= \left[\psi^*{}_1(x) + \psi^*{}_2(x)\right]\left[\psi_1(x) + \psi_2(x)\right]$$

$$= \psi^*{}_1(x)\psi_1(x) + \psi^*{}_2(x)\psi_2(x) + \psi^*{}_1(x)\psi_2(x) + \psi^*{}_2(x)\psi_1(x)$$

and $A\psi_1(x)+A\psi_2(x)=\psi^*{}_1(x)\psi_1(x)+\psi^*{}_2(x)\psi_1(x)$

Thus, $A[\psi_1(x)+_2(x)]=\psi^*{}_1(x)+A\psi_2(x)$ and hence A is not a linear operator.

Example 12. Prove that $[Xp_x, H]=\frac{i\hbar}{m}p_x^2+X[p_x,V]$ where $H=\frac{p_x^2}{2m}+V$, and V is potential energy operator.

Soln. $[Xp_x, H]=X[p_x,H]+[X,H]p_x = X\left[p_x,\frac{p_x^2}{2m}+V\right]+\left[X,\frac{p_x^2}{2m}+V\right]p_x$

$$=X[p_x,V]+\frac{1}{2m}\{p_x[X,p_x]+[X,p_x]p_x\}p_x$$

$$=X[p_x,V]+\frac{1}{2m}(2i\hbar p_x)p_x=\frac{i\hbar}{m}p_x^2+X[p_x,V]$$

Example 13. $|\phi_1\rangle$ and $|\phi_2\rangle$ be two ortonormal state vectors. Let $A=|\phi_1\rangle\langle\phi_2|+|\phi_2\rangle\langle\phi_1|$. Is a projection operator?

Soln. $A^\dagger=[|\phi_1\rangle\langle\phi_2|+|\phi_2\rangle\langle\phi_1|]^\dagger=[|\phi_1\rangle\langle\phi_2|]^\dagger+[|\phi_2\rangle\langle\phi_1|]^\dagger=|\phi_2\rangle\langle\phi_1|+|\phi_1\rangle\langle\phi_2|=A$

Hence, A is hermitian.

Now, $A^2=[|\phi_1\rangle\langle\phi_2|+|\phi_2\rangle\langle\phi_1|]+[|\phi_1\rangle\langle\phi_2|+|\phi_2\rangle\langle\phi_1|]$

$$=|\phi_1\rangle\langle\phi_2|[|\phi_1\rangle|\phi_2\rangle+|\phi_2\rangle\langle\phi_1|]+\langle\phi_2|\langle\phi_1|[|\phi_1\rangle\langle\phi_2|+|\phi_2\rangle\langle\phi_1|]$$

$$=[|\phi_1\rangle\langle\phi_2|\phi_1\rangle\langle\phi_2|+|\phi_1\rangle\langle\phi_2|\phi_2\rangle\langle\phi_1|]+[|\phi_2\rangle\langle\phi_1|\phi_1\rangle+|\phi_2\rangle\langle\phi_1|\phi_2\rangle\langle\phi_1|]$$

Since, $|\phi_1\rangle$ and $|\phi_2\rangle$ are orthonormal,

$$A^2=|\phi_1\rangle\langle\phi_1|+|\phi_2\rangle\langle\phi_2|\neq A$$

Therefore, A is not a projection operator.

Example 14. Prove that $\frac{d}{dt}\langle x^2\rangle=\frac{1}{m}\langle Xp_x+p_xX\rangle$

Soln. $\frac{d}{dt}\langle x^2\rangle=\frac{1}{i\hbar}\langle[X^2,H]\rangle=\frac{1}{i\hbar}\left\langle\left[X^2,\frac{p_x^2}{2m}+V(x)\right]\right\rangle$

$$=\frac{1}{2mi\hbar}\langle[X^2,p_x^2]\rangle=\frac{1}{2mi\hbar}\langle p_x[X^2,p_x]+[X^2,p_x]p_x\rangle$$

$$=\frac{1}{2mi\hbar}\langle p_x(2i\hbar X)+(2i\hbar X)p_x\rangle=\frac{1}{m}\langle p_xX+Xp_x\rangle=\frac{1}{m}\langle Xp_x+p_xX\rangle$$

Example 15. Prove that the operators $i(d/dx)$ and d^2/dx^2 are Hermitian.

