

# Analysis of the NMR through-space coupling mechanism between $^{19}\text{F}$ atoms

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Received 29 April 2004; in final form 18 June 2004

Available online 17 July 2004

## Abstract

The through-space NMR spin–spin coupling mechanism between  $^{19}\text{F}$  nuclei was investigated at the coupled perturbed density functional level using a BLYP(60:40) functional and a large basis set. Through-space coupling decays exponentially with the distance  $R(\text{F},\text{F})$  and is strongly angular dependent. The  $\text{lp}(\sigma)$  and  $\text{lp}(\sigma)\text{--lp}(\sigma)$  contributions to the FC term are larger than the corresponding  $\text{lp}(\pi_{\text{ip}})$  contributions. The passive  $\text{lp}(\pi)$  contributions are responsible for 10% of the FC mechanism. The PSO term is not negligible. In 1,8-difluoronaphthalene, the FC term of 56 Hz results from through-space coupling (75 Hz) and  $\sigma$  through-bond coupling (–19 Hz). The magnitude of through-space coupling can be predicted with a suitable model.

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## 1. Introduction

The physical properties of fluorine (small size, spin of  $^{19}\text{F}$  is  $\frac{1}{2}$ , 100% natural abundance of  $^{19}\text{F}$ ) coupled with its large gyromagnetic ratio, [1] makes long range NMR spin–spin coupling constants (SSCCs)  ${}^nJ(^{19}\text{F},^{19}\text{F}) = {}^nJ(\text{F},\text{F})$  important parameters for studying the structure of polycyclic aliphatic carbons, steroids, and aromatic molecules [1–4]. Indeed, SSCCs  ${}^nJ(\text{F},\text{F})$  with large  $n$  have for some time already been used as important probes in biochemical investigations [2,4]. However, the mechanism by which the spin information is transferred from one fluorine atom to the other via a long chain of bonds (through-bond) or alternatively via a direct through-space route is not yet fully understood.

For coupling fluorine nuclei that are proximate to one another (i.e., within the van der Waals distance of 2.94 Å [5]) the transfer of spin information is generally

thought to occur through the lone pairs (lp) of the F atoms. [4] However, several cases exist where sizable couplings occur between F nuclei that have a separation larger than 2.94 Å. These long-range couplings have generally been explained by a through-bond mechanism – either via a hydrogen bond [6] or a  $\pi$ -electron system [7]. More recently, the pure through-space limit has been further extended to the outer limit of the van der Waals distance, where  ${}^{398}J(\text{F},\text{F}) = 17 \pm 2$  Hz detected within a dihydrofolate reductase–NADPH–MTX complex [8], was determined to be transmitted purely through-space [9].

It is the general understanding that the Fermi contact (FC) coupling mechanism dominates F,F coupling, but it is still not well understood which orbitals are in which way responsible for the through-space coupling mechanism and whether this is exclusively a FC coupling mechanism or whether the non-contact interactions (paramagnetic spin orbit, PSO; diamagnetic spin orbit, DSO; spin dipole, SD) also contribute. The FC coupling mechanism requires that there is spin density at the coupling nuclei, which cannot be expected if  $\pi$ -orbitals are involved. Therefore, a consideration of the  $\pi$ - or

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$\sigma$ -character of the interacting F lp-orbitals is essential for an understanding of the F,F coupling mechanism.

The initial proposal, by Mallory et al. [10,11] that the lp interactions carry the predominant through-space transmission mechanism, was based upon the concept of the overlapping in plane lp( $\pi$ ) orbitals, as an explanation for the observed dependence of  ${}^nJ(\text{F},\text{F})$  on F,F separation  $R(\text{F},\text{F})$ .

Peralta et al. [12] performed an NJC (natural- $J$ -coupling) analysis of the FH dimer using finite perturbation theory. The NJC analysis sought to decompose the total FC(FF) term into contributions from the core, bond, and lp orbitals. The decomposition of the SSCC in this way suggested that the total FC term of the SSCC was dominated by the lp orbital interactions and that a sizable core contribution existed. An angular dependence was also established and this dependence was in line with the lp overlap theory of Mallory [10].

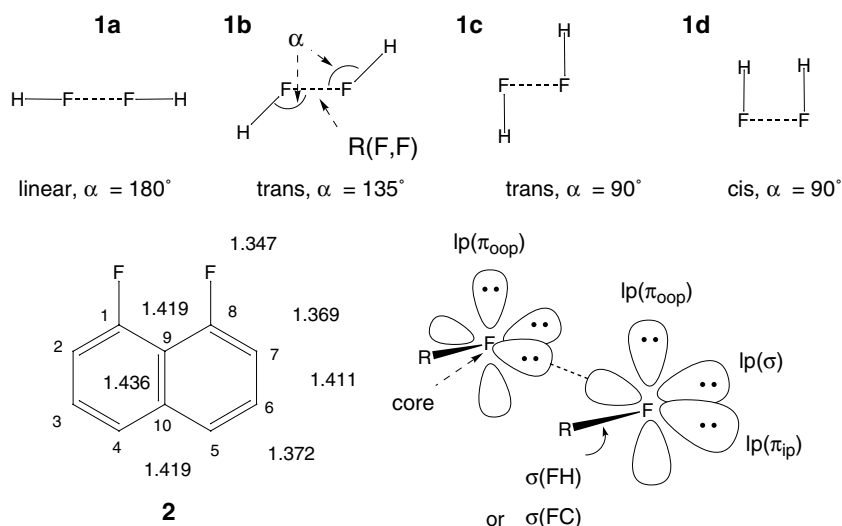
In this work, we will review the F,F long-range coupling mechanism using the FH dimer as a suitable model. For this purpose, we will apply the recently developed J-OC-PSP (=J-OC-OC-PSP: decomposition of  $J$  into orbital contributions using orbital currents and partial spin polarization) analysis, which decomposes the spin–spin coupling interactions into one-, two-, and  $m$ -orbital terms. It was one of the disadvantages of previous investigations that spin–spin coupling was viewed from a one-orbital analysis, which cannot single out steric exchange interactions between two-orbitals or the passive contributions of lp( $\pi$ ) orbitals to the F,F coupling mechanism involving three-orbital terms. Also, the relatively large contributions of the core orbitals to the F,F coupling mechanism seems to be an artifact of recent analyses rather than typical of the true coupling mechanism. Hence, we will determine the individual

