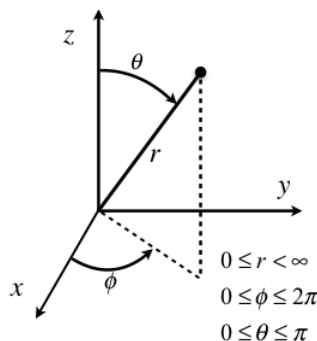


7.3: Central Forces

Separation of Variables

Working in spherical coordinates is significantly more difficult than working in Cartesian coordinates. So why do it? Because point-like particles are sources for spherically-symmetric potentials that affect other particles. Understanding how to work in spherical coordinates is essential for solving the hydrogen atom in particular. First a reminder of the coordinates themselves:

Figure 7.3.1 – Spherical Coordinates



We begin with the stationary-state Schrödinger equation in three dimensions. We need to write the Laplacian operator found in the Hamiltonian (Equation 7.1.7) in spherical coordinates. This we can simply look up (deriving it from the transformation between coordinate systems is no fun):

$$\nabla^2 = \frac{1}{r^2} \left[\frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \left(\frac{1}{\sin \theta} \right) \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \left(\frac{1}{\sin^2 \theta} \right) \frac{\partial^2}{\partial \phi^2} \right] \quad (7.3.1)$$

The stationary-state Schrodinger equation in spherical coordinates is therefore:

$$-\frac{\hbar^2}{2mr^2} \left[\frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \left(\frac{1}{\sin \theta} \right) \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \left(\frac{1}{\sin^2 \theta} \right) \frac{\partial^2}{\partial \phi^2} \right] \psi(r, \theta, \phi) + V(r, \theta, \phi) \psi(r, \theta, \phi) = E \psi(r, \theta, \phi) \quad (7.3.2)$$

Our goal is to collect similar variables, and before we use our usual trick, we can get a head start on that by removing the r^{-2} factor from the second and third terms. Collecting all the terms with factors of r on one side of the equation then gives:

$$\left(\frac{1}{\sin \theta} \right) \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) \psi(r, \theta, \phi) + \left(\frac{1}{\sin^2 \theta} \right) \frac{\partial^2}{\partial \phi^2} \psi(r, \theta, \phi) = \frac{2mr^2}{\hbar^2} [V(r, \theta, \phi) - E] \psi(r, \theta, \phi) - \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) \psi(r, \theta, \phi) \quad (7.3.3)$$

Now follow our two-step separation trick: Write the wave function as a product of single-variable functions...

$$\psi(r, \theta, \phi) = R(r) \Theta(\theta) \Phi(\phi) \quad (7.3.4)$$

...and divide the whole equation by the wave function:

$$\frac{1}{\Theta} \left(\frac{1}{\sin \theta} \right) \frac{d}{d\theta} \left(\sin \theta \frac{d}{d\theta} \right) \Theta + \frac{1}{\Phi} \left(\frac{1}{\sin^2 \theta} \right) \frac{d^2}{d\phi^2} \Phi = \frac{2mr^2}{\hbar^2} [V(r, \theta, \phi) - E] - \frac{1}{R} \frac{d}{dr} \left(r^2 \frac{d}{dr} \right) R \quad (7.3.5)$$

We haven't quite separated the angular variables yet, but let's come back to that in a bit. First, we note that the only thing keeping the right-hand side of the equation from containing only functions of r is the potential. This method therefore only helps us when the potential is a function of r , which is the case for point-source potentials, as discussed above. With the left-hand side only a function of the angular coordinates, and the right hand side only functions of r , they must both equal a common constant (which we will for the time being call " C_1 "), giving us (after a bit of rearranging) what is known as the **radial equation**:

$$-\frac{\hbar^2}{2mr^2} \frac{d}{dr} \left(r^2 \frac{d}{dr} \right) R(r) + \frac{\hbar^2 C_1}{2mr^2} R(r) + V(r) R(r) = E R(r) \quad (7.3.6)$$

Plugging C_1 into the right-hand side of Equation 7.3.5, we now set out to separate the angular functions:

$$\frac{1}{\Theta} \left(\frac{1}{\sin \theta} \right) \frac{d}{d\theta} \left(\sin \theta \frac{d}{d\theta} \right) \Theta + \frac{1}{\Phi} \left(\frac{1}{\sin^2 \theta} \right) \frac{d^2}{d\phi^2} \Phi = C_1 \quad (7.3.7)$$

Multiply the equation by $\sin^2 \theta$ and collect the functions of each variable to get:

$$\frac{1}{\Theta} \left[\sin \theta \frac{d}{d\theta} \left(\sin \theta \frac{d}{d\theta} \right) \Theta - C_1 \sin^2 \theta \right] = -\frac{1}{\Phi} \frac{d^2}{d\phi^2} \Phi \quad (7.3.8)$$

