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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/R⁵ and 1/R⁷ terms. A comparison of the multipolar terms with nonmultipolar results shows that the 1/R⁵ term contributes dominantly to the NMR shift and there is in good agreement between the exact solution and the multipolar results when R ≥ 0.25. A temperature dependence analysis may lead to the results that the 1/T² 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 dipolar-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 3dⁿ and a 4fⁿ systems has been interpreted as arising through the Fermi 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 McConnell and Robertson⁸ in the form

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

where R is the distance between the paramagnetic center and

the NMR nucleus and θ is the angle between the principal axis 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 McGravey⁹ extended this expression and showed that the pseudo contact shift may be expressed in terms of the magnetic susceptibility components, $X_{\alpha\alpha}$, namely,

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

This expression has extensively been used in interpreting the pseudo contact shift in paramagnetic 3dⁿ and 4fⁿ systems.¹⁰ Thereafter, attention has been focused on the higher multipolar terms¹¹⁻¹³ and the NMR shift may be expressed as

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

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 Stubbs¹⁴ and this method was applied to investigate the NMR chemical shift

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) \\ &\quad - (6048/t^3) (\pi/21)^{\frac{1}{2}} [(7/12)^{\frac{1}{2}} Y_{00}(\theta, \phi) \\ &\quad + (5/24)^{\frac{1}{2}} \{Y_{2-2}(\theta, \phi) + Y_{22}(\theta, \phi)\}] P_1(t) \\ &\quad + (518400/t^7) (\pi/26)^{\frac{1}{2}} [(1/8)^{\frac{1}{2}} Y_{00}(\theta, \phi) \\ &\quad - (\sqrt{7}/4) \{Y_{2-2}(\theta, \phi) + Y_{22}(\theta, \phi)\}] Q(t) \\ F_2 &= -(9/140) \sqrt{\pi} Y_{00}(\theta, \phi) F_2(t) \\ &\quad + (2016/t^3) (\pi/21)^{\frac{1}{2}} [(7/12)^{\frac{1}{2}} Y_{00}(\theta, \phi) \\ &\quad + (5/24)^{\frac{1}{2}} \{Y_{2-2}(\theta, \phi) + Y_{22}(\theta, \phi)\}] P_2(t) \\ &\quad - (518400/t^7) (\pi/26)^{\frac{1}{2}} [(1/8)^{\frac{1}{2}} Y_{00}(\theta, \phi) \\ &\quad - (\sqrt{7}/4) \{Y_{2-2}(\theta, \phi) + Y_{22}(\theta, \phi)\}] Q(t) \\ F_3 &= 0 \\ H_1 &= (39/70) \sqrt{\pi} Y_{00}(\theta, \phi) H_1(t) \\ &\quad + (17472/t^3) (\pi/21)^{\frac{1}{2}} [(7/12)^{\frac{1}{2}} Y_{00}(\theta, \phi) \\ &\quad + (5/24)^{\frac{1}{2}} \{Y_{2-2}(\theta, \phi) + Y_{22}(\theta, \phi)\}] R_1(t) \\ &\quad - (2073600/t^7) (\pi/26)^{\frac{1}{2}} [(1/8)^{\frac{1}{2}} Y_{00}(\theta, \phi) \\ &\quad - (\sqrt{7}/4) \{Y_{2-2}(\theta, \phi) + Y_{22}(\theta, \phi)\}] Q(t) \\ H_2 &= (33/70) \sqrt{\pi} Y_{00}(\theta, \phi) H_2(t) \\ &\quad - (28224/t^3) (\pi/21)^{\frac{1}{2}} [(7/12)^{\frac{1}{2}} Y_{00}(\theta, \phi) \\ &\quad + (5/24)^{\frac{1}{2}} \{Y_{2-2}(\theta, \phi) + Y_{22}(\theta, \phi)\}] R_2(t) \\ &\quad + (6220800/t^7) (\pi/26)^{\frac{1}{2}} [(1/8)^{\frac{1}{2}} Y_{00}(\theta, \phi) \\ &\quad - (\sqrt{7}/4) \{Y_{2-2}(\theta, \phi) + Y_{22}(\theta, \phi)\}] Q(t) \\ H_3 &= -(32/35) \sqrt{\pi} Y_{00}(\theta, \phi) H_3(t) \\ &\quad + (10752/t^3) (\pi/21)^{\frac{1}{2}} [(7/12)^{\frac{1}{2}} Y_{00}(\theta, \phi) \\ &\quad + (5/24)^{\frac{1}{2}} \{Y_{2-2}(\theta, \phi) + Y_{22}(\theta, \phi)\}] R_3(t) \\ &\quad - (4147200/t^7) (\pi/26)^{\frac{1}{2}} [(1/8)^{\frac{1}{2}} Y_{00}(\theta, \phi) \\ &\quad - (\sqrt{7}/4) \{Y_{2-2}(\theta, \phi) + Y_{22}(\theta, \phi)\}] Q(t) \end{aligned} \quad (10)$$

