

## 2.6: Problems in Multiple Dimensions

As luck would have it, not all quantum mechanical problems are expressible in terms of a single dimension. In fact, most problems will require multiple "dimensions" as they will involve not only electronic state descriptions, but also vibrational descriptions and rotational descriptions as well. In this section, we will discuss how variables are separated in the multidimensional problems, using a particle in a three-dimensional box as an example.

### The Particle in a Rectangular Box

Consider a particle of mass  $m$  constrained to a three dimensional rectangular box with sides of lengths  $a$ ,  $b$  and  $c$  in the  $x$ ,  $y$  and  $z$  directions respectively. For this problem, the Hamiltonian will look as follows

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

One important thing to notice is that this Hamiltonian can be written as a sum of three separate operators, each affecting only a single variable.

$$\begin{aligned}\hat{H} &= -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} - \frac{\hbar^2}{2m}\frac{\partial^2}{\partial y^2} - \frac{\hbar^2}{2m}\frac{\partial^2}{\partial z^2} \\ &= \hat{H}_x + \hat{H}_y + \hat{H}_z\end{aligned}$$

When the Hamiltonian takes a form like this, it will also be possible to express the eigenfunctions as a product of functions. Let's give it a try.

The time independent Schrödinger equation looks as follows

$$\begin{aligned}\hat{H}\Psi(x, y, z) &= E\Psi(x, y, z) \\ -\frac{\hbar^2}{2m}\nabla^2\Psi(x, y, z) &= E\Psi(x, y, z) \\ -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\Psi(x, y, z) &= E\Psi(x, y, z)\end{aligned}$$

To simplify things, let's gather variables and make the substitution

$$-\frac{2mE}{\hbar^2} = -k^2$$

To proceed, we make an assumption that the wavefunction can be expressed as a product of functions.

$$\Psi(x, y, z) = X(x)Y(y)Z(z)$$

The wave equation then becomes

$$\begin{aligned}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)X(x)Y(y)Z(z) &= -k^2X(x)Y(y)Z(z) \\ Y(y)Z(z)\frac{d^2}{dx^2}X(x) + X(x)Z(z)\frac{d^2}{dy^2}Y(y) + X(x)Y(y)\frac{d^2}{dz^2}Z(z) &= -k^2X(x)Y(y)Z(z)\end{aligned}$$

Dividing both sides by  $X(x)Y(y)Z(z)$  yields

$$\frac{1}{X(x)}\frac{d^2}{dx^2}X(x) + \frac{1}{Y(y)}\frac{d^2}{dy^2}Y(y) + \frac{1}{Z(z)}\frac{d^2}{dz^2}Z(z) = -k^2$$

Since each of these terms is in a different variable, the only way the equation can be true is if each term on the left is equal to a constant. These constants are chosen in a convenient way so as to make the solution of the problem simple. So again, to proceed, we make a substitution.

$$\begin{aligned}\frac{1}{X(x)} \frac{d^2}{dx^2} X(x) &= -k_x^2 \\ \frac{1}{Y(y)} \frac{d^2}{dy^2} Y(y) &= -k_y^2 \\ \frac{1}{Z(z)} \frac{d^2}{dz^2} Z(z) &= -k_z^2\end{aligned}$$

where

$$-k_x^2 - k_y^2 - k_z^2 = -k^2$$

These substitutions allow us to separate the problem into three problems in single variables. Further, we know what the solutions to these equations are!

$$\begin{aligned}X(x) &= \sqrt{\frac{2}{a}} \sin\left(\frac{n_x \pi x}{a}\right) \quad n_x = 1, 2, 3, \dots \\ Y(y) &= \sqrt{\frac{2}{b}} \sin\left(\frac{n_y \pi y}{b}\right) \quad n_y = 1, 2, 3, \dots \\ Z(z) &= \sqrt{\frac{2}{c}} \sin\left(\frac{n_z \pi z}{c}\right) \quad n_z = 1, 2, 3, \dots\end{aligned}$$

The total wavefunction, therefore is

$$\Psi(x, y, z) = \sqrt{\frac{8}{abc}} \sin\left(\frac{n_x \pi x}{a}\right) \sin\left(\frac{n_y \pi y}{b}\right) \sin\left(\frac{n_z \pi z}{c}\right)$$

And the energy levels can be expressed as

$$\begin{aligned}E &= E_x + E_y + E_z \\ &= \left(\frac{n_x^2 h^2}{8ma^2}\right) + \left(\frac{n_y^2 h^2}{8mb^2}\right) + \left(\frac{n_z^2 h^2}{8mc^2}\right)\end{aligned}$$

The key element to notice here is that the wavefunctions are expressed as a product and the eigenfunction as a sum. This is a common pattern as it always happens when the operator can be expressed as a sum as was the case for this operator.

