Quantum Mechanics

According to de-Broglie hypothesis, whenever a material particle is in motion, a wave is associated with it.

material means nonzero rest mass.
motion means position of the particle is changing w.r.t. something or we can say particle is not at rest
[i.e we are not talking about photons, whose rest mass is zero]
or we are talking about matter i.e e^-, proton, neutron etc. whose rest mass $\neq 0$.
wave means something is changing whose change is creating a wave, and we call it wavefn Ψ. eg in case of em waves, Ψ is electric field or mag field. $\Psi(x y z t)$. Then what is changing in de-Broglie waves?
It is actually the probability to locate the particle at $(x y z t)$ per unit volume that is changing & this change will generate a wave.

We can consider the example of a moving football in ground. Football is continuously moving in ground, so probability to locate football at a given point xyz & time t is changing all the time. This change in probability is going to generate a wave, associated with motion of football.

In general, we represent the wave fn. as $\psi(xyzt) = A e^{-i(\omega t - \vec{k}\cdot\vec{r})}$

for 1-D motion,

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

To be more specific, ~~to~~ discuss motion alone, we can take consider only real part of the wave fn. i.e

$$\psi(x,t) = A \sin(\omega t - kx)$$

Now wave fn. can have both positive & negative values but probability can have only positive values $(0 < P < 1)$.

therefore we say It is the square of the absolute value of Ψ which is proportional to the prob. to locate the particle per unit volume and not the wave fn. itself.

$$\therefore \rho(x,y,z,t) \propto |\Psi|^2$$

$\downarrow$

prob./volume

(prob. density)

This statement is known as Max Born's interpretation of wave fn. Ψ.

In quantum mechanics, we discuss the motion ~~have to apply~~ of microscopic particles (eg electron). So, we have to apply uncertainty principle to discuss the motion.

& Uncertainty means the parameter cannot be measured with 100% certainty, we have to talk in terms of $x \pm \Delta x$, $p \pm \Delta p$. Since values are not certain, they keep on changing and we take the help of probability.

<u>Operator</u> → set of mathematical rules which when act on some function, change its value or form.

eg $\frac{d}{dx}\sin x = \cos x$

∴ In quantum mech., to every physical quantity, there is associated a corresponding operator, which will act on wavefunction.

i.e values of x, p, E may keep on changing in QM (as nothing can be measured with certainty), so these ~~op~~ physical quantities have their corresponding operators.

$\wedge$ → symbol of operator

$\wedge$ → symbol of operator

$\hat{x} = x$

$\hat{E} = i\hbar\frac{\partial}{\partial t}$ (motion is time dependent)

$\hat{E} = \hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + U$ (motion is time independent)

$\hat{H}$ is known as Hamiltonian Operator

& $\hat{p}_x = -i\hbar\frac{\partial}{\partial x}$

Given $\psi(x,t) = A e^{-i(\omega t - kx)}$ — ① (5)

$$\Rightarrow \psi(x,t) = A e^{-\frac{i}{\hbar}(Et - px)}$$

$$\frac{\partial \psi}{\partial t} = -\frac{i}{\hbar} E A e^{-\frac{i}{\hbar}(Et - px)}$$

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

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

$$\Rightarrow \boxed{\hat{E} = i\hbar \frac{\partial}{\partial t}}$$ time dependent

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

$$\omega = \frac{E}{\hbar} \quad \text{where } \hbar = \frac{h}{2\pi}$$

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

$$\frac{\partial \psi}{\partial x} = \frac{i}{\hbar} p \psi \quad \text{—②}$$

$$\Rightarrow p\psi = -i\hbar \frac{\partial \psi}{\partial x}$$

$$\Rightarrow \hat{p}_x = -i\hbar \frac{\partial}{\partial x}, \quad \hat{p}_y = -i\hbar \frac{\partial}{\partial y}, \quad \hat{p}_z = -i\hbar \frac{\partial}{\partial z}$$

differentiating ② again w.r.t x

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

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

$$\Rightarrow \hat{p}_x^2 = -\hbar^2 \frac{\partial^2}{\partial x^2}$$

When motion is time independent (eg electron ~~~~ revolving around the nucleus in a given orbit) and speed is very less than 'c' (i.e nonrelativistic speeds)

then $E = KE + PE$

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

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

$\Rightarrow \hat{E}\psi = -\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} + U\psi$ $\quad \hat{U} = U$ (scalar)

$\hat{p}^2 = -\hbar^2\frac{\partial^2}{\partial x^2}$

$\Rightarrow \hat{E} = \hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + U$ $\quad m = m_0 =$ rest mass.

