

# Core-dependent and ligand-dependent relativistic corrections to the nuclear magnetic shieldings in $MH_{4-n}Y_n$ ( $n=0-4$ ; $M = Si, Ge, Sn$ , and $Y = H, F, Cl, Br, I$ ) model compounds

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**Abstract** The nuclear magnetic shieldings of Si, Ge, and Sn in  $MH_{4-n}Y_n$  ( $M = Si, Ge, Sn$ ;  $Y = F, Cl, Br, I$  and  $n=1-4$ ) molecular systems are highly influenced by the substitution of one or more hydrogens by heavy-halogen atoms. We applied the linear response elimination of small components (LRESC) formalism to calculate those shieldings and learn whether including only a few of the leading relativistic correction terms is sufficient to be able to quantitatively reproduce the full relativistic value. It was observed that the nuclear magnetic shieldings change as the number of heavy halogen substituents and their weights vary, and the pattern of  $\sigma(M)$  generally does not exhibit the normal halogen dependence (NHD) behavior that can be seen in similar molecular systems containing carbon atoms. We also analyzed each relativistic correction afforded by the LRESC method and split them in two: core-dependent and ligand-dependent contributions; we

then looked for the electronic mechanisms involved in the different relativistic effects and in the total relativistic value. Based on this analysis, we were able to study the electronic mechanism involved in a recently proposed relativistic effect, the “heavy atom effect on vicinal heavy atom” (HAVHA), in more detail. We found that the main electronic mechanism is the spin-orbit or  $\sigma_p^{T(3)}$  correction, although other corrections such as  $\sigma_p^{S(1)}$  and  $\sigma_p^{S(3)}$  are also important. Finally, we analyzed proton magnetic shieldings and found that, for molecules containing Sn as the central atom,  $\sigma(H)$  decreases as the number of heavy halogen substituents (of the same type: either F, Cl, or Br) increases, albeit at different rates for different halogens.  $\sigma(H)$  only increase as the number of halogen substituents increases if the halogen is iodine.

**Keywords** LRESC · Relativistic effects · Polarization propagators · NMR

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## Introduction

The theoretical analysis of NMR magnetic shieldings of heavy-atom-containing molecules should include relativistic effects, which are widely known to affect the magnetic behavior of both heavy and light atoms. These effects appear due to the presence of heavy atoms, HAs. Two type of HA-dependent effects were postulated in the late 1980s based on the seminal work of Pekka Pyykkö and coauthors [1, 2]. They were the first group to show that there is a heavy-atom effect on the chemical shift of a vicinal light atom “through spin-orbit-induced changes in the wavefunction” [2]. This effect was coined the HALA (heavy atom on light atom) effect [2, 3]. However, almost simultaneously, they introduced another HA effect. The differences in the relativistic and nonrelativistic contributions from the Pb 6s orbitals to the Pb chemical shift in a  $PbH_3$  model compounds was interpreted as being due to the HAVA (heavy atom on

heavy atom) effect [1]. This is essentially a heavy-atom effect on the shielding of the same heavy atom.

These two effects are now well established and have been studied in a number of different molecular systems since their discovery [4–13]. However, very recently, a third HA effect was proposed by us, termed the HAVHA (heavy atom on vicinal heavy atoms) effect [8, 14]. New studies were then needed to obtain enough evidence of this effect to allow it to be analyzed. Thus, even though some authors have studied the NMR spectroscopic parameters for heavy-atom containing molecules, the relatively recent unearthing of the HAVHA effect has meant that it was not included in any of their analyses. One of the main reasons for the rather late discovery of the HAVHA effect (compared to the HALA and HAHA effects) this may be the appearance of more versatile and accurate two-component methods, such as the linear response elimination of small component (LRESC) formalism [4, 15] and the Breit–Pauli perturbation theory (BPPT) [16, 17], which allows the analysis of magnetic properties in molecules with three or more heavy atoms. It is important to note that HA-type effects can only be analyzed using two-component methods because, even though they are included in the results obtained with four-component methods, they are included in the total relativistic effects.

Perhaps the first study to indicate a link between the spin-orbit contribution to the chemical shift of a lead atom and the atomic number of atoms directly coordinated to the metal was published by Ziegler and coauthors in 1999 [18]. They found that the presence of heavier atoms led to a larger absolute value of the SO contribution to the chemical shift. However, they did not assign this SO contribution to a new HA effect. Ten years later, Autschbach and Zheng, in a review article [9], proposed that those findings were due to HAOHA (heavy atom on other heavy atom) and HAHA effects.

We now know that, when the molecule contains two or more heavy atoms, the whole set of heavy atoms can influence (via different electronic mechanisms) the nuclear magnetic shielding of a given vicinal heavy atom belonging to the same molecule [14, 19]. We found that this effect is related to the atomic number of the (halogen) substituents present, and is mostly due to paramagnetic-like contributions.

Following our previous studies, we were then interested in obtaining answers to some long-unanswered questions, such as: what are the main electronic mechanisms involved in the HAVHA effect? Are HAHA-type effects modified by the HAVHA effect? Or, in other words, does the presence of heavy atoms in close proximity to the studied atom modify its shielding? What about HALA-type effects? Is the mechanism of the HAVHA effect similar to that of the HALA effect? Is the SO contribution of a central heavy atom modified by the presence of other heavy atoms in its vicinity? Some of the aims of the work described in the present article are to explore and answer these questions.

In order to analyze relativistic effects on NMR shieldings, we applied the LRESC formalism [4, 15]. This starts from fully relativistic (four-component) expressions, making use of Rayleigh–Schrödinger perturbation theory. Then, applying some particular prescriptions to eliminate the small component scheme, four-component terms are reduced to two-component ones.

Calculations performed with codes that implement such a two-component scheme and the other equivalent two-component method, BPPT [16, 17], as well as others that have recently been published by some of the present authors [20], have shown that the LRESC methodology gives results that are close to those afforded by four-component calculations, at least for atoms as heavy as those belonging to the fifth row of the periodic table [4, 21].

The family of molecular systems we studied in the work reported here has the formula  $MH_{4-n}Y_n$  ( $n=0-4$ ;  $M = \text{Si, Ge, Sn, and } Y = \text{H, F, Cl, Br, I}$ ). These systems may show what is known as normal halogen dependence (NHD). This implies that the SO effects increase the shielding as both the atomic number of the halogen substituent bonded to the NMR-active atom and the number of (heavy-atom) substituents increase. Thus, the chemical shift of the active atom,  $\delta(M) = \sigma^{\text{ref}} - \sigma(M)$ , decreases upon changing the substituent from Cl to Br to I [5, 22, 23]. In line with this fact, the  $^{13}\text{C}$  chemical shifts of the halogen-substituted methanes  $\text{CH}_{4-n}Y_n$  ( $Y = \text{Br, I}$ ) exhibit nonlinear NHD with increasing  $n$ , whereas the corresponding mixed complexes  $\text{CH}_{4-n}Y_n$  ( $Y = \text{Br, I}$  for example) show an essentially linear decrease [13, 24]. Another aim of the present research was to investigate this issue further.

The article is structured as follows. Next, in the “Theory” section, an overview of the methods applied in this work is provided. We then present results from shielding calculations for the central atom. In the “LRESC vs. four-component RelPPA-RPA calculations” section, the performance of the LRESC method is compared with that of the more accurate four-components approach, and an analysis the halogen dependence of heavy central atoms (i.e., to determine if there is a normal or inverse halogen dependence) is summarized. Then, in the “Leading LRESC relativistic corrections” section, we present an analysis in which the leading relativistic corrections are split in two, leading to both core-dependent and ligand-dependent contributions. This approach provides the foundations for studying the HAVHA effect in a more realistic way. An investigation of the dependence of the hydrogen shielding on the halogen substituents is also discussed. Finally, concluding remarks are provided in the “Conclusions” section.

## Theory

The nuclear magnetic shielding constant may be thought of as the proportionality coefficient between an external (uniform)

magnetic field and the additional local fields generated by the interaction of this applied field with surrounding electrons. The nuclear magnetic shielding tensor of the nucleus M ( $\sigma_{ij}(\text{M})$ ) is then defined as the response of the electronic molecular system to both the external magnetic field ( $\mathbf{B}$ ) and the nuclear magnetic moment of the nucleus M.

$$\sigma_{ij}(\text{M}) = \frac{\partial^2 E}{\partial \mu_i^{\text{M}} \partial \mathbf{B}_j} \quad (1)$$

This property is usually obtained as the second derivative of the molecular electronic energy ( $E$ ) under the action of both the magnetic moment and the field ( $\mu_{\text{M}}$ ,  $\mathbf{B}$ ). The vector potential  $\mathbf{A}$  gives rise to the magnetic field as  $\mathbf{B} = \nabla \times \mathbf{A}$ , which is given by

$$\mathbf{A} = \sum_K^{\text{nuc}} \mathbf{A}_K = \sum_K^{\text{nuc}} \left( \mu_K \times \frac{\mathbf{r}_K}{r_K^3} \right) + \mathbf{B} \times \frac{\mathbf{r}}{2}, \quad (2)$$

where  $\mathbf{r}_K = \mathbf{r} - \mathbf{R}_K$  (from nucleus “K”),  $\mathbf{r}$  is taken from the gauge origin, and  $c$  is the speed of light in a vacuum.

### Relativistic polarization propagator

Some second-order molecular properties (i.e., those that are theoretically obtainable by applying second-order perturbation theory to the electronic energy, and thus depend on two “external” fields) can be calculated using polarization propagators [25]. The formal equation that relates the correction to the energy with these propagators is

$$E_{\text{PQ}}^2 = 1/2 \text{Re} \langle \langle H^{\text{P}}; H^{\text{Q}} \rangle \rangle_{E=0} \quad (3)$$

where  $H^{\text{P}}$  and  $H^{\text{Q}}$  are perturbative Hamiltonians that describe the external perturbations to the system, the response to which (observable through the molecular properties that are modified by them) we are interested in calculating and analyzing. In the relativistic polarization propagator approach (RelPPA), the explicit shorthand expression for the nuclear magnetic shielding is [25].

$$\sigma_{\text{M}} = e^2 \left\langle \left\langle \frac{\alpha \times \mathbf{r}_{\text{M}}}{r_{\text{M}}^3}; \alpha \times \mathbf{r}_{\text{G}} \right\rangle \right\rangle. \quad (4)$$

This equation can be re-expressed in such a way that all of the considered virtual electronic excitations are written explicitly. The excitations involving occupied electronic states and virtual positive-energy electronic states will give the paramagnetic component and those involving negative-energy electronic states will give the diamagnetic component in a nonrelativistic regime [25].

