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Calculation of the NMR Chemical Shift for a 3d² System in a Strong Crystal Field of Octahedral Symmetry

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The NMR chemical shift arising from 3d electron spin dipolar nuclear spin angular momentum interactions for a 3d² system in a strong crystal field environment of octahedral symmetry has been investigated when the fourfold axis is chosen to be our axis of quantization. The NMR shift is separated into the contribution of $1/R^5$ and $1/R^7$ terms. A comparision of the multipolar terms with nonmultipolar results shows that the $1/R^6$ term contributes dominantly to the NMR shift and there is in good agreement between the exact solution and the multipolar results when $R \geqslant 0.25$. A temperature dependence analysis may lead to the results that the $1/T^2$ term has the dominant contribution to the NMR shift for a paramagnetic 3d² system but the contribution of the $1/T$ term may not be negligible.

1. Introduction

Since our interest is centered on the NMR chemical shift arising from the electron angular momentum and the electron spin diploar-nuclear spin angular momentum interactions for a 3d² system in a strong crystal field environment of octahedral symmetry, it is necessary to examine the NMR chemical shift in a 3d² paramagnetic system. The effects of paramagnetism on the characteristics of nuclear magnetic resonances have been investigated by the various methods.[1-3] The NMR shift in a $3d^n$ and a $4f^n$ systems has been interpreted as arising through the Fermic contact interaction between the electron bearing nucleus and the NMR nucleus.[4,5] In other cases,[6,7] the NMR shift has been interpreted as arising dominantly through pseudo contact interaction.

In this paper we investigate in detail the pseudo contact contribution of a 3d² system to the NMR shift for a 3d² system in a strong crystal field environment of octahedral symmetry.

The pseudo contact NMR shift, B, was first given by McConell and Robertson[8] in the form

$$\frac{\Delta B}{B} = -\mu_B^2 \frac{S(S+1)}{3kT} \frac{(3\cos^2\theta - 1)}{R^3} F(g) \qquad (1)$$

where R is the distance between the paramagnetic center and the NMR nucleus and θ is the angle between the pricipal asix of the complex and the vector between the paramagnetic center and the NMR nucleus. $F(g)$ is a function of the principal g-values. Kurland and McGravey[9] extended this expression and showed that the pseudo contact shift may be expressed in terms of the magnetic susceptibility components, $X_{\alpha\alpha}$, namely,

$$\frac{\Delta B}{B} = \frac{1}{3R^3} [\{X_{zz} - \frac{1}{2}(X_{xx}+X_{yy})\}(3\cos^2\theta - 1) + \frac{3}{2}(X_{xx} - X_{yy}) \sin^2\theta \cos^2\phi] \qquad (2)$$

This expression has extensively been used in interpreting the pseudo contact shift in paramagnetic $3d^n$ and $4f^n$ systems.[10] Thereafter, attention has been focused on the higher multipolar terms[11-13] and the NMR shift may be expressed as

$$\frac{\Delta B}{B} = \sum_{L=2}^{k} \sum_{M=0}^{L} \frac{\{A_{LM}\cos M\phi + B_{LM}\sin M\phi\} P_L^M(\cos\theta)}{R^{L+1}} \qquad (3)$$

where $K=2(\ell+1)$ for a specific ℓ-electron, $P_L^M(\cos\theta)$, the associated Legendre polynomials and the coefficients A_{LM} and B_{LM} measure the anisotropy in the multipolar magnetic susceptibilities of the molecule. Recently, nonmultipole expansion method has been developed by Golding and Stubbs[14] and this method was applied to investigate the NMR chemical shift for $3d^1$,[15] $3d^2$,[16] $4d^1$,[17] and $4f^1$ systems.[18,19]

