

# Free Study Material from All Lab Experiments



## Elements of Modern Physics Chapter - 3 Probability in Quantum Mechanics

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## Chapter-3

Two slit interference experiment with photons, atoms and particles; linear superposition principle as a consequence; Matter waves and wave amplitude; Schrodinger equation for non-relativistic particles; Momentum and Energy operators; stationary states; physical interpretation of a wave function, probabilities and normalization; Probability and probability current densities in one dimension. (10 Lectures)

**Q:**

Describe the double-slit experiment using an electron beam. Show that the results of this experiment can be explained only if the uncertainty principle is assumed to be valid.

**Ans:**

that if we employ a detector that can tell which slit an electron goes through, the interference pattern disappears. We shall now see that the uncertainty principle ensures that this is exactly the case.

Figure 5.5 shows a schematic diagram of the double-slit experiment. The distance between the slits  $A$  and  $B$  is  $d$  and the distance between the slits and the screen is  $D$ .

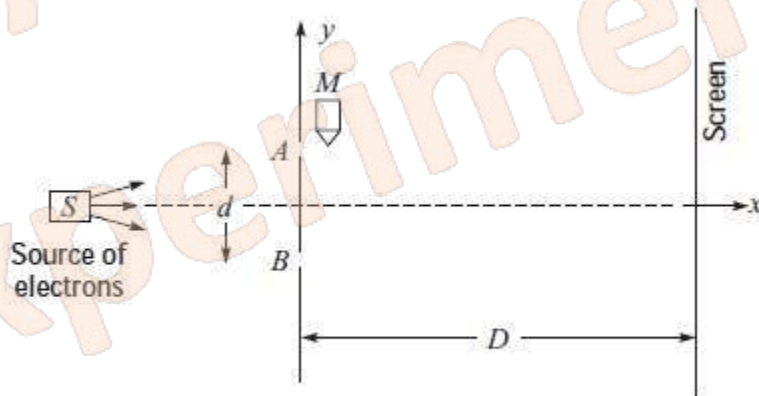


Figure 5.5 Double-slit experiment with a detector.

The distance between successive maxima on the screen would be

$$\beta = \frac{\lambda D}{d} \quad (5.33)$$

where  $\lambda$  is the de Broglie wavelength of the electron, that is,

$$\lambda = \frac{h}{p}$$

$p$  being the momentum of the electron.

The detector is placed just behind the slits. It is a microscope along with an illumination device. In order that the microscope tells which slit the electron came through, it should measure the  $y$ -component of the electron's position to a precision better than half the distance between the slits. That is

$$\Delta y < \frac{d}{2}$$

In order to detect the electron, an illumination photon must bounce off the electron into the microscope. This will impart to the electron a momentum in the  $y$ -direction and thereby introduce an uncertainty  $\Delta p_y$  in the  $y$ -component of the electron's momentum. According to the uncertainty principle

$$\Delta p_y \geq \frac{\hbar}{\Delta y}$$

$$\Delta p_y \geq \frac{2\hbar}{d}$$

As a consequence, the direction of motion of the electron becomes uncertain by an angle  $\Delta\theta$  given by

$$\Delta\theta \approx \frac{\Delta p_y}{p} \geq \frac{2\hbar}{d(h/\lambda)} = \frac{\lambda}{\pi d}$$

This angular uncertainty produces an uncertainty in the position of the electron on the screen given by

$$\Delta y = D\Delta\theta \geq \frac{\lambda D}{\pi d}$$

This is comparable with  $\beta$ , the distance between successive maxima of the interference pattern (see Equation 5.33). Thus, the uncertainty principle leads to the conclusion that if an attempt is made to determine through which slit the electron passes, the interference pattern disappears. Since this is known to be correct experimentally, the uncertainty principle must be true.

