6.2 THE TIME-DEPENDENT SCHRÖDINGER EQUATION

To begin with, we consider the one-dimensional motion of a free particle of mass m, moving in the positive x direction with momentum p and energy E. Such a particle can be described by the monochromatic plane wave

$$\Psi(x, t) = A\, e^{i(px - Et)/\hbar} \tag{6.1}$$

where A is a constant. Differentiating with respect to t, we have

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

or

$$i\hbar\frac{\partial \Psi}{\partial t} = E\Psi \tag{6.2}$$

Differentiating twice with respect to x, we have

$$-i\hbar\frac{\partial \Psi}{\partial x} = p\Psi \tag{6.3}$$

and

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

or

$$-\frac{\hbar^2}{2m}\frac{\partial^2 \Psi}{\partial x^2} = \frac{p^2}{2m}\Psi \tag{6.4}$$

Now, for a nonrelativistic free particle

$$E = \frac{p^2}{2m} \tag{6.5}$$

Therefore, (6.2), (6.4) and (6.5) give

$$\boxed{i\hbar\frac{\partial \Psi(x,t)}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2 \Psi(x,t)}{\partial x^2}} \tag{6.6}$$

This is the *one-dimensional time-dependent Schrödinger equation for a free particle*.

Since (6.6) is linear and homogeneous, it will also be satisfied by the wave packet

$$\Psi(x,\ t) = \frac{1}{\sqrt{2\pi\hbar}} \int \phi(p)\, e^{i(px-Et)/\hbar}\, dp \tag{6.7}$$

which is a linear superposition of plane waves and is associated with a 'localised' free particle. We have

$$i\hbar\frac{\partial\Psi(x,t)}{\partial t} = \frac{1}{\sqrt{2\pi\hbar}} \int E\phi(p)\, e^{i(px-Et)/\hbar}\, dp$$

and

$$-\frac{\hbar^2}{2m}\frac{\partial^2\Psi(x,t)}{\partial x^2} = \frac{1}{\sqrt{2\pi\hbar}} \int \frac{p^2}{2m}\phi(p)\ e^{i(px-Et)/\hbar}\, dp$$

Using (6.5), the right hand sides of the above two equations are equal, and hence we obtain (6.6).

It is clear that the Schrödinger equation for a free particle satisfies the three restrictions that we mentioned in section 6.1. To see how it satisfies the correspondence principle, we note that this equation is, in a sense, the quantum mechanical 'translation' of the classical equation (6.5), where the energy E, and the momentum p are represented by **differential operators**[†]

$$\boxed{\hat{E} = i\hbar\frac{\partial}{\partial t}} \tag{6.8}$$

and

$$\boxed{\hat{p} = -i\hbar\frac{\partial}{\partial x}} \tag{6.9}$$

respectively, acting on the wave function:

$$\hat{E}\,\Psi(x,\ t) = \frac{\hat{p}^2}{2m}\Psi(x,\ t) \tag{6.10}$$

As we shall see later, it is a *postulate* of quantum mechanics that even when the particle is not free, E and p are still represented by the operators in (6.8) and (6.9), respectively.

The above treatment can be easily extended to three dimensions. Instead of (6.1), the expression for the plane wave is

$$\Psi(\mathbf{r},\ t) = Ae^{i(\mathbf{p}\cdot\mathbf{r}-Et)/\hbar} \tag{6.11}$$

The operator representation of **p** would be

$$\boxed{\hat{\mathbf{p}} = -i\hbar\nabla} \tag{6.12}$$

[†] It is customary to represent a variable and its operator by the same symbol. Wherever there is confusion, a hat is put on the symbol to represent the operator, e.g., $\hat{E}$, $\hat{p}$.

which is equivalent to

$$\boxed{\begin{aligned}\hat{p}_x &= -i\hbar\frac{\partial}{\partial x}\\ \hat{p}_y &= -i\hbar\frac{\partial}{\partial y}\\ \hat{p}_z &= -i\hbar\frac{\partial}{\partial z}\end{aligned}} \tag{6.13}$$

Therefore, the Schrödinger equation becomes

$$\boxed{i\hbar\frac{\partial\Psi(\mathbf{r},t)}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\Psi(\mathbf{r},t)} \tag{6.14}$$

