Theory of NMR Shifts and ENDOR Spectroscopy in Paramagnetic l^n Complexes

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The interactions of magnetic hyperfine spectroscopy are expressed in irreducible tensor-operator form, suitable for applications to configurations l^n with n equivalent electrons outside closed shells. The matrix elements are evaluated on the basis of Racah's techniques. The familiar point-dipole approximation of the pseudocontact interaction is valid for $n \leqq 2l+1$; a minus sign, however, must be introduced in this formula for $n > 2l+1$.

1. Introduction

It was shown in two previous papers [1, 2] that the relevant interactions of nuclear magnetic resonance spectroscopy may be simplified by the introduction of tensor operators. Formulae were given for the pseudocontact interaction $H_L + H_D$ and the Fermi contact term H_F, suitable for applications to one-electron states.

The present paper deals with the application of the powerful techniques of Racah [3] to calculations within configurations with n equivalent electrons outside closed shells. The interactions are expressed in irreducible tensor-operator form, and the matrix elements are evaluated for any configuration l^n. For definitions and notations we refer to [1].

2. Matrix Elements of $h_\mu(H_L, H_D, H_F)$ within the Configuration l^n

The totality of states of the configuration l^n for a given spin form a basis for a single irreducible representation of U_{2l+1} [4]. The base vectors of l^n can be characterized by the irreducible representations of various groups according to the reduction $U_5 \to R_5 \to R_3$ and $U_7 \to R_7 \to G_2 \to R_3$ for d- and f-electrons, respectively. Base vectors of the iron-series are defined by the quantum numbers $|d^n v\, LM_L\, SM_S\rangle$, where the seniority number v is unambiguously determined by an irreducible representation of R_5 and the spin S. For the present we limit the number of equivalent electrons to $n \leqq 2l+1$.

2.1. $h_\mu(L)$

Matrix elements of $h_\mu(L)$ within one-electron states $|l, m\rangle$ are given in (7) and (11) of [2]. In order to extend the calculation to the configurations l^n, we shall express the operator $h_\mu(L)$ in irreducible tensor form, yielding

$$h_\mu(L) = 8\pi\gamma_N \hbar\beta R^{-3}(-1)^{\mu+1} \sum_{\substack{K=0 \\ (\text{even})}}^{(2l-2)} \left(\frac{r}{R}\right)^K \langle l \| Y^{(K)} \| l\rangle$$
$$\cdot \{l(l+1)(2l+1)(K+1)(2K+3)/(K+2)\}^{1/2}$$
$$\cdot \begin{Bmatrix} K+1 & K & 1 \\ l & l & l \end{Bmatrix} \tag{1}$$
$$\cdot \sum_{m=-(K+1)}^{(K+1)} X_{\mu-m}^{K+2} \begin{pmatrix} K+2 & K+1 & 1 \\ m-\mu & -m & \mu \end{pmatrix} V_m^{(K+1)}.$$

The three-j and six-j symbols are tabulated in [5], and

$$\langle l \| Y^{(K)} \| l\rangle \tag{2}$$
$$= (-1)^l (2l+1)\,[(2K+1)/4\pi]^{1/2} \begin{pmatrix} l & K & l \\ 0 & 0 & 0 \end{pmatrix}.$$

The required matrix elements are given by

$$\langle l^n v\, SM_S\, LM_L | V_m^{(K+1)} | l^n v'\, S' M_S'\, L' M_L'\rangle$$
$$= \delta(SS')\,\delta(M_S M_S')(-1)^{L-M_L} \begin{pmatrix} L & K+1 & L' \\ -M_L & m & M_L' \end{pmatrix}$$
$$\cdot \langle l^n \theta \| V^{(K+1)} \| l^n \theta'\rangle, \tag{3}$$

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where the abbreviation $\theta = (v, S, L)$ is made. Since it is intended to apply the techniques to configurations of electrons that are equivalent, we introduced the tensor operators V^K [4] for which

$$\langle l \| V^{(K)} \| l' \rangle = (2K+1)^{1/2} \delta(l\, l'). \tag{4}$$

The reduced matrix elements within l^n to be evaluated are

$$\langle l^n \theta \| V^{(K)} \| l^n \theta' \rangle = n\, \delta(SS')[(2L+1)(2K+1)(2L'+1)]^{1/2} \cdot \sum_{\bar{\theta}} (\theta | \bar{\theta})(\theta' | \bar{\theta})(-1)^{\bar{L}+l+L+K} \begin{Bmatrix} L & K & L' \\ l & \bar{L} & l \end{Bmatrix}. \tag{5}$$

