3.4 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

$$\Psi(x,\ t) = A\, e^{i(px-Et)/\hbar} \qquad \ldots(3.1)$$

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

$$\frac{\partial \Psi}{\partial t} = -\frac{iE}{\hbar}\Psi \qquad \ldots(3.2)$$

or

$$i\hbar\frac{\partial \Psi}{\partial t} = E\Psi \qquad \ldots(3.3)$$

Differentiating twice with respect to x, we have

$$-i\hbar\frac{\partial \Psi}{\partial x} = p\Psi \qquad \ldots(3.4)$$

and

$$-\hbar^2\frac{\partial^2 \Psi}{\partial x^2} = p^2\Psi \qquad \ldots(3.5)$$

or

$$-\frac{\hbar^2}{2m}\frac{\partial^2 \Psi}{\partial x^2} = \frac{p^2}{2m}\Psi \qquad \ldots(3.6)$$

Now, for a nonrelativistic free particle

$$E = \frac{p^2}{2m} \qquad \ldots(3.7)$$

Therefore;

$$\boxed{i\hbar\frac{\partial \Psi(x,t)}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2 \Psi(x,t)}{\partial x^2}} \qquad \ldots(3.8)$$

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

Since the Schrodinger equation is linear and homogeneous, it will also be satisfied by the wave packet

$$\Psi(x,\ t) = \frac{1}{\sqrt{2\pi\hbar}}\int \phi(p)\, e^{i(px-Et)/\hbar}\, dp \qquad \ldots(3.9)$$

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

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

The righthand sides of the above two equations are equal, (where $E = \frac{p^2}{2m}$) and hence we obtain equation (3.8).

To see how it satisfies the **correspondence principle**, we note that this equation is the quantum mechanical 'translation' of the classical equation ($E = \frac{p^2}{2m}$), where the energy E, and the momentum p are represented by differential operators

$$\boxed{\begin{aligned}\hat{E} &= i\hbar\frac{\partial}{\partial t}\\ \hat{p} &= -i\hbar\frac{\partial}{\partial x}\end{aligned}} \qquad \ldots(3.10)$$

and

respectively, acting on the wave function:

$$\hat{E}\,\Psi(x,\ t) = \frac{\hat{p}^2}{2m}\Psi(x,\ t) \qquad \ldots(3.11)$$

The expression for the plane wave in three dimensions

$$\Psi(\mathbf{r},\ t) = Ae^{i(\mathbf{p}\cdot\mathbf{r}-Et)/\hbar} \qquad \ldots(3.12)$$

The **operator representation** of **p** would be

$$\boxed{\hat{\mathbf{p}} = -i\hbar\nabla} \qquad \ldots(3.13)$$

which is equivalent to

$$
\boxed{\begin{aligned}\hat{p}_x &= -i\hbar\frac{\partial}{\partial x}\\ \hat{p}_y &= -i\hbar\frac{\partial}{\partial y}\\ \hat{p}_z &= -i\hbar\frac{\partial}{\partial z}\end{aligned}} \qquad \ldots(3.14)
$$

Therefore, the Schrödinger equation becomes

$$
\boxed{i\hbar\frac{\partial\Psi(\mathbf{r},t)}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\Psi(\mathbf{r},t)} \qquad \ldots(3.15)
$$

where

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

3.5 Particle in a Force-field

The case of a particle acted by a force which is derivable from a potential V(r, t). According to classical mechanics, the total energy of the particle would be given by;

$$
E = \frac{p^2}{2m} + V(\mathbf{r},\ t) \qquad \ldots(3.16)
$$

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

$$
\hat{E}\Psi = \left(\frac{\hat{p}^2}{2m} + V\right)\Psi \qquad \ldots(3.17)
$$

so that, the Schrödinger equation generalizes to

$$
\boxed{\begin{gathered} i\hbar\frac{\partial}{\partial t}\Psi(\mathbf{r},t) = \left(-\frac{\hbar^2\nabla^2}{2m} + V(\mathbf{r},t)\right)\Psi(\mathbf{r},t)\\ \textbf{(Time-dependent Schrödinger equation)}\end{gathered}} \qquad \ldots(3.18)
$$

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

$$
\boxed{\begin{gathered} H = -\frac{\hbar^2\nabla^2}{2m} + V(\mathbf{r},t)\\ \textbf{(Hamiltonian operator)}\end{gathered}} \qquad \ldots(3.19)
$$

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.

