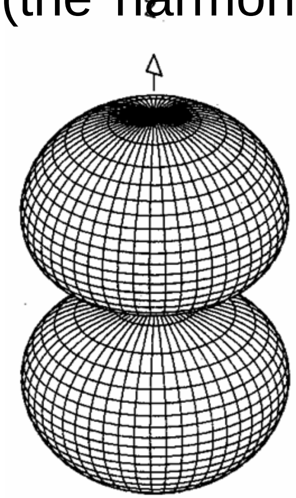
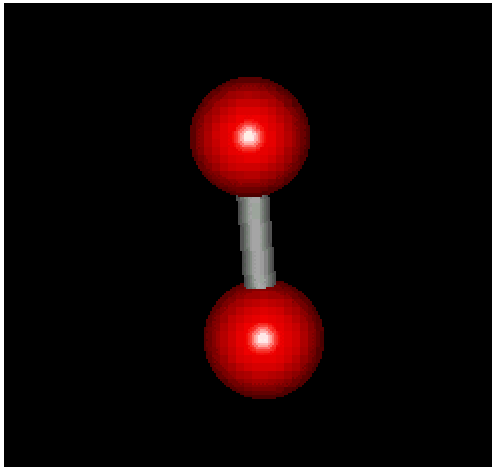
3-Dimensional and Multi-Dimensional Systems

We've looked at one-dimensional problems, or at least problems that could be reduced to 'effective' one-dimensional problems (the harmonic oscillator).

Most problems of interest occur in three-dimensional space and involve multi-dimensional spaces. For example, molecules are 3-dimensional structures.



p_z orbital of hydrogen



rotation of H_2

Before we look at those systems, we will examine some general techniques for solving multi-dimensional problems.

The Useful Theorem of Separability

The **separability theorem** can help us to solve **multi-dimensional** Schrödinger equations.

We'll first discuss two-dimensional systems, but this is easily extended to multidimensional problems.

Consider a two-dimensional system where the wave function is a function of two coordinates:

$$\psi(x, y)$$

This wave function is the solution to the Schrödinger equation:

$$\hat{H}\psi(x, y) = E_{\text{tot}}\psi(x, y) \qquad\qquad \hat{H}$$

$\hat{H}$ is the Hamiltonian and E_{tot} is the energy. We'll see shortly why we subscript this energy with 'tot' for total energy.

If (*not always possible!*) we can write the total Hamiltonian as a sum of independent terms that act on separate variables only, such as:

$$\hat{H} = \hat{H}_x + \hat{H}_y$$

the Hamiltonian is separable

where

$\hat{H}_x$ depends on or acts only on x

$\hat{H}_y$ depends on or acts only on y

then we can write the wave function $\psi(x,y)$ as a product of independent wave functions that each depend only on one of the independent variables:

$$\psi(x,y) = \psi_x(x) \cdot \psi_y(y)$$

Let's look at some examples of separable Hamiltonians and product wave functions.

Not only can we write the wave function as a product wave function,

$$\boxed{\psi(x,y)=\psi_x(x)\cdot\psi_y(y)}$$

each of these product wave functions are solutions to their own corresponding one-dimensional Schrödinger equations:

$$\boxed{\begin{array}{c}\hat{H}_x\psi_x(x)=E_x\psi_x(x)\\[2ex] \hat{H}_y\psi_y(y)=E_y\psi_y(y)\end{array}}$$

They combine to be a solution of the total Schrödinger equation:

$$\hat{H}\psi_x(x)\cdot\psi_y(y)=E_{\text{tot}}\psi_x(x)\cdot\psi_y(y)$$

where

$$E_{\text{tot}}=E_x+E_y$$

proof will not be given, but we will demonstrate it is valid.

How do we use the Separability Theorem?

