Particle in a Box

Schrodinger Equation and Solution

Recapitulate

Under separation of variables, wave function can be written as a product

$$\Psi(x,t) = \psi(x)\phi(t)$$

$$\phi(t) = e^{-iEt/\hbar}$$

$$\Psi(x,t) = \psi(x)e^{-iEt/\hbar}$$

Now find *E* from time independent Schrödinger Equation

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi(x)}{\partial x^2} + V(x)\psi(x) = E\psi(x)$$

Time independent Schrodinger equation (TISE)

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi(x)}{\partial x^2}+V(x)\psi(x)=E\psi(x)$$

Important points to note:

Given V(x), solve TISE to obtain E and ψ(x)

Solution is subjected to the 'boundary' conditions.

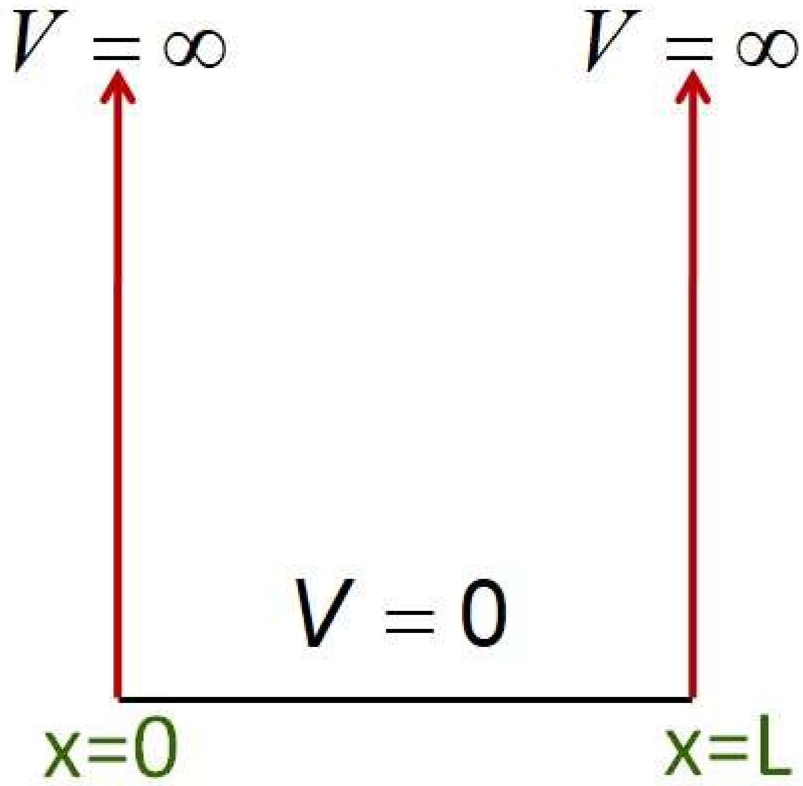
Acceptable solution [ψ(x)] must be continuous, single valued, and its derivative must be continuous.

*Ideas on '**How to proceed to find the acceptable solution**' were discussed while working with 'Free Particle'.*

Particle in a Box

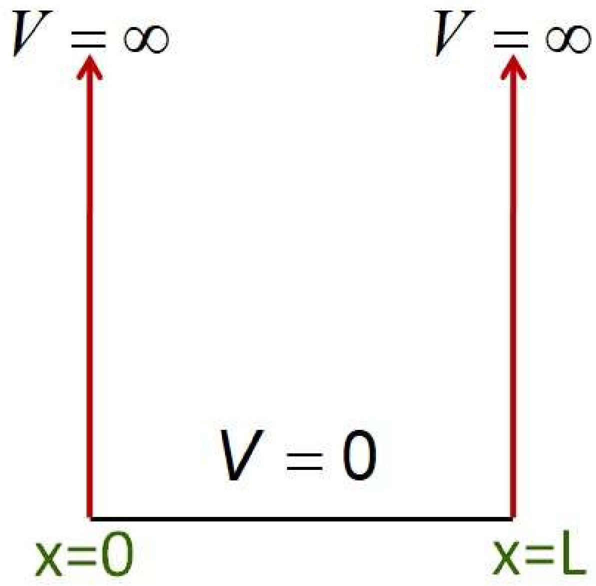
$$V(x) = 0 \quad for \quad 0 \le x \le L$$

$$= \infty \quad for \quad x < 0 \text{ or } x > L$$



Particle of mass m is placed in the potential

Particle is free to move in side the box; however at the boundary, it experiences a strong force.



