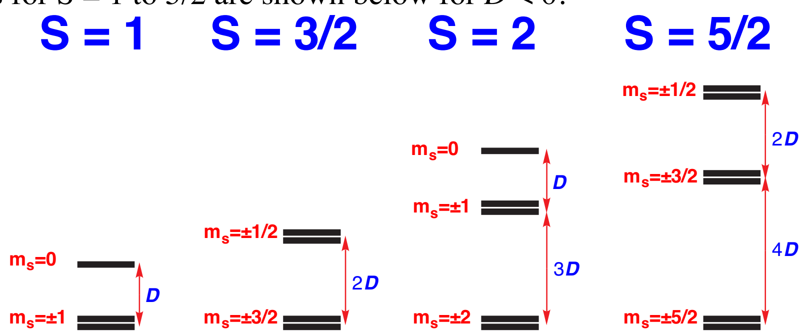
Zero-field splitting (zfs) is the removal spin microstate degeneracy for systems with S > 1/2 in the absence of an applied field. That is, the degeneracy is removed as a consequence of molecular electronic structure and/or spin density distribution. For odd-electron systems, axial zfs (the "*D*" zfs parameter) removes the microstate degeneracy and produces Kramer's doublets. Rhombic zfs (the "*E*" zfs parameter) splits the Kramer's doublets. Zero-field splitting causes magnetic anisotropy, and has profound effects on magnetic *properties*. For example, magnetic hardness (≈ the width of a hysteresis loop) is related to the magnetoanisotropy. At the molecular level, understanding zfs is essential for rational design of single-molecule magnets since the energy barrier separating the $+m_s$ and $-m_s$ microstates is equal to $|S^2D|$.[1] The energies of spin microstates in units of D are given by equation 1, assuming $E = 0$.

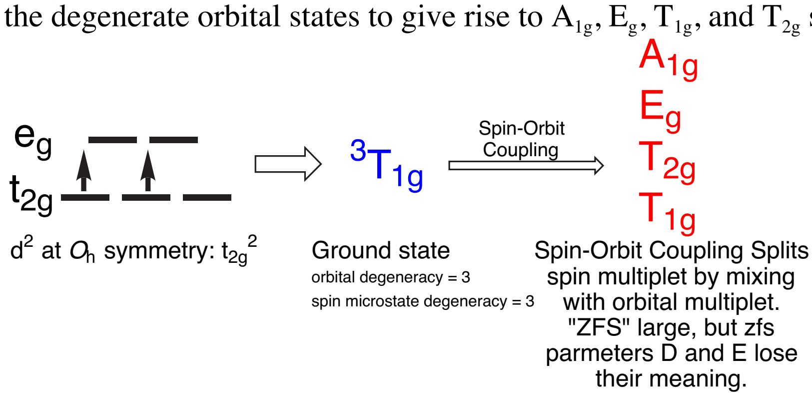
$$E_{m_s} = D\left[S_z^2 - \frac{S(S+1)}{3}\right] \qquad (1)$$

Energy level spacings for S = 1 to 5/2 are shown below for $D < 0$.

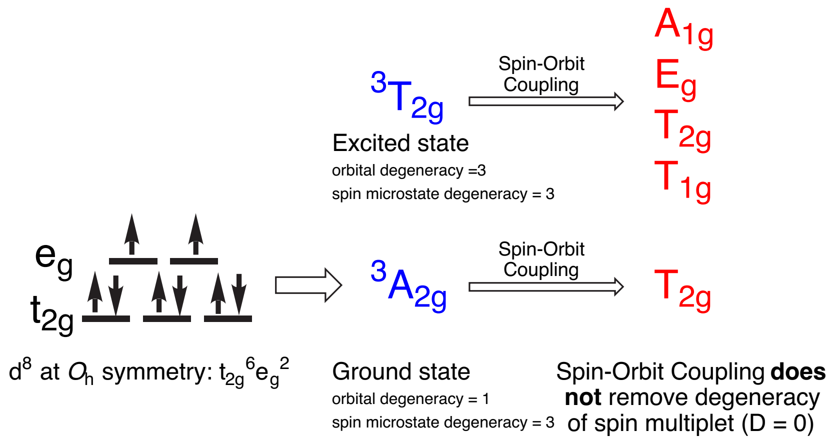


Orbital angular momentum can be of primary contributor to zfs, and can make the zfs quite large (≈1-10 cm^{-1})compared to spin-dipolar contributions (≈10^{-3} - 10^{-1} cm^{-1}). There are two scenarios in which orbital angular momentum manifests itself in zfs: in-state orbital angular momentum (*e.g.*, orbital T states in O_h symmetry), and out-of state orbital angular momentum (*e.g.*, spin-orbit mixing of certain excited states into the ground state).

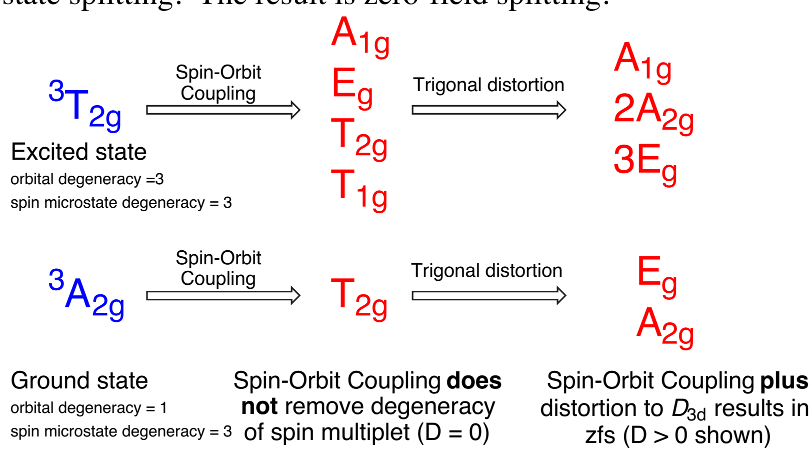
In-state orbital angular momentum can give rise to very large zfs. However, in such cases, the zfs parameters lose their traditional meanings. Consider the d^2 electron configuration at O_h symmetry. The ground state is $^3T_{1g}$. At O_h symmetry, the spin-orbit coupling operator (which always transforms as the rotations) transforms at t_{1g}. Thus, spin-orbit coupling breaks the triplet microstate degeneracy (S = 1; m_s = ±1, 0) by coupling to the degenerate orbital states to give rise to A_{1g}, E_g, T_{1g}, and T_{2g} states.



