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NMR Chemical Shift for 4d^n Systems (I). Evaluation of the Required Hyperfine Integrals

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The hyperfine integrals for 4d orbitals have been evaluated adopting a general method which is applicable to a general vector, $\boldsymbol{R}$, pointing arbitrary direction in space. The operator and the spherical harmonic part of 4d orbitals are expressed in terms of $\boldsymbol{R}$ and r_N and the exponential part, $r^2\exp(-2\beta r)$, of 4d orbitals is also translated as a function of $\boldsymbol{R}$ and r_N and then intergration is performed. The radial integrals for 4d orbitals are tabulated in analytical forms. The hyperfine integrals for 4d orbitals are also represented in analytical forms, using the specific formulas of radial series which we found.

1. Introduction

Since our interest is centered on the NMR shift arising from the electron orbital angular momentum, and the electron spin dipolar-nuclear spin angular momentum interactions for $4d^n$ systems in the octahedral crystal field, it is necessary to evaluate the hyperfine integrals of the hamiltonian representing the pseudo contact part of hyperfine integrals.[1]

$$H = H_1 + H_2 \quad (1)$$

where

$$H_1 = \frac{2\mu_0}{4\pi} g_N \mu_B \mu_N \{ \boldsymbol{l}_N \cdot \boldsymbol{I} / r_N^3 \} \quad (2a)$$

$$H_2 = \frac{\mu_0}{4\pi} g_S g_N \mu_B \mu_N \left\{ \frac{3(\boldsymbol{r}_N \cdot \boldsymbol{S}) \boldsymbol{r}_N \cdot \boldsymbol{I}}{r_N^5} - \frac{\boldsymbol{S} \cdot \boldsymbol{I}}{r_N^3} \right\} \quad (2b)$$

Here the first part represents the Fermi contact term and the second part, H_2, the pseudo contact term. $\boldsymbol{r}_N$ is the radius vector of the electron about the nucleus with nuclear spin angular momentum, $\boldsymbol{I}$, as shown in Figure 1.

In order to evaluate the hyperfine integrals involving 4d orbitals, we adopt the general method which has been developed by Golding and Stubbs.[2] This method is applicable to a general vector, $\boldsymbol{R}$, pointing in any direction in space, which

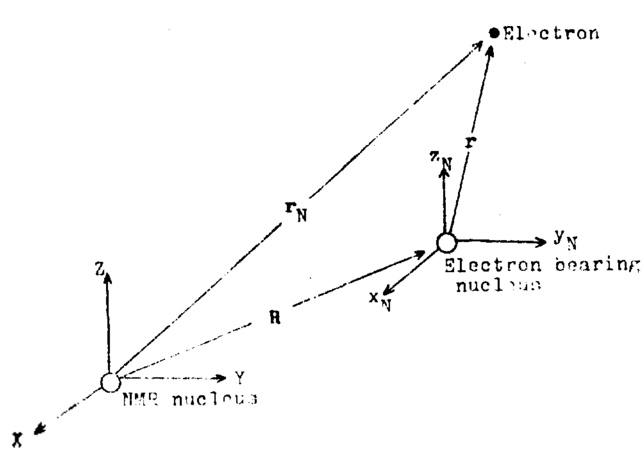

Figure 1. The coordinate system.

is different from the other methods developed previously.[3]

The purpose of this work is to evaluate the hyperfine integrals involving 4d orbitals which are required to investigate the NMR shift for $4d^n$ systems in a strong crystal field of octahedral and tetragonal symmetries. As far as we are aware no previous attempt has been made to evaluate the hyperfine integrals involving 4d orbitals.

2. Evaluation of the Hyperfine Integrals

We choose SCF function of the form,

$$\phi_{lm}=Nr^{l+1}\exp(-\beta r)\,Y_{lm}(\theta,\phi) \tag{3}$$

where l and m are usual quantum numbers which have integer values, N a normalizing constant, β the optimized orbital exponent.[4] Therefore the electronic wave functions in real notation for 4*d* orbitals are,

$$\left|4d_{yz}\right>=\left(\frac{\beta^9}{21\pi}\right)^{\frac{1}{2}}yzr\exp(-\beta r)$$

$$\left|4d_{xz}\right>=\left(\frac{\beta^9}{21\pi}\right)^{\frac{1}{2}}xzr\exp(-\beta r)$$

$$\left|4d_{xy}\right>=\left(\frac{\beta^9}{21\pi}\right)^{\frac{1}{2}}xyr\exp(-\beta r)$$

$$\left|4d_{z^2}\right>=\left(\frac{\beta^9}{252\pi}\right)^{\frac{1}{2}}(3z^2-r^2)\exp(-\beta r)$$

$$\left|4d_{x^2-y^2}\right>=\left(\frac{\beta^9}{84\pi}\right)^{\frac{1}{2}}(x^2-y^2)\exp(-\beta r) \tag{4}$$

The hyperfine integrals are evaluated by expressing the electron coordinate system 0_{xyz} in terms of R and r_N (Figure 1) Using the following identities[5]

$$r^l\,Y_{lm}(\theta,\phi)=\sum_{l_1=0}^{l}\sum_{l_2=0}^{l}\sum_{m_1=-l_1}^{l_1}\sum_{m_2=-l_2}^{l_2}(-1)^{l_1}\delta(l_1+l_2,\ l)\times\left\{\frac{4\pi(2l+1)!}{(2l_1+1)!(2l_2+1)!}\right\}^{\frac{1}{2}}\left<l_1l_2m_1m_2|l_1l_2lm\right>\times R^{l_1}Y_{l_1m_1}(\Theta,\Phi)r_N^{l_2}Y_{l_2m_2}(\theta_N,\phi_N) \tag{5}$$

and

$$r^2\exp(-2\beta r)=4\pi\sum_{n=0}^{\infty}h_N(R,r_N)\sum_{k=-n}^{n}Y_{nk}^*(\Theta,\Phi)\,Y_{nk}(\theta_N,\phi_N) \tag{6}$$

where[6]

$$\begin{aligned}h_n(R,r_N)=(r_<r_>)^{\frac{1}{2}}\{&r_>^3I_{n+\frac{1}{2}}(2\beta r_<)K_{n-\frac{1}{2}}(2\beta r_>)\\&-r_<^3I_{n+\frac{3}{2}}(2\beta r_<)K_{n+\frac{1}{2}}(2\beta r_>)\\&+\left(\frac{4n+1}{2n+1}\right)r_>^2r_<\,I_{n+\frac{1}{2}}(2\beta r_<)K_{n-\frac{1}{2}}(2\beta r_>)\\&-\left(\frac{4n+3}{2n+1}\right)r_<\,r_>^2\,I_{n+\frac{3}{2}}(2\beta r_<)K_{n+\frac{1}{2}}(2\beta r_>)\\&+\left(\frac{2(n+1)}{2n+1}\right)r_<^2r_>\,I_{n+\frac{5}{2}}(2\beta r_<)K_{n+\frac{3}{2}}(2\beta r_>)\\&-\left(\frac{2n}{2n+1}\right)r_<\,r_>^2\,I_{n-\frac{1}{2}}(2\beta r_<)K_{n-\frac{3}{2}}(2\beta r_>)\end{aligned} \tag{7}$$

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

Since we are interested in the hyperfine interactions arising from the electron orbital angular momentum and the electron spin dipolor-nuclear spin angular momentum interactions, it is necessary to evaluate the hyperfine integrals involving the electron orbital angular momentum-nuclear spin hyperfine interaction (the integrals of $l_{N\alpha}/r_N^3$) and the hyperfine integrals arising from the electron spin dipolar-nuclear spin angular momentum interaction (dipolar integrals). We shall evaluate the two hyperfine integrals separately.

Dipolar Integrals. The hamiltonian representing the dipolar hyperfine interaction may be written in dyadic notation as

$$H_2=\frac{\mu_0}{4\pi}g_Sg_N\,\mu_B\mu_N\,\boldsymbol{S}\cdot\boldsymbol{T}\cdot\boldsymbol{I} \tag{8}$$

where T is a symmetric tensor whose components are given by

$$T_{\alpha\beta}=(3r_{N\alpha}r_{N\beta}-r_N^2\delta_{\alpha\beta})/r_N^5 \tag{9}$$

In calculating integrals of H_2, it is required to consider integrals of form,

$$\left<\phi_{lm'}|T_{\alpha\beta}|\phi_{lm}\right> \tag{10}$$

To evaluate the above integral, the 4d orbitals are expressed as a function of R and r_N using equation (5) and (6). As an example, the $4d_{yz}$ which is expressed as a function of R and and r_N takes the following form,

$$\begin{aligned}\left|4d_{yz}\right>=\left(\frac{\beta^9}{21\pi}\right)^{\frac{1}{2}}&\{(x_N-X)^2+(y_N-Y)^2+(z_N-Z)^2\}^{\frac{1}{2}}\\&\times(y_N-Y)(z_N-Z)\exp[-\beta\{(x_N-X)^2\\&+(y_N-Y)^2+(z_N-Z)^2\}^{\frac{1}{2}}]\end{aligned} \tag{11}$$

where X, Y and Z are the components of vector R and x_N, y_N and z_N the components of vector r_N in Figure 1. The dipolar operator, $T_{\alpha\beta}$, is also expressed in terms of r_N. For example,

$$T_{xx}=(3x_N^2/r_N^2-1)/r_N^3 \tag{12}$$

Therefore

$$\begin{aligned}&\left<4d_{yz}|T_{xx}|4d_{yz}\right>\\&=N^2\int_0^\infty(3x_N^2/r_N^2-1)(y_N-Y)^2(z_N-Z)^2\\&\times r^2\frac{\exp(-2\beta r)}{r_N^3}dx_N\,dy_N\,dz_N\end{aligned} \tag{13}$$

