JOURNAL OF MAGNETIC RESONANCE **40**, 115–133 (1980)

The Theory of the Pseudocontact Contribution to NMR Shifts of d^1 and d^2 Transition Metal Ion Systems in Sites of Octahedral Symmetry

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Received October 12, 1979

This paper is an extension of our work in the evaluation of NMR shifts in paramagnetic transition metal ions using a non-multipole expansion technique. For the first time we present the NMR shifts for a d^1 system without assuming a strong crystal field. This work requires the evaluation of a number of further matrix elements which complete the set required for any d^n system. A compact general expression has been developed to obtain analytical expressions for all the required matrix elements. Finally, the NMR shifts in a d^2 system in a strong crystal field of octahedral symmetry are determined and the effect of configurational mixing is examined in detail.

INTRODUCTION

In recent years increasing attention has been focused on the theoretical evaluation of the NMR shifts in paramagnetic systems that arise from the electron-nuclear interaction represented by the theoretical Hamiltonian

$$\mathcal{H} = \frac{\mu_0}{4\pi} g_N \mu_B \mu_N \sum_{i=1}^{n} \left[g_s \left(\frac{3(\mathbf{r}_{Ni} \cdot \mathbf{s}_i)\mathbf{l}_{Ni} \cdot \mathbf{I}}{r_{Ni}^5} - \frac{\mathbf{s}_i \cdot \mathbf{I}}{r_{Ni}^3} \right) + \frac{2\mathbf{l}_{Ni} \cdot \mathbf{I}}{r_{Ni}^3} \right]. \qquad [1]$$

In Eq. [1], $\mathbf{r}_{Ni}$ is the radius vector of the ith electron about a nucleus, say N, with nuclear spin angular momentum $\mathbf{I}$, $\mathbf{l}_{Ni}$ is its orbital angular momentum about this nucleus, N, g_s is the free-electron Landé splitting factor (which for the purposes of this paper we shall take equal to 2 exactly), and the other terms have their usual meanings. Buckingham and Stiles (*1*) used a multipole expansion approach to evaluate the NMR shifts, which is a significant improvement on the results gained using the point–dipole approximation (*2, 3*). The multipole expansion results are valid for $R > 0.2$ nm, the point–dipole approximation results for $R > 0.3$ nm. ($\mathbf{R}$ is the vector pointing from the NMR nucleus to the electron-bearing nucleus, as shown in Fig. 1.) Recently (*4, 5*) we gave a method of evaluating the contribution from [1] to the NMR shift which is valid for all distances R, thus overcoming the limitations of the aforementioned results (*1–3*). In the first paper (*4*), we treated a d^1 system in a strong crystal field environment, where the crystal field was of octahedral, tetragonal,

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0022-2364/80/100115-19$02.00/0

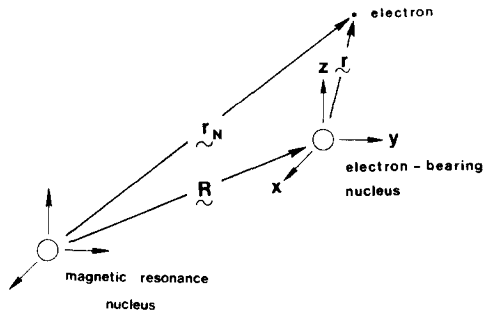

FIG. 1. The coordinate system.

or trigonal symmetry. In the second (*5*), ligand field effects were considered for a d^1 system in a strong crystal field of octahedral symmetry.

In this paper we present calculations for a d^1 system in a crystal field of octahedral symmetry, the condition of strong field coupling having been removed, and for a d^2 system in a strong crystal field of octahedral symmetry. The effect of Coulomb repulsion mixing is incorporated in the latter case. Results for the d^1 system have previously been given by Stiles (*6*), using the multipole expansion approach, and by Golding *et al.* (*7*), who treated the special case with **R** along the z axis, although they were able to infer from their results the multiple expansion results valid for sufficiently large R.

THEORY

In calculating the contribution from [1] to the NMR shift, a crystal field approach was adopted and the eigenfunctions and eigenvalues of the appropriate theoretical Hamiltonian were calculated. The principal values σ_{xx}, σ_{yy}, and σ_{zz} of the nuclear shielding tensor $\boldsymbol{\sigma}$ were determined by considering the magnetic field interaction as parallel to the x, y, and z directions and averaged assuming a Boltzmann distribution. The contribution from [1] to the NMR shift, ΔB, is given by

$$\Delta B = \tfrac{1}{3}B(\sigma_{xx} + \sigma_{yy} + \sigma_{zz}),$$

where

$$\sigma_{\alpha\beta} = \left(\frac{\partial^2\langle\mathscr{H}\rangle}{\partial\mu_\alpha\,\partial B_\beta}\right)_{\boldsymbol{\mu}=\mathbf{B}=\mathbf{0}},$$

where

$$\boldsymbol{\mu} = g_{\mathrm{N}}\mu_{\mathrm{N}}\mathbf{I},$$

and $\mathscr{H}$ is the Hamiltonian given in Eq. [1]. Slater-type $3d$ orbitals were chosen, defined by

$$|\xi\rangle = (2\beta^7/3\pi)^{1/2} yz\, e^{-\beta r},$$
$$|\eta\rangle = (2\beta^7/3\pi)^{1/2} zx\, e^{-\beta r},$$

$$|\zeta\rangle = (2\beta^7/3\pi)^{1/2} xy\, e^{-\beta r},$$
$$|\theta\rangle = (\beta^7/18\pi)^{1/2}(3z^2 - r^2)\, e^{-\beta r},$$
$$|\varepsilon\rangle = (\beta^7/6\pi)^{1/2}(x^2 - y^2)\, e^{-\beta r}.$$

This NMR shift ΔB, is referred to as the pseudocontact shift.

In calculating ΔB, molecular hyperfine integrals in addition to those given by us in Ref. (*4*) had to be evaluated. In the process of evaluating these integrals using the method given in Ref. (*4*), we developed a more streamlined method for evaluating the integrals of the Hamiltonian

$$\mathcal{H} = \frac{\mu_0}{4\pi} g_s g_N \mu_B \mu_N \left\{ \frac{3(\mathbf{r}_N \cdot \mathbf{s})\mathbf{r}_N \cdot \mathbf{I}}{r_N^5} - \frac{\mathbf{s} \cdot \mathbf{I}}{r_N^3} \right\}. \quad [2]$$

Equation [2] may be expressed in dyadic notation as

$$\mathcal{H} = \frac{\mu_0}{4\pi} g_s g_N \mu_B \mu_N \mathbf{s} \cdot \mathbf{T} \cdot \mathbf{I},$$

where

$$T_{\alpha\beta} = (3 r_{N\alpha} r_{N\beta} - r_N^2 \delta_{\alpha\beta})/r_N^5,$$

which may be expressed as

$$T_{\alpha\beta} = \sum_{M=-2}^{2} C_{\alpha\beta}^{(M)} Y_{2M}(\theta_N, \phi_N)/r_N^3.$$

A master formula was developed for the integrals,

$$\langle \psi_{2m'}(\mathbf{r}) | Y_{2M}(\theta_N, \phi_N)/r_N^3 | \psi_{2m}(\mathbf{r}) \rangle, \quad [3]$$

where $|\psi_{2m}(\mathbf{r})\rangle$ and $|\psi_{2m'}(\mathbf{r})\rangle$ are $3d$ Slater-type orbitals defined by

$$|\psi_{2m}(\mathbf{r})\rangle = (8\beta^7/45)^{1/2} r^2\, e^{-\beta r} Y_{2m}(\theta, \phi).$$

