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Hyperfine Interaction Integrals for NMR Chemical Shifts in 5f Paramagnetic Systems

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To study the NMR chemical shift arising from the 5f-electron orbital angular momentum and the 5f-electron spin dipolar-nuclear spin angular momentum interactions, the evaluation of the hyperfine integrals has been extended to any pairs of SCF type 5f orbitals adopting a general method which is applicable to a general vector *R,* pointing in any direction in space. From the electronic wavefunctions for 5f orbitals expressed in common coordinate system, the radial part of the hyperfine interaction integrals are derived by translating the exponential part, $r^2 \exp(-2\beta r)$, in terms of R, r_N and the modified Bessel functions. The radial integals for 5f orbitals are tabulated in analytical forms. When two of the hyperfine integrals along the (100), (010), (001), (110), and (111) axes are calculated using the derived radial integrals, the calculated values for the 5f system change sign for R-values larger than R$\simeq$0.35 nm. But the calculated values for the 4f systems change sign for R-values larger than R$\simeq$0.20 nm.

Introduction

In the past two decades a substantial amount of work has been devoted toward evaluation of the contact and pseudo contact contributions to the observed isotropic shifts in the ^{1}H nuclear magnetic resonance (NMR) spectra of uranium (IV) organometallic compounds.[1-5] Nuclei in different molecular electronic environments experience different shielding field and such differences in shielding field give rise to the chemical shifts in high resolution NMR spectroscopy. The chemical shifts are extremely important in the applications of NMR to molecular structure studies. The interpretation of the NMR shift in 5f paramagnetic systems has been based on the Fermi contact interactions and pseudo contact interactions. A large number of organometallic actinide compounds have been synthesized and their NMR spectra in solution are studied. Much of this NMR work has been reviewed by Fischer[6] and by Luke and Streitwieser.[7] In those cases in which the pseudo contact shift could be reliably estimated, it was found that when the pseudo contact shift was subtracted from the experimental shift a sizeable shift, which has generally been called the contact shift, remained. The results of the pseudo contact interaction were interpreted using the dipolar approximation expressed in terms of the magnetic susceptibility components.[8] But Golding *et al.,* [9-11,14] Ahn *et al.* [12,13] and Lee and Lee *et al.* [15] have shown that the use of such an expression may lead to serious errors in the interpretation of the NMR shift through this mechanism, especially if only the dipolar term is considered.

Since our interest is centered on the NMR shift arising from the 5f-electron orbital angular momentum and the 5f-electron spin dipolar-nuclear spin angular momentum interactions for an 5f-electron in a crystal field environment centered at $O_{NxNyNzN}$, it is necessary to evaluate the theoretical hamiltonian representing the pseudo contact part,[10]

$$H_H = H_L + H_D \tag{1}$$

where

$$H_L = \frac{2\mu_0}{4\pi} g_N \mu_B \mu_N \{l_{N'} \cdot I / r_N^3\} \tag{2a}$$

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$$H_D = \frac{\mu_0}{4\pi}\, g_N\, \mu_B\, \mu_N g_S \left\{ \frac{3(r_N \cdot S)r_N \cdot I}{r_N^5} - \frac{S \cdot I}{r_N^3} \right\} \qquad (2b)$$

In equations (2a) and (2b), μ_0 is the permeability constant of free space, g_N the nuclear g-value of the nucleus being shielded (that is, the NMR nucleus), μ_B the Bohr magneton, μ_N the nuclear magneton, g_s the free electron Lande' splitting factor (g_s=2.20023 ⋯), and S the spin angular momentum of the electron. r_N is the radius vector of the electron about the nucleus with nuclear spin angular momentum, I. Here the first part represents the electron orbital angular momentum-nuclear spin angular momentum interaction and the second part, H_D, the electron spin dipolar-nuclear spin angular momentum interaction. Thus taken together equations (2a) and (2b) define the operators which account for pseudo contact interactions between nuclei and unpaired electrons.

The position of the nucleus on which the f-electrons are centered, with respect to the NMR nucleus N, is given by the vector R, as shown in Figure 1.