The homogenous polynomial in equation (13) is expanded in a series of products of form using digital computer,

$$X^lY^mZ^n\,x_N^p\,y_N^q\,z_N^r \tag{14}$$

where $(l+m+n+p+q+r)=6$ or 4 for dipolar integrals. Using the following identities[7]

$$x=\left(\frac{2\pi}{3}\right)^{\frac{1}{2}}r\{Y_{1-1}(\theta,\phi)-Y_{11}(\theta,\phi)\}$$

$$y=\left(\frac{2\pi}{3}\right)^{\frac{1}{2}}ir\{Y_{1-1}(\theta,\phi)+Y_{11}(\theta,\phi)\}$$

$$z=\left(\frac{4\pi}{3}\right)^{\frac{1}{2}}r\ Y_{10}(\theta,\phi) \tag{15}$$

and the relationship[8]

$$Y_{l_1m_1}\,Y_{l_2m_2}=\sum_{l=|l_1-l_2|}^{l_1+l_2}\sum_{m=-l}^{l}(-1)^m\left\{\frac{(2l_1+1)(2l_2+1)(2l+1)}{4\pi}\right\}^{\frac{1}{2}}\begin{pmatrix}l_1&l_2&l\\0&0&0\end{pmatrix}\begin{pmatrix}l_1&l_2&l\\m_1&m_2&m\end{pmatrix}Y_{l-m}(\theta,\phi) \tag{16}$$

The product functions represented by equation (14) are transformed to products of spherical harmonics,

$$X^l Y^m Z^n x_N{}^p y_N{}^q z_N{}^r = \sum_{L_1, L_2} \sum_{M_1, M_2} C_{mm'}(L_1, M_1;\ L_2, M_2)\, Y_{L_1 M_1}(\Theta, \Phi)\, Y_{L_2 M_2}(\theta_N, \phi_N) \qquad (17)$$

where the $C_{mm'}(L_1M_1;\ L_2M_2)$ are functions of R and r_N. Next, the radial part of $r^2\exp(-2\beta r)$ is translated using equation(6), resulting in the integral being a large sum,

$$\begin{aligned} &\langle \phi_{lm} | T_{\alpha\beta} | \phi_{lm'} \rangle \\ &= N^2 \sum_{L_1, L_2} \sum_{M_1, M_2} \sum_{n=0}^{\infty} 4\pi \int_0^{\infty} C_{mm'}(L_1M_1;\ L_2M_2)\, h_n(R, r_N) \\ &\times \frac{dr_N}{r_N} \sum_{k=-n}^{n} Y_{nk}{}^*(\Theta, \Phi)\, Y_{L_1 M_1}(\Theta, \Phi) \\ &\int_0^{2\pi} \int_0^{\pi} Y_{nk}(\theta_N, \phi_N)\, Y_{L_2 M_2}(\theta_N, \phi_N) \times \sin\theta_N\, d\theta_N\, d\phi_N \end{aligned} \qquad (18)$$

where the radial and angular parts are separated. Using the formula,

$$\begin{aligned} &\int_0^{\pi} \int_0^{2\pi} Y_{l_1 m_1}(\theta_N, \phi_N)\, Y_{l_2 m_2}(\theta_N, \phi_N) \sin\theta_N\, d\theta_N\, d\phi_N \\ &= \left[\frac{(2l_1+1)(2l_2+1)(2l+1)}{4\pi} \right]^{\frac{1}{2}} \\ &\begin{pmatrix} l_1 & l_2 & l \\ m_1 & m_2 & m \end{pmatrix} \begin{pmatrix} l_1 & l_2 & l \\ 0 & 0 & 0 \end{pmatrix} \end{aligned} \qquad (19)$$

selection rules are obtained on n and h. The reqired dipolar integrals are listed in appendix.

The Radial Integral. For the 4d orbitals, we define the radial integrals as

$$R_N{}^{(L)}(t) = 4\beta^9 (-R)^L \int_0^{\infty} r_N{}^{5-L-2} h_n(R, r_N)\, dr_N \qquad (20)$$

where $t = 2\beta R$ and further, for convenience

$$\begin{aligned} u_n(t) &= R_n{}^{(4)}(t) \\ v_n(t) &= R_n{}^{(3)}(t) \\ w_n(t) &= R_n{}^{(2)}(t) \\ x_n(t) &= R_n{}^{(1)}(t) \\ y_n(t) &= R_n{}^{(0)}(t) \end{aligned} \qquad (21)$$

This definition provides a suitable notation that enables easy handling of the radial parts of the hyperfine integrals. From the angular parts of the hyperfine integrals we obtain selection rules on n. The required radial integrals are listed in Table 1.

The Integrals of $l_{N\alpha}/r_N{}^3$. To evaluate the hyperfine integrals arising from the electron angular momentum-nuclear spin interaction, it is necessary to evaluate the following two center integrals,

$$\langle \phi_{lm'} | l_{N\alpha} / r_N{}^3 | \phi_{lm} \rangle$$

where

$$l_N = -i\hbar r_N \times \Delta_N$$

Here the wave function

$$\phi_{lm} = N r^{l+1} \exp(-\beta r)\, Y_{lm}(\theta, \phi) \qquad (22)$$

is expressed as a function of the cartesian coordinates of R and r_N and the differentiation is performed. The net result is that

$$\begin{aligned} &\phi_{lm'}^* \frac{l_{N\alpha}}{r_N{}^3} \phi_{lm} \\ &= \{ f_{m'm}^{(l)}(R, r_N) e^{-2\beta r} + g_{m'm}^{(l)}(R, r_N) r^2 e^{-2\beta r} \\ &+ h_{m'm}(R, r_N) e^{-2\beta r} \} / r_N{}^3 \end{aligned} \qquad (23)$$

where $f_{m'm}^{(l)}$, $g_{m'm}^{(l)}$ and $h_{m'm}^{(l)}$ are homogenous polynomials of the cartesian coordinates of R and r_N,[9] respectively. The two center hyperfine integral is therefore transformed to the form,

$$\begin{aligned} &\langle \phi_{lm'} | l_{N\alpha} / r_N{}^3 | \phi_{lm} \rangle \\ &= N^2 \int_0^{\infty} \frac{dx_N\, dy_N\, dz_N}{r_N{}^3} \{ f_{m'm}^{(l)}(R, r_N) e^{-2\beta r} + g_{m'm}^{(l)}(R, r_N) \\ &\times r^2 e^{-2\beta r} + h_{m'm}^{(l)}(R, r_N) e^{-2\beta r} \} \end{aligned} \qquad (24)$$

The integral $\langle \phi_{lm'} | \frac{l_{N\alpha}}{r_N{}^3} | \phi_{lm} \rangle$ where $\langle \phi_{lm'} |$ and $| \phi_{lm} \rangle$

TABLE 1: The Required Radial Inetgrals for 4d Orbitals

$$u_2(t) = \beta^3 \left\{ \frac{3}{2}t - e^{-t}\left(\frac{t^6}{48} + \frac{t^5}{16} + \frac{t^4}{4} + \frac{3}{4}t^3 + \frac{3}{2}t^2 + \frac{3}{2}t \right) \right\}$$

$$v_1(t) = -\beta^3 \left\{ \frac{3}{2}t - e^{-t}\left(\frac{t^5}{16} + \frac{t^4}{4} + \frac{3}{4}t^3 + \frac{3}{2}t^2 + \frac{3}{2}t \right) \right\}$$

$$\begin{aligned} v_3(t) = -\beta^3 \Big\{ &\left(\frac{3}{2}t - \frac{75}{t} \right) + e^{-t}\Big(\frac{t^5}{24} + \frac{3}{8}t^4 + \frac{19}{8}t^3 \\ &+ 11t^2 + 36t + 75 + \frac{75}{t} \Big) \Big\} \end{aligned}$$

$$w_0(t) = \beta^3 \left\{ \frac{3}{2}t - e^{-t}\left(\frac{t^4}{16} + \frac{3}{8}t^3 + \frac{9}{8}t^2 + \frac{3}{2}t \right) \right\}$$

$$w_2(t) = \beta^3 \left\{ \left(\frac{3}{2}t - \frac{45}{t} \right) + e^{-t}\left(-\frac{t^4}{8} + \frac{9}{8}t^3 + 6t^2 + 21t + 45 + \frac{45}{t} \right) \right\}$$

$$\begin{aligned} w_4(t) = \beta^3 \Big\{ &\left(\frac{3}{2}t - \frac{150}{t} + \frac{5880}{t^3} \right) - e^{-t}\Big(\frac{t^4}{6} + \frac{8}{3}t^3 + \frac{51}{2}t^2 \\ &+ \frac{343}{2}t + 830 + \frac{2790}{t} + \frac{5880}{t^2} + \frac{5880}{t^3} \Big) \Big\} \end{aligned}$$

$$x_1(t) = -\beta^3 \left\{ \left(\frac{3}{2}t - \frac{15}{t} \right) + e^{-t}\left(\frac{t^3}{8} + \frac{5}{4}t^2 + 6t + 15 + \frac{15}{t} \right) \right\}$$

$$\begin{aligned} x_3(t) = -\beta^3 \Big\{ &\left(\frac{3}{2}t - \frac{90}{t} + \frac{2520}{t^3} \right) - e^{-t}\Big(\frac{t^3}{2} + \frac{15}{2}t^2 + \frac{123}{2}t \\ &+ 330 + \frac{1170}{t} + \frac{2520}{t^2} + \frac{2520}{t^3} \Big) \Big\} \end{aligned}$$

$$\begin{aligned} x_5(t) = -\beta^3 \Big\{ &\left(\frac{3}{2}t - \frac{225}{t} + \frac{17640}{t^3} - \frac{680400}{t^5} \right) \\ &+ e^{-t}\Big(t^3 + 24t^2 + 321t + 2955 + \frac{19755}{t} + \frac{95760}{t^2} \\ &+ \frac{322560}{t^3} + \frac{680400}{t^4} + \frac{680400}{t^5} \Big) \Big\} \end{aligned}$$

$$y_0(t) = \beta^3 \left\{ \left(\frac{3}{2}t + \frac{15}{t} \right) - e^{-t}\left(\frac{t^2}{8} + \frac{3}{2}t + \frac{15}{2} + \frac{15}{t} \right) \right\}$$

$$\begin{aligned} y_2(t) = \beta^3 \Big\{ &\left(\frac{3}{2}t - \frac{30}{t} + \frac{504}{t^3} \right) - e^{-t}\Big(\frac{t^2}{2} + \frac{15}{2}t \\ &+ 54 + \frac{222}{t} + \frac{504}{t^2} + \frac{504}{t^3} \Big) \Big\} \end{aligned}$$

$$\begin{aligned} y_4(t) = \beta^3 \Big\{ &\left(\frac{3}{2}t - \frac{135}{t} + \frac{7560}{t^3} - \frac{226800}{t^5} \right) \\ &+ e^{-t}\Big(3t^2 + 66t + 765 + \frac{5805}{t} + \frac{30240}{t^2} + \frac{105840}{t^3} \\ &+ \frac{226800}{t^4} + \frac{226800}{t^5} \Big) \Big\} \end{aligned}$$

$$\begin{aligned} y_6(t) = \beta^3 \Big\{ &\left(\frac{3}{2}t - \frac{300}{t} + \frac{35280}{t^3} - \frac{2721600}{t^5} + \frac{109771200}{t^7} \right) \\ &- e^{-t}\Big(8t^2 + 264t + 4680 + \frac{56400}{t} + \frac{496440}{t^2} + \frac{3248280}{t^3} \\ &+ \frac{15573600}{t^4} + \frac{52164000}{t^5} + \frac{109771200}{t^6} + \frac{109771200}{t^7} \Big) \Big\} \end{aligned}$$

are real wave functions, is a purely imaginary quantity and is equal to

$$\frac{1}{2}\langle\phi_{lm'}|l_{N\alpha}/r_N^3|\phi_{lm}\rangle-\frac{1}{2}\langle\phi_{lm}|l_{N\alpha}/r_N^3|\phi_{lm'}\rangle \qquad (25)^9$$

