❖ Derivation of Schrodinger Wave Equation

The Schrodinger wave equation can be derived from the classical wave equation as well as from the third postulate of quantum mechanics. Now though the two routes may appear completely different, the final result is just the same indicating the objectivity of the quantum mechanical system.

➢ *The Derivation of Schrodinger Wave Equation from Classical Wave Equation*

After the failure of the Bohr atomic model to comply with the Heisenberg's uncertainty principle and dual character proposed by Louis de Broglie in 1924, an Austrian physicist Erwin Schrodinger developed his legendary equation by making the use of wave-particle duality and classical wave equation. In order to understand the concept involved, consider a wave traveling in a string along the *x*-axis with velocity *v*.

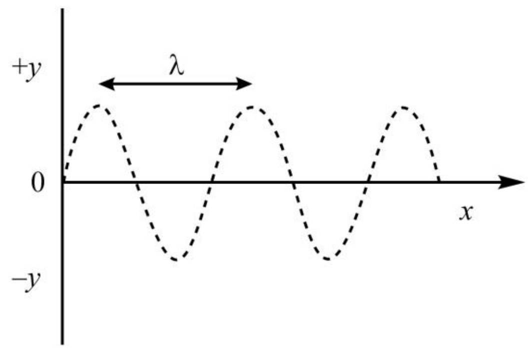

Figure 1. The wave motion in a string.

It can be clearly seen that the amplitude of the wave at any time *t* is the function of displacement *x*, and the equation for wave motion can be formulated as given below.

$$\frac{\partial^2 y}{\partial x^2} = \frac{1}{v^2}\frac{\partial^2 y}{\partial t^2} \tag{13}$$

Therefore, we can say that y is a function of *x* well at *t*.

$$y = f(x)f'(t) \tag{14}$$

Where *f(x)* and *f′(t)* are the functions of coordinate *x* and time, respectively. The nature of the function *f(x)* can be understood by taking the example of stationary or the standing wave.

A standing wave is created in a string fixed between two points with a wave traveling in one direction, and when it strikes the other end, it gets reflected with the same velocity but in negative amplitude. This would create vibrations in that string with or without nodes depending upon the frequency incorporated. We can create fundamental mode (0 node), first overtone (1 node) or second overtone (2 nodes) just by changing the vibrational frequency. The nature of these standing or stationary waves can be understood more clearly by the diagram given below.

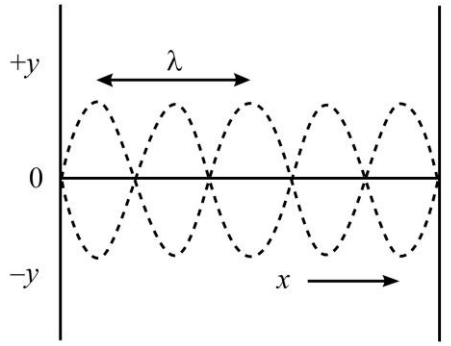

Figure 2. Standing waves in a string.

The mathematical description for such a wave motion is

$$f'(t) = A \sin 2\pi\nu t \tag{15}$$

Where *A* is a constant representing maximum amplitude and *ν* is the frequency of the vibration. Now putting the value of *f′(t)* from equation (15) in equation (14), we get

$$y = f(x)\, A\, Sin\, 2\pi\nu t \tag{16}$$

Differentiating the above equation w.r.t. *t*, we are left with

$$\frac{\partial y}{\partial t} = f(x)\, A 2\pi\nu\, Cos\, 2\pi\nu t \tag{17}$$

Differentiating again

$$\frac{\partial^2 y}{\partial t^2} = -f(x)\, 4\pi^2\nu^2\, A\, Sin\, 2\pi\nu t \tag{18}$$

$$\frac{\partial^2 y}{\partial t^2} = -4\pi^2\nu^2 f(x)\, f'(t) \tag{19}$$

Now differentiating equation (14) w.r.t. *x* only, we get

$$\frac{\partial y}{\partial x} = f'(t)\frac{\partial f(x)}{\partial x} \tag{20}$$

Differentiating again

$$\frac{\partial^2 y}{\partial x^2} = f'(t)\frac{\partial^2 f(x)}{\partial x^2} \tag{21}$$

Now put the value of equation (19) and (21) in equation (13), we get

$$f'(t)\frac{\partial^2 f(x)}{\partial x^2} = \left(\frac{1}{v^2}\right)[-4\pi^2\nu^2 f(x)\, f'(t)] \tag{22}$$

$$\frac{\partial^2 f(x)}{\partial x^2} = \frac{-4\pi^2\nu^2}{v^2} f(x) \tag{23}$$

