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 Cite this: *Phys. Chem. Chem. Phys.*,  
2016, **18**, 23572

# Toward an absolute NMR shielding scale using the spin-rotation tensor within a relativistic framework

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One of the most influential articles showing the best way to get the absolute values of NMR magnetic shieldings,  $\sigma$  (non-measurables) from both accurate measurements and theoretical calculations, was published a long time ago by Flygare. His model was shown to break down when heavy atoms are involved. This fact motivated the development of new theories of nuclear spin-rotation (SR) tensors, which consider electronic relativistic effects. One was published recently by some of us. In this article we take another step further and propose three different models that generalize Flygare's model. All of them are written using four-component relativistic expressions, though the two-component relativistic SO-S term also appears in one. The first clues for these developments were built from the relationship among  $\sigma$  and the SR tensors within the two-component relativistic LRESC model. Besides, we had to introduce a few other well defined assumptions: (i) relativistic corrections must be included in a way to best reproduce the relationship among the (e-e) term (called "paramagnetic" within the non-relativistic domain) of  $\sigma$  and its equivalent part of the SR tensor, (ii) as happens in Flygare's rule, the shielding of free atoms shall be included to improve accuracy. In the highest accurate model, a new term known as Spin-orbit due to spin, SO-S (in this mechanism the spin-Zeeman Hamiltonian replaces the orbital-Zeeman Hamiltonian), is included. We show the results of the application of those models to halogen containing linear molecules.

 Received 14th January 2016,  
Accepted 18th July 2016

DOI: 10.1039/c6cp03355e

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## 1 Introduction

The nuclear magnetic shielding,  $\sigma$ , is one of the most important NMR spectroscopic parameters. It can be related to the modification of the nuclear Zeeman effect due to the presence of electrons that surround the nucleus of interest.

When the isotope Y of a given nucleus with spin 1/2 is subject to a magnetic field  $\mathbf{B}_0$ , there its interaction energy value will be split into two. This effect is known as the Zeeman effect. The difference in energy depends on the gyromagnetic ratio of the nucleus,  $\gamma_Y$ , and  $\mathbf{B}_0$ . Because nuclei are surrounded by electrons in atoms and molecules, the actual field  $\mathbf{B}$  at the place of each isotope Y is different from  $\mathbf{B}_0$ ,

$$\mathbf{B} = \mathbf{B}_0(\mathbf{1} - \sigma_Y),$$

where  $\sigma$  is a tensor that describes the electronic shielding. So, in an isotropic medium the frequency of resonance is

$$\nu_0 = \frac{\gamma \mathbf{B}_0(1 - \sigma_Y)}{2\pi}.$$

The absolute shielding constant  $\sigma_Y$  is hardly obtainable by experiments given the difficulties in getting accurate values for  $\nu_0/\mathbf{B}_0$ .

The quantity usually reported is the chemical shift,  $\delta$ , which is defined as

$$\delta_Y = (\sigma_Y^{\text{ref}} - \sigma_Y)/(1 - \sigma_Y^{\text{ref}}) \approx \sigma_Y^{\text{ref}} - \sigma_Y, \quad (1)$$

where  $\sigma_Y^{\text{ref}}$  and  $\sigma_Y$  are the shieldings of reference and sample nuclei. They both refer to the same isotope though belonging to different molecules. The approximate expression of  $\delta$  is reasonably accurate for small shielding constants, meaning  $\sigma_Y < 10^{-3}$ . Each magnetic nucleus Y has its own shielding scale. To establish this scale one needs to know the theoretical/experimental absolute shielding of the given isotope in its reference compound.

The long-standing Flygare's relation, which was derived within the non-relativistic, NR, framework, allows one to know the absolute shielding  $\sigma_Y$  in a molecular system, starting from

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the measured value of the nuclear spin-rotation constant,  $M_Y$ .<sup>1-4</sup> A widely known relationship between these properties was first obtained by Ramsey within a NR picture in the Schrödinger representation.<sup>1</sup> Its expression links the paramagnetic (so called within the NR domain) contribution to the  $\sigma_Y$  tensor and the electronic part of the  $M_Y$  tensor according to:

$$\sigma_Y^{\text{NR-para}} = \frac{m_p \mathbf{I}}{g_Y} M_Y^{\text{NR-elec}} = \frac{m_p \mathbf{I}}{g_Y} (M_Y^{\text{NR}} - M_Y^{\text{nuc}}). \quad (2)$$

Atomic units are used in the last expression, where  $m_p$  is the proton mass,  $g_Y$  the nuclear  $g$ -value of nucleus  $Y$ , and  $\mathbf{I}$  the molecular moment of the inertia tensor at its equilibrium geometry with respect to the center of mass.

For molecules in their equilibrium positions, it holds that the nuclear spin-rotation tensor  $M_Y^{\text{NR}}$  can be expressed as the sum of a purely nuclear contribution and an electronic one related to a second order energy correction,<sup>4</sup>  $M_Y^{\text{NR}} = M_Y^{\text{nuc}} + M_Y^{\text{NR-elec}}$ . This separation is also valid in a relativistic framework.<sup>5</sup> It is also known that the  $M_Y$  tensor is independent of the origin of coordinates (according to both NR and relativistic theories), because the operators it involves depend on the positions of the center of mass together with the position of the nucleus  $Y$ .<sup>5</sup> Eqn (2) is valid only when the gauge origin for the calculation of shielding constants is taken in the center of mass.