This equation corresponds with (7-52) of [4]. The coefficients of fractional parentage $(\theta | \bar{\theta})$ for d-electrons are tabulated in [3]. In lowest approximation of (1), the tensor operator $V_m^{(1)}$ is independent of n, and proportional to the angular momentum operator

$$V_m^{(1)} = \vec{L}_m [l(l+1)(2l+1)/3]^{-1/2}, \quad \text{or} \tag{6}$$

$$\langle l^n \theta \| V^{(1)} \| l^n \theta' \rangle = \delta(\theta\theta') \left[\frac{3L(L+1)(2L+1)}{l(l+1)(2l+1)} \right]^{1/2}. \tag{6a}$$

The reduced matrix elements $\langle d^3\theta \| V^{(3)} \| d^3\theta' \rangle$ are given in Table 1. All tensors $V^{(K)}$ of odd degree are diagonal with respect to the seniority v [3].

2.2. $h_\mu(D)$

In (28) of [1] a formula was given for the dipolar interaction within one-electron states, where the spin is an exact quantum number. The concept of double-tensor operators [3, 4] gives the possibility of calculating matrix elements of more complex configurations l^n, yielding

$$h_\mu(D) = 4\pi g\, \gamma_N \hbar\, \beta R^{-3} \sum_{q=-1}^{1} (-1)^q \begin{pmatrix} 2 & 1 & 1 \\ \mu - q & q & -\mu \end{pmatrix} \cdot \sum_{\substack{K=0 \\ (\text{even})}}^{2l} \left(\frac{r}{R} \right)^K [5(K+1)(K+2)(2K+3)/(4K+2)]^{1/2} \cdot \langle l \| Y^{(K)} \| l \rangle \cdot \sum_{m=-K}^{K} \begin{pmatrix} K+2 & K & 2 \\ m-\mu+q & -m & \mu-q \end{pmatrix} X^{K+2}_{\mu-m-q}\, W^{(1,K)}_{q,m}. \tag{7}$$

The general matrix element will be

$$\langle l^n v\ S M_S L M_L |\ W^{(i,K)}_{q,m} |\ l^n v'\ S' M'_S L' M'_L \rangle = (-1)^{S-M_S} \begin{pmatrix} S & i & S' \\ -M_S & q & M'_S \end{pmatrix} (-1)^{L-M_L} \begin{pmatrix} L & K & L' \\ -M_L & m & M'_L \end{pmatrix} \cdot \langle l^n \theta \| W^{(i,K)} \| l^n \theta' \rangle. \tag{8}$$

The reduced matrix elements between single-electron states are, in analogy to (4),

$$\langle s l \| W^{(i,K)} \| s' l' \rangle = [(2i+1)(2K+1)]^{1/2} \delta(ss')\, \delta(l\, l'), \tag{9}$$

so that the reduced matrix elements within l^n can be obtained from (7-54) of [4]:

$$\langle l^n \theta \| W^{(i,K)} \| l^n \theta' \rangle = [(2S+1)(2i+1)(2S'+1)(2L+1)(2K+1)(2L'+1)]^{1/2} \cdot n \sum_{\bar{\theta}} (\theta | \bar{\theta})(\theta' | \bar{\theta})(-1)^{\bar{S}+1/2+S+i+\bar{L}+l+L+K} \cdot \begin{Bmatrix} S & i & S' \\ 1/2 & \bar{S} & 1/2 \end{Bmatrix} \begin{Bmatrix} L & K & L' \\ l & \bar{L} & l \end{Bmatrix}. \tag{9a}$$

Table 1. The reduced matrix elements $\langle d^3\theta \| V^{(3)} \| d^3\theta' \rangle$

