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The evaluation of the hyperfine interaction tensor components in molecular systems

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In this paper a general method is developed to evaluate the nine hyperfine interaction tensor components, $A_{\alpha\beta}$, arising from the electron orbital angular momentum and the electron spin dipolar-nuclear spin angular momentum interactions of an electron associated dominantly with one nucleus coupling with a nucleus with a non-zero magnetic moment, where the electronic wavefunction is described by a Slater-type orbital. The method handles long range and short range coupling including the free atom case. From the results the degree of non-coincidence of the principal axes of the $\mathbf{g}$ and $\mathbf{A}$ tensors and the n.m.r. shifts are evaluated. As an illustration the molecular system examined is a molecule containing a d^1 transition metal ion in a strong crystal field.

1. INTRODUCTION

The interactions of an electron and a nucleus with a magnetic moment with an applied magnetic field and the interaction between the electron and the nucleus may be represented by the spin hamiltonian

$$\mathscr{H} = \mu_B \boldsymbol{s}\cdot\mathbf{g}\cdot\boldsymbol{B} - \mu_N g_N \boldsymbol{I}\cdot\boldsymbol{B} + \mu_N g_N \boldsymbol{I}\cdot\boldsymbol{\sigma}\cdot\boldsymbol{B} + \boldsymbol{I}\cdot\mathbf{A}\cdot\boldsymbol{s}, \tag{1}$$

where the $\mathbf{g}$, $\boldsymbol{\sigma}$ and $\mathbf{A}$ tensors may not necessarily be coincident nor symmetric. We shall examine the case when the first term in hamiltonian (1) is the dominant term and the third term is insignificant. We shall determine the degree of coincidence of the $\mathbf{g}$ and $\mathbf{A}$ tensors and the asymmetry of the $\mathbf{A}$ tensor for a one electron system. Hence, we shall develop a method whereby the nine $A_{\alpha\beta}$ components may be calculated for any system where the electron-nuclear interaction is represented by the hamiltonian

$$\mathscr{H}' = 2g_N\mu_B\mu_N\{-\mathrm{i}\hbar\boldsymbol{I}\cdot\boldsymbol{r}_N\times\nabla/r_N^3 - \boldsymbol{s}\cdot\boldsymbol{I}/r_N^3 + 3(\boldsymbol{r}_N\cdot\boldsymbol{s})\,\boldsymbol{r}_N\cdot\boldsymbol{I}/r_N^5\}\mu_0/4\pi. \tag{2}$$

In equation (2) $\boldsymbol{r}_N$ is the radius vector of the electron about the nucleus with nuclear spin angular momentum, $\boldsymbol{I}$.

The nine components of the hyperfine tensor will be calculated by equating the eigenvalues of the spin hamiltonian (1) to the eigenvalues of the appropriate hamiltonian for the molecular system including hamiltonian (2). Much of the work involved is in the evaluation of the two centre molecular hyperfine interaction integrals and the system we shall explore is shown in figure 1.

The electronic wavefunction $\psi(lm_l)$ will be chosen as a Slater-type of the form

$$\psi(lm_l) = r^l \exp(-\beta r) Y_{lm_l}(\theta, \phi). \tag{3}$$

McConnell & Strathdee (1959) gave a method of evaluating the integrals for the special case when the two nuclei lie along the z-axis. The operator was expressed as a function of $\boldsymbol{R}$ and $\boldsymbol{r}$ and the integration performed in the $Oxyz$ system. However, the singular nature of the operator at the nucleus with the magnetic moment causes problems, and there is a δ-function type contribution (Pitzer, Kern & Lipscomb 1962).

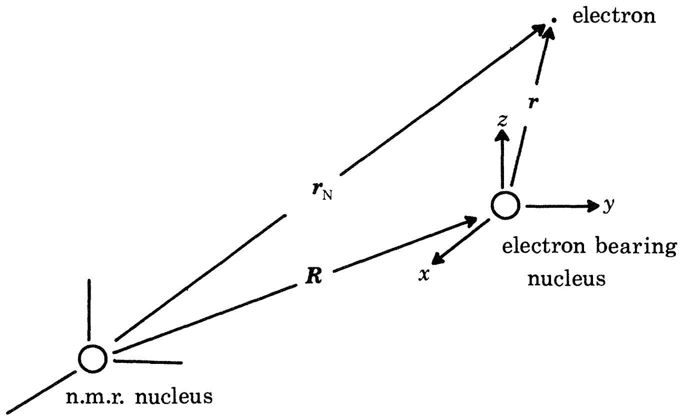

FIGURE 1. The coordinate system.

We shall evaluate these hyperfine integrals for the general case, namely when $\boldsymbol{R}$ can point anywhere in space, not necessarily along the z-axis. The corrections given to the results of McConnell & Strathdee (1959) by Pitzer *et al.* (1962) are automatically incorporated in our answer since the integration is performed in the $O_N x_N y_N z_N$ system and the singularity at O_N is easily handled. The hyperfine interaction integrals are evaluated by expressing the electron coordinate system $Oxyz$ in the coordinate system $O_N x_N y_N z_N$ using the following identities:

$$r^l Y_{lm}(\theta, \phi) = \sum_{l_1=0}^{l} \sum_{l_2=0}^{l} \sum_{m_1=-l_1}^{l_1} \sum_{m_2=-l_2}^{l_2} (-1)^{l_1} \delta(l_1+l_2, l) \times \left(\frac{4\pi(2l+1)!}{(2l_1+1)!\,(2l_2+1)!}\right)^{\frac{1}{2}} \langle l_1 l_2 m_1 m_2 | l_1 l_2 l m\rangle \times R^{l_1} Y_{l_1 m_1}(\Theta, \Phi) r_N^{l_2} Y_{l_2 m_2}(\theta_N, \phi_N), \tag{4a}$$

$$\exp(-2\beta r) = 4\pi \sum_{n=0}^{\infty} b_n(R, r_N) \sum_{k=-n}^{n} Y_{nk}^*(\Theta, \Phi) Y_{nk}(\theta_N, \phi_N),$$

where

$$b_n(R, r_N) = \sqrt{(r_>/r_<)}\, I_{n+\frac{1}{2}}(2\beta r_<)\, K_{n+\frac{3}{2}}(2\beta r_>) - \sqrt{(r_</r_>)}\, I_{n-\frac{1}{2}}(2\beta r_<)\, K_{n+\frac{1}{2}}(2\beta r_>), \tag{4b}$$

where $r_<$ is the smaller of R and r_N, $r_>$ is the larger of R and r_N and I_ν and K_ν are the modified Bessel functions.

To illustrate the results we shall examine the case when the hyperfine interaction arises from the interaction of a d-electron in a strong crystal field with the nucleus with spin angular momentum. From a knowledge of the hyperfine interaction components we shall determine the degree of non-coincidence of the **g** and **A** tensors. Also, in this paper we shall derive expressions for the n.m.r. shift arising from this interaction which will lead to generalised results of our previous work on the pseudocontact contribution to the n.m.r. screening constant in d^1 transition metal ion complexes (Golding, Pascual & Vrbancich 1976; Golding, Pascual & Stubbs 1976).

2. Theory

Since we are examining the interaction of a d-electron centred at O in a strong crystal field we shall express the required electronic wavefunctions as

$$\left.\begin{aligned}|\xi\rangle &= (2\beta^7/3\pi)^{\frac{1}{2}}\, yz \exp(-\beta r),\\ |\eta\rangle &= (2\beta^7/3\pi)^{\frac{1}{2}}\, zx \exp(-\beta r),\\ |\zeta\rangle &= (2\beta^7/3\pi)^{\frac{1}{2}}\, xy \exp(-\beta r),\end{aligned}\right\} \tag{5}$$

where $\beta = 2.2/a_0$.

To evaluate the hyperfine interaction integrals, the integrand is expressed as a function of $\boldsymbol{R}$ and $\boldsymbol{r}_N$ using equations (4*a*) and (4*b*). For the radial part of the integrals we introduce, for convenience, the following notation

$$\left.\begin{aligned} r_n^{(L)}(t) &= 4\beta^7(-R)^L \int_0^\infty r_N^{3-L} b_n(R, r_N)\, dr_N\\ \text{and}\quad u_n(t) &= r_n^{(4)}(t), \quad x_n(t) = r_n^{(1)}(t),\\ v_n(t) &= r_n^{(3)}(t), \quad y_n(t) = r_n^{(0)}(t),\\ w_n(t) &= r_n^{(2)}(t),\end{aligned}\right\} \tag{6}$$

where $t = 2\beta R$.

From the angular parts of the hyperfine interaction integrals we gain selection rules on n. The required radial integrals are listed in table 1. The integrals are then readily evaluated.

(*a*) *Hyperfine interaction tensor components*

A d^1 system in a strong crystal field of octahedral symmetry results in a $^2T_2$ ground state. The spin–orbit coupling interactions and a crystal field component of lower symmetry results in a splitting of the $^2T_2$ ground state into three doubly spin degenerate energy levels E_k ($k = 1, 2, 3$) where the eigenfunctions may be written as (Golding 1969)

$$\left.\begin{aligned}|\psi_k^+\rangle &= A_k|1^+\rangle + B_k|\zeta_1^-\rangle + C_k|-1^+\rangle,\\ |\psi_k^-\rangle &= A_k|-1^-\rangle - B_k|\zeta_1^+\rangle + C_k|1^-\rangle.\end{aligned}\right\} \tag{7}$$

Hence, the $\mathbf{g}$ tensor for each energy level E_k is diagonalized and the principal g-values are given as

$$\left.\begin{aligned} g_{xx}^{(k)} &= 2\{B_k^2 - 2A_k C_k + \surd 2B_k(A_k - C_k)\}, \\ g_{yy}^{(k)} &= 2\{B_k^2 + 2A_k C_k + \surd 2B_k(A_k + C_k)\}, \\ g_{zz}^{(k)} &= 2\{2A_k^2 - B_k^2\}. \end{aligned}\right\} \tag{8}$$

Table 1. The required radial integrals

$$u_2(t) = \beta^3 \left[\frac{t}{2} - \left(\frac{t^4}{12} + \frac{t^3}{4} + \frac{t^2}{2} + \frac{t}{2}\right) \mathrm{e}^{-t}\right],$$

$$v_1(t) = -\beta^3 \left[\frac{t}{2} - \left(\frac{t^3}{4} + \frac{t^2}{2} + \frac{t}{2}\right) \mathrm{e}^{-t}\right],$$

$$v_3(t) = -\beta^3 \left[\left(\frac{t}{2} - \frac{10}{t}\right) + \left(\frac{t^3}{6} + \frac{7t^2}{6} + \frac{9t}{2} + 10 + \frac{10}{t}\right) \mathrm{e}^{-t}\right],$$

$$w_0(t) = \beta^3 \left[\frac{t}{2} - \left(\frac{t^2}{4} + \frac{t}{2}\right) \mathrm{e}^{-t}\right],$$

$$w_2(t) = \beta^3 \left[\left(\frac{t}{2} - \frac{6}{t}\right) + \left(\frac{t^2}{2} + \frac{5t}{2} + 6 + \frac{6}{t}\right) \mathrm{e}^{-t}\right],$$

$$w_4(t) = \beta^3 \left[\left(\frac{t}{2} - \frac{20}{t} + \frac{420}{t^3}\right) - \left(\frac{2t^2}{3} + 8t + 50 + \frac{190}{t} + \frac{420}{t^2} + \frac{420}{t^3}\right) \mathrm{e}^{-t}\right],$$

$$x_1(t) = -\beta^3 \left[\left(\frac{t}{2} - \frac{2}{t}\right) + \left(\frac{t}{2} + 2 + \frac{2}{t}\right) \mathrm{e}^{-t}\right],$$

$$x_3(t) = -\beta^3 \left[\left(\frac{t}{2} - \frac{12}{t} + \frac{180}{t^3}\right) - \left(2t + 18 + \frac{78}{t} + \frac{180}{t^2} + \frac{180}{t^3}\right) \mathrm{e}^{-t}\right],$$

$$x_5(t) = -\beta^3 \left[\left(\frac{t}{2} - \frac{30}{t} + \frac{1260}{t^3} - \frac{30240}{t^5}\right) + \left(4t + 72 + \frac{660}{t} + \frac{3780}{t^2} + \frac{13860}{t^3} + \frac{30240}{t^4} + \frac{30240}{t^5}\right) \mathrm{e}^{-t}\right],$$

$$y_0(t) = \beta^3 \left[\left(\frac{t}{2} + \frac{2}{t}\right) - \left(\frac{1}{2} + \frac{2}{t}\right) \mathrm{e}^{-t}\right],$$

$$y_2(t) = \beta^3 \left[\left(\frac{t}{2} - \frac{4}{t} + \frac{36}{t^3}\right) - \left(2 + \frac{14}{t} + \frac{36}{t^2} + \frac{36}{t^3}\right) \mathrm{e}^{-t}\right],$$

$$y_4(t) = \beta^3 \left[\left(\frac{t}{2} - \frac{18}{t} + \frac{540}{t^3} - \frac{10080}{t^5}\right) + \left(12 + \frac{168}{t} + \frac{1140}{t^2} + \frac{4500}{t^3} + \frac{10080}{t^4} + \frac{10080}{t^5}\right) \mathrm{e}^{-t}\right],$$

$$y_6(t) = \beta^3 \left[\left(\frac{t}{2} - \frac{40}{t} + \frac{2520}{t^3} - \frac{120960}{t^5} + \frac{3326400}{t^7}\right) - \left(32 + \frac{800}{t} + \frac{10080}{t^2} + \frac{80640}{t^3} + \frac{433440}{t^4} + \frac{1542240}{t^5} + \frac{3326400}{t^6} + \frac{3326400}{t^7}\right) \mathrm{e}^{-t}\right].$$

