9

OPERATORS IN QUANTUM MECHANICS

During discussion of the Schrodinger equation in Chapter 7 we introduced an operator $-i\hbar\vec{\nabla}$ for momentum $\vec{p}$ of a particle, and an operator $i\hbar\,\partial/\partial t$ for energy E of the particle.

What is an operator?

An operator is a rule to change a given function into some other function. An operator is a mathematical operation on a function on the right hand side of the operator, which in general results in another function:[1]

$$\hat{A}\,\psi = \phi \quad ,$$

where $\hat{A}$ is the operator and ψ and ϕ are functions.[2]

For example, operator $\hat{A} = \partial/\partial x$ represents differentiation with respect to *x*. Consider a function, $\psi(x) = a e^{ikx} + b e^{-ikx}$, where a and k are constants. Then

$$\hat{A}\,\psi(x) = \frac{\partial}{\partial x}\left(a e^{ikx} + b e^{-ikx}\right) \quad ,$$

$$= ik\left(a e^{ikx} - b e^{-ikx}\right) \quad ,$$

$$= \phi(x)$$, a different function.

(See **Example 9. 1**)

9.1 LINEAR OPERATOR

Let for an operator $\hat{A}$ we have $\hat{A}\,\psi_1 = \phi_1$ and $\hat{A}\,\psi_2 = \phi_2$. The operator $\hat{A}$ is called a linear operator if it satisfies the following condition:

$$\hat{A}\left(c_1\psi_1 + c_2\psi_2\right) = c_1\left(\hat{A}\psi_1\right) + c_2\left(\hat{A}\psi_2\right) \quad ,$$

$$= c_1\phi_1 + c_2\phi_2 \quad ,$$

where c_1 and c_2 are constants.

That is (i) the action of a linear operator operating on superposition of two functions is equivalent to the sum of the action of the operator on the individual functions:

$$\hat{A}\left(\psi_1 + \psi_2\right) = \left(\hat{A}\psi_1\right) + \left(\hat{A}\psi_2\right)$$, and

(ii) the action of a linear operator operating on a constant multiple of a function is equivalent to the constant times the action of the operator on the individual function:

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1 *We use the notation hat A, that is* $\hat{A}$ *for representing an operator corresponding to the dynamical variable A of classical mechanics.*

2 *In quantum mechanics, unless mentioned, we consider only those functions which are square integrable.*

$$\hat{A}\,(c\,\psi) = c\,(\hat{A}\,\psi)\quad .$$ [3,4]

PROPERTIES OF LINEAR OPERATORS

(I) Additive Linear Operators

(i) If $\hat{A}$ and $\hat{B}$ are two linear operators, then their sum $(\hat{A} + \hat{B})$ is also a linear operator:

$$(\hat{A} + \hat{B})\,\psi = (\hat{A}\,\psi) + (\hat{B}\,\psi)\quad .$$

Similarly $(\hat{A} - \hat{B})$ is also a linear operator.

(ii) The sum of two linear operators obey commutative property, that is

$$(\hat{A} + \hat{B})\,\psi = (\hat{B} + \hat{A})\,\psi\quad .$$

(**Proof**: Let $\hat{A}\,\psi = \phi_1$ and $\hat{B}\,\psi = \phi_2$, then

$$(\hat{A} + \hat{B})\,\psi = (\hat{A}\,\psi) + (\hat{B}\,\psi)\quad ,$$

$$= \phi_1 + \phi_2 \equiv \phi_2 + \phi_1\quad ,$$

$$= (\hat{B}\,\psi) + (\hat{A}\,\psi) = (\hat{B} + \hat{A})\psi\quad .$$

Thus $(\hat{A} + \hat{B})\,\psi = (\hat{B} + \hat{A})\,\psi\quad .$

(iii) The sum of linear operators obey associative property:

$$(\hat{A} + \hat{B}) + \hat{C} = \hat{A} + (\hat{B} + \hat{C})\quad .$$

(II) Multiplicative Linear Operators

(iv) When two or more linear operators acts one after the other on a function, then it is equivalent to a multiplicative linear operator. Let $\hat{A}$ and $\hat{B}$ are two linear operators, then the multiplicative operators formed from these two are

$$\hat{C} = \hat{A}\,\hat{B}\ ,\ \text{and}\quad \hat{D} = \hat{B}\,\hat{A}\quad .$$

Let $\hat{A}\,\psi = \phi_1$ and $\hat{B}\,\psi = \phi_2$, then

$$\hat{C}\,\psi = \hat{A}\,\hat{B}\psi = \hat{A}\,(\hat{B}\,\psi) = \hat{A}\,\phi_1\quad ,$$

and $$\hat{D}\,\psi = \hat{B}\,\hat{A}\psi = \hat{B}\,(\hat{A}\,\psi) = \hat{B}\,\phi_2\quad .$$

Therefore, in general,

$$\hat{A}\,\hat{B} \neq \hat{B}\,\hat{A}\quad .$$

The multiplicative operators do not obey the commutation law (See Examples 9.2 &9.3).

(v) If an operator appears as a product, such as $\hat{C} = \hat{A}\,\hat{A}\,\hat{A}$, then it can be expressed as $\hat{C} = \hat{A}^3$. In this sense,

$$e^{\hat{A}} = 1 + \hat{A} + \frac{\hat{A}^2}{2!} + \dots\quad .$$

(vi) An operator operates on the function in front of the operator, it does not operate on the func-

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3 *An anti-linear operator is defined by the relation* $\hat{A}'\,(a\,\psi_1 + b\,\psi_2) = a^*(\hat{A}'\,\psi_1) + b^*(\hat{A}'\,\psi_2)$,
where a^* *is the complex conjugate of the constant a, etc.*

4 *In quantum mechanics, unless mentioned, we consider only linear operators.*

tion on the backside of the operator, that is

$$\left(\hat{A}\ \psi\right) \neq \left(\psi\ \hat{A}\right) \quad .$$

For example,

$$\hat{p}_x\left(e^{ikx}\right) = \left(-i\hbar\frac{\partial(e^{ikx})}{\partial x}\right) = \hbar k\ e^{ikx} \quad ,$$

but $$\left(e^{ikx}\right)\ \hat{p}_x = \left(e^{ikx}\right)\left(-i\hbar\frac{\partial}{\partial x}\right) \neq \left(e^{ikx}\right)\hbar k \quad .$$

(III) Unit (Identity) Operator

A unit (or identity) operator $\hat{I}$ is that operator whose action leaves the function unchanged, that is the action of the unit operator is to multiply the function by unity,

$$\hat{I}\ \psi = \psi \quad .$$

A unit operator commutes with any linear operator

$$\hat{I}\ \hat{A} = \hat{A}\ \hat{I} = \hat{A} \quad .$$

Each operator $\hat{A}$ has an inverse denoted by $\hat{A}^{-1}$ such that

$$\hat{A}\ \hat{A}^{-1} = \hat{A}^{-1}\ \hat{A} = I \quad .$$

(IV) Null Operator

A null (or zero) operator is that operator which gives zero when acting on a function,

$$\hat{0}\ \psi = 0 \quad .$$

(V) Function of Linear Operator

The algebraic function of a linear operator is also a linear operator. For example, the total energy of a particle moving in one-dimension in a potential energy region $V(x)$ is a function of momentum p_x and position *x,*

$$E = \frac{p_x^2}{2m} + V(x)$$

The operators corresponding to momentum and position are, respectively,

$$\hat{p}_x = -\,i\hbar\,\frac{\partial}{\partial x} \quad \text{, and} \quad \hat{x} \quad ,$$

the operator for the total energy is

$$\hat{E} = -\frac{\hbar^2}{2m}\,\frac{\partial^2}{\partial x^2} + V(\hat{x}) \quad ,$$

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

where we have used $V(x)$ in place of $V(\hat{x})$ because the action of operator $\hat{x}$ on any function of *x* is to multiply that function by *x* only,

$$\hat{x}\ \psi(x) = x\ \psi(x) \quad .$$

In quantum mechanics, for every dynamical variable that relates to the motion of a particle, like position, velocity, momentum, energy, angular momentum,... an operator is assigned.[5] Let $A(\vec{r},\vec{p})$ is a function of dynamical variables $\vec{r}$ and $\vec{p}$. We construct the corresponding operator $\hat{A}$ by replacing the quantities $\vec{r}$ and $\vec{p}$ in the expression for A by the assigned operators $\hat{\vec{r}} = \vec{r}$ and $\hat{\vec{p}} = -i\hbar\vec{\nabla}$. Here the position operator is identical to the position vector. Some of the operators in x-, y-, z- coordinate space (Cartesian coordinate space) are given in the **Table 9.1** below.

Table 9.1 Quantum Mechanical Operators

Classical dynamical variable (Physical quantity)	**Quantum mechanical operator (in Cartesian coordinate representation)**
Position x, y, z	$\hat{x} = x$, $\hat{y} = y$, $\hat{z} = z$
Position vector $\vec{r}$	$\hat{\vec{r}} = \vec{r}$
Components of momentum, p_x , p_y , p_z	$\hat{p}_x = -i\hbar\frac{\partial}{\partial x}$, $\hat{p}_y = -i\hbar\frac{\partial}{\partial y}$, $\hat{p}_z = -i\hbar\frac{\partial}{\partial z}$
Momentum, $\vec{p}$	$\hat{\vec{p}} = -i\hbar\vec{\nabla}$
Kinetic energy (non-relativistic), $\frac{p^2}{2m}$	$\frac{\hat{p}^2}{2m} = -\frac{\hbar^2}{2m}\nabla^2$
Potential energy, $V(\vec{r},t)$	$\hat{V}(\hat{\vec{r}},t) = V(\vec{r},t)$
Total energy (non-relativistic), $H = \frac{p^2}{2m} + V(\vec{r},t)$	$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r},t)$
Angular momentum, $\vec{L} = \vec{r}\times\vec{p}$	$\hat{\vec{L}} = -i\hbar\,\vec{r}\times\vec{\nabla}$
Components of angular momentum, $L_x = y\,p_z - z\,p_y$, $L_y = z\,p_x - x\,p_z$, $L_z = x\,p_y - y\,p_x$.	$\hat{L}_x = -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)$, $\hat{L}_y = -i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)$, $\hat{L}_z = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$.
Total energy (the Hamiltonian), H	$\hat{H} = i\hbar\frac{\partial}{\partial t}$

9.2 ADJOINT OPERATOR

Let two linear operators $\hat{A}$ and $\hat{B}$, satisfy the following volume integral relation for

5 *In quantum mechanics, unless mentioned, we consider only linear operators. The operators given in Table 1 are defined using Cartesian coordinates. For any other coordinate system, these are then changed using coordinate transformation relations.*

two independent functions $\psi \equiv \psi(x, y, z, t)$ and $\phi \equiv \phi(x, y, z, t)$,

$$\int \left(\hat{B}\,\psi\right)^* \phi \, dV = \int \psi^* \left(\hat{A}\,\phi\right) dV$$

then the operator $\hat{B}$ is called the adjoint of operator $\hat{A}$.

The conventional symbol for adjoint of operator $\hat{A}$ is $\hat{A}^\dagger$. Therefore, the relation between operator $\hat{A}$ and its adjoint operator $\hat{A}^\dagger$ is

$$\int \left(\hat{A}^\dagger\,\psi\right)^* \phi \, dV = \int \psi^* \left(\hat{A}\,\phi\right) dV \quad .$$

The adjoint operators have the following properties:

(i) $\left(\hat{A} \pm \hat{B}\right)^\dagger = \hat{A}^\dagger \pm \hat{B}^\dagger$.

(ii) $\left(c\,\hat{A}\right)^\dagger = c^*\,\hat{A}^\dagger$, where c is a complex number.

(iii) $\left(\hat{A}^\dagger\right)^\dagger = \hat{A}$,

(iv) $\left(\hat{A}\,\hat{B}\right)^\dagger = \hat{B}^\dagger\,\hat{A}^\dagger$,

(v) $\left(\hat{A}\,\hat{B} - \hat{B}\,\hat{A}\right)^\dagger = \hat{B}^\dagger\,\hat{A}^\dagger - \hat{A}^\dagger\,\hat{B}^\dagger$

9.3 HERMITIAN OPERATOR

If an operator $\hat{A}$ satisfies the following relation for volume integral of two independent functions $\psi \equiv \psi(x, y, z, t)$ and $\phi \equiv \phi(x, y, z, t)$, then it is called a Hermitian operator:

$$\int \left(\hat{A}\,\psi\right)^* \phi \, dV = \int \psi^* \left(\hat{A}\,\phi\right) dV \quad .$$

This means that

$$\hat{A}^\dagger = \hat{A} \quad .$$

Thus a Hermitian operator is a self-adjoint operator.

The Hermitian operators have the following properties:

(i) $\left(\hat{A} \pm \hat{B}\right)^\dagger = \left(\hat{A} \pm \hat{B}\right)$.

(ii) $\left(c\,\hat{A}\right)^\dagger = c^*\,\hat{A}$, where c is a complex number.

(iii) $\left(\hat{A}\,\hat{B}\right)^\dagger = \hat{B}^\dagger\,\hat{A}^\dagger = \hat{B}\,\hat{A}$; that is the product of two Hermitian operators need not be Hermitian.

(iv) $\left(\hat{A}\,\hat{B} + \hat{B}\,\hat{A}\right)^\dagger = \left(\hat{A}\,\hat{B} + \hat{B}\,\hat{A}\right)$; that is for two Hermitian operators, $\hat{A}\,\hat{B} + \hat{B}\,\hat{A}$ is Hermitian.

(v) $\left[i\left(\hat{A}\,\hat{B} - \hat{B}\,\hat{A}\right)\right]^\dagger = i\left(\hat{A}\,\hat{B} - \hat{B}\,\hat{A}\right)$; that is for two Hermitian operators, $i\left(\hat{A}\,\hat{B} - \hat{B}\,\hat{A}\right)$ is Hermitian.

In quantum mechanics, for each physical measurable variable A, there is a corresponding Hermitian operator $\hat{A}$. The momentum operator $\hat{p}_x = -i\hbar\,\partial/\partial x$, the energy operator $\hat{E} = i\hbar\,\partial/\partial t$ are examples of Hermitian operators (see **Examples 9.4 to 9.7**). The Hermitian operators have real eigenvalues and mutually orthogonal eigenfunctions. See section 9.11 for a proof.

9.4 UNITARY OPERATOR

An operator $\hat{U}$ for which,

$$\hat{U}^\dagger\,\hat{U} = \hat{U}\,\hat{U}^\dagger = \hat{I}$$

is called a unitary operator.

A unitary operator satisfies the property

$$\hat{U}^\dagger = \hat{U}^{-1}$$

An identity operator $\hat{I}$ is also a unitary operator.

If $\hat{H}$ is the Hamiltonian operator, having dimensions of energy, then $\hat{U} = e^{-i\hat{H}\,t/\hbar}$ is a unitary operator. If $\hat{p}_x = -i\hbar\,\partial/\partial x$ is the momentum operator, then $\hat{U} = e^{-i\,\hat{p}_x x/\hbar}$ is a unitary operator.[6]

9.5 STATE FUNCTION

The state of a physical system is represented by a wave function $\Psi(x,y,z,t)$ also known as the state function. The state function is square integrable and in general complex. It may be multiplied by an arbitrary complex number without altering its physical significance. It contains all the information that can be known about the system. It is a function which is used to find the expectation values of dynamical variables describing the state of the system.

For a normalized state function, that is,

$$\int \Psi^*(x,y,z,t)\,\Psi(x,y,z,t)\;dx\,dy\,dz = 1 \quad ,$$

or

$$\int \Psi^*(\vec{r},t)\,\Psi(\vec{r},t)\;dV = 1 \quad .$$

The state function plays the role of probability amplitude. If system consists of a particle moving in the potential energy region $V(x,y,z,t)$, then the probability of finding the particle in a volume element dV around the point x,y,z at time t is (assuming normalized state function)

$$|\Psi(\vec{r},t)|^2\;dV \quad .$$

The state function may be multiplied by a phase factor $e^{i\alpha}$ without altering its physical significance, here α is a constant.

If Ψ_1 and Ψ_2 are state functions representing state 1 and state 2 of a physical system, respectively, then the principle of superposition requires that a linear superposition of the two wave functions

$$\Psi = c_1\Psi_1 + c_2\Psi_2$$

also represent a possible state of the system, here c_1, c_2 are constants (may be complex in general). Two understand it, imagine an ensemble of identical systems, out of which many are in state 1 represented by the state function Ψ_1 and many are in state 2 represented by the state function Ψ_2 .

9.6 EXPECTATION VALUE

Meaning of Expectation Value

In the sense of probability theory, the expectation value is the mathematical expectation

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6 *Unitary operators play an important role in the study of quantum mechanics. Symmetry transformation operators are unitary.*

for the result of a single measurement. Also it is the average of the results of a large number of measurements on equivalent, identically prepared independent systems. Consider an ensemble of a very large number of equivalent, identically prepared independent systems, each in a state represented by the wave function (state function) $\Psi(\vec{r},t)$. Then the expectation value of a measurable dynamical variable A is the average value of the measurement of A performed on these large number of identical systems of the ensemble.

Definition of Expectation Value

The expectation value of an operator $\hat{A}$ assigned to a measurable dynamical variable A of a physical system in a state described by the wave function (state function) $\Psi(\vec{r},t)$ is defined by the following relation:

$$\langle\hat{A}\rangle = \frac{\int \Psi^*(\vec{r},t)\,\hat{A}\,\Psi(\vec{r},t)\,dV}{\int \Psi^*(\vec{r},t)\,\Psi(\vec{r},t)\,dV} \quad . \qquad ...(1)$$

If the wave function is normalized, that is

$$\int \Psi^*(\vec{r},t)\,\Psi(\vec{r},t)\,dV = 1 \quad , \qquad ...(2)$$

then

$$\langle\hat{A}\rangle = \int \Psi^*(\vec{r},t)\,\hat{A}\,\Psi(\vec{r},t)\,dV \quad . \qquad ...(3)$$

In general, the expectation value is a function of time only, as space coordinates have been integrated. However, if an operator does not explicitly depend on time, then its expectation value is independent of time.

For one-dimensional motion, if the physical system is in a state described by the wave function $\Psi(x,t)$, the expectation value for a measurable dynamical variable A is

$$\langle\hat{A}\rangle = \frac{\int_{-\infty}^{\infty} \Psi^*(x,t)\,\hat{A}\,\Psi(x,t)\,dx}{\int_{-\infty}^{\infty} \Psi^*(x,t)\,\Psi(x,t)\,dx} \quad . \qquad ...(4)$$

For a normalized wave function $\int \Psi^*(x,t)\,\Psi(x,t)\,dx = 1$, and

$$\langle\hat{A}\rangle = \int_{-\infty}^{\infty} \Psi^*(x,t)\,\hat{A}\,\Psi(x,t)\,dx \quad . \qquad ...(5)$$

Expectation Value of Position

Let the state function for a particle moving in some potential energy region is $\Psi \equiv \Psi(\vec{r},t)$. Then the expectation value of the position vector of the particle is[7] (for convenience we write $\langle\hat{\vec{r}}\rangle$ as $\langle\vec{r}\rangle$)

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7 *For convenience, the hat on operator is often not written, i.e.,* $\langle\hat{x}\rangle$, $\langle\hat{p}_x\rangle$, $\langle\hat{E}\rangle$, $\langle\hat{\vec{r}}\rangle$, $\langle\hat{\vec{p}}\rangle$ *etc. are written as* $\langle x\rangle$, $\langle p_x\rangle$, $\langle E\rangle$, $\langle\vec{r}\rangle$, $\langle\vec{p}\rangle$ *etc. At many places, we also drop the hat over operator symbol.*

$$\langle \vec{r} \rangle = \frac{\int \Psi^* \hat{\vec{r}}\ \Psi\ dV}{\int \Psi^*\ \Psi\ dV} = \frac{\int \Psi^* \vec{r}\ \Psi\ dV}{\int \Psi^*\ \Psi\ dV} \quad . \qquad ...(6)$$

For normalized wave function, $\int \Psi^*\ \Psi\ dV = 1$, therefore,

$$\langle \vec{r} \rangle = \int \Psi^*\ \vec{r}\ \Psi\ dV = \int \vec{r}\ |\Psi|^2\ dV \quad . \qquad ...(7)$$

The above relation is equivalent to three equations,

$$\langle x \rangle = \int x\ |\Psi|^2\ dV \quad , \quad \langle y \rangle = \int y\ |\Psi|^2\ dV \quad , \quad \langle z \rangle = \int z\ |\Psi|^2\ dV \quad . \qquad ...(8)$$

That is, the expectation value of the position vector of a particle is the vector whose components are the weighted averages of the components of the position of the particle.

