Critical analysis of the through-space transmission of NMR JFH spin-spin coupling constants

5 AUTHORS, INCLUDING:

Rubén H Contreras
University of Buenos Aires
200 PUBLICATIONS **2,943** CITATIONS

SEE PROFILE

Lucas C Ducati
University of São Paulo
41 PUBLICATIONS **210** CITATIONS

SEE PROFILE

Claudio Tormena
University of Campinas
144 PUBLICATIONS **1,259** CITATIONS

SEE PROFILE

Critical Analysis of the Through-Space Transmission of NMR J_{FH} Spin–Spin Coupling Constants

Rubén H. Contreras,[a] Lucas C. Ducati,[b] and Cláudio F. Tormena*[b]

NMR J_{FH} coupling constants transmitted through space are known to show several unusual peculiarities. The main three are (a) in many cases their experimental values are reported to be positive and in others, negative; (b) theoretical values show that in some cases they are substantially contributed not only from the Fermi contact (FC) term but also from the paramagnetic spin orbit (PSO) term, and their respective signs could be either like or unlike; (c) in many cases it can hardly be expected that the corresponding F—H proximate interactions could be considered a "hydrogen bond," whereas in other cases it is evident that they are. For discussing points (a) and (b), characteristics of both the FC and PSO terms are discussed performing qualitative analyses based on their expressions given in terms of the polarization propagator formalism. Point (c) is discussed in terms of the well-known Bader's QTAIM method as well as recalling the known relationship between the transmissions of the Fermi hole and of the FC interaction of spin–spin coupling constants. © 2012 Wiley Periodicals, Inc.

DOI: 10.1002/qua.24100

Introduction

In isotropic phase indirect spin–spin coupling constants, SSCCs, are built up from four contributions[1] Fermi contact (FC), paramagnetic spin orbit (PSO), spin–dipolar (SD), and diamagnetic spin orbit (DSO), terms, Eq. (1)

$$^{n}J_{AB} = {}^{n}J_{AB}^{FC} + {}^{n}J_{AB}^{PSO} + {}^{n}J_{AB}^{SD} + {}^{n}J_{AB'}^{DSO} \tag{1}$$

where n stands for the number of formal bonds separating the A and B coupling nuclei. In anisotropic phase the only isotropic contribution is the FC term, whereas the other three show second rank tensor character.

The possibility that SSCCs be transmitted through-space (TS), between two proximate moieties was first reported about 50 years ago.[2,3] Later, many other cases were reported and discussed in detail during these last five decades. Many examples are quoted in a large number of review articles; for the sake of brevity, only a few of them are cited here.[4] More recently, it was discussed the possibility that SSCCs could be transmitted through a hydrogen bond (HB),[5,6] and with the important works by Dingley and Grzesiek,[7] the transmission of J_{NN} SSCCs in Watson–Crick base pairs started a new era.[8] To emphasize the way these SSCCs are transmitted, the following notation was coined $^{nh}J_{AB}$ where n stands for the number of bonds (including the HB) between the A and B coupling nuclei.

In this work, a detailed study about J_{FH} SSCCs transmitted through-space, $^{nTS}J_{FH}$, is undertaken being motivated by some peculiarities known for these parameters; among them the following are worth mentioning. Sometimes such SSCCs are reported to be negative and in others, positive, as briefly discussed by Rae et al.[9] For instance in compound **1,** the $^{5}J_{FH}$ SSCC is negative, whereas in compound **2**, it is positive, see Figure 1, as it is also the case reported by Yamamoto and co-workers[9,10] in 8,13-dichloro-1,2,3,4-tetrafluoro-9-methyltripty-cene (**3**) where at -70 °C the rotation of the methyl group is sufficiently slowed down to observe separately $^{5}J_{FH}$ for the two types of methyl protons (**3a**), that is, $\pm$ sc and ap, respectively (Fig. 1), that is, $^{5}J_{FH}^{(\pm SC)} = +6.1$ Hz and $^{5}J_{FH}^{(ap)} = +8.7$ Hz.[9]

Sometimes $^{nTS}J_{FH}$ SSCCs are contributed significantly not only by the FC term but also by noncontact contributions, especially by the PSO and/or DSO terms. Of course, these contributions to SSCCs are not amenable to be measured directly, but at present times the precision of SSCC calculations is reasonable enough the get reliable trends of each contribution. Another point to be clarified in this work is this, when observing $^{n}J_{FH}$ SSCCs in proximate F—H—X moieties, is it an indication that a hydrogen-bond of type F—H is operating? In a recent work,[11] it was shown that $^{4}J_{FH} = -4.4$ Hz[12] in o-fluorophenol is not transmitted through a hydrogen bond and it was rationalized that this transmission takes place owing to exchange interactions taking place within the region where the F and H electronic clouds overlap as a consequence of their spatial proximity. This rationalization suggests that the different signs observed for proximate $^{nTS}J_{FH}$ SSCCs originates in the competition between the overlaps of the X—H bond with the C—F bond and with the F nonbonding electron pairs. There could be another positive contribution originating in charge transfer interactions involving the two proximate

