

## 2.13 THE SCHRODINGER WAVE EQUATION

In 1926 Erwin Schrodinger, an Austrian Physicist developed the *wave mechanical model* of the atom. This model takes into account the wave and particle nature of the electron. In his model, he visualized the atom as a positively charged nucleus surrounded by a standing electron wave which extends round the nucleus.

Schrodinger proposed that if the electron has wave-like nature, it would obey the same equation of motion as all other known types of waves obey. On the basis of this simple idea, he derived an equation which describes the wave motion of an electron wave along any of the three axes viz. x, y and z axis and is called *Schrodinger Wave Equation*. This equation cannot be proved or derived. Rather, it

may be taken as the starting point for a discussion of modern quantum theory. It is possible, however, to make an argument for the Schrodinger equation in the following way.

Let us consider a particle P moving with uniform angular velocity  $\omega$  rad  $s^{-1}$  in a circular path of radius A, which is executing simple harmonic motion. We measure time from the instant when P passes O and then after a time t second, we imagine P to have described an angle  $\theta = \omega t$  radians. The variation of displacement with time can be represented by a simple harmonic wave as shown in Fig. 2.9.

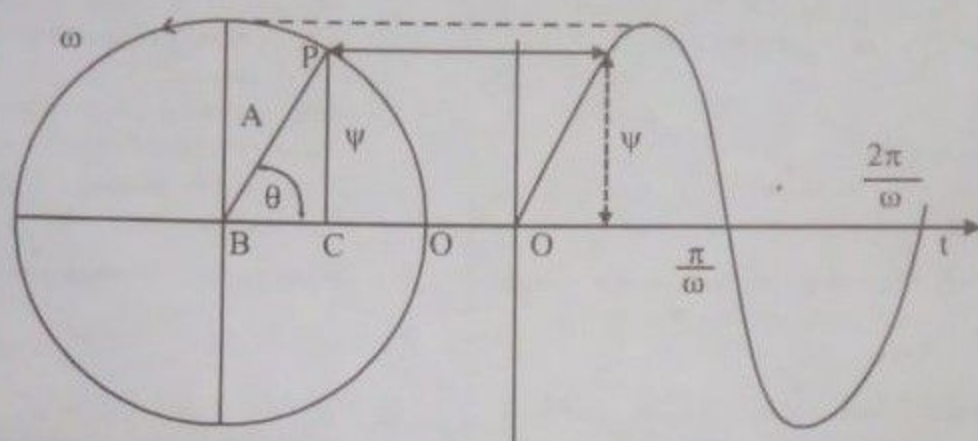


Fig. 2.9 The representation of simple harmonic motion and harmonic wave

A simple harmonic wave may be produced in a medium by a body executing simple harmonic motion. By considering the right angled triangle PBC, we can write

$$\frac{PC}{PB} = \frac{\Psi}{A} = \sin \theta$$

$$\Psi = A \sin \theta = A \sin \omega t \quad (\because \theta = \omega t) \quad 2.35$$

Where  $\Psi$  (pronounced a psi) represents the vertical displacement of the harmonic wave. We can plot this displacement against time as on the right hand side of Fig. 2.9

The angular velocity,  $\omega = 2\pi\nu$

Where  $\nu$  is the frequency

$$\Psi = A \sin 2\pi\nu t \quad (2.36)$$

In order to consider the nature of progressive waves, we are more interested in the distance variation of displacement. For this purpose we need the fundamental distance — time relationship.

$$x = vt$$

$$(2.37)$$

Where x is distance covered in time t at speed v.

$$\begin{aligned} t &= \frac{\theta}{\omega} \\ \theta &= 2\pi \\ \text{or } t &= \frac{2\pi}{\omega} \\ \nu &= \frac{1}{t} \\ \nu &= \frac{\omega}{2\pi} \\ \omega &= 2\pi\nu \end{aligned}$$