These values, together with the NR free atom shielding tensor  $\sigma_Y^{\text{NR-free}}$  (which has only diamagnetic contributions within the NR domain), provided a way to find experimental values of absolute shieldings using measured spin-rotation constants,

$$\begin{aligned} \sigma_Y &= \sigma_Y^{\text{NR-para}} + \sigma_Y^{\text{NR-dia}} \\ &\approx \frac{m_p \mathbf{I}}{g_Y} M_Y^{\text{NR}} + \sigma_Y^{\text{NR-free}}. \end{aligned} \quad (3)$$

Eqn (3) is the famous Flygare's relationship broadly used until now to get absolute NMR shielding scales, and is valid only when molecules are restricted to be considered as rigid rotors. In this equation it is also implicitly considered that the paramagnetic contributions to NR shieldings of free atoms are zero. It is worth mentioning here that such paramagnetic contributions are transformed into the (e-e) contributions within the relativistic domain. The contributions named (e-e) and (e-p) will be defined in Section 2.1.

There is also another relationship, shown also by Flygare, from which the free atomic shielding is related to both the diamagnetic term of the shielding and the nuclear contribution to the spin-rotation tensor (only when the rigid rotor model is considered).<sup>4,6</sup>

Within the relativistic framework both eqn (2) and (3) are not valid any longer because:

(1) Paramagnetic-like contributions to the  $\sigma$  tensor of free atoms are no longer zero, therefore, it is not valid to consider that the shielding of a free atom is of purely diamagnetic nature,

(2) for linear molecules, the  $M$  tensor has null elements corresponding to the symmetry axis of the molecule, while relativistic  $\sigma$  has not,<sup>7</sup> and

(3) the equivalence between the perturbative Hamiltonian of a molecular system in a uniform magnetic field and that describing rotational effects is now broken.<sup>5</sup>

In ref. 5 we had considered the fact that the formal expressions of both magnetic properties, *e.g.* the NMR magnetic shielding and the spin rotation tensors cannot explicitly be related to each other within the relativistic regime. This is contrary to what happens within the non-relativistic framework, where a simple relationship was found. There is no way to obtain an exact theoretical relation among both properties that would be valid within the relativistic regime. So one cannot get a top-down scheme from which eqn (3) would be obtained starting from a relativistic expression. In other words, if one wants to obtain a relativistic generalization of Flygare's relationship, one should try following a different route that may resemble a bottom-up scheme. This is what we have done and its first results are shown in this article.

Being a bottom-up scheme and one that is intrinsically approximate, our proposal has a weakness that is not present in Flygare's scheme: we do not know from the outset which is the exact formal expression that relates both properties. Still we will show in this article that we can get theoretical results for absolute shieldings that are as close as possible to the best theoretical values we have at hand at the moment, using a natural generalization of Flygare's relation.

As mentioned above in the present contribution we seek a relativistic generalization of eqn (3). To get it we decided to work within two different relativistic frameworks: two-component and four-component. At the end, results from both should match each other. From a theoretical point of view four-component expressions shall be the most reliable when properly derived, though two-component relativistic expressions highlight electronic mechanisms that could be used to better understand the physics that underlies the likely relationship among those molecular response properties. We choose to work with the four-component relativistic polarization propagator<sup>8</sup> and one of the two-component formalisms available, known as the linear-response within the elimination of small component (LRESC) model.<sup>9</sup> Both have been shown to be highly accurate in the calculations of NMR spectroscopic parameters<sup>10-13</sup> and spin-rotation constants, SRCs,<sup>14</sup> though the LRESC model gives not quite accurate results for shieldings when the molecule contains heavy elements belonging to the 6th row of the Periodic Table. The SRC was calculated using a formalism developed a few years ago, which actually introduces four-component relativistic expressions.<sup>5</sup> Another formalism was proposed a little later by Liu and collaborators.<sup>15</sup> Then we realized that it was the time to try to take one step further by proposing models that could generalize Flygare's model in an appropriate way. It should be mentioned here that we have a previous work published recently in which we study a relation, valid within the relativistic framework, among magnetizability and the  $g$ -tensor. It was performed using a scheme that is similar to that used here, to identify the electronic mechanisms which underlie the relativistic effects of both properties.<sup>16</sup>

In the last few years some articles were published using as a recipe eqn (3) though within the relativistic domain.

Malkin *et al.* obtained “quasi-experimental” absolute shielding constants combining experimental nuclear spin-rotation data with NR free atom diamagnetic shielding constants (and also comparing this last contribution with diamagnetic shielding constants of nucleus in molecules).<sup>17</sup> Liu *et al.* have also proposed a relativistic extension of the NMR absolute shielding scale,<sup>18</sup> which is based on the NR Flygare’s one, with the addition of three kinds of relativistic effects belonging to  $M_Y$  and  $\sigma_Y$  constants. These three effects are all naturally included in our work, though the LRESC model allows us to go one crucial step further. Furthermore, using the LRESC model one can be aware of the physical mechanisms that underlie each contribution to both properties, and also one can identify contributions that are null as in the case of  $M_Y^{(e-p)}$ .

In line with these findings, nuclear SRCs, absolute NMR shielding constants and shielding spans were calculated using coupled-cluster singles-and-doubles with a perturbative triples (CCSD(T)) correction theory, four-component relativistic density functional theory (relativistic DFT), and non-relativistic DFT.<sup>19,20</sup> It was shown that the straightforward application of the NR formula which relates the electronic contribution to the nuclear SRC and the paramagnetic contribution to  $\sigma$  does not yield correct results. In the case of light-atom containing systems, such as water and hydrogen sulfide, studies that include relativistic effects provide accurate absolute shielding scales for oxygen and sulfur.<sup>21</sup> Another way of getting absolute shieldings of heavy atoms was recently proposed by Adrjan and coauthors.<sup>22</sup>

Nowadays 4-component relativistic calculations are carried out routinely, using for example the DIRAC program package.<sup>23</sup> In this package the actual expressions of the relativistic polarization propagator formalism at the random phase level of approach, RPPA-RPA, are implemented.