[a] R. H. Contreras
    Department of Physics, FCEyN, University of Buenos Aires and IFIBA-CONICET, Ciudad Universitaria, Pab.1, 1428, Buenos Aires, Argentina

[b] L. C. Ducati, C. F. Tormena
    Chemistry Institute, University of Campinas, P. O. 6154, 13084-971, Campinas-SP, Brazil
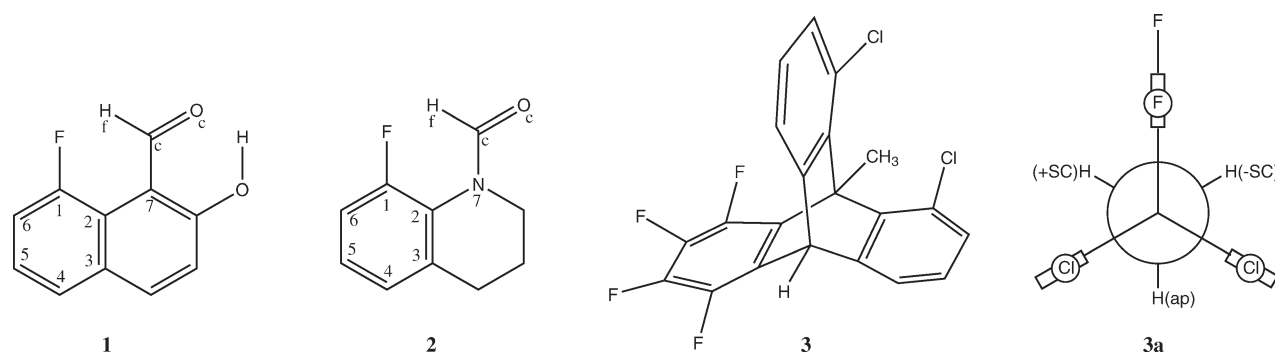   E-mail: tormena@iqm.unicamp.br

Figure 1. Structure for compounds **1**, **2**, and **3**. **3a** is a view from top showing the $\pm s\,c$ and *ap* methyl proton orientations for compound **3**.

molecular fragments. To get insight into electronic molecular features defining such effects, the QTAIM Bader's[13] method together with a qualitative approach described in previous papers[14] are used in this work.

Computational Details

Geometries of compounds **1** and **2** were optimized as isolated molecules at the MP2/aug-cc-pVDZ level. $^{TS}J_{FH}$ couplings in compounds **1** and **2** were calculated using the CP-DFT/B3LYP methodology as implemented in the Gaussian03 package of programs,[15] using EPR-III basis set.[16] The NBO analysis was performed using NBO 5.0[17] at the B3LYP/cc-pVDZ level. QTAIM analysis was performed using the AIMALL[18] program with the wave function obtained at the MP2/aug-cc-pVDZ level.

Results and Discussion

Compounds **1** and **2**, Figure 1, are taken as model compounds for obtaining insight into molecular aspects determining the sign of the FC term of J_{FH} SSCC between proximate F and H atoms. For their optimized geometries at MP2/aug-cc-pVDZ level, QTAIM analyses were performed, Figure 2, where in both compounds a bond critical point is observed in the F—H bonding path. This can be described saying that in **1** and **2** hydrogen bonds of type F—H operate. These results show that the sign of $^{TS}J_{FH}$ SSCCs is not indicative of the presence or absence of an F—H hydrogen bond.

Different relative configurations between the F atom and the H_f—C=O aldehyde group are evident in Figure 2. In fact, while compound **1** is planar and the aldehyde group is included in that plane, in compound **2** only the aromatic carbon ring is approximately planar. In the latter, the following distances are referred to the aromatic ring plane. The F atom is about 0.4 Å below; the O atom is about 0.5 Å above; the N atom is about 0.2 below, carbonyl carbon is about 0.4 Å above, and the formyl proton, H_f is about 1.0 Å above (Fig. 2).

