10 The Quantum Mechanics of Angular Momentum

10.1 General Angular Momentum[1]

The following discussion is very involved and uses much of the vector algrebra and complex number algebra that we have learned so far. There is much here and the reader will be excused for being intimidated by it. However, there is nothing that has not been explained in detail in previous chapters and as long as the reader has a firm understanding of complex numbers and vectors there will be no surprises (well, maybe one or two).

In classical physics, the angular momentum of a particle is given by the vector cross product, **L** = **r**X**p**, where **r** is the position vector of the particle and **p** is the tangential linear momentum, m**v** (see chapter 8, the Bloch equations).

The components of **L** are (by the determinant method, chapter 2):

$$\boldsymbol{L}=\boldsymbol{r}\times\boldsymbol{p}=\begin{bmatrix}\boldsymbol{i} & \boldsymbol{j} & \boldsymbol{k}\\ x & y & z\\ p_x & p_y & p_z\end{bmatrix}=\boldsymbol{i}(yp_z-zp_y)+\boldsymbol{j}(zp_x-xp_z)+\boldsymbol{k}(xp_y-yp_x)$$

and the magnitude of each component:

$$L_x=yp_z-zp_y$$
$$L_y=zp_x-xp_z$$
$$L_z=xp_y-yp_x$$

To get the corresponding operators we replace the momentum term, p, with $-i\hbar\frac{\partial}{\partial x}(\text{or}\frac{\partial}{\partial y}\text{or}\frac{\partial}{\partial z})$ (see chapter 9). *i* is the root of minus one and ħ is the *reduced* Planck constant or Dirac constant and is equal to h/2π. Why do this? Recall from the chapter on waves that natural frequency units in radians per second and ordinary frequency units in cycles per second or hertz are related by equation [6-2]:

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[1] The substance of this discussion owes much to talks with Professor J. A. Weil and to his book, ref. 2.

$$2\pi\omega=\nu$$
$$\omega=\frac{\nu}{2\pi}$$

In dividing h by 2π we are specifying that our frequency results will be in natural frequency units, radians per second. The coordinates remain the same:

$$\begin{aligned}\hat{\boldsymbol{J}}_{\boldsymbol{x}}&=-i\hbar\left(y\cdot\frac{\partial}{\partial z}-z\cdot\frac{\partial}{\partial y}\right)\\ \hat{\boldsymbol{J}}_{\boldsymbol{y}}&=-i\hbar\left(z\cdot\frac{\partial}{\partial x}-x\cdot\frac{\partial}{\partial z}\right)\\ \hat{\boldsymbol{J}}_{\boldsymbol{z}}&=-i\hbar\left(x\cdot\frac{\partial}{\partial y}-y\cdot\frac{\partial}{\partial x}\right)\end{aligned}\qquad [10\text{-}1]$$

We have switched to **J** from **L** here, as **J** is the general angular momentum symbol.

We can also define **J²** by summing the squares of each of the angular momentum component operators:

$$\hat{\boldsymbol{J}}^{\boldsymbol{2}}=\hat{\boldsymbol{J}}_{\boldsymbol{x}}^{\boldsymbol{2}}+\hat{\boldsymbol{J}}_{\boldsymbol{y}}^{\boldsymbol{2}}+\hat{\boldsymbol{J}}_{\boldsymbol{z}}^{\boldsymbol{2}}\qquad [10\text{-}2]$$

Do these operators commute? Let's find out ... :

$$[\hat{\boldsymbol{J}}_{\boldsymbol{x}},\hat{\boldsymbol{J}}_{\boldsymbol{y}}]=\hat{\boldsymbol{J}}_{\boldsymbol{x}}\hat{\boldsymbol{J}}_{\boldsymbol{y}}-\hat{\boldsymbol{J}}_{\boldsymbol{y}}\hat{\boldsymbol{J}}_{\boldsymbol{x}}$$

from the above definitions [10-1]:

$$\begin{aligned}\hat{\boldsymbol{J}}_{\boldsymbol{x}}\hat{\boldsymbol{J}}_{\boldsymbol{y}}&=-\hbar^2\left(y\cdot\frac{\partial}{\partial z}-z\cdot\frac{\partial}{\partial y}\right)\left(z\cdot\frac{\partial}{\partial x}-x\cdot\frac{\partial}{\partial z}\right)\\ &=-\hbar^2\left[\left(y\cdot\frac{\partial}{\partial z}\right)\left(z\cdot\frac{\partial}{\partial x}\right)-\left(z\cdot\frac{\partial}{\partial y}\right)\left(z\cdot\frac{\partial}{\partial x}\right)-\left(y\cdot\frac{\partial}{\partial z}\right)\left(x\cdot\frac{\partial}{\partial}z\right)+\left(z\cdot\frac{\partial}{\partial y}\right)\left(x\cdot\frac{\partial}{\partial z}\right)\right]\\ &=-\hbar^2\left[y\cdot\frac{\partial}{\partial x}+yz\cdot\frac{\partial^2}{\partial z\partial x}-z^2\cdot\frac{\partial^2}{\partial y\partial x}-yx\cdot\frac{\partial^2}{\partial z^2}+zx\cdot\frac{\partial^2}{\partial y\partial z}\right]\end{aligned}$$

