

# The Quantum Mechanics of Angular Momentum

"Round and round we go .."

*childrens' rhyme*

## A Brief History

The Stern-Gerlach experiment, performed in 1922, showed that a beam of silver atoms passed through an inhomogeneous magnetic field was split into two and only two beams (Figure 15-1). Why silver atoms? Silver atoms have a single unpaired electron and, of course, are neutral so that they can be passed through a magnetic field without tracing a curved path (see chapter 10, section 10.2 and Figure 10-8). Why an inhomogeneous field? An inhomogeneous magnetic field will have a field gradient which, after the application of the gradient operator of chapter 4, will result in a force in the direction of the gradient. This would not be so in a homogeneous field. The Bohr-Sommerfeld theory of the atom at the time proposed quantized *orbital* angular momenta and the experiment was designed to test this hypothesis (not spin angular momentum as many texts seem to imply). The reasoning was that if the angular momentum behaved classically then as a atom passed through the inhomogeneous field there would be a larger deflection at one end of the magnetic dipole than the other and the atom would be deflected by an angle depending on the orientation of the dipole as it entered the field. Thus one would expect to see an even spread of deflections. Quantized orbital angular momenta on the other hand would result in only specific deflections. Furthermore, orbital angular momentum quantum calculations of the time indicated that if the electron behaved "quantum mechanically" it would have in integral angular momentum quantum number and would be in one of an odd number of states; one of three, five, seven etc. Thus the expectation was that if orbital angular momentum is quantized one should see the beam of atoms deflected such that there were an odd number of patches on the detector. This was not observed. There were *two* patches which could not be explained by the understanding of the time. We now know however that it was actually the first observation of the effects of intrinsic angular momentum or spin.

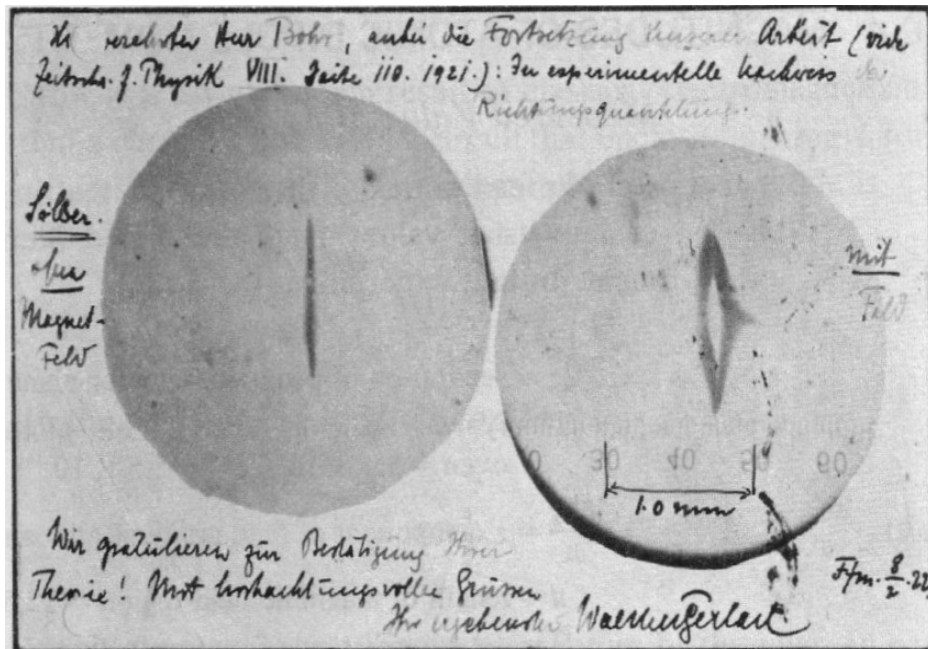
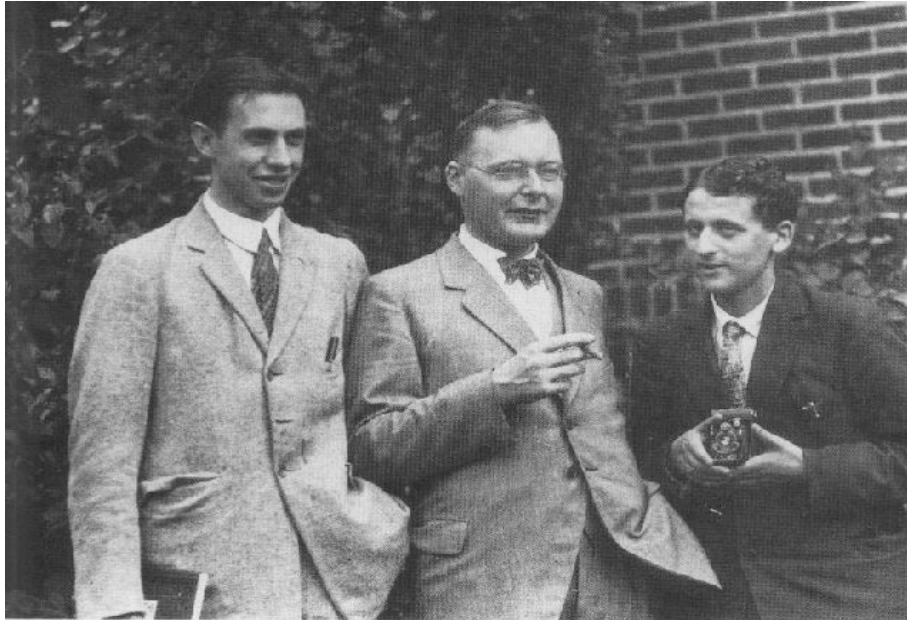


Figure 15-1 The Stern-Gerlach experimental results showing the photo of the split beam on the right

The idea that microscopic particles have a property corresponding to angular momentum was first proposed by two young Dutch-American graduate students George Ulenbeck and Samuel Goudsmid in 1925.



*Figure 15-2 G. Ulenbeck, H. Kramers and S. Goudsmit*

The background to this hypothesis was the observation that, when in a magnetic field, the hydrogen emission spectrum (see Figure 12-3) lines were each split into a fine structure of lines around the positions where the (non-magnetic) lines were observed. Quantum mechanics was successful in explaining the non-magnetic hydrogen emission spectrum but was unable to account for the observed splittings. The suggestion that the hydrogen electron behaves as though it has angular momentum and, since it is charged, a magnetic moment led to the injection of the concept into the then still developing field of quantum mechanics. Wolfgang Pauli later named it 'spin' which is still used today.

An interesting side story is that Ulenbeck and Goudsmit sent their hypothesis for publication and then had a discussion about it with Hendrik Lorentz (of Lorentz transform fame), one of the most eminent physicists of the time who argued that electron-spin would be impossible. They then tried to stop publication but were too late. Of course, they were right and Lorentz was wrong. So much for experts.

## **General Angular Momentum<sup>1</sup>**

The following discussion is very involved and uses much of the vector algebra and complex number algebra that we have learned so

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<sup>1</sup> The substance of this discussion owes much to discussions with Professor J. A. Weil and to his book, (see ref. 2). There is much here and you will certainly be excused for being intimidated by the quantity. However, there is nothing that has not been explained in detail in previous chapters and as long as you have a reasonably firm understanding of complex numbers and vectors there will be no surprises (well, maybe one or two). Stay with it and you will be a different person at the end.

far. Note that we switch from using the operator " $\hat{\mathbf{J}}$ " for general angular momentum to using " $\hat{\mathbf{I}}$ " for spin angular momentum part way through the chapter. The form of the equations for both are identical, only the symbol changes.

In classical physics, the angular momentum of a particle is given by the vector cross product,  $\vec{\mathbf{L}} = \vec{\mathbf{r}} \times \vec{\mathbf{p}}$ , where  $\vec{\mathbf{r}}$  is the position vector of the particle and  $\vec{\mathbf{p}}$  is the tangential linear momentum,  $m\vec{\mathbf{v}}$  (see chapter 10, the Bloch equations).

