1

(B) Schrödinger Eq^n (A basic physical principle that cannot be derived from anything else)

Time-dependent form:-

The wavefunction ψ for a particle moving freely in the $+x$-direction is specified by

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

wave vector $k = \frac{p_x}{\hbar}$, $\omega = \frac{E}{\hbar}$

$$\boxed{\psi(x,t) = A e^{\frac{i}{\hbar}(p_x x - Et)}} \quad \text{--- (2)}$$

or $A e^{-\frac{i}{\hbar}(Et - p_x x)}$

$E = h\nu$
$2\pi E = 2\pi h\nu$
$\frac{2\pi E}{h} = 2\pi\nu$
$\frac{E}{\hbar} = \omega$

$k = \frac{2\pi}{\lambda}$
$\lambda = \frac{h}{p}$
$k = \frac{2\pi p}{h}$
$= p/\hbar$

This eq^n describes the wave equivalent of an unrestricted particle of total energy E and momentum p moving in the $+x$ direction.

Eq^n (2) correct only for freely moving particles.

However we are most interested in situations where the motion of a particle is subject to various restriction.

e.g., • electron bound to an atom by the electric field of its nucleus.
• particle in a box.

Fundamental diff eq^n of ψ, which we can then solve for ψ in specific situation

Schrödinger eq^n

Differentiating eq^n (2), twice, w.r.to x.

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

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

$-i\hbar\frac{\partial}{\partial x}$

$E = \frac{p^2}{2m} + V(x,t)$

$E\psi = \frac{p^2}{2m}\psi + U\psi$

Differentiating eq^n ② w.r. to t

$$\frac{\partial \psi}{\partial t} = -\frac{iE}{\hbar}\psi$$

$$E\psi = -\frac{\hbar}{i}\frac{\partial \psi}{\partial t} \quad \text{or} \quad \hbar i\frac{\partial \psi}{\partial t} \quad \text{--- ④}$$

or
now ope
operator
$+i\hbar\frac{\partial}{\partial t}$ on ψ

At speeds small compared with that of light, the total energy E of a particle is sum of its kinetic energy $\frac{p^2}{2m}$ and its potential energy U.

$$E = \frac{p^2}{2m} + U(x,t) \quad \text{--- ⑤}$$

multiplying both side of eq^n ⑤ by ψ.

$$E\psi = \frac{p^2}{2m}\psi + U\psi \quad \text{--- ⑥}$$

Now if we put $E\psi$ and $p^2\psi$ from previous eq^{n}s

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

→ Time-dep. Schrödinger eq^n in one-dimension.

In three dimensions.

$$i\hbar\frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m}\left[\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2}\right] + U\psi$$

Schrödinger's Eqⁿ :- Steady-State form (Time independent form)

In a many situations the potential energy of a particle does not depend on time explicitly; the forces that act on it, and hence U, vary with the position of the particle only,

$\Downarrow$

Schrödinger eqⁿ may be simplified by removing all reference to t.

$$\psi = A e^{\frac{i}{\hbar}(p_x x - Et)} \quad \text{or} \quad A e^{-\frac{i}{\hbar}(Et - p_x x)}$$

$$= \underbrace{A e^{\frac{i}{\hbar}\frac{p_x x}{\hbar}}} e^{-\frac{iE}{\hbar}t}$$

$$\psi = \psi' e^{-\frac{iE}{\hbar}t} \quad \text{--- (7)}$$

ψ' ↓ position dep. only

Subsituting this eqⁿ into time dependent Schrödinger eqⁿ

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

E

$$E\psi e^{-\frac{iEt}{\hbar}} = -\frac{\hbar^2}{2m} e^{-\left(\frac{iE}{\hbar}\right)t} \frac{\partial^2 \psi}{\partial x^2} + U \psi e^{-\left(\frac{iE}{\hbar}\right)t}$$

$E\psi$ ↓ pos. dep — $U\psi$ ↓ pos. dep.

Dividing through by the common exponential facter gives

$$\boxed{\frac{\partial^2 \psi}{\partial x^2} + \frac{2m}{\hbar^2}(E-U)\psi = 0}$$

ψ ↓ position dep.

