Lecture Notes in Quantum Mechanics

Unit - I: Concepts and Formalisms

II M.Sc Physics
III Semester

Dr. A. Ishaq Ahamed

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Chapter 1

Schrö̈edinger's Wave Equation

1.1 Old Quantum Theory

For a long time in the past, people knew that despite appearing continuous, matter has a definite structure on a microscope scale. They also knew that this microscopic structure was beyond the reach of their direct senses. However in the past one century and a half, the existence of atoms and molecules and their own constitutent particles - the electrons, protons, neutrons etc., have been identified and studied.

Every atom consists of a small nucleus containing protons and neutrons and a few number of electrons circling the nucleus at some distance from it. It is tempting to think that the electrons circle the nucleus as do the planets around the sun. But the classical electromagnetic theory denies this possibility. It tells that an electron - a charged particle, on orbiting (that is following a circular path) will radiate and loose its energy. Hence instead of the path being a stable orbit, will be a spiralling trajectory of successively decreasing radius that embeds the electron directly into the nucleus. Therefore an atom as an entity will be highly unstable and hence will not exist.

It is in order to resolve this paradox that Neils Bohr proposed in 1913 the quantum structure of the Hydrogen atom. His theory was entirely empirical in nature. He assumed that

- the electrons revolve around the nucleus in certain *non-radiating* orbits, having an angular momentum in integral multiples of $\hbar$, that is $L = n\hbar$.

- the electrons in making a transition from a higher orbit to a lower orbit will emit an emission spectral line. Similarly the electrons in making a transition from a lower orbit to a higher orbit will emit an absorption spectral line.

Using these ideas, Bohr was able to account for all the spectral series known at that time, namely Lymann, Balmer, Paschen, Brackett and Pfund series of Hydrogen atom. This theory of the atomic structure of Hydrogen is now known as the *Old Quantum* theory.

1.2   Inadequacy of the Old Quantum Theory

Though Bohr's theory accounts for many aspects of atomic phenomena such as stability of the atoms, atomic spectra etc., has severe limitations as well.

1. It applies to Hydrogen and Hydrogen-like atoms (that is one electron atoms such as the He^+ ion, Li^{2+} ion $\cdots$). It does not explain even an ordinary Helium atom.

2. It does not explain why certain spectral lines are more intense than others, that is why transitions between certain energy levels have more probability of occurrence than others.

3. It does not account for the hyperfine structure of spectral lines, that is why many spectral lines on observing through high resolution spectroscopes are made up of several closely spaced spectral lines.

4. It does not help us understand how individual atoms interact with each other to endow macroscopic aggregates with the physical and chemical properties we observe.

1.3   Wavefunction ψ

The quantum theory of light developed by Max Planck and Albert Einstein in 1905 established the particulate properties of light waves (that is the particle nature of light or corpuscular nature of light). In 1924 Louis de Broglie speculated that material particles have a wave like nature and that this wave nature is imperciptible to us because of the smallness of the Planck's constant $h = 6.626 \times 10^{-34}$Joules seconds. This wave particle duality was the starting point for Shcröedinger's development of new *Quantum Mechanics* or *Wave Mechanics*.

If matter were to behave as a wave then, Schröedinger reasoned out that this matter wave should be describable mathematically by a wave equation in terms of a variable quantity. In water waves the quantity that varies is the height of the water surface from the bottom. In sound waves, its the pressure that varies. In light waves, it's the intensities of the electric and magnetic fields that vary.

The quantity whose variations that make up the matter waves is an unknown one. Hence Schröedinger called this unknown function of a wave as a *wave function* and denoted it by the Greek letter ψ. Later on the value of this wave function ψ associated with a moving particle at a particular point x, y, z in space at an instant t of time, was related to the likelihood (probability) of locating the particle at that point in space at that particular instant of time. Thus this wave function is not a real quantity but has a probabilistic nature.

1.4   Schröedinger's Time Dependent Wave Equation

Let us derive, as a simple case, the Schröedinger's time dependent wave equation for a free particle in one dimension and then extend it to three dimensions. Then let us derive the wave equation for a bound particle using the correspondance principle.

1.4.1   Schröedinger's Time Dependent Wave Equation for a Free Particle in One Dimension

Let us consider a free particle moving with a velocity v, momentum p and energy E along the positive direction of the $x - axis$.

Note: A particle is free if it has no forces acting on it or that its potential energy is zero. In such a case, the total energy of the particle will be purely kinetic in nature.

Then the momentum and energy of the particle can be given as

$$E = \frac{m}{m}\left(\frac{1}{2}mv^2\right)$$

$$= \frac{(mv)^2}{2m}$$

$$= \frac{p^2}{2m}$$

$$p = mv \qquad (1.1)$$

$$E = \frac{1}{2}mv^2 \qquad (1.2)$$

Comparing the above two Eqns. gives

$$E = \frac{p^2}{2m} \qquad (1.3)$$

According to de Broglie hypothesis, this free particle will have associated with it, a harmonic wave of propagation constant k and angular frequency ω such that

$$p = \frac{h}{\lambda}, \left(\frac{h}{2\pi}\right)\left(\frac{2\pi}{\lambda}\right)$$

$$= \hbar k,$$

$$E = h\nu, \left(\frac{h}{2\pi}\right)2\pi\nu$$

$$= \hbar \omega$$

$$p = \hbar k \qquad (1.4)$$

$$E = \hbar \omega \qquad (1.5)$$

Substituting the above two equations in Eqn. (1.3) gives

$$\hbar \omega = \frac{\hbar^2 k^2}{2m}. \qquad (1.6)$$

The matter wave associated with the free particle can be given as a linear combination of harmonic terms, say $\cos(kx - \omega t)$ and $\sin(kx - \omega t)$, that is

$$\psi(x, t) = a\cos(kx - \omega t) + b\sin(kx - \omega t). \qquad (1.7)$$

Here a and b are arbitrary constants that are to be determined.

Our aim is to derive an equation that will describe the temporal and spatial advancement of the harmonic wave as the particle moves. Hence we differentiate $\psi(x, t)$ with respect

to space and time. Thus we have

$$\frac{\partial \psi}{\partial x} = k\left[-a\sin\left(kx - \omega t\right) + b\cos\left(kx - \omega t\right)\right] \tag{1.8}$$

$$\frac{\partial^2 \psi}{\partial x^2} = -k^2\left[a\cos\left(kx - \omega t\right) + b\sin\left(kx - \omega t\right)\right], \quad \text{or} \tag{1.9}$$

$$\frac{\partial^2 \psi}{\partial x^2} = -k^2\psi \tag{1.10}$$

$$\frac{\partial \psi}{\partial t} = -\omega\left[-a\sin\left(kx - \omega t\right) + b\cos\left(kx - \omega t\right)\right] \tag{1.11}$$

$$\frac{\partial^2 \psi}{\partial t^2} = -\omega^2\left[a\cos\left(kx - \omega t\right) + b\sin\left(kx - \omega t\right)\right], \quad \text{or} \tag{1.12}$$

$$\frac{\partial^2 \psi}{\partial t^2} = -\omega^2\psi \tag{1.13}$$

The desired wave equation can be constructed by

- equating the first order space derivative of ψ, with its first order time derivative, that is that is $\frac{\partial \psi}{\partial x} = \frac{\partial \psi}{\partial t}$ or

- equating the second order space derivative of ψ, with its second order time derivative, that is $\frac{\partial^2 \psi}{\partial x^2} = \frac{\partial^2 \psi}{\partial t^2}$ or

- a cross combination of these, that is equating the first order space derivative with the second order time derivative, $\frac{\partial \psi}{\partial x} = \frac{\partial^2 \psi}{\partial t^2}$ or

- equating first order time derivative with the second order space derivative, that is $\frac{\partial \psi}{\partial t} = \frac{\partial^2 \psi}{\partial x^2}$

Out of these four possibilities, the first three are ruled out based on what are called as the *admissibiliy conditions*. Hence the desired wave equation should be

$$\frac{\partial \psi}{\partial t} = \frac{\omega}{k^2}\left(\frac{\partial^2 \psi}{\partial x^2}\right). \tag{1.14}$$

If Eqn. (1.14) is to be satisfied mathematically, then we require the ratio of the coefficients of the cosine terms to be equal to the ratio of the coefficients of the sine terms, that is

$$\frac{a}{b} = -\frac{b}{a} \quad \text{or}$$

$$b^2 = -a^2 \quad \text{or}$$

$$b = \pm ia. \tag{1.15}$$

Proof:

Dividing the first order time derivative of ψ with its second order space derivative using the above equations and rearranging gives

$$\frac{-\left(\frac{1}{\omega}\right)\frac{\partial\psi}{\partial t}}{-\left(\frac{1}{k^2}\right)\frac{\partial^2\psi}{\partial x^2}} = \frac{\left[-a\sin\left(kx-\omega t\right)+b\cos\left(kx-\omega t\right)\right]}{\left[a\cos\left(kx-\omega t\right)+b\sin\left(kx-\omega t\right)\right]},$$

$$= \frac{b\left[-\left(\frac{a}{b}\right)\sin\left(kx-\omega t\right)+\cos\left(kx-\omega t\right)\right]}{b\left[\left(\frac{a}{b}\right)\cos\left(kx-\omega t\right)+\sin\left(kx-\omega t\right)\right]},$$

If the RHS is to be unity, we require the coefficients of the sine and cosine terms in both the numerator and denominator of the RHS to be same, that is

$$\frac{-a}{b} = 1,$$

$$\frac{b}{a} = 1, \qquad \text{or}$$

$$\left(\frac{-a}{b}\right) = \left(\frac{b}{a}\right), \qquad \text{or}$$

$$b^2 = -a^2. \qquad \text{or}$$

In that case we have

$$\frac{-\left(\frac{1}{\omega}\right)\frac{\partial\psi}{\partial t}}{-\left(\frac{1}{k^2}\right)\frac{\partial^2\psi}{\partial x^2}} = 1,$$

or

$$\frac{\partial\psi}{\partial t} = \frac{\omega}{k^2}\left(\frac{\partial^2\psi}{\partial x^2}\right).$$

Hence the proof.

Substituting the coefficients given by the Eqn. (1.15) in Eqn. (1.7), gives

$$\psi(x,t) = a\left[\cos\left(kx-\omega t\right)\pm i\sin\left(kx-\omega t\right)\right], \tag{1.16}$$

or

$$\psi(x,t) = ae^{\pm i(kx-\omega t)}. \tag{1.17}$$

The equation (1.17) tells that the matter waves for a particle of momentum p are to be represented by a complex harmonic function of x and t. The positive sign for the exponent denotes an outgoing wave, while the negative sign for the exponent denotes an incoming wave. As we have assumed the particle to move along the positive direction of the $x-axis$, Eqn. (1.17) can be rewritten as

$$\psi(x,t) = ae^{+i(kx-\omega t)}. \tag{1.18}$$

Differentiating the Eqn. (1.18) with respect to time t, gives

$$\frac{\partial \psi}{\partial t} = -i\omega\psi. \tag{1.19}$$

Similarly differenting the Eqn. (1.18) twice with respect to position x,

$$\frac{\partial^2 \psi}{\partial x^2} = -k^2\psi. \tag{1.20}$$

Multiplying Eqn. (1.19) by $i\hbar$ gives

$$i\hbar\frac{\partial \psi}{\partial t} = \hbar\omega\psi. \tag{1.21}$$

Similarly multiplying Eqn. (1.20) by $-\left(\frac{\hbar^2}{2m}\right)$ gives

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2 \psi}{\partial x^2}\right) = \frac{\hbar^2 k^2}{2m}\psi. \tag{1.22}$$

Substituting Eqn. (1.6) in Eqn. (1.22) gives

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2 \psi}{\partial x^2}\right) = \hbar\omega\psi. \tag{1.23}$$

Comparing Eqns. (1.21) and (1.23) gives

$$\boxed{i\hbar\frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2 \psi}{\partial x^2}\right).} \tag{1.24}$$

The Eqn. (1.24) is the required Schröedinger's equation for a free particle in one dimension.

Note:

- The Schröedinger's equation is a linear homogenous equation obeying the linear superposition principle. This means that not only $\psi(x,t) = ae^{i(kx-\omega t)}$ a solution but any linear combination of these is also a solution of the wave equation, that is,

$$\psi(x,t) = \int a(k)e^{i(kx-\omega t)}dk. \tag{1.25}$$

- The Schröedinger's equation is different from other differential equations of classical physics in that it is a complex function of harmonic terms.

1.4.2 Extension to Three Dimensions

In three dimensions, the energy-momentum relation is given as

$$
\begin{aligned}
E &= \frac{p^2}{2m} \quad \text{or} \\
E &= \frac{1}{2m}\left(p_x^2 + p_y^2 + p_z^2\right) \quad \text{or} \\
E &= \frac{-\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)
\end{aligned}
\tag{1.26}
$$

where p_x, p_y and p_z are the components of the momentum p along the three directions x, y and z. Therefore the free particle wave equation can be extended to three dimensional case as

$$
i\hbar\frac{\partial \psi(r,t)}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\psi(r,t).
\tag{1.27}
$$

whose solution can be given as

$$
\psi(r,t) = ae^{i(kr-\omega t)}.
\tag{1.28}
$$

Note: As in case of one dimension, the linear superposition of harmonic waves in three dimensions is given as

$$
\psi(r,t) = \int a(k)e^{i(kr-\omega t)}dk.
\tag{1.29}
$$

1.4.3 Schröedinger's Time Dependent Wave Equation for a Bound Particle

We have seen that a particle is said to be *free* if no forces are acting on the particle, that is if the potential energy of the particle is zero, $(V(r,t)=0)$. Now let us consider the case of a particle acted upon by some forces. We know that any external force acting on a particle is related to its potential energy as $F = -\nabla V$, that is the negative gradient of the potential energy $V(r,t)$ equals the force F. The total energy of the particle will now be a sum of its kinetic energy E as well as its potential energy $V(r,t)$, that is

$$
\mathcal{E} = E + V(r,t).
\tag{1.30}
$$

In quantum mechanics, we consider any measurable quantity as an observable which can be represented by quantum mechanical operators. Thus for momentum the operator is $\hat{p} = -i\hbar\nabla$, for kinetic energy it is $\hat{E} = \frac{-\hbar^2}{2m}\nabla^2$, for potential energy it is $\hat{V}(r,t)$ and for

the total energy the operator is given as $\mathcal{E} = \frac{-\hbar^2}{2m}\nabla^2 + \hat{V}(r,t)$. Allowing these operators to act upon the particle in a particular state $\psi(r,t)$, the Schröedinger's equation for a bound particle can be given as

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

or

$$i\hbar\frac{\partial\psi(r,t)}{\partial t} = \left[-\frac{\hbar^2}{2m}\nabla^2 + V(r,t)\right]\psi(r,t). \tag{1.31}$$

The equation 1.31 is the Schröedinger equation for a bound particle moving in three dimensions.

1.4.4 Validity of the Schröedinger's Wave Equation

The Schröedinger's Wave Equation, just like Newton's laws of motion, is a basic principle in itself. It cannot be derived from any other principles of Physics.

To test the validity of this equation, we solve it for a variety of physical problems and compare the results of calculations with the results of experiments. If both are in agreement, then we can consider the Schröedinger's Wave Equation to be valid in the range of applicability by virtue of the agreement with experimental results.

1.5 The Bohr's Correspondance Principle

By assigning operators to physical quantities and allowing them to act upon quantum states, the quantum mechanical relationships can be made to correspond to classical relationships. This is known as the *Correspondance Principle* and was first given by Neils Bohr.

> *Note:* The correspondance principle does not mean that the classical relation $E = \left(\frac{p^2}{2m}\right)$, implies an operator identity $i\frac{\partial}{\partial t} = \frac{-\hbar^2}{2m}\nabla^2$. Rather the correspondance principle can be realized only when the operators are allowed to act upon quantum states.

Chapter 2

Physical Interpretation of Wave Function

2.1 Physical Interpretation of the Wave Function ψ

We have seen that the motion of a free particle or a bound particle can be studied using Schröedinger's wave equation. As this is a second order differential equation, it has infinite number of possible solutions as per mathematical theory. However all of these solutions do not describe the actual behaviour of the particle. Only a few solutions, satisfying the *admissibility conditions*, can successfully explain the behaviour of the particle. This leads us to the *physical interpretation* or the *probabilistic interpretation* or *statistical interpretation* of the wave function ψ.

