



## Unit-IV: Wave Mechanics (Part-I)

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## Reference Books and other sources

- Concept of Modern Physics, by Arthur Beiser, Tata McGraw-Hill, 6th edition (2003).
- Quantum Physics for Scientists and Technologists, by Paul Sanghera, John Wiley & Sons (2011).
- Notes of Anjani Sir.

# Failures of Classical Physics

- Classical Physics on its own can not explain many natural/ observed phenomena.
- There are two main drawbacks of Classical Physics:
  - 1 Einstein's theory of relativity: Newtonian mechanics failed at very high speed phenomena, where a body moves with speed of light.
  - 2 Classical Physics fails to work microscopic level: It fails to explain the structure of atom and how light interacts with particles.

# Introduction

- The original formulation of quantum mechanics is generally credited to Werner Heisenberg and Erwin Schrodinger, who presented essentially the same theory in two different mathematical formulations.
- Heisenberg developed quantum mechanics, in 1925, along with Max Born and Pascual Jordan, in the form of matrices, whereas Schrodinger developed the quantum mechanics, in 1926, in the form of wave mechanics.
- Paul Dirac, Schrodinger, and others later demonstrated that both formulations yield identical results even though they use a different mathematical structure.

# Wave function: building block of quantum mechanics

- In wave mechanics, a particle (or a physical system) can be represented by a wave and it must have a wave function associated with it.
- In quantum mechanics, such a wave function,  $\Psi$ , represents the probability of finding the particle at a given point in space and time.
- To be precise, we will learn later that  $\Psi$ , as being a complex number, does not have any direct physical significance. However, the square of its absolute magnitude  $|\Psi|^2 = \Psi^*\Psi$  evaluated at a specific point in space and time represents the probability density ( $P$ ) of experimentally finding the particle at that point in space and time. Here  $\Psi^*$  is the complex conjugate of  $\Psi$ .

## Normalization Condition

- Because the particle must be somewhere in the space, the integration of  $|\Psi|^2$  over total space and time must be equal to 1. This can be represented mathematically as:

$$\int_{-\infty}^{+\infty} |\Psi|^2 dV = 1 \Rightarrow \int_{-\infty}^{+\infty} \Psi^*(\vec{r}, t) \Psi(\vec{r}, t) dV = 1 \Rightarrow \int_{-\infty}^{+\infty} P dV = 1$$

where  $dV = dx dy dz = d^3r$  represents infinitesimal volume in 3D at time  $t$  in which the particle can be found with the probability of  $|\Psi|^2$ . This is also called the **normalization condition** for the wave function. The wave function that meets this condition is called a **normalized wave function**.

- If  $\int_{-\infty}^{+\infty} |\Psi|^2 dV = 0$  particle does not exist there.

# Acceptable or Well-Behaved wave function

- $\Psi$  must be finite, single-valued every where. Also  $\Psi$  is continuous every where (except in the region where P.E:  $U = \infty$ ).
- $\frac{\partial \Psi}{\partial x}$ ,  $\frac{\partial \Psi}{\partial y}$  and  $\frac{\partial \Psi}{\partial z}$  must be finite, continuous and single valued everywhere.
- $\Psi$  must be normalizable, which means that  $\Psi$  must go to 0 as  $x \rightarrow \pm\infty$ ,  $y \rightarrow \pm\infty$  and  $z \rightarrow \pm\infty$  in order that  $\int |\Psi|^2 dV$  over all space be a finite constant.



## Operator: information extractor

- We know that a wave function has all the information about the system that it represents. How do we extract information from it? That is where operators come into the picture.
- Operator is a rule which changes a function to another function. For example, derivative is an operator which shows:  $\frac{d}{dx}(\sin x) = \cos x$ .
- In quantum mechanics, a physical observable (e.g. position, momentum, energy etc.) is represented by an operator that operates on a wave function to predict the value of the measurements of the observable. That is  $\hat{A}\Psi = a\Psi'$ , where  $\hat{A}$  is the operator and  $a$  is the value of the measurement of the observable.