The components of  $\vec{\mathbf{L}}$  are (by the determinant method, chapter 2):

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

and the magnitude of each component:

$$\begin{aligned} L_x &= yp_z - zp_y \\ L_y &= zp_x - xp_z \\ L_z &= xp_y - yp_x \end{aligned}$$

To get the corresponding Hamiltonian operators we replace the momentum term,  $p$ , with  $-i\hbar \frac{\partial}{\partial x}$  (or  $-i\hbar \frac{\partial}{\partial y}$  or  $-i\hbar \frac{\partial}{\partial z}$ ) (see chapter 12).  $i$  is the root of minus one and  $\hbar$  is the *reduced* Planck constant or Dirac constant and is equal to  $h/2\pi$ . 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 [8-2]:

$$\begin{aligned} 2\pi\omega &= \nu \\ \omega &= \frac{\nu}{2\pi} \end{aligned}$$

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

$$\begin{aligned} \hat{\mathbf{J}}_x &= -i\hbar \left( y \cdot \frac{\partial}{\partial z} - z \cdot \frac{\partial}{\partial y} \right) \\ \hat{\mathbf{J}}_y &= -i\hbar \left( z \cdot \frac{\partial}{\partial x} - x \cdot \frac{\partial}{\partial z} \right) \\ \hat{\mathbf{J}}_z &= -i\hbar \left( x \cdot \frac{\partial}{\partial y} - y \cdot \frac{\partial}{\partial x} \right) \end{aligned} \quad [15-1]$$

We have switched to  $\hat{\mathbf{J}}$  from  $L$  here, as  $\hat{\mathbf{J}}$  is the general angular momentum

symbol. One often sees  $\hat{L}$  used for orbital angular momentum,  $\hat{S}$  for electron spin angular momentum and  $\hat{I}$  for nuclear angular momentum, as well as the more general  $\hat{J}$ .

We can also define  $\hat{J}^2$  by summing the squares of each of the angular momentum component operators:

$$\hat{J}^2 = \hat{J}_x^2 + \hat{J}_y^2 + \hat{J}_z^2 \quad [15-2]$$

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

$$[\hat{J}_x, \hat{J}_y] = \hat{J}_x \hat{J}_y - \hat{J}_y \hat{J}_x$$

from the above definitions [15-1]:

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

What happened to the 'i'? It's there, hiding in the minus sign. Don't forget that we have multiplied  $\hat{J}_x$  times  $\hat{J}_y$ , each of which contains  $i$  and the product of  $i$  times  $i$  is  $-1$ . Using the product rule of the differential calculus (see Appendix II), the first term is:

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

so that the last line becomes:

$$\hat{J}_x \hat{J}_y = -\hbar^2 \left[ y \cdot \frac{\partial}{\partial x} + zy \cdot \frac{\partial^2}{\partial z \partial x} - z^2 \cdot \frac{\partial^2}{\partial y \partial x} - yx \cdot \frac{\partial^2}{\partial z^2} + zx \cdot \frac{\partial^2}{\partial y \partial z} \right]$$

similarly:

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

and so:

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

using the definition of  $\hat{J}_z$  above and the fact that  $i^2 = -1$ . Similarly we can write:

$$\begin{aligned}
[\hat{J}_x, \hat{J}_y] &= i \hbar \hat{J}_z \\
[\hat{J}_z, \hat{J}_x] &= i \hbar \hat{J}_y \\
[\hat{J}_y, \hat{J}_z] &= i \hbar \hat{J}_x
\end{aligned} \tag{15-3}$$

We note the cyclic permutation in these commutation relationships and that the components of the angular momenta 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 discussion of the uncertainty principle in chapter 13. Put another way, there are no functions that are simultaneously eigenfunctions of all three angular momentum operators. One will often see these commutation relationships written in 'frequency' notation. Recalling from chapter 13 that Planck's energy equation relates the energy of a photon to its frequency  $E = h\nu$  where  $\nu$  is in hertz. Alternatively:

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

where  $\omega$  is in radians per second. Dividing by  $\hbar$  gives the frequency notation which is more useful to us as nmr spectroscopists. We shall however have occasion to temporarily switch back to the energy notation in a later chapter. If we divide our commutation relationships, [15-3], by  $\hbar$  we get the frequency notation:

$$\begin{aligned}
[\hat{J}_x, \hat{J}_y] &= i \hat{J}_z \\
[\hat{J}_z, \hat{J}_x] &= i \hat{J}_y \\
[\hat{J}_y, \hat{J}_z] &= i \hat{J}_x
\end{aligned} \tag{15-4}$$

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

$$\begin{aligned}
[\hat{J}^2, \hat{J}_x] &= 0 \\
[\hat{J}^2, \hat{J}_y] &= 0 \\
[\hat{J}^2, \hat{J}_z] &= 0
\end{aligned}$$

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

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

$$\hat{J}_+ = \hat{J}_x + i\hat{J}_y \quad \text{and} \quad \hat{J}_- = \hat{J}_x - i\hat{J}_y \quad [15-5]$$

Their commutation relationships are:

$$\begin{aligned}
[\hat{J}^2, \hat{J}_+] &= [\hat{J}^2, \hat{J}_-] = 0 \\
[\hat{J}_z, \hat{J}_+] &= \hat{J}_+ \quad \text{or} \\
\hat{J}_z \hat{J}_+ - \hat{J}_+ \hat{J}_z &= \hat{J}_+ \\
[\hat{J}_z, \hat{J}_-] &= -\hat{J}_- \\
[\hat{J}_+, \hat{J}_-] &= 2\hat{J}_z
\end{aligned} \quad [15-6]$$

and inspection will show that:

$$\hat{J}_+ = \hat{J}_-^* \quad \hat{J}_- = \hat{J}_+^*$$

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

$$\begin{aligned}
\hat{J}^2 |j, m\rangle &= \lambda_j |j, m\rangle \\
\hat{J}_z |j, m\rangle &= \lambda_m |j, m\rangle
\end{aligned} \quad [15-7]$$

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

$$\begin{aligned}\hat{J}^2 \Psi_{j,m} &= \lambda_j \Psi_{j,m} \\ \hat{J}_z \Psi_{j,m} &= \lambda_m \Psi_{j,m}\end{aligned}$$

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

Note that these are or can be made to be *orthonormal* functions where:

$$\langle j',m' | j,m \rangle = 1 \quad \text{if } j'=j \text{ and } m'=m$$

or

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

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

Now, from the definition of  $\hat{J}^2$  ([15-2]):

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

and, using this in our eigenvalue equation [15-7]:

$$\begin{aligned}(\hat{J}_x^2 + \hat{J}_y^2) | j,m \rangle &= (\hat{J}^2 - \hat{J}_z^2) | j,m \rangle \\ &= (\lambda_j - \lambda_m^2) | j,m \rangle\end{aligned}$$

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

$$\lambda_j - \lambda_m^2 \geq 0 \quad [15-8]$$

Recalling the commutator  $[\hat{J}_z, \hat{J}_+] = \hat{J}_+$  or  $\hat{J}_z \hat{J}_+ - \hat{J}_+ \hat{J}_z = \hat{J}_+$  (from [15-6]) we can write:

$$\langle j,m' | \hat{J}_z \hat{J}_+ - \hat{J}_+ \hat{J}_z | j,m \rangle = \langle j,m' | \hat{J}_+ | j,m \rangle$$

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:

$$\begin{aligned}
\hat{J}_z \hat{J}_+ |j, m\rangle &= (\hat{J}_+ + \hat{J}_+ \hat{J}_z) |j, m\rangle \\
&\text{(using } \hat{J}_z \hat{J}_+ - \hat{J}_+ \hat{J}_z = \hat{J}_+ \text{)} \\
&= (\hat{J}_+ + \hat{J}_+ \lambda_m) |j, m\rangle \\
&= (\lambda_m + 1) \hat{J}_+ |j, m\rangle
\end{aligned}$$

This shows us that  $\hat{J}_z \hat{J}_+$ , operating on the eigenfunction,  $|j, m\rangle$ , produces an eigenvalue of  $\lambda_m$  plus one. **Wow!** What a result! Let's think about it for a moment. The result of  $\hat{J}_z |j, m\rangle$  is  $\lambda_m |j, m\rangle$  ... we said this earlier in equation [15-7]. Contrast this with  $\hat{J}_z \hat{J}_+ |j, m\rangle$  which gives  $(\lambda_m + 1) \hat{J}_+ |j, m\rangle$ . If you consider  $\hat{J}_+ |j, m\rangle$  as a whole to be just another eigenfunction of  $\hat{J}_z$ , then this result indicates that  $\hat{J}_+$  must operate on  $|j, m\rangle$  to give  $|j, m+1\rangle$ :

$$\hat{J}_+ |j, m\rangle = \zeta_m |j, m+1\rangle \quad [15-10]$$

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  $\hat{J}_z$  whose eigenvalues are separated from each other by one.

