Unrestricted Hartree–Fock Instabilities in Semiempirical CNDO/S and INDO/S Calculations of Spin–Spin Coupling Constants*

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It is shown that non-convergent calculations of the Fermi contact term of spin-spin coupling constants within the self-consistent and finite perturbation schemes used to solve the coupled Hartree–Fock equations, are originated in non-singlet Hartree–Fock instabilities of the closed-shell restricted Hartree–Fock wavefunction. In CNDO/S and INDO/S wavefunctions, where the electronic system response has been successfully reproduced, all investigated molecules containing π MOs were found to be unstable. Results of spin-spin coupling constants are given and compared with experimental as well as FP and SOS INDO values.

Key words: UHF instabilities – CNDO/S – INDO/S – NMR spin-spin coupling constants.

1. Introduction

The most common theoretical calculations of NMR spin-spin coupling constants have been performed using two different approaches, namely the Sum-Over-States (SOS) [1] and the Coupled Hartree–Fock (CHF) methods [2]. Two schemes, giving identical numerical results, are used to implement the latter, i.e. the Finite Perturbation (FP) [3] and the Self-Consistent Perturbation (SCP) schemes [4]. Calculations have been carried out with these methods employing the semiempirical INDO level of approximation to compare several

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parameterizations [5, 6] and it has been found that, in so far as NMR coupling constants are concerned, the best performance is obtained with the standard one of Pople et al [7]. However, this is not the case when other molecular properties are calculated [8, 9].

In the last few years the INDO/S [10–12] and the CNDO/S [13–15] methods have been successfully employed by Webb et al. [16], to calculate the paramagnetic component of screening tensors. This success [17] is supposed to rest upon the satisfactory prediction of orbital energies given by these semiempirical methods [10]. Since coupling constants are another second order property, a similar improvement can be expected when INDO/S wavefunctions are used to calculate them. However, when calculations of the Fermi contact term are carried out using either the FP or SCP methods, it is found that in molecules containing a π electron system, convergence problems arise in the iterative procedure. In this work it is shown that these convergence problems originate in non-singlet Hartree–Fock instabilities of the wavefunction. Nuclear spin-spin coupling constants are calculated for a set of molecules with INDO/S wavefunction and a special technique is developed for the unstable cases. The numerical results obtained for this term are compared with those of the standard FP INDO method, which is found to remain valid.

2. Theoretical Considerations

The first order perturbation matrix $C^{(1)}$, to the MO coefficient matrix C used in a LCAO MO scheme may be written [4] as:

$$C_{\mu i}^{(1)} = - \sum_{l=M+1}^{N} \sum_{\lambda,\nu} (\varepsilon_l - \varepsilon_i)^{-1} C_{\mu l} C_{\nu l}^* F_{\nu\lambda}^{(1)} C_{\lambda i}, \tag{1}$$

where: Greek letters indicate atomic basis functions; Roman letters stand for molecular orbitals; M and N are the occupied and total number of MOs, respectively; $F^{(1)}$ is the first order change in the Fock matrix due to the perturbation being considered; ε_l and ε_i are the orbital energies of the HF equations.

Eq. (1) can be transformed into the unperturbed MO basis,

$$U_{li}^{(1)} = (\varepsilon_l - \varepsilon_i)^{-1} G_{li}^{(1)} \tag{2}$$

where the transformed quantities $G_{li}^{(1)}$ and $U_{li}^{(1)}$ are related to the old ones by Eqs. (3) and (4):

$$G_{li}^{(1)} = \sum_{\nu,\lambda} C_{\nu l}^* F_{\nu\lambda}^{(1)} C_{\lambda i} \tag{3}$$

$$U_{li}^{(1)} = \sum_{\mu} C_{\mu l}^* C_{\mu i}^{(1)}. \tag{4}$$

It may be shown that $G_{li}^{(1)}$ can also be written as [18]:

$$G_{li}^{(1)} = \sum_{j=1}^{M} \sum_{m=M+1}^{N} [(ij, lm) U_{mj}^{(1)} + (im, lj) U_{mj}^{(1)*}] + H_{li}^{(1)} \tag{5}$$

where: $H^{(1)}$ is the one electron contribution giving the first order electron-nucleus interaction and it depends on the particular perturbation; and:

$$(ij, \, lm) = \int \int \varphi_i^*(1)\varphi_j(1)r_{12}^{-1}\varphi_i^*(2)\varphi_m(2) \, d\tau_1 \, d\tau_2. \tag{6}$$

