

# The Use of Partially Restricted Molecular Orbitals to Investigate Transmission Mechanisms of Spin–Spin Coupling Constants. I. The $\sigma$ and $\pi$ Contributions within the FPT INDO Method

Alejandro R. Engelmann, Rubén H. Contreras\* and Julio C. Facelli\*\*

Departamento de Física, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Ciudad Universitaria, Pabellón I, 1428, Buenos Aires, Argentina

Partially restricted INDO MO Calculations have been carried out to separate the  $\pi$ -electron contributions to spin–spin coupling constants in ethylene, butadiene, benzene and toluene. Results reproduce very well known trends such as the pathway invariance, the alternation in sign and the methyl group replacement rule.

**Key words:** Coupling constants – Transmission mechanisms.

## 1. Introduction

One of the most commonly used approaches to calculate spin–spin coupling constants is that based on the finite perturbation theory (FPT) [1] and in general, it is used at different levels of approximation [2, 3]. Within this scope the wave function is calculated as a spin-unrestricted self-consistent molecular orbital function. This requirement must be fulfilled in order to accommodate the uneven distribution of electron spins induced by the nuclear magnetic moment introduced as a finite perturbation. In this series of papers calculations of wave functions performed with partially restricted molecular orbitals (PRMO) will be carried out in order to study transmission mechanisms of nuclear spin–spin coupling constants.

\* Author to whom correspondence should be addressed.

\*\* Comisión de Investigaciones Científicas (CIC, Pcia.Bs.As.) fellow.

Most experimental as well as theoretical investigations concerned with transmission mechanisms of coupling constants were particularly directed towards estimations of the  $\sigma$ - and  $\pi$ -electron contributions [4, 5, 6]. For this reason, the aim of this paper is to apply the PRMO method at the INDO level of approximation to separate these two contributions in ethylene, butadiene, benzene and toluene. At the same INDO level of approximation other methods of evaluating  $\pi$ -electron contributions to coupling constants are found in the literature. Briefly, these other methods are:

- 1) A comparison of CNDO/2 and INDO calculations. Since in the CNDO method the one-center exchange integrals are excluded, no  $\pi$ -spin density can be induced [2]. Therefore, an FPT-CNDO/2 calculation gives an only  $\sigma$ -transmitted coupling constant. However, objections to this treatment have been found [5].
- 2) Wasylishen and Schaefer [7] separated the  $\sigma$ - and  $\pi$ -contributions to benzylic couplings in toluene and inter-benzylic couplings in xylenes performing FPT-INDO calculations for different orientations of the methyl group. The results thus obtained were averaged assuming that these groups undergo a free rotation. Afterwards, these averaged values were compared with those obtained by averaging the sine square dihedral dependence [4] of the  $\pi$ -electron contribution.
- 3) The Bacon and Maciel method [8] where a full FPT INDO calculation is compared with another one in which, for plane systems, the  $\sigma - \pi$  exchange integrals are set equal to zero in the two electron part of the Fock operator.
- 4) The modified version of the Bacon and Maciel method given by Steiger et al. [9] where the  $\sigma - \pi$  exchange integrals that appear in the core hamiltonian matrix elements are also set equal to zero.

## 2. $\sigma$ -unrestricted and $\pi$ -restricted molecular orbitals

For an unrestricted LCAO-SCF calculation the Fock hamiltonian can be written:

$$F_{\mu\nu}^{\alpha} = H_{\mu\nu}^{\text{core}} + \sum_{\lambda\sigma} [P_{\lambda\sigma}(\mu\nu|\lambda\sigma) - P_{\lambda\sigma}^{\alpha}(\mu\sigma|\lambda\nu)] \quad (1)$$

with a similar expression for beta orbitals. The different symbols in Eq. (1) have their usual meanings [2].

