Angular Momentum: Key Results

Before reading this handout, you should review *Survival Facts from Quantum Mechanics* if necessary. The last section of that handout is of particular importance for the developments discussed below, so it is repeated here:

From *Survival Facts*:

Commuting operators have common eigenfunctions. Suppose $\hat{A}$ and $\hat{B}$ commute: $[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A} = 0$.

Let $\{\varphi_i\}$ be the set of eigenfunctions of $\hat{A}$:

$$\hat{A}\varphi_i = a_i\varphi_i$$
$$\text{then } \hat{B}\left(\hat{A}\varphi_i\right) = \hat{B}\left(a_i\varphi_i\right) = a_i\left(\hat{B}\varphi_i\right)$$
$$\text{but } \hat{A}\hat{B} = \hat{B}\hat{A}\text{, so } \hat{A}\left(\hat{B}\varphi_i\right) = a_i\left(\hat{B}\varphi_i\right)$$
$$\therefore \text{ The function } \hat{B}\varphi_i \text{ is an eigenfunction of with eigenvalue } a_i.$$

If φ_i is the only eigenfunction of $\hat{A}$ with eigenvalue a_i, then $\hat{B}\varphi_i \propto \varphi_i$ (in other words, $\hat{B}\varphi_i$ can only be an eigenfunction of $\hat{A}$ with eigenvalue a_i if it differs from φ_i by at most a constant multiplicative factor – see p. 2 of Survival Facts). Thus,

$$\hat{B}\varphi_i = b_i\varphi_i \text{ for some constant } b_i.$$

If a_i is a degenerate eigenvalue, i.e. there are more than one eigenfunctions of $\hat{A}$ with eigenvalue a_i, then we can take linear combinations of these eigenfunctions to satisfy this condition.

Angular Momentum

For quantum mechanical problems involving angular momentum, $\hat{\mathbf{M}}$, the key operators of interest are $\hat{M}^2$ and $\hat{M}_z$ in that they are two commuting operators for which angular momentum eigenfunctions and eigenvalues apply. [We use the general symbols $\hat{M}^2$ and $\hat{M}_z$ for any angular momentum. In specific applications these could be orbital angular momentum operators (for which the symbols $\hat{L}^2$ and $\hat{L}_z$ are used), electron spin angular momentum ($\hat{S}^2$ and $\hat{S}_z$), the sum of spin and orbital angular momentum ($\hat{J}^2$ and $\hat{J}_z$), or nuclear spin angular momentum ($\hat{I}^2$ and $\hat{I}_z$).] The commutation properties of angular momentum operators are sufficient to establish the eigenvalues of these operators, as we shall see below. Also important are the angular momentum *ladder operators* ($\hat{M}_+$ and $\hat{M}_-$) that are useful in achieving this goal and in calculations involving angular momentum generally. We begin with the definition of the angular momentum operators and their commutation relations (see *Survival Facts*, p. 4):

$$\hat{M}^2 = \hat{\mathbf{M}} \bullet \hat{\mathbf{M}} = \hat{M}_x^2 + \hat{M}_y^2 + \hat{M}_z^2 \tag{1}$$

$$[\hat{M}_x, \hat{M}_y] = i\hbar\hat{M}_z \text{ and cyclic permutations, } [\hat{M}_y, \hat{M}_z] = i\hbar\hat{M}_x \quad [\hat{M}_y, \hat{M}_z] = i\hbar\hat{M}_x \tag{2}$$

$$[\hat{M}_x, \hat{M}^2] = [\hat{M}_y, \hat{M}^2] = [\hat{M}_z, \hat{M}^2] = 0 \tag{3}$$

Proof that $\hat{M}^2$ and $\hat{M}_x$ commute involves repeated application of the first commutation relations:

$[\hat{M}_x, \hat{M}^2] = [\hat{M}_x, \hat{M}_y^2] + [\hat{M}_x, \hat{M}_z^2]$

1st term: $[\hat{M}_x, \hat{M}_y^2] = \hat{M}_x\hat{M}_y^2 - \hat{M}_y^2\hat{M}_x = \hat{M}_x\hat{M}_y^2 - \hat{M}_y(\hat{M}_x\hat{M}_y - i\hbar\hat{M}_z) = \hat{M}_x\hat{M}_y^2 - (\hat{M}_y\hat{M}_x)\hat{M}_y + i\hbar\hat{M}_y\hat{M}_z$