Eqs. (1) were proposed by Blizzard and Santry [4] in the SCP method as an iterative procedure to compute the $C^{(1)}$ matrix and thereby to calculate coupling constants. Alternatively, the self-consistent calculation could be performed using Eqs. (2). Let Eqs. (2) be written as (for the real case):

$$U_{li}^{(1)} = \sum_{j=1}^{M} \sum_{m=M+1}^{N} A_{li,mj} U_{mj}^{(1)} + (\varepsilon_l - \varepsilon_i)^{-1} H_{li}^{(1)} \tag{7}$$

where the matrix A is not symmetric

$$A_{li,mj} = (\varepsilon_l - \varepsilon_i)^{-1}[(ij, \, lm) + (im, \, lj)]. \tag{8}$$

For the iteration process to converge with any initial $U^{(1)}$, and any value of the second term of the right hand side of Eq. (7), it is necessary and sufficient that the modulus of all the eigenvalues of matrix A is less than unity [19]. The linear equation system (7) can also be written in the usual form of the CHF equations [2]:

$$\sum_{j=1}^{M} \sum_{m=M+1}^{N} B_{li,mj} U_{mj}^{(1)} = H_{li}^{(1)} \tag{9}$$

where the symmetric matrix B is:

$$B_{li,mj} = (\varepsilon_l - \varepsilon_i)\delta_{ij}\delta_{lm} - (ij, \, lm) - (im, \, lj) \tag{10}$$

and if all eigenvalues of A are less than unity in modulus, then all eigenvalues of B must be positive (see Appendix).

Paldus and Cizek [20, 21] have studied the stability conditions of Hartree–Fock solutions when, for example, spin symmetry constraints are eliminated. From their work, instabilities can be classified in three different types: singlet, non-singlet (or triplet) and non-real [22]. The stability conditions correspond to the positiveness of all eigenvalues of certain matrices which, in the triplet case become matrix B of Eq. (10) [22]. As shown above, this is also a necessary and sufficient condition in order to obtain convergent calculations of the Fermi contact term with the SCP method.

Similarly, with the FP method the HF equations are solved in the presence of a finite spin-dependent perturbation that breaks the spin closed-shell symmetry. If the calculations converge, then this means that the molecular energy has remained unchanged, whereas non-convergent calculations are always accompanied by a growth of α spin in one MO and of β spin in another. The absolute value of coupling constants become larger and larger in every iteration, thus reflecting a tendency of the molecule to accommodate a non-singlet or unpaired spin wavefunction in view of the energy decrease that this new situation signifies.

Therefore, it must be concluded that whenever a nonconvergent calculation of the Fermi contact term appears, the RHF wavefunction has an UHF instability of the non-singlet type.

3. Results and Discussions

All results presented in this work were performed with special programs written in this group and based on standard programs FINITE, CNINDO and CNDO/M (programs number 224, 141 and 315 from QCPE, Indiana University respectively), in order to calculate spin-spin coupling constants within the FP, SCP and SOS methods according to the formulations of Refs. [7, 4 and 1], respectively.

3.1. Non-Singlet CNDO/S and INDO/S Instabilities

In order to study the stability conditions of CNDO/S and INDO/S wavefunctions in planar hydrocarbon systems, it is convenient to divide matrix B into a 4×4 block form. Each block is labelled with two of four possible groups formed by a virtual MO followed by an occupied MO: $\pi^*\pi$, $\sigma^*\sigma$, $\sigma^*\pi$ and $\pi^*\sigma$. Further, the integrals appearing in Eq. (10) can be expressed in terms of atomic basis functions:

$$(ij, lm) = \sum_{A,B} \sum_{\mu}^{A} \sum_{\lambda}^{B} C_{\mu i}^* C_{\mu j} C_{\lambda l}^* C_{\lambda m} (\mu\mu, \lambda\lambda)$$

$$+ \sum_{A} \sum_{\mu}^{A} \sum_{\nu \neq \mu}^{A} C_{\mu i}^* C_{\nu j} (C_{\mu l}^* C_{\nu m} + C_{\nu l}^* C_{\mu m})(\mu\nu, \mu\nu) \tag{11}$$

where A and B are atomic centers and $(\mu\nu, \lambda\sigma)$ is defined in the same way as (ij, lm).