Time independent Schrodinger equation

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi(x)}{\partial x^2}+V(x)\psi(x)=E\psi(x)$$

$$\frac{\partial^2\psi(x)}{\partial x^2}=-\frac{2m(E-V(x))}{\hbar^2}\psi(x)$$

for $x<0$ *and* $x>L,\quad V(x)=\infty \Rightarrow \psi(x)=0$

Particle can not exists for x <0 and x > L

for $0\le x\le L,\quad V(x)=0 \Rightarrow \frac{\partial^2\psi(x)}{\partial x^2}=-\frac{2mE}{\hbar^2}\psi(x)$

$$\frac{\partial^2 \psi(x)}{\partial x^2} = -\frac{2mE}{\hbar^2}\psi(x) \qquad \textit{for} \quad 0 \le x \le L,$$

The general solution is

$$\psi(x) = A\sin(kx) + B\cos(kx)$$

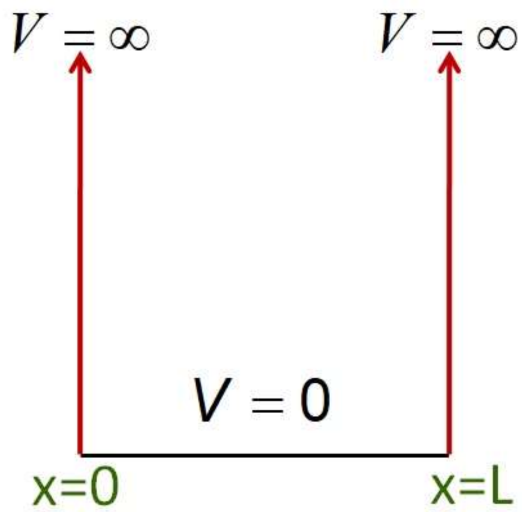
$$k^2 = \frac{2mE}{\hbar^2} \quad \text{Since } E \ge 0, \ \ k \text{ is real}$$

Note: We could choose a general solution of the form

$$\psi(x) = Ae^{ikx} + Be^{-ikx}$$

This choice will give same results since sin(kx) and cos(kx) are each superpositions of exp(±kx). Algebra will be a little more involved.

$$\psi(x) = A\sin(kx) + B\cos(kx)$$



Boundary Conditions

The wave function must be continuous

$\psi(x) = 0$ for $x < 0$ and $x > L$,

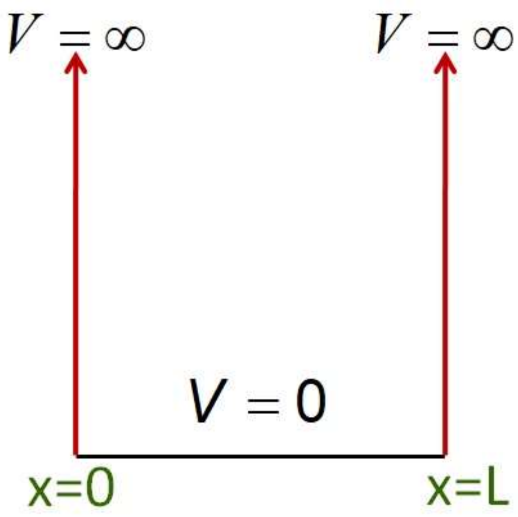
$$\Rightarrow \psi(x=0) = \psi(x=L) = 0$$

$$\psi(0) = 0 \Rightarrow A\sin(0) + B\cos(0) = 0 \Rightarrow B = 0$$

$$\psi(L) = 0 \Rightarrow A\sin(kL) = 0 \Rightarrow kL = n\pi$$

$$\therefore \frac{\sqrt{2mE}}{\hbar} L = n\pi \Rightarrow \boxed{E = \frac{n^2\pi^2\hbar^2}{2mL^2} \quad n \geq 1}$$

Energy is quantized!



What we obtain is

$$\psi(x) = A\sin(kx) \qquad k = \frac{n\pi}{L}$$

$$E_n = \frac{n^2\pi^2\hbar^2}{2mL^2} \qquad n \geq 1$$

Normalization of Wave function

$$\int_{-\infty}^{\infty} \psi^*(x)\psi(x)dx = |A|^2 \int_0^L \sin^2(kx)dx = 1$$

$$\therefore \quad |A|^2 \int_0^L \sin^2\left(\frac{n\pi}{L}x\right)dx = 1$$

$$|A|^2 \int_0^L \sin^2\left(\frac{n\pi}{L}x\right)dx = 1$$

Use $\sin^2\theta = (1-\cos^2\theta)/2$

$$\therefore \frac{|A|^2}{2}\int_0^L \left[1-\cos\left(\frac{2n\pi}{L}x\right)\right]dx = 1$$

$$\therefore \frac{|A|^2}{2}\left[x-\frac{L}{2n\pi}\sin\left(\frac{2n\pi x}{L}\right)\right]_0^L = 1$$

$$\therefore \frac{|A|^2}{2}L = 1$$

$$A = e^{i\theta}\sqrt{\frac{2}{L}}$$

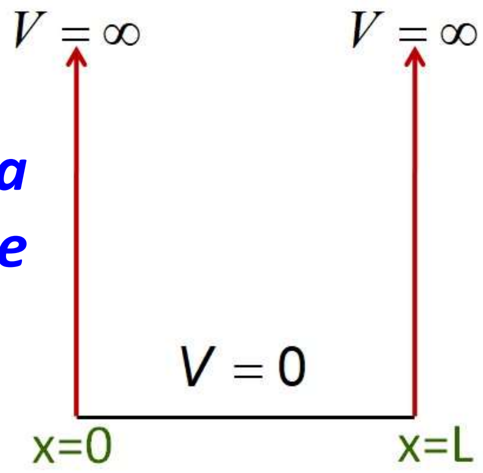
Let us take real A, i.e., $A = \sqrt{\frac{2}{L}}$

$$\boxed{\begin{aligned} \psi(x) &= \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi}{L}x\right) && \textit{for} \quad 0 \le x \le L \\ &= 0 && \textit{elsewhere} \end{aligned}}$$

Now let us start with the wave function

$$\psi(x) = Ae^{ikx} + Be^{-ikx}$$

The particle is a free particle inside the box!



