

Semiempirical Calculations of Spin-spin Coupling Constants.

A Comparison of some Parametrizations

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The CNDO/2 and INDO semiempirical calculation schemes have been used to obtain correlation diagrams between experimental and calculated spin-spin coupling constants through one, two and three bonds in molecules at equilibrium geometries. The calculation scheme included a variable screening in the Slater atomic orbitals depending on electron populations. The CNDO, INDO parametrizations suggested by Boyd have been used to evaluate molecular orbitals and energies for calculation of spin-spin coupling constants.

Since the first semiempirical calculations of spin-spin coupling constants were published by Karplus and Anderson¹ and by McConnell² a large number of applications of the sum over states (SOS) method has been published. However, first the development of CNDO/2 and INDO by Pople *et al.*³ indicated that within modest computational requirements the calculations would provide sensible results.⁴ The results obtained by the SOS method were refined by inclusion of configuration interaction⁵ and by including spin-spin and spin-orbit contributions.⁴ Alternatively to this method Pople *et al.* later introduced the finite perturbation method.⁶ Also with this method acceptable predictions could be established, and it was for several types of spin-spin couplings found to be superior to the SOS method.

Simultaneous with the semiempirical calculations *ab initio* type of calculations were developed primarily for small systems.⁷ It was, however, found that the greatly improved wave functions did not produce equally better numerical results for the spin-spin coupling constants. In most calculations it has been

found that the dominating term is the Fermi contact term, in coupling calculations involving hydrogen it is the only one. In 1971 Jeu⁸ mentioned that the mathematical expression for the Fermi contact term is an approximation to the real relativistic equation and that it is only valid to first order in the theory of perturbation. Later Wooley⁹ presented a critical discussion of the same problem and concluded that "one cannot give a precise meaning to the idea of spin-spin coupling within a molecule". In view of the controversial state of interpretation and due to the significantly higher cost of *ab initio* calculations it therefore seems obvious that semiempirical calculations still will be valuable for some time.

In the non relativistic approximation used the Fermi contact term depends on the electron density at the site of the nucleus, $\langle \psi^2(0) \rangle$. This term has been handled in three different manners. The basis set used in CNDO/2 and INDO calculations of spin-spin coupling constants is Slater type orbitals, where the functions are evaluated to reproduce the experimental values for atomic energy levels in X-ray studies and atomic and ion radii.¹⁰ For this type the behaviour near the center position of the nucleus is known to be poor for the orbitals $2s$, $3s$ etc. So alternatively the integral, $\langle \psi^2(0) \rangle$ can be handled as a semiempirical parameter, the value of which depends only on the nature of the atom.⁸ The third approach is to use the mathematical expression for the integral and evaluate $\langle \psi^2(0) \rangle$ after an improvement of the basis set.¹¹ In this expression the exponential factor in the radial part

of the orbital appears. The exponential factor can be chosen as a fixed value, which only depends on the nature of the atom, or one can use a value, which depends both on the atom and the molecule. However, it has been found that the integral is rather sensitive to variation in the exponential factor.¹² When scaled, exponential factors are used in the calculation of the Fermi contact term, a logical extension would be to introduce a scaling of the atomic orbitals in the SCF scale itself and finally apply them in the calculation of the spin-spin coupling constants. This idea has been investigated as one of the parametrizations below.

It has been found by several authors¹³ that the spin-spin coupling constants calculated depend strongly on the molecular geometry used. To provide a consistent set of geometries Pople *et al.*³ have suggested use of standard bond lengths and angles. Alternatively calculations have been published¹¹ where experimental geometries were used. Both methods reflect the reluctance towards use of the minimal energy configuration that might be determined within the CNDO/2 and INDO method itself. This reflects the unrealistic geometries that in some papers have been found by energy minimization using the two methods.¹⁴

We found that conceptually it would be attractive if a semiempirical method would exist that allowed fairly good estimates of geometries and at the same time lead to acceptable values for spin-spin coupling constants.

In a number of papers^{15,16} Whitehead and coworkers have developed a modification of the CNDO and INDO methods with the aim of providing a route to more realistic estimates of geometries. One of the programs is described in Ref. 16a, in the thesis of Boyd^{16d} and some private communications. The method has been extensively applied for estimates of geometries and mechanistic reaction pathways by Snyder *et al.*¹⁷ as well as Boyd.^{16b,16c} From these papers it can be concluded that capability of estimating geometries is significantly improved. The energy minimized geometries are in general very close to the experimental data. In the present paper we have investigated how the CNDO/B¹⁸ and INDO/B¹⁸ methods are reflected in the calculation of spin-spin coupling constants.

THEORY AND CALCULATION

In the CNDO/2 and INDO calculations reported in the following section the parametrization is identical with the one given by Pople,³ Santry⁴ and Segal.^{14a}

In the two methods presented by Boyd¹⁶ the parametrizations differ substantially. The basis set is *s* and *p* Slater orbitals, but for hydrogen the exponent factor is 1.0, whereas 1.2 is used by Pople.

Overlap integrals are calculated explicitly.

The repulsion integrals, γ_{AB} , have been introduced according to the formula given by Ohno,¹⁶

$$\gamma_{AB} = \frac{1}{(R_{AB}^2 + \alpha^2)^2}, \text{ where } \alpha = \frac{2}{\gamma_{AA}^* + \gamma_{BB}^*}$$

the * means the atomic limit.^{15a}

The one center Coulomb integrals are determined as reported by Sichel and Whitehead^{15a} based on spectroscopic data previously given by Hinze and Jaffé.¹⁹

While the parametrization by Pople allows calculations involving third period atoms for CNDO/2 and involving hydrogen and second period for INDO, Boyd's parametrization of the CNDO approximation is rather sporadic, but that of the INDO is complete. Calculations using the two schemes were carried out until the energy minimization showed consistency better than 10^{-6} a.u.