When considering plane molecules, in order to perform an unrestricted calculation on  $\sigma$ -electrons and a restricted one on  $\pi$ -electrons the following procedure is adopted: the density matrix elements  $P_{\mu\nu}^{\alpha}$  and  $P_{\mu\nu}^{\beta}$  obtained in each SCF cycle are dealt with in different ways depending on whether both  $\mu$  and  $\nu$  refer to atomic orbitals that belong to the  $\pi$ -molecular system or whether any of them does not belong to that system. In the first case their arithmetic mean value is taken to form the  $\alpha$  and  $\beta$  Fock matrices to start the next SCF cycle, whereas in the second case the density matrix elements are not modified. This procedure is repeated until convergence is achieved. In toluene the  $\pi$ -restriction is imposed only on the ring carbon atomic orbitals.

**Table 1.**  $\sigma$ - and  $\pi$ -contributions to spin-spin coupling constants of ethylene according to different methods. (All values are given in Hz)

Type of Coupling	Exp. <sup>a</sup>	INDO <sup>b</sup>	PRMO <sup>c</sup>	this work	$\pi$ -contribution <sup>d</sup>				
					I	II	III	IV	V
H-C-H	2.5	3.23	4.50	-1.27	-5.24	1.53	-0.98	-0.99	-1.35
H-C-C-H (cis)	11.7	9.31	8.04	1.27	1.27	0.40	1.18	0.99	1.35
H-C-C-H (trans)	19.1	25.14	23.87	1.27	5.64	2.36	1.32	0.99	1.35
C-H	156.4	156.70	152.34	4.35	29.07	4.78	4.52	—	—
C-C-H	-2.4	-11.57	-7.21	-4.35	-7.73	3.51	-4.29	—	—

<sup>a</sup> taken from Ref. [11].<sup>b</sup> Calculations were carried out using the geometric data given by the Pople and Gordon model [12].<sup>c</sup> Partially restricted molecular orbital calculations.  $\pi$ -orbitals are restricted as explained in the text.<sup>d</sup> Values obtained using different methods : I: INDO - CNDO; II: Bacon and Maciel [8]; III: Steiger et al. [9]; IV and V: Cuntliffe et al. [13].

### 3. Results and Discussion

To implement the above outlined method the pertinent modifications were introduced into the FINITE program [10].  $\sigma$ - and  $\pi$ -electron contributions to some proton–proton as well as carbon–proton couplings in ethylene, butadiene, benzene and toluene were calculated.

Table 1 shows the results obtained for ethylene. They are compared with those obtained using several different methods. It is observed that, within the INDO level of approximation, the  $\pi$ -contributions obtained in this work are the only ones whose absolute values do not depend either on the zig-zag path or on the number of bonds that separate both interacting nuclei. The absolute values of the  $\pi$ -component of interproton coupling constants are close to those obtained by Steiger et al. [9] and Cunliffe et al. [13].

It must be observed that while the method of Steiger et al. [9] whereby some exchange integrals are set equal to zero yields a modification in the final molecular orbital wave function, in the PRMO method the restriction on the  $\pi$ - orbitals does not modify the final wave function. This could explain the better performance of the PRMO method as compared with that of Steiger et al. [9].

In Table 2 the PRMO  $\sigma$ - and  $\pi$ -electron contributions to the interproton coupling constants in butadiene (see Fig. 1) are compared with those given by the Steiger et al. [9] method (SGR). To obtain the SGR results the Fock hamiltonian of the FINITE program [10] has been modified according to Ref. [9]. Calculations were performed using the standard geometry [12]. There is an exact agreement between the  $\sigma$ -components thus calculated and those reported in reference [9].

**Table 2.**  $\sigma$ - and  $\pi$ -components of the proton-proton couplings in butadiene: Comparison between the results obtained using the PRMO and the Steiger et al. [9] methods<sup>a,b,c</sup>

	Exp. <sup>d</sup>	INDO	$\sigma$ -PRMO	$\sigma$ -SGR	$\pi$ -PRMO <sup>e</sup>	$\pi$ -SGR <sup>e</sup>
<sup>2</sup> $J_{13}$	1.74	4.84	6.44	6.17	-1.59	-1.33
<sup>3</sup> $J_{12}$	10.17	9.21	7.84	7.95	1.36	1.26
<sup>3</sup> $J_{23}$	17.05	25.72	24.30	24.25	1.42	1.46
<sup>3</sup> $J_{26}$	10.41	17.65	17.18	17.16	0.47	0.49
<sup>4</sup> $J_{16}$	-0.86	-1.26	-0.64	-0.64	-0.61	-0.62
<sup>4</sup> $J_{36}$	-0.83	-1.46	-0.85	-0.87	-0.60	0.59
<sup>5</sup> $J_{38}$	0.69	0.87	0.04	0.04	0.83	0.82
<sup>5</sup> $J_{18}$	0.60	1.00	0.16	0.17	0.83	0.83
<sup>5</sup> $J_{17}$	1.30	2.42	1.58	1.56	0.84	0.86

<sup>a</sup> All values are given in Hz.