**Q: Write the time-dependent Schrödinger equation for a particle of mass  $m$  moving under a force which is derivable from a potential  $V(r, t)$ . What is the physical interpretation of the wave function? Why should the wave function be normalized?**

**Ans:**

According to classical mechanics, the total energy of the particle would be given by

$$E = \frac{p^2}{2m} + V(\mathbf{r}, t) \quad (6.15)$$

Since  $V$  does not depend on  $E$  or  $\mathbf{p}$ , the above discussion for the free particle suggests that the wave function should satisfy

$$\hat{E}\Psi = \left( \frac{\hat{p}^2}{2m} + V \right) \Psi$$

so that, the Schrödinger equation generalizes to

$$i\hbar \frac{\partial}{\partial t} \Psi(\mathbf{r}, t) = \left( -\frac{\hbar^2 \nabla^2}{2m} + V(\mathbf{r}, t) \right) \Psi(\mathbf{r}, t) \quad (6.16)$$

**(Time-dependent Schrödinger equation)**

The operator on the right-hand side is called the *Hamiltonian operator* and is denoted by the symbol  $H$ :

$$H = -\frac{\hbar^2 \nabla^2}{2m} + V(\mathbf{r}, t) \quad (6.17)$$

**(Hamiltonian operator)**

The name follows from the fact that in classical mechanics the sum of the kinetic and the potential energies of a particle is called its *Hamiltonian*.

#### Interpretation:

If a particle is described by a wave function  $\Psi(\mathbf{r}, t)$ , then the probability of finding the particle, at time  $t$ , within the volume element  $d\mathbf{r} = dx dy dz$  about the point  $\mathbf{r} \equiv (x, y, z)$  is

$$P(\mathbf{r}, t) d\mathbf{r} = |\Psi(\mathbf{r}, t)|^2 d\mathbf{r} = \Psi^*(\mathbf{r}, t) \Psi(\mathbf{r}, t) d\mathbf{r} \quad (6.18)$$

The quantity

$$P(\mathbf{r}, t) = |\Psi(\mathbf{r}, t)|^2 = \Psi^*(\mathbf{r}, t) \Psi(\mathbf{r}, t) \quad (6.19)$$

is obviously called the **position probability density**. Since the probability of finding the particle somewhere at time  $t$  is unity, the wave function is chosen to satisfy the **normalization condition**

$$\int |\Psi(\mathbf{r}, t)|^2 d\mathbf{r} = 1 \quad (6.20)$$

where the integral extends over all space. The wave functions for which the above integral exists are said to be square integrable.

**Q: What is the Hamiltonian operator? Show that the conservation of probability implies that the Hamiltonian is an Hermitian operator.**

**Ans:**

The operator on the right-hand side is called the *Hamiltonian operator* and is denoted by the symbol  $H$ :

$$H = -\frac{\hbar^2 \nabla^2}{2m} + V(\mathbf{r}, t) \quad (6.17)$$

**(Hamiltonian operator)**

The name follows from the fact that in classical mechanics the sum of the kinetic and the potential energies of a particle is called its *Hamiltonian*.

In terms of  $H$ , the Schrödinger equation can be written as

$$i\hbar \frac{\partial \Psi}{\partial t} = H\Psi \quad (6.29)$$

The complex conjugate of this equation is

$$-i\hbar \frac{\partial \Psi^*}{\partial t} = (H\Psi)^* \quad (6.30)$$

Using these equations, we can write

$$\begin{aligned} \frac{\partial}{\partial t} \int \Psi^* \Psi d\mathbf{r} &= \int \left( \Psi^* \frac{\partial \Psi}{\partial t} + \Psi \frac{\partial \Psi^*}{\partial t} \right) d\mathbf{r} \\ &= (i\hbar)^{-1} \int [\Psi^* (H\Psi) - \Psi (H\Psi)^*] d\mathbf{r} \end{aligned}$$

Since the left-hand side is zero, we obtain

$$\int \Psi^* (H\Psi) d\mathbf{r} = \int (H\Psi)^* \Psi d\mathbf{r} \quad (6.31)$$

Operators which satisfy this condition are called **Hermitian operators**. ~~Thus~~

**Q: Define the position probability density and the probability current density in the context of a quantum mechanical wave function. Obtain the equation connecting these quantities and give the physical interpretation of this equation.**

