

2.7: Angular Momentum

Orbital Angular Momentum

A particle moving with momentum \mathbf{p} at a position \mathbf{r} relative to some coordinate origin has so-called orbital 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 \mathbf{r} and \mathbf{p} as follows:

$$L_z = xp_y - yp_x, \quad (2.7.1)$$

$$L_x = yp_z - zp_y, \quad (2.7.2)$$

$$L_y = zp_x - xp_z. \quad (2.7.3)$$

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

$$[q_k, p_j] = q_k p_j - p_j q_k = i\hbar \delta_{j,k} (j, k = x, y, z), \quad (2.7.4)$$

which are proven by considering quantities of the form

$$(xp_x - p_x x)f = -i\hbar \left[x \frac{\partial f}{\partial x} - \frac{\partial(xf)}{\partial x} \right] = i\hbar f, \quad (2.7.5)$$

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

$$[\mathbf{L}_x, \mathbf{L}_y] = i\hbar \mathbf{L}_z, \quad (2.7.6)$$

$$[\mathbf{L}_y, \mathbf{L}_z] = i\hbar \mathbf{L}_x, \quad (2.7.7)$$

$$[\mathbf{L}_z, \mathbf{L}_x] = i\hbar \mathbf{L}_y. \quad (2.7.8)$$

Although the components of \mathbf{L} do not commute with one another, they can be shown to commute with the operator \mathbf{L}^2 defined by

$$\mathbf{L}^2 = \mathbf{L}_x^2 + \mathbf{L}_y^2 + \mathbf{L}_z^2. \quad (2.7.9)$$

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 \mathbf{L}^2 and of one, but not more than one, component of \mathbf{L} . It is convention to select this one component as \mathbf{L}_z , and to label the resulting simultaneous eigenstates of \mathbf{L}^2 and \mathbf{L}_z as $|l, m\rangle$ according to the corresponding eigenvalues:

$$\mathbf{L}^2 |l, m\rangle = \hbar^2 l(l+1) |l, m\rangle, l = 0, 1, 2, 3, \dots \quad (2.7.10)$$

$$\mathbf{L}_z |l, m\rangle = \hbar m |l, m\rangle, m = \pm l, \pm(l-1), \pm(l-2), \dots, \pm(l-(l-1)), 0. \quad (2.7.11)$$

These eigenfunctions of \mathbf{L}^2 and of \mathbf{L}_z will not, in general, be eigenfunctions of either \mathbf{L}_x or of \mathbf{L}_y . This means that any measurement of \mathbf{L}_x or \mathbf{L}_y will necessarily change the wave function if it begins as an eigenfunction of \mathbf{L}_z .

The above expressions for \mathbf{L}_x , \mathbf{L}_y , and \mathbf{L}_z can be mapped into quantum mechanical operators by substituting x , y , and z as the corresponding coordinate operators and $-i\hbar \frac{\partial}{\partial x}$, $-i\hbar \frac{\partial}{\partial y}$, and $-i\hbar \frac{\partial}{\partial z}$ for p_x , p_y , and p_z , respectively. The resulting operators can then be transformed into spherical coordinates the results of which are:

$$\mathbf{L}_z = -i\hbar \frac{\partial}{\partial \phi}, \quad (2.7.12)$$

$$\mathbf{L}_x = i\hbar \left[\sin \phi \frac{\partial}{\partial \theta} + \cot \theta \cos \phi \frac{\partial}{\partial \phi} \right], \quad (2.7.13)$$

$$\mathbf{L}_y = -i\hbar \left[\cos \phi \frac{\partial}{\partial \theta} - \cot \theta \sin \phi \frac{\partial}{\partial \phi} \right], \quad (2.7.14)$$

$$\mathbf{L}^2 = -\hbar^2 \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right]. \quad (2.7.15)$$

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^1 , H^2 , C^{13} , 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^- ion, which has a 2P ground electronic state (its electronic configuration is $1s^2 2s^2 3s^2 2p_{\pi x}^2 2p_{\pi y}^1$) has electronic spin, electronic orbital, and molecular rotational angular momenta. The full Hamiltonian H contains terms that couple the electronic spin and orbital angular momenta, thereby causing them individually to not 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 operators \mathbf{J}^2 and \mathbf{J}_z . The total angular momentum of a collection of individual angular momenta is defined, component-by-component, as follows:

$$\mathbf{J}_k = \sum_i \mathbf{J}_k(i), \quad (2.7.16)$$

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

For the remainder of this Section, 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 $\{\mathbf{J}(i)\}$ to produce eigenfunctions of the total \mathbf{J} .