## Continued...

- Let's Consider the wave function of a particle having momentum  $p$  and energy  $E$  is given by:  $\Psi(x, t) = e^{i(kx - \omega t)}$ , where  $k$  and  $\omega$  are determined from momentum:  $p = \hbar k$  and energy  $E = \hbar\omega$  respectively.

Now we are going to extract information from the wave function using a simple operator, i.e., derivative. So differentiating  $\Psi$  with respect to  $x$  we get:  $\frac{\partial}{\partial x}[\Psi(x, t)] = \frac{\partial}{\partial x}[e^{i(kx - \omega t)}] = ik\Psi. \Rightarrow \frac{\hbar}{i} \frac{\partial}{\partial x}[\Psi(x, t)] = \hbar k\Psi(x, t).$   
 $\Rightarrow p = \frac{\hbar}{i} \frac{\partial}{\partial x}.$

As  $\Psi = \Psi(x, t)$ , so again differentiating  $\Psi$  with respect to  $t$  we get:  
 $\frac{\partial}{\partial t}[\Psi(x, t)] = \frac{\partial}{\partial t}[e^{i(kx - \omega t)}] = -i\omega\Psi. \Rightarrow i\hbar \frac{\partial}{\partial t}[\Psi(x, t)] = \hbar\omega\Psi(x, t).$   
 $\Rightarrow E = i\hbar \frac{\partial}{\partial t}.$

So the operator form of momentum:  $\hat{p} = \frac{\hbar}{i} \frac{\partial}{\partial x}$  and energy:  $\hat{E} = i\hbar \frac{\partial}{\partial t}.$

## Eigen value equation

- It is an expression in which an operator  $\hat{A}$  acting on a wave function  $\Psi$  representing the same wave function  $\Psi$  multiplied by a constant factor  $\lambda$ . That is  $\hat{A}\Psi = \lambda\Psi$ , here  $\lambda$  is called the eigen value.
- For example: suppose  $\frac{d}{dx}$  is an operator acting on the wave function  $e^{2x}$ , then it yields:  $\frac{d}{dx}(e^{2x}) = 2e^{2x}$ , where 2 is the eigen value and it satisfies the eigen value equation.
- The only possible results in the measurement of a physical observable  $A$  are the eigenvalues  $\lambda$  of the corresponding operator  $\hat{A}$  operating on the wave function  $\Psi$ .
- If two or more wave functions corresponds to same eigen value, then these wave functions are called degenerate wave functions or simply degenerate states.

# Problems

- 1 Select the acceptable wave functions from the following: (a)  $\Psi = x^n$ , (b)  $\Psi = e^x$ , (c)  $\Psi = e^{-x}$ , (d)  $\Psi = e^{-x^2}$ , (e)  $\Psi = A \sin(x)$ .
- 2 Show that the wave function  $\Psi(x) = e^{-\frac{\alpha^2 x^2}{2}}$  is an eigen function of operator  $\hat{A} = -\frac{d^2}{dx^2} + \alpha^4 x^2$  with an eigen value of  $\alpha^2$ .
- 3 Which of the following functions are eigen function of the operator  $\frac{d^2}{dx^2}$ ? Find the eigen value in each case, if exists. (a)  $\Psi = A \sin(mx)$ , (b)  $\Psi = B \cos(nx)$ , (c)  $\Psi = A e^{-mx}$ , (d)  $\Psi = B e^{x^2}$ , (e)  $\Psi = ex$ , (f)  $\Psi = \frac{\alpha}{x}$ .
- 4 The normalized state of free particle is given by wave function  $\psi(x) = N e^{-\frac{x^2}{2a^2}} e^{ikx}$ . (a) Find the normalization factor  $N$ , (b) In what region of space, the particle is most likely to found.

