4.3 Solution of the Schrödinger Equation Using Spherical Coordinates

If the potential function has spherical symmetry, such that $V(\mathbf{r}) = V(r)$, (a central force) it is natural to express the Schrödinger Equation in terms of spherical coordinates:

$$x = r\sin\theta\cos\phi, \qquad y = r\sin\theta\sin\phi, \qquad z = r\cos\theta \tag{4.23}$$

$$r \geq 0, \qquad 0 \leq \theta \leq \pi, \qquad 0 \leq \phi < 2\pi \tag{4.24}$$

with the inverse transformations:

$$r^2 = x^2 + y^2 + z^2, \qquad \cos\theta = \frac{z}{\sqrt{x^2+y^2+z^2}}, \qquad \tan(\phi) = \frac{y}{x} \tag{4.25}$$

A volume element in spherical coordinates is:

$$dV = d^3r = r^2 \sin\theta \, dr \, d\theta \, d\phi \tag{4.26}$$

It is frequently convenient to make a change of variables, $\mu = \cos\theta$. Then $d\mu = -\sin\theta d\theta$. As θ varies from 0 to π, $\cos\theta$ varies from 1 to -1. In volume integrals:

$$\int_0^\infty \int_0^\pi \int_0^{2\pi} f(r,\theta,\phi)\, r^2 \sin\theta \, dr \, d\theta \, d\phi$$

$$= -\int_0^\infty \int_1^{-1} \int_0^{2\pi} f(r,\mu,\phi) r^2 dr \, d\mu \, d\phi =$$

$$= \int_0^\infty \int_{-1}^{1} \int_0^{2\pi} f(r,\mu,\phi) r^2 dr \, d\mu \, d\phi$$

In spherical coordinates:

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r}\right) + \frac{1}{r^2 \sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta \frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\left(\frac{\partial^2}{\partial\phi^2}\right) \tag{4.27}$$

Changing from θ to $\mu = \cos\theta$, so that:

$$\frac{\partial}{\partial\theta} = \frac{\partial}{\partial\mu}\frac{d\mu}{d\theta} = -\sin\theta \frac{\partial}{\partial\mu} \tag{4.28}$$

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r}\right) + \frac{1}{r^2 \sin\theta}\sin\theta\frac{\partial}{\partial\mu}\left(\sin^2\theta \frac{\partial}{\partial\mu}\right) + \frac{1}{r^2\sin^2\theta}\left(\frac{\partial^2}{\partial\phi^2}\right) \tag{4.29}$$

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2}\frac{\partial}{\partial \mu}\left((1-\mu^2)\frac{\partial}{\partial \mu}\right) + \frac{1}{r^2(1-\mu^2)}\left(\frac{\partial^2}{\partial \phi^2}\right) \quad (4.30)$$

We can now write the time-independent Schrödinger Equation as:

$$\begin{aligned} &\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial \psi}{\partial r}\right) + \frac{1}{r^2}\frac{\partial}{\partial \mu}\left((1-\mu^2)\frac{\partial \psi}{\partial \mu}\right) \\ &+\frac{1}{r^2(1-\mu^2)}\left(\frac{\partial^2 \psi}{\partial \phi^2}\right) + \frac{2m}{\hbar^2}(E - V(r))\psi = 0 \quad (4.31) \end{aligned}$$

Multiplying by r^2:

$$\begin{aligned} &\frac{\partial}{\partial r}\left(r^2\frac{\partial \psi}{\partial r}\right) + \frac{2mr^2}{\hbar^2}(E - V(r))\psi \\ &+\frac{\partial}{\partial \mu}\left((1-\mu^2)\frac{\partial \psi}{\partial \mu}\right) + \frac{1}{(1-\mu^2)}\left(\frac{\partial^2 \psi}{\partial \phi^2}\right) = 0 \quad (4.32) \end{aligned}$$

Using operator notation we can write this as:

$$\hat{D}(r)\psi + \hat{K}(\mu, \phi)\psi = 0 \quad (4.33)$$

$$\hat{D}(r) = \frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{2mr^2}{\hbar^2}(E - V(r))$$

$$\hat{K}(\mu, \phi) = +\frac{\partial}{\partial \mu}\left((1-\mu^2)\frac{\partial}{\partial \mu}\right) + \frac{1}{(1-\mu^2)}\left(\frac{\partial^2}{\partial \phi^2}\right)$$

The operator $\hat{D}$ depends only on r and the operator $\hat{K}$ depends only on the angle variables (μ and ϕ).

