

Quantum Mechanical Description of “Simple” 1-D Systems

We will now apply the postulates of QM to some “simple” systems.

The results from these systems will help us understand the methodology and the of interpretive nature of quantum mechanics.

We'll start with **stationary states** for systems with Hamiltonians that are **time-independent**.

$$\begin{aligned}\hat{H} &= -\frac{\hbar^2}{2m} \nabla^2 + V(x, y, z; t) \\ &= -\frac{\hbar^2}{2m} \nabla^2 + V(x, y, z)\end{aligned}$$

The time-independent Schrödinger equation applies:

$$\hat{H}\psi = E\psi$$

For now, we'll only deal with a **single particle** in one-dimension.

Not too common in practice, but the math is simple and the interpretive value is very important.

The time-independent Schrödinger equation for a one-dimensional system is

$$\hat{H}\psi(x) = E\psi(x)$$

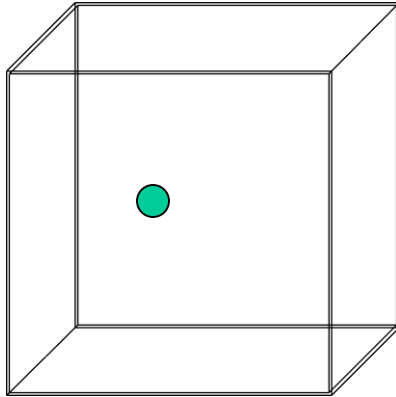
one-dimension (x)

What changes between different physical systems is the Hamiltonian operator and the boundary conditions of the problem.

$$\hat{H} = -\frac{\hbar^2}{2m} \nabla^2 + V(x)$$

These factors define the problem and therefore the resulting wave functions for the particle.

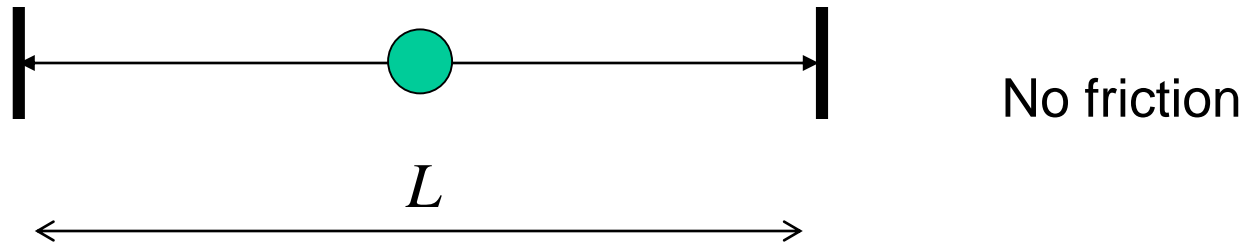
A Particle in a One-Dimensional Box



This is quantum mechanical system is used for introductory purposes.

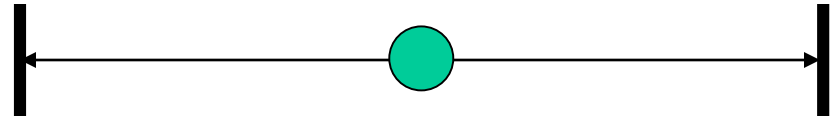
In 3-Dimensions, it's a box.

In one-dimension, we have a particle in a line bounded by impenetrable walls. (It is still called a box though!)



It could serve as a crude model for an electron in a wire.

The Classical Mechanical Picture



The classical state can be solved in Hamilton's formulation:

$$H = T + V = \frac{p^2}{2m} + V(x)$$

$V(x) = 0$	inside box
$V(x) = \infty$	outside box

If we have a conservative system where the energy is constant, then we assume the particle has perfectly elastic collisions with the walls.

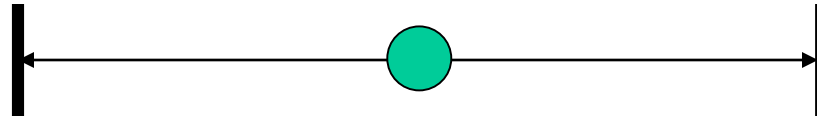
Without actually solving the equations of motion, we would expect that the lowest energy state of the system to be

$$E = 0$$

when the particle is not moving.

Classically, the particle could assume any velocity and therefore we would have a **continuum** of energy states with $E \geq 0$.

The Quantum Mechanical Description



We'll find that the quantum mechanical description has some surprises.

If we want the QM description, what do we need?

From Postulate 1

The state of a quantum mechanical system is completely specified by a function $\Psi(x,y,z,t)$ that depends on the coordinates of the particle and on time. This function is called the **wave function** of the system.

We need to find the quantum mechanical wave function for a one-dimensional system:

$$\Psi(x,t)$$

How do we find or solve for the wave function?

From Postulate 5 we have

The wave function of a system evolves in time according to the time-dependent Schrödinger equation:

$$\hat{H}\Psi(x, y, z; t) = i\hbar \frac{\partial}{\partial t} \Psi(x, y, z; t)$$

If the Hamiltonian operator is not time-dependent, then we can apply the time-independent Schrödinger equation:

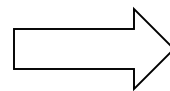
$$\hat{H}\psi(x, y, z) = E\psi(x, y, z)$$

$$V(x) = 0$$

inside box

$$V(x) = \infty$$

outside box



Time-independent

So, we need to solve Schrödinger's time-independent equation for the wave function:

$$\hat{H}\psi(x) = E\psi(x)$$

In general, the Hamiltonian operator is different for each system.

The Hamiltonian for a conservative system is given by:

$$\hat{H} = \hat{T} + \hat{V}$$

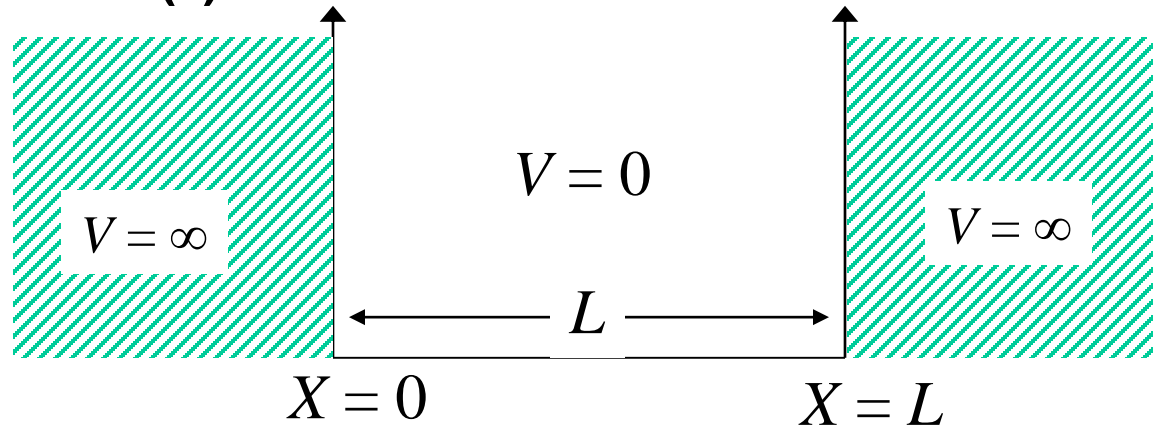
$$\hat{T} = -\frac{\hbar^2}{2m} \nabla^2 \quad \xrightarrow{\text{1-D}} \quad \hat{T} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2}$$

For a single particle in 1-dimension.

