# On the Usage of Locally Dense Basis Sets in the Calculation of NMR Indirect Nuclear Spin–Spin Coupling Constants: Vicinal Fluorine–Fluorine Couplings

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## Abstract

Locally dense basis sets (<DBSs) were developed for correlated *ab initio* calculations of vicinal fluorine–fluorine indirect nuclear spin–spin couplings in several saturated and unsaturated fluorinated hydrocarbons. We find that the choice of the basis set for each atom belonging to our studied model compounds depends on its location with respect to the coupled fluorine atoms and on the *cis/trans* or *synperiplanar/antiperiplanar* conformation of the molecule. Carbon atoms in the bonding path connecting the coupled fluorine atoms have to be described with better basis sets than the carbon atoms outside this path. For the hydrogen atoms directly connected to the coupling pathway in molecules with *trans* or *antiperiplanar* conformations and for all hydrogen atoms not directly connected to the coupling pathway one can employ a minimal basis set with only one s-function. Employing these type of LDBSs we can reduce the number of necessary basis functions by about 30% without losing more than about 1 Hz in accuracy. The analysis of the four contributions to the vicinal fluorine–fluorine coupling constants shows that the non-contact orbital paramagnetic term is the most important contribution followed by the also non-contact spin-dipolar term. The Fermi contact term is the largest contribution only in the *synperiplanar* conformations of 1,2-difluoroethane and -propane.

## Contents

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## 1. INTRODUCTION

The parameters of nuclear magnetic resonance (NMR) spectroscopy, i.e., chemical shift and indirect nuclear spin–spin coupling constant $J$, are useful tools in the analysis of chemical structures. As an example, important progress was recently made in the determination of three-dimensional structures of proteins and nucleic acids in solution by NMR spectroscopy [1]. Vicinal spin–spin coupling constants hereby play an important role in the determination of torsional angles. Theoretical predictions of chemical shifts and coupling constants can give the necessary insight into the physical mechanism involved.

However, accurate calculations of indirect nuclear spin–spin coupling constants are computationally very demanding. Jens Oddershede has contributed substantially to this field over the years [2–22]. One of the questions he addressed so far was the selection of an optimal basis set of Gaussian-type functions [10,20] which plays an important role in obtaining converged results within reasonable computational cost. The search for optimized basis sets which allow for the quantitative reproduction of experimental results has recently attracted much attention again [20,23–27]. The optimized basis sets turn out to be rather large, too large for accurate calculations on anything but small molecules. Provasi *et al.* [25] therefore proposed recently to make use of the old idea of locally dense basis sets (LDBSs) [28,29] also in the calculation of spin–spin couplings. This approach has in the meantime been used in several theoretical studies [30–40]. The evident advantages of this approach are: (i) the reduction of the computational cost without significant loss in the accuracy; (ii) the possibility of increasing the level of approximation, mainly of electronic correlation, in the calculations; and (iii) to obtain information about the way the coupling constants are transmitted in the molecule. Apart from the first LDBS study by Provasi *et al.* on the vicinal proton–proton couplings in monohalogen substituted ethane [25] no systematic investigation of couplings between other nuclei has been reported so far. The purpose of the present work is therefore to study the performance of LDBSs in the calculation of vicinal fluorine–fluorine coupling constants, ${}^{3}J_{\mathrm{F-F}}$, in saturated and unsaturated hydrocarbons. As model systems we have chosen difluoroethyne (**1**), *trans*-1,2-difluoroethene (**2**), *trans*-1,2-difluoropropene (**3**), *cis*-1,2-difluoroethene (**4**), *cis*-1,2-difluoropropene (**5**), *antiperiplanar*-1,2-difluoroethane (**6**)[1], *antiperiplanar*-1,2-difluoropropane (**7**), *synperiplanar*-1,2-difluoroethane (**8**) and *synperiplanar*-1,2-difluoropropane (**9**). The study is focused on two main purposes:

(a) To analyze the sensitivity of this coupling on the basis set employed.
(b) To design optimized LDBSs for the calculation of vicinal F–F couplings

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[1] The prefixes *synperiplanar* and *antiperiplanar* will often be abbreviated as *spp* and *app* in the following.

which maximize the ratio between the accuracy of the results and the size of the basis set.

Fluorinated organic compounds and their NMR spectra have recently attracted much attention due to their important biological activity and as promising candidates for quantum computers [41]. Fluorine has been incorporated into alpha-helices [42,43], proteins [44,45] and bioactive small molecules [46–49] as NMR probes for aggregation, microenvironmental structure and binding site interactions. Several classes of medicines contain fluorine atoms, which allow to monitor their transport *in vivo* in the human body by magnetic resonance imaging techniques [50]. Furthermore, unusually large F–F coupling constants have been predicted for conjugated systems [39].

We have employed the second-order polarization propagator approximation (SOPPA) in this study, a method which was mainly developed by Jens Oddershede and his co-workers [3,4,20,51–56]. Barone *et al.* [32] have recently shown that SOPPA reproduces the vicinal F–F couplings reasonably well in 1,2-difluoroethene.

The remaining chapter is divided into four sections. The following two sections review briefly the theory of spin–spin coupling constant calculations, report the computational details of the calculations and describe the nomenclature used in this work. In Section 4, the results of the LDBS study are discussed. It starts with a subsection on the converged results for the model systems studied here. Finally, the last section summarizes the conclusions of the present work.

## 2. THEORY

The non-relativistic theory of the indirect spin–spin coupling constant between two nuclei M and N was formulated by Ramsey, who proposed four contributions for it [57]. These four contributions arise from two different mechanisms by which a nuclear magnetic moment perturbs the surrounding electrons and the induced electronic current or spin polarization generates a magnetic field in the region close to the other nucleus that interacts with its nuclear magnetic moment. The interaction of the nuclear spin with the spin of the electrons is accounted for by the Fermi contact (FC) and spin dipolar (SD) contributions, while their interaction with the orbital angular momentum of the electrons is given by the orbital paramagnetic (OP) and orbital diamagnetic (OD) contributions.

The first three contributions, which depend on the first-order wave function, can be expressed as sum over states:

$$J^{\mathrm{A}}_{\mathrm{MN}} = \frac{2}{3}\frac{\gamma_{\mathrm{M}}\gamma_{\mathrm{N}}}{h}\sum_{\alpha=x,y,z}\sum_{n\neq 0}\frac{\langle 0|(\vec{O}^{\mathrm{A}}_{\mathrm{M}})_{\alpha}|n\rangle\langle n|(\vec{O}^{\mathrm{A}}_{\mathrm{N}})_{\alpha}|0\rangle}{E_0 - E_n} \tag{1}$$

$$(\vec{O}^{\mathrm{OP}}_{\mathrm{M}})_{\alpha} = \left(\frac{\mu_0}{4\pi}\right)\left(\frac{e\hbar}{m_e}\right)\sum_i \frac{(\vec{l}_{i\mathrm{M}})_{\alpha}}{r^3_{i\mathrm{M}}} \tag{2}$$

$$(\vec{O}_{\mathrm{M}}^{\mathrm{FC}})_\alpha = \left(\frac{\mu_0}{4\pi}\right)\left(\frac{4\pi g_e e\hbar}{3m_e}\right)\sum_i (\vec{s}_i)_\alpha \delta(\vec{r}_{i\mathrm{M}}) \tag{3}$$

$$(\vec{O}_{\mathrm{M}}^{\mathrm{SD}})_\alpha = \left(\frac{\mu_0}{4\pi}\right)\left(\frac{g_e e\hbar}{2m_e}\right)\sum_i \frac{3(\vec{s}_i \cdot \vec{r}_{iK})(\vec{r}_{iK})_\alpha - r_{iK}^2(\vec{s}_i)_\alpha}{r_{iK}^5} \tag{4}$$

The magnetogyric ratio of the nucleus M is $\gamma_{\mathrm{M}}$, $\vec{r}_{i\mathrm{M}} = \vec{r}_i - \vec{r}_{\mathrm{M}}$ is the difference between the position vectors of the electron $i$ and the nucleus M, $\vec{s}_i$ is the spin angular momentum operator and $\vec{l}_i$ the orbital angular momentum operator of the $i$th electron, $\delta(x)$ is the Dirac delta function and all the other symbols have their usual meaning [58].