Therefore the integrals involving exp $(-2\beta r)$ vanish in equation (24). The remaining integrals can be written as

$$\langle\phi_{lm'}|l_{N\alpha}/r_N^3|\phi_{lm}\rangle=\frac{N^2}{2}\int_0^\infty\int_0^{2\pi}\int_0^\pi r^2e^{-2\beta r}[g^{(l)}_{m'm}(R,r_N)+g^{(l)}_{mm'}(R,r_N)]\frac{dr_N}{r_N}\sin^2\theta_N\,d\theta_N\,d\phi_N \qquad (26)$$

Using equation(15) and (16), the homogenous polynomials, $g^{(l)}_{mm'}$ and $g^{(l)}_{m'm}$, are expanded in terms of a sum of products of the harmonic polynomials and the radial part, r^2exp $(-2\beta r)$, is translated using equations(6), and then integrations are performed. The required integrals of $l_{N\alpha}/r_N^3$ are listed in appendix.

3. Results and Discussion

A number of the hyperfine integrals are evaluated using the method in the previous section and then a general expression is derived for the integrals

$$\langle\phi_{lm'}|T_{\alpha\beta}|\phi_{lm}\rangle \text{ and } \langle\phi_{lm'}|l_{N\alpha}/r_N^3|\phi_{lm}\rangle$$

by extracting the coefficients of the various radial integrals from the quite general expression for the above integrals. One example for 4d dipolar integrals is given in the following.

$$\begin{aligned}&\langle\phi_{lm'}|T_{\alpha\beta}|\phi_{lm}\rangle\\&=C_6\{u_2+4v_3+6w_4+4x_5+y_6\}Y_{6p}(\Theta,\Phi)\\&\quad+C_4\{u_2+(4-A)v_1+Av_3+(6-B)w_2+Bw_4\\&\quad+(4-C)x_3+Cx_5+y_4\}Y_{4p}(\Theta,\Phi)\\&\quad+C_2\{u_2+(4-A')v_1+A'v_3+(6-B'-C')w_0+B'w_2\\&\quad+C'w_4+(4-A')x_1+A'x_3+y_2\}Y_{2p}(\Theta,\Phi)\\&\quad+C_0\left\{u_2+\left(\frac{14}{5}v_1+\frac{6}{5}v_3\right)+\left(\frac{7}{3}w_0+\frac{11}{3}w_2\right)\right.\\&\quad\left.+4x_1+y_0\right\}Y_{00}(\Theta,\Phi)\end{aligned} \qquad (27)$$

In equation (27), the eleven unknowns p, A, B, C, A', B', C', C_6, C_4, C_2 and C_0 are determined using a computer program which was written to evaluate the large number of the required integrals in an analytical form. The specific formulas for the dipolar integrals and $l_{N\alpha}/r_N^3$ are listed in appendix. From appendix, it was found that the radial series for the dipolar integrals and the integrals of $l_{N\alpha}/r_N^3$ follow 1 : 4 : 6 : 4 : 1 and 1 : 3 : 3 : 1 patterns, respectively. Such patterns were also found in the radial series of 3d orbitals.[2]

The dipolar integrals and the integrals of $l_{N\alpha}/r_N^3$ listed in the appendix can be used to evaluate the NMR shift arising from the electron angular momentum and electron spin dipolar-nuclear spin angular momentum interactions and the hyperfine interaction tensor components for $4d^n$ systems.

Appendix A. Radial Series

(a) Specific formulas for the integrals of $l_{\alpha N}/r_N^3$.

$n_1=y_0+3x_1+\left(\frac{5}{3}w_0+\frac{4}{3}w_2\right)+v_1$

$t_1=y_2+\left(\frac{21}{5}x_1-\frac{6}{5}x_3\right)+\left(\frac{14}{3}w_0-\frac{5}{3}w_2\right)+v_1$

$t_2=y_2+\left(\frac{7}{3}x_1+\frac{2}{3}x_3\right)+\left(\frac{14}{9}w_0+\frac{13}{8}w_2\right)+v_1$

$t_3=y_2+\left(\frac{28}{15}x_1+\frac{17}{15}x_3\right)+\left(\frac{7}{9}w_0+\frac{20}{9}w^2\right)+v_1$

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

(b) Specific formulas for the dipolar integrals

$N_1=y_0+4x_1+\left(\frac{7}{3}w_0+\frac{11}{3}w_2\right)+\left(\frac{14}{5}v_1+\frac{6}{5}v_3\right)+u_2$

$T_1=y_2+\left(\frac{8}{5}x_1+\frac{12}{5}x_3\right)+\left(\frac{14}{5}w_0+\frac{74}{21}w_2+\frac{54}{35}w_4\right)$
$\quad+\left(\frac{8}{5}v_1+\frac{12}{5}v_3\right)+u_2$

$T_2=y_2+4x_3+\left(-\frac{14}{5}w_0+\frac{46}{7}w_2+\frac{78}{35}w_4\right)+4v_3+u_2$

$T_3=(x_1-x_3)+\frac{1}{21}(49w_0-40w_2-9w_4)+(v_1-v_3)$

$T_5=y_2+\left(-\frac{4}{5}x_1+\frac{24}{5}x_3\right)+\left(-\frac{14}{3}w_0+\frac{170}{21}w_2+\frac{18}{7}w_4\right)$
$\quad+\left(-\frac{4}{5}v_1+\frac{24}{5}v_3\right)+u_2$

$T_4=y_2+\left(\frac{2}{5}x_1+\frac{18}{5}x_3\right)+\left(-\frac{28}{15}w_0+\frac{122}{21}w_2+\frac{72}{35}w_4\right)$
$\quad+\left(\frac{2}{5}v_1+\frac{18}{5}v_3\right)+u_2$

$T_6=y_2+\left(\frac{4}{5}x_1+\frac{16}{5}x_3\right)+\left(\frac{14}{15}w_0+\frac{106}{21}w_2+\frac{66}{35}w_4\right)$
$\quad+\left(\frac{4}{5}v_1+\frac{16}{5}v_3\right)+u_2$

$T_7=y_2+\left(\frac{6}{5}x_1+\frac{14}{5}x_3\right)+\left(\frac{30}{7}w_2+\frac{12}{7}w_4\right)+\left(\frac{6}{5}v_1+\frac{14}{5}v_3\right)+u_2$

$T_8=y_2+\left(\frac{12}{5}x_1+\frac{8}{5}x_3\right)+\left(\frac{28}{15}w_0+\frac{10}{3}w_2+\frac{4}{5}w_4\right)$
$\quad+\left(\frac{12}{5}v_1+\frac{8}{5}v_3\right)+u_2$

$T_9=y_2+(3x_1+x_3)+\left(\frac{14}{5}w_0+\frac{20}{7}w_2+\frac{12}{35}w_4\right)+(3v_1+v_3)+u_2$

$F_1=y_4+\left(\frac{286}{69}x_3-\frac{10}{69}x_5\right)+\left(\frac{957}{161}w_2+\frac{9}{161}w_4\right)$
$\quad+\left(\frac{352}{115}v_1+\frac{108}{115}v_3\right)+u_2$

$F_2=y_4+\left(\frac{10}{3}x_3+\frac{2}{3}x_5\right)+\left(\frac{27}{7}w_2+\frac{15}{7}w_4\right)+\left(\frac{8}{5}v_1+\frac{12}{5}v_3\right)+u_2$

$F_3=y_4+\left(\frac{22}{9}x_3+\frac{14}{9}x_5\right)+\left(\frac{11}{7}w_2+\frac{31}{7}w_4\right)+4v_3+u_2$

$F_4=y_4+\left(\frac{22}{3}x_3-\frac{10}{3}x_5\right)+\left(\frac{99}{7}w_2-\frac{57}{7}w_4\right)+\left(\frac{44}{5}v_1-\frac{24}{5}v_3\right)+u_2$

$F_5=y_4+\left(\frac{22}{7}x_3+\frac{6}{7}x_5\right)+\left(\frac{165}{49}w_2+\frac{129}{49}w_4\right)$
$\quad+\left(\frac{44}{35}v_1+\frac{96}{35}v_3\right)+u_2$

$F_6=y_4+\left(\frac{242}{63}x_3+\frac{10}{63}x_5\right)+\left(\frac{253}{49}w_2+\frac{41}{49}w_4\right)$
$\quad+\left(\frac{88}{35}v_1+\frac{52}{35}v_3\right)+u_2$

$F_7=y_4+\left(\frac{66}{19}x_3+\frac{10}{19}x_5\right)+\left(\frac{561}{133}w_2+\frac{237}{133}w_4\right)$
$\quad+\left(\frac{176}{95}v_1+\frac{204}{95}v_3\right)+u_2$

$F_8=y_4+\left(\frac{11}{3}x_3+\frac{1}{3}x_5\right)+\left(\frac{33}{7}w_2+\frac{9}{7}w_4\right)+\left(\frac{11}{5}v_1+\frac{9}{5}v_3\right)+u_2$

