# Angular Momentum Operator Identities G

## I. Orbital Angular Momentum

A particle moving with momentum **p** at a position **r** relative to some coordinate origin has so-called <u>orbital</u> angular momentum equal to  $\mathbf{L} = \mathbf{r} \times \mathbf{p}$ . The three components of this angular momentum vector in a cartesian coordinate system located at the origin mentioned above are given in terms of the cartesian coordinates of **r** and **p** as follows:

$$\begin{split} L_z &= x \ p_y - y \ p_x \ , \\ L_x &= y \ p_z - z \ p_y \ , \\ L_y &= z \ p_x - x \ p_z \ . \end{split}$$

Using the fact that the quantum mechanical coordinate operators  $\{q_k\} = x, y, z$  as well as the conjugate momentum operators  $\{p_j\} = p_x, p_y, p_z$  are Hermitian, it is possible to show that  $L_x, L_y$ , and  $L_z$  are also Hermitian, as they must be if they are to correspond to experimentally measurable quantities.

Using the fundamental commutation relations among the cartesian coordinates and the cartesian momenta:

$$[q_k, p_j] = q_k p_j - p_j q_k = ih_{j,k} (j, k = x, y, z),$$

it can be shown that the above angular momentum operators obey the following set of commutation relations:

$$\begin{split} [L_x, L_y] &= ih L_z , \\ [L_y, L_z] &= ih L_x , \\ [L_z, L_x] &= ih L_y . \end{split}$$

Although the components of **L** do not commute with one another, they can be shown to commute with the operator  $L^2$  defined by

$$L^2 = L_x^2 + L_y^2 + L_z^2 .$$

This new operator is referred to as the square of the total angular momentum operator.

The commutation properties of the components of  $\mathbf{L}$  allow us to conclude that complete sets of functions can be found that are eigenfunctions of  $L^2$  and of one, but not more than one, component of  $\mathbf{L}$ . It is convention to select this one component as  $L_z$ , and to label the resulting simultaneous eigenstates of  $L^2$  and  $L_z$  as  $|l,m\rangle$  according to the corresponding eigenvalues:

$$L^{2} |l,m\rangle = h^{2} l(l+1) |l,m\rangle, l = 0,1,2,3,...$$
  
$$L_{z} |l,m\rangle = h m |l,m\rangle, m = \pm l, \pm (l-1), \pm (l-2), ... \pm (l-(l-1)), 0.$$

That these eigenvalues assume the values specified in these identities is proven in considerable detail below. These eigenfunctions of  $L^2$  and of  $L_z$  will not, in general, be eigenfunctions of either  $L_x$  or of  $L_y$ . This means that any measurement of  $L_x$  or  $L_y$  will necessarily change the wavefunction if it begins as an eigenfunction of  $L_z$ .

The above expressions for  $L_x$ ,  $L_y$ , and  $L_z$  can be mapped into quantum mechanical operators by substituting x, y, and z as the corresponding coordinate operators and -ih / x, -ih / y, and -ih / z for  $p_x$ ,  $p_y$ , and  $p_z$ , respectively. The resulting operators can then be transformed into spherical coordinates by using the techniques provided in Appendix (A), the results of which are:

$$\begin{split} L_z &= -i\hbar \ / \ , \\ L_x &= i\hbar \left\{ \sin \ / \ + \cot \ \cos \ / \ \right\} \, , \\ L_y &= -i\hbar \left\{ \cos \ / \ - \cot \ \sin \ / \ \right\} \, , \\ L^2 &= - \, \hbar^2 \left\{ (1/\sin \ ) \ / \ (\sin \ / \ ) + (1/\sin^2 \ ) \ ^2/ \ ^2 \right\} \, . \end{split}$$

At this point, it should be again stressed that the above form for L<sup>2</sup> appears explicitly when the kinetic energy operator -  $h^2/2m^2$  is expressed in spherical coordinates; in particular, the term L<sup>2</sup>/2mr<sup>2</sup> is what enters. This means that our study of the properties of angular momenta will also help us to understand the angular-motion components of the Hamiltonian for spherically symmetric systems (i.e., those for which the potential V contains no angle dependence, and hence for which the total angle dependence is contained in the kinetic energy term L<sup>2</sup>/2mr<sup>2</sup>).

## II. Properties of General Angular Momenta

There are many types of angular momenta that one encounters in chemistry. Orbital angular momenta, such as that introduced above, arise in electronic motion in atoms, in atom-atom and electron-atom collisions, and in rotational motion in molecules. Intrinsic spin angular momentum is present in electrons, H<sup>1</sup>, H<sup>2</sup>, C<sup>13</sup>, and many other nuclei. In this section, we will deal with the behavior of any and all angular momenta and their corresponding eigenfunctions.

At times, an atom or molecule contains more than one type of angular momentum. The Hamiltonian's interaction potentials present in a particular species may or may not cause these individual angular momenta to be coupled to an appreciable extent (i.e., the Hamiltonian may or may not contain terms that refer simultaneously to two or more of these angular momenta). For example, the NH<sup>-</sup> ion, which has a <sup>2</sup> ground electronic state (its electronic configuration is  $1 \text{s}_{\text{N}}^{22}$  <sup>23</sup> <sup>22</sup>p  $_{\text{x}}^{22}\text{p}_{\text{py}}^{1}$ ) has electronic spin, electronic orbital, and molecular rotational angular momenta. The full Hamiltonian H contains spinorbit coupling terms that couple the electronic spin and orbital angular momenta, thereby causing them individually to not commute with H. H also contains terms that couple the ion's rotational and electronic angular momenta, thereby making these quantities no longer "good" quantum numbers (i.e., making the corresponding operators no longer commute with H).

In such cases, the eigenstates of the system can be labeled rigorously only by angular momentum quantum numbers j and m belonging to the total angular momentum **J**. The total angular momentum of a collection of individual angular momenta is defined, component-by-component, as follows:

$$\mathbf{J}_{\mathbf{k}} = \mathbf{i} \ \mathbf{J}_{\mathbf{k}}(\mathbf{i}),$$

where k labels x, y, and z, and i labels the constituents whose angular momenta couple to produce J.

For the remainder of this Appendix, we will study eigenfunction-eigenvalue relationships that are characteristic of all angular momenta and which are consequences of the commutation relations among the angular momentum vector's three components. We will also study how one combines eigenfunctions of two or more angular momenta  $\{J(i)\}$  to produce eigenfunctions of the total J.

A. Consequences of the Commutation Relations

Any set of three Hermitian operators that obey

$$\begin{split} [\mathbf{J}_{\mathbf{X}}, \, \mathbf{J}_{\mathbf{y}}] &= \mathbf{i}\mathbf{h} \, \mathbf{J}_{\mathbf{Z}} \,, \\ [\mathbf{J}_{\mathbf{y}}, \, \mathbf{J}_{\mathbf{Z}}] &= \mathbf{i}\mathbf{h} \, \mathbf{J}_{\mathbf{X}} \,, \\ [\mathbf{J}_{\mathbf{Z}}, \, \mathbf{J}_{\mathbf{X}}] &= \mathbf{i}\mathbf{h} \, \mathbf{J}_{\mathbf{y}} \,, \end{split}$$

will be taken to define an angular momentum **J**, whose square  $J^2 = J_x^2 + J_y^2 + J_z^2$  commutes with all three of its components. It is useful to also introduce two combinations of the three fundamental operators:

$$\mathbf{J}_{\pm} = \mathbf{J}_{\mathbf{X}} \pm \mathbf{i} \, \mathbf{J}_{\mathbf{y}} \,,$$

and to refer to them as <u>raising</u> and <u>lowering operators</u> for reasons that will be made clear below. These new operators can be shown to obey the following commutation relations:

$$[J^2, J_{\pm}] = 0,$$
  
 $[J_z, J_{\pm}] = \pm \frac{1}{2} J_z$ 

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These two operators are <u>not</u> Hermitian operators (although  $J_x$  and  $J_y$  are), but they are adjoints of one another:

$$J_{+}^{+} = J_{-},$$
  
 $J_{-}^{+} = J_{+},$ 

as can be shown using the self-adjoint nature of  $J_x$  and  $J_y$ .