Consequences of the Commutation Relations

Any set of three operators that obey

$$[\mathbf{J}_x, \mathbf{J}_y] = i\hbar\mathbf{J}_z, \quad (2.7.17)$$

$$[\mathbf{J}_y, \mathbf{J}_z] = i\hbar\mathbf{J}_x, \quad (2.7.18)$$

$$[\mathbf{J}_z, \mathbf{J}_x] = i\hbar\mathbf{J}_y, \quad (2.7.19)$$

will be taken to define an angular momentum \mathbf{J} , whose square $\mathbf{J}^2 = \mathbf{J}_x^2 + \mathbf{J}_y^2 + \mathbf{J}_z^2$ commutes with all three of its components. It is useful to also introduce two combinations of the three fundamental operators \mathbf{J}_x and \mathbf{J}_y :

$$\mathbf{J}_{\pm} = \mathbf{J}_x \pm i\mathbf{J}_y, \quad (2.7.20)$$

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

$$[\mathbf{J}^2, \mathbf{J}_{\pm}] = 0, \quad (2.7.21)$$

$$[\mathbf{J}_z, \mathbf{J}_{\pm}] = \pm\hbar\mathbf{J}_{\pm}. \quad (2.7.22)$$

Using only the above commutation properties, it is possible to prove important properties of the eigenfunctions and eigenvalues of \mathbf{J}^2 and \mathbf{J}_z . Let us assume that we have found a set of simultaneous eigenfunctions of \mathbf{J}^2 and \mathbf{J}_z ; the fact that these two operators commute tells us that this is possible. Let us label the eigenvalues belonging to these functions:

$$\mathbf{J}^2|j, m\rangle = \hbar^2 f(j, m)|j, m\rangle, \quad (2.7.23)$$

$$\mathbf{J}_z|j, m\rangle = \hbar m|j, m\rangle, \quad (2.7.24)$$

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 \mathbf{J}^2 and \mathbf{J}_z are Hermitian, eigenfunctions belonging to different $f(j, m)$ or m quantum numbers must be orthogonal:

$$\langle j, m|j', m'\rangle = \delta_{m,m'}\delta_{j,j'}. \quad (2.7.25)$$

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 Section, the essential results are summarized.

There is a Maximum and a Minimum Eigenvalue for \mathbf{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:

$$\langle j, m | \mathbf{J}_x^2 + \mathbf{J}_y^2 | j, m \rangle = \langle \mathbf{J}_x | j, m \rangle \langle \mathbf{J}_x | j, m \rangle + \langle \mathbf{J}_y | j, m \rangle \langle \mathbf{J}_y | j, m \rangle \geq 0. \quad (2.7.26)$$

However, $\mathbf{J}_x^2 + \mathbf{J}_y^2$ is equal to $\mathbf{J}^2 - \mathbf{J}_z^2$, so this inequality implies that

$$\langle j, m | \mathbf{J}^2 - \mathbf{J}_z^2 | j, m \rangle = \hbar^2 f(j, m) - m^2 \geq 0, \quad (2.7.27)$$

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 .

The Raising and Lowering Operators Change the \mathbf{J}_z Eigenvalue but not the \mathbf{J}^2 Eigenvalue When Acting on $|j, m\rangle$

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

$$\mathbf{J}_z \mathbf{J}_\pm |j, m\rangle - \mathbf{J}_\pm \mathbf{J}_z |j, m\rangle = \pm \hbar \mathbf{J}_\pm |j, m\rangle, \quad (2.7.28)$$

$$\mathbf{J}^2 \mathbf{J}_\pm |j, m\rangle - \mathbf{J}_\pm \mathbf{J}^2 |j, m\rangle = 0. \quad (2.7.29)$$

Now, using the fact that $|j, m\rangle$ is an eigenstate of \mathbf{J}^2 and of \mathbf{J}_z , these identities give

$$\mathbf{J}_z \mathbf{J}_\pm |j, m\rangle = (m\hbar \pm \hbar) \mathbf{J}_\pm |j, m\rangle = \hbar(m \pm 1) \mathbf{J}_\pm |j, m\rangle, \quad (2.7.30)$$

$$\mathbf{J}^2 \mathbf{J}_\pm |j, m\rangle = \hbar^2 f(j, m) \mathbf{J}_\pm |j, m\rangle. \quad (2.7.31)$$

