

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

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NMR nuclear magnetic shieldings of Si, Ge and Sn in $MH_{4-n}Y_n$ molecular systems (M = Si, Ge, Sn; Y = F, Cl, Br, I and $n = 1, \dots, 4$) are highly influenced by the substitution of one or more hydrogen by halogen heavy atoms. We applied the linear response elimination of small components (LRESC) formalism to calculate those shieldings and learn whether including only few leading relativistic correcting terms is enough for getting quantitative reproduction of the full relativistic value. It was observed that the nuclear magnetic shieldings change when the number and weight of the substituent heavy-halogen atoms varies, and in general the pattern of $\sigma(M)$ does not exhibit the normal halogen dependence (NHD) behaviour that can be found in similar molecular systems containing carbon atom. We analysed also each relativistic correction given by the LRESC method and splitted them in two: core-dependent and ligands-dependent, looking for the electronic mechanisms involved in the different relativistic effects and in the total relativistic value. From this analysis we were able to study in more detail the electronic mechanism involved in a new relativistic effect recently proposed, and named “heavy atom effect on vicinal heavy atom” (HAVHA). We found that the main electronic mechanism is the Spin-orbit or $\sigma_p^{T(3)}$ correction, although other corrections like $\sigma_p^{S(1)}$ and $\sigma_p^{S(3)}$ are also important. Finally we analysed proton magnetic shieldings and found that for molecules containing Sn as central atom, $\sigma(H)$ decreases when the number of the same heavy-halogen substituent atom increases from F, to Cl and Br though with different rate of increase. Only for iodine atoms $\sigma(H)$ increases when the number of atoms grows up.

Keywords: LRESC, Relativistic effects, Polarization propagators, NMR

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I. INTRODUCTION

The theoretical analysis of NMR magnetic shieldings of heavy-atom containing molecules should include relativistic effects, which are widely proved to affect the magnetic behavior of both, the heavy and the light atoms. These effects do appear due to the presence of heavy atoms, HA. Two type of HA dependent effects were postulated in the late eighties by 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 HALA (heavy atom effect on light atom).^{2,3} Almost at the same time they introduced another HA effect. The differences in the relativistic and non relativistic contributions from Pb 6s orbitals to the Pb chemical shift in a PbH_3^- model compounds, was interpreted due to the HAVA effect (heavy atom effect on heavy atom)¹. It arises as a modification of the shielding of heavy atoms due to themselves.

These two effects are well established and were studied in a number of different molecular systems since their discovery.^{4–13} It was not until the past few recent years that the third HA effect was proposed by us. The development of new studied was needed to have enough evidence to start thinking on such kind of effects. Twenty five years elapsed among those two previous HA effects and the one we are treating here in some detail, coined as HAVHA (heavy atom effect on vicinal heavy atoms). Even though some authors have studied the NMR spectroscopic parameters in heavy-atom containing molecules, the HAVHA effect was never included in their analysis. In fact this last HAVHA effect was just proposed few years ago.^{8,14} One of the main reasons for this may be rooted in the appearance of more versatile and accurate two component methods, like the linear response elimination of small component, LRESC^{4,15} and the Breit-Pauli Perturbation Theory, BPPT^{16,17}, which allows the analysis of magnetic properties in three or more than three heavy-atom containing molecules. We should be aware that one can analyse the HA-type effects only with two-component methods because even though they are included in results performed with four-component methods they are included in the total relativistic effects.

Perhaps the first time where the spin-orbit contribution to the chemical shift of a lead atom was attributed to the atomic number of atoms directly coordinated to the metal, was published by Ziegler and coauthors in 1999.¹⁸ They found that for heavier atoms, the larger absolute value of the SO contribution to the chemical shift. Such SO contribution was not properly assigned to a new HA effect. Ten years later Autschbach and Zheng, in a review article,⁹ considered such

isolated findings as due to HAOHA (heavy atom effect on other heavy atom) + HAHA.

So, we know now that, when the molecules are composed of two or more than two heavy atoms, the whole set of heavy atoms can influence, by 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 with the atomic number of the (halogen) substituents and it is mostly due to paramagnetic-like contributions.

Following our previous studies we were then interested in giving new answers to some still open questions, like: Which are the main electronic mechanisms involved in the HAVHA effects? Do the HAHA-type effects be modified by the HAVHA effects? Or, in other words, does the presence of heavy atoms in the close vicinity of the studied atom modify its shielding? In line with this, what about the HALA-type effects? Is the mechanism of HAVHA similar to HALA? Is the SO correction of a central heavy atom modified by the presence of another heavy atoms in its vicinity? Some of the aims of this article are the discussion of all these enquires.

In order to analyse the relativistic effects on NMR shieldings we applied the LRESC formalism.^{4,15} Which starts from fully relativistic (four component) expressions making use of the Rayleigh-Schrödinger perturbation theory, and applying some given prescriptions in the elimination of the small component scheme, 4-component terms are reduced to 2-component ones.

Calculations performed with codes that implemented such two-component scheme and the other equivalent two-component method named Breit-Pauli Perturbation Theory, BPPT^{16,17}, and others just published by some of the present authors²⁰ have shown that the LRESC methodology gives results which are close to those of 4-component calculations at least for atoms as heavy as that belonging to the fifth row of the periodic table^{4,21}.

The family of molecular systems we have studied is $MH_{4-n}Y_n$ ($n = 0, \dots, 4$; $M = \text{Si, Ge, Sn}$ and $Y = \text{H, F, Cl, Br, I}$). For those systems it may appear what is known as normal halogen dependence, NHD. It is such that the Spin-orbit, SO, effects increases the shielding when both the atomic number of the halogen substituent bonded to the NMR active atom, and the number of (heavy-atom) substituents also increases. In this way the chemical shift of the active atom, $\delta(M) = \sigma^{ref} - \sigma(M)$, decreases when the substituent goes from Cl to Br and to I.^{5,22,23} In line with this fact the ^{13}C chemical shifts of halogen-substituted methanes $\text{CH}_{4-n}Y_n$ ($Y = \text{Br, I}$) exhibit “non-linear NHD” with increasing n , whereas the corresponding mixed complexes $\text{CH}_{4-n}Y_n$ (*e. g.* $Y = \text{Br, } Y = \text{I}$) show essentially a linear decrease.^{13,24} Another aim of this research is to discuss

this enquires.

The structure of the article is as follows. Firstly we give, in section II, a schematic overview of the applied methods. Then we start presenting results of shielding calculations on the central atom. First showing in section IV A the performance of the LRESC method as compared with more accurate 4-components and the analysis of whether we should find normal or inverse halogen dependence for heavy central atoms. Then in section IV B we show an analysis that splits the leading relativistic corrections in two: core-dependent and ligands-dependent. It shall give us the basement for studying the HAVHA effect in a more realistic way. The hydrogen shielding dependence with halogen substituents will also be analysed. Finally concluding remarks are given in section V.

II. THEORY

The nuclear magnetic shielding constant might 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. Then the nuclear magnetic shielding tensor of the nucleus M ($\sigma_{ij}(M)$) is 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.

$$\sigma_{ij}(M) = \frac{\partial^2 E}{\partial \mu_i^M \partial B_j} \quad (1)$$

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

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

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

A. Relativistic polarization propagator

Some second-order molecular property, *i.e.* those which are theoretically obtainable applying second-order perturbation theory to the electronic energy (and so depending on two “external”

fields), can be calculated using polarization propagators.²⁵ The equation which relates the correction to the energy with such propagators is formally the following

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

where H^P and H^Q are perturbative Hamiltonians describing the external perturbations to the system whose response (observable by the molecular properties that are modified by them) one is interested in to calculate, and analyse. Within the relativistic polarization propagator approach, RelPPA the explicit and short hand expression of the nuclear magnetic shielding is²⁵

$$\sigma_M = e^2 \left\langle \left\langle \frac{\alpha \times \mathbf{r}_M}{r_M^3}; \alpha \times \mathbf{r}_G \right\rangle \right\rangle \quad (4)$$

This last equation can be reexpressed in such a way that all virtual electronic excitations to be considered 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 level of approach is the random phase approximation (RPA) which is obtained when the reference state is chosen as the Dirac-Hartree-Fock state and the manifold of excitation operators considered is truncated up to the first set of elements, meaning the single-excitation operators.²⁵

B. Relativistic corrections to the shielding constants

The starting point to appropriately include all relativistic corrections to σ is to consider a molecular system under the action of both an uniform external magnetic field (\vec{B}) and the magnetic moments of all nuclei ($\vec{\mu}_M$) in a many-body relativistic regime¹⁵. In this way, all interactions are taken into account when the full relativistic Hamiltonian of the total system is transformed from four to two components. In doing so, one gets the unperturbed molecular Hamiltonian and a perturbation containing both magnetic interactions. For the LRESC scheme one takes into account the transformation named elimination of the small component for all matrix elements involved in a response function; and also the contributions that come 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 Refs.^{4,15}).

