Quantum Mechanics – Part II

Operators

In mathematics, operators provide us with tools for obtaining new functions from a given function. An operator $\hat{\boldsymbol{\alpha}}$ operating on the function f(x) generates a new function g(x):

$$\hat{\boldsymbol{\alpha}}\, \boldsymbol{f}(\boldsymbol{x}) = \boldsymbol{g}(\boldsymbol{x}) \ldots (\mathbf{47})$$

As an example let, $\hat{\alpha} = \frac{d}{dx}$ $and\ f(x) = x^3$.

Then, $$\hat{\boldsymbol{\alpha}}\, \boldsymbol{f}(\boldsymbol{x}) = \frac{d}{dx}x^3 = 3x^2 = \boldsymbol{g}(\boldsymbol{x})$$

In quantum mechanics each dynamical variable (which represents a measurable quantity like, position, linear momentum, total energy etc.) is represented by an operator.

Form of the operators of different dynamical variables is provided in the table below:

Dynamical Variable	Corresponding Operator
Position	$\hat{\boldsymbol{x}} = \boldsymbol{x}$
	$\hat{\boldsymbol{y}} = \boldsymbol{y}$
	$\hat{\boldsymbol{z}} = \boldsymbol{z}$
Linear Momentum (Component wise)	$\widehat{\boldsymbol{p_x}} = -\boldsymbol{i}\hbar\boldsymbol{\partial}/\boldsymbol{\partial x}$
	$\widehat{\boldsymbol{p_y}} = -\boldsymbol{i}\hbar\boldsymbol{\partial}/\boldsymbol{\partial y}$
	$\widehat{\boldsymbol{p_z}} = -\boldsymbol{i}\hbar\boldsymbol{\partial}/\boldsymbol{\partial z}$
Kinetic Energy (in 1-D)	$\widehat{\boldsymbol{E_k}} = \widehat{\boldsymbol{p_x}}.\widehat{\boldsymbol{p_x}}/\boldsymbol{2m} = \frac{-\hbar^{\mathbf{2}}}{\boldsymbol{2m}}\frac{\boldsymbol{d^2}}{\boldsymbol{dx^2}}$
Angular Momentum **(L=r x p)**	$\widehat{\boldsymbol{L_x}} = \hat{\boldsymbol{y}}\widehat{\boldsymbol{p_z}} - \hat{\boldsymbol{z}}\widehat{\boldsymbol{p_y}}$
	$\widehat{\boldsymbol{L_y}} = \hat{\boldsymbol{z}}\widehat{\boldsymbol{p_x}} - \hat{\boldsymbol{x}}\widehat{\boldsymbol{p_z}}$
	$\widehat{\boldsymbol{L_z}} = \hat{\boldsymbol{x}}\widehat{\boldsymbol{p_y}} - \hat{\boldsymbol{y}}\widehat{\boldsymbol{p_x}}$
Potential Energy	$\widehat{\boldsymbol{V}} = \boldsymbol{V}$
Hamiltonian	$\widehat{\boldsymbol{H}} = \widehat{\boldsymbol{E_k}} + \widehat{\boldsymbol{V}}$

Linear Operator : An operator is said to be linear if it satisfies the following two conditions:

(a) $\hat{\boldsymbol{\alpha}}\,(\boldsymbol{\psi_1} + \boldsymbol{\psi_2}) = \hat{\boldsymbol{\alpha}}\boldsymbol{\psi_1} + \hat{\boldsymbol{\alpha}}\boldsymbol{\psi_2}\ \ \boldsymbol{and}$

$(\boldsymbol{b})\ \hat{\boldsymbol{\alpha}}\,(\boldsymbol{C\psi}) = \boldsymbol{C}\hat{\boldsymbol{\alpha}}\,(\boldsymbol{\psi}), \boldsymbol{where\ C\ is\ a\ constatnt\ and\ \psi_1, \psi_2\ are\ two\ functions} \ldots\ldots (\mathbf{48})$

Example : ***d/dx*** is a linear operator where ***log*** is not .

Hermitian Operator

An operator is said to be Hermitian if it satisfies the following conditions:

$\int_{-\infty}^{\infty}(\hat{\boldsymbol{\alpha}}\boldsymbol{\psi})^*\boldsymbol{\psi}\, \boldsymbol{dx} = \int_{-\infty}^{\infty}\boldsymbol{\psi}^*\hat{\boldsymbol{\alpha}}\boldsymbol{\psi}\, \boldsymbol{dx}\ \ldots\ldots\ldots (\mathbf{49})$, **where * denotes the complex conjugate**

All quantum mechanical operators are Hermitian and Linear.

Eigen Value and Eigen Function

In general if we consider an operator $\hat{\alpha}$ which operating on a function **φ(x)** multiplies the latter by a constant a, then **φ(x)** is called an eigenfunction of $\hat{\alpha}$ belonging to the eiegenvalue a.

To each operator $\hat{\alpha}$, there belongs in general a set of eigenvalues a_n and a set of eigenfunctions φ_n defined by the equation

$$\hat{\alpha}\, \varphi_n(x) = a_n \varphi_n(x) \ldots\ldots\ldots\ldots (50)$$

Eigenvalue represents the result of a measurement of the corresponding dynamical variable.

Problem: Find the eigenfunction of the momentum operator $\widehat{p_x} = -i\hbar d/dx$ corresponding to the eigenvalue p.

