# Calculation of Nuclear Spin-Spin Coupling Constants by SCF Perturbation Theory with MINDO/3 Approximation[*]

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LCAO-MO-SCF-MINDO/3 approximation is used to calculate nuclear spin-spin couplings, $^nJ^{AB}$, between magnetic nuclei A and B (A, B ≡ $^1H$, $^{13}C$, $^{19}F$) separated by $n$ bonds in a number of molecules. The theory predicts reasonably good values for directly bonded couplings (except those involving fluorine), but the results for multi-bond couplings are not so encouraging. Reasons for this deficiency of the theory are examined in the text.

**Key words:** MINDO/3 nuclear spin-spin couplings

## 1. Introduction

Several semiempirical schemes involving the approximation of zero differential overlap within the framework of the SCF LCAO MO theory have been applied in the study of various molecular properties during the last decade with varying degree of success. Out of these, two schemes INDO [1] and MINDO/3 [2] which involve calculations at the same level of sophistication differ only in the method of evaluation of certain integrals. In particular, MINDO/3, which is parameterized to reproduce the experimental heats of formation of molecules is found to be fairly successful in reproducing several experimental ground state properties [3]. In order to examine the range of applicability of this approximation, we have studied two first order properties (dipole moment derivatives [4] and isotropic hyperfine coupling constants [5]) and we find MINDO/3 to be reasonably successful in giving the values in agreement with the experiment for these properties, but results of the calculation of magnetic susceptibility [6], a second order property, are not so encouraging. Employing MINDO/3, a calculation [7] of nuclear spin couplings

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has been published but a clear picture of the applicability of MINDO/3 to this property does not emerge.

Presently, we report the results of MINDO/3 calculations of nuclear spin-spin couplings, another second order property. The calculations involve the coupling constants $^nJ_{AB}$ between magnetic nuclei A and B (A, B $\equiv$ $^1$H, $^{13}$C, $^{19}$F) separated by $n$ bonds in a large number of molecules. Wherever possible, the results are compared with those of INDO calculations as well as with experimental data.

## 2. Theory

The general theory of nuclear spin-spin interactions, as given by Ramsey [8], has been used to calculate coupling constants using both molecular orbital [9] and valence bond theories [10]. In the present work we have followed the SCF perturbation extension of Ramsey's theory due to Blizzard and Santry [11] (hereafter abbreviated as "BSPT" Blizzard Santry perturbation theory).

Following Blizzard and Santry [11], the spin coupling constant, $J_{AB}$ in Hz between two nuclear spins $I_A$ and $I_B$ is given by

$$J_{AB} = E_{AB}^{(2)} \gamma_A \gamma_B / 2\pi \tag{1}$$

where $\gamma_A$ and $\gamma_B$ are magnetogyric ratios of the two coupling nuclei A and B, respectively, and $E_{AB}^{(2)}$ is the second order perturbation energy. Employing the Hellman-Feynmann theorem [12] and assuming $I_A$ to lie in $z$-direction, the explicit expressions for the contributions to $E_{AB}^{(2)}$ from contact, orbital and spin dipolar mechanisms at the INDO (MINDO/3) level of approximation are given by

$$E_{AB}^{(2)}(\text{contact}) = 2P_{s_B s_B}^{\alpha(1)} (8\pi\beta/3)^2 S_A^2(0) S_B^2(0) \tag{2}$$

$$E_{AB}^{(2)}(\text{orbital} = 2P_{x_B y_B}^{\alpha(1)} (2\beta)^2 \langle r^{-3} \rangle_A \langle r^{-3} \rangle_B \tag{3}$$

$$E_{AB}^{(2)}(\text{dipolar}) = \tfrac{4}{5}[2P_{z_B z_B}^{\alpha\alpha(1)} - P_{x_B x_B}^{\alpha\alpha(1)} - P_{y_B y_B}^{\alpha(1)} + 3P_{x_B x_B}^{\alpha\beta(1)}$$
$$+ 3Q_{y_B y_B}^{\alpha\beta(1)}]\langle r^{-3} \rangle_A \langle r^{-3} \rangle_B \hbar^2 \beta^2 \tag{4}$$

where the symbols have the same meaning as in Ref. [11]. Since the orbital and dipolar terms are anisotropic, their values with nuclear spin $I_A$ in $x$- and $y$-directions are evaluated through expressions similar to Eqs. (3) and (4), and from these average orbital and dipolar contributions to $E_{AB}^{(2)}$ are evaluated. The total second order energy is the sum of the contact and the average orbital and the average dipolar contributions.