A general expression was derived by setting up in quite general terms the expression for the above integral, [3], and then extracting the coefficients of the various radial integrals $u_n(t)$, $v_n(t)$, $w_n(t)$, $x_n(t)$, and $y_n(t)$ (where $t = 2\beta R$) defined in Ref. (*4*). The general expression is

$$\langle \psi_{2m'}(\mathbf{r}) | Y_{2M}(\theta_N, \phi_N)/r_N^3 | \psi_{2m}(\mathbf{r}) \rangle = C_6 S_1 Y_{6q}(\Theta, \Phi) + C_4 F(\mu) Y_{4q}(\Theta, \Phi) + C_2 T(\mu', \lambda') Y_{2q}(\Theta, \Phi) + C_0 N_1 Y_{0q}(\Theta, \Phi),$$

where

$$q = M - m' + m,$$
$$S_1 = [5u_2 + 20v_3 + 30w_4 + 20x_5 + 5y_6],$$
$$F(\mu) = [5u_2 + (20 - A)v_1 + Av_3 + (30 - B)w_2 + Bw_4 + (20 - C)x_3 + Cx_5 + 5y_4],$$

where

$$A=\mu, \qquad B=(1/7)(10\mu-45), \qquad C=(1/9)(5\mu-30),$$

$$T(\mu',\lambda')=[5u_2+(20-A')v_1+A'v_3+(30-B'-C')w_0+B'w_2$$
$$+C'w_4+(20-A')x_1+A'x_3+5y_2],$$

where

$$A'=\mu', \qquad B'=(10/3)(\mu'-\lambda'+1), \qquad C'=\lambda',$$

and

$$N_1=[5u_2+14v_1+6v_3+(5/3)(7w_0+11w_2)+20x_1+5y_0].$$

The seven unknowns C_6, C_4, C_2, C_0, μ, μ', and λ' are determined from

$$\text{coefficient of } u_2(t)=\tfrac{8}{45}\pi Y^*_{2m'}(\Theta,\Phi)Y_{2M}(\Theta,\Phi)Y_{2m}(\Theta,\Phi);$$

$$\text{coefficient of } v_1(t)=\tfrac{16}{9}\pi\sum_{\mu=-1}^{1}\begin{pmatrix}2 & 1 & 1\\ M & -M-\mu & \mu\end{pmatrix}\Bigg\{(-1)^{M+m+\mu}\begin{pmatrix}2 & 1 & 1\\ -m & m-\mu & \mu\end{pmatrix}$$
$$\times Y^*_{2m'}(\Theta,\Phi)Y_{1,m-\mu}(\Theta,\Phi)Y_{1,M+\mu}(\Theta,\Phi)+(-1)^{M+m'}$$
$$\times\begin{pmatrix}2 & 1 & 1\\ m' & -m'-\mu & \mu\end{pmatrix}Y^*_{1,m'+\mu}(\Theta,\Phi)Y_{2m}(\Theta,\Phi)Y_{1,M+\mu}(\Theta,\Phi)\Bigg\};$$

$$\text{coefficient of } w_0(t)=\frac{2}{9(5)^{1/2}}\begin{pmatrix}2 & 2 & 0\\ M & m & 0\end{pmatrix}Y^*_{2m'}(\Theta,\Phi)+(-1)^M\frac{2}{9(5)^{1/2}}\begin{pmatrix}2 & 2 & 0\\ M & -m' & 0\end{pmatrix}$$
$$\times Y_{2m}(\Theta,\Phi)+\frac{40}{9}\left(\frac{2\pi}{3}\right)^{1/2}\sum_{\mu=-1}^{1}(-1)^{m+m'+\mu}$$
$$\times\begin{pmatrix}2 & 1 & 1\\ -m & M+m+\mu & -M-\mu\end{pmatrix}\begin{pmatrix}2 & 1 & 1\\ M & \mu & -M-\mu\end{pmatrix}$$
$$\times\begin{pmatrix}2 & 1 & 1\\ m' & -m'-\mu & \mu\end{pmatrix}Y^*_{1,m'+\mu}(\Theta,\Phi)Y_{1,M+m+\mu}(\Theta,\Phi).$$

As an example $\langle\psi_{20}(\mathbf{r})|Y_{20}(\theta_N,\phi_N)|r_N^3|\psi_{20}(\mathbf{r})\rangle$ is evaluated. The coefficient of $u_2(t)$ is $(8\pi/45)Y^3_{20}(\Theta,\Phi)$, which is equal to

$$\frac{4}{77}\left(\frac{5}{13}\right)^{1/2}Y_{60}(\Theta,\Phi)+\frac{8}{77(5)^{1/2}}Y_{40}(\Theta,\Phi)+\frac{2}{21}Y_{20}(\Theta,\Phi)+\frac{4}{63(5)^{1/2}}Y_{00}(\Theta,\Phi),$$

from which it follows that $C_6=4/(77(65)^{1/2})$, $C_4=8/(385(5)^{1/2})$, $C_2=2/105$, and $C_0=4/(315(5)^{1/2})$. The coefficient of $v_1(t)$ is

$$\frac{16}{105(5)^{1/2}}Y_{40}(\Theta,\Phi)+\frac{8}{35}Y_{20}(\Theta,\Phi)+\frac{8}{45(5)^{1/2}}Y_{00}(\Theta,\Phi)$$
$$=C_4\left[\frac{22}{3}\right]Y_{40}(\Theta,\Phi)+C_2[12]Y_{20}(\Theta,\Phi)+C_0[14]Y_{00}(\Theta,\Phi),$$

from which it follows that $\mu = 38/3$ and $\mu' = 8$. Finally, the coefficient of $w_0(t)$ is

$$\frac{8}{45} Y_{20} + \frac{4}{27(5)^{1/2}} Y_{00} = C_2\left[\frac{28}{3}\right] Y_{20}(\Theta, \Phi) + C_0\left[\frac{35}{3}\right] Y_{00}(\Theta, \Phi),$$

whence $\lambda' = 4$. This completes the evaluation of the integral.

RESULTS

(a) d^1 System, Crystal Field of Octahedral Symmetry

For a d^1 transition metal ion in a crystal field of octahedral symmetry, the theoretical Hamiltonian representing the various interactions we need consider is given by

$$\mathscr{H} = -\frac{\hbar^2\nabla^2}{2m_e} - \frac{Ze^2}{r} + \zeta\mathbf{l}\cdot\mathbf{s} + V(\mathbf{r}) + \mu_B(\mathbf{l}+2\mathbf{s})\cdot\mathbf{B} + \mathscr{H}_{\text{hyperfine}},$$

where $V(\mathbf{r})$ is the crystal field term, the strength of which is defined by the crystal field parameter Δ; $\mathscr{H}_{\text{hyperfine}}$ is the Hamiltonian of Eq. [1]; and the other terms have their usual meanings. Results are given for the contribution to the NMR shift for two cases, namely, (i) $\Delta = 0$; and (ii) $\Delta \neq 0$.

(i) Zero Crystal Field

When there is zero crystal field present, the ^2D ground-state level is split by spin–orbit coupling into two levels with J values of $\frac{5}{2}$ and $\frac{3}{2}$ and with eigenvalues of ζ and $-\frac{3}{2}\zeta$, respectively. The contribution to the NMR shift is given by[1]

$$\frac{\Delta B}{B} = -\frac{2}{75}\frac{\mu_0}{4\pi}\frac{\mu_B^2}{kT}\frac{[K_0 + G_0\exp(5\zeta/2kT) + M_0\{1-\exp(5\zeta/2kT)\}kT/\zeta]}{3+2\exp(5\zeta/2kT)},$$

where

$$K_0 = 36\beta^3 e^{-t}\left(\frac{t^4}{108} + \frac{t^3}{3!} + \frac{t^2}{2!} + t + 1\right),$$

$$G_0 = 16\beta^3 e^{-t}\left(-\frac{t^4}{72} + \frac{t^3}{3!} + \frac{t^2}{2!} + t + 1\right),$$

$$M_0 = \frac{4}{5}\beta^3 e^{-t}\left(\frac{t^4}{18} + \frac{t^3}{3!} + \frac{t^2}{2!} + t + 1\right),$$

where $t = 2\beta R$. The condition of zero crystal field is reflected by the absence of any angular dependence of the final result for $\Delta B/B$. This must be so since in this case the system is isotropic.

[1] This result was previously given by Golding *et al.* (*7*), and is given here for completeness. Note that in their Eq. [*6*], B_0 is in error and should be

$$B_0 = -\frac{\exp(-2\alpha)}{5R^3}\left(\frac{32\alpha^7}{27} + \frac{16\alpha^6}{9} + \frac{8\alpha^5}{3} + \frac{8\alpha^4}{3} + \frac{4\alpha^3}{3}\right).$$

The NMR shift for $\mathbf{R}=\mathbf{0}$ is readily determined from the above. As $R\to 0$,

$$\frac{\Delta B}{B}\to -\frac{2}{5}\langle r^{-3}\rangle\frac{\mu_0}{4\pi}\frac{\mu_B^2}{kT}\frac{[36+16\exp(5\zeta/2kT)+\frac{4}{5}\{1-\exp(5\zeta/2kT)\}kT/\zeta]}{3+2\exp(5\zeta/2kT)},$$

where $\langle r^{-3}\rangle=\beta^3/15$.