$= \hat{M}_x\hat{M}_y^2 - (\hat{M}_x\hat{M}_y - i\hbar\hat{M}_z)\hat{M}_y + i\hbar\hat{M}_y\hat{M}_z = i\hbar(M_yM_z + M_zM_y)$

2nd term: $[\hat{M}_x, \hat{M}_z^2] = \hat{M}_x\hat{M}_z^2 - \hat{M}_z^2\hat{M}_x = \hat{M}_x\hat{M}_z^2 - \hat{M}_z(\hat{M}_x\hat{M}_z + i\hbar\hat{M}_y) = \hat{M}_x\hat{M}_y^2 - (\hat{M}_z\hat{M}_x)\hat{M}_z - i\hbar\hat{M}_z\hat{M}_y$

$= \hat{M}_x\hat{M}_y^2 - (\hat{M}_x\hat{M}_z + i\hbar\hat{M}_y)\hat{M}_z - i\hbar\hat{M}_z\hat{M}_y = -i\hbar(\hat{M}_y\hat{M}_z + \hat{M}_z\hat{M}_y)$

$\therefore [\hat{M}_x, \hat{M}^2] = 0$

The other two relations are proved analogously.

$\hat{M}_x$, $\hat{M}_y$, and $\hat{M}_z$ do not commute with each other, so simultaneous eigenfunctions of all three operators and $\hat{M}^2$ cannot be found. We therefore seek simultaneous eigenfunctions of $\hat{M}^2$ and $\hat{M}_z$. Let us introduce the *ladder operators*, which are defined as

$$\hat{M}_+ = \hat{M}_x + i\hat{M}_y \quad ; \quad \hat{M}_- = \hat{M}_x - i\hat{M}_y \tag{4}$$

both commute with $\hat{M}^2$: $[\hat{M}_\pm, \hat{M}^2] = [\hat{M}_x, \hat{M}^2] \pm i[\hat{M}_y, \hat{M}^2] = 0$ (5)

Because $\hat{M}_+$ and $\hat{M}_-$ commute with $\hat{M}^2$, the result of operating on an eigenfunction of $\hat{M}^2$ with $\hat{M}_+$ or $\hat{M}_-$ is still an eigenfunction of $\hat{M}^2$ with an unchanged eigenvalue. In other words, if a_l and b_m are the respective eigenvalues of $\hat{M}^2$ and $\hat{M}_z$ for an eigenfunction we call $|lm\rangle$, then a_l is also the eigenvalue of $\hat{M}^2$ for the eigenfunctions $\hat{M}_+|lm\rangle$ or $\hat{M}_-|lm\rangle$ (see the argument at the beginning of this handout). However, the ladder operators do not commute with $\hat{M}_z$,

$$[\hat{M}_\pm, \hat{M}_z] = [\hat{M}_x \pm i\hat{M}_y, \hat{M}_z] = [\hat{M}_x, \hat{M}_z] \pm i[\hat{M}_y, \hat{M}_z] = -i\hbar\hat{M}_y \mp \hbar\hat{M}_x = \mp\hbar\hat{M}_+$$

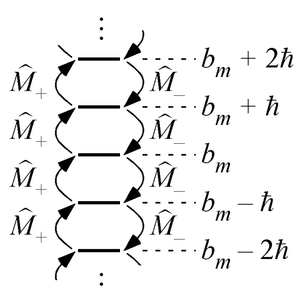
$$\hat{M}_\pm\hat{M}_z = \hat{M}_z\hat{M}_\pm \mp \hbar\hat{M}_\pm \quad \text{Rearranging,}$$

$$\boxed{\hat{M}_z\hat{M}_\pm = \hat{M}_\pm(\hat{M}_z \pm \hbar)} \tag{6}$$

Operating on $|lm\rangle$ with both sides of equation (6),

$$\hat{M}_z\hat{M}_\pm|lm\rangle = \hat{M}_\pm(\hat{M}_z \pm \hbar)|lm\rangle = (b_m \pm \hbar)\hat{M}_\pm|lm\rangle$$

$$\text{or } \hat{M}_z\left[\hat{M}_\pm|lm\rangle\right] = (b_m \pm \hbar)\left[\hat{M}_\pm|lm\rangle\right]$$



