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Relativistic effects on nuclear magnetic shieldings of $\text{CH}_n\text{X}_{4-n}$ and CHXYZ ($\text{X}, \text{Y}, \text{Z} = \text{H}, \text{F}, \text{Cl}, \text{Br}, \text{I}$)

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Nuclear magnetic shieldings of both carbon and hydrogen atoms of haluro methyl molecules 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 such shieldings and learn whether including only few terms is enough for getting quantitative reproduction of the total shieldings or not. First, we discuss the contribution of all leading relativistic corrections to $\sigma(\text{C})$, in CHX_2I molecular models with $\text{X} = \text{H}, \text{F}$, and Cl , and show that spin-orbit (SO) effects are the main ones. After adding the SO effects to the non-relativistic (NR) results, we obtain $\sim 97\%$ (93%) of the total LRESC values for $\sigma(\text{C})$ ($\sigma(\text{H})$). The magnitude of SO terms increases when the halogen atom becomes heavier. In this case, such contributions to $\sigma(\text{C})$ can be extrapolated as a function of Z , the halogen atomic number. Furthermore, when paramagnetic spin-orbit (PSO) contributions are also considered, we obtain results that are within 1% of the total LRESC value. Then we study in detail the main electronic mechanisms involved to contribute C and H shieldings on $\text{CH}_n\text{X}_{4-n}$ ($n = 1, 3$), and CHXYZ ($\text{X}, \text{Y}, \text{Z} = \text{F}, \text{Cl}, \text{Br}, \text{I}$) model compounds. The pattern of $\sigma(\text{C})$ for all series of compounds follows a normal halogen dependence (NHD), though with different rate of increase. A special family of compounds is that of CHF_2X for which $\sigma^{\text{nr}}(\text{C})$ follows an inverse halogen dependence though the total shielding have a NHD due to the SO contributions. For the series CH_3X ($\text{X} = \text{F}, \text{Cl}, \text{Br}$ and I), we found that $\sigma^{\text{SO}} \sim Z_X^{2.53}$. Another important finding of this work is the logarithmic dependence of $\sigma^{\text{SO}}(\text{C})$ with the substituent atomic number: $\ln \sigma^{\text{SO}}(\text{C}) = A_X + a_X Z_Y$ for both family of compounds CH_2XY and CHX_2Y . We also performed four-component calculations using the spin-free Hamiltonian to obtain SO contributions within a four-component framework. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4768470>]

I. INTRODUCTION

During the last few decades relativistic effects were investigated on different theoretical grounds in order to get general patterns concerning its influence on molecular properties, specially on nuclear magnetic resonance (NMR) spectroscopic parameters.^{1–5} A great deal of efforts were oriented to learn on these matters, though until quite recently only molecules containing one heavy atom were treated with *ab initio* methods.^{6–9} Shielding calculations of Sn, Pb, and Hg in more than two-heavy-atom-containing molecules were published during the last two years.^{10–12}

For molecular systems containing halogen substituents, the normal halogen dependence, NHD, is such that the spin-orbit, SO, effects increase the shielding when both the atomic number of the halogen substituent bonded to the NMR active atom and the number of (heavy atom) substituents are larger. In this way, the active atom chemical shift, $\delta(\text{X}) = \sigma^{\text{ref}} - \sigma(\text{X})$, decreases when running the substituent from Cl to Br to I.^{13–15} In line with this finding, ^{13}C chemical shifts of halogen-substituted methanes $\text{CH}_{4-n}\text{X}_n$ ($\text{X} = \text{Br}, \text{I}$) exhibits “nonlinear NHD” with increasing n , whereas the

corresponding mixed complexes $\text{CX}_{4-n}\text{Y}_n$ (e.g., $\text{X} = \text{Br}, \text{Y} = \text{I}$) shows essentially a linear decrease.¹⁶

On the other hand, when bonds tend to have p -] mostly, the Fermi contact (FC) mechanism is very inefficient and so the SO shifts are expected to be small. Here, paramagnetic contributions (σ^p) dominate the overall shielding, resulting in an inverse halogen dependence (IHD).¹⁴

In 2005, Nakatsuji and coauthors published carbon shielding constants of methyl halides within the application of a relativistic singles and doubles configuration interaction method and relativistic coupled cluster using four-component spinors.¹⁸ They found that may not be so satisfactory because they cannot apply large enough basis sets. For equivalent tin containing molecules, Bagno and coauthors applied density functional theory methods and Slater all electron basis sets to include relativistic effects by means of the zeroth order regular approximation method up to spin-orbit coupling.¹⁷ They investigated the SO contribution to $\sigma(\text{Sn})$ in $\text{Me}_{4-n}\text{SnX}_n$ ($n = 1–4$, $\text{X} = \text{Cl}, \text{Br}$, and I), and found that such effects are quite large and positive when $n = 4$. In all cases, the SO contribution grows when n goes from $1 \rightarrow 4$. The greatest contribution occurs for $\text{X} = \text{I}$ being $|\sigma^{\text{SO}}| \simeq |\sigma^p|$. When SO terms are included, theoretical and experimental chemical shifts fit together in very good agreement. Diamagnetic terms

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are almost constant in the whole series of compounds they studied.

Relativistic effects on NMR spectroscopy shieldings, due to heavy atoms, may be of three types: (a) Effects on light atoms due to vicinal heavy atoms (HALA), which were shown to arise mainly from SO interactions.¹⁹ This electronic mechanism was first explained by Pyykkö and coauthors.²⁰ HALA effects arise mostly from “passive” third-order spin-orbit corrections through contributions of external magnetic field-free operators.^{21,22} (b) Effects of heavy atoms on themselves, known as heavy-atom effect on heavy-atom, HABA. They can be observed on heavy atom shieldings of halogen halides. In these shieldings, there is a nuclear charge scaling factor proportional to $Z^{3.0}$ for non-SO, and $Z^{3.5}$ for SO effects.^{23–25} It is worth to mention that for the hydrides series such scaling was found to be quite similar.^{25,26} The search for scaling dependences with Z for the carbon shielding at halo methyl compounds is still lacking in the literature. The HABA effect mainly arises due to the “active” second-order cross term of the Fermi contact hyperfine interaction and the kinetic energy correction to the electronic spin-Zeeman (SZ) interaction; though one should also include passive SO corrections (SO-I) to better describe them.^{23,25–28} Finally, (c) recently discovered heavy-atom effect on vicinal heavy atoms²⁹ which arises due to the proximity of a heavy atom on another heavy atom and it is not an enhancement of HALA-type effects.

One of the aims of this work is to go deeper on the analysis of SO effects on both carbon and hydrogen shieldings in halomethyl derivatives when containing more than one heavy halogen. In doing so, we choose the whole family: XCH_3X , CH_2X_2 , CHX_3 , CH_2XY and CHX_2Y ($\text{X}, \text{Y} = \text{F}, \text{Cl}, \text{Br}, \text{I}$) as model compound systems. For this purpose, we apply three different methods: (a) the linear response elimination of small component formalism (LRESC), (b) the spin-free (SF) scheme, and (c) full-relativistic calculations based on the relativistic polarization propagator theory at the random phase level of approach (4c-RPA). We aim to answer the following questions:

- Which are the leading relativistic effects one must include in order to get results within 5% from those obtained via LRESC scheme?
- Do they follow a scaling dependence with Z_X or Z_Y ?
- Are substituent effects additive for carbon shieldings?
- What can be learned when applying the spin-free methodology to the NMR shielding calculations? In other words, is it possible to obtain an effective four-component SO contribution for carbon shieldings within spin-free methodology?