In order to evaluate the hyperfine integrals involving 5f orbitals, we adopt the general method, which is applicable to a general vector R, pointing in any direction in space, developed by Gelding *et al.* [9] In this method, the integrand is expressed as a function of R and r_N using the translation and the integration is performed in the $O_N x_N y_N z_N$ system. This method is applied to derive the required radial integrals of the hyperfine integrals to 3d^n systems, [11] 4d^n systems, [12] 5d^n systems [13] and 4f systems. [14] As far as we are aware no previous attempt has been made to evaluate the hyperfine integrals involving SCF 5f orbitals.

The purpose of this work is to evaluate the required radial integrals of the hyperfine integrals involving 5f orbitals which are required to investigate the NMR chemical shift in analytical form for 5f^n-electrons systems in a crystal field environment adopting the nonmultipole expansion method.

Evaluation of the required radial integrals of the hyperfine integrals

We choose a SCF type function of the form,
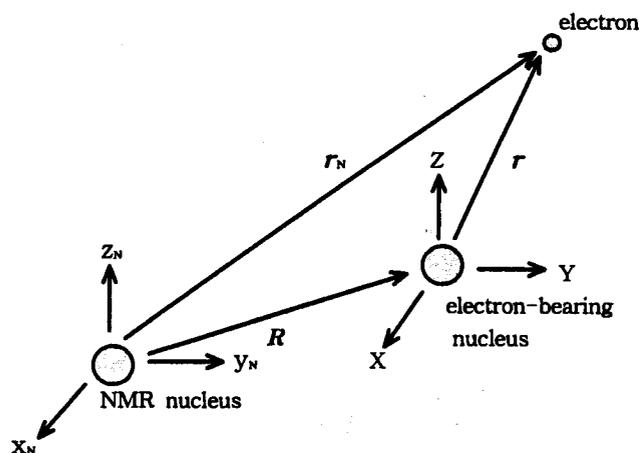
Figure 1. The coordinate system for calculation of the NMR chemical shift.

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

where l and m are the usual quantum numbers which have integer values, N a normalization constant, and β the optimized orbital exponent. [16] Therefore the electronic wave functions in real notation for 5f orbitals are

$$| 5fz^3 > = N(7/16\pi)^{1/2} z(5z^2\text{-}3r^2)\, r \exp(-\beta r)$$
$$| 5fxz^2 > = N(21/32\pi)^{1/2} x(5z^2\text{-}r^2)\, r \exp(-\beta r)$$
$$| 5fyz^2 > = N(21/32\pi)^{1/2} y(5z^2\text{-}r^2)\, r \exp(-\beta r)$$
$$| 5fxyz > = N(105/4\pi)^{1/2} xyz\, r \exp(-\beta r)$$
$$| 5fz(x^2\text{-}y^2) > = N(105/16\pi)^{1/2} z(x^2\text{-}y^2)\, r \exp(-\beta r)$$
$$| 5fx(x^2\text{-}y^2) > = N(35/32\pi)^{1/2} x(x^2\text{-}3y)\, r \exp(-\beta r)$$
$$| 5fy(x^2\text{-}y^2) > = N(35/32\pi)^{1/2} y(3x^2\text{-}y^2)\, r \exp(-\beta r) \qquad (4)$$

where N is the normalization constant defined by

$$\frac{1}{N^2} = \int_0^\infty r^{10} \exp(-2\beta r)dr \qquad (5)$$

The hyperfine interaction integrals are evaluated by expressing the electron coordinate system O_{xyz} in the coordinate system $O_N x_N y_N z_N$ in terms of R and r_N using the following two mathematical identities. [9~14]

