ANGULAR MOMENTUM

Now that we have obtained the general eigenvalue relations for angular momentum directly from the operators, we want to learn about the associated wave functions. Returning to spherical polar coordinates, we recall that the angular momentum operators are given by:

$$\hat{L}_x = -i\hbar\left(-\sin\phi\frac{\partial}{\partial\theta} - \cot\theta\cos\phi\frac{\partial}{\partial\phi}\right)$$

$$\hat{L}_y = -i\hbar\left(\cos\phi\frac{\partial}{\partial\theta} - \cot\theta\sin\phi\frac{\partial}{\partial\phi}\right)$$

$$\hat{L}_z = -i\hbar\frac{\partial}{\partial\phi}$$

$$\hat{L}^2 = \hat{L}_x^2 + \hat{L}_Y^2 + \hat{L}_z^2 \quad \Rightarrow \hat{L}^2 = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]$$

In terms of these, our original Schrödinger Equation for rigid rotations was

$$\hat{H}Y_l^m = \frac{\hat{L}^2}{2I}Y_l^m = E_l Y_l^m$$

$$\Rightarrow \frac{-\hbar^2}{2I}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]Y_l^m(\theta,\phi) = E_l Y_l^m(\theta,\phi)$$

where l was the quantum number for $\hat{L}^2$ and m was the quantum number for $\hat{L}_z$. Taking what we learned in the last section about the eigenvalues of $\hat{L}^2$ and $\hat{L}_z$ we can say that at most we can have

$$l = 0, \tfrac{1}{2}, 1, \tfrac{3}{2}, 2, \ldots \qquad m = -l, -l+1, \ldots, l$$

We will see that there is an additional restriction on the possible values of l in the present case, but these are the possible values for the quantum numbers. In terms of the quantum numbers, we have the eigenvalue relations

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

$$\hat{L}_z Y_l^m = \hbar m Y_l^m$$

Now, the functions, Y_l^m, that satisfy these relations for rigid rotations are called **Spherical Harmonics**. It is possible to derive the spherical harmonics by solving the 2D differential equation above. McQuarrie goes through a fairly complete derivation and we outline that solution in the appendix to these notes (below). The result is that:

$$Y_l^m(\theta,\phi) = A_{lm} P_l^{|m|}(\cos\theta)\, e^{im\phi}$$

where A_{lm} is a normalization constant and $P_l^{|m|}(x)$ is an associated Legendre Polynomial. The first few Associated Legendre Polynomials are:

$$P_0^0(\cos\theta) = 1 \qquad P_1^0(\cos\theta) = \cos\theta$$

$$P_1^1(\cos\theta) = \sin\theta \qquad P_2^0(\cos\theta) = \tfrac{1}{2}\left(3\cos^2\theta - 1\right)$$

$$P_2^1(\cos\theta) = 3\cos\theta\sin\theta \qquad P_2^2(\cos\theta) = 3\sin^2\theta$$

There are a number of important features of the Spherical Harmonics we can recognize simply by inspecting these solutions:

- The wavefunctions factorize into a product of a function of θ and a function of ϕ.

  $$Y_l^m(\theta,\phi) \propto f(\theta)\, g(\phi)$$

  This result is very reminiscent of the result we found for separable Hamiltonians, which is somewhat surprising because the Hamiltonian certainly did not appear at first sight to be separable into a Hamiltonian for θ and a Hamiltonian for ϕ:

  $$\hat{H} = \frac{-\hbar^2}{2I}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right] \neq \hat{H}_\theta + \hat{H}_\phi$$

  However, physically it makes some sense for the motion along θ and ϕ to separate: we haven't applied any potential that links them together so particles should be free to move along θ and ϕ independently, just as particles in a separable potential in x and y can move independently along those axes. The θ-ϕ cross terms above reflect the **curvature** of the 2D surface the particles are moving on.
- It is easy to verify that these functions are eigenstates of $\hat{L}_z$:

  $$\hat{L}_z Y_l^m = -i\hbar\frac{\partial}{\partial\phi}Y_l^m = -i\hbar\frac{\partial}{\partial\phi}A_{lm}P_l^{|m|}(\cos\theta)e^{im\phi} = \hbar m A_{lm}P_l^{|m|}(\cos\theta)e^{im\phi} = \hbar m Y_l^m$$