This paper is organized in five sections. After this one, we give a brief sketch on both the LRESC method and the relativistic polarization propagator theory at RPA level. Introducing, in this way, the theoretical background and terminology needed for the rest of this work. Computational details used for all calculations are given in Sec. III. Section IV is devoted to the results and discussion. We start showing theoretical values of $\sigma(\text{C})$ and $\sigma(\text{H})$ in CH_2XI ($\text{X} = \text{H}, \text{F}, \text{Cl}$) molecular systems with LRESC method including some and all of its contributions. For such systems, relativistic calculations at RPA level

of approach with unrestricted kinetic balance (UKB) prescription and with spin-free Hamiltonian are given. We also show the SO contribution to $\sigma(\text{C})$ and $\sigma(\text{H})$ in different molecular systems containing heavy halogen atoms. Concluding remarks are presented in Sec. V.

II. THEORY

A. The linear response elimination of small component formalism

The LRESC method was first published in Refs. 21 and 22. A brief survey of it will be given in this section in order to highlight the electronic origin of the operators involved and the nomenclature used for identifying them. They would explain the pattern that relativistic corrections of magnetic properties follow, in different molecular electronic environments.

Within a full relativistic domain, molecular properties arising from charge conserving operators can be obtained as corrections to the relativistic ground-state molecular energy, via the Rayleigh-Schrödinger perturbation theory. This is the case for the NMR magnetic shielding constant, which is a bilinear property depending on both an external (applied) magnetic field (\mathbf{B}) and the magnetic moments of molecular nuclei (μ_M).

In order to introduce the LRESC methodology, we should start with an electronic molecular framework described by the Breit Hamiltonian, for a molecule in the presence of an external and uniform magnetic field and the nuclear magnetic moments all of them as the perturbation (V)

$$V = \boldsymbol{\alpha} \cdot \mathbf{A}, \quad (1)$$

$$\begin{aligned} \mathbf{A} &= \sum_M^{nuc} \mathbf{A}_M + \mathbf{A}_B \\ &= \sum_M^{nuc} \left(\boldsymbol{\mu}_M \times \frac{\mathbf{r}_M}{r_M^3} \right) + \mathbf{B} \times \frac{\mathbf{r}}{2}, \end{aligned} \quad (2)$$

where $\mathbf{r}_M = \mathbf{r} - \mathbf{R}_M$ (electronic distance from the nucleus M), \mathbf{r} is the distance taken from the gauge origin, and c is the speed of light at vacuum.

The leading relativistic correcting terms of magnetic molecular properties arise, within the LRESC method, after considering the following assumptions:

- We assume the existence of a complete set of eigenstates of the Breit Hamiltonian in the Dirac-Fock space

$$H^B = h^D + V^C + V^B, \quad (3)$$

where h^D is the one-body Dirac Hamiltonian of a particle in the field of the (fixed) nuclei; V^C and V^B are the Coulomb and Breit operators.^{30–33}

- The second-order correction to the energy is written as

$$\begin{aligned} E^{(2)} &= \sum_{n \neq 0} \frac{\langle 0|V|n\rangle \langle n|V|0\rangle}{E_0 - E_n} \\ &\quad - \sum_{n \neq vac} \frac{\langle vac|V|n\rangle \langle n|V|vac\rangle}{E_{vac} - E_n}. \end{aligned} \quad (4)$$

States $|n\rangle$ are those in the Dirac-Fock space that can be connected with $|0\rangle$ (or $|vac\rangle$, in the second term) by the perturbation V of Eq. (1). The second term of the rhs of Eq. (4) means the vacuum polarization due to the presence of the external (magnetic) field represented by the operator V . This term appears only in a full relativistic scheme (there is no, and cannot be, such term within the non-relativistic (NR) regime) and should be subtracted in order to properly account for the modifications that a magnetic field produce in an atomic or molecular electronic system.^{31,32,34}

- Starting from full relativistic matrix elements, a two-component model is obtained by expanding them as a power series in c^{-1} , up to order c^{-4} .
- The rhs of Eq. (4) is divided in two terms. They are defined according to its NR limit

$$E^{(2)} = E_a + E_b, \quad (5)$$

where E_a contains those terms for which $\lim_{c \rightarrow \infty} (E_0 - E_n)^{-1} \neq 0$, i.e., $\{|n_a\rangle\}$ so hereafter they will represent those molecular states which generates the Schrödinger-type molecular spectrum.

On the other hand, E_b contains those terms obtained from states $\{|n_b\rangle\}$ that in the $\lim_{c \rightarrow \infty} (E_0 - E_n)^{-1} = 0$, i.e., they contain at least one electron-positron pair created or annihilated in $|0\rangle$. The effects of the vacuum polarization that arise due to the presence of the external potential V , and the Breit operator, are included in E_b .

It is worth it to mention that in a relativistic regime, the spectrum of states $|0\rangle$, $|n\rangle$ must conserve the total charge $Q = -eN$, for a system that contain N electrons in the non-relativistic limit. When interactions are turned-on the total number of particles is not necessarily conserved. In our case, this is because the operators V and H^B provides the creation/destruction of virtual pairs. In this sense, $|vac\rangle$ represents the vacuum state in the QED representation.³³

Relativistic corrections on E_a and E_b to the lowest order will appear at c^{-2} level. As mentioned above, expanding E_a will lead to paramagnetic term and its corrections; and working out E_b , will give diamagnetic terms. Both E_a and E_b give rise to one-body and two-body operators. We will focus from now on in one-body correcting terms to $E^{(2)}$.

In short, the LRESC model considers the leading relativistic correcting terms of the NR limit of $E^{(2)}$ as a power series of c^{-1} . The way this is done is based on two main steps. First, rewriting the sum of Eq. (4), depending on the behavior of $(E_0 - E_n)^{-1}$ in the NR limit. Second, transforming the expressions of the full relativistic operators V and H^B , with special consideration of the creation/annihilation of virtual pairs on the ground-state $|0\rangle$ and the vacuum $|vac\rangle$. For a further and detailed description of the LRESC scheme, we suggest the reading of Refs. 21 and 22.

The whole set of the one-body leading correcting terms that appears in the LRESC method are given in Table I.

Which are the electronic effects that these operators describes? (i) $O(\mu_M)$ are those operators which come from the magnetic perturbations related with the magnetic vector potential originated at nucleus M ($\alpha \cdot A_{\mu_M}$); (ii) the operators

TABLE I. Leading correcting terms to σ within the LRESC method.

	$O(\mu_M)^a$	$O(B)^b$	$O(D)^c$	Correcting term
Paramagnetic terms	H^{PSO}	H^{OZ}	...	σ_p^{nr}
	H^{PSO}	H^{OZ}	$H^{MV} + H^{DW}$	σ_p^{PSO}
	$H^{FC} + H^{SD}$	H^{OZ}	H^{SO}	σ_p^{SO}
	H^{PSO}	H^{OZ-K}		σ_p^{OZK}
	H^{PSO-K}	H^{OZ}		σ_p^{PSOK}
	$H^{FC} + H^{SD}$	H^{SZ-K}		σ_p^{SZK}
	$H^{FC} + H^{SD}$	H^{BSO}		σ_p^{BSO}
Diamagnetic terms	A_{μ_M}	A_B		σ_d^{nr}
	A_{μ_M}	A_B	$H^{MV} + H^{DW}$	$\sigma_d^{MV} + \sigma_d^{DW}$
	H^{DIAK}			σ_d^{DIAK}

^a $O(\mu_M)$: terms correcting the energy due to the nuclear magnetic moment of nucleus M .

^b $O(B)$: terms correcting the energy due to the external and uniform magnetic field.

^c $O(D)$: terms arising from the one-body Dirac Hamiltonian, e.g., Darwin, mass-velocity, and spin orbit.

$O(B)$ arise from the external and uniform magnetic perturbation ($\alpha \cdot A_B$), and (iii) the operators $O(D)$ arise from the one-body Dirac Hamiltonian. In Table I, we give the explicit form of the operators $O(\mu_M)$, $O(B)$, $O(D)$ we actually use, due to the shielding tensor is obtained by the second derivative of the corrected energy up to second order in perturbation theory. Derivatives are applied with respect to the external magnetic field and the three components of the nuclear magnetic moments.

