# Research Article

# The electronic origin of unusually large $^nJ_{FN}$ coupling constants in some fluoroximes

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SOPPA(CCSD) calculations show that the FC term is the most important contribution to the through-space transmission of $J_{FN}$ coupling constants for the fluoroximes studied in this work. Because of the well-known behavior of FC term, a new rationalization for the experimental $^{TS}J_{FN}$ SSCC is presented. It is mainly based on the overlap matrix ($S_{ij}$) between fluorine and nitrogen lone pairs obtained from NBO analyses. An expression is proposed to take into account the influence of the electronic density ($D_{ij}$) between coupled nuclei as well as the s% character at the site of the coupling nuclei of bonds and non-bonding electron pairs involved in $D_{ij}$. In using this approach, a linear correlation between $^{TS}J_{FN}$ versus $D_{ij}$ is obtained. The most important aspect of this rationalization is related to the facility for understanding the behavior of some unusual experimental coupling constants. It is shown that, at least in this case, the electronic origin of the so-called through-space coupling is transmitted through to the overlap of orbitals on the coupled atoms, suggesting that, at least for these compounds, instead of through-space coupling, it should better be dubbed as 'through overlapping orbital coupling'. Copyright © 2013 John Wiley & Sons, Ltd.

**Keywords:** $^nJ_{FN}$ through space coupling constants; *overlap* matrix; lone pairs interaction; $d_{FN}$ dependence

## Introduction

Nuclear spin-spin coupling constants (SSCCs) measured in isotropic phase by high-resolution NMR spectroscopy were rationalized, using a non-relativistic formulation, by Ramsey[1] as originating in four different terms, namely, Fermi contact (FC), spin-dipolar (SD), paramagnetic spin-orbit (PSO) and diamagnetic spin-orbit (DSO).

About 50 years ago, it was reported for the first time the possibility that through-space interactions between proximate moieties[2–8] could be responsible for the especially large *spin-spin* coupling constants, SSCCs, observed in many different systems. However, the mechanism by which the spin information is transferred from one atom to the other via a direct through-space route is not yet fully understood.[9]

Contreras *et al.* showed, in 1984, that the through-space (TS) transmission of $^{19}F$-$^{13}C$ coupling constants can be greatly enhanced if a hydrogen atom bonded to the carbon atom is close to the fluorine atom.[10,11] In that case, the coupling pathway was called indirect TS transmission via an intermediate C-H bond. On the other hand, for proximate non-bonding electron pair bearing atoms, the corresponding SSCC is strongly influenced by a TS transmission mechanism.[12]

In 1985, Mallory *et al.* reported the first example of 'through-space' *spin-spin* coupling involving $^{15}N$ and $^{19}F$ nuclei.[13,14] They found that oxime **1** has the exceptionally large $J_{FN}$ value of 22.4 Hz, whereas the oxime **2b**, which possess the same bond connectivity as the former shows only a $J_{FN}$ value of 3.2 Hz (Fig. 1).

Based on their previous observations, Mallory *et al.* developed a corollary based on the lone pair overlap.[13] On this corollary, they had predicted that the overlap between the lone pair on the nitrogen with the 2p orbital of the fluorine atom could give rise to the through-space $^{19}F$-$^{15}N$ coupling in oxime **1**. The key feature of this assumption is the effectiveness of the lone-pairs overlap, where the main points are the distance between these atoms and the orientation of their C-F and C=N bonds. Furthermore, on the literature, it is not found a deeper investigation

about this relationship or a more accurate insight involving other bond orientation such as N-O and their contribution for the coupling transmission.

Recently, Tomoda *et. al.*[15] have reported the importance of non-bonded interactions to explain the $^{77}Se$-$^{19}F$ coupling constants in selenyl derivatives. In this case, the authors assigned the difference on the coupling values to the difference in the energy of the orbital interactions LP(F) $\rightarrow \sigma^*_{SeY}$ (Y = halogens).

