The Particle in a Box

Overview

The Schrödinger wave equation, $\hat{H}\Psi = E\Psi$, lies at the heart of the quantum mechanical description of atoms. $\hat{H}$ represents an operator (called the Hamiltonian) that "extracts" the total energy $E$ (the sum of the potential and kinetic energies) from the wave function $\Psi$. The wave function $\Psi$ depends on the $x$, $y$, and $z$ coordinates of the electron's position in space.

Note that the Schrödinger equation requires that when $\Psi$ is operated on by $\hat{H}$, the result is $\Psi$ multiplied by a constant, $E$, which represents the total energy of the particular state described by a given $\Psi$. As we will see, there are many possible solutions to the Schrödinger equation for a given system. For example, for the hydrogen atom there are many functions that satisfy the Schrödinger equation, each one corresponding to a particular energy for hydrogen's electron. Each of these specific wave functions for the hydrogen atom is called an orbital. In the case of hydrogen we denote these orbitals as "1s", "2s", "2p", etc. In this case, solving the Schrödinger equation using the wave function $\Psi$ that describes each of these orbitals in hydrogen would yield the relative energies of an electron in such orbitals. This information could then be used to calculate values requiring these energies, such as predicting the spectrum of the atom.

Although the detailed solution of the Schrödinger equation for the hydrogen atom is not appropriate to the level of this course, we will illustrate some of the properties of wave mechanics and wave functions by using the wave equation to describe a very simple, hypothetical system commonly called "the particle in a box," a situation where a particle is trapped in a one-dimensional box that has infinitely high "sides." It is important to recognize that this situation is not an accurate physical model for the hydrogen atom. That is, the hydrogen atom is really not much like this particle in a box. The reasons for treating the particle in a box are that (1) it illustrates the mathematics of wave mechanics, (2) it gives an indication of the characteristics of wave functions, and (3) it shows how energy quantization arises. Thus this treatment of a particle in a box illustrates the "flavor" of the wave mechanical description of the hydrogen atom, but it should not be taken to be an accurate representation of the hydrogen atom itself.
Finally, please note that while this discussion utilizes calculus, the logic and conclusions of the derivations presented herein may be understood without knowledge of the methods used to solve calculus problems. Students will be responsible for the concepts and conclusions of this material, and the application of the derived equations (see the sample problem at the end), but will not be held responsible for their derivation. These are presented only as an illustration of the practice of solving problems in quantum mechanics.

The Particle in a Box as a Model

Consider a particle with mass $m$ that is free to move back and forth along one dimension (we arbitrarily choose $x$) between the values $x = 0$ and $x = L$ (that is, we are considering a one-dimensional "box" of size $L$ meters). We will assume that the potential energy $V(x)$ of the particle is zero at all points along its path, except at the end points $x = 0$ and $x = L$, where $V(x)$ is infinitely large. In effect, we have a repulsive barrier of infinite strength at each end of the box. Thus the particle is trapped in a one-dimensional box with impenetrable walls (see Fig. 1).

As we mentioned before, the Schrödinger equation contains the energy operator $\hat{H}$. In this case, since the potential energy is zero inside the box, the only energy possible is the kinetic energy of the particle as it moves back and forth along the $x$ axis. The operator for this kinetic energy is

$$-\frac{\hbar^2}{2m} \frac{d^2}{dx^2}$$

where $\hbar$ is Planck's constant $\hbar$ divided by $2\pi$, $m$ is the mass of the particle, and $d^2/dx^2$ is the second derivative with respect to $x$. The form of this operator comes from the description of
waves in classical physics. Inserting this operator into the Schrödinger equation \( \hat{H}\psi = E\psi \) gives

\[
-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} = E\psi
\]

where \( \psi \) is a function of \( x \) (\( \psi(x) \)). We can rearrange this equation to give

\[
\frac{d^2\psi}{dx^2} = -\frac{2mE}{\hbar^2}\psi
\]