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x)$$

In the Hamiltonian, it is the potential that is different for each system.

The potential $V(x)$

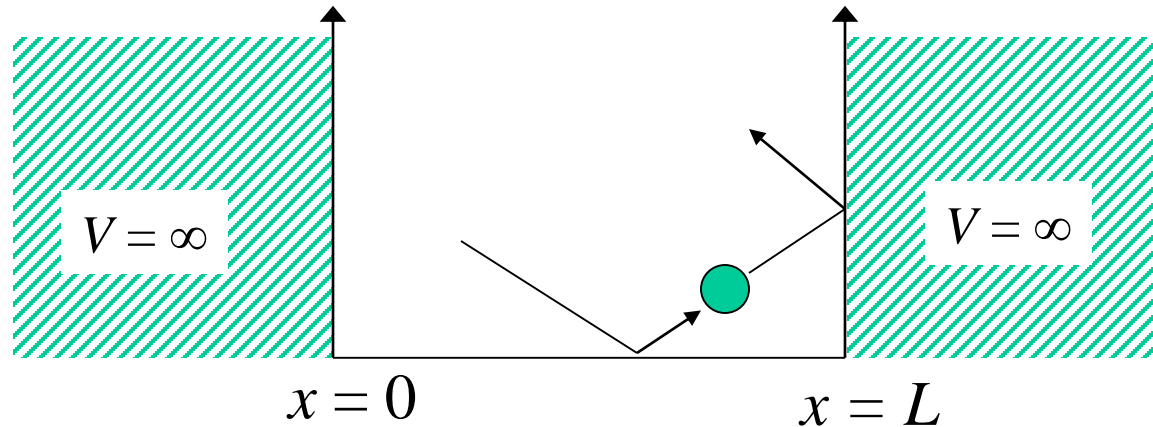


$$V(x) = 0 \quad \text{for} \quad 0 < x < L$$

$$V(x) = \infty \quad \text{for} \quad 0 \geq x \quad \text{and} \quad x \geq L$$

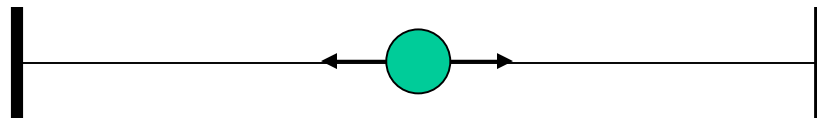
Note: $V(x)$ is not finite valued or smooth! That's ok (the QM postulates impose restrictions on the wave functions, *not the potential!*)

Note also: This is a plot of the potential, NOT the box. Recall that the box is 1-dimensional.



The above interpretation of the particle bouncing around in the potential is incorrect.

The particle is restricted to move in one-dimension as depicted below.



We only have restrictions on $\psi(x)$. Recall for the first postulate we have:

1. $\psi(x)$ must be a continuous function.
2. $\psi(x)$ must be bounded and single valued.
3. $\psi(x)$ must be normalizable.

$$1 = \int_{-\infty}^{\infty} \psi^*(x)\psi(x)dx$$

We can use all of the above to help us solve for the appropriate solutions:

$$\hat{H}\psi(x) = E\psi(x)$$

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

$$V(x) = 0 \quad 0 < x < L$$

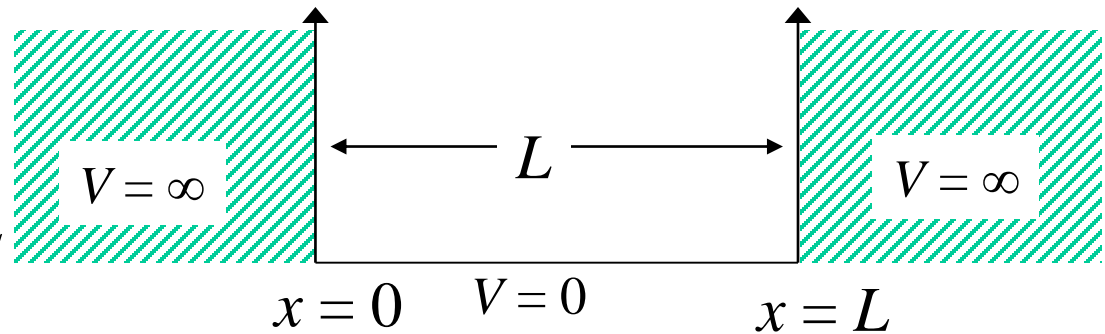
$$V(x) = \infty \quad 0 \geq x \text{ and } x \geq L$$

Since $V(x)$ is discontinuous and piecewise, it is useful to solve for, or at least to think about the solution, in a piecewise manner.

Just remember that the wave function must be continuous at the boundaries ($x = 0$ and $x = L$)

Outside the box

$$V(x) = \infty \quad 0 \geq x \text{ and } x \geq L$$



- Qualitatively, the barrier is impenetrable, with an infinite potential.
- So the particle will require an infinite amount of energy to get out of the box.
- We can therefore assume that there is a **zero probability** of finding the particle outside of the box.

From the Born interpretation of the wave function we have:

$$|\psi|^2 = \psi^* \psi = 0 \text{ outside of the box.}$$

And hence:

$$\psi(x) = 0 \text{ outside of the box.}$$

$\psi(x) = 0$ outside of the box.

Starting from Schrödinger's equation we can also arrive at this result.

$$\left[-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \infty \right] \psi(x) = E \psi(x)$$

rearranging

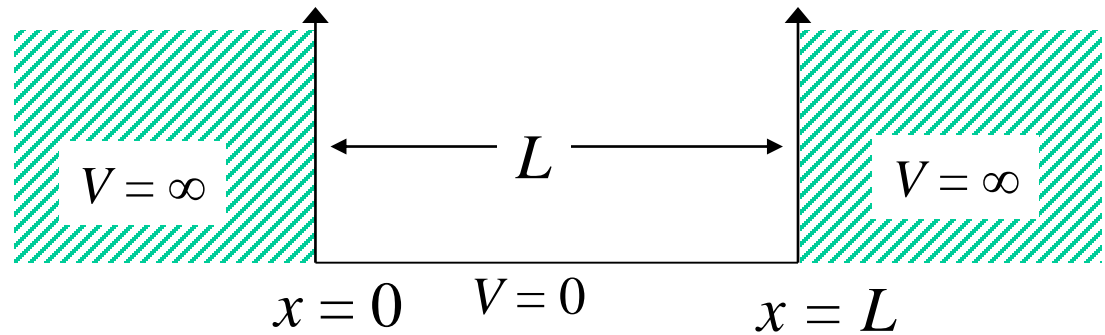
$$-\frac{\hbar^2}{2m} \frac{d^2 \psi(x)}{dx^2} = (E - \infty) \psi(x)$$

A finite second derivative requires $\psi(x) = 0$ as the only solution.

$\psi(x) = 0$ outside the box ($x < 0$ and $x > L$)

Inside the box

$$V(x) = 0 \quad 0 < x < L$$



$$\left[-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + 0 \right] \psi(x) = E \psi(x)$$

This is an ordinary 2nd order differential equation.

