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INDO Calculation of ^{13}C Chemical Shifts by the Finite Perturbation Method

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Synopsis. The approximate SCF-MO calculation of ^{13}C nuclear magnetic shielding constants was performed using the finite perturbation method. The results indicated that the INDO finite perturbation method calculates ^{13}C chemical shifts in poor agreement with experiment.

The previous theories of the ^{13}C chemical shifts[1,2] have referred the shifts to the changes in the effective nuclear charge, the mobile bond order, and the average excitation energy and have given good results in many cases. However, in these semiempirical calculations, there is a certain degree of arbitrariness in the choice of an appropriate average excitation energy value. Especially the comparison of the shieldings between different types of molecules depends greatly on the choice of excitation energies. In the finite perturbation theory[3] this arbitrariness is eliminated. Ditchfield, Miller, and Pople[4] have presented *ab initio* results for the shieldings of small molecules using the finite perturbation method. The aim of this note is to examine the effectiveness of the finite perturbation calculation of ^{13}C chemical shifts in the simple molecular orbital method.[5]

In the finite perturbation theory, the shielding constant of the nucleus, A, in a liquid sample is expressed as:

$$\sigma^{\mathrm{A}} = \sigma_{\mathrm{d}}{}^{\mathrm{A}} + \sigma_{\mathrm{p}}{}^{\mathrm{A}},$$

$$\sigma_{\mathrm{d}}{}^{\mathrm{A}} = \frac{e^2}{3mc^2}\sum_{\mu\nu} P_{\mu\nu}(0)\langle\phi_\mu|r_{\mathrm{A}}{}^{-1}|\phi_\nu\rangle,$$

$$\sigma_{\mathrm{p}}{}^{\mathrm{A}} = -\frac{1}{3}\sum_{\mu\nu}\sum_{\alpha}(H^{(0,1)}_{\mathrm{A}\mu\nu})_\alpha(\partial/\partial H_\alpha[P^{\mathrm{Im}}_{\mu\nu}(H_\alpha)])_{\mathrm{H}=0},$$

$$(H^{(0,1)}_{\mathrm{A}\mu\nu})_\alpha = (e\hbar/mc)\langle\phi_\mu|(\boldsymbol{r}_{\mathrm{A}}\wedge\boldsymbol{\nabla})_\alpha r_{\mathrm{A}}{}^{-3}|\phi_\nu\rangle,$$

$$(\alpha = x, y, z), \qquad (1)$$

where the gauge origin of the vector potential is set at the position of the nucleus, A. $P_{\mu\nu}(0)$ and $P_{\mu\nu}(H_\alpha)$ are the density-matrix elements without and with the magnetic perturbation, H_α, respectively. $P_{\mu\nu}(H_\alpha)$ is allowed to be complex to accommodate the purely imaginary nature of the perturbation, and $P_{\mu\nu}{}^{\mathrm{Im}}(H_\alpha)$ represents its imaginary part. Then,

$$P_{\mu\nu}(H_\alpha) = 2\sum_{i}^{\mathrm{occ}} C^{*}_{\mu i}C_{\nu i} = P^{\mathrm{Re}}_{\mu\nu} + iP^{\mathrm{Im}}_{\mu\nu}. \qquad (2)$$

The LCAO coefficients, $C_{\mu\mathrm{i}}$, are found by solving the Roothaan equation with the finite perturbation. The Fock matrix with the perturbation is given by:

$$F_{\mu\nu}(H_\alpha) = H^{\mathrm{core}}_{\mu\nu} + iH_\alpha(H^{(1,0)}_{\mu\nu})_\alpha + \sum_{\lambda\sigma}P_{\lambda\sigma}(H_\alpha)[(\mu\nu|\lambda\sigma) - 1/2(\mu\sigma|\lambda\nu)],$$

$$(H^{(1,0)}_{\mu\nu})_\alpha = (e\hbar/2mc)\langle\phi_\mu|(\boldsymbol{r}_{\mathrm{A}}\wedge\boldsymbol{\nabla})_\alpha|\phi_\nu\rangle. \qquad (3)$$

The equation used in the present calculation was simplified by means of the Alger, Grant, and Paul assumption[2] for the angular momentum operators. Then,

$$\langle\phi_\mu{}^{\mathrm{A}}|\phi_\nu{}^{\mathrm{B}}\rangle = \langle\phi_\mu{}^{\mathrm{A}}|l_\alpha{}^{\mathrm{A}}|\phi_\nu{}^{\mathrm{B}}\rangle = 0,$$

$$\langle\phi_\mu{}^{\mathrm{A}}|r_{\mathrm{A}}{}^{-3}l_\alpha{}^{\mathrm{A}}|\phi_\nu{}^{\mathrm{B}}\rangle = \langle\phi_\mu{}^{\mathrm{B}}|r_{\mathrm{A}}{}^{-3}l_\alpha{}^{\mathrm{A}}|\phi_\nu{}^{\mathrm{B}}\rangle = 0,$$

$$l_\alpha{}^{\mathrm{A}} = (\boldsymbol{r}_{\mathrm{A}}\wedge\boldsymbol{\nabla})_\alpha. \qquad (4)$$