Clearly we can separate out the dependence on r by writing:

$$\psi = R(r)Y(\theta, \phi) = R(r)Y(\mu, \phi)$$

which by substitution into Eq. 4.33 yields:

$$\left(\hat{D}(r)R(r)\right)Y(\mu, \phi) + \left(\hat{K}(\mu, \phi)Y(\theta, \phi)\right)R(r) = 0$$

Dividing through by RY:

$$\frac{1}{R(r)}\hat{D}(r)R(r) + \frac{1}{Y(\mu, \phi)}\hat{K}(\mu.\phi)Y(\mu, \phi) = 0$$

This can be valid only if the two terms are equal and opposite constants. Denote the constant by C:

$$\hat{D}(r)R = CR, \qquad \hat{K}(\mu,\phi)Y = -CY$$

Looking ahead to the solution of the radial equation, we write the separation constant in the form, $C = l(l+1)$, where l at this point is just another constant. The explicit radial equation is:

$$\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) + \left[\frac{2mr^2}{\hbar^2}(E - V(r)) - l(l+1)\right]R = 0 \tag{4.34}$$

4.3.1 The angular equation

The angular part of the equation is independent of the potential, provided of course that the potential is a central force potential depending only on r. Thus this part of the equation is the same for a large variety of problems, so we investigate its solution first. The angular equation is:

$$\frac{\partial}{\partial \mu}\left((1-\mu^2)\frac{\partial Y}{\partial \mu}\right) + \frac{1}{1-\mu^2}\left(\frac{\partial^2 Y}{\partial \phi^2}\right) = -l(l+1) \tag{4.35}$$

Multiplying by $1-\mu^2$:

$$(1-\mu^2)\frac{\partial}{\partial \mu}\left((1-\mu^2)\frac{\partial Y}{\partial \mu}\right) + l(l+1)(1-\mu^2)Y + \left(\frac{\partial^2 Y}{\partial \phi^2}\right) = 0 \tag{4.36}$$

which we can write in operator form as:

$$\hat{L}(\mu)Y + \hat{M}(\phi)Y = 0 \tag{4.37}$$

where:

$$\hat{L} \equiv (1-\mu^2)\frac{\partial}{\partial \mu}\left((1-\mu^2)\frac{\partial}{\partial \mu}\right) + l(l+1)(1-\mu^2)$$

and:

$$\hat{M} \equiv \frac{\partial^2 Y}{\partial \phi^2}$$

We can now write $Y = \Theta(\mu)\Phi(\phi)$ to obtain:

$$\frac{1}{\Theta}\hat{L}\Theta + \frac{1}{\Phi}\hat{M}\Phi = 0$$

Each term must separately be constant:

$$\frac{1}{\Phi}\hat{M}\Phi = C = -\frac{1}{\Theta}\hat{L}\Theta$$

Solutions for $\Phi(\phi)$

The solution for Φ is immediate. The differential equation is:

$$\frac{\partial^2 \Phi}{\partial \phi^2} = C\Phi \tag{4.38}$$

so that:

$$\Phi = e^{\pm\sqrt{C}\phi} \tag{4.39}$$

There is a special boundary condition associated with the variable ϕ, namely that $\phi + 2\pi$ is the same as ϕ. Therefore:

$$e^{\pm\sqrt{C}\phi + 2\pi} = e^{\pm\sqrt{C}\phi}$$

$$e^{\pm\sqrt{C}2\pi} = 1 = e^{\pm 2m\pi i}, \qquad m = 0, 1, 2, \cdots$$

so $\sqrt{(C)} = im$, and $C = -m^2$. We can eliminate the $\pm$ symbol in the solution for Φ by allowing m to be any integer from $-\infty$ to ∞. The final result is:

$$\Phi = e^{im\phi}, \quad m = 0, \pm 1, \pm 2, \cdots \tag{4.40}$$

Solutions for $\Theta(\mu)$

Substituting $C = -m^2$ into the equation for Θ:

$$\left[\frac{\partial}{\partial \mu}\left((1-\mu^2)\frac{\partial \Theta}{\partial \mu}\right)\right] + \left[l(l+1) - \frac{m^2}{1-\mu^2}\right]\Theta = 0 \tag{4.41}$$

$$(1-\mu^2)\frac{\partial^2 \Theta}{\partial \mu^2} - 2\mu\frac{\partial \Theta}{\partial \mu} + \left[l(l+1) - \frac{m^2}{1-\mu^2}\right]\Theta = 0 \tag{4.42}$$

Since this equation depends only on m^2, its solution for negative and positive values of m will be the same. In the following we will take $m \geq 0$.

The solution for Θ (which is not a polynomial):

$$\Theta_l^m(\mu) = C(1-\mu^2)^{m/2}\frac{d^m P_l(\mu)}{d\mu^m} \tag{4.43}$$

where C is an arbitrary constant. The solutions for $m \neq 0$ are called the associated Legendre functions

The solutions for $\Theta(\mu)$ with the classical normalization can be represented by the Rodriguez formula:

$$P_l^m = \frac{(1-\mu^2)^{m/2}}{2^l l!}\frac{d^{\,l+m}}{dx^{l+m}}(\mu^2 - 1)^l \tag{4.44}$$

If we set $m = 0$ we get the Legendre polynomials. There are a number of useful recursion relations relating successive orders of the Legendre and associated Legendre polynomials. Some of these are listed in your text book.