Hamiltonian Operator

Hamiltonian op $\hat{H}$ is energy op. when motion is time independent & non relativistic. If particle is free, $U = 0$, $\quad \hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$

For free particle, we consider only K.E and P.E. = 0

For restricted particle, E = KE + PE
i.e. P.E. ≠ 0

Also note when $v \to c$, then motion is relativistic and if $v << c$, then motion is non relativistic

---

When we say total probability to locate particle in this universe is one it means

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} P\,dV = 1$$

$P \propto |\psi|^2$

$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \to$ represents Universe

if $P = |\psi|^2$

$P \to \frac{\text{prob.}}{\text{volume}}$

then $\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} |\psi|^2 dV = 1$ This condition is known as Normalization of wave fn. ψ.

for 1-D case $\int_{-\infty}^{\infty} |\psi|^2 dx = 1$ then $P = \frac{\text{prob.}}{\text{length}}$

Significance of Normalization → It ensures particle is present in universe and calculations done related to particle will not go in waste. Secondly it helps us to find the value of unknown constant A in the expression of ψ.

Conditions to be satisfied by a wave fn. ψ so that it becomes well behaved or acceptable : ① ψ must be normalizable. i.e $\int_{-\infty}^{\infty} |\psi|^2 dx = 1$
(1-D motion)

② ψ & its partial derivatives $\left(\frac{\partial \psi}{\partial x}, \frac{\partial \psi}{\partial y}, \frac{\partial \psi}{\partial z}\right)$ must be single valued, finite valued and continuous.

③ when $x \to \pm\infty$, $\psi(x) \to 0$.

Eigen fn. & Eigen operator → If $\hat{X}$ is some operator acting on wavefn. ψ such that in answer we get a constant A multiplied by wave fn. ψ, i.e. $\hat{X}\psi = A\psi$, ①

Eigen → (means proper)

then $\hat{X}$ is known as eigen operator
ψ is known as eigen fn.
A is known as eigen value
& eqn ① is known as eigen eqn.

eg $\frac{d}{dx} e^{2x} = 2e^{2x}$

$\frac{d}{dx}$ → eigen op.
e^{2x} → eigen fn.
2 → eigen value.

Time Independent Schrodinger eqn for a restricted particle in 1-D:- Let a particle of rest mass m be moving along $+x$-axis. Then acc. to de-Broglie hypothesis, a wave is associated with the motion of particle. Let $\psi(x,t)$ be the wave fn. describing the wave. Then $\psi(x,t) = A e^{-i(\omega t - kx)}$ — ①

and eqn. of motion of a progressive wave can be written as

$$\frac{\partial^2 \psi}{\partial x^2} - \frac{1}{u^2}\frac{\partial^2 \psi}{\partial t^2} = 0, \quad \psi = \psi(x,t) \quad \text{— ②}$$

& $u \rightarrow$ phase velocity or wave velocity

Also note $u = \nu\lambda = \frac{\omega}{k}$ $\quad \omega = 2\pi\nu$, $k = \frac{2\pi}{\lambda}$

∴ ② becomes $\frac{\partial^2 \psi}{\partial x^2} - \frac{k^2}{\omega^2}\frac{\partial^2 \psi}{\partial t^2} = 0$ — ③

Now from ① $\psi(x,t) = A e^{-i\omega t} e^{ikx}$

$$\Rightarrow \psi(x,t) = \underbrace{A e^{ikx}}_{\phi(x)} e^{-i\omega t}$$

$$\Rightarrow \psi(x,t) = \phi(x) e^{-i\omega t}$$

where $\phi(x) = A e^{ikx}$ [space dependent]

& $e^{-i\omega t} \rightarrow$ time dependent term

(Separation of variables)

$\therefore\ \psi(x,t) = \phi(x)\, e^{-i\omega t}$

$$\frac{\partial \psi}{\partial x} = \frac{d\phi}{dx} e^{-i\omega t} \Rightarrow \frac{\partial^2 \psi}{\partial x^2} = \frac{d^2\phi}{dx^2} e^{-i\omega t}$$

& $$\frac{\partial \psi}{\partial t} = -i\omega\, \phi(x) e^{-i\omega t} \Rightarrow \frac{\partial^2 \psi}{\partial t^2} = (-i\omega)^2 \phi(x) e^{-i\omega t}$$
$$= -\omega^2 \phi(x) e^{-i\omega t}$$

