Lecture 4
Particle in a box

In the last class, we found that for a free particle: when the particle has momentum $p_x = \pm \hbar k$, then its

corresponding energy is given by $\dfrac{p_x^2}{2m}$, which is continuous.

There is no difference from classical mechanics (CM) since here in quantum mechanics (QM) case also p_x can take arbitrary values (integer, non-integer) & we get continuous energy values.

However, as soon as this free particle is "confined" to certain part in space, things are different!

Let us look at the simplest possible case → Particle confined in a one-dimensional (i.e., 1-D) box.

The potential energy is zero for x between

zero and L and infinite everywhere else.

"Hard walls" are put at the boundaries of

$x = 0$ and $x = L$.

CM picture: A particle of mass m, bouncing

between two fixed walls.
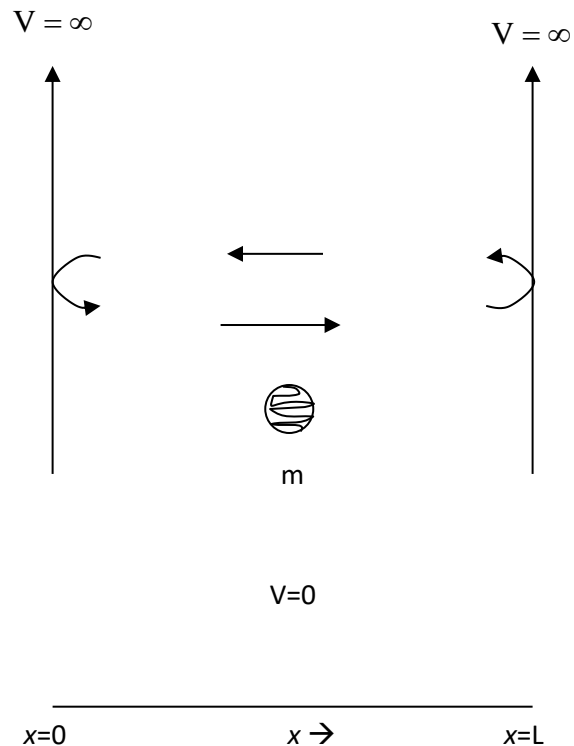
Given some momentum p_x, the classical

particle has some energy $\dfrac{p_x^2}{2m}$ and simply

reflects between the two hard walls continually

radiating energy→ continuous energy.

What happens in the QM picture?

For the particle within the box, the Schrödinger equation for the particle inside the box is the same as in case of the free particle. We were not interested in Hamiltonian operator of the particle outside the box, as particle will have zero probability to be outside the box (and thus wavefunction = 0) which is forced by the infinite potential at x = 0 and x = L. Solve the Schrödinger equation to get $\Psi(x)$. $\because$ there is

no force or potential inside the box, the Schrödinger equation for the particle inside the box is the same as in case of the free particle:

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

Similar to the free particle, we have the general solution as:

$$\Psi(x) = Ae^{ikx} + Be^{-ikx}; \qquad k = \sqrt{\frac{2mE}{\hbar^2}}$$

However, we cannot throw away either A or B & consider only one of the cases as in the free particle case! In fact, it is like the wave (classical!) is traveling back & forth between the two "hard walls" essentially forward & reflected on top of each other & results in superposition of waves $\Rightarrow$ Stable solution should be standing waves!

The recipe that we are using for solving Schrödinger equation is as follows:
- Define the potential energy function (system dependent)
- Define the boundary conditions (system dependent)
- Write down the Hamiltonian operator for the system and solve the resulting SE to obtain a general solution for the differential equation.
- Find particular solution applying the boundary conditions

The wavefunction $\Psi(x)$ is a superposition of both forward and backward moving waves to result in standing waves. But now the main questions are:

(i)   What are A & B? How to determine them?
(ii)   Energy is still continuous or not?