What do we do about $-m$? There are various conventions. Griffiths sets $P_l^{-m} = P_l^m$.

4.3.2 Spherical Harmonics

We can multiply the solutions for $\Theta(\mu)$ by the functions $\Phi = e^{im\phi}$ to obtain the solutions:

$$Y_l^m(\theta, \phi) = C_l^m P_l^m(\cos\theta) e^{im\phi} \tag{4.45}$$

for the angular part of the Schrödinger Equation in spherical coordinates.

All that remains is to determine the normalization constant. It is customary to normalize the angular part of the solution separately from the radial part. We can think of this as normalizing the angular functions on the unit sphere. The normalization condition is:

$$1 = \int |\psi|^2\, r^2\, \sin\theta\, d\theta\, d\phi = \int |\psi|^2 r^2\, d\mu d\phi = \int_0^\infty |R(r)|^2 r^2\, dr \int |Y_l^m|^2 d\mu\, d\phi \tag{4.46}$$

We normalize $R(r)$ and $Y(\theta, \phi)$ separately:

$$\int_0^\infty |R(r)|^2 r^2\, dr = 1 \tag{4.47}$$

and:

$$\int_{-1}^1 \int_0^{2\pi} |Y_l^m|^2\, d\mu\, d\phi = 1 \tag{4.48}$$

The normalized functions are:

$$Y_l^m(\theta, \phi) = \epsilon \sqrt{\frac{(2l+1)}{4\pi} \frac{(l-|m|)!}{(l+|m|)!}} e^{im\phi} P_l^m(\mu) \tag{4.49}$$

where $\epsilon = (-1)^m$ for $m \geq 0$, and $\epsilon = 1$ for $m < 0$.

4.4 Angular Momentum: Operators and Eigenfunctions

How can we interpret the angular dependence (which can get quite complicated for increasing values of l and m) of the wave function. Clearly the angular functions are eigenfunctions of differential operators. For example:

$$\frac{d\Phi}{d\phi} = im\Phi, \qquad \left[\frac{1}{i}\frac{d}{d\phi}\right] \Phi(\phi) = m\Phi \tag{4.50}$$

To understand this operator in terms of a physical observable, recall that the derivatives arose from the presence of $p^2/2m$ in the Hamiltonian. We will interpret the differential operator in terms of momentum.

Recalling that $x = r\sin\theta\cos\phi$ and that $y = r\sin\theta\sin\phi$, it follows that:

$$\frac{\partial}{\partial\phi} = -r\sin\theta\sin\phi\frac{\partial}{\partial x} + r\sin\theta\cos\phi\frac{\partial}{\partial y} = -y\frac{\partial}{\partial x} + x\frac{\partial}{\partial y} \tag{4.51}$$

Then, using the operator interpretation of the Cartesian derivatives, it follows that:

$$\frac{\hbar}{i}\frac{\partial}{\partial\phi} = xp_y - yp_x = L_z \tag{4.52}$$

where L_z is the z component of the angular momentum of the particle. We then have the eigenvalue equation:

$$L_z\Phi = m\hbar\Phi \tag{4.53}$$

If ϕ dependence is described by eigenfunction Φ_m, then it follows that:

$$L_z\Psi = m\hbar\Psi \tag{4.54}$$

and $\langle L_z\rangle = m\hbar$. The eigenvalues associated with a measurement of the z component of the angular momentum are $m\hbar$. The choice of the z axis is arbitrary, but certain physical situations can lead to a natural choice, as we will see later.

Now that we have had so much success in interpreting Φ_m let us see what we can do with the θ eigenfunctions.

Let's pursue the angular momentum connection farther. The classical definition of the components of angular momentum is:

$$L_x = yp_z - zp_y, \qquad L_y = zp_x - xp_z, \qquad L_z = xp_y - yp_x \tag{4.55}$$

Before trying to express these operators in spherical coordinates, we can investigate their commutative properties:

$$[L_x, L_y] = [yp_z - zp_y, zp_x - xp_z] = [yp_z, zp_x] - [yp_z, xp_z] - [zp_y, zp_x] + [zp_y, xp_z]$$

Remembering that x doesn't commute with p_x and does commute with p_y and p_z, i.e. $[x_i, p_j] = i\hbar\delta_{ij}$, this reduces to:

$$[L_x, L_y] = [yp_z, zp_x] + [zp_y, xp_z] = yp_x[p_z, z] + xp_y[z, p_z]$$

$$= i\hbar(xp_y - yp_x) = i\hbar L_z$$

so:

$$[L_x, L_y] = i\hbar L_z \tag{4.56}$$

Similarly, by permuting the indices:

$$[L_y, L_z] = i\hbar L_x, \qquad [L_z, L_x] = i\hbar L_y \tag{4.57}$$

Neither L_x nor L_y commute with L_z, so there is no possibility for the eigenfunctions of L_z to be eigenfunctions of L_x or L_y.

