2-11 Schrödinger's Wave Equations

To describe the motion of a particle of atomic dimensions in space and time, Schrödinger derived differential equations, which control the space–time behaviour of the wavefunction ψ of de Broglie waves associated with that particle. These differential equations are known as Schrödinger's wave equations.

Erwin Schrödinger (1887–1961)

Erwin Schrödinger, the famous Austrian physicist, contributed to the creation of quantum mechanics and formulated the famous Schrödinger wave equation.

Derivation of time-independent and time-dependent one-dimensional Schrödinger's wave equations

Suppose that $\psi(r, t)$ is the wave displacement of de Broglie waves associated with a moving particle of rest mass m_0. Then the one-dimensional general wave-equation for these waves can be expressed as

$$\frac{\partial^2 \psi}{\partial x^2} = \frac{1}{v^2}\frac{\partial^2 \psi}{\partial t^2} \tag{2.73}$$

where v is the particle velocity.

The general solution of Eq. (2.73) is given by

$$\psi = \exp\{i(kx - \omega t)\} \tag{2.74}$$

where ω is the angular frequency and k the propagation constant.

If E is the energy and p the momentum of the particle, then we have

$$E = h\nu = \frac{h}{2\pi} 2\pi\nu = \hbar\omega \qquad \left(\text{since } \hbar = \frac{h}{2\pi} \text{ and } \omega = 2\pi\upsilon\right)$$

and

$$p = \frac{h}{\lambda} = \frac{h}{2\pi}\frac{2\pi}{\lambda} = \hbar k \qquad \left(\text{since } \hbar = \frac{h}{2\pi} \text{ and } k = \frac{2\pi}{\lambda}\right).$$

Using these relations in Eq. (2.74), we have

$$\psi = \exp\left\{\frac{i}{\hbar}(px - Et)\right\} \tag{2.75}$$

Differentiating partially Eq. (2.75) w.r.t. x, we have

$$\frac{\partial \psi}{\partial x} = \frac{\partial}{\partial x}\left[\exp\left\{\frac{i}{\hbar}(px - Et)\right\}\right]$$

or

$$\frac{\partial \psi}{\partial x} = \frac{ip}{\hbar}\exp\left\{\frac{i}{\hbar}(px - Et)\right\}$$

or

$$\frac{\partial \psi}{\partial x} = \frac{ip}{\hbar}\psi \tag{2.76}$$

Differentiating partially Eq. (2.76) w.r.t. x, we have

$$\frac{\partial^2 \psi}{\partial x^2} = \frac{\partial}{\partial x}\left(\frac{ip}{\hbar}\psi\right)$$

or

$$\frac{\partial^2 \psi}{\partial x^2} = \frac{ip}{\hbar}\frac{\partial \psi}{\partial x}$$

or

$$\frac{\partial^2 \psi}{\partial x^2} = \frac{ip}{\hbar}\left(\frac{ip}{\hbar}\right)\psi \qquad \text{[from Eq. (2.76)]}$$

or

$$\frac{\partial^2 \psi}{\partial x^2} = \left(\frac{ip}{\hbar}\right)^2\psi$$

or

$$\frac{\partial^2 \psi}{\partial x^2} = -\frac{p^2}{\hbar^2}\psi \tag{2.77}$$

Differentiating partially Eq. (2.75) w.r.t. time t, we have

$$\frac{\partial \psi}{\partial t} = \frac{\partial}{\partial t}\left[\exp\left\{\frac{i}{\hbar}(px - Et)\right\}\right]$$

or

$$\frac{\partial \psi}{\partial t} = \frac{-iE}{\hbar}\exp\left\{\frac{i}{\hbar}(px - Et)\right\}$$

or

$$\frac{\partial \psi}{\partial t} = \frac{-iE}{\hbar}\psi \tag{2.78}$$

The energy of a particle is expressed as

$$E = \text{KE} + \text{PE}$$

i.e.

