5 Angular Momentum

Molecules are 3-dimensional objects that rotate in space. To understand the rotational motion of molecules, we must first understand how angular momentum is treated in quantum mechanics. To do this we need to look at the properties of angular momentum operators.

Let us look back at the Schrödinger equation for the rigid rotor

$$\hat{H}Y_l^m(\theta,\varphi) = EY_l^m(\theta,\varphi) = \frac{\hbar^2 l(l+1)}{2I}Y_l^m(\theta,\varphi)$$

Recall that since classically we find for the energy

$$E = \frac{L^2}{2I}$$

we could represent the Hamiltonian for the rigid rotor in terms of the $\hat{L}^2$ operator:

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

Since the $\hat{H}$ and $\hat{L}^2$ operators only differ by a constant, $\frac{1}{2I}$, we can also write

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

This says that the spherical harmonics are also eigenfunctions of the $\hat{L}^2$ operator and that the square of the angular momentum can only have quantized values given by

$$L^2 = \hbar^2 l(l+1) \qquad l = 0,1,2,3,\ldots$$

I would like to consider further the implications of the quantization of the square of the magnitude of the angular momentum, $\hat{L}^2$. But first, I would like to make a brief digression to give you some commutator identities that we will need.

Digression: Commutator Identities

$$\left[\hat{A},\hat{A}^n\right] = 0 \qquad n = 0,1,2,3,\ldots$$

$$\left[k\hat{A},\hat{B}\right] = \left[\hat{A},k\hat{B}\right] = k\left[\hat{A},\hat{B}\right]$$

$$\left[\hat{A},\hat{B}+\hat{C}\right] = \left[\hat{A},\hat{B}\right] + \left[\hat{A},\hat{C}\right]$$

$$\left[\hat{A},\hat{B}\hat{C}\right] = \left[\hat{A},\hat{B}\right]\hat{C} + \hat{B}\left[\hat{A},\hat{C}\right]$$

$$\left[\hat{A}\hat{B},\hat{C}\right] = \left[\hat{A},\hat{C}\right]\hat{B} + \hat{A}\left[\hat{B},\hat{C}\right]$$

Since angular momentum is a vector quantity, we need to think about vectors as operators.

Consider the position vector operator:

$$\hat{\mathbf{r}} = \left(\hat{x}, \hat{y}, \hat{z}\right)$$

or the momentum vector operator:

$$\hat{\mathbf{p}} = \left(\hat{p}_x, \hat{p}_y, \hat{p}_z\right)$$

where $\hat{x} \to x$ $\qquad\qquad$ $\hat{p}_x \to -i\hbar\dfrac{\partial}{\partial x}$

Each component of the vector is an operator. When we make a measurement of a vector quantity, we can measure its magnitude or one of its components (projection).

It will be helpful to know the commutators of the coordinates and the different components of the momenta with respect to one another:

$$\left[\hat{x}, \hat{y}\right] = 0$$

$$\left[\hat{p}_x, \hat{p}_y\right] = 0 \qquad \text{(because mixed partial derivatives commute)}$$

$$\left[\hat{x}, \hat{p}_y\right] = 0 \qquad \text{(all mixed terms like this commute)}$$

$$\left[\hat{x}, \hat{p}_x\right] = -i\hbar\left[x, \frac{\partial}{\partial x}\right]$$

To evaluate this, must operate on a function:

$$\left[x, \frac{\partial}{\partial x}\right] f(x) = x\frac{\partial f(x)}{\partial x} - \frac{\partial x f(x)}{\partial x} = x\frac{\partial f(x)}{\partial x} - f(x) - x\frac{\partial f(x)}{\partial x} = -f(x)$$

Thus $\qquad \left[\hat{x}, \hat{p}_x\right] = i\hbar$

One could also show

$$\left[\hat{p}_x, \hat{x}\right] = -i\hbar$$

and similarly for the other coordinates.

