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NMR Chemical Shift for a $4d^1$ System when the Threefold Axis is Chosen to be the Axis of Quantization

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The NMR chemical shift arising from 4d electron angular momentum and 4d electron spin dipolar-nuclear spin angular momentum interaction for a $4d^1$ system in a strong crystal field of octahedral symmetry, when the threefold axis is chosen as the quantization axis, has been investigated. A general expression using a nonmultipole expansion method is derived for the NMR chemical shift. From this expression all the multipolar terms are determined. We find that the nonmultipolar results for the NMR chemical shift, ΔB, is exactly in agreement with the multipolar results when $R \geqslant 0.20$ nm. It is also found that the $1/R^7$ term contributes to the NMR chemical shift almost the same as the $1/R^5$ in magnitude. The temperature dependence analysis of $\Delta B/B$(ppm) at various values of R shows that the $1/T^2$ term has the dominant contribution to the NMR chemical shift but the contributions of other two terms are certainly significant for a $4d^1$ system in a strong crystal field of octahedral symmetry when the threefold axis is chosen to be the axis of quantization.

Introduction

For a decade a great deal of interest has been focussed on the interpretation of the NMR shift in $3d^n$ and $4f^n$ paramagnetic systems. From NMR studies of paramagnetic molecules[1-4] detailed information about the electronic structure and, in certain cases, the conformation of molecules can be yielded. For instance, we can determine, from the NMR spectra, the magnitude and sign of the various electron-nuclear hyperfine interaction constants throughout a paramagnetic molecule.

Theoretically the NMR shift has been classified as arising from the Fermi contact interaction,[5-7] the electron angular momentum, and the electron spin dipolar-nuclear spin angular momentum interaction. The latter two terms have been treated as a multipole expansion in $\underset{\sim}{R}$, where $\underset{\sim}{R}$ is the distance between the NMR nucleus and the electron bearing atom.[8] Dipolar expansion method[9] has been used almost exclusively to interpret the NMR chemical shifts in $3d^n$ and $4f^n$ systems,[10-13] although the higher multipole expansion method[14,15] has been developed recently and was applied to calculate (2L + 1) independent anisotropy coefficients for each harmonic order L.[15] More recently, nonmultipole expansion method has been developed whereby, from a set of experimental results, an estimate might be made of the various contributions to the NMR shifts.[10]

We adopted the nonmultipole expansion method to calculate the NMR shifts for $4d^1$ and $4d^2$ systems in a strong crystal field environment of octahedral symmetry[16,17] when the fourfold axis was chosen as the quantization axis.

In this work, we derive a general formula for the NMR chemical shift in a $4d^1$ system in a strong crystal field environment of octahedral symmetry, when the threefold axis is chosen as the quantization axis, adopting the nonmultipole expansion method. We calculate the NMR chemical shifts, using this formula and compare the NMR results with the multipolar results.

As far as we are aware no previous calculation has been performed to detemine the NMR chemical shift arising from the 4d electron angular momentum and the 4d electron spin dipolar-nuclear spin angular momentum interaction when the threefold axis is chosen to be the axis of quantization.

Theory

The hamiltonian representing the various interaction in this work may be written as[18]

$$H=-\frac{\hbar^2}{2m}\nabla^2-\frac{Ze^2}{4\pi e_0 r}+V(\underset{\sim}{r})+\zeta\,\underset{\sim}{l}\cdot S+\mu_B(\underset{\sim}{l}+2S)\cdot\underset{\sim}{B}+H_h \qquad (1)$$

where

$$V(\underset{\sim}{r})=a_4\{\frac{1}{3}\sqrt{\frac{7}{3}}\,Y_{40}(\Theta,\Phi)-\frac{1}{3}\sqrt{\frac{10}{3}}\,[Y_{4-3}(\Theta,\Phi)-Y_{43}(\Theta,\Phi)]\}$$

$$H_h=\frac{\mu_0}{4\pi}\,g_N\mu_B\mu_N\,\{\frac{2\underset{\sim}{l}_N\cdot I}{r_N^3}+2[\frac{3(r_N\cdot\underset{\sim}{S})r_N\cdot I}{r_N^5}-\frac{S\cdot I}{r_N^3}]\} \qquad (3)$$

Here $\underset{\sim}{r}$ and r_N are the electron radius vectors about the electron bearing atom and the nucleus with nuclear spin angular momentum $\underset{\sim}{l}$, respectively.

The quantity $\underset{\sim}{B}$ is the applied magnetic field, $V(\underset{\sim}{r})$ is the crystal field potential of octahedral symmetry when the threefold axis is chosen as the quantization axis and a_4 is the required crystal field parameter for the 4d electron system. The other symbols have their usual meaning.

When the threefold axis is taken as the quantization axis the required axial wave function may be expressed in the real notation as[20]

$$\phi_0=|4dz^2>$$

$$\phi_1=\frac{1}{\sqrt{3}}\,4d_{x^2-y^2}+\frac{i}{\sqrt{3}}\,4d_{xy}-\frac{1}{\sqrt{6}}\,4d_{xz}+\frac{i}{\sqrt{6}}\,4d_{yz}$$

$$\phi_2=\frac{1}{\sqrt{3}}\,4d_{x^2-y^2}-\frac{i}{\sqrt{3}}\,4d_{xy}-\frac{1}{\sqrt{6}}\,4d_{xz}-\frac{i}{\sqrt{6}}\,4d_{yz} \qquad (4)$$

Here we adopt SCF wave functions[23] for 4d orbitals expressed, in the real from, as

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

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

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

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

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

A $4d^1$ system in a strong crystal field environment of octahedral symmetry results in a $^2T_2$ ground state. This ground state is split by the spin orbit coupling interactions with relative eigenvalues of $-\frac{1}{2}\zeta$ and ζ where ζ is the spin orbit coupling constant.

Hyperfine integrals. In order to investigate the NMR chemical shifts for a $4d^1$ system in a strong crystal field environment of octahedral symmetry, it is required to evaluate the hyperfine integrals for all pairs of 4d orbitals in addition to the hyperfine integrals for any pair of $4d_{xz}$, $4d_{yz}$ and $4d_{xy}$.

The hyperfine integrals are evaluated using the method reported previously.[21] The required hyperfine integrals are listed in appendix A and B.

Calculation of the NMR chemical shift. To determine the NMR chemical shift in liquid solution we calculate the principal values $\sigma_{\alpha\alpha}$ of the NMR screening tensor by considering the magnetic field interaction parallel to the x, y and z directions and averaged assuming a Boltzmann distribution. It follows that the contribution to the NMR chemical shift, ΔB, is given by

$$\Delta B=\frac{1}{3}B(\sigma_{xx}+\sigma_{yy}+\sigma_{zz}) \qquad (5)$$

where

$$\sigma_{\alpha\alpha}=(\frac{\delta^2<H_h>}{\delta\mu_\alpha\,\delta B_\alpha})_{\mu=B=0} \qquad (6)$$

and $\mu=g_N\mu_N I$

The term $<H_h>$ refers to the Boltzmann average of the hyperfine interaction represented by eq.(3). To calculate the hyperfine interaction, we use the hyperfine integrals evaluated in this work and the previous work.[21] When the threefold axis is chosen as the quantization axis, the NMR chemical shift arising from the electron angular momentum and the electron spin dipolar-nuclear spin angular momentum interactions is given by

$$\frac{\Delta B}{B}=\frac{\mu_0}{4\pi}\,\frac{\mu_B^2}{KT}\,\{\frac{d(R)+[1-\exp(3\zeta/2KT)]KT/\zeta S(R)}{1+2\exp(3\zeta/2KT)}\} \qquad (7)$$

where

$$d(R)=\frac{36\sqrt{\pi}}{441}\,Y_{00}(\Theta,\Phi)E(t)-\frac{17280}{t^5}(\frac{\pi}{21})^{\frac{1}{2}}Y_3H(t)-\frac{22809600}{7t^7}(\frac{\pi}{26})^{\frac{1}{2}}Y_4\,J(t)$$

$$S(R)=-\frac{60\sqrt{\pi}}{441}\,Y_{00}(\Theta,\Phi)M(t)+\frac{7680}{t^5}(\frac{\pi}{21})^{\frac{1}{2}}Y_3H(t)-\frac{15206400}{7t^7}(\frac{\pi}{26})^{\frac{1}{2}}Y_4\,J(t)$$