using the product rule from differential calculus (see the appendix):

$$\frac{\partial^2 yz}{\partial z\partial x}=y\cdot\frac{\partial^2 z}{\partial z\partial x}+z\cdot\frac{\partial^2 y}{\partial z\partial x}=y\cdot\frac{\partial}{\partial x}+z\cdot\frac{\partial^2 y}{\partial z\partial x}\;\;)$$

similarly:

$$\begin{aligned}\hat{\boldsymbol{J}}_y\hat{\boldsymbol{J}}_x &= -\hbar^2(z\cdot\frac{\partial}{\partial x}-x\cdot\frac{\partial}{\partial z})(y\cdot\frac{\partial}{\partial z}-z\cdot\frac{\partial}{\partial y})\\ &= -\hbar^2[(z\cdot\frac{\partial}{\partial x})(y\cdot\frac{\partial}{\partial z})-(x\cdot\frac{\partial}{\partial z})(y\cdot\frac{\partial}{\partial z})-(z\cdot\frac{\partial}{\partial x})(z\cdot\frac{\partial}{\partial y})+(x\cdot\frac{\partial}{\partial z})(z\cdot\frac{\partial}{\partial y})]\\ &= -\hbar^2[zy\cdot\frac{\partial^2}{\partial x\partial z}+xy\cdot\frac{\partial^2}{\partial z^2}-z^2\cdot\frac{\partial^2}{\partial x\partial y}-x\cdot\frac{\partial}{\partial y}+xz\cdot\frac{\partial^2}{\partial z\partial y}]\end{aligned}$$

and:

$$\begin{aligned}\hat{\boldsymbol{J}}_x\hat{\boldsymbol{J}}_y-\hat{\boldsymbol{J}}_y\hat{\boldsymbol{J}}_x &= -\hbar^2[y\cdot\frac{\partial}{\partial x}-x\cdot\frac{\partial}{\partial y}]\\ &= \hbar^2[x\cdot\frac{\partial}{\partial y}-y\cdot\frac{\partial}{\partial x}]\\ &= i\hbar\hat{\boldsymbol{J}}_z\end{aligned}$$

(using the definition of $\hat{\boldsymbol{J}}_z$ above)

So:

$$\begin{aligned}[\hat{\boldsymbol{J}}_x,\hat{\boldsymbol{J}}_y] &= i\hbar\hat{\boldsymbol{J}}_z\\ [\hat{\boldsymbol{J}}_z,\hat{\boldsymbol{J}}_x] &= i\hbar\hat{\boldsymbol{J}}_y\\ [\hat{\boldsymbol{J}}_y,\hat{\boldsymbol{J}}_z] &= i\hbar\hat{\boldsymbol{J}}_x\end{aligned} \qquad [10\text{-}3]$$

We note the cyclic permutation in these commutation relationships. Also, note that the components of the angular momentum do not commute with each other. This means that we cannot assign definite values to any two of these at once as we saw in our dicussion of the uncertainty principle in chapter 9. Put another way, there are no functions that are simultaneously eigenfunctions of all three angular momentum operators. Frequently, one will see these commutation relationships written in 'frequency' notation. Recalling from chapter 9 that Planck's energy equation relates the energy of a photon to its frequency $E=h\nu$ where n is in hertz. Alternatively:

$$E=\frac{h\omega}{2\pi}=\hbar\omega$$

where ω is in radians per second. Dividing by $\hbar$ gives the (equivalent) frequency notation. If we divide our commutation relationships, [10-3], by ħ we get the frequency notation:

$$[\hat{\boldsymbol{J}}_x, \hat{\boldsymbol{J}}_y] = i\hat{\boldsymbol{J}}_z$$
$$[\hat{\boldsymbol{J}}_z, \hat{\boldsymbol{J}}_x] = i\hat{\boldsymbol{J}}_y \qquad [10\text{-}4]$$
$$[\hat{\boldsymbol{J}}_y, \hat{\boldsymbol{J}}_z] = i\hat{\boldsymbol{J}}_x$$

