CHAPTER 5

Quantum Mechanics – II

❖ Schrodinger Wave Equation for a Particle in a Three Dimensional Box

In the first chapter of this book, we derived and discussed the Schrodinger wave equation for a particle in the one-dimensional box. In this chapter, we will extend that procedure to the particle in a three-dimensional box. In order to do so, consider a particle trapped in a 3-dimensional box of length, breadth, and height as *a*, *b* and *c*, respectively. This means that this particle can travel in any direction i.e. along *x-, y- and z*-axis. The potential inside the box is 0, while outside to the box it is infinite.

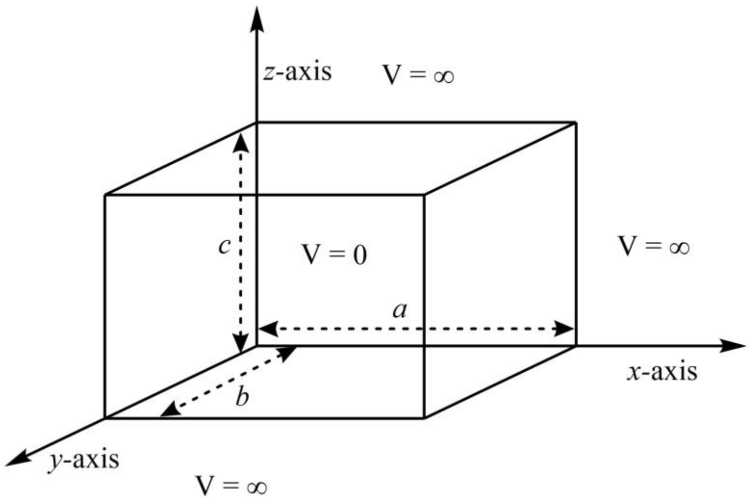

Figure 1. The particle in a three-dimensional box.

So far we have considered a quantum mechanical system of a particle trapped in a three-dimensional box. Now suppose that we need to find various physical properties associated with different states of this system. Had it been a classical system, we would use simple formulas from classical mechanics to determine the value of different physical properties. However, being a quantum mechanical system, we cannot use those expressions because they would give irrational results. Therefore, we need to use the postulates of quantum mechanics to evaluate various physical properties.

Let ψ be the function that describes all the states of the particle in a three-dimensional box. At this point we have no information about the exact mathematical expression of ψ; nevertheless, we know that there is one operator that does not need the absolute expression of wave function but uses the symbolic form only, the Hamiltonian operator. The operation of Hamiltonian operator over this symbolic form can be rearranged to give to construct the Schrodinger wave equation; and we all know that the wave function as well the energy, both are obtained as this second-order differential equation is solved. Mathematically, we can say that

$$\hat{H}\psi = E\psi \qquad (1)$$

After putting the value of three-dimensional Hamiltonian in equation (1), we get

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

or

$$\frac{-h^2}{8\pi^2 m}\left(\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}\right)+V\psi = E\psi \qquad (3)$$

$$\frac{-h^2}{8\pi^2 m}\left(\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}\right)+V\psi - E\psi = 0 \qquad (4)$$

or

$$\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}+\frac{8\pi^2 m}{h^2}(E-V)\psi = 0 \qquad (5)$$

The above-mentioned second order differential equation is the Schrodinger wave equation for a particle moving along three dimensions. Since the conditions outside and inside the box are different, the equation (5) must be solved separately for both cases.

1. The solution of Schrodinger wave equation for outside the box: After putting the value of potential outside the box in equation (5) i.e. V = ∞, we get

$$\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}+\frac{8\pi^2 m}{h^2}(E-\infty)\psi = 0 \qquad (6)$$

Since E is negligible in comparison to the ∞, the above equation becomes

$$\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}-\infty\psi = 0 \qquad (7)$$

$$\infty\psi = \frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2} \qquad (8)$$

$$\psi = \frac{1}{\infty}\left(\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}\right) = 0 \qquad (9)$$

The physical significance of the equation (9) is that the particle cannot go outside the box, and is always reflected back when it strikes the boundaries. In other words, as the function describing the existence of particles is zero outside the box, the particle cannot exist outside the box.