Here

$$Y_3=\{\frac{1}{3}\sqrt{\frac{7}{3}}\,Y_{40}(\Theta,\Phi)-\frac{1}{3}\sqrt{\frac{10}{3}}[Y_{4-3}(\Theta,\Phi)-Y_{43}(\Theta,\Phi)]\}$$

$$Y_4=\frac{4\sqrt{2}}{9}Y_{60}(\Theta,\Phi)+\frac{1}{9}\sqrt{\frac{35}{3}}[Y_{6-3}(\Theta,\Phi)-Y_{63}(\Theta,\Phi)]+\frac{1}{9}\sqrt{\frac{77}{6}}[Y_{6-6}(\Theta,\Phi)+Y_{66}(\Theta,\Phi)]\}$$

$$E(t)=\beta^3e^{-t}(\frac{1}{3}\,\frac{t^6}{6!}+\sum_{n=0}^{5}\frac{t^n}{n!})$$

$$H(t)=\beta^3\{1-e^{-t}(\frac{8}{9}\,\frac{t^{11}}{11!}+\sum_{n=0}^{10}\frac{t^n}{n!})\}$$

$$J(t)=\beta^3\{1-e^{-t}(\frac{13}{11}\,\frac{t^{13}}{13!}+\sum_{n=0}^{12}\frac{t^n}{n!})\}$$

$$M(t)=\beta^3e^{-t}(-\frac{2}{13}\,\frac{t^6}{6!}+\sum_{n=0}^{5}\frac{t^n}{n!})$$

$$N(t)=\beta^3e^{-t}(\frac{4}{3}\,\frac{t^{11}}{11!})$$

with $t=2\beta R$

For the case of the free atom we may take $\underset{\sim}{R} \to O$ to find

$$\frac{\Delta B}{B} \to -\frac{\mu_0}{4\pi}\frac{2}{441}\frac{\mu_B^2}{KT}\left\{\frac{9-15\{1-\exp(3\zeta/2KT)\}KT/\zeta}{1+2\ \exp(3\zeta/2KT)}\right\} \tag{8}$$

When we have long range coupling, the term in eq.(7) may be expressed as

$$d(\underset{\sim}{R}) = -\frac{1}{R^5}\frac{540}{\beta^2}\left(\frac{\pi}{21}\right)^{\frac{1}{2}} Y_4 - \frac{1}{R^7}\ \frac{128200}{7\beta^4}\left(\frac{\pi}{26}\right)^{\frac{1}{2}} Y_6 \tag{9}$$

$$S(\underset{\sim}{R}) = -\frac{1}{R^7}\cdot\frac{118800}{7\beta^4}\left(\frac{\pi}{26}\right)^{\frac{1}{2}} Y_6$$

When the threefold axis is chosen to be our axis of quantization the calculated NMR chemical shifts along the x, y and z axes for a $4d^1$ system in a strong crystal field environment of octahedral symmetry are listed in Table 1 and 2. We also list the calculated NMR chemical shifts along the <1,1,1>, <-1,-1,-1>, <-1,1,-1>, <1,-1,1>, <1,-1,-1>, <-1,-1,1>, <1,1,-1>, and <-1,1,1> directions in Table 3 and 4, respectively.

Temperature dependence of the NMR chemical shifts. We may separate the contributions of the Fermi contact interaction and the pseudo contact interaction to the NMR chemical shift for a $4d^1$ system in a strong crystal field environment of octahedral symmetry by the temperature dependence for $\Delta B/B$ and the NMR chemical shift may be expressed as

$$\Delta B/B = A + B/T + C/T^2 \tag{10}$$

In eq.(10) the last two terms arise from the Fermi and the pseudo contact terms, respectively.

The NMR chemical shift over the temperature range from 200 to 400K from the nonmultipole results of $\Delta B/B$ given by eq.(7) may be fitted almost precisely to an expression of the form given by eq.(10) some vaules of A, B and C are given in Table 5.

Results and Discussion

To calculate the NMR chemical shift for specific R-values for a $4d^1$ system in a strong crystal environment of octahedral symmetry when the threefold axis is chosen as the quantization axis, we choose the spin orbit coupling constant, ζ as 500 cm^{-1} and β as $3.2679/a_0$, which are the appropriate values for the Zr^{3+} ion, where a_0 is the Bohr radius and the temperature T is taken as 300 K.[23]

As shown in Table 1, the NMR chemical shift, $\Delta B/B$, decreases in magnitude rapidly, as R increases. Along the <1,0,0> axis $\Delta B/B$(ppm) changes sign around R≃0.20 nm. Along the <0,1,0> and <0,0,1> axes, $\Delta B/B$(ppm), however, changes sign around 0.10 nm, the $\Delta B/B$(ppm) values being negative for small R values and positive for greater R values. However, along the <1,0,0> and <1,1,0> axes, $\Delta B/B$(ppm) is positive for all values of R while along the <0,0,1> axis, $\Delta B/B$(ppm) changes sign around R≃0.10 nm for all $3d^1$ system.[22] Along the <1,0,0>, <0,1,0> and <0,0,1> axes, a comparison of the multipolar terms with the nonmultipolar NMR chemical shift obtained from eq.(7) shows that $1/R^5$ term and $1/R^7$ term contribute almost equally to the chemical NMR shift, while for a $3d^1$ system, $1/R^7$ term contributes dominantly to the NMR chemical shift for all values of R.[22] Along the <1,1,1> axis, the NMR chemical shift, $\Delta B/B$(ppm), is negative for all values of R while along the <1,1,0> axis $\Delta B/B$(ppm)

Table 1. A Comparision of the Nonmultipole Result of $\Delta B/B$(ppm) Obtained using Equation (7) with the Multipolar Terms for Specific R-values when the Threefold Axis is Chosen to be the Axis of Quantization

1a) Along the <1,0,0> Axis ($\zeta = 500cm^{-1}$, $\beta = 3.2679/a_0$ and T = 300 K)

R(nm)	$\Delta B/B$(ppm)			
	$1/R^5$	$1/R^7$	Sum of all multipolar terms	from eq.(7)
0.05	360.137	-79.846	280.291	-1316.584
0.10	68.872	-60.194	8.678	-45.587
0.15	6.590	-9.158	-2.568	-3.181
0.20	1.389	-1.386	0.0028	-0.001
0.25	0.452	-0.293	0.1590	0.159
0.30	0.1817	-0.0818	0.0999	0.0999
0.35	0.0841	-0.0278	0.0562	0.0562
0.40	0.0431	-0.0109	0.0322	0.0322
0.45	0.0293	-0.0048	0.0191	0.0191
0.50	0.0141	-0.0023	0.0118	0.0118

1b) Along the <0,1,0> Axis ($\zeta = 500cm^{-1}$, $\beta = 3.2679/a_0$ and T = 300 K)

R(nm)	$\Delta B/B$(ppm)				
	$Y_{\infty}(\theta,\phi)$	$1/R^5$	$1/R^7$	Sum of all multipolar terms	from eq.(7)
0.05	-1596.875	135.052	18.631	153.683	-1443.192
0.10	-54.265	25.827	14.046	39.874	-14.392
0.15	-0.6129	2.471	2.713	4.608	3.995
0.20	-0.004	0.521	0.324	0.845	0.841
0.25	0	0.1696	0.0684	0.2380	0.2380
0.30	0	0.0681	0.0191	0.0872	0.0872
0.35	0	0.0315	0.0065	0.0380	0.0380
0.40	0	0.0162	0.0025	0.0187	0.0187
0.45	0	0.0090	0.0011	0.0101	0.0101
0.50	0	0.0053	0.0005	0.0058	0.0058

1c) Along the <0,0,1> Axis ($\zeta = 500cm^{-1}$, $\beta = 3.2679/a_0$ and T = 300 K)