(ii) Nonzero Crystal Field

For the case of nonzero crystal field, the contribution to the NMR shift is given by

$$\frac{\Delta B}{B}=\frac{2}{3}\frac{\mu_0}{4\pi}\frac{\mu_B^2}{kT}\frac{\sum_{i=1}^{3}(A_i+B_ikT)\exp(-\varepsilon_i/kT)}{\sum_{i=1}^{3}\rho_i\exp(-\varepsilon_i/kT)},$$

where

$$\rho_1=\rho_2=2 \qquad \text{and} \qquad \rho_3=1,$$

$$\varepsilon_1=-\frac{\zeta}{4}+\frac{\Delta}{10}+\frac{X}{2},$$

$$\varepsilon_2=-\frac{\zeta}{4}+\frac{\Delta}{10}-\frac{X}{2},$$

$$\varepsilon_3=\zeta-\tfrac{2}{5}\Delta,$$

and

$$X^2=\tfrac{25}{4}\zeta^2+\Delta\zeta+\Delta^2.$$

We shall express A_i and B_i using matrix notation. If we define

$$a^2=\frac{1}{2}+\frac{1}{2}\left(\frac{5}{2}\zeta+\frac{\Delta}{5}\right)X^{-1},$$

$$b^2=\frac{1}{2}-\frac{1}{2}\left(\frac{5}{2}\zeta+\frac{\Delta}{5}\right)X^{-1},$$

$$ab=-\frac{6^{1/2}}{5}\Delta X^{-1},$$

we may then define matrices $g_m^{(i)}$ and $h_m^{(i)}$ as shown in Tables 1 and 2, respectively. A_i and B_i are given by

$$A_i=\tfrac{1}{75}\sum_{m=1}^{5}a_m g_m^{(i)}, \qquad i=1,2,$$

$$A_3=\tfrac{1}{3}(A_0+2B_0-2E_0),$$

$$B_i=\tfrac{1}{75}\sum_{m=1}^{6}b_m h_m^{(i)}, \qquad i=1,2,3,$$

TABLE 1

THE MATRIX ELEMENTS $g_m^{(i)}$

m	$i=1$	$i=2$
1	a^4	b^4
2	$(6)^{1/2}a^3b$	$-(6)^{1/2}b^3a$
3	a^2b^2	b^2a^2
4	$-(6)^{1/2}ab^3$	$(6)^{1/2}ba^3$
5	b^4	a^4

where the coefficients a_m and b_m are given by

$$\begin{pmatrix} a_1 \\ a_2 \\ a_3 \\ a_4 \\ a_5 \end{pmatrix} = \begin{pmatrix} -32 & 44 & -12 & -36 & 4 & -132 \\ -\frac{82}{3} & \frac{124}{3} & -4 & 18 & \frac{44}{3} & -14 \\ -8 & 26 & 22 & 36 & 46 & 212 \\ -19 & 28 & -4 & 28 & 8 & -4 \\ 18 & -36 & -12 & 24 & -36 & -72 \end{pmatrix} \begin{pmatrix} A_0 \\ B_0 \\ C_0 \\ D_0 \\ E_0 \\ F_0 \end{pmatrix},$$

$$\begin{pmatrix} b_1 \\ b_2 \\ b_3 \\ b_4 \\ b_5 \\ b_6 \end{pmatrix} = \begin{pmatrix} -14 & 8 & 1 & -12 & -32 & -4 \\ -16 & 52 & 94 & 72 & 92 & 824 \\ \frac{139}{3} & -\frac{208}{3} & 8 & -46 & -\frac{68}{3} & 18 \\ 20 & 40 & -30 & 0 & 80 & 120 \\ \frac{35}{3} & \frac{70}{3} & \frac{15}{2} & 0 & \frac{140}{3} & -30 \\ 5 & 10 & 5 & 0 & 20 & -20 \end{pmatrix} \begin{pmatrix} A_0 \\ B_0 \\ C_0 \\ D_0 \\ E_0 \\ F_0 \end{pmatrix},$$

TABLE 2

THE MATRIX ELEMENTS $h_m^{(i)}$

m	$i=1$	$i=2$	$i=3$
1	$\frac{a^4+b^4}{\varepsilon_1-\varepsilon_2}$	$\frac{b^4+a^4}{\varepsilon_2-\varepsilon_1}$	0
2	$\frac{a^2b^2}{\varepsilon_1-\varepsilon_2}$	$\frac{b^2a^2}{\varepsilon_2-\varepsilon_1}$	0
3	$\frac{(6)^{1/2}ab^3-(6)^{1/2}a^3b}{\varepsilon_1-\varepsilon_2}$	$\frac{(6)^{1/2}ab^3-(6)^{1/2}a^3b}{\varepsilon_2-\varepsilon_1}$	0
4	$\frac{a^2}{\varepsilon_1-\varepsilon_3}$	$\frac{b^2}{\varepsilon_2-\varepsilon_3}$	$\frac{a^2}{\varepsilon_3-\varepsilon_1}+\frac{b^2}{\varepsilon_3-\varepsilon_2}$
5	$\frac{(6)^{1/2}ab}{\varepsilon_1-\varepsilon_3}$	$-\frac{(6)^{1/2}ab}{\varepsilon_2-\varepsilon_3}$	$\frac{(6)^{1/2}ab}{\varepsilon_3-\varepsilon_1}-\frac{(6)^{1/2}ab}{\varepsilon_3-\varepsilon_2}$
6	$\frac{b^2}{\varepsilon_1-\varepsilon_3}$	$\frac{a^2}{\varepsilon_2-\varepsilon_3}$	$\frac{b^2}{\varepsilon_3-\varepsilon_1}+\frac{a^2}{\varepsilon_3-\varepsilon_2}$

and the six functions A_0, B_0, C_0, D_0, E_0, and F_0 which are functions of the vector $\mathbf{R}$ are defined in terms of the molecular hyperfine integrals by

$$A_0(\mathbf{R}) = \langle\xi|T_{xx}|\xi\rangle + \langle\eta|T_{yy}|\eta\rangle + \langle\zeta|T_{zz}|\zeta\rangle,$$

$$B_0(\mathbf{R}) = \langle\xi|T_{xy}|\eta\rangle + \langle\eta|T_{yz}|\zeta\rangle + \langle\zeta|T_{zx}|\xi\rangle,$$

$$C_0(\mathbf{R}) = 3^{1/2}\langle\eta|T_{zx}|\theta\rangle + 3^{1/2}\langle\xi|T_{yz}|\theta\rangle - 2(3)^{1/2}\langle\zeta|T_{xy}|\theta\rangle + 3\langle\eta|T_{zx}|\varepsilon\rangle - 3\langle\xi|T_{yz}|\varepsilon\rangle,$$

$$D_0(\mathbf{R}) = \frac{3}{4}\langle\varepsilon|T_{zz}|\varepsilon\rangle - \frac{3}{4}\langle\theta|T_{zz}|\theta\rangle + \frac{3^{1/2}}{2}\langle\theta|T_{xx}|\varepsilon\rangle - \frac{3^{1/2}}{2}\langle\theta|T_{yy}|\varepsilon\rangle,$$

$$E_0(\mathbf{R}) = i[\langle\zeta|l_{Nx}/r_N^3|\eta\rangle + \langle\xi|l_{Ny}/r_N^3|\zeta\rangle + \langle\eta|l_{Nz}/r_N^3|\xi\rangle],$$

$$F_0(\mathbf{R}) = i\left[\frac{3^{1/2}}{2}\langle\xi|l_{Nx}/r_N^3|\theta\rangle + \frac{1}{2}\langle\xi|l_{Nx}/r_N^3|\varepsilon\rangle - \frac{3^{1/2}}{2}\langle\eta|l_{Ny}/r_N^3|\theta\rangle + \frac{1}{2}\langle\eta|l_{Ny}/r_N^3|\varepsilon\rangle - \langle\zeta|l_{Nz}/r_N^3|\varepsilon\rangle\right].$$