Steady-State Schrödinger eqⁿ in one dimension

In three dimensions

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

Eigen values and Eigen functions:-

$$H\psi = E\psi$$

H ↓ operator, E ↓ eigenvalues

The value of energy E_n for which Schrödinger steady-State eqn can be solved are called eigenvalues and corresponding wave function ψ_n are called eigenfunctions

Q:- An eigenfunction of the operator $\frac{d^2}{dx^2}$ is $\psi = e^{2x}$, Find the corresponding eigen value.

Soln

$$\frac{d^2}{dx^2}(e^{2x}) = \frac{d}{dx}(2e^{2x}) = \underset{\text{eigenvalue}}{4}\ \underset{\psi}{e^{2x}}$$

$| H\psi = E\psi$

Q:- The eigenfunction of the operator $\left(\frac{d^2}{dx^2} + 2\frac{d}{dx}\right)$ is e^{3x}. Find its corresponding eigenvalues.

Soln

$$\left(\frac{d^2}{dx^2} + 2\frac{d}{dx}\right)e^{3x}$$

$$9e^{3x} + 6e^{3x}$$

$$= 15e^{3x}$$

$$= E\psi$$

↓ eigenvalue $\underline{15}$

4-4

Postulates of Quantum Mechanics

wave function

Postulate 1:-

"The state of a quantum mechanical system is completely specified by a function $\psi(r,t)$ that depends on the co-ordinates of the particle (s) and on time."

$\downarrow$

This function, called the wave function or state function, has important property that $\psi^*(r,t)\,\psi(r,t)\,d\tau$ is the probability that the particle lies in the volume $d\tau$ located at ~~t~~ r and at time t.

$\downarrow$ Also normalization condition

$$\int_{-\infty}^{\infty} \psi^*(r,t)\ \psi(r,t)\ d\tau = 1$$

orthonormal

$\int \psi_m^*(x)\,\psi_n(x)\,dx = \delta_{mn}$ orthogonal

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

$\downarrow$

Kronecker delta

operator

Postulate 2:-

"To every observable in classical mechanics there corresponds a linear, Hermitian operator in quantum mechanics."

$\downarrow$ Real eigen value

$\hat{A}^{+} = \hat{A}$ (Hermitian)

$\hat{A}^{+} = -\hat{A}$ (anti-Hermitian)

Observable name (symbol)		operator symbol	operator
Position	(r)	$\hat{r}$	r
momentum	(p)	$\hat{p}$	$-i\hbar \frac{\partial}{\partial x}$
energy of the particle	(E)	$\hat{E}$	$i\hbar \frac{\partial}{\partial t}$
kinetic energy	(T)	$\hat{T}$	$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$
Potential energy	$(V(r))$	$\hat{V}(r)$	$V(r)$
Total energy	E	$\hat{H}$	$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}\right) + V(r)$
Angular momentum	l_x	$\hat{l}_x$	$-i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)$
	l_y	$\hat{l}_y$	$-i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)$
	l_z	$\hat{l}_z$	$-i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$

eigen value **Postulate 3:-**

"In any measurement of the observable associated with operator $\hat{A}$, the only values that will be observed are the eigen-values a, which satisfy the eigenvalue eqn.

$$\hat{A}\psi = a\psi$$ "

↓

quantized value.

expectation value **Postulate 4:-** "If ~~there~~ a system is in a state described by a normalized wave function ψ, then the average value of the observable corresponding to $\hat{A}$ is given by"

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

Time evolution of a system **Postulate 5:-** "The wavefunction or state function of a system evolves in time according to the time-dependent Schrödinger eqn

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

↓

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

$\nabla \Rightarrow$ Laplacian operator

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

Postulate 6:- "The total wavefunction must be antisymmetric with respect to the interchange of all coordinates of one fermion with those of another."

The Pauli exclusion principle is a direct result of this antisymmetric principle.

Symmetric $\psi(r_1, r_2) = \psi(r_2, r_1)$ → Boson (integral spin) e.g. electron

anti-symmetric $\psi(r_1, r_2) = -\psi(r_2, r_1)$ → Fermion: (half-integral spin)

"No two fermions occupy the same state."

↓

But Boson may occupy

Physical interpretation of ψ and the Probability current density:-

Probability current density
Conservation of probability
continuity eq^n.

