

7.1: Schrödinger's Equation in 3-Dimensions

Adding Degrees of Freedom

When we extend our work on quantum mechanics in one dimension to three dimensions, we have to take into account what happens to how we describe quantum states. The main difference that arises is that we still need to get to a single number (probability) from three times as many dimensions as before. Instead of describing the wave function in terms of a single number x , we require three numbers, x , y , and z . For cases when we want to remain ambiguous about the coordinate system in use, we will replace explicit use of variables like (x, y, z) with the more generic position vector \vec{r} .

$$\Psi(x, y, z, t) \rightarrow \Psi(\vec{r}, t) \quad (7.1.1)$$

As before, the magnitude-squared of the wave function is a probability density, but in three dimensions, this becomes a volume density instead of a line density. Computations of probabilities in three dimensions requires integration over a three dimensional space:

$$\text{probability that particle is found in a tiny volume } dV \text{ located at position } \vec{r} = |\Psi(\vec{r}, t)|^2 dV \quad (7.1.2)$$

The tiny volume element dV takes on different forms depending upon the coordinate system used. In this class, we will only be using Cartesian and spherical coordinates:

$$dV = \begin{matrix} \text{Cartesian} & \text{spherical} \\ dx \, dy \, dz & r^2 \, dr \, \sin \theta \, d\theta \, d\phi \end{matrix} \quad (7.1.3)$$

Naturally the normalization condition is:

$$\int_{\text{all space}} |\Psi(\vec{r}, t)|^2 dV = 1 \quad (7.1.4)$$

Written out explicitly for Cartesian and spherical coordinates, this is:

$$\begin{aligned} \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} dz |\Psi(x, y, z, t)|^2 &= 1 \\ \int_0^{\infty} r^2 \, dr \int_0^{\pi} \sin \theta \, d\theta \int_0^{2\pi} d\phi |\Psi(r, \theta, \phi, t)|^2 &= 1 \end{aligned} \quad (7.1.5)$$

As before, we can use eigenstates of momentum (plane waves) as our "unit vectors," and the relationship between the y and z components of momentum with the y and z coordinates is exactly the same as it was for the case of x in one dimension, which means that position space and momentum space wave functions are related through a Fourier transform, which now must be performed in all three directions.

One interesting effect arises from the extension to three dimensions. In the case of one dimension, the stationary-state wave function was completely defined by a single number x , the position along the one dimension. The wave function also contained all of the information about the stationary state, namely the energy. This is also reversible – if we know the energy of the particle (say we know that a particle-in-a-box is in its ground state), then we also have its full wave function and all of the information about its state.

When we get to three dimensions, however, knowing the wave function requires knowing the three numbers that define position. These three numbers will provide all the information about the particle's state, including its energy, but this time it is not reversible – knowing the energy (a single number) cannot possibly tell us everything about the state of the particle. There has to be two other such numbers. If the particle is bound, these numbers will – like the energy – be quantized, and we will label them with integers as we already do with the energy. These integer labels are called *quantum numbers*, and are frequently used to label eigenstates in the same way that n labeled the energy eigenstates in one dimension.

Schrödinger's Equation

Schrödinger's equation is easy to expand to three dimensions. All that is required is to use the kinetic and potential energy operators in three dimensions in the Hamiltonian. In Cartesian coordinates, we have:

$$\widehat{H} = \frac{1}{2m} (\hat{p}_x^2 + \hat{p}_y^2 + \hat{p}_z^2) + \widehat{V} = -\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) + V(x, y, z) \quad (7.1.6)$$

We can write this without reference to a choice of coordinate system by replacing the set of second derivatives with the Laplacian operator (which we can look up for whatever coordinate system we like):

$$\widehat{H} = -\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}) \quad (7.1.7)$$

Once again, we are faced with a partial differential equation, this time in *four* variables. Just as before, we can use the separation of variables method to select-out the stationary-state subset of solutions:

$$\Psi(\vec{r}, t) = \psi(\vec{r}) e^{-i\omega t}, \quad \text{where:} \quad -\frac{\hbar^2}{2m} \nabla^2 \psi(\vec{r}) + V(\vec{r}) \psi(\vec{r}) = E \psi(\vec{r}), \quad \omega = \frac{E}{\hbar} \quad (7.1.8)$$

Okay, now we have a differential equation with three variables to solve. If the separation of variables trick is so effective, why not just use it again? Not so fast! Unlike separating the time variable from the spatial variables, separating the spatial variables from each other is trickier business, because we can choose any set of coordinates we like. That is, there is nothing about the Schrödinger equation written above in Cartesian coordinates that is any more "correct" than if it is written in spherical coordinates, so how do we know whether we can (or should) do a separation of variables in Cartesian coordinates?

