THE ESRg MATRIX FOR STRONG FIELD d^5 SYSTEMS

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This review has tried to collect and correlate all the various equations for the g matrix of strong field d^5 systems obtained from different basis sets using full electron and hole formalism calculations. It has corrected mistakes found in the literature and shown how the failure to properly take in symmetry boundary conditions has produced a variety of apparently inconsistent equations in the literature. The review has reexamined the problem of spin-orbit interaction with excited t^4e states and finds that the earlier reports that it is zero in octahedral symmetry is not correct. It has shown how redefining what x, y, and z are in the principal coordinate system simplifies, compared to previous methods, the analysis of experimental g values with the equations.

Keywords: ESR; g matrix; strong field d^5.

INTRODUCTION

This review of the theory of the g matrix for strong field d^5 systems was undertaken after an extended stay at the Instituto de Química de São Carlos, Universidade de São Paulo where extensive studies on Ru(III) and Os(III) complexes were being done. On reviewing the literature, I found that although it was done correctly in the beginning by Bleaney and O'Brien[1] many confusing and not always correct versions have been employed since. This review is undertaken to correlate the various approaches and to correct some errors and mistaken concepts that have appeared in the past forty years.

Most treatments have been for a tetragonal distortion from octahedral symmetry[1-15,18,19], which is most appropriate for monodentate ligands, but some treatments for trigonal a distortion, appropriate for tris bidentate complexes, have appeared[1,16,17]. Bleaney and O'Brien[1] showed that the equations for a trigonal distortion are formally identical to those for the tetragonal distortion, but some of the parameters have a somewhat different meaning. For this reason, several treatments of trigonal complexes have been treated with the tetragonal equations. It will be shown here that this formal similarity is true only for systems close to true octahedral symmetry, which is often not the case with the tris bidentate complexes.

For a tetragonal distortion, two different basis sets have been used in the literature leading to different appearing equations. The most common basis set is the use of $d_{\pm1}$ and d_{xy} for the t_2 orbitals[1-9,12-15] but some authors have used d_{xz}, d_{yz}, and d_{xy} as the basis set[11,12,18,19]. Some interesting variations of these two sets have been used to obtain real instead of complex matrices.

Many of the derivations[1-4,6,8-14,16,19] have used the hole formalism for d^5 where the single electron problem is solved with a change in sign for the ligand field and spin-orbit parameters. Others have, for a variety of reasons, used the d^5 equations themselves[5,7,15,17,18]. It will be shown here that unless care is exercised, the hole formalism often leads to equations that appear different from those obtained by the full electron approach. If done properly, they are not wrong but some of the parameters will have opposite signs.

Finally, most treatments have ignored spin-orbit interaction with the excited states. Hill[5], Griffiths[4], and Thornley[2] have examined the effect of both this spin-orbit interaction and configuration interaction. Their conclusion was that configuration interaction was significant but spin-orbit interaction was not. Hill[5] states that configuration interaction does not change the basic nature of the equations but produces small changes in the mixing parameters and the orbital momentum reduction parameter k. These calculations assumed near octahedral symmetry and may not apply to large distortions in the ligand fields. The spin-orbit interaction with excited states has been required to explain why $g_{\parallel}$ is less than 2 in magnitude and $g_{\perp}$ is greater than 2 in the d^5 $[M(CN)_5NO]^{n+}$ complexes[20-22]. It would appear that one should reexamine this question of the spin-orbit interaction with the t_2^4e states, particularly as it applies to those metal ions of the second and third transition series, which have very large spin-orbit parameters (>1000 cm^{-1}).

APPLICATION OF THE HOLE FORMALISM

We will treat this for each situation, but a general discussion of the treatment will be useful at the beginning. As an illustration, consider the case of the d^9 configuration. A general treatment would use the ten Slater functions $|m_l, m_s\rangle$ where

$$\left|+2,+\frac{1}{2}\right\rangle = d_2^+ d_1^+ d_1^- d_0^+ d_0^- d_{-1}^+ d_{-1}^- d_{-2}^+ d_{-2}^- \qquad (1)$$

It is generally assumed in the hole formalism, that the appropriate matrix elements of these functions can be represented by the matrix elements of the ten single electron functions $d_m^{\pm}$ as long as you change the sign of all crystal field interactions and the spin-orbit interaction parameter ξ. This is not completely correct unless care is exercised in the choice of what $d_m^{\pm}$ represents. Let us examine the relevant matrix elements for both sets of functions. In Table 1 are listed non-zero matrix elements for the spin, orbital momentum, and spin-orbit operators assuming $|m,\pm1/2\rangle$ and $d_m^{\pm}$ are equivalent. We note that an exact correspondence can be achieved only when is designated as the replacement for $|m,\pm1/2\rangle$. The correspondence is complete only when we use $(-1)^m d_{-m}^+$ as the replacement. We now have a hole function that reproduces all matrix element of d^9 if we use - ξ for ξ and change the sign for all crystal field parameters.

The failure of many authors, including this author, to not carefully note the proper relation between the hole functions and the full electron functions they represent produces spin-orbit interaction matrices in which the off diagonal terms are of opposite sign from those obtained using the full electron wave functions. This does not produce invalid equations for the g values since the

Table 1. Comparison of matrix elements[a] for d^9 and d^1.

