Nuclear magnetic resonance spin–spin coupling constants from density functional theory: Problems and results

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Our recently developed method for the calculation of indirect nuclear spin–spin coupling constants is studied in more detail. For the couplings between nuclei other than N, O, and F (which have lone pairs) the method yields very reliable results. The results for ^1J(Si–H) couplings are presented and their dependence on the basis set quality is analyzed. Also, ^2J(H–H) and ^1J(X–H) couplings (X=C, Si, Ge, Sn) in XH_4 molecules are presented and the relativistic effects on ^1J(X–H) are discussed. The limitations of the method, which is based on density functional theory, are connected with the inability of the present LDA and GGA exchange-correlation functionals to describe properly the spin-perturbations (through the Fermi-contact mechanism) on atoms to the right of the periodic table (containing lone pairs). However, the deviations from experiment of the calculated couplings for such nuclei are systematic, at least for one-bond couplings, and therefore these calculated couplings should still be useful for NMR structure determinations. [S0021-9606(96)03942-6]

INTRODUCTION

In our previous paper[1] we introduced a new approach for the calculation of NMR indirect nuclear spin–spin coupling constants using density functional theory (DFT). For a test set of molecules this approach produces results as good as those of the coupled cluster method for H–H, H–C, and C–C couplings with moderate computational effort.[2] For this reason, this approach is already being applied by several groups for many types of couplings in a variety of compounds.[1–8] The ability to calculate properly the H–H, H–C, and C–C couplings covers most of the needs of specialists in organic chemistry and biochemistry (except for very important couplings with nitrogen). However, since some of the studies cited above already include other types of couplings (with Li, B, N, P) with reasonable success, we thought it appropriate to provide further insight into the progress and the problems associated with such calculations.

In this paper, we examine further the performance of our methodology on a variety of molecules and nuclei, and we present an analysis of the different contributions to the coupling constants as functions of the bond lengths in CO and N_2. We will show that the limitations of the method are connected with the inability of the present LDA (local density approximation) and GGA (general gradient approximation) exchange-correlation functionals to describe properly the spin perturbations (through the Fermi-contact mechanism) for molecules containing these atoms (lying at the right of the Periodic Table and containing lone pairs).

However, even at its present stage of development, our approach gives quite systematic results for couplings with such nuclei. For the couplings between nuclei of atoms without lone pairs our method yields very reliable results for a wide range of compounds and nuclei. As a demonstration, the results for ^1J(Si–H) couplings in a set of molecules and for ^2J(H–H) and ^1J(H–X) couplings (X=C, Si, Ge, Sn) in XH_4 molecules are presented and their dependence on the basis set quality is analyzed. These results are compared with those of the random phase approximation (RPA) and the multiconfigurational linear response methods [the latter with complete (CAS) and restricted active spaces (RAS)]. The importance of relativistic effects for the proper calculation of spin–spin couplings is discussed.

COMPUTATIONAL DETAILS

The method for the calculation of the NMR spin–spin coupling constants has been described in detail previously[1,3] and therefore it is outlined below only very briefly. There are four main contributions: the Fermi contact (FC), the paramagnetic spin–orbit (PSO), the spin–dipolar (SD), and the diamagnetic spin–orbit (DSO) contributions. The Fermi contact term is usually the most important of these and also the most sensitive to the geometry. It arises from the interaction between the two nuclei through spin polarization of the electronic system (even if formally one is treating a closed-shell

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system). To calculate the FC contribution we use finite perturbation theory.[9,10] These calculations require high quality basis sets, enlarged grids for numerical integration (approximately twice as large as for the PSO and DSO contributions) and the ''spin-unrestricted'' approach which normally is applied for open shell systems.[1,3] Therefore, in the present realization, the calculation of the FC contribution is the most time-consuming part of the whole calculation (since we neglect the SD contribution).

The second most important contribution, the PSO term, is calculated using the sum-over-states density functional perturbation theory (SOS-DFPT) method.[3,11] This step is very similar to the SOS-DFPT procedure for the NMR chemical shift calculation but with the common gauge origin for all MOs at the position of the nucleus selected as the center of perturbation (for chemical shift calculations, we usually use the IGLO choice of gauge origins[2,3,12]). Using SOS-DFPT one has to perform a ''spin-restricted'' calculation for the ground state only once and then calculate the PSO term with a sum-over-states approach [which is much faster than any (DFT or Hartree–Fock) coupled calculations]. Hence, this is not the bottleneck of our calculations. Also, the PSO contribution is not as sensitive as the FC contribution to the quality of the basis set and grid. Therefore, we use a smaller grid for the PSO calculations to reduce the total computational effort.