R(nm)	$\Delta B/B$(ppm)				
	$Y_{\infty}(\theta,\phi)$	$1/R^5$	$1/R^7$	Sum of all multipolar terms	from eq.(7)
0.05	-1596.875	135.052	31.272	166.324	-1430.551
0.10	-54.265	25.827	23.576	49.403	-4.862
0.15	-0.623	2.471	3.587	6.058	5.445
0.20	-0.004	0.521	0.543	1.064	1.060
0.25	0	0.1696	0.1148	0.2855	0.2844
0.30	0	0.0681	0.0321	0.1002	0.1002
0.35	0	0.0315	0.0109	0.0424	0.0424
0.40	0	0.0162	0.0042	0.0204	0.0204
0.45	0	0.0090	0.0018	0.0108	0.0108
0.50	0	0.0053	0.0009	0.0062	0.0062

Table 2. A Comparision of the Nonmultipole Result of $\Delta B/B$(ppm) using Equation (7) with the Multipolar Terms for Specific R-Values when the Threefold Axis is Chosen as the Quantization Axis

2a) Along the <1,0,0> Axis ($\zeta = 500 cm^{-1}$, $\beta = 3.2679/a_o$ and T = 300 K)

R(nm)	$\Delta B/B$(ppm)				
	$Y_{\infty}(\theta,\phi)$	$1/R^5$	$1/R^7$	Sum of all multipolar terms	from eq.(7)
0.05	-1596.875	360.137	-79.846	280.291	-1316.584
0.10	-54.265	68.872	-60.194	8.678	-45.597
0.15	-0.6129	6.590	-9.158	-2.568	-3.181
0.20	-0.004	1.389	-1.387	0.003	-0.001
0.25	0	0.2541	-0.2931	0.1590	0.1590
0.30	0	0.1817	-0.0818	0.0999	0.0999
0.35	0	0.0841	-0.0279	0.0562	0.0562
0.40	0	0.0431	-0.0109	0.0322	0.0322
0.45	0	0.0191	0.0048	0.0191	0.0191
0.50	0	0.0141	0.0023	0.0118	0.0118

2b) Along the <1,1,0> Axis ($\zeta = 500 cm^{-1}$, $\beta = 3.2679/a_o$ and T = 300 K)

R(nm)	$\Delta B/B$(ppm)				
	$Y_{\infty}(\theta,\phi)$	$1/R^5$	$1/R^7$	Sum of all multipolar terms	from eq.(7)
0.05	-1596.875	135.052	24.951	160.003	-1436.872
0.10	-54.265	25.827	18.811	44.638	-9.627
0.15	-0.613	2.4712	2.862	5.333	4.720
0.20	-0.004	0.521	0.433	0.954	0.950
0.25	0	0.1696	0.0916	0.2612	0.2612
0.30	0	0.0681	0.0256	0.0937	0.0937
0.35	0	0.0315	0.0087	0.0402	0.0402
0.40	0	0.0162	0.0034	0.0196	0.0196
0.45	0	0.0090	0.0015	0.0105	0.0105
0.50	0	0.0053	0.0007	0.0060	0.0060

2c) Along the <1,1,1> Axis ($\zeta = 500 cm^{-1}$, $\beta = 3.2679/a_o$ and T = 300 K)

R(nm)	$\Delta B/B$(ppm)				
	$Y_{\infty}(\theta,\phi)$	$1/R^5$	$1/R^7$	Sum of all multipolar terms	from eq.(7)
0.05	-1596.875	-140.032	-17.753	-157.785	-1754.660
0.10	-54.265	-26.779	-13.384	-40.163	-94.428
0.15	-0.613	-2.562	-2.036	-4.599	-5.212
0.20	-0.040	-0.5402	-0.308	-0.813	-0.853
0.25	0	-0.1758	-0.0652	-0.2410	-0.2410
0.30	0	-0.0706	-0.0182	-0.0888	-0.0888
0.35	0	-0.0327	-0.0060	-0.0389	-0.0389
0.40	0	-0.0168	-0.0024	-0.0192	-0.0192
0.45	0	-0.0093	-0.0011	-0.0104	-0.0104
0.50	0	-0.0055	-0.0005	-0.0060	-0.0060

Table 3. A Nonmultipolar Results of $\Delta B/B$(ppm) Obtained from Equation (7) for Specific R-Values along the <1,1,1>, <-1,-1,-1>, <-1,1,-1> and <1,-1,1> Axes when the Threefold Axis is Chosen to be the Axis of Quantization

R(nm)	$\Delta B/B$(ppm)			
	<1,1,1>	<-1,-1,-1>	<-1,1,-1>	<1,-1,1>
0.05	-1754.660	-1754.660	-1754.660	-1754.660
0.10	-94.428	-94.428	-94.428	-94.428
0.15	-5.212	-5.212	-5.212	-5.212
0.20	-0.853	-0.853	-0.853	-0.853
0.25	-0.2410	-0.2410	-0.2410	-0.2410
0.30	-0.0888	-0.0888	-0.0888	-0.0888
0.35	-0.0389	-0.0389	-0.0389	-0.0389
0.40	-0.0192	-0.0192	-0.0192	-0.0192
0.45	-0.0104	-0.0104	-0.0104	-0.0104
0.50	-0.0060	-0.0060	-0.0060	-0.0060

Table 4. A Nonmultipolar Results of $\Delta B/B$(ppm) Obtained using Equation (7) for Specific R-Values along the <-1,-1,1>, <1,1,-1>, <1,-1,-1> and <-1,1,1> Axes when the Threefold Axis is Chosen to be the Axis of Quantization

R(nm)	$\Delta B/B$(ppm)			
	<-1,-1,1>	<1,1,-1>	<1,-1,-1>	<-1,1,1>
0.05	-1754.660	-1754.660	-1754.660	-1754.660
0.10	-94.428	-94.428	-94.428	-94.428
0.15	-5.212	-5.212	-5.212	-5.212
0.20	-0.8526	-0.8526	-0.8526	-0.8526
0.25	-0.2410	-0.2410	-0.2410	-0.2410
0.30	-0.0888	-0.0888	-0.0888	-0.0888
0.35	-0.0389	-0.0389	-0.0389	-0.0389
0.40	-0.0192	-0.0192	-0.0192	-0.0192
0.45	-0.0104	-0.0104	-0.0104	-0.0104
0.50	-0.0060	-0.0060	-0.0060	-0.0060

changes sign around R≃0.10 nm, $\Delta B/B$(ppm) being negative for small R values and positive for greater R values as shown Table 2. For $3d^1$ system, $\Delta B/B$(ppm) is positive for all values of R. A comparison of $\Delta B/B$(ppm) obtained from eq.(7) with multipolar results also shows that the $1/R^5$ term and $1/R^7$ term contribute almost the same magnitude to the NMR chemical shift along the <1,1,0> and <1,1,1> axes while the $1/R^7$ term contributes dominantly to $\Delta B/B$(ppm) for all values of R for a $3d^1$ system. However, for a $3d^1$ system, the $1/R^7$ term is inadequate to describe accurately the NMR chemical shift for R⩽0.50 nm, and the nonmultipolar NMR results are in agreement with the multipolar results when R⩾0.20 nm. Such the large difference between nonmultipolar and multipolar NMR chemical shift arises because the multipolar terms only include the long range coupling term[24] represented by eq.(9) and constant term represented by eq.(8) is neglected.

The multipolar results of $\Delta B/B$(ppm) obtained from eq.(7) for specific R values along the <1,1,1>, <-1,-1,-1>, <-1,1,-1> and <1,-1,1> axes are listed in Table 3 when the threefold axis is chosen as the quantization axis. $\Delta B/B$(ppm) are exactly in agreement with those along the

Table 5. The Temperature Dependence of $\Delta B/B$(ppm) at Various Values of R expressed in Terms of the Coefficients along <1,1,1>, when the Threefold Axis is Chosen to be the Axis of Quantization, $\zeta = 500 cm^{-1}$, $\beta = 3.2679/a_0$

R(nm)	A(ppm)	B(ppm·K)×10^2	C(ppm·K^2)×10^4
0.10	1439	−21900	106400
0.20	−4.553	37.36	−215.80
0.30	−0.1303	−1.567	4.460
0.40	−2.295	18.694	−8.600
0.50	0.0503	−1.044	5.3610

<−1,−1,1>, <1,1,−1>, <1,−1,−1> and <−1,1,1> axes as shown in Table 4.