As $^5J_{FH}$ SSCC in compounds **1** and **2** are of opposite signs, the geometric differences shown in Figure 2 seem to be consistent with the rationalization made for *o*-fluorophenols describing the negative FC term of $^{4TS}J_{FH}$ SSCC.[11] According to that rationalization, the proximity between the F and H atoms makes their electronic clouds close enough to overlap to a considerable extent. In that overlapping region, exchange

interactions take place determining a direct pathway for transmitting the FC interaction. There are two different types of contributions originating in that exchange mechanism, that is, those coming from the $\sigma_{C-F}/\sigma_{C-Hf}$ overlap and that from the $LP_n(F)/\sigma_{C-Hf}$ (n = 1, 2, 3) overlap. As localized orbitals corresponding to the F lone pairs and the σ_{C-F} bond at the F site show opposite phases,[19] the latter contribution to the FC term is expected to be negative, whereas the former is expected to be positive. Therefore, the FC term transmitted by exchange interactions owing to the overlap of the F and H_f
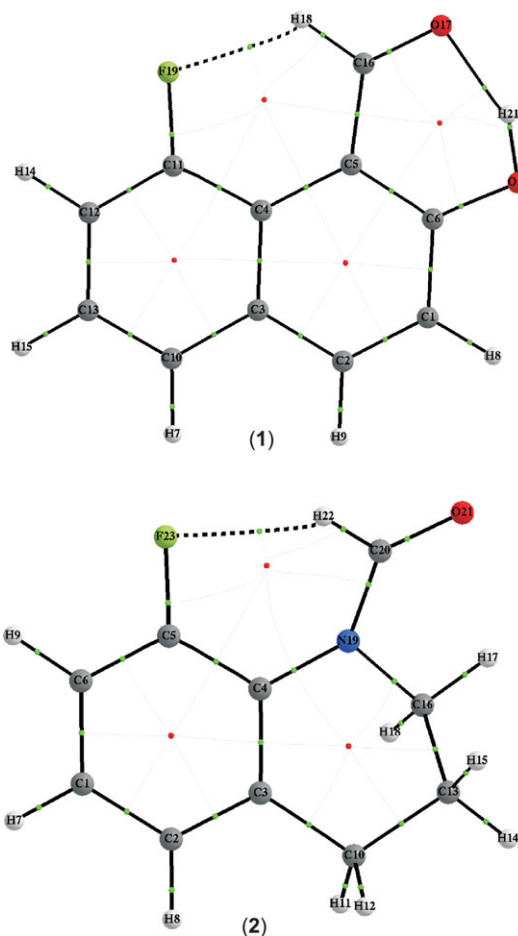

Figure 2. QTAIM molecular graphics for compounds **1** and **2**. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

International Journal of **QUANTUM CHEMISTRY**

Table 1. Overlap of NBOs defining the electronic clouds surrounding the F and H_f coupling nuclei.

	S(i,j) (a.u.)	
NBOs	**1**	**2**
$\sigma_{C-F}/\sigma_{C-Hf}$	0.0559	0.0589
$LP_1(F)/\sigma_{C-Hf}$	−0.0528	−0.0350
$LP_2(F)/\sigma_{C-Hf}$	−0.1038	−0.0596
$LP_3(F)/\sigma_{C-Hf}$	0.0000	−0.371

As expected, the signs of the $\sigma_{C-F}/\sigma_{C-Hf}$ and $LP_n(F)/\sigma_{C-Hf}$ (n = 1, 2, 3) overlaps are opposite to each other.

Table 3. Sequences of HIs and their back donation (BD) (kcal/mol) in compounds **1** and **2** which define through-bond coupling pathways for the FC term of $^{5TS}J_{FHf}$ SSCC.

	HI//BD	**1**	**2**
I	$LP_1(F) \rightarrow \sigma^*_{C1-C2}$	2.15	1.44
II	$LP_2(F) \rightarrow \sigma^*_{C1-C2}$	5.30	6.15
III	$\sigma_{C1-F} \rightarrow \sigma^*_{C2-C3}$	1.72//4.84	2.01//3.88
IV	$\sigma_{C7/N7-Cc} \rightarrow \sigma^*_{C2-C3}$	2.86//2.03	1.24//2.24
V	$\sigma_{C1-C2} \rightarrow \sigma^*_{C2-C7/N7}$	3.81//3.13	1.45//1.31
VI	$\sigma_{C2-C/N7} \rightarrow \sigma^*_{C/N7-Cc}$	2.03//2.86	2.24//1.24
VII	$LP_1(Oc) \rightarrow \sigma^*_{Cc-Hf}$	5.16	1.28
VIII	$LP_1(Oc) \rightarrow \sigma^*_{Cc-C,N7}$	5.62	1.29
IX	$LP_2(Oc) \rightarrow \sigma^*_{Cc-Hf}$	15.46	24.60
X	$LP_2(Oc) \rightarrow \sigma^*_{Cc-C,N7}$	9.41	18.53

Atoms are labeled as shown in Figure 1, and interactions are labeled with Roman numbers.

electronic clouds is built up by the competition between these two opposite contributions. This assertion indicates that the FC absolute value cannot be correlated with the F—H distance, as it depends strongly on the σ_{C-F} and σ_{C-Hf} relative orientations. The overlaps between the corresponding NBO orbitals, S(i,j) were calculated using the NBO 5.0 program.[17] They are displayed in Table 1.