Answer: As per the given problem, $\widehat{p_x}\, \varphi(x) = p\varphi(x),\ thus, -\frac{i\hbar d\varphi(x)}{dx} = p\varphi(x)$

Or, $-i\hbar \int \frac{d\varphi(x)}{\varphi(x)} = p \int dx + C$

Or, $\ln \varphi(x) = \frac{ip}{\hbar} x - \frac{C}{i\hbar} = \frac{ip}{\hbar} x + \ln K, (where\ \ln K = -\frac{C}{i\hbar})$

Or, $\varphi(x) = K e^{\frac{ip}{\hbar}x}$

Eigenvalues of a Hermitian operator are real.

Proof: Let $\hat{\alpha}$ is a Hermitian operator which satisfies the following eigenvalue equation:

$\hat{\alpha}\, \varphi_n(x) = a_n \varphi_n(x) \ldots. (51\, a)$,

Therefore, the complex conjugate of the previous equations gives,

$$\left(\hat{\alpha}\, \varphi_n(x)\right)^* = a_n^* \varphi_n^*(x) \ldots\ldots (51b)$$

As $\hat{\alpha}$ is a Hermitian, then it must obey equation (49), thus replacing equ (51a) and (51 b) in equ(49), we get,

$$\int_{-\infty}^{\infty} a_n^* \varphi_n^*(x)\varphi(x)\, dx = \int_{-\infty}^{\infty} \varphi_n^*(x)\, a_n \varphi_n(x) dx$$

Or, $(a_n^* - a_n) \int_{-\infty}^{\infty} \varphi_n^*(x)\varphi(x) dx = 0$

As, $\int_{-\infty}^{\infty} \varphi_n^*(x)\varphi(x)dx$ **denotes the total probability, therefore it can't be zero. Thus,** $(a_n^* - a_n) = 0$. **or,** $a_n^* = a_n$. **Therefore,** a_n ***has to be real.***

In 1-D Time-Independent Schrödinger equation is given by,

$$\frac{-\hbar^2}{2m} \, {d^2\varphi(x)}/{dx^2} + V(x)\varphi(x) = E\varphi(x)$$

$$\text{or,} \quad \left[\frac{-\hbar^2}{2m}\ d^2/_{dx^2} + \mathrm{V(x)}\right] \varphi(x) = \mathrm{E}\varphi(x)$$

$$\text{Or, } \hat{H}\ \varphi(x) = E\varphi(x) \ldots\ldots (52)$$

We have seen before [for example :1-D and 3-D infinite potential well], that equation (52) gives rise to different possible solutions, with different eigenvalues.

Time-Independent Schrödinger equation represents an eigenvalue equation for Hamiltonian operator ($\hat{H}$): $\hat{H}\ \varphi_n(x) = E_n\varphi_n(x)$ solution of which gives the enegy eigenvalues (E_n) and the energy eigenfunctions (φ_n).

Therefore, the general wave-function **[ψ(x,t)]** will be a linear superposition of all possible eigenfunctions (eigenstates): $\psi_n(x,t) = \sum_n C_n\varphi_n\,(x)e^{-iE_nt/\hbar} \ldots\ldots (53)$**,** where C_n are constants.

[In the process of deduction of time-independent Schrödinger equation from time-dependent Schrödinger equation, we considered the wavefunction $\psi(x,t)$ ***to be*** $\psi(x,t) = \varphi(x)f(t)$ ***and by separation of variable method, we obtain*** $f(t) = Ce^{-\frac{iE_nt}{\hbar}}$, ***where the constant C is now absorbed within the constant*** C_n ***in equation*** (53) **]**

Solutions of time-independent Schrödinger equation $\varphi_n(x)$ represents the stationary states as the probability density, $P(x,t) = \psi_n^*(x,t)\psi_n(x,t) = \varphi_n^*(x)\varphi_n(x)$ is independent of time.

Orthogonality of eigenfunctions (Proof not required)

Complete set of eigenfunctions of a Hamiltonian operator are orthogonal which can be expressed (in 1-D) by the following relation:

$$\int_{-\infty}^{\infty} \varphi_m^*(x)\varphi_n(x)\,dx = \begin{cases} 0 \ for\ m \neq n \\ 1 \ for\ m = n \end{cases} \ldots\ldots\ldots (54)\,,$$

where φ_n's are the normalized eigenfunctions and φ_m^*(x) represents the complex conjugate of $\varphi_m(x)$.

<u>Proof:-</u> Let us consider that $\varphi_m\,(x)$ *and* $\varphi_n\,(x)$ are two energy eigen functions which satisfy the time-independent Schrödinger equation, thus can be written as,

$$\frac{-\hbar^2}{2m}\ d^2\varphi_m(x)\big/_{dx^2} + \mathrm{V(x)}\varphi_m(x) = \mathrm{E_m}\varphi_m(x) \ldots.(i)$$

and

$$\frac{-\hbar^2}{2m}\ d^2\varphi_n(x)\big/_{dx^2} + \mathrm{V(x)}\varphi_n(x) = \mathrm{E_n}\varphi_n(x) \ldots.(ii)$$

Now, complex conjugate of equation (i) gives,

$$\frac{-\hbar^2}{2m}\ d^2\varphi_m^*(x)\big/_{dx^2} + \mathrm{V(x)}\varphi_m^*(x) = \mathrm{E_m}\varphi_m^*(x) \ldots.(iii)$$

In equation (iii), potential energy V(x) is considered as a real function. Moreover, as E_m or E_n are different energy eigenvalues of Hamiltonian operator (which is a Hermitian operator), thus they are real numbers.