$$E = \frac{p^2}{2m_0} + V \tag{2.79}$$

Operating wavefunction ψ on both sides of Eq. (2.79), we have

$$E\psi = \frac{p^2\psi}{2m_0} + V\psi \tag{2.80}$$

Using Eq. (2.77) in Eq. (2.80), we get

$$E\psi = \frac{1}{2m_0}\left(-\hbar^2 \frac{\partial^2\psi}{\partial x^2}\right) + V\psi$$

or

$$E\psi - V\psi = \frac{-\hbar^2}{2m_0}\frac{\partial^2\psi}{\partial x^2}$$

or

$$\frac{-2m_0}{\hbar^2}(E - V)\psi = \frac{\partial^2\psi}{\partial x^2}$$

or

$$\frac{\partial^2\psi}{\partial x^2} + \frac{2m_0}{\hbar^2}(E - V)\psi = 0$$

This is the one-dimensional time-independent Schrödinger's wave equation. The three-dimensional generalization of this equation is given by

$$\nabla^2\psi + \frac{2m_0}{\hbar^2}(E - V)\psi = 0$$

Now, using Eqs. (2.77) and (2.78) in Eq. (2.80), we get

$$\frac{\hbar}{i}\frac{\partial\psi}{\partial t} = \frac{1}{2m_0}\left(-\hbar^2 \frac{\partial^2\psi}{\partial x^2}\right) + V\psi$$

i.e.

$$i\hbar\frac{\partial\psi}{\partial t} = \frac{-\hbar^2}{2m_0}\frac{\partial^2\psi}{\partial x^2} + V\psi$$

This is the one-dimensional time-dependent Schrödinger's wave equation. The three-dimensional generalization of this equation is given by

$$i\hbar\frac{\partial\psi}{\partial t} = \frac{-\hbar^2}{2m_0}\nabla^2\psi + V\psi$$

Significance of Schrödinger's wave equation

Schrödinger presented his famous wave equation as a development of de Broglie ideas of the wave properties. Schrödinger's equation is the fundamental equation of wave mechanics in the same sense as the Newton's second law of motion of classical mechanics. It is the differential equation for the de Broglie waves associated with particles and it describes the motion of particles.

Physical interpretation of wavefunction ψ

The time-dependent Schrödinger's wave equation is given by

$$i\hbar\frac{\partial\psi}{\partial t} = \frac{-\hbar^2}{2m_0}\frac{\partial^2\psi}{\partial x^2} + V\psi$$

In this equation, the wavefunction $\psi(x, t)$ gives the behaviour of a particle at a given point x in one dimension at a given time. The magnitude of wavefunction ψ is large in regions, where the probability of finding the particle is high and its magnitude is small in regions, where the probability of finding the particle is low. Thus, we can regard ψ as a measure of the probability of finding the particle around a particular position. Now since, the probability of finding the particle at a particular region must be real and positive, but the wavefunction ψ is, in general, a complex quantity; so we take $\psi\psi^* = |\psi|^2$ (where ψ^* is the complex conjugate of ψ) as a measure of the probability of finding the particle at a particular region. The quantity $|\psi|^2$ is known as the probability density.

Thus, the probability of finding the particle in a particular linear region dx is given by

$$P(x) = |\psi(x)|^2\, dx$$

Similarly, the probability of finding the particle in an elementary volume dV is given by

$$P(x, y, z) = |\psi(x, y, z)|^2\, dV$$

Conditions for acceptable wavefunction ψ

To be an acceptable solution of Schrödinger's wave equation, the wave function ψ must fulfil the following requirements:

1. For an infinite value of $\psi(x, y, z)$, the uncertainty principle does not obey. Hence, the wavefuction must be finite everywhere for all values of x, y and z.
2. If the wavefunction ψ has two or more values at a point then there will be two or more probabilities of finding the particle at this particular point. Hence, the wavefunction must be single-valued.
3. It must be continuous in all regions except in those regions where the potential energy $V(x, y, z) = \infty$.
4. It must have a continuous first derivative everywhere. This is the necessary condition for the Schrödinger equation.

Important features of wavefunction ψ

1. The wavefunction ψ contains all the measurable information about the particle.
2. It can interfere with itself. This property explains the phenomenon of electron diffraction.
3. The integration of ψ and its complex conjugate ψ^* over all space is equal to one, i.e. $\int_{-\infty}^{+\infty} \psi(x)\psi^*(x)dx = 1$, which indicates that if the particle exists, then the probability of finding it somewhere is one.

4. The wavefunction ψ allows energy calculation via the Schrödinger equation.
5. The wavefunction ψ permits the calculation of most probable value (expectation value) of a given variable.