orbital contributions to identify those orbital interactions that really carry the F,F mechanism.

## 2. Computational details

For the purpose of investigating through-space F,F coupling, the dimer HF...FH (**1**) was used as a suitable model. The FH distance in the monomer was set to the experimental value [13] and then the distance  $R(\text{F},\text{F})$  between the F atoms increased from 2 to 3.4 Å. Four different forms of **1** (see Scheme 1) were considered: **1a**: linear arrangement, **1b**: planar *trans*-arrangement with HFF angles  $\alpha = 135^\circ$ , **1c**: planar *trans*-arrangement with  $\alpha = 90^\circ$ , and **1d**: planar *cis*-arrangement with  $\alpha = 90^\circ$ . In total, 32 different configurations of **1** were investigated with regard to F,F through-space spin–spin coupling. The investigation of the FH dimer by Peralta et al. [12] focused on conformation **1d**, which will be considered in the following when comparing our results with those of [12].

The indirect SSCCs  $J(\text{F},\text{F})$  were calculated with the coupled perturbed DFT (CP-DFT) approach of Sychrovsky et al. [14], which leads to the four Ramsey terms FC, SD, DSO, and PSO in an analytical way. For the purpose of obtaining reliable  $J(\text{F},\text{F})$  values, an XC functional was used consisting of 60% exact exchange, 40% Becke 88 DFT exchange [15], and the Lee–Yang–Parr (LYP) correlation functional [16] (called henceforth BLYP(60:40)). The basis set was constructed starting from Dunning's augmented cc-pVTZ basis set [17,18], decontracting the  $s$  functions, and adding to the  $s$ -function of the cc-pVTZ basis with the largest exponent an even-tempered set of four steep  $s$  function at each nucleus with a ratio of 6. The polarization functions



Scheme 1.

with the highest angular momentum were omitted for each atom. In this way a (15s6p3d1f/10s3p1d)[15s4p3d1f/10s3p1d] basis set resulted. Using CP-DFT/BLYP(60:40)/[15s4p3d1f/10s3p1d] the SSCC  ${}^1J({}^{19}\text{F}^1\text{H}) = {}^1J(\text{F},\text{H})$  of FH is calculated to be 557 Hz. The measured SSCC  ${}^1J(\text{F},\text{H})$  is 529 Hz (value obtained for the gas phase [1]), which has to be corrected for a vibrational contribution of 26 Hz [19] thus leading to a value of 555 Hz in reasonable agreement with the calculated value. Based on this result, we assume that the method used in this work leads also to reliable  ${}^nJ(\text{F},\text{F})$  values, Ramsey terms, and orbital contributions.

For the purpose of comparing the ratio of through-space and through-bond coupling in a compound with a SSCC  ${}^4J(\text{F},\text{F})$ , difluoronaphthalene (**2**, Scheme 1) was investigated. The F,F coupling mechanism in **2** was recently investigated by Contreras and co-workers [20] and therefore it was desirable to facilitate a comparison of the results of these authors with those of the current work by using the same molecular geometry determined with B3LYP [21] and the 6-311G(d,p) basis set [22] and the same procedure for calculating SSCCs, i.e. CP-DFT/B3LYP was used in connection with an aug-cc-pCVDZ basis set [23] at the F atoms and a cc-pVDZ basis set [17] at the C and H atoms. A suitable model for **2** was constructed with the help of **1** by freezing distance  $R(\text{F},\text{F})$  and angle  $\alpha$  (Scheme 1) at the values of **2** and reoptimizing the FH distances at the B3LYP/6-311G(d,p) level.

The analysis of the F,F-coupling mechanism was carried out with the J-OC-PSP1 and J-OC-PSP2 methods described recently [24]. An orbital analysis of the nuclear spin–spin coupling at the J-OC-PSP1 level leads to the active one-orbital and two-orbital contributions of the spin transfer mechanisms. The one-orbital terms describe predominantly the effect of the Ramsey distortions of the orbitals (FC, PSO, SD), i.e., the direct transfer of spin information between the coupling nuclei by one and the same orbital; the two-orbital terms represent the steric-exchange interactions of the distorted orbitals, i.e. processes where the spin information is transferred by a pair of orbitals, each of which interacts directly with one of the coupling nuclei. Technically, J-OC-PSP1 con-

tributions can be obtained by selected orbital SSCC calculations where for a given SSCC one orbital is kept active whereas all others are set passive [24].

