Theor Chem Acc (1998) 100:275–284
DOI 10.1007/s00214980m149

Theoretical
Chemistry Accounts

Regular article

Correlated calculations of indirect nuclear spin-spin coupling constants using second-order polarization propagator approximations: SOPPA and SOPPA(CCSD)

Thomas Enevoldsen[1], **Jens Oddershede**[1], **Stephan P.A. Sauer**[2]

[1] Department of Chemistry, Odense University, Campusvej 55, DK-5230 Odense M, Denmark
[2] Chemistry Laboratory IV, Department of Chemistry, University of Copenhagen,
Universitetsparken 5, DK-2100 Copenhagen ∅ , Denmark

Received: 6 July 1998 / Accepted: 8 September 1998 / Published online: 23 November 1998

Abstract. We present correlated calculations of the indirect nuclear spin-spin coupling constants of HD, HF, H_2O, CH_4, C_2H_2, BH, AlH, CO and N_2 at the level of the second-order polarization propagator approximation (SOPPA) and the second-order polarization propagator approximation with coupled-cluster singles and doubles amplitudes – SOPPA(CCSD). Attention is given to the effect of the so-called W_4 term, which has not been included in previous SOPPA spin-spin coupling constant studies of these molecules. Large sets of Gaussian basis functions, optimized for the calculation of indirect nuclear spin-spin coupling constants, were used instead of the in general rather small basis sets used in previous studies. We find that for nearly all couplings the SOPPA(CCSD) method performs better than SOPPA.

Key words: NMR parameters – Spin-spin coupling constants – Second-order polarization propagator approximation – Second-order polarization propagator approximation with coupled-cluster singles and doubles amplitudes – Basis set

1 Introduction

The indirect nuclear spin-spin coupling constant depends critically upon the molecular electronic structure close to the coupled nuclei, more so than most other molecular properties. Calculations of this quantity thus serve as a measure of the quality of the wavefunction both at the nuclear position and – as it turns out – also in general. This can, for instance, be seen from the fact that the standard zeroth-order method of electronic structure calculations, the Hartree-Fock method, may give NMR spin-spin coupling constants that are off by orders of magnitude. It thus becomes a challenge to develop reliable methods for the calculation of this difficult property.

Since the early days of polarization propagator methods [1] we have had an interest in the calculation of indirect spin-spin coupling constants [2–7] primarily because the Ramsey expressions [8] for three out of the four non-relativistic contributions to the coupling are second-order energy expressions and thus optimally suited for polarization propagator calculations. More recently a relativistic variant of the method has also been formulated [9]. Since the publication of our earliest calculations of couplings both theoretical methods and computational possibilities have improved considerably. In particular, the basis set problem which has been one of the major reasons for inaccurate theoretical results is now nearly eliminated for smaller molecules [10].

The main purpose of the present paper is to present up-to-date non-relativistic calculations of the spin-spin couplings of the molecules for which we have previously reported couplings at lower levels of approximation [5, 6, 11–17] using new optimized basis sets and the latest implementation [18] of the second-order polarization propagator approximation (SOPPA). We have tested the importance of a previously ignored second-order term in the propagator, the so-called W_4 term [19], as well as corrected an incorrect second-order contribution to the triplet transition moments in our original implementation [5] of the SOPPA method for the calculation of couplings.

In addition, we investigate the relative merit of the original [19], now fully second-order, SOPPA method and its coupled-cluster generalization [20], the recent version of which is referred to as the SOPPA(CCSD) method [21].

In Sect. 2 we give the relevant equations for the indirect nuclear spin-spin coupling constants in SOPPA.

Correspondence to: S.P.A. Sauer
e-mail: sps@ithaka.ki.ku.dk

Section 3 is devoted to the choice of basis functions for coupling constant calculations. In Sect. 4 our results are presented and discussed in comparison with experimental and other theoretical values.

2 Theory

The indirect spin-spin coupling constant between two nuclei K and L consists according to Ramsey [8] of four contributions: the orbital diamagnetic (or diamagnetic spin-orbit) term

$$J_{\mathrm{KL}}^{\mathrm{OD}} = \frac{1}{3} \sum_{\alpha = x,y,z} \left(\frac{\mu_0}{4\pi}\right)^2 \frac{e^2\hbar^2}{m_{\mathrm{e}}} \frac{\gamma_{\mathrm{K}}\gamma_{\mathrm{L}}}{h} \times \left\langle 0 \middle| \sum\nolimits_i \left(\frac{\mathbf{r}_{i\mathrm{L}} \cdot \mathbf{r}_{i\mathrm{K}} - (\mathbf{r}_{i\mathrm{L}})_\alpha (\mathbf{r}_{i\mathrm{K}})_\alpha}{r_{i\mathrm{L}}^3 r_{i\mathrm{K}}^3} \right) \middle| 0 \right\rangle \quad , \tag{1}$$

the orbital paramagnetic (or paramagnetic spin-orbit) term

$$J_{\mathrm{KL}}^{\mathrm{OP}} = \frac{2}{3} \sum_{\alpha = x,y,z} \left(\frac{\mu_0}{4\pi}\right)^2 \left(\frac{e\hbar}{m_{\mathrm{e}}}\right)^2 \frac{\gamma_{\mathrm{K}}\gamma_{\mathrm{L}}}{h} \times \sum_{n \neq 0} \frac{\left\langle 0 \middle| \sum\nolimits_i \frac{(\mathbf{l}_{i\mathrm{K}})_\alpha}{r_{i\mathrm{K}}^3} \middle| n \right\rangle \left\langle n \middle| \sum\nolimits_i \frac{(\mathbf{l}_{i\mathrm{L}})_\alpha}{r_{i\mathrm{L}}^3} \middle| 0 \right\rangle}{E_0 - E_n} \quad , \tag{2}$$

the Fermi contact term

$$J_{\mathrm{KL}}^{\mathrm{FC}} = \frac{2}{3} \sum_{\alpha = x,y,z} \left(\frac{\mu_0}{4\pi}\right)^2 \left(\frac{4\pi g_e e\hbar}{3m_{\mathrm{e}}}\right)^2 \frac{\gamma_{\mathrm{K}}\gamma_{\mathrm{L}}}{h} \times \sum_{n \neq 0} \frac{\left\langle 0 \middle| \sum\nolimits_i (\mathbf{s}_i)_\alpha \delta(\mathbf{r}_{i\mathrm{K}}) \middle| n \right\rangle \left\langle n \middle| \sum\nolimits_i (\mathbf{s}_i)_\alpha \delta(\mathbf{r}_{i\mathrm{L}}) \middle| 0 \right\rangle}{E_0 - E_n} \quad , \tag{3}$$

and the spin-dipolar term

$$J_{\mathrm{KL}}^{\mathrm{SD}} = \frac{2}{3} \sum_{\alpha = x,y,z} \left(\frac{\mu_0}{4\pi}\right)^2 \left(\frac{g_e e\hbar}{2m_{\mathrm{e}}}\right)^2 \frac{\gamma_{\mathrm{K}}\gamma_{\mathrm{L}}}{h} \times \sum_{n \neq 0} \frac{\langle 0 | (\mathbf{O}_{\mathrm{K}}^{\mathrm{SD}})_\alpha | n \rangle \langle n | (\mathbf{O}_{\mathrm{L}}^{\mathrm{SD}})_\alpha | 0 \rangle}{E_0 - E_n} \quad , \tag{4}$$

where

$$(\mathbf{O}_{\mathrm{K}}^{\mathrm{SD}})_\alpha = \sum_i \frac{3(\mathbf{s}_i \cdot \mathbf{r}_{i\mathrm{K}})(\mathbf{r}_{i\mathrm{K}})_\alpha - r_{i\mathrm{K}}^2 (\mathbf{s}_i)_\alpha}{r_{i\mathrm{K}}^5} \quad . \tag{5}$$

The magnetogyric ratio of nucleus K is γ_{K}, $\mathbf{r}_{i\mathrm{K}} = \mathbf{r}_i - \mathbf{r}_{\mathrm{K}}$ is the difference of the position vectors of electron i and nucleus K, $\mathbf{s}_i$ and $\mathbf{l}_i$ are the spin and orbital angular momentum operators of electron i in units Js, $\delta(x)$ is the Dirac delta function and all other symbols have their usual meaning [22].

