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Absolute value of the nuclear magnetic shielding of silicon and germanium atoms in $Si/Ge(CH_3)_4$

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ABSTRACT

The reference value of NMR magnetic shieldings, $\sigma^{ref}(X)$, of a nucleus X is of highest importance when theoretical analysis of chemical shifts are envisaged. For light atoms the absolute scale can be obtained using an old relationship among spin–rotation constants and magnetic shieldings, though for heavy-atom-containing molecules such nonrelativistic relationship is not valid any longer. Then, for such molecules the search for σ^{ref} needs new strategies to be followed. We present here new values of σ^{ref}(Si) and σ^{ref}(Ge) for tetramethyl silane and tetramethyl germanium that were obtained applying a simple procedure which mix accurate experimental chemical shifts and theoretically obtained magnetic shieldings in a set of selected molecular systems. We considered that in experiments one usually measures chemical shifts, (δ). We calculated σ^{ref}(Si) and σ^{ref}(Ge) from a set of seventeen and sixteen heavy-halogen-containing molecules, respectively. We found out that σ^{ref}[Si; $Si(CH_3)_4$] in gas phase should be close to 410.49 ± 6.77 ppm and σ^{ref}[Ge; $Ge(CH_3)_4$] should be close to 1705.29 ± 19.51 ppm. Such theoretical values were obtained by performing calculations within the relativistic polarization propagator method, RelPPA, at RPA level of approach. Based on those values of σ^{ref}, we recalculated the chemical shifts of the whole set of molecular systems obtaining a good reproduction of known experimental results. We also obtained a highly correlated relationship among the absolute values of the nuclear magnetic shieldings of Si and Ge atoms in halogen substituted tetrahedral compounds.

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1. Introduction

Atoms belonging to IV main group of the Periodic Table are very important to explain what one finds in Nature, specially in Chemistry. Silicates constitute the main material of the earths crust, and organo silicon compounds are often used in organic chemistry or as building blocks in material science. In the last thirty years the amount of data for different compounds of this group increased exponentially. For such atoms containing compounds the determination of structural geometries needs reliable results of NMR spectroscopic parameters. They provide valuable information about the molecular electronic structure, together with information of great usefulness in structure elucidation. It is therefore necessary to get as accurate as possible theoretical values of both, chemical shifts, $\delta(X)$ and absolute value of magnetic shieldings in their reference compounds, $\sigma[X; X(CH_3)_4]$ (X = C, Si, Ge, Sn, Pb).

The application of NMR spectroscopy to characterize medium- and large-size molecules containing nuclei of the IV main group elements is highly useful, with exception of the central element germanium. ^{13}C NMR spectroscopy is an invaluable tool for the characterization of organic compounds. ^{29}Si NMR spectroscopy gives structural information for organosilicon compounds and provides a direct observation of the silicon nucleus itself. Tin has two NMR-active nuclei with spin 1/2, ^{117}Sn and ^{119}Sn and they have been extensively used to characterize organotin compounds. ^{207}Pb is the only NMR-active nucleus for this element with also spin 1/2 and it has been regularly used to characterize organolead compounds. This was reported in several works published by Wrackmayer [1–4]. On the other hand germanium is an extremely challenging nucleus to study because the only NMR-active nucleus is ^{73}Ge which has a spin 9/2, and so a relatively large quadrupole moment that produces quadrupolar relaxation and a low resonance frequency.

NMR spectroscopic parameters of silicon and germanium nuclei were studied from the early 1950s for different model compounds and there are lot of experimental data in literature [5–8]. Reasonable correlations among NMR chemical shifts of different elements belonging to the IV main group elements of the Periodic Table were found [9–12]. In this manner the NMR analysis of molecules that contain these atoms can usually be made together, using always

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the chemical shifts. Some of these correlations were used in a recent paper (see Ref. [13]).

Most of ^{29}Si NMR chemical shifts are in a range between + 50 and − 350 ppm. In the case of the germanium chemical shifts this range for tetrahalides molecules spans 1117 ppm (between $GeC1_4$ and GeI_4). In the case of tin-containing compounds such a range is close to 1550 ppm, and for the corresponding carbon compounds it is close to 395 ppm. The mentioned germanium tetrahalides constitute the best set of model compounds for studying ^{73}Ge-containing compounds due to their straightforward comparison with the whole set of analogous compounds belonging to the IV main group elements which have been broadly studied using NMR spectroscopy.

