

ANISOTROPY OF THE INDIRECT NUCLEAR SPIN-SPIN COUPLING CONSTANT.
 II. TREATMENT BY THE FINITE PERTURBATION METHOD *

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The finite perturbation method is applied to the calculation of the anisotropy of the indirect nuclear spin-spin coupling constants. For CH_3F , all the elements of the calculated coupling tensors become larger than those reported in Paper I of this series. However, for the C-H coupling anisotropy, the calculated value is still too small to compare with the experimentally estimated value as large as 1890 Hz. It seems that the effects other than the electronic one is important.

The finite perturbation method (FPM), theoretically equivalent to the coupled Hartree-Fock perturbation method, has only been used for the calculation of the electrical polarizabilities [2, 3] and shielding factors [4] of atoms and molecules. However, more recently, Pople and his co-workers applied this method to the calculation of the isotropic nuclear spin-spin coupling constant, stressing many important advantages of this method [5]. We have investigated the possibility of applying it to the calculation of the other properties of atoms and molecules. In this communication, the FPM is applied to the calculation of the anisotropy in the indirect nuclear spin-spin coupling constant which has attracted attention because of the experimental studies of high resolution nuclear magnetic resonance (NMR) spectra in nematic solvents [6].

The theory of the indirect nuclear spin-spin coupling constant, originally formulated by Ramsey [7] is based on the three types of interaction:

i) an electron orbital-nuclear dipole interaction

$$\mathcal{H}_1^{(a)} = (e\hbar\beta/c) \sum_{A, B, k} \gamma_A \gamma_B \gamma_{kA}^{-3} \gamma_{kB}^{-3} [(I_A \cdot I_B) (r_{kA} \cdot r_{kB}) - (I_A \cdot r_{kB}) (I_B \cdot r_{kA})],$$

$$\mathcal{H}_1^{(b)} = (2\beta\hbar/i) \sum_{A, k} \gamma_A \gamma_{kA}^{-3} I_A \cdot (r_{kA} \times \nabla_k).$$

ii) a magnetic dipole interaction

$$\mathcal{H}_2 = 2\beta\hbar \sum_{A, k} \gamma_A [3(S_k \cdot r_{kA}) (I_A \cdot r_{kA}) r_{kA}^{-5} - S_k \cdot I_A r_{kA}^{-3}].$$

iii) a Fermi contact interaction

$$\mathcal{H}_3 = (16\pi\beta\hbar/3) \sum_{A, k} \gamma_A \delta(r_{kA}) S_k \cdot I_A.$$

These one electron operators may be grouped into two classes; a spin independent operator, \mathcal{H}_1 , and spin linear operators, \mathcal{H}_2 and \mathcal{H}_3 . In the FPM, when the perturbation belongs to the former type, we use the restricted Hartree-Fock (RHF) wavefunction since $\Psi^{\text{rf}}(\text{SCF})$ is expressed to first order as a sum of the unperturbed wavefunction Ψ_0^{rf} and the singly excited singlet wavefunctions [eq. (1)]. This point may easily be understood from the Brillouin's theorem.

* Part II of ref. [1] which is hereafter called Paper I.

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$$\Psi^{\text{rf}}(\text{SCF}) = \Psi_0^{\text{rf}} + \sum_{i,k} C_{ik} |S_{ik}\rangle, \quad |S_{ik}\rangle = |\dots \varphi_i \varphi_k \frac{1}{\sqrt{2}}(\alpha\beta - \beta\alpha) \dots| \quad (1)$$

On the other hand, when the perturbation belongs to the latter type, the singlet wavefunction for the ground state gets mixed with the singly excited triplet wavefunctions. As shown by our previous study [8], the same can be done more easily by using the unrestricted Hartree-Fock (UHF) method, since

$$\Psi^{\text{uhf}} = \Psi_0^{\text{rf}} + \sum_i C_i |T_i\rangle + \dots, \quad |T_i\rangle = |\dots \lambda_i \nu_i \frac{1}{\sqrt{2}}(\alpha\beta + \beta\alpha) \dots| \quad (2)$$

where $|T_i\rangle$ is the triplet function. Thus the UHF method is applicable to the perturbation of the latter type.

The origins for the anisotropy of the indirect nuclear spin-spin coupling constants have already been studied in the previous report of this series. (See table 1 of paper I.) Among those sources, we formulate here the Fermi-spin dipolar interaction term rather fully along the line of the FPM. Taking the fixed magnetic dipoles μ_A and μ_B oriented along the z direction, the total hamiltonian is given by

$$\mathcal{H} = \mathcal{H}_0 + \mu_A \mathcal{H}_A + \mu_B \mathcal{H}_B, \quad (3)$$

where

$$\mathcal{H}_A = 2\beta \sum_k [3(S_k \mathbf{r}_{kA}) Z_{kA} r_{kA}^{-5} - S_{kz} r_{kA}^{-3}], \quad (4)$$

$$\mathcal{H}_B = (16\pi\beta/3) \sum_k \delta(\mathbf{r}_{kB}) S_{kz}. \quad (5)$$