The time dependent Schrödinger eq^n for a particle in a field characterized by the potential energy function $V(r,t)$:

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

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

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

$$i\hbar\frac{\partial\psi}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\psi + V\psi \quad \text{---}(1)$$

and its complex conjugate

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

multiplying eq^n (1) by ψ^* and eq^n (2) by ψ and substracting (1) - (2)

$$i\hbar\left[\psi^*\frac{\partial\psi}{\partial t} + \psi\frac{\partial\psi^*}{\partial t}\right] = -\frac{\hbar^2}{2m}\left[\psi^*\nabla^2\psi - \psi\nabla^2\psi^*\right] \quad \text{---}(3)$$

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

We can rewrite eq^n (3) in the form

$$\frac{\partial}{\partial t}(\psi^*\psi) + \left[\frac{\partial J_x}{\partial x} + \frac{\partial J_y}{\partial y} + \frac{\partial J_z}{\partial z}\right] = 0 \quad \text{--}(4)$$

Where
$$J_x = \frac{i\hbar}{2m}\left[\psi\frac{\partial\psi^*}{\partial x} - \psi^*\frac{\partial\psi}{\partial x}\right]$$
$$J_y = \frac{i\hbar}{2m}\left[\psi\frac{\partial\psi^*}{\partial y} - \psi^*\frac{\partial\psi}{\partial y}\right]$$
$$J_z = \frac{i\hbar}{2m}\left[\psi\frac{\partial\psi^*}{\partial z} - \psi^*\frac{\partial\psi}{\partial z}\right]$$

Eq^n (4) can be written in the form

$$\underbrace{\boxed{\frac{\partial\rho(\bar{r},t)}{\partial t} + \vec{\nabla}\cdot\vec{J} = 0}}_{\text{(Conservation of probability)}} \quad \text{---}(5) \rightarrow \text{Continuity eqn}$$

$$\vec{\nabla}\cdot\vec{J} = -\frac{\partial\rho}{\partial t}$$
Charge Conservation in electrodynamics

$\rho(\bar{r},t)$ $(\psi^*\psi)$ $\rightarrow$ Probability density $\rightarrow$ The number of particles per unit volume.

$\bar{J}(\bar{r},t)$ $\rightarrow$ Probability current density / ~~probability~~ or simply current density (~~or~~ particle density flux)

Probability current density → (Conservation of probability)

It should give information about the no. of particles crossing unit area per unit time.

$\rho = \psi^* \psi$ --- (6)

$\bar{J} = \frac{i\hbar}{2m} [\psi \nabla \psi^* - \psi^* \nabla \psi]$ -- (7)

$$\bar{J} = \frac{i\hbar}{2m} [\psi \nabla \psi^* - \psi^* \nabla \psi] = Re\left[\psi^* \frac{\hbar}{im}\right] \nabla \psi \text{ -- (9)}$$

$$\cancel{= Re\left[\psi^* \frac{\hbar}{im}\right] \psi}$$

$$\bar{J} = Re\,[\psi^* \bar{v} \psi] \text{ -- (10)}$$

$p = \frac{\hbar}{i} \nabla$

$= -i\hbar \nabla$

Velocity Operator $\bar{v} = \frac{\bar{p}}{m}$

eqn (6) and (10) are consistent with the fact that in fluid dynamics

$$\boxed{\vec{J} = \rho \vec{v}}$$

Q:- Find probability current density in case a particle is in state

a) $\psi(x,t) = A \sin kx \, e^{-\frac{i\hbar k^2 t}{2m}}$

b) $\psi(x,t) = A e^{i\left(kx - \frac{\hbar k^2 t}{2m}\right)}$

Soln:-

$$J(x,t) = Re\left[\psi^*(x,t) \frac{\hbar}{im} \frac{d}{dx} \psi(x,t)\right]$$

(a) $$J(x,t) = Re\left[A \sin kx \, e^{\left(\frac{i\hbar k^2}{2m}\right)t} \left(\frac{\hbar}{im}\right) Ak \cos kx \, e^{-\left(\frac{i\hbar k^2}{2m}\right)t}\right]$$

$$= Re\left[A^2 \sin kx \cos kx \left(\frac{\hbar k}{im}\right)\right]$$

$$= 0$$

(b) $$J(x,t) = Re\left[A e^{-i\left(kx - \frac{\hbar k^2 t}{2m}\right)} \left(\frac{\hbar}{im}\right) A (ik) e^{i\left(kx - \frac{\hbar k^2 t}{2m}\right)}\right]$$

$$= A^2 \frac{\hbar k}{m}$$ Ans