The comparison of NMR data for 29 pairs of analogous silicon and germanium compounds, together with 26 pairs of analogous germanium- and tin-containing compounds were reported in 1984 [10]. Two correlation equations were derived:

$$\delta(\mathrm{Ge}) = 3.32[\delta(\mathrm{Si})] + 39.9 (r = 0.967)$$

$$\delta(\mathrm{Sn}) = 1.56[\delta(\mathrm{Ge})] - 87.4 (r = 0.991)$$

Recently Weinert published a review on NMR spectroscopy of germanium compounds with a large amount of data collected during almost sixty years. It includes the observation of the fluxional behavior of hypervalent germanium species having five or six attached ligands, the spectral properties of linear and branched oligogermanes that contain single germanium–germanium bonds, and the relatively new field of solid-state ^{73}Ge NMR [14].

Few years ago Makulski et al. published a paper with gas-phase ^{29}Si and ^{79}Ge NMR experimental data. With that starting point they proposed an absolute shielding scales for those nuclei extrapolated to zero density to obtain accurate isolated molecule values [15]. With the absolute shielding values, SiH_4 and GeH_4 respectively, and measured chemical shifts, they obtained the absolute shielding values of the reference compound for the tetramethylsilane and tetramethyl germanium. This procedure was applied only for one molecular system to obtain the reference value of each atom: $\sigma^{ref}(\mathrm{Si}) = 378.51$ ppm and $\sigma^{ref}(\mathrm{Ge}) = 1662.40$ ppm. At that time the absolute shielding value for liquid tetramethylsilane was known with low accuracy, 368.5 ppm ± 10 ppm [16].

For light-atom containing molecules the absolute value of σ are indirectly obtained through a relationship among the measured spin–rotation constant and the paramagnetic component of the shielding first published by Flygare [17]. The diamagnetic component is obtained by an as accurate as possible calculation of the free atom under study. This mix of experimental/theoretical relationship used to get semiempirical magnetic shieldings gives reliable results for that molecules, but it does not work properly when heavy-atom containing molecules are involved [18]. To overcome this weakness Martín Ruiz de Azúa et al. proposed a new relationship between the spin–rotation constant and the absolute nuclear magnetic shielding for heavy atoms [19]. Applying this new relationship Malkin et al. obtained the absolute value of σ(Sn) in its reference model compound, $Sn(CH_3)_4$ [20]. They furthermore proposed a new shielding scale for SnH_4, $Sn(CH_3)_4$ and $SnCl_4$ model compounds which have a difference of around 1000 ppm with respect to the old shielding scale obtained by applying the nonrelativistic relationship with spin–rotation constants. This was also improved by including non-collinear spin magnetization and employing London atomic orbitals to ensure gauge origin independence [21].

An experimental new method was recently published to obtain magnetic shieldings of few small compounds directly [22,23], though the chemical shift is the parameter most usually measured. The nuclear magnetic shieldings are routinely obtained by theoretical calculations and the chemical shifts as a difference between magnetic shieldings of a given nucleus in an specific molecule with that of the same nucleus in another molecule taken as a reference. An equivalent procedure is used by experimentalists, giving a great coherence in order to compare results obtained from both sides, experimental and theoretical [24].

We recently published a method that mix experimental chemical shifts and accurate calculations of the nuclear magnetic shieldings in order to obtain the reference value, σ^{ref}, of Sn and Pb atoms in heavy-halogen-containing molecules. Fifteen different molecular systems were used to obtain average values which have very small dispersions. Then the chemical shifts calculated with those reference values fitted very well with experimental results [13,25].

We shall show here results for a new absolute scale of σ^{ref}(Si) and σ^{ref}(Ge) applying quite a similar procedure. Calculations were performed using the relativistic polarization propagator formalism (RelPPA) [26–28]. This is one of the most reliable methods for the calculation of molecular properties; specially for the nuclear magnetic shieldings at the four-component relativistic level [25,29,30]. This formalism was implemented at the random phase approximation, RPA, or consistent first order of approach in the DIRAC code [31] and benchmark shielding calculations of usual elements were published during the last ten years [29,30,32–36].