The NR contribution to the shielding constant (σ^{nr}) is usually divided, in a two-component scheme, in the following paramagnetic (σ_p^{nr}) and diamagnetic (σ_d^{nr}) NR response functions, namely,

$$\sigma = \sigma_p^{nr} + \sigma_d^{nr}, \quad (6)$$

$$\sigma_p^{nr} = \langle \langle H^{OZ}, H^{PSO} \rangle \rangle, \quad (7)$$

$$\sigma_d^{nr} = \langle 0 | H^{DIA} | 0 \rangle, \quad (8)$$

where

$$H^{OZ} = \frac{e}{2m} LB, \quad (9)$$

$$H^{PSO} = \frac{e}{m} \mu_M \frac{L_M}{r_M^3}, \quad (10)$$

$$\begin{aligned} H^{DIA} &= A_{\mu_M} \cdot A_B \\ &= \frac{e}{2mc} \cdot \left[(\mu_M B) \left(\frac{r_M r_0}{r_M^3} \right) - (\mu_M r_0) \left(\frac{r_M B}{r_M^3} \right) \right]. \end{aligned} \quad (11)$$

The commonest corrections to σ_p^{nr} and σ_d^{nr} are those terms obtainable from the consideration of operators arising from a perturbed series of the NR limit of the one-body Dirac Hamiltonian, up to first order in α , and operators due to the nuclear magnetic vector potential (including “Fermi contact” terms)

$$\sigma_p^{PSO} = \langle \langle H^{OZ}, H^{PSO}, H^{MV} + H^{DW} \rangle \rangle, \quad (12)$$

$$\sigma_p^{SO} = \langle \langle H^{OZ}, H^{FC} + H^{SD}, H^{SO} \rangle \rangle, \quad (13)$$

TABLE II. LRESC corrections to shielding constant.

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

$$\sigma_d^{MV} = \langle \langle H^{DIA}, H^{MV} \rangle \rangle, \quad (14)$$

$$\sigma_d^{DW} = \langle \langle H^{DIA}, H^{DW} \rangle \rangle. \quad (15)$$

In these equations, the perturbative Hamiltonians that arise from the magnetic perturbations due to the nuclear dipole moment are

$$H^{FC} = \frac{e}{2m} \sigma \left(\frac{8\pi}{3} \mu_M \delta(r_M) \right), \quad (16)$$

$$H^{SD} = \frac{e}{2m} \sigma \left(\frac{3(\mu_M r_M) r_M - r_M^2 \mu_M}{r_M^5} \right), \quad (17)$$

and the correcting terms of the Dirac Hamiltonian of a singlet-type, i.e., mass velocity (H^{MV}) and Darwin (H^{DW}) operators, and of a triplet-type or spin-orbit (H^{SO}) operator, are

$$H^{MV} = -\frac{1}{8m^3 c^2} p^4, \quad (18)$$

$$H^{DW} = \frac{1}{4m^2 c^2} \nabla^2 V_C, \quad (19)$$

$$H^{SO} = \frac{1}{8m^3 c^3} \sigma (\nabla V_C \times p). \quad (20)$$

On the other hand, we should also use those terms which arise from magnetic field-dependent operators yielding relativistic corrections. They are those which arise from both the consideration of the effects due to the small component wave functions and those from the “normalization” of the large component of the wave functions. We split them up according to their spin character, i.e., triplet-type and singlet-type terms

$$\sigma_p^{SZK} = \langle \langle H^{FC+SD}; H^{SZK} \rangle \rangle, \quad (21)$$

$$\sigma_p^{BSO} = \langle \langle H^{FC+SD}; H^{BSO} \rangle \rangle, \quad (22)$$

$$\sigma_p^{OZK} = \langle \langle H^{PSO}; H^{OZK} \rangle \rangle, \quad (23)$$

$$\sigma_p^{PSOK} = \langle \langle H^{PSOK}; H^{OZ} \rangle \rangle, \quad (24)$$

$$\sigma_d^{DIAK} = \langle H^{diaK} \rangle, \quad (25)$$

where

$$H^{SZK} = \frac{-e}{8m^3 c^2} [3(\sigma B) p^2 - (\sigma p)(pB)], \quad (26)$$

$$H^{BSO} = \frac{e}{4m^2 c^2} \nabla V_C \times (B \times r_0), \quad (27)$$

$$H^{OZK} = \frac{-e}{4m^3 c^2} (LB) p^2, \quad (28)$$

$$H^{PSOK} = -\frac{e}{4m^3 c^2} \left\{ \frac{\mu_M L_M}{r_M^3}, p^2 \right\}, \quad (29)$$

$$H^{DIAK} = -\frac{1}{4m^3 c^4} \left[2 \left(\frac{\mu_M L_M}{r_M^3} \right) (BL_M) + BB_M + 2(A_M A_B) p^2 + 2\pi (\mu_M B) \delta(r_M) \right]. \quad (30)$$

From now on we shall express the leading relativistic corrections of the LRESC model in terms of their response order and spin character. In Table II, we show all the corrections. All presentations of our results will be based on this terminology.

B. Relativistic polarization propagator and the spin-free scheme

Any second-order molecular property, i.e., properties which are theoretically obtained from second-order perturbation theory applied to the energy (and so depending on two “external” fields) can be calculated by using polarization propagators.³ The equation which relates the correction to the energy with such propagators is formally the following:

$$E_{PQ}^2 = 1/2 \text{Re} \langle \langle H^P; H^Q \rangle \rangle_{E=0}, \quad (31)$$

where H^P and H^Q are interaction Hamiltonians which describe the external perturbations to the system whose response (observable through molecular properties) one is interested to calculate and analyze.

Within the relativistic polarization propagator approach the explicit short hand expression of the nuclear magnetic shielding is³

$$\sigma_M = e^2 \left\langle \left\langle \frac{\alpha \times \mathbf{r}_M}{r_M^3}; \alpha \times \mathbf{r}_G \right\rangle \right\rangle. \quad (32)$$

The 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 state and virtual positive-energy electronic states will give the paramagnetic component; the excitations which involve negative-energy electronic states will give the diamagnetic component.³ Then, it is evident that there is only one electronic mechanism involved in this NMR spectroscopic parameter. In this way, there is no distinction between diamagnetic and paramagnetic terms.

The consistent first-order level of approach, the random phase approximation, is obtained when the reference state is chosen as the Dirac-Hartree-Fock state and the manifold of

excitations operators considered is truncated up to the first set of elements, meaning the single-excitation operators.³ Results of calculations at this level of approach will be referred as 4c-RPA.

The SF formalism was developed by Dyall.³⁵ Substituting the prescription which define Φ^L , $2mc\Psi^S = (\boldsymbol{\sigma} \cdot \mathbf{p})\Phi^L$ into the Dirac equation written in terms of large (Ψ^L) and small (Ψ^S) components³⁵

$$\begin{aligned}(V - E)\Psi^L + c(\boldsymbol{\sigma} \cdot \mathbf{p})\Psi^S &= 0, \\ c(\boldsymbol{\sigma} \cdot \mathbf{p})\Psi^L + (V - E - 2mc^2)\Psi^S &= 0,\end{aligned}\quad (33)$$

one gets a modified Dirac equation with the following modified Dirac Hamiltonian:

$$h_D = h^{SF} + h^{SO}, \quad (34)$$

$$h^{SF} = \begin{pmatrix} V & T \\ T & (\frac{1}{4m^2c^2})(\mathbf{p} \cdot V\mathbf{p}) - T \end{pmatrix}, \quad (35)$$

$$h^{SO} = \begin{pmatrix} 0 & 0 \\ 0 & (\frac{1}{4m^2c^2})i\boldsymbol{\sigma} \cdot (\mathbf{p}V \times \mathbf{p}) \end{pmatrix}. \quad (36)$$

The h^{SF} Hamiltonian does include all scalar corrections which does not involve any SO operator. Then, the solution of a reduced Dirac equation which contain only the first term of h_D , will give molecular orbitals and energies corresponding to the SF contributions to the electronic spectra. In this manner, the SF term shall include non-relativistic and mass-velocity and Darwin terms.