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

We can rearrange this into a more 'familiar' DE form:

$$\frac{d^2}{dx^2} \psi(x) + k^2 \psi(x) = 0 \quad \text{where} \quad k = \frac{1}{\hbar} (2mE)^{1/2}$$

$$\frac{d^2}{dx^2} \psi(x) + k^2 \psi(x) = 0$$

The general solution of the differential equation is given by:

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

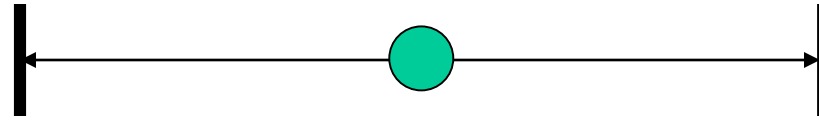


Where A and B are constants to be determined.

Hint. Remember the boundary conditions:

The wave function must be zero at $x = 0$ and $x = L$.

The particle in a box wave function



outside box $\psi(x) = 0$

Inside box $\psi_n(x) = \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{n\pi}{L}x\right) \quad n = 1, 2, 3, \dots$

L is the length of the box

- There is an infinite number of solutions ($n = 1, 2, 3, \dots$)

The Energy

To find the wave function $\psi(x)$ we solved the time independent Schrödinger equation, which is an **eigenvalue equation**. The energy is the eigenvalue.

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

Typically, when you solve an eigenvalue equation, you get both the eigenfunction and the eigenvalue.

Recall that we rearranged the above into a more 'familiar' DE (differential equation) form:

$$\frac{d^2}{dx^2} \psi(x) + k^2 \psi(x) = 0$$

with

$$k = \frac{1}{\hbar} (2mE)^{1/2}$$

Also recall, in applying our 2nd boundary requirement we had:

$$kL = n\pi \quad n = 1, 2, 3\dots$$

This gives us:

$$k = \frac{n\pi}{L} \quad n = 1, 2, 3\dots$$

And from before

$$k = \frac{1}{\hbar} (2mE)^{1/2} = \frac{n\pi}{L}$$

Therefore, solving for E_n gives:

$$E_n = \frac{n^2 \pi^2 \hbar^2}{2mL^2} \quad n = 1, 2, 3\dots$$

Usually, this is written as: $h = 2\pi\hbar$

$$E_n = \frac{n^2 h^2}{8mL^2} \quad n = 1, 2, 3\dots$$

The Particle in a Box - Wave Function and Energy

$$\psi_n(x) = \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{n\pi}{L}x\right)$$

$$E = \frac{n^2 h^2}{8mL^2} \quad \text{with } n = 1, 2, 3, \dots$$

- ***The energy is quantized.*** It can only have discrete values.
- ***n*** is called a quantum number.
- Quantization and quantum numbers appear naturally in quantum mechanics by solving Schrödinger's equation.
- There are quantum numbers for each degree of freedom of a system.

The Particle in a Box - Wave Function and Energy

$$\psi_n(x) = \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{n\pi}{L}x\right)$$

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

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

Lowest energy solution, is called the ground state.