**Ans:**

If a particle is described by a wave function  $\Psi(\mathbf{r}, t)$ , then the probability of finding the particle, at time  $t$ , within the volume element  $d\mathbf{r} = dx dy dz$  about the point  $\mathbf{r} \equiv (x, y, z)$  is

$$P(\mathbf{r}, t) d\mathbf{r} = |\Psi(\mathbf{r}, t)|^2 d\mathbf{r} = \Psi^*(\mathbf{r}, t) \Psi(\mathbf{r}, t) d\mathbf{r} \quad (6.18)$$

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$$\int |\Psi(\mathbf{r}, t)|^2 d\mathbf{r} = 1 \quad (6.20)$$

### Probability Current Density

It says that the rate of change of the probability of finding the particle in a volume  $V$  is equal to the probability flux passing through the surface  $S$  bounding  $V$ . It is reasonable, therefore, to interpret the vector  $\mathbf{j}(\mathbf{r}, t)$  as probability current density. Since this equation is true for any arbitrary volume, we have

$$\frac{\partial}{\partial t} P(\mathbf{r}, t) + \nabla \cdot \mathbf{j}(\mathbf{r}, t) = 0 \quad (6.32)$$

This equation has the familiar form associated with the conservation of matter in a fluid of density  $P$  and current density  $\mathbf{j}$  in a medium in which there are no sources or sinks. This is called the **equation of continuity**.

If  $\nabla \cdot \mathbf{j}$  is zero in a state, then for that state the probability density is constant in time. Such states are called **stationary states**.

The probability current density (6.26) may also be written as

$$\mathbf{j}(\mathbf{r}, t) = \text{Re} \left[ \Psi^* \frac{\hbar}{im} \nabla \Psi \right] \quad (6.33)$$

where 'Re' indicates 'real part of'.

It may be noted that the operator  $(\hbar/im)\nabla$  represents  $\mathbf{p}/m$ , that is, the velocity  $\mathbf{v}$  of the particle. Thus,  $\mathbf{j}$  corresponds to the product of the probability density  $P$  and the velocity  $\mathbf{v}$ :

$$\mathbf{j} = P\mathbf{v}$$

Thus, it is appropriate to interpret  $\mathbf{j}$  as a probability current density.

**Q:**

- What is meant by the expectation value of a dynamical variable? How is it obtained mathematically?
- Show that the expectation value of a physical quantity can be real only if the corresponding operator is Hermitian.
- Show by actual integration that  $\langle p_x \rangle$  is real.

**Ans:**

the *expectation value* of a quantity, which is the average value of the

measurements of the quantity performed on a very large number of independent identical systems represented by the wave function  $\Psi$ . Or, equivalently, it is the average of a large number of measurements on the same system.

First, let us consider the measurement of the position of the particle. Since  $P(\mathbf{r}, t) = \Psi^*(\mathbf{r}, t) \Psi(\mathbf{r}, t)$  is interpreted as the position probability density at the point  $\mathbf{r}$  at the time  $t$ , the *expectation value* of the position vector  $\mathbf{r}$  is given by

$$\begin{aligned}\langle \mathbf{r} \rangle &= \int \mathbf{r} P(\mathbf{r}, t) d\mathbf{r} \\ &= \int \Psi^*(\mathbf{r}, t) \mathbf{r} \Psi(\mathbf{r}, t) d\mathbf{r}\end{aligned}\quad (6.34)$$

where  $\Psi(\mathbf{r}, t)$  is normalized. This equation is equivalent to the three equations

$$\langle x \rangle = \int \Psi^* x \Psi d\mathbf{r} \quad (6.35a)$$

$$\langle y \rangle = \int \Psi^* y \Psi d\mathbf{r} \quad (6.35b)$$

$$\langle z \rangle = \int \Psi^* z \Psi d\mathbf{r} \quad (6.35c)$$

The expectation value is a function only of the time because the space coordinates have been integrated out. Further, the expectation value of a physical quantity is always real. Note the order of the factors in the integrand—the vector  $\mathbf{r}$  (or each of  $x, y, z$ ) has been sandwiched between  $\Psi^*$  on the left and  $\Psi$  on the right. This is immaterial at this stage but is chosen for reason which will be clear shortly.