We applied it in order to separate as much as possible, the SO contributions within a four-component scheme. In a previous work, an effective four-component SO contribution to the NMR magnetic shielding was defined and applied to HF and FX compounds,⁴⁹

$$\sigma^{4c-SO} = \sigma^{4c} - \sigma^{SF} \approx \sigma^{SO-I}. \quad (37)$$

The SO mechanism which is independent of the external magnetic field is known as passive-SO or SO-I. It may be of a HALA-type, when light atoms are close to heavy-atom or of a HABA type when it is included on the shielding of the heavy atom itself.

III. COMPUTATIONAL DETAILS

The calculation of NR and the leading LRESC contributions to the shielding constant were carried out with the DALTON v2.0 code³⁷ at RPA level. Some contributions were calculated with a local implementation of the DALTON code.³⁸ Full relativistic calculations were performed with the DIRAC⁴⁰ program package; where small components of the basis set were generated by applying the UKB prescription, as done in Ref. 29. As in all our previous works, we saturated as much as possible all basis set lately used. The spin-free calculations were also performed with the DIRAC code applying the .SPIN-FREE option.

All the geometries were optimized at the electron correlation level within mp2=fc keyword in the GAUSSIAN98

code.⁴¹ This means that only valence orbitals, on each molecular system, are taken into account for the MP2 wave function evaluation.

The aug-cc-pVTZ-J spherical basis set was used⁴² in the last step of all structural geometry optimization, and also to obtain NR and LRESC contributions to shielding constants. We also used some other basis sets for getting converged results like Sadlej-J^{42,43} and aug-cc-pVTZ-Jun3²¹ basis sets.

Although it was previously shown that LRESC is gauge origin independent^{12,44} the use of a finite basis set leads to errors concerning gauge origin elections. In this sense, as we did on all of our previous works, we use for all calculations the gauge origin placed at the nucleus of interest for all LRESC calculations. In the case of NR results, we used gauge-including atomic orbitals as implemented in DALTON v2.0.⁴⁵ For relativistic calculations, Sadlej basis sets were used in all cases⁴⁶ with the addition of some tight and diffuse functions to *s*, *p*, *d*, and *f* blocks, with the following relation between exponents: $\alpha_i/\alpha_{i-1} = 3$. The scheme of both the original and the optimized Sadlej basis functions for each atom are as follows: H[6s4p-6s4p]; C[10s6p4d-11s8p5d]; F[10s6p4d-11s8p5d]; Cl[13s10p4d-14s11p6d1f] and I[19s15p12d4f-21s17p13d6f].

The whole basis sets with all previous considerations and all geometrical parameters used in calculations are given as the supplementary material.³⁹

IV. RESULTS AND DISCUSSION

Our aim is to find the minimal set of LRESC correcting terms which quantitatively may reproduce the total $\sigma(\text{C})$ and $\sigma(\text{H})$ values, in a given set of molecular environments. In such a case, the analysis of its dependence with the number and type of (halogen) substituent would be easier; in addition to finding new physical insights. We had chosen the usual methyl halogen-substituted systems as model compounds because of its interest in chemistry, because there are few previous studies, and because we aim to describe shieldings of light atoms on large-size molecular systems containing one, or more than one, heavy (halogen) atoms.

We shall start showing the whole set of contributions obtained within LRESC for three closely related model compounds: CH_3I , CHF_2I , and CHCl_2I . We found that the NR contribution together with third-order triplet-type SO contributions (σ_p^{SO} , Table II, and Eq. (13)) reproduce more than 97% for the total LRESC value for $\sigma(\text{C})$. These results are then used as a reference for the analysis that follows for the whole set of related compounds: $\text{CH}_n\text{X}_{4-n}$ ($n = 1, 3$), CHXYZ and also CH_2XY and CHX_2Y ($\text{X}, \text{Y} = \text{F}, \text{Cl}, \text{Br}$, and I).

A. Leading relativistic effects on $\sigma(\text{C})$ and $\sigma(\text{H})$ of CHX_2I with $\text{X} = \text{H}, \text{F}$, and Cl

As mentioned above, in this section we present the contributions to $\sigma(\text{C})$ and $\sigma(\text{H})$ of the leading relativistic corrections arising from the LRESC formalism in CH_3I , CHF_2I , and CHCl_2I model compounds. Table III shows results of calculations with different basis sets, and also the convergence of the obtained results.

TABLE III. Leading LRESC relativistic corrections to σ for CHX_2I ($\text{X} = \text{H}, \text{F}, \text{Cl}$).

System	Basis functions	σ^{nr}	σ_p^{1T}	σ_p^{1S}	σ_p^{3T}	σ_p^{3S}	σ_d^{1S}	σ_d^{0S}	LRESC	LR ₁ ^a	LR ₂ ^b	4c-RPA
CH₃I												
$\sigma(\text{C})$	246	191.78	2.64	1.91	47.11	-6.29	0.38	-3.99	233.52	238.87	232.60	
	435	189.99	2.75	2.42	46.44	-6.89	0.38	-3.99	231.08 ^c	236.43	229.63	234.02
$\sigma(\text{H})$	246	29.09	0.00	1.52	-0.93	-1.59	0.02	-2.04	26.08	28.16	26.57	
	435	29.08	0.00	1.87	-0.93	-2.03	0.02	-2.04	25.99	28.17	26.14	27.83
CHF₂I												
$\sigma(\text{C})$	354	77.29	2.71	2.46	84.57	-4.86	0.38	-4.50	158.10	161.86	156.89	
	497	73.45	2.81	2.57	84.52	-4.60	0.38	-3.28	154.63	157.97	153.56	
	569	73.28	2.81	2.71	84.57	-4.61	0.38	-3.28	155.86	157.85	153.24	151.80
$\sigma(\text{H})$	354	24.46	-0.01	1.59	-0.04	-1.94	0.00	-1.82	22.30	24.42	22.48	
	497	24.45	-0.01	1.61	-0.03	-1.69	0.01	-1.82	22.52	24.42	22.73	
	569	24.44	-0.01	1.61	-0.04	-1.69	0.01	-1.82	21.58	24.40	22.71	24.19
CHCl₂I												
$\sigma(\text{C})$	309	124.93	2.51	2.22	126.49	-6.15	0.34	-4.55	245.80	251.39	245.26	
	569	123.48	2.41	2.72	124.73	-6.85	0.35	-4.78	242.11	248.21	241.38	
	673	115.19	2.89	2.89	124.68	-7.15	0.39	-4.86	234.05	239.87	232.90	223.79
$\sigma(\text{H})$	309	25.30	-0.01	1.50	-0.82	-1.50	0.02	-1.91	22.50	24.18	22.68	
	569	25.09	-0.01	1.85	-0.85	-1.99	0.02	-2.06	22.07	24.24	22.25	
	673	24.88	0.00	1.86	-0.92	-2.00	0.02	-2.06	21.78	23.96	21.96	23.67

^aLR₁ \equiv NR + σ_p^{3T} (NR + SO).^bLR₂ \equiv NR + σ_p^{3T} + σ_p^{3S} (NR + SO + PSO).^c $\sigma(\text{C})$ is 235.57 ppm when taken from Ref. 22. Its exp value at 300 K taken from Ref. 36 is 220.59 ppm.

Both σ^{nr} and σ_p^{3T} contributions to $\sigma(\text{C})$ (Eqs. (6)–(8), and (13)) are highly dependent on the halogen substituent, X. σ_p^{3T} grows up when increasing the atomic number Z_X . It is interesting to observe that the paramagnetic, PSO term (σ_p^{PSO} , Table II, and Eq. (12)) contribution is also X-dependent, where all the other terms are almost non-X-dependent. The values of σ_p^{PSO} are smaller and have an opposite sign as compared to the SO ones (σ_p^{SO} on Table II and Eq. (13)).