Total FC terms of $^5J_{FH}$ SSCCs in compounds **1** and **2** could also be contributed by the following pathways (a) $LP_{1,2}(F) \rightarrow \sigma^*_{Cc-Hf}$ hyperconjugative interactions(HIs), and (b) concatenated sequences of HIs.[20] For compound **2**, the former is below the printing threshold of the NBO program. Relevant data for analyzing such possible FC coupling pathways in **1** and **2** as well as possible mechanisms to transmit the PSO contribution are displayed in Table 2 together with the four contributions, FC, SD, PSO, and DSO, to $^{5TS}J_{FH}$ SSCCs calculated at the B3LYP/EPR-III//MP2/aug-cc-pVDZ level.

It is highlighted that in **1,** the proximity interaction between the σ_{Cc-Hf} and the $LP_2(F)$ nonbonding electron pair yields a significant increase in the latter s % character. A similar effect, although with notable stronger intensity, is observed for the $LP_2(O_c)$ nonbonding electron pair in the same compound as a consequence of the $C_c = O—H—O$ hydrogen bond. In fact, while in **2** the $LP_2(O_c)$ s % character is 0.01%, in compound **1** it is 5.90%. As discussed below, the increase in the $LP_2(F)$ s % character due to the F—H_f—C_c proximity interaction in

Table 2. Comparison of calculated data obtained using the optimized structures for compounds **1** and **2**.

Compound	**1**	**2**
Total $^5J_{FHf}$ (Hz)	−4.2	+9.1
Exp.	−3.3	+4.5
FC	−2.3	+9.6
SD	+1.0	+0.23
PSO	−6.0	−4.12
DSO	+3.1	+2.57
$\sigma(^{19}F)$(ppm).	307.81	327.05
s % at F (C—F)	33.03	32.58
s % $LP_1(F)$	66.46	67.35
s % $LP_2(F)$	0.66	0.04
s % $LP_3(F)$	0.00	0.01
$d(F—H_f)$ (Å)	2.0069	2.1762
Delocalization index, δ_{FH}	0.0359 a.u.	0.0618 a.u.
$LP_1(F) \rightarrow \sigma^*_{Cc-Hf}$	0.93 kcal/mol	–
$LP_2(F) \rightarrow \sigma^*_{Cc-Hf}$	1.74 kcal/mol	–
$LP_2(F) \rightarrow \sigma^*_{Cc-O}$	0.51 kcal/mol	0.66 kcal/mol

compound **1** affects notably both the through-space transmission of the PSO term of $^5J_{FHf}$ as well as the fluorine paramagnetic nuclear magnetic shielding constant. The calculated total σ_F shielding constant obtained with the gauge included atomic orbitals method that does not allow to calculate separately the paramagnetic contribution was displayed in Table 1. However, it can be expected that by far the main difference between both compounds originates in the paramagnetic component. The total effect corresponds to a deshielding effect of about 20 ppm for the F atom in **1** compared with that in **2**. Similar fluorine deshielding effect on an F atom in the proximity to the protons of a methyl group was experimentally reported about 20 years ago.[21]

In Table 2, it is observed that in **1**, FC = −2.3 Hz and in **2** it is + 9.6 Hz, whereas the respective QTAIM δ_{FH} delocalization indices are 0.0359 and 0.0618 a.u. The disparate trend between these two quantities suggests that both the positive and the negative FC contributions in **1** yield positive contributions to the delocalization index. This observation calls for some caution when intending to correlate in a set of SSCCs their FC contributions with the corresponding QTAIM delocalization indices.

In Table 3 are compared for compounds **1** and **2** a set of HIs that are expected to define sequences of concatenated HIs defining through-bond coupling pathways for transmitting the FC spin information corresponding to the $^5J_{FH}$ SSCC. It is observed that there are two main through-bond coupling pathways, **A** and **B**, defined by the following sequences of HIs. (**A**) III–IV–VIII + X–VII + IX and **B**) I + II–V–VI–VIII + X–VII + IX, see Table 3. These two types of through-bond coupling pathways are considered somewhat similar in both compounds. Therefore, the observed differences in Table 1 seem to originate mainly in the "through-space" interaction.

Additional insight into comments made above is obtained with a qualitative analysis described previously;[14] some of its basic aspects are shortly described in the next subsection.

Qualitative approach to get insight into transmission mechanisms of SSCCs

Only a very brief description is given here as the main features of this approach were discussed in previous papers.[14] Within

the polarization propagator (PP), approach the four terms in Eq. (1) can be decomposed into canonical molecular orbital (CMO), contributions. In this work, this study is limited to analyzing the FC and PSO terms; their expansions in terms of CMOs are shown in Eq. (2), where i and j stand for occupied and a and b for virtual CMOs, and X stands for either the FC term or for the $\alpha\alpha$ diagonal component of the second rank PSO tensor.[22] Although Eq. (1) holds only for SSCCs measured in isotropic phase, for analyzing the PSO term care must be taken to consider its second rank tensor character.

