A particle in a 1-dimensional box is a fundamental quantum mechanical approximation describing the translational motion of a single particle confined inside an infinitely deep well from which it cannot escape.

**Introduction**

The particle in a box problem is a common application of a quantum mechanical model to a simplified system consisting of a particle moving horizontally within an infinitely deep well from which it cannot escape. The solutions to the problem give possible values of E and $|\psi(x)|$ that the particle can possess. E represents allowed energy values and $|\psi(x)|$ is a wavefunction, which when squared gives us the probability of locating the particle at a certain position within the box at a given energy level.

To solve the problem for a particle in a 1-dimensional box, we must follow our **Big, Big recipe for Quantum Mechanics**:

1. Define the Potential Energy, $V$
2. Solve the Schrödinger Equation
3. Define the wavefunction
4. Define the allowed energies

**Step 1: Define the Potential Energy $V$**

*A particle in a 1D infinite potential well of dimension $L$.*

The potential energy is *0 inside the box* ($V=0$ for $0<x<L$) and *goes to infinity at the walls of the box* ($V=\infty$ for $x<0$ or $x>L$). We assume the walls have infinite potential energy to ensure that the particle has zero probability of being at the walls or outside the box. Doing so significantly simplifies our later mathematical calculations as we employ these **boundary conditions** when solving the Schrödinger Equation.
Step 2: Solve the Schrödinger Equation

The time-independent Schrödinger equation for a particle of mass $m$ moving in one direction with energy $E$ is

\[-\frac{\hbar^2}{2m} \frac{d^2 \psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x) \tag{5.5.1}\]

with

- $\hbar$ is the reduced Planck Constant where $\hbar = \frac{h}{2\pi}$
- $m$ is the mass of the particle
- $\psi(x)$ is the stationary time-independent wavefunction
- $V(x)$ is the potential energy as a function of position
- $E$ is the energy, a real number

This equation can be modified for a particle of mass $m$ free to move parallel to the x-axis with zero potential energy ($V = 0$ everywhere) resulting in the quantum mechanical description of free motion in one dimension:

\[-\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} = E\psi(x) \tag{5.5.2}\]

This equation has been well studied and gives a general solution of:

\[\psi(x) = A\sin(kx) + B\cos(kx) \tag{5.5.3}\]

where $A$, $B$, and $k$ are constants.

Step 3: Define the wavefunction

The solution to the Schrödinger equation we found above is the general solution for a 1-dimensional system. We now need to apply our **boundary conditions** to find the solution to our particular system. According to our boundary conditions, the probability of finding the particle at $x=0$ or $x=L$ is zero. When $x=0$, $\sin(0)=0$, and $\cos(0)=1$; therefore, $B$ must equal 0 to fulfill this boundary condition giving:

\[\psi(x) = A\sin(kx) \tag{5.5.4}\]

We can now solve for our constants ($A$ and $k$) systematically to define the wavefunction.

**Solving for $k$**

Differentiate the wavefunction with respect to $x$:

\[\frac{d\psi}{dx}(x) = kA\cos(kx) \tag{5.5.5}\]

\[\frac{d^2\psi}{dx^2}(x) = -k^2A\sin(kx) \tag{5.5.6}\]

Since $\int\psi(x) = A\sin(kx)$, then
If we then solve for $k$ by comparing with the Schrödinger equation above, we find:

$$k = \left( \frac{8\pi^2 mE}{\hbar^2} \right)^{1/2} \label{5.5.8}$$

Now we plug $k$ into our wavefunction:

$$\psi = A \sin \left( \frac{8\pi^2 mE}{\hbar^2} \right)^{1/2} x \label{5.5.9}$$

**Solving for $A$**

To determine $A$, we have to apply the boundary conditions again. Recall that the *probability of finding a particle at $x = 0$ or $x = L$ is zero.*