The largest value of $\sigma^{nr}(\text{C})$ for CH_3I , CHF_2I , and CHCl_2I was found for CH_3I though the largest SO contribution was obtained for CHCl_2I . As will be shown in Subsections IV B–IV D, the NR terms are less dependent on the substituent, as compared with the SO terms.

The SO contributions grow with both the number of halogen substituents and the increasing of the substituents atomic number, showing a higher sensitivity of the variation on the vicinity of the central carbon atom.

A similar pattern was obtained for the NR contributions to $\sigma(\text{H})$ but not for $\sigma^{SO}(\text{H})$. This last term gives negative contributions and the smallest value was obtained for $\text{X} = \text{F}$. One may argue that this is because of the electronegativity of fluorine atoms that diminishes the electronic s-type density at the hydrogen atom.

So forth, the addition of NR and triplet third-order SO terms gives more than 97% (93%) for the total LRESC C (H) shielding value, named LR₁ in Table III.

The next step to almost reproduce total LRESC values is to add PSO contributions, namely, LR₂, obtaining values within 1% for both C and H shieldings with the exception of $\sigma(\text{H}; \text{CHF}_2\text{I})$ in which the difference is close to 5% (or 1.13 ppm).

With this background we decided to consider, and show, in Subsections IV B–IV D only the passive SO relativistic contributions to the shieldings (LR₁). First in the molecu-

lar systems $\text{CH}_n\text{X}_{4-n}$ ($n = 1, 3$) and CHXYZ , and then in CH_2XY and CHX_2Y ($\text{X}, \text{Y} = \text{F}, \text{Cl}, \text{Br}, \text{I}$).

B. NR and SO contributions to $\sigma(\text{C})$ and $\sigma(\text{H})$ on $\text{CH}_n\text{X}_{4-n}$ ($n = 1, 3$) and CHXYZ ($\text{X}, \text{Y}, \text{Z} = \text{F}, \text{Cl}, \text{Br}, \text{I}$)

We want to answer the following two questions: (a) How large is the influence of vicinal halogen atoms on both, NR and SO contributions to carbon and hydrogen shieldings? and (b) Is it possible to find out a relationship $\sigma(\text{C}; \text{H}) \sim Z_{X,Y,Z}$.

As observed in Fig. 1, $\sigma^{nr}(\text{C})$ and $\sigma^{SO}(\text{C})$ follow a definite pattern in the CH_3X family where the SO contribution becomes important for $\text{X} = \text{Br}$ and I .

Relativistic effects on the shielding of carbon atoms are of HALA-type in this series of model compounds. The best

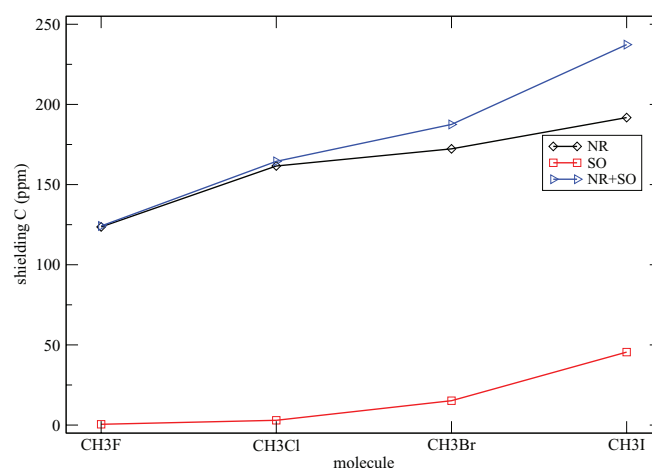


FIG. 1. Non-relativistic $\sigma^{nr}(\text{C})$, spin orbit $\sigma^{SO}(\text{C})$ and the addition of both $\sigma^T(\text{C}) = \sigma^{nr}(\text{C}) + \sigma^{SO}(\text{C})$, for the CH_3X model compounds.

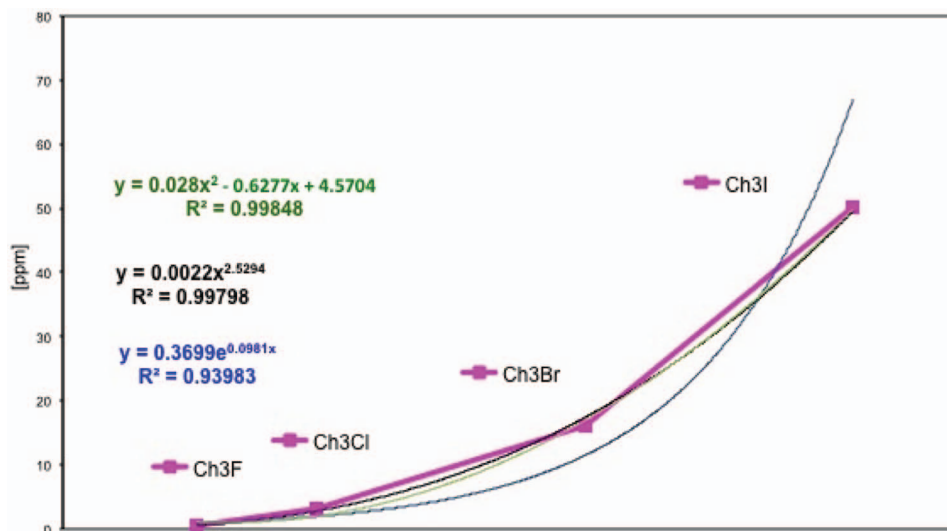


FIG. 2. Spin orbit contribution to carbon shielding, $\sigma^{SO}(C)$, for CH_3X model compounds and extrapolated trend lines. Quadratic, exponential, and potential trends with the corresponding equations are shown.

fitting for such behavior is shown in Fig. 2, where we include three different functional dependences of $\sigma(C)$ in terms of the halogen substituent atomic number, Z_X

$$\sigma_p^{SO}(C) = 0.0022Z_X^{2.53}, \quad (38)$$

$$R^2 = 0.998.$$

One may compare such scaling factor for SO effects, with those previously found for heavy atoms on hydrogen halides and hydrides: $Z^{3.5}$, although in the last case it refers to HAH-type effects.²³ In line with this, $\sigma(X) \sim Z^{3.2}$ for systems like XH_2 ($X = \text{O}, \text{S}, \text{Se}, \text{Te}, \text{and Po}$) and XH_3 ($X = \text{N}, \text{P}, \text{As}, \text{Sb}, \text{and Bi}$). The influence of the mass-correction terms are higher in these last systems because one is considering relativistic effects on the heavy elements.²⁵

Nakatsuji and coauthors published NR and SO contributions to $\sigma(C)$ of some compounds of the following families: CH_3X , CH_2X_2 , and CHX_3 ($X = \text{Br}$ and I).¹⁶ Our results are close to their NR but not so close to the SO ones. We should emphasize here the fact that they include correlation in a similar manner as done for the NR case.

The contributions $\sigma^{nr}(C)$ have an inverse halogen dependence, IHD. Such IHD behavior can be related to large inductive effects that are clearly larger than the relativistic effects.¹⁴

The SO effects are close to that of the NR contributions for systems with $X = \text{Br}$ and $n \geq 2$. The rate of increase for SO contributions is not large enough to reverse the NR trend (decreasing) within the series $\text{CH}_{4-n}\text{X}_n$ for $X = \text{F}, \text{Cl}$ and $n = 1, 2, 3$. It changes for systems with $X = \text{Br}$ and I , where the trend of the total shielding follows that of SO, as seen in Fig. 3.

The variation of the chemical shift, $\delta(C) = \sigma_{ref}(C; \text{CH}_4) - \sigma(C)$, shows a pattern which depends on the family and substituents. For each family of compounds, meaning a family those systems having the same number of substituents (same value for n), the chemical shift grows from $X = \text{I}$ to $X = \text{F}$ (see Table IV). On the other hand, when n increases, the chemical shift also increases for $X = \text{F}$ and Cl , meaning that

the total shielding follows the NR behavior. In the other two cases ($X = \text{Br}$ and I), the trend for the chemical shift follows that one of SO terms.

