Analytical methods and d–s mixing in the ligand-field molecular-mechanics method

David L FOULIS and Robert J DEETH[†]

Department of Chemistry, University of Warwick, Coventry CV4 7AL, UK

e-mail: r.j.deeth@warwick.ac.uk

WWW: http://www.warwick.ac.uk/~mssbq

July 26, 2002

1   Theory

We give first an outline of LF theory, to set the notation for later sections, following broadly the approach of Schäffer and Jørgensen [1]. We quote some standard formulae explicitly so that the development presented here may be relatively self-contained and easily reproduced by the interested researcher. One is interested in the effect of a set of ligands on the d orbitals of the central, transition-metal atom. One may approach the problem by postulating a perturbing potential v^{LF} due to the ligands, and calculating the effect of this potential on the energies of the d orbitals by first-order, degenerate perturbation theory. This requires diagonalisation of the (symmetric) matrix

$$V_{ab}^{\mathrm{LF}} \equiv \langle d_a | v^{\mathrm{LF}} | d_b \rangle \tag{1}$$

$(a, b = 1, 2, 3, 4, 5)$ where each orbital $|d_a\rangle$ consists of a radial function multiplied by the usual real, $l{=}2$, spherical harmonics d_i defined in terms of the standard, complex ones as follows:

$$
\begin{aligned}
d_{z^2} &\equiv Y_{2\,0}(\hat{\mathbf{r}}) = \frac{1}{2}\sqrt{\frac{5}{4\pi}}(3z^2 - r^2)/r^2 \\[2mm]
d_{xz} &\equiv -\frac{1}{\sqrt{2}}(Y_{2\,1}(\hat{\mathbf{r}}) - Y_{2\,-1}(\hat{\mathbf{r}})) = \sqrt{\frac{15}{4\pi}}(xz)/r^2 \\[2mm]
d_{yz} &\equiv i\frac{1}{\sqrt{2}}(Y_{2\,1}(\hat{\mathbf{r}}) + Y_{2\,-1}(\hat{\mathbf{r}})) = \sqrt{\frac{15}{4\pi}}(yz)/r^2 \\[2mm]
d_{x^2-y^2} &\equiv \frac{1}{\sqrt{2}}(Y_{2\,2}(\hat{\mathbf{r}}) + Y_{2\,-2}(\hat{\mathbf{r}})) = \frac{1}{2}\sqrt{\frac{15}{4\pi}}(x^2 - y^2)/r^2
\end{aligned}
$$

1

$$d_{xy} \equiv -i\frac{1}{\sqrt{2}}(Y_{2\,2}(\hat{\mathbf{r}}) - Y_{2\,-2}(\hat{\mathbf{r}})) = \sqrt{\frac{15}{4\pi}}(xy)/r^2 \,. \tag{2}$$

These angular parts may therefore be written

$$\mathbf{d} \equiv \begin{pmatrix} d_1 \\ d_2 \\ d_3 \\ d_4 \\ d_5 \end{pmatrix} \equiv \begin{pmatrix} d_{z^2} \\ d_{xz} \\ d_{yz} \\ d_{x^2-y^2} \\ d_{xy} \end{pmatrix} \equiv \begin{pmatrix} 0 & 0 & 1 & 0 & 0 \\ 0 & -1/\sqrt{2} & 0 & 1/\sqrt{2} & 0 \\ 0 & i/\sqrt{2} & 0 & i/\sqrt{2} & 0 \\ 1/\sqrt{2} & 0 & 0 & 0 & 1/\sqrt{2} \\ -i/\sqrt{2} & 0 & 0 & 0 & i/\sqrt{2} \end{pmatrix} \begin{pmatrix} Y_{2\,2}(\hat{\mathbf{r}}) \\ Y_{2\,1}(\hat{\mathbf{r}}) \\ Y_{2\,0}(\hat{\mathbf{r}}) \\ Y_{2\,-1}(\hat{\mathbf{r}}) \\ Y_{2\,-2}(\hat{\mathbf{r}}) \end{pmatrix} \equiv \mathbf{Cy} \tag{3}$$

and we note that the matrix $\mathbf{C}$ here defined is unitary, *i.e.* $\mathbf{C}^\dagger\mathbf{C} = \mathbf{I}$.

There are two key approximations in the version of LF theory used here. Firstly, each ligand contributes linearly to the potential v^{LF}; *i.e.*

$$v^{\mathrm{LF}} = \sum_\lambda v_\lambda^{\mathrm{LF}} \,, \tag{4}$$

where the index λ runs through the ligands. Secondly, in the local frame of a particular ligand λ (where the local z_λ-axis is along the metal–ligand axis pointing away from the metal atom), the matrix $(V_\lambda^{\mathrm{LF}})_{ab} \equiv \langle d_{\lambda a}|v_\lambda^{\mathrm{LF}}|d_{\lambda b}\rangle$ is diagonal. The diagonal elements are taken as parameters

$$
\begin{aligned}
\langle d_{\lambda,z^2}|v_\lambda^{\mathrm{LF}}|d_{\lambda,z^2}\rangle &\equiv e_\sigma(\lambda) \equiv e_1(\lambda) \\
\langle d_{\lambda,xz}|v_\lambda^{\mathrm{LF}}|d_{\lambda,xz}\rangle &\equiv e_{\pi x}(\lambda) \equiv e_2(\lambda) \\
\langle d_{\lambda,yz}|v_\lambda^{\mathrm{LF}}|d_{\lambda,yz}\rangle &\equiv e_{\pi y}(\lambda) \equiv e_3(\lambda) \\
\langle d_{\lambda,x^2-y^2}|v_\lambda^{\mathrm{LF}}|d_{\lambda,x^2-y^2}\rangle &\equiv e_{\delta x^2-y^2}(\lambda) \equiv e_4(\lambda) \\
\langle d_{\lambda,xy}|v_\lambda^{\mathrm{LF}}|d_{\lambda,xy}\rangle &\equiv e_{\delta xy}(\lambda) \equiv e_5(\lambda) \,,
\end{aligned}
\tag{5}
$$

which within the context of the LFMM calculations will be assumed to be transferable for a given metal–ligand combination.

To find an expression for the LF matrix (1) we must consider the rotation of a local ligand frame (and the associated $d_{\lambda,a}$) into the global molecular frame. This may be done with the usual spherical harmonic rotation matrices [2]

$$D^j_{m'm}(\alpha\beta\gamma) = e^{-im'\alpha}\, d^j_{m'm}(\beta)\, e^{-im\gamma} \,, \tag{6}$$

where the Euler angles α, β and γ relate to a rotation of the coordinate system performed in the following manner:
(1) a rotation made about the z-axis through an angle α; the new coordinate axes are x', y', z';
(2) a rotation made about the y'-axis through an angle β; the new coordinate axes are x'', y'', z'';

(3) a rotation made about the z''-axis through an angle γ; the new (final) coordinate axes are x''', y''', z'''.

The rotation matrices for the Euler angle β (pertaining to rotation about the intermediate y'-axis) have the symmetries

$$d^j_{m'm}(\beta) = d^j_{mm'}(-\beta) = (-1)^{m'-m}d^j_{mm'}(\beta) = (-1)^{m'-m}d^j_{-m',-m}(\beta)\,. \tag{7}$$

and were given explicitly by Wigner as follows:

$$
\begin{aligned}
d^j_{m'm}(\beta) &= [(j+m)!(j-m)!(j+m')!(j-m')!]^{1/2} \\
&\times \sum_t (-1)^t/[(j-m'-t)!(j+m-t)!(t+m'-m)!t!] \\
&\times \left(\cos\frac{\beta}{2}\right)^{2j+m-m'-2t}\left(-\sin\frac{\beta}{2}\right)^{m'-m+2t}. \tag{8}
\end{aligned}
$$

For the case $l = 2$, of interest to us here, Table 1 gives the formulae for these matrix elements.