J-OC-PSP2 was used to determine the passive contributions of orbitals, which carry the spin information through the coupling path but do not interact with either the perturbing or responding nucleus. For instance, out-of-plane  $\pi$  electrons cannot make any active contribution to the FC coupling mechanism but can participate in the latter passively. This is possible either by an *echo effect*, where the passive orbital modifies the Ramsey distortion of another, active orbital, or by *spin transport* effects, where the spin information is transferred through a chain of three or more orbitals [24]. J-OC-PSP2 contributions can be determined by freezing selected orbitals in the SSCC calculation, i.e. their interactions to both the coupling nuclei and to the other orbitals are suppressed. By comparing the SSCCs obtained from calculations where a certain orbital once is frozen and once is set passive, the various contributions of this orbital are found by forming appropriate differences. All SSCC calculations and the J-OC-PSP analyses were carried out with the program package Cologne 03 [25].

### 3. Analysis of through-space spin–spin coupling between F atoms

The SSCC  ${}^1J(\text{F},\text{F})$  of dimer **1** is always positive and varies at  $R(\text{F},\text{F})=2$  Å between 2106 (**1a**) and 713 Hz (**1d**) depending on the arrangement of the FH monomers. Increase of  $R(\text{F},\text{F})$  leads in each case to an exponential decay of  ${}^1J(\text{F},\text{F})$ . The through-space SSCC is dominated by the FC term (2084–880 Hz at 2 Å, Tables 1 and 2: in the following, we will always refer to the 2 Å values in direct comparisons), which is shown for the four different configurations of **1** in Fig. 1 as a function of  $R(\text{F},\text{F})$ . Also shown is the distance dependence of the PSO term (inset in Fig. 1). This adopts at  $R(\text{F},\text{F})=2$  Å values between 18.5 and –155 Hz for  $\alpha$  decreasing from 180 to 90° (**1a** to **1d**). Not shown are DSO and SD terms, which turn out to be rather small.

Table 1  
Active and passive contributions to the FC term of  ${}^1J(\text{F},\text{F})$  in **1a**, **1c**, and **1d**<sup>a</sup>

Orbital	<b>1a</b>		<b>1c</b>		<b>1d</b>	
	Active	Passive	Active	Passive	Active	Passive
Core	0	–	0	–	0	–
$\sigma(\text{FH})$	–451.5	263.9	282.2	–63.1	167.2	–36.1
$\text{lp}(\sigma)$	1539.5	16.9	125.5	–72.9	194.5	–58.8
$\text{lp}(\pi_{\text{ip}})$	0	27.5	–28.8	59.5	42.1	55.5
$\text{lp}(\pi_{\text{oop}})$	0	27.5	0	24.5	0	23.4
$\sum_{\sigma}$	1088.0	280.8	407.7	–136.0	361.6	–94.9
$\sum_{\text{one}}$	1088.0	330.8	378.9	–52.0	403.8	–16.0

<sup>a</sup> All values in Hz.  $\sum_{\sigma}$  and  $\sum_{\text{one}}$  denote the sum of  $\sigma$ -orbital and all one-orbital contributions. Calculations done at the CP-DFT level of theory with the B3LYP(60:40) functional and the basis set described in Section 2.

Table 2  
Two-orbital contributions to the FC term of  ${}^1J(\text{F},\text{F})$  in **1a**, **1c**, and **1d**<sup>a</sup>

Orbital	<b>1a</b>	<b>1c</b>	<b>1d</b>
Core–core	2.8	–1.4	1.1
Core– $\sigma(\text{FH})$	–101.4	–27.6	–38.7
Core– $\text{lp}(\sigma)$	234.2	90.8	86.6
Core– $\text{lp}(\pi_{\text{ip}})$	0	–184.9	–155.1
$\sigma(\text{FH})$ – $\sigma(\text{FH})$	319.3	–123.6	167.0
$\sigma(\text{FH})$ – $\text{lp}(\sigma)$	–1711.5	277.7	–430.6
$\sigma(\text{FH})$ – $\text{lp}(\pi_{\text{ip}})$	0	166.1	147.9
$\text{lp}(\sigma)$ – $\text{lp}(\sigma)$	2252.9	–92.2	381.8
$\text{lp}(\sigma)$ – $\text{lp}(\pi_{\text{ip}})$	0	321.4	285.7
$\text{lp}(\pi_{\text{ip}})$ – $\text{lp}(\pi_{\text{ip}})$	0	41.7	30.5
$\sum_{\text{core}-\sigma}$	132.8	63.2	47.9
$\sum_{\sigma-\sigma}$	860.7	61.9	118.2
$\sum_{\sigma-\pi}$	0	487.5	433.5
$\sum_{\text{diag}}$	2575.0	–175.5	580.4
$\sum_{\text{cross}}$	–1578.8	643.5	–104.3
$\sum_{\text{two}}$	996.2	468.0	476.1
FC(F,F)	2084.2	846.9	879.8
$J(\text{F},\text{F})$	2106.2	738.2	713.8

<sup>a</sup> All values in Hz.  $R(\text{F},\text{F})=2 \text{ \AA}$ .  $\sum_{\text{core}-\sigma}$ ,  $\sum_{\sigma-\sigma}$ ,  $\sum_{\sigma-\pi}$ ,  $\sum_{\text{diag}}$ ,  $\sum_{\text{cross}}$ , and  $\sum_{\text{two}}$  denote the sums of all core– $\sigma$ ,  $\sigma$ – $\sigma$ , and  $\sigma$ – $\pi$  two orbital contributions, the sum of all orbital  $i$ –orbital  $i$ , orbital  $i$ –orbital  $j$  ( $i \neq j$ ), all two-orbital contributions, respectively. Calculations done at the CP–DFT level of theory with the BLYP(60:40) functional and the basis set described in Section 2.