2.1.1 Normalization and Probability Interpretation of the Wave Function ψ

The wave function ψ, which is the solution of the Schröedinger's wave equation has no physical relevance. This is because it is a complex quantity. However the square of its absolute magnitude $|\psi(r,t)|^2$ evaluated at a particular point in space at a particular time is to be taken as the measure of the probability $P(r,t)$ of finding the particle at that point is space at that instant of time, that is

$$P(r,t) = |\psi|^2. \tag{2.1}$$

As the total probability of finding the particle somewhere in space is unity, we require

$$\int P(r,t)d\tau = 1, \tag{2.2}$$

or

$$\int |\psi(r,t)|^2 dr = 1, \tag{2.3}$$

$$\int \psi^*(r,t)\psi(r,t)d\tau = 1. \tag{2.4}$$

Hence the wave function $\psi(r,t)$ determines the corpuscular characteristics like position, momentum (angular and linear), charge density etc., in a statistical sense. This is known as the *Probabilistic Interpretation* of wave functions and was first given by Max Born.

2.1.2 Normalization Constant and Normalized Wave Functions

Let $\psi(r,t)$ be a wave function representing the motion of a particle. Let

$$\int |\psi(r,t)|^2 d\tau = N. \tag{2.5}$$

As $\psi(r,t)$ is a complex function, the square of its absolute magnitude should always be a real and positive quantity. This means N should be a real and positive number. This number is called as the *Normalization Costant* or *Norm* of the wave function.

A wave function whose norm is unity, that is $N = 1$, is called as a *Normalized Wave Function*. On the other hand if the normalization constant of a wave function is not unity, that is if $N \neq 1$, then it is called as an *unnormalized wave function*.

2.1.3 Normalization Procedure

Any unnormalized wave function, that is a wave function whose norm is not equal to unity can be normalized by a process called as *Normalization Procedure*. This is based on the *Linear Superposition Principle*.

Let us consider the $\psi'(r,t)$ be a solution of the Schröedinger wave equation describing the motion of a particle. Let

$$\int |\psi'(r,t)|^2 d\tau = N. \tag{2.6}$$

Let us now define a new wave function $\psi(r,t)$ such that

$$\psi(r,t) = \frac{1}{\sqrt{N}}\psi'(r,t). \tag{2.7}$$

As the Schröedinger wave equation is a linear second order differential equation, its solution $\psi'(r,t)$ should obey the *Linear Superposition Principle*. As $\psi(r,t)$ differs from $\psi'(r,t)$ only by a constant factor $\frac{1}{\sqrt{N}}$, by the linear superposition principle, $\psi(r,t)$ should also be a solution of the same Schröedinger equation. Taking the square of the absolute values of the quantities on both sides of Eqn. (2.7) and integrating them over the whole space gives

$$\int |\psi(r,t)|^2 d\tau = \frac{1}{N}\left\{\int |\psi'(r,t)|^2 d\tau\right\}. \tag{2.8}$$

Substituting Eqn. (2.6) in Eqn. (2.8) gives

$$\int |\psi(r,t)|^2 d\tau = \frac{1}{N}\{N\} \qquad \text{or}$$

$$\int |\psi(r,t)|^2 d\tau = 1. \tag{2.9}$$

The Eqn. (2.9) tells that the normalization constant of the wave function $\psi(r,t)$ is unity, that is $N = 1$. Hence it is a normalized wave function.

Note-1: The Eqn. (2.9) makes sense only if the normalization constant is a finite quantity. This finiteness of the normalization constant implies that

$$\psi(r,t) \longrightarrow 0, \qquad \text{as} \qquad r \longrightarrow \infty.$$

This is a boundary condition applicable to all wave functions.

Note-2: If Eqn. (2.9) is to be valid the integral on the Left Hand Side has to be the same at all times.

The motivation for normalizing a given wave function, arises from probability considerations. We know that unlike as in Classical Mechanics, the precise position of a particle cannot be defined. We can only say that there is a certain probability that the particle is likely to be found within a particular specified volume element. This propability of occurrence is given as $P(r,t) = |\psi(r,t)|^2$. Since the particle is sure to be found some where in space, the total probability should always be unity, that is $\mathcal{P} = \int P(r,t)dt = \int |\psi(r,t)|^2 d\tau = 1$ or $\mathcal{P} = 1$. This is the real meaning and probability interpretation of the Eqn. (2.9).

Example Problem 1:

   A particle limited to the $(x-axis)$ has a wave function given as $\psi = ax$ between $x = 0$ and $x = 1$ and $\psi = 0$ elsewhere. Find the probability for locating the particle in the range $0.45 < x < 0.55$.

Solution:

The wave function is given as

$$\psi(x,t) = \begin{cases} ax & \text{for} \quad 0 < x < 1 \\ 0 & \text{for} \quad x < 0, x > 1 \end{cases}$$

The probability is defined as

$$\mathcal{P}(r,t) = \int_{x_1}^{x_2} |\psi(x,t)|^2 dx$$

Substituting for $\psi(x,t)$ and simplifying the equation gives

$$\mathcal{P}(r,t) = a^2 \int_{0.45}^{0.55} x^2 dx$$

$$= a^2 \left[\frac{x^3}{3} \right]_{0.45}^{0.55}$$

$$= 0.0251 \, a^2.$$

Example Problem 2:

Normalize the wave function

$$\psi'(x,t) = e^{-|x|} \sin \alpha x, \qquad x > 0.$$

Hint: The wave function has the explicit form

$$\psi(x,t) = \begin{cases} e^{x} \sin \alpha x, & x < 0 \\ e^{-x} \sin \alpha x, & x > 0 \end{cases}$$

Answer: The normalization constant is

$$N = \sqrt{\frac{\alpha^2}{2(1+\alpha^2)}}$$

Hence the normalized wave function is

$$\psi(x,t) = \sqrt{\frac{2(1+\alpha^2)}{\alpha^2}} e^{-|x|} \sin \alpha x.$$

Example 3:

If a particle has a wave function given as

$$\psi'(x,t) = e^{-|x|} \sin \alpha x, \qquad x > 0.$$

what will be the probability of finding the particle to the right of $x = 1$?

Answer :

$$\int_1^\infty |\psi(x,t)|^2 dx = \frac{e^{-2}}{2\,\alpha^2}\left[1 + \alpha^2 - \cos\,2\alpha + \alpha\sin\,2\alpha\right].$$

2.1.4   Box Normalization

The condition for normalization is

$$\int |\psi(r,t)|^2 d\tau = 1. \tag{2.10}$$

This equation is satisfied only if the integral itself is not infinte. The wave functions whose integrals over the whole space are not finite are called as *un-normalizable wave functions.*

The un-normalizable wave functions can be handled and visualized clearly by a procedure called **Box Normalization**. Let us imagine a partilce is confined to a box. Let the norm of the wave function is defined as the integral of $|\psi(r,t)|^2$ taken over the box only. This causes the norm to take on a finite value. Making use of the usual normalization process, the wave function can be normalized. Then the integral can be extended to cover all space by increasing the volume of the box to infinity. This procedure is called as the *Box Normalization.*

For example let us consider a particle of definite momentum be confined to a box of dimension L. Then the probability of locating the particles is given by

$$\mathcal{P}(r,t) = \int\!\!\!\int\!\!\!\int_{-\frac{1}{2}L}^{+\frac{1}{2}L} |\psi(r,t)|^2\,dx\,dy\,dz. \tag{2.11}$$

Let the momentum wave functions of the particles be given as

$$\psi_k(r,t) = ae^{i(k\,r-\omega\,t)}. \tag{2.12}$$

Then at some initial time $t = 0$

$$\psi_k(r,0) = ae^{ik\,r}, \tag{2.13}$$

where we assume $a = \frac{1}{L^{3/2}}$. Then the probability of locating the particle in the box is

$$
\begin{aligned}
\mathcal{P}(r,t) &= \int\!\!\!\int\!\!\!\int_{-\frac{1}{2}L}^{+\frac{1}{2}L} \left| \left(\frac{1}{L}\right)^{3/2} e^{i\vec{k}.\vec{r}} \right|^2 dx\,dy\,dz, \\
&= \frac{1}{L^3} \left\{ \int\!\!\!\int\!\!\!\int_{-\frac{1}{2}L}^{+\frac{1}{2}L} dx\,dy\,dz \right\}, \qquad \text{since} \qquad |e^{i(\vec{k}.\vec{r})}| = 1 \\
&= \frac{1}{L^3} \left\{ L^3 \right\}, \qquad \text{or}
\end{aligned}
$$

$$
\mathcal{P}(r,t) = 1. \tag{2.14}
$$

2.1.5 Quantization Condition for Momentum Values

In the preceding section refering Eqn. (2.13) and assumuing $a = \frac{1}{L^{3/2}}$ we obtain the momentum wave function to have the form

$$
\psi_k(r,0) = \left(\frac{1}{L^{3/2}}\right) e^{ik\,r}, \tag{2.15}
$$

This means it can be split explicitly in three dimensions as

$$
\psi_k(r,0) = \left(\frac{1}{L^{3/2}}\right) \left\{ e^{i(k_x\,x + k_y\,y + k_z\,z)} \right\}. \tag{2.16}
$$

The Eqn. (2.16) tells that for the integral of this momentum wave function over the volume of the box to be unity, we require the wave function to be periodic with respect to the size of the box. This means that if x, y or z were to be increased by L, the wave function should remain unchanged. This is possible only if

$$
e^{ik_x\,L} = e^{ik_y\,L} = e^{ik_z\,L} = 1.
$$

Here $e^{ik_x\,L} = \cos(k_x\,L) + i\sin(k_x\,L)$

If $e^{ik_x\,L} = 1$, then we should have $\cos(k_x\,L) = 1$ and $\sin(k_x\,L) = 0$.