The answer is utility – we trust that like the case of separation of the time variable, we will be able to construct more general solutions from linear combinations of whatever solutions we arrive at after separating variables, so we are free to try the separation in any coordinate system. The system we choose should be the one that is easiest to work with for the physical situation given. If the potential is easy to work with in a specific coordinate system (typically due to some spatial symmetry inherent in the potential), then that is the one to use. Ultimately whatever separation we choose will lead to its own set of three quantum numbers, as we will see with our two cases of Cartesian and spherical coordinates.

Separation of Variables in Cartesian Coordinates

Potentials with particular properties encourage us to separate variables in the Cartesian coordinate system, so let's look at how this works. We seek solutions to the stationary-state Schrödinger equation that admit wave functions which can be written as a product of three functions of single variables:

$$\psi(x, y, z) = X(x) Y(y) Z(z) \quad (7.1.9)$$

Plugging this into the stationary-state Schrödinger equation, and dividing the whole equation by the wave function separates it into terms that are functions of only x , y , and z , along with a potential that so far we have not restricted:

$$\begin{aligned} -\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) X(x) Y(y) Z(z) + V(x, y, z) X(x) Y(y) Z(z) &= E X(x) Y(y) Z(z) \\ \Rightarrow \frac{1}{X} \frac{\partial^2 X}{\partial x^2} + \frac{1}{Y} \frac{\partial^2 Y}{\partial y^2} + \frac{1}{Z} \frac{\partial^2 Z}{\partial z^2} - \frac{2m}{\hbar^2} V(x, y, z) &= -\frac{2mE}{\hbar^2} \end{aligned} \quad (7.1.10)$$

For this method to be useful, we need to be able to separate the entire equation into a sum of terms that are exclusively functions of one variable at a time (x , y , or z). To see how this works, consider the following:

$$f(x) + g(y) + h(z) = \text{constant} \quad (7.1.11)$$

We can plug any x value we like into $f(x)$, without changing any of the y or z values. For this equation to remain correct, it must mean that $f(x)$ is the same constant value for all choices of x . The same argument can be made for $g(y)$ and $h(z)$. This gives us three separate equations, each in a single variable.

The first three terms are already separated into x , y , and z , but the potential function poses a problem. This method is only really effective in two cases: When the potential is a constant (universally, or piecewise), or when it splits up into a sum of functions of

single variables. We will look at examples of each of these cases, starting with the simplest – where there is essentially no potential function at all.

Free Particle

If the potential is universally constant, then the particle is obviously free. As with the one-dimensional free particle, the stationary-state Schrödinger's equation gives us wave functions of energy eigenstates, but we can filter-out the momentum eigenstates (plane waves) if we wish. Plugging zero in for the potential allows us to separate the equation into three differential equations in single variables. The choices for the form of the constants below will become quickly apparent:

$$\frac{1}{X} \frac{d^2 X}{dx^2} = -k_x^2, \quad \frac{1}{Y} \frac{d^2 Y}{dy^2} = -k_y^2, \quad \frac{1}{Z} \frac{d^2 Z}{dz^2} = -k_z^2, \quad k_x^2 + k_y^2 + k_z^2 = \frac{2mE}{\hbar^2} \quad (7.1.12)$$

The plane wave solutions of each of the separate differential equations are:

$$X(x) = A_x e^{ik_x x}, \quad Y(y) = A_y e^{ik_y y}, \quad Z(z) = A_z e^{ik_z z} \quad (7.1.13)$$

Reconstructing the full momentum eigenstate wave function, we get:

$$\psi(x, y, z) = X(x) Y(y) Z(z) = A e^{i(k_x x + k_y y + k_z z)} \quad (7.1.14)$$

If we define the momentum vector \vec{p} in terms of a wave vector $\vec{k} = k_x \hat{i} + k_y \hat{j} + k_z \hat{k}$, we get the rather compact plane wave solution moving in a specific direction:

$$\psi(\vec{r}) = A e^{i\vec{k} \cdot \vec{r}}, \quad \vec{k} = \frac{\vec{p}}{\hbar}, \quad E = \frac{p^2}{2m} = \frac{\hbar^2}{2m} (\vec{k} \cdot \vec{k}) \quad (7.1.15)$$

This plane wave is also an energy eigenstate, so the full time-dependent wave function can also be written:

$$\psi(\vec{r}, t) = A e^{i(\vec{k} \cdot \vec{r} - \omega t)}, \quad \omega = \frac{E}{\hbar} \quad (7.1.16)$$

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