We see that operating on $|lm\rangle$ with $\hat{M}_+$ and $\hat{M}_-$ generates $\hat{M}_z$ eigenfunctions, $\hat{M}_+|lm\rangle$ and $\hat{M}_-|lm\rangle$, that have $\hat{M}_z$ eigenvalues that are respectively $b_m + \hbar$ and $b_m - \hbar$. $\hat{M}_+$ moves us up the 'ladder' by a rung, $\hat{M}_-$ moves us down the 'ladder' by a rung. Repeated operation with $\hat{M}_+$ and $\hat{M}_-$ will generate a whole 'ladder' of $\hat{M}_z$ eigenfunctions, each with eigenvalues that differ by $\hbar$. The 'ladder' is bounded at both the low and high ends, which can be seen by considering the operator $\hat{M}_x^2 + \hat{M}_y^2$. On physical grounds, the eigenvalues of $\hat{M}_x^2 + \hat{M}_y^2$ cannot be negative and it has the same eigenfunctions as $\hat{M}^2$ and $\hat{M}_z$ since it is identical to $\hat{M}^2 - \hat{M}_z^2$:

$$(\hat{M}_x^2 + \hat{M}_y^2)|lm\rangle = (\hat{M}^2 - \hat{M}_z^2)|lm\rangle = (a_l - b_m^2)|lm\rangle \;\Rightarrow\; a_l \ge b_m^2 \;\Rightarrow\; -\sqrt{a_l} \le b_m \le \sqrt{a_l}$$

If $\hat{M}_+$ operates on the eigenfunction at the 'top of the ladder', $\left| l\, max \right\rangle$ with eigenvalue b_{max}, it must annihilate it. Likewise, $\hat{M}_-$ must annihilate the eigenfunction at the 'bottom of the ladder', $\left| l\, min \right\rangle$ with eigenvalue b_{min}. We can use a little operator algebra to establish the relationship between b_{max} and b_{min}:

$$\hat{M}_\mp \hat{M}_\pm = \left(\hat{M}_x \mp i\hat{M}_y\right)\left(\hat{M}_x \pm i\hat{M}_y\right) = \hat{M}_x^2 + \hat{M}_y^2 \pm i[\hat{M}_x, \hat{M}_y]$$

$$\hat{M}_\mp \hat{M}_\pm = \hat{M}^2 - \hat{M}_z^2 \mp \hbar \hat{M}_z \qquad (7)$$

$$\hat{M}_- \hat{M}_+ \left| l\, max \right\rangle = \left(\hat{M}^2 - \hat{M}_z^2 - \hbar\hat{M}_z\right)\left| l\, max \right\rangle = (a_l - b_{\max}^2 - \hbar b_{\max})\left| l\, max \right\rangle = 0$$

$$\therefore b_{max}^2 + \hbar b_{max} = a_l \ \text{ and similarly, } \ b_{min}^2 - \hbar b_{min} = a_l$$

Setting these equal and rearranging we find $(b_{max} + b_{min})(b_{max} - b_{min} + \hbar) = 0$

Since $b_{max} \geq b_{min}$, the only acceptable root for this equation is $b_{max} = -b_{min}$.

Since the ladder operators generate adjacent $\hat{M}_z$ eigenfunctions with eigenvalues that differ by $\hbar$, it follows that $b_{max} = b_{min} + n\hbar = -b_{max} + n\hbar$, where n is an integer. Then,

$$b_{max} = \tfrac{1}{2} n\hbar \qquad b_{min} = -\tfrac{1}{2} n\hbar \qquad n = 0,1,2,3,\ldots$$

$$a_l = b_{\max}^2 + \hbar b_{max} = (\tfrac{1}{4} n^2 + \tfrac{1}{2} n)\hbar^2$$

If we let $l = ½\, n$, then

$$\boxed{b_{max} = l\hbar \qquad b_{min} = -l\hbar \qquad l = 0, \tfrac{1}{2}, 1, \tfrac{3}{2}, \ldots \ \text{ and } \ a_l = l(l+1)\hbar^2} \qquad (8)$$

Recalling that the eigenvalues of $\hat{M}_z$ form a 'ladder' with steps spaced by $\hbar$, we conclude

$$\boxed{b_m = m\hbar \qquad m = -l, -l+1, \ldots, l-1, l} \qquad (9)$$

The possibility that l is half-integral arises naturally; for orbital angular momentum only integral values occur, for spin angular momentum half-integral values may occur.