The calculation of the DSO term in DFT involves only a straightforward numerical integration because this contribution depends only on the unperturbed ground-state density.[1,3,13]

The last term is the SD (spin–dipolar) contribution.[1,3,13] As pointed out in the review by Kowalewski,[13] the calculation of the SD term is the most time-consuming among the second-order terms because in this case one deals with a perturbation which contains both real and imaginary components. At the same time, the SD contribution is relatively small (at least for long-range couplings). Also, this term is usually smaller than the error in the DFT calculations of the FC term. Since the calculation of the SD term would be the most expensive part of the nuclear spin–spin coupling constant calculations using DFT, it is neglected in the present approach.

Besides the four contributions discussed above, the FC–SD (Fermi contact–spin–dipolar) cross term must also be taken into account in calculations of the nuclear spin–spin coupling tensor. This cross term usually produces the dominant contribution to the anisotropy and can be calculated together with the FC term using the FPT approach (that is using the spin-density calculated by FPT with the FC operator as a perturbation for the calculation of the expectation values of the spin–dipolar operator). In contrast to the SD term, the calculation of the FC–SD cross term requires only a very small additional computational effort.

The calculations have been carried out using a modified version of the deMon-KS program[14–16] along with the deMon-NMR code.[1,3,11] All calculated couplings have been obtained with the Perdew and Wang exchange[17] and the Perdew correlation functional[18] (PP) except for the data presented in Fig. 3, where other exchange-correlation functionals implemented in the deMon code were tested: the Vosko, Wilk, and Nusair exchange-correlation functional (VWN),[19] Becke exchange[20] with Perdew correlation functional[18] (BP), and the newer Perdew and Wang exchange-correlation functional (PW91).[21] See Refs. 1 and 3 for further computational details. Unless otherwise indicated, the basis set BIII of Kutzelnigg *et al.*[12] (also known as IGLO-III) was used. In addition to the basis set BIII, we also used a large fully uncontracted basis sets of Partridge (UP)[22] with four additional polarization functions (for H, C, N, F, and Si) and diffuse functions (for Ge and Sn): $(16s0p0d)+4p$ for H, $(18s13p0d)+4d$ for C,N,F; $(20s15p0d)+4d$ for Si; $(21s16p10d)+spd$ for Ge and $(26s19p13d)+spd$ for Sn.

A FINE grid with 32 (for the calculation of the PSO and DSO contributions) and 64 (for the FC term) points of radial quadrature[23] was employed. We used the experimental molecular geometries.[24]

RESULTS AND DISCUSSION

In our previous publications[1,3] we demonstrated that our approach leads to very reliable results for hydrogen–hydrogen, carbon–hydrogen, and carbon–carbon couplings in a broad set of organic compounds. The presence of N, O, or F atoms in the molecules under study does not worsen significantly the agreement between our results and experimental data as far as the C–C, C–H, and H–H couplings are concerned. However, we found a general trend that the results go from good to worse in the series H, C, N, O, and F, the errors increasing as one goes to the right in the Periodic Table and, hence, as the number of lone pairs increases. The discrepancy with experiment arises from the FC contribution,[1,3,25] whereas the calculated PSO and DSO contributions are in very good agreement with results of post-Hartree–Fock (HF) calculations.[26–28] To illustrate this, we present the dependencies of the, usually most important, FC and PSO contributions to one-bond couplings (calculated with the DFT method in comparison with CAS results[26]) in N_2 and CO molecules as functions of the bond lengths (see Figs. 1 and 2).

The PSO contribution calculated with the SOS-DFPT method is in perfect agreement with the CAS results. In contrast, the results for the FC contribution with DFT and CAS methods differ noticeably in absolute value, but DFT reproduces the general dependence of the FC contribution on the geometry very well. This is a general tendency: DFT with LDA or GGA exchange-correlation potentials (which are currently in use) underestimates the FC contribution to the reduced one-bond coupling because of the inability of such exchange-correlation functionals to produce the very high accuracy spin densities required for these properties (see also Ref. 29). Since FPT is, in principle, an exact DFT perturbation theory with respect to calculation of the FC contribution to the nuclear spin–spin coupling constant, improved results will require a better exchange-correlation functional to describe the spin polarization more precisely. One might rationalize the increasing difficulty in the series N,O,F as arising,