$$^{n}J^{X}_{AB} = \sum_{ia,jb} {}^{n}J^{X}_{ia,jb}(AB) \qquad (2)$$

The Fermi contact term

Equation (2) for the FC term contributing to $^{n}J_{AB}$ SSCC can be written as

$$^{n}J^{FC}_{AB} = -\Omega^{FC}\gamma_{A}\gamma_{B}\sum_{ia,jb} {}^{n}J^{FC}_{ia,jb}(AB) \qquad (3)$$

where Ω^{FC} is a positive constant involving universal and numerical constants; its expression is not given explicitly as this is only a qualitative analysis and it is not affected by a constant. γ_{A} and γ_{B} are the magnetogyric ratios of each coupling nuclei. As shown previously,[23] CMO contributions to the FC term can be written as in Eq. (4)

$$^{n}J^{FC}_{ia,jb}(AB) = {}^{3}W_{ia,jb}[U^{FC}_{ia,A}U^{FC}_{jb,B} + U^{FC}_{ia,B}U^{FC}_{jb,A}] \qquad (4)$$

where $^{3}W_{ia,jb} = ({}^{3}A + {}^{3}B)^{-1}_{ia,jb}$ are the elements of the inverse of the triplet PP matrix; they involve the $i \rightarrow a$ and $j \rightarrow b$ virtual excitations. Matrices ^{3}A and ^{3}B can be expressed in terms of bielectronic molecular integrals, $^{3}A_{ia,jb} = (\varepsilon_{a} - \varepsilon_{i})\delta_{ab}\delta_{ij} - \langle aj|bi \rangle$ and $^{3}B_{ia,jb} = \langle ab|ji \rangle$, respectively. It is observed that only diagonal elements of the ^{3}W matrix, $^{3}W_{ia,ia}$, depend explicitly on the energy gap between the occupied and virtual MOs determining each virtual excitation. Such dependence shows that interactions increasing that energy gap yield a decrease in the $^{3}W_{ia,ia}$ diagonal matrix element, and vice versa. It is recalled that diagonal elements ^{3}W are the largest, followed by "quasi-diagonal" elements, for example, $^{3}W_{ia,ib}$ and $^{3}W_{ia,ja}$.

In Eq. (4), $U^{FC}_{ia,A}(U^{FC}_{ia,B'})$ are the matrix elements of the FC operator, between the occupied i (j) and virtual a (b) MOs evaluated at the A and B sites of the coupling nuclei. The term "perturbator" was coined for them, and they are given by Eq. (5)

$$U^{FC}_{ia,A} = \langle i|\delta(\vec{r}_{A})|a \rangle \quad \text{and} \quad U^{FC}_{jb,B} = \langle j|\delta(\vec{r}_{B})|b \rangle \qquad (5)$$

where $\delta(\vec{r}_{N})$ is the Dirac's delta function and $N = A, B$.

Equations (2)–(5) are particularly useful when comparing the FC terms of analogous SSCCs. In this work, they are used to compare the through-space contributions to the FC term of $^{5}J_{FH}$ SSCCs in **1** and **2**. It must be recalled that the FC spin information is transmitted like the Fermi hole.[24] This means that FC spin information corresponding to a given SSCC spans

Table 4. Comparison of NBO expansions of occupied CMOs contributing to $^{5TS}J_{FH}$ SSCC in **1** and **2**.	
Compound **1**	Compound **2**
MO 26 (occ): orb. energy = −0.711418 a.u.	MO 24 (occ): orb. energy = −0.701886 a.u.
0.425*[27]: BD (1) C_c—H_f	**−0.401*[45]: LP (1) F**
0.333*[44]: LP (1) F	**−0.363*[23]: BD (1) C_1—F**
−0.316*[14]: BD (1) C_1—F	−0.352*[1]: BD (1) C 1—C 5
−0.270*[49]: LP (3) O_{OH}	0.256*[4]: BD (1) C_1—N
−0.257*[19]: BD (1) C11—C13	**−0.248*[28]: BD (1) C_c—H_f**
−0.243*[43]: LP (2) O_c	0.244*[20]: BD (1) C13—H17
−0.232*[1]: BD (1) C 1—C 2	
MO 28 (occ): orb. energy = −0.635865 a.u.	MO 30 (occ): orb. energy = −0.565434 a.u.
0.369*[16]: BD (1) H 7—C10	**−0.398*[46]: LP (2) F**
−0.359*[10]: BD (1) C 4—C 5	−0.381*[8]: BD (1) C 2—N19
0.297*[47]: LP (1) O20(lp)	−0.279*[11]: BD (1) C 3—H 8
−0.281*[23]: BD (1) C13—O20	0.274*[19]: BD (1) C12—H16
0.274*[12]: BD (1) C 4—C11	−0.239*[25]: BD (1) N19—C20
−0.265*[45]: LP (2) F	**−0.238*[28]: BD (1) C_c—H_f**
0.255*[27]: BD (1) C_c—H_f	0.228*[7]: BD (1) C 2—H11
0.235*[49]: LP (3) O20(lp)	−0.227*[6]: BD (1) C 2—H 6
	0.227*[10]: BD (1) C 3—H 7
MO 32 (occ): orb. energy = −0.589300 a.u.	
0.447*[24]: BD (1) C14—H15	
0.390*[27]: BD (1) C_c—H_f	
−0.324*[21]: BD (1) C11—C16	
0.317*[45]: LP (2) F	
−0.246*[8]: BD (1) C 3—C 4	
0.230*[19]: BD (1) C11—C13	
MO 37 (occ): orb. energy = −0.519051 a.u.	
−0.427*[4]: BD (1) C 1—H 8	
0.347*[45]: LP (2) F	
0.326*[17]: BD (1) C10—C14	
−0.316*[27]: BD (1) C_c—H_f	
0.306*[16]: BD (1) H 7—C10	
0.273*[24]: BD (1) C14—H15	
0.229*[15]: BD (1) C 6—H12	