2. Theory

For a $3d^n$ system in a strong crystal field environment of octahedral symmetry when the fourfold axis is chosen to be our axis of quantization, appropriate hamiltonian representing the various interactions is given by[20]

$$H = \sum_{i=1}^{n} \left\{ -\frac{h^2}{2m} \nabla_i^2 - \frac{Ze^2}{4\pi\varepsilon_0 r_i} \right\} + \sum_{i<j} \frac{e^2}{r_{ij}} + \sum_{i=1}^{n} V(r_i) + \sum_{i=1}^{n} \zeta \boldsymbol{l}_i \boldsymbol{s}_i + \sum_{i=1}^{n} \mu_B (\boldsymbol{l}_i + 2\boldsymbol{s}_i) \boldsymbol{B} + H_{hy} \quad (4)$$

where

$$\sum_{i=1}^{n} V(r_i) = a_4 [(7/12)^{\frac{1}{2}} Y_{40}(\Theta, \Phi) + (5/24)^{\frac{1}{2}} \{ Y_{4-4}(\Theta, \Phi) + Y_{44}(\Theta, \Phi) \}] \quad (5)^{21}$$

and

$$H_{hy} = \frac{\mu_0}{4\pi} g_N \mu_B \mu_N \left(\frac{2\boldsymbol{l} \cdot \boldsymbol{I}}{r_N^3} + g_S \left\{ \frac{3(\boldsymbol{r}_N \cdot \boldsymbol{I}) \boldsymbol{r}_N \cdot \boldsymbol{I}}{r_N^5} - \frac{\boldsymbol{s} \cdot \boldsymbol{I}}{r_N^3} \right\} \right) \quad (6)^{22}$$

Here $\boldsymbol{r}$ and $\boldsymbol{r}_N$ are the electron radius vector about the electron and a_4 is the required crystal field parameter for the 3d system. tum 1, respectively. The quantity $\boldsymbol{B}$ is the applied magnetic field and a_4 is the required crystal field parameter for the 3d system. The other symbols have their usual meaning. Since we are examining the NMR shift arising from the electron orbital angular momentum and the electron spin dipolar-nuclear spin angular momentum interactions for a $3d^2$ system when the fourfold axis is chosen as the quantization axis (refer Figure 1 to 1st. series of this work), we choose the electron wavefunctions for the ground state as[20,26]

$$X_1 = \frac{1}{\sqrt{2}} |\phi_1 \phi_3|$$
$$X_2 = \frac{1}{\sqrt{2}} |\phi_2 \phi_4|$$
$$X_3 = \frac{1}{\sqrt{2}} |\phi_1 \phi_5|$$
$$X_4 = \frac{1}{\sqrt{2}} |\phi_2 \phi_6|$$
$$X_5 = \frac{1}{2} \{ |\phi_4 \phi_5| + |\phi_3 \phi_6| \}$$
$$X_6 = \frac{1}{\sqrt{2}} |\phi_3 \phi_5|$$
$$X_7 = \frac{1}{2} \{ |\phi_1 \phi_6| + |\phi_2 \phi_5| \}$$
$$X_8 = \frac{1}{2} \{ |\phi_1 \phi_4| + |\phi_2 \phi_3| \}$$
$$X_9 = \frac{1}{\sqrt{2}} |\phi_4 \phi_6| \quad (7)^{23,24}$$

where

$$|\phi_1 \phi_2| = \begin{vmatrix} \phi_1(1) & \phi_1(2) \\ \phi_2(1) & \phi_2(2) \end{vmatrix}$$

Here

$$|\phi_1\rangle = \frac{1}{\sqrt{2}} \{ |3d_2^+\rangle - |3d_{-2}^+\rangle \}$$
$$|\phi_2\rangle = \frac{1}{\sqrt{2}} \{ |3d_2^-\rangle - |3d_{-2}^-\rangle \}$$
$$|\phi_3\rangle = |3d_1^+\rangle$$
$$|\phi_4\rangle = |3d_1^-\rangle$$
$$|\phi_5\rangle = |3d_{-1}^+\rangle$$
$$|\phi_6\rangle = |3d_{-1}^-\rangle$$

It is stressed that the contribution (t_2^1, e^1) electron contribution to the ground state for $3d^2$ system is neglected and the contribution of (t_2^2) is only considered.[25]

As described in the previous work[27], the spin orbit coupling interaction is treated as a perturbation acting on the crystal field potential and repulsion between 3d electrons. The spin orbit coupling interaction matrix for the ground state wave functions of a $3d^2$ system is represented, when the fourfold axis is chosen to be our axis of qunatization, in Table 1A.

