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The analysis of NMR J-couplings of saturated and unsaturated compounds by the localized second order polarization propagator approach method

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Calculations of NMR J-coupling with polarization propagators are not invariant under unitary transformations at second order level of approach, second order polarization propagator approach (SOPPA). They are only invariant at first order or random phase level of approach (RPA). We performed "localized" SOPPA (Loc-SOPPA), calculations of J-couplings applying two different schemes for the localization of molecular orbitals(LMO): Foster-Boys and Pipek-Mezey. We show here that results of such Loc-SOPPA calculations are different though not much: they are less than 6% different in the worst case. Therefore it is possible to apply them with confidence in the analysis of the transmission of different coupling mechanisms within the molecule. We are able now to get reliable information on what LMOs are the most important (and so which are not important) for a given J-coupling in a molecule. This information can then be used for selecting which are the paths that should be described with the highest possible accuracy for that J-coupling calculation. A few unsaturated compounds are analyzed: ethene, trans-difluoroethene or DiF-ethene, and imine. It is shown that different lone pairs (of p_z or $p_{x/y}$ type) are responsible for the vicinal F-F J-coupling in DiF-ethene; and also the fact that the main LP contributor is not the same for the fermi contact and the spin-dipolar mechanisms. We also studied phosphorous containing compounds such as phosphine and cis-propylene phosphine. In both cases the analysis of the main LMO contributing to one-bond P-H coupling and through-space P-C coupling were performed. The above mentioned unsaturated molecular systems have quasiinstability problems that arise at RPA level of approach. We show here that they are mostly originated in the antibonding π^* LMO, corresponding to the C=C or C=N double bonds. We performed the analysis of the origin of quasiinstabilities for the SD mechanism. The contribution of each kind of excitation terms to SOPPA calculations were considered, meaning the main contributions by single and double excitations. It is shown that one can get more than 97% of the total electron correlation contribution when including terms that mainly contain single excitations (though double-excitation matrix elements should still be calculated). © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.3697844]

I. INTRODUCTION

Two spectroscopic parameters obtained from nuclear magnetic resonance, i.e., magnetic shieldings and indirect nuclear spin-spin couplings (J-couplings) are quite sensitive to the electronic molecular structure and also to its geometrical conformation. The actual J-coupling values depend on both, the whole molecular structure and specially, on the path the perturbation follows to put both coupled nuclei in contact. Therefore it contains a large amount of local information concerning the electronic structure of the molecule.

When theoretical J-coupling expressions are decomposed in terms which explicitly depend on localized molecular orbitals (LMOs), the analysis of the origin of some electronic effects that have an influence on them is easier. Another advantage concerns the identification of the region of the molecule which is more involved in the transmission of a given J-coupling, and so, to know where the description of the electronic density should be improved in order to get more accurate results. This could optimize calculations on large molecular systems or still make them possible by *ab initio* methods.

The importance of using LMOs to describe the transmission of spin information originated in the nuclear dipole moment interactions with the electronic framework was first pointed out few decades ago by Schulman and Venanzy.[1,2] Recently several reviews or invited articles were devoted to highlight the benefit of such kind of analysis, which illustrate its advantages getting insight in the electronic mechanisms that are involved in the sign and the absolute value of NMR J-couplings.[3–8]

During the last three decades Contreras and co-workers highlighted the physical insights that are obtained when one analyze the contributions to J-couplings from LMOs. They first developed two schemes: the IPPP method (inner projection of polarization propagators) (Refs. 9 and 10) and the CLOPPA method (contributions from localized orbitals within polarization propagators).[11] The last one was applied to different semiempirical wave functions at random phase approximation level of approach (RPA),[12,13] and was also

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applied on heavy-atom containing molecules.[14] A short review with the formalism and results was published in 1993.[15] Its implementation in an *ab initio* scheme was published few years later and applied to study the influence of LMO for ^{1}J(N-H) in NH_3.[16] An interesting analysis of the origin of cooperative effects on linear chains of NCH monomers, with IPPP-CLOPPA method was published by Giribet and Azúa.[17]

Another methodology for the analysis of J-coupling contributions was then developed in Contrera´s group. This new procedure was based on previous ideas that were introduced in the CLOPPA scheme. It uses natural bond orbitals within finite perturbation theory and density functional theory (DFT); the so called natural J-couplings (NJC).[18] Its application on a large variety of compounds together with the dependence of J-couplings on the angle between bonded nuclei was shown in a review by Contreras and Peralta.[19] A variant of the NJC method was introduced by Weinhold and co-workers.[20] They also showed that J-couplings contributions can be related to the localized features of the molecular electronic structure.

Lazzeretti and Soncini developed a model based on current and energy densities, which are property density functions of the position in three-dimensional space.[21] From this model they were able to obtain the path whereby coupling takes place.

Cremer and co-workers have also largely contributed to the analysis of J-couplings through LMOs. They developed the J decomposition into orbital contributions with the help of orbital currents and partial spin polarization (JOC-PSP) method.[22] They were able to learn on the π-character of a C–C bond by studying non-contact terms,[23] the origin of large SD components of J-couplings in fluorinated polyenes,[24,25] by the π-mechanism involved in J-couplings in polyenes previously studied by Provasi *et al.*[26] The JOC-PSP method makes it possible to analyze the four J-coupling transmission mechanisms in terms of orbital contributions in the framework of DFT.[4]

Sauer and Provasi had also applied LMOs in the analysis of isotope effects on NMR J-couplings[27,28] Their scheme is actually an *ab initio* implementation of the CLOPPA approach in the DALTON code[29] at RPA and TD-DFT level of theory.

Malkin and co-workers presented a new method[30] which considers the coupling electron deformation densities (CDD) (Ref. 31) with Foster-Boys[32] or Pipek-Mezey[33] localized molecular orbitals. They discussed the contribution of σ-bonds, π-bonds, and lone pairs to J-couplings in isomers of Adenine. They found that it is the σ-bond of the C=N bond which has an exclusive contribution to the FC term for ^{1}H–C=^{15}N coupling.

