# Fundamental postulates of wave mechanics

The fundamental postulates on which Schrödinger's formulation of wave mechanics is based are as follows:

## Postulate I

A system consisting of a single particle moving in a conservative force field is associated with a complex wave function $\psi(r,t)$ which completely describes the space-time behaviour of the particle consistent with the uncertainty principle.

## Postulate II

Every dynamical variable (e.g. position, velocity, momentum angular momentum, energy etc.) of the system is represented by an operator in quantum mechanics. These operators are linear and Hermitian.

## Postulate III

The only possible values of dynamical variables A that may be experimentally measured are the eigen values $\lambda$ of the operator $\hat{A}$ corresponding to the eigen value equation.

$$\hat{A}\psi_n = \lambda_n \psi_n$$

where, $\psi_n$ is the eigen function of $\hat{A}$ belonging to the eigen value $\lambda_n$.

i) The eigen values $\lambda_n$ must be real as the observable physical quantities have real magnitude.

ii) The eigen functions $\psi_n$ are well-behaved and form a complete set which is orthogonal.

iii) An observation on a dynamical variable represented by $\hat{A}$ on an eigen state $\psi$ of a system definitely leads to the result $\lambda_n$.

## Postulate IV

The probability density of the finding a particle at $(x, y, z)$ at time $t$ is $P = \psi^* \psi$, where $\psi^* \psi$ is always real as $P$ is real. The total probability of finding the particle over the entire volume is

$$P = \int_\tau \rho \, d\tau = \int_\tau \psi^* \psi \, d\tau = 1$$

In this case $\psi$ is said to be normalized.

## Postulate V

The average or expectation value of a dynamical variable $A$ associated with the operator $\hat{A}$ is given by

$$\langle A \rangle = \int_\tau \psi^* \hat{A} \psi \, d\tau$$

if $\psi$ is normalized. If $\psi$ is not normalised then,

$$\langle A \rangle = \frac{\int \psi^* \hat{A} \psi \, d\tau}{\int_\tau \psi^* \psi \, d\tau}$$

## One-dimensional time-dependent Schrödinger equation:

The wave function for such a particle along the position x-axis is

$$\psi(x,t) = A e^{-i(\omega t - Kx)} \quad \text{——— (1)}$$

$$= A e^{i(Kx - \omega t)}$$

where, $A$ is a constant & $K = \frac{\omega}{v}$

The wave function $\psi(x,t)$ in terms of $P_x$ & $E$ is

$$\psi(x,t) = A e^{i/\hbar (P_x x - Et)} \quad \text{——— (2)}$$

where, $E = \hbar\omega$, $P = \hbar K$, $K = \frac{2\pi}{\lambda}$

Diff. $\psi$ w.r.t $x$ & we get

$$\frac{\partial \psi}{\partial x} = A\left(\frac{i}{\hbar}\right) P_x e^{i/\hbar(P_x x - Et)}$$

$$= \frac{i}{\hbar} P_x \psi$$

& $$\frac{\partial^2 \psi}{\partial x^2} = \frac{i}{\hbar} P_x \frac{\partial \psi}{\partial x} = \frac{i}{\hbar} P_x \left(\frac{i}{\hbar} P_x \psi\right)$$

$$= -\frac{1}{\hbar^2} P_x^2 \psi$$

$\Rightarrow$

$$P_x^2 \psi = -\hbar^2 \frac{\partial^2 \psi}{\partial x^2} \quad \text{--- (3)}$$

Again diff. $\psi$ w.r.t $t$ & we get

$$\frac{\partial \psi}{\partial t} = A\left(\frac{i}{\hbar}\right)(-E) e^{i/\hbar(P_x x - Et)}$$

$$= -\frac{i}{\hbar} E \psi$$

$$= \frac{E\psi}{i\hbar}$$

$$\Rightarrow E\psi = i\hbar \frac{\partial \psi}{\partial t}$$

$$\Rightarrow \frac{P_x^2}{2m} \psi = i\hbar \frac{\partial \psi}{\partial t}$$

$$\therefore P_x^2 \psi = 2m\, i\hbar \frac{\partial \psi}{\partial t} \quad \text{--- (4)}$$

From eqn 3 & 4 we get,

$$-\hbar^2 \frac{\partial^2 \psi}{\partial x^2} = 2m i\hbar \frac{\partial \psi}{\partial t}$$

$$\therefore \boxed{-\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} = i\hbar \frac{\partial \psi}{\partial t}}$$

→ This is one dimensional time depend schrödinger eqn for a free particle.