The full list of relativistic corrections arising within the LRESC model, to paramagnetic and diamagnetic terms (σ_p , σ_d), that comes from one body operators, are presented in Table I. Detailed descriptions about this separation and the origin of all that LRESC corrections is straightforwardly discussed in Ref.¹³.

The corrections can be clustered as both, first and third order in response theory, and also depending on their spin character being singlet or triplet. From now on we shall express the LRESC corrections in line with such a criteria, which is explained in Table I. All physical insights that arise from the application of such criteria are presented and discussed in Section IV.

TABLE I. Classification of LRESC corrections to the NMR shielding constant

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

We now present a brief account of LRESC corrections. The commonest corrections to the shielding constant, are those terms obtainable from : 1) a perturbed series of the one-body Dirac Hamiltonian, when taking its nonrelativistic limit up to the first order in α ; and 2) operators which contain the nuclear magnetic vector potential (including “Fermi-type” terms):

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

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

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

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

Corrections to the Dirac Hamiltonian are of singlet-type, *i.e* Mass velocity (H^{MV}) and Darwin

(H^{DW}) operators, and 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 those terms coming from the external magnetic field-dependent operators yielding relativistic corrections and those arising from both, the inclusion of effects due to the small components and due to the “normalization” of large components. We split them according to their spin character, *i.e.* 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

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

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

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

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

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

III. COMPUTATIONAL DETAILS

A. Geometry Optimizations

The complete set of molecular systems under study in this work are : $MH_{4-n}Y_n$ ($n = 0, \dots, 4$; $M = \text{Si, Ge, Sn}$ and $Y = \text{H, F, Cl, Br, I}$). Most of them were optimized at the 4 component level of approach with the module OPTIMIZE of the DIRAC code²⁶. For the rest of the systems experimental geometrical structures were used and taken from Ref.²⁷ In Table II we show some bond distances between central atoms and sustituent halogens, showing also which geometries were optimized. In all cases geometrical optimizations were performed considering Sadlej basis set²⁸.

TABLE II. Experimental/optimized geometries. d(M-Y) and d(M-H) bond distances

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

^a Experimental geometry taken from Ref.²⁷

^b Theoretically optimized geometry

To learn about whether the quality of the optimization procedure was good enough, we compare the optimized geometries for three of the molecular systems whose geometries were obtained by

experiments. They are: SiF_4 , SiCl_4 and SnCl_4 . Their theo/exp d(M-Y) bond lengths are, for SiF_4 , $r = 1.537/1.553 \text{ \AA}$; for SiCl_4 , $r = 2.018/2.019 \text{ \AA}$ and finally, for SnCl_4 , $r = 2.311/2.325 \text{ \AA}$. We observe that the differences are small enough to be confident on the use of theoretically optimized geometries.

B. Shielding calculations with the 4 component method

Benchmark calculations of shielding constants were performed with the RelPPA-RPA formalism. The basis set used in this work are the same as the ones used in previous works.^{14,29,30} We considered Sadlej’s basis sets in a first step²⁸, and then included some tight and diffuse Gaussian-type functions searching for converged results. The scheme for including such orbitals is as follows: tight basis functions were added to s, p, d, f blocks with the relationship $\alpha_{i+1}/\alpha_i = 3$ among exponents, starting from the largest exponent of each block.^{14,29,30} No diffuse basis functions were necessary for d and f blocks, because they do not change the shielding values significantly. The small components of the basis set were generated applying the unrestricted kinetic balance, UKB, prescription.⁸

C. Shieldings calculations with the LRESC model

LRESC shielding calculations were carried out with Dalton program³¹. In this work we present a new version of the basis set used for LRESC calculations in previous papers^{4,11,13–15}. This new basis set is smaller than the previous one though it holds the same quality for calculations within the LRESC scheme. In this case, we have taken out tight functions of s and p character; namely: 2 s -type tight functions for H and F, and 2 s -type and p -type tight functions for Si, Cl, Ge, Br, Sn and I. The basis set is presented in the supplementary material.

IV. RESULTS AND DISCUSSION

We first analyse the accuracy of total LRESC results in the whole set of molecules we considered in this work. Then the analysis of the electronic mechanisms that contribute to the leading relativistic effects we divided in two sets: core-dependent and ligands-dependent; which are composed of three different mechanisms each. Then we shall show how large are each one of the three

heavy-atom effects (HALA, HABA and HAVHA) on the central light/heavy atom. The latest analysis is dedicated to the hydrogen shieldings.

A. LRESC vs 4 component RelPPA-RPA calculations

In order to assess LRESC accuracy to describe which electronic mechanisms are responsible for the relativistic effects on many heavy atom containing molecules, we will firstly compare it with 4c calculations.

LRESC results of $\sigma(\text{Si})$, $\sigma(\text{Ge})$ and $\sigma(\text{Sn})$ are presented in Tables III, IV and V, respectively to asses it's accuracy with respect to 4-component shielding calculations. As already mentioned, the model compounds are $M\text{H}_{4-n}\text{Y}_n$ ($n = 0, \dots, 4$; $M = \text{Si, Ge, Sn}$; $Y = \text{H, F, Cl, Br, I}$).

The second column shows the nonrelativistic values of the nuclear magnetic shieldings in the whole set of molecules. From the third to the eighth columns the LRESC corrections are presented. The ninth and tenth columns represents LRESC corrections grouped as core- or ligands-dependent. Last three columns show the nonrelativistic values plus SO corrections, the total LRESC values and the 4component ones.

LRESC values are close enough to the 4-component ones, even for molecules with several substituents belonging to the fifth row of the Periodic Table. The largest absolute difference (LRESC – 4c) was found for $\sigma(\text{Sn})$ in SnI_4 molecule, which contains five heavy atoms, giving 415 ppm of difference ($\simeq 7.5\%$). On the other hand, the largest percentual difference was obtained in the SiI_4 system, which is of 8.9 %, being of 8.7 % when Si is replaced with Ge. Even though the difference between LRESC and 4-component values are higher than 8%, the absolute values of such differences are lower than 70 ppm and 250 ppm, respectively.

Much smaller differences (in absolute values) are obtained for $\sigma(\text{Si})$ in some lighter molecular systems shown in Table III. They can be lower than 2 ppm, as happens for SiF_4 .

It was shown in previous works that the largest differences among LRESC and 4-componet 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 until five atoms belonging to the same row of the Periodic Table, at least for this kind of molecular geometries.

From the analysis given above, we are confident on the fact that the addition of the whole set of

TABLE III. Nuclear magnetic shielding constant for central Si atom, at different levels of theory, for $\text{SiH}_{4-n}\text{Y}_n$ ($Y = \text{F, Cl, Br, I; } n = 0, \dots, 4$).

system	σ^{nr}	$\sigma_d^{S(0)}$	$\sigma_d^{S(1)}$	$\sigma_p^{T(1)}$	$\sigma_p^{S(1)}$	$\sigma_p^{S(3)}$	$\sigma_p^{T(3)}$	core ^a	ligand ^b	$\sigma^{nr} + \sigma_p^{T(3)}$	LRESC	4c
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
SiH_3F	414.27	5.95	-22.22	35.89	2.98	-5.29	0.24	19.62	-2.07	414.51	431.81	430.80
SiH_3Cl	422.95	5.95	-22.31	35.92	3.16	-5.62	2.46	19.56	-0.01	425.41	442.50	442.64
SiH_3Br	424.89	5.95	-22.83	35.98	3.91	-7.87	14.01	19.10	10.04	438.90	454.03	453.74
SiH_3I	437.27	5.95	-23.76	36.02	4.97	-11.67	42.11	18.21	35.41	479.38	490.90	494.69
SiH_2F_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
SiH_2Cl_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
SiH_2Br_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
SiH_2I_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
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
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
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
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
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
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
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
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

^a The core-dependent contribution, defined as $\sigma_p^{T(1)} + \sigma_d^{S(1)} + \sigma_d^{S(0)}$

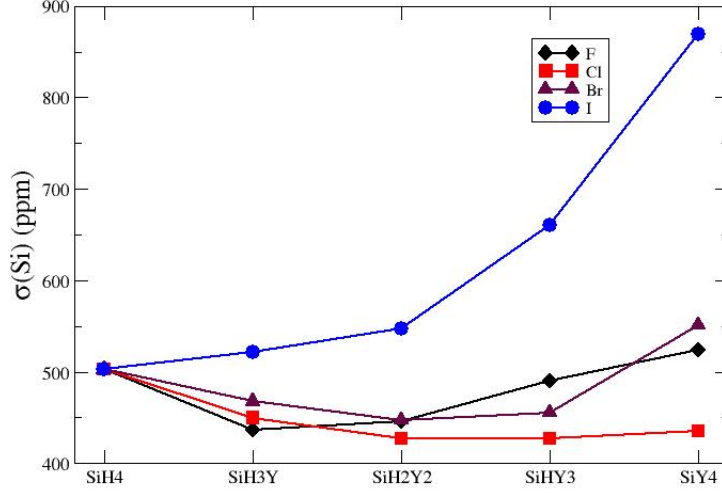
^b The ligand-dependent contribution, defined as $\sigma_p^{S(1)} + \sigma_p^{T(3)} + \sigma_p^{S(3)}$

relativistic corrections obtained within the LRESC scheme matches very close to the 4-component relativistic values of $\sigma(M)$, even for the heaviest systems which contains five heavy atoms. Then we are in a good position to start with the analysis of the electronic origin of the relativistic corrections.