The aim of this work is to rationalize the electronic influence in the transmission mechanisms for such $J_{FN}$ SSCCs in oximes shown in Fig. 1. To this end, the following approaches are employed to determine the main trends of such couplings, namely, the Pre-orthogonal Natural Bond Orbital (PNBO) method proposed by Weinhold *et al.*[16] for studying the relationship between the NBO matrix overlap elements and occupancy of those orbitals with the respective FC terms to study features of the proximity interaction between N and F atoms. This aim includes also establishing, using oxime **2a** as a model compound, the relationship between the (N=C-C-C(F)) dihedral angle and $J_{FN}$ values.

To carry out such study, first of all, using a high level of theory, the relative importance of the four isotropic terms contributing to these $J_{FN}$ SSCCs were determined because each of these four terms are transmitted by different mechanisms through the molecular electronic system. Because in all cases, the FC contribution is the most significant one, special emphasis is put in rationalizing its transmission. It is important to recall that recently,[17] it was found that the transmission of the coupling constant $^{nTS}J_{FH}$ SSCCs

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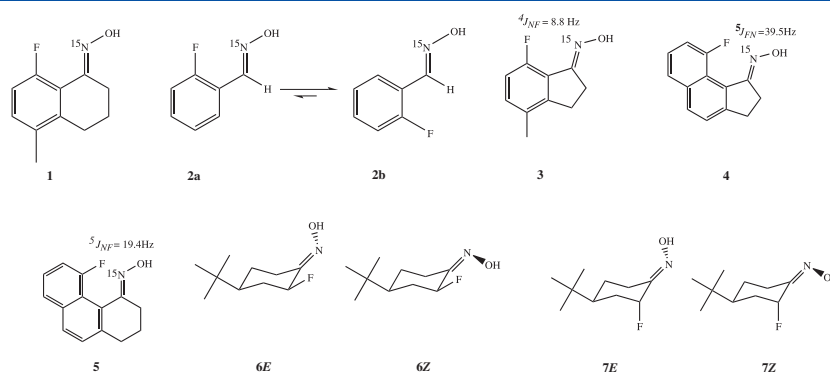b Department of Physics, FCEyN, University of Buenos Aires and IFIBA-CONICET, Buenos Aires, Argentina

**Figure 1.** Structures for fluoroximes studied in this work.

originates in the competition between the overlaps of the X-H bond with the C-F bond and with the F non-bonding electron pairs. In those cases, the proximity between fluorine lone pair $LP_2(F)$ and hydrogen atom increases the *s*% character of the $LP_2(F)$ playing an important contribution to the through-space transmission of the FC term for some $J_{FH}$ SSCCs. For this reason, in this work, special attention is paid to the *s*% character of fluorine lone pairs.

As shown below, the main contribution to the $J_{FN}$ SSCC in compounds listed in Scheme 1 are those originating in the FC term. During the past few years, a qualitative approach was developed to get insight into different aspects of high-resolution NMR parameters. Theoretical aspect of this approach can be found in previous papers.[18–23]

programs.[28] Calculations for all four isotropic terms of $^nJ_{FN}$ SSCC, that is, Fermi contact (FC), spin dipolar (SD), paramagnetic spin orbit (PSO), and diamagnetic spin orbit (DSO), were carried out using the SOPPA(CCSD) approach[29,30] using a locally dense basis set consisting in EPR-III[31] for F and N atoms and aug-cc-pVTZ for all remaining atoms. These last calculations were carried out using the Dalton2011 program.[32]

The importance played by overlap interactions on the through-space transmission of SSCCs is remarkable;[17,33] thus, the overlap matrix (S) elements were evaluated using the natural bond orbital (NBO)[34] analysis, implemented in the Gaussian 09 suite of programs. These calculations were performed with the B3LYP hybrid functional using the EPR-III basis set.

## Experimental and Computational Details

### NMR measurements

The experimental $^3J_{FN}$ coupling constants for compounds **6–7** were measured using a $^{15}N$-{$^1H$} pulse sequence with $^1H$ decoupling only during the acquisition ($^{15}N$ has a negative magnetogiric ratio). The $^{15}N$ 1D spectra were acquired on a Bruker Avance III 500 spectrometer equipped with a BBO SmartProbe.