In Table IV, the NR and SO contributions to $\sigma(\text{H})$ are also shown. The NR terms follow an IHD pattern when the number of the same halogen substituent is increased. On the other hand, the NR contributions grow up as the halogen substituent has a higher atomic number.

The passive SO contributions to $\sigma(\text{H})$ are quite small in all cases, only for molecular systems with $X = \text{Br}$ (in CH_2X_2 and CHX_3) and $X = \text{I}$ such terms becomes non-vanishingly small.

C. NR and SO contributions to $\sigma(C)$ for CH_2XY and CHX_2Y ($X, Y = \text{F}, \text{Cl}, \text{Br}$ and I)

In this section, we analyze NR and SO results of $\sigma(C)$ for CH_2XY and CHX_2Y family of model compounds. The

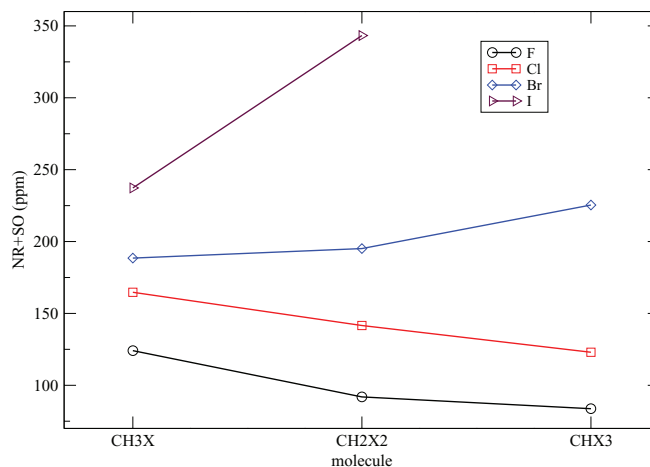


FIG. 3. Total NR plus SO contributions to carbon shielding $\sigma^T(C) = \sigma^{nr}(C) + \sigma^{SO}(C)$, for CH_3X , CH_2X_2 , and CHX_3 ($X = \text{F}, \text{Cl}, \text{Br}, \text{I}$) model compounds.

TABLE IV. NR and SO effects on $\sigma(\text{C})$ and $\sigma(\text{H})$ as a function of the number and type of halogen substituents.^{a,b}

Molecule	$\sigma(\text{C})$											
	NR				SO				NR + SO			
	F	Cl	Br	I	F	Cl	Br	I	F	Cl	Br	I
CH_3X	123.62 [122.40]	161.56 [162.30]	172.29 [170.50] (174.35)	193.98 [191.70] (190.48)	0.51 [0.51]	3.01 [2.96]	15.15 [14.79] (11.52)	45.58 [44.60] (36.22)	124.13	164.57	187.44 ^c	239.56
δ									72.46	32.02	9.15	−42.97
CH_2X_2	90.57	132.91	146.94 (146.42)	185.35 (170.72)	1.33	8.53	46.71 (34.90)	157.97 (115.63)	91.90	141.44	193.65	343.32
δ									104.69	55.15	2.94	−146.73
CHX_3	83.20	104.70	117.41 (117.73)		−0.23	18.24	106.77 (88.18)		82.97	122.94	224.18	
δ									113.62	73.65	−27.59	
CHFClBr	86.94				34.20				121.14			
δ									75.45			
Molecule	$\sigma(\text{H})$											
	NR				SO				NR + SO			
	F	Cl	Br	I	F	Cl	Br	I	F	Cl	Br	I
CH_3X	27.55	28.59	28.87	29.50	0.06	0.05	−0.02	−0.87	27.61	28.64 ^d	28.85 ^c	28.63
CH_2X_2	26.44	26.57	26.77	27.85	0.04	0.03	−0.16	−1.81	26.48	26.60	26.61	26.04
CHX_3	25.76	24.85	24.84		−0.05	−0.10	−0.49		25.71	24.75	24.35	

^aOur value of $\sigma_{\text{ref}}(\text{C}; \text{CH}_4) = 196.59$ ppm, and $\delta(\text{C}) = \sigma_{\text{ref}}(\text{C}; \text{CH}_4) - \sigma(\text{C})$.^bBetween brackets are the values taken from Ref. 47 and between parenthesis those from Ref. 16.^c $\sigma^{\text{exp}}(\text{C}) = 182.35$ ppm and $\sigma^{\text{exp}}(\text{H}) = 28.29$ ppm, both at 300 K and taken from Ref. 48.^d $\sigma^{\text{exp}}(\text{H}) = 28.75$ ppm at 300 K and taken from Ref. 36 and $\sigma(\text{H}) = 28.92$ ppm taken from Ref. 22.

effect of halogen substituents on NR contributions are shown in Figs. 4 and 5. They follow a definite pattern for CH_2XY and CHX_2Z with the exception of CHF_2X for which $\sigma^{\text{nr}}(\text{C})$ falls down with an IHD behavior for all $\text{X} \neq \text{F}$.

In the case of the CH_2XY family of compounds, both NR and SO contributions increase when X or Y are fixed and the other substituent varies from F to I, as shown in Fig. 6. The largest spin orbit effects appear when the substituent X (or Y) is iodine. It is worth to highlight the fact that such contributions maintain quite similar differences between its values when Y goes from F to Cl, and so on, and X is replaced by any of the halogens. The difference on $\sigma^{\text{SO}}(\text{C})$ between CH_2BrCl and CH_2ICl is 50.02 ppm; which is close to that between CH_2Br_2 and CH_2IBr : 53.37 ppm and to that between CH_2BrI and CH_2I_2 : 57.98 ppm. These numbers are taken from

Table V. Figure 6 shows that all curves have an equivalent rate of increase, depending on the weight of the varying heavy-atom halogen substituent. Quite a similar behavior is observed for the family of compounds CHX_2Y as seen in Fig. 7.

It is interesting to observe that the NR contributions to $\sigma(\text{C})$ are larger for CH_2XY as compared to CHX_2Y , for the same X and Y halogen substituents. As an example, the value of $\sigma^{\text{nr}}(\text{C})$ for CH_2ClBr is 139.49 ppm and $\sigma^{\text{nr}}(\text{C})$ for CHCl_2Br is 108.34 ppm or 112.34 ppm for CHBr_2Cl . This tendency is opposite to that which appears from a similar analysis of SO contributions: $\sigma_p^{\text{SO}}(\text{C})$ for CH_2ClBr is 26.91 ppm but it is 42.39 ppm for CHCl_2Br and 75.42 ppm for CHBr_2Cl .