It has previously been found that configuration interaction including the single excited states leads to improvement in the calculated spin-spin coupling constants.⁵ For the small molecules selected here it has been possible to perform this calculation.

The use of variable electron density at the site of the nucleus, $\langle \psi^2(0) \rangle$, was introduced as a scaling mechanism by Towl and Schaumburg.¹¹ This first order correction for unequal charge distribution did not require any modification of the SCF calculation. In the present case we have introduced a self-consistent electro-negativity type of scaling²⁰ but for all sorts of valence electrons, whereby the atomic orbitals in the basis set are scaled according to eqns. (2)–(4). The iterative scheme has been modified such that consistency for eqns. (2)–(4) was obtained as well as a minimum energy for that particular set of AO's.

For hydrogen:

$$\xi = 1.2(1.0 - 0.3(P_H - 1.0)) \quad (2)$$

For second period atoms:

$$\xi = (Z_A - 1.7 - 0.35(P_A - 1.0))/2 \quad (3)$$

For third period atoms:

$$\xi = (Z_A - 8.8 - 0.35(P_A - 1.0))/3 \quad (4)$$

Where ξ is the exponential factor in the radial part of Slater type orbitals, Z_A is the atomic number, and P_A is the electron population on the atom A.

It was not obvious to us what convergence properties such a calculation scheme would possess if any. Experimentally it was found that the iterative scheme would converge leading to exponential factor constant within 10^{-4} charge unit within 6–8 cycles.

The calculation of coupling constant was, irrespective of the choice of the preceding options, performed using the sum over states method (SOS) using the perturbing Hamiltonian given by Towl and Schaumburg¹¹ including spin-spin and spin-orbit contributions.

In the formula the electron densities at the site of the nuclei still appear as a factor. It is therefore possible to apply yet one alternative set of parameters, since Clementi and Raymond¹² have published a set of optimized values for the exponential factors based on *ab initio* calculations.

The possible parametrizations based on the options above are represented in Table 1.

To be able to compare the values of the spin-spin coupling constants calculated in the different manners all the calculations were carried out using the experimentally determined geometries of the molecules.

The programs used in the calculations were a symmetry adopted version of the program used by Towl and Schaumburg¹¹ and programs used by Boyd and Snyder.^{16,17} The calculations were carried out on an IBM 370/165.

RESULTS AND DISCUSSION

The molecules chosen for the present comparison have been selected according to three criteria. Firstly, the experimental geometry

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Table 1. An inventory of the 24 calculation schemes used. FD means that the electron density only depends on the nature of the atom. VD means that the electron density both depends on the nature of the atom and on the molecule. DI means diagonal approximation, *i.e.* no configuration interaction.

| | The approximation of CNDO | | | | The approximation of INDO | | | |
|--|-----------------------------|-----------------------------|-----------------------------|-----------------------------|---------------------------|---------------------------|---------------------------|---------------------------|
| | Without CI | | With CI | | Without CI | | With CI | |
| | Using FD | Using VD | Using FD | Using VD | Using FD | Using VD | Using FD | Using VD |
| With the parametrization of Pople | CNDO/2 with DI and FD | CNDO/2 with DI and VD | CNDO/2 with CI and FD | CNDO/2 with CI and VD | INDO with DI and FD | INDO with DI and VD | INDO with CI and FD | INDO with CI and VD |
| With the parametrization of Pople and scaling (V.O.) | CNDO/2 with V.O., DI and FD | CNDO/2 with V.O., DI and VD | CNDO/2 with V.O., CI and FD | CNDO/2 with V.O., CI and VD | INDO with V.O., DI and FD | INDO with V.O., DI and VD | INDO with V.O., CI and FD | INDO with V.O., CI and VD |
| With the parametrization of Boyd | CNDO/B with DI and FD | CNDO/B with DI and VD | CNDO/B with CI and FD | CNDO/B with CI and VD | INDO/B with DI and FD | INDO/B with DI and VD | INDO/B with CI and FD | INDO/B with CI and VD |

Table 2. Calculated and experimental values for ${}^1K_{\text{AH}}$. All the values are to be multiplied by 10^{30} cm^{-3} .

