22. The Radial Equation

Now that we know all about angular momentum, let's go back to the time-independent Schrödinger equation, in spherical coordinates, for a particle subject to an r-dependent potential energy function:

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

If you compare the terms with angular derivatives to the expression for L^2 from the previous lesson, you'll see that every θ and ϕ matches perfectly, so we can write the TISE more simply as

$$\left[-\frac{\hbar^2}{2mr^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{L^2}{2mr^2}+V(r)\right]\psi=E\psi. \tag{2}$$

But since L^2 commutes with the Hamiltonian, we know we can find solutions to the TISE that are also eigenfunctions of L^2. We can also take them to be eigenfunctions of L_z (which commutes with both L^2 and H), so that they are the spherical harmonics, $Y_l^m(\theta,\phi)$, multiplied by factors that are independent of θ and ϕ but presumably still dependent on r. We'll call these r-dependent functions $R(r)$, so that

$$\psi(r,\theta,\phi)=R(r)\,Y_l^m(\theta,\phi). \tag{3}$$

Plugging this separable solution into the TISE, replacing L^2 with its known eigenvalue, and canceling the factor of Y_l^m, we obtain the *radial Schrödinger equation*,

$$\left[-\frac{\hbar^2}{2mr^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right)+\frac{\hbar^2 l(l+1)}{2mr^2}+V(r)\right]R(r)=ER(r). \tag{4}$$

The radial Schrödinger equation simplifies somewhat if we make a change of variables from $R(r)$ to the function

$$u(r)=rR(r), \tag{5}$$

which is sometimes called the *reduced radial wavefunction*. Notice that

$$\begin{aligned}\frac{d}{dr}\left(r^2\frac{d}{dr}\left(r^{-1}u(r)\right)\right)&=\frac{d}{dr}\left(r^2\left(-r^{-2}u(r)+r^{-1}\frac{du}{dr}\right)\right)\\&=\frac{d}{dr}\left(-u(r)+r\frac{du}{dr}\right)\\&=-\frac{du}{dr}+\frac{du}{dr}+r\frac{d^2u}{dr^2}\\&=r\frac{d^2u}{dr^2}.\end{aligned} \tag{6}$$

Plugging this simplification into the radial Schrödinger equation and multiplying through by r, we obtain the *reduced radial equation*,

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dr^2} + \frac{\hbar^2 l(l+1)}{2mr^2} + V(r)\right]u(r) = Eu(r). \tag{7}$$

The first term in brackets now looks just like the familiar one-dimensional kinetic energy operator. The second term, for any fixed l value, is a known function of r, which we can group with the potential energy to form the *effective potential energy* function,

$$V_{\text{eff}}(r) = \frac{\hbar^2 l(l+1)}{2mr^2} + V(r), \tag{8}$$

just as we often do in classical mechanics problems with central forces. Then the reduced radial equation becomes simply

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dr^2} + V_{\text{eff}}(r)\right]u(r) = Eu(r), \tag{9}$$

which is identical to the one-dimensional TISE but with x replaced by r, ψ replaced by u, and V replaced by V_{eff}.

Because of their mathematical similarity, we can analyze and solve the reduced radial equation using all of the techniques that we learned for the one-dimensional TISE earlier in this course. We can sketch qualitative graphs of the solutions. In a few cases we can find exact solutions. And we can solve the equation numerically using either the shooting method or the matrix diagonalization method. The only mathematical difference is that whereas x normally ranges from $-\infty$ to ∞, negative r values are not allowed. In fact, $u(r)$ must equal zero at $r = 0$, as is almost obvious from the definition $u(r) = rR(r)$. (The only question that requires thought is whether $R(r)$ can ever by infinite at $r = 0$, and the answer is "no" in all the examples we'll encounter.) There's also a difference when we interpret the solutions, because the full wavefunction is $u(r)/r$ times the applicable spherical harmonic. And we need to remember that V_{eff} depends on l, so we get to solve the reduced radial equation separately for $l = 0$, $l = 1$, $l = 2$, and so on.

The l-dependent term in V_{eff} is called the *centrifugal term* (as it is in classical mechanics). It's zero for $l = 0$, but for $l > 0$ it creates an effective repulsive force that becomes infinite as $r \to 0$, pushing the particle out from the origin. (Of course this "force" is just a useful fiction that we invent so we can pretend that this is a one-dimensional problem; in three dimensions, we would instead say that assuming a nonzero angular momentum entails assuming that the particle avoids the origin.)

As a first example of solving the radial Schrödinger equation, consider the *spherical infinite square well*, with $V(r) = 0$ out to some radius a and $V = \infty$ beyond that. You should be able to write down the solutions for $l = 0$ almost immediately. For $l > 0$ the solutions are harder to find, but they can still be expressed exactly in terms of sines and cosines. Griffiths lays out the solutions at the end of Section 4.1, so please look over his presentation.