❖ Schrodinger Wave Equation for a Particle in One Dimensional Box

In the first section of this chapter, we discussed the postulates of quantum mechanics i.e. the step-by-step procedure to solve a quantum mechanical problem. Now it's the time to implement those rules to the simplest quantum mechanical problem i.e. particle in a one-dimensional box. Consider a particle trapped in a one-dimensional box of length "*a*", which means that this particle can travel in only one direction only, say along *x*-axis. The potential inside the box is V, while outside to the box it is infinite.

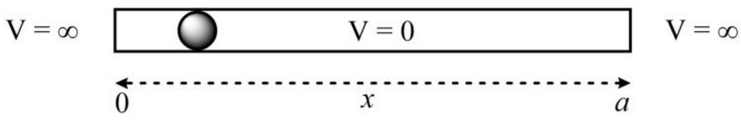

Figure 7. The particle in a one-dimensional box.

One other popular depiction of the particle in a one-dimensional box is also given in which the potential is shown vertically while the displacement is projected along the horizontal line.

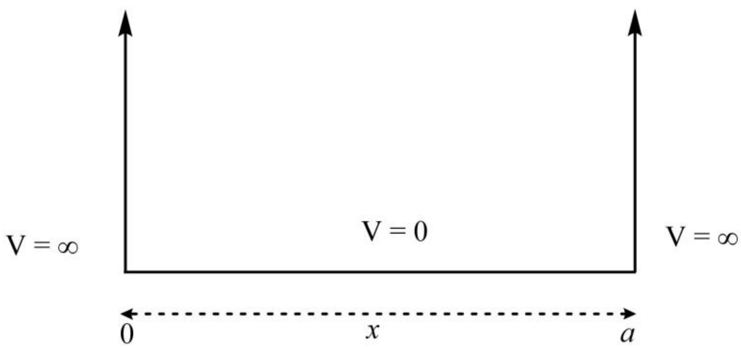

Figure 8. The second representation particle in a one-dimensional box.

So far we have considered a quantum mechanical system of a particle trapped in a one-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 one-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 the obtained as this second-order differential equation is solved. Mathematically, we can say that

$$\hat{H}\psi = E\psi \tag{415}$$

After putting the value of one-dimensional Hamiltonian in equation (415), we get

$$\left[\frac{-h^2}{8\pi^2 m}\frac{\partial^2}{\partial x^2} + V\right]\psi = E\psi \tag{416}$$

or

$$\frac{-h^2}{8\pi^2 m}\frac{\partial^2\psi}{\partial x^2} + V\psi = E\psi \tag{417}$$

$$\frac{-h^2}{8\pi^2 m}\frac{\partial^2\psi}{\partial x^2} + V\psi - E\psi = 0 \tag{418}$$

$$\frac{\partial^2\psi}{\partial x^2} + \frac{8\pi^2 m}{h^2}E\psi - \frac{8\pi^2 m}{h^2}V\psi = 0 \tag{419}$$

or

$$\frac{\partial^2\psi}{\partial x^2} + \frac{8\pi^2 m}{h^2}(E - V)\psi = 0 \tag{420}$$

The above-mentioned second order differential equation is the Schrodinger wave equation for a particle moving along one dimension only. Since the conditions outside and inside the box are different, the equation (420) 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 (420) i.e. V = ∞, we get

$$\frac{\partial^2\psi}{\partial x^2} + \frac{8\pi^2 m}{h^2}(E - \infty)\psi = 0 \tag{421}$$

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

$$\frac{\partial^2\psi}{\partial x^2} - \infty\psi = 0 \tag{422}$$

$$\infty\psi = \frac{\partial^2\psi}{\partial x^2} \tag{423}$$

$$\psi = \frac{1}{\infty}\frac{\partial^2\psi}{\partial x^2} = 0 \tag{424}$$

The physical significance of the equation (424) 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. Solution of Schrodinger wave equation for inside the box: After putting the value of potential inside the box in equation (420) i.e. V = 0, we get

$$\frac{\partial^2\psi}{\partial x^2}+\frac{8\pi^2 m}{h^2}(E-0)\psi=0 \tag{425}$$

or

$$\frac{\partial^2\psi}{\partial x^2}+\frac{8\pi^2 mE}{h^2}\psi=0 \tag{426}$$

Now consider

$$k^2=\frac{8\pi^2 mE}{h^2} \tag{427}$$

After using the value from equation (427) in equation (426), we get

$$\frac{\partial^2\psi}{\partial x^2}+k^2\psi=0 \tag{428}$$

The general solution of the above equation is

$$\psi=A\,Sin\,kx+B\,Cos\,kx \tag{429}$$

Hence, from just the symbolic form we have obtained some kind of expression for the wave function defining quantum mechanical states. However, the function given by equation (429) cannot be used to find different physical properties or the nature of corresponding quantum mechanical states. The reason is that this expression does have some unknown parameters like *A*, *B* and *k*. Since the function describing any quantum mechanical state must be single-valued, finite and continuous; the function ψ must also follow these conditions to become a "wave-function". Therefore, these boundary conditions are fulfilled only if the magnitude of ψ is zero at the start and at the end of the box (function outside is zero).