The consistent first-order approach is the random phase approximation (RPA), which is obtained when the reference

state is chosen to be the Dirac–Hartree–Fock state and the manifold of excitation operators considered is truncated up to the first set of elements, i.e., the single-excitation operators [25].

### Relativistic corrections to the shielding constants

The starting point for correctly including all relativistic corrections to  $\sigma$  is to consider a molecular system under the influence of both a uniform external magnetic field ( $\vec{B}$ ) and the magnetic moments of all nuclei ( $\vec{\mu}_{\text{M}}$ ) in a many-body relativistic regime [15]. In this way, all of the interactions are taken into account when the full relativistic Hamiltonian of the total system is transformed from four to two components. In doing so, we obtain the unperturbed molecular Hamiltonian and a perturbation containing both magnetic interactions. For the LRESC scheme, we take into account the transformation termed “elimination of the small component” for all matrix elements involved in a response function, as well as the contributions that derive from the manifold space where  $N$  electron–positron pairs are created over the ground state. These states are coupled with the  $N$ -electron ground state via the magnetic interaction and the Breit operator in the unperturbed molecular Hamiltonian. A detailed description of this scheme is presented elsewhere; see [4, 15].

The full list of the relativistic corrections that arise within the LRESC model to paramagnetic and diamagnetic terms ( $\sigma_{\text{p}}$ ,  $\sigma_{\text{d}}$ ), which come from one-body operators, is presented in Table 1. A straightforward, detailed description of this separation and the origin of all the LRESC corrections is provided in [13].

The corrections can be clustered according to whether they are first- or third-order in response theory and also depending on their spin character, either singlet or triplet. From now on we shall express the LRESC corrections in line with these criteria, which are explained in Table 1. All physical insights that arise from the application of these criteria are presented and discussed in the “Results and discussion” section.

We now present a brief account of the LRESC corrections. The commonest corrections to the shielding constant are those terms obtainable from (i) a perturbed series of the one-body Dirac Hamiltonian, taking its nonrelativistic limit up to the first order in  $\alpha$ , and (ii) operators that contain the nuclear magnetic vector potential (including “Fermi-type” terms):

$$\sigma_{\text{p}}^{\text{PSO}} = \langle \langle H^{\text{OZ}}, H^{\text{PSO}}, H^{\text{MV}} + H^{\text{DW}} \rangle \rangle \quad (5)$$

$$\sigma_{\text{p}}^{\text{SO}} = \langle \langle H^{\text{OZ}}, H^{\text{FC}} + H^{\text{SD}}, H^{\text{SO}} \rangle \rangle \quad (6)$$

$$\sigma_{\text{d}}^{\text{MV}} = \langle \langle H^{\text{DIA}}, H^{\text{MV}} \rangle \rangle \quad (7)$$

**Table 1** Classification of the LRESC corrections to the NMR shielding constant

$\sigma = \sigma_p + \sigma_d$	Zeroth-order	First-order		Third-order	
	Singlet	Singlet	Triplet	Singlet	Triplet
$\sigma_p$	–	$\sigma_p^{S(1)} = \sigma_p^{OZK} + \sigma_p^{PSOK}$	$\sigma_p^{T(1)} = \sigma_p^{SZK} + \sigma_p^{BSO}$	$\sigma_p^{S(3)} = \sigma_p^{PSO}$	$\sigma_p^{T(3)} = \sigma_p^{SO}$
$\sigma_d$	$\sigma_d^{S(0)} = \sigma_d^{DIAK}$	$\sigma_d^{S(1)} = \sigma_d^{MV} + \sigma_d^{DW}$	–	–	–

$$\sigma_d^{DW} = \langle\langle H^{DIA}, H^{DW} \rangle\rangle. \quad (8)$$

Corrections to the Dirac Hamiltonian are either of singlet type, i.e., mass velocity ( $H^{MV}$ ) and Darwin ( $H^{DW}$ ) operators, or of triplet type, which in this case are the spin-orbit ( $H^{SO}$ ) operators:

$$H^{OZ} = \frac{e}{2mc} L \cdot B \quad (9)$$

$$H^{MV} = -\frac{1}{8m^3c^2} p^4 \quad (10)$$

$$H^{DW} = \frac{1}{4m^2c^2} \nabla^2 V_C \quad (11)$$

$$H^{SO} = \frac{1}{8m^3c^3} \sigma(\nabla V_C \times p). \quad (12)$$

The operators that are constructed from the magnetic perturbation due to the nuclear spin are

$$H^{FC} = \frac{e}{2m} \sigma \left( \frac{8\pi}{3} \mu_M \delta(r_M) \right) \quad (13)$$

$$H^{SD} = \frac{e}{2m} \sigma \left( \frac{3(\mu_M r_M) r_M - r_M^2 \mu_M}{r_M^5} \right). \quad (14)$$

Finally, we use terms arising from the external-magnetic-field-dependent operators that yield relativistic corrections as well as those arising from the inclusion of effects due to small components and due to the “normalization” of large components. We split these terms up according to their spin character, i.e., into singlet- and triplet-type terms:

$$\sigma_p^{SZK} = \langle\langle H^{FC+SD}, H^{SZK} \rangle\rangle \quad (15)$$

$$\sigma_p^{BSO} = \langle\langle H^{FC+SD}, H^{BSO} \rangle\rangle \quad (16)$$

$$\sigma_p^{OZK} = \langle\langle H^{PSO}, H^{OZK} \rangle\rangle \quad (17)$$

$$\sigma_p^{PSOK} = \langle\langle H^{PSOK}, H^{OZ} \rangle\rangle \quad (18)$$

$$\sigma_d^{DIAK} = \langle H^{DIAK} \rangle \quad (19)$$

where

$$H^{SZK} = \frac{-e}{8m^3c^2} [3(\sigma B)p^2 - (\sigma p)(pB)] \quad (20)$$

$$H^{BSO} = \frac{e}{4m^2c^2} \nabla V_C \times (B \times r_0) \quad (21)$$

$$H^{OZK} = \frac{-e}{4m^3c^2} (LB)p^2 \quad (22)$$

$$H^{PSOK} = -\frac{e}{4m^3c^2} \left\{ \frac{\mu_M L_M}{r_M^3}, p^2 \right\} \quad (23)$$

$$H^{DIAK} = -\frac{1}{4m^3c^4} \left\langle 2 \left( \frac{\mu_M L_M}{r_M^3} \right) (BL_M) + BB_M + 2(A_M A_B) p^2 + 2\pi(\mu_M B) \delta(r_M) \right\rangle. \quad (24)$$

## Computational details

### Geometry optimizations

The complete set of molecular systems under study in this work are defined by the formula  $MH_{4-n}Y_n$  ( $n=0-4$ ;  $M = \text{Si, Ge, Sn}$ , and  $Y = \text{H, F, Cl, Br, I}$ ). Most of them were optimized at the four-component level with the module OPTIMIZE of the DIRAC code [26]. Experimental geometries, as taken from [27], were used for the other systems. Table 2 presents some bond distances between central atoms and substituent halogens, and also indicates which of the geometries were optimized. Geometry optimizations were performed considering the Sadlej basis set [28] in all cases.

To check that the quality of the optimization procedure is good enough, we compared the optimized geometries for three of the molecular systems for which there are experimentally obtained geometries:  $\text{SiF}_4$ ,  $\text{SiCl}_4$ , and  $\text{SnCl}_4$ . Their

**Table 2** Experimental/optimized geometries

M	Molecule	Y				
		H	F	Cl	Br	I
Si	SiH <sub>3</sub> Y	1.480 <sup>a</sup>	1.593 <sup>a</sup>	2.048 <sup>a</sup>	2.210 <sup>a</sup>	2.437 <sup>a</sup>
	SiH <sub>2</sub> Y <sub>2</sub>		1.561 <sup>b</sup>	2.040 <sup>b</sup>	2.204 <sup>b</sup>	2.435 <sup>b</sup>
	SiHY <sub>3</sub>		1.562 <sup>a</sup>	2.028 <sup>b</sup>	2.199 <sup>b</sup>	2.447 <sup>b</sup>
	SiY <sub>4</sub>		1.553 <sup>a</sup>	2.019 <sup>a</sup>	2.197 <sup>b</sup>	2.440 <sup>b</sup>
Ge	GeH <sub>3</sub> Y	1.525 <sup>a</sup>	1.732 <sup>a</sup>	2.150 <sup>a</sup>	2.299 <sup>a</sup>	2.533 <sup>b</sup>
	GeH <sub>2</sub> Y <sub>2</sub>		1.697 <sup>b</sup>	2.139 <sup>b</sup>	2.291 <sup>b</sup>	2.520 <sup>b</sup>
	GeHY <sub>3</sub>		1.678 <sup>b</sup>	2.123 <sup>b</sup>	2.285 <sup>b</sup>	2.511 <sup>b</sup>
	GeY <sub>4</sub>		1.660 <sup>b</sup>	2.113 <sup>a</sup>	2.272 <sup>a</sup>	2.531 <sup>b</sup>
Sn	SnH <sub>3</sub> Y	1.711 <sup>a</sup>	1.904 <sup>b</sup>	2.256 <sup>b</sup>	2.331 <sup>b</sup>	2.574 <sup>b</sup>
	SnH <sub>2</sub> Y <sub>2</sub>		1.890 <sup>b</sup>	2.256 <sup>b</sup>	2.471 <sup>b</sup>	2.614 <sup>b</sup>
	SnHY <sub>3</sub>		1.870 <sup>b</sup>	2.297 <sup>b</sup>	2.479 <sup>b</sup>	2.689 <sup>b</sup>
	SnY <sub>4</sub>		1.854 <sup>b</sup>	2.325 <sup>a</sup>	2.487 <sup>b</sup>	2.709 <sup>b</sup>

$d(M-Y)$  and  $d(M-H)$  bond distances

<sup>a</sup> Experimental geometry taken from [27]

<sup>b</sup> Theoretically optimized geometry

theoretical/experimental bond lengths  $d(M-Y)$  are: for SiF<sub>4</sub>,  $r = 1.537/1.553$  Å; for SiCl<sub>4</sub>,  $r = 2.018/2.019$  Å; for SnCl<sub>4</sub>,  $r = 2.311/2.325$  Å. We can see that the differences are small enough that we can be confident in the use of theoretically optimized geometries.