Combining Equation (2.35) and Equation (2.36), we have

$$\Psi = A \sin \frac{2\pi v x}{v} \quad (\because t = x/v) \quad (2.38)$$

and wave is shown in Fig. 2.10

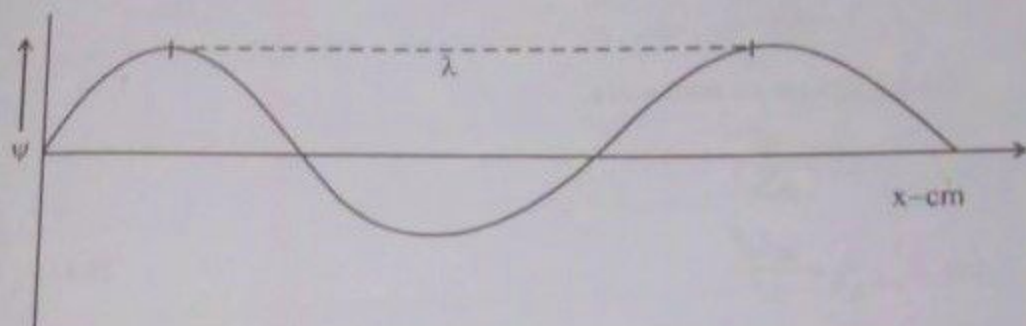


Fig. 2.10 The concept of progressive wave with wavelength  $\lambda$ .

Besides the frequency  $\nu$ , we now have another property by which we can characterize the wave — its wavelength  $\lambda$ , which is the distance traveled during a complete cycle.

$$\nu = \frac{v}{\lambda} \quad (\because v = \nu\lambda)$$

So, we have

$$\Psi = A \sin \frac{2\pi x}{\lambda} \quad (2.39)$$

On differentiating Equation (2.39) with respect to  $x$ , we get

$$\begin{aligned} \frac{d\Psi}{dx} &= \left( A \cos \frac{2\pi x}{\lambda} \right) \left( \frac{2\pi}{\lambda} \right) \\ &= \frac{2\pi}{\lambda} A \cos \frac{2\pi x}{\lambda} \end{aligned}$$

Differentiating again, we get

$$\begin{aligned} \frac{d^2\Psi}{dx^2} &= \frac{2\pi A}{\lambda} \left( -\sin \frac{2\pi x}{\lambda} \right) \left( \frac{2\pi}{\lambda} \right) \\ &= \frac{-4\pi^2}{\lambda^2} \left( A \sin \frac{2\pi x}{\lambda} \right) \\ &= \frac{-4\pi^2}{\lambda^2} \Psi \quad \left( \because \Psi = A \sin \frac{2\pi x}{\lambda} \right) \end{aligned}$$

$$\text{or} \quad \frac{d^2\Psi}{dx^2} + \frac{4\pi^2}{\lambda^2} \Psi = 0 \quad (2.40)$$



This is the *classical wave equation* describing the wave motion of any particle along x-axis. Since the electron is proved to have a wave character, let us assume that the same behavior is shown by electron waves. To apply this equation to a particle,  $\lambda$  must be replaced by the momentum of the particle using de-Broglie's relationship i.e.,

$$\lambda = \frac{h}{mv}$$

Taking square on both sides

$$\lambda^2 = \frac{h^2}{m^2 v^2}$$

$$\text{or } \frac{1}{\lambda^2} = \frac{m^2 v^2}{h^2} \quad (2.41)$$

Substituting this value in equation 2.40, we get

$$\frac{d^2\Psi}{dx^2} + \frac{4\pi^2 m^2 v^2}{h^2} \Psi = 0 \quad (2.42)$$

In order to express this equation in terms of energy, we make use of the fact that total energy (E) is the sum of kinetic energy and potential energy (Bohr's theory).

