Orbital Angular Momentum

Classically, we define angular momentum as $\underline{L} = \underline{r} \times \underline{p}$

$$\underline{L} = \begin{vmatrix} \hat{\underline{i}} & \hat{\underline{j}} & \hat{\underline{k}} \\ \hat{x} & \hat{y} & \hat{z} \\ \hat{p}_x & \hat{p}_y & \hat{p}_z \end{vmatrix} \quad \text{so} \quad \begin{aligned} \hat{L_x} &= \hat{y}\hat{p}_z - \hat{z}\hat{p}_y \\ \hat{L_y} &= \hat{z}\hat{p}_x - \hat{x}\hat{p}_z \\ \hat{L_z} &= \hat{x}\hat{p}_y - \hat{y}\hat{p}_x \end{aligned}$$

in spherical coordinates, these are:

$$\hat{L_x} = i\hbar\left(\sin\phi \frac{\partial}{\partial\theta} + \cot\theta\cos\phi \frac{\partial}{\partial\phi}\right)$$

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

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

This is the orbital angular momentum. We can define an operator corresponding to the square of total angular momentum:

$$\hat{L}^2 = \hat{L_x}^2 + \hat{L_y}^2 + \hat{L_z}^2$$

$$= -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right] \quad \text{in spherical coordinates}$$

None of the components of angular momentum commute but they all commute with the total angular momentum operator. So, when discussing orbital angular momentum, we will use the eigenvalues of the total angular momentum operator and one of the components, choosing $\hat{L_z}$ since it is the simplest.

The angular momentum of a particle which experiences no external forces is conserved. So all the operators above commute with the kinetic part of the hamiltonian. If the potential is uniform in space, or spherically symmetric, the operators commute with the full Hamiltonian.

Let's start by solving for the eigenfunctions of the total angular momentum operator. Suppose that $Y(\theta,\phi)$ is an eigenfunction, using separation of variables, we can write $Y(\theta,\phi) = \Theta(\theta)\,\Phi(\varphi)$

so if $\hat{L}^2 Y(\theta,\varphi) = \Lambda Y(\theta,\varphi)$

$$\Rightarrow \hat{L}^2 \Theta(\theta)\Phi(\varphi) = \Lambda \Theta(\theta)\Phi(\varphi)$$

$$-\hbar^2\left[\Phi(\varphi)\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right) + \Theta(\theta)\frac{1}{\sin^2\theta}\frac{\partial^2\Phi}{\partial\varphi^2}\right] = \Lambda\,\Theta(\theta)\,\Phi(\varphi)$$

$$\Rightarrow -\frac{\hbar^2}{\Theta}\frac{1}{\sin\theta}\left(\frac{\partial}{\partial\theta}\sin\theta\frac{\partial\Theta}{\partial\theta}\right) - \frac{\hbar^2}{\Phi\sin^2\theta}\frac{\partial^2\Phi}{\partial\varphi^2} = \Lambda$$

$$-\frac{\hbar^2\sin\theta}{\Theta}\left(\frac{\partial}{\partial\theta}\sin\theta\frac{\partial\Theta}{\partial\theta}\right) - \Lambda\sin^2\theta = \frac{\hbar^2}{\Phi}\frac{\partial^2\Phi}{\partial\varphi^2}$$

since the two sides of this equation don't depend on the same variables, the expression can only be true if both sides equal the same constant.

$$\therefore \quad -\frac{\hbar^2\sin\theta}{\Theta}\left(\frac{\partial}{\partial\theta}\sin\theta\frac{\partial\Theta}{\partial\theta}\right) - \Lambda\sin^2\theta = b \qquad (1)$$

$$\frac{\hbar^2}{\Phi}\frac{\partial^2\Phi}{\partial\varphi^2} = b \qquad (2)$$

We will solve (2) first since it is simpler. It should also be clear that although we started with $\hat{L}^2$, the eigenfunctions of $\hat{L}_z$ should also solve this equation.

In order for the eigenfunctions to be physically reasonable, we require that they are single-valued so:

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

so $\frac{\hbar^2}{\phi}\frac{\partial^2\phi}{\partial\varphi^2} = b$ and we require $\phi(\varphi) = \phi(\varphi + 2\pi)$

In this case, the solution is: $\phi(\varphi) = e^{im\varphi}$

where m is an integer. The associated eigenvalue is $\hbar m$.

So what is the value of b?

$$\frac{\partial^2\phi}{\partial\varphi^2} = i^2 m^2 e^{im\varphi} = -m^2 e^{im\varphi} = -m^2\phi$$

$$\Rightarrow \frac{\hbar^2}{\phi}\frac{\partial^2\phi}{\partial\varphi^2} = -\hbar^2 m^2 \phi \quad \text{so} \quad b = -\hbar^2 m^2$$

Now we can solve the other equation (1).

$$-\frac{\hbar^2 \sin(\theta)}{\Theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right) - \Lambda\sin^2\theta = -\hbar^2 m^2$$

Unfortunately, this is very hard to solve by hand so we do it computationally. The solutions to this introduce another integer l (just as we introduced m earlier). It turns out $\Lambda = \hbar^2 l(l+1)$ and physically reasonable solutions exist only for $-l \leq m \leq l$

The $Y(\theta, \phi)$ are known as spherical harmonics and are listed below in the form $Y_{l,m}$. They correspond to different orbitals of electrons.

s $\quad Y_{0,0} = \sqrt{\frac{1}{4\pi}}$

p $\quad Y_{1,0} = \sqrt{\frac{3}{4\pi}}\cos\theta \qquad Y_{1,\pm1} = \mp\sqrt{\frac{3}{8\pi}}\sin\theta\exp(\pm i\phi)$

d $\quad Y_{2,0} = \sqrt{\frac{5}{16\pi}}(3\cos^2\theta - 1) \qquad Y_{2,\pm1} = \mp\sqrt{\frac{15}{8\pi}}\cos\theta\sin\theta\exp(\pm i\phi)$

$\quad Y_{2,\pm2} = \sqrt{\frac{15}{32\pi}}\sin^2\theta\exp(\pm i2\phi)$

In cases where $m = 0$, there is azimuthal symmetry in the orbital shape.