If the CNDO approximation is used the second term in Eq. (11) vanishes. It is easy to verify in this case that for the type of molecules under consideration, all integrals containing ij or lm equal to a pair of MOs $\pi\sigma$, $\pi^*\sigma$, $\pi\sigma^*$ or $\pi^*\sigma^*$ also vanish. Therefore matrix B takes on the simple form:

$$B = \begin{bmatrix} \boxed{\diagdown} & 0 & 0 & 0 \\ 0 & \boxed{\diagdown} & 0 & 0 \\ 0 & 0 & \boxed{\diagdown} & \boxed{\diagdown} \\ 0 & 0 & \boxed{\diagdown} & \boxed{\diagdown} \end{bmatrix}$$

that is to say, it is divided into three blocks: one concerning only the π system, another only the σ one and a third one that mixes the $\pi^*\sigma$ and $\sigma^*\pi$ groups together.

On the other hand, at the INDO level the retention of one center exchange integrals in the second term of Eq. (11), causes the appearance of off-diagonal terms which couple the π and σ systems. Two examples are given, namely, the ethylene and benzene molecules.

3.1.1. Ethylene

In this molecule the dimension of the $\pi^*\pi$-$\pi^*\pi$ block is 1×1 and its eigenvalue is found to be:

$$\lambda_\pi = \varepsilon_{\pi^*} - \varepsilon_\pi - (\pi\pi, \pi^*\pi^*) - (\pi\pi^*, \pi\pi^*) \tag{13}$$

but these molecular integrals can also be expressed in terms of atomic integrals:

$$(\pi\pi, \pi^*\pi^*) = \tfrac{1}{2}(\gamma + \gamma') \tag{14a}$$

$$(\pi\pi^*, \pi\pi^*) = \tfrac{1}{2}(\gamma - \gamma'). \tag{14b}$$

On the other hand, the difference between orbital energies can be written as:

$$\varepsilon_{\pi^*} - \varepsilon_\pi = 2K\beta S + \gamma' \tag{15}$$

where β is the absolute value of the carbon bonding parameter [7]; S, γ and γ' are, respectively, overlap, Coulomb one center, and Coulomb two center integrals between the two p_π AOs; and K is the carbon–carbon screening constant characteristics of the "S" methods.

In this case the condition $\lambda_\pi > 0$ leads to:

$$K > (2\beta S)^{-1}(\gamma - \gamma') = 0.584 \tag{16}$$

when the standard geometrical model is used [23]. This critical value is very close to that of 0.585 selected for this screening constant in the CNDO/S parameterization [13]. Besides, Eq. (16) recovers the Paldus and Cizek result obtained for this molecule in the Pariser–Parr–Pople approximation [21]. This agreement is expected owing to the symmetry properties of the ethylene π system.

3.1.2. Benzene

Benzene is somewhat more complicated. However, the rotational symmetry invariance can be used to treat the Fock matrix for the π system separately, which leads to:

$$\Delta\varepsilon = 2K\beta(S_1 - S_3) + \tfrac{1}{3}(2\gamma_1 + \gamma_3) \tag{17a}$$

$$\Delta\varepsilon' = 2K\beta(2S_1 + S_3) + \tfrac{1}{3}(4\gamma_1 - \gamma_3) \tag{17b}$$

where the subindices 1, 2 and 3 stand for the number of bonds that separate the two p_π AOs that are being considered in the respective integral. The $\pi^*\pi$–$\pi^*\pi$ block of matrix B takes on the form:

$$B_\pi = \begin{bmatrix} a & b & 2b \\ b & a & -2b \\ 2b & -2b & c \end{bmatrix} \tag{18}$$

where:

$$a = \Delta\varepsilon - \tfrac{1}{2}(\gamma + \gamma_2) \tag{19a}$$

$$b = \tfrac{1}{6}(\gamma - \gamma_2) \tag{19b}$$

$$c = \Delta\varepsilon' - \tfrac{1}{3}(\gamma + 2\gamma_2). \tag{19c}$$

It follows that a necessary condition for all B_π eigenvalues to be larger than zero, is:

$$\det [B_\pi] = -8b^2(a+b) + c(a^2 - b^2) > 0. \tag{20}$$

This condition leads to a quadratic inequality in K, the screening constant:

$$a_1 K^2 + a_2 K + a_3 > 0 \tag{21}$$

where:

$$a_1 = 4\beta^2 (2S_1 + S_3)(S_1 - S_3) \tag{22a}$$

$$a_2 = -\tfrac{2}{3}\beta [S_1(5\gamma - 8\gamma_1 + 4\gamma_2 - \gamma_3) + S_3(\gamma + 2\gamma_1 - \gamma_2 - 2\gamma_3)] \tag{22b}$$

$$a_3 = \tfrac{1}{9}[(\gamma - 4\gamma_1 + 2\gamma_2 + \gamma_3)(2\gamma - 2\gamma_1 + \gamma_2 - \gamma_3) - 2(\gamma - \gamma_2)^2] \tag{22c}$$

When the relevant quantities are calculated using the standard geometrical model, condition (21) is obtained to be:

$$K > 0.652. \tag{23}$$

This condition is not satisfied by the CNDO/S method since its screening constant is $K = 0.585$. Therefore, the CNDO/S wavefunction also presents a non-singlet HF instability for benzene.

This analysis should be modified if it is to be valid at the INDO/S level, since there are small off-diagonal terms that contaminate different blocks in the whole matrix B. These terms depend only on one center exchange integrals. Therefore, closed forms for eigenvalues cannot be found. For this reason calculations were carried out in order to obtain numerical values.

Table 1. Influence of the screening constant K on the stability, energies and ordering of the molecular orbitals of the benzene molecule[a] as calculated by the INDO/S method

Sym.	Exptl.[b] K	Calculated 0.57	0.60	Orbital 0.70	Energies (eV) 0.80	0.90	1.00
$e_{2u}(\pi^*)$	$\cdots$	+0.04	+0.09	+0.53	+0.97	+1.42	+1.86
$e_{1g}(\pi)$	9.24	−9.19	−9.30	−9.66	−10.02	−10.38	−10.74
e_{2g}	11.49	−11.98	−11.91	−11.67	−11.43	−11.21	−10.99
$a_{2u}(\pi)$	12.3	−13.52	−13.83	−14.85	−15.87	−16.88	−17.90
e_{1u}	13.8	−15.31	−15.32	−15.35	−15.39	−15.43	−15.47
b_{2u}	14.7	−15.78	−15.84	−16.02	−16.19	−16.36	−16.54
b_{1u}	15.4	−17.87	−17.82	−17.65	−17.49	−17.34	−17.19
a_{1g}	16.85	−22.70	−22.83	−23.26	−23.68	−24.11	−24.54
e_{2g}	19.2	−25.53	−25.56	−25.68	−25.80	−25.93	−26.05
	λ^c	1.086	1.058	0.974	0.904	0.845	0.793

[a] Standard geometry is used (C—C = 1.40 Å, C—H = 1.08 Å).
[b] Ref. [10].
[c] Largest eigenvalue of the iteration matrix $D^{1/2} S D^{1/2}$ (see Appendix). For $\lambda > 1$ the SCP calculation is non-convergent, and matrix B has a negative eigenvalue which indicates the presence of an UHF instability of the non-singlet type in the wavefunction.

