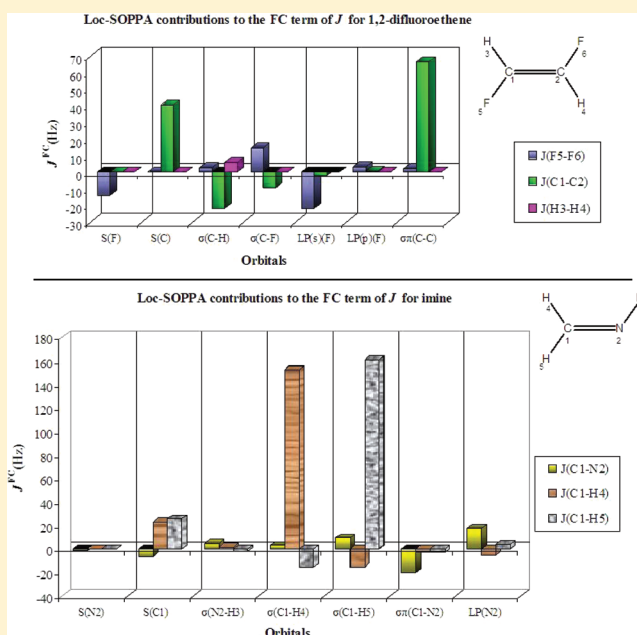


Analysis of Electron Correlation Effects and Contributions of NMR J-Couplings from Occupied Localized Molecular Orbitals

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ABSTRACT: NMR J-coupling calculations at the second-order of polarization propagator approach, SOPPA, are among the most reliable. They include a high percentage of the total electron correlation effects in saturated and unsaturated molecular systems. Furthermore, J-couplings are quite sensitive to the whole electronic molecular framework. We present in this article the first study of all three response mechanisms, Fermi contact, FC, spin-dipolar, SD and paramagnetic spin-orbital, PSO, for J-couplings with occupied localized molecular orbitals at the SOPPA level of approach. Even though SOPPA results are not invariant under unitary transformations, the difference between results obtained with canonical and localized molecular orbitals, LMOs, are small enough to permit its application with confidence. The following small-size saturated and unsaturated compounds were analyzed: CH₄, CH₃F, C₂H₆, NH₃, C₂H₄, CH₂NH, H₂C=CHF, and FHC=CHF. The local character of the FC mechanism that appears in J-couplings of these molecular models is shown through the analysis of contributions from LMOs. The importance of including the electron correlation on the engaged bonding orbitals for one-bond couplings is emphasized. Almost all electron correlation effects are included in such orbitals. Interesting findings were the large contributions by s-type LMOs to the C–H and C–C J-couplings; they are responsible for the variation of ¹J(C–C) when going from ethane to ethene and to 1,2-difluoroethene. The previously proposed hyperconjugative transfer mechanism has been tested. Among other tests we found the difference anti-syn of one-bond ¹J(C–H) in imine as due to both the corresponding σ (C–H) and the lone-pair, LP, contribution. Geminal and vicinal J-couplings were also analyzed. Our findings are in accord with a previous work by Pople and Bothner-by, who considered results taken from calculations or empirical data. For all geminal couplings the pattern of J-couplings, like the change of sign, is originated in the main bondings that participate in the coupling pathways. The finding of asymmetric contributions of LP to vicinal H–H couplings in imine is highlighted. The analysis of J-couplings by contributions from LMOs to the noncontact mechanisms, SD and PSO, show that the π electronic framework makes both terms grow in the specific case of the model compounds studied here. The PSO mechanism is more efficient when a σ bond is vicinal to a π bond. We found in this way an efficient and powerful scheme to get a deeper insight on the electronic molecular framework on which J-couplings are transmitted.



1. INTRODUCTION

Electron correlation effects must be included when one wants to get accurate result of calculations of NMR indirect nuclear spin couplings, J-couplings.^{1–4} This originates from two facts: one should include two triplet-type excitation operators and the restricted Hartree–Fock (HF) wave functions are not good enough for describing the ground state of unsaturated molecular systems. Then instability or quasi-instability problems^{5–12} may arise making it mandatory to include enough electron correlation in such calculations.

The polarization propagator methodology at the second-order level of approach, SOPPA,^{13–16} has shown to be one of the most reliable tools for J-coupling calculations.¹⁷ On the

contrary the fact that computational efforts grow as N^5 with N the number of Gaussian functions for a given basis set makes its application limited to medium-size molecules.

When J-couplings are analyzed in terms of localized molecular orbitals, LMOs, its understanding by excitations from occupied to vacant molecular orbitals (MOs) is easier. Then, it is possible to identify which region of the molecule is more involved in the transmission of a given J-coupling (and this for each of the four electronic mechanisms) and then highlighting it to improve the

Received: October 13, 2011

Revised: January 4, 2012

description of the electronic density. This could also be used to optimize calculations on large molecular systems and still makes them possible by ab initio methods.

The advantage of analyzing J-couplings in terms of localized molecular orbitals (LMOs) has been shown by its applications with semiempirical methods like the CLOPPA model (contributions from localized orbitals within the polarization propagator approach),¹⁸ and density functional theory (DFT)-based methodologies. There were several attempts of working with LMOs within DFT methods such as the natural J-coupling, NJC, of Contreras and coauthors,¹⁹ the J-OC-PSP1(2) of Cremer and coauthors,²⁰ the coupling deformation method of Malkin and coauthors,²¹ and the method of Sauer and Provasi,^{22,23} which is close to the original CLOPPA model. There were also more basic models applied to describe specific J-couplings like that of Mallory²⁴

The model that introduces the decomposition of J into orbital contributions using orbital currents and partial spin polarization, J-OC-PSP,²⁰ decomposes J-couplings into one-, two-, and *m*-orbital terms. They can be active orbital contributions, J-OC-PSP1, and passive orbital contributions, J-OC-PSP2. This scheme permits to detect the most important orbital contributions to the J-couplings as the calculations performed within the coupled perturbed DFT approach.

The natural J-coupling model was developed to decompose the total J^{FC} term into contributions from the core, bond, and LP orbitals. It was applied to the analysis of F–F J-couplings in some molecular systems and for different transmission mechanisms.¹⁹

Another recent model was introduced by Marek and coauthors for the interpretation of J-couplings with the coupling electron deformation density, CDD,²¹ and using LMOs. They applied this model to the understanding of how the magnetic polarization due to the electron–nucleus interaction propagates through the electronic framework of adenine²⁵

In this article we show results of calculations at SOPPA level of approach applying localized MOs. This represents a first step in the development of an strategy to work with molecules of large size. We shall show the analysis of the contributions of both bonding and lone-pairs to the electron correlation of J-couplings of saturated compounds; and the correlated localized contributions in unsaturated compounds containing H, C, N, and F atoms. We studied small-sized molecules to learn the performance of our strategy and then in the future will apply it to larger systems. We compared calculations at the random phase approximation (RPA) and SOPPA level of approach with molecular orbitals localized with the Foster–Boys localization procedure.²⁶

In section 2 we sketch the theoretical models we worked with and all computational details. Results of calculations with canonical and localized MOs are given in section 3 together with the analysis of electron correlation involved in each localized MO and the importance of such LMOs in the transmission of the J-couplings. Concluding remarks are given in section 4.