By using the Born interpretation of the wavefunction, we can determine A & B (Boundary values).

Since the potential is ∞ at both x = 0 and x = L; the probability of finding particle at $x < 0$ and $x > L$ is zero.

$$\Rightarrow \left|\Psi(x)\right|^2\Big|_{x=0,L} = 0; \text{ otherwise discontinuity etc.}$$

$$\Rightarrow \Psi(0) = 0 = \Psi(L)$$

$$\Rightarrow A + B = 0 \quad \text{and} \quad Ae^{ikL} + Be^{-ikL} = 0$$

Putting $B = -A$ in the second expression, we get: $A(e^{ikL} - e^{-ikL}) = 0$

$\because e^{\pm ikL} = \cos(kL) \pm i\sin(kL)$, we get $2iA\sin(kL) = 0$,

which $\Rightarrow \sin(kL) = 0 = \sin(n\pi)$ i.e., $kL = n\pi$, with n being an integer.

$\because k = \sqrt{\frac{2mE}{\hbar^2}}$, it implies that only certain Energies, $E_n = \frac{\pi^2\hbar^2}{2mL^2}n^2$ are allowed !

The eigenstates of $\hat{H}$ for this case are:

$$\Psi_n(x) = 2iA\sin\left(\frac{n\pi x}{L}\right) \qquad \text{standing wave solution! with } n = 1,2,3,...$$

$$i = \sqrt{-1} \qquad\qquad\qquad n = 0 \text{ not allowed}$$

$$\because for\ n = 0,\ \Psi_n(x) = 0 \text{ for all } x \Rightarrow \text{no particle!}$$

& the corresponding eigen-energies $E_n = \dfrac{\pi^2\hbar^2}{2mL^2}n^2$; $\qquad\qquad n = 1,2,3,...$

Energy can only take discrete values $\Rightarrow$ Quantized; "Quanta" $\Rightarrow$ units of "packets" & integer n is the Quantum number.

Thus, confining the particle between $x = 0$ and $x = L$ quantizes the energy. The magnitude of the constant in the wavefunction $\Psi(x)$ can be found from the normalization condition which means that total probability of finding the particle within the box is always going to be unity, i.e.,