One, first given in the literature by Moshinsky [17] in 1959, translates the harmonic polynomial $r^l Y_{lm}(\theta, \phi)$:

$$r^l Y_{lm}(\theta, \phi) = \sum_{l_1=0}^{l} \sum_{l_2=0}^{l} \sum_{m_1=-l_1}^{l_1} \sum_{m=-l_2}^{l_2} (-1)^{l_1}\, \delta(l_1+l_2, l)$$
$$\times \left\{ \frac{4\pi(2l+1)!}{2l_1+1)!(2l_2+1)!} \right\}^{1/2} <l_1 l_2 m_1 m_2 | l_1 l_2 lm>$$
$$\times R^{l_1} Y_{l_1 m_1}(\theta, \phi)\, r_N^{l_2} Y_{l_2 m_2}(\theta_N, \phi_N) \qquad (6)$$

where the symbol $\delta(l_1 + l_2, l)$ is the so-called kronecker delta, it has the value 1 when $l_1 + l_2 = l$ and the value 0 when $l_1 + l_2 \neq l$, and $<l_1 l_2 m_1 m_2|l_1 l_2 lm>$ is the Clebsch-Gordan coefficient.

Secondly, the exponential part may also be transformed into the following form:

$$r^2 \exp(-2\beta r) = 4\pi \sum_{n=0}^{\infty} h_n(R, r_N) \sum_{h=-n}^{n} Y^*_{nh}(\theta, \phi)\, Y_{nh}(\theta_N, \phi_N) \qquad (7)$$

where

$$h_n(R, r_N) = (r_< r_>)^{-1/2} \{ r_<^3 I_{n+1/2}(2\beta r_<)\, K_{n-1/2}(2\beta r_>)$$
$$- r_<^3 I_{n+3/2}(2\beta r_<)\, K_{n+1/2}(2\beta r_>)$$
$$+ (4n+1/2n+1)\, r_>^2 r_< I_{n+1/2}(2\beta r_<)\, K_{n-1/2}(2\beta r_>)$$
$$- (4n+3/2n+1)\, r_< r_>^2 I_{n+3/2}(2\beta r_<)\, K_{n+1/2}(2\beta r_>)$$
$$+ (2(n+1)/2n+1)\, r_>^2 r_< I_{n+5/2}(2\beta r_<)\, K_{n+3/2}(2\beta r_>)$$
$$- (2n/2n+1)\, r_< r_>^2 I_{n-1/2}(2\beta r_<)\, K_{n-3/2}(2\beta r_>) \qquad (8)$$

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

To evaluate the hyperfine interaction integrals, the integrand is expressed as a function of R and r_N using equations (6) and (7). For the angular part constitution, the required computer program [18] are already set up. Thus we only need to derive the analytical formulas for the radial integral.

For the radial part of integrals for 5f orbitals, we define the radial integral as

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$$R_N^{(L)}(t) = 4\,\beta^{11}(-R)^L \int_0^\infty r_N^{5-L}\; h_N(R, r_N)\, dr \qquad (9)$$

where $t = 2\beta r$ and further for convenience

$$\begin{aligned}
U_n(t) &= R_n^{(6)}(t)\\
V_n(t) &= R_n^{(5)}(t)\\
W_n(t) &= R_n^{(4)}(t)\\
X_n(t) &= R_n^{(3)}(t)\\
Y_n(t) &= R_n^{(2)}(t)\\
Z_n(t) &= R_n^{(1)}(t)\\
B_n(t) &= R_n^{(0)}(t) \qquad\qquad (10)
\end{aligned}$$

This definition provides a suitable notation that enables handling of the radial parts of the hyperfine integrals. From the angular parts of the hyperfine interaction integrals we obtain selection rules on n. Due to this selection rules on n, only a few radial integrals were required.

The required radial integrals are list in Table 1.

Since $h_N(R, r_N)$ is a Green's function type expression, the integration was conducted in two parts,

$$\lim_{\varepsilon\to 0}\int_\varepsilon^R \cdots dr_N \quad\text{and}\quad \int_R^\infty \cdots dr_N$$

Table 1. The required radial integrals for 5f-orbitals

$U_2(t)= \beta^3\{3t^8/8 - e^{-t}(t^8/192+t^7/64+t^6/16+3t^5/16+3t^4/8+3t^3/8)\}$

$V_1(t)=- \beta^3\{3t^3/8 - e^{-t}(t^7/64+t^6/16+3t^5/16+3t^4/8+3t^3/8)\}$

$V_3(t)=- \beta^3\{(3t^3/8-75t/4)+e^{-t}(t^7/96+3t^6/32+19t^5/32+11t^4/4+9t^3+75t^2/4+75t/4)\}$