These equations prove that the functions $\mathbf{J}_\pm |j, m\rangle$ must either themselves be eigenfunctions of \mathbf{J}^2 and \mathbf{J}_z , with eigenvalues $\hbar^2 f(j, m)$ and $\hbar(m \pm 1)$, respectively, or $\mathbf{J}_\pm |j, m\rangle$ must equal zero. In the former case, we see that \mathbf{J}_\pm acting on $|j, m\rangle$ generates a new eigenstate with the same \mathbf{J}^2 eigenvalue as $|j, m\rangle$ but with one unit of \hbar higher or lower in \mathbf{J}_z eigenvalue. It is for this reason that we call \mathbf{J}_\pm raising and lowering operators. Notice that, although $\mathbf{J}_\pm |j, m\rangle$ is indeed an eigenfunction of \mathbf{J}_z with eigenvalue $(m \pm 1)\hbar$, $\mathbf{J}_\pm |j, m\rangle$ is not identical to $|j, m \pm 1\rangle$; it is only proportional to $|j, m \pm 1\rangle$:

$$\mathbf{J}_\pm |j, m\rangle = C_{j,m}^\pm |j, m \pm 1\rangle. \quad (2.7.32)$$

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

iii. The \mathbf{J}^2 Eigenvalues are Related to the Maximum and Minimum \mathbf{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 $\mathbf{J}_\pm |j, m\rangle = 0$ applies. In particular,

$$\mathbf{J}_+ |j, m_{\max}\rangle = 0, \quad (2.7.33)$$

$$\mathbf{J}_- |j, m_{\min}\rangle = 0. \quad (2.7.34)$$

Applying the following identities:

$$\mathbf{J}_- \mathbf{J}_+ = \mathbf{J}^2 - \mathbf{J}_z^2 - \hbar \mathbf{J}_z, \quad (2.7.35)$$

$$\mathbf{J}_+ \mathbf{J}_- = \mathbf{J}^2 - \mathbf{J}_z^2 + \hbar \mathbf{J}_z, \quad (2.7.36)$$

respectively, to $|j, m_{\max}\rangle$ and $|j, m_{\min}\rangle$ gives

$$\hbar^2 \{ f(j, m_{\max}) - m_{\max}^2 - m_{\max} \} = 0, \quad (2.7.37)$$

$$\hbar^2 \{f(j, m_{\min}) - m_{\min}^2 + m_{\min}\} = 0, \quad (2.7.38)$$

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

$$f(j, m_{\max}) = m_{\max}(m_{\max} + 1), \quad (2.7.39)$$

$$f(j, m_{\min}) = m_{\min}(m_{\min} - 1). \quad (2.7.40)$$

So, we now know the \mathbf{J}^2 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 \mathbf{J}^2 eigenvalue (when we treated the effect of \mathbf{J}_{\pm} on $|j, m\rangle$) and that the \mathbf{J}^2 eigenvalue is independent of m . If we therefore define the quantum number j to be m_{\max} , we see that the \mathbf{J}^2 eigenvalues are given by

$$\mathbf{J}^2 |j, m\rangle = \hbar^2 j(j+1) |j, m\rangle. \quad (2.7.41)$$

We also see that

$$f(j, m) = j(j+1) = m_{\max}(m_{\max} + 1) = m_{\min}(m_{\min} - 1), \quad (2.7.42)$$

from which it follows that

$$m_{\min} = -m_{\max}. \quad (2.7.43)$$

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 \mathbf{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 $-j, -j+1, -j+2, \dots, -j+(j-1), 0, 1, 2, \dots, j$;

in the latter, m runs over $-j, -j+1, -j+2, \dots, -j+(j-\frac{1}{2}), \frac{1}{2}, \frac{3}{2}, \dots, j$. Only integer and half-integer values can range from j to $-j$ in steps of unity. Species whose intrinsic angular momenta are integers are known as Bosons and those with half-integer spin are called Fermions.

