Learning Objectives

- To demonstrate how the particle in 1-D box problem can extend to a particle in a 3D box
- Introduction to nodal surfaces (e.g., nodal planes)

The quantum particle in the 1D box problem can be expanded to consider a particle within a higher dimensions as demonstrated elsewhere for a quantum particle in a 2D box. Here we continue the expansion into a particle trapped in a 3D box with three lengths \(L_x\), \(L_y\), and \(L_z\). As with the other systems, there is NO FORCE (i.e., no potential) acting on the particles inside the box (Figure \(\PageIndex{1}\)).

![3D box diagram](image)

The potential for the particle inside the box

\[
V(\vec{r}) = 0
\]

- \(0 \leq x \leq L_x\)
- \(0 \leq y \leq L_y\)
- \(0 \leq z \leq L_z\)
- \(L_x < x < 0\)
- \(L_y < y < 0\)
- \(L_z < z < 0\)

\(\vec{r}\) is the vector with all three components along the three axes of the 3-D box: \(\vec{r} = L_x\hat{x} + L_y\hat{y} + L_z\hat{z}\). When the potential energy is infinite, then the wavefunction equals zero. When the potential energy is zero, then the wavefunction obeys the Time-Independent Schrödinger Equation

\[
-\frac{\hbar^2}{2m}\nabla^2\psi(r) + V(r)\psi(r) = E\psi(r) \label{3.9.1}
\]

Since we are dealing with a 3-dimensional figure, we need to add the 3 different axes into the Schrödinger equation:
\[ -\frac{\hbar^2}{2m} \left( \frac{d^2\psi(r)}{dx^2} + \frac{d^2\psi(r)}{dy^2} + \frac{d^2\psi(r)}{dz^2} \right) = E \psi(r) \] 

The easiest way in solving this partial differential equation is by having the wavefunction equal to a product of individual function for each independent variable (e.g., the separation of variables technique):

\[ \psi(x,y,z) = X(x)Y(y)Z(z) \]

Now each function has its own variable:

- \(X(x)\) is a function of variable \(x\) only
- \(Y(y)\) is a function of variable \(y\) only
- \(Z(z)\) is a function of variable \(z\) only

Now substitute Equation \(\ref{3.9.3}\) into Equation \(\ref{3.9.2}\) and divide it by the \(xyz\) product:

\[ \frac{d^2\psi}{dx^2} = YZ \frac{d^2X}{dx^2} \Rightarrow \frac{1}{X} \frac{d^2X}{dx^2} \]

\[ \frac{d^2\psi}{dy^2} = XZ \frac{d^2Y}{dy^2} \Rightarrow \frac{1}{Y} \frac{d^2Y}{dy^2} \]

\[ \frac{d^2\psi}{dz^2} = XY \frac{d^2Z}{dz^2} \Rightarrow \frac{1}{Z} \frac{d^2Z}{dz^2} \]

\[ \left( -\frac{\hbar^2}{2mX} \frac{d^2X}{dx^2} \right) + \left( -\frac{\hbar^2}{2mY} \frac{d^2Y}{dy^2} \right) + \left( -\frac{\hbar^2}{2mZ} \frac{d^2Z}{dz^2} \right) = E \]

\(E\) is an energy constant, and is the sum of \(x\), \(y\), and \(z\). For this to work, each term must equal its own constant. For example,

\[ \frac{d^2X}{dx^2} + \frac{2m}{\hbar^2} \varepsilon_x X = 0 \]

\(\varepsilon\) is an energy constant, and is the sum of \(x\), \(y\), and \(z\). For this to work, each term must equal its own constant. For example,

\[ \frac{d^2X}{dx^2} + \frac{2m}{\hbar^2} \varepsilon_x X = 0 \]

Now separate each term in Equation \(\ref{3.9.4}\) to equal zero:

\[ \frac{d^2X}{dx^2} + \frac{2m}{\hbar^2} \varepsilon_x X = 0 \]

\[ \frac{d^2Y}{dy^2} + \frac{2m}{\hbar^2} \varepsilon_y Y = 0 \]

\[ \frac{d^2Z}{dz^2} + \frac{2m}{\hbar^2} \varepsilon_z Z = 0 \]