	$^2_3$P	$^4_3$P	$^2_1$D	$^2_3$D	$^2_3$F	$^4_3$F	$^2_3$G	$^2_3$H
$^2_3$P	0	0	0	$-(60/7)^{1/2}$	$(3/20)^{1/2}$	0	$-(243/28)^{1/2}$	0
$^4_3$P	0	0	0	0	0	$(42/5)^{1/2}$	0	0
$^2_1$D	0	0	$7^{1/2}$	0	0	0	0	0
$^2_3$D	$(60/7)^{1/2}$	0	0	$-(9/7)^{1/2}$	$-(15/2)^{1/2}$	0	$(3/14)^{1/2}$	$-(66/7)^{1/2}$
$^2_3$F	$(3/20)^{1/2}$	0	0	$(15/2)^{1/2}$	$(189/20)^{1/2}$	0	$(33/4)^{1/2}$	$-(33/4)^{1/2}$
$^4_3$F	0	$(42/5)^{1/2}$	0	0	0	$-(21/5)^{1/2}$	0	0
$^2_3$G	$(243/28)^{1/2}$	0	0	$(3/14)^{1/2}$	$-(33/4)^{1/2}$	0	$-(99/28)^{1/2}$	$-(429/28)^{1/2}$
$^2_3$H	0	0	0	$(66/7)^{1/2}$	$-(33/4)^{1/2}$	0	$(429/28)^{1/2}$	0

In lowest approximation of (7), the matrix elements are independent of n, and the double-tensor is proportional to the spin operator

$$W^{(1,0)}_{q,0} = \boldsymbol{S}_q [(2l+1)/2]^{-1/2}, \quad \text{or} \tag{10}$$

$$\langle l^n \theta \| W^{(1,0)} \| l^n \theta' \rangle = \delta(\theta\theta') [2S(S+1)(2S+1)(2L+1)/(2l+1)]^{1/2}. \tag{10a}$$

According to (6) and (10), the familiar point-dipole approximation of the pseudocontact interaction $H_L + H_D$ is guaranteed if $n \leqq 2l+1$.

For d-electrons, the reduced matrix elements of $W^{(1,2)}$ are proportional to those calculated by Racah [3]

$$\langle d^n \theta \| W^{(1,2)} \| d^n \theta' \rangle = (490)^{-1/2} \langle d^n \theta \| 70\, V^{(12)} \| d^n \theta' \rangle, \tag{11}$$

and the reduced matrix elements of $W^{(1,4)}$ within the d^3 configuration are listed in Table 2. The tensors of (1) and (7) have odd degree and must be diagonal with respect to the seniority v.

If spin-orbit coupling is treated as a perturbation, the first-order approximation requires the evaluation of matrix elements for which $S = S'$. For this case, we can separate the double-tensors in a spin and orbital part:

$$W^{(1,K)}_{q,m} = \boldsymbol{S}_q\, T^{(K)}_m; \tag{12}$$

$\boldsymbol{S}_q$ is the spin operator, and the quantities $T^{(K)}_m$ possess the same transformation properties as the tensors $V^{(K)}_m$ in (3); the reduced matrix elements are now given by

$$\langle l^n \theta \| T^{(K)} \| l^n \theta' \rangle = \delta(SS')[S(S+1)(2S+1)]^{-1/2} \langle l^n \theta \| W^{(1,K)} \| l^n \theta' \rangle. \tag{13}$$

2.3. $h_\mu(F)$

The spin density operator $h_\mu(F)$ of the Fermi contact interaction for single-electron states in (32) of [1] is assumed to be proportional to the electron density $\delta(\boldsymbol{R} - \boldsymbol{r})$. It is obvious that the separation of the spin- and δ-operator is incorrect for configurations with more than one equivalent electron. In order to generalize the calculation, we first expand the δ-operator in a series of normalized spherical harmonics Y^K_m, being proportional to the tensor-operators $V^{(K)}_m$:

$$\delta(\boldsymbol{R} - \boldsymbol{r}) = U^2_{3d}(R) \sum_{\substack{K=0 \\ (\text{even})}}^{2l} \sum_{m=-K}^{K} (-1)^m X^K_{-m}\, Y^K_m. \tag{14}$$

The spin density for a single-electron state is now defined by the products $S_\mu \cdot Y^K_m$, which clearly form the components of a double tensor as outlined in (6-4) of [4]; hence for l^n configurations, the Fermi contact operator is given by

$$h_\mu(F) = \frac{8\pi}{3} g\, \gamma_N \hbar\, \beta\, U^2_{3d}(R) \cdot \sum_{\substack{K=0 \\ (\text{even})}}^{2l} \langle l \| Y^{(K)} \| l \rangle [2(2K+1)]^{-1/2} \cdot \sum_{m=-K}^{K} (-1)^m X^K_{-m}\, W^{(1,K)}_{\mu,m}, \tag{15}$$

where the matrix elements of the double-tensor are defined in (8). The multipole expansion coefficients of (15) have the same order of magnitude.