The polarization propagator method, at its second order level of approach, second order polarization propagator approach (SOPPA)[34–37] had shown to be one of the most reliable theoretical tools for getting accurate J-coupling results for calculations on unsaturated compounds.[38–40] This model was successfully applied recently to calculate J-couplings in medium-size molecular systems.[41]

An old assumption that was not explicitly proved until this year, was the fact that SOPPA results were not invariant under unitary transformations of MOs.[42] Moreover calculations with the "localized" version of SOPPA, Loc-SOPPA, have shown results that are quite close to that obtained with its "canonical" version, at least for small molecules.[42]

In this article we make a step forward in the analysis of J-couplings with the Loc-SOPPA scheme. We studied (i) how dependent J-couplings are when different localization procedures are considered; (ii) the transmission path of fermi-contact (FC) and spin-dipolar (SD) electron-nucleus interaction mechanism in few unsaturated compounds, e.g., ethene, trans-difluoroethene (DiF-ethene) and imine; (iii) the importance of the π^* antibonding LMO for quasiinstability problems in such unsaturated compounds, and (iv) how important are the single excitation contributions to the total SOPPA results.

In Sec. II, we introduce the basis of our Loc-SOPPA procedure and also few computational details necessary for doing calculations. Results are given in Sec. III starting with the analysis of how large are the differences when different localization schemes are considered. In Sec. IV, we highlight the main results of our work.

II. THEORETICAL MODEL AND COMPUTATIONAL DETAILS

The non relativistic theory of J-couplings was first formulated by Ramsey who considered four terms

$$J_{MN} = J^{FC}_{MN} + J^{SD}_{MN} + J^{PSO}_{MN} + J^{DSO}_{MN} \tag{1}$$

being FC, the fermi-contact, SD, the spin-dipolar and the PSO (DSO) the paramagnetic (diamagnetic) spin-orbital. These contributions arise from two different mechanisms of interaction between the electronic magnetic moments and the nuclear magnetic moments transmitted through electrons: the electron spin-nuclear spin interaction and the electronic orbital-nuclear magnetic moment interaction.

These J-coupling terms can be obtained from the polarization propagator theory, applying perturbation theory. Consistent first- and second-order calculations are named as RPA (random phase approximation)and SOPPA (second order polarization propagator approach), respectively.[35] All terms of Eq. (1) are then obtained at those different levels, being them defined by the fluctuation potential.

When calculated within the non relativistic polarization propagator theory each of the first three terms of the rhs of Eq. (1) are written as

$$\mathbf{J}^X_{MN} = \gamma_M \gamma_N \langle\langle \mathbf{V}^X_M ; \mathbf{V}^X_N \rangle\rangle_{E=0}, \tag{2}$$

where X = FC, SD, or PSO.

The FC mechanism depends on the electronic density at the site of the nuclei. So its contributions may be related to the electronic densities at the sites of two different nuclei, say M and N. This term 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 mechanisms[7] are more important than the FC one. They are the SD and PSO.

To calculate molecular properties within polarization propagators, one apply the non partitioned matrices at SOPPA level as implemented in the DALTON code[29] and described in

the work of Packer *et al.*[36] Accordingly when partitioning is not applied the linear response can be expressed as

$$\langle\langle P;Q\rangle\rangle_\omega = (P^\dagger|\mathbf{h})(\tilde{\mathbf{h}}|\omega\hat{I}-\hat{H}|\mathbf{h})^{-1}(\tilde{\mathbf{h}}|Q), \tag{3}$$

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 term of basic excitation operators that belong to that excitation manifold.

Then

$$\begin{aligned}\langle\langle P;Q\rangle\rangle_\omega &= \sum_{\mu\nu} -P_\mu^{[1]}\left(\mathbf{E}^{[2]}-\omega\mathbf{S}^{[2]}\right)^{-1}_{\mu\nu}Q_\nu^{[1]} \\ &= \sum_{\mu} -P_\mu^{[1]}N_\mu^{Q}(\omega).\end{aligned} \tag{4}$$

When $\mathbf{h}=\mathbf{h}_2+\mathbf{h}_4$ (the manifold containing single and double excitation operators) and the reference state includes first- and second-order corrections, Eq. (3) becomes the original expression of polarization propagators at SOPPA level of approach written within the super operator formalism, and Eq. (4) is short-hand expression of that given first by Olsen and Jørgensen.[43] In the first term of Eq. (4), one can see the response as a product of a property gradient vector (PGV) or perturbator $P_\mu^{[1]}$ times the inverse of the principal propagator $(\mathbf{E}^{[2]}-\omega\mathbf{S}^{[2]})$ and another perturbator $Q_\nu^{[1]}$. The meaning of subindices μ and ν in such equations are of being particle-hole, ph, or two particle-two hole, 2p2h, operators.

In its actual implementation in the DALTON program package,[36] the calculation of response functions at SOPPA level of approach use an smart procedure by which one calculate the vector $\mathbf{N}^Q(\omega)$ of Eq. (4) in a tricky way. They are obtained from the following equation:

$$(\mathbf{E}^{[2]}-\omega\mathbf{S}^{[2]})\mathbf{N}^Q(\omega)=\mathbf{Q}^{[1]}. \tag{5}$$

Equation (5) was solved by Packer and co-workers using an iterative technique previously applied by Olsen and Jørgensen in MCSCF methods.[44,45] In such a method, the vector $\mathbf{N}^Q(\omega)$ is obtained by iteration, as a sum of terms which contain coefficients multiplying trial vectors **b**, of dimensions ph and 2p2h (those with subindices K and J in Eq. (6))

$$\mathbf{N}^{Q(SOPPA)} = \sum c_K\mathbf{b}_K^{ph} + \sum c_J\mathbf{b}_J^{2p2h}. \tag{6}$$

There are mandatory mathematical reasons by which each coefficient $c_{K,J}$ appears within the interactive procedure, and also its convergency. They are determined in a way that single and double excitation contributions are mixed in intermediate steps.

