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Calculation of Directly-Bonded Nuclear Spin-Spin Coupling Constants with Localized Orbitals

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Synopsis. The directly-bonded nuclear spin-spin coupling constants were calculated by a perturbation method involving the summing over singly-excited states using localized orbitals. It is shown that a localized representation of orbitals in the perturbation expansion can be of considerable value both for interpretative purposes and for assessing the rate at which the pertubation expansion converges.

Although the Hartree-Fock (HF) variational condition selects the occupied and virtual manifolds, it does not completely determine the individual orbitals belonging to each manifold.[1] This orbital ambiguity yields the possibility of obtaining a new set of orbitals, within unitary transformations, which may be more suitable for the investigation of a particular physical problem than the original set of canonical molecular orbitals (CMO). The most interesting case is that of a transformation in which the orbitals are localized as much as possible.

One can employ the perturbation theory starting with a wave function constructed from localized molecular orbitals (LMO) as easily as CMO constructed wave functions. There is a theoretical advantage in using LMO- rather than CMO-based wave functions, since the LMO can often be chosen to be localized in a particular region of space, whereas the CMO are usually delocalized. If the perturbation can be expressed as a series of local perturbations which affect only a relatively small region of space, then there may be some advantages in choosing the original orbitals to reflect this localization.[2,3]

The second-order property of a system may be calculated in the perturbation approach employing a summing over excited states from the second-order energy $E^{(2)}$ or the first-order wave function $\Psi^{(1)}$:

$$E^{(2)} = \langle \Psi_0 | H' | \Psi^{(1)} \rangle$$

$$\Psi^{(1)} = \sum_n{}' C_n \Psi_n, \quad C_n = \langle \Psi_0 | H' | \Psi_n \rangle / (E_0 - E_n) \qquad (1)$$

where H' is the operator describing the perturbation and $\{\Psi_n\}$ is a complete set of eigenfunctions of the zeroth-order Hamiltonian H_0 with the set of eigenvalues $\{E_n\}$

$$H_0 \Psi_n = E_n \Psi_n \quad (n=0, 1, \cdots). \qquad (2)$$

Here the sum in Eq. 1 is over an infinite number of excited states. However, since it is impossible to obtain a set of exact wave functions satisfying Eq. 2, some approximation must be introduced. The most frequent approximation to Eq. 1 is to replace Ψ_0 by the HF wave function and Ψ_n by singly-excited configurations, cutting off from the sum other excited configurations. To this approximation, $E^{(2)}$ depends on the unitary transformation of the singly-excited configurations. It would be expected that an LMO set would guarantee a more rapid convergence of the perturbation expansion than a CMO set.

TABLE 1. RESULTS OF J_{AB} (Hz) FOR THE DIRECTLY-BONDED NUCLEI IN SOME HYDROCARBONS FOR INDO-MO CALCULATIONS

Molecule		Fermi	Spin dipolar	Orbital	Total	Exptl.[a]
CH coupling						
CH_4	CMO[b]	64.6	0.0	0.0	64.6	
	LMO[c]	117.1	0.0	0.0	117.1	125
	FPM[d]	121.0	0.0	0.0	121.0	
C_2H_6	CMO	57.8	0.0	0.0	57.8	
	LMO	112.2	0.0	0.0	112.2	125
	FPM	119.8	0.0	0.0	119.8	
C_2H_4	CMO	80.1	0.0	0.0	80.1	
	LMO	132.8	0.0	0.0	132.8	156.2
	σ-π[e]	133.3	0.0	0.0	133.3	
	FPM	150.2	0.0	0.0	150.2	
C_2H_2	CMO	141.9	0.0	0.0	141.9	
	LMO	186.1	0.0	0.0	186.1	249
	σ-π	189.4	0.0	0.0	189.4	
	FPM	226.4	0.0	0.0	226.4	
CC coupling						
C_2H_6	CMO	6.6	0.4	−0.8	6.2	
	LMO	27.2	0.2	−1.3	26.2	34.6
	FPM	18.6	0.6	−1.0	18.3	
C_2H_4	CMO	20.8	1.4	−5.4	16.8	
	LMO	71.6	0.5	−3.2	68.9	67.6
	σ-π	45.6	1.9	−2.6	43.1	
	FPM	36.7	2.4	−3.4	35.7	
C_2H_2	CMO	56.1	4.2	6.1	66.5	
	LMO	141.1	2.2	1.4	144.7	171.5
	σ-π	75.8	4.5	7.0	87.3	
	FPM	73.4	4.6	7.4	85.4	

