Chapter 3

The Schrödinger Wave Equation

We obtained; $i\hbar \dfrac{\partial \Psi(x,t)}{\partial t} = -\dfrac{\hbar^2}{2m} \dfrac{\partial^2 \Psi(x,t)}{\partial x^2}$ (1)

with the most general sol. $\Psi(x,t) = \dfrac{1}{\sqrt{2\pi\hbar}} \int dp\, \varphi(p)\, e^{i[px - \frac{p^2}{2m}t]/\hbar}$ (2)

Equ (1) is of first order in the time-derivative.

$\xrightarrow{\text{so}}$ if $\Psi(x,0)$ is known, then $\Psi(x,t)$ can be found either

1) from ; $i\hbar \dfrac{\Psi(x,t+\Delta t) - \Psi(x,t)}{\Delta t} = -\dfrac{\hbar^2}{2m} \dfrac{\partial^2 \Psi(x,t)}{\partial x^2}$

$\rightarrow \Psi(x,t+\Delta t) = \Psi(x,t) + \dfrac{i\hbar}{2m} \dfrac{\partial^2 \Psi(x,t)}{\partial x^2} \Delta t$ (3)

This can be evaluated by the computer.

2) or from the form of the most general sol.

i.e. Given $\Psi(x,0)$, the func. $\varphi(p)$ may be found from;

(2) $\rightarrow$ $\Psi(x,0) = \dfrac{1}{\sqrt{2\pi\hbar}} \int dp\, \varphi(p)\, e^{i\,px/\hbar}$ (4)

and once $\varphi(p)$ is known, $\Psi(x,t)$ may be found by using the equ (2).

Note that:

i) $\Psi(x,t)$ is in general a complex func.

ii) $|\Psi(x,t)|$ is large where the particle is supposed to be.

The suggestion of Max Born:

$$\underbrace{P(x,t)}_{\text{probability density}}dx = |\Psi(x,t)|^2 dx \quad (5)$$

the probability that the particle described by $\Psi(x,t)$ may be found between x and $x+dx$ at time t.

What does the spreading of $\Psi(x,t)$ mean (as time goes)?

It means that as times goes, one is <u>less</u> likely to find the particle where one put it at $t=0$.

For this interpretation to hold, we must require that:

$$\int_{-\infty}^{\infty} P(x,t)\,dx = 1 \quad (6)$$

Since the equ.(1) is linear $\xrightarrow{\text{then}}$ $c\Psi(x,t)$ is also a sol. (c=const.)

$$(6) \longrightarrow \int_{-\infty}^{\infty} |\Psi(x,t)|^2 dx = 1 \quad (7)$$

($\Psi(x,t)$ must be square integrable)

We shall see that it is enough to require that:

$$\int_{-\infty}^{\infty} |\Psi(x,0)|^2 dx < \infty \quad (8)$$

(square integrable)

With an *infinite* integration interval this means that;

$$\psi(x,0) \xrightarrow[\substack{\text{at least as} \\ \text{fast as } \frac{1}{x^{\frac{1}{2}+\epsilon}}}]{\text{must}} 0 \quad \text{as } x \to \pm\infty \qquad (9)$$

($\epsilon > 0$ an arbitrary small number)

We shall also require that, $\psi(x,t)$ be continuous in x

Remark:

Since equ (1) is linear, if $\psi_1(x,t)$ and $\psi_2(x,t)$ are sols.,

so is, $$\psi(x,t) = \alpha_1 \psi_1(x,t) + \alpha_2 \psi_2(x,t) \qquad (10)$$ α_1, α_2: complex numbers

$$\longrightarrow \quad |\psi(x,t)|^2 = f(\alpha_1, \alpha_2) \qquad (11)$$

{For example, the interference pattern is determined by the phase relation between the two parts of the wave func. associated with the two slits in a two-slit experiment.

But $$|\alpha\psi(x,t)|^2 \sim |\psi(x,t)|^2 \qquad (12)$$ α: complex number

i.e. an overall phase factor can be ignored.