# Schrodinger's equation

- It is a fundamental equation of wave mechanics having two forms: Time dependent and time independent Schrodinger equations.
- Time dependent Schrodinger equation: 
$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \Psi + U\Psi$$
, where  $\Psi = \Psi(x, y, z; t)$  and  $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$ .
- Time independent Schrodinger equation: 
$$\nabla^2 \Psi + \frac{2m}{\hbar^2} (E - V)\Psi = 0$$
, where  $\Psi = \Psi(x, y, z)$
- The general form of Schrodinger equation:  $\hat{H}\Psi = E\Psi$ , where  $H$  is the Hamiltonian operator equal to the sum of K.E ( $\frac{p^2}{2m}$ ) and P.E ( $U$ ) and  $E$  is the energy eigen value or in some cases it is called as the energy operator.

# Time dependent Schrodinger equation (TDSE)

Let us consider a particle which is moving (with non-relativistic speed) freely in +ve  $x$  direction. Then the corresponding wave equation for the particle can be written as:

$$\Psi = Ae^{i(kx - \omega t)}$$

Since we know  $p = \hbar k$  and  $E = \hbar\omega$ , then the above equation can be written as:

$$\Psi = Ae^{\frac{i}{\hbar}(px - Et)} \quad (1)$$

Although the above equation is correct for a freely moving particle, but we are interested in the situations where the particle is bound by some restrictions. Now we are going to obtain a differential equation for  $\Psi$ .

## Continued...

Now let us begin by Differentiating eq-1 twice with respect to  $x$ , which

$$\text{gives: } \frac{\partial^2 \Psi}{\partial x^2} = -\frac{p^2}{\hbar^2} \Psi. \quad \Rightarrow p^2 \Psi = -\hbar^2 \frac{\partial^2 \Psi}{\partial x^2} \dots\dots\dots(2)$$

Again differentiating eq-1 once wrt  $t$ , we get:  $\frac{\partial \Psi}{\partial t} = -\frac{iE}{\hbar} \Psi$ .

$$E\Psi = i\hbar \frac{\partial \Psi}{\partial t} \dots\dots\dots(3)$$

As we know that the total energy  $E$  of a particle is equal to the sum of its K.E ( $\frac{p^2}{2m}$ ) and P.E ( $U(x,t)$ ), so we can write  $E = \frac{p^2}{2m} + U(x,t)$ .

By multiplying  $\Psi$  on both sides of the equation we get:

$$E\Psi = \frac{p^2}{2m} \Psi + U(x,t)\Psi \dots\dots\dots(4)$$

Substituting the eq-(2) and eq-(3) in eq-(4) it becomes the time

$$\text{dependent Schrodinger equation in 1-D: } i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + U\Psi$$

Schrodinger's equation in 3D is:

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \left( \frac{\partial^2 \Psi}{\partial x^2} + \frac{\partial^2 \Psi}{\partial y^2} + \frac{\partial^2 \Psi}{\partial z^2} \right) + U(x, y, z, t)\Psi$$

$$\Rightarrow i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \Psi + U(x, y, z, t)\Psi$$

# Time independent Schrodinger equation (TISE)

Here we will prove the TISE from TDSE using the separation of variables technique in 1D.

When the potential energy ( $U$ ) is independent of time, then the wave function can be written as:

$$\Psi(x, t) = \psi(x)\phi(t).$$

We begin by taking the wave function of a particle moving in +x direction as:  $\Psi(x, t) = Ae^{\frac{i}{\hbar}(px - Et)} = Ae^{\frac{i}{\hbar}px} e^{-\frac{i}{\hbar}Et} = \psi e^{-\frac{i}{\hbar}Et}$ .

Substituting the  $\Psi$  in TDSE, we get:

$$i\hbar \frac{\partial}{\partial t}(\psi e^{-\frac{i}{\hbar}Et}) = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2}(\psi e^{-\frac{i}{\hbar}Et}) + U\psi e^{-\frac{i}{\hbar}Et}$$

$$E\psi e^{-\frac{i}{\hbar}Et} = -\frac{\hbar^2}{2m} e^{-\frac{i}{\hbar}Et} \frac{\partial^2 \Psi}{\partial x^2} + U\psi e^{-\frac{i}{\hbar}Et}.$$