  They are also eigenfunctions of $\hat{L}^2$, as can be proven for any given Y_l^m (after some algebra) by computing $\hat{L}^2 Y_l^m$ and verifying that the result is just $\hbar^2 l(l+1)Y_l^m$.
- We can now see why half-integer values of l are not allowed here. Recall that ϕ is the angle in the x-y plane and it varies from 0 to 2π. What should happen to $Y_l^m(\theta,\phi)$ when $\phi \to \phi + 2\pi$? Of course, the value of the wavefunction should not change because by incrementing ϕ by 2π: we've

just moved the particle around in a full circle. Thus, for the wave function to be **single-valued**, we must have:

$$Y_l^m(\theta,\phi) = Y_l^m(\theta,\phi+2\pi)$$

$$\Rightarrow \cancel{A_{lm}P_l^{|m|}}(\cos\theta)e^{im\phi} = \cancel{A_{lm}P_l^{|m|}}(\cos\theta)e^{im(\phi+2\pi)}$$

$$\Rightarrow e^{im\phi} = e^{im(\phi+2\pi)}$$

$$\Rightarrow \cancel{e^{im\phi}} = \cancel{e^{im\phi}} e^{im2\pi}$$

$$\Rightarrow 1 = e^{im2\pi}$$

$$\Rightarrow m = \text{an integer}$$

thus, m must be an integer, no matter what value of l we choose. However, since the minimal value for m <u>**is**</u> l, l must also be an integer. This continuity argument is the reason why half integer values of l are not allowed for rigid rotations.

- Note that there are a few interesting algebraic features of the spherical harmonics: 1) the ϕ part of the wavefunction does not depend on l 2) The l^{th} order Legendre polynomial always involves sums of products of sines and cosines such that the sum of the sine and cosine powers is less than or equal to l 3) for $m \neq 0$ the spherical Harmonics are complex and $Y_l^m{}^* = Y_l^{-m}$. Thus, one can obtain two real functions from each $\pm m$ pair via

$$R_l^m = \tfrac{1}{\sqrt{2}}\left(Y_l^m + Y_l^{-m}\right) \qquad I_l^m = \tfrac{1}{i\sqrt{2}}\left(Y_l^m - Y_l^{-m}\right)$$

  These features are helpful in trying to identify, when given an arbitrary function of the angles, which spherical harmonics might contribute to that function.

- Typically, the spherical Harmonics are associated with letters as you have seen in your previous chemistry courses. Thus, l=0 is 's', l=1 is 'p', l=2 is 'd' ….
- In the absence of a potential, as is the case for rigid rotations, the spherical Harmonics are $2l+1$-fold degenerate:

$\underline{l}$	$\underline{m}$	$\underline{Y_l^m\text{'s}}$	$\underline{2l+1}$
0	0	Y_0^0	1
1	-1, 0, 1	$Y_1^{-1},\ Y_1^0,\ Y_1^1$	3
2	-2, -1, 0, 1, 2	$Y_2^{-2},\ Y_2^{-1},\ Y_2^0,\ Y_2^1,\ Y_2^2$	5
3	-3, -2, -1, 0, 1, 2, 3	$Y_3^{-3},\ Y_3^{-2},\ Y_3^{-1},\ Y_3^0,\ Y_3^1,\ Y_3^2,\ Y_3^3$	7

As discussed previously, we should expect this degeneracy to be broken if we apply a potential that is not spherically symmetric. In the presence of a potential, we expect these levels to be split.

Thus, to summarize, for the spherical Harmonics we have:

$$\boxed{\begin{gathered} Y_l^m(\theta,\phi) = A_{lm} P_l^{|m|}(\cos\theta)\, e^{im\phi} \\ \hat{L}^2 Y_l^m = L^2 Y_l^m = \hbar^2 l(l+1) Y_l^m \qquad l = 0,1,2,3\ldots \\ \hat{L}_z Y_l^m = \hbar m Y_l^m \qquad m = -l, -l+1, \ldots, l \end{gathered}}$$

APPENDIX: SOLVING FOR THE SPHERICAL HARMONICS

We need to solve the differential equation

$$-\frac{\hbar^2}{2I}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right] Y(\theta,\phi) = EY(\theta,\phi)$$

This is $\hat{H}Y(\theta,\phi) = EY(\theta,\phi)$ for Rigid rotations. Rearranging the Equation,

$$\underbrace{\left[\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{2IE}{\hbar^2}\sin^2\theta\right]}_{\text{only } \theta} Y(\theta,\phi) = \underbrace{-\frac{\partial^2}{\partial\phi^2}}_{\text{only } \phi} Y(\theta,\phi)$$

We've separated the variables, just as in the 3D harmonic oscillator.