As shown in Table 3 and 4, the sign of the nonmultipolar results of $\Delta B/B$(ppm) for specific R values along the <1,1,1>, <−1,−1,−1>, <−1,1,−1> and <1,−1,1> axes are exactly same as those along the <−1,−1,1>, <1,1,−1>, <1,−1,−1> and <−1,1,1> axes while the NMR chemical shift, $\Delta B/B$(ppm) along the <1,1,1>, <−1,−1,−1>, <−1,1,−1> and <1,−1,1> axes has the opposite sign for a $3d^1$ system.

The temperature dependence analysis of $\Delta B/B$(ppm) at various values of R expressed in term of A, B and C along the <1,1,1> axis over the temperature range from 200 to 400 K shows that the values of A, B and C depend markedly on the R values. We find that the major contribution to the NMR chemical shift arises from the $1/T^2$ term but the contributions of other two terms are certainly significant and the temperature dependence analysis of $\Delta B/B$(ppm) for a $4d^1$ system is not simply proportional to $1/T^2$ when the threefold axis is chosen as the quantization axis.

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Appendix A. Radial series

a) Specific formulas for $I_{\alpha N}/r_N^3$ integrals

$$t_4 = y_2 + (\frac{49}{25}x_1 + \frac{26}{25}x_3) + (\frac{14}{15}w_0 + \frac{31}{15}w_2) + v_1$$

$$t_5 = y_2 + (\frac{14}{5}x_1 + \frac{1}{5}x_3) + (\frac{7}{3}w_0 + \frac{2}{3}w_2) + v_1$$

$$t_6 = y_2 + (\frac{21}{10}x_1 + \frac{9}{10}x_3) + (\frac{7}{6}w_0 + \frac{11}{6}w_2) + v_1$$

$$t_7 = \frac{4}{5}(x_1 - x_3) + \frac{4}{3}(w_0 - w_2)$$

$$t_8 = y_2 + (\frac{7}{5}x_1 + \frac{8}{5}x_3) + 3w_2 + v_1$$

$$t_9 = y_2 + (-\frac{21}{5}x_1 + \frac{36}{5}x_3) + (-\frac{28}{3}w_0 + \frac{37}{3}w_2) + v_1$$

$$t_{10} = y_2 + (-\frac{7}{5}x_1 + \frac{22}{5}x_3) + (-\frac{14}{3}w_0 + \frac{23}{3}w_2) + v_1$$

$$t_{11} = y_2 + (\frac{42}{25}x_1 + \frac{33}{25}x_3) + (\frac{7}{15}w_0 + \frac{38}{15}w_2) + v_1$$

$$t_{12} = y_2 + (\frac{56}{25}x_1 + \frac{19}{25}x_3) + (\frac{7}{5}w_0 + \frac{8}{5}w_2) + v_1$$

Here we define the radial integrals as[21]

$$R_N^{(L)}(t) = 4\beta^{*}(-R)^L \int_0^\infty r_N^{5-L-2} h_n(\underset{\sim}{R}, \underset{\sim}{r}_N) dr_N$$

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

$$u_n(t) = R_n^{(4)}(t)$$
$$v_n(t) = R_n^{(3)}(t)$$
$$w_n(t) = R_n^{(2)}(t)$$
$$x_n(t) = R_n^{(1)}(t)$$
$$y_n(t) = R_n^{(0)}(t)$$

b) Specific formulas for dipolar integrals

$$T_{10} = y_2 + (\frac{14}{5}x_1 + \frac{6}{5}x_3) + (\frac{7}{3}w_0 + \frac{68}{21}w_2 + \frac{3}{7}w_4) + (\frac{14}{5}v_1 + \frac{6}{5}v_3) + u_2$$

$$T_{11}=y_2+(\frac{18}{5}x_1+\frac{2}{5}x_3)+(\frac{21}{5}w_0+\frac{12}{7}w_2+\frac{3}{35}w_4)+(\frac{18}{5}v_1+\frac{2}{5}v_3)+u_2$$

$$T_{12}=y_2+(\frac{16}{5}x_1+\frac{4}{5}x_3)+(\frac{49}{15}w_0+\frac{52}{21}w_2+\frac{9}{35}w_4)+(\frac{16}{5}v_1+\frac{4}{5}v_3)+u_2$$

$$T_{13}=y_2+(\frac{12}{5}x_1+\frac{8}{5}x_3)+(\frac{7}{5}w_0+4w_2+\frac{3}{5}w_4)+(\frac{12}{5}v_1+\frac{8}{5}v_3)+u_2$$

$$T_{14}=y_2+(\frac{8}{5}x_1+\frac{12}{5}x_3)+(\frac{7}{30}w_0+\frac{95}{21}w_2+\frac{87}{70}w_4)+(\frac{8}{5}v_1+\frac{12}{5}v_3)+u_2$$

$$T_{15}=y_2+(\frac{13}{5}x_1+\frac{7}{5}x_3)+(\frac{28}{15}w_0+\frac{76}{21}w_2+\frac{13}{35}w_4)+(\frac{13}{5}v_1+\frac{7}{5}v_3)+u_2$$

$$T_{16}=\frac{2}{35}\{(x_1-x_3)+\frac{10}{7}(w_2-w_4)+(v_1-v_3)\}$$

$$T_{17}=y_2+(\frac{17}{5}x_1+\frac{3}{5}x_3)+(\frac{56}{15}w_0+\frac{44}{21}w_2+\frac{6}{35}w_4)+(\frac{17}{5}v_1+\frac{3}{5}v_3)+u_2$$

$$F_{23}=y_4+(\frac{253}{72}x_3+\frac{35}{72}x_5)+(\frac{121}{28}w_2+\frac{47}{28}w_4)+(\frac{77}{40}v_1+\frac{83}{40}v_3)+u_2$$

$$F_{24}=y_4(\frac{242}{75}x_3+\frac{58}{75}x_5)+(\frac{627}{175}w_2+\frac{423}{175}w_4)+(\frac{176}{125}v_1+\frac{324}{125}v_3)+u_2$$

$$F_{25}=y_4+(\frac{682}{183}x_3+\frac{50}{183}x_5)+(\frac{297}{61}w_2+\frac{69}{61}w_4)+(\frac{704}{305}v_1+\frac{516}{305}v_3)+u_2$$

$$F_{26}=y_4+(\frac{286}{93}x_3+\frac{86}{93}x_5)+(\frac{99}{31}w_2+\frac{87}{31}w_4)+(\frac{176}{155}v_1+\frac{444}{155}v_3)+u_2$$

$$F_{27}=y_4+4x_3+(\frac{39}{7}w_2+\frac{3}{7}w_4)+(\frac{14}{5}v_1+\frac{6}{5}v_3)+u_2$$

$$F_{28}=y_4+(\frac{22}{15}x_3+\frac{38}{15}x_5)+(-\frac{33}{35}w_2+\frac{243}{35}w_4)+(-\frac{44}{25}v_1+\frac{144}{25}v_3)+u_2$$

$$F_{29}=y_4+(\frac{154}{57}x_3+\frac{74}{57}x_5)+(\frac{297}{133}w_2+\frac{501}{133}w_4)+(\frac{44}{95}v_1+\frac{336}{95}v_3)+u_2$$

$$F_{30}=y_4+(\frac{209}{63}x_3+\frac{43}{63}x_5)+(\frac{187}{49}w_2+\frac{107}{49}w_4)+(\frac{11}{7}v_1+\frac{17}{7}v_3)+u_2$$

$$F_{31}=y_4+(\frac{11}{9}x_3+\frac{25}{9}x_5)+(-\frac{11}{7}w_2+\frac{53}{7}w_4)+(-\frac{11}{5}v_1+\frac{31}{5}v_3)+u_2$$