If we can separate the Hamiltonian:

$$\hat{H} = \hat{H}_x + \hat{H}_y$$

then we can solve for the total wave function $\psi(x,y)$ by simply solving the one-dimensional Schrödinger equations:

$$\hat{H}_x \psi_x(x) = E_x \psi_x(x)$$

$$\hat{H}_y \psi_y(y) = E_y \psi_y(y)$$

The total wave function is the product of the independent wave functions

$$\psi(x, y) = \psi_x(x) \cdot \psi_y(y)$$

and the total energy is the sum of the individual energies!

$$E_{\text{tot}} = E_x + E_y$$

So, for separable Hamiltonians, we can simplify the two-dimensional problem into two separate one-dimensional problems.

$$\hat{H}_x \psi_x(x) = E_x \psi_x(x)$$

$$\hat{H}_y \psi_y(y) = E_y \psi_y(y)$$

Each of the wave functions ψ_x and ψ_y must satisfy the normal conditions of being well behaved, including being normalized.

Examples:

If the individual wave functions are ψ_x and ψ_y normalized, is the total product wave function also normalized?

Show that the product wave function is an eigenfunction of the total Hamiltonian with eigenvalue $E_{tot}=E_x+E_y$.

The Theorem is General to Multi-Dimensional Problems

$$\psi(q_1, q_2, q_3 ... q_n) = \psi_1(q_1) \cdot \psi_2(q_2) \cdot \psi_3(q_3) ... \psi_n(q_n)$$

$$\hat{H} = \hat{H}_{q_1} + \hat{H}_{q_2} + \hat{H}_{q_3} + ... + \hat{H}_{q_n}$$

$$E_{tot} = E_1 + E_2 + E_3 + ... + E_n$$

and to Various Combinations of Independent Variables:

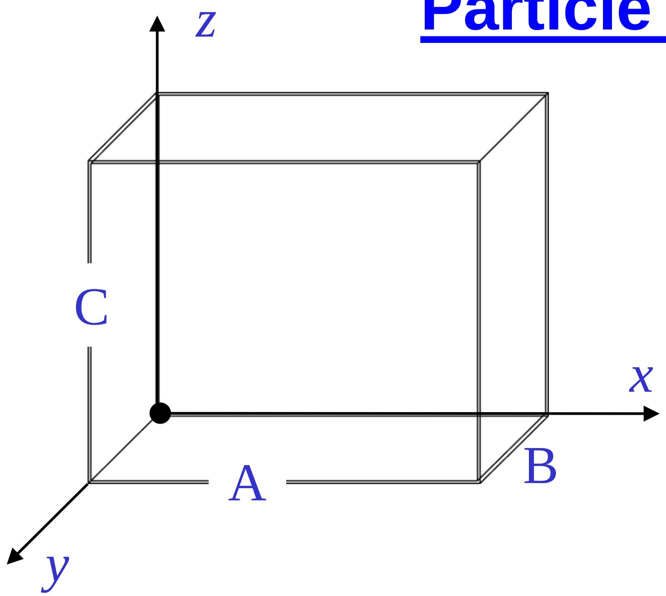
$$\hat{H} = \hat{H}_{xy} + \hat{H}_z$$

$$\psi(x, y, z) = \psi_{xy}(x, y) \cdot \psi_z(z)$$

$$E_{\text{tot}} = E_{xy} + E_z$$

The resulting Schrödinger equations are called **separable**.

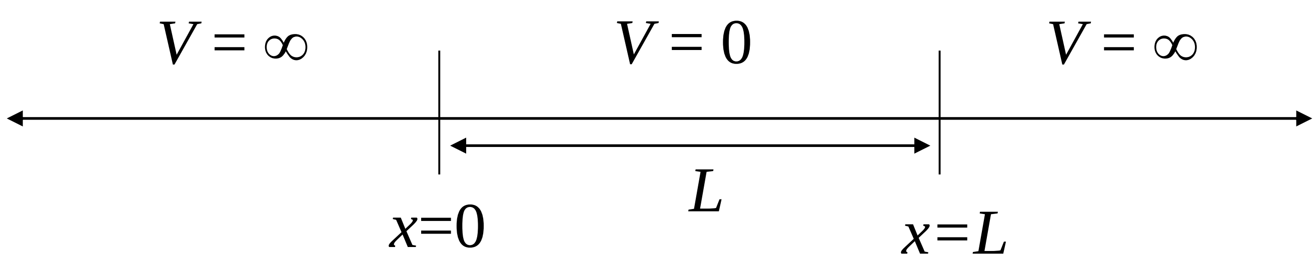
Particle in a 3-Dimensional Box



The particle in a box is easily generalized to three dimensions.