Thus, $\varphi_m^*(x) \times$ equ (ii) gives,

$$\frac{-\hbar^2}{2m}\varphi_m^*(x)\ d^2\varphi_n(x)\big/_{dx^2} + \mathrm{V(x)}\varphi_m^*(x)\varphi_n(x) = \mathrm{E_n}\varphi_m^*(x)\varphi_n(x) \ldots.(iv)$$

and $equ\ (iii) \times\ \varphi_n(x)\ gives,$

$$\frac{-\hbar^2}{2m}\frac{d^2\varphi_m^*(x)}{dx^2}\varphi_n(x) + \mathrm{V(x)}\varphi_m^*(x)\varphi_n(x) = \mathrm{E_m}\varphi_m^*(x)\varphi_n(x) \ldots.(v)$$

Therefore, equ (iv) – equ (v) becomes,

$$\frac{-\hbar^2}{2m}\left[\varphi_m^*(x)\frac{d^2\varphi_n(x)}{dx^2} - \frac{d^2\varphi_m^*(x)}{dx^2}\varphi_n(x)\right] = (\mathrm{E_n} - \mathrm{E_m})\varphi_m^*(x)\varphi_n(x)$$

$$\frac{-\hbar^2}{2m}\frac{d}{dx}\left[\varphi_m^*(x)\frac{d\varphi_n(x)}{dx} - \frac{d\varphi_m^*(x)}{dx}\varphi_n(x)\right] = (\mathrm{E_n} - \mathrm{E_m})\varphi_m^*(x)\varphi_n(x) \ldots(vi)$$

Integrating equ (vi) on both side over all values of x, we get,

$$\frac{-\hbar^2}{2m}\int_{-\infty}^{\infty}\frac{d}{dx}\left[\varphi_m^*(x)\frac{d\varphi_n(x)}{dx} - \frac{d\varphi_m^*(x)}{dx}\varphi_n(x)\right]dx = (\mathrm{E_n} - \mathrm{E_m})\int_{-\infty}^{\infty}\varphi_m^*(x)\varphi_n(x)\,dx$$

$$\mathbf{0} = (\mathrm{E_n} - \mathrm{E_m})\int_{-\infty}^{\infty}\varphi_m^*(x)\varphi_n(x)\,dx \text{ as both } \varphi_n(x)\ and\ \varphi_m^*(x) \to \mathbf{0},\ as\ x \to \pm\infty.$$

$$\textbf{Thus, when } \mathrm{E_n} \neq \mathrm{E_m}, \int_{-\infty}^{\infty}\varphi_m^*(x)\varphi_n(x)\,dx = 0$$

Orthonormality of wavefunction $\boldsymbol{\psi_n(x,t)}$

If $\boldsymbol{\psi_n(x,t)}'s$ **are orthogonal as well as normalized (orthonormal), then they must follow**

$$\int_{-\infty}^{\infty} \boldsymbol{\psi_m^*(x,t)\psi_n(x,t)\, dx} = \begin{cases} 0 \; for\; m \neq n \\ 1 \; for \; m = n \end{cases} \quad \ldots.(55)$$

Therefore, equation (53) gives us,

$$\int_{-\infty}^{\infty} \sum_{\boldsymbol{m}} \boldsymbol{C_m^* \varphi_m^*(x) e^{iE_m t/\hbar}} \sum_{\boldsymbol{n}} \boldsymbol{C_n \varphi_n\,(x) e^{-iE_n t/\hbar}\, dx} = \begin{cases} 0 \; for \; m \neq n \\ 1 \; for \; m = n \end{cases}$$

Or, $\int_{-\infty}^{\infty} \left[\, C_1^* \varphi_1^*(x) e^{iE_1 t/\hbar} + \; C_2^* \varphi_2^*(x) e^{iE_2 t/\hbar} + \cdots + \; C_m^* \varphi_m^*(x) e^{iE_m t/\hbar}\right] \left[C_1 \varphi_1(x) e^{-iE_1 t/\hbar} + C_2 \varphi_2(x) e^{-iE_2 t/\hbar} + \cdots + C_m \varphi_m(x) e^{-iE_m t/\hbar}\right] \, dx = 1$

Or,

$$\int_{-\infty}^{\infty} \; C_1^* C_1 \varphi_1^*(x) \varphi_1(x) dx + \int_{-\infty}^{\infty} \; C_1^* \varphi_1^*(x) e^{iE_1 t/\hbar} \; C_2 \varphi_2(x) e^{-iE_2 t/\hbar}\, dx + \int_{-\infty}^{\infty} \; C_2^* \varphi_2^*(x) e^{iE_2 t/\hbar} \; C_1 \varphi_1(x) e^{-iE_1 t/\hbar}\, dx + \int_{-\infty}^{\infty} \; C_2^* C_2 \varphi_2^*(x) \varphi_2(x) dx + \cdots = 1$$

Or,

$$|C_1|^2 \int_{-\infty}^{\infty} \varphi_1^*(x) \varphi_1(x) dx + \; C_1^* C_2 e^{i(E_1 - E_2)t/\hbar} \int_{-\infty}^{\infty} \varphi_1^*(x) \; \varphi_2(x)\, dx + C_2^* C_1 e^{i(E_2 - E_1)t/\hbar} \int_{-\infty}^{\infty} \varphi_2^*(x) \; \varphi_1(x)\, dx + |C_2|^2 \int_{-\infty}^{\infty} \varphi_2^*(x) \varphi_2(x) dx + \cdots = 1$$

Or, $\boldsymbol{|C_1|^2 + \; |C_2|^2 + \cdots + |C_m|^2 \, = 1}$ **.....(56) (Important)**

[Summation of probabilities of occurrence of all the eigenstates: total probability is one]

[As orthogonality of eigenfunction demands (equation(54)],

$$\int_{-\infty}^{\infty} \varphi_2^*(x) \varphi_2(x) dx = 1\,, \int_{-\infty}^{\infty} \varphi_2^*(x) \; \varphi_1(x)\, dx = 0 \; and \; so \; on.]$$

The probability of occurrence of the eigenstate $\boldsymbol{\varphi_m}$ is given by $\boldsymbol{|C_m|^2}$.