The hyperfine interaction tensor components, $A_{\alpha\beta}$, are obtained from the solution of the following six simultaneous equations, namely

$$\sum_\alpha (A_{\alpha x}^{(k)})^2 = \sum_\alpha (R_\alpha^{(k)})^2,$$
$$\sum_\alpha (A_{\alpha y}^{(k)})^2 = \sum_\alpha (I_\alpha^{(k)})^2,$$
$$\sum_\alpha (A_{\alpha z}^{(k)})^2 = \sum_\alpha (D_\alpha^{(k)})^2,$$
$$\sum_\alpha A_{\alpha y}^{(k)} A_{\alpha z}^{(k)} = \sum_\alpha I_\alpha^{(k)} D_\alpha^{(k)},$$
$$\sum_\alpha A_{\alpha z}^{(k)} A_{\alpha x}^{(k)} = \sum_\alpha D_\alpha^{(k)} R_\alpha^{(k)},$$
$$\sum_\alpha A_{\alpha x}^{(k)} A_{\alpha y}^{(k)} = \sum_\alpha R_\alpha^{(k)} I_\alpha^{(k)},$$

where

$$\begin{aligned} R_\alpha^{(k)} = 2g_{\mathrm{N}}\mu_B\mu_{\mathrm{N}}[&-2\sqrt{2}B_k(C_k-A_k)\,\mathrm{i}\,\langle\zeta|\, l_{\mathrm{N}\alpha}/r_{\mathrm{N}}^3|\eta\rangle - \tfrac{1}{2}(C_k+A_k)^2\langle\xi|\,T_{\alpha x}\,|\xi\rangle \\ &+\tfrac{1}{2}(C_k-A_k)^2\langle\eta|\,T_{\alpha x}\,|\eta\rangle + B_k^2\langle\zeta|\,T_{\alpha x}\,|\zeta\rangle + (C_k^2-A_k^2)\langle\xi|\,T_{\alpha y}\,|\eta\rangle \\ &-\sqrt{2}B_k(C_k+A_k)\langle\zeta|\,T_{\alpha z}\,|\xi\rangle]\,\mu_0/4\pi, \end{aligned}$$

$$\begin{aligned} D_\alpha^{(k)} = 2g_{\mathrm{N}}\mu_B\mu_{\mathrm{N}}[&-2(C_k^2-A_k^2)\,\mathrm{i}\,\langle\eta|l_{\mathrm{N}\alpha}/r_{\mathrm{N}}^3|\,\xi\rangle - \sqrt{2}B_k(C_k+A_k)\langle\zeta|\,T_{\alpha x}\,|\xi\rangle \\ &+\sqrt{2}B_k(C_k-A_k)\langle\eta|\,T_{\alpha y}\,|\zeta\rangle + \tfrac{1}{2}(C_k+A_k)^2\langle\xi|\,T_{\alpha z}\,|\xi\rangle \\ &+\tfrac{1}{2}(C_k-A_k)^2\langle\eta|\,T_{\alpha z}\,|\eta\rangle - B_k^2\langle\zeta|\,T_{\alpha z}\,|\zeta\rangle]\,\mu_0/4\pi, \end{aligned}$$

$$\begin{aligned} I_\alpha^{(k)} = 2g_{\mathrm{N}}\mu_B\mu_{\mathrm{N}}[&2\sqrt{2}B_k(C_k+A_k)\,\mathrm{i}\,\langle\xi|\,l_{\mathrm{N}\alpha}/r_{\mathrm{N}}^3\,|\zeta\rangle + (C_k^2-A_k^2)\langle\xi|\,T_{\alpha x}\,|\eta\rangle \\ &+\tfrac{1}{2}(C_k+A_k)^2\langle\xi|\,T_{\alpha y}\,|\xi\rangle - \tfrac{1}{2}(C_k-A_k)^2\langle\eta|\,T_{\alpha y}\,|\eta\rangle + B_k^2\langle\zeta|\,T_{\alpha y}\,|\zeta\rangle \\ &+\sqrt{2}B_k(C_k-A_k)\langle\eta|\,T_{\alpha z}\,|\zeta\rangle]\,\mu_0/4\pi, \end{aligned}$$

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

The integrals are given in the appendices.

When $\boldsymbol{R}$ lies along one of the coordinate axes the solution is chosen such that the **A** tensor is diagonal. A consistent set of solutions for all directions of the $\boldsymbol{R}$ vector in space is then

$$\left.\begin{aligned} A_{\alpha x}^{(k)} &= R_\alpha^{(k)}, \\ A_{\alpha y}^{(k)} &= I_\alpha^{(k)}, \\ A_{\alpha z}^{(k)} &= D_\alpha^{(k)}. \end{aligned}\right\} \tag{10}$$

Therefore, in general the **A** tensor is asymmetric. However, it follows that a symmetric tensor **S** can be constructed where

$$\mathbf{S} = \mathbf{A}^T\mathbf{A}.$$

(*b*) *N.m.r. pseudocontact shift*

From a knowledge of the hyperfine interaction tensor components we may determine the n.m.r. shifts arising from the electron-nuclear interaction represented by equation (2) when the n.m.r. results of the paramagnetic system are determined in liquid solution. The principal values σ_{xx}, σ_{yy} and σ_{zz} of the n.m.r. screening tensor,

$\boldsymbol{\sigma}$, are determined by considering the magnetic field, $\boldsymbol{B}$, interaction as parallel to the x, y and z axes and averaged assuming a Boltzmann distribution. It follows that the contribution to the n.m.r. shift, ΔB, is given by

$$\Delta B = \tfrac{1}{3}B(\sigma_{xx}+\sigma_{yy}+\sigma_{zz}), \tag{11}$$

where
$$\sigma_{\alpha\alpha} = \frac{1}{g_{\mathrm{N}}\mu_{\mathrm{N}}}\left(\frac{\partial^2}{\partial I_\alpha\,\partial B_\alpha}\,\frac{\sum_i \langle \Psi_i|\mathscr{H}'|\Psi_i\rangle \exp(-E_i/kT)}{\sum_i \exp(-E_i/kT)}\right)_{B=0},$$

where Ψ_i are the eigenfunctions (7) and E_i the corresponding eigenvalues. $\mathscr{H}'$ is the hamiltonian operator (2).

We shall examine three cases; namely, when the d-electron is in a strong crystal field of (i) octahedral symmetry, (ii) with a tetragonal crystal field component along the z axis and (iii) with a trigonal crystal field component along the [111] axis.

(i) *Octahedral case*

In this case the n.m.r. shift is given by

$$\frac{\Delta B}{B} = -\frac{\mu_0}{4\pi}\frac{\mu_B^2}{kT}\left[\frac{d(\boldsymbol{R})+(1-\exp(3\zeta/2kT))\,kT/\zeta\,s(\boldsymbol{R})}{1+2\exp(3\zeta/2kT)}\right], \tag{12}$$

where

$$d(\boldsymbol{R}) = \frac{921600}{t^7}\sqrt{\left(\frac{\pi}{26}\right)}\left[\frac{\sqrt{7}}{4}Y_{64}(\Theta,\Phi)-\frac{1}{2\sqrt{2}}Y_{60}(\Theta,\Phi)+\frac{\sqrt{7}}{4}Y_{6-4}(\Theta,\Phi)\right]M(t)$$
$$+\frac{7168}{t^5}\sqrt{\left(\frac{\pi}{21}\right)}\left[\tfrac{1}{2}\sqrt{(\tfrac{5}{6})}Y_{44}(\Theta,\Phi)+\tfrac{1}{2}\sqrt{(\tfrac{7}{3})}Y_{40}(\Theta,\Phi)+\tfrac{1}{2}\sqrt{(\tfrac{5}{6})}Y_{4-4}(\Theta,\Phi)\right]E(t)$$
$$+\tfrac{16}{105}\sqrt{\pi}[Y_{00}(\Theta,\Phi)]\,J(t),$$

$$s(\boldsymbol{R}) = \frac{614400}{t^7}\sqrt{\left(\frac{\pi}{26}\right)}\left[\frac{\sqrt{7}}{4}Y_{64}(\Theta,\Phi)-\frac{1}{2\sqrt{2}}Y_{60}(\Theta,\Phi)+\frac{\sqrt{7}}{4}Y_{6-4}(\Theta,\Phi)\right]M(t)$$
$$-\frac{7168}{t^5}\sqrt{\left(\frac{\pi}{21}\right)}\left[\tfrac{1}{2}\sqrt{(\tfrac{5}{6})}\,Y_{44}(\Theta,\Phi)+\tfrac{1}{2}\sqrt{(\tfrac{7}{3})}\,Y_{40}(\Theta,\Phi)+\tfrac{1}{2}\sqrt{(\tfrac{5}{6})}\,Y_{4-4}(\Theta,\Phi)\right]G(t)$$
$$-\tfrac{16}{63}\sqrt{\pi}[Y_{00}(\Theta,\Phi)]\,P(t),$$

where
$$M(t) = \beta^3\left[1-\mathrm{e}^{-t}\sum_{n=0}^{11}\frac{t^n}{n!}\right],$$

$$E(t) = \beta^3\left[1-\mathrm{e}^{-t}\left(\frac{8}{11}\frac{t^9}{9!}+\sum_{n=0}^{8}\frac{t^n}{n!}\right)\right],$$

$$J(t) = \beta^3\mathrm{e}^{-t}\left(\frac{2}{9}\frac{t^4}{4!}+\frac{t^3}{3!}+\frac{t^2}{2!}+t+1\right),$$

$$G(t) = \beta^3\mathrm{e}^{-t}\left(\frac{16}{33}\frac{t^9}{9!}\right),$$

$$P(t) = \beta^3\mathrm{e}^{-t}\left(-\frac{4}{45}\frac{t^4}{4!}+\frac{t^3}{3!}+\frac{t^2}{2!}+t+1\right).$$

For the case of the free atom we may take $R \to 0$ to find

$$\frac{\Delta B}{B} \to -\frac{8\beta^3}{315}\frac{\mu_B^2}{kT}\left[\frac{3-5[1-\exp(3\zeta/2kT)]\,kT/\zeta}{1+2\exp(3\zeta/2kT)}\right]\frac{\mu_0}{4\pi}. \tag{13a}$$

When R is large, that is when we have long range coupling

$$d(\boldsymbol{R}) = \frac{1}{R^7}\left[\frac{7200}{\beta^4}\sqrt{\left(\frac{\pi}{26}\right)}\left(\frac{\sqrt{7}}{4}Y_{64}(\Theta,\Phi) - \frac{1}{2\sqrt{2}}Y_{60}(\Theta,\Phi) + \frac{\sqrt{7}}{4}Y_{6-4}(\Theta,\Phi)\right)\right]$$

$$+\frac{1}{R^5}\left[\frac{224}{\beta^2}\sqrt{\left(\frac{\pi}{21}\right)}\left(\tfrac{1}{2}\sqrt{(\tfrac{5}{6})}Y_{44}(\Theta,\Phi) + \tfrac{1}{2}\sqrt{(\tfrac{7}{3})}\,Y_{40}(\Theta,\Phi) + \tfrac{1}{2}\sqrt{(\tfrac{5}{6})}\,Y_{4-4}(\Theta,\Phi)\right)\right]$$

and $$s(\boldsymbol{R}) = \frac{1}{R^7}\left[\frac{4800}{\beta^4}\sqrt{\left(\frac{\pi}{26}\right)}\left(\frac{\sqrt{7}}{4}Y_{64}(\Theta,\Phi) - \frac{1}{2\sqrt{2}}Y_{60}(\Theta,\Phi) + \frac{\sqrt{7}}{4}Y_{6-4}(\Theta,\Phi)\right)\right]. \tag{13b}$$