$$E_{AB}^{(2)} = E_{AB}^{(2)}(\text{contact}) + E_{AB}^{(2)}(\text{orbital}) + E_{AB}^{(2)}(\text{dipolar}) \tag{5}$$

Blizzard and Santry treated $S_A^2(0)$ and $\langle r^{-3} \rangle_A$ as a characteristic of the nucleus A and obtained them through least square fitting between calculated and experimental couplings. Here, $S_A^2(0) S_B^2(0)$ and $\langle r^{-3} \rangle_A \langle r^{-3} \rangle_B$ are treated as least square parameters, characteristic of the pair of coupled nuclei A and B.

## 3. Molecular Geometry

Wherever possible, experimental bond lengths and bond angles were employed to describe the molecular structure of the molecules [13, 14]. In other cases geometrical model "A" of Pople and Beveridge [1] was used.

## 4. Results

Since a valence basis set has been used in these calculations, the evaluation of spin-spin couplings involving the proton is restricted to the contact term only

**Table 1.** Proton-proton coupling constants (in Hz)
$S_H^2(0)S_H^2(0) = 0.7621$ a.u.

| Molecule | Coupling type | MINDO/3 couplings | INDO[a] couplings | Experimental couplings | |
|---|---|---|---|---|---|
| $H_2$ | H–H | 248.34 | 408.6 | 280 | [15] |
| *Geminal couplings* | | | | | |
| $H_2O$ | H–O–H | −6.08 | −8.07 | (−)7.2 | [16] |
| $CH_4$ | H–C–H | −5.10 | −6.13 | −12.4 | [17] |
| $C_2H_6$ | H–C–H | −5.40 | −5.22 | – | |
| $C_2H_4$ | H–C–H | 5.11 | 3.24 | 2.5 | [18] |
| $H_2CO$ | H–C–H | 91.15 | 31.86 | 40.2 | [19] |
| $CH_3F$ | H–C–H | 10.73 | −1.86 | −9.6 | [20] |
| $H_2CF_2$ | H–C–H | 52.92 | – | – | |
| Cyclopropane | H–C–H | 3.52 | 0.69[b] | −7.0 | [21a] |
| Oxirane | H–C–H | 23.05 | 8.43[b] | 5.5 | [21b] |
| Aziridine | H–C–H | 12.08 | 5.35[b] | 2.0 | [21b] |
| $HFCCH_2$ | H–C–H | −6.91 | – | −3.2 | [22] |
| $F_2CCH_2$ | H–C–H | 5.23 | – | – | |
| *Vicinal couplings* | | | | | |
| | H–C–C–H (*cis*) | 4.52 | | | |
| $C_2H_6$ | H–C–C–H (*gauche*) | 0.64 | 3.25 | | |
| | H–C–C–H (*trans*) | 16.70 | 18.63 | | |
| | H–C–C–H (average) | 5.99 | 8.37 | 8.0 | [18] |
| $C_2H_4$ | H–C–C–H (*cis*) | 7.17 | 9.31 | 11.7 | [18] |
| | H–C–C–H (*trans*) | 39.10 | 25.15 | 19.1 | [18] |
| $C_2H_2$ | H–C–C–H | 34.68 | 10.99 | 9.5 | [18] |
| $HFCCH_2$ | H–C–C–H (*cis*) | 0.85 | | 4.65 | [22] |
| | H–C–C–H (*trans*) | 32.59 | | 12.75 | [22] |
| HFCCHF | H–C–C–H (*cis*) | 0.41 | | −2.0 | [22] |
| | H–C–C–H (*trans*) | 40.89 | | 9.5 | [22] |
| Cyclopropane | H–C–C–H (*cis*) | 1.85 | 7.16[b] | 9.5 | [21a] |
| | H–C–C–H (*trans*) | 5.87 | 6.75[b] | 5.5 | [21a] |
| Oxirane | H–C–C–H (*cis*) | −1.43 | 3.98[b] | 4.45 | [21b] |
| | H–C–C–H (*trans*) | 6.09 | 6.30[b] | 3.1 | [21b] |
| Aziridine | H–C–C–H (*cis*) | −0.42 | 4.49[b] | 6.3 | [21b] |
| | H–C–C–H (*trans*) | 6.45 | 6.60[b] | 3.8 | [21b] |
| | H–C–N–H (*cis*) | −3.79 | 7.69 (*trans*) | – | |
| $C_6H_6$ | H–C–C–H | 4.88 | 8.15[b] | 7.54 | [23] |

[a] Ref. [1].     [b] Ref. [42].

and these are listed in Tables 1–3. For $J_{CC}$, $J_{CF}$ and $J_{FF}$, all the three coupling mechanisms are considered and the results are collected in Tables 4 and 5. The values of necessary parameters are given at appropriate places in the tables. The experimental couplings are taken from the literature [15–38]. The INDO couplings are either taken from literature [1, 39–41] or from those calculated by the authors of [42].