We can do the same investigations into the commutation relationships between $\hat{\boldsymbol{J}}^2$ and $\hat{\boldsymbol{J}}_x$, $\hat{\boldsymbol{J}}_y$ and $\hat{\boldsymbol{J}}_z$. When we do so, using the above definitions for these operators, we get:

$$[\hat{\boldsymbol{J}}^2, \hat{\boldsymbol{J}}_x] = 0$$
$$[\hat{\boldsymbol{J}}^2, \hat{\boldsymbol{J}}_y] = 0$$
$$[\hat{\boldsymbol{J}}^2, \hat{\boldsymbol{J}}_z] = 0$$

In these cases we see that $\hat{\boldsymbol{J}}^2$ commutes with all three angular momentum operators. Thus, it is possible to measure simultaneous values using $\hat{\boldsymbol{J}}^2$ and ***one*** of the angular momentum operators. Equivalently, there exists an eigenfunction that can be used simultaneously with $\hat{\boldsymbol{J}}^2$ and one of the angular momentum operators.

Now, all this talk of eigenfunctions and angular momentum operators leads one to think "what about the eigenvalues of these eigenfunctions" (well, maybe not but ...). Since there is a set of eigenfunctions that satisfy *both* J^2 and one of $\hat{\boldsymbol{J}}_x$, $\hat{\boldsymbol{J}}_y$ or $\hat{\boldsymbol{J}}_z$, we can try to find out what it might be or to find the corresponding eigenvalues. The choice that is generally made is to use $\hat{\boldsymbol{J}}^2$ and $\hat{\boldsymbol{J}}_z$.

In the following discussion it is convenient/necessary to introduce a couple of new operator definitions. These are the so-called ladder or raising and lowering operators:

$$\hat{\boldsymbol{J}}_+ = \hat{\boldsymbol{J}}_x + i\hat{\boldsymbol{J}}_y \text{ and } \hat{\boldsymbol{J}}_- = \hat{\boldsymbol{J}}_x - i\hat{\boldsymbol{J}}_y \qquad [10\text{-}5]$$

Their commutation relationships are:

$$[\hat{\boldsymbol{J}}^2,\hat{\boldsymbol{J}}_+]=[\hat{\boldsymbol{J}}^2,\hat{\boldsymbol{J}}_-]=0$$
$$[\hat{\boldsymbol{J}}_z,\hat{\boldsymbol{J}}_+]=\hat{\boldsymbol{J}}_+ \quad \text{or}$$
$$\hat{\boldsymbol{J}}_z\hat{\boldsymbol{J}}_+-\hat{\boldsymbol{J}}_+\hat{\boldsymbol{J}}_z=\hat{\boldsymbol{J}}_+ \qquad [10\text{-}6]$$
$$[\hat{\boldsymbol{J}}_z,\hat{\boldsymbol{J}}_-]=-\hat{\boldsymbol{J}}_-$$
$$[\hat{\boldsymbol{J}}_+,\hat{\boldsymbol{J}}_-]=2\hat{\boldsymbol{J}}_z$$

Now let's try for some eigenvalues of $\hat{\boldsymbol{J}}^2$ and $\hat{\boldsymbol{J}}_z$. First, remembering that these two operators have common eigenfunctions, we can call the eigenvalues of $\hat{\boldsymbol{J}}^2$ and $\hat{\boldsymbol{J}}_z$, λ_j and λ_m respectively and we can write:

$$\hat{\boldsymbol{J}}^2|j,m>=\lambda_j|j,m>$$
$$\hat{\boldsymbol{J}}_z|j,m>=\lambda_m|j,m> \qquad [10\text{-}7]$$

This is our familiar Dirac notation that has been used here to represent the common eigenfunction of $\hat{\boldsymbol{J}}^2$ and $\hat{\boldsymbol{J}}_z$. $|j,m>$ represents the spin wavefunction with emphasis on j and m, rather that writing $|\Psi>$. It helps us to keep clear what we are talking about. Another way to write this using Schroedinger notation would be:

$$\hat{\boldsymbol{J}}^2\Psi_{j,m}=\lambda_j\Psi_{j,m}$$
$$\hat{\boldsymbol{J}}_z\Psi_{j,m}=\lambda_m\Psi_{j,m}$$

The Dirac notation is rather more compact and is useful in developing the matrix representation of operators.

Note that these are *orthonormal* functions where:

$$<j',m'|j,m>=1 \quad if\ j'=j \text{ and } m'=m$$

or

$$<j',m'|j,m>=0 \quad if\ j'\neq j \text{ and/or } m'\neq m$$

You will need to remember these when we talk about matrix representations of operators.