Using only the above commutation properties, it is possible to prove important properties of the eigenfunctions and eigenvalues of  $J^2$  and  $J_z$ . Let us assume that we have found a set of simultaneous eigenfunctions of  $J^2$  and  $J_z$ ; the fact that these two operators

commute tells us that this is possible. Let us label the eigenvalues belonging to these functions:

$$J^{2} |j,m\rangle = h^{2} f(j,m) |j,m\rangle,$$
$$J_{z} |i,m\rangle = h m |i,m\rangle.$$

in terms of the quantities m and f(j,m). Although we certainly "hint" that these quantities must be related to certain j and m quantum numbers, we have not yet proven this, although we will soon do so. For now, we view f(j,m) and m simply as symbols that represent the respective eigenvalues. Because both  $J^2$  and  $J_z$  are Hermitian, eigenfunctions belonging to different f(j,m) or m quantum numbers must be orthogonal:

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

We now prove several identities that are needed to discover the information about the eigenvalues and eigenfunctions of general angular momenta that we are after. Later in this Appendix, the essential results are summarized.

1. There is a Maximum and a Minimum Eigenvalue for  $J_z$ 

Because all of the components of  $\mathbf{J}$  are Hermitian, and because the scalar product of any function with itself is positive semi-definite, the following identity holds:

$$=  +  0$$

However,  $J_x^2 + J_y^2$  is equal to  $J^2 - J_z^2$ , so this inequality implies that

$$\langle j,m | J^2 - J_z^2 | j,m \rangle = h^2 \{ f(j,m) - m^2 \} = 0$$

which, in turn, implies that  $m^2$  must be less than or equal to f(j,m). Hence, for any value of the total angular momentum eigenvalue f, the z-projection eigenvalue (m) must have a maximum and a minimum value and both of these must be less than or equal to the total angular momentum squared eigenvalue f.

2. The Raising and Lowering Operators Change the  $J_z$  Eigenvalue but not the  $J^2$  Eigenvalue When Acting on  $|j,m\rangle$ 

Applying the commutation relations obeyed by  $J_{\pm}$  to  $|j,m\rangle$  yields another useful result:

$$\begin{split} &J_{z}\,J_{\pm}\;|j,m\!\!> \text{-}\;J_{\pm}\,J_{z}\;|j,m\!\!> = \pm\, h\;J_{\pm}\;|j,m\!\!>,\\ &J^{2}\,J_{\pm}\;|j,m\!\!> \text{-}\;J_{\pm}\,J^{2}\;|j,m\!\!> = 0. \end{split}$$

Now, using the fact that  $|j,m\rangle$  is an eigenstate of J<sup>2</sup> and of J<sub>z</sub>, these identities give

$$J_{z} J_{\pm} |j,m\rangle = (mh \pm h) J_{\pm} |j,m\rangle = h (m \pm 1) |j,m\rangle,$$

$$J^2 J_{\pm} |j,m\rangle = h^2 f(j,m) J_{\pm} |j,m\rangle.$$

These equations prove that the functions  $J_{\pm}$  |j,m> must either themselves be eigenfunctions of  $J^2$  and  $J_z$ , with eigenvalues  $h^2$  f(j,m) and h (m+1) or  $J_{\pm}$  |j,m> must equal zero. In the former case, we see that  $J_{\pm}$  acting on |j,m> generates a new eigenstate with the same  $J^2$  eigenvalue as |j,m> but with one unit of h higher in  $J_z$  eigenvalue. It is for this reason that we call  $J_{\pm}$  raising and lowering operators. Notice that, although  $J_{\pm}$  |j,m> is indeed an eigenfunction of  $J_z$  with eigenvalue

 $(m\pm 1)$  h,  $J_{\pm}$  |j,m> is not identical to |j,m±1>; it is only proportional to |j,m±1>:

 $J_{\pm} |j,m\rangle = C^{\pm}_{j,m} |j,m\pm 1\rangle.$ 

Explicit expressions for these  $C^{\pm}_{j,m}$  coefficients will be obtained below. Notice also that because the  $J_{\pm}$  |j,m>, and hence |j,m±1>, have the same J<sup>2</sup> eigenvalue as |j,m> (in fact, sequential application of  $J_{\pm}$  can be used to show that all |j,m'>, for all m', have this same J<sup>2</sup> eigenvalue), the J<sup>2</sup> eigenvalue f(j,m) must be independent of m. For this reason, f can be labeled by one quantum number j.

3. The  $J^2$  Eigenvalues are Related to the Maximum and Minimum  $J_z$  Eigenvalues Which are Related to One Another

Earlier, we showed that there exists a maximum and a minimum value for m, for any given total angular momentum. It is when one reaches these limiting cases that  $J_{\pm} |j,m\rangle = 0$  applies. In particular,

 $J_{+} |j,m_{max}\rangle = 0,$  $J_{-} |j,m_{min}\rangle = 0.$ 

Applying the following identities:

$$J_{-} J_{+} = J^{2} - J_{z}^{2} - h J_{z} ,$$
  
$$J_{+} J_{-} = J^{2} - J_{z}^{2} + h J_{z} ,$$

respectively, to |j,m<sub>max</sub>> and |j,m<sub>min</sub>> gives

$$h^{2} \{ f(j,m_{max}) - m_{max}^{2} - m_{max} \} = 0,$$
  
$$h^{2} \{ f(j,m_{min}) - m_{min}^{2} + m_{min} \} = 0,$$

which immediately gives the  $J^2$  eigenvalue  $f(j,m_{max})$  and  $f(j,m_{min})$  in terms of  $m_{max}$  or  $m_{min}$ :

 $f(j,m_{max}) = m_{max} (m_{max}+1),$  $f(j,m_{min}) = m_{min} (m_{min}-1).$  So, we now know the J<sup>2</sup> eigenvalues for  $|j,m_{max}\rangle$  and  $|j,m_{min}\rangle$ . However, we earlier showed that  $|j,m\rangle$  and  $|j,m-1\rangle$  have the same J<sup>2</sup> eigenvalue (when we treated the effect of J<sub>±</sub> on  $|j,m\rangle$ ) and that the J<sup>2</sup> eigenvalue is independent of m. If we therefore define the quantum number j to be  $m_{max}$ , we see that the J<sup>2</sup> eigenvalues are given by

$$J^2 |j,m\rangle = h^2 j(j+1) |j,m\rangle.$$

We also see that

 $f(j,m) = j(j+1) = m_{max} (m_{max}+1) = m_{min} (m_{min}-1),$ 

from which it follows that

 $m_{\min} = -m_{\max}$ .

4. The j Quantum Number Can Be Integer or Half-Integer

The fact that the m-values run from j to -j in unit steps (because of the property of the  $J_{\pm}$  operators), there clearly can be only integer or half-integer values for j. In the former case, the m quantum number runs over -j, -j+1, -j+2, ..., -j+(j-1), 0, 1, 2, ... j; in the latter, m runs over -j, -j+1, -j+2, ...-j+(j-1/2), 1/2, 3/2, ... j. Only integer and half-integer values can range from j to -j in steps of unity. Species with integer spin are known as Bosons and those with half-integer spin are called Fermions.

5. More on  $J_{\pm}$  |j,m>

Using the above results for the effect of  $J_{\pm}$  acting on  $|j,m\rangle$  and the fact that  $J_{+}$  and  $J_{-}$  are adjoints of one another, allows us to write:

 $\langle j,m| J_{-} J_{+} | j,m \rangle = \langle j,m| (J^2 - J_z^2 - h J_z) | j,m \rangle$ =  $h^2 \{ j(j+1)-m(m+1) \} = \langle J_{+} \langle j,m| J_{+} | j,m \rangle = (C^+_{i,m})^2,$ 

where  $C^+_{j,m}$  is the proportionality constant between  $J_+|j,m>$  and the normalized function |j,m+1>. Likewise, the effect of  $J_-$  can be

$$\langle j,m| J_+ J_- |j,m\rangle = \langle j,m| J_+ (J^2 - J_z^2 + J_z) |j,m\rangle$$
  
 $h^2 \{j(j+1)-m(m-1)\} = \langle J_- \langle j,m| J_- |j,m\rangle = (C^-_{j,m})^2,$ 

where  $C_{j,m}$  is the proportionality constant between  $J_{-}|j,m\rangle$  and the normalized  $|j,m-1\rangle$ . Thus, we can solve for  $C^{\pm}_{i,m}$  after which the effect of  $J_{\pm}$  on  $|j,m\rangle$  is given by:

 $J_+|j,m\rangle = h \{j(j+1) - m(m\pm 1)\}^{1/2} |j,m\pm 1\rangle.$ 

### B. Summary

The above results apply to <u>any</u> angular momentum operators. The essential findings can be summarized as follows:

(i)  $J^2$  and  $J_z$  have complete sets of simultaneous eigenfunctions. We label these eigenfunctions  $|j,m\rangle$ ; they are orthonormal in both their m- and j-type indices:  $\langle j,m| j',m'\rangle$ 

= m,m' j,j'.