The structure of this article is as follows. We first give an schematic overview of the method applied. Then we start presenting results of NMR shieldings for silicon- and germanium-containing molecules. From those results, together with experimental chemical shifts we are able to obtain absolute magnetic shieldings of those atoms applying the proposed method in Ref. [25]. Finally, we show the correlation between the absolute nuclear magnetic shielding of silicon and germanium atoms in equivalent molecular systems. In the last section we present some conclusions of the present work.

2. Theoretical methods and computational details

Our model is based on accurate calculations of NMR magnetic shieldings using the relativistic polarization propagator formalism at consistent first order or RPA level of approach, RelPPA-RPA. In the following section we give a very short introduction to this formalism. More details are given elsewhere [28,37].

2.1. Relativistic polarization propagator formalism

The NMR spectroscopic parameters, like the nuclear magnetic shielding constant can be calculated within both, relativistic and nonrelativistic frameworks using the polarization propagator approach. The perturbative Hamiltonians that shall be considered for such calculations do arise from both, the external magnetic field and the magnetic moment of the nucleus of interest [28]. Within the nonrelativistic regime the paramagnetic term do arise by considering the perturbative excitations from occupied to virtual electronic states. On the other hand within the relativistic regime one has to consider two different kind of excitations, *i,e,* from the occupied electronic states to two kind of virtual electronic states, positive and negative.

Within the RelPPA formalism the explicit and usual expression of the nuclear magnetic shielding is given by Aucar et al. [28]

$$\sigma_M = e^2 \left\langle\left\langle \frac{\boldsymbol{\alpha} \times \mathbf{r}_M}{r_M^3}; \alpha \times \mathbf{r}_G \right\rangle\right\rangle \quad (1)$$

were $\mathbf{r}_M$ means the position of the nucleus M, $\mathbf{r}_G$ is the gauge origin and $\boldsymbol{\alpha}$ is the 4×4 Dirac matrix.

This last equation can be reexpressed in such a way that all virtual electronic excitations to be considered are written explicitly.

The addition of contributions due to excitations involving occupied electronic states and virtual positive-energy electronic states gives rise the paramagnetic component; and those involving negative-energy electronic states give rise the diamagnetic component. They are known as *e-e* and *e-p* contributions, respectively [28].

Calculations with the RelPPA formalism can include electron correlation at different levels, but only the random phase approximation (RPA), which is consistent till first order in the fluctuation potential, is actually implemented in computational codes [31].

2.2. Absolute value of Si/Ge magnetic shieldings in compounds of reference

In few earlier papers we presented the same theoretical scheme from which the absolute value of $\sigma^{ref}(\mathrm{Sn})$ in the tetramethyltin compound, $\mathrm{Sn(CH_3)_4}$ was obtained [13,25]. In this article, we use the same procedure to obtain an accurate average value for $\sigma^{ref}(\mathrm{Si})$ and $\sigma^{ref}(\mathrm{Ge})$ in $\mathrm{Si/Ge(CH_3)_4}$ compounds.

The chemical shift of a nucleus is obtained as the difference of magnetic shieldings in two different molecular environments; one of them is taken as a reference

$$\delta^{theo}(X) = \frac{\sigma^{ref}(X) - \sigma(X)}{1 - \sigma^{ref}(X)} \tag{2}$$

The main difficulty lies in obtaining reliable reference values. Both, relativistic and electron correlation effects should be included altogether for getting accurate reference values. At the moment there is no any method that can do it. So we proposed a mixed scheme that consider on the same grounds, accurate theoretical and experimental results.

From Eq. (2) and considering experimental instead of theoretical chemical shifts, the reference shieldings are calculated as

$$\sigma^{ref}(X) = \frac{\delta^{exp}(X) + \sigma(X)}{1 + \delta^{exp}(X)}$$

In the case of $\sigma(X)$ (X = Si, Ge) we considered the following expression

$$\sigma^{ref}[X; X(\mathrm{CH_3})_4] = \frac{\delta^{exp}(X) + \sigma(X)}{1 + \delta^{exp}(X)} \tag{3}$$

Applying the last equation we are then able to calculate $\sigma^{ref}(\mathrm{Si/Ge})$ in many molecular systems at four-component relativistic level for obtaining an average value as final result.