The molecular hyperfine integrals for A_0, B_0, and E_0 were given by us in Ref. (*4*); those for C_0, D_0, and F_0 are listed in Appendix B. In terms of their specific radial and angular dependences, these six functions are given by

$$A_0(\mathbf{R}) = -\frac{32}{385}\left(\frac{\pi}{26}\right)^{1/2} Z_6(\Theta, \Phi)S_1(R) + \frac{16}{825}\left(\frac{\pi}{21}\right)^{1/2} Z_4(\Theta, \Phi)F_7(R) - \frac{16\pi^{1/2}}{525} Z_0(\Theta, \Phi)N_1(R),$$

$$B_0(\mathbf{R}) = -\frac{32}{385}\left(\frac{\pi}{26}\right)^{1/2} Z_6(\Theta, \Phi)S_1(R) - \frac{24}{275}\left(\frac{\pi}{21}\right)^{1/2} Z_4(\Theta, \Phi)F_{12}(R) + \frac{4\pi^{1/2}}{175} Z_0(\Theta, \Phi)N_1(R),$$

$$C_0(\mathbf{R}) = \frac{96}{385}\left(\frac{\pi}{26}\right)^{1/2} Z_6(\Theta, \Phi)S_1(R) - \frac{16}{275}\left(\frac{\pi}{21}\right)^{1/2} Z_4(\Theta, \Phi)F_{23}(R) + \frac{16\pi^{1/2}}{175} Z_0(\Theta, \Phi)N_1(R),$$

$$D_0(\mathbf{R}) = \frac{24}{385}\left(\frac{\pi}{26}\right)^{1/2} Z_6(\Theta, \Phi)S_1(R) - \frac{48}{275}\left(\frac{\pi}{21}\right)^{1/2} Z_4(\Theta, \Phi)F_{12}(R) - \frac{16\pi^{1/2}}{525} Z_0(\Theta, \Phi)N_1(R),$$

$$E_0(\mathbf{R}) = -\frac{8}{15}\left(\frac{\pi}{21}\right)^{1/2} Z_4(\Theta, \Phi)f_1(R) + \frac{4\pi^{1/2}}{15} Z_0(\Theta, \Phi)\, n_1(R),$$

$$F_0(\mathbf{R}) = \frac{4}{15}\left(\frac{\pi}{21}\right)^{1/2} Z_4(\Theta, \Phi)f_1(R) + \frac{8\pi^{1/2}}{15} Z_0(\Theta, \Phi)\, n_1(R).$$

The three functions Z_0, Z_4, and Z_6 have been defined as the appropriate combinations of the spherical harmonics $Y_{lm}(\Theta, \Phi)$ that transform as the irreducible representation A_1a_1 of group O for $l = 0$, 4, and 6:

$$Z_6(\Theta, \Phi) = \frac{7^{1/2}}{4} Y_{64}(\Theta, \Phi) - \frac{1}{2(2)^{1/2}} Y_{60}(\Theta, \Phi) + \frac{7^{1/2}}{4} Y_{6-4}(\Theta, \Phi)$$

$$Z_4(\Theta, \Phi) = \frac{1}{2}\left(\frac{5}{6}\right)^{1/2} Y_{44}(\Theta, \Phi) + \frac{1}{2}\left(\frac{7}{3}\right)^{1/2} Y_{40}(\Theta, \Phi) + \frac{1}{2}\left(\frac{5}{6}\right)^{1/2} Y_{4-4}(\Theta, \Phi)$$

$$Z_0(\Theta, \Phi) = Y_{00}(\Theta, \Phi).$$

The functions of radial dependence are given in Appendix A, with $F_7 = F(-24)$, $F_{12} = F(38/3)$, and $F_{23} = F(31)$.

(b) d^2 System, Octahedral Symmetry

For a d^2 system in a strong crystal field of octahedral symmetry the Hamiltonian

$$\mathcal{H} = \sum_{i=1}^{2} \left\{ -\frac{\hbar^2 \nabla_i^2}{2m_e} - \frac{Ze^2}{r_i} + V(\mathbf{r}_i) \right\} + \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|}$$

results in a $^3T_1$ ground state (*8*) whose relative energy for the t_2^2 configuration is given by

$$E(^3T_1) = -\tfrac{4}{5}\Delta + A - 5B,$$

where A and B are the Racah parameters and Δ is the crystal field parameter. (Mixing due to the Coulomb repulsion interaction between the $^3T_1$ state of the t_2^2 configuration and the $^3T_1$ state of the et_2 configuration is considered in Section (c).) The spin–orbit coupling interaction splits this $^3T_1$ term into three levels E_1, E_2, and E_3.

The pseudocontact contribution to the NMR shift is given by

$$\frac{\Delta B}{B} = \frac{2}{3} \frac{\mu_0}{4\pi} \frac{\mu_B^2}{kT} \frac{\sum_{i=1}^{3} (A_i + B_i kT/\zeta) \exp(-E_i/kT)}{\sum_{i=1}^{3} \rho_i \exp(-E_i/kT)},$$

where

$$E_1 = \zeta,$$
$$E_2 = \tfrac{1}{2}\zeta,$$
$$E_3 = -\tfrac{1}{2}\zeta,$$

$\rho_1 = 1$, $\rho_2 = 3$, $\rho_3 = 5$, and

$$A_1 = 0,$$
$$A_2 = \tfrac{1}{2}A_0 + B_0 + \tfrac{1}{2}E_0,$$
$$A_3 = -\tfrac{1}{2}A_0 - B_0 + \tfrac{5}{2}E_0,$$
$$B_1 = 4A_0 + 8B_0 + 8E_0,$$

$$B_2 = -6A_0 - 12B_0 - 3E_0,$$
$$B_3 = 2A_0 + 4B_0 - 5E_0,$$

where A_0, B_0, and E_0 are the functions of $\mathbf{R}$ defined above.

(c) d^2 System, Incorporating Coulomb Repulsion Mixing

The results given in the previous section for a d^2 system in a strong crystal field of octahedral symmetry were extended to incorporate mixing due to the Coulomb repulsion interaction between the $^3T_1$ state of the t_2^2 configuration and the $^3T_1$ state of the et_2 configuration. Wavefunctions of the form

$$|\psi\rangle = a|t_2^2:{}^3T_1\rangle + b|et_2:{}^3T_1\rangle$$

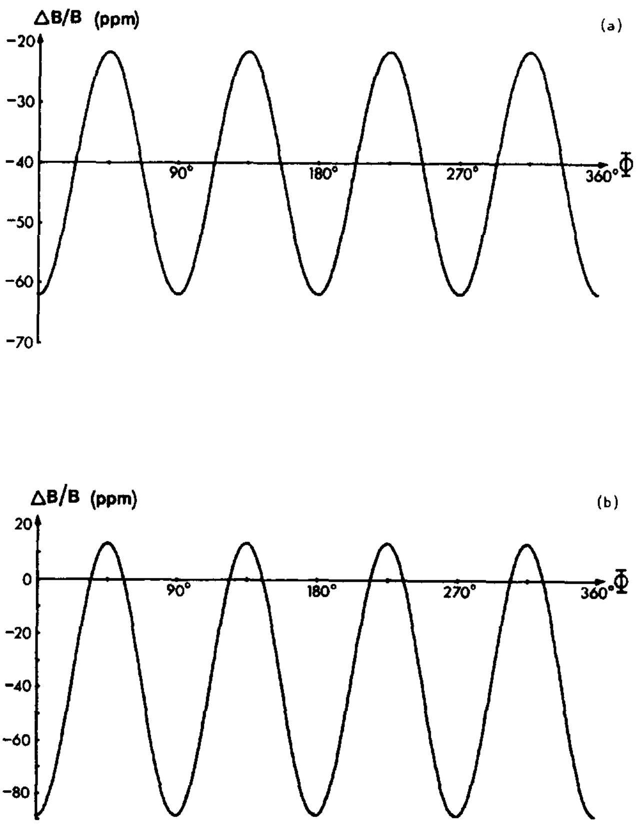

FIG. 2. The Φ dependence of $\Delta B/B$ (ppm) for a d^1 system in a crystal field of octahedral symmetry where (a) $\Delta = 500\ \text{cm}^{-1}$; and (b) $\Delta = 5000\ \text{cm}^{-1}$. The NMR nucleus is in the xy plane 0.2 nm from the d-electron-bearing nucleus ($T = 300\ K$).