More on $\mathbf{J}_{\pm}|j, m\rangle$

Using the above results for the effect of \mathbf{J}_{\pm} acting on $|j, m\rangle$ and the fact that \mathbf{J}_{+} and \mathbf{J}_{-} are adjoints of one another (two operators \mathbf{F} and \mathbf{G} are adjoints if $\langle\psi|\mathbf{F}|\chi\rangle = \langle\mathbf{G}\psi|\chi\rangle$, for all ψ and all χ) allows us to write:

$$\langle j, m | \mathbf{J}_{-} \mathbf{J}_{+} | j, m \rangle = \langle j, m | (\mathbf{J}^2 - \mathbf{J}_z^2 - \hbar \mathbf{J}_z) | j, m \rangle \quad (2.7.44)$$

$$= \hbar^2 j(j+1) - m(m+1) = \langle \mathbf{J}_{+} \langle j, m | \mathbf{J}_{+} | j, m \rangle = (C_{j,m}^{+})^2, \quad (2.7.45)$$

where $C_{j,m}^{+}$ is the proportionality constant between $\mathbf{J}_{+}|j, m\rangle$ and the normalized function

$|j, m+1\rangle$. Likewise, the effect of \mathbf{J}_{-} can be expressed as

$$\langle j, m | \mathbf{J}_{+} \mathbf{J}_{-} | j, m \rangle = \langle j, m | (\mathbf{J}^2 - \mathbf{J}_z^2 + \hbar \mathbf{J}_z) | j, m \rangle \quad (2.7.46)$$

$$= \hbar^2 j(j+1) - m(m-1) = \langle \mathbf{J}_{-} \langle j, m | \mathbf{J}_{-} | j, m \rangle = (C_{j,m}^{-})^2, \quad (2.7.47)$$

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

$$\mathbf{J}_{\pm} |j, m\rangle = \hbar \sqrt{j(j+1) - m(m \pm 1)} |j, m \pm 1\rangle. \quad (2.7.48)$$

Summary

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

- (i) \mathbf{J}^2 and \mathbf{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:

$$\langle j, m | j', m' \rangle = \delta_{m,m'} \delta_{j,j'}. \quad (2.7.49)$$

- (ii) These $|j, m\rangle$ eigenfunctions obey:

$$\mathbf{J}^2 |j, m\rangle = \hbar^2 j(j+1) |j, m\rangle, \{j = \text{integer or half-integer}\}, \quad (2.7.50)$$

$$\mathbf{J}_z |j, m\rangle = \hbar m |j, m\rangle, \{m = -j, \text{ in steps of } 1 \text{ to } +j\}. \quad (2.7.51)$$

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

$$\mathbf{J}_{\pm} |j, m\rangle = \hbar \sqrt{j(j+1) - m(m \pm 1)} |j, m \pm 1\rangle. \quad (2.7.52)$$

(iv) When \mathbf{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 \mathbf{J}^2 , \mathbf{J}^z , and \mathbf{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 \mathbf{L}^2 and \mathbf{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 \mathbf{J}^2 and \mathbf{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 \mathbf{J}^2 and \mathbf{J}^z .

Coupling of Angular Momenta

If the Hamiltonian under study contains terms that couple two or more angular momenta $\mathbf{J}(i)$, then only the components of the total angular momentum $\mathbf{J} = \sum_i \mathbf{J}(i)$ and the total \mathbf{J}^2 will commute with \mathbf{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 wave functions 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 $\prod_i |j_i, m_i\rangle$, to form eigenfunctions of \mathbf{J}^2 and \mathbf{J}_z .

Eigenfunctions of \mathbf{J}_z

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

$$\mathbf{J}_z = \sum_i \mathbf{J}_z(i); \quad (2.7.53)$$

simple products of the form $\prod_i |j_i, m_i\rangle$ are eigenfunctions of \mathbf{J}_z :

$$\mathbf{J}_z \prod_i |j_i, m_i\rangle = \sum_k \mathbf{J}_z(k) \prod_i |j_i, m_i\rangle = \sum_k \hbar m_k \prod_i |j_i, m_i\rangle, \quad (2.7.54)$$

and have \mathbf{J}_z eigenvalues equal to the sum of the individual $m_k \hbar$ eigenvalues. Hence, to form an eigenfunction with specified J and M eigenvalues, one must combine only those product states $\prod_i |j_i, m_i\rangle$ whose $m_i \hbar$ sum is equal to the specified M value.