$F_9=y_4+\left(\frac{11}{4}x_3+\frac{5}{4}x_5\right)+\left(\frac{33}{14}w_2+\frac{51}{14}w_4\right)$
$\quad+\left(\frac{11}{20}v_1+\frac{69}{20}v_3\right)+u_2$

$F_{10}=y_4+\left(\frac{187}{63}x_3+\frac{65}{63}x_5\right)+\left(\frac{143}{49}w_2+\frac{151}{49}w_4\right)$
$\quad+\left(\frac{33}{35}v_1+\frac{107}{35}v_3\right)u+u_2$

$$F_{11}=\frac{1}{9}(x_3-x_5)+\frac{2}{7}(w_2-w_4)+\frac{1}{5}(v_1-v_3)$$

$$F_{12}=y_4+\left(\frac{154}{45}x_3+\frac{26}{45}x_5\right)+\left(\frac{143}{35}w_2+\frac{67}{35}w_4\right)+\left(\frac{44}{25}v_1+\frac{56}{25}v_3\right)+u_2$$

$$F_{13}=y_4+\left(\frac{143}{45}x_3+\frac{37}{45}x_5\right)+\left(\frac{121}{35}w_2+\frac{89}{35}w_4\right)+\left(\frac{33}{25}v_1+\frac{67}{25}v_3\right)+u_2$$

$$F_{14}=y_4+\left(\frac{187}{54}x_3+\frac{29}{54}x_5\right)+\left(\frac{88}{21}w_2+\frac{38}{21}w_4\right)+\left(\frac{11}{6}v_1+\frac{13}{6}v_3\right)+u_2$$

$$F_{15}=y_4+\left(\frac{55}{18}x_3+\frac{17}{18}x_5\right)+\left(\frac{22}{7}w_2+\frac{20}{7}w_4\right)+\left(\frac{11}{10}v_1+\frac{29}{10}v_3\right)+u_2$$

$$F_{16}=y_4+\left(\frac{55}{21}x_3+\frac{29}{21}x_5\right)+\left(\frac{99}{49}w_2+\frac{105}{49}w_4\right)+\left(\frac{11}{35}v_1+\frac{129}{35}v_3\right)+u_2$$

$$F_{17}=y_4+\left(\frac{44}{21}x_3+\frac{40}{21}x_5\right)+\left(\frac{33}{49}w_2+\frac{261}{49}w_4\right)+\left(-\frac{22}{35}v_1+\frac{162}{35}v_3\right)+u_2$$

$$F_{18}=y_4+\left(\frac{44}{15}x_3+\frac{16}{15}x_5\right)+\left(\frac{99}{35}w_2+\frac{111}{35}w_4\right)+\left(\frac{22}{25}v_1+\frac{78}{25}v_3\right)+u_2$$

$$F_{19}=y_4+\left(\frac{88}{27}x_3+\frac{20}{27}x_5\right)+\left(\frac{11}{3}w_2+\frac{7}{3}w_4\right)+\left(\frac{22}{15}v_1+\frac{38}{15}v_3\right)+u_2$$

$$F_{20}=y_4+4x_5+\left(-\frac{33}{7}w_2+\frac{75}{7}w_4\right)+\left(-\frac{22}{5}v_1+\frac{42}{5}v_3\right)+u_2$$

$$F_{21}=y_4+\left(\frac{77}{27}x_3+\frac{31}{27}x_5\right)+\left(\frac{55}{21}w_2+\frac{71}{21}w_4\right)+\left(\frac{11}{15}v_1+\frac{44}{15}v_3\right)+u_2$$

$$F_{22}=y_4+\left(\frac{44}{9}x_3-\frac{8}{9}x_5\right)+\left(\frac{55}{7}w_2-\frac{13}{7}w_4\right)+\left(\frac{22}{5}v_1-\frac{2}{5}\right)v_3+u_2$$

$$S_1=y_6+4x_6+6w_4+4v_3+u_2$$

Appendix B. The Hyperfine Integrals

(a) The integrals of $\langle\psi_i|l_{N\alpha}/r_N^3|\psi_j\rangle$

$$\langle 4d_{xz}|l_{Nz}/r_N^3|4d_{xy}\rangle=-i\Big\{-\frac{2\sqrt{\pi}}{315}n_1Y_{00}(\Theta,\Phi)+\frac{1}{441}\sqrt{\frac{\pi}{5}}t_1Y_{20}(\Theta,\Phi)-\frac{1}{294}\sqrt{\frac{2\pi}{15}}t_1(Y_{2-2}(\Theta,\Phi)+Y_{22}(\Theta,\Phi))+\frac{\sqrt{\pi}}{735}f_1Y_{40}(\Theta,\Phi)-\frac{2}{441}\sqrt{\frac{\pi}{10}}f_1(Y_{4-2}(\Theta,\Phi)+Y_{42}(\Theta,\Phi))+\frac{1}{126}\sqrt{\frac{2\pi}{35}}f_1(Y_{4-4}(\Theta,\Phi)+Y_{44}(\Theta,\Phi)\Big\}$$

$$\langle 4d_{xz}|l_{Nz}/r_N^3|4d_{yz}\rangle=i\Big\{-\frac{2\sqrt{\pi}}{315}n_1Y_{00}(\Theta,\Phi)-\frac{2}{441}\sqrt{\frac{\pi}{5}}t_1Y_{20}(\Theta,\Phi)+\frac{8\sqrt{\pi}}{2205}Y_{40}(\Theta,\Phi))\Big\}$$

$$\langle 4d_{yz}|l_{Ny}/r_N^3|4d_{xy}\rangle=i\Big\{-\frac{2\sqrt{\pi}}{315}n_1Y_{00}(\Theta,\Phi)+\frac{1}{441}\sqrt{\frac{\pi}{5}}t_1Y_{20}(\Theta,\Phi)+\frac{1}{294}\sqrt{\frac{2\pi}{15}}t_1(Y_{2-2}(\Theta,\Phi)+Y_{22}(\Theta,\Phi))+\frac{\sqrt{\pi}}{735}f_1Y_{40}(\Theta,\Phi)+\frac{2}{441}\sqrt{\frac{\pi}{10}}f_1(Y_{4-2}(\Theta,\Phi)+Y_{42}(\Theta,\Phi))+\frac{1}{186}\sqrt{\frac{2\pi}{35}}f_1(Y_{4-4}(\Theta,\Phi)+Y_{44}(\Theta,\Phi))\Big\}$$

$$\langle 4d_{xy}|l_{Ny}/r_N^3|4d_{xz}\rangle=-\frac{3}{294}\sqrt{\frac{2\pi}{15}}t_2(Y_{2-2}(\Theta,\Phi)-Y_{22}(\Theta,\Phi))+\frac{1}{441}\sqrt{\frac{\pi}{10}}f_1(Y_{4-2}(\Theta,\Phi)-Y_{42}(\Theta,\Phi))-\frac{1}{126}\sqrt{\frac{2\pi}{35}}(Y_{4-4}(\Theta,\Phi)-Y_{44}(\Theta,\Phi))$$

$$\langle 4d_{yz}|l_{Nz}/r_N^3|4d_{xy}\rangle=-\frac{3}{294}\sqrt{\frac{2\pi}{15}}t_2(Y_{2-1}(\Theta,\Phi)+Y_{21}(\Theta,\Phi))+\frac{1}{294}\sqrt{\frac{\pi}{5}}f_1(Y_{4-1}(\Theta,\Phi)+Y_{41}(\Theta,\Phi))+\frac{1}{126}\sqrt{\frac{\pi}{35}}f_1(Y_{4-3}(\Theta,\Phi)+Y_{43}(\Theta,\Phi))$$

$$\langle 4d_{xz}|l_{Nx}/r_N^3|4d_{yz}\rangle=i\Big\{\frac{3}{294}\sqrt{\frac{2\pi}{15}}t_2(Y_{2-1}(\Theta,\Phi)-Y_{21}(\Theta,\Phi))+\frac{2}{441}\sqrt{\frac{\pi}{5}}f_1(Y_{4-1}(\Theta,\Phi)-Y_{41}(\Theta,\Phi))\Big\}$$

$$\langle 4d_{xz}|l_{Ny}/r_N^3|4d_{yz}\rangle=-\frac{1}{294}\sqrt{\frac{2\pi}{15}}t_3(Y_{2-1}(\Theta,\Phi)+Y_{21}(\Theta,\Phi))+\frac{1}{147}\sqrt{\frac{\pi}{10}}f_1(Y_{4-1}(\Theta,\Phi)+Y_{41}(\Theta,\Phi))$$

$$\langle 4d_{xy}|l_{Nz}/r_N^3|4d_{xz}\rangle=i\Big\{\frac{3}{294}\sqrt{\frac{2\pi}{15}}t_2(Y_{2-1}(\Theta,\Phi)-Y_{21}(\Theta,\Phi))-\frac{1}{294}\sqrt{\frac{\pi}{5}}f_1(Y_{4-1}(\Theta,\Phi)-Y_{41}(\Theta,\Phi))+\frac{1}{126}\sqrt{\frac{\pi}{35}}f_1(Y_{4-3}(\Theta,\Phi)-Y_{43}(\Theta,\Phi))\Big\}$$

$$\langle 4d_{xy}|l_{Nx}/r_M^3|3d_{yz}\rangle=-\frac{3}{294}\sqrt{\frac{2\pi}{15}}t_2(Y_{2-2}(\Theta,\Phi)+Y_{22}(\Theta,\Phi))+\frac{1}{441}\sqrt{\frac{\pi}{10}}f_1(Y_{4-2}(\Theta,\Phi)-Y_{42}(\Theta,\Phi))+\frac{1}{126}\sqrt{\frac{2\pi}{35}}f_1(Y_{4-4}(\Theta,\Phi)-Y_{44}(\Theta,\Phi))$$