Shielding calculations performed using the four-component method

Benchmark calculations of shielding constants were performed with the RelPPA-RPA formalism. The basis sets used in this work are the same as those used in previous works [14, 29, 30]. We considered Sadlej's basis sets in a first step [28], and then included some tight and diffuse Gaussian-type functions in order to obtain converged results. We used these orbitals in the following fashion: tight basis functions were added to  $s$ ,  $p$ ,  $d$ ,  $f$  blocks with the relationship among exponents of  $\alpha_{i+1}/\alpha_i = 3$ , starting from the largest exponent in each block [14, 29, 30]. No diffuse basis functions were necessary for  $d$  and  $f$  blocks because they do not significantly change the shielding values. The small components of the basis set were generated by applying the unrestricted kinetic balance (UKB) prescription [8].

Calculating shieldings with the LRESC model

LRESC shielding calculations were carried out with the Dalton program [31]. In this work, we present a new version of the basis set used for LRESC calculations in previous papers [4, 11, 13, 14, 15]. This new basis set is smaller than

the previous one although it achieves the same quality of data for calculations performed within the LRESC scheme. In this case, we have taken out tight functions of  $s$  and  $p$  character, namely two  $s$ -type tight functions for H and F and two  $s$ - and  $p$ -type tight functions for Si, Cl, Ge, Br, Sn, and I. This basis set is presented in the "Electronic supplementary material" (ESM).

## Results and discussion

We first present our analysis of the accuracy of the LRESC results for the whole set of molecules we considered in this work. We then discuss our analysis of the electronic mechanisms that contribute to the leading relativistic effects. We divided them in two sets: core-dependent and ligand-dependent contributions, each of which comprises three different mechanisms. We then consider the magnitude of each of the three heavy-atom effects (HALA, HAAA, and HAVHA) on the central light/heavy atom. The final analysis presented in this work focuses on the hydrogen shieldings.

### LRESC vs. four-component RelPPA-RPA calculations

In order to assess the accuracy of LRESC in describing the electronic mechanisms responsible for the relativistic effects on many heavy-atom-containing molecules, we first compare it with 4c calculations.

The LRESC results for  $\sigma(\text{Si})$ ,  $\sigma(\text{Ge})$ , and  $\sigma(\text{Sn})$  are presented in Tables 3, 4, and 5, respectively, as well as the results from four-component shielding calculations for comparison. As already mentioned, the model compounds studied have the formula MH<sub>4-n</sub>Y<sub>n</sub> ( $n=0-4$ ; M = Si, Ge, Sn; Y = H, F, Cl, Br, I).

The second column shows the nonrelativistic values of the nuclear magnetic shieldings for the whole set of molecules. The LRESC corrections are presented from the third to the eighth column. The ninth and tenth columns show core- and ligand-dependent LRESC corrections. The last three columns show the nonrelativistic values plus the SO corrections, the total LRESC values, and the four-component values.

The LRESC values are close enough to the four-component values, even for molecules with several substituents that belong to the fifth row of the periodic table. The largest absolute difference (LRESC - 4c) was found for  $\sigma(\text{Sn})$  in the SnI<sub>4</sub> molecule, which contains five heavy atoms, giving a difference of 414 ppm ( $\approx 7.5$  %). On the other hand, the largest percentage difference, 8.9 %, was obtained for the SiI<sub>4</sub> system; this decreased to 8.7 % when Si was replaced with Ge. Even though the differences between the LRESC and the four-component



**Table 3** Nuclear magnetic shielding constants for the central Si atom, obtained at different levels of theory, in  $\text{SiH}_{4-n}\text{Y}_n$  ( $\text{Y} = \text{F}, \text{Cl}, \text{Br}, \text{I}; n=0-4$ )

System	$\sigma^{\text{nr}}$	$\sigma_{\text{d}}^{\text{S}(0)}$	$\sigma_{\text{d}}^{\text{S}(1)}$	$\sigma_{\text{p}}^{\text{T}(1)}$	$\sigma_{\text{p}}^{\text{S}(1)}$	$\sigma_{\text{p}}^{\text{S}(3)}$	$\sigma_{\text{p}}^{\text{T}(3)}$	Core <sup>a</sup>	Ligand <sup>b</sup>	$\sigma^{\text{nr}} + \sigma_{\text{p}}^{\text{T}(3)}$	LRESC	4c
$\text{SiH}_4$	473.91	5.95	-22.19	35.89	2.71	-4.46	-0.71	19.66	-2.46	473.20	491.10	489.04
$\text{SiH}_3\text{F}$	414.27	5.95	-22.22	35.89	2.98	-5.29	0.24	19.62	-2.07	414.51	431.81	430.80
$\text{SiH}_3\text{Cl}$	422.95	5.95	-22.31	35.92	3.16	-5.62	2.46	19.56	-0.01	425.41	442.50	442.64
$\text{SiH}_3\text{Br}$	424.89	5.95	-22.83	35.98	3.91	-7.87	14.01	19.10	10.04	438.90	454.03	453.74
$\text{SiH}_3\text{I}$	437.27	5.95	-23.76	36.02	4.97	-11.67	42.11	18.21	35.41	479.38	490.90	494.69
$\text{SiH}_2\text{F}_2$	424.06	5.95	-22.25	35.87	3.02	-5.29	1.08	19.56	-1.19	425.14	442.43	442.33
$\text{SiH}_2\text{Cl}_2$	396.36	5.95	-22.44	35.94	3.54	-6.43	7.26	19.46	4.37	403.62	420.19	422.25
$\text{SiH}_2\text{Br}_2$	388.71	6.02	-23.48	36.09	5.00	-10.72	38.66	18.62	32.94	427.37	440.28	440.69
$\text{SiH}_2\text{I}_2$	399.06	5.94	-25.33	36.20	7.17	-18.78	122.09	16.82	110.49	521.15	526.37	526.89
$\text{SiHF}_3$	466.81	5.95	-22.29	35.82	2.96	-4.93	1.77	19.48	-0.20	468.58	486.08	486.62
$\text{SiHCl}_3$	387.85	5.96	-22.56	35.96	3.69	-6.99	14.01	18.35	10.72	401.86	417.93	421.83
$\text{SiHBr}_3$	362.97	5.96	-24.13	36.23	7.37	-13.11	80.09	18.06	74.35	443.06	455.38	453.25
$\text{SiHI}_3$	355.51	5.95	-26.87	36.48	9.38	-25.58	275.29	15.56	259.10	630.80	630.17	612.70
$\text{SiF}_4$	501.27	5.94	-22.32	35.72	2.92	-4.70	1.48	19.34	-0.31	502.75	520.31	521.72
$\text{SiCl}_4$	384.56	5.96	-22.68	35.95	4.19	-7.46	22.77	19.23	19.50	407.33	423.29	428.09
$\text{SiBr}_4$	335.57	5.97	-24.72	36.47	7.08	-15.41	169.74	17.72	161.41	505.31	514.70	492.78
$\text{SiI}_4$	318.44	5.96	-28.45	36.82	11.62	-32.11	514.56	14.33	494.07	833.00	826.83	759.13

<sup>a</sup> The core-dependent contribution, defined as  $\sigma_{\text{p}}^{\text{T}(1)} + \sigma_{\text{d}}^{\text{S}(1)} + \sigma_{\text{d}}^{\text{S}(0)}$

<sup>b</sup> The ligand-dependent contribution, defined as  $\sigma_{\text{p}}^{\text{S}(1)} + \sigma_{\text{p}}^{\text{T}(3)} + \sigma_{\text{p}}^{\text{S}(3)}$

values are higher than 8 %, the absolute values of these differences are less than 70 ppm and 250 ppm, respectively.

Much smaller differences (in absolute values) were obtained for  $\sigma(\text{Si})$  in some of the lighter molecular systems shown in Table 3. They can be less than 2 ppm, as seen for  $\text{SiF}_4$ .

It was shown in previous works that the largest differences between the LRESC and four-component calculations are less than 10 % for molecular systems containing only one heavy atom belonging to the fifth row of the periodic table [4, 13, 15]. That conclusion can be extended to molecular systems containing up to five atoms belonging to the same row of the periodic table, at least for this type of molecular geometry.

From the analysis given above, we can be confident that the addition of the whole set of relativistic corrections obtained within the LRESC scheme leads to values very close to the four-component relativistic values of  $\sigma(\text{M})$ , even for the heaviest systems, which contain five heavy atoms. We are therefore in a good position to start the analysis of the electronic origin of the relativistic corrections.

The halogen dependence (normal or inverse) with respect to  $n$  and the nature of substituent  $\text{Y}$  is now (as compared with the equivalent carbon systems [13]) very much dependent on the central atom  $\text{M}$ . For  $\text{SiH}_{4-n}\text{I}_n$  ( $n=1 \rightarrow 4$ ),  $\text{GeH}_{4-n}\text{Y}_n$  ( $n=2 \rightarrow 4$ ;  $\text{Y} = \text{Br}, \text{I}$ ), and  $\text{SnH}_{4-n}\text{Y}_n$  ( $n=2 \rightarrow 4$ ;  $\text{Y} = \text{F}, \text{Cl}, \text{Br}, \text{I}$ ), the shielding of the central atom follows an NHD dependence.

If we fix the number  $n$  of substituents but modify the type of halogen ( $\text{Y}$ ) present, we find that (i) for  $\text{SiHY}_3$  and  $\text{SiY}_4$  ( $\text{Y} = \text{F} \rightarrow \text{I}$ ),  $\sigma^{\text{nr}}(\text{Si})$  presents IHD behavior whereas  $\sigma^{\text{LRESC}}(\text{Si})$  shows NHD behavior for  $\text{Y} = \text{Cl} \rightarrow \text{I}$ ; (ii) for  $\text{GeY}_4$  ( $\text{Y} = \text{F} \rightarrow \text{I}$ ),  $\sigma^{\text{nr}}(\text{Ge})$  presents IHD behavior whereas  $\sigma^{\text{LRESC}}(\text{Ge})$  shows NHD behavior for  $\text{Y} = \text{Cl} \rightarrow \text{I}$ ; (iii) for  $\text{SnHY}_3$  and  $\text{SnY}_4$  ( $\text{Y} = \text{F} \rightarrow \text{I}$ ),  $\sigma^{\text{nr}}(\text{Sn})$  presents IHD behavior whereas  $\sigma^{\text{LRESC}}(\text{Sn})$  shows NHD behavior for  $\text{Y} = \text{Cl} \rightarrow \text{I}$ .