Now, from the definition of $\hat{\boldsymbol{J}}^2$, [10-2]:

$$\hat{\boldsymbol{J}}_x^2+\hat{\boldsymbol{J}}_y^2=\hat{\boldsymbol{J}}^2-\hat{\boldsymbol{J}}_z^2$$

and, using this in our eigenvalue equation [10-7]:

$$(\hat{\boldsymbol{J}}_x^2+\hat{\boldsymbol{J}}_y^2)|j,m>=(\hat{\boldsymbol{J}}^2-\hat{\boldsymbol{J}}_z^2)|j,m>$$
$$=(\lambda_j-\lambda_m^2)|j,m>$$

Since $\hat{\boldsymbol{J}}_x$ and $\hat{\boldsymbol{J}}_y$ correspond to experimental observables (and are therefore hermitian) they must give real, non-negative numbers so that ($\hat{\boldsymbol{J}}_x^2$ + $\hat{\boldsymbol{J}}_y^2$) will also give real, non-negative numbers:

$$\lambda_j-\lambda_m^2\geqslant 0 \qquad [10\text{-}8]$$

Since $[\hat{\boldsymbol{J}}_z,\hat{\boldsymbol{J}}_+]=\hat{\boldsymbol{J}}_+ \text{or} \hat{\boldsymbol{J}}_z\hat{\boldsymbol{J}}_+-\hat{\boldsymbol{J}}_+\hat{\boldsymbol{J}}_z=\hat{\boldsymbol{J}}_+$ (from [10-6]) we can write:

$$<j,m'|\hat{\boldsymbol{J}}_z\hat{\boldsymbol{J}}_+-\hat{\boldsymbol{J}}_+\hat{\boldsymbol{J}}_z|j,m>=<j,m'|\hat{\boldsymbol{J}}_+|j,m>$$

where j has the same value in the bra and ket but m' may (or may not) be different from m. That this is so is because:

$$\hat{\boldsymbol{J}}_z\hat{\boldsymbol{J}}_+|j,m>=(\hat{\boldsymbol{J}}_++\hat{\boldsymbol{J}}_+\hat{\boldsymbol{J}}_z)|j,m>$$
$$(using \quad \hat{\boldsymbol{J}}_z J_+-\hat{\boldsymbol{J}}_+\hat{\boldsymbol{J}}_z=\hat{\boldsymbol{J}}_+)$$
$$=(\hat{\boldsymbol{J}}_++\hat{\boldsymbol{J}}_+\lambda_m)|j,m>$$
$$=(\lambda_m+1)\hat{\boldsymbol{J}}_+|j,m>$$

This shows us that $\hat{\boldsymbol{J}}_z\hat{\boldsymbol{J}}_+$, operating on the eigenfunction, $|j,m>$, produces an eigenvalue of λ_m *plus* one. ***Wow***! What a result! Let's think about it for a moment. The result of $\hat{\boldsymbol{J}}_z|j,m>$ is $\lambda_m|j,m>$ ... we said this earlier in equation [10-7]. Contrast this with $\hat{\boldsymbol{J}}_z\hat{\boldsymbol{J}}_+|j,m>$ which gives $(\lambda+1)\hat{\boldsymbol{J}}_+|j,m>$. If you consider $\hat{\boldsymbol{J}}_+|j,m>$ as a whole to be just another eigenfunction of $\hat{\boldsymbol{J}}_z$, then this result indicates that $\hat{\boldsymbol{J}}_+$ must operate on $|j,m>$ to give $|j,m+1>$:

$$\hat{\boldsymbol{J}}_+|j,m>=\zeta_m|j,m+1> \qquad [10\text{-}10]$$

Only m is affected by this operation .. j, related to the total angular momentum, is unaffected. Furthermore, there must be a whole set of eigenfunctions of J_z whose eigenvalues are separated from each other by one.

Similarly:

$$\hat{\boldsymbol{J}}_-|j,m>=\xi_m|j,m-1> \qquad [10\text{-}11]$$

Now, since we have shown that $\lambda_j-\lambda_m^2\geqslant 0$ (equation [10-8]), this means that there must be a maximum and a minimum value for λ_m . In other words:

$$-\sqrt{\lambda_j}\leqslant\lambda_m\leqslant\sqrt{\lambda_j}$$

If we try to use the raising operator on an eigenfunction that already has a maximum value of m we cannot generate one with m_{max} + 1 and we are forced to write:

$$J_+|j,m_{max}>=0$$

and

$$J_-|j,m_{min}>=0$$

Now:

$$\hat{\boldsymbol{J}}_-\hat{\boldsymbol{J}}_+|j,m_{max}>=(\hat{\boldsymbol{J}}^2-\hat{\boldsymbol{J}}_z^2-\hat{\boldsymbol{J}}_z)|j,m_{max}>$$

$$\text{(from the definitions of } \hat{\boldsymbol{J}}_- \text{ and } \hat{\boldsymbol{J}}_+\text{)}$$

$$=(\lambda_j-\lambda_{m-max}^2-\lambda_{m-max})|j,m>=0$$

Why you ask, is it equal to zero?