This spin orbit coupling interaction matrix is different from that for the axial wave functions of a $3d^2$ system when the threefold axis is chosen as the quantization axis. Solving the spin orbit coupling interaction matrix given in Table 1A, we obtain the five fold degenerate eigenfunctions with the corresponding eigenvalue, the threefold degenerate eigenfunctions with the eigenvalue and the non-degenerate eigenfunction with the corresponding eigenvalue, respectively.

To determine the NMR shift for a $3d^2$ system in a strong crystal field environment of octahedral symmetry, we calculate the principal values of NMR screening tensor by considering the magnetic field interaction parallel to the x,y and z directions and averaged assuming a Boltzmann distribution. The contribution to the NMR shift, ΔB, is given by

$$\Delta B = \frac{B\sigma_{\alpha\alpha}}{3} \quad (8)$$

where

$$\sigma_{\alpha\alpha} = \left\{ \frac{\partial^2 \langle H_{hf} \rangle}{\partial \mu_\alpha \partial B_\alpha} \right\}_{\mu = B = 0} \text{ and } \mu = g_N \mu_N \boldsymbol{I}$$

The term $\langle H_{hf} \rangle$ refers to the Boltzmann average of the hyperfine interaction represented by Eq(6).[18] In a crystal field environment of octahedral symmetry, the NMR shift for a $3d^2$ system is given by

$$\frac{\Delta B}{B} = -\frac{2}{3} \frac{\mu_0}{4\pi} \frac{\mu_B^2}{kT} \left\{ \frac{\sum_{i=1}^{3} (F_i + H_i kT/\zeta) \exp(-E_i/kT)}{\sum_{i=1}^{3} g_i \exp(-E_i/kT)} \right\} \quad (9)$$

TABLE 1A: The Spin Orbit coupling Matrix for the Ground State of $^3T_1$ wave Functions when the Four fold axis is Chosen as the Quantization Axis

	$\|x_1\rangle$	$\|x_2\rangle$	$\|x_3\rangle$	$\|x_4\rangle$	$\|x_5\rangle$	$\|x_6\rangle$	$\|x_7\rangle$	$\|x_8\rangle$	$\|x_9\rangle$
$\|x_1\rangle$	$-\xi/2-e$	0							
$\|x_2\rangle$		$-\xi/2-e$							
$\|x_3\rangle$			$\xi/2-e$	0	$\xi/2$				
$\|x_4\rangle$				$-e$	$\xi/2$				
$\|x_5\rangle$					$\xi/2-e$				
$\|x_6\rangle$						$-e$	$\xi 1/2$		
$\|x_7\rangle$							$-e$		
$\|x_8\rangle$								$-e$	$\xi 1/2$
$\|x_9\rangle$									$-e$

where

$$E_1 = -\zeta/2,\ E_2 = \zeta/2,\ E_3 = \zeta,\ g_1 = 5,\ g_2 = 3,\ \text{and}\ g_3 = 1$$

In equation (9). F_i and H_i are expressed as a function of spherical harmonics as given in the following.