There is only one integral which survives the assumptions of Eq. (4) and that does not place all the orbitals on the A atom. It is the integral of the $\langle\phi_\mu{}^{\mathrm{B}}|l_\alpha{}^{\mathrm{A}}|\phi_\nu{}^{\mathrm{B}}\rangle$ form, whose evaluation requires a translation of the coordinates, $l_\alpha{}^{\mathrm{A}} = \mathrm{L}_\alpha{}^{\mathrm{AB}} + l_\alpha{}^{\mathrm{B}}$. The term arising from the $\mathrm{L}_\alpha{}^{\mathrm{AB}}$ portion of $l_\alpha{}^{\mathrm{A}}$ could be shown to be negligible; then:

$$\langle\phi_\mu{}^{\mathrm{B}}|l_\alpha{}^{\mathrm{A}}|\phi_\nu{}^{\mathrm{B}}\rangle = \langle\phi_\mu{}^{\mathrm{B}}|l_\alpha{}^{\mathrm{B}}|\phi_\nu{}^{\mathrm{B}}\rangle. \qquad (5)$$

It was assumed here that the diamagnetic contribution, $\sigma_{\mathrm{d}}{}^{\mathrm{A}}$, is determined by the carbon 1s electrons. This assumption led to the value of 202.4 ppm for the diamagnetic contribution. The paramagnetic contribution, $\sigma_{\mathrm{P}}{}^{\mathrm{A}}$, was calculated from the INDO approximate molecular orbitals with Eqs. (1)—(5). The integral of $\langle\phi_\mu{}^{\mathrm{A}}|r_{\mathrm{A}}{}^{-3}l_\alpha{}^{\mathrm{A}}|\phi_\nu{}^{\mathrm{A}}\rangle$ in Eq. (1) reduces to the evaluation of $\langle r_{\mathrm{A}}{}^{-3}\rangle_{2\mathrm{p}}$. This was estimated by using the Slater 2p orbitals and by choosing the appropriate nuclear charge, Z_{A}. The effective nuclear charge was given by Eq. (6):

$$Z_{\mathrm{A}} = 3.25 - 0.35(P_{\mathrm{A}} - 4), \quad P_{\mathrm{A}} = \sum_{\lambda}^{\mathrm{A}} P_{\lambda\lambda}(0). \qquad (6)$$

Since $P_{\mu\nu}{}^{\mathrm{Im}}(H_\alpha)$ is an odd function of H_α, the derivatives in Eq. (1) are given approximately by:

$$(\partial/\partial H_\alpha[P^{\mathrm{Im}}_{\mu\nu}(H_\alpha)])_{\mathrm{H}=0} = P^{\mathrm{Im}}_{\mu\nu}(H_\alpha)/H_\alpha. \qquad (7)$$

The magnitude of H_α used was 5×10^6 Gauss; this gave about 10^{-3} a.u. as the perturbation energy. The diagonalization of the Hermitian matrix, F, was performed by means of a FACOM 230-60 computer in the Hok-

TABLE 1. CALCULATED AND EXPERIMENTAL VALUES OF ^{13}C CHEMICAL SHIFT (ppm)

		σ_{p}	σ	Exptl σ
C_2H_2		-103.6	98.8	-76[a]
C_2H_4		-158.7	43.7	-126[a]
C_2H_6		-120.5	81.9	-8.0[a]
C_6H_6		-161.3	41.1	0[b]
C_6H_5F	C–F	-164.1	38.3	-34.8[b]
	o	-160.2	42.2	12.9[b]
	m	-162.8	39.6	-1.4[b]
	p	-160.9	41.5	4.5[b]

a) Shielding constant relative to CH_4. Ref. 4.
b) Shielding constant relative to C_6H_6. G. L. Nelson, G. C. Levy, and J. D. Cargioli, *J. Amer. Chem. Soc.*, **94**, 3089 (1972).

kaido University Computer Center, using a CDIAG program written by the author. The results are given in Table 1.

Although the approximation of the above calculation is of the same degree as that of Karplus and Pople1b) or of Alger, Grant, and Paul's2) semiempirical calculations, the estimated values of σ_p in Table 1 are about a half the values obtained by the latter average excitation approximation. Ditchfield, Miller, and Pople's *ab initio* calculation by the finite perturbation indicated an excellent agreement with the experimental values. However, the finite perturbation calculation in the simple molecular orbital method indicates rather poorer agreement with the experiment than does the average excitation method. This seems to be because the average excitation approximation cancels the neglect of the overlap integrals of the angular momentum operators. Recently Maciel *et al.*5) have reported that he INDO finite perturbation calculation of ^{13}C chemical shifts with an altered set of parameters reproduced successfully the experimental results. However, they have not shown clearly why the standard INDO parameters should be altered.

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