TABLE 3

THE VARIATION OF THE NMR SHIFT WITH RESPECT TO THE CRYSTAL FIELD PARAMETER, Δ, FOR A d^1 SYSTEM IN A CRYSTAL FIELD OF OCTAHEDRAL SYMMETRY

Δ (cm^{-1})	$\Delta B/B$ (ppm) at $\Phi = 0°$	$\Delta B/B$ (ppm) at $\Phi = 45°$
0	−38.40	−38.40
250	−51.75	−31.40
500	−62.07	−21.63
750	−69.00	−13.23
1,000	−73.63	−6.97
1,500	−79.19	0.87
2,500	−84.36	8.01
5,000	−88.47	13.46
7,500	−89.86	15.22
10,000	−90.54	16.08
12,500	−90.95	16.56
15,000	−91.22	16.92
25,000	−91.75	17.58
50,000	−92.15	18.06

were used, with the coefficients a and b calculated from the matrix (*9*)

$^3T_1$	t_2^2	et_2
t_2^2	$A-5B-\frac{4}{5}\Delta$	$6B$
et_2	$6B$	$A+4B+\frac{1}{5}\Delta$

[4]

The spin–orbit coupling interaction splits the $^3T_1$ ground-state term into three levels with relative values for the energy of

$$E_1 = \zeta'',$$
$$E_2 = \tfrac{1}{2}\zeta'',$$
$$E_3 = -\tfrac{1}{2}\zeta'',$$

where

$$\zeta'' = (a^2 - 2ab - \tfrac{1}{2}b^2)\zeta.$$

The contribution to the shift is given by

$$\frac{\Delta B}{B} = \frac{2}{3}\frac{\mu_0}{4\pi}\frac{\mu_B^2}{kT}\frac{\sum_{i=1}^{3}\{A_i f(a,b) + B_i g(a,b)kT/\zeta''\}\exp(-E_i/kT)}{\sum_{i=1}^{3}\rho_i \exp(-E_i/kT)},$$

where $\rho_1 = 1$, $\rho_2 = 3$, $\rho_3 = 5$, and

$$f(a,b) = a^2 - \tfrac{2}{3}ab + \tfrac{1}{2}b^2,$$
$$g(a,b) = a^2 + 2ab + \tfrac{5}{2}b^2,$$

and

$$A_1 = 0,$$
$$A_2 = \tfrac{1}{2}k(a, b, \mathbf{R}) + \tfrac{1}{2}m(a, b, \mathbf{R}),$$
$$A_3 = -\tfrac{1}{2}k(a, b, \mathbf{R}) + \tfrac{5}{2}m(a, b, \mathbf{R}),$$
$$B_1 = 4k(a, b, \mathbf{R}) + 8m(a, b, \mathbf{R}),$$
$$B_2 = -6k(a, b, \mathbf{R}) - 3m(a, b, \mathbf{R}),$$
$$B_3 = 2k(a, b, \mathbf{R}) - 5m(a, b, \mathbf{R}),$$

where

$$k(a, b, \mathbf{R}) = a^2(A_0 + 2B_0) + abC_0 + b^2(-A_0 + B_0 - D_0),$$
$$m(a, b, \mathbf{R}) = a^2E_0 - abF_0 - \tfrac{1}{2}b^2E_0.$$

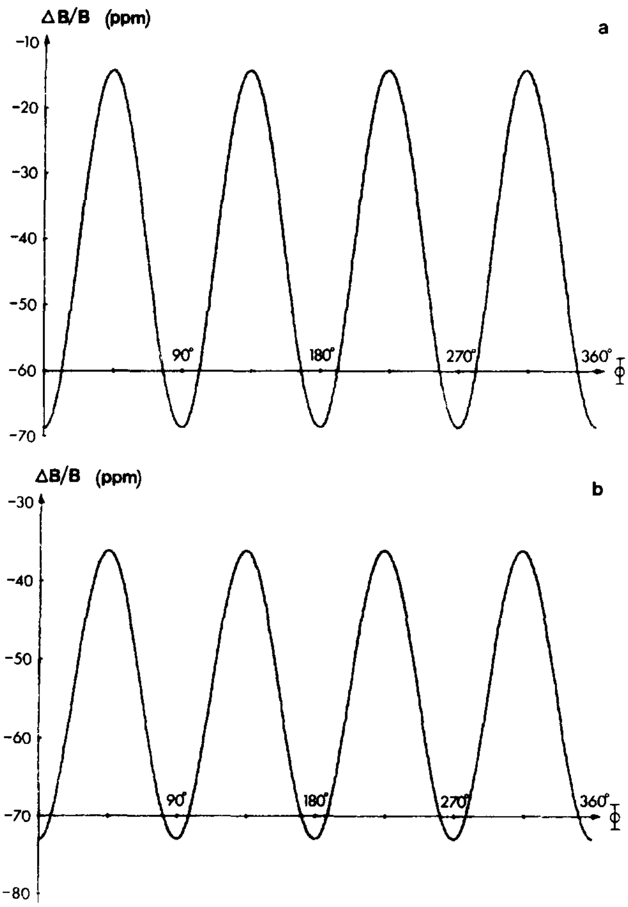

FIG. 3. The Φ dependence of $\Delta B/B$ (ppm) for a d^2 system in a strong crystal field of octahedral symmetry for the case when the NMR nucleus is in the xy plane 0.2 nm from the d-electron-bearing nucleus for the two cases: (a) t_2^2 configuration only; and (b) t_2^2 and et_2 configurations ($T = 300\ K$).

DISCUSSION

To illustrate the results for a d^1 system, $\Delta B/B$ is plotted in Fig. 2 as a function of the angle Φ for two values of the crystal field parameter Δ: $\Delta = 500\ \mathrm{cm}^{-1}$ and $\Delta = 5000\ \mathrm{cm}^{-1}$. The central metal ion is taken to lie in the xy plane 0.2 nm from the NMR nucleus. The case of a Ti^{3+} ion is considered, for which the value of the spin–orbit coupling constant, ζ (calculated from the appropriate spectroscopic data (*10*)), is $\zeta = 154\ \mathrm{cm}^{-1}$, and from Slater's rules $\beta = 4/(3a_0)$. In the xy plane $\Delta B/B$ has a sinusoidal dependence on Φ, varying between −62.07 and −21.63 ppm for $\Delta = 500\ \mathrm{cm}^{-1}$, and between −88.47 and 13.46 ppm for $\Delta = 5000\ \mathrm{cm}^{-1}$. Thus, for intermediate strengths of the crystal field, we see that there is a noticeable dependence of the NMR shift ΔB upon the crystal field parameter Δ. This is further shown in Table 3, where $\Delta B/B$ is given for a range of values of Δ. The central metal ion is once more

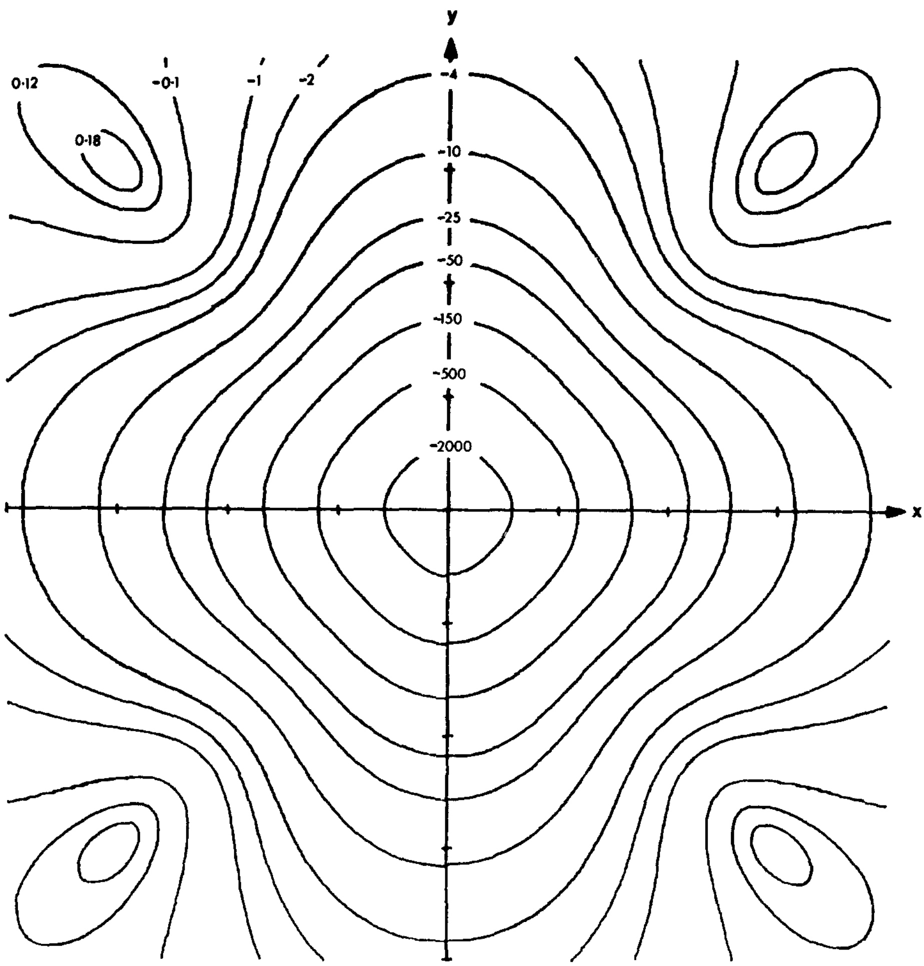

FIG. 4. The isoshielding diagram for a d^2 system (t_2^2 and et_2 configurations considered) for the case when the NMR nucleus lies in the xy plane. The scale on the axes is in units of 0.1 nm ($T = 300\ K$).