This will be possible only if $k_x L = 2\pi$ or $k_x = \left(\frac{2\pi}{L}\right)$

Hence in general we require k_x, k_y and k_z to be integral multiples of $\left(\frac{2\pi}{L}\right)$ or

$$
k_i = n_i \left(\frac{2\pi}{L}\right), \qquad \text{where} \qquad n_i = 0, \pm 1, \pm 2 \cdots \qquad \text{and} \qquad i = x, y, z \tag{2.17}
$$

The above condition (2.17) gives the quantization rule or the admissibility condition for the momentum wave functions.

Chapter 3

Conservation of Probability: Equation of Continuity

3.1 Introduction

In this chapter we will be seeing the concept of conservation of probability density which results in the equation of continuity. The equation of continuity arises in any theory in which an extensive quantity such as mass, charge or heat energy is known to satisfy a law of conservation. In quantum dynamics it is given mathematically as

$$\frac{\partial \vec{\mathcal{P}}}{\partial t} + \nabla.\vec{S} = 0.$$

where $\vec{\mathcal{P}}$ denotes probability density and $\vec{S}$ denotes the probability current density for a system of particles.

3.2 Conservation of Probability

According to the probability interpretation of the wave functions, we have

$$\int |\psi(r,t)|^2 d\tau = 1. \tag{3.1}$$

This equation (3.1) says that the particle is sure to be found some where in space. As long as the particle is stable and does not decay or disappear, Eqn. (3.1) will be true always. This means that the total probability must be time independent and the

derivative of this probability with time should be zero, that is

$$\frac{\partial}{\partial t}\mathcal{P}(r,t) = 0, \qquad \text{or} \qquad \frac{\partial}{\partial t}\int |\psi(r,t)|^2 d\tau = 0 \qquad \text{or} \qquad \frac{\partial}{\partial t}\int \psi^*\psi d\tau = 0.$$

This is known as the *Law of Conservation of Probability Density.*

Proof:

We know that

$$|\psi|^2 \;\; = \;\; \psi^*\psi \qquad \text{or}$$

$$\frac{\partial}{\partial t}|\psi|^2 \;\; = \;\; \frac{\partial}{\partial t}(\psi^*\psi) \qquad \text{or}$$

$$\frac{\partial}{\partial t}|\psi|^2 \;\; = \;\; \psi^*\left(\frac{\partial \psi}{\partial t}\right) + \left(\frac{\partial \psi^*}{\partial t}\right)\psi. \tag{3.2}$$

From the Schröedinger's equation we have

$$\frac{\partial \psi}{\partial t} = \frac{1}{i\hbar}\left\{-\frac{\hbar^2}{2m}\nabla^2 + V(r,t)\right\}\psi \tag{3.3}$$

Taking the complex conjugate of Eqn. (3.3), gives

$$\frac{\partial \psi^*}{\partial t} = -\frac{1}{i\hbar}\left\{-\frac{\hbar^2}{2m}\nabla^2 + V(r,t)\right\}\psi^* \tag{3.4}$$

Pre-multiplying Eqn. (3.3) by ψ^*, gives

$$\psi^*\left(\frac{\partial \psi}{\partial t}\right) = \frac{1}{i\hbar}\left\{-\frac{\hbar^2}{2m}\psi^*\nabla^2\psi + \psi^*V\psi\right\}. \tag{3.5}$$

Post-multiplying Eqn. (3.4) by ψ, gives

$$\left(\frac{\partial \psi^*}{\partial t}\right)\psi = -\frac{1}{i\hbar}\left\{-\frac{\hbar^2}{2m}\left(\nabla^2\psi\right)\psi + (V\psi^*)\psi\right\} \tag{3.6}$$

Substituting Eqns. (3.5) & (3.6) in (3.2) gives

$$\frac{\partial}{\partial t}|\psi|^2 = \frac{1}{i\hbar}\left\{-\frac{\hbar^2}{2m}\left[\psi^*\left(\nabla^2\psi\right) - \left(\nabla^2\psi^*\right)\psi\right]\right\}, \tag{3.7}$$

$$\text{since} \qquad \psi^*V(r,t)\psi = (V(r,t)\psi^*)\,\psi.$$

3.3   Equation of Continuity

Rearranging Eqn. (3.7) gives

$$\frac{\partial}{\partial t}|\psi|^2 = \frac{i\hbar}{2m}\nabla.\left[\psi^*\left(\nabla\psi\right)-\left(\nabla\psi^*\right)\psi\right].$$
$$(3.8)$$

Let

$$\mathcal{P}(r,t) = |\psi|^2$$
$$(3.9)$$

and

$$\mathcal{S}(r,t) = -\frac{i\hbar}{2m}\left[\psi^*\left(\nabla\psi\right)-\left(\nabla\psi^*\right)\psi\right].$$
$$(3.10)$$

Proof:

Let us assume that the probability current density $\mathcal{S}(r,t)$ to be given as

$$
\begin{aligned}
\mathcal{S}(r,t) &= -\frac{i\hbar}{2m}\left[\psi^*\left(\nabla\psi\right)-\left(\nabla\psi^*\right)\psi\right]\\
&= \frac{1}{2m}\left[\psi^*\left(-i\hbar\nabla\right)\psi-\left(-i\hbar\nabla\psi^*\right)\psi\right]\\
&= \frac{1}{2m}\left[\psi^*\left(\vec{p}\,\psi\right)-\left(\vec{p}\psi^*\right)\psi\right] \qquad \text{as} \qquad \vec{p}=\left(-i\hbar\nabla\right)\\
&= \frac{1}{2m}\,2\,Real\,\left[\psi^*\vec{p}\,\psi\right]\\
&= Real\left[\psi^*\left(\frac{\vec{p}}{m}\right)\psi\right]\\
&= Real\left[\psi^*\vec{v}\,\psi\right] \qquad \text{since} \qquad \vec{v}\longrightarrow\left(\frac{p}{m}\right)\\
&= \int \psi^*\vec{v}\,\psi d\tau \qquad \text{or}\\
\mathcal{S}(r,t) &= \rho\vec{v}, \qquad \text{since} \int \psi^*\psi d\tau \longrightarrow \rho \longrightarrow 1.
\end{aligned}
$$

The quantity ρ is to be assumed as the particle denisty and its product with $\vec{v}$ is to be assumed as the *probability current density*, $\mathcal{S}(r,t) = \rho\vec{v}$.

Substituting Eqns. (3.9) and (3.10) in Eqn. (3.8) gives

$$\frac{\partial\mathcal{P}}{\partial t} = -\nabla.\mathcal{S}$$

or

$$\boxed{\frac{\partial\mathcal{P}}{\partial t} + \nabla.\mathcal{S} = 0}.$$
$$(3.11)$$

This Eqn. (3.11) is called as the *Equation of Continuity* in quantum dynamics. This equation tells that there is no creation of destruction of probability densities. Any

increase or decrease in the probability density $\mathcal{P}$ of finding a particle inside a closed volume V, should be compensated by a corresponding decrease or increase elsewhere through an inflow or outflow of the probability current $\vec{S}$ across the boundary of the volume V.