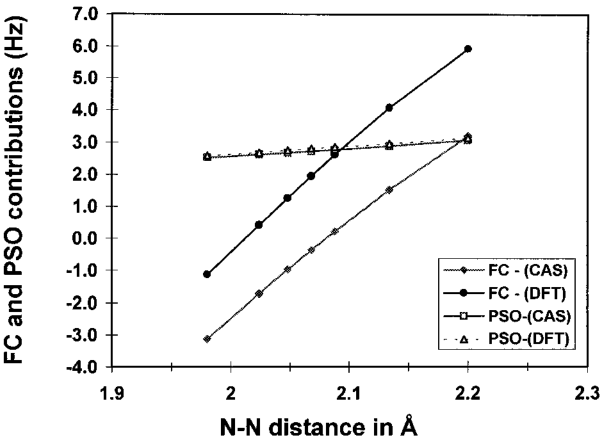

FIG. 1. Dependence of the FC and PSO contributions to ${}^1J$(N–N) on the bond length in N_2 calculated with the CAS and DFT methods.

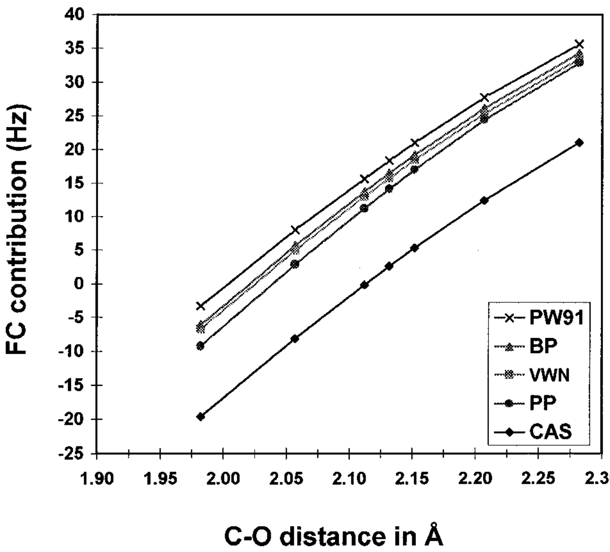

FIG. 3. Comparison of the FC contribution to ${}^1J$(C–O) in CO calculated with CAS and DFT methods (employing different exchange-correlation functionals) as a function of the bond length.

in addition to the general increase in the difficulty of the correlation problem, from the presence of polarizable lone pairs. These could be especially sensitive to the known long-range shortcomings of currently used functionals.[30] A wider base of calculations, some of which are in progress, including studies of the heavier homologs of these atoms could be enlightening in this respect.

Earlier we found that the FC contribution depends strongly on the choice of exchange-correlation functional.[1] However, the results for the FC contribution calculated with different exchange-correlation potentials usually show the same geometry dependence and are just shifted with respect to each other (see Fig. 3). Therefore, the calculated spin–spin couplings are usually also shifted with respect to experimental data (the slopes and correlation coefficients for these graphs are close to one) as one can see from Table I and on Fig. 4 where the calculated F–C one-bond couplings are compared with experiment. Despite the significant shift (about 110 Hz) the calculated couplings correlate with experiment very well and the ''shift'' is nearly independent of the type of molecule. Similar trends take place for some other types of couplings (including couplings with P).[2,5] Although this situation is not fully satisfactory from the theoretical point of view, in practice, this method is found to be useful because it predicts unknown values of couplings and may be used to identify unknown compounds (isomers) using a correlation between calculated and experimental couplings (as presented on Fig. 4) for a given type of coupling. Hence, with due caution, one should be able to use coupling constants calculated with our methodology for NMR structure determination even when N, O, F, and other nuclei are involved in the coupling. Such studies are now in progress.

A new exchange-correlation functional may significantly improve the agreement with experiment for calculated spin–spin couplings with atoms containing lone pair(s). Barone reported that the B3LYP functional improves agreement with experiment for calculated hyperfine structures.[31] The same functional might improve the results for FC contributions to

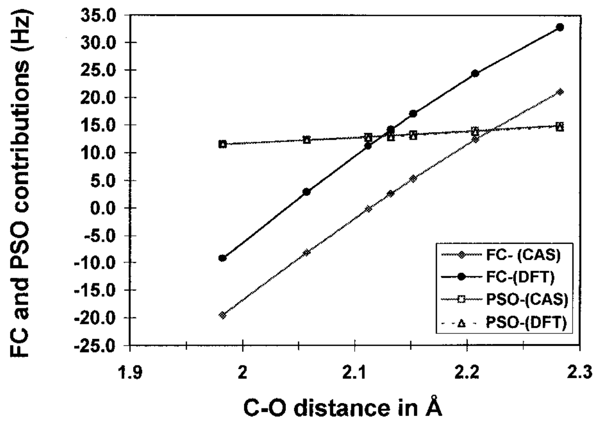

FIG. 2. Dependence of the FC and PSO contributions to ${}^1J$(C–O) on the bond length in CO calculated with the CAS and DFT methods.