For one-dimensional motion and normalized state function

$$\langle x \rangle = \int_{-\infty}^{\infty} \Psi^*(x,t)\ x\ \Psi(x,t)\ dx = \int_{-\infty}^{\infty} x\ |\Psi(x,t)|^2\ dx \qquad ...(9)$$

When the potential energy is independent of time, the wave function separates into parts, $\Psi(x,t) = \psi(x)\ e^{-iEt/\hbar}$, and the expectation value of position of the particle is obtained from the relation

$$\langle x \rangle = \int_{-\infty}^{\infty} \psi^*(x)\ x\ \psi(x)\ dx = \int_{-\infty}^{\infty} x\ |\psi(x)|^2\ dx \quad . \qquad ...(10)$$

Expectation Value of Momentum

Let the state of a particle is described by a normalized state function. $\Psi \equiv \Psi(\vec{r},t)$ Then, the expectation value of the momentum of the particle in this state is (dropping, for convenience, the hat over the operator symbol)

$$\langle \vec{p} \rangle = \int \Psi^*\ \hat{\vec{p}}\ \Psi\ dV = \int \Psi^* \left(-i\hbar \vec{\nabla} \Psi\right) dV \quad . \qquad ...(11)$$

The expectation values of the components of the momentum are

$$\langle p_x \rangle = \int \Psi^*\ \hat{p}_x\ \Psi\ dV = \int \Psi^* \left(-i\hbar \frac{\partial \Psi}{\partial x}\right) dV \quad ,$$

$$\langle p_y \rangle = \int \Psi^*\ \hat{p}_y\ \Psi\ dV = \int \Psi^*(\vec{r},t) \left(-i\hbar \frac{\partial \Psi}{\partial y}\right) dV \quad ,$$

$$\langle p_z \rangle = \int \Psi^*\ \hat{p}_z\ \Psi\ dV = \int \Psi^* \left(-i\hbar \frac{\partial \Psi}{\partial z}\right) dV \quad . \qquad ...(12)$$

For one-dimensional motion and normalized state function $\Psi(x,t)$,

$$\langle p_x \rangle = \int_{-\infty}^{\infty} \Psi^*(x,t) \left(-i\hbar \frac{\partial \Psi(x,t)}{\partial x}\right) dx \quad . \qquad ...(13)$$

For one-dimension motion in a time independent potential energy region,

$$\langle p_x \rangle = \int_{-\infty}^{\infty} \psi^*(x) \left(-i\hbar \frac{\partial \psi(x)}{\partial x}\right) dx \quad . \qquad ...(14)$$

Expectation Value of Energy

The total energy operator is $\hat{E} = i\hbar \frac{\partial}{\partial t}$. Let the state of a particle is described by the normalized wave function $\Psi \equiv \Psi(\vec{r}, t)$. Then, the expectation value of the total energy of the particle in this state is

$$\langle E \rangle = \int \Psi^* \hat{E} \ \Psi \ dV = \int \Psi^* \left(i\hbar \frac{\partial \Psi}{\partial t} \right) dV \ .$$

For one-dimensional motion and normalized state function $\Psi(x, t)$,

$$\langle E \rangle = \int_{-\infty}^{\infty} \Psi^*(x, t) \left(i\hbar \frac{\partial \Psi(x, t)}{\partial t} \right) dx \ . \qquad ...(15)$$

When the potential energy is independent of time, the wave function separates into parts, $\Psi(x, t) = \psi(x) \ e^{-iEt/\hbar}$. Then for a normalized wave function,

$$\langle E \rangle = E \ .$$

The particle in a stationary state has a definite energy.

Expectation Value of Kinetic Energy

The kinetic energy operator is $\hat{T} = -\frac{\hbar^2}{2m} \nabla^2$. Let the state of a particle is described by the normalized wave function . $\Psi \equiv \Psi(\vec{r}, t)$ Then, the expectation value of the kinetic energy of the particle in this state is

$$\langle T \rangle = \int \Psi^* \left(-\frac{\hbar^2}{2m} \nabla^2 \Psi \right) dV \ . \qquad ...(16)$$

Expectation Value of Potential Energy

The potential energy operator is $\hat{V} = V(\hat{\vec{r}}, t) = V(\vec{r}, t)$. The expectation value of the potential energy is (we use symbol $d\tau$ for volume element, as we are using the symbol V for potential energy)

$$\langle V \rangle = \int \Psi^* \ V(\vec{r}, t) \ \Psi \ d\tau \ ,$$

$$= \int V(\vec{r}, t) \ |\Psi|^2 \ d\tau \ . \qquad ...(17)$$

(see **Examples 9.8 to 9.11**)

9.7 EHRENFEST'S THEOREM[8]

Statement of Ehrenfest theorem

The Ehrenfest theorem states that if the dynamical variables in the equation of motion of a particle in classical mechanics are replaced by the expectation values of the corresponding operators, then the expectation values of the operators obey the same equation in quantum mechanics as the dynamical variables in classical mechanics. That is

8 *P. Ehrenfest, Z. Physik, vol. 45, 455 (1927)*

$$\langle \vec{p} \rangle = m \frac{d}{dt} \langle \vec{r} \rangle \quad , \qquad \ldots (I)$$

and

$$\frac{d}{dt} \langle \vec{p} \rangle = \langle -\vec{\nabla} V \rangle = \langle \vec{F} \rangle \quad . \qquad \ldots (II)$$

In the component form, these relations are

$$\langle p_x \rangle = m \frac{d}{dt} \langle x \rangle \quad , \quad \text{and} \quad \frac{d}{dt} \langle p_x \rangle = \langle -\frac{\partial V}{\partial x} \rangle = \langle F_x \rangle \quad ;$$

$$\langle p_y \rangle = m \frac{d}{dt} \langle y \rangle \quad , \quad \text{and} \quad \frac{d}{dt} \langle p_y \rangle = \langle -\frac{\partial V}{\partial y} \rangle = \langle F_y \rangle \quad ;$$

$$\langle p_z \rangle = m \frac{d}{dt} \langle z \rangle \quad , \quad \text{and} \quad \frac{d}{dt} \langle p_z \rangle = \langle -\frac{\partial V}{\partial z} \rangle = \langle F_z \rangle \quad .$$

Proof of Ehrenfest theorem - relation (I): $\frac{d}{dt} \langle x \rangle = \frac{1}{m} \langle p_x \rangle$.

Consider a particle moving in a potential energy region $V(\vec{r}, t)$ and described by a normalized wave function $\psi(\vec{r}, t)$. The expectation value of *x*-component of the position vector is, by definition, (we use symbol $d\tau$ for volume element, as we are using the symbol *V* for potential energy)

$$\langle x \rangle = \int \psi^*(\vec{r}, t)\, x\, \psi(\vec{r}, t)\, d\tau \quad . \qquad \ldots (1)$$

The *x* in the integrand of Eq.(1) is a variable of integration. The expectation value $\langle x \rangle$ depends only on time. Therefore, the time rate of change of $\langle x \rangle$ is (we use $\psi \equiv \psi(\vec{r}, t)$ and $\psi^* \equiv \psi^*(\vec{r}, t)$ for notational simplicity)

$$\frac{d}{dt} \langle x \rangle = \int \left(\frac{\partial \psi^*}{\partial t} \right) x\, \psi\, d\tau + \int \psi^*\, x \left(\frac{\partial \psi}{\partial t} \right) d\tau \quad . \qquad \ldots (2)$$

The time-dependent Schrodinger equation is

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

Therefore,

$$\frac{\partial \psi}{\partial t} = -\frac{\hbar}{2mi} \nabla^2 \psi + \frac{V}{i\hbar} \psi \quad , \qquad \ldots (3a)$$

and

$$\frac{\partial \psi^*}{\partial t} = \frac{\hbar}{2mi} \nabla^2 \psi^* - \frac{V}{i\hbar} \psi^* \quad . \qquad \ldots (3b)$$

We use (3a & 3b) in (2), and note that the potential energy function is $V = V(\vec{r}, t)$, that is it depends on x, y, z and t . Therefore, we can write $V \psi^* x \psi = x V \psi^* \psi$, and $\psi^* x V \psi = x V \psi^* \psi$. So the terms involving the potential energy *V* cancel out, and we get

$$\frac{d}{dt} \langle x \rangle = \frac{\hbar}{2mi} \left[\int \left(\nabla^2 \psi^* \right) x\, \psi\, d\tau - \int \psi^*\, x \left(\nabla^2 \psi \right) d\tau \right] \quad . \qquad \ldots (4)$$

To solve it further, first we prove that the first integral satisfies the following relation,[9]

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9 ∇^2 *is a Hermitian and real operator. Therefore, for two complex wave functions,* ϕ_1 *and*

$$\int \left(\nabla^2 \psi^*\right) x \ \psi \ d\tau = \int \psi^* \ \nabla^2 (x \psi) \ d\tau \quad . \qquad ...(5)$$

Using the vector identity $\vec{\nabla} \cdot (\phi \ \vec{A}) = \vec{\nabla} \phi \cdot \vec{A} + \phi \left(\vec{\nabla} \cdot \vec{A}\right)$, where ϕ is some scalar function and $\vec{A}$ is some vector function, we note that

$$\vec{\nabla} \cdot \left((x\psi)\,(\vec{\nabla}\psi^*)\right) = \vec{\nabla}(x\psi) \cdot (\vec{\nabla}\psi^*) + (x\psi)\,(\nabla^2\psi^*) \quad . \qquad ...(6)$$

Further, the first integral in (4) can be written as

$$\int \left(\nabla^2 \psi^*\right) x \ \psi \ d\tau = \int (x\psi) \left(\nabla^2 \psi^*\right) d\tau \quad .$$

Now using the relation (6), we get

$$\int \left(\nabla^2 \psi^*\right) x \ \psi \ d\tau = \int \vec{\nabla} \cdot \left((x\psi)\,(\vec{\nabla}\psi^*)\right) d\tau - \int \vec{\nabla}(x\psi) \cdot (\vec{\nabla}\psi^*) \ d\tau \quad . \qquad ...(7)$$

The Gauss divergence theorem converts volume integral of a divergence into surface integral. According to it the first integral of relation (7) becomes

$$\int_V \vec{\nabla} \cdot \left((x\psi)\,(\vec{\nabla}\psi^*)\right) d\tau = \int_S (x\psi)\,(\vec{\nabla}\psi^*) \cdot d\vec{S} = 0 \quad . \qquad ...(8)$$

Here S is the surface enclosing the volume V. Since the volume integral is over the entire space, the surface lies at infinity where the wave function vanishes. Therefore, the result of the surface integral is zero. On using (8) in (7) we find

$$\int \left(\nabla^2 \psi^*\right) x \ \psi \ d\tau = - \int \vec{\nabla}(x\psi) \cdot (\vec{\nabla}\psi^*) \ d\tau \quad ,$$

$$= - \int (\vec{\nabla}\psi^*) \cdot \vec{\nabla}(x\psi) \ d\tau \quad . \qquad ...(9)$$

In a similar manner, using vector identity $\vec{\nabla} \cdot (\phi \ \vec{A}) = \vec{\nabla} \phi \cdot \vec{A} + \phi \left(\vec{\nabla} \cdot \vec{A}\right)$, we find that

$$\int \vec{\nabla} \cdot \left(\psi^* \,(\vec{\nabla}(x\psi))\right) d\tau = \int (\vec{\nabla}\psi^*) \cdot (\vec{\nabla}(x\psi)) \ d\tau + \int \psi^* \ \nabla^2 (x\psi) \ d\tau \quad . \qquad ...(10)$$

Again using Gauss divergence theorem for the left hand side integral, we find

$$\int_V \vec{\nabla} \cdot \left(\psi^* \,(\vec{\nabla}(x\psi))\right) d\tau = \int_S \psi^* \,(\vec{\nabla}(x\psi)) \cdot d\vec{S} = 0 \quad .$$

Therefore, relation (10) gives

$$\int \psi^* \ \nabla^2 (x\psi) \ d\tau = - \int (\vec{\nabla}\psi^*) \cdot (\vec{\nabla}(x\psi)) \ d\tau \quad . \qquad ...(11)$$

Comparing (9) and (11), we find

$$\int \left(\nabla^2 \psi^*\right) x \ \psi \ d\tau = \int \psi^* \ \nabla^2 (x \psi) \ d\tau \quad .$$

Thus we proved the relation (5). Using it in (4) we get

$$\frac{d}{dt}\langle x \rangle = \frac{\hbar}{2mi} \left[\int \psi^* \ \nabla^2 (x\psi) \ d\tau - \int \psi^* \ x \left(\nabla^2 \psi\right) d\tau\right] \quad ,$$

$$= - \frac{i\hbar}{2m} \left\{\int \psi^* \left[\nabla^2 (x\psi) - x \left(\nabla^2 \psi\right)\right] d\tau\right\} \quad . \qquad ...(12)$$

We note that

$$\nabla^2 (x\psi) = \vec{\nabla} \cdot \vec{\nabla}(x\psi) = \vec{\nabla} \cdot \left[(\vec{\nabla} x)\psi + x(\vec{\nabla}\psi)\right] \quad .$$

ϕ_2 , it satisfies the property $\int \left(\nabla^2 \phi_1^*\right) \phi_2 \ d\tau = \int \phi_1^* \left(\nabla^2 \phi_2\right) d\tau$. Substituting $\phi_1 = \psi$ and $\phi_2 = x\psi$, we get Eq.(5). Here we are presenting in detail a proof of Eq.(5) without using the fact that ∇^2 is Hermitian.

$$= \frac{\partial \psi}{\partial x} + \left(\frac{\partial \psi}{\partial x} + x \, \nabla^2 \psi \right) \quad .$$

Therefore,

$$\nabla^2 (x \psi) - x \left(\nabla^2 \psi \right) = 2 \, \frac{\partial \psi}{\partial x} \quad . \qquad \ldots(13)$$

Using (13) in (12), we get

$$\frac{d}{dt} \langle x \rangle = - \frac{i \hbar}{2 m i} \left[\int \psi^* \, 2 \, \frac{\partial \psi}{\partial x} \, d\tau \right] \quad ,$$

$$= \frac{1}{m} \left[\int \psi^* \left(-i \hbar \frac{\partial}{\partial x} \right) \psi \; d\tau \right] \quad ,$$

or $$\frac{d}{dt} \langle x \rangle = \frac{1}{m} \left[\int \psi^* \; \hat{p}_x \psi \; d\tau \right] \quad , \qquad \ldots(14)$$

or $$\frac{d}{dt} \langle x \rangle = \frac{1}{m} \, \langle \hat{p}_x \rangle \quad .$$

Proof of Ehrenfest theorem - relation (II) : $\frac{d}{dt} \langle p_x \rangle = \langle - \frac{\partial V}{\partial x} \rangle = \langle F_x \rangle$

Consider a particle moving in a potential energy region $V(\vec{r}, t)$ and described by a normalized wave function $\psi(\vec{r}, t)$. The expectation value of x-component of the momentum vector is, by definition, (we use symbol $d\tau$ for volume element, as we are using the symbol V for potential energy)

$$\langle p_x \rangle = -i \hbar \int \psi^* (\vec{r}, t) \, \frac{\partial \psi(\vec{r}, t)}{\partial x} \, d\tau \quad . \qquad \ldots(1)$$

Using $\psi \equiv \psi(\vec{r}, t)$ and $\psi^* \equiv \psi^* (\vec{r}, t)$ for notational simplicity, the time rate of change of $\langle p_x \rangle$ is

$$\frac{d}{dt} \langle p_x \rangle = -i \hbar \int \left[\frac{\partial \psi^*}{\partial t} \, \frac{\partial \psi}{\partial x} + \psi^* \, \frac{\partial}{\partial x} \left(\frac{\partial \psi}{\partial t} \right) \right] d\tau \quad . \qquad \ldots(2)$$

The time-dependent Schrodinger equation is

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

Therefore,

$$\frac{\partial \psi}{\partial t} = - \frac{\hbar}{2 m i} \, \nabla^2 \psi + \frac{V}{i \hbar} \psi \quad , \qquad \ldots(3a)$$

and

$$\frac{\partial \psi^*}{\partial t} = \frac{\hbar}{2 m i} \, \nabla^2 \psi^* - \frac{V}{i \hbar} \psi^* \quad . \qquad \ldots(3b)$$

We substitute (3a & 3b) in (2) and simplify to get

$$\frac{d}{dt} \langle p_x \rangle = - \frac{\hbar^2}{2 m} \int \left[\left(\nabla^2 \psi^* \right) \frac{\partial \psi}{\partial x} - \psi^* \frac{\partial}{\partial x} \left(\nabla^2 \psi \right) \right] d\tau - \int \psi^* \, \frac{\partial V}{\partial x} \, \psi \; d\tau \quad . \qquad \ldots(4)$$

The Laplacian ∇^2 is a Hermitian and real operator, therefore, for two complex wave functions, ϕ_1 and ϕ_2, it satisfies the property

$$\int \left(\nabla^2 \, \phi_1^* \right) \phi_2 \, d\tau = \int \phi_1^* \left(\nabla^2 \, \phi_2 \right) d\tau \quad .$$

Substituting $\phi_1 = \psi$ and $\phi_2 = \partial\psi/\partial x$, we get

$$\int \left(\nabla^2 \psi^*\right) \frac{\partial \psi}{\partial x}\, d\tau = \int \psi^* \nabla^2 \left(\frac{\partial \psi}{\partial x}\right) d\tau \quad ,$$

$$= \int \psi^* \frac{\partial}{\partial x}\left(\nabla^2 \psi\right) d\tau \quad . \qquad \ldots(5)$$

Using (5) in (4) gives

$$\frac{d}{dt}\langle p_x \rangle = -\int \psi^* \frac{\partial V}{\partial x}\, \psi \, d\tau \quad ,$$

or
$$\frac{d}{dt}\langle p_x \rangle = -\left\langle \frac{\partial V}{\partial x} \right\rangle \quad ,$$

or
$$\frac{d}{dt}\langle p_x \rangle = \langle F_x \rangle \quad .$$

(See **Example 9.12** (book 26)also)

Significance of Ehrenfest theorem

Ehrenfest theorem provides an example of the correspondence principle, since it shows that a wave packet moves like a classical particle in the macroscopic limit in which the finite size and the internal structure of the wave packet is ignored. According to Ehrenfest theorem, the motion of a wave packet representing a particle in quantum mechanics agrees with the motion of the corresponding classical particle if we mean by the “position” and “momentum” vectors of the wave packet the expectation values of these quantities. This is true whenever the potential energy changes by a negligible amount over the dimensions of the packet.

Complementarity Principle

The complementary principle was given by Bohr in 1928. It states that the wave and particle aspects of physical systems are complimentary, both aspects being needed for a complete description of nature. In no single experiment does a photon show both the wave and the particle properties, nor does a particle simultaneously show both the wave and particle properties.

The wave and particle aspects are related by Planck constant *h*. In the limit $h \to 0$, the quantum physics tends to classical physics, this means that for the electron it results into particle picture and for the light it results into wave picture. In atomic domains we can not neglect *h*, and large deviations from classical physics are observed. In atomic domains, the electron shows wave properties and the light shows particle properties. Thus both wave and particle aspects are needed for a complete description of nature.

According to complementarity principle, the electron should be thought of as a wave-particle displaying either wave or particle properties according to the experiment. A single experiment can not show together both the wave and particle aspects.

9.8 EIGENVALUE AND EIGENFUNCTION

Let an operator $\hat{A}$ acts on some function ψ and the result is that we obtain the same function or a multiple of the same function, then we have

$$\hat{A}\, \psi = a\, \psi \quad , \qquad \ldots(1)$$

where the number a is in general complex. Then ψ is called the eigenfunction of the operator $\hat{A}$ and a is called the corresponding eigenvalue of the operator $\hat{A}$.

Eq.(1) is known as the eigenvalue equation.[10]

For example: Consider the differential operator $\hat{A} \equiv \partial/\partial x$, and an exponential function $\phi(x) = N e^{ikx}$, where N and k are constants. Since,

$$\hat{A}\ \phi(x) = \frac{\partial(N e^{ikx})}{\partial x} = ik N e^{bx} \quad ,$$

or $$\hat{A}\ \phi(x) = (ik)\ \phi(x) \quad .$$

Thus is $\phi(x) = N e^{ikx}$ an eigenfunction of operator $\hat{A} \equiv \partial/\partial x$ and the corresponding eigenvalue is ik. Note that the operator $\hat{A} \equiv \partial/\partial x$ is not Hermitian, and the eigenvalue ($i\,k$) is complex.

For an arbitrary operator, in general, the eigenvalue may be complex. But in quantum mechanics, for any physical measurable dynamical variable A the operator is Hermitian, and for a Hermitian operator the eigenvalues are real. (See section 9.11 for proof).

For example, consider the time independent Schrodinger equation for a particle in a potential energy region $V(\vec{r})$. The eigenvalue equation is

$$\hat{H}\ \psi_n(\vec{r}) = E_n\ \psi_n(\vec{r}) \quad ,$$

where $\psi_n(\vec{r})$ is an eigenfunction of the Hamiltonian operator $\hat{H} = (-\hbar^2/2m)\nabla^2 + V(\vec{r})$, and E_n is the corresponding eigenvalue. For many types of $V(\vec{r})$, there exists more than one eigenfunctions and eigenvalues, so the subscript n is used to specify them, $n = 1, 2, 3, \ldots$. Thus an operator can in general have many different eigenfunctions. The eigenfunctions of a Hermitian operator belonging to different eigenvalues are orthogonal to each other. (See section 9.11 for proof)

(see Example 9.13-9.16(book 14,15,16,17)

9.9 DEGENERACY

Let there exists an operator $\hat{A}$ for which,

$$\hat{A}\ \psi_1 = a\ \psi_1 \quad ,$$

$$\hat{A}\ \psi_2 = a\ \psi_2 \quad ,$$

.... ,

$$\hat{A}\ \psi_n = a\ \psi_n \quad .$$

That is there exists many (in above example n) different linearly independent eigenfunctions of the operator $\hat{A}$ and all of these eigenfunctions corresponds to one eigenvalue a. Then we say that the eigenvalue is degenerate. This property is called degeneracy. The number of linearly independent eigenfunctions belonging to that eigenvalue is called the degree of degeneracy. In this example the degree of degeneracy is n. The eigenvalue is n-fold degenerate.