The main aim of this work is to introduce new models that generalize the relationship among tensors  $\sigma$  and  $M$ , and then apply them to a few molecular systems. The strongest constraint that must be fulfilled is that their expressions and results of calculations should fit the well-known NR relationship of eqn (2) and (3) in the NR limit. We shall show that our models fulfill such a constraint.

In Flygare’s model one has a very useful replacement of molecular calculations by atomic calculations, to get diamagnetic terms. Another aim of this work is our search for continuing to use this kind of replacement, so that this is introduced in the new relativistic models.

In our development we used two related formalisms, the LRESC and the RPPA, as the basic theoretical structures. In the LRESC model, relativistic corrections to the NR expressions of both response molecular tensors,  $\sigma_Y$  and  $M_Y$ , are well defined.<sup>5,9</sup> In addition, its application to calculate them on different molecules has shown that relativistic effects are quantitatively well reproduced.<sup>13,14</sup> The straightforward separation of those relativistic corrections, depending on whether they are core- or ligand-dependent,<sup>24</sup> is one of the key points in the assumptions used as a support to our proposal. Another relevant consideration is related to the fact that all contributions can be divided into electron–electron (e–e) and electron–positron (e–p) terms,

which are related to positive energy–positive energy and positive energy–negative energy coupling terms of the linear response functions, respectively.<sup>8</sup> Given that the LRESC formalism can be related to the RPPA formalism, one can use it to make new assumptions and so, starting from a relationship among  $\sigma$  and  $M$  that is valid within the NR framework, one can go one step further and find some other relationships that are more general and valid within the relativistic framework. We show here a few such relationships and analyze the results of their applications to linear molecules.

Similar to Flygare’s formulation, where the paramagnetic term of  $\sigma$  is not related to the diamagnetic term (one is related to the total SRC and the other to the shielding of free atoms), in our models the (e–e) contributions are not related to the (e–p) ones.

This article is organized as follows. In Section 2 we give a brief account of the main characteristics of the LRESC model, together with the actual expressions for both molecular properties obtained within such a model. This is necessary to expose what are the considerations and prescriptions that guide us to propose three different models to generalize Flygare’s relation. After giving the Computational details in Section 3, in Section 4 we start making an analysis of the core-dependent terms for perpendicular components of shieldings and spin-rotation constants of the HX (X = F, Cl, Br, I), XF and IX (X = Cl, Br, I) family of compounds. Afterwards we give the results of calculations of the same components applying our three models. The main characteristics of the new term, the SO–S, are also analyzed. At the end of Section 4 we give the analysis of the isotropic values of  $\sigma$ . The main results are highlighted in the last Section.

## 2 Theory and models

As was mentioned above, Ramsey<sup>1</sup> and then Flygare<sup>4</sup> were able to introduce a relationship among  $\sigma$  and  $M$ . Such a relationship is not valid within the relativistic regime. In order to lift this restriction we proposed recently a theoretical formalism from which a relativistic expression of the spin-rotation tensor was found.<sup>5</sup> The application of the LRESC model strengthened what was found within the more general four-component relativistic formalism.

In this article we shall go one step forward and concentrate our focus on the development of models that shall establish new relations among  $\sigma$  and  $M$ , these relationships being valid within the relativistic framework. These different models are conceived to introduce more relativistic effects from one to the next one, *i.e.* to become more and more accurate.

We start this section with the basic definitions of the LRESC formalism and then we give expressions of both tensors,  $\sigma$  and  $M$ . Finally we shall show three different models from which some new insights can be obtained.

### 2.1 The LRESC model

The formal expressions of response properties that the LRESC model provides are obtained after considering some well

defined assumptions.<sup>9</sup> To get a better understanding of what we shall show in this section we only need to consider that

(1) Within the relativistic regime, the second-order correction to the energy of a perturbed system can be written as

$$E^{(2)} = \sum_{n \neq 0} \frac{\langle \psi_0 | V | \psi_n(N) \rangle \langle \psi_n(N) | V | \psi_0 \rangle}{E_0 - E_n} + \sum_{n \neq 0} \frac{\langle \psi_0 | V | \psi_n(N+2) \rangle \langle \psi_n(N+2) | V | \psi_0 \rangle}{E_0 - E_n} - \sum_{n \neq \text{vac}} \frac{\langle \text{vac} | V | \psi_n(2) \rangle \langle \psi_n(2) | V | \text{vac} \rangle}{E_{\text{vac}} - E_n} \quad (4)$$

where states  $|\psi_n\rangle$  are those in the Dirac–Fock space that are connected with  $|\psi_0\rangle$  (or  $|\text{vac}\rangle$ , in the second term) by the magnetic perturbation  $V$ . The excited states  $|\psi_n(N)\rangle$  belong to the  $N$ -particle manifold of states, which are built from Slater determinants containing  $N$  “electronic” solutions, *i.e.* made up of positive energy solutions of a starting one-particle Dirac Hamiltonian; and also  $|\psi_n(N+2)\rangle$  belong to all states of the  $N+2$  particles manifold containing an extra electron–positron pair (see ref. 9 and Section II C of ref. 5).

(2) Starting from four-component relativistic matrix elements, a two-component model can be obtained by expanding them as a power series in  $c^{-1}$ , up to order  $c^{-2}$  (using cgs gaussian units) for getting the leading relativistic effects. All other higher-order relativistic effects require to go further in the expansion of the series.