### Computational details

All geometry optimizations were carried out at the B3LYP[24–26]/ aug-cc-pVTZ[27] level of theory by using the Gaussian09 suite of

## Results and Discussion

In Table 1, the four isotropic terms of $J_{FN}$ SSCCs for compounds (**1–7**) are collected and compared, whenever possible, with their experimental values.

A good agreement between experimental and theoretical $J_{FN}$ SSCCs is observed in Table 1. This agreement suggests that theoretical values can be used with confidence when experimental data are not available. It can also be observed that the FC term is the most important contribution to these $J_{FN}$ SSCCs and can easily be rationalized, recalling that the FC term is transmitted like the 'Fermi hole'.[35] Recently, it was shown[33] that the proximity between F and H atoms can lead to a significant overlap of their electronic clouds when they are close to each other. In that

**Table 1.** For fluoroximes **1–7** experimental and theoretical (SOPPA(CCSD)/EPR-III) $^nJ_{NF}$ (Hz) are compared. Their respective FC, SD, PSO and DSO contributions as well as the respective optimized $d_{NF}$ distances (in Å) are also displayed. The latter are compared with their X-ray experimental values

| Compounds | FC | SD | PSO | DSO | Total | |Exp.| | $d_{NF}$ | $d_{NF}$ (X-ray) |
|---|---|---|---|---|---|---|---|---|
| **1** | −18.19 | −0.92 | −1.25 | −0.17 | −20.53 | 22.4 | 2.678 | 2.595 |
| **2a** | −15.00 | −2.11 | −1.30 | −0.14 | −18.55 | 3.2[a] | 2.755 | -[c] |
| **2b** | 0.24 | −1.44 | 0.52 | 0.08 | −0.60 | 3.2 | 4.057 | -[c] |
| **3a** | −6.87 | −1.68 | −0.66 | −0.13 | −9.34 | 8.8 | 2.946 | 2.897 |
| **4** | −36.42 | 0.38 | 0.43 | −0.21 | −35.82 | 39.5 | 2.645 | 2.627 |
| **5** | −17.79 | 0.08 | 0.97 | −0.19 | −16.93 | 19.4 | 2.672 | 2.642 |
| **6E** | −9.00 | −0.01 | 0.81 | −0.10 | −8.31 | 10.7 | 2.644 | -[c] |
| **7Z** | −2.62 | 1.11 | 1.85 | 0.08 | 0.43 | 0 | 3.656 | -[c] |
| **7E** | −6.51 | 0.01 | −0.55 | 0.04 | −7.01 | -[b] | 3.232 | -[c] |

[a]Experimental $J_{FN}$ value is the average between those for conformers 2a and 2b.
[b]Not determined experimentally.
[c]X-ray analyses were not obtained.

overlapping region, exchange interactions take place, determining a direct pathway for transmitting the FC interaction.

It is well known[36] that only MOs with a significant **s**% character on both coupled nuclei can contribute significantly to the FC transmission mechanism. According to previous studies,[13] the $^{TS}J_{FN}$ SSCC is transmitted by exchange interactions because of the overlap of the F and N lone pairs. As it is observed in Table 1, the FC term is dominant in the transmission mechanism of SSCCs, which reinforce the importance for determining the **s**% character for lone pairs of the coupled nuclei.

Taking into account comments made above the following points can be concluded about geometric and electronic factors defining the efficiency for transmitting through-space $J_{FN}$ SSCCs: (i) the $d_{F-N}$ distance, (ii) the relative orientation of bonds containing the F and N atoms, and (iii) the s% character of the overlapping fluorine and nitrogen lone-pairs and the extension of their overlaps, which strongly depend on the orientation, proximity and occupancy of the NBOs representing them. At this point, it is interesting to recall that any steric compression on $LP_2(F)$ and $LP_3(F)$ lone pairs increase their s% character at the F nucleus. Besides the three points mentioned previously, an important contribution to $J_{NF}$ coupling could originate in hyperconjugative interactions, such as $LP(F_{1,2}) \rightarrow \sigma^*_{(NO)}$, which strongly depend on the relative orientation between the N-O bond and the LP(F)s. However, in compounds studied in this work, such hyperconjugative interactions are below the threshold of the NBO program. Therefore, they are not taken into account.