Dividing through by the common exponential factor we get the TISE in

1D:  $\frac{\partial^2 \psi}{\partial x^2} + \frac{2m}{\hbar^2} (E - U)\psi = 0$ . It is also called as the steady-state form of Schrodinger's equation. In three dimension, it becomes:

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{2m}{\hbar^2} (E - U)\psi = 0 \Rightarrow \nabla^2 \psi + \frac{2m}{\hbar^2} (E - U)\psi = 0.$$



# Short-comings and properties of Schrodinger equation

- Properties of Schrodinger equation:
  - ① The differential equation is first order in time. This means that for an initial condition it suffices to know the wavefunction completely at some initial time  $t_0$  and the Schrodinger equation then determines the wave function for all times.
  - ② Schrodinger equation is linear in the wave function  $\Psi$ . If  $\Psi_1$  and  $\Psi_2$  are two solutions of Schrodinger's equation, then  $\Psi = a_1\Psi_1 + a_2\Psi_2$  is also a solution, where  $a_1$  and  $a_2$  are constants. Thus the wave functions  $\Psi_1$  and  $\Psi_2$  obey the superposition principle that other waves do.
- Short-comings of Schrodinger equation:
  - ① Time dependent Schrodinger's equation is not symmetric with respect to space and time. Because it contains second order derivative of space and first order derivative of time.

# Physical interpretation of wave function

- Properties of Schrodinger's Interpretation:
  - 1 Schrodinger thought that  $\Psi$  represents particles that disintegrate. You have a wave function and the wave function is spread all over space, so the particle has disintegrated completely. And wherever you find more  $\Psi$ , more of the particle is there. That was his interpretation.
  - 2 In 1926, Schrdinger believed that electron waves were always spread out across all of space and that the square of the wave function gave the charge density of the electron wave in any particular location. This was a reasonable assumption since the wave appeared to be densest in the places where Bohr's theory predicted electrons would be. Yet Schrdinger's interpretation could not explain quantum tunnelling.

## Continued.....

- Max-Born Interpretation:

- 1 Max Born proposed a different interpretation in the same year. Born stated that the square of the wave function does not represent the physical density of electron waves, but their probability density. This is the probability of finding an electron in any particular state, that is, with any particular position, momentum, or energy, at any particular time. The de Broglie model of the atom was now replaced with the idea that electrons exist in a superpositional 'probability cloud'.
- 2 Born's statistical interpretation of the wave function, which says that  $|\Psi(x, t)|^2$  gives the probability of finding the particle at point  $x$ , at time  $t$ ,  
or more precisely,  $|\Psi(x, t)|^2 dx =$  Probability of finding the particle between  $x$  and  $(x + dx)$ , at time  $t$ .

## Stationary states

- The state of the system for which the probability density is independent of time is called as **stationary states** (i.e.,  $\frac{dP}{dt} = 0$ ). Such systems are known as stationary systems.
- Example: for a wave function which satisfies the Schrodinger equation, its probability density is always independent of time.

The solution of Schrodinger equation is:  $\Psi(x, t) = \psi(x)e^{-\frac{i}{\hbar}Et}$  and the probability density is:

$P = \Psi^*(x, t) \cdot \Psi(x, t) = \psi^*(x)e^{\frac{i}{\hbar}Et} \cdot \psi(x)e^{-\frac{i}{\hbar}Et} = \psi^*(x) \cdot \psi(x)$  independent of time.

## Orthogonal and orthonormal wave function

- Two wave functions  $\Psi_m(x, t)$  and  $\Psi_n(x, t)$  are said to be mutually orthogonal if  $\int_{-\infty}^{+\infty} \Psi_m^*(x, t) \cdot \Psi_n(x, t) dx = 0$  when  $m \neq n$ .
- The normalized and the orthogonal wave functions are called orthonormal wave functions. Mathematically  $\int_{-\infty}^{+\infty} \Psi_m^*(x, t) \cdot \Psi_n(x, t) dx = \delta_{mn}$ . Where  $\delta_{mn}$  is called as Kronecker delta and is defined as follows:

$$\delta_{mn} = \begin{cases} 1, & m = n \\ 0, & m \neq n \end{cases}$$

## Complete (closed) wave function

- It is a wave function whose value at one point is independent of its value at any other point.

$$\int_{-\infty}^{+\infty} \psi_m^*(x) \cdot \psi_n(x') dx = \begin{cases} 0, & x \neq x' \\ 1, & x = x' \end{cases}$$

- If  $\int_{-\infty}^{+\infty} \psi_m^*(x) \psi_n(x') dx = 0$  for  $m \neq n$  and  $x = x'$ , then the wave function  $\psi$  is said to be complete as well as orthonormal.