(b) Dipolar Integrals

$$\langle 4d_{yz}|T_{xx}|4d_{yz}\rangle=\frac{8\sqrt{\pi}}{2205}N_1Y_{00}(\Theta,\Phi)-\frac{2}{441}\sqrt{\frac{\pi}{5}}T_1Y_{20}(\Theta,\Phi)+\frac{1}{147}\sqrt{\frac{2\pi}{15}}T_1(Y_{2-2}(\Theta,\Phi)+Y_{22}(\Theta,\Phi))+\frac{46\sqrt{\pi}}{24255}F_1Y_{40}(\Theta,\Phi)+\frac{4}{441}\sqrt{\frac{\pi}{10}}F_2(Y_{4-2}(\Theta,\Phi)+Y_{42}(\Theta,\Phi))-\frac{1}{231}\sqrt{\frac{2\pi}{35}}F_3(Y_{4-4}(\Theta,\Phi)+Y_{44}(\Theta,\Phi))+\frac{4}{1617}\sqrt{\frac{\pi}{13}}S_1Y_{60}(\Theta,\Phi)-\frac{2}{231}\sqrt{\frac{2\pi}{91}}S_1(Y_{6-4}(\Theta,\Phi)+Y_{64}(\Theta,\Phi))$$

$$\langle 4d_{yz}|T_{yy}|4d_{yz}\rangle=\frac{4\sqrt{\pi}}{2205}N_1Y_{00}(\theta,\Phi)-\frac{2}{441}\sqrt{\frac{\pi}{5}}T_5Y_{20}(\theta,\Phi)-\frac{1}{147}\sqrt{\frac{2\pi}{15}}T_6(Y_{2-2}(\theta,\Phi)+Y_{22}(\theta,\Phi))-\frac{38\sqrt{\pi}}{24255}F_7Y_{40}(\theta,\Phi)$$
$$-\frac{16}{4851}\sqrt{\frac{\pi}{10}}F_8(Y_{4-2}(\theta,\Phi)+Y_{42}(\theta,\Phi))+\frac{1}{231}\sqrt{\frac{2\pi}{35}}F_3(Y_{4-4}(\theta,\Phi)+Y_{44}(\theta,\Phi))+\frac{2}{1617}\sqrt{\frac{\pi}{13}}S_1Y_{60}(\theta,\Phi)$$
$$+\frac{16}{231}\sqrt{\frac{\pi}{1365}}S_1(Y_{6-2}(\theta,\Phi)+Y_{62}(\theta,\Phi))+\frac{2}{231}\sqrt{\frac{2\pi}{91}}S_1(Y_{6-4}(\theta,\Phi)+Y_{64}(\theta,\Phi))$$

$$\langle 4d_{yz}|T_{zz}|4d_{yz}\rangle=\frac{4\sqrt{\pi}}{2205}N_1Y_{00}(\theta,\Phi)+\frac{4}{441}\sqrt{\frac{\pi}{5}}T_4Y_{20}(\theta,\Phi)-\frac{4}{735}\sqrt{\frac{2\pi}{15}}T_3(Y_{2-2}(\theta,\Phi)+Y_{22}(\theta,\Phi))-\frac{8\sqrt{\pi}}{24255}F_4Y_{40}(\theta,\Phi)$$
$$-\frac{4}{693}\sqrt{\frac{\pi}{10}}F_5(Y_{4-2}(\theta,\Phi)+Y_{42}(\theta,\Phi))-\frac{16}{1617}\sqrt{\frac{\pi}{13}}S_1Y_{60}(\theta,\Phi)-\frac{16}{231}\sqrt{\frac{\pi}{1365}}S_1(Y_{6-2}(\theta,\Phi)+Y_{62}(\theta,\Phi))$$

$$\langle 4d_{xz}|T_{xx}|4d_{xz}\rangle=\frac{4\sqrt{\pi}}{2205}N_1Y_{00}(\theta,\Phi)-\frac{2}{441}\sqrt{\frac{\pi}{5}}T_5Y_{20}(\theta,\Phi)+\frac{1}{147}\sqrt{\frac{2\pi}{15}}T_6(Y_{2-2}(\theta,\Phi)+Y_{22}(\theta,\Phi))-\frac{38\sqrt{\pi}}{24255}F_7Y_{40}(\theta,\Phi)$$
$$+\frac{16}{4851}\sqrt{\frac{\pi}{10}}F_8(Y_{4-2}(\theta,\Phi)+Y_{42}(\theta,\Phi))+\frac{1}{231}\sqrt{\frac{2\pi}{35}}F_3(Y_{4-4}(\theta,\Phi)+Y_{44}(\theta,\Phi))+\frac{12}{1617}\sqrt{\frac{\pi}{13}}S_1Y_{60}(\theta,\Phi)$$
$$+\frac{16}{231}\sqrt{\frac{\pi}{1365}}S_1(Y_{6-2}(\theta,\Phi)+Y_{62}(\theta,\Phi))+\frac{2}{231}\sqrt{\frac{2\pi}{91}}S_1(Y_{6-4}(\theta,\Phi)+Y_{64}(\theta,\Phi))$$

$$\langle 4d_{xz}|T_{yy}|4d_{xz}\rangle=-\frac{8\sqrt{\pi}}{2205}N_1Y_{00}(\theta,\Phi)-\frac{2}{441}\sqrt{\frac{\pi}{5}}T_1Y_{20}(\theta,\Phi)-\frac{1}{147}\sqrt{\frac{2\pi}{15}}T_1(Y_{2-2}(\theta,\Phi)+Y_{22}(\theta,\Phi))+\frac{46}{24255}F_1Y_{40}(\theta,\Phi)$$
$$-\frac{4}{441}\sqrt{\frac{\pi}{10}}F_2(Y_{4-2}(\theta,\Phi)+Y_{42}(\theta,\Phi))-\frac{\sqrt{\pi}}{231}F_3(Y_{4-4}(\theta,\Phi)+Y_{44}(\theta,\Phi))+\frac{4}{1617}\sqrt{\frac{\pi}{13}}S_1Y_{60}(\theta,\Phi)$$
$$-\frac{2}{231}\sqrt{\frac{2\pi}{91}}S_1(Y_{6-4}(\theta,\Phi)+Y_{64}(\theta,\Phi))$$

$$\langle 4d_{xz}|T_{zz}|4d_{xz}\rangle=\frac{4\sqrt{\pi}}{2205}N_1Y_{00}(\theta,\Phi)+\frac{4}{441}\sqrt{\frac{\pi}{5}}T_4Y_{20}(\theta,\Phi)+\frac{4}{735}\sqrt{\frac{2\pi}{15}}T_3(Y_{2-2}(\theta,\Phi)+Y_{22}(\theta,\Phi))-\frac{8\sqrt{\pi}}{24255}F_4Y_{40}(\theta,\Phi)$$
$$+\frac{4}{693}\sqrt{\frac{\pi}{10}}F_5(Y_{4-2}(\theta,\Phi)+Y_{42}(\theta,\Phi))-\frac{16}{1617}\sqrt{\frac{\pi}{13}}S_1Y_{60}(\theta,\Phi)+\frac{16}{231}\sqrt{\frac{\pi}{1365}}S_1(Y_{6-2}(\theta,\Phi)+Y_{62}(\theta,\Phi))$$

$$\langle 4d_{xy}|T_{xx}|4d_{xy}\rangle=\frac{4\sqrt{\pi}}{2205}N_1Y_{00}(\theta,\Phi)-\frac{2}{441}\sqrt{\frac{\pi}{5}}T_1Y_{20}(\theta,\Phi)+\frac{1}{147}\sqrt{\frac{2\pi}{15}}T_6(Y_{2-2}(\theta,\Phi)+Y_{22}(\theta,\Phi))+\frac{32\sqrt{\pi}}{24255}F_9Y_{40}(\theta,\Phi)$$
$$+\frac{4}{1617}\sqrt{\frac{\pi}{10}}F_3(Y_{4-2}(\theta,\Phi)+Y_{42}(\theta,\Phi))-\frac{4\sqrt{\pi}}{693}F_8(Y_{4-4}(\theta,\Phi)+Y_{44}(\theta,\Phi))-\frac{2}{1617}\sqrt{\frac{\pi}{13}}S_1Y_{60}(\theta,\Phi)$$
$$+\frac{1}{231}\sqrt{\frac{\pi}{1365}}S_1(Y_{6-2}(\theta,\Phi)+Y_{62}(\theta,\Phi))+\frac{1}{231}\sqrt{\frac{2\pi}{91}}S_1(Y_{6-4}(\theta,\Phi)+Y_{64}(\theta,\Phi))$$
$$+\frac{1}{7}\sqrt{\frac{\pi}{3003}}S_1(Y_{6-6}(\theta,\Phi)+Y_{66}(\theta,\Phi))$$

$$\langle 4d_{xy}|T_{yy}|4d_{xy}\rangle=\frac{4\sqrt{\pi}}{2205}N_1Y_{00}(\theta,\Phi)-\frac{2}{441}\sqrt{\frac{\pi}{5}}T_1Y_{20}(\theta,\Phi)-\frac{1}{147}\sqrt{\frac{2\pi}{15}}T_2(Y_{2-2}(\theta,\Phi)+Y_{22}(\theta,\Phi))+\frac{32\sqrt{\pi}}{24255}F_9Y_{40}(\theta,\Phi)$$
$$+\frac{4}{1617}\sqrt{\frac{\pi}{10}}F_3(Y_{4-2}(\theta,\Phi)+Y_{42}(\theta,\Phi))-\frac{4\sqrt{\pi}}{693}F_8(Y_{4-4}(\theta,\Phi)+Y_{44}(\theta,\Phi))-\frac{2}{1617}\sqrt{\frac{\pi}{13}}S_1Y_{60}(\theta,\Phi)$$
$$-\frac{1}{231}\sqrt{\frac{\pi}{1365}}S_1(Y_{6-2}(\theta,\Phi)+Y_{62}(\theta,\Phi))+\frac{1}{231}\sqrt{\frac{2\pi}{91}}S_1(Y_{6-4}(\theta,\Phi)+Y_{64}(\theta,\Phi))$$
$$+\frac{1}{7}\sqrt{\frac{\pi}{3003}}S_1(Y_{6-6}(\theta,\Phi)+Y_{66}(\theta,\Phi))$$