Similarly:

$$\hat{J}_- |j, m\rangle = \xi_m |j, m-1\rangle \quad [15-11]$$

Now, since we have shown that  $\lambda_j - \lambda_m^2 \geq 0$  (equation [15-8]), this means that there must be a maximum and a minimum value for  $\lambda_m$ . In other words:

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

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:

$$\begin{aligned}
\hat{J}_+ |j, m_{\max}\rangle &= 0 \\
\hat{J}_- |j, m_{\min}\rangle &= 0
\end{aligned} \quad [15-12]$$

Now:

$$\begin{aligned}
\hat{J}_- \hat{J}_+ |j, m_{\max}\rangle &= (\hat{J}^2 - \hat{J}_z^2 - \hat{J}_z) |j, m_{\max}\rangle \\
&\text{(from the definitions of } \hat{J}_- \text{ and } \hat{J}_+ \text{)} \\
&= (\lambda_j - \lambda_{m(\max)}^2 - \lambda_{m(\max)}) |j, m_{\max}\rangle = 0
\end{aligned}$$

Why you ask, is it equal to zero?

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

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

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

or:

$$\begin{aligned} \lambda_j &= \lambda_{m(max)}^2 + \lambda_{m(max)} \\ \lambda_j &= \lambda_{m(max)} (\lambda_{m(max)} + 1) \end{aligned}$$

Similarly, for  $\hat{J}_- \hat{J}_+ |j, m_{min}\rangle$ , 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  $\hat{J}_z |j, m\rangle$  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  $\hat{J}_z |j, m\rangle$  can take only the values  $\dots -3/2, -1, -1/2, 0, +1/2, +1, +3/2 \dots$ . 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  $\lambda_m$  ranges from  $\lambda_{m(min)}$  to  $\lambda_{m(max)}$  in steps of one, the values that  $j$  can take are  $0, 1/2, 1, 3/2, 2 \dots$

The possible values of  $\lambda_m$  depend on  $j$  and the fact that they differ by one from each other. So, if  $j=1$ , then  $\lambda_m$  or  $m$  for short<sup>2</sup>, can be  $-1, 0, +1$ . More generally, for a given value of  $j$ ,  $m$  ranges from  $-j$  to  $+j$  in steps of one.

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<sup>2</sup> This is one of the things that some books fail to point out explicitly! I guess you are supposed to already know it.

So now we have the eigenvalues of  $\hat{J}^2$  and  $\hat{J}_z$ ,  $j(j+1)$  and  $m$  respectively.

Ready for more? Lets look at  $\zeta_m$  and  $\xi_m$ . As you will no doubt instantly recall:

$$\langle j, m | \hat{J}_- \hat{J}_+ | j, m \rangle = \zeta_m \langle j, m | \hat{J}_- | j, m+1 \rangle = \zeta_m \xi_{m+1} \langle j, m | j, m \rangle = \zeta_m \xi_{m+1}$$

also, burned into your mind is:

$$\langle j, m | \hat{J}_- \hat{J}_+ | j, m \rangle = \langle j, m | \hat{J}^2 - \hat{J}_z^2 - \hat{J}_z | j, m \rangle$$

and since we now know what the eigenvalues of  $\hat{J}^2$  and  $\hat{J}_z$  are:

$$\begin{aligned} \langle j, m | \hat{J}^2 - \hat{J}_z^2 - \hat{J}_z | j, m \rangle &= j(j+1) - m^2 - m \\ &= j(j+1) - m(m+1) \\ &= \zeta_m \xi_{m+1} \end{aligned}$$

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

$$\begin{aligned} \langle j, m | \hat{J}_- \hat{J}_+ | j, m \rangle &= \zeta_m \langle j, m | \hat{J}_- | j, m+1 \rangle \\ &= \zeta_m [\langle j, m+1 | \hat{J}_+ | j, m \rangle]^* \\ &= \zeta_m \zeta_m^* \langle j, m+1 | j, m+1 \rangle \\ &= \zeta_m \zeta_m^* \end{aligned}$$

(since  $\hat{J}_+$  is hermitian,  $\hat{J}_-^* = \hat{J}_+$  )

So:

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

and:

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

Similarly, for  $\langle j, m | \hat{J}_+ \hat{J}_- | j, m \rangle$  :

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

In summary we now have four eigenvalue equations:

1.  $\hat{J}_z |j, m\rangle = m |j, m\rangle$  and there will be  $2j+1$  possible eigenvalues of  $\hat{J}_z$ .
2.  $\hat{J}^2 |j, m\rangle = j(j+1) |j, m\rangle$
3.  $\hat{J}_+ |j, m\rangle = (\sqrt{j(j+1)-m(m+1)}) |j, m+1\rangle$
4.  $\hat{J}_- |j, m\rangle = (\sqrt{j(j+1)-m(m-1)}) |j, m-1\rangle$

Also, we can derive expressions using  $\hat{J}_x$  and  $\hat{J}_y$ . From the definitions of the ladder operators:

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

and

$$\hat{J}_y = \frac{\hat{J}_+ - \hat{J}_-}{2i}$$

So:

$$\begin{aligned} \hat{J}_x |j, m\rangle &= \frac{(\hat{J}_+ + \hat{J}_-)}{2} |j, m\rangle \\ &= \frac{\hat{J}_+}{2} |j, m\rangle + \frac{\hat{J}_-}{2} |j, m\rangle \\ &= \frac{1}{2} (\sqrt{j(j+1)-m(m+1)}) |j, m+1\rangle + \frac{1}{2} (\sqrt{j(j+1)-m(m-1)}) |j, m-1\rangle \end{aligned} \quad [15-13a]$$

Similarly:

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

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

$$\begin{aligned} \hat{J}_y |j, m\rangle &= \\ &= -\frac{i}{2} (\sqrt{j(j+1)-m(m+1)}) |j, m+1\rangle + \frac{i}{2} (\sqrt{j(j+1)-m(m-1)}) |j, m-1\rangle \end{aligned} \quad [15-13b]$$

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

The symbol,  $\mathbf{J}$ , 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  $\mathbf{L}$  or when the nuclear spin is of interest,  $\mathbf{I}$  or  $\mathbf{S}$  would be used. The math and the results do not

change however.

## Coupling of Angular Momenta

Let's review our commutation relations from equation [15-3] for a moment. We have, in general:

$$[\hat{J}_i, \hat{J}_j] = i\hbar \sum \epsilon_{ij} \hat{J}_k$$

where  $i$ ,  $j$  and  $k$  stand for  $x$ ,  $y$  and  $z$ <sup>3</sup>. The symbol  $\epsilon_{ij}$  is the Levi-Cervita permutation symbol. The possible values are:

$$\begin{aligned} \epsilon_{ij} &= 0 \quad (\text{i and j equal}) \\ \epsilon_{ij} &= 1 \quad (\text{i and j and k cyclicly permuted}) \\ \epsilon_{ji} &= -1 \quad (\text{i and j swapped}) \end{aligned}$$

Thus we can easily find for example, that:

$$[\hat{J}_y, \hat{J}_x] = -i\hbar \hat{J}_z$$

since the order of  $x$  and  $y$  has been swapped. These commutation relations can be used to find the commutation relations for the ladder operators:

$$\begin{aligned} [\hat{J}_+, \hat{J}_-] &= 2\hbar \hat{J}_z \\ [\hat{J}_\pm, \hat{J}_z] &= \mp \hbar \hat{J}_\pm \end{aligned}$$

Now let's consider two *independent* angular momenta,  $\hat{J}_1$  and  $\hat{J}_2$ . By independent, we mean that if some change happens to  $\hat{J}_1$ , nothing happens to  $\hat{J}_2$  and *vice versa*. Since they are independent they will each have their own state space and will therefore commute:

$$[\hat{J}_1, \hat{J}_2] = 0$$

We can take it a bit further and look at the commutators of the components of  $\hat{J}_1$  and  $\hat{J}_2$ . Again, because they each have their own space independent of the other the commutators will be zero:

$$[\hat{J}_{1i}, \hat{J}_{2j}] = 0 \quad (i, j = 1, 2, 3)$$

Also, given our above analysis, we can say something about the effect

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<sup>3</sup> Note that "i" used in this context is a subscript, *not* the square root of minus one!

of operators,  $\hat{J}_i^2$  and  $\hat{J}_{iz}$  on the eigenvectors for their respective states:

$$\begin{aligned}\hat{J}_i^2 |j_i m_i\rangle &= j_i(j_i+1) |j_i m_i\rangle \\ \hat{J}_{iz} |j_i m_i\rangle &= m_i |j_i m_i\rangle\end{aligned}$$

The sum of these angular momenta is:

$$\hat{J}_T = \hat{J}_1 + \hat{J}_2$$

Now, we consider two angular momenta that are *not* independent. In other words, when a change occurs to angular momentum vector 1 an effect on angular momentum 2 is felt. We then say that the two momenta are *coupled*. From Newton's third law, we find that linear momentum and by extension, angular momentum are conserved. Thus, if for some reason there is a change in angular momentum 1 there will be a change in angular momentum 2 such the sum of their momenta remains constant (unless energy from an external source is added).

$$\hat{J}_T = \hat{J}_1 + \hat{J}_2$$

Coupling of angular momenta is treated in the literature in a .. shall we say, rather disjointed way. There is no apparent agreement on how states are written which makes reading by the uninitiated that much more difficult.