2. THEORETICAL MODEL AND COMPUTATIONAL DETAILS

The non relativistic theory of J-couplings was first formulated by Ramsey who considered four terms. Two are electron spin-dependent: Fermi contact, FC, and spin-dipolar, SD. The other two are not electron spin-dependent: paramagnetic spin–orbital,

PSO, and diamagnetic spin–orbital, DSO. Then, the total indirect nuclear spin coupling, the J-coupling, can be written as

$$J_{MN} = J_{MN}^{\text{FC}} + J_{MN}^{\text{SD}} + J_{MN}^{\text{PSO}} + J_{MN}^{\text{DSO}} \quad (1)$$

One may obtain the explicit polarization propagators by solving its equation of motion. A more practical way to do it consists of the application of the usual perturbation theory. In this case one should use the fluctuation potential as the perturbative term. Then it will give the different orders through which one include electron correlation in the calculation of properties. The consistent first-order approach is named the RPA level of approximation.²⁷ The second-order approach is named SOPPA.^{13,28}

When calculated by the nonrelativistic polarization propagator theory each of the first three terms of eq 1 are written as

$$\mathbf{J}_{MN}^X = \gamma_M \gamma_N \langle \langle \mathbf{V}_M^X; \mathbf{V}_N^X \rangle \rangle_{E=0} \quad (2)$$

where $X = \text{FC}, \text{SD}, \text{or PSO}$. All terms of eq 2 can be calculated at different levels of approach depending on the fluctuation potential.

$$\begin{aligned} H^{\text{FC}} &= \frac{8}{3} \pi \mu_B \hbar g_e \sum_N \gamma_N \sum_i \delta(\mathbf{r}_{iN}) s_i \mathbf{I}_N \\ &= \sum_N \gamma_N \mathbf{I}_N \mathbf{V}_N^{\text{FC}} \end{aligned} \quad (3)$$

where μ_B is the nuclear magneton, γ_N is the gyromagnetic constant of nucleus N, g_e is the electronic g-factor, and

$$\mathbf{V}_N^{\text{FC}} = \frac{8}{3} \pi \mu_B \hbar g_e \sum_i \delta(\mathbf{r}_{iN}) s_i \quad (4)$$

The Fermi contact perturbative Hamiltonian of eq 3 depends on the electronic density at the site of the nuclei. One should include two of these Hamiltonians for calculating the NMR J-coupling. The Fermi contact interaction is usually the most important, though there are several molecular systems where this is not a valid assumption, and the other two “paramagnetic-like” perturbative Hamiltonians are more important than the FC one. They are the so-called SD and PSO, which can be expressed in the same manner as for the FC within polarization propagators.

To calculate molecular properties one applies the non-partitioned matrices at SOPPA level as is implemented in the DALTON code²⁹ and described in the work of Packer et al.¹⁴ Accordingly when partitioning is not applied the linear response can be expressed as

$$\langle \langle P; Q \rangle \rangle_\omega = (P^\dagger | \mathbf{h} (\tilde{\mathbf{h}} | \omega \hat{I} - \hat{H} | \mathbf{h})^{-1} (\tilde{\mathbf{h}} | Q) \quad (5)$$

\mathbf{h} is a complete operator manifold of basic excitation operators from which it is possible to describe the whole branch of excited states that may come from a reference state $|0\rangle$. The operators P and Q should also be described in terms of basic excitation operators that belongs to that excitation manifold.

Then

$$\begin{aligned} \langle \langle P; Q \rangle \rangle_\omega &= \sum_{\mu\nu} -P_\mu^{[1]} (E^{[2]} - \omega S^{[2]})_{\mu\nu}^{-1} Q_\nu^{[1]} \\ &= \sum_{\mu} -P_\mu^{[1]} N_\mu^Q(\omega) \end{aligned} \quad (6)$$

Equation 5 is the original SOPPA expression written within the superoperator formalism, and eq 6 is that of Olsen and Jorgensen.³⁰ In the first term of eq 6 one can see the response as a product of a property gradient vector (PGV) or perturber $P_{ai}^{[1]}$ times the inverse of the principal propagator $(E^{[2]} - \omega S^{[2]})$ and another perturber $Q_{\nu}^{[1]}$. The meaning of subindices μ and ν in such equations are of being particle-hole, ph, or two particle-two hole, 2p-2h, operators.

In the actual implementation on the DALTON program package,¹⁴ the calculation of response functions at the SOPPA level of approach is made from the calculation of the vector $N_{\mu}^Q(\omega)$ of eq 6 by solving the following set of linear equations

$$N_{\mu}^Q(\omega) = \sum_{\nu} (E^{[2]} - \omega S^{[2]})_{\mu\nu}^{-1} Q_{\nu}^{[1]} = \sum_{\nu} N_{\mu\nu}^Q \quad (7)$$

To solve eq 7 Packer and coauthors used an iterative technique that was previously applied in MCSCF methods.^{31,32} Then the scalar product of eq 6 can be written in the following way

$$\begin{aligned} \langle\langle P; Q \rangle\rangle_{\omega}^{(\text{SOPPA})} &= \sum_{ai} -\mathbf{P}_{ai}^{[1](\text{SOPPA})} \mathbf{N}_{ai}^Q(\text{SOPPA})(\omega) \\ &+ \sum_{aibj} -\mathbf{P}_{aibj}^{[1](\text{SOPPA})} \mathbf{N}_{aibj}^Q(\text{SOPPA})(\omega) \end{aligned} \quad (8)$$

where subindices i, j, k, \dots (a, b, c, \dots) indicate occupied (virtual) HF molecular orbitals. Because the solution vector contains the inverse of the principal propagator matrix, both terms of eq 8 would contain contributions from the whole matrix $E^{[2]}$.²⁸ The contribution to the solution vector of the first term of eq 8 is dominated by simple excitations and that of the second term, by double excitations.^{13,33} This means that the first term of eq 8 can be obtained from the multiplication of the ph contribution to $\mathbf{P}_{\mu}^{[1]}$ with $N_{\mu}^Q(\omega)$ of eq 7 that are dominated by simple excitations. The second term is obtained by the multiplication of the 2p-2h contribution to $\mathbf{P}_{\mu}^{[1]}$ by that contributions of the solution vector dominated by double excitations. The explicit expressions for vectors $\mathbf{P}_{\mu}^{[1](\text{SOPPA})}$ and $\mathbf{N}_{\mu}^Q(\omega)^{(\text{SOPPA})}$ are given in ref 14.

In our approach LMOs are introduced at the beginning of the response module of calculations. It means that we carry out the whole SOPPA calculation within the framework of localized orbitals. We did not modified any module of the DALTON code for our Loc-SOPPA calculations.

How do we obtain the contribution of each occupied MO? The actual contribution corresponding to each occupied LMO, in our case the i th LMO, is given by the expression

$$\begin{aligned} \langle\langle P; Q \rangle\rangle_i^{(\text{SOPPA})} &= \sum_a -\mathbf{P}_{ai}^{[1](\text{SOPPA})} \mathbf{N}_{ai}^Q(\text{SOPPA})(\omega) \\ &+ \sum_{ab,j=i} -\mathbf{P}_{aibj}^{[1](\text{SOPPA})} \mathbf{N}_{aibj}^Q(\text{SOPPA})(\omega) \\ &+ \frac{1}{2} \sum_{ab,j \neq i} -\mathbf{P}_{aibj}^{[1](\text{SOPPA})} \mathbf{N}_{aibj}^Q(\text{SOPPA})(\omega) \end{aligned} \quad (9)$$

Within the RPA level of approach the \mathbf{P} vector does contain only p-h terms. Then the polarization propagator can be

written formally as the first terms of eq 8

$$\langle\langle P; Q \rangle\rangle_{\omega}^{(\text{RPA})} = \sum_{ia} -\mathbf{P}_{ai}^{[1](\text{RPA})} \mathbf{N}_{ai}^Q(\text{RPA})(\omega) \quad (10)$$

In this case the solution vector only contains terms that are obtained from the ph block of trial vectors given in eq 3.3 of ref 14. This means that $\mathbf{P}_{\mu}^{[1]}$ and $N_{\mu}^Q(\omega)$ are evaluated without any correction to the HF wave function, which is different from what is proposed to obtain the first sumation of eq 8 where the calculation involves first- and second-order corrections to the HF wave function as observed in the work of Packer and coauthors.

The contribution of each occupied LMO at RPA level of approach is obtained from

$$\langle\langle P; Q \rangle\rangle_i^{(\text{RPA})} = \sum_a -\mathbf{P}_{ai}^{[1](\text{RPA})} \mathbf{N}_{ai}^Q(\text{RPA})(\omega) \quad (11)$$

J-coupling calculations with both canonical and localized MOs were done with the cc-pVTZ basis set.³⁴ This basis set is not the best option to obtain results comparable with experiments, but all calculations with them give numbers that follow the trends of J-couplings on different molecular structures. Our main concern in this respect was obtaining semiquantitative results to be able to perform the analysis of the pattern of contributions of each localized bonding to the total J-couplings.