The halogen dependence (normal or inverse) with n and the nature of the substituent Y is now (as compared with the equivalent carbon systems¹³) very much dependent on the central atom M . For $\text{SiH}_{4-n}\text{I}_n$ ($n = 1 \rightarrow 4$), $\text{GeH}_{4-n}\text{Y}_n$ ($n = 2 \rightarrow 4$; $Y = \text{Br, I}$) and $\text{SnH}_{4-n}\text{Y}_n$ ($n = 2 \rightarrow 4$; $Y = \text{F, Cl, Br, I}$) the shielding of the central atom follows an NHD dependence.

If one fixes the number n of substituents but modifies the type of halogen, Y , it is found that: i) for SiHY_3 and SiY_4 ($Y = \text{F} \rightarrow \text{I}$) $\sigma^{nr}(\text{Si})$ follows an IHD behavior though $\sigma^{LRESC}(\text{Si})$ follows an NHD behavior for $Y = \text{Cl} \rightarrow \text{I}$; ii) for GeY_4 ($Y = \text{F} \rightarrow \text{I}$) $\sigma^{nr}(\text{Ge})$ follows an IHD behavior though

FIG. 1. σ^{LRESC} for Si atom, at $SiH_{4-n}Y_n$ ($n = 0 - 4$; $Y = F, Cl, Br, I$) model compounds



$\sigma^{LRESC}(\text{Ge})$ follows an NHD behavior for $Y = \text{Cl} \rightarrow \text{I}$ and iii) for SnHY_3 and SnY_4 ($Y = \text{F} \rightarrow \text{I}$) $\sigma^{nr}(\text{Sn})$ follows an IHD behavior though $\sigma^{LRESC}(\text{Sn})$ follows an NHD behavior for $Y = \text{Cl} \rightarrow \text{I}$.

In Figs.1, 2 and 3 we show the dependence $\sigma^{LRESC}(M)$ in terms of the number n and the atomic number of the substituted halogen atoms, Y . When the number n of the same type of heavy-halogen atoms increases, the nuclear magnetic shielding grows up too, except for shieldings in $MH_{4-n}Cl_n$ ($M = \text{Si}, \text{Ge}$; $n = 1, 2, 3$) molecules for which $\sigma^{LRESC}(M)$ decreases.

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

Figs. 4 and 5 shows the pattern of the functional dependence of $\sigma(M)$ in MY_4 molecular systems as a function of M (Fig.4) and Y (Fig.5). It is interesting to highlight the fact that there is a clear distinction of the shieldings in the systems with $Y = \text{I}$ as compared with the other systems. In such cases relativistic effects do increase as the number of iodine atoms increase.

FIG. 2. σ^{LRESC} for Ge atom, at $GeH_{4-n}Y_n$ ($n = 0 - 4$; $Y = F, Cl, Br, I$) model compounds

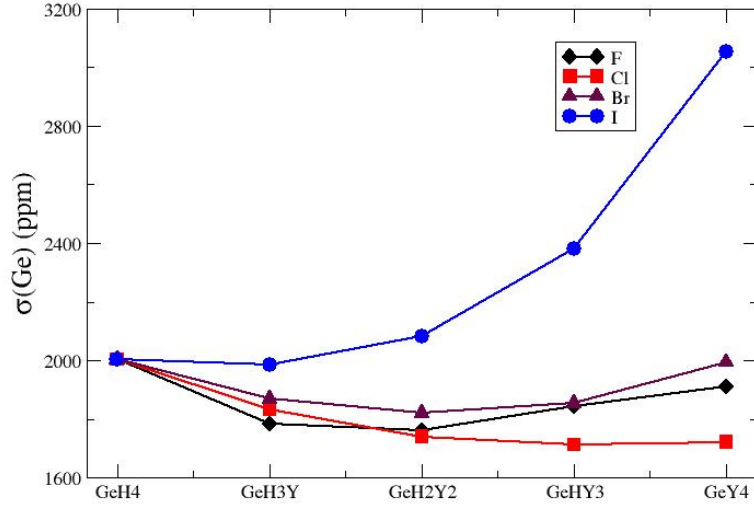


FIG. 3. σ^{LRESC} for Sn atom, at $SnH_{4-n}Y_n$ ($n = 0 - 4$; $Y = F, Cl, Br, I$) model compounds

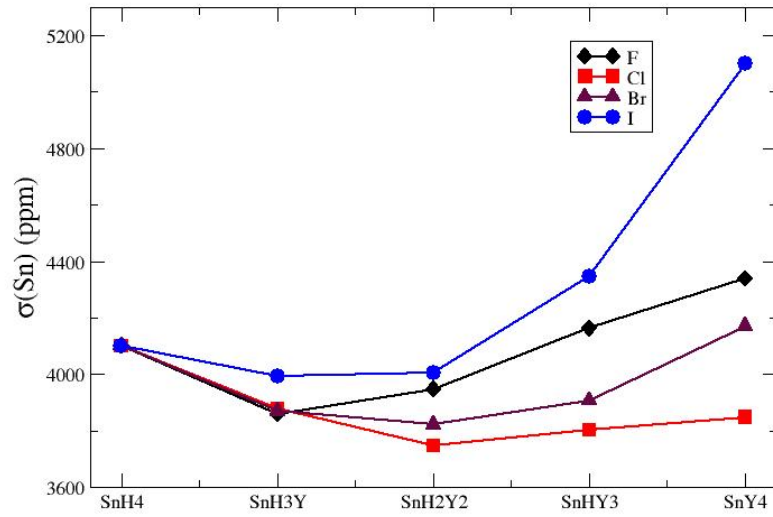
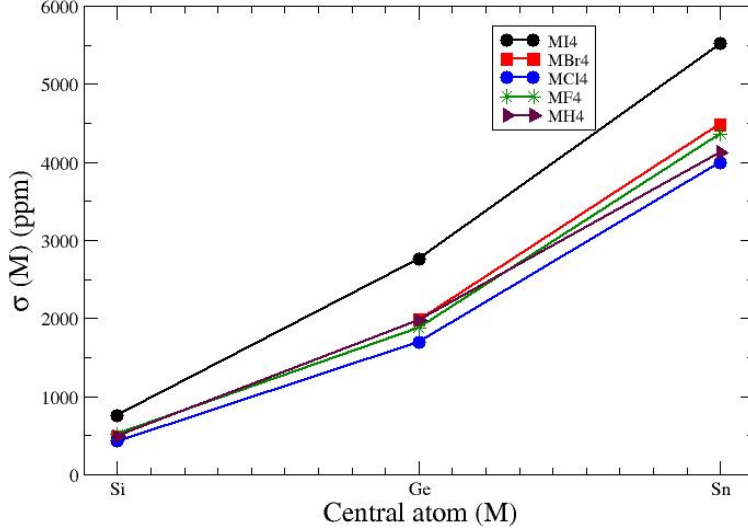


FIG. 4. σ^{LRESC} for central M atom, at MY_4 model compounds ($M = \text{Si, Ge, Sn}$; $Y = \text{F, Cl, Br, I}$) in terms of M central atom



B. Leading LRESC relativistic corrections

There are several leading relativistic corrections that arise within LRESC method. We shall divide them in terms of core- and ligands-dependent. Meaning, those corrections that have almost the same value when the number or type of halogen-substituent varies, grouped as core-dependent. On the other hand we call ligand-dependent to those corrections which have a strong dependence with the substituents.

