3.7 Probability Conservation and the Hermiticity of the Hamiltonian

If the operator $\hat{A}$ satisfy the condition $$\boxed{\int \Psi^* \hat{A} \Psi \, d\mathbf{r} = \int (\hat{A}\Psi)^* \Psi \, d\mathbf{r}}$$

is called Hermitian operator.

We shall now show that the conservation of probability implies that the Hamiltonian operator **H** appearing in the Schrödinger equation is **Hermitian**.

In terms of **H**, the Schrödinger equation can be written as

$$i\hbar \frac{\partial \Psi}{\partial t} = H\Psi \quad \text{...(3.30)}$$

The complex conjugate of this equation is

$$-i\hbar \frac{\partial \Psi^*}{\partial t} = (H\Psi)^* \quad \text{...(3.31)}$$

Using these equations, we can write

$$\frac{\partial}{\partial t} \int \Psi^* \Psi d\mathbf{r} = \int \left(\Psi^* \frac{\partial \Psi}{\partial t} + \Psi \frac{\partial \Psi^*}{\partial t} \right) d\mathbf{r} \quad \text{...(3.32)}$$

$$= (i\hbar)^{-1} \int [\Psi^*(H\Psi) - \Psi(H\Psi)^*] d\mathbf{r}$$

Since the left-hand side is zero, we obtain

$$\boxed{\int \Psi^*(H\Psi) d\mathbf{r} = \int (H\Psi)^* \Psi \, d\mathbf{r}} \quad \text{...(3.33)}$$

Operators which satisfy this condition are called Hermitian. Thus, H is an Hermitian operator.

3.8 Probability Current Density

From equation (3.28)

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

and since this equation is true for any arbitrary volume, we have

$$\boxed{\frac{\partial}{\partial t} P(\mathbf{r}, t) + \nabla \cdot \mathbf{j}(\mathbf{r}, t) = 0} \quad \text{...(3.34)}$$

This is called the equation of continuity.

The vector $\boldsymbol{j}(\boldsymbol{r}, t)$ is called the probability current density.

If $\nabla \cdot \boldsymbol{j} = 0$, then for that state the probability density is constant in time. Such states are called stationary states.

3.8 Expectation Values of Dynamical Variables

- In quantum mechanics a particle is represented by a wave function which can be obtained by solving the Schrödinger equation and contains all the available information about the particle.
- The dynamical variables of the particle (position, momentum, ….) can be extracted from the wave function Ψ.
- Since Ψ has a probabilistic interpretation, so that exact information about the variables cannot be obtained.
- We obtain only the expectation value of a quantity, which is the average of a large number of measurements on the same system.
- The expectation value of a physical quantity is always real.

To find the position expectation value $\langle r \rangle$:

Since $P(\mathbf{r}, t) = \Psi^*(\mathbf{r}, t)\,\Psi(\mathbf{r}, t)$ is interpreted as the position probability density at the point $\mathbf{r}$ at the time t, the *expectation value* of the position vector $\mathbf{r}$ is given by

$$\langle \mathbf{r} \rangle = \int \mathbf{r}\, P(\mathbf{r}, t)\, d\mathbf{r} \qquad \ldots(3.35)$$

$$= \int \Psi^*(\mathbf{r}, t)\, \mathbf{r}\, \Psi(\mathbf{r}, t)\, d\mathbf{r} \qquad \ldots(3.36)$$

where $\Psi(\mathbf{r}, t)$ is normalized. This equation is equivalent to the three equations

$$\langle x \rangle = \int \Psi^* \, x \, \Psi \; d\mathbf{r}$$

$$\langle y \rangle = \int \Psi^* \, y \, \Psi \; d\mathbf{r} \qquad \ldots(3.37)$$

$$\langle z \rangle = \int \Psi^* \, z \, \Psi \; d\mathbf{r}$$

- The expectation value is a function only of the time because the space coordinates have been integrated out.
- The expectation value of a physical quantity is always real.