The equation (23) is now time-independent; and therefore, shows the amplitude dependence only upon the coordinate *x*. Since $c = \nu\lambda$ ($\nu = c/\lambda$), the velocity of the wave can also be replaced by the multiplication of frequency and wavelength i.e. $v = \nu\lambda$.

$$\frac{\partial^2 f(x)}{\partial x^2} = \frac{-4\pi^2\nu^2}{\nu^2\lambda^2} f(x) \tag{24}$$

$$\frac{\partial^2 f(x)}{\partial x^2} = \frac{-4\pi^2}{\lambda^2} f(x) \tag{25}$$

The symbol of the function *f(x)* is replaced by popular $\psi(x)$ or simply the ψ.

$$\frac{\partial^2 \psi}{\partial x^2} = \frac{-4\pi^2}{\lambda^2}\psi \tag{26}$$

Also, as we know that $\lambda = h/mv$, the equation (26) becomes

$$\frac{\partial^2 \psi}{\partial x^2} = \frac{-4\pi^2 m^2 v^2}{h^2}\psi \tag{27}$$

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{4\pi^2 m^2 v^2}{h^2}\psi = 0 \tag{28}$$

Furthermore, as the total energy (*E*) is simply the sum of the potential (*V*) and kinetic energy, we can say that

$$E = \frac{mv^2}{2} + V \tag{29}$$

$$mv^2 = 2(E - V) \tag{30}$$

After putting the value of mv^2 from equation (30) in equation (28), we get

$$\frac{\partial^2 \psi}{\partial x^2} - \frac{8\pi^2 m}{h^2}(E - V)\psi = 0 \tag{31}$$

For three-dimension i.e. $\psi(x, y, z)$, the above equation can be extended to following

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} - \frac{8\pi^2 m}{h^2}(E - V)\psi = 0 \tag{32}$$

The above-mentioned second order differential equation i.e. equation (32) is our popular form of the Schrodinger wave equation.

➢ ***The Derivation of Schrodinger Wave Equation from the Postulates of Quantum Mechanics***

The Schrodinger wave equation can be derived using the first three postulates of quantum mechanics. In other words, we can say that the Schrodinger wave equation is nothing but the rearranged form of the following equation:

$$\hat{H}\psi = E\psi \tag{12}$$

In order to prove the above claim, consider a single particle having "*m*" mass that moves with a velocity "*v*" in the three-dimensional region. The sum of its kinetic and potential energy can be given as:

$$E = T + V \tag{13}$$

However, we know that

$$T = \frac{1}{2}mv^2 = \frac{p^2}{2m} \tag{14}$$

Where "p" represents the total linear momentum of the particle under consideration. Furthermore, as we also know that

$$p^2 = p_x^2 + p_y^2 + p_z^2 \tag{15}$$

Where p_x, p_y and p_z are the magnitudes of total linear momentum along *x*, *y* and *z*-axis, respectively. Now putting the value of p^2 from equation (15) into equation (14), we get the following

$$T = \frac{p_x^2 + p_y^2 + p_z^2}{2m} \tag{16}$$

And now put the value of kinetic energy from equation (16) into equation (13). We get

$$E = \frac{p_x^2 + p_y^2 + p_z^2}{2m} + V \tag{17}$$

However, from the second postulate of quantum mechanics, we know that the expressions for linear momentum operator along three different directions are:

$$\widehat{p_x} = \frac{h}{2\pi i}\frac{\partial}{\partial x} \tag{18}$$

$$\widehat{p_y} = \frac{h}{2\pi i}\frac{\partial}{\partial y} \tag{19}$$

$$\widehat{p_z} = \frac{h}{2\pi i}\frac{\partial}{\partial z} \tag{20}$$

The operator of "V" is simply itself as it is a function of position coordinates only.

Hence, after putting values of linear momentum operators and potential energy operator in equation (17), the operator for total energy (Hamiltonian operator) becomes

$$\hat{H} = \frac{1}{2m}\left[\left(\frac{h}{2\pi i}\frac{\partial}{\partial x}\right)^2 + \left(\frac{h}{2\pi i}\frac{\partial}{\partial y}\right)^2 + \left(\frac{h}{2\pi i}\frac{\partial}{\partial z}\right)^2\right] + V \tag{21}$$

$$\hat{H} = -\frac{h^2}{8\pi^2 m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + V \tag{22}$$

$$\hat{H} = -\frac{h^2}{8\pi^2 m}\nabla^2 + V \tag{23}$$

Where

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

represents the Laplacian operator.