$$\begin{aligned}
F_1 = &-(33/140)\sqrt{\pi}\, Y_{00}(\theta,\Phi) F_1(t) \\
&-(6048/t^5)(\pi/21)^{\frac{1}{2}}[(7/12)^{\frac{1}{2}} Y_{40}(\theta,\Phi) \\
&+(5/24)^{\frac{1}{2}}\{Y_{4-4}(\Theta,\Phi)+Y_{44}(\Theta,\Phi)\}] P_1(t) \\
&+(518400/t^7)(\pi/26)^{\frac{1}{2}}[(1/8)^{\frac{1}{2}} Y_{40}(\Theta,\Phi) \\
&-(\sqrt{7}/4)\{Y_{4-4}(\Theta,\Phi)+Y_{44}(\Theta,\Phi)\}] Q(t) \\
F_2 = &-(9/140)\sqrt{\pi}\, Y_{00}(\Theta,\Phi)\ F_2(t) \\
&+(2016/t^5)(\pi/21)^{\frac{1}{2}}[(7/12)^{\frac{1}{2}} Y_{40}(\Theta,\Phi) \\
&+(5/24)^{\frac{1}{2}}\{Y_{4-4}(\Theta,\Phi)+Y_{44}(\Theta,\Phi)\}]\ P_2(t) \\
&-(518400/t^7)(\pi/26)^{\frac{1}{2}}[(1/8)^{\frac{1}{2}} Y_{40}(\Theta,\Phi) \\
&-(\sqrt{7}/4)\{Y_{4-4}(\Theta,\Phi)+Y_{44}(\Theta,\Phi)\}]\ Q(t) \\
F_3 = &\ 0 \\
H_1 = &\ (39/70)\sqrt{\pi}\, Y_{00}(\Theta,\Phi)\ H_1(t) \\
&+(17472/t^5)\ (\pi/21)^{\frac{1}{2}}[(7/12)^{\frac{1}{2}} Y_{40}(\Theta,\Phi) \\
&+(5/24)^{\frac{1}{2}}\{Y_{4-4}(\Theta,\Phi)+Y_{44}(\Theta,\Phi)\}]\ R_1(t) \\
&-(2073600/t^7)\ (\pi/26)^{\frac{1}{2}}[(1/8)^{\frac{1}{2}} Y_{40}(\Theta,\Phi) \\
&-(\sqrt{7/4})\ \{Y_{4-4}(\Theta,\Phi)+Y_{44})\Theta,\Phi)\}]\ Q(t) \\
H_2 = &\ (33/70)\sqrt{\pi}\ Y_{00}(\Theta,\Phi)\ H_2(t) \\
&-(28224/t^5)(\pi/21)^{\frac{1}{2}}[(7/12)^{\frac{1}{2}} Y_{40}(\Theta,\Phi) \\
&+(5/24)^{\frac{1}{2}}\{Y_{4-4}(\Theta,\Phi)+Y_{44}(\Theta,\Phi)\}]\ R_2(t) \\
&+(6220800/t^7)\ (\pi/26)^{\frac{1}{2}}[(1/8)^{\frac{1}{2}} Y_{40}(\Theta,\Phi) \\
&-(\sqrt{7/4})\ \{Y_{4-4}(\Theta,\Phi)+Y_{44}(\Theta,\Phi)\}]\ Q(t) \\
H_3 = &-(32/35)\sqrt{\pi}\ Y_{00}(\Theta,\Phi)\ H_3(t) \\
&+(10752/t^5)\ (\pi/21)^{\frac{1}{2}}[(7/12)^{\frac{1}{2}} Y_{40}(\Theta,\Phi) \\
&+(5/24)^{\frac{1}{2}}\{Y_{4-4}(\Theta,\Phi)+Y_{44}(\Theta,\Phi)\}]\ R_3(t) \\
&-(4147200/t^7)\ (\pi/26)^{\frac{1}{2}}[(1/8)^{\frac{1}{2}} Y_{40}(\Theta,\Phi) \\
&-(\sqrt{7/4})\ \{Y_{4-4}(\Theta,\Phi)+Y_{44}(\Theta,\Phi)\}]\ Q(t)
\end{aligned} \quad (10)$$