The systems having the largest SO effects are CHBr_2I and CH_2I_2 . In the case of CHBr_2I , the $\sigma_p^{\text{SO}}(\text{C})$ value is 81.0%

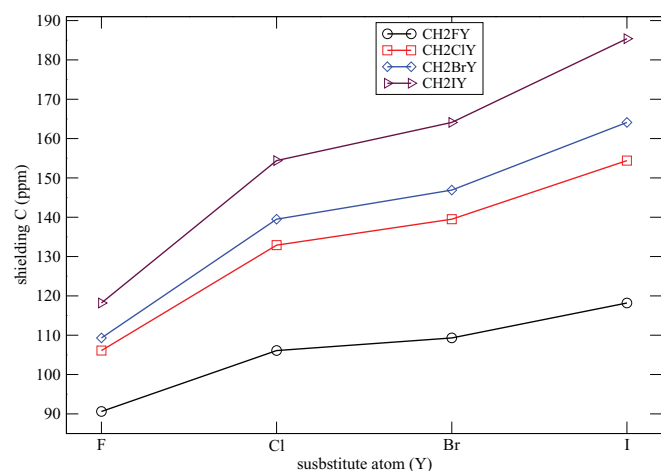
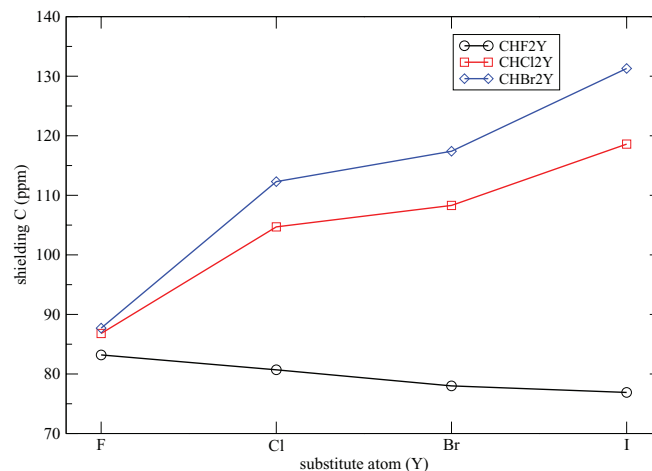
FIG. 4. Non-relativistic contribution to carbon shielding, $\sigma^{\text{nr}}(\text{C})$, for CH_2XY ($\text{X}, \text{Y} = \text{F}, \text{Cl}, \text{Br}, \text{I}$) model compounds.FIG. 5. Non-relativistic contribution to carbon shielding, $\sigma^{\text{nr}}(\text{C})$, for CHX_2Y ($\text{X}, \text{Y} = \text{F}, \text{Cl}, \text{Br}, \text{I}$) model compounds.

TABLE V. NR and SO contributions to $\sigma(C)$ for CH_2XY and CHX_2Y ($X, Y = F, Cl, Br, I$).

Molecule	$\sigma(C)$									
CH_2XY	F, F	F, Cl	F, Br	F, I	Cl, Cl	Cl, Br	Cl, I	Br, Br	Br, I	I, I
NR	90.57	106.06	109.31	118.21	132.91	139.49	154.41	146.94	164.05	185.35
SO	1.33	4.35	19.36	60.92	8.53	26.91	76.96	46.71	100.08	157.97
NR + SO	91.91	110.41	128.67	179.13	141.44	166.40	231.37	193.65	264.12	343.32
δ^a	104.68	86.18	67.92	17.46	55.15	30.19	-34.78	2.94	-67.53	-146.73
CHF_2Y	F ₂ , F	F ₂ , Cl	F ₂ , Br	F ₂ , I						
NR	83.20	80.73	77.89	76.94						
SO	-0.23	6.04	26.03	85.58						
NR + SO	82.97	86.95	103.92	162.52						
δ^a	113.62	109.64	92.67	34.07						
$CHCl_2Y$	Cl ₂ , F	Cl ₂ , Cl	Cl ₂ , Br	Cl ₂ , I						
NR	86.82	104.70	108.34	118.56						
SO	11.47	18.24	42.39	124.78						
NR + SO	98.29	122.94	150.73	243.34						
δ^a	98.30	73.65	45.86	-46.75						
$CHBr_2Y$	Br ₂ , F	Br ₂ , Cl	Br ₂ , Br	Br ₂ , I						
NR	87.68	112.34	117.41	131.32						
SO	60.45	75.42	106.77	193.40						
NR + SO	148.13	187.76	224.18	324.72						
δ^a	48.46	8.83	-27.59	-128.13						

^aSee the footnote of Table IV for the calculation of chemical shifts, δ .

larger than its value for $CHBr_3$, which in turn is only 42.8% larger than the value of the carbon shielding in $CHBr_2Cl$.

Another interesting effect becomes apparent when we analyze the chemical shift of the family of molecular models CH_2XY (see Table V). When two or more hydrogens are substituted by heavy-halogen atoms belonging to the fourth row of the Periodic Table or below, the chemical shift $\delta(C)$ becomes smaller as compared with the chemical shift corresponding to the systems with only one of that heavy atoms (NHD behavior). This fact does not depend on whether the other substituents are F or Cl. This is the case of the $\delta(C)$ for the systems $CHBr_2Y$ as compared with that of the systems $CHBrY_2$, being $Y = F$ or Cl. On the other hand, $\delta(C)$ becomes larger when only one heavy atom substitute one hydrogen and the other substituents are F or Cl, like what hap-

pens for CH_2BrY and $CHBrY_2$ systems, being $Y = F$ or Cl (IHD behavior).

D. Relationship between total LRESC, passive SO and SF calculations

It is worth to search for any relationship that may arise from triplet-type LRESC terms matching 4c and/or spin-free formalisms. In order to do so we selected three systems from the above section: CH_3I , CH_2FI , and CH_2CI . In Table VI, we show triplet-type LRESC corrections, relativistic four-component calculations at RPA level and spin-free values for both $\sigma(C)$ and $\sigma(I)$. We also include the total LRESC values and the difference between four-component and SF (4c-SF) results for comparison.

The spin-free values are related with passive SO corrections, but not only with them.^{12,49} As observed in Table VI

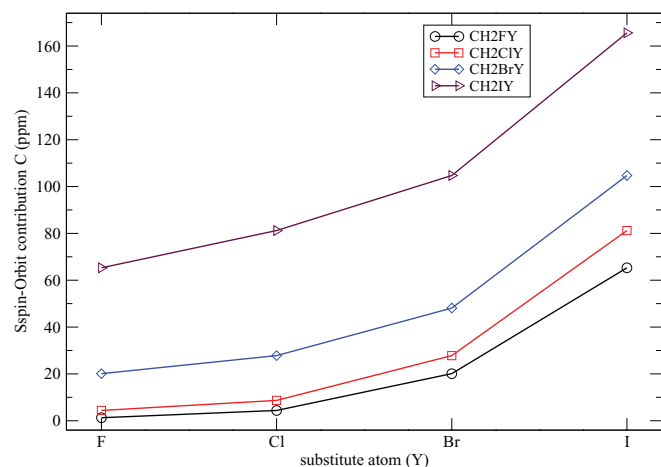


FIG. 6. Spin orbit contribution to carbon shielding, $\sigma^{SO}(C)$, for CH_2XY ($X, Y = F, Cl, Br, I$) model compounds.

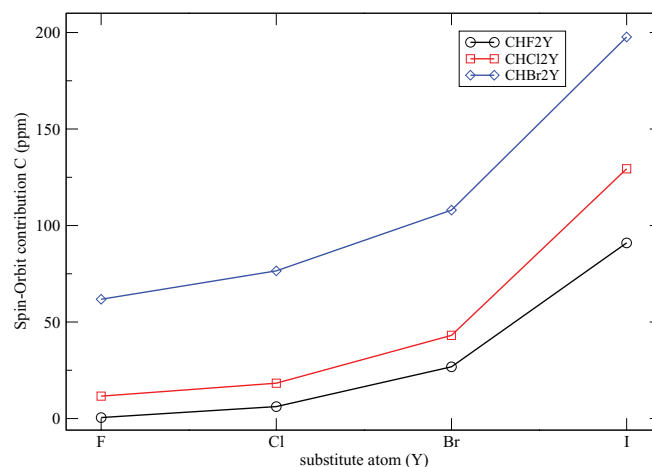


FIG. 7. Spin orbit contribution to carbon shielding, $\sigma^{SO}(C)$, for CHX_2Y ($X, Y = F, Cl, Br, I$) model compounds.

TABLE VI. Contributions to $\sigma(C)$ and $\sigma(I)$ from different approaches for CHX_2I ($X = \text{H, F, Cl}$).