$$E_4 = \frac{16h^2}{8mL^2} \quad 4$$

$\psi_4(x)$

third excited state

$$E_3 = \frac{9h^2}{8mL^2} \quad 3$$

$\psi_3(x)$

second excited state

$$E_2 = \frac{4h^2}{8mL^2} \quad 2$$

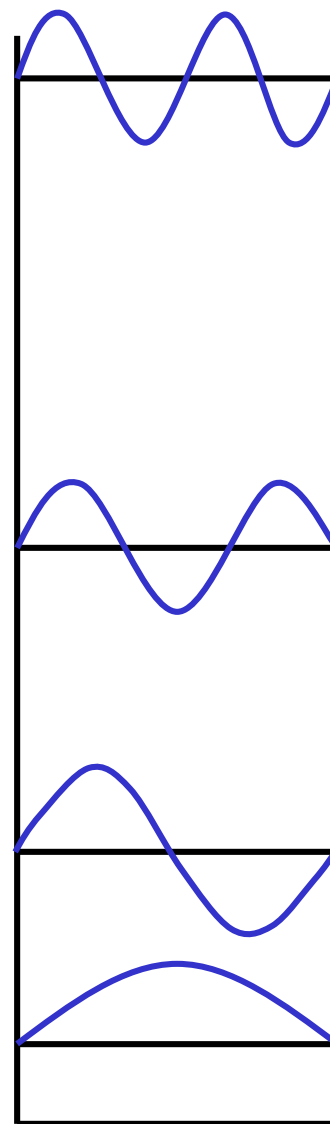
$\psi_2(x)$

first excited state

$$E_1 = \frac{h^2}{8mL^2} \quad 1$$

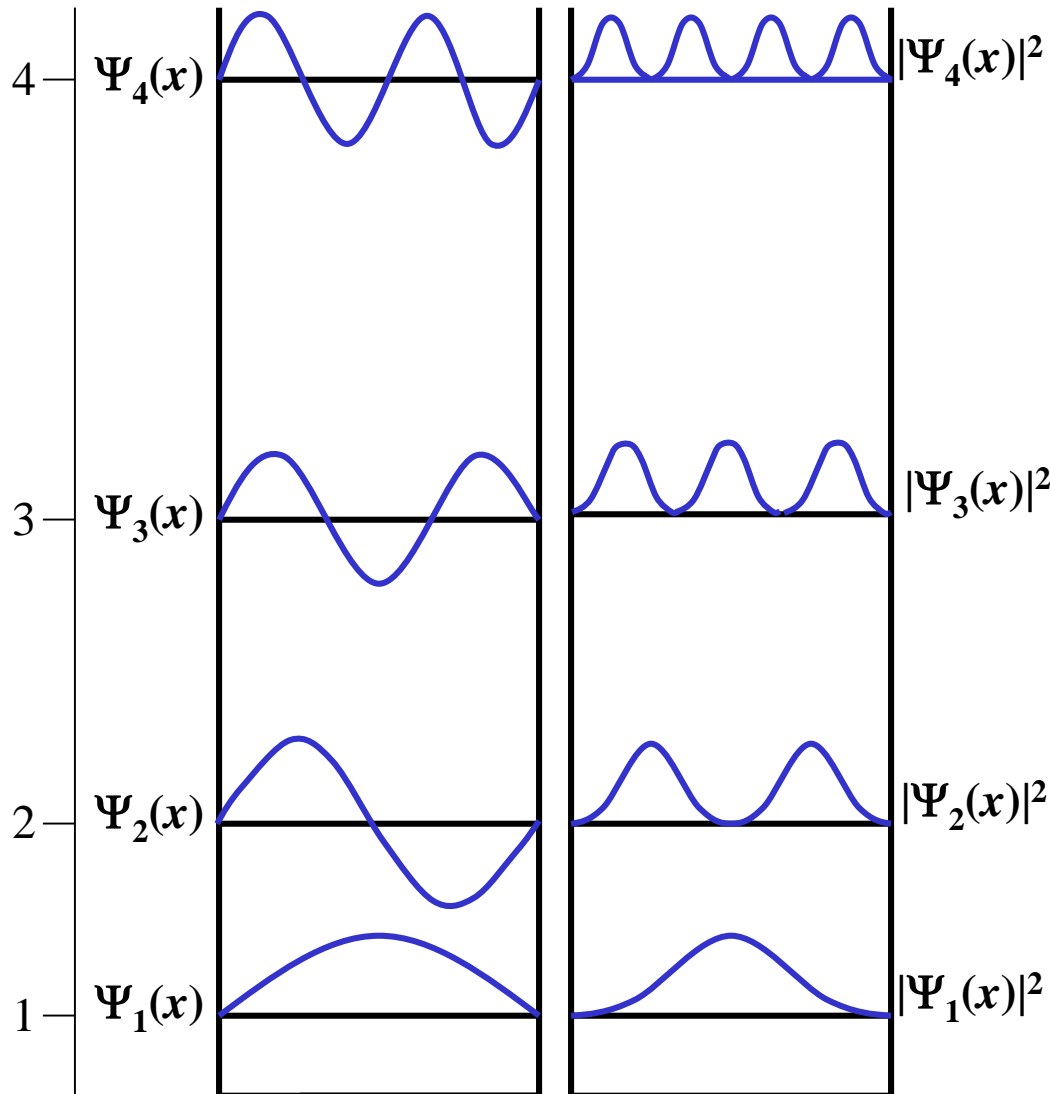
$\psi_1(x)$

ground state

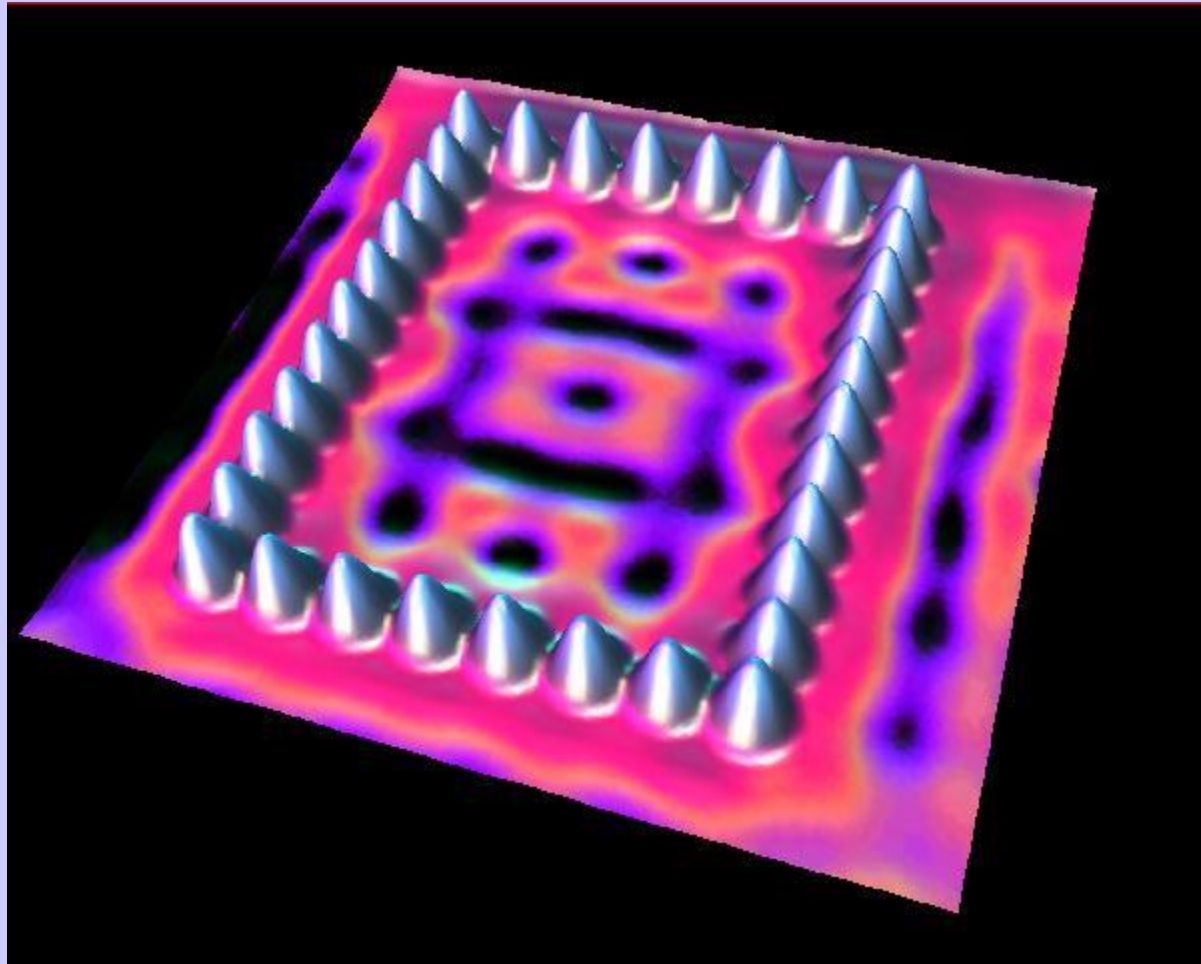


*wave
function*

*probability
distribution
function*



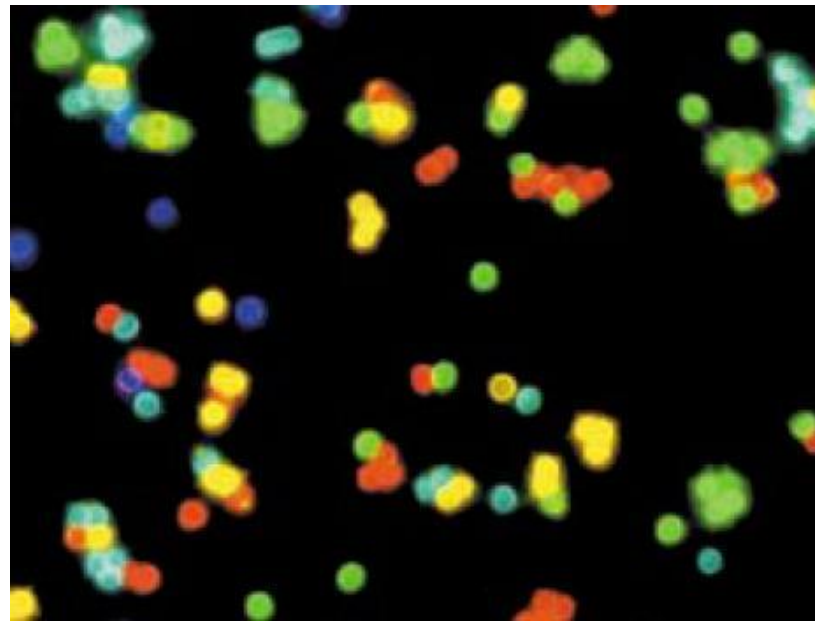
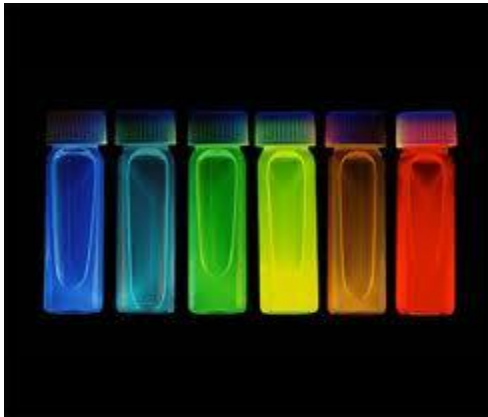
- The wave function is positive and negative
- The probability distribution function is only positive
- excited state solutions have **nodes** where there is zero probability of finding the particle
- Nodes increase with energy