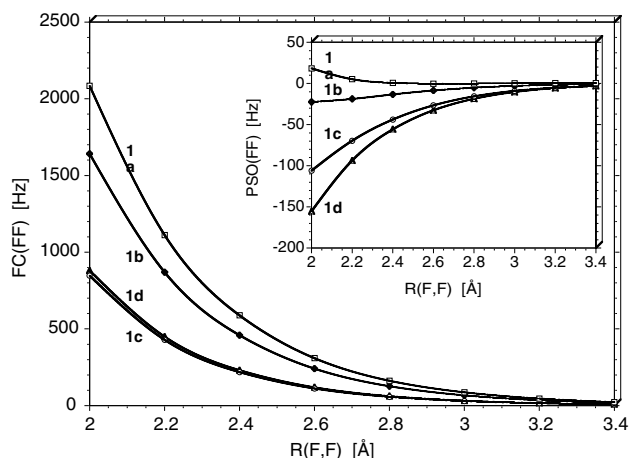


Fig. 1. The variation of FC(F,F) (inset: PSO(F,F)) in **1** with respect to the angle  $\alpha$  and the distance  $R(\text{F},\text{F})$  (Scheme 1). All calculations were done at the CP–DFT level of theory with the BLYP(60:40) functional and the basis set, as described in Section 2.

The  ${}^1\text{FC}(\text{FF})$  values for the four configurations also depend exponentially on  $R(\text{F},\text{F})$  (average  $R^2$  of 0.9997). The exponential decay with increasing  $R(\text{F},\text{F})$  becomes smaller for **1d** rearranging to **1c** and **1d** (Fig. 1). The coincidence of the lines for **1c** and **1d** is a further striking feature of the results presented in Fig. 1. This fact may suggest that the transmission mechanism between the coupling nuclei remains the same in the two forms, which implies that the interactions of the orbitals in both arrangements must be equivalent. However, the alignment of the orbitals in the *trans*-orientation is only retained for the in plane and out of

plane  $\text{lp}$  orbitals ( $\text{lp}(\pi_{\text{ip}})$  and  $\text{lp}(\pi_{\text{oop}})$ , see Scheme 1) of the *cis* arrangement. Since the  $\text{lp}(\pi_{\text{oop}})$  orbitals cannot contribute actively to the FC coupling mechanism, the coupling between the two nuclei appears *prima facie* to be solely dependent upon the overlap of the  $\text{lp}(\pi_{\text{ip}})$  orbitals. For the purpose of quantifying this dependence we performed a J–OC–PSP1 analysis on **1a** and **1d**, obtaining one orbital (core,  $\text{lp}(\sigma)$ , etc.) and two orbital (e.g. core–core, core– $\text{lp}(\sigma)$ , etc.) contributions.

In Fig. 2, the one orbital contributions are shown for the **1d** and **1a** (inset). Each of the one orbital terms in **1d** contributes positively to the FC(F,F) term with the largest contribution arising from the  $\text{lp}(\sigma)$  (195 Hz) and the  $\sigma(\text{FH})$  orbitals (167 Hz, Table 1). In the linear form **1a**, the  $\text{lp}(\sigma)$  orbital contribution dominates strongly (1540 Hz), which is only partly compensated by the  $\sigma(\text{FH})$  contribution of –452 Hz (Fig. 2). Contrary to previous proposals [10], we find that for **1d** the  $\text{lp}(\pi_{\text{ip}})$  one orbital contribution is less significant (42 Hz for **1d**, 0 Hz for **1a**, Table 1) than those of the  $\sigma$  orbitals. Furthermore, the results show that the one orbital contribution of the core orbitals to the FC term is zero. However, in a previous investigation [12] the core orbitals were calculated to have a contribution of ca. 110 Hz to the FC term of  ${}^1J(\text{F},\text{F})$  at  $R(\text{F},\text{F})=2.1 \text{ \AA}$ . This large discrepancy between the two methods is resolved in the following.

In Fig. 3, the two orbital contributions to the FC term of  ${}^1J(\text{F},\text{F})$  are shown for **1d** and **1a** (inset). Clearly, these contributions are much larger in magnitude than the one orbital contributions. However, the cross terms cancel each other largely out (**1d**: core– $\text{lp}(\sigma)$ =87;  $\text{ip}$ )=–155;  $\sigma(\text{FH})$ – $\text{lp}(\sigma)$ =–431;  $\sigma(\text{FH})$ – $\text{lp}(\pi_{\text{ip}})$ =148;  $\text{lp}(\sigma)$ – $\text{lp}(\pi_{\text{ip}})$ =286 Hz; Table 2). Thus, the major contri-

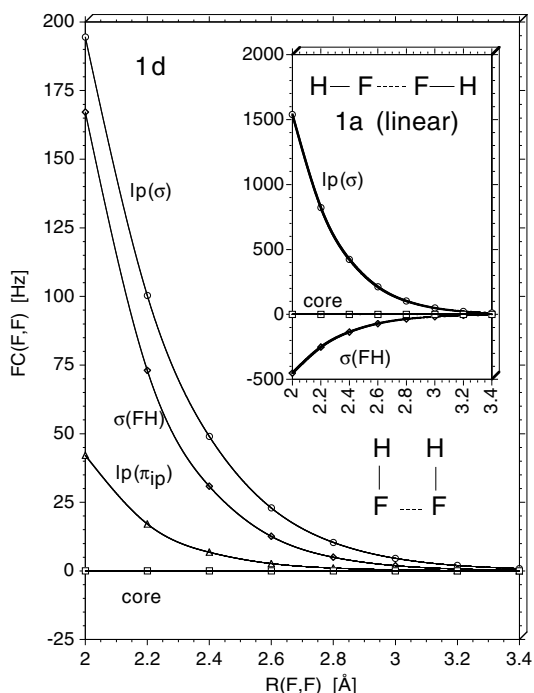


Fig. 2. The one orbital contributions to the FC term of  ${}^1J(F,F)$  in **1d** (inset: **1a**), and their dependence on  $R(F,F)$ . All calculations were done at the CP-DFT level of theory with the BLYP(60:40) functional and the basis set, as described in Section 2.

