The use of locally dense basis sets in the calculation of indirect nuclear spin−spin coupling constants: The vicinal coupling constants in $H_3C–CH_2X$ (X=H, F, Cl, Br, I)

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We have calculated the vicinal indirect nuclear spin-spin coupling constants $^3J_{^1H^1H}$ in the series of molecules $H_3C–CH_2X$ with X=H, F, Cl, Br, and I at the self-consistent field level and using the second order polarization propagator approximation (SOPPA). We have studied the effect of electron correlation and of the substituents (X=F, Cl, Br, and I) on all four contributions to the coupling constants. But in particular we have investigated the possibility of using locally dense basis sets, i.e., we have carried out calculations with basis sets, where the basis functions on the hydrogen atoms were optimized for the calculation of spin−spin coupling constants whereas on the other atoms smaller, contracted sets of basis functions were used. This changes the results for the couplings by ∼0.3 Hz or 3%. However, the change is almost entirely due to the orbital paramagnetic term and is independent of electron correlation, which enables one to estimate the SOPPA results in the full basis sets. Furthermore we find that the Fermi contact term is the dominant contribution to the vicinal coupling constants, because it is about an order of magnitude larger than the other contributions and because the two orbital angular moment terms almost cancel each other completely. Also the changes in the calculated couplings due to electron correlation are solely due to the Fermi contact term. However, the shifts in the coupling constants caused by the different substituents arise in equal amounts from the Fermi contact and the orbital diamagnetic term, whereas the changes in the orbital paramagnetic term are smaller and are in the opposite direction. In comparison with the experimental data we find very good agreement for C_2H_6 and C_2H_5F. However, the agreement becomes less good with increasing nuclear charge of the substituent X. © *2000 American Institute of Physics.* [S0021-9606(00)30211-2]

I. INTRODUCTION

The indirect nuclear spin–spin coupling constant is known to depend strongly on the molecular electronic structure close to the coupled nuclei, which makes this parameter difficult to calculate. Only recently the importance of a careful optimization of the basis set has been stressed again.[1–3] In particular the inclusion of s-type functions with very large exponents is essential.[4] Helgaker *et al.*[1] as well as Enevoldsen *et al.*[3] investigated how the series of correlation consistent basis sets of Dunning and co-workers[5–9] have to be modified for the calculation of spin–spin coupling constants. Enevoldsen *et al.*[3] suggested the use of a modified aug-cc-pVTZ basis set, where the contraction is completely removed and a set of four even tempered s-type functions with very large exponents is added. It was also found that the set of the most diffuse second polarization functions could be removed. However, these basis sets are rather large and cannot routinely be used in calculations on larger molecules. Guilleme and San Fabián[2] studied, on the other hand, the possibility of reducing the size of the basis sets by contract-

ing them with the molecular orbital coefficients of the molecule in question. This idea had previously successfully been used by Geertsen *et al.*[10] Another possibility in cases where only the coupling constants between selected atoms are required, is to make use of the concept of locally dense basis sets.[11,12] One of the purposes of this work was thus to investigate how much the results for the vicinal $^3J_{^1H^1H}$ coupling constants in ethane (C_2H_6) and halogen mono-substituted ethane (C_2H_5X) are influenced by the basis set on the carbon and halogen atoms.

Apart from the basis set, the results for coupling constants also depend strongly on the inclusion of electron correlation. Nowadays Hartree–Fock based methods for the calculation of coupling constants are mainly improved by variational, perturbative or coupled cluster procedures, like, e.g., the multiconfigurational linear response method (MCLR),[13] the second order polarization propagator approximation (SOPPA)[3] or the equation-of-motion coupled cluster method (EOM–CCSD).[14] Of these methods SOPPA and EOM–CCSD can be considered as ''black box'' methods, as only the basis set has to be chosen. The selection of the configurations in the multiconfigurational self-consistent field (MCSCF) wave function, on the other hand, requires a lot of test calculations and for larger systems becomes quite

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difficult. Furthermore in a recent publication[3] SOPPA has been shown to give good agreement with the experimental values for a variety of small molecules. In the present work SOPPA was therefore used to investigate the effect of electron correlation on the vicinal coupling constants and its contributions in ethane and halogen monosubstituted ethane.

Vicinal proton–proton coupling constants and in particular their torsion-angle dependence expressed as the Karplus equation[15] or variants of it have been the subject of many studies. One of the major factors influencing the vicinal coupling constants is the electronegativity of the substitutents X and Y in CH_2XCH_2Y. Several modifications of the original Karplus equation[15] have thus been proposed in order to account for this (see, e.g., Ref. 16). A third purpose of our study was therefore to analyze how the four contributions to the vicinal coupling constants are influenced by the inductive effects due to the change in the electronegativity of the substituents.

Finally a detailed study of the vicinal coupling constants in C_2H_6 and C_2H_5X should give some information about how coupling constants in larger molecules are affected and how they can be calculated efficiently.

II. THEORY

Ramsey[17] formulated the nonrelativistic theory of the indirect spin–spin coupling constant between two nuclei M and N proposing for it four contributions. It arises by means of a mechanism, whereby one nucleus perturbs the electrons surrounding it and the induced electronic currents produce a magnetic field at the site of the other nucleus. If the nucleus interacts with the spin of the electrons the Fermi-contact (FC) and spin-dipolar (SD) contributions arise, whereas the interactions with the orbital angular moment of the electrons is given by the orbital paramagnetic (OP) and orbital diamagnetic (OD) contributions.