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

Particle in a Force-field

Let us now generalize the free-particle Schrödinger equation (6.14) to the case of a particle acted upon by a force which is derivable from a potential $V(\mathbf{r}, t)$. According to classical mechanics, the total energy of the particle would be given by

$$E = \frac{p^2}{2m} + V(\mathbf{r}, t) \tag{6.15}$$

Since V does not depend on E or p, the above discussion for the free particle suggests that the wave function should satisfy

$$\hat{E}\Psi = \left(\frac{\hat{p}^2}{2m} + V\right)\Psi$$

so that, the Schrödinger equation generalizes to

$$\boxed{\begin{gathered}i\hbar\frac{\partial}{\partial t}\Psi(\mathbf{r},t) = \left(-\frac{\hbar^2\nabla^2}{2m} + V(\mathbf{r},t)\right)\Psi(\mathbf{r},t)\\ \textbf{(Time-dependent Schrödinger equation)}\end{gathered}} \tag{6.16}$$

The operator on the right-hand side is called the *Hamiltonian operator* and is denoted by the symbol H:

$$\boxed{\begin{gathered}H = -\frac{\hbar^2\nabla^2}{2m} + V(\mathbf{r},t)\\ \textbf{(Hamiltonian operator)}\end{gathered}} \tag{6.17}$$

The name follows from the fact that in classical mechanics the sum of the kinetic and the potential energies of a particle is called its *Hamiltonian*.

The Schrödinger Equation (6.16), is the *basic equation* of nonrelativistic quantum mechanics. It must be emphasized that we have *not derived* it. Like

Time Dependent Schrodinger equ. for non Relativistic free Particle (1D)

Total Energy of non relativistic Particle (no external force)

$$E = \frac{1}{2}mv^2 = \frac{p^2}{2m}$$

$\hbar = \frac{2\pi}{h}$

moving Particle associated with wave fre. & wavelength

$E = h\nu$, $\nu = \hbar/h$ $\lambda = h/p$. and $k = P/\hbar$

$$\omega = \frac{E}{\hbar} = \frac{p^2}{2m\hbar} = \frac{\hbar k^2}{2m} \quad \text{--- (1)}$$

wave equ. of plane monochromatic wave

$$\psi(r,t) = A\exp[i(k \cdot r - \omega t)] \quad \text{--- (2)}$$

If we assume the Propogation to be along x axis

$$\psi(x,t) = A\exp[i(kx - \omega t)] \quad \text{--- (3)}$$

from equ (3)

$P = \hbar k$ and $E = \hbar\omega$

$$\psi(x,t) = A\exp\left[\frac{i}{\hbar}(px - Et)\right] \quad \text{--- (4)}$$

So equ (2) & (3) shows the wave fun of plane wave moving along the +ve direction of x axis associated with free particle. By Superposition of such waves a wave packet can be constructed which is the wave function of a localized free particle.

$$\psi(x,t) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} a(p) \exp\left[\frac{i}{\hbar}(px - Et)\right] dP \quad \text{--- (5)}$$

where $a(p)$, the amplitude of the component of momentum P.

$$a(p) = \frac{1}{\sqrt{\pi\hbar}} \int_{-\infty}^{\infty} \psi(x,t) \exp\left[-\frac{i}{\hbar}(px - Et)\right] dx \quad \text{--- (6)}$$

diff. equ. (5) w.r.t. t

$$\frac{d\psi}{dt} = \frac{1}{\sqrt{2\pi\hbar}}\left(\frac{-i}{\hbar}\right)\int_{-\infty}^{\infty} E\, a(p) \exp\left[\frac{i}{\hbar}(px-Et)\right] dp$$

$$\frac{d\psi}{dt} = \frac{-i}{\hbar} E\psi \quad \text{or} \quad \text{from equ } (5)$$

$$i\hbar \frac{\partial\psi}{dt} = E\psi \quad \text{——— } (6)$$

diff equ (5) w.r. to x.

$$\frac{\partial\psi}{\partial x} = \frac{p}{\sqrt{2\pi\hbar}} \cdot \frac{i}{\hbar} \int_{-\infty}^{\infty} a(p) \exp\left[\frac{i}{\hbar}(px-Et)\right] dp$$

Again diff

$$\frac{\partial^2\psi}{\partial x^2} = \frac{p^2}{\sqrt{2\pi\hbar}} \frac{i^2}{\hbar^2} \int_{-\infty}^{\infty} a(p) \exp\left[\frac{i}{\hbar}[px-Et)\right] dp$$

$$-\hbar^2 \frac{\partial^2\psi}{\partial x^2} = p^2\psi \quad \text{——— } (7)$$

for non relativstic free particle

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

so from equ (6) & (7)

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

This is 1D time dependent Schroedinger equ for non relativstic free Particle.