On the other hand, each term of the perturbator vector $\mathbf{P}^{[1]}$ can be divided into two groups. The one which contains only single excitations operators and the other one containing double excitation operators. Then the scalar product of Eq. (4) can be written in the following way:

$$\begin{aligned}\sum_\mu P_\mu^{[1]}N_\mu^Q(\omega) &= \begin{bmatrix} P_{ph}^{[1]} & P_{2p2h}^{[1]}\end{bmatrix}\begin{pmatrix} N_{ph}^Q(\omega) \\ N_{2p2h}^Q(\omega)\end{pmatrix} \\ &= \sum_{ai} P_{ai}^{[1](SOPPA)}N_{ai}^{Q(SOPPA)}(\omega) \\ &\quad + \sum_{aibj} P_{aibj}^{[1](SOPPA)}N_{aibj}^{Q(SOPPA)}(\omega).\end{aligned} \tag{7}$$

where subindices i, j, k, ... (a, b, c, ...) means occupied (virtual) Hartree-Fock molecular orbitals. The contribution to the solution vector of the first term of the second line of Eq. (7) is dominated by single excitations and that of the second term, by double excitations.[35,46] We like to stress here that for calculations of the ph terms of the direct linear transformation of $\mathbf{E}^{[2]}$ on the trial vector **b**, $[\mathbf{E}^{[2]}\mathbf{b}]_{ph}$, matrices **A**(0, 1, 2), **B**(1, 2), and $\tilde{\mathbf{C}}(1)$ are considered. The calculation of $[\mathbf{E}^{[2]}\mathbf{b}]_{2p2h}$ includes matrices **C**(1) and **D**(0) (see Ref. 35 for definition of matrices **A**, **B**, **C,** and **D**). Both, $[\mathbf{E}^{[2]}\mathbf{b}]_{ph}$ and $[\mathbf{E}^{[2]}\mathbf{b}]_{2p2h}$ are used in the iterative algorithm which gives the final solution vector $\mathbf{N}^{Q(SOPPA)}(\omega)$. This means that electron correlation effects are introduced within the first term of second line of Eq. (7) at a higher level than Higher RPA.[35] The explicit expressions for vectors $\mathbf{P}_\mu^{[1](SOPPA)}$ and $\mathbf{N}_\mu^Q(\omega)^{(SOPPA)}$ are given in Ref. 36.

Canonical and localized calculation of J-couplings were performed with cc-pVTZ basis sets[47] for all compounds but in case of phosphine the cc-pCVTZ basis set was applied.[47,48] The basis sets used are not the best option to obtain results comparable with experiments but all calculations with this basis set give numbers that follow the tendency of J-couplings on different molecular structures. Our main concern in this respect was to obtain semiquantitatively correct results in order to analyse the pattern of contributions of each localized bonding to the total J-couplings.

The localization of MOs was performed with the methods of Foster and Boys[32] and and Pipek-Mezey.[33] The geometry of all compounds were optimized at DFT-B3LYP/6-311++G** level of approach.[49,50]

For the implementation of our scheme we have introduced small modifications to the DALTON suite of programs in order to work with LMOs.

III. RESULTS

The SOPPA method is not invariant under unitary transformations of MOs. In Sec. III A, we show how large the expected deviation is when calculations are performed with two different schemes of localization: Foster-Boys, FB and Pipek-Mezey, PM. In this second article on Loc-SOPPA we had concentrated our studies on three typical unsaturated molecular systems and phosphorus containing molecules, shown in Fig. 1.

Different pattern of *coupling pathways* for the transmission of J-couplings may be expected when considering different electron-nucleus interactions. They are analysed in Secs. III B and III C.

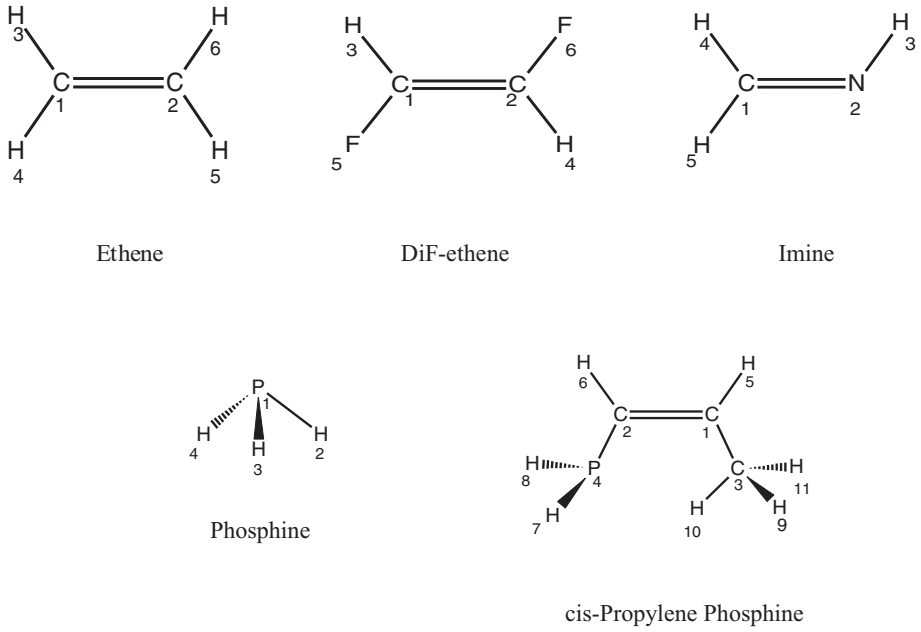

FIG. 1. Saturated and unsaturated molecular models analysed.

