

11.8: Particle in a One-Dimensional Box

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 ψ 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.

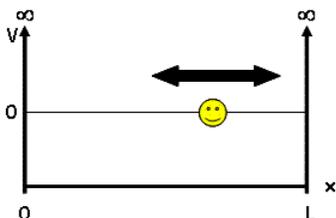
recipe for Quantum Mechanics

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. Solve for the wavefunctions
4. Solve for the allowed energies

Step 1: Define the Potential Energy V

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

$$-\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x) \quad (11.8.1)$$

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:

$$-\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} = E\psi(x) \quad (11.8.2)$$

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

$$\psi(x) = A \sin(kx) + B \cos(kx) \quad (11.8.3)$$

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 $x = 0$, then $\sin(0) = 0$ and $\cos(0) = 1$; therefore, B must equal 0 to fulfill this boundary condition giving:

$$\psi(x) = A \sin(kx) \quad (11.8.4)$$

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 :

$$\frac{d\psi}{dx} = kA \cos(kx) \quad (11.8.5)$$

Differentiate the wavefunction again with respect to x :

$$\frac{d^2\psi}{dx^2} = -k^2 A \sin(kx) \quad (11.8.6)$$

Since $\psi(x) = A \sin(kx)$, then

$$\frac{d^2\psi}{dx^2} = -k^2 \psi \quad (11.8.7)$$

If we then solve for k by comparing with the Schrödinger equation above, we find:

$$k = \left(\frac{8\pi^2 m E}{h^2} \right)^{1/2} \quad (11.8.8)$$

Now we plug k into our wavefunction (Equation 11.8.4):

$$\psi = A \sin \left(\frac{8\pi^2 m E}{h^2} \right)^{1/2} x \quad (11.8.9)$$

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 $x = L$:

$$0 = A \sin \left(\frac{8\pi^2 m E}{h^2} \right)^{1/2} L \quad (11.8.10)$$

This is only true when

$$\left(\frac{8\pi^2 m E}{h^2} \right)^{1/2} L = n\pi \quad (11.8.11)$$

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

Plugging this back in gives us:

$$\psi = A \sin \frac{n\pi}{L} x \quad (11.8.12)$$

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.

$$\int_0^L \psi^2 dx = 1 \quad (11.8.13)$$

For our system, the normalization looks like:

$$A^2 \int_0^L \sin^2\left(\frac{n\pi}{L}x\right) dx = 1 \quad (11.8.14)$$

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

$$A = \sqrt{\frac{2}{L}} \quad (11.8.15)$$

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

$$\psi_n = \sqrt{\frac{2}{L}} \sin \frac{n\pi}{L} x \quad (11.8.16)$$

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

Step 4: Determine the Allowed Energies

Solving for the energy of each ψ requires substituting Equation 11.8.16 into Equation 11.8.2 to get the allowed energies for a particle in a box:

$$E_n = \frac{n^2 h^2}{8mL^2} \quad (11.8.17)$$

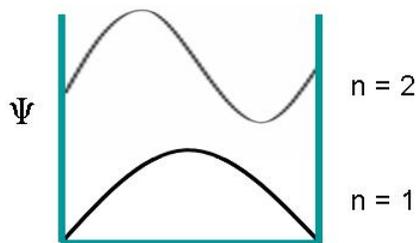
Equation 11.8.17 is a very important result and tells us that:

1. The energy of a particle is quantized.
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.

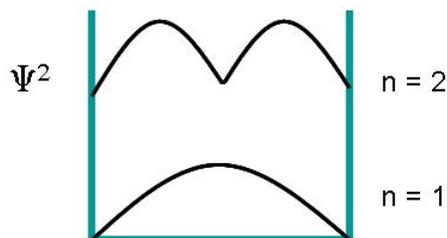
This is also consistent with the [Heisenberg Uncertainty Principle](#): if the particle had zero energy, we would know where it was in both space and time.

What does all this mean?

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



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



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](#).

✓ Example 11.8.1

What is the ΔE between the $n = 4$ and $n = 5$ states for an F_2 molecule trapped within in a one-dimension well of length 3.0 cm? At what value of n does the energy of the molecule reach $\frac{1}{4}k_B T$ at 450 K, and what is the separation between this energy level and the one immediately above it?

Solution

Since this is a one-dimensional particle in a box problem, the particle has only kinetic energy ($V = 0$), so the permitted energies are:

$$E_n = \frac{n^2 h^2}{8mL^2}$$

with $n = 1, 2, \dots$

The energy difference between $n = 4$ and $n = 5$ is then

$$\Delta E = E_5 - E_4 = \frac{5^2 h^2}{8mL^2} - \frac{4^2 h^2}{8mL^2}$$

Using Equation 11.8.17 with the mass of F_2 ($37.93 \text{ amu} = 6.3 \times 10^{-26} \text{ kg}$) and the length of the box ($L = 3 \times 3.0 \times 10^{-2} \text{ m}^2$):

$$\Delta E = \frac{9h^2}{8mL^2} = \frac{9(6.626 \times 10^{-34} \text{ kg} \cdot \text{m}^2 \cdot \text{s}^{-1})^2}{8(6.30938414 \times 10^{-26} \text{ kg})(3.0 \times 10^{-2} \text{ m}^2)^2}$$

$$\Delta E = 8.70 \times 10^{-39} \text{ J}$$

The n value for which the energy reaches $\frac{1}{4}k_B T$:

$$\frac{n^2 h^2}{8mL^2} = \frac{1}{4}k_B T$$

$$n = 1.79 \times 10^9$$

The separation between $n + 1$ and n :

$$\Delta E = E_{n+1} - E_n = \frac{(n+1)^2 h^2 - (n)^2 h^2}{8mL^2}$$

$$\Delta E = \frac{(2n+1)h^2}{8mL^2}$$

$$\Delta E = 3.47 \times 10^{-30} \text{ J}$$

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

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

1. Chang, Raymond. *Physical Chemistry for the Biosciences*. Sausalito, CA: University Science, 2005.

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