Let for the eigenvalue equation

---

10 *Eigen is a German word which mean characteristic.*

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

there are n linearly independent eigenfunctions for one energy value E. Then the energy level is n-fold degenerate. The fine structure and hyperfine structure of spectral lines are due to degenrate energy levels.

(see **Example 9.17**)

*(**Comment:** For a free particle moving in one-dimension, the Hamiltonian operator is*

$$\hat{H} = \frac{\hat{p}_x^2}{2m} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} \quad .$$

The eigenvalue equation is

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi = E\,\psi \quad , \qquad or \qquad \frac{d^2\psi}{dx^2} + k^2\psi = 0 \quad ,$$

where $k = \frac{\sqrt{2mE}}{\hbar}$ *. There are two independent solutions of the above equation. These are* e^{ikx} *and* e^{-ikx} *. So each eigenvalue* E *is doubly degenerate.)*

9.10 ORTHOGONALITY OF EIGENFUNCTIONS

Orthogonality condition

Two state functions (or wave functions), $\psi(\vec{r},t)$ and $\phi(\vec{r},t)$, are said to be orthogonal when they satisfy the following orthogonality condition:

$$\int \psi^*(\vec{r},t)\,\phi(\vec{r},t)\,dV = 0 \quad ,$$

where the volume integration is over the entire space.

Orthogonality of Energy Eigenfunctions

Two energy eigenfunctions belonging to two unequal (different) eigenvalues are orthogonal.

Proof: Let us consider the energy eigenvalue equation

$$\hat{H}\,\psi_n = E_n\,\psi_n \quad , \qquad \ldots(1)$$

where $\hat{H}$ is the Hamiltonian operator for total energy, ψ_n is eigenfunction and E_n is corresponding energy eigenvalue. It is assumed that the eigenvalues are non-degenerate, that means for each eigenvalue there exists only one linearly independent eigenfunction. Let us consider two energy eigenfunctions, ψ_n and ψ_m belonging to two unequal eigenvalues, E_n and E_m , respectively. That is

$$\hat{H}\,\psi_n = E_n\,\psi_n \quad , \qquad \ldots(2)$$

and

$$\hat{H}\,\psi_m = E_m\,\psi_m \quad . \qquad \ldots(3)$$

Multiplying (2) by ψ_m^* from left and volume integrating over entire space gives

$$\int \psi_m^*\left(\hat{H}\,\psi_n\right)dV = E_n \int \psi_m^*\,\psi_n\,dV \quad . \qquad \ldots(4)$$

The complex conjugate of Eq.(3) is

$$\left(\hat{H}\,\psi_m\right)^* = E_m\,\psi_m^* \quad , \qquad \ldots(5)$$

where we have used the fact the Hamiltonian (total energy operator) is Hermitian and its energy eigenvalues are real, $E^* = E$. Multiplying (5) by ψ_n from right side and volume integrating over the entire space, we get

$$\int \left(\hat{H}\ \psi_m\right)^* \psi_n\ dV = E_m \int \psi_m^* \psi_n\ dV \quad . \qquad \text{...(6)}$$

Because, $\hat{H}$ is a Hermitian operator, therefore, it obeys the Hermiticity condition

$$\int \left(\hat{H}\ \psi_m\right)^* \psi_n\ dV = \int \psi_m^* \left(\hat{H}\,\psi_n\right) dV \quad . \qquad \text{...(7)}$$

Using (7) in(6), we find

$$\int \psi_m^* \left(\hat{H}\,\psi_n\right) dV = E_m \int \psi_m^*\ \psi_n\ dV \quad . \qquad \text{...(8)}$$

Subtracting (4) from (8), we find

$$\left(E_m - E_n\right) \int \psi_m^*\ \psi_n\ dV = 0 \quad . \qquad \text{...(9)}$$

Since $E_m \neq E_n$, therefore,

$$\int \psi_m^*\ \psi_n\ dV = 0 \quad . \qquad \text{...(10)}$$

Thus two energy eigenfunctions belonging to two unequal eigenvalues are orthogonal.

*(**Comment**: The linearly independent solutions* $\psi_n\,(n = 1,\ 2,\ 3,\ ...)$ *of the Schrodinger equation*

$$\hat{H}\ \psi_n = E_n\ \psi_n \quad ,$$

belonging to different eigenvalues are orthogonal, as shown above.

This prove does not apply if there is a degeneracy in any eigenvalue. For a degenerate eigenvalue there are more than one linearly independent eigenfunctions for that eigenvalue. Let us assume that the degeneracy of E_n *is of the order* α *and* $\psi_{n1}, \psi_{n2}, \cdots, \psi_{n\alpha}$ *are the* α *linearly independent normalized eigenfunctions corresponding to that energy. The orthogonality proof given above is not valid because in this case eigenvalue for two different eigenfunctions is the same. Further, in general, the eigenfunctions* $\psi_{n1}, \psi_{n2}, \cdots, \psi_{n\alpha}$ *need not be orthogonal. However, given a set of* α *linearly independent, normalizable functions, it is always possible to construct a new set of* α *mutually orthogonal functions by using a procedure known as the Schmidt orthogonalisation procedure.)*

Orthonormality Condition

The normalization condition for an eigenfunction (or wave function) ψ_n is

$$\int \psi_n^*\ \psi_n\ dV = 1 \quad . \qquad \text{...(1)}$$

The orthogonality condition for two eigenfunctions (or wave functions), ψ_m and ψ_n , is

$$\int \psi_m^*\ \psi_n\ dV = 0 \quad . \qquad \text{...(2)}$$

The two conditions (1) and (2) can be written as follows in a combined manner:

$$\int \psi_m^*\ \psi_n\ dV = \delta_{mn} \quad , \qquad \text{...(3)}$$

where δ_{mn} is the Kronecker delta-symbol, such that

$$\delta_{mn} = 1 \quad \text{if} \quad m = n \quad ,$$

$$\delta_{mn} = 0 \quad \text{if} \quad m \neq n \quad . \qquad \text{...(4)}$$

The condition (3), namely $\int \psi_m^* \, \psi_n \, dV = \delta_{mn}$, is called the orthonormality consition.

9.11 EIGENVALUES AND EIGENFUNCTIONS OF HERMITIAN OPERATORS[11]

The eigenvalues of a Hermitian operator are always real.

Proof: Consider a Hermitian operator $\hat{A}$. Let ψ is an eigenfunction of operator $\hat{A}$ and the corresponding eigenvalue is a , that is,

$$\hat{A}\,\psi = a\,\psi \quad . \qquad ...(1)$$

From the condition of Hermiticity, we can write

$$\int \left(\hat{A}\,\psi\right)^* \psi \, dV = \int \psi^* \left(\hat{A}\,\psi\right) dV \quad . \qquad ...(2)$$

The left hand term of (2), using (1), is

$$\int \left(\hat{A}\,\psi\right)^* \psi \, dV = \int (a\,\psi)^* \, \psi \, dV \quad ,$$

$$= \int a^* \, \psi^* \, \psi \, dV \quad ,$$

$$= a^* \int \psi^* \, \psi \, dV \quad . \qquad ...(4)$$

The right-hand term of (3), using (1), is

$$\int \psi^* \left(\hat{A}\,\psi\right) dV = \int \psi^* \,(a\,\psi)\, dV \quad ,$$

$$= a \int \psi^* \, \psi \, dV \quad . \qquad ...(5)$$

Using (4) and (5) in (2) gives

$$a^* \int \psi^* \, \psi \, dV = a \int \psi^* \, \psi \, dV \quad ,$$

or $$\left(a^* - a\right) \int \psi^* \, \psi \, dV = 0 \quad . \qquad ...(6)$$

For an eigenfunction ψ , the normalization integral is a constant, that is,

$$\int \psi^* \, \psi \, dV = constant \quad . \qquad ...(7)$$

Using the above in (6), implies that

$$\left(a^* - a\right) = 0 \quad ,$$

or $$a^* = a \quad . \qquad ...(8)$$

That means a is real. Thus the eigenvalues of a Hermitian operator are always real.

The eigenfunctions of a Hermitian operator belonging to different eigenvalues are orthogonal to each other.

Proof: Let $\hat{A}$ is a Hermitian operator, and a_n and a_m are two different eigenvalues with corresponding eigenfunction ψ_n and ψ_m , respectively, that is

$$\hat{A}\,\psi_n = a_n \psi_n \quad , \qquad ...(1)$$

and $$\hat{A}\,\psi_m = a_m \psi_m \quad . \qquad ...(2)$$

A Hermitian operator $\hat{A}$ satisfies the following property,

$$\int \left(\hat{A}\,\psi_n\right)^* \psi_m \, dV = \int \psi_n^* \left(\hat{A}\,\psi_m\right) dV \quad . \qquad ...(3)$$

11 *Hermitian operators have real eigenvalues and mutually orthogonal eigenfunctions.*

Using (1) and (2) in the above, we find,

$$\int (a_n \, \psi_n)^* \, \psi_m \, dV = \int \psi_n^* \, (a_m \, \psi_m) \, dV \quad ,$$

or $$a_n^* \int \psi_n^* \, \psi_m \, dV = a_m \int \psi_n^* \, \psi_m \, dV \quad . \qquad ...(4)$$

The eigenvalues of a Hermitian operator are real, that is, $a_n^* = a_n$. Therefore, (4) gives,

$$(a_n - a_m) \int \psi_n^* \, \psi_m \, dV = 0 \quad .$$

Since the eigenvalues are different, $a_n \neq a_m$, therefore, the above relation gives

$$\int \psi_n^* \, \psi_m \, dV = 0 \quad .$$

That is, for a Hemitian operator, the wave functions belonging to different eigenvalues are orthogonal.

(***Comments:*** *(1) For a Hermitian operator, it is always possible to fine a complete set of mutually orthogonal and normal eigenfunctions,*

$$\int \psi_n^* \, \psi_m \, dV = \delta_{nm} \quad .$$

(2) An arbitrary wave-function $\phi(x)$ *can always be expressed as a linear combination of a complete set of orthonormal eigenfunctions* $\psi_k(x)$ *of a Hermitian operator,*

$$\phi(x) = \sum_k C_k \, \psi_k(x) \quad ,$$

where C_k *are complex constants.*

(3) If $\hat{A} \, \psi = a \, \psi$ *, then* $(\hat{A})^n \, \psi = (a)^n \, \psi$ *. This means that* $\langle A^n \rangle = a^n = \langle A \rangle^n$ *. That is in a state described by the wave-function* ψ *, the expectation value of the* n^{th} *power of* A *is just the* n^{th} *power of* $\langle A \rangle$ *.)*

9.12 FUNDAMENTAL POSTULATES OF QUANTUM MECHANICS

The quantum mechanics can be developed based on certain postulates. These postulates are applicable for an ensemble of physical systems. For the sake of convenience, many a times we consider only one physical system. The postulates are:

1. To a physical system one can associate a wave function or state function $\psi(x, y, z, t)$ which contains all the information that can be known about the system. This function is in general complex; it may be multiplied by an arbitrary complex number without altering its physical significance.

The complex wave-function $\psi(\vec{r}, t)$ should be single valued, finite and continuous. The function should be square integrable and so that it can be normalized,

$$\int |\psi(\vec{r}, t)|^2 dV = 1 \quad .$$

The quantity

$$P(\vec{r}, t) = |\psi(\vec{r}, t)|^2$$

is interpreted as position probability density, in the sense that $P(\vec{r}, t) \, dV$ is the probability of finding at time t the particle in volume element dV around position $\vec{r}$.

For a physical system containing two particles[12], the wave function is $\psi(\vec{r}_1, \vec{r}_2, t)$ which depends on the position vectors of the particles and the time. Let the wave-function is normalized to unity, that is,

$$\int |\psi(\vec{r}_1, \vec{r}_2, t)|^2 \, dV_1 \, dV_2 = 1 \quad .$$

When the wave-function is normalized to unity, the quantity

$$P(\vec{r}_1, \vec{r}_2, t) = |\psi(\vec{r}_1, \vec{r}_2, t)|^2$$

can be interpreted as a position probability density, in the sense that $P(\vec{r}_1, \vec{r}_2, t) dV_1 dV_2$ is the probability of finding at time t particle 1 in the volume element dV_1 about $\vec{r}_1$ and particle 2 in the volume element dV_2 about $\vec{r}_2$.

$$P_1(\vec{r}_1, t) = \int |\psi(\vec{r}_1, \vec{r}_2, t)|^2 \, dV_2$$

is the position probability density of particle 1 at the point $\vec{r}_1$ at time t , independently of the positions of the other particle.

Momentum space wave-function:

Instead of using the configuration space wave-function $\psi(\vec{r}, t)$ to describe the state of one-particle system, we could as well use the corresponding momentum space wave function $\phi(\vec{p}, t)$, the Fourier transform of $\psi(\vec{r}, t)$, that is,

$$\phi(\vec{p}, t) = \frac{1}{(2\pi\hbar)^{3/2}} \int e^{i\vec{p}\cdot\vec{r}/\hbar} \, \psi(\vec{r}, t) \, d\vec{r} \quad . \qquad (\text{Here } \; d\vec{r} \equiv d^3 r = dx \; dy \; dz \equiv dV \;)$$

If the configuration space wave-function $\psi(\vec{r}, t)$ is normalized to unity, the corresponding momentum space wave-function $\phi(\vec{p}, t)$ will also be normalized to unity in momentum space:

$$\int |\phi(\vec{p}, t)|^2 \, d\vec{p} = 1 \quad .$$

The quantity

$$\Pi(\vec{p}, t) = |\phi(\vec{p}, t)|^2$$

can be interpreted as the probability density in momentum space for finding the momentum of the particle in the volume $d\vec{p}$ about $\vec{p}$.

2. Superposition principle: If the state function ψ_1 is associated with one possible state of a statistical ensemble of physical systems, and the state function ψ_2 with another state of this ensemble, then any linear combination

$$\psi = c_1 \psi_1 + c_2 \psi_2$$

where c_1 and c_2 are complex constants, is also a state function associated with a possible state of the ensemble.[13]

3. With every measurable dynamical variable is associated a linear Hermitian operat-

12 *We ignore spin or other internal degrees of freedom.*

13 *The relative phase of* ψ_1 *and* ψ_2 *in* $\psi = c_1\psi_1 + c_2\psi_2$ *is important, since it does affect the physical quantity* $|\psi|^2$.

or.

For example, for the canonical momentum p_x the operator correspondence in a coordinate realization is

$$p_x \to -i\hbar \frac{\partial}{\partial x} \quad .$$

Table 9.1 contains some measurable classical dynamical variables and associated quantum mechanical operators in Cartesian coordinate representation. A Hermitian operator is a self-adjoint operator. It has real eigenvalues.

4. The only result of a precise measurement of the dynamical variable A is one of the eigenvalues a_n of the Hermitian operator $\hat{A}$ associated with A .

The set of all the eigenvalues, $\{a_n\}$, of an operator $\hat{A}$ is called the spectrum of $\hat{A}$. The eigenvalues of an observable are real. The spectrum may consists of only discrete eigenvalues, or of a continuous range of eigenvalues, or a mixture of both.

If the wave function of a system is one of the eigenfunctions ψ_n of the operator $\hat{A}$, corresponding to the eigenvalue a_n , then a measurement of the dynamical variable A will certainly produce the result a_n . In this case we say that the system is in an eigenstate of $\hat{A}$ characterized by the eigenvalue a_n . If the wave function is not an eigenfunction of $\hat{A}$, then in a measurement of A any one of the results $a_1, a_2, \ldots,$ can be obtained.

5. If a series of measurements is made of the dynamical variable A on an ensemble of systems, described by the wave function ψ , the expectation or average value of this dynamical variable is

$$\langle A \rangle = \frac{\int \psi^* \hat{A} \psi \, dV}{\int \psi^* \psi \, dV} \quad .$$

6. A wave function representing any dynamical state can be expressed as a linear combination of the eigenfunctions of $\hat{A}$, where $\hat{A}$ is the operator associated with a dynamical variable.

Let $\{\psi_n\}$ is a complete set of the eigenfunctions of a Hermitian operator associated with a dynamical variable. For an arbitrary dynamical state described by a wave-function Ψ , we can write, according to the above postulate,

$$\Psi = \sum_n c_n \psi_n \quad ,$$

where the coefficient of expansions are

$$c_m = \int \psi_m^* \Psi \, dV \quad .$$

The quantity

$$P_n = |c_n|^2$$

is interpreted as the probability that in a given measurement the particular value a_n will be obtained. The coefficients c_n are called probability amplitudes.

7. The time evolution of a wave-function of a system is determined by the time-dependent Schrodinger equation

$$i\hbar \frac{\partial \Psi}{\partial t} = \hat{H}\, \Psi \quad ,$$

where $\hat{H}$ is the Hamiltonian, or total energy operator of the system.

For example, for a particle of mass m , position coordinate $\vec{r}$, momentum $\vec{p}$ moving in a region such that its potential energy $V(\vec{r},t)$ depends only on the position $\vec{r}$ and time t , the Hamiltonian operator (non-relativistic) is given by

$$\hat{H} = \frac{\hat{\vec{p}}^2}{2m} + V(\hat{\vec{r}},t) = -\frac{\hbar^2}{2m}\vec{\nabla}^2 + V(\vec{r},t) \quad .$$

As a second example, consider a particle of mass m and charge q moving in an electromagnetic field described by a vector potential $\vec{A}(\vec{r},t)$ and a scalar potential $\phi(\vec{r},t)$. Its non-relativistic classical Hamiltonian can be obtained by starting from the field free expression $E=\vec{p}^2/2m$ between the energy and the momentum of the particle, and making in it the substitutions

$$E \to E - q\phi \quad , \qquad \vec{p} \to \vec{p} - q\vec{A} \quad .$$

The resulting classical Hamiltonian is

$$H = \frac{1}{2m}\left(\vec{p} - q\vec{A}\right)^2 + q\phi \quad ,$$

$$= \frac{\vec{p}^2}{2m} - \frac{q}{2m}\left(\vec{A}\cdot\vec{p} + \vec{p}\cdot\vec{A}\right) + \frac{q^2}{2m}\vec{A}^2 + q\phi \quad .$$

The quantum mechanical operator is obtained by replacement (in the position representation)

$$\vec{p} \to -i\hbar\vec{\nabla} \quad , \quad \vec{r} \to \hat{\vec{r}} \equiv \vec{r} \quad , \quad \hat{\vec{A}}(\hat{\vec{r}},t) \to \vec{A}(\vec{r},t) \quad , \quad \hat{\phi}(\hat{\vec{r}},t) \to \phi(\vec{r},t) \quad .$$

9.13 COMMUTATION RELATIONS

The commutator of two operators $\hat{A}$ and $\hat{B}$ is defined as the difference $\hat{A}\hat{B} - \hat{B}\hat{A}$ and is denoted by the symbol $[\hat{A},\hat{B}]$:

$$[\hat{A},\hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A} \quad . \qquad ...(1)$$

If $$[\hat{A},\hat{B}] = 0 \quad , \qquad ...(2)$$

the two operators $\hat{A}$ and $\hat{B}$ commute, and $\hat{A}\hat{B} = \hat{B}\hat{A}$. For example the differential operators $\frac{\partial}{\partial x}$ and $\frac{\partial}{\partial y}$ commute:

$$\frac{\partial}{\partial x}\left(\frac{\partial}{\partial y}\right)\psi = \frac{\partial}{\partial y}\left(\frac{\partial}{\partial x}\right)\psi \quad .$$

But many operators do not commute. For example, the position operator $\hat{x} \equiv x$ and momentum operator $\hat{p}_x \equiv -i\hbar\frac{\partial}{\partial x}$ do not commute. For an arbitrary wave-function $\psi(x)$, we have

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

$$= -i\hbar\left(x\frac{\partial\psi}{\partial x}\right) \quad , \qquad \ldots(3)$$

and $$\hat{p}_x\,\hat{x}\,\psi = \left(-i\hbar\frac{\partial}{\partial x}\right)(x\,\psi) \quad ,$$

$$= -i\hbar\left(\psi + x\frac{\partial\psi}{\partial x}\right) \quad . \qquad \ldots(4)$$

Using (3) and (4), we find

$$\left[\hat{x}\,,\hat{p}_x\right]\psi = \hat{x}\,\hat{p}_x\psi - \hat{p}_x\,\hat{x}\,\psi = i\hbar\,\psi \quad .$$

Therefore,

$$\left[\hat{x}\,,\hat{p}_x\right] = i\hbar \quad . \qquad \ldots(5)$$

Thus $\left[\hat{x}\,,\hat{p}_x\right] \neq 0$, i.e., $\hat{x}$ and $\hat{p}_x$ do not commute.