The localization was performed with the method of Foster and Boys,²⁶ and the geometry of all compounds was optimized at the DFT-B3LYP/6-311++G** level of approach.^{35,36}

For the implementation of our scheme we have introduced small modifications of the DALTON suite of programs to work with LMOs. Actually only the occupied MOs were localized. We did not apply the previous implementation of Sauer and Provasi.²²

3. RESULTS

We first shall show results of the calculations performed to search for the reliability of J-coupling calculations with both canonical and localized orbitals at both the RPA and SOPPA level of approach. We studied saturated and unsaturated molecular systems as shown in Figure 1.

We show an analysis of the amount of electron correlation each LMO contributes to the total J-couplings and how important they are at the SOPPA level of approach.

3.1. J-Couplings at the RPA and SOPPA Levels with Canonical and Localized MOs. We first performed calculations at the RPA level of approach and found that exactly the same numbers are obtained when both types of orbitals were considered, as the theory predicted. Then we performed SOPPA calculations, and the results are shown in Tables 1 and 2

As observed in those tables, results of SOPPA calculations with localized and canonical MOs are in good accord each other. The largest differences are found, as expected, for FC and SD terms in unsaturated compounds due to quasi-instability problems.^{1,8} On the other hand, it is important to highlight the fact that results of calculations with the two types of MOs for singlet-type terms, i.e., PSO and DSO, are very close to each other with the differences large in percentage though quite small in absolute values, for unsaturated compounds. As an example for ethane the largest difference

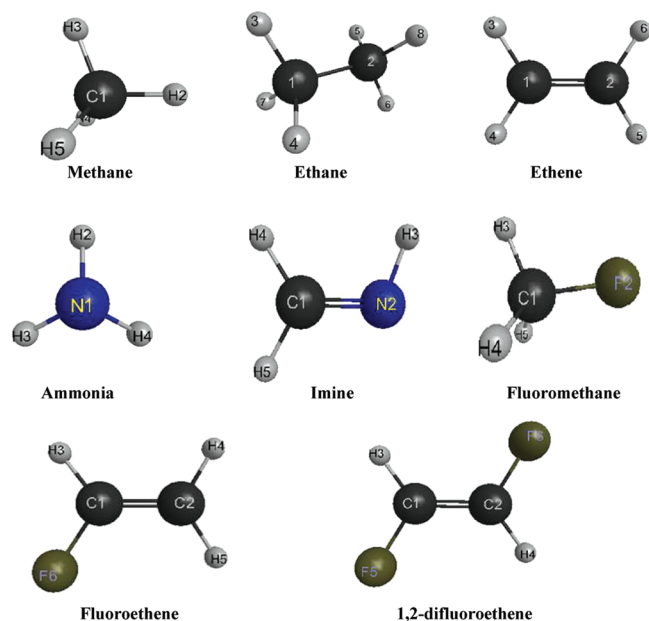


Figure 1. Molecular models.

was found for ${}^3J^{\text{FC}}(\text{H}_4\text{--H}_5)$ (0.66 Hz or 4.53%) being larger in ethene for ${}^1J^{\text{SD}}(\text{C}_1\text{--C}_2)$ (1.56 Hz or 47.27%) and ${}^3J^{\text{FC}}(\text{trans H}_3\text{--H}_5)$ (1.51 Hz or 8.96%).

In the case of the saturated compound, CH_3F , the largest difference (11.82 Hz) was obtained for $J^{\text{FC}}(\text{C}_1\text{--F}_2)$ with its percentage of 5%. For the coupling $J^{\text{FC}}(\text{C}_1\text{--F}_6)$ of $\text{C}_2\text{H}_3\text{F}$ we found a similar difference. In the case of $\text{C}_2\text{H}_2\text{F}_2$ the largest differences was obtained for the SD terms though the PSO electronic mechanism is the most important for the total couplings. In these last terms there are good matching between contributions from canonical and LMOs.

The PSO electronic mechanism is the main contributor for vicinal ${}^3J(\text{F--F})$ in 1,2-difluoroethene. For this J-coupling the SD term is as large as the FC one. This is in line with previous findings.^{37–39} As will be shown in section 3.4 this pattern is due to the contributions of fluorine LPs. In all other J-couplings of 1,2-difluoroethene the contribution of the FC mechanism is by far the largest one.

3.2. Local Electron Correlation Contributions to J^{FC} . Given that at the SOPPA level of approach most of the dynamical electron correlation contributions are included² and the fact that we are now able to divide the total J-coupling of all nonrelativistic perturbative mechanisms in terms of contributions from each occupied LMO, we shall start analyzing the local electron correlation contribution, LeCC, to J-couplings in few typical saturated molecules: methane, ethane, F-methane, and ammonia. For all unsaturated compounds studied here we were unable to obtain the amount of correlation involved in the FC and SD mechanisms due to the appearance of triplet-type quasi-instability problems.

Table 1. SOPPA and RPA (between Square Brackets) Results of J-Coupling (Hz) Calculations on Saturated Compounds with Canonical (Localized between Parenthesis) Orbitals and cc-pVTZ Basis Set

	canonical/localized				
	FC	SD	PSO	DSO	total
	methane				
$J(\text{C}_1\text{--H}_2)$	111.74 (111.69) [138.76]	0.07 (0.06) [−0.16]	1.59 (1.57) [1.52]	0.24 (0.24) [0.23]	113.64 (113.56) [140.35]
$J(\text{H}_2\text{--H}_3)$	−13.40 (−13.68) [−23.66]	0.37 (0.38) [0.47]	3.37 (3.37) [3.35]	−3.50 (−3.49) [−3.49]	−13.15 (−13.42) [−23.32]
	F-methane				
$J(\text{H}_3\text{--H}_4)$	−10.26 (−10.55) [−19.50]	0.50 (0.51) [0.62]	2.76 (2.75) [2.74]	−3.03 (−3.02) [−3.02]	−10.03 (−10.31) [−19.16]
$J(\text{H}_3\text{--F}_2)$	29.81 (31.11) [42.11]	−3.45 (−3.65) [−4.64]	12.08 (12.08) [10.74]	−1.80 (−1.80) [−1.79]	36.64 (37.73) [46.42]
$J(\text{C}_1\text{--H}_3)$	132.94 (133.62) [165.47]	0.09 (0.08) [−0.17]	0.01 (−0.01) [0.07]	0.61 (0.61) [0.60]	133.66 (134.30) [165.96]
$J(\text{C}_1\text{--F}_2)$	−229.25 (−241.08) [−200.81]	21.53 (22.45) [24.78]	39.81 (40.62) [34.37]	0.43 (0.43) [0.44]	−167.48 (−177.57) [−141.23]
	ethane				
$J(\text{H}_3\text{--H}_5)$	3.65 (3.76) [5.35]	0.07 (0.07) [0.09]	0.84 (0.84) [0.85]	−0.94 (−0.94) [−0.95]	3.62 (3.73) [5.34]
$J(\text{H}_3\text{--H}_4)$	−13.67 (−14.03) [−24.14]	0.41 (0.43) [0.53]	2.85 (2.85) [2.84]	−2.89 (−2.89) [−2.90]	−13.30 (−13.64) [−23.67]
$J(\text{H}_4\text{--H}_5)$	14.57 (15.23) [18.28]	0.02 (0.03) [0.05]	2.76 (2.77) [2.73]	−3.08 (−3.08) [−3.07]	14.28 (14.94) [17.98]
$J(\text{C}_1\text{--C}_2)$	28.10 (28.16) [49.80]	1.17 (1.18) [1.26]	0.23 (0.20) [0.01]	0.11 (0.11) [0.11]	29.62 (29.65) [51.17]
$J(\text{C}_1\text{--H}_4)$	110.66 (110.54) [138.48]	0.03 (0.01) [−0.26]	1.27 (1.26) [1.26]	0.48 (0.48) [0.47]	112.44 (112.29) [139.95]
	ammonia				
$J(\text{N}_1\text{--H}_2)$	−47.59 (−46.55) [−60.42]	−0.13 (−0.12) [0.03]	−3.07 (−3.08) [−3.13]	−0.08 (−0.08) [−0.08]	−50.86 (−49.83) [−63.59]
$J(\text{H}_2\text{--H}_3)$	−12.15 (−12.55) [−22.65]	0.55 (0.57) [0.75]	5.75 (5.77) [5.74]	−5.35 (−5.35) [−5.38]	−11.20 (−11.56) [−21.55]