In Table 1 values thus obtained for the largest eigenvalue of the iteration matrix $(D^{1/2}SD^{1/2}$, see Appendix) are shown for carbon-carbon screening constants ranging from 0.57 to 1.00. It is interesting to recall that the screening constant in the "S" methods tends to raise the energy of occupied π orbitals, counteracting the tendency of CNDO/2 and INDO occupied π MOs to fall spuriously far below those with σ symmetry. In Table 1, where the ordering of orbital energies for different screening constants are shown, this trend is also depicted. It is observed that for $K = 0.57$ the ordering of MOs is in agreement with experimental values. However, the largest eigenvalue of the iteration matrix is 1.086 which shows that the wavefunction presents a non-singlet instability. In this case it is also found that the SCP or the FP calculations of spin-spin coupling constants are non-convergent. As the screening constant is increased, the largest eigenvalue diminishes, yielding an UHF stable wavefunction, but the ordering of orbital energies is no longer in agreement with the experimental one since the π MO a_{2u} lies below the σMOs e_{1u} and b_{2u}. As in the CNDO/S case, the critical value of this screening constant lies somewhere between $K = 0.60$ and $K = 0.70$.

3.2. Spin-Spin Coupling Constants

The coupled Hartree–Fock method is known to give the best possible results for second-order properties based on the zeroth-order wavefunction [24]. Therefore, calculations of spin-spin coupling constants were carried out within this scheme in molecules with INDO/S UHF stable wavefunctions. However, when UHF instabilities are present, as pointed out before, no convergence is found in the process of iteration. Therefore, other methods were required to cope with this situation. Two procedures for obtaining the couplings, J_T, within the same CHF method, in spite of UHF inestabilities, were devised. First, extrapolated values were found using an adequate damping factor procedure [25, 26]. As in every iteration the spin polarization is increased, the solution is sought in the "backward" region. For this reason, the "adequate" damping factor turns out to be negative. Secondly the linear CHF equations were solved by the inversion of matrix B. This procedure is more time-consuming than the first one.

As these non-singlet instabilities originate in the INDO/S π systems, a quite different behaviour of σ- and π-electron transmitted components of coupling constants must be expected. To study both components separately, a level shifting procedure [25, 26] was adopted to eliminate the virtual π orbitals of the molecule under consideration. To this end, these vacant orbitals are not taken into account in the summation (or, equivalently, they are taken to be in the continuum) when the reduced propagator Q [27] of Eq. (1) is constructed:

$$Q_{\mu\nu,i} = \sum_{l=m+1}^{N} (\varepsilon_l - \varepsilon_i)^{-1} C_{\mu l} C_{\nu l}^*. \tag{24}$$

In this way, the ground-state wavefunction is not altered [28], and the π channels of transmission are eliminated. Therefore, with this procedure the CHF equations yield only the σ-transmitted component, J_σ, and the π-electron contribution is

obtained as:

$$J_\pi = J_T - J_\sigma.$$

3.2.1. SCP Results in INDO/S Stable Wavefunctions

Calculations were carried out using the semiempirical INDO/S parameters given in Ref. [10], with $\beta_F^0 = -50$ eV and $K(C, O) = 0.75$ [11]. Geometrical data were taken from the Pople and Gordon model [23]. As no reparametrization of the electronic densities at the nucleus was undertaken, the standard FP INDO values were chosen, i.e. $S_0^2(H) = 0.3724$ a.u. and $S_0^2(C) = 4.0318$ a.u. Results for geminal and vicinal H—H couplings are presented in Table 2. Though there is a slight improvement in the geminal couplings in the isoelectronic series CH_4, NH_3 and OH_2 in that they follow the experimental sequence, in general INDO/S values seem to be poorer than those obtained with the standard FP INDO method. The difference between the two methods can be partially rationalized in terms of the different numerical values of their semi-empirical parameters [29].

Table 3 shows the results for one bond C—H couplings which seem to be somewhat near the INDO values. In molecules whose couplings are shown in Tables 2 and 3, the screening constants play a minor role (as in ethane) or do not appear at all (as in methane).