| | CNDO/2 | | CNDO/2 with V.O. | | CNDO/B | | INDO | | INDO with V.O. | | INDO/B | | Exp. values for ${}^1K_{\text{AH}}$ | Refs. to exp. for ${}^1K_{\text{AH}}$ geom. |
|---|--------|-------|------------------|-------|--------|--------|-------|-------|----------------|-------|--------|--------|-------------------------------------|---|
| | DI | CI | DI | CI | DI | CI | DI | CI | DI | CI | DI | CI | | |
| BH_4^- | 13.84 | 16.31 | 12.93 | 14.97 | 24.12 | 29.26 | 13.94 | 17.86 | 13.03 | 16.37 | 23.38 | 34.76 | 20.95 | 44 |
| VD | 10.80 | 12.73 | 10.00 | 11.58 | 19.53 | 23.69 | 11.05 | 14.15 | 10.27 | 12.90 | 18.49 | 27.50 | | 25 |
| CH_4 | 22.71 | 26.48 | 22.68 | 26.45 | 32.30 | 38.65 | 22.61 | 29.71 | 22.64 | 29.76 | 32.05 | 50.36 | 41.41 | 46 |
| VD | 23.31 | 27.19 | 23.28 | 27.15 | 32.69 | 39.01 | 23.50 | 30.88 | 23.52 | 30.92 | 32.04 | 50.34 | | 26 |
| CH_3F | 25.89 | 31.24 | 26.07 | 31.72 | | B | 26.39 | 35.10 | 26.70 | 35.97 | 41.12 | 62.21 | 49.40 | 49 |
| VD | 28.67 | 34.59 | 28.81 | 35.05 | | | 29.80 | 39.64 | 30.06 | 40.49 | 48.97 | 74.07 | | 31 |
| $\text{H}_2\text{C}=\text{CH}_2$ | 27.96 | 35.74 | 27.88 | 35.65 | 39.36 | 51.71 | 27.88 | 38.54 | 27.90 | 38.56 | 40.58 | 64.47 | 51.75 | 59 |
| VD | 28.97 | 37.02 | 28.88 | 36.93 | 40.98 | 53.83 | 28.80 | 39.81 | 28.82 | 39.84 | 42.31 | 67.22 | | 40 |
| $\text{H}_2\text{C}=\text{C}=\text{CH}_2$ | 27.32 | 37.02 | 27.34 | 37.03 | 42.31 | 58.50 | 27.37 | 39.99 | 27.41 | 39.99 | 42.51 | 69.30 | 55.72 | 62 |
| VD | 28.04 | 38.01 | 28.08 | 38.03 | 43.43 | 60.04 | 28.12 | 41.08 | 28.16 | 41.08 | 43.59 | 71.07 | | 42 |
| NH_3^+ | 32.93 | 37.64 | 33.11 | 38.56 | 43.31 | 49.21 | 32.40 | 42.90 | 32.70 | 44.17 | 39.30 | 59.96 | 60.80 | 47 |
| VD | 42.43 | 48.49 | 42.79 | 49.84 | 51.54 | 58.57 | 42.05 | 55.67 | 42.53 | 57.45 | 49.29 | 75.20 | | 27 |
| CH_2F_2 | 30.84 | 37.95 | 31.12 | 39.01 | | B | 32.73 | 42.94 | 33.19 | 44.73 | 59.65 | 83.92 | 61.12 | 49 |
| VD | 36.59 | 45.03 | 36.75 | 46.06 | | | 39.72 | 52.12 | 40.04 | 53.95 | 81.13 | 114.13 | | 34 |
| $\text{H}_2\text{C}=\text{N}=\text{N}$ | 36.74 | 46.49 | 36.90 | 46.35 | 57.96 | 60.32 | 37.79 | 49.80 | 37.92 | 49.61 | 56.99 | 63.64 | (±)64.64 | 55 |
| VD | 36.34 | 45.98 | 36.61 | 45.98 | 63.61 | 66.19 | 37.18 | 49.00 | 37.44 | 48.98 | 56.74 | 63.36 | | 35 |
| CHF_3 | 39.38 | 47.47 | 39.65 | 49.25 | | B | 43.71 | 55.53 | 44.51 | 58.39 | 107.44 | 135.00 | 79.21 | 49 |
| VD | 49.69 | 60.16 | 49.74 | 61.77 | | | 56.39 | 71.65 | 57.08 | 74.88 | 163.98 | 206.04 | | 32 |
| $\text{HC}\equiv\text{CH}$ | 49.18 | 60.37 | 48.72 | 60.00 | 72.27 | 91.36 | 49.53 | 63.05 | 49.15 | 62.77 | 75.64 | 102.16 | 82.49 | 59 |
| VD | 52.58 | 64.54 | 52.05 | 64.09 | 80.25 | 101.45 | 52.67 | 67.06 | 52.23 | 66.70 | 84.01 | 113.46 | | 41 |
| RMS | 3.64 | 3.40 | 3.19 | 2.65 | 5.70 | 6.52 | 3.91 | 2.25 | 3.46 | 1.47 | 6.66 | 6.78 | | I |
| Error | 4.61 | 2.43 | 4.56 | 2.67 | 4.27 | 4.35 | 4.39 | 3.55 | 4.37 | 4.10 | 4.32 | 5.71 | | |
| RMS | 4.32 | 4.56 | 3.86 | 3.50 | | B | 3.47 | 2.52 | 2.98 | 1.34 | 8.91 | 8.70 | | II |
| Error | 3.87 | 2.05 | 3.82 | 2.25 | | | 4.28 | 3.49 | 4.36 | 4.21 | 10.76 | 10.71 | | |

Explanations of symbols used in Tables 1-8. A. The value of this spin-spin coupling constant is not calculated because it cannot be derived in a meaningful way with method DI. B. The value is not calculated because of the sporadic parametrization of CNDO/B. ^a This coupling is a *cis* coupling. ^b This coupling is a *trans* coupling. ^c This coupling is transmitted via a nitrogen atom. ^d This coupling constant is ${}^2K_{\text{HH}}$ in pyridazine, where the hydrogens are in *ortho* and *meta* positions to the nearest nitrogen. ^e This coupling constant is ${}^2K_{\text{HH}}$ in pyridazine, where the hydrogens are in *meta* and *para* positions to the nitrogens. ^f This coupling constant is of the type ${}^2K_{\text{NH}}$. ^g This coupling constant is of the type ${}^2K_{\text{FH}}$. ^h This coupling is ${}^2K_{\text{HH}}$ between the hydrogens in positions 2 and 3. ⁱ This coupling is ${}^2K_{\text{HH}}$ between the hydrogens in positions 3 and 4. ^j The RMS errors are calculated on the basis of the coupling constants which can be calculated in all the CNDO/B methods. ^k The RMS errors are calculated on the basis of the coupling constants which can be calculated in all methods but the CNDO/B methods. ^l As I, but only for methods using CI. ^m As II, but only for methods using CI.