Matrix Element	d^9	d^1
$\left\langle m,\pm\frac{1}{2}\middle\vert S_z\middle\vert m,\pm\frac{1}{2}\right\rangle$	$\pm\frac{1}{2}$	$\pm\frac{1}{2}$
$\left\langle m,\pm\frac{1}{2}\middle\vert S_x\middle\vert m,\mp\frac{1}{2}\right\rangle$	$\frac{1}{2}$	$\frac{1}{2}$
$\left\langle m,\pm\frac{1}{2}\middle\vert S_y\middle\vert m,\mp\frac{1}{2}\right\rangle$	$\mp\frac{i}{2}$	$\mp\frac{i}{2}$
$\left\langle m,\pm\frac{1}{2}\middle\vert L_z\middle\vert m,\pm\frac{1}{2}\right\rangle$	$-m$	m
$\left\langle m+1,\pm\frac{1}{2}\middle\vert L_x\middle\vert m,\pm\frac{1}{2}\right\rangle$	$-\frac{1}{2}\sqrt{6-m(m+1)}$	$\frac{1}{2}\sqrt{6-m(m+1)}$
$\left\langle m+1,\pm\frac{1}{2}\middle\vert L_y\middle\vert m,\pm\frac{1}{2}\right\rangle$	$-i\frac{1}{2}\sqrt{6-m(m+1)}$	$-i\frac{1}{2}\sqrt{6-m(m+1)}$
$\left\langle m,\pm\frac{1}{2}\middle\vert \Sigma\,\xi\ell_z s_z\middle\vert m,\pm\frac{1}{2}\right\rangle$	$\pm\frac{1}{2}m\xi$	$\pm\frac{1}{2}m\xi$
$\left\langle m+1,-\frac{1}{2}\middle\vert \Sigma\frac{1}{2}\xi(\ell_+ s_- + \ell_- s_+)\middle\vert m,+\frac{1}{2}\right\rangle$	0	$\frac{1}{2}\sqrt{6-m(m+1)}\xi$
$\left\langle m+1,-\frac{1}{2}\middle\vert \Sigma\frac{1}{2}\xi(\ell_+ s_- + \ell_- s_+)\middle\vert m,-\frac{1}{2}\right\rangle$	$\frac{1}{2}\sqrt{6-m(m+1)}\xi$	0

[a]See text for definition of symbols.

change in sign of the off diagonal orbital momentum matrix elements cancels out the change in sign of the spin-orbit elements, but it can produce g matrix equations which appear different from those obtained from the complete functions, particularly in the sign of the mixing coefficients in the Kramer's doublets. It was essential in this review to examine the relation of the hole function to the complete function when comparing different treatments of the same problem.

TETRAGONAL DISTORTION IN d^5

Full Electron Treatment using $d_{\pm1}$ and d_{xy} Basis Functions for t_2.

Most of the treatments have followed Hill[5] using basis functions $|\ell,s\rangle$

$$\left|-1,\pm\frac{1}{2}\right\rangle = d_1^+ d_1^- d_{xy}^+ d_{xy}^- d_{-1}^{\pm} \tag{2}$$

$$\left|+1,\pm\frac{1}{2}\right\rangle = d_{-1}^+ d_{-1}^- d_{xy}^+ d_{xy}^- d_1^{\pm} \tag{3}$$

$$\left|0,\pm\frac{1}{2}\right\rangle = \pm i d_1^+ d_1^- d_{-1}^+ d_{-1}^- d_{xy}^{\pm} \tag{4}$$

in which the sign convention plus use of the imaginary number *i* in eq. 4 were chosen to give two identical and real 3x3 spin-orbit matrices. If H_C is the crystal or ligand field operator, Hill defined the Δ and V parameters in terms of the one electron matrix elements

$$\langle d_{xy}|H_c|d_{xy}\rangle = \Delta \tag{5}$$

$$\langle d_{xz}|H_c|d_{xz}\rangle = \frac{V}{2} = -\langle d_{yz}|H_c|d_{yz}\rangle \tag{6}$$

Eq. 6 is opposite in sign to what Hill[5] and many others since have used. This change in definition was necessary because rather late in the preparation of this manuscript, I discovered that his definition gave a negative sign to the off diagonal matrix elements involving V in eq. 8 below, not the plus sign that appears in his and many others papers. It was then decided to use the definition above to keep the resulting equations as close as possible to those appearing in the literature. Using these definitions, and the spin-orbit interaction operator H_{LS}

$$H_{LS} = \sum_i \xi(\ell_i . s_i) \tag{7}$$

we obtain the determinant

$$\begin{array}{ccc} \left|-1,\frac{1}{2}\right\rangle & \left|0,-\frac{1}{2}\right\rangle & \left|+1,\frac{1}{2}\right\rangle \\ \left|+1,-\frac{1}{2}\right\rangle & \left|0,\frac{1}{2}\right\rangle & \left|-1,-\frac{1}{2}\right\rangle \end{array}$$

$$\begin{vmatrix} \left(2\Delta-\frac{1}{2}\xi-E\right) & -\frac{\xi}{\sqrt{2}} & \frac{V}{2} \\ -\frac{\xi}{\sqrt{2}} & (\Delta-E) & 0 \\ \frac{V}{2} & 0 & \left(2\Delta+\frac{1}{2}\xi-E\right) \end{vmatrix} = 0 \tag{8}$$

The wave-functions for the ground state are chosen to be

$$\psi_+ = a\left|+1,-\frac{1}{2}\right\rangle + b\left|0,\frac{1}{2}\right\rangle + c\left|-1,-\frac{1}{2}\right\rangle$$
$$\psi_- = a\left|-1,\frac{1}{2}\right\rangle + b\left|0,-\frac{1}{2}\right\rangle + c\left|+1,\frac{1}{2}\right\rangle \tag{9}$$

Neglecting spin orbit admixtures with the excited states ($t_2^4 e$ etc.), the principal g-values can be calculated from the Zeeman interaction, $H_z = \beta \mathbf{B}.(k\mathbf{L}+2\mathbf{S})$, where k is the orbital reduction factor and the wave functions are given by eq. 9.