TABLE I. DFT calculations of ${}^1J$(C–F) NMR spin–spin coupling constants in a number of compounds in comparison with experimental data. All values are in Hz. The experimental geometries for CH_3F, CH_2F_2, CH_3F, $H_3C–CF_3$, $SeCF_2$ and CF_2O were taken from Ref. 24 and for CF_4, CF_3Cl, $CFCl_3$, $CHCl_2F$ and HCOF from Ref. 34.

Molecule	Formula	Calc.	Expt.	Refs.
Fluoromethane	CH_3F	−268.12	−157.5	35
Difluoromethane	CH_2F_2	−343.11	−234.8	35
Tetrafluoromethane	CF_4	−379.37	−259.2	35
1,1,1-Trifluoroethane	$H_3C–CF_3$	−379.06	−271	36
Trifluoromethane	CHF_3	−390.72	−274.3	35
Dichlorofluoromethane	$CHCl_2F$	−388.50	−293.8	36
Chlorotrifluoromethane	CF_3Cl	−415.33	−299	36
Cabonic difluoride	CF_2O	−426.22	−308.4	35
Trichlorofluoromethane	$CFCl_3$	−448.83	−337	36
Formyl fluoride	HCOF	−455.01	−369	35
Selenocarbony difluoride	$SeCF_2$	−510.87	−408	36

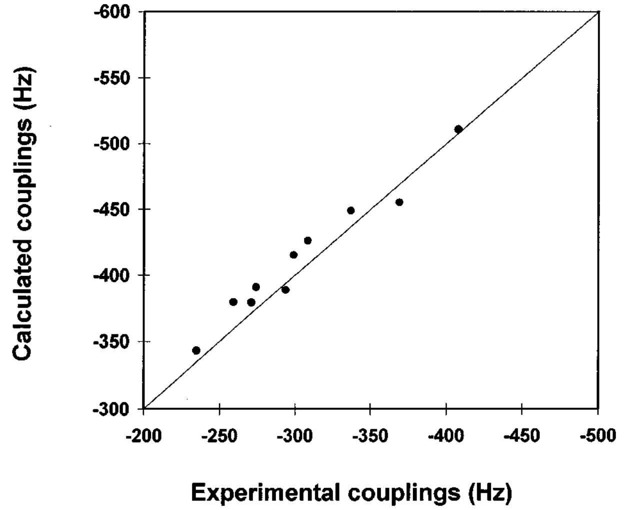

FIG. 4. Comparison between calculated and experimental ^{1}J(C–F) couplings for the set of molecules presented in Table I.

TABLE II. DFT calculations of ^{1}J(Si–H) NMR spin–spin coupling constants in a number of compounds in comparison with experimental data. All values are in Hz.

Molecule[b]	BIII	UP	Expt.[a]
SiH_3CH_3	−179.48	−196.94	−194.3
$SiH_2(CH_3)_2$	−174.27	−189.80	−188.6
SiH_3SiH_3	−181.08	−198.28	−198.2
SiH_3F	−212.12	−232.70	−229.0
SiH_2F_2	−258.82	−281.32	−282.0
$SiHF_3$	−347.34	−379.45	−381.7
SiH_3CN	−212.65	−232.04	−238.0

[a] The experimental geometries are taken from Ref. 24. The experimental data for couplings in SiH_3CH_3.

[b] $SiH_2(CH_3)_2$, SiH_3SiH_3 are taken from the review of Kowalewski (Ref. 13), for SiH_3F, SiH_2F_2, $SiHF_3$ from Ref. 37, and for SiH_3CN from Ref. 38.

spin–spin coupling as well because the calculation of the FC term involves the same operator. However, the use of B3LYP increases the computational cost significantly (since Hartree–Fock exchange must be calculated) and likely its use will not fix the problem completely. In any event, the B3LYP functional is not included in the deMon code and therefore we will not pursue the issue further at this time.

