The Eigenvalues and Eigenfunctions of $\hat{L}^2$ and $\hat{L}_z$

Using the usual definitions

$x = r\sin\theta\cos\phi$

$y = r\sin\theta\sin\phi$

$z = r\cos\theta$

It's a straightforward but tedious exercise to show that

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

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

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

Squaring each and summing results in

$$\hat{L}^2 = -\hbar^2\left(\frac{\partial^2}{\partial\theta^2} + \cot\theta\frac{\partial}{\partial\theta} + \left(1+\cot^2\theta\right)\frac{\partial^2}{\partial\phi^2}\right)$$

Which is often written as

$$\hat{L}^2 = -\hbar^2\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)$$

The eigenvalue problem for $\hat{L}_z$ is

$$\hat{L}_z\chi = m\hbar\chi$$

So

$$-i\hbar\frac{d\chi}{d\phi} = m\hbar\chi$$

And if we normalize χ to 1 (over the interval $0 \le \phi \le 2\pi$) we have

$$\chi = \frac{1}{\sqrt{2\pi}}\exp(im\phi)$$

If this is to be single valued $\chi(\phi)=\chi(\phi+2\pi)$ then m must be an integer, either positive or negative. Since the eigenfunctions of $\hat{\vec{L}}^2$ are also eigenfunctions of $\hat{L}_z$ they must have the form $f(\theta)\chi_m(\phi)$ so

$\hat{\vec{L}}^2 f(\theta)\chi_m(\phi)=\lambda\hbar^2 f(\theta)\chi_m(\phi)$ where we extract the units from the eigenvalue so λ is a pure number. Continuing

$$\hat{\vec{L}}^2 f(\theta)\chi_m(\phi)=-\hbar^2\chi_m(\phi)\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}-\frac{m^2}{\sin^2\theta}\right)f(\theta)=\lambda\hbar^2 f(\theta)\chi_m(\phi)$$

and so $f(\theta)$ is determined by the differential equation

$$-\left(\frac{1}{\sin\theta}\frac{d}{d\theta}\sin\theta\frac{d}{d\theta}-\frac{m^2}{\sin^2\theta}\right)f(\theta)=\lambda f(\theta)$$

This solutions differential equation are called the associated Legendre polynomials and are written as $P_\ell^{|m|}(\cos\theta)$ where ℓ is 0 or any positive integer and the eigenvalue $\lambda=\ell(\ell+1)$. Note that these polynomials depend on the absolute value of m since it appears squared in the differential equation. $P_\ell^{|m|}\left(\cos\theta\right)$ may be written in terms of the Legendre polynomials $P_\ell(x)$ as

$$P_\ell^{|m|}(x)=(1-x^2)^{|m|/2}\frac{d^{|m|}P_\ell(x)}{dx}$$

The first five Legendre polynomials are collected below.

$$P_0(x)=1$$
$$P_1(x)=x$$
$$P_2(x)=\frac{1}{2}(3x^2-1)$$
$$P_3(x)=\frac{1}{2}(5x^3-3x)$$
$$P_4(x)=\frac{1}{8}(35x^4-30x^2+3)$$

If we normalize $f_{\ell m}\left(\theta\right)$ to 1 by requiring

$$\int_0^{\pi} f_{\ell m}(\theta) f_{\ell m}^*(\theta) \sin\theta d\theta = 1$$

We get

$$f_{\ell m}(\theta) = \delta_m \left\{ \frac{(2\ell+1)(\ell-|m|)!}{2(\ell+|m|)!} \right\}^{\frac{1}{2}} P_\ell^{|m|}(\cos\theta)$$

δ_m in this definition of $f_{\ell m}(\theta)$ is an arbitrary phase factor which is not universally agreed upon. We will choose it to be $(-1)^m$ when $m > 0$ and +1 when $m < 0$. This is often called the Condon-Shortly choice of phase. The product $f_{\ell m}(\theta)\chi_m(\phi)$ is called a spherical harmonic and is written as

$$Y_\ell^m(\theta,\phi) = f_{\ell m}(\theta)\chi_m(\phi) = \delta_m \left\{ \frac{(2\ell+1)(\ell-|m|)!}{2(\ell+|m|)!} \right\}^{\frac{1}{2}} P_\ell^{|m|}(\cos\theta) \frac{e^{im\phi}}{\sqrt{2\pi}}$$

Note that the phase convention requires that $Y_\ell^{-m} = (-1)^m \left(Y_\ell^m\right)^*$.

In summary we have

$$\hat{\vec{L}}^2 Y_\ell^m(\theta,\phi) = \ell(\ell+1)\hbar^2 Y_\ell^m(\theta,\phi) \quad \ell = 0,1,2,3,\cdots$$
$$\hat{L}_z Y_\ell^m(\theta,\phi) = m\hbar Y_\ell^m(\theta,\phi) \quad -\ell \le m \le \ell$$

And since the eigenfunctions of $\hat{H}$ can be chosen to be eignfunctions of $\hat{\vec{L}}^2$ & $\hat{L}_z$ they must have the form $R(r)Y_\ell^m(\theta,\phi)$ where $R(r)$ is determined by

$$\left(-\frac{\hbar^2}{2\mu r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right) + \frac{\ell(\ell+1)\hbar^2}{2\mu r^2} + V(r) \right) R(r) = ER(r)$$

The solutions of this equation are considered in the section of these notes dealing with one-electron atoms.

It's common to identify an orbital angular momentum with a letter corresponding to the orbital angular momentum quantum number ℓ. This convention is of historical origin and refers to the nature of the spectroscopic lines in the hydrogen atom. The first four were called sharp, primary, diffuse and fundamental. The remaining letters continue in sequence with j being omitted.

ℓ	0	1	2	3	4	5	6
letter	s	p	d	f	g	h	i

s orbitals , ℓ=0

$$Y_0^0 = \frac{1}{\sqrt{4\pi}}$$

p orbitals, ℓ=1

$$Y_1^0 = \sqrt{\frac{3}{4\pi}}\cos\theta = \sqrt{\frac{3}{4\pi}}\frac{z}{r}$$

$$Y_1^{\pm 1} = \mp\sqrt{\frac{3}{8\pi}}\sin\theta e^{\pm i\phi} = \mp\sqrt{\frac{3}{8\pi}}\frac{x+iy}{r}$$

d orbitals, ℓ=2

$$Y_2^0 = \sqrt{\frac{5}{16\pi}}(3\cos^2\theta - 1) = \sqrt{\frac{5}{16\pi}}\frac{\left(2z^2 - x^2 - y^2\right)}{r^2}$$

$$Y_2^{\pm 1} = \mp\sqrt{\frac{15}{8\pi}}\cos\theta\sin\theta e^{\pm i\phi} = \mp\sqrt{\frac{15}{8\pi}}\frac{\left(x+iy\right)z}{r^2}$$

$$Y_2^{\pm 2} = \sqrt{\frac{15}{32\pi}}\sin^2\theta e^{\pm 2i\phi} = \sqrt{\frac{15}{32\pi}}\frac{\left(x+iy\right)^2}{r^2}$$

The spherical harmonics are orthonormal in the sense

$$\int_0^{\pi}\sin\theta\, d\theta\int_0^{2\pi} d\phi\ Y_\ell^m(\theta,\phi)Y_{\ell'}^{m'*}(\theta,\phi) = \delta_{\ell\ell'}\delta_{mm'}$$