Consider a rectangular box whose dimensions are A times B times C.

Before we solve the **3-D** problem, first let's review the **1-D** particle in a box problem:



Outside the box, we required the wave function to be zero (infinite potential there), and then we solved for the wave function inside of the 'box'.

Wave Functions and Energies of the 1-D particle in a Box

inside the box

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + 0 \quad \Rightarrow \quad -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x) = E\psi(x)$$

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

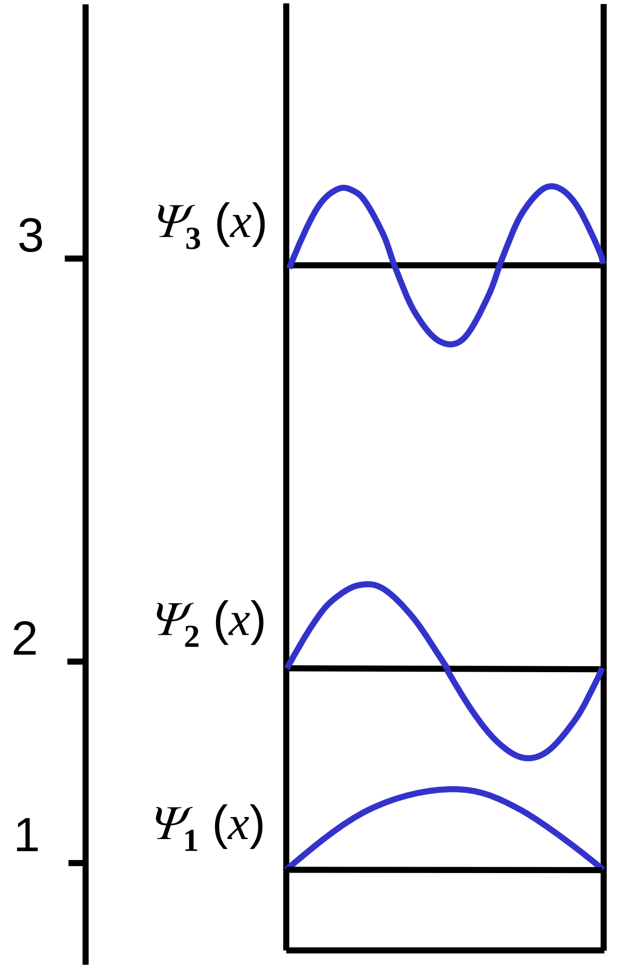
$$E = \frac{n^2 h^2}{8mL^2}$$

$$n = 1, 2, 3, \ldots.$$

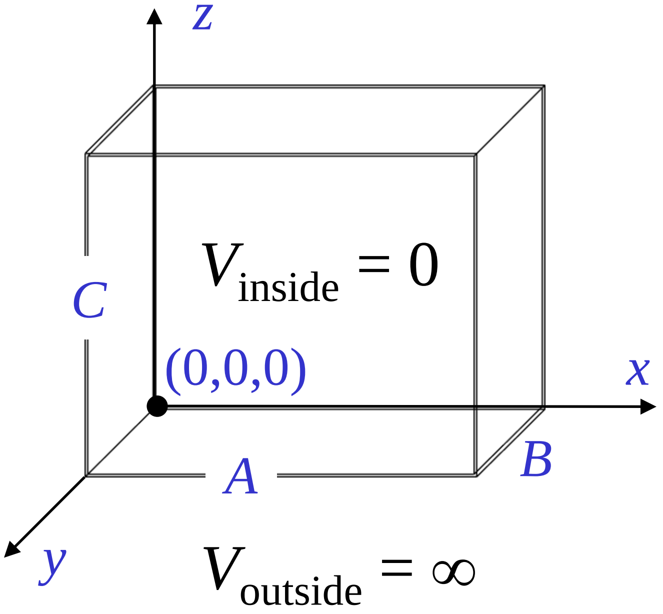
$$E_3 = \frac{9h^2}{8mL^2}$$

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

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



A Particle in a 3-Dimensional Box



Consider a rectangular box whose dimensions are ABC and whose origin is at one corner of the box as shown.

As for the 1-D box, the potential energy is $V(x,y,z) = 0$ inside the box and infinite outside of the box.

Again, we simply apply the principles and postulates we have used previously.

So we need to simply solve the Schrödinger equation for this problem.

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