a) R.M.Lynden Bell and N. Sheppard, *Proc. R. Soc. London, Ser. A*, **269**, 385 (1962). b) CMO-SOSP results. c) unconstrained LMO-SOSP results. d) FP results. e) σ-π constrained LMO-SOSP results.

In order to test the LMO effects, model calculations were made of nuclear spin-spin coupling constants using INDO-MO[4] and the sum-over-singly excited-state perturbation (SOSP) method. Computational details have been described in a previous paper.[5] The LMO are obtained by minimizing the off-diagonal exchange energy according to the Edminton-Ruedenberg procedure.[6] The virtual orbitals were also transformed in the same manner. The calculated nuclear spin-spin coupling constants are summarized in Table 1. In the table, LMO denotes the SOSP values with a complete LMO set (*i.e.*, banana-type CC bonding orbitals are obtained for C_2H_4 and C_2H_2) and σ-π denotes the results of σ-π constrained LMO. In order to examine the refinement of LMO perturbation approximation, the coupling constants calculated with the SOSP method using CMO and those using the finite perturbation (FP) method[7] are also listed. It is to be noted here that the FP treatment which is equivalent to the coupled HF perturbation theory is the most accurate of the three different approaches, since in the FP approximation some doubly-excited states, in addition to the singly-excited states, can be included in the perturbed wave function.[8]

The LMO and σ-π results for CH coupling constants show a significant shift towards the FP results. Especially LMO values for CH_4 and C_2H_6 (saturated molecules) are in good agreement with the FP values. The Fermi contributions calculated using the FP method are always larger than those obtained using the SOSP method. It has been suggested that the difference in the second-order properties calculated by the FP method and those by the SOSP method is essentially due to the fact that in the FP treatment one cannot introduce singly-excited states without introducing at the same time doubly-excited states in a restricted manner.[8] That is, if we take the Ψ_n to be singly-excited triplet states, $^3\Psi_{i\to a}$, for spin-dependent perturbations like the Fermi interaction, the approximate equation for C_{ia} in Eq. 1 is

$$C_{ia} = -\langle\Psi_0|H'|^3\Psi_{i\to a}\rangle/(^3\Delta E_{i\to a}) \tag{3}$$

in the SOSP method. Here $^3\Delta E_{i\to a}$ is the triplet excitation energy. On the other hand, in the FP approximation, C_{ia} takes the first-order form

$$C_{ia} = -\langle\Psi_0|H'|^3\Psi_{i\to a}\rangle/(^3\Delta E_{i\to a}-K_{ia}), \tag{4}$$

where the exchange integral K_{ia} comes from the doubly-excited configuration. Taking this into consideration, the reproduced trend in the CH coupling which is that the LMO-SOSP results are shifted from the CMO-SOSP results toward the FP values, would indicate that an LMO set gives a more rapid convergence of the perturbation expansion than a CMO set.

In CC couplings, σ-π constrained LMO results are also shifted towards the FP results, although the former exceed the latter in magnitude, while unconstrained LMO values are somewhat too large.

A comparison with the FP results indicates that better results would be obtained for C_2H_4 and C_2H_2 with σ-π constrained LMO than those obtained with banana-type LMO, although the latter agree well with the experimental results. In view of the energy localization criterion, the banana-type LMO are more localized than the σ-π constrained LMO. Nevertheless, maintaining the σ-π constraint and hence using less localized orbitals appears to be a better starting point of the perturbation expansion based on HF wave functions.