3. Configurations of Almost Closed Shells

The approach of the previous section for $n \leqq 2l+1$ can be extended to deal with any con-

Table 2. The reduced matrix elements $\langle d^3 \theta \| W^{(1,4)} \| d^3 \theta' \rangle$.

	$^2_3$P	$^4_3$P	$^2_1$D	$^2_3$D	$^2_3$F	$^4_3$F	$^2_3$G	$^2_3$H
$^2_3$P	0	0	0	0	$(3/140)^{1/2}$	$-(60/7)^{1/2}$	$-51\,(140)^{-1/2}$	$-(66/35)^{1/2}$
$^4_3$P	0	0	0	0	$(30)^{1/2}$	$(12)^{1/2}$	$-(18/5)^{1/2}$	$-2(33/5)^{1/2}$
$^2_1$D	0	0	$(27)^{1/2}$	0	0	0	0	0
$^2_3$D	0	0	0	$(363/49)^{1/2}$	$3\,(15/14)^{1/2}$	$2\,(30/7)^{1/2}$	$-9(11/98)^{1/2}$	$(66/7)^{1/2}$
$^2_3$F	$(3/140)^{1/2}$	$-(30)^{1/2}$	0	$-3(15/14)^{1/2}$	$-3(33/20)^{1/2}$	0	$(99/140)^{1/2}$	$3(429/140)^{1/2}$
$^4_3$F	$(60/7)^{1/2}$	$(12)^{1/2}$	0	$2(30/7)^{1/2}$	0	$(66)^{1/2}$	$12(11/35)^{1/2}$	$2(429/35)^{1/2}$
$^2_3$G	$51\,(140)^{-1/2}$	$-(18/5)^{1/2}$	0	$-9(11/98)^{1/2}$	$-(99/140)^{1/2}$	$12(11/35)^{1/2}$	$9(429/980)^{1/2}$	$-3(143/140)^{1/2}$
$^2_3$H	$-(66/35)^{1/2}$	$2(33/5)^{1/2}$	0	$-(66/7)^{1/2}$	$3(429/140)^{1/2}$	$-2(429/35)^{1/2}$	$3(143/140)^{1/2}$	$-2(429/35)^{1/2}$

figuration l^n. According to the complementary nature of electrons and holes, the base vectors of l^n and l^{4l+2-n} are identical. The relevant interactions for $n > 2l+1$ can be evaluated by means of the conjugated eigenfunctions of the hole-configuration l^{4l+2-n}. The corresponding reduced matrix elements of tensor operators are related by [6]

$$\langle l^{4l+2-n}\,\theta \| \; W^{(i,K)} \| \, l^{4l+2-n}\,\theta' \rangle = (-1)^{i+K+1} \langle l^n\,\theta \| \; W^{(i,K)} \| l^n\,\theta' \rangle; \quad (16)$$

i.e., matrix elements of odd tensors have the same sign in both configurations.

The hamiltonian of ENDOR and NMR spectroscopy can be expressed in the form [1]

$$H = -\gamma_N \hbar \, \boldsymbol{H} \cdot \boldsymbol{I} + \sum_{\mu} (-1)^{\mu} h_{\mu} I_{-\mu} + \beta \, \boldsymbol{H}(\boldsymbol{L} + g\,\boldsymbol{S}), \quad (17)$$

where $h_{\mu} = h_{\mu}(L + D + F)$. The first two terms remain unaffected by the electron-hole transformation because the first term does not act on the paramagnetic electrons, and the second term contains solely tensors of odd degree. The third term, however, changes sign. The interaction of an externally applied magnetic field with n equivalent holes is opposite to its interaction with the conjugated state of n equivalent electrons.

According to (41) of [1], the NMR shift is proportional to the matrix elements of the third term, whereas the paramagnetic susceptibility is proportional to the square of these matrix elements and remains of course a positive definite quantity. It follows that a minus sign must be introduced in the point dipole approximation [7–10] for $n > 2l+1$.

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