i) The first boundary condition: ψ must vanish when $x = 0$ i.e.

$$0=A\,Sin\,k(0)+B\,Cos\,k(0) \tag{430}$$

$$0=0+B\,Cos\,k(0) \tag{431}$$

$$B=0 \tag{432}$$

So, the function ψ is acceptable only if the value of the constant *B* is zero. After putting the value of *B* in equation (429), we get

$$\psi=A\,Sin\,kx+(0)\,Cos\,kx \tag{433}$$

$$\psi=A\,Sin\,kx \tag{434}$$

ii) The second boundary condition: ψ must vanish when $x = a$, i.e.,

$$0 = A\,Sin\,ka \tag{435}$$

$$Sin\,ka = 0 \tag{436}$$

Moreover, as we know that

$$Sin\,0 = 0 \quad or \quad Sin\,0\pi = 0 \tag{437}$$

$$Sin\,180 = 0 \quad or \quad Sin\,1\pi = 0 \tag{438}$$

$$Sin\,360 = 0 \quad or \quad Sin\,2\pi = 0 \tag{439}$$

$$Sin\,540 = 0 \quad or \quad Sin\,3\pi = 0 \tag{440}$$

or

$$Sin\,n\pi = 0 \tag{441}$$

Where $n = 0, 1, 2, 3, 4, 5 \ldots \infty$. Comparing equation (436) and equation (441), we conclude that

$$Sin\,ka = Sin\,n\pi = 0 \tag{442}$$

Which eventually means that

$$ka = n\pi \tag{443}$$

$$k = \frac{n\pi}{a} \tag{444}$$

After putting the value of k in equation (434), we get

$$\psi = A\,Sin\frac{n\pi x}{a} \tag{445}$$

The only parameters that is still unknown in equation (445) is A, which can also be obtained by the condition of normalization i.e. the function must define the state completely. Therefore, we can say that

$$\int_0^a \psi^2 = A^2 \int_0^a Sin^2\left(\frac{n\pi x}{a}\right) = 1 \tag{446}$$

$$A^2.\frac{a}{2} = 1 \tag{447}$$

$$A^2 = \frac{2}{a} \quad or \quad A = \sqrt{\frac{2}{a}} \tag{448}$$

After putting the value of A in equation (445), we get

$$\psi = \sqrt{\frac{2}{a}}\, Sin\frac{n\pi x}{a} \tag{449}$$

Since the function ψ also depends upon the discrete variable *n*, it is better to write the above equation given as

$$\psi_n = \sqrt{\frac{2}{a}}\, Sin\frac{n\pi x}{a} \tag{450}$$

The equation (450) represents all the quantum mechanical states of a particle in one-dimensional box. We can obtain functions for individual states just by putting different values of "*n*" allowed by the boundary conditions. For first quantum mechanical state i.e $n = 1$

$$\psi_1 = \sqrt{\frac{2}{a}}\, Sin\frac{\pi x}{a} \tag{451}$$

For second quantum mechanical state i.e $n = 2$

$$\psi_2 = \sqrt{\frac{2}{a}}\, Sin\frac{2\pi x}{a} \tag{452}$$

For third quantum mechanical state i.e $n = 3$

$$\psi_3 = \sqrt{\frac{2}{a}}\, Sin\frac{3\pi x}{a} \tag{453}$$

Similarly, we can write the expression for ψ_4, ψ_5, ψ_6 and so on. It is also worthy to note that even though the $n = 0$ is permitted by the boundary condition, we still didn't use it in equation (450); which is obviously because it makes the whole function to collapse to zero.

One of the most remarkable results of this procedure that we have not discussed yet is the correlation of equation (427) and equation (444).

$$k^2 = \frac{8\pi^2 mE}{h^2} = \frac{n^2\pi^2}{a^2} \tag{454}$$

$$E_n = \frac{n^2h^2}{8ma^2} \tag{455}$$

The energy of different quantum mechanical states can be obtained by putting n = 1, 2, 3.... ∞ in equation (455). Hence, we have obtained the wave-function as well as the energy for a particle in one-dimensional box.