The OD term is an average value of the ground state:

$$J_{\mathrm{MN}}^{\mathrm{OD}} = \frac{1}{3}\frac{\gamma_{\mathrm{M}}\gamma_{\mathrm{N}}}{h}\sum_{\alpha,\beta=x,y,z}\langle 0|(\vec{O}_{\mathrm{MN}}^{\mathrm{OD}})_{\alpha\beta}|0\rangle \tag{5}$$

with

$$(\vec{O}_{\mathrm{MN}}^{\mathrm{OD}})_{\alpha\beta} = \left(\frac{\mu_0}{4\pi}\right)^2 \frac{e^2\hbar^2}{m_e}\sum_i \left(\frac{\vec{r}_{i\mathrm{N}} \cdot \vec{r}_{i\mathrm{M}} - (\vec{r}_{i\mathrm{N}})_\alpha(\vec{r}_{i\mathrm{M}})_\beta}{r_{i\mathrm{N}}^3 r_{i\mathrm{M}}^3}\right) \tag{6}$$

although it can also be formulated as a sum over states [59].

Excited triplet states $|n\rangle$ with energy $E_n$ are included in the sum for the FC and SD terms, while excited singlet states contribute to the OP term. Recalling the spectral representation of the polarization propagator for zero frequency $\omega$ [60]

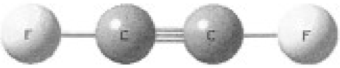
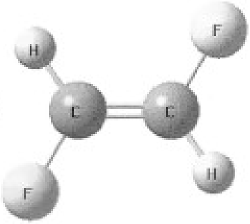
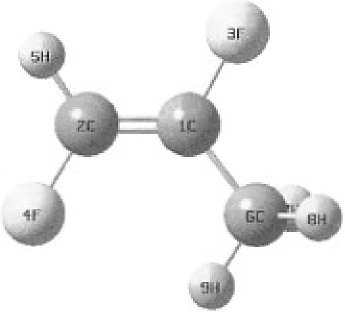
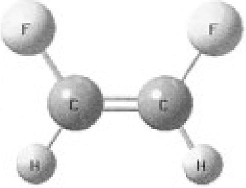
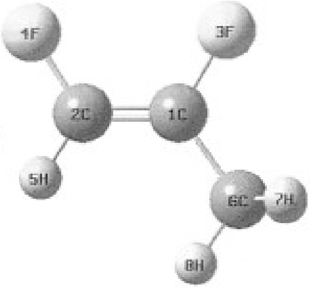
$$\langle\langle P; Q\rangle\rangle_{\omega=0} = 2\sum_{n\neq 0}\frac{\langle 0|P|n\rangle\langle n|Q|0\rangle}{E_0 - E_n} \tag{7}$$

it can be seen that those three contributions can be calculated without knowing explicitly the excited states. Within the random phase approximation (RPA) [61] or time-dependent Hartree–Fock theory [62] the polarization propagator is evaluated consistently through first order in the fluctuation potential, i.e., the difference between the instantaneous interelectron interaction and the average interaction of the Hartree–Fock approximation. In the SOPPA [52] the single excitation contributions to the polarization propagator are evaluated through second order in Møller–Plesset perturbation theory [63,64]. Explicit expressions for SOPPA have been given elsewhere [4,20,53–56].

## 3. COMPUTATIONAL DETAILS AND NOMENCLATURE

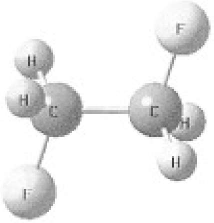
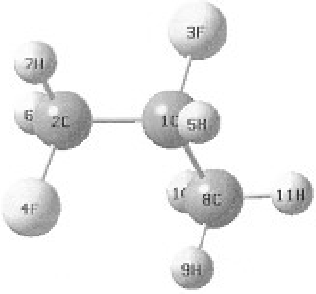
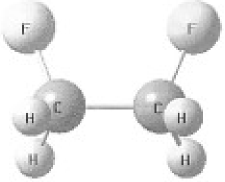
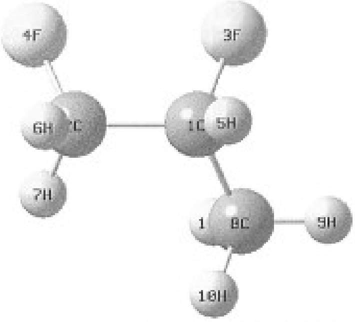
The geometry for all the studied model compounds was optimized with the Gaussian98 program [65] at the MP2/cc-pVTZ level using the very tight option. The internal coordinates of the optimized geometries are given in Table 1. The total $J_{\mathrm{F-F}}$ coupling constants and their four contributions were calculated with

**Table 1.** Geometries (in Å and degrees) calculated at MP2/cc-pVTZ level

| Compound | Salient geometric parameters |
|---|---|
| **(1)**  | $r$(FF) = 3.7673, $r$(CF) = 1.2864,<br>$r$(CC) = 1.1945 |
| **(2)**  | $r$(FF) = 3.5372, $r$(CF) = 1.3400,<br>$r$(CC) = 1.3258, $r$(CH) = 1.0778,<br>$\angle$(FCC) = 120.1701,<br>$\angle$(FCH) = 115.1236 |
| **(3)**  | $r$(FF) = 3.5338, $r$(1C3F) = 1.3505,<br>$r$(2C4F) = 1.3443, $r$(1C2C) = 1.3293,<br>$r$(1C6C) = 1.4790, $r$(2C5H) = 1.0772,<br>$\angle$(3F1C2C) = 117.1972,<br>$\angle$(4F2C1C) = 120.6879,<br>$\angle$(2C1C6C) = 128.1424,<br>$\angle$(4F2C5H) = 114.9643 |
| **(4)**  | r(FF) = 2.7740, r(FC) = 1.3350,<br>r(CC) = 1.3264, r(CH) = 1.0773,<br>$\angle$(FCC) = 122.8302,<br>$\angle$(FCH) = 115.2188 |
| **(5)**  | $r$(FF) = 3.5338, $r$(1C3F) = 1.3443,<br>$r$(2C4F) = 1.3386, $r$(1C2C) = 1.3299,<br>$r$(1C6C) = 1.4813, $r$(2C5H) = 1.0768,<br>$\angle$(3F1C2C) = 119.9497,<br>$\angle$(4F2C1C) = 122.3318,<br>$\angle$(2C1C6C) = 125.5068,<br>$\angle$(4F2C5H) = 114.9868 |