$$\langle 4d_{xy}|T_{zz}|4d_{xy}\rangle=-\frac{8\sqrt{\pi}}{2205}N_1Y_{00}(\theta,\Phi)+\frac{4}{441}\sqrt{\frac{2\pi}{5}}T_1Y_{20}(\theta,\Phi)-\frac{64\sqrt{\pi}}{24255}F_9Y_{40}(\theta,\Phi)+\frac{8}{693}\sqrt{\frac{2\pi}{35}}F_8(Y_{4-4}(\theta,\Phi)+Y_{44}(\theta,\Phi))$$
$$+\frac{4}{1617}\sqrt{\frac{\pi}{13}}S_1Y_{60}(\theta,\Phi)-\frac{2}{231}\sqrt{\frac{2\pi}{91}}S_1(Y_{6-4}(\theta,\Phi)+Y_{64}(\theta,\Phi))$$

$$\langle 4d_{xz}|T_{xy}|4d_{xz}\rangle=i\Big\{\frac{1}{147}\sqrt{\frac{2\pi}{15}}T_7(Y_{2-2}(\theta,\Phi)-Y_{22}(\theta,\Phi))+\frac{10}{1617}\sqrt{\frac{2\pi}{5}}F_{12}(Y_{4-2}(\theta,\Phi)-Y_{42}(\theta,\Phi))$$
$$+\frac{1}{231}\sqrt{\frac{2\pi}{35}}F_3(Y_{4-4}(\theta,\Phi)-Y_{44}(\theta,\Phi))-\frac{8}{231}\sqrt{\frac{\pi}{1365}}S_1(Y_{6-2}(\theta,\Phi)-Y_{62}(\theta,\Phi))$$
$$+\frac{2}{231}\sqrt{\frac{2\pi}{91}}S_1(Y_{6-4}(\theta,\Phi)-Y_{64}(\theta,\Phi))\Big\}$$

$$\langle 4d_{yz}|T_{xy}|4d_{yz}\rangle=i\Big\{\frac{1}{147}\sqrt{\frac{2\pi}{15}}T_7(Y_{2-2}(\theta,\Phi)-Y_{22}(\theta,\Phi))+\frac{10}{1617}\sqrt{\frac{\pi}{10}}F_{12}(Y_{4-2}(\theta,\Phi)-Y_{42}(\theta,\Phi))$$
$$-\frac{1}{231}\sqrt{\frac{2\pi}{35}}F_3(Y_{4-4}(\theta,\Phi)-Y_{44}(\theta,\Phi))-\frac{8}{231}\sqrt{\frac{\pi}{136}}S_1(Y_{6-2}(\theta,\Phi)-Y_{62}(\theta,\Phi))$$
$$-\frac{2}{231}\sqrt{\frac{2\pi}{91}}S_1(Y_{6-4}(\theta,\Phi)-Y_{64}(\theta,\Phi))\Big\}$$

$$\langle 4d_{xy}|T_{xy}|4d_{xy}\rangle=i\Big\{\frac{3}{147}\sqrt{\frac{2\pi}{15}}T_8(Y_{2-2}(\theta,\Phi)-Y_{22}(\theta,\Phi))-\frac{12}{1617}\sqrt{\frac{\pi}{10}}(Y_{4-2}(\theta,\Phi))-Y_{42}(\theta,\Phi)$$
$$+\frac{1}{77}\sqrt{\frac{\pi}{1365}}S_1(Y_{6-2}(\theta,\Phi)-Y_{62}(\theta,\Phi))-\frac{1}{7}\sqrt{\frac{\pi}{3003}}S_1(Y_{6-6}(\theta,\Phi)-Y_{66}(\theta,\Phi))\Big]$$

$$\langle 4d_{xz}|T_{zz}|4d_{xy}\rangle=i\Big\{\frac{1}{147}\sqrt{\frac{2\pi}{15}}T_9(Y_{2-2}(\theta,\Phi)-Y_{22}(\theta,\Phi))+\frac{10}{1617}\sqrt{\frac{\pi}{10}}F_{13}(Y_{4-2}(\theta,\Phi)-Y_{42}(\theta,\Phi))$$
$$+\frac{1}{231}\sqrt{\frac{2\pi}{35}}F_8(Y_{4-4}(\theta,\Phi)-Y_{44}(\theta,\Phi))-\frac{8}{231}\sqrt{\frac{\pi}{1365}}S_1(Y_{6-2}(\theta,\Phi)-Y_{62}(\theta,\Phi))$$

$$+\frac{2}{231}\sqrt{\frac{2\pi}{91}}\,S_1\,(Y_{6-4}(\theta,\Phi)-Y_{64}(\theta,\Phi))\Big\}$$

$$<4d_{yz}|T_{yz}|4d_{xy}>=i\Big\{\frac{1}{147}\sqrt{\frac{2\pi}{15}}\,T_9\,(Y_{2-2}(\theta,\Phi)-Y_{22}(\theta,\Phi))+\frac{10}{1617}\sqrt{\frac{\pi}{10}}\,F_{13}\,(Y_{4-2}(\theta,\Phi)-Y_{42}(\theta,\Phi))$$
$$-\frac{1}{231}\sqrt{\frac{2\pi}{35}}\,F_8\,(Y_{4-4}(\theta,\Phi)-Y_{44}(\theta,\Phi))-\frac{8}{231}\sqrt{\frac{\pi}{1365}}\,S_1\,(Y_{6-2}(\theta,\Phi))-Y_{62}(\theta,\Phi))$$
$$-\frac{2}{231}\sqrt{\frac{2\pi}{91}}\,S_1\,(Y_{6-4}(\theta,\Phi)-Y_{64}(\theta,\Phi))\Big\}$$

$$<4d_{yz}|T_{xy}|4d_{xy}>=\frac{1}{147}\sqrt{\frac{2\pi}{15}}\,T_9\,(Y_{2-1}(\theta,\Phi)-Y_{21}(\theta,\Phi))-\frac{2}{539}\sqrt{\frac{\pi}{5}}\,F_{14}\,(Y_{4-1}(\theta,\Phi)-Y_{41}(\theta,\Phi))$$
$$-\frac{2}{231}\sqrt{\frac{\pi}{35}}\,F_{15}\,(Y_{4-3}(\theta,\Phi)-Y_{43}(\theta,\Phi))+\frac{1}{231}\sqrt{\frac{2\pi}{273}}\,S_1\,(Y_{6-1}(\theta,\Phi)-Y_{61}(\theta,\Phi))$$
$$+\frac{1}{77}\sqrt{\frac{\pi}{1365}}\,S_1\,(Y_{6-3}(\theta,\Phi)-Y_{63}(\theta,\Phi))-\frac{1}{21}\sqrt{\frac{\pi}{1001}}\,S_1\,(Y_{6-5}(\theta,\Phi)-Y_{65}(\theta,\Phi))$$

$$<4d_{xy}|T_{xy}|4d_{yz}>=\frac{6\sqrt{\pi}}{2205}\,N_1\,Y_{00}(\theta,\Phi)+\frac{4}{735}\sqrt{\frac{\pi}{5}}\,T_3\,Y_{20}(\theta,\Phi)-\frac{2\sqrt{\pi}}{1155}\,F_6\,Y_{40}(\theta,\Phi)-\frac{1}{231}\sqrt{\frac{2\pi}{35}}\,F_3\,(Y_{4-4}(\theta,\Phi)+Y_{44}(\theta,\Phi))$$
$$+\frac{4}{1617}\sqrt{\frac{\pi}{13}}\,S_1\,Y_{60}(\theta,\Phi)-\frac{2}{231}\sqrt{\frac{2\pi}{91}}\,S_1\,(Y_{6-4}(\theta,\Phi)+Y_{64}(\theta,\Phi))$$

$$<4d_{xz}|T_{xz}|4d_{xy}>=\frac{6\sqrt{\pi}}{2205}\,N_1\,Y_{00}(\theta,\Phi)-\frac{2}{735}\sqrt{\frac{\pi}{5}}\,T_3\,Y_{20}(\theta,\Phi)+\frac{3}{735}\sqrt{\frac{2\pi}{15}}\,T_3\,(Y_{2-2}(\theta,\Phi)+Y_{22}(\theta,\Phi))-\frac{2\sqrt{\pi}}{1155}\,F_{10}\,Y_{40}(\theta,\Phi)$$
$$+\frac{4}{147}\sqrt{\frac{\pi}{10}}\,F_{11}\,(Y_{4-2}(\theta,\Phi)+Y_{42}(\theta,\Phi))-\frac{1}{231}\sqrt{\frac{2\pi}{35}}\,(Y_{4-4}(\theta,\Phi)+Y_{44}(\theta,\Phi))+\frac{4}{1617}\sqrt{\frac{\pi}{13}}\,Y_{60}(\theta,\Phi)$$
$$-\frac{2}{231}\sqrt{\frac{2\pi}{91}}\,S_1\,(Y_{6-4}(\theta,\Phi)+Y_{64}(\theta,\Phi))$$

$$<4d_{yz}|T_{xz}|4d_{xy}>=\frac{6\sqrt{\pi}}{2205}\,N_1\,Y_{00}(\theta,\Phi)-\frac{2}{735}\sqrt{\frac{\pi}{5}}\,T_3\,Y_{20}(\theta,\Phi)-\frac{3}{735}\sqrt{\frac{2\pi}{15}}\,T_3\,(Y_{2-2}(\theta,\Phi)+Y_{22}(\theta,\Phi))-\frac{2\sqrt{\pi}}{1155}\,F_{10}\,Y_{40}(\theta,\Phi)$$
$$-\frac{4}{147}\sqrt{\frac{\pi}{10}}\,F_{11}\,(Y_{4-2}(\theta,\Phi)+Y_{42}(\theta,\Phi))-\frac{1}{231}\sqrt{\frac{2\pi}{35}}\,F_8\,(Y_{4-4}(\theta,\Phi)+Y_{44}(\theta,\Phi))+\frac{4}{1617}\sqrt{\frac{\pi}{13}}\,S_1\,Y_{60}(\theta,\Phi)$$
$$-\frac{2}{231}\sqrt{\frac{2\pi}{91}}\,S_1\,(Y_{6-4}(\theta,\Phi)+Y_{64}(\theta,\Phi))$$