Table 2. SOPPA and RPA (between Square Brackets) Results of J-Coupling (Hz) Calculations on Unsaturated Compounds with Canonical (Localized between Parenthesis) Orbitals and cc-pVTZ Basis Set

	FC	SD	PSO	DSO	total
ethene					
J(H ₄ -H ₅)	10.18 (11.36) [159.50]	-0.07 (-0.10) [-2.76]	0.68 (0.68) [0.69]	-1.09 (-1.09) [-1.09]	9.70 (10.85) [156.34]
J(H ₃ -H ₅)	16.86 (18.37) [167.80]	0.28 (0.42) [12.55]	2.60 (2.60) [2.56]	-3.54 (-3.54) [-3.53]	16.20 (17.84) [179.38]
J(H ₃ -H ₄)	-1.06 (-1.79) [-152.75]	0.40 (0.43) [3.17]	3.61 (3.62) [3.59]	-3.60 (-3.80) [-3.79]	-0.86 (-1.53) [-149.78]
J(C ₁ -C ₂)	95.60 (96.50) [427.01]	3.30 (4.86) [118.61]	-9.97 (-10.20) [-10.33]	0.07 (0.07) [0.06]	89.00 (91.23) [535.35]
J(C ₁ -H ₄)	148.50 (149.37) [389.28]	0.10 (0.02) [-4.48]	0.46 (0.40) [0.30]	0.42 (0.42) [0.41]	149.49 (150.22) [385.51]
F-ethene					
J(F ₆ -H ₅)	17.12 (14.76) [-107.32]	-0.60 (-0.33) [7.77]	-3.70 (-3.65) [-3.55]	-0.60 (-0.60) [-0.60]	12.22 (10.18) [-103.70]
J(H ₃ -H ₄)	5.04 (6.21) [77.43]	-0.14 (-0.19) [-1.94]	0.68 (0.68) [0.69]	-0.95 (-0.95) [-0.95]	4.62 (5.74) [75.22]
J(H ₄ -F ₆)	38.65 (35.36) [-75.14]	1.06 (1.14) [-3.28]	-2.96 (-2.91) [-2.59]	-2.50 (-2.50) [-2.48]	34.25 (31.10) [-83.50]
J(H ₃ -H ₅)	11.79 (13.30) [89.23]	0.30 (0.43) [5.82]	2.63 (2.62) [2.57]	-3.49 (-3.49) [-3.48]	11.22 (12.86) [94.15]
J(C ₁ -C ₂)	113.27 (115.07) [304.31]	3.73 (5.45) [59.89]	-9.03 (-9.25) [-9.52]	0.16 (0.16) [0.15]	108.14 (111.43) [354.83]
J(C ₁ -F ₆)	-268.31 (-280.78) [-423.38]	1.79 (-2.37) [-138.82]	-3.70 (-2.82) [-8.28]	0.60 (0.60) [0.60]	-269.64 (-285.38) [-569.89]
1,2-difluoroethene					
J(H ₃ -H ₄)	9.58 (11.51) [314.24]	0.37 (0.56) [21.93]	2.46 (2.45) [2.40]	-3.41 (-3.40) [-3.39]	9.01 (11.12) [335.17]
J(F ₅ -F ₆)	-24.05 (-21.53) [780.55]	23.04 (35.65) [1198.11]	-156.84 (-158.60) [-142.85]	-1.71 (-1.71) [-1.69]	-159.55 (-146.19) [1834.11]
J(H ₃ -F ₆)	0.48 (-1.83)	0.04 (0.42)	1.19 (1.33)	-0.47 (-0.47)	1.25 (-0.55)
J(C ₁ -C ₂)	145.94 (149.57) [902.53]	4.53 (6.95) [231.70]	-9.69 (-9.99) [-10.31]	0.26 (0.26) [0.25]	141.04 (146.78) [1124.17]
imine					
J(H ₃ -H ₅)	22.75 (24.45) [433.02]	0.34 (0.50) [54.36]	3.19 (3.18) [3.17]	-4.49 (-4.49) [-4.48]	21.79 (23.64) [486.06]
J(H ₃ -H ₄)	17.41 (18.74) [435.22]	0.08 (0.08) [-2.39]	0.28 (0.28) [0.29]	-0.93 (-0.93) [-0.94]	16.84 (18.17) [432.18]
J(H ₄ -H ₅)	15.74 (15.43) [-383.54]	0.42 (0.44) [7.81]	3.29 (3.29) [3.25]	-3.64 (-3.64) [-3.64]	15.81 (15.52) [-376.12]
J(C ₁ -H ₃)	-10.37 (-11.43) [-620.15]	-0.09 (-0.07) [-0.25]	-2.61 (-2.72) [-2.72]	-0.85 (-0.85) [-0.86]	-13.92 (-15.07) [-623.99]
J(C ₁ -N ₂)	-13.94 (-13.95) [-429.69]	-1.42 (-2.40) [-284.64]	8.99 (9.41) [9.50]	-0.01 (-0.01) [-0.01]	-6.38 (-6.96) [-704.85]
J(N ₂ -H ₄)	2.53 (2.95) [285.12]	-0.23 (-0.31) [-7.75]	1.07 (1.10) [1.14]	0.35 (0.35) [0.35]	3.71 (4.09) [278.85]
J(N ₂ -H ₅)	-10.47 (-10.44) [264.72]	-0.15 (-0.21) [-9.62]	1.40 (1.46) [1.49]	0.29 (0.30) [0.29]	-8.93 (-8.90) [256.88]
J(C ₁ -H ₄)	149.51 (150.81) [769.98]	0.16 (0.10) [-13.70]	-0.08 (-0.19) [-0.37]	0.51 (0.51) [0.50]	150.11 (151.22) [756.41]
J(C ₁ -H ₅)	166.48 (167.08) [771.47]	0.14 (0.07) [-15.35]	-0.20 (-0.30) [-0.35]	0.50 (0.50) [0.49]	166.93 (167.35) [756.26]

In the case of saturated compounds the RPA calculations are not quasi-instable, so it is possible, within the polarization propagators approach, to make use of the following definition of LeCC: it is the difference between SOPPA and RPA results. In our case this was done by considering only each occupied LMO. We are currently working to include also the localized virtual orbitals in our scheme.

Results of LeCC to FC mechanism are given in Table 3. The largest LeCC contribution for the one-bond coupling in methane is given by the σ bond, i.e. σ , -21.10 Hz. The second one is that of the core s-type MO, $s(C_1)$, -3.63 Hz. In both cases the LeCC is negative and follow the same pattern. As observed in previous studies with semiempirical⁴¹ and DFT methodologies^{4,19,22} the so-called other bond contributions, ob,