Some Commutation Relations:

(i) For operators corresponding to the components of position and momentum:

$$\left[\hat{x}\,,\hat{p}_x\right] = i\hbar \;\; , \;\; \left[\hat{x}\,,\hat{p}_y\right] = 0 = \left[\hat{x}\,,\hat{p}_z\right] \;\; , \;\; [\hat{x}\,,\hat{y}] = 0 = [\hat{x}\,,\hat{z}] \;\; , \;\; \left[\hat{p}_x\,,\hat{p}_y\right] = 0 = \left[\hat{p}_x\,,\hat{p}_z\right] \;\; ; \quad \ldots(6a)$$

$$\left[\hat{y}\,,\hat{p}_y\right] = i\hbar \;\; , \;\; \left[\hat{y}\,,\hat{p}_x\right] = 0 = \left[\hat{y}\,,\hat{p}_z\right] \;\; , \;\; [\hat{y}\,,\hat{x}] = 0 = [\hat{y}\,,\hat{z}] \;\; , \;\; \left[\hat{p}_y\,,\hat{p}_x\right] = 0 = \left[\hat{p}_y\,,\hat{p}_z\right] \;\; ; \quad \ldots(6b)$$

$$\left[\hat{z}\,,\hat{p}_z\right] = i\hbar \;\; , \;\; \left[\hat{z}\,,\hat{p}_x\right] = 0 = \left[\hat{z}\,,\hat{p}_y\right] \;\; , \;\; [\hat{z}\,,\hat{y}] = 0 = [\hat{z}\,,\hat{x}] \;\; , \;\; \left[\hat{p}_z\,,\hat{p}_y\right] = 0 = \left[\hat{p}_z\,,\hat{p}_x\right] \;\; . \quad \ldots(6c)$$

(ii) For operators corresponding to the components of angular momentum:

The operators corresponding to the components of angular momentum are:

$$\hat{L}_x = -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right) \;\; ; \;\; \hat{L}_y = -i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right) \;\; ; \;\; \hat{L}_z = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) \;\; . \qquad \ldots(7)$$

The commutation relations are: (see solved Example 9.25)

$$\left[\hat{L}_x,\hat{L}_y\right] = i\hbar\,\hat{L}_z \;\; ; \;\; \left[\hat{L}_y,\hat{L}_z\right] = i\hbar\,\hat{L}_x \;\; ; \;\; \left[\hat{L}_z,\hat{L}_x\right] = i\hbar\,\hat{L}_y \;\; . \qquad \ldots(8)$$

The above three commutation relations are written in a combined form as

$$\hat{\vec{L}} \times \hat{\vec{L}} = i\hbar\hat{\vec{L}} \;\; . \qquad \ldots(9)$$

The commutation relations for the operator $\hat{\vec{L}}^2 \equiv \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$ and components of $\hat{\vec{L}}$ are: (see solved example 9.25)

$$\left[\hat{\vec{L}}^2,\hat{L}_x\right] = 0 \;\; ; \;\; \left[\hat{\vec{L}}^2,\hat{L}_y\right] = 0 \;\; ; \;\; \left[\hat{\vec{L}}^2,\hat{L}_z\right] = 0 \;\; . \qquad \ldots(9)$$

(Comments: For two free particles (one-dimensional motion), if position and momentum operators are, $\hat{x}_1\,,\hat{p}_{1x}$ *and* $\hat{x}_2\,,\hat{p}_{2x}$ *, then for canonically conjugate pairs,* $\left[\hat{x}_1,\hat{p}_{1x}\right] = i\hbar$ *and* $\left[\hat{x}_2,\hat{p}_{2x}\right] = i\hbar$ *. All other pairs commute, such as* $\left[\hat{x}_1,\hat{p}_{2x}\right] = 0$ *,* $\left[\hat{x}_2,\hat{p}_{1x}\right] = 0$ *, etc.)*

Commutator Algebra

$$[A\,,B] = -[B\,,A] \quad , \qquad \ldots(10a)$$

$$[A\,,B+C] = [A\,,B] + [A\,,C] \quad , \qquad \ldots(10b)$$

$$[A\,,BC] = [A\,,B]C + B[A\,,C] \quad , \qquad \ldots(10c)$$

$$[A\,,[B\,,C]] + [B\,,[C\,,A]] + [C\,,[A\,,B]] = 0 \quad . \qquad \ldots(10d)$$

(see **Example 9.18 to 9.25**)

9.14 COMPATIBLE OBSERVABLES

In quantum mechanics, one can associate a Hermitian operator with a dynamical variable. A Hermitian operator which possess a complete set of eigenfunctions is called an **observable**.

Two observables $\hat{A}$ and $\hat{B}$ are said to be **compatible**, if there exists a complete set of functions ψ_n such that each function is simultaneously an eigenfunction of $\hat{A}$ and $\hat{B}$.

Compatible observables commute.

Proof: If the eigenvalues of $\hat{A}$ and $\hat{B}$ corresponding to the eigenfunction ψ_n are denoted by a_n and b_n , respectively, then

$$\hat{A}\,\psi_n = a_n\psi_n \text{ , and } \hat{B}\psi_n = b_n\psi_n \quad . \qquad \ldots(1)$$

So for compatible observables having common eigenfunction ψ_n ,

$$\hat{A}\,\hat{B}\,\psi_n = a_n b_n\psi_n \quad ,$$

$$= b_n a_n\psi_n \quad ,$$

$$= \hat{B}\,\hat{A}\,\psi_n \quad ,$$

or $$\left(\hat{A}\hat{B} - \hat{B}\hat{A}\right)\psi_n = 0 \quad . \qquad \ldots(2)$$

Since an observable is a Hermitian operator possessing a complete set of eigenfunctions, $\{\psi_n\}$ forms a complete set. An arbitrary wave-function Φ can be expanded in the complete set of eigenfunctions ψ_n ,

$$\Phi = \sum_n c_n\,\psi_n \quad .$$

Using (2), we write

$$\left(\hat{A}\hat{B} - \hat{B}\hat{A}\right)\Phi = \sum_n c_n\left(\hat{A}\hat{B} - \hat{B}\hat{A}\right)\psi_n = 0 \quad .$$

Since the above is true for any arbitrary Φ , therefore,

$$\left(\hat{A}\hat{B} - \hat{B}\hat{A}\right) = 0 \quad ,$$

or $$\left[\hat{A},\hat{B}\right] = 0 \quad .$$

Thus two compatible observables commute. This means that the two compatible observables can be measured simultaneously.

Two operators which commute possess a complete set of common eigenfunctions.

Proof: Let two Hermitian operators (observables), $\hat{A}$ and $\hat{B}$ commute, that is,

$$\hat{A}\,\hat{B} = \hat{B}\,\hat{A} \quad .$$

We consider the case for which $\hat{A}$ has non-degenerate eigenvalues a_n . Then,

$$\hat{A}(\hat{B}\,\psi_n) = \hat{B}\,\hat{A}\,\psi_n = a_n(\hat{B}\,\psi_n) \quad .$$

Therefore $(\hat{B}\,\psi_n)$ is an eigenfunction of $\hat{A}$ belonging to the eigenvalue a_n . Since a_n is non-degenerate, $(\hat{B}\,\psi_n)$ can only differ from ψ_n by a multiplicative constant which we call b_n :

$$\hat{B}\psi_n = b_n\psi_n \quad .$$

Thus we say that ψ_n is simultaneously an eigenfunction of the operators $\hat{A}$ and $\hat{B}$ belonging to the eigenvalues a_n and b_n , respectively.

9.15 DIRAC BRA-KET NOTATION

Dirac introduced the symbol $\langle\psi_1 \mid \psi_2\rangle$ for the scalar product of two square integrable functions $\psi_1(\vec{r},t)$ and $\psi_2(\vec{r},t)$:

$$\langle\psi_1 \mid \psi_2\rangle \equiv \int \psi_1^*(\vec{r},t)\,\psi_2(\vec{r},t)\,d\vec{r} \quad . \qquad ...(1)$$

The symbol $|\,\rangle$ is known as a ***ket*** while $\langle\,|$ is known as a ***bra***. $\langle\,\psi_1\,|$ is $bra\,\psi_1$, and $|\psi_2\,\rangle$ is $ket\,\psi_2$. From the definition (1) we have

$$\langle\psi_1 \mid \psi_2\rangle = \langle\psi_2 \mid \psi_1\rangle^* \quad .$$

Moreover, if c is a complex number and ψ_3 a third wave-function, we also have

$$\langle\psi_1 \mid c\ \psi_2\rangle = c\,\langle\psi_1 \mid \psi_2\rangle \quad ,$$

$$\langle c\ \psi_1 \mid \psi_2\rangle = c^*\,\langle\psi_1 \mid \psi_2\rangle \quad ,$$

$$\langle\psi_3 \mid \psi_1 + \psi_2\rangle = \langle\psi_3 \mid \psi_1\rangle + \langle\psi_3 \mid \psi_2\rangle \quad .$$

Examples of use of bra-ket notation:

Normalization condition: $\langle\psi \mid \psi\rangle = 1$.

Orthogonality condition: $\langle\psi_1 \mid \psi_2\rangle = 0$.

Orthonormality condition: $\langle\psi_n \mid \psi_m\rangle = \delta_{nm}$.

Expectation value: $\langle A\rangle = \dfrac{\langle\psi \mid \hat{A} \mid \psi\rangle}{\langle\psi \mid \psi\rangle}$.

Hermiticity condition: $\langle\phi \mid \hat{A}\,\psi\rangle = \langle\hat{A}\,\phi \mid \psi\rangle$, here $\langle\phi \mid \hat{A}\,\psi\rangle \equiv \langle\phi \mid (\hat{A}\,\psi)\rangle$ and $\langle\hat{A}\,\phi \mid \psi\rangle \equiv \langle(\hat{A}\,\phi) \mid \psi\rangle$.

Eigenvalue equation: $\hat{A}\mid\psi_n\,\rangle = a_n \mid \psi_n\,\rangle$, $\langle\,\psi_n \mid \hat{A} = a_n^*\,\langle\,\psi_n\,|$.

Eigenvalue: $\langle\,\psi_n \mid \hat{A} \mid \psi_n\rangle \equiv \langle\,\psi_n \mid (\hat{A}\,\psi_n)\,\rangle = a_n\,\langle\,\psi_n \mid \psi_n\,\rangle$,

$$\langle\,\hat{A}\,\psi_n \mid \psi_n\rangle = a_n^*\,\langle\,\psi_n \mid \psi_n\,\rangle \quad .$$

Adjoint operator: Defining relation: For any pair of square integrable functions,

$$\langle\,\phi \mid \hat{A}^\dagger \mid \psi\,\rangle = \langle\,(\hat{A}\,\phi) \mid \psi\,\rangle \quad ,$$

$$= \langle\,\psi \mid \hat{A} \mid \phi\,\rangle^* \quad .$$

If we define a bra $\langle\Phi|$ by the relation $\langle\Phi| = \langle\phi|\,\hat{A}^\dagger$ where the operator $\hat{A}^\dagger$ acts to the left on the bra $\langle\phi|$, then the ket $|\Phi\rangle$ is $|\Phi\rangle = \hat{A}|\phi\rangle$.

9.16 HEISENBERG UNCERTAINTY RELATIONS

Let $\langle A\rangle \equiv \langle\psi|A|\psi\rangle$ be the expectation value[14] of A in a given state ψ (normalized to unity), and $\langle B\rangle \equiv \langle\psi|B|\psi\rangle$ be the expectation value of B in the state ψ . The mean square de-

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14 For simplicity, we drop the hat ^ notation in this section.

viation about the expectation value $\langle A \rangle$ is

$$(\Delta A)^2 = \left\langle (A - \langle A \rangle)^2 \right\rangle = \langle A^2 \rangle - \langle A \rangle^2 \quad .$$

The uncertainty ΔA is defined as

$$\Delta A = \left(\langle (A - \langle A \rangle)^2 \rangle \right)^{1/2} = \sqrt{\langle A^2 \rangle - \langle A \rangle^2} \quad .$$

Similarly, the uncertainty ΔB is

$$\Delta B = \left(\langle (B - \langle B \rangle)^2 \rangle \right)^{1/2} = \sqrt{\langle B^2 \rangle - \langle B \rangle^2} \quad .$$

Then, it can be proved that

$$\Delta A \, \Delta B \geq \frac{1}{2} \, | \langle [A, B] \rangle | \quad . \qquad ...(1)$$

For two observables which are canonically conjugate, so that $[A, B] = i\hbar$ we have

$$\langle [A, B] \rangle = i\hbar \quad . \qquad ...(2)$$

Then, use of (5) in (4) gives,

$$\Delta A \, \Delta B \geq \frac{\hbar}{2} \quad . \qquad ...(3)$$

This is Heisenberg uncertainty principle. In particular, for pairs of canonically conjugate variables (x, p_x) , (y, p_y) and (z, p_z) , we can state the position-momentum uncertainty relations in the precise form:

$$\Delta x \, \Delta p_x \geq \frac{\hbar}{2} \quad , \qquad \Delta y \, \Delta p_y \geq \frac{\hbar}{2} \quad , \qquad \Delta z \, \Delta p_z \geq \frac{\hbar}{2}$$

with

$$\Delta x = \sqrt{\langle x^2 \rangle - \langle x \rangle^2} \quad , \quad \Delta p_x = \sqrt{\langle p_x^2 \rangle - \langle p_x \rangle^2}$$

and similar definitions for Δy , Δp_y , Δz and Δp_z .

Proof of $\boldsymbol{\Delta A \, \Delta B \geq \frac{1}{2} |\langle [A, B] \rangle|}$

Let us consider the linear Hermitian operators

$$\overline{A} = A - \langle A \rangle \quad , \quad \overline{B} = B - \langle B \rangle \quad .$$

Their expectation values vanish, $\langle \overline{A} \rangle = 0$, $\langle \overline{B} \rangle = 0$. In terms of these operators, we have

$$(\Delta A)^2 = \left\langle (A - \langle A \rangle)^2 \right\rangle = \langle \overline{A}^2 \rangle \quad , \qquad (\Delta B)^2 = \left\langle (B - \langle B \rangle)^2 \right\rangle = \langle \overline{B}^2 \rangle \quad . \qquad ...(4)$$

We also note that

$$[\overline{A}, \overline{B}] = [A - \langle A \rangle, B - \langle B \rangle] = [A, B] \quad . \qquad ...(5)$$

Next, we consider the linear (but not Hermitian) operator

$$C = \overline{A} + i\lambda \overline{B} \quad , \qquad ...(6)$$

where λ is a real constant. The adjoint of C is the operator $C^\dagger = \overline{A} - i\lambda \overline{B}$. The expectation value of $C C^\dagger$ is

$$\langle C C^\dagger \rangle = \langle \psi | C C^\dagger | \psi \rangle = \langle C^\dagger \psi | C^\dagger \psi \rangle \geq 0 \quad . \qquad ...(7)$$

It is real and non-negative. From (6) the expectation value is

$$\langle C C^\dagger \rangle = \langle (\overline{A} + i\lambda \overline{B})(\overline{A} - i\lambda \overline{B}) \rangle = \left\langle \overline{A}^2 + \lambda^2 \overline{B}^2 - i\lambda \, [\overline{A}, \overline{B}] \right\rangle$$

Comparing with (7) we find that the expectation value

$$\langle \overline{A}^2 + \lambda^2 \overline{B}^2 - i\lambda\, [\overline{A}, \overline{B}] \rangle \geq 0 \quad ,$$

it is real and non-negative. That is the function

$$f(\lambda) = \langle \overline{A}^2 + \lambda^2 \overline{B}^2 - i\lambda\, [\overline{A}, \overline{B}] \rangle \geq 0 \quad ,$$

or
$$f(\lambda) = \langle \overline{A}^2 \rangle + \lambda^2 \langle \overline{B}^2 \rangle - i\lambda\, \langle [\overline{A}, \overline{B}] \rangle \geq 0 \quad . \qquad \text{...(8)}$$

Using (4) and (5) in (8), we find

$$f(\lambda) = (\Delta A)^2 + \lambda^2 (\Delta B)^2 - i\lambda \langle [A, B] \rangle \geq 0 \quad . \qquad \text{...(9)}$$

The function $f(\lambda)$ is also real and non-negative. Thus (9) implies that $\langle [A, B] \rangle$ is purely imaginary. Now, the function $f(\lambda)$ has a minimum for

$$\lambda_0 = \frac{i}{2} \frac{\langle [A, B] \rangle}{(\Delta B)^2}$$

and the value of $f(\lambda)$ at the minimum is

$$f(\lambda_0) = (\Delta A)^2 + \frac{1}{4} \frac{(\langle [A, B] \rangle)^2}{(\Delta B)^2} \quad . \qquad \text{...(10)}$$

Since this value is non-negative, we must have

$$(\Delta A)^2 + \frac{1}{4} \frac{(\langle [A, B] \rangle)^2}{(\Delta B)^2} \geq 0 \quad ,$$

or
$$(\Delta A)^2 (\Delta B)^2 \geq -\frac{1}{4} (\langle [A, B] \rangle)^2 \quad . \qquad \text{...(11)}$$

Since $\langle [A, B] \rangle$ is purely imaginary, using this fact in above gives

$$(\Delta A)^2 (\Delta B)^2 \geq \frac{1}{4} |\langle [A, B] \rangle|^2 \quad , \qquad \text{...(12)}$$

or
$$\Delta A\, \Delta B \geq \frac{1}{2} |\langle [A, B] \rangle| \quad . \qquad \text{...(13)}$$

9.17 PARITY OPERATOR

The parity operator P is defined by specifying its effect on wave-functions. The parity operator causes the function $\psi(\vec{r}, t)$ to go over to a new function $\psi'(\vec{r}, t)$ whose value at $\vec{r}$ is the same as that of ψ at $-\vec{r}$, that is

$$P\psi(\vec{r}, t) \equiv \psi'(\vec{r}, t) = \psi(-\vec{r}, t) \quad . \qquad \text{...(1)}$$

Parity operation is also called space inversion, because $\vec{r}$ and $-\vec{r}$ are inverse points, equidistant from the origin but in opposite directions.[15]

In one-dimension, the operation which transforms x to $-x$, is called the Parity operation. The behavior of the function under the parity operation determines the parity of the function. A function $f(x)$ has even parity if $f(-x) = f(x)$ and odd parity if $f(-x) = -f(x)$, whereas it has no definite parity if $f(-x) \neq \pm f(x)$.

Eigenvalues of Parity operator

Let $\psi(\vec{r})$ is eigenfunction of the parity operator P and λ is the corresponding eigenvalue. Then,

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15 *Parity operator has no classical counterpart; there is no classical dynamical variable from which it can be obtained by the operator correspondence* $\vec{r} \to \hat{\vec{r}} \equiv \vec{r}$ *and* $\vec{p} \to -i\hbar\vec{\nabla}$.

$$P\,\psi(\vec{r}) = \lambda\,\psi(\vec{r}) \quad . \qquad \ldots(2)$$

Further

$$P^2\,\psi(\vec{r}) = \lambda\,P\,\psi(\vec{r}) \quad ,$$

$$= \lambda^2\,\psi(\vec{r}) \quad . \qquad \ldots(3)$$

From the definition of the parity operator,

$$P\,\psi(\vec{r}) = \psi(-\vec{r}) \quad ,$$

and

$$P^2\,\psi(\vec{r}) = P\,\psi(-\vec{r}) \quad ,$$

$$= \psi(\vec{r}) \quad . \qquad \ldots(4)$$

Comparing (3) and (4), we find

$$\lambda^2 = 1 \quad .$$

Since the parity operator is Hermitian (see solved Example 9.29), its eigenvalues are real. Therefore,

$$\lambda = \pm 1 \quad . \qquad \ldots(5)$$

Therefore, the eigenvalues of parity operator are $+1$ and -1 .

Parity of a function (symmetric and anti-symmetric wave-functions):

Consider an inversion of the coordinate system, i.e., reflection of the coordinate axes in the origin. A point with position vector $\vec{r}$ has the position vector $-\vec{r}$ after inversion. Thus, under the inversion, the function $\psi(\vec{r}, t)$ becomes transformed into $\psi(-\vec{r}, t)$.

If

$$\psi(-\vec{r}, t) = \psi(\vec{r}, t) \quad , \qquad \ldots(6)$$

then the function is called **symmetric or even function** and the parity of the function is even or $+1$. But if

$$\psi(-\vec{r}, t) = -\,\psi(\vec{r}, t) \quad , \qquad \ldots(7)$$

then the function is called **anti-symmetric or odd function** and the parity of the function is odd or -1 .

For example, consider the normalized one dimensional wave-functions,

$$(\psi_1)_n(x) = \sqrt{\frac{1}{a}}\cos\left(\frac{n\pi x}{2a}\right) \quad \text{, where} \quad n{=}1,\,3,\,5,\,\ldots \qquad \ldots(8)$$

and

$$(\psi_2)_m(x) = \sqrt{\frac{1}{a}}\sin\left(\frac{m\pi x}{2a}\right) \quad \text{, where} \quad m{=}2,\,4,\,6,\,\ldots \quad . \qquad \ldots(9)$$

The function $(\psi_1)_n$ is an even or symmetric function. Its parity is $+1$. The function $(\psi_2)_m$ is an odd function or anti-symmetric function. Its parity is -1 .

In general, a function may be a linear combination of the two types of functions (symmetric and anti-symmetric). Then the function does not have a definite parity.

Energy eigenfunctions and Parity

Consider motion of a particle of mass m in one dimension. Let the Hamiltonian operator is

$$H = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x) \quad . \qquad ...(10)$$

If $V(x)$ is symmetric under the parity transformation ($x \to -x$), then, $V(-x) = V(x)$ and $H(-x) = H(x)$. In this situation, when the Hamiltonian is symmetric under parity transformation.