Atoms that do not belong to any side-chain are numbered as in Figure 1.

the whole spatial region covered by a CMO, that is, any pair of magnetic nuclei belonging to that region will show a SSCC if at the site of each magnetic nucleus there is an important electron density. The key question to be answered is this: how it can be known if there is an important electron density at the sites of the two chosen magnetic nuclei within a given CMO? This question is answered by expanding CMOs in terms of Weinhold coworkers.[17] Natural bond orbitals (NBOs) as given by the NBO 5.0 program. The NBO expansions of CMOs defining the through-space transmission of $^{5}J_{FH}$ SSCCs are displayed in Table 4. It is important to note that there is no virtual CMO containing simultaneously in their NBO expansions the (C—F)* and (C_c—H_f)* antibonding orbitals. This means that neither in compound **1** nor in compound **2** there is a diagonal matrix element contributing to the TS transmission of the FC term of $^{5}J_{FH}$ SSCCs. Taking into account the s % character at the F atom (Table 1), contribution coming from CMO 26 in **1**, is similar to that of CMO 24 in **2**. Conversely, contribution from CMO 28 in **1**, which is negative, is notable more important than that of CMO 30 in **2**, as the s % character of $LP_{2}(F)$ in the latter is much smaller than in **1**, see Table 2. Conversely, in **2**

there are no similar contributions to those of CMO 32 and CMO 37 in **1**, which correspond also to negative contributions as the overlap between the C_1—F bond and $LP_2(F)$ is negative. Data displayed in Table 4, support the results reported above showing that the negative $^{5TS}J_{FH}$ SSCC in **1** originates mainly in the smaller $\sigma_{C-F}/\sigma_{C-Hf}$ overlap than those originating in the $LP_n(F)/\sigma_{C-Hf}$ ($n = 1, 2, 3$) overlap.

The Paramagnetic Spin-Orbit Term

As SSCCs measured in isotropic phase are considered in this work, only diagonal elements of the **PSO** tensor are considered,

$$^n J_{AB}^{PSO} = \frac{1}{3} \sum_\alpha {}^n J_{AB}^{PSO,\alpha\alpha}$$

and the analogous to Eq. (3) for diagonal elements of the **PSO** second-rank tensor corresponding to $^n J_{AB}$ SSCC can be written as in Eq. (6)

$$^n J_{AB}^{PSO,\alpha\alpha} = -\Omega^{PSO} \gamma_A \gamma_B \sum_{ia,jb} {}^n J_{ia,jb}^{PSO,\alpha\alpha}(AB) \tag{6}$$

where Ω^{PSO} is a positive constant, and

$$^n J_{ia,jb}^{PSO\alpha\alpha} = U_{ia,A}^{PSO,\alpha 1} W_{ia,jb} U_{jb,B}^{PSO,\alpha} \tag{7}$$

where $^1 W_{ia,jb} = (^1 A + ^1 B)_{ia,jb}^{-1}$ are the elements of the inverse of the singlet PP matrix. The corresponding "perturbators" are

$$U_{ia,A}^{PSO,\alpha} = \left\langle i \left| \frac{(\vec{r}_A \times \vec{\nabla})_\alpha}{r_A^3} \right| a \right\rangle \text{ and } U_{jb,B}^{PSO,\alpha} = \left\langle i \left| \frac{(\vec{r}_B \times \vec{\nabla})_\alpha}{r_B^3} \right| a \right\rangle \tag{8}$$

It is highlighted that these perturbators show vector character, and therefore, they are much easier to rationalize than those corresponding to the SD term, where each perturbator show second-rank tensor.