2-13 Application of Time-independent Schrödinger's Wave Equation

Particle in a one-dimensional potential box

Consider a particle of rest mass m_0 in a one-dimensional potential box of length a as shown in Figure 2.8. For such a particle the potential energy function can be expressed as

$$V(x) = \begin{cases} 0 & \text{for } 0 < x < a \\ \infty & \text{for } x < 0 \text{ and } a < x \end{cases} \tag{2.84}$$

The corresponding boundary conditions for wavefunction of de Broglie waves associated with this particle are as follows:

$$\psi(x) = \begin{cases} 0 & \text{for } x = 0 \\ 0 & \text{for } x = a \end{cases} \tag{2.85}$$

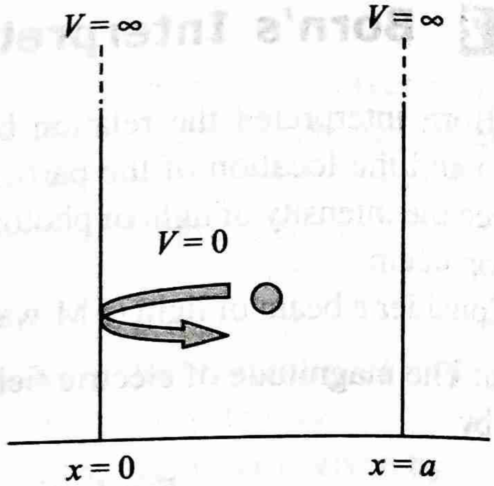

Figure 2.8 Particle in a one-dimensonal potential box.

The time-independent Schrödinger equation

$$\frac{\partial^2\psi}{\partial x^2} + \frac{2m_0}{\hbar^2}(E - V)\,\psi = 0$$

for such a particle can be written as

$$\frac{\partial^2\psi}{\partial x^2} + \frac{2m_0}{\hbar^2}E\psi = 0 \qquad [\text{since } V = 0 \text{ for } 0 < x < a] \tag{2.86}$$

The propagation constant of the de Broglie waves is given by

$$k = \frac{p}{\hbar} = \frac{\sqrt{2m_0E}}{\hbar}$$

or

$$k^2 = \frac{2m_0E}{\hbar^2} \tag{2.87}$$

Using Eq. (2.87) in Eq. (2.86), we have

$$\frac{\partial^2\psi}{\partial x^2} + k^2\psi = 0 \tag{2.88}$$

The general solution of Eq. (2.88) can be expressed as

$$\psi(x) = A\sin kx + B\cos kx \tag{2.89}$$

where A and B are constants to be determined by using the boundary conditions of Eq. (2.85).

Applying the first boundary condition $\psi(0) = 0$ to Eq. (2.89), we have

$$\psi(0) = A\sin k0 + B\cos k0$$

or

$$0 = A0 + B1$$

or

$$B = 0$$

Then Eq. (2.89) reduces to

$$\psi(x) = A\sin kx \tag{2.90}$$

Applying the second boundary condition, $\psi(a) = 0$ to Eq. (2.90), we have

$$\psi(a) = A \sin ka$$

or

$$0 = A \sin ka$$

i.e.

$$\text{either } A = 0 \quad \text{or} \quad \sin ka = 0$$

But A cannot be equal to zero because in this condition $\psi(x)$ will be zero for the region $0 < x < a$, which shows the absence of the particle in the box. Hence, we must have

$$\sin ka = 0$$

i.e.

$$\sin ka = \sin n\pi \qquad (\text{where } n = 1, 2, 3, \ldots \text{ but } n \neq 0)$$

i.e.

$$ka = n\pi$$

i.e.