The method used to calculate the g values must be explained in detail, because failure to understand the process has led to considerable confusion in the literature with a plethora of apparently inconsistent equations and a variety of signs for the g values. The process is to match up equivalent elements in the 2x2 matrix of the Zeeman operator H_z of eq. 9 with those in a spin only Hamiltonian. This results in the following equations:

$$g_z = 2\langle \psi_+ | kL_z + 2S_z | \psi_+ \rangle$$
$$g_x = 2\langle \psi_+ | kL_x + 2S_x | \psi_- \rangle$$
$$g_y = 2i\langle \psi_+ | kL_y + 2S_y | \psi_- \rangle \tag{10}$$

where $\psi\pm$ are the two Kramer's functions, eq. 9. Unfortunately the choice of which function we label as plus and minus, is arbitrary. Also, the magnitudes of the coefficients a, b, and c in ψ_+ and ψ_- must be the same but the signs can be the same or opposite. We thus end up with four possible sets of solutions, which are set out in Table 2. In the table Case 1a is for the plus and minus labels to be assigned as shown in eqs. 9 and for the two sets of mixing coefficients a, b, c having the same sign. Case 2a is the solution for interchanging the plus and minus labels but having both sets of coefficients with the same sign. Cases 1b and 2b are for the solutions in which the signs of the two set of coefficients are opposite. When there is more than one solution to a mathematical problem, it is customary to use boundary conditions to select the more physically reasonable solution. In this case we use symmetry. For axial symmetry (V = 0), the coefficient c = 0 and we expect $g_x = g_y$. This rules out Cases 2a and 2b because they give $g_x = -g_y$. In octahedral symmetry, where $a = \sqrt{2/3}; b = 1/\sqrt{3}$ one would expect all three g values to be identical and this can only happen for Case 1a. In this case, all three g values are -2. Experiments[23] have shown in a few instances, that the g is indeed negative for octahedral strong field d^5 systems. Equations for Case 1a in Table 2 are not original, several authors[1,6,13,15] have used the same set of equations, but many authors[3-5,9] have chosen to use Case 2a, probably to get a positive g_z and ended up with g_x and g_y of opposite sign. In two cases[5,7] x and y were interchanged somehow.

Hole Treatment using $d_{\pm 1}$ and d_{xy} Basis Functions for t_2.

The hole formalism will give the determinants of eq. 8, if we represent the $|\ell, s\rangle$ functions by the one electron functions

$$\left|+1,\pm\frac{1}{2}\right\rangle = d_1^{\pm}; \quad \left|-1,\pm\frac{1}{2}\right\rangle = d_{-1}^{\pm}; \quad \left|0,\pm\frac{1}{2}\right\rangle = \pm i d_{xy}^{\pm} \tag{11}$$

and replace ξ, Δ, and V by their negative values. It is also necessary to change the zero of energy to ε = E - 2Δ to accommodate going from five electrons to one electron. Using these basis functions will give the equations in Table 2 for the g values.

Full Electron Treatment using d_{xz}, d_{yz}, and d_{xy} Basis Functions for t_2.

I have found one full electron treatment[18] for the basis set of d_{xz}, d_{yz}, and d_{xy} but they chose to rotate the coordinate system 45° so that the set became $d_{x^2-y^2}$, d_{yz}, d_{xy}. There are two hole treatments[11,12] using d_{xz}, d_{yz}, d_{xy} and one[19] using $d_{x^2-y^2}$, d_{yz}, d_{xy}. I will present the full treatment using d_{xz}, d_{yz}, d_{xy} here. The five electron functions will be defined as

$$\left|xy,\pm\frac{1}{2}\right\rangle = d_{xz}^{+} d_{xz}^{-} d_{yz}^{+} d_{yz}^{-} d_{xy}^{\pm} \tag{12}$$

$$\left|xz,\pm\frac{1}{2}\right\rangle = i d_{yz}^{+} d_{yz}^{-} d_{xy}^{+} d_{xy}^{-} d_{xz}^{\pm} \tag{13}$$

$$\left|yz,\pm\frac{1}{2}\right\rangle = d_{xz}^{+} d_{xz}^{-} d_{xy}^{+} d_{xy}^{-} d_{yz}^{\pm} \tag{14}$$

where the i in $|xy,1/2\rangle$ is put in to give real determinants for the spin-orbit interaction. For consistency and ease of comparison, we will use the same crystal field parameters of eq. 5, 6.

$$\begin{array}{ccc} \left|xy,\frac{1}{2}\right\rangle & \left|yz,-\frac{1}{2}\right\rangle & \left|xz,-\frac{1}{2}\right\rangle \\ \left|xy,-\frac{1}{2}\right\rangle & \left|yz,\frac{1}{2}\right\rangle & \left|xz,\frac{1}{2}\right\rangle \end{array}$$

$$\begin{vmatrix} (\Delta-E) & \mp\frac{\xi}{2} & -\frac{\xi}{2} \\ \mp\frac{\xi}{2} & \left(2\Delta+\frac{1}{2}V-E\right) & \mp\frac{\xi}{2} \\ -\frac{\xi}{2} & \mp\frac{\xi}{2} & \left(2\Delta-\frac{1}{2}V-E\right) \end{vmatrix} = 0 \tag{15}$$

The wave-functions for the ground state are chosen to be

Table 2. Equations for the g matrix for the four possible cases using the $d_{\pm1}$ and d_{xy} basis functions for t_2.