Explicitly, what is the Hamiltonian in 3-dimensions?

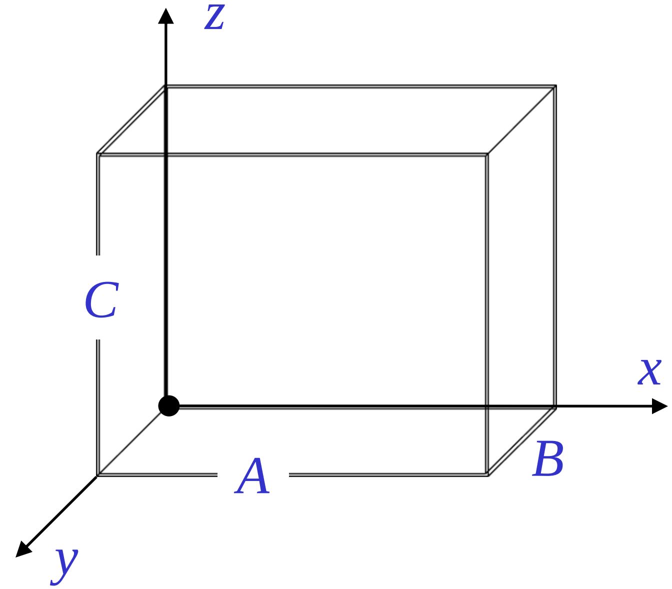
Inside the box only

$0 \le x \le A$

$0 \le y \le B$

$0 \le z \le C$

$$-\frac{\hbar^2}{2m}\nabla^2\psi(x,y,z) = E\psi(x,y,z)$$



The boundary conditions are:

$\psi(0,y,z) = 0$ for all y and z

$\psi(x,0,z) = 0$ for all x and z

$\psi(x,y,0) = 0$ for all x and y

With these boundary conditions, all we have to do is now solve this multidimensional Schrödinger equation.

Are we missing any boundary conditions?

$$\hat{H} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} - \frac{\hbar^2}{2m}\frac{\partial^2}{\partial y^2} - \frac{\hbar^2}{2m}\frac{\partial^2}{\partial z^2}$$

This can be written as:

$$\hat{H} = \hat{H}_x + \hat{H}_y + \hat{H}_z$$

where:

$$\hat{H}_x = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} \qquad \hat{H}_y = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial y^2} \qquad \hat{H}_z = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial z^2}$$

Therefore, we can use the theorem, and write our total wave function as a product of three independent wave functions:

$$\psi(x, y, z) = \psi_x(x) \cdot \psi_y(y) \cdot \psi_z(z)$$

$$= \psi_x \cdot \psi_y \cdot \psi_z$$

Now we just have to solve the individual one-dimensional Schrödinger equations.