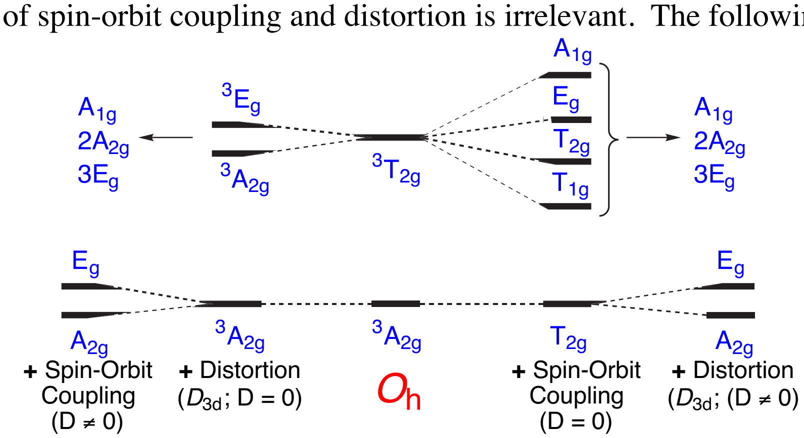
Out-of state orbital angular momentum can also give rise to zfs, but not alone. Consider the d^8 electron configuration at O_h symmetry. The ground state is $^3A_{2g}$, with low-lying $^3T_{2g}$ and $^3T_{1g}$ excited states. Both excited states have orbital angular momentum, but the interaction that mixes these states into the ground state must transform as $A_{2g} \otimes T_{1g} = T_{2g}$ or as $A_{2g} \otimes T_{2g} = T_{1g}$. Since the spin-orbit coupling operator transforms as t_{1g}, then spin-orbit coupling can mix the $^3T_{2g}$ state into the ground state. However, this mixing does not break the spin degeneracy of the ground state since $A_{2g} \otimes T_{1g} = T_{2g}$, and the degeneracy is retained.



Now consider the effect of a ligand field distortion. A trigonal distortion lowers the symmetry to D_{3d}, *and* splits the ground T_{1g} state into an A_{2g} and an E_g. Any distortion that removes the degeneracy of t_{1g} will work. Thus, the spin-orbit coupling plus the distortion combine as perturbations to allow the ground state "feel" the excited state splitting. The result is zero-field splitting.

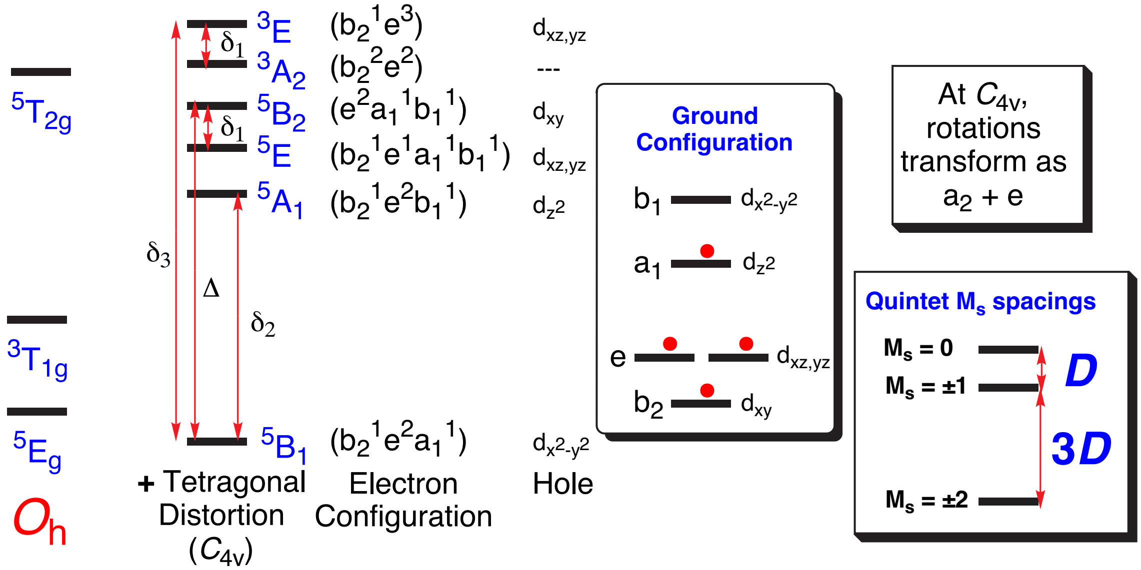


Note that the order of spin-orbit coupling and distortion is irrelevant. The following illustrates.



Diagrams like those on the last page can be drawn for any orbital singlet state with $S > 1/2$. The issues are (1) the symmetry, (2) the number, and (3) energies of excited states. For example, Cr^{III} has only one low-lying excited state that can impart orbital angular momentum to the ground state via spin-orbit-induced configuration interaction. However, this state is high-lying, so the mixing is weak and $|D| < 1$ cm^{-1}. However, distorted six- and five-coordinate Mn^{III} has three low-lying states that can mix with the ground state, so the mixing is relatively strong and $|D| > 1$ cm^{-1}. However, even when more than one excited state contributes to ground state zfs, different excited states can provide contributions to D of opposite signs. The sign of each contribution arises from the particular spin-orbit coupling matrix elements.

As an example, consider the diagrams below for five-coordinate Mn^{III} at C_{4v} symmetry.[2]



The ground-state term symbol is $^5B_1$. Excited states can mix with the ground state and give rise to zfs. The expression for the *axial* zfs in the $^5B_1$ ground state of Mn^{III} (at C_{4v} symmetry) is given by equation 1:

$$D = \lambda^2\left[-\frac{4}{\Delta} - \frac{4}{\delta_3} + \frac{1}{(\Delta - \delta_1)}\right] \tag{1}$$

Equation 1 comes from evaluating the mixing of every M_S level for each excited state with each M_S level of the $^5B_1$ ground state. As such, there are 145 terms to consider! However, since $B_1 \otimes (a_2 + e) = B_2 + E$, only three of the five excited states will mix with the $^5B_1$ ground state via spin-orbit coupling. These are the ^5E, the $^5B_2$, and the ^3E. Now, we're down to 105 terms. Fortunately, as will be shown, many of these need not be computed. So, let's derive equation 1 beginning with writing down the orbital functions for each electronic state.

$$^5B_1 = d_{xy}d_{xz}d_{yz}d_{z2} \tag{2}$$

$$^5A_1 = d_{xy}d_{xz}d_{yz}d_{x2-y2} \tag{3}$$

$$^5E = d_{xy}d_{xz}d_{z2}d_{x2-y2} \tag{4}$$

$$\text{and } = d_{xy}d_{yz}d_{z2}d_{x2-y2} \tag{5}$$

$$^5B_2 = d_{xz}d_{yz}d_{x2-y2}d_{z2} \tag{6}$$

$$^3A_2 = d_{xy}\bar{d}_{xy}d_{xz}d_{yz} \tag{7}$$

$$^3E = d_{xy}d_{xz}\bar{d}_{xz}d_{yz} \tag{8}$$

$$\text{and } = d_{xy}d_{yz}\bar{d}_{yz}d_{xz}$$

Now let's write down the M_S wavefunctions for each electronic state. For the $^5B_1$ (ground state), we have:

$$M_s = 2;\left[xy\ xz\ yz\ z^2\right] \tag{9}$$

$$M_s = 1;\frac{1}{2}\left[\overline{xy}\ xz\ yz\ z^2 + xy\ \overline{xz}\ yz\ z^2 + xy\ xz\ \overline{yz}\ z^2 + xy\ xz\ yz\ \overline{z}^2\right] \tag{10}$$

$$M_s = 0;\frac{1}{\sqrt{6}}\left[\overline{xy}\ \overline{xz}\ yz\ z^2 + \overline{xy}\ xz\ \overline{yz}\ z^2 + \overline{xy}\ xz\ yz\ \overline{z}^2 + xy\ \overline{xz}\ \overline{yz}\ z^2 + xy\ \overline{xz}\ yz\ \overline{z}^2 + xy\ xz\ \overline{yz}\ \overline{z}^2\right] \tag{11}$$

$$M_s = -1;\frac{1}{2}\left[xy\ \overline{xz}\ \overline{yz}\ \overline{z}^2 + \overline{xy}\ xz\ \overline{yz}\ \overline{z}^2 + \overline{xy}\ \overline{xz}\ yz\ \overline{z}^2 + \overline{xy}\ \overline{xz}\ \overline{yz}\ z^2\right] \tag{12}$$

$$M_s = -2;\left[\overline{xy}\ \overline{xz}\ \overline{yz}\ \overline{z}^2\right] \tag{13}$$