Case[1]	g_x	g_y	g_z
1a	$-2\left[-2ac+b^2+k\sqrt{2}b(a-c)\right]$	$-2\left[2ac+b^2+k\sqrt{2}b(a+c)\right]$	$-2\left[a^2-b^2+c^2+k(a^2-c^2)\right]$
2a	$-2\left[-2ac+b^2+k\sqrt{2}b(a-c)\right]$	$2\left[2ac+b^2+k\sqrt{2}b(a+c)\right]$	$2\left[a^2-b^2+c^2+k(a^2-c^2)\right]$
1b	$2\left[-2ac+b^2+k\sqrt{2}b(a-c)\right]$	$2\left[2ac+b^2+k\sqrt{2}b(a+c)\right]$	$-2\left[a^2-b^2+c^2+k(a^2-c^2)\right]$
2b	$2\left[-2ac+b^2+k\sqrt{2}b(a-c)\right]$	$-2\left[2ac+b^2+k\sqrt{2}b(a+c)\right]$	$2\left[a^2-b^2+c^2+k(a^2-c^2)\right]$

[1]Defined in main text of article.

$$\psi_+ = A_+\left|xy,\frac{1}{2}\right\rangle + B_+\left|yz,-\frac{1}{2}\right\rangle + C_+\left|xz,-\frac{1}{2}\right\rangle$$
$$\psi_- = A_-\left|xy,-\frac{1}{2}\right\rangle + B_-\left|yz,\frac{1}{2}\right\rangle + C_-\left|xz,\frac{1}{2}\right\rangle \qquad (16)$$

Using eqs. 10 we find that the only consistent solution is for A+ = -A- = A, $B_+ = B_- = B$. and $C_+ = -C_- = C$, which gives the following equations for the g values.

$$g_x = 2\left[B^2 - A^2 - C^2 - 2kAC\right]$$
$$g_y = 2\left[C^2 - B^2 - A^2 - 2kAB\right] \qquad (17)$$
$$g_z = 2\left[A^2 - C^2 - B^2 - 2kBC\right]$$

In octahedral symmetry $A = B = C = 1/\sqrt{3}$ and the above equations give - 2 for all three g values. These equations have a nice cyclic symmetry that is not present in other treatments[11,12,18,19] due to their inversion of the choice for ψ_+ and ψ_-.

The conversion that converts the equations in Table 2 to eqs. 17 is:

$$A = b; \quad B = \frac{(a+c)}{\sqrt{2}}; \quad B = \frac{(a-c)}{\sqrt{2}}$$

which allows us to relate the two sets of coefficients in the two approaches.

Hole Treatment using d_{xz}, d_{yz}, and d_{xy} Basis Functions for t_2.

The hole formalism will give the determinants of eq. 15, if we represent the functions by the one electron functions

$$\left|xy,\pm\frac{1}{2}\right\rangle = d^{\pm}_{xy}; \quad \left|xz;\pm\frac{1}{2}\right\rangle = id^{\pm}_{xz}; \quad \left|yz,\pm\frac{1}{2}\right\rangle = d^{\pm}_{xz} \qquad (18)$$

and replace ξ, Δ, and V by their negative. It is also necessary to change the zero of energy to ε = E - 2Δ to accommodate going from five electrons to one electron. Using these basis functions gives eqs. 17 for the g values.

TRIGONAL DISTORTION IN d^5

This occurs, primarily, in the tris-bidentate metal complexes which have C_3 or D_{3d} symmetry in which the distortion is along the three-fold rotation axis of the octahedron. Symmetry arguments tell us that the t_2 orbitals split into an A and E irreducible representation in which the orbitals can be written as:

$$t_2(0) = d_0$$
$$t_2(\pm) = \pm\alpha d_{\pm 2} - \beta d_{\mp 1} \qquad (19)$$

where in octahedral symmetry $\alpha = \sqrt{2/3}$; $\beta = 1/\sqrt{3}$. Most treatments in the literature[1,16,17] have used the octahedral values but this may be unwise for bidentate ligands with bite angles considerably different than 90°. Please note that the d_m orbitsls in eq. 19 are quantized along the C_3 axis and are not the same as those used in the tetragonal distortion problem. For the full electron treatment we will define the following basis set.

$$\left|+,\pm\frac{1}{2}\right\rangle = t_2^{\pm}(+)t_2^{+}(-)t_2^{-}(-)t_2^{+}(0)t_2^{-}(0)$$
$$\left|-,\pm\frac{1}{2}\right\rangle = t_2^{+}(+)t_2^{-}(+)t_2^{\pm}(-)t_2^{+}(0)t_2^{-}(0) \qquad (20)$$
$$\left|0,\pm\frac{1}{2}\right\rangle = t_2^{+}(+)t_2^{-}(+)t_2^{+}(-)t_2^{-}(-)t_2^{\pm}(0)$$

