# 3.9: A Particle in a Three-Dimensional Box

> 🧠 **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 3.9.1 ).
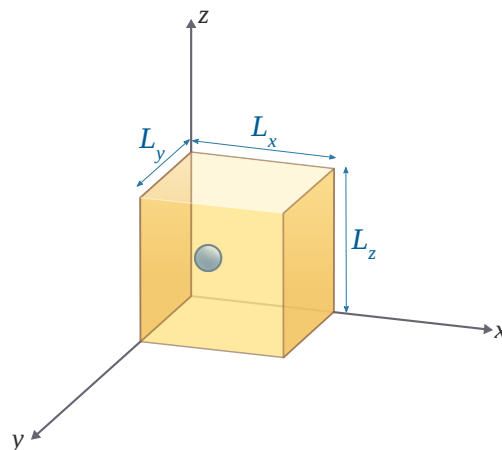


Figure 3.9.1 : A particle in 3D box with three lengths $L_x$, $L_y$, and $L_z$. (CC BY-NC 4.0; Ümit Kaya via LibreTexts)

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

$$-\frac{\hbar^2}{2m}\nabla^2\psi(r) + V(r)\psi(r) = E\psi(r) \tag{3.9.1}$$

Since we are dealing with a 3-dimensional figure, we need to add the 3 different axes into the Schrondinger equation:

$$-\frac{\hbar^2}{2m}\left(\frac{d^2\psi(r)}{dx^2} + \frac{d^2\psi(r)}{dy^2} + \frac{d^2\psi(r)}{dz^2}\right) = E\psi(r) \tag{3.9.2}$$

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):

$$\psi(x, y, z) = X(x)Y(y)Z(z) \tag{3.9.3}$$

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 $3.9.3$ into Equation $3.9.2$ and divide it by the $xyz$ product:

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

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

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

$$\left(-\frac{\hbar^2}{2mX}\frac{d^2X}{dx^2}\right) + \left(-\frac{\hbar^2}{2mY}\frac{d^2Y}{dy^2}\right) + \left(-\frac{\hbar^2}{2mZ}\frac{d^2Z}{dz^2}\right) = E \tag{3.9.4}$$

$E$ 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,

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

Now separate each term in Equation $3.9.4$ 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:

$$\varepsilon_x + \varepsilon_y + \varepsilon_z = E \tag{3.9.5}$$

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

$$\frac{d^2X}{dx^2} + \frac{2m}{\hbar^2}E_x X = 0 \approx \frac{d^2\psi}{dx^2} = -\frac{4\pi^2}{\lambda^2}\psi \tag{3.9.6}$$

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:

$$\psi(x) = \begin{cases} \sqrt{\dfrac{2}{L_x}}\sin\dfrac{n\pi x}{L_x} & \text{if } 0 \leq x \leq L \\ 0 & \text{if } L < x < 0 \end{cases}$$

Normalization wavefunction equation for each variable (that substitute into Equation $3.9.3$):

$$X(x) = \sqrt{\frac{2}{L_x}}\sin\left(\frac{n_x\pi x}{L_x}\right) \tag{3.9.7}$$

$$Y(y) = \sqrt{\frac{2}{L_y}}\sin\left(\frac{n_y\pi y}{L_y}\right) \tag{3.9.8}$$

$$Z(z) = \sqrt{\frac{2}{L_z}}\sin\left(\frac{n_z\pi z}{L_z}\right) \tag{3.9.9}$$

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:

$$\varepsilon_x = \frac{n_x^2 h^2}{8 m L_x^2} \tag{3.9.10}$$

with $n_x = 1 \ldots \infty$

Do the same for variables $n_y$ and $n_z$. Combine Equation 3.9.3 with Equations 3.9.7-3.9.9 to find the wavefunctions inside a 3D box.

$$\psi(r) = \sqrt{\frac{8}{V}} \sin\left(\frac{n_x \pi x}{L_x}\right) \sin\left(\frac{n_y \pi y}{L_y}\right) \sin\left(\frac{n_z \pi z}{L_z}\right) \tag{3.9.11}$$

with

$$V = \underbrace{L_x \times L_y \times L_z}_{\text{volume of box}}$$

To find the Total Energy, add Equation 3.9.10 and Equation 3.9.5.