When $(x = L)$:

$$0 = A \sin \left( \frac{8\pi^2 mE}{\hbar^2} \right)^{1/2} L \label{5.5.10}$$

This is only true when

$$\left( \frac{8\pi^2 mE}{\hbar^2} \right)^{1/2} L = n\pi \label{5.5.11}$$

where $n = 1, 2, 3, \ldots$

Plugging this back in gives us:

$$\psi = A \sin \left( \frac{n\pi}{L} \right) x \label{5.5.12}$$

To determine $(A)$, recall that the total probability of finding the particle inside the box is 1, meaning there is no probability of it being outside the box. When we find the probability and set it equal to 1, we are *normalizing* the wavefunction.

$$\int_{0}^{L} \psi \, dx = 1 \label{5.5.13}$$

For our system, the normalization looks like:

$$A^2 \int_{0}^{L} \sin^2 \left( \frac{n\pi x}{L} \right) \, dx = 1 \label{5.5.14}$$

Using the solution for this integral from an integral table, we find our normalization constant, $(A)$:

$$A = \sqrt{\frac{2}{L}} \label{5.5.15}$$

Which results in the normalized wavefunction for a particle in a 1-dimensional box:

$$\psi = \sqrt{\frac{2}{L}} \sin \left( \frac{n\pi}{L} \right) x \label{5.5.16}$$
Step 4: Determine the Allowed Energies

Solving for $E$ results in the allowed energies for a particle in a box:

$$E_n = \frac{n^2 \hbar^2}{8mL^2} \label{5.5.17}$$

This is an important result that tells us:

1. The energy of a particle is quantized and
2. The lowest possible energy of a particle is **NOT** zero. This is called the zero-point energy and means the particle can **never be at rest** because it always has some kinetic energy.

This is also consistent with the Heisenberg Uncertainty Principle: if the particle had zero energy, we would know where it was in both space and time.

What does all this mean?

The wavefunction for a particle in a box at the $\langle n=1 \rangle$ and $\langle n=2 \rangle$ energy levels look like this:

![Wavefunction](image)

The probability of finding a particle a certain spot in the box is determined by squaring $|\psi\rangle$. The probability distribution for a particle in a box at the $\langle n=1 \rangle$ and $\langle n=2 \rangle$ energy levels looks like this:

![Probability Distribution](image)

Notice that the number of nodes (places where the particle has zero probability of being located) increases with increasing energy $n$. Also note that as the energy of the particle becomes greater, the quantum mechanical model
breaks down as the energy levels get closer together and overlap, forming a continuum. This continuum means the particle is free and can have any energy value. At such high energies, the classical mechanical model is applied as the particle behaves more like a continuous wave. Therefore, the particle in a box problem is an example of Wave-Particle Duality.

Important Facts to Learn from the Particle in the Box

- The energy of a particle is quantized. This means it can only take on discrete energy values.
- The lowest possible energy for a particle is NOT zero (even at 0 K). This means the particle always has some kinetic energy.
- The square of the wavefunction is related to the probability of finding the particle in a specific position for a given energy level.
- The probability changes with increasing energy of the particle and depends on the position in the box you are attempting to define the energy for.
- In classical physics, the probability of finding the particle is independent of the energy and the same at all points in the box.

Questions

1. Draw the wave function for a particle in a box at the \( n = 4 \) energy level.
2. Draw the probability distribution for a particle in a box at the \( n = 3 \) energy level.
3. What is the probability of locating a particle of mass \( m \) between \( x = L/4 \) and \( x = L/2 \) in a 1-D box of length \( L \)? Assume the particle is in the \( n=1 \) energy state.
4. Calculate the electronic transition energy of acetylaldehyde (the stuff that gives you a hangover) using the particle in a box model. Assume that aspirin is a box of length \( 300 \, \text{pm} \) that contains 4 electrons.
5. Suggest where along the box the \( n=1 \) to \( n=2 \) electronic transition would most likely take place.

Helpful Links

- Provides a live quantum mechanical simulation of the particle in a box model and allows you to visualize the solutions to the Schrödinger Equation: www.falstad.com/qm1d/

References