(3) The rhs of eqn (4) can be divided into two other terms that are defined according to its NR limit. Eqn (4) is re-expressed as

$$E^{(2)} = E^{(e-e)} + E^{(e-p)}. \quad (5)$$

The first term  $E^{(e-e)}$  contain those terms for which  $(E_0 - E_n)^{-1} \neq 0$  in the NR limit. On the other hand,  $E^{(e-p)}$  contain those terms for which  $(E_0 - E_n)^{-1} = 0$  in the same limit.

The leading relativistic corrections of  $E^{(e-e)}$  and  $E^{(e-p)}$  do appear at order  $c^{-2}$ . In the language of relativistic polarization propagators,  $E^{(e-e)}$  is related to contributions from positive energy–positive energy coupling terms of the linear response functions. It yields the so called “electron–electron” (e–e) corrections. The expansion of  $E^{(e-e)}$  will lead to the paramagnetic term (NR) and its (relativistic) corrections.  $E^{(e-p)}$  is related to contributions from positive energy–negative energy coupling terms of the linear response functions, yielding the so called “electron–positron” (e–p) corrections. The  $E^{(e-p)}$  will give the diamagnetic terms at the NR limit in addition to its relativistic corrections.

The electronic mechanisms that arise within the LRESC model, from the (e–e) terms, are obtained expanding the matrix elements of two given four-component operators  $V$  and  $W$  between positive energy four-component spinors  $|\phi_j^{(4)}\rangle$ ; and afterwards applying the elimination of small components (ESC) approach. As a result they are expressed as matrix elements of new operators acting in the space spanned by Pauli spinors  $|\phi_j^P\rangle$ ,

$$\langle \phi_i^{(4)} | V | \phi_j^{(4)} \rangle \approx \langle \phi_i^P | O(V) | \phi_j^P \rangle. \quad (6)$$

Every static second-order molecular property, *i.e.* those arising from a second-order correction to the energy and depending on

two external static fields like the NMR spectroscopic parameters or the spin-rotation constants, can be calculated by using polarization propagators. This is apparent from the following equation

$$E_{VW}^{(2)} = \text{Re}(\langle \langle V; W \rangle \rangle_{E=0}), \quad (7)$$

where  $V$  and  $W$  are the interaction Hamiltonians that consider external perturbations acting on the unperturbed system.  $E_{VW}^{(2)}$  stands for the second-order correction to the atomic or molecular electronic energy. The response properties are obtained from these expressions.<sup>8</sup> Besides, they have an equivalent form to eqn (7) within the LRESC model

$$E_{O(V)O(W)}^{(2)} = \text{Re}(\langle \langle O(V); O(W) \rangle \rangle_{E=0}), \quad (8)$$

where  $O(V)$  and  $O(W)$  are the operators  $V$  and  $W$  written in the framework of the two-component LRESC model.

The derivation of the actual expressions of the LRESC model is based on the perturbation theory technique. The particular technique used is not relevant in order to identify the operators involved in first and second order perturbation theory. Furthermore we want to stress here the fact that perturbation theory was applied in such a way that the likely problems related to the mixing of positive energy and negative energy states that may arise in many-electron systems (mentioned in ref. 25) do not appear. For the (e–p) contribution to the second-order correction to the energy, actual expressions use a projector onto negative-energy states that, at the end, is written in terms of positive-energy orbitals. So that final expressions are always expressed in terms of positive-energy orbitals.

## 2.2 Spin-rotation and shielding tensors within the LRESC model

The nuclear spin-rotation tensor can be expressed as the sum of nuclear and electronic contributions. In a relativistic framework, the latter includes a term originating in the Breit electron–nucleus interaction. This contribution is negligible,<sup>5,26</sup> so it is not considered hereafter.

We adopt Gaussian atomic units throughout this work because an easier track of relativistic effects can be kept in this system of units, in which the fine structure constant is directly given as  $1/c$ . Within the relativistic polarization propagator approach, the electronic contribution to the nuclear spin-rotation tensor can be calculated as the sum of two different terms which considers excitations to positive- and negative-energy orbitals.<sup>25,27</sup> The former is expressed as:

$$M_Y^{(e-e)} = \frac{g_Y}{m_p c} \langle \langle \left( \frac{\mathbf{r} - \mathbf{r}_Y}{|\mathbf{r} - \mathbf{r}_Y|^3} \times \boldsymbol{\alpha} \right); \mathbf{J}_e \rangle \rangle^{(e-e)} \mathbf{I}^{-1}, \quad (9)$$

with the usual interpretation that (e–e) refers to excitations to positive-energy orbitals. The operator  $\boldsymbol{\alpha}$  refers to the Dirac matrices, whereas the relativistic electronic total angular momentum operator is  $\mathbf{J}_e = \mathbf{r} \times \mathbf{p} + \frac{1}{2}\boldsymbol{\Sigma}$ , where the position operator must be defined with respect to the molecular center of mass, and  $\boldsymbol{\Sigma}$  is the four-component extension of the Pauli matrices.

On the other hand, (e-e) contribution to the  $\sigma$  tensor is defined as:

$$\sigma_Y^{(e-e)} = \frac{1}{2} \langle \langle \left( \frac{\mathbf{r} - \mathbf{r}_Y}{|\mathbf{r} - \mathbf{r}_Y|^3} \times \boldsymbol{\alpha} \right); (\mathbf{r} - \mathbf{r}_G) \times \boldsymbol{\alpha} \rangle \rangle^{(e-e)}, \quad (10)$$

where  $\mathbf{r}_G$  stands for the vector position of the (arbitrary) gauge origin of the magnetic potential.