## 4.1. Couplings Involving Protons

Table 1 gives the proton-proton couplings across one, two and three bonds. It is seen from this table that a number of experimental trends are qualitatively reproduced by the theory. Geminal proton-proton couplings ($^2J_{HH}$) in many cases are calculated to be negative (in agreement with experiment) in $sp^3$ hybridizations

**Table 2.** $^{13}$Carbon proton coupling constants (in Hz)
$S_C^2(0)S_H^2(0) = 0.90442$ a.u.

| Molecule | Coupling type | MINDO/3 couplings | INDO couplings | Experimental couplings | |
|---|---|---|---|---|---|
| Methane | C–H | 112.47 | 122.92 | 125 | [24] |
| Ethane | C–H | 109.43 | 122.12 | 124.9 | [18] |
| | C–C–H | −4.98 | −7.20 | −4.5 | [18] |
| Ethylene | C–H | 151.48 | 156.71 | 156.4 | [18] |
| | C–C–H | −22.63 | −11.57 | −2.4 | [18] |
| Acetylene | C–H | 206.13 | 232.65 | 248.7 | [18] |
| | C–C–H | −2.91 | 2.52 | 49.3 | [18] |
| HFCO | C–H | 367.92 | 244.77[a] | 267.0 | [25] |
| H$_2$CO | C–H | 140.00 | 180.51[a] | 172.0 | [26] |
| CHF$_3$ | C–H | 540.78 | 212.29[a] | 239.1 | [27] |
| CH$_3$F | C–H | 132.15 | 140.08[a] | 149.1 | [27] |
| CH$_2$F$_2$ | C–H | 178.88 | 166.79[a] | 184.5 | [27] |
| 1,2-Difluoroethylene (trans) | C–H | 211.89 | 179.51[a] | − | |
| | C–C–H | −24.94 | − | − | |
| 1,2-Difluoroethylene (cis) | C–H | 179.17 | − | − | |
| | C–C–H | −7.19 | − | − | |
| 1,1-Difluoroethylene | C–H | 143.36 | 160.11 | − | |
| | C–C–H | 1.20 | − | − | |
| Vinyl fluoride | C–H | 168.80 | 183.11[a] | 200.2 | [28] |
| Benzene | C–H | 134.13 | 140.29 | 157.5 | [29] |
| | C–C–H | −14.07 | −4.94 | 1.0 | [29] |
| | C–C–C–H | 23.23 | 9.40 | 7.4 | [29] |
| | C–C–C–C–H | −14.94 | −2.27 | −1.1 | [29] |
| Cyclopropane | C–H | 141.47 | 163.44[c] | 162.0 | [21a] |
| | C–C–H | −6.24 | −5.19[c] | − | |
| Oxirane | C–H | 141.10 | 167.75[b] | 175.8 | [21b] |
| | C–C–H | −1.46 | −4.75[b] | − | |
| Aziridine | C–H | 132.66 | 161.4[b] | 168.1 | [21b] |
| | C–C–H | −3.27 | −4.14[b] | − | |

[a] Ref. [39].       [b] Ref. [41].       [c] Ref. [42].

