

Relativistic effects on the shielding of SnH_2XY and PbH_2XY ($\text{X}, \text{Y} = \text{F}, \text{Cl}, \text{Br}$ and I) heavy atom-containing molecules

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Abstract The relativistic polarization propagator approach is one of the most reliable methods available today for the calculation of NMR spectroscopic parameters on heavy atom-containing molecules, though its implementation is still at RPA or FOPPA (first-order) level of approach. Two-component methods like the LR-ESC method make possible the analysis of the electronic origin of relativistic effects due to its splitting in several mechanisms which are (or not) sensitive to the molecular structure or the nature of the chemical environment of the atom under study. In this article we present the study of some nuclear magnetic shieldings on the heavy atom for the following systems: SnXH_3 ($\text{X} = \text{H}, \text{F}, \text{Cl}, \text{Br}, \text{I}$), SnXYH_2 ($\text{X}, \text{Y} = \text{F}, \text{Cl}, \text{Br}, \text{I}$) and PbXH_3 ($\text{X} = \text{H}, \text{F}, \text{Br}, \text{I}$). Total LR-ESC calculations are confronted to benchmark RPA calculations and then analyzed in order to get the main

trends and discuss the electronic origin of the shielding of two kinds of atoms involved in such systems: central and substituent atoms. The electronic origin of the heavy atom effects on vicinal heavy atoms (HAVHA), recently proposed, is analyzed. It is shown that the passive third-order Spin orbit mechanism does not explain the total pattern though is still the most important. There are two other mechanisms involved: the so called here PSO-OZ and the L-PSO-K. Both mechanisms do contain the PSO perturbative Hamiltonian (which also include kinetic energy correcting terms). In the case of SnH_2I_2 , the HAVHA effect on $\sigma(\text{Sn})$ is of the order of 16%. When the central atom is as heavy as Sn, the active SO contribution on the shielding of such atom becomes larger than the passive SO, which is small in this case. This would mean that the HALA-type effect is strongly diminished when applied on a vicinal heavy atom. Quite a similar pattern though with larger relativistic effects is observed for the central lead atom.

Dedicated to Professor Pekka Pyykkö on the occasion of his 70th birthday and published as part of the Pyykkö Festschrift Issue.

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1 Introduction

The NMR spectroscopic parameters (nuclear magnetic shielding σ and nuclear spin couplings transmitted through electrons, J) are powerful tools to get information on both electronic and geometrical structures. In particular on tin atom-containing molecules, tin being one of the most common elements that appears in Organic and Inorganic Chemistry. Then, it is of interest to learn more about its magnetic properties like the NMR spectroscopic parameters.

Given the last developments concerning the calculation of such NMR spectroscopic parameters in heavy atom-containing molecules, where relativity plays a central role, it becomes necessary to pursue a better understanding of the electronic origin (i.e., the underlying electronic mechanisms) of leading relativistic contributions to σ . Several recent studies were published with calculations based on 4-component, quasirelativistic and semirelativistic different and novel formalisms [1–18]. Most of them give results which do not converge to the same numbers. In the case of the two more used semirelativistic models, LR-ESC coined by Melo et al. [6, 19] and the Breit-Pauli perturbational approach, BPPA, of Manninen et al. [7, 13], one finds some different ways to perturbatively express the total contribution to σ . When the sum rule shown in Ref. [6] is considered, both schemes give completely equivalent results.

The relativistic polarization propagator formalism (fully developed up to RPA level of approach) [20–22] and its implementation in the DIRAC code [21, 23, 24] is the method that has proved to be the most accurate and giving deep physical insights into such spectroscopic parameters, though it has practical restrictions on the size and the number of heavy atoms of the systems to which it can be applied [25, 26]. In a recent article, we have shown that applying the UKB prescription the nuclear magnetic shielding for two heavy atom-containing molecules can accurately be obtained [25]. This is the main reason why our 4-component *ab initio* calculations can be used as benchmark calculations of magnetic molecular properties.

The LR-ESC formalism starts from fully relativistic (four component) expressions. Making use of the Rayleigh-Schrödinger perturbation theory and applying some given prescriptions, and the elimination of the small component scheme 4-component terms are reduced to 2-component terms. Gauge-invariant theoretical expressions for nuclear magnetic shieldings [1, 2] plus additional terms that were not included in Fukui and Baba's formulation are then obtained. This formulation does not suffer from change of picture problems. Recent calculations with that generalized two-component schemes by Melo et al. [6, 19] and Manninen et al. [7, 14] and others just published by some of the present authors [27] have shown that the LR-ESC 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 [19, 24]. Nevertheless, for the sixth row elements in both diamagnetic and paramagnetic terms of σ , semiquantitative differences between approximate methods and four-component RPA results were found [27, 28]. We explained the reason for these differences [31] from the contributions of excitations to the branch of negative-energy electronic states. Quite recently, an alternative approach, named Generalized elimination of small component approach,

GESC, was developed to overcome the overestimation of such contributions [32]. Within the GESC approximation, the inner shell s-type orbitals yield a smaller contribution in absolute value compared with LR-ESC scheme. Then, a better agreement with the four-component polarization propagator approach was found.

On the other hand, there are, in the literature, some reports concerning the Sn chemical shift and the values of magnetic shieldings in different compounds [33–36]. They have been calculated with different methods and approximations. The Spin-orbit mechanism plays an important role in all of them even though this is not the unique contribution to consider in order to reproduce total relativistic corrections.

For nuclear shieldings of systems which contain only one heavy atom, one must consider two kind of relativistic effects: the HALA effect [37, 38] which is the effect of the heavy on the vicinal lighter atom, and the HAVA effect [39] which is a relativistic effect of the heavy atom on itself. HALA effects arise mainly from “passive” third-order spin-orbit corrections through contributions of external magnetic field-free operators, [6, 7, 14, 19, 40], and the HAVA effect arise mainly due to the “active” second-order cross-term of the Fermi contact (FC) hyperfine interaction and the kinetic energy correction to the electronic spin-Zeeman interaction (FC/SZ-KE terms) though one should also include passive SO corrections (SO-I) to better describe them [5, 24, 28, 41, 42]. We want to emphasize here that both effects, HALA and HAVA, were proposed by Pekka Pyykkö and coauthors when the study of relativistic effects on nuclear shieldings was in their very first stage of development. After few years they were confirmed by several other authors. An updated and extensive analysis of their electronic origin was published recently by Kaupp [43].

The main aim of this work is to give a possible answer for an still open question on whether a new pattern appears for the nuclear shieldings of molecular systems like Sn (and Pb)H₂XY (X, Y = F, Cl, Br and I) which contain two or more than two heavy atoms. In a previous article, it was shown that a new effect, the heavy-atom effect on vicinal heavy atoms (HAVA) does appear when molecular systems like XYH₃ (X = C, Si, Ge, Sn; Y = F, Cl, Br, I) are considered [25]. Such effects were observed on both the central atoms and the halogen substituents being its magnitude smaller than the HALA effect [37] though significant: for SnIH₃, HAVA effects on Sn are close to 4.5% of the total $\sigma(\text{Sn})$. Is the origin of such effect the same as the HALA effect though scaled? We will show here that we need to consider new mechanisms like both PSO mechanisms (which include kinetic energy correcting terms) in order to reproduce the pattern of the total shielding of the central atom, Sn or Pb.