Calculation within polarization propagators can be performed at different level of approach. At second-order there are contributions which depend mostly on single or double excitations. They may have quite different weights concerning the final result and they are also much different in the time-consumption of computational resources. In Sec. III D their analysis is performed.

A. Canonical vs localized SOPPA, Loc-SOPPA results

As illustrated in Ref. 42 results of calculations at RPA level of approach are exactly the same when using either, canonical or localized MOs. They could give different relative contributions when the localization of MOs are performed with FB or PM procedures (see Ref. 51, where the relative contributions of LMOs at RPA level of approach are shown).

As observed in Table I, results of SOPPA calculations depend on whether the scheme of MOs are localized or canonical, and also on the procedure of localization adopted. Differences in the FC values are, in percentage, larger for H-H couplings than for C–C ones. For example, in DiF-ethene $J^{FC}(C_1\text{-}C_2)$ has a difference of 3% when calculations are performed with canonical MOs or LMOs, being of 6% for $J^{FC}((H_3\text{-}H_4)$. It is interesting to observe that the J(P-H) values in phosphine have a difference of 6% between canonical and Loc-SOPPA with PM localization. Such a difference may be due to the localization of the core of P atoms.

SD contributions at SOPPA level are usually small in all kind of compounds and couplings studied here, though they become smoothly larger for J(F-F) in DiF-ethene (it contributes with more than 10% of the total). For this last coupling the difference among all three type of calculations (with canonical and the two different LMOs) are also large and much larger than what is obtained for the FC contribution.

As happens for FC and SD terms, the largest differences among all three type of calculations are found for the PSO term of the J(F-F) coupling in DiF-ethene. Still the PSO results are not much influenced by the localization procedure. On the other hand, calculations of the PSO term at SOPPA level give results not much different with canonical and localized MOs for all couplings and molecular systems studied here.

Even though we can apply our Loc-SOPPA procedure on top of any localization scheme it is by far more relevant to choose schemes which clearly separate the whole branch of occupied MOs. The Pipek-Mezey scheme is then more useful than the Foster-Boys for the analysis of J-couplings in unsaturated compounds. In Ref. 42 results of Loc-SOPPA calculations with Foster-Boys were presented. There were no difference between σ-π contribution what is now done. As an example, if one compares the contributions of the σ - π bonding orbitals to all different J-couplings in our set of unsaturated compounds (see Table II) it becomes apparent that (i) the $\sigma(C_1\text{-}C(N)_2)$ LMO do mostly contribute to the FC mechanism and (ii) the $\pi(C_1\text{-}C(N)_2)$ LMO do that for the SD mechanism. Actually for all FC terms of J-couplings there are no contributions from the π-type LMO. These facts would not be found by the application of Foster-Boys´ localization scheme.

B. Transmission of the FC nucleus-electron interacting mechanism

In Table II, we show the contributions of each Pipek-Mezey LMO to both, FC and SD terms of J-couplings. It is interesting to highlight the fact that the π LMO gave the largest contribution to $J^{SD}(C_1\text{-}C_2)$ in ethene and $J^{SD}(C_1\text{-}N_2)$ in imine. For DiF-ethene the π-type LMO is also important in both $J^{SD}(C_1\text{-}C_2)$ and $J^{SD}(F_5\text{-}F_6)$.

In the three unsaturated model compounds studied here the main contributions to the FC term for C–C and C–N

TABLE I. SOPPA and Loc-SOPPA[a] values for all electronic mechanisms. All values are in Hz.

Methane	FC	SD	PSO	DSO	Total
$J(C_1\text{-}H_2)$	111.736	0.073	1.588	0.241	113.638
	(111.686) [115.404]	(0.062) [0.036]	(1.572) [1.574]	(0.241) [0.233]	(113.560) [117.248]
$J(H_2\text{-}H_3)$	−13.398	0.373	3.371	−3.494	−13.149
	(−13.678) [−14.893]	(0.380) [0.394]	(3.372) [3.372]	(−3.493) [−3.488]	(−13.419) [−14.616]
Ethane					
$J(C_1\text{-}C_2)$	28.098	1.169	0.238	0.111	29.616
	(28.159) [29.702]	(1.185) [1.199]	(0.196) [0.219]	(0.111) [0.109]	(29.651) [31.229]
$J(H_4\text{-}H_5)$	14.573	0.028	2.758	−3.083	14.276
	(15.227) [15.593]	(0.029) [0.029]	(2.765) [2.765]	(−3.082) [−3.075]	(14.939) [15.313]
Ethene					
$J(C_1\text{-}C_2)$	95.598	3.301	−9.968	0.066	88.997
	(96.501) [97.368]	(4.855) [3.299]	(−10.195) [−10.175]	(0.066) [0.066]	(91.227) [90.558]
$J(H_3\text{-}H_5)$	16.861	0.282	2.603	−3.544	16.201
	(18.367) [17.491]	(0.418) [0.281]	(2.597) [2.600]	(−3.542) [−3.545]	(17.839) [16.828]
DiF-ethene					
$J(C_1\text{-}C_2)$	145.941	4.531	−9.692	0.258	141.038
	(149.567) [150.338]	(6.951) [4.930]	(−9.991) [−9.903]	(0.258) [0.258]	(146.785) [145.623]
$J(H_3\text{-}H_4)$	9.585	0.374	2.463	−3.411	9.010
	(11.513) [10.194]	(0.565) [0.406]	(2.449) [2.460]	(−3.409) [−3.405]	(11.121) [9.650]
$J(F_5\text{-}F_6)$	−24.046	23.045	−156.837	−1.708	−159.546
	(−21.530) [−22.300]	(35.650) [27.498]	(−158.603) [−160.979]	(−1.706) [−1.702]	(146.188) [−157.483]
Imine					
$J(C_1\text{-}N_2)$	−13.937	−1.422	8.992	−0.014	−6.380
	(−13.954) [−14.113]	(−2.399) [−1.349]	(9.408) [9.458]	(−0.014) [−0.014]	(−6.958) [−6.017]
$J(H_3\text{-}H_5)$	22.749	0.339	3.191	−4.486	21.793
	(24.447) [23.841]	(0.500) [0.335]	(3.179) [3.169]	(−4.485) [−4.488]	(23.641) [22.857]
Phosphine					
J(P-H)	162.799	−1.415	5.407	−0.022	166.769
	(155.612) [154.225]	(−1.553) [−1.720]	(5.180) [5.199]	(−0.022) [−0.020]	(159.218) [157.686]
Propylene phosphine					
$J(P_4\text{-}C_3)$	25.830	0.161	−0.540	−0.003	25.449
	(25.831) [26.030]	(0.173) [0.195]	(−0.520) [−0.524]	(−0.003) [−0.003]	(25.480) [25.698]