(ii) *Tetragonal case*

With a tetragonal distortion along the z axis the n.m.r. shift is given by

$$\frac{\Delta B}{B} = \frac{2}{3}\frac{\mu_B^2}{kT}\frac{\mu_0}{4\pi}\frac{\sum_{i=1}^{3}(A_i + B_i kT)\exp(-\epsilon_i/kT)}{\sum_{i=1}^{3}\exp(-\epsilon_i/kT)}, \tag{14}$$

where
$$\epsilon_1 = \tfrac{1}{4}\zeta + \tfrac{1}{2}\delta - \tfrac{1}{2}A,$$
$$\epsilon_2 = \tfrac{1}{4}\zeta + \tfrac{1}{2}\delta + \tfrac{1}{2}A,$$
$$\epsilon_3 = -\tfrac{1}{2}\zeta - \delta,$$
$$A^2 = 9\zeta^2/4 - 3\delta\zeta + 9\delta^2,$$

where δ is the distortion parameter. A_i and B_i may be expressed in terms of spherical harmonics,

$$A_i = a_1^{(i)}\sqrt{(2\pi/91)}\,(Y_{6-4}(\Theta,\Phi) + Y_{64}(\Theta,\Phi)) + a_2^{(i)}\sqrt{(\pi/13)}\,Y_{60}(\Theta,\Phi)$$
$$+ a_3^{(i)}\sqrt{(2\pi/35)}\,(Y_{4-4}(\Theta,\Phi) + Y_{44}(\Theta,\Phi)) + a_4^{(i)}\sqrt{\pi}\,Y_{40}(\Theta,\Phi)$$
$$+ a_5^{(i)}\sqrt{(\pi/5)}\,Y_{20}(\Theta,\Phi) + a_6^{(i)}\sqrt{\pi}\,Y_{00}(\Theta,\Phi),$$

$$B_i = b_1^{(i)}\sqrt{(2\pi/91)}\,(Y_{6-4}(\Theta,\Phi) + Y_{64}(\Theta,\Phi)) + b_2^{(i)}\sqrt{(\pi/13)}\,Y_{60}(\Theta,\Phi)$$
$$+ b_3^{(i)}\sqrt{(2\pi/35)}\,(Y_{4-4}(\Theta,\Phi) + Y_{44}(\Theta,\Phi)) + b_4^{(i)}\sqrt{\pi}\,Y_{40}(\Theta,\Phi)$$
$$+ b_5^{(i)}\sqrt{(\pi/5)}\,Y_{20}(\Theta,\Phi) + b_6^{(i)}\sqrt{\pi}\,Y_{00}(\Theta,\Phi)$$

for $i = 1, 2, 3$.

The coefficients $a_l^{(i)}$ and $b_l^{(i)}$ for $l = 1$–6 are functions of the internuclear separation R, the spin-orbit coupling constant ζ and the distortion parameter δ.

We shall express the coefficients using matrix notation. If we define

$$a^2 = \tfrac{1}{2} - \tfrac{1}{2}(\zeta/2 - 3\delta)\,A^{-1},$$
$$b^2 = \tfrac{1}{2} + \tfrac{1}{2}(\zeta/2 - 3\delta)\,A^{-1},$$
$$ab = (\zeta/\sqrt{2})\,A^{-1},$$

we may then define matrices $g_m^{(i)}$ and $h_m^{(i)}$ as shown in tables 2 and 3 respectively.

The coefficients $a_l^{(i)}$ and $b_l^{(i)}$ may be expressed in terms of these matrices $g_m^{(i)}$ and $h_m^{(i)}$ and two matrices $c_{lm}(t)$ and $d_{lm}(t)$ of radial dependence. That is,

$$a_l^{(i)} = \sum_{m=1}^{4} c_{lm}(t)\, g_m^{(i)},$$

$$b_l^{(i)} = \sum_{m=1}^{6} d_{lm}(t)\, h_m^{(i)},$$

where $t = 2\beta R$.

TABLE 2. THE MATRIX ELEMENTS $g_m^{(i)}$

m	$i = 1$	$i = 2$	$i = 3$
1	a^4	b^4	0
2	$\sqrt{2}\,a^3b$	$-\sqrt{2}\,ab^3$	0
3	a^2b^2	a^2b^2	0
4	$-\sqrt{2}\,ab^3$	$\sqrt{2}\,a^3b$	0

TABLE 3. THE MATRIX ELEMENTS $h_m^{(i)}$

m	$i = 1$	$i = 2$	$i = 3$
1	$\frac{a^4+b^4}{\epsilon_1-\epsilon_2}$	$\frac{b^4+a^4}{\epsilon_2-\epsilon_1}$	0
2	$\frac{a^2b^2}{\epsilon_1-\epsilon_2}$	$\frac{b^2a^2}{\epsilon_2-\epsilon_1}$	0
3	$\frac{(\sqrt{2}\,ab^3-\sqrt{2}\,a^3b)}{\epsilon_1-\epsilon_2}$	$\frac{(\sqrt{2}\,ab^3-\sqrt{2}\,a^3b)}{\epsilon_2-\epsilon_1}$	0
4	$\frac{a^2}{\epsilon_1-\epsilon_3}$	$\frac{b^2}{\epsilon_2-\epsilon_3}$	$\frac{a^2}{\epsilon_3-\epsilon_1}+\frac{b^2}{\epsilon_3-\epsilon_2}$
5	$\frac{\sqrt{2}\,ab}{\epsilon_1-\epsilon_3}$	$-\frac{\sqrt{2}\,ab}{\epsilon_2-\epsilon_3}$	$\frac{\sqrt{2}\,ab}{\epsilon_3-\epsilon_1}-\frac{\sqrt{2}\,ab}{\epsilon_3-\epsilon_2}$
6	$\frac{b^2}{\epsilon_1-\epsilon_3}$	$\frac{a^2}{\epsilon_2-\epsilon_3}$	$\frac{a^2}{\epsilon_3-\epsilon_2}+\frac{b^2}{\epsilon_3-\epsilon_1}$

The matrix elements $c_{lm}(t)$ and $d_{lm}(t)$, together with their asymptotic expansions for $R \to \infty$, are listed in tables 4 and 5 respectively. They are given in terms of series which are linear combinations of the radial integrals of table 1. These series are listed in appendix A.

(iii) *Trigonal case*

The next case we shall treat is the one where there is a trigonal distortion along the [111] axis, the distortion being measured by the parameter δ and the eigenvalues are the ϵ_i values of the previous section. The n.m.r. shift is given by

$$\frac{\Delta B}{B} = \frac{2}{3}\frac{\mu_B^2}{kT}\frac{\mu_0}{4\pi}\frac{\sum_{i=1}^{3}(A_i'+B_i'kT)\exp(-\epsilon_i/kT)}{\sum_{i=1}^{3}\exp(-\epsilon_i/kT)}, \tag{15}$$

TABLE 4. THE MATRIX ELEMENTS $c_{lm}(t)$

(The asymptotic expansion for $R \to \infty$ for each $c_{lm}(t)$ is given in parentheses.)

$$c_{11} = 0,$$
$$c_{12} = \tfrac{16}{165}S_1 \quad \left(\frac{12\,600}{R^7\beta^4}\right),$$
$$c_{13} = -\tfrac{4}{33}S_1 \quad \left(-\frac{15\,750}{R^7\beta^4}\right),$$
$$c_{14} = -\tfrac{2}{165}S_1 \quad \left(-\frac{1575}{R^7\beta^4}\right),$$
$$c_{21} = \tfrac{32}{1155}S_1 \quad \left(\frac{3600}{R^7\beta^4}\right),$$
$$c_{22} = -\tfrac{16}{1155}S_1 \quad \left(-\frac{1800}{R^7\beta^4}\right),$$
$$c_{23} = \tfrac{8}{1155}S_1 \quad \left(\frac{900}{R^7\beta^4}\right),$$
$$c_{24} = \tfrac{4}{1155}S_1 \quad \left(\frac{450}{R^7\beta^4}\right),$$
$$c_{31} = 0,$$
$$c_{32} = \tfrac{4}{165}F_1 + \tfrac{4}{165}F_4 \quad \left(\frac{140}{R^5\beta^2}\right),$$
$$c_{33} = -\tfrac{4}{165}F_1 + \tfrac{4}{495}F_4 + \tfrac{4}{9}f_1 \quad \left(-\frac{280}{R^5\beta^2}\right),$$
$$c_{34} = \tfrac{8}{495}F_4 + \tfrac{2}{9}f_1 \quad \left(-\frac{70}{R^5\beta^2}\right),$$
$$c_{41} = \tfrac{16}{17325}F_7 + \tfrac{32}{315}f_1 \quad \left(-\frac{48}{R^5\beta^2}\right),$$
$$c_{42} = \tfrac{8}{825}F_2 - \tfrac{46}{17325}F_3 - \tfrac{38}{17325}F_5 + \tfrac{4}{825}F_8 \quad \left(\frac{32}{R^5\beta^2}\right),$$
$$c_{43} = -\tfrac{8}{825}F_2 + \tfrac{76}{17325}F_5 - \tfrac{128}{17325}F_6 - \tfrac{4}{825}F_8 + \tfrac{8}{315}f_1 \quad \left(-\frac{64}{R^5\beta^2}\right),$$
$$c_{44} = -\tfrac{64}{17325}F_6 + \tfrac{4}{105}f_1 \quad \left(-\frac{28}{R^5\beta^2}\right),$$
$$c_{51} = -\tfrac{8}{315}T_2 - \tfrac{8}{63}t_1 \quad \left(-\frac{8}{R^3}\right),$$
$$c_{52} = \tfrac{2}{315}T_1 - \tfrac{2}{315}T_3 \quad (0),$$
$$c_{53} = \tfrac{8}{315}T_1 + \tfrac{4}{315}T_3 + \tfrac{4}{21}t_1 \quad \left(\frac{12}{R^3}\right),$$
$$c_{54} = \tfrac{4}{315}T_1 + \tfrac{4}{63}t_1 \quad \left(\frac{4}{R^3}\right),$$
$$c_{61} = -\tfrac{8}{1575}N_1 - \tfrac{8}{45}n_1 \quad (0),$$
$$c_{62} = -\tfrac{8}{525}N_1 \quad (0),$$
$$c_{63} = \tfrac{4}{525}N_1 - \tfrac{4}{15}n_1 \quad (0),$$
$$c_{64} = -\tfrac{8}{1575}N_1 - \tfrac{8}{45}n_1 \quad (0).$$

TABLE 5. THE MATRIX ELEMENTS $d_{lm}(t)$

(The asymptotic expansion for $R \to \infty$ for each $d_{lm}(t)$ is given in parentheses).

$$d_{11} = \tfrac{4}{165}S_1 \quad \left(\frac{3150}{R^7\beta^4}\right),$$

$$d_{12} = -\tfrac{32}{165}S_1 \quad \left(-\frac{25\,200}{R^7\beta^4}\right),$$

$$d_{13} = -\tfrac{14}{165}S_1 \quad \left(-\frac{11\,025}{R^7\beta^4}\right),$$

$$d_{14} = 0,$$

$$d_{15} = \tfrac{4}{165}S_1 \quad \left(\frac{3150}{R^7\beta^4}\right),$$

$$d_{16} = -\tfrac{4}{165}S_1 \quad \left(-\frac{3150}{R^7\beta^4}\right),$$

$$d_{21} = -\tfrac{8}{1155}S_1 \quad \left(-\frac{900}{R^7\beta^4}\right),$$

$$d_{22} = -\tfrac{64}{1155}S_1 \quad \left(-\frac{7200}{R^7\beta^4}\right),$$

$$d_{23} = \tfrac{4}{385}S_1 \quad \left(\frac{1350}{R^7\beta^4}\right),$$

$$d_{24} = \tfrac{32}{1155}S_1 \quad \left(\frac{3600}{R^7\beta^4}\right),$$

$$d_{25} = -\tfrac{24}{1155}S_1 \quad \left(-\frac{2700}{R^7\beta^4}\right),$$

$$d_{26} = \tfrac{8}{1155}S_1 \quad \left(\frac{900}{R^7\beta^4}\right),$$

$$d_{31} = \tfrac{2}{165}F_4 - \tfrac{2}{9}f_1 \quad \left(\frac{70}{R^5\beta^2}\right),$$

$$d_{32} = -\tfrac{8}{165}F_1 + \tfrac{4}{99}F_4 + \tfrac{4}{9}f_1 \quad \left(-\frac{420}{R^5\beta^2}\right),$$

$$d_{33} = -\tfrac{4}{165}F_1 - \tfrac{4}{99}F_4 - \tfrac{2}{9}f_1 \quad \left(-\frac{70}{R^5\beta^2}\right),$$

$$d_{34} = 0,$$

$$d_{35} = \tfrac{2}{165}F_4 + \tfrac{2}{9}f_1 \quad \left(-\frac{70}{R^5\beta^2}\right),$$

$$d_{36} = -\tfrac{2}{165}F_4 - \tfrac{2}{9}f_1 \quad \left(\frac{70}{R^5\beta^2}\right),$$

$$d_{41} = \tfrac{4}{825}F_2 - \tfrac{4}{105}f_1 \quad \left(\frac{28}{R^5\beta^2}\right),$$

$$d_{42} = -\tfrac{8}{825}F_2 + \tfrac{152}{17325}F_5 - \tfrac{256}{17325}F_6 - \tfrac{63}{17325}F_7 - \tfrac{8}{825}F_8 - \tfrac{8}{35}f_1 \quad \left(\frac{24}{R^5\beta^2}\right),$$

$$d_{43} = -\tfrac{8}{825}F_2 + \tfrac{46}{17325}F_3 + \tfrac{38}{17325}F_5 + \tfrac{64}{17325}F_6 - \tfrac{4}{825}F_8 - \tfrac{4}{105}f_1 \quad \left(-\frac{4}{R^5\beta^2}\right),$$