Another aim of this article is related with the analysis of the pattern of $\sigma(Y)$ in SnH_2XY ($X, Y = \text{H, F, Br, I}$) compounds. It will be shown that $\sigma(Y)$ follows the qualitative NR behavior due to different relativistic mechanisms which compensate each other, though they should be included for a reliable and more accurate description of $\sigma(Y)$.

This article is organized as follows: in Sect. 2, a brief description of both methods, the full relativistic polarization propagator at RPA level of approach and the LR-ESC, is presented. Then, computational details are given in Sect. 3. The main results concerning the pattern for central, hydrogen and halogen substituent atoms are given in Sect. 4. Concluding remarks are given in Sect. 5.

2 Theory

Within the relativistic framework, the description of the electronic structure of a molecule, in the absence of any external magnetic field, is given by the Dirac-Coulomb-Breit hamiltonian

$$H^B = H^D + V^C + V^B, \quad (1)$$

where H^D stands for the one-body Dirac Hamiltonian for a particle in the field of the fixed nuclei of the molecule,

$$H^D = \sum h^D(i) \quad (2)$$

where

$$h^D(i) = c\boldsymbol{\alpha}\cdot\mathbf{p}_i + (\beta - 1)c^2 - \sum_A \frac{Z_A}{r_{iA}}, \quad (3)$$

and V^C and V^B stand for the Coulomb and Breit two-body interaction operators, respectively, written in atomic units ($e = \hbar = m = 1$, i.e., $\alpha = 1/c$). The energy spectra of the Dirac equation

$$H^D\Psi = E\Psi \quad (4)$$

have two different solutions; a branch of positive energy states containing bonded and virtual states, and a branch of negative-energy states that can be considered as virtual states for perturbative calculation of properties.

The interaction of that system with an external magnetic field is accounted for by the minimal coupling prescription leading to the introduction of the perturbative Hamiltonian

$$V = c\boldsymbol{\alpha}\cdot\mathbf{A}, \quad (5)$$

describing the interaction between the electrons and the external magnetic field $\mathbf{B} = \nabla \times \mathbf{A}$, where $\boldsymbol{\alpha} = (\alpha_x, \alpha_y, \alpha_z)$ are the 4×4 Dirac matrices, which can be written in terms of the 2×2 Pauli matrices $\boldsymbol{\sigma} = (\sigma_x, \sigma_y, \sigma_z)$ as

$$\boldsymbol{\alpha} = \begin{pmatrix} 0 & \boldsymbol{\sigma} \\ \boldsymbol{\sigma} & 0 \end{pmatrix} \quad (6)$$

and $\mathbf{A} = \mathbf{A}_N + \mathbf{A}_B$ is the vector potential that involves the sum of the nuclear and external vector potentials

$$\mathbf{A}_N = \frac{1}{c^2} \sum_K \frac{\boldsymbol{\mu}_K \times \mathbf{r}_K}{r_K^3}, \quad (7)$$

$$\mathbf{A}_B = \frac{1}{2}\mathbf{B} \times \mathbf{r}_G = \frac{1}{2}\mathbf{B} \times (\mathbf{r} - \mathbf{R}_G). \quad (8)$$

$\boldsymbol{\mu}_K$ represents the nuclear magnetic dipole moment of the nuclear spin \mathbf{I}_K , \mathbf{r}_K is the nuclear position and the gauge origin of the external magnetic field set at the point \mathbf{R}_G .

In the relativistic regime, the magnetic molecular properties which depends bilinearly on the magnetic potential V of Eq. 5 such as the nuclear magnetic shielding can be obtained from relativistic linear response theory [20]

$$\sigma(K) = \langle\langle \mathbf{V}_K; \mathbf{V}_B \rangle\rangle \quad (9)$$

$$\mathbf{V}_K = \boldsymbol{\alpha} \times \frac{\mathbf{r}_K}{r_K^3} \quad (10)$$

$$\mathbf{V}_B = \frac{1}{2}\boldsymbol{\alpha} \times \mathbf{r}_G \quad (11)$$

or explicitly, the total tensor is written as

$$\sigma = \sum_{ij,ab} \mathbf{V}_{\text{Bia}}(\mathbf{P}^{-1})_{ia,jb} \mathbf{V}_{Njb} + c.c. \quad (12)$$

In Eq. 12, \mathbf{P}^{-1} is the principal propagator matrix, (i, j) indices run over all occupied molecular orbitals, and (a, b) indices run over all virtual positive or negative-energy molecular states. The actual form of the principal propagator depends on the level of approximation in which it is calculated.

For the calculation of response properties like the NMR spectroscopic parameters, the first-order approximation to the polarization propagator is the same as the time-dependent HF approximation and the fully coupled HF method. At the first-order or random-phase approximation (RPA), first-order correlation is included in both the ground and the excited states [26]. Within this level of approach, the matrix \mathbf{A} is calculated to first order and \mathbf{B} to zeroth order in the so called fluctuation potential. Then,

$$\mathbf{P} = \begin{pmatrix} \mathbf{A} & \mathbf{B}^* \\ \mathbf{B} & \mathbf{A}^* \end{pmatrix} \quad (13)$$

where \mathbf{A} and \mathbf{B} are given by

$$\begin{aligned} \mathbf{A}_{ia,jb} &= (\epsilon_i - \epsilon_a)\delta_{ij}\delta_{ab} + (ai|bj) - (ab|ij) \\ \mathbf{B}_{ia,jb} &= (ja|ib) - (jb|ia) \end{aligned} \quad (14)$$

Within the complete relativistic polarization propagator approach (RPPA) [20], it has non-sense to consider

separately both kind of contributions, e.g., para- and diamagnetic to the nuclear magnetic shielding. In fact, only the total shielding is gauge independent. Within RPPA theory that separation arises naturally when mixed contributions (virtual positive- and virtual negative-energy electronic states) to the perturbed matrix elements are neglected [21].

The LR-ESC method was presented with some detail elsewhere [6, 19]. The Breit-Pauli perturbative theory is completely equivalent to it [7, 14]. We give here a very brief introduction to it for completeness and also an idea of GESC scheme. All interacting Hamiltonians are given in SI units. In the second paper on the LR-ESC method, relativistic effects were splitted up in two kind of terms (in line with the proposal of Ref. [7]): (A) passive and (B) active. Within the passive effects, we collect such relativistic effects that arise from the unperturbed molecular states. They can also be divided in two: (a) spin dependent

$$\sigma^{\text{SO-I}} = \langle\langle H^{\text{FC+SD}}; H^{\text{OZ}}; H^{\text{SO}} \rangle\rangle = \sigma^{\text{SO-I(FC+SD)}} \quad (15)$$

and (b) scalar

$$\begin{aligned} \sigma^{\text{MV(Dw)}} &= \sigma^{p,\text{MV(Dw)}} + \sigma^{d,\text{MV(Dw)}} \\ &= \langle\langle H^{\text{PSO}}; H^{\text{OZ}}; H^{\text{MV(Dw)}} \rangle\rangle + \langle\langle H_{\text{dia}}; H^{\text{MV(Dw)}} \rangle\rangle \end{aligned} \quad (16)$$

