Theoret. Chim. Acta (Berl.) 61, 49–57 (1982)

THEORETICA CHIMICA ACTA

Unrestricted Hartree–Fock Instabilities in Nuclear Spin–Spin Coupling Calculations. The MNDO Method*

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The MNDO wavefunction is used to calculate the Fermi contact term of nuclear spin–spin coupling constants. Owing to the presence of non-singlet unrestricted Hartree–Fock instabilities of the wavefunction, convergence problems arise in a rather large set of molecules, especially those containing π molecular orbitals. A special technique to cope with this situation is presented. The MNDO π and σ transmitted components of the coupling constants in the ethylene molecule are also calculated and compared with those previously obtained with the INDO and INDO/S methods.

Key words: UHF instabilities – MNDO – NMR spin–spin coupling constants.

1. Introduction

The theoretical calculation of nuclear spin–spin coupling constants has proved to be a very difficult task for the molecular orbital theory [1]. In general *ab initio* results are better than those obtained with semiempirical calculations only when extended basis sets are used and CI is included [2]. These calculations are too expensive, and therefore, for large molecular systems semiempirical methods are frequently sought. The best agreement with experiment was found with INDO wavefunctions. Calculations have been performed with the FP [3] and SCP [4] schemes, both within the coupled Hartree–Fock, CHF [5] theory, and with a double perturbation method [6]. However, the shortcomings of these

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* Part of a Ph.D. thesis (G.E.S.) to be presented to the University of Buenos Aires.

** Commission of Scientific Research (CIC, Pcia. Bs. As.) fellow.

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results are very well known [1] and experimental trends are at most qualitatively reproduced. In order to overcome these shortcomings several attempts were made either to improve the INDO method performance [7–9] or to use other semiempirical wavefunctions, especially those which proved to be more suitable to describe different molecular properties. Regarding the latter approach, the use of the MINDO/3 [10, 11] method and the previous paper on the use of CNDO/S and INDO/S wavefunctions are worth mentioning [12]. None of them, within the monocentric approximation [13], have achieved the performance of the FP INDO method of Pople et al. [3].

In this paper attention is focused on the MNDO method [14] which successfully reproduces a number of molecular properties and so far it remains untested against experimental results for coupling constants.

Only couplings where at least one proton is involved are considered. Therefore, calculations are restricted only to the Fermi contact term, and they are implemented using the SCP scheme of Blizzard and Santry [4] of the CHF theory. Convergence difficulties are found in a large set of molecules containing a π-electron system. In a previous paper [12] the origin of such convergence problems was thoroughly analyzed and it was found that in the case concerning the present problem, they originate from Unrestricted Hartree–Fock (UHF) instabilities of the closed-shell Restricted Hartree–Fock (RHF) wavefunction [16]. The connection between both phenomena can be easily understood in physical terms: when a perturbation breaking the spin-symmetry constraints is introduced into a system with a non-singlet unstable closed-shell wavefunction, the iterative procedure of the SCP method is non-convergent or "error increasing" since the opening of the shell is advantageous for the wavefunction to decrease the total molecular energy.

The MNDO Fermi contact term of the spin–spin coupling constants in molecules with stable wavefunctions will be presented elsewhere [17]. In this paper attention is paid only to molecules with unstable or with "quasi-unstable" MNDO wavefunctions. A method to enforce convergence in these difficult cases is employed. As it is also the case with the CNDO/S and INDO/S [12] methods, UHF instabilities are found to be related to the π-electronic system. For this reason, the π-electron transmitted component of the Fermi contact term of spin–spin couplings was also calculated. This decomposition of σ- and π-transmitted components was accomplished with a modified version of the PRMO (Partially Restricted Molecular Orbitals) method which was reported elsewhere [18]. These modifications were required since in the previous paper [18] the FP instead of the SCP method was used.

2. Methods of Calculation

2.1. The Perturbation Scheme

The MNDO program [19] was modified in order to include a subroutine that allows the calculation of the Fermi contact term of spin–spin coupling constants within the SCP procedure [4]. The perturbation equations used are:

$$c^{(1)}_{\mu i} = -\sum_{l}^{\text{unocc}} \sum_{\nu,\lambda} \frac{c_{\mu l} c_{\nu l}}{\varepsilon_l - \varepsilon_i} F^{(1)}_{\nu\lambda} c_{\lambda i} \tag{1}$$

where $c^{(1)}_{\mu i}$ are the first order corrections to the MO coefficients, $c_{\lambda i}$; $F^{(1)}_{\nu\lambda}$ is the first order correction to the Fock operator matrix and ε_i are the orbital energies. The first summation is over the unoccupied MO's and those with Greek indices are over the whole AO basis.