The angular momentum is a vector containing the components

$$\hat{L} = \left(\hat{L}_x, \hat{L}_y, \hat{L}_z\right)$$

and is defined in classical mechanics as:

$$\mathbf{L} = \mathbf{r} \times \mathbf{p}$$

We showed earlier in the course while discussing postulate 2 that

$$\mathbf{r} \times \mathbf{p} = \left(yp_z - zp_y\right)\mathbf{i} + \left(zp_x - xp_z\right)\mathbf{j} + \left(xp_y - yp_x\right)\mathbf{k}$$

Thus

$$\hat{L}_x = \hat{y}\hat{p}_z - \hat{z}\hat{p}_y = -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)$$

$$\hat{L}_y = \hat{z}\hat{p}_x - \hat{x}\hat{p}_z = -i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)$$

$$\hat{L}_z = \hat{x}\hat{p}_y - \hat{y}\hat{p}_x = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$$

It is important to know how these operators commute with each other.

$$\left[\hat{L}_x,\hat{L}_y\right] = \left[\left(\hat{y}\hat{p}_z - \hat{z}\hat{p}_y\right),\left(\hat{z}\hat{p}_x - \hat{x}\hat{p}_z\right)\right]$$

$$= \left[\hat{y}\hat{p}_z,\hat{z}\hat{p}_x\right] - \left[\hat{y}\hat{p}_z,\hat{x}\hat{p}_z\right] - \left[\hat{z}\hat{p}_y,\hat{z}\hat{p}_x\right] + \left[\hat{z}\hat{p}_y,\hat{x}\hat{p}_z\right]$$

$$= \hat{y}\left[\hat{p}_z,\hat{z}\hat{p}_x\right] + \left[\hat{y},\hat{z}\hat{p}_x\right]\hat{p}_z + \hat{z}\left[\hat{p}_y,\hat{x}\hat{p}_z\right] + \left[\hat{z},\hat{x}\hat{p}_z\right]\hat{p}_y$$

$$= \hat{y}\hat{z}\left[\hat{p}_z,\hat{p}_x\right] + \hat{y}\left[\hat{p}_z,\hat{z}\right]\hat{p}_x + \hat{x}\left[\hat{z},\hat{p}_z\right]\hat{p}_y + \left[\hat{z},\hat{x}\right]\hat{p}_z\hat{p}_y$$

$$= -i\hbar\hat{y}\hat{p}_x + i\hbar\hat{x}\hat{p}_y$$

$$= i\hbar\left(\hat{x}\hat{p}_y - \hat{y}\hat{p}_x\right)$$

$$= i\hbar\hat{L}_z$$

Note that several terms are omitted above because certain commutators are zero. Remember that mixed partial derivatives commute, different position operators commute, and position operators commute with momenta in other coordinates

So

$$\left[\hat{L}_x,\hat{L}_y\right] = i\hbar\hat{L}_z$$

$$\left[\hat{L}_y,\hat{L}_z\right] = i\hbar\hat{L}_x$$

$$\left[\hat{L}_z,\hat{L}_x\right] = i\hbar\hat{L}_y$$

Note that it is cyclic (*xyz*, *yzx*, *zxy*). This cyclic pattern is a property of all types of angular momentum.

Since these operators do not commute, they do not have a complete set of common eigenfunctions. We therefore cannot simultaneously define precise values to these quantities**.**

Remember: $$\Delta A^2 \Delta B^2 = \sigma_A^2\sigma_B^2 \geq -\frac{1}{4}\left(\int \psi^*(x)\left[\hat{A},\hat{B}\right]\psi(x)dx\right)^2$$

However, consider the operator

$$\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$$

This represents the square of the magnitude of the total angular momentum.