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi_x(x) = E_x\psi_x(x) \qquad \underbrace{\psi_x(0)=0 \quad \psi_x(A)=0}_{\text{boundary conditions}}$$

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial y^2}\psi_y(y) = E_y\psi_y(y) \qquad \psi_y(0)=0 \quad \psi_y(B)=0$$

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial z^2}\psi_z(z) = E_z\psi_z(z) \qquad \psi_z(0)=0 \quad \psi_z(C)=0$$

Each of these three sets of equations and boundary conditions are identical to the one-dimensional particle-in-a-box Schrödinger equation that we have already solved with a length L.

For the original one-dimensional particle in a box of length L we had:

$$\psi_n(x) = \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{n\pi}{L}x\right) \qquad E = \frac{n^2h^2}{8mL^2} \qquad n = 1, 2, 3, \ldots.$$

So, for our 3-D problem, we have:

$$\psi_{n_x}(x) = \left(\frac{2}{A}\right)^{1/2} \sin\left(\frac{n_x\pi}{A}x\right) \qquad E_{n_x} = \frac{n_x^2h^2}{8mA^2} \qquad n_x = 1, 2, 3, \ldots.$$

$$\psi_{n_y}(y) = \left(\frac{2}{B}\right)^{1/2} \sin\left(\frac{n_y\pi}{B}y\right) \qquad E_{n_y} = \frac{n_y^2h^2}{8mB^2} \qquad n_y = 1, 2, 3, \ldots.$$

$$\psi_{n_z}(z) = \left(\frac{2}{C}\right)^{1/2} \sin\left(\frac{n_z\pi}{C}z\right) \qquad E_{n_z} = \frac{n_z^2h^2}{8mC^2} \qquad n_z = 1, 2, 3, \ldots.$$

Notice that we have **three independent quantum numbers**: n_x, n_y, n_z.

Using the separability theorem, we can simply write the total wave function and energies as:

$$\psi_{n_x n_y n_z}(x,y,z) = \left(\frac{8}{ABC}\right)^{1/2} \sin\left(\frac{n_x\pi}{A}x\right) \sin\left(\frac{n_y\pi}{B}y\right) \sin\left(\frac{n_z\pi}{C}z\right)$$

$$E_{n_x n_y n_z} = \frac{h^2}{8m}\left(\frac{n_x^2}{A^2} + \frac{n_y^2}{B^2} + \frac{n_z^2}{C^2}\right)$$

$$n_x = 1,2,3\ldots$$
$$n_y = 1,2,3\ldots$$
$$n_z = 1,2,3\ldots$$

Notice we have three quantum numbers, one for each degree of freedom of the system. The states and energies are typically specified with these indices.

e.g.

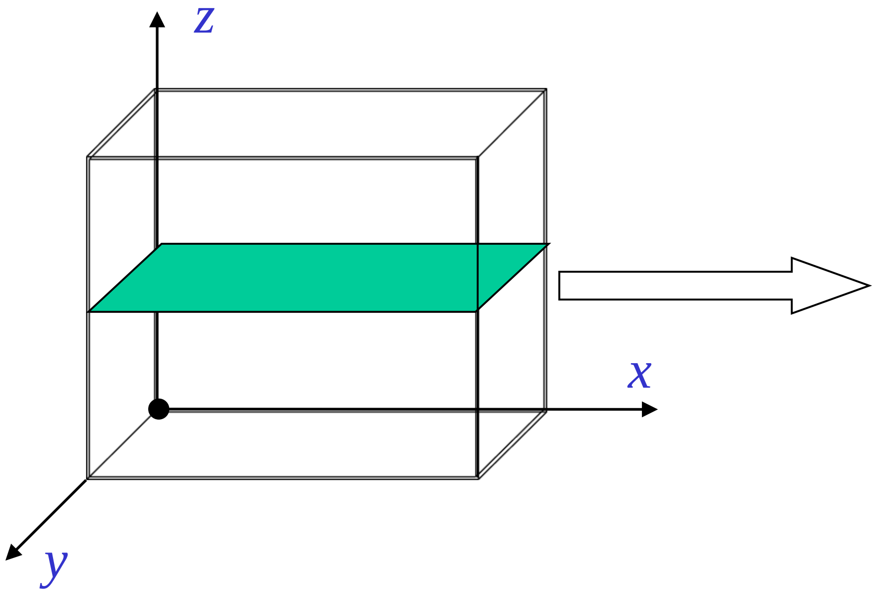
$$\psi_{111} \quad \psi_{121} \quad \psi_{133} \quad \psi_{512}$$
$$E_{111} \quad E_{121} \quad E_{133} \quad E_{512}$$