As shown in Table 1, for almost all compounds, the $d_{FN}$ distance is shorter than the sum of the F and N van der Waals radii, that is, $(1.47 + 1.55 = 3.02$ Å) and is observed an almost exponential relationship between $d_{FN}$ and the FC term of $J_{NF}$ SSCCs (Fig. 2). This exponential relationship suggests that this coupling pathway is notably dominated by the F and N lone pairs overlap.

In Fig. 2, it is observed that $J_{FN}$ SSCC in compound **6E** is an 'outsider'. It is noted that this $J_{FN}$ SSCC corresponds to a three-bond SSCC, $^3J_{FN}$, and therefore, other transmission mechanisms for its FC term are expected. In fact, besides that mentioned above for compounds like, for instance, **1**, **2a**, **2b**, **3** and **4**, it is evident that a three-bond contribution is operating, which must be of opposite sign to that corresponding to the F and N lone-pairs overlapping. In fact, it is observed that the concatenated hyperconjugative interactions $LP(N) \rightarrow \sigma^*_{C1C6}/\sigma_{C1C6} \rightarrow \sigma^*_{C2F}$
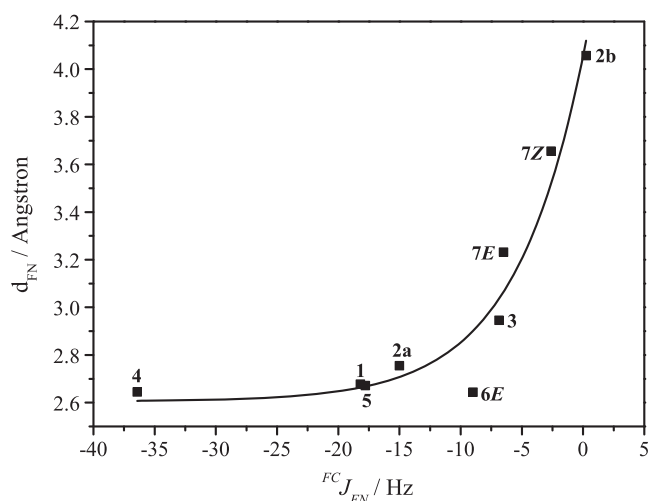
should increase the absolute value of the FC term of $^3J_{FN}$ SSCC. This assertion is supported by calculating the FC term of $^3J_{FN}$ SSCC for different bond angles, $\theta = C2\text{-}C1\text{-}C6$, changing it in 5° steps from 100 to 125°, allowing to relax all other geometrical parameters (Fig. 3).

It is observed in Fig. 3, that increasing $\theta$ from 100° to 125°, the distance between fluorine and nitrogen increases, as does the absolute value of the FC term of $J_{FN}$ SSCC. For $\theta = 100°$ and $\theta° = 125°$, both plots are very close to each other. Between these two extremes, both plots depart from each other, suggesting that TS and TB mechanisms are working.

For oxime **2a**, a similar analysis was performed, but in this case, the $J_{FN}$ coupling constant is calculated using the same basis set for all atoms, that is, EPR-III for different (C$_1$-C$_2$-C$_3$ = N) dihedral angle values (Fig. 4).

As observed in Fig. 4, when increasing the C$_1$-C$_2$-C$_3$ = N dihedral angle, the overlap between LP(F) and LP(N) is reduced, and therefore the $J_{NF}$ 'through space' decreases, supporting that in this type of compounds, the $J_{FN}$ coupling is transmitted mainly by this mechanism.