$$k = \frac{n\pi}{a} \tag{2.91}$$

Using Eq. (2.91) in (2.90), we have

$$\psi(x) = A \sin\frac{n\pi x}{a} \tag{2.92}$$

Now applying the normalization condition

$$\int_{-\infty}^{+\infty} \psi(x)\,\psi^*(x)\,dx = 1$$

to Eq. (2.92), we have

$$\int_0^a \psi(x)\,\psi^*(x)\,dx = 1$$

or

$$\int_0^a \left(A\sin\frac{n\pi x}{a}\right)\left(A\sin\frac{n\pi x}{a}\right)^* dx = 1$$

or

$$A^2 \int_0^a \left(\sin^2\frac{n\pi x}{a}\right) dx = 1$$

or

$$\frac{A^2}{2}\int_0^a \left(2\sin^2\frac{n\pi x}{a}\right) dx = 1$$

or

$$\frac{A^2}{2}\int_0^a \left(1-\cos\frac{2n\pi x}{a}\right) dx = 1$$

or

$$\frac{A^2}{2}\left[x - \frac{a}{2n\pi}\sin\frac{2n\pi x}{a}\right]_0^a = 1$$

or

$$\frac{A^2}{2}\left[\left\{a - \frac{a}{2n\pi}\sin\frac{2n\pi a}{a}\right\} - \left\{0 - \frac{a}{2n\pi}\sin 0\right\}\right] = 1$$

or

$$\frac{A^2}{2}\,a = 1$$

or

$$A = \sqrt{\frac{2}{a}} \tag{2.93}$$

Substituting the value of normalization constant A in Eq. (2.92), the normalized eigenfunctions for the particle confined in one-dimensional potential box of length a are given by

$$\psi(x) = \psi_n(x) \text{ (say)} = \sqrt{\frac{2}{a}} \sin \frac{n\pi x}{a}$$

The first three eigenfunctions are shown in Figure 2.9.

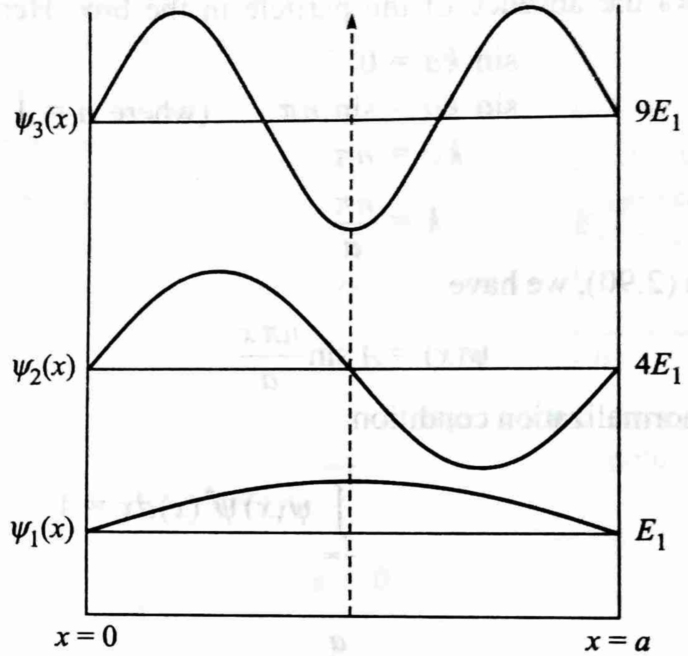

Figure 2.9 Eigenfunctions of a particle confined in one-dimensional box.

The corresponding energy eigenvalues and the momentum eigenvalues are given by

$$E = E_n \text{ (say)} = \frac{\hbar^2 k^2}{2m_0} = \frac{n^2\pi^2\hbar^2}{2m_0 a^2} = \frac{n^2 h^2}{8m_0 a^2}$$

$$p = p_n \text{ (say)} = \sqrt{2m_0 E} = \sqrt{2m_0 \frac{n^2\pi^2\hbar^2}{2m_0 a^2}} = \frac{n\pi\hbar}{a}$$

For $n = 1$, we have

$$E_1 = \frac{\pi^2\hbar^2}{2m_0 a^2} = \frac{h^2}{8m_0 a^2}$$

This is the lowest possible energy of the particle, which is known as zero-point energy.

Physical significance of zero-point energy: The zero-point energy is a fundamental characteristic of quantum mechanics, which indicates that in quantum mechanics the minimum energy of the particle confined in one-dimensional potential box cannot be zero. If the minimum energy of the particle is zero, then the particle will be completely located at a particular position (i.e. uncertainty in its position will be zero, i.e. $\Delta x = 0$) with zero momentum (in this case, uncertainty in its momentum will be zero, i.e. $\Delta p = 0$). This violates the Heisenberg uncertainty principle. The existence of zero-point energy, therefore, preserves the Heisenberg uncertainty principle.