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Department of Chemistry

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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

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

Ψ is a function of spatial coordinates (x, y, z) or (r, θ, φ) for a particular energy state (E).

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

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

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

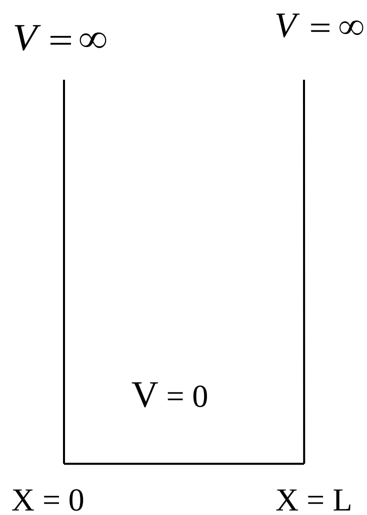
In one dimension, $\hat{T} = \dfrac{p_x^2}{2m} = -\dfrac{\hbar^2}{2m}\dfrac{d^2}{dx^2}$

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

For Coulombic potential: $\hat{V} = -\dfrac{Ze^2}{4\pi\varepsilon_0 r}$ (between an electron and nucleus with charge Z)

For Harmonic Oscillator potential: $\hat{V}$ = ½ 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 = nπ; where n = 1, 2, 3, 4……

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 $$\int_0^L \Psi^*(x)\,\Psi(x)\,\mathrm{dx} = 1$$

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

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

Hence, $$\Psi(x) = \sqrt{\frac{2}{L}}\sin\frac{n\pi x}{L};$$ 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

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

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

The expression for energy is

$$E_n = \frac{n^2h^2}{8mL^2}$$; where n is the quantum numbers, n = 1, 2, 3, 4,…..

Home work:

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

Hint: Evaluate the following integral

$$\langle x\rangle = \int_0^L \Psi(x)^*\,\mathrm{x}\Psi(x)dx$$

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

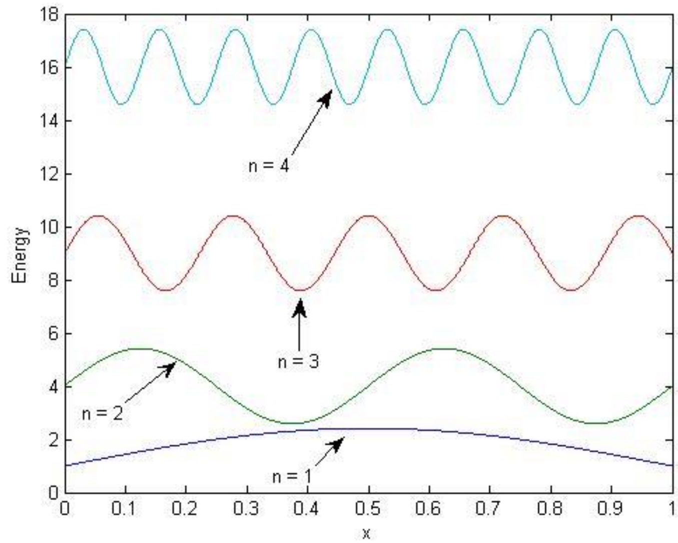


Figure 2. The probability densities of the electron inside the box at various location in x and for different energy states.