where

$$\begin{aligned} H^{\text{FC+SD}} &= \frac{1}{2mc} \boldsymbol{\sigma} \cdot \left(\frac{8\pi}{3} \boldsymbol{\mu}_M \delta(r_M) + \frac{3(\boldsymbol{\mu}_M \cdot \mathbf{r}_M) \mathbf{r}_M - r_M^2 \boldsymbol{\mu}_M}{r_M^5} \right) \\ H^{\text{OZ}} &= \frac{1}{2mc} \mathbf{L} \cdot \mathbf{B} \\ H^{\text{SO}} &= \frac{1}{4m^2 c^2} \boldsymbol{\sigma} (\nabla V_C \times \mathbf{p}) \end{aligned} \quad (17)$$

and

$$\begin{aligned} H^{\text{PSO}} &= \frac{1}{mc} \boldsymbol{\mu}_M \cdot \frac{\mathbf{L}_M}{r_M^3} \\ H^{\text{MV}} &= -\frac{1}{8m^3 c^2} p^4 \\ H^{\text{Dw}} &= \frac{1}{4m^2 c^2} \nabla^2 V_C \\ H_{\text{dia}} &= \frac{1}{2mc^2} \left[(\boldsymbol{\mu}_M B) \left(\frac{r_M r_0}{r_M^3} \right) - (\boldsymbol{\mu}_M r_0) \left(\frac{r_M B}{r_M^3} \right) \right] \end{aligned} \quad (18)$$

Active relativistic effects come from magnetic field-dependent operators yielding relativistic corrections. They arise from the effects of small components and the “normalization” of the large component within the ESC approach.

Again they are (a) spin-dependent

$$\begin{aligned} \sigma^{\text{SZ-K}} &= \langle\langle H^{\text{FC+SD}}; H^{\text{SZ-K}} \rangle\rangle \\ \sigma^{\text{BSO}} &= \langle\langle H^{\text{FC+SD}}; H^{\text{BSO}} \rangle\rangle \end{aligned} \quad (19)$$

and (b) scalar

$$\begin{aligned} \sigma^{p,\text{OZ-K}} &= \langle\langle H^{\text{PSO}}; H^{\text{OZ-K}} \rangle\rangle \\ \sigma^{p,\text{PSO-K}} &= \langle\langle H^{\text{PSO-K}}; H^{\text{OZ}} \rangle\rangle \\ \sigma^{\text{dia-K}} &= \langle H^{\text{dia-K}} \rangle \\ &= \left\langle -\frac{1}{4m^3 c^4} \left[2 \left(\frac{\boldsymbol{\mu}_M \cdot \mathbf{L}_M}{r_M^3} \right) (\mathbf{B} \cdot \mathbf{L}_M) + \mathbf{B} \cdot \mathbf{B}_M \right. \right. \\ &\quad \left. \left. + 2(\mathbf{A}_M \cdot \mathbf{A}_B) p^2 + 2\pi(\boldsymbol{\mu}_M \cdot \mathbf{B}) \delta(r_M) \right] \right\rangle \end{aligned} \quad (20)$$

where

$$\begin{aligned} H^{\text{SZ-K}} &= \frac{-1}{8m^3 c^3} [3(\boldsymbol{\sigma} \cdot \mathbf{B}) p^2 - (\boldsymbol{\sigma} \cdot \mathbf{p})(\mathbf{p} \cdot \mathbf{B})] \\ H^{\text{BSO}} &= \frac{1}{4m^2 c^3} \nabla V_C \times (\mathbf{B} \times r_0) \\ H^{\text{OZ-K}} &= \frac{-1}{4m^3 c^3} (L_B) p^2 \\ H^{\text{PSO-K}} &= -\frac{1}{4m^3 c^3} \left\{ \frac{\boldsymbol{\mu}_M L_M}{r_M^3}, p^2 \right\} \end{aligned} \quad (21)$$

The electronic mechanisms that underlie few of these perturbative Hamiltonians need more explanation. The $H^{\text{OZ-K}}$ Hamiltonian refers to the orbital-Zeeman interaction scaled by $\frac{1}{c}$ of the kinetic energy, KE, operator. There is another interesting Hamiltonian, the $H^{\text{PSO-K}}$ which refers to the paramagnetic nuclear spin-electron orbital mechanism scaled by $\frac{1}{c}$ of the KE operator.

In Sect. 4, we will need to consider the addition of some terms in order to better analyze the electronic origin of the shieldings. Then, we shall have the following terms:

$$\begin{aligned} \sigma^{\text{LPK}} &= \sigma^{p,\text{OZ-K}} + \sigma^{p,\text{PSO-K}} = \sigma^{\text{L-PSO-K}} \\ \sigma^{\text{PSO-OZ}} &= \sigma^{p,\text{MV}} + \sigma^{p,\text{Dw}} \\ \sigma^{\text{Dia}} &= \sigma^{d,\text{MV}} + \sigma^{d,\text{Dw}} + \sigma^{\text{dia-K}} \end{aligned} \quad (22)$$

σ^{LPK} is a passive, scalar, and third-order contribution to the shielding which combines both the PSO and the orbital-Zeeman mechanisms with the Mass-velocity and Darwin perturbative Hamiltonians.

It is important at last to give an introduction to the Generalized elimination of small component (GESC) approach which is an alternative scheme developed to evaluate the electron-positron contribution to magnetic shielding tensor [32]. This scheme is based on two-component Breit-Pauli spinors, where the elimination of the small component is applied to the inverse propagator matrix of e-p pairs. In this way, the effect of the positronic manifold is expressed as an operator acting on Breit-Pauli

spinors. Such operator resumes the relativistic correction arising from the e-p part as a geometric series and introduces the whole account of such terms.

3 Computational details

All calculations of NMR nuclear magnetic shieldings were performed with DIRAC [23] program package in a cluster of 9 nodes of Sun Fire X2200 M2 with two dual-core processors each, and the non-relativistic calculation with all corrections given by the LR-ESC was performed with DALTON program package [44], with the exception of some contributions [40] which were implemented in a local version of DALTON v2.0.

For NR-limit calculations, the speed of light was taken as 10 times c ($c = 137.0359998$ a.u.). The geometries for the SnH_3X ($\text{X} = \text{F}, \text{Br}, \text{I}$), SnH_2XY ($\text{X}, \text{Y} = \text{F}, \text{Br}, \text{I}$), and PbH_3X ($\text{X} = \text{F}, \text{Br}, \text{I}$) model compounds were optimized using the module OPTIMIZE of the DIRAC code. For the calculation of relativistic corrections, the gauge origin was placed at the position of the atom for which the corrections were calculated.

The gaussian nuclear model was used in all calculations though perturbative hamiltonians do not include the correction due to such option about the nuclear model. In order to be completely coherent in the theoretical model, one should introduce the same nuclear model in both the unperturbed wavefunction and the perturbation operators. Still our option is more realistic than such which consider in both cases a nuclear point charge.

The UKB prescriptions were applied to generate small components basis set from large components basis set in the four-component calculations. Sadlej basis sets [45–48] were chosen in most cases in the four-component calculations. Several more tight and diffuse Gaussian functions were included to get converged results. The scheme for including more Gaussian functions was the usual one: (1) tight basis functions were added to s, p, d, f and g (only for Pb atom) blocks, in the four-component calculations, with exponents related as $\alpha_{i+1}/\alpha_i = 3$ from the largest exponent of the each block; (2) diffuse basis functions were not necessary to include in the d and f blocks because they do not change the shieldings values significantly.