Our goal is to find specific functions \( \psi(x) \) that satisfy this equation. Notice that the solutions to this equation are functions such that \( \frac{d^2\psi}{dx^2} = (\text{constant})\psi \). That is, each solution must be a function whose second derivative has the same form as the original function. One function that behaves this way is the sine function. For example, consider the function \( A \sin(kx) \), where \( A \) and \( k \) are constants. We will now take the second derivative of this function with respect to \( x \):

\[
\frac{d^2}{dx^2} (A \sin kx) = A \frac{d}{dx} \left( \frac{d}{dx} \sin kx \right) = A \frac{d}{dx} (k \cos kx)
\]

\[
= A(k \frac{d}{dx} \cos kx) = A(k(-k \sin kx))
\]

\[
= -Ak^2 \sin kx = -Ak^2 \sin kx
\]

Thus we have shown that

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

This is just the type of function that will satisfy the Schrödinger equation for the particle in a box. In fact, when we compare the general form of the Schrödinger equation

\[
\frac{d^2\psi}{dx^2} = -\frac{2mE}{\hbar^2}\psi
\]

with

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

we see that

\[
-k^2 = -\frac{2mE}{\hbar^2}
\]

which can be rearranged to give an expression for energy
\[ E = \frac{\hbar^2 k^2}{2m} \]

What does this equation mean? We have simply specified that \( A \) and \( k \) are constants. What values can these constants have? Note that if they could assume any values, this equation would lead to an infinite number of possible energies—that is, a continuous distribution of energy levels. However, this is not correct. For reasons we will discuss presently, we find that only certain energies are allowed. That is, this system is quantized. In fact, the ability of wave mechanics to account for the observed (but initially unexpected) quantization of energy in nature is one of the most important factors in convincing us that it may be a correct description of the properties of matter.

Quantization enters the wave mechanical description of the particle in a box via the boundary conditions. Boundary conditions arise from the physical requirements of natural systems. That is, we must insist that our descriptions of natural systems make physical sense. For example, assume that in describing an aqueous solution containing an acid, we arrive at the expression \([H^+]^2 = 4.0 \times 10^{-8} \text{ M}^2\). The solutions to this expression are

\[
[H^+] = 2.0 \times 10^{-4} \text{ M} \quad \text{and} \quad [H^+] = -2.0 \times 10^{-4} \text{ M}
\]

In doing such a problem, we automatically reject the second possibility because there is no physical meaning for a negative concentration. What we have done here is apply a type of boundary condition to this situation.

The boundary conditions for the particle in a box enforce the following facts:

1. The particle cannot be outside the box—it is bound inside the box.
2. In a given state the total probability of finding the particle in the box must be 1 (or 100%).
3. The wave function must be continuous.

We have seen that the function \( \Psi = A \sin(kx) \) satisfies the Schrödinger equation \( \hat{H}\Psi = E\Psi \). We will now define the constants \( k \) and \( A \) so that this function also satisfies the boundary conditions based on the three constraints listed above. Because the particle must stay inside the box and because the wave function must be continuous, the value of \( \Psi(x) \) must be zero at each wall. That is,

\[
\Psi(0) = 0 \quad \text{and} \quad \Psi(L) = 0
\]
Recall that the sine function is zero at angles of $0^\circ$, $180^\circ$ ($\pi$ radians), $360^\circ$ ($2\pi$ radians), and so on. Thus the function $A \sin kx$ is automatically zero when $x = 0$.

The requirement that the wave function must also be zero at the other wall, which can be stated as $\Psi(L) = A \sin (kL) = 0$, means that $k$ is limited to the values of $n\pi/L$, where $n$ is an integer ($1, 2, 3, \ldots$). That is,

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

then

$$\Psi(L) = A \sin \left( \frac{n\pi}{L} L \right) = A \sin(n\pi) = 0$$

To assign the value of the constant $A$, we need to introduce a new idea. In the application of wave mechanics to the description of matter, scientists have learned to associate the square of the wave function ($\Psi^2$) with probability. As we will discuss in more detail below, this means that the square of the wave function evaluated at a given point gives the relative probability of finding a particle near that point. In fact, the three dimensional pictures of orbitals (such as 1s, 2s, 2p, etc.) that we are familiar with for atoms comes from plotting the regions in space where the values of $\Psi^2$ are greater than 0.9 (or 90%). This concept is relevant to the boundary conditions for the particle in a box because the total probability in a given state must be 1 (or 100%). To be more precise, the probability of finding the particle on a segment of the $x$ axis of length $dx$ surrounding point $x$ is $\Psi^2(x) \, dx$. Because there is one particle in the box the sum of all of these probabilities along the $x$ axis from $x = 0$ to $x = L$ must be 1. We sum these probabilities over the length of the box (from $x = 0$ to $x = L$) by integration from $x = 0$ to $x = L$:

$$\text{Total probability of finding the particle in the box} = \int_0^L \Psi^2(x) \, dx = 1$$

Substituting $\Psi(x) = A \sin \left[ (n\pi/L)x \right]$, we have

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

or

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

The value of the integral is $L/2$, which means that
\[ \frac{L}{2} = \frac{1}{A^2} \quad \text{and} \quad A = \sqrt{\frac{2}{L}} \]

Now that we know the allowed values of \( k \) and \( A \), we can specify the wave function for the particle in a one-dimensional box as

\[ \Psi(x) = \frac{2}{\sqrt{L}} \sin \left( \frac{n\pi}{L} x \right) \]

We can also substitute the value of \( k \) into the expression for energy:

\[ E = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2 (n\pi / L)^2}{2m} \]

Substituting \( \hbar = \hbar / 2\pi \) gives

\[ E = \frac{n^2 \hbar^2}{8mL^2} \quad \text{where} \quad n = 1, 2, 3, 4, \ldots \]

Note that this analysis leads to a series of solutions to the Schrödinger equation, where each function corresponds to a given energy state:

<table>
<thead>
<tr>
<th>( n )</th>
<th>Function</th>
<th>Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>( \Psi_1 = \frac{2}{\sqrt{L}} \sin \left( \frac{\pi}{L} x \right) )</td>
<td>( E_1 = \frac{\hbar^2}{8mL^2} )</td>
</tr>
<tr>
<td>2</td>
<td>( \Psi_2 = \frac{2}{\sqrt{L}} \sin \left( \frac{2\pi}{L} x \right) )</td>
<td>( E_2 = \frac{4\hbar^2}{8mL^2} = \frac{\hbar^2}{2mL^2} )</td>
</tr>
<tr>
<td>3</td>
<td>( \Psi_3 = \frac{2}{\sqrt{L}} \sin \left( \frac{3\pi}{L} x \right) )</td>
<td>( E_3 = \frac{9\hbar^2}{8mL^2} )</td>
</tr>
<tr>
<td>4</td>
<td>( \Psi_4 = \frac{2}{\sqrt{L}} \sin \left( \frac{4\pi}{L} x \right) )</td>
<td>( E_4 = \frac{16\hbar^2}{8mL^2} = \frac{2\hbar^2}{mL^2} )</td>
</tr>
<tr>
<td>( \vdots )</td>
<td>( \vdots )</td>
<td>( \vdots )</td>
</tr>
</tbody>
</table>

Notice something very important about these results. The application of the boundary conditions has led to a series of quantized energy levels. That is, only certain energies are allowed for the particle bound in the box. This result fits very nicely with the experimental evidence, such as the hydrogen emission spectrum, that nature does not allow continuous energy
levels for bound systems, as classical physics had led us to expect. Note that the energies are quantized, because the boundary conditions require that \( n \) assume only integer values. Consequently, we call \( n \) the quantum number for this system.

We can diagram the solutions to the particle-in-a-box problem conveniently by showing a plot of the wave function that corresponds to each energy level. The energy level, wave function, and probability distribution are shown in Fig. 2 for the first three levels.

![Figure 2](image)

(a) The first three energy levels for a particle in a one-dimensional box in increments of \( \hbar^2/(8mL^2) \).
(b) The wave functions for the first three levels plotted as a function of \( x \). Note that the maximum value is \( \sqrt{2}/L \) in each case.
(c) The square of the wave functions for the first three levels plotted as a function of \( x \). Note that the maximum value is \( 2/L \) in each case.