$$\hat{\boldsymbol{J}}_{-}\hat{\boldsymbol{J}}_{+}|j,m_{max}>=\hat{\boldsymbol{J}}_{-}(\hat{\boldsymbol{J}}_{+}|j,m_{max}>)=J_{-}(0)=0$$

so, assuming that $|j,m_{max}>$ has a non-zero value:

$$(\lambda_j-\lambda_{m-max}^2-\lambda_{m-max})=0$$

or:

$$\lambda_j=\lambda_{m-max}^2+\lambda_{m-max}$$
$$\lambda_j=\lambda_{m-max}(\lambda_{m-max}+1)$$

Similarly, for $J_+J_-|j,m_{min}>$, we obtain:

$$\lambda_j=\lambda_{m-min}(\lambda_{m-min}-1)$$

and we can then say:

$$\lambda_{m-max}^2+\lambda_{m-max}=\lambda_{m-min}^2+\lambda_{m-min}$$

This can only be true if $\lambda_{m(max)} = -\lambda_{m(min)}$.

Combined with our knowledge that the eigenvalues of $\hat{\boldsymbol{J}}_z|j,m>$ differ from each other by *exactly* one, the fact that there is a maximum and a minimum eigenvalue for the set of eigenfunctions and the fact that the maximum value equals the negative of the minimum value means that the eigenvalues of $\hat{\boldsymbol{J}}_z|j,m>$ can take only the values ...-3/2, -1, -1/2, 0, +1/2, +1, +3/2 ... No other values are possible. Thus, there are $2\lambda_{m(max)} + 1$ possible values of m.

It is customary to define $j = \lambda_{m(max)}$ and $-j = \lambda_{m(min)}$. This gives us:

$$\lambda_j=j(j+1)$$

Now, since j is defined in terms of $\lambda_{m(max)}$ and λ_m ranges from $\lambda_{m(min)}$ to $\lambda_{m(max)}$ in steps of one, the values that j can take are 0, 1/2, 1, 3/2, 2 ...

The possible values of λ_m depend on j and the fact that they differ by one from each other. So, if j = 1, then λ_m or m for short (which is one of the things that some books fail to point out explicitly!), can be -1, 0, +1. More generally, for a given value of j, m ranges from -j to +j in steps of one.

So now we have the eigenvalues of J^2 and J_z, j(j+1) and m respectively.

Ready for more? Lets look at z_m and c_m. As you will no doubt instantly recall:

$$< j,m|\hat{\boldsymbol{J}}_{-}\hat{\boldsymbol{J}}_{+}X|j,m> = \zeta_m < j,m|\hat{\boldsymbol{J}}_{-}|j,m+1> = \zeta_m \xi_{m+1} < j,m|j,m> = \zeta_m \xi_{m+1}$$

also, burned into your mind is:

$$< j,m|\hat{\boldsymbol{J}}_{-}\hat{\boldsymbol{J}}_{+}|j,m> = < j,m|\hat{\boldsymbol{J}}^{2}-\hat{\boldsymbol{J}}_{z}^{2}-\hat{\boldsymbol{J}}_{z}|j,m>$$

and since we now know what the eigenvalues of J^2 and J_z are:

$$\begin{gathered}< j,m|\hat{\boldsymbol{J}}^{2}-\hat{\boldsymbol{J}}_{z}^{2}-\hat{\boldsymbol{J}}_{z}|j,m> = j(j+1)-m(m+1)\\ =\zeta_m \xi_{m+1}\end{gathered}$$

We can also call up the hermitian operator 'trick':

$$\begin{gathered}< j,m|\hat{\boldsymbol{J}}_{-}\hat{\boldsymbol{J}}_{+}|j,m> = \zeta_m < j,m|\hat{\boldsymbol{J}}_{-}|j,m+1>\\ =\zeta_m\left[< j,m+1|\hat{\boldsymbol{J}}_{+}|j,m>\right]^{*}\\ =\zeta_m \zeta_m^{*} < j,m+1||j,m+1>\\ =\zeta_m \zeta_m^{*}\end{gathered}$$

(since **J_-** is hermitian, **J_-^* =** J_+)

So:

$$\zeta_m \zeta_m^* = \zeta_m \xi_{m+1}$$

and:

$$\zeta_m^* = \xi_{m+1}$$
$$\zeta_m \zeta_m^* = |\zeta_m|^2 = j(j+1) - m(m+1)$$
$$\zeta_m = \sqrt{j(j+1) - m(m+1)}$$