$W_0(t)= \beta^3\{3t^3/8 - e^{-t}(t^6/64+3t^5/32+9t^4/32+3t^3/8)\}$

$W_2(t)= \beta^3\{(3t^3/8-45t/4)+e^{-t}(t^6/32+9t^5/32+3t^4/2+21t^3/4+45t^2/4+45t/4)\}$

$W_4(t)= \beta^3\{(3t^3/8-75t/4+1470/2)-e^{-t}(t^6/24+2t^5/3+51t^4/8+343t^3/8+415t^2/2+2790t+1470+1470/t)\}$

$X_1(t)=- \beta^3\{(3t^3/8-15t/4)+e^{-t}(t^5/32+5t^4/16+3t^3/2+15t^2/4+15t/4)\}$

$X_3(t)=- \beta^3\{(3t^3/8-45t/2+630/t)-e^{-t}(t^5/8+15t^4/8+123t^3/8+165t^2/2+585t/2+630+630/t)\}$

$X_5(t)=- \beta^3\{(3t^3/8-225t/4+4410/t-170100/t^3)+e^{-t}(t^5/4+6t^4+321t^3/4+2955t^2/4+19755t/4+23940+80640/t+170100/t^2+170100/t^3)\}$

$Y_0(t)= \beta^3\{(3t^3/8+15t/4)-e^{-t}(t^4/32+3t^3/8+15t^2/8+15t/4)\}$

$Y_2(t)= \beta^3\{(3t^3/8-15t/2+1\,26/t)-e^{-t}(t^4/8+15t^3/8+27t^2/2+111t/2+126+126/t)\}$

$Y_4(t)= \beta^3\{(3t^3/8-135t/4+1890/t-56700/t^3)+e^{-t}(3t^4/4+33t^3/2+765t^2/4+5805t/4+7560+26460/t+56700/t^2+56700/t^3)\}$

$Y_6(t)= \beta^3\{(3t^3/8-75t+8820/t+680400/t^3+27442800/t^5)-e^{-t}(2t^4+66t^3+1170t^2+14100t+124110+812070/t+389400/t^2+13041000/t^3+27442800/t^4+27442800/t^5)\}$

$Z_1(t)=- \beta^3\{(3t^3/8+15t/2-42/t)+e^{-t}(t^3/8+2t^2+27t/2+42+42/t)\}$

$Z_3(t)=- \beta^3\{(3t^3/8-45t/4+378/t-8100/t^3)+e^{-t}(3t^3/4+63t^2/4+1253/8t+972+3672/t+8100/t^2+8100/t^3)\}$

$Z_5(t)=- \beta^3\{(3t^3/8-45t+3780/t-226800/t^3+7484400/t^5)-e^{-t}(6t^3+180t^2+2790t+28350+202230/t+1020600/t^2+3515400/t^3+7484400/t^4+7484400/t^5)\}$

$B_0(t)= \beta^3\{(3t^3/8+45t/2+126/t)-e^{-t}(3t^2/8+27t/4+189/4+126/t)\}$

$B_2(t)= \beta^3\{(3t^3/8-45t/4-126/t+1620/t^3)-e^{-t}(3t^2/4+63t/4+144+684/t+1620/t^2+1620/t^3)\}$

$B_4(t)= \beta^3\{(3t^3/8-15t+756/t-32400/t^3+831600/t^5)-e^{-t}(6t^2+168t+2286+19206/t+106200/t^2+383400/t^3+831600/t^4+831600/t^5)\}$

$B_6(t)= \beta^3\{(3t^3/8-225t/4+6300/t-567000/t^3+37422000/t^5-1362160800/t^7)+e^{-t}(60t^2+2340t+46620+609840/t+5681340/t^2+38612700/t^3+18960480/t^4+643658400/t^5+1362160800/t^6+1362160800/t^7)\}$

where by taking the limit as $\varepsilon \to 0$ the singularity at the magnetic resonance nucleus was dealt with.