To be consistent with the MNDO approximation the first order correction to the electron repulsion part (which appears in $F^{(1)}_{\mu\nu}$ added to the perturbation) should be written as:

$$G^{\alpha(1)}_{\mu\mu} = -g_{\mu\mu} P^{\alpha(1)}_{\mu\mu} - \sum_{\nu \neq \mu}^{A} h_{\mu\nu} P^{\alpha(1)}_{\nu\nu} \tag{2}$$

$$G^{\alpha(1)}_{\mu\nu} = -(g_{\mu\nu} + h_{\mu\nu}) P^{\alpha(1)}_{\mu\nu} \tag{3}$$

$$G^{\alpha(1)}_{\mu\lambda} = -\sum_{\nu}^{A} \sum_{\sigma}^{B} (\mu\nu, \lambda\sigma) P^{\alpha(1)}_{\nu\sigma} \tag{4}$$

where: μ and ν indicate atomic orbitals of atom A, λ and σ indicate atomic orbitals of atom B, $P^{\alpha^{(1)}}$ is the first order correction to the α bond-order, $g_{\mu\nu}$ and $h_{\mu\nu}$ are the one-center two-electron Coulomb and exchange integrals of the MNDO parametrization, $(\mu\nu, \lambda\sigma)$ are the two center two-electron repulsion integrals of the MNDO method.

Therefore, also with the MNDO approximation, the perturbation equations constitute a linear system, which is solved using an iterative procedure. In matrix form these equations may be written as before [12]

$$U = DSU + DH \tag{5}$$

where U is a column matrix which contains the first order corrections to the MO coefficients and it has a dimension equal to the number of single excitations; D is a diagonal matrix whose elements are the inverse of the difference of the eigenvalues associated with the excitation; S is a symmetrical matrix representing the electronic interaction, and H is a column matrix containing the matrix elements of the perturbation Hamiltonian between the MO's involved. The monocentric approximation for the Fermi contact term has been used throughout the calculations reported here.

For the present purpose Eq. (5) can also be written in terms of a new unknown matrix, $X = D^{-1/2}U$,

$$X = TX + J \tag{6}$$

where $T = D^{1/2}SD^{1/2}$ is a symmetric matrix and the perturbation is contained in $J = D^{1/2}H$.

Instead of reparametrizing the electronic densities at the nucleus, the corresponding values of the FP INDO method have been used, i.e. $S^2_{\mathrm{H}}(0) = 0.3724$ a.u. and $S^2_{\mathrm{C}}(0) = 4.0318$ a.u.

2.2. *The Enforcement of Convergence*

In all calculations of coupling constants reported in this paper, convergence problems were found in the iterative procedure used to solve Eq. (6). These problems were of two kinds, namely: (a) a slowly convergent process, (b) a non-convergent calculation. The latter case, as shown before, [12] implies that the wavefunction has an Unrestricted Hartree–Fock instability of the non-singlet type. On the other hand, in the former case one may speak of a "quasi-instability" of the wavefunction. To obtain convergence in one case and to save computing time in the other, the following procedure was adopted: it is known [15] that the convergence of the iterative procedure is ruled out by the size of the absolute value of the largest eigenvalue of matrix T. If it is larger than unity, then convergence is not achieved. If it is slightly smaller than unity, then the convergence is slower the closer to unity its value is.

The column matrix X_n, solution of the nth iteration, is:

$$X_n = \sum_{i=0}^{n} T^i J. \tag{7}$$

When the spectral resolution of the operator T is used explicitly, it is found that:

$$X_n = \sum_{i=1}^{n} \frac{1-\lambda_i^{n+1}}{1-\lambda_i} P_i J \tag{8}$$

where λ_i are the T eigenvalues, and P_i are their projectors.

If there is only one eigenvalue larger or close to unity, as the iterations progress the main variation of the unknown matrix X takes place in the subspace to which it belongs. Let λ_1 be this largest eigenvalue.

Then it is possible to extrapolate a better approximation to the solution, in the kth iteration, as:

$$X_\infty^{(k)} = \frac{X_k - \lambda_1^{(k)} X_{k-1}}{1-\lambda_1^{(k)}} \tag{9}$$

where

$$\lambda_1^{(k)} = \frac{\|X_k - X_{k-1}\|}{\|X_{k-1} - X_{k-2}\|} \tag{10}$$

is an estimation of the largest eigenvalue (the double bars indicate a suitable norm).