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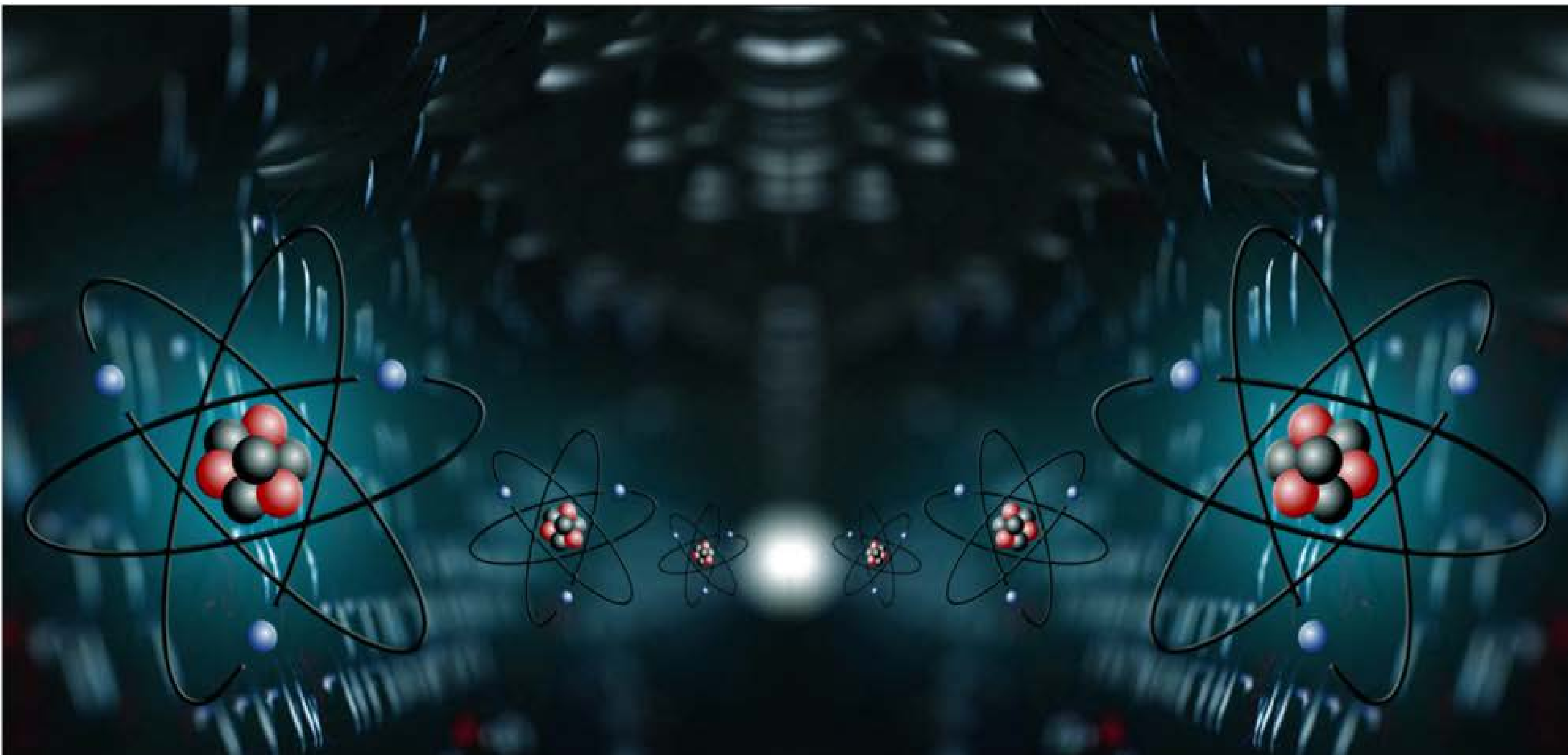

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Mandeep Dalal
(M.Sc, Ph.D, CSIR UGC - NET JRF, IIT - GATE)
Founder & Director, Dalal Institute
Contact No: +91-9802825820
Homepage: www.mandeepdalal.com
E-Mail: dr.mandeep.dalal@gmail.com

Mandeep Dalal is an Indian research scholar who is primarily working in the field of Science and Philosophy. He received his Ph.D in Chemistry from Maharshi Dayanand University, Rohtak, in 2018. He is also the Founder and Director of "Dalal Institute", an India-based educational organization which is trying to revolutionize the mode of higher education in Chemistry across the globe. He has published more than 40 research papers in various international scientific journals, including mostly from Elsevier (USA), IOP (UK) and Springer (Netherlands) .

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