Consider the eigenvalue equation for H ,

$$H(x)\psi(x) = E\,\psi(x) \quad . \qquad ...(11)$$

Consider the parity transformation $x \to -x$. Then the above equation changes to

$$H(-x)\psi(-x) = E\,\psi(-x) \quad .$$

For a symmetric Hamiltonian $H(-x) = H(x)$, therefore, the above equation becomes

$$H(x)\psi(-x) = E\,\psi(-x) \quad . \qquad ...(12)$$

Eqs.(11) &(12) shows that $\psi(x)$ and $\psi(-x)$ both are eigenfunctions of the symmetric Hamiltonian and the corresponding eigenvalue is E . If $\psi(x)$ and $\psi(-x)$ are linearly independent functions, then the energy E is degenerate. If E is non degenerate, the $\psi(x)$ and $\psi(-x)$ are not linearly independent. Then we can write

$$\psi(x) = c\,\psi(-x) \quad , \qquad ...(13)$$

where c is some constant. Replacement $x \to -x$ gives

$$\psi(-x) = c\,\psi(x) \quad .$$

Using (13) in the above, we get

$$\psi(x) = c^2\,\psi(x) \quad ,$$

or $\qquad c^2 = 1 \quad .$

Thus $c = +1$ or $c = -1$, that is, for a non-degenerate energy eigenvalue, the corresponding eigenfunction is either even ($\psi(-x) = \psi(x)$) or odd ($\psi(-x) = -\psi(x)$).

(*Comment: In solved example 9.26 we show that a symmetric Hamiltonian operator H commutes with the parity operator P , i.e.,*

$$[H, P] = 0 \quad .$$

Two operators which commute possess a complete set of common eigenfunctions. Therefore, the eigenfunctions of H are also eigenfunctions of P . That is, the energy eigenfunctions for a symmetric Hamiltonian have definite parity, either $+1$ or -1 .)

(see **Examples 9.26 to 9.29**)

SOLVED EXAMPLES

Example 9.1 The momentum operator $\hat{p}_x = -i\hbar\partial/\partial x$, the energy operator $\hat{E} = i\hbar\partial/\partial t$ and the function $\psi(x,t) = x^2\exp(-i\omega t)$ are given, where $\hbar$ and ω are constants. What are $\hat{p}_x\psi$ and $(b)\hat{E}\,\psi$?

Ans. (i) $\hat{p}_x \psi(x,t) = -i\hbar \frac{\partial}{\partial x}\left(x^2 \exp(-i\omega t)\right) = -2i\hbar x \exp(-i\omega t)$,

or $\hat{p}_x \psi(x,t) = \phi(x,t)$,

where $\phi(x,t) = -2i\hbar x \exp(-i\omega t)$ is a function different from $\psi(x,t)$.

(ii) $\hat{E}\,\psi(x,t) = i\hbar \frac{\partial}{\partial t}\left(x^2 \exp(-i\omega t)\right) = (\hbar\omega)\, x^2 \exp(-i\omega t)$,

or $\hat{E}\,\psi(x,t) = (\hbar\omega)\,\psi(x,t)$.

This example shows that when an operator acts on a function we may obtain a different function as in (i), or a multiple of the same function as in (ii).

Example 9.2 (a) Prove that for a well behaved wave function $\psi(x)$, the action of operators (i) $\hat{x}\,\hat{p}_x$ and (ii) $\hat{p}_x\hat{x}$ gives different results. (b) Find an operator whose action on $\psi(x)$ is equivalent to the action of operator $(\hat{x}\,\hat{p}_x - \hat{p}_x\hat{x})$.

Ans. (a) The action of operator $\hat{x}$ is to multiply the function by x , that is

$$\hat{x}\,\psi(x) = x\,\psi(x) \quad , \quad \hat{x}\left(\frac{\partial\psi}{\partial x}\right) = x\left(\frac{\partial\psi}{\partial x}\right) \; .$$

The momentum operator is $\hat{p}_x = -i\hbar\partial/\partial x$. Therefore,

(i) $$\hat{x}\,\hat{p}_x\,\psi(x) = \hat{x}\left(-i\hbar\frac{\partial\psi(x)}{\partial x}\right) = -i\hbar\, x\frac{\partial\psi(x)}{\partial x} \; . \qquad \text{...(1)}$$

And

(ii) $$\hat{p}_x\hat{x}\,\psi(x) = -i\hbar\frac{\partial}{\partial x}\left(\hat{x}\,\psi(x)\right) = -i\hbar\frac{\partial}{\partial x}\left(x\,\psi(x)\right) \; ,$$

or $$= -i\hbar\psi(x) - i\hbar\, x\frac{\partial\psi(x)}{\partial x} \; . \qquad \text{...(2)}$$

Thus we find that

$$\hat{x}\,\hat{p}_x\,\psi(x) \neq \hat{p}_x\hat{x}\,\psi(x) \; . \qquad \text{...(3)}$$

Since it it true for any $\psi(x)$, therefore, from (3) we write

$$\hat{x}\,\hat{p}_x \neq \hat{p}_x\hat{x} \; . \qquad \text{...(4)}$$

(b) In order to find an operator equivalent to $(\hat{x}\,\hat{p}_x - \hat{p}_x\hat{x})$, let us consider

$$(\hat{x}\,\hat{p}_x - \hat{p}_x\hat{x})\psi(x) = \hat{x}\,\hat{p}_x\psi(x) - \hat{p}_x\hat{x}\,\psi(x) \; .$$

Using

$$\hat{x}\,\hat{p}_x\psi(x) = -i\hbar\, x\frac{\partial\psi(x)}{\partial x} \; ,$$

and

$$\hat{p}_x\hat{x}\,\psi(x) = -i\hbar\psi(x) - i\hbar x\frac{\partial\psi(x)}{\partial x} \; ,$$

we find that

$$(\hat{x}\,\hat{p}_x - \hat{p}_x\hat{x})\psi(x) = -i\hbar\, x\frac{\partial\psi(x)}{\partial x} - \left\{-i\hbar\psi(x) - i\hbar x\frac{\partial\psi(x)}{\partial x}\right\} \; ,$$

$$= i\hbar\,\psi(x) \; .$$

Since $\psi(x)$ is any arbitrary wave function, therefore we can write

$$\hat{x}\,\hat{p}_x - \hat{p}_x\hat{x} = i\hbar\hat{I} \quad , \qquad ...(1)$$

where $\hat{I}$ is a identity (unit) operator. Relation (1) is simply written as

$$\hat{x}\,\hat{p}_x - \hat{p}_x\hat{x} = i\hbar \quad . \qquad ...(2)$$

(Comment: For the sake of simplicity of notation, sometimes the hat on the operator is not written, then the relation (2) for the position and the momentum operators is written as,

$$x\,p_x - p_x x = i\hbar \quad .$$

Example 9.3 For the position and momentum operators $\hat{x}$ and $\hat{p}_x$, show that

(a) $\hat{x}^2\,\hat{p}_x \neq \hat{p}_x\,\hat{x}^2$,

(b) $\hat{x}^2\,\hat{p}_x - \hat{p}_x\,\hat{x}^2 = 2i\hbar\hat{x}$.

Ans. (a) Consider a well behaved wave function $\psi(x)$. Then,

$$\hat{x}^2\,\hat{p}_x\;\psi(x) = \hat{x}^2\left(-i\hbar\frac{\partial\,\psi(x)}{\partial x}\right) = -i\hbar\,x^2\,\frac{\partial\,\psi(x)}{\partial x} \quad . \qquad ...(1)$$

And

$$\hat{p}_x\,\hat{x}^2\;\psi(x) = \left(-i\hbar\frac{\partial}{\partial x}\right)\left(\hat{x}^2\;\psi(x)\right) = \left(-i\hbar\frac{\partial}{\partial x}\right)\left(x^2\;\psi(x)\right) \quad ,$$

$$= -2\,i\hbar x\,\psi(x) - i\hbar\,x^2\,\frac{\partial\psi(x)}{\partial x} \quad . \qquad ...(2)$$

Comparing (1) and (2) we find that

$$\hat{x}^2\,\hat{p}_x\psi(x) \neq \hat{p}_x\hat{x}^2\;\psi(x) \quad . \qquad ...(3)$$

Since (3) is true for any wave function $\psi(x)$, therefore,

$$\hat{x}^2\,\hat{p}_x \neq \hat{p}_x\,\hat{x}^2 \quad . \qquad ...(4)$$

(b) Consider $\left(\hat{x}^2\,\hat{p}_x - \hat{p}_x\,\hat{x}^2\right)\psi(x) = \hat{x}^2\,\hat{p}_x\;\psi(x) - \hat{p}_x\,\hat{x}^2\;\psi(x)$.

Using (1) and (2) in the above, we find that

$$\left(\hat{x}^2\,\hat{p}_x - \hat{p}_x\,\hat{x}^2\right)\psi(x) = -i\hbar x^2\,\frac{\partial\psi(x)}{\partial x} - \left[-2\,i\hbar x\,\psi(x) - i\hbar\,x^2\,\frac{\partial\psi(x)}{\partial x}\right] \quad ,$$

$$= 2\,i\hbar\,x\;\psi(x) \quad ,$$

$$\equiv 2\,i\hbar\,\hat{x}\psi(x) = \left(2\,i\hbar\,\hat{x}\right)\psi(x) \quad .$$

Since $\psi(x)$ is any arbitrary wave function, therefore, we can write

$$\hat{x}^2\,\hat{p}_x - \hat{p}_x\,\hat{x}^2 = 2\,i\hbar\,\hat{x} \quad .$$

Example 9.4 (a) Show that the position operator $\hat{x}$ is Hermitian.

(b) Show that the momentum operator $p_x = -i\hbar\,\partial/\partial x$ is a Hermitian operator.

Ans. (a) Let $\psi \equiv \psi(x,y,z,t)$ and $\phi \equiv \phi(x,y,z,t)$ are two well behaved wave functions. Consider the volume integral

$$\int\left(\hat{x}\psi\right)^*\,\phi\;dV \quad ,$$

which when simplified as

$$\int\left(\hat{x}\psi\right)^*\,\phi\;dV = \int\left(x\psi\right)^*\,\phi\;dV = \int\psi^*\;x\;\psi\;dV = \int\psi^*\left(x\,\psi\right)dV$$

$$= \int \psi^* (\hat{x}\psi)\, dV \quad .$$

Thus

$$\int (\hat{x}\psi)^* \, \phi \; dV = \int \psi^* (\hat{x}\psi)\, dV \quad .$$

The condition of Hermiticity is satisfied by the position operator $\hat{x}$. Thus it is Hermitian.

(b) Let $\psi \equiv \psi(x, y, z, t)$ and $\phi \equiv \phi(x, y, z, t)$ are two well behaved wave functions. Consider the volume integral

$$\iiint \left(\frac{\partial}{\partial x} (\psi^* \, \phi) \right) dx\; dy\; dz = \iint [\psi^* \, \phi]_{-\infty}^{\infty} \; dy\; dz \quad . \qquad ...(1)$$

Since well behaved wave functions vanish at infinity, that is for $x = \pm\infty$, the wave functions tend to zero, $\psi \to 0,\ \phi \to 0$, we have (using $\int \equiv \iiint$)

$$\int \left(\frac{\partial}{\partial x} (\psi^* \, \phi) \right) dV = 0 \quad ,$$

or

$$\int \left(\frac{\partial \psi^*}{\partial x} \right) \phi \; dV + \int \psi^* \left(\frac{\partial \phi}{\partial x} \right) dV = 0 \quad . \qquad ...(2)$$

Multiplying the above by $i\hbar$ and rearranging the terms we find

$$\int i\hbar \left(\frac{\partial \psi^*}{\partial x} \right) \phi \; dV = - \int \psi^* \, i\hbar \left(\frac{\partial \phi}{\partial x} \right) dV \quad ,$$

or

$$\int \left(-i\hbar \, \frac{\partial \psi}{\partial x} \right)^* \phi \; dV = \int \psi^* \left(-i\hbar \, \frac{\partial \phi}{\partial x} \right) dV \quad . \quad ...(3)$$

Using $\hat{p}_x = -i\hbar\, \partial / \partial x$ in (3), we find

$$\int (\hat{p}_x \psi)^* \, \phi \; dV = \int \psi^* \, (\hat{p}_x \phi) \; dV \quad . \qquad ...(4)$$

This is the defining relation for Hermitian operator, thus $\hat{p}_x$ is a Hermitian operator.

(In a similar manner it can be shown that the other components of the momentum operator $\hat{\vec{p}} = -i\hbar\vec{\nabla}$, namely $\hat{p}_y = -i\hbar\partial/\partial y$ and $\hat{p}_z = -i\hbar\partial/\partial z$ are Hermitian. Therefore, $\hat{\vec{p}} = -i\hbar\vec{\nabla}$ is Hermitian.)

Example 9.5 Show that the Laplacian operator ∇^2 is a Hermitian operator.

Ans. Let $\psi \equiv \psi(x, y, z, t)$ and $\phi \equiv \phi(x, y, z, t)$ are two well behaved wave functions. Then

$$\vec{\nabla} \cdot (\phi \, \vec{\nabla} \psi^*) = \vec{\nabla} \phi \cdot \vec{\nabla} \psi^* + \phi \, \nabla^2 \psi^* \quad , \qquad ...(1)$$

and

$$\vec{\nabla} \cdot (\psi^* \vec{\nabla} \phi) = \vec{\nabla} \psi^* \cdot \vec{\nabla} \phi + \psi^* \, \nabla^2 \phi \quad . \qquad ...(2)$$

Subtracting (2) from (1), and using $\vec{\nabla} \phi \cdot \vec{\nabla} \psi^* = \vec{\nabla} \psi^* \cdot \vec{\nabla} \phi$, we get

$$\vec{\nabla} \cdot (\phi \, \vec{\nabla} \psi - \psi^* \, \vec{\nabla} \phi) = \phi \, \nabla^2 \psi^* - \psi^* \, \nabla^2 \phi \quad . \qquad ...(3)$$

Taking volume integral of (3), we find

$$\int \vec{\nabla} \cdot (\phi \vec{\nabla} \psi - \psi^* \, \vec{\nabla} \phi) \; dV = \int \phi \; \nabla^2 \psi^* \; dV - \int \psi^* \, \nabla^2 \phi \; dV \quad . \qquad ...(4)$$

Use of Gauss divergence theorem converts the volume integral on the LHS into a surface integral, that is

$$\int_V \vec{\nabla}\cdot\left(\phi\vec{\nabla}\psi - \psi^*\vec{\nabla}\phi\right)\,dV = \int_S \left(\phi\vec{\nabla}\psi - \psi^*\vec{\nabla}\phi\right)\cdot d\vec{S} \quad , \qquad \ldots(5)$$

where the surface *S* encloses the volume *V*. Since the volume integration is over the entire space (universe), the surface lies at infinity. The well behaved wave functions vanish at infinity, thus the RHS of (5) vanishes. Using this fact in (4), we find

$$0 = \int \phi\,\nabla^2\psi^*\,dV - \int \psi^*\,\nabla^2\phi\,dV \quad ,$$

or $$\int \phi\left(\nabla^2\psi^*\right)dV = \int \psi^*\left(\nabla^2\phi\right)dV \quad ,$$

or $$\int \left(\nabla^2\psi^*\right)\phi\,dV = \int \psi^*\left(\nabla^2\phi\right)dV \quad ,$$

or $$\int \left(\nabla^2\psi\right)^*\phi\,dV = \int \psi^*\left(\nabla^2\phi\right)dV \quad . \ldots(6)$$

Comparing (6) with the definition of Hermitian operator, we find that the Laplacian ∇^2 satisfies the condition for Hermiticity (relation (6)). Therefore, it is a Hermitian operator.

Example 9.6 Show that the energy operator $\hat{E} = i\hbar\,\partial/\partial t$ is a Hermitian operator.

Ans. For a well behaved wave function, $\psi(x,y,z,t)$, the conservation of probability requires that

$$\frac{\partial}{\partial t}\left(\int \psi^*\,\psi\,dV\right) = 0 \quad , \qquad \ldots(1)$$

where the volume integral is over the entire space. Therefore,

$$\int \frac{\partial\psi^*}{\partial t}\,\psi\,dV + \int \psi^*\,\frac{\partial\psi}{\partial t}\,dV = 0 \quad ,$$

or $$\int \frac{\partial\psi^*}{\partial t}\,\psi\,dV = -\int \psi^*\,\frac{\partial\psi}{\partial t}\,dV \quad . \qquad \ldots(2)$$

Multiplying (2) by $-i\hbar$, we get

$$\int \left(-i\hbar\frac{\partial\psi^*}{\partial t}\right)\psi\,dV = \int \psi^*\left(i\hbar\frac{\partial\psi}{\partial t}\right)dV \quad ,$$

or $$\int \left(i\hbar\frac{\partial\psi}{\partial t}\right)^*\psi\,dV = \int \psi^*\left(i\hbar\frac{\partial\psi}{\partial t}\right)dV \quad ,$$

or $$\int \left(\hat{E}\psi\right)^*\psi\,dV = \int \psi^*\left(\hat{E}\psi\right)dV \quad . \qquad \ldots(3)$$

Thus operator $\hat{E}$ obeys the Hermiticity condition (3). Therefore, $\hat{E} = i\hbar\,\partial/\partial t$ is a Hermitian operator.

Example 9.7 Show that the Hamiltonian operator

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

is a Hermitian operator.

Ans. The Hamiltonian operator is

$$\hat{H} = \hat{T} + \hat{V} \quad ,$$

where the kinetic energy operator $\hat{T}$ and the potential energy operator $\hat{V}$ are, respectively,

$$\hat{T} = \frac{\hat{\vec{p}}^2}{2m} = -\frac{\hbar^2}{2m}\nabla^2 \quad \text{, and} \quad \hat{V} = V(\hat{x},\hat{y},\hat{z}) = V(x,y,z) \quad .$$

We have used $\hat{\vec{p}} = -i\hbar\vec{\nabla}$. Further, $V(\hat{x},\hat{y},\hat{z}) = V(x,y,z)$ because the action of a position operator is simply to multiply by respective position coordinate.

The kinetic energy operator is Hermitian as shown below:

$$\int \left(\hat{T}\psi\right)^* \phi\, dV = \frac{1}{2\text{m}}\int \left(\hat{\vec{p}}\cdot\left(\hat{\vec{p}}\psi\right)\right)^* \phi\, dV \quad ,$$

$$= \frac{1}{2\text{m}}\int \left(\hat{\vec{p}}\psi\right)^* \cdot \hat{\vec{p}}\phi\, dV \quad \text{(because } \hat{p} \text{ is Hermitian)}$$

$$= \frac{1}{2\text{m}}\int \psi^*\, \hat{\vec{p}}\cdot\hat{\vec{p}}\phi\, dV \quad \text{(because } \hat{p} \text{ is Hermitian)}$$

$$= \int \psi^*\, \hat{T}\phi\, dV \quad .$$

Thus

$$\int \left(\hat{T}\psi\right)^* \phi\, dV = \int \psi^*\, \hat{T}\phi\, dV \quad ,$$

therefore, $\hat{T}$ is Hermitian.

The potential energy operator $\hat{V}$ is Hermitian by virtue of being a function of Hermitian operators $\hat{x},\hat{y},\hat{z}$. Therefore, the Hamiltonian

$$\hat{H} = \hat{T} + \hat{V}$$

is Hermitian.

Example 9.8 The wave function of a particle is given by

$$\psi(x) = \sqrt{\frac{2}{a}}\sin\left(\frac{\pi x}{a}\right) \quad \text{, for} \quad 0 \le x \le a \quad \text{, and} \quad \psi(x) = 0 \quad \text{outside this region.}$$

Calculate the expectation value of (i) position, and (ii) momentum of the particle.

Ans. (i) For a one-dimensional wave function, the expectation value of position is

$$\langle\hat{x}\rangle = \frac{\int \psi^*(x)\,\hat{x}\,\psi(x)\,dx}{\int \psi^*(x)\,\psi(x)\,dx} = \frac{\int \psi^*(x)\,x\,\psi(x)\,dx}{\int \psi^*(x)\,\psi(x)\,dx} \quad .$$

Here

$$\int \psi^*(x)\,\psi(x)\,dx = \frac{2}{a}\int_0^a \sin^2\left(\frac{\pi x}{a}\right)dx = \frac{1}{a}\int_0^a \left[1 - \cos\left(\frac{2\pi x}{a}\right)\right]dx \quad ,$$

$$= \frac{1}{a}\left[x - \frac{a}{2\pi}\sin\left(\frac{2\pi x}{a}\right)\right]_0^a = 1 \quad .$$

That is , $\psi(x)$ is a normalized wave function. Therefore,

$$\langle\hat{x}\rangle = \int \psi^*(x)\,x\psi(x)\,dx = \frac{2}{a}\int_0^a x\sin^2\left(\frac{\pi x}{a}\right)dx \quad ,$$

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

$$= \frac{1}{a}\left[\frac{x^2}{2} - \left(\frac{a}{2\pi}\right)x\sin\left(\frac{2\pi x}{a}\right) - \left(\frac{a}{2\pi}\right)^2\cos\left(\frac{2\pi x}{a}\right)\right]_0^a \quad ,$$

$$= \frac{a}{2} \quad .$$

Thus

$$\langle \hat{x} \rangle = \frac{a}{2} \quad .$$

(ii) The expectation value of momentum is

$$\langle \hat{p}_x \rangle = \frac{\int \psi^*(x)\, \hat{p}_x \psi(x)\, dx}{\int \psi^*(x)\, \psi(x)\, dx} = \frac{\int \psi^*(x) \left(-i\hbar \frac{\partial}{\partial x}\right) \psi(x)\, dx}{\int \psi^*(x)\, \psi(x)\, dx}$$

Here,

$$\int \psi^*(x)\, \psi(x)\, dx = 1 \quad ,$$

therefore,

$$\langle \hat{p}_x \rangle = -i\hbar \int \psi^*(x) \left(\frac{\partial \psi(x)}{\partial x}\right) dx \quad .$$

Substituting values we find

$$\langle \hat{p}_x \rangle = -i\hbar \left(\frac{2}{a}\right) \int_0^a \sin\left(\frac{\pi x}{a}\right) \left(\frac{\partial}{\partial x} \sin\left(\frac{\pi x}{a}\right)\right) dx \quad ,$$

$$= -i\hbar \left(\frac{2\pi}{a^2}\right) \int_0^a \sin\left(\frac{\pi x}{a}\right) \cos\left(\frac{\pi x}{a}\right) dx \quad ,$$

$$= -i\hbar \left(\frac{\pi}{a^2}\right) \int_0^a \sin\left(\frac{2\pi x}{a}\right) dx \quad ,$$

$$= 0 \quad .$$

Thus $\langle \hat{p}_x \rangle = 0$.