**Table 3.** MINDO/3 proton [19]fluorine coupling constants (in Hz)[a]
$S_H^2(0)S_F^2(0) = 7.9368$ a.u.

| Molecule | Coupling type | MINDO/3 couplings | INDO couplings (Ref. 1) | Experimental couplings | |
|---|---|---|---|---|---|
| HF | H–F | −228.25 | −150.22 | (−)521.0 | [30] |
| $CH_3F$ | H–C–F | −5.17 | 4.68 | 46.4 | [27] |
| $CH_2F_2$ | H–C–F | −10.99 | – | 50.2 | [27] |
| $CHF_3$ | H–C–F | 72.40 | – | 79.7 | [27] |
| 1,2-Difluoroethylene (*cis*) | H–C–F | −8.19 | | 72.7 | [31] |
| | H–C–C–F (*trans*) | −89.33 | | 20.4 | [31] |
| 1,2-Difluoroethylene (*trans*) | H–C–F | −10.44 | | 74.3 | [31] |
| | H–C–C–F (*cis*) | −8.97 | | 4.4 | [31] |
| 1,1-Difluoroethylene | H–C–C–F (*cis*) | −13.96 | | | |
| | H–C–C–F (*trans*) | 31.72 | | | |
| Vinyl fluoride | H–C–F | −30.15 | 16.61 | 84.7 | [32] |
| | H–C–C–F (*cis*) | −7.63 | 26.7 | 20.1 | [32] |
| | H–C–C–F (*trans*) | −33.57 | 66.20 | 52.4 | [32] |

[a] $S_H^2(0)S_F^2(0)$ value due to Pople *et al.* was used, see Ref. [1].

**Table 4.** MINDO/3 [13]carbon [13]carbon coupling constants (in Hz)[a, b]

| Molecule | Coupling type | Contact term | Orbital term | Dipolar term | Total | Contact[c] term only | Experimental |
|---|---|---|---|---|---|---|---|
| $C_2H_6$ | C–C | 29.88 | −3.18 | 3.41 | 30.11 | 39.66 | 34.6 [33] |
| | | (35.63) | (−2.91) | (0.73) | (33.45) | | |
| $C_2H_4$ | C–C | 72.25 | −28.58 | 31.10 | 74.77 | 95.89 | 67.6 [33] |
| | | (70.61) | (−18.58) | (3.92) | (55.95) | | |
| $C_2H_2$ | C–C | 84.03 | 48.91 | 38.56 | 171.50 | 111.52 | 171.5 [18] |
| | | (140.80) | (23.59) | (8.31) | (172.70) | | |
| Benzene | C–C | 63.00 | −21.90 | 19.11 | 60.21 | 83.62 | 57.0 [34] |
| | | (64.30) | (−12.83) | (1.59) | (53.10) | | |
| | C–C–C | −32.75 | 1.14 | −17.50 | −49.11 | 43.47 | |
| | C–C–C–C | 32.39 | 0.38 | 20.09 | 52.86 | 42.99 | |
| Vinyl fluoride | C–C | 91.77 | −21.41 | 35.94 | 106.30 | 121.30 | |
| | | | | | (95.4)[d] | | |
| 1,2-Difluoroethylene (*cis*) | C–C | 103.34 | −16.87 | 40.19 | 126.66 | 137.16 | |
| | | | | | (108.3)[d] | | |
| 1,2-Difluoroethylene (*trans*) | C–C | 132.45 | −43.06 | 51.98 | 141.37 | 175.79 | |
| | | | | | (119.8)[d] | | |
| 1,1-Difluoroethylene | C–C | 81.81 | −8.53 | 22.43 | 95.71 | 108.53 | |
| | | | | | (118.9)[d] | | |

[a] $S_C^2(0)S_C^2(0) = 12.5851$ a.u., $\langle r^{-3} \rangle_C \langle r^{-3} \rangle_C = 3.5901$ a.u.
[b] INDO values taken from Ref. [11], except when stated otherwise.
[c] Only "Contact term" was considered, $S_C^2(0)S_C^2(0) = 8.0338$ a.u.
[d] Ref. [39].

but fluorination changes the theoretical signs. For example, while in $CH_4$, $C_2H_6$ and $H_2O$, $^2J_{HH}$ are negative it is positive in $CH_3F$ in disagreement with experiment. In trigonal groups such as $C_2H_4$ and $H_2CO$, however, these are calculated to be positive in agreement with experiment though the magnitude differs considerably. In three-membered rings, calculated $^2J_{HH}$ are negative in contrast to positive observed values. The same type of sign reversal is observed with the INDO formalism [40–42]. The observed vicinal proton couplings are positive and largest in *trans*-configuration in straight chain systems. This experimental trend is reproduced by the theory in all straight-chain molecules studied here. In three-membered rings such as cyclopropane, aziridine and oxirane the calculated vicinal *cis*-proton couplings are negative whereas they are positive experimentally. INDO [40–42] gives the sign of these couplings to be positive. Quantitatively, even in straight-chain molecules, although the vicinal couplings are calculated to be positive, the theory fails to reproduce dihedral angle dependence of the couplings, e.g. in the ethane fragment the experimental ratio of $^3J_{HH}$ *trans*/$^3J_{HH}$