As the expression given in Eq. (6) is invariant under unitary transformations, these perturbators can be rationalized much easier considering that occupied i and vacant a orbitals are localized, LMOs, representing chemical functions like bonding; nonbonding electron pairs, and antibonding orbitals. In this way, each perturbator in Eq. (8) will be significant if the occupied i orbital rotated around the α axis centered at a coupling nuclei overlaps significantly with the a antibonding orbital. When comparing compounds **1** and **2**, it is observed that the main differences in both PSO terms could originate either in perturbator changes or in the ^1W matrix changes. It is easy to verify that in this case the main differences originate in the perturbators, especially in that centered at the F atom. This can easily be rationalized considering that in fluorobenzene the principal axes (PAs) of the **PSO** tensor corresponding to the $^1J_{FC}$ SSCC tensor are those shown in Figure 3. The vector perturbators at F for the $^5PSO_{FH}$ term in **1** and **2**, $U_{jb,B}^{PSO,\alpha} = \left\langle i \left| \frac{(\vec{r}_B \times \vec{\nabla})_\alpha}{r_B^3} \right| a \right\rangle$ should have similar orientations and, looking at Table 2, it is expected that the most affected
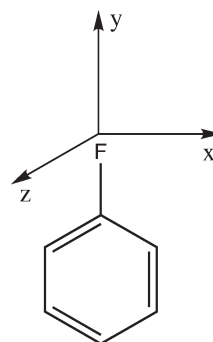

Figure 3. PAs of the PSO term at the F atom in fluorobenzene. Similar PAs are expected at the F atom in compounds **1** and **2**.

perturbator should be that satisfying $i = LP_2(F)$; $B = F$; $a = \sigma^*_{CF}$ as rotating the σ^*_{CF} antibonding orbital in $+90°$, it overlaps to an important extent with $LP_2(F)$. Besides, in the denominator appears the quadratic distance of LP_2 electrons to the F nucleus. As the s % character of $LP_2(F)$ increases from 0.04 in **2** to 0.66 in **1**, that is, about 16 times, on average the LP_2 electron distance to F is reduced, increasing the perturbator absolute value. Taking into account the minus sign in Eq. (6), the **z** component is more negative in **1** than in **2**. As it is expected that the **x** and **y** perturbator components are much less affected when going from **2** to **1**, this qualitative description seems to take into account the main difference in the PSO term of $^{5TS}J_{FH}$ SSCC displayed in Table 2.

It is noted that in the paramagnetic component of the nuclear magnetic shielding tensor appears a term like that shown in Eq. (8).[25] It is highlighted that such term does not depend on the electromagnetic gauge used for describing both the spectrometer and the nuclei magnetic fields. Therefore, should a similar trend to that described for the PSO term corresponding to $^{5TS}J_{FH}$ is observed in the ^{19}F magnetic shielding constant in compounds **2** and **1**, the assumptions made above are nicely supported. In fact, this qualitative description predicts that the ^{19}F nucleus should be less shielded in **1** than in **2**, as displayed in Table 2.

Concluding remarks

The analyses of $^5J_{FH}$ SSCCs in compounds **1** and **2** support the hypothesis presented previously, that the "through-space" transmission of $^{TS}J_{FH}$ SSCCs are built up from different types of contributions, namely, (a) those originated by exchange interactions taking place in the region where electronic clouds surrounding the F and H atoms overlap; (b) direct charge transfer interactions between either $LP_{1,2,3}(F)$ or σ_{C-F} occupied and σ_{C-Hf} vacant orbitals; (c) long-range charge transfer interactions mediated by concatenated sequences of HIs. Type (a) contributions are positive for $\sigma_{C-F}/\sigma_{C-Hf}$ overlapping orbitals, whereas they are negative when they correspond to $LP_{1,2,3}(F)/\sigma_{C-Hf}$ overlapping orbitals. Conversely, contributions of types (b) and (c) correspond to positive contributions to the FC term of $^{TS}J_{FH}$.

The through space transmission of the FC term due to exchange interactions in the region where electronic clouds of

two proximate molecular fragments overlap could also lead to either negative or positive reduced coupling constants for other isotopic species, especially when one of the nuclei involved in that SSCC belongs to a lone-pair bearing atom. A point in case seems to be $^4J_{PH_f} = -7.1$ Hz reported by Schaefer et al.[26] for 2-(diphenylphosphino)benzaldehyde, where the preferential conformation corresponds to the C—H formyl bond placed in an all-cis conformation with respect to the P lone pair.

Discussions presented in this article support results previously reported indicating that, at least in several instances, proximate interactions on a fluorine atom bonded to an aromatic system can affect the s % character of the $LP_2(F)$ non-bonding electron pair.[22]

[1] N. F. Ramsey, *Phys. Rev.* **1953**, *91*, 303.

[2] D. R. Davis, R. P. Lutz, J. D. Roberts, *J. Am. Chem. Soc.* **1961**, *83*, 246.

[3] L. Petrakis, C. H. Sederholm, *J. Chem. Phys.* **1961**, *35*, 1243.

