

3.11 The Time-Independent Schrödinger Equation (Stationary States)

There are many physically interesting problems in which the potential energy of the particle does not depend on the time, that is, $V = V(\mathbf{r})$. In such cases the solution of the Schrödinger equation

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

It is possible to use the *method of separation of variables*. This method consists of assuming that the wave function $\Psi(\mathbf{r}, t)$ can be written as a product of two functions a function of position only, $\Psi(\mathbf{r})$, and a function of time only, $f(t)$:

$$\Psi(\mathbf{r}, t) = \psi(\mathbf{r}) f(t) \quad \dots(3.59)$$

Then the Schrödinger Equation becomes

$$i\hbar \psi(\mathbf{r}) \frac{df(t)}{dt} = f(t) \left[-\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}) \right] \psi(\mathbf{r})$$

Dividing both sides by $\psi(\mathbf{r}) f(t)$, we get

$$i\hbar \frac{1}{f(t)} \frac{df(t)}{dt} = \frac{1}{\psi(\mathbf{r})} \left[-\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}) \right] \psi(\mathbf{r})$$

Note that the left-hand side depends only on t and right-hand side only on \mathbf{r} . Therefore, both sides must be equal to a constant. We shall denote this constant by E because, this constant is equal to the energy of the particle, we thus obtain the two equations

$$\boxed{\begin{aligned} i\hbar \frac{df(t)}{dt} &= E f(t) && \dots(3.60) \\ \left[-\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}) \right] \psi(\mathbf{r}) &= E \psi(\mathbf{r}) && \dots(3.61) \end{aligned}}$$

The first of these equations depends only on the time t . It can be immediately integrated to give

$$f(t) = \exp\left(-\frac{iEt}{\hbar}\right) \quad \dots(3.62)$$

The second equation depends only on the space coordinates. It is called the **time-independent Schrödinger equation**. The solution of this equation depends on the particular form of the potential $V(\mathbf{r})$.

The full solution of the time-dependent Schrödinger equation can be written as

$$\boxed{\Psi(\mathbf{r}, t) = \psi(\mathbf{r}) \exp(-iEt/\hbar)} \quad \dots(3.63)$$

We may write time-independent Schrödinger equation as

$$\boxed{H \psi(\mathbf{r}) = E \psi(\mathbf{r})} \quad \dots(3.64)$$

where H is the Hamiltonian operator

$$H = -\frac{\hbar^2 \nabla^2}{2m} + V(\mathbf{r}) \quad \dots(3.65)$$

Equation (3.64) has the following special property:

- The operator H acting on the function $\Psi(r)$ gives the function multiplied by the constant E . $\hat{H}\Psi = E\Psi$. Such an equation is called an **eigenvalue equation**.
- The function Ψ is called an **eigenfunction of the operator H** and E is the **eigenvalue**.
- In general, many eigenfunctions and eigenvalues may correspond to a given H . The set of all the eigenvalues is called the eigenvalue spectrum of H .
- Since H is the Hamiltonian, the eigenvalues E are called the energy eigenvalues because these are the possible energies of the system.
- To indicate that an eigenfunction corresponds to a particular eigenvalue E_n , we put a subscript n with $\Psi(r)$, that is, we write it as $\Psi_n(r)$.
- The problem of solving the Schrödinger equation thus reduces to finding the eigenvalues and eigenfunctions of the Hamiltonian H .

3.12 Degeneracy

Sometimes it happens that more than one linearly independent eigenfunctions correspond to the same eigenvalue. The eigenvalue is then said to be degenerate.

- If there are k linearly independent eigenfunctions corresponding to the same eigenvalue, then this eigenvalue is said to be k -fold degenerate.
- Any linear combination of the degenerate eigenfunctions is also an eigenfunction corresponding to the same eigenvalue.
- If $\Psi_1, \Psi_2, \dots, \Psi_k$ are linearly independent eigenfunctions corresponding to an eigenvalue E , then $\Psi = c_1\Psi_1 + c_2\Psi_2 + \dots + c_k\Psi_k$ is also an eigenfunction corresponding to E .

3.13 Reality of Eigenvalues

To prove that all the energy eigenvalues are real.

Let E be the eigenvalue corresponding to the eigenfunction Ψ . Then

$$H\Psi = E\Psi$$

Since the Hamiltonian H is a Hermitian operator, we have

$$\int \psi^* H \psi \, d\mathbf{r} = \int (H\psi)^* \psi \, d\mathbf{r}$$

These equations give

$$\int \psi^* E \psi \, d\mathbf{r} = \int E^* \psi^* \psi \, d\mathbf{r}$$

or
$$(E - E^*) \int \psi^* \psi \, d\mathbf{r} = 0$$

Since the probability integral $\int \psi^* \psi \, d\mathbf{r}$ is necessarily positive, it follows that

$$E = E^*$$

Hence the eigenvalues of H are *real*.

3.14 Stationary States

The position probability density corresponding to the states represented by ‘separable’ wave functions $\Psi(\mathbf{r}, t) = \psi(\mathbf{r}) \exp(-iEt/\hbar)$ is independent of time:

$$\begin{aligned} P(\mathbf{r}, t) &= \Psi^*(\mathbf{r}, t) \Psi(\mathbf{r}, t) \\ &= \psi^*(\mathbf{r}) e^{iEt/\hbar} \psi(\mathbf{r}) e^{-iEt/\hbar} \\ &= \psi^*(\mathbf{r}) \psi(\mathbf{r}) \end{aligned}$$

Therefore, these states are called stationary states.