[a]Between parenthesis Foster-Boys values are given and between square brackets are Pipek-Mezey values.

couplings are given by the $\sigma(C_1\text{-}C_2)$ or $\sigma(C_1\text{-}N_2)$. The next most important contribution is that of the s-type LMO, though its relative value with respect to $\sigma(C_1\text{-}X_2; X = C, N)$ depends on the molecule: it is of 67% for DiF-ethene, 56% for ethene, and 46.8% for imine. The total contribution of the bonding C-H (plus that of the C-F bonding in DiF-ethene) follows an opposite behavior. It is of 58.4% for ethene, 48% for DiF-ethene and 43% imine though adding the LP contribution it grows to 92%.

The transmission of the FC mechanism in the vicinal H-H and F-F couplings follows different patterns. For $^3J^{FC}$(H-H), the contribution of the bonding σ(C-H) (plus that of σ(N-H) in imine) is the largest one (and almost unique). This is not the case for F-F J-coupling. The contribution of both fluorine atoms through its s(F) and the s-type LP are the largest one. They are both negative, so the $^3J^{FC}$(F-F) is negative being $^3J^{FC}$(H-H) positive. The contribution of σ(C-F) is close to that of σ(C-H) for ^{3}J(H-H) in both, ethene and imine.

The difference of the LP contribution to both (syn/anti) one-bond J(C-H) couplings in imine is known as one particular case of the Perlin effect.[52,53] The difference (syn-anti) of the total J-coupling calculated with our Loc-SOPPA scheme is close to 16 Hz. Such a difference was found close to 18 Hz by the application of the original NJC scheme.[54] Contreras and co-workers analyzed only the FC mechanism, and that was enough given that the other contributions were found vanishingly small. They have also shown that one should consider solvent effects in order to get a better agreement between theoretical calculations and experimental results.

When considering each LMO contribution to the difference (syn-anti) of the one-bond J(C-H) couplings, we observe that our results show a less pronounced influence of the LP and bonding contributions: 6.6 Hz (ours) vs 14.3 Hz (NJC) for the LP, and 5.6 Hz (ours) vs 10 Hz (NJC) for the bonding or (C-H) contribution. On the other hand, within the NJC scheme the contributions to that difference of the bonding σ(C=N) and the core s(C) are small or vanishingly small respectively. Our results show that they are close to 4.5 Hz. The differences in individual (occupied) LMO contributions obtained by NJC or by our scheme may be due to that both methods are based on different theoretical grounds.

These results indicate that the LP orientational effects would also influence the contributions of both the C=N

TABLE II. Contributions to the FC and SD J-coupling terms by Pipek-Mezey LMOs in saturated and unsaturated compounds.[a]