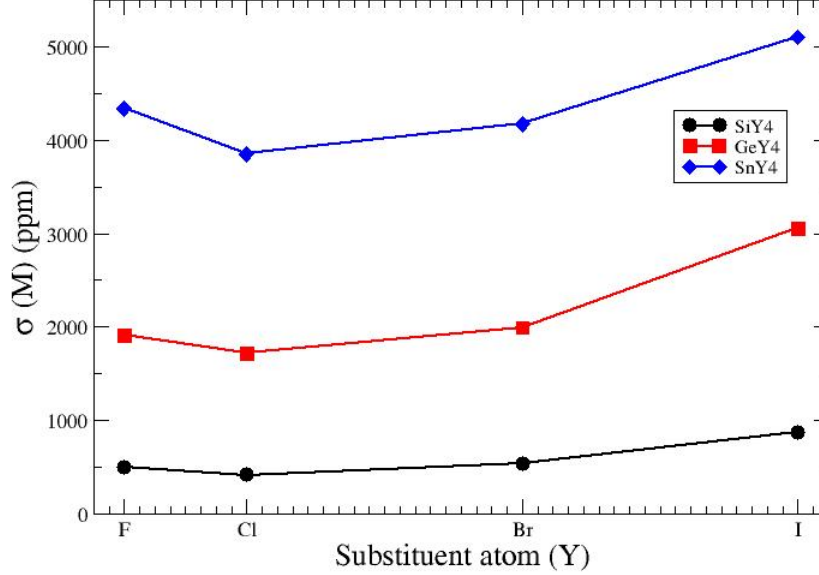
Core-dependent terms

In Tables III, IV and V we show the whole set of relativistic corrections to $\sigma(M)$ together with their nonrelativistic contributions and the addition of some specific terms.

The core-dependent corrections are $\sigma_p^{T(1)}$, $\sigma_d^{S(1)}$ and $\sigma_d^{S(0)}$. Each one will be analysed separately as they do not behave in the same way, having opposite signs and same order of magnitude. On the other hand, each one arises from different electronic mechanisms. Two of them modifies the diamagnetic component of the nuclear magnetic shielding, and the third one modifies the

paramagnetic part.

FIG. 5. σ^{LRESC} for central M atom, at MY_4 model compounds ($M = \text{Si, Ge, Sn}$; $Y = \text{F, Cl, Br, I}$) in terms of Y_4 substituent atom



In molecular systems that contain silicon as central atoms, the correction $\sigma_p^{T(1)}$ represents among 7.1% and 11.6% of the nonrelativistic shielding (σ^{nr}). However, for molecular systems containing germanium as central atom, this correction represents between 25.5% and 34.3% of the σ^{nr} value. Finally, when the central atom is heavier, like the tin atom, we found the largest variation for this correction, among 50.9% and 65.8% of σ^{nr} . According to the variations mentioned above, $\sigma_p^{T(1)}$ is strongly core-dependent and for heavy atoms, like Sn, it has the same order of magnitude as σ^{nr} , as shown in Table V.

The behavior of $\sigma_d^{S(1)}$ is similar to that of $\sigma_p^{T(1)}$, though less important than the latter, and also with opposite sign. For molecular systems containing silicon as central atom, $\sigma_d^{S(1)}$ correction represents among 4.5% and 8.9% of σ^{nr} values; but for molecules containing germanium as central atom such percentage grows up, being among 16.3% and 22.2%. The highest variations appear for molecular systems containing tin as central atom, to which the correction represents among 32.9% and 42.6% of σ^{nr} . The third core-dependent correction is $\sigma_d^{S(0)}$, mainly its contribution is less important than the other two ones. The variations with respect to the nonrelativistic shielding

TABLE IV. Nuclear magnetic shielding constant for central Ge atom, at different levels of theory, for $\text{GeH}_{4-n}\text{Y}_n$ ($Y = \text{F, Cl, Br, I; } n = 0, \dots, 4$).

system	σ^{nr}	$\sigma_d^{S(0)}$	$\sigma_d^{S(1)}$	$\sigma_p^{T(1)}$	$\sigma_p^{S(1)}$	$\sigma_p^{S(3)}$	$\sigma_p^{T(3)}$	core ^a	ligand ^b	$\sigma^{nr} + \sigma_p^{T(3)}$	LRESC	4c
GeH ₄	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 ₃ 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 ₃ 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 ₃ 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 ₃ 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 ₂ F ₂	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 ₂ Cl ₂	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 ₂ Br ₂	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 ₂ I ₂	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 ₃	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 ₃	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 ₃	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 ₃	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 ₄	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 ₄	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 ₄	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 ₄	1319.63	83.86	-293.62	453.13	68.28	-149.91	1518.13	243.37	1436.49	2838.03	2999.49	2758.28

^a The core-dependent contribution is defined as $\sigma_p^{T(1)} + \sigma_d^{S(1)} + \sigma_d^{S(0)}$

^b The ligand-dependent contribution is defined as $\sigma_p^{S(1)} + \sigma_p^{T(3)} + \sigma_p^{S(3)}$

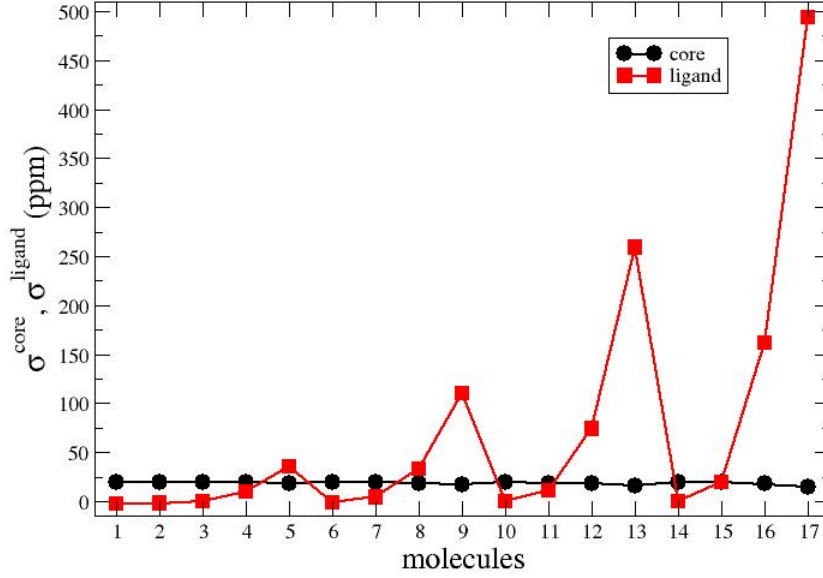
constant are: among 1.2% and 1.9% for molecules containing silicon atom; 4.7% and 6.4% for germanium and among 10.1% and 12.9% for tin containing molecules.

The total value that results from the addition of the three core-dependent relativistic corrections is small for molecules which have light central atoms like silicon and germanium. Such value is quite larger in the case of molecules with tin as central atom. This is because $\sigma_p^{T(1)}$ and $\sigma_d^{S(1)}$ have opposite sign each other and they are of the same order of magnitude. Then, the total core-dependent contribution is not so important for light central atom systems, but for molecules containing tin atoms σ^{core} contribution is almost of the same order of magnitude as σ^{nr} .

The total contribution of the core-dependent corrections on the central atom in the different systems under study varies among 3.9% and 4.5% of $\sigma^{nr}(\text{Si})$ value; 14.0% and 18.4% for $\sigma^{nr}(\text{Ge})$ and 27.9% and 36.0% for $\sigma^{nr}(\text{Sn})$. The range of variations come from different nonrelativistic

shielding values. As an example, the total core-dependent relativistic contribution to $\sigma(\text{Sn})$ in SnF_4 is 964.76 ppm and for SnI_4 it is 964.77 ppm. However $\sigma^{nr}(\text{Sn})$ is 3455.42 ppm in the former case and 2676.59 ppm in the latter.

FIG. 6. σ^{core} and σ^{ligand} behavior, for central Si atom, at the whole set of compounds



The dependence of the core-dependent terms with respect to the central atom M is nicely seen in Figs. 6, 7 and 8. One can see that such contributions grow up from $M = \text{Si}$ and Ge to Sn .