TABLE 5. (*cont.*)

$$d_{44} = \tfrac{16}{17325}F_7 \quad \left(-\frac{16}{R^5\beta^2}\right),$$

$$d_{45} = \tfrac{4}{825}F_2 - \tfrac{8}{17325}F_7 + \tfrac{4}{105}f_1 \quad \left(\frac{12}{R^5\beta^2}\right),$$

$$d_{46} = -\tfrac{4}{825}F_2 - \tfrac{4}{105}f_1 \quad \left(-\frac{4}{R^5\beta^2}\right),$$

$$d_{51} = \tfrac{4}{105}T_4 - \tfrac{4}{63}t_1 \quad \left(-\frac{2}{R^3}\right),$$

$$d_{52} = \tfrac{16}{315}T_1 + \tfrac{16}{315}T_2 + \tfrac{8}{315}T_3 + \tfrac{8}{105}T_4 + \tfrac{32}{63}t_1 \quad \left(\frac{36}{R^3}\right),$$

$$d_{53} = -\tfrac{2}{105}T_1 + \tfrac{2}{315}T_3 - \tfrac{4}{63}t_1 \quad \left(-\frac{4}{R^3}\right),$$

$$d_{54} = -\tfrac{8}{315}T_2 \quad \left(-\frac{4}{R^3}\right),$$

$$d_{55} = \tfrac{4}{315}T_2 + \tfrac{4}{105}T_4 + \tfrac{4}{63}t_1 \quad \left(\frac{4}{R^3}\right),$$

$$d_{56} = -\tfrac{4}{105}T_4 - \tfrac{4}{63}t_1 \quad \left(-\frac{2}{R^3}\right),$$

$$d_{61} = -\tfrac{4}{525}N_1 + \tfrac{8}{45}n_1 \quad (0),$$

$$d_{62} = \tfrac{16}{1575}N_1 + \tfrac{8}{45}n_1 \quad (0).$$

$$d_{63} = \tfrac{32}{1575}N_1 + \tfrac{8}{45}n_1 \quad (0),$$

$$d_{64} = -\tfrac{8}{1575}N_1 \quad (0),$$

$$d_{65} = -\tfrac{8}{1575}N_1 - \tfrac{8}{45}n_1 \quad (0),$$

$$d_{66} = \tfrac{4}{525}N_1 + \tfrac{8}{45}n_1 \quad (0).$$

where
$$A'_i = \frac{1}{3}\sum_{m=1}^{4} a_m g_m^{(i)},$$

$$B'_i = \frac{1}{3}\sum_{m=1}^{6} b_m h_m^{(i)},$$

where $g_m^{(i)}$ and $h_m^{(i)}$ are listed in tables 2 and 3, and the a_m and b_m are given in table 6 in terms of the combinations of the hyperfine interaction integrals defined as follows:

$$A_0 = \sum_{\alpha,\beta} A_{\alpha\beta},$$

$$B_0 = \sum_{\alpha,\beta} B_{\alpha\beta},$$

$$C_0 = \sum_{\alpha,\beta} C_{\alpha\beta}^{(\beta)},$$

$$D_0 = \sum_{\alpha} D_{\alpha\alpha}^{(\alpha)} + \sum_{\alpha,\beta,\gamma}{}' D_{\alpha\beta}^{(\gamma)} \quad (\Sigma' \text{ implies } \alpha \neq \beta, \beta \neq \gamma, \gamma \neq \alpha),$$

$$E_0 = \mathrm{i}\sum_{\alpha}\{\langle\xi|\, l_{\mathrm{N}\alpha}/r_{\mathrm{N}}^3\,|\zeta\rangle + \langle\eta|\, l_{\mathrm{N}\alpha}/r_{\mathrm{N}}^3\,|\xi\rangle + \langle\zeta|\, l_{\mathrm{N}\alpha}/r_{\mathrm{N}}^3\,|\eta\rangle\},$$

$$F_0 = 3\mathrm{i}\{\langle\zeta|\, l_{\mathrm{N}x}/r_{\mathrm{N}}^3\,|\eta\rangle + \langle\xi|\, l_{\mathrm{N}y}/r_{\mathrm{N}}^3\,|\zeta\rangle + \langle\eta|\, l_{\mathrm{N}z}/r_{\mathrm{N}}^3\,|\xi\rangle\} - E_0,$$

$$A_{\alpha\beta} = \tfrac{1}{6}\{\langle\xi|\,T_{\alpha\beta}\,|\xi\rangle + \langle\eta|\,T_{\alpha\beta}\,|\eta\rangle + \langle\zeta|\,T_{\alpha\beta}\,|\zeta\rangle + 2\,\langle\xi|\,T_{\alpha\beta}|\,\eta\rangle + 2\,\langle\eta|\,T_{\alpha\beta}\,|\zeta\rangle + 2\,\langle\zeta|\,T_{\alpha\beta}\,\xi\rangle\},$$

$$B_{\alpha\beta} = \tfrac{1}{6}\{\langle\xi|\,T_{\alpha\beta}\,|\xi\rangle + \langle\eta|\,T_{\alpha\beta}|\eta\rangle + \langle\zeta|\,T_{\alpha\beta}\,|\zeta\rangle - \langle\xi|\,T_{\alpha\beta}\,|\eta\rangle - \langle\eta|\,T_{\alpha\beta}\,|\zeta\rangle - \langle\zeta|\,T_{\alpha\beta}\,|\xi\rangle\},$$

$$C^{(x)}_{\alpha\beta} = \tfrac{1}{6}\{2\,\langle\xi|\,T_{\alpha\beta}\,|\xi\rangle - \langle\eta|\,T_{\alpha\beta}\,|\eta\rangle - \langle\zeta|\,T_{\alpha\beta}\,|\zeta\rangle - 2\,\langle\eta|\,T_{\alpha\beta}\,|\zeta\rangle + \langle\zeta|\,T_{\alpha\beta}\,|\xi\rangle + \langle\xi|\,T_{\alpha\beta}\,|\eta\rangle\},$$

$$C^{(y)}_{\alpha\beta} = \tfrac{1}{6}\{2\,\langle\eta|\,T_{\alpha\beta}\,|\eta\rangle - \langle\zeta|\,T_{\alpha\beta}\,|\zeta\rangle - \langle\xi|\,T_{\alpha\beta}\,|\xi\rangle - 2\,\langle\zeta|\,T_{\alpha\beta}\,|\xi\rangle + \langle\xi|\,T_{\alpha\beta}\,|\eta\rangle + \langle\eta|\,T_{\alpha\beta}\,|\zeta\rangle\},$$

$$C^{(z)}_{\alpha\beta} = \tfrac{1}{6}\{2\,\langle\zeta|\,T_{\alpha\beta}\,|\zeta\rangle - \langle\xi|\,T_{\alpha\beta}\,|\xi\rangle - \langle\eta|\,T_{\alpha\beta}\,|\eta\rangle - 2\,\langle\xi|\,T_{\alpha\beta}\,|\eta\rangle + \langle\eta|\,T_{\alpha\beta}\,|\zeta\rangle + \langle\zeta|\,T_{\alpha\beta}\,|\xi\rangle\},$$

$$D^{(x)}_{\alpha\beta} = \tfrac{1}{6}\{2\,\langle\xi|\,T_{\alpha\beta}\,|\xi\rangle - \langle\eta|\,T_{\alpha\beta}\,|\eta\rangle - \langle\zeta|\,T_{\alpha\beta}\,|\zeta\rangle + 4\,\langle\eta|\,T_{\alpha\beta}\,|\zeta\rangle - 2\,\langle\zeta|T_{\alpha\beta}\,|\xi\rangle - 2\,\langle\xi|\,T_{\alpha\beta}\,|\eta\rangle\},$$

$$D^{(y)}_{\alpha\beta} = \tfrac{1}{6}\{2\,\langle\eta|\,T_{\alpha\beta}\,|\eta\rangle - \langle\zeta|\,T_{\alpha\beta}\,|\zeta\rangle - \langle\xi|\,T_{\alpha\beta}\,|\xi\rangle + 4\,\langle\zeta|\,T_{\alpha\beta}\,|\xi\rangle - 2\,\langle\xi|\,T_{\alpha\beta}\,|\eta\rangle - 2\,\langle\eta|\,T_{\alpha\beta}\,|\zeta\rangle\},$$

$$D^{(z)}_{\alpha\beta} = \tfrac{1}{6}\{2\,\langle\zeta|\,T_{\alpha\beta}\,|\zeta\rangle - \langle\xi|\,T_{\alpha\beta}\,|\xi\rangle - \langle\eta|\,T_{\alpha\beta}\,|\eta\rangle + 4\,\langle\xi|\,T_{\alpha\beta}\,|\eta\rangle - 2\,\langle\eta|\,T_{\alpha\beta}\,|\zeta\rangle - 2\,\langle\zeta|\,T_{\alpha\beta}\,|\xi\rangle\}.$$

Table 6. The appropriate a_m and b_m values of equation (15)

m	a_m	b_m
1	$-2B_0-2E_0$	$-C_0+F_0$
2	$2C_0+D_0$	$2B_0+2C_0+2D_0+6E_0-2F_0$
3	$2A_0+B_0+2C_0+D_0+E_0-2F_0$	$A_0-D_0-F_0$
4	$-A_0+F_0$	$-2B_0$
5	—	$C_0-B_0+F_0$
6	—	C_0+F_0

3. Discussion

To illustrate the results from these calculations we shall examine the electron–nuclear interaction as represented by the hamiltonian (2) when the nucleus with a magnetic moment is in the xy plane 0.2 nm from the d-electron bearing nucleus.

First, we shall consider the case when the d-electron bearing atom is in a strong crystal field of octahedral symmetry and examine the hyperfine interaction tensor components $A_{\alpha\beta}$ in the ${}^2T_2E''$ level. (In this case in equation (7) $A_k = \sqrt{2}/\sqrt{3}$, $B_k = 1/\sqrt{3}$ and $C_k = 0$.) In this example $A_{xz} = A_{zx} = A_{yz} = A_{zy} = 0$. The remaining hyperfine interaction tensor components are evaluated from equation (10) and are markedly angular dependent as shown in figure 2. As a specific example, when $R = 0.2\,\text{nm}$, $\Theta = 90°$ and $\Phi = 30°$ the $\mathbf{A}$ tensor, in units of $2g_{\text{N}}\mu_{\text{N}}\mu_B\mu_0/4\pi \times 10^{28}$ joules, is

$$\begin{pmatrix} 18.7881 & 13.9944 & 0 \\ 25.1413 & -7.1676 & 0 \\ 0 & 0 & -3.4486 \end{pmatrix}.$$

The principal values of the symmetric tensor, $\mathbf{S}$, ($\mathbf{S} = \mathbf{A}^T\mathbf{A}$) S_1, S_2 and S_3 are 994.2373, 238.0557 and 11.8929 respectively and the corresponding principal axes are when $\Theta = 90°$ and $\Phi = 6.319°$; $\Theta = 90°$ and $\Phi = 96.319°$ and $\Theta = 0°$ and $\Phi = 0°$ respectively. Hence the principal hyperfine interaction constants are

$$A_1 = S_1^{\frac{1}{2}} = 31.5316,$$
$$A_2 = -S_2^{\frac{1}{2}} = -15.4291,$$
$$A_3 = A_{zz} = -S_3^{\frac{1}{2}} = -3.4486.$$

The signs of A_1 and A_2 were ascertained by considering a range of R values – when $R \to 0$ $A_1 = A_2 = A_3$ and when $R \to \infty$ $A_1 + A_2 + A_3 = 0$.

The n.m.r. shift arising from the electron–nuclear interaction when the n.m.r. nucleus is at a position (R, Θ Φ,) from the d-electron bearing atom is given by equation (12) when the d-electron is in a strong crystal field of octahedral symmetry. The results for the case when $\zeta = 400\,\mathrm{cm}^{-1}$ and $T = 300\,\mathrm{K}$ when $R = 0.2\,\mathrm{nm}$ and $\Theta = \frac{1}{2}\pi$ for a range of Φ values are given in figure 3. From the results $\Delta B/B$ is markedly angular dependent and can be positive or negative depending on the Φ value. The maximum negative value occurs when the n.m.r. nucleus is along the x and y axes and the maximum positive value occurs when the Φ value for the n.m.r. nucleus is $\frac{1}{4}\pi + \frac{1}{2}n\pi$ ($n = 0, 1, 2, 3, \ldots$).