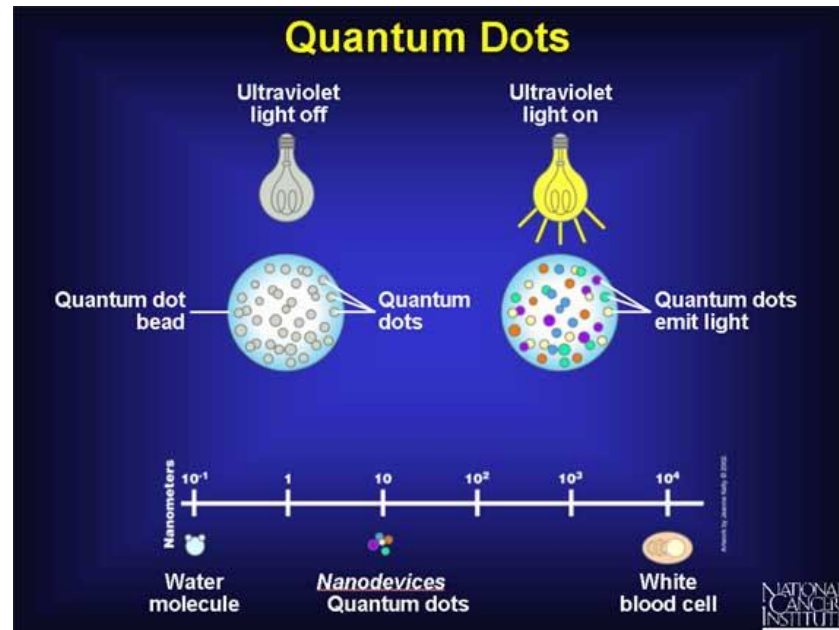
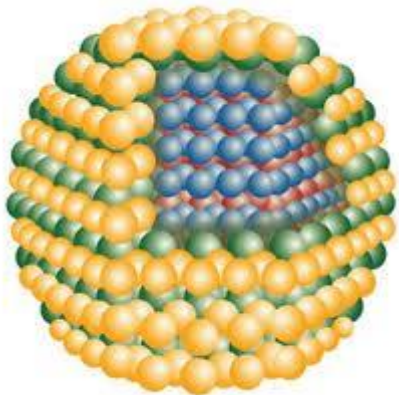
iron atoms on a copper surface

Fe atoms are arranged in a square box to 'corral' surface electrons, like a 2D 'particle-in-a-box'.

The resulting electron density has nodes

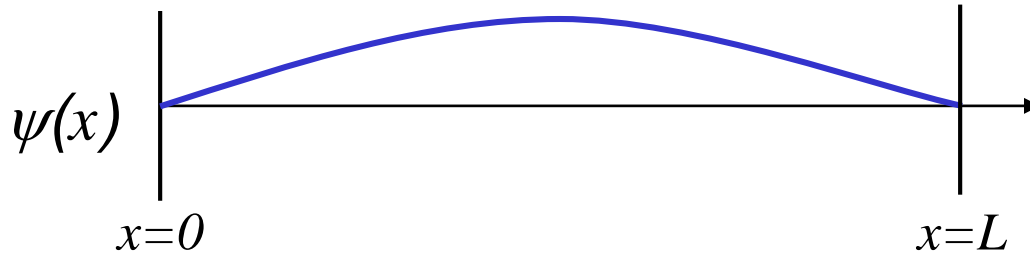


Particles in a Dot!



The Ground State

- Let's look at the $n = 1$ solution, the ground state solution.



$$\psi_1(x) = \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{\pi}{L}x\right)$$

$$E = \frac{h^2}{8mL^2}$$

- Does the wave function satisfy all of our minimum requirements?

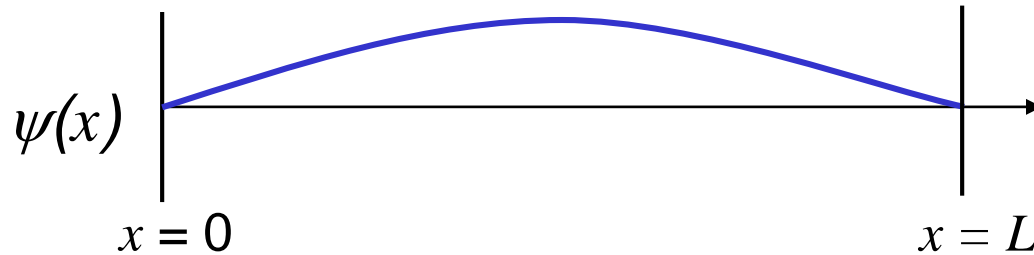
It is continuous, single valued, and finite valued everywhere. We have already shown it can be normalized.

- Notice that the wave function is smooth everywhere except at the boundaries.

This means that the derivative of the wave function will have discontinuities at $x = 0$ and $x = L$ where our potential has discontinuities at these points (changes from zero to infinity instantly)

Recall this was a “loose” requirement.

Zero-point energy



$$\psi_1(x) = \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{\pi}{L}x\right)$$
$$E_1 = \frac{h^2}{8mL^2}$$

- Consider the classical particle in a box.

Without actually solving the equations of motion, we would expect that the lowest energy state of the system to be zero with the particle not moving.

- The lowest energy quantum mechanical state has a non-zero energy (even at absolute zero). *There is no classical explanation for this!*

$$E = \frac{h^2}{8mL^2}$$

This is called the **zero-point energy**

We will see zero-point energies frequently in quantum mechanics.

There are common experimentally measurable effects that are due to the quantum mechanical zero-point energy.

The mysterious zero-point energy is a direct consequence of the Uncertainty Principle:

$$\sigma_x \sigma_{p_x} \geq h/4\pi$$

The particle is “somewhere” in the box, between $x = 0$ and $x = L$, so σ_x is roughly L , the box width (but *not zero!*)