Soln. $\int_{-\infty}^{\infty}\psi_m^*\left(i\frac{d}{dx}\right)\psi_n dx=i[\psi_m^*\psi_n]_{-\infty}^{\infty}-i\int_{-\infty}^{\infty}\psi_n\frac{d}{dx}\psi_m^* dx=\int_{-\infty}^{\infty}\left(i\frac{d}{dx}\psi_m\right)^*\psi_n dx$

Therefore, id/dx is Hermitian.

$$\int_{-\infty}^{\infty}\psi_m^*\frac{d^2\psi_n}{dx^2}dx=\left[\psi_m^*\frac{d\psi_n}{dx}\right]_{-\infty}^{\infty}-\int_{-\infty}^{\infty}\frac{d\psi_n}{dx}\frac{d\psi_m^*}{dx}dx$$

$$= \left[\frac{d\psi_m^*}{dx} \psi_n \right]_{-\infty}^{\infty} + \int_{-\infty}^{\infty} \psi_n \frac{d^2\psi_m^*}{dx^2} dx = \int_{-\infty}^{\infty} \frac{d^2\psi_m^*}{dx^2} \psi_n dx$$

Thus, d^2/dx^2 is Hermitian.

Example 16: Find the following commutation relations:

(i) $\left[\frac{\partial}{\partial x}, \frac{\partial^2}{\partial x^2} \right]$ (ii) $\left[\frac{\partial}{\partial x}, F(x) \right]$

Soln. (i) $\left[\frac{\partial}{\partial x}, \frac{\partial^2}{\partial x^2} \right]\psi = \left(\frac{\partial}{\partial x}\frac{\partial^2}{\partial x^2} - \frac{\partial^2}{\partial x^2}\frac{\partial}{\partial x} \right)\psi = \left(\frac{\partial^3}{\partial x^3} - \frac{\partial^3}{\partial x^3} \right)\psi = 0$

(iii) $\left[\frac{\partial}{\partial x}, F(x) \right]\psi = \frac{\partial}{\partial x}(F\psi) - F\frac{\partial}{\partial x}\psi = \frac{\partial F}{\partial x}\psi + F\frac{\partial \psi}{\partial x} - F\frac{\partial \psi}{\partial x} = \frac{\partial F}{\partial x}\psi$

Thus, $\left[\frac{\partial}{\partial x}, F(x) \right] = \frac{\partial F}{\partial x}$

Example 17: Find the equivalence of the following operators:

(i) $\left(\frac{d}{dx} + x \right)\left(\frac{d}{dx} + x \right)$ (ii) $\left(\frac{d}{dx} + x \right)\left(\frac{d}{dx} - x \right)$

Soln. (i) $\left(\frac{d}{dx} + x \right)\left(\frac{d}{dx} + x \right)\psi(x) = \left(\frac{d}{dx} + x \right)\left(\frac{d\psi}{dx} + x\psi \right)$

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

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

(ii) Similarly, $\left(\frac{d}{dx} + x \right)\left(\frac{d}{dx} - x \right) = \frac{d^2}{dx^2} - x^2 - 1$

Example 18. By what factors do the operators $(x^2 p_x^2 + p_x^2 x^2)$ and $1/2(xp_x + p_x x)^2$ differ?