*(continued)*

**Table 1.** *(continued)*

| Compound | Salient geometric parameters |
|---|---|
| **(6)**  | $r(\mathrm{FF}) = 3.5419$, $r(\mathrm{CF}) = 1.3838$,<br>$r(\mathrm{CC}) = 1.5107$, $r(\mathrm{CH}) = 1.0878$,<br>$\angle(\mathrm{FCC}) = 108.1414$,<br>$\angle(\mathrm{FCH}) = 108.8924$,<br>$\angle(\mathrm{HCH}) = 109.5053$ |
| **(7)**  | $r(\mathrm{FF}) = 3.5404$, $r(\mathrm{1C3F}) = 1.3936$,<br>$r(\mathrm{2C4F}) = 1.3846$, $r(\mathrm{1C2C}) = 1.5143$,<br>$r(\mathrm{1C5H}) = 1.0900$, $r(\mathrm{1C8C}) = 1.5056$,<br>$r(\mathrm{2C6H}) = 1.0894$, $r(\mathrm{2C7H}) = 1.0877$,<br>$\angle(\mathrm{3F1C2C}) = 105.8568$,<br>$\angle(\mathrm{4F2C1C}) = 109.1488$,<br>$\angle(\mathrm{2C1C8C}) = 112.9819$,<br>$\angle(\mathrm{2C1C5H}) = 109.7840$,<br>$\angle(\mathrm{4F2C6H}) = 108.6942$,<br>$\angle(\mathrm{4F2C7H}) = 108.7976$ |
| **(8)**  | $r(\mathrm{FF}) = 2.5163$, $r(\mathrm{CF}) = 1.3754$,<br>$r(\mathrm{CC}) = 1.5425$, $r(\mathrm{CH}) = 1.0880$,<br>$\angle(\mathrm{FCC}) = 110.7310$,<br>$\angle(\mathrm{FCH}) = 108.0009$,<br>$\angle(\mathrm{HCH}) = 108.8507$ |
| **(9)**  | $r(\mathrm{FF}) = 2.5022$, $r(\mathrm{1C3F}) = 1.3832$,<br>$r(\mathrm{2C4F}) = 1.3754$, $r(\mathrm{1C2C}) = 1.5453$,<br>$r(\mathrm{1C5H}) = 1.0901$, $r(\mathrm{1C8C}) = 1.5079$,<br>$r(\mathrm{2C6H}) = 1.0887$, $r(\mathrm{2C7H}) = 1.0897$,<br>$\angle(\mathrm{3F1C2C}) = 109.3907$,<br>$\angle(\mathrm{4F2C1C}) = 111.2098$,<br>$\angle(\mathrm{2C1C8C}) = 112.0529$,<br>$\angle(\mathrm{2C1C5H}) = 109.4548$,<br>$\angle(\mathrm{4F2C6H}) = 108.1834$,<br>$\angle(\mathrm{4F2C7H}) = 107.6864$ |

the Dalton program package [66]. Electronic correlation was included in all calculations by the SOPPA method [4,20,52].

In the calculations of the F–F spin–spin couplings we employed the following basis sets:

(i) standard basis sets, cc-pVXZ (with X=D or T) and their augmented versions, aug-cc-pVXZ (which include diffuse functions) [67–69],
(ii) optimized NMR-*J* basis sets, aug-cc-pVTZ-J [26,70], which permit an adequate treatment of the cusp of the wave function at the nucleus and give therefore a very good description of the FC term (Ref. [26] and references cited therein),
(iii) a minimal basis set, containing only one s-type Gaussian function with coefficient 1.159 for hydrogen and two s-type Gaussian functions with coefficients 3.319 and 0.9059 and one p-type Gaussian function with coefficient 0.3827 for carbon.

We have investigated several series of LDBSs which were generated as different combinations of these basis sets for the non-coupled atoms and the aug-cc-pVTZ-J basis set for the coupled fluorine atoms. The results are presented graphically in Figs 1–10.

In order to simplify the discussion of the different LDBSs we use the following acronyms for the basis sets:

apTJ : for aug-cc-pVTZ-J
apT : for aug-cc-pVTZ
pT : for cc-pVTZ
apD : for aug-cc-pVDZ
pD : for cc-pVDZ
m : for the minimal basis set of only one *s*-type function with coefficient 1.159 for hydrogen and two *s*-type Gaussian functions with coefficients 3.319 and 0.9059 and one *p*-type Gaussian function with coefficient 0.3827 for carbon

A LDBS is then identified by listing the labels for the basis sets separated by '/'. The first label is for the coupled fluorine atoms, the second is for the atoms in the structure of interest, i.e., in this work the coupling path (here always carbon), the third labels are for atoms directly bond to the atoms in the coupling path and the last is for atoms not directly bond to the coupling path. When more than one type of atoms belong to a group, e.g., '6C' and '5H' in (**3**), the basis set labels will then appear in order of decreasing atomic number. The label LDBS apTJ/apTJ/[pT/pD]/m for 1,2-difluoropropen (**3**) or (**5**), e.g., stands therefore for a LDBS with the aug-cc-pVTZ-J basis set on the fluorine atoms and on the doubly bonded carbon atoms, the cc-pVTZ basis set on the carbon atom in the methyl group, the cc-pVDZ basis set on the vinyl hydrogen and the minimal basis set on the hydrogen atoms in the methyl group. In the figures the first label representing the basis set for the coupled fluorine atoms was dropped for the sake of readability. In Table 2 the best basis set for each molecule is given.

**Table 2.** The best basis sets for the molecules included in this study

| Molecule | Basis[a] | Number |
|---|---|---|
| (**1**) Difluoroethyne | apTJ/apTJ | 184 |
| (**2**) *trans*-1,2-difluoroethene | apTJ/apTJ/apTJ | 224 |
| (**3**) *trans*-1,2-difluoropropene | apTJ/apTJ/[apTJ/pD]/m | 238 |
| (**4**) *cis*-1,2-difluoroethene | apTJ/apTJ/apTJ | 224 |
| (**5**) *cis*-1,2-difluoropropene | apTJ/pT/[pT/m]/m | 186 |
| (**6**) *antiperiplanar*-1,2-difluoroethane | apTJ/apTJ/pT | 240 |
| (**7**) *antiperiplanar*-1,2-difluoropropane | apTJ/apTJ/[apTJ/pD]/m | 248 |
| (**8**) *synperiplanar*-1,2-difluoroethane | apTJ/apTJ/pT | 240 |
| (**9**) *synperiplanar*-1,2-difluoropropane | apTJ/apTJ/[apTJ/pD]/m | 248 |

[a] See Section 3 for nomenclature used.

## 4. RESULTS

The results of the LDBS study are presented graphically in Figs 1–10. The figures show the deviation of the results for the total vicinal F–F couplings as well as the OP, SD and FC contributions obtained with the given LDBS from the corresponding result obtained with the largest basis set as given in Table 2. The OD contribution is not included in the figures, because the changes in OD term are for most basis sets smaller than 0.01 Hz and the largest change is only 0.02 Hz. The label representing the basis set for the coupled fluorine atoms is not included in the figures.

The whole set of values for $^3J_{F-F}$ in the studied compounds are available on request.

### 4.1. Difluoroethyne

From Table 3 we can see that the negative OP contribution is the most important term in the vicinal F–F coupling in difluoroethyne (**1**). The SD and FC terms are

**Table 3.** $^3J_{^{19}F-^{19}F}$ coupling constants and their four contributions (in Hz) calculated with the best set (see Table 2) at the SOPPA level at MP2/cc-pVTZ geometry

| | $J^{OD}$ | $J^{OP}$ | $J^{SD}$ | $J^{FC}$ | $J$ | Exp. |
|---|---|---|---|---|---|---|
| (**1**) | −1.82 | −54.64 | 28.39 | 6.55 | −21.52 | 2.1[a] |
| (**2**) | −1.77 | −143.27 | 22.69 | −11.28 | −133.62 | −132.7[b] |
| (**3**) | −1.70 | −134.90 | 18.44 | −12.02 | −130.18 | |
| (**4**) | −0.42 | −38.44 | 24.21 | 0.58 | −14.06 | −18.7[c] |
| (**5**) | −0.21 | −29.50 | 22.31 | 0.96 | −6.43 | |
| (**6**) | −1.55 | −39.18 | 14.34 | −10.54 | −36.93 | −30.0[d] |
| (**7**) | −1.50 | −29.23 | 15.13 | −12.22 | −27.82 | |
| (**8**) | 0.19 | −12.60 | 8.94 | 35.80 | 32.32 | |
| (**9**) | 0.35 | −18.73 | 7.37 | 40.25 | 29.24 | |

[a] Ref. [71].
[b] Ref. [72].
[c] Ref. [73].
[d] Estimated [74].