The preceding shows that the commutation relations alone are sufficient to generate the characteristics of angular momenta in quantum mechanics. However, while we know that $\hat{M}_\pm \left| lm \right\rangle \propto \left| l\, m \pm 1 \right\rangle$, we need the proportionality constants for use in calculations. Let $\hat{M}_\pm \left| lm \right\rangle \propto \hbar c_\pm^{lm} \left| l\, m \pm 1 \right\rangle$ where c_+^{lm} and c_-^{lm}, where are as yet undetermined constants, though we do know that since $-l \leq m \leq l$, c_+^{ll} and $c_-^{l-l} = 0$. First, when the top and bottom rungs of the 'ladder' are not involved,

$$\left\langle \hat{M}_\pm \psi_{lm} \middle| \hat{M}_\pm \psi_{lm} \right\rangle = \hbar^2 \left| c_\pm^{lm} \right|^2 \left\langle \psi_{l\, m\pm1} \middle| \psi_{l\, m\pm1} \right\rangle = \hbar^2 \left| c_\pm^{lm} \right|^2.$$

We then make use of the fact that $\hat{M}_+$ and $\hat{M}_-$ are adjoint, $(\hat{M}_\pm)^\dagger = \hat{M}_\mp$, which yields

$$\left\langle \hat{M}_\pm \psi_{lm} \middle| \hat{M}_\pm \psi_{lm} \right\rangle = \left\langle \psi_{lm} \middle| \hat{M}_\pm \hat{M}_\mp \middle| \psi_{lm} \right\rangle = \left\langle \psi_{lm} \middle| \hat{M}^2 - \hat{M}_z(\hat{M}_z \pm \hbar) \middle| \psi_{lm} \right\rangle$$

$$\therefore \left| c_\pm^{lm} \right|^2 = [l(l+1) - m(m \pm 1)]$$

We have the magnitudes of the proportionality constants, but they are undetermined to within a 'phase factor', $e^{-i\alpha}$, but the choice of this 'phase factor' has no physical consequences and α equal to zero is usually chosen. Thus we have the final relations,

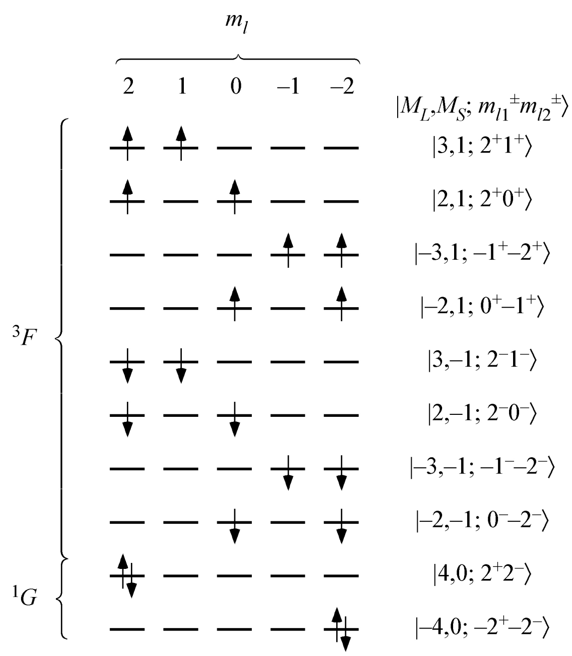
$$\hat{M}_+ \left| lm \right\rangle = \sqrt{l(l+1) - m(m+1)} \left| l\ m+1 \right\rangle \quad (= 0 \text{ when } m = l) \qquad (10)$$

$$\hat{M}_- \left| lm \right\rangle = \sqrt{l(l+1) - m(m-1)} \left| l\ m-1 \right\rangle \quad (= 0 \text{ when } m = -l) \qquad (11)$$

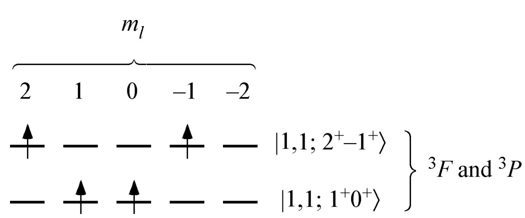
Practical Use of Ladder Operators

The ladder operators can be quite useful in working out the eigenfunctions of summed angular momenta. Working out some examples in detail can show the way they are applied. Let us consider the following question: how are the eigenfunctions of $\hat{L}^2$, $\hat{L}_z$, $\hat{S}^2$, and $\hat{S}_z$ obtained for a two-electron configuration? To address this question, let's look at specific problem: what Slater determinants or combinations of Slater determinants are used to write the electronic states of a d^2 configuration?