Next, let us examine the electronic origin of the coupling mechanisms. In the conventional perturbation theory with delocalized orbitals, the calculated result are determined by a very complicated cancellation of a number of large values and hence it is not easy to interpret the results. However, the LMO perturbation theory allows an easier qualitative interpretation of the results. As summarized in Table 2, the Fermi term for the CH couplings are determined by only one transition from the localized CH bonding orbital to the corresponding antibonding orbital. That is, the CH coupling can be expressed as a "local" contribution. The same is true for CC couplings. In the σ-π constrained LMO perturbation method, the transition from a localized CC bonding orbital to an antibonding orbital determines the Fermi term of the CC coupling. For the perturbation with banana-type orbitals, the transitions from banana-type CC bonding orbitals to the corresponding antibonding orbitals play an important role. Moreover, each contribution has the same sign, implying that there is no partial cancellation. Thus, the results can always be expressed as the sum of "local" contributions. Namely, the LMO perturbation results are useful for describing local properties and are of conceptual simplicity. This is an essential advantage in employing LMO perturbation theory. From this point of view, the σ-π constrained LMO appear to be more suitable than the unconstrained LMO.

TABLE 2. CONTRIBUTIONS OF "local" TRANSITIONS TO THE FERMI TERM

Molecule		Local transitions[a)]	Transition energy (eV)	Contribution of local transition (Hz)	Total Fermi term (Hz)
CH coupling					
CH_4	LMO	ω (2.67)[b)] $\to\omega^*$ (3.38)	16.74	117.3	117.1
C_2H_6	LMO	ω (2.81) $\to\omega^*$ (3.40)	16.95	112.3	112.2
C_2H_4	LMO	ω (2.09) $\to\omega^*$ (2.77)	17.44	130.0	132.8
	σ-π	ω (1.95) $\to\omega^*$ (2.61)	17.61	134.8	133.3
C_2H_2	LMO	ω (1.19) $\to\omega^*$ (1.69)	18.21	176.5	186.1
	σ-π	ω (0.97) $\to\omega^*$ (1.43)	18.49	193.2	189.4
CC coupling					
C_2H_6	LMO	σ (2.67) $\to\sigma^*$ (2.73)	22.92	31.8	27.2
C_2H_4	LMO	λ_1 (3.60) $\to\lambda_1^*$ (4.05)	18.59	23.1	
		λ_1 (3.60) $\to\lambda_2^*$ (4.05)	19.93	21.5	
		sum[c)]		89.2	71.6
	σ-π	σ (1.47) $\to\sigma^*$ (1.68)	28.84	52.2	45.6
C_2H_2	LMO	λ_1 (3.75) $\to\lambda_1^*$ (4.64)	18.29	20.3	
		λ_1 (3.75) $\to\lambda_2^*$ (4.64)	19.55	19.0	
		sum		174.6	141.1
	σ-π	σ (0.72) $\to\sigma^*$ (1.09)	33.09	86.4	75.8

a) Explanation of notation: $\omega\to\omega^*$ the transition from a CH bonding orbital to the corresponding antibonding orbital, $\sigma\to\sigma^*$ the transition from a CC bonding orbital to an antibonding orbital in $\sigma\to\pi$ constrained LMO form, $\lambda\to\lambda^*$ the transition from CC banana type orbitals to the corresponding antibonding orbitals in unconstrained LMO form. b) Carbon atom hybrids of CH and CC bonds (sp^x) are shown in parenthesis. c) The sum denotes the sum over local transitions (*i.e.* sum$=2\{(\lambda_1\to\lambda_1^*)+(\lambda_1\to\lambda_2^*)\}$ in C_2H_4 and sum$=3\{(\lambda_1\to\lambda_1^*)+2(\lambda_1\to\lambda_2^*)\}$ in C_2H_2).

In this note, the advantages of the LMO in perturbation theory were stressed, using the case of directly-bonded nuclear spin-spin coupling constants as an example and it was shown that a localized representation of orbitals in the perturbation expansion can be of considerable value both for interpretative purposes and in assessing the rate at which perturbation expansion converges. The σ-π constrained LMO for unsaturated molecules seem to be, in every respect, better than the banana-type orbitals as a starting point for the perturbation expansion. The success of LMO perturbation theory in describing local properties should provide a justification of the additivity of such bond properties as the polarizability and the susceptibility.

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