## Complete (closed) wave function

According to this theorem, a single-valued, continuous, finite and normalizable orthogonal wave function  $\Phi$  can be expanded as series of orthogonal wave functions  $\psi_n$  of same variable.

Mathematically:  $\Phi = \sum a_n \psi_n(x)$ , where  $a_n$  are known as co-efficients and  $\psi_n$  are known as basis set.

$$\Phi = a_1 \psi_1 + a_2 \psi_2 + \dots + a_n \psi_n.$$

Multiplying the above equation by  $\psi_n^*$  and integrating over the entire space, we get

$$\int_{-\infty}^{+\infty} \psi_n^* \cdot \Phi dx = a_1 \int_{-\infty}^{+\infty} \psi_n^* \cdot \psi_1 dx + a_2 \int_{-\infty}^{+\infty} \psi_n^* \cdot \psi_2 dx + \dots + a_n \int_{-\infty}^{+\infty} \psi_n^* \cdot \psi_n dx$$

Again we know that:

$$\int_{-\infty}^{+\infty} \psi_m^*(x) \cdot \psi_n(x) dx = \begin{cases} 1, & m = n \\ 0, & m \neq n \end{cases}$$

.

$$\text{So } a_n = \int_{-\infty}^{+\infty} \psi_n^* \cdot \Phi dx$$

# Expectation Values

- When we perform an experiment, we get a definite value and not a probability. But the predictions of quantum mechanics are in terms of probabilities. So, then, how do we associate these predictions with experimental measurements?
- This is where the concept of expectation values comes into the picture. We will derive the expectation value from the wave function and compare it to experimental results.
- Expectation value of an observable ( $\langle A \rangle$ ) is defined as the average of large number of measurements on the observables ( $A$ ) and it is

mathematically written as: 
$$\langle A \rangle = \frac{\int_{-\infty}^{+\infty} \Psi^* \hat{A} \Psi dx}{\int_{-\infty}^{+\infty} \Psi^* \cdot \Psi dx}.$$

If  $\Psi$  is normalized, then  $\int_{-\infty}^{+\infty} \Psi^* \cdot \Psi dx = 1$ , then the above equation

becomes: 
$$\langle A \rangle = \int_{-\infty}^{+\infty} \Psi^* \hat{A} \Psi dx.$$



## Expectation Value of known operators

- The expectation value of the position of a single particle is:

$$\langle x \rangle = \int_{-\infty}^{+\infty} \Psi^* x \Psi dx = \int_{-\infty}^{+\infty} x |\Psi|^2 dx.$$

- The expectation value of momentum of a particle in 1D is:

$$\langle p \rangle = \int_{-\infty}^{+\infty} \Psi^* \hat{p} \Psi dx = \int_{-\infty}^{+\infty} \Psi^* \left( \frac{\hbar}{i} \frac{\partial}{\partial x} \right) \Psi dx = \frac{\hbar}{i} \int_{-\infty}^{+\infty} \Psi^* \frac{\partial \Psi}{\partial x} dx, \text{ since}$$

the operator form of  $\hat{p} = \frac{\hbar}{i} \frac{\partial}{\partial x}$ .

- The expectation value of energy of a particle is:

$$\langle E \rangle = \int_{-\infty}^{+\infty} \Psi^* \hat{E} \Psi dx = \int_{-\infty}^{+\infty} \Psi^* \left( i\hbar \frac{\partial}{\partial t} \right) \Psi dx = i\hbar \int_{-\infty}^{+\infty} \Psi^* \frac{\partial \Psi}{\partial t} dx, \text{ since}$$

the operator form of  $\hat{E} = i\hbar \frac{\partial}{\partial t}$ . Here in all cases we assume that  $\Psi$  is normalized.