First, recall that the states of a d^2 configuration are ^3F, ^3P, ^1G, ^1D, and ^1S. Before going further, we observe that 10 of the 45 determinants that can be written for a d^2 configuration can be assigned immediately to the ^3F and ^1G states. These are illustrated here and are immediately assignable because they exhibit extreme values of M_L and/or M_S. The determinants with $M_L = m_{l1} + m_{l2} = \pm 4$ must be two of 9 degenerate eigenfunctions that belong to the ^1G state simply because the ^1G state is the only state with a large enough value of L (= 4). Similarly, subject to the constraint that $M_S = m_{s1} + m_{s2} = \pm 1$, determinants with $M_L = m_{l1} + m_{l2} = \pm 3, \pm 2$ must belong to the ^3F state because the ^3F state is the only state with a large enough value of L (= 3) that also has $S = 1$.



Getting (combinations of) determinants for the other states is an indirect process. No single determinant can be unambiguously assigned to the ^3P state, for example, because there are at least two determinants for every pair of M_L and M_S values for the ^3P state. The ^3P state must have one component with $M_L = 1$ and $M_S = 1$, but there are two determinants with these characteristics: $|\, 2^{+}{-1}^{+}\rangle$ and $|1^{+}0^{+}\rangle$ (the notation is a shortening of that used in the illustrations; the numbers give the m_l values and the + and – signs respectively refer to α and β eigenfunctions of the individual electrons). Both the states ^3P and ^3F have components with $M_L = 1$ and $M_S = 1$, but as we shall see, neither of these two determinants belongs solely to ^3P or ^3F. We do, however, have the component of ^3F with $M_L = 2$ and $M_S = 1$ and our strategy is to operate on this determinant with an appropriate *lowering operator*, $\hat{L}_-$, which will generate an eigenfunction with $M_L = 1$ (and $M_S = 1$) that still belongs to ^3F because a lowering operator does not change the value of L, it just lowers M_L by one step.



The total angular momentum operators $\hat{\mathbf{L}}$ and $\hat{\mathbf{S}}$ are just the vector sum of the individual electron operators (the "hats" on the unit vectors do *not* indicate operators, next page):

$$\hat{\mathbf{L}} = \hat{L}_x\hat{\mathbf{x}} + \hat{L}_y\hat{\mathbf{y}} + \hat{L}_z\hat{\mathbf{z}} = \hat{\mathbf{L}}_1 + \hat{\mathbf{L}}_2 = (\hat{L}_{x1} + \hat{L}_{x2})\hat{\mathbf{x}} + (\hat{L}_{y1} + \hat{L}_{y2})\hat{\mathbf{y}} + (\hat{L}_{z1} + \hat{L}_{z2})\hat{\mathbf{z}} \quad (12)$$

$$\hat{\mathbf{S}} = \hat{S}_x\hat{\mathbf{x}} + \hat{S}_y\hat{\mathbf{y}} + \hat{S}_z\hat{\mathbf{z}} = \hat{\mathbf{S}}_1 + \hat{\mathbf{S}}_2 = (\hat{S}_{x1} + \hat{S}_{x2})\hat{\mathbf{x}} + (\hat{S}_{y1} + \hat{S}_{y2})\hat{\mathbf{y}} + (\hat{S}_{z1} + \hat{S}_{z2})\hat{\mathbf{z}} \quad (13)$$

i.e., the operator components add: $\hat{L}_z = \hat{L}_{z1} + \hat{L}_{z2} \quad \hat{S}_z = \hat{S}_{z1} + \hat{S}_{z2}$, etc… (14)

It follows that the ladder operators add: $\hat{L}_\pm = \hat{L}_{\pm1} + \hat{L}_{\pm2} \quad \hat{S}_\pm = \hat{S}_{\pm1} + \hat{S}_{\pm2}$ (15)

The general relations (10) and (11) for the ladder operators hold for *both* the total angular momenta *and* the individual angular momenta:

$$\hat{L}_\pm \left| LM_LSM_S \right\rangle = \sqrt{L(L+1) - M_L(M_L \pm 1)}\left| L\ M_L \pm 1\ SM_S \right\rangle \quad (16)$$

$$\hat{S}_\pm \left| LM_LSM_S \right\rangle = \sqrt{S(S+1) - M_S(M_S \pm 1)}\left| LM_LS\ M_S \pm 1 \right\rangle \quad (17)$$

$$\hat{L}_{1\pm} \left| m_{l1}m_{l1}m_{s1}m_{s2} \right\rangle = \sqrt{l_1(l_1+1) - m_{l1}(m_{l1} \pm 1)}\left| m_{l1} + 1\ m_{l2}m_{s1}m_{s2} \right\rangle \quad (18)$$