In the FPM, the zz -component of the reduced coupling constant tensor K_{AB} (the coupling constant per unit magnetic moments) can be written as

$$(K_{AB})_{zz} = \left[\frac{\partial}{\partial \mu_A} \langle \Psi(\mu_A, 0) | \mathcal{H}_B | \Psi(\mu_A, 0) \rangle \right]_{\mu_A=0}, \quad (6)$$

where $\Psi(\mu_A, 0)$ is the wavefunction when only the spin dipolar perturbation is present at nucleus A and can be calculated by means of the UHF method. The Fock operator for $\Psi(\mu_A, 0)$ is

$$F(1) = h^{\text{core}}(1) + \mu_A \mathcal{H}_A(1) + \sum_{j=1}^N \langle \chi_j(2) | r_{12}^{-1} (1 - P_{12}) | \chi_j(2) \rangle, \quad (7)$$

where χ_j is the UHF spin orbital. On practical calculation, we adopted the one-center integral approximation for the atomic orbital (AO) matrix elements of \mathcal{H}_A and \mathcal{H}_B . Then we obtain from eq. (6) the following;

$$(K_{AB})_{zz} = (16\pi/15) \beta^2 \langle r^{-3} \rangle_A S_B^2(0) \left[\frac{\partial}{\partial h_A} \rho_{S_B S_B}(h_A) \right]_{h_A=0}, \quad h_A = (2/5) \beta \mu_A \langle r^{-3} \rangle_A. \quad (8)$$

The spin density at the s_B AO, $\rho_{S_B S_B}(h_A)$ is calculated by adding the small quantity h_A to the diagonal $2p_{x_A}$, $2p_{y_A}$ and $2p_{z_A}$ elements of the F^α matrix in the ratio of $-1:-1:2$, respectively and at the same time, by subtracting the same quantities from the corresponding elements of F^β . The physical meaning of eq. (8) is that adding the perturbation h_A at nucleus A, the orbitals of atom A are spin-polarized and this effect propagates to nucleus B, resulting in the induced spin density at nucleus B, and the coupling is calculated by taking the derivative of the spin density $\rho_{S_B S_B}(h_A)$ with respect to the added perturbation h_A . The xx -, yy - components of the coupling tensor K_{AB} are derived similarly by rotating the x, y, z suffixes. Note that the same interaction can be obtained by interchanging the terms $\mu_A \mathcal{H}_A$ and $\mu_B \mathcal{H}_B$ in the above treatment. In this case, the result becomes

$$(K_{AB})_{zz} = (16/15) \pi \beta^2 \langle r^{-3} \rangle_A S_B^2(0) \left[\frac{\partial}{\partial h_B} (2\rho_{z_A z_A}(h_B) - \rho_{x_A x_A}(h_B) - \rho_{y_A y_A}(h_B)) \right]_{h_B=0},$$

$$h_B = (8/3) \pi \beta \mu_B S_B^2(0), \quad (9)$$

where h_B is added to the diagonal s_B element of the F^α matrix and is subtracted at the same time from the corresponding β -element.

The other sources of the coupling constant tensor can easily be formulated as above by means of the FPM, and we give here only the resultant formulae. The spin dipolar contribution to the $\xi\xi$ element of K_{AB} is given by,

$$\begin{aligned} (K_{AB})_{\xi\xi} = & (9/25)\beta^2 \langle r^{-3} \rangle_A \langle r^{-3} \rangle_B \left[\frac{\partial}{\partial h_{A1}} \rho_{\eta B \xi B}(h_{A1}) \right] h_{A1=0} \\ & + (9/25)\beta^2 \langle r^{-3} \rangle_A \langle r^{-3} \rangle_B \left[\frac{\partial}{\partial h_{A2}} \rho_{\zeta B \xi B}(h_{A2}) \right] h_{A2=0} \\ & + (4/25)\beta^2 \langle r^{-3} \rangle_A \langle r^{-3} \rangle_B \left[\frac{\partial}{\partial h_{A3}} (2\rho_{\xi B \xi B}(h_{A3}) - \rho_{\eta B \eta B}(h_{A3}) - \rho_{\zeta B \zeta B}(h_{A3})) \right] h_{A3=0}, \quad (10) \end{aligned}$$

$$h_{A1} = h_{A2} = (3/5)\beta\mu \langle r^{-3} \rangle_A, \quad h_{A3} = (2/5)\beta\mu \langle r^{-3} \rangle_A,$$