3.2.2. SCP Results in INDO/S Unstable Wavefunctions

INDO/S coupling constants for ethylene are shown in Table 4. They are given for values of the screening constant ranging from 0.57 to 1.00. σ and π electron transmitted components for each coupling are also shown. Some interesting

Table 2. H—H couplings as calculated by the CHF INDO/S method[a]

Molecule and coupling	INDO/S	INDO[b]	Exptl[b]
Hydrogen H—H	257.53	408.60	278.2
Water H—O—H	−2.14	−8.07	−7.2
Ammonia H—N—H	−3.62	−6.37	−10.35
Methane H—C—H	−3.98	−6.13	−12.4
Methyl Fluoride H—C—H	−1.17	−1.86	−9·6
Acetonitrile H—C—H	−4.83	−7.73	−16.9
Methanol H—C—H	−0.94	−2.12	−10.8
Ethane H—C—H	−3.40	−5.22	· · ·
Ethanoic Acid H—C—H	−3.55	−5.84	−14.6
Formaldehyde H—C—H	33.12	31.86	40.3
Cyclopropane H—C—H	3.36	2.04	−3.9
Ethane H—C—C—H *gauche*	−0.11	3.25	· · ·
Ethane H—C—C—H *trans*	4.01	18.63	· · ·
Ethane H—C—C—H average	1.27	8.37	8
Methanol H—C—O—H	5·09	6·41	2.83

[a] Standard geometry is used in all cases. All values in Hz.
[b] Values taken from Ref. [33].

Table 3. One bond C—H coupling constants as calculated by the CHF INDO/S method[a]

Molecule	INDO/S	INDO[b]	Exptl[b]
Methane	114.25	122.91	125
Methyl Fluoride	127.80	140.08	149.1
Acetonitrile	115.45	122.47	136.1
Methanol	126.37	135.27	141.0
Methylamine	118.25	129.92	133.0
Acetaldehyde	105.05	121.36	127.0
Ethanoic Acid	120.58	127.78	130.0
Ethane	113.01	122.12	124.9
Formic Acid	200.07	214.05	222.0
Formaldehyde	167.13	180.51	172
Cyclopropane	148.34	163.13	160.45

[a] Standard Geometry is used in all cases. All values are in Hz.
[b] Values taken from Ref. [33].

Table 4. Pi and Sigma transmitted components of the coupling constants in the ethylene molecule[a] as calculated by the CHF INDO/S method
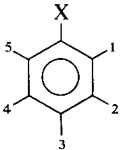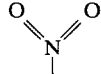
Screening Constant		0.57	0.60	0.70	0.80	0.90	1.00
Total	Exptl[b]						
$^2J_{HH}^{gem}$	2.3	12.71	18.61	−0.89	4.26	5.92	6.93
$^3J_{HH}^{cis}$	11.5	−7.77	−13.29	7.59	4.03	4.14	5.07
$^3J_{HH}^{trans}$	19.1	0.87	−4.18	18.26	16.26	17.95	20.47
$^1J_{CH}$	156.2	113.08	89.51	172.86	154.14	149.72	147.80
$^2J_{CH}$	−2.4	29.81	53.26	−30.55	−12.37	−8.55	−7.28
Sigma							
$^2J_{HH}^{gem}$		5.75	5.94	6.56	7.17	7.74	8.27
$^3J_{HH}^{cis}$		−0.80	−0.62	0.14	1.12	2.32	3.74
$^3J_{HH}^{trans}$		7.84	8.49	10.80	13.35	16.13	19.14
$^1J_{CH}$		141.99	142.01	142.09	142.18	142.27	142.37
$^2J_{CH}$		0.90	0.75	0.21	−0.41	−1.09	−1.85
Pi							
$^2J_{HH}^{gem}$		6.97	12.67	−7.45	−2.91	−1.82	−1.33
$^3J_{HH}^{cis}$		−6.97	−12.67	7.45	2.91	1.82	1.33
$^3J_{HH}^{trans}$		−6.97	−12.67	7.45	2.91	1.82	1.33
$^1J_{CH}$		−28.91	−52.51	30.76	11.96	7.45	5.43
$^2J_{CH}$		28.91	52.51	−30.76	−11.96	−7.45	−5.43
λ^{c}		−0.023	−0.012	0.021	0.055	0.088	0.021

[a] Standard Geometry is used (C=C = 1.34 Å, C—H = 1.08 Å, HCH = 120°). All values are in Hz.
[b] Values taken from Ref. [33].
[c] Lowest eigenvalue of matrix B.

features deserve comment. For instance, for any value of the screening constant the π-components satisfy very well known trends in spite of their unphysical values, e.g. they do not depend either on the zig-zag path or (in absolute value) on the number of bonds that separate the two interacting nuclei. The alternating sign rule is satisfied, although there is a sign inversion when K takes the critical value which yields a non-singlet unstable wavefunction. This sign inversion can be rationalized as follows: when the "screening factor" leads to a stable wavefunction, the energy surface belonging to both the σ and π systems has a minimum. However, when K crosses the critical point the wavefunction becomes unstable and the surface energy acquires a saddle-point structure. Therefore, the non-convergent calculation of coupling constants can be interpreted as the result of performing a series expansion around a minimum for the σ system but around a maximum for the π.