$$\hat{L}_{2\pm} \left| m_{l1}m_{l1}m_{s1}m_{s2} \right\rangle = \sqrt{l_2(l_2+1) - m_{l2}(m_{l2} \pm 1)}\left| m_{l1}\ m_{l2} + 1\ m_{s1}m_{s2} \right\rangle \quad (19)$$

$$\begin{matrix} \hat{S}_{1+}\alpha_1\sigma_2 = 0 & \hat{S}_{1+}\beta_1\sigma_2 = \alpha_1\sigma_2 & \hat{S}_{1-}\alpha_1\sigma_2 = \beta_1\sigma_2 & \hat{S}_{1-}\beta_1\sigma_2 = 0 \\ \hat{S}_{2+}\sigma_1\alpha_2 = 0 & \hat{S}_{2+}\sigma_1\beta_2 = \sigma_1\alpha_2 & \hat{S}_{2-}\sigma_1\alpha_2 = \sigma_1\beta_2 & \hat{S}_{2-}\sigma_1\beta_2 = 0 \end{matrix} \quad (20)$$

The symbol "σ" has been used in (20) to signify either α or β and the square root factors have been evaluated for the case of individual spins; $\sqrt{s_j(s_j+1) - m_{sj}(m_{sj} \pm 1)} = 1$ or 0 in all individual electron cases.

As an example, let's apply $\hat{L}_-$ to the ^3F determinant with $M_L = 2$ and $M_S = 1$:

$$\hat{L}_-\left| {}^3F; M_LM_S \right\rangle = (\hat{L}_{1-} + \hat{L}_{2-})\left| m_{l1}m_{l1}m_{s1}m_{s2} \right\rangle$$

$$\hat{L}_-\left| {}^3F; 2\,1 \right\rangle = (\hat{L}_{1-} + \hat{L}_{2-})\left| 2^+0^+ \right\rangle$$

$$\sqrt{3(3+1) - 2(2-1)}\left| {}^3F; 1\,1 \right\rangle = \sqrt{2(2+1) - 2(2-1)}\left| 1^+0^+ \right\rangle + \sqrt{2(2+1) - 0(-1-1)}\left| 2^+ -1^+ \right\rangle$$

$$\boxed{\left| {}^3F; 1\,1 \right\rangle = \sqrt{\tfrac{2}{5}}\left| 1^+0^+ \right\rangle + \sqrt{\tfrac{3}{5}}\left| 2^+ -1^+ \right\rangle}$$

On the left-hand side of these equations, the *total* orbital angular momentum lowering operator is applied using L and M_L as in equation (16); on the right-hand side of these equations, the *individual* orbital angular momentum lowering operators are applied using l_i (= 2 for d electrons) and m_{li} values as in equation (18). When simplified, we obtain the normalized combination of the two determinants identified above. Because the ^3P and ^3F state wavefunctions must be orthogonal to each other, the correct combination of the two determinants for ^3P can be found be setting $\langle {}^3P; 1\,1 | {}^3F; 1\,1 \rangle = 0$ and requiring that the ^3P combination also be normalized,

$$\left.\begin{matrix} \left| {}^3P; 1\,1 \right\rangle = c_1\left| 1^+0^+ \right\rangle + c_2\left| 2^+ -1^+ \right\rangle \ ; \ c_1^2 + c_2^2 = 1 \\ \left\langle {}^3P; 1\,1 \right| {}^3F; 1\,1 \rangle = \sqrt{\tfrac{2}{5}}c_1 + \sqrt{\tfrac{3}{5}}c_2 = 0 \end{matrix}\right\} \Rightarrow c_1 = \sqrt{\tfrac{3}{5}} \quad c_2 = -\sqrt{\tfrac{2}{5}}$$

$$\left| {}^3P; 1\,1 \right\rangle = \sqrt{\tfrac{3}{5}}\left| 1^+0^+ \right\rangle - \sqrt{\tfrac{2}{5}}\left| 2^+ -1^+ \right\rangle$$

Spin lowering operators are very easily applied. Any spin wavefunction of the form $\alpha_1\alpha_2$ ($S = 1$, $M_S = 1$) can be lowered with by applying $\hat{S}_-$:

$$\hat{S}_-\left|S=1, M_S=1\right\rangle = (\hat{S}_{1-}+\hat{S}_{2-})\left|\alpha_1\alpha_2\right\rangle$$
$$\sqrt{1(1+1)-1(1-1)}\left|S=1, M_S=0\right\rangle = \left|\beta_1\alpha_2\right\rangle + \left|\alpha_1\beta_2\right\rangle$$
$$\left|S=1, M_S=0\right\rangle = \sqrt{\tfrac{1}{2}}\left(\left|\beta_1\alpha_2\right\rangle + \left|\alpha_1\beta_2\right\rangle\right)$$