where the suffixes (ξ , η and ζ) appearing in the right-hand side of eq. (10) correspond to ($2p_x$, $2p_y$ and $2p_z$). Practically, the above three terms in eq. (10) are calculated separately. That is, $\rho_{\eta B \xi B}(h_{A1})$ is calculated by adding h_{A1} ($-h_{A1}$) to the $F_{\eta A \xi A}^\alpha$ and $F_{\xi A \eta A}^\alpha$ ($F_{\eta A \xi A}^\beta$ and $F_{\xi A \eta A}^\beta$) elements, $\rho_{\zeta B \xi B}(h_{A2})$ by adding h_{A2} ($-h_{A2}$) to the $F_{\zeta A \xi A}^\alpha$ and $F_{\xi A \zeta A}^\alpha$ ($F_{\zeta A \xi A}^\beta$ and $F_{\xi A \zeta A}^\beta$) elements, and the third term, $2\rho_{\xi B \xi B}(h_{A3}) - \rho_{\eta B \eta B}(h_{A3}) - \rho_{\zeta B \zeta B}(h_{A3})$ is calculated in the same way as in the Fermi-spin dipolar cross term [eq. (8)]. For the orbital term, the RHF method is employed and h_A becomes imaginary [9].

$$(K_{AB})_{\xi\xi} = 16\beta^2 \langle r^{-3} \rangle_A \langle r^{-3} \rangle_B \left[\frac{\partial}{\partial h_A} \text{Im} \left(\sum_i C_{i\eta B}^* C_{i\xi B} \zeta_B(h_A) \right) \right] h_{A=0}, \quad h_A = 2\beta\mu \langle r^{-3} \rangle_A i,$$

where h_A is added to $F_{\zeta A \eta A}^\alpha$ and $-h_A$ to $F_{\eta A \zeta A}^\alpha$.

In the present communication, the above treatment is applied to the calculation of the coupling constants of CH_3F and the results are summarized in table 1. In these we used the INDO method of Pople et al. [10], and the values of integrals introduced by perturbation are the same as those given in table 3 of paper I. The values in parentheses are those calculated by the method reported in paper I. As can be seen from this table, the Fermi and the Fermi-spin dipolar cross terms make the dominant contributions to the isotropic and anisotropic couplings respectively. Note however that, for the C-F coupling, the other terms make 10-15% contribution to the total isotropic and anisotropic coupling constants and are not negligible. As shown by Pople, McIver and Ostlund [5], the agreement of the calculated isotropic C-H coupling constant with the experimental value becomes fairly satisfactory in this FPM treatment.

Table 1
Results of J_{AB} (Hz) for the directly bonded nuclei in CH_3F with INDO MO's

Isotropic (J_{AB}) _{iso}					
A-B	Fermi	Spin dipolar	Orbital	Total	Exptl. b)
C-H	147(75)	0(0)	0(0)	145(75)	148.8
C-F	- 97(-99)	15(9.4)	-15(-6.3)	- 97(- 96)	-161.9
Anisotropic ($J_{\parallel} - J_{\perp}$) _{AB} c)					
A-B	Fermi Spin dipolar	Spin dipolar	Orbital	Total	Exptl. b)
C-H	- 19(-11)	0(0)	0(0)	- 19(- 11)	1890 ± 130
C-F	208(94)	26(16.2)	27(4.5)	261(115)	700 ± 130

a) $J_{AB} = (h/2\pi)\gamma_A\gamma_B K_{AB}$.

b) Ref. [6].

c) The axis is chosen to be parallel with the molecular symmetry axis.

However, for the anisotropy of the C-H couplings, the disagreement between theory and experiment is still extraordinary even in the present FPM treatment as in the previous one reported in paper I. A similar discrepancy was also reported by Barfield by means of the valence-bond method [11]. It seems that these discrepancies between theory and experiment are far beyond the accuracy of the calculated values. Since the anisotropy of the indirect coupling was obtained experimentally by subtracting the direct coupling anisotropy, calculated with the gas phase microwave geometry, from the observed total anisotropy, some uncertainty may still remain owing to the neglect of the vibrational effects and of the change in molecular geometry from the gas state to the solute state in nematic solvent [12]. Thus, at present we believe that this discrepancy may suggest that the experimental values of the coupling anisotropy still contain some important effects other than the electronic one. In fact, the substituent effect to the C-H coupling anisotropies of the methyl derivatives, obtained from the NMR spectra by using gas phase microwave geometry [12], was extraordinarily large to interpret only from the electronic effect, and then a possibility of change of molecular geometry in nematic solvent from that in gas phase was suggested previously [12]. For the C-F coupling constant considerably large anisotropy can be expected from the present calculation although it is still small to compare with experiment.

Now, compare the present results with those calculated by the method reported in paper I: the signs of coupling constants obtained by these two methods are the same, but the absolute values obtained by the FPM are about 1-5 times as large as the ones obtained by the method reported in paper I. Since the FPM is equivalent to the coupled Hartree-Fock perturbation method in the small perturbation limit, and since the previous method is almost equivalent to the alternative uncoupled Hartree-Fock perturbation method of Langhoff et al. [13], this refinement in the FPM may be attributed to the inclusion of the self-consistency requirement for the calculation of the coupling constant. In fact, a similar trend was also seen in the model calculations [13] of the properties which lay stress on the electron distribution near the nucleus, as the present coupling constant does.

More details of the present method and fuller examinations of the coupling anisotropy will be published in the near future.

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