2.3. Computational details

All calculations were carried out using DIRAC program [31]. The geometry of tetrahedral model compounds, $\mathrm{Si/GeY_4}$ (Y = H, F, Cl, Br, I), were obtained from experimental measurements [38] or from calculations. In Table 1 we specify which molecules were optimized.

The geometry optimization was carried out at relativistic level with optimized Sadlej's [39] basis set and Dirac–Hartree–Fock Hamiltonian. Gaussian-type finite-size nucleus model and uncontracted basis sets were used. The basis set for small components were obtained from the large components applying the restricted kinetic balance scheme (RKB).

Calculations of nuclear magnetic shieldings were performed with the RelPPA formalism at RPA level of approach, which included electron correlation till first order. For molecular systems that contain mix of Cl, Br and I atoms, the bond angles were assumed to be tetrahedral and distances of *X*-Cl, *X*-Br and *X*-I are assumed to be the same as the corresponding distances in $\mathrm{XCl_4}$, $\mathrm{XBr_4}$ and $\mathrm{XI_4}$, respectively (X = Si, Ge). The gauge origin was placed at the position of the center of the molecule for all tetrahedral compounds.

For property calculations, the set of small components were generated applying the unrestricted kinetic balance prescription (UKB) because it increases the size of the small component basis set and so improves the description of the negative-energy space and the diamagnetic component [29]. The chosen basis sets were the same as that previously used [13,25,30,40,41]. Sadlej's basis sets were chosen for the whole set of systems with several tight and diffuse Gaussian functions included for each block of angular momentum to get converged results. The scheme for including more Gaussian-type functions was the usual one: i) tight basis functions were added to s, p, d, f blocks with exponents related as $\alpha_{i+1}/\alpha_i = 3$ from the largest exponent of each block; ii) diffuse basis functions were not necessary to include in shielding calculations in the *d* and *f* blocks because when they were included the values of the shielding did not change significantly.

Table 1
Experimental/optimized geometries. $d(X–Y)$ bond distances.

Molecule	Y				
	H	F	Cl	Br	I
$\mathrm{SiY_4}$	1.480[a]	1.553[a]	2.019[a]	2.197[b]	2.440[b]
$\mathrm{GeY_4}$	1.525[a]	–	2.113[a]	2.272[a]	2.531[b]

[a] Experimental geometry taken from Ref. [38]
[b] Theoretically optimized geometry

3. Results and discussion

There exist in the literature a great amount of experimental data for silicon- and germanium-containing molecules, though for many of them theoretical calculations at four-component relativistic level are still quite expensive. In some cases such calculations are not feasible to do. The experimental value of $\delta(\mathrm{Si; SiH_4})$ with respect to $\mathrm{Si(CH_3)_4}$ compound did have different values: 91.9 ppm [6]; 93.1 ppm [7]; 106.8 ppm [16]; 104.34 ppm [15]. For the other systems analyzed here there are also different experimental values. So, in this work we considered the experimental data taken from Ref. [10].

In Tables 2 and 3 the second column shows the experimental chemical shifts of the molecules listed in the first column. The third one corresponds to our calculated nuclear magnetic shieldings obtained with RelPPA-RPA method, and the fourth column shows

Table 2
Experimental chemical shifts, and calculated magnetic shieldings and reference values of Si atom in a series of heavy-atom-containing molecules.

Molecule	δ^{exp}[a]	σ	$\sigma[\mathrm{SiMe_4}]$[b]
$\mathrm{SiCl_4}$	−20.0	428.42	408.43
$\mathrm{SiCl_3Br}$	−34.3	441.03	406.74
$\mathrm{SiCl_2Br_2}$	−50.7	456.15	405.47
$\mathrm{SiClBr_3}$	−69.8	473.51	403.74
$\mathrm{SiCl_3I}$	−75.4	493.87	418.50
$\mathrm{SiBr_4}$	−92.7	492.78	400.12
$\mathrm{SiH_4}$	−93.1	489.04	395.98
$\mathrm{SiCl_2BrI}$	−98.9	513.36	414.50
$\mathrm{SiF_4}$	−109.0	521.72	412.76
$\mathrm{SiClBr_2I}$	−122.8	534.49	411.74
$\mathrm{SiBr_3I}$	−149.5	556.95	407.51
$\mathrm{SiCl_2I_2}$	−151.5	574.85	423,41
$\mathrm{SiClBrI_2}$	−181.9	598.59	416.77
$\mathrm{SiBr_2I_2}$	−212.3	623.19	410.98
$\mathrm{SiClI_3}$	−245.9	664.49	418.69
$\mathrm{SiBrI_3}$	−280.1	690.61	410.63
$\mathrm{SiI_4}$	−346.2	758.39	412.33

[a] Experimental data taken from Ref. [10].
[b] The reference values are obtained applying Eq. (3) for RelPPA-RPA.