## Angular Momentum Operator Matrices

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

$$\begin{aligned}\langle j, m | \hat{J}_z | j, m \rangle &= \langle j, m | m | j, m \rangle \\ &= \langle j, m | j, m \rangle \\ &= m \\ (\langle j, m | j, m \rangle \text{ normalized and equal to one})\end{aligned}$$

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 use a  $3 \times 3$  matrix (3 because of the three values of  $m$ ). The columns in the matrix would be labeled  $|j, +j\rangle$  to  $|j, -j\rangle$  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 ...  $\langle j,+j|$  to  $\langle j,-j|$  .

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  $J_z$  would be:

$$\langle 1,1| J_z | 1,1\rangle = \langle 1,1| 1 | 1,1\rangle = 1 \langle 1,1| 1,1\rangle = 1$$

The whole  $J_z$  matrix for our  $j=1$  spin is:

$$J_z = \begin{matrix} & | 1,1\rangle & | 1,0\rangle & | 1,-1\rangle \\ \begin{matrix} \langle 1,1| \\ \langle 1,0| \\ \langle 1,-1| \end{matrix} & \begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{bmatrix} \end{matrix}$$

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:

$$\begin{aligned} \langle j,m | \hat{J}_z | j,m\rangle &= \langle j,m | m | j,m\rangle \\ &= m \langle j,m | j,m\rangle \\ &= m \end{aligned}$$

$$\begin{aligned} \langle j,m | \hat{J}^2 | j,m\rangle &= \langle j,m | j(j+1) | j,m\rangle \\ &= j(j+1) \langle j,m | j,m\rangle \\ &= j(j+1) \end{aligned}$$

$$\begin{aligned} \langle j,m+1 | \hat{J}_+ | j,m\rangle &= \langle j,m+1 | \sqrt{[j(j+1)-m(m+1)]} | j,m+1\rangle \\ &= \frac{(\sqrt{j(j+1)-m(m+1)}) \langle j,m+1 | j,m+1\rangle}{\sqrt{j(j+1)-m(m+1)}} \end{aligned}$$

and similarly:

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

There are two ways that the element of  $\hat{J}_x$  can be constructed, depending on the value of  $m$  in the bra:

$$\begin{aligned}
\langle j, m+1 | \hat{J}_x | j, m \rangle &= \langle j, m+1 | \frac{\sqrt{j(j+1)-m(m+1)}}{2} | j, m+1 \rangle \\
&= \left(\frac{1}{2}\right) (\sqrt{j(j+1)-m(m+1)}) \langle j, m+1 | j, m+1 \rangle \\
&= \left(\frac{1}{2}\right) \sqrt{j(j+1)-m(m+1)}
\end{aligned}$$

or

$$\begin{aligned}
\langle j, m-1 | \hat{J}_x | j, m \rangle &= \langle j, m-1 | \frac{\sqrt{j(j+1)-m(m-1)}}{2} | j, m-1 \rangle \\
&= \left(\frac{1}{2}\right) (\sqrt{j(j+1)-m(m-1)}) \langle j, m-1 | j, m-1 \rangle \\
&= \left(\frac{1}{2}\right) \sqrt{j(j+1)-m(m-1)}
\end{aligned}$$

Similarly for  $\hat{J}_y$  :

$$\begin{aligned}
\langle j, m+1 | \hat{J}_y | j, m \rangle &= \langle j, m+1 | \frac{i\sqrt{j(j+1)-m(m+1)}}{2} | j, m+1 \rangle \\
&= \left(\frac{i}{2}\right) (\sqrt{j(j+1)-m(m+1)}) \langle j, m+1 | j, m+1 \rangle \\
&= \left(\frac{i}{2}\right) \sqrt{j(j+1)-m(m+1)}
\end{aligned}$$

or

$$\begin{aligned}
\langle j, m-1 | \hat{J}_y | j, m \rangle &= \langle j, m-1 | \frac{i\sqrt{j(j+1)-m(m-1)}}{2} | j, m-1 \rangle \\
&= \left(\frac{i}{2}\right) (\sqrt{j(j+1)-m(m-1)}) \langle j, m-1 | j, m-1 \rangle \\
&= \left(\frac{i}{2}\right) \sqrt{j(j+1)-m(m-1)}
\end{aligned}$$

This is *lot* of stuff for what turns out to be some really rather simple matrices. In the case of spin- $\frac{1}{2}$  nuclei (spin- $\frac{1}{2}$  refers of course to  $j=\frac{1}{2}$ ) we can calculate what the expectation values of the nuclear spin angular momentum operators,  $\hat{I}_z$ ,  $\hat{I}_x$  and  $\hat{I}_y$  are. For  $\hat{I}_z$  the calculation is particularly simple. Since:

$$\begin{aligned}
\langle \frac{1}{2}, \frac{1}{2} | \hat{I}_z | \frac{1}{2}, \frac{1}{2} \rangle &= \frac{1}{2} \\
\langle \frac{1}{2}, \frac{1}{2} | \hat{I}_z | \frac{1}{2}, -\frac{1}{2} \rangle &= 0 \\
\langle \frac{1}{2}, -\frac{1}{2} | \hat{I}_z | \frac{1}{2}, -\frac{1}{2} \rangle &= -\frac{1}{2} \\
&\text{and} \\
\langle \frac{1}{2}, -\frac{1}{2} | \hat{I}_z | \frac{1}{2}, \frac{1}{2} \rangle &= 0
\end{aligned}$$

the matrix is:

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

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

$$\begin{array}{cc} & |\frac{1}{2}, \frac{1}{2}\rangle & |\frac{1}{2}, -\frac{1}{2}\rangle \\ \begin{array}{l} \langle \frac{1}{2}, \frac{1}{2} | \\ \langle \frac{1}{2}, -\frac{1}{2} | \end{array} & \begin{bmatrix} a & b \\ c & d \end{bmatrix} \end{array}$$

As you will recall from a few lines back, there are two expressions for the expectation value of  $\hat{I}_x$  ( $\hat{J}_x$  actually, since it was a general angular momentum operator then) depending on whether m increases by one or decreases by one. If you look at row 1, column 1, this is  $\langle \frac{1}{2}, \frac{1}{2} | \hat{I}_x | \frac{1}{2}, \frac{1}{2} \rangle$ . 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  $\langle \frac{1}{2}, \frac{1}{2} | \sqrt{[j(j+1)-m(m-1)]} | \frac{1}{2}, -\frac{1}{2} \rangle$  or  $\sqrt{[j(j+1)-m(m-1)]} \langle \frac{1}{2}, \frac{1}{2} | \frac{1}{2}, -\frac{1}{2} \rangle$  and since the basis functions are assumed orthonormal to one another the expression  $\langle \frac{1}{2}, \frac{1}{2} | \frac{1}{2}, -\frac{1}{2} \rangle$  is equal to zero. Similar calculations for the other matrix elements lead to the  $\hat{I}_x$  matrix:

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

and similarly,  $\hat{I}_y$ :

$$I_y = \begin{bmatrix} 0 & -\frac{i}{2} \\ \frac{i}{2} & 0 \end{bmatrix} = \frac{1}{2} \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}$$