Remember, the magnitude of the angular momentum is quantized.

$$\hat{L}^2 Y_l^m(\theta,\varphi) = \hbar^2 l\left(l+1\right)Y_l^m(\theta,\varphi)$$

We want to find the commutator of $\hat{L}^2$ with $\hat{L}_x$, $\hat{L}_y$, or $\hat{L}_z$.

$$\begin{aligned}
\left[\hat{L}^2,\hat{L}_z\right] &= \left[\hat{L}_x^2+\hat{L}_y^2+\hat{L}_z^2,\hat{L}_z\right] \\
&= \left[\hat{L}_x^2,\hat{L}_z\right]+\left[\hat{L}_y^2,\hat{L}_z\right]+\left[\hat{L}_z^2,\hat{L}_z\right] \\
&= \hat{L}_x\left[\hat{L}_x,\hat{L}_z\right]+\left[\hat{L}_x,\hat{L}_z\right]\hat{L}_x+\hat{L}_y\left[\hat{L}_y,\hat{L}_z\right]+\left[\hat{L}_y,\hat{L}_z\right]\hat{L}_y \\
&= \hat{L}_x\left(-i\hbar\hat{L}_y\right)+\left(-i\hbar\hat{L}_y\right)\hat{L}_x+\hat{L}_y\left(i\hbar\hat{L}_x\right)+\left(i\hbar\hat{L}_x\right)\hat{L}_y \\
&= 0
\end{aligned}$$

We could similarly show that

$$\left[\hat{L}^2,\hat{L}_x\right]=0 \qquad \left[\hat{L}^2,\hat{L}_y\right]=0$$

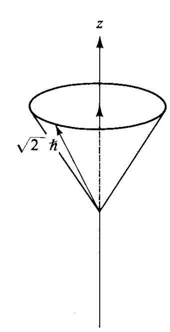
So each component of the angular momentum commutes with the $\hat{L}^2$ operator.

Since each component commutes with $\hat{L}^2$ but no component commutes with each other, we can only simultaneously specify one component along with $\hat{L}^2$ (with infinite precision, that is). We can therefore choose the eigenfunctions of $\hat{L}^2$ to also be eigenfunctions of one of these operators, and by convention this is chosen to be $\hat{L}_z$.

One could take L_x or L_y as well, but the set of eigenfunctions they share is different. I will say more on this later. Note that in specifying $L^2 = |\mathbf{L}|^2$ we are not specifying **L**, only its magnitude. A complete specification of **L** requires specification of its components, and in general we cannot do that (because all the operators don't commute).

In classical mechanics, when **L** is conserved each component has a definite value. In quantum mechanics, when **L** is conserved, we can only specify its magnitude and one of its components.

This is an important concept to understand.



So what we are doing is constraining the vector **L** to lie anywhere on a cone, since we know its magnitude and its L_z component (or any one of the three components).

We will often call the *z*-component of the angular momentum vector the projection of **L** on the *z*-axis or merely the projection of **L**.

I have already shown that the magnitude of the angular momentum vector is quantized, that is we showed that the eigenvalues of $\hat{L}^2$ were $\hbar^2 l(l+1)$. We can also show that the *z*-projection of the angular momentum is quantized. The easiest way to see this is to look at the $\hat{L}_z$ operator in spherical polar coordinates. To find this we simply need to take the expression in Cartesian coordinates and substitute the polar equivalent for the coordinates and the partial derivatives.

The result is

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

By inspection we can see that the eigenfunctions of this operator are $\propto e^{im\varphi}$

$$\hat{L}_z\left(e^{im\varphi}\right) = -i\hbar\frac{\partial}{\partial\varphi}\left(e^{im\varphi}\right) = m\hbar\left(e^{im\varphi}\right) \qquad m = 0, \pm1, \pm2, \ldots$$

You should recognize that these are just the functions describing the Φ part of the spherical harmonics. Consequently the eigenfunctions of the of the $\hat{L}^2$ operator are also eigenfunctions of the $\hat{L}_z$ operator.