The first three contributions depend on the first order wave function and are thus given as sum-over-states expressions

$$J^A_{MN} = \frac{2}{3} \frac{\gamma_M \gamma_N}{h} \sum_{\alpha=x,y,z} \sum_{n \neq 0} \frac{\langle 0|(\vec{O}^A_M)_\alpha|n\rangle\langle n|(\vec{O}^A_N)_\alpha|0\rangle}{E_0 - E_n},$$ (1)

where A can be OP, FC, SD and the corresponding operators are defined as

$$(\vec{O}^{OP}_M)_\alpha = \left(\frac{\mu_0}{4\pi}\right)\left(\frac{e\hbar}{m_e}\right) \sum_i \frac{(\vec{l}_{iM})_\alpha}{r^3_{iM}},$$ (2)

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

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

The magnetogyric ratio of nucleus M is γ_M, $\vec{r}_{iM} = \vec{r}_i - \vec{r}_M$ is the difference of the position vectors of electron i and nucleus M, $\vec{s}_i$ the spin angular momentum operator and $\vec{l}_i$ the

orbital angular momentum operator of electron i in units Js, $\delta(x)$ the Dirac delta function and all other symbols have their usual meaning.[18]

The orbital diamagnetic term, on the other hand, is a ground state average value,

$$J^{OD}_{MN} = \frac{1}{3} \frac{\gamma_M \gamma_N}{h} \sum_{\alpha=x,y,z} \langle 0|(\vec{O}^{OD}_{MN})_{\alpha\alpha}|0\rangle$$ (5)

with

$$(\vec{O}^{OD}_{MN})_{\alpha\alpha} = \left(\frac{\mu_0}{4\pi}\right)^2 \frac{e^2\hbar^2}{m_e} \sum_i \left(\frac{\vec{r}_{iN} \cdot \vec{r}_{iM} - (\vec{r}_{iN})_\alpha(\vec{r}_{iM})_\alpha}{r^3_{iN} r^3_{iM}}\right)$$ (6)

although it is also possible to express it as a sum-over-states.[19]

All excited triplet states $|n\rangle$ with energy E_n are included in the sum for the FC and SD terms, whereas excited singlet states contribute to the OP term. Recalling the spectral representation of the polarization propagator[20] taken at $\omega = 0$

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

it can be seen that these three contributions can be evaluated without explicit calculation of the excited states by using propagator methods. In the random phase approximation (RPA)[21] the polarization propagator is evaluated through first order in the fluctuation potential, i.e., the difference between the instantaneous interaction of the electrons and the averaged interaction as used in the Hartree–Fock approximation. The polarization propagator in RPA is often also called the self-consistent field (SCF) linear response function and can thus also be derived by time dependent Hartree–Fock (TDHF) theory.[22] Requiring that the single excitation dominated part of the polarization propagator is evaluated through second order the second order polarization propagator approximation (SOPPA)[23] is obtained. Detailed expressions for SOPPA have been given elsewhere.[24,25]

III. RESULTS

A. Details of the calculations

All the calculations in the present study have been performed with version 1.1 of the DALTON program package.[26] Experimental equilibrium geometries[27–31] were used for all molecules. Details of the geometries are shown in Fig. 1 and are contained in Tables I– V.

The basis set optimization was performed in two stages. First, calculations with a larger number of different basis sets were performed on C_2H_6. Then a smaller number of basis sets was selected for the calculations on the haloethanes C_2H_5X. The calculations were carried out at the SCF as well as at the SOPPA level. Apart from the correlation consistent (cc) basis sets of Dunning and co-workers[6,7] with the modifications suggested by Enevoldsen et al.,[3] the medium size polarized (MSP) basis sets of Sadlej[32–35] were also investigated. The latter have the advantage over other choices that they contain basis sets for all the halogen atoms, whereas for

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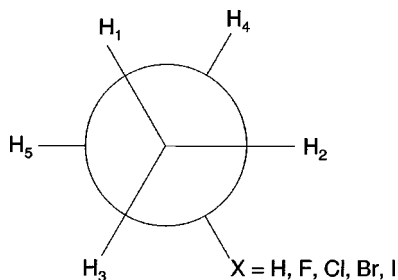
FIG. 1. Geometry of C_2H_5X

Br and I we had to use correlation consistent basis sets obtained by Visscher and Dyall.[36] For C_2H_6 the basis set used in previous studies on CH_4 (Refs. 10 and 37) was also used.

B. Basis set study for C_2H_6

The results of the basis set study on C_2H_6 are presented in Table I. Basis sets A–D are based on the aug-cc-pVTZ basis sets[6] with the exception of the carbon basis set in D which is the aug-cc-pVDZ set.[6] The 4 tight s-type functions on carbon in basis A and of hydrogen in basis A–D are taken from Ref. 3. Basis sets E–M are based on Sadlej's medium size polarized basis sets.[32] The exponents of the additional 4 s-type functions on hydrogen are $\zeta_s = 222.713\,91$, 1472.5090, 9735.7312, and 64 369.360. Finally, basis set N is the basis set used in a previous study on CH_4.[37] Further details of the basis sets are given in the footnotes of Table I.

From all the basis sets in Table I we consider basis set A proposed by Enevoldsen et al.[3] to be the best. It gives at the SCF level a slightly larger total coupling constant than basis set N. However, Guilleme and San Fabián[2] could show that the hydrogen part of basis set N is not optimal and leads to coupling constants which are slightly too small. It can only be incidentally that basis sets A and N give at the SOPPA level the same results for the total vicinal coupling constant despite differences in the individual four contributions.