For spin 1/2 nuclei we often abbreviate  $|\frac{1}{2}, \frac{1}{2}\rangle$  to  $|\alpha\rangle$  and  $|\frac{1}{2}, -\frac{1}{2}\rangle$  to  $|\beta\rangle$

and the nuclear spin operators are  $\hat{I}_z$  or  $\hat{I}_x$  or  $\hat{I}_y$ . There are, of course, corresponding ladder operators,  $\hat{I}_+$  and  $\hat{I}_-$ . Hopefully, from the above discussion and the discussion of angular momentum operators you can see that:

$$\begin{aligned} \hat{I}_z |\alpha\rangle &= \frac{1}{2} |\alpha\rangle \\ \text{and} & \\ \hat{I}_z |\beta\rangle &= -\frac{1}{2} |\beta\rangle \end{aligned} \quad [15-14a]$$

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

$$\begin{aligned} \hat{I}_+ &= \hat{I}_x + i\hat{I}_y \\ \hat{I}_- &= \hat{I}_x - i\hat{I}_y \end{aligned}$$

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

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

So:

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

and since these are linear operators:

$$\hat{I}_x |\alpha\rangle = \frac{1}{2} \hat{I}_+ |\alpha\rangle + \frac{1}{2} \hat{I}_- |\alpha\rangle$$

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

$$\hat{I}_x |\alpha\rangle = 0 + \frac{1}{2} |\beta\rangle$$

The "0" comes about because the eigenvalue of  $\hat{I}_+ |\alpha\rangle$  works out to be zero for spin  $\frac{1}{2}$ . This is, of course, because the ladder operator,  $\hat{I}_+$ , increases m by one but for the  $|\alpha\rangle$  spin state m is already as high as it can be. Thus, operating on it with a 'raising' operator returns

nothing.

Thus:

$$\hat{I}_x |\alpha\rangle = \frac{1}{2} |\beta\rangle \quad [15-14b]$$

and similarly:

$$\begin{aligned} \hat{I}_x |\beta\rangle &= \frac{1}{2} |\alpha\rangle \\ \hat{I}_y |\alpha\rangle &= \frac{i}{2} |\beta\rangle \\ \hat{I}_y |\beta\rangle &= -\frac{i}{2} |\alpha\rangle \end{aligned} \quad [15-14c]$$

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

## Expectation Values

We can now write the state of our single spin-1/2 as a superposition of basis states  $|\alpha\rangle$  and  $|\beta\rangle$ :

$$|\Psi\rangle = c_\alpha |\alpha\rangle + c_\beta |\beta\rangle$$

followed by an expectation value calculation:

$$\begin{aligned} \langle I_z \rangle &= \langle \Psi | I_z | \Psi \rangle = \langle \alpha | c_\alpha^* + \langle \beta | c_\beta^* \rangle I_z [c_\alpha |\alpha\rangle + c_\beta |\beta\rangle] \\ &= \langle \alpha | c_\alpha^* + \langle \beta | c_\beta^* \rangle \left[ c_\alpha \cdot \frac{1}{2} |\alpha\rangle - c_\beta \cdot \frac{1}{2} |\beta\rangle \right] \\ &= \frac{1}{2} c_\alpha^* c_\alpha \langle \alpha | \alpha \rangle - \frac{1}{2} c_\alpha^* c_\beta \langle \alpha | \beta \rangle + \frac{1}{2} c_\beta^* c_\alpha \langle \beta | \alpha \rangle - \frac{1}{2} c_\beta^* c_\beta \langle \beta | \beta \rangle \\ &= \frac{1}{2} c_\alpha^* c_\alpha - 0 + 0 - \frac{1}{2} c_\beta^* c_\beta \\ &= \frac{1}{2} (c_\alpha^* c_\alpha - c_\beta^* c_\beta) \\ &= \frac{1}{2} (c_\alpha^2 - c_\beta^2) \end{aligned} \quad [15-15a]$$

where  $c_\alpha^2$  and  $c_\beta^2$  represent the probabilities of finding the spin in state  $|\alpha\rangle$  or  $|\beta\rangle$  respectively. Thus the expectation value is half the difference between these two probabilities.

Similarly for  $I_x$  and  $I_y$  :

$$\begin{aligned}
 \langle I_x \rangle &= [\langle \alpha | c_\alpha^* + \langle \beta | c_\beta^* ] I_x [ c_\alpha | \alpha \rangle + c_\beta | \beta \rangle ] \\
 &= [\langle \alpha | c_\alpha^* + \langle \beta | c_\beta^* ] \left[ \frac{1}{2} c_\alpha | \beta \rangle + \frac{1}{2} c_\beta | \alpha \rangle \right] \\
 &= \frac{1}{2} c_\alpha^* c_\alpha \langle \alpha | \beta \rangle + \frac{1}{2} c_\alpha^* c_\beta \langle \alpha | \alpha \rangle + \frac{1}{2} c_\beta^* c_\alpha \langle \beta | \beta \rangle + \frac{1}{2} c_\beta^* c_\beta \langle \beta | \alpha \rangle \quad [15-15b] \\
 &= 0 + \frac{1}{2} c_\alpha^* c_\beta + \frac{1}{2} c_\beta^* c_\alpha + 0 \\
 &= \frac{1}{2} (c_\alpha^* c_\beta + c_\beta^* c_\alpha)
 \end{aligned}$$

$$\begin{aligned}
 \langle I_y \rangle &= [\langle \alpha | c_\alpha^* + \langle \beta | c_\beta^* ] I_y [ c_\alpha | \alpha \rangle + c_\beta | \beta \rangle ] \\
 &= [\langle \alpha | c_\alpha^* + \langle \beta | c_\beta^* ] \left[ \frac{i}{2} c_\alpha | \beta \rangle - \frac{i}{2} c_\beta | \alpha \rangle \right] \\
 &= \frac{i}{2} c_\alpha^* c_\alpha \langle \alpha | \beta \rangle - \frac{i}{2} c_\alpha^* c_\beta \langle \alpha | \alpha \rangle + \frac{i}{2} c_\beta^* c_\alpha \langle \beta | \beta \rangle - \frac{i}{2} c_\beta^* c_\beta \langle \beta | \alpha \rangle \quad [15-15c] \\
 &= 0 - \frac{i}{2} c_\alpha^* c_\beta + \frac{i}{2} c_\beta^* c_\alpha - 0 \\
 &= \frac{i}{2} (c_\beta^* c_\alpha - c_\alpha^* c_\beta)
 \end{aligned}$$

A moment's reflection (and a review of the chapter on complex numbers) will reveal that:

$$\begin{aligned}
 \langle I_x \rangle &= \frac{1}{2} [c_\alpha^* c_\beta + c_\beta^* c_\alpha] = \text{Re} [c_\alpha^* c_\beta] \\
 \langle I_y \rangle &= \frac{i}{2} [c_\beta^* c_\alpha - c_\alpha^* c_\beta] = \text{Im} [c_\alpha^* c_\beta]
 \end{aligned} \quad [15-16]$$

From the discussion of complex numbers in chapter one we recall that complex numbers may be represented in Argand notation or polar notation. If we choose polar notation we can write our complex coefficients as:

$$\begin{aligned}
 c_\alpha &= r_\alpha e^{i\phi_\alpha} & c_\alpha^* &= r_\alpha e^{-i\phi_\alpha} \\
 c_\beta &= r_\beta e^{i\phi_\beta} & c_\beta^* &= r_\beta e^{-i\phi_\beta}
 \end{aligned}$$

and then rewrite our expectation values in polar notation and using trigonometric identity [A-12] from Appendix II:

$$\begin{aligned} \langle I_z \rangle &= \frac{1}{2} (c_\alpha^2 - c_\beta^2) \\ &+ \frac{1}{2} (r_\alpha^2 e^{i2\phi_\alpha} - r_\beta^2 e^{i2\phi_\beta}) \end{aligned} \quad [15-17a]$$

$$\begin{aligned} \langle I_x \rangle &= \frac{1}{2} (c_\alpha^* c_\beta + c_\beta^* c_\alpha) \\ &+ \frac{1}{2} (r_\alpha e^{-i\phi_\alpha} r_\beta e^{i\phi_\beta} + r_\beta e^{-i\phi_\beta} r_\alpha e^{i\phi_\alpha}) \\ &= \frac{1}{2} (r_\alpha r_\beta [e^{i(\phi_\beta - \phi_\alpha)} + e^{-i(\phi_\beta - \phi_\alpha)}]) \\ &= r_\alpha r_\beta \cos(\phi_\beta - \phi_\alpha) \end{aligned} \quad [15-17b]$$

$$\begin{aligned} \langle I_y \rangle &= \frac{i}{2} (c_\beta^* c_\alpha - c_\alpha^* c_\beta) \\ &+ \frac{i}{2} (r_\beta e^{-i\phi_\beta} r_\alpha e^{i\phi_\alpha} - r_\alpha e^{-i\phi_\alpha} r_\beta e^{i\phi_\beta}) \\ &= \frac{i}{2} (r_\alpha r_\beta [e^{-i(\phi_\beta - \phi_\alpha)} - e^{i(\phi_\beta - \phi_\alpha)}]) \\ &= \frac{i}{2} (-2i \sin(\phi_\beta - \phi_\alpha)) \\ &= r_\alpha r_\beta \sin(\phi_\beta - \phi_\alpha) \end{aligned} \quad [15-17c]$$

We shall have occasion to look more closely at these expressions in a later chapter.