Now, after putting the value of Hamiltonian operator from equation (22) into equation (12) i.e. given by the third postulate of quantum mechanics, get

$$\left[-\frac{h^2}{8\pi^2 m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + V\right]\psi = E\psi \tag{24}$$

$$\left[-\frac{h^2}{8\pi^2 m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + V\right]\psi - E\psi = 0 \tag{25}$$

$$-\frac{h^2}{8\pi^2 m}\frac{\partial^2 \psi}{\partial x^2} - \frac{h^2}{8\pi^2 m}\frac{\partial^2 \psi}{\partial y^2} - \frac{h^2}{8\pi^2 m}\frac{\partial^2 \psi}{\partial z^2} + V\psi - E\psi = 0 \tag{26}$$

Multiplying the equation (26) throughout by

$$-\frac{8\pi^2 m}{h^2}$$

we get

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} - \frac{8\pi^2 m}{h^2}V\psi + \frac{8\pi^2 m}{h^2}E\psi = 0 \tag{27}$$

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi^2 m}{h^2}(E - V)\psi = 0 \tag{28}$$

Equation (28) is the most popular form of the Schrodinger wave equation for three dimensional systems. In the case of two and one dimensional systems first three terms can be reduced to two and one, respectively.

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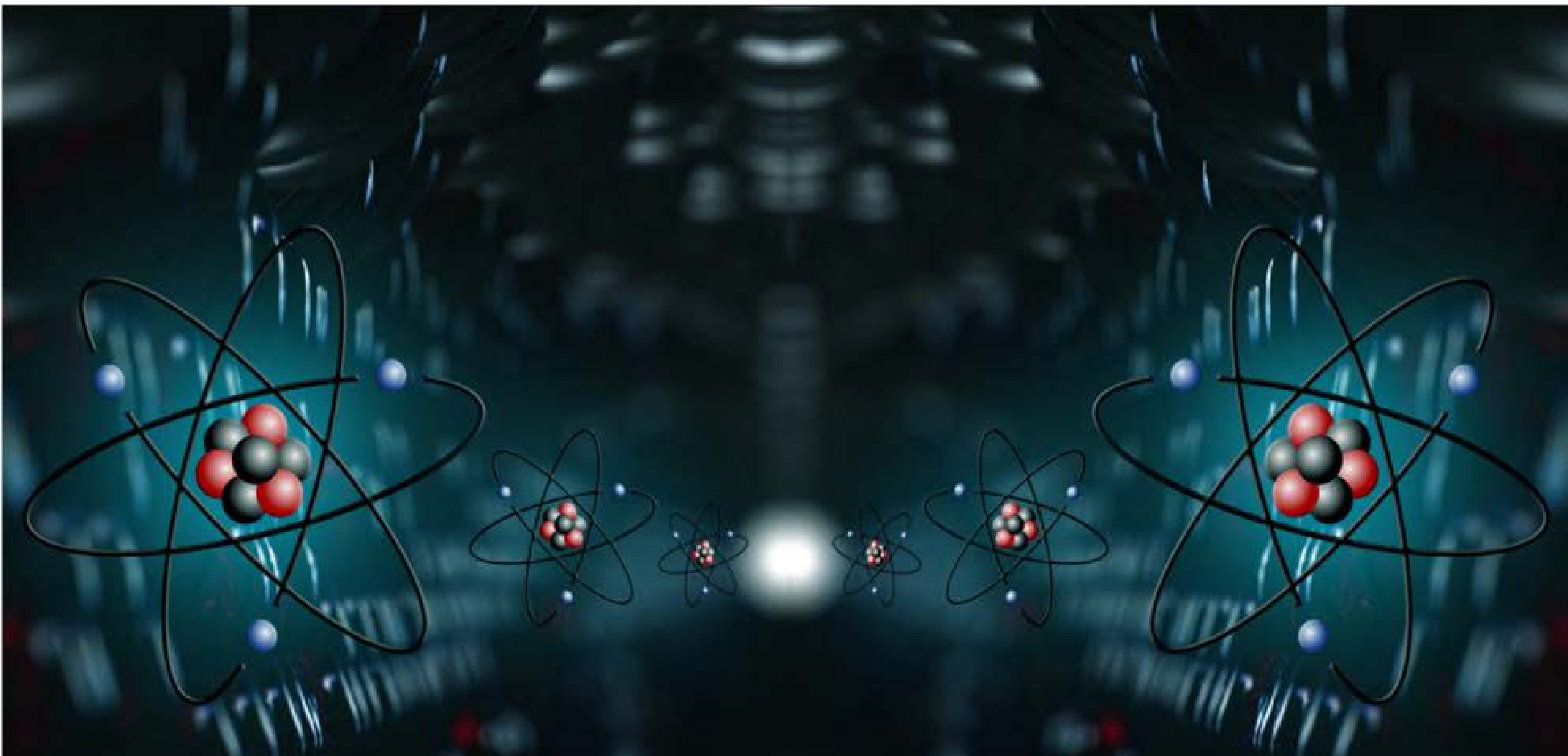
Volume I

MANDEEP DALAL



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