The most important result from this basis set investigation is that the changes in the dominant contribution to $^3J_{H-H}$, the Fermi contact term are less than 1% as long as a good hydrogen basis set is used. For example, one can see from basis sets N and O, where the four most compact s-type functions on the carbon atoms in basis set N were removed, that these functions have no effect at all on $^3J_{^1H-^1H}$ Even replacing the uncontracted aug-cc-pVTZ basis set for carbon (A) with an aug-cc-pVDZ set (D) or replacing the totally uncontracted MSP basis set for carbon (E,G) by the contracted MSP basis set (J) changes the Fermi contact contribution to $^3J_{^1H-^1H}$ by less than 0.05 Hz or 1% at the SCF level and about 0.1 Hz or 1% at the SOPPA level. On the other hand, basis sets M, L, and J prove again the necessity to include s-type functions with very large exponents on the atoms of interest. The FC term is thus well described in the locally dense basis sets. However, the two locally dense basis sets, D and J do not behave in the same way. Whereas basis set D predicts a slightly larger FC term at the SCF and SOPPA level than basis set A, basis set J gives a smaller FC term than basis set E or G at the SCF level.

The changes in the spin-dipolar contribution are almost an order of magnitude smaller than the changes in the Fermi contact term. Although the agreement between the modified cc basis sets or basis set N on one side and the modified MSP basis sets on the other side is not as good as for the Fermi contact term, the smallness of the spin-dipolar contribution renders this unimportant.

The orbital diamagnetic term is basically unaffected by the changes in the basis sets at the SCF level, although there is a very small discrepancy between the result of the cc and MSP basis sets. At the SOPPA level a small change is observed on going from the aug-cc-pVTZ (A) to the aug-cc-pVDZ set (D) basis set for carbon and from the totally uncontracted MSP basis set for carbon (G) to the contracted MSP basis set (J). However, the differences are still less than 1% of the OD term.

Finally, the orbital paramagnetic term shows a different behavior. Already the largest basis sets of the three types of basis sets differ by up to 0.04 Hz or 2.5%. This is a consequence of the fact that basis set A has a set of d-type functions on the hydrogen atoms in contrast to basis sets E and N. Using the different locally dense basis sets the changes become even larger. The contraction of the p-type functions on the carbon atoms in basis set B and basis set I, e.g., reduces the OP term by 0.2 Hz (12%) and 0.3 Hz (20%), respectively. Also replacing the aug-cc-pVTZ basis set for carbon (B) by an aug-cc-pVDZ set (D) basis set further reduces the OP term by 0.1 Hz (7%). However, the relative changes in the total coupling constants amount to only about 3% and more importantly the basis set dependence of the orbital paramagnetic contribution is nearly independent of electron correlation. This makes it possible to estimate the SOPPA result for the OP term in the large basis set from results in smaller basis sets.

This investigation thus shows that using locally dense basis sets, i.e., using basis sets optimized for the calculation of spin–spin coupling constants only on the atoms of interest, is a real possibility for reducing the basis set size, if an error of about 0.3 Hz or 3% in the total coupling constant is acceptable. A comparison of the two locally dense basis sets, D and J, shows that the total basis set effect is smaller at the SOPPA level despite larger changes in the individual contributions due to a cancellation of errors in the FC and OP terms. Further, one can see that the differences between basis sets D and A at the SCF (0.27 Hz) and SOPPA (0.20 Hz) level are smaller than the differences between basis sets J and E/G/H (SCF : 0.37 Hz, SOPPA : 0.27 Hz), which makes basis set D the better choice.

C. Basis set study for C_2H_5X

In Tables II–V the results of the basis set investigation on C_2H_5X (X=F, Cl, Br, I) at the SCF and SOPPA level are presented. The basis set study on C_2H_6 showed that a good short list of basis sets would be A, B, H, D, and J. However, we are only aware of an aug-cc-pVDZ basis set[36] for Br and I and not an aug-cc-pVTZ basis set. Furthermore due to program limitations it was not possible to perform SOPPA calculations with basis A for F and Cl and with basis H for Br and I.

TABLE I. Basis-set[a] and correlation study on $^3J_{^1H-^1H}$ (in Hz) in C_2H_6,[b] where $^3J_{^1H-^1H}$ was calculated as $(^3J_{^1H_1-^1H_4}+^3J_{^1H_2-^1H_4}+^3J_{^1H_3-^1H_4})/3$.

Method	Basis	#	$^3J_{^1H-^1H}^{OD}$	$^3J_{^1H-^1H}^{OP}$	$^3J_{^1H-^1H}^{SD}$	$^3J_{^1H-^1H}^{FC}$	$^3J_{^1H-^1H}$
SCF	A	254	−1.6448	1.6010	0.0742	10.5795	10.6099
	B	222	−1.6445	1.4039	0.0755	10.5800	10.4155
	C	210	−1.6445	1.4036	0.0755	10.5803	10.4150
	D	190	−1.6442	1.3011	0.0740	10.6066	10.3375
	E	228	−1.6392	1.5721	0.0690	10.5873	10.5895
	F	200	−1.6391	1.5717	0.0690	10.5874	10.5890
	G	182	−1.6391	1.5704	0.0692	10.5866	10.5870
	H	172	−1.6390	1.5590	0.0673	10.5948	10.5821
	I	200	−1.6392	1.2545	0.0718	10.5519	10.2391
	J	180	−1.6391	1.2305	0.0731	10.5535	10.2180
	K	144	−1.6390	1.2205	0.0693	10.5605	10.2112
	L	156	−1.6391	1.2305	0.0731	8.6853	8.3499
	M	102	−1.6202	1.1637	0.0633	8.4793	8.0861
	N	162	−1.6447	1.5599	0.0768	10.5908	10.5827
	O	162	−1.6447	1.5599	0.0768	10.5908	10.5827
SOPPA	A	254	−1.6459	1.6090	0.0562	7.8910	7.9102
	B	222	−1.6441	1.4100	0.0573	7.9088	7.7322
	D	190	−1.6357	1.2910	0.0569	8.0061	7.7183
	G	182	−1.6350	1.5641	0.0524	7.9508	7.9324
	H	172	−1.6352	1.5525	0.0505	7.9490	7.9169
	J	180	−1.6293	1.2150	0.0571	8.0185	7.6613
	K	144	−1.6290	1.2036	0.0534	8.0182	7.6462
	N	162	−1.6417	1.5553	0.0598	7.9368	7.9102
EXPT.							8.02[c]