So far we have analyzed the spin–spin couplings between H, C, N, O, and F nuclei only. The calculation of spin–spin couplings with heavier elements is an exciting challenge. A large basis set is necessary for a proper description of the wave function [or the electron density and Kohn–Sham (KS) MOs in DFT] at the nucleus and near the nucleus as well as in the bond areas and correlation effects should be taken into account. Also, relativistic effects influence the NMR parameters much earlier than they do, for example, for the geometry of the molecule due to the strong dependence of the NMR parameters on the electronic structure in the core region. Since, in general, calculations of spin–spin couplings at the post-HF level are quite demanding, the number of such calculations for molecules containing nuclei heavier than F is very limited.

We started the study of the ability of our method to calculate couplings with heavy elements with calculations of Si–H couplings. We used the BIII basis set which is usual in our calculations and also the UP basis set in order to study the basis set dependence. The results are collected in Table II and shown visually on Fig. 5. Even the couplings calculated with the BIII basis set are in reasonably good agreement with experiment though they are shifted by 7%–11%. The use of the larger UP basis set brings the calculated couplings into excellent agreement with experiment. Unfortunately, such calculations with the uncontracted Partridge basis set are quite demanding and the development of a suitable contraction scheme is desirable. Another exciting possibility to reduce computational efforts is to use a locally concentrated basis.[39] However, this idea has not yet been tested carefully for the calculation of spin-spin coupling constants.

These benchmark calculations demonstrate that our approach gives very reliable data for such types of couplings. In fact, the results are ''too good'' because there is no room for relativistic corrections (see the discussion below) which are expected to be about 2%–3%.[13,32] Since solvation and rovibration effects might also be of the same order of magnitude as these relativistic corrections our almost perfect agreement with experiment (obtained with the UP basis set) should probably be viewed as somewhat fortuitous. Nevertheless, it is clear that useful accuracy has been attained.

Recently, Kirpekar *et al.* published the couplings for XH_4(X=C, Si, Ge, and Sn) molecules calculated with the CAS and RAS methods using different types of active space.[33] They also discussed the importance of relativistic corrections. We found it very interesting to compare our results with those of the post-HF approaches and with experiment. The results for ^{2}J(H–H) and ^{1}J(X–H) couplings are presented in Tables III and IV.

Let us start with the discussion of the results for ^{2}J(H–H) (Table III). First of all, we note that judging by the CAS results[33] the SD contribution is the smallest one for these molecules and in many cases it is really negligible.

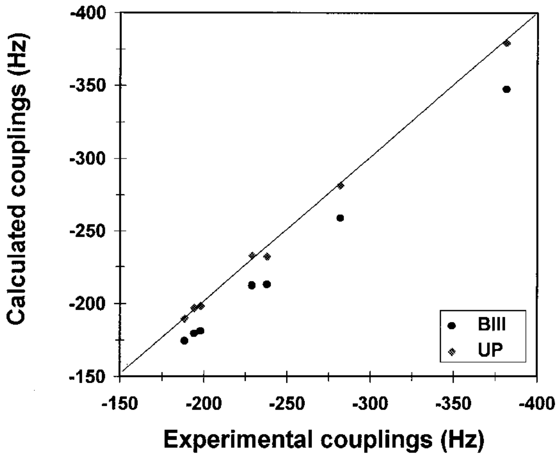

FIG. 5. Comparison between calculated and experimental ^{1}J(Si–H) couplings for the set of molecules presented in Table II.

TABLE III. DFT calculations of ${}^{2}J(\mathrm{H{-}H})$ NMR spin–spin coupling constants in XH_4 (X=C, Si, Ge, Sn) in comparison with the results of RPA and CAS methods and with experimental data.[a] All values are in Hz.