<sup>b</sup> All calculations were carried out at the standard geometry given by the Pople and Gordon model [12].

<sup>c</sup> To obtain in the SGR values the Fock hamiltonian of the FINITE program [10] has been modified according to Steiger et al. [9].

<sup>d</sup> Ref. [14].

<sup>e</sup>  $\pi$ -contributions are obtained subtracting the respective  $\sigma$ -components from the FPT INDO values.

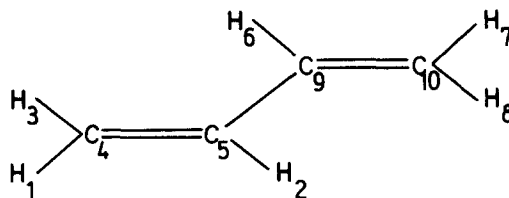


Fig. 1. Numbering of nuclei in butadiene

This agreement shows that the modifications were correctly introduced into the FINITE program [10]. However, slight differences are found in the  $\sigma$ -components due to different values obtained in the full INDO calculation. Apparently, Steiger et al. [9] used the standard geometry [12] to calculate the  $\sigma$ -component but a different one for the full INDO calculation.

In butadiene a noteworthy agreement between both methods is displayed. However, as it is the case in ethylene, the PRMO method reproduced slightly better than the SGR method the pathway invariance of the  $\pi$  component.

In Table 3 the benzene  $\pi$ -components according to the PRMO and SGR methods are compared with the valence bond results of Barfield and Chakrabarti [16] for interproton couplings. The PRMO method yield a trend in better agreement with those valence bond results than the SGR method. It is also observed that the agreement between the PRMO and SGR methods is better the larger the number of bonds that separate both interacting nuclei. Unfortunately, to the authors' knowledge, in the current literature there are no calculations of the  $\pi$ -contributions to the  $^{13}\text{C}$ - $^1\text{H}$  coupling constants in benzene and therefore a direct comparison cannot be made. However, according to Brey et al. [6] the " $^4J(\text{CH})$  in benzene, although not completely dominated, apparently involves a high degree of  $\pi$ -electron contribution". The results of both methods agree with this statement. Also, the  $\pi$ -contributions to Carbon-Hydrogen couplings calculated in this

Table 3.  $\sigma$ - and  $\pi$ -contributions to spin-spin coupling constants in benzene as calculated by the PRMO and SGR methods<sup>a,b</sup>

	Exp. <sup>c</sup>	INDO	$\sigma$ -PRMO	$\pi$ -PRMO	$\pi$ -SGR <sup>d</sup>	$\pi$ -VB <sup>e</sup>
$J_o$	7.540	8.15	7.54	0.60	0.47	0.76
$J_m$	1.380	2.12	2.56	-0.43	-0.38	-0.61
$J_p$	0.653	1.14	0.62	0.51	0.53	0.65
$^1J_{\text{CH}}$	158.45	140.28	137.29	2.99	3.69	—
$^2J_{\text{CH}}$	1.14	-4.94	-2.70	-2.24	-2.04	—
$^3J_{\text{CH}}$	7.60	9.40	7.77	1.63	1.64	—
$^4J_{\text{CH}}$	-1.29	-2.27	-0.48	-1.78	-1.78	—

<sup>a</sup> All values are given in Hz.

<sup>b</sup> All calculations were carried out at the geometry given by the Pople and Gordon model [12].

<sup>c</sup> Ref. [15].

<sup>d</sup> Values obtained using the Steiger et al. method [9]. To carry them out the FINITE program [10] was modified according to Ref. [9].