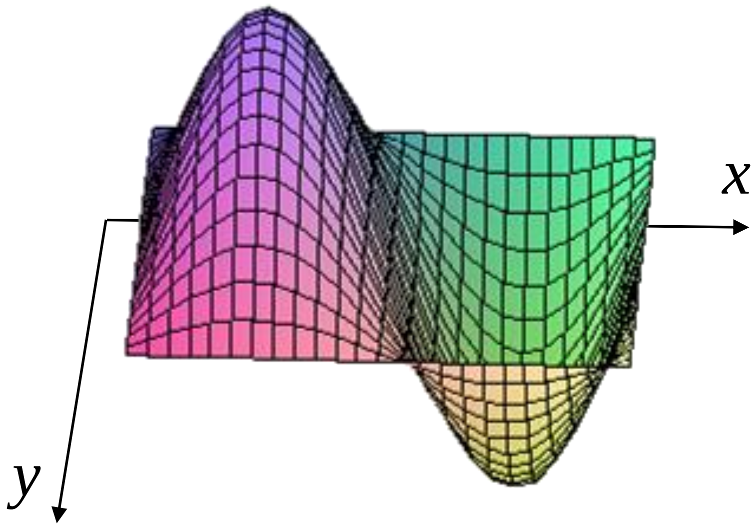
Visualization of the Wave Functions

$$\psi_{n_x n_y n_z}(x,y,z) = \left(\frac{8}{ABC}\right)^{1/2} \sin\left(\frac{n_x \pi}{A} x\right) \sin\left(\frac{n_y \pi}{B} y\right) \sin\left(\frac{n_z \pi}{C} z\right)$$

Visualizing a 3-D function is difficult since it would require a 4-dimensional plot.

However, 2-D slices of the wave function can be plotted.





Degeneracy

<u>Definition:</u> Two or more wave functions (of the same system) are **degenerate** if they have the same energy. It is important to realize that the wave functions and states are distinct. They just have the same energy.

If the 3-D box has equal sides, such that $A = B = C = L$, then some of the states of the 3-D particle in a box will be degenerate.

If $A = B = C = L$ (a **cube**), then the energy is given by:

$$E_{n_x n_y n_z} = \frac{h^2}{8m}\left(\frac{n_x^2}{A^2} + \frac{n_y^2}{B^2} + \frac{n_z^2}{C^2}\right)$$

$$= \frac{h^2}{8mL^2}\left(n_x^2 + n_y^2 + n_z^2\right)$$

$$E_{n_x n_y n_z} = \frac{h^2}{8mL^2}\left(n_x^2 + n_y^2 + n_z^2\right)$$

For example, the first excited state, has a three-fold degeneracy:

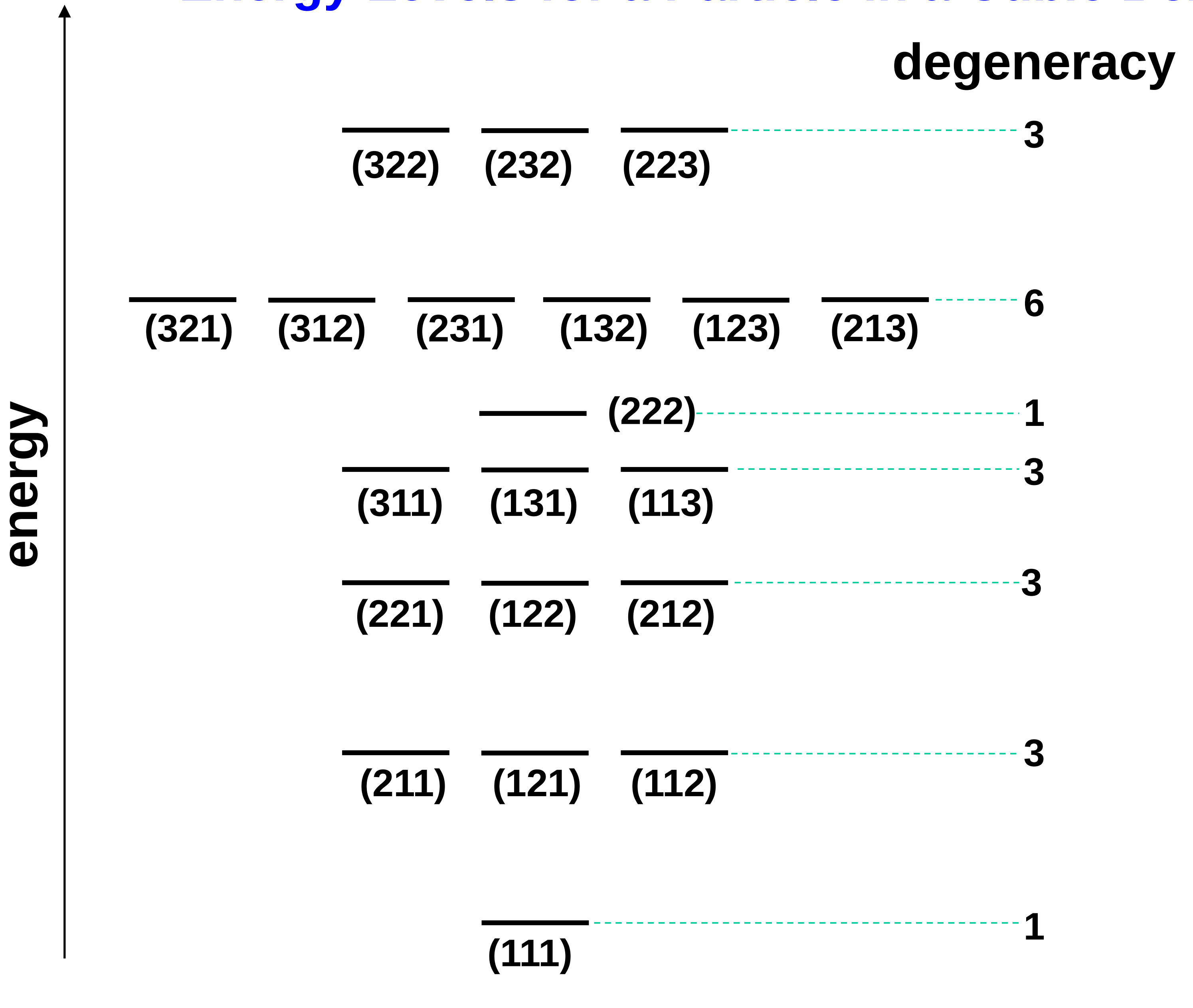
$$E_{211} = E_{121} = E_{112} = \frac{h^2}{8mL^2}(1 + 1 + 2^2)$$

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

There are three **distinct** states that have the same energy. In other words, there are three different wave functions that happen to have the same energy.

$$\psi_{211} \quad \text{and} \quad \psi_{121} \quad \text{and} \quad \psi_{112}$$

Energy Levels for a Particle in a Cubic Box



The ground state of the particle in a cubic box is **non-degenerate**, meaning there is only one state with that energy. Zero-point energy:

$$E_{111} = \frac{3h^2}{8mL^2}$$

The first excited state, has a three-fold degeneracy, meaning that there are three **distinct** states with the same energy.

$$E_{211} = E_{121} = E_{112} = \frac{6h^2}{8mL^2}$$

Note: These wave functions have the same energy, but they are still orthogonal to one another.