Appendix B. The hyperfine integrals

a) The integrals of $\langle \Psi_i | l_{N\alpha}/r_N^3 | \Psi_j \rangle$

$$i\langle 4dx^2-y^2 | l_{Nx}/r_N^3 | 4dxy\rangle$$

$$=\frac{4\sqrt{\pi}}{315}n_1 Y_{00}(\Theta,\Phi)-\frac{8}{441}\sqrt{\frac{\pi}{5}}Y_{20}(\Theta,\Phi)\,t_4+\frac{4\sqrt{\pi}}{2205}Y_{40}(\Theta,\Phi)\,f_1$$

$$i\langle 4dx^2-y^2 | l_{Nz}/r_N^3 | 4dyz\rangle$$

$$=\frac{3}{294}\sqrt{\frac{2\pi}{15}}[Y_{2-1}(\Theta,\Phi)-Y_{21}(\Theta,\Phi)]t_2-\frac{1}{588}\sqrt{\frac{\pi}{5}}[Y_{4-1}(\Theta,\Phi)$$

$$-Y_{41}(\Theta,\Phi))$$

$$f_1-\frac{1}{126}\sqrt{\frac{\pi}{35}}[Y_{4-3}(\Theta,\Phi)-Y_{43}(\Theta,\Phi)]f_1$$

$$i\langle 4dxy | l_{Nz}/r_N^3 | 4dxz\rangle$$

$$=-\frac{3}{294}\sqrt{\frac{2\pi}{15}}[Y_{2-1}(\Theta,\Phi)-Y_{2-1}(\Theta,\Phi)]t_2+\frac{1}{588}\sqrt{\frac{\pi}{5}}[Y_{4-1}(\Theta,\Phi)-$$

$$Y_{41}(\Theta,\Phi)]f_1-\frac{1}{126}\sqrt{\frac{\pi}{35}}[Y_{4-3}(\Theta,\Phi)-Y_{43}(\Theta,\Phi)]f_1$$

$$i\langle 4dx^2-y^2 | l_{Nx}/r_N^3 | 4dyz\rangle$$

$$=-\frac{2\sqrt{\pi}}{315}Y_{00}(\Theta,\Phi)n_1+\frac{1}{441}\sqrt{\frac{\pi}{5}}Y_{20}(\Theta,\Phi)t_1+\frac{1}{98}\sqrt{\frac{2\pi}{15}}[Y_{2-2}$$

$$+Y_{22}(\Theta,\Phi)]t_2+\frac{\sqrt{\pi}}{735}Y_{40}(\Theta,\Phi)f_1-\frac{1}{441}\sqrt{\frac{\pi}{10}}[Y_{4-2}(\Theta,\Phi)$$

$$+Y_{42}(\Theta,\Phi)]f_1-\frac{1}{126}\sqrt{\frac{2\pi}{35}}[Y_{4-4}(\Theta,\Phi)+Y_{44}(\Theta,\Phi)]f_1$$

$$i\langle 4dxy | l_{Nx}/r_N^3 | 4dz^2\rangle$$

$$=\frac{2}{441}\sqrt{\frac{2\pi}{5}}[Y_{2-1}(\Theta,\Phi)-Y_{21}(\Theta,\Phi)]t_5+\frac{1}{294}\sqrt{\frac{2\pi}{15}}[Y_{4-1}(\Theta,\Phi)$$

$$-Y_{41}(\Theta,\Phi)]f_1-\frac{1}{42}\sqrt{\frac{\pi}{105}}[Y_{4-3}(\Theta,\Phi)-Y_{43}(\Theta,\Phi)]f_1$$

$$i\langle 4dyz | l_{Nx}/r_N^3 | 4dz^2\rangle$$

$$=\frac{2}{105}\sqrt{\frac{\pi}{3}}Y_{00}(\Theta,\Phi)n_1+\frac{3}{147}\sqrt{\frac{\pi}{15}}Y_{20}(\Theta,\Phi)t_2-\frac{5}{294}\sqrt{\frac{2\pi}{45}}[Y_{2-2}(\Theta,\Phi)$$

$$+Y_{22})]t_3+\frac{2}{735}\sqrt{\frac{\pi}{3}}Y_{40}(\Theta,\Phi)f_1-\frac{1}{147}\sqrt{\frac{\pi}{30}}[Y_{4-2}(\Theta,\Phi)$$

$$+Y_{42}(\Theta,\Phi)]f_1$$

$$i\langle 4dx^2-y^2 | l_{Ny}/r_N^3 | 4dz^2\rangle$$

$$=-\frac{2}{441}\sqrt{\frac{2\pi}{5}}[Y_{2-1}(\Theta,\Phi)-Y_{21}(\Theta,\Phi)]t_5-\frac{1}{294}\sqrt{\frac{2\pi}{15}}[Y_{4-1}(\Theta,\Phi)$$

$$-Y_{41}(\Theta,\Phi)]f_1-\frac{1}{42}\sqrt{\frac{\pi}{105}}[Y_{4-3}(\Theta,\Phi)-Y_{43}(\Theta,\Phi)]f_1$$

$$i\langle 4dx^2-y^2 | l_{Ny}/r_N^3 | 4dxz\rangle$$

$$=-\frac{2}{315}\sqrt{\frac{\pi}{3}}Y_{00}(\Theta,\Phi)n_1+\frac{1}{441}\sqrt{\frac{\pi}{15}}Y_{20}(\Theta,\Phi)t_1-\frac{3}{294}\sqrt{\frac{2\pi}{45}}$$

$$[Y_{2-2}(\Theta,\Phi)+Y_{22}(\Theta,\Phi)]t_2+\frac{1}{735}\sqrt{\frac{\pi}{3}}Y_{40}(\Theta,\Phi)f_1+\frac{1}{441}\sqrt{\frac{\pi}{30}}$$

$$[Y_{4-2}(\Theta,\Phi)+Y_{42}(\Theta,\Phi)]f_1-\frac{1}{126}\sqrt{\frac{2\pi}{105}}[Y_{4-4}(\Theta,\Phi)+Y_{44}(\Theta,\Phi)]f_1$$

$$i\langle 4dxz | l_{Ny}/r_N^3 | 4dz^2\rangle$$

$$=-\frac{2}{105}\sqrt{\frac{\pi}{3}}Y_{00}(\Theta,\Phi)n_1-\frac{3}{147}\sqrt{\frac{\pi}{15}}Y_{20}(\Theta,\Phi)t_2-\frac{5}{294}\sqrt{\frac{2\pi}{45}}$$

$$[Y_{2-2}(\Theta,\Phi)+Y_{22}(\Theta,\Phi)]t_3-\frac{2}{735}\sqrt{\frac{\pi}{3}}Y_{40}(\Theta,\Phi)f_1$$

$$-\frac{1}{147}\sqrt{\frac{\pi}{30}}Y_{4-2}(\Theta,\Phi)+Y_{42}(\Theta,\Phi)f_1$$