When a sign of a coupling constant is not established experimentally, then a sign is chosen, which to a lesser degree alters the correlation between calculated and experimentally determined spin-spin coupling constants.

should be accurately known, since the calculated values for the coupling constants are depending on the geometries and since these variations for the different calculation schemes are not well known. Secondly, the experimental data for the spin-spin coupling constants should be well determined in magnitude as well as sign. Thirdly, a wide variety of compounds with regard to elements and chemical bonding should be covered in order to make the evaluation as general as possible. In order to bring the data on a common scale it has been chosen to report the reduced spin-spin coupling constants $K_{AB} = 4\pi^2 \cdot J_{AB}/(h\gamma_A\gamma_B)$ as has become usual in recent papers (K_{AB} in cm^{-3} and J_{AB} in Hz). γ is the gyromagnetic ratio.

The large number of K_{AB} that have been calculated will not be treated as one group, but separated into classes according to criteria given below:

The importance of mechanism. It can be expected that coupling between two protons only involving Fermi contact term might display a type of correlation between experimental and calculated values different from what is found in the case of coupling between two second period atoms.

The importance of basis set. It can be expected that this will influence the coupling between protons and second period atoms in a way different from two protons. For inter proton coupling it has been found by Kowalewski²² that the size of the basis set is very important for the obtained numerical results. Furthermore it can be seen²² that an increase in basis set does not influence inter proton coupling over different numbers of valence bonds equally. It would therefore be likely that semiempirical calculations would only show an acceptable correlation to experiments if the data are further subdivided into classes ${}^nK_{AB}$ depending on n .

${}^1K_{AH}$. In Table 2 and Fig. 1 results obtained for ${}^1K_{AH}$, $A \neq H$ are reported. For all the methods investigated good correlations can be established between the calculated and experimental values.

When the strong dependence on ξ is taken into account, it is surprising to observe that only minor changes are introduced by the variable orbital exponent modification, V.O.

The values obtained by the Boyd methods are considerably larger, but the correlation

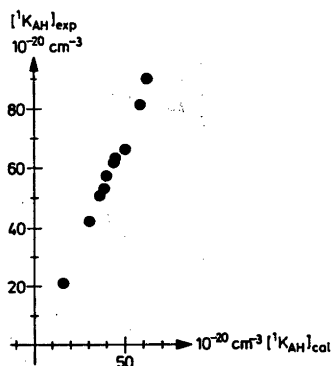


Fig. 1. One of the correlations between calculated and experimentally determined spin-spin coupling constants is shown for the type of coupling ${}^1K_{AH}$. The calculation scheme used is: INDO with V.O., CI and FD.

has not improved. The best result was obtained using the INDO method with V.O., CI and FD leading to the formula:

$${}^1K_{AH} = 1.32({}^1K_{AH})_{\text{calc}} + 1.21 \times 10^{20} \text{ cm}^{-3}$$

$$\text{RMS error: } 1.3 \times 10^{20} \text{ cm}^{-3}$$

${}^1K_{AB}$. In Table 3 and Fig. 2 data for the ${}^1K_{AB}$, $A, B \neq H$, coupling are reported. The range spanned by the experimental data is from $(-195.95 \text{ to } 183.57)10^{20} \text{ cm}^{-3}$. The Boyd parametrization of the CNDO approximation has not been completed for fluorine interaction with other atoms, and here the column is omitted. Since charge distribution in, e.g., CF_4

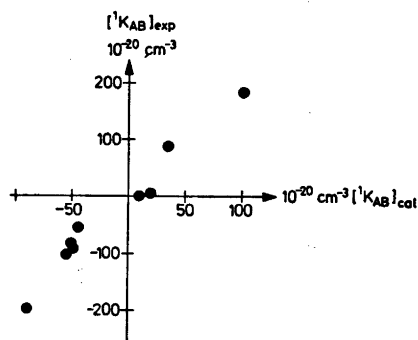


Fig. 2. One of the correlations between calculated and experimentally determined spin-spin coupling constants is shown for the type of coupling ${}^1K_{AB}$. The calculation scheme used is: INDO with V.O., CI and VD.

Table 3. Calculated and experimental values for ${}^1K_{AB}$. All the values are to be multiplied by 10^{20} cm^{-3} .