[4] (a) J. Hilton, L. H. Sutcliffe, *Prog. NMR Spectrosc.* **1975**, *10*, 27; (b) R. H. Contreras, M. A. Natiello, G. E. Scuseria, *Magn. Reson. Rev.* **1985**, *9*, 239; (c) F. B. Mallory, C. W. Mallory, In Encyclopedia of Nuclear Magnetic Resonance; D. M. Grant, R. K. Harris, Eds.; Wiley: Chichester, **1996**; p. 1491.

[5] (a) N. Platzer, J.-P. Buisson, P. Demerseman, *J. Heterocycl. Chem.* **1992**, *29*, 1149; (b) H. Duddeck, A. Biallas, *Magn. Reson. Chem.* **1994**, *32*, 303; (c) R. H. Contreras, J. C. Facelli, *Ann. Rep. NMR Spectrosc.* **1993**, *27*, 255.

[6] I. Alkorta, J. E. Elguero, H. H. Limbach, I. G. Shenderovich, T. Winkler, *Magn. Reson. Chem.* **2009**, *47*, 585.

[7] A. J. Dingley, S. Grzesiek, *J. Am. Chem. Soc.* **1998**, *120*, 8293.

[8] I. Alkorta, J. Elguero, G. S. Denisov, *Magn. Reson. Chem.* **2008**, *46*, 599.

[9] I. D. Rae, J. A. Weigold, R. H. Contreras, G. Yamamoto, *Magn. Reson. Chem.* **1992**, *30*, 1047.

[10] (a) G. Yamamoto, M. Oki, *J. Org. Chem.* **1984**, *49*, 1913; (b) G. Yamamoto, M. Oki, *Tetrahedron Lett.* **1985**, 457; (c) G. Yamamoto, M. Oki, *Bull. Chem. Soc. Jpn.* **1990**, *63*, 3550; (d) G. Yamamoto, *Chem. Lett.* **1991**, 1161.

[11] R. A. Cormanich, M. A. Moreira, M. P. Freitas, T. C. Ramalho, C. P. A. Anconi, R. Rittner, R. H. Contreras, C. F. Tormena, *Magn. Reson. Chem.* **2011**, *49*, 763.

[12] J. B. Rowbotham, M. Smith, T. Schaefer, *Can. J. Chem.* **1975**, *53*, 986.

[13] R. F. W. Bader, Atoms in Molecules: A Quantum Theory; Clarendor: Oxford, **1990**.

[14] P. R. Anizelli, D. C. Favaro, R. H. Contreras, C. F. Tormena, *J. Phys. Chem. A* **2011**, *115*, 5684; and references cited therein.

[15] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, Al-Laham, M. A.; C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian 03 Revision E.01; Gaussian: Wallingford CT, **2004**.

[16] V. Barone, *J. Chem. Phys.* **1994**, *10*, 6834.

[17] NBO 5.0. E. D. Glendening, J. K. Badenhoop, A. E. Reed, J. E. Carpenter, J. A. Bohmann, C. M. Morales, F. Weinhold, Theoretical Chemistry Institute, University of Wisconsin: Madison, **2001**.

[18] AIMAll (Version 11.06.19), T. A. Keith, Gristmill T. K., Software, Overland Park KS, USA, **2011**, http://aim.tkgristmill.com.

[19] R. H. Contreras, M. C. Ruiz de Azúa, C. G. Giribet, G. A. Aucar, R. Lobayan de Bonczok, *J. Mol. Struct. Theochem.* **1993**, *284*, 249.

[20] R. H. Contreras, A. L. Esteban, E. Díez, N. J. Head, E. W. Della, *Mol. Phys.* **2006**, *104*, 485.

[21] G. W. Gribble, D. J. Keavy, E. R. Olson, I. D. Rae, A. Staffa, T. E. Herr, M. B. Ferraro, R. H. Contreras, *Magn. Reson. Chem.* **1991**, *29*, 422.

[22] J. D. Vilcachagua, L. C. Ducati, R. Rittner, R. H. Contreras, C. F. Tormena, *J. Phys. Chem. A* **2011**, *115*, 7762.

[23] R. H. Contreras, G. Gotelli, L. C. Ducati, T. M. Barbosa, C. F. Tormena, *J. Phys. Chem. A* **2010**, *114*, 1044.

[24] A. Soncini, P. Lazzeretti, *J. Chem. Phys.* **2003**, *119*, 1343.

[25] R. H. Contreras, C. G. Giribet, M. C. Ruiz de Azúa, M. B. Ferraro, In Computational Chemistry: Structure, Interactions and Reactivity, Vol. *77(B)*, Fraga, S. Ed.; Elsevier Science Publishers B.V, **1992**; p. 212.

[26] T. Schaefer, R. Sebastian, R. W. Schurko, F. E. Hruska, *Can, J. Chem.* **1993**, *71*, 1384.