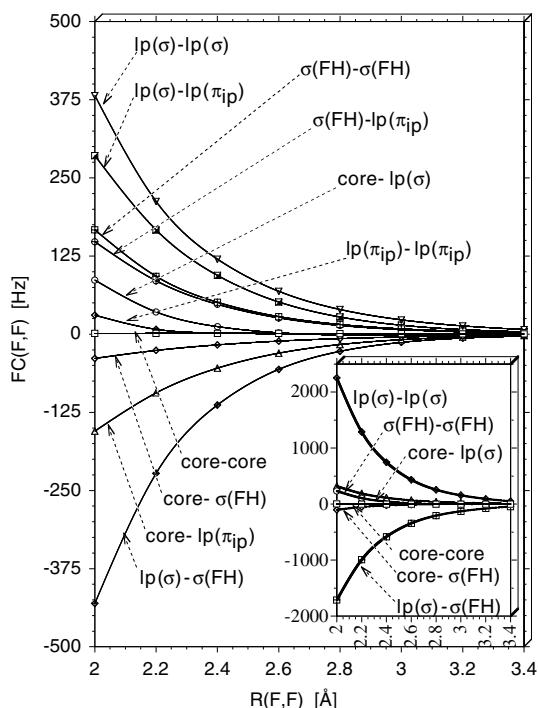


Fig. 3. The two orbital contributions to the FC term of  ${}^1J(F,F)$  in **1d** (inset: **1a**), and their dependence on  $R(F,F)$ . All calculations were done at the CP-DFT level of theory with the BLYP(60:40) functional and the basis set, as described in Section 2.

Contributions in the two orbital terms result from the  $lp(\sigma)-lp(\sigma)$  (382 Hz) and  $\sigma(FH)-\sigma(FH)$  (167 Hz), with the  $lp(\pi_{ip})-lp(\pi_{ip})$  interaction proving minor (31 Hz). In the linear arrangement **1a**, the analysis is even clearer, with the overwhelming contribution arising from the  $lp(r)-lp(r)$  term (2253 Hz) although this is partly compensated by the  $r(FH)-lp(r)$  (-1712 Hz) interaction.

At  $R(F,F)=2.0$  Å, the one-orbital and two-orbital contributions are comparable (**1d**: sum of one-orbital contributions  $\sum_{one}=404$  Hz; sum of two-orbital contributions  $\sum_{two}=476$  Hz; **1a**:  $\sum_{one}=1088$  Hz;  $\sum_{two}=996$  Hz). As the distance increases the steric exchange interactions and thus the two orbital terms begin to dominate the total FC value (e.g. at 3.0 Å, **1d**:  $\sum_{one}=7$  Hz;  $\sum_{two}=26$  Hz; **1a**:  $\sum_{one}=32$  Hz;  $\sum_{two}=55$  Hz).

Of special interest is the interaction of the core orbitals, which were previously proposed to have a sizable, positive contribution to the FC term [12]. The steric exchange between the two cores is negligible, although we do find sizable interactions between the core orbitals and the other orbitals, which lead to a total contribution of -106 Hz. Thus, we find that the core orbitals do contribute to the transmission of the spin information between the two  ${}^{19}F$  nuclei. However, this transfer is only possible through their interaction with the valence orbitals. Our analysis predicts the total core contribution to be negative, in contradiction to the results of Peralta et al. [12]. As we demonstrated recently [26], this discrepancy can be traced back to the use of natural LMOs (NLMOs) [27] in the NJC analysis. The core NLMOs have non-negligible orthogonalization tails, which result in chemically unreasonable contributions from these orbitals to the Ramsey terms. The NJC analysis is thus misleading in that it predicts a large positive contribution that results from the core orbitals alone, whereas the actual core and core-core interaction (i.e. the 'pure' core contribution) is less than 3 Hz (Tables 1 and 2) and the core contribution mediated by other orbitals is negative.

Next we compare the FC through-space coupling mechanism for **1c** and **1d**. Fig. 1 reveals that the FC term changes only slightly between **1c** and **1d**. Table 1 shows that the FC coupling in these cases is dominated by contributions from the  $\sigma$  orbitals and that the individual J-OC-PSP1 contributions undergo large changes between **1c** and **1d**. However, if one summarizes the contributions from the  $\sigma(FH)$  and  $lp(\sigma)$  orbitals into one common term ( $\sum_{\sigma}$ ,  $\sum_{c-\sigma}$ ,  $\sum_{\sigma-\sigma}$ ,  $\sum_{\sigma-\pi}$  in Table 2), one finds that the resulting terms change by no more than 60 Hz each between **1c** and **1d**. That is, the  $\sigma(FH)$  and  $lp(\sigma)$  orbitals change their roles between **1c** and **1d**, whereas their total contribution to the FC coupling is about the same. This view is supported by the signs of the two-orbital terms involving the  $\sigma(FH)$  and  $lp(\sigma)$  orbitals in **1c** and **1d**: These terms are positive when the two orbitals involved are parallel and negative