Soln. $(x^2 p_x^2 + p_x^2 x^2) f = -\hbar^2 \left[x^2 \frac{\partial^2 f}{\partial x^2} + \frac{\partial^2 (x^2 f)}{\partial x^2} \right]$

$$= -\hbar^2 x^2 \frac{\partial^2 f}{\partial x^2} - \hbar^2 \frac{\partial}{\partial x}\frac{\partial (x^2 f)}{\partial x} = -\hbar^2 x^2 \frac{\partial^2 f}{\partial x^2} - \hbar^2 \frac{\partial}{\partial x}\left(2xf + x^2 \frac{\partial f}{\partial x} \right)$$

$$= -\hbar^2 \left(x^2 \frac{\partial^2 f}{\partial x^2} + 2f + 2x\frac{\partial f}{\partial x} + x^2 \frac{\partial^2 f}{\partial x^2} + 2x\frac{\partial f}{\partial x} \right) = -\hbar^2 \left(2x^2 \frac{\partial^2}{\partial x^2} + 4x\frac{\partial}{\partial x} + 2 \right) f$$

$$\frac{1}{2}(xp_x + p_x x)^2 f = -\frac{i\hbar}{2}(xp_x + p_x x)\left[x\frac{\partial f}{\partial x} + \frac{\partial (xf)}{\partial x} \right]$$

$$= -\frac{i\hbar}{2}(xp_x + p_x x)\left(2x\frac{\partial f}{\partial x} + f\right)$$

$$= -\frac{\hbar^2}{2}\left[x\frac{\partial}{\partial x}\left(2x\frac{\partial f}{\partial x}\right) + x\frac{\partial f}{\partial x} + \frac{\partial}{dx}\left(2x^2\frac{\partial f}{\partial x}\right) + \frac{\partial(xf)}{\partial x}\right]$$

$$= -\frac{\hbar^2}{2}\left(2x^2\frac{\partial^2 f}{\partial x^2} + 2x\frac{\partial f}{\partial x} + x\frac{\partial f}{\partial x} + 2x^2\frac{\partial^2 f}{\partial x^2} + 4x\frac{\partial f}{\partial x} + x\frac{\partial f}{\partial x} + f\right)$$

$$= -\frac{\hbar^2}{2}\left(8x\frac{\partial f}{\partial x} + 2x^2\frac{\partial^2 f}{\partial x^2} + f\right) = -\hbar^2\left(2x^2\frac{\partial^2}{\partial x^2} + 4x\frac{\partial}{\partial x} + \frac{1}{2}\right)f$$

The two operators differ by a term $-(3/2)\hbar^2$

Example 19. Find the eigenvalues and eigenfunctions of the operator d/dx.

Soln. Eigenvalue equation: $\frac{d}{dx}\psi(x) = k\psi(x)$ (where k is the eigenvalue and $\psi(x)$ is the eigenfunction)

$$\Rightarrow \frac{d\psi}{\psi} = kdx \quad \Rightarrow \psi = Ce^{kx}.$$

Case 1: k is a real positive quantity, ψ is not an acceptable function since it tends to ∞ or $-\infty$ as $x \to \infty$ or $-\infty$.

Case 2: k is purely imaginary (say ia), then $\psi = Ce^{iax}$ which will be finite for all values of x.

Hence, $y = ce^{kx}$ is the eigenfunction of the operator d/dx with eigenvalues $k = ia$, where a is real.

Expectation value of dynamic variables:

It is defined as the average of the result of a large number of independent measurements of a physical observable on the same system.

$$\langle\hat{A}\rangle = \frac{\int_{-\infty}^{\infty}\psi^*\hat{A}\psi\,dx}{\int_{-\infty}^{\infty}\psi^*\psi\,dx} = \frac{\langle\psi|\hat{A}|\psi\rangle}{\langle\psi|\psi\rangle}$$

Note:

(1) If the state of the particle is an eigenfunction of the operator $\hat{A}$, then the expectation value of the physical observable corresponding to $\hat{A}$ will be equal to the eigenvalue of $\hat{A}$ corresponding to the state of the particle.

(2) The state of the particle is given as:

$$|\psi\rangle = C_1|\phi_1\rangle + C_2|\phi_2\rangle + C_3|\phi_3\rangle + \ldots\ldots\ldots\ldots\ldots\ldots = \sum_n C_n|\phi_n\rangle$$

where $|\phi_1\rangle, |\phi_2\rangle$.......... are the eigenfunction of the operator $\hat{A}$, then expectation value of the the physical observable corresponding to $\hat{A}$ will be

$$\langle\hat{A}\rangle = \sum_n |C_n|^2 \lambda_n$$

where λ_n are the eigenvalues of operator $\hat{A}$ corresponding to $|\phi_n\rangle$.