$$E_{n_x, n_y, n_z} = \frac{h^2}{8m}\left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2}\right) \tag{3.9.12}$$

Notice the similarity between the energies a particle in a 3D box (Equation 3.9.12) 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 3.9.12 with $n_x = 1$, $n_y = 1$, and $n_z = 1$. This energy ($E_{1,1,1}$) is hence

$$E_{1,1,1} = \frac{3h^2}{8mL^2}$$

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 3.9.11). The particle having a particular value of energy in the excited state *MAY* has 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:

$$E_{2,1,1} = E_{1,2,1} = E_{1,1,2} = \frac{6h^2}{8mL^2}$$

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

$$n^2 = n_x^2 + n_y^2 + n_z^2$$

as well as the degree of degeneracy are depicted in Table 3.9.1 .

Table 3.9.1 : Degeneracy properties of the particle in a 3-D cube with $L_x = L_y = L$ .

| $n_x^2 + n_y^2 + n_z^2$ | Combinations of Degeneracy $(n_x, n_y, n_z)$ | | Total Energy $(E_{n_x, n_y, n_z})$ | Degree of Degeneracy |
|---|---|---|---|---|
| | | | | |

| $n_x^2 + n_y^2 + n_z^2$ | Combinations of Degeneracy $(n_x, n_y, n_z)$ | | | | | | Total Energy $(E_{n_x,n_y,n_z})$ | Degree of Degeneracy |
|---|---|---|---|---|---|---|---|---|
| 3 | (1,1,1) | | | | | | $\dfrac{3h^2}{8mL^2}$ | 1 |
| 6 | (2,1,1) | (1,2,1) | (1,1,2) | | | | $\dfrac{6h^2}{8mL^2}$ | 3 |
| 9 | (2,2,1) | (1,2,2) | (2,1,2) | | | | $\dfrac{9h^2}{8mL^2}$ | 3 |
| 11 | (3,1,1) | (1,3,1) | (1,1,3) | | | | $\dfrac{11h^2}{8mL^2}$ | 3 |
| 12 | (2,2,2) | | | | | | $\dfrac{12h^2}{8mL^2}$ | 1 |
| 14 | (3,2,1) | (3,1,2) | (2,3,1) | (2,1,3) | (1,3,2) | (1,2,3) | $\dfrac{14h^2}{8mL^2}$ | 6 |
| 17 | (2,2,3) | (3,2,2) | (2,3,2) | | | | $\dfrac{17h^2}{8mL^2}$ | 3 |
| 18 | (1,1,4) | (1,4,1) | (4,1,1) | | | | $\dfrac{18h^2}{8mL^2}$ | 3 |
| 19 | (1,3,3) | (3,1,3) | (3,3,1) | | | | $\dfrac{19h^2}{8mL^2}$ | 3 |
| 21 | (1,2,4) | (1,4,2) | (2,1,4) | (2,4,1) | (4,1,2) | (4,2,1) | $\dfrac{21h^2}{8mL^2}$ | 6 |

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### ✔ Example 3.9.1 : 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 3.9.12 or Table 3.9.1 , 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

$$\frac{n_x^2}{L_x^2} = \frac{n_y^2}{L_y^2}$$

there will be a degeneracy. Also degeneracies will exist if

$$\frac{n_y^2}{L_y^2} = \frac{n_z^2}{L_z^2}$$

or if

$$\frac{n_x^2}{L_x^2} = \frac{n_z^2}{L_z^2}$$

and especially if

$$\frac{n_x^2}{L_x^2} = \frac{n_y^2}{L_y^2} = \frac{n_z^2}{L_z^2}.$$

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 3.9.1**
>
> The 6$^{th}$ energy level of a particle in a 3D Cube box is 6-fold degenerate.
>
> a. What is the energy of the 7th energy level?
> b. What is the degeneracy of the 7th energy level?
>
> **Answer a**
>
> $$\frac{17h^2}{8mL^2}$$
>
> **Answer b**
>
> three-fold (i.e., there are three wavefunctions that share the same energy.

## References

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