Faegri's basis sets [49] were used for Pb atom with more tight and diffuse basis functions added following the scheme mentioned above.

For the non-relativistic calculations, the augJun3 basis set was used [6]. This basis is built up from the total uncontraction and the addition of both tight and diffuse functions of the aug-cc-pVTZ-J basis set of Ref. [50]. Tight and diffuse functions were included following the relations between exponents given by $\alpha_{i+1}/\alpha_i = 2$, though in few

cases, this relation was taken as equal to 3. The criteria for selecting a factor 2 or 3 were the consideration of the value of the new exponent being this large enough or not. For Pb atom, the Faegri basis set was applied.

The whole basis sets with all previous considerations and all geometrical parameters used in calculations are given as Supporting Information.

4 Results and discussion

All fully relativistic calculations were performed within the relativistic polarization propagator scheme at RPA level of approach and semi-relativistic calculations within the LR-ESC approach. We show nuclear magnetic shieldings of central heavy atoms (Sn and Pb) and substituents (H, F, Br and I).

It is worth to express that GESC corrections were only calculated for the SnH_4 system, though included as an estimate in all results of tin-containing molecules. Such corrections should vary with the inclusion of different substituents.

We have chosen good enough basis set for all our common origin shielding calculations. As observed in Table 1, the basis set used in our work (the second in the Table) for SnH_2F_2 is such that converged results are obtained. A similar behavior is obtained for all other molecular systems containing atoms of H, F, Cl, Br, I, Sn, and Pb.

As shown in Table 2, we have studied the gauge origin dependence and found that the quality of the basis set is such that there is no significant difference when calculations are performed with the gauge origin at the nucleus of interest or in a vicinal heavy atom.

4.1 The nuclear magnetic shielding on the central (Sn and Pb) atom

We first analyze the pattern of relativistic effects on Sn. As shown in the last two columns of Table 3, the total LR-ESC results corrected by GESC closely reproduce benchmark calculations by the RPPA method for systems as heavy as SnH_2I_2 . Differences are close to $\pm 1\%$, and its largest value is 1.5% for the SnH_4 being the difference of -1.3% for SnH_2I_2 , which is the heaviest system studied right now with ab initio 4-component MO methods.

Our full relativistic results are in line with few of previous available calculations like that from Jaszunski and Ruud [35]. They have calculated the shielding of Sn and Pb for XH_4 systems at SCF and CAS level of approach. Our RPA and their SCF results are close to each other for Sn: 4,126.10 ppm versus 3,972.23 ppm but not so close for Pb: 12,931.8 ppm versus 10,004.06 ppm. In this last case, our

Table 1 Basis set convergence for all LR-ESC mechanisms

Sn	F	H	X	lresc	Shield	SZ-K	BSO	LPK	SO-FC	PSO-OZ	Dia
[21s15p11d2f]	[10s5p1d]	[4s1p] ^a	Sn	3,703.2	3,084.5	2,169.8	-513.8	336.8	16.9	-355.1	-1,036.0
[25s21p16d5f]	[15s9p6d2f]	[10s3p2d] ^b	Sn	3,817.5	3,098.8	2,220.4	-460.6	349.0	9.8	-359.9	-1,040.0
[33s27p18d5f3g1h]	[15s9p6d2f]	[10s3p2d] ^c	Sn	3,801.4	3,100.7	2,206.2	-467.7	350.9	8.5	-360.1	-1,037.1
[21s15p11d2f]	[10s5p1d]	[4s1p] ^d	F	444.1	445.1	11.3	-3.0	1.7	3.1	-7.6	-6.4
[25s21p16d5f]	[15s9p6d2f]	[10s3p2d] ^e	F	452.2	450.2	12.2	-3.0	1.7	2.5	-4.7	-6.6
[33s27p18d5f3g1h]	[15s9p6d2f]	[10s3p2d] ^f	F	452.2	450.1	12.2	-3.0	1.7	2.4	-4.6	-6.7

In all cases uncontracted basis set were used

^a cv2z for Sn and cc-pCVDZ for F, H. (135/30/7 = 209)

^b augJun3 for Sn, F and H. (203/86/29 = 433)

^c cv4z for Sn and augJun3 for F, H. (277/86/29 = 507)

^d cv2z for Sn and cc-pCVDZ for F, H (135/30/7 = 209)

^e augJun3 for Sn, F and H (203/86/29 = 433)

^f cv4z for Sn and augJun3 for f, H (277/86/29 = 507)

Table 2 Gauge origin dependence for LR-ESC calculations on SnH₂F₂ with augJun3 basis set

SnH ₂ F ₂	Atom	LRESC	NR-shield	SZ-K	BSO	LPK	SO-FC	PSO-OZ	Dia
Gauge on Sn	Sn	3,817.5	3,098.8	2,220.4	-460.6	349.0	9.8	-359.9	-1,040.0
Gauge on F	Sn	3,816.9	3,098.8	2,220.4	-461.4	347.0	10.0	-358.4	-1,039.6
Gauge on F	F	452.2	450.2	12.2	-3.0	1.7	2.5	-4.7	-6.6
Gauge on Sn	F	453.5	450.2	12.2	-3.1	0.2	2.5	-3.3	-5.2

Table 3 Nuclear magnetic shielding on Sn atom in SnH₂XY model compounds (X, Y = H, F, Cl, Br, I)

Molecule	NR	SZ-K	BSO	LPK ^a	SO ^b	SO ^c	PSO-OZ	Dia	GESC	Total	4c
SnH ₄	3,270.2	2,220.8	-461.1	333.7	19.0	-57.7	-307.5	-1,039.8	210.4	4,188.1	4,126.1 ^d
SnH ₃ F	3,039.0	2,220.7	-460.9	361.5	71.5	-73.4	-367.9	-1,040.0	210.4	3,961.1	3,908.3
SnH ₃ Cl	3,055.3	2,220.7	-460.9	356.1	62.3	-68.3	-356.7	-1,040.0	210.4	3,978.9	3,912.4
SnH ₃ Br	3,027.8	2,220.6	-460.6	355.5	66.5	-60.9	-351.6	-1,039.8	210.4	3,967.0	3,921.0
SnH ₃ I	3,083.4	2,220.7	-460.6	352.8	130.7	-56.3	-351.0	-1,042.1	210.4	4,088.1	4,076.0
SnH ₂ F ₂	3,098.8	2,220.4	-460.6	353.0	85.4	-75.6	-359.9	-1,040.0	210.4	4,027.9	3,979.0
SnH ₂ Cl ₂	2,936.5	2,220.5	-460.6	365.3	93.9	-74.2	-383.8	-1,040.2	210.4	3,867.8	3,824.2
SnH ₂ FBr	2,993.0	2,220.5	-460.5	365.6	144.1	-77.6	-385.3	-1,040.8	210.4	3,969.5	3,943.4
SnH ₂ Br ₂	2,921.9	2,220.5	-460.2	376.3	190.3	-73.8	-399.8	-1,041.6	210.4	3,944.2	3,932.4
SnH ₂ FI	2,965.2	2,220.5	-460.3	371.4	253.1	-77.8	-393.3	-1,041.9	210.4	4,047.3	4,065.7
SnH ₂ BrI	2,922.3	2,220.5	-460.0	378.7	308.3	-71.7	-407.6	-1,042.8	210.4	4,058.2	4,092.1
SnH ₂ I ₂	2,939.8	2,220.6	-460.0	373.0	328.5	-59.4	-398.6	-1,044.2	210.4	4,110.4	4,162.6
PbH ₄	6,868.6	9,904.1	-2,003.3	1,642.5	64.6	-263.9	-1,485.9	-4,676.1		10,050.8	1,2931.8 ^e
PbFH ₃	6,476.3	9,903.9	-2,003.0	1,786.5	330.4	-344.1	-1,816.8	-4,676.2		9,657.1	12,937.0
PbBrH ₃	6,428.8	9,903.8	-2,002.5	1,746.6	203.2	-293.4	-1,695.4	-4,677.0		9,614.0	12,727.0
PbIH ₃	6,561.0	9,713.3	-2,185.3	1,585.5	316.5	-275.6	-1,615.8	-4,657.3		9,442.3	13,262.2