With

$$F_1(t) = \beta^3 e^{-t}\left(\frac{8}{99}\frac{t^4}{4!} + \sum_{n=0}^{3}\frac{t^n}{n!}\right)$$

$$P_1(t) = \beta^3\left\{1 - e^{-t}\left(\frac{16}{33}\frac{t^9}{9!} + \sum_{n=0}^{8}\frac{t^n}{n!}\right)\right\}$$

$$F_2(t) = \beta^3 e^{-t}\left(-\frac{2}{105}\frac{t^4}{4!} + \sum_{n=0}^{3}\frac{t^n}{n!}\right)$$

$$P_2(t) = \beta^3\left\{1 - e^{-t}\left(\frac{16}{11}\frac{t^9}{9!} + \sum_{n=0}^{8}\frac{t^n}{n!}\right)\right\}$$

$$Q(t) = \beta^3\left(1 - e^{-t}\sum_{n=0}^{11}\frac{t^n}{n!}\right)$$

$$H_1(t) = \beta^3 e^{-t}\left(-\frac{16}{117}\frac{t^4}{4!} + \sum_{n=0}^{3}\frac{t^n}{n!}\right)$$

$$R_1(t) = \beta^3\left\{1 - e^{-t}\left(\frac{96}{143}\frac{t^9}{9!} + \sum_{n=0}^{8}\frac{t^n}{n!}\right)\right\}$$

$$H_2(t) = \beta^3 e^{-t}\left(-\frac{16}{33}\frac{t^4}{4!} + \sum_{n=0}^{3}\frac{t^n}{n!}\right)$$

$$R_2(t) = \beta^3\left\{1 - e^{-t}\left(\frac{96}{77}\frac{t^9}{9!} + \sum_{n=0}^{8}\frac{t^n}{n!}\right)\right\}$$

$$H_3(t) = \beta^3 e^{-t}\left(-\frac{1}{6}\frac{t^4}{4!} + \sum_{n=0}^{3}\frac{t^n}{n!}\right)$$

$$R_3(t) = \beta^3\left\{1 - e^{-t}\left(\frac{24}{11}\frac{t^9}{9!} + \sum_{n=0}^{8}\frac{t^n}{n!}\right)\right\}$$

Since this expression for $\Delta B/B$ is applicable for all values of R we may determine from equation (9) the case when $R \rightarrow 0$, namely,

$$\begin{aligned}
\frac{\Delta B}{B} = \frac{\mu_0}{4\pi}\frac{\beta^3}{420}\frac{\mu_B^2}{kT}[\{(33-78kT/\zeta)+(9-66kT/\zeta) \\
\exp(-\zeta/kT)+(128kT/\zeta)\ \exp(-3\zeta/2kT)\}/ \\
\{5+3\exp(-\zeta/kT)+\exp(-3\zeta/kT)\}]
\end{aligned} \quad (11)$$