(ii) These |j,m> eigenfunctions obey:

 $J^2 |j,m\rangle = h^2 j(j+1) |j,m\rangle$ , { j= integer or half-integer},

 $J_{z}|j,m\rangle = h m |j,m\rangle, \{ m = -j, in steps of 1 to +j \}.$ 

(iii) The raising and lowering operators  $J_{\pm}$  act on  $|j,m\rangle$  to yield functions that are eigenfunctions of  $J^2$  with the same eigenvalue as  $|j,m\rangle$  and eigenfunctions of  $J_z$  with eigenvalue of  $(m\pm 1)$  h :

 $J_{\pm} |j,m\rangle = h \{j(j+1) - m(m\pm 1)\}^{1/2} |j,m\pm 1\rangle.$ 

(iv) When  $J_{\pm}$  acts on the "extremal" states  $|j,j\rangle$  or  $|j,-j\rangle$ , respectively, the result is zero.

The results given above are, as stated, general. Any and all angular momenta have quantum mechanical operators that obey these equations. It is convention to designate specific kinds of angular momenta by specific letters; however, it should be kept in mind that no matter what letters are used, there are operators corresponding to  $J^2$ ,  $J_z$ , and  $J_{\pm}$  that obey relations as specified above, and there are eigenfunctions and eigenvalues that have all of the properties obtained above. For electronic or collisional orbital angular momenta, it is common to use  $L^2$  and  $L_z$ ; for electron spin,  $S^2$  and  $S_z$  are used; for nuclear spin  $I^2$  and  $I_z$  are most common; and for molecular rotational angular momentum,  $N^2$  and  $N_z$  are most common (although sometimes  $J^2$  and  $J_z$  may be used). Whenever two or more angular momenta are combined or coupled to produce a "total" angular momentum, the latter is designated by  $J^2$  and  $J_z$ .

# III. Coupling of Angular Momenta

If the Hamiltonian under study contains terms that couple two or more angular momenta  $\mathbf{J}(\mathbf{i})$ , then only the components of the total angular momentum  $\mathbf{J} = -\mathbf{i} \mathbf{J}(\mathbf{i})$  and  $\mathbf{J}^2$ will commute with H. It is therefore essential to label the quantum states of the system by the eigenvalues of  $\mathbf{J}_z$  and  $\mathbf{J}^2$  and to construct variational trial or model wavefunctions that are eigenfunctions of these total angular momentum operators. The problem of angular momentum coupling has to do with how to combine eigenfunctions of the uncoupled angular momentum operators, which are given as simple products of the eigenfunctions of the individual angular momenta  $\mathbf{J}_i | \mathbf{j}, \mathbf{m}_i >$ , to form eigenfunctions of  $\mathbf{J}^2$  and  $\mathbf{J}_z$ .

A. Eigenfunctions of Jz

Because the individual elements of J are formed additively, but  $J^2$  is  $\underline{not}$  , it is straightforward to form eigenstates of

$$J_z = i J_z(i);$$

simple products of the form  $i |j_i, m_i > are eigenfunctions of J_z$ :

$$J_{z} \quad i \mid j_{i}, m_{i} \rangle = \quad k J_{z}(k) \quad i \mid j_{i}, m_{i} \rangle = \quad k h m_{k} \quad i \mid j_{i}, m_{i} \rangle,$$

and have  $J_z$  eigenvalues equal to the sum of the individual  $m_k h$  eigenvalues. Hence, to form an eigenfunction with specified J and M eigenvalues, one must combine only those product states  $i_j |j_j, m_j\rangle$  whose  $m_j h$  sum is equal to the specified M value.

B. Eigenfunctions of J<sup>2</sup>; the Clebsch-Gordon Series

The task is then reduced to forming eigenfunctions  $|J,M\rangle$ , given particular values for the  $\{j_i\}$  quantum numbers (e.g., to couple the <sup>3</sup>P states of the Si atom, which are eigenfunctions of L<sup>2</sup> and of S<sup>2</sup>, to produce a <sup>3</sup>P<sub>1</sub> state which is an eigenfunction of J<sup>2</sup>, where J=L+S). When coupling pairs of angular momenta {  $|j,m\rangle$  and  $|j',m'\rangle$ }, the total angular momentum states can be written, according to what we determined above, as

$$|J,M\rangle = m,m' C^{J,M}_{j,m;j',m'} |j,m\rangle |j',m'\rangle,$$

where the coefficients  $C^{J,M}_{j,m;j',m'}$  are called vector coupling coefficients (because angular momentum coupling is viewed much like adding two vectors **j** and **j'** to produce another vector **J**), and where the sum over m and m' is restricted to those terms for which m+m' = M. It is more common to express the vector coupling or so-called **Clebsch-Gordon** (CG) **coefficients** as <j,m;j'm'|J,M> and to view them as elements of a "matrix" whose columns are labeled by the coupled-state J,M quantum numbers and whose rows are labeled by the quantum numbers characterizing the uncoupled "product basis" j,m;j',m'. It turns out (see Chapt. 2 of <u>Angular Momentum</u>, by R. N. Zare, John Wiley and Sons, New York, N.Y., (1988)) that this matrix can be shown to be unitary so that the CG coefficients obey:

$$_{m,m'} < j,m;j'm'|J,M>* < j,m;j'm'|J',M'> = _{J,J'} _{M,M'}$$

and

$$J_{J,M} < j,n;j'n'|J,M> < j,m;j'm'|J,M>^* = n,m,n',m'.$$

This unitarity of the CG coefficient matrix allows the inverse of the relation giving coupled functions in terms of the product functions:

 $|J,M\rangle = m,m' < j,m;j'm'|J,M\rangle |j,m\rangle |j',m'\rangle$ 

to be written as:

$$|j,m\rangle |j',m'\rangle = -_{J,M} \langle j,m;j'm'|J,M\rangle * |J,M\rangle$$

$$= J,M < J,M | j,m;j'm' > | J,M >.$$

This result expresses the product functions in terms of the coupled angular momentum functions.

C. Generation of the CG Coefficients

The CG coefficients can be generated in a systematic manner; however, they can also be looked up in books where they have been tabulated (e.g., see Table 2.4 of Zare's book on angular momentum; the reference is given above). Here, we will demonstrate the technique by which the CG coefficients can be obtained, but we will do so for rather limited cases and refer the reader to more extensive tabulations.

The strategy we take is to generate the  $|J,J\rangle$  state (i.e., the state with maximum M-value) and to then use J<sub>-</sub> to generate  $|J,J-1\rangle$ , after which the state  $|J-1,J-1\rangle$  (i.e., the state with one lower J-value) is constructed by finding a combination of the product states in terms of which  $|J,J-1\rangle$  is expressed (because both  $|J,J-1\rangle$  and  $|J-1,J-1\rangle$  have the same M-value M=J-1) which is orthogonal to  $|J,J-1\rangle$  (because

 $|J-1,J-1\rangle$  and  $|J,J-1\rangle$  are eigenfunctions of the Hermitian operator  $J^2$  corresponding to different eigenvalues, they must be orthogonal). This same process is then used to generate  $|J,J-2\rangle$   $|J-1,J-2\rangle$  and (by orthogonality construction)  $|J-2,J-2\rangle$ , and so on.

1. The States With Maximum and Minimum M-Values

We begin with the state  $|J,J\rangle$  having the highest M-value. This state must be formed by taking the highest m and the highest m' values (i.e., m=j and m'=j'), and is given by:

$$|J,J\rangle = |j,j\rangle |j'j'\rangle.$$

Only this one product is needed because only the one term with m=j and m'=j' contributes to the sum in the above CG series. The state

|J,-J> = |j,-j> |j',-j'>

with the minimum M-value is also given as a single product state.

Notice that these states have M-values given as  $\pm(j+j')$ ; since this is the maximum M-value, it must be that the J-value corresponding to this state is J=j+j'.