The expectation value of any quantity which is a function of **r** *and t* would be;

$$\boxed{\langle f(\mathbf{r}, t) \rangle = \int \Psi^*(\mathbf{r}, t) \, f(\mathbf{r}, t) \; \Psi(\mathbf{r}, t) \; d\mathbf{r}} \qquad \ldots(3.38)$$

As an example, the expectation value of the potential energy is

$$\langle V(\mathbf{r}, t) \rangle = \int \Psi^* \; (\mathbf{r}, \; t) \; V(\mathbf{r}, \; t) \; \Psi(\mathbf{r}, \; t) d\mathbf{r} \qquad \ldots(3.39)$$

The expectation values for quantities which are functions of momentum or of both position and momentum by using the ***operator representations***

$$\hat{\mathbf{p}} = -i\hbar \; \nabla$$

$$p^2 = -\hbar^2 \; \nabla^2$$

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

Q: How these differential operators are to be combined with the position probability density $\Psi^* \; \Psi$ to obtain the total energy expressions?

Answer: by using the classical expression for the total energy

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

And the expectation values;

$$\langle E \rangle = \left\langle \frac{p^2}{2m} \right\rangle + \langle V \rangle \qquad \ldots(3.40)$$

Replacing E and p^2 by the corresponding operators, we get

$$\left\langle i\hbar\frac{\partial}{\partial t}\right\rangle = \left\langle -\frac{\hbar^2}{2m}\nabla^2\right\rangle + \langle V\rangle \qquad \ldots(3.41)$$

This equation must be consistent with the Schrödinger equation

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

Multiplying by Ψ^* on the left and integrating, we get

$$\int\Psi^*\left(i\hbar\frac{\partial}{\partial t}\right)\Psi\,d\mathbf{r} = \int\Psi^*\left(-\frac{\hbar^2\nabla^2}{2m}\right)\Psi\,d\mathbf{r} + \int\Psi^*V\Psi\,d\mathbf{r} \qquad \ldots(3.42)$$

From (3.40) -(3.42) we have;

$$\langle V\rangle = \int\Psi^*\,\mathrm{V}\,\Psi\,d\mathrm{r} \qquad \ldots(3.43)$$

$$\langle E\rangle = \int\Psi^*\,i\hbar\,\frac{\partial\Psi}{\partial t}\,d\mathbf{r} \qquad \ldots(3.44)$$

$$\langle\mathbf{p}\rangle = \int\Psi^*\,(-i\hbar)\,\nabla\Psi\,d\mathbf{r} \qquad \ldots(3.45)$$

The last equation is equivalent to

$$\left.\begin{aligned}\langle p_x\rangle &= -i\hbar\int\Psi^*\frac{\partial\Psi}{\partial x}\,d\mathbf{r}\\ \langle p_y\rangle &= -i\hbar\int\Psi^*\frac{\partial\Psi}{\partial y}\,d\mathbf{r}\\ \langle p_z\rangle &= -i\hbar\int\Psi^*\frac{\partial\Psi}{\partial z}\,d\mathbf{r}\end{aligned}\right] \qquad \ldots(3.46)$$

Generalizing the above results:

$\Psi(\boldsymbol{r},t)$ The normalized wave function which describes the dynamical state of a particle.

$A(\boldsymbol{r},\boldsymbol{p},t)$ the dynamical variable representing a physical quantity associated with the particle.

We calculate the expectation value of A from the expression;

$$\langle A \rangle = \int \Psi^*(\boldsymbol{r}, t)\, \hat{A}\, \Psi(\mathbf{r}, \mathrm{t})\, \mathrm{d}\mathbf{r}\,, \qquad \text{or}$$

$$\boxed{\langle A \rangle = \int \Psi^*(\mathbf{r}, t)\, \hat{A}(\mathbf{r}, -i\hbar\nabla, t)\, \Psi(\mathbf{r}, t)\, d\mathbf{r}} \qquad \ldots(3.46)$$

Since the *expectation value of a physical quantity is always real*, i.e., $\langle A \rangle^* = \langle A \rangle$

Then the operator $\hat{A}$ must satisfy;

$$\boxed{\int \Psi^* \hat{A} \Psi\, d\mathbf{r} = \int (\hat{A}\Psi)^*\, \Psi\, d\mathbf{r}} \qquad \ldots(3.47)$$

Thus, the operator associated with a dynamical quantity must be **Hermitian**.