Eigenfunctions of \mathbf{J}^2 ; the Clebsch-Gordon Series

The task is then reduced to forming eigenfunctions $|J, M\rangle$, given particular values for the $\{j_i\}$ quantum numbers. 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

$$|J, M\rangle = \sum_{m, m'} C_{j, m; j', m'}^{J, M} |j, m\rangle |j', m'\rangle, \quad (2.7.55)$$

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 \mathbf{j} and \mathbf{j}' to produce another vector \mathbf{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 $\langle j, m; j', m' | J, M \rangle$ 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 that this matrix can be shown to be unitary so that the CG coefficients obey:

$$\sum_{m,m'} \langle j, m; j' m' | J, M \rangle^* \langle j, m; j' m' | J', M' \rangle = \delta_{j,j'} \delta_{m,m'} \quad (2.7.56)$$

and

$$\sum_{J,M} \langle j, n; j' n' | J, M \rangle \langle j, m; j' m' | J, M \rangle^* = \delta_{n,m} \delta_{n',m'}. \quad (2.7.57)$$

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

$$|J, M\rangle = \sum_{m,m'} \langle j, m; j' m' | J, M \rangle |j, m\rangle |j', m'\rangle \quad (2.7.58)$$

to be written as:

$$|j, m\rangle |j', m'\rangle = \sum_{J,M} \langle j, m; j' m' | J, M \rangle^* |J, M\rangle \quad (2.7.59)$$

$$= \sum_{J,M} \langle J, M | j, m; j' m' \rangle |J, M\rangle. \quad (2.7.60)$$

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

Generation of the Clebsch-Gordon Coefficients

The Clebsch-Gordon 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 R. N. Zare, Angular Momentum, John Wiley, New York (1988)). 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 for more cases.

The strategy we take is to generate the $|J, J\rangle$ state (i.e., the state with maximum M -value) and to then use \mathbf{J}_- to generate $|J, J-1\rangle$, after which the state $|J-1, J-1\rangle$ (i.e., the state with one lower \mathbf{J}_- value) is constructed by finding a combination of the product states in terms of which $|J-1, J-1\rangle$ is expressed (because both $|J-1, J-1\rangle$ and $|J, J-1\rangle$ 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 \mathbf{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.

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:

$$|J, J\rangle = |j, j\rangle |j', j'\rangle. \quad (2.7.61)$$

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

$$|J, -J\rangle = |j, -j\rangle |j', -j'\rangle \quad (2.7.62)$$

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 $J = j + j'$.

States With One Lower M -Value But the Same \mathbf{J}_- Value

Applying \mathbf{J}_- to $|J, J\rangle$, and expressing \mathbf{J}_- as the sum of lowering operators for the two individual angular momenta:

$$\mathbf{J}_- = \mathbf{J}_-(1) + \mathbf{J}_-(2) \quad (2.7.63)$$

gives

$$\mathbf{J}_- |J, J\rangle = \hbar \sqrt{J(j+1) - J(j-1)} |J, J-1\rangle \quad (2.7.64)$$

$$= (\mathbf{J}_-(1) + \mathbf{J}_-(2)) |j, j\rangle |j', j'\rangle \quad (2.7.65)$$

$$= \hbar \sqrt{j(j+1) - j(j-1)} |j, j-1\rangle |j', j'\rangle + \hbar \sqrt{j'(j'+1) - j'(j'-1)} |j, j\rangle |j', j'-1\rangle. \quad (2.7.66)$$

This result expresses $|J, J-1\rangle$ as follows:

$$|J, J-1\rangle = \frac{\sqrt{j(j+1) - j(j-1)} |j, j-1\rangle |j', j'\rangle + \sqrt{j'(j'+1) - j'(j'-1)} |j, j\rangle |j', j'-1\rangle}{\sqrt{J(J+1) - J(J-1)}}; \quad (2.7.67)$$

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.

iii. States With One Lower \mathbf{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 \mathbf{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:

$$|J-1, J-1\rangle = \frac{\sqrt{j(j+1) - j(j-1)} |j, j\rangle |j', j'-1\rangle - \sqrt{j'(j'+1) - j'(j'-1)} |j, j-1\rangle |j', j'\rangle}{\sqrt{J(J+1) - J(J-1)}}. \quad (2.7.68)$$

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

States With Even One Lower \mathbf{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 $|J-2, J-2\rangle$ are analogous to those taken above:

- One first applies \mathbf{J}_- 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 $|j, j-1\rangle |j', j'-1\rangle$.
- 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 \mathbf{J}_- 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 $\mathbf{J}^2(1)$, $\mathbf{J}_z(1)$, $\mathbf{J}^2(2)$, and $\mathbf{J}_z(2)$ as well as \mathbf{J}^2 and \mathbf{J}_z are Hermitian operators which have complete sets of orthonormal eigenfunctions). 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.

Example

Example 1

Let us consider an example in which the spin and orbital angular momenta of the Si atom in its 3P ground state can be coupled to produce various 3P_J 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 wave functions obtained would span the same space as those we are about to determine.