The error in the extrapolated result introduced by the assumed value of the eigenvalue may be calculated as follows:

$$\delta X^{(k)} = \left\| \frac{\partial X^{(k)}}{\partial \lambda_1^{(k)}} \right\| |\delta \lambda_1^{(k)}| \cong \frac{\|X_k - X_{k-1}\|}{(1-\lambda_1^{(k)})^2} |\lambda_1^{(k)} - \lambda_1^{(k-1)}|. \tag{11}$$

In the present work this extrapolation procedure was carried out when the error defined in Eq. (11) was 0.1 times the required precision in coupling constants. Self consistency was always achieved one or two cycles after the extrapolation was carried out, both for molecules with unstable and quasi-unstable wave functions. In general the solution of Eq. (5), using this extrapolation procedure, was obtained after 15–20 iterations, and simultaneously the largest eigenvalue of matrix T was found.

2.3. The PRMO *Method Within the* SCP *Scheme*

A method for separating the σ- and π-electron transmitted components of coupling constants within a SCF-LCAO-MO calculation was reported elsewhere [18]. However, in that paper it was applied to the FP INDO method. As in the present work coupling constants are calculated within the SCP scheme, it was necessary to adapt the idea of a partially restricted molecular orbital (PRMO) calculation to this formalism.

The PRMO procedure consists in partitioning the space spanned by the AO's into two subspaces, from which only one is allowed to be polarized by a spin-dependent perturbation, while the other one remains unpolarized. This goal is accomplished in the SCP scheme by restricting summations over Greek indices in Eq. (1) to those AO's which span the subspace which is allowed to be polarized. In other words, Eq. (1) is used in a smaller dimension space.

An equivalent procedure would be to project the MO's onto the unrestricted subspace, without renormalization, and to use Eq. (1) in full. It is interesting to remark that the AO's which are not allowed to be spin-polarized may be not only basis functions but combinations of them, like hybridized orbitals, for example.

The π-component of coupling constants were calculated by subtracting from the values given by the SCP-MNDO method those obtained with a PRMO calculation in which the AO's belonging to the π-electron system were restricted (hence giving the σ-transmitted component).

3. Results and Discussion

In Table 1 a set of H—H and C—H coupling constants as calculated with the SCP MNDO method are displayed. Calculations were carried out with the MNDO optimized geometry obtained with the Davidson, Fletcher and Powell (DFP) procedure [14]. While those molecules marked with footnote c were found to have an UHF MNDO unstable wavefunction, those of the remaining

Table 1. H—H and C—H couplings as calculated by the SCP MNDO method[a]

Molecule and coupling		MNDO (DFP)	INDO[b] (PG)	Exptl.[b]
Ethylene	*gem*	−61.81	3.24	2.5
	cis	58.67	9.31	11.7
	trans	70.33	25.15	19.0
	^{1}C—H	325.67	156.71	156.4
	^{2}C—H	−158.24	−11.57	−2.4
Vinyl Fluoride[c]	*gem*	62.26	−3.20	−3.2
	trans	−53.94	20.73	14.6
Ketene	*gem*	−426.99	−11.92	−15.8
	^{1}C—H	1361.75	168.75	
Allene	*gem*	−44.02		
	^{3}H—H	−435.93	−9.69	−7.0
	^{1}C—H	926.14		
Benzene[c]	*ortho*	−4.48	8.15	7.54
	meta	7.42	2.13	1.37
	para	−6.49	1.15	0.69
	^{1}C—H	169.20	140.29	157.5
	^{2}C—H	17.57	−4.94	1.0
	^{3}C—H	−18.61	9.40	7.4
	^{4}C—H	21.65	−2.27	−1.1

[a] All values are in Hz. Geometry is given in brackets, DFP stands for the optimum obtained with the MNDO method and PG is that of the standard model.
[b] Values taken from Ref. [21].
[c] Molecules with unstable MNDO wavefunctions.

molecules are of a "quasi-unstable" type. For comparison, in the same Table the experimental and the FP INDO calculated values are also given. INDO calculations were carried out with the geometry given by the Pople and Gordon (PG) [20] standard model. In all cases MNDO results are conspicuously in disagreement with experiment as well as with those of the INDO method. Although both sets of calculations were carried out at different geometries, it is important to point out that the stability features of the MNDO wavefunction do not depend upon these geometrical data.