In the case of the orbital paramagnetic contribution the sum includes all excited electronic singlet states $|n\rangle$ with energy E_n, whereas excited triplet states contribute to the Fermi contact and spin-dipolar terms. Recalling the spectral representation of the polarization propagator [1] taken at $\omega = 0$

$$\langle\langle P; Q \rangle\rangle_{\omega = 0} = 2 \sum_{n \neq 0} \frac{\langle 0|P|n\rangle\langle n|Q|0\rangle}{E_0 - E_n} \tag{6}$$

it can be seen that these three contributions can be evaluated without explicit calculation of the excited states by using propagator methods. The orbital diamagnetic term, on the other hand, is a ground-state average value, although it is also possible to express it as a propagator [23].

In SOPPA and SOPPA(CCSD) the polarization propagator of an operator P in the presence of a static perturbation, represented by the operator Q, is defined as [24]

$$\langle\langle P; Q \rangle\rangle_{\omega = 0} = \begin{pmatrix} \langle 0|[P, \tilde{\mathbf{q}}^\dagger]|0\rangle^{(0,2)} \\ \langle 0|[P, \tilde{\mathbf{q}}]|0\rangle^{(0,2)} \\ \langle 0|[P, \tilde{\mathbf{q}}^\dagger\tilde{\mathbf{q}}^\dagger]|0\rangle^{(1)} \\ \langle 0|[P, \tilde{\mathbf{q}}\tilde{\mathbf{q}}]|0\rangle^{(1)} \end{pmatrix}^{\mathrm{T}} \times \begin{pmatrix} -\mathbf{A}^{(0,1,2)} & -\mathbf{B}^{(1,2)^*} & -\tilde{\mathbf{C}}^{(1)} & 0 \\ -\mathbf{B}^{(1,2)} & -\mathbf{A}^{(0,1,2)^*} & 0 & -\tilde{\mathbf{C}}^{(1)^*} \\ -\mathbf{C}^{(1)} & 0 & -\mathbf{D}^{(0)} & 0 \\ 0 & -\mathbf{C}^{(1)^*} & 0 & -\mathbf{D}^{(0)^*} \end{pmatrix}^{-1} \times \begin{pmatrix} \langle 0|[\mathbf{q}, Q]|0\rangle^{(0,2)} \\ \langle 0|[\mathbf{q}^\dagger, Q]|0\rangle^{(0,2)} \\ \langle 0|[\mathbf{q}\mathbf{q}, Q]|0\rangle^{(1)} \\ \langle 0|[\mathbf{q}^\dagger\mathbf{q}^\dagger, Q]|0\rangle^{(1)} \end{pmatrix} \quad , \tag{7}$$

where the superscripts (n) denote the order, in terms of the fluctuation potential, to which the individual matrices have to be evaluated. The dimension of the matrix equations to be solved can be reduced by partitioning of the second-order polarization propagator [5, 24]

$$\langle\langle P; Q \rangle\rangle_{\omega = 0} = W_2 + W_4 \tag{8}$$

$$W_2 = \mathbf{T}(P) \times \begin{pmatrix} -\mathbf{A}^{(0,1,2)} + \mathbf{A}' & -\mathbf{B}^{(1,2)^*} \\ -\mathbf{B}^{(1,2)} & -\mathbf{A}^{(0,1,2)^*} + \mathbf{A}'^* \end{pmatrix}^{-1} \tilde{\mathbf{T}}(Q) \tag{9}$$

$$W_4 = -\langle 0|[P, \tilde{\mathbf{q}}^\dagger\tilde{\mathbf{q}}^\dagger]|0\rangle^{(1)} \mathbf{D}^{(0)^{-1}} \langle 0|[\mathbf{q}\mathbf{q}, Q]|0\rangle^{(1)} - \langle 0|[P, \tilde{\mathbf{q}}\tilde{\mathbf{q}}]|0\rangle^{(1)} \mathbf{D}^{(0)^{*-1}} \langle 0|[\mathbf{q}^\dagger\mathbf{q}^\dagger, Q]|0\rangle^{(1)} \quad , \tag{10}$$

where

$$\mathbf{A}' = \tilde{\mathbf{C}}^{(1)} \mathbf{D}^{(0)^{-1}} \mathbf{C}^{(1)} \tag{11}$$

and

$$\mathbf{T}(P) = \begin{pmatrix} \langle 0|[P, \tilde{\mathbf{q}}^{\dagger}]|0\rangle^{(0,2)} \\ \langle 0|[P, \tilde{\mathbf{q}}]|0\rangle^{(0,2)} \end{pmatrix}^{\mathrm{T}} - \begin{pmatrix} \langle 0|[P, \tilde{\mathbf{q}}^{\dagger}\tilde{\mathbf{q}}^{\dagger}]|0\rangle^{(0,2)} \mathbf{D}^{(0)^{-1}} \mathbf{C}^{(1)} \\ \langle 0|[P, \tilde{\mathbf{q}}\tilde{\mathbf{q}}]|0\rangle^{(0,2)} \mathbf{D}^{(0)^{*-1}} \mathbf{C}^{(1)^{*}} \end{pmatrix}^{\mathrm{T}} \tag{12}$$

and

$$\tilde{\mathbf{T}}(Q) = \begin{pmatrix} \langle 0|[\mathbf{q}, Q]|0\rangle^{(0,2)} \\ \langle 0|[\mathbf{q}^{\dagger}, Q]|0\rangle^{(0,2)} \end{pmatrix} - \begin{pmatrix} \tilde{\mathbf{C}}^{(1)} \mathbf{D}^{(0)^{-1}} \langle 0|[\mathbf{q}\mathbf{q}, Q]|0\rangle^{(1)} \\ \tilde{\mathbf{C}}^{(1)^{*}} \mathbf{D}^{(0)^{*-1}} \langle 0|[\mathbf{q}^{\dagger}\mathbf{q}^{\dagger}, Q]|0\rangle^{(1)} \end{pmatrix} \tag{13}$$

In previous implementations [17, 25] this partitioned form was used and the W_4 term (Eq. 10) was omitted, whereas the new implementation [18] is based on Eq. (7) and thus always includes the W_4 term. Explicit expressions for all the matrices can be found elsewhere [18, 21, 24][1]. Therefore we only note here that the original expressions [5] for the $2p$-$2h$ property gradient vectors of a triplet operator P (e.g. $\langle 0|[P, \tilde{\mathbf{q}}^{\dagger}\tilde{\mathbf{q}}^{\dagger}]|0\rangle^{(1)}$) were recently corrected [18]. The orbital diamagnetic term is evaluated as an average value using the same unrelaxed one-density matrix ρ [18, 21] as used elsewhere in the SOPPA and SOPPA(CCSD) approaches. Evaluation of the polarization propagator through first order yields the random phase approximation (RPA).

All calculations were carried out with a version of the DALTON program package [27], whose properties module ABACUS had been modified to perform SOPPA and SOPPA(CCSD) calculations of indirect nuclear spin-spin coupling constants and which is interfaced to the integral-direct coupled-cluster program of Koch and co-workers [28, 29].

3 Basis set study

The sets of Gaussian basis functions used in previous studies [5, 6, 11, 13–16] were of very different origin and quality. Apart from HD [14] and CH_4 [16, 30] none of them was optimized for calculation of indirect nuclear spin-spin coupling constants. For the present study we could also have used the carbon and hydrogen basis set of CH_4 for carbon and hydrogen in the other molecules. However, generalization of these basis sets to other atoms is not straightforward, since the contraction coefficients of carbon were chosen from self-consistent-field (SCF) molecular orbital coefficients obtained for CH_4 [16].