For $^5B_2$ we have:

$$M_s = 2;\left[x^2 - y^2\ xz\ yz\ z^2\right] \tag{14}$$

$$M_s = 1;\frac{1}{2}\left[\overline{x}^2 - \overline{y}^2\ xz\ yz\ z^2 + x^2 - y^2\ \overline{xz}\ yz\ z^2 + x^2 - y^2\ xz\ \overline{yz}\ z^2 + x^2 - y^2\ xz\ yz\ \overline{z}^2\right] \tag{15}$$

$$M_s = 0;\frac{1}{\sqrt{6}}\left[\begin{array}{l}\overline{x}^2 - \overline{y}^2\ \overline{xz}\ yz\ z^2 + \overline{x}^2 - \overline{y}^2\ xz\ \overline{yz}\ z^2 + \overline{x}^2 - \overline{y}^2\ xz\ yz\ \overline{z}^2 + \\ x^2 - y^2\ \overline{xz}\ \overline{yz}\ z^2 + x^2 - y^2\ \overline{xz}\ yz\ \overline{z}^2 + x^2 - y^2\ xz\ \overline{yz}\ \overline{z}^2\end{array}\right] \tag{16}$$

$$M_s = -1;\frac{1}{2}\left[x^2 - y^2\ \overline{xz}\ \overline{yz}\ \overline{z}^2 + \overline{x}^2 - \overline{y}^2\ xz\ \overline{yz}\ \overline{z}^2 + \overline{x}^2 - \overline{y}^2\ \overline{xz}\ yz\ \overline{z}^2 + \overline{x}^2 - \overline{y}^2\ \overline{xz}\ \overline{yz}\,\Sigma z^2\right] \tag{17}$$

$$M_s = -2;\left[\overline{x}^2 - \overline{y}^2\ \overline{xz}\ \overline{yz}\ \overline{z}^2\right] \tag{18}$$

For ^3E we get,

$$M_s = 1;\left[xy\ xz\ yz\ \overline{yz}\right] \tag{19}$$

$$M_s = 0;\frac{1}{\sqrt{2}}\left[\overline{xy}\ xz\ yz\ \overline{yz} + xy\ \overline{xz}\ yz\ \overline{yz}\right] \tag{20}$$

$$M_s = -1;\left[\overline{xy}\ \overline{xz}\ yz\ \overline{yz}\right] \tag{21}$$

and:

$$M_s = 1;\left[xy\ xz\ yz\ \overline{xz}\right] \tag{22}$$

$$M_s = 0;\frac{1}{\sqrt{2}}\left[\overline{xy}\ xz\ yz\ \overline{xz} + xy\ xz\ \overline{yz}\ \overline{xz}\right] \tag{23}$$

$$M_s = -1;\left[\overline{xy}\ xz\ \overline{yz}\ \overline{xz}\right] \tag{24}$$

For ^5E:

$$M_s = 2;\left[xy\ xz\ x^2-y^2\ z^2\right] \tag{25}$$

$$M_s = 1;\frac{1}{2}\left[\overline{xy}\ xz\ x^2-y^2\ z^2 + xy\ \overline{xz}\ x^2-y^2\ z^2 + xy\ xz\ \overline{x}^2-\overline{y}^2\ z^2 + xy\ xz\ x^2-y^2\ \overline{z}^2\right] \tag{26}$$

$$M_s = 0;\frac{1}{\sqrt{6}}\begin{bmatrix}\overline{xy}\ \overline{xz}\ x^2-y^2\ z^2 + \overline{xy}\ xz\ \overline{x}^2-\overline{y}^2\ z^2 + \overline{xy}\ xz\ x^2-y^2\ \overline{z}^2 \\ +xy\ \overline{xz}\ \overline{x}^2-\overline{y}^2\ z^2 + xy\ \overline{xz}\ x^2-y^2\ \overline{z}^2 + xy\ xz\ \overline{x}^2-\overline{y}^2\ \overline{z}^2\end{bmatrix} \tag{27}$$

$$M_s = -1;\frac{1}{2}\left[xy\ \overline{xz}\ \overline{x}^2-\overline{y}^2\ \overline{z}^2 + \overline{xy}\ xz\ \overline{x}^2-\overline{y}^2\ \overline{z}^2 + \overline{xy}\ \overline{xz}\ x^2-y^2\ \overline{z}^2 + \overline{xy}\ \overline{xz}\ \overline{x}^2-\overline{y}^2\ z^2\right] \tag{28}$$

$$M_s = -2;\left[\overline{xy}\ \overline{xz}\ \overline{x}^2-\overline{y}^2\ \overline{z}^2\right] \tag{29}$$

and:

$$M_s = 2;\left[xy\ yz\ x^2-y^2\ z^2\right] \tag{30}$$

$$M_s = 1;\frac{1}{2}\left[\overline{xy}\ yz\ x^2-y^2\ z^2 + xy\ \overline{yz}\ x^2-y^2\ z^2 + xy\ yz\ \overline{x}^2-\overline{y}^2\ z^2 + xy\ yz\ x^2-y^2\ \overline{z}^2\right] \tag{31}$$

$$M_s = 0;\frac{1}{\sqrt{6}}\begin{bmatrix}\overline{xy}\ \overline{yz}\ x^2-y^2\ z^2 + \overline{xy}\ yz\ \overline{x}^2-\overline{y}^2\ z^2 + \overline{xy}\ yz\ x^2-y^2\ \overline{z}^2 \\ +xy\ \overline{yz}\ \overline{x}^2-\overline{y}^2\ z^2 + xy\ \overline{yz}\ x^2-y^2\ \overline{z}^2 + xy\ yz\ \overline{x}^2-\overline{y}^2\ \overline{z}^2\end{bmatrix} \tag{32}$$

$$M_s = -1;\frac{1}{2}\left[xy\ \overline{yz}\ \overline{x}^2-\overline{y}^2\ \overline{z}^2 + \overline{xy}\ yz\ \overline{x}^2-\overline{y}^2\ \overline{z}^2 + \overline{xy}\ \overline{yz}\ x^2-y^2\ \overline{z}^2 + \overline{xy}\ \overline{yz}\ \overline{x}^2-\overline{y}^2\ z^2\right] \tag{33}$$

$$M_s = -2;\left[\overline{xy}\ \overline{yz}\ \overline{x}^2-\overline{y}^2\ \overline{z}^2\right] \tag{34}$$

As shown in the figure on page 1, for a quintet state, D is given by the energy gap between the $M_s = 1$ and $M_s = 0$ microstates. Therefore, only matrix elements that include these $^5B_1$ M_s levels need to be calculated. Strictly speaking, that means that we have to compute only 42 terms. As you'll see, symmetry demands that many of these terms make the same contribution.