If we define $\Delta = \langle t_2(0)|H_c|t_2(0)\rangle$ for the one electron energy, the spin-orbit interaction plus the crystal field yield the following determinants

$$\begin{array}{ccc} \left|+,-\frac{1}{2}\right\rangle & \left|0,\frac{1}{2}\right\rangle & \left|-,-\frac{1}{2}\right\rangle \\ \left|-,+\frac{1}{2}\right\rangle & \left|0,-\frac{1}{2}\right\rangle & \left|+,\frac{1}{2}\right\rangle \end{array}$$

$$\begin{vmatrix} \left(2\Delta-\frac{1}{2}\left(2\alpha^2-\beta^2\right)\xi-E\right) & -\frac{\sqrt{6}}{2}\beta\xi & 0 \\ \frac{\sqrt{6}}{2}\beta\xi & (\Delta-E) & 0 \\ 0 & 0 & \left(2\Delta+\frac{1}{2}\left(2\alpha^2-\beta^2\right)\xi-E\right) \end{vmatrix} = 0 \qquad (21)$$

If we use the octahedral values of α and β, the above determinants

are formally identical to eq. 8 when V = 0. The identity remains the same if we add an off diagonal crystal field term to split the E orbitals by V. Bleaney and O'Brien[1] pointed this out very early, which has resulted in many authors using, for the trigonal systems, the tetragonal equations for the $d_{\pm1}$ and d_{xy} basis functions. The difficulty they have encountered fitting some of the trigonal systems with these equations may be due the assumption that α and β have the octahedral values.

If we use the following functions for the ground state Kramer's doublet

$$\psi_+ = a_t\left|+,\frac{1}{2}\right\rangle + b_t\left|0,\frac{1}{2}\right\rangle$$
$$\psi_- = -a\left|-,+\frac{1}{2}\right\rangle - b_t\left|0,-\frac{1}{2}\right\rangle \qquad (22)$$

we get for the two g values

$$g_{\parallel} = 2\left[b_t^2 - a_t^2 - \left(2\alpha^2 - \beta^2\right)ka_t^2\right]$$
$$g_{\perp} = 2\left[-b_t^2 - \sqrt{6}ka_tb_t\beta\right] \qquad (23)$$

The same equations can be obtained in the hole formalism if we represent the above functions by the one electron functions

$$\left|+,\pm\frac{1}{2}\right\rangle = \alpha\, d^{\pm}_{2} + \beta\, d^{\pm}_{1}$$
$$\left|-,\pm\frac{1}{2}\right\rangle = -\alpha\, d^{\pm}_{2} + \beta\, d^{\pm}_{1} \qquad (24)$$
$$\left|0,\pm\frac{1}{2}\right\rangle = d^{\pm}_{0}$$

and replace ξ and Δ by their negative values. The hole treatment of DeSimone and Drago[16] gave equations identical to eqs. 23 except they used the octahedral values of α and β. The full electron treatment Merrithew, *et al*[17] followed Hill[5] and made the same mistake of using Case 2a.

SPIN-ORBIT INTERACTION WITH t_2^4e STATES

Most of the literature ignores this as unimportant or uses equations from the work of Hill[5]. Interestingly, his equations for this interaction predict a zero contribution for octahedral symmetry and therefore a small contribution for systems that have small distortions from this symmetry. The interaction has, however, been found important for the nitrosyl d^5 systems[20-22] to explain the fact that $g_{\parallel}$ is found to be less than 2 in magnitude, while $g_{\perp}$ is greater than 2 in magnitude in these systems. Only the $g_{\perp}$ values are explained by the equations discussed above where only the spin-orbit interaction within the ground state d^5 configuration is considered. In view of the rather large spin-orbit parameters for Ru(III) and Os(III) atoms, it was considered important to reexamine this interaction.

Hill[5] used an approach more appropriate to weak ligand field problems, so it was decided to use a strong field approach using eqs. 12-14 for the full electron problem. The hole formalism cannot be used here. There are, in fact, a large number of states that fall under the loose classification of t_2^4e. The ones that first come to mind are the doublet states that result from the promotion of the unpaired electron in d^5 to one of the two *e* states. These 12 states can be designated as

$$d^{+}_{xz}\, d^{-}_{xz} d^{+}_{yz} d^{-}_{yz} d^{\pm}_{x^2-y^2};\ d^{+}_{xz} d^{-}_{xz} d^{+}_{yz} d^{-}_{yz} d^{\pm}_{z^2} \qquad (25)$$
$$d^{+}_{yz}\, d^{-}_{yz} d^{+}_{xy} d^{-}_{xy} d^{\pm}_{x^2-y^2};\ d^{+}_{yz} d^{-}_{yz} d^{+}_{xy} d^{-}_{xy} d^{\pm}_{z^2} \qquad (26)$$
$$d^{+}_{xz}\, d^{-}_{xz} d^{+}_{xy} d^{-}_{xy} d_{x^2-y^2};\ d^{+}_{xz} d^{-}_{xz} d^{+}_{xy} d^{-}_{xy} d^{\pm}_{z^2} \qquad (27)$$

In addition, there are the following states:

$$d^2_{xy}\, d_{xz} d_{yz} d_{x^2-y^2};\ d^2_{xy} d_{xz} d_{yz} d_{z^2} \qquad (28)$$
$$d^2_{xz}\, d_{xy} d_{yz} d_{x^2-y^2};\ d^2_{xz} d_{xy} d_{yz} d_{z^2} \qquad (29)$$
$$d^2_{yz}\, d_{xz} d_{xy} d^{\pm}_{x^2-y^2};\ d^2_{yz} d_{xz} d_{xy} d_{z^2} \qquad (30)$$

which exist as a quartet state and two doublet states.