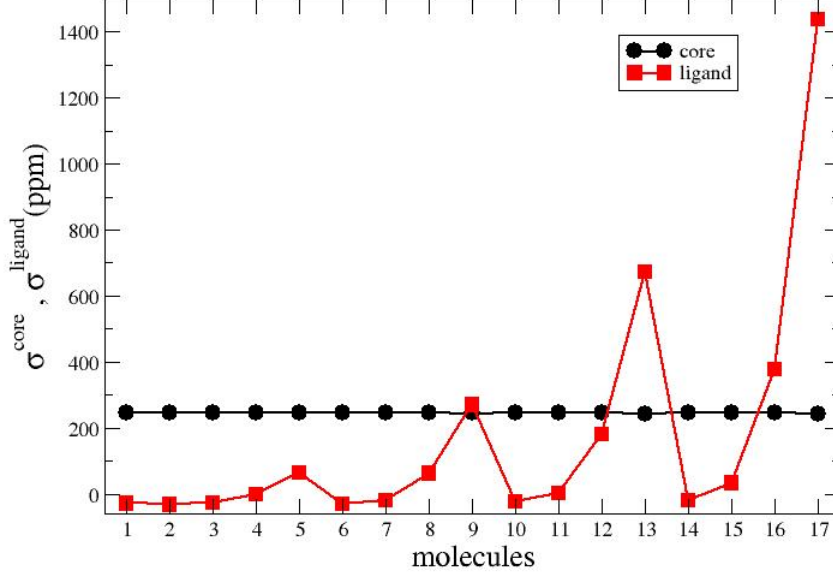
Ligand-dependent terms

There are several corrections that change their values when the central atom is fixed and the molecular ligands are modified. They are termed as *ligands-dependent* corrections (see Tables III, IV and V) and arises from the following σ^{LRESC} corrections: $\sigma_p^{S(1)}$, $\sigma_p^{S(3)}$ and $\sigma_p^{T(3)}$.

The $\sigma_p^{S(1)}$ term increases its value when the central atom becomes heavier, but it does not change very much when the ligands are modified, even for molecules which contain several heavy atoms. Large differences are obtained going from SnF_4 to SnI_4 (60 ppm). For molecular systems containing central silicon atoms the correction is such that it varies among 0.6% and 3.6% of the

$\sigma^{nr}(\text{Si})$ value. When the central atom is germanium the percentage grows up from 2.6% to 5.2%; and for tin central atom the range of variations is from 5.5% to 9.3% of $\sigma^{nr}(\text{Sn})$.

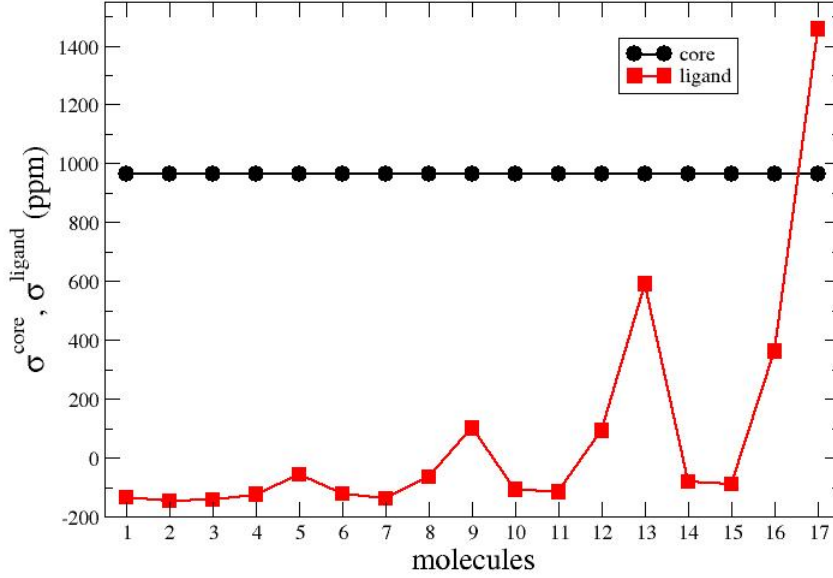
FIG. 7. σ^{core} and σ^{ligand} behavior, for central Ge atom, at the whole set of compounds



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

The most important of the three ligand-dependent relativistic corrections is $\sigma_p^{T(3)}$, which is responsible of the electronic origin of many relativistic effects. Such a correction includes the FC and SD contributions to $\sigma_p^{T(3)}$ as was shown in section II. Such FC contributing term has a very large range of variation when the weight of the molecule grows up and it can be of the same order of magnitude as the nonrelativistic value. For SnI_4 it represents 68% of $\sigma^{nr}(\text{Sn})$, though for the SiI_4 molecule, $\sigma_p^{T(3)}(\text{Si})$ has a value that is larger than that of $\sigma^{nr}(\text{Si})$ and represents a correction that is 162% of the nonrelativistic term.

FIG. 8. σ^{core} and σ^{ligand} behavior, for central Sn atom, at the whole set of compounds



The FC contributing terms are positive and their contributions are very large for heavy systems. On the other hand the SD contributing terms have opposite sign and they are not as important as the former, except for molecular systems with the light substituents. All this is in line with previous findings, by Nakatsuji and coauthors, for tin tetrahalides³² and for lighter systems like $CY_{4-n}Z_n$ ($Y = H, Cl, Br$; $Z = Br, I$ and $n = 0 - 4$).²⁴ Still, for tin tetrahalides they got values that are 1000 ppm smaller than ours. We should emphasise 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 analyse the different behavior of each σ^{ligand} term, $\sigma_p^{S(1)}$, $\sigma_p^{S(3)}$, and $\sigma_p^{T(3)}$. For molecules like SiH_3I , the addition of $\sigma_p^{S(1)}$ and $\sigma_p^{S(3)}$ terms, gives -6.7 ppm which is close to 16% of $\sigma_p^{T(3)}$. When the central atom is Sn and the molecule has the same substituents, such a relationship becomes opposite: the absolute value of $\sigma_p^{T(3)}$ is smaller than the addition of $\sigma_p^{S(1)}$ and $\sigma_p^{S(3)}$. This last relationship is again reversed for systems with two or more than two iodines. The contribution due to SO effects grows up much faster than the other two ligand-dependent terms. Due to the large variation of $\sigma_p^{T(3)}$ in this kind of compounds, it has no sense to take into account percentage changes. For light systems, like MH_4 ($M = Si, Ge$ and Sn) $\sigma_p^{T(3)}$ is negative because

TABLE V. Nuclear magnetic shielding constant for central Sn atom, at different levels of theory, for $\text{SnH}_{4-n}Y_n$ ($Y = \text{F, Cl, Br, I; } n = 0, \dots, 4$).

system	σ^{nr}	$\sigma_d^{S(0)}$	$\sigma_d^{S(1)}$	$\sigma_p^{T(1)}$	$\sigma_p^{S(1)}$	$\sigma_p^{S(3)}$	$\sigma_p^{T(3)}$	core ^a	ligand ^b	$\sigma^{nr} + \sigma_p^{T(3)}$	LRESC	4c
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
SnH ₃ 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
SnH ₃ 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
SnH ₃ 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
SnH ₃ 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
SnH ₂ 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
SnH ₂ 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
SnH ₂ 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
SnH ₂ 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
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
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
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
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
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
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
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
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

^a The core-dependent contribution is defined as $\sigma_p^{T(1)} + \sigma_d^{S(1)} + \sigma_d^{S(0)}$

^b The ligand-dependent contribution is defined as $\sigma_p^{S(1)} + \sigma_p^{T(3)} + \sigma_p^{S(3)}$

the contributing SD terms are larger than the FC ones (in absolute value).

For the systems like $M\text{H}_3\text{F}$ both values are almost the same cancelling each other, and so forth giving then almost null total values. When the weight of the molecule grows up, the FC correcting term, belonging to the SO mechanism, increases its value considerably and, at the same time, the SD term becomes not so very important.

For molecular systems that contain four iodine atoms this correction may be quite large. As was mentioned above, for SiI_4 the $\sigma_p^{T(3)}(\text{Si})$ is larger than $\sigma^{nr}(\text{Si})$; the nonrelativistic value is 318.44 ppm and its relativistic SO correction is 514.56 ppm (being 161.6%). For GeI_4 , $\sigma^{nr}(\text{Ge}) = 1319.63$ ppm and its SO correction is 1518.13 ppm which represents 115.0%. Finally for SnI_4 , $\sigma^{nr}(\text{Sn}) = 2676.59$ ppm and $\sigma_p^{T(3)}(\text{Sn}) = 1715.75$ ppm representing 64.1%. This percentage is smaller than the others for Si and Ge, even though as an absolute value it is the largest.

Then we are able to state that there exists a compensation of the contributions due to their different electronic mechanisms being as core- and ligand-dependent. Only the correction $\sigma_p^{T(3)}$ has a very different behaviour. The addition of core-dependent corrections plus two of the three ligand-dependent corrections (not including $\sigma_p^{T(3)}$) gives very small values for light systems. Reaching its largest absolute value (26.4%) for the heaviest molecular system under study, SnI_4 .

From this analysis one can understand why the leading term $\sigma_p^{T(3)}$ was considered the main electronic mechanism responsible of ligand relativistic effects. However, we should highlight that this is only true for light, or not so heavy-atom, containing molecules; since for heavy ones $\sigma_p^{T(3)}$ does not reproduce the total relativistic effect for the nuclear magnetic shielding. The other relativistic corrections increase their contribution, especially those that are core-dependent, as shown in tables IV and V (eleventh and last columns). For most heavy systems, the contribution of $\sigma^{nr}(\text{Sn}) + \sigma_p^{T(3)}(\text{Sn})$ does not give good enough reproduction of the 4 component relativistic value since the differences are close to 25%, and then the others contributions become important.