Similarly, for $<j,m|\hat{\boldsymbol{J}}_+ \hat{\boldsymbol{J}}_-|j,m>$:

$$\xi_m = \sqrt{j(j+1) - m(m-1)}$$

In summary we now have four eigenvalue equations:

$$\hat{\boldsymbol{J}}_{\boldsymbol{z}} |j,m> = m|j,m>$$
$$\hat{\boldsymbol{J}}^{\boldsymbol{2}} |j,m> = j(j+1)|j,m>$$

There will be 2j+1 possible eigenvalues of $\mathbf{J_z}$

$$\hat{\boldsymbol{J}}_+ |j,m> = (\sqrt{j(j+1) - m(m+1)})|j,m+1>$$
$$\hat{\boldsymbol{J}}_- |j,m> = (\sqrt{j(j+1) - m(m-1)})|j,m-1>$$

Also, we can derive expressions using J_x and J_y. From the definitions of the ladder operators:

$$\hat{\boldsymbol{J}}_{\boldsymbol{x}} = \frac{\hat{\boldsymbol{J}}_+ + \hat{\boldsymbol{J}}_-}{2}$$

and

$$\hat{\boldsymbol{J}}_{\boldsymbol{y}} = \frac{\hat{\boldsymbol{J}}_+ - \hat{\boldsymbol{J}}_-}{2\mathrm{i}}$$

So:

$$\hat{\boldsymbol{J}}_x|j,m> = \frac{(\hat{\boldsymbol{J}}_+ + \hat{\boldsymbol{J}}_-)}{2}|j,m>$$

$$= \frac{\hat{\boldsymbol{J}}_+}{2}|j,m> + \frac{\hat{\boldsymbol{J}}_-}{2}|j,m>$$

$$= \frac{1}{2}(\sqrt{j(j+1)-m(m+1)})|j,m> + \frac{1}{2}(\sqrt{j(j+1)-m(m-1)})|j,m>$$

Similarly:

$$\hat{\boldsymbol{J}}_y|j,m> = \frac{1}{2\mathrm{i}}(\sqrt{j(j+1)-m(m+1)})|j,m> - \frac{1}{2\mathrm{i}}(\sqrt{j(j+1)-m(m-1)})|j,m>$$

or (remembering that 1/i = -i):

$$\hat{\boldsymbol{J}}_y|j,m> = -\frac{i}{2}(\sqrt{j(j+1)-m(m+1)})|j,m> + \frac{i}{2}(\sqrt{j(j+1)-m(m-1)})|j,m>$$

The orthonormality of the eigenfunctions will considerably simplify these expressions when looking at operator matrices.

The symbol, **J**, is a generalized symbol for an angular momentum operator. When one wishes to talk about a specific type of angular momentum one generally changes the symbol for the operator (but not the math!). For example when the orbital angular momentum of an electron is being discussed one would use L or when the nuclear spin is of interest, **I** or **S** would be used. The math and the results do not change however.

10.2 Coupling of Angular Momenta

10.3 Angular Momentum Operator Matrices

We can do some expectation value calculations using the angular momentum operators that we previously developed:

$$<j,m|\hat{\boldsymbol{J}}_z|j,m>=<j,m|m|j,m>$$

$$=<j,m|j,m>$$

$$=m$$

(<j,m|j,m> normalized and equal to one)

As we have seen, generally, for a spin with spin quantum number j, there are 2j + 1 values for m, ranging from -j to +j in increments of one. For example, for a spin of 1, m can be -1, 0 or +1. We can use this to represent all of the possible expectation values for an operator in a matrix. So, for a single spin with j=1 we would do a 3 x 3 matrix (3 because of the three values of m). The columns in the matrix would be labeled |j,+j> to |j,-j> in steps of one (of course!) or just +j to -j, which are the possible values of m. For our spin with j=1 these would be 1, 0, -1. The rows are labeled similarly except that bras are used ... <j,+j| to <j,-j| .

Each matrix element is then the expectation value of the operator using the corresponding bra and ket. So, for row 1 and column 1 the expectation value of I_z would be:

$$<1,1|I_z|1,1>=<1,1|1|1,1>=1<1,1|1,1>=1$$

The whole I_z matrix for our j=1 spin is:

$$<I_z> = \begin{array}{r|ccc|} & |1,1> & |1,0> & |1,-1> \\ <1,1| & 1 & 0 & 0 \\ <1,0| & 0 & 0 & 0 \\ <1,-1| & 0 & 0 & -1 \end{array}$$

The 'basis' functions in bra and ket form are shown beside the appropriate rows and above the appropriate columns. Columns 2 and 3, row 1 are zero since the eigenfunctions are orthonormal and collapse to zero.