3.6 Statistical Interpretation of The Wave Function and Conservation of Probability

If a particle is described by a wave function $\Psi(\mathbf{r}, t)$, then the probability of finding the particle, at time t, within the volume element $d\boldsymbol{r} = dx\, dy\, dz$ about the point $\boldsymbol{r} \equiv (x, y, z)$ is

$$P(\mathbf{r}, t)\, d\mathbf{r} = |\Psi(\mathbf{r}, t)|^2\, d\mathbf{r} = \Psi^*(\mathbf{r}, t)\Psi(\mathbf{r}, t)\, d\mathbf{r} \qquad \ldots(3.20)$$

The quantity

$$P(\mathbf{r}, t) = |\Psi(\mathbf{r}, t)|^2 = \Psi^*(\mathbf{r}, t)\, \Psi(\mathbf{r}, t) \qquad \ldots(3.21)$$

is obviously called the position probability density. Since the probability of finding the particle somewhere at time t is unity, the normalization condition,

$$\boxed{\int |\Psi(\mathbf{r}, t)|^2\, d\mathbf{r} = 1} \qquad \ldots(3.22)$$

where the integral extends over all space.

What happens as time changes.?

It is clear that the probability of finding the particle somewhere must remain conserved. That is, the normalization integral in (3.22) must be independent of time.

$$\frac{\partial}{\partial t}\int P(\mathbf{r}, t) d\mathbf{r} = \frac{\partial}{\partial t}\int \Psi^*(\mathbf{r}, t)\, \Psi(\mathbf{r}, t) d\mathbf{r} = 0 \qquad \ldots(3.23)$$

In order to prove this,

By use the Schrödinger equation

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\Psi + V\Psi \qquad \ldots(3.24)$$

and its complex conjugate

$$-i\hbar \frac{\partial \Psi^*}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\Psi^* + V\Psi^* \qquad \ldots(3.25)$$

where $V(\mathbf{r}, t)$ is assumed to be real.

Multiplying (3.24) by Ψ^* and (3.25) by Ψ on the left and then subtracting, we get

$$i\hbar\left[\Psi^*\frac{\partial\Psi}{\partial t}+\Psi\frac{\partial\Psi^*}{\partial t}\right]=-\frac{\hbar^2}{2m}[\Psi^*\nabla^2\Psi-\Psi\nabla^2\Psi^*] \qquad \ldots(3.26)$$

Now, consider the time derivative of the integral of $\Psi^*\Psi$ over a finite volume *V*. We have,

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

$$=\frac{i\hbar}{2m}\int_V[(\Psi^*\nabla^2\Psi-\Psi\nabla^2\Psi^*)]d\mathbf{r}$$

By using (3.26)

$$=\frac{i\hbar}{2m}\int_V \boldsymbol{\nabla}\cdot(\Psi^*\boldsymbol{\nabla}\Psi-\Psi\boldsymbol{\nabla}\Psi^*)d\mathbf{r} \qquad \ldots(3.27)$$

Let us define a vector

$$\boldsymbol{j}(\boldsymbol{r},t)=\frac{-i\hbar}{2m}(\Psi^*\boldsymbol{\nabla}\Psi-\Psi\boldsymbol{\nabla}\Psi^*) \qquad \ldots(3.28)$$

Substituting in (3.27),

$$\frac{\partial}{\partial t}\int_V P(\mathbf{r},\ t)\ d\mathbf{r}=-\int_V \boldsymbol{\nabla}\cdot\mathbf{j}\ d\mathbf{r} \qquad \ldots(3.29)$$

Using Green's theorem (also called Gauss' divergence theorem) we can convert the volume integral on the right into an integral over the surface S bounding the volume V:

$$\frac{\partial}{\partial t}\int_V P(\mathbf{r},\ t)d\mathbf{r}=-\int_S \mathbf{j}\cdot d\mathbf{S} \qquad \ldots(*)$$

Since a square integrable wave function vanishes at large distances, the surface integral becomes zero and hence (3.23) is proved.