To solve

$$\frac{\partial^2 \psi(x)}{\partial x^2} = -k^2 \psi(x) \qquad \textit{for} \quad 0 \le x \le L, \qquad k^2 = \frac{2mE}{\hbar^2}$$

$$\psi(x) = 0 \qquad \textit{for} \quad x < 0 \quad \textit{and} \quad x > L,$$

$$\psi(0) = 0 \Rightarrow A + B = 0 \Rightarrow A = -B \Rightarrow \psi(x) = 2iA\sin(kx)$$

$$\psi(L) = 0 \Rightarrow 2iA\sin(kL) = 0 \Rightarrow kL = n\pi$$

$$\therefore \frac{\sqrt{2mE}}{\hbar} L = n\pi \qquad \therefore E = \frac{n^2\pi^2\hbar^2}{2mL}$$

Normalization of wave function

$$\psi(x) = 2iA\sin(kx)$$

$$\int_{-\infty}^{\infty} \psi^*(x)\psi(x)dx = 4|A|^2 \int_0^L \sin^2(kx)dx = 1$$

$$\therefore 2|A|^2 L = 1 \qquad A = \frac{e^{i\theta}}{\sqrt{2L}}$$

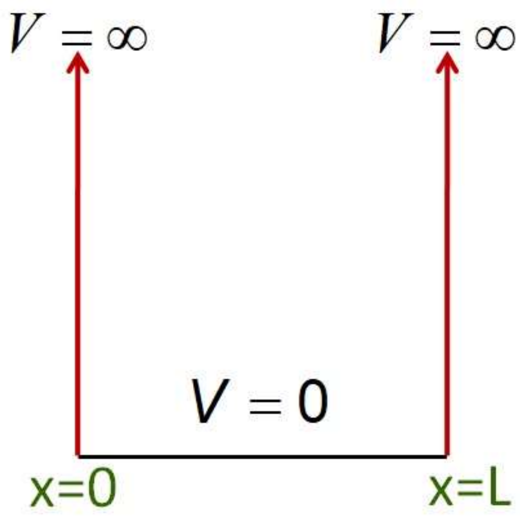
$$\psi(x) = \frac{2ie^{i\theta}\sin(kx)}{\sqrt{2L}} = \sqrt{\frac{2}{L}}e^{i(\theta+\pi/2)}\sin(kx)$$

Now choose phases to make wave function real

$$\psi(x) = \sqrt{\frac{2}{L}}\sin(kx) = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi}{L}x\right)$$

Answer is same.

You can choose the phase since what matters is $\psi^*(x)\ \psi(x)$



Summary of Results

Since the energy levels are quantized (n=1,2,3..), we denote energy (E) and wave function [ψ(x)] by subscript 'n'

$$\psi_n(x)=\sqrt{\frac{2}{L}}\sin\left(\frac{n\pi}{L}x\right) \quad for \quad 0\le x\le L \qquad E_n=\frac{n^2\pi^2\hbar^2}{2mL^2}$$

$$=0 \qquad elsewhere$$

We may also write

$$H\psi_n(x)=E_n\psi_n(x)$$

E_n is the eigenvalue corresponding to wave function $\psi_n(x)$

How do these wave functions look like?