Recall the definition of the spherical harmonics:

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

$$N_{lm} = \left[\frac{(2l+1)}{4\pi}\frac{\left(l-|m|\right)!}{\left(l+|m|\right)!}\right]^{\frac{1}{2}}$$

Thus,

$$\hat{L}_z\, Y_l^m(\theta,\varphi) = -i\hbar\frac{\partial\left(N_{lm}P_l^{|m|}(\cos\theta)e^{im\varphi}\right)}{\partial\varphi} = m\hbar\left(N_{lm}P_l^{|m|}(\cos\theta)e^{im\varphi}\right) = m\hbar\, Y_l^m(\theta,\varphi)$$

The last thing we need to do is to see the connection between the allowable values of *m* and those of *l*.

Consider the following equation

$$\left(\hat{L}^2 - \hat{L}_z^2\right)Y_l^m(\theta,\varphi) = \left(\hat{L}_x^2 + \hat{L}_y^2\right)Y_l^m(\theta,\varphi) = \left[l\left(l+1\right) - m^2\right]\hbar^2 Y_l^m(\theta,\varphi)$$

I operated on the $Y_l^m(\theta,\varphi)$ functions to get the eigenvalues indicated, but I also used the relationship

$$\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$$

to convert $\left(\hat{L}^2 - \hat{L}_z^2\right)$ to $\left(\hat{L}_x^2 + \hat{L}_y^2\right)$

Since $\hat{L}_x^2 + \hat{L}_y^2$ is the sum of two squared real terms it cannot be negative, so

$$\left[l\left(l+1\right) - m^2\right]\hbar^2 \geq 0$$

or $\quad l\left(l+1\right) \geq m^2$

This says that

$$|m| \leq l$$

or that the only possible values of *m* are:

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

Consequently, there are 2*l*+1 values of *m* for each value of *l* (*l* positive values, *l* negative values and 0).
Thus,

$$\hat{L}^2 Y_l^m(\theta,\varphi) = l(l+1)\hbar^2 Y_l^m(\theta,\varphi) \qquad l = 0,1,2,3,\ldots$$

$$\hat{L}_z Y_l^m(\theta,\varphi) = m\hbar\, Y_l^m(\theta,\varphi) \qquad m = 0,\pm 1,\pm 2,\ldots,\pm l$$

Let us now consider the implications of the commutators of these operators on the measurement process. Recall that $\hat{H}_{rr}$ and $\hat{L}^2$ are simply related by a constant and thus commute.

The fact that the three operators

$\hat{H}_{rr}$, $\hat{L}^2$ and $\hat{L}_z$

all commute has important implications on the measurement process. It says that the stationary states of the system (the eigenfunctions of $\hat{H}_{rr}$) can simultaneously have definite total energy, angular momentum (in magnitude), and have a well-defined projection on one axis (chosen by convention to be the *z* axis). They cannot, however, simultaneously have well defined values of L_x and L_y.

The fact that we can choose one axis to be special arises from the fact that the eigenvalues of $\hat{H}$ (the rigid rotor Hamiltonian) or of $\hat{L}^2$ only depend upon the quantum number *l*. Remember the theorem we introduced when we started multi-dimensional systems. Any linear combination of functions with the same eigenvalue with respect to a particular operator is also and eigenfunction of that operator.

For example, we said that there are 2*l*+1 allowable values of *m* for each *l*,

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

but we know that the energy of the Rigid Rotor depends only upon *l*:

$$E = \frac{\hbar^2}{2I} l(l+1) \qquad l = 0,1,2,3,\ldots$$

This says that each level is (2*l*+1)-fold degenerate.

Any linear combination of the 2*l*+1 degenerate eigenfunctions of $\hat{H}_{rr}$ and $\hat{L}^2$ are also eigenfunctions of $\hat{H}_{rr}$ and $\hat{L}^2$. By choosing *z* to be the special axis, we choose the linear combinations in such a way that they are eigenfunctions of $\hat{L}_z$. We could have chosen those linear combinations of $\hat{H}_{rr}$ and $\hat{L}^2$ eigenfunctions to be eigenfunctions of $\hat{L}_x$ or $\hat{L}_y$. However, since $\hat{L}_z$ is a simple operator in spherical polar coordinates, the mathematical form of the eigenfunctions is simplest if we choose them in as eigenfunctions of $\hat{L}_z$.