We now show the condition (6), imposed at $t=0$, holds true for all times.

$$(1) \longrightarrow \quad -i\hbar \frac{\partial \psi^*(x,t)}{\partial t} = \frac{-\hbar^2}{2m} \frac{\partial^2 \psi^*(x,t)}{\partial x^2} \qquad (13)$$

Now $$\frac{\partial}{\partial t} P(x,t) = \frac{\partial}{\partial t}(\psi \psi^*) = \frac{\partial \psi^*}{\partial t}\psi + \psi^* \frac{\partial \psi}{\partial t}$$

$$\frac{\partial}{\partial t} P(x,t) = \frac{1}{i\hbar}\left(\frac{\hbar^2}{2m}\frac{\partial^2\psi^*}{\partial x^2}\psi - \frac{\hbar^2}{2m}\psi^*\frac{\partial^2\psi}{\partial x^2}\right)$$

$$= -\frac{\partial}{\partial x}\left[\frac{\hbar}{2im}\left(\psi^*\frac{\partial\psi}{\partial x} - \frac{\partial\psi^*}{\partial x}\psi\right)\right]$$

Define $\quad j(x,t) = \frac{\hbar}{2im}\left(\psi^*\frac{\partial\psi}{\partial x} - \frac{\partial\psi^*}{\partial x}\psi\right)$ flux or current density

$$\rightarrow \frac{\partial}{\partial t} P(x,t) + \frac{\partial}{\partial x} j(x,t) = 0 \qquad (14)$$

$$\rightarrow \frac{\partial}{\partial t}\int_{-\infty}^{\infty} dx\, P(x,t) = -\int_{-\infty}^{\infty} dx\, \frac{\partial}{\partial x} j(x,t) = 0 \qquad (15)$$

Since for square integrable funcs., $j(x,t) \to 0$ as $x \to \pm\infty$

Remark: If there is discontinuities in $\psi(x)$ $\xrightarrow{\text{then}}$ there will be δ-func singularities in $j(x)$ $\xrightarrow{\text{and hence}}$ in $P(x)$, which is unacceptable in a physically observable quantity.

Equation (14) is a conservation law.
It expresses the fact that a change in the density in a region x is compensated by a net change in flux into that region;

$$\frac{\partial}{\partial t}\int_a^b dx\, P(x,t) = -\int_a^b dx\, \frac{\partial}{\partial x} j(x,t) = j(a,t) - j(b,t) \qquad (16)$$

The definition of $\rho(x,t)$, $j(x,t)$ and the conservation law are maintained if the eqn (1) is changed to;

$$i\hbar\frac{\partial\psi(x,t)}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\psi(x,t)}{\partial x^2} + V(x)\psi(x,t) \quad (17)$$

provided that $V(x)$ is real.

The generalization;

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

In compact form; $$i\hbar\frac{\partial\psi(\bar{r},t)}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\psi(\bar{r},t) + V(\bar{r})\psi(\bar{r},t) \quad (18)$$

And the generalization of eqn (16)

$$\frac{\partial P(\bar{r},t)}{\partial t} + \nabla\cdot J(\bar{r},t) = 0 \quad (19)$$

where $$J(\bar{r},t) = \frac{\hbar}{2im}\left[\psi^*(\bar{r},t)\nabla\psi(\bar{r},t) - [\nabla\psi^*(\bar{r},t)]\psi(\bar{r},t)\right] \quad (20)$$

and $$P(\bar{r},t) = |\psi(\bar{r},t)|^2 \quad (21)$$

$$\nabla\cdot J = \frac{\partial J_x}{\partial x} + \frac{\partial J_y}{\partial y} + \frac{\partial J_z}{\partial z}$$

Expectation value of $f(x)$ with a given probability density $\rho(x,t)$ is given by;

$$< f(x) > = \int dx\, f(x)\, \rho(x,t) = \int dx\, \psi^*(x,t)\, f(x)\, \psi(x,t) \tag{22}$$

Remark: For a finite, discrete space, with $\sum P_i = 1$

$$< f > = \sum f_i\, P_i \qquad \text{mean value}$$

What about $< p > = ?$

Classically; $p = mv = m\frac{dx}{dt}$

$$< p > = m\frac{d}{dt} < x > = m\frac{d}{dt}\int dx\, \psi^*(x,t)\, x\, \psi(x,t)$$

$$\rightarrow < p > = m\int_{-\infty}^{\infty} dx \left(\frac{\partial \psi^*}{\partial t} x \psi + \psi^* x \frac{\partial \psi}{\partial t} \right) \tag{23}$$