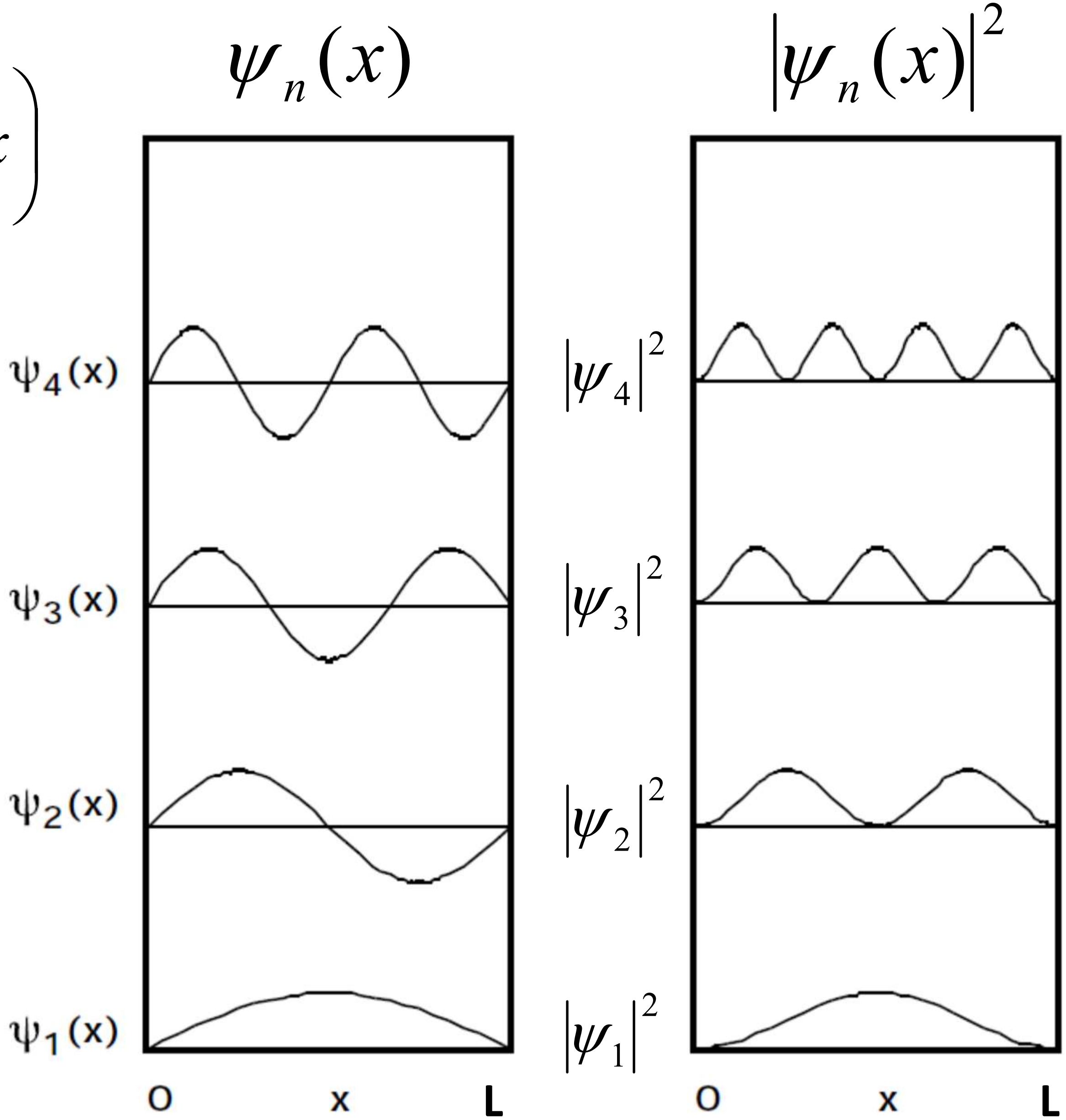
$$\psi_n(x) = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi}{L}x\right)$$

$$\psi_4(x) = \sqrt{\frac{2}{L}}\sin\left(\frac{4\pi}{L}x\right)$$

$$\psi_3(x) = \sqrt{\frac{2}{L}}\sin\left(\frac{3\pi}{L}x\right)$$

$$\psi_2(x) = \sqrt{\frac{2}{L}}\sin\left(\frac{2\pi}{L}x\right)$$

$$\psi_1(x) = \sqrt{\frac{2}{L}}\sin\left(\frac{\pi}{L}x\right)$$



How are the energy levels organized?