Total Energy = Kinetic Energy + Potential Energy

$$E = \frac{1}{2} mv^2 + V$$

$$\text{or } \frac{1}{2} mv^2 = E - V$$

$$mv^2 = 2(E - V)$$

$$v^2 = \frac{2(E - V)}{m}$$

Substituting this value of  $v^2$  in equation (2.42), we get

$$\frac{d^2\Psi}{dx^2} + \frac{8\pi^2 m}{h^2} (E - V) \Psi = 0 \quad (2.43)$$

This is the wave equation when the particle is moving in one dimensional system, i.e., the wave is moving in one direction x. For electrons which can have their wave motion along any of the three, axes, x, y, z, we can similarly write the wave equation as

$$\frac{\partial^2\Psi}{\partial x^2} + \frac{\partial^2\Psi}{\partial y^2} + \frac{\partial^2\Psi}{\partial z^2} + \frac{8\pi^2 m}{h^2} (E - V) \Psi = 0 \quad (2.44)$$

$$\nabla^2 \Psi + \frac{8\pi^2 m}{h^2} (E - V) \Psi = 0 \quad (2.45)$$

where  $\nabla^2$  (del squared) is known as the *Laplacian operator*.

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

Equations (2.43), (2.44) and (2.45) are different forms of the Schrodinger wave equation.

Equation (2.45) can be written in another way as

$$\nabla^2 \Psi = \frac{-8\pi^2 m}{h^2} (E - V) \Psi$$

$$\text{or } \nabla^2 \Psi = \frac{-8\pi^2 m}{h^2} E \Psi + \frac{8\pi^2 m}{h^2} V \Psi$$

Multiply this equation by  $\frac{h^2}{8\pi^2 m}$

$$\frac{h^2}{8\pi^2 m} \nabla^2 \Psi = -E\Psi + V\Psi$$

$$\text{or } E\Psi = \frac{-h^2}{8\pi^2 m} \nabla^2 \Psi + V\Psi$$

$$\text{or } E\Psi = \left( -\frac{h^2}{8\pi^2 m} \nabla^2 + V \right) \Psi$$

$$\text{or } H\Psi = E\Psi \quad (2.46)$$

where  $H = -\frac{h^2}{8\pi^2 m} \nabla^2 + V$ , and is known as *Hamiltonian operator*. It represents a certain way of expressing the total energy of a system and  $E$  is the numerical value of that energy.

### Applications of Schrodinger Wave Equation

Important applications of the equation are:

- (i) This equation is used to calculate the energy and wave function of a particle such as electron in a one-dimensional box.
- (ii) This equation is used to calculate the energy and wave function of particle in a three dimensional box.
- (iii) This equation introduces the concept of degeneracy in atomic orbitals.



- (iv) This equation has been used to derive an expression for an electron in H-atom.
- (v) This equation has been used to derive various quantum numbers which represent the postal address of an electron in an atom.
- (vi) This equation has been used to calculate the energy of  $\pi$ -electrons in conjugated systems like benzene.
- (vii) This is also used to calculate the resonance energy of molecules.

## 2.14 THE INTERPRETATION OF WAVE FUNCTION ( $\Psi$ )

The wave function  $\Psi$  is a sort of an *amplitude function*. In the case of a light wave, the intensity of a light at any point is proportional to the square of the amplitude of wave at that point. In terms of light quanta or photon  $h\nu$ , the more intense the light at any place, the more photons are falling on that place. This fact can be expressed in another way by saying that the greater the value of amplitude of a light wave in any region the greater is the probability of a photon being within that region.

$\Psi$  being a mathematical function has no physical meaning by itself. Max Born suggested in 1927 that the product  $\Psi^2$  does have physical meaning, since it gives the probability of finding the particle (or the product of the wave function  $\Psi$  and its complex conjugate  $\Psi^*$  is a probability density). The probability of finding the electron in space is not given by  $\Psi$  only, even though  $\Psi$  is considered to be a complete function which has a real value and always zero or positive. The complex conjugate of  $\Psi$  is obtained by changing  $i$  to  $-i$  everywhere in  $\Psi$ . If the behaviour of the electron is represented by a wave equation, we can equate the square of the function with either (a) the electron density and (b) the probability that the electron will be found in a given volume element, we thus get a physical significance for the function  $\Psi(x, y, z)$  in that

$$\Psi^2 \cdot dx \cdot dy \cdot dz (= \Psi^2 dv)$$

measures the probability that the electron will be found in the volume element  $dv$  surrounding the point whose coordinates are  $(x, y, z)$ .