Results and Discussion

The analytical expansion formulas for $r^2 \exp(-2\beta r)$ of the hyperfine integrals arising from the pseudo contact interaction for a 5f system, adopting the nonmultipole expansion method are derived as shown in Table 1. The angular part of f systems was reported in reference 18, The hyperfine integrals for SCF type 5f atomic orbitals have been derived separately by expressing the spherical harmonics part in terms of the coordinate (R, r_N) of the reference point, and by translating the exponential part, $r^2 \exp(-2\beta r)$, in terms of R, r_N and the modified Bessel functions. Some calculated $l \cdot I$ hyperfine interaction integrals for the 5f system in a crystal field environment at different values of R along the (100), (010), (001), (110) and (111) axes are given in Tables 2 and 3. Here we choose $\beta =3.866$. In addition, we compare the results for the 4f hyperfine integrals and the 5f hyperfine integrals, respectively.

Table 2. Calculated values for $\langle f_{yz}^2 | l_{Nz}/r_N^3 | f_{xz}^2 \rangle$ of 4f hyperfine integrals with those of 5f hyperfine integrals for specific R-values along (001), (100), (010), (110), and (111) axes ($\beta =3.866$)

	4f			5f		
r (nm)	[001]	[100][a]	[111]	[001]	[100][a]	[111]
0.05	1.848	1.161	1.390	14.315	14.197	14.236
0.10	1.594	1.035	1.221	13.782	13.360	13.500
0.15	1.179	0.831	0.946	12.767	12.016	12.263
0.20	0.489	0.569	0.541	11.068	10.225	0.497
0.25	-0.611	0.270	-0.024	8.403	8.060	8.156
0.30	-2.269	-0.050	-0.786	4.418	5.599	5.176
0.35	-4.635	-0.378	-1.785	-1.301	2.922	1.477
0.40	-7.856	-0.705	-3.062	-9.213	0.100	-3.041
0.45	-12.071	-1.024	-4.660	-19.806	-2.809	-8.493
0.50	-17.413	-1.332	-6.619	-33.578	-5.753	-15.002

[a]Here, the calculated values along the [100] axis are the same to those along the [010] and [110] axes.

Table 3. Calculated values for $\langle f_{z(x2-y2)} | l_{Nz}/r_N^3 | f_{xyz} \rangle$ of 4f hyperfine integrals with those of 5f hyperfine integrals for specific R-values along (001), (100), (010), (110), and (111) axes ($\beta = 3.866$)

	4f			5f		
r (nm)	[001]	[010][a]	[111]	[001]	[010][a]	[111]
0.05	-2.958	-2.690	-2.780	-28.417	-28.499	-28.472
0.10	-2.574	-2.372	-2.444	-26.927	-27.028	-27.003
0.15	-1.962	-1.843	-0.898	-24.430	-24.540	-24.547
0.20	-1.064	-1.063	-1.091	-20.811	-20.979	-21.051
0.25	0.188	0.017	0.046	-15.929	-16.269	-16.428
0.30	1.866	1.457	1.595	-9.610	-10.306	-10.541
0.35	4.047	3.322	3.647	-1.661	-2.970	-3.197
0.40	6.809	5.684	6.291	8.129	5.884	5.843
0.45	10.228	8.620	9.616	19.984	16.419	16.862
0.50	14.382	12.211	13.703	34.132	28.812	30.164

[a]Here, the calculated values along the [010] axis are the same to those along the [100] and [110] axes.

As shown in Tables 2 and 3, the calculated values along the (100) axis are in agreement with those along (010) and (110) axes. The calculated values along the (001), (010), and (111) axes are different from each other for all values of R. Along the (001), (100), and (111) axes, the calculated values in 4f and 5f systems are found to change sign when R≃0.20 nm and 0.35 nm, respectively. Here, the values are found to be positive for smaller R values and negative for greater R values in Table 2 From Table 3 along the (001), (010), (100), (110), and (111) axes, the calculated values in 4f and 5f systems also change sign when R≃0.20 nm and 0.35 nm, respectively. But the values are negative for smaller R values and positive for greater R values.

This work is applied to investigate the paramagnetic NMR shift for 5f systems and enables, for the first time, an estimate of errors coming from the usually used approximation.

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