$$E_n = \frac{n^2\pi^2\hbar^2}{2mL^2} \qquad n \geq 1$$

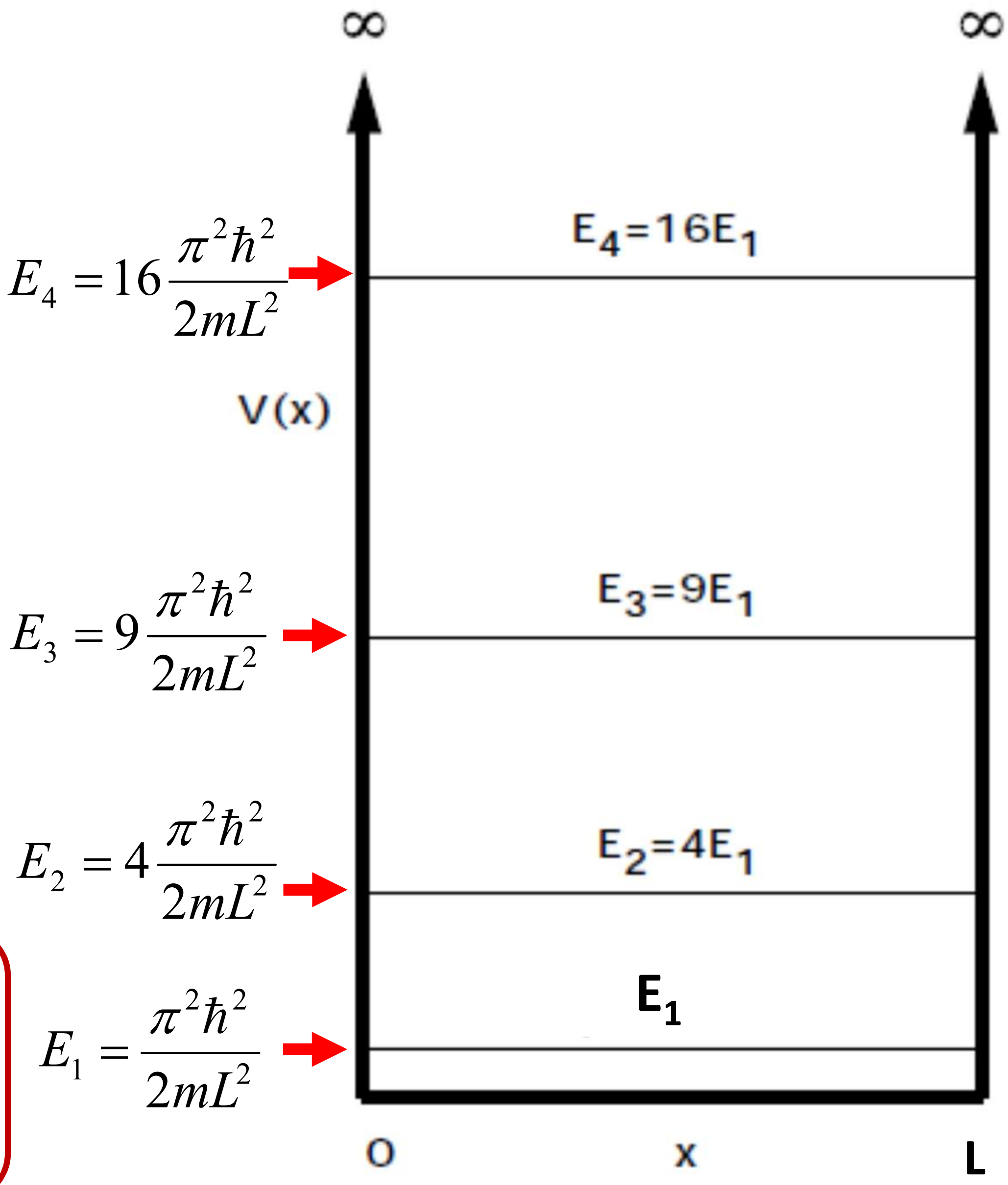
- **Occurrence of quantized energy levels.**

- **Lowest energy**

$$E_1 = \frac{\pi^2\hbar^2}{2mL^2} > 0$$

Classically, $E_1 = 0$

Quantum particle possesses "Zero point energy"



Energy levels of a particle in a box can be obtained using de Broglie equation

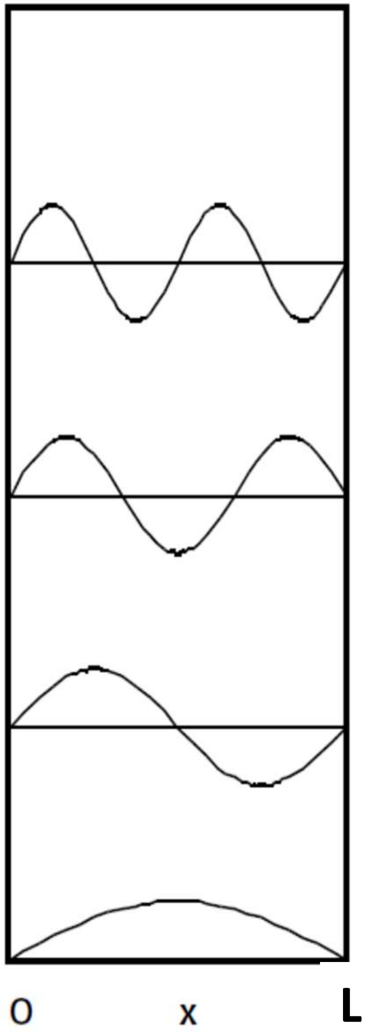
$$\lambda_{dB} = \frac{h}{p}$$

Amplitude of oscillation at both ends must be zero. Therefore, integer number of half waves must fit into the box

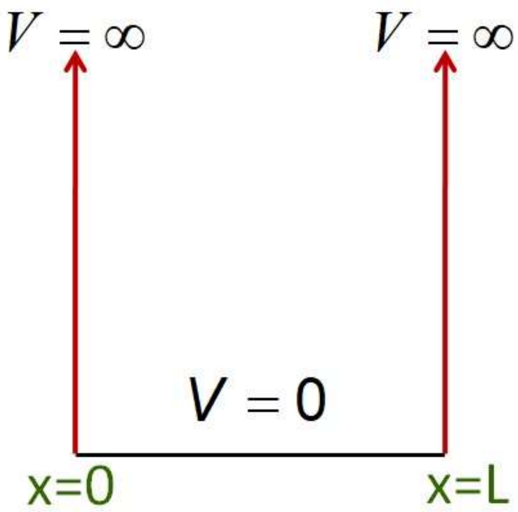
$$n\frac{\lambda_{dB}}{2} = L \Rightarrow n\frac{h}{2p} = L \Rightarrow p = \frac{nh}{2L}$$