<sup>e</sup> Ref. [16].

work follow the same trend as the experimental methyl-protons ring-carbons couplings in toluene [17], which according to the methyl group replacement method [7, 18] would equal the  $\pi$ -contributions to these couplings in benzene.

The PRMO method was also used to carry out calculations of the  $\pi$ -electron contribution of the methyl proton–ring proton coupling constants in toluene. These calculations were performed at  $30^\circ$  intervals for the dihedral angle  $\theta$  formed by the plane determined by the interacting methyl proton, the methyl carbon and the ring carbon in position 1, and the ring plane. Plots of these results are shown in Fig. 2. These plots follow closely the  $\sin^2 \theta$  dependence on the dihedral angle expected for these  $\pi$ -electron contributions [4]. The expression that fits all three curves is:

$$f(\theta) = J_{0^\circ} + (J_{90^\circ} - J_{0^\circ}) \sin^2 \theta$$

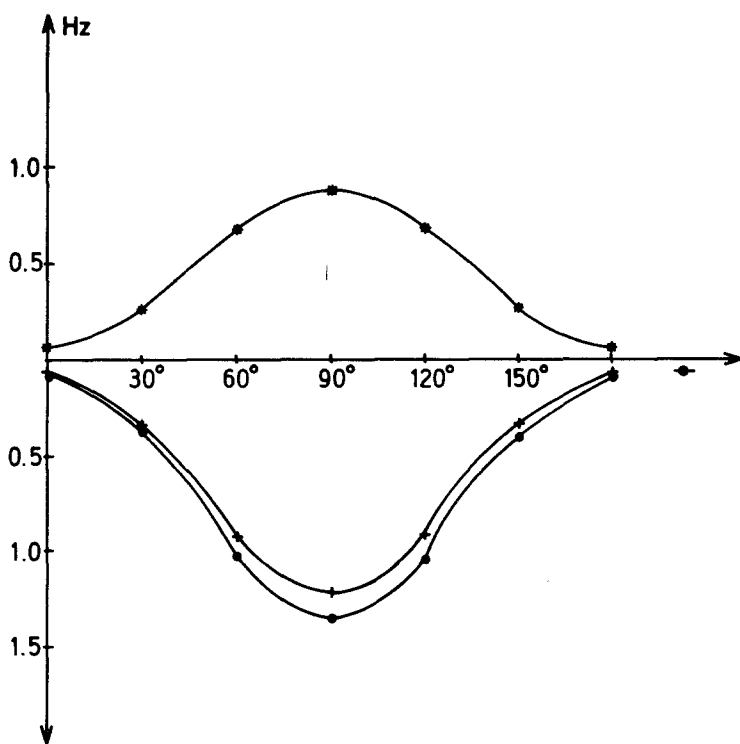


Fig. 2. Dihedral dependence of the PRMO  $\pi$ -electron contribution of the benzylic couplings in toluene

$o$ :  ${}^4J_{o,CH_3}$ ;  $*$ :  ${}^5J_{m,CH_3}$ ;  $+$ :  ${}^6J_{p,CH_3}$

$\theta$ : dihedral angle determined by the ring plane and that formed by the methyl proton, the methyl carbon and the ring carbon in position 1

**Table 4.** Averaged values of  $\pi$ -electron contributions to methyl proton-ring proton coupling constants in toluene. The  $\pi$ -electron contributions to  $J_o$ ,  $J_m$  and  $J_p$  of benzene are also shown in order to verify how closely the methyl group replacement method is satisfied within the PRMO approach<sup>a,b</sup>

	Exp. <sup>c</sup>	INDO <sup>d</sup>	$\pi$ -PRMO	$\pi$ -ii <sup>e</sup>	Benzene $\pi$ -PRMO	
<sup>4</sup> $J(\text{H},\text{CH}_3)$	-0.75	-0.92	-0.67	-0.73	$J_o$	0.60
<sup>5</sup> $J(\text{H},\text{CH}_3)$	0.36	0.69	0.41	0.45	$J_m$	-0.43
<sup>6</sup> $J(\text{H},\text{CH}_3)$	-0.62	-0.64	-0.57	-0.61	$J_p$	0.51

<sup>a</sup> All values are given in Hz.