2. States With One Lower M-Value But the Same J-Value

Applying  $J_{-}$  to |J,J>, and expressing  $J_{-}$  as the sum of lowering operators for the two individual angular momenta:

 $J_{-} = J_{-}(1) + J_{-}(2)$ 

gives

$$J_{J}J_{J} = h \{ J(J+1) - J(J-1) \}^{1/2} | J, J-1 >$$

$$= (J_{-}(1) + J_{-}(2)) |j,j\rangle |j'j'\rangle$$

$$= \mathbf{h}\{\mathbf{j}(\mathbf{j}+1) - \mathbf{j}(\mathbf{j}-1)\}^{1/2} | \mathbf{j}, \mathbf{j}-1\rangle | \mathbf{j}', \mathbf{j}'\rangle + \mathbf{h}\{\mathbf{j}'(\mathbf{j}'+1) - \mathbf{j}'(\mathbf{j}'-1)\}^{1/2} | \mathbf{j}, \mathbf{j}\rangle | \mathbf{j}', \mathbf{j}'-1\rangle.$$

This result expresses |J,J-1> as follows:

$$|J,J-1\rangle = [\{j(j+1)-j(j-1)\}^{1/2} | j,j-1\rangle | j',j'\rangle]$$

+ {j'(j'+1)-j'(j'-1)}<sup>1/2</sup> |j,j > |j',j'-1>] {J(J+1) - J(J-1)}<sup>-1/2</sup>;

that is, the  $|J,J-1\rangle$  state, which has M=J-1, is formed from the two product states  $|j,j-1\rangle$  $|j',j'\rangle$  and  $|j,j\rangle$   $|j',j'-1\rangle$  that have this same M-value.

#### 3. States With One Lower J-Value

To find the state  $|J-1,J-1\rangle$  that has the same M-value as the one found above but one lower J-value, we must construct another combination of the two product states with M=J-1 (i.e.,  $|j,j-1\rangle |j',j'\rangle$  and  $|j,j\rangle |j',j'-1\rangle$ ) that is orthogonal to the combination representing  $|J,J-1\rangle$ ; after doing so, we must scale the resulting function so it is properly normalized. In this case, the desired function is:

$$\begin{aligned} |J-1,J-1\rangle &= [\{j(j+1)-j(j-1)\}^{1/2} | j,j\rangle | j',j'-1\rangle \\ &- \{j'(j'+1)-j'(j'-1)\}^{1/2} | j,j-1\rangle | j',j'\rangle ] \{J(J+1) - J(J-1)\}^{-1/2}. \end{aligned}$$

It is straightforward to show that this function is indeed orthogonal to |J,J-1>.

4. States With Even One Lower J-Value

Having expressed  $|J,J-1\rangle$  and  $|J-1,J-1\rangle$  in terms of  $|j,j-1\rangle |j',j'\rangle$  and  $|j,j\rangle |j',j'-1\rangle$ , we are now prepared to carry on with this stepwise process to generate the states  $|J,J-2\rangle$ ,  $|J-1,J-2\rangle$  and  $|J-2,J-2\rangle$  as combinations of the product states with M=J-2. These product states are  $|j,j-2\rangle |j',j'\rangle$ ,  $|j,j\rangle |j',j'-2\rangle$ , and  $|j,j-1\rangle |j',j'-1\rangle$ . Notice that there are precisely as many product states whose m+m' values add up to the desired M-value as there are total angular momentum states that must be constructed (there are three of each in this case).

The steps needed to find the state |J-2,J-2> are analogous to those taken above:

a. One first applies J<sub>-</sub> to  $|J-1,J-1\rangle$  and to  $|J,J-1\rangle$  to obtain  $|J-1,J-2\rangle$  and  $|J,J-2\rangle$ , respectively as combinations of  $|j,j-2\rangle |j',j'\rangle$ ,  $|j,j\rangle |j',j'-2\rangle$ , and  $|j,j-1\rangle |j',j'-1\rangle$ .

b. One then constructs  $|J-2,J-2\rangle$  as a linear combination of the  $|j,j-2\rangle |j',j'\rangle$ ,  $|j,j\rangle |j',j'-2\rangle$ , and  $|j,j-1\rangle |j',j'-1\rangle$  that is orthogonal to the combinations found for  $|J-1,J-2\rangle$  and  $|J,J-2\rangle$ .

Once  $|J-2,J-2\rangle$  is obtained, it is then possible to move on to form  $|J,J-3\rangle$ ,  $|J-1,J-3\rangle$ , and  $|J-2,J-3\rangle$  by applying J<sub>-</sub> to the three states obtained in the preceding application of the process, and to then form  $|J-3,J-3\rangle$  as the combination of  $|j,j-3\rangle$   $|j',j'\rangle$ ,  $|j,j\rangle$   $|j',j'-3\rangle$ ,  $|j,j-2\rangle$   $|j',j'-1\rangle$ ,  $|j,j-1\rangle$   $|j',j'-2\rangle$  that is orthogonal to the combinations obtained for  $|J,J-3\rangle$ ,  $|J-1,J-3\rangle$ , and  $|J-2,J-3\rangle$ .

Again notice that there are precisely the correct number of product states (four here) as there are total angular momentum states to be formed. In fact, the product states and the total angular momentum states are equal in number and are both members of orthonormal function sets (because  $J^2(1)$ ,  $J_z(1)$ ,  $J^2(2)$ , and  $J_z(2)$  as well as  $J^2$  and  $J_z$  are Hermitian operators). This is why the CG coefficient matrix is unitary; because it maps one set of orthonormal functions to another, with both sets containing the same number of functions.

### D. An Example

Let us consider an example in which the spin and orbital angular momenta of the Si atom in its <sup>3</sup>P ground state can be coupled to produce various <sup>3</sup>P<sub>J</sub> states. In this case, the specific values for j and j' are j=S=1 and j'=L=1. We could, of course take j=L=1 and

j'=S=1, but the final wavefunctions obtained would span the same space as those we are about to determine.

The state with highest M-value is the  ${}^{3}P(M_{s}=1, M_{L}=1)$  state. As shown in Chapter 10 which deals with electronic configurations and states, this particular product

wavefunction can be represented by the product of an spin function (representing S=1,  $M_s=1$ ) and a  $3p_13p_0$  spatial function (representing L=1,  $M_L=1$ ), where the first function corresponds to the first open-shell orbital and the second function to the second open-shell orbital. Thus, the maximum M-value is M= 2 and corresponds to a state with J=2:

$$|J{=}2,M{=}2{>}=|2,2{>}=\qquad 3p_13p_0\;.$$

Clearly, the state  $|2,-2\rangle$  would be given as  $3p_{-1}3p_0$ .

The states  $|2,1\rangle$  and  $|1,1\rangle$  with one lower M-value are obtained by applying  $J_{-} = S_{-} + L_{-}$  to  $|2,2\rangle$  as follows:

$$J_{-}|2,2\rangle = h\{2(3)-2(1)\}^{1/2} |2,1\rangle$$
$$= (S_{-} + L_{-}) \qquad 3p_{1}3p_{0}.$$

To apply  $S_0$  or  $L_1$  to  $3p_13p_0$ , one must realize that each of these operators is, in turn, a sum of lowering operators for each of the two open-shell electrons:

$$S_{-} = S_{-}(1) + S_{-}(2),$$
  
 $L_{-} = L_{-}(1) + L_{-}(2).$ 

The result above can therefore be continued as

$$(S_{-} + L_{-}) \qquad 3p_{1}3p_{0} = h\{1/2(3/2) - 1/2(-1/2)\}^{1/2} \qquad 3p_{1}3p_{0}$$
$$+ h\{1/2(3/2) - 1/2(-1/2)\}^{1/2} \qquad 3p_{1}3p_{0}$$
$$+ h\{1(2) - 1(0)\}^{1/2} \qquad 3p_{0}3p_{0}$$
$$+ h\{1(2) - 0(-1)\}^{1/2} \qquad 3p_{1}3p_{-1}.$$

So, the function  $|2,1\rangle$  is given by

 $|2,1\rangle = [ 3p_13p_0 + 3p_13p_0 + \{2\}^{1/2} 3p_03p_0$ 

+  $\{2\}^{1/2}$  3p<sub>1</sub>3p<sub>-1</sub>]/2,

which can be rewritten as:

$$|2,1\rangle = [(+)3p_13p_0 + \{2\}^{1/2} (3p_03p_0 + 3p_13p_{-1})]/2.$$

Writing the result in this way makes it clear that  $|2,1\rangle$  is a combination of the product states  $|S=1,M_S=0\rangle |L=1,M_L=1\rangle$  (the terms containing  $|S=1,M_S=0\rangle = 2^{-1/2}(+)$ ) and  $|S=1,M_S=1\rangle |L=1,M_L=0\rangle$  (the terms containing  $|S=1,M_S=1\rangle =$ ).