Note that each wave function goes to zero at the edges of the box, as required by the boundary conditions. Another way to say this is that the standing waves that represent the particle must have wavelengths such that an integral number of half-wavelengths exactly equals the size of the box. Waves with any other wavelengths could not exist because they would destructively interfere over time. Also, note from Figure 2 that the probability distribution is significantly different for the three levels. For \( n = 1 \) (the lowest energy or ground state) the particle is most likely to be found near the center of the box. In contrast, for \( n = 2 \) the particle has zero probability of being found in the center of the box. This zero point is called a node. Notice that the number of nodes increases with \( n \).

Another interesting characteristic of the particle in a box is that the particle cannot have zero energy (that is, \( n \) cannot equal zero). For example, if \( n \) were equal to zero, \( \Psi_0 \) would be zero everywhere in the box (\( \sin 0 = 0 \)). This would mean that \( \Psi_0^2 \) would also be zero. In this
case there could be no particle in the box, which contradicts the boundary conditions. This fact that the particle must have a nonzero energy in its ground state is a characteristic of all particles with quantized energies. In addition, for the particle in a box, a value of zero for the energy would mean that the particle was sitting still (zero kinetic energy). This condition would violate the uncertainty principle, because we would simultaneously know the exact values of the momentum (zero) and the position of the particle. For similar reasons all quantized particles must possess a minimum energy, often called the zero-point energy.

While the particle in the box is a simple one-dimensional model, the same sort of analysis presented here is applied to an electron in a spherical potential well around a positively charged nucleus when solving for the energies and wave functions of the hydrogen atom.

Although the particle in the box is not a good model for the atom, it does approximate the energy levels found in simple covalent bonds (where a electron shared between two nuclei is very similar to one trapped in a "box") and it helps to explain resonance stability. Both of these applications of the particle in the box will be explored later in class.

**Sample Problem**

Assume that an electron is confined to a one-dimensional box 1.50 nm in length. Calculate the lowest three energy levels for this electron, and calculate the wavelength of light necessary to promote the electron from the ground state to the first excited state.

**Solution**

To solve this problem, we need to substitute appropriate values into the general expression for energy:

\[
E = \frac{n^2 \hbar^2}{8mL^2}
\]

The mass of an electron \(m\) is \(9.11 \times 10^{-31}\) kg; the dimension of the box \(L\) is 1.50 nm, or \(1.50 \times 10^{-9}\) m; and the value of Planck's constant is \(6.626 \times 10^{-34}\) J s.

For \(n = 1\) we get,

\[
E_1 = \frac{(1)^2 (6.626 \times 10^{-34} \text{ J} \cdot \text{s})^2}{(8)(9.11 \times 10^{-31} \text{ kg})(1.50 \times 10^{-9} \text{ m})^2} = 2.68 \times 10^{-20}\text{ J}
\]

Similarly, for \(n = 2\) we get

\[
E_2 = 1.07 \times 10^{-19}\text{ J}
\]

And for \(n = 3\) we get
\[ E_3 = 2.41 \times 10^{-19} \text{ J} \]

Note that since
\[ E_n = n^2 \frac{h^2}{8mL^2} = n^2 E_1 \]

then \[ E_2 = (2)^2 \frac{h^2}{8mL^2} = 4E_1 \quad \text{and} \quad E_3 = 9E_1 \]

To calculate the wavelength of light necessary to excite the electron from level 1 to level 2 (the first excited state), we first need to obtain the energy difference between the two levels:

\[ \Delta E = E_2 - E_1 = (n_2^2 - n_1^2) \frac{h^2}{8mL^2} \]
\[ = (3)(2.68 \times 10^{-20} \text{ J}) = 8.04 \times 10^{-20} \text{ J} \]

Then we find the wavelength using Plank's equation
\[ \Delta E = \frac{hc}{\lambda} \]

Inserting the appropriate values gives
\[ \lambda = \frac{hc}{\Delta E} = \frac{(6.626 \times 10^{-34} \text{ J} \cdot \text{s})(2.9979 \times 10^8 \text{ m/s})}{8.04 \times 10^{-20} \text{ J}} \]
\[ = 2.47 \times 10^{-6} \text{ m} = 2470 \text{ nm} \]