Example 9.9 The normalized wave function of a particle is given by

$$\psi(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{\pi x}{a}\right) \quad \text{, for} \quad 0 \le x \le a \quad \text{, and} \quad \psi(x) = 0 \quad \text{outside this region.}$$

(i) Calculate the expectation value of $\hat{x}^2$. (ii) Is $\langle \hat{x}^2 \rangle = \langle \hat{x} \rangle^2$?

Ans. (ii) The wave function is normalized, therefore,

$$\langle \hat{x}^2 \rangle = \int \psi^*(x)\, x^2 \psi(x)\, dx = \frac{2}{a} \int_0^a x^2 \sin^2\left(\frac{\pi x}{a}\right) dx \quad .$$

On solving the integral, we find

$$\langle \hat{x}^2 \rangle = \frac{2}{a}\left[\frac{a^3}{6} - \frac{a^3}{4\pi^2}\right] = a^2 \left(\frac{1}{3} - \frac{1}{2\pi^2}\right) \quad . \qquad ...(1)$$

(ii) The expectation value $\langle \hat{x} \rangle$ is

$$\langle \hat{x} \rangle = \int \psi^*(x)\, x \psi(x)\, dx = \frac{2}{a} \int_0^a x \sin^2\left(\frac{\pi x}{a}\right) dx$$

On solving the integral (see example 9.8(i)) we find

$$\langle \hat{x} \rangle = \frac{a}{2} \quad .$$

Therefore,

$$\langle \hat{x} \rangle^2 = \frac{a^2}{4} \quad . \qquad \ldots(2)$$

Comparing (1) and (2) we conclude

$$\langle \hat{x}^2 \rangle \neq \langle \hat{x} \rangle^2 \quad .$$

Example 9.10 Show that, for any observable A of a system, the expectation value of the square of A is positive and real.

Ans. Let the system is in a state described by the normalized state function ψ , and operator is $\hat{A}$. Then the expectation value of the square of A is

$$\langle A^2 \rangle = \int \psi^* \hat{A}^2 \psi \, dV = \int \psi^* \hat{A} \left(\hat{A} \psi \right) dV \quad . \qquad \ldots(1)$$

Since an observable is a Hermitian operator, therefore,

$$\int \psi^* \hat{A} \left(\hat{A} \psi \right) dV = \int \left(\hat{A} \psi \right)^* \left(\hat{A} \psi \right) dV = \int \left| \left(\hat{A} \psi \right) \right|^2 dV \quad .$$

Using it in (1), we get

$$\langle A^2 \rangle = \int \left| \left(\hat{A} \psi \right) \right|^2 dV \quad . \qquad \ldots(2)$$

Although $\hat{A} \psi = \phi$, in general, may be a complex quantity but its modulus square $\phi^* \phi$ is always real. Therefore, from (2) we infer,

$$\langle A^2 \rangle = \int \left| \hat{A} \psi \right|^2 dV \geq 0 \quad .$$

Example 9.11 For some state of a system the state function (wave function) is

$$\psi(x) = A \, e^{-x^2/2a^2} \, e^{-i p x/\hbar} \quad .$$

Find (i) the normalization constant and (ii) the expectation value of potential energy $V(x) = (1/2) k x^2$. Here A and a are constants and other symbols have conventional meanings. You may use the following standard integral:

$$\int_{-\infty}^{\infty} y^{2n} \exp(-y^2) \, dy = \frac{1 \cdot 3 \cdot 5 \cdot \ldots\ldots (2n-1)}{2^n} \sqrt{\pi} \quad .$$

Ans. (i) Using normalization conditions

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

we find

$$|A|^2 \int_{-\infty}^{\infty} \exp(-x^2/a^2) \, dx = 1 \quad . \qquad \ldots(1)$$

Using the given standard integral, we find

$$\int_{-\infty}^{\infty} \exp(-x^2/a^2) \, dx = a \sqrt{\pi} \quad .$$

Using it in (1), we get

$$|A|^2 \, a \sqrt{\pi} = 1 \quad ,$$

or $$A = \left(\frac{1}{a\sqrt{\pi}}\right)^{1/2} . \qquad ...(2)$$

(ii) The expectation value of the potential energy is

$$\langle V(x)\rangle = \int_{-\infty}^{\infty} \psi^* \left(\frac{1}{2}kx^2\right)\psi\, dx ,$$

$$= \frac{1}{2}k\,|A|^2 \int_{-\infty}^{\infty} x^2 \exp(-x^2/a^2)\, dx . \qquad ...(3)$$

Using the given standard integral, we find

$$\int_{-\infty}^{\infty} x^2 \exp(-x^2/a^2)\, dx = a^3\frac{\sqrt{\pi}}{2} .$$

Using it and the value of the normalization constant A in (3), we get

$$\langle V(x)\rangle = \frac{1}{2}k\left(\frac{1}{a\sqrt{\pi}}\right)\left(\frac{a^3\sqrt{\pi}}{2}\right) ,$$

or $$\langle V(x)\rangle = \frac{1}{4}k\,a^2 . \qquad ...(4)$$

Example 9.12 (a) For a physical system show that a dynamical variable q satisfies the relation

$$\frac{d}{dt}\langle q\rangle = \frac{i}{\hbar}\langle[\hat{H}, \hat{Q}]\rangle + \left\langle\frac{\partial\hat{Q}}{\partial t}\right\rangle ,$$

where $\hat{Q}$, is the operator corresponding to the dynamical variable, and $\hat{H}$ is the Hamiltonian operator for the physical system.

(b) Using the above relation, if (i) $q=x$, and (ii) $q=p_x$, where x and p_x do not depend explicitly on t, then prove the Ehrenfest relations:

(I) $\frac{d\langle x\rangle}{dt} = \frac{1}{m}\langle p_x\rangle$, and **(II)** $\frac{d\langle p_x\rangle}{dt} = -\left\langle\frac{\partial V}{\partial x}\right\rangle$.

Ans. (a) Let $\hat{Q}$ is an operator corresponding to the dynamical variable q and the physical system is in a state described by the normalized wave function ψ. The expectation value of q is

$$\langle q\rangle = \int \psi^* \hat{Q}\,\psi\, dx . \qquad ...(1)$$

Differentiating with respect to time, we get

$$\frac{d}{dt}\langle q\rangle = \int\left[\frac{\partial\psi^*}{\partial t}\hat{Q}\,\psi + \psi^*\frac{\partial\hat{Q}}{\partial t}\psi + \psi^*\hat{Q}\frac{\partial\psi}{\partial t}\right]d\tau . \qquad ...(2)$$

We use the Schrodinger equation

$$i\hbar\frac{\partial\psi}{\partial t} = \hat{H}\psi , \qquad ...(3)$$

and its complex conjugate equation

$$-i\hbar\frac{\partial\psi^*}{\partial t} = \hat{H}\psi^* , \qquad ...(4)$$

in (2). Here,

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V(r) , \qquad ...(5)$$

is the Hamiltonian operator. So we get

$$\frac{d}{dt}\langle q\rangle = \int \frac{i}{\hbar}\left[(\hat{H}\psi^*)\,(\hat{Q}\,\psi) - \psi^*(\hat{Q}\hat{H}\psi)\right] d\tau + \int \psi^* \frac{\partial \hat{Q}}{\partial t}\,\psi\, d\tau \quad . \qquad ...(6)$$

Since potential is real, i.e., $V^*(r)=V(r)$, the Hamiltonian satisfies the Hermitian operator property,

$$\int (\hat{H}\psi^*)(\hat{Q}\psi)\, d\tau = \int \psi^*(\hat{H}\hat{Q}\psi)\, d\tau \quad . \qquad ...(7)$$

Using (7) in (6), we find

$$\frac{d}{dt}\langle q\rangle = \int \frac{i}{\hbar}\left[\psi^*(\hat{H}\;\hat{Q}\;\psi) - \psi^*(\hat{Q}\hat{H}\psi)\right] d\tau + \int \psi^* \frac{\partial \hat{Q}}{\partial t}\,\psi\, d\tau \quad ,$$

$$= \int \psi^*\left(\frac{i}{\hbar}(\hat{H}\hat{q} - \hat{q}\;\hat{H})\right)\psi\, d\tau + \int \psi^* \frac{\partial \hat{Q}}{\partial t}\psi\, d\tau \quad ,$$

$$= \int \psi^*\left(\frac{i}{\hbar}[\hat{H}\;,\;\hat{Q}] + \frac{\partial \hat{Q}}{\partial t}\right)\psi\, d\tau \quad , \qquad ...(8)$$

where $[\hat{H}\;,\;\hat{Q}] = \hat{H}\hat{Q} - \hat{Q}\hat{H}$, is the commutator of $\hat{H}$ and $\hat{Q}$. Therefore, from (8), we get

$$\frac{d}{dt}\langle q\rangle = \left\langle \frac{i}{\hbar}[\hat{H}\;,\;\hat{Q}] + \frac{\partial \hat{Q}}{\partial t}\right\rangle \quad ,$$

or

$$\frac{d}{dt}\langle q\rangle = \left\langle \frac{i}{\hbar}[\hat{H}\;,\;\hat{Q}]\right\rangle + \left\langle \frac{\partial \hat{Q}}{\partial t}\right\rangle \quad . \qquad ...(9)$$

(b) (I) Using $q=x$ in (9) and the fact in Cartesian coordinate representation $\hat{x} = x$, we get

$$\frac{d}{dt}\langle x\rangle = \left\langle \frac{i}{\hbar}[\hat{H}\;,\;x]\right\rangle + \left\langle \frac{\partial x}{\partial t}\right\rangle \quad . \qquad ...(10)$$

It is given that x does not depend on time t explicitly, therefore,

$$\frac{\partial x}{\partial t} = 0 \quad .$$

Using it in (10), we find

$$\frac{d}{dt}\langle x\rangle = \frac{i}{\hbar}\,\langle[\hat{H}\;,\;x]\rangle \quad . \qquad ...(11)$$

Now

$$\left[\hat{H}\;,\;x\right] = \left[\frac{\hat{p}^2}{2m} + V(r)\;,\;x\right] \quad ,$$

$$= \frac{1}{2m}\left(\left[\hat{p}_x{}^2\;,\;x\right] + \left[\hat{p}_y{}^2\;,\;x\right] + \left[\hat{p}_z{}^2\;,\;x\right]\right) + \left[V(r)\;,\;x\right] \quad .$$

Since $\left[V(r)\;,\;x\right] = V(r)\;x - x\;V(r) = 0$, the above relation becomes

$$\left[\hat{H}\;,\;x\right] = \frac{1}{2m}\left(\left[\hat{p}_x{}^2\;,\;x\right] + \left[\hat{p}_y{}^2\;,\;x\right] + \left[\hat{p}_z{}^2\;,\;x\right]\right) \quad . \qquad ...(12)$$

Using identity

$$\left[\hat{A}\,\hat{B}\;,\hat{C}\right] = \hat{A}\left[\hat{B}\;,\;\hat{C}\right] + \left[\hat{A}\;,\;\hat{C}\right]\hat{B} \quad ,$$

and relation

$$\left[\hat{p}_x\;,\;x\right] = -i\hbar \quad , \quad \left[\hat{p}_y\;,\;x\right] = 0 \quad , \quad \left[\hat{p}_z\;,\;x\right] = 0 \quad ,$$

we find from (12),

$$\left[\hat{H}\;,\;x\right] = \frac{1}{2m}\left(-i\hbar(2\,\hat{p}_x) + 0 + 0\right) \quad ,$$

or $$\left[\hat{H}\ ,\ x\right] = -\frac{i\hbar}{m}\ \hat{p}_x \quad . \qquad \text{...(13)}$$

Using (13) in (11), we get

$$\frac{d}{dt}\langle x\rangle = \frac{i}{\hbar}\left(-\frac{i\hbar}{m}\right)\langle \hat{p}_x\rangle \quad ,$$

or

$$\frac{d\langle x\rangle}{dt} = \frac{1}{m}\ \langle p_x\rangle \quad . \qquad \text{...(14)}$$

(b) (II) Using $q = x$ in (9), we find

$$\frac{d}{dt}\langle p_x\rangle = \left\langle \frac{i}{\hbar}[\hat{H}\ ,\ \hat{p}_x]\right\rangle + \left\langle \frac{\partial\, \hat{p}_x}{\partial\, t}\right\rangle \quad . \qquad \text{...(15)}$$

It is given that p_x does not depend on time t explicitly, therefore,

$$\frac{\partial\, \hat{p}_x}{\partial t} = 0 \quad .$$

Therefore,

$$\frac{d}{dt}\langle p_x\rangle = \left\langle \frac{i}{\hbar}[\hat{H}\ ,\ \hat{p}_x]\right\rangle \quad . \qquad \text{...(16)}$$

Now

$$\left[\hat{H}\ ,\ \hat{p}_x\right] = \left[\frac{\hat{p}^2}{2m} + V(r)\ ,\ \hat{p}_x\right] = 0 + \left[V(r)\ ,\ \hat{p}_x\right] = i\hbar\ \frac{\partial V(r)}{\partial x} \quad .$$

Using it in (16), we find

$$\frac{d}{dt}\langle p_x\rangle = \left\langle \frac{i}{\hbar}\left(i\hbar\frac{\partial\, V(r)}{\partial x}\right)\right\rangle \quad ,$$

or

$$\frac{d}{dt}\langle p_x\rangle = -\left\langle \frac{\partial\, V}{\partial\, x}\right\rangle \quad .$$

Example 9.13 If for any state of a physical system, ψ is the eigenfunction of operator $\hat{A}$ corresponding to the dynamical variable A , then, show that the expectation value of A in that state is equal to the corresponding eigenvalue of the operator $\hat{A}$.

Ans. Let a is the eigenvalue corresponding to the eigenfunction ψ of the operator $\hat{A}$. The eigenvalue equation is

$$\hat{A}\ \psi = a\ \psi \quad . \qquad \text{...(1)}$$

Multiplying by ψ^* from left and integrating over volume gives,

$$\int\ \psi^*\ \hat{A}\ \psi\ dV = a \int\ \psi^*\ \psi\ dV \quad . \qquad \text{...(2)}$$

Thus, the expectation value

$$\langle A\rangle = \frac{\int \psi^*\ \hat{A}\ \psi\ dV}{\int\ \psi^*\ \psi\ dV} \quad . \qquad \text{...(3)}$$

Using (2) in (3) givens

$$\langle A \rangle = \frac{a \int \psi^* \, \psi \, dV}{\int \psi^* \, \psi \, dV} = a \quad .$$

Example 9.14 If e^{ix} is an eigenfunction of operator $\frac{d}{dx}$ with eigenvalue i, then determine the eigenfunction and eigenvalue of the operator $-2i\frac{d}{dx}$.

Ans. The eigenvalue equation has the form, $\hat{A}\,\psi = a\,\psi$, therefore,

$$\frac{d}{dx}\left(e^{ix}\right) = i\left(e^{ix}\right) \quad .$$

Multiplying it by $-2i$, we find

$$-2i\,\frac{d}{dx}\left(e^{ix}\right) = 2\left(e^{ix}\right) \quad ,$$

or

$$\left(-2i\,\frac{d}{dx}\right)\left(e^{ix}\right) = 2\left(e^{ix}\right)$$

Therefore, e^{ix} is the eigenfunction of the operator $\left(-2i\frac{d}{dx}\right)$, and 2 is the eigenvalue.

Example 9.15 Show that $e^{-x^2/2}$ is an eigenfunction of the the operator $\left(\frac{\partial^2}{\partial x^2} - x^2\right)$. What is the corresponding eigenvalue?

Ans. Consider the function,

$$\psi = e^{-x^2/2} \quad , \qquad \ldots(1)$$

then $$\frac{\partial \psi}{\partial x} = -x\,e^{-x^2/2} \quad ,$$

and $$\frac{\partial^2 \psi}{\partial x^2} = \left(x^2 - 1\right) e^{-x^2/2} \quad . \qquad \ldots(2)$$

Therefore, using (1) and (2), we get

$$\left(\frac{\partial^2}{\partial x^2} - x^2\right) e^{-x^2/2} = (-1)\,e^{-x^2/2} \quad . \qquad \ldots(3)$$

Thus $e^{-x^2/2}$ is the eigenfunction of the operator $\left(\frac{\partial^2}{\partial x^2} - x^2\right)$, and the corresponding eigenvalue is (-1) .

Example 9.16 Show that the wave-functions

$$\psi_1(x) = A_1 \cos(n\pi x/a) \quad \text{and} \quad \psi_2(x) = A_2 \sin(n\pi x/a)$$

are orthogonal wave-functions.

Ans. The orthogonality condition for the wave-functions is

$$\int_V \psi_1^* \, \psi_2 \, d\tau = 0 \quad ,$$

where $d\tau$ is the volume element. For one dimensional wave-functions, the orthogonality condition reduces to

$$\int_{-\infty}^{\infty} \psi_1^* \, \psi_2 \, dx = 0 \quad .$$

Here, the wave-functions belong to a particle confined in a box of dimension $0 < x < a$, so the orthogonality condition reduces to

$$\int_0^a \psi_1^* \, \psi_2 \, dx = 0 \quad .$$

For the given wave-functions,

$$\int_0^a \psi_1^* \, \psi_2 \, dx = A_1^* \, A_2 \int_0^a \cos\left(\frac{n\pi x}{a}\right) \sin\left(\frac{n\pi x}{a}\right) dx \quad ,$$

$$= \frac{1}{2} A_1^* \, A_2 \int_0^a \sin\left(\frac{2n\pi x}{a}\right) dx \quad ,$$

$$= \frac{1}{2} A_1^* \, A_2 \frac{a}{2n\pi} \left[\cos 2n\pi - \cos 0\right] \quad ,$$

$$= 0 \quad .$$

Thus the given wave-functions are orthogonal.

Example 9.17 Let three linearly independent eigenfunctions ψ_1, ψ_2, ψ_3 belong to a 3-fold degenerate eigenvalue a. (i) Show that a linear combination

$$\phi = c_1 \psi_1 + c_2 \psi_2 + c_3 \psi_3$$

is also an eigenfunction belonging to the eigenvalue a. (ii) Does it increase the degeneracy of a?

Ans. (i) Let three linearly independent eigenfunctions ψ_1, ψ_2, ψ_3 belong to a 3-fold degenerate eigenvalue a of an operator $\hat{A}$. That is

$$\hat{A}\,\psi_1 = a\,\psi_1 \quad , \quad \hat{A}\,\psi_2 = a\,\psi_2 \quad , \quad \hat{A}\,\psi_3 = a\,\psi_3 \quad . \qquad \text{...(1)}$$

Consider a linear combination

$$\phi = c_1 \psi_1 + c_2 \psi_2 + c_3 \psi_3 \quad , \qquad \text{...(2)}$$

where c_i (with $i = 1, 2, 3$) are some constants. Then

$$\hat{A}\,\phi = c_1 \hat{A}\,\psi_1 + c_2 \hat{A}\,\psi_2 + c_3 \hat{A}\,\psi_3 \quad . \qquad \text{...(3)}$$

Using (1) in (3), we find

$$\hat{A}\,\phi = a\left(c_1 \psi_1 + c_2 \psi_2 + c_3 \psi_3\right) = a\,\phi \quad . \qquad \text{...(4)}$$

Thus ϕ is also an eigenfunction belonging to the eigenvalue a.

(ii) No. ϕ is not linearly independent from the given three functions ψ_1, ψ_2, ψ_3. Therefore, it does not contribute to the degeneracy.

Example 9.18 Show that if two operators $\hat{A}$ and $\hat{B}$ have a complete set of simultaneous eigenfunctions then the two operators commute.