If the crystal field has a tetragonal component along the z axis $\Delta B/B$ for a specific $\boldsymbol{R}$ is given by equation (14). The results for the case when $\delta = 1000\,\mathrm{cm}^{-1}$, $\zeta = 400\,\mathrm{cm}^{-1}$ and $T = 300\,\mathrm{K}$ when $R = 0.2\,\mathrm{nm}$ and $\theta = \frac{1}{2}\pi$ for a range of Φ values are given in figure 4.

If the crystal field has a trigonal component along the [111] axis $\Delta B/B$ for a specific $\boldsymbol{R}$ is given by equation (15). The results for the case when $\delta = 1000\,\mathrm{cm}^{-1}$, $\zeta = 400\,\mathrm{cm}^{-1}$ and $T = 300\,\mathrm{K}$ when $R = 0.2\,\mathrm{nm}$ and $\Theta = \frac{1}{2}\pi$ for a range of Φ values are given in figure 5.

We shall next compare these results with the multipole expansion approach in determining $\Delta B/B$ – see, for example, McConnell (1957), McConnell & Robertson (1958) and Stiles (1975). For the case of octahedral symmetry the angular dependence of the first term in the multipole expansion, the $1/R^5$ term of equation (13*b*), is

$$35\cos^4\Theta - 30\cos^2\Theta + 3 + 5\sin^4\Theta\cos 4\Phi.$$

In the xy plane this reduces to $(3 + 5\cos 4\Phi)$ and the ratio of the values when $\Phi = 0$ and $\frac{1}{4}\pi$ is -4. The results in figure 3 follow the $\cos 4\Phi$ dependence but the ratio of $\Delta B/B$ when $\Phi = 0$ and $\frac{1}{4}\pi$ is -1.117. For the tetragonal case the angular dependence of the first term in the multipole expansion, the $1/R^3$ term, is $(3\cos^2\Theta - 1)$ and is Φ independent. The results in figure 4 reflect a Φ dependence.

The inclusion of the higher multipole terms improves the comparison of the results but still the results differ significantly. Thus these results confirm our early work (Golding, Pascual & Vrbancich 1976; Golding, Pascual & Stubbs 1976) and hence in this particular case the multiple expansion method of evaluating the electron–nuclear interation should not be used.

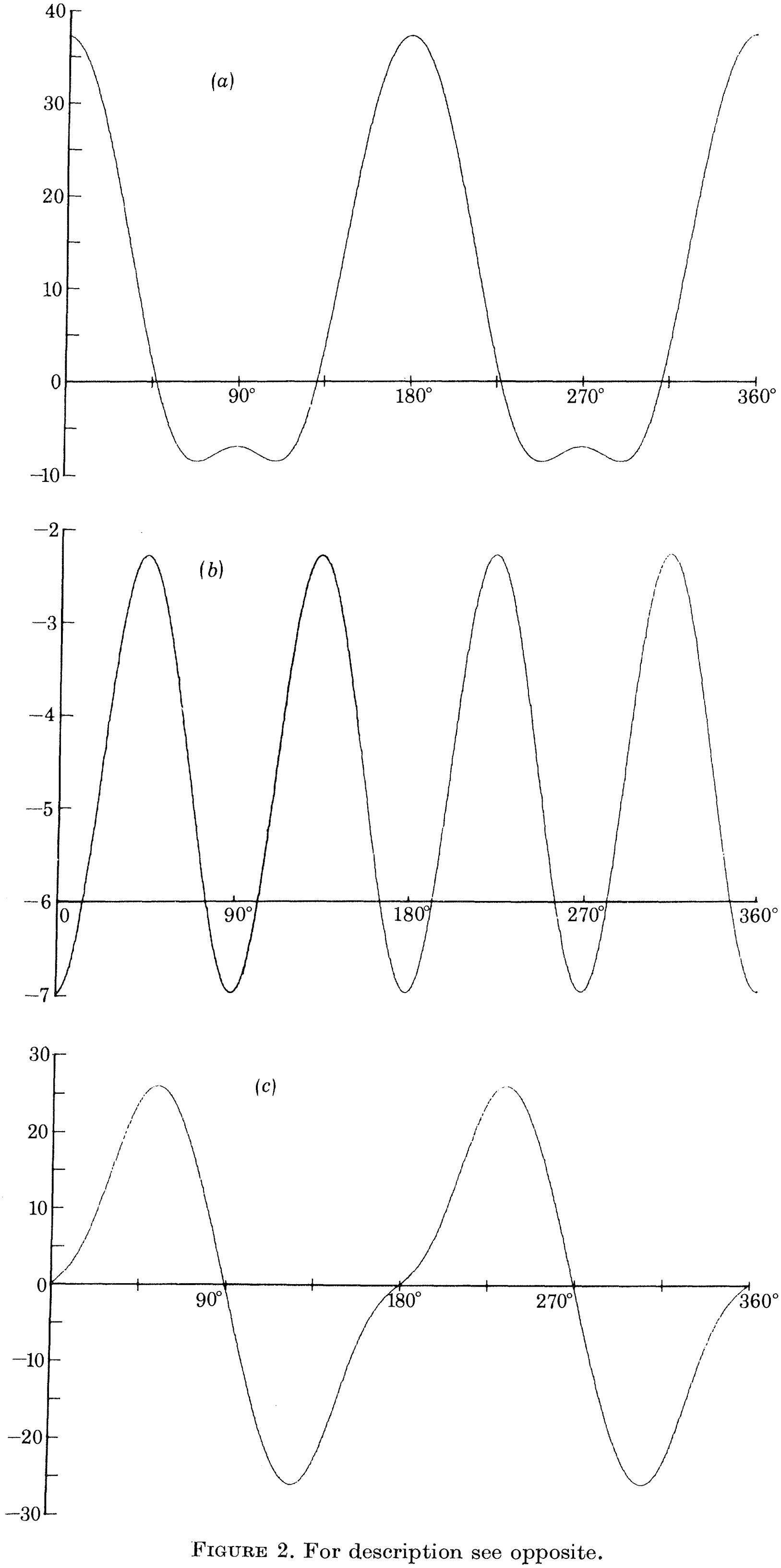

FIGURE 2. For description see opposite.

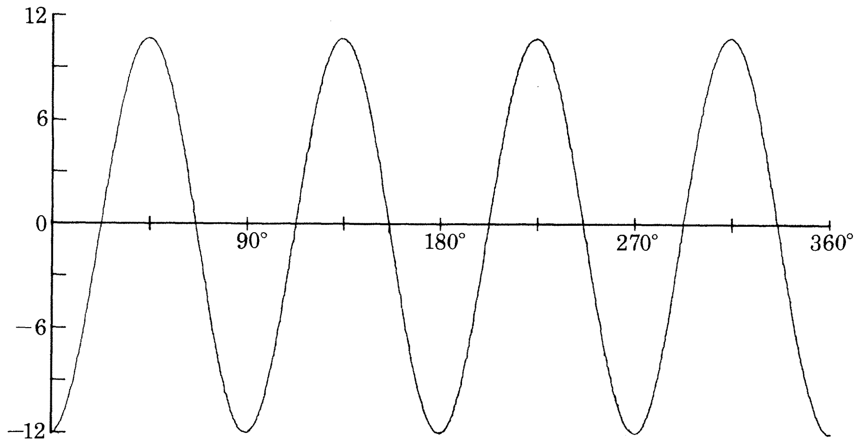

FIGURE 3. The Φ dependence of $\Delta B/B$ (ppm) when the n.m.r. nucleus is 0.2 nm in the xy plane from the d-electron bearing atom in a crystal field of octahedral symmetry when $\zeta = 400\,\text{cm}^{-1}$ and $T = 300\,\text{K}$.

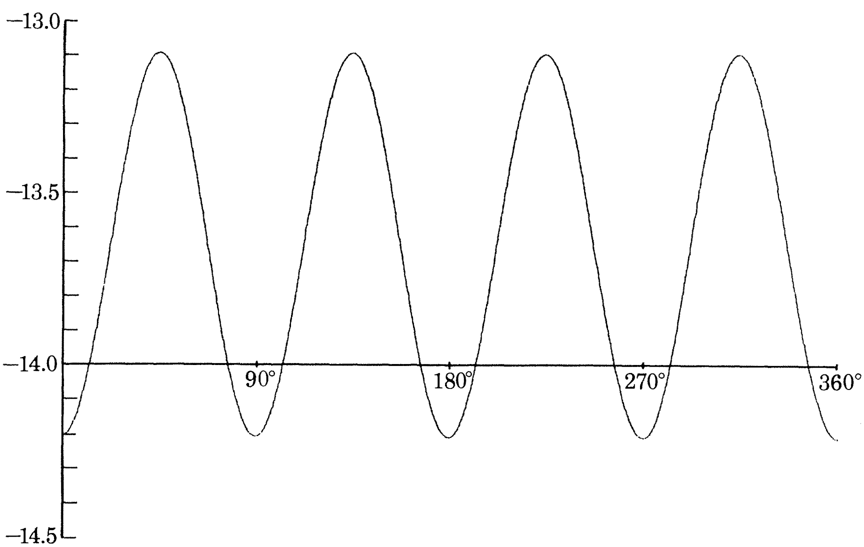

FIGURE 4. The Φ dependence of $\Delta B/B$ (ppm) when the n.m.r. nucleus is 0.2 nm in the xy plane from the d-electron bearing atom in a crystal field with a tetragonal component along the z axis when $\delta = 1000\,\text{cm}^{-1}$, $\zeta = 400\,\text{cm}^{-1}$ and $T = 300\,\text{K}$.

FIGURE 2. (*a*) The Φ dependence of A_{xx} for the $^2T_2E''$ level when the n.m.r. nucleus is 0.2 nm in the xy plane from the d-electron bearing atom in a crystal field of octahedral symmetry. $A_{yy}(\Phi) = A_{xx}(\Phi + \frac{1}{2}\pi)$. (*b*) The Φ dependence of A_{zz} for the $^2T_2E''$ level when the n.m.r. nucleus is 0.2 nm in the xy plane from the d-electron bearing atom in a crystal field of octahedral symmetry. (*c*) The Φ dependence of A_{xy} for the $^2T_2E''$ level when the n.m.r. nucleus is 0.2 nm in the xy plane from the d-electron bearing atom in a crystal field of octahedral symmetry. $A_{yx}(\Phi) = -A_{xy}(\Phi + \frac{1}{2}\pi)$. All in units of $2g_N\mu_N\mu_B\mu_0/4\pi \times 10^{28}$ joules.

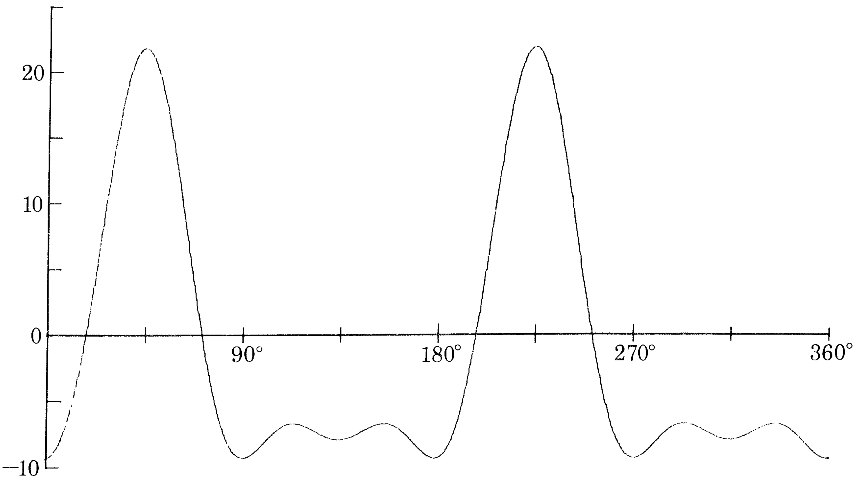

FIGURE 5. The Φ dependence of $\Delta B/B$ (ppm) when the n.m.r. nucleus is 0.2 nm in the xy plane from the d-electron bearing atom in a crystal field with a trigonal component along the [111] axis when $\delta = 1000\,\mathrm{cm}^{-1}$, $\zeta = 400\,\mathrm{cm}^{-1}$ and $T = 300$ K.