| | CNDO/2 | | CNDO/2 with V.O. | | INDO | | INDO with V.O. | | INDO/B | | Exp. values for ${}^1K_{BB}$ | Refs. to exp. for ${}^1K_{BB}$ geom. | |
|----------------------------------|--------------|--------|------------------|--------|--------|--------|----------------|--------|---------|---------|------------------------------|--------------------------------------|----|
| | DI | CI | DI | CI | DI | CI | DI | CI | DI | CI | | | |
| NF ₃ | FD -54.27 | -59.19 | -51.96 | -55.89 | -72.16 | -80.50 | -66.12 | -73.65 | -167.79 | -171.11 | -195.95 | 54 | 33 |
| CHF ₃ | VD -14.86 | -22.72 | -18.54 | -26.04 | -33.32 | -36.68 | -37.93 | -41.56 | -107.12 | -100.04 | - | 49 | 32 |
| CF ₄ | VD -18.68 | -28.79 | -23.01 | -32.48 | -44.50 | -49.02 | -49.36 | -54.13 | -161.78 | -150.99 | -96.55 | 49 | 29 |
| CH ₂ F ₂ | VD -2.64 | -12.81 | -9.05 | -19.52 | -19.95 | -25.65 | -27.65 | -35.41 | -57.16 | -52.65 | -91.23 | 49 | 29 |
| CH ₃ F | VD -3.13 | -16.96 | -11.62 | -25.51 | -28.14 | -36.27 | -37.85 | -48.60 | -95.75 | -88.02 | - | 49 | 34 |
| CH ₃ F | VD -20.75 | -26.62 | -22.62 | -33.09 | -38.30 | -39.69 | -40.04 | -41.74 | -103.88 | -95.68 | -82.64 | 49 | 31 |
| BF ₃ | VD -24.57 | -31.65 | -26.22 | -33.09 | -47.58 | -49.36 | -48.95 | -51.11 | -138.33 | -127.37 | - | 49 | 31 |
| BF ₃ | VD -19.77 | -25.70 | -19.94 | -26.18 | -36.16 | -37.85 | -37.44 | -38.51 | -88.56 | -80.79 | -55.44 | 49 | 31 |
| H ₂ C=CH ₂ | VD -21.98 | -28.54 | -22.15 | -29.01 | -41.54 | -43.48 | -42.79 | -44.02 | -100.67 | -91.89 | - | 48 | 28 |
| HC≡CH | VD 19.17 | 17.85 | 14.65 | 13.31 | 11.88 | 13.75 | 6.22 | 7.58 | 5.11 | 10.71 | 1.32 | 48 | 30 |
| RMS Error | VD 24.73 | 23.07 | 18.52 | 16.88 | 16.33 | 18.89 | 8.43 | 10.24 | 9.17 | 18.79 | 4.14 | 50 | 40 |
| | VD 32.56 | 29.95 | 23.71 | 20.66 | 23.06 | 24.93 | 12.38 | 13.25 | 14.41 | 21.53 | 89.06 | 59 | 52 |
| | VD 45.48 | 41.94 | 32.48 | 28.44 | 33.58 | 36.34 | 17.75 | 19.03 | 26.10 | 38.80 | 183.57 | 59 | 41 |
| | VD 29.27 | 30.01 | 29.70 | 30.45 | 27.59 | 33.09 | 27.48 | 32.99 | -8.32 | 12.99 | - | 52 | 40 |
| | VD 30.94 | 31.72 | 31.41 | 32.19 | 29.86 | 35.79 | 29.75 | 35.68 | -7.68 | 13.38 | - | 52 | 41 |
| | VD 96.17 | 98.20 | 98.00 | 100.10 | 91.18 | 98.47 | 92.71 | 99.99 | 59.44 | 85.68 | - | 52 | 41 |
| | VD 97.46 | 99.54 | 99.45 | 101.60 | 93.07 | 100.55 | 94.76 | 102.24 | 56.15 | 81.32 | - | 52 | 41 |
| | VD 30.94 | 28.02 | 27.22 | 25.54 | 26.60 | 23.34 | 24.39 | 20.71 | 42.93 | 35.65 | - | 52 | 41 |
| | VD 34.35 | 30.42 | 26.84 | 24.35 | 28.86 | 26.25 | 23.09 | 20.04 | 46.04 | 41.72 | - | 52 | 41 |

Table 4. Calculated and experimental values for ${}^2K_{\text{HH}}$. All the values are to be multiplied by 10^{20} cm^{-3} . For explanation of A, I, II, III and IV see below Table 2.

| | | INDO with V.O. | | INDO/B | | Exp. values for ${}^2K_{\text{HH}}$ | Refs. to exp. for ${}^2K_{\text{HH}}$ | geom. |
|--|----|----------------|-------|--------|-------|---|--|-------|
| | | DI | CI | DI | CI | | | |
| CH_4 | FD | | -0.13 | | -1.38 | -1.033 | 45 | 26 |
| | VD | A | -0.12 | A | -1.53 | | | |
| NH_4^+ | FD | | -0.16 | | -1.46 | -0.922 | 47 | 27 |
| | VD | A | -0.25 | A | -2.59 | | | |
| BH_4^- | FD | | 0.024 | | 1.25 | -0.871 | 44 | 25 |
| | VD | A | 0.016 | A | 0.84 | | | |
| CH_3F | FD | | 0.35 | | 1.27 | -0.800 | 51 | 31 |
| | VD | A | 0.34 | A | 1.27 | | | |
| H_2O | FD | 0.27 | -0.19 | 0.72 | -0.50 | -0.600 | 57 | 37 |
| | VD | 0.35 | -0.26 | 1.14 | -0.80 | | | |
| $\text{H}_2\text{C}=\text{CF}_2$ | FD | 0.43 | 0.43 | 0.85 | 0.58 | (+) - 0.400 | 56 | 36 |
| | VD | 0.48 | 0.48 | 1.09 | 0.74 | | | |
| $\text{H}_2\text{C}=\text{CH}_2$ | FD | 0.74 | 0.83 | 2.42 | 2.33 | 0.192 | 52 | 40 |
| | VD | 0.74 | 0.82 | 2.67 | 2.58 | | | |
| HCONH_2 | FD | 0.93 | 1.20 | 1.60 | 0.97 | 0.192 | 63 | 43 |
| | VD | 1.17 | 1.51 | 2.39 | 1.46 | | | |
| $\text{H}_2\text{C}=\overset{+}{\text{N}}=\overset{-}{\text{N}}$ | FD | 0.96 | 1.11 | 2.20 | 2.05 | (+) - 0.380 | 55 | 35 |
| | VD | 1.02 | 1.19 | 2.76 | 2.57 | | | |
| RMS | FD | 0.054 | 0.013 | 0.126 | 0.114 | | I | |
| Error | VD | 0.107 | 0.028 | 0.057 | 0.077 | | | |
| RMS | FD | 0.084 | 0.131 | 0.151 | 0.175 | | II | |
| Error | VD | 0.172 | 0.172 | 0.088 | 0.139 | | | |
| RMS | FD | | 0.169 | | 0.314 | | III | |
| Error | VD | A | 0.188 | A | 0.281 | | | |
| RMS | FD | | 0.199 | | 0.361 | | IV | |
| Error | VD | A | 0.226 | A | 0.323 | | | |

is significantly different from neutrality some effect of the V.O. method is observed, but still it remains smaller than the effect of CI. How-

ever, both are small compared to the changes from the CNDO/2 and INDO to the INDO/B method. The best method is again INDO with V.O. and CI but VD:

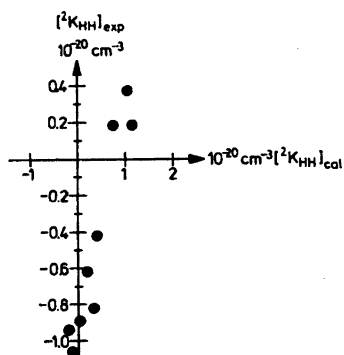


Fig. 3. One of the correlations between calculated and experimentally determined spin-spin coupling constants is shown for the type of coupling ${}^2K_{\text{HH}}$. The calculations scheme used is: INDO with V.O., CI and FD.

$${}^1K_{\text{AB}} = 1.85({}^1K_{\text{AB}})_{\text{calc}} - 2.47 \times 10^{20} \text{ cm}^{-3}$$

RMS error: $20.0 \times 10^{20} \text{ cm}^{-3}$

${}^2K_{\text{HH}}$. Table 4 and Fig. 3 reproduce the data observed for geminal proton coupling, ${}^2K_{\text{HH}}$. They have in many previous calculations been found most difficult to calculate. The present results do not differ from previous results in this respect. It is possible to establish a reasonable correlation but again the Pople parametrization is superior to the method of Boyd. Again the best result is obtained using INDO with V.O., CI and FD:

$${}^2K_{\text{HH}} = 0.92({}^2K_{\text{HH}})_{\text{calc}} - 0.78 \times 10^{20} \text{ cm}^{-3}$$

RMS error: $0.2 \times 10^{20} \text{ cm}^{-3}$

Table 5. In this table it is shown that not all properties are calculated in a meaningful way, when the calculation scheme includes the DI method (without CI). The results quoted below for models I, II and III, see Fig. 4, are obtained using the CNDO/2 method without CI and with FD.

| Energy in unit of a.u. | | | | | | |
|---------------------------------------|----------------------------|----------------------------|----------------------------|----------------------------|----------------------------|----------------------------|
| Model | Total- | Electronic- | | Bonding | | |
| I } II } III } | -10.11369014 | -19.629820 | | -1.39377553 | | |
| Valence electronic population of atom | | | | | | |
| Model | C | H | | | | |
| I } II } III } | 4.04933 | 0.98767 | | | | |
| Spin-spin coupling constants in Hz | | | | | | |
| Model | J_{CH_1} | J_{CH_2} | J_{CH_3} | J_{CH_4} | | |
| I } II } III } | 68.5522 | 68.5522 | 68.5522 | 68.5522 | | |
| Model | $J_{\text{H}_1\text{H}_2}$ | $J_{\text{H}_1\text{H}_3}$ | $J_{\text{H}_1\text{H}_4}$ | $J_{\text{H}_2\text{H}_3}$ | $J_{\text{H}_2\text{H}_4}$ | $J_{\text{H}_3\text{H}_4}$ |
| I | 1.5255 | 1.7824 | 1.2592 | -1.2350 | 0.7088 | 0.7677 |
| II | 0.4415 | 0.4006 | 1.4865 | 0.4612 | 1.3111 | 0.1246 |
| III | 1.6659 | 2.5196 | 1.2740 | 0.3221 | 0.2025 | 1.3370 |

Table 6. Calculated and experimental values for ${}^3K_{\text{HH}}$. All values are to be multiplied by 10^{20} cm^{-3} . For explanation of I, II, a, b, c, d, e, h and i see below Table 2.

| | | INDO with V.O. | | INDO/B | | Exp. values for ${}^3K_{\text{HH}}$ | Refs. to exp. for ${}^3K_{\text{HH}}$ | geom. |
|--------------------------------------|----|----------------|-------|--------|--------|---|--|-------|
| | | DI | CI | DI | CI | | | |
| <i>cis</i> | FD | 0.15 | 0.19 | 0.67 | 0.55 | +0.167 (-) | 56 | 36 |
| FHC=CHF | VD | 0.15 | 0.20 | 0.62 | 0.59 | | | |
| HCONH ₂ , a | FD | 0.19 | 0.29 | -0.73 | -0.35 | 0.175 | 63 | 43 |
| | VD | 0.19 | 0.30 | -0.86 | -0.41 | | | |
| Pyrrole h | FD | 0.14 | 0.15 | 0.005 | -0.088 | 0.225 | 58 | 39 |
| | VD | 0.14 | 0.14 | 0.005 | -0.088 | | | |
| Pyrrole i | FD | 0.14 | 0.35 | -0.27 | -0.17 | 0.279 | 58 | 39 |
| | VD | 0.13 | 0.34 | -0.30 | -0.19 | | | |
| Pyridazine d | FD | 0.41 | 0.65 | -0.074 | 0.044 | 0.421 | 55 | 38 |
| | VD | 0.39 | 0.62 | -0.079 | 0.047 | | | |
| Pyridazine e | FD | 0.56 | 0.83 | 0.012 | 0.31 | 0.685 | 55 | 38 |
| | VD | 0.55 | 0.81 | 0.013 | 0.34 | | | |
| HC≡CH | FD | 0.91 | 1.03 | 4.29 | 4.92 | 0.816 | 52 | 41 |
| | VD | 1.00 | 1.13 | 5.48 | 6.29 | | | |
| H ₂ C=CH ₂ , a | FD | 0.78 | 1.01 | 0.47 | 0.69 | 0.958 | 52 | 40 |
| | VD | 0.78 | 1.00 | 0.51 | 0.77 | | | |
| HCONH ₂ , b | FD | 1.55 | 2.57 | 4.29 | 5.89 | 1.158 | 63 | 43 |
| | VD | 1.64 | 2.71 | 5.13 | 7.05 | | | |
| H ₂ C=CH ₂ , b | FD | 2.14 | 2.73 | 4.88 | 6.52 | 1.591 | 52 | 40 |
| | VD | 2.13 | 2.71 | 5.38 | 7.20 | | | |
| RMS | FD | 0.101 | 0.112 | 0.274 | 0.247 | | I | |
| Error | VD | 0.105 | 0.107 | 0.295 | 0.269 | | | |
| RMS | FD | 0.108 | 0.153 | 0.265 | 0.242 | | II | |
| Error | VD | 0.115 | 0.163 | 0.279 | 0.258 | | | |