In addition, it is well known that steric and hyperconjugative effects play important rules for conformational preferences, with
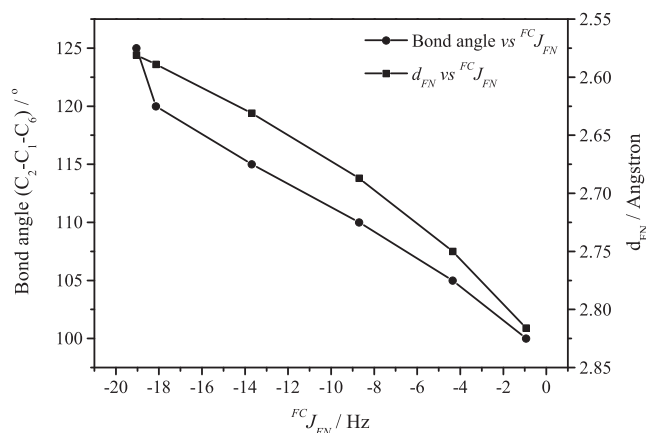
**Figure 3.** FC term for JFN SSCC *versus* bond angle and *versus* dFN for E-cis-2-fluoro-4-tbutylcyclohexanoxime (**6E**).
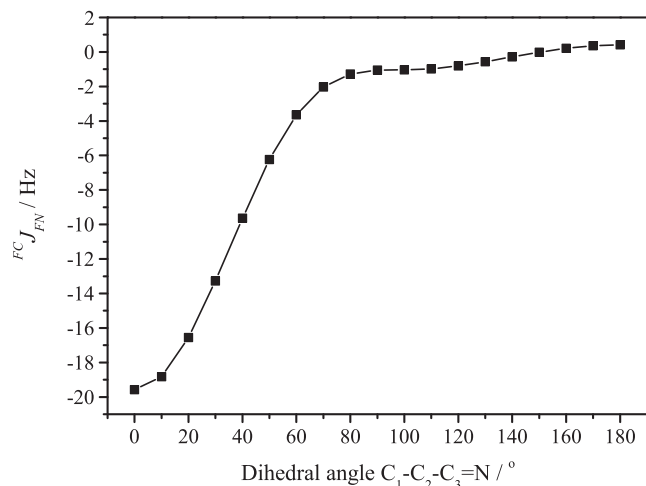
**Figure 2.** The FC term of JNF SSCC *versus* the optimized dFN distance fits in general an exponential decay.

**Figure 4.** FC term for JFN *versus* dihedral angle C1-C2-C3 = N for oxime **2a**.

different extension, depending on the molecular system.[37] However, the relative importance of 'steric' *versus* 'hyperconjugative' contributions is *reversed* in *J*-coupling because occupied orbitals (LPs and σ) carry a much stronger Fermi contact amplitude at the nuclei than low-occupancy σ*.[16] Because the through-space coupling constant between fluorine and nitrogen is transmitted mainly by the Fermi contact term (Table 1), its magnitude should depend on the extension of the *overlap* interactions among the lone pairs of these two atoms (Table 2), weighted by occupancy (ρ) (Table 3) and s% character of orbitals (Table 4)

**Table 2.** Absolute values for overlap matrix ($S_{ij}$) elements between $LP_{1,2,3}(F)$ and LP(N) for fluoroximes **1–7** calculated at the B3LYP/EPR-III level

| Compounds | Overlap matrix ($S_{ij}$) | | |
| | $LP_1(N) - LP_1(F)$ | $LP_1(N) - LP_2(F)$ | $LP_1(N) - LP_3(F)$ |
|---|---|---|---|
| **1** | 0.0280 | 0.0621 | 0.0161 |
| **2a** | 0.0245 | 0.0366 | 0 |
| **2b** | 0.0021 | 0.0008 | 0 |
| **3a** | 0.0133 | 0.0382 | 0 |
| **4** | 0.0422 | 0.0597 | 0.0324 |
| **5** | 0.0235 | 0.0344 | 0.0360 |
| **6E** | 0.0167 | 0.0046 | 0.0520 |
| **7Z** | 0.0042 | 0.0014 | 0.0045 |
| **7E** | 0.0019 | 0.0037 | 0.0011 |