Since V=0, all energy is kinetic energy

$$E = \frac{p^2}{2m} \Rightarrow E = \frac{n^2h^2}{8mL^2} = \frac{n^2\pi^2\hbar^2}{2mL^2}$$



'Zero point energy' is a consequence of 'Uncertainty Relation'



Particle is restricted within the box of dimension L

$$\Delta x = L$$

Momentum uncertainty

$$\Delta p = \frac{\hbar}{2\Delta x} = \frac{\hbar}{2L}$$

For the minimum energy state,

$$p = \Delta p = \frac{\hbar}{2L}$$

$$E_{\text{minimum}} = \frac{p^2}{2m} = \frac{\hbar^2}{8mL^2} > 0$$

Numerical Example:

An electron confined in a box of dimension 0.5 nm. Find lowest energy level and the energy difference between the second and first level.

$$E_1 = \frac{\pi^2\hbar^2}{2mL^2} = \left(\frac{\hbar^2}{2m_e}\right)\left(\frac{\pi}{5\times 10^{10}}\right)^2 = 2.4\times 10^{-19} J \sim 1.5eV$$

Separation between second and first energy levels

$$E_2 = 4\frac{\pi^2\hbar^2}{2mL^2}$$

$$E_2 - E_1 = 3\frac{\pi^2\hbar^2}{2mL^2} = 3E_1 \quad \sim 4.5eV$$

Orthogonality

Two functions $\psi_1(x)$ and $\psi_2(x)$ are said to be **orthogonal** if

$$\int_{-\infty}^{\infty} \psi_1^*(x)\psi_2(x)dx = 0$$

For a particle in box

$$\psi_n(x) = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi}{L}x\right)$$ and energy is $$E_n = \frac{n^2\pi^2\hbar^2}{2mL^2}$$

Let us test the orthogonality of $\psi_l(x)$ and $\psi_n(x)$

We need to find out $$\int_{-\infty}^{\infty} \psi_l^*(x)\psi_n(x)dx = \int_0^L \psi_l^*(x)\psi_n(x)dx$$

$$\psi_n(x) = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi}{L}x\right)$$

$$\int_0^L \psi_l^*(x)\psi_n(x)dx = \frac{2}{L}\int_0^L \sin\left(\frac{l\pi}{L}x\right)\sin\left(\frac{n\pi}{L}x\right)dx$$

$$Use\ \ \mathrm{sinAsinB} = \left[\cos(\mathrm{A}-\mathrm{B}) - \cos(\mathrm{A}+\mathrm{B})\right]/2$$

$$= \frac{1}{L}\int_0^L \left[\cos\frac{(l-n)\pi}{L}x - \cos\frac{(l+n)\pi}{L}x\right]dx \qquad = \delta_{\mathrm{ln}}$$

Kronecker-Delta function $\delta_{\mathrm{ln}} = \begin{cases} 1 & \text{for } l = n \\ 0 & \text{for } l \neq n \end{cases}$

Eigen functions belonging to different eigenvalues are orthogonal

Time dependent wave functions

$$\psi_n(x) = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi}{L}x\right)$$

$$\Psi(x,t) = \psi(x)e^{-iE/\hbar}$$

$$E_n = \frac{n^2\pi^2\hbar^2}{2mL^2}$$

$$\Psi_n(x,t) = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi}{L}x\right)e^{-iE_n/\hbar}$$

$$\Psi_n^*(x,t)\Psi_n(x,t) = \frac{2}{L}\sin^2\left(\frac{n\pi}{L}x\right)$$

Probability of observing the particle at x

Independent of time

$\Psi_n(x,t)$ *is a Stationary state*

Particle in a box:
Quantum Particle vs Classical Particle

- **For a quantum particle the energy levels are quantized.**

$$E_n = \frac{n^2 \pi^2 \hbar^2}{2mL^2}$$

A classical particle can assume any value of E

- **For a quantum particle the lowest energy is**

$$E_1 = \frac{\pi^2 \hbar^2}{2mL^2} > 0$$

Quantum particle possesses "Zero point energy"

For a classical particle the lowest energy =0

• Probability of finding a particle in an interval [L/4, 3L/4]

$$P_n[L/4, 3L/4] = \int_{L/4}^{3L/4} \psi_n^*(x)\psi(x)dx = \frac{2}{L}\int_{L/4}^{3L/4} \sin^2\left(\frac{n\pi x}{L}\right)dx$$