The state with highest M -value is the ($^3P(M_s = 1, M_L = 1)$) state, which can be represented by the product of an $\alpha\alpha$ spin function (representing $S = 1, M_s = 1$) and a $3p_1 3p_0$ 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 $J = 2$:

$$|J = 2, M = 2\rangle = |2, 2\rangle = \alpha\alpha 3p_1 3p_0. \quad (2.7.69)$$

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

The states $|2, 1\rangle$ and $|1, 1\rangle$ with one lower M -value are obtained by applying $\mathbf{J}_- = \mathbf{S}_- + \mathbf{L}_-$ to $|2, 2\rangle$ as follows:

$$\mathbf{J}_-|2, 2\rangle = \hbar\sqrt{J(J+1) - M(M-1)}|2, 1\rangle = \hbar\sqrt{2(3) - 2(1)}|2, 1\rangle \quad (2.7.70)$$

$$= (\mathbf{S}_- + \mathbf{L}_-)\alpha\alpha 3p_1 3p_0. \quad (2.7.71)$$

To apply \mathbf{S}_- or \mathbf{L}_- to $\alpha\alpha 3p_1 3p_0$, one must realize that each of these operators is, in turn, a sum of lowering operators for each of the two open-shell electrons:

$$\mathbf{S}_- = \mathbf{S}_-(1) + \mathbf{S}_-(2), \quad (2.7.72)$$

$$\mathbf{L}_- = \mathbf{L}_-(1) + \mathbf{L}_-(2). \quad (2.7.73)$$

The result above can therefore be continued as

$$(\mathbf{S}_- + \mathbf{L}_-)\alpha\alpha 3p_1 3p_0 = \hbar\sqrt{\frac{1}{2}\left(\frac{3}{2}\right) - \frac{1}{2}\left(-\frac{1}{2}\right)}\beta\alpha 3p_1 3p_0 \quad (2.7.74)$$

$$+ \hbar\sqrt{\frac{1}{2}\left(\frac{3}{2}\right) - \frac{1}{2}\left(-\frac{1}{2}\right)}\alpha\beta 3p_1 3p_0 \quad (2.7.75)$$

$$+ \hbar\sqrt{1(2) - 1(0)}\alpha\alpha 3p_0 3p_0 \quad (2.7.76)$$

$$+ \hbar\sqrt{1(2) - 0(-1)}\alpha\alpha 3p_1 3p_{-1}. \quad (2.7.77)$$

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

$$|2, 1\rangle = \frac{1}{2}[\beta\alpha 3p_1 3p_0 + \alpha\beta 3p_1 3p_0 + \sqrt{2}\alpha\alpha 3p_0 3p_0 + \sqrt{2}\alpha\alpha 3p_1 3p_{-1}], \quad (2.7.78)$$

which can be rewritten as:

$$|2, 1\rangle = \frac{1}{2}[(\beta\alpha + \alpha\beta)^3 p_1 3p_0 + \sqrt{2}\alpha\alpha(3p_0 3p_0 + 3p_1 3p_{-1})]. \quad (2.7.79)$$

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 $|S = 1, M_S = 0\rangle = \frac{1}{\sqrt{2}}(\alpha\beta + \beta\alpha)$) and $|S = 1, M_S = 1\rangle|L = 1, M_L = 0\rangle$ (the terms containing $|S = 1, M_S = 1\rangle = \alpha\alpha$).

There is a good chance that some readers have noticed that some of the terms in the $|2, 1\rangle$ function would violate the Pauli exclusion principle. In particular, the term $\alpha\alpha 3p_0 3p_0$ places two electrons into the same orbitals and with the same spin. Indeed, this electronic function would indeed violate the Pauli principle, and it should not be allowed to contribute to the final Si 3P_J wave functions we are trying to form. The full resolution of how to deal with this paradox is given in the following Subsection, but for now let me say the following:

(i) Once you have learned that all of the spin-orbital product functions shown for $|2, 1\rangle$ (e.g., $\alpha\alpha 3p_0 3p_0$, $(\beta\alpha + \alpha\beta)^3 p_1 3p_0$, and $\alpha\alpha 3p_1 3p_{-1}$) represent Slater determinants (we deal with this in the next Subsection) that are antisymmetric with respect to permutation of any pair of electrons, you will understand that the Slater determinant corresponding to $\alpha\alpha 3p_0 3p_0$ vanishes.