$$\int_0^L \Psi_n^*(x)\Psi_n(x)dx = \int_0^L |\Psi_n(x)|^2\, dx = 1$$

Since we are going to take the mod-square of the complex wavefunction, we can easily simplify the problem by using: $\Psi_n(x) = 2iA\sin\left(\dfrac{n\pi x}{L}\right) = C\sin\left(\dfrac{n\pi x}{L}\right)$, where $C = 2iA$
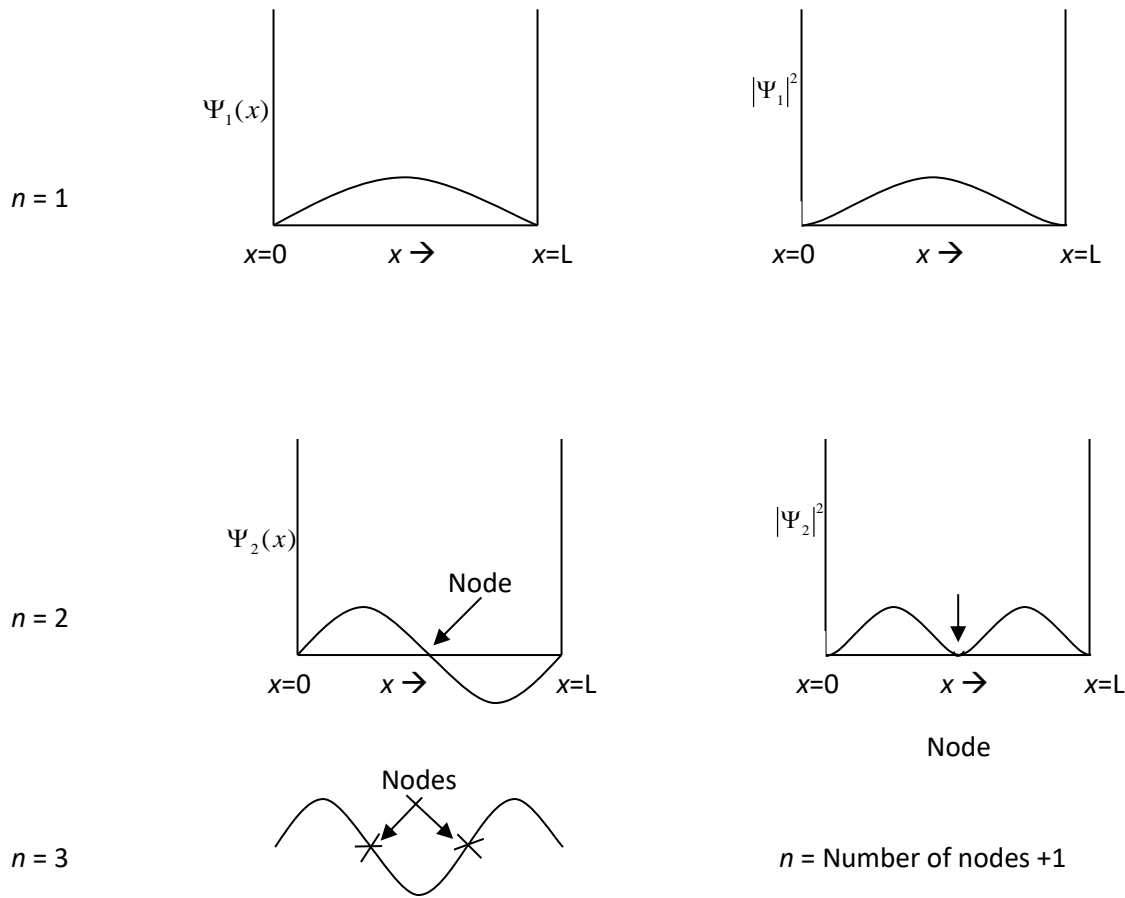
$$\text{So, } \int_0^L |\Psi_n(x)|^2\, dx = C^2\int_0^L \sin^2\left(\frac{n\pi}{L}\right)dx = 1$$

$$\text{which} \Rightarrow C^2\frac{L}{2} - 0 = 1\text{, and }\therefore C = \sqrt{\frac{2}{L}}$$

Thus, the wavefunction $\Psi_n(x)$ is given by

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

Plots of the first few eigenstates $\Psi_n(x)$ and their corresponding probability density $\left|\Psi_n\right|^2$ are as follows:

n = 1

$\Psi_1(x)$

x=0   x→   x=L

$\left|\Psi_1\right|^2$

x=0   x→   x=L

n = 2

$\Psi_2(x)$

Node

x=0   x→   x=L

$\left|\Psi_2\right|^2$

x=0   x→   x=L

Node

Nodes

n = 3

n = Number of nodes +1

Classically, all locations for the particle in the box are equally likely. Quantum mechanically, the probability density is not uniform but shows oscillations. Also, classically, the minimum energy of the particle is zero.

Quantum mechanically, the particle in a box has a non-zero minimum in energy $\dfrac{\pi^2\hbar^2}{2mL^2}$ which is known as the zero-point energy as a consequence of the uncertainty principle.

Nodes are the points, except the boundaries, where y(x) = 0. Number of nodes increases with n for a particle in a box wave function. It may be also noted that the distance between maxima decreases with n, thus a nearly uniform probability density is achieved when n → ∞.