To form the other function with M=1, the  $|1,1\rangle$  state, we must find another combination of  $|S=1,M_S=0\rangle$   $|L=1,M_L=1\rangle$  and  $|S=1,M_S=1\rangle$   $|L=1,M_L=0\rangle$  that is orthogonal to  $|2,1\rangle$  and is normalized. Since

$$|2,1\rangle = 2^{-1/2} [|S=1,M_S=0\rangle |L=1,M_L=1\rangle + |S=1,M_S=1\rangle |L=1,M_L=0\rangle],$$

we immediately see that the requisite function is

$$|1,1\rangle = 2^{-1/2} [|S=1,M_S=0\rangle |L=1,M_L=1\rangle - |S=1,M_S=1\rangle |L=1,M_L=0\rangle].$$

In the spin-orbital notation used above, this state is:

$$|1,1\rangle = [( + )3p_13p_0 - \{2\}^{1/2} (3p_03p_0 + 3p_13p_{-1})]/2.$$

Thus far, we have found the  ${}^{3}P_{J}$  states with J=2, M=2; J=2, M=1; and J=1, M=1.

To find the <sup>3</sup>P<sub>J</sub> states with J=2, M=0; J=1, M=0; and J=0, M=0, we must once again apply the J. tool. In particular, we apply J. to |2,1> to obtain |2,0> and we apply J. to |1,1> to obtain |1,0>, each of which will be expressed in terms of  $|S=1,M_S=0>$  |L=1,M<sub>L</sub>=0>,  $|S=1,M_S=1>|L=1,M_L=-1>$ , and  $|S=1,M_S=-1>|L=1,M_L=1>$ . The |0,0> state is then constructed to be a combination of these same product states which is orthogonal to |2,0> and to |1,0>. The results are as follows:

$$\begin{split} |J=2,M=0> &= 6^{-1/2} [2 \ |1,0> |1,0> + |1,1> |1,-1> + |1,-1> |1,1>], \\ |J=1,M=0> &= 2^{-1/2} [|1,1> |1,-1> - |1,-1> |1,1>], \\ |J=0, M=0> &= 3^{-1/2} [|1,0> |1,0> - |1,1> |1,-1> - |1,-1> |1,1>], \end{split}$$

where, in all cases, a short hand notation has been used in which the  $|S,M_S\rangle |L,M_L\rangle$  product stated have been represented by their quantum numbers with the spin function always appearing first in the product. To finally express all three of these new functions in terms of spin-orbital products it is necessary to give the  $|S,M_S\rangle |L,M_L\rangle$  products with M=0 in terms of these products. For the spin functions, we have:

$$|S=1,M_S=1>=$$
 ,  
 $|S=1,M_S=0>=2^{-1/2}(+)$ .  
 $|S=1,M_S=-1>=$  .

For the orbital product function, we have:

$$|L=1, M_L=1>=3p_13p_0,$$

$$|L=1, M_L=0> = 2^{-1/2}(3p_03p_0 + 3p_13p_{-1}),$$
  
 $|L=1, M_L=-1> = 3p_03p_{-1}.$ 

E. CG Coefficients and 3-j Symbols

As stated above, the CG coefficients can be worked out for any particular case using the raising and lowering operator techniques demonstrated above. Alternatively, as also stated above, the CG coefficients are tabulated (see, for example, Zare's book on angular momentum the reference to which is given earlier in this Appendix) for several values of j, j', and J.

An alternative to the CG coefficients is provided by the so-called 3-j coefficients (see Sec. 2.2 of Zare's book) which are defined in terms of the CG coefficients as follows:

$$\frac{j \quad j' \quad J}{m \ m' - M} = (-1)^{j - j' - M} < j, m; \ j', m' | J, M > (2J + 1)^{-1/2}$$

Clearly, these coefficients contain no more or less information than do the CG coefficients. However, both sets of symbols have symmetries under interchange of the j and m quantum number that are more easily expressed in terms of the 3-j symbols. In particular, odd permutations of the columns of the 3-j symbol leave the magnitude unchanged and change the sign by  $(-1)^{j+j'+J}$ , whereas even permutations leave the value unchanged. Moreover, replacement of all of the m-values (m, m', and M) by their negatives leave the magnitude the same and changes the sign by  $(-1)^{j+j'+J}$ . Table 2.5 in Zare's book (see above for reference) contains 3-j symbols for J=0, 1/2, 1, 3/2, and 2.

# IV. How Angular Momentum Arises in Molecular Quantum Chemistry

## A. The Hamiltonian May Commute With Angular Momentum Operators

As is illustrated throughout this text, angular momentum operators often commute with the Hamiltonian of the system. In such cases, the eigenfunctions of the Hamiltonian can be made to also be eigenfunctions of the angular momentum operators. This allows one to label the energy eigenstates by quantum numbers associated with the angular momentum eigenvalues.

1. Electronic Atomic Hamiltonia Without Spin-Orbit Coupling

For example, the electronic Hamiltonian of atoms, as treated in Chapters 1 and 3 in which only kinetic and coulombic interaction energies are treated, commutes with  $L^2$ , and  $L_7$ , where

$$L_z = i L_z(j)$$

and

$$L^2 = L_z^2 + L_x^2 + L_y^2 .$$

The fact that H commutes with  $L_z$ ,  $L_x$ , and  $L_y$  and hence  $L^2$  is a result of the fact that the total coulombic potential energies among all the electrons and the nucleus is invariant to rotations of <u>all</u> electrons about the z, x, or y axes (H does not commute with  $L_z(j)$  since if

only the j<sup>th</sup> electron's coordinates are so rotated, the total coulombic potential is altered because inter-electronic distances change). The invariance of the potential to rotations of all electrons is, in turn, related to the spherical nature of the atom. As a result, atomic energy levels for such a Hamiltonian can be labeled by their total L and M quantum numbers.

2. Electronic Linear-Molecule Hamiltonia Without Spin-Orbit Coupling

For linear molecules, the coulombic potential is unchanged (because the set of all inter-particle distances are unchanged) by rotations about the molecular axis (the z axis); hence H commutes with  $L_z$ . H does not commute with  $L_x$  or  $L_y$ , and thus not  $L^2$ , because the potential is altered by rotations about the x or y axes. As a result, linear-molecule energy levels for such a Hamiltonian can be labeled by their total M quantum number, which in this context is usually replaced by the quantum number = |M|.

#### 3. Spin-Orbit Effects

When spin-orbit couplings are added to the electrostatic Hamiltonian considered in the text, additional terms arise in H. These terms have the form of a one-electron additive operator:

$$H_{SO} = j \{ g_{e}/2m_{e}^{2}c^{2} \} r_{j}^{-1} \quad V/R_{j} S(j) \cdot L(j)$$

where V is the total coulombic potential the that electron j feels due to the presence of the other electrons and the nuclei. S(j) and L(j) are the spin- and orbital- angular momentum operators of electron j, and  $g_e$  is the electron magnetic moment in Bohr magneton units ( $g_e = 2.002319$ ). For atoms in which these spin-orbit terms are considered (they are important for "heavy atoms" because  $r_j^{-1}$  V/  $R_j$  varies as Z  $r_j^{-3}$  for atoms, whose expectation value varies as Z<sup>4</sup>), it turns out that neither L<sup>2</sup> nor S<sup>2</sup> commute with H<sub>SO</sub>. However, the "combined" angular momentum

$$J = L + S$$
$$J_z = L_z + S_z$$
$$J^2 = J_z^2 + J_x^2 + J_y^2$$

does commute with  $H_{SO}$ , and hence with the full  $H + H_{SO}$  Hamiltonian including spinorbit coupling. For this reason, the eigenstates of atoms in which spin-orbit coupling is important can not be labeled by L, M, S, and M<sub>S</sub>, but only by J and M<sub>J</sub>.

B. The Hamiltonian May Contain Angular Momentum Operators

1. Electronic Hamiltonia for Atoms Without Spin-Orbit Effects

There are cases in which the angular momentum operators themselves appear in the Hamiltonian. For electrons moving around a single nucleus, the total kinetic energy operator T has the form:

$$T = j \{ -\frac{\hbar^2}{2m_e} j^2 \}$$
  
= j \ - \frac{\hbar^2}{2m\_e} [ r\_j^{-2} / r\_j(r\_j^2 / r\_j) ]

- 
$$(r_j^2 \sin j)^{-1} / j(\sin j / j)$$
  
-  $(r_j \sin j)^{-2} 2 / j^2$ .