(ii) If, instead of considering the $3s^2 3p^2$ configuration of Si, we wanted to generate wave functions for the $3s^2 3p^1 4p^1$ 3P_J states of Si, the same analysis as shown above would pertain, except that now the $|2, 1\rangle$ state would have a contribution from $\alpha\alpha 3p_0 4p_0$. This contribution does not violate the Pauli principle, and its Slater determinant does not vanish.

So, for the remainder of this treatment of the 3P_J states of Si, don't worry about terms arising that violate the Pauli principle; they will not contribute because their Slater determinants will vanish.

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

$$|2, 1\rangle = \frac{1}{\sqrt{2}}[|S = 1, M_S = 0\rangle|L = 1, M_L = 1\rangle + |S = 1, M_S = 1\rangle|L = 1, M_L = 0\rangle], \quad (2.7.80)$$

we immediately see that the requisite function is

$$|1, 1\rangle = \frac{1}{\sqrt{2}}[|S = 1, M_S = 0\rangle|L = 1, M_L = 1\rangle - |S = 1, M_S = 1\rangle|L = 1, M_L = 0\rangle]. \quad (2.7.81)$$

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

$$|1, 1\rangle = \frac{(\beta\alpha + a\beta)^3 p_1 3p_0 - \sqrt{2}\alpha\alpha(3p_0 3p_0 + 3p_1 3p_{-1})}{2}. \quad (2.7.82)$$

Thus far, we have found the 3P_J states with $J = 2, M = 2$; $J = 2, M = 1$; and $J = 1, M = 1$.

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

$$|J = 2, M = 0\rangle = \frac{1}{\sqrt{6}}[2|1, 0\rangle|1, 0\rangle + |1, 1\rangle|1, -1\rangle + |1, -1\rangle|1, 1\rangle], \quad (2.7.83)$$

$$|J = 1, M = 0\rangle = \frac{1}{\sqrt{2}}[|1, 1\rangle|1, -1\rangle - |1, -1\rangle|1, 1\rangle], \quad (2.7.84)$$

$$|J = 0, M = 0\rangle = \frac{1}{\sqrt{3}}[|1, 0\rangle|1, 0\rangle - |1, 1\rangle|1, -1\rangle - |1, -1\rangle|1, 1\rangle], \quad (2.7.85)$$

where, in all cases, a short hand notation has been used in which the $|S, M_S\rangle|L, M_L\rangle$ product states 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:

$$|S = 1, M_S = 1\rangle = \alpha\alpha, \quad (2.7.86)$$

$$|S = 1, M_S = 0\rangle = \frac{1}{\sqrt{2}}(\alpha\beta + \beta\alpha). \quad (2.7.87)$$

$$|S = 1, M_S = -1\rangle = \beta\beta. \quad (2.7.88)$$

For the orbital product function, we have:

$$|L = 1, M_L = 1\rangle = 3p_1 3p_0, \quad (2.7.89)$$

$$|L = 1, M_L = 0\rangle = \frac{1}{\sqrt{2}}(3p_0 3p_0 + 3p_1 3p_{-1}), \quad (2.7.90)$$

$$|L = 1, M_L = -1\rangle = 3p_0 3p_{-1}. \quad (2.7.91)$$

Coupling Angular Momenta of Equivalent Electrons

If equivalent angular momenta are coupled (e.g., to couple the orbital angular momenta of a p^2 or d^3 configuration), there is a tool one can use to determine which of the term symbols violate the Pauli principle. To carry out this step, one forms all possible unique (determinantal) product states with non-negative M_L and M_S values and arranges them into groups according to their M_L and M_S values. For example, the "boxes" appropriate to the p^2 orbital occupancy that we considered earlier for Si are shown below:

$M_S \ M_L$	2	1	0
1		$ p_1\alpha \ p_0\alpha $	$ p_1\alpha \ p_{-1}\alpha $
0	$ p_1\alpha \ p_1\beta $	$ p_1\alpha \ p_0\beta , p_0\alpha \ p_1\beta $	$ p_1\alpha \ p_{-1}\beta ,$ $ p_{-1}\alpha \ p_1\beta ,$ $ p_0\alpha \ p_0\beta $

There is no need to form the corresponding states with negative M_L or negative M_S values because they are simply "mirror images" of those listed above. For example, the state with $M_L = -1$ and $M_S = -1$ is $|p_{-1}\beta \ p_0\beta|$, which can be obtained from the

$M_L = 1, M_S = 1$ state $|p_1\alpha p_0\alpha\rangle$ by replacing a by b and replacing p_1 by p_{-1} .