2. The solution of Schrodinger wave equation for inside the box: After putting the value of potential inside the box in equation (5) i.e. V = 0, we get

$$\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}+\frac{8\pi^2 m}{h^2}(E-0)\psi=0 \tag{10}$$

$$\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}+\frac{8\pi^2 mE}{h^2}\psi=0 \tag{11}$$

The above equation has three variables and is difficult to solve directly. Therefore, it is better to separate variable, we already know the steps to solve a one-variable equation. To do so, consider that the wave function ψ is the multiplication of three individual functions as

$$\psi(x,y,z)=\psi(x)\times\psi(y)\times\psi(z)=XYZ \tag{12}$$

Using the above expression in equation (11), we get

$$\frac{\partial^2 XYZ}{\partial x^2}+\frac{\partial^2 XYZ}{\partial y^2}+\frac{\partial^2 XYZ}{\partial z^2}+\frac{8\pi^2 mE}{h^2}XYZ=0 \tag{13}$$

From the rules of partial derivative, the equation (13) takes the form

$$YZ\frac{\partial^2 X}{\partial x^2}+XZ\frac{\partial^2 Y}{\partial y^2}+XY\frac{\partial^2 Z}{\partial z^2}+\frac{8\pi^2 mE}{h^2}XYZ=0 \tag{14}$$

Now divide the above equation by XYZ on both side i.e.

$$\frac{1}{X}\frac{\partial^2 X}{\partial x^2}+\frac{1}{Y}\frac{\partial^2 Y}{\partial y^2}+\frac{1}{Z}\frac{\partial^2 Z}{\partial z^2}+\frac{8\pi^2 mE}{h^2}=0 \tag{15}$$

Assuming

$$k^2=\frac{8\pi^2 mE}{h^2} \tag{16}$$

The equation (15) becomes

$$\frac{1}{X}\frac{\partial^2 X}{\partial x^2}+\frac{1}{Y}\frac{\partial^2 Y}{\partial y^2}+\frac{1}{Z}\frac{\partial^2 Z}{\partial z^2}+k^2=0 \tag{17}$$

Also fragmenting the constant k^2 along three *x*-, *y*- and *z*-axis i.e. $k^2=k_x^2+k_y^2+k_z^2$, the equation (17) can

$$\frac{1}{X}\frac{\partial^2 X}{\partial x^2}+\frac{1}{Y}\frac{\partial^2 Y}{\partial y^2}+\frac{1}{Z}\frac{\partial^2 Z}{\partial z^2}+k_x^2+k_y^2+k_z^2=0 \tag{18}$$

The above equation can be written as the sum of three equations with only one variable in each i.e.

$$\frac{\partial^2 X}{\partial x^2} + k_x^2 X = 0 \tag{19}$$

$$\frac{\partial^2 Y}{\partial y^2} + k_y^2 Y = 0 \tag{20}$$

$$\frac{\partial^2 Z}{\partial z^2} + k_z^2 Z = 0 \tag{21}$$

The equations (19-21) are simple one-dimensional differential equations whose solutions can be obtained just like in the one-dimensional box. The solution of equation (19) will give the *x*-dependent wave function as well the energy distribution along *x*-axis i.e.

$$\psi_{n_x}(x) = X = \sqrt{\frac{2}{a}}\, Sin\frac{n_x \pi x}{a} \quad and \quad E_{n_x} = \frac{n_x^2 h^2}{8ma^2} \tag{22}$$

Similarly, the solution of equation (20) will be

$$\psi_{n_y}(y) = Y = \sqrt{\frac{2}{b}}\, Sin\frac{n_y \pi y}{b} \quad and \quad E_{n_y} = \frac{n_y^2 h^2}{8mb^2} \tag{23}$$

Just like the above two, the solution of equation (21) will be

$$\psi_{n_z}(z) = Z = \sqrt{\frac{2}{c}}\, Sin\frac{n_z \pi z}{c} \quad and \quad E_{n_z} = \frac{n_z^2 h^2}{8mc^2} \tag{24}$$

After putting the expressions of individual wave functions from equation (22-24) in equation (12), the total wave function can be obtained i.e.

$$\psi_{n_x n_y n_z}(x, y, z) = \sqrt{\frac{8}{abc}}\, Sin\frac{n_x \pi x}{a}\, Sin\frac{n_y \pi y}{b}\, Sin\frac{n_z \pi z}{c} \tag{25}$$

Since $k^2 = k_x^2 + k_y^2 + k_z^2$, the total energy must be the sum of individual energies i.e.

$$E_{n_x n_y n_z} = \left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right)\frac{h^2}{8m} \tag{26}$$

Where n_x, n_y, n_y are the discrete variable whose permitted values from boundary conditions can be 0, 1, 2, 3, 4….∞. Nevertheless, it is worthy to note that even though the *n* = 0 is permitted by the boundary conditions, we still don't use it in equation (25); which is obviously because it makes the whole function zero.