Application of perturbation theory to the doublet states represented in eqs. 25-27 gives for Δg:

$$\Delta g_x = -2\xi B^2/\Delta E\left(d^2_{xz} d^2_{xy} d_{x^2-y^2}\right) - 6\xi B^2/\Delta E\left(d^2_{xz} d^2_{xy} d_{z^2}\right) \qquad (31)$$
$$\Delta g_y = -2\xi C^2/\Delta E\left(d^2_{yz} d^2_{xy} d_{x^2-y^2}\right) - 6\xi C^2/\Delta E\left(d^2_{yz} d^2_{xy} d_{z^2}\right) \qquad (32)$$
$$\Delta g_z = -8\xi A^2/\Delta E\left(d^2_{xz} d^2_{yz} d_{x^2-y^2}\right) \qquad (33)$$

In octahedral symmetry this reduces to $\Delta g = -\frac{8\xi}{3\Delta E}$ which makes

$$g = -2 - \frac{8\xi}{3\Delta E} \qquad (34)$$

which is not what Hill[5] found. No contribution to g came from the states represented by eqs. 28-30 but this conclusion depends upon an assumption made as to the form of the two doublet states. To get the form of these equations 31-33 for the $d_{\pm1}$ and d_{xy} basis functions you can use the conversion formulas given earlier.

In the case of large and positive Δ for the d^5 nitrosyls, the parameter A approaches unity and g_z from eq. 17 becomes positive. Thus the correction term proposed[20-22] for $g_{\parallel}$ in these systems, that makes $g_{\parallel}$ less than 2 in magnitude, is predicted by these equations.

PROPER USE OF THE EQUATIONS

Most of the problems encountered in the literature with using the g matrix equations is due to not knowing what the signs are for the various g values and which g values to assign to x, y, and z. Since most compounds have been measured in powders or frozen liquids, the three principal g values cannot even be related to any molecular coordinate system. The sign problem has been compounded by the different selections of the four possible solutions listed in Table 2. Therefore researchers have opted to solve the equations they are using for all 48 possible combinations of signs and coordinate assignments. They then reject solutions that give unreasonable values of the parameters Δ/ξ, V/ξ, and k which often narrows the choice to about two sets of the parameters. My aim in this section is to show that this shotgun technique is not necessary, if you use the equations proposed here and carefully define x, y, and z in the principal coordinate system.

I propose that we define the z axis as the axis associated with the major distortion Δ. Further we also assume that V is always the same sign as Δ and this will define x relative to y. These assumptions require that $|V| \le 2|\Delta|/3$. These restrictions give a new meaning to the sign of Δ. A positive sign is for a

elongation along the tetragonal axis in which two of the three one electron states for t_2 are close together and below the third state, while a negative sign is for the compression distortion which produces two upper energy levels close together and one lower energy state. In fact our definition has d_{xy} as the upper orbital and d_{yz} as the lowest orbital when Δ is positive and the reverse for Δ negative. The d_{xz} orbital is always the intermediate one with the definitions used here. When $V = 2\Delta/3$ we have the situation in which one of the three energy levels is halfway between the upper and lower level. A similar treatment to this has been proposed by LaChance-Galang, etc.[18] in which they label the three states as 1, 2, 3 with one for the highest one electron energy. They then use the two positive parameters δ_{13} and $R = \delta_{12}/\delta_{13}$. For positive Δ, they have $R > 0.5$ and for negative Δ, $R < 0.5$.

Using eq. 8, 9, and those for Case 1a in Table 2, we have plotted in Figure 1 the three g values versus Δ/ξ for the range of $-10 \leq \Delta/\xi \leq 10$ for $k = 1$. In these plots $V = F\infty\Delta$ and values of F used were F = 0, 1/6, 1/3, and 2/3. In this plot the special case of F = 0 is represented by filled and open circles while the other special case of F = 2/3 is represented by thicker lines. Since we measure only the absolute values of g, Figure 2 shows a similar plot to Figure 1 for the absolute values. It is clear from these plots that $|g_z| < |g_y| \leq g_x|$ for $\Delta > 0$ and $|g_z| > |g_y| \bullet g_x|$ for $\Delta < 0$. Note the mirror plane symmetry, for the three g values, about zero for F = 2/3. For $\Delta > 0$ g_z goes from negative to positive at $\Delta/\xi = 1$, and for $\Delta < 0$ g_x eventually goes from negative to positive as Δ becomes increasingly negative, when F > 0. Thus in solving the equations we have only four possible cases to consider; (1) $\Delta > 0$, $g_z < 0$, (2) $\Delta > 0$, $g_z > 0$, (3) $\Delta < 0$, $g_x < 0$, and (4) $\Delta < 0$, $g_x > 0$. In practice the solutions for one sign of Δ will violate the condition that $(V/\Delta) < 2/3$, so there will only be two solutions from which one must choose.