**Table 3.** Occupancy of the lone pairs of the fluorine ($LP_{1,2,3}$) and of the nitrogen for fluoroximes **1–7** calculated using B3LYP/EPR-III

| Compounds | Occupancy (ρ) | | | |
| | $LP_1(N)$ | $LP_1(F)$ | $LP_2(F)$ | $LP_3(F)$ |
|---|---|---|---|---|
| **1** | 1.9588 | 1.9891 | 1.9669 | 1.9193 |
| **2a** | 1.9607 | 1.9891 | 1.9669 | 1.9154 |
| **2b** | 1.9607 | 1.9891 | 1.9683 | 1.9259 |
| **3a** | 1.9533 | 1.9887 | 1.9659 | 1.9192 |
| **4** | 1.9547 | 1.9893 | 1.9675 | 1.9184 |
| **5** | 1.9569 | 1.9890 | 1.9677 | 1.9221 |
| **6E** | 1.9533 | 1.9924 | 1.9697 | 1.9660 |
| **7Z** | 1.9557 | 1.9930 | 1.9739 | 1.9687 |
| **7E** | 1.9531 | 1.9928 | 1.9783 | 1.9685 |

**Table 4.** *s* % character at the respective nucleus for $LP_{1,2,3}(F)$ and LP(N) in fluoroximes **1–7**, calculated at the B3LYP/EPR-III level

| Compounds | *s* % character | | | |
| | $LP_1(N)$ | $LP_1(F)$ | $LP_2(F)$ | $LP_3(F)$ |
|---|---|---|---|---|
| **1** | 42.29 | 70.19 | 0.15 | 0.01 |
| **2a** | 42.44 | 70.28 | 0.03 | - |
| **2b** | 41.78 | 70.48 | 0.02 | - |
| **3a** | 42.26 | 70.37 | 0.03 | - |
| **4** | 42.46 | 70.58 | 0.04 | 0.01 |
| **5** | 42.2 | 70.35 | 0.21 | 0.04 |
| **6E** | 42.13 | 73.22 | 0.18 | 0.02 |
| **7Z** | 41.71 | 74.02 | 0.42 | 0.34 |
| **7E** | 41.57 | 74.05 | 0.24 | 0.46 |

involved in the coupling pathway because FC term is directly dependent of **s**% character.[33] This can be used with confidence because, in this case, only the overlap between fluorine and nitrogen lone-pairs is responsible for $^{TS}J_{FN}$ SSCC transmission.

The values for overlap between nitrogen and fluorine lone pairs are too small (10 times smaller) in comparison, for example, with overlap between carbon 2pz with nitrogen 2pz atomic orbitals (obtained from NAO analysis), responsible for C = N double bond; although overlap between nitrogen and fluorine lone pairs is too small, this pathway can be used efficiently to transmit $^{TS}J_{FN}$ coupling constant.

To obtain a much better rationalization for the TS transmission of $J_{FN}$ instead of just plotting distance between coupled nuclei (in this case, distance between fluorine and nitrogen nuclei *versus* experimental $J_{FN}$) as suggested[13] in the current literature, the present study is proposed to use Eqn (1) to take into account the influence of the electronic density ($D_{ij}$) between coupled nuclei.

$$D_{ij} = S_{ij}\left\{ \left[ \rho_i(s_i\%char/100) \right] \times \left[ \rho_j(s_j\%char/100) \right] \right\} \quad (1)$$

where the LP(N) occupancy, $\rho_i$, is weighted with the LP(N) s% character at the site of N nucleus, and similarly, the $LP_n(F)$ occupancy is weighted with its s% character at the site of nucleus