Energy & momentum diff. operator

wave function for plane wave

$$\psi(x,t) = \exp\left[\frac{i}{\hbar}(px-Et)\right]$$

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

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

So. Energy diff operator. & Momentum diff operator

$$E = i\hbar \frac{\partial}{\partial t} \qquad P = -i\hbar \frac{\partial}{\partial x}$$

If external force acting on the particle [Use P.E fun]

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

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

from equ 6 & 7

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

Fourier Transformation of wave function :-

wave packet is constructed by the superposition of a group of wave of slightly diff wave length. we consider 1D wave packet associated with the particle along x axis

$$\psi(x,t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \phi(k)\, e^{i(kx-\omega t)}\, dk$$

$$\psi(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \phi(k)\, e^{ikx}\, dk$$

$$\phi(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \psi(x)\, e^{-ikx}\, dx.$$

Satistical Interpretation of the wave function & Conservation of Probability. :-

If the Particle is described by a wave function $\psi(r,t)$, then the probability of finding the particle, with in the volume element $dr = dx\,dy\,dz$ at the time t, about the point $r = (x,y,z)$ is

$$P(r,t)\,dr = |\psi(r,t)|^2 dr = \psi^*(r,t)\,\psi(r,t)\,dr$$

$$P(r,t) = |\psi(r,t)|^2 = \psi^*(r,t)\,\psi(r,t).$$

Probability of finding the particle some where at time t is unity. So. $\int |\psi(r,t)|^2 dr = 1$

$$P(r,t) = \psi^*(r,t)\,\psi(r,t)$$

$$\frac{\partial}{\partial t}\int P(r,t)\,d\tau = \frac{\partial}{\partial t}\int \psi^*(r,t)\,\psi(r,t)\,d\tau$$

Schroedinger Equ.

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

complex Conjugate

$$-i\hbar\frac{\partial\psi^*}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\psi^* + V\psi^*.$$

$$i\hbar\left[\psi^*\frac{\partial\psi}{\partial t} + \psi\frac{\partial\psi^*}{\partial t}\right] = -\frac{\hbar^2}{2m}\left[\psi^*\nabla^2\psi - \psi\nabla^2\psi^*\right] \quad \text{--- (1)}$$

Consider the time derivative of the integral of $\psi^*\psi$ over a finite volume V

$$\frac{\partial}{\partial t}\int_V \psi^*\psi\,d\tau = \int_V \left[\left(\psi^*\frac{\partial\psi}{\partial t} + \psi\frac{\partial\psi^*}{\partial t}\right)\right]d\tau$$

from equ (1)

$$= \frac{i\hbar}{2m}\int_V \left[\left(\psi^*\nabla^2\psi - \psi\nabla^2\psi^*\right)\right]d\tau$$

$$= \frac{-i\hbar}{2m}\int_V \nabla\cdot\left(\psi^*\nabla\psi - \psi\nabla\psi^*\right)dr$$

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

$$\frac{\partial}{\partial t}\int_V P(r,t)\,dr = -\int_V \nabla\cdot J\,dr$$

Using Green's theoram

$$\boxed{\frac{\partial}{\partial t}\int_V P(r,t)\,dr = -\int_S J\cdot dS}$$

$$\frac{\partial}{\partial t}\int_V \psi^*\psi\,d\tau = \frac{-i\hbar}{2m}\int_V \left(\psi\nabla^2\psi^* - \psi^*\nabla^2\psi + \nabla\psi^*\nabla\psi - \nabla\psi\cdot\nabla\psi^*\right)d\tau$$

we have

$$\nabla\cdot(fA) = f(\nabla\cdot A) + A(\nabla\cdot f)$$

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