Using equ (1) and equ (13);

$$< p > = \frac{\hbar}{2i}\int_{-\infty}^{\infty} dx \left(\frac{\partial^2 \psi^*}{\partial x^2} x \psi - \psi^* x \frac{\partial^2 \psi}{\partial x^2} \right) \tag{24}$$

Now, $\frac{\partial^2 \psi^*}{\partial x^2} x \psi = \frac{\partial}{\partial x}\left(\frac{\partial \psi^*}{\partial x} x \psi \right) - \frac{\partial \psi^*}{\partial x} \psi - \frac{\partial \psi^*}{\partial x} x \frac{\partial \psi}{\partial x}$

$$= \frac{\partial}{\partial x}\left(\frac{\partial \psi^*}{\partial x} x \psi \right) - \frac{\partial}{\partial x}(\psi^* \psi) + \psi^* \frac{\partial \psi}{\partial x}$$

$$- \frac{\partial}{\partial x}\left(\psi^* x \frac{\partial \psi}{\partial x} \right) + \psi^* \frac{\partial \psi}{\partial x} + \psi^* x \frac{\partial^2 \psi}{\partial x^2}$$

Hence the integrand has the form;

$$\frac{\partial}{\partial x}\left(\frac{\partial \psi^*}{\partial x} x\psi - \psi^* x \frac{\partial \psi}{\partial x} - \psi^*\psi\right) + 2\psi^* \frac{\partial \psi}{\partial x}$$

$$\rightarrow \quad \langle p \rangle = \int dx\, \psi^*(x,t) \underbrace{\frac{\hbar}{i}\frac{\partial}{\partial x}} \psi(x,t) \qquad (25)$$

Since $\int \frac{\partial}{\partial x}\left(\frac{\partial \psi^*}{\partial x} x\psi - \psi^* x \frac{\partial \psi}{\partial x} - \psi^*\psi\right) dx$

$$= \left(\frac{\partial \psi^*}{\partial x} x\psi - \psi^* x \frac{\partial \psi}{\partial x} - \psi^*\psi\right)\Big|_{-\infty}^{\infty} = 0 \qquad \begin{cases} \psi \to 0 & \text{as } x \to \pm\infty \\ \psi^* \to 0 \end{cases}$$

This suggests that $\quad p = \frac{\hbar}{i}\frac{\partial}{\partial x} \qquad (26)$

More generally; $\quad \langle f(p) \rangle = \int dx\, \psi^*(x,t)\, f\left(\frac{\hbar}{i}\frac{\partial}{\partial x}\right) \psi(x,t)$

(27)

What is the physical significance of $\varphi(p)$?

At $t=0 \quad \psi(x) = \frac{1}{\sqrt{2\pi\hbar}} \int dp\, \varphi(p)\, e^{ipx/\hbar} = \sqrt{\frac{\hbar}{2\pi}} \int dk\, \varphi(\hbar k)\, e^{ikx}$

Using the inversion formula for a Fourier integral; (28)

$$\varphi(\hbar k) = \frac{1}{\sqrt{2\pi\hbar}} \int dx\, \psi(x)\, e^{-ikx} \quad \rightarrow \varphi(p) = \frac{1}{\sqrt{2\pi\hbar}} \int dx\, \psi(x)\, e^{-ipx/\hbar}$$

(29)

Now; $\int dp\, \varphi^*(p)\varphi(p) = \int dp \frac{1}{\sqrt{2\pi\hbar}} \int dx\, e^{+ipx/\hbar} \psi^*(x) \frac{1}{\sqrt{2\pi\hbar}} \int dx'\, e^{-ipx'/\hbar} \psi(x')$

$$\rightarrow \int dp\, \varphi^*(p)\varphi(p) = \int dx\, \psi^*(x) \int dx'\, \psi(x') \underbrace{\frac{1}{2\pi\hbar}\int_{-\infty}^{\infty} dp\, e^{ip(x-x')/\hbar}}_{\delta(x-x')}$$

$$= \int dx\, \psi^*(x)\psi(x) = 1 \qquad (29')$$

This is just Parseval's theorem in the mathematical literature. It states that if a func. is normalized to $\underline{1}$, so is its Fourier tr. .