We can now write out the generalized expectation values for all of our angular momentum operators for all ***non-zero*** matrix elements:

$$<j,m|\hat{\boldsymbol{J}}_z|j,m>=<j,m|m|j,m>$$

$$=m<j,m|j,m>$$

$$=m$$

$$<j,m|\hat{\boldsymbol{J}}^2|j,m>=<j,m|j(j+1)|j,m>$$

$$=j(j+1)<j,m|j,m>$$

$$=j(j+1)$$

$$<j,m+1|\hat{\boldsymbol{J}}_+|j,m>=<j,m+1|\sqrt{[j(j+1)-m(m+1)]}|j,m+1>$$

$$=(\sqrt{j(j+1)-m(m+1)})<j,m+1|j,m+1>$$

$$\sqrt{j(j+1)-m(m+1)}$$

and similarly:

$$<j,m-1|\hat{\boldsymbol{J}}_{-}|j,m>=\sqrt{j(j+1)-m(m-1)}$$

There are two ways that the element of J_x can be constructed, depending on the value of m in the bra:

$$<j,m+1|\hat{\boldsymbol{J}}_{\boldsymbol{x}}|j,m>=<j,m+1|\frac{\sqrt{j(j+1)-m(m+1)}}{2}|j,m+1>$$
$$=(\frac{1}{2})(\sqrt{j(j+1)-m(m+1)})<j,m+1|j,m+1>$$
$$=(\frac{1}{2})\sqrt{j(j+1)-m(m+1)}$$

or

$$<j,m-1|\hat{\boldsymbol{J}}_{\boldsymbol{x}}|j,m>=<j,m-1|\frac{\sqrt{j(j+1)-m(m-1)}}{2}|j,m-1>$$
$$=(\frac{1}{2})(\sqrt{j(j+1)-m(m-1)})<j,m-1|j,m-1>$$
$$=(\frac{1}{2})\sqrt{j(j+1)-m(m-1)}$$

Same for J_y:

$$<j,m+1|\hat{\boldsymbol{J}}_{\boldsymbol{y}}|j,m>=<j,m+1|\frac{i\sqrt{j(j+1)-m(m+1)}}{2}|j,m+1>$$
$$=(\frac{i}{2})(\sqrt{j(j+1)-m(m+1)})<j,m+1|j,m+1>$$
$$=(\frac{i}{2})\sqrt{j(j+1)-m(m+1)}$$

or

$$<j,m-1|\hat{\boldsymbol{J}}_{\boldsymbol{y}}|j,m>=<j,m-1|\frac{i\sqrt{j(j+1)-m(m-1)}}{2}|j,m-1>$$
$$=(\frac{i}{2})(\sqrt{j(j+1)-m(m-1)})<j,m-1|j,m-1>$$
$$=(\frac{i}{2})\sqrt{j(j+1)-m(m-1)}$$

This is lot of stuff for what turns out to be some rather simple matrices. In the case of spin-½ nuclei (spin-½ refers of course to j=½) we can calculate what the expectation values of the nuclear spin angular momentum operators, $\mathbf{I_z}$, $\mathbf{I_x}$ and $\mathbf{I_y}$ are. For $\mathbf{I_z}$ the calculation is particularly simple. Since:

$$< \frac{1}{2},\frac{1}{2} | I_z | \frac{1}{2},\frac{1}{2} > = \frac{1}{2}$$
$$< \frac{1}{2},\frac{1}{2} | I_z | \frac{1}{2},-\frac{1}{2} > = 0$$
$$< \frac{1}{2},-\frac{1}{2} | I_z | \frac{1}{2},-\frac{1}{2} > = -\frac{1}{2}$$
$$\text{and}$$
$$< \frac{1}{2},-\frac{1}{2} | I_z | \frac{1}{2},\frac{1}{2} > = 0$$

the matrix is:

$$< I_z > = \begin{bmatrix} \frac{1}{2} & 0 \\ 0 & -\frac{1}{2} \end{bmatrix}$$

where $<I_Z>$ represents the expectation value of $\mathbf{I_z}$.

For $\mathbf{I_x}$ the calculation is a bit more complicated (but not much!). First, we visualize the basis functions along side the initially empty matrix:

$$< I_z > = \begin{array}{c|cc} & |\frac{1}{2},\frac{1}{2}> & |\frac{1}{2},-\frac{1}{2}> \\ \hline < \frac{1}{2},\frac{1}{2}| & a & b \\ < \frac{1}{2},\frac{1}{2}| & c & d \end{array}$$