$$<4d_{xz}|T_{xy}|4d_{yz}>=i\Big\{-\frac{2}{735}\sqrt{\frac{2\pi}{15}}\,T_3\,(Y_{2-2}(\theta,\Phi)-Y_{22}(\theta,\Phi))-\frac{2}{693}\sqrt{\frac{\pi}{10}}\,F_3\,(Y_{4-2}(\theta,\Phi)-Y_{42}(\theta,\Phi))$$
$$+\frac{1}{231}\sqrt{\frac{2\pi}{35}}\,F_3\,(Y_{4-4}(\theta,\Phi)-Y_{44}(\theta,\Phi))-\frac{8}{231}\sqrt{\frac{\pi}{1365}}\,S_1\,(Y_{6-2}(\theta,\Phi)-Y_{62}(\theta,\Phi))$$
$$+\frac{2}{231}\sqrt{\frac{2\pi}{91}}\,S_1\,(Y_{6-4}(\theta,\Phi)-Y_{64}(\theta,\Phi))\Big\}$$

$$<4d_{xz}|T_{yy}|4d_{yz}>=i\Big\{-\frac{2}{735}\sqrt{\frac{2\pi}{15}}\,T_3\,(Y_{2-2}(\theta,\Phi)-Y_{22}(\theta,\Phi))-\frac{2}{693}\sqrt{\frac{\pi}{10}}\,F_3\,(Y_{4-2}(\theta,\Phi)-Y_{42}(\theta,\Phi))$$
$$-\frac{1}{231}\sqrt{\frac{2\pi}{35}}\,F_3\,(Y_{4-4}(\theta,\Phi)-Y_{44}(\theta,\Phi))-\frac{8}{231}\sqrt{\frac{\pi}{1365}}\,S_1\,(Y_{6-2}(\theta,\Phi)-Y_{62}(\theta,\Phi))$$
$$-\frac{2}{231}\sqrt{\frac{2\pi}{91}}\,S_1\,(Y_{6-4}(\theta,\Phi)-Y_{64}(\theta,\Phi))\Big\}$$

$$<4d_{xz}|T_{zz}|4d_{yz}>=i\Big\{\frac{4}{735}\sqrt{\frac{2\pi}{15}}\,T_3\,(Y_{2-2}(\theta,\Phi)-Y_{22}(\theta,\Phi))+\frac{4}{693}\sqrt{\frac{\pi}{10}}\,F_3\,(Y_{4-2}(\theta,\Phi)-Y_{42}(\theta,\Phi))$$
$$+\frac{16}{231}\sqrt{\frac{\pi}{1365}}\,S_1\,(Y_{6-2}(\theta,\Phi)-Y_{62}(\theta,\Phi))\Big\}$$

$$<4d_{yz}|T_{xy}|4d_{xy}>=i\Big\{\frac{1}{147}\sqrt{\frac{2\pi}{15}}\,T_9\,(Y_{2-1}(\theta,\Phi)+Y_{21}(\theta,\Phi))-\frac{2}{539}\sqrt{\frac{\pi}{5}}\,F_{14}\,(Y_{4-1}(\theta,\Phi)+Y_{41}(\theta,\Phi))$$
$$+\frac{2}{231}\sqrt{\frac{\pi}{35}}\,(Y_{4-3}(\theta,\Phi)+Y_{43}(\theta,\Phi))+\frac{1}{231}\sqrt{\frac{2\pi}{273}}\,S_1\,(Y_{6-1}(\theta,\Phi)+Y_{61}(\theta,\Phi))$$
$$-\frac{1}{77}\sqrt{\frac{\pi}{1365}}\,S_1\,(Y_{6-3}(\theta,\Phi)+Y_{63}(\theta,\Phi))-\frac{1}{21}\sqrt{\frac{\pi}{1001}}\,S_1\,(Y_{6-5}(\theta,\Phi)+Y_{65}(\theta,\Phi))\Big\}$$

$$<4d_{yz}|T_{yy}|4d_{xy}>=-\frac{4}{735}\sqrt{\frac{2\pi}{15}}\,T_3\,(Y_{2-1}(\theta,\Phi)-Y_{21}(\theta,\Phi))-\frac{1}{693}\sqrt{\frac{\pi}{5}}\,F_5\,(Y_{4-1}(\theta,\Phi)-Y_{41}(\theta,\Phi))$$
$$-\frac{1}{99}\sqrt{\frac{\pi}{35}}\,F_5\,(Y_{4-3}(\theta,\Phi)-Y_{43}(\theta,\Phi))+\frac{1}{231}\sqrt{\frac{2\pi}{273}}\,S_1\,(Y_{6-1}(\theta,\Phi)-Y_{61}(\theta,\Phi))$$
$$+\frac{3}{77}\sqrt{\frac{\pi}{1365}}\,S_1\,(Y_{6-3}(\theta,\Phi)-Y_{63}(\theta,\Phi))+\frac{1}{21}\sqrt{\frac{\pi}{1001}}\,S_1\,(Y_{6-5}(\theta,\Phi)-Y_{65}(\theta,\Phi))$$

$$<4d_{yz}|T_{zz}|4d_{xy}>=-\sqrt{\frac{2\pi}{15}}\,T_3\,(Y_{2-1}(\theta,\Phi)-Y_{21}(\theta,\Phi))+\frac{2}{693}\sqrt{\frac{\pi}{5}}\,F_{16}\,(Y_{4-1}(\theta,\Phi)-Y_{41}(\theta,\Phi))$$
$$+\frac{2}{693}\sqrt{\frac{\pi}{35}}\,F_8\,(Y_{4-3}(\theta,\Phi)-Y_{43}(\theta,\Phi))-\frac{2}{231}\sqrt{\frac{2\pi}{273}}\,S_1\,(Y_{6-1}(\theta,\Phi)-Y_{61}(\theta,\Phi))$$
$$-\frac{4}{77}\sqrt{\frac{\pi}{1365}}\,S_1\,(Y_{6-3}(\theta,\Phi)-Y_{63}(\theta,\Phi))$$

$$<4d_{yz}|T_{xy}|4d_{xy}>=-\frac{2}{735}\sqrt{\frac{2\pi}{15}}\,T_3\,(Y_{2-1}(\theta,\Phi)-Y_{21}(\theta,\Phi))-\frac{1}{693}\sqrt{\frac{\pi}{5}}\,F_{17}\,(Y_{4-1}(\theta,\Phi)-Y_{41}(\theta,\Phi))$$

$$+\frac{5}{693}\sqrt{\frac{\pi}{35}}F_{18}(Y_{4-3}(\theta,\Phi)-Y_{43}(\theta,\Phi))+\frac{1}{231}\sqrt{\frac{2\pi}{273}}S_1(Y_{6-1}(\theta,\Phi)-Y_{61}(\theta,\Phi))$$

$$+\frac{1}{77}\sqrt{\frac{\pi}{1365}}S_1(Y_{6-3}(\theta,\Phi)-Y_{63}(\theta,\Phi))-\frac{1}{21}\sqrt{\frac{\pi}{1001}}S_1(Y_{6-5}(\theta,\Phi)-Y_{65}(\theta,\Phi))$$

$$<4d_{xz}|T_{zz}|4d_{xy}>=i\Big\{-\frac{2}{735}\sqrt{\frac{2\pi}{15}}T_3(Y_{2-1}(\theta,\Phi)+Y_{21}(\theta,\Phi))+\frac{2}{693}\sqrt{\frac{\pi}{5}}F_{18}(Y_{4-1}(\theta,\Phi)+Y_{41}(\theta,\Phi))$$

$$-\frac{2}{693}\sqrt{\frac{\pi}{35}}F_8(Y_{4-3}(\theta,\Phi)+Y_{43}(\theta,\Phi))-\frac{2}{231}\sqrt{\frac{2\pi}{273}}S_1(Y_{6-1}(\theta,\Phi)+Y_{61}(\theta,\Phi))$$

$$+\frac{4}{77}\sqrt{\frac{\pi}{1365}}S_1(Y_{6-3}(\theta,\Phi)+Y_{63}(\theta,\Phi))\Big\}$$

$$<4d_{zz}|T_{xz}|4d_{xz}>=\frac{1}{49}\sqrt{\frac{2\pi}{15}}T_8(Y_{2-1}(\theta,\Phi)+Y_{21}(\theta,\Phi))+\frac{1}{539}\sqrt{\frac{\pi}{5}}F_{19}(Y_{4-1}(\theta,\Phi)-Y_{41}(\theta,\Phi))$$

$$+\frac{1}{77}\sqrt{\frac{\pi}{35}}F_{19}(Y_{4-3}(\theta,\Phi)-Y_{43}(\theta,\Phi))-\frac{2}{77}\sqrt{\frac{2\pi}{273}}S_1(Y_{6-1}(\theta,\Phi)-Y_{61}(\theta,\Phi))$$

$$+\frac{4}{77}\sqrt{\frac{\pi}{1365}}S_1(Y_{6-3}(\theta,\Phi)-Y_{63}(\theta,\Phi))$$

$$<4d_{xz}|T_{yz}|4d_{xz}>=i\Big\{\frac{1}{147}\sqrt{\frac{2\pi}{15}}T_7(Y_{2-1}(\theta,\Phi)+Y_{21}(\theta,\Phi))+\frac{1}{1617}\sqrt{\frac{\pi}{5}}F_{20}(Y_{4-1}(\theta,\Phi)+Y_{41}(\theta,\Phi))$$

$$+\frac{1}{77}\sqrt{\frac{\pi}{35}}F_{19}(Y_{4-3}(\theta,\Phi)+Y_{43}(\theta,\Phi))-\frac{2}{231}\sqrt{\frac{2\pi}{273}}S_1(Y_{6-1}(\theta,\Phi)+Y_{61}(\theta,\Phi))$$

$$+\frac{4}{77}\sqrt{\frac{\pi}{1365}}S_1(Y_{6-3}(\theta,\Phi)+Y_{63}(\theta,\Phi))\Big\}$$

$$<4d_{yz}|T_{yz}|4d_{yz}>=i\Big\{\frac{1}{49}\sqrt{\frac{2\pi}{15}}T_8(Y_{2-1}(\theta,\Phi)+Y_{21}(\theta,\Phi))+\frac{1}{539}\sqrt{\frac{\pi}{5}}F_{19}(Y_{4-1}(\theta,\Phi)+Y_{41}(\theta,\Phi))$$