In Figs. 1, 2, and 3 we show the dependence of  $\sigma^{\text{LRESC}}(\text{M})$  on  $n$  and the atomic number of the substituted halogen ( $\text{Y}$ ) atoms. When the number  $n$  of the same type of heavy-halogen atom is increased, the nuclear magnetic shielding also increases, except in  $\text{MH}_{4-n}\text{Cl}_n$  ( $\text{M} = \text{Si}, \text{Ge}; n=1, 2, 3$ ) molecules, where  $\sigma^{\text{LRESC}}(\text{M})$  decreases.

**Table 4** Nuclear magnetic shielding constants for the central Ge atom, obtained at different levels of theory, in GeH<sub>4-n</sub>Y<sub>n</sub> (Y = F, Cl, Br, I; n=0–4)

System	$\sigma^{\text{nr}}$	$\sigma_{\text{d}}^{\text{S}(0)}$	$\sigma_{\text{d}}^{\text{S}(1)}$	$\sigma_{\text{p}}^{\text{T}(1)}$	$\sigma_{\text{p}}^{\text{S}(1)}$	$\sigma_{\text{p}}^{\text{S}(3)}$	$\sigma_{\text{p}}^{\text{T}(3)}$	Core <sup>a</sup>	Ligand <sup>b</sup>	$\sigma^{\text{nr}} + \sigma_{\text{p}}^{\text{T}(3)}$	LRESC	4c
GeH <sub>4</sub>	1765.68	83.75	-287.85	450.81	46.36	-65.05	-9.30	246.71	-27.98	1756.38	1984.40	1979.67
GeH <sub>3</sub> F	1561.10	83.74	-287.87	450.83	50.31	-82.12	0.47	246.70	-31.35	1561.57	1776.45	1756.47
GeH <sub>3</sub> Cl	1601.30	83.75	-287.96	450.87	49.83	-79.38	3.84	246.65	-25.71	1605.14	1822.24	1802.71
GeH <sub>3</sub> Br	1614.55	83.75	-288.47	451.01	50.67	-81.33	29.80	246.29	-0.86	1644.35	1859.98	1850.29
GeH <sub>3</sub> I	1655.51	83.75	-289.36	451.10	51.54	-85.24	99.26	245.49	65.56	1754.77	1966.56	1954.32
GeH <sub>2</sub> F <sub>2</sub>	1535.53	83.73	-287.90	450.82	50.20	-83.86	4.26	246.66	-29.41	1539.79	1752.78	1735.75
GeH <sub>2</sub> Cl <sub>2</sub>	1501.61	83.75	-288.08	450.94	51.85	-88.23	17.12	246.61	-19.26	1518.73	1728.96	1717.31
GeH <sub>2</sub> Br <sub>2</sub>	1500.23	83.76	-289.09	451.27	54.36	-95.18	103.08	245.94	62.26	1603.31	1808.44	1797.51
GeH <sub>2</sub> I <sub>2</sub>	1559.87	83.80	-290.88	451.48	56.95	-106.36	320.39	244.40	270.98	1880.26	2075.24	2041.82
GeHF <sub>3</sub>	1609.29	83.72	-287.92	450.73	47.93	-78.41	6.80	246.53	-23.68	1616.09	1832.14	1814.32
GeHCl <sub>3</sub>	1451.55	83.75	-288.20	450.98	52.87	-94.06	43.74	246.53	2.54	1495.29	1700.63	1689.15
GeHBr <sub>3</sub>	1414.43	83.78	-289.71	451.62	57.53	-106.86	230.76	245.68	181.43	1645.19	1841.55	1838.48
GeHI <sub>3</sub>	1428.89	83.82	-292.41	452.15	62.55	-127.96	737.78	243.56	672.37	2166.67	2344.82	2293.84
GeF <sub>4</sub>	1669.04	83.74	-287.93	450.47	45.99	-74.81	9.88	246.28	-18.94	1678.92	1896.38	1879.46
GeCl <sub>4</sub>	1424.42	83.76	-288.31	450.97	52.64	-98.22	78.64	246.42	33.06	1503.06	1703.90	1696.82
GeBr <sub>4</sub>	1353.75	83.79	-290.34	452.07	60.23	-115.58	433.80	245.53	378.44	1787.55	1977.72	1982.35
GeI <sub>4</sub>	1319.63	83.86	-293.62	453.13	68.28	-149.91	1518.13	243.37	1436.49	2838.03	2999.49	2758.28

<sup>a</sup> The core-dependent contribution is defined as  $\sigma_{\text{p}}^{\text{T}(1)} + \sigma_{\text{d}}^{\text{S}(1)} + \sigma_{\text{d}}^{\text{S}(0)}$

<sup>b</sup> The ligand-dependent contribution is defined as  $\sigma_{\text{p}}^{\text{S}(1)} + \sigma_{\text{p}}^{\text{T}(3)} + \sigma_{\text{p}}^{\text{S}(3)}$

On the other hand, when the number of halogen atoms is fixed but the nuclear charge of each halogen is increased (from F to I),  $\sigma^{\text{LRESC}}(\text{M})$  does not show the normal halogen dependence behavior (NHD) for any central atoms: M = Si, Ge, and Sn.

Figures 4 and 5 shows the functional dependence of  $\sigma(\text{M})$  in MY<sub>4</sub> molecular systems on M (Fig. 4) and Y (Fig. 5). It is worth highlighting the fact that there is a clear distinction between the shieldings in the systems with Y = I and those calculated for the other systems. Relativistic effects increase as the number of iodine atoms increases.

#### Leading LRESC relativistic corrections

There are several leading relativistic corrections that arise within the LRESC method. We divided them into core-dependent and ligand-dependent contributions. This means that corrections which remain almost constant as the number or type of halogen substituent(s) varies are grouped together

and termed “core-dependent.” On the other hand, corrections that strongly depend on the substituents are termed “ligand-dependent.”

#### Core-dependent terms

In Tables 3, 4, and 5, we show the whole set of relativistic corrections to  $\sigma(\text{M})$  together with 4c, non relativistic, and also grouped as core, ligand and nr+SO corrections.

The core-dependent corrections are  $\sigma_{\text{p}}^{\text{T}(1)}$ ,  $\sigma_{\text{d}}^{\text{S}(1)}$ , and  $\sigma_{\text{d}}^{\text{S}(0)}$ . Each of these will be analyzed here separately as they do not behave in the same way: they have opposite signs but the same order of magnitude. Each arises from different electronic mechanisms. Two of them modify the diamagnetic component of the nuclear magnetic shielding, while the third modifies the paramagnetic part.

In molecular systems that contain silicon as the central atom, the correction  $\sigma_{\text{p}}^{\text{T}(1)}$  represents 7.1–11.6 % of

**Table 5** Nuclear magnetic shielding constants for the central Sn atom, obtained at different levels of theory, in  $\text{SnH}_{4-n}\text{Y}_n$  ( $\text{Y} = \text{F}, \text{Cl}, \text{Br}, \text{I}; n=0-4$ )

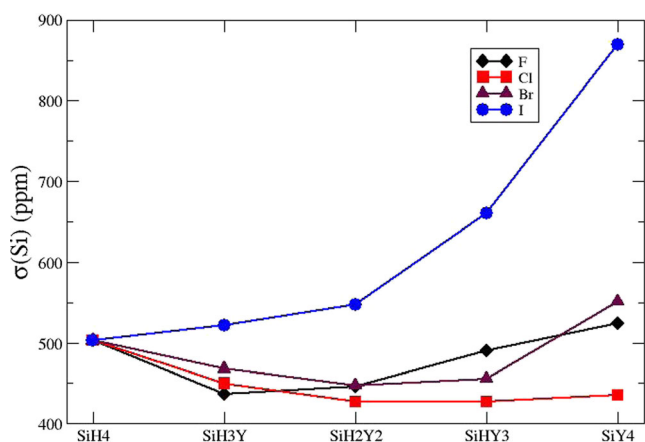
System	$\sigma^{\text{nr}}$	$\sigma_{\text{d}}^{\text{S}(0)}$	$\sigma_{\text{d}}^{\text{S}(1)}$	$\sigma_{\text{p}}^{\text{T}(1)}$	$\sigma_{\text{p}}^{\text{S}(1)}$	$\sigma_{\text{p}}^{\text{S}(3)}$	$\sigma_{\text{p}}^{\text{T}(3)}$	Core <sup>a</sup>	Ligand <sup>b</sup>	$\sigma^{\text{nr}} + \sigma_{\text{p}}^{\text{T}(3)}$	LRESC	4c
$\text{SnH}_4$	3270.26	345.16	-1137.66	1757.93	208.29	-304.29	-33.83	965.43	-134.33	3236.43	4101.36	4126.14
$\text{SnH}_3\text{F}$	3039.06	345.15	-1137.68	1757.96	219.95	-364.24	-1.51	965.43	-145.80	3037.55	3858.69	3908.30
$\text{SnH}_3\text{Cl}$	3055.27	345.16	-1137.76	1757.97	217.77	-353.17	-5.68	965.37	-141.08	3049.59	3879.55	3912.40
$\text{SnH}_3\text{Br}$	3027.76	345.15	-1138.26	1758.21	217.94	-348.03	6.02	965.10	-124.07	3033.78	3868.79	3921.07
$\text{SnH}_3\text{I}$	3083.40	345.16	-1139.08	1758.28	217.45	-347.46	74.62	964.36	-55.39	3158.02	3992.37	4076.03
$\text{SnH}_2\text{F}_2$	3103.66	345.12	-1137.68	1757.85	210.52	-346.67	14.99	965.28	-121.16	3118.65	3947.78	3979.00
$\text{SnH}_2\text{Cl}_2$	2936.50	345.15	-1137.87	1758.06	221.78	-380.14	20.12	965.33	-138.23	2956.62	3747.75	3845.90
$\text{SnH}_2\text{Br}_2$	2921.90	345.17	-1138.74	1758.55	231.82	-411.89	115.09	964.98	-64.98	3036.99	3821.89	3932.40
$\text{SnH}_2\text{I}_2$	2939.86	345.17	-1140.45	1758.69	227.05	-394.81	269.29	963.63	101.53	3209.15	4004.81	4162.60
$\text{SnHF}_3$	3304.71	345.09	-1137.69	1757.79	201.14	-317.50	8.98	965.18	-107.38	3313.69	4162.52	4180.73
$\text{SnHCl}_3$	2952.62	345.15	-1137.96	1758.06	222.55	-395.84	58.42	965.25	-114.83	3011.04	3803.00	3859.23
$\text{SnHBr}_3$	2869.18	345.19	-1139.34	1758.93	231.83	-429.36	291.26	964.77	93.73	3161.11	3907.36	4090.20
$\text{SnHI}_3$	2835.56	345.21	-1141.74	1759.53	239.07	-456.28	808.02	963.01	590.81	3643.58	4346.10	4657.34
$\text{SnF}_4$	3455.42	345.03	-1137.69	1757.41	189.34	-291.25	20.00	964.76	-81.92	3475.42	4337.66	4364.52
$\text{SnCl}_4$	2972.37	345.15	-1138.06	1757.93	220.63	-401.14	91.62	965.02	-88.89	3063.99	3848.51	3988.53
$\text{SnBr}_4$	2842.30	345.23	-1139.89	1759.50	234.63	-450.95	579.22	964.83	362.89	3421.52	4170.03	4480.72
$\text{SnI}_4$	2676.59	345.26	-1141.24	1760.75	249.24	-507.85	1715.75	964.77	1457.14	4392.34	5098.50	5512.86