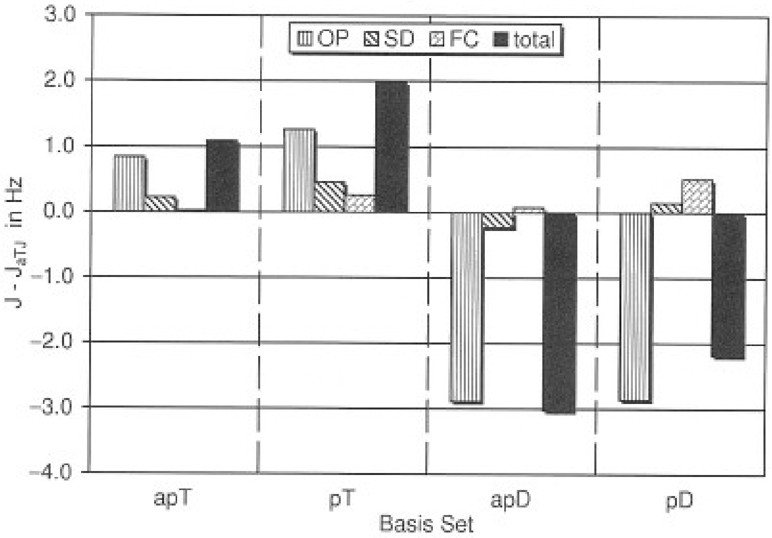


**Fig. 1.** Dependence of the vicinal F–F coupling constant in difluoroethyne on the basis set used for the carbon atoms: Deviation (in Hz) of the locally dense basis set result from the calculation with the apTJ/apTJ basis set. Only the basis sets on the non-coupled atoms are used as labels on the basis set axis. The apTJ basis set was used for fluorine in all calculations.

positive in this molecule and amount to only about 50 and 10% of the OP term, respectively.

In Fig. 1, the results of the LDBS study are shown. Usage of standard basis sets of valence triple and double $\zeta$ quality on the carbon atoms changes the vicinal F–F couplings by at most 3 Hz while the basis set can be reduced by 64 functions or 35%. The changes are a lot more important for the OP term than for the FC and SD terms. It is interesting to note that employing the apT or pT basis sets on carbon increases the OP term by ~1 Hz whereas the apD and pD basis sets reduce it by ~3 Hz. The additional diffuse functions in the apT and apD basis sets on the carbon atoms seem to be of no importance for the vicinal F–F couplings in difluoroethyne. The LDBS apTJ/pT (aug-cc-pVTZ-J on fluorine and cc-pVTZ on carbon) reproduces each term quite well with respect to the calculation with the most complete basis set. As pointed out in our previous paper on long-range F–F couplings [39] there is a large difference between our SOPPA result and the only available experimental result. Earlier semi-empirical calculations [75] predict −85.4 Hz, which is further away from the experimental value. The reason for this disagreement should be investigated further.

## 4.2. *trans*-1,2-difluoroethene and *trans*-1,2-difluoropropene

Analyzing the four contributions to the vicinal F–F couplings in *trans*-1,2-difluoroalkanes, (**2**) and (**3**), in Table 3 one sees that the large and negative OP term is the all dominating contribution, whereas the SD and FC term amount to only about 16 and 8% of the OP term. The FC term is negative as for all *trans* or *app* vicinal couplings.

Despite the dominance of the OP term it is primarily the FC term which is influenced by the choice of the basis set on the non-coupled atoms in *trans*-1,2-difluoroethene (**2**). Only when we reduce the basis set on the carbon atoms to the cc-pVDZ level (LDBS apTJ/pD/pD), the change in the OP term (1.9 Hz) becomes larger than the change in the FC term (1.8 Hz) and the error in the total coupling exceeds 4 Hz. Similarly we observe larger changes in the OP and SD term when the basis set on the hydrogen atoms is reduced to the minimal basis set (LDBS apTJ/pT/m). However, the errors in the OP and SD term cancel nearly, so that the change in the total coupling is almost identical in the apTJ/pT/pD and apTJ/pT/m basis sets and is still $<1$ Hz.

Using the aug-cc-pVTZ-J basis set for fluorine, cc-pVTZ for carbon and cc-pVDZ for hydrogen (LDBS apTJ/pT/pD) it is possible to reproduce each contribution to the vicinal F–F coupling from the most complete basis set apTJ/apTJ/apTJ without considerable loss of accuracy ($<1$ Hz) while reducing the size of the basis set by 62 functions or 28%.

Turning our attention now to *trans*-1,2-difluoropropene (**3**) we can see that the methyl group induces only minor changes in the vicinal *trans*-F–F coupling constant. The absolute values of the OP and SD terms are reduced while the FC becomes numerically larger. Comparing the individual terms we can set that the changes increase in the order FC < total < SD < OP.

With the LDBS study on *trans*-1,2-difluoropropene, Fig. 3, we wanted to investigate primarily the effect of the basis sets for the carbon atom in the methyl group. Therefore, we used the minimal basis set for the methyl hydrogens in all

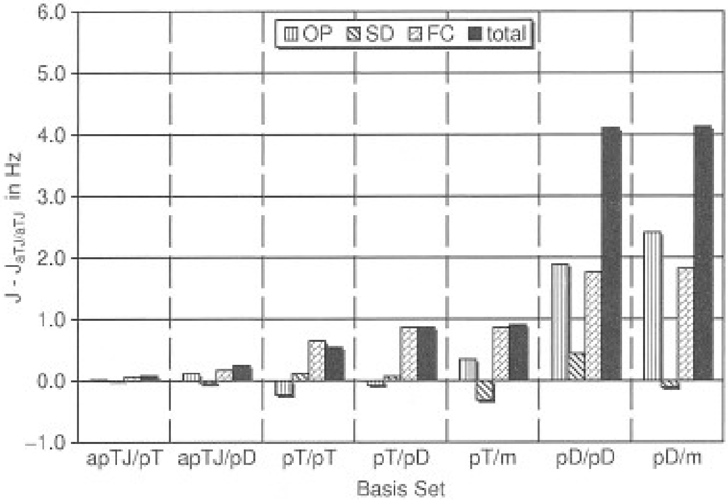


**Fig. 2.** Dependence of the vicinal *trans* F–F coupling constant in *trans*-1,2-difluoroethene on the basis set used for the carbon atoms and hydrogen atoms: Deviation (in Hz) of the locally dense basis set result from the calculation with the apTJ/apTJ/apTJ basis set. Only the basis sets on the non-coupled atoms are used as labels on the basis set axis. The apTJ basis set was used for fluorine in all calculations.

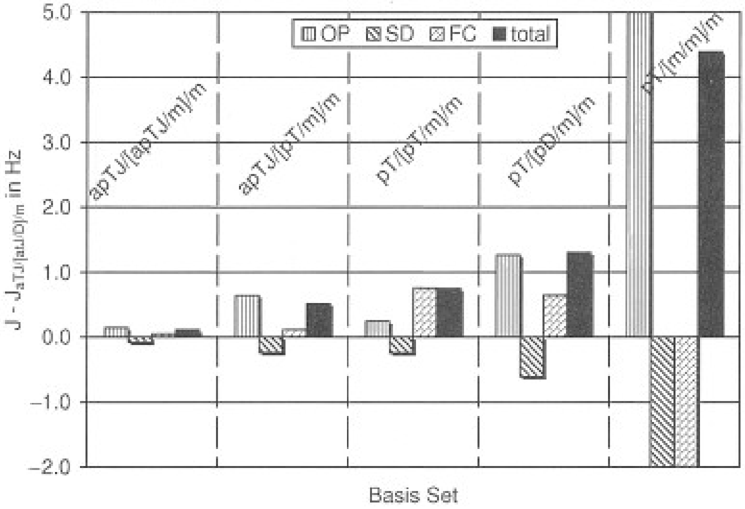


**Fig. 3.** Dependence of the vicinal *trans* F–F coupling constant in *trans*-1,2-difluoropropene calculated at the SOPPA level on the basis set used for the carbon atoms and hydrogen atoms: Deviation (in Hz) of the locally dense basis set result from the calculation with the apTJ/apTJ/[apTJ/pD]/m basis set. Only the basis sets on the non-coupled atoms are used as labels on the basis set axis. The apTJ basis set was used for fluorine in all calculations.

calculations shown in Fig. 3. Reducing the basis set for the vinyl hydrogen from cc-pVDZ to the minimal basis set introduces only insignificant changes in the order of 0.1 Hz and this basis set was thus used in all the other calculations for this molecule. Similarly the changes in the total coupling constant introduced by reducing the basis set for the two doubly bonded carbon atoms to the cc-pVTZ level are small. However, using the minimal basis for the carbon of the methyl group produces important changes in the OP, SD and FC contributions (LDBS apTJ/pT/[m/m]/m) and a total error of ~4 Hz, whereas the basis set cc-pVDZ (LDBS apTJ/pT/[pD/m]/m) gives good results for each term and a total error of only 1.3 Hz while reducing the size of the basis set by 68 functions or 29% with respect to the apTJ/apTJ/[apTJ/pD]/m basis set.