For $M_S = 1$ of $^5B_1$ we have:

$$M_s = 1;\frac{1}{2}\left[\overline{xy}\ xz\ yz\ z^2 + xy\ \overline{xz}\ yz\ z^2 + xy\ xz\ \overline{yz}\ z^2 + xy\ xz\ yz\ \overline{z}^2\right] \tag{10}$$

For $^5B_1$ mixing with $^5B_2$ (only $l_z s_z$)

$$M_s = 2;\left[x^2-y^2\ xz\ yz\ z^2\right] \tag{14}$$

gives

$$\frac{1}{2}\left[\left\langle \overline{xy}\middle| l\bullet s \middle| x^2-y^2\right\rangle\right] = \frac{1}{2}\left[\left\langle xy\middle| l_z \middle| x^2-y^2\right\rangle\left\langle \beta\middle| s_z\middle|\alpha\right\rangle\right] = 0 \tag{35}$$

$$M_s = 1;\frac{1}{2}\left[\overline{x}^2-\overline{y}^2\ xz\ yz\ z^2 + x^2-y^2\ \overline{xz}\ yz\ z^2 + x^2-y^2\ xz\ \overline{yz}\ z^2 + x^2-y^2\ xz\ yz\ \overline{z}^2\right] \tag{15}$$

gives

$$\boxed{\begin{array}{l}\frac{1}{4}\left[\left\langle\overline{xy}\middle|l\bullet s\middle|\overline{x}^2-\overline{y}^2\right\rangle+3\left\langle xy\middle|l\bullet s\middle|x^2-y^2\right\rangle\right]\\=\frac{1}{4}\left[\left\langle xy\middle|l_z\middle|x^2-y^2\right\rangle\left\langle\beta\middle|s_z\middle|\beta\right\rangle+3\left\langle xy\middle|l_z\middle|x^2-y^2\right\rangle\left\langle\alpha\middle|s_z\middle|\alpha\right\rangle\right]=\frac{1}{4}\left[(2i)\left(-\frac{1}{2}\right)+3(2i)\left(+\frac{1}{2}\right)\right]=\frac{i}{2}\end{array}} \quad (36)$$

$$M_s=0;\frac{1}{\sqrt{6}}\begin{bmatrix}\overline{x}^2-\overline{y}^2\ \overline{xz}\ yz\ z^2+\overline{x}^2-\overline{y}^2\ xz\ \overline{yz}\ z^2+\overline{x}^2-\overline{y}^2\ xz\ yz\ \overline{z}^2\\+x^2-y^2\ \overline{xz}\ \overline{yz}\ z^2+x^2-y^2\ \overline{xz}\ yz\ \overline{z}^2+x^2-y^2\ xz\ \overline{yz}\ \overline{z}^2\end{bmatrix} \quad (16)$$

gives

$$\frac{1}{2}\left[\left\langle\overline{xy}\middle|l\bullet s\middle|x^2-y^2\right\rangle\right]=\frac{1}{2}\left[\left\langle xy\middle|l_z\middle|x^2-y^2\right\rangle\left\langle\beta\middle|s_z\middle|\alpha\right\rangle\right]=0 \quad (37)$$

$$M_s=-1;\frac{1}{2}\left[x^2-y^2\ \overline{xz}\ \overline{yz}\ \overline{z}^2+\overline{x}^2-\overline{y}^2\ xz\ \overline{yz}\ \overline{z}^2+\overline{x}^2-\overline{y}^2\ \overline{xz}\ yz\ \overline{z}^2+\overline{x}^2-\overline{y}^2\ \overline{xz}\ \overline{yz}\ \Sigma z^2\right] \quad (17)$$

gives 0 (38)

$$M_s=-2;\left[\overline{x}^2-\overline{y}^2\ \overline{xz}\ \overline{yz}\ \overline{z}^2\right] \quad (18)$$

gives 0 (39)

For $M_s = 1$ of $^5B_1$ mixing with ^3E (only $l_x s_x$ and $l_y s_y$) we have:

$$M_s=1;\frac{1}{2}\left[\overline{xy}\ xz\ yz\ z^2+xy\ \overline{xz}\ yz\ z^2+xy\ xz\ \overline{yz}\ z^2+xy\ xz\ yz\ \overline{z}^2\right] \quad (10)$$

For ^3E:

$$M_s=1;\left[xy\ xz\ yz\ \overline{yz}\right] \quad (19)$$

gives

$$\frac{1}{2}\left[\left\langle\overline{z}^2\middle|l\bullet s\middle|\overline{yz}\right\rangle\right]=\frac{1}{2}\left[\left\langle z^2\middle|l_x\middle|yz\right\rangle\left\langle\beta\middle|s_x\middle|\beta\right\rangle\right]=0 \quad (40)$$

$$M_s=0;\frac{1}{\sqrt{2}}\left[\overline{xy}\ xz\ yz\ \overline{yz}+xy\ \overline{xz}\ yz\ \overline{yz}\right] \quad (20)$$

gives

$$\boxed{\frac{1}{2\sqrt{2}}\left[2\left\langle z^2\middle|l\bullet s\middle|\overline{yz}\right\rangle\right]=\frac{1}{2\sqrt{2}}\left[2\left\langle z^2\middle|l_x\middle|yz\right\rangle\left\langle\alpha\middle|s_x\middle|\beta\right\rangle\right]=\frac{1}{\sqrt{2}}\left[\left(i\sqrt{3}\right)\left(\frac{1}{2}\right)\right]=i\sqrt{\frac{3}{8}}} \quad (41)$$

$$M_s=-1;\left[\overline{xy}\ \overline{xz}\ yz\ \overline{yz}\right] \quad (21)$$

gives 0 (42)

and:

$$M_s=1;\left[xy\ xz\ yz\ \overline{xz}\right] \quad (22)$$

gives

$$\frac{1}{2}\left[\left\langle\overline{xz}\middle|l\bullet s\middle|\overline{z}^2\right\rangle\right]=\frac{1}{2}\left[\left\langle xz\middle|l_y\middle|z^2\right\rangle\left\langle\beta\middle|s_y\middle|\beta\right\rangle\right]=0 \quad (43)$$

$$M_s=0;\frac{1}{\sqrt{2}}\left[\overline{xy}\ xz\ yz\ \overline{xz}+xy\ xz\ \overline{yz}\ \overline{xz}\right] \quad (23)$$

gives

$$\boxed{\frac{1}{2\sqrt{2}}\left[2\left\langle z^2\middle|l\bullet s\middle|\overline{xz}\right\rangle\right]=\frac{1}{2\sqrt{2}}\left[2\left\langle z^2\middle|l_y\middle|xz\right\rangle\left\langle\alpha\middle|s_y\middle|\beta\right\rangle\right]=\frac{1}{\sqrt{2}}\left[\left(-i\sqrt{3}\right)\left(\frac{-i}{2}\right)\right]=-\sqrt{\frac{3}{8}}} \quad (44)$$

$$M_s = -1;\left[\overline{xy}\ xz\ \overline{yz}\ \overline{xz}\right] \quad (24)$$

gives 0 (45)

For $M_s = 1$ of $^5B_1$ mixing with ^5E (only $l_x s_x$ and $l_y s_y$), we have:

$$M_s = 1;\frac{1}{2}\left[\overline{xy}\ xz\ yz\ z^2 + xy\ \overline{xz}\ yz\ z^2 + xy\ xz\ \overline{yz}\ z^2 + xy\ xz\ yz\ \overline{z}^2\right] \quad (10)$$