Expectation Value

The expectation value or the expected average of the results of a large number of measurements of a physical property α, is given by,

$$\langle \alpha \rangle = \int_{-\infty}^{\infty} \psi^* \hat{\alpha} \psi \, dx \ \ldots\ldots (57a),$$

where $\hat{\alpha}$ is the operator representing the dynamical variable α and ψ is the normalized wavefunction.

If ψ is not normalized, then the expectation value can be found out,

$$\langle \alpha \rangle = \int_{-\infty}^{\infty} \psi^* \hat{\alpha} \psi \, dx \Big/ \int_{-\infty}^{\infty} \psi^* \psi \, dx \ \ldots\ldots (57b)$$

Note: Expectation value of different operators (in 1-D),

Position : $\langle x \rangle = \int_{-\infty}^{\infty} \psi^* \hat{x} \psi \, dx = \int_{-\infty}^{\infty} \psi^* x \psi \, dx$ **.....(58)**

$$\langle x^2 \rangle = \int_{-\infty}^{\infty} \psi^* \widehat{x^2} \psi \, dx = \int_{-\infty}^{\infty} \psi^* x^2 \psi \, dx \ \ldots . (59)$$

Linear Momentum: $\langle p_x \rangle = \int_{-\infty}^{\infty} \psi^* \widehat{p_x} \psi \, dx = -i\hbar \int_{-\infty}^{\infty} \psi^* \frac{d\psi}{dx} dx \ \ldots (60)$

$\langle p_x^2 \rangle = \int_{-\infty}^{\infty} \psi^* \widehat{p^2} \psi \, dx = -\hbar^2 \int_{-\infty}^{\infty} \psi^* \frac{d^2\psi}{dx^2} \, dx$ **....(61)**

Hamiltonian:

$\langle E \rangle = \int_{-\infty}^{\infty} \psi^* \hat{H} \psi \, dx = -\frac{\hbar^2}{2m} \int_{-\infty}^{\infty} \psi^* \frac{d^2\psi}{dx^2} \, dx$ for free partcile, ie., V = 0 .... (62)

Important: Expectation value of Hamiltonian operator gives the energy expectation value.

Problem (important) : A system has two energy eigenstates ε_0 and $3\varepsilon_0$. φ_1 **and** φ_2 are the corresponding normalized eigenfunction. At an instant the system is in a superposed state,
$\varphi = c_1 \varphi_1 + c_2 \varphi_2$ and $c_1 = 1/\sqrt{2}$.

i) Find c_2 if φ is normalized.

ii) What is the **probability** that an energy measurement would yield a value $3\varepsilon_0$.

iii) Find out the **energy expectation** value.

Answer: **i)** As **φ is normalized,** then equation **(56)** gives that $|C_1|^2 + |C_2|^2 = 1$
It is given that, **$c_1 = 1/\sqrt{2}$, therefore $c_2 = 1/\sqrt{2}$…(63)**

ii) Since φ_2 **is the energy eigenstate corresponding to the enrgy eigenvalue** $3\varepsilon_0$, therefore the probability of occurrence of that state (ie. An energy measurement would yield a value of $3\varepsilon_0$) is given by $|C_2|^2 = \frac{1}{2}$. [using equ (63)]

iii) As per the problem, φ_1 and φ_2 satisfy the following eigenvalue equations,

$$\boldsymbol{\hat{H}\varphi_1 = \varepsilon_0\varphi_1 \text{ and } \hat{H}\varphi_2 = 3\varepsilon_0\varphi_2} \ldots\ldots (64)$$

Thus, the energy expectation value can be evaluated as (equ (62))

$$\langle \boldsymbol{E} \rangle = \int_{-\infty}^{\infty} \boldsymbol{\varphi^* \hat{H}\varphi\, dx} = \int_{-\infty}^{\infty} [\boldsymbol{c_1^*\varphi_1^* + c_2^*\varphi_2^*}]\, \boldsymbol{\hat{H}}[\mathbf{c_1\varphi_1 + c_2\varphi_2}]\, \boldsymbol{dx}$$

or, $\langle \boldsymbol{E} \rangle = \int_{-\infty}^{\infty} [\boldsymbol{c_1^*\varphi_1^* + c_2^*\varphi_2^*}]\, [\boldsymbol{\varepsilon_0 c_1\varphi_1 + 3\varepsilon_0\, c_2\varphi_2}]\, \boldsymbol{dx}$ $(using\ equation\ 64)$

or, $\langle \boldsymbol{E} \rangle = \boldsymbol{\varepsilon_0|C_1|^2 \int_{-\infty}^{\infty} \varphi_1^*\, \varphi_1\, dx + 3\varepsilon_0|C_2|^2 \int_{-\infty}^{\infty} \varphi_2^*\, \varphi_2\, dx} = \boldsymbol{{\varepsilon_0}/{2} + {3\varepsilon_0}/{2}}$

$$\text{or, } \langle \boldsymbol{E} \rangle = \boldsymbol{2\varepsilon_0} \text{ using eqn(63)}$$

[where, orthogonality of eigenfunction gives,
$\boldsymbol{\int_{-\infty}^{\infty} \varphi_1^*\, \varphi_1\, dx = \int_{-\infty}^{\infty} \varphi_2^*\, \varphi_2\, dx = 1 \text{ and } \int_{-\infty}^{\infty} \varphi_2^*\, \varphi_1\, dx = \int_{-\infty}^{\infty} \varphi_1^*\, \varphi_2\, dx = 0}$]

