



CH101

Classes 3; Physical Chemistry

**Schrödinger Wave Equation**

Time –dependent Schrödinger Wave Equation

$$\hat{H}\Psi(r,t) = i\hbar \frac{\partial \Psi}{\partial t}$$

Time – independent Schrödinger Wave Equation

$$\hat{H} \Psi = E \Psi$$

$\Psi$  is a function of spatial coordinates (x, y, z) or (r,  $\theta$ ,  $\phi$ ) for a particular energy state (E).

$\hat{H}$  is known as the Hamiltonian operator or simply Hamiltonian.

$$\hat{H} = (\text{Kinetic Energy} + \text{potential Energy}) \text{ operators} = \hat{T} + \hat{V}$$

Typically,  $\hat{T} = \frac{p^2}{2m} = -\frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right)$  in three dimensions

In one dimension,  $\hat{T} = \frac{p_x^2}{2m} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2}$

$\hat{V}$  depends on the system and interaction involved.

For Coulombic potential:  $\hat{V} = -\frac{Ze^2}{4\pi\epsilon_0 r}$  (between an electron and nucleus with charge Z)

For Harmonic Oscillator potential:  $\hat{V} = \frac{1}{2} kX^2$

**Solving Problems: Particle in a BOX.** One-Dimensional Box. The particle is an electron and it does not have enough energy to climb the barrier; therefore remains confined to the box. What are the energy states that the particle can occupy?

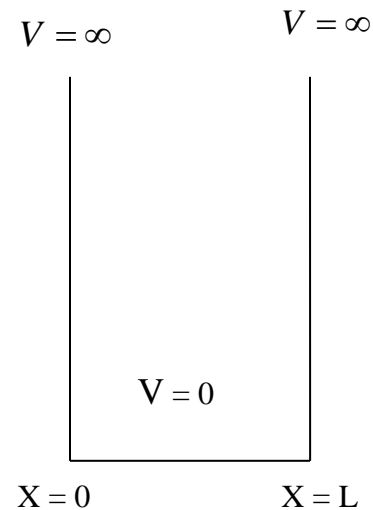
Hamiltonian,  $\hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2}$

$$\hat{H} \Psi = E \Psi$$

Or,  $-\frac{\hbar^2}{2m} \frac{d^2 \Psi}{dx^2} = E \Psi$

Or,  $\frac{d^2 \Psi}{dx^2} = -\frac{2mE}{\hbar^2} \Psi = -k^2 \Psi;$

where  $k = \frac{(2mE)^{1/2}}{\hbar}$



Solutions:  $\Psi = Ae^{ikx}; \Psi = Be^{-ikx}$  and  $\Psi = Ae^{ikx} + Be^{-ikx}$

However,  $\Psi = Ae^{ikx} + Be^{-ikx}$  is the most general solution.

$\Psi = Ae^{ikx} + Be^{-ikx}$ , however, can be rewritten as  $\Psi = C \cos kx + D \sin kx$

Boundary conditions:

At  $x = 0; \Psi = 0$  and at  $x = L; \Psi = 0$ .

When  $x = 0; \Psi = 0$ ; then  $\Psi = C \cos kx + D \sin kx = C = 0$

Hence,  $\Psi = D \sin kx$

However, at  $x = L; \Psi = 0$ ; then  $\Psi = D \sin kL = 0$

This is possible only when  $kL = n\pi$ ; where  $n = 1, 2, 3, 4, \dots$

Hence,  $\Psi = D \sin \frac{n\pi x}{L}$ ; the solution of the equation under the above boundary

conditions. One can also write  $\Psi(x) = D \sin \frac{n\pi x}{L}$

However, D is still unknown. How to find D?

Since the particle must be inside the box, the total probability of finding the particle inside the box must be unity.

Thus

$$\int_0^L \Psi^*(x) \Psi(x) dx = 1$$

$$\int_0^L D \sin \frac{n\pi x}{L} D \sin \frac{n\pi x}{L} dx = 1$$

$$D = \sqrt{\frac{2}{L}}$$

Hence,

$$\Psi(x) = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L}; \text{ complete solution.}$$

One can see the solution is expressed in terms of the dimension of the box (L), position (x) and quantum numbers (n=1, 2, 3, ...).

One can derive the expression for energy of the particle in the box from

$$-\frac{\hbar^2}{2m} \frac{d^2\Psi}{dx^2} = E \Psi$$

**With the wavefunction**  $\Psi(x) = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L};$

The expression for energy is

$$E_n = \frac{n^2 \hbar^2}{8mL^2}; \text{ where n is the quantum numbers, } n = 1, 2, 3, 4, \dots$$

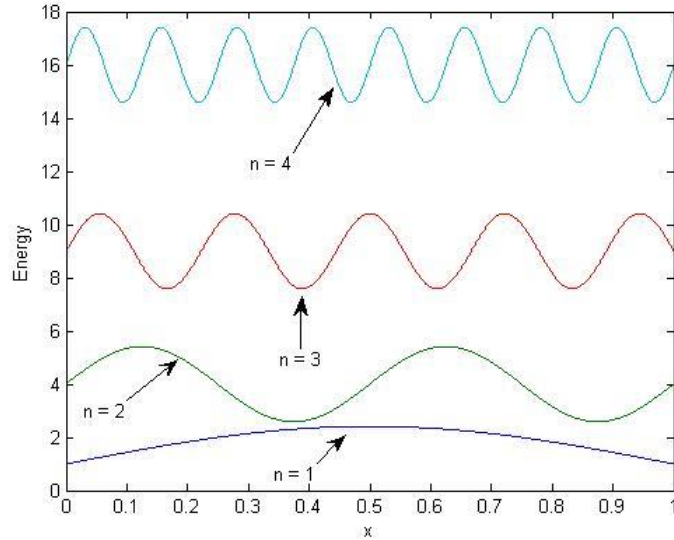
### Home work:

Find the average position of the particle in the one-dimensional box with the length L.

Hint: Evaluate the following integral

$$\langle x \rangle = \int_0^L \Psi(x)^* x \Psi(x) dx$$

**Figure 1. Energy and Wavefunctions of particle in a one-dimensional box (first four states shown).**



**Figure 2. The probability densities of the electron inside the box at various location in  $x$  and for different energy states.**