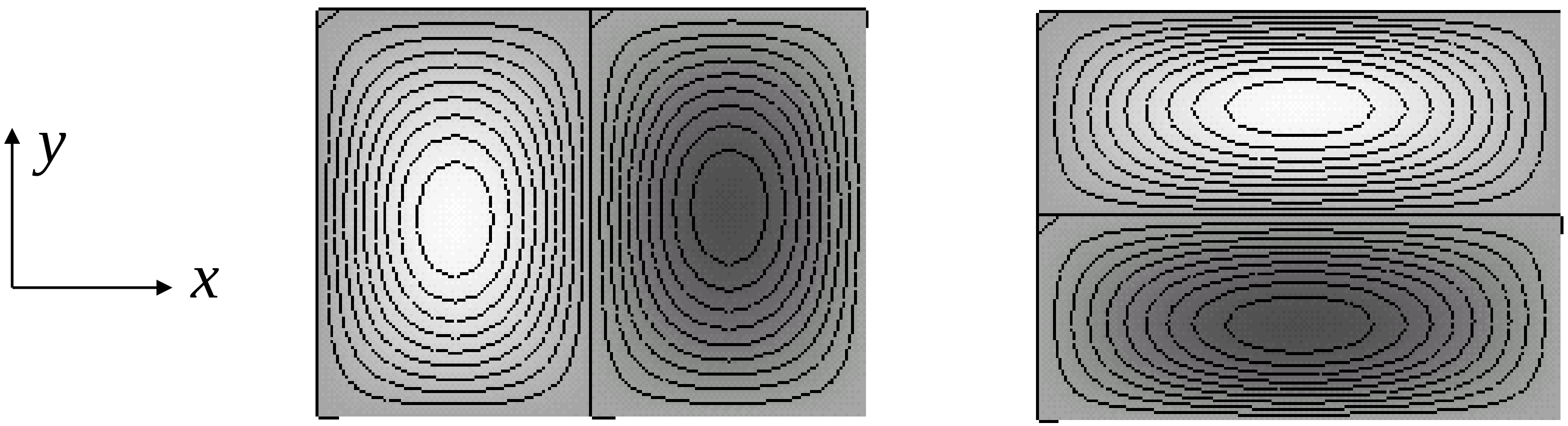
It is a general principle in quantum mechanics that degeneracies are the result of the underlying **symmetry** of a physical system.

We can demonstrate this if we consider the wave functions of the particle in a 2-D particle in a box which we can plot.

$$\psi_{n_x n_y}(x, y) = \frac{2}{L}\sin\left(\frac{n_x \pi}{L}x\right)\sin\left(\frac{n_y \pi}{L}y\right)$$

The Ψ_{21} and Ψ_{12} states are degenerate such that $E_{21} = E_{12}$.

Plotted below are the wave functions of these states. Notice the symmetry.



ψ_{21} ψ_{12}

3-D Particle In a Box Serves as a Model For an Ideal Gas

The 3-D particle in a box serves as a model for an ideal gas in a container.

Why an ideal gas?

The 3-D particle in a box can be used to treat and discuss the translational motion of molecules in a container within the ideal gas approximation.

Used in the derivation of the Maxwell Boltzmann Distribution Law for molecular speeds or kinetic energies.

3-Dimensional Harmonic Oscillator

We can also extend the Harmonic Oscillator to 3-dimensions, by assuming that the potential has the form:

$$V(x,y,z) = \frac{1}{2}k_x\,x^2 + \frac{1}{2}k_y\,y^2 + \frac{1}{2}k_z\,z^2$$

The resulting Hamiltonian is separable, as you can see.

Using the 1-D harmonic oscillator wave functions and energies, we can immediately write down the solutions. (First done by Einstein.)

The 3-D harmonic oscillator can serve as a simple model for a molecule embedded in a solid or an atomic crystal.