Molecule	Method (Basis)	FC	PSO	DSO	SD	Sum
CH_4	RPA	−27.69	3.63	−3.54	0.44	−27.16
	CAS (A)	−21.26	3.56	−3.50	0.36	−20.84
	CAS (B)	−15.73	3.59	−3.51	0.35	−15.30
	DFT (H:BIII;C:BII)	−10.80	3.37	−3.42		−10.75
	DFT (H:BIII;C:TZV2)	−10.69	3.55	−3.43		−10.58
	DFT (H:BIII;C:BIII)	−10.83	3.56	−3.43		−10.71
	DFT (UP)	−13.31	3.68	−3.45		−13.08
	Exp.					−12.4
SiH_4	RPA	0.40	1.42	−2.37	0.86	−0.39
	CAS (A)	−0.34	1.42	−2.35	0.10	−1.45
	CAS (B)	−0.05	1.40	−2.35	0.05	−0.95
	DFT (H:BIII;Si:BII)	1.54	1.76	−2.35		0.95
	DFT (H:BIII;Si:TZV2)	2.78	2.02	−2.36		2.44
	DFT (H:BIII;Si:BIII)	1.93	2.02	−2.35		1.60
	DFT (UP)	1.24	2.20	−2.36		1.09
	Exp.					+2.75
GeH_4	RPA	−0.57	2.52	−4.84	0.06	−2.83
	CAS (A)	−0.86	2.51	−4.82	0.06	−3.12
	RAS (B)	2.18	2.50	−4.82	0.05	−0.09
	DFT (H:BIII;Ge:BII)	8.04	2.23	−4.84		5.44
	DFT (H:BIII;Ge:TZV2)	8.42	2.60	−4.83		6.19
	DFT (UP)	9.45	2.72	−4.84		7.33
	Exp.					
SnH_4	RPA	2.45	2.93	−4.80	0.00	0.58
	CAS (A)	0.77	2.92	−4.79	0.00	−1.10
	RAS (A)	0.81	2.93	−4.79	0.00	−1.05
	RAS (B)	3.38	2.91	−4.88	0.01	1.42
	DFT (H:BIII;Sn:BII)	11.16	1.98	−4.79		8.35
	DFT (UP)	13.20	2.13	−4.79		10.54
	Exp.					±15.3

[a] Experimental values are taken from Ref. 33 and [for ${}^{2}J(\mathrm{H{-}H})$ in SiH_4] from the review of Kowalewski (Ref. 13).

Hence, these CAS results provide an additional argument to justify the neglect of the SD term in our approach. Also, as one can see, the PSO and DSO contributions almost cancel each other, especially for lighter molecules. The agreement between the CAS and DFT results for these two terms is apparent. Indeed, the difference between the CAS and DFT results for the PSO term is within the difference associated with the use of different basis sets in the DFT method. The results for DSO are absolutely independent of the method and basis set quality for all these molecules.

In contrast, the CAS/RAS and DFT methods give quite different values for the FC term. The data presented in Table III show that the DFT results for the ${}^{2}J(\mathrm{H{-}H})$ couplings are closer to experiment in all molecules for which data are available. It is difficult to explain the discrepancy between the CAS/RAS results and the experimental data. Judging by the fact that the CAS results are in quite good agreement with experiment for CH_4 and the agreement worsens for heavier systems and based on our experience that the dependence of the calculated couplings on the basis set quality is stronger for the systems with heavier elements one might suspect that basis set problems could contribute to the error. However, most probably the reason is the neglect of correlation for the core electrons in the CAS calculations. In general, we conclude that the DFT results are reliable for the whole set of molecules with somewhat larger deviation from experiment for SnH_4 where we suspect the importance of relativistic effects. However, based on our calculations for the whole series we predict the unknown experimental value for ${}^{2}J(\mathrm{H{-}H})$ in GeH_4 to be about $+8\pm2$ Hz.

The results for ${}^{1}J(\mathrm{X{-}H})$ couplings for the same set of molecules are collected in Table IV. Once more one can see that the SD contribution is negligible for all molecules as well as is the DSO contribution. Again, the results for DSO are independent of the basis set and method used. The PSO contributions calculated by SOS-DFPT are in agreement with those from the CAS/RAS methods. However, the PSO contribution to ${}^{1}J(\mathrm{X{-}H})$ couplings is also quite small in these molecules in comparison with the leading FC contribution. The latter completely defines the trend of ${}^{1}J(\mathrm{X{-}H})$ couplings for this set of molecules. The FC contribution in CH_4 calculated with DFT using the largest UP basis set (129.44 Hz) is in good agreement with the results of the CAS method (123.53–130.78 Hz). The same remarkable agreement between DFT and CAS methods is found for the FC contribution to ${}^{1}J(\mathrm{Si{-}H})$ in the case of SiH_4. Also, for CH_4 and SiH_4

TABLE IV. DFT calculations of ^1J(X–H) NMR spin–spin coupling constants in XH_4 (X=C, Si, Ge, Sn) in comparison with the results of RPA and CAS methods and with experimental data.[a] All values are in Hz.