We decided therefore to develop a new basis set for carbon and hydrogen in CH_4, which would reproduce the results of the previous basis sets, and to generate corresponding basis sets for all the other atoms. Since the basis sets should also be used in correlated calculations the correlation consistent basis sets of Dunning and co-workers [31–33] seem to be an appropriate choice for a starting set in agreement with the recent basis set study of Helgaker et al. [10]. Although Schulman and Kaufman [34] noticed in 1972 that s-type functions with very large exponents are of utmost importance for the convergence of the Fermi contact term, this does not seem to be widely known. Consequently we investigated not only which level of the correlation-consistent basis sets, such as polarized valence double-, triple-, quadruple-zeta, is necessary or by how many sets of diffuse functions the basis set has to be augmented, but we also added s-type functions with large exponents and decontracted the s and p set. The exponents of the additional s-type functions were chosen as an even tempered series $\zeta_i = \alpha\beta^i$, where α is the exponent of the s-type function with the largest exponent ζ_n in the original basis set and β is the ratio of the exponents of the s-type functions with the two largest exponents $\beta = \zeta_n/\zeta_{n-1}$. Up to five compact s functions were thus added to the correlation-consistent basis sets. Some of the results from our basis set study at the RPA level are shown in Table 1.

Comparing the three original aug-cc-pVDZ/-pVTZ/-pVQZ basis sets shows that the results at the valence triple- and quadruple-zeta level are similar, whereas the valence double-zeta result is very different. Also the effect of totally decontracting the basis sets is not the same for the three basis sets. Whereas the absolute value of both coupling constants is strongly reduced in the aug-cc-pVDZ basis set (20% for ${}^{1}J_{{}^{13}\mathrm{C}-{}^{1}\mathrm{H}}$ and 11% for ${}^{2}J_{{}^{1}\mathrm{H}-{}^{1}\mathrm{H}}$) and only very slightly reduced in the aug-cc-pVTZ basis set (1% for ${}^{1}J_{{}^{13}\mathrm{C}-{}^{1}\mathrm{H}}$ and 3% for ${}^{2}J_{{}^{1}\mathrm{H}-{}^{1}\mathrm{H}}$), it is actually increased in the aug-cc-pVQZ basis set (4% for ${}^{1}J_{{}^{13}\mathrm{C}-{}^{1}\mathrm{H}}$ and 4% for ${}^{2}J_{{}^{1}\mathrm{H}-{}^{1}\mathrm{H}}$). On the other hand, addition of the five compact s functions increases the absolute value of the coupling constants in all basis sets. The changes amount to 37% (${}^{1}J_{{}^{13}\mathrm{C}-{}^{1}\mathrm{H}}$) and 43% (${}^{2}J_{{}^{1}\mathrm{H}-{}^{1}\mathrm{H}}$) for the aug-cc-pVDZ basis set, 15% (${}^{1}J_{{}^{13}\mathrm{C}-{}^{1}\mathrm{H}}$) and 23% (${}^{2}J_{{}^{1}\mathrm{H}-{}^{1}\mathrm{H}}$) for the aug-cc-pVTZ basis set and 10% (${}^{1}J_{{}^{13}\mathrm{C}-{}^{1}\mathrm{H}}$) and 16% (${}^{2}J_{{}^{1}\mathrm{H}-{}^{1}\mathrm{H}}$) for the aug-cc-pVQZ basis set. Combining both modifications shows a nicely converging pattern for the aug-cc-pVQZ basis set, an oscillatory behavior for the aug-cc-pVDZ basis set and a very small effect of the decontraction for the aug-cc-pVTZ basis set. An explanation for this might be:

1. The sp set of the aug-cc-pVDZ basis set is much too small and too strongly contracted for calculations of coupling constants.
2. The aug-cc-pVTZ basis set is very well contracted, i. e. without a significant change in the results for the coupling constants.
3. The aug-cc-pVQZ basis set already contains s-type functions with large enough exponents, which cannot, however, contribute if the contraction is optimized for energy calculations.

Since the differences between basis sets H and O are less than 0.4% and basis sets L, M, N and O are prohibitively large for correlated calculations, we continued the basis set optimization with basis set H. Inclusion of an extra set of diffuse functions for each angular momentum, so-called doubly augmented basis sets, in basis set K, did not change the results. Comparison of basis sets H, I and J shows that the fifth compact s-type function and the additional diffuse second polarization

---

[1] Notice the corrections to the W_4 term given in Ref. [26] and that the $C^{(1)}$ matrix in Eq. (C.16) of Ref. [24] has the wrong sign

Table 1. CH_4: basis set study for ${}^1J_{{}^{13}C-{}^1H}$ and ${}^2J_{{}^1H-{}^1H}$ (in Hz) at the (RPA) level[a]

Basis set[b]			#	${}^1J^{FC}_{{}^{13}C-{}^1H}$	${}^1J_{{}^{13}C-{}^1H}$	${}^2J^{FC}_{{}^1H-{}^1H}$	${}^2J_{{}^1H-{}^1H}$
A	aug-cc-pVDZ[c]	$4s3p2d/3s2p$	59	157.5460	158.7467	−22.0307	−22.3829
B	A + $5s/5s$[d]	$9s3p2d/8s2p$	84	216.0453	217.3378	−31.4753	−31.8216
C	A uncontracted	$10s5p2d/5s2p$	79	126.8648	128.3376	−19.6475	−19.2780
D	C + $5s/5s$[d]	$15s5p2d/10s2p$	104	156.4555	157.9259	−27.3726	−27.0038
E	aug-cc-pVTZ[c]	$5s4p3d2f/4s3p2d$	138	136.7036	138.3495	−23.4219	−23.1605
F	E + 5s/5s[e]	$10s4p3d2f/9s3p2d$	163	156.5600	158.2049	−28.7498	−28.4890
G	E uncontracted	$11s6p3d2f/6s3p2d$	158	135.7405	137.2445	−22.7491	−22.0892
H	G + $5s/5s$[e]	$16s6p3d2f/11s3p2d$	183	155.6459	157.1490	−27.7513	−27.0915
I	G + $4s/4s$[e]	$15s6p3d2f/10s3p2d$	178	155.3898	156.8929	−27.6854	−27.0257
J	I − $1f/1d$[f]	$15s6p3d1f/10s3p1d$	151	155.4226	156.9232	−27.6748	−27.0273
K	daug-cc-pVTZ uncontracted + $5s/5s$[e]	$17s7p4d3f/12s4p3d$	235	155.6492	157.1514	−27.7479	−27.0864
L	aug-cc-pVQZ[c]	$6s5p3d3f2g/5s4p3d2f$	264	138.6513	140.1672	−23.5812	−23.0022
M	L + $5s/5s$[g]	$11s5p3d3f2g/10s4p3d2f$	289	152.6952	154.2109	−27.4007	−26.8218
N	L uncontracted	$13s7p4d3f2g/7s4p3d2f$	285	143.6748	145.2671	−24.5418	−23.8216
O	N + $5s/5s$[g]	$18s7p4d3f2g/12s4p3d2f$	310	155.8447	157.4369	−27.8364	−27.1163

[a] $R_{C-H} = 1.0858$ Å; all basis sets consist of spherical Gaussian functions

[b] The specifications of the contracted basis set in front and after the solidus refer to the basis sets centered on the heavy atoms and on the hydrogen atoms, respectively

[c] Ref. [32]

[d] The exponents of the additional s-type functions are $\zeta_s(C) = 44422.0, 296074.0, 1973334.0, 13152271.0, 87659890.0$ for carbon and $\zeta_s(H) = 86.0, 572.0, 3793.0, 25153.0, 166789.0$ for hydrogen

[e] The exponents of the additional s-type functions are $\zeta_s(C) = 54924.0, 366281.0, 2442668.0, 16289729.0, 108633300.0$ for carbon and $\zeta_s(H) = 225.0, 1496.0, 9950.0, 66145.0, 439713.0$ for hydrogen

[f] One f-type function $[\zeta_f(C) = 0.268]$ centered on carbon and one d-type function $[\zeta_d(H) = 0.247]$ centered on hydrogen were removed

[g] The exponents of the additional s-type functions are: $\zeta_s(C) = 226889.0, 1514974.0, 10115704.0, 67544045.0, 451001506.0$ for carbon and $\zeta_s(H) = 550.0, 3664.0, 24403.0, 162504.0, 1082138.0$ for hydrogen

Table 2. H_2: results[a] of different methods for ${}^1J_{{}^1H-{}^2H}$ (in Hz) using basis sets I[b] and II[c]