Although results for other molecules such as benzene, acethylene, vinyl fluoride, acrylonitrile, propene, allene, ketene and butadiene were also obtained, they are not reported in detail. In all cases the π components were found to follow a behaviour similar to that discussed for ethylene. When setting the screening constant equal to one, convergence was achieved in all cases. This shows clearly that the responsibility for non-singlet Hartree–Fock instabilities rests upon the screening constant and not on the particular values of bonding parameters and electronegativities that the "S" methods adopt, nor on the Mataga-Nishimoto

Table 5. H—H couplings in substituted benzenes[a] as calculated by the SOS INDO/S method

		H[b]	F	O\H	N≡C	O=C\H	O=N=O
	INDO/S[e]	−2.33	−0.28	−0.29	0.14	−0.10	−0.09
J_{12}	INDO[c,e]	8.15	6.24	5.39	5.49	5.13	6.02
	Exptl[d]	7.56	8.36	8.17	7.79	7.71	8.36
	INDO/S	3.86	2.78	2.92	2.02	2.29	1.75
J_{13}	INDO	2.13	1.71	2.03	1.60	2.04	1.47
	Exptl	1.38	1.07	1.09	1.28	1.35	1.18
	INDO/S	−1.66	0.09	0.01	−0.26	0.11	0.18
J_{14}	INDO	1.15	0.11	−0.25	0.44	0.33	−0.20
	Exptl	0.68	0.43	0.49	0.63	0.62	0.55
	INDO/S	3.86	1.58	1.89	1.79	0.92	1.32
J_{15}	INDO	2.13	1.44	2.22	1.01	0.88	1.77
	Exptl	1.38	2.74	2.71	1.76	1.75	2.40

[a] Standard Geometry is used in all cases. All values are in Hz.
[b] Due to symmetry problems with the SOS method [5] these are extrapolated SCP values.
[c] These values were also calculated for this work.
[d] Values taken from Ref. [33].
[e] S_0^2 values taken from Ref. [1] ($S_0^2(H) = 0.5500$ a.u.).

expression for the two-center Coulomb integrals [10] that are also used. It is also interesting to point out that in all cases it was found that the influence of semiempirical parameters on coupling constants in the CNDO/S and INDO/S methods follows the same trends as those observed before when using their standard versions [29].

3.2.3. SOS Results with INDO/S Unstable Wavefunctions

The SOS method was used to study the trends of H—H coupling constants in substituted benzenes. The purpose of this calculation was to check the ability of INDO/S to improve the standard SOS INDO values. The reason for this comparison is easily understood in terms of the successful results obtained for the paramagnetic component of the screening tensor using similar SOS formulae for this second order property. However, as shown by results presented in Table 5, there is no improvement in the spin-spin coupling calculations. In this set of molecules the general trend of the INDO/S results is poorer than that obtained with the standard INDO, which gives acceptable results in most cases. In other molecules like ethylene, vinyl fluoride, propene, butadiene, acrylonitrile, and nitroethylene the same behavior for the H—C—C—H coupling was found: the values obtained were nearly zero and in most cases with the incorrect sign.

4. Conclusion

As has been shown above, there exists a close relation between the UHF instabilities of the closed-shell restricted Hartree–Fock wavefunction and non-convergent calculations of nuclear spin-spin coupling constants.

