

14.1: Multidimensional Free waves and the Particle in a Cube

We begin our understanding on multidimensional quantum mechanics with the kinetic energy operator $\frac{-\hbar^2}{2 \cdot mass} \frac{\partial^2}{\partial x^2}$, as most of the complexity of quantum mechanics originates from here as we saw back in Ch. 12. The operator must be augmented with additional terms, likely the same expression except with y : $\frac{-\hbar^2}{2 \cdot mass} \frac{\partial^2}{\partial y^2}$ and z : $\frac{-\hbar^2}{2 \cdot mass} \frac{\partial^2}{\partial z^2}$. Now the question is how- are these terms added into the operator? Or do they all multiply? Let's use an analogy- recalling the equipartition theorem from your earlier introduction to thermodynamics, the energy of a particle increases by $\frac{1}{2}k_B T$ for every degree of freedom that particle has. The ability of a particle to move in x , y and z counted as three degrees of freedom, and as a result all the $\frac{1}{2}k_B T$ energies were summed. This leads us to conclude that the kinetic energy operator must likewise sum energies for each accessible dimension, which is:

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

This expression is the full 3D kinetic energy operator, and we will use it to revisit our old problems of the freewave and particle in a box once we know a little bit more about how to solve the wavefunctions.

14.1.1. Multidimensional wavefunctions and separability in the 3D freewave problem

With the kinetic energy operator in hand, let's solve a simple system such as the freewave in 3D, which describes a particle that moves in any direction, forever, without encountering any potential energy. The Schrödinger equation for the 3D freewave is then:

$$\frac{-\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \Psi(x, y, z) = E \cdot \Psi(x, y, z)$$

To make further progress we must know more about the total wavefunction $\Psi(x, y, z)$. Could it be a simple summation of "mini" wavefunctions in different dimensions: $\Psi(x, y, z) = \Psi_x(x) + \Psi_y(y) + \Psi_z(z)$ or perhaps they multiply: $\Psi(x, y, z) = \Psi_x(x) \cdot \Psi_y(y) \cdot \Psi_z(z)$? Instead of guessing, we can review some mathematical principles of differential equations to resolve between the two possibilities.

Separability is a method for solving differential equations, and what it means is that the Hamiltonian can be cast into a form whereby distinct terms that contain only an x , y or z are added or subtracted. A separable Hamiltonian is significantly easier to solve, and fortunately most (but not all) operators are in fact separable. To check for separability, first act on a wavefunction to the right of the Hamiltonian: $\hat{H}\Psi$ and then divide it out on the left: $\frac{1}{\Psi}\hat{H}\Psi$. What you are trying to see is if you can write out the Hamiltonian as:

$\frac{1}{\Psi}$

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$\frac{1}{\Psi} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \Psi = \frac{1}{\Psi} \left(\frac{\partial^2 \Psi}{\partial x^2} + \frac{\partial^2 \Psi}{\partial y^2} + \frac{\partial^2 \Psi}{\partial z^2} \right) = \frac{1}{\Psi} \left(\frac{\partial^2 \Psi_x}{\partial x^2} + \frac{\partial^2 \Psi_y}{\partial y^2} + \frac{\partial^2 \Psi_z}{\partial z^2} \right)$

and, if so, then the total wavefunction is: $\Psi(x, y, z) = \Psi_x(x) \cdot \Psi_y(y) \cdot \Psi_z(z)$.

Separability has two consequences. First, the wavefunction *cannot* look like $\Psi(x, y, z) \approx \sin(k_x x + k_y y + k_z z)$ or $e^{i \cdot k_x \cdot x} + e^{i \cdot k_y \cdot y} + e^{i \cdot k_z \cdot z}$. Second, the method of separability gives us a way to solve the Schrödinger equation as each of the terms becomes a smaller and easier differential equation. Beginning with the definition of separability:

$\frac{1}{\Psi}$

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$\frac{1}{\Psi} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \Psi = \frac{1}{\Psi} \left(\frac{\partial^2 \Psi}{\partial x^2} + \frac{\partial^2 \Psi}{\partial y^2} + \frac{\partial^2 \Psi}{\partial z^2} \right) = \frac{1}{\Psi} \left(\frac{\partial^2 \Psi_x}{\partial x^2} + \frac{\partial^2 \Psi_y}{\partial y^2} + \frac{\partial^2 \Psi_z}{\partial z^2} \right)$

$\frac{1}{\Psi}$

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$\Psi_x(x) \cdot \Psi_y(y) \cdot \Psi_z(z) +$

$$\frac{1}{\Psi_x(x) \cdot \Psi_y(y) \cdot \Psi_z(z)} \left(\frac{-\hbar^2}{2m} \right) \frac{\partial^2}{\partial y^2} \Psi(x) \cdot \Psi(y) \cdot \Psi(z) +$$

$\frac{1}{\Psi_x(x) \cdot \Psi_y(y) \cdot \Psi_z(z)}$

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$\Psi_x(x) \cdot \Psi_y(y) \cdot \Psi_z(z)$

One simple rule of calculus is concerning derivatives is that functions of other variables are not “caught up” by the derivative operation, i.e. $\frac{\partial}{\partial x} f(x) f(y) = f(y) \frac{\partial f(x)}{\partial x}$. When we apply that to the 1st term above we find:

$\frac{1}{\Psi_x(x) \cdot \Psi_y(y) \cdot \Psi_z(z)}$

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$\Psi_x(x) \cdot \Psi_y(y) \cdot \Psi_z(z) = \frac{1}{\Psi_x(x) \cdot \Psi_y(y) \cdot \Psi_z(z)}$

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$\Psi_x(x)$

which simplifies to $\frac{1}{\Psi_x(x)} \left(\frac{-\hbar^2}{2m} \right) \frac{\partial^2 \Psi_x(x)}{\partial x^2}$. Applying these across-the-board yields:

$$\left\{ \frac{1}{\Psi_x(x)} \left(\frac{-\hbar^2}{2m} \right) \frac{\partial^2 \Psi_x(x)}{\partial x^2} \right\} + \left\{ \frac{1}{\Psi_y(y)} \left(\frac{-\hbar^2}{2m} \right) \frac{\partial^2 \Psi_y(y)}{\partial y^2} \right\} + \left\{ \frac{1}{\Psi_z(z)} \left(\frac{-\hbar^2}{2m} \right) \frac{\partial^2 \Psi_z(z)}{\partial z^2} \right\}$$

Success! We see three distinct terms, whereby only an x appears in the 1st one and so on. Furthermore, each term is now a min-Schrödinger equation to be solved. The last step is to realize that all three terms add up to the energy. You can see this starting with: $\hat{H}\Psi = E\Psi$ and dividing out the wavefunction on the left $\frac{1}{\Psi}\hat{H}\Psi = \frac{1}{\Psi}E\Psi = \frac{E}{\Psi} = E$. Since each term adds to a constant (the energy), then each term must be a constant in its own right. As a result, we divide the energy into three parts, one for x, for y and for z as: $E = E_x + E_y + E_z$, and then give each energy to the corresponding term (and using a little algebra to bring the wavefunctions to the right):

$\frac{1}{\Psi_x(x)}$

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$\Psi_x(x) = E_x \Psi_x(x)$

$\frac{1}{\Psi_x(x)}$

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$\Psi_y(y) = E_y \Psi_y(y)$

$\frac{1}{\Psi_y(y)}$

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$\Psi(x,y,z) = e^{\pm i k_x x} \cdot e^{\pm i k_y y} \cdot e^{\pm i k_z z}$