	Method	J^{OD}	J^{OP}	J^{SD}	J^{FC}	J[d]
I	RPA	−0.33	0.83	0.57	53.23	54.30
	SOPPA	−0.32	0.83	0.51	43.11	44.12
	SOPPA(CCSD)	−0.31	0.81	0.49	40.33	41.33
II	RPA	−0.31	0.78	0.59	52.99	54.05
	SOPPA	−0.30	0.78	0.52	42.94	43.93
	SOPPA(CCSD)	−0.29	0.76	0.50	40.19	41.17

[a] $R_{H-H} = 0.740848$ Å; The ground state total energies for basis set I are: $E_{SCF} = -1.133619\ \hbar/m_e a_0^2$, $E_{MP2} = -1.165876\ \hbar/m_e a_0^2, E_{CCSD} = -1.173406\ \hbar/m_e a_0^2$; and for basis set II: $E_{SCF} = -1.133318\ \hbar/m_e a_0^2, E_{MP2} = -1.165288\ \hbar/m_e a_0^2$, $E_{CCSD} = -1.172986\ \hbar/m_e a_0^2$

[b] Cartesian Gaussian basis set H from Ref. [14]: ($14s5p2d$)

[c] Basis set J from Table 1

[d] Experimental values: 42.94 ± 0.04 at 300 K [46]; 41.13 ± 0.04 equilibrium value obtained by subtracting the computed [14] rovibrational correction at $T = 300$ K (1.81 Hz) from the experimental value in Ref. [46]

functions (f-type function on C and d-type function on H) in the augmented basis set changes the results by at most 0.2 % and can therefore be omitted. Our final basis set is thus basis set J, which is called II in Tables 2–15. Basis sets for the other atoms B, Al, N, O and F were constructed accordingly. Details of the basis sets are given in the footnotes to Tables 3, 4, 12, 13 and 15.

After the completion of this work, Helgaker and coworkers [10] published a similar study of basis set effects on the coupling constants of HF and H_2O. Besides the aug-cc-pVXZ basis sets they also investigated the cc-pCVXZ basis sets, which include an additional function meant to describe the core valence region. They also extended the basis sets by decontracting the s functions and by adding additional tight s functions. Their findings fully agree with our conclusions.

4 Results and discussion

4.1 Earlier SOPPA numbers and the W_4 term

There are three main differences between the previous SOPPA and the present SOPPA numbers. The present SOPPA uses the unrelaxed second-order density rather than Hartree-Fock densities to obtain the J^{OD} contribution. It includes the W_4 term and finally the correct formulas for the triplet $2p$-$2h$ property gradient vectors are used [18]. One of the purposes of this paper is to determine the importance of the W_4 term.

The present SOPPA implementation without the W_4 term is labeled SOPPA(W2). Comparing SOPPA and SOPPA(W2) showed that inclusion of the W_4 term in the J^{OP} contribution is of no importance for all the molecules considered here. This confirmed the findings of a previous study [19], where the importance of the W_4 term for another singlet response function, the polarizability, was investigated.

However, this is not completely the case for the triplet properties J^{FC} and J^{SD}. The largest relative difference in J^{SD} of 14% is observed for HF. The W_4 contribution to J^{FC} is largest for AlH (7%), N_2 (3%) and CO (1%). In absolute terms the W_4 term is, however, only important for AlH, where $W_4(J^{FC})$ is 10% of the total J and for N_2, where the change in J^{FC} is 2% of the total J.

Table 3. HF: results[a] of different methods for $^1J_{^{19}F-^1H}$ (in Hz) using basis sets I[b] and II[c]

	Method	J^{OD}	J^{OP}	J^{SD}	J^{FC}	J^{d}
I	RPA	−0.06	199.41	−12.43	468.65	655.57
	SOPPA	0.02	195.88	−0.65	339.74	534.99
	SOPPA(CCSD)	0.03	194.58	−1.12	331.91	525.40
II	RPA	−0.03	195.05	−11.73	483.62	666.91
	SOPPA(W2)	0.04	190.52	−0.64	348.43	538.34
	SOPPA	0.04	190.65	−0.56	349.40	539.52
	SOPPA(CCSD)	0.05	189.82	−0.94	340.50	529.43

[a] $R_{H-F} = 0.916958$ Å; The ground-state total energies for basis set I are: $E_{SCF} = -100.069693\ \hbar/m_e a_0^2$, $E_{MP2} = -100.369908\ \hbar/m_e a_0^2, E_{CCSD} = -100.371882\ \hbar/m_e a_0^2$; and for basis set II: $E_{SCF} = -100.061758\ \hbar/m_e a_0^2, E_{MP2} = -100.392090\ \hbar/m_e a_0^2, E_{CCSD} = -100.394003\ \hbar/m_e a_0^2$

[b] Cartesian Gaussian basis set from Ref. [6]: $(13s8p4d/8s3p1d)$ contracted to $[9s6p4d/6s3p1d]$

[c] Spherical Gaussian basis set $(15s6p3d1f/10s3p1d)$. Hydrogen: basis set J from Table 1; fluorine: uncontracted aug-cc-pVTZ augmented by four s-type functions with exponents $\zeta_s(F) = 130088.0$, 867853.0, 5789645.0, 38624049.0 and without the f-type function with exponent $\zeta_f(F) = 0.724$

[d] Experimental values: 529 ± 23 [47]; 558 ± 23 equilibrium value obtained by subtracting the computed [45] zero-point rovibrational correction (−28.9 Hz) from the experimental value in Ref. [47]

Table 4. H_2O: results[a] of different methods for $^1J_{^{17}O-^1H}$ (in Hz) using basis sets I[b] and II[c]

	Method	J^{OD}	J^{OP}	J^{SD}	J^{FC}	J^{d}
I	RPA	−0.07	−12.25	0.39	−85.00	−96.94
	SOPPA	−0.08	−11.51	−0.17	−67.01	−78.77
	SOPPA(CCSD)	−0.08	−11.42	−0.18	−65.55	−77.23
II	RPA	−0.04	−12.27	−0.01	−91.12	−103.44
	SOPPA	−0.05	−11.56	−0.47	−70.34	−82.42
	SOPPA(CCSD)	−0.05	−11.51	−0.47	−68.56	−80.60

[a] $R_{O-H} = 0.958390$ Å, $\angle_{HOH} = 104.45$; The ground-state total energies for basis set I are: $E_{SCF} = -76.060784\ \hbar/m_e a_0^2$, $E_{MP2} = -76.310968\ \hbar/m_e a_0^2$, $E_{CCSD} = -76.317357\ \hbar/m_e a_0^2$; and for basis set II: $E_{SCF} = -76.061259\ \hbar/m_e a_0^2$, $E_{MP2} = -76.377714\ \hbar/m_e a_0^2$, $E_{CCSD} = -76.383475\ \hbar/m_e a_0^2$

[b] Cartesian Gaussian basis set from Ref. [48]: $(11s7p2d/5s1p)$ contracted to $[6s5p1d/3s1p]$

[c] Spherical Gaussian basis set $(15s6p3d1f/10s3p1d)$. Hydrogen: basis set J from table 1; oxygen: uncontracted aug-cc-pVTZ augmented by four s-type functions with exponents $\zeta_s(O) = 102222.0$, 681629.0, 4545186.0, 30307833.0 and without the f-type function with exponent $\zeta_f(O) = 0.500$

[d] Experimental values: −78.70 ± 0.02 measured in cyclohexane-d_{12} at 293 K [49]; −83.04 ± 0.02 equilibrium value obtained by subtracting the computed [40] rovibrational correction at 300 K (4.34 Hz) from the experimental value in Ref. [49]; −80.62 ± 0.06 measured in nitromethane-d_3 at 323 K [50]; −85.01 ± 0.06 equilibrium value obtained by subtracting the computed [40] rovibrational correction at 340 K (4.39 Hz) from the experimental value in Ref. [50]

Table 5. H_2O: results[a] of different methods for $^2J_{^1H-^1H}$ (in Hz) using basis sets I[b] and II[c]

	Method	J^{OD}	J^{OP}	J^{SD}	J^{FC}	J^{d}
I	RPA	−7.17	8.12	1.47	−25.05	−22.63
	SOPPA	−7.02	8.25	1.10	−13.90	−11.57
	SOPPA(CCSD)	−7.05	8.26	1.09	−13.44	−11.14
II	RPA	−7.23	9.09	1.25	−25.50	−22.39
	SOPPA	−7.13	9.29	0.90	−12.19	−9.14
	SOPPA(CCSD)	−7.14	9.31	0.89	−11.87	−8.81

[a–c] See footnotes [a–c] to Table 4

[d] Experimental values: −7.2 ± 0.7 at ambient temperature in organic solvent [51]; −7.8 ± 0.7 equilibrium value obtained by subtracting the computed [40] rovibrational correction at 300 K (0.55 Hz) from the experimental value in Ref. [51]; −7.34 ± 0.03 nitromethane-d_3 at 297 K [50]; −7.89 ± 0.03 equilibrium value obtained by subtracting the computed [40] rovibrational correction at 300 K (0.55 Hz) from the experimental value in Ref. [50]

4.2 Results with the new basis sets

We now discuss the results obtained using the extended correlation-consistent basis sets described in Sect. 3.