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

We will first introduce some considerations about the heavy-atom effects on the central atom; and then we shall discuss the results of relativistic effects, for the set of molecules analysed in this work.

We are interested to understand which could be the proper ligand heavy-atom effects on the central atom when it is not a light one. If the central atom were not heavy, there would be HALA effects. So we asked ourselves how large the HALA effects would be in the case of having two vicinal heavy atoms. We are not aware of any research oriented to answer this enquire. It may be that proper HAVHA effects should arise from electronic (HALA type) mechanisms, that become vanishingly small when the central atoms are not heavy, and turn out to be important when the central atoms become heavier. The SO effects depend on the substituent and, for heavy substituents, they are always important with independence of whether the central atom is light or not.

From the whole set of molecular systems we have studied, relativistic effects are mostly due to HALA type in the subset of si containing molecular systems. In Table III it is observed that $\sigma_p^{T(3)}$ is the most important relativistic correction. Its contribution are in very good agreement with

those of previous studies.⁸

When considering molecules with several heavy atoms, like SiBr_4 , SiHI_3 or SiI_4 , relativistic corrections are such that σ^{LRESC} results are little overestimated when compared with 4 component calculations.

In addition to that, for SiH_2I_2 $\sigma_p^{T(3)} = 122.09$ ppm and when this value is added to σ^{nr} the result is quite close to the total LRESC value, with a difference less than 1%. Furthermore, for SiI_4 $\sigma_p^{T(3)} = 514.56$ ppm and when this value is added to σ^{nr} , the result is also close to the LRESC (less than 1 % of difference) though the difference among LRESC and the 4 component value is $\simeq 9\%$. Then, when the contribution of $\sigma_p^{T(3)}$ becomes an important fraction of the nonrelativistic shielding value, the addition of the $\sigma_p^{T(3)}$ (SO) term plus σ^{nr} contribution gives a value that has a difference less than 1 % (with the exception of SiBr_4 where the difference is 1.8 %) when compared with the total LRESC value.

On the other hand, as was previously shown, the HAHA effect is mainly due to the core-dependent corrections, as they are related with the weight of the central atoms. Still it is well-known that the whole set of relativistic corrections increases their values when the central atom becomes heavier.

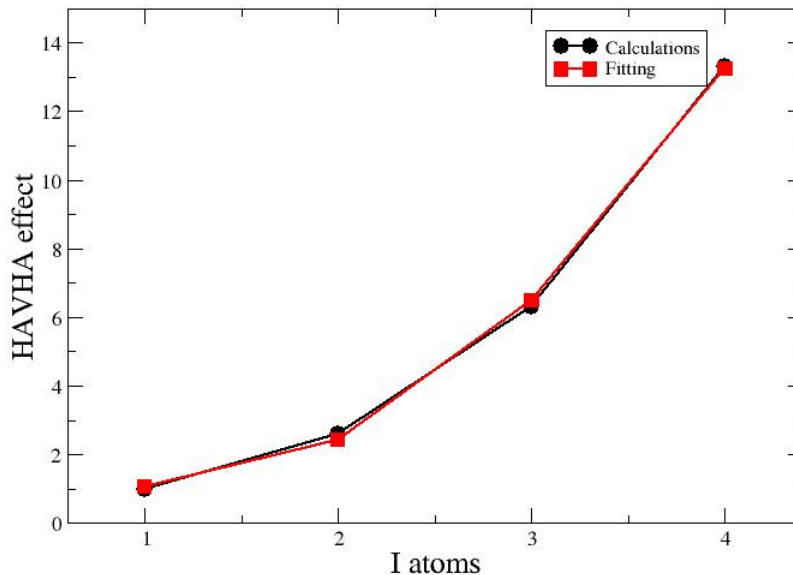
What kind of functional dependence, with the atomic number of the whole set of substituents, does this effects have? Can it be addressed as a HALA + other ligand-dependent effects? Or is it only just of HALA type? The newest proposed heavy-atom effect, the HAVHA effect,^{8,14} seems to appear on systems containing more than one heavy atom. It should appear when light vicinal atoms are substituted by heavy analogues. As shown in previous sections the nuclear magnetic shielding of one central heavy atom is modified in a tetrahalide molecule due to vicinal heavy atoms effect.

Let us start considering that relativistic effects on $\sigma(\text{Sn})$ atoms may be analysed following the usual definition for percentual contributions: $(\sigma^R - \sigma^{nr})/\sigma^{nr}$, where R means relativistic. In our case, given that nonrelativistic contributions are also both, core and ligand dependent, we shall consider in this case the nonrelativistic contribution due to the unsubstituted molecular system. For SnH_4 , relativistic effects amount 25.4% of the total $\sigma(\text{Sn})$ (it is a pure HAHA-type effect), while for SnH_3I their contributions grow to 29.5% (they are of both types, HAHA + HAVHA). This means that 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 increase its value with the weight of the substituents, being its largest values that which are obtained for the heavier molecular systems, like SnBr_4 (21.3%), SnHI_3 (27.9%) and SnI_4 (65.1%). It is healthy to emphasise here that, in this analysis the HAVHA effect was taken as the total relativistic effect that appears after the replacement of vicinal light atoms by heavy atoms. In a way the HAVHA effect would include a likely different HAHA effect also is involved when the central atom is not the same.

An interesting feature of this effect is that when the number of the same kind of substituent heavy-halogen atoms increases, an enhancement appears as a non linear function on the number of substituents. This can be seen by analysing molecular systems containing iodine atoms. For SnH_3I the HAVHA effect is 4.1%; for SnH_2I_2 it is 15.4%; 27.9% for SnHI_3 and 65.1% for SnI_4 . This set of values shows a quadratic behaviour for $\sigma(\text{Sn})$ as a function of the number of iodine atoms (see Fig. 9). The functional dependence of the HAVHA effect is quadratic: $1.58 n^2 - 3.11 n + 2.83$, where n is the number of iodine atoms.

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



How much of the HAVHA effect calculated in the above mentioned way 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

TABLE VI. Nonrelativistic (in ppm) and relativistic (in percentage) ligand-dependent corrections to $\sigma(M)$ for $MH_{4-n}I_n$ ($M = \text{Si, Ge and Sn; } n = 1, \dots, 4$)

$MH_{4-n}I_n$	Si			Ge			Sn		
$n \setminus M$	(nr, nc) ^a	%SO ^b	non-SO ^c	(nr, nc)	%SO	non-SO	(nr, nc)	%SO	non-SO
	[ppm]	[%]	[%]	[ppm]	[%]	[%]	[ppm]	[%]	[%]
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

^a Non relativistic non core contributions: $\sigma^{(nr,nc)} = \sigma^{nr}(M : MH_{4-n}I_n) - \sigma^{nr}(M : MH_4)$, in [ppm]

^b Relativistic ligand Spin-orbit contribution: $\sigma^{(\%SO)} = \frac{\sigma^{SO}}{\sigma^{(nr,nc)}} * 100$

^c Relativistic ligand Non SO contribution : $\sigma^{(\%SO)} = \frac{\sigma^{ligand} - \sigma^{SO}}{\sigma^{(nr,nc)}} * 100$

electronic mechanism may or may not be modified due to it's action on a heavy, instead of light, nucleus.

In line with previous reasoning, in Table VI we show how large are the contributions of the SO and the addition of both non-SO ($\sigma_p^{S(1)}$ and $\sigma_p^{S(3)}$) mechanisms, in percentage, with respect to the nonrelativistic contribution to $\sigma(M)$ for $MH_{4-n}I_n$ ($M = \text{Si, Ge and Sn; and } n = 1, \dots, 4$) molecular systems. Some new features are now apparent. First, the main HALA effect becomes less important as the central atom belongs to lower rows of the Periodic Table. Second, the other non-SO mechanisms grows up in the series from $M = \text{Si}$ to $M = \text{Sn}$.

The HAVHA effect is obviously more related to the ligand-dependent corrections than with core-dependent ones. Furthermore, as it was mentioned above, the $\sigma_p^{T(3)}$ contribution greatly varies and represents the most important relativistic correction obtained with LRESC method. For SnI_4 molecule, the combined contribution of $\sigma_p^{S(1)} + \sigma_p^{S(3)}$, is close to 15% of $\sigma_p^{T(3)}$. The total ligand-dependent contribution (nr + relativistic) is, in this case, of 73.8 % being then the total HAVHA effect of 42.54 %. There is also a non core-dependent nonrelativistic contribution that appears when hydrogen atoms are replaced by heavy-halogens.