$\therefore$ Try $Y(\theta,\phi) = \Theta(\theta)\Phi(\phi)$ as a solution

Define $\beta \equiv \dfrac{2IE}{\hbar^2}$ $\quad (\text{note } \beta \propto E)$

$$\left[\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \beta\sin^2\theta\right]\Theta(\theta)\Phi(\phi) = -\frac{\partial^2}{\partial\phi^2}\Theta(\theta)\Phi(\phi)$$

Dividing by $\Theta(\theta)\Phi(\phi)$ and simplifying

$$\underbrace{\frac{\sin\theta}{\Theta(\theta)}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)\Theta(\theta)+\beta\sin^2\theta}_{\text{only }\theta}=\underbrace{-\frac{1}{\Phi(\phi)}\frac{\partial^2}{\partial\phi^2}\Phi(\phi)}_{\text{only }\phi}$$

Since θ and ϕ are independent variables, each side of the equation must be equal to a constant $\equiv m^2$.

$$\Rightarrow \qquad \boxed{\frac{1}{\Phi(\phi)}\frac{\partial^2}{\partial\phi^2}\Phi(\phi)=-m^2} \qquad \text{I}$$

and $$\Rightarrow \qquad \boxed{\frac{\sin\theta}{\Theta(\theta)}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)\Theta(\theta)+\beta\sin^2\theta=m^2} \qquad \text{II}$$

First solve for $\Phi(\phi)$ using I

$$\frac{\partial^2\Phi(\phi)}{\partial\phi^2}=-m^2\Phi(\phi)$$

Solutions are $\Phi(\phi)=A_m e^{im\phi}$ and $A_{-m}e^{-im\phi}$

Boundary conditions $\Rightarrow$ quantization

$$\Phi(\phi+2\pi)=\Phi(\phi)$$

$$\Rightarrow \qquad A_m e^{im(\phi+2\pi)}=A_m e^{im\phi} \quad \text{and} \quad A_{-m}e^{-im(\phi+2\pi)}=A_{-m}e^{-im\phi}$$

$$\therefore \qquad e^{im(2\pi)}=1 \quad \text{and} \quad e^{-im(2\pi)}=1$$

This is only true if $\boxed{m=0,\ \pm1,\ \pm2,\ \pm3,....}$

m is the "magnetic" quantum number

$$\therefore \qquad \Phi(\phi)=A_m e^{im\phi} \qquad m=0,\ \pm1,\ \pm2,\ \pm3,....$$

Normalization: $\int_0^{2\pi} \Phi^*(\phi)\Phi(\phi)\,d\phi = 1$

$$\Rightarrow \qquad \Phi(\phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi} \qquad m = 0,\ \pm 1,\ \pm 2,\ \pm 3, \ldots$$

Now let's look at $\Theta(\theta)$. Need to solve II

$$\frac{\sin\theta}{\Theta(\theta)} \frac{\partial}{\partial\theta}\left(\sin\theta \frac{\partial}{\partial\theta}\right)\Theta(\theta) + \beta \sin^2\theta = m^2$$

Change variables: $x = \cos\theta \qquad \Theta(\theta) = P(x) \qquad \dfrac{dx}{-\sin\theta} = d\theta$

Since $0 \le \theta \le \pi \quad \Rightarrow \quad -1 \le x \le +1$

Also $\sin^2\theta = 1 - \cos^2\theta = 1 - x^2$

This equation turns out to be Legendre's equation in terms of Θ:

$$\sin\theta \frac{d}{d\theta}\left[\sin\theta \frac{d\Theta}{d\theta}\right] + \left(\beta \sin^2\theta - m^2\right)\Theta(\theta) = 0$$

which we can re-write:

$$\sin^2\theta \frac{d^2\Theta}{d\theta^2} + \sin\theta\cos\theta \frac{d\Theta}{d\theta} + \left(\beta \sin^2\theta - m^2\right)\Theta(\theta) = 0$$

Let $x = \cos\theta$ and $\Theta(\theta) = P(x)$.

$$\frac{d\Theta}{d\theta} = \frac{dP}{dx}\frac{dx}{d\theta} = -\sin\theta \frac{dP}{dx} = -\left(1 - x^2\right)^{1/2} \frac{dP}{dx}$$

$$\frac{d^2\Theta}{d\theta^2} = \frac{d}{d\theta}\left[\frac{d\Theta}{d\theta}\right] = \left[\frac{dx}{d\theta}\right]\frac{d}{dx}\left[-\left(1 - x^2\right)^{1/2}\frac{dP}{dx}\right]$$

$$= -\sin\theta \left[\frac{x}{\left(1 - x^2\right)^{1/2}}\frac{dP}{dx} - \left(1 - x^2\right)^{1/2}\frac{d^2P}{dx^2}\right]$$

$$= -x\frac{dP}{dx} + \left(1 - x^2\right)\frac{d^2P}{dx^2}$$

Substituting these results into Legendre's equation gives

$$\left(1-x^2\right)^2 \frac{d^2P}{dx^2} - 2x\left(1-x^2\right)\frac{dP}{dx} + \left(\beta\left(1-x^2\right) - m^2\right)P(x) = 0$$