In the CNDO/S and INDO/S methods, the screening constant is found to be responsible for successful predictions about the excited-state electronic system and as shown in Table 1 this success rests mainly on it. This is particularly reflected on the MOs with π symmetry since this constant acts only on the p_π atomic orbitals when local diatomic basis are used to construct the overlap integral matrix [10]. However, in this case the choice of a particular value of the screening factor could lead to a wavefunction with UHF instabilities of the non-singlet type as it frequently happens with near Hartree–Fock calculations [30]. These instabilities have a well established physical meaning since they demark a situation of broken symmetry [31]. In the Fermi contact calculation the appearance of non-singlet instabilities is connected with the breaking of the spin-symmetry of the wavefunction since there exists a state with components of higher multiplicities and lower energy than that of the singlet RHF one. This instability arises from the presence of a pole of the propagator at energies below zero. Under these conditions, the physical meaning of the perturbation schemes used to calculate a second order spin-dependent property no longer applies. Moreover, owing to the convergence problems of the usual methods of calculation (SCP and FP), if some special procedures are developed to enforce convergence, it is found that the numerical results obtained are unrealistic and that they violate some very well known rules. It is important to point out that the main reason of these unrealistic

results rests upon the use of a single determinant wavefunction which is not adequate to study these properties, since a multiple-determinant one should be used.

It must be recalled that "S" methods are successful in predicting photoelectron spectra and screening tensors, but nuclear spin-spin coupling calculations are not satisfactory especially in molecules containing π MOs where the difference between these methods and their standard versions without screening becomes important.

In a very recent paper [31] calculation problems together with a sign inversion were found when estimating the spin-dipolar term of the C—C coupling constant in ethylene and acetylene, using the CHF method with an *ab initio* wavefunction. As a final remark we note that the present analysis can be extended to include the spin-dipolar and the orbital terms of coupling constants. SCP convergence problems with the calculation of these terms would indicate non singlet instabilities in the first case, but a non-real instability in the latter case. This conclusion follows since in Eq. (5) $U^{(1)}$ for the spin-dipolar term is real as in the Fermi contact case, while for the orbital term it is pure imaginary, leading matrix B of Eq. (10) to become the one whose eigenvalues are used to test for non-real instability [22].

Appendix

Here it will be shown that if all eigenvalues of A are less than unity in modulus then all eigenvalues of B must be positive. To see this, note first that A (which it is not symmetric) is the product of a diagonal matrix, D, and a symmetric one, S:

$$A = DS \tag{A1}$$

and

$$B = D^{-1} - S \tag{A2}$$

where D^{-1} is the inverse of the diagonal matrix D and:

$$D_{li,mj} = (\varepsilon_l - \varepsilon_i)^{-1} \delta_{ij} \delta_{lm} \tag{A3}$$

$$S_{mj,nk} = (jk, mn) + (jn, mk). \tag{A4}$$

The subindices i, j, k refer to occupied MOs, while l, m, n indicate virtual ones. The set of SCP Eqs. [4] in the unperturbed MO basis (see Eq. (7) in the text) may be written in matrix notation as:

$$U = DSU + DH. \tag{A5}$$

Premultiplying by $D^{-1/2}$ and inserting the unity matrix $D^{1/2} D^{-1/2}$ between S and U one obtains

$$D^{-1/2} U = (D^{1/2} S D^{1/2}) D^{-1/2} U + D^{1/2} H. \tag{A6}$$

It is easy to see that the process of iteration involved in Eq. (A6) is equivalent to

that of Eq. (A5) since the successive application of both iteration matrices, i.e.

$$(D^{1/2} S D^{1/2})(D^{1/2} S D^{1/2}) \cdots (D^{1/2} S D^{1/2}) \quad \text{and} \quad (D S)(D S) \cdots (D S)$$

leads to the same results. Nevertheless, the former has real eigenvalues owing to its symmetric nature, while the latter is clearly non-symmetric.

After a new premultiplication of Eq. (A6) by $D^{-1/2}$ it can be rearranged as follows:

$$D^{-1/2}(1 - D^{1/2} S D^{1/2})D^{-1/2} U = B U = H.$$

Then, if all eigenvalues of matrix $D^{1/2} S D^{1/2}$ are less than unity all the eigenvalues of matrix $1 - D^{1/2} S D^{1/2}$ will be positive, and so will B since it is related to the latter by a pre and postmultiplication by $D^{-1/2}$ which does not change the sign of its eigenvalues.

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