3.4 Law of Conservation of Probability from the Equation of Continuity

Integrating Eqn. (3.11) with respect to the whole space gives

$$\frac{\partial}{\partial t} \int_{\tau} \mathcal{P} d\tau = - \int_{\tau} \nabla.\mathcal{S} d\tau. \tag{3.12}$$

Using the Gauss Divergence theorem, we have

$$\int_{\tau} \nabla.\mathcal{S} d\tau = \int_{\sigma} \mathcal{S}.\hat{n}.d\sigma \tag{3.13}$$

or

$$\frac{\partial}{\partial t} \int_{\tau} \mathcal{P} d\tau = - \int_{\sigma} \mathcal{S}.\hat{n}.d\sigma \tag{3.14}$$

As the volume integral on the left hand side (LHS) is with respect to whole space, the surface σ should lie at infinity. But according to boundary conditions, ψ and $\nabla\psi \longrightarrow 0$ as $r \longrightarrow \pm\infty$. Hence $\int_{\sigma} \mathcal{S}.\hat{n}d\sigma = 0$. Therefore

$$\frac{\partial}{\partial t} \int_{\tau} \mathcal{P}(r,t) d\tau = 0, \tag{3.15}$$

or

$$\frac{\partial}{\partial t} \int_{\tau} \left(\psi^*\psi\right) d\tau = 0. \tag{3.16}$$

The above equation (3.16) tells that the total probability of locating a particle in the whole space must be conserved. This is the mathematical statement of the *Law of Conservation of Probability.*

Equation of Continuity

The equation of continuity arises in any theory in which an extensive quantity such as mass, charge or heat energy is known to satisfy a law of conservation. Mathematically it is given as

$$\frac{\partial \vec{\rho}}{\partial t} + \nabla . \vec{S} = 0.$$

Here if we assume ρ as the density of an incompressible fluid and $\vec{S} = \vec{\rho} v$ as the current of fluid crossing unit area normal to the direction of the fluid velocity v, then the above equation can be assumed as the equation of continuity in fluid dynamics. It tells that the total amount of fluid contained in a small fixed volume element is a constant with respect to time. However if there arises an increase or decrease in the total amount of fluid in the volume element, then it has to be accounted as due to a nett inflow or outflow of fluid across the surface enclosing the volume element.

Similarly the above equation can also be considered as the equation of continuity in electrodynamics. If we assume ρ as charge density and $J = nev$ as the charge current density, then

$$\frac{\partial \vec{\rho}}{\partial t} + \nabla . \vec{J} = 0.$$

This equation tells us that the total charge in a given volume element is a conserved quantity. If at all there is any change in the charge density ρ then it has to be accounted for as arising due to either an inflow or outflow of charges across the surface enclosing the volume element.

Chapter 4

Expectation Values:Ehrenfest's Theorem

4.1 Expectation Values

Let us consider a large number of measurements of a dynamical variable, say $\hat{A}$ are made on a system which is prepared to be in the same state ψ before each measurement. The results of these individual measurements may in general be different from each other. However the average of all the observed values is expected to be given as

$$
\begin{aligned}
< \hat{A} >_{\psi} &= \int \psi^* \hat{A} \psi d\tau \\
&\equiv \ < \psi, \hat{A}\psi >
\end{aligned}
\tag{4.1}
$$

The quantity $< \hat{A} >_{\psi}$ is known as the *expectation value* of the dynamical variable $\hat{A}$. It is integral of all possible results A, weighted by the function $|\psi|^2$. Therefore it is the weighted average of all possible measurements of $\hat{A}$. If the wave function ψ is not normalized, then the expectation value is given as

$$
< \hat{A} >_{\psi} = \frac{\int \psi^* \hat{A} \psi d\tau}{\int \psi^* \psi d\tau}
\tag{4.2}
$$

For example the expectation values of position and momentum etc., are given as

$$
< \hat{x} > \ = \ \int \psi^* \left(\hat{x}\psi \right) d\tau
\tag{4.3}
$$

$$
< \hat{p_x} > \ = \ \int \psi^* \left(-i\hbar \frac{\partial}{\partial x} \psi \right) d\tau
\tag{4.4}
$$

$$
< \hat{p} > \ = \ \int \psi^* \left(-i\hbar \nabla \psi \right) d\tau
\tag{4.5}
$$

> *Note:*
>
> The expectation value may be a real or complex quantity. However in quantum mechanical context, only those dynamical variables whose expectation values are real should be considered as directly measurable or observable quantities.

Problem:

The wave function for a particle is given as $\psi = \left(\frac{1}{\pi a^3}\right)^{1/2} . e^{-r/a}$, where a is a constant. Evaluate the expectation of $\hat{r}$, that is $< \hat{r} >$.

Solution:

Let

$$
\begin{aligned}
< \hat{r} > \ &= \ \int \psi^* \hat{r} \psi d\tau \\[2mm]
&= \ \int \left\{ \left(\frac{1}{\pi a^3}\right)^{1/2} e^{-r/a} \right\}^* \hat{r} \left\{ \left(\frac{1}{\pi a^3}\right)^{1/2} e^{-r/a} \right\} d\tau \\[2mm]
&= \ \left(\frac{1}{\pi a^3}\right) \int \hat{r} e^{-2r/a} d\tau
\end{aligned}
$$

$$
\begin{aligned}
&= \ \left(\frac{1}{\pi a^3}\right) \int_0^\infty \int_0^\pi \int_0^{2\pi} \hat{r} e^{-2r/a} \, r^2 \, \sin(\theta) \, dr \, d\theta \, d\phi \qquad \text{since} \\[2mm]
&\qquad d\tau \Longrightarrow r^2 \, \sin(\theta) \, dr \, d\theta \, d\phi \\[2mm]
&= \ \left(\frac{1}{\pi a^3}\right) \int_0^\infty r^3 \, e^{-2r/a} \, dr \, \int_0^\pi \sin(\theta) \, d\theta \, \int_0^{2\pi} d\phi \\[2mm]
< \hat{r} > \ &= \ (3a/2)
\end{aligned}
$$

> Integrating the azimuthal angle ϕ part $\Longrightarrow \int_0^{2\pi} d\phi = [\phi]_0^{2\pi} = 2\pi$

Let $p = \cos(\theta)$, then $dp = -\sin(\theta) \, d\theta$

If $\theta \longrightarrow 0, p \longrightarrow +1$ while if $\theta \longrightarrow \pi, p \longrightarrow -1$

> Therefore the integral for the orbital angle θ can be written as
>
> $\int_0^\pi \sin(\theta) \, d\theta = -\int_{+1}^{-1} dp$ or $\int_{-1}^{+1} dp = [p]_{-1}^{+1} = 2.$

We know from the theory of Laplace Transforms, $\int_0^\infty t^n \, e^{-st} \, dt = \frac{n!}{s^{n+1}}$. Let $t = r$, $n = 3$ and $s = 2/a$.

Then the integral in r can be written as $\int_0^\infty t^n \, e^{-st} \, dt = \int_0^\infty r^3 \, e^{-2r/a} \, dr = \frac{3!}{(2/a)^4}$

Therefore the expectation value of $\hat{r}$ is

$$
\begin{aligned}
<\hat{r}> \;&=\; \left(\frac{1}{\pi a^3}\right) \times \frac{3!}{(2/a)^4} \times 2 \times 2\pi \\
&=\; (3a/2)
\end{aligned}
$$

4.2 Motion of a Classical Particle: Wave Packet Approximation

Classically we consider a free particle as a point object endowed with a precise position and momentum at every instant of time. However de Broglie's hypothesis says that a particle of momentum p has associated with it a harmonic wave of wave length $\lambda = \dfrac{h}{p}$. As a harmonic wave extends over the whole space, it is not possible to get any idea of the position of the particle described by such a wave. To overcome this difficulty, the
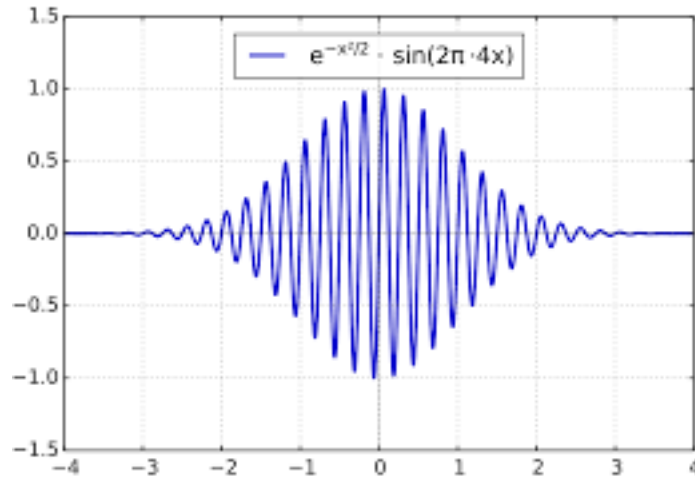

FIGURE 4.1: The superposition of a large number of waves having a large range of momenta values giving rise to a localized wave formed due to constructive and destructive interferences.