**Table 5.** Electronic density for each orbital overlap and their sum for fluoroximes **1–7**

| Compounds | $D_{LP1(F)} - LP1$ (N) | $D_{LP2(F)} - LP1$ (N) | $D_{LP3(F)} - LP1$ (N) | $\sum D_{ij}$ |
|---|---|---|---|---|
| **1** | 0.03238 | 0.00015 | 0 | 0.03253 |
| **2a** | 0.02850 | 0.00002 | 0 | 0.02851 |
| **2b** | 0.00241 | 0.0 | 0 | 0.00241 |
| **3a** | 0.01536 | 0.00002 | 0 | 0.01538 |
| **4** | 0.04917 | 0.00004 | 0 | 0.049221 |
| **5** | 0.02715 | 0.00012 | 0.00002 | 0.02729 |
| **6E** | 0.02005 | 0.00001 | 0.00001 | 0.02007 |
| **7Z** | 0.00505 | 0.0 | 0.00002 | 0.00508 |
| **7E** | 0.00227 | 0.00001 | 0 | 0.00228 |



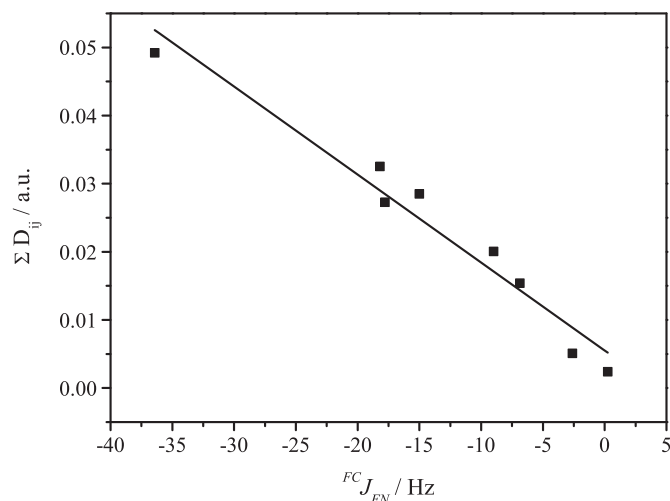**Figure 5.** Sum of electronic density (ΣDiJ) *versus* $^{FC}J_{FN}$ calculated at the SOPPA(CCSD)/EPR-III level ($r^2 = 0.95$).

F, and so on. Using this expression, it is possible to estimate the quantity of overlapping electronic density by the two atoms ($D_{ij}$), in this case, fluorine and nitrogen. These values as well as their sum are presented in Table 5.

Results displayed in Table 5 are plotted *versus* the respective FC term of $J_{FN}$ in Fig. 5 where the sum of the overlapped electronic density by fluorine and nitrogen was correlated with the Fermi contact term for the $J_{FN}$ SSCC calculated at the SOPPA(CCSD)/EPR-III level.

As can be seen from Fig. 5, a good correlation was obtained. It is possible to observe that a higher overlapping by the two nuclei is associated with a higher coupling constant, which highlights the existence of a through-space transmission of the fluorine-nitrogen coupling constant for all compounds studied here.

## Conclusion

In this paper, it is shown that the $J_{FN}$ coupling constant is not governed only by the $d_{FN}$ distance as frequently described in the literature, but it also depends on the relative orientation of the fluorine and nitrogen, and specially, the *s*% character of the F and N associated with an effective overlap strongly affecting the FC term and consequently the $J_{FN}$. Moreover, in this paper, it is shown that the electronic density between the two coupled nuclei is the best way to rationalize $J_{FN}$ coupling values, as it is observed (Fig. 5) if two atoms (in this case, nitrogen and fluorine) overlap with a larger electronic density with non-negligible *s*% character, a larger coupling constant is associated with it. These results highlight the remarkable importance played by the overlap interactions in the through space transmission of SSCCs, which should be dubbed through overlapping orbitals coupling instead of through-space coupling.

Furthermore, the existence of a linear correlation between the $D_{i,j}$ values and the FC term makes the determination of one property easier to be done based on the knowlegment of the other. Its is noted that the mechanisms involved in the transmission of this coupling constant can be described as a sum of the interactions between $LP_{1,2}(F)$ and $\sigma^*_{N-O}$ and the overlap between $LP_{1,2}(F)$ and $LP(N)$. However, it is highlighted that this approach is only valid if there are no other FC coupling pathways connecting both coupling nuclei. For instance, in compound **6E**, there is an FC transmission for $J_{FN}$ SSCC that does not correspond to the overlap of their respective lone pairs.

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