when they are oriented antiparallel. In addition, there is a partial compensation e.g. between  $\sum_{\sigma}$  and  $\text{lp}(\pi_{\text{ip}})$  or  $\sum_{\text{core}-\sigma}$  and  $\text{core}-\text{lp}(\pi)$ , which finally leads to the small difference for the FC term in **1c** and **1d**. Hence, the assumption that the coupling mechanism is the same for **1c** and **1d** and involves just the  $\text{lp}(\pi_{\text{ip}})$  orbitals is misleading. The through-space mechanism is dominated by  $\sigma$  orbital interactions, which change their role from **1c** to **1d**.

For the purpose of assessing the passive contributions of the various orbitals, we performed a J-OC-PSP2 analysis for the p orbitals of **1** in the way that both the active and the passive contributions for the  $\sigma(\text{FH})$  and each type of lp LMO ( $\sigma$ , in-plane  $\pi$ , out-of-plane  $\pi$ ) were determined (Table 1). The (purely passive) contribution of the  $\text{lp}(\pi_{\text{oop}})$  orbitals vary from 23 Hz to 27 Hz (there cannot be any active contribution because the F nuclei are positioned in the nodal plane of these orbitals) which indicates that these contributions are largely independent of the configurations of **1**. They are relatively small because the  $\text{lp}(\pi_{\text{oop}})$ - $\text{lp}(\pi_{\text{oop}})$  overlap is, even at 2 Å, rather small.

The  $\text{lp}(\pi_{\text{ip}})$  orbitals have larger passive contributions (27 Hz for **1a**, 60 Hz for **1c**, 55 Hz for **1d**, Table 1) to FC(F,F). For **1c** and **1d**, the two  $\text{lp}(\pi_{\text{ip}})$  orbitals penetrate each other more intensely than the  $\text{lp}(\pi_{\text{oop}})$  orbitals, thus leading to a much stronger steric interaction. Hence, the  $\text{lp}(\pi_{\text{ip}})$  can bridge the gap between e.g. two  $\sigma$  orbitals at each fragment by spin transport and enhance the FC coupling mechanism.

The passive contributions of the  $\sigma$  orbitals vary much stronger with the configuration of **1** than those of the  $\pi$  orbitals. Two different mechanisms are operative: For instance, in **1a**, the  $\text{lp}(\sigma)$  orbitals function in the linear form primarily as active orbitals via direct exchange interactions (one-orbital: 1540 Hz, Table 1; two-orbital: 2253 Hz, Table 2) but also passively establishing the following orbital paths:  $\text{F1} \rightarrow \sigma(\text{F1H}) \rightarrow \text{lp}(\sigma, \text{F1}) \rightarrow \text{lp}(\sigma, \text{F2}) \rightarrow \sigma(\text{F2H}) \rightarrow \text{F2}$  or  $\text{F1} \rightarrow \sigma(\text{F1H}) \rightarrow \text{lp}(\sigma, \text{F1}) \rightarrow$

$\text{lp}(\sigma, \text{F2}) \rightarrow \text{F2}$ . This passive spin transport leads to just a 28 Hz contribution in the case of **1a**. There is a much stronger passive contribution of the  $\sigma(\text{FH})$  orbitals (264 Hz) where their active contributions involving their tails (one-orbital –451 Hz, Table 1; two-orbital: 319 Hz, Table 2) are of similar magnitude. The relatively large passive contribution results from an echo effect based on the following spin polarization path:  $\text{F1} \rightarrow \text{lp}(\sigma, \text{F1}) \rightarrow \sigma(\text{F1H}) \rightarrow \text{lp}(\sigma, \text{F1}) \rightarrow \text{lp}(\sigma, \text{F2}) \rightarrow \text{F2}$ , i.e., the Ramsey distortion of the  $\text{lp}(\sigma, \text{F})$  orbital is enhanced by the response of the neighboring passive  $\sigma(\text{FH})$  orbital. Clearly, this echo effect depends strongly on the configuration of **1** and decreases for  $\alpha \rightarrow 0^\circ$  (Table 1).

The total passive contribution is 16% (331 Hz, Table 1) of the FC(F,F) term (2084 Hz) in the case of **1a** ( $R(\text{F}, \text{F}) = 2 \text{ \AA}$ ), becomes however substantially smaller for decreasing  $\alpha$  because positive and negative passive contributions partially cancel. Nevertheless, it is comparable to that found for  ${}^1\text{FC}(\text{C}, \text{C})$  in ethylene ( $\pi$  contribution: 5.9 Hz, total FC term: 79.1 Hz [24]). Clearly, echo effects of the passive orbitals are more important than spin transport effects.

The difluoro derivative **2** is a prototype for molecules with the possibility of through-space and through-bond F,F coupling. The F atoms are separated by about 2.5 Å, i.e. well below the van der Waals distance of 2.94 Å, whereas the bond path involves four bonds (Scheme 1). F,F spin–spin coupling in **2** was studied previously [9] by comparing **2** with model systems such as **1d** that exclude any through-bond coupling. These studies provided estimates for the through-space contributions to the coupling but did not allow any conclusions on the role of the  $\pi$  orbitals. We performed therefore a J-OC-PSP2 analysis of the F,F coupling in **2** focusing on the role of the  $\pi$  system in the coupling. The results are summarized in Table 3.