As you will recall from a few lines back, there are two expressions for the expectation value of $\mathbf{I_x}$ ($\mathbf{J_x}$ actually, since it was a general angular momentum operator then, but I digress) depending on whether m increases by one or decreases by one. If you look at row 1, column 1, this is $<\frac{1}{2},\frac{1}{2}|\hat{\boldsymbol{I}}_x|\frac{1}{2},\frac{1}{2}>$. You can't use the first of the two equations since this would raise 1/2 to 3/2 but m cannot be larger than j (remember the maximum value of m is +j and the minimum value is -j). If you use the second of the two expressions you will get $<\frac{1}{2},\frac{1}{2}|\sqrt{[j(j+1)-m(m-1)]}|\frac{1}{2},-\frac{1}{2}>$ or $\sqrt{[j(j+1)-m(m-1)]}<\frac{1}{2},\frac{1}{2}|\frac{1}{2},-\frac{1}{2}>$ and since the basis functions are orthonormal the expression $<\frac{1}{2},\frac{1}{2}|\frac{1}{2},-\frac{1}{2}>$ is equal to zero. Similar calculations for the other matrix elements lead to the I_x matrix:

$$<I_x>=\begin{bmatrix} 0 & \frac{1}{2} \\ \frac{1}{2} & 0 \end{bmatrix}$$

Similarly for I_y:

$$<I_y>=\begin{bmatrix} 0 & -\frac{i}{2} \\ \frac{i}{2} & 0 \end{bmatrix}$$

For spin 1/2 nuclei we often abbreviate $|\frac{1}{2},\frac{1}{2}>$ to $|\alpha>$ and $|\frac{1}{2},-\frac{1}{2}>$ to $|\beta>$ and the nuclear spin operators are $\hat{\boldsymbol{I}}_z$ or $\hat{\boldsymbol{I}}_x$ or $\hat{\boldsymbol{I}}_y$. There are, of course, corresponding ladder operators, $\hat{\boldsymbol{I}}_+$ and $\hat{\boldsymbol{I}}_-$. Hopefully, from the above discussion and the discussion of angular momentum operators you can see that:

$$\hat{\boldsymbol{I}}_z|\alpha>=\frac{1}{2}|\alpha>$$

and

$$\hat{\boldsymbol{I}}_z|\beta>=-\frac{1}{2}|\beta>$$

One of those frustrating "it can be shown that" statements that one runs across is "it can be shown that $\hat{\boldsymbol{I}}_x|\alpha>=\frac{1}{2}|\beta>$ " but then it is not shown or stated where it is shown. We show it here using the ladder operator definitions:

$$\hat{\boldsymbol{I}}_+=\hat{\boldsymbol{I}}_x+i\hat{\boldsymbol{I}}_y$$
$$\hat{\boldsymbol{I}}_-=\hat{\boldsymbol{I}}_x-i\hat{\boldsymbol{I}}_y$$

Adding these together and solving for $\hat{\boldsymbol{I}}_x$:

$$\hat{\boldsymbol{I}}_x=\frac{\hat{\boldsymbol{I}}_+ + \hat{\boldsymbol{I}}_-}{2}$$

So:

$$\hat{\boldsymbol{I}}_x|\alpha>=\frac{\hat{\boldsymbol{I}}_+ + \hat{\boldsymbol{I}}_-}{2}|\alpha>$$

and since these are linear operators:

$$=\frac{1}{2}\hat{\boldsymbol{I}}_+|\alpha>+\frac{1}{2}\hat{\boldsymbol{I}}_-|\alpha>$$

Remembering our definitions of $|\alpha>$ and $|\beta>$ and the effect of the ladder operators from above:

$$=0+\frac{1}{2}|\beta>$$

The "0" comes about because the eigenvalue of $\hat{\boldsymbol{I}}_+|\alpha>$ works out to be zero for spin ½ (why?).

Thus:

$$\hat{\boldsymbol{I}}_x|\alpha>=\frac{1}{2}|\beta>$$

and similarly:

$$\hat{\boldsymbol{I}}_x|\beta>=\frac{1}{2}|\alpha>$$

$$\hat{\boldsymbol{I}}_y|\alpha>=\frac{i}{2}|\beta>$$

$$\hat{\boldsymbol{I}}_y|\beta>=-\frac{i}{2}|\alpha>$$

As you can see, $|\alpha>$ and $|\beta>$ are *not* eigenfunctions of $\hat{\boldsymbol{I}}_x$ and $\hat{\boldsymbol{I}}_y$. as we should expect to be the case since they do not commute with $\hat{\boldsymbol{I}}_z$.

10.4 References

1. *I.N. Levine,Quantum Chemistry,* Allyn and Bacon Inc., 1974.
2. J.A. Weil, J.R. Bolton and J.E. Wertz*, Electron Paramagnetic Resonance,* John Wiley and Sons Ltd., 1994.
3. N. Zettili*, Quantum Mechanics,* John Wiley and Sons, 2001.