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One-bond ^{29}Si - ^1H spin-spin coupling constants in the series of halosilanes: benchmark SOPPA and DFT calculations, relativistic effects, and vibrational corrections

Yury Yu. Rusakov and Leonid B. Krivdin*

A number of most representative second order polarization propagator approach (SOPPA) based wavefunction methods, SOPPA, SOPPA(CC2) and SOPPA(CCSD), and density functional theory (DFT) based methods, B3LYP, PBE0, KT2, and KT3, have been benchmarked in the calculation of the one-bond ^{29}Si - ^1H spin-spin coupling constants in the series of halosilanes $\text{SiH}_n\text{X}_{4-n}$ ($X = \text{F}, \text{Cl}, \text{Br}, \text{I}$), both at the non-relativistic and full four-parameter Dirac's relativistic levels taking into account vibrational corrections. At the non-relativistic level, the wavefunction methods showed much better results as compared with those of DFT. At the DFT level, out of four tested functionals, the Perdew, Burke, and Ernzerhof's PBE0 showed best performance. Taking into account, relativistic effects and vibrational corrections noticeably improves wavefunction methods results, but generally worsens DFT results. Copyright © 2013 John Wiley & Sons, Ltd.

Keywords: NMR; ^{29}Si - ^1H spin-spin coupling constants; relativistic effects; vibrational corrections; SOPPA; SOPPA(CC2); SOPPA(CCSD); B3LYP; PBE0; KT2; KT3; aug-cc-pVTZ-J; halosilanes

Introduction

Recently, a major breakthrough has been achieved in the high-level calculations of different types of spin-spin coupling constants.^[1] In a long chain of our recent publications, we have successfully applied a general second order polarization propagator approach, SOPPA,^[2] to calculate element-hydrogen spin-spin coupling constants involving carbon,^[3] nitrogen,^[4] silicon,^[5] phosphorous,^[6] selenium,^[7] and most recently, tellurium.^[8] Alternatively, a number of papers reports the implementation of another efficient high-level non-empirical method, coupled clusters with single and double amplitudes within the equation-of-motion framework, EOM-CCSD,^[9] for the accurate calculations of spin-spin coupling constants of different types (for key references, see reviews^[11]). In this communication, we report the results on the benchmark calculations of the one-bond ^{29}Si - ^1H spin-spin coupling constants in the series of halosilanes, $\text{SiH}_n\text{X}_{4-n}$ ($X = \text{F}, \text{Cl}, \text{Br}, \text{I}$), including parent silane ($n = 4$), performed at the SOPPA level in comparison with much computationally cheaper (density functional theory) DFT calculations and, in the final diagnosis, with experiment. In the two cited papers,^[5] a systematic study of geminal and vicinal silicon-hydrogen coupling constants across double bond has been carried out in the series of alkenyl and chloroalkenyl silanes. However, to the best of our knowledge, apart from several single results, such as those by Sauer *et al.*^[10] for silane, no systematic calculations of the one-bond ^{29}Si - ^1H spin-spin coupling constants has ever been published. In the series of halosilanes under study 1–13, one has to expect the noticeable contribution of relativistic effects and vibrational corrections. In this connection, apart from evaluating the relative merits of different theoretical methods used to calculate one-bond ^{29}Si - ^1H spin-spin coupling constants at the non-relativistic level, we also performed the four-component

Dirac's calculations of relativistic effects together with the zero point vibrational (ZPV) corrections contributing to the overall values of $^1J(\text{Si}, \text{H})$.

Results and Discussion

To test the reliability and the effectiveness of different theoretical methods used to calculate one-bond ^{29}Si - ^1H spin-spin coupling constants, we examined several most promising DFT functionals and, on the other hand, the wavefunction-based genuine *ab initio* methods derived from a general SOPPA formalism in the series of halosilanes 1–13 (enumeration of compounds is given in the tables). All one-bond ^{29}Si - ^1H spin-spin coupling constants were calculated both within the SOPPA scheme and within the DFT framework taking into account four non-relativistic Ramsey's coupling contributions to the total coupling, J , namely, Fermi contact, J_{FC} , spin-dipolar, J_{SD} , diamagnetic spin-orbital, J_{DSO} , and paramagnetic spin-orbital, J_{PSO} , terms. These theoretical results together with related experimental data^[11–13] are compiled in Tables 1 and 2. Given in Table 1 are also calculated in this study relativistic and vibrational corrections to the values of $^1J(\text{Si}, \text{H})$, which are discussed later.