The other interpretation  $\Psi^2 dv$  represents the electron density in the volume element  $dv$  cannot be justified so vigorously as the probability interpretation, but it has proved to be very useful in practice. But difficulties arise when applied to single electron system.

The probability density at some point multiplied by a differential is the probability that a particle will be found there. For example, if a particle can move along the  $x$ -axis and has a wave function  $\Psi(x)$ , then

the probability density,  $f(x) = \Psi^*(x) \Psi(x)$ .

The probability that the particle is between  $x$  and  $x + dx$  is

$$f(x)dx = \Psi^*(x) \cdot \Psi(x) \cdot dx$$

The probability that it is between  $x_1$  and  $x_2$  is

$$\int_{x_1}^{x_2} \Psi^*(x) \cdot \Psi(x) dx$$

The probability that the particle is between  $x = -\infty$  and  $+\infty$  is of course, unity

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

When the integral of the wave function times its complex conjugate over the entire space available is equal to unity, the wave function is said to be normalized.

In calculating probability densities, the wave function is multiplied by its complex conjugate so that the probability density is always real and positive. The function  $\Psi$  as a matter of fact may involve an imaginary part i.e.  $\Psi$  may be a complex quantity.

$$\text{Let } \Psi = a + ib$$

where  $a$  is real quantity and  $b$  is an imaginary part.

Then its complex conjugate

$$\Psi^* = a - ib$$

where  $i$  (iota) is an imaginary part.

These two values of  $\Psi$  and  $\Psi^*$

$$\therefore i^2 = -1$$

$$i = \sqrt{-1}$$

may be imaginary, in order to get a real quantity we multiply them

$$\begin{aligned} \Psi\Psi^* &= (a + ib)(a - ib) = a^2 - (ib)^2 \\ &= a^2 + b^2 \end{aligned}$$

$$\text{or } |\Psi|^2 = a^2 + b^2$$

$$\text{or } \Psi^2 = a^2 + b^2$$

Strictly speaking that  $\Psi^2$  should be the square of the absolute value of the wave function i.e.  $|\Psi|^2$ . However most of the wave functions in atomic or molecular structural problems contain real terms only, and so  $\Psi^2$  may be employed.

"The quantity  $\Psi^2$  tells us where the particle/electron is likely to be (not where it is)."

A wave function not only contains the information about where a particle may be located, but it contains all the information that can be learned about the system this is represented by the wave function. Other physical quantities can be obtained from wave function.



Since  $\Psi\Psi^*$  is a probability density, a wave function must have certain general properties.

or

The physical interpretation of the wave function as a probability amplitude implies that it must obey certain mathematical conditions.

Following are the mathematical requirements which must be met by physically acceptable wave functions.

1. The wave function must be *normalized*, the integral of  $\Psi\Psi^*$  over all the space is unity, since the particle must exist somewhere in that interval if it to exist at all.

$$\int_{-\infty}^{+\infty} \Psi^2(x) \cdot dx = 1$$

or 
$$\int_{-\infty}^{+\infty} \Psi(x)\Psi^*(x) \cdot dx = 1$$

2.  $\Psi(x)$  and  $\frac{d\Psi(x)}{dx}$  must be everywhere *single-valued*. It must be single-valued because the probability of finding the electron at any point must have only one value. If the  $\Psi$  were double-valued, there would be two probabilities for the same position which would be physically meaningless.
3.  $\Psi(x)$  and  $d\Psi(x)/dx$  must be *everywhere finite*. It cannot be infinite at any point, for then the electron would be fixed at exactly that point which would be *inconsistent* with its wave properties or  $\Psi$  cannot become infinite since that would correspond to certainty of particle being at some definite points.
4.  $\Psi(x)$  and  $\frac{d\Psi(x)}{dx}$  must be everywhere *continuous*. The reason for that is that certain properties (e.g. momentum) are calculated by taking the derivatives of the wave function. If the wave function is discontinuous at some point. Its first derivative is infinite at this point. But values of physical properties cannot be infinite, so the wave function cannot be discontinuous. Moreover the requirement of continuity is helpful in the selection of physically reasonable solutions for the wave equation.