To see how to solve the equations, we shall examine the case of $Os[Cl_3(PEt_2Ph)_3]$ that was reported by Hill[5]. The absolute g values reported for a single crystal of $Rh[Cl_3(PEt_2Ph)_3]$ containing some Os(III) were $g_1 = 3.32$, $g_2 = 1.44$, and $g_3 = 0.32$. From Figures 1 and 2 we see that if $\Delta/\xi < 0$, then $g_z = -3.32$, $g_x = \pm 0.32$, and $g_y = -1.44$ and if $\Delta/\xi > 0$, then $g_z = \pm 0.32$, $g_x = -3.32$, and $g_y = -1.44$. Since the g_y value in the second set cannot be realized in Figure 1 where k = 1 and F is between 0 and 2/3, it is that this second set will give k values much different than one or F values much larger than 2/3.

The method of solving the three equations in Table 2 plus the normalization equation of $(a^2 + b^2 + c^2) = 1$, which make up four non-linear simultaneous equations, is rarely indicated. There can be various approaches but let me give one of the simplest, which involves a cyclic successive approximation method that is easy to program in BASIC. The three equations for Case 1a in Table 2 can be rewritten into the following three equations:

$$a^2 = \frac{(2-g_z)}{2(2+k)} - \frac{(2-k)}{(2-k)}c^2 \tag{35}$$

$$k = \frac{\left[2b^2 + \frac{1}{2}(g_x + g_y)\right]}{2\sqrt{2}ab} \tag{36}$$

$$c = \frac{(g_x + g_y)}{4(2a + \sqrt{2}kb)} \tag{37}$$

We now do a cyclic four step calculation in which we assume to start with that k = 1 and c = 0 and use eq. 35 to estimate a. From a and c we calculate b from the normalization condition and then use eq. 36 to estimate k. The fourth step is to use eq. 37 to estimate c. We then return to Eq. 35 and repeat the process until we get the same value of k, to a specified precision, as was used in the previous

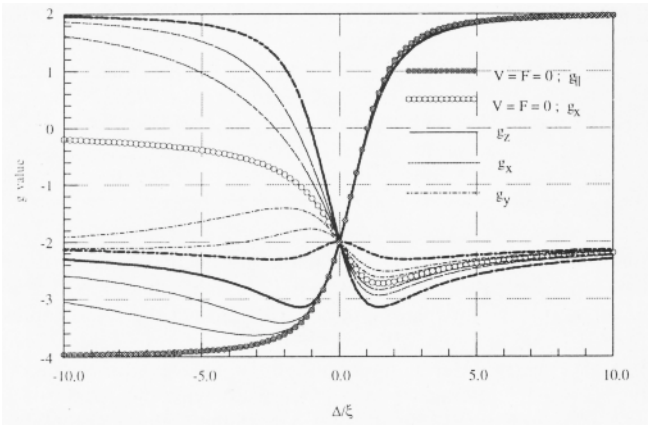

Figure 1. *Plot of g values versus Δ/ξ for strong field d^5 system using equations in paper. In the calculation k = 1 and $V = F\infty\Delta$ for F = 0, 1/6, 1/3, and 2/3. The filled open circles are for $g_z = g_{||}$ for F = 0 and the open circles are for $g_\perp$ The thick lines are for the other extreme of F = 2/3. The thin lines are for F = 1/6 and 1/3.*

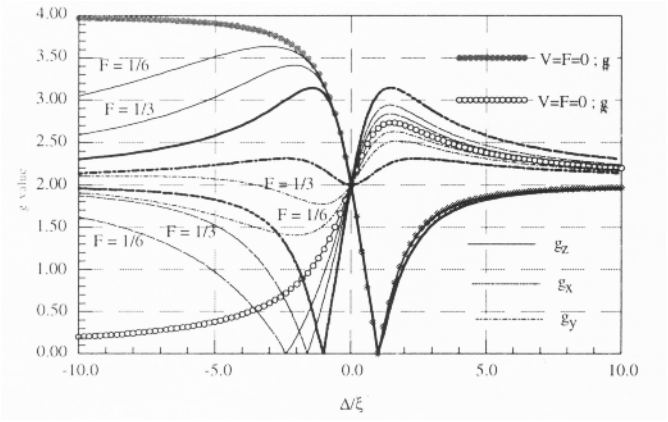

Figure 2. *Plot of the absolute values of $|g|$ versus Δ/ξ for strong field d^5 system using equations in paper. In the calculation k = 1 and $V = F\infty\Delta$ for F = 0, 1/6, 1/3, and 2/3. The symbols are the same as those given in the caption for Figure 1.*

cycle. Since k tends to oscillate in this calculation, conversion is more rapid if you use for k in the next cycle, the average of the k from eq. 36 and the k value from the previous cycle. When c is small this method converges in a few cycles to give a k good to 0.0001. For larger values, twenty or more cycles could be required. For a PC the calculation is nearly instantaneous. At this point we have only a, b, c, and k. Values of Δ/ξ, V/ξ, and E_0/ξ (the ground state energy) can then be obtained from the equations;

$$\frac{\Delta}{\xi} = \frac{\left[b(1-b^2) + \sqrt{2}a(1-2a^2)\right]}{2b(a^2 - c^2)} \tag{38}$$

$$\frac{V}{\xi} = \frac{c(2a + \sqrt{2}b)}{(c^2 - a^2)} \tag{39}$$

$$\frac{E_0}{\xi} = \Delta - \frac{a}{\sqrt{2}b} \tag{40}$$

In Table 3 are given the various solutions for $Os[Cl_3(PEt_2Ph)_3]$. Only three of the four possibilities considered, yield a solution and the two assuming $\Delta > 0$ have, as expected, a value of V/ξ too large relative to Δ/ξ to be acceptable. Thus there are only two possible solutions! Other factors are needed to choose the best solution. Both k values are acceptable but one Δ/ξ is