At the *ab initio* level, we used the mostly effective and well-approved for different types of spin-spin coupling constants,

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Table 1. The total values of $^1J(\text{Si,H})$ in the series of halosilanes calculated at different levels of theory taking into account relativistic and vibrational corrections ^a

Entry number	Compound	SOPPA	SOPPA (CC2)	SOPPA (CCSD)	B3LYP	PBE0	KT2	KT3	Δ_{rel}	Δ_{ZPV}	J_{exp}^b
1	SiH ₄	-203.8	-200.9	-193.2	-211.3	-195.3	-220.1	-227.1	-3.1	-3.9	-202.5 ^c
2	SiFH ₃	-232.3	-229.5	-221.9	-242.7	-224.4	-250.9	-258.3	-3.9	-3.4	-233.6
3	SiF ₂ H ₂	-282.9	-279.9	-271.9	-301.4	-279.2	-312.1	-319.0	-5.4	-4.1	-288.2
4	SiF ₃ H	-377.4	-373.7	-363.6	-407.5	-386.6	-428.4	-433.1	-8.4	-6.6	-388.0
5	SiClH ₃	-238.9	-235.9	-227.5	-248.5	-230.0	-258.2	-264.9	-3.9	-3.1	-240.0 ^d
6	SiCl ₂ H ₂	-287.6	-284.3	-274.7	-304.8	-282.7	-318.6	-324.4	-5.2	-3.3	-293.0 ^d
7	SiCl ₃ H	-356.7	-353.1	-341.2	-391.9	-364.5	-417.2	-420.6	-7.4	-5.2	-373.0 ^d
8	SiBrH ₃	-241.3	-238.3	-229.7	-250.1	-231.6	-259.9	-266.2	-4.1	-2.9	-240.8
9	SiBr ₂ H ₂	-289.8	-286.8	-276.8	-305.5	-283.8	-319.3	-323.9	-5.1	-2.8	-290.0
10	SiBr ₃ H	-352.2	-349.8	-337.4	-386.4	-360.5	-411.9	-412.8	-6.4	-4.2	-357.1
11	SiIH ₃	-242.7	-239.7	-230.8	-250.9	-232.8	-261.6	-267.1	-3.0	-2.8	-239.5
12	SiI ₂ H ₂	-284.7	-282.2	-271.8	-298.8	-279.3	-315.1	-318.1	-1.7	-2.5	-280.8
13	SiI ₃ H	-327.1	-326.1	-313.5	-339.1	-336.8	-387.7	-385.8	+3.5	-3.9	-324.7

^aAll couplings and coupling contributions are in hertz.^bTaken from ^[11] if not indicated otherwise.^cTaken from ^[12]^dTaken from ^[13]

the SOPPA-based family of methods, namely parent SOPPA^[2] itself and that in combination with CC2, known as SOPPA(CC2)^[14] and also that with CCSD, referred to as SOPPA(CCSD).^[15] In a general SOPPA formalism, the ground-state wavefunction used for the calculation of spin-spin coupling constant as the linear-response property is approximated with the MP2 wavefunction, whereas in SOPPA(CC2) and SOPPA(CCSD) methods, the MP2 correlation coefficients are replaced with accordingly, CC2 and CCSD single and double amplitudes that is regarded^[14,15] to generally improve the description of the electron correlation effects at the MP2 level. At the DFT level, we used the most common three-parameter hybrid functional of Becke^[16] in combination with the correlation functional of Lee, Yang and Parr,^[17] the so-called B3LYP. At the same time, we used some more NMR-oriented functionals – the parameter-free generalized gradient functional of Perdew, Burke and Ernzerhof, PBE,^[18] with a predetermined amount of exact exchange, known as PBE0,^[19] together with the generalized gradient approximation exchange-correlation functional of Keal and Tozer, KT2,^[20] and that with the additional gradient-corrected exchange and correlation terms, the so-called KT3.^[21]

