19. Spherical Coordinates

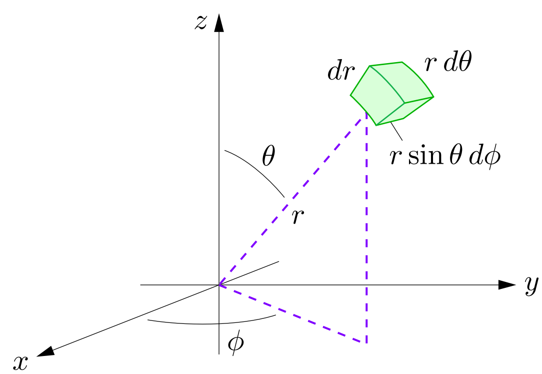
We now begin a major new unit of this course, in which we will study the behavior of a single quantum particle in three dimensions, subject to a potential energy function V that is spherically symmetric—that is, V depends only on the distance r from some fixed center:

$$V(x,y,z) = V(r,\theta,\phi) = V(r) \qquad \text{(independent of } \theta \text{ and } \phi). \tag{1}$$

The most important example of a spherically symmetric potential is the attractive Coulomb potential, proportional to $-1/r$, between an atomic nucleus (which we can treat as a fixed center of force) and an electron. But there are other interesting central potentials as well, and we can get pretty far in our analysis without assuming a specific formula for $V(r)$.

As usual, our goal is to solve the time-independent Schrödinger equation to find the allowed energy levels and the associated wavefunctions. Once we have these, it is a straightforward exercise to combine these wavefunctions with their associated wiggle factors to build solutions to the time-dependent Schrödinger equation.

As you can probably guess, solving the TISE in this case is much easier if we use spherical coordinates, (r, θ, ϕ):



Note that θ is the polar angle, measured down from the z axis and ranging from 0 to π, while ϕ is the azimuthal angle, projected onto the xy plane, measured counter-clockwise, when viewed from above, from the positive x axis, and ranging from 0 to 2π. When setting up integrals, you also need to know that the infinitesimal volume element is $(dr)(r\,d\theta)(r\sin\theta\,d\phi)$, as shown in the illustration (note that $r\sin\theta$ is the projection of the length r onto the xy plane).

To write down the TISE, we also need to express the Laplacian operator, ∇^2, in spherical coordinates—and this is harder than you might think. The naive guess turns out to be *wrong*:

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial y^2} \neq \frac{\partial^2}{\partial r^2} + \frac{\partial^2}{\partial \theta^2} + \frac{\partial^2}{\partial \phi^2}. \tag{2}$$

(How can you tell?) The correct expression still has three terms, each with two derivatives with respect to one of the three variables, but, as in the volume element, there are a bunch of stray factors of r and $\sin\theta$. The correct expression is

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}, \tag{3}$$

and if you want to see a derivation, you can look in *Introduction to Electrodynamics* by Griffiths or in any good book on vector calculus.

The kinetic energy operator is the Laplacian times $-\hbar^2/2m$, so the TISE for a single particle subject to a central potential is

$$-\frac{\hbar^2}{2mr^2}\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}\right] + V(r)\psi = E\psi, \tag{4}$$

where ψ is a function of r, θ, and ϕ.

At this point there are two ways to proceed. The more mathematical approach is to solve this partial differential equation by the method of separation of variables, looking for solutions $\psi(r,\theta,\phi)$ that factor into a function of r times a function of θ times a function of ϕ. (There will be other solutions that don't factor in this way, but the separable solutions form a basis so we can build the other solutions as linear combinations of the separable solutions.) This method works fine, but it requires a fair amount of labor with very little reward in the form of physical insight. If you'd like to see it, you can find all the details in Section 4.1 of Griffiths.

The alternative is to realize that in any problem with spherical symmetry we expect the solutions to have a physical interpretation in terms of angular momentum. Recall that in classical mechanics, when a particle moves under the influence of a central potential $V(r)$, its angular momentum vector $\vec{L} = \vec{r}\times\vec{p}$ must be conserved. The quantum mechanical counterpart to this conservation law is more subtle, but we can ultimately find the separable solutions to the TISE (or more precisely, their angular dependence) by focusing first on the three components of the angular momentum operator, and by looking for their eigenfunctions and eigenvalues. This approach is just as laborious as the purely mathematical approach described above, but we'll gain much more physical understanding along the way.