This pattern arises often in chemistry, where, for example, the total wavefunction of a molecule might be described as the product of wavefunctions describing the electronic state, the vibrational state and the rotational state.

$$\Psi_{\text{tot}} = \psi_{\text{elec}} \psi_{\text{vib}} \psi_{\text{rot}}$$

In the limit that this is a good description, the energy of the molecule can be expressed as a sum of energies.

$$E_{\text{tot}} = E_{\text{elec}} + E_{\text{vib}} + E_{\text{rot}}$$

## Degeneracy

Let's now consider the case where the particle is confined to a cubic space - a rectangular solid where all edges have the same length. If that length is  $a$ , the wavefunction becomes

$$\Psi(x, y, z) = \sqrt{\frac{8}{a^3}} \sin\left(\frac{n_x \pi x}{a}\right) \sin\left(\frac{n_y \pi y}{a}\right) \sin\left(\frac{n_z \pi z}{a}\right)$$

The energy levels are given by

$$E = (n_x^2 + n_y^2 + n_z^2) \frac{h^2}{8ma^2}$$

This result leads to an important possibility. Specifically, several eigenstates of the system can have the same energy. Consider the set of quantum numbers and energies shown in the following table.

Notice that several energies can be generated by a number of combinations of quantum numbers. The degeneracy is indicated by the number of quantum states that yield the same energy. There are many examples in quantum mechanics where several eigenstates yield the same energy. This can have important consequences on the nature of the system being described. This is perhaps the simplest system in which this phenomenon is observed. (Well, a particle in a 2-D box is simpler.)

Level	$n_x$	$n_y$	$n_z$	$E / (\hbar^2 / 8ma^2)$	Degeneracy
1	1	1	1	3	1
2	1	1	2	6	3
3	1	2	1	6	3
4	2	1	1	6	3
5	1	2	2	9	3
6	2	1	2	9	3
7	2	2	1	9	3
8	1	1	3	11	3
9	1	3	1	11	3
10	3	1	1	11	3
11	2	2	2	12	1
12	1	2	3	14	6
13	2	3	1	14	6
14	3	2	1	14	6
15	1	3	2	14	6
16	3	2	1	14	6
17	2	1	3	14	6

## Linear Combinations of Degenerate Wavefunctions

Oftentimes, it is convenient to describe systems using linear combinations of wavefunctions. An example of this is the creation of molecular orbitals as linear combinations of atomic orbitals. Another is the construction of hybrid orbitals such as the  $sp^3$  hybrid set that is often used to describe the bonding in methane or other hydrocarbons.

These linear combinations have important properties. In the case that the basis wavefunctions are degenerate eigenfunctions of the same operator (say, the Hamiltonian operator for instance) the linear combinations will also be eigenfunctions of that operator. However, this will not generally be the case for linear combinations of non-degenerate eigenfunctions. The proof of this is fairly straight forward.

### Theorem 2.6.1

**Proof:** Show that any linear combination of two functions that are eigenfunctions of the same operator, and have the same eigenvalues is also an eigenfunction of the operator.

**Solution:** Consider two functions  $f$  and  $g$  that are eigenfunctions of the operator  $\hat{A}$ .

$$\hat{A}f = af \quad \text{and} \quad \hat{A}g = ag$$

Any linear combination of the functions  $f$  and  $g$  will also be an eigenfunction of the operator  $\hat{A}$ .

$$\begin{aligned}\hat{A}(c_1 f + c_2 g) &= c_1 \hat{A}f + c_2 \hat{A}g \\ &= ac_1 f + ac_2 g \\ &= a(c_1 f + c_2 g)\end{aligned}$$