The energy difference (or gap) between the states can be probed through spectroscopy.

$$E_{n+1} - E_n = \left(\frac{\pi^2\hbar^2}{2mL^2}\right)(2n+1)$$ The spacing between the states increases with higher quantum

number, *n*.

spacing increases with *n*
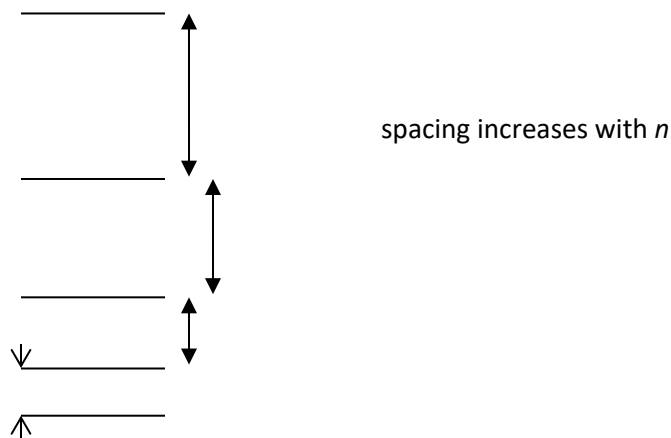
This quantization of energy levels is quite general and can be quite effectively used as a model for dealing with π-electrons in conjugated molecules.

So seemingly, it gets more difficult to get classical character for higher energies of the particle in 1-D box! However, it is not the absolute value of the energy gap that matters. It is the ratio of the energy gap to the particular energy state being considered, i.e., $\dfrac{E_{n+1} - E_n}{E_n}$. For higher energy states, therefore, the separation $E_{n+1} - E_n$ would become insignificant with respect to the value of the energy E_n leading to almost continuous energies and hence the classical case.

In summary, what we have learned so far is as below:

The dynamics of a free particle is the same in either Classical Mechanics or Quantum Mechanics case.

As soon as the free particle is confined or its motion is restricted, discretization or Quantum Mechanics sets in and the discrete energy levels are determined from the solution of the Eigenvalue form of the Schrodinger equation: $\hat{H}\Psi = E\Psi$

We solved for the 1D particle in a box and found that many possible solutions exist, of which the ones as per the Born interpretation are admissible. Born interpretation is important since it provides physical meaning in terms of the fact that only the square of wavefunction makes sense as it represents the probability of finding the particle. Even within the Born interpretation more than one wavefunctions can be admissible. We have already seen superposition of wavefuntions in the 1D potential when we mentioned that there left moving wavefunction simultaneously was present with the right moving wavefunction resulting in standing wave solutions.

So, in general $\Psi = a_1\phi_1 + a_2\phi_2 + ...$ where $a_1, a_2,...$ are the coefficients of the superposing wavefunctions $\phi_1, \phi_2,...$ and would represent their respective contribution or weightage to the total wavefunction.

We know for normalized total wavefunction Ψ, we have $\left|\Psi\right|^2 = 1$.

Similarly, two wavefunctions are orthogonal if the integral of their product vanishes, i.e.,
$\int \Psi_i^*(x)\Psi_j(x)dx = 0$ for all $i \neq j$

In general, wavefunctions corresponding to different energies are orthogonal.

Thus, for an orthonormal set, we have: $1 = \left|\Psi\right|^2 = \left|a_1\right|^2 + \left|a_2\right|^2 + ..., \because$ all $a_i^* a_j = 0$

Square of the coefficients, therefore, represent the contribution of the individual wavefunctions to the total wavefunction.

Origin of Quantization

We realized while solving particle in a box problem that we solve the wave functions only for some values of E. In general, it is impossible to find a quantum mechanically acceptable solution to the problem for an arbitrary value of E. Note that for any arbitrary value of E we can have a mathematically acceptable solution, but this might not give us a well behaving solution, which is required by quantum mechanics.

The quantized energy levels or quantum numbers is a consequence of the boundary conditions. Quantization will occur only when the particle is confined to a finite region of space by the potential.

It is possible to make straight forward extension to 2 and higher dimensional systems from the particle in a 1D box model.