Comparison of the results obtained with the two different basis sets shows the variable quality of the basis sets used in previous studies [5, 6, 11, 13–16]. Since the basis set for C_2H_2 is the smallest the largest basis set effect at the RPA level is observed for the one-bond coupling constants $^1J_{^{13}C-^{13}C}$ (33.9 Hz, 9%) and $^1J_{^{13}C-^1H}$ (16.7 Hz, 4%) in this molecule. However, the one-bond coupling constants in HF (11 Hz, 2%), H_2O (6.5 Hz,

Table 6. CH_4: results[a] of different methods for ${}^1J_{{}^{13}C-{}^1H}$ (in Hz) using basis sets I[b] and II[c]

	Method	J^{OD}	J^{OP}	J^{SD}	J^{FC}	J^{d}
I	RPA	0.25	1.39	−0.24	155.96	157.37
	SOPPA	0.26	1.49	−0.01	126.92	128.65
	SOPPA(CCSD)	0.26	1.44	0.01	122.15	123.86
II	RPA	0.24	1.47	−0.21	155.42	156.92
	SOPPA	0.25	1.54	0.02	125.07	126.88
	SOPPA(CCSD)	0.25	1.50	0.03	120.58	122.32

[a] $R_{C-H} = 1.0858$ Å; The ground-state total energies for basis set I are: $E_{SCF} = -40.215277\ \hbar/m_e a_0^2, E_{MP2} = -40.438357\ \hbar/m_e a_0^2, E_{CCSD} = -40.460402\ \hbar/m_e a_0^2$; and for basis set II: $E_{SCF} = -40.214507\ \hbar/m_e a_0^2$, $E_{MP2} = -40.458618\ \hbar/m_e a_0^2$, $E_{CCSD} = -40.480654\ \hbar/m_e a_0^2$

[b] Cartesian Gaussian basis set from Ref. [30]: $(15s7p4d/9s2p)$ contracted to $[10s5p4d/6s2p]$

[c] Basis set J from Table 1

[d] Experimental value: 120.87 ± 0.05 equilibrium value [52]

Table 7. CH_4: results[a] of different methods for ${}^2J_{{}^1H-{}^1H}$ (in Hz) using basis sets I[b] and II[c]

	Method	J^{OD}	J^{OP}	J^{SD}	J^{FC}	J^{d}
I	RPA	−3.54	3.63	0.44	−27.69	−27.16
	SOPPA	−3.54	3.63	0.35	−16.26	−15.83
	SOPPA(CCSD)	−3.51	3.60	0.34	−14.87	−14.45
II	RPA	−3.54	3.73	0.46	−27.68	−27.03
	SOPPA	−3.55	3.75	0.37	−15.85	−15.28
	SOPPA(CCSD)	−3.53	3.72	0.36	−14.53	−13.98

[a–c] See footnotes [a–c] to Table 6

[d] Experimental values: −12.564 ± 0.004 [53]; −11.878 ± 0.004 equilibrium value obtained by subtracting the computed [30] zero-point rovibrational correction (−0.686 Hz) from the experimental value in Ref. [53]

Table 8. C_2H_2: results[a] of different methods for ${}^1J_{{}^{13}C-{}^{13}C}$ (in Hz) using basis sets I[b] and II[c]

	Method	J^{OD}	J^{OP}	J^{SD}	J^{FC}	J^{d}
I	RPA	0.01	15.60	29.87	347.41	392.90
	SOPPA	0.02	6.77	8.48	164.83	180.09
	SOPPA(CCSD)	0.01	6.21	8.28	164.58	179.08
II	RPA	0.01	15.05	29.06	365.35	409.47
	SOPPA	0.01	6.73	8.55	173.97	189.25
	SOPPA(CCSD)	0.01	6.34	8.46	173.92	188.72

[a] $R_{C-C} = 2.27391a_0, R_{C-H} = 2.00406a_0$; The ground-state total energies for basis set I are: $E_{SCF} = -76.840569\ \hbar/m_e a_0^2, E_{MP2} = -77.151410\ \hbar/m_e a_0^2, E_{CCSD} = -77.167593\ \hbar/m_e a_0^2$; and for basis set II: $E_{SCF} = -76.851242\ \hbar/m_e a_0^2, E_{MP2} = -77.251388\ \hbar/m_e a_0^2, E_{CCSD} = -77.266707\ \hbar/m_e a_0^2$

[b] 6-31G** [54] called basis set II in Ref. [11]: cartesian Gaussian basis set $(11s5p1d/5s1p)$ contracted to $[4s3p1d/3s1p]$

[c] Basis set J from Table 1

[d] Experimental value: 171.5 [55]

Table 9. C_2H_2: results[a] of different methods for ${}^1J_{{}^{13}C-{}^1H}$ (in Hz) using basis sets I[b] and II[c]

	Method	J^{OD}	J^{OP}	J^{SD}	J^{FC}	J^{d}
I	RPA	0.33	−3.55	4.19	376.26	377.21
	SOPPA	0.33	−0.59	0.47	237.64	237.84
	SOPPA(CCSD)	0.33	−0.58	0.44	228.49	228.69
II	RPA	0.27	−3.60	3.04	411.41	411.11
	SOPPA	0.26	−0.83	0.46	263.04	262.94
	SOPPA(CCSD)	0.27	−0.85	0.43	253.73	253.58

[a–c] See footnotes [a–c] to Table 8

[d] Experimental value: 248.7 [55]

7%), AlH [5.8 Hz, 84% at the SOPPA(CCSD) level] and the geminal coupling constants ${}^2J_{{}^{13}C-{}^1H}$ C_2H_2 [5.5 Hz, 12% in SOPPA(CCSD)] and ${}^2J_{{}^1H-{}^1H}$ H_2O [2.3 Hz, 21% in SOPPA(CCSD)] are also significantly affected by the use of an improved basis set. Furthermore, the effect of the enlarged basis set manifests itself differently at the uncorrelated and the correlated level. With the exception of N_2 we find that the correlation correction to the coupling constants is larger in extended basis set II. This is in contrast to what is found, for example, for polar-

Table 10. C_2H_2: results[a] of different methods for $^2J_{^{13}C-^1H}$ (in Hz) using basis sets I[b] and II[c]

	Method	J^{OD}	J^{OP}	J^{SD}	J^{FC}	J^{d}
I	RPA	−1.34	7.98	−3.04	−57.57	−53.98
	SOPPA	−1.34	5.28	0.64	42.44	47.02
	SOPPA(CCSD)	−1.33	5.08	0.65	41.82	46.21
II	RPA	−1.35	8.28	−1.52	−55.25	−49.85
	SOPPA	−1.35	5.75	0.97	47.24	52.62
	SOPPA(CCSD)	−1.35	5.60	0.98	46.47	51.71

[a–c] See footnotes [a–c] to Table 8
[d] Experimental value: 49.2 [55]

Table 11. C_2H_2: results[a] of different methods for $^3J_{^1H-^1H}$ (in Hz) using basis sets I[b] and II[c]

	Method	J^{OD}	J^{OP}	J^{SD}	J^{FC}	J^{d}
I	RPA	−3.58	4.67	3.32	77.23	81.64
	SOPPA	−3.57	3.93	0.61	10.60	11.57
	SOPPA(CCSD)	−3.55	3.87	0.59	9.67	10.58
II	RPA	−3.60	5.54	3.02	79.93	84.88
	SOPPA	−3.60	4.85	0.60	10.31	12.16
	SOPPA(CCSD)	−3.58	4.81	0.59	9.49	11.31