Example 20: A particle of mass 'm' is confined in a 1-D box from $x=-2L$ to $x=2L$. The wave function of the particle in this state is $\psi(x)=\psi_0\cos\left(\frac{\pi x}{4L}\right)$

(i) Find the normalization factor.

(ii) The expectation value of P^2 in this state.

Soln. (i) $\int_{-\infty}^{\infty}\psi^*\psi\,dx=1 \quad\Rightarrow |\psi_0|^2\int_{-2L}^{2L}\cos^2\left(\frac{\pi x}{4L}\right)dx=1 \quad\Rightarrow |\psi_0|^2\int_{-2L}^{2L}\frac{1}{2}\left(1+\cos\frac{2\pi x}{4L}\right)dx$

$$\Rightarrow\frac{|\psi_0|^2}{2}\left[x-\sin\left(\frac{2\pi x}{4L}\right)\times\frac{4L}{2\pi}\right]_{-2L}^{+2L}=1\Rightarrow\frac{|\psi_0|^2}{2}\left[(2L+2L)\right]=1\Rightarrow|\psi_0|=\frac{1}{\sqrt{2L}}$$

$$\left\langle P^2\right\rangle=\int_{-2L}^{2L}\psi^*\left[-\hbar^2\frac{d^2}{dx^2}\right]\psi\,dx\;=\;=\frac{\hbar^2}{2L}\int_{-2L}^{2L}\cos^2\left(\frac{\pi x}{4L}\right)\left(\frac{\pi}{4L}\right)^2dx$$

$$=\frac{\hbar^2}{2L}\cdot\frac{\pi^2}{16L^2}\frac{1}{2}\int_{-2L}^{+2L}\left(1+\cos\frac{\pi x}{2L}\right)dx=\frac{\pi^2\hbar^2}{32L^3}\int_0^{2L}\left(1+\cos\frac{\pi x}{2L}\right)dx=\frac{\pi^2\hbar^2}{16L^2}$$

Example 21: Find the expected value of position and momentum of a particle whose wave function is $\psi(x)=e^{-x^2/a^2+ikx}$ in all space

Soln. Expected position of the particle $\langle x\rangle=\dfrac{\int_{-\infty}^{\infty}\psi^*x\psi\,dx}{\int_{-\infty}^{\infty}\psi^*\psi\,dx}=\dfrac{\int_{-\infty}^{\infty}e^{-2x^2/a^2}.xdx}{\int_{-\infty}^{\infty}e^{-2x^2/a^2}dx}=0$

Expected momentum of the particle

$$\langle p\rangle=\frac{\int_{-\infty}^{\infty}e^{-x^2/a^2-ikx}\left(-i\hbar\frac{\partial}{\partial x}\right)e^{-x^2/a^2+ikx}dx}{\int_{-\infty}^{\infty}e^{-2x^2/a^2}dx}=-i\hbar\frac{\int_{-\infty}^{\infty}e^{-2x^2/a^2}\left(-\frac{2x}{a^2}+ik\right)dx}{e^{-2x^2/a^2}dx}=\hbar k\frac{\int_{-\infty}^{\infty}e^{-2x^2/a^2}dx}{\int_{-\infty}^{\infty}e^{-2x^2/a^2}dx}=\hbar k$$

Example 22. The wavefunction of a particle in a state is $\psi=N\exp(-x^2/2\alpha)$, where $N=(1/\pi\alpha)^{1/4}$. Evaluate $(\Delta x)(\Delta p)$.