In Table 2 the convergence properties of the SCP procedure for different molecules are illustrated by showing the relationship between the largest eigenvalue of the iteration matrix used when calculating the Fermi contact term (matrix T in Eq. (6)) and the RMS error of the diagonal elements of the first order correction to the bond-order matrix for a different number of iterations. This calculation becomes non-convergent when this largest eigenvalue is greater than unity, and in this case, as it was shown before [12], the corresponding eigenvalue of the matrix used to test for non-singlet instabilities, is negative, indicating the presence of an MNDO RHF unstable wavefunction. For comparison, values for cyclopropane and formaldehyde are also presented, although their MNDO wavefunctions are stable.

Table 2. Convergence characteristics of SCP calculations in some selected molecules

			RMS Error[a]		
Molecule	Geometry	λ_1^b	$k=5$	$k=10$	$k=20$
Cyclopropane	DFP	0.749	$5.09\ 10^{-3}$	$2.57\ 10^{-4}$	$1.40\ 10^{-6}$
Formaldehyde	DFP	0.836	$9.80\ 10^{-3}$	$1.47\ 10^{-3}$	$4.95\ 10^{-5}$
Methylimine	PG	0.953	$1.91\ 10^{-2}$	$1.24\ 10^{-2}$	$5.26\ 10^{-3}$
Ethylene	DFP	0.985	$2.56\ 10^{-2}$	$2.24\ 10^{-2}$	$1.72\ 10^{-2}$
Allene	DFP	0.997	$3.04\ 10^{-2}$	$2.96\ 10^{-2}$	$2.78\ 10^{-2}$
Ketene	DFP	0.998	$2.13\ 10^{-2}$	$2.06\ 10^{-2}$	$1.99\ 10^{-2}$
Vinyl Fluoride	DFP	1.012	$2.55\ 10^{-2}$	$2.84\ 10^{-2}$	$3.48\ 10^{-2}$
Trans Butadiene	PG	1.036	$2.05\ 10^{-2}$	$2.52\ 10^{-2}$	$4.50\ 10^{-2}$
Benzene	DFP	1.049	$1.34\ 10^{-2}$	$1.98\ 10^{-2}$	$4.47\ 10^{-2}$

[a] RMS error of the perturbed density matrix in iteration k.
[b] Largest eigenvalue of the iteration matrix.

As in the case of the CNDO/S and INDO/S wavefunctions, these non-singlet instabilities are closely related to the electronic π system. For this reason, the π- and σ-transmitted components of the Fermi contact term have been analyzed separately by means of the PRMO method. Basically, with this method the π-orbital was not allowed to be spin-polarized. With this restriction on the π-system, the SCP method yields a convergent calculation, and the coupling constants thus obtained are considered to be the σ-transmitted components. Results for ethylene are shown in Table 3. Several features are worthy of note. The path invariance is strictly satisfied and so is the sign alternation with the number of bonds that separate both interacting nuclei. For comparison, in the same Table 3 the FP INDO and the INDO/S π-components calculated in previous papers [12, 18] are also shown. It may be observed that the signs of the MNDO π-components are the same as those obtained with the FP INDO method, while in the INDO/S method they are reversed. However, in the previous paper on INDO/S [12] it was observed that when changing the screening

Table 3. π and σ transmitted components of the Fermi contact term in the ethylene molecule as calculated by the CHF method[a]

		MNDO (DFP)		INDO (PG)	INDO/S (PG)
Coupling	J_T	J_σ	J_π	J_π	J_π
gem	−61.81	−7.53	−54.28	−1.27	4.20
cis	58.67	4.39	54.28	1.27	−4.20
trans	70.33	16.05	54.28	1.27	−4.20
^{1}C—H	325.67	169.74	155.94	4.36	−17.41
^{2}C—H	−158.24	−2.30	−155.94	−4.36	17.41

[a] All values are in Hz. Geometry is given in brackets (see Table 1).

constant so as to render an INDO/S stable wavefunction, the π-transmitted component is of the same sign as that of FP INDO. It is interesting to recall that although the MNDO wavefunction of ethylene is almost unstable, it does not actually present a UHF instability.

4. Conclusions

In this paper instabilities of the UHF non-singlet type in MNDO wavefunctions of some molecules containing a π-electronic system are discussed. For this reason, the quality of spin–spin coupling constants calculated with the MNDO method, in molecules where no instability problems are present, will be reported elsewhere [17].