### 4.3. *cis*-1,2-difluoroethene and *cis*-1,2-difluoropropene

The OD and OP contributions and the total value of the vicinal F–F coupling constants in *cis*-1,2-difluoroethene (**4**) and *cis*-1,2-difluoropropene (**5**) are all negative, whereas the SD and FC terms are positive, as can be seen from Table 3. The OP and SD terms are of the same order of magnitude whereas the FC terms are close to zero.

The basis set study for *cis*-1,2-difluoroethene (**4**), Fig. 4, shows that the hydrogens are well described with the cc-pVDZ basis set (e.g., LDBS apTJ/apTJ/pD, apTJ/apT/pD or apTJ/pT/pD), whereas with the minimal basis set the changes in the OP term and thus the total vicinal F–F coupling become about −3 Hz (e.g., LDBS apTJ/apTJ/m, apTJ/apT/m or apTJ/pT/m). It is interesting to note that

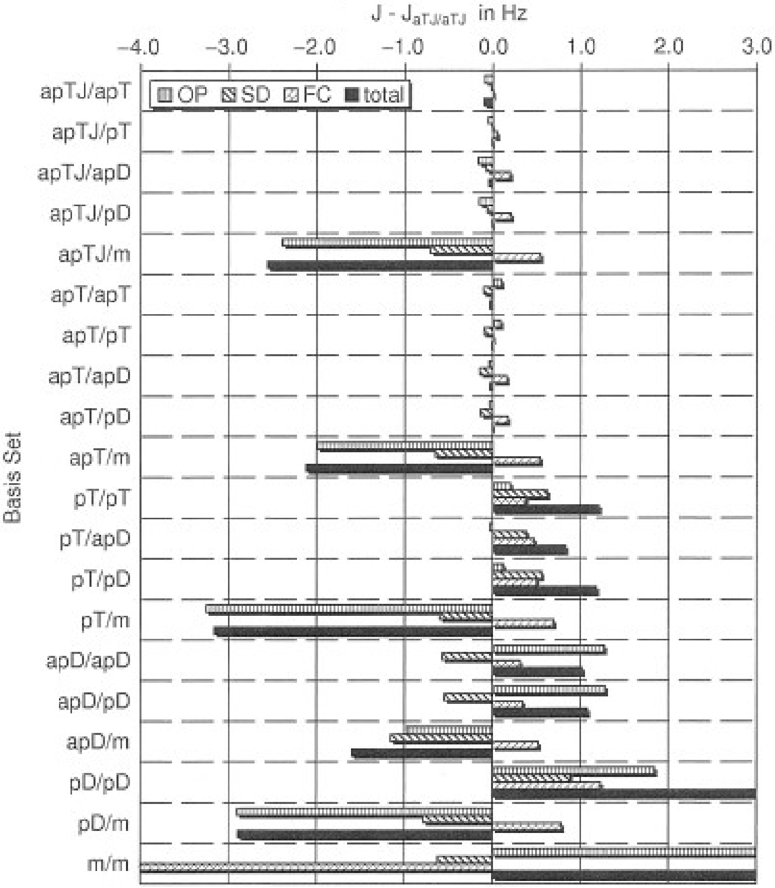


**Fig. 4.** Dependence of the vicinal *cis* F–F coupling constant in *cis*-1,2-difluoroethene calculated at the SOPPA level on the basis set used for the carbon atoms and hydrogen atoms: Deviation (in Hz) of the locally dense basis set result from the calculation with the apTJ/apTJ/apTJ basis set. Only the basis sets on the non-coupled atoms are used as labels on the basis set axis. The apTJ basis set was used for fluorine in all calculations.

all the calculations with the minimal basis for hydrogen give larger errors in the total F–F couplings in the *cis*-isomers than it was the case for the *trans*-isomers.

Comparing the LDBS calculations with the cc-pVTZ and aug-cc-pVDZ basis set on the carbon atoms shows that in the former case the changes are mainly in the SD and FC term, whereas in the latter case there are large changes in the OP term, which are partially reduced by a now negative change in the SD term. The errors in the FC term are actually slightly smaller in the aug-cc-pVDZ basis set. The changes in the total vicinal F–F coupling constants are comparable in both basis sets (~1 Hz). Nevertheless, the cc-pVTZ basis should be preferred for carbon (LDBS apTJ/pT/pD) due to the smaller changes in the individual contributions.

Calculations of the vicinal F–F coupling constant for *cis*-1,2-difluoropropene (**5**) suffer from triplet instabilities, when the aug-cc-pVTZ-J basis set is used

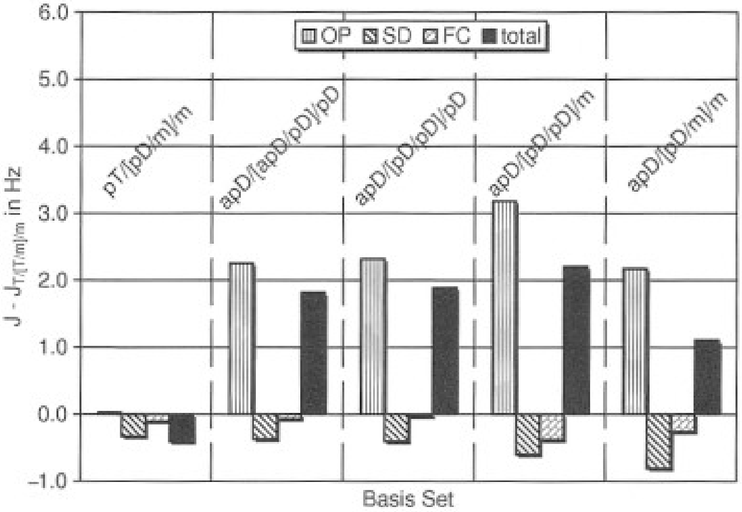


**Fig. 5.** Dependence of the vicinal *cis* F–F coupling constant in *cis*-1,2-difluoropropene on the basis set used for the carbon and hydrogen atoms: Deviation (in Hz) of the locally dense basis set result from the calculation with the apTJ/pT/[pT/m]/m basis set. Only the basis sets on the non-coupled atoms are used as labels on the basis set axis. The apTJ basis set was used for fluorine in all calculations.

for the doubly bonded carbon atoms (LDBS apTJ/apTJ/[apTJ/pD]/m, apTJ/apTJ/[apTJ/m]/m, apTJ/apTJ/[pT/m]/m). We choose therefore the apTJ/pT/[pT/m]/m basis set as reference. From Table 3 one can see that the methyl group induces only minor changes in the vicinal *cis* F–F coupling constant. The absolute values of the OP and SD terms are reduced while the FC becomes larger. However, the changes in the FC and SD are rather small and of opposite sign such that the change in the total coupling is dominated by the OP term.