Table 3. Contributions from LMOs to the FC Term of Saturated Compounds

orbital	RPA	SOPPA	LeCC	RPA	SOPPA	LeCC
methane						
		${}^2J(\text{H}_2\text{-H}_3)$			${}^1J(\text{C}_1\text{-H}_2)$	
$s(\text{C}_1)$	-0.02	-0.02	0.01	18.98	15.36	-3.63
$\sigma(\text{C}_1\text{-H}_2)$	-11.78	-6.82	4.97	131.94	110.84	-21.10
$\sigma(\text{C}_1\text{-H}_{4,5})$	-0.03	-0.01	0.02	-4.06	-4.84	-0.78
total	-23.66	-13.68	9.98	138.76	111.69	-27.07
F-methane						
		${}^2J(\text{H}_3\text{-H}_4)$			${}^1J(\text{C}_1\text{-H}_3)$	
$s(\text{C}_1)$	-0.03	-0.03	0.00	24.34	19.84	-4.50
$s(\text{F}_2)$	0.0	0.0	0.0	0.0	0.0	0.0
$\sigma(\text{C}_1\text{-H}_{5(3)})^a$	-0.21	-0.14	0.07	155.83	130.99	-24.83
$\sigma(\text{C}_1\text{-F}_2)$	-0.04	-0.05	0.00	-1.65	-2.56	-0.91
$\sigma(\text{C}_1\text{-H}_4\text{H}_{3(5)})^a$	-9.61	-5.17	4.43	-6.59	-7.31	-0.72
total	-19.50	-10.55	8.95	165.47	133.62	-31.85
ammonia						
		${}^2J(\text{H}_2\text{-H}_3)$			${}^1J(\text{N}_1\text{-H}_2)$	
$s(\text{N}_1)$	-0.02	-0.01	0.00	-3.33	-2.36	0.97
$\sigma(\text{N}_1\text{-H}_2)$	-11.26	-6.24	5.02	-70.86	-57.88	12.98
$\sigma(\text{N}_1\text{-H}_4)$	-0.03	-0.03	0.00	3.03	3.56	0.53
$\text{LP}(\text{N}_1)$	-0.08	-0.02	0.07	7.72	6.57	-1.14
total	-22.65	-12.55	10.11	-60.42	-46.55	13.86
ethane						
		${}^3J(\text{H}_4\text{-H}_5)$			${}^1J(\text{C}_1\text{-H}_4)$	
$s(\text{C}_1)$	0.00	0.00	0.00	19.19	15.45	-3.75
$s(\text{C}_2)$	0.00	0.00	0.00	0.00	0.00	0.00
$\sigma(\text{C}_1\text{-H}_3)$	0.17	0.17	0.00	-3.81	-4.62	-0.81
$\sigma(\text{C}_1\text{-H}_4)$	8.62	7.12	-1.50	129.96	108.53	-21.43
$\sigma(\text{C}_1\text{-C}_2)$	0.35	0.32	-0.03	-3.30	-4.35	-1.05
total	18.28	15.23	-3.06	138.48	110.54	-27.94
		${}^1J(\text{C}_1\text{-C}_2)$			${}^2J(\text{H}_3\text{-H}_4)$	
$S(\text{C}_1)$	5.42	2.95	-2.47	-0.02	-0.02	0.00
$\sigma(\text{C}_1\text{-H}_3)$	-4.30	-4.67	-0.37	-12.00	-6.98	5.02
$\sigma(\text{C}_1\text{-C}_2)$	64.76	50.26	-14.50	0.00	0.00	0.00
total	49.80	28.16	-21.64	-24.14	-14.03	10.11

^aNumbers between parentheses are for $J^{\text{FC}}(\text{C}_1\text{-H}_3)$

are opposite in sign and smaller in magnitude. The LeCC contribution to the other two mechanisms are similar each other: the C–H σ bond is the most important, though the total SD contribution is vanishingly small, and all other C–H bonds contribute with an amount that is much larger than the contribution of the coupled C–H bonding for the PSO mechanism (Table 4). Quite a similar behavior is observed for the one-bond C–H coupling in ethane and F-methane. Furthermore, all LeCCs have negative values.

It is interesting to observe that the absolute value of the sum of all other C–H bond contributions is larger than the core s-type MO, $s(\text{C}_1)$ contribution in both methane and ethane. This relationship is reversed in F-methane. On the other hand the total ${}^1J(\text{C-H})$ in all three compounds is almost completely given by the contribution of the LMO corresponding to the coupled nuclei.

In the case of ${}^1J(\text{C-C})$, by far the largest SOPPA contribution is given by the $\sigma(\text{C-C})$ bonding orbital, which is positive, as are also the contributions from the $s(\text{C}_i, i = 1, 2)$ LMOs. All other contributions to that one-bond coupling are small.

For one-bond (C–H) J-couplings there are two sensitive LMOs that feel the electron correlation effects more. They are the core $s(\text{C})$ of the carbon atom and the bonding C–H. Both are negative though more negative for F-methane.

LeCC does not necessarily follow the same pattern as the contributions from LOMs to the SOPPA values. A clear example is observed in ethane. For ${}^1J(\text{C-C})$ the LeCC of both s-type LMOs are much larger than the corresponding LeCC of all $\sigma(\text{C-H})$ bonding orbitals, though the hierarchy of contributions of that LMOs at SOPPA level are opposite. The contributions of all $\sigma(\text{C-H})$ bonding orbitals to ${}^1J(\text{C-C})$ are larger than that of the s-type.

Comparative studies of LMO contributions are shown in Figures 2–5, for one-bond, geminal, and vicinal couplings. The $\sigma(\text{C-H})$ contribution to the ${}^1J(\text{C-H})$ in F-methane is clearly larger than its contribution in both methane and ethane. This pattern is similar to that of unsaturated compounds. For them the $\sigma(\text{C-H})$ contribution becomes the largest for 1,2-difluoroethene. It may be due to the electronegativity of fluorine atoms that makes the growing of the electron density at the site of the carbon atom. This hypothesis is enforced when

Table 4. Contributions from LMOs to the SD and PSO Terms of Saturated Compounds

orbital	SD						PSO		
	RPA	SOPPA	LeCC	RPA	SOPPA	LeCC	RPA	SOPPA	LeCC
methane									
		$^2J(\text{H}_2-\text{H}_3)$		$^1J(\text{C}_1-\text{H}_2)$			$^2J(\text{H}_2-\text{H}_3)$		
$s(\text{C}_1)$	0.00	0.00	0.00	-0.01	-0.01	0.00	0.74	0.74	0.00
$\sigma(\text{C}_1-\text{H}_2)$	0.17	0.14	-0.03	-0.95	-0.69	0.26	1.03	1.03	0.00
$\sigma(\text{C}_1-\text{H}_{4,5})$	0.06	0.05	-0.01	0.27	0.25	-0.01	0.28	0.29	0.01
total	0.47	0.38	-0.09	-0.16	0.06	0.22	3.35	3.37	0.02
F-methane									
		$^2J(\text{H}_3-\text{H}_4)$		$^1J(\text{C}_1-\text{H}_3)$			$^1J(\text{C}_1-\text{H}_3)$		
$s(\text{C}_1)$	0.00	0.00	0.00	-0.01	-0.01	0.00	-0.05	-0.05	0.00
$s(\text{F}_2)$	0.00	0.00	0.00	0.00	0.00	0.00	-0.07	-0.07	0.00
$\sigma(\text{C}_1-\text{H}_{5(3)})^a$	0.04	0.03	-0.01	-0.61	-0.34	0.27	0.73	0.66	-0.06
$\sigma(\text{C}_1-\text{F}_2)$	0.03	0.03	0.00	0.14	0.13	-0.01	0.04	0.07	0.03
$\sigma(\text{C}_1-\text{H}_{4,3(5)})^a$	0.27	0.22	-0.05	0.15	0.14	-0.01	-0.09	-0.11	-0.02
total	0.63	0.51	-0.12	-0.17	0.08	0.25	0.07	-0.01	-0.09
ammonia									
		$^2J(\text{H}_2-\text{H}_3)$		$^1J(\text{N}_1-\text{H}_2)$			$^1J(\text{N}_1-\text{H}_2)$		
$s(\text{N}_1)$	0.00	0.00	0.00	0.00	0.00	0.00	-0.15	-0.15	0.00
$\sigma(\text{N}_1-\text{H}_2)$	0.26	0.20	-0.07	1.26	0.98	-0.28	0.29	0.39	0.10
$\sigma(\text{N}_1-\text{H}_4)$	0.12	0.10	-0.02	-0.36	-0.32	0.04	-0.95	-0.97	-0.02
$\text{LP}(\text{N}_1)$	0.10	0.09	-0.01	-0.52	-0.47	0.05	-1.37	-1.38	-0.01
total	0.75	0.58	-0.18	0.03	-0.12	-0.15	-3.13	-3.08	0.05
ethane									
		$^3J(\text{H}_4-\text{H}_5)$		$^1J(\text{C}_1-\text{C}_2)$			$^1J(\text{C}_1-\text{H}_4)$		
$s(\text{C}_1)$	0.00	0.00	0.00	0.00	0.00	0.00	-0.01	-0.01	0.00
$s(\text{C}_2)$	0.00	0.00	0.00	0.00	0.00	0.00	-0.07	-0.07	0.00
$\sigma(\text{C}_1-\text{H}_3)$	-0.01	-0.01	0.00	0.04	0.05	0.01	0.43	0.45	0.02
$\sigma(\text{C}_1-\text{H}_4)$	0.00	0.00	0.00	0.04	0.05	0.01	0.25	0.17	-0.08
$\sigma(\text{C}_1-\text{C}_2)$	0.08	0.06	-0.02	0.99	0.88	0.11	0.41	0.45	0.05
total	0.05	0.03	-0.02	1.26	1.19	0.07	1.26	1.26	0.00