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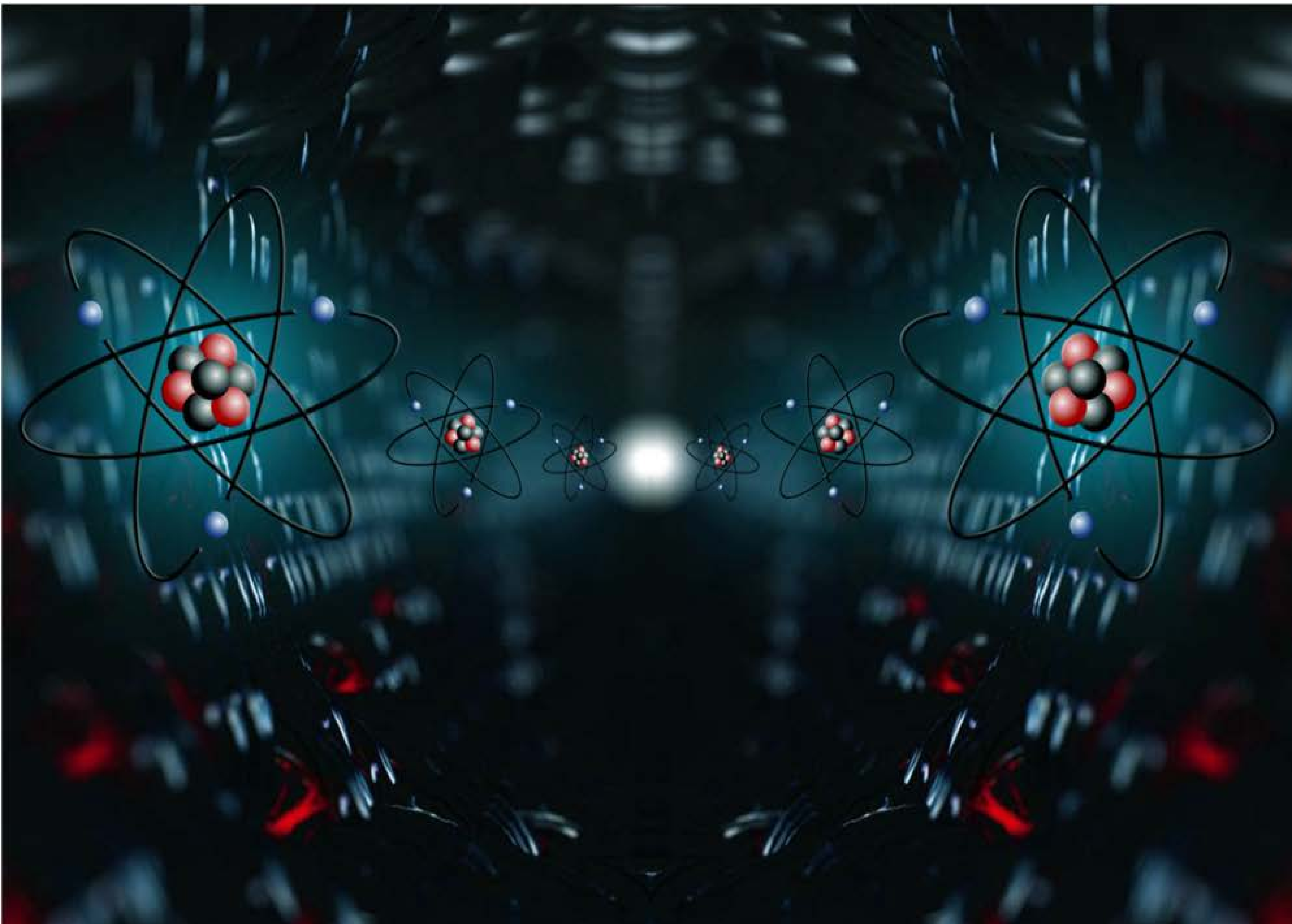

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Table of Contents

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