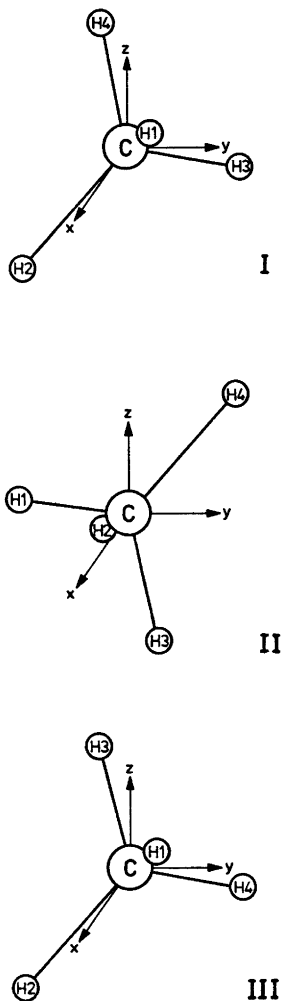


Fig. 4. This figure shows a methane molecule placed in three different manners in a coordinate system ($a = 0.63164 \text{ \AA}$). For each of the three sets of coordinates calculations are performed using the method CNDO/2 without CI but with FD. The results are shown in Table 5.

Model I: The coordinates are for C: (0,0,0); H1: (a, a, a); H2: ($a, -a, -a$); H3: ($-a, a, -a$); H4: ($-a, -a, a$).

Model II: The coordinates are for C: (0,0,0); H1: ($a, -a, a$); H2: ($-a, -a, -a$); H3: ($a, a, -a$); H4: ($-a, a, a$).

Model III: The coordinates are for C: (0,0,0); H1: (a, a, a); H2: ($a, -a, -a$); H3: ($-a, -a, a$); H4: ($-a, a, -a$).

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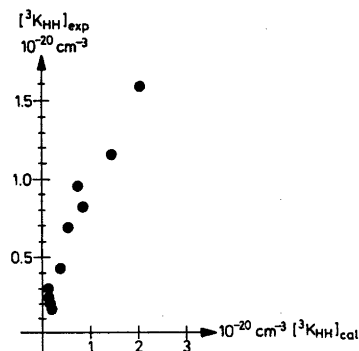


Fig. 5. One of the correlations between calculated and experimentally determined spin-spin coupling constants is shown for the ${}^3K_{HH}$ type of coupling. The calculation scheme used is: INDO without CI and with FD.

In this case the results obtained without CI are not reported in the table. This is due to the fundamental defect in the CNDO and INDO methods in handling degenerate orbitals. This was first pointed out by Ditchfield and Murrell²³ and later mentioned by Pouzard *et al.*²⁴

In calculations reported by Murrell the degenerate molecular orbitals were chosen in such a way that all triplet excited states arising from a degenerate configuration had the same energy.²³ This procedure seems somewhat arbitrary since these energies are not invariant under coordinate transformations.

In Table 5 and Fig. 4 data for CH_4 in three different coordinate systems are quoted.

No problem is encountered in calculations employing CI since the resulting wavefunctions for the triplet excited states are projected into the irreducible species of the molecular point group.

${}^3K_{HH}$. Most geometrical considerations have been focused on ${}^3K_{HH}$. In Table 6 and Fig. 5 the results obtained for vicinal coupling constants are reported. For this coupling the Boyd methods show definitely poor performance, since the RMS error is two times bigger than the ones found in the Pople parametrization. The best correlation was found for the INDO. The correlation is slightly better in the case without CI than with CI, but the difference is insignificant. The calculated relationship is given as (in the method INDO without CI and with FD):

Table 7. Calculated and experimental values for ${}^2K_{AH}$. All the values are to be multiplied by 10^{20} cm^{-3} . For explanation of I, II, *f* and *g* see below Table 2.