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

$$\langle 4d_{yz} | T_{xz} | 4d_{xy}\rangle$$

$$=\frac{2\sqrt{\pi}}{735}Y_{00}(\Theta,\Phi)N_1-\frac{2}{735}\sqrt{\frac{\pi}{5}}Y_{20}(\Theta,\Phi)T_3-\frac{1}{245}\sqrt{\frac{2\pi}{15}}[Y_{2-2}(\Theta,\Phi)$$

$$+Y_{22}(\Theta,\Phi)]T_3-\frac{2\sqrt{\pi}}{1155}Y_{40}(\Theta,\Phi)F_{10}-\frac{4}{147}\sqrt{\frac{\pi}{10}}[Y_{4-2}(\Theta,\Phi)$$

$$+Y_{42}(\Theta,\Phi)]F_{11}-\frac{1}{231}\sqrt{\frac{2\pi}{35}}[Y_{4-4}(\Theta,\Phi)+Y_{44}(\Theta,\Phi)]F_6+\frac{4}{1617}\sqrt{\frac{\pi}{13}}$$

$$Y_{60}(\Theta,\Phi)S_1-\frac{2}{231}\sqrt{\frac{2\pi}{91}}[Y_{6-4}(\Theta,\Phi)+Y_{64}(\Theta,\Phi)]S_1$$

$$\langle 4d_{z^2}|T_{xx}|4d_{z^2}\rangle$$
$$=-\frac{4\sqrt{\pi}}{2205}Y_{00}(\Theta,\Phi)N_1-\frac{2}{147}\sqrt{\frac{\pi}{5}}Y_{20}(\Theta,\Phi)T_8+\frac{1}{147}\sqrt{\frac{2\pi}{15}}[Y_{2-2}(\Theta,\Phi)$$
$$+Y_{22}(\Theta,\Phi)]T_1-\frac{8\sqrt{\pi}}{2695}Y_{40}(\Theta,\Phi)F_{19}-\frac{4}{1617}\sqrt{\frac{\pi}{10}}[Y_{4-2}(\Theta,\Phi)$$
$$-Y_{42}(\Theta,\Phi)]F_{22}-\frac{4}{539}\sqrt{\frac{\pi}{13}}Y_{60}(\Theta,\Phi)S_1+\frac{4}{77}\sqrt{\frac{\pi}{1365}}[Y_{6-2}(\Theta,\Phi)$$
$$+Y_{62}(\Theta,\Phi)]S_1$$

$$\langle 4d_{z^2}|T_{yy}|4d_{z^2}\rangle$$
$$=-\frac{4\sqrt{\pi}}{2205}Y_{00}(\Theta,\Phi)N_1-\frac{2}{147}\sqrt{\frac{\pi}{5}}Y_{20}(\Theta,\Phi)T_8-\frac{1}{147}\sqrt{\frac{2\pi}{15}}[Y_{2-2}(\Theta,\Phi)$$
$$+Y_{22}(\Theta,\Phi)]T_1-\frac{8\sqrt{\pi}}{2695}Y_{40}(\Theta,\Phi)F_{19}+\frac{4}{1617}\sqrt{\frac{\pi}{10}}[Y_{4-2}(\Theta,\Phi)+$$
$$+Y_{42}(\Theta,\Phi)]F_{22}-\frac{4}{539}\sqrt{\frac{\pi}{13}}Y_{60}(\Theta,\Phi)S_1-\frac{4}{77}\sqrt{\frac{\pi}{1365}}[Y_{6-2}(\Theta,\Phi)$$
$$-Y_{62}(\Theta,\Phi)]S_1$$

$$\langle 4d_{x^2-y^2}|T_{zz}|4d_{x^2-y^2}\rangle$$
$$=-\frac{8\sqrt{\pi}}{2205}Y_{00}(\Theta,\Phi)N_1+\frac{4}{441}\sqrt{\frac{\pi}{5}}Y_{20}(\Theta,\Phi)T_1-\frac{64\sqrt{\pi}}{24255}Y_{40}(\Theta,\Phi)F_9$$
$$-\frac{8}{693}\sqrt{\frac{2\pi}{35}}[Y_{4-4}(\Theta,\Phi)+Y_{44}(\Theta,\Phi)]F_9+\frac{4}{1617}\sqrt{\frac{\pi}{13}}Y_{60}(\Theta,\Phi)S_1$$
$$+\frac{2}{231}\sqrt{\frac{2\pi}{91}}[Y_{6-4}(\Theta,\Phi)+Y_{64}(\Theta,\Phi)]S_1$$

$$\langle 4d_{x^2-y^2}|T_{xx}|4d_{x^2-y^2}\rangle$$
$$=\frac{4\sqrt{\pi}}{2205}Y_{00}(\Theta,\Phi)N_1-\frac{2}{441}\sqrt{\frac{\pi}{5}}Y_{20}(\Theta,\Phi)T_1+\frac{1}{49}\sqrt{\frac{2\pi}{15}}[Y_{2-2}(\Theta,\Phi)$$
$$+Y_{22}(\Theta,\Phi)]T_8+\frac{32\sqrt{\pi}}{24255}Y_{40}(\Theta,\Phi)F_9-\frac{4}{539}\sqrt{\frac{\pi}{10}}[Y_{4-2}(\Theta,\Phi)$$
$$+Y_{42}(\Theta,\Phi)]F_{19}+\frac{4}{693}\sqrt{\frac{2\pi}{35}}[Y_{4-4}(\Theta,\Phi)+Y_{44}(\Theta,\Phi)]F_8-\frac{2}{1617}\sqrt{\frac{\pi}{13}}$$
$$Y_{60}(\Theta,\Phi)S_1+\frac{1}{77}\sqrt{\frac{\pi}{1365}}[Y_{6-2}(\Theta,\Phi)+Y_{62}(\Theta,\Phi)]S_1-\frac{1}{231}\sqrt{\frac{2\pi}{91}}$$
$$[Y_{6-4}(\Theta,\Phi)+Y_{64}(\Theta,\Phi)]S_1+\frac{1}{7}\sqrt{\frac{\pi}{3003}}[Y_{6-6}(\Theta,\Phi)+Y_{66}(\Theta,\Phi)]S_1$$

$$\langle 4d_{x^2-y^2}|T_{yy}|4d_{x^2-y^2}\rangle$$
$$=\frac{4\sqrt{\pi}}{2205}Y_{00}(\Theta,\Phi)N_1-\frac{2}{441}\sqrt{\frac{\pi}{5}}Y_{20}(\Theta,\Phi)T_1-\frac{1}{49}\sqrt{\frac{2\pi}{15}}[Y_{2-2}(\Theta,\Phi)$$
$$+Y_{22}(\Theta,\Phi)]T_8+\frac{32\sqrt{\pi}}{24255}Y_{40}(\Theta,\Phi)F_9+\frac{4}{593}\sqrt{\frac{\pi}{10}}[Y_{4-2}(\Theta,\Phi)$$
$$+Y_{42}(\Theta,\Phi)]F_{19}+\frac{4}{693}\sqrt{\frac{2\pi}{35}}[Y_{4-4}(\Theta,\Phi)+Y_{44}(\Theta,\Phi)]F_8-\frac{2}{1617}\sqrt{\frac{\pi}{13}}$$
$$Y_{60}(\Theta,\Phi)S_1-\frac{1}{77}\sqrt{\frac{\pi}{1365}}[Y_{6-2}(\Theta,\Phi)+Y_{62}(\Theta,\Phi)]S_1-\frac{1}{231}\sqrt{\frac{2\pi}{91}}$$
$$[Y_{6-4}(\Theta,\Phi)+Y_{64}(\Theta,\Phi)]S_1-\frac{1}{7}\sqrt{\frac{\pi}{3003}}[Y_{6-6}(\Theta,\Phi)+Y_{66}(\Theta,\Phi)]S_1$$

$$\langle 4d_{z^2}|T_{zz}|4d_{z^2}\rangle$$
$$=\frac{8\sqrt{\pi}}{2205}Y_{00}(\Theta,\Phi)N_1+\frac{4}{147}\sqrt{\frac{\pi}{5}}Y_{20}(\Theta,\Phi)T_8+\frac{16\sqrt{\pi}}{2695}Y_{40}(\Theta,\Phi)F_{19}$$
$$+\frac{8}{539}\sqrt{\frac{\pi}{13}}Y_{60}(\Theta,\Phi)S_1$$