Within the LRESC model, relativistic corrections are expressed as a series power expansion in terms of  $1/c$ . At its lowest order, the operators involved in the expression of  $\sigma$  are the paramagnetic (nuclear) spin-orbit  $H^{\text{PSO}}$  (PSO), Fermi-contact  $H^{\text{FC}}$  (FC) and spin-dipolar  $H^{\text{SD}}$  (SD), together with the orbital-Zeeman  $H^{\text{OZ}}$  (OZ) and spin-Zeeman  $H^{\text{SZ}}$  (SZ) operators.<sup>9,28</sup>

In the case of the  $\mathbf{M}$  tensor the nuclear spin operator is also involved, so PSO, FC and SD operators shall be considered in the LRESC expansion of this property.<sup>5</sup>

When the LRESC procedure is applied to the matrix elements of the 4-component total angular momentum operator  $\mathbf{J}_e^{(4)}$  of eqn (9), the following expansion is obtained:<sup>29</sup>

$$O(-\omega \mathbf{J}_e^{(4)}) = H^{\text{BO-J}} = H^{\text{BO-L}} + H^{\text{BO-S}}, \quad (11)$$

where

$$H^{\text{BO-J}} = -\omega \mathbf{J}_e^{(2)}, \quad (12)$$

$$H^{\text{BO-L}} = -\omega \cdot \mathbf{L}_e, \quad (13)$$

$$H^{\text{BO-S}} = -\omega \cdot \mathbf{S}_e, \quad (14)$$

with no contributions of order  $1/c^2$ , as pointed out in previous works.<sup>5,14</sup> In eqn (11)–(14), BO stands for ‘‘Born-Oppenheimer’’. In the previous equations,  $\omega$  corresponds to the molecular angular velocity, which is related to the molecular angular momentum according to  $\omega = \mathbf{I}^{-1} \mathbf{L}$ .

At the next order in  $1/c$ , relativistic corrections to operators mentioned above should be considered.<sup>5,9,30</sup> They are the following: kinetic-paramagnetic spin-orbit  $H^{\text{PSO-K}}$  (PSO-K), kinetic-Fermi contact  $H^{\text{FC-K}}$  (FC-K), kinetic-spin dipolar  $H^{\text{SD-K}}$  (SD-K), kinetic-orbital Zeeman  $H^{\text{OZ-K}}$  (OZ-K), kinetic-spin Zeeman  $H^{\text{SZ-K}}$  (SZ-K) and magnetic induced spin-orbit  $H^{\text{B-SO}}$  (B-SO) operators. The perturbative Hamiltonian  $H^{\text{FC/SD}} = H^{\text{FC}} + H^{\text{SD}}$  where FC/SD means FC + SD is used throughout the present work.

For all operators derived from the external magnetic field, the gauge origin is placed in the molecular center of mass in such a way that the so-called paramagnetic contribution to the NR absolute shielding tensor is equivalent to the electronic contribution to the NR spin-rotation tensor.

Taking into account that up to order  $1/c^2$  there are no (e-p) contributions to  $\mathbf{M}_Y^{\text{elec}}$  tensors<sup>5</sup> ( $\mathbf{M}_Y^{(e-p)\text{-LRESC}} = 0$ ) we have

$$\mathbf{M}_Y^{\text{LRESC}} = \mathbf{M}_Y^{(e-e)\text{-LRESC}}. \quad (15)$$

As a consequence, the leading order relativistic corrections to  $\mathbf{M}_Y^{\text{elec}}$  that appear from (e-e) excitations are

$$\mathbf{M}_Y^{\text{LRESC}} = \mathbf{M}_Y^{\text{NR-elec}} + \mathbf{M}_Y^{\text{PSO-K}} + \mathbf{M}_Y^{\text{para-Mv/Dw}} + \mathbf{M}_Y^{\text{SO-L}} + \mathbf{M}_Y^{\text{SO-S}}, \quad (16)$$

with

$$\mathbf{M}_Y^{\text{PSO-K}} = -\frac{\partial^2}{\partial \mathbf{I}_Y \partial \mathbf{L}} \langle \langle H^{\text{PSO-K}}; H^{\text{BO-L}} \rangle \rangle \quad (17)$$

$$\mathbf{M}_Y^{\text{para-Mv/Dw}} = -\frac{\partial^2}{\partial \mathbf{I}_Y \partial \mathbf{L}} \langle \langle H^{\text{PSO}}; H^{\text{Mv/Dw}}; H^{\text{BO-L}} \rangle \rangle \quad (18)$$

$$\mathbf{M}_Y^{\text{SO-L}} = -\frac{\partial^2}{\partial \mathbf{I}_Y \partial \mathbf{L}} \langle \langle H^{\text{FC/SD}}; H^{\text{SO}}; H^{\text{BO-L}} \rangle \rangle \quad (19)$$

$$\mathbf{M}_Y^{\text{SO-S}} = -\frac{\partial^2}{\partial \mathbf{I}_Y \partial \mathbf{L}} \langle \langle H^{\text{FC/SD}}; H^{\text{SO}}; H^{\text{BO-S}} \rangle \rangle, \quad (20)$$

where  $\mathbf{M}_Y^{\text{NR-elec}}$  is the non-relativistic electronic contribution to the  $\mathbf{M}_Y$  tensor. The operators  $H^{\text{PSO}}$ ,  $H^{\text{FC/SD}}$ ,  $H^{\text{PSO-K}}$ ,  $H^{\text{BO-L}}$  and  $H^{\text{BO-S}}$  were mentioned above, while the operators  $H^{\text{Mv}}$ ,  $H^{\text{Dw}}$  and  $H^{\text{SO}}$  correspond to the usual mass-velocity, Darwin and spin-orbit (only the one-body part is considered in our actual model) operators, respectively.  $\mathbf{I}_Y$  is the nuclear spin of nucleus Y and  $\mathbf{L}$  is the angular momentum due to the rotation of the nuclei.