<sup>a</sup> The core-dependent contribution is defined as  $\sigma_{\text{p}}^{\text{T}(1)} + \sigma_{\text{d}}^{\text{S}(1)} + \sigma_{\text{d}}^{\text{S}(0)}$

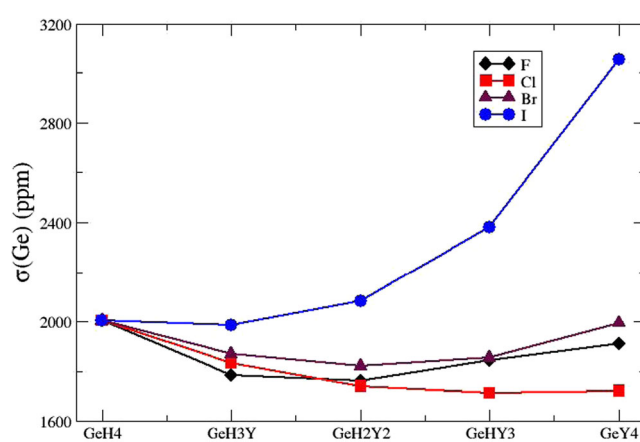
<sup>b</sup> The ligand-dependent contribution is defined as  $\sigma_{\text{p}}^{\text{S}(1)} + \sigma_{\text{p}}^{\text{T}(3)} + \sigma_{\text{p}}^{\text{S}(3)}$

the nonrelativistic shielding ( $\sigma^{\text{nr}}$ ). However, for molecular systems containing germanium as the central atom, this correction represents 25.5–34.3 % of the  $\sigma^{\text{nr}}$  value. Finally, when the central atom is heavier, such as tin, we see the largest corrections, 50.9–65.8 % of  $\sigma^{\text{nr}}$ . Based on these corrections,  $\sigma_{\text{p}}^{\text{T}(1)}$  is strongly core-dependent, and for heavy atoms such as Sn, it has the same order of magnitude as  $\sigma^{\text{nr}}$ , as shown in Table 5.

$\sigma_{\text{d}}^{\text{S}(1)}$  behaves similarly to that of  $\sigma_{\text{p}}^{\text{T}(1)}$ , albeit less strongly, and also shows the opposite sign. For molecular systems containing silicon as the central atom, the  $\sigma_{\text{d}}^{\text{S}(1)}$  correction represents 4.5–8.9 % of  $\sigma^{\text{nr}}$ , but for molecules containing germanium as the central atom, this percentage rises to 16.3–22.2 %. The largest corrections appear for molecular systems containing tin as the central atom: 32.9–42.6 % of  $\sigma^{\text{nr}}$ . The third core-dependent correction is  $\sigma_{\text{d}}^{\text{S}(0)}$ , although its

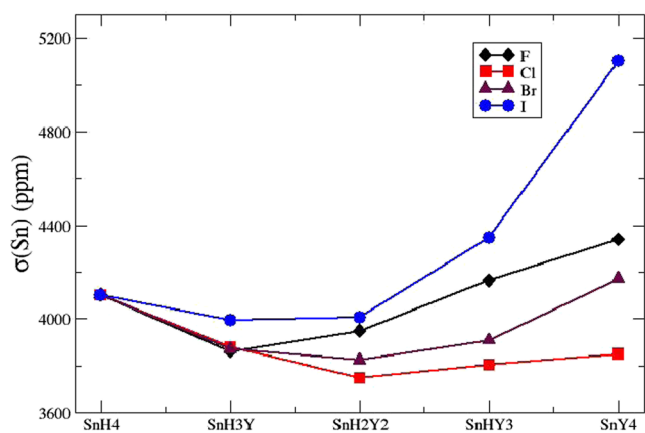


**Fig. 1**  $\sigma^{\text{LRESC}}$  for the Si atom in  $\text{SiH}_{4-n}\text{Y}_n$  ( $n=0-4$ ;  $\text{Y} = \text{F}, \text{Cl}, \text{Br}, \text{I}$ ) model compounds



**Fig. 2**  $\sigma^{\text{LRESC}}$  for the Ge atom in  $\text{GeH}_{4-n}\text{Y}_n$  ( $n=0-4$ ;  $\text{Y} = \text{F}, \text{Cl}, \text{Br}, \text{I}$ ) model compounds



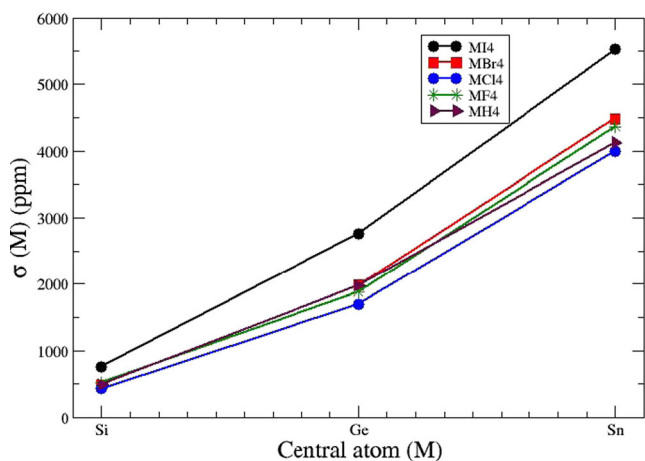


**Fig. 3**  $\sigma^{\text{LRESC}}$  for the Sn atom in  $\text{SnH}_{4-n}\text{Y}_n$  ( $n=0-4$ ;  $Y = \text{F, Cl, Br, I}$ ) model compounds

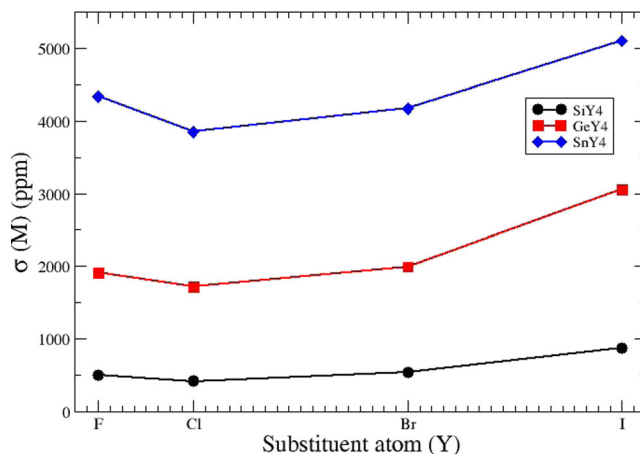
contribution is usually less important than the other two corrections. The variations with respect to the nonrelativistic shielding constant are: 1.2–1.9 % for silicon-containing molecules; 4.7–6.4 % for germanium-containing molecules, and 10.1–12.9 % for tin-containing molecules.

The total value that results from the addition of the three core-dependent relativistic corrections is small for molecules with light central atoms such as silicon and germanium. This value is quite large in molecules with tin as the central atom. This is because  $\sigma_p^{\text{T}(1)}$  and  $\sigma_d^{\text{S}(1)}$  have opposite signs and are of the same order of magnitude. Therefore, the total core-dependent contribution is not very important for systems with a light central atom, but the  $\sigma^{\text{core}}$  contribution is almost the same order of magnitude as  $\sigma^{\text{nr}}$  for molecules containing tin atoms.

The total contribution of the core-dependent corrections to the central atom in the different systems under study is 3.9–4.5 % of  $\sigma^{\text{nr}}(\text{Si})$ , 14.0–18.4 % for  $\sigma^{\text{nr}}(\text{Ge})$ , and 27.9–36.0 % for  $\sigma^{\text{nr}}(\text{Sn})$ . These different ranges arise due to different nonrelativistic shielding values. As an example, the total core-dependent



**Fig. 4**  $\sigma^{\text{LRESC}}$  for the central M atom in  $\text{MY}_4$  model compounds ( $M = \text{Si, Ge, Sn}$ ;  $Y = \text{F, Cl, Br, I}$ ) in terms of the central M



**Fig. 5**  $\sigma^{\text{LRESC}}$  for the central M atom in  $\text{MY}_4$  model compounds ( $M = \text{Si, Ge, Sn}$ ;  $Y = \text{F, Cl, Br, I}$ ) in terms of the substituent atom Y

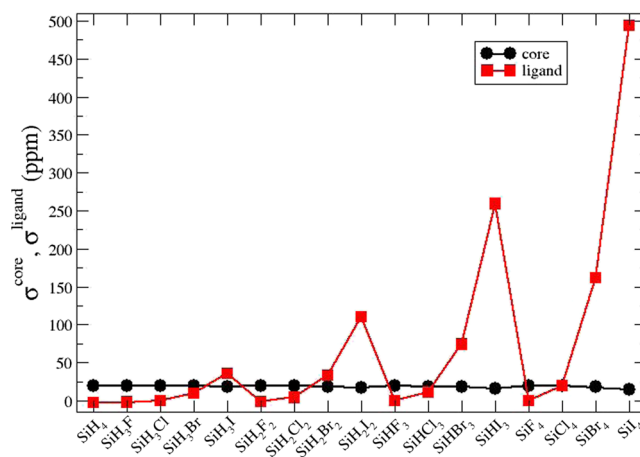
relativistic contribution to  $\sigma(\text{Sn})$  in  $\text{SnF}_4$  is 964.76 ppm, and that for  $\text{SnI}_4$  it is 964.77 ppm. However,  $\sigma^{\text{nr}}(\text{Sn})$  is 3455.42 ppm in the former case and 2676.59 ppm in the latter.