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

$$\begin{aligned}
F_1 = &-(189/R^5\beta^2)\ (\pi/21)^{\frac{1}{2}}[(7/12)^{\frac{1}{2}}\ Y_{40}(\Theta,\Phi)+ \\
&(5/24)^{\frac{1}{2}}\ \{Y_{4-4}(\Theta,\Phi)+Y_{44}(\Theta,\Phi)\}] \\
&+(4045/R^7\beta^4)\ (\pi/26)^{\frac{1}{2}}[(1/8)^{\frac{1}{2}}\ Y_{40}(\Theta,\Phi)- \\
&(\sqrt{7}/4)^{\frac{1}{2}}\ \{Y_{4-4}(\Theta,\Phi)+Y_{44}(\Theta,\Phi)\}] \\
F_2 = &\ (63/R^5\beta^2)\ (\pi/21)^{\frac{1}{2}}[(7/12)^{\frac{1}{2}}\ Y_{40}(\Theta,\Phi)+(5/24)^{\frac{1}{2}} \\
&\{Y_{4-4}(\Theta,\Phi)+Y_{44}(\Theta,\Phi)\}] \\
&-(4050/R^7\beta^4)\ (\pi/26)^{\frac{1}{2}}[(1/8)^{\frac{1}{2}}\ Y_{40}(\Theta,\Phi)-(\sqrt{7}/4) \\
&\{Y_{4-4}(\Theta,\Phi)+Y_{44}(\Theta,\Phi)\}] \\
H_1 = &\ (546/R^5\beta^2)\ (\pi/12)^{\frac{1}{2}}[(7/12)^{\frac{1}{2}}\ Y_{40}(\Theta,\Phi)+(5/24)^{\frac{1}{2}} \\
&\{Y_{4-4}(\Theta,\Phi)+Y_{44}(\Theta,\Phi)\}] \\
&-(16200/R^7\beta^4)\ (\pi/26)^{\frac{1}{2}}[(1/8)^{\frac{1}{2}}\ Y_{40}(\Theta,\Phi)-(\sqrt{7}/4) \\
&\{Y_{4-4}(\Theta,\Phi)+Y_{44}(\Theta,\Phi)\}] \\
H_2 = &-(882/R^5\beta^2)\ (\pi/21)^{\frac{1}{2}}[(7/12)^{\frac{1}{2}}\ Y_{40}(\Theta,\Phi)+(5/24)^{\frac{1}{2}} \\
&\{Y_{4-4}(\Theta,\Phi)+Y_{44}(\Theta,\Phi)\}] \\
&+(48600/R^7\beta^4)\ (\pi/26)^{\frac{1}{2}}[(1/8)^{\frac{1}{2}}\ Y_{40}(\Theta,\Phi)-(\sqrt{7}/4) \\
&\{Y_{4-4}(\Theta,\Phi)+Y_{44}(\Theta,\Phi)\}] \\
H_3 = &\ (336/R^5\beta^2)\ (\pi/21)^{\frac{1}{2}}[(7/12)^{\frac{1}{2}}\ Y_{40}(\Theta,\Phi)+(5/24)^{\frac{1}{2}} \\
&\{Y_{4-4}(\Theta,\Phi)+Y_{44}(\Theta,\Phi)\}] \\
&-(32400/R^7\beta^4)\ (\pi/26)^{\frac{1}{2}}[(1/8)^{\frac{1}{2}}\ Y_{40}(\Theta,\Phi)-(\sqrt{7}/4) \\
&\{Y_{4-4}(\Theta,\Phi)+Y_{44}(\Theta,\Phi)\}]
\end{aligned} \quad (12)$$

As shown in equations (10) and (12), the only combinations of spherical harmonics, $Y_{lm}(\Theta,\Phi)$, that transform as the irreducible representation A_1a_g of the octahedral group occur. This is also the case for 3d² system when threefold axis is chosen to be our axis of quantization.[16]

3. Results and Discussion

The calculated NMR shift along the x, y and z axes for a 3d² system in a strong crystal field environment of octahedral symmetry are listed in Table 1, when the fourfold axis is chosen as the quantization axis. Here we choose $\beta = 2.9943/a_0$, the spin-orbit coupling constant, ζ as 210 cm^{-1}. The temperature is taken as T = 300K. As shown in Table 1, the calculated NMR shift values for specific R-avalues along the x, y and z axes are equal. It is found that $\Delta B/B$ (ppm) decreases in magnitude rapidly as R increases.