Particle moving in a force field

If the particle of mass m moves with velocity v in a path V then its total energy is

$$E = \frac{P_x^2}{2m} + V \quad \text{or,} \quad \frac{P_x^2}{2m}\psi + V\psi = E\psi \quad \text{--- (1)}$$

Scanned by CamScanner

The wave function representing the particle is

$$\psi(x,t) = A e^{i/\hbar (P_x x - Et)} \quad \text{—— (2)}$$

Diff. twice w.r.t $x$ we get

$$\frac{\partial^2 \psi}{\partial x^2} = -\frac{1}{\hbar^2} P_x^2 \psi$$

$$\Rightarrow P_x^2 \psi = -\hbar^2 \frac{\partial^2 \psi}{\partial x^2} \quad \text{—— (3)}$$

again, diff. w.r.t $t$

$$\frac{\partial \psi}{\partial t} = \frac{E\psi}{i\hbar}$$

$$\Rightarrow E\psi = i\hbar \frac{\partial \psi}{\partial t} \quad \text{—— (4)}$$

Substituting the values of $P_x^2 \psi$ and $E\psi$ in eqn. (1) we get,

$$\boxed{-\frac{\hbar^2}{2m}\frac{\partial^2 \psi}{\partial x^2} + V\psi = i\hbar \frac{\partial \psi}{\partial t}}$$

→ This is the schrödinger's time dependent wave eqn for a particle moving in a poth $V$.

## Three dimensional Schrödinger eqn

The wave function is give by

$$\psi(\vec{r}, t) = A e^{-i/\hbar (\vec{P}\cdot\vec{r} - Et)}$$

here, $P$ is the momentum and $E$ the total energy of the particle.

$$E = \frac{P^2}{2m} + V(\vec{r}, t)$$

$$\Rightarrow E\psi = \frac{1}{2m}(P_x^2 + P_y^2 + P_z^2)\psi + V(\vec{r}, t)\psi$$

$\psi(\vec{r},t) = A e^{i/\hbar (P_x x + P_y y + P_z z - Et)}$

$\therefore$ Diff w.r.t $x$ we get

$$\frac{\partial \psi}{\partial x} = A\left(\frac{i}{\hbar}\right) P_x e^{i/\hbar (P_x x + P_y y + P_z z - Et)}$$

$$= \frac{i}{\hbar} P_x \psi$$

& $$\frac{\partial^2 \psi}{\partial x^2} = \frac{i}{\hbar} P_x \frac{\partial \psi}{\partial x}$$

$$= \left(\frac{i}{\hbar} P_x\right)\left(\frac{i}{\hbar} P_x\right)\psi$$

$$= -\frac{P_x^2}{\hbar^2}\psi$$

$$\therefore P_x^2 \psi = -\hbar^2 \frac{\partial^2 \psi}{\partial x^2}$$

Similarly $P_y^2 \psi = -\hbar^2 \frac{\partial^2 \psi}{\partial y^2}$

& $P_z^2 \psi = -\hbar^2 \frac{\partial^2 \psi}{\partial z^2}$

& Diff. w.r.t $t$ we get

$$\frac{\partial \psi}{\partial t} = A\left(\frac{i}{\hbar}\right)(-E) e^{i/\hbar (P_x x + P_y y + P_z z - Et)}$$

$$= -\left(\frac{i}{\hbar}\right) E \psi$$

$$\therefore E\psi = -\frac{\hbar}{i}\frac{\partial \psi}{\partial t} = i\hbar \frac{\partial \psi}{\partial t}$$

$$\therefore -\frac{\hbar^2}{2m}\left(\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2}\right) + V(\vec{r},t)\psi = i\hbar \frac{\partial \psi}{\partial t}$$

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

here, $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$

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

here, $\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r},t) \rightarrow$ 3D Harmiltonian operator