In a similar discussion on the ability of CNDO/S and INDO/S wavefunctions to reproduce coupling constants [12] it was found that the inclusion of the "screening constant" that makes the semiempirical Hamiltonian more flexible so as to reproduce correctly the photoelectron spectra, yields, in some cases, UHF unstable wavefunctions. In the MNDO method responsibility for this fact lies on the way the carbon bonding parameters are chosen, since this parameter is different for carbon p orbitals and for carbon s orbitals ($\beta_s^0(\mathrm{C}) = -18.985044$ eV; $\beta_p^0(\mathrm{C}) = -7.934122$ eV). It must be noted that using a bonding parameter on p orbitals that is so much smaller has the same influence on the non-diagonal core-Hamiltonian matrix elements as using a screening constant smaller than unity in the p_π-p_π overlap integrals [21]. This assertion is not amenable of an analytical description as it was the case with the CNDO/S method [12] because the π and σ blocks of the matrix used to test for instabilities are no longer disconnected. In this case it was necessary to carry out numerical calculations changing the bonding parameter $\beta_p^0(\mathrm{C})$ to confirm this statement.

The unrealistic results obtained for the π-electron transmitted components of spin–spin coupling constants are not surprising at all since the perturbation theory has no physical meaning in the case of unstable wavefunctions. Nevertheless, the saddle-point structure of the energy surface where the σ electronic system is in a minimum while the π system is in a maximum, does not invalidate the π-restricted molecular calculation where the σ transmitted component of those constants are obtained.

Acknowledgments. The authors are deeply indebted to the authorities of DISCAD (Argentine Air Force Data Processing Centre) and specially to V.C. Rafael E. Sequeiros, for kindly allowing the use of the B6700 system where calculations were carried out. Grants from the Argentine Research Council (CONICET) and from the Argentine Science and Technology Secretariat (SECYT) are gratefully acknowledged.

References

1. Kowalewski, J.: Prog. NMR Spectroscopy **11**, 1 (1977)
2. Kowalewski, J., Laaksonen, A.: J. Chem. Phys. **71**, 2896 (1979)

3. Pople, J. A., McIver, J. W., Ostlund, N. S.: J. Chem. Phys. **49**, 2960 (1968)
4. Blizzard, A. C., Santry, D. P.: J. Chem. Phys. **55**, 950 (1971)
5. Thomsen, K., Swanstrøm, P.: Mol. Phys. **26**, 735 (1973)
6. Denis, A., Malrieu, J. P.: Mol. Phys. **23**, 581 (1972)
7. Contreras, R. H., Engelmann, A. R., Scuseria, G. E., Facelli, J. C.: Org. Magn. Reson. **13**, 137 (1980)
8. Facelli, J. C., Contreras, R. H.: Int. J. Quantum Chem. **18**, 1175 (1980); Int. J. Quantum Chem. **20**, 909 (1981); J. Mol. Struct. (Theochem), **85**, 99 (1981)
9. Tarpø, A., Bildsøe, H., Schaumburg, K.: Acta Chem. Scand. Ser. A **31**, 6 (1977)
10. Dewar, M. J. S., Landman, D., Suck, S. H., Weiner, P. K.: J. Am. Chem. Soc. **99**, 3951 (1977)
11. Pandey, P. K. K., Chandra, P.: Theoret. Chim. Acta (Berl.) **50**, 211 (1978)
12. Scuseria, G. E., Contreras, R. H.: Theoret. Chim. Acta. (Berl.) **59**, 437 (1981)
13. Archirel, P., Barbier, C.: J. Chim. Phys. **75**, 1003 (1978)
14. Dewar, J. M. S., Thiel, W.: J. Am. Chem. Soc. **99**, 4899 (1977); J. Am. Chem. Soc. **99**, 4907 (1977).
15. Fadeeva, V. N.: Computational methods of linear algebra. New York: Dover 1959
16. Chambaud, G., Levy, B., Millie, P.: Theoret. Chim. Acta (Berl.) **48**, 104 (1978) and references cited therein
17. Scuseria, G. E., Facelli, J. C., Giribet, C., Contreras, R. H.: to be published
18. Engelmann, A. R., Contreras, R. H., Facelli, J. C.: Theoret. Chim. Acta (Berl.) **59**, 17 (1981)
19. Thiel, W.: QCPE **10**, 353 (1978)
20. Pople, J. A., Gordon, M.: J. Am. Chem. Soc. **89**, 4253 (1967)
21. Pople, J. A., Beveridge, D. L.: Approximate Molecular Orbital Theory. New York: McGraw-Hill 1970

Received July 22, 1981/October 19, 1981