Since $\bar{E}_i$ for large polyatomic molecules can be quite large, it is important that consideration be given to the effect that the method of determining AE_T(exptl) has on $\Delta H_f{}^\circ{}_T$(ion). If AE_T(exptl) is determined by any method other than that based on an extrapolation of a linear post-threshold region, the relationship between AE_T(exptl), AE_0(exptl), and $\bar{E}_i$ must be reestablished and the appropriate modifications made to eq IX. Work is underway in our laboratory to assess the difficulties associated with the application of the above method to larger systems, particularly fragmentations involving the loss of a diatomic or polyatomic neutral species.

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Calculation of the Nuclear Spin-Spin Coupling Constants. 3. σ- and π-Electron Contributions in Some Simple Unsaturated Hydrocarbons

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Abstract: The sum-over-states calculations of the nuclear spin-spin coupling constants by Nakatsuji's formula, including doubly excited configurations, have reproduced exact finite perturbation results. in addition, a new method of separation of the coupling constants into σ- and π-electron contributions has been proposed. It has been shown that π-electron coupling constants alternate in sign with the number of bonds while their magnitudes are approximately independent of the number of bonds.

Introduction

In papers 1[1] and 2[2] of this series, we showed that the finite perturbation (FP) method is superior to the sum-over-states (SOS) one in the calculation of the nuclear spin-spin coupling constants. This is because FP calculations show a clear convergence to experimental values as the size of the basis set is increased. On the other hand, the SOS calculations show divergence even if the singly excited triplet configuration interaction calculation (we denote as SOS1) is invoked.[3] Ditchfield et al.[4] studied the relation between the SOS and FP methods and pointed out that the FP theory corresponds to introducing doubly excited states in a restricted way (see the following section). We thus conjectured that the doubly excited states introduced into the FP calculation brought about the convergent trend. However, no proof of this could be presented directly in our previous papers. It would therefore seem important to confirm whether the SOS calculations with double excitations (we denote as SOS2) can reproduce the FP results, and this we do in this paper. Moreover, the SOS2 method makes it possible to estimate the π contribution to the nuclear spin-spin coupling constant, which is quite difficult in the FP method. Thus we will show the separation of the nuclear spin-spin coupling constant into the sum of the σ and π-contributions.

Method

Nakatsuji[5] showed that eq 50 of his paper is the best expression of the second-order SOS perturbation energy based on the Hartree-Fock (HF) wave function. From this expression for the second-order perturbation energy, we can write the SOS2 formula for the nuclear spin-spin coupling constants, $J_{NN'}$ (in Hz), in the INDO level as follows (in SI units):

$$J_{NN'} = -\frac{64}{9}\mu_B{}^2 h\left(\frac{\mu_0}{4\pi}\right)^2 \gamma_N\gamma_{N'}S_N(0)^2 S_{N'}(0)^2 \times \sum_n \sum_{ij}^{\substack{\sigma\\ \text{occ}}} \sum_{ab}^{\substack{\sigma\\ \text{unocc}}} T_n{}^{-1} V_{i\to a,n} V_{j\to b,n} C_{Ni} C_{Na} C_{N'b} C_{N'j} \quad (1)$$

where T_n is the nth eigenvalue of the **H** matrix defined below. $V_{i\to a,n}$ is the coefficient of the triplet excitation i → a in the nth eigenvector of H. μ_0 is the magnetic permeability in vacuo. The other notations are the same as in eq 3.2 in the review by Kowalewski.[6] The matrix **H** is defined as follows:

$$\mathbf{H}_{i\to a,j\to b} = \langle {}^3\Psi_{i\to a}|\mathbf{H}_0|{}^3\Psi_{j\to b}\rangle + \langle {}^1\Psi_0|\mathbf{H}_0|\Psi_{i\to a,j\to b}\rangle - \delta_{ij}\delta_{ab}\langle {}^1\Psi_0|\mathbf{H}_0|{}^1\Psi_0\rangle \quad (2)$$

where $\mathbf{H}_0$ is the unperturbed Hamiltonian and ${}^1\Psi_0$ is the ground-state wave function approximated by the single determinant composed of doubly occupied SCF MO's. The triplet states ${}^3\Psi_{i\to a}$ are formed by promoting one electron from an occupied MO, ψ_i, to an unoccupied one, ψ_a. $\Psi_{i\to a,j\to b}$ are the doubly excited wave functions which are not the eigenfunctions of the total electronic spin operator $\hat{S}^2$. They are written explicitly as $\Psi_{i\to a,j\to b} = \|\ldots iajb(\alpha\beta\alpha\beta + \alpha\beta\beta\alpha + \beta\alpha\alpha\beta + \beta\alpha\beta\alpha)/2\ldots\|$ in standard notation.

Using the SCF MO energies ϵ_i associated with ψ_i and the molecular integrals of electron repulsion, we can rewrite the matrix elements of **H** as

$$\mathbf{H}_{i\to a,j\to b} = \delta_{ij}\delta_{ab}(\epsilon_a - \epsilon_i) - [ij|ab] - [ib|ja]$$

where $[ij|ab] = \int \psi_i(1)\psi_j(1)r_{12}{}^{-1}\psi_a(2)\psi_b(2)\, d\tau_1 d\tau_2$. The real symmetric matrix **H** is diagonalized to give the diagonal matrix **T** by the orthogonal matrix **V** whose nth column vector gives the coefficients $V_{i\to a,n}$ in eq 1. Thus $HV = VT$.