TABLE II. Basis-set[a] and correlation study on $^3J_{^1H-^1H}$ (in Hz) of C_2H_5F.[b] where $^3J_{^1H-^1H}$ was calculated as $(^3J_{^1H_1-^1H_4}+^3J_{^1H_2-^1H_4}+^3J_{^1H_3-^1H_4})/3$.

Method	Basis	#	$^3J_{^1H-^1H}^{OD}$	$^3J_{^1H-^1H}^{OP}$	$^3J_{^1H-^1H}^{SD}$	$^3J_{^1H-^1H}^{FC}$	$^3J_{^1H-^1H}$
SCF	A	285	−1.4834	1.4222	0.0871	9.4870	9.5128
	B	237	−1.4832	1.2472	0.0883	9.4869	9.3393
	D	189	−1.4833	1.1524	0.0862	9.5212	9.2765
	H	194	−1.4780	1.4011	0.0789	9.4872	9.4891
	J	182	−1.4782	1.0940	0.0841	9.4624	9.1623
SOPPA	B	237	−1.4841	1.2546	0.0686	7.1172	6.9563
	D	189	−1.4772	1.1452	0.0676	7.1982	6.9337
	H	194	−1.4754	1.3979	0.0610	7.1400	7.1235
	J	182	−1.4709	1.0818	0.0669	7.2038	6.8816
EXPT.							7.00[c]

[a]For references see Secs. III B and III C. For the details of the basis sets on carbon and hydrogen see the footnotes of Table I.
A: F [15s6p3d1f|15s6p3d1f]: uncontracted aug-cc-pVTZ, diffuse 2. Polarization function removed, 4 tight *s*-type functions added.
B: F [11s6p3d1f|5s4p3d1f]: aug-cc-pVTZ, diffuse 2. Polarization function removed.
D: F [10s5p2d|4s3p2d]: aug-cc-pVDZ.
H: F [10s6p2d|10s6p2d]: uncontracted MSP basis set, two most diffuse *d*-type functions removed.
J: F [10s6p4d|5s3p2d]: MSP basis set.
[b]$R_{CC}=1.512$ Å, $R_{C_2F}=1.387$ Å, $\angle_{FC_2C_1}=109.567°$, $R_{C_1H_{1/2/3}}=1.093$ Å, $\angle_{H_1C_1C_2}=109.717°$, $\angle_{H_{2/3}C_1C_2}=110.267°$, $\angle_{H_1C_1H_{2/3}}=108.833°$, $\angle_{H_2C_1H_3}=108.889°$, $R_{C_2H_{4/5}}=1.094$ Å, $\angle_{H_{4/5}C_2C_1}=112.233°$, $\angle_{H_{4/5}C_2F}=106.817°$, $\angle_{H_4C_2H_5}=108.891°$ (Ref. 28).
[c]Reference 16.