Each of these are simply freewave Schrödinger equations. We know from the last chapter that the solutions are: $\Psi_x(x) = e^{\pm i k_x x}$, etc., which means that the full solution is:

$$\Psi(x, y, z) = e^{\pm i k_x x} \cdot e^{\pm i k_y y} \cdot e^{\pm i k_z z}$$

It is interesting to note that three separate momentum components now add to the total like a vector: $k^2 = k_x^2 + k_y^2 + k_z^2$. This is especially apparent if you use the wavefunction to calculate the total energy:

$$E = \frac{\hbar^2}{2m} (k_x^2 + k_y^2 + k_z^2) = \frac{\hbar^2 k^2}{2m}$$

If for some reason the individual wavevectors were not of equal magnitude, then it would have to be true that the total energy wasn't divided equally between the three dimensions: $E_x \neq E_y \neq E_z$. This is a very unlikely scenario, but if it was true you would be aware of it due to the fact that you must have some basic understanding of the system under study. Or, if you are solving a problem this information would be given to you as an initial condition of the system.

14.1.2. The Particle in a 3D Box and Degeneracy

The quantum particle in a box can be extended to multiple dimensions as visually represented in Figure 14.1. From the last chapter, this problem was defined by a potential that is 0 inside the box and infinite outside. Boundary conditions allow us to define the wavefunctions: $\Psi = \sin\left(\frac{n\pi}{L}x\right)$ with the quantum number $n=1,2,3,\dots$ that characterize the number of nodes and the energy. Extending this to multiple dimensions is straightforward. Given the previous discussion the total wavefunction is just the multiple of individual particle in a box functions for x , y and z :

$$\Psi_{2D}(x, y, z) = N_{2D} \cdot \sin(k_x x) \cdot \sin(k_y y) \quad \Psi_{3D}(x, y, z) = N_{3D} \cdot \sin(k_x x) \cdot \sin(k_y y) \cdot \sin(k_z z)$$

where the normalization constants are $N_{2D} = \frac{2}{\sqrt{L_x L_y}}$, $N_{3D} = \frac{2\sqrt{2}}{\sqrt{L_x L_y L_z}}$, and $k_x = \frac{n_x \pi}{L_x}$, $k_y = \frac{n_y \pi}{L_y}$, and $k_z = \frac{n_z \pi}{L_z}$. We will limit further discussion to the 3D case from here on. Inserting the wavefunction back into the particle in a box Hamiltonian reveals the energy to be:

$$E = \frac{\hbar^2}{2m} (k_x^2 + k_y^2 + k_z^2) = \frac{\hbar^2 \pi^2}{2m} \left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2} \right)$$

which can be simplified to $E = \frac{\hbar^2 \pi^2}{2m L^2} (n_x^2 + n_y^2 + n_z^2)$ if all the box lengths are the same. As in the one-dimensional particle in a box problem, the quantum numbers are limited to whole numbers: $n_{x,y,z} = 1, 2, 3, \dots$ due to the need to satisfy boundary conditions imposed by infinite potential energies past the barriers. Various wavefunctions are depicted in Figure 14.2, where we have made the simplification that $L = L_x = L_y = L_z$. It can be seen that there is only one wavefunction that gives the lowest energy ground state for which $n_{x,y,z} = 1$. However, there are three potential 1st and 2nd excited states; since for example:

$$E = \frac{\hbar^2 \pi^2}{2m \cdot L^2} \left\{ (n_x = 2)^2 + 1^2 + 1^2 \right\} = \frac{\hbar^2 \pi^2}{2m \cdot L^2} \left\{ 1^2 + (n_y = 2)^2 + 1^2 \right\} = \frac{\hbar^2 \pi^2}{2m \cdot L^2} \left\{ 1^2 + 1^2 + (n_z = 2)^2 \right\}$$

This is referred to as a degeneracy, multiple distinct states that all have the same energy. One way to recognize degeneracy is if you can rotate the wavefunctions such that they all look the same.

There isn't much more to say about these simple multidimensional systems. For example, one can generate interesting problems by mixing and matching potential surfaces in different dimensions- a freewave surface in x and a parabolic (spring) potential in y . However, the solutions are rather trivial, as the total wavefunction in this example is just the freewave in x times the harmonic oscillator function in y . Such problems are left for your effort at the end of the chapter, and as such we move on to discuss a quantum particle rotating.

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