Substituting these values in eqn. (3), we get

$$\frac{d^2\phi(x)}{dx^2} e^{-i\omega t} + \omega^2 \frac{k^2}{\omega^2} \phi(x) e^{-i\omega t} = 0$$

$$\Rightarrow \left[\frac{d^2\phi(x)}{dx^2} + k^2 \phi(x)\right] e^{-i\omega t} = 0$$

as $e^{-i\omega t} \neq 0$

$$\therefore\ \frac{d^2\phi(x)}{dx^2} + k^2 \phi(x) = 0 \qquad \lambda = \frac{h}{p}$$

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

we have $$\frac{d^2\phi(x)}{dx^2} + \frac{p^2}{\hbar^2}\phi(x) = 0.$$

Now $E = \frac{p^2}{2m} + U \Rightarrow p^2 = 2m(E-U)$

$$\therefore\ \boxed{\frac{d^2\phi(x)}{dx^2} + \frac{2m}{\hbar^2}(E-U)\phi(x) = 0 \quad (4)}$$

This is Time independent Schrodinger eqn. for a restricted particle for 1-D motion.

For 3-D motion, it will be

$$\nabla^2 \phi(xyz) + \frac{2m}{\hbar^2}(E-U)\phi(xyz) = 0.$$

For free particle, $U = 0$

$$\therefore \frac{d^2\phi(x)}{dx^2} + \frac{2m}{\hbar^2} E\phi(x) = 0$$

or $$\nabla^2 \phi(xyz) + \frac{2mE}{\hbar^2}\phi(xyz) = 0$$

We can replace symbol ϕ with ψ, but then ψ will be fn of (xyz) or x only and not time t.

$\therefore$ Time independent Sch. eqn. is

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}(E-U)\psi(x) = 0 \qquad \psi = \psi(x)$$

$$\Rightarrow \frac{2m}{\hbar^2}(E-U)\psi(x) = -\frac{d^2\psi}{dx^2}$$

$$\Rightarrow (E-U)\psi(x) = \frac{-\hbar^2}{2m}\frac{d^2\psi}{dx^2}$$

$$\Rightarrow E\psi(x) = -\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + U\psi(x)$$

$$\Rightarrow E\psi(x) = \left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + U\right]\psi(x)$$

$$\Rightarrow E\psi(x) = \hat{H}\psi(x)$$

where $\hat{H}$ is Hamiltonian op. for time independent motion.

i.e now we have $\hat{H}\psi = E\psi$ which is eigen eqn., E is energy eigen value and ψ is eigen wave function.

$\therefore$ Time Indepedent Sch. eqn. can be written as $\hat{H}\psi = E\psi$.

Time dependent Schrodinger Eqn.

for time dependent motion

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

Now time independent Sch. eqn. is

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

multiplying both sides by $e^{-i\omega t}$

$$\frac{d^2\psi(x)}{dx^2} e^{-i\omega t} + \frac{2m}{\hbar^2}(E-U)\psi(x)e^{-i\omega t} = 0$$

$$\Rightarrow \frac{d^2\psi(x,t)}{dx^2} + \frac{2m}{\hbar^2}(E-U)\psi(x,t) = 0$$

where

$$\psi(x,t) = \psi(x)e^{-i\omega t}$$

$$\Rightarrow E\psi(x,t) = -\frac{\hbar^2}{2m}\frac{d^2\psi(x,t)}{dx^2} + U\psi(x,t)$$

Now $\hat{E} = i\hbar\frac{\partial}{\partial t}$

$\therefore$ Time dependent Sch. eqn. will be

$$\hat{E}\psi(x,t) = -\frac{\hbar^2}{2m}\frac{d^2\psi(x,t)}{dx^2} + U\psi(x,t)$$

or $$i\hbar\frac{\partial\psi(x,t)}{\partial t} = -\frac{\hbar^2}{2m}\frac{d^2\psi(x,t)}{dx^2} + U\psi$$

for 3-D motion, it will be

$$i\hbar\frac{\partial\psi(xyzt)}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\psi(xyzt) + U\psi(xyzt)$$

For free particle put $U=0$.

i.e $$i\hbar\frac{\partial\psi(x,t)}{\partial t} = -\frac{\hbar^2}{2m}\frac{d^2\psi(x,t)}{dx^2} \quad (1\text{-D})$$

or $$i\hbar\frac{\partial\psi(x,t)}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\psi(x,t) \quad (3\text{-D})$$