Table 3
Experimental chemical shifts, and calculated magnetic shieldings and reference values of Ge atom in a series of heavy-atom-containing molecules.

Molecule	δ^{exp} [a]	σ	$\sigma[GeMe_4]$ [b]
$GeCl_4$	30.9	1696.82	1727.67
$GeCl_3Br$	−47.8	1764.34	1716.62
$GeCl_2Br_2$	−131.3	1834.07	1703.99
$GeClBr_3$	−219.4	1907.94	1688.91
$GeCl_3I$	−235.9	1975.56	1740.07
GeH_4	−283.7	1979.67	1696.45
$GeBr_4$	−311.3	1982.35	1671.57
$GeCl_2BrI$	−326.2	2048.87	1723.23
$GeClBr_2I$	−417.6	2123.41	1706.52
$GeBr_3I$	−509.3	2197.19	1688.75
$GeCl_2I_2$	−523.7	2256.85	1734.06
$GeClBrI_2$	−613.5	2328.50	1716.05
$GeBr_2I_2$	−707.4	2399.08	1692.88
$GeClI_3$	−809.9	2520.17	1711.66
$GeBrI_3$	−899.8	2586.14	1687.85
GeI_4	−1081.8	2758.28	1678.30

[a] Experimental data taken from Ref. [10]. The quoted precision of the chemical shifts (±3 ppm) takes account of the calibration uncertainty.
[b] The reference values are obtained applying Eq. (3) with RelPPA-RPA method.

the nuclear magnetic shielding for the reference compound applying Eq. (3).

In Table 2 we show results of σ^{ref}[Si; $Si(CH_3)_4$] for seventeen different molecular systems. The smallest value is 395.98 ppm corresponding to SiH_4 and the largest is 423.41 ppm for $SiCl_2I_2$; this means that the amplitude is 27.43 ppm. From these results the corresponding $\sigma^{ref}[Si(CH_3)_4]$ are obtained applying Eq. (3). The RelPPA-RPA average value is $\sigma[Si(CH_3)_4] = 410.49 \pm 6.77$ ppm. Its dispersion is very small, meaning that a reliable average value is obtained.

In Table 3 we show results of the corresponding σ^{ref}[Ge; $Ge(CH_3)_4$] for sixteen different molecular systems. The smallest value is 1671.57 ppm corresponding to $GeBr_4$ and the largest one is 1740.07 ppm for $SiCl_3I$. Then the amplitude is 68.50 ppm. The RelPPA-RPA average value obtained is $\sigma[Ge(CH_3)_4] = 1705.29 \pm 19.51$ ppm. There is also a very small dispersion as happens in the case of Si-containing molecules, meaning a reliable average value.

We now compare our results, taken from Tables 2 and 3, with those of the literature. For ^{29}Si, a value of 368.5 ppm was reported for $\sigma^{ref}(Si)$ in liquid phase [16]; in 2006 Antusek et al. obtained a value of 376.6 ppm [42] and Makulski et al. reported 378.51 ppm for the reference system in gas phase [15]. The last two values were obtained applying a similar procedure used in this work combining high accurate calculations of $\sigma(Si)$ in SiH_4 model compound and the experimental chemical shift with respect to tetramethylsilane. Antusek et al. combined accurate calculation of $\sigma(Si)$ in SiH_4 (483.4 ppm) with experimental chemical shift taken from Ref. [16] (106.8 ppm), and Makulski et al. combined accurate value for $\sigma(Si)$ in SiH_4 (482.85 ppm) and a new measured value for the experimental chemical shift (104.34 ppm).

Temperature, vibrational and electron correlation effects can be estimated as being close to −4.4 ppm from Ref. [42]. The incompleteness of the basis set would give an error close to −2 ppm (see Ref. [29]) for Si in SiH_4. When all these effects and errors are taken into account, our corrected result for $\sigma(Si; SiH_4)$ is 482.64 ppm, which is in very good agreement with high accurate calculations reported previously.