$$\langle 4d_{z^2}|T_{xx}|4d_{x^2-y^2}\rangle$$
$$=-\frac{4}{735}\sqrt{\frac{\pi}{3}}Y_{00}(\Theta,\Phi)N_1+\frac{2}{147}\sqrt{\frac{\pi}{15}}Y_{20}(\Theta,\Phi)T_{10}-\frac{1}{441}\sqrt{\frac{2\pi}{5}}[Y_{2-2}(\Theta,\Phi)$$
$$+Y_{22}(\Theta,\Phi)]T_{10}-\frac{32}{8085}\sqrt{\frac{\pi}{3}}Y_{40}(\Theta,\Phi)F_{23}+\frac{4}{1617}\sqrt{\frac{\pi}{30}}[Y_{4-2}(\Theta,\Phi)$$
$$+Y_{42}(\Theta,\Phi)]F_3-\frac{4}{231}\sqrt{\frac{2\pi}{105}}[Y_{4-4}(\Theta,\Phi)+Y_{44}(\Theta,\Phi)]F_{15}+\frac{2}{539}\sqrt{\frac{\pi}{39}}$$
$$Y_{60}(\Theta,\Phi)S_1-\frac{4}{231}\sqrt{\frac{\pi}{455}}[Y_{6-2}(\Theta,\Phi)+Y_{62}(\Theta,\Phi)]S_1$$
$$+\frac{1}{77}\sqrt{\frac{2\pi}{273}}[Y_{6-4}(\Theta,\Phi)+Y_{64}(\Theta,\Phi)]S_1$$

$$\langle 4d_{z^2}|T_{yy}|4d_{x^2-y^2}\rangle$$
$$=\frac{4}{735}\sqrt{\frac{\pi}{3}}Y_{00}(\Theta,\Phi)N_1-\frac{2}{147}\sqrt{\frac{\pi}{15}}Y_{20}(\Theta,\Phi)T_{10}-\frac{1}{441}\sqrt{\frac{2\pi}{5}}[Y_{2-2}(\Theta,\Phi)$$
$$+Y_{22}(\Theta,\Phi)]T_{10}+\frac{32}{8085}\sqrt{\frac{\pi}{3}}Y_{40}(\Theta,\Phi)F_{23}+\frac{4}{1617}\sqrt{\frac{\pi}{30}}[Y_{4-2}(\Theta,\Phi)$$
$$+Y_{42}(\Theta,\Phi)]F_3+\frac{4}{231}\sqrt{\frac{2\pi}{105}}[Y_{4-4}(\Theta,\Phi)+Y_{44}(\Theta,\Phi)]F_{15}-\frac{2}{539}\sqrt{\frac{\pi}{39}}$$
$$Y_{60}(\Theta,\Phi)S_1-\frac{4}{231}\sqrt{\frac{\pi}{455}}[Y_{6-2}(\Theta,\Phi)+Y_{62}(\Theta,\Phi)]S_1-\frac{1}{77}\sqrt{\frac{2\pi}{273}}$$
$$[Y_{6-4}(\Theta,\Phi)+Y_{64}(\Theta,\Phi)]S_1$$

$$\langle 4d_{xy}|T_{xy}|4d_{z^2}\rangle$$
$$=\frac{4}{735}\sqrt{\frac{\pi}{3}}Y_{00}(\Theta,\Phi)N_1+\frac{2}{147}\sqrt{\frac{\pi}{15}}Y_{20}(\Theta,\Phi)T_{10}-\frac{32}{8085}\sqrt{\frac{\pi}{3}}Y_{40}(\Theta,\Phi)F_{23}$$
$$+\frac{4}{231}\sqrt{\frac{2\pi}{105}}[Y_{4-4}(\Theta,\Phi)+Y_{44}(\Theta,\Phi)]F_{15}+\frac{2}{539}\sqrt{\frac{\pi}{39}}Y_{60}(\Theta,\Phi)S_1$$
$$-\frac{1}{77}\sqrt{\frac{2\pi}{273}}[Y_{6-4}(\Theta,\Phi)+Y_{64}(\Theta,\Phi)]S_1$$

$$\langle 4d_{yz}|T_{yz}|4d_{x^2-y^2}\rangle$$
$$=-\frac{2\sqrt{\pi}}{735}Y_{00}(\Theta,\Phi)N_1-\frac{2}{735}\sqrt{\frac{\pi}{5}}Y_{20}(\Theta,\Phi)T_3+\frac{1}{147}\sqrt{\frac{2\pi}{15}}[Y_{2-2}(\Theta,\Phi)$$
$$+Y_{22}(\Theta,\Phi)]T_9+\frac{2\sqrt{\pi}}{1155}Y_{40}(\Theta,\Phi)F_{19}+\frac{10}{1617}\sqrt{\frac{\pi}{10}}[Y_{4-2}(\Theta,\Phi)$$
$$+Y_{42}(\Theta,\Phi)]F_{13}-\frac{2}{462}\sqrt{\frac{2\pi}{35}}[Y_{6-4}(\Theta,\Phi)+Y_{64}(\Theta,\Phi)]F_8-\frac{4}{1617}\sqrt{\frac{\pi}{13}}$$
$$Y_{60}(\Theta,\Phi)S_1-\frac{8}{231}\sqrt{\frac{\pi}{1365}}[Y_{6-2}(\Theta,\Phi)+Y_{62}(\Theta,\Phi)]S_1-\frac{2}{231}\sqrt{\frac{2\pi}{91}}$$
$$[Y_{6-4}(\Theta,\Phi)+Y_{64}(\Theta,\Phi)]S_1$$

$$\langle 4d_{x^2-y^2}|T_{xx}|4d_{xz}\rangle$$
$$=\frac{1}{147}\sqrt{\frac{2\pi}{15}}[Y_{2-1}(\Theta,\Phi)-Y_{21}(\Theta,\Phi)]T_{12}-\frac{25}{4851}\sqrt{\frac{\pi}{5}}[Y_{4-1}(\Theta,\Phi)$$
$$-Y_{41}(\Theta,\Phi)]F_{24}+\frac{1}{99}\sqrt{\frac{\pi}{35}}[Y_{4-3}(\Theta,\Phi)-Y_{43}(\Theta,\Phi)]F_5+\frac{2}{231}\sqrt{\frac{\pi}{273}}$$
$$[Y_{6-1}(\Theta,\Phi)-Y_{61}(\Theta,\Phi)]S_1-\frac{3}{77}\sqrt{\frac{\pi}{1365}}[Y_{6-3}(\Theta,\Phi)-Y_{63}(\Theta,\Phi)]S_1$$
$$+\frac{1}{21}\sqrt{\frac{\pi}{1001}}[Y_{6-5}(\Theta,\Phi)-Y_{65}(\Theta,\Phi)]S_1$$

$$\langle 4d_{xy}|T_{xy}|4d_{x^2-y^2}\rangle$$

$$=\frac{1}{147}\sqrt{\frac{2\pi}{15}}[Y_{2-2}(\theta,\Phi)+Y_{22}(\theta,\Phi)]T_{11}-\frac{4}{1617}\sqrt{\frac{\pi}{10}}[Y_{4-2}(\theta,\Phi)+Y_{42}(\theta,\Phi)]F_{8}+\frac{1}{231}\sqrt{\frac{\pi}{1365}}[Y_{6-2}(\theta,\Phi)+Y_{62}(\theta,\Phi)]S_1-\frac{1}{7}\sqrt{\frac{\pi}{3003}}[Y_{6-6}(\theta,\Phi)+Y_{66}(\theta,\Phi)]S_1$$

$$\langle 4d_{x^2-y^2}|T_{yy}|4d_{xz}\rangle$$

$$=-\frac{1}{147}\sqrt{\frac{2\pi}{15}}[Y_{2-1}(\theta,\Phi)-Y_{21}(\theta,\Phi)]T_{10}+\frac{1}{441}\sqrt{\frac{\pi}{5}}[Y_{4-1}(\theta,\Phi)-Y_{41}(\theta,\Phi)]F_{27}-\frac{5}{693}\sqrt{\frac{\pi}{35}}[Y_{4-3}(\theta,\Phi)-Y_{43}(\theta,\Phi)]F_{18}-\frac{1}{77}\sqrt{\frac{\pi}{1365}}[Y_{6-3}(\theta,\Phi)-Y_{63}(\theta,\Phi)]S_1-\frac{1}{21}\sqrt{\frac{\pi}{1001}}[Y_{6-5}(\theta,\Phi)-Y_{65}(\theta,\Phi)]S_1$$