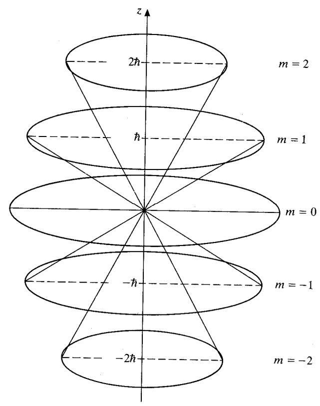
Consider an example where *l*=2. Because *l*=2, *m* can only have the values 0, ±1, ±2

Thus the magnitude of the vector **L**, that is |L| is

$$|L| = \sqrt{L^2} = \sqrt{l(l+1)}\hbar = \sqrt{6}\hbar$$

and the projection $\hat{L}_z$ can have the values: $-2\hbar$, $-\hbar$, 0, $\hbar$, $2\hbar$

We therefore have the following picture:



$$|L| = \sqrt{l(l+1)}\hbar = \sqrt{6}\hbar$$

$$m = -2, -1, 0, 1, 2$$

$$L_z = m\hbar$$

If we specify the magnitude of the angular momentum vector and only one component, L_z, then we restrict the vector **L** to lie somewhere on a cone.

Remember that we cannot simultaneously specify L^2, L_x, L_y, and L_z because the components $\hat{L}_x$, $\hat{L}_y$, and $\hat{L}_z$ do not commute. Any one commutes with $\hat{L}^2$, so we can choose the eigenfunctions of $\hat{L}^2$ to simultaneously be eigenfunctions of one of those components.

By convention we chose $\hat{L}_z$. The vector can lie anywhere on a cone, since if we specify $\hat{L}_z$, we know nothing of $\hat{L}_x$ and $\hat{L}_y$ except that $\hat{L}_x^2 + \hat{L}_y^2 = \hat{L}^2 - \hat{L}_z^2$. (Since the eigenvalues of $\hat{L}^2$ and $\hat{L}_z$ are a constant $\hat{L}_x^2 + \hat{L}_y^2$ = constant just defines the circle at the top of the cone.)

Note that the maximum value of L_z is less than |**L**|, which says that L_z cannot point in the same direction as **L**. If it did, it would violate the Heisenberg Uncertainty Principle in that we could simultaneously know L_x, L_y, and L_z with infinite precision.

Remember, each vector that I have drawn represents the angular momentum of a particular eigenfunction. There are 5 vectors here since for l=2, there are $2l$+1=5 eigenfunctions. All of these functions are degenerate (they have the same energy eigenvalue). I will speak more about degeneracy later. This is an important picture to keep in your mind. We will run into it again.

It is also important to realize that this picture is not specific to the Rigid Rotor. It just depends upon the angular momentum operators, their commutators and their eigenvalues, which is independent of the system. All angular momentum in quantum mechanics can be viewed this way. That is, the relationship between the angular momentum operators is the same for all systems. However, the fact that $\hat{H}$ commutes with the angular momentum operators need not be true. It will be true whenever the potential is spherically symmetric.

To summarize:
Since $\hat{H}_{rr}$, $\hat{L}^2$ and $\hat{L}_z$ all commute they have a common set of eigenfunctions, the spherical harmonics, and we can make simultaneous measurements of any of these and not affect the other. Each of these quantities has quantized eigenvalues, and we determined what the allowed values were.

Also we determined that since the energy doesn't depend upon m, all states with the same l but different m have the same energy. These states are ($2l$+1)-fold degenerate. The $2l$+1 degenerate eigenfunctions correspond, for example, to the different positions of the vector **L** in the figure above.