Given the box entries, one can identify those term symbols that arise by applying the following procedure over and over until all entries have been accounted for:

- One identifies the highest M_S value (this gives a value of the total spin quantum number that arises, S) in the box. For the above example, the answer is $S = 1$.
- For all product states of this M_S value, one identifies the highest M_L value (this gives a value of the total orbital angular momentum, L , that can arise for this S). For the above example, the highest M_L within the $M_S = 1$ states is $M_L = 1$ (not $M_L = 2$), hence $L = 1$.
- Knowing an S, L combination, one knows the first term symbol that arises from this configuration. In the p^2 example, this is 3P .
- Because the level with this L and S quantum numbers contains $(2L+1)(2S+1)$ states with M_L and M_S quantum numbers running from $-L$ to L and from $-S$ to S , respectively, one must remove from the original box this number of product states. To do so, one simply erases from the box one entry with each such M_L and M_S value. Actually, since the box need only show those entries with non-negative M_L and M_S values, only these entries need be explicitly deleted. In the 3P example, this amounts to deleting nine product states with M_L, M_S values of 1,1; 1,0; 1,-1; 0,1; 0,0; 0,-1; -1,1; -1,0; -1,-1.
- After deleting these entries, one returns to step 1 and carries out the process again. For the p^2 example, the box after deleting the first nine product states looks as follows (those that appear in italics should be viewed as already deleted in counting all of the 3P states):

$M_S M_L$	2	1	0
1		$ p_1\alpha p_0\alpha\rangle$	$ p_1\alpha p_{-1}\alpha\rangle$
0	$ p_1\alpha p_1\beta\rangle$	$ p_1\alpha p_0\beta\rangle, p_0\alpha p_1\beta\rangle$	$ p_1\alpha p_{-1}\beta\rangle,$ $ p_{-1}\alpha p_1\beta\rangle,$ $ p_0\alpha p_0\beta\rangle$

It should be emphasized that the process of deleting or crossing off entries in various M_L, M_S boxes involves only counting how many states there are; by no means do we identify the particular L, S, M_L, M_S wave functions when we cross out any particular entry in a box. For example, when the $|p_1\alpha p_0\beta\rangle$ product is deleted from the $M_L = 1, M_S = 0$ box in accounting for the states in the 3P level, we do not claim that $|p_1\alpha p_0\beta\rangle$ itself is a member of the 3P level; the $|p_0\alpha p_1\beta\rangle$ product state could just as well been eliminated when accounting for the 3P states.

Returning to the p^2 example at hand, after the 3P term symbol's states have been accounted for, the highest M_S value is 0 (hence there is an $S = 0$ state), and within this M_S value, the highest M_L value is 2 (hence there is an $L = 2$ state). This means there is a 1D level with five states having $M_L = 2, 1, 0, -1, -2$. Deleting five appropriate entries from the above box (again denoting deletions by italics) leaves the following box:

$M_S M_L$	2	1	0
1		$ p_1\alpha p_0\alpha\rangle$	$ p_1\alpha p_{-1}\alpha\rangle$
0	$ p_1\alpha p_1\beta\rangle$	$ p_1\alpha p_0\beta\rangle, p_0\alpha p_1\beta\rangle$	$ p_1\alpha p_{-1}\beta\rangle,$ $ p_{-1}\alpha p_1\beta\rangle,$ $ p_0\alpha p_0\beta\rangle$

The only remaining entry, which thus has the highest M_S and M_L values, has $M_S = 0$ and $M_L = 0$. Thus there is also a 1S level in the p^2 configuration.

Thus, unlike the non-equivalent $3p_1 4p_1$ case, in which $^3P, ^1P, ^3D, ^1D, ^3S$, and 1S levels arise, only the $^3P, ^1D$, and 1S arise in the p^2 situation. This "box method" is useful to carry out whenever one is dealing with equivalent angular momenta.

If one has mixed equivalent and non-equivalent angular momenta, one can determine all possible couplings of the equivalent angular momenta using this method and then use the simpler vector coupling method to add the non-equivalent angular momenta to each of these coupled angular momenta. For example, the $p^2 d^1$ configuration can be handled by vector coupling (using the

straightforward non-equivalent procedure) $L = 2$ (the d orbital) and $S = \frac{1}{2}$ (the third electron's spin) to each of 3P , 1D , and 1S arising from the p^2 configuration. The result is 4F , 4D , 4P , 2F , 2D , 2P , 2G , 2F , 2D , 2P , 2S , and 2D .

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