We can also check out the magnitude of the angular momentum to see if it might commute with L_z.

$$[L^2, L_z] = [L_x^2, L_z] + [L_y^2, L_z]$$

$$= L_x[L_x, L_z] + [L_x, L_z]L_x + L_y[L_y, L_z] + [L_y, L_z]L_y$$

$$= -i\hbar L_x L_y - i\hbar L_y L_x + i\hbar L_y L_x + i\hbar L_x L_y = 0$$

$$[L^2, L_z] = 0 \tag{4.58}$$

Since the two operators commute, it should be possible to find simultaneous eigenfunctions of L^2 and L_z. Perhaps we have already found them. We know that:

$$L_z Y_l^m = m\hbar Y_l^m \tag{4.59}$$

What are the simultaneous eigenfunctions of L^2 and L_z?

$$L^2 F = \alpha F, \qquad L_z F = m\hbar F \tag{4.60}$$

$$(L_x^2 + L_y^2 + L_z^2)F = (L_x^2 + L_y^2)F + m^2\hbar^2 F = \alpha F \tag{4.61}$$

We want to find the solutions of:

$$(L_x^2 + L_y^2)F + (m^2\hbar^2 - \alpha)F = 0 \tag{4.62}$$

First, let's express the operators L_x and L_y in terms of derivatives. We need:

$$\frac{\partial r}{\partial x} = \frac{x}{r} = \sin\theta\cos\phi \tag{4.63}$$

$$\frac{\partial r}{\partial y} = \frac{y}{r} = \sin\theta\sin\phi \tag{4.64}$$

$$\frac{\partial r}{\partial z} = \frac{z}{r} = \cos\theta \tag{4.65}$$

$$\frac{\partial \theta}{\partial x} = \frac{zx}{r^3\sin\theta} = \frac{\cos\theta\cos\phi}{r} \tag{4.66}$$

$$\frac{\partial\theta}{\partial y} = \frac{zy}{r^3\sin\theta} = \frac{\cos\theta\sin\phi}{r} \tag{4.67}$$

$$\frac{\partial\theta}{\partial z} = \frac{z^2 - r^2}{r^3\sin\theta} = -\frac{\sin\theta}{r} \tag{4.68}$$

$$\frac{\partial\phi}{\partial x} = -\frac{\sin\phi}{r\sin\theta} \tag{4.69}$$

$$\frac{\partial\phi}{\partial y} = \frac{\cos\phi}{r\sin\theta} \tag{4.70}$$

$$\frac{i}{\hbar}yp_z = r\sin\theta\sin\phi[\frac{\partial r}{\partial z}\frac{\partial}{\partial r} + \frac{\partial\theta}{\partial z}\frac{\partial}{\partial\theta} + \frac{\partial\phi}{\partial z}\frac{\partial}{\partial\phi}] \tag{4.71}$$

$$\frac{i}{\hbar}yp_z = \sin\theta\sin\phi[r\cos\theta\frac{\partial}{\partial r} - \sin\theta\frac{\partial}{\partial\theta}] \tag{4.72}$$

$$\frac{i}{\hbar}zp_y = \cos\theta[r\sin\theta\sin\phi\frac{\partial}{\partial r} + \cos\theta\sin\phi\frac{\partial}{\partial\theta} + \frac{\cos\phi}{\sin\theta}\frac{\partial}{\partial\phi}] \tag{4.73}$$

$$\frac{i}{\hbar}L_x = -\sin\phi\frac{\partial}{\partial\theta} - \frac{\cos\phi}{\sin\theta}\frac{\partial}{\partial\phi} \tag{4.74}$$

Similarly:

$$\frac{i}{\hbar}L_y = \cos\phi\frac{\partial}{\partial\theta} - \frac{\sin\phi}{\sin\theta}\frac{\partial}{\partial\phi} \tag{4.75}$$

The angular momentum operators depend only on the angles, θ and ϕ. Thus, the common eigenfunctions of L^2 and L_z must depend only on θ and ϕ.

Using these results we can show that:

$$L^2Y_l^m = l(l+1)\hbar^2Y_l^m$$

Rather than doing this now, we will derive this result later using a more general algebraic argument.

4.5 The Radial Equation

$$\frac{d}{dr}\left(r\frac{dR}{dr}\right) - \frac{2mr^2}{\hbar^2}[V(r) - E]R = l(l+1)R \tag{4.76}$$

The equation is simpler with the following change:

$$u(r) = rR(r) \tag{4.77}$$