[a–c] See footnotes [a–c] to Table 8
[d] Experimental value: 9.6 [55]

Table 12. BH: results[a] of different methods for $^1J_{^{11}B-^1H}$ (in Hz) using basis sets I[b] and II[c]

	Method	J^{OD}	J^{OP}	J^{SD}	J^{FC}	J
I	RPA	−0.52	−0.40	[d]	66.00	
	SOPPA	−0.51	−0.66	[d]	53.52	
	SOPPA(CCSD)	−0.51	−1.06	−1.21	52.06	49.27
II	RPA	−0.51	−0.32	[d]	66.95	
	SOPPA	−0.51	−0.61	[d]	53.32	
	SOPPA(CCSD)	−0.51	−1.01	1.04	51.92	51.44

[a] $R_{B-H} = 2.336 a_0$; The ground-state total energies for basis set I are: $E_{SCF} = -25.131332\ \hbar/m_e a_0^2, E_{MP2} = -25.239271\ \hbar/m_e a_0^2, E_{CCSD} = -25.267231\ \hbar/m_e a_0^2$; and for basis set II: $E_{SCF} = -25.130563\ \hbar/m_e a_0^2, E_{MP2} = -25.245099\ \hbar/m_e a_0^2, E_{CCSD} = -25.272104\ \hbar/m_e a_0^2$
[b] Cartesian Gaussian basis set from Ref. [56]: $(13s8p4d/10s3p)$ contracted to $[8s6p4d/6s3p]$
[c] Spherical Gaussian basis set $(15s6p3d1f/10s3p1d)$. Hydrogen: basis set J from table 1; boron: uncontracted aug-cc-pVTZ augmented by four s-type functions with exponents $\zeta_s(B) = 36488$, 243274, 1621926, 10813498 and without the f-type function with exponent $\zeta_f(B) = 0.163$
[d] Triplet instability

Table 13. AlH: results[a] of different methods for $^1J_{^{27}Al-^1H}$ (in Hz) using basis sets I[b] and II[c]

	Method	J^{OD}	J^{OP}	J^{SD}	J^{FC}	J
I	RPA	−0.10	−2.30	[d]	−18.26	
	SOPPA	−0.10	−2.58	0.45	1.63	−0.61
	SOPPA(CCSD)	−0.10	−2.58	0.42	9.15	6.90
II	RPA	−0.10	−2.29	[d]	−17.61	
	SOPPA(W2)	−0.09	−2.60	0.38	7.91	5.60
	SOPPA	−0.09	−2.61	0.38	8.46	6.14
	SOPPA(CCSD)	−0.09	−2.66	0.36	15.09	12.70

[a] $R_{Al-H} = 3.114\, a_0$; The ground-state total energies for basis set I are: $E_{SCF} = -242.458417\ \hbar/m_e a_0^2$, $E_{MP2} = -242.737791\ \hbar/m_e a_0^2$, $E_{CCSD} = -242.758264\ \hbar/m_e a_0^2$; and for basis set II: $E_{SCF} = -242.462214\ \hbar/m_e a_0^2$, $E_{MP2} = -242.697400\ \hbar/m_e a_0^2$, $E_{CCSD} = -242.717984\ \hbar/m_e a_0^2$
[b] Cartesian Gaussian basis set from Ref. [15]: $(16s10p5d/12s6p4d)$ contracted to $[12s7p4d/8s4p2d]$
[c] Spherical Gaussian basis set $(20s10p3d1f/10s3p1d)$. Hydrogen: basis set J from Table 1; aluminum: uncontracted aug-cc-pVTZ augmented by four s-type functions with exponents $\zeta_s(Al) = 1372002$, 9160058, 61156336, 408304972 and without the f-type function with exponent $\zeta_f(Al) = 0.0858$
[d] Triplet instability

izabilities [35]. Finally it is interesting to note that the spin-dipolar contribution to $^1J_{^{11}B-^1H}$ in BH has different signs in the two basis sets.

Comparing the four contributions to the coupling constants and their correlation dependence we can see that with the exception of the geminal or vicinal hydrogen-hydrogen coupling constants $J_{^1H-^1H}$ in H_2O, CH_4 and C_2H_2, the orbital diamagnetic term gives a small contribution to the total coupling constants. J^{OD} is calculated as an average value and it turns out that it

Table 14. CO: results[a] of different methods for $^{1}J_{^{13}\mathrm{C}-^{17}\mathrm{O}}$ (in Hz) using basis sets I[b] and II[c]

	Method	J^{OD}	J^{OP}	J^{SD}	J^{FC}	J^{d}
I	RPA	0.10	12.25	−9.29	−8.15	−5.09
	SOPPA	0.09	14.81	−4.41	9.43	19.92
	SOPPA(CCSD)	0.09	14.49	−4.45	8.10	18.23
II	RPA	0.10	11.81	−9.07	−8.53	−5.69
	SOPPA(W2)	0.10	14.43	−4.29	10.34	20.58
	SOPPA	0.10	14.42	−4.31	10.20	20.41
	SOPPA(CCSD)	0.10	14.11	−4.37	8.76	18.60

[a] $R_{\mathrm{C-O}} = 2.132\,a_0$; The ground-state total energies for basis set I are: $E_{\mathrm{SCF}} = -112.785795\,\hbar/m_{\mathrm{e}}a_0^2$, $E_{\mathrm{MP2}} = -113.169439\,\hbar/m_{\mathrm{e}}a_0^2$, $E_{\mathrm{CCSD}} = -113.173724\,\hbar/m_{\mathrm{e}}a_0^2$; and for basis set II : $E_{\mathrm{SCF}} = -112.782411\,\hbar/m_{\mathrm{e}}a_0^2$, $E_{\mathrm{MP2}} = -113.234629\,\hbar/m_{\mathrm{e}}a_0^2$, $E_{\mathrm{CCSD}} = -113.23985\,\hbar/m_{\mathrm{e}}a_0^2$

[b] Cartesian Gaussian basis set from Ref. [13]: $(12s7p3d)$ contracted to $[8s4p3d]$

[c] Spherical Gaussian basis set $(15s6p3d1f/10s3p1d)$. Carbon: basis set J from table 1; oxygen: see footnote [c] of Table 4

[d] Experimental values: 16.4±0.1 [57]; 15.6±0.1 equilibrium value obtained by subtracting the zero-point rovibrational correction computed [13] at the SOPPA level (0.76 Hz) from the experimental value in Ref. [57]

Table 15. N_2 : results[a] of different methods for $^{1}J_{^{15}\mathrm{N}-^{14}\mathrm{N}}$ (in Hz) using basis sets I[b] and II[c]

	Method	J^{OD}	J^{OP}	J^{SD}	J^{FC}	J^{d}
I	RPA	0.03	0.50	−8.16	−7.67	−15.31
	SOPPA	0.03	3.25	−1.69	0.98	2.56
	SOPPA(CCSD)	0.03	3.17	−1.78	0.58	2.00
II	RPA	0.03	0.43	−7.84	−7.49	−14.87
	SOPPA(W2)	0.03	3.09	−1.66	1.25	2.72
	SOPPA	0.03	3.09	−1.65	1.21	2.67
	SOPPA(CCSD)	0.03	3.00	−1.76	0.79	2.06

[a] $R_{\mathrm{N-N}} = 2.068\,a_0$; The ground-state total energies for basis set I are: $E_{\mathrm{SCF}} = -108.988608\,\hbar/m_{\mathrm{e}}a_0^2$, $E_{\mathrm{MP2}} = -109.391950\,\hbar/m_{\mathrm{e}}a_0^2$, $E_{\mathrm{CCSD}} = -109.391767\,\hbar/m_{\mathrm{e}}a_0^2$; and for basis set II: $E_{\mathrm{SCF}} = -108.986727\,\hbar/m_{\mathrm{e}}a_0^2$, $E_{\mathrm{MP2}} = -109.457078\,\hbar/m_{\mathrm{e}}a_0^2$, $E_{\mathrm{CCSD}} = -109.457556\,\hbar/m_{\mathrm{e}}a_0^2$