As was previously shown, the expansion of the (e-e) contribution to  $\sigma_Y$  within the LRESC model is written as:<sup>9,28</sup>

$$\sigma_Y^{(e-e)\text{-LRESC}} = \sigma_Y^{\text{para-NR}} + \sigma_Y^{\text{PSO-K}} + \sigma_Y^{\text{para-Mv/Dw}} + \sigma_Y^{\text{SO-L}} + \sigma_Y^{\text{SO-S}} + \sigma_Y^{\text{OZ-K}} + \sigma_Y^{\text{SZ-K}} + \sigma_Y^{\text{B-SO}} \quad (21)$$

where a similar definition as in the case of the  $\mathbf{M}$  tensor was applied. In particular,  $\sigma_Y^{\text{SO-L}}$  and  $\sigma_Y^{\text{SO-S}}$  can be expressed as:

$$\sigma_Y^{\text{SO-L}} = \frac{\partial^2}{\partial \boldsymbol{\mu}_Y \partial \mathbf{B}} \langle \langle H^{\text{FC/SD}}; H^{\text{SO}}; H^{\text{OZ}} \rangle \rangle, \quad (22)$$

$$\sigma_Y^{\text{SO-S}} = \frac{\partial^2}{\partial \boldsymbol{\mu}_Y \partial \mathbf{B}} \langle \langle H^{\text{FC/SD}}; H^{\text{SO}}; H^{\text{SZ}} \rangle \rangle, \quad (23)$$

with  $\boldsymbol{\mu}_Y$  and  $\mathbf{B}$  being the magnetic moment of nucleus Y and the external uniform magnetic field, respectively. It is important to note that  $H^{\text{OZ}} + H^{\text{SZ}} = \frac{1}{2c} (\mathbf{L}_e + 2\mathbf{S}_e) \cdot \mathbf{B}$ .

### 2.3 Relationships among $\sigma$ and $\mathbf{M}$ within the LRESC model

In addition to the well-known NR Flygare’s relation of eqn (2), there is a close relation between some contributions to  $\mathbf{M}_Y^{(e-e)\text{-LRESC}}$  and  $\sigma_Y^{(e-e)\text{-LRESC}}$  in eqn (16) and (21) given by:

$$\sigma_Y^\alpha = \frac{m_p \mathbf{I}}{g_Y} \mathbf{M}_Y^\alpha, \quad (24)$$

where the superscript  $\alpha$  stands for the PSO-K, para-Mv/Dw and SO-L mechanisms. Although the SO-S term fulfills a similar relation, a difference of a factor of 2 appears:

$$\sigma_Y^{\text{SO-S}} = 2 \frac{m_p \mathbf{I}}{g_Y} \mathbf{M}_Y^{\text{SO-S}}. \quad (25)$$

Following these expressions, it is possible to state a new relationship that links both tensors,  $\sigma$  and  $\mathbf{M}$ , in a



two-component relativistic domain according to the LRESC model:

$$\sigma_Y^{(e-e)\text{-LRESC}} = \frac{m_p I}{g_Y} M_Y^{(e-e)\text{-LRESC}} + \frac{1}{2} \sigma_Y^{\text{SO-S}} + \sigma_Y^{\text{OZ-K}} + \sigma_Y^{\text{SZ-K}} + \sigma_Y^{\text{B-SO}}. \quad (26)$$

This eqn shows that there are several mechanisms which avoid the full equivalence between such properties. In addition, two important remarks shall be made:

- The usual Spin-orbit mechanism (SO-L), which is the main responsible for the so called HALA (heavy-atom effect on light atoms) effect,<sup>31–33</sup> follows Flygare's relation; therefore, one should expect that for light elements in a heavy-atom environment (where all other contributions are close to zero) this relation will still be fulfilled.<sup>14</sup>

- The OZ-K, SZ-K and B-SO mechanisms are core-dependent and belong to what was coined as HAAA (heavy-atom effect on heavy atom) effects.<sup>31–33</sup> They are not influenced by the environment. As a result, these contributions may be introduced by means of atomic calculations. This prescription is taken in the present work.

Due to the spherical symmetry of isolated atoms, there can be only a few non-zero contributions to the (e-e) component of shieldings within the LRESC model. They are

$$\sigma_Y^{\text{atom}(e-e)\text{-LRESC}} = \sigma_Y^{\text{atom-OZ-K}} + \sigma_Y^{\text{atom-SZ-K}} + \sigma_Y^{\text{atom-B-SO}}. \quad (27)$$

Given that the OZ-K, SZ-K and B-SO mechanisms are core-dependent, their contributions are almost equal to their corresponding atomic counterparts. So eqn (26) can be rewritten as

$$\sigma_Y^{(e-e)\text{-LRESC}} \cong \frac{m_p I}{g_Y} M_Y^{(e-e)\text{-LRESC}} + \sigma_Y^{\text{atom}(e-e)\text{-LRESC}} + \frac{1}{2} \sigma_Y^{\text{SO-S}}. \quad (28)$$

As was mentioned in Section 1, one of the aims of this work is to replace the core-dependent molecular contributions by atomic calculations. The last equation is in line with such a proposal.

#### 2.4 Relativistic generalization of previous relationships

We are interested in obtaining a relationship among both tensors,  $\sigma$  and  $M$  that must be valid within the relativistic domain. As observed in eqn (28) there is a two-component relativistic relationship among both tensors though there only the (e-e) part is involved. The inclusion of the (e-p) part on both tensors within the relativistic domain is straightforward.