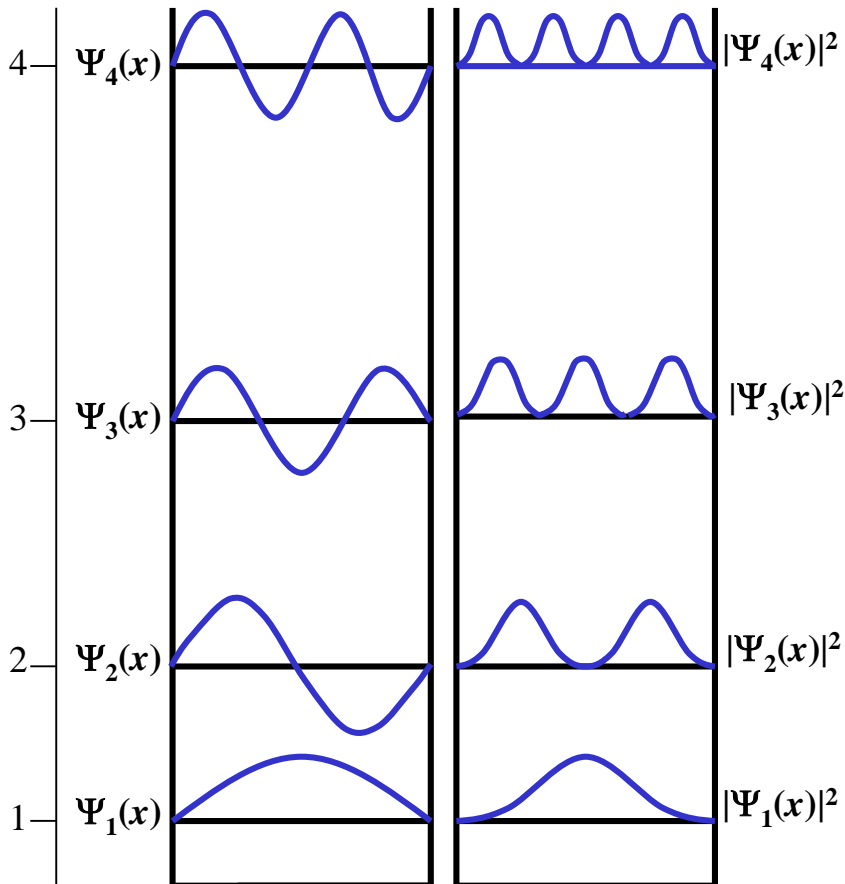
If the the ground-state energy

$$E_1 = p_{x1}^2/(2m)$$

is zero, then the momentum p_x is exactly zero, in which case $\sigma_{p_x} = 0$, violating the Uncertainty Principle.

- The energy of the ‘particle-in-a-box’ problem is all kinetic energy.
- This is reasonable since our potential was zero inside of the box.

$$\hat{H} = \hat{T} + \hat{V} = \hat{T} + 0$$



- The kinetic energy increases with the number of nodes.
- The curvature of the wave function is related to the kinetic energy.
- Qualitatively, the more nodes a wave function has, the more curved it is, and the higher the kinetic energy.

Obtaining Observables from the Wave Function

- The wave function for the particle in a box problem are real-valued and relatively simple.
- This is a good opportunity to examine the mathematical machinery for deriving measurable properties from quantum mechanical wave functions.

Example:

Using the wave function, what is the probability of finding the particle between $x = 0$ and $x = L/2$ (i.e. the first half of the box)?



The integral given below will be useful:

$$\int \sin^2(ax) dx = \frac{1}{2} x - \frac{1}{4a} \sin(2ax)$$

Example:

What is the average momentum that we would measure for the particle in a box?

Recall that the 2nd postulate gives us that for every observable there is a corresponding operator in quantum mechanics:

$$p_x \rightarrow \hat{p}_x = -i\hbar \frac{\partial}{\partial x}$$

Postulate 4, gives us that the average value of an observable is determined from the expectation value:

$$\langle a \rangle = \int_{\text{all space}} \Psi^* \hat{A} \Psi d\tau \quad (\text{where } \Psi \text{ is normalized})$$

In this case, notice that the momentum operator operating on Ψ gives a cosine function, which is orthogonal to the wave function (a sine function).



Average momentum of a particle in a box (**notice that $\psi(x)$ is not an eigenfunction of the momentum operator**):

$$\begin{aligned}\langle p_x \rangle &= \int_0^L \psi^*(x) \hat{p}_x \psi(x) dx \\ &= \int_0^L \psi^*(x) \left(\frac{-i\hbar}{2\pi} \right) \frac{\partial}{\partial x} \psi(x) dx \\ &= \int_0^L \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L} \left(\frac{-i\hbar}{2\pi} \frac{\partial}{\partial x} \right) \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L} dx \\ &= \frac{2}{L} \int_0^L \sin \frac{n\pi x}{L} \left(\frac{-i\hbar}{2\pi} \frac{n\pi}{L} \right) \cos \frac{n\pi x}{L} dx \\ &= -\frac{i\hbar}{L^2} \int_0^L \sin \frac{n\pi x}{L} \cos \frac{n\pi x}{L} dx \\ &= \mathbf{0}\end{aligned}$$

But the average squared momentum is *not zero!*

$$\begin{aligned}\langle p_x^2 \rangle &= \int_0^L \psi^*(x) \hat{p}_x^2 \psi(x) dx = \int_0^L \psi^*(x) \left(\frac{-i\hbar}{2\pi} \right)^2 \frac{\partial^2}{\partial x^2} \psi(x) dx \\ &= \int_0^L \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L} \left(\frac{-i\hbar}{2\pi} \right) \left(\frac{-i\hbar}{2\pi} \right) \left(\frac{\partial}{\partial x} \right) \left(\frac{\partial}{\partial x} \right) \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L} dx \\ &= \frac{2}{L} \int_0^L \sin \frac{n\pi x}{L} \left(\frac{-i\hbar n\pi}{2\pi L} \right) \left(\frac{-i\hbar n\pi}{2\pi L} \right) \sin \frac{n\pi x}{L} dx \\ &= -\frac{2}{L} \left(-\frac{i\hbar}{2\pi} \right)^2 \left(\frac{n\pi}{L} \right)^2 \int_0^L \sin \frac{n\pi x}{L} \sin \frac{n\pi x}{L} dx \\ &= -\frac{2}{L} \left(-\frac{i\hbar}{2\pi} \right)^2 \left(\frac{n\pi}{L} \right)^2 \left(\frac{L}{2} \right) = \frac{n^2 \hbar^2}{4L^2} \\ &= \frac{n^2 \hbar^2}{4L^2} (= 2mE_n)\end{aligned}$$

$$\langle p_x \rangle = \int \psi^* \hat{p}_x \psi dx = 0$$

Interpretation: The average momentum we measure is zero. As expected, the particle is equally likely to be moving in either direction.

But notice that $\langle p_x^2 \rangle = n^2 h^2 / 4L^2$ is not zero.

Also, the variance in the momentum is not zero:

$$\sigma_{px}^2 = \langle p_x^2 \rangle - \langle p_x \rangle^2 = n^2 h^2 / 4L^2$$

Important: This means the momentum does not have a fixed value.

Due to the probabilistic nature of quantum mechanics, in general, we can't foretell what the results of the individual measurements will be. This is true even if we know what the exact wave function is.