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APPENDIX A. RADIAL SERIES

(a) General formulae

$$F_j = 5u_2 + (20-A)\,v_1 + Av_3 + (30-B)\,w_2 + Bw_4 + (20-C)\,x_3 + Cx_5 + 5y_4,$$

where $$A = \mu, \quad B = \tfrac{10}{7}\mu - \tfrac{45}{7}, \quad C = \tfrac{5}{9}\mu - \tfrac{10}{3}.$$

$$T_j = 5u_2 + (20-A)\,v_1 + Av_3 + (30-B-C)\,w_0 + Bw_2 + Cw_4 + (20-A)\,x_1 + Ax_3 + 5y_2,$$

where $$A = \mu, \quad B = \tfrac{10}{3}(\mu - \lambda + 1), \quad C = \lambda.$$

(b) Specific formulae

$$S_1 = 5u_2 + 20v_3 + 30w_4 + 20x_5 + 5y_6,$$
$$F_{21} = \tfrac{1}{5}(v_1 - v_3) + \tfrac{2}{7}(w_2 - w_4) + \tfrac{1}{9}(x_3 - x_5),$$
$$T_4 = v_1 - v_3 + \tfrac{1}{21}(49w_0 - 40w_2 - 9w_4) + x_1 - x_3,$$
$$N_1 = 5u_2 + 14v_1 + 6v_3 + \tfrac{5}{3}(7w_0 + 11w_2) + 20x_1 + 5y_0,$$

$$f_1 = v_1 + 3w_2 + 3x_3 + y_4,$$
$$t_1 = v_1 + \tfrac{1}{3}(14w_0 - 5w_2) + \tfrac{3}{5}(7x_1 - 2x_3) + y_2,$$
$$t_2 = v_1 + \tfrac{1}{9}(14w_0 + 13w_2) + \tfrac{1}{3}(7x_1 + 2x_3) + y_2,$$
$$n_1 = v_1 + \tfrac{1}{3}(5w_0 + 4w_2) + 3x_1 + y_0.$$

(*c*) Parameter values for the F_j and T_j series

F_j	F_1	F_2	F_3	F_4	F_5	F_6	F_7
μ	20	$\frac{107}{7}$	$\frac{108}{23}$	9	$\frac{204}{19}$	$\frac{69}{4}$	-24
F_j	F_8	F_9	F_{10}	F_{11}	F_{12}	F_{13}	F_{14}
μ	$\frac{52}{7}$	12	$\frac{96}{7}$	$\frac{56}{5}$	$\frac{38}{3}$	42	$\frac{49}{3}$
F_j	F_{15}	F_{16}	F_{17}	F_{18}	F_{19}	F_{20}	F_{22}
μ	-2	$\frac{78}{5}$	$\frac{162}{7}$	$\frac{129}{7}$	$\frac{29}{2}$	$\frac{65}{6}$	$\frac{67}{5}$

T_j	T_1	T_2	T_3	T_5	T_6	T_7	T_8	T_9
μ	12	18	24	16	14	8	20	5
λ	$\frac{54}{7}$	$\frac{72}{7}$	$\frac{90}{7}$	$\frac{66}{7}$	$\frac{60}{7}$	4	$\frac{78}{7}$	$\frac{12}{7}$

Appendix B. The hyperfine integrals

Define

$$Q^{(\pm)}_{LM_L} = \frac{1}{\sqrt{2}}[Y_{L-M_L}(\Theta, \Phi) \pm Y_{LM_L}(\Theta, \Phi)], \quad M_L \neq 0,$$
$$Q_{L0} = Y_{L0}(\Theta, \Phi).$$

(*a*) The integrals $\langle \Psi_i | \, l_{\mathrm{N}\alpha}/r^3_{\mathrm{N}} \, | \Psi_j \rangle$

$$\langle \eta | \, l_{\mathrm{N}x}/r^3_{\mathrm{N}} \, | \xi \rangle = \mathrm{i}\left[\frac{4}{63}\sqrt{\left(\frac{2\pi}{5}\right)} Q^{(-)}_{41} f_1 + \frac{2}{7}\sqrt{\left(\frac{\pi}{15}\right)} Q^{(-)}_{21} t_2\right],$$

$$\langle \eta | \, l_{\mathrm{N}y}/r^3_{\mathrm{N}} \, | \xi \rangle = -\frac{4}{63}\sqrt{\left(\frac{2\pi}{5}\right)} Q^{(+)}_{41} f_1 - \frac{2}{7}\sqrt{\left(\frac{\pi}{15}\right)} Q^{(+)}_{21} t_2,$$

$$\langle \eta | \, l_{\mathrm{N}z}/r^3_{\mathrm{N}} \, | \xi \rangle = \mathrm{i}\left[\frac{16\sqrt{\pi}}{315} Q_{40} f_1 - \frac{4}{63}\sqrt{\left(\frac{\pi}{5}\right)} Q_{20} t_1 - \frac{4\sqrt{\pi}}{45} Q_{00} n_1\right],$$

$$\langle \zeta | \, l_{\mathrm{N}x}/r^3_{\mathrm{N}} \, | \eta \rangle = \mathrm{i}\left[\frac{2}{9}\sqrt{\left(\frac{\pi}{35}\right)} Q^{(+)}_{44} f_1 - \frac{4}{63}\sqrt{\left(\frac{\pi}{5}\right)} Q^{(+)}_{42} f_1 + \frac{2\sqrt{\pi}}{105} Q_{40} f_1 - \frac{2}{21}\sqrt{\left(\frac{\pi}{15}\right)} \right.$$
$$\left. \times Q^{(+)}_{22} t_1 + \frac{2}{63}\sqrt{\left(\frac{\pi}{5}\right)} Q_{20} t_1 - \frac{4\sqrt{\pi}}{45} Q_{00} n_1\right],$$

$$\langle \zeta | \, l_{\mathrm{N}y}/r^3_{\mathrm{N}} \, | \eta \rangle = -\frac{2}{9}\sqrt{\left(\frac{\pi}{35}\right)} Q^{(-)}_{44} f_1 + \frac{2}{63}\sqrt{\left(\frac{\pi}{5}\right)} Q^{(-)}_{42} f_1 - \frac{2}{7}\sqrt{\left(\frac{\pi}{15}\right)} Q^{(-)}_{22} t_2,$$

$$\langle \zeta | \, l_{\mathrm{N}z}/r^3_{\mathrm{N}} \, | \eta \rangle = \mathrm{i}\left[\frac{1}{9}\sqrt{\left(\frac{2\pi}{35}\right)} Q^{(-)}_{43} f_1 - \frac{1}{21}\sqrt{\left(\frac{2\pi}{5}\right)} Q^{(-)}_{41} f_1 + \frac{2}{7}\sqrt{\left(\frac{\pi}{15}\right)} Q^{(-)}_{21} t_2,\right],$$

$$\langle\xi|\,l_{Nx}/r^3\,|\zeta\rangle = \frac{2}{9}\sqrt{\left(\frac{\pi}{35}\right)}\,Q_{44}^{(-)}f_1+\frac{2}{63}\sqrt{\left(\frac{\pi}{5}\right)}\,Q_{42}^{(-)}f_1-\frac{2}{7}\sqrt{\left(\frac{\pi}{15}\right)}\,Q_{22}^{(-)}t_2,$$

$$\langle\xi|\,l_{Ny}/r_N^3\,|\zeta\rangle = \mathrm{i}\left[\frac{2}{9}\sqrt{\left(\frac{\pi}{35}\right)}\,Q_{44}^{(+)}f_1+\frac{4}{63}\sqrt{\left(\frac{\pi}{5}\right)}\,Q_{42}^{(+)}f_1+\frac{2\sqrt{\pi}}{105}Q_{40}f_1\right.$$
$$\left.+\frac{2}{21}\sqrt{\left(\frac{\pi}{15}\right)}\,Q_{22}^{(+)}t_1+\frac{2}{63}\sqrt{\left(\frac{\pi}{5}\right)}\,Q_{20}t_1-\frac{4\sqrt{\pi}}{45}Q_{00}n_1\right],$$

$$\langle\xi|l_{N\,z}/r_N^3\,|\zeta\rangle = \frac{1}{9}\sqrt{\left(\frac{2\pi}{35}\right)}\,Q_{43}^{(+)}f_1+\frac{1}{21}\sqrt{\left(\frac{2\pi}{5}\right)}\,Q_{41}^{(+)}f_1-\frac{2}{7}\sqrt{\left(\frac{\pi}{15}\right)}\,Q_{21}^{(+)}t_2.$$

(*b*) The integrals $\langle\Psi_i|\,T_{\alpha\beta}\,|\Psi_j\rangle$

$$\langle\xi|\,T_{xx}\,|\xi\rangle = -\frac{8}{165}\sqrt{\left(\frac{\pi}{91}\right)}\,Q_{64}^{(+)}S_1+\frac{8}{1155}\sqrt{\left(\frac{\pi}{13}\right)}\,Q_{60}S_1-\frac{4}{165}\sqrt{\left(\frac{\pi}{35}\right)}\,Q_{44}^{(+)}F_1$$
$$+\frac{8}{315}\sqrt{\left(\frac{\pi}{5}\right)}\,Q_{42}^{(+)}F_9+\frac{92\sqrt{\pi}}{17325}Q_{40}F_3+\frac{4}{105}\sqrt{\left(\frac{\pi}{15}\right)}\,Q_{22}^{(+)}T_1$$
$$-\frac{4}{315}\sqrt{\left(\frac{\pi}{5}\right)}\,Q_{20}T_1-\frac{16\sqrt{\pi}}{1575}Q_{00}N_1,$$

$$\langle\xi|\,T_{yy}\,|\xi\rangle = \frac{8}{165}\sqrt{\left(\frac{\pi}{91}\right)}\,Q_{64}^{(+)}S_1+\frac{32}{165}\sqrt{\left(\frac{2\pi}{1365}\right)}\,Q_{62}^{(+)}S_1+\frac{8}{385}\sqrt{\left(\frac{\pi}{13}\right)}Q_{60}S_1$$
$$+\frac{4}{165}\sqrt{\left(\frac{\pi}{35}\right)}\,Q_{44}^{(+)}F_1-\frac{32}{3465}\sqrt{\left(\frac{\pi}{5}\right)}\,Q_{42}^{(+)}F_4-\frac{76\sqrt{\pi}}{17325}Q_{40}F_5$$
$$-\frac{4}{105}\sqrt{\left(\frac{\pi}{15}\right)}\,Q_{22}^{(+)}T_5-\frac{4}{315}\sqrt{\left(\frac{\pi}{5}\right)}\,Q_{20}T_3+\frac{8\sqrt{\pi}}{1575}Q_{00}N_1,$$

$$\langle\xi|\,T_{zz}\,|\xi\rangle = -\frac{32}{165}\sqrt{\left(\frac{2\pi}{1365}\right)}\,Q_{62}^{(+)}S_1-\frac{32}{1155}\sqrt{\left(\frac{\pi}{13}\right)}\,Q_{60}S_1-\frac{8}{495}\sqrt{\left(\frac{\pi}{5}\right)}\,Q_{42}^{(+)}F_{10}$$
$$-\frac{16\sqrt{\pi}}{17325}Q_{40}F_7-\frac{16}{105}\sqrt{\left(\frac{\pi}{15}\right)}\,Q_{22}^{(+)}T_4+\frac{8}{315}\sqrt{\left(\frac{\pi}{5}\right)}Q_{20}T_2+\frac{8\sqrt{\pi}}{1575}Q_{00}N_1,$$

$$\langle\xi|T_{xy}\,|\xi\rangle = \mathrm{i}\left[-\frac{8}{165}\sqrt{\left(\frac{\pi}{91}\right)}\,Q_{64}^{(-)}S_1-\frac{16}{165}\sqrt{\left(\frac{2\pi}{1365}\right)}\,Q_{62}^{(-)}S_1-\frac{4}{165}\sqrt{\left(\frac{\pi}{35}\right)}\,Q_{44}^{(-)}F_1\right.$$
$$\left.+\frac{4}{231}\sqrt{\left(\frac{\pi}{5}\right)}\,Q_{42}^{(-)}F_{11}+\frac{4}{105}\sqrt{\left(\frac{\pi}{15}\right)}\,Q_{22}^{(-)}T_6\right],$$

$$\langle\xi|\,T_{yz}\,|\xi\rangle = \mathrm{i}\left[-\frac{8}{55}\sqrt{\left(\frac{2\pi}{1365}\right)}\,Q_{63}^{(+)}S_1-\frac{8}{55}\sqrt{\left(\frac{\pi}{273}\right)}\,Q_{61}^{(+)}S_1-\frac{2}{55}\sqrt{\left(\frac{2\pi}{35}\right)}\,Q_{43}^{(+)}F_{12}\right.$$
$$\left.+\frac{2}{385}\sqrt{\left(\frac{2\pi}{5}\right)}\,Q_{41}^{(+)}F_{12}+\frac{4}{35}\sqrt{\left(\frac{\pi}{15}\right)}\,Q_{21}^{(+)}T_7\right],$$