Still, Flygare's relationship includes the atomic contribution because such a part is purely diamagnetic, within the NR domain, plus the  $M^{\text{nuc}}$  component of  $M$ , and some other terms that are neglected.<sup>6</sup>

So, we shall propose a relativistic generalization of Flygare's relationship starting from eqn (28). We assume that the LRESC model adequately reproduces the leading relativistic corrections of molecular properties in both terms, (e-e) and (e-p). Then we consider that the diamagnetic-like terms of the atomic shielding in the molecule are approximately equal to those

terms though in the free atom in addition to the nuclear part of the SRC. In other words,  $\sigma_Y^{(e-p)} \cong \sigma_Y^{\text{atom}(e-p)} + \frac{m_p I}{g_Y} M_Y^{\text{nuc}}$ .

With those considerations the last equation can be generalized to get a new one, valid within the relativistic domain:

$$\sigma_Y \cong \frac{m_p I}{g_Y} M_Y + \sigma_Y^{\text{atom}} + \frac{1}{2} \sigma_Y^{\text{SO-S}}. \quad (29)$$

This new relationship is the natural relativistic generalization of Flygare's model. From it Flygare's model is recovered in the NR limit. One important point to highlight is the appearance of the last term, SO-S, that arises from the two-component relativistic LRESC model.

What one usually do in the treatment of NMR spectroscopic parameters is to consider isotropic values. They are involved in the measurable quantities, the chemical shifts. From eqn (29) such isotropic values are obtained.

In the special case of linear molecules, the two usual components of the  $\sigma$  tensor (perpendicular and parallel to the molecular axis) are expressed as:

$$\sigma_{\perp,Y}^{(e-e)} \cong \frac{m_p I}{g_Y} M_{\perp,Y}^{\text{elec}(e-e)} + \sigma_Y^{\text{atom}(e-e)} + \frac{1}{2} \sigma_{\perp,Y}^{\text{SO-S}} \quad (30)$$

$$\sigma_{\perp,Y}^{(e-p)} \cong \frac{m_p I}{g_Y} M_{\perp,Y}^{\text{nuc}} + \sigma_Y^{\text{atom}(e-p)},$$

and

$$\sigma_{\parallel,Y}^{(e-e)} \cong \sigma_Y^{\text{atom}(e-e)} + \frac{1}{2} \sigma_{\parallel,Y}^{\text{SO-S}} \quad (31)$$

$$\sigma_{\parallel,Y}^{(e-p)} \cong \sigma_Y^{\text{atom}(e-p)}.$$

As it was shown in a previous work authored by some of us, the isotropic SO-S contribution is zero.<sup>34</sup> Therefore, the isotropic shielding constant can be expressed as:

$$\sigma_Y^{\text{iso}} \cong \frac{2}{3} \frac{m_p I}{g_Y} M_Y + \sigma_Y^{\text{iso-atom}}, \quad (32)$$

where  $M_{\perp,Y}$  was replaced by the "spin-rotation constant"  $M_Y$ , as they are equal when linear molecules are considered.

One of our main concern is the accuracy of the relationships given in eqn (28) for the (e-e) parts, and eqn (29) for both parts. We shall compare results of our models with that of four-component relativistic calculations. The relationship given in the first row of eqn (30) is the most complete concerning the dependence of (e-e) terms of the shielding on the SRC, the atomic contribution to the shielding and the SO-S electronic mechanism. Then we will give an exhaustive analysis of perpendicular components of  $\sigma^{(e-e)}$  for the whole set of molecules studied here.

With this in mind we shall propose now three models that consider differently the (e-e) and (e-p) parts. They are given from the lowest to highest level. The first approach is to consider that eqn (28) is still valid though taking the relativistic values of the tensor  $M$  (as considered in eqn (29)). Given that within the NR regime the atomic contributions to the shieldings

**Table 1** New models for the relationship between  $\sigma$  and  $\mathbf{M}$  tensors, according to eqn (29)

Approximation	$\sigma_Y$
M-I	$\frac{m_p \mathbf{I}}{g_Y} \mathbf{M}_Y$
M-II	$\frac{m_p \mathbf{I}}{g_Y} \mathbf{M}_Y + \sigma_Y^{\text{atom}}$
M-III	$\frac{m_p \mathbf{I}}{g_Y} \mathbf{M}_Y + \sigma_Y^{\text{atom}} + \frac{1}{2} \sigma_Y^{\text{SO-S}}$

are purely diamagnetic (see eqn (3)) the first model will consider only the relation among the (e-e) parts of  $\sigma$  and the  $\mathbf{M}$  tensors.

The next step is obtained adding to the model I a corrective term associated with atomic contributions. They are non zero within the relativistic regime. Lastly, eqn (29) shows that an additional SO-S contribution should be made to the last approach in order to get a still more accurate relationship among  $\sigma$  and the SRC.

All three models are explicitly shown in Table 1. Their names were coined as a recognition of the work of the late Martín Ruiz de Azúa.

It may be useful to stress that, in addition to the  $\sigma^{\text{SO-S}}$  term which considers an electronic mechanism derived from the LRESC model, all other terms of eqn (29) correspond to their four-component relativistic definitions.

Our proposal can be compared with the one of Liu *et al.*<sup>15,18</sup> In their relativistic mapping, the total shielding is obtained from the experimental SRC and the calculated value of the NR diamagnetic shielding. They consider three terms, namely:  $\Delta_A$ , which is close to the relativistic effect on the paramagnetic-like mapping;  $\Delta_B$ , the relativistic effect on the (e-p) diamagnetic-like shielding; and  $\Delta_C$ , which gives the relativistic effects on the nuclear contribution to the SRC, when molecules in their equilibrium position are considered. It is important to state that  $\Delta_C$  is negligibly small, and corresponds to the slight difference in the molecular geometry due to the inclusion of relativistic considerations.