Soln. Since ψ is symmetrical about $x=0,\langle x\rangle=0$

$$\left\langle x^2\right\rangle=N^2\int_{-\infty}^{\infty}x^2\exp\left(\frac{-x^2}{\alpha}\right)dx=\frac{\alpha}{2}$$

Since, ψ is a real wave function, $\langle p\rangle=0$

$$\left\langle p^2\right\rangle=(-i\hbar)^2N^2\int_{-\infty}^{\infty}\exp\left(\frac{-x^2}{2\alpha}\right)\frac{d^2}{dx^2}\exp\left(\frac{-x^2}{2\alpha}\right)dx$$

$$=\frac{\hbar^2N^2}{\alpha}\int_{-\infty}^{\infty}\exp\left(\frac{-x^2}{\alpha}\right)dx-\frac{\hbar^2N^2}{\alpha^2}\int_{-\infty}^{\infty}x^2\exp\left(\frac{-x^2}{\alpha}\right)dx$$

$$= \frac{\hbar^2}{\alpha} - \frac{\hbar^2}{2\alpha} = \frac{\hbar^2}{2\alpha}$$

Therefore, $\Delta x \Delta p = \left[\sqrt{\langle x^2\rangle - \langle x\rangle^2}\right]\left[\sqrt{\langle p^2\rangle - \langle p\rangle^2}\right] = \sqrt{\frac{\alpha}{2}}\sqrt{\frac{\hbar^2}{2\alpha}} = \frac{\hbar}{2}$

Example 23. The Hamiltonian operator of a system is $H = -(d^2/dx^2) + x^2$. Show that $Nx\exp(-x^2/2)$ is an eigenfunction of H and determine the eigenvalue. Also evaluate N by normalization of the function.

Soln. $\psi = Nx\exp(-x^2/2), N$ being a constant

$$H\psi = \left(-\frac{d^2}{dx^2} + x^2\right)Nx\exp\left(-\frac{x^2}{2}\right) = Nx^3\exp\left(-\frac{x^2}{2}\right)\frac{d}{dx}\left[\exp\left(-\frac{x^2}{2}\right) - x^2\exp\left(-\frac{x^2}{2}\right)\right]$$

$$= 3Nx\exp\left(-\frac{x^2}{2}\right) = 3\psi$$

Thus, the eigenvalue of H is 3. The normalization condition gives

$$N^2\int_{-\infty}^{\infty} x^2 e^{-x^2}dx = 1 \Rightarrow N^2\frac{\sqrt{\pi}}{2} = 1 \Rightarrow N = \left(\frac{2}{\sqrt{\pi}}\right)^{1/2}$$

The normalized function $\psi = \left(\frac{2}{\sqrt{\pi}}\right)^{1/2} x\exp\left(-\frac{x^2}{2}\right)$

Example 24. Consider the wave function $\psi(x) = A\exp\left(-\frac{x^2}{a^2}\right)\exp(ikx)$, where A is a real constant.

(i) Find the value of A, (ii) calculate $\langle p\rangle$ for this wave function.

Soln. (i) Normalization condition: $A^2\int_{-\infty}^{\infty}\exp\left(-\frac{2x^2}{a^2}\right)dx = 1$

$$\Rightarrow A^2\left(\frac{\pi}{2/a^2}\right)^{1/2} = 1 \quad \Rightarrow A = \sqrt{\frac{2}{\pi}}a$$

(ii) $\langle p\rangle = \int \psi^*\left(-i\hbar\frac{d}{dx}\right)\psi dx = (-i\hbar)A^2\int_{-\infty}^{\infty}\exp\left(-\frac{x^2}{a^2}\right)e^{-ikx}\left(-\frac{2x}{a^2} + ik\right)\exp\left(-\frac{x^2}{a^2}\right)e^{-ikx}dx$

$$= (-i\hbar)\left(-\frac{2}{a^2}\right)\int_{-\infty}^{\infty}\exp\left(\frac{-2x^2}{a^2}\right)xdx + (-i\hbar)(ik)A^2\int_{-\infty}^{\infty}\exp\left(\frac{-2x^2}{a^2}\right)dx$$

In the first term, the integrand is odd and the integral is from $-\infty$ to ∞. Hence the integral vanishes.

Therefore, $\langle p\rangle = \hbar k$, since $A^2\int_{-\infty}^{\infty}\exp\left(\frac{-2x^2}{a^2}\right)dx = 1$