Figure 5 shows that the best overall description of the coupling constants is obtained with the combination of cc-pVTZ on the doubly bonded carbon atoms, cc-pVDZ on the methyl carbon atom and the minimal basis set on all hydrogens (LDBS apTJ/pT/[pD/m]/m) – the same basis set as for the *trans*-isomer.

### 4.4. *app*-1,2-difluoroethane and *app*-1,2-difluoropropane

There are several similarities between the vicinal F–F coupling constants in *antiperiplanar* conformers of 1,2-difluoroalkanes, (**6**) and (**7**), and the corresponding *trans*-1,2-difluoroalkenes, (**2**) and (**3**). The sign of the four contributions is the same, the SD is positive and all other contributions as well as the total coupling constant are negative. Furthermore, the FC terms are almost identical and thus do not depend on the character of the C–C bond in the coupling pathway. The SD and OP contributions on the other hand are smaller in the *app*-1,2-difluoroalkanes, the SD term is only about 2/3 and the OP roughly 1/4 of the values in the *trans*-1,2-difluoroalkenes. Furthermore, the FC and SD contributions are very similar but of different sign and the total coupling constant becomes

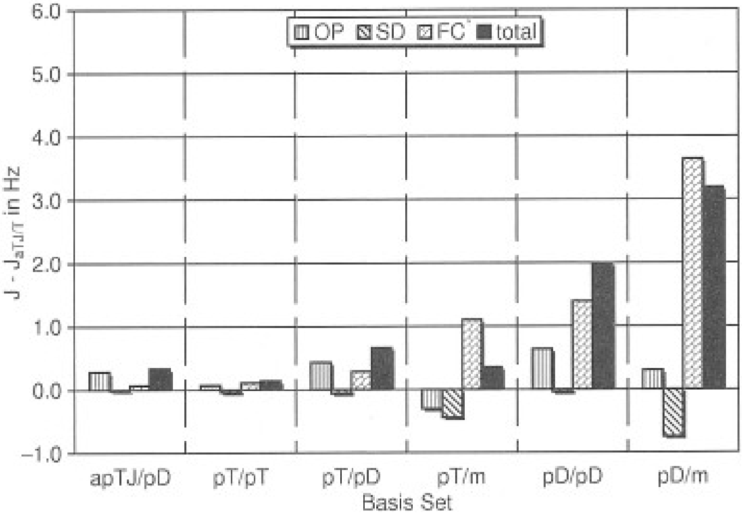


**Fig. 6.** Dependence of the vicinal *app* F–F coupling constant in *antiperiplanar*-1,2-difluoroethane on the basis set used for the carbon and hydrogen atoms: Deviation (in Hz) of the locally dense basis set result from the calculation with the apTJ/apTJ/pT basis set. Only the basis sets on the non-coupled atoms are used as labels on the basis set axis. The apTJ basis set was used for fluorine in all calculations.

therefore very close in value to the OP contribution. The introduction of the methyl group in *app*-1,2-difluoropropane (**7**) leads again to a reduction of the absolute value of the OP and a much smaller increase in the absolute value of the FC and SD term.

From Fig. 6 for *app*-1,2-difluoroethane (**6**) it can be seen that it is enough to describe each hydrogen with the cc-pVDZ basis set (LDBS apTJ/pT/pD), whereas with the minimal basis set on the hydrogen atoms the FC term change by more than 1 Hz (LDBS apTJ/pT/m). Nevertheless, the changes in the total coupling constant is still much less than 1 Hz due to a cancellation of errors. The carbon atoms are also well described by the cc-pVTZ basis set (LDBS apTJ/pT/pD). With this LDBS it is possible to reduce the size of the basis set by 68 functions (28%) without considerable loss of accuracy (<1 Hz). Using a smaller carbon basis sets, (LDBS apTJ/pD/pD) leads to larger errors in the FC term and the total coupling constant (~2 Hz). The extra diffuse functions in the augmented basis sets are again not necessary for describing the electronic densities around the carbon atoms in this molecule.

In the case of the *antiperiplanar* conformer of 1,2-difluoropropane (**7**) we studied again the influence of the basis for the carbon atom in the methyl group. For all hydrogen atoms we used the minimal basis set apart from the reference calculation where the cc-pVDZ basis set was employed on hydrogens '5H', '6H' and '7H'. The result, shown in Fig. 7, is the same as for *trans*-1,2-difluoropropene (**3**). The electron density around the methyl carbon, although it is out of the F–F bonding path, is not properly described with the minimal basis set. The OP, SD and FC terms are all not well reproduced by this calculation

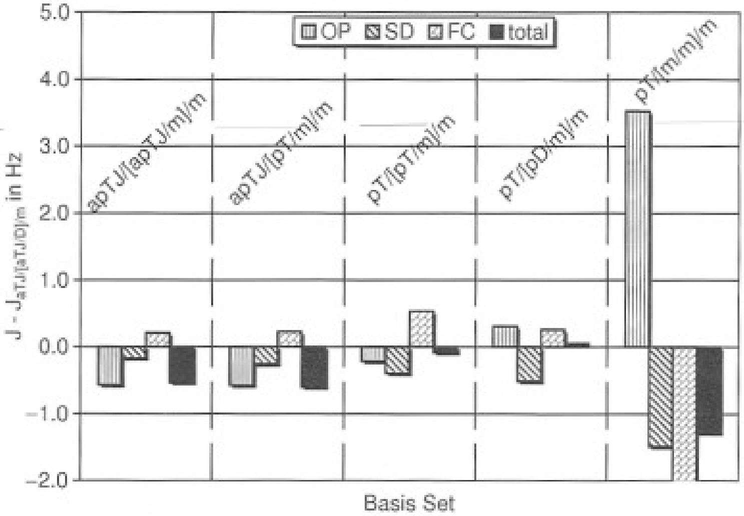


**Fig. 7.** Dependence of the vicinal *app* F–F coupling constant in *antiperiplanar*-1,2-difluoropropane on the basis set used for the carbon and hydrogen atoms: Deviation (in Hz) of the locally dense basis set result from the calculation with the apTJ/apTJ/[apTJ/pD]/m basis set. Only the basis sets on the non-coupled atoms are used as labels on the basis set axis. The apTJ basis set was used for fluorine in all calculations.

(LDBS apTJ/pT/[m/m]/m). Nevertheless, due to a cancellation of the errors, the change in the total coupling constant is only −1.3 Hz. With the cc-pVDZ basis set on the carbon in the methyl group, on the other hand, all terms are correctly reproduced (LDBS apTJ/pT/[pD/m]/m), which allows to reduce the basis set by 76 functions (31%) with respect to the more complete calculation.

A comparison of Figs 2 and 6 or 3 and 7 shows that the changes in the FC and often also in the OP term due to the smaller basis sets are generally smaller in the alkanes than in the alkenes.

### 4.5. *spp*-1,2-difluoroethane and *spp*-1,2-difluoropropane

Contrary to all the other molecules studied here, the FC term is the largest contribution to the vicinal F–F coupling constants in the *synperiplanar* conformers of the 1,2-difluoroalkanes (**8**) and (**9**). This is quite remarkable, because it is a factor of 40–50 larger than in the corresponding difluoroalkenes, (**4**) and (**5**), and because there is no significant difference between the *trans*-difluoroalkenes, (**2**) and (**3**), and the *app*-difluoroalkanes, (**6**) and (**7**). The second largest contribution is the negative OP term. However, the total F–F coupling constants are quite similar to the FC term, because the OP and SD terms are of the same order of magnitude but have opposite signs.