Let's apply this, for example, to obtain two $M_S = 0$ components of ^3F,

$$\hat{S}_-\left|{}^3F;3\,1\right\rangle = (\hat{S}_{1-}+\hat{S}_{2-})\left|2^+1^+\right\rangle \qquad \hat{S}_-\left|{}^3F;2\,1\right\rangle = (\hat{S}_{1-}+\hat{S}_{2-})\left|2^+0^+\right\rangle$$
$$\sqrt{1(1+1)-1(1-1)}\left|{}^3F;3\,0\right\rangle = \left|2^-1^+\right\rangle + \left|2^+1^-\right\rangle \qquad \sqrt{1(1+1)-1(1-1)}\left|{}^3F;2\,1\right\rangle = \left|2^-0^+\right\rangle + \left|2^+0^-\right\rangle$$
$$\boxed{\left|{}^3F;3\,0\right\rangle = \sqrt{\tfrac{1}{2}}\left(\left|2^-1^+\right\rangle + \left|2^+1^-\right\rangle\right) \qquad \left|{}^3F;2\,0\right\rangle = \sqrt{\tfrac{1}{2}}\left(\left|2^-0^+\right\rangle + \left|2^+0^-\right\rangle\right)}$$

We can confirm that the ^1G state wavefunction $|^1G;\,3\,0\rangle$ is orthogonal to $|^3F;\,3\,0\rangle$:

$$\hat{L}_-\left|{}^1G;M_L M_S\right\rangle = (\hat{L}_{1-}+\hat{L}_{2-})\left|{}^1G;m_{l1}m_{l1}m_{s1}m_{s2}\right\rangle$$
$$\hat{L}_-\left|{}^1G;4\,0\right\rangle = (\hat{L}_{1-}+\hat{L}_{2-})\left|2^+2^-\right\rangle$$
$$\sqrt{4(4+1)-4(4-1)}\left|{}^1G;3\,0\right\rangle = \sqrt{2(2+1)-2(2-1)}\left(\left|2^+1^-\right\rangle - \left|1^+2^-\right\rangle\right)$$

Swapping the columns in the last determinant changes its sign,

$$\boxed{\left|{}^1G;3\,0\right\rangle = \sqrt{\tfrac{1}{2}}\left(\left|2^+1^-\right\rangle - \left|2^-1^+\right\rangle\right)}$$

This can be lowered once again with $\hat{L}_-$ to obtain $|^1G;\,2\,0\rangle$,

$$\hat{L}_-\left|{}^1G;3\,0\right\rangle = (\hat{L}_{1-}+\hat{L}_{2-})\sqrt{\tfrac{1}{2}}\left(\left|2^+1^-\right\rangle - \left|2^-1^+\right\rangle\right)$$
$$\sqrt{4(4+1)-4(4-1)}\left|{}^1G;3\,0\right\rangle = \left[\sqrt{\tfrac{2(2+1)-2(2-1)}{2}}\left(\left|1^+1^-\right\rangle - \left|1^-1^+\right\rangle\right) + \sqrt{\tfrac{2(2+1)-1(1-1)}{2}}\left(\left|2^+0^-\right\rangle - \left|2^-0^+\right\rangle\right)\right]$$

recalling that $\left|1^+1^-\right\rangle = -\left|1^-1^+\right\rangle$ this simplifies to

$$\boxed{\left|{}^1G;2\,0\right\rangle = \tfrac{2}{\sqrt{7}}\left|1^+1^-\right\rangle + \sqrt{\tfrac{3}{14}}\left(\left|2^+0^-\right\rangle - \left|2^-0^+\right\rangle\right)}$$

Continuing in this manner we can generate the combinations of determinants appropriate for any other of the d^2 configuration wavefunctions: ^3F, ^3P, ^1G, ^1D, and ^1S.