[a]For references see Sec. III B.
A: C [15s6p3d1f|15s6p3d1f]: uncontracted aug-cc-pVTZ, diffuse 2. Polarization function removed, 4 tight *s*-type functions added; H [10s3p1d|10s3p1d]: uncontracted aug-cc-pVTZ, diffuse 2. Polarization function removed, 4 tight *s*-type functions added.
B: C [11s6p3d1f|5s4p3d1f]: aug-cc-pVTZ, diffuse 2. Polarization function removed; H [10s3p1d|10s3p1d]: uncontracted aug-cc-pVTZ, diffuse 2. Polarization function removed, 4 tight *s*-type functions added.
C: C [11s6p3d1f|5s4p3d1f]: aug-cc-pVTZ, diffuse 2. Polarization function removed; H [6s3p1d|4s3p1d]: aug-cc-pVTZ, diffuse 2. Polarization function removed; H (coupled) [10s3p1d|10s3p1d]: uncontracted aug-cc-pVTZ, diffuse 2. Polarization function removed, 4 tight *s*-type functions added.
D: C [10s5p2d|4s3p2d]: aug-cc-pVDZ; H [10s3p1d|10s3p1d]: uncontracted aug-cc-pVTZ, diffuse 2. Polarization function removed, 4 tight *s*-type functions added.
E: C [10s6p4d|10s6p4d]: uncontracted MSP basis set; H [10s4p|10s4p]: uncontracted MSP basis set, 4 tight *s*-type functions added.
F: C [10s6p3d|10s6p3d]: uncontracted MSP basis set, most diffuse *d*-type function removed; H [10s3p|10s3p]: uncontracted MSP basis set, most diffuse *p*-type function removed, 4 tight *s*-type functions added.
G: C [10s6p3d|10s6p3d]: uncontracted MSP basis set, most diffuse *d*-type function removed; H [10s2p|10s2p]: uncontracted MSP basis set, two most diffuse *p*-type functions removed, 4 tight *s*-type functions added.
H: C [10s6p2d|10s6p2d]: uncontracted MSP basis set, two most diffuse *d*-type functions removed; H [10s2p|10s2p] uncontracted MSP basis set, two most diffuse *p*-type functions removed, 4 tight *s*-type functions added.
I: C [10s6p4d|5s3p4d]: MSP basis set, *d*-type functions uncontracted; H [10s4p|10s4p]: uncontracted MSP basis set, 4 tight *s*-type functions added.
J: C [10s6p4d|5s3p2d]: MSP basis set; H [10s4p|10s4p]: uncontracted MSP basis set 4 tight *s*-type functions added.
K: C [10s6p4d|5s3p2d]: MSP basis set; H [10s2p|10s2p]: uncontracted MSP basis set, two most diffuse *p*-type functions removed, 4 tight *s*-type functions added.
L: C [10s6p4d|5s3p2d]: MSP basis set; H [6s4p|6s4p]: uncontracted MSP basis set.
M: C [10s6p4d|5s3p2d]: MSP basis set; H [6s4p|3s2p]: MSP basis set.
N: C [15s7p4d|10s5p4d]: Ref. 37; H [9s2p|6s2p]: Ref. 37.
O: C [11s7p4d|10s5p4d]: Ref. 37, 4 tight *s*-type functions removed; H [9s2p|6s2p]: Ref. 37.
[b]$R_{CC}=1.536$ Å, $R_{CH}=1.091$ Å, $\angle_{HCH}=108.00°$, $\angle_{HCC}=110.905°$ (Ref. 27).
[c]Reference 16.

From Tables II–III we can see that the main conclusions of the basis set investigation for C_2H_5F and C_2H_5Cl are the same as for C_2H_6. Using the locally dense basis sets D and J increases the FC term by less than 0.1 Hz ($\sim$1%) at the SOPPA level and reduces the OP term by about 0.3 Hz. The absolute changes are slightly smaller in C_2H_5F and C_2H_5Cl than in C_2H_6, but so are the OP and FC terms, yielding similar relative changes. The changes in the SD term are irrelevant due to the smallness of the SD term and there is a very small difference between the cc and MSP basis sets for the OD term, which is a bit larger at the SOPPA level. In more detail, we can see that the changes in the FC term in C_2H_5F and C_2H_5Cl are almost identical with the exception of basis D at the SCF level in C_2H_5Cl yielding a slightly smaller FC term than basis set A. The basis set effect for the FC term for both molecules is larger at the SOPPA level than it was for C_2H_6. Also for the OP term the pattern observed in C_2H_6 is repeated. Basis set H gives a smaller OP term than basis A. Contracting the aug-cc-pVTZ basis sets for carbon and halogen reduces the OP term by 0.18 Hz (F) and 0.15 Hz (Cl) at the SCF level. Replacing the aug-cc-pVTZ by an aug-cc-pVDZ basis sets further reduces it by 0.10 Hz at SCF and 0.11 Hz at SOPPA in both molecules. Going from basis set H to J the changes are 0.31 Hz (SCF) / 0.32 Hz (SOPPA) for F and 0.29 Hz (SCF) / 0.30 Hz (SOPPA) for Cl.

This very systematic behavior allows us to estimate the SOPPA results in basis set A from the results of basis D corrected with the differences between the SCF results for the OP term in basis set A and D and the differences between the SOPPA results for the FC term in basis set B and D:

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TABLE III. Basis-set [a] and correlation study on $^3J_{^1H-^1H}$ (in Hz) of C_2H_5Cl[b], where $^3J_{^1H-^1H}$ was calculated as $(^3J_{^1H_1-^1H_4}+^3J_{^1H_2-^1H_4}+^3J_{^1H_3-^1H_4})/3$.

Method	Basis	#	$^3J^{OD}_{^1H-^1H}$	$^3J^{OP}_{^1H-^1H}$	$^3J^{SD}_{^1H-^1H}$	$^3J^{FC}_{^1H-^1H}$	$^3J_{^1H-^1H}$
SCF	A	302	−1.3416	1.4113	0.0876	9.9548	10.1123
	B	241	−1.3413	1.2658	0.0888	9.9553	9.9686
	D	193	−1.3416	1.1657	0.0866	9.9503	9.8610
	H	210	−1.3357	1.3822	0.0805	9.9476	10.0747
	J	190	−1.3364	1.0946	0.0862	9.9082	9.7527
SOPPA	B	241	−1.3398	1.2717		7.3098	7.2416[c]
	D	193	−1.3332	1.1597	0.0673	7.3918	7.2856
	H	210	−1.3314	1.3801	0.0616	7.3440	7.4544
	J	190	−1.3266	1.0840	0.0680	7.4069	7.2322
EXPT.							7.26[d]

[a]For references see Secs. III B and III C. For the details of the basis sets on carbon and hydrogen see the footnotes of Table I.

A: Cl [20s10p3d1f|20s10p3d1f]: uncontracted aug-cc-pVTZ, diffuse 2. Polarization function removed, 4 tight s-type functions added.

B: Cl [16s10p3d1f|6s5p3d1f]: aug-cc-pVTZ, diffuse 2. Polarization function removed.

D: Cl [13s9p2d|5s4p2d]: aug-cc-pVDZ.