[b] Cartesian Gaussian basis set from Ref. [13]: $(12s7p3d)$ contracted to $[8s4p3d]$. Note that contrary to the statement in Ref. [13] the exponents for the *s*- and *p*-type functions are taken from the van Duijneveldt [58] $12s7p$ basis set for nitrogen, the contraction coefficients are the ones given in Table II of Ref. [13] and the exponents of the *d*-type functions are $\zeta_d(\mathrm{N}) = 0.11, 0.45, 1.51$

[c] Spherical Gaussian basis set $(15s6p3d1f/10s3p1d)$. Nitrogen: uncontracted aug-cc-pVTZ augmented by four *s*-type functions with exponents $\zeta_s(\mathrm{N}) = 76177, 508148, 3389636, 22610777$ and without the *f*-type function with exponent $\zeta_f(\mathrm{N}) = 0.364$

[d] Experimental values: 1.8 ± 0.6[59]; 1.4 ± 0.6 equilibrium value obtained by subtracting the zero-point rovibrational correction computed [13] at the SOPPA level (0.43 Hz) from the experimental value in Ref. [59]

hardly makes any difference whether the SCF density, the unrelaxed second order density with Møller-Plesset correlation coefficients or coupled-cluster amplitudes are used. The largest change between the correlated and uncorrelated results are observed for $J_{^{1}\mathrm{H}-^{1}\mathrm{H}}$ in H_2O (0.1 Hz) and for the coupling constant in HF (0.7 Hz). In the latter case the sign of J^{OD} is also altered at the correlated level. Otherwise the changes are 0.02 Hz or less.

The three other contributions to the total coupling constant are calculated as polarization propagators as described in Sect. 2 and they are therefore as expected more dependent on electron correlation. There is a moderate correlation contribution to the J^{OP} term. It is most pronounced for the triply bonded molecules. The difference between SOPPA and SOPPA(CCSD) orbital paramagnetic results is very modest. The largest absolute difference is found in the HF molecule where the SOPPA number is 0.83 Hz larger than the SOPPA(CCSD) result. However, the relative difference is less than 0.5% . For the BH molecule there is a relatively larger difference: SOPPA(CCSD) is numerically larger by 66% . This is not surprising since SOPPA is known to have difficulties describing the near degeneracy effects in BH [15, 36–38]. The spin-dipolar term is even unstable for SOPPA.

It is well-known that RPA gives unreliable triplet properties and in this study we see no exceptions from this general observation. In two of the molecules, BH and AlH, we even get instabilities for the spin-dipolar contribution.

The contributions to the spin-dipolar term from SOPPA and SOPPA(CCSD) differ by at most 0.1 Hz except in one case. For the HF molecule the difference is 0.38 Hz. In this molecule we also have a large absolute correlation contribution to J^{OP}.

The main difference between the SOPPA and SOPPA (CCSD) numbers comes from the Fermi contact contribution. In all cases but AlH ($\Delta J^{\mathrm{FC}} = 6.63$ Hz) the absolute SOPPA(CCSD) value of J^{FC} is smaller than the corresponding SOPPA result. For the HF molecule the change is 9.0 Hz. This is only exceeded by the change in $^{1}J^{\mathrm{FC}}_{^{13}\mathrm{C}-^{1}\mathrm{H}}$ for C_2H_2 which is 9.3 Hz.

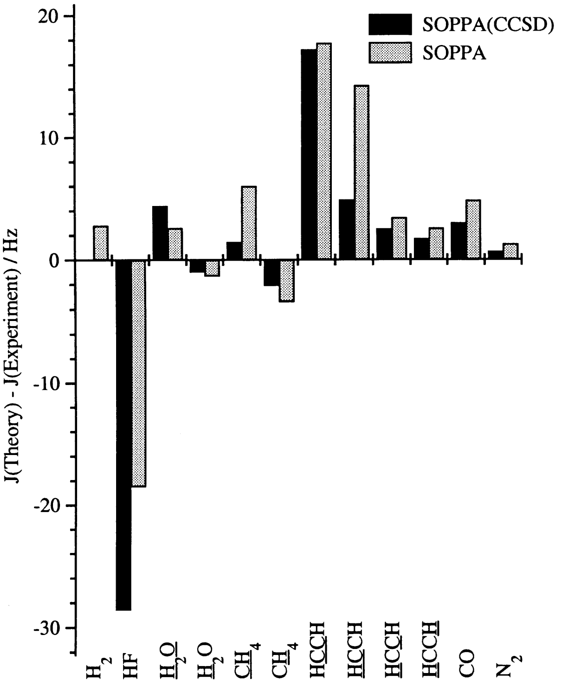

Fig. 1. Deviation from experiment of calculated coupling constants using SOPPA and SOPPA(CCSD) with basis sets II. The coupling is between the *underlined atoms*, where choices exist

4.3 Comparison with experiment and other correlated calculations

In Fig. 1 we show the deviation of the SOPPA and SOPPA(CCSD) coupling constants from experimental data. When available we have subtracted the rovibrational correction from the experimental couplings in order to consider comparable quantities. The figure demonstrates that the SOPPA(CCSD) results are generally in better agreement with experiments than the SOPPA results with the exceptions of HF and ${}^1J_{^{17}\mathrm{O}-^1\mathrm{H}}$ in H_2O. For all molecules but HF and C_2H_2 SOPPA(CCSD) gives coupling constants which differ by less than 2.5 Hz from the experimental data. It should, however, be noted that not all the experimental numbers are obtained from gas-phase experiments nor have the rovibrational contributions been taken into account in all cases. The latter effects are investigated in another series of papers [30, 39–41] and may amount to as much as 5% .

For some of the molecules we can also compare our SOPPA (CCSD) values with other theoretical results. In particular for CH_4, HF, CO and N_2 we can compare our results obtained with basis set I directly with the multicon figurational random phase approximation (MCRPA) ones of Vahtras and coworkers [7, 42] and the equation-of-motion coupled cluster singles and doubles (EOM-CCSD) results of Perera et al. [43] as in principle, they used the same basis sets. Fukui et al. [44] reported finite-field second-order perturbation theory calculations of the coupling constants of HF, H_2O and CH_4. Unfortunately the basis sets used were quite small and their uncorrelated results thus differ too much from our RPA results for a meaningful comparison. In the case of HF [45] and H_2O [40] MCRPA calculations with larger basis sets have recently been reported.

Using the EOM-CCSD method Perera et al. [43] computed ${}^1J_{\mathrm{HF}}$ to be 516.3 Hz. The correlation correction was -140.7 Hz, which is larger than the -130.2 Hz we find at the SOPPA(CCSD) level. However, the large error bars (± 23 Hz) on the experimental value make it impossible to say which method performs better. Åstrand et al. [45] using an atomic natural orbital basis set obtained 647.3 at the RPA level and 516.3 with a large MCRPA calculation, which amounts to a correlation correction of -131 Hz in close agreement with our SOPPA(CCSD) result.

For ${}^1J_{^{17}\mathrm{O}-^1\mathrm{H}}$ (${}^2J_{^1\mathrm{H}-^1\mathrm{H}}$) in H_2O Perera et al. [43] obtained -95.44 Hz (-22.44 Hz) at the RPA and -74.90 Hz (-10.81 Hz) at the EOM-CCSD level using a basis set of size comparable to our basis set I. The correlation correction at the EOM-CCSD level is thus only slightly larger than ours in SOPPA(CCSD). Using an even larger basis set than basis set II, Wigglesworth et al. [40] obtained MCRPA results of -83.93 Hz (-9.60 Hz) and SOPPA(CCSD) results of -81.56 Hz (-8.58 Hz).

The MCRPA results of Vahtras et al. [7] for CH_4, 125.3 Hz for ${}^1J_{^{13}\mathrm{C}-^1\mathrm{H}}$ and -15.30 Hz for ${}^2J_{^1\mathrm{H}-^1\mathrm{H}}$, are slightly larger than our SOPPA(CCSD) results and thus further away from experiments.

For CO and N_2 the EOM-CCSD method [43] using basis set I gives 15.5 Hz and 1.4 Hz, respectively, and thus in this case (as opposed to the case of H_2O and HF) a smaller correlation correction than SOPPA(CCSD). Vahtras et al. [42] reported MCRPA results of 12.11 Hz (CO) and 0.22 (N_2) using a complete active space wavefunction, which clearly underestimates the correlation correction. Including more active orbitals in the form of a restricted active space calculation they obtained 16.10 Hz (CO) and 0.77 Hz (N_2).