Table 1: Explicit form of $d^2_{m'm}(\beta)$

m' \ m	2	1	0
2	$[1+\cos(\beta)]^2/4$	$-\sin(\beta)[1+\cos(\beta)]/2$	$\sqrt{3/8}\sin^2(\beta)$
1	$\sin(\beta)[1+\cos(\beta)]/2$	$[2\cos^2(\beta)+\cos(\beta)-1]/2$	$-\sqrt{3/2}\sin(\beta)\cos(\beta)$
0	$\sqrt{3/8}\sin^2(\beta)$	$\sqrt{3/2}\sin(\beta)\cos(\beta)$	$[3\cos^2(\beta)-1]/2$
-1	$\sin(\beta)[1-\cos(\beta)]/2$	$-[2\cos^2(\beta)-\cos(\beta)-1]/2$	$\sqrt{3/2}\sin(\beta)\cos(\beta)$
-2	$[1-\cos(\beta)]^2/4$	$\sin(\beta)[1-\cos(\beta)]/2$	$\sqrt{3/8}\sin^2(\beta)$

m' \ m	-1	-2
2	$-\sin(\beta)[1-\cos(\beta)]/2$	$[1-\cos(\beta)]^2/4$
1	$-[2\cos^2(\beta)-\cos(\beta)-1]/2$	$-\sin(\beta)[1-\cos(\beta)]/2$
0	$-\sqrt{3/2}\sin(\beta)\cos(\beta)$	$\sqrt{3/8}\sin^2(\beta)$
-1	$[2\cos^2(\beta)+\cos(\beta)-1]/2$	$-\sin(\beta)[1+\cos(\beta)]/2$
-2	$\sin(\beta)[1+\cos(\beta)]/2$	$[1+\cos(\beta)]^2/4$

Thus a spherical harmonic $Y_{lm}(\hat{\mathbf{r}})$ in the original coordinate system will become, under this rotation R, carried with the coordinate frame rotation, the new function

$$RY_{lm}(\hat{\mathbf{r}}) = \sum_{m'} D^l_{m'm}(\alpha\beta\gamma)Y_{lm'}(\hat{\mathbf{r}}) \tag{9}$$

of the old coordinates.

Returning to our LF development we must first specify the direction of the x_λ-axis, which we take to point away from the global z-axis. Thus, if the position of the ligand has polar coordinates r, θ and ϕ in the global frame, the Euler angles of the required coordinate rotation may be taken to be

$$\alpha = 0 \,, \beta = -\theta \,, \gamma = -\phi \,. \tag{10}$$

With these definitions the spherical harmonics ($\mathbf{y}_\lambda$) in the local frame are related to those ($\mathbf{y}$) in the global frame by

$$\mathbf{y}^{\mathrm{T}} = \mathbf{y}_\lambda{}^{\mathrm{T}} \mathbf{D}_\lambda \tag{11}$$

(where we have expressed Eqn. 9 in an obvious matrix form) and the matrix elements of $\mathbf{D}_\lambda$ are given by (6) and Tab. 1 in the matrix sense of the latter. Likewise we may therefore write

$$\mathbf{d}_\lambda{}^{\mathrm{T}} \equiv \mathbf{d}^{\mathrm{T}} \mathbf{F}_\lambda \tag{12}$$

so that, using (3), we find that

$$\mathbf{F}_\lambda = \mathbf{C}^* \mathbf{D}_\lambda{}^\dagger \mathbf{C}^{\mathrm{T}} \,. \tag{13}$$

Therefore,

$$E_{\lambda,ab} \equiv e_a(\lambda)\delta_{ab} = \langle d_{\lambda a}|v_\lambda^{\mathrm{LF}}|d_{\lambda b}\rangle = \sum_c \sum_d F_{\lambda,ca}^* \langle d_c|v_\lambda^{\mathrm{LF}}|d_d\rangle F_{\lambda,db} \,. \tag{14}$$

And finally,

$$\mathbf{V}^{\mathrm{LF}} = \sum_\lambda \mathbf{F}_\lambda \mathbf{E}_\lambda \mathbf{F}_\lambda{}^\dagger \,. \tag{15}$$

In the case of solely σ bonding, the parameter e_1 is the only non-zero one for all ligands, so that (15) becomes

$$V_{ab}^{\mathrm{LF}} = \sum_\lambda F_{\lambda,a1} e_\sigma(\lambda) F_{\lambda,b1}{}^* \,. \tag{16}$$

The matrix elements $F_{\lambda,ab}$ may be calculated explicitly from the above definitions (and turn out to be real), although the calculation is tedious. We have made use of the symbolic algebra package Maple to check the calculations. We quote here the results for $F_{\lambda,a1}$:

$$\begin{aligned}
F_{\lambda,11} &= (1/2)(3\cos^2\theta - 1) \\
F_{\lambda,21} &= \sqrt{3}\sin\theta\cos\theta\cos\phi \\
F_{\lambda,31} &= \sqrt{3}\sin\theta\cos\theta\sin\phi \\
F_{\lambda,41} &= (1/2)\sqrt{3}(1 - \cos^2\theta)\cos 2\phi \\
F_{\lambda,51} &= (1/2)\sqrt{3}(1 - \cos^2\theta)\sin 2\phi \,,
\end{aligned} \tag{17}$$

which correspond exactly to those of Schäffer and Jørgensen [1]. It is interesting to note from (17) and (2) that

$$F_{\lambda,a1} = \sqrt{4\pi/5}\, d_a(\theta,\phi) \,. \tag{18}$$

To include the effect of non-zero parameters, $e_{\pi x}(\lambda)$ and $e_{\pi y}(\lambda)$, one must take into account the geometrical arrangement of the subsidiary atoms bonded to the main π bonding ligand atom. If these two parameters are equal, then our analysis above suffices to give the appropriate matrix elements $F_{\lambda,ab}$. If not, then we must include an extra rotation of the local ligand frame. The local frame is now defined so that its x- and y- axes are appropriate for the definitions of $e_{\pi x}(\lambda)$ and $e_{\pi y}(\lambda)$ separately. In particular, for a planar ligand group, the local xz-plane would be in that plane. A new angle ψ (see Ref. [3]) is now the angle between the former local x-axis from above and the new local x-axis.