With

$$\begin{aligned} F_1(t) &= \beta^3 e^{-t} \left(\frac{8}{99} \frac{t^4}{4!} + \sum_{n=0}^{\infty} \frac{t^n}{n!} \right) \\ P_1(t) &= \beta^3 \left\{ 1 - e^{-t} \left(\frac{16}{33} \frac{t^3}{9!} + \sum_{n=0}^{\infty} \frac{t^n}{n!} \right) \right\} \\ F_2(t) &= \beta^3 e^{-t} \left(-\frac{2}{105} \frac{t^4}{4!} + \sum_{n=0}^{\infty} \frac{t^n}{n!} \right) \\ P_2(t) &= \beta^3 \left\{ 1 - e^{-t} \left(\frac{16}{119} \frac{t^3}{9!} + \sum_{n=0}^{\infty} \frac{t^n}{n!} \right) \right\} \\ Q(t) &= \beta^3 \left(1 - e^{-t} \sum_{n=0}^{\infty} \frac{t^n}{n!} \right) \\ H_1(t) &= \beta^3 e^{-t} \left(-\frac{16}{117} \frac{t^4}{4!} + \sum_{n=0}^{\infty} \frac{t^n}{n!} \right) \\ R_1(t) &= \beta^3 \left\{ 1 - e^{-t} \left(\frac{96}{143} \frac{t^3}{9!} + \sum_{n=0}^{\infty} \frac{t^n}{n!} \right) \right\} \\ H_2(t) &= \beta^3 e^{-t} \left(-\frac{16}{33} \frac{t^4}{4!} + \sum_{n=0}^{\infty} \frac{t^n}{n!} \right) \\ R_2(t) &= \beta^3 \left\{ 1 - e^{-t} \left(\frac{96}{77} \frac{t^3}{9!} + \sum_{n=0}^{\infty} \frac{t^n}{n!} \right) \right\} \\ H_3(t) &= \beta^3 e^{-t} \left(-\frac{1}{6} \frac{t^4}{4!} + \sum_{n=0}^{\infty} \frac{t^n}{n!} \right) \end{aligned}$$