chosen to lie in the xy plane 0.2 nm from the NMR nucleus. The second column contains the minimum value of $\Delta B/B$ (at $\Phi = 0°$) and the third column the maximum (at $\Phi = 45°$). For values of Δ larger than 10,000 cm^{-1}, the change in the NMR shift with respect to Δ is slight.

To illustrate the results for the d^2 system, we consider the case of a V^{3+} ion, in which $\zeta = 210\ cm^{-1}$ (*10*) and $\beta = 1.55/a_0$. The quantity $\Delta B/B$ is plotted in Fig. 3 as a function of the angle Φ for the case when the central metal ion is in the xy plane 0.2 nm from the NMR nucleus. Figure 3a gives the results for the case when Coulomb repulsion mixing is ignored, Fig. 3b for the case when it is incorporated into the calculations. In the latter case the crystal field parameter Δ is taken to be 20,000 cm^{-1} and the value of the Racah parameter B as $B = 860\ cm^{-1}$(*9*). Diagonalizing the matrix [4] yielded values of $a = 0.9842$ and $b = -0.1771$ for the mixing coefficients. Even though the amount of mixing is quite small, a comparison of

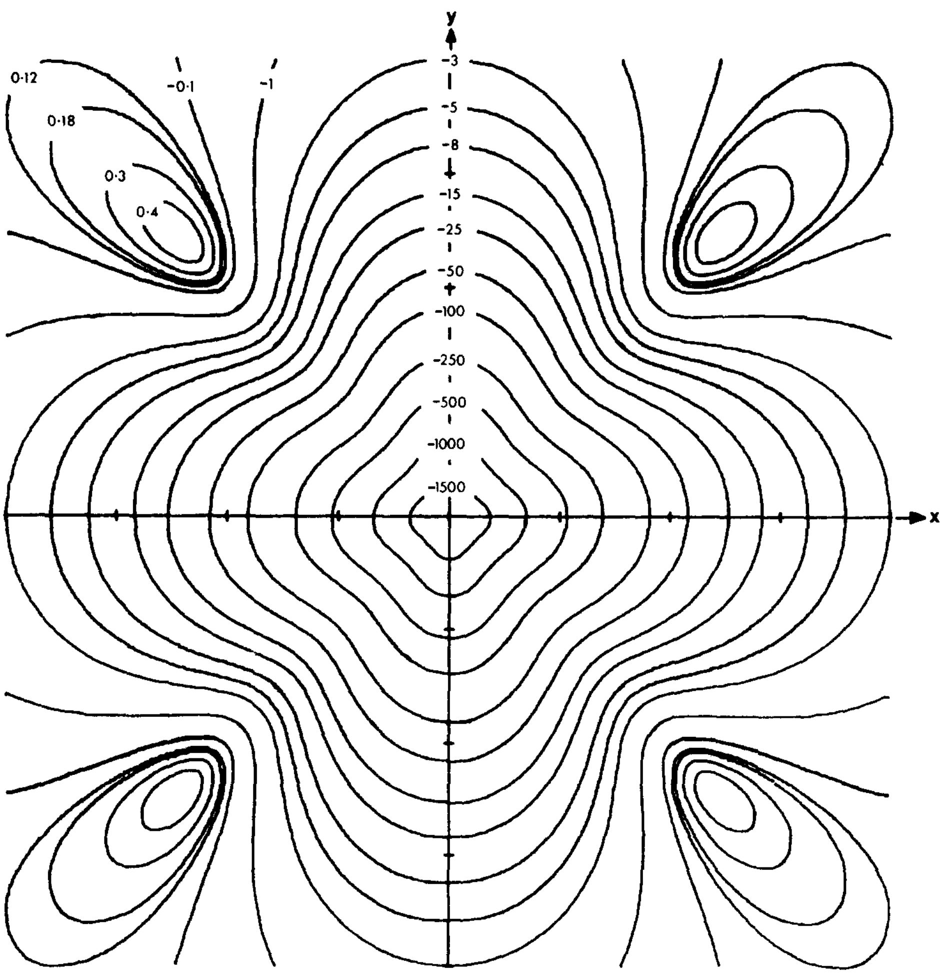

FIG. 5. The isoshielding diagram for a dt_2^2 system for the case when the NMR nucleus lies in the xy plane. The scale on the axes is in units of 0.1 nm ($T = 300\ K$).

Figs. 3a and b shows that there has been a marked effect on the value of the NMR shift ΔB by incorporating the effect of Coulomb repulsion mixing.

Finally, we present in Figs. 4 and 5 isoshielding diagrams for a d^2 system for the case when the NMR nucleus lies in the xy plane. The values of ζ, β, Δ, and the Racah parameter B were chosen as above. An isoshielding diagram is a contour map in which the contours are lines of equal chemical shifts (*5, 11*). Figure 4 gives the results for the case when Coulomb repulsion mixing is incorporated, Fig. 5 for that when it is not, the dt_2^2 system. There are regions where ΔB becomes slightly positive, of the order of 0.45 ppm in Fig. 5. A comparison with an isoshielding diagram for a d^1 system in a strong crystal field of octahedral symmetry—see Ref. (*5*), in which there are "lobes" in the map where ΔB reaches 50 ppm—highlights the dissimilarities that may occur in the isoshielding diagrams of three seemingly similar functions, that is, those of the form

$$\Delta B/B = \alpha Z_0(\Theta, \Phi) + \beta Z_4(\Theta, \Phi) + \delta Z_6(\Theta, \Phi).$$

APPENDIX A: THE RADIAL SERIES

For integrals of $l_{N\alpha}/r_N^3$ define

$$f_1 = v_1 + 3w_2 + 3x_3 + y_4,$$

$$n_1 = v_1 + \tfrac{1}{3}(5w_0 + 4w_2) + 3x_1 + y_0,$$

$$t(\mu) = v_1 + (3-A)w_0 + Aw_2 + (3-B)x_1 + Bx_3 + y_2,$$

where $A = \mu$ and $B = \frac{1}{5}(3\mu - 1)$. The explicit forms of the radial series in terms of $t = 2\beta R$ are

$$S_1 = \frac{16{,}632{,}000\beta^3}{t^7}\left[1 - e^{-t}\sum_{n=0}^{11} t^n/n!\right],$$

$$F(\mu) = \frac{16{,}800\beta^3}{t^5}\left[(\mu-9) - e^{-t}\left\{\frac{t^9}{8!} + (\mu-9)\sum_{n=0}^{8} t^n/n!\right\}\right],$$

$$T(\mu',\lambda') = \frac{60\beta^3}{t^3}\left[(7\lambda' - 3\mu' + 3)\right.$$
$$\left. - e^{-t}\left\{\frac{t^7}{144} + \frac{(\mu'-9)}{144}t^6 + \frac{(7\lambda' - 2\mu' - 6)}{144}t^5 + (7\lambda' - 3\mu' + 3)\sum_{n=0}^{4} t^n/n!\right\}\right],$$

$$N_1 = \frac{15\beta^3}{2}\left[e^{-t}\left\{-\frac{t^4}{18} + \frac{t^3}{3!} + \frac{t^2}{2!} + t + 1\right\}\right],$$

$$f_1 = -\frac{10{,}080\beta^3}{t^5}\left[1 - e^{-t}\sum_{n=0}^{8} t^n/n!\right],$$

$$t(\mu) = \frac{36\beta^3}{t^3}\left[(2-3\mu) - e^{-t}\left\{-\frac{t^6}{144} + \frac{(1-3\mu)}{144}t^5 + (2-3\mu)\sum_{n=0}^{4} t^n/n!\right\}\right],$$

$$n_1 = \frac{3\beta^3}{2}\left[e^{-t}\left\{\frac{t^3}{3!} + \frac{t^2}{2!} + t + 1\right\}\right].$$

The appearance of the incomplete factorial function,

$$i_N(t) = N!\left[1 - e^{-t}\sum_{n=0}^{N} t^n/n!\right],$$

ties in with results of Gottlieb *et al.* (*12*).