	RPA	SOPPA	RPA	SOPPA	RPA	SOPPA	RPA	SOPPA
Ethene	$J^{FC}(C_1\text{-}C_2)$		$J^{SD}(C_1\text{-}C_2)$		$J^{FC}(H_3\text{-}H_5)$		$J^{SD}(H_3\text{-}H_5)$	
$s(C_1)$	16.66	32.16	0.06	0.00	0.08	0.00	0.00	0.00
$\sigma(C_1\text{-}H_3)$	33.71	− 11.97	− 0.55	− 0.09	85.43	8.05	1.07	− 0.03
$\sigma(C_1\text{-}H_4)$	33.71	− 11.97	− 0.55	− 0.09	− 0.52	0.35	0.13	0.00
$\sigma(C_1\text{-}C_2)$	258.82	82.17	− 3.04	− 0.53	− 2.19	0.48	0.51	0.03
$\pi(C_1\text{-}C_2)$	0.03	0.00	123.72	4.11	0.00	0.00	9.65	0.30
Total[b]	427.01	98.62	118.61	3.21	167.80	17.29	12.56	0.28
DiF-ethene	$J^{FC}(C_1\text{-}C_2)$		$J^{SD}(C_1\text{-}C_2)$		$J^{FC}(F_5\text{-}F_6)$		$J^{SD}(F_5\text{-}F_6)$	
$s(F_5)$	− 0.01	0.00	0.00	0.00	105.16	− 13.57	− 0.54	− 0.01
$s(C_1)$	− 7.55	42.98	0.23	0.01	− 0.49	0.00	0.08	0.00
$\sigma(C_1\text{-}H_3)$	128.67	− 21.37	− 0.20	− 0.06	21.50	1.80	− 3.63	− 0.10
$\sigma(C_1\text{-}F_5)$	25.76	− 9.41	− 1.31	− 0.02	− 209.41	9.50	95.51	4.50
$LP(s)(F_5)$	5.63	− 0.31	− 0.07	− 0.00	447.79	− 10.91	34.57	1.09
$LP(p_z)(F_5)$	− 0.01	0.00	1.14	0.01	0.00	0.00	443.48	6.32
$LP(p_x\text{-}p_y)(F_5)$	2.69	− 0.09	0.03	0.00	2.70	0.73	− 8.20	0.92
$\sigma(C_1\text{-}C_2)$	592.07	128.30	− 4.11	− 0.43	46.00	2.26	− 11.35	0.27
$\pi(C_1\text{-}C_2)$	0.06	0.00	236.19	5.39	0.07	0.00	86.91	1.05
Total[b]	902.53	151.92	231.70	4.82	780.55	− 22.66	1198.11	26.75
Imine	$J^{FC}(C_1\text{-}N_2)$		$J^{SD}(C_1\text{-}N_2)$		$J^{FC}(H_3\text{-}H_5)$		$J^{SD}(H_3\text{-}H_5)$	
$s(N_2)$	5.72	− 5.19	0.27	0.00	0.46	− 0.01	0.02	0.00
$s(C_1)$	22.97	− 7.24	− 0.10	0.00	0.26	0.00	0.02	0.00
$\sigma(N_2\text{-}H_3)$	− 35.19	2.19	2.39	0.05	216.86	11.75	4.03	− 0.10
$\sigma(C_1\text{-}H_4)$	− 66.41	1.75	1.12	0.29	− 2.99	0.60	0.57	− 0.01
$\sigma(C_1\text{-}H_5)$	− 53.59	7.52	1.23	0.14	223.91	10.20	4.61	− 0.04
$LP(N_2)$	− 80.56	12.89	− 2.05	0.24	− 0.80	0.51	0.69	0.06
$\sigma(C_1\text{-}N_2)$	− 222.59	− 26.48	7.90	0.60	− 4.69	0.47	2.25	0.04
$\pi(C_1\text{-}N_2)$	− 0.04	0.00	− 295.40	− 2.61	0.00	0.00	42.19	0.37
Total[b]	− 429.70	− 14.57	− 284.64	− 1.31	433.02	23.53	54.36	0.33
	$J^{FC}(C_1\text{-}H_4)$				$J^{FC}(C_1\text{-}H_5)$			
$s(N_2)$	0.30	0.01			0.24	− 0.03		
$s(C_1)$	− 15.79	24.66			− 10.38	29.18		
$\sigma(N_2\text{-}H_3)$	2.47	1.95			− 0.93	− 1.82		
$\sigma(C_1\text{-}H_4)$	588.59	153.83			75.97	− 16.04		
$\sigma(C_1\text{-}H_5)$	71.22	− 15.42			573.52	158.37		
$LP(N_2)$	− 6.56	− 3.11			− 0.55	3.50		
$\sigma(C_1\text{-}N_2)$	129.61	− 11.79			133.59	− 7.19		
Total[b]	769.98	150.13			771.47	165.97		

[a]Contributions of each occupied LMO was obtained applying Eq. (9) of Ref. 42.
[b]The total value correspond to the contribution of only the single excitations. See Sec. III D.

bonding and the core s(C) on $^1J(C\text{-}H)$ in imine. There would be a direct (LP) and more than one indirect (σ(C-H), σ(C-N) and s(C)) contribution to the Perlin effect in imine.

For both J-couplings of P-containing molecules studied here the FC mechanism is by far the largest one. In the case of $J(P_4\text{-}C_3)$ in cis-propylene phosphine, the Loc-SOPPA method shows which are the main occupied LMO that intervene in the transmission of such coupling (see Table III). The main LMO are: (i) the core s(P) and $\sigma(C_3\text{-}H_{10})$ which together give more than 57% of the total, and (ii) the LP of phosphorus and the sigma bondings $\sigma(C_2\text{-}P_4)$ and $\sigma(C_1\text{-}C_3)$ which together give around 40% of the total J-coupling. It is then clear that the transmission is through-space.

C. Transmission of the SD nucleus-electron interacting mechanism and analysis of quasiinstabilities

The SD electron-nucleus interacting mechanism involves an interaction between the electron spin with the nuclear magnetic dipole moment, that does not occur at the nuclear site. This is the underlying feature that becomes apparent from the analysis of contributions from LMOs for $J^{SD}(C_1\text{-}C_2)$ and $J^{SD}(C_1\text{-}N_2)$. For ethene and DiF-ethene, the π-type LMO is by far the main contributor. In the imine molecule, there are three other LMOs of less importance, though necessary to be included: $\sigma(C_1\text{-}N_2)$, $\sigma(C_1\text{-}H_4)$, and the LP (N_2).

TABLE III. Contributions of each occupied LMO to the FC term of $J(P_4\text{-}C_3)$ in cis-propylene-phosphine. Pipek-Mezey localization scheme was used.[a]

	$J^{FC}(P_4\text{-}C_3)$	
LMO	RPA	Loc-SOPPA
$s(P_4)$	14.34	7.23
$s(C_1)$	0.03	0.02
$s(C_2)$	0.03	0.01
$s(C_3)$	9.82	2.86
$\sigma(C_1\text{-}H_5)$	1.00	1.29
$\sigma(C_2\text{-}H_6)$	0.60	0.60
$\sigma(C_3\text{-}H_9)$	0.72	− 1.05
$\sigma(C_3\text{-}H_{10})$	7.45	7.68
$\sigma(C_3\text{-}H_{11})$	− 0.16	− 1.37
$\sigma(C_1\text{-}C_2)$	− 3.11	− 1.75
$\pi(C_1\text{-}C_2)$	0.00	0.03
$\sigma(C_1\text{-}C_3)$	12.41	3.41
$\sigma(C_2\text{-}P_4)$	21.13	4.23
$\sigma(P_4\text{-}H_7)$	0.82	− 1.11
LP	− 1.03	5.16
Total	60.92	26.03

[a]Contributions of each occupied LMO was obtained applying Eq. (9) of Ref. 42.