Table 3. Solutions of g equations for $Os[Cl_3(PEt_2Ph)_3]$ for four possible assignments.

g_x	g_y	g_z	a	b	c	k	Δ/ξ	V/ξ
+ 0.32	- 1.44	- 3.32	0.957	0.206	0.204	0.852	-2.578	-0.513
- 0.32	- 1.44	- 3.32	0.950	0.287	0.123	0.929	-1.609	-0.319
- 3.32	- 1.44	+ 0.32	0.523	0.821	-0.231	0.852	1.674	2.321
- 3.32	- 1.44	- 0.32	0.616	0.759	-0.211	0.929	1.044	1.450

considerably larger than the other. Hill did get the same values for a, b, c, k, Δ/ξ, and V/ξ for the first solution in Table 3, but x and y were interchanged and only one g was negative, because his equations were for Case 2b with the labels of x and y interchanged. He did not report the second acceptable solution in the table. He also had no good reasons for rejecting some solutions, such as those for $\Delta/\xi > 0$ in Table 3. The appropriate A, B, C parameters for the d_{xz}, d_{yz}, and d_{xy} basis set are A = 0.287, B = 0.759, C = 0.585 for the first acceptable solution in Table 3 and are A = 0.206, B = 0.821, C = 0.533 for the second acceptable solution.

It is worth examining a trigonal example to see the affect of configuration interaction. We will take the example of $[M(phen)_3](PF_6)_3$ as reported by DeSimone and Drago[16]. In this system we know that Δ is positive since $g_\perp$ is greater than 2 in magnitude and $g_\parallel$ is less than 2 in magnitude. A positive Δ means an elongated trigonal distortion in which the X-M-X angle is greater than 90°. Thus $g_\perp$ is negative but in principle $g_\parallel$ could be plus or minus. We chose positive for M = Fe and Ru because we expect Δ to decrease as we go from Fe to Os due to the increasing size of the central metal ion. The value of $g_\parallel$ could be plus or minus for the Os complex. In eq. 23 we have two equations and three variables, b_t, β, k. In Table 4 are given possible solutions for b_t and β along with Δ/ξ for different values of k. The octahedral value of β, which has been used by everyone up to now, is 0.58 and is included in Table 4. There is a lower limit of k below which there is no solution. For increasing elongation or increasing Δ, we would expect the $d_{\pm 2}$ orbitals to become more stable and therefore β to decrease from the 0.58 for octahedral symmetry. In Table 4 we see that k must increase if β is to decrease. Thus the k we get from assuming octahedral orbitals is the lower limit and would be higher if there is any configuration interaction. This is consistent with Hill's[5] calculations for tetragonal systems in which he found that configuration interaction increases the effective value of k in these d^5 equations.

It is worth examining further here the question of which of the four cases tabulated in Table 2 are the appropriate ones to choose. I have chosen the boundary conditions of octahedral symmetry to make the choice and this, I maintain is the proper choice for systems with small distortions from octahedral symmetry but is it the proper choice for strong distortions, such as those found in the $M(CN)_5NO^{n+}$ complexes? These were treated by simple second order perturbation theory which gave all g values as positive. In this case of large positive Δ, it would probably be better to use as the boundary conditions, that $g_x = g_y$ in axial symmetry and all g's be positive. This is true for Case 1b and these equations would be more appropriate in this case. For the case of a large rhombic distortion with large negative Δ, perturbation theory would also yield three positive g values, and Case 2a would appear to be the better choice as it would give all positive g values in this case. It might be mentioned that the case of large negative Δ with no rhombic distortion is not worth considering since the Jahn-Teller theorem would predict its non-existence.

Table 4. Trigonal parameters for $M(phen)_3(PF_6)_3$ assuming different k values.

M	$g_\parallel$[a]	$g_\perp$[a]	k	b_t	β	Δ/ξ
Fe	+1.19	-2.69	1.00	0.93	0.57	2.01
			0.99	0.93	0.58	2.01
			0.90	0.92	0.63	1.93
			0.80	0.91	0.70	1.79
			0.70	0.90	0.79	1.55
			0.60	0.87	0.93	1.02
Ru	+1.00	-2.63	1.00	0.92	0.53	1.79
			0.91	0.91	0.58	1.73
			0.90	0.91	0.59	1.72
			0.80	0.90	0.66	1.59
			0.70	0.88	0.75	1.35
			0.60	0.84	0.91	0.79
Os	+0.40	-2.43	1.00	0.88	0.43	1.39
			0.90	0.86	0.49	1.32
			0.80	0.85	0.56	1.19
			0.78	0.84	0.58	1.17
			0.70	0.82	0.67	0.93
Os	-0.40	-2.34	1.00	0.80	0.49	0.97
			0.90	0.77	0.58	0.75
			0.82	0.68	0.75	0.03

[a]Reference 16

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