Another context where the ladder operators are used is in the evaluation of matrix elements in involving $\hat{L}_x$ and $\hat{L}_y$ or $\hat{S}_x$ and $\hat{S}_y$ operators. Since we usually choose the z-axis as our "quantization axis" (i.e., we deal with simultaneous eigenfunctions of $\hat{L}_z$ or $\hat{S}_z$ along with $\hat{L}^2$ or $\hat{S}^2$), operations with $\hat{L}_z$ are usually straightforward. We deal with the $\hat{L}_x$ and $\hat{L}_y$ operators using $\hat{L}_+ \pm \hat{L}_-$. Table 2 on the following page is derived with just a modest effort. For example, if we freely interconvert the real with the complex forms of d-orbitals and $\hat{L}_x$ and $\hat{L}_y$ with $\hat{L}_+$ and $\hat{L}_-$, we can write

$$\hat{L}_x\left|z^2\right\rangle \equiv \hat{L}_x\left|0\right\rangle = \left(\hat{L}_+ + \hat{L}_-\right)\left|0\right\rangle = \sqrt{\tfrac{3}{2}}\left[\left|1\right\rangle + \left|-1\right\rangle\right] = -i\sqrt{3}\times\tfrac{i}{\sqrt{2}}\left[\left|1\right\rangle + \left|-1\right\rangle\right] \equiv -i\sqrt{3}\left|yz\right\rangle$$

where we've made use of a d-orbital conversion given in Table 1.

Table 1. Complex d orbitals ($\hat{L}_z$ eigenfunctions)* and Real d orbitals

$$
\sqrt{\frac{15}{8\pi}} \times f(r) \times \left\{
\begin{array}{cc}
\frac{1}{4}\sin^2\theta e^{2i\varphi} = |2\rangle & |x^2-y^2\rangle = \sqrt{\tfrac{1}{2}}\left[|2\rangle + |-2\rangle\right] \\
-\sin\theta\cos\theta e^{i\varphi} = |1\rangle & |yz\rangle = \tfrac{i}{\sqrt{2}}\left[|1\rangle + |-1\rangle\right] \\
\sqrt{\tfrac{1}{6}}(3\cos^2\theta - 1) = |0\rangle & |z^2\rangle = |0\rangle \\
\sin\theta\cos\theta e^{-i\varphi} = |-1\rangle & |xz\rangle = \tfrac{1}{\sqrt{2}}\left[-|1\rangle + |-1\rangle\right] \\
\frac{1}{4}\sin^2\theta e^{-2i\varphi} = |-2\rangle & |xy\rangle = \tfrac{-i}{\sqrt{2}}\left[|2\rangle - |-2\rangle\right]
\end{array}
\right.
$$

*Signs chosen vary, but a consistent set must be used.

All of the entries in Table 2 can be verified by repeated application of operations like the one illustrated above, along with the use of Table 1, the ladder operator definitions (4), and equations (18) and (19).

Table 2. Effect of orbital angular momentum operators on the real d orbitals

$\hat{L}_x d_{xz} = -id_{xy}$	$\hat{L}_y d_{xz} = -i\sqrt{3}d_{z^2} + id_{x^2-y^2}$	$\hat{L}_z d_{xz} = id_{yz}$
$\hat{L}_x d_{yz} = i\sqrt{3}d_{z^2} + id_{x^2-y^2}$	$\hat{L}_y d_{yz} = id_{xy}$	$\hat{L}_z d_{yz} = -id_{xz}$
$\hat{L}_x d_{xy} = id_{xz}$	$\hat{L}_y d_{xy} = -id_{yz}$	$\hat{L}_z d_{xy} = -2id_{x^2-y^2}$
$\hat{L}_x d_{x^2-y^2} = -id_{yz}$	$\hat{L}_y d_{x^2-y^2} = -id_{xz}$	$\hat{L}_z d_{x^2-y^2} = 2id_{xy}$
$\hat{L}_x d_{z^2} = -i\sqrt{3}d_{yz}$	$\hat{L}_y d_{z^2} = i\sqrt{3}d_{xz}$	$\hat{L}_z d_{z^2} = 0$

Reference: Ballhausen, C. J. *Introduction to Ligand Field Theory*

When computing g-values in EPR, a formula from 2nd order perturbation theory emerges wherein excited states, ψ_n, are coupled to the ground state, ψ_0, via the angular momentum operators:

$$
g_{ij} = g_e - 2\zeta \sum_n \frac{\langle \psi_0 | \hat{L}_i | \psi_n \rangle \langle \psi_n | \hat{L}_j | \psi_0 \rangle}{E_n - E_0} \quad \text{where } i \text{ and } j \text{ are } x, y \text{ or } z
$$

For the real d orbitals, the operator relations in Table 2 are of the most direct use. These are used to build the 'magic pentagon' discussed in lecture. The $\hat{L}_z$ operator couples real orbitals that are combinations of complex orbitals with the same value of m_l (Table 1), while the $\hat{L}_x$ and the $\hat{L}_y$ operators couple orbitals with values of m_l separated by 1 – because these operators are expressible as combinations of the ladder operators.