Molecule	$\sigma_p^{1T\text{a}}$	σ_p^{3T}	$\sigma_p^{1T} + \sigma_p^{3T}$	LRESC	4-comp ^b	SF ^c	Diff (4c-SF) ^d	% ^e
$\sigma(C)$								
CH_3I	2.75	46.44	49.19	231.08	234.02	196.60	37.42	(−)19.4
CH_2FI	2.81	84.57	87.38	150.21	151.80	83.40	68.40	(−)21.0
CH_2ClI	2.89	124.68	127.57	234.05	223.79	126.79	97.00	(−)22.2
$\sigma(I)$								
CH_3I	2099.00	181.30	2280.30	5471.90	5722.61	5448.95	273.66	(+)33.8
CH_2FI	2098.31	295.08	2393.39	4559.70	4807.32	4380.30	427.02	(+)30.9
CH_2ClI	2087.26	389.20	2476.46	4110.21	4357.24	3853.37	503.87	(+)22.8

^a σ_p^{1T} (related to σ_p^{SZK} , Eqs. (21) and (22)) represents the correction terms due to the first-order triplet-type paramagnetic component. σ_p^{3T} represents the equivalent third-order corrections.

^bResults of full relativistic calculations at RPA level of approach.

^cResults of spin-free calculations.

^dDifferences between four-component and SF calculations.

^ePercentage of $\sigma_p^{3T}/\text{Diff (4c-SF)}$.

the contributions of σ_p^{3T} are close to 20% larger than the difference between full relativistic (4c-RPA) and SF results for $\sigma(C)$, i.e., 19.4%, 21.0%, and 22.2% when $X = \text{H, F}$ and Cl in CH_2XI , respectively. In the case of $\sigma(I)$, such relationship is opposite, in the sense that the passive SO contributions are smaller, being their percentage higher: 33.7%, 30.9%, and 22.7% for the same sequence of substituents, though both are of the same order of magnitude.

It is worth to emphasize here that passive SO contributions are the most important for $\sigma(C)$ being larger than the NR values, but quite small for $\sigma(I)$, close to 10% of σ_p^{1T} .

V. CONCLUDING REMARKS

As a continuation of our previous works dealing with relativistic effects on magnetic shieldings, we have analyzed the nuclear magnetic shielding of carbon and hydrogen atoms in the following series of compounds: $\text{CH}_n\text{X}_{4-n}$ with $n = 1, 2$, and 3, and CHXYZ ($X, Y, Z = \text{H, F, Cl, Br, I}$). To our knowledge this last broad family of compounds was never studied in the way we did it, though few authors studied them considering a shorten range of substitutions. As an example, the shieldings of the family of compounds CH_2XY with $X, Y = \text{F, Cl, Br}$ or I was never studied in full detail.

Different patterns for the passive SO contribution to the shieldings of carbon central atoms were obtained. A clear dependence with the number and type of substituents was found.

In other words, the overall behavior of $\sigma^{SO}(C)$ does not depend on the special family of compounds (studied here). Anyway, it depends on few parameters which are related with the given family of compounds like $\ln[\sigma^{SO}(C)] = A_X + a_X Z_Y$; for families with two or more than two halogen substituents. They are shown in Figs. 8 and 9, but we give two examples here:

- $\ln[\sigma^{SO}(C)] = 0.0646 + 0.9721 Z_Y$ for CH_2ClIY , $R^2 = 0.9952$,
- $\ln[\sigma^{SO}(C)] = 0.0256 + 3.8572 Z_Y$ for CHBr_2Y , $R^2 = 0.9846$.

In all cases, the slope goes down as Z_X (not Z_Y) grows up. This means that additivity effects arises for $\ln[\sigma^{SO}(C)]$

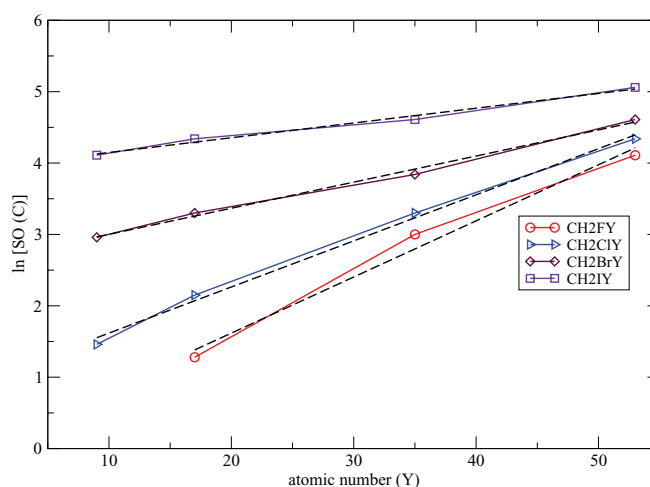


FIG. 8. Logarithmic extrapolation for spin orbit contribution to carbon shielding, $\ln(\sigma^{SO}(C))$, for CH_2XY ($X, Y = \text{F, Cl, Br, I}$) model compounds. Equations are shown in text.

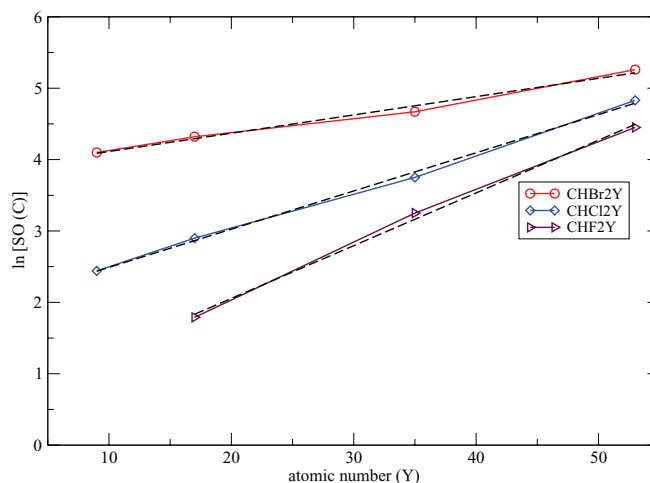


FIG. 9. Logarithmic extrapolation for spin orbit contribution to carbon shielding, $\ln(\sigma^{SO}(C))$, for CHX_2Y ($X, Y = \text{F, Cl, Br, I}$) model compounds. Equations are shown in text.

depending on the Y-substituent. Such additivity is more important when the X-substituents are lighter.

In general, only few LRESC terms are needed to properly describe the results, giving an overall performance within few percentage for $\sigma(\text{C})$ and $\sigma(\text{H})$. In the case of CHF_2I , CHCl_2I , and CHX_2 ($\text{X} = \text{F}, \text{Cl}, \text{Br}$ and I), we show here that such percentage is 3% (7%) for $\sigma(\text{C})$ ($\sigma(\text{H})$).

The normal halogen dependence, NHD of $\sigma(\text{C})$ in the CH_3X , CH_2X_2 , and CHX_3 family of compounds, was found to be originated in the passive SO mechanism, while from the NR contribution one obtain an IHD behavior. This is in line with previous findings published in the literature.¹⁵ Such NHD behavior have different rate of increase, depending on the family of compounds and halogen substituents.

The best functional dependence of the SO contribution in CH_3X series is

$$\sigma^{\text{SO}}(\text{C}) = 0.0022Z_{\text{X}}^{2.53}, \quad (39)$$

though it fits quite well also as a logarithmic function.

Searching for an application of the spin-free formalism to magnetic shieldings like $\sigma(\text{C})$, we found that the difference between four-component relativistic calculations and SF ones on CH_3I , CHF_2I , and CHCl_2I model compounds, gives a value that is close to $\simeq 20\%$ of σ_p^{3T} (the passive SO contribution). Such difference is very meaningful, because SF formalism would give most of the “active” contributions to the shielding when applying our way to compute passive SO to the heaviest elements of such model compounds. We have found that the difference is of the same order of magnitude though in the opposite side; meaning, for $\sigma(\text{C})$ the difference ($4\text{c-SF}) < \sigma_p^{3T}$ but it becomes larger for $\sigma(\text{I})$.

Our results are in good agreement with previous calculations for the NR terms. The values of SO contributions are not so close to that of Nakatsuji because we did not include electron correlation on SO terms, which are of 20%.

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