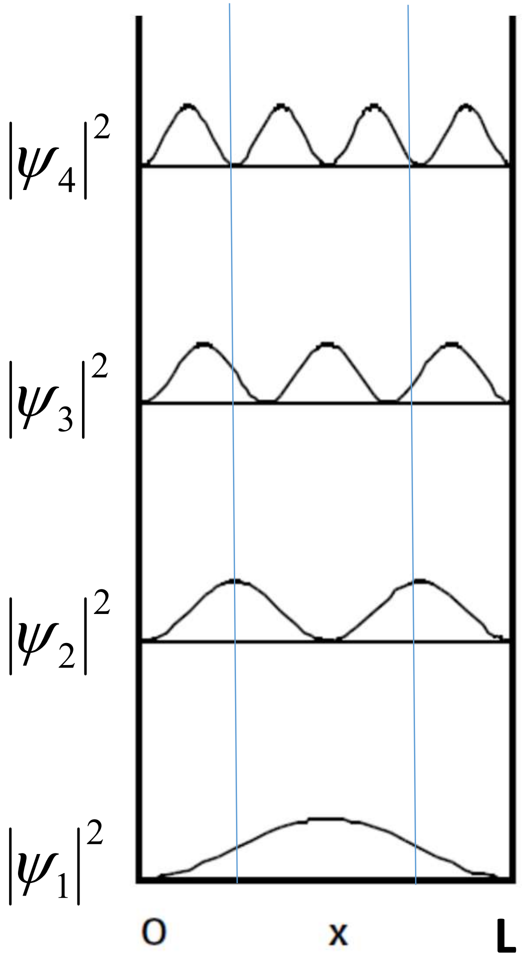
$$= \frac{1}{2} - \frac{1}{2n\pi}\left[\sin\left(\frac{3}{2}n\pi\right) - \sin\left(\frac{1}{2}n\pi\right)\right]$$

$$P_n[L/4, 3L/4] = \frac{1}{2} + \frac{1}{\pi} = 0.818 \quad for \;\; n = 1$$

$$P_n[L/4, 3L/4] = \frac{1}{2} \quad for \;\; n = even$$

$P_n[L/4, 3L/4] =$ Oscillating around 1/2 $\; for \;\; n = odd$

$$P_n[L/4, 3L/4] = \frac{1}{2} \quad as \;\; n \to \infty$$



For a classical particle, the probability of finding it at any x is 1/L

$$\therefore P_{class}[L/4, 3L/4] = 1/2$$

For large n, quantum probability tends to classical probability

- **Momentum uncertainty**

$$\langle p_x \rangle = \int_0^L \psi_n^*(x)\left(-i\hbar\frac{\partial}{\partial x}\right)\psi(x)dx \;= \frac{-2i\hbar}{L}\int_0^L \frac{n\pi}{L}\sin\left(\frac{n\pi x}{L}\right)\cos\left(\frac{n\pi x}{L}\right)dx$$

$$= 0$$

$$\langle p_x^2 \rangle = \int_0^L \psi_n^*(x)\left(-\hbar^2\frac{\partial^2}{\partial x^2}\right)\psi(x)dx \;= \frac{2\hbar^2}{L}\left(\frac{n\pi}{L}\right)^2\int_0^L \sin^2\left(\frac{n\pi x}{L}\right)dx$$

$$= \left(\frac{n\hbar\pi}{L}\right)^2$$

$$\boxed{\Delta p_x = \sqrt{\langle p^2 \rangle - \langle p \rangle^2} \;= \frac{n\hbar\pi}{L}}$$

- **Position uncertainty**

$$\langle x \rangle = \int_0^L \psi_n^*(x)\, x\, \psi(x)\, dx = \frac{2}{L}\int_0^L x \sin^2\left(\frac{n\pi x}{L}\right) dx = \frac{L}{2}$$

$$\langle x^2 \rangle = \int_0^L \psi_n^*(x)\, x^2 \psi(x)\, dx = \frac{2}{L}\int_0^L x^2 \sin^2\left(\frac{n\pi x}{L}\right) dx = \frac{L^3}{3}\left[1 - \frac{3}{2n^2\pi^2}\right]$$

$$\boxed{\Delta x = \sqrt{\langle x^2 \rangle - \langle x \rangle^2} = \sqrt{\frac{L^2}{12n^2\pi^2}(n^2\pi^2 - 6)}}$$