concept of a *wave packet* approximation for a free particle was proposed. A wave packet is a localized wave which is confined to a small region of space, as shown in Fig. 4.1. It is made up of a superposition of a large numbers of de Broglie waves such that, its wave function is given as

$$\psi(x,t) = \int a(k)e^{i(kx-\omega t)}dk, \tag{4.6}$$

where $a(k)$ is the amplitude and k is the propagation constant of the wave and ω is its angular frequency. The profile of a wave packet is shown in Fig. (4.2). It has a maximum at say, $x = X(t)$, where the particle is likely to be. If the particle moves in space, then the position of the wave packet changes with time thereby causing the point of maximum amplitude to also change with time. The rate at which the point of maximum amplitude changes with time defines the group velocity of the wave packet.
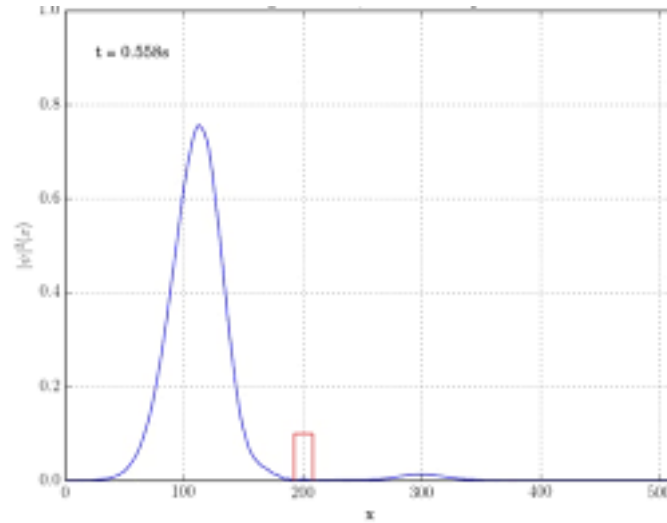
FIGURE 4.2: The profile of a wavepacket in the $(\psi - x)$ plane showing a maximum at $x = X(t)$ at the point at which the particle is likely to be.

It can be shown that the group velocity v_g of the wave packet is given by

$$
\begin{aligned}
v_g(x) &= \frac{dX(t)}{dt} \\
&= \frac{d\omega(k)}{dk} \\
&= \frac{d\hbar\omega}{\hbar k} \qquad \text{or} \\
v_g(x) &= \frac{dE}{dp},
\end{aligned}
\tag{4.7}
$$

since $E = \hbar\omega$ and $p = \hbar k$.

We know that the energy of a free classical particle is given as $E = \dfrac{p^2}{2m}$. Differentiating this gives $dE = \dfrac{2pdp}{2m}$, or $dE = \dfrac{pdp}{m}$, or $dE = \dfrac{(mv)dp}{m}$, or $dE = vdp$. Rearranging this equation gives the expression for the velocity for the free particle as

$$
v = \frac{dE}{dp}
\tag{4.8}
$$

Thus from Eqns. (4.7) and (4.8) we find that the group velocity of a wave packet becomes identical to the velocity of a classical particle when the particle parameters E and p are related to the wave parameters ω and k through the de Broglie's relations $E = \hbar\omega$ and $p = \hbar k$. Therefore under these restraining conditons, a wavepacket approximates the motion of a classical particle.

4.3   Ehrenfest Theorem

Whenever the changes in the potential energy $V(r,t)$ over the dimensions of a wavepacket is negligibly small, the motion of a wave packet agrees well with the motion of a corresponding classical particle. Under such conditions, the quantum analogues of the Newton's equations of motion may be given as

$$\frac{d\langle \hat{x} \rangle}{dt} = \frac{1}{m}\langle p_x \rangle \tag{4.9}$$

$$\frac{d\langle \hat{p_x} \rangle}{dt} = -\left\langle \frac{\partial V}{\partial x} \right\rangle. \tag{4.10}$$

These equations are together known as the Ehrenfest's Theorem.

4.3.1   Proof of Ehrenfest's First Equation

We know that the expectation value of position is

$$\langle \hat{x} \rangle = \int \psi^* \left(\hat{x}\psi \right) d\tau \tag{4.11}$$

Then the time rate of change of the expectation value of position is

$$\frac{\partial \langle \hat{x} \rangle}{\partial t} = \int \psi^* \hat{x} \left(\frac{\partial \psi}{\partial t} \right) d\tau + \int \left(\frac{\partial \psi^*}{\partial t} \right) \hat{x}\psi d\tau \tag{4.12}$$

From the Schröedinger's equation we have

$$\frac{\partial \psi}{\partial t} = \frac{1}{i\hbar} \left\{ -\frac{\hbar^2}{2m}\nabla^2 + V(r,t) \right\} \psi \tag{4.13}$$

Taking the complex conjugate of Eqn. (4.13), gives

$$\frac{\partial \psi^*}{\partial t} = -\frac{1}{i\hbar} \left\{ -\frac{\hbar^2}{2m}\nabla^2 + V(r,t) \right\} \psi^* \tag{4.14}$$

Substituting Eqns. (4.13) and (4.14) in Eqn. (4.12) and rearranging it gives

$$\frac{\partial \langle \hat{x} \rangle}{\partial t} = \frac{i\hbar}{2m} \int \left[\psi^* \hat{x}\nabla^2\psi - \nabla^2\psi^* \left(x\psi \right) \right] d\tau + \frac{1}{i\hbar} \int \left[\psi^* \hat{x}V(x,t)\psi - V(x,t)\psi^* \hat{x}V(x,t)\psi \right] d\tau \tag{4.15}$$

As $V(x,t)$ is a Self-adjoint operator we have

$$V(x,t)\psi - V(x,t)\psi^*$$

Hence Eqn. (4.15) simplifies to

$$\frac{\partial \langle \hat{x} \rangle}{\partial t} = \frac{i\hbar}{2m} \int \psi^* \hat{x} \nabla^2 \psi d\tau - \frac{i\hbar}{2m} \int \left(\nabla^2 \psi^* \right) x \psi d\tau \qquad (4.16)$$

Applying the integrating by parts rule twice, the second integral on the right side of Eqn. (4.16) gives

$$\int \left(\nabla^2 \psi^* \right) x \psi d\tau = 2 \int \psi^* \nabla \psi d\tau + \int \psi^* \hat{x} \nabla^2 \psi d\tau \qquad (4.17)$$

> *Note:* The proof of this is given at the end of this section for reference.

Substituting Eqn. (4.17) in Eqn. (4.16), gives

$$\frac{\partial \langle \hat{x} \rangle}{\partial t} = \frac{i\hbar}{2m} \left\{ \int \psi^* \hat{x} \nabla^2 \psi d\tau - 2 \int \psi^* \nabla \psi d\tau + \int \psi^* \hat{x} \nabla^2 \psi d\tau \right\} \qquad (4.18)$$

When we cancel off the first and third integrals in the RHS of the Eqn. (**??**), we obtain

$$\begin{aligned}
\frac{\partial \langle \hat{x} \rangle}{\partial t} &= \frac{i\hbar}{2m} \times \left\{ -2 \int \psi^* \nabla \psi d\tau \right\} \qquad \text{or} \\
\frac{\partial \langle \hat{x} \rangle}{\partial t} &= \frac{1}{m} \int \psi^* \left(-i\hbar \nabla \right) \psi d\tau \qquad \text{or} \\
\frac{\partial \langle \hat{x} \rangle}{\partial t} &= \frac{1}{m} \int \psi^* \left(\hat{p} \right) \psi d\tau
\end{aligned}$$

$$(4.19)$$

Since $\hat{p} = (-i\hbar \nabla)$ and $\hat{p}_x$ is the xth component of $\hat{p}$, we have

$$\boxed{\frac{\partial \langle \hat{x} \rangle}{\partial t} = \frac{1}{m} \langle \hat{p}_x \rangle ,} \qquad (4.20)$$

This equation relates the rate of change of the expectation value of position of a particle to the expectation value of its momentum.