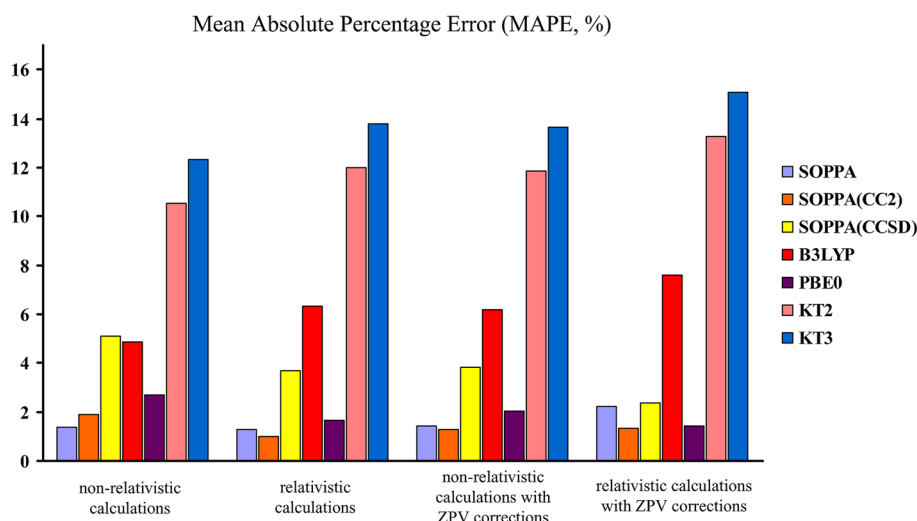
In all calculations, both at the SOPPA and DFT levels, Sauer's contracted aug-cc-pVTZ-J basis set (derived elsewhere for hydrogen^[22] and silicon^[23]), which is specially optimized for and very well-approved in the high-level correlated calculations of spin-spin coupling constants, was used for silicon and hydrogens, whereas Pople's 6-311G** basis set^[24] was used for all halogens (F, Cl, Br, and I) throughout. It was expected that Sauer's aug-cc-pVTZ-J basis should provide better performance in the calculations of $^1J(\text{Si,H})$ due to the improved description of the electron density on the silicon nucleus that is of major importance for the adequate evaluation of the Fermi contact contribution to the total value of spin-spin coupling constant, as was shown earlier for spin-spin couplings involving carbon,^[25] nitrogen,^[26] phosphorus,^[27] and selenium.^[28] It follows from the data presented in Table 2 that the overall contribution of the non-contact terms of $^1J(\text{Si,H})$ is almost negligible in all compounds **1–13**. Indeed, out of the three non-contact contributions, only the paramagnetic spin-orbital term is of any noticeable magnitude (*ca.* 1 Hz), whereas the rest of the non-contact terms are negative and even smaller in absolute value, so that the Fermi contact contribution by far dominates in the total values of $^1J(\text{Si,H})$ that justifies the usage of aug-cc-pVTZ-J having four tight *s*-functions with large exponents for silicon.

Coming back to Table 1, it is clearly seen that in general, the wavefunction-based methods, SOPPA, SOPPA(CC2), and SOPPA(CCSD), show much better results than any of the DFT methods. This is illustratively shown in Fig. 1 where the mean absolute percentage errors (MAPE) calculated with account of all 13 coupling constants in the series of **1–13** are presented for different DFT and SOPPA methods.

For the non-relativistic calculations, best results are achieved within the SOPPA and SOPPA(CC2) schemes, which are characterized by MAPE being less than 2%. On the other hand, more sophisticated and time consuming SOPPA(CCSD) method shows less reliable results characterized by MAPE of about 5%. Out of the four tested DFT functionals presented in Fig. 1, the PBE0 functional of Perdew, Burke, and Ernzerhof demonstrates the best performance with the MAPE of less than 3%, whereas the most popular B3LYP functional is characterized by MAPE of about 5%. This is not surprising because it is well documented that PBE functionals are less affected by the well known triplet

Table 2. Individual non-relativistic contributions to the total values of $^1J(\text{Si,H})$ in the series of halosilanes calculated at the SOPPA(CC2)/aug-cc-pVTZ-J level ^a

Entry number	Compound	J_{DSO}	J_{PSO}	J_{SD}	J_{FC}	J	$J_{\text{exp}}^{\text{b}}$
1	SiH_4	-0.02	0.45	-0.03	-201.29	-200.89	-202.5
2	SiFH_3	-0.19	1.04	-0.16	-230.16	-229.47	-233.6
3	SiF_2H_2	-0.38	1.13	-0.29	-280.40	-279.94	-288.2
4	SiF_3H	-0.57	1.15	-0.41	-373.90	-373.73	-388.0
5	SiClH_3	-0.18	0.91	-0.19	-236.39	-235.85	-240.0
6	SiCl_2H_2	-0.36	1.01	-0.34	-284.64	-284.33	-293.0
7	SiCl_3H	-0.54	1.01	-0.45	-353.13	-353.11	-373.0
8	SiBrH_3	-0.30	0.93	-0.21	-238.70	-238.28	-240.8
9	SiBr_2H_2	-0.59	1.11	-0.36	-286.99	-286.83	-290.0
10	SiBr_3H	-0.90	1.18	-0.47	-349.59	-349.78	-357.1
11	SiIH_3	-0.32	0.92	-0.21	-240.09	-239.70	-239.5
12	SiI_2H_2	-0.65	1.18	-0.36	-282.34	-282.17	-280.8
13	SiI_3H	-0.98	1.34	-0.45	-326.01	-326.10	-324.7