To find the new expression for the LF matrix (1) our previous analysis applies, except for the rotation that we perform. The new Euler angles of the required coordinate rotation are now

$$\alpha = -\psi \,, \beta = -\theta \,, \gamma = -\phi \,. \tag{19}$$

Where both σ and π bonding are present, (15) becomes

$$V_{ab}^{\mathrm{LF}} = \sum_{\lambda} \left[F_{\lambda,a1} e_{\sigma}(\lambda) F_{\lambda,b1}{}^{*} + F_{\lambda,a2} e_{\pi x}(\lambda) F_{\lambda,b2}{}^{*} + F_{\lambda,a3} e_{\pi y}(\lambda) F_{\lambda,b3}{}^{*} \right] \,. \tag{20}$$

The matrix elements $F_{\lambda,ab}$ may be calculated explicitly as before, with the new rotations, and checked with Maple. The results for $F_{\lambda,a1}$ are unaltered. Those for $F_{\lambda,a2}$ and $F_{\lambda,a3}$ are:

$$
\begin{aligned}
F_{\lambda,12} &= -\sqrt{3}\sin\theta\cos\theta\cos\psi \\
F_{\lambda,22} &= \cos 2\theta\cos\phi\cos\psi - \cos\theta\sin\phi\sin\psi \\
F_{\lambda,32} &= \cos 2\theta\sin\phi\cos\psi + \cos\theta\cos\phi\sin\psi \\
F_{\lambda,42} &= \sin\theta\cos\theta\cos 2\phi\cos\psi - \sin\theta\sin 2\phi\sin\psi \\
F_{\lambda,52} &= \sin\theta\cos\theta\sin 2\phi\cos\psi + \sin\theta\cos 2\phi\sin\psi \,,
\end{aligned}
\tag{21}
$$

and

$$
\begin{aligned}
F_{\lambda,13} &= \sqrt{3}\sin\theta\cos\theta\sin\psi \\
F_{\lambda,23} &= -\cos\theta\sin\phi\cos\psi - \cos 2\theta\cos\phi\sin\psi \\
F_{\lambda,33} &= \cos\theta\cos\phi\cos\psi - \cos 2\theta\sin\phi\sin\psi \\
F_{\lambda,43} &= -\sin\theta\sin 2\phi\cos\psi - \sin\theta\cos\theta\cos 2\phi\sin\psi \\
F_{\lambda,53} &= \sin\theta\cos 2\phi\cos\psi - \sin\theta\cos\theta\sin 2\phi\sin\psi \,,
\end{aligned}
\tag{22}
$$

which correspond exactly to those of Figgis and Hitchman ([3], page 61).

1.1   The CLF Stabilisation Energy and the Crystal Field Barycentre

Having prepared the matrix $\mathbf{V}^{\mathrm{LF}}$ according to the foregoing algebra, one must diagonalise it to find the perturbed energy eigenvalue shifts. Since it is a symmetric matrix, the

eigenvectors can be chosen to form a complete, orthonormal set, the eigenvalues are real, and the diagonalisation may be performed with an orthogonal matrix, $\mathbf{Q}$ (such that $\mathbf{Q}^T\mathbf{Q} = \mathbf{I}$). Therefore, we have

$$\mathbf{W} = \mathbf{Q}\mathbf{V}^{\text{LF}}\mathbf{Q}^T \tag{23}$$

where the diagonal matrix $\mathbf{W}$ is defined in terms of the energy eigenvalues w_a of $\mathbf{V}^{\text{LF}}$ (with the requirement that $w_1 \leq w_2 \leq w_3 \leq w_4 \leq w_5$) by

$$W_{ab} \equiv w_a\delta_{ab}. \tag{24}$$

We note that the matrix $\mathbf{Q}^T$ may be taken to have its columns as the orthonormal eigenvectors of $\mathbf{V}^{\text{LF}}$.

The main quantity of interest is the CLF stabilisation energy, $\mathcal{E}$, which is a sum of the energy eigenvalues, w_a, weighted by constants, n_a, depending on the occupation of the levels. Thus,

$$\mathcal{E} \equiv \sum_a n_a w_a. \tag{25}$$

It is more useful for further development to write this last equation as the trace of a matrix product

$$\mathcal{E} \equiv \text{tr}(\mathbf{N}\mathbf{W}), \tag{26}$$

where the constant, diagonal matrix $\mathbf{N}$ is given by

$$N_{ab} \equiv n_a\delta_{ab}. \tag{27}$$

At this point we recognise that the CLF (or AOM) and crystal field theory (CFT) barycentres are different. The original tensor operator mathematics employed Gerloch's formalism which automatically gave the CFT result. Here, our use of the S-J approach means that the sum of the d-orbital energies is not zero. Rather, it is the sum of the CLF parameter values. We envisage that for organometallic species, this will be the preferred reference point for the molecular orbital stabilisation energy (MOSE) as defined by Burdett. For Werner-type complexes where the CFT barycentre is more usual, we can easily convert the barycentre by replacing the matrix $\mathbf{W}$ above in (26) with a barycentred version $\mathbf{W}_B$ defined by

$$\mathbf{W}_B \equiv \mathbf{W} - \frac{1}{5}(\text{tr}\mathbf{W})\mathbf{I}. \tag{28}$$

For our development below we wish to keep to the previous definition of $\mathbf{W}$. This may be achieved in the following manner. Note that now

$$
\begin{aligned}
\mathcal{E} &= \text{tr}(\mathbf{N}\mathbf{W}_B) \\
&= \text{tr}(\mathbf{N}(\mathbf{W} - \frac{1}{5}(\text{tr}\mathbf{W})\mathbf{I})) \\
&= \text{tr}(\mathbf{N}\mathbf{W}) - \frac{1}{5}\text{tr}(\mathbf{W})\text{tr}(\mathbf{N}) \\
&= \text{tr}((\mathbf{N} - \frac{1}{5}(\text{tr}\mathbf{N})\mathbf{I})\mathbf{W}) \\
&= \text{tr}(\mathbf{N}_B\mathbf{W}),
\end{aligned} \tag{29}
$$

where

$$\mathbf{N}_B \equiv \mathbf{N} - \frac{1}{5}(\mathrm{tr}\mathbf{N})\mathbf{I}. \tag{30}$$

1.2 The Inclusion of d–s Mixing

In certain circumstances, and most famously for square-planar complexes, it is known that the ligand field gives rise to an interaction between the nd and $(n+1)s$ orbitals [4, 5]. In this case it is necessary to include the $(n+1)s$ orbital in the perturbation procedure. An important point to note is that the d–s-interaction that we wish to take into account arises from second order perturbation theory, a point made by Riley [7] in his usefully explicit treatment.

In this work we proceed in a direct manner by considering the full, perturbed Hamiltonian, $h \equiv h_0 + v^{\mathrm{LF}}$; where the unperturbed Hamiltonian, h_0, is spherically symmetric, and the nd and $(n+1)s$ orbitals are eigenstates of h_0. Our task is then to diagonalise the matrix of h expressed in the eigenstates of h_0. The assumption that v^{LF} is a small perturbation which mixes the nd and $(n+1)s$ orbitals, but no others with them, allows us to restrict our attention to the six-dimensional subspace of these orbitals. Thus, we must diagonalise the 6×6 matrix

$$H_{\alpha\beta} \equiv \langle u_\alpha | h | u_\beta \rangle \tag{31}$$

$(\alpha, \beta = 0, 1, 2, 3, 4, 5)$, where $|u_0\rangle \equiv |s\rangle$ and $|u_a\rangle \equiv |d_a\rangle$ for $a = 1, \ldots, 5$. Now we may subtract from this 6×6 Hamiltonian matrix any multiple of the identity matrix without affecting the diagonalisation process. Therefore, let us define the 6×6 LF matrix

$$V_{\alpha\beta}^{(ds)} \equiv H_{\alpha\beta} - E_d^{(0)}\delta_{\alpha\beta}, \tag{32}$$

where $E_d^{(0)} \equiv \langle d_a | h_0 | d_a \rangle$ is the unperturbed (degenerate) d orbital energy (and for the remainder of this work we drop the LF label). The eigenvectors of $\mathbf{V}^{(ds)}$ are the same as those of $\mathbf{H}$, while the eigenvalues are the energy shifts relative to $E_d^{(0)}$ that we seek.