The average value for $\sigma^{ref}(Si)$ can be re calculated considering all corrections mentioned above (which give a value close to −6.4 ppm). It gives a final result of 404.09 ppm. For $\sigma^{ref}(Ge)$ there is no dependence with temperature or any other corrections to consider to improve the result of this work. Only the incompleteness of the basis set can reduce the final value in 1 ppm. Makulski et al. reported $\sigma^{ref}(Ge) = 1662.40$ ppm combining one not very accurate calculation of $\sigma(Ge)$ in GeH_4 with a new measured value of its chemical shift.

At this stage we have to mention that the values of σ^{ref} reported by Antusek [42] and Makulski [15] were obtained applying a similar procedure as ours though they applied it only to one molecular system, while we did it to seventeen (for Si) and sixteen (for Ge) different molecular systems to obtain a reliable averaged value which has a dispersion as small as possible.

We shall give another source of errors in our procedure: we used experimental chemical shifts that were obtained in liquid samples and our theoretical calculations are valid in gas phase. Still the difference among δ^{exp} in liquid and gas phase should not be very important. Makulski has shown that the gas-to-solution shift of $\sigma(Si)$ in SiF_4 is close to 1 ppm [43]. We can expect that a similar behavior should occur for the other (Si/Ge)-containing tetrahedral molecules.

We are able now to go one step further and calculate again chemical shifts within the RelPPA-RPA level though using the values of reference, $\sigma^{ref}(Si)$ and $\sigma^{ref}(Ge)$ computed above. In Tables 4 and 5 we show results of $\delta(Si)$ and $\delta(Ge)$ obtained applying Eq. (2). The data were taken from Tables 2 and 3 and the corresponding reference values, $\sigma^{ref}(Si) = 410.49$ ppm and $\sigma^{ref}(Ge) = 1705.29$ ppm.

A good fitting between theoretical and experimental values of $\delta(Si)$ and $\delta(Ge)$ is obtained at the RelPPA-RPA level. As observed in Table 4, for silicon containing molecules the largest difference is now less than 15 ppm (SiH_4) and the smallest one is close to zero ($SiBr_2I_2$ and $SiBrI_3$). In the case of the germanium atom (see Table 5), the largest difference is of only 34 ppm ($GeCl_3I$) and such a difference is close to zero for $GeClBr_2I$. The averaged deviation for the whole set of molecular systems analyzed is only 5 ppm for silicon containing molecules and 17 ppm for germanium containing molecules. In Figs. 1 and 2 we show the excellent agreement with experimental values that arises when we use the calculated $\sigma^{ref}(Si)$ and $\sigma^{ref}(Ge)$ with RelPPA-RPA as the reference value.

From the analysis given above, we can say that our results can be taken as benchmark values for the absolute nuclear magnetic shielding, as well as chemical shift, even for the heavier molecular systems.

In several papers a relationship between chemical shifts of silicon and germanium atom in equivalent systems was reported [10,11]. We are now able to propose a similar relationship between the absolute nuclear magnetic shieldings for both nuclei in the

Table 4
Magnetic shieldings and chemical shifts of silicon atom computed with respect to the reference value.

Molecule	RelPPA-RPA	δ^{theo}	δ^{exp} [a]
$SiCl_4$	428.42	−17.93	−20.0
$SiCl_3Br$	441.03	−30.54	−34.3
$SiCl_2Br_2$	456.15	−45.66	−50.7
$SiClBr_3$	473.51	−63.02	−69.8
$SiCl_3I$	493.87	−83.38	−75.4
$SiBr_4$	492.78	−82.29	−92.7
SiH_4	489.04	−78.55	−93.1
$SiCl_2BrI$	513.36	−102.87	−98.9
SiF_4	521.72	−111.23	−109.0
$SiClBr_2I$	534.49	−124.00	−122.8
$SiBr_3I$	556.95	−146.46	−149.5
$SiCl_2I_2$	574.85	−164.36	−151.5
$SiClBrI_2$	598.59	−188.10	−181.9
$SiBr_2I_2$	623.19	−212.70	−212.3
$SiClI_3$	664.49	−254.00	−245.9
$SiBrI_3$	690.61	−280.12	−280.1
SiI_4	758.39	−347.90	−346.2

[a] Experimental data taken from Ref. [10]

Table 5
Magnetic shieldings and chemical shifts of germanium atom computed with respect to the reference value.