Remark
$$\begin{cases} f(x) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty} A(k)e^{ikx}\,dk \\ A(k) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty} f(x)e^{-ikx}\,dx \end{cases}$$

Next consider;

$$\langle p \rangle = \int dx\, \psi^*(x)\frac{\hbar}{i}\frac{d\psi(x)}{dx}$$

$$= \int dx\, \psi^*(x)\frac{\hbar}{i}\frac{d}{dx}\frac{1}{\sqrt{2\pi\hbar}}\int dp\, \varphi(p)e^{ipx/\hbar}$$

$$= \int dp\, \varphi(p)\, p\, \frac{1}{\sqrt{2\pi\hbar}}\int dx\, \psi^*(x)\, e^{ipx/\hbar} = \int dp\, \varphi(p)\, p\, \varphi^*(p)$$

$$(30)$$

$\xrightarrow{\text{suggests}}$ $\varphi(p)$: wave func in the mom. space.

$|\varphi(p)|^2$: probability density of finding particle with mom. p .

When $\psi(x,t)$ is a sol. of (17), we may define $\varphi(p,t)$ by;

$$\psi(x,t) = \frac{1}{\sqrt{2\pi\hbar}}\int dp\, \varphi(p,t)\, e^{ipx/\hbar} \qquad (31)$$

Equ (29') and (30) are valid with t-dep φ and ψ.

Now, consider;

$$\langle x \rangle = \int \psi^*(x,t)\, x\, \psi(x,t)\, dx$$

$$\langle x \rangle = \int dx \frac{1}{\sqrt{2\pi\hbar}} \int dp\, \varphi^*(x,t)\, e^{-ipx/\hbar} \times \frac{1}{\sqrt{2\pi\hbar}} \int dp'\, \varphi(p',t)\, e^{ip'x/\hbar}$$

$$\langle x \rangle = \frac{1}{2\pi\hbar} \int dx \int dp \int dp'\, \varphi^*(p,t)\, \varphi(p',t)\, x\, e^{i(p'-p)x/\hbar}$$

$$x\, e^{i(p'-p)x/\hbar} = \frac{\hbar}{i} \frac{\partial}{\partial p'} e^{i(p'-p)x/\hbar}$$

$$\langle x \rangle = \frac{1}{2\pi\hbar} \int dx \int dp\, \varphi^*(p,t) \int dp'\, \varphi(p',t)\, \frac{\hbar}{i} \frac{\partial}{\partial p'} e^{i(p'-p)x/\hbar}$$

$$= \frac{1}{2\pi\hbar} \int dx \int dp\, \varphi^*(p,t) \left\{ \underbrace{\varphi(p',t) \frac{\hbar}{i} e^{i(p'-p)x/\hbar} \Big|_{p'=-\infty}^{p'=\infty}}_{=0} - \int dp' \frac{\hbar}{i} \left(\frac{\partial}{\partial p'} \varphi(p',t)\right) \cdot e^{i(p'-p)x/\hbar} \right\}$$

$$= \int dp \int dp'\, \varphi^*(p,t) \left(-\frac{\hbar}{i}\frac{\partial}{\partial p'}\right) \varphi(p',t)\, \underbrace{\frac{1}{2\pi\hbar} \int e^{i(p'-p)x/\hbar} dx}_{\delta(p'-p)}$$

$$= \int dp\, \varphi^*(p,t) \left(-\frac{\hbar}{i}\right) \frac{\partial}{\partial p} \varphi(p,t) \quad (32)$$

$$\langle x \rangle = \int \varphi^*(\bar{p},t) \left(-\frac{\hbar}{i} \nabla_p\right) \varphi(\bar{p},t)\, d^3p \quad \text{(In 3-dim.)} \quad (33)$$

In general;

$$\langle f(x) \rangle = \int dp\, \varphi^*(p,t)\, f\left(-\frac{\hbar}{i}\frac{\partial}{\partial p}\right) \varphi(p,t) \quad (34)$$

Conclusion:

a) In position space $\begin{cases} \text{Position operator} = x \\ \text{Momentum} \quad " \quad = \frac{\hbar}{i}\frac{\partial}{\partial x} \end{cases}$

b) In Momentum " $\begin{cases} \text{Position operator} = -\frac{\hbar}{i}\frac{\partial}{\partial p} \\ \text{Momentum} \quad " \quad = p \end{cases}$

Two points:

1- In general $[A,B] = AB - BA \neq 0$

Example: $[p,x]\psi(x,t) = \frac{\hbar}{i}\frac{\partial}{\partial x}[x\psi(x,t)] - x\frac{\hbar}{i}\frac{\partial\psi(x,t)}{\partial x}$

$$= \frac{\hbar}{i}(1)\psi(x,t) + \frac{\hbar}{i}x\frac{\partial\psi(x,t)}{\partial x} - x\frac{\hbar}{i}\frac{\partial\psi(x,t)}{\partial x} = \frac{\hbar}{i}\psi(x,t)$$

$\longrightarrow [p,x] = \frac{\hbar}{i}$

In transcribing a classical func. $f(x,p)$ into operator form, we shall adopt the rule that $f(x,p)$ be symmetrized in x and p

Example: $xp \longrightarrow \frac{1}{2}(xp + px)$

$x^2 p \longrightarrow x\left\{\frac{1}{2}(xp + px)\right\}$

$$= \frac{1}{2}\left\{\frac{1}{2}[x^2p + xpx] + \frac{1}{2}[xpx + px^2]\right\} = \frac{1}{4}(x^2p + 2xpx + px^2)$$

2- The reality of $\langle p \rangle$:

$$\langle p \rangle - \langle p \rangle^* = \int dx\, \psi^* \frac{\hbar}{i} \frac{\partial \psi}{\partial x} - \int dx\, \psi(x) \left(-\frac{\hbar}{i} \frac{\partial \psi^*}{\partial x} \right)$$

$$= \frac{\hbar}{i} \int dx \left(\psi^* \frac{\partial \psi}{\partial x} + \frac{\partial \psi^*}{\partial x} \psi \right) = \frac{\hbar}{i} \int dx \frac{\partial}{\partial x} (\psi^* \psi)$$

$$= \frac{\hbar}{i} (\psi^* \psi) \Big|_{x=-\infty}^{x=\infty} = 0 \qquad \rightarrow \langle p \rangle = \langle p \rangle^* \quad \text{real}$$

Remark: Sometimes $\psi(x)$ is not square integrable but has certain periodicity conditions, for example:

$$\psi(x) = \psi(x+L)$$

If one restricts oneself working in the region $0 \leq x \leq L$, then $\frac{\hbar}{i} \frac{d}{dx}$ is still a Hermitian op.;

i.e. $$\langle p \rangle - \langle p \rangle^* = \frac{\hbar}{i} \int_0^L dx \frac{\partial}{\partial x} (\psi^*(x) \psi(x))$$

$$= \frac{\hbar}{i} |\psi(L)|^2 - \frac{\hbar}{i} |\psi(0)|^2 = 0 \qquad \rightarrow \langle p \rangle = \langle p \rangle^*$$

Def. - A Hermitian op. is an op. with the following properties:

i) $\langle A \rangle = \langle A \rangle^*$

ii) The eigenkets belonging to different eigenvalues are orthogonal.

Note: The operators representing the observables must be Hermitian.

Now note that; $i\hbar \dfrac{\partial \Psi(x,t)}{\partial t} = \dfrac{\hbar^2}{2m} \dfrac{\partial^2 \Psi(x,t)}{\partial x^2}$

with the identification $P_{op} \equiv \dfrac{\hbar}{i} \dfrac{\partial}{\partial x}$

$$\rightarrow i\hbar \frac{\partial \Psi(x,t)}{\partial t} = \underbrace{\frac{P_{op}^2}{2m}}_{\text{the energy for a free particle}} \Psi(x,t)$$

The generalization;

$$i\hbar \frac{\partial \Psi(x,t)}{\partial t} = \left[\frac{P_{op}^2}{2m} + V(x) \right] \Psi(x,t)$$

or more explicitly;

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

or $\quad i\hbar \dfrac{\partial \Psi(x,t)}{\partial t} = \underset{\text{energy op (Hamiltonian)}}{H} \Psi(x,t)$ Shrödigerequ. (non-rel.)

Since p : Hermitian $\longrightarrow$ p^2 : Harmitian

$\longrightarrow$ H: Hermitian if $V(x)$ is real $\qquad H = \dfrac{p^2}{2m} + V(x)$

Now we abandon the notion of a wave packet representing a particle. This notion was helpful in making the Schrödinger equ. plausible, but <u>now</u> it is $\Psi(x,t)$ and its probabilitistic interpretation that tells us where the particle is, without the particle being thought as "made up out of waves".