**Table 5.** MINDO/3 $^{13}C$ $^{19}F$ and $^{19}F$ $^{19}F$ coupling constants (in Hz)

| Molecule | Coupling type | Calculated | | | | Experimental | |
| --- | --- | --- | --- | --- | --- | --- | --- |
| | | Contact term | Orbital term | Dipolar term | Total | | |
| *CF couplings* | | | | | | | |
| $CH_3F$ | C–F | −129.83 | 202.47 | 503.89 | 576.21 | −157.5 | [27] |
| $CH_2F_2$ | C–F | −93.42 | −249.97 | 308.40 | −34.99 | −234.8 | [27] |
| $CHF_3$ | C–F | −148.78 | | | | −274.3 | [27] |
| $CF_4$ | C–F | −102.99 | −428.13 | | | −259.2 | [27] |
| FCHO | C–F | −294.89 | −306.66 | 208.69 | −392.86 | −369.0 | [35] |
| FCFO | C–F | −148.22 | −363.67 | 401.82 | −110.07 | −308.4 | [27] |
| $FCHCH_2$ | C–F | −177.94 | 284.46 | 293.40 | 409.92 | | |
| | C–C–F | 142.89 | −196.41 | 112.16 | 58.64 | | |
| FCHFCH (*cis*) | C–F | −212.93 | 535.10 | 490.10 | 812.27 | | |
| | C–C–F | 39.40 | −143.30 | 117.00 | 13.10 | | |
| FCHFCH | C–F | −145.44 | 681.86 | 590.24 | 1126.66 | | |
| (*trans*) | C–C–F | 0.26 | 346.10 | 90.20 | 436.56 | | |
| $H_2CCF_2$ | C–F | −125.93 | −231.46 | 239.32 | −118.07 | −287.0 | [35] |
| | C–C–F | −6.05 | −254.97 | 11.21 | −249.81 | | |
| *FF couplings* | | | | | | | |
| $CHF_3$ | F–C–F | 101.69 | | | | 150.0 | [36] |
| $CF_4$ | F–C–F | 118.87 | −579.01 | | | | |
| $CH_2F_2$ | F–C–F | 73.06 | 310.07 | 643.10 | 1026.23 | | |
| FCFO | F–C–F | 608.37 | −618.79 | 566.95 | 556.53 | | |
| FCHFCH | F–C–C–F | 1.20 | −1077.55 | 585.79 | −490.46 | −124.8 | [37] |
| | (*trans*) | | | | | | |
| | F–C–C–F | 1.83 | −102.59 | 5.79 | −94.93 | | |
| | (*cis*) | | | | | | |
| $H_2CCF_2$ | F–C–F | 88.22 | 86.88 | 727.12 | 902.22 | 36.4 | [37] |

$^a S^2(0)$ and $\langle r^{-3} \rangle$ parameters taken from Ref. [11].

*gauche* is 5.9 [19] but the MINDO/3 value is 26.1. In the identical situation INDO gives a correct *trans/gauche* ratio of 5.77 [42].

Like proton-proton couplings, carbon-proton couplings are reproduced by MINDO/3 with variable degree of success. Directly bonded carbon-proton couplings, which are always positive, are fairly well reproduced. Experimental $^1J_{CH}$ is seen to increase in magnitude in the series: ethane, methane, ethylene and acetylene. Exactly the same trend is observed in MINDO/3 spin couplings (and also by the INDO approach [1]). The MINDO/3 values of $^1J_{CH}$ in benzene and ethylene are 134.13 Hz and 151.48 Hz, respectively, i.e. $^1J_{CH}$ in benzene is smaller than $^1J_{CH}$ in ethylene (and the same is observed with INDO), but the reverse order is observed experimentally. In formaldehyde and formylfluoride the observed $^1J_{CH}$ values are 172.0 Hz and 267.0 Hz, respectively, whereas in MINDO/3 the corresponding values are 140.04 Hz and 367.92 Hz, and in INDO these are 180.51 Hz and 244.77 Hz, respectively. Comparison of MINDO/3 and experiment shows that $^1J_{CH}$, in the presence of fluorine, is overestimated. The difference of $^1J_{CH}$ in formaldehyde and formyl fluoride is considerably larger in MINDO/3 than in experiment. The reverse is true for INDO where the calculated $^1J_{CH}$ value in the presence of fluorine is smaller than the experimental value. In fluoromethanes, the observed $^1J_{CH}$ value increases as the number of fluorines increases. The same trend is repeated in MINDO/3 and in INDO. Again the presence of fluorine increases the MINDO/3 and decreases INDO couplings in comparison with experiment. $^1J_{CH}$ values in vinyl fluoride are almost the same in MINDO/3 and INDO, both being smaller than the experimental value. In other fluoroethylenes MINDO/3 and INDO show similar trends. MINDO/3 also gives reasonable $^1J_{CH}$ values in three-membered rings.