The calculated total SSCC for **2** is 62.3 Hz (# 1 in Table 3), i.e., just 3 Hz off the experimental value of 59 Hz [1]. The accuracy of the calculations is sufficient

Table 3  
Ramsey terms for  $J(\text{F}, \text{F})$  in 1,8-difluoronaphthalene **2** and the  $\text{HF} \cdots \text{FH}$  dimer **1**<sup>a</sup>

#	Molecule	Frozen orbitals	Contribution	FC	SD	PSO	DSO	Total
1	<b>2</b>	None	Total	56.5	0.5	4.4	0.9	62.3
2	<b>2</b>	$\pi(\text{naphthalene})$	Partial	57.1	5.5	5.4	0.8	68.8
3	<b>2</b>	$\pi(\text{naphthalene}), \pi(\text{F})$	Partial	55.8	6.5	7.5	0.4	70.3
4	<b>2</b>	All except those of F <sup>b</sup>	THS	75.3	5.0	3.7	0.2	84.2
5	<b>1</b>	None	THS	84.9	0.2	–37.1	0.0	47.5
1–2	<b>2</b>		$\pi(\text{Naphthalene})$	–0.6	–5.0	–1.4	0.1	–6.5
2–3	<b>2</b>		$\pi(\text{F})$	1.3	–1.0	–2.1	0.4	–1.5
3–4	<b>2</b>		All $\sigma(\text{CC}), \sigma(\text{CH}), 1s(\text{C})$ <sup>b</sup>	–19.5	1.5	3.8	0.2	–13.9
1–4	<b>2</b>		THB	–10.4	–4.5	0.8	0.7	–11.9

<sup>a</sup> All values in Hz. Calculations done at the CP-DFT level of theory with the B3LYP functional and the basis set described in Section 2. Geometries optimized at the B3LYP/6-311G(d,p) level. The geometry of **1** was adjusted to that of **2** (see text). THS and THB denote the through-space and through bond contributions, respectively.

<sup>b</sup> The orbitals frozen are the  $\pi(\text{naphthalene}), \sigma(\text{CC}), \sigma(\text{CH})$ , and the  $1s(\text{C})$  orbitals with the exception of the  $1s$  orbitals at the C atoms bound to the F atoms.

to guarantee a reliable analysis of the coupling mechanism. The results of Contreras and co-workers [20] deviate somewhat from ours, which is due to the use of spherical [20] rather than Cartesian basis functions (this work). The SSCC is dominated by the FC term (56.5 Hz) and on first sight there seems to be a considerable difference between the F,F coupling in model **1** and that in **2**.

If the  $\pi$  orbitals of the naphthalene unit in **2** are frozen, the total SSCC will increase from 62.3 to 68.8 Hz (# 2 in Table 3). The strongest change arises from the SD term, which increases from 0.5 to 5.5 Hz, i.e., the  $\pi$  system in the naphthalene part contributes  $-5$  Hz to the SD coupling mechanism. The FC term increases to 57.1 Hz, which corresponds to a  $\pi$ (naphthalene) contribution to the FC coupling mechanism of just  $-0.6$  Hz. (Table 3). This small contribution is in line with the fact that bonds C1C9 and C8C9 have the weakest  $\pi$  character of all peripheral CC bonds in **2** (see Scheme 1). The result indicates that the  $\pi$  system in the naphthalene part of **2** allows for an efficient spin-information transport between the F atoms in first instance by the SD rather than the FC mechanism. This is in line with the findings by Gräfenstein and Cremer [29]:  $\pi$  systems with low-lying  $\pi^*$  orbitals make active contributions to the SD term. The small total SD term in **2** results from a compensation of positive and negative contributions. Substitutions in **2** may break this compensation and lead to total SD terms of several Hz [20]. It is not justified to neglect the SD term a priori as was done in previous investigations (see e.g. [9]). Freezing in addition the  $\pi$ (F) lone-pair orbitals (# 3 in Table 3) leads only to small changes in the Ramsey terms of SSCC  ${}^4J$ (F,F) (FC: 1.3; SD:  $-1.0$ ; PSO:  $-2.1$  Hz; Table 3).

If all orbitals except the  $\sigma$ (FC),  $lp$ (F),  $1s$ (F), and the  $1s$ (C) at the two C atoms bonded to F are frozen (# 4 in Table 3), the through-space part of the FF coupling can be isolated, which for the FC term corresponds to 75.3 Hz. A comparison with Table 3, reveals that  $\sigma$  through-bond coupling contributes  $-19.5$  Hz to the FC coupling mechanism.

Contreras and co-workers [20] performed an NJC orbital decomposition of  ${}^4J$ (F,F) in **2**, which sums all  $n$ -orbital contributions into one-orbital contributions. A direct comparison between our results and those of [20] is therefore not possible, because NJC does not allow an explicit separation of through-space and through-bond terms. However, the results in [20] combined with the calculations of this work suggest a through-space part of the FC term of about 60 Hz and a through-bond part of about  $-10$  Hz, which is in qualitative agreement with our findings.