- **Uncertainty relation**

$$\Delta x = \sqrt{\frac{L^2}{12n^2\pi^2}(n^2\pi^2 - 6)}$$

$$\Delta p_x = \frac{n\hbar\pi}{L}$$

$$\boxed{\Delta x \Delta p_x = \hbar\sqrt{\frac{(n^2\pi^2 - 6)}{12}}}$$

$$= 0.57\hbar \quad \text{for} \quad n = 1$$

$$= 1.67\hbar \quad \text{for} \quad n = 2$$

- **Symmetry of wave functions**

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L}x\right)$$

Odd n $\psi_1, \psi_3, \psi_5 \ldots\ldots$ $\boxed{\psi(x) = \psi(-x)}$

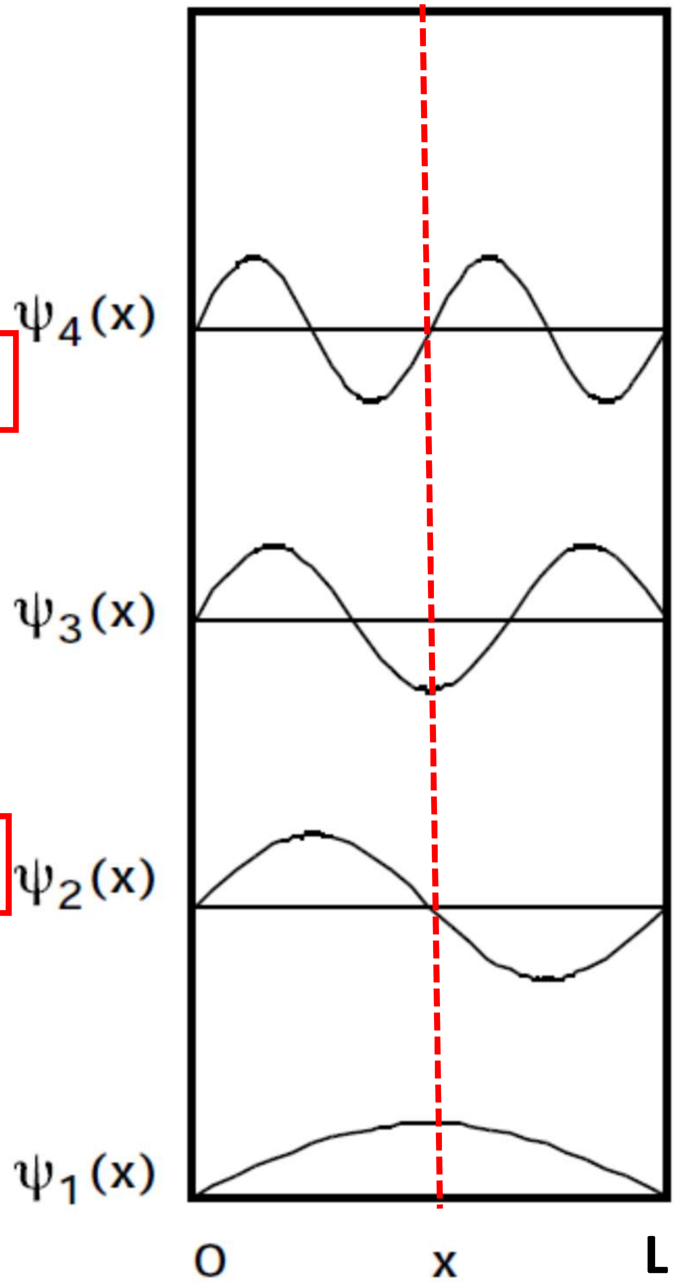
$\psi(x)$ on the right half is exactly mirror image of the $\psi(x)$ in the left half.

Such wave functions are called '**Even Parity**' wave functions

Even n $\psi_2, \psi_4, \psi_6 \ldots\ldots$ $\boxed{\psi(x) = -\psi(-x)}$

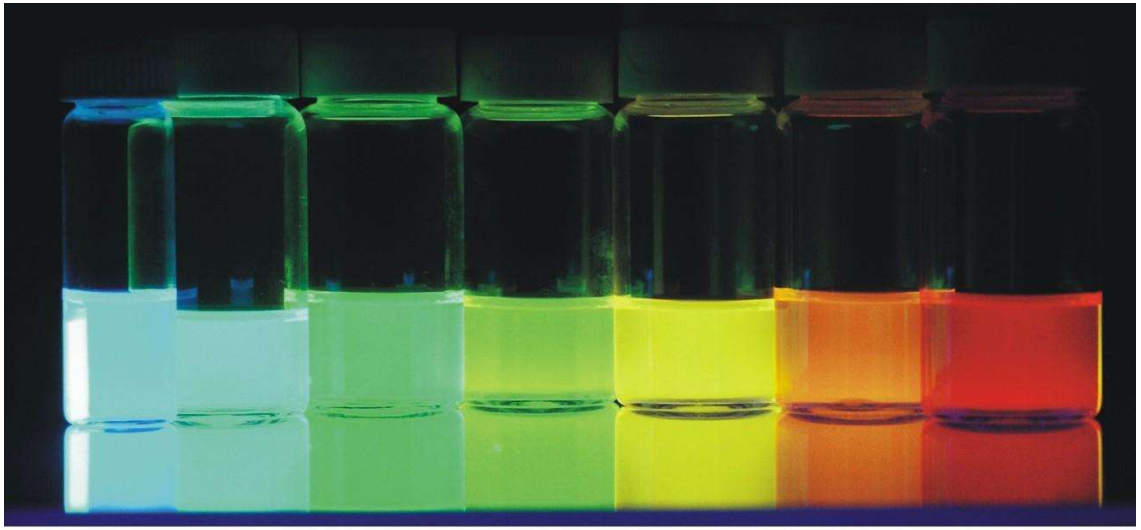
$\psi(x)$ on the right half is negative of the mirror image of the $\psi(x)$ in the left half.

Such wave functions are called '**odd Parity**' wave functions



Colours from Quantum Dots

A nanoscale semiconductor arrangement is called a quantum dot. They exhibit size dependent colours.



$$E_n = \frac{n^2\pi^2\hbar^2}{2mL^2}$$

L = size of the quantum dot

2.3 → 5.5

Size (nanometers)

$$E_2 - E_1 = \frac{3\pi^2\hbar^2}{2m}\frac{1}{L^2}$$

Size increases, emission shifts to red side.