<sup>b</sup> All calculations were carried out at the geometry given by Pople and Gordon [12].

<sup>c</sup> Ref. [19].

<sup>d</sup> Ref. [17].

<sup>e</sup> Average according to the above-mentioned 2) method [7].

where

	$J_{0^\circ}$ (Hz)	$J_{90^\circ}$ (Hz)
4-bond coupling	-0.08	-1.35
5-bond coupling	0.06	0.89
6-bond coupling	-0.06	-1.21

In Table 4 the average values obtained from plots of Fig. 2 are compared with the experimental long-range coupling constants [19], with the average INDO values and with the average  $\pi$ -electron component taken from the work of Wasylishen and Schaefer [7]. In the last column of Table 4 the PRMO  $\pi$ -electron components of the benzene interproton coupling constants are given to show how closely the methyl group replacement method [7, 18] is, verified by the PRMO method proposed in this work.

As a final remark it should be pointed out that when the  $\pi$ -partially restricted calculation is carried out at the CNDO/2 level of approximation the calculated coupling constants are equal to those obtained using the FPT CNDO/2 method.

*Acknowledgements.* The authors are deeply indebted to the authorities of DISCAD (Argentina Air Force Data Processing Centre) for kindly allowing the use of the B6700 computer system with which the calculations were carried out, and to the operators of that system for their assistance. Grants from the Argentine Research Council (CONICET) and from the Argentine Science and Technology Secretariat (SECYT) are gratefully acknowledged. The authors thank Prof. V. J. Kowalewski for his keen interest in this work.

## References

1. Pople, J. A., McIver, J. W., Ostlund, N. S.: J. Chem. Phys. **49**, 2960 (1968)
2. Pople, J. A., Beveridge, D. L.: Approximate molecular orbital theory, New York: McGraw Hill 1970
3. Kowalewski, J., Laaksonen, A., Roos, B., Siegbahn, P.: J. Chem. Phys. **71**, 2896 (1979)

4. Barfield, M., Chakrabarti, B.: *Chem. Rev.* **69**, 757 (1969)
5. Kowalewski, J., in: *Progress in NMR spectroscopy*, Vol. 11, eds. Emsley, J. W., Feeney, J., Sutcliffe, L. H., Oxford: Pergamon 1977
6. Brey, W. S., Jaques, L. W., Jakobsen, H. J.: *Org. Magn. Reson.* **12**, 243 (1979)
7. Wasylshen, R., Schaefer, T.: *Can. J. Chem.* **50**, 1852 (1972)
8. Bacon, M., Maciel, G. E.: *Mol. Phys.* **21**, 257 (1971)
9. Steiger, Th., Gey, E., Radeglia, R.: *Mol. Phys.* **30**, 1729 (1975)
10. Ostlund, N. S.: *FINITE Program. QCPE* **9**, 224 (1972)
11. Lynden-Bell, R. M., Sheppard, N.: *Proc. R. Soc. (London) Ser. A* **269** 385 (1962)
12. Pople, J. A., Gordon, M.: *J. Am. Chem. Soc.* **89**, 4253 (1967)
13. Cunliffe, A. V., Grinter, R., Harris, R. K.: *J. Magn. Reson.* **3**, 299 (1970)
14. Hobgood, R. T., Jr., Goldstein, J. H.: *J. Mol. Spectry.* **17**, 76 (1964)
15. Wray, V., Ernst, L., Lustig, E.: *J. Magn. Reson.* **27**, 1 (1977)
16. Barfield, M., Chakrabarti, B.: *J. Am. Chem. Soc.* **91**, 4346 (1969)
17. Hansen, M., Jakobsen, H. J.: *J. Magn. Reson.* **20**, 520 (1975)
18. Rowbotham, J. B., Schaefer, T.: *Can. J. Chem.* **52**, 489 (1974)
19. Williamson, M. P., Kostelnik, R., Castellano, S. M.: *J. Chem. Phys.* **49**, 2218 (1968)

Received July 30, 1980