To do

1a) Eigenfunction of a particle in 1-D infinite potential well of length L is given by,
$\varphi_n(x) = \sqrt{2/L}\, \sin {n\pi x}/{L}$. For the ground state eigenfunction (n=1) show that
i) $\langle \boldsymbol{x^2} \rangle = \boldsymbol{{L^4}/{6\pi^2}}$, **ii)** $\langle \boldsymbol{x} \rangle = \boldsymbol{1/2}$, iii) $\langle \boldsymbol{p_x} \rangle = \boldsymbol{0}$ **and** $\langle \boldsymbol{p_x^2} \rangle = \boldsymbol{\pi^2}\hbar^{\boldsymbol{2}}/\boldsymbol{L^2}$ **Important**

Hint: ii) $\langle \boldsymbol{x} \rangle = \frac{2}{L}\int_0^L \sin {\pi x}/{L}\; x\; \sin {\pi x}/{L}\, dx = \frac{2}{L}\int_0^L x\sin^2 {\pi x}/{L}\, dx$
Or, $\langle \boldsymbol{x} \rangle = \frac{1}{L}\int_0^L \mathrm{x}(1 - \cos {2\pi x}/{L}) = \frac{1}{2}$.

1b) Prove that the eigenfunctions are orthogonal to each other. **Important**

Hint: $\frac{2}{L}\int_0^L \sin {m\pi x}/{L}\; \sin {n\pi x}/{L}\, dx = 0, for\ m \neq n$
$and = 1\ for\ m = n$

Commutator

The commutator of two operators $\hat{A}$ *and* $\hat{B}$ is defined as, $\left[\hat{A},\hat{B}\right] = \hat{A}\hat{B} - \hat{B}\hat{A}$.
If, $\left[\hat{A},\hat{B}\right] = 0$, *then* $\hat{A}$ *and* $\hat{B}$ *are said to commute with each other.*

If two operators commute then they will have simultaneous eigenfunctions

Proof: Let us consider that two operators $\hat{A}$ *and* $\hat{B}$ have a common eigenfunction φ corresponding to different eigenvalues ***a*** and ***b***, thus their eigenvalue equations become,

$$\hat{A}\varphi = a\varphi \quad and \ \hat{B}\varphi = b\varphi \ \ldots\ldots\ (64)$$

We will now prove that $\hat{A}$ *and* $\hat{B}$ *commute with each other* : $\left[\hat{A},\hat{B}\right] = 0$

Operating $\left[\hat{A},\hat{B}\right]$ *on* φ we get,

$$\left[\hat{A},\hat{B}\right]\varphi = (\hat{A}\hat{B} - \hat{B}\hat{A})\varphi = \hat{A}\left(\hat{B}\varphi\right) - \hat{B}\left(\hat{A}\varphi\right) = \hat{A}\,b\varphi - \hat{B}\,a\varphi\ (from\ equ\ 64)$$

$$= b\,\hat{A}\varphi - a\,\hat{B}\varphi = ba\varphi - ab\varphi = 0\ [as\ a\ and\ b\ are\ numbers, so\ ab = ba]$$

Therefore, $\left[\hat{\boldsymbol{A}},\hat{\boldsymbol{B}}\right] = \mathbf{0}$ **….(65)**

Properties of commutator

1) $\left[\hat{\boldsymbol{A}},\hat{\boldsymbol{B}}\right] = -\left[\hat{\boldsymbol{B}},\hat{\boldsymbol{A}}\right]$ **…(66)**

2) $\left[\hat{\boldsymbol{A}},\hat{\boldsymbol{A}}\right] = \mathbf{0}$ **…(67)**

3) $\left[\hat{\boldsymbol{A}}\hat{\boldsymbol{B}},\hat{\boldsymbol{C}}\right] = \hat{\boldsymbol{A}}\left[\hat{\boldsymbol{B}},\hat{\boldsymbol{C}}\right] + \left[\hat{\boldsymbol{A}},\hat{\boldsymbol{C}}\right]\hat{\boldsymbol{B}}$ **…(68)**

4) $\left[\hat{\boldsymbol{B}},\hat{\boldsymbol{C}}\hat{\boldsymbol{A}}\right] = \hat{\boldsymbol{C}}\left[\hat{\boldsymbol{B}},\hat{\boldsymbol{A}}\right] + \left[\hat{\boldsymbol{B}},\hat{\boldsymbol{C}}\right]\hat{\boldsymbol{A}}$ **….(69)**

5) $\left[\hat{\boldsymbol{A}}+\hat{\boldsymbol{B}},\hat{\boldsymbol{C}}\right] = \left[\hat{\boldsymbol{A}},\hat{\boldsymbol{C}}\right] + \left[\hat{\boldsymbol{B}},\hat{\boldsymbol{C}}\right]$ **….(70)**

Evaluate the following commutators

1) $[\hat{x},\ \widehat{p_x}] = i\hbar$ ….(71) **Important**

Ans. $[\hat{x},\ \widehat{p_x}]\varphi(x) = [\hat{x}\widehat{p_x} - \widehat{p_x}\hat{x}\,]\varphi(x) = \left[x\left(-i\hbar\frac{d}{dx}\right) - i\hbar\frac{d}{dx}\right)x\,\varphi(x)$

$$= (-i\hbar)\left[x\frac{d\varphi(x)}{dx} - \left\{\frac{d}{dx}\left(x\varphi(x)\right)\right\}\right] = (-i\hbar)\left[x\frac{d\varphi(x)}{dx} - x\frac{d\varphi(x)}{dx} - \varphi(x)\right]$$