H: Cl [14s10p2d|14s10p2d]: uncontracted MSP basis set, two most diffuse d-type functions removed.

J: Cl [14s10p4d|7s5p2d]: MSP basis set.

[b]$R_{CC}=1.520$ Å, $R_{C_2Cl}=1.789$ Å, $\angle ClC_2C_1=111.000°$, $R_{C_1H_{1/2/3}}=1.092$Å, $\angle H_1C_1C_2=109.267°$, $\angle H_{2/3}C_1C_2=110.433°$, $\angle H_1C_1H_{2/3}=109.217°$, $\angle H_2C_1H_3=108.24°$, $R_{C_2H_{4/5}}=1.089$Å, $\angle H_{4/5}C_2C_1=111.600°$, $\angle H_{4/5}C_2Cl=106.550°$, $\angle H_4C_2H_5=109.291°$ (Ref. 29).

[c]Without the SD contribution.

[d]Reference 16.

TABLE IV. Basis-set [a] and correlation study on $^3J_{^1H-^1H}$ (in Hz) of C_2H_5Br[b], where $^3J_{^1H-^1H}$ was calculated as $(^3J_{^1H_1-^1H_4}+^3J_{^1H_2-^1H_4}+^3J_{^1H_3-^1H_4})/3$.

Method	Basis	#	$^3J^{OD}_{^1H-^1H}$	$^3J^{OP}_{^1H-^1H}$	$^3J^{SD}_{^1H-^1H}$	$^3J^{FC}_{^1H-M^1H}$	$^3J_{^1H-^1H}$
SCF	D	209	−1.0403	1.0198	0.0859	10.2133	10.2787
	H	266	−1.0345	1.1034	0.0803	10.2159	10.3651
	H–f	252	−1.0345	1.2241	0.0803	10.2152	10.4851
	J	222	−1.0346	0.7518	0.0854	10.1927	9.9952
	J–f	208	−1.0349	0.9728	0.0853	10.1762	10.1994
SOPPA	D	209	−1.0323	1.0146	0.0660	7.5313	7.5796
	H–f	252	−1.0306	1.2220		7.4845	7.6759[c]
	J	222	−1.0240	0.7392	0.0665	7.5333	7.3150
	J–f	208	−1.0253	0.9608	0.0664	7.5465	7.5484
EXPT.							7.35[d]

[a]For references see Secs. III B and III C. For the details of the basis sets on carbon and hydrogen see the footnotes of Table I.

D: Br [17s14p8d1f|6s5p3d1f]: aug-cc-pVDZ Ref. 36.

H: Br [15s12p9d2f|15s12p9d2f]: uncontracted MSP basis set, two most diffuse f-type functions removed.

H–f: Br [15s12p9d|15s12p9d]: uncontracted MSP basis set without f-type functions.

J: Br [15s12p9d4f|9s7p4d2f]: MSP basis set.

J–f: Br [15s12p9d|9s7p4d]: MSP basis set without f functions.

[b]$R_{CC}=1.519$ Å, $R_{C_2Br}=1.950$ Å, $\angle BrC_2C_1=111.050°$, $R_{C_1H_{1/2}}=1.092$ Å, $\angle H_1C_1C_2=108.833°$, $\angle H_{2/3}C_1C_2=110.617°$, $\angle H_1C_1H_{2/3}=109.267°$, $\angle H_2C_1H_3=108.217°$, $R_{C_2H_{4/5}}=1.087$ Å, $\angle H_{4/5}C_2C_1=112.333°$, $\angle H_{4/5}C_2Br=105.417°$, $\angle H_4C_2H_5=109.848°$ (Ref. 30).

[c]Without the SD contribution.

[d]Reference 16.

TABLE V. Basis-set [a] and correlation study on $^3J_{^1H-^1H}$ (in Hz) of C_2H_5I[b], where $^3J_{^1H-^1H}$ was calculated as $(^3J_{^1H_1-^1H_4}+^3J_{^1H_2-^1H_4}+^3J_{^1H_3-^1H_4})/3$.

Method	Basis	#	$^3J^{OD}_{^1H-^1H}$	$^3J^{OP}_{^1H-^1H}$	$^3J^{SD}_{^1-^1H}$	$^3J^{FC}_{^1H-^1H}$	$^3J_{^1H-^1H}$
SCF	D	218	−0.8364	1.0039	0.0859	10.4432	10.6966
	H	294	−0.8277	0.9935	0.0809	10.6861	10.9328
	H–f	280	−0.8278	1.2149	0.0809	10.6831	11.1511
	J	240	−0.8278	0.6779	0.0862	10.6519	10.5883
	J–f	226	−0.8282	0.9377	0.0861	10.6338	10.8294
SOPPA	D	218	−0.8286	1.0050	0.0648	7.6218	7.8630
	J	240	−0.8166	0.6719	—	7.7313	7.5866[c]
	J–f	226	−0.8183	0.9254	0.0652	7.7551	7.9274
EXPT.							7.47[d]

[a]For references see Secs. III B and III C. For the details of the basis sets on carbon and hydrogen see the footnotes of Table I.

D: I [34s14p9d1f|7s6p4d1f]: aug-cc-pVDZ Ref. 36.

H: I [19s15p12d2f|19s15p12d2f]: uncontracted MSP basis set, two most diffuse f-type functions removed.

H-f: I [19s15p12d|19s15p12d]: uncontracted MSP basis set without f-type functions.

J: I [19s15p12d4f|11s9p6d2f]: MSP basis set.

J-f: I [19s15p12d|11s9p6d]: MSP basis set without f-type functions.