$$\langle\xi|\,T_{zx}\,|\xi\rangle = -\frac{8}{55}\sqrt{\left(\frac{2\pi}{1365}\right)}\,Q_{63}^{(-)}S_1 - \frac{8}{165}\sqrt{\left(\frac{\pi}{273}\right)}\,Q_{61}^{(-)}S_1 - \frac{2}{55}\sqrt{\left(\frac{2\pi}{35}\right)}\,Q_{43}^{(-)}F_{12} + \frac{2}{1155}\sqrt{\left(\frac{2\pi}{5}\right)}\,Q_{41}^{(-)}F_{13} + \frac{4}{105}\sqrt{\left(\frac{\pi}{15}\right)}\,Q_{21}^{(-)}T_6,$$

$$\langle\eta|\,T_{xx}\,|\eta\rangle = \frac{8}{165}\sqrt{\left(\frac{\pi}{91}\right)}\,Q_{64}^{(+)}S_1 - \frac{32}{165}\sqrt{\left(\frac{2\pi}{1365}\right)}\,Q_{62}^{(+)}S_1 + \frac{8}{385}\sqrt{\left(\frac{\pi}{13}\right)}\,Q_{60}S_1 + \frac{4}{165}\sqrt{\left(\frac{\pi}{35}\right)}\,Q_{44}^{(+)}F_1 + \frac{32}{3465}\sqrt{\left(\frac{\pi}{5}\right)}\,Q_{42}^{(+)}F_4 - \frac{76\sqrt{\pi}}{17325}\,Q_{40}F_5 + \frac{4}{105}\sqrt{\left(\frac{\pi}{15}\right)}\,Q_{22}^{(+)}T_5 - \frac{4}{315}\sqrt{\left(\frac{\pi}{5}\right)}\,Q_{20}T_3 + \frac{8\sqrt{\pi}}{1575}\,Q_{00}N_1,$$

$$\langle\eta|\,T_{yy}\,|\eta\rangle = -\frac{8}{165}\sqrt{\left(\frac{\pi}{91}\right)}\,Q_{64}^{(+)}S_1 + \frac{8}{1155}\sqrt{\left(\frac{\pi}{13}\right)}\,Q_{60}S_1 - \frac{4}{165}\sqrt{\left(\frac{\pi}{35}\right)}\,Q_{44}^{(+)}F_1 - \frac{8}{315}\sqrt{\left(\frac{\pi}{5}\right)}\,Q_{42}^{(+)}F_9 + \frac{92\sqrt{\pi}}{17325}\,Q_{40}F_3 - \frac{4}{105}\sqrt{\left(\frac{\pi}{15}\right)}\,Q_{22}^{(+)}T_1 - \frac{4}{315}\sqrt{\left(\frac{\pi}{5}\right)}\,Q_{20}T_1 - \frac{16\sqrt{\pi}}{1575}\,Q_{00}N_1,$$

$$\langle\eta|\,T_{zz}\,|\eta\rangle = \frac{32}{165}\sqrt{\left(\frac{2\pi}{1365}\right)}\,Q_{62}^{(+)}S_1 - \frac{32}{1155}\sqrt{\left(\frac{\pi}{13}\right)}\,Q_{60}S_1 + \frac{8}{495}\sqrt{\left(\frac{\pi}{5}\right)}\,Q_{42}^{(+)}F_{10} - \frac{16\sqrt{\pi}}{17325}\,Q_{40}F_7 + \frac{16}{105}\sqrt{\left(\frac{\pi}{15}\right)}\,Q_{22}^{(+)}T_4 + \frac{8}{315}\sqrt{\left(\frac{\pi}{5}\right)}\,Q_{20}T_2 + \frac{8\sqrt{\pi}}{1575}\,Q_{00}N_1,$$

$$\langle\eta|\,T_{xy}\,|\eta\rangle = \mathrm{i}\left[\frac{8}{165}\sqrt{\left(\frac{\pi}{91}\right)}\,Q_{64}^{(-)}S_1 - \frac{16}{165}\sqrt{\left(\frac{2\pi}{1365}\right)}\,Q_{62}^{(-)}S_1 + \frac{4}{165}\sqrt{\left(\frac{\pi}{35}\right)}\,Q_{44}^{(-)}F_1 + \frac{4}{231}\sqrt{\left(\frac{\pi}{5}\right)}\,Q_{42}^{(-)}F_{11} + \frac{4}{105}\sqrt{\left(\frac{\pi}{15}\right)}\,Q_{22}^{(-)}T_6\right],$$

$$\langle\eta|\,T_{yz}\,|\eta\rangle = \mathrm{i}\left[\frac{8}{55}\sqrt{\left(\frac{2\pi}{1365}\right)}\,Q_{63}^{(+)}S_1 - \frac{8}{165}\sqrt{\left(\frac{\pi}{273}\right)}\,Q_{61}^{(+)}S_1 + \frac{2}{55}\sqrt{\left(\frac{2\pi}{35}\right)}\,Q_{43}^{(+)}F_{12} + \frac{2}{1155}\sqrt{\left(\frac{2\pi}{5}\right)}\,Q_{41}^{(+)}F_{13} + \frac{4}{105}\sqrt{\left(\frac{\pi}{15}\right)}\,Q_{21}^{(+)}T_6\right],$$

$$\langle\eta|\,T_{zx}\,|\eta\rangle = \frac{8}{55}\sqrt{\left(\frac{2\pi}{1365}\right)}\,Q_{63}^{(-)}S_1 - \frac{8}{55}\sqrt{\left(\frac{\pi}{273}\right)}\,Q_{61}^{(-)}S_1 + \frac{2}{55}\sqrt{\left(\frac{2\pi}{35}\right)}\,Q_{43}^{(-)}F_{12} + \frac{2}{385}\sqrt{\left(\frac{2\pi}{5}\right)}\,Q_{41}^{(-)}F_{12} + \frac{4}{35}\sqrt{\left(\frac{\pi}{15}\right)}\,Q_{21}^{(-)}T_7,$$

$$\langle\zeta|\,T_{xx}\,|\zeta\rangle = -\frac{2}{5}\sqrt{\left(\frac{2\pi}{3003}\right)}\,Q_{66}^{(+)}S_1 + \frac{4}{165}\sqrt{\left(\frac{\pi}{91}\right)}\,Q_{64}^{(+)}S_1 + \frac{2}{165}\sqrt{\left(\frac{2\pi}{1365}\right)}\,Q_{62}^{(+)}S_1 - \frac{4}{1155}\sqrt{\left(\frac{\pi}{13}\right)}\,Q_{60}S_1 - \frac{16}{495}\sqrt{\left(\frac{\pi}{35}\right)}\,Q_{44}^{(+)}F_4 - \frac{8}{1155}\sqrt{\left(\frac{\pi}{5}\right)}\,Q_{42}^{(+)}F_1 + \frac{64\sqrt{\pi}}{17325}\,Q_{40}F_6 + \frac{4}{105}\sqrt{\left(\frac{\pi}{15}\right)}\,Q_{22}^{(+)}T_8 - \frac{4}{315}\sqrt{\left(\frac{\pi}{5}\right)}\,Q_{20}T_1 + \frac{8\sqrt{\pi}}{1575}\,Q_{00}N_1,$$

$$\langle\zeta|\,T_{yy}\,|\zeta\rangle = \frac{2}{5}\sqrt{\left(\frac{2\pi}{3003}\right)}\,Q_{66}^{(+)}S_1 + \frac{4}{165}\sqrt{\left(\frac{\pi}{91}\right)}\,Q_{64}^{(+)}S_1 - \frac{2}{165}\sqrt{\left(\frac{2\pi}{1365}\right)}\,Q_{62}^{(+)}S_1$$

$$- \frac{4}{1155}\sqrt{\left(\frac{\pi}{13}\right)}\,Q_{60}S_1 - \frac{16}{495}\sqrt{\left(\frac{\pi}{35}\right)}\,Q_{44}^{(+)}F_4 + \frac{8}{1155}\sqrt{\left(\frac{\pi}{5}\right)}\,Q_{42}^{(+)}F_1$$

$$+ \frac{64\sqrt{\pi}}{17325}Q_{40}F_6 - \frac{4}{105}\sqrt{\left(\frac{\pi}{15}\right)}\,Q_{22}^{(+)}T_8 - \frac{4}{315}\sqrt{\left(\frac{\pi}{5}\right)}\,Q_{20}T_1 + \frac{8\sqrt{\pi}}{1575}Q_{00}N_1,$$

$$\langle\zeta|\,T_{zz}\,|\zeta\rangle = -\frac{8}{165}\sqrt{\left(\frac{\pi}{91}\right)}\,Q_{64}^{(+)}S_1 + \frac{8}{1155}\sqrt{\left(\frac{\pi}{13}\right)}\,Q_{60}S_1 + \frac{32}{495}\sqrt{\left(\frac{\pi}{35}\right)}\,Q_{44}^{(+)}F_4$$

$$- \frac{128\sqrt{\pi}}{17325}Q_{40}F_6 + \frac{8}{315}\sqrt{\left(\frac{\pi}{5}\right)}\,Q_{20}T_1 - \frac{16\sqrt{\pi}}{1575}Q_{00}N_1,$$

$$\langle\zeta|\,T_{xy}\,|\zeta\rangle = \mathrm{i}\left[-\frac{2}{5}\sqrt{\left(\frac{2\pi}{3003}\right)}\,Q_{66}^{(-)}S_1 + \frac{2}{55}\sqrt{\left(\frac{2\pi}{1365}\right)}\,Q_{62}^{(-)}S_1 - \frac{8}{385}\sqrt{\left(\frac{\pi}{5}\right)}\,Q_{42}^{(-)}F_{12}\right.$$

$$\left. + \frac{4}{35}\sqrt{\left(\frac{\pi}{15}\right)}\,Q_{22}^{(-)}T_7\right],$$

$$\langle\zeta|\,T_{yz}\,|\zeta\rangle = \mathrm{i}\left[-\frac{2}{15}\sqrt{\left(\frac{2\pi}{1001}\right)}\,Q_{65}^{(+)}S_1 - \frac{2}{55}\sqrt{\left(\frac{2\pi}{1365}\right)}\,Q_{63}^{(+)}S_1 + \frac{4}{165}\sqrt{\left(\frac{\pi}{273}\right)}\,Q_{61}^{(+)}S_1\right.$$

$$\left. + \frac{4}{165}\sqrt{\left(\frac{2\pi}{35}\right)}\,Q_{43}^{(+)}F_4 - \frac{4}{385}\sqrt{\left(\frac{2\pi}{5}\right)}\,Q_{41}^{(+)}F_{14} + \frac{4}{105}\sqrt{\left(\frac{\pi}{15}\right)}\,Q_{21}^{(+)}T_6\right],$$

$$\langle\zeta|\,T_{zx}\,|\zeta\rangle = -\frac{2}{15}\sqrt{\left(\frac{2\pi}{1001}\right)}\,Q_{65}^{(-)}S_1 + \frac{2}{55}\sqrt{\left(\frac{2\pi}{1365}\right)}\,Q_{63}^{(-)}S_1 + \frac{4}{165}\sqrt{\left(\frac{\pi}{273}\right)}\,Q_{61}^{(-)}S_1$$

$$- \frac{4}{165}\sqrt{\left(\frac{2\pi}{35}\right)}\,Q_{43}^{(-)}F_4 - \frac{4}{385}\sqrt{\left(\frac{2\pi}{5}\right)}\,Q_{41}^{(-)}F_{14} + \frac{4}{105}\sqrt{\left(\frac{\pi}{15}\right)}\,Q_{21}^{(-)}T_6,$$

$$\langle\xi|\,T_{xx}\,|\eta\rangle = \mathrm{i}\left[\frac{8}{165}\sqrt{\left(\frac{\pi}{91}\right)}\,Q_{64}^{(-)}S_1 - \frac{16}{165}\sqrt{\left(\frac{2\pi}{1365}\right)}\,Q_{62}^{(-)}S_1 + \frac{4}{165}\sqrt{\left(\frac{\pi}{35}\right)}\,Q_{44}^{(-)}F_1\right.$$

$$\left. - \frac{4}{495}\sqrt{\left(\frac{\pi}{5}\right)}\,Q_{42}^{(-)}F_{10} - \frac{8}{105}\sqrt{\left(\frac{\pi}{15}\right)}\,Q_{22}^{(-)}T_4\right],$$

$$\langle\xi|\,T_{yy}\,|\eta\rangle = \mathrm{i}\left[-\frac{8}{165}\sqrt{\left(\frac{\pi}{91}\right)}\,Q_{64}^{(-)}S_1 - \frac{16}{165}\sqrt{\left(\frac{2\pi}{1365}\right)}\,Q_{62}^{(-)}S_1 - \frac{4}{165}\sqrt{\left(\frac{\pi}{35}\right)}\,Q_{44}^{(-)}F_1\right.$$

$$\left. - \frac{4}{495}\sqrt{\left(\frac{\pi}{5}\right)}\,Q_{42}^{(-)}F_{10} - \frac{8}{105}\sqrt{\left(\frac{\pi}{15}\right)}\,Q_{22}^{(-)}T_4\right],$$