Along the (100) axis, $\Delta B/B$ is positive while along the (111) axis $\Delta B/B$ is negative for all values of R. $\Delta B/B$ changes in sign to negative around $R \cong 0.20$ nm. Such the NMR results are different from those cases when the threefold axis is chosen as the quantization axis.[16]

A comparision of the multipolar terms with nonmultipolar expansion results (the exact values of $\Delta B/B$ (ppm) given by

TABLE 1. $\Delta B/B$(ppm) for Specific R-Values for a 3d² System Along the x, y and z Axes in a Strong Crystal Field Environment of Octahedral Symmetry when Fourfold Axis is Chosen as the Quantization Axis

	$\Delta B/B$(ppm)		
R(nm)	x	y	z
0.05	12543.535	12543.535	12543.535
0.10	1623.685	1623.685	1623.685
0.15	308.373	308.373	308.373
0.20	80.715	80.715	80.715
0.25	27.501	27.501	27.501
0.30	11.280	11.280	11.280
0.35	5.282	5.282	5.282
0.40	2.730	2.730	2.730
0.45	1.523	1.523	1.523
0.50	0.903	0.903	0.903

TABLE 2. $\Delta B/B$(ppm) for Specific R-Values for a 3d² System in a Strong Crystal Field Environment of Octahedral Symmetry When Fourfold Axis is Chosen to be Our Axis of Quantization

	$\Delta B/B$(ppm)		
R(nm)	(100)	(110)	(111)
0.05	12543.535	7677.011	−2257.474
0.10	1623.685	344.259	−2298.666
0.15	308.373	4.992	−354.850
0.20	80.715	−8.126	−75.284
0.25	27.501	−4.331	−22.859
0.30	11.280	−2.109	−8.783
0.35	5.282	−1.079	−3.951
0.40	2.730	−0.588	−1.989
0.45	1.523	−0.339	−1.089
0.50	0.903	−0.206	−0.637

equation (9) shows that the first multipolar term, $1/R^5$ in this case, contributes dominantly to the NMR shift and there is in good agreement between the exact solutions and the multipolar results when $R \geqslant 0.25$ nm. It is interesting to note that along the (100) and (110) axes, the $1/R^5$ term gives values opposite in sign to that of $1/R^7$ term.

In addition, NMR results show that the NMR shift arising from the interaction described by hamiltonian (6) in 3d² system in a strong crystal field environment of octahedral symmetry is large for significant distances between the NMR nucleus and the d-electron bearing atom. For distances less than 0.40 nm it should not be neglected.

To examine the contribution of the Fermi contact interaction and the Pseudo contact interaction to the NMR shift for a 3d² system, it is usual to express a temperature dependence for $\Delta B/B$ as follows:

$$\frac{\Delta B}{B} = b_0 + b_1/T + b_2/T^2 \qquad (13)$$

The NMR results over temperature range 240 to 360K from the exact solution of $\Delta B/B$ given by Eq(9), where $\beta = 2.9943/a_0$, $\zeta = 210\text{cm}^{-1}$, may be fitted almost precisely to an expression given by Eq(13). The values of b_0, b_1 and b_2 depend markedly on the location of the NMR nucleus and some of values are listed in Table 4.

TABLE 3: A Comparision of the Exact Value of $\Delta B/B$(ppm) with Multipolar Terms for Specific R Values

(a) Along the (100) Axis

	$\Delta B/B$(ppm)			
R(nm)	$1/R^5$	$1/R^7$	Sum of all multipolar terms	from eq.(9)
0.05	7973.808	−518.137	−6030.670	12543.535
0.10	2111.617	−518.131	1593.486	1623.685
0.15	369.710	−60.479	309.231	308.373
0.20	89.512	−8.780	80.731	80.715
0.25	29.353	−1.851	27.501	27.501
0.30	11.280	−0.517	11.280	11.280
0.35	5.458	−0.176	5.282	5.282
0.40	2.799	−0.069	2.730	2.730
0.45	1.553	−0.030	1.523	1.523
0.50	0.917	−0.014	0.902	0.902

(b) Along the (110) Axis

0.05	−1993.452	3175.598	1164.146	7677.011
0.10	−527.904	841.963	314.059	344.259
0.15	−92.428	98.278	5.851	4.992
0.20	−22.378	14.268	−8.110	−8.126
0.25	−7.338	3.008	−4.330	−4.330
0.30	−2.949	0.840	−2.109	−2.109
0.35	−1.364	0.285	−1.079	−1.079
0.40	−0.700	0.112	−0.588	−0.588
0.45	−0.388	0.049	−0.339	−0.339
0.50	−0.229	0.024	−0.206	−0.206