[b]$R_{CC}=1.521$ Å, $R_{C_2I}=2.151$ Å, $\angle IC_2C_1=111.617°$, $R_{C_1H_{1/2/3}}=1.093$ Å, $\angle H_1C_1C_2=108.600°$, $\angle H_{2/3}C_1C_2=110.800°$, $\angle H_1C_1H_{2/3}=109.317°$, $\angle H_2C_1H_3=107.985°$, $R_{C_2H_{4/5}}=1.086$ Å, $\angle H_{4/5}C_2C_1=112.567°$, $\angle H_{4/5}C_2I=104.833°$, $\angle H_4C_2H_5=109.879°$ (Ref. 31).

[c]Without the SD contribution.

[d]Reference 16.

$$J(A/SOPPA) \approx J(D/SOPPA) + J^{OP}(A/SCF) - J^{OP}(D/SCF)$$
$$+ J^{FC}(B/SOPPA) - J^{FC}(D/SOPPA). \qquad (8)$$

Encouraged by the very good agreement between the estimate 7.92 Hz [from Eq. (8)] and the calculated result 7.91 Hz for C_2H_6 (from Table I), we estimate the SOPPA results of basis set A for C_2H_5F and C_2H_5Cl to be 7.12 Hz and 7.45 Hz, respectively.

In Tables IV and V, finally the results for C_2H_5Br and C_2H_5I are shown. It was already mentioned that from the cc basis sets only calculations with the locally dense basis set D could be carried out and that using the MSP basis sets a SOPPA calculation with a full basis set was also only possible for C_2H_5Br without the polarization functions (f-type functions) on Br (basis set H–f).

In addition to the performance of the locally dense basis sets D and J we wanted to investigate the importance of the polarization (f-type) functions on the halogen atoms in the MSP basis sets, as the MSP basis sets for Br and I are often used without the f-type functions, which we denote then as H–f and J–f. The effect on the FC term is very small, although it is a bit larger in the locally dense basis set J. The OP term, on the other hand, is changed by about 0.2 Hz. However removing the polarization functions the OP term is increased, which implies that the error introduced by using the locally dense basis set J is partly canceled and the results of basis set H and J–f differ thus by only about 0.1 Hz.

Comparison of the locally dense basis sets D and J with the full basis set H shows in general the same changes as for C_2H_5F and C_2H_5Cl with two exceptions. First, the difference

between the results for the FC term of the two locally dense basis sets D and J as well as between basis sets D and H is one order of magnitude larger in C_2H_5I than in C_2H_5Br and the other molecules. This is probably due to a deficiency in basis set D as basis sets H and J follow the same pattern as observed for all the other molecules. Second, the difference between the results for the OP term of basis sets D and J is about 0.27 Hz for Br and 0.33 Hz for I and thus much larger than about 0.07 Hz for the other systems. On the other hand, the difference between H and D (-0.01 Hz for Br and 0.08 Hz for I) is much smaller than the 0.25 Hz found for the other molecules. This raises again the question of whether the aug-cc-pVDZ basis sets for Br and I used in basis set D are comparable to the aug-cc-pVDZ basis sets of F and Cl.

It might therefore be better to estimate a large basis set SOPPA result for C_2H_5Br and C_2H_5I from the results of basis J instead of from basis set D. An estimate of the SOPPA results for basis set H could be obtained from the results of basis set J in the following way:

$$J(\text{H/SOPPA}) \approx J(\text{J/SOPPA}) + J^{\text{OP}}(\text{H/SCF}) - J^{\text{OP}}(\text{J/SCF}). \tag{9}$$

Applied to C_2H_6 one would obtain 7.98 Hz instead of 7.92 Hz, which is an error of less than 1%. For fluorine and chlorine the estimated values from Eq. (9) agree to within 1% with the calculated results for basis set H. For C_2H_5Br and C_2H_5I the results of basis set H are thus estimated to 7.67 Hz and 7.97 Hz, respectively.

D. Electron correlation

It is well known that a proper description of electron correlation is needed to quantitatively reproduce the triplet contributions FC and SD to the indirect nuclear spin–spin coupling constants. The second order polarization propagator approximation, used in this study, has been shown to give good agreement with experiments for one and two bond couplings constants for small molecules.[38,3,39] However, apart from ethene[38] and ethyne[3,38] it has not been used in the calculation of vicinal couplings.

The effects of electron correlation on the vicinal coupling constants are basically independent of the substituent X and of the basis set. The electron correlation corrections to the two orbital angular momentum terms, OD and OP, are ~ 0.01 Hz or $\sim 1\%$ and are therefore irrelevant. The unimportance of electron correlation for the OD term is well known,[3,40–42] whereas the correlation contribution to the OP term depends in general very much on the molecule and the type of coupling considered. In the previous SOPPA calculations of vicinal coupling constants in ethyne,[3,38] the OP term was reduced by $\sim 12\%$, whereas in ethene[38] the correlation corrections seem to be negligible again.

The electron correlation corrections to the two electron spin terms, FC and SD, on the other hand, are much larger percentage wise and in the case of the FC term also in absolute terms. The SD term is reduced by 0.02 Hz independent of the molecule and basis set, which is about 24% of the corresponding SCF values. The changes in the FC term are between 2.3 Hz or 25% in C_2H_5F and 2.9 Hz or 27% in C_2H_5I. This is not a particularly large change, if one com-

pares with the correlation correction of 69.62 Hz or 87% calculated for FC contributions to the vicinal coupling constants in ethyne.[3] Nevertheless, it shows again that the FC contact term is the dominant contribution in absolute terms as well as basis set and electron correlation effects are concerned.