$$-\frac{1}{77}\sqrt{\frac{\pi}{35}}F_{19}(Y_{4-3}(\theta,\Phi)+Y_{43}(\theta,\Phi))-\frac{2}{77}\sqrt{\frac{2\pi}{273}}S_1(Y_{6-1}(\theta,\Phi)+Y_{61}(\theta,\Phi))$$

$$-\frac{4}{77}\sqrt{\frac{\pi}{1365}}S_1(Y_{6-3}(\theta,\Phi)+Y_{63}(\theta,\Phi))\Big\}$$

$$<4d_{yz}|T_{xz}|4d_{yz}>=\frac{1}{147}\sqrt{\frac{2\pi}{15}}T_7(Y_{2-1}(\theta,\Phi)-Y_{21}(\theta,\Phi))+\frac{1}{1617}\sqrt{\frac{\pi}{5}}F_{20}(Y_{4-1}(\theta,\Phi)-Y_{41}(\theta,\Phi))$$

$$-\frac{1}{77}\sqrt{\frac{\pi}{35}}F_{19}(Y_{4-3}(\theta,\Phi)-Y_{43}(\theta,\Phi))-\frac{2}{231}\sqrt{\frac{2\pi}{273}}S_1(Y_{6-1}(\theta,\Phi)-Y_{61}(\theta,\Phi))$$

$$-\frac{4}{77}\sqrt{\frac{\pi}{1365}}S_1(Y_{6-3}(\theta,\Phi)-Y_{63}(\theta,\Phi))$$

$$<4d_{xy}|T_{xz}|4d_{xy}>=\frac{1}{147}\sqrt{\frac{2\pi}{15}}T_7(Y_{2-1}(\theta,\Phi)-Y_{21}(\theta,\Phi))-\frac{2}{539}\sqrt{\frac{\pi}{5}}F_{21}(Y_{4-1}(\theta,\Phi)-Y_{41}(\theta,\Phi))$$

$$-\frac{2}{231}\sqrt{\frac{\pi}{35}}F_8(Y_{4-3}(\theta,\Phi)-Y_{43}(\theta,\Phi))+\frac{1}{231}\sqrt{\frac{2\pi}{273}}S_1(Y_{6-1}(\theta,\Phi)-Y_{61}(\theta,\Phi))$$

$$+\frac{1}{77}\sqrt{\frac{\pi}{1365}}S_1(Y_{6-3}(\theta,\Phi)-Y_{63}(\theta,\Phi))-\frac{1}{21}\sqrt{\frac{\pi}{1001}}S_1(Y_{6-5}(\theta,\Phi)-Y_{65}(\theta,\Phi))$$

$$<4d_{xy}|T_{yz}|4d_{xy}>=i\Big\{\frac{1}{147}\sqrt{\frac{2\pi}{15}}T_7(Y_{2-1}(\theta,\Phi)+Y_{21}(\theta,\Phi))-\frac{2}{539}\sqrt{\frac{\pi}{5}}F_{21}(Y_{4-1}(\theta,\Phi)+Y_{41}(\theta,\Phi))$$

$$+\frac{2}{21}\sqrt{\frac{\pi}{35}}F_8(Y_{4-3}(\theta,\Phi)+Y_{43}(\theta,\Phi))+\frac{1}{231}\sqrt{\frac{2\pi}{273}}S_1(Y_{6-1}(\theta,\Phi)+Y_{61}(\theta,\Phi))$$

$$-\frac{1}{77}\sqrt{\frac{\pi}{1365}}S_1(Y_{6-3}(\theta,\Phi)+Y_{63}(\theta,\Phi))-\frac{1}{21}\sqrt{\frac{\pi}{1001}}S_1(Y_{6-5}(\theta,\Phi)+Y_{65}(\theta,\Phi)\Big\}$$

$$<4d_{xz}|T_{xz}|4d_{yz}>=i\Big\{\frac{1}{147}\sqrt{\frac{2\pi}{15}}T_9(Y_{2-1}(\theta,\Phi)+Y_{21}(\theta,\Phi))+\frac{1}{539}\sqrt{\frac{\pi}{5}}F_{22}(Y_{4-1}(\theta,\Phi)+Y_{41}(\theta,\Phi))$$

$$+\frac{1}{77}\sqrt{\frac{\pi}{35}}F_{19}(Y_{4-3}(\theta,\phi)+Y_{43}(\theta,\phi))-\frac{2}{231}\sqrt{\frac{2\pi}{273}}S_1(Y_{6-1}(\theta,\Phi)+Y_{61}(\theta,\Phi))$$

$$+\frac{4}{77}\sqrt{\frac{\pi}{1365}}S_1(Y_{6-3}(\theta,\Phi)+Y_{63}(\theta,\Phi))\Big\}$$

$$<4d_{xz}|T_{yz}|4d_{yz}>=\frac{1}{147}\sqrt{\frac{2\pi}{15}}T_9(Y_{2-1}(\theta,\Phi)-Y_{21}(\theta,\Phi))+\frac{1}{539}\sqrt{\frac{\pi}{5}}F_{22}(Y_{4-1}(\theta,\Phi)-Y_{41}(\theta,\Phi))$$

$$-\frac{1}{77}\sqrt{\frac{\pi}{35}}F_{19}(Y_{4-3}(\theta,\Phi)-Y_{43}(\theta,\Phi))-\frac{2}{231}\sqrt{\frac{2\pi}{273}}S_1(Y_{6-1}(\theta,\Phi)-Y_{61}(\theta,\Phi))$$

$$-\frac{4}{77}\sqrt{\frac{\pi}{1365}}S_1(Y_{6-3}(\theta,\Phi)-Y_{63}(\theta,\Phi))$$

$$<4d_{xx}|T_{xx}|4d_{xy}>=i\Big\{\frac{4}{735}\sqrt{\frac{2\pi}{15}}T_3(Y_{2-1}(\theta,\Phi)+Y_{21}(\theta,\Phi))-\frac{1}{693}\sqrt{\frac{\pi}{5}}F_5(Y_{4-1}(\theta,\Phi)+Y_{41}(\theta,\Phi))$$

$$+\frac{7}{99}\sqrt{\frac{\pi}{35}}F_8(Y_{4-3}(\theta,\Phi)+Y_{43}(\theta,\Phi))+\frac{1}{231}\sqrt{\frac{2\pi}{273}}S_1(Y_{6-1}(\theta,\Phi)+Y_{61}(\theta,\Phi))$$

$$-\frac{3}{77}\sqrt{\frac{\pi}{1365}}S_1(Y_{6-3}(\theta,\Phi)+Y_{63}(\theta,\Phi))+\frac{1}{21}\sqrt{\frac{\pi}{1001}}S_1(Y_{6-5}(\theta,\Phi)+Y_{65}(\theta,\Phi))\Big\}$$

$$<4d_{zz}|T_{yy}|4d_{xy}>=i\Big\{\frac{2}{735}\sqrt{\frac{2\pi}{15}}T_3(Y_{2-1}(\theta,\Phi)+Y_{21}(\theta,\Phi))-\frac{1}{693}\sqrt{\frac{\pi}{5}}F_{17}(Y_{4-1}(\theta,\Phi)+Y_{41}(\theta,\Phi)$$

$$-\frac{5}{693}\sqrt{\frac{\pi}{35}}F_{18}\left(Y_{4-3}(\Theta,\Phi)+Y_{43}(\Theta,\Phi)\right)+\frac{1}{231}\sqrt{\frac{2\pi}{273}}S_1\left(Y_{6-1}(\Theta,\Phi)+Y_{61}(\Theta,\Phi)\right)$$
$$-\frac{1}{77}\sqrt{\frac{\pi}{1365}}S_1\left(Y_{6-3}(\Theta,\Phi)+Y_{63}(\Theta,\Phi)\right)-\frac{1}{21}\sqrt{\frac{\pi}{1001}}S_1\left(Y_{6-5}(\Theta,\Phi)+Y_{65}(\Theta,\Phi)\right)\Big]$$

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Molecular Reorientation in the Presence of the Extended Diffusion of Internal Rotation in Liquid Perdeuterotoluene

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The effect of internal rotation of methyl group in liquid perdeuterotoluene on nuclear quadrupole relaxation of methyl deuterons is investigated. A model of a spherical diffusor undergoing rotational diffusion is extended to include the extended diffusion of internal rotation. The overall reorientational correlation time in the presence of internal rotation is explicitly given as an analytical function of the angular momentum correlation time. Also, the degree of inertial effect in the internal rotation is evaluated.

1. Introduction

Nuclear magnetic relaxation measurements are widely used in understanding molecular dynamics in liquids.[1-6] Interpretation of the experimental data in terms of the rotational diffusion model[7-9] is a common practice. However, this model is based on the assumption of small angular step diffusion and can not describe the inertial effect properly. In 1966 Gordon[10] proposed an extended version of the rotational diffusion model and applied it to linear molecules. His model is free of the restriction on the size of angular steps but assumes that both the magnitude and direction of angular momentum are randomized at the end of each free rotational step (J-diffusion) or only the direction is randomized (M-diffusion). Since then, Gordon's extended diffusion theory was developed further to deal with spherical top molecules[11] and symmetric top molecules.[12,13]

Recently, Versmold[4] studied the internal rotation of a side group attached to a spherical diffusor in terms of the extended diffusion model. He treated the overall rotation of a spherical diffusor by the isotropic rotational diffusion and proposed a scheme to incorporate the inertial effect of the extended internal rotation. His theory is limited, however, to a certain range of the angular momentum correlation time. Furthermore, all the calculations in his theory have to be carried out by numerical integrations. We have reported earlier[11] a general scheme of calculating the internal correlation time and the overall reorientational correlation time as analytic functions of the angular momentum correlation time without any restriction on the range of validity. The purpose of this work is to apply our general scheme to the nuclear quadrupolar relaxation of methyl group deuterons in liquid perdeuterotoluene and evaluate the degree of inertial effect of the internal rotation.

2. Theoretical Background

Application of the extended diffusion model to describe the internal rotation of a side group such as the methyl group in toluene can be simplified if we assume that the internal rotation about the z-axis of molecular coordinate system is one dimensional. In this case, a modified version of the extended diffusion model of Spiess, *et al.*[2] may be adopted. In this modified version, only the magnitude of angular momentum is randomized at the end of each free rotational step.