The expectation value of the total energy operator in a state described by the wave function $\Psi(\mathbf{r}, t) = \psi(\mathbf{r}) \exp(-iEt/\hbar)$ is equal to the energy eigenvalue of that state for all time if the wave function is normalized:

$$\begin{aligned} &\int \Psi^*(\mathbf{r}, t) H \Psi(\mathbf{r}, t) \, d\mathbf{r} \\ &= \int \psi^*(\mathbf{r}) e^{iEt/\hbar} H \psi(\mathbf{r}) e^{-iEt/\hbar} \, d\mathbf{r} \\ &= \int \psi^*(\mathbf{r}) E \psi(\mathbf{r}) \, d\mathbf{r} \\ &= E \int \psi^*(\mathbf{r}) \psi(\mathbf{r}) \, d\mathbf{r} \\ &= E \end{aligned}$$

3.15 Orthogonality of Eigenfunctions

The eigenfunctions corresponding to distinct eigenvalues are orthogonal. We prove it below.

Let ψ_k and ψ_n be the eigenfunctions corresponding to the eigenvalues E_k and E_n , respectively. Then

$$H\psi_k = E_k\psi_k \quad \dots(3.66)$$

and
$$H\psi_n = E_n\psi_n \quad \dots(3.67)$$

Taking complex-conjugate of (3.67) and remembering that E_n is real,

$$(H\psi_n)^* = E_n\psi_n^* \quad \dots(3.68)$$

Pre-multiplying (3.66) by ψ_n^* and post-multiplying (3.68) by ψ_k , we obtain

$$\psi_n^*(H\psi_k) = E_k\psi_n^*\psi_k \quad \dots(3.69)$$

and
$$(H\psi_n)^*\psi_k = E_n\psi_n^*\psi_k \quad \dots(3.70)$$

Subtracting (3.70) from (3.67) and integrating, we obtain

$$(E_k - E_n) \int \psi_n^* \psi_k d\mathbf{r} = \int [\psi_n^*(H\psi_k) - (H\psi_n)^*\psi_k] d\mathbf{r}$$

Since H is Hermitian, the integral on the right-hand side is zero. Therefore,

$$(E_k - E_n) \int \psi_n^* \psi_k d\mathbf{r} = 0$$

Since $E_k \neq E_n$, this gives

$$\int \psi_k^* \psi_n d\mathbf{r} = 0$$

This shows that the eigenfunctions are orthogonal.

If the eigenfunctions are normalized, then combining the normalization condition with the orthogonality condition, we have

$$\boxed{\int \psi_k^* \psi_n d\mathbf{r} = \delta_{kn}} \quad \dots(3.71)$$

$$\delta_{kn} = 1 \text{ for } k = n \quad \delta_{kn} = 0 \text{ for } k \neq n$$

This equation is known as the **orthonormality condition**.

3.16 Parity

For simplicity we shall discuss the one-dimensional case. Suppose the potential function is symmetric about the origin, i.e., it is an even function:

$$V(x) = V(-x) \quad \dots(3.72)$$

Let us study the behavior of the Schrödinger equation under the *operation of reflection* through the origin, $x \rightarrow -x$. This operation is called the *parity operation*. The Schrödinger equation is

$$-\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x) \quad \dots(3.73)$$

Replacing x by $-x$, we get

$$-\frac{\hbar^2}{2m} \frac{d^2\psi(-x)}{dx^2} + V(x)\psi(-x) = E\psi(-x) \quad \dots(3.74)$$

where we have used (3.72). Comparing these equations we note that $\psi(x)$ and $\psi(-x)$ are eigenfunctions corresponding to the same eigenvalue E . There are two possible cases:

Case 1: If the eigenvalue is nondegenerate then $\psi(x)$ and $\psi(-x)$ can differ only by a multiplicative constant:

$$\psi(-x) = c\psi(x)$$

Changing the sign of x in this equation, we get

$$\psi(x) = c\psi(-x)$$

Combining these two equations,

$$\psi(x) = c^2\psi(x)$$

so that

$$c^2 = 1$$

or

$$c = \pm 1$$

Therefore,

$$\psi(-x) = \pm \psi(x) \quad \dots(3.75)$$

This shows that the eigenfunctions can be divided into two classes. The one for which

$$\psi(-x) = \psi(x) \quad \dots(3.76)$$

are said to have **even parity**. The other, for which

$$\psi(-x) = -\psi(x) \quad \dots(3.77)$$

are said to have **odd parity**.

Case 2: If the eigenvalue is **degenerate** then $\psi(-x)$ need not be a multiple of $\psi(x)$. In that case, $\psi(x)$ and $\psi(-x)$ are two linearly independent solutions corresponding to the same eigenvalue. Therefore, any linear combination of $\psi(x)$ and $\psi(-x)$ is also a possible eigenfunction. We can choose two linear combinations as

$$\psi_+(x) = \psi(x) + \psi(-x)$$

and

$$\psi_-(x) = \psi(x) - \psi(-x)$$

Clearly $\psi_+(x)$ has **even** parity while $\psi_-(x)$ has **odd** parity.