We may write the matrix $\mathbf{V}^{(ds)}$ in partitioned form as

$$\mathbf{V}^{(ds)} = \begin{pmatrix} \Delta + \xi & \mathbf{c}^T \\ \mathbf{c} & \mathbf{V} \end{pmatrix}, \tag{33}$$

where $\Delta \equiv E_s^{(0)} - E_d^{(0)}$, $E_s^{(0)} \equiv \langle s | h_0 | s \rangle$, $\xi \equiv \langle s | v | s \rangle$, $\mathbf{V}$ is our 5×5 LF matrix from (1), and $\mathbf{c}$ is a 5-dimensional vector with elements

$$c_a \equiv \langle d_a | v | s \rangle. \tag{34}$$

A non-trivial d–s hybridisation means a non-zero $\mathbf{c}$, so that we are obliged to consider the full 6×6 problem. However, the parameters Δ and ξ are usually not available separately. We may nonetheless proceed by considering directly the 6×6 eigenvalue problem

$$\begin{pmatrix} \Delta + \xi & \mathbf{c}^T \\ \mathbf{c} & \mathbf{V} \end{pmatrix} \begin{pmatrix} \mu \\ \mathbf{m} \end{pmatrix} = \epsilon \begin{pmatrix} \mu \\ \mathbf{m} \end{pmatrix}, \tag{35}$$

where we note that neither the scalar μ nor the vector $\mathbf{m}$ can be zero for a non-trivial eigenvector, since this would imply that the vector $\mathbf{c}$ were zero, contradicting our assumption of some d–s interaction. Therefore we may eliminate μ between the scalar and vector equations of (35) to obtain

$$\mathbf{V}\mathbf{m} - \mathbf{c}\left(\frac{\mathbf{c}^T\mathbf{m}}{\Delta + \xi - \epsilon}\right) = \epsilon\mathbf{m} \,. \tag{36}$$

If we assume that the original d–s energy difference Δ is much greater than the difference of perturbation shifts $\xi - \epsilon$, then the last equation becomes approximately

$$\left(\mathbf{V} - \left(\frac{\mathbf{c}\mathbf{c}^T}{\Delta}\right)\right)\mathbf{m} = \epsilon\mathbf{m} \,, \tag{37}$$

which is an eigenvalue equation for the 5×5 matrix

$$\widetilde{\mathbf{V}} \equiv \mathbf{V} - \left(\frac{\mathbf{c}\mathbf{c}^T}{\Delta}\right) \,, \tag{38}$$

which we take to be our new LF matrix in the case of d–s mixing.

The new term in the LF matrix may be evaluated as follows. Note first from (4,34) that

$$c_a = \sum_\lambda c_{\lambda,a} \,, \tag{39}$$

where $c_{\lambda,a} \equiv \langle d_a|v_\lambda|s\rangle$. Using (12) and noting the rotational symmetry of the s orbital, we find that

$$\sum_b F_{\lambda,ba}^* c_{\lambda,b} = \langle d_{\lambda,a}|v_\lambda|s_\lambda\rangle \,. \tag{40}$$

This may be inverted to give

$$c_{\lambda,a} = \sum_b F_{\lambda,ab}\langle d_{\lambda,b}|v_\lambda|s_\lambda\rangle \,. \tag{41}$$

From considerations of local symmetry, only the term $\langle d_{\lambda,z^2}|v_\lambda|s_\lambda\rangle$ is significant, so that

$$c_{\lambda,a} = F_{\lambda,a1}\langle d_{\lambda,1}|v_\lambda|s_\lambda\rangle \,. \tag{42}$$

Defining the parameter $e_{ds}(\lambda)$ in the usual way

$$e_{ds}(\lambda) \equiv e_0(\lambda) \equiv \langle d_{\lambda,1}|v_\lambda|s_\lambda\rangle^2/\Delta \,, \tag{43}$$

and setting

$$b_a \equiv \sum_\lambda F_{\lambda,a1}\sqrt{e_{ds}(\lambda)} \,, \tag{44}$$

leads finally to

$$\widetilde{\mathbf{V}} = \mathbf{V} - \mathbf{b}\mathbf{b}^T \,. \tag{45}$$

1.3 Evaluation of the Ligand Field Matrix

The key to the practical implementation of the ligand field algebra is its expression in terms of the Cartesian coordinates of the atoms of the molecule. We need consider only those atoms involved in generating the CLFSE. Thus, we start with the central transition metal atom having position vector, $\vec{x}^{(0)}$, with components, $x_i^{(0)}$, for $i = 1, 2, 3$. Then we have the L ligand atoms directly bonded to the metal, with position vectors $\vec{x}^{(\lambda)}$, for $\lambda = 1, 2, \ldots, L$. Finally, we have possible subsidiary atoms bonded to the ligand atoms. So for main ligand atom λ we have K_λ subsidiary atoms, where $K_\lambda \geq 0$. In this work we consider no more than two subsidiary atoms, whose positions determine the local coordinate frame for asymmetric π bonding. In practice, the maximum number of subsidiary atoms is three as in, for example, phosphine ligands, PR_3. In these cases, there is local C_3 symmetry and we consider the π bonding to be cylindrical and thus equivalent to the case of no subsidiary atoms. The position vectors of the subsidiary atoms we write as $\vec{x}^{(\lambda\kappa)}$, for $\kappa = 1, \ldots, K_\lambda$.

The coefficients in the LF matrix are given, of course, in terms of relative position vectors. So we define therefore

$$
\begin{aligned}
\vec{r}^{(\lambda)} &\equiv \vec{x}^{(\lambda)} - \vec{x}^{(0)}, \\
\vec{s}^{(\lambda)} &\equiv \vec{x}^{(\lambda 1)} - \vec{x}^{(\lambda)} \text{ (if it exists)}, \\
\vec{t}^{(\lambda)} &\equiv \vec{x}^{(\lambda 2)} - \vec{x}^{(\lambda)} \text{ (if it exists)}.
\end{aligned}
\tag{46}
$$

We consider separately the terms in the ligand field matrix (taken straightforwardly from (20) and (45))

$$
\mathbf{V} = \mathbf{V}^\sigma + \mathbf{V}^{\pi x} + \mathbf{V}^{\pi y} - \mathbf{b}\mathbf{b}^T.
\tag{47}
$$

The first term may be written, using (20) with (2) and (18), as

$$
V_{ab}^\sigma = \sum_\lambda G_a^{(\sigma)}(\vec{r}^{(\lambda)}) \left[\frac{e_\sigma(\lambda)}{r^{(\lambda)4}} \right] G_b^{(\sigma)}(\vec{r}^{(\lambda)}),
\tag{48}
$$

and the $G_a^{(\sigma)}(\vec{r})$ are defined by

$$
\begin{aligned}
G_1^{(\sigma)}(\vec{r}) &\equiv \frac{1}{2}(2z^2 - x^2 - y^2) \\
G_2^{(\sigma)}(\vec{r}) &\equiv \sqrt{3}(xz) \\
G_3^{(\sigma)}(\vec{r}) &\equiv \sqrt{3}(yz) \\
G_4^{(\sigma)}(\vec{r}) &\equiv \frac{1}{2}\sqrt{3}(x^2 - y^2) \\
G_5^{(\sigma)}(\vec{r}) &\equiv \sqrt{3}(xy).
\end{aligned}
\tag{49}
$$

(For ease of reading the formulae, we have used (x, y, z) as the components of $\vec{r}$, instead of

(r_1, r_2, r_3).) The vector $\mathbf{b}$ in the d–s mixing term of (45) may be now written as

$$b_a \equiv \sum_\lambda G_a^{(\sigma)}(\vec{r}^{(\lambda)}) \left[\frac{\sqrt{e_{ds}(\lambda)}}{r^{(\lambda)2}} \right]. \tag{50}$$

The advantages of writing the terms of the ligand field matrix in this way become apparent when we come to taking the derivative of the matrix. In particular, the quantities $G_a^{(\sigma)}(\vec{r})$ are simple polynomials in x, y and z, and the expressions in square brackets are purely functions of the magnitude r of the vector $\vec{r}$.