However, we can tell what the average of the measure values is. This average is given by the expectation value. (4th postulate)

The Spread in Our Measurements

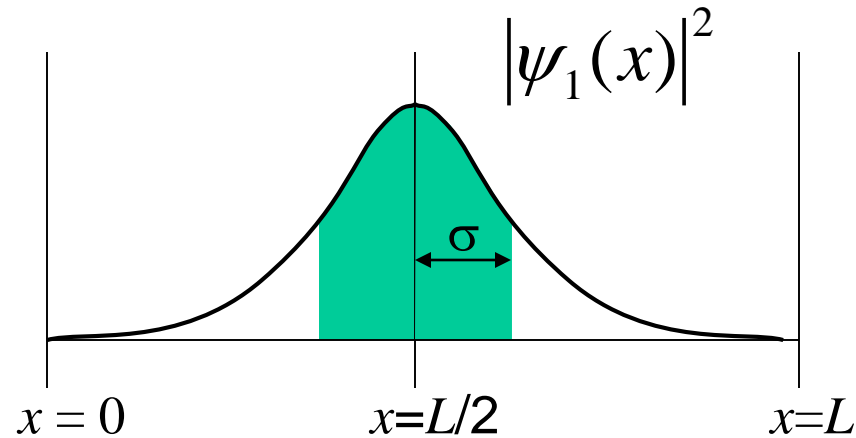
The spread in our measurements about the mean value (expectation value) is given by the variance σ^2 , defined as:

variance:
$$\sigma_a^2 = \langle a^2 \rangle - \langle a \rangle^2$$
$$= \int \psi^* \hat{A}^2 \psi d\tau - \left(\int \psi^* \hat{A} \psi d\tau \right)^2$$

standard deviation:
$$\sigma_a = \sqrt{\sigma_a^2}$$

Recall that the conventional measure of statistical spread is the standard deviation σ . The above expression is derived directly from the expression for the standard deviation, σ in statistics.

Exercise: Determine the variance in the measurements of the position of the particle-in-a-box in the ground state.



$$\langle x \rangle = \int \psi^* \hat{x} \psi d\tau = L/2 \qquad \langle x^2 \rangle = \frac{L^2}{3} - \frac{L^2}{2\pi^2 n^2}$$

$$\text{variance of } x = \langle x^2 \rangle - \langle x \rangle^2 = \frac{L^2}{12} - \frac{L^2}{2\pi^2 n^2}$$



What is the variance in the measurement of the energy of a particle in a box in the ground state?

Before we calculate this by brute force, let's think about the situation more closely.

The energy of the quantum mechanical particle in a box in the ground state is given by the equation:

$$E_1 = \frac{h^2}{8mL^2}$$

If the system is really isolated, then the energy of the system should be constant and we should always measure the same energy.

Indeed, the energy of the system is definite and we will find that the variance is zero.



Summary

Consider a property, a , whose corresponding operator is given by $\underline{\mathbf{A}}$. If the wave function of the system happens to be an eigenfunction of the operator $\underline{\mathbf{A}}$, then the variance in the measurement of that property is zero. In other words, the property ' a ' of that state is definite.

$$\text{If } \hat{A}\psi = a\psi \text{ then } \sigma_a^2 = \langle a^2 \rangle - \langle a \rangle^2 = 0$$

$$\langle a \rangle = \int \psi^* \hat{A}\psi d\tau = \int \psi^* a\psi d\tau = a$$

$$\langle a^2 \rangle = \int \psi^* \hat{A}^2\psi d\tau = \int \psi^* \hat{A}a\psi d\tau = \int \psi^* aa\psi d\tau = a^2$$

So $\langle a^2 \rangle - \langle a \rangle^2 = a^2 - a^2 = 0$. Also, the value that will be measured is the eigenvalue ' a '.

Correspondence Principle

Classical mechanics works very well for macroscopic systems, but fails for microscopic bodies, such as electrons.

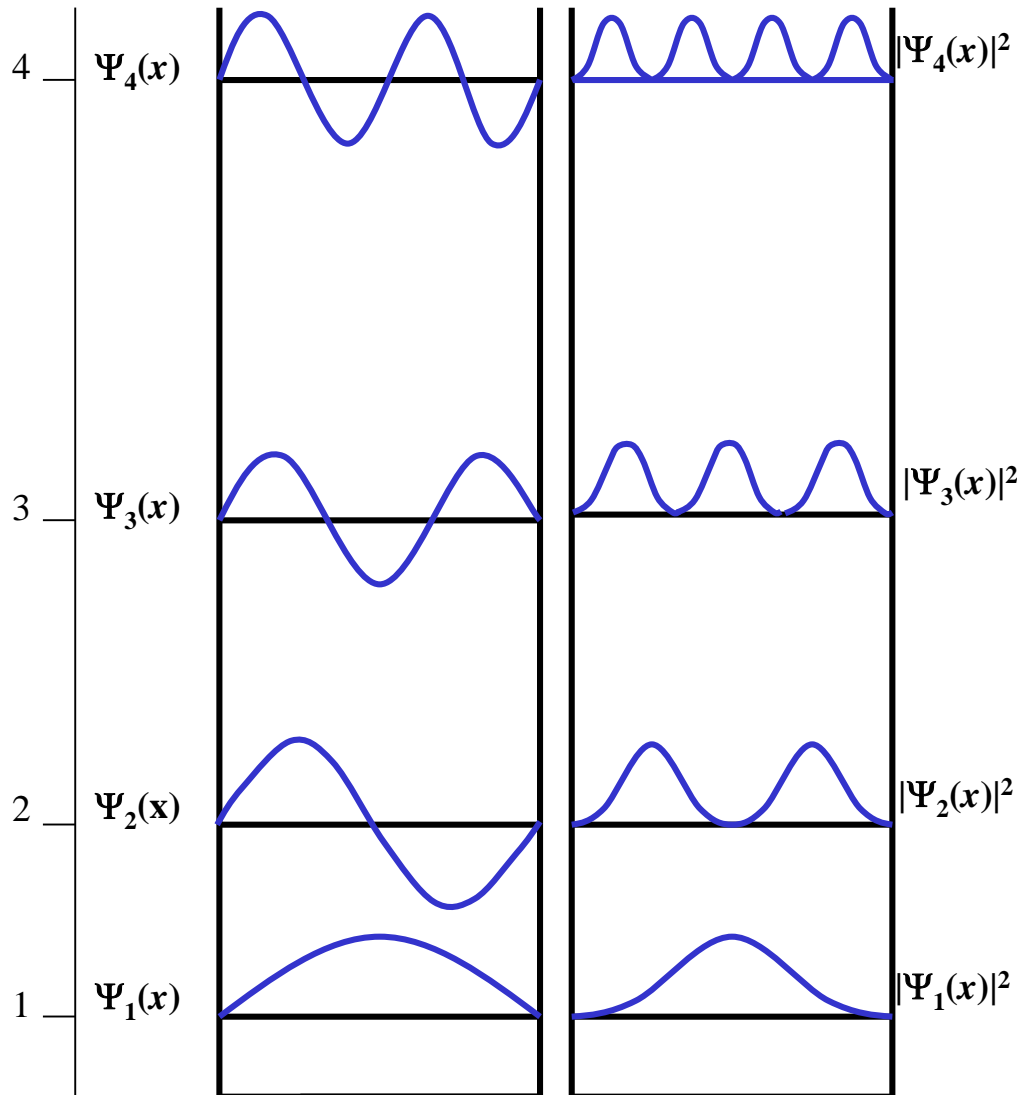
Quantum mechanics is valid for both the microscopic and macroscopic.

The Correspondence Principle states that the behavior of quantum mechanical systems reduces to that of classical systems in the limit of large quantum numbers.

As one might expect, this occurs when we start dealing with macroscopic lengths and masses.

This idea was first developed by Neils Bohr and is sometimes called the Bohr Correspondence Principle.

Consider the probability distribution function for the classical particle in a box and compare this to the probability distribution function as $n \rightarrow \infty$.