TABLE IV. Contributions of the excitation $\pi \rightarrow \pi^*$ to the SD term of different couplings in unsaturated compounds.[a]

	RPA	SOPPA	RPA	SOPPA
Ethene	$J(C_1\text{-}C_2)$		$J(H_3\text{-}H_5)$	
$\pi(C_1\text{-}C_2)$	123.72	4.11	9.65	0.30
Total	118.61	3.21	12.56	0.28
$\pi \rightarrow \pi^*$	115.12	4.62	9.50	0.35
Total[b]	3.49	3.21	3.06	0.28
Di-F ethene	$J(C_1\text{-}C_2)$		$J(H_3\text{-}H_4)$	
$\pi(C_1\text{-}C_2)$	236.19	5.39	16.08	0.35
Total	231.70	4.82	21.93	0.40
$\pi \rightarrow \pi^*$	215.37	5.95	15.67	0.41
Total[b]	16.34	4.82	6.26	0.40
Imine	$J(C_1\text{-}N_2)$		$J(H_3\text{-}H_5)$	
$\pi(C_1\text{-}N_2)$	− 295.40	− 2.61	42.19	0.37
Total	− 284.64	− 1.31	54.36	0.33
$\pi \rightarrow \pi^*$	− 266.81	− 2.75	40.00	0.35
Total[b]	− 17.83	− 1.31	14.36	0.33

[a]Contributions of each occupied LMO was obtained applying Eq. (7) and Eq. (8).
[b]Without the contribution from $\pi \rightarrow \pi^*$.

The SD contribution to ^3J(F-F) in DiF-ethene is larger than the corresponding FC one. The p_z-type of LP(F) and the σ(C-F) give together a contribution of 21.60 Hz out of the total 26.75 Hz. This is in line with a previous work published by Gräfenstein and Cremer,[25] though our procedure is more straightforward in obtaining similar physical insights.

In this J-coupling the core s(F) does not contribute, and the p_x-p_y type LP(F) gives a contribution close to that of the FC mechanism, 0.92 Hz. Furthermore the LMOs which correspond to the C=C double bond do not contribute significantly. Therefore there are only two LMO of importance for $^3J^{SD}$(F-F), which are of less importance for the transmission of the FC electron-nucleus interacting mechanism. We give the picture of all LPs for DiF-ethene as a supplementary material (see Ref. 51).

In the case of ^3J(H-H) in both, ethene and imine, there is only one LMO of importance, the π-type C=C or C=N.

When RPA and SOPPA values are considered, one can observe (see Table II) that both FC and SD contributions at the RPA level are artificially exaggerated. Previous studies have shown that this is due to quasiinstability problems being the $\pi \rightarrow \pi^*$ excitation the main source for it. In Table IV, we show how large are the contributions of such excitations to SD. The contribution of $\pi \rightarrow \pi^*$ to the total value of the π-type contribution to all J-couplings studied represent more than 93%. It means that the quasiinstability problem is located in such excitations. When the $\pi \rightarrow \pi^*$ contribution is not included, the RPA values become more reliable.

From the analysis of results with and without the $\pi \rightarrow \pi^*$ contribution, one observes that vicinal couplings are more affected by quasiinstability problems originated in such excitation than the one-bond couplings.

D. Contributions from single and double excitations

As mentioned in Sec. II, terms which mainly contain single excitations are by far the most important contributions to the first term of Eq. (7), and terms that mainly arise from double excitations are the most important for the second term of such equation. We were then interested to learn whether one of these two terms could be larger or much larger than the other.

As observed in Table V, the total contributions from single excitations contain almost the whole actual value of SOPPA results of all couplings studied in this work.

In all cases the addition of the total contributions which are connected to the vector $\mathbf{P}^{[1](SOPPA)}_{aibj}$ gives less than 5% of the total SOPPA value. So

$$\langle\langle P;Q\rangle\rangle^{(SOPPA)}_{\omega} \simeq \sum_{ai} -\mathbf{P}^{[1](SOPPA)}_{ai}\mathbf{N}^{Q(SOPPA)}_{ai}(\omega). \quad (8)$$

For the FC term, the largest deviation was found for $J^{FC}(C_1\text{-}N_2)$ with a value of 3.12%. In all other cases it is never larger than 2%. In the case of SD and PSO terms, percentual differences are larger but arise from small contributions, and so they do not have any influence to the total coupling. In the case of the PSO contribution to J(F-F) in DiF-ethene (which is large enough) the double-excitation contribution is close to 3%.

This is a remarkable result. It shows that the 2p2h terms of Eq. (7) may be neglected in a semiquantitative calculation.

TABLE V. Percentual contributions to the three different terms, FC, SD, and PSO, corresponding of single and double excitations. All values are given in Hz.