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Table I. Calculated and Experimental Values of the Nuclear Spin-Spin Coupling Constants (Hz)

	J^{σ}-(SOS2)[a]	J^{π}-(SOS2)[a]	J-(SOS2)[a]	J-(FP)[b]	(exptl)[b]
		Ethylene			
C-C	67.19	14.95	82.14	82.14	67.6
C-H	152.33	4.36	156.69	156.71	156.4
C-C-H	−7.22	−4.36	−11.58	−11.57	−2.4
H-C-H	4.51	−1.27	3.24	3.24	2.5
H-C-C-H (cis)	8.04	1.27	9.31	9.31	11.7
H-C-C-H (trans)	23.88	1.27	25.15	25.15	19.1
		Acetylene			
C-C	143.66	20.07	163.73	163.75	171.5
C-H	226.91	5.71	232.62	232.65	248.7
C-C-H	8.24	−5.72	2.52	2.52	49.3
H-C-C-H	9.36	1.63	10.99	10.99	9.5
		Benzene			
C-C	67.90	8.20	76.10		
C-C-C	−4.88	−6.05	−10.93		
C-C-C-C	5.48	6.19	11.67		
C-H	137.16	2.99	140.15	140.29	157.5
C-C-H	−2.70	−2.24	−4.94	−4.94	1.0
C-C-C-H	7.77	1.63	9.40	9.40	7.4
C-C-C-C-H	−0.49	−1.78	−2.27	−2.27	−1.1
H-C-C-H	7.54	0.60	8.14	8.15	7.54
H-C-C-C-H	2.56	−0.43	2.13	2.13	1.37
H-C-C-C-C-H	0.63	0.52	1.15	1.15	0.69

[a] See Method. [b] Cited from ref 8.

We have to turn our attention to the fact that the form of the doubly excited terms of the second-order wave function $\Psi_{(2)}$ in the Nakatsuji's perturbation theory (on which our SOS2 formula is based) is restricted. This restriction is the same as that on the doubly excited states included in the FP theory, which Ditchfield et al.[4] have already discussed in comparison with SOS and FP theories.[7] The terms included in $\Psi_{(2)}$ are not free from the singly excited terms of the first-order wave function $\Psi_{(1)}$. Although there are the other doubly excited states not included in $\Psi_{(2)}$, they do not contribute to the second-order energy $E_{(2)}$ as shown in Appendix B of Nakatsuji's paper. This fact is very fortunate for our SOS2 calculation.

We can divide the possible promotions of an electron, i → a, into three classes. Namely, the first category includes $\sigma \rightarrow \sigma^*$ excitations only, if we denote unoccupied MO's by *. The second one is for $\pi \rightarrow \pi^*$ excitations, and the third is for $\sigma \rightarrow \pi^*$ and $\pi \rightarrow \sigma^*$ ones. It is clearly seen in eq 3 that the promotions belonging to the third category do not mix with the first- and second-type promotions. Therefore, we can neglect the third-type excitations in the calculation of nuclear spin–spin coupling constants because both i and a in promotions i → a have to be σ-type MO's to include valence s-type AO's.

It is obvious that the π-electron contribution $J^{\pi}{}_{NN'}$ to $J_{NN'}$ originates from the $H_{\sigma\rightarrow\sigma^*,\pi\rightarrow\pi^*}$ elements of **H**, which produce σ–π configuration interaction. So we can estimate the σ contribution $J^{\sigma}{}_{NN'}$ if we neglect the above elements, that is, configurational mixing between first- and second-type promotions. We define here $J^{\pi}{}_{NN'}$ as $J^{\pi}{}_{NN'} = J_{NN'} - J^{\sigma}{}_{NN'}$.

Results and Discussion

We calculated $J^{\sigma}{}_{NN'}$, $J^{\pi}{}_{NN'}$, and $J_{NN'}$ for the three typical unsaturated hydrocarbons, that is, ethylene, acetylene, and benzene molecules using the SOS2 formula in INDO level and compared them with the FP results of Pople et al.[8] We used the same parameters as did Pople et al. in their FP calculations and standard molecular geometry. Our calculated results are presented and compared with Pople et al.'s FP values and experimental ones in Table I. The computational times of the two methods, SOS2 and FP ones, were not so different. For example, for C_2H_4 SOS2 took 7.2 s; FP, 8.7 s.

Table I shows that the SOS2 formula reproduces the FP values quite exactly. Therefore, now it has been proved that the convergent trend of J's calculated by FP comes from inclusion of the double excitations. We have to include a contribution from the doubly excited configurations to get the correct excited states and energies.

The calculated π-electron coupling constants show clearly the alternation in sign with the number of intervening bonds. The odd numbers of bonds correspond to positive π couplings and the even numbers to negative ones. This result is the same as that concluded by Barfield[9] about the J^{π}'s of octatetraene calculated by the SOS VB (valence-bond) method. From Table I it is concluded that J^{σ} is dominant in the directly bonded coupling constants, ${}^1J_{CC}$ and ${}^1J_{CH}$, and proton–proton coupling constants, J_{HH}. However, in ${}^2J_{CC}$ and ${}^2J_{CH}$ two parts equally contribute. The magnitude of J^{π} is approximately independent of the number of bonds while that of J^{σ} attenuates rapidly (as a function of the number of bonds). Therefore, in the long-range proton–proton couplings, J^{π} will be dominant.

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(7) The two restrictions stated by Nakatsuji[5] and Ditchfield et al.,[4] respectively, are equal to each other. This is because eq 38 of the Nakatsuji's paper is equivalent to eq 13 and 29 of the Ditchfield paper.

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