All values are given in ppm

^a LPK means the L-PSO-K mechanism

^b FC contribution to the passive SO-I correcting term

^c SD contribution to the passive SO-I correcting term

^d The SCF (CAS) value from Ref. [35] is 3,972.23 (4,017.54) ppm

^e The SCF (CAS) value from Ref. [35] is 10,004.06 (10,091.51) ppm

LR-ESC calculation gives 10,050 ppm without corrections from GESC model.

Our results are also in a qualitative agreement with that of Nakatsuji et al. [33, 34] and Bagno et al. [36] for $X = \text{Sn}$. They applied the SO-UHF/finite perturbation and ZORA SO methods, respectively. A difference between ours and theirs is of around 15 % that may come from the inclusion within the LR-ESC/BPPT methods of some non-SO correcting terms. As will be shown in the next subsection, there is no electron correlation effect that could explain this difference.

The NR behavior of $\sigma(\text{Sn})$ is such that it becomes less and less shielded as substitutes become heavier. This is not the case when relativistic effects are included. It is worth to mention that $\sigma(\text{Sn})$ has its largest full relativistic value when $X = Y = \text{I}$.

As observed in Table 3 most of relativistic corrections are quite similar to each other with no dependence of the molecular system under study. There are only three correcting terms that have variations with the halogen substitutes, being one of them of SO-type, SO-I(FC), and two non-SO terms, the PSO-OZ (columns 6 and 8) and the L-PSO-K (column 5) terms. In the case of PSO-OZ, it arise as the sum of two related terms: PSO-OZ-X ($X = \text{MV}$ or DW) and the L-PSO-K term arise from the sum of L-PSO-K and L-K-PSO terms. The SO-I(FC) contribution is the largest and specially for substitutes like Br and I [34, 36]. All these three contributions are of paramagnetic type and are different in magnitude. The SO-I(FC) term is modified at last in one order of magnitude when substituents are changed.

Do these three mechanisms have any interaction in common? The OZ Hamiltonian of Eq. 17 is involved in all of them. Two are passive and of third-order: $\sigma^{SO-I(FC+SD)}$ and $\sigma^{p,(MV+Dw)}$; and one is active and of second-order: $\sigma^{L-PSO-K}$. The $\sigma^{SO-I(FC+SD)}$ contribution, which corresponds to the HALA effect, has the largest variation: around +300 ppm, and its effect is shielding with the halogen substituent and increases when the atomic number of such substituents is increased. The other passive mechanism, PSO-OZ, is of deshielding type with its largest variation of around -100 ppm. The active mechanism, L-PSO-K, is of shielding type with a maximum variation of +40 ppm. As observed in Figs. 1 and 2, results of calculations with the LR-ESC method follow closely the benchmark results, though there appears a difference that grows with both the weight of the halogen substituent and the number of heavy substituents.

For SnH_3X ($X = \text{H}, \text{F}, \text{Br}, \text{I}$) molecular systems, the value of SO-I(FC + SD) (columns 6 and 7 of Table 3) grows as its halogen substituent becomes heavier. It starts with -38.7 ppm for $X = \text{H}$ and goes to 74.4 for $X = \text{I}$: it changes its sign and varies 113.1 ppm. A similar pattern

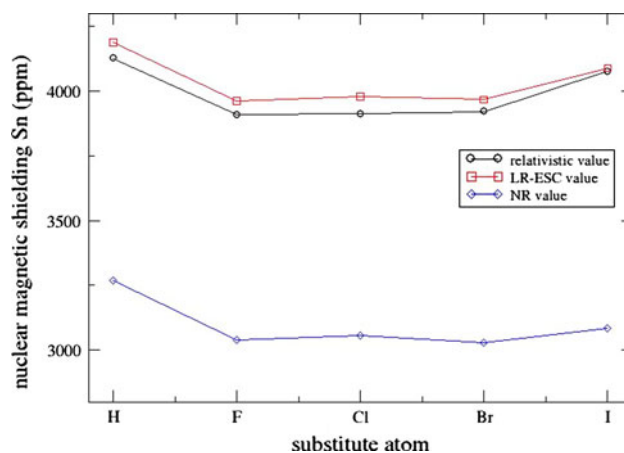


Fig. 1 Nuclear magnetic shielding on Sn atom in SnH_3X model compounds

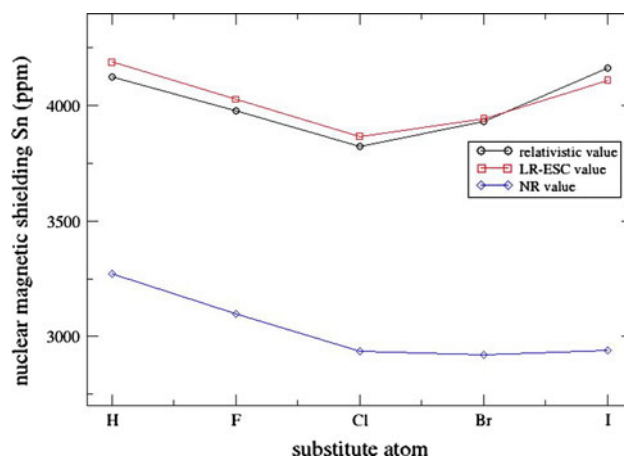


Fig. 2 Nuclear magnetic shielding on Sn atom in SnH_2X_2 model compounds

can be observed for SnH_2X_2 and SnH_2XY systems, though in these cases, there is no a change of sign but an increment that is of 300 ppm for the highest variation. The SO-I contributions we have obtained from LR-ESC model can be compared with calculations by Bagno et al. [36]. In their study they worked with SnMe_3X and SnMe_2X_2 . They found that the variation of the SO contribution for $\sigma(\text{Sn})$ when considering both molecular systems is 19 ppm for $X = \text{Cl}$, 140 ppm for $X = \text{Br}$ and 372 ppm for $X = \text{I}$. In our case where the molecular systems does not have Me but H, the values are close to 14, 120, and 200 ppm, respectively.