The situation becomes more complicated when we come to consider the π bonding terms. Here we must take into account several different cases. Furthermore, we may have different cases for each ligand λ. Thus we must consider separate expressions for each $\mathbf{V}^{\pi x(\lambda)}$ and $\mathbf{V}^{\pi y(\lambda)}$ (defined in an obvious way).

The simplest case is that of cylindrical π bonding for which we need consider no subsidiary ligand atoms. We can thus set the angle ψ arbitrarily to zero. If we now define

$$\rho^{(\lambda)} \equiv \sqrt{r_1^{(\lambda)2} + r_2^{(\lambda)2}} = \sqrt{x^{(\lambda)2} + y^{(\lambda)2}}, \tag{51}$$

then from (21) and (22) we can derive

$$V_{ab}^{\pi x(\lambda)} = G_a^{(\pi x)}(\vec{r}^{(\lambda)}) \left[\frac{e_{\pi x}(\lambda)}{r^{(\lambda)4}} \right] \left(\frac{1}{\rho^{(\lambda)2}} \right) G_b^{(\pi x)}(\vec{r}^{(\lambda)}), \tag{52}$$

and

$$V_{ab}^{\pi y(\lambda)} = G_a^{(\pi y)}(\vec{r}^{(\lambda)}) \left[\frac{e_{\pi y}(\lambda)}{r^{(\lambda)2}} \right] \left(\frac{1}{\rho^{(\lambda)2}} \right) G_b^{(\pi y)}(\vec{r}^{(\lambda)}), \tag{53}$$

where $G_a^{(\pi x)}(\vec{r})$ and $G_a^{(\pi y)}(\vec{r})$ are defined by

$$
\begin{array}{llll}
G_1^{(\pi x)}(\vec{r}) & \equiv & -\sqrt{3}(x^2 + y^2)z & \qquad G_1^{(\pi y)}(\vec{r}) \equiv 0 \\
G_2^{(\pi x)}(\vec{r}) & \equiv & x(z^2 - x^2 - y^2) & \qquad G_2^{(\pi y)}(\vec{r}) \equiv -yz \\
G_3^{(\pi x)}(\vec{r}) & \equiv & y(z^2 - x^2 - y^2) & \qquad G_3^{(\pi y)}(\vec{r}) \equiv xz \\
G_4^{(\pi x)}(\vec{r}) & \equiv & z(x^2 - y^2) & \qquad G_4^{(\pi y)}(\vec{r}) \equiv -2xy \\
G_5^{(\pi x)}(\vec{r}) & \equiv & 2xyz & \qquad G_5^{(\pi y)}(\vec{r}) \equiv x^2 - y^2
\end{array}
\tag{54}
$$

The next possibility is that of one subsidiary atom. Here we take the local xz-plane to be that determined by the metal, ligand donor atom and subsidiary atom, such that the local x-axis is given by the projection of the ligand to subsidiary atom vector, $\vec{s}^{(\lambda)}$, on to the plane perpendicular to the metal to ligand vector, $\vec{r}^{(\lambda)}$. Defining

$$\sigma^{(\lambda)} \equiv \sqrt{s^{(\lambda)2} r^{(\lambda)2} - (\vec{s}^{(\lambda)} \cdot \vec{r}^{(\lambda)})^2} \tag{55}$$

we find that

$$V_{ab}^{\pi x(\lambda)} = \left(\vec{g}_a^{(x)}(\vec{r}^{(\lambda)}) \cdot \vec{s}^{(\lambda)} \right) \left[\frac{e_{\pi x}(\lambda)}{r^{(\lambda)4}} \right] \left(\frac{1}{\sigma^{(\lambda)2}} \right) \left(\vec{g}_b^{(x)}(\vec{r}^{(\lambda)}) \cdot \vec{s}^{(\lambda)} \right), \tag{56}$$

10

and

$$V_{ab}^{\pi y(\lambda)} = \left(\vec{g}_a^{(y)}(\vec{r}^{(\lambda)}) \cdot \vec{s}^{(\lambda)}\right) \left[\frac{e_{\pi y}(\lambda)}{r^{(\lambda)2}}\right] \left(\frac{1}{\sigma^{(\lambda)2}}\right) \left(\vec{g}_b^{(y)}(\vec{r}^{(\lambda)}) \cdot \vec{s}^{(\lambda)}\right), \tag{57}$$

where the components of $\vec{g}_a^{(x)}(\vec{r})$ are given in Table 2, and those of $\vec{g}_a^{(y)}(\vec{r})$ in Table 3.

Table 2: Vector components of $\vec{g}_a^{(x)}(\vec{r})$

a	$g_{a,1}^{(x)}(\vec{r})$	$g_{a,2}^{(x)}(\vec{r})$	$g_{a,3}^{(x)}(\vec{r})$
1	$-\sqrt{3}xz^2$	$-\sqrt{3}yz^2$	$\sqrt{3}z(x^2+y^2)$
2	$z(z^2-x^2+y^2)$	$-2xyz$	$x(x^2+y^2-z^2)$
3	$-2xyz$	$z(x^2-y^2+z^2)$	$y(x^2+y^2-z^2)$
4	$x(2y^2+z^2)$	$-y(2x^2+z^2)$	$-z(x^2-y^2)$
5	$y(z^2-x^2+y^2)$	$x(x^2-y^2+z^2)$	$-2xyz$

Table 3: Vector components of $\vec{g}_a^{(y)}(\vec{r})$

a	$g_{a,1}^{(y)}(\vec{r})$	$g_{a,2}^{(y)}(\vec{r})$	$g_{a,3}^{(y)}(\vec{r})$
1	$-\sqrt{3}yz$	$\sqrt{3}xz$	0
2	$-xy$	x^2-z^2	yz
3	z^2-y^2	xy	$-xz$
4	$-yz$	$-xz$	$2xy$
5	xz	$-yz$	y^2-x^2