^aAll couplings and coupling contributions are in hertz.^bTaken from [11–13], see footnote to Table 1.**Figure 1.** Mean absolute percentage errors of different DFT and SOPPA methods versus experiment derived from the benchmark calculations of the one-bond ^{29}Si - ^1H spin-spin coupling constants in the series of halosilanes **1–13**.

instabilities problem in Kohn–Sham theory, especially in the calculations of NMR indirect spin-spin coupling constants.^[29] Unexpectedly, both NMR-oriented functionals of Keal and Tozer, KT2, and KT3, known to perform very good in the calculations of chemical shifts,^[30] in this case show much worse results with MAPE of about 10–12%.

Relativistic calculations of $^1J(\text{Si,H})$ in the series of **1–13** were performed using the four-component Dirac's method within the Gaussian nuclear charge distribution scheme,^[31] as realized in DIRAC program code^[32] at the DFT-PBE0 level. Thus, to evaluate relativistic corrections, ΔJ_{rel} , given in Table 1, the non-relativistic values of $^1J(\text{Si,H})$ obtained from the Levy-Leblond Hamiltonian^[33] were subtracted from their total relativistic values obtained from the Dirac–Coulomb Hamiltonian, calculated both at the same DFT-PBE0 level using DIRAC code.^[32]

It follows from the MAPE diagram shown in Fig. 1 that taking into account relativistic corrections (calculated as described earlier) improves the performance of all three wavefunction-based methods, SOPPA, SOPPA(CC2), and SOPPA(CCSD), but

worsens the results of all DFT functionals with the exception of PBE0. The smallest values of MAPE of about 1% are achieved with SOPPA and SOPPA(CC2) methods, whereas the largest values of MAPE (12–14%) are obtained with KT2 and KT3 DFT functionals. Basically, relativistic corrections to $^1J(\text{Si,H})$ are negative (except for the positive one of +3.5 Hz in triiodosilane **13**) being in average of around 4–6 Hz in absolute value.

It is noteworthy that PBE0 functional demonstrates very good performance in the calculation of $^1J(\text{Si,H})$, which is characterized by the MAPE of less than 2%. We think that this could be accounted for the fact that the PBE0 functional is less affected by the DFT triplet instabilities problem in the calculations of spin-spin coupling constants^[29], as has already been mentioned with respect to the non-relativistic data. Indeed, this is a very encouraging result in view of the fact that the DFT-PBE0 calculations are dramatically less demanding as compared with any of the SOPPA methods.

Zero point vibrational corrections to the total non-relativistic values of $^1J(\text{Si,H})$ were calculated as described in the original

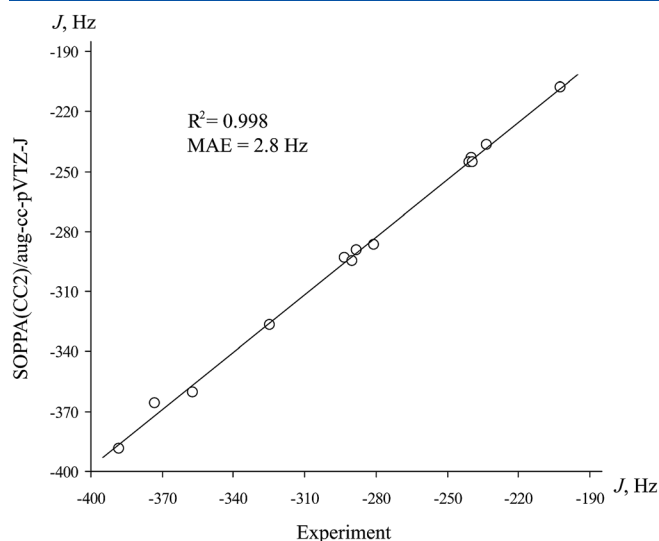


Figure 2. Correlation plot of the one-bond ^{29}Si - ^1H spin-spin coupling constants in the series of halosilanes **1–13** calculated at the SOPPA(CC2)/aug-cc-pVTZ-J level taking into account relativistic and vibrational corrections versus experiment (best results).