If we observe Tables III, IV and V we see that the nonrelativistic contributions to $\sigma(M; M = \text{Si, Ge and Sn})$ varies with the substituents. On the other hand the relativistic core-dependent contributions are almost the same in each family of compounds. So, we can assume that the

core-dependent nonrelativistic contribution to the shielding of central atoms is not modified by the ligands. Then we are able to analyse the relationship between relativistic and nonrelativistic ligand dependent contributions. In other words, how the HALA-type effect becomes a HAVHA-type effect.

In Table VI we show the non-core (ligand) nonrelativistic contribution to $\sigma(M; MI_4)$ taken from Tables III, IV and V: -155.47 ppm, -446.05 ppm and -593.67 ppm for $M = \text{Si}$, Ge and Sn , respectively. Their spin-orbital contributions are 3.31 times, 3.40 times and 2.89 times, respectively. So, the HALA effect seems to be of the same order of magnitude, though little smaller for Sn . In the case of the other two ligand-dependent effects, they grow up quite strongly.

As shown in Table VI the percent increase of the SO effect grows up when the number of heavy-halogen substituents grows up, though with different rate of increase (higher for heavier central atoms), and the non-SO contributions falls down, though quite slowly, as compared with the SO counterpart.

Proton shielding

Table VII shows the nuclear magnetic shielding of the proton ^1H in the whole set of molecular systems studied in this work. It has different behavior when the central atom becomes heavier.

In Si atom containing molecules, $\sigma(\text{H})$ increases its value when the weight of each substituent heavy-halogen atom grows up. For SiH_3Y molecules there is a small raising from F to Br atoms (26.76 ppm and 28.02 ppm respectively), but such raising is larger for I atom, 32.02 ppm. This pattern is similar in SiH_2Y_2 and SiHY_3 molecular systems; the largest variation is obtained for the shieldings in SiHF_3 (27.67 ppm) and SiHI_3 (39.71 ppm), difference corresponding to 44%.

On the other hand, it is interesting to analyse $\sigma(\text{H})$ when the number of the same heavy-halogen atom increases. When the number of fluorine, chlorine and bromine atoms varies, there is a very small variation on the shielding values; less than 1 ppm from SiH_3Y to SiHY_3 . When the number of iodine atoms varies, the shielding grows up from SiH_3I (32.02 ppm) to SiHI_3 (39.71 ppm) and this corresponds to an increase of 24%.

For tin atom containing molecules, the $\sigma(\text{H})$ behavior is different. When the weight of the substituent heavy-halogen atom grows up $\sigma(\text{H})$ value increases a little more than what happens for molecules containing silicon atoms. Such behavior is enhanced when the number of the same

TABLE VII. Proton shieldings at relativistic level. All values are given in ppm

M	molecule	Y				
		H	F	Cl	Br	I
Si	SiH ₃ Y	27.96	26.76	27.61	28.02	32.02
	SiH ₂ Y ₂	—	27.29	28.07	28.33	36.11
	SiHY ₃	—	27.67	28.49	28.34	39.71
Ge	GeH ₃ Y	27.93	26.04	27.09	28.01	32.92
	GeH ₂ Y ₂	—	25.75	27.08	27.74	36.09
	GeHY ₃	—	25.83	27.16	27.86	41.19
Sn	SnH ₃ Y	27.48	24.22	26.07	27.66	31.33
	SnH ₂ Y ₂	—	23.29	25.00	25.89	33.81
	SnHY ₃	—	23.15	24.33	25.59	37.24

heavy-halogen substituent atom increases. The largest variation is found out for SnHF₃ ($\sigma(\text{H}) = 23.15$ ppm) and SnHI₃ ($\sigma(\text{H}) = 37.24$ ppm) with an increase of 61%. However if the number of the same heavy-halogen atoms increases, $\sigma(\text{H})$ decreases few ppm; only for the iodine atom the shielding value increases, from SnH₃I (32.33 ppm) to SnHI₃ (37.24 ppm), which is close to 19%. This is shown in Fig. 10.

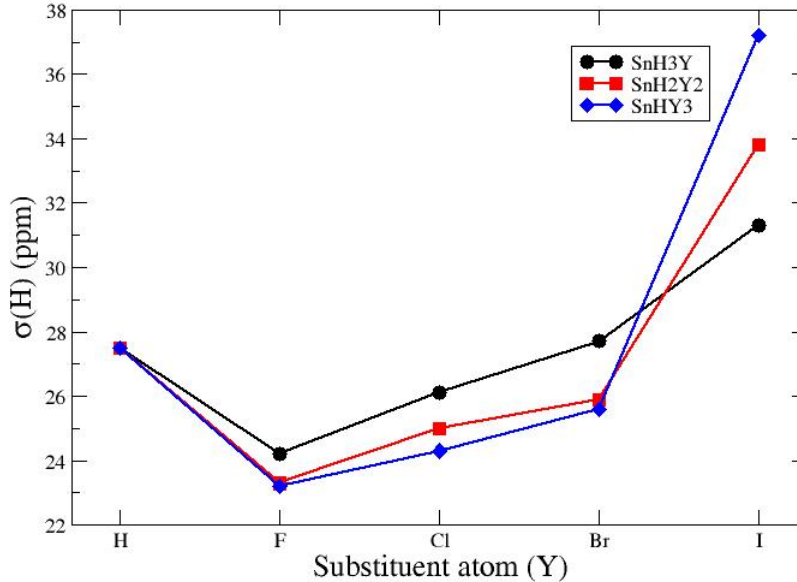
For molecular systems containing germanium as central atom, the behavior of $\sigma(\text{H})$ is between that of silicon and tin cases. Only for iodine-halogen substituent atom there is a variation of 25% from GeH₃I to GeHI₃.

V. CONCLUSIONS

The increasing use of semirelativistic methods, like LRESC, gives the opportunity to calculate and analyse electronic mechanisms underlying relativistic effects contributing to magnetic molecular properties in molecules with several heavy atoms, atoms belonging to the fifth or sixth row in the Periodic Table.

We presented here the analysis by contributions of the LRESC relativistic effects on the shieldings of $M\text{H}_{4-n}\text{Y}_n$ molecular systems ($M = \text{Si, Ge, Sn}$; $Y = \text{F, Cl, Br, I}$ and $n = 1, \dots, 4$). We first

FIG. 10. Proton nuclear magnetic shielding at relativistic level. All values are given in ppm.



compared the total central atom magnetic shieldings calculated with LRESC model, with benchmark results of the relativistic polarization propagator formalism at RPA level, RelPPA-RPA, and also with some other previous calculations taken from the literature. We found an excellent performance of the LRESC formalism. Their values are close to the 4-component ones, even for molecular systems containing five heavy atoms, *e.g.* belonging to the fifth row of the Periodic Table. The largest difference is of 414 ppm (7.5%) and corresponds to SnI_4 .

We divided the relativistic corrections into two groups: the core- and the ligand-dependent corrections. The electronic mechanisms that belongs to the core-dependent corrections are $\sigma_p^{T(1)}$, $\sigma_d^{S(1)}$ and $\sigma_d^{S(0)}$. The first one is the most important. For the heaviest system analysed here, *i.e.* SnI_4 , it reaches 66% of $\sigma^{nr}(\text{Sn})$. However the addition of all core-dependent corrections does not give a large value as compared to the total shielding because they have opposite signs. For the lightest system they almost cancel each other reaching a percentage of 4%.

The ligand-dependent corrections are found to be due to $\sigma_p^{S(1)}$, $\sigma_p^{S(3)}$ and $\sigma_p^{T(3)}$ mechanisms. Both singlet type corrections have opposite sign and also equivalent absolute values. Then the total relativistic contribution is at the end very small for systems with lightest substituents; its highest value is less than -10% of σ^{nr} . The $\sigma_p^{T(3)}$ (or Spin-orbit) correction is the most important

one and can be larger than σ^{nr} for systems with heavy substituents.

We show here that ligand-dependent relativistic corrections are the main ones for MI_4 ($M = \text{Si, Ge and Sn}$) molecular systems, being the SO the main term in σ^{ligand} . However, the other corrections (core- and ligand-dependent) reach 26.4% of σ^{nr} for the heaviest system. This means that they must be introduced when one wants to get reliable reproduction of the total relativistic shielding, in molecules with few heavy-halogen containing substituents and heavy central atoms.

In line with what we expressed above, the recently proposed HAVHA effect is mainly dependent of the term $\sigma_p^{T(3)}$. Still the largest contribution of $\sigma_p^{S(1)}$ plus $\sigma_p^{S(3)}$ reach 15% of $\sigma_p^{T(3)}$. The electronic mechanisms that underlies these last two terms are then important in the HAVHA effect. We showed that the HAVHA effect is due to all three ligand-dependent relativistic effects. As one may expect, the SO effect has the same size for all systems when the number of heavy-halogen substituents is the same (it goes down a little bit for tin systems) though the other two grows up quite a bit. This finding is based on the analysis of relativistic versus nonrelativistic ligand-dependent effects.