Finally, we have the case of two subsidiary atoms. Here we define the local x-axis as being the intersection of the plane of the ligand donor atom and the subsidiary atoms (*i.e.* that containing $\vec{s}^{(\lambda)}$ and $\vec{t}^{(\lambda)}$) with the plane perpendicular to $\vec{r}^{(\lambda)}$. Thus, defining

$$\tau^{(\lambda)} \equiv \sqrt{(\vec{s}^{(\lambda)} \times \vec{t}^{(\lambda)})^2 r^{(\lambda)2} - ((\vec{s}^{(\lambda)} \times \vec{t}^{(\lambda)}) \cdot \vec{r}^{(\lambda)})^2}, \tag{58}$$

we find that

$$V_{ab}^{\pi x(\lambda)} = \left(\vec{h}_a^{(x)}(\vec{r}^{(\lambda)}) \cdot (\vec{s}^{(\lambda)} \times \vec{t}^{(\lambda)})\right) \left[\frac{e_{\pi x}(\lambda)}{r^{(\lambda)2}}\right] \left(\frac{1}{\tau^{(\lambda)2}}\right) \left(\vec{h}_b^{(x)}(\vec{r}^{(\lambda)}) \cdot (\vec{s}^{(\lambda)} \times \vec{t}^{(\lambda)})\right) \tag{59}$$

and

$$V_{ab}^{\pi y(\lambda)} = \left(\vec{h}_a^{(y)}(\vec{r}^{(\lambda)}) \cdot (\vec{s}^{(\lambda)} \times \vec{t}^{(\lambda)})\right) \left[\frac{e_{\pi y}(\lambda)}{r^{(\lambda)4}}\right] \left(\frac{1}{\tau^{(\lambda)2}}\right) \left(\vec{h}_b^{(y)}(\vec{r}^{(\lambda)}) \cdot (\vec{s}^{(\lambda)} \times \vec{t}^{(\lambda)})\right), \tag{60}$$

where

$$\vec{h}_a^{(x)}(\vec{r}) \equiv \vec{g}_a^{(y)}(\vec{r}) \tag{61}$$

and

$$\vec{h}_a^{(y)}(\vec{r}) \equiv -\vec{g}_a^{(x)}(\vec{r}). \tag{62}$$

11

1.4 Degenerate Cases

It is clear from the expressions (48), (50), (52), (53), (56), (57), (59) and (60) for the parts of the ligand field matrix, that there may be problems when quantities in the denominators become zero. Firstly, in all these expressions, the case $r^{(\lambda)} \to 0$ is a singularity. However, we may ignore this possibility in the molecular mechanics context since it corresponds to the ligand hitting the metal atom. This would normally be ruled out by the corresponding large bond stretch energy term.

Potentially more serious is the case where $\rho^{(\lambda)} \to 0$ in (52) and (53), corresponding to the ligand atom lying along the global z-axis, an entirely possible and acceptable occurrence. We may however remove this singularity by expanding the sum $V_{ab}^{\pi x(\lambda)} + V_{ab}^{\pi y(\lambda)}$ in full, noting that we must have $e_{\pi x}(\lambda) = e_{\pi y}(\lambda) \equiv e_\pi(\lambda)$, to obtain

$$V_{ab}^{\pi x(\lambda)} + V_{ab}^{\pi y(\lambda)} = \left[\frac{e_\pi(\lambda)}{r^{(\lambda)4}} \right] \Gamma_{ab}^{\pi(\lambda 0)}, \tag{63}$$

where the matrix $\mathbf{\Gamma}^{\pi(\lambda 0)}$ is given by

$$\mathbf{\Gamma}^{\pi(\lambda 0)} \equiv \begin{pmatrix} 3(x^2 + y^2)z^2 & -\sqrt{3}xz(z^2 - x^2 - y^2) & -\sqrt{3}yz(z^2 - x^2 - y^2) \\ -\sqrt{3}xz(z^2 - x^2 - y^2) & (x^2 - z^2)^2 + y^2(x^2 + z^2) & xy(x^2 + y^2 - 3z^2) \\ -\sqrt{3}yz(z^2 - x^2 - y^2) & xy(x^2 + y^2 - 3z^2) & (y^2 - z^2)^2 + x^2(y^2 + z^2) \\ -\sqrt{3}z^2(x^2 - y^2) & xz(z^2 - x^2 + 3y^2) & yz(y^2 - z^2 - 3x^2) \\ -2\sqrt{3}xyz^2 & yz(z^2 - 3x^2 + y^2) & xz(z^2 + x^2 - 3y^2) \end{pmatrix}$$

$$\begin{pmatrix} -\sqrt{3}z^2(x^2 - y^2) & -2\sqrt{3}xyz^2 \\ xz(z^2 - x^2 + 3y^2) & yz(z^2 - 3x^2 + y^2) \\ yz(y^2 - z^2 - 3x^2) & xz(z^2 + x^2 - 3y^2) \\ 4x^2y^2 + z^2(x^2 + y^2) & -2xy(x^2 - y^2) \\ -2xy(x^2 - y^2) & (x^2 - y^2)^2 + z^2(x^2 + y^2) \end{pmatrix}. \tag{64}$$

Setting $x, y \to 0$ in this last equation leads us to the result that

$$\mathbf{V}^{\pi x(\lambda)} + \mathbf{V}^{\pi y(\lambda)} \to e_\pi(\lambda) \begin{pmatrix} 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \end{pmatrix}, \tag{65}$$

as one might have expected from the local-frame definition (5) of the ligand field parameters.

In the case of one subsidiary atom, the possibility that $\sigma^{(\lambda)} \to 0$ corresponds to this atom being collinear with the metal and ligand donor atom. While this is always possible in a real molecular geometry, our assumption that we have non-cylindrical π bonding (*i.e.* $e_{\pi x}(\lambda) \neq e_{\pi y}(\lambda)$) to begin with, suggests that it would be unlikely for the metal–ligand–subsidiary atom angle to straighten out. However, in a molecular mechanics simulation there would have to be an explicit angular potential included to resist this possibility.

Similarly, in the case of two subsidiary atoms, the possibility that $\tau^{(\lambda)} \to 0$ corresponds to the three-atom ligand plane becoming perpendicular to the metal–ligand direction. Again this is a possible geometry in real molecules. Our π bonding model is inappropriate in this eventuality, it being intended more for the case where the metal and the three atoms of the ligand are nearly coplanar, with the assumption that other, angular potentials would tend to keep it nearly so.

1.5 Analytic First Derivatives of the Ligand-Field Matrix and CLFSE

In the process of geometry optimisation within the molecular mechanics method one requires derivatives of the total molecular energy with respect to each atomic coordinate. Apart from the CLFSE, the formulae for the other force field terms are simple enough that one may calculate their derivatives analytically. Until now we have been obliged to calculate the derivatives of the CLFSE numerically with a finite difference approximation, which is cumbersome, time consuming and prone to inaccuracy. In this section we develop the formalism for obtaining these derivatives analytically from the previous expressions for the ligand field matrix.