Calculated two-bond carbon-proton couplings, $^2J_{CH}$ are invariably negative in sign. Not much experimental data is available for this class of couplings; wherever possible, it appears that in saturated molecules MINDO/3 couplings are satisfactory e.g., $^2J_{CH}$ in ethane (Table 2). But, the calculated couplings are not satisfactory when any bond in the coupling path is of multiple character e.g. double, triple or aromatic. In oxirane and aziridine, however, no experimental results are known. Comparing MINDO/3 with INDO, it is seen that the difference between $^1J_{CH}$ and $^2J_{CH}$ in MINDO/3 is less pronounced than the corresponding difference in INDO. The relative magnitude of long-range carbon-proton couplings in benzene are well reproduced by the theory. The signs of MINDO/3 calculated couplings in this molecule are alternately positive and negative as the number of bonds become odd or even in the coupling path. This trend is not followed strictly in experiments. Thus, $^2J_{CH}$ and $^3J_{CH}$ both are observed to be positive whereas $^4J_{CH}$ is seen to be negative. If we consider only magnitudes the theory correctly reproduces the experimental observation of $|^2J_{CH}| < |^4J_{CH}| < |^3J_{CH}|$. INDO [1], however, fails to reproduce the sign and the magnitude of the couplings in this case.

It is generally assumed that CH couplings increase with the increase in *s*-character of the bond between the coupled nuclei. A rough measure of the *s*-character of the

bond can be taken as the square of the bond order between $s$-orbitals of the coupled nuclei. A statistical analysis through the correlation coefficient between the square of this bond order and the MINDO/3 bond order shows this trend to be roughly followed.

MINDO/3 proton-flourine couplings do not exhibit any well-defined trend. In this case, least square fitting was not done; instead, the value of the required parameter was taken from the work of Pople *et al.* [1]. From Table 3 it is clear that in contrast to $J_{CH}$, $J_{HF}$ values are not very reliable.

## 4.2. Couplings involving Nuclei other than Protons

Blizzard and Santry [11] have shown that although $^{13}C-^{13}C$ couplings are dominated by the contact term, the inclusion of the orbital and dipolar term contributions improves the agreement between theory and experiment. MINDO/3 carbon-carbon couplings are presented in Table 4 where in parentheses the corresponding INDO figures are also given. It is clear from this table that in MINDO/3 calculations also the inclusion of orbital and dipolar contributions improves the agreement between calculated and experimental couplings as compared with the case when only the contact term contribution is considered (columns 6 and 7). Wherever the experimental results are available, it is seen that MINDO/3 is reasonably successful in reproducing corresponding experimental couplings. At least in these cases it does not seem that INDO has got an edge over MINDO/3. The $^2J_{CC}$ and $^3J_{CC}$ in benzene are negative and positive respectively in accordance with the alternation of sign with the change in number of intervening bonds. In fluoroethylenes, MINDO/3 $^1J_{CC}$ values are larger than their INDO counterpart in all but 1,1-difluoroethylene where the MINDO/3 value is smaller than corresponding INDO value. The signs of the individual contributions in MINDO/3 and in INDO are similar but the general trend of the magnitude $J_{con} > J_{orb} > J_{dipolar}$ observed in INDO [11] differs in MINDO/3 ($J_{con} > J_{orb} \sim J_{dipolar}$). Since MINDO/3 dipolar and orbital contributions to $J_{CC}$ in general, are of comparable magnitude but of opposite sign (except acetylene) they largely cancel each other and in such cases, the contact term determines the sign as well as the magnitude of the couplings.