publications by Ruud *et al.*^[34] at the DFT-PBE0/6-311G** level using DALTON package.^[35] In this formulation, ZPV correction to the value of spin-spin coupling constant is a sum of harmonic and anharmonic contributions. The former is calculated using the so-called *effective geometry*^[36] that corresponds to the vibrationally averaged molecular geometry corresponding to the second order perturbation theory level. On the other hand, anharmonic contribution is determined as a difference of spin-spin coupling constant calculated using equilibrium and effective molecular geometries. ZPV corrections to the values of $^1J(\text{Si,H})$ in the series of **1–13** (ΔJ_{ZPV}) calculated in this way are given in Table 1. It follows that all ZPV corrections in this series are negative being in average $-(3\text{--}4)\text{ Hz}$. The largest ZPV correction of -6.6 Hz was found for trifluorosilane **4**. Expectedly, ZPV corrections decrease in absolute value with the increase of the atomic number of a halogen that is mostly pronounced in the series of trihalosilanes, SiHX_3 : $\Delta J_{\text{ZPV}} = -6.6\text{ Hz}$ (**4**, $X = \text{F}$); -5.2 Hz (**7**, $X = \text{Cl}$); -4.2 Hz (**10**, $X = \text{Br}$); and -3.9 Hz (**13**, $X = \text{Cl}$).

Coming back to Fig. 1, it is clearly seen that taking into account ZPV corrections noticeably improves the results of the wavefunction-based methods, but slightly worsens the results of all DFT functionals with the exception of PBE0. However, the best result is achieved when both relativistic and vibrational corrections are taken into account, and this is illustrated in Fig. 2 for a most efficient SOPPA(CC2) method. This is indeed a very encouraging result giving rise to a mean average error of only 2.8 Hz for a size of changing of $^1J(\text{Si,H})$ of around 200 Hz.

Concluding Remarks

A number of most representative SOPPA-based wavefunction methods, SOPPA, SOPPA(CC2) and SOPPA(CCSD), and DFT-based methods, B3LYP, PBE0, KT2, and KT3, have been benchmarked in the calculation of the one-bond ^{29}Si - ^1H spin-spin coupling constants in the series of halosilanes $\text{SiH}_n\text{X}_{4-n}$ ($X = \text{F}, \text{Cl}, \text{Br}, \text{I}$), both at the non-relativistic and full four-parameter Dirac's relativistic levels taking into account vibrational corrections. At the non-relativistic level, the wavefunction methods showed much

better results as compared with those of DFT, with a MAPE of about 2% calculated for a set of 13 coupling constants in 13 halosilanes (including parent unsubstituted silane) falling into range of ca 200–400 Hz. At the DFT level, out of the tested functionals, the Perdew, Burke, and Ernzerhof's PBE0 showed best performance characterized with the MAPE of about 2.5%. However, other functionals, especially those of Keal and Tozer, KT2, and KT3, known to perform very good in the calculations of chemical shifts, are characterized with much higher MAPE reaching as much as 15%. Taking into account relativistic effects and vibrational corrections noticeably improves wavefunction methods results, especially those of SOPPA(CCSD), but generally worsens DFT results (except for PBE0 functional). However, the best result is achieved when both relativistic and vibrational corrections are taken into account. Thus, for the most efficient SOPPA(CC2) method, a mean average error is only 2.8 Hz for a size of changing of $^1J(\text{Si,H})$ of around 200 Hz, and this is indeed a very encouraging result for the future studies in this field.

Computational Details

Geometry optimizations of **1–13** were performed with the GAMESS code^[37] at the MP2/6-311G** level without symmetry constraints. Non-relativistic DFT and SOPPA calculations of ^{29}Si - ^1H spin-spin coupling constants have been carried out with the DALTON package^[35] using the stationary equilibrium MP2/6-311G** geometries. Relativistic calculations of ^{29}Si - ^1H spin-spin coupling constants were performed within the four-component Dirac's method at the DFT-PBE0 level using DIRAC code.^[32] In all calculations of ^{29}Si - ^1H spin-spin coupling constants, Sauer's aug-cc-pVTZ-J basis set was used for silicon and hydrogens, whereas all halogens were specified with Pople's 6-311G** basis. ZPV corrections were calculated at the DFT-PBE0/6-311G** level with the DALTON package.^[35]

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