Molecule	Method (Basis)	FC	PSO	DSO	SD	Sum
CH_4	RPA	157.90	1.39	0.25	−0.23	159.31
	CAS (A)	130.78	1.31	0.26	−0.08	132.27
	CAS (B)	123.53	1.48	0.27	0.02	125.30
	DFT (H:BIII;C:BII)	117.92	1.59	0.25		119.77
	DFT (H:BIII;C:TZV2)	118.27	1.66	0.25		120.17
	DFT (H:BIII;C:BIII)	119.45	1.68	0.25		121.38
	DFT (UP)	129.44	1.72	0.24		131.39
	Exp.					120.78
SiH_4	RPA	−257.75	0.72	−0.02	0.05	−257.00
	CAS (A)	−212.76	0.98	−0.01	−0.06	−211.85
	CAS (B)	−207.66	0.61	−0.04	−0.11	−207.20
	DFT (H:BIII;Si:BII)	−190.52	0.32	−0.03		−190.23
	DFT (H:BIII;Si:TZV2)	−185.01	0.29	−0.02		−184.74
	DFT (H:BIII;Si:BIII)	−188.46	0.35	−0.03		−188.14
	DFT (UP)	−206.24	0.30	−0.03		−205.96
	Exp.					−202.5
GeH_4	RPA	−126.50	0.23	−0.01	0.18	−126.10
	CAS (A)	−102.52	0.20	−0.01	0.12	−102.21
	RAS (B)	−97.86	0.21	−0.01	0.10	−97.56
	DFT (H:BIII;Ge:BII)	−85.96	0.16	−0.01		−85.80
	DFT (H:BIII;Ge:TZV2)	−76.62	0.21	−0.01		−76.42
	DFT (UP)	−81.06	0.17	−0.01		−80.09
	Exp.					−97.6
SnH_4	RPA	−2184.39	6.27	−0.03	1.21	−2176.94
	CAS (A)	−1715.07	5.81	−0.04	0.44	−1708.86
	RAS (A)	−1749.45	5.87	−0.04	0.51	−1743.10
	RAS (B)	−1897.65	5.52	−0.03	0.87	−1891.29
	DFT (H:BIII;Sn:BII)	−1366.02	4.86	−0.04		−1361.20
	DFT (UP)	−1412.48	4.64	−0.04		−1407.88
	Exp.					−1930

[a] Experimental values are taken from Ref. 33.

both DFT and CAS methods agree well with experiment.

However, the FC contribution for GeH_4 and especially for SnH_4 calculated with the DFT and CAS methods differ significantly. Taken at face value, the CAS results are in better agreement with experiment than are our DFT results. However, for couplings with such heavy elements as Ge and Sn one should expect that relativistic corrections might be important. The importance of relativistic effects was discussed in the literature quite extensively in the past (see the reviews of Kowalewski,[13] for example). In 1930 Breit[40] introduced simple *a posteriori* relativistic corrections to the nonrelativistic expectation values of the FC operator. Following the papers of Pyykkö *et al.*[32] a relativistic correction factor (depending on the principal quantum number of the atomic s-state ''n'' and the nuclear charge ''Z'') $B(n,Z)$ can be presented in the following form:

$$B(n,Z)=\frac{\langle\psi_{\mathrm{rel}}|H_{\mathrm{rel}}^{\mathrm{hfs}}|\psi_{\mathrm{rel}}\rangle}{\langle\psi_{\mathrm{nonrel}}|H_{\mathrm{nonrel}}^{\mathrm{FC}}|\psi_{\mathrm{nonrel}}\rangle},$$

where H^{hfs} includes the nuclear spin–electron orbit, the dipole–dipole, and the Fermi contact (FC) terms (see Ref. 32 for more details). Using such corrections one can estimate the relativistic value by multiplying the nonrelativistic expectation value of the FC operator by a corresponding $B(n,Z)$ factor. Here, we neglect the new relativistic, isotropic $s-p$ term introduced by Pyykkö[32(c)] (which is not large, as found in the original paper[32(c)]).

Further progress in this field was made by Pyykkö.[32] Based on his calculations for ''hydrogen-like'' (Breit type) corrections one can estimate that nonrelativistic calculations will underestimate the FC contribution to the couplings with C, Si, Ge, and Sn by a factor of 1.004, 1.023, 1.125, and 1.348, respectively (see Refs. 13 and 32). Such a correction is small for ^1J(C–H) coupling (the correction will be less than 0.5 Hz) but it will already affect the agreement with experiment for ^1J(Si–H) couplings (the correction will be about 5 Hz). It will slightly reduce the level of agreement of our results ^1J(Si–H), presented in Tables II and IV (calculated with UP basis set) with experiment. But such corrections will influence the CAS results for ^1J(Ge–H) and ^1J(Sn–H) much more significantly, pushing them away from their experimental counterparts.