The PSO-OZ term is much less dependent of the chemical environment, and the largest variation appears when the substituents are not heavy. For the SnH_3X systems when $X = \text{H}$ is replaced by F, the contribution of this term changes -60.4 ppm but then for $X = \text{Br}$, such variation is of -44.1 ppm which is the same when $X = \text{I}$. This

behavior is similar for the other two systems: SnH_2X_2 and SnH_2XY .

Even though the SO-I(FC) terms show the largest variations, they are attenuated by the variations of the PSO-OZ terms (both have opposite behavior). When we include the SO-I(SD) terms, from SnH_4 to $\text{SnH}_3\text{I}\sigma(\text{Sn})^{\text{SO-I(FC+SD)}}$ varies 113.1 ppm but $\sigma(\text{Sn})^{\text{SO-I+PSO-OZ}}$ varies 69.6 ppm. On the other hand when considering what happens for SnH_2H_2 , such variations are 307.8 ppm and 216.7 ppm, respectively.

The L-PSO-K correcting term modifies its values as the whole molecular system becomes heavier though quite smoothly: only grows 45 ppm (from 333.7 ppm to 378.7 ppm) when SnH_4 is replaced by SnH_2BrI . At the same time, the PSO-OZ mechanism give more negative contributions. Its largest variation is given for the same molecular systems: SnH_4 , -307.5 ppm and SnH_2BrI , -407.6 ppm. Then, the PSO-OZ mechanism becomes more paramagnetic when the substitutes are heavier. The opposite is observed for the L-PSO-K mechanism. $\sigma^{p,\text{OZ-K}}$ and $\sigma^{p,\text{PSO-K}}$ have a difference of which operator is enhanced by the KE operator. It seems that the enlargement of the PSO contribution due to the effect on it of the KE operator is more efficient when the molecular systems do have a central heavy atom like Sn or Pb. In the case of the Sn shieldings, $\sigma^{p,\text{PSO-K}}$ varies 42.0 ppm between SnH_4 and SnH_2BrI , and $\sigma^{p,\text{OZ-K}}$ varies in this two systems only 2.9 ppm. The corresponding tables are given as Supporting Information. A similar pattern is observed for the shielding on halogen substitutes but it also occurs that when the system has three non-hydrogen atoms, $\sigma^{p,\text{PSO-K}}$ has quite similar values. It is also observed that $\sigma^{p,\text{PSO-K}} \approx 2 \sigma^{p,\text{OZ-K}}$.

In the CH_3X ($\text{X} = \text{Br}, \text{I}$) systems, both terms contribute with small and close results [19]. The it is clear that there is a proper relativistic effect on the central heavy atom that is also affected by the presence of more than one vicinal heavy atom.

On the other hand, the diamagnetic relativistic corrections are almost the same in the whole set of systems under study which means that they are not affected by the chemical environment.

In Fig. 1, we show the pattern of relativistic, non-relativistic, and the LR-ESC values of $\sigma(\text{Sn})$ as a function of the substituent in SnH_3X ($\text{X} = \text{H}, \text{F}, \text{Br}, \text{I}$) model compounds. The largest variation on $\sigma(\text{Sn})$ is found when H is replaced by F. Then, the NR results grows up slowly as the other substituents are introduced though they grow more quickly for both LR-ESC and 4c methods. There is a difference of 917.9 ppm between NR and LR-ESC results and a difference of less than 70 ppm (less than 2%) between LR-ESC and full relativistic results in SnH_4 . More important is the fact that LR-ESC numbers can follow quite

closely its full relativistic numbers. A similar pattern is observed in Fig. 2 where the system can contain three heavy atoms. In the same figure, we also observe that the difference between LR-ESC and full relativistic results grows up as the X substituent becomes heavier. Still such a difference is lower than 2% for the heaviest molecular system: SnH_2I_2 .

In a recent work, we have proposed a new effect that appears on systems which contain more than one heavy atom, i.e., the heavy atom effect on a vicinal heavy atom or HAVHA effect [25]. We can now express that such effect arises from spin-orbit interactions.

Relativistic effects on Sn atoms can be analyzed following the usual procedure $\sigma^{\text{R-NR}}(\text{X},\text{Y})/\sigma^{\text{NR}}(\text{X},\text{Y})$. In the case of SnH_4 , relativistic effects amount 26.2% (HAHA effect). From this result, we can analyze the HAVHA effects considering the heavier substituents. For SnH_3I , relativistic effects on Sn grow to 32.2% (contributions from HAVHA and HAHA effects) which means that the contribution of the HAVHA effect is close to 6% in a clear agreement with our previous results [25]. Let us see now which is the effect of a second substituent on the central atom. When the second substituent is F (SnFIH_2), the total relativistic effects are of 37.1%, when Br (SnH_2BrI) they are of 40.0%, and when I (SnH_2I_2) they are of 41.6%. This shows that the HAVHA effect grows with the weight of the heavy substitutes, being of 16.4% for the heaviest system under study here.

In Table 3, it is observed that all other mechanisms, SZ-K and BSO are insensitive to the chemical environment.

4.1.1 Electron correlation contributions

From previous studies, it is known that electron correlation effects are important for SO-I contributions [29] though negligibly small for SO-II or BSO (in our notation) contributions in the series CH_3X ($\text{X} = \text{H}, \text{F}, \text{Br}, \text{I}$) [30] and also the fact that $\sigma_{\text{C}}^{\text{SO-I}} \gg \sigma_{\text{C}}^{\text{SO-II}}$. In such systems $\sigma_{\text{C}}^{\text{SO-I}}$ represents the main HALA effect which diminishes the NR results.

The largest electron correlation effects on $\sigma_{\text{C}}^{\text{SO-I}}$ of CH_3X were obtained for CH_3I . For FC-I, it means 30% or $\sigma_{\text{C}}^{\text{FC-I}} = 49.17$ (36.81) ppm at SCF (RAS) level of approach. This SCF contribution of $\sigma_{\text{C}}^{\text{FC-I}}$ represents 25% of its σ^{NR} contribution. In the case of CH_3Br , the $\sigma_{\text{C}}^{\text{FC-I}}$ contribution is 10% of its NR value.

When the central atom is Sn (instead of C), the relative contribution between SO-I and BSO is reversed as observed in Table 3. In this last case, $\sigma_{\text{Sn}}^{\text{BSO}} \gg \sigma_{\text{Sn}}^{\text{SO-I}}$ in absolute values. It happens also that the SO-I contribution represents 4.2% of the NR counterpart for SnH_3I . This may mean that the HALA-type contribution is strongly

diminished when such kind of effects is applied on two vicinal heavy atoms. On the other hand the BSO contribution grows from 0.2% with respect to its NR contribution in CH_3I to 14.94% in SnH_3I . The BSO contribution is almost the same in the whole set of systems we have studied here. The largest FC-I type contribution was obtained for SnH_2I_2 which represents 11.2% of its NR contribution.

Then, if electron correlation has a similar percentual contribution to SO-I in our family of molecular systems, it will not change the overall behavior just commented. In line with this there is the study by Jaszunski and Ruud [35] where they have shown that electron correlation effects on Sn or Pb central atom for XH_4 ($X = \text{Sn}$ and Pb) are almost zero. Electron correlation affects only the NR contributions.

4.1.2 Magnetic shielding of Pb

We want now to analyze the shieldings on the central atom when it (tin) is replaced by lead for PbH_3X ($X = \text{H}, \text{F}, \text{Br}, \text{I}$) molecular systems. Non-relativistic shieldings are given in Table 3.