| | | INDO with V.O. | | INDO/B | | Exp. values for ${}^2K_{AH}$ | Refs. to exp. for | |
|----------------------------------|-------------|----------------|-------|--------|-------|------------------------------------|-------------------|-------|
| | | DI | CI | DI | CI | | ${}^2K_{AH}$ | geom. |
| $\text{H}_2\text{C}=\text{CH}_2$ | FD | 0.61 | -0.41 | 2.66 | -0.24 | -0.80 | 60 | 40 |
| | VD | 0.63 | -0.42 | 2.78 | -0.25 | | | |
| Pyrrole <i>f</i> | FD | 1.30 | 2.07 | 5.51 | 6.31 | + (-) 3.72 | 58 | 39 |
| | VD | 1.32 | 2.10 | 5.64 | 6.46 | | | |
| CH_3F | FD | 0.77 | 0.20 | 1.09 | 0.91 | 4.12 | 53 | 31 |
| | VD | 0.75 | 0.20 | 1.04 | 0.87 | | | |
| CH_2F_2 | FD | 0.59 | 0.41 | 2.13 | 2.31 | 4.46 | 53 | 34 |
| | VD | 0.57 | 0.40 | 1.96 | 2.13 | | | |
| <i>cis</i> | FD | 0.24 | 0.55 | 1.48 | 2.33 | 6.43 | 56 | 36 |
| HFC=CFH <i>g</i> | VD | 0.24 | 0.55 | 1.49 | 2.34 | | | |
| CHF_3 | FD | 1.36 | 1.24 | 8.12 | 8.77 | 6.99 | 53 | 32 |
| | VD | 1.31 | 1.20 | 7.38 | 7.97 | | | |
| Pyridazine | FD | 6.33 | 10.45 | 8.34 | 12.54 | 9.90 | 55 | 38 |
| | <i>f</i> VD | 6.26 | 10.34 | 8.61 | 12.95 | | | |
| HCONH_2 <i>f</i> | FD | 5.19 | 7.97 | 23.38 | 25.13 | 11.90 | 63 | 43 |
| | VD | 4.75 | 7.30 | 20.28 | 21.80 | | | |
| $\text{HC}\equiv\text{CH}$ | FD | 2.42 | 2.31 | 9.95 | 8.66 | 16.33 | 60 | 41 |
| | VD | 2.58 | 2.46 | 11.05 | 9.62 | | | |
| RMS | FD | 5.57 | 5.87 | 1.20 | 4.23 | I | | |
| Error | VD | 5.47 | 5.82 | 0.69 | 3.93 | | | |
| RMS | FD | 3.83 | 3.99 | 3.66 | 3.60 | II | | |
| Error | VD | 3.79 | 3.98 | 3.37 | 3.34 | | | |

Table 8. Calculated and experimental values for ${}^3K_{AH}$. All values are to be multiplied by 10^{20} cm^{-3} . For explanation of I, II, *a*, *b*, *c* and *f* see below Table 2.

| | | INDO with V.O. | | INDO/B | | Exp. values for ${}^3K_{AH}$ | Refs. to exp. for | |
|---|----------------|----------------|-------|--------|-------|------------------------------------|-------------------|-------|
| | | DI | CI | DI | CI | | ${}^3K_{AH}$ | geom. |
| $\text{H}_2\text{C}=\text{CF}_2$ <i>a</i> | FD | 0.80 | 0.70 | 1.16 | -0.33 | 0.06 | 56 | 36 |
| | VD | 0.83 | 0.74 | 1.26 | -0.35 | | | |
| $\text{H}_2\text{C}=\text{N}=\text{N}$ | FD | 0.02 | 0.14 | -0.42 | 0.09 | + (-) 0.90 | 55 | 35 |
| | VD | 0.02 | 0.15 | -0.46 | 0.10 | | | |
| Pyridazine | FD | -0.70 | -0.36 | -0.53 | -1.04 | 0.92 | 55 | 38 |
| | <i>f</i> VD | -0.70 | -0.36 | -0.56 | -1.09 | | | |
| <i>cis</i> | FD | 2.08 | 2.10 | 4.45 | 5.54 | 1.81 | 56 | 36 |
| HFC=CFH | VD | 2.09 | 2.11 | 4.47 | 5.58 | | | |
| $\text{H}_2\text{C}=\text{CF}_2$ <i>b</i> | FD | 2.21 | 2.48 | 6.02 | 7.61 | 3.00 | 56 | 36 |
| | VD | 2.31 | 2.59 | 6.53 | 8.26 | | | |
| Pyridazine | FD | 0.42 | 0.35 | 0.14 | -0.54 | 3.04 | 55 | 38 |
| | <i>c, f</i> VD | 0.42 | 0.34 | 0.14 | -0.56 | | | |
| Pyrrole <i>f</i> | FD | 4.52 | 6.37 | 5.93 | 8.37 | + (-) 4.43 | 58 | 39 |
| | VD | 4.61 | 6.48 | 6.12 | 8.63 | | | |
| RMS | FD | 0.69 | 0.79 | 0.75 | 0.89 | I | | |
| Error | VD | 0.69 | 0.79 | 0.75 | 0.89 | | | |
| RMS | FD | 0.93 | 0.90 | 1.07 | 0.99 | II | | |
| Error | VD | 0.93 | 0.90 | 1.07 | 0.99 | | | |

$${}^3K_{\text{HH}} = 0.69({}^3K_{\text{HH}})_{\text{cal}} + 0.16 \times 10^{20} \text{ cm}^{-3}$$

$$\text{RMS error: } 0.1 \times 10^{20} \text{ cm}^{-3}$$

${}^2K_{\text{AH}}, {}^3K_{\text{AH}}$. Recently considerable interest has been given to K_{AH} with A = ${}^{13}\text{C}$, ${}^{15}\text{N}$, ${}^{31}\text{P}$ etc. In Table 7 data are given for ${}^2K_{\text{AH}}$ and in Table 8 for ${}^3K_{\text{AH}}$. The Boyd parametrization again reduces the number of data available in CNDO/B. Also for these two types of coupling constants is it possible to obtain a reasonable correlation, but the RMS errors are not acceptable.

In the test molecules a number of ${}^4K_{\text{HH}}$ coupling constants are available, but the correlations obtainable are not sufficiently accurate to warrant any predictions.

CONCLUSION

Based on a selected set of molecules it seems unlikely that the parametrization introduced by Boyd, Sichel and Whitehead will serve as an attractive alternative to CNDO/2 and INDO calculations with conventional parametrization. The use of the concept of variable orbital exponents can be incorporated in an iterative scheme with stable convergence behaviour. The result obtained is not substantially different from the standard calculation but a marginal improvement is found when the correlation of experimental and calculated results are considered. In all cases but one the CI improves the correlations. For systems having n fold symmetry axis, $n > 3$, it is necessary to introduce a procedure that yields symmetry adapted excited states in order to obtain well defined results.

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