Now we can add all the energies together to get the total energy:

\[ \varepsilon_x + \varepsilon_y + \varepsilon_z = E \]

Do these equations look familiar? They should because we have now reduced the 3D box into three particle in a 1D box problems!

\[ \frac{d^2X}{dx^2} + \frac{2m}{\hbar^2} \varepsilon_x X \approx \frac{d^2\psi}{dx^2} = -\frac{4\pi^2}{\lambda^2} \psi \]
Now the equations are very similar to a 1-D box and the boundary conditions are identical, i.e.,
\[n = 1, 2, \ldots, \infty\]

Use the normalization wavefunction equation for each variable:
\[
\psi(x) =
\begin{cases}
\sqrt{\frac{2}{L_x}} \sin\left(\frac{n \pi x}{L_x}\right) & \text{if } 0 \leq x \leq L \\
0 & \text{if } L < x < 0
\end{cases}
\]

Normalization wavefunction equation for each variable (that substitute into Equation \ref{3.9.3}):
\[
X(x) = \sqrt{\frac{2}{L_x}} \sin \left(\frac{n_x \pi x}{L_x}\right) \tag{3.9.8a}
\]
\[
Y(y) = \sqrt{\frac{2}{L_y}} \sin \left(\frac{n_y \pi y}{L_y}\right) \tag{3.9.8b}
\]
\[
Z(z) = \sqrt{\frac{2}{L_z}} \sin \left(\frac{n_z \pi z}{L_z}\right) \tag{3.9.8c}
\]

The limits of the three quantum numbers
- \(n_x = 1, 2, 3, \ldots, \infty\)
- \(n_y = 1, 2, 3, \ldots, \infty\)
- \(n_z = 1, 2, 3, \ldots, \infty\)

For each constant use the de Broglie Energy equation:
\[
\varepsilon_x = \frac{n_x^2 \hbar^2}{8mL_x^2} \tag{3.9.9}
\]

with \(n_x = 1, 2, 3, \ldots, \infty\)

Do the same for variables \(n_y\) and \(n_z\). Combine Equation \ref{3.9.3} with Equations \ref{3.9.8a}-\ref{3.9.8c} to find the wavefunctions inside a 3D box.
\[
\psi(r) = \sqrt{\frac{8}{V}} \sin \left(\frac{n_x \pi x}{L_x}\right) \sin \left(\frac{n_y \pi y}{L_y}\right) \sin \left(\frac{n_z \pi z}{L_z}\right) \tag{3D wave}
\]

with
\[
V = \underbrace{L_x \times L_y \times L_z}_{\text{volume of box}}
\]

To find the Total Energy, add Equation \ref{3.9.9} and Equation \ref{3.9.6}.
\[
E_{n_x,n_y,n_z} = \frac{\hbar^2}{8m} \left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2}\right) \tag{3.9.10}
\]
Notice the similarity between the energies a particle in a 3D box (Equation \ref{3.9.10}) and a 1D box.

**Degeneracy in a 3D Cube**

The energy of the particle in a 3-D cube (i.e., \(L_x=L_y=L\)) in the ground state is given by Equation \ref{3.9.10} with \((n_x=1), (n_y=1), and (n_z=1)\). This energy \(\langle E\{1,1,1\}\rangle\) is hence

\[
\langle E\{1,1,1\}\rangle = \frac{3 \hbar^2}{8mL^2}
\]

The ground state has only one wavefunction and no other state has this specific energy; the ground state and the energy level are said to be **non-degenerate**. However, in the 3-D cubical box potential the energy of a state depends upon the sum of the squares of the quantum numbers (Equation \ref{3D wave}). The particle having a particular value of energy in the excited state MAY have several different stationary states or wavefunctions. If so, these states and energy eigenvalues are said to be **degenerate**.