Molecule	RelPPA-RPA	δ^{theo}	δ^{exp} [a]
$GeCl_4$	1696.82	8.47	30.9
$GeCl_3Br$	1764.34	−59.05	−47.8
$GeCl_2Br_2$	1834.07	−128.78	−131.3
$GeClBr_3$	1907.94	−202.65	−219.4
$GeCl_3I$	1975.56	−270.27	−235.9
GeH_4	1979.67	−274.38	−283.7
$GeBr_4$	1982.35	−277.06	−311.3
$GeCl_2BrI$	2048.87	−343.58	−326.2
$GeClBr_2I$	2123.41	−418.12	−417.6
$GeBr_3I$	2197.19	−491.90	−509.3
$GeCl_2I_2$	2256.85	−551.56	−523.7
$GeClBrI_2$	2328.50	−623.21	−613.5
$GeBr_2I_2$	2399.08	−693.79	−707.4
$GeClI_3$	2520.17	−814.88	−809.9
$GeBrI_3$	2586.14	−880.85	−899.8
GeI_4	2758.28	−1052.99	−1081.8

[a] Experimental data taken from Ref. [10]. The quoted precision of the chemical shifts (±3 ppm) takes account of the calibration uncertainty.

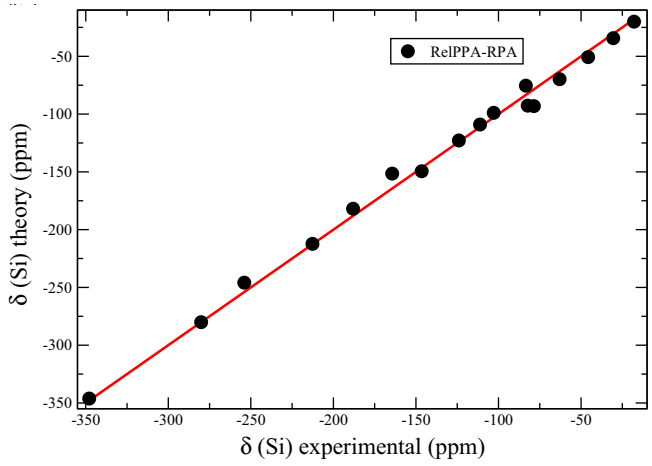

Fig. 1. Experimental vs theoretical chemical shifts of Si in the seventeen molecular systems from Table 4.

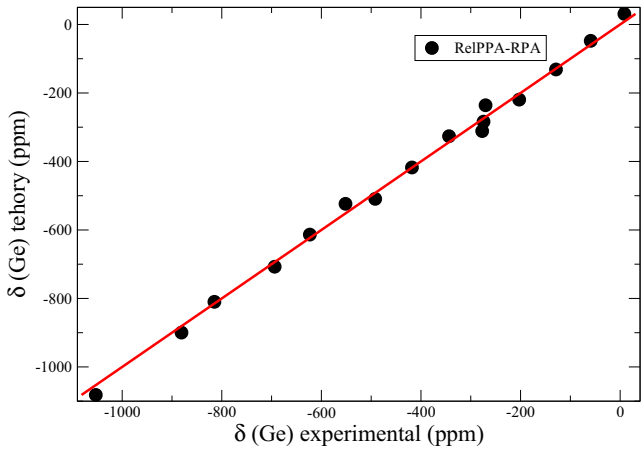

Fig. 2. Experimental vs theoretical chemical shifts of Ge in the sixteen molecular systems from Table 5.