## The Particle on a Ring Problem

Consider a quantum mechanical particle of mass  $m$  constrained to a circular path of radius  $a$ . In Cartesian coordinates, we can write the potential energy function for this system as

$$V(x, y) = \begin{cases} \infty & \text{for } x^2 + y^2 \neq a^2 \\ 0 & \text{for } x^2 + y^2 = a^2 \end{cases}$$

However, it is much more convenient to work in coordinates that reflect the symmetry of the problem. In plane polar coordinates, the potential energy function is defined as

$$V(r, \theta) = \begin{cases} \infty & \text{for } r \neq a \\ 0 & \text{for } r = a \end{cases}$$

And since the Laplacian operator is given by

$$\nabla^2 = \frac{1}{r^2} \frac{\partial^2}{\partial \theta^2}$$

we can write the time-independent Schrödinger equation as

$$-\frac{\hbar^2}{2m} \cdot \frac{1}{r^2} \cdot \frac{\partial^2}{\partial \theta^2} \psi(r, \theta) = E \psi(r, \theta)$$

As usual, we proceed by separating variables. Let's let  $\psi(r, \theta) = R(r)\Theta(\theta)$ . We now get

$$-\frac{\hbar^2}{2m} \cdot \frac{R(r)}{r^2} \cdot \frac{d^2}{d\theta^2} \Theta(\theta) = ER(r)\Theta(\theta)$$

Now we can divide both sides by the function  $R(r)$  and simply get rid of it. In this problem the only thing we need to know about the  $r$  is that it is a constant ( $r = a$ .)

So after a trivial rearrangement, we see

$$\frac{d^2}{d\theta^2} \Theta(\theta) = -\frac{2mr^2 E}{\hbar^2} \Theta(\theta)$$

This is starting to look more like something we can manage to solve by inspection! Let's make a substitution. Let

$$m_l = \pm \frac{(2mr^2 E)^{1/2}}{\hbar}$$

We'll evaluate  $m_l$  later. But now it is easy to show that

$$\Theta(\theta) = Ae^{im_l \theta}$$

is a solution to the eigenvalue, eigenfunction problem. Let's try!

$$\begin{aligned}\frac{d}{d\theta} Ae^{im_l \theta} &= iAm_l e^{im_l \theta} \\ \text{and} \\ \frac{d}{d\theta} iAm_l e^{im_l \theta} &= -Am_l^2 e^{im_l \theta}\end{aligned}$$

So the eigenfunctions are given by  $\Theta(\theta) = Ae^{im_l \theta}$  and the eigenvalues are given by  $-m_l^2$ .

To proceed, we will employ a cyclical boundary condition. Since all wavefunctions must be single valued, we see that

$$\Theta(\theta) = \Theta(\theta + 2\pi)$$

So ...

$$\begin{aligned} Ae^{im_l\theta} &= Ae^{im_l(\theta+2\pi)} \\ &= Ae^{im_l\theta} e^{i2\pi m_l} \end{aligned}$$

Or dividing both sides by  $Ae^{im_l\theta}$ , we see

$$1 = e^{i2\pi m_l}$$

This is going to quantize the possible values which  $m_l$  can take. And since the Euler relation tells us that

$$e^{i\pi} = -1$$

we see that

$$1 = (-1)^{2m_l}$$

which can only be true if  $m_l$  is an integer. As it turns out, it doesn't matter if  $m_l$  is positive or negative. It just has to be an integer.

$$m_l = 0, \pm 1, \pm 2 \dots$$

As promised, this quantizes the energies possible for the system.

$$\frac{m_l^2 \hbar^2}{2I} = E$$

where the moment of inertia  $I$  is given by the mass times the radius squared.

$$I = mr^2$$

Finally, we can obtain the value of the normalization constant  $A$  to normalize the wavefunctions.

$$1 = A^2 \int_0^{2\pi} e^{im_l\theta} e^{im_l\theta} d\theta$$

And we see that

$$A = \left( \frac{1}{2\pi} \right)^{1/2}$$

So, in summary, the wavefunctions are given by

$$\psi(r, \theta) = \left( \frac{1}{2\pi} \right)^{1/2} e^{im_l\theta} \quad m_l = 0, \pm 1, \pm 2, \dots$$

And the energies are given by

$$E_{m_l} = \frac{m_l^2 \hbar^2}{2I} \quad \text{where } I = mr^2$$

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