One can use **1** as a model for the through-space interaction in **2** (# 5 in Table 3). All orbitals are kept active in the calculation of **1**, hence, the results should

be compared to those of # 4 for **2**. (Strictly speaking, there is a slight difference in that the  $\pi$ (F) orbitals are active in # 5 but not in # 4, however, a comparison of # 2 and #3 shows that the impact of these orbitals on  ${}^4J$ (F,F) is small.) The FC term for # 5 is 84.9 Hz, i.e. 9.4 Hz larger than for # 4, i.e., **1** models the through-space FC coupling in **2** reasonably well. The PSO term for # 5 is  $-37.1$  Hz, i.e. 42.3 Hz off the value found in # 4. Hence, model system **1** features a strong through-space PSO coupling not present in **2**. The coupling in **1** is provided  $lp(\pi_{ip},F) \rightarrow \sigma^*(FH)$  excitations. The  $\sigma^*(FH)$  has distinct p character at the F site, which allows for an effective PSO coupling [29]. In **2**, the corresponding virtual orbital has a less distinct p character (due to the different electronegativities of H and C( $sp^2$ ) atom), and the corresponding PSO coupling is weaker.

#### 4. Conclusions

Our investigation of the through-space F,F spin–spin coupling mechanism in **1** and **2** leads to a number of new insights:

- (1) The through-space F,F spin–spin coupling in **1** decays exponentially with the distance  $R$ (F,F) and is strongly angular dependent. The head-to-head arrangement of the F atoms in **1a** provides the largest SSCCs (about three times the corresponding values for **1d**). The angular dependence is caused by a strong decrease of the  $lp(\sigma)$  and  $lp(\sigma)-lp(\sigma)$  contributions with the angle  $\alpha$ , counteracted only partly by an increase of the  $lp(\pi_{ip})$  one- and two-orbital contributions.
- (2) At  $R$ (F,F) = 2 Å, one- and two-orbital terms are about of the same magnitude. With increasing  $R$ (F,F), the one-orbital terms decrease more rapidly in magnitude reflecting the limited extent of the orbitals. Some of the two-orbital terms representing steric exchange interactions are considerably larger, however there is a large cancellation among the cross terms at all values of  $\alpha$ .
- (3) Contrary to general expectations, the  $lp(\sigma)$  and  $lp(\sigma)-lp(\sigma)$  contributions are larger than the corresponding  $lp(\pi_{ip})$  contributions at all values of  $\alpha$ . Although the  $lp(\pi_{ip})$  contributions lead to stronger through-space overlap and therefore to stronger steric interactions, spin polarization cannot be effectively transferred because of the rather small amplitudes of these orbitals at the position of the nuclei. The  $lp(\pi_{ip})$  orbitals gain however importance in cross terms such as  $lp(\pi_{ip})-lp(\sigma)$  or  $lp(\pi_{ip})-core$  when  $\alpha$  decreases to  $90^\circ$ . These cross terms cancel each other partly.

- (4) There are sizable contributions to the FC coupling including the core orbitals. All these contributions are two-orbital terms involving a core orbital and a non-core orbital. This is not reflected in the results given in [12].
- (5) Contrary to the predictions of Mallory [10], the passive contributions of the  $lp(\pi)$  orbitals are relatively small. The same observation was made for the passive  $\pi$  contributions in polyenes [24] and in so far the passive  $lp$  contributions of 84 Hz (**1c**) and 79.3 Hz (**1d**) are not unexpected.
- (6) Through-space F,F spin–spin coupling is generally dominated by the FC term. Only for  $\alpha=90^\circ$  does the PSO term play a major role due to excitations from  $lp(\pi_{ip})$  to  $\sigma^*(FH)$  orbitals. These excitations are typical of **1**, but become less efficient for C–F bonds of **2** where the PSO coupling mechanism is not significant.
- (7) FC coupling represents the leading contribution to  ${}^4J(F,F)$  in **2**. The FC term in turn is dominated by through-space coupling (75.3 Hz), which by  $\sigma$  through-bond coupling (–19.5 Hz) is compensated to the final FC term of 56.5 Hz. Model studies of **1** show that the through-space FC coupling mechanism is provided mainly by  $lp(\sigma)$ – $lp(\sigma)$  coupling.
- (8) The SD contributions from the  $\pi$  system on the one hand and the  $\sigma(CF)$  bonds on the other hand are non-negligible, and it is not justified to neglect them as has been done in previous investigations [9,12]. The leading contributions from the naphthalene  $\pi$  system (–5 Hz) and the  $\sigma(CH)$  bonds (5 Hz) cancel each other in **2**. Substitutions in **2** may disturb this compensation and lead to sizable SD terms as shown by Contreras and co-workers [20].
- (9) Dimer **1** is suitable as a model for **2** only as far as the through-space part of the FC term is concerned. Model **1** fails to fully describe the spin-spin coupling in **2** in two ways: First, the FC term in **2** has large through-bond contributions, which of course cannot be described by a model for through-space coupling. Secondly, **1** fails also to reproduce the through-space part of the coupling in **2** because model **1** possesses a large PSO term, which has no counterpart in **2**. This dependence of the non-contact terms on the chemical environment of the coupling F nuclei is in line with the findings of Barone et al. in [30].
- (10) Generalizing (9), model systems as **1** are suitable for the description of FF coupling only if (i) the through-bond path between the two F atoms is long enough to exclude through-bond coupling in the real system and (ii) non-contact coupling

terms play no major role. Both conditions are fulfilled in systems where the two coupling F atoms are positioned head-to-head, i.e. for  $\alpha \approx 180^\circ$ .

## Acknowledgement

Calculations were done on the supercomputers of the Nationellt Superdatorcentrum (NSC), Linköping, Sweden. D.C. thanks the NSC for a generous allotment of computer time. J.G. thanks Carl Tryggers Stiftelse for financial support.

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