The factor  $h^2 [(\sin_j)^{-1} / j(\sin_j / j) + (\sin_j)^{-2} / j^2]$  is  $L^2(j)$ , the square of the angular momentum for the j<sup>th</sup> electron. In this case, the Hamiltonian contains  $L^2(j)$  for the individual electrons, not the total  $L^2$ , although it still commutes with the total  $L^2$  (which thus renders L and M good quantum numbers).

#### 2. Linear Rigid-Molecule Rotation

The rotational Hamiltonian for a diatomic molecule as given in Chapter 3 is

 $H_{rot} = h^2/2\mu \{ (R^2 sin )^{-1} / (sin / ) + (R^2 sin^2 )^{-1} ^{2}/^{2} \},\$ 

where  $\mu$  is the reduced mass of the molecule, and R is its bond length. Again, the square of the total rotational angular momentum operator appears in H<sub>rot</sub>

$$H_{\rm rot} = L^2/2\mu R^2.$$

In this case, the Hamiltonian both contains and commutes with the total  $L^2$ ; it also commutes with  $L_z$ , as a result of which L and M are both good quantum numbers and the spherical harmonics  $Y_{L,M}($ , ) are eigenfunctions of H. These eigenfunctions obey orthogonality relations:

because they are eigenfunctions of two Hermitian operators ( $L^2$  and  $L_z$ ) with (generally) different eigenvalues.

3. Non-Linear Molecule Rotation

For non-linear molecules, when treated as rigid (i.e., having fixed bond lengths, usually taken to be the equilibrium values or some vibrationally averaged values), the rotational Hamiltonian can be written in terms of rotation about three axes. If these axes (X,Y,Z) are located at the center of mass of the molecule but fixed in space such that they do not move with the molecule, then the rotational Hamiltonian can be expressed as:

$$H_{rot} = 1/2 \quad K,K' \quad K^{'} \quad K'$$

where  $_{K}$  is the angular velocity about the K<sup>th</sup> axis and

$$I_{K,K} = j m_j (R_j^2 - R^2_{K,j}) \quad (\text{for } K = K')$$
$$I_{K,K'} = -j m_j R_{K,j} R_{K',j} \quad (\text{for } K - K')$$

are the elements of the so-called moment of inertia tensor. This tenor has components along the axes labeled K and K' (each of which runs over X, Y, and Z). The  $m_j$  denote the masses of the atoms (labeled j) in the molecule,  $R_{K,j}$  is the coordinate of atom j along the K-axis relative to the center of mass of the molecule, and  $R_j$  is the distance of atom j from

the center of mass  $(R_j^2 = K(R_{K,j})^2)$ .

Introducing a new set of axes x, y, z that also have their origin at the center of mass, but that rotate with the molecule, it is possible to reexpress  $H_{rot}$  in terms of motions of these axes. It is especially useful to choose a particular set of such molecule-fixed axes, those that cause the moment of inertial tensor to be diagonal. This symmetric matrix can, of course, be made diagonal by first computing  $I_{k,k'}$  (where k and k' run over x, y, and z) for an arbitrary x, y, z axis choice and then finding the orthogonal transformation (i.e., the eigenvectors of the I matrix) that brings I to diagonal form. Such molecule-fixed axes (which we denote as a, b, and c) in which I is diagonal are called **principal axes**; in terms of them,  $H_{rot}$  becomes:

$$H_{rot} = 1/2 [I_a a^2 + I_b b^2 + I_c c^2].$$

The angular momentum conjugate to each of these three angular coordinates (each is the time rate of change of an angle of rotation about an axis: = d (angle)/dt) is obtained, as usual, from the Lagrangian function L = T - V of classical mechanics:

$$p = L/q = (Kinetic Energy-Potential Energy)/(dq/dt)$$

or (using  $J_a$  to denote the angular momentum conjugate to a and realizing that since this free rotational motion has no potential energy,  $L = T = H_{rot}$ )

$$J_a = H_{rot} / a = I_a a$$
$$J_b = I_b b$$
$$J_c = I_c c.$$

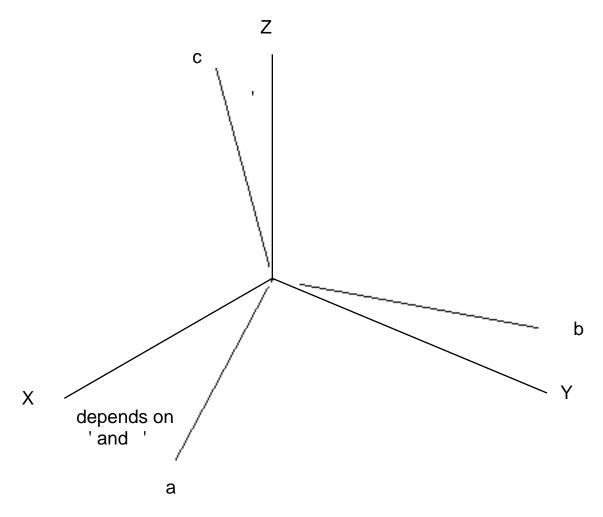
The rotational Hamiltonian can then be written in terms of angular momenta and principalaxis moments of inertia as:

$$H_{rot} = J_a^2/2I_a + J_b^2/2I_b + J_c^2/2I_c.$$

With respect to this principal axis point of view, the rotation of the molecule is described in terms of three angles (it takes three angles to specify the orientation of such a rigid body) that detail the movement of the a, b, and c axes relative to the lab-fixed X, Y, and Z axes. It is convention to call these angles '(which can be viewed as the angle

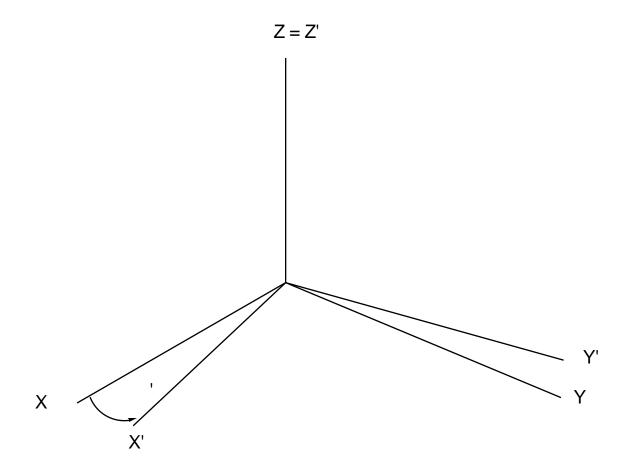
between the lab-fixed Z axis and one of the principal axes- say c- in the molecule), ', and

'. The volume element for integration over these three angles is sin d d d , with and running between 0 and 2 , and going from 0 to . These coordinates are described visually below.

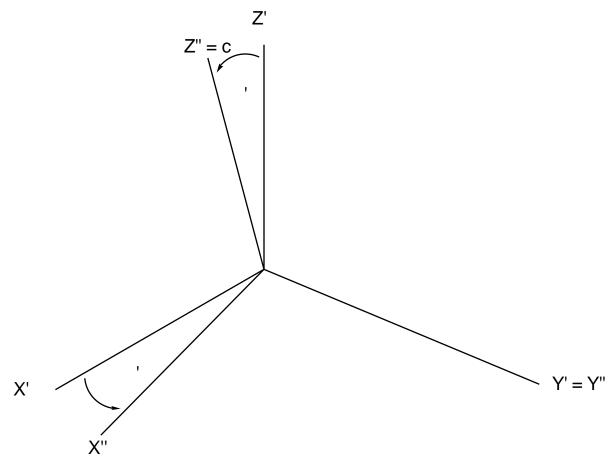


The a, b, c, coordinate system can be formed by beginning with the original X, Y, Z system and sequentially:

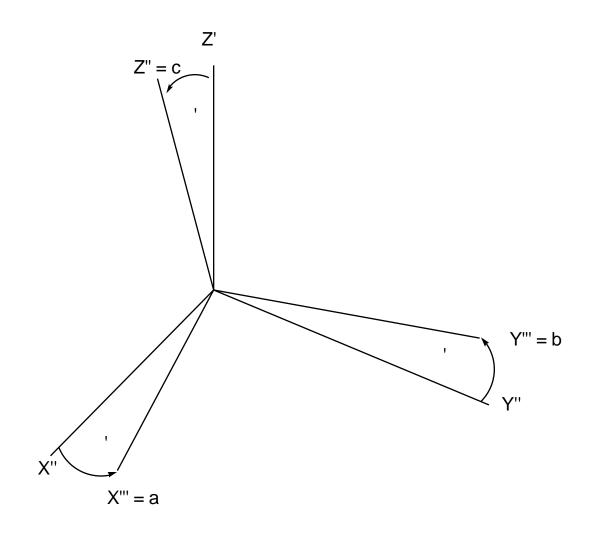
(i) rotating about the Z axis by an amount ', to generate intermediate X' Y', and Z = Z' axes (X' and Y' being rotated by ' relative to X and Y);