Divide by $\left(1-x^2\right)$ to obtain the Legendre equation in a convenient form:

$$\left(1-x^2\right)\frac{d^2P}{dx^2} - 2x\frac{dP}{dx} + \left[\beta - \frac{m^2}{1-x^2}\right]P(x) = 0$$

The solutions to this equation are known, but very messy. They are called the associated Legendre polynomials, $P_l^{|m|}(x)$. Note that they only depend on $|m|$ because the equation depends on m^2:

$$P_l^{|m|}(x) = P_l^{|m|}(\cos\theta)$$

$$P_0^0(\cos\theta) = 1 \qquad P_2^0(\cos\theta) = \frac{1}{2}\left(3\cos^2\theta - 1\right)$$

$$P_1^0(\cos\theta) = \cos\theta \qquad P_2^1(\cos\theta) = 3\cos\theta\sin\theta$$

$$P_1^1(\cos\theta) = \sin\theta \qquad P_2^2(\cos\theta) = 3\sin^2\theta$$

etc.

So $\Theta(\theta) = A_{lm} P_l^{|m|}(\cos\theta) \qquad A_{lm} = \left[\left(\frac{2l+1}{2}\right)\frac{(l-|m|)!}{(l+|m|)!}\right]^{\frac{1}{2}}$

where A_{lm} is the normalization constant

$$\Rightarrow \qquad A_{lm}^2 \int_0^\pi \left[P_l^{|m|}(\cos\theta)\right]^2 \sin\theta d\theta = 1$$

So now putting it all together:

$$\psi_{lm}(r_0,\theta,\phi) = Y_l^m(\theta,\phi) = \Theta_l^{|m|}(\theta)\Phi_m(\phi)$$

$$Y_l^m(\theta,\phi) = \left[\left(\frac{2l+1}{4\pi}\right)\frac{(l-|m|)!}{(l+|m|)!}\right]^{\frac{1}{2}} P_l^{|m|}(\cos\theta)e^{im\phi}$$

These functions are the <u>spherical harmonics</u>.

SPHERICAL HARMONICS SUMMARY

$$Y_l^m(\theta,\phi) = \Theta_l^{|m|}(\theta)\Phi_m(\phi)$$

$$Y_l^m(\theta,\phi) = \left[\left(\frac{2l+1}{4\pi}\right)\frac{(l-|m|)!}{(l+|m|)!}\right]^{\frac{1}{2}} P_l^{|m|}(\cos\theta)e^{im\phi}$$

$$l = 0,\ 1,\ 2,\ldots \qquad m = 0,\ \pm 1,\ \pm 2,\ \pm 3,\ldots \pm l$$

Y_l^m's are the eigenfunctions to $\hat{H}\psi = E\psi$ for the rigid rotor problem.

$$Y_0^0 = \frac{1}{(4\pi)^{1/2}} \qquad Y_2^0 = \left(\frac{5}{16\pi}\right)^{\frac{1}{2}}\left(3\cos^2\theta - 1\right)$$

$$Y_1^0 = \left(\frac{3}{4\pi}\right)^{\frac{1}{2}}\cos\theta \qquad Y_2^{\pm 1} = \left(\frac{15}{8\pi}\right)^{\frac{1}{2}}\sin\theta\cos\theta e^{\pm i\phi}$$

$$Y_1^1 = \left(\frac{3}{8\pi}\right)^{\frac{1}{2}}\sin\theta e^{i\phi} \qquad Y_2^{\pm 2} = \left(\frac{15}{32\pi}\right)^{\frac{1}{2}}\sin^2\theta e^{\pm 2i\phi}$$

$$Y_1^{-1} = \left(\frac{3}{8\pi}\right)^{\frac{1}{2}}\sin\theta e^{-i\phi}$$

Y_l^m's are <u>orthonormal</u>: $\iint Y_{l'}^{m'*}(\theta,\phi)Y_l^m(\theta,\phi)\sin\theta d\theta d\phi = \delta_{ll'}\delta_{mm'}$

Krönecker delta $\delta_{ll'} = \begin{cases} 1 & \text{if } l = l' \\ 0 & \text{if } l \neq l' \end{cases}$ $\quad \delta_{mm'} = \begin{cases} 1 & \text{if } m = m' & \text{normalization} \\ 0 & \text{if } m \neq m' & \text{orthogonality} \end{cases}$

Note: Switch $l \to J$ conventional for molecular rotational quantum number (e.g.: $l(l+1) \Rightarrow J(J+1) \qquad J = 0,\ 1,\ 2,\ldots.$)