The *expectation value* of any quantity which is a function of  $\mathbf{r}$  and  $t$  would be

$$\langle f(\mathbf{r}, t) \rangle = \int \Psi^*(\mathbf{r}, t) f(\mathbf{r}, t) \Psi(\mathbf{r}, t) d\mathbf{r} \quad (6.36)$$

Suppose, the dynamical state of a particle is described by the normalized wave function  $\Psi(\mathbf{r}, t)$ . Let  $A(\mathbf{r}, \mathbf{p}, t)$  be a dynamical variable representing a physical quantity associated with the particle. We obtain the operator  $\hat{A}(\mathbf{r}, -i\hbar \nabla, t)$  by performing the substitution  $\mathbf{p} \rightarrow -i\hbar \nabla$ , and then calculate the expectation value of  $A$  from the expression

$$\langle A \rangle = \int \Psi^*(\mathbf{r}, t) \hat{A}(\mathbf{r}, -i\hbar \nabla, t) \Psi(\mathbf{r}, t) d\mathbf{r} \quad (6.43)$$

Since the expectation value of a physical quantity is always *real*, i.e.,  $\langle A \rangle^* = \langle A \rangle$ , it follows that the operator  $\hat{A}$  must satisfy

$$\int \Psi^* \hat{A} \Psi d\mathbf{r} = \int (\hat{A}\Psi)^* \Psi d\mathbf{r} \quad (6.44)$$

Thus, the operator associated with a dynamical quantity must be *Hermitian*.

**Q: State and prove Ehrenfest's theorem.**

**Ans:** According to Ehrenfest's theorem, the equations of motion of the expectation values of the position and momentum vectors for a wave packet are formally identical to Newton's equations of classical mechanics. That is,

$$\frac{d}{dt} \langle \mathbf{r} \rangle = \frac{\langle \mathbf{p} \rangle}{m} \quad (6.45)$$

$$\frac{d}{dt} \langle \mathbf{p} \rangle = -\langle \nabla V \rangle \quad (6.46)$$

In order to prove (6.45), let us first consider the expectation value of the  $x$ -component of the position vector  $\mathbf{r}$ . Assuming that the wave function  $\Psi$  representing the wave packet is normalized to unity, we have

$$\langle x \rangle = \int \Psi^* x \Psi d\mathbf{r}$$

The time rate of change of  $\langle x \rangle$  is

$$\begin{aligned} \frac{d}{dt} \langle x \rangle &= \frac{d}{dt} \int \Psi^* x \Psi d\mathbf{r} \\ &= \int \Psi^* x \frac{\partial \Psi}{\partial t} d\mathbf{r} + \int \frac{\partial \Psi^*}{\partial t} x \Psi d\mathbf{r} \end{aligned}$$

The right-hand side can be transformed by using the Schrödinger equation (6.22) and its complex conjugate (6.23). We obtain

$$\begin{aligned} \frac{d}{dt} \langle x \rangle &= \frac{1}{i\hbar} \left[ \int \Psi^* x \left( -\frac{\hbar^2}{2m} \nabla^2 \Psi + V\Psi \right) d\mathbf{r} - \int \left( -\frac{\hbar^2}{2m} \nabla^2 \Psi^* + V\Psi^* \right) x \Psi d\mathbf{r} \right] \\ &= \frac{i\hbar}{2m} \int [\Psi^* x (\nabla^2 \Psi) - (\nabla^2 \Psi^*) x \Psi] d\mathbf{r} \quad (6.47) \end{aligned}$$

Let us consider the second part of the integral. Using Green's first identity<sup>†</sup>, we obtain

$$\int (\nabla^2 \Psi^*) x \Psi d\mathbf{r} = \int_S x \Psi (\nabla \Psi^*) \cdot d\mathbf{S} - \int (\nabla \Psi^*) \cdot \nabla (x \Psi) d\mathbf{r}$$