We consider the partial derivative of $\mathcal{E}$ with respect to one of the atomic coordinates $x_i^{(\lambda\kappa)}$ (for $\lambda = 0, 1, \ldots, L$; $\kappa = 0, 1, \ldots, K_\lambda$; and $i = 1, 2, 3$). Let us for the moment denote this derivative with a prime, so that we have from (26) that

$$\mathcal{E}' = \text{tr}(\mathbf{N}\mathbf{W}')\,, \tag{66}$$

where we use the fact that $\mathbf{N}$ is a constant matrix (barycentred or otherwise). Differentiating (23) we have

$$\mathbf{W}' = \mathbf{Q}'\mathbf{V}\mathbf{Q}^T + \mathbf{Q}\mathbf{V}'\mathbf{Q}^T + \mathbf{Q}\mathbf{V}\mathbf{Q}^{T'}\,. \tag{67}$$

Now $\mathbf{Q}$ is an orthogonal matrix, so that

$$\mathbf{Q}^T\mathbf{Q} = \mathbf{Q}\mathbf{Q}^T = \mathbf{I}\,, \tag{68}$$

from which we obtain

$$\mathbf{Q}'\mathbf{Q}^T + \mathbf{Q}\mathbf{Q}^{T'} = \mathbf{0} = \mathbf{Q}^{T'}\mathbf{Q} + \mathbf{Q}^T\mathbf{Q}'\,. \tag{69}$$

The equation for $\mathbf{W}'$ may now be rearranged as follows:

$$\begin{aligned}
\mathbf{W}' &= \mathbf{Q}\mathbf{V}'\mathbf{Q}^T + \mathbf{Q}'(\mathbf{Q}^T\mathbf{Q})\mathbf{V}\mathbf{Q}^T + \mathbf{Q}\mathbf{V}(\mathbf{Q}^T\mathbf{Q})\mathbf{Q}^{T'} \\
&= \mathbf{Q}\mathbf{V}'\mathbf{Q}^T + \mathbf{Q}'\mathbf{Q}^T\mathbf{W} + \mathbf{W}\mathbf{Q}\mathbf{Q}^{T'} \\
&= \mathbf{Q}\mathbf{V}'\mathbf{Q}^T + \mathbf{Q}'\mathbf{Q}^T\mathbf{W} - \mathbf{W}\mathbf{Q}'\mathbf{Q}^T\,.
\end{aligned} \tag{70}$$

Therefore

$$\text{tr}(\mathbf{N}\mathbf{W}') = \text{tr}(\mathbf{N}\mathbf{Q}\mathbf{V}'\mathbf{Q}^T) + \text{tr}(\mathbf{N}\mathbf{Q}'\mathbf{Q}^T\mathbf{W} - \mathbf{N}\mathbf{W}\mathbf{Q}'\mathbf{Q}^T)$$

$$\begin{aligned}
&= \text{tr}(\mathbf{N}\mathbf{Q}\mathbf{V}'\mathbf{Q}^T) + \text{tr}(\mathbf{N}\mathbf{Q}'\mathbf{Q}^T\mathbf{W} - \mathbf{W}\mathbf{N}\mathbf{Q}'\mathbf{Q}^T) \\
&= \text{tr}(\mathbf{N}\mathbf{Q}\mathbf{V}'\mathbf{Q}^T) + \text{tr}\left[\mathbf{N}\mathbf{Q}'\mathbf{Q}^T, \mathbf{W}\right] \\
&= \text{tr}(\mathbf{N}\mathbf{Q}\mathbf{V}'\mathbf{Q}^T),
\end{aligned} \tag{71}$$

where the square bracketed expression is a matrix commutator whose trace is therefore zero. (We may go even further than this last equation by noting that, since $\mathbf{N}$ is an arbitrary constant matrix, it follows that $\mathbf{W}'$ is equal to the diagonal part of $\mathbf{Q}\mathbf{V}'\mathbf{Q}^T$.)

Writing our result now in full we have

$$\frac{\partial \mathcal{E}}{\partial x_i^{(\lambda\kappa)}} = \text{tr}\left(\mathbf{N}\mathbf{Q}\frac{\partial \mathbf{V}}{\partial x_i^{(\lambda\kappa)}}\mathbf{Q}^T\right). \tag{72}$$

1.6 Evaluation of the First Derivatives

The CLFSE part of the calculational task of the molecular mechanics method now consists of finding $\mathbf{V}$, diagonalizing it to give the eigenvalues, w_a; using these with $\mathbf{N}$ to give the energy $\mathcal{E}$; using the eigenvectors to construct $\mathbf{Q}$; finding $\mathbf{V}'$ and then using (72) to give $\mathcal{E}'$ for each atomic coordinate.

At this point we demonstrate a useful general result. We note from the relative coordinate definitions (46) and the subsequent formulae for the parts of the ligand field matrix, that the CLFSE may be written as a function of all the atomic positions relative to the metal position. Formally, this is

$$\mathcal{E} = \mathcal{R}(r_i^{(\lambda\kappa)}), \tag{73}$$

where $r_i^{(\lambda\kappa)} \equiv x_i^{(\lambda\kappa)} - x_i^0$; $\lambda = 1,\ldots,L$; $\kappa = 0,1,\ldots,K_\lambda$; and $i = 1,2,3$. Using the chain rule of partial differentiation on this last equation gives us

$$\begin{aligned}
\frac{\partial \mathcal{E}}{\partial x_i^{(0)}} &= \sum_{\lambda\kappa}\sum_j \frac{\partial \mathcal{R}}{\partial r_j^{(\lambda\kappa)}}\frac{\partial r_j^{(\lambda\kappa)}}{\partial x_i^{(0)}} \\
&= \sum_{\lambda\kappa}\sum_j \frac{\partial \mathcal{R}}{\partial r_j^{(\lambda\kappa)}}(-\delta_{ji}) \\
&= -\sum_{\lambda\kappa} \frac{\partial \mathcal{E}}{\partial x_i^{(\lambda\kappa)}}.
\end{aligned} \tag{74}$$

Another useful point to note is that, since the parts $\mathbf{V}^\sigma$, $\mathbf{V}^{\pi x}$, $\mathbf{V}^{\pi y}$ and $\mathbf{b}$ consist of sums over the main ligand atom index λ, the derivatives with respect to a coordinate of any atom in the ligand group annihilates the terms from all other main ligand groups.

With these last two simplifications in mind one may come to the details of finding the derivatives of individual parts of the ligand field matrix for which formulae were developed above. Beginning with $\mathbf{V}^{\sigma(\lambda)}$ from (48), we use the Leibniz product rule, and derivatives of

$G_a^{(\sigma)}(\vec{r}^{(\lambda)})$ and $\left[e_\sigma(\lambda)/r^{(\lambda)4}\right]$ to construct the result. The former is easy since it is expressed in polynomial form (49). For the latter we have

$$\frac{\partial}{\partial x_i^{(\lambda)}}\left[\frac{e_\sigma(\lambda)}{r^{(\lambda)4}}\right] = \frac{d}{dr^{(\lambda)}}\left[\frac{e_\sigma(\lambda)}{r^{(\lambda)4}}\right]\frac{\partial r^{(\lambda)}}{\partial x_i^{(\lambda)}} = \frac{d}{dr^{(\lambda)}}\left[\frac{e_\sigma(\lambda)}{r^{(\lambda)4}}\right]\frac{x_i^{(\lambda)}}{r^{(\lambda)}}, \tag{75}$$

since $e_\sigma(\lambda)$ is a function of $r^{(\lambda)}$, via a typical parametrisation such as our own

$$e_\sigma(\lambda) = a_0 + a_1 r + a_2 r^{-2} + a_3 r^{-3} + a_4 r^{-4} + a_5 r^{-5} + a_6 r^{-6}. \tag{76}$$

Similar terms in the other parts of the ligand field matrix may be treated thus. In particular, the vector **b** from the d–s mixing term is quickly disposed of with a similar approach to the foregoing.