## Time Evolution

In chapter 12 we developed the stationary Schrodinger equations in terms of the superposition principle. We did not, however, discuss the time evolution of states but rather deferred it until we have a specific form for the Hamiltonian operator. We will now develop the Hamiltonians for  $I_z$ ,  $I_x$ , and  $I_y$  and, coupling them with the effect of these operators on the states of a single spin-1/2 (equation [10-14]), we shall be able to obtain some expressions for the behavior of a spin system with respect to time. We will not include relaxation in our calculations and so will produce equations that are artificial models of the physics of a spin system. Nonetheless, they will prove very useful.

Recall from equation [12-16] that the classical expression for the energy of a magnetic moment in an external magnetic field is:

$$\begin{aligned}
E &= -\vec{\mu} \cdot \vec{B} \\
&= -\mu_x B_x - \mu_y B_y - \mu_z B_z
\end{aligned}$$

where  $\vec{\mu}$  is the magnetic moment vector and  $\vec{B}$  is the external field vector. Recall also from equation [12-13] that the magnetic moment is proportional to the angular momentum:

$$\begin{aligned}
\vec{\mu} &= \frac{q}{2m} \cdot \vec{L} \\
&= \gamma \cdot \vec{L} \\
&= \gamma L_x + \gamma L_y + \gamma L_z \\
&= \mu_x + \mu_y + \mu_z
\end{aligned}$$

where  $\gamma$  is the gyromagnetic ratio. What we want to do, of course, is convert this to the corresponding Hamiltonian expression.

Substituting the proportionality equation into the energy equation:

$$E = -\gamma L_x B_x - \gamma L_y B_y - \gamma L_z B_z$$

and from the beginning of this chapter:

$$\begin{aligned}
L_x &= yp_z - zp_y \\
L_y &= zp_x - xp_z \\
L_z &= xp_y - yp_x
\end{aligned}$$

Our energy equation now can be written:

$$E = -\gamma B_x (yp_z - zp_y) - \gamma B_y (zp_x - xp_z) - \gamma B_z (xp_y - yp_x) \quad [15-18]$$

Remember that this is still the classical energy expression. If we want the analogous quantum mechanical operators we replace the momenta,  $p_x$ ,  $p_y$  and  $p_z$  with  $-i\hbar \frac{\partial}{\partial x}$ ,  $-i\hbar \frac{\partial}{\partial y}$  and  $-i\hbar \frac{\partial}{\partial z}$  respectively. So, the quantum mechanical energy Hamiltonian for a magnetic moment in an external field is:

$$\begin{aligned}
H &= -i\hbar \gamma B_x \left( y \cdot \frac{\partial}{\partial z} - z \cdot \frac{\partial}{\partial y} \right) \\
&\quad - i\hbar \gamma B_y \left( z \cdot \frac{\partial}{\partial x} - x \cdot \frac{\partial}{\partial z} \right) \\
&\quad - i\hbar \gamma B_z \left( x \cdot \frac{\partial}{\partial y} - y \cdot \frac{\partial}{\partial x} \right)
\end{aligned}$$

or, using equation [15-1]:

$$\begin{aligned}
H &= -\gamma B_x I_x \\
&\quad -\gamma B_y I_y \\
&\quad -\gamma B_z I_z
\end{aligned}$$

where we have used  $I$  as the symbol for angular momentum operator instead of  $J$ . In practice, the direction of the external field is defined as the z-direction and there will therefore be no x or y component to the external field. The  $\vec{B}_z$  component is often written  $\vec{B}_0$ , as we have seen in the discussion of the Bloch equations. Thus, the Hamiltonian simplifies to:

$$H = -\gamma B_0 I_z$$

Also, recalling equation [12-15], we can write the Hamiltonian in terms of the Larmor precession frequency:

$$H = \omega_0 I_z$$

The fifth postulate of quantum mechanics listed in chapter 13 gave us the time-dependent Schrodinger equation:

$$H | \Psi(t) \rangle = i\hbar \frac{d}{dt} | \Psi(t) \rangle$$

or in units of  $\hbar$ :

$$\begin{aligned}
H | \Psi(t) \rangle &= i \frac{d}{dt} | \Psi(t) \rangle \\
\frac{d}{dt} | \Psi(t) \rangle &= -iH | \Psi(t) \rangle
\end{aligned}$$

Since we now have an explicit Hamiltonian we can insert it into the equation:

$$\frac{d}{dt} | \Psi(t) \rangle = -i\omega_0 I_z | \Psi(t) \rangle$$

Substituting the superposition state terms gives us:

$$\frac{d}{dt} (c_\alpha(t) | \alpha \rangle + c_\beta(t) | \beta \rangle) = -i\omega_0 I_z (c_\alpha(t) | \alpha \rangle + c_\beta(t) | \beta \rangle)$$

Note here that we have assumed the time dependence to be wholly in the coefficients  $c_\alpha$  and  $c_\beta$ . This is similar to the situation with classical coordinate systems. There, the basis vectors don't change

with time but the coordinates of position vectors do change with time when describing motion. In other words, the coefficients of the position vectors change but the basis vectors are time invariant<sup>4</sup>. We assume the basis states  $|\alpha\rangle$  and  $|\beta\rangle$  to be time-invariant as well which means the time-dependence is in the coefficients.

We now cast the problem as an inner product calculation using  $\langle\alpha|$  as the bra:

$$\begin{aligned} \langle\alpha| \frac{d}{dt}(c_\alpha(t)|\alpha\rangle + c_\beta(t)|\beta\rangle) &= \langle\alpha| -i\omega_0 \mathbf{I}_z (c_\alpha(t)|\alpha\rangle + c_\beta(t)|\beta\rangle) \\ \frac{d}{dt}c_\alpha(t)\langle\alpha|\alpha\rangle + \frac{d}{dt}c_\beta(t)\langle\alpha|\beta\rangle &= \langle\alpha| -i\omega_0 \mathbf{I}_z c_\alpha(t)|\alpha\rangle + \langle\alpha| -i\omega_0 \mathbf{I}_z c_\beta(t)|\beta\rangle \\ \frac{dc_\alpha(t)}{dt} &= \frac{-i\omega_0 c_\alpha(t)}{2} \langle\alpha|\alpha\rangle + \frac{i\omega_0 c_\beta(t)}{2} \langle\alpha|\beta\rangle \\ \frac{dc_\alpha(t)}{dt} &= \frac{-i\omega_0 c_\alpha(t)}{2} \end{aligned}$$

This is a simple first-order differential equation which is easily solved (see Appendix II):

$$c_\alpha(t) = c_\alpha(0) e^{\frac{-i\omega_0 t}{2}}$$

A similar analysis (using  $|\beta\rangle$ ) for  $c_\beta$  gives us:

$$c_\beta(t) = c_\beta(0) e^{\frac{i\omega_0 t}{2}}$$

So we now have:

$$|\Psi(t)\rangle = c_\alpha(0) e^{\frac{-i\omega_0 t}{2}} |\alpha\rangle + c_\beta(0) e^{\frac{i\omega_0 t}{2}} |\beta\rangle$$

We ask now 'what is the time-dependence, if any, of the expectation values?'. For  $\langle I_z \rangle$ :

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<sup>4</sup> This need not be the case. We can reverse things and have the basis vectors change with time and the coordinate coefficients be static however this is not the usual approach, at least for introductory nmr spectroscopy.