The dependence of the core-dependent terms on the central atom M is nicely seen in Figs. 6, 7, and 8. It is clear that these contributions increase as M changes from Si to Ge to Sn.

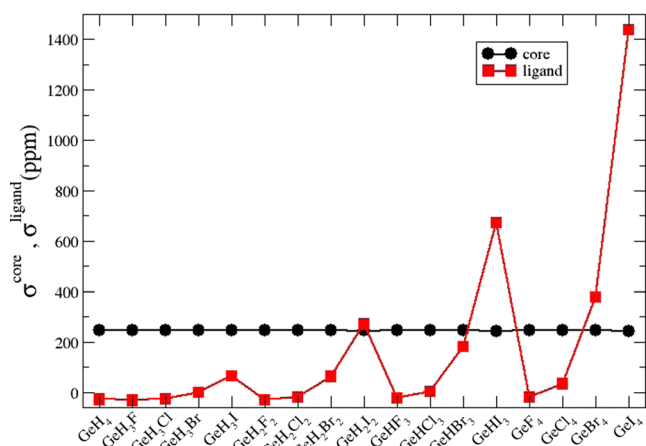
### Ligand-dependent terms

There are several corrections that change their values when the central atom is fixed and the molecular ligands are modified; these are termed “ligand-dependent” corrections (see Tables 3, 4, and 5), and they arise from the following  $\sigma^{\text{LRESC}}$  corrections:  $\sigma_p^{\text{S}(1)}$ ,  $\sigma_p^{\text{S}(3)}$ , and  $\sigma_p^{\text{T}(3)}$ .

The  $\sigma_p^{\text{S}(1)}$  term increases as the central atom becomes heavier, but it does not change very much when the ligands are modified, even in molecules with several heavy atoms. Large differences are observed upon going from  $\text{SnF}_4$  to  $\text{SnI}_4$  (60 ppm). For



**Fig. 6** Behavior of  $\sigma^{\text{core}}$  and  $\sigma^{\text{ligand}}$  for the central Si atom across the whole set of compounds

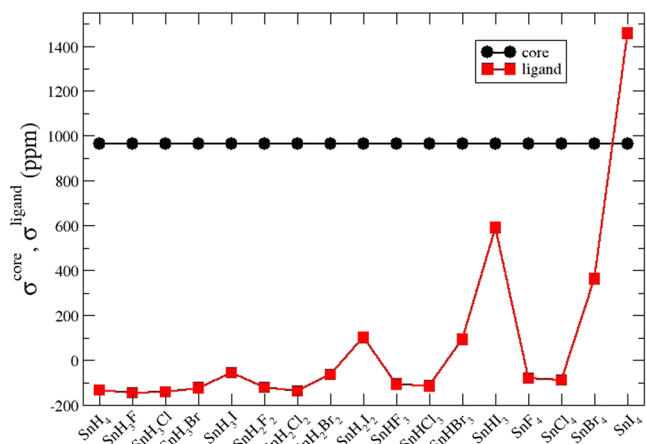


**Fig. 7** Behavior of  $\sigma^{\text{core}}$  and  $\sigma^{\text{ligand}}$  for the central Ge atom across the whole set of compounds

molecular systems containing a central silicon atom, the correction is such that it is 0.6–3.6 % of the  $\sigma^{\text{nr}}(\text{Si})$  value. When the central atom is germanium, the correction is 2.6–5.2 %; and when tin is the central atom it is 5.5–9.3 % of  $\sigma^{\text{nr}}(\text{Sn})$ .

On the other hand, the contributions of  $\sigma_p^{\text{S}(3)}$  are larger than those of  $\sigma_p^{\text{S}(1)}$ , but they have opposite signs. If we fix the central atom, we find that the percentages with respect to  $\sigma^{\text{nr}}$  are 0.9–10.1 % for Si, 3.7–11.4 % for Ge, and 8.4–19.0 % for Sn. Due to its negative sign, this correction decreases the contribution arising from  $\sigma_p^{\text{S}(1)}$ , leading to a total contribution that is less than 10 % (negative) for the heaviest molecular system and decreasing the total shielding. In some of the lighter molecular systems, both of these contributions cancel each other.

The most important of the three ligand-dependent relativistic corrections is  $\sigma_p^{\text{T}(3)}$ , which is responsible for the electronic origin of many relativistic effects. Such a correction includes the FC and SD contributions to  $\sigma_p^{\text{T}(3)}$ , as shown in the “Theory” section. This contribution from FC varies widely as the weight of the molecule increases; it can be of the same



**Fig. 8** Behavior of  $\sigma^{\text{core}}$  and  $\sigma^{\text{ligand}}$  for the central Sn atom across the whole set of compounds

order of magnitude as the nonrelativistic value. For  $\text{SnI}_4$  it represents 68 % of  $\sigma^{\text{nr}}(\text{Sn})$ . However, for the  $\text{SiI}_4$  molecule,  $\sigma_p^{\text{T}(3)}(\text{Si})$  is larger than that of  $\sigma^{\text{nr}}(\text{Si})$  and represents a correction that is 162 % of the nonrelativistic term.

The FC contributions are positive and very large for heavy systems. On the other hand, the SD contributions have the opposite sign and they are not as important as the former, except in molecular systems with light substituents. All of this is in line with previous findings obtained by Nakatsuji and coauthors for tin tetrahalides [32] and for lighter systems such as  $\text{CY}_{4-n}\text{Z}_n$  ( $Y = \text{H}, \text{Cl}, \text{Br}; Z = \text{Br}, \text{I}; n=0-4$ ) [24]. For tin tetrahalides, they got values that were 1,000 ppm smaller than ours. We should emphasize that they only included the SO relativistic corrections. The total ligand-dependent corrections are shown in Figs. 6, 7, and 8.

It is worth to analyzing the different behaviors of each  $\sigma^{\text{ligand}}$  term:  $\sigma_p^{\text{S}(1)}$ ,  $\sigma_p^{\text{S}(3)}$ , and  $\sigma_p^{\text{T}(3)}$ . For molecules such as  $\text{SiH}_3\text{I}$ , addition of the  $\sigma_p^{\text{S}(1)}$  and  $\sigma_p^{\text{S}(3)}$  terms gives  $-6.7$  ppm, which is close to 16 % of  $\sigma_p^{\text{T}(3)}$ . When the central atom is Sn and the molecule has the same substituents, the opposite relationship is observed: the absolute value of  $\sigma_p^{\text{T}(3)}$  is smaller than the combination of  $\sigma_p^{\text{S}(1)}$  and  $\sigma_p^{\text{S}(3)}$ . This latter relationship is again reversed for systems with two or more than two iodines. The contribution due to SO effects rises much more rapidly than the other two ligand-dependent terms. Due to the large variation of  $\sigma_p^{\text{T}(3)}$  in this kind of compound, it makes no sense to take percentage changes into account. For light systems such as  $\text{MH}_4$  ( $M = \text{Si}, \text{Ge}, \text{and Sn}$ ),  $\sigma_p^{\text{T}(3)}$  is negative because the contributing SD terms are larger (in absolute value) than the FC ones.

For systems such as  $\text{MH}_3\text{F}$ , both values are almost the same, meaning that they essentially cancel each other, leading to total values of almost zero. As the weight of the molecule increases, the FC correcting term (associated with the SO mechanism) increases considerably, whereas the SD term decreases in importance.

This correction may be quite large for molecular systems that contain four iodine atoms. As was mentioned above, for  $\text{SiI}_4$ ,  $\sigma_p^{\text{T}(3)}(\text{Si})$  is larger than  $\sigma^{\text{nr}}(\text{Si})$ ; the nonrelativistic value is 318.44 ppm and its relativistic SO correction is 514.56 ppm (i.e., 161.6 % the size of the nonrelativistic value). For  $\text{GeI}_4$ ,  $\sigma^{\text{nr}}(\text{Ge})=1319.63$  ppm, and its SO correction is 1518.13 ppm (i.e., 115.0 %). Finally for  $\text{SnI}_4$ ,  $\sigma^{\text{nr}}(\text{Sn})=2676.59$  ppm and  $\sigma_p^{\text{T}(3)}(\text{Sn})=1715.75$  ppm (i.e., 64.1 %). This percentage is smaller than the others seen for Si and Ge, even though it is the largest absolute value.

We can therefore state that the contributions cancel each other out to some degree due to the different electronic mechanisms of the core- and ligand-dependent contributions. Only

the  $\sigma_p^{T(3)}$  correction shows very different behaviour. Adding the core-dependent corrections to two of the three ligand-dependent corrections (not including  $\sigma_p^{T(3)}$ ) yields very small values for light systems. The largest absolute value (26.4 %) is seen for the heaviest molecular system studied here,  $\text{SnI}_4$ .

Based on this analysis, we can understand why the leading term  $\sigma_p^{T(3)}$  is considered the main electronic mechanism responsible for ligand relativistic effects. However, we should highlight that this is only true for molecules containing light or not very heavy atoms; for molecules containing heavy atoms,  $\sigma_p^{T(3)}$  does not reproduce the total relativistic effect for the nuclear magnetic shielding. The other relativistic corrections increase their contributions, especially those that are core-dependent, as shown in Tables 4 and 5 (eleventh and last columns). For most heavy systems, the contribution from  $\sigma^{\text{nr}}(\text{Sn}) + \sigma_p^{T(3)}(\text{Sn})$  does not provide a sufficiently good reproduction of the four-component relativistic value—the differences are close to 25 %. For such systems, the other contributions become important.

Ligand heavy-atom effects on the central light or heavy atom

In this section, we first introduce some considerations about heavy-atom effects on the central atom, and then we discuss the results for relativistic effects for the set of molecules analyzed in this work.