(c) Along the (111) Axis

0.05	−5315.872	−3454.466	−8770.338	−2257.474
0.10	1407.744	−921.122	−2328.866	−2298.666
0.15	−246.473	−107.518	−353.991	−354.850
0.20	−59.675	−15.609	−75.284	−75.300
0.25	−19.568	−3.291	−22.859	−22.859
0.30	−7.864	−0.919	−8.783	−8.783
0.35	−3.638	−0.312	−3.951	−3.951
0.40	−1.866	−0.123	−1.989	−1.989
0.45	−1.036	−0.054	−1.089	−1.089
0.50	−0.612	−0.013	−0.637	−0.637

TABLE 4: The Termperature Dependence of $\Delta B/B$(nm) using Eq(9) at Various Values of (R, Θ, Φ) Expressed in Terms of the Coefficients in Eq(13), $\xi = 210\text{cm}^{-1}$, $\beta = 2.9943/a_0$

R(nm)	Axis	b_0(ppm)	b_1(ppm)	b_2(ppm)
0.1	<100>	−820.382	631763.00	23820145.63
0.2	<100>	−28.196	26290.483	1943733.545
0.3	<100>	−3.820	3548.115	294468.509
0.4	<100>	0.910	852.267	71899.737
0.5	<100>	−0.304	278.862	24939.845
0.2	<110>	−28.485	26264.978	1947237.980
0.2	<110>	−28.520	26290.483	1943733.545

For the case when the NMR shift in 3d² paramagnetic system has been interpreted as arising through the Fermi contact interaction between the electron bearing nucleus and the NMR nucleus[18], the expression for the NMR shift, ΔB, was described by

$$\frac{\Delta B}{B}=-\frac{a\mu_B}{3g_N\mu_N\lambda}\frac{2}{}(g-1)\ (g-2)+(g-1)g\frac{J(J+1)}{kT} \qquad (14)$$

where

$$g=1+[J(J+1)-L(L+1)+S(S+1)]/2J(J+1)$$

Here ζ is the spin orbit coupling constant and only the $(2s+1)_L$ ground state is considered with no bonding effects.

In other case[6,7] the NMR shifts have been expounded as a result of the pseudo contact interaction as expressed in terms of the dipolar approximation. Bleaney[10], using the dipolar approximation represented in terms of the magnetic susceptibility components of Kurland and McGravey[9], derived an equation for the NMR shift, ΔB, given by

$$\frac{\Delta B}{B}=\frac{N\mu_B^2 g^2(2l+1-4s)\ \{3X(X-1)-4J\ (J+1)\ (L+1)\}}{24\sqrt{5}(2l+3)\ (2l-1)\ (2L-1)\ \sqrt{\pi}R^3k^2T^2}\cdot\frac{(1-3\cos^2\theta)\ a_2^\circ}{} \qquad (15)$$

where $\ell=2$, a_2° is a crystal field parameter. In equations (14) and (15) $1/T$ and $1/T^2$ terms arise from the Fermi and the pseudo contact terms, respectively.

As shown in Table 4, the major contribution to the NMR shift arises from the $1/T^2$ term but the other two terms are certainly significant. Hence a temperature dependence analysis may lead to almost correct interpretation of the origin of the NMR shift for a $3d^2$ system when the fourfold axis is chosen as our axis of quantization.

This work may be applied to investigate the isotropic shielding arising from 3d electron angular momentum and the 3d electron spin dipolar-nuclear spin angular momentum interactions for a $3d^n$ system in a strong crystal field environment of octahedral symmetry. As far as we are aware no attemt has been made to examine the NMR shift for a $3d^2$ system in a strong crystal field environment of octahedral symmetry.

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