$$\langle\xi|\,T_{zz}\,|\eta\rangle = \mathrm{i}\left[\frac{32}{165}\sqrt{\left(\frac{2\pi}{1365}\right)}\,Q_{62}^{(-)}S_1 + \frac{8}{495}\sqrt{\left(\frac{\pi}{5}\right)}\,Q_{42}^{(-)}F_{10} + \frac{16}{105}\sqrt{\left(\frac{\pi}{15}\right)}\,Q_{22}^{(-)}T_4\right],$$

$$\langle\xi|\,T_{xy}\,|\eta\rangle = -\frac{8}{165}\sqrt{\left(\frac{\pi}{91}\right)}\,Q_{64}^{(+)}S_1 + \frac{8}{1155}\sqrt{\left(\frac{\pi}{13}\right)}\,Q_{60}S_1 - \frac{4}{165}\sqrt{\left(\frac{\pi}{35}\right)}\,Q_{44}^{(+)}F_1$$

$$- \frac{4\sqrt{\pi}}{825}Q_{40}F_8 + \frac{8}{105}\sqrt{\left(\frac{\pi}{5}\right)}\,Q_{20}T_4 + \frac{4\sqrt{\pi}}{525}Q_{00}N_1,$$

$$\langle\xi|\,T_{yz}\,|\eta\rangle = -\frac{8}{55}\sqrt{\left(\frac{2\pi}{1365}\right)}\,Q_{63}^{(-)}S_1 - \frac{8}{165}\sqrt{\left(\frac{\pi}{273}\right)}\,Q_{61}^{(-)}S_1 - \frac{2}{55}\sqrt{\left(\frac{2\pi}{35}\right)}\,Q_{43}^{(-)}F_{12} + \frac{2}{1155}\sqrt{\left(\frac{2\pi}{5}\right)}\,Q_{41}^{(-)}F_{15} + \frac{4}{105}\sqrt{\left(\frac{\pi}{15}\right)}\,Q_{21}^{(-)}T_9,$$

$$\langle\xi|\,T_{zx}\,|\eta\rangle = \mathrm{i}\left[\frac{8}{55}\sqrt{\left(\frac{2\pi}{1365}\right)}\,Q_{63}^{(+)}S_1 - \frac{8}{165}\sqrt{\left(\frac{\pi}{273}\right)}\,Q_{61}^{(+)}S_1 + \frac{2}{55}\sqrt{\left(\frac{2\pi}{35}\right)}\,Q_{43}^{(+)}F_{12} + \frac{2}{1155}\sqrt{\left(\frac{2\pi}{5}\right)}\,Q_{41}^{(+)}F_{15} + \frac{4}{105}\sqrt{\left(\frac{\pi}{15}\right)}\,Q_{21}^{(+)}T_9\right],$$

$$\langle\eta|\,T_{xx}\,|\zeta\rangle = \mathrm{i}\left[\frac{2}{15}\sqrt{\left(\frac{2\pi}{1001}\right)}\,Q_{65}^{(+)}S_1 - \frac{6}{55}\sqrt{\left(\frac{2\pi}{1365}\right)}\,Q_{63}^{(+)}S_1 + \frac{4}{165}\sqrt{\left(\frac{\pi}{273}\right)}\,Q_{61}^{(+)}S_1 + \frac{14}{495}\sqrt{\left(\frac{2\pi}{35}\right)}\,Q_{43}^{(+)}F_{10} - \frac{2}{495}\sqrt{\left(\frac{2\pi}{5}\right)}\,Q_{41}^{(+)}F_{10} + \frac{16}{105}\sqrt{\left(\frac{\pi}{15}\right)}\,Q_{21}^{(+)}T_4\right],$$

$$\langle\eta|\,T_{yy}\,|\zeta\rangle = \mathrm{i}\left[-\frac{2}{15}\sqrt{\left(\frac{2\pi}{1001}\right)}\,Q_{65}^{(+)}S_1 - \frac{2}{55}\sqrt{\left(\frac{2\pi}{1365}\right)}\,Q_{63}^{(+)}S_1 + \frac{4}{165}\sqrt{\left(\frac{\pi}{273}\right)}\,Q_{61}^{(+)}S_1 - \frac{2}{99}\sqrt{\left(\frac{2\pi}{35}\right)}\,Q_{43}^{(+)}F_{16} - \frac{2}{495}\sqrt{\left(\frac{2\pi}{5}\right)}\,Q_{41}^{(+)}F_{17} - \frac{8}{105}\sqrt{\left(\frac{\pi}{15}\right)}\,Q_{21}^{(+)}T_4\right],$$

$$\langle\eta|\,T_{zz}\,|\zeta\rangle = \mathrm{i}\left[\frac{8}{55}\sqrt{\left(\frac{2\pi}{1365}\right)}\,Q_{63}^{(+)}S_1 - \frac{8}{165}\sqrt{\left(\frac{\pi}{273}\right)}\,Q_{61}^{(+)}S_1 - \frac{4}{495}\sqrt{\left(\frac{2\pi}{35}\right)}\,Q_{43}^{(+)}F_4 + \frac{4}{495}\sqrt{\left(\frac{2\pi}{5}\right)}\,Q_{41}^{(+)}F_{18} - \frac{8}{105}\sqrt{\left(\frac{\pi}{15}\right)}\,Q_{21}^{(+)}T_4\right],$$

$$\langle\eta|\,T_{xy}\,|\zeta\rangle = -\frac{2}{15}\sqrt{\left(\frac{2\pi}{1001}\right)}\,Q_{65}^{(-)}S_1 + \frac{2}{55}\sqrt{\left(\frac{2\pi}{1365}\right)}\,Q_{63}^{(-)}S_1 + \frac{4}{165}\sqrt{\left(\frac{\pi}{273}\right)}\,Q_{61}^{(-)}S_1 - \frac{4}{165}\sqrt{\left(\frac{2\pi}{35}\right)}\,Q_{43}^{(-)}F_{19} - \frac{4}{385}\sqrt{\left(\frac{2\pi}{5}\right)}\,Q_{41}^{(-)}F_{20} + \frac{4}{105}\sqrt{\left(\frac{\pi}{15}\right)}\,Q_{21}^{(-)}T_9,$$

$$\langle\eta|\,T_{yz}\,|\zeta\rangle = -\frac{8}{165}\sqrt{\left(\frac{\pi}{91}\right)}\,Q_{64}^{(+)}S_1 + \frac{8}{1155}\sqrt{\left(\frac{\pi}{13}\right)}\,Q_{60}S_1 - \frac{4}{165}\sqrt{\left(\frac{\pi}{35}\right)}\,Q_{44}^{(+)}F_4 + \frac{8}{21}\sqrt{\left(\frac{\pi}{5}\right)}\,Q_{42}^{(+)}F_{21} - \frac{4\sqrt{\pi}}{825}Q_{40}F_2 + \frac{4}{35}\sqrt{\left(\frac{\pi}{15}\right)}\,Q_{22}^{(+)}T_4 - \frac{4}{105}\sqrt{\left(\frac{\pi}{5}\right)} \times Q_{20}T_4 + \frac{4\sqrt{\pi}}{525}Q_{00}N_1,$$

$$\langle\eta|\,T_{zx}\,|\zeta\rangle = \mathrm{i}\left[\frac{8}{165}\sqrt{\left(\frac{\pi}{91}\right)}\,Q_{64}^{(-)}S_1 - \frac{16}{165}\sqrt{\left(\frac{2\pi}{1365}\right)}\,Q_{62}^{(-)}S_1 + \frac{4}{165}\sqrt{\left(\frac{\pi}{35}\right)}\,Q_{44}^{(-)}F_4 + \frac{4}{231}\sqrt{\left(\frac{\pi}{5}\right)}\,Q_{42}^{(-)}F_{22} + \frac{4}{105}\sqrt{\left(\frac{\pi}{15}\right)}\,Q_{22}^{(-)}T_9\right],$$

$$\langle\zeta|\,T_{xx}\,|\xi\rangle = -\frac{2}{15}\sqrt{\left(\frac{2\pi}{1001}\right)}\,Q_{65}^{(-)}S_1+\frac{2}{55}\sqrt{\left(\frac{2\pi}{1365}\right)}\,Q_{63}^{(-)}S_1+\frac{4}{165}\sqrt{\left(\frac{\pi}{273}\right)}\,Q_{61}^{(-)}S_1$$
$$+\frac{2}{99}\sqrt{\left(\frac{2\pi}{35}\right)}\,Q_{43}^{(-)}F_{16}-\frac{2}{495}\sqrt{\left(\frac{2\pi}{5}\right)}\,Q_{41}^{(-)}F_{17}-\frac{8}{105}\sqrt{\left(\frac{\pi}{15}\right)}\,Q_{21}^{(-)}T_4,$$

$$\langle\zeta|\,T_{yy}\,|\xi\rangle = \frac{2}{15}\sqrt{\left(\frac{2\pi}{1001}\right)}\,Q_{65}^{(-)}S_1+\frac{6}{55}\sqrt{\left(\frac{2\pi}{1365}\right)}\,Q_{63}^{(-)}S_1+\frac{4}{165}\sqrt{\left(\frac{\pi}{273}\right)}\,Q_{61}^{(-)}S_1$$
$$-\frac{14}{495}\sqrt{\left(\frac{2\pi}{35}\right)}\,Q_{43}^{(-)}F_{10}-\frac{2}{495}\sqrt{\left(\frac{2\pi}{5}\right)}\,Q_{41}^{(-)}F_{10}+\frac{16}{105}\sqrt{\left(\frac{\pi}{15}\right)}\,Q_{21}^{(-)}T_4,$$

$$\langle\zeta|\,T_{zz}\,|\xi\rangle = -\frac{8}{55}\sqrt{\left(\frac{2\pi}{1365}\right)}\,Q_{63}^{(-)}S_1-\frac{8}{165}\sqrt{\left(\frac{\pi}{273}\right)}\,Q_{61}^{(-)}S_1+\frac{4}{495}\sqrt{\left(\frac{2\pi}{35}\right)}\,Q_{43}^{(-)}F_4$$
$$+\frac{4}{495}\sqrt{\left(\frac{2\pi}{5}\right)}\,Q_{41}^{(-)}F_{18}-\frac{8}{105}\sqrt{\left(\frac{\pi}{15}\right)}\,Q_{21}^{(-)}T_4,$$

$$\langle\zeta|\,T_{xy}\,|\xi\rangle = \mathrm{i}\left[-\frac{2}{15}\sqrt{\left(\frac{2\pi}{1001}\right)}\,Q_{65}^{(+)}S_1-\frac{2}{55}\sqrt{\left(\frac{2\pi}{1365}\right)}\,Q_{63}^{(+)}S_1+\frac{4}{165}\sqrt{\left(\frac{\pi}{273}\right)}\,Q_{61}^{(+)}S_1\right.$$
$$\left.+\frac{4}{165}\sqrt{\left(\frac{2\pi}{35}\right)}\,Q_{43}^{(+)}F_{19}-\frac{4}{385}\sqrt{\left(\frac{2\pi}{5}\right)}\,Q_{41}^{(+)}F_{20}+\frac{4}{105}\sqrt{\left(\frac{\pi}{15}\right)}\,Q_{21}^{(+)}T_9\right],$$

$$\langle\zeta|\,T_{yz}\,|\xi\rangle = \mathrm{i}\left[-\frac{8}{165}\sqrt{\left(\frac{\pi}{91}\right)}\,Q_{64}^{(-)}S_1-\frac{16}{165}\sqrt{\left(\frac{2\pi}{1365}\right)}\,Q_{62}^{(-)}S_1-\frac{4}{165}\sqrt{\left(\frac{\pi}{35}\right)}\,Q_{44}^{(-)}F_4\right.$$
$$\left.+\frac{4}{231}\sqrt{\left(\frac{\pi}{5}\right)}\,Q_{42}^{(-)}F_{22}+\frac{4}{105}\sqrt{\left(\frac{\pi}{15}\right)}\,Q_{22}^{(-)}T_9\right],$$

$$\langle\zeta|\,T_{zx}\,|\xi\rangle = -\frac{8}{165}\sqrt{\left(\frac{\pi}{91}\right)}\,Q_{64}^{(+)}S_1+\frac{8}{1155}\sqrt{\left(\frac{\pi}{13}\right)}\,Q_{60}S_1-\frac{4}{165}\sqrt{\left(\frac{\pi}{35}\right)}\,Q_{44}^{(+)}F_4$$
$$-\frac{8}{21}\sqrt{\left(\frac{\pi}{5}\right)}\,Q_{42}^{(+)}F_{21}-\frac{4\sqrt{\pi}}{825}Q_{40}F_2-\frac{4}{35}\sqrt{\left(\frac{\pi}{15}\right)}\,Q_{22}^{(+)}T_4-\frac{4}{105}\sqrt{\left(\frac{\pi}{5}\right)}$$
$$\times Q_{20}T_4+\frac{4\sqrt{\pi}}{525}Q_{00}N_1.$$