$$\begin{aligned}
\langle I_z \rangle(t) &= \frac{1}{2} (c_\alpha^*(t) c_\alpha(t) - c_\beta^*(t) c_\beta(t)) \\
&= \frac{1}{2} \left( \left[ c_\alpha(0) e^{-\frac{i\omega_0 t}{2}} \right]^* \left[ c_\alpha(0) e^{-\frac{i\omega_0 t}{2}} \right] - \left[ c_\beta(0) e^{\frac{i\omega_0 t}{2}} \right]^* \left[ c_\beta(0) e^{\frac{i\omega_0 t}{2}} \right] \right) \\
&= \frac{1}{2} \left( c_\alpha(0)^* e^{\frac{i\omega_0 t}{2}} c_\alpha(0) e^{-\frac{i\omega_0 t}{2}} - c_\beta(0)^* e^{-\frac{i\omega_0 t}{2}} c_\beta(0) e^{\frac{i\omega_0 t}{2}} \right) \\
&= \frac{1}{2} (c_\alpha(0)^* c_\alpha(0) - c_\beta(0)^* c_\beta(0))
\end{aligned}$$

The  $c(0)$ 's are constants which means that under the influence of  $\mathbf{B}_0$  the expectation value of  $I_z$  is constant. Thinking in terms of the vector model of chapter 12, this is exactly what we would expect. For  $\langle I_x \rangle$  and  $\langle I_y \rangle$  :

$$\begin{aligned}
\langle I_x \rangle(t) &= \frac{1}{2} (c_\alpha^*(t) c_\beta(t) + c_\beta^*(t) c_\alpha(t)) \\
&= \frac{1}{2} \left( \left[ c_\alpha(0) e^{-\frac{i\omega_0 t}{2}} \right]^* \left[ c_\beta(0) e^{\frac{i\omega_0 t}{2}} \right] + \left[ c_\beta(0) e^{\frac{i\omega_0 t}{2}} \right]^* \left[ c_\alpha(0) e^{-\frac{i\omega_0 t}{2}} \right] \right) \\
&= \frac{1}{2} (c_\alpha(0)^* c_\beta(0) e^{i\omega_0 t} + c_\beta(0)^* c_\alpha(0) e^{-i\omega_0 t}) \\
&= \frac{1}{2} c_\alpha(0)^* c_\beta(0) (\cos(\omega_0 t) + i \sin(\omega_0 t)) + \frac{1}{2} c_\beta(0)^* c_\alpha(0) (\cos(\omega_0 t) - i \sin(\omega_0 t)) \\
&= \cos(\omega_0 t) \left( \frac{1}{2} c_\alpha(0)^* c_\beta(0) + \frac{1}{2} c_\beta(0)^* c_\alpha(0) \right) - \sin(\omega_0 t) \left( \frac{i}{2} c_\beta(0)^* c_\alpha(0) - \frac{i}{2} c_\alpha(0)^* c_\beta(0) \right) \\
&= \langle I_x \rangle(0) \cos(\omega_0 t) - \langle I_y \rangle(0) \sin(\omega_0 t) \\
\langle I_y \rangle(t) &= \frac{i}{2} (c_\beta^*(t) c_\alpha(t) - c_\alpha^*(t) c_\beta(t)) \\
&= \frac{i}{2} \left( \left[ c_\beta(0) e^{\frac{i\omega_0 t}{2}} \right]^* \left[ c_\alpha(0) e^{-\frac{i\omega_0 t}{2}} \right] - \left[ c_\alpha(0) e^{-\frac{i\omega_0 t}{2}} \right]^* \left[ c_\beta(0) e^{\frac{i\omega_0 t}{2}} \right] \right) \\
&= \frac{i}{2} (c_\beta(0)^* c_\alpha(0) e^{-i\omega_0 t} - c_\alpha(0)^* c_\beta(0) e^{i\omega_0 t}) \\
&= \frac{i}{2} c_\beta^*(0) c_\alpha(0) (\cos(\omega_0 t) - i \sin(\omega_0 t)) - \frac{i}{2} c_\alpha^*(0) c_\beta(0) (\cos(\omega_0 t) + i \sin(\omega_0 t)) \\
&= \cos(\omega_0 t) \left( \frac{i}{2} c_\beta^*(0) c_\alpha(0) - \frac{i}{2} c_\alpha^*(0) c_\beta(0) \right) + \sin(\omega_0 t) \left( \frac{1}{2} c_\alpha^*(0) c_\beta(0) + \frac{1}{2} c_\beta^*(0) c_\alpha(0) \right) \\
&= \langle I_y \rangle(0) \cos(\omega_0 t) + \langle I_x \rangle(0) \sin(\omega_0 t)
\end{aligned}$$

Recalling the precession of a magnetic moment from chapter 12 and specifically, figure 12-10, these are exactly what we would expect under the influence of an external magnetic field,  $\vec{\mathbf{B}}_0$ . The first equation says that  $\langle I_x \rangle(t)$  is a combination of  $\langle I_x \rangle(0)$  and  $\langle I_y \rangle(0)$  and that

as time progresses the mixture of the two changes in an oscillatory fashion. In terms of the vector model of chapter 12, we can picture a vector rotating in a right-hand sense about the z axis.

This sense of rotation is a bit difficult to visualize. At first glance it appears that it should be a left-hand rotation but keep in mind that the equation is describing the time-evolution of  $\langle I_x \rangle$  which is a scalar value (or a magnitude if you like) *not* a vector, and that the value of  $\langle I_x \rangle(t)$  is a *magnitude* calculation which depends on both  $\langle I_x \rangle(0)$  and  $\langle I_y \rangle(0)$  and the amount of time that has passed since  $t=0$ . The result of the calculation tells us the magnitude of the *projection* of the vector onto the  $\langle I_x \rangle(t)$ -axis (see figure 15-3).

So, at  $t=0$ :

$$\begin{aligned}\langle I_x \rangle(0) &= \langle I_x \rangle(0) \cos(\omega_0 0) - \langle I_y \rangle(0) \sin(\omega_0 0) \\ &= \langle I_x \rangle(0)\end{aligned}$$

(obviously). At  $t = \frac{\pi}{2\omega_0}$ :

$$\begin{aligned}\langle I_x \rangle\left(\frac{\pi}{2\omega_0}\right) &= \langle I_x \rangle(0) \cos\left(\omega_0 \frac{\pi}{2\omega_0}\right) - \langle I_y \rangle(0) \sin\left(\omega_0 \frac{\pi}{2\omega_0}\right) \\ &= -\langle I_y \rangle(0)\end{aligned}$$

and (the scalar)  $\langle I_x \rangle$  is equal to the negative of the initial value of  $\langle I_y \rangle$ . This can *only* be the case if, in a vector-picture the vector describes a rotation in the right-handed sense. You can use figure 15-3 to help in seeing this.

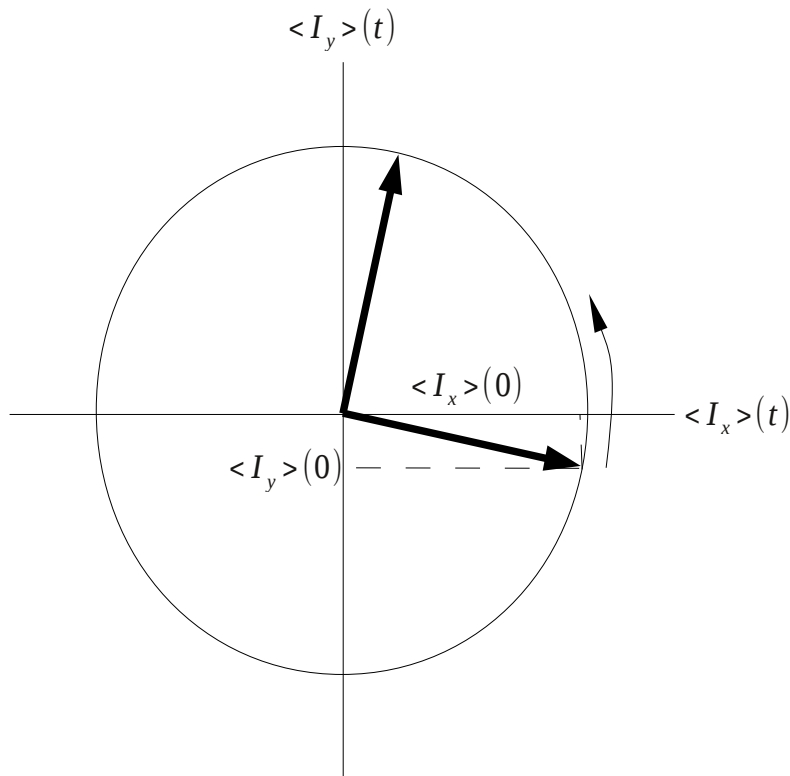


Figure 15-3: Vector picture of the time-evolution of  $\langle I_x \rangle$

The second equation says much the same for  $\langle I_y \rangle$  and implies the same handedness in the associated vector rotation.