4.3.2 Proof of Ehrenfest's Second Equation:

We know the expectation of momentum along the $x-$direction is given as

$$\langle \hat{p}_x \rangle = \int \psi^* \left(-i\hbar \frac{\partial}{\partial x} \right) \psi d\tau \qquad (4.21)$$

Then the rate of change of the expectation value of momentum with respect to time is given as

$$\frac{\partial \langle \hat{p_x} \rangle}{\partial t} = \frac{\partial}{\partial t} \int \psi^* \left(-i\hbar \frac{\partial}{\partial x} \right) \psi d\tau \tag{4.22}$$

Expanding this we have

$$\frac{\partial \langle \hat{p_x} \rangle}{\partial t} = -i\hbar \int \left(\frac{\partial \psi^*}{\partial t} \right) \frac{\partial \psi}{\partial x} d\tau - i\hbar \int \psi^* \frac{\partial}{\partial t} \left(\frac{\partial \psi}{\partial x} \right) d\tau \qquad \text{or}$$

$$\frac{\partial \langle \hat{p_x} \rangle}{\partial t} = -i\hbar \int \left(\frac{\partial \psi^*}{\partial t} \right) \frac{\partial \psi}{\partial x} d\tau - i\hbar \int \psi^* \frac{\partial}{\partial x} \left(\frac{\partial \psi}{\partial t} \right) d\tau, \tag{4.23}$$

since $\dfrac{\partial}{\partial x}$ and $\dfrac{\partial}{\partial t}$ are differential operators and can be interchanged.

From the Schröedinger's equation we have

$$\frac{\partial \psi}{\partial t} = \frac{1}{i\hbar} \left\{ -\frac{\hbar^2}{2m} \nabla^2 + V(r,t) \right\} \psi \tag{4.24}$$

Taking the complex conjugate of Eqn. (4.24), gives

$$\frac{\partial \psi^*}{\partial t} = -\frac{1}{i\hbar} \left\{ -\frac{\hbar^2}{2m} \nabla^2 + V(r,t) \right\} \psi^* \tag{4.25}$$

Substituting Eqns. (4.24) and (4.25) in Eqn. (4.23) and rearranging it gives

$$\frac{\partial \langle \hat{p_x} \rangle}{\partial t} = -i\hbar \int \left\{ \frac{-1}{i\hbar} \left[-\frac{\hbar^2}{2m} \nabla^2 \psi^* + V(r,t)\psi^* \right] \right\} \frac{\partial \psi}{\partial x} d\tau$$

$$-i\hbar \int \psi^* \frac{\partial}{\partial x} \left\{ \frac{1}{i\hbar} \left[\frac{-\hbar^2}{2m} \nabla^2 \psi + V(r,t)\psi \right] \right\} d\tau \tag{4.26}$$

Rearranging Eqn. (4.26) we have

$$\frac{\partial \langle \hat{p_x} \rangle}{\partial t} = \frac{-\hbar^2}{2m} \int \left[\nabla^2 \psi^* \left(\frac{\partial \psi}{\partial x} \right) - \psi^* \frac{\partial}{\partial x} \left(\nabla^2 \psi \right) \right] d\tau$$

$$+ \int \left[\psi^* V \left(\frac{\partial \psi}{\partial x} \right) - \psi^* \frac{\partial}{\partial x} \left(V\psi \right) \right] d\tau \tag{4.27}$$

Integrating by parts twice and applying the boundary conditions the first integral in the RHS of Eqn. (4.27) vanishes. Hence we have

$$\frac{\partial \langle \hat{p_x} \rangle}{\partial t} = \int \left[\psi^* V \left(\frac{\partial \psi}{\partial x} \right) - \psi^* \frac{\partial}{\partial x} \left(V\psi \right) \right] d\tau \tag{4.28}$$

But

$$\frac{\partial}{\partial x}(V\psi) = \frac{\partial V}{\partial x}\psi + V\frac{\partial \psi}{\partial x} \qquad (4.29)$$

Substituting Eqn. (4.29) in Eqn. (4.28) gives

$$\frac{\partial \langle \hat{p_x} \rangle}{\partial t} = \int \left[\psi^* V \left(\frac{\partial \psi}{\partial x} \right) - \psi^* \left(\frac{\partial V}{\partial x} \right) \psi - \psi^* V \left(\frac{\partial \psi}{\partial x} \right) \right] d\tau \qquad (4.30)$$

Simplifying the above equation gives

$$\frac{\partial \langle \hat{p_x} \rangle}{\partial t} = - \int \psi^* \left(\frac{\partial V}{\partial x} \right) \psi d\tau$$

or

$$\frac{\partial \langle \hat{p_x} \rangle}{\partial t} = \int \psi^* \left(-\frac{\partial V}{\partial x} \right) \psi d\tau$$

or

$$\boxed{\frac{\partial \langle \hat{p_x} \rangle}{\partial t} = \left\langle -\frac{\partial V}{\partial x} \right\rangle} \qquad (4.31)$$

The Eqn. (4.31) gives the rate of change of expectation value of momentum of a particle in terms of the expectation value of the negative gradient of its potential enerby V.

The Eqns. (4.20) and (4.31) along with their y and z components constitute the Ehrenfest's Theorem. They are analogous to the classical Newton's laws of motion, namely

$$\boxed{\frac{dr}{dt} = \frac{p}{m}}$$

and

$$\boxed{\frac{dp}{dt} = -\nabla V.}$$

> **Note-1:** Ehrenfest's Theorem provides an example of the Correspondance Principle. This is because it tells us that a wave packet moves like a classical particle whenever the expectation values give a good representation of the dynamical variables.
>
> **Note-2:** The *Correspondance Principle* tells that under appropriate conditions, all quantum mechanical calculations should reduce to classical results. This was first ennunciated by Neils Bohr.

Proof of Eqn. (4.17)

$$\int \left(\nabla^2\psi^*\right)x\psi d\tau = 2\int \psi^*\nabla\psi d\tau + \int \psi^*\hat{x}\nabla^2\psi d\tau$$

We know that the integrations by parts rule is

$$\int u dv = [uv] - \int v du.$$

Using this rule, the integral $\int \left(\nabla^2\psi^*\right)d\tau$ can be solved.

Let $u = (x\psi)$, $du = \nabla(x\psi)$,

$dv = \left(\nabla^2\psi^*\right)$ and $v = (\nabla\psi^*)$.

Then

$$\int_\tau \left(\nabla^2\psi^*\right)(x\psi)\, d\tau = \int_\sigma (\nabla\psi^*)(x\psi)\, d\sigma - \int_\tau (\nabla\psi^*)\nabla(x\psi)\, d\tau \qquad (4.34)$$

We know from the boundary conditons, $\psi \longrightarrow 0$ and $\nabla\psi \longrightarrow 0$ as $r \longrightarrow \pm\infty$. As the surface enclosing the whole universe lies at infinite distance from the origin, the surface integral vanishes. Hence we have

$$\int_\tau \left(\nabla^2\psi^*\right)(x\psi)\, d\tau = -\int_\tau (\nabla\psi^*)\nabla(x\psi)\, d\tau \qquad (4.35)$$

Let $u = \nabla(x\psi)$, $du = \nabla^2(x\psi)$,

$dv = (\nabla\psi^*)$ and $v = \psi^*$.

Then

$$\int_\tau (\nabla\psi^*)\nabla(x\psi)\, d\tau = \int_\sigma \psi^*\nabla(x\psi)\, d\sigma - \int_\tau \psi^*\nabla^2(x\psi)\, d\tau \qquad (4.36)$$

Using the boundary conditons $\psi \longrightarrow 0$ and $\nabla\psi \longrightarrow 0$ as $r \longrightarrow \pm\infty$ once again, the surface integral becomes zero. Hence we have

$$\int_\tau (\nabla\psi^*)\nabla(x\psi)\, d\tau = -\int_\tau \psi^*\nabla^2(x\psi)\, d\tau \qquad (4.37)$$

Substituting Eqn. (4.37) in Eqn. (4.34) gives

$$\int_\tau \left(\nabla^2\psi^*\right)(x\psi)\, d\tau = \int_\tau \psi^*\nabla^2(x\psi)\, d\tau \qquad (4.38)$$

Let

$$
\begin{aligned}
\nabla\left(x\psi\right) &= \left(\nabla x\right)\psi + x\nabla\psi \\
&= \psi + x\nabla\psi \qquad \text{since} \nabla x = 1
\end{aligned}
\tag{4.39}
$$

Then

$$
\begin{aligned}
\nabla^2\left(x\psi\right) &= \nabla\left(\psi + x\nabla\psi\right) \\
&= \nabla\psi + \nabla x\nabla\psi x\nabla^2\psi \\
&= 2\nabla\psi + x\nabla^2\psi
\end{aligned}
\tag{4.40}
$$

Substituting Eqn. (4.40) we have

$$
\int_\tau \psi^*\nabla^2\left(x\psi\right)d\tau = \int_\tau \psi^*\left[2\nabla\psi + x\nabla^2\psi\right]d\tau
\tag{4.41}
$$

Substituting Eqn. (4.41) in Eqn. (4.38) will then give

$$
\int_\tau \left(\nabla^2\psi^*\right)\left(x\psi\right)d\tau = 2\int_\tau \psi^*\nabla\psi d\tau + \int_\tau \psi^* x\nabla^2\psi d\tau
\tag{4.42}
$$

Hence the proof.