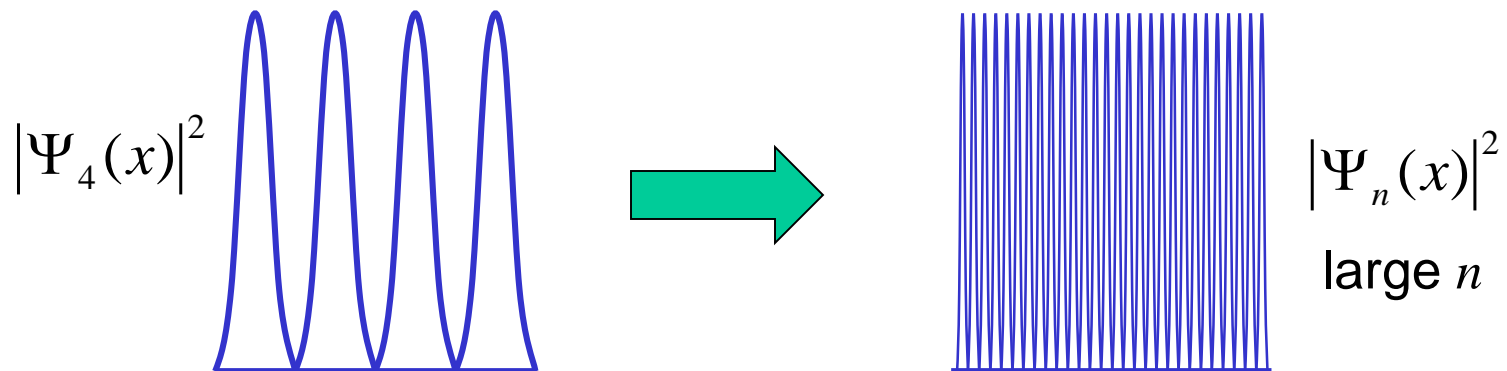
For our particle in a box problem it is not difficult to show that as we begin to deal with macroscopic masses or lengths we will be dealing with large n quantum numbers.

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

- as $m \rightarrow \infty$ (mass), the energy spacings approach zero.
- as $L \rightarrow \infty$ (length), the energy spacings approach zero.

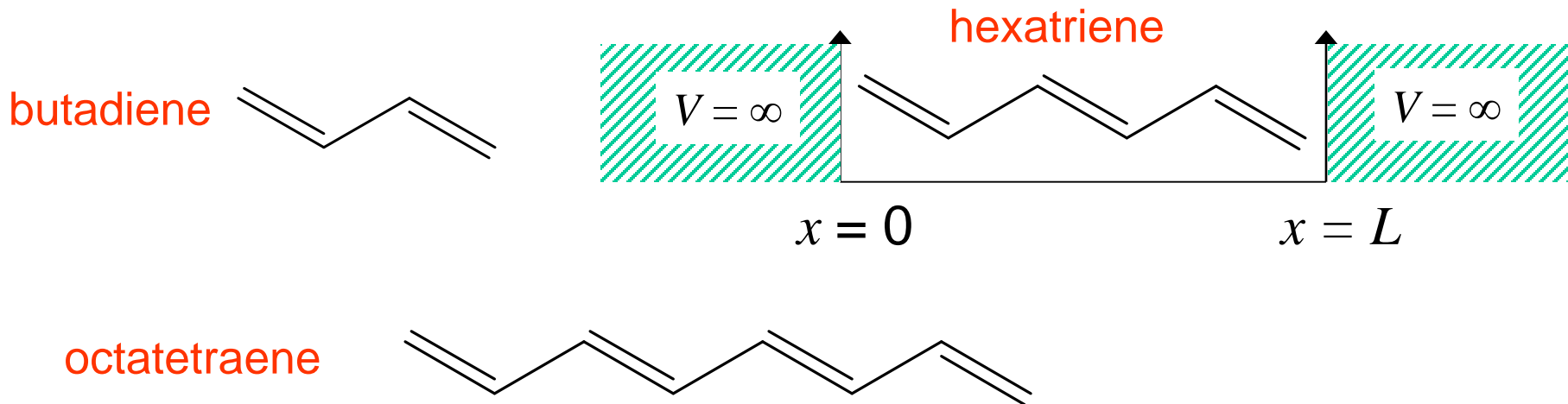
Thus, even at moderate temperatures (300 K), the system is most likely to be in a highly excited state (very large n) where the spacings are small.

- as $n \rightarrow \infty$, the local probability density $|\Psi|^2$ is the same for all x .



π -electrons in Linear Conjugated Hydrocarbons

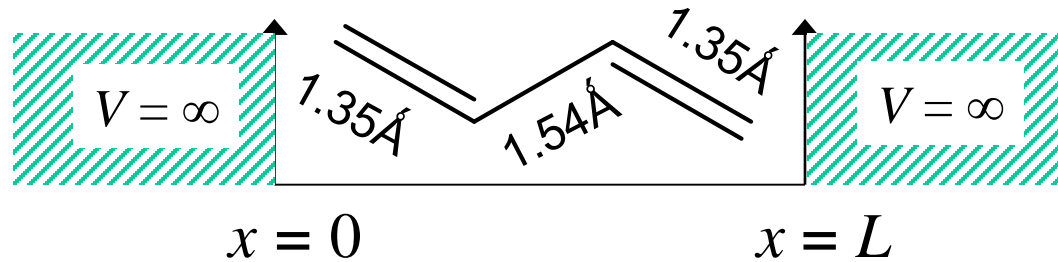
The one-dimensional particle-in-a-box is a very idealized system. However, it acts as a crude model for π -electrons in linear conjugated hydrocarbons.



For a molecule in the gas-phase (isolated), it would be difficult for the electron to escape. Thus, an electron that is ‘delocalized’ in the conjugated π -system is in a situation similar to that of a particle in a box.

Although these polyenes are not linear, we can model π -electrons with a 1-D particle in a box with the box length given by the sum of the C-C bonds in the hydrocarbon.

Consider butadiene:



— $n = 3$

●● $n = 2$

●● $n = 1$

Using our model of a 1-D particle in a box and the approximate C-C single and double bond lengths given above, we have a box of length 4.24 Å.

Butadiene has 4 π electrons, occupying 2 orbitals (Pauli exclusion principle). Thus in our model particle in a box the first 2 levels are occupied.

The energy required to excite the system to the first excited state is given by:

$$\Delta E = \frac{h^2}{8mL^2} (3^2 - 2^2)$$

Using the mass of an electron $m_e = 9.109 \times 10^{-31}$ kg and the length of our box $L = 4.24 \times 10^{-10}$ m

○ $n = 3$

●● $n = 2$

●● $n = 1$

$$\Delta E = \frac{h^2}{8mL^2} (3^2 - 2^2)$$

$$= \frac{(6.626 \times 10^{-34} \text{ J}\cdot\text{s})^2 (9 - 4)}{8(9.109 \times 10^{-31} \text{ kg})(4.24 \times 10^{-10} \text{ m})^2} = 1.676 \times 10^{-18} \text{ J}$$

Experimentally, butadiene has an absorption band at 210 nm.

Using $E = \frac{hc}{\lambda}$

Our particle in a box model gives 118 nm.

Our result is not great, but we have assumed the end of our box corresponds to the position of the terminal carbon atoms. However, one would expect that the electron should be able to go beyond the position of the end nuclei.

If we use a slightly longer distance to account for this, we will actually get a result that is in better agreement with experiment.