We have just described the situation with respect to the time evolution of the system under the influence of an external magnetic field. There is another field to consider ... the applied  $\vec{B}_1$  field. In other words we now wish to know about the time evolution of the spin system under the influence of a pulse of rf energy.

The Hamiltonian that we use is very similar to the one we used to determine the time dependence of the spin system on the external field. Recall that the  $\vec{B}_1$  field is at right angles to the  $\vec{B}_0$  field and, as is usual, the coordinate system is such that the z-axis is parallel to the  $\vec{B}_0$  field. Also, recall that in the rotating frame of reference, the  $\vec{B}_0$  field disappears from the equations (at the rotating frame frequency, that is). So, using the rotating frame of reference we can write a Hamiltonian expression:

$$H = \omega_1 I_x$$

Of course, we have arbitrarily assumed that the  $\vec{B}_1$  field is aligned

with the x-axis but then we are free to choose where the x and y axes lie in the transverse plane. We could just as well have chosen the  $\vec{B}_1$  field to lie along the y-axis in which case we would write:

$$H = \omega_1 I_y$$

Note that the frequency here is  $\omega_1$  not  $\omega_0$  because the frequency of rotation is determined by the field strength and the  $\vec{B}_1$  field is (presumably!) appreciably different from that of the  $\vec{B}_0$  external field.

Our analysis proceeds much as above:

$$\begin{aligned} \langle \alpha | \frac{d}{dt} (c_\alpha(t) | \alpha \rangle + c_\beta(t) | \beta \rangle) &= \langle \alpha | -i\omega_1 I_x (c_\alpha(t) | \alpha \rangle + c_\beta(t) | \beta \rangle) \\ \frac{d}{dt} c_\alpha(t) \langle \alpha | \alpha \rangle + \frac{d}{dt} c_\beta(t) \langle \alpha | \beta \rangle &= \langle \alpha | -i\omega_1 I_x c_\alpha(t) | \alpha \rangle - \langle \alpha | -i\omega_1 I_x c_\beta(t) | \beta \rangle \\ \frac{d c_\alpha(t)}{dt} &= \frac{-i\omega_1 c_\alpha(t)}{2} \langle \alpha | \beta \rangle - \frac{i\omega_1 c_\beta(t)}{2} \langle \alpha | \alpha \rangle \\ \frac{d c_\alpha(t)}{dt} &= \frac{-i\omega_1 c_\beta(t)}{2} \end{aligned}$$

and similarly:

$$\begin{aligned} \langle \beta | \frac{d}{dt} (c_\alpha(t) | \alpha \rangle + c_\beta(t) | \beta \rangle) &= \langle \beta | -i\omega_1 I_x (c_\alpha(t) | \alpha \rangle + c_\beta(t) | \beta \rangle) \\ \frac{d}{dt} c_\alpha(t) \langle \beta | \alpha \rangle + \frac{d}{dt} c_\beta(t) \langle \beta | \beta \rangle &= \langle \beta | -i\omega_1 I_x c_\alpha(t) | \alpha \rangle + \langle \beta | -i\omega_1 I_x c_\beta(t) | \beta \rangle \\ \frac{d c_\beta(t)}{dt} &= \frac{-i\omega_1 c_\alpha(t)}{2} \langle \beta | \beta \rangle + \frac{i\omega_1 c_\beta(t)}{2} \langle \beta | \alpha \rangle \\ \frac{d c_\beta(t)}{dt} &= \frac{-i\omega_1 c_\alpha(t)}{2} \end{aligned}$$

These are *coupled* differential equations somewhat reminiscent of equations 15-14c. Their solutions are:

$$\begin{aligned} c_\alpha(t) &= c_\alpha(0) \cos\left(\frac{\omega_1 t}{2}\right) - i c_\beta(0) \sin\left(\frac{\omega_1 t}{2}\right) \\ c_\beta(t) &= c_\beta(0) \cos\left(\frac{\omega_1 t}{2}\right) - i c_\alpha(0) \sin\left(\frac{\omega_1 t}{2}\right) \end{aligned}$$

You are encouraged to work this out for yourself using the example in Appendix II (and being very, very careful with signs!).

Now, what do the expectation values look like? Starting with equation 15-15 and using trigonometric identities A-6 and A-7 from Appendix II:

$$\begin{aligned}
\langle I_z \rangle(t) &= \frac{1}{2} (c_\alpha^*(t)c_\alpha(t) - c_\beta^*(t)c_\beta(t)) \\
&= \frac{1}{2} \left[ \left( c_\alpha^*(0) \cos\left(\frac{\omega_1 t}{2}\right) + i c_\beta^*(0) \sin\left(\frac{\omega_1 t}{2}\right) \right) \left( c_\alpha(0) \cos\left(\frac{\omega_1 t}{2}\right) - i c_\beta(0) \sin\left(\frac{\omega_1 t}{2}\right) \right) \right] \\
&\quad - \frac{1}{2} \left[ \left( c_\beta^*(0) \cos\left(\frac{\omega_1 t}{2}\right) + i c_\alpha^*(0) \sin\left(\frac{\omega_1 t}{2}\right) \right) \left( c_\beta(0) \cos\left(\frac{\omega_1 t}{2}\right) - i c_\alpha(0) \sin\left(\frac{\omega_1 t}{2}\right) \right) \right] \\
&= \frac{1}{2} [c_\alpha(0)^* c_\alpha(0) - c_\beta(0)^* c_\beta(0)] \left[ \cos^2\left(\frac{\omega_1 t}{2}\right) - \sin^2\left(\frac{\omega_1 t}{2}\right) \right] \\
&\quad + [c_\beta^*(0)c_\alpha(0) - c_\alpha^*(0)c_\beta(0)] i \sin\left(\frac{\omega_1 t}{2}\right) \cos\left(\frac{\omega_1 t}{2}\right) \\
&= \frac{1}{2} [c_\alpha(0)^* c_\alpha(0) - c_\beta(0)^* c_\beta(0)] \cos^2(\omega_1 t) \\
&\quad + \frac{i}{2} [c_\beta^*(0)c_\alpha(0) - c_\alpha^*(0)c_\beta(0)] \sin(\omega_1 t)
\end{aligned}$$

Using equations 15-15a and 15-15c:

$$\langle I_z \rangle(t) = \langle I_z \rangle(0) \cos(\omega_1 t) + \langle I_y \rangle(0) \sin(\omega_1 t)$$

Similar calculations for  $\langle I_x \rangle(t)$  and  $\langle I_y \rangle(t)$  give:

$$\begin{aligned}
\langle I_x \rangle(t) &= \langle I_x \rangle(0) \\
\langle I_y \rangle(t) &= \langle I_y \rangle(0) \cos(\omega_1 t) - \langle I_z \rangle(0) \sin(\omega_1 t)
\end{aligned}$$

We can now see that using the Hamiltonian  $H = \omega_1 I_x$  on our single spin system, the expectation values correspond to a rotation of a vector about the x-axis at a frequency of  $\omega_1$  radians per second. As might be anticipated, a vector lying along the x-axis will not rotate about the x-axis and this is reflected in the expectation value for  $I_x$ . A vector lying along the y-axis will be rotated towards the +z-axis and a vector lying along the +z-axis will be rotated towards the -y-axis.

Given the results of the above analyses for  $I_z$  and  $I_x$  and our vector picture, we can predict what the results will be for  $I_y$ :

$$\begin{aligned}
\langle I_z \rangle(t) &= \langle I_z \rangle(0) \cos(\omega_1 t) - \langle I_x \rangle(0) \sin(\omega_1 t) \\
\langle I_y \rangle(t) &= \langle I_y \rangle(0) \\
\langle I_x \rangle(t) &= \langle I_x \rangle(0) \cos(\omega_1 t) + \langle I_z \rangle(0) \sin(\omega_1 t)
\end{aligned}$$

## Problems

## References

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