For the first excited state, three combinations of the quantum numbers \((n_x, n_y, n_z)\) are \((2,1,1), (1,2,1), (1,1,2)\). The sum of squares of the quantum numbers in each combination is same (equal to 6). Each wavefunction has same energy:

\[
\langle E\{2,1,1\}\rangle = \langle E\{1,2,1\}\rangle = \langle E\{1,1,2\}\rangle = \frac{6 \hbar^2}{8mL^2}
\]

Corresponding to these combinations three different wavefunctions and **three** different states are possible. Hence, the first excited state is said to be three-fold or triply degenerate. The number of independent wavefunctions for the stationary states of an energy level is called as the **degree of degeneracy** of the energy level. The value of energy levels with the corresponding combinations and sum of squares of the quantum numbers

\[
\langle n^2 \rangle = \langle n_x^2+n_y^2+n_z^2\rangle
\]

as well as the degree of degeneracy are depicted in Table \ref{Degeneracy properties of the particle in a 3-D cube with \(L_x=L_y=L\)\\(\text{Table} \ref{Degeneracy properties of the particle in a 3-D cube with \(L_x=L_y=L\)\).}}.

**Table** \ref{Degeneracy properties of the particle in a 3-D cube with \(L_x=L_y=L\)\\(\text{Table} \ref{Degeneracy properties of the particle in a 3-D cube with \(L_x=L_y=L\)\).}}: Degeneracy properties of the particle in a 3-D cube with \(L_x=L_y=L\).

<table>
<thead>
<tr>
<th>((n_x^2+n_y^2+n_z^2))</th>
<th>Combinations of Degeneracy</th>
<th>Total Energy (\langle E{n_x,n_y,n_z}\rangle)</th>
<th>Degree of Degeneracy</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>((1,1,1))</td>
<td>(\frac{3 \hbar^2}{8mL^2})</td>
<td>1</td>
</tr>
<tr>
<td>6</td>
<td>((2,1,1)), ((1,2,1)),((1,1,2))</td>
<td>(\frac{6 \hbar^2}{8mL^2})</td>
<td>3</td>
</tr>
<tr>
<td>9</td>
<td>((2,2,1)), ((1,2,2)),((2,1,2))</td>
<td>(\frac{9 \hbar^2}{8mL^2})</td>
<td>3</td>
</tr>
<tr>
<td>11</td>
<td>((3,1,1)), ((1,3,1)),((1,1,3))</td>
<td>(\frac{11 \hbar^2}{8mL^2})</td>
<td>3</td>
</tr>
<tr>
<td>12</td>
<td>((2,2,2))</td>
<td>(\frac{12 \hbar^2}{8mL^2})</td>
<td>1</td>
</tr>
</tbody>
</table>
Example \(\PageIndex{1}\): Accidental Degeneracies

When is there degeneracy in a 3-D box when none of the sides are of equal length (i.e., \((L_x \neq L_y \neq L_z)\))? 

Solution 

From simple inspection of Equation \ref{3.9.10} or Table \(\PageIndex{1}\), it is clear that degeneracy originates from different combinations of \((n_x^2/L_x^2)\), \((n_y^2/L_y^2)\), and \((n_z^2/L_z^2)\) that give the same value. These will occur at common multiples of at least two of these quantities (the Least Common Multiple is one example). For example:

if

\[
\frac{n_x^2}{L_x^2} = \frac{n_y^2}{L_y^2} \nonumber
\]

there will be a degeneracy. Also degeneracies will exist if

\[
\frac{n_y^2}{L_y^2} = \frac{n_z^2}{L_z^2} \nonumber
\]

or if

\[
\frac{n_x^2}{L_x^2} = \frac{n_z^2}{L_z^2} \nonumber
\]

and especially if

\[
\frac{n_x^2}{L_x^2} = \frac{n_y^2}{L_y^2} = \frac{n_z^2}{L_z^2} \nonumber.
\]

There are two general kinds of degeneracies in quantum mechanics: degeneracies due to a symmetry (i.e., \((L_x=L_y)\)) and accidental degeneracies like those above.
Exercise (PageIndex{1})

The 6\textsuperscript{th} energy level of a particle in a 3D Cube box is 6-fold degenerate.

a. What is the energy of the 7\textsuperscript{th} energy level?

b. What is the degeneracy of the 7\textsuperscript{th} energy level?

Answer a

\[ \frac{17 h^2}{8mL^2} \]

Answer b

three-fold (i.e., there are three wavefunctions that share the same energy.

References