Since the volume under consideration is the entire space, the surface  $S$  in the first integral on the right is at infinity. Hence, this integral is zero because the wave function vanishes at large distances. Therefore,



$$\int (\nabla^2 \Psi^*) x \Psi d\mathbf{r} = - \int (\nabla \Psi^*) \cdot \nabla (x\Psi) d\mathbf{r}$$

Using Green's first identity again, we get

$$- \int (\nabla \Psi^*) \cdot \nabla (x\Psi) d\mathbf{r} = - \int_S \Psi^* \nabla (x\Psi) \cdot d\mathbf{S} + \int \Psi^* \nabla^2 (x\Psi) d\mathbf{r}$$

The surface integral again vanishes. Thus,

$$\int (\nabla^2 \Psi^*) x \Psi d\mathbf{r} = \int \Psi^* \nabla^2 (x\Psi) d\mathbf{r}$$

Substituting this back into (6.47), we obtain

$$\frac{d}{dt} \langle x \rangle = \frac{i\hbar}{2m} \int \Psi^* [x \nabla^2 \Psi - \nabla^2 (x\Psi)] d\mathbf{r}$$

It can be easily shown that

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

Therefore,

$$\begin{aligned} \frac{d}{dt} \langle x \rangle &= -\frac{i\hbar}{m} \int \Psi^* \frac{\partial \Psi}{\partial x} d\mathbf{r} \\ &= \frac{1}{m} \int \Psi^* \left( -i\hbar \frac{\partial}{\partial x} \right) \Psi d\mathbf{r} \\ &= \frac{\langle p_x \rangle}{m} \end{aligned}$$

Similarly, we can prove that

$$\frac{d}{dt} \langle y \rangle = \frac{\langle p_y \rangle}{m}, \quad \frac{d}{dt} \langle z \rangle = \frac{\langle p_z \rangle}{m}$$

These three equations are the three components of Equation (6.45), which was to be proved.

Let us calculate the time rate of change of the expectation value of the  $x$ -component of the momentum of the particle. We have

$$\begin{aligned} \frac{d}{dt} \langle p_x \rangle &= -i\hbar \frac{d}{dt} \int \Psi^* \frac{\partial \Psi}{\partial x} d\mathbf{r} \\ &= -i\hbar \left[ \int \Psi^* \frac{\partial}{\partial x} \frac{\partial \Psi}{\partial t} d\mathbf{r} + \int \frac{\partial \Psi^*}{\partial t} \frac{\partial \Psi}{\partial x} d\mathbf{r} \right] \end{aligned}$$

Using the Schrödinger equation (6.22) and its complex conjugate (6.23) to replace  $\partial\Psi/\partial t$  and  $\partial\Psi^*/\partial t$ , respectively, we get

$$\begin{aligned}\frac{d}{dt}\langle p_x \rangle &= -\int \Psi^* \frac{\partial}{\partial x} \left( -\frac{\hbar^2}{2m} \nabla^2 \Psi + V\Psi \right) d\mathbf{r} + \int \left( -\frac{\hbar^2}{2m} \nabla^2 \Psi^* + V\Psi^* \right) \frac{\partial \Psi}{\partial x} d\mathbf{r} \\ &= \frac{\hbar^2}{2m} \int \left[ \Psi^* \left( \nabla^2 \frac{\partial \Psi}{\partial x} \right) - (\nabla^2 \Psi^*) \frac{\partial \Psi}{\partial x} \right] d\mathbf{r} - \int \Psi^* \left[ \frac{\partial}{\partial x} (V\Psi) - V \frac{\partial \Psi}{\partial x} \right] d\mathbf{r}\end{aligned}$$

Using Green's second identity<sup>†</sup> the first integral on the right is zero because  $\Psi$  and  $\partial\Psi/\partial x$  vanish at large distances. The second integral gets simplified as

$$\begin{aligned}-\int \Psi^* \left[ \frac{\partial}{\partial x} (V\Psi) - V \frac{\partial \Psi}{\partial x} \right] d\mathbf{r} &= -\int \Psi^* \frac{\partial V}{\partial x} \Psi d\mathbf{r} \\ &= -\left\langle \frac{\partial V}{\partial x} \right\rangle\end{aligned}$$

Thus,

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

Similarly we can prove that

$$\frac{d}{dt}\langle p_y \rangle = -\left\langle \frac{\partial V}{\partial y} \right\rangle, \quad \frac{d}{dt}\langle p_z \rangle = -\left\langle \frac{\partial V}{\partial z} \right\rangle$$

These three equations are the three components of Equation (6.46). Thus, the proof of Ehrenfest's theorem is complete.