- Problems: If  $\Psi = \frac{e^{ikx}}{\sqrt{b-a}}$  then over the limit  $a$  to  $b$  calculate the expectation value of (i) position ( $\langle x \rangle$ ), (ii) momentum ( $\langle p \rangle$ ) and (iii) kinetic energy ( $\langle T \rangle$ ).

## Conservation of Probability density or Equation of Continuity

Probability density is defined as:  $P(r, t) = \Psi^*(r, t)\Psi(r, t)$ . Then taking the integration of the equation over all space, we get

$\Rightarrow \int_V P dV = \int_V \Psi^*(r, t)\Psi(r, t) dV$ . Then differentiating this equation with respect to  $t$  we get:  $\int_V \frac{\partial P}{\partial t} dV = \int_V (\Psi^* \frac{\partial \Psi}{\partial t} + \Psi \frac{\partial \Psi^*}{\partial t}) dV \dots\dots(1)$

Now we are going to simplify the RHS of eq-(1) using Schrodinger equation.

The time dependent Schrodinger equation is:

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \Psi + U\Psi \dots\dots\dots(2a).$$

Multiplying  $\Psi^*$  on both sides of above equation:

$$i\hbar \Psi^* \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \Psi^* \nabla^2 \Psi + \Psi^* U\Psi \dots\dots\dots(2b).$$

Taking complex conjugate of eq-(2a) we get:

$$-i\hbar \frac{\partial \Psi^*}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \Psi^* + U\Psi^* \dots\dots\dots(3a).$$

Multiplying  $\Psi$  on both sides of above equation, we get:

## Continued.....

$$-i\hbar\Psi\frac{\partial\Psi^*}{\partial t} = -\frac{\hbar^2}{2m}\Psi\nabla^2\Psi^* + \Psi U\Psi^* \dots\dots\dots(3b).$$

Then subtracting eq-(3b) from eq-(2b) and then doing some simplification, we get:

$$(\Psi^*\frac{\partial\Psi}{\partial t} + \Psi\frac{\partial\Psi^*}{\partial t}) = \frac{i\hbar}{2m}(\Psi^*\nabla^2\Psi - \Psi\nabla^2\Psi^*).$$

Then eq-(1) implies:

$$\int_V \frac{\partial P}{\partial t} dV = \int_V \frac{i\hbar}{2m}(\Psi^*\nabla^2\Psi - \Psi\nabla^2\Psi^*)dV$$

Using the Green's theorem:  $\Psi^*\nabla^2\Psi - \Psi\nabla^2\Psi^* = \nabla\cdot(\Psi^*\nabla\Psi - \Psi\nabla\Psi^*)$ , the above equation becomes:  $\int_V \frac{\partial P}{\partial t} dV = -\frac{\hbar}{2im} \int_V [\nabla\cdot(\Psi^*\nabla\Psi - \Psi\nabla\Psi^*)] dV$

$$\Rightarrow \int_V \frac{\partial P}{\partial t} dV = -\int_V (\nabla\cdot J) dV = \oint_S J\cdot dS \dots\dots\dots(4) \text{ using Gauss divergence theorem.}$$

where  $J = \frac{\hbar}{2im}(\Psi^*\nabla\Psi - \Psi\nabla\Psi^*)$  is called as current density.

$\Rightarrow \int_V [\frac{\partial P}{\partial t} + (\nabla\cdot J)] dV = 0$  So we can also write  $\frac{\partial P}{\partial t} + (\nabla\cdot J) = 0$  which is the equation of continuity. As from the normalization condition, it is clear that:  $\int_V \frac{\partial P}{\partial t} dV = 0$ . Here  $dV$  is arbitrary and can not be zero, so  $\frac{\partial P}{\partial t} = 0$  and that implies  $P$  is conserved.