E. Effects of Halogen Substituents

One of the purposes of this study was to investigate the effects of the substituents X on the vicinal coupling constants and in particular to check whether there is a systematic behavior. Since the indirect nuclear spin–spin coupling constants consist in nonrelativistic theory of four contributions, the experimentally observed trends cannot be interpreted in a simple manner. Theory on the other hand, can study each of the four contributions individually.

An analysis of Tables II–V thus shows that going from C_2H_5F to C_2H_5I the OD and FC terms increase whereas the OP and SD terms decrease. Furthermore, one can see that the substituent effect on OD and FC are of equal size and larger than the effect on the OP term. The smallness of the SD term renders its substituent effect irrelevant. The effect on the total coupling constant is therefore dominated by the effects on the OD and FC term which have the same sign. It is interesting to note that, because of the opposite sign of the OD and OP term and the opposite sense of their substituent effects the total orbital angular momentum contribution is very small ($< |0.2|$ Hz) and changes sign on going from C_2H_5F to C_2H_5I.

C_2H_6, however, does not fit very well in this series. It has the most negative OD term and the most positive OP and FC terms.

IV. SUMMARY AND DISCUSSION

We have investigated theoretically the indirect vicinal hydrogen–hydrogen spin–spin coupling constants in C_2H_6 and C_2H_5X (X=F, Cl, Br, I). All four contributions to the couplings, the Fermi contact, spin-dipolar, orbital diamagnetic, and paramagnetic terms, have been calculated at the self-consistent field level as well as using the second order polarization propagator approximation. The latter method is known[3] to describe the main part of the electron correlation effects on spin–spin couplings.

Large uncontracted basis sets have been used. They are based on the correlation consistent aug-cc-pVTZ basis set of Dunning and co-workers[6,7] and on the medium size polarized basis sets of Sadlej[32–35] but have been augmented with four very tight s-type functions. Furthermore we have investigated the possibility of using locally dense basis sets, where basis sets optimized for the calculation of spin–spin couplings are only used on the atoms of interest and smaller basis sets are employed on all other atoms.

We find that the FC term is the largest and dominant contribution to the vicinal, three bond coupling constants in these molecules, as it is the case for most one bond coupling constants. The SD term is smaller than 0.1 Hz and therefore completely unimportant, whereas the OD and OP terms are

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between 1 Hz and 2 Hz. However, the sum of the two orbital angular momentum terms is also only 0.2 Hz at most.

With respect to the basis sets, we find that the tight s-type functions are of course only necessary on the atoms for which coupling constants are to be calculated. Furthermore using contracted basis sets of only valence double zeta quality on the other atoms, i.e., using locally dense basis sets, changes the coupling constants in these molecules by about 0.3 Hz. This basis set effect is almost completely due to the OP term and is independent of electron correlation. One is therefore able to estimate the SOPPA results in the larger basis set from SOPPA calculations with the locally dense basis sets and SCF calculation with both basis sets. In general we can conclude that the results of large basis set calculations can be reproduced quite accurately by using properly designed locally dense basis sets. This allows the reduction of the size of the basis sets in cases in which coupling constants only between some nuclei are to be calculated, a fact which is important for *ab initio* calculations of coupling constants in medium-size molecules.

Electron correlation, treated with SOPPA, changes the FC term by ~2.6 Hz or 25%. The SD term is also changed by ~25%, whereas the two orbital angular momentum terms are unaffected by electron correlation.

Comparison with experiment[16] shows very good agreement between the SOPPA results 7.91 Hz/7.92 Hz obtained with basis set A / H and the experimental value of 8.02 Hz. The agreement between the measured 7.00 Hz for C$_2$H$_5$F and the SOPPA result 7.12 Hz (calculated with basis set H and estimated result of basis set A) is also very good. However, theory now predicts a larger coupling contrary to what was found for C$_2$H$_6$. In the case of C$_2$H$_5$Cl the difference is slightly larger between the experimental 7.26 Hz and the SOPPA result 7.45 Hz obtained with basis set H and estimated for basis set A. The discrepancies become larger for the other two molecules where 7.67 Hz was estimated for basis set H versus the measured 7.35 Hz (C$_2$H$_5$Br) and the estimated 7.97 Hz (basis set H) versus the experimental 7.47 Hz (C$_2$H$_5$I). However, the error in the estimates for C$_2$H$_5$Br and C$_2$H$_5$I is probably 0.1 Hz. Besides the remaining electron correlation corrections not included in SOPPA and the remaining basis set error, which we expect to be rather small, there are two other contributions which probably account for the differences. All our results are for experimental equilibrium geometries and we have thus not included any corrections due to the rotational and vibrational motion of the nuclei. These effects are typically of the order of 5% for one bond and two bond coupling constants.[37,39,43,44] For the vicinal coupling constants in ethyne[45] the nuclear motion correction at 300 K was found to be −0.5 Hz or −4.4 %. Our calculations are based on the Schrödinger equation and relativistic effects present in C$_2$H$_5$Br and C$_2$H$_5$I are therefore not included in our results.

The good agreement with experimental data nevertheless allows us to interpret the experimentally observed shifts in the coupling constants on going from C$_2$H$_5$F to C$_2$H$_5$I based on our results for the four contributions to the coupling constants. We find that the changes are due to equal changes in the Fermi contact term and the orbital diamagnetic contribu-

tion. The shifts in the orbital paramagnetic term, on the other hand, are smaller and have the opposite sign.

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