It is observed that the LR-ESC method gives results that are 20% smaller than that of the 4c method. This difference was observed previously [31] though we did not include in this comparison the extra diamagnetic contribution that arises from GESC model. We are unable to do it at the moment. In any case, we stress here the fact that the total relativistic effects are of the same size of NR contributions in these systems. The tendency of $\sigma(\text{Pb})$ is observed in Fig. 3 where we display the shielding as a function of substitutes.

As happens to $\sigma(\text{Sn})$, the electronic mechanisms that are affected by the electronic environment are SO-I(FC+SD) and PSO-OZ; there are also variations in the L-PSO-K

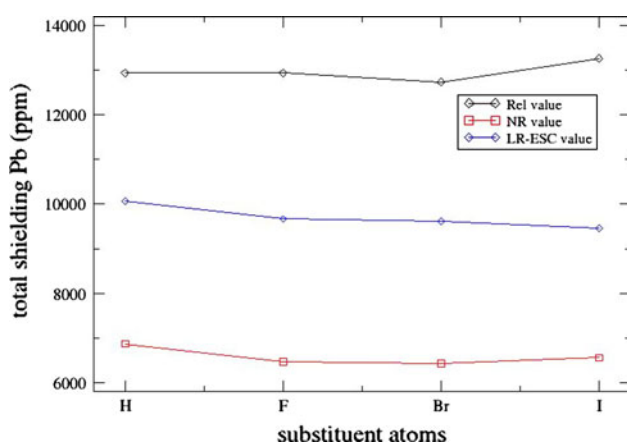


Fig. 3 Nuclear magnetic shielding on Pb atom in PbH_3X model compounds

mechanism. The SO-I(FC+SD) mechanism is largely modified though they do not have an strong influence on the total values. Such contributions are of -199.3 ppm for PbH_4 and -13.7 ppm for PbH_3F ; this variation represent only 1.4% of the total. When we substitute one H by Br or I the variation is even smaller.

On the other hand, the contributions of the PSO-OZ terms are modified little larger though they do not have influence on the total shieldings. For PbH_4 , its value is $-1,485.9$ ppm, and $-1,816.8$ ppm for PbH_3F . The amount of this variation is of 2.6% when compared with the variation of the total shielding. For the other substitutes like Br and I, the variation is even smaller. The last term which is also varying is L-PSO-K, but its contribution is smaller than 1%. Then, the three terms which are modified by substitutes in PbH_3X do not contribute much to the total variations of $\sigma(\text{Pb})$. It should be stressed here that the variation of SO-I is opposite to that of PSO-OZ mechanism though of a similar size.

The magnitude of relativistic effects on Pb is a lot larger than on Sn. The non-relativistic contribution to $\sigma(\text{Sn})$ is half its contribution to $\sigma(\text{Pb})$, though the relativistic effects on $\sigma(\text{Sn})$ are 1/3 of that on $\sigma(\text{Pb})$. This shows how important the latter are when one goes one row down in the periodic table. In line with this, the relativistic contributions on the different mechanisms are four to five times larger for Pb than for Sn. The mechanism that is more influenced by relativity is SZ-K.

4.2 Analysis of the nuclear magnetic shielding on the substituent atom

In Table 4 $\sigma(X)$ ($X = \text{F}, \text{Br}, \text{I}$) is given. As happens for Sn and Pb, most of correcting terms do not change its values with the variation of the other substituent. Only SO-I(FC), PSO-OZ, and L-PSO-K are sensitive to such variations. The LR-ESC method gives close values to the four-component calculations.

The pattern of variations of the three terms mentioned above is such that the full relativistic values follow their NR counterparts. Both PSO-OZ and L-PSO-K have opposite signs and close absolute values. Still they feel the presence of another non-hydrogen in the same molecule with a different response. Let us analyze the system SnH_2XBr in some more detail. When $X = \text{H}$, the absolute value of L-PSO-K is larger than PSO-OZ, but this relationship is reversed when X is any of the halogen. Then, the total value of $\sigma(\text{Br})$ becomes more negative when X is any of the halogen substituent. The SO-I(FC) contribution is positive in all cases though in SnH_2F_2 .

As can be seen in Figs. 4 and 5 the overall tendency is the same in both regimes, relativistic and non-relativistic. For the shielding of F, relativistic effects becomes more

Table 4 Nuclear magnetic shielding on the substituent atom in SnH₂XY model compounds (X, Y = H, F, Cl, Br, I)

Molecule	X	NR	SZ-K	BSO	LPK ^a	SO-I ^b	PSO-OZ	Dia	Total	4c
SnH ₃ F	F	499.8	12.2	-3.0	1.5	4.0	-1.4	-5.9	507.1	507.6
SnH ₂ F ₂	F	450.2	12.2	-3.0	1.5	2.5	-4.7	-9.0	452.2	453.2
SnH ₂ FBr	F	455.2	12.2	-3.0	2.1	4.9	-5.6	-7.2	458.6	461.0
SnH ₂ FI	F	458.1	12.2	-3.0	1.8	7.1	-6.7	-7.9	461.6	468.7
SnH ₃ Cl	Cl	1,170.5	83.9	-19.2	3.0	7.3	-11.3	-39.2	1,195.0	1,200.1
SnH ₂ Cl ₂	Cl	1,097.2	83.8	-19.2	4.2	7.3	-17.4	-39.2	1,116.9	1,116.1
SnH ₃ Br	Br	3,180.4	752.6	-161.1	30.5	18.4	-18.9	-350.3	3,451.6	3,475.4
SnH ₂ FBr	Br	2,917.9	752.6	-161.0	48.6	31.1	-72.5	-350.2	3,166.4	3,184.0
SnH ₂ Br ₂	Br	2,920.1	752.6	-161.0	48.6	34.5	-76.4	-350.7	3167.7	3,185.4
SnH ₂ BrI	Br	2,922.2	752.6	-160.9	49.1	38.1	-81.0	-351.3	3135.2	3,189.2
SnH ₃ I	I	5,472.6	2,642.5	-551.9	93.9	48.1	-72.7	-1,241.9	6,390.7	6,688.0
SnH ₂ FI	I	5,105.5	2,649.5	-551.8	202.2	90.4	-211.1	-1,241.6	6,042.9	6,288.8
SnH ₂ BrI	I	5,080.8	2,649.5	-551.8	206.5	99.6	-228.8	-1,242.1	6,013.6	6,253.6
SnH ₂ I ₂	I	5,126.6	2,649.5	-551.8	199.2	79.8	-193.0	-1,242.9	6,077.7	6,312.2

All values are given in ppm

^a LPK means the L-PSO-K mechanism

^b FC + SD contribution to the passive SO-I correcting term

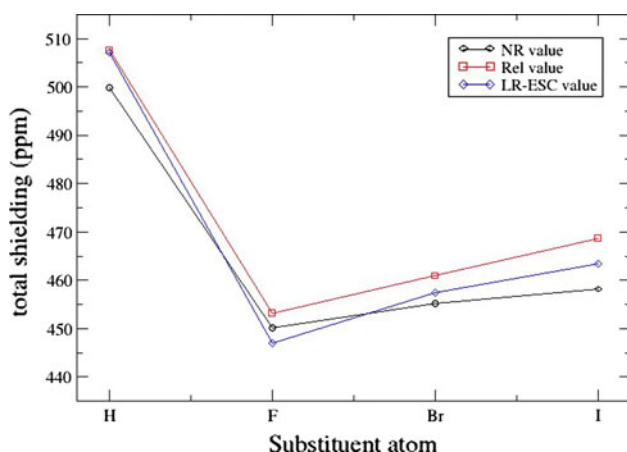


Fig. 4 Nuclear magnetic shielding on F atom in SnH₂XF model compounds

important when the other halogen substituent is more heavier. This is not the case for the shielding of I where relativistic effects are almost the same and it does not matter whether the other halogen substituent is heavy or not.