APPENDIX B: SOME MOLECULAR HYPERFINE INTEGRALS INVOLVING THE e ORBITALS

Employing the notation of Griffith (*8*) define

$$Z_{L0}(\Theta, \Phi) = Y_{L0}(\Theta, \Phi),$$

$$Z_{LM}^{(c)}(\Theta, \Phi) = \frac{1}{2^{1/2}}\{Y_{L-M}(\Theta, \Phi) + Y_{L-M}^{*}(\Theta, \Phi)\},$$

$$Z_{LM}^{(s)}(\Theta, \Phi) = \frac{i}{2^{1/2}}\{Y_{L-M}(\Theta, \Phi) - Y_{L-M}^{*}(\Theta, \Phi)\}.$$

We also require one additional radial series defined by

$$T_4 = v_1 - v_3 + (1/21)(49w_0 - 40w_2 - 9w_4) + x_1 - x_3.$$

The additional molecular hyperfine integrals involving the e orbitals are

$$\begin{aligned}\langle\xi|T_{yz}|\varepsilon\rangle = &-\frac{8}{165}\left(\frac{\pi}{91}\right)^{1/2} S_1 Z_{64}^{(c)}(\Theta, \Phi) - \frac{16}{165}\left(\frac{2\pi}{1365}\right)^{1/2} S_1 Z_{62}^{(c)}(\Theta, \Phi)\\ &-\frac{8}{1155}\left(\frac{\pi}{13}\right)^{1/2} S_1 Z_{60}(\Theta, \Phi) - \frac{4}{165}\left(\frac{\pi}{35}\right)^{1/2} F(9) Z_{44}^{(c)}(\Theta, \Phi)\\ &+\frac{4}{231}\left(\frac{\pi}{5}\right)^{1/2} F\left(\frac{67}{5}\right) Z_{42}^{(c)}(\Theta, \Phi) + \frac{4\pi^{1/2}}{825} F\left(\frac{107}{7}\right) Z_{40}(\Theta, \Phi)\\ &+\frac{4}{105}\left(\frac{\pi}{15}\right)^{1/2} T\left(5, \frac{12}{7}\right) Z_{22}^{(c)}(\Theta, \Phi) + \frac{4}{105}\left(\frac{\pi}{5}\right)^{1/2} T_4 Z_{20}(\Theta, \Phi)\\ &-\frac{4\pi^{1/2}}{525} N_1 Z_{00}(\Theta, \Phi),\end{aligned}$$

$$\begin{aligned}\langle\eta|T_{zx}|\varepsilon\rangle = &\frac{8}{165}\left(\frac{\pi}{91}\right)^{1/2} S_1 Z_{64}^{(c)}(\Theta, \Phi) - \frac{16}{165}\left(\frac{2\pi}{1365}\right)^{1/2} S_1 Z_{62}^{(c)}(\Theta, \Phi)\\ &+\frac{8}{1155}\left(\frac{\pi}{13}\right)^{1/2} S_1 Z_{60}(\Theta, \Phi) + \frac{4}{165}\left(\frac{\pi}{35}\right)^{1/2} F(9) Z_{44}^{(c)}(\Theta, \Phi)\\ &+\frac{4}{231}\left(\frac{\pi}{5}\right)^{1/2} F\left(\frac{67}{5}\right) Z_{42}^{(c)}(\Theta, \Phi) - \frac{4\pi^{1/2}}{825} F\left(\frac{107}{7}\right) Z_{40}(\Theta, \Phi)\end{aligned}$$

$$+\frac{4}{105}\left(\frac{\pi}{15}\right)^{1/2}T\left(5,\frac{12}{7}\right)Z_{22}^{(c)}(\Theta,\Phi)-\frac{4}{105}\left(\frac{\pi}{5}\right)^{1/2}T_4Z_{20}(\Theta,\Phi)$$

$$+\frac{4\pi^{1/2}}{525}N_1Z_{00}(\Theta,\Phi),$$

$$\langle\eta|T_{zx}|\theta\rangle=\frac{1}{3^{1/2}}\left[\frac{16}{55}\left(\frac{2\pi}{1365}\right)^{1/2}S_1Z_{62}^{(c)}(\Theta,\Phi)-\frac{16}{385}\left(\frac{\pi}{13}\right)^{1/2}S_1Z_{60}(\Theta,\Phi)\right.$$

$$+\frac{4}{165}\left(\frac{\pi}{5}\right)^{1/2}F\left(\frac{85}{7}\right)Z_{42}^{(c)}(\Theta,\Phi)-\frac{8\pi^{1/2}}{5775}F(31)Z_{40}(\Theta,\Phi)$$

$$-\frac{4}{35}\left(\frac{\pi}{15}\right)^{1/2}T_4Z_{22}^{(c)}(\Theta,\Phi)$$

$$\left.+\frac{4}{105}\left(\frac{\pi}{5}\right)^{1/2}T\left(3,\frac{6}{7}\right)Z_{20}(\Theta,\Phi)+\frac{4\pi^{1/2}}{525}N_1Z_{00}(\Theta,\Phi)\right],$$

$$\langle\xi|T_{yz}|\theta\rangle=\frac{1}{3^{1/2}}\left[-\frac{16}{55}\left(\frac{2\pi}{1365}\right)^{1/2}S_1Z_{62}^{(c)}(\Theta,\Phi)-\frac{16}{385}\left(\frac{\pi}{13}\right)^{1/2}S_1Z_{60}(\Theta,\Phi)\right.$$

$$-\frac{4}{165}\left(\frac{\pi}{5}\right)^{1/2}F\left(\frac{85}{7}\right)Z_{42}^{(c)}(\Theta,\Phi)-\frac{8\pi^{1/2}}{5775}F(31)Z_{40}(\Theta,\Phi)$$

$$+\frac{4}{35}\left(\frac{\pi}{15}\right)^{1/2}T_4Z_{22}^{(c)}(\Theta,\Phi)+\frac{4}{105}\left(\frac{\pi}{5}\right)^{1/2}T\left(3,\frac{6}{7}\right)Z_{20}(\Theta,\Phi)$$

$$\left.+\frac{4\pi^{1/2}}{525}N_1Z_{00}(\Theta,\Phi)\right],$$

$$\langle\zeta|T_{xy}|\theta\rangle=\frac{1}{3^{1/2}}\left[-\frac{4}{55}\left(\frac{\pi}{91}\right)^{1/2}S_1Z_{64}^{(c)}(\Theta,\Phi)+\frac{4}{385}\left(\frac{\pi}{13}\right)^{1/2}S_1Z_{60}(\Theta,\Phi)\right.$$

$$+\frac{16}{165}\left(\frac{\pi}{35}\right)^{1/2}F\left(\frac{29}{2}\right)Z_{44}^{(c)}(\Theta,\Phi)-\frac{64\pi^{1/2}}{5775}F\left(\frac{83}{8}\right)Z_{40}(\Theta,\Phi)$$

$$\left.+\frac{4}{105}\left(\frac{\pi}{5}\right)^{1/2}T\left(6,\frac{15}{7}\right)Z_{20}(\Theta,\Phi)-\frac{8\pi^{1/2}}{525}N_1Z_{00}(\Theta,\Phi)\right],$$

$$\langle\theta|T_{xx}|\varepsilon\rangle=\frac{1}{3^{1/2}}\left[\frac{4}{55}\left(\frac{\pi}{91}\right)^{1/2}S_1Z_{64}^{(c)}(\Theta,\Phi)-\frac{8}{55}\left(\frac{2\pi}{1365}\right)^{1/2}S_1Z_{62}^{(c)}(\Theta,\Phi)\right.$$

