Schrödinger theory of quantum mechanics

In trying to find the wave associated with the particle, de Broglie's postulates give us the first guideline. We have seen that if a particle has a well-defined momentum and energy, we can use a sinusoidal traveling wave, that is, either

$$\psi = A\sin(kx - wt) \quad \text{or} \quad \psi = A\cos(kx - wt)$$

or a linear combination of both. As we have seen, if we want to describe a free particle, which is partially localized, we could use a wave packet.

De Broglie's hypothesis does not tell us what type of wave one can associate with a particle that is not free and that is acted on by a force. If a particle is acted on by a force, its momentum and its energy will not be constant. Therefore, it is meaningless to talk about a λ and a ν, because these quantities are changing. The Schrödinger theory tells us how to obtain the wavefunction $\psi(x, t)$ associated with a particle, when we specify the forces acting on the particle, by giving the potential energy associated with the forces. (In quantum mechanics the potential energy is often referred to simply as the potential). The Schrödinger theory also tells us how to extract information about the particle from the associated wavefunction.

Schrödinger developed a differential equation whose solutions yield the possible wavefunctions that can be associated with a particle in a given physical situation. This equation, known as the *Schrödinger equation*, tells us how the wavefunction changes as a result of the forces acting on the particle. Because the wavefunction ψ is a function of space and time, the equation contains derivatives (remember that a derivative represents the rate of change) with respect to x, y, and z and with respect to t.

The total energy of a particle is equal to the kinetic energy plus the potential energy,

$$E = \frac{1}{2}mv^2 + E_p \quad = \frac{p^2}{2m} + E_p$$

Therefore,

$$E\psi = \frac{p^2}{2m}\psi + E_p\psi \cdots\cdots\cdots (1)$$

In quantum mechanics physical observables are generally expressed as operators. Operators for some of the observables are

Observable		Operator
$Energy(E)$	$\rightarrow$	$i\hbar\frac{\partial}{\partial t}$
$Momentum(p)$	$\rightarrow$	$-i\hbar\frac{\partial}{\partial x}$

Substituting the operators in equation (1), we get,

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

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

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} + E_p\psi = i\hbar\frac{\partial\psi}{\partial t}\cdots\cdots\cdots(2)$$

Equation (2) is known as the one-dimensional time-dependent Schrödinger equation. If the potential energy E_p is known, this equation can be solved in principle, and the solution will yield the possible wavefunctions that we can associate with the particle. The Schrödinger equation is to quantum mechanics what Newton's second law is to classical physics.

The Schrödinger Equation for a Free Particle

Let us consider a free particle moving along the x axis with definite momentum $p = mv$ and definite energy $E = 1/2mv^2$. If no force acts on the particle, that is, $F = 0$, the potential energy is $E_p = constant$, which we can choose to be 0. Thus, the condition $F = 0$ requires that $E = constant$. The Schrödinger equation (Eq. 2) in this case may be written for $E_p = 0$ as

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} = i\hbar\frac{\partial\psi}{\partial t}\cdots\cdots\cdots(3)$$

Since we are dealing with a particle of well-defined momentum and energy, we might expect that the solution would be in the form of a traveling wave, that is, either

$$\psi = A\sin(kx - wt) \quad \text{or} \quad \psi = A\cos(kx - wt)$$

or some linear combination of these two functions. There is a particular combination of these two functions that does satisfy the Schrödinger equation. This combination is

$$\psi = A\left[\cos(kx - \omega t) + i\sin(kx - \omega t)\right]$$

which, by mathematical definition, may be written as

$$\psi = Ae^{i(kx-\omega t)}\cdots\cdots\cdots(4)$$

Differentiating equation (4) twice with respect to x, we get

$$\frac{\partial\psi}{\partial x} = \frac{\partial}{\partial x}\left[Ae^{i(kx-\omega t)}\right] = ikAe^{i(kx-\omega t)}$$

$$\frac{\partial^2\psi}{\partial x^2} = \frac{\partial}{\partial x}\left[ikAe^{i(kx-\omega t)}\right] = (ik)^2\,Ae^{i(kx-\omega t)} = -k^2Ae^{i(kx-\omega t)}$$

Differentiating (4) with respect to t, we get

$$\frac{\partial\psi}{\partial t} = \frac{\partial}{\partial t}\left[Ae^{i(kx-\omega t)}\right] = -i\omega Ae^{i(kx-\omega t)}$$

Substituting into equation (3), we get

$$\frac{\hbar^2 k^2}{2m} Ae^{i(kx-\omega t)} = \hbar\omega \; Ae^{i(kx-\omega t)}$$

$$\frac{\hbar^2 k^2}{2m} = \hbar\omega \cdots\cdots\cdots (5)$$

The kinetic energy of a particle is given by

$$E = \frac{1}{2}mv^2 = \frac{p^2}{2m} \cdots\cdots\cdots (i)$$

From Planck's theory,

$$E = h\nu = h\frac{\omega}{2\pi} = \hbar\omega \cdots\cdots\cdots (ii)$$

From de Broglie's hypothesis

$$p = \frac{h}{\lambda} = \frac{h}{2\pi/k} = \hbar k \cdots\cdots\cdots (iii)$$

Substituting (ii) and (iii) in (i)

$$\hbar\omega = \frac{\hbar^2 k^2}{2m} \cdots\cdots\cdots (iv)$$

which is same as equation (5)

The consistency of the formulation has been demonstrated.