For ^5E:

$$M_s = 2;\left[xy\ xz\ x^2 - y^2\ z^2\right] \quad (25)$$

gives

$$\boxed{\frac{1}{2}\left[\left\langle \overline{yz}\middle| l \bullet s \middle| x^2 - y^2\right\rangle\right] = \frac{1}{2}\left[\left\langle yz\middle| l_x \middle| x^2 - y^2\right\rangle\left\langle \beta\middle| s_x \middle|\alpha\right\rangle\right] = \frac{1}{2}\left[(-i)\left(\frac{1}{2}\right)\right] = -\frac{i}{4}} \quad (46)$$

$$M_s = 1;\frac{1}{2}\left[\overline{xy}\ xz\ x^2 - y^2\ z^2 + xy\ \overline{xz}\ x^2 - y^2\ z^2 + xy\ xz\ \overline{x}^2 - \overline{y}^2\ z^2 + xy\ xz\ x^2 - y^2\ \overline{z}^2\right] \quad (26)$$

gives

$$\frac{1}{4}\left[3\left\langle x^2 - y^2\middle| l \bullet s\middle| yz\right\rangle + \left\langle \overline{x}^2 - \overline{y}^2\middle| l \bullet s\middle|\overline{yz}\right\rangle\right] = \left[3\left\langle x^2 - y^2\middle| l_x\middle| yz\right\rangle\left\langle\alpha\middle| s_x\middle|\alpha\right\rangle + \left\langle x^2 - y^2\middle| l_x\middle| yz\right\rangle\left\langle\beta\middle| s_x\middle|\beta\right\rangle\right] = 0 \quad (47)$$

$$M_s = 0;\frac{1}{\sqrt{6}}\left[\begin{array}{l}\overline{xy}\ \overline{xz}\ x^2 - y^2\ z^2 + \overline{xy}\ xz\ \overline{x}^2 - \overline{y}^2\ z^2 + \overline{xy}\ xz\ x^2 - y^2\ \overline{z}^2 \\ +xy\ \overline{xz}\ \overline{x}^2 - \overline{y}^2\ z^2 + xy\ \overline{xz}\ x^2 - y^2\ \overline{z}^2 + xy\ xz\ \overline{x}^2 - \overline{y}^2\ \overline{z}^2\end{array}\right] \quad (27)$$

gives

$$\boxed{\frac{1}{2\sqrt{6}}\left[3\left\langle yz\middle| l \bullet s\middle|\overline{x}^2 - \overline{y}^2\right\rangle\right] = \frac{1}{2\sqrt{6}}\left[3\left\langle yz\middle| l_x\middle| x^2 - y^2\right\rangle\left\langle\alpha\middle| s_x\middle|\beta\right\rangle\right] = \frac{1}{2\sqrt{6}}\left[3(-i)\left(\frac{1}{2}\right)\right] = -\frac{i}{2}\sqrt{\frac{3}{8}}} \quad (48)$$

$$M_s = -1;\frac{1}{2}\left[xy\ \overline{xz}\ \overline{x}^2 - \overline{y}^2\ \overline{z}^2 + \overline{xy}\ xz\ \overline{x}^2 - \overline{y}^2\ \overline{z}^2 + \overline{xy}\ \overline{xz}\ x^2 - y^2\ \overline{z}^2 + \overline{xy}\ \overline{xz}\ \overline{x}^2 - \overline{y}^2\ z^2\right] \quad (28)$$

gives 0 (49)

$$M_s = -2;\left[\overline{xy}\ \overline{xz}\ \overline{x}^2 - \overline{y}^2\ \overline{z}^2\right] \quad (29)$$

gives 0 (50)

and, $M_s = 1$ of $^5B_1$:

$$M_s = 1;\frac{1}{2}\left[\overline{xy}\ xz\ yz\ z^2 + xy\ \overline{xz}\ yz\ z^2 + xy\ xz\ \overline{yz}\ z^2 + xy\ xz\ yz\ \overline{z}^2\right] \quad (10)$$

with ^5E:

$$M_s = 2;\left[xy\ yz\ x^2 - y^2\ z^2\right] \quad (30)$$

gives

$$\boxed{\frac{1}{2}\left[\left\langle \overline{xz}\middle| l \bullet s\middle| x^2 - y^2\right\rangle\right] = \frac{1}{2}\left[\left\langle xz\middle| l_y\middle| x^2 - y^2\right\rangle\left\langle\beta\middle| s_y\middle|\alpha\right\rangle\right] = \frac{1}{2}\left[(-i)\left(\frac{i}{2}\right)\right] = \frac{1}{4}} \quad (51)$$

$$M_s = 1;\frac{1}{2}\left[\overline{xy}\ yz\ x^2 - y^2\ z^2 + xy\ \overline{yz}\ x^2 - y^2\ z^2 + xy\ yz\ \overline{x}^2 - \overline{y}^2\ z^2 + xy\ yz\ x^2 - y^2\ \overline{z}^2\right] \quad (31)$$

gives 0 (52)

$$M_s = 0;\frac{1}{\sqrt{6}}\left[\begin{array}{l}\overline{xy}\ \overline{yz}\ x^2 - y^2\ z^2 + \overline{xy}\ yz\ \overline{x}^2 - \overline{y}^2\ z^2 + \overline{xy}\ yz\ x^2 - y^2\ \overline{z}^2 \\ +xy\ \overline{yz}\ \overline{x}^2 - \overline{y}^2\ z^2 + xy\ \overline{yz}\ x^2 - y^2\ \overline{z}^2 + xy\ yz\ \overline{x}^2 - \overline{y}^2\ \overline{z}^2\end{array}\right] \quad (32)$$

gives $\boxed{\frac{1}{2\sqrt{6}}\left[3\left\langle xz|l\bullet s|\bar{x}^2-\bar{y}^2\right\rangle\right]=\frac{1}{2\sqrt{6}}\left[3\left\langle xz|l_y|x^2-y^2\right\rangle\left\langle\alpha|s_y|\beta\right\rangle\right]=\frac{1}{2\sqrt{6}}\left[3(-i)\left(-\frac{i}{2}\right)\right]=-\frac{1}{2}\sqrt{\frac{3}{8}}}$ (53)

$$M_s=-1;\frac{1}{2}\left[xy\ \bar{y}\bar{z}\ \bar{x}^2-\bar{y}^2\ \bar{z}^2+\bar{x}\bar{y}\ yz\ \bar{x}^2-\bar{y}^2\ \bar{z}^2+\bar{x}\bar{y}\ \bar{y}\bar{z}\ x^2-y^2\ \bar{z}^2+\bar{x}\bar{y}\ \bar{y}\bar{z}\ \bar{x}^2-\bar{y}^2\ z^2\right] \quad (33)$$

gives 0 (54)

$$M_s=-2;\left[\bar{x}\bar{y}\ \bar{y}\bar{z}\ \bar{x}^2-\bar{y}^2\ \bar{z}^2\right] \quad (34)$$

gives 0 (55)

The net energy lowering of M_s = 1 of $^5B_1$ (ΔE) is given by a second order correction. The numerator of the second-order correction is a summation of each matrix element computed above multiplied by its complex conjugate, and the denominator is the excited state energy. Thus, the energy lowering is:

$\Delta E(M_s = 1 \text{ of } {}^5B_1) =$

$$-\lambda^2\left[\frac{\left(i/2\right)\left(-i/2\right)}{E(^5B_2)-E(^5B_1)}+\left(\frac{\left(i\sqrt{\frac{3}{8}}\right)\left(-i\sqrt{\frac{3}{8}}\right)+\left(-\sqrt{\frac{3}{8}}\right)^2}{E(^3E)-E(^5B_1)}\right)+\left(\frac{\left(\frac{-i}{4}\right)\left(\frac{i}{4}\right)+\left(\frac{-i}{2}\sqrt{\frac{3}{8}}\right)\left(\frac{i}{2}\sqrt{\frac{3}{8}}\right)+\left(\frac{1}{4}\right)^2+\left(\frac{-1}{2}\sqrt{\frac{3}{8}}\right)^2}{E(^5E)-E(^5B_1)}\right)\right]$$

$$=-\lambda^2\left[\frac{1/4}{E(^5B_2)-E(^5B_1)}+\frac{6/8}{E(^3E)-E(^5B_1)}+\frac{5/16}{E(^5E)-E(^5B_1)}\right] \quad (56)$$

Now to calculate the corresponding terms for $M_s = 0$ of $^5B_1$:

$$M_s=0;\frac{1}{\sqrt{6}}\left[\bar{x}\bar{y}\ \bar{x}\bar{z}\ yz\ z^2+\bar{x}\bar{y}\ xz\ \bar{y}\bar{z}\ z^2+\bar{x}\bar{y}\ xz\ yz\ \bar{z}^2+xy\ \bar{x}\bar{z}\ \bar{y}\bar{z}\ z^2+xy\ \bar{x}\bar{z}\ yz\ \bar{z}^2+xy\ xz\ \bar{y}\bar{z}\ \bar{z}^2\right] \quad (11)$$

For $^5B_1$ mixing with $^5B_2$ (only $l_z s_z$),

$$M_s=2;\left[x^2-y^2\ xz\ yz\ z^2\right] \quad (14)$$

gives 0 (57)

$$M_s=1;\frac{1}{2}\left[\bar{x}^2-\bar{y}^2\ xz\ yz\ z^2+x^2-y^2\ \bar{x}\bar{z}\ yz\ z^2+x^2-y^2\ xz\ \bar{y}\bar{z}\ z^2+x^2-y^2\ xz\ yz\ \bar{z}^2\right] \quad (15)$$

gives $\frac{1}{2\sqrt{6}}\left[3\left\langle x^2-y^2|l\bullet s|\bar{x}\bar{y}\right\rangle\right]=\frac{1}{2\sqrt{6}}\left[3\left\langle x^2-y^2|l_z|xy\right\rangle\left\langle\alpha|s_z|\beta\right\rangle\right]=0$ (58)

$$M_s=0;\frac{1}{\sqrt{6}}\left[\begin{array}{l}\bar{x}^2-\bar{y}^2\ \bar{x}\bar{z}\ yz\ z^2+\bar{x}^2-\bar{y}^2\ xz\ \bar{y}\bar{z}\ z^2+\bar{x}^2-\bar{y}^2\ xz\ yz\ \bar{z}^2\\+x^2-y^2\ \bar{x}\bar{z}\ \bar{y}\bar{z}\ z^2+x^2-y^2\ \bar{x}\bar{z}\ yz\ \bar{z}^2+x^2-y^2\ xz\ \bar{y}\bar{z}\ \bar{z}^2\end{array}\right] \quad (16)$$

gives $\frac{1}{6}\left[3\left\langle\bar{x}^2-\bar{y}^2|l\bullet s|\bar{x}\bar{y}\right\rangle+2\left\langle x^2-y^2|l\bullet s|xy\right\rangle\right]=\frac{1}{6}\left[3\left\langle x^2-y^2|l_z|xy\right\rangle\left\langle\beta|s_z|\beta\right\rangle+3\left\langle x^2-y^2|l_z xy\right\rangle\left\langle\alpha|s_z|\alpha\right\rangle\right]$

$$=\frac{1}{6}\left[3(2i)\left(-\frac{1}{2}\right)+3(2i)\left(\frac{1}{2}\right)\right]=\frac{1}{6}\left[-3(i)+(3i)\right]=0 \quad (59)$$

$$M_s = -1; \frac{1}{2}\left[x^2-y^2\ \bar{x}\bar{z}\ \bar{y}\bar{z}\ \bar{z}^2 + \bar{x}^2-\bar{y}^2\ xz\ \bar{y}\bar{z}\ \bar{z}^2 + \bar{x}^2-\bar{y}^2\ \bar{x}\bar{z}\ yz\ \bar{z}^2 + \bar{x}^2-\bar{y}^2\ \bar{x}\bar{z}\ \bar{y}\bar{z}\ \Sigma z^2 \right] \quad (17)$$

gives $$\frac{1}{2\sqrt{6}}\left[3\langle \bar{x}^2-\bar{y}^2|l\bullet s|xy\rangle\right] = \frac{1}{2\sqrt{6}}\left[3\langle x^2-y^2|l_z|xy\rangle\langle\beta|s_z|\alpha\rangle\right] = 0 \quad (60)$$

$$M_s = -2; \left[\bar{x}^2-\bar{y}^2\ \bar{x}\bar{z}\ \bar{y}\bar{z}\ \bar{z}^2\right] \quad (18)$$

gives 0 (61)

For $M_s = 0$ of $^5B_1$ mixing with ^3E (only $l_x s_x$ and $l_y s_y$):

$$M_s = 0; \frac{1}{\sqrt{6}}\left[\overline{xy}\ \bar{x}\bar{z}\ yz\ z^2 + \overline{xy}\ xz\ \bar{y}\bar{z}\ z^2 + \overline{xy}\ xz\ yz\ \bar{z}^2 + xy\ \bar{x}\bar{z}\ \bar{y}\bar{z}\ z^2 + xy\ \bar{x}\bar{z}\ yz\ \bar{z}^2 + xy\ xz\ \bar{y}\bar{z}\ \bar{z}^2\right] \quad (11)$$