We are interested in understanding the heavy-atom effects on the central atom when it is not light. If the central atom is not heavy, there are HALA effects. So we then wondered how large the HALA effects would be when there are two vicinal heavy atoms. We are not aware of any research that has been done that can answer this query. It may be that HAVHA effects arise from electronic (HALA-type) mechanisms, become vanishingly small when the central atoms are not heavy, and become increasingly important as the central atoms become heavier. The SO effects depend on the substituent and, for heavy substituents, they are always important independent of whether the central atom is light or heavy.

Among the whole set of molecular systems we studied, relativistic effects were mostly found to be of HALA type in the subset of Si-containing molecular systems. In Table 3 it is clear that  $\sigma_p^{T(3)}$  is the most important relativistic correction. Its contribution is in very good agreement with those found in previous studies [8].

When molecules with several heavy atoms, such as  $\text{SiBr}_4$ ,  $\text{SiHI}_3$ , or  $\text{SiI}_4$ , are considered, the relativistic corrections are such that the  $\sigma^{\text{LRESC}}$  results are little overestimated when compared with four-component calculations.

In addition, for  $\text{SiH}_2\text{I}_2$ ,  $\sigma_p^{T(3)} = 122.09$  ppm; when this value is added to  $\sigma^{\text{nr}}$ , the result is quite close to the total LRESC value (the difference is less than 1 %). Furthermore, for  $\text{SiI}_4$ ,  $\sigma_p^{T(3)} = 514.56$  ppm; when this value is added to  $\sigma^{\text{nr}}$ , the result

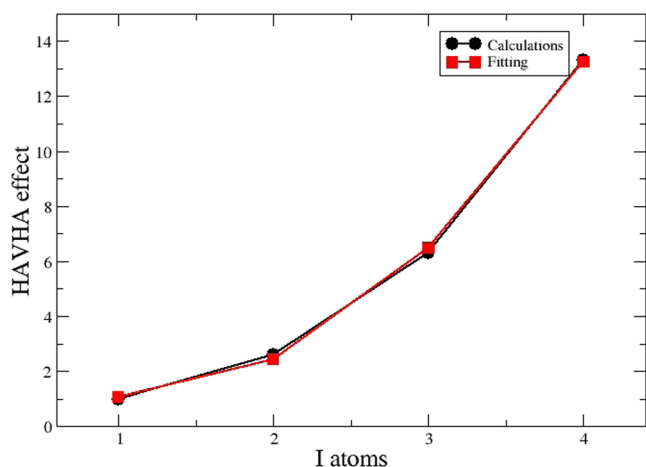
is again very close to the LRESC value (less than 1 % difference), whereas the difference between the LRESC value and the four-component value is  $\approx 9$  %. Therefore, when the contribution of  $\sigma_p^{T(3)}$  becomes a substantial fraction of the nonrelativistic shielding value, adding the  $\sigma_p^{T(3)}$  (SO) term to the  $\sigma^{\text{nr}}$  contribution gives a value that is within 1 % (with the exception of  $\text{SiBr}_4$ , where the difference is 1.8 %) of the total LRESC value.

On the other hand, as was previously shown, the HAVA effect is mainly due to the core-dependent corrections, as they are related to the weight of the central atom. Still, it is well known that all of the relativistic corrections increase as the central atom becomes heavier.

What kind of functional dependence on the atomic number of the whole set of substituents does this effect have? Can it be considered a HALA + other ligand-dependent effect, or is it only a HALA-type effect? The recently proposed heavy-atom effect, the HAVHA effect [8, 14], seems to appear in systems containing more than one heavy atom. It should appear when light vicinal atoms are substituted by heavy analogs. As shown in previous sections, the nuclear magnetic shielding of one central heavy atom is modified in a tetrahalide molecule due to an effect of the vicinal heavy atoms.

Let us start by noting that relativistic effects on  $\sigma(\text{Sn})$  atoms may be analyzed by utilizing the usual definition for percentage contributions:  $(\sigma^{\text{R}} - \sigma^{\text{nr}}) / \sigma^{\text{nr}}$ , where R means relativistic. In our case, given that nonrelativistic contributions are both core- and ligand-dependent, we shall consider the nonrelativistic contribution due to the unsubstituted molecular system in this case. For  $\text{SnH}_4$ , relativistic effects amount to 25.4 % of the total  $\sigma(\text{Sn})$  (this is a pure HALA-type effect), while the corresponding contribution for  $\text{SnH}_3\text{I}$  is a little larger, 29.5 % (this is a HALA + HAVHA effect). This means that the HAVHA effect should be close to 4 % for such molecule. If we perform the analysis in this way, we can find that, for most of our selected heavy-atom-containing molecules, the HAVHA effect increases in strength with the weight of the substituent. The strongest HAVHA effects were obtained for the heavier molecular systems, such as  $\text{SnBr}_4$  (21.3 %),  $\text{SnHI}_3$  (27.9 %), and  $\text{SnI}_4$  (65.1 %). It is important to emphasize that, in this analysis, the HAVHA effect was taken to be the total relativistic effect that appears after replacing vicinal light atoms with heavy atoms. In a way, the HAVHA effect would likely include a different HALA effect when the central atom is not the same.

An interesting feature of this effect is that when the number of (the same kind of) heavy-halogen substituent atoms increases, an enhancement occurs as a nonlinear function of the number of substituents. This can be seen by analyzing molecular systems containing iodine atoms. For  $\text{SnH}_3\text{I}$ , the



**Fig. 9** HAVHA effect on  $\sigma(\text{Sn})$  as a function of the number of iodine atoms in  $\text{SnH}_{4-n}\text{I}_n$  ( $n=1-4$ )

HAVHA effect is 4.1 %; for  $\text{SnH}_2\text{I}_2$ , it is 10.8 %; for  $\text{SnHI}_3$ , it is 27.9 %; and for  $\text{SnI}_4$  it is 65.1 %. This set of values indicates that  $\sigma(\text{Sn})$  is a quadratic function of the number of iodine atoms (see Fig. 9). Thus, the functional dependence of the HAVHA effect is quadratic:  $1.58n^2 - 3.11n + 2.83$ , where  $n$  is the number of iodine atoms.

How much of the HAVHA effect calculated in the manner described above is due to ligand-dependent mechanisms? Or, in other words, are the core-dependent mechanisms also modified by the presence of vicinal heavy atoms? What about the well-known SO HALA-type effect? Its electronic mechanism may or may not be modified due to its action on a heavy rather than a light nucleus.

In line with previous reasoning, Table 6 shows the magnitudes of the contributions of the SO and both non-SO mechanisms combined ( $\sigma_p^{S(1)}$  and  $\sigma_p^{S(3)}$ ) as a percentage with respect to the nonrelativistic contribution to  $\sigma(\text{M})$  for  $\text{MH}_{4-n}\text{I}_n$  ( $\text{M} = \text{Si}, \text{Ge}, \text{and Sn}$ ; and  $n=1-4$ ) molecular systems. Some new features are now apparent. First, the main HALA effect becomes less important as we increase the weight of the central atom from  $\text{M} = \text{Si}$  to  $\text{M} = \text{Sn}$ . Second, the other non-SO

mechanisms increase in influence as we increase the weight of the central atom.

The HAVHA effect is obviously more closely related to the ligand-dependent corrections than the core-dependent ones. Furthermore, as mentioned above, the  $\sigma_p^{T(3)}$  contribution varies and is the most important relativistic correction obtained with the LRESC method. For  $\text{SnI}_4$ , the combined contribution of  $\sigma_p^{S(1)} + \sigma_p^{S(3)}$  is close to 15 % of  $\sigma_p^{T(3)}$ . The HAVHA effect for Sn at  $\text{SnI}_4$ , is obtained as the difference between relativistic corrections on  $\text{SnI}_4 - \text{SnH}_4$  (corresponding to 90.5–25.4 %). In this way, the total HAVHA effect is 65.1 %; composed as 54.4 % of ligand corrections and 10.7 % of core ones. There is also a non-core-dependent nonrelativistic contribution that appears when hydrogen atoms are replaced by heavy halogens.

The data in Tables 3, 4, and 5 show that the nonrelativistic contributions to  $\sigma(\text{M})$ ; ( $\text{M} = \text{Si}, \text{Ge}, \text{and Sn}$ ) vary with the substituent. On the other hand, the relativistic core-dependent contributions are almost the same for each family of compounds. Therefore, we can assume that the core-dependent nonrelativistic contribution to the shielding of central atoms is not modified by the ligands. We are able to analyze the relationship between the relativistic and nonrelativistic ligand dependent contributions; in other words, how the HALA-type effect becomes a HAVHA-type effect.

In Table 6, we show the non-core (ligand) nonrelativistic contribution to  $\sigma(\text{M})$ ; ( $\text{M} = \text{Si}, \text{Ge}, \text{and Sn}$ ), taken from Tables 3, 4, and 5:  $-155.5$  ppm ( $\text{SiI}_4$ ),  $-446.1$  ppm ( $\text{GeI}_4$ ), and  $-593.7$  ppm ( $\text{SnI}_4$ ) for M. Their spin-orbit contributions are 3.31, 3.40 and 2.89 times the corresponding non-core nonrelativistic contributions. Therefore, the HALA effect seems to be of the same order of magnitude, albeit a little smaller, for Sn. The other two ligand-dependent effects increase quite rapidly.

As shown in Table 6, the percentage increase in the SO effect rises as the number of heavy halogen substituents increases, albeit at different rates of increase

**Table 6** Nonrelativistic (in ppm) and relativistic (in percentage) ligand-dependent corrections to  $\sigma(\text{M})$  for  $\text{MH}_{4-n}\text{I}_n$  ( $\text{M} = \text{Si}, \text{Ge}, \text{and Sn}$ ;  $n=1-4$ )

$\text{MH}_{4-n}\text{I}_n$	$\text{M} = \text{Si}$			$\text{M} = \text{Ge}$			$\text{M} = \text{Sn}$		
	(nr, nc) <sup>a</sup> (ppm)	%SO <sup>b</sup> (%)	Non-SO <sup>c</sup> (%)	(nr, nc) (ppm)	%SO (%)	Non-SO (%)	(nr, nc) (ppm)	%SO (%)	Non-SO (%)
1	-36.6	-115.1	18.3	-110.2	-90.1	30.6	-186.9	-39.9	69.6
2	-74.9	-163.0	15.5	-205.8	-155.7	24.0	-330.4	-81.5	50.8
3	-118.4	-232.5	13.7	-336.8	-219.1	19.4	-434.7	-185.9	50.0
4	-155.5	-331.0	13.2	-446.1	-340.3	18.3	-593.7	-289.0	43.6

<sup>a</sup> Nonrelativistic non-core contributions:  $\sigma^{(\text{nr,nc})} = \sigma^{\text{nr}}(\text{M}; \text{MH}_{4-n}\text{I}_n) - \sigma^{\text{nr}}(\text{M}; \text{MH}_4)$ , in ppm

<sup>b</sup> Relativistic ligand spin-orbit contribution:  $\sigma^{(\% \text{SO})} = \frac{\sigma^{\text{SO}}}{\sigma^{(\text{nr,nc})}} \times 100$

<sup>c</sup> Relativistic ligand non-SO contribution:  $\sigma^{(\% \text{SO})} = \frac{\sigma^{\text{ligand}-\sigma^{\text{SO}}}}{\sigma^{(\text{nr,nc})}} \times 100$



(higher for heavier central atoms), and the non-SO contributions decrease—quite slowly—as compared with their SO counterparts.