It can be seen from Fig. 8 that the minimal basis set on the hydrogen atoms produces larger errors in the OP term and FC term of 1,2-difluoroethane in the *synperiplanar* conformation (**8**) than in the *antiperiplanar* conformation (**6**). The same difference was also observed between the *trans* and *cis* couplings in the

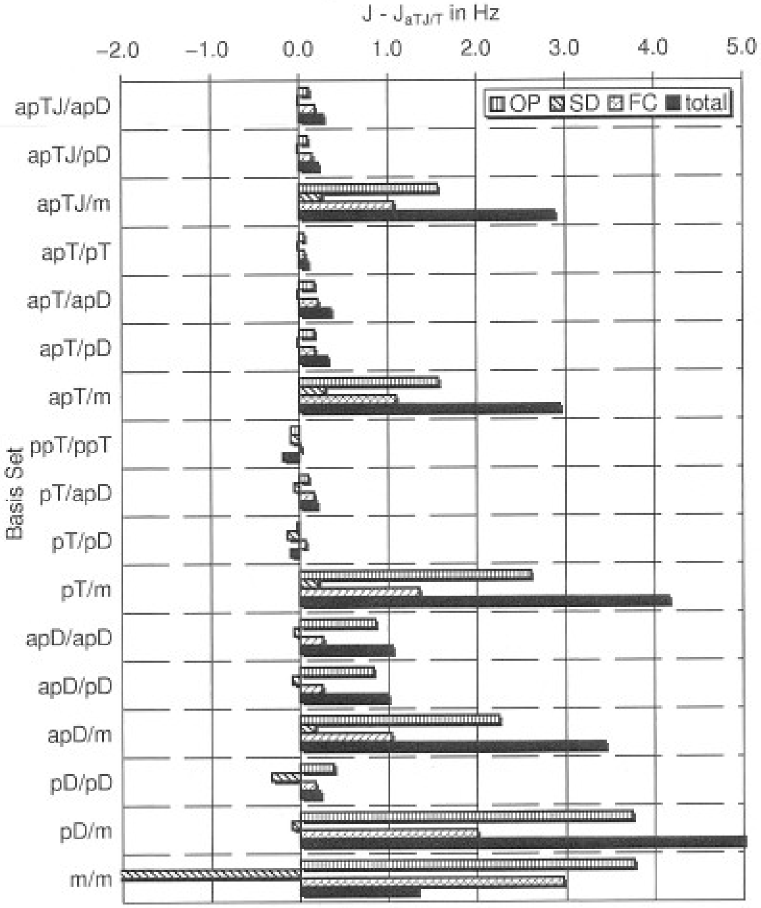


**Fig. 8.** Dependence of the vicinal *spp* F–F coupling constant in *synperiplanar*-1,2-difluoroethane on the basis set used for the carbon and hydrogen atoms: Deviation (in Hz) of the locally dense basis set result from the calculation with the apTJ/apTJ/pT basis set. Only the basis sets on the non-coupled atoms are used as labels for the basis set axis. The apTJ basis set was used for fluorine in all calculations.

difluoroalkanes, (**2**) and (**4**), and indicates a difference in the coupling pathway. But with the cc-pVDZ basis set for the hydrogen atoms one obtains good results (LDBS apTJ/apTJ/pD, apTJ/pT/pD, apTJ/apD/pD).

The carbon atoms are well described by the cc-pVTZ basis set. The F–F coupling is almost identical to the large basis set value. However, the size of the basis set can further be reduced by using the aug-ccpVDZ basis sets for the carbon atoms. Although the error in the OP term increases in this case, the change in the total coupling constants is still about 1 Hz only (LDBS apTJ/apD/pD).

Reducing the basis set for the non-methyl hydrogens to the minimal basis set gives also in *spp*-1,2-difluoropropane (**9**) a larger error as shown in Fig. 9. We have therefore carried out two series of basis set studies – one with the cc-pVDZ

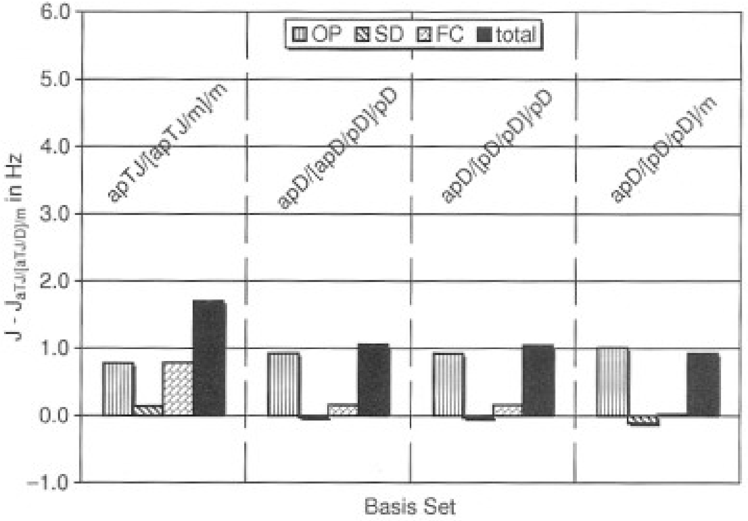


**Fig. 9.** Dependence of the vicinal *spp* F–F coupling constant in *synperiplanar*-1,2-difluoropropane on the basis set used for the carbon and hydrogen atoms: Deviation (in Hz) of the locally dense basis set result from the calculation with the apTJ/apTJ/ [apTJ/pD]/m basis set. Only the basis sets on the non-coupled atoms are used as labels for the basis set axis. The apTJ basis set was used for fluorine in all calculations.

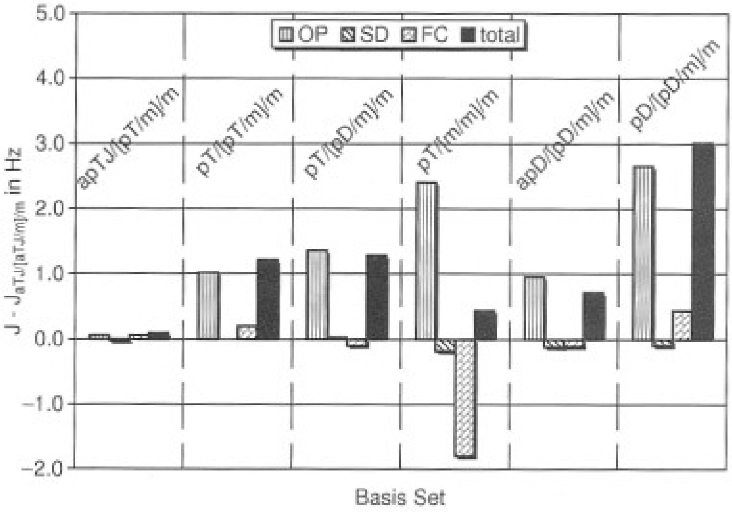


**Fig. 10.** Dependence of the vicinal *spp* F–F coupling constant in *synperiplanar*-1,2-difluoropropane on the basis set used for the carbon and hydrogen atoms: Deviation (in Hz) of the locally dense basis set result from the calculation with the apTJ/apTJ/[pT/m]/m basis set. Only the basis sets on the non-coupled atoms are used as labels on the basis set axis. The apTJ basis set was used for fluorine in all calculations.

basis set on these hydrogen atoms (remaining columns in Fig. 9) and the second with only the minimal basis set. In the latter case, **10**, we choose then LDBS apTJ/apTJ/[apTJ/m]/m as the reference basis set. In this way, we can study the influence of the carbon basis sets. The conclusion is that the cc-pVDZ basis set is good enough to describe the carbon atoms of the methyl group, whereas the minimal basis set gives again larger changes in the OP and FC term, which however partly cancel out (Fig. 10). Secondly, reducing the basis set for the methyl hydrogens to the minimal basis set has not significant effect (see Fig. 9).

## 4.6. Physical implications

From an analysis of the LDBSs developed in the previous sections one can also gain insight on which parts of the electronic structure of the molecules are relevant or irrelevant for the transmission of the indirect nuclear spin coupling through the molecule.