Chapter 5

Admissibility Conditions and Time Independent Schröedinger Equation

5.1 Admissibility Conditions on ψ

The probability interpretation of wave functions makes it necessary that wave function ψ satisfies certain general conditions, namely

1. finiteness

2. single valuedness

3. continuity

These conditions are called as *admissibility conditions* and are intended to ensure that $|\psi|^2$ has the propertied of a probability magnitude.

Finiteness:
   The function ψ should take a single value at every point. This finiteness is required in order that $|\psi|^2$ takes a value between 0 and 1 as any probability should even for an infinitesemal volume element $d\tau$.

Single Valuedness:
   The single valuedness is the requirement that at any given physical point the wavefunction should have a unique value in order that the probability density $|\psi|^2$ may be uniquely defined.

Continuity:

The wavefunction ψ and all its first order derivatives, namely $\dfrac{\partial \psi}{\partial x}$, $\dfrac{\partial \psi}{\partial y}$, $\dfrac{\partial \psi}{\partial z}$ should be continuous functions of x for all values of x.

Note: This condition arises because of the nature of the potential $V(r,t)$. As $V(r,t)$ is a continuous function of r, the consistency of the Schröeinger equation requires that ψ is also continuous.

Any wavefunction which satisfies all the three requirements is considered to be eligible to describe a physical system. Hence these conditions are called as *admissiblilty conditions.*

Note: The continuity of $\psi = e^{-|x|} \sin{(\alpha x)}$ and its first order partial derivatives and the discontinuity of its second order derivatives are shown in Fig. 5.1

5.2 Stationary States

The stationary states are those quantum states in which none of the particle characteristics change with time. The wave function of the particle in these states is given as

$$\psi(r,t) = u(r)e^{\frac{-iEt}{\hbar}} \tag{5.1}$$

In these states the position probability density $|\psi|^2$ at every point r in space remains independent of time. Similarly the expectation values of all its dynamical variables remain time independen. Further the energy that the particle takes will be a definite value. The energy spectrum of the particle will be atleast partially discrete in nature.

Note: The discreteness of the energy spectrum was first used by Neils Bohr to describe the atomic spectra of the Hydrogen atom.

5.3 Time Independent Schröedinger Wave Equation

The time independent Schröedinger equation can be obtained from the time dependent Schröedinger equation by

1. factorizing the wavefunction $\psi(r,t)$ into space dependent part, say $u(r)$ and time dependent part, say $f(t)$
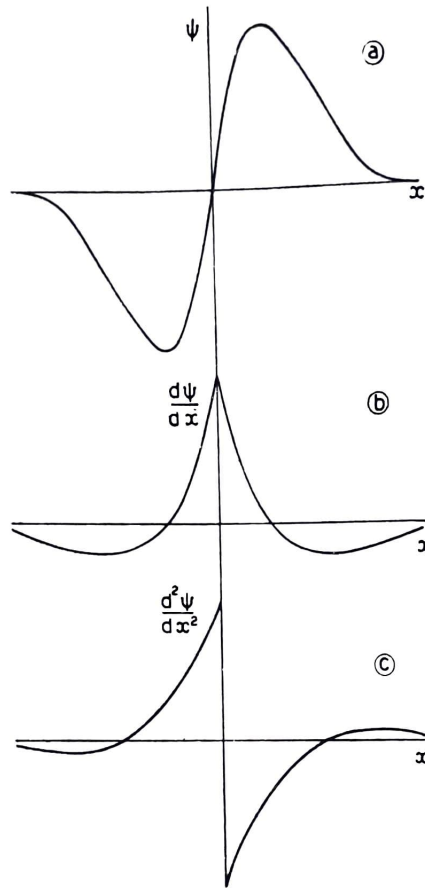
FIGURE 5.1: (a) and (b) show the continuity of the wavefunction $\psi = e^{-|x|} \sin(\alpha x)$ and its first order partial derivative respectively while (c) shows the discontinuity of its second order partial derivative. *Note:* THough the first order partial derivative is continuous, it shows a kink at the origin $x = 0$.

2. by applying the method of separation of variables method.

Let the time dependent Schröedinger equation be given as

$$i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2 \psi(r,t) + V(r,t)\psi(r,t) \tag{5.2}$$

Let us assume the potential to be time independent, that is

$$V \equiv v(r) \tag{5.3}$$

Let us factorize the wavefunction as

$$\psi(r,t) = u(r)f(t) \tag{5.4}$$

Substituting Eqn. (5.4) in Eqn. (5.2) gives

$$i\hbar u(r)\frac{\partial f(t)}{\partial t} = -\frac{\hbar^2}{2m}f(t)\nabla^2 u(r,t) + V(r)u(r)f(t) \tag{5.5}$$

Dividing the above Eqn. (5.5) by $u(r)f(t)$ gives

$$\frac{1}{f(t)}i\hbar\frac{\partial f(t)}{\partial t} = -\frac{\hbar^2}{2m}\frac{1}{u(r)}\nabla^2 u(r) + V(r) \tag{5.6}$$

The Eqn. (5.6) tells us that the RHS is independent of time t and the LHS is independent of space r. But their equality denotes that they are equal to some separation constant, say E.

Separating the Eqn. (5.6) into the time part and the space part we have

$$\frac{1}{f(t)}i\hbar\frac{df(t)}{dt} = E \quad \text{or}$$

$$i\hbar\frac{df(t)}{dt} = Ef(t) \tag{5.7}$$

and

$$-\frac{\hbar^2}{2m}\frac{1}{u(r)}\nabla^2 u(r) + V(r) = E \quad \text{or} \tag{5.8}$$

or mutiplying the above equation Eqn. (5.8) by $u(r)$ gives

$$\boxed{-\frac{\hbar^2}{2m}\nabla^2 u(r) + V(r)u(r) = Eu(r)} \tag{5.9}$$

The above Eqn. (5.9) is called as the **Time Independent Schröedinger's Wave Equation.** As the solution of this equation depends on the value E, the wavefunction can be written as $u_E(r)$

5.3.1   Finding the Time Dependent Part of the Wavefunction

Rearranging the Eqn. (5.7) and rearranging it gives

$$\frac{df}{f} = \frac{-iEdt}{\hbar} \tag{5.10}$$

Taking the integral of Eqn. (5.10) gives

$$log_e(f) = \frac{-iEt}{\hbar}log_e(e) \tag{5.11}$$

Getting rid of the logarithm gives

$$f(t) = e^{-iEt/\hbar} \tag{5.12}$$

Substituting Eqn. (5.12) in Eqn. (5.4) gives the total wavefunction as

$$\psi(r,t) = u_E(r)e^{-iEt/\hbar} \tag{5.13}$$

Using Eqn. (5.13) the position probability density is given as

$$|\psi|^2 = |u(r)|^2 \tag{5.14}$$

This means that the probability density is independent of time. Similarly the expectation values of all dynamical variables will be time independent. Therefore Eqn. (5.13) gives the wavefunction of a system in a stationary state.

5.3.2 Energy Spectrum

The time independent wave equation given by Eqn. (5.9) can be written as

$$\mathcal{H}u_E(r) = Eu_E(r), \tag{5.15}$$

where

$$\mathcal{H} = \left[\frac{-\hbar^2}{2m}\nabla^2 + V(r)\right] \tag{5.16}$$

is known as the *Hamiltonian Operator*. It is equal to the sum of the kinetic and potential energies of the particle or system. The Eqn. (5.15) is similar to the eigen value equation of matrix theory, namely

$$Mu = \lambda u$$

where M refers to a matrix operator, λ is the eigen value for the system and u refers to an eigen vector pertaining to the eigen value λ.

The Eqn. (5.15) implies that the action of the Hamilton operator on the particle wavefunction $u_E(r)$ is to simply reproduce the wavefunction $u_E(r)$ multiplied by a constant E. Here E is called as the *energy eigen value* and $u_E(r)$ is considered as the energy eigen function. According to mathematical theory, the energy eigen value E can take on all possible values. But the admissibility conditons restrict the energy to a discrete set. This discrete set of all allowed energy values is called as the *energy eigen spectrum*.