Ans. Let $\{\psi_n\}$ is a complete set of simultaneous eigenfunctions of the two operators $\hat{A}$ and $\hat{B}$. Further let

$$\hat{A}\,\psi_n = a_n \psi_n \quad , \qquad \text{...(1a)}$$

and

$$\hat{B}\,\psi_n = b_n \psi_n \quad . \qquad \text{...(1b)}$$

Consider an arbitrary function Φ. It can be expanded in the form of a linear combination of the eigenfunctions ψ_n forming a complete set. That is

$$\Phi = \sum_n C_n \psi_n \quad . \qquad ...(2)$$

Therefore,

$$\hat{A}\hat{B}\Phi = \hat{A}\left(\hat{B}\sum_n C_n\psi_n\right) = \hat{A}\left(\sum_n C_n \hat{B}\psi_n\right) = \hat{A}\left(\sum_n C_n b_n \psi_n\right) \quad ,$$

$$= \sum_n C_n b_n \hat{A}\psi_n = \sum_n C_n b_n a_n \psi_n \quad ,$$

$$= \sum_n a_n b_n C_n \psi_n \quad . \qquad ...(3)$$

Similarly,

$$\hat{B}\hat{A}\Phi = \hat{B}\left(\hat{A}\sum_n C_n\psi_n\right) = \hat{B}\left(\sum_n C_n \hat{A}\psi_n\right) = \hat{B}\left(\sum_n C_n a_n \psi_n\right) \quad ,$$

$$= \sum_n C_n a_n \hat{B}\psi_n = \sum_n C_n a_n b_n \psi_n \quad ,$$

$$= \sum_n a_n b_n C_n \psi_n \quad . \qquad ...(4)$$

Therefore, using (3) and (4), we find that the commutator

$$\left[\hat{A}, \hat{B}\right]\Phi = \hat{A}\hat{B}\Phi - \hat{B}\hat{A}\Phi = \sum_n a_n b_n C_n \psi_n - \sum_n a_n b_n C_n \psi_n \quad ,$$

$$= 0 \quad . \qquad ...(5)$$

Since Φ is an arbitrary function, therefore, (5) implies that

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

That is the two operators commute.

Example 9.19 If two operators $\hat{A}$ and $\hat{B}$ are Hermitian and commute, then show that $(\hat{A}\hat{B})$ is also a Hermitian operator.

Ans. For two wave functions ψ_1 and ψ_2, and the Hermitian operators $\hat{A}$ and $\hat{B}$, consider the integral

$$\int \psi_1^* \hat{A}\,\hat{B}\psi_2 \, d\tau \quad .$$

From the Hermitian property of operator $\hat{A}$, we find

$$\int \psi_1^* \hat{A}\,\hat{B}\psi_2 \, d\tau = \int \left(\hat{A}\psi_1\right)^* \hat{B}\psi_2 \, d\tau \quad . \qquad ...(1)$$

From the Hermitian property of operator $\hat{B}$, (1) can be written as

$$\int \left(\hat{A}\psi_1\right)^* \hat{B}\psi_2 \, d\tau = \int \left(\hat{B}\,\hat{A}\psi_1\right)^* \psi_2 \, d\tau \quad . \qquad ...(2)$$

Comparing (1) and (2), we find that

$$\int \psi_1^* \left(\hat{A}\,\hat{B}\psi_2\right) d\tau = \int \left(\hat{B}\,\hat{A}\psi_1\right)^* \psi_2 \, d\tau \quad . \qquad ...(3)$$

Since $\hat{A}$ and $\hat{B}$ commute, that is $\hat{A}\hat{B} = \hat{B}\hat{A}$, therefore (3) gives

$$\int \psi_1^* \left(\hat{A}\,\hat{B}\psi_2\right) d\tau = \int \left(\hat{A}\,\hat{B}\psi_1\right)^* \psi_2 \, d\tau \quad .$$

It is the condition for Hermiticity of the operator $\hat{C} \equiv \hat{A}\hat{B}$. Thus $\hat{A}\hat{B}$ is Hermitian.

Example 9.20 Establish the commutation relation for operators[16] x and $\frac{d}{dx}$.

Ans. Consider an arbitrary wave-function $\psi(x)$. Then for the given operators, we find

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

$$= x\frac{d\psi(x)}{dx} - \psi(x) - x\frac{d\psi(x)}{dx} \quad ,$$

or $$\left[x, \frac{d}{dx}\right]\psi(x) = -\psi(x) \quad .$$

Since $\psi(x)$ is an arbitrary wave-function, therefore, the above relation gives

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

Example 9.21 Show that

$$[f(r), p_x] = i\hbar\frac{\partial f(r)}{\partial x} \quad ,$$

where $r = (x, y, z)$.

Ans. For any wave-function $\psi(r)$, we have

$$[f(r), p_x]\psi(r) = f(r)\left(-i\hbar\frac{\partial}{\partial x}\right)\psi(r) - \left(-i\hbar\frac{\partial}{\partial x}\right)(f(r)\psi(r)) \quad ,$$

$$= -i\hbar f(r)\frac{\partial\psi(r)}{\partial x} + i\hbar\frac{\partial f(r)}{\partial x}\psi(r) + i\hbar f(r)\frac{\partial\psi(r)}{\partial x} \quad ,$$

$$= i\hbar\frac{\partial f(r)}{\partial x}\psi(r) \quad .$$

Since $\psi(r)$ is any arbitrary function, therefore, the above relation gives

$$[f(r), p_x] = i\hbar\frac{\partial f(r)}{\partial x} \quad .$$

Example 9.22 Show that the Hamiltonian operator and the momentum operator for a free particle commute.

Ans. Consider a particle of mass m moving along the x-axis with a momentum p . Then the Hamiltonian and the momentum operators are, respectively,

$$H = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} \quad \text{and} \quad p = -i\hbar\frac{\partial}{\partial x} \quad .$$

For any wave-function $\psi(x)$, we have

$$[H, p]\psi = Hp\psi - pH\psi \quad ,$$

$$= \left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\right)\left(-i\hbar\frac{\partial\psi(x)}{\partial x}\right) - \left(-i\hbar\frac{\partial}{\partial x}\right)\left(-\frac{\hbar^2}{2m}\frac{\partial^2\psi(x)}{\partial x^2}\right) \quad ,$$

$$= \frac{i\hbar^3}{2m}\frac{\partial^3\psi(x)}{\partial x^3} - \frac{i\hbar^3}{2m}\frac{\partial^3\psi(x)}{\partial x^3} \quad ,$$

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16 *For convenience of notation we drop the hat ^ over operators in this and other examples.*

$= 0$

Since $\psi(x)$ is an arbitrary function, the above relation implies that

$$[H,\, p] = 0 \quad .$$

Thus for a free particle, the Hamiltonian operator and the momentum operator commute.

Example 9.23 In quantum mechanics, the commutator of two operators A and B is defined by the relation $[A,\, B] = AB - BA$. Show that

$$[x,\, p_x] = i\hbar \quad .$$

Ans. Consider any wave-function $\psi(x)$, then we have

$$[x,\, p_x]\psi(x) = x\, p_x \psi(x) - p_x x\, \psi(x) \quad ,$$

$$= x\left(-i\hbar \frac{\partial \psi(x)}{\partial x}\right) - \left(-i\hbar \frac{\partial}{\partial x}(x\,\psi(x))\right) \quad ,$$

$$= -i\hbar x \frac{\partial \psi(x)}{\partial x} + i\hbar\, \psi(x) + i\hbar x \frac{\partial \psi(x)}{\partial x} \quad ,$$

$$= i\hbar\, \psi(x) \quad .$$

Since $\psi(x)$ is an arbitrary wave-function, therefore, the above relation is equivalent to

$$[x,\, p_x] = i\hbar \quad .$$

Example 9.24 If any two operators A and B commute with their commutator $[A,\, B]$, then show that $[A,\, B^n] = n B^{n-1}[A,\, B]$.

Ans. It is given that the operators A and B commute with $[A,\, B]$, therefore,

$$A[A,\, B] = [A,\, B]A \quad , \qquad \ldots(1)$$

and

$$B[A,\, B] = [A,\, B]B \quad . \qquad \ldots(2)$$

In order to prove that

$$[A,\, B^n] = n B^{n-1}[A,\, B] \quad . \qquad \ldots(3)$$

We use the principle of mathematical induction. Let us consider $n=2$, then,

$$[A,\, B^2] = [A,\, B\, B] \quad ,$$

$$= B[A,\, B] + [A,\, B]B \quad ,$$

$$= B[A,\, B] + B[A,\, B] \quad , \text{(we used (2))}$$

Thus

$$[A,\, B^2] = 2B[A,\, B] \quad . \qquad \ldots(4)$$

Therefore, (3) is true for $n = 2$.

Now we assume that (3) is true for $n=k$ that is

$$[A,\, B^k] = kB^{k-1}[A,\, B] \quad , \qquad \ldots(5)$$

and then show that it is true for $n=k+1$.

Consider

$$[A,\, B^{k+1}] = [A,\, B^k B] \quad ,$$

$$= B^k[A,\, B] + [A,\, B^k]B \quad .$$

Using (5) in the second term on the right hand side, we find

$$[A,\, B^{k+1}] = B^k[A,\, B] + kB^{k-1}[A,\, B]B \quad ,$$

$= B^k[A, B] + k B^k[A, B]$, (we used (2)),

$= (k+1)B^k [A, B]$.

Therefore, if the relation $[A, B^n] = n B^{n-1} [A, B]$ is true for $n=k$, then it is true for $n=k+1$. We have earlier showed that the relation is true for $n=2$, therefore it should be true for $n=3$. If it is true for $n=3$ then it is true for $n=4$, and so on. Thus by the principle of mathematical induction,

$$[A, B^n] = n B^{n-1} [A, B] \quad .$$

Example 9.25 If $\vec{L}$ is the angular momentum operator of a particle L_x , L_y and L_z are its Cartesian components, then show that[17]

(I) $\vec{L} \times \vec{L} = i\hbar \vec{L}$, (II) $[\vec{L}^2, L_x] = [\vec{L}^2, L_y] = [\vec{L}^2, L_z] = 0$.

Ans. The angular momentum operator of a particle of mass m moving with momentum $\vec{p}$ at position $\vec{r}$ is,

$$\vec{L} = \vec{r} \times \vec{p} = -i\hbar(\vec{r} \times \vec{\nabla}) \quad ,$$

where momentum operator in coordinate representation is $\vec{p} \equiv -i\hbar\vec{\nabla}$. The Cartesian components of the angular momentum operator are

$$L_x = y\,p_z - z\,p_y = -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right) \quad ,$$

$$L_y = z\,p_x - x\,p_z = -i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right) \quad ,$$

$$L_z = x\,p_y - y\,p_x = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) \quad .$$

(I) Consider,

$$[L_x, L_y] = [(y\,p_z - z\,p_y), (z\,p_x - x\,p_z)] \quad ,$$

$$= [y\,p_z, z\,p_x] + [z\,p_y, x\,p_z] - [y\,p_z, x\,p_z] - [z\,p_y, z\,p_x] \quad . \qquad ...(1)$$

The first commutator on the right of this equation (1) is

$$[y\,p_z, z\,p_x] = y\,p_z z\,p_x - z\,p_x y\,p_z \quad .$$

Since y and p_x commute with each other and with z and p_z , we can write

$$[y\,p_z, z\,p_x] = y\,p_x [p_z, z] \quad ,$$

$$= -i\hbar\, y\,p_x \quad . \qquad ...(2)$$

Similarly, the second commutator on the right hand side of (1) is

$$[z\,p_y, x\,p_z] = z\,p_y x\,p_z - x\,p_z z\,p_y \quad ,$$

$$= x\,p_y [z, p_z] \quad ,$$

$$= i\hbar x\,p_y \quad . \qquad ...(3)$$

The third commutator on the right hand side of Eq.(1) vanishes because y , x and p_z mutually commute

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17 *For simplicity of notation, we drop the hat ^ sign on operators.*

$$[y\,p_z, x\,p_z] = y\,p_z x\,p_z - x\,p_z y\,p_z = x\,y\,p_z^2 - x\,y\,p_z^2 \quad ,$$
$$= 0 \quad . \qquad \ldots(4)$$

Similarly the fourth commutator on the right hand side of Eq.(1) vanishes because z , p_y and p_x mutually commute:

$$[z\,p_y, z\,p_x] = z\,p_y z\,p_x - z\,p_x z\,p_y = z^2\,p_x p_y - z^2\,p_x p_y \quad ,$$
$$= 0 \quad . \qquad \ldots(5)$$

Thus, using (2) to (5) in (1), we find that

$$[L_x\,,\,L_y] = -i\hbar\,y\,p_x + i\hbar\,x\,p_y = i\hbar\left(x\,p_y - y\,p_x\right) \quad ,$$
$$= i\hbar L_z \quad . \qquad \ldots(6a)$$

Similarly we obtain

$$[L_y,\,L_z] = i\hbar\,L_x \quad , \qquad \ldots(6b)$$

and $$[L_z,\,L_x] = i\hbar\,L_y \quad . \qquad \ldots(6c)$$

Consider the vector commutation relation

$$\vec{L}\times\vec{L} = \begin{vmatrix} \hat{i} & \hat{j} & \hat{k} \\ L_x & L_y & L_z \\ L_x & L_y & L_z \end{vmatrix} \quad ,$$
$$= \hat{i}\left(L_y L_z - L_z L_y\right) + \hat{j}\left(L_z L_x - L_x L_z\right) + \hat{k}\left(L_x L_y - L_y L_x\right) \quad ,$$
$$= \hat{i}\left[L_y,\,L_z\right] + \hat{j}\left[L_z,\,L_x\right] + \hat{k}\left[L_x,\,L_y\right] \quad ,$$
$$= i\hbar\left(\hat{i}L_x + \hat{j}L_y + \hat{k}L_z\right) \quad ,$$
$$= i\hbar\vec{L} \quad . \qquad \ldots(9)$$

(II) The operator representing the square of the magnitude of the orbital angular momentum is defined as

$$\vec{L}^2 = L_x^2 + L_y^2 + L_z^2 \quad . \qquad \ldots(10)$$

Consider

$$\left[\vec{L}^2,\,L_x\right] = \left[L_x^2,\,L_x\right] + \left[L_y^2,\,L_x\right] + \left[L_z^2,\,L_x\right] \quad . \qquad \ldots(11)$$

Using

$$[AB\,,\,C] = A\,[B\,,\,C] + [A\,,\,C]\,B \quad ,$$

and commutation relations (6a, 6b, 6c), we find that

$$\left[L_x^2,\,L_x\right] = L_x\left[L_x,\,L_x\right] + \left[L_x,\,L_x\right]L_x = 0 \quad , \quad \text{(because } \left[L_x,\,L_x\right] = 0 \text{);} \qquad \ldots(12a)$$
$$\left[L_y^2,\,L_x\right] = L_y\left[L_y,\,L_x\right] + \left[L_y,\,L_x\right]L_y \quad ,$$
$$= -i\hbar\left(L_y L_z + L_z L_y\right) \quad , \quad \text{(because } \left[L_x,\,L_y\right] = i\hbar\,L_z \text{);} \qquad \ldots(12b)$$
$$\left[L_z^2,\,L_x\right] = L_z\left[L_z,\,L_x\right] + \left[L_z,\,L_x\right]L_z \quad ,$$
$$= i\hbar\left(L_z L_y + L_y L_z\right) \quad , \quad \text{(because } \left[L_z,\,L_x\right] = i\hbar\,L_y \text{).} \qquad \ldots(12c)$$

Substituting (12a, 12b,12c) in (11), we get

$$\left[\vec{L}^2,\,L_x\right] = 0 + \left(-i\hbar\left(L_y L_z + L_z L_y\right)\right) + i\hbar\left(L_z L_y + L_y L_z\right) \quad ,$$

$$= 0 \quad . \qquad \text{...(13a)}$$

Thus $\vec{L}^2$ commutes with L_x . Similarly, we can show that

$$\left[\vec{L}^2, L_y\right] = 0 \quad , \qquad \text{...(13b)}$$

$$\left[\vec{L}^2, L_z\right] = 0 \quad . \qquad \text{...(13c)}$$

That is $\vec{L}^2$ commutes with each of the three components of $\vec{L}$. We may summarize relations (13a, 13b, 134c) as

$$\left[\vec{L}^2, \vec{L}\right] = 0 \quad .$$

Example 9.26 If a particle is moving under the influence of one dimensional potential $V(x)$ which is symmetric under the transformation $x \to -x$, then show that the Hamiltonian operator

$H(x) = -\hbar^2 \dfrac{d^2}{dx^2} + V(x)$ for the particle commutes with the parity operator P .

Ans. The Hamiltonian operator is

$$H(x) = -\hbar^2 \frac{d^2}{dx^2} + V(x) \quad . \qquad \text{...(1)}$$

Under the transformation $x \to -x$, the above equation becomes

$$H(-x) = -\hbar^2 \frac{d^2}{dx^2} + V(-x) \quad .$$

Since $V(x)$ is symmetric, i.e., $V(-x) = V(x)$, therefore,

$$H(-x) = -\hbar^2 \frac{d^2}{dx^2} + V(x) \quad ,$$

or $\quad H(-x) = H(x) \quad . \qquad \text{...(2)}$

Now consider for any arbitrary function $\psi(x)$, the action of parity operator on $H(x)\psi(x)$:

$$P H(x)\, \psi(x) = H(-x)\psi(-x) \quad ,$$

$$= H(x)\psi(-x) \quad , \text{(because } H(-x)=H(x) \text{)},$$

$$= H(x)P\, \psi(x) \quad , \text{(because } \psi(-x)=P\, \psi(x) \text{)}.$$

Therefore,

$$P H(x)\, \psi(x) - H(x)P(x)\, \psi(x) = 0 \quad ,$$

or $\quad [P, H(x)]\, \psi(x) = 0 \quad ,$

or $\quad [P, H(x)] = 0$, (because $\psi(x)$ is any arbitrary function).

Thus a symmetric Hamiltonian operator commutes with the parity operator.

(*Comment: This result is true for a 3-dimensional case also. That is if* $H(-\vec{r}) = H(\vec{r}) \equiv H$ *, then* $[P, H] = 0$.)

Example 9.27 For a particle moving in a symmetric potential energy region, the solutions of the Schrodinger equation can be chosen to have a definite parity, even or odd.

Ans. For a symmetric potential energy, $V(-x) = V(x)$. Then the Hamiltonian is also symmetric, i.e., $H(-x) = H(x)$, where

$$H(x) = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x) \quad . \qquad ...(1)$$

Consider the Schrodinger equation

$$H\,\psi(x) = E\,\psi(x) \quad ,$$

or $$(H - E)\psi(x) = 0 \quad . \qquad ...(2)$$

A general wave function $\psi(x)$ can be written as

$$\psi(x) = \psi_+(x) + \psi_-(x) \quad , \qquad ...(3)$$

where

$$\psi_+(x) = \frac{1}{2}\left(\psi(x) + \psi(-x)\right) \quad , \qquad ...(4a)$$

and $$\psi_-(x) = \frac{1}{2}\left(\psi(x) - \psi(-x)\right) \quad . \qquad ...(4b)$$

The function $\psi_+(x)$ has even parity,

$$\psi_+(-x) = \psi_+(x) \quad , \qquad ...(5a)$$

and the function $\psi_-(x)$ has odd parity,

$$\psi_-(-x) = -\,\psi_-(x) \quad . \qquad ...(5b)$$

Using (3) in (2), we find

$$(H - E)\psi_+(x) + (H - E)\psi_-(x) = 0 \quad . \qquad ...(6)$$

Under parity transformation (in one dimension), $x \to -x$, Eq.(6) becomes (knowing the fact that H is symmetric)

$$(H - E)\psi_+(-x) + (H - E)\psi_-(-x) = 0 \quad .$$

Using (5) in the above, we get

$$(H - E)\psi_+(x) - (H - E)\psi_-(x) = 0 \quad . \qquad ...(7)$$

Adding (6) and (7), we find

$$(H - E)\psi_+(x) = 0 \quad ,$$

or $$H\,\psi_+(x) = E\,\psi_+(x) \quad . \qquad ...(8)$$

Subtracting (7) from (6) gives

$$(H - E)\psi_-(x) = 0 \quad ,$$

or $$H\,\psi_-(x) = E\,\psi_-(x) \quad . \qquad ...(9)$$

Eqs.(8) & (9) shows that $\psi_+(x)$ and $\psi_-(x)$ are also solutions of the Schrodinger equation. These solutions have definite parity. Thus the solutions of the Schrodinger equation can be chosen to have a definite parity, even or odd.

(*Comment: If we know a general solution* $\psi(x)$ *of the Schrodinger equation, then the combinations* $\psi_+(x) = \frac{1}{2}\left(\psi(x) + \psi(-x)\right)$ *, and* $\psi_-(x) = \frac{1}{2}\left(\psi(x) - \psi(-x)\right)$ *, are also solutions corresponding to the same eigenvalue. These solutions have a definite parity.*)

Example 9.28 What is the parity of the following spherical harmonics:

(I) $Y_1^0 = \left(\frac{3}{4\pi}\right)^{1/2} \cos\theta$, (II) $Y_1^1 = -\left(\frac{3}{8\pi}\right)^{1/2} \sin\theta\, e^{i\phi}$, and (III) $Y_2^1 = -\left(\frac{15}{8\pi}\right)^{1/2} \cos\theta \sin\theta\, e^{i\phi}$.

Ans. The parity of the spherical harmonics is found from the fact that an inversion which transforms $\vec{r}$ into $-\vec{r}$ is expressed in polar coordinates by the transformation

$$\theta \to \pi-\theta \quad , \quad \phi \to \phi+\pi \quad . \qquad ...(1)$$

So under parity transformation,

$$P(\cos\theta)=\cos(\pi-\theta)=-\cos\theta \quad , \qquad ...(2a)$$

$$P(\sin\theta)=\sin(\pi-\theta)=\sin\theta \quad , \qquad ...(2b)$$

$$P(e^{i\phi}) \to e^{i(\phi+\pi)}=-e^{i\phi} \quad . \qquad ...(2c)$$

(I) Under parity transformation

$$P\,Y_1^0 = \left(\frac{3}{4\pi}\right)^{1/2} P(\cos\theta) \quad .$$

Using (2) in the above we find

$$P\,Y_1^0 = \left(\frac{3}{4\pi}\right)^{1/2} (-\cos\theta) \quad ,$$

$$= -\,Y_1^0 \quad .$$

Thus parity of Y_1^0 is odd (-1).