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

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,

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

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

$$\begin{aligned} F_1 &= -(189/R^3 \beta^3) (\pi/21)^{\frac{1}{2}} [(7/12)^{\frac{1}{2}} Y_{00}(\theta, \phi) + \\ &\quad (5/24)^{\frac{1}{2}} \{Y_{2-2}(\theta, \phi) + Y_{22}(\theta, \phi)\}] \\ &\quad + (4045/R^3 \beta^3) (\pi/26)^{\frac{1}{2}} [(1/8)^{\frac{1}{2}} Y_{00}(\theta, \phi) - \\ &\quad (\sqrt{7}/4)^{\frac{1}{2}} \{Y_{2-2}(\theta, \phi) + Y_{22}(\theta, \phi)\}] \\ F_2 &= (63/R^3 \beta^3) (\pi/21)^{\frac{1}{2}} [(7/12)^{\frac{1}{2}} Y_{00}(\theta, \phi) + (5/24)^{\frac{1}{2}} \\ &\quad \{Y_{2-2}(\theta, \phi) + Y_{22}(\theta, \phi)\}] \\ &\quad - (4050/R^3 \beta^3) (\pi/26)^{\frac{1}{2}} [(1/8)^{\frac{1}{2}} Y_{00}(\theta, \phi) - (\sqrt{7}/4) \\ &\quad \{Y_{2-2}(\theta, \phi) + Y_{22}(\theta, \phi)\}] \\ H_1 &= (546/R^3 \beta^3) (\pi/12)^{\frac{1}{2}} [(7/12)^{\frac{1}{2}} Y_{00}(\theta, \phi) + (5/24)^{\frac{1}{2}} \\ &\quad \{Y_{2-2}(\theta, \phi) + Y_{22}(\theta, \phi)\}] \\ &\quad - (16200/R^3 \beta^3) (\pi/26)^{\frac{1}{2}} [(1/8)^{\frac{1}{2}} Y_{00}(\theta, \phi) - (\sqrt{7}/4) \\ &\quad \{Y_{2-2}(\theta, \phi) + Y_{22}(\theta, \phi)\}] \\ H_2 &= -(882/R^3 \beta^3) (\pi/21)^{\frac{1}{2}} [(7/12)^{\frac{1}{2}} Y_{00}(\theta, \phi) + (5/24)^{\frac{1}{2}} \\ &\quad \{Y_{2-2}(\theta, \phi) + Y_{22}(\theta, \phi)\}] \\ &\quad + (48600/R^3 \beta^3) (\pi/26)^{\frac{1}{2}} [(1/8)^{\frac{1}{2}} Y_{00}(\theta, \phi) - (\sqrt{7}/4) \\ &\quad \{Y_{2-2}(\theta, \phi) + Y_{22}(\theta, \phi)\}] \\ H_3 &= (336/R^3 \beta^3) (\pi/21)^{\frac{1}{2}} [(7/12)^{\frac{1}{2}} Y_{00}(\theta, \phi) + (5/24)^{\frac{1}{2}} \\ &\quad \{Y_{2-2}(\theta, \phi) + Y_{22}(\theta, \phi)\}] \\ &\quad - (32400/R^3 \beta^3) (\pi/26)^{\frac{1}{2}} [(1/8)^{\frac{1}{2}} Y_{00}(\theta, \phi) - (\sqrt{7}/4) \\ &\quad \{Y_{2-2}(\theta, \phi) + Y_{22}(\theta, \phi)\}] \end{aligned} \quad (12)$$

As shown in equations (10) and (12), the only combinations of spherical harmonics, $Y_{lm}(\theta, \phi)$, that transform as the irreducible representation A_{1g} 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 $T = 300\text{K}$. As shown in Table 1, the calculated NMR shift values for specific R -values 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 comparison of the multipolar terms with nonmultipolar expansion results (the exact values of $\Delta B/B$ (ppm) given by

TABLE 1. $\Delta B/B(\text{ppm})$ for Specific R -Values for a $3d^2$ 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

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

$R(\text{nm})$	$\Delta B/B(\text{ppm})$		
	(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 $R \geq 0.25$ 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 $3d^2$ 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 $3d^2$ system, it is usual to express a temperature dependence for $\Delta B/B$ as follows:

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

The NMR results over temperature range 240 to 360K from the exact solution of $\Delta B/B$ given by Eq(9), where $\beta = 2.9943/a_0$, $\xi = 210\text{cm}^{-1}$, 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 Comparison of the Exact Value of $\Delta B/B(\text{ppm})$ with Multipolar Terms for Specific R Values

(a) Along the (100) Axis

$R(\text{nm})$	$\Delta B/B(\text{ppm})$			
	$1/R^5$	$1/R^7$	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 Temperature Dependence of $\Delta B/B(\text{nm})$ using Eq(9) at Various Values of (R, θ, ϕ) Expressed in Terms of the Coefficients in Eq(13), $\xi = 210\text{cm}^{-1}$, $\beta = 2.9943/a_0$

$R(\text{nm})$	Axis	$b_0(\text{ppm})$	$b_1(\text{ppm})$	$b_2(\text{ppm})$
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 $3d^2$ paramagnetic system has been interpreted as arising through the Fermi contact interaction between the electron bearing nucleus and the NMR nucleus¹⁸, the expression for the NMR shift, ΔB , was described by

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

where

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

Here ξ is the spin orbit coupling constant and only the $(2s+1)\ell_j$ 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. Bleaney¹⁰, using the dipolar approximation represented in terms of the magnetic susceptibility components of Kurland and McGravey⁹, derived an equation for the NMR shift, ΔB , given by

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

where $\ell = 2$, a_2^2 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 3d² 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 3dⁿ system in a strong crystal field environment of octahedral symmetry. As far as we are aware no attempt has been made to examine the NMR shift for a 3d² system in a strong crystal field environment of octahedral symmetry.

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