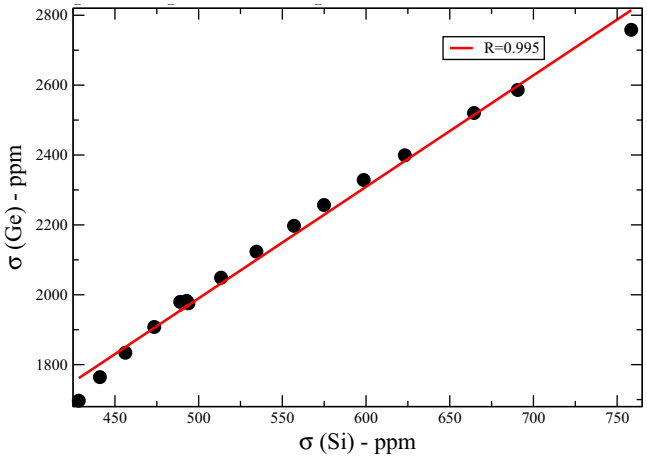

Fig. 3. Correlation of ^{29}Si nuclear magnetic shieldings in silicon compounds with ^{73}Ge nuclear magnetic shieldings in their germanium analogs.

equivalent molecular systems worked out here. In Fig. 3 we show the correlation of σ(Si) in silicon compounds with σ(Ge) in their germanium analogs and it yields a straight line. However, the interpretation of the individual data shows that the values for XCl_4, XCl_3Br and XI_4 compounds (X = Si, Ge) lie away from the overall line. If one take them out the regression analysis improves the correlation.

The relationship among the shieldings of Ge and Si obtained from Fig. 3 is

$$\sigma(\mathrm{Ge}) = 3.191[\sigma(\mathrm{Si})] + 394.32 (r = 0.995)$$

that corresponds to a very good correlation between nuclear magnetic shieldings for Si and Ge nuclei for the molecular systems studied in this work. Its equivalence for chemical shifts is

$$\delta(\mathrm{Ge}) = 3.19[\delta(\mathrm{Si})] + 1.01 (r = 0.995)$$

which is little better than the experimental one mentioned in Section 1 [10].

Why it happens this kind of linear relationship among σ(Ge) and σ(Si)? Geometrical and electronic effects on both set of halogen substituted tetrahedral (Si/Ge)-containing compounds are completely equivalent. So it seems natural to consider that such kind of dependence should appear. We should not expect a similar dependence for other kind of (Si/Ge)-containing compounds, though it may occur.

4. Concluding remarks

The search for reliable absolute values of the NMR shieldings for silicon and germanium containing molecules is still underway. There is no pure experimental results available and so, one needs to search for an accurate theoretical method for obtaining such reference values in tetramethylsilane and tetramethylgermanium. Such theoretical method needs also to include the likely dependence of such spectroscopic parameter with few effects as temperature, vibrational effects, incompleteness of basis set, and relativistic and electron correlation effects. Relativistic effects must be included even for Si-containing molecules because some halogen substituents, like Br and I should be considered as heavy atoms. So they need to be treated within relativistic frameworks. We have chosen one of the most accurate methods we have at hand, the relativistic polarization propagator at the random phase level of approach, RelPPA-RPA.

The main aims of this article have been oriented to answering the following enquiries:

(i) Which are the most accurate values (or short range of values) of $\sigma^{ref}[Si(CH_3)_4]$ and $\sigma^{ref}[Ge(CH_3)_4]$ to consider as the reference for the shieldings of silicon and germanium atoms?

(ii) Which are the best theoretical estimate of the corresponding chemical shifts in different halogen substituted silicon/germanium molecular systems?
(iii) What relationship can be proposed for the absolute nuclear magnetic shieldings of both nuclei in equivalent molecular systems?

We found that the best theoretical reference values for the shieldings of Si and Ge are:

σ[Si; $Si(CH_3)_4$] = 410.49 ± 6.77 ppm.

σ[Ge; $Ge(CH_3)_4$] = 1705.29 ± 19.51 ppm.

These values do not contain corrections due to different effects mentioned above. If we do so, including the gas-to-solution shift, for Si atom the corrected value should be close to 403.1 ppm. In the case of Ge this is not possible due to all corrections are not known.

Once we have the accurate absolute reference values of Si and Ge, and the theoretical values of the nuclear magnetic shieldings for all molecular systems, we can calculate the corresponding theoretical chemical shifts. We found that they are close to the experimental ones. This fact is an indication that we obtained reliable theoretical values for σ^{ref}(Si) and σ^{ref}(Ge).

Another finding of this work is related with the linear relationship that we propose and found for the nuclear magnetic shieldings of both nuclei in equivalent molecular environments with good enough correlation. Such a relationship seems to be natural due to we are considering that central atoms (Si and Ge) belongs to equivalent molecular structures.

Conflict of interest

There is no conflict of interest.

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