If the percentual HAVHA effect is taken as a difference among the total relativistic and the nonrelativistic effects, it grows from 4.1% for SnH_3I , to 15.4% for SnH_2I_2 ; 27.9% for SnHI_3 and 65.1% for SnI_4 . These values show a cuadratic dependence of $\sigma(\text{Sn})$ with 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 silicon atom and when the number of the same heavy-halogen substituent atom increases, $\sigma(\text{H})$ increases a little for F, Cl and Br atoms from SiH_3X to SiHX_3 . On the other hand, such behavior is opposite for Sn atom; when the number of the same heavy-halogen substituent atom increases, $\sigma(\text{H})$ decreases few ppm. Only when the substituents are iodine atoms $\sigma(\text{H})$ increases for both kind of central atoms.

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REFERENCES

- ¹U. Edlund, T. Lejon, P. Pyykkö, T. K. Venkatachalam, and E. Buncel, *J. Am. Chem. Soc.* **109**, 5982 (1987).
- ²P. Pyykkö, A. Görling, and N. Rösch, *Mol. Phys.* **61**, 195 (1987).
- ³M. Kaupp, O. L. Malkina, V. G. Malkin, and P. Pyykkö, *Chem. Eur. J.* **4**, 118 (1998).
- ⁴J. I. Melo, M. C. Ruiz de Azúa, C. G. Giribet, G. A. Aucar, and P. F. Provasi, *J. Chem. Phys.* **121**, 6798 (2004).
- ⁵M. Kaupp, “Relativistic electronic structure theory II: Applications,” (Elsevier, Amsterdam, 2004) Chap. 9.
- ⁶P. Lantto, R. H. Romero, S. S. Gomez, G. A. Aucar, and J. Vaara, *J. Chem. Phys.* **125**, 184113 (2006).
- ⁷J. Vaara, *Phys. Chem. Chem. Phys.* **9**, 5399 (2007).
- ⁸A. F. Maldonado and G. A. Aucar, *Phys. Chem. Chem. Phys.* **11**, 5615 (2009).
- ⁹J. Autschbach and S. Zheng, *Annu. Rep. NMR Spectrosc.* **67**, 1 (2009).
- ¹⁰A. M. Kantola, P. Lantto, J. Vaara, and J. Jokisaari, *Phys. Chem. Chem. Phys.* **12**, 2679 (2010).
- ¹¹V. Arcisauskaite, J. I. Melo, L. Hemmingsen, and S. P. A. Sauer, *J. Chem. Phys.* **135**, 044306 (2011).
- ¹²J. Roukala, A. F. Maldonado, J. Vaara, G. A. Aucar, and P. Lantto, *Phys. Chem. Chem. Phys.* **13**, 21016 (2011).
- ¹³J. I. Melo, A. F. Maldonado, and G. A. Aucar, *J. Chem. Phys.* **137**, 214319 (2012).
- ¹⁴J. I. Melo, A. F. Maldonado, and G. A. Aucar, *Theor. Chem. Acc.* **129**, 483 (2011).
- ¹⁵J. I. Melo, M. C. Ruiz de Azúa, C. G. Giribet, G. A. Aucar, and R. H. Romero, *J. Chem. Phys.* **118**, 471 (2003).
- ¹⁶P. Manninen, P. Lantto, J. Vaara, and K. Ruud, *J. Chem. Phys.* **119**, 2623 (2003).
- ¹⁷P. Manninen, K. Ruud, P. Lantto, and J. Vaara, *J. Chem. Phys.* **122**, 114107 (2005).
- ¹⁸A. Rodriguez-Fortez, P. Alemany, and T. Ziegler, *J. Phys. Chem. A* **103**, 8288 (1999).
- ¹⁹A. F. Maldonado and G. A. Aucar, *J. Phys. Chem. A*, Submitted(2014).
- ²⁰S. S. Gomez, A. F. Maldonado, and G. A. Aucar, *J. Chem. Phys.* **123**, 214108 (2005).

- ²¹L. Visscher, T. Enevoldsen, T. Saue, H. J. Aa. Jensen, and J. Oddershede, *J. Comput. Chem.* **20**, 1262 (1999).
- ²²C. J. Jameson, *Multinuclear NMR* (Plenum Press, New York, 1998).
- ²³M. Kaupp, “Calculation of NMR and EPR parameters. Theory and applications,” (Wiley-VCH Verlag GmbH & Co, Weinheim, FRG, 2004) Chap. 18.
- ²⁴S. Fukawa, M. Hada, R. Fukuda, S. Tanaka, and H. Nakatsuji, *J. Comp. Chem.* **22**, 528 (2001).
- ²⁵G. A. Aucar, R. H. Romero, and A. F. Maldonado, *Int. Rev. on Phys. Chem.* **29**, 1 (2010).
- ²⁶T. Saue, L. Visscher, with contributions from R. Bast H.J. Aa. Jensen, K.G. Dyall, U. Ekstrom, E. Eliav, T. Enevoldsen, T. Fleig, A.S.P. Gomes, J. Henriksson, M. Iliaš, Ch. R. Jacob, S. Knecht, H.S. Nataraj, P. Norman, J. Olsen, M. Pernpointner, K. Ruud, B. Schimmelpfennig, J. Sikkema, A. Thorvaldsen, J. Thyssen, S. Villaume, and S. Yamamoto, *dirac is a relativistic ab initio electronic structure program*, Release DIRAC10 (University of Southern Denmark, Odense, 2010), <http://dirac.chem.sdu.dk>.
- ²⁷N. B. Kagakkai, “Kagaku benran, 3rd edition,” (Maruzen Company, 1984) p. 649.
- ²⁸A. J. Sadlej, *Theor. Chim. Acta* **79**, 123 (1991).
- ²⁹A. F. Maldonado, C. A. Gimenez, and G. A. Aucar, *Chem. Phys.* **395**, 75 (2012).
- ³⁰A. F. Maldonado, C. A. Gimenez, and G. A. Aucar, *J. Chem. Phys.* **136**, 224110 (2012).
- ³¹Kestutis Aidas, Celestino Angeli, Keld L. Bak, Vebjørn Bakken, Radovan Bast, Linus Boman, Ove Christiansen, Renzo Cimiraglia, Sonia Coriani, Pål Dahle, Erik K. Dalskov, Ulf Ekström, Thomas Enevoldsen, Janus J. Eriksen, Patrick Ettenhuber, Berta Fernández, Lara Ferrighi, Heike Fliegl, Luca Frediani, Kasper Hald, Asger Halkier, Christof Hättig, Hanne Heiberg, Trygve Helgaker, Alf Christian Hennum, Hinne Hettema, Eirik Hjertenæs, Stinne Høst, Ida-Marie Høyvik, Maria Francesca Iozzi, Branislav Jansík, Hans Jørgen Aa. Jensen, Dan Jonsson, Poul Jørgensen, Joanna Kauczor, Sheela Kirpekar, Thomas Kjærgaard, Wim Klopper, Stefan Knecht, Rika Kobayashi, Henrik Koch, Jacob Kongsted, Andreas Krapp, Kasper Kristensen, Andrea Ligabue, Ola B. Lutnæs, Juan I. Melo, Kurt V. Mikkelsen, Rolf H. Myhre, Christian Neiss, Christian B. Nielsen, Patrick Norman, Jeppe Olsen, Jógvan Magnus H. Olsen, Anders Osted, Martin J. Packer, Filip Pawłowski, Thomas B. Pedersen, Patricio F. Provasi, Simen Reine, Zilvinas Rinkevicius, Torgeir A. Ruden, Kenneth Ruud, Vladimir V. Rybkin, Paweł Sałek, Claire C. M. Samson, Alfredo Sánchez de Merás, Trond Saue, Stephan P. A. Sauer, Bernd Schimmelpfennig, Kristian Sneskov, Arnfinn H. Steindal, Kristian O. Sylvester-Hvid, Peter R. Taylor,

Andrew M. Teale, Erik I. Tellgren, David P. Tew, Andreas J. Thorvaldsen, Lea Thøgersen, Olav Vahtras, Mark A. Watson, David J. D. Wilson, Marcin Ziolkowski, and Hans Ågren, “The Dalton quantum chemistry program system,” Wiley Interdisciplinary Reviews: Computational Molecular Science, n/a–n/a(2013), ISSN 1759-0884, <http://dx.doi.org/10.1002/wcms.1172>.

³²H. Kaneko, M. Hada, T. Nakajima, and H. Nakatsuji, Chem. Phys. Lett. **261**, 1 (1996).