$$+\frac{4}{385}\left(\frac{\pi}{13}\right)^{1/2}S_1Z_{60}(\Theta,\Phi)-\frac{16}{165}\left(\frac{\pi}{35}\right)^{1/2}F\left(\frac{29}{2}\right)Z_{44}^{(c)}(\Theta,\Phi)$$

$$+\frac{8}{1155}\left(\frac{\pi}{5}\right)^{1/2}F(20)Z_{42}^{(c)}(\Theta,\Phi)-\frac{64\pi^{1/2}}{5775}F\left(\frac{83}{8}\right)Z_{40}(\Theta,\Phi)$$

$$-\frac{4}{105}\left(\frac{\pi}{15}\right)^{1/2}T\left(6,\frac{15}{7}\right)Z_{22}^{(c)}(\Theta,\Phi)+\frac{4}{105}\left(\frac{\pi}{5}\right)^{1/2}T\left(6,\frac{15}{7}\right)Z_{20}(\Theta,\Phi)$$

$$\left.-\frac{8\pi^{1/2}}{525}N_1Z_{00}(\Theta,\Phi)\right],$$

$$\langle\theta|T_{yy}|\varepsilon\rangle=\frac{1}{3^{1/3}}\Big[-\frac{4}{55}\Big(\frac{\pi}{91}\Big)^{1/2}S_1Z_{64}^{(c)}(\Theta,\Phi)-\frac{8}{55}\Big(\frac{2\pi}{1365}\Big)^{1/2}S_1Z_{62}^{(c)}(\Theta,\Phi)$$
$$-\frac{4}{385}\Big(\frac{\pi}{13}\Big)^{1/2}S_1Z_{60}(\Theta,\Phi)+\frac{16}{165}\Big(\frac{\pi}{35}\Big)^{1/2}F\Big(\frac{29}{2}\Big)Z_{44}^{(c)}(\Theta,\Phi)$$
$$+\frac{8}{1155}\Big(\frac{\pi}{5}\Big)^{1/2}F(20)Z_{42}^{(c)}(\Theta,\Phi)+\frac{64\pi^{1/2}}{5775}F\Big(\frac{83}{8}\Big)Z_{40}(\Theta,\Phi)$$
$$-\frac{4}{105}\Big(\frac{\pi}{15}\Big)^{1/2}T\Big(6,\frac{15}{7}\Big)Z_{22}^{(c)}(\Theta,\Phi)-\frac{4}{105}\Big(\frac{\pi}{5}\Big)^{1/2}T\Big(6,\frac{15}{7}\Big)Z_{20}(\Theta,\Phi)$$
$$+\frac{8\pi^{1/2}}{525}N_1Z_{00}(\Theta,\Phi)\Big],$$

$$\langle\theta|T_{zz}|\theta\rangle=\frac{16}{385}\Big(\frac{\pi}{13}\Big)^{1/2}S_1Z_{60}(\Theta,\Phi)+\frac{32\pi^{1/2}}{1925}F\Big(\frac{38}{3}\Big)Z_{40}(\Theta,\Phi)$$
$$+\frac{8}{108}\Big(\frac{\pi}{5}\Big)^{1/2}T(8,4)Z_{20}(\Theta,\Phi)+\frac{16\pi^{1/2}}{1575}N_1Z_{00}(\Theta,\Phi),$$

$$\langle\varepsilon|T_{zz}|\varepsilon\rangle=\frac{8}{165}\Big(\frac{\pi}{91}\Big)^{1/2}S_1Z_{64}^{(c)}(\Theta,\Phi)+\frac{8}{1155}\Big(\frac{\pi}{13}\Big)^{1/2}S_1Z_{60}(\Theta,\Phi)$$
$$-\frac{32}{495}\Big(\frac{\pi}{35}\Big)^{1/2}F(9)Z_{44}^{(c)}(\Theta,\Phi)-\frac{128\pi^{1/2}}{17325}F\Big(\frac{69}{4}\Big)Z_{40}(\Theta,\Phi)$$
$$+\frac{8}{315}\Big(\frac{\pi}{5}\Big)^{1/2}T\Big(12,\frac{54}{7}\Big)Z_{20}(\Theta,\Phi)-\frac{16\pi^{1/2}}{1575}N_1Z_{00}(\Theta,\Phi),$$

$$i\langle\zeta|l_{Nz}/r_N^3|\varepsilon\rangle=-\frac{8\pi^{1/2}}{315}f_1Z_{40}(\Theta,\Phi)+\frac{16}{63}\Big(\frac{\pi}{5}\Big)^{1/2}t\Big(\frac{11}{6}\Big)Z_{20}(\Theta,\Phi)$$
$$-\frac{8\pi^{1/2}}{45}n_1Z_{00}(\Theta,\Phi),$$

$$i\langle\xi|l_{Nx}/r_N^3|\varepsilon\rangle=\frac{2}{9}\Big(\frac{\pi}{35}\Big)^{1/2}f_1Z_{44}^{(c)}(\Theta,\Phi)+\frac{2}{63}\Big(\frac{\pi}{5}\Big)^{1/2}f_1Z_{42}^{(c)}(\Theta,\Phi)-\frac{2\pi^{1/2}}{105}f_1Z_{40}(\Theta,\Phi)$$
$$-\frac{2}{7}\Big(\frac{\pi}{15}\Big)^{1/2}t\Big(\frac{13}{9}\Big)Z_{22}^{(c)}(\Theta,\Phi)-\frac{2}{63}\Big(\frac{\pi}{5}\Big)^{1/2}t\Big(-\frac{5}{3}\Big)Z_{20}(\Theta,\Phi)$$
$$+\frac{4\pi^{1/2}}{45}n_1Z_{00}(\Theta,\Phi),$$

$$i\langle\eta|l_{Ny}/r_N^3|\varepsilon\rangle=\frac{2}{9}\Big(\frac{\pi}{35}\Big)^{1/2}f_1Z_{44}^{(c)}(\Theta,\Phi)-\frac{2}{63}\Big(\frac{\pi}{5}\Big)^{1/2}f_1Z_{42}^{(c)}(\Theta,\Phi)-\frac{2\pi^{1/2}}{105}f_1Z_{40}(\Theta,\Phi)$$
$$+\frac{2}{7}\Big(\frac{\pi}{15}\Big)^{1/2}t\Big(\frac{13}{9}\Big)Z_{22}^{(c)}(\Theta,\Phi)-\frac{2}{63}\Big(\frac{\pi}{5}\Big)^{1/2}t\Big(-\frac{5}{3}\Big)Z_{20}(\Theta,\Phi)$$
$$+\frac{4\pi^{1/2}}{45}n_1Z_{00}(\Theta,\Phi),$$

$$i\langle\xi|l_{Nx}/r_N^3|\theta\rangle = \frac{1}{3^{1/2}}\Big[-\frac{2}{21}\Big(\frac{\pi}{5}\Big)^{1/2} f_1 Z_{42}^{(c)}(\Theta,\Phi) + \frac{4\pi^{1/2}}{105} f_1 Z_{40}(\Theta,\Phi)$$
$$-\frac{10}{21}\Big(\frac{\pi}{15}\Big)^{1/2} t\Big(\frac{1}{15}\Big) Z_{22}^{(c)}(\Theta,\Phi) + \frac{2}{7}\Big(\frac{\pi}{5}\Big)^{1/2} t\Big(\frac{13}{9}\Big) Z_{20}(\Theta,\Phi)$$
$$+\frac{4\pi^{1/2}}{15} n_1 Z_{00}(\Theta,\Phi)\Big],$$

$$i\langle\eta|l_{Ny}/r_N^3|\theta\rangle = \frac{1}{3^{1/2}}\Big[-\frac{2}{21}\Big(\frac{\pi}{5}\Big)^{1/2} f_1 Z_{42}^{(c)}(\Theta,\Phi) - \frac{4\pi^{1/2}}{105} f_1 Z_{40}(\Theta,\Phi)$$
$$-\frac{10}{21}\Big(\frac{\pi}{15}\Big)^{1/2} t\Big(\frac{1}{15}\Big) Z_{22}^{(c)}(\Theta,\Phi) - \frac{2}{7}\Big(\frac{\pi}{5}\Big)^{1/2} t\Big(\frac{13}{9}\Big) Z_{20}(\Theta,\Phi)$$
$$-\frac{4\pi^{1/2}}{15} n_1 Z_{00}(\Theta,\Phi)\Big].$$

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