For the cylindrical π bonding term one may proceed, like the σ term just treated, from the expressions (52) and (53). One requires only the extra result for the derivative of the term involving $\rho^{(\lambda)}$. Thus,

$$\frac{\partial}{\partial x_i^{(\lambda)}}\left(\frac{1}{\rho^{(\lambda)2}}\right) = \left(-\frac{1}{\rho^{(\lambda)4}}\right)\frac{\partial}{\partial x_i^{(\lambda)}}\left(\rho^{(\lambda)2}\right) \tag{77}$$

and

$$\frac{\partial}{\partial x_i^{(\lambda)}}\left(\rho^{(\lambda)2}\right) = \left(2x_1^{(\lambda)}, 2x_2^{(\lambda)}, 0\right). \tag{78}$$

In the degenerate case, where $\rho^{(\lambda)} \to 0$, we again consider the full matrix $\mathbf{\Gamma}^{\pi(\lambda 0)}$, taking the appropriate derivatives (this being easy since the matrix elements are polynomials) and setting $x, y \to 0$.

In the cases involving subsidiary atoms, one must bear in mind that the dependence of the LF matrix expressions on the ligand atom positions and subsidiary atom positions is different. Thus, for one subsidiary atom, we have that, for example,

$$\frac{\partial}{\partial x_i^{(\lambda)}}\left(\vec{g}_a^{(x)}(\vec{r}^{(\lambda)}) \cdot \vec{s}^{(\lambda)}\right) = \sum_{j=1}^{3}\left(\frac{\partial}{\partial r_i^{(\lambda)}}g_{a,j}^{(x)}(\vec{r}^{(\lambda)})\right)s_j^{(\lambda)} - g_{a,i}^{(x)}(\vec{r}^{(\lambda)}), \tag{79}$$

but

$$\frac{\partial}{\partial x_i^{(\lambda 1)}}\left(\vec{g}_a^{(x)}(\vec{r}^{(\lambda)}) \cdot \vec{s}^{(\lambda)}\right) = g_{a,i}^{(x)}(\vec{r}^{(\lambda)}). \tag{80}$$

In this case we also require the term involving $\sigma^{(\lambda)}$, similar to (77), for which we have

$$\frac{\partial}{\partial x_i^{(\lambda)}}\left(\sigma^{(\lambda)2}\right) = 2\left(s^{(\lambda)2}r_i^{(\lambda)} - r^{(\lambda)2}s_i^{(\lambda)} - (\vec{s}^{(\lambda)} \cdot \vec{r}^{(\lambda)})(s_i^{(\lambda)} - r_i^{(\lambda)})\right), \tag{81}$$

and, for the subsidiary atom,

$$\frac{\partial}{\partial x_i^{(\lambda 1)}}\left(\sigma^{(\lambda)2}\right) = 2\left(r^{(\lambda)2}s_i^{(\lambda)} - (\vec{s}^{(\lambda)} \cdot \vec{r}^{(\lambda)})r_i^{(\lambda)}\right). \tag{82}$$

For the case of two subsidiary atoms it is useful to write the expressions (59) and (60) in Cartesian tensor form before evaluating the derivatives. In this way one is led to, for example,

$$\frac{\partial}{\partial x_i^{(\lambda)}} \left(\vec{h}_a^{(x)}(\vec{r}^{(\lambda)}) \cdot (\vec{s}^{(\lambda)} \times \vec{t}^{(\lambda)}) \right) = \sum_{j=1}^{3} \left(\frac{\partial}{\partial r_i^{(\lambda)}} h_{a,j}^{(x)}(\vec{r}^{(\lambda)}) \right) (\vec{s}^{(\lambda)} \times \vec{t}^{(\lambda)})_j + \left((\vec{s}^{(\lambda)} - \vec{t}^{(\lambda)}) \times \vec{h}_a^{(x)} \right)_i ; \tag{83}$$

while, for the two subsidiary atoms,

$$\frac{\partial}{\partial x_i^{(\lambda 1)}} \left(\vec{h}_a^{(x)}(\vec{r}^{(\lambda)}) \cdot (\vec{s}^{(\lambda)} \times \vec{t}^{(\lambda)}) \right) = \left(\vec{t}^{(\lambda)} \times \vec{h}_a^{(x)} \right)_i , \tag{84}$$

and

$$\frac{\partial}{\partial x_i^{(\lambda 2)}} \left(\vec{h}_a^{(x)}(\vec{r}^{(\lambda)}) \cdot (\vec{s}^{(\lambda)} \times \vec{t}^{(\lambda)}) \right) = - \left(\vec{s}^{(\lambda)} \times \vec{h}_a^{(x)} \right)_i . \tag{85}$$

For the term involving $\tau^{(\lambda)}$, we require the further expressions

$$\frac{\partial}{\partial x_i^{(\lambda 1)}} \left(\tau^{(\lambda)2} \right) = 2 \left(t^{(\lambda)2} r^{(\lambda)2} s_i^{(\lambda)} - (\vec{s}^{(\lambda)} \cdot \vec{t}^{(\lambda)}) r^{(\lambda)2} t_i^{(\lambda)} - \left((\vec{s}^{(\lambda)} \times \vec{t}^{(\lambda)}) \cdot \vec{r}^{(\lambda)} \right) (\vec{t}^{(\lambda)} \times \vec{r}^{(\lambda)})_i \right) , \tag{86}$$

$$\frac{\partial}{\partial x_i^{(\lambda 2)}} \left(\tau^{(\lambda)2} \right) = 2 \left(s^{(\lambda)2} r^{(\lambda)2} t_i^{(\lambda)} - (\vec{s}^{(\lambda)} \cdot \vec{t}^{(\lambda)}) r^{(\lambda)2} s_i^{(\lambda)} - \left((\vec{s}^{(\lambda)} \times \vec{t}^{(\lambda)}) \cdot \vec{r}^{(\lambda)} \right) (\vec{r}^{(\lambda)} \times \vec{s}^{(\lambda)})_i \right) , \tag{87}$$

and, finally,

$$\begin{aligned}
\frac{\partial}{\partial x_i^{(\lambda)}} \left(\tau^{(\lambda)2} \right) &= 2 \left(s^{(\lambda)2} t^{(\lambda)2} r_i^{(\lambda)} - (\vec{s}^{(\lambda)} \cdot \vec{t}^{(\lambda)})^2 r_i^{(\lambda)} - \left((\vec{s}^{(\lambda)} \times \vec{t}^{(\lambda)}) \cdot \vec{r}^{(\lambda)} \right) (\vec{s}^{(\lambda)} \times \vec{t}^{(\lambda)})_i \right) \\
&\quad - \frac{\partial}{\partial x_i^{(\lambda 1)}} \left(\tau^{(\lambda)2} \right) - \frac{\partial}{\partial x_i^{(\lambda 2)}} \left(\tau^{(\lambda)2} \right) .
\end{aligned} \tag{88}$$

References

[1] Schäffer, C.E., and Jørgensen, C.K., 1965, *Molecular Physics*, **9**, 401.

[2] Rose, M.E., 1957, *Elementary Theory of Angular Momentum* (New York: Wiley).

[3] Figgis, B.N., and Hitchman, M.A., 2000, *Ligand Field Theory and Its Applications* (New York: Wiley-VCH)

[4] Smith, D.W., 1977, *Inorganica Chimica Acta*, **22**, 107.

[5] Ceulemans, A., Beyens, D., and Vanquickenborne, L.G., 1982, *Inorganica Chimica Acta*, **61**, 199.

[6] Burton, V.J., Deeth, R.J., Kemp, C.M., and Gilbert, P.J., 1995, *J. Am. Chem. Soc.*, **117**, 8407.

[7] Riley, M.J., 1998, *Inorganica Chimica Acta*, **268**, 55.

[8] Rodger, P.M., 1999, pers. comm.