^aNumbers between parentheses are for $J^{\text{SD,PSO}}(\text{C}_1-\text{H}_3)$

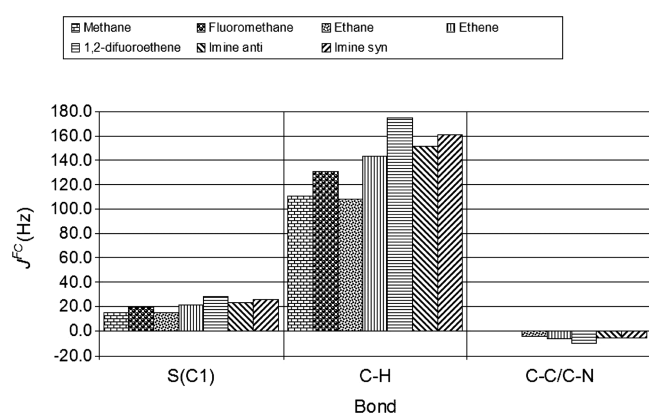


Figure 2. Bonding contribution to $^1J^{\text{FC}}(\text{C}-\text{H})$ at the SOPPA level of approach for different compounds.

considering the core s-type contributions, which follow exactly the same pattern as the $\sigma(\text{C}-\text{H})$ contributions (see Figure 2).

Geminal H-H couplings are almost completely defined through each of the two bonding $\sigma(\text{C}-\text{H})$ LMOs in all compounds we have studied. Still the LeCC contribution varies from close to 60% for methane and ethane to around 44% for ammonia. These geminal couplings are all negative, but they become positive for a few unsaturated compounds. They follow the same pattern as proposed long ago by Pople and Bothner-by.⁴⁰

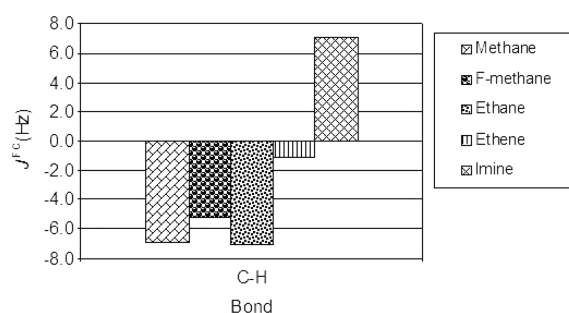


Figure 3. Bonding contribution to $^2J^{\text{FC}}(\text{H}-\text{H})$ at the SOPPA level of approach for different compounds.

As we will see in Section 4.4 the change of the sign is completely defined by the behavior of the occupied $\sigma(\text{C}-\text{H})$. We do not observe a direct influence of the π framework, though it is surely indirect.

It is worth to mention that all our results are in good accord with previous findings of Pople and Bothner-by⁴⁰ for geminal J-couplings, though we are able now to go deeper on the search of its electronic origin.

In Figure 3 it is observed that the pattern of contributions to $^2J(\text{H}-\text{H})$ is opposite to the pattern for $^1J(\text{C}-\text{H})$. The largest $\sigma(\text{C}-\text{H})$ LMO contribution is found for ethane and the smallest for F-methane.

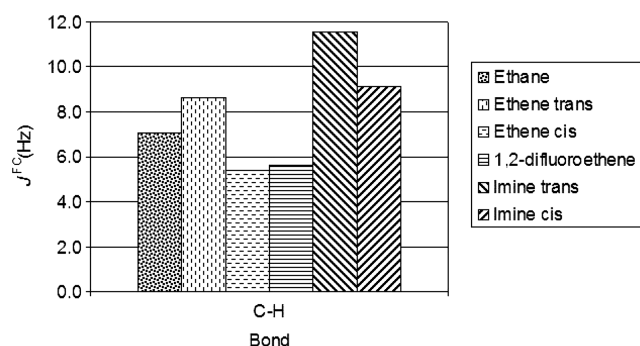


Figure 4. Bonding contribution to $^3J^{\text{FC}}(\text{H-H})$ at the SOPPA level of approach for different compounds.

For the staggered ($\text{H}_4\text{-H}_5$) J-coupling in ethane almost all electron correlation effects are on $\sigma(\text{C-H})$ bondings.

3.3. Local Electron Correlation Contributions to J^{SD} and J^{PSO} . It is known that for our set of model compounds the SD and PSO electronic mechanisms are related with the π electronic structure. Cremer and coauthors have shown that the SD term has exponential growth when the C-C bond changes from a simple to a double bond.⁴² The $^1J^{\text{PSO}}(\text{C-C})$ in ethane is small (positive or negative) but much larger and negative in ethene.

Our results are in line with previous findings. At the SOPPA level of approach they show that the SD term changes its value from 1.19 Hz in ethane to 4.86 Hz in ethene. In ref 42, such values are 1.08 and 3.94 Hz, respectively. By application of the LMO analysis to our SOPPA values we observe that its variation is due to the contribution of the C-C bond, with its contribution in ethane of 0.88 Hz and of 5.26 Hz in ethene. This means that the π -character of the double bond makes the SD contributions grow. A similar insight can be applied to the PSO terms. The $^1J^{\text{PSO}}(\text{C-C})$ term in ethane have a contribution of -0.35 Hz from the C-C bond which grows to -7.34 Hz for a double bond in ethene.

It is interesting to note that the total contribution of C-H bonds in ethane is 0.53 Hz though -2.83 Hz in ethene. This shows that the transmission of information for the PSO mechanism is more effective when a σ bond is vicinal to a π bond.⁴³

3.4. Local Origin of the FC Electronic Mechanism in Few Unsaturated Compounds. How large is the electron

correlation contribution to J-couplings in unsaturated compounds? Which are the main LMOs that contribute to it?

First of all we should mention that in all unsaturated compounds we have studied there are triplet-type instability problems. This is clearly observed in Table 2 where the contributions of FC and SD terms have unreasonable large values at RPA level of approach as compared to their SOPPA values. This is not the case for both singlet-type mechanisms, PSO and DSO. Then we are able only to analyze the relative contributions of each LMO to a given J-coupling at SOPPA level of approach.

In Table 5 results of FC contributions to J-couplings in 1,2-difluoroethene and imine are shown.

The analysis of the electronic origin of variations of $^1J^{\text{FC}}(\text{C-C})$ in the series ethane, ethene, and 1,2-difluoroethene can illustrate the advantages of dividing the total J-coupling in contributions from occupied LMOs.

In *trans*-1,2-difluoroethene the $\sigma(\text{C-C})$ bonding is the LMO which gives the largest contribution (133 Hz out of 149.57 Hz). In this case the contributions of both $s(\text{C}_i, i = 1, 2)$ LMOs give 81 Hz, which represents a larger percentage when compared with equivalent contributions in ethene. The total value of $^1J^{\text{FC}}(\text{C-C})$ grows 3.43 times from ethane to ethene and 1.55 times from ethene to 1,2-difluoroethene. Why does it grow this way? We can consider the relationship between contributions of the same LMOs in different molecules. The contribution which varies most is the s-type LMO: 8.74 times from ethane to ethene and 1.56 times from ethene to DiF-ethene. The contribution of the double C=C bond varies 1.95 times and 1.36 times, respectively. These variations are similar to that from the C-H bonds: 2.84 and 1.65. Then it is the growing of the contribution of s-type LMOs that justifies the differences of $^1J^{\text{FC}}(\text{C-C})$ from ethane to ethene. This is not the case for the differences of the same kind of coupling when going from ethene to DiF-ethene. In this last case the contributions of almost all LMOs grows like the total coupling, though the contribution of the double C=C bond grows little less than the total: 1.36 times.

Another one-bond coupling that deserves analysis is that of $^1J^{\text{FC}}(\text{C-N})$ in imine. Its pattern is partially different from that of $^1J^{\text{FC}}(\text{C-C})$ in ethene. For the imine the largest contributions is given by the double C=N bond though the LP contribute with a large value compared with what happens for C-H bonds in ethene.

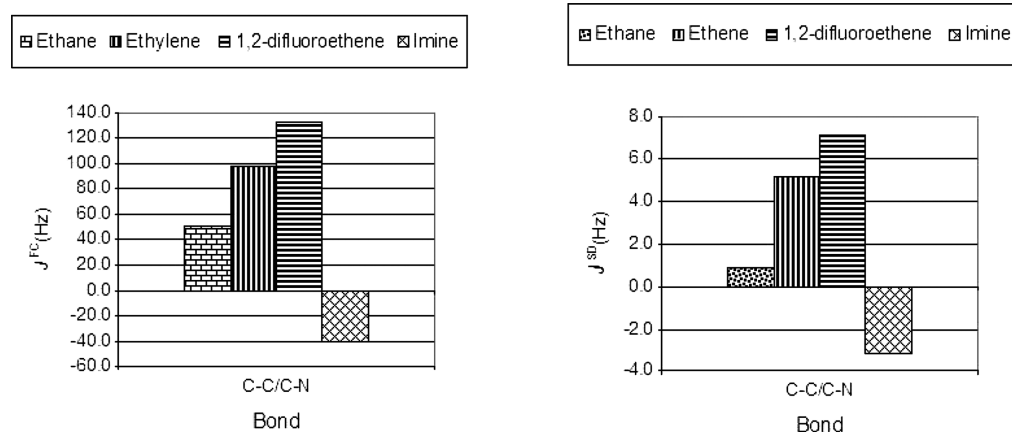


Figure 5. Bonding contribution at the SOPPA level for $J^{\text{FCorSD}}(\text{C-X})$ (to the left/right) with $X = \text{C}, \text{N}$.

Table 5. LeCC Contributions to the FC Term of Unsaturated Compounds

orbital	RPA	SOPPA	RPA	SOPPA	RPA	SOPPA
	ethene		1,2-difluoroethene		imine	
	${}^{\text{trans}}J(\text{H}_3\text{-H}_5)$		${}^1J(\text{C}_1\text{-C}_2)$		${}^1J(\text{C}_1\text{-H}_4)$	
$s(\text{C}_1)$	0.07	0.00	2.16	25.77	7.59	21.95
$s(\text{C}_2)$	0.07	0.00	2.16	25.77	0.08	-0.01
$\sigma(\text{C}_1\text{-H}_3)$	85.07	8.73	29.51	-13.28	18.40	-10.12
$\sigma(\text{C}_1\text{-H}_4)$	-0.46	0.34	29.51	-13.28	304.61	144.21
$\sigma(\text{C}_2\text{-H}_5)$	85.07	8.73	29.51	-13.28	0.82	1.29
$\sigma\pi(\text{C}_1\text{-C}_2)$	-0.78	0.11	152.20	49.04	29.78	-3.18
total	167.80	18.37	427.01	96.50	389.28	149.37
	${}^{\text{trans}}J(\text{F}_5\text{-F}_6)$		${}^1J(\text{C}_1\text{-C}_2)$		${}^{\text{trans}}J(\text{H}_3\text{-H}_4)$	
$s(\text{F}_5)$	71.65	-14.26	-0.01	0.00	0.00	0.00
$s(\text{C}_1)$	-0.27	0.00	-0.59	40.31	0.16	0.00
$\sigma(\text{C}_1\text{-H}_3)$	25.67	2.57	95.41	-21.94	159.86	5.67
$\sigma(\text{C}_1\text{-F}_5)$	-313.29	14.80	38.49	-9.28	-0.50	0.04
LP(s)(F ₅)	161.61	-22.13	0.81	-2.12	0.43	-0.01
LP(p)(F ₅)	205.97	3.05	3.17	0.64	-0.09	0.00
$\sigma\pi(\text{C}_1\text{-C}_2)$	32.97	2.15	310.80	66.55	-2.65	0.07
total	780.55	-21.53	902.53	149.57	314.24	11.51
	${}^1J(\text{C}_1\text{-H}_5)$		${}^1J(\text{C}_1\text{-H}_4)$		${}^1J(\text{C}_1\text{-N}_2)$	
$s(\text{N}_2)$	0.12	-0.01	0.15	0.00	74.22	-1.62
$s(\text{C}_1)$	-31.08	25.72	-34.92	23.23	35.80	-6.50
$\sigma(\text{N}_2\text{-H}_3)$	-0.95	-2.04	2.70	1.74	-54.41	4.73
$\sigma(\text{C}_1\text{-H}_4)$	67.36	-15.83	573.71	152.18	-59.16	2.82
$\sigma(\text{C}_1\text{-H}_5)$	572.29	161.05	69.67	-15.32	-50.31	9.25
$\sigma\pi(\text{C}_1\text{-N}_2)$	80.70	-2.92	82.85	-2.89	-156.52	-20.05
LP(N ₂)	2.32	4.05	-7.01	-5.24	-62.79	17.48
total	771.47	167.08	769.98	150.81	-429.70	-13.95
	${}^{\text{cis}}J(\text{H}_3\text{-H}_4)$		${}^{\text{trans}}J(\text{H}_3\text{-H}_5)$		${}^{\text{gem}}J(\text{H}_4\text{-H}_5)$	
$s(\text{N}_2)$	0.19	0.00	0.18	0.00	0.01	0.00
$s(\text{C}_1)$	0.22	0.01	0.21	0.00	-0.46	-0.04
$\sigma(\text{N}_2\text{-H}_3)$	221.21	7.94	220.03	10.92	-0.63	0.38
$\sigma(\text{C}_1\text{-H}_4)$	226.93	9.13	-2.11	0.71	-195.03	7.48
$\sigma(\text{C}_1\text{-H}_5)$	-2.02	0.78	224.51	11.65	-195.30	7.07
$\sigma\pi(\text{C}_1\text{-N}_2)$	-2.40	-0.15	-2.12	0.16	2.36	-0.07
LP(N ₂)	-6.53	1.17	-5.57	0.85	3.15	0.69
total	435.22	18.74	433.02	24.45	-383.54	15.43

For the one-bond J-coupling, ${}^1J(\text{C-H})$, the most important contribution is given by the $\sigma(\text{C-H})$ bonding which is 108.53 Hz (out of 110.54 Hz) for ethane and 144.20 Hz (out of 149.37 Hz) for ethene. The second important contribution is that of the closest $s(\text{C})$ to the coupled nuclei, though much less important ($\approx 15\%$ of the total).

In Figure 2 we show the pattern of contributions due to different bondings to the ${}^1J(\text{C-H})$. As happens between F-methane compared with 1,2-difluoroethene, in fluorinated compounds its contribution is larger than in the others. A similar behavior is observed for the $s(\text{C})$ LMO.

In a recent review, Contreras and Peralta analyzed the angular dependence of J-couplings with intramolecular interactions.⁴⁴ Hyperconjugative interactions, which are by definition electronically nonlocalized, can be important for J-couplings. In ref 44 only the FC mechanism is analyzed given that it is this mechanism the most involved in the angular dependence. The authors show that one must consider the contributions of LPs close to the coupled nuclei given that they

could define the difference in couplings. This is the case of the LP in the imine and its influence to the one-bond couplings.

We can then analyze the influence of the hyperconjugative transfer mechanism. This involves a partial electronic transfer mechanism from an occupied (bonding) orbital to an unoccupied (antibonding) orbital. One of them is the $n \rightarrow \sigma^*$, where n is a LP and σ^* the antibonding of a σ bonding orbital.⁴⁵ In the case of an antiperiplanar configuration between the LP and an antibonding ($A \rightarrow B$)* this is the strongest interaction. If it involves an antibonding $\sigma^*(\text{C-H})$ it produces a decrease of the corresponding ${}^1J^{\text{FC}}(\text{C-H})$. This is the well-known Perlin effect.⁴⁶⁻⁴⁸ On the other hand, for a synperiplanar configuration this interaction is vanishingly small.

From a CLOPPA analysis (contributions from localized orbitals within polarization propagator approach) it is possible to show that the Perlin effect on the ${}^1J^{\text{FC}}(\text{C-H})$ in imine is mainly originated from the nitrogen LP. This contribution is positive for a syn periplanar arrangement between the LP and the C-H bonding and negative for an anti periplanar arrangement. Furthermore this interaction does show that the

contribution of the orbital that bonds the carbon atom with the hydrogen atom that are coupled in the anti arrangement decreases.

In line with these previous findings our SOPPA calculations show that the origin of the difference anti/syn of $^1J^{\text{FC}}(\text{C}-\text{H})$ is mainly due to the contribution of the LP and the (C–H) bonding between the coupled nuclei. In the case of the LP, it is positive (4.05 Hz) for the syn configuration and negative (–5.24 Hz) for the anti. The contribution of the (C–H) bonding is 8.87 Hz larger when the C–H bonding is in the *syn* configuration.

Another feature that is also observed in our results is the fact that all other bonding contributions are negative.

In the case of the geminal $^2J^{\text{FC}}(\text{H}_4-\text{H}_5)$ coupling the electron correlation modifies the FC mechanism and also the SD, but much less. As observed in Table 5 the bondings $\sigma(\text{C}_1-\text{H}_4)$ and $\sigma(\text{C}_1-\text{H}_5)$ are the main contributors to that coupling. The contribution of both C–H bondings is similar in absolute values, though different in sign to that of methane and ethane though larger than for F-methane and ethene (see Figure 3).

We turn now to the analysis of three-bond couplings. It is nicely seen that for the vicinal H–H coupling only the $\sigma(\text{C}-\text{H})$ bonding contribute to the FC mechanism. In the case of ethene and *trans*-1,2-difluoroethene the corresponding $\sigma(\text{C}-\text{H})$ bondings give almost the total value of such coupling. All other bondings contribute with less than 2% of the total.

As was shown by Gräfenstein and Cremer³⁸ the growing of the noncontact contributions to $^3J(\text{F}-\text{F})$ is due to an interaction between the p-type LPs of fluorine atoms and the C=C double bond. Furthermore the higher p character of the $\sigma(\text{C}-\text{F})$ bond contributes to increase the values of the FC and SD terms.

In a previous work published by Peruchena et al.³⁹ it was shown that the coupling pathway that contributes most to the SD term of $^5J(\text{F}-\text{F})$ in unsaturated compounds is the one which arise as an excitation from p-type fluorine LPs to π^* virtual orbitals. They applied in their studies the CLOPPA scheme.¹⁸ In our work we found the same pattern for the $^3J(\text{F}-\text{F})$. In addition we observe that the $\sigma(\text{C}-\text{F})$ bond contribute with 4.72 Hz to the SD term and –19.10 Hz to the PSO.

Moreover Gräfenstein and Cremer suggested that when hydrogen atoms are replaced by fluorines this fact does not modify the efficiency of the information transmitted within the π electronic framework. The growing of the coupling should be due to the larger overlapping between the coupled nuclei with the π -framework. Our results are in line with these suggestions. Both terms, SD and PSO, do contribute with similar values to the *trans* H–H coupling in ethene, F-ethene and 1,2 difluoroethene; meaning that the efficiency of the coupling mechanism through the double bond is not affected by the presence of fluorine atoms for SD and PSO electronic mechanisms.

In the case of *trans*- $^3J(\text{H}-\text{H})$ for 1,2-difluoroethene there is only one type of LMO that contributes to the total J-coupling: the corresponding $\sigma(\text{C}-\text{H})$. This pattern is not entirely the same for ethene and imine. For this last molecule there are a few other contributions that are also a little nonsymmetric. The LP contribution is much larger than the equivalent $\sigma(\text{C}-\text{H})$. The whole contributions from $\sigma(\text{C}-\text{H})$ and $\sigma(\text{N}-\text{H})$ are equivalent to the LP contribution. Another difference between imine and ethene is observed for the contributions of s-type LMOs. In the case of imine they give a much smaller contribution as compared with ethene and also the contribution

of s(C) is much larger than that of s(N) meaning that the electronic density at the site of C is larger than that of N.

Other interesting features are related with the relationship between vicinal H–H couplings in the same molecules, like imine. For the *cis*- $^3J(\text{H}-\text{H})$ coupling the contributions of the $\sigma(\text{C}-\text{H})$ and $\sigma(\text{N}-\text{H})$ bondings are smaller than their contributions in the case of the *trans*- $^3J(\text{H}-\text{H})$ coupling. Moreover the nitrogen LP contributes twice in the *cis* coupling as compared with the *trans* coupling, though the values are quite small.

4. CONCLUDING REMARKS

In this article we analyzed the LeCC of J-couplings of small-sized and saturated compounds by applying LMOs to calculate them at the SOPPA level of approach. Such LeCCs are obtained as a difference between SOPPA and RPA results. For unsaturated compounds there appear to be quasi-instability problems, and then such a difference is meaningless. For unsaturated compounds only an analysis of LMO contributions to J-couplings is possible.

We have chosen the Foster–Boys localization procedure as the first one. We know that it is not appropriate for separating σ and π contributions. In a future work we shall study the likely (though probably quite small) dependence of each LMO contribution with the localization procedure.

It was suspected (never analytically proven) that the explicit SOPPA formulas actually implemented in the DALTON program package were not invariant under unitary transformations. Our first finding was the confirmation of its noninvariance. Now, how large can be the difference between results with canonical and localized orbitals? We are showing in this work that such a difference is small, and affects mostly the FC and SD mechanisms. Given that the total values do not differ in more than 5% we were able to make with confidence the study of J-couplings with LMOs at the SOPPA level.

All electronic mechanisms were analyzed, with the FC the most important for all J-couplings studied here. The PSO mechanism is (almost) not affected by electron correlation.

Our main results were the finding of typical patterns for describing the LeCC contribution to one, two, and three-bond couplings in saturated molecules. The main LMOs are that which bonds the coupled nuclei. They are also the ones which need more the inclusion of electron correlation. We were then able to identify the most important occupied LMOs that contribute to a given J-coupling. In the case of one-bond J-couplings they are first, the bonding orbitals between the coupled nuclei and, second, the core s-type orbitals. For two-bond H–H J-couplings the localized occupied $\sigma(\text{C}-\text{H})$ is the most important. For three-bond H–H J-couplings a similar pattern is found, though when considering *trans* $J(\text{F}-\text{F})$ the s-type LP contribution becomes the most important (and negative) one. In this last case both LMO contributions, the core s(F) and the $\sigma(\text{C}-\text{F})$, are close in magnitude but of opposite sign.

The amount the electron correlation would contribute to the total J-coupling depends on the nature of the coupled nuclei and also on the electronic framework through which the perturbation is transmitted. We found that the *trans* F–F coupling is the most sensitive to electron correlation.

Another important finding is related to the SD contributions which are important when the largest contributions arise from LMOs with high p-character, like that of the double bonds and LPs. A typical example is the F–F J-coupling in unsaturated compounds.

We have shown in this work that the analysis of the contributions given by each localized molecular orbital to NMR J-couplings could offer an efficient way to get a deeper understanding of the electronic structure of the molecules.

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ACKNOWLEDGMENTS

We appreciate important comments of professor Stephan P. A. Sauer on the actual implementation of the SOPPA scheme. We gratefully acknowledge partial support from the Argentinian National Research Council for Science and Technology (CONICET, PIP 11220090100654/2010).

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