In order to get a deeper and clear understanding of relativistic effects involved in these shieldings, it is worth to define two parameters: (a) the absolute variation of the shielding $\Delta\sigma^{R(Y,X)} = \sigma^{R(Y,X)} - \sigma^{R(Y,H)}$, being the last term that corresponding to SnH₃Y, (b) the relative variation or $\delta\sigma^{R(Y,X)} = \Delta\sigma^{R(Y,X)}/\sigma^{R(Y,H)}$.

For Y = F; X = F, one obtain $\Delta\sigma^{R(F,F)} = -54.4$ ppm and $\delta\sigma^{R(F,F)} = -10.7\%$; though for Y = F; X = I se tiene $\Delta\sigma^{R(F,I)} = -38.9$ ppm and $\delta\sigma^{R(F,I)} = -7.7\%$ what means

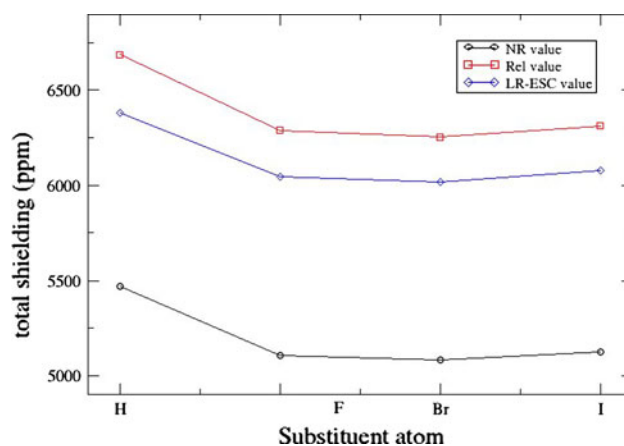


Fig. 5 Nuclear magnetic shielding on I atom in SnH₂XI model compounds

that a fluorine atom is more affected by the substitution of another fluorine than for a heavy halogen atom like I. On the other hand, if the studied shielded atom is heavier as I (Y = I) and X = F, $\Delta\sigma^{R(I,F)} = -399.2$ ppm and $\delta\sigma^{R(I,F)} = -6.0\%$, when Y = I; X = I, one has $\Delta\sigma^{R(I,I)} = -375.8$ ppm and $\delta\sigma^{R(I,I)} = -5.6\%$ which means that the shielding on the iodine atom does not change much with different halogen substituents.

Relativistic effects on a substituent atoms due to the other substituent atom ca also be analyzed through the usual manner: considering $\sigma^{R-NR(Y,X)}/\sigma^{NR(Y,X)}$. For the molecule SnFH₃ (Y = F; X = H), relativistic effects are of the order of 1.56%, though for SnIH₃ (Y = I; X = H), they are of the order of 22.2%. For Y = F; X = I,

relativistic effects are of the order of 2.31% which means that HALA effects of one substituent on the other are small, of the order of 0.75%; being the relativistic effects (HAHA + HAVHA) for $X = I$; $Y = I$ of the order of 23.1% which means that the HAVHA effects are also small in this case: of the order of 0.9% and then the HAVHA effect is less important on the substituent atom when compared to what happens for central atoms.

5 Concluding remarks

The analysis of leading relativistic corrections on the nuclear magnetic shielding of both central atoms and substitutes of SnH_2XY and PbH_3X ($X = \text{H, F, Cl, Br, I}$) with the LR-ESC scheme (including a correction that arise from the recent developed GESC formalism) is presented. The total shieldings are compared with benchmark calculations with the relativistic polarization propagator method and also with previous calculations from the literature. We found an excellent performance of LR-ESC formalism when diamagnetic terms are corrected via GESC.

The main advantage that two-component methods, like the LR-ESC/BPPT, introduce in the study of magnetic shieldings of (few) heavy atom-containing molecules is the appearance of several electronic mechanisms that can be used to get deeper insights into the electronic structure of such molecules. When a proper analysis of the pattern of variations of the shieldings can be done by considering only few electronic mechanisms, it becomes very convenient to apply the LR-ESC method for such an analysis. This is the case for the nuclear magnetic shielding of molecular models studied in this work.

We have found that most of relativistic correcting terms are not sensitive to the chemical environment. Only three of them are affected by substitutes: SO-I(FC), L-PSO-K (or LPK in short), and PSO-OZ. Only one of them is of SO-type. The other two reflect the enhancement of the PSO electronic mechanism due to a kinetic energy correcting term. The last term is always negative and opposite to the LPK. Then, its contributions are attenuated though when added to the SO-I(FC) it gives a fine tuning for reproducing the total relativistic corrections to the shieldings of central and substituent atoms. We conclude here that the HAVHA effect is due to the appearance of that contributions different of SO-I.

The largest variation of $\sigma(\text{Sn})$ corresponds to the difference of the shieldings in SnH_4 and SnH_2BrI . The HALA effect (SO-I) is of +300 ppm. The PSO-OZ term gives -100 ppm and L-PSO-K gives +40 ppm. Given that the total variation from LR-ESC is of -130 ppm we observe that the largest variation is not due to relativistic effects but due to the NR contributions: -348 ppm! Of course, one

should include relativistic effects in order to reproduce the total variations.

If relativistic effects are considered as $\sigma^{R-NR}(X, Y)/\sigma^{NR}(X, H)$, the HAHA effect for SnH_4 is $\simeq 26\%$; the HAVHA + HAHA effects for SnH_3I are $\simeq 32\%$ which imply that the pure HAVHA effect is for this last molecule of $\simeq 6\%$. When considering two heavy substitutes like SnH_2I_2 , the HAVHA + HAHA effect is $\simeq 42\%$. Then, the HAVHA effect grows now to $\simeq 16\%$ and we can conclude that the HAVHA effect grows as the weight of heavy substitutes.

The typical HALA effect is the passive third-order, SO-I term. For CH_3I molecular system the contribution of SO-I(FC) to the $\sigma(\text{C})$ is $\simeq 25\%$ of its NR contribution. When considering SnH_3I the SO-I(FC) mechanism gives a contribution of $\simeq 4\%$. Then the HALA effect is lower when the central atom is heavier, but grows with the number of vicinal heavy atoms.

When studying the behavior of the shielding of substituents, we observe that for $\sigma(\text{I})$ of SnH_3I and SnH_2I_2 systems the variation of LPK + PSO-OZ terms is vanishingly small, and SO-I terms grow around 30 ppm. Then, $\Delta\sigma^{\text{LR-ESC}} \simeq \Delta\sigma^{\text{NR}}$.

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