To demonstrate the general trends we present the results of RPA and CAS (A) together with DFT (UP) for ^1J(Sn–H) before and after the relativistic correction in comparison with experimental data in Fig. 6 (all data are taken from Table IV). Now it is easy to see that the RPA and CAS results are in good agreement with experimental data *before* the relativ-

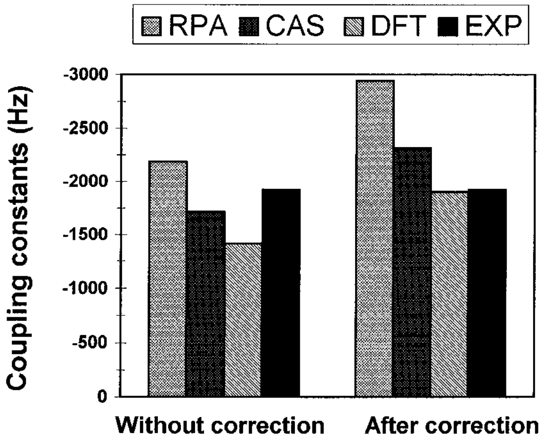

FIG. 6. ^1J(Si–H), calculated with the RPA, CAS, and DFT methods, before and after the *a posteriori* relativistic correction in comparison with the experimental value.

istic correction. However, *after* the correction RPA and CAS significantly overestimate the Sn–H coupling. Our DFT result with the UP basis set is far below the experimental value *before* the correction but it is in excellent agreement with experiment *after* the relativistic (Breit type) correction[13,32] was applied.

The same conclusion was deduced for the ^1J(Ge–H) coupling in GeH_4 but the relativistic correction is less pronounced [about 10–15 Hz depending on the calculated ^1J(Ge–H) value]. Taking into account the overall very good agreement between our DFT results for such types of couplings (between atoms without lone pairs) we believe that our results are superior to the CAS results published by Kirpekar *et al.*[33] Probably, these CAS calculations are sensitive to shortcomings of the basis set and/or the active space.

Judging by the results presented on Fig. 6 we conclude that the multiplicative relativistic corrections proposed by Pyykkö [32] work very well and their use on top of the DFT nonrelativistic calculations of spin–spin coupling constants is, at present, the most efficient way to calculate couplings with heavy elements. Of course, this does not eliminate the need for fully relativistic calculations of spin–spin coupling constants which are extremely important for better understanding of these interactions and for benchmark calculations.

CONCLUSIONS

The DFT-based approach to NMR spin–spin coupling constants recently developed by the authors was applied to a wider set of molecules and nuclei. This additional study clearly demonstrates that DFT with LDA and GGA exchange-correlation potentials underestimate the spin perturbation for N, O, and F, which contain lone pairs, and therefore fails to predict quantitatively the FC contribution to the couplings for such nuclei. However, even in such cases our approach is usually able to reproduce the trends (with respect to geometry changes, for example) quite well. This indicates that our DFT-based method can, in fact, be applied to a wider range of compounds than we have suggested previously.[1]

Also, our approach yields very good results for couplings involving Si and, after the inclusion of relativistic corrections, for couplings with Ge and Sn. This supports our conclusion that the present method works very well for the atoms without lone pairs so far examined (we have experience with H, C, Si, Ge, and Sn and we are aware of good results, obtained with our method, for couplings with Li and B).[2] Unfortunately, spin–spin couplings with heavy elements tend to be more sensitive to the basis set quality in the core region. However, as follows from our experience, the use of a smaller basis set [for example, BIII instead of the uncontracted Partridge (UP) basis set [22]] leads just to a systematic shift of the results and the data with a larger basis set can be easily estimated. We found that relativistic effects are important for couplings even with such relatively light elements as Si and Ge and extremely important for Sn. The use of the ‘‘hydrogenlike’’ (Breit type) corrections proposed by Pyykkö[32] on top of our DFT-based method is the most efficient way to treat couplings with heavy elements. However, fully relativistic calculations of these couplings would be extremely interesting as reliable reference points for benchmark calculations.

In conclusion, we predict that the DFT method for spin–spin coupling constant calculations will be a very popular and extremely useful practical tool for NMR studies in the coming years. This approach will benefit significantly from the development of new exchange-correlation potentials.

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