Or, $[\hat{x},\ \widehat{p_x}]\varphi(x) = i\hbar\varphi(x)$ *gives*, $[\hat{\boldsymbol{x}},\ \widehat{\boldsymbol{p_x}}] = \boldsymbol{i}\hbar$ **[$\hat{\boldsymbol{x}}$ *and* $\widehat{\boldsymbol{p_x}}$** follows **uncertainty principle]**

Similarly, $\left[\hat{\boldsymbol{y}},\ \widehat{\boldsymbol{p_y}}\right] = \boldsymbol{i}\hbar\ \boldsymbol{and}\ [\hat{\boldsymbol{z}},\ \widehat{\boldsymbol{p_z}}] = \boldsymbol{i}\hbar$

2) $[\hat{y},\ \widehat{p_x}] = 0$ **[**have **simultaneous eigenfunctions**, equation (65)]

Ans. $[\hat{y},\ \widehat{p_x}]\varphi(x) = [\hat{y}\widehat{p_x} - \widehat{p_x}\hat{y}\,]\varphi(x) = \left[y\left(-i\hbar\frac{d}{dx}\right) - i\hbar\frac{d}{dx}\right)y\,\varphi(x)$

$= (-i\hbar)\left[y\frac{d\varphi(x)}{dx} - \left\{\frac{d}{dx}\left(y\varphi(x)\right)\right\}\right] = (-i\hbar)\left[y\frac{d\varphi(x)}{dx} - y\frac{d\varphi(x)}{dx} - 0\right] = 0$

Similarly, $\left[\hat{x},\ \widehat{p_y}\right] = [\hat{y},\ \widehat{p_z}] = \left[\hat{z},\ \widehat{p_y}\right] = [\hat{x},\ \widehat{p_z}] = \left[\hat{Z},\ \widehat{p_x}\right] = 0$

3) **Important** $[\hat{\boldsymbol{x}}, \ \widehat{\boldsymbol{p}_{\boldsymbol{x}}^{\boldsymbol{n}}}] = \boldsymbol{n i}\hbar\widehat{\boldsymbol{p}_{\boldsymbol{x}}^{\boldsymbol{n-1}}}$

Ans. Let us put n=1, $[\hat{\boldsymbol{x}}, \ \widehat{\boldsymbol{p}_{\boldsymbol{x}}}] = \boldsymbol{i}\hbar$ (from equ (71))

For n=2, $\left[\hat{\boldsymbol{x}}, \ \widehat{\boldsymbol{p}_{\boldsymbol{x}}^{\boldsymbol{2}}}\right] = [\hat{\boldsymbol{x}}, \ \widehat{\boldsymbol{p}_{\boldsymbol{x}}}\widehat{\boldsymbol{p}_{\boldsymbol{x}}}] = \widehat{\boldsymbol{p}_{\boldsymbol{x}}}[\hat{\boldsymbol{x}}, \ \widehat{\boldsymbol{p}_{\boldsymbol{x}}}] + [\hat{\boldsymbol{x}}, \ \widehat{\boldsymbol{p}_{\boldsymbol{x}}}]\widehat{\boldsymbol{p}_{\boldsymbol{x}}}$ $(using\ equation\ 69)$

$\left[\hat{x}, \widehat{p_x^2}\right] = \widehat{p_x}\ i\hbar + i\hbar\widehat{p_x} = 2i\hbar\widehat{p_x}$ (equn(71)) …….(72)

For n=3, $\left[\hat{\boldsymbol{x}}, \ \widehat{\boldsymbol{p}_{\boldsymbol{x}}^{\boldsymbol{3}}}\right] = \left[\hat{\boldsymbol{x}}, \ \widehat{\boldsymbol{p}_{\boldsymbol{x}}}\widehat{\boldsymbol{p}_{\boldsymbol{x}}^{\boldsymbol{2}}}\right] = \widehat{\boldsymbol{p}_{\boldsymbol{x}}}\left[\hat{\boldsymbol{x}}, \ \widehat{\boldsymbol{p}_{\boldsymbol{x}}^{\boldsymbol{2}}}\right] + [\hat{\boldsymbol{x}}, \ \widehat{\boldsymbol{p}_{\boldsymbol{x}}}]\widehat{\boldsymbol{p}_{\boldsymbol{x}}^{\boldsymbol{2}}} = \boldsymbol{2i}\hbar\widehat{\boldsymbol{p}_{\boldsymbol{x}}^{\boldsymbol{2}}} + \boldsymbol{i}\hbar\widehat{\boldsymbol{p}_{\boldsymbol{x}}^{\boldsymbol{2}}} = \boldsymbol{3i}\hbar\widehat{\boldsymbol{p}_{\boldsymbol{x}}^{\boldsymbol{2}}}$

Thus, method of induction proves that, $[\hat{\boldsymbol{x}}, \ \widehat{\boldsymbol{p}_{\boldsymbol{x}}^{\boldsymbol{n}}}] = \boldsymbol{ni}\hbar\widehat{\boldsymbol{p}_{\boldsymbol{x}}^{\boldsymbol{n-1}}}$

4) **Important** $[\widehat{\boldsymbol{x}^{\boldsymbol{n}}}, \ \widehat{\boldsymbol{p}_{\boldsymbol{x}}}] = \boldsymbol{ni}\hbar\widehat{\boldsymbol{x}^{\boldsymbol{n-1}}}$

