Chapter Three

Particle in a Potential Well

4.1 The Free Particle

The one-dimensional time-independent Schrodinger equation for a free particle is,

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} = E\psi(x) \qquad \ldots(4.1)$$

or

$$\frac{d^2\psi}{dx^2} + \frac{2mE}{\hbar^2}\psi = 0$$

or

$$\frac{d^2\psi}{dx^2} + k^2\psi = 0; \quad k = \left(\frac{2mE}{\hbar^2}\right)^{1/2}$$

The general solution is,

$$\psi(x) = Ae^{ikx} + Be^{-ikx} \qquad \ldots(4.2)$$

Where A and B are arbitrary constants. For a solution to be physically acceptable, k must be real, otherwise $\psi(x)$ would become unbounded at one of the limits $x = \infty$ or $x = -\infty$. Therefore, we must have $E \geq 0$, so *the energy spectrum is continuous*.

The energy eigenvalues are given by,

$$E = \frac{\hbar^2 k^2}{2m} \qquad \ldots(4.3)$$

Each eigenvalue is doubly degenerate because two linearly independent eigenfunction e^{ikx} and e^{-ikx} correspond to it.

The full wave function for a free particle is,

$$\Psi(x,t) = \psi(r)e^{-iEt/\hbar}$$

$$\Psi(x,\ t) = (Ae^{ikx} + Be^{-ikx})\,e^{-iEt/\hbar}$$
$$= Ae^{i(kx-\omega t)} + Be^{-i(kx+\omega t)} \qquad \ldots(4.4)$$

where $\omega = E/\hbar$ is the angular frequency. Let us now consider the case when $B = 0$. The resulting wave function is

$$\Psi(x,\ t) = Ae^{i(kx-\omega t)} \qquad \ldots(4.5)$$

This is a plane wave travelling in the positive x-direction. Therefore, it must be associated with a free particle of mass m moving along the x-axis in the positive direction with momentum $p = \hbar k$ and energy $E = \hbar^2 k^2/2m$.

If $A = 0$, the resulting wave function would be

$$\Psi(x, t) = Be^{-i(kx+\omega t)} \qquad \ldots(4.6)$$

This represents a plane wave traveling in the negative x-direction.

Momentum eigenfunction

Let us now operate on the eigenfunctions exp (ikx) and exp $(-ikx)$ with the momentum operator

$$p = -i\hbar \frac{d}{dx}$$

We have

$$-i\hbar \frac{d}{dx}(e^{ikx}) = \hbar k(e^{ikx})$$

and

$$-i\hbar \frac{d}{dx}(e^{-ikx}) = -\hbar k\,(e^{-ikx})$$

We find that the functions exp (ikx) and exp $(-ikx)$ are eigenfunctions of the momentum operator with the eigenvalues $\hbar k$ and $-\hbar k$, respectively. Thus, these functions are not only energy eigenfunctions, but also *momentum eigenfunctions*.

The position probability density

$$P = |\Psi(x, t)|^2 = |A|^2$$

We find that P is independent of time t as well as the position x of the particle.

The probability current density

$$j = \text{Re}\left[\psi^* \frac{\hbar}{im}\frac{\partial \psi}{\partial x}\right]$$

$$= \text{Re}\left[A^* e^{-ikx}\left(\frac{\hbar}{im}\right)(ik)\,Ae^{ikx}\right]$$

$$j = \frac{\hbar k}{m}|A|^2 = \frac{p}{m}|A|^2 \qquad \ldots(4.7)$$

This is independent of *t* and *x*, as expected for stationary states.

H.W.: In the case of a plane wave traveling in the *negative x-direction* $\left(Be^{-i(kx+\omega t)}\right)$, find the position probability density and the probability current density for this wavefunction.

Normalization of Momentum Eigenfunctions

Let us consider the momentum eigenfunction

$$\psi_k(x) = Ae^{ikx}$$

It is easy to see that $\psi_k(x)$ cannot be normalized in the usual way because:

$$\int_{-\infty}^{\infty} \psi_k^*(x)\psi_k(x)\, dx = \int_{-\infty}^{\infty} A^* e^{-ikx} A\, e^{ikx}\, dx = |A|^2 \int_{-\infty}^{\infty} dx = \infty$$

Therefore, it is necessary to have alternative ways of normalizing it.

Box Normalization

It is assumed that the particle is enclosed in a large one-dimensional box of length *L*, at the walls of which the wave functions satisfy the periodic boundary condition

$$\psi_k(x + L) = \psi_k(x) \qquad \ldots(4.8)$$

or

$$e^{ik(x+L)} = e^{ikx}$$

or

$$e^{ikL} = 1$$

This restricts k to the discrete values

$$k = \frac{2\pi n}{L}, \quad n = 0, \pm 1, \pm 2, \ldots \qquad \ldots(4.9)$$

Therefore, the energy levels also become discrete:

$$E_n = \frac{2\pi^2\hbar^2 n^2}{mL^2} \qquad \ldots(4.10$$

As *L* increases, the spacings of the energy levels decrease. So, for a very large box, the energy level spectrum is practically continuous.

The normalization of $\psi_k(x)$ is,

$$\int_{-L/2}^{L/2} |\psi_k(x)|^2\, dx = 1$$

$$\int_{-L/2}^{L/2} \psi_k^*(x)\psi_k(x)\,dx = \int_{-L/2}^{L/2} A^* e^{-i(k+L)x} A\, e^{i(k+L)x}\,dx = |A|^2 \int_{-L/2}^{L/2} dx = 1$$

Then $|A|^2 = \frac{1}{L}$, we have $A = \frac{1}{\sqrt{L}}$

Therefore, the normalized momentum eigenfunctions are given by,

$$\psi_k(x) = \frac{1}{\sqrt{L}}\, e^{ikx}$$

The eigenfunctions are, in fact, **orthonormal**:

$$\int_{-\frac{L}{2}}^{\frac{L}{2}} \psi_{\acute{k}}^*(x)\psi_k(x)\,dx = \frac{1}{L}\int_{-\frac{L}{2}}^{\frac{L}{2}} e^{i(k-\acute{k})x}\,dx = \delta_{k\acute{k}} \qquad \ldots(4.11)$$

$\delta_{k\acute{k}} = 1$ for $k = \acute{k}$

$\delta_{k\acute{k}} = 0$ for $k \neq \acute{k}$