Table 5 gives CF and FF couplings. The value of necessary parameters $S^2(0)$ and $\langle r^{-3} \rangle$ are those obtained by INDO [11]. The independent least-square fitting was not done because the couplings obtained by MINDO/3 do not follow the regular experimental trend and also the convergence was not achieved in the calculation of perturbed eigenvectors even in 30 cycles in many cases when the perturbing nucleus was fluorine. Even without parameterization qualitative assessment of the couplings indicate that they are not satisfactory. Similar worsening of isotropic hyperfine couplings is observed [5] whenever fluorine is present in the system.

## 5. Discussion

An examination of Table 1 reveals that the MINDO/3 $^1J_{HH}$ of 248.34 Hz in hydrogen molecule agrees fairly well with experimental value of 280 Hz, the INDO

value being 408.6 Hz. This apparently good result of MINDO/3 calculations is due to the fact that we have employed a least-square value of $S_H^2(0) = 0.2761$ a.u. compared to that of 0.3724 a.u. in INDO [1]. The orbital exponent, $Z$, of hydrogen is taken to be 1.3 in MINDO/3 and 1.2 in INDO. Employing an atomic orbital of the type $\sqrt{(z^3/\pi a_0^3)} \exp(-zr/a_0)$, we should expect $S_H^2(0)$ MINDO/3/$S_H^2(0)$ INDO $= (1.3/1.2)^3 = 1.2714$ whereas we have used the value of this quantity as 0.7414. Thus it is not fair to compare MINDO/3 and INDO coupling constants in this system. The quantity that can be compared in the two approximations is $^1J_{HH}/S_H^2(0)S_H^2(0)$. The values of this quantity turn out to be 3259 and 2946 in MINDO/3 and INDO, respectively. Since all other quantities in coupling constant expressions (Ref. [1]) are constants multiplied by the derivative of spin density, this difference implies that the quantity $[\partial/\partial\mu_B P_{s_A s_A}^{spin}(\mu_B)]_{\mu_B} = 0$, the derivative of the diagonal element of spin density matrix corresponding to the valence $s$-orbital on atom "A" with respect to the perturbation on atom "B", is larger in MINDO/3 than in INDO. Thus in MINDO/3 the diagonal elements of the $s$-orbital spin density matrix at one centre are seen to be more rapidly varying functions of the perturbation on the other centre than their INDO counterparts.

In an earlier paper [5] it was shown that MINDO/3 spin densities are greater than the INDO spin densities, but by choosing appropriate parameters, the resulting hyperfine couplings turn out fairly satisfactory. However, it is the derivative of the spin density with respect to the perturbation on a second nucleus which differs considerably in MINDO/3 and INDO approximations and makes the approximation (MINDO/3) less reliable for spin coupling calculations. Similar remarks apply to $^1J_{CC}$ where $S_C^2(0) = 3.5476$ and 3.7387 a.u. in MINDO/3 and INDO, respectively. The HMNC (hyperfine magnetic nucleus constant) [5] for $^{13}C$ hyperfine couplings in MINDO/3 and INDO approximations are 757.63 G and 820.10 G respectively [1, 5]. A similar trend is seen in the evaluation of $^1J_{CH}$ couplings where the derivative of spin density matrix is larger in MINDO/3 than in INDO as is reflected in the least squares parameters $S_C^2(0)S_H^2(0) = 0.9044$ a.u. and 1.5014 a.u. for MINDO/3 and INDO, respectively.

A comparison of orbital energies [6] as obtained from MINDO/3 and INDO calculations shows that the separation of the MINDO/3 virtual orbitals and occupied orbitals is much smaller than that in INDO. Since the calculations of the perturbed density matrix requires the knowledge of $(E_{unocc} - E_{occ})^{-1}$, the MINDO/3 perturbed density matrix would be a more sensitive function of any perturbation than its INDO counterpart. This accounts for the larger spin density derivatives in MINDO/3 as compared to those obtained in the INDO calculation.

When the coupling nuclei are separated by more than one bond, the spin density derivative does not follow any well-defined trend in MINDO/3 as is exhibited by the erratic dihedral angle dependence of vicinal proton couplings.

Thus, it is seen that although MINDO/3 gives good values (because of the least-square parameters used) of $^1J_{HH}$, $^1J_{CH}$, $^1J_{CC}$ (poor agreement for $J_{XF}$ is attributed to poor fluorine parameters), it gives poor results for two-bond and three-bond couplings. Therefore we conclude that while MINDO/3 can give reasonably good

zero- and first-order properties, it cannot be relied upon to give an equally good description of second-order properties which are dependent on virtual orbitals.

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