Ans. Let us put n=1, $[\hat{\boldsymbol{x}}, \ \widehat{\boldsymbol{p}_{\boldsymbol{x}}}] = \boldsymbol{i}\hbar$ (from equ (71))

For n=2, $\left[\widehat{\boldsymbol{x}^{\boldsymbol{2}}}, \ \widehat{\boldsymbol{p}_{\boldsymbol{x}}}\right] = [\hat{\boldsymbol{x}}\hat{\boldsymbol{x}}, \ \widehat{\boldsymbol{p}_{\boldsymbol{x}}}] = \hat{\boldsymbol{x}}[\hat{\boldsymbol{x}}, \ \widehat{\boldsymbol{p}_{\boldsymbol{x}}}] + [\hat{\boldsymbol{x}}, \ \widehat{\boldsymbol{p}_{\boldsymbol{x}}}]\hat{\boldsymbol{x}}$ $(using\ equation\ 68)$

$\left[\widehat{\boldsymbol{x}^{\boldsymbol{2}}}, \ \widehat{\boldsymbol{p}_{\boldsymbol{x}}}\right] = \hat{x}\ i\hbar + i\hbar\hat{x} = 2i\hbar\hat{x}$ (equn(71)) …….(72)

For n=3, $\left[\widehat{\boldsymbol{x}^{\boldsymbol{3}}}, \ \widehat{\boldsymbol{p}_{\boldsymbol{x}}}\right] = \left[\hat{\boldsymbol{x}}\widehat{\boldsymbol{x}^{\boldsymbol{2}}}, \ \widehat{\boldsymbol{p}_{\boldsymbol{x}}}\right] = \hat{\boldsymbol{x}}\left[\widehat{\boldsymbol{x}^{\boldsymbol{2}}}, \ \widehat{\boldsymbol{p}_{\boldsymbol{x}}}\right] + [\hat{\boldsymbol{x}}, \ \widehat{\boldsymbol{p}_{\boldsymbol{x}}}]\widehat{\boldsymbol{x}^{\boldsymbol{2}}} = \boldsymbol{2i}\hbar\widehat{\boldsymbol{x}^{\boldsymbol{2}}} + \boldsymbol{i}\hbar\widehat{\boldsymbol{x}^{\boldsymbol{2}}} = \boldsymbol{3i}\hbar\widehat{\boldsymbol{x}^{\boldsymbol{2}}}$

Thus, method of induction proves that, $[\widehat{\boldsymbol{x}^{\boldsymbol{n}}}, \ \widehat{\boldsymbol{p}_{\boldsymbol{x}}}] = \boldsymbol{ni}\hbar\widehat{\boldsymbol{x}^{\boldsymbol{n-1}}}$

5) $\left[\hat{\boldsymbol{x}}, \ \widehat{\boldsymbol{L}_{\boldsymbol{y}}}\right] = \boldsymbol{i}\hbar\boldsymbol{z}$ **(Important)**

$$\left[\hat{x}\, , \widehat{L_y}\right]\varphi(x,y,z) = \left[\hat{x}\widehat{L_y} - \widehat{L_y}\hat{x}\right]\varphi(x,y,z) = \left[\hat{x}\left(\hat{z}\widehat{p_x} - \hat{x}\widehat{p_z}\right) - \left(\hat{z}\widehat{p_x} - \hat{x}\widehat{p_z}\right)\hat{x}\right]\varphi(x,y,z)$$

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

$$= (-i\hbar)\left[xz\frac{\partial\varphi(x,y,z)}{\partial x} - x^2\frac{\partial\varphi(x,y,z)}{\partial z}\right] + (i\hbar)\left[zx\frac{\partial\varphi(x,y,z)}{\partial x} + z\varphi(x,y,z) - x^2\frac{\partial\varphi(x,y,z)}{\partial z}\right]$$

$$= -i\hbar xz\frac{\partial\varphi(x,y,z)}{\partial x} + i\hbar x^2\frac{\partial\varphi(x,y,z)}{\partial z} + i\hbar zx\frac{\partial\varphi(x,y,z)}{\partial x} - i\hbar x^2\frac{\partial\varphi(x,y,z)}{\partial z} + i\hbar z\varphi(x,y,z) = i\hbar z\varphi(x,y,z)$$

Thus, $\left[\hat{\boldsymbol{x}}, \ \widehat{\boldsymbol{L}_{\boldsymbol{y}}}\right] = \boldsymbol{i}\hbar\boldsymbol{z}.$

Similarly, $\left[\hat{\boldsymbol{y}}, \ \widehat{\boldsymbol{L}_{\boldsymbol{z}}}\right] = \boldsymbol{i}\hbar\boldsymbol{x}$ $\ \boldsymbol{and}\ \left[\hat{\boldsymbol{z}}, \ \widehat{\boldsymbol{L}_{\boldsymbol{x}}}\right] = \boldsymbol{i}\hbar\boldsymbol{y}$

6) **To do,** $\left[\hat{\boldsymbol{x}}, \widehat{\boldsymbol{L}_{\boldsymbol{x}}}\right] = \left[\hat{\boldsymbol{y}}, \widehat{\boldsymbol{L}_{\boldsymbol{y}}}\right] = \left[\hat{\boldsymbol{z}}, \widehat{\boldsymbol{L}_{\boldsymbol{z}}}\right] = \boldsymbol{0}$

7) Given, $[\widehat{L_x}, \widehat{L_y}] = i\hbar\widehat{L_z}$; $[\widehat{L_y}, \widehat{L_z}] = i\hbar\widehat{L_x}$ *and* $[\widehat{L_z}, \widehat{L_x}] = i\hbar\widehat{L_y}$