Separated at last, we can state that both sides of this equation equal a constant (which we will call " C_2 "), giving us two more differential equations in single variables, the *polar equation* (in θ) and the *azimuthal equation* (in ϕ):

$$\sin \theta \frac{d}{d\theta} \left(\sin \theta \frac{d}{d\theta} \right) \Theta(\theta) - (C_1 \sin^2 \theta + C_2) \Theta(\theta) = 0 \quad (7.3.9)$$

$$\frac{d^2}{d\phi^2} \Phi(\phi) + C_2 \Phi(\phi) = 0 \quad (7.3.10)$$

While the solution to the radial equation depends upon the details of the potential, the solutions to the polar and azimuthal equations do not (other than the fact that the potential is strictly a function of r). We have seen the azimuthal differential equation before, and we can write the solution this way:

$$\Phi(\phi) = A e^{\pm i \sqrt{C_2} \phi} \quad (7.3.11)$$

We cannot go any further to determine constants in this solution without boundary conditions. In our previous encounters with this differential equation, we found our boundary conditions from the potential (e.g. the wave function must vanish at the walls of the infinite square well). That is not the case here, but we *do* have a condition we can impose: If r and θ are held fixed and we change ϕ by some multiple of 2π , then we come back to the same point in space. We therefore insist that the function Φ returns to the same value every time ϕ changes by some multiple of 2π . This is ensured by insisting that the constant $\sqrt{C_2}$ is an integer. For reasons that will become clear later (and with the ancillary benefit of not confusing it with the mass of the particle), we name this integer " m_l ," giving us:

$$\Phi_{m_l}(\phi) = A e^{i m_l \phi}, \quad m_l = 0, \pm 1, \pm 2, \dots \quad (7.3.12)$$

The solution to the polar equation, while it doesn't depend upon the potential, is no picnic, and we will not delve into that bit of mathematics. Its solution is called a *Legendre polynomial*, and like the azimuthal case, there is a periodic boundary condition involved, which once again introduces an integer-valued variable, this time related to the constant C_1 , which we call " l ." Specifically, it turns out:

$$C_1 = -l(l+1), \quad l = 0, 1, 2, \dots \quad (7.3.13)$$

Notice that the polar equation also includes the constant C_2 , which means its solution also depends upon m_l . Indeed, this links the integers l and m_l intimately, which explains the subscript on m_l . For this reason, the functions $\Theta_{l m_l}(\theta)$ and $\Phi_{m_l}(\phi)$ are usually thrust together to make a single function (called *spherical harmonic* functions, which have been solved, and can simply be looked-up) of both variables, and this new function includes both quantum numbers (typically the " l " subscript in m_l is suppressed in the variable representing this function, as the relationship between the two quantum numbers m and l is understood, and in this context m is not going to be confused with the mass):

$$Y_{lm}(\theta, \phi) = \Theta_{l m_l}(\theta) \Phi_{m_l}(\phi) \quad (7.3.14)$$

[Note: In the literature, the indices defining spherical harmonics are frequently written with the m_l index raised: $Y_l^{m_l}$.]

For a given value of l , it so happens that m_l can take on only a limited number of values:

$$m_l = 0, \pm 1, \pm 2, \dots, \pm l \quad (7.3.15)$$

That is, the absolute value of m_l can never exceed l .

Plugging in for the value of C_1 removes the unknown constant from the radial equation:

$$-\frac{\hbar^2}{2mr^2} \frac{d}{dr} \left(r^2 \frac{d}{dr} \right) R(r) - \frac{\hbar^2 l(l+1)}{2mr^2} R(r) + V(r) R(r) = E R(r) \quad (7.3.16)$$

If the particle is bound, then this equation will give quantized partial wave functions $R_{nl}(r)$ (from the presence of the $l(l+1)$ in the radial equation, it seems clear that the radial wave function will have dependence on the quantum number l as well as the quantum number n that comes from its own differential equation), and we will once again have three quantum numbers: n , l , and m_l .

Just for completeness, we can put the wave function of the stationary state back together:

$$\psi_{nlm_l}(r, \theta, \phi) = AR_{nl}(r) Y_{lm}(\theta, \phi) \quad (7.3.17)$$

All that remains is to plug in the radial potential and use the boundary conditions to solve the differential equation for $R_{nl}(r)$.

While these names may not make sense just yet, these quantum numbers are referred to as the **principle quantum number** (n), the **orbital quantum number** (l), and the **magnetic quantum number** (m_l).

The Free Particle

From our work with the free particle in Cartesian coordinates, it is clear that it is the easiest coordinate system to use when one wishes to discuss plane waves. But as we have mentioned many times before, plane waves are not the only energy eigenstate wave functions. There is in fact a common energy eigenstate for which spherical coordinates are ideal. It is called a **spherical wave**, as it emanates radially outward from (or inward toward) a single point, which of course is the origin of our spherical coordinates. This is more often encountered when discussing light rather than massive particles (as light is frequently emitted from a point source), but as we have seen before, quantum mechanics treats both as "quanta."

For reasons we will see when we discuss the hydrogen atom next, a radially spreading (or contracting) wave function has an l -value equal to zero (and therefore a zero m_l -value as well), and it is left as an exercise to show that this wave function satisfies the free-particle ($V(r) = 0$), radially-outward ($l = 0$) radial equation:

$$\psi(r) = A \frac{e^{\pm ikr}}{r}, \quad E = \frac{\hbar^2 k^2}{2m} \quad (7.3.18)$$

The positive-valued exponent corresponds to the wave that moves radially-outward. Notice that the probability density is simply $\frac{1}{r^2}$, which reflects an inverse-square reduction in intensity when one converts this single particle wave function to a steady-state stream of particles. Also notice that like the plane wave, this wave function cannot be normalized. And finally, as is always the case with energy eigenstates, we can attach the time-dependence by multiplying the stationary-state solution by the usual $e^{-i\omega t}$.

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