For *trans*-1,2-difluoroethene, (**2**), and the *antiperiplanar* conformation of 1,2-difluoroethane, (**6**), a good LDBS consists of the aug-cc-pVTZ-J basis set for fluorine, cc-pVTZ for carbon and cc-pVDZ or a minimal basis set for the hydrogen atoms (LDBS apTJ/pT/pD or apTJ/pT/m). These basis sets lead to an error smaller than 1 Hz (see Table 4). They ensure an adequate treatment of the cusp of the wavefunction at the site of F nuclei [26] as well as a good description of the valence orbitals of the coupled fluorine atoms, even far away from the nuclei, due to the presence of four very tight *s*-functions and large number of diffuse and polarization functions in the aug-cc-pVTZ-J basis set. A good description of the valence orbitals of the carbon atoms is also ensured by the use of the cc-pVTZ basis set; however, this basis set does not contain tight or extra diffuse functions. The hydrogens can be described adequately by the cc-pVDZ basis set or even by a single *s*-function.

This analysis shows that in order to get a quantitative reproduction of the *trans*-vicinal F–F coupling it is necessary to describe properly the core orbitals of the coupled fluorine atoms as well as the valence orbitals of the whole system

**Table 4.** Errors in the vicinal F–F coupling constants and reduction in the number of basis functions for various locally dense basis sets in comparison with the apTJ/apTJ/apTJ basis set for difluoroethyne (**1**) and the 1,2-difluoroalkanes, (**2**) and (**4**), and the apTJ/apTJ/pT basis set for the 1,2-difluoroalkanes, (**6**) and (**8**). All calculations were carried out using SOPPA

| | apTJ/pT/pD | | apTJ/pT/m | | apTJ/pD/pD | | apTJ/pD/m | |
|---|---|---|---|---|---|---|---|---|
| | Hz | % | Hz | % | Hz | % | Hz | % |
| (**1**) | 2.0 | 17 | | | 2.2 | 35 | | |
| (**2**) | 0.9 | 28 | 0.9 | 31 | 4.1 | 42 | 4.1 | 46 |
| (**4**) | 1.2 | 28 | −3.2 | 31 | 4.0 | 42 | −2.9 | 46 |
| (**6**) | 0.7 | 28 | 0.4 | 35 | 2.0 | 42 | 3.2 | 48 |
| (**8**) | −0.1 | 28 | 4.2 | 35 | 0.2 | 42 | 5.7 | 48 |

**Table 5.** Errors in the vicinal F–F coupling constants and reduction in the number of basis functions for various locally dense basis sets in comparison with the apTJ/apTJ/[apTJ/pD]/m basis set for *trans*-1,2-difluoropropene (**3**) and *app*-1,2-difluoropropane (**7**). All calculations were carried out using SOPPA

| | apTJ/pT/[pD/m]/m | | apTJ/pT[m/m]/m | |
|---|---|---|---|---|
| | Hz | % | Hz | % |
| (**3**) | 1.3 | 29 | 4.4 | 32 |
| (**7**) | 0.1 | 31 | −1.3 | 34 |

F–C–C–F of F–C=C–F. This suggest that the *J* coupling is transmitted, in both systems, mainly via the core and valence electrons of coupled fluorine atoms and the valence electrons of intermediate atoms. The orbitals of the hydrogen atoms, which are located in the region of the backloops of the C–F single bonds, on the other hand, play a minor role in the quantitative reproduction of the *trans*-vicinal F–F coupling. These results are in accord with previous findings based on different grounds (Ref. [32]).

By a similar analysis of the results for the *trans*-1,2-difluoropropene, (**3**), and the *antiperiplanar* conformation of 1,2-difluoropropane, (**7**), (see also Table 5) one can see that the previous findings are still valid when the LDBS scheme is apTJ/pT/[pD/m]/m. However, it can be seen in Figs 3 and 7 that for quantitative reproduction of the vicinal F–F coupling it is necessary to describe the carbon atom of the $CH_3$ substituent with a larger than a minimal basis set. In both cases, the cc-pVDZ basis set was used.

On the other hand, a quantitative reproduction of the vicinal F–F couplings in *cis*-1,2-difluoroethene (**4**) and the *synperiplanar* conformation of 1,2-difluoroethane (**8**) is only obtained when the basis set on the hydrogens is at least of valence double $\zeta$ quality (see Table 4 and Figs 4 and 8). This LDBS scheme shows the necessity to describe properly not only both the core and valence orbitals of the coupled fluorine atoms with the aug-cc-pVTZ-J basis and the valence orbitals of the carbon atoms with a cc-pVTZ basis set, but also the hydrogenic orbitals which are in the region of the backloops of the fluorine–carbon single bonds. This suggest that the main transmission mechanism of the coupling is slightly shifted to a side, closer to the hydrogens and away from the main F–C–C–F and F–C=C–F structure.

## 5. CONCLUSIONS

In this work, results of high level *ab initio* SOPPA calculations of vicinal fluorine–fluorine indirect nuclear spin couplings are presented for 1,2-difluoroethene, -propene, -ethane and -propane. The four contributions (OD, OP, SD, FC) and the total value of the coupling constant are analyzed.

We find that the OP is the most important term and the absolute values of the four contributions follow the order $|OP|>|SD|>|FC|>|OD|$ for all the molecules studied here with the exception of the *synperiplanar* conformations of 1,2-difluoroethane and 1,2-difluoropropane, where the FC term is the most important one. In all multiply bonded systems, the FC term amounts to only 16% or less of the OP term. The SD term is generally of the same order of magnitude than the OP term with the exception of the *trans* couplings in the difluoroalkenes. The smallest non-contact terms are found for the *spp* F–F couplings in 1,2-difluoroalkanes. For the same molecules we find also the largest FC terms. Furthermore, we found that the OP terms are generally larger by a factor between 1.5 and 4.5 in the *trans* or *app* couplings than in the corresponding *cis* or *spp* couplings. The OP terms are also larger in the difluoroalkenes than in the difluoroalkanes and particularly large values of the OP term are found for the *trans* F–F couplings in the difluoroalkenes. The SD term is smaller in the *trans* than in the *cis* couplings, but larger in the *app* couplings than in the *spp* couplings. On the other hand, it is always larger across the C–C double bond than across the single bond.

With respect to the sign of the four contributions or the total coupling constants we can see that the FC term is positive in difluoroethyne and for all *cis* or *spp* couplings and negative for the *trans* or *app* couplings. An earlier natural *J*-coupling analysis at the DFT level showed that the latter is mainly due to the fluorine lone pairs [76]. The SD term, on the other hand, is positive for all the molecules, whereas the OP term is negative. The total F–F coupling is consequently negative with the exception of the *synperiplanar* conformations of the 1,2-difluoroalkanes.

The main purpose of this study, however, was the development of LDBSs which will closely reproduce the results of large basis set for spin–spin coupling constant calculations with a much reduced number of basis functions. We find that the best choice of basis set for each atom belonging to the studied model compounds depends on its location with respect to those nuclei whose coupling are being calculated and depends also on the conformation of the latter atoms. The carbon atoms located out of the bonding path which connects the coupled nuclei may be described with smaller basis sets (cc-pVDZ) than those located in the coupling pathway (cc-pVTZ), although a good basis set on the latter atoms is more important for the structures in *trans* F–F conformation than for those in *cis* F–F conformation. A decent basis on the hydrogen atoms directly bound to the coupling pathway is more important for molecules with *cis* or *spp* F–F conformation (cc-pVDZ) than for molecules with *trans* or *app* F–F conformation. Hydrogen atoms not directly connected to the coupling pathway can safely be described by a minimal basis set.

We recommend therefore the following LDBS scheme for compounds and couplings equivalent to the ones studied in this paper:

- aug-cc-pVTZ-J for the coupled atoms, here fluorine
- cc-pVTZ for all atoms in the coupling pathway, here carbon
- cc-pVDZ for carbon and hydrogen atoms (only for *cis*- or *spp*-couplings) directly bonded to the coupling pathway
- a minimal basis set for hydrogens not directly connect to the coupling path and for the directly connected hydrogens in the case of *trans*- or *app*-couplings.

Our recommendation should not be applied without further tests to a phenyl group attached to the coupling pathway.

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