On the other hand, the addition of our terms,  $\sigma^{\text{atom(e-e)}}$  (which is of pure relativistic nature) and  $\frac{1}{2} \sigma^{\text{SO-S}}$  can be related to the  $\Delta_A$  term. This is because the (e-p) diamagnetic-like contribution to the SRC (which is included formally in  $\Delta_A$ ) is completely negligible, as shown theoretically and in a few applications by some of us,<sup>5,14</sup> and later also by Liu *et al.*<sup>18</sup> Under this consideration,  $\Delta_A$  is related to our  $\Delta \sigma^{\text{II}}$ , which will be defined in eqn (35).

Finally,  $\Delta_B$  can be approximated as  $\sigma^{\text{atom(e-p)}} - \sigma^{\text{NR-free}}$ , in the same spirit as the original Flygare's relation, where the diamagnetic shielding of a free atom serves as an approximation for the diamagnetic component of the shielding of a nucleus in its molecular environment.

Even though Liu and coauthor's proposal introduces relativistic corrections by means of the four-component definitions of both properties, shielding and SRC, our model goes one important step further. It resembles as much as possible

Flygare's criteria of getting an absolute scale from accurate experimental measurements together with the state-of-the-art atomic calculations.

### 3 Computational details

Relativistic four-component calculations of  $\sigma$  and  $\mathbf{M}$  tensors were carried out in model molecular systems HX (X = F, Cl, Br, I), XF (X = Cl, Br, I) and IX (X = Cl, Br, I) following expressions of eqn (9) and (10).

Due to the molecular symmetry, the  $\mathbf{M}$  tensor (in both relativistic and NR cases) has only two equal diagonal non-zero components, which are those perpendicular to the molecular axis of symmetry, referred to as the “ $M$  constant”. On the other hand, for the relativistic  $\sigma$  tensor, both components (parallel and perpendicular to the molecular axis) are non-zero in the relativistic domain. However, in its NR limit it has a zero parallel component.

In addition, calculations corresponding to the LRESC analysis of relativistic corrections of both properties were carried out following eqn (16) and (21).

Relativistic calculations of  $M$  constants, and perpendicular and parallel components of the  $\sigma$  tensor were performed at the RPA level of approach of the polarization propagator formalism with Dirac-Hartree-Fock wave functions as implemented in the DIRAC code.<sup>23</sup> NR calculations were performed using the DALTON program package,<sup>35,36</sup> also at the RPA level of approach for molecular properties.

Although quadratic response calculations involving three triplet operators cannot be performed with the DALTON code, the SO-S mechanism can be obtained using another response calculations implemented in it, following the arguments developed in ref. 34. They were previously used in the calculation of LRESC contributions to nuclear SRC.<sup>14</sup> It is important to highlight here that the arguments discussed in ref. 34 are valid only for linear molecules.

The molecular center of mass was taken as the gauge origin of magnetic potentials in all calculations. Furthermore, an electron was added to each halogen free atom in order to be able to perform relativistic shielding calculations of closed shell atoms using the DIRAC code.

Experimental geometric distances in gaseous phase compounds were used for HX (X = F, Cl, Br, I),<sup>37</sup> XF (X = Cl,<sup>37</sup> Br,<sup>37</sup> I<sup>38</sup>) and IX (X = Cl, Br, I)<sup>37</sup> series. The same geometries were used both in the NR and relativistic calculations. The HX, XF and IX bond distances in Å are: 0.9170 (HF), 1.2746 (HCl), 1.6283 (ClF), 2.3210 (ICl), 1.4145 (HBr), 1.7590 (BrF), 2.4691 (IBr), 1.6090 (HI), 1.9098 (IF) and 2.6663 (I<sub>2</sub>).

In relativistic and NR calculations we employed the non-relativistic Dunning's augmented correlation-consistent aug-cc-pCV5Z basis set for H, F and Cl atoms.<sup>39</sup> For Br and I we used the relativistic acv4z basis sets of Dyall, dyall.acv4z.<sup>40</sup> In relativistic calculations, the small component basis sets were obtained by applying restricted kinetic balance (RKB) prescription as implemented in the DIRAC package.

Unless otherwise indicated, uncontracted gaussian basis sets were used with the common gauge-origin (CGO) approach in all calculations. The rate of convergence of shielding values was studied comparing results that use conventional orbitals with those obtained using London atomic orbitals in both NR and relativistic regimes. Results of relativistic isotropic shielding calculations with and without London atomic orbitals are displayed for comparison in the last column of Table 3.

To describe the coulombic electron–nucleus interaction, a point nuclear model was employed in all calculations. This nuclear model was used in the derivation of the LRESC operators of eqn (16) and (21). In line with this, nuclear size effects were not considered in the present work. They are small or very small and do not affect the main conclusions of this work. Nevertheless, in the last column of Table 3 we include the results of isotropic shieldings using finite nuclei in the electrostatic electron–nucleus interaction, modeled by Gaussian charge distributions as implemented in the DIRAC package.

Relativistic Dirac–Coulomb Hartree–Fock wave functions and linear response calculations were performed excluding bi-electronic (SS|SS) and Gaunt (SL|SL) integrals in all cases (L and S denote large and small component basis functions, respectively). The value of the speed of light used throughout all four-component calculations was 137.0359998 a.u.

We have performed different kinds of relativistic linear response calculations, considering: (i) both (e–e) and (e–p) coupling terms, *i.e.* terms arising from transitions between occupied and unoccupied positive-energy orbitals, and between the occupied positive-energy and the unoccupied negative-energy orbitals, respectively; (ii) only the (e–e) coupling terms; and (iii) only the (e–p) coupling terms.<sup>41</sup> These different