**Q: Show that the wave packet having the minimum uncertainty product has a gaussian shape.**

**Ans: the uncertainty product is minimum when the following two conditions are satisfied:**

$$A\Psi = \alpha B\Psi \quad (6.56)$$

$$\text{and} \quad \int \Psi^*(AB + BA)\Psi dx = 0 \quad (6.57)$$

Using Equation (6.49), Equation (6.56) gives

$$(x - \langle x \rangle)\Psi = \alpha \left[ -i\hbar \frac{d\Psi}{dx} - \langle p \rangle \Psi \right]$$

Rearranging, we get the differential equation

$$\frac{d\Psi}{dx} = \left[ \frac{i}{\alpha\hbar} (x - \langle x \rangle) + \frac{i}{\hbar} \langle p \rangle \right] \Psi$$

which on integration gives

$$\Psi(x) = N \exp \left[ \frac{i}{2\alpha\hbar} (x - \langle x \rangle)^2 + \frac{i\langle p \rangle x}{\hbar} \right] \quad (6.58)$$

where  $N$  is an arbitrary constant.

Equation (6.57) gives

$$\int \Psi^* A B \Psi dx + \int B^* \Psi^* A \Psi dx = 0$$

Using (6.56), this becomes

$$\left( \frac{1}{\alpha} + \frac{1}{\alpha^*} \right) \int \Psi^* A^2 \Psi dx = 0$$

Since the integral is not zero, this yields

$$\frac{1}{\alpha} + \frac{1}{\alpha^*} = 0$$

which requires that  $\alpha$  be purely imaginary. Further, since the integral of  $|\Psi|^2$  should converge,  $\alpha$  must be negative imaginary. In order to determine  $\alpha$ , we require

$$\int (x - \langle x \rangle)^2 |\Psi|^2 dx = (\Delta x)^2$$

Evaluating the integral and substituting the value of  $\alpha$  in (6.58), we obtain

$$\Psi(x) = N \exp \left[ -\frac{(x - \langle x \rangle)^2}{4(\Delta x)^2} + \frac{i\langle p \rangle x}{\hbar} \right] \quad (6.59)$$

which is a gaussian function. Thus we find that *the wave packet having the minimum uncertainty product has a gaussian shape.*

### Q:

Show that the eigenvalues of the time-independent Schrödinger equation  $H\psi = E\psi$  are real.

### Ans:

Let  $E$  be the eigenvalue corresponding to the eigenfunction  $\psi$ .

Then

$$H\psi = E\psi$$

Since the Hamiltonian  $H$  is a Hermitian operator, we have from Equation (6.31),

$$\int \psi^* H \psi \, d\mathbf{r} = \int (H\psi)^* \psi \, d\mathbf{r}$$

These equations give

$$\int \psi^* E \psi \, d\mathbf{r} = \int E^* \psi^* \psi \, d\mathbf{r}$$

or  $(E - E^*) \int \psi^* \psi \, d\mathbf{r} = 0$

Since the probability integral  $\int \psi^* \psi \, d\mathbf{r}$  is necessarily positive, it follows that

$$E = E^*$$

Hence the eigenvalues of  $H$  are *real*.