For ^3E:

$$M_s = 1; \left[xy\ xz\ yz\ \bar{y}\bar{z}\right] \quad (19)$$

gives $$\boxed{\frac{1}{\sqrt{6}}\left[\langle z^2|l\bullet s|\bar{y}\bar{z}\rangle\right] = \frac{1}{\sqrt{6}}\left[\langle z^2|l_x|yz\rangle\langle\alpha|s_x|\beta\rangle\right] = \frac{1}{\sqrt{6}}\left[\left(i\sqrt{3}\right)\left(\frac{1}{2}\right)\right] = i\sqrt{\frac{1}{8}}} \quad (62)$$

$$M_s = 0; \frac{1}{\sqrt{2}}\left[\overline{xy}\ xz\ yz\ \bar{y}\bar{z} + xy\ \bar{x}\bar{z}\ yz\ \bar{y}\bar{z}\right] \quad (20)$$

gives $$\frac{1}{\sqrt{12}}\left[2\langle \bar{y}\bar{z}|l\bullet s|\bar{z}^2\rangle\right] = \frac{1}{\sqrt{12}}\left[2\langle yz|l_x|z^2\rangle\langle\beta|s_x|\beta\rangle\right] = 0 \quad (63)$$

$$M_s = -1; \left[\overline{xy}\ \bar{x}\bar{z}\ yz\ \bar{y}\bar{z}\right] \quad (21)$$

gives $$\boxed{\frac{1}{\sqrt{6}}\left[\langle z^2|l\bullet s|\bar{y}\bar{z}\rangle\right] = \frac{1}{\sqrt{6}}\left[\langle z^2|l_x|yz\rangle\langle\alpha|s_x|\beta\rangle\right] = \frac{1}{\sqrt{6}}\left[\left(i\sqrt{3}\right)\left(\frac{1}{2}\right)\right] = i\sqrt{\frac{1}{8}}} \quad (64)$$

and:

$$M_s = 1; \left[xy\ xz\ yz\ \bar{x}\bar{z}\right] \quad (22)$$

gives $$\boxed{\frac{1}{\sqrt{6}}\left[\langle \bar{z}^2|l\bullet s|xz\rangle\right] = \frac{1}{\sqrt{6}}\left[\langle z^2|l_x|xz\rangle\langle\beta|s_x|\alpha\rangle\right] = \frac{1}{\sqrt{6}}\left[\left(-i\sqrt{3}\right)\left(\frac{1}{2}\right)\right] = -i\sqrt{\frac{1}{8}}} \quad (65)$$

$$M_s = 0; \frac{1}{\sqrt{2}}\left[\overline{xy}\ xz\ yz\ \bar{x}\bar{z} + xy\ xz\ \bar{y}\bar{z}\ \bar{x}\bar{z}\right] \quad (23)$$

gives $$\frac{1}{\sqrt{12}}\left[2\langle xz|l\bullet s|z^2\rangle\right] = \frac{1}{2\sqrt{2}}\left[2\langle xz|l_y|z^2\rangle\langle\alpha|s_y|\alpha\rangle\right] = 0 \quad (66)$$

$$M_s = -1; \left[\overline{xy}\ xz\ \bar{y}\bar{z}\ \bar{x}\bar{z}\right] \quad (24)$$

gives $$\boxed{\frac{1}{\sqrt{6}}\left[\langle z^2|l\bullet s|\bar{x}\bar{z}\rangle\right] = \frac{1}{\sqrt{6}}\left[\langle z^2|l_y|xz\rangle\langle\beta|s_y|\alpha\rangle\right] = \frac{1}{\sqrt{6}}\left[\left(-i\sqrt{3}\right)\left(\frac{i}{2}\right)\right] = \sqrt{\frac{1}{8}}} \quad (67)$$

For $M_s = 0$ of $^5B_1$ mixing with ^5E (only $l_x s_x$ and $l_y s_y$):

$$M_s = 0; \frac{1}{\sqrt{6}}\left[\overline{xy}\ \bar{x}\bar{z}\ yz\ z^2 + \overline{xy}\ xz\ \bar{y}\bar{z}\ z^2 + \overline{xy}\ xz\ yz\ \bar{z}^2 + xy\ \bar{x}\bar{z}\ \bar{y}\bar{z}\ z^2 + xy\ \bar{x}\bar{z}\ yz\ \bar{z}^2 + xy\ xz\ \bar{y}\bar{z}\ \bar{z}^2\right] \quad (11)$$

For ^5E:

$$M_s = 2;\left[xy\ xz\ x^2-y^2\ z^2\right] \tag{25}$$

gives 0 (68)

$$M_s = 1;\frac{1}{2}\left[\overline{xy}\ xz\ x^2-y^2\ z^2 + xy\ \overline{xz}\ x^2-y^2\ z^2 + xy\ xz\ \overline{x}^2-\overline{y}^2\ z^2 + xy\ xz\ x^2-y^2\ \overline{z}^2\right] \tag{26}$$

gives $\boxed{\frac{1}{2\sqrt{6}}\left[3\langle \overline{yz}|l\bullet s|x^2-y^2\rangle\right] = \frac{1}{2\sqrt{6}}\left[3\langle yz|l_x|x^2-y^2\rangle\langle\beta|s_x|\alpha\rangle\right] = \frac{1}{2\sqrt{6}}\left[3(-i)\left(\frac{1}{2}\right)\right] = \frac{-i}{2}\sqrt{\frac{3}{8}}}$ (69)

$$M_s = 0;\frac{1}{\sqrt{6}}\begin{bmatrix}\overline{xy}\ \overline{xz}\ x^2-y^2\ z^2 + \overline{xy}\ xz\ \overline{x}^2-\overline{y}^2\ z^2 + \overline{xy}\ xz\ x^2-y^2\ \overline{z}^2 \\ +xy\ \overline{xz}\ \overline{x}^2-\overline{y}^2\ z^2 + xy\ \overline{xz}\ x^2-y^2\ \overline{z}^2 + xy\ xz\ \overline{x}^2-\overline{y}^2\ \overline{z}^2\end{bmatrix} \tag{27}$$

gives $\frac{1}{6}\left[3\langle x^2-y^2|l\bullet s|yz\rangle + 3\langle \overline{x}^2-\overline{y}^2|l\bullet s|\overline{yz}\rangle\right]$

$$= \frac{1}{6}\left[3\langle x^2-y^2|l_x|yz\rangle\langle\alpha|s_x|\alpha\rangle + 3\langle x^2-y^2|l_x|yz\rangle\langle\beta|s_x|\beta\rangle\right] = 0 \tag{70}$$

$$M_s = -1;\frac{1}{2}\left[xy\ \overline{xz}\ \overline{x}^2-\overline{y}^2\ \overline{z}^2 + \overline{xy}\ xz\ \overline{x}^2-\overline{y}^2\ \overline{z}^2 + \overline{xy}\ \overline{xz}\ x^2-y^2\ \overline{z}^2 + \overline{xy}\ \overline{xz}\ \overline{x}^2-\overline{y}^2\ z^2\right] \tag{28}$$

gives $\boxed{\frac{1}{2\sqrt{6}}\left[3\langle yz|l\bullet s|\overline{x}^2-\overline{y}^2\rangle\right] = \frac{1}{2\sqrt{6}}\left[3\langle yz|l_x|x^2-y^2\rangle\langle\alpha|s_x|\beta\rangle\right] = \frac{1}{2\sqrt{6}}\left[3(-i)\left(\frac{1}{2}\right)\right] = \frac{-i}{2}\sqrt{\frac{3}{8}}}$ (71)

$$M_s = -2;\left[\overline{xy}\ \overline{xz}\ \overline{x}^2-\overline{y}^2\ \overline{z}^2\right] \tag{29}$$

gives 0 (72)

and, $M_s = 0$ of $^5B_1$:

$$M_s = 0;\frac{1}{\sqrt{6}}\left[\overline{xy}\ \overline{xz}\ yz\ z^2 + \overline{xy}\ xz\ \overline{yz}\ z^2 + \overline{xy}\ xz\ yz\ \overline{z}^2 + xy\ \overline{xz}\ \overline{yz}\ z^2 + xy\ \overline{xz}\ yz\ \overline{z}^2 + xy\ xz\ \overline{yz}\ \overline{z}^2\right] \tag{11}$$

with ^5E:

$$M_s = 2;\left[xy\ yz\ x^2-y^2\ z^2\right] \tag{30}$$

gives 0 (73)

$$M_s = 1;\frac{1}{2}\left[\overline{xy}\ yz\ x^2-y^2\ z^2 + xy\ \overline{yz}\ x^2-y^2\ z^2 + xy\ yz\ \overline{x}^2-\overline{y}^2\ z^2 + xy\ yz\ x^2-y^2\ \overline{z}^2\right] \tag{31}$$

gives $\boxed{\frac{1}{2\sqrt{6}}\left[3\langle \overline{xz}|l\bullet s|x^2-y^2\rangle\right] = \frac{1}{2\sqrt{6}}\left[3\langle xz|l_y|x^2-y^2\rangle\langle\beta|s_y|\alpha\rangle\right] = \frac{1}{2\sqrt{6}}\left[3(-i)\left(\frac{i}{2}\right)\right] = \frac{1}{2}\sqrt{\frac{3}{8}}}$ (74)

$$M_s = 0;\frac{1}{\sqrt{6}}\begin{bmatrix}\overline{xy}\ \overline{yz}\ x^2-y^2\ z^2 + \overline{xy}\ yz\ \overline{x}^2-\overline{y}^2\ z^2 + \overline{xy}\ yz\ x^2-y^2\ \overline{z}^2 \\ +xy\ \overline{yz}\ \overline{x}^2-\overline{y}^2\ z^2 + xy\ \overline{yz}\ x^2-y^2\ \overline{z}^2 + xy\ yz\ \overline{x}^2-\overline{y}^2\ \overline{z}^2\end{bmatrix} \tag{32}$$

gives 0 (75)

$$M_s = -1;\frac{1}{2}\left[xy\ \overline{yz}\ \overline{x}^2-\overline{y}^2\ \overline{z}^2 + \overline{xy}\ yz\ \overline{x}^2-\overline{y}^2\ \overline{z}^2 + \overline{xy}\ \overline{yz}\ x^2-y^2\ \overline{z}^2 + \overline{xy}\ \overline{yz}\ \overline{x}^2-\overline{y}^2\ z^2\right] \tag{33}$$

gives $\boxed{\frac{1}{2\sqrt{6}}\left[3\langle xz|l\bullet s|\overline{x}^2-\overline{y}^2\rangle\right] = \frac{1}{2\sqrt{6}}\left[3\langle xz|l_y|x^2-y^2\rangle\langle\alpha|s_y|\beta\rangle\right] = \frac{1}{2\sqrt{6}}\left[3(-i)\left(\frac{-i}{2}\right)\right] = -\frac{1}{2}\sqrt{\frac{3}{8}}}$ (76)

$$M_s = -2;\left[\overline{xy}\ \overline{y}\overline{z}\ \overline{x}^2 - \overline{y}^2\ \overline{z}^2\right] \tag{34}$$

gives 0 (77)

The net energy change of $M_s = 0$ of $^5B_1$ is:

$$\Delta E(M_s = 0 \text{ of } ^5B_1) = -\lambda^2 \frac{(0)^2}{E(^5B_2) - E(^5B_1)} - \lambda^2 \left(\frac{2\left(i\sqrt{\frac{1}{8}}\right)\left(-i\sqrt{\frac{1}{8}}\right) + \left(-\sqrt{\frac{1}{8}}\right)^2 + \left(\sqrt{\frac{1}{8}}\right)^2}{E(^3E) - E(^5B_1)} \right)$$

$$-\lambda^2 \left(\frac{2\left(\frac{-i}{2}\sqrt{\frac{3}{8}}\right)\left(\frac{i}{2}\sqrt{\frac{3}{8}}\right) + \left(\frac{1}{2}\sqrt{\frac{3}{8}}\right)^2 + \left(-\frac{1}{2}\sqrt{\frac{3}{8}}\right)^2}{E(^3E) - E(^5B_1)} \right)$$

$$= -\lambda^2 \left[\frac{0}{E(^5B_2) - E(^5B_1)} + \frac{1/2}{E(^3E) - E(^5B_1)} + \frac{3/8}{E(^3E) - E(^5B_1)} \right] \tag{78}$$

The energy difference between the of $M_s = 0$ of $^5B_1$ and $M_s = 1$ of $^5B_1$ is *D*:

$\Delta E(M_s = 1 \text{ of } ^5B_1)$ - $\Delta E(M_s = 0 \text{ of } ^5B_1)$=

$$D = -\lambda^2 \left[\frac{1/4}{E(^5B_2) - E(^5B_1)} + \frac{6/8}{E(^3E) - E(^5B_1)} + \frac{5/16}{E(^5E) - E(^5B_1)} \right]$$

$$-\lambda^2 \left[-\frac{0}{E(^5B_2) - E(^5B_1)} - \frac{1/2}{E(^3E) - E(^5B_1)} - \frac{3/8}{E(^3E) - E(^5B_1)} \right]$$

$$= \lambda^2 \left[\frac{-1/4 + 0}{E(^5B_2) - E(^5B_1)} + \frac{-6/8 + 1/2}{E(^3E) - E(^5B_1)} + \frac{-5/16 + 3/8}{E(^3E) - E(^5B_1)} \right] = \lambda^2 \left[\frac{-1/4}{E(^5B_2) - E(^5B_1)} + \frac{-1/4}{E(^3E) - E(^5B_1)} + \frac{+1/16}{E(^3E) - E(^5B_1)} \right]$$

$$= \lambda^2 \left[-\frac{4}{E(^5B_2) - E(^5B_1)} - \frac{4}{E(^3E) - E(^5B_1)} + \frac{1}{E(^3E) - E(^5B_1)} \right] \tag{79}$$

Using the notation from the figure on page 1, we get,

$$D = \lambda^2 \left[-\frac{4}{\Delta} - \frac{4}{\partial_3} + \frac{1}{\Delta - \partial_1} \right] \tag{80}$$

which is identical to equation 1.

Indeed, this is a cumbersome calculation, but it shows the paramount importance of the ligand field contribution in second order to zfs. Moreover, when there are paramagnetic ligands, there are other important terms to consider: contributions due to charge transfer and excited state exchange. For obvious reasons, the latter term is called the exchange contribution, $\boldsymbol{D}^{ex}$, which results in a third-order correction that contributes to the zfs,

$$D^{ex} = J(e_M g_{PL})\lambda_M^2 \sum \frac{\langle g_M | l \bullet s | e_M \rangle^2}{E_M^2} + J(e_{PL} g_M)\lambda_{RL}^2 \sum \frac{\langle g_{RL} | l \bullet s | e_{RL} \rangle^2}{E_{PL}^2} \tag{81}$$

where $\boldsymbol{J}(e_M g_{PL})$ is the exchange term of the metal excited state(s) with the ground state of the paramagnetic ligand, and $\boldsymbol{J}(e_{PL} g_M)$ is the exchange term of the metal ground state with the excited state(s) of the paramagnetic ligand. As can be seen, this term is directly proportional to the excited state exchange parameter, $\boldsymbol{J}^{ex}$. In addition, unless the paramagnetic ligand has heavy atoms, the second term in (81) can be ignored. As such, the $\boldsymbol{D}^{ex}$ contribution is proportional to the single-ion contribution (given by eqn. 80) times $\boldsymbol{J}(e_M g_{PL})/E_M$.

References

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