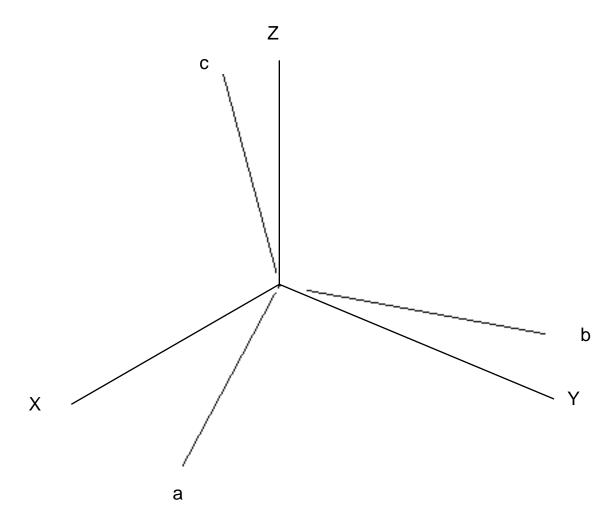
(ii) next rotating about the Y' axis by an amount  $\ ',$  to generate X'', Y', and Z'' = c axes



(iii) and finally rotating about the new Z'' = c axis by an amount  $\ '$  to generate the final X''' = a and Y''' = b axes



Thus, the original and final coordinates can be depicted as follows:



The explicit expressions for the components of the quantum mechanical angular momentum operators along the three new axes are:

$$\begin{split} J_a &= -i h \, \cos \ [ cot \ / \ - (sin \ )^{-1} \ / \ ] - -i h \, sin \ / \\ J_b &= i h \, sin \ [ cot \ / \ - (sin \ )^{-1} \ / \ ] - -i h \, cos \ / \\ J_c &= - \, i h \ / \ . \end{split}$$

The corresponding total angular momentum operator J<sup>2</sup> can be obtained as

$$J^2 = J_a^2 + J_b^2 + J_c$$
  
= - 2/ 2 - cot /

$$-(1/\sin)(2/2+2/2-2\cos 2/),$$

and the component along the original Z axix  $J_Z$  is still - ih / .

Returning now to the rigid-body rotational Hamiltonian shown above, there are two special cases for which exact eigenfunctions and energy levels can be found using the general properties of angular momentum operators.

# a. Spherical and Symmetric Top Energies

The special cases for which  $I_a = I_b = I_c$  (the **spherical top**) and for which  $I_a = I_b > I_c$  (the oblate symmetric top) or  $I_a > I_b = I_c$  (the prolate symmetric top) are covered in Chapter 3. In the former case, the rotational Hamiltonian can be expressed in terms of  $J^2 = J_a^2 + J_b^2 + J_c^2$  because all three moments of inertia are identical:

$$H_{rot} = J^2/2I$$
,

as a result of which the eigenfunctions of  $H_{rot}$  are those of  $J^2$  (and  $J_a$  as well as  $J_Z$  both of which commute with  $J^2$  and with one another;  $J_Z$  is the component of **J** along the lab-fixed Z-axis and commutes with  $J_a$  because  $J_Z = -i\hbar$  / and  $J_a = -i\hbar$  / act on different angles). The energies associated with such eigenfunctions are

$$E(J,K,M) = h^2 J(J+1)/2I^2,$$

for all K (i.e.,  $J_a$  quantum numbers) ranging from -J to J in unit steps and for all M (i.e.,  $J_Z$  quantum numbers) ranging from -J to J. Each energy level is therefore  $(2J + 1)^2$ **degenarate** because there are 2J + 1 possible K values and 2J + 1 M values for each J.

In the **symmetric top** cases,  $H_{rot}$  can be expressed in terms of  $J^2$  and the angular momentum along the axis with the unique moment of inertia (denoted the a-axis for prolate tops and the c-axis of oblate tops):

$$H_{rot} = J^2/2I + J_a^2 \{1/2I_a - 1/2I\}$$
, for prolate tops

$$H_{rot} = J^2/2I + J_c^2 \{ 1/2I_c - 1/2I \}$$
, for oblate tops.

 $H_{rot}$ , along with  $J^2$  and  $J_a$  (or  $J_c$  for oblate tops) and  $J_Z$  (the component of J along the lab-fixed Z-axis) form a mutually commutative set of operators.  $J_Z$ , which is - i h/, and  $J_a$  (or c), which is - i h/, commute because they act on different angles. As a result, the eigenfunctions of  $H_{rot}$  are those of  $J^2$  and  $J_a$  or  $J_c$  (and of  $J_Z$ ), and the corresponding energy levels are:

$$E(J,K,M) = \ h^2 \ J(J+1)/2I^2 + \ h^2 \ K^2 \ \{1/2I_a \text{ - } 1/2I\},$$

for prolate tops

$$E(J,K,M) = h^2 J(J+1)/2I^2 + h^2 K^2 \{1/2I_c - 1/2I\},\$$

for oblate tops,

again for K and M (i.e.,  $J_a$  or  $J_c$  and  $J_Z$  quantum numbers, respectively) ranging from -J to J in unit steps. Since the energy now depends on K, these levels are only 2J + 1 **degenerate** due to the

2J + 1 different M values that arise for each J value.

b. Spherical and Symmetric Top Wavefunctions

The eigenfunctions of J<sup>2</sup>,  $J_a$  (or  $J_c$ ) and  $J_Z$  clearly play important roles in polyatomic molecule rotational motion; they are the eigenstates for spherical-top and symmetric-top species, and they can be used as a basis in terms of which to expand the eigenstates of asymmetric-top molecules whose energy levels do not admit an analytical solution. These eigenfunctions  $|J,M,K\rangle$  are given in terms of the set of so-called "**rotation matrices**" which are denoted  $D_{J,M,K}$ :

$$|J,M,K\rangle = \sqrt{\frac{2J + 1}{8}} D^*_{J,M,K}(\ ,\ ,\ ).$$

They obey

 $J^{2} |J,M,K\rangle = h^{2} J(J+1) |J,M,K\rangle,$   $J_{a} (or J_{c} for oblate tops) |J,M,K\rangle = h K |J,M,K\rangle,$  $J_{Z} |J,M,K\rangle = h M |J,M,K\rangle.$ 

It is demonstrated below why the symmetric and spherical top wavefunctions are given in terms of these  $D_{J,M',M}$  functions.

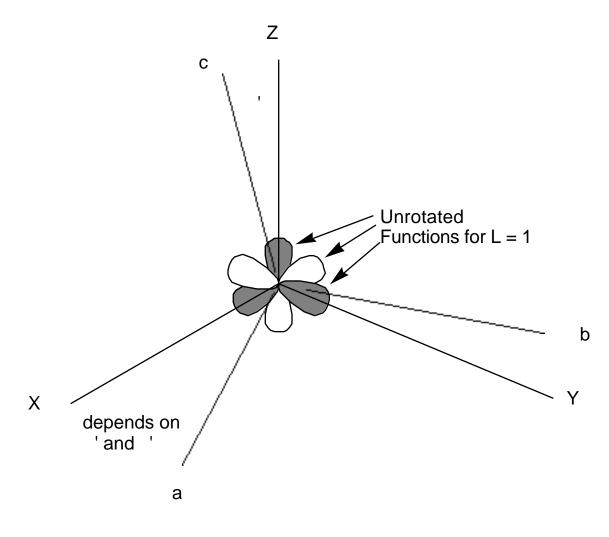
### c. Rotation Matrices

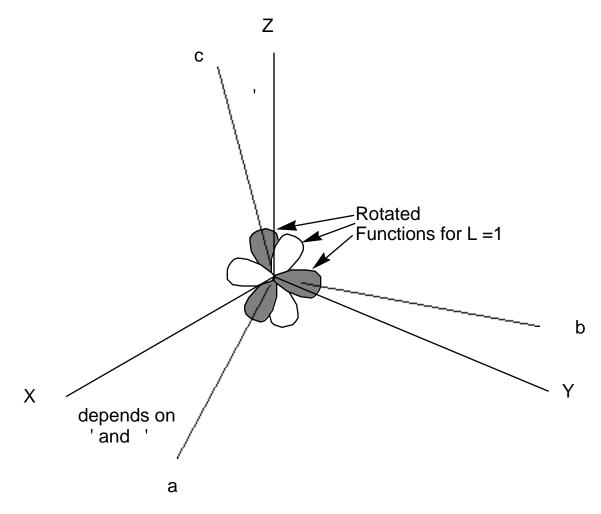
These same rotation matrices arise when the transformation properties of spherical harmonics are examined for transformations that rotate coordinate systems. For example, given a spherical harmonic  $Y_{L,M}(,)$  describing the location of a particle in terms of polar angles , within the X, Y, Z axes, one might want to rotate this function by Euler angles ', ', ' and <u>evaluate this rotated function at the same physical point</u>. As shown in Zare's text on angular momentum, the rotated function  $Y_{L,M}$  evaluated at the angles , can be expressed as follows:

$$Y_{L,M}(,) = M' D_{L,M',M}(', ', ') Y_{L,M'}(, ).$$

In this form, one sees why the array  $D_{J,M',M}$  is viewed as a unitary matrix, with M' and M as indices, that describes the effect of rotation on the set of functions  $\{Y_{L,M}\}$ . This mapping from the unrotated set  $\{Y_{L,M}\}$  into the rotated set of functions  $\{Y_{L,M}\}$  must be

**unitary** if the sets  $\{Y_{L,M}\}$  and  $\{Y_{L,M}\}$  are both orthonormal. The unitary matrix carries an additional index (L in this example) that details the dimension (2L + 1) of the space of functions whose transformations are so parameterized. An example, for L =1, of a set of unrotated and rotated functions is shown below.







An identity that proves very useful when treating coupled angular momenta that are subjected to rotations of the axes with respect to which their eigenfunctions are quantized can be derived by combining the above result:

$$Y_{L,M}(,) = M' D_{L,M',M}(', ', ') Y_{L,M'}(, )$$

and the expression for couping two angular momenta:

 $|J,M\!\!>\!= \quad _{m,n}<\!\!j,m;l,n|J,M\!\!>|j,m\!\!>|l,n\!\!>.$ 

Applying the rotation to the left and right sides of the equation defining |J,M>, gives:

$$M' D_{J, M, M'}() |J, M'>$$

 $= \quad _{m',n'} <\!\! j,\!m;l,\!n|J,\!M\!\!>\!D_{j,\ m,\ m'}(\quad)D_{l,\ n,\ n'}(\quad)\ |j,\!m'\!\!>|l,\!n'\!\!>.$ 

Multiplying both sides of this equation by <J,M'| and using the orthonormality of the angular momentum eigenfunctions gives:

$$D_{J, M, M'} = m', n' < j, m; l, n | J, M > D_{j, m, m'} D_{l, n, n'} < J, M' | j, m'; l, n' >.$$

This result expresses one  $D_{J,M,M'}$  in terms of sums of products of D matrix elements for angular momenta j, m, m' and l, n, n' that can be coupled to for J, M, M'.

If the above series of operations is applied to the angular momentum coupling expression in the form:

$$|j,m\rangle |l,n\rangle = J,M < J,M|j,m;l,n\rangle |J,M\rangle,$$

one can obtain:

$$m',n' D_{j,m,m'}() D_{l,n,n'}() |j,m'>|l,n'>$$

$$= J_{,M} < J,M|j,m;l,n> M' D_{J,M,M'} () |J,M'>.$$

Multiplying by <j,m'| <l,n'| then yields:

D<sub>j, m, m</sub>' D<sub>l, n, n</sub>'

 $= \quad _{J,M,M'} <\!\! J,M|j,m;l,n\!> <\!\! j,m';\ l,n'|J,M'\!> D_{J,\ M,\ M'}$ 

which expresses the product of two D matrices as a sum of D matrices whose angular momentum indices are related to those of the product.

e. Rigid Body Rotational Wavefunctions as Rotation Matrices

This same analysis can be used to describe how a set of functions  $_{J,M}(,,)$  (labeled by a total angular momentum quantum number that determines the number of functions in the set and an M quantum number that labels the Z-axis projection of this angular momentum) that are functions of three coordinates , , , transform under rotation. In particular, one obtains a result analogous to the spherical harmonic expression:

 $J_{,M} \left( \ , \ , \ \right) = \quad _{M'} D_{J,M',M} ( \ ', \ ', \ ') \quad _{J,M'} ( \ , \ , \ ).$ 

Here  $_{J,M}(,,)$  is the original unrotated function evaluated at a point whose angular coordinates are ,, ; ', ', ' are the Euler angles through which this function is rotated to obtain the rotated function  $_{J,M}$  whose value at the above point is denoted  $_{J,M}(,,)$ .

Now, if the angles ', ', ' through which the original function is rotated were <u>chosen</u> to equal the angular coordinates , , of the point discussed here, then the rotated function  $J_{,M}$  evaluated at this point could easily be identified. Its value would be nothing more than the unrotated function  $_{J,M}$  evaluated at = 0, = 0, = 0. In this case, we can write:

$$J_{,M}( , , ) = J_{,M}(0, 0, 0) = M' D_{J,M',M}( , , ) J_{,M'}( , , ).$$

Using the unitary nature of the  $D_{L,M^\prime,M}$  array, this equation can be solved for the  $_{J,M^\prime}($  , , ) functions:

$$J_{M'}(, , ) = M D^* J_{M',M}(, , ) J_{M}(0, 0, 0).$$

This result shows that the functions that describe the rotation of a rigid body through angles

, , must be a combination of rotation matrices (actually  $D^*{}_{L,M',M}(\ ,\ ,\ )$  functions). Because of the normalization of the  $D_{L,M,M'}(\ ,\ ,\ )$  functions:

$$(D^*_{L',M',K'}(, , ) D_{L,M,K}(, , ) \sin d d )$$
  
=  $\frac{8^2}{2L+1}$  L,L' M,M' K,K'

the properly normalized rotational functions that describe spherical or symmetric tops are:

$$|J,M,K\!> = \sqrt{\frac{2J \ + \ 1}{8}} \ D^*{}_{J,M,K}(\ , \ , \ )$$

as given above. For asymmetric top cases, the correct eigenstates are combinations of these  $\{|J,M,K>\}$  functions:

$$J_{J,M}(,,) = K \sqrt{\frac{2J+1}{8^2}} D^* J_{J,M,K}(,,) C_K$$

with amplitudes  $\{C_K\}$  determined by diagonalizing the full  $H_{rot}$  Hamiltonian within the basis consisting of the set of

$$\sqrt{\frac{2J+1}{8}} D^*_{J,M,K}(,,)$$

functions.

4. Electronic and Nuclear Zeeman Interactions

When magnetic fields are present, the intrinsic spin angular momenta of the electrons  $\mathbf{S}(\mathbf{j})$  and of the nuclei  $\mathbf{I}(\mathbf{k})$  are affected by the field in a manner that produces additional energy contributions to the total Hamiltonian H. The Zeeman interaction of an external magnetic field (e.g., the earth's magnetic field of 4. Gauss or that of a NMR

machine's magnet) with such intrinsic spins is expressed in terms of the following contributions to H:

$$H_{\text{zeeman}} = (g_e e/2m_ec) \quad j S_z(j) H$$
$$- (e/2m_pc) \quad k g_k I_z(k) H.$$

Here  $g_k$  is the so-called nuclear g-value of the k<sup>th</sup> nucleus, *H* is the strength of the applied field,  $m_p$  is the mass of the proton,  $g_e$  is the electron magnetic moment, and c is the speed of light. When chemical shieldings (denoted \_k), nuclear spin-spin couplings (denoted J<sub>k,l</sub>), and electron-nuclear spin couplings (denoted  $a_{i,k}$ ) are considered, the following spin-

dependent Hamiltonian is obtained:

$$H = (g_{e} e/2m_{e}c) \quad {}_{j} S_{z}(j) H - (e/2m_{p}c) \quad {}_{k} g_{k} (1-{}_{k})I_{z}(k) H.$$
  
+ h  ${}_{j,k} (a_{j,k}/\hbar^{2}) \mathbf{I}(k) \cdot \mathbf{S}(j) + h {}_{k,l} (J_{k,l}/\hbar^{2}) \mathbf{I}(k) \cdot \mathbf{I}(l).$ 

Clearly, the treatment of electron and nuclear spin angular momenta is essential to analyzing the energy levels of such Hamiltonia, which play a central role in NMR and ESR spectroscopy.