**Q: What are stationary states? Show that the probability current density is divergence less for such states.**

**Ans:**

An important consequence of the reality of eigenvalues is that the position probability density corresponding to the states represented by 'separable' wave functions (6.64) is independent of time:

$$\begin{aligned} P(\mathbf{r}, t) &= \Psi^*(\mathbf{r}, t) \Psi(\mathbf{r}, t) \\ &= \psi^*(\mathbf{r}) e^{iEt/\hbar} \psi(\mathbf{r}) e^{-iEt/\hbar} \\ &= \psi^*(\mathbf{r}) \psi(\mathbf{r}) \end{aligned}$$

Therefore, these states are called *stationary states*. This name is further justified by the fact that the expectation value of the total energy operator in a state described by the wave function (6.64) is equal to the energy eigenvalue of that state for all time if the wave function is normalized:

$$\begin{aligned} &\int \Psi^*(\mathbf{r}, t) H \Psi(\mathbf{r}, t) \, d\mathbf{r} \\ &= \int \psi^*(\mathbf{r}) e^{iEt/\hbar} H \psi(\mathbf{r}) e^{-iEt/\hbar} \, d\mathbf{r} \\ &= \int \psi^*(\mathbf{r}) E \psi(\mathbf{r}) \, d\mathbf{r} \\ &= E \int \psi^*(\mathbf{r}) \psi(\mathbf{r}) \, d\mathbf{r} \\ &= E \end{aligned}$$

**Q: Show that the eigenfunctions corresponding to distinct eigenvalues of the Hamiltonian are orthogonal.**

**Ans:**

Let  $\psi_k$  and  $\psi_n$  be the eigenfunctions corresponding to the eigenvalues  $E_k$  and  $E_n$ , respectively. Then

$$H\psi_k = E_k\psi_k \quad (6.67)$$

and

$$H\psi_n = E_n\psi_n \quad (6.68)$$

Taking complex-conjugate of (6.68) and remembering that  $E_n$  is real,

$$(H\psi_n)^* = E_n\psi_n^* \quad (6.69)$$

Premultiplying (6.67) by  $\psi_n^*$  and postmultiplying (6.69) by  $\psi_k$ , we obtain

$$\psi_n^*(H\psi_k) = E_k\psi_n^*\psi_k \quad (6.70)$$

and

$$(H\psi_n)^*\psi_k = E_n\psi_n^*\psi_k \quad (6.71)$$

Subtracting (6.71) from (6.70) and integrating, we obtain

$$(E_k - E_n) \int \psi_n^* \psi_k d\mathbf{r} = \int [\psi_n^*(H\psi_k) - (H\psi_n)^*\psi_k] d\mathbf{r}$$

Since  $H$  is Hermitian, the integral on the right-hand side is zero. Therefore,

$$(E_k - E_n) \int \psi_n^* \psi_k d\mathbf{r} = 0$$

Since  $E_k \neq E_n$ , this gives

$$\int \psi_k^* \psi_n d\mathbf{r} = 0$$

This shows that the eigenfunctions are orthogonal.

**Q: What are the continuity and boundary conditions that must be satisfied for a wave function to be physically acceptable?**

**Ans:** In order for a wave function to be physical acceptable, it must satisfy certain continuity and boundary conditions. We mention these below:

- 1) the wave function and its gradient be single-valued, finite and continuous at every point in space.
- 2) The wave functions are bounded at large distances in all directions.
- 3) If there is an infinite potential step at a surface, then the wave function at the surface is zero and the component of the gradient of the wave function normal to the surface is not determined.

**Q: What are momentum eigenfunctions?**

**Ans:**

Let us now operate on the eigenfunctions  $\exp(ikx)$  and  $\exp(-ikx)$  with the momentum operator

$$p = -i\hbar \frac{d}{dx}$$

We have

$$-i\hbar \frac{d}{dx} (e^{ikx}) = \hbar k (e^{ikx}) \quad (6.82)$$

and

$$-i\hbar \frac{d}{dx} (e^{-ikx}) = -\hbar k (e^{-ikx}) \quad (6.83)$$

We find that the functions  $\exp(ikx)$  and  $\exp(-ikx)$  are eigenfunctions of the momentum operator with the eigenvalues  $\hbar k$  and  $-\hbar k$ , respectively. Thus, these functions are not only energy eigenfunctions, but also *momentum eigenfunctions*.