### Proton shielding

Table 7 shows the nuclear magnetic shielding of the protons in all of the molecular systems studied in this work. Note that the behavior of the shielding changes as the central atom becomes heavier.

In Si-containing molecules,  $\sigma(\text{H})$  increases as the weight of each heavy halogen substituent increases. For  $\text{SiH}_3\text{Y}$ , molecules there is a small rise upon shifting from F to Br (26.76 and 28.02 ppm, respectively), and then a larger rise upon shifting to I, 32.02 ppm. Similar patterns are observed for  $\text{SiH}_2\text{Y}_2$  and  $\text{SiHY}_3$ ; the largest difference in shielding occurs between  $\text{SiHF}_3$  (27.67 ppm) and  $\text{SiHI}_3$  (39.71 ppm)—a difference of 44 %.

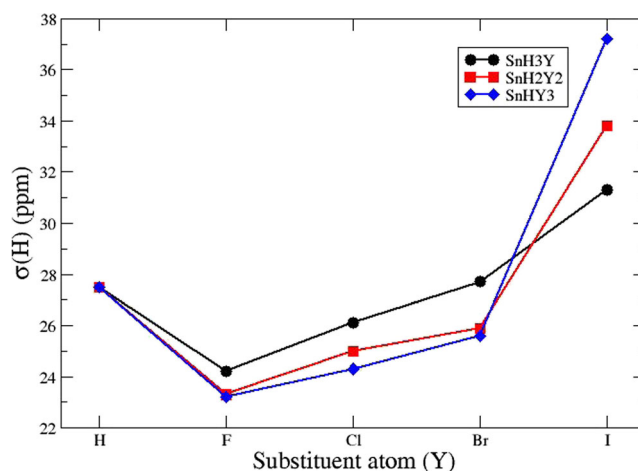
On the other hand, it is interesting to analyze  $\sigma(\text{H})$  when the number of heavy halogen substituents (of the same type) increases. As the number of fluorine, chlorine, or bromine atoms rises, there are very small changes in the shielding; this change is less than 1 ppm upon shifting from  $\text{SiH}_3\text{Y}$  to  $\text{SiHY}_3$ . As the number of iodine atoms increases, the shielding rises from 32.02 ppm (for  $\text{SiH}_3\text{I}$ ) to 39.71 ppm (for  $\text{SiHI}_3$ ), which corresponds to an increase of 24 %.

The behavior of  $\sigma(\text{H})$  for tin-containing molecules is, however, different. As the weight of the heavy halogen substituent increases,  $\sigma(\text{H})$  rises slightly more rapidly than it does for molecules containing silicon atoms. This trend is enhanced when the number of heavy halogen substituents (of the same type) increases. The largest difference in shielding is seen for  $\text{SnHF}_3$  ( $\sigma(\text{H})=23.15$  ppm) and  $\text{SnHI}_3$  ( $\sigma(\text{H})=37.24$  ppm), which represents an increase of 61 %. However, as the number of heavy halogen substituents increases,  $\sigma(\text{H})$  decreases by a

**Table 7** Proton shieldings (in ppm) at the relativistic level

M	Molecule	Y				
		H	F	Cl	Br	I
Si	$\text{SiH}_3\text{Y}$	27.96	26.76	27.61	28.02	32.02
	$\text{SiH}_2\text{Y}_2$	–	27.29	28.07	28.33	36.11
	$\text{SiHY}_3$	–	27.67	28.49	28.34	39.71
Ge	$\text{GeH}_3\text{Y}$	27.93	26.04	27.09	28.01	32.92
	$\text{GeH}_2\text{Y}_2$	–	25.75	27.08	27.74	36.09
	$\text{GeHY}_3$	–	25.83	27.16	27.86	41.19
Sn	$\text{SnH}_3\text{Y}$	27.48	24.22	26.07	27.66	31.33
	$\text{SnH}_2\text{Y}_2$	–	23.29	25.00	25.89	33.81
	$\text{SnHY}_3$	–	23.15	24.33	25.59	37.24

All values are given in ppm



**Fig. 10** Proton nuclear magnetic shielding at the relativistic level. All values are in ppm

few ppm, except when the substituents are iodine atoms; for instance, the rise in shielding upon shifting from  $\text{SnH}_3\text{I}$  (32.33 ppm) to  $\text{SnHI}_3$  (37.24 ppm) is close to 19 %; see also Fig. 10.

For molecular systems containing germanium as the central atom, the trend in  $\sigma(\text{H})$  lies between those of the silicon and tin cases. When the substituents are iodine atoms, there is a variation of 25 % in the shielding upon shifting from  $\text{GeH}_3\text{I}$  to  $\text{GeHI}_3$ .

### Conclusions

The increasing use of semirelativistic methods such as LRESC provides the opportunity to calculate and analyze the electronic mechanisms that underlie the relativistic effects that contribute to the magnetic properties of molecules with several heavy atoms (i.e., atoms belonging to the fifth or sixth row in the periodic table).

In this paper, we have presented an analysis of the contributions of LRESC relativistic effects to the shieldings of  $\text{MH}_4 - \text{Y}_n$  molecular systems ( $M = \text{Si, Ge, Sn}$ ;  $Y = \text{F, Cl, Br, I}$ , and  $n = 1-4$ ). We first compared the total central atom magnetic shielding calculated with the LRESC model with benchmark results from the relativistic polarization propagator formalism at RPA level, RelPPA-RPA, as well as with some other calculations taken from the literature. We found that the LRESC formalism provides excellent performance. The resulting values are close to those obtained using the four-component approach, even for molecular systems containing five heavy atoms (where “heavy” implies that the atom belongs to the fifth row of the periodic table). The largest difference between the LRESC and four-component values was 414 ppm (7.5 %), which was obtained for  $\text{SnI}_4$ .



We divided the relativistic corrections into two groups: core-dependent and ligand-dependent corrections. The electronic mechanisms that are associated with the core-dependent corrections are  $\sigma_p^{T(1)}$ ,  $\sigma_d^{S(1)}$ , and  $\sigma_d^{S(0)}$ . The first is the most important. For the heaviest system analyzed here,  $\text{SnI}_4$ , it represents 66 % of  $\sigma^{\text{nr}}(\text{Sn})$ . However, adding together all core-dependent corrections does not result in a large value compared to the total shielding because these corrections have opposite signs. Indeed, they almost cancel each other for the lightest system, yielding only 4 %.

The ligand-dependent corrections were found to be due to the  $\sigma_p^{S(1)}$ ,  $\sigma_p^{S(3)}$ , and  $\sigma_p^{T(3)}$  mechanisms. The two singlet-type corrections have opposite signs and equivalent absolute values. The total relativistic contribution is therefore very small for systems with light substituents; at its highest, it is less than -10 % of  $\sigma^{\text{nr}}$ . The  $\sigma_p^{T(3)}$  (or spin-orbit) correction is the most important one; it can be larger than  $\sigma^{\text{nr}}$  for systems with heavy substituents.

In this work, we have shown that ligand-dependent relativistic corrections are the main relativistic corrections for  $\text{MI}_4$  ( $\text{M} = \text{Si}, \text{Ge}, \text{and Sn}$ ) molecular systems, with SO being the main term in  $\sigma^{\text{ligand}}$ . However, the other corrections (core-dependent and ligand-dependent) reach 26.4 % of  $\sigma^{\text{nr}}$  for the heaviest system. This means that they must be included to achieve a reliable reproduction of the total relativistic shielding in molecules with a few heavy halogen substituents and heavy central atoms.

In line with our discussion above, the recently proposed HAVHA effect is mainly dependent on the term  $\sigma_p^{T(3)}$ . The largest contribution of  $\sigma_p^{S(1)}$  plus  $\sigma_p^{S(3)}$  is only 15 % of the contribution of  $\sigma_p^{T(3)}$ . The electronic mechanisms that underlie these two terms are thus important in the HAVHA effect. We showed that the HAVHA effect is due to all three ligand-dependent relativistic effects. The percentages of SO effect for molecular systems containing silicon and germanium as the central atom are close each other, when the number of heavy halogen substituents is the same. But for molecular systems containing tin as the central atom, the percentage of SO effect goes down. This finding is based on the analysis of relativistic versus nonrelativistic ligand-dependent effects.

When the HAVHA effect was quantified as the difference between the total relativistic and the total nonrelativistic effects, it was found to rise from 4.1 % for  $\text{SnH}_3\text{I}$  to 15.4 % for  $\text{SnH}_2\text{I}_2$  to 27.9 % for  $\text{SnHI}_3$  to 65.1 % for  $\text{SnI}_4$ . These values show a quadratic dependence of  $\sigma(\text{Sn})$  on the number of iodine atoms.

The behavior of  $\sigma(\text{H})$  depends on whether the central atom of the molecule is light (Si) or heavy (Sn). For a central silicon atom, as the number of heavy halogen substituents (of the same type) increases,  $\sigma(\text{H})$  increases a little from  $\text{SiH}_3\text{X}$  to  $\text{SiHX}_3$  ( $\text{X} = \text{F}, \text{Cl}, \text{Br}$ ). On the other hand, the opposite behavior is observed when the central atom is Sn: as the number of heavy halogen substituents (of the same type)

increases,  $\sigma(\text{H})$  decreases by a few ppm. Only when the substituents are iodine atoms does  $\sigma(\text{H})$  increase (regardless of whether the central atom is Si or Sn).

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