5 Conclusion

Following the same genearal rules as Helgaker et al. [10] we have developed new basis sets for use in spin-spin coupling constant calculations. The basis sets are constructed from the correlation consistent basis sets of Dunning and coworkers [31–33]. These new sets have great flexibility and include the all-important tight *s* functions.

The new basis sets have been used to get up-to-date non-relativistic results for the spin-spin couplings of nine molecules. In particular we have investigated the performance of the latest coupled-cluster generalization of SOPPA, SOPPA(CCSD).

Compared with experimental coupling constants SOPPA(CCSD) in general improves on the SOPPA results. For the majority of the coupling constants calculated the deviation from experiment is less than 2.5 Hz. The most noticeable exception from this rule is the carbon-carbon coupling in acetylene. The origin of this disagreement is not clear. In comparison with EOM-CCSD the correlation corrections obtained with SOP-

PA(CCSD) are smaller for HF and H_2O and larger for CO and N_2, whereas they are larger than what was previously obtained for H_2O, CH_4, CO and N_2 using medium-sized complete or restrictive active space calculations.

The SOPPA(CCSD) method serves as a cost efficient improvement over SOPPA for calculating reliable spin-spin coupling constants. Even though the step necessary to obtain the correlation coefficient scales as N^6 the rest of the calculation is no more expensive than N^5 as in a regular SOPPA calculation.

Analyzing contributions to the polarization propagator at the SOPPA level we found that the second-order W_4 term is of little importance, but exceptions were observed for triplet response properties of the AlH and N_2 molecules.

Acknowledgements. SPAS is grateful to Henrik Koch for making the integral-direct coupled-cluster program available. This work was supported by grants Nos. 9600856, 93133141 and 9701136 from the Danish National Sciences Research Council.

References

1. Linderberg J, Öhrn Y (1973) Propagators in quantum chemistry, Academic Press, London
2. Oddershede J, Jørgensen P, Beebe NHF (1975) J Chem Phys 63:2996
3. Oddershede J, Jørgensen P, Beebe NHF (1977) Chem Phys 25:451
4. Albertsen P, Jørgensen P, Yeager DL (1980) Chem Phys Lett 76:354
5. Geertsen J, Oddershede J (1984) Chem Phys 90:301
6. Geertsen J, Oddershede J, Scuseria GE (1987) Int J Quantum Chem Symp 21:475
7. Vahtras O, Ågren H, Jørgensen P, Jensen HJAa, Padkjær SB, Helgaker T (1992) J Chem Phys 96:6120
8. Ramsey NF (1953) Phys Rev 91:303
9. Aucar GA, Oddershede J (1993) Int J Quantum Chem 47:425
10. Helgaker T, Jaszuński M, Ruud K, Górska A (1998) Theor Chem Acc 99:175
11. Geertsen J, Oddershede J (1986) Chem Phys 104:67
12. Geertsen J (1987) Chem Phys Lett 134:400
13. Geertsen J, Oddershede J, Scuseria GE (1987) J Chem Phys 87:2138
14. Oddershede J, Geertsen J, Scuseria GE (1988) J Phys Chem 92:3056
15. Scuseria GE, Geertsen J, Oddershede J (1989) J Chem Phys 90:2338
16. Geertsen J, Oddershede J, Raynes WT, Scuseria GE (1991) J Magn Reson 93:458
17. Scuseria GE (1986) Chem Phys Lett 127:236
18. Packer MJ, Dalskov EK, Enevoldsen T, Jensen HJA, Oddershede J (1996) J Chem Phys 105:5886
19. Nielsen ES, Jørgensen P, Oddershede J (1980) J Chem Phys 73:6238
20. Geertsen J, Eriksen S, Oddershede J (1991) Adv Quantum Chem 22:167
21. Sauer SPA (1997) J Phys B 30:3773
22. Mills I, Cvitaš T, Homann K, Kallay N, Kuchitsu K (1993) Qantities, units and symbols in physical chemistry. Blackwell, Oxford
23. Sauer SPA (1993) J Chem Phys 98:9220
24. Oddershede J, Jørgensen P, Yeager DL (1984) Comput Phys Rep 2:33
25. Diercksen GHF, Kraemer WP MUNICH, Molecular Program System. Max-Planck-Institut für Physik und Astrophysik, Munich
26. Sauer SPA, Diercksen GHF, Oddershede J (1991) Int J Quantum Chem 39:667
27. Helgaker T, Jensen HJAa, Jørgensen P, Olsen J, Ruud K, Ågren H, Andersen T, Bak KL, Bakken V, Christiansen O, Dahle P, Dalskov EK, Enevoldsen T, Fernandez B, Heiberg H, Hettema H, Jonsson D, Kirpekar S, Kobayashi R, Koch H, Mikkelsen KV, Norman P, Packer MJ, Saue T, Taylor PR, Vahtras O (1997) DALTON, an electronic structure program, release 1.0. http://www.kjemi.uio.no/software/dalton/dalton.html
28. Koch H, Christiansen O, Kobayashi R, Jørgensen P, Helgaker T (1994) Chem Phys Lett 228:233
29. Koch H, de Merás AS, Helgaker T, Christiansen O (1996) J Chem Phys 104:4157
30. Wigglesworth RD, Raynes WT, Sauer SPA, Oddershede J (1997) Mol Phys 92:77
31. Dunning Jr. TH (1989) J Chem Phys 90:1007
32. Kendall RA, Dunning TH, Harrison RJ (1992) J Chem Phys 96:6796
33. Woon DE, Dunning Jr TH (1993) J Chem Phys 98:1358
34. Schulman JM, Kaufman DN (1972) J Chem Phys 57:2328
35. Dalskov EK, Sauer SPA (1998) J Phys Chem A 102:5269
36. Sauer SPA, Oddershede J, Geertsen J (1992) Mol Phys 76:445
37. Sauer SPA, Enevoldsen T, Oddershede J (1993) J Chem Phys 98:9748
38. Sauer SPA, Paidarová I (1995) Chem Phys 201:405
39. Kirpekar S, Enevoldsen T, Oddershede J, Raynes WT (1997) Mol Phys 91:897
40. Wigglesworth RD, Raynes WT, Sauer SPA, Oddershede J (1998) Mol Phys 94:851
41. Sauer SPA, Møller CK, Koch H, Paidarová I, Špirko V Chem Phys (1998) 238:385
42. Vahtras O, Ågren H, Jørgensen P, Helgaker T, Jensen HJAa (1993) Chem Phys Lett. 209:201
43. Perera SA, Sekino H, Bartlett RJ (1994) J Chem Phys 101:2186
44. Fukui H, Miura K, Matsuda H, Baba T (1992) J Chem Phys 97:2299
45. Åstrand PO, Ruud K, Mikkelsen KV, Helgaker T (1998) J Chem Phys (submitted)
46. Beckett JR (1979) PhD thesis. Rutgers University.
47. Muenter JS, Klemperer W (1970) J Chem Phys 52:6033
48. Lazzeretti P, Zanasi R (1982) J Chem Phys 77:2448
49. Wasylishen R, Friedrich J (1987) Can J Chem 65:2238
50. Sergeyev NM, Sergeyeva ND, Strelenko YuA, Raynes WT (1997) Chem Phys Lett 277:142
51. Holmes JR, Kivelson D, Drinkard WC (1962) J Chem Phys 37:150
52. Raynes WT, Geertsen J, Oddershede J (1992) Chem Phys Lett 197:516
53. Anet FAL, O'Leary DJ (1989) Tetrahedron Lett 30:2755
54. Krishnan R, Binkley JS, Seeger R, Pople JA (1980) J Chem Phys 72:650
55. Lynden-Bell RM, Sheppard N (1962) Proc R Soc London A 269:385
56. Diercksen GHF, Grüner NE, Sabin JR, Oddershede J (1987) Chem Phys 115:15
57. Wasylishen RE, Friedrich JO, Mooibroek S, MacDonald JB (1985) J Chem Phys 83:548
58. van Duijneveldt FB (1971) IBM Technical Report RJ945
59. Friedrich JO, Wasylishen RE (1985) J Chem Phys 83:3707