$$\langle 4dx^2-y^2|Tzz|4dxz\rangle$$

$$=-\frac{2}{735}\sqrt{\frac{2\pi}{15}}[Y_{2-1}(\theta,\Phi)-Y_{21}(\theta,\Phi)]T_3+\frac{2}{693}\sqrt{\frac{\pi}{5}}[Y_{4-1}(\theta,\Phi)-Y_{41}(\theta,\Phi)]F_{16}-\frac{2}{693}\sqrt{\frac{\pi}{35}}[Y_{4-3}(\theta,\Phi)-Y_{43}(\theta,\Phi)]F_8-\frac{2}{231}\sqrt{\frac{2\pi}{273}}[Y_{6-1}(\theta,\Phi)-Y_{61}(\theta,\Phi)]S_1+\frac{4}{77}\sqrt{\frac{\pi}{1365}}[Y_{6-3}(\theta,\Phi)-Y_{63}(\theta,\Phi)]S_1$$

$$\langle 4dx^2-y^2|Txz|4dxz\rangle$$

$$=\frac{2\sqrt{\pi}}{735}Y_{00}(\theta,\Phi)N_1+\frac{2}{735}\sqrt{\frac{\pi}{5}}Y_{20}(\theta,\Phi)T_3+\frac{1}{147}\sqrt{\frac{2\pi}{15}}[Y_{2-2}(\theta,\Phi)+Y_{22}(\theta,\Phi)]F_{13}-\frac{2\sqrt{\pi}}{1155}Y_{40}(\theta,\Phi)F_{16}+\frac{10}{1617}\sqrt{\frac{\pi}{10}}[Y_{4-2}(\theta,\Phi)+Y_{42}(\theta,\Phi)]F_{13}+\frac{1}{231}\sqrt{\frac{2\pi}{35}}[Y_{4-4}(\theta,\Phi)+Y_{44}(\theta,\Phi)]F_8+\frac{4}{1617}\sqrt{\frac{\pi}{13}}Y_{40}(\theta,\Phi)S_1-\frac{8}{231}\sqrt{\frac{\pi}{1365}}[Y_{6-2}(\theta,\Phi)]+Y_{62}(\theta,\Phi)]S_1+\frac{2}{231}\sqrt{\frac{2\pi}{91}}[Y_{4-4}(\theta,\Phi)+Y_{44}(\theta,\Phi)]S_1$$

$$\langle 4dz^2|Tyz|4dxy\rangle$$

$$=\frac{2}{735}\sqrt{\frac{2\pi}{5}}[Y_{2-1}(\theta,\Phi)-Y_{21}(\theta,\Phi)]T_3+\frac{11}{231}\sqrt{\frac{\pi}{15}}[Y_{4-1}(\theta,\Phi)-Y_{41}(\theta,\Phi)]F_{30}+\frac{1}{231}\sqrt{\frac{\pi}{105}}[Y_{4-3}(\theta,\Phi)-Y_{43}(\theta,\Phi)]F_{31}-\frac{1}{231}\sqrt{\frac{2\pi}{91}}[Y_{6-1}(\theta,\Phi)-Y_{61}(\theta,\Phi)]S_1-\frac{2}{77}\sqrt{\frac{\pi}{455}}[Y_{6-3}(\theta,\Phi)-Y_{63}(\theta,\Phi)]S_1$$

$$\langle 4dx^2-y^2|T_{xy}|4dyz\rangle$$

$$=\frac{1}{245}\sqrt{\frac{2\pi}{15}}[Y_{2-1}(\theta,\Phi)-Y_{21}(\theta,\Phi)]T_3-\frac{1}{1323}\sqrt{\frac{2\pi}{5}}[Y_{4-1}(\theta,\phi)-Y_{41}(\theta,\Phi)]T_{16}+\frac{2}{231}\sqrt{\frac{\pi}{35}}[Y_{4-3}(\theta,\Phi)-Y_{43}(\theta,\Phi)]F_{15}-\frac{1}{77}\sqrt{\frac{\pi}{1365}}[Y_{6-3}(\theta,\Phi)-Y_{63}(\theta,\Phi)]S_1-\frac{1}{21}\sqrt{\frac{\pi}{1001}}[Y_{6-5}(\theta,\Phi)-Y_{65}(\theta,\Phi)]S_1$$

$$\langle 4dz^2|Txz|4dxz\rangle$$

$$=\frac{2}{735}\sqrt{\frac{\pi}{3}}Y_{00}(\theta,\Phi)N_1+\frac{2}{147}\sqrt{\frac{\pi}{15}}Y_{20}(\theta,\Phi)T_{17}-\frac{1}{735}\sqrt{\frac{2\pi}{5}}[Y_{2-2}(\theta,\Phi)+Y_{22}(\theta,\phi)]T_3-\frac{4}{8085}\sqrt{\frac{\pi}{3}}Y_{40}(\theta,\Phi)F_{31}+\frac{2}{231}\sqrt{\frac{\pi}{30}}[Y_{4-2}(\theta,\Phi)+Y_{42}(\theta,\Phi)]F_{30}-\frac{8}{539}\sqrt{\frac{\pi}{39}}Y_{60}(\theta,\Phi)S_1+\frac{8}{231}\sqrt{\frac{\pi}{455}}[Y_{6-2}(\theta,\Phi)+Y_{62}(\theta,\Phi)]S_1$$

$$\langle 4dyz|Tyz|4dz^2\rangle$$

$$=\frac{2}{735}\sqrt{\frac{\pi}{3}}Y_{00}(\theta,\Phi)N_1+\frac{2}{147}\sqrt{\frac{\pi}{15}}Y_{20}(\theta,\Phi)T_{17}-\frac{1}{735}\sqrt{\frac{2\pi}{5}}[Y_{2-2}(\theta,\Phi)+Y_{22}(\theta,\Phi)]T_3-\frac{4}{8085}\sqrt{\frac{\pi}{3}}Y_{40}(\theta,\Phi)F_{31}-\frac{2}{231}\sqrt{\frac{\pi}{30}}[Y_{4-2}(\theta,\Phi)+Y_{42}(\theta,\Phi)]F_{30}-\frac{8}{539}\sqrt{\frac{\pi}{39}}Y_{60}(\theta,\Phi)S_1-\frac{8}{231}\sqrt{\frac{\pi}{455}}[Y_{6-2}(\theta,\Phi)+Y_{62}(\theta,\Phi)]S_1$$

$$\langle 4dxy|Txy|4dx^2-y^2\rangle$$

$$=-\frac{1}{147}\sqrt{\frac{2\pi}{15}}[Y_{2-2}(\theta,\Phi)+Y_{22}(\theta,\Phi)]T_{11}-\frac{4}{1617}\sqrt{\frac{\pi}{10}}[Y_{4-2}(\theta,\Phi)+Y_{42}(\theta,\Phi)]F_8+\frac{1}{231}\sqrt{\frac{\pi}{1365}}[Y_{6-2}(\theta,\Phi)+Y_{62}(\theta,\Phi)]S_1-\frac{1}{7}\sqrt{\frac{\pi}{3003}}[Y_{6-6}(\theta,\Phi)+Y_{66}(\theta,\Phi)]S_1$$

$$\langle 4dx^2-y^2|Txz|4dz^2\rangle$$

$$=\frac{2}{735}\sqrt{\frac{2\pi}{5}}[Y_{2-1}(\theta,\Phi)-Y_{21}(\theta,\Phi)]T_{16}+\frac{1}{231}\sqrt{\frac{\pi}{15}}[Y_{4-1}(\theta,\Phi)-Y_{41}(\theta,\Phi)]F_{30}-\frac{1}{231}\sqrt{\frac{\pi}{105}}[Y_{4-3}(\theta,\Phi)-Y_{43}(\theta,\Phi)]F_{31}-\frac{1}{231}\sqrt{\frac{2\pi}{91}}[Y_{6-1}(\theta,\Phi)-Y_{61}(\theta,\Phi)]S_1+\frac{2}{77}\sqrt{\frac{\pi}{455}}[Y_{6-3}(\theta,\Phi)-Y_{63}(\theta,\Phi)]S_1$$