(II) Under parity transformation

$$P\,Y_1^1 = -\left(\frac{3}{8\pi}\right)^{1/2} P\left(\sin\theta\, e^{i\phi}\right) \quad .$$

Using (2) in the above we find

$$P\,Y_1^1 = -\left(\frac{3}{8\pi}\right)^{1/2} \sin\theta \left(-e^{i\phi}\right) \quad ,$$

$$= +\left(\frac{3}{8\pi}\right)^{1/2} \sin\theta\, e^{i\phi} \quad ,$$

$$= -Y_1^1 \quad .$$

Thus parity of Y_1^1 is odd (-1).

(III) Under parity transformation

$$P\,Y_2^1 = -\left(\frac{15}{8\pi}\right)^{1/2} P\left(\cos\theta \sin\theta\, e^{i\phi}\right) \quad .$$

Using (2) we find

$$P\,Y_2^1 = -\left(\frac{15}{8\pi}\right)^{1/2} (-\cos\theta)(\sin\theta)\left(-e^{i\phi}\right) \quad ,$$

$$= -\left(\frac{15}{8\pi}\right)^{1/2} \cos\theta \sin\theta\, e^{i\phi} \quad ,$$

$$= Y_2^1 \quad .$$

Thus parity of Y_2^1 is even ($+1$).

(*Comment: The parity of spherical harmonic* Y_l^m *is* $(-1)^l$.)

Example 9.29 Show that parity operator is Hermitian.

Ans. The parity operator is $\hat{P}$ Hermitian if it satisfies the condition of Hermiticity, that is if

$$\int \left(\hat{P}\,\psi(\vec{r})\right)^* \psi(\vec{r})\, dV = \int \psi^*(\vec{r}) \left(\hat{P}\,\psi(\vec{r})\right) dV \quad .$$

By definition,

$$LHS = \int \left(\hat{P}\,\psi(\vec{r})\right)^* \psi(\vec{r})\, dV \quad ,$$

$$= \int \psi^*(-\vec{r})\, \psi(\vec{r})\, dV \quad ,$$

$$= \int \psi^*(\vec{r}\,')\, \psi(-\vec{r}\,')\, dV\,' \quad , \text{(by changing the integration variable } \vec{r}\,' = -\vec{r} \text{)}$$

$$= \int \psi^*(\vec{r}\,')\left(\hat{P}\,\psi(\vec{r}\,')\right) dV\,' \quad ,$$

$$\equiv \int \psi^*(\vec{r})\left(\hat{P}\,\psi(\vec{r})\right) dV \quad ,$$

$$= RHS \quad .$$

Thus $\hat{P}$ is Hermitian.

QUESTIONS

THEORY

9.1 Define Hermitian operator and prove that $i(p_x^2 x - x\,p_x^2)$ is a Hermitian operator. (similar **RU 2014**) (Hint: $i(p_x^2 x - x\,p_x^2) \equiv 2\hbar\, p_x$ and p_x is Hermitian.)

9.2 What is an operator? Define (a) linear operator, (b) Hermitian operator. Show that (i) $\hat{p}_x$, and (ii) ∇^2 are Hermitian operators. (similar **Bikaner 2012**) (see **Solved Examples 9.4(b) and 9.5**)

9.3 Define Hermitian operator. Show that the momentum operator $-i\hbar\frac{\partial}{\partial x}$ is Hermitian. (similar **Bikaner 2013, Ajmer 2014**)(see **Solved Examples 9.4(b)**)

9.4 (a) Define adjoint operator. (b) State Ehrenfest theorem. (c) What is the meaning of degeneracy of an energy eigenvalue? (similar **Kota 2014**)

9.5 Define parity operator and prove that the eigenvalues of parity operator are ± 1 . (similar **Kota 2013, 2010, Ajmer 2014**)

9.6 (a) What do you understand by Hermitian operator? Show that the eigenvalue of a Hermitian operator is real. (b) Show that $e^{-x^2/2}$ is an eigenfunction of the operator

$$\left(\frac{\partial^2}{\partial x^2} - x^2\right) \quad .$$
(similar **Bikaner 2010**)(see **Solved Examples 9.15**)

9.7 (a)What do you mean by an Hermitian operator? Prove that the eigenvalues of Hermitian operator are real and eigenfunctions corresponding to different eigenvalues are orthogonal. (similar **Kota 2012**) (b) What is the physical meaning of expectation value of physical parameter of a quantum system? Explain. (similar **RU 2013**)

9.8 (a) Define a Hermitian operator. Prove that $\hat{x}$ and $\hat{p}_x$ are Hermitian operators. (b) Prove that eigenvalures of a Hermitian operator are real. (c) Prove that eigenfunctions of a Hermitian operator for two distinct eigenvalues are orthogonal. (similar **RU 2011**)

9.9 Explain the meaning of expectation value of a physical variable. Prove that the rate of change of expectation value of linear momentum is equal to the expectation value of negative gradient of potential energy. (similar **Bikaner 2014**)

9.10 Differentiate between eigenvalue and expectation value. (similar **RU 2012**).

9.11 What do you mean by expectation value? The wave function of a particle is

$$\psi(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{\pi x}{a}\right) \text{ , for } \quad 0 \le x \le a \text{ , and } \quad \psi(x) = 0 \text{ outside this region.}$$

Determine the expectation values of position and momentum of the particle. (similar **Bikaner 2013, Kota 2013**)(see **Solved Examples 9.8**)

9.12 Prove that the expectation value of square of any observable quantity is always positive and real. (similar **Kota 2009**) (see **Solved Examples 9.10**)

9.13 State Ehrenfest theorem and prove that

$$\frac{d}{dt}\langle x \rangle = \frac{1}{m}\langle p_x \rangle \ .$$ (similar **Bikaner 2013, RU 2013, 2010, Kota 2009**)

$$\frac{d}{dt}\langle p_x \rangle = -\left\langle \frac{\partial V}{\partial x} \right\rangle \ .$$ (similar **RU 2014, RU 2013, 2010**)

9.14 (a)Define expectation value of an operator. Give its physical significance. (similar **RU 2011**)

9.15 State and Prove Ehrenfest theorem. What is its significance? (similar **RU 2011**)

9.16 State Ehrenfest theorem and with the help of this theorem prove that the wave nature and particle nature of matter are complimentary. (similar **Kota 2010**)

9.17 For one dimensional motion of a particle of mass m, prove that the expectation value of particles kinetic energy K is given by

$$\langle K \rangle = \frac{\hbar^2}{2m} \int_{-\infty}^{\infty} \frac{\partial \psi}{\partial x} \frac{\partial \psi^*}{\partial x} dx$$ (similar **Bikaner 2011**)

9.18 State and prove Ehrenfest theorems:(a) $\frac{d}{dt}\langle x \rangle = \frac{1}{m}\langle p_x \rangle$ and(b) $\frac{d}{dt}\langle p_x \rangle = -\left\langle \frac{\partial V}{\partial x} \right\rangle$. (similar **Bikaner 2011**)

9.19 Prove that the Hamiltonian and the linear momentum operator for a free particle commute. (similar **RU 2009**) (see **Solved Examples 9.22**)

9.20 Establish the following equation

$$\frac{d}{dt}\langle \hat{A} \rangle = \frac{1}{i\hbar}\langle [\hat{A} , \hat{H}] \rangle + \left\langle \frac{\partial \hat{A}}{\partial t} \right\rangle \ ,$$

where $\hat{A}$ is an operator and $\hat{H}$ is Hamiltonian, and other symbols have their usual meanings. From the above equation deduce the following relations:

(i) $\frac{d}{dt}\langle x \rangle = \frac{1}{m}\langle p_x \rangle$,

(ii) $\frac{d}{dt}\langle p_x \rangle = \langle F_x \rangle$.

(similar **Bikaner 2008)**(see **Solved Examples 9.12**)

9.21 (a) One-line-answer type (not more than 20 words) questions:

(i) If an operator $\hat{p}$ operates on ψ according to equation $\hat{p}\psi=\lambda\psi$, then what is λ in this equation?(similar **Ajmer 2012**) (Ans. Eigenvalue)

(ii) Define linear operator. (similar **Ajmer 2014, 2011**) (see section 9.1)

(iii) Write operators for energy and momentum. (similar **Ajmer 2012**) (Ans. $i\hbar\frac{\partial}{\partial t}$, $-i\hbar\vec{\nabla}$)

(iv) What is the value of the commutator $[\hat{z}, \hat{p}_z]$?(similar **Ajmer 2012**) (Ans. $i\hbar$)

(b) Small answer type Questions;

(i) What do you understand by adjoint operator? (similar **Kota 2014**)

(ii) State Ehrenfest theorem. (similar **Kota 2014**)

(iii) Define symmetric and anti-symmetric wave-functions. (similar **Kota 2013**)

(iv) Evaluate the commutator $\left[x, \frac{d}{dx}\right]$ by operating it on a wave-function. (similar **Kota 2012**)

(v) Explain the concept of parity. (similar **Kota 2010**)

9.22 State and explain the postulates of quantum mechanics. What are orthogonal functions? Explain. (similar **Bikaner 2010, RU 2010**)

9.23 (a) Define parity operator. Show that the parity operator commutes with a symmetric Hamiltonian.

(b) What are symmetric and anti-symmetric wave-functions? What is parity of each? (similar **Kota 2014**)

NUMERICAL

9.24 Prove that $\exp(-\frac{x^2}{2})$ is an eigenfunction of the operator $\left(\frac{d^2}{dx^2}-x^2\right)$. (similar **RU 2014**) (see **Solved Examples 9.15**)

9.25 A certain system is described by the Hamiltonian $H=-\frac{d^2}{dx^2}+x^2$. Show that $Axe^{-x^2/2}$ is an eigenfunction of *H* and determine the eigenvalue. (similar **Kota 2012**) (Ans. 3)

9.26 Prove that $\hat{x}^2\hat{p}_x-\hat{p}_x\hat{x}^2=2i\hbar\hat{x}$. (similar **Kota 2011**) (Ans. See **solved Example 9.3(b)**)

9.27 Show that $\hat{p}_x$ operator is Hermitian. (similar **Ajmer 2011**)(see **Solved Examples 9.4(b)**)

9.28 Prove that the wave functions $\psi_1(x)=A_1\cos\left(\frac{n\pi x}{L}\right)$ and $\psi_2(x)=A_2\sin\left(\frac{n\pi x}{L}\right)$ are orthogonal. (similar **Bikaner 2014**)

9.29 The wave function of a particle is given by

$$\psi(x)=\sqrt{\frac{2}{a}}\sin\left(\frac{\pi x}{a}\right) \text{ , for } 0\le x\le a \text{ , and } \psi(x)=0 \text{ outside this region.}$$

Show that the expectation value of position is $a/2$. (similar **Bikaner 2012**) (see **Solved Example 9.8**)

9.30 Show that $(\hat{x}\hat{p}-\hat{p}\hat{x})f(x)=i\hbar f(x)$, where $f(x)$ is any differentiable function of *x*.

9.31 If $\psi(x,t)=x^2\exp(-i\omega t)$ then find $\hat{E}\psi$.(similar **Kota 2013**) (see **Solved Example 9.1**)

9.32 If **A** and **B** are Hermitian operators then show that (**AB** + **BA**) is also a Hermitian operator.

(similar **RU 2012**)

9.33 Prove commutation relation $\left[L_x , L_y\right] = i\hbar L_z$. (similar Ajmer **2013**) (see **Solved Example 9.25**, establishment of Eq.(6a))

9.34 Prove that

$$\vec{L} \times \vec{L} = i\hbar \vec{L} \quad ,$$

where $\vec{L}$ is orbital angular momentum operator. (similar **Kota 2013**, **2009**, **RU 2009**) ((see **Solved Example 9.25**)

9.35 For angular momentum operator L , prove that $\left[L^2 , L_x\right]=0$, given that $\left[L_x , L_y\right] = i\hbar L_z$.(similar **Kota 2010**) (see **Solved Example 9.25**)

9.36 Find commutator of x and p_x operators. (similar **RU 2009**) (Ans. $\left[\hat{x} , \hat{p}_x\right]=i\hbar$)(see **Solved Example 9.23**)

9.37 Prove that $\left[x , \dfrac{\partial}{\partial x}\right]=-1$. (similar **Kota 2009**)(see **Solved Example 9.20**)

9.38 Write the parity of the following wave-functions: (i) $\psi=A e^{-ax}$, (ii) $\psi=A x e^{-x}$, (iii) $\psi=A x e^{-x^2}$, (iv) $\psi=A\cos x$. (similar **Kota 2010**) (Ans.(i) and (ii) no definite parity, because $\psi(-x)\neq\pm\psi(x)$ (iii) odd , that is -1 , (iv) even, that is $+1$)

9.39 Using the basic relation $[x, p]=i\hbar$, show that

(a) $\left[x, p^n\right]=i\hbar n p^{n-1}$, (b) $\left[p , x^n\right]=-i\hbar n x^{n-1}$.

9.40 The normalized wave function of a particle is given by

$$\psi(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{\pi x}{a}\right) \text{ , for } 0 \le x \le a \text{ , and } \psi(x) = 0 \text{ outside this region.}$$

Calculate the expectation value of p^2 . (Ans. $\dfrac{\pi^2\hbar^2}{a^2}$)

SOLUTIONS OF SELECTED QUESTIONS

9.25 Consider the action of the given operator $H=-\dfrac{d^2}{dx^2}+x^2$ on the given wave-function $\psi(x) = A x e^{-x^2/2}$:

$$H \psi(x) = \left(-\frac{d^2}{dx^2}+x^2\right)\left(A x e^{-x^2/2}\right) \quad ,$$

$$= -A\frac{d^2}{dx^2}\left(x e^{-x^2/2}\right) + A x^3 e^{-x^2/2} \quad ,$$

$$= -A\left\{-3x e^{-x^2/2} + x^3 e^{-x^2/2}\right\} + A x^3 e^{-x^2/2} \quad ,$$

$$= 3 A x e^{-x^2/2} \quad ,$$

$$= 3\psi(x) \quad .$$

Thus the function $\psi(x) = A x e^{-x^2/2}$ is an eigenfunction of $H=-\dfrac{d^2}{dx^2}+x^2$ and the eigenvalue is 3.

9.28 Two wave functions are orthogonal if they satisfy the condition,

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

For the given wave functions, consider the integral[18]

$$\int_{-\infty}^{\infty} \psi_1^*(x)\, \psi_2(x)\, dx = \lim_{\frac{L}{2} \to \infty} \left(A_1 A_2 \int_{-\frac{L}{2}}^{\frac{L}{2}} \cos(a x) \sin(a x)\, dx \right) \quad , \qquad \ldots(1)$$

where

$$a = \frac{n\pi}{L} \quad .$$

Using in (1),

$$\int \cos(a x) \sin(a x) dx = \frac{1}{2a} \sin^2(a x) \quad ,$$

we find

$$\int_{-\infty}^{\infty} \psi_1^*(x)\, \psi_2(x)\, dx = \lim_{\frac{L}{2} \to \infty} \quad A_1 A_2 \frac{1}{2a} \left[\sin^2(a x)\right]_{-L/2}^{L/2} \quad ,$$

$$= \lim_{L/2 \to \infty} \quad A_1 A_2 \frac{1}{2a} \times 0 = 0 \quad .$$

Thus the two functions are orthogonal.

(see **Solved Example 9.16** also.)

9.30 $$(\hat{x}\, \hat{p} - \hat{p}\, \hat{x})\, f(x) = \hat{x}\left(-i\hbar \frac{\partial f(x)}{\partial x}\right) - \left(-i\hbar \frac{\partial}{\partial x}(\hat{x}\, f(x))\right) \quad ,$$

$$= -i\hbar\, x \frac{\partial f(x)}{\partial x} + i\hbar \frac{\partial}{\partial x}(x\, f(x)) \quad ,$$

$$= -i\hbar\, x \frac{\partial f(x)}{\partial x} + i\hbar\, f(x) + i\hbar\, x \frac{\partial f(x)}{\partial x} \quad ,$$

$$= i\hbar\, f(x) \quad .$$

Thus

$$(\hat{x}\, \hat{p} - \hat{p}\, \hat{x})\, f(x) = i\hbar\, f(x) \quad .$$

9.32 For two wave functions ψ_1 and ψ_2, and the Hermitian operators **A** and **B**, consider the integral

$$\int \psi_1^* (\mathbf{A}\mathbf{B} + \mathbf{B}\mathbf{A}) \psi_2\, d\tau = \int \psi_1^* \mathbf{A}\mathbf{B} \psi_2\, d\tau + \int \psi_1^* \mathbf{B}\mathbf{A} \psi_2\, d\tau \quad . \qquad \ldots(1)$$

Consider the first integral on RHS:

$$\int \psi_1^* \mathbf{A}\, \mathbf{B} \psi_2\, d\tau = \int \left(\mathbf{A}\psi_1\right)^* \mathbf{B} \psi_2\, d\tau$$, (from the Hermitian property of operator **A**),

$$= \int \left(\mathbf{B}\mathbf{A}\psi_1\right)^* \psi_2\, d\tau$$, (from the Hermitian property of operator **B**). ...(2)

Similarly consider the second integral on RHS of Eq.(1):

$$\int \psi_1^* \mathbf{B}\mathbf{A} \psi_2\, d\tau = \int \left(\mathbf{B}\psi_1\right)^* \mathbf{A}\, \psi_2\, d\tau$$, (from the Hermitian property of operator **B**),

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18 *See box normalization.*

$$= \int \left(\mathbf{A}\mathbf{B}\psi_1\right)^* \psi_2 \, d\tau \quad \text{, (from the Hermitian property of operator } \mathbf{A} \text{).} \quad ...(3)$$

Using (2) and (3) on the RHS of (1), we find that

$$\int \psi_1^* (\mathbf{AB}+\mathbf{BA})\psi_2 \, d\tau = \int \left(\mathbf{BA}\psi_1\right)^* \psi_2 \, d\tau + \int \left(\mathbf{AB}\psi_1\right)^* \psi_2 \, d\tau \quad ,$$

$$= \int \left((\mathbf{AB} + \mathbf{BA})\psi_1\right)^* \psi_2 \, d\tau \quad . \quad ...(4)$$

The Eq.(4) shows that the operator $(\mathbf{AB} + \mathbf{BA})$ satisfies the condition of Hermiticity. Therefore, $(\mathbf{AB} + \mathbf{BA})$ is also a Hermitian operator.

9.39 (a) In order to prove that

$$\left[x,\ p^n\right] = i\hbar n\, p^{n-1} \quad ,. \quad ...(1)$$

we use the principle of mathematical induction. Let us consider $n=2$, then,

$$\left[x,\ p^2\right] = [x\,,\ p\ p] \quad ,$$

$$= p[x,\ p] + [x,\ p]p \quad ,$$

$$= 2\,i\hbar\, p \quad \text{, (we used } [x,\ p] = i\hbar$$

Thus $\quad \left[x,\ p^2\right] = 2\,i\hbar\, p \quad . \quad ...(2)$

Therefore, (1) is true for $n = 2$.

Now we assume that (1) is true for $n=k$ that is

$$\left[x,\ p^k\right] = i\hbar k\, p^{k-1} \quad , \quad ...(3)$$

and then show that it is true for $n=k+1$.

Consider

$$\left[x,\ p^{k+1}\right] = \left[x\,,\ p^k\ p\right] \quad ,$$

$$= p^k[x,\ p] + \left[x,\ p^k\right]p \quad .$$

Using $[x,\ p] = i\hbar$ in the first term and (3) in the second term on the right hand side, we find

$$\left[x,\ p^{k+1}\right] = i\hbar\, p^k + i\hbar k\, p^{k-1}\ p \quad ,$$

$$= i\hbar(k+1)p^k \quad .$$

Therefore, if the relation $\left[x,\ p^n\right] = i\hbar n\, p^{n-1}$ is true for $n=k$, then we have proved that it is true for $n=k+1$. We have earlier proved that the relation is true for $n=2$, therefore it should be true for $n=3$. If it is true for $n=3$ then it is true for $n=4$, and so on. Thus by the principle of mathematical induction,

$$\left[x,\ p^n\right] = i\hbar n\, p^{n-1}$$

true for all $n=1, 2, 3, \dots$.

(b) Use a process similar to (a) to show that

$$\left[p\,,\ x^n\right] = -i\hbar n\, x^{n-1} \quad .$$

9.40 The expectation value of p^2 is

$$\langle p^2 \rangle = \int_{-\infty}^{\infty} \psi^*(x) \left(-\hbar^2 \frac{d^2\psi(x)}{dx^2}\right) dx \quad ,$$

$$= \int_0^a \left(\sqrt{\frac{2}{a}} \sin\left(\frac{\pi x}{a}\right) \right)^* \left(-\hbar^2 \frac{d^2}{dx^2} \left(\sqrt{\frac{2}{a}} \sin\left(\frac{\pi x}{a}\right) \right) \right) dx \quad ,$$

$$= \frac{2}{a} \frac{\pi^2 \hbar^2}{a^2} \int_0^a \sin^2\left(\frac{\pi x}{a}\right) dx \quad ,$$

$$= \frac{2}{a} \frac{\pi^2 \hbar^2}{a^2} \left[\frac{x}{2} - \frac{a}{4\pi} \sin\left(\frac{2\pi x}{a}\right) \right]_0^a \quad ,$$

$$= \frac{\pi^2 \hbar^2}{a^2} \quad .$$