Prove that, $[\widehat{L_x}, \widehat{L^2}] = 0$ where, $\widehat{L^2} = \widehat{L_x^2} + \widehat{L_y^2} + \widehat{L_z^2}$. **(Important)**

Ans. $[\widehat{L_x}, \widehat{L^2}] = [\widehat{L_x}, \widehat{L_x^2} + \widehat{L_y^2} + \widehat{L_z^2}] = [\widehat{L_x}, \widehat{L_x^2}] + [\widehat{L_x}, \widehat{L_y^2}] + [\widehat{L_x}, \widehat{L_z^2}]$ $(using\ equation\ (70))$

Or, $[\widehat{L_x}, \widehat{L^2}] = [\widehat{L_x}, \widehat{L_x}\widehat{L_x}] + [\widehat{L_x}, \widehat{L_y}\widehat{L_y}] + [\widehat{L_x}, \widehat{L_z}\widehat{L_z}] = \widehat{L_x}[\widehat{L_x}, \widehat{L_x}] + [\widehat{L_x}, \widehat{L_x}]\widehat{L_x} + \widehat{L_y}[\widehat{L_x}, \widehat{L_y}]$ $+ [\widehat{L_x}, \widehat{L_y}]\widehat{L_y} + \widehat{L_z}[\widehat{L_x}, \widehat{L_z}] + [\widehat{L_x}, \widehat{L_x}]\widehat{L_z}$ (using equation (69))

Or, $[\widehat{L_x}, \widehat{L^2}] = 0 + 0 + i\hbar\widehat{L_y}\widehat{L_z} + i\hbar\widehat{L_z}\widehat{L_y} - i\hbar\widehat{L_y}\widehat{L_z} - i\hbar\widehat{L_z}\widehat{L_y} = 0$ {since, $[\widehat{L_z}, \widehat{L_x}] = -[\widehat{L_x}, \widehat{L_z}]$}

Postulates of Quantum Mechanics

I] There is a **wave function ψ(x,y,z,t)** which completely describes the space-time behavior of the particle, consistent with the uncertainty principle**.**

II] Dynamical variables or **observables** which are the **physically measurable (like position, momentum, energy etc)** properties of the particle are represented by **mathematical operators** in quantum mechanics**. These operators are linear and Hermitian.**

III] The only possible result of measurement of a dynamical variable **α** are the **eigenvalues of the operator $\hat{\alpha}$,** satisfying the eigen value equation $\hat{\alpha}\,\varphi_n = a_n\varphi_n$, where φ_n is the **eigen function** of the operator $\hat{\alpha}$**,** belonging to **the eigen value a_n.**

The eigen functions are well-behaved, i.e., **they must be single-valued and square-integrable (for bound state) (means eigen-function must vanish at boundaries).** They also form a **complete set** and are **orthogonal.**

The **eigen value equation** satisfied by the **Hamiltonian operator** is known as the **Schrödinger** equation and can be written as**,** $\hat{H}\,\psi_n(x) = E_n\psi_n(x)$**,** where E_n is the **energy of the system.**

IV] The probability ***Pdv*** of finding a particle in the volume element ***dv*** is given by,

$Pdv = \psi^*\,\psi\,dv = |\psi|^2 dv$, where $P = \psi^*\,\psi = |\psi|^2$ is known as the **probability density**.

In a finite region of space the probability of finding the particle is obtained by integrating the above expression over the volume under consideration, $\int Pdv = \int \psi^*\,\psi\,dv = \int |\psi|^2 dv$

The integral r.h.s must always remain **finite since the probability must be finite** for any physically admissible state. In particular if **we multiply ψ by a suitable complex number**, we can make the total probability of finding the particle somewhere in space as unity, so that we get, $\int_{-\infty}^{\infty} \psi^*\,\psi\,dv = \int_{-\infty}^{\infty} |\psi|^2 dv = 1$, the **wave function ψ** is said to be **normalized** in this case**.**

V] The **expectation value** or the expected average of the results of a large number of measurements of a physical property α, is given by,

$$\langle \boldsymbol{\alpha} \rangle = \int_{-\infty}^{\infty} \boldsymbol{\psi^* \hat{\alpha} \psi \, dx}$$

where $\hat{\alpha}$ is the operator representing the dynamical variable α and **ψ is the normalized** wavefunction.

If ψ is not a normalized wavefunction, then the expectation value is given by,

$$\langle \boldsymbol{\alpha} \rangle = \left. \int_{-\infty}^{\infty} \boldsymbol{\psi^* \hat{\alpha} \psi \, dv} \middle/ \int_{-\infty}^{\infty} \boldsymbol{\psi^* \psi \, dv} \right.$$

VI] It may be noted that the state (general wave function) ψ of the system can be built up by applying the **principle of superposition**, thus

$$\boldsymbol{\psi_{n_x n_y n_z}(x, y, z)} = \sum_{\boldsymbol{n_x n_y n_z}} \boldsymbol{C_{n_x n_y n_z} \, \varphi_{n_x n_y n_z}(x, y, z)}$$

where, $\varphi_{n_x n_y n_z}(x, y, z)$ are the solutions of the 3-D Time-independent Schrödinger equation (eigenvalue equation) and $C_{n_x n_y n_z}$'s are the complex numbers such that $\left|\boldsymbol{C_{n_x n_y n_z}}\right|^{\boldsymbol{2}}$ gives the **probability of finding the particle in the eigenstate** represented by the **eigen function $\boldsymbol{\varphi_{n_x n_y n_z}}$**. They can evaluated by utilizing the orthogonality property of eigen functions.