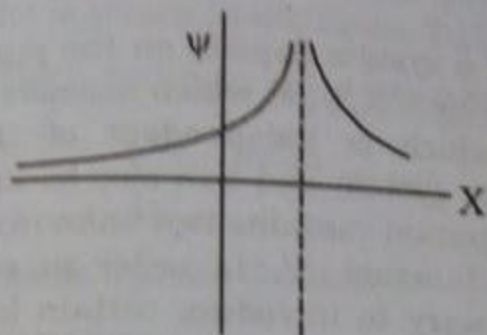
Because of these limitations only certain solutions of Schrodinger equation are of physical interest.

A discontinuous  $\Psi$  cannot correspond to a physically acceptable situation, because it leads to find derivative infinite.

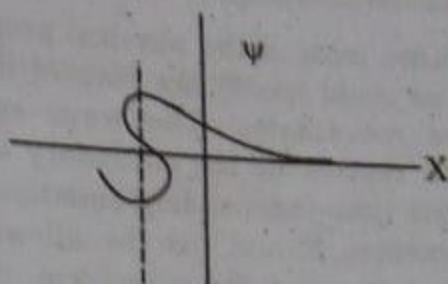
The wave function  $\Psi$  gives information on the outcome of a measurement of any property, not just position, e.g. momentum, energy and angular momentum.  $\Psi$  is not to be thought of as a physical wave. Instead  $\Psi$  is an abstract mathematical entity that gives information about the state of a system. Everything that can be known about the system in a given state is contained in the state function  $\Psi$ . Instead of saying "the state described by the function  $\Psi$ " we can just as well say "the state  $\Psi$ ."



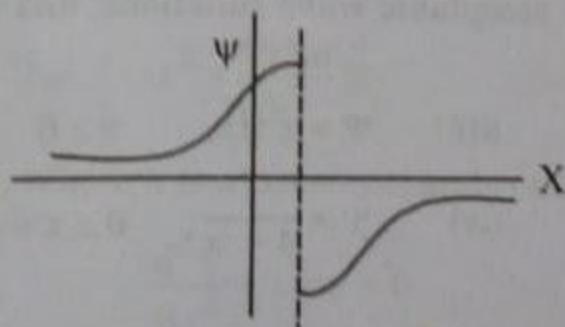
The information given by  $\psi$  is the probabilities of the possible outcomes of measurements of the systems, physical properties.



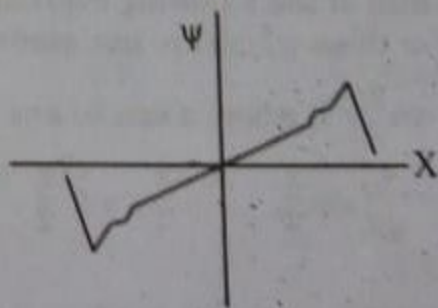
(a) This function becomes infinite at certain value of  $x$



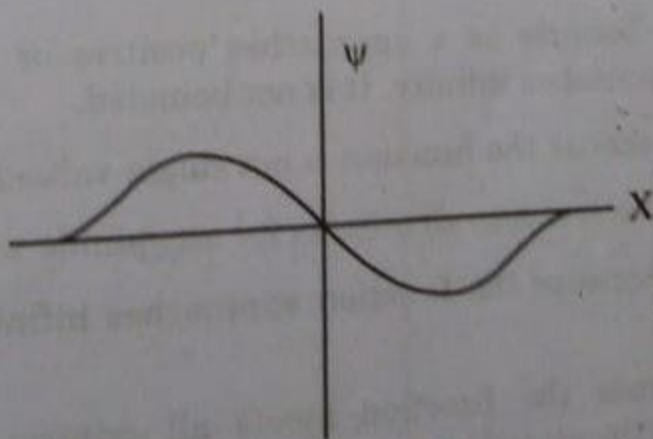
(b) This function is not single valued at every position over the allowed range of  $x$



(c) This function is not everywhere continuous



(d) This function has discontinuous derivative at each cusp.



(d) This meets all the requirements and hence is acceptable.

Fig.2.11. Examples of the wave functions that do and do not meet requirement, for physically acceptable solutions.