	FC	SD	PSO		FC	SD	PSO
Methane							
$J(C_1\text{-}H_2)$				$J(H_2\text{-}H_3)$			
One exc	111.27 (99.63)	0.05 (72.87)	1.54 (98.14)		−13.90 (101.60)	3.33 (98.87)	3.33 (98.87)
Two exc	0.41 (0.37)	0.02 (27.13)	0.03 (1.86)		0.22 (−1.60)	0.04 (1.13)	0.04 (1.13)
Total	111.69	0.06	1.57		−13.68	3.37	3.37
Ethane							
$J(H_3\text{-}H_4)$				$J(H_4\text{-}H_5)$			
One exc	−14.23 (101.44)	0.42 (99.52)	2.82 (98.84)		15.01 (98.59)	0.03 (99.43)	2.73 (98.61)
Two exc	0.20 (−1.44)	0.00 (0.48)	0.03 (1.16)		0.22 (1.41)	0.00 (0.57)	0.04 (1.39)
Total	−14.03	0.43	2.85		15.23	0.03	2.77
$J(C_1\text{-}C_2)$				$J(C_1\text{-}H_4)$			
One exc	28.34 (100.63)	1.17 (98.39)	0.17 (88.64)		110.09 (99.59)	−0.01 (−102.21)	1.24 (98.36)
Two exc	−0.18 (−0.63)	0.02 (1.61)	0.02 (11.36)		0.45 (0.41)	0.02 (202.21)	0.02 (1.64)
Total	28.16	1.19	0.20		110.54	0.01	1.26
Ethene							
$J(H_3\text{-}H_5)$				$J(H_4\text{-}H_5)$			
One exc	18.18 (98.97)	0.41 (98.28)	−2.56 (98.74)		11.26 (99.08)	−0.10 (99.38)	−0.68 (100.11)
Two exc	0.19 (1.03)	0.01 (1.72)	−0.03 (1.26)		0.10 (0.92)	−0.00 (0.62)	0.00 (−0.11)
Total	18.37	0.42	−2.60		11.36	−0.10	−0.68
$J(C_1\text{-}C_2)$				$J(C_1\text{-}H_4)$			
One exc	97.74 (101.28)	4.75 (97.86)	−9.97 (97.83)		148.89 (99.67)	0.00 (2.56)	0.39 (96.03)
Two exc	−1.23 (−1.28)	0.10 (2.14)	−0.22 (2.17)		0.49 (0.33)	0.03 (97.44)	0.02 (3.97)
Total	96.50	4.86	−10.20		149.37	0.03	0.40
DiF-ethene							
$J(C_1\text{-}C_2)$				$J(H_3\text{-}H_4)$			
One exc	151.11 (101.03)	6.82 (98.19)	−9.80 (98.03)		11.50 (99.90)	0.56 (98.49)	2.41 (98.59)
Two exc	−1.55 (−1.03)	0.13 (1.81)	−0.20 (1.97)		0.01 (0.10)	0.01 (1.51)	0.03 (1.41)
Total	149.57	6.95	−9.99		11.51	0.57	2.45
$J(F_5\text{-}F_6)$							
One exc	−21.91 (101.77)	34.86 (97.80)	−153.54 (96.81)				
Two exc	0.38 (−1.77)	0.79 (2.20)	−5.06 (3.19)				
Total	−21.53	35.65	−158.60				
Imine							
$J(H_3\text{-}H_4)$				$J(H_3\text{-}H_5)$			
One exc	18.57 (99.08)	0.08 (96.42)	0.29 (105.22)		24.15 (98.79)	0.49 (98.08)	3.14 (98.79)
Two exc	0.17 (0.92)	0.00 (3.58)	−0.01 (−5.22)		0.30 (1.21)	0.01 (1.92)	0.04 (1.21)
Total	18.74	0.08	0.28		24.45	0.50	3.18
$J(C_1\text{-}H_4)$				$J(C_1\text{-}H_5)$			
One exc	150.52 (99.81)	0.07 (71.46)	−0.21 (105.87)		166.41 (99.60)	0.04 (62.56)	−0.30 (99.78)
Two exc	0.29 (0.19)	0.03 (28.54)	0.01 (−5.87)		0.67 (0.40)	0.03 (37.44)	−0.00 (0.22)
Total	150.81	0.10	−0.19		167.08	0.07	−0.30
$J(C_1\text{-}N_2)$							
One exc	−14.39 (103.12)	−2.35 (97.77)	9.19 (97.64)				
Two exc	0.44 (−3.12)	−0.05 (2.23)	0.22 (2.36)				
Total	−13.95	−2.40	9.41				

IV. CONCLUDING REMARKS

Calculation of J-couplings with polarization propagators at SOPPA level are not invariant under unitary transformations of molecular orbitals. The new Loc-SOPPA method is able to highlight it with numerical results.

We show in this article that one can apply different localization schemes to obtain semiquantitative results of J-couplings at SOPPA level (only due to the small basis set employed here). There are few advantages of using the Pipek-Mezey scheme compared to that of Foster-Boys. The main one is the clear σ-π separation when localizing double bonds. This fact permits one to learn about the different role of π-type MOs for the transmission of FC and SD J-coupling terms in unsaturated compounds.

Our analysis show on better grounds what was known from the previous application of DFT and semiempirical theoretical models and experimental evidence: that the FC electron spin-nucleus spin interacting mechanism is mainly transmitted through the σ electronic framework. And also the fact that this is opposite to what happens for the transmission of the SD mechanism.

In the case of F-F vicinal J-couplings, the contributions of the s(F) and the s-type LP(F) are the largest one. Given that they are both negative, the $^3J^{FC}$(F-F) is negative, being $^3J^{FC}$(H-H) positive. This is a nice explanation of why the F-F vicinal J-coupling becomes negative: the contributions of both s-type LMOs belonging to fluorine atoms are necessary for getting the total $^1J^{FC}$(F-F) coupling negative.

The main electronic source for the SD term of the vicinal J(F-F) coupling is the p_z-type of LP(F). The addition of its contribution to that of the σ(C-F) give 21.60 Hz, out of the total 26.75 Hz. This shows the importance of both LMOs for explaining the anomalous behaviour of the SD mechanism in molecular systems with a well defined π-electronic framework.

A new pattern of contributions from the core LMO, specially for imine, was found. It shows that also the contribution of the core is affected by the closest electronic environment. As mentioned above, we were also able to show that fluorine LPs are important sources of the vicinal F-F couplings, being their contributions different for each of both coupling mechanisms, PSO and SD.

In the case of two P-containing molecules, phosphine and cis-propylene phosphine, we found the FC as the most important mechanism for J(PH) in phosphine and J(P_4-C_3) (see Fig. 1) in cis-propylene phosphine. In the last case the application of Loc-SOPPA shows that the transmission of the FC coupling is mainly through-space. There are two main LMOs: the core s(P) and the σ(C_3-H_{10}) wich together give more than 55% of the total J-coupling.

The last important finding was the percentage to which the single excitations part of the solution vector $\mathbf{N}^{Q(SOPPA)}$ contribute to the total response function in Eq. (7) and so to the total J-couplings at SOPPA level. They are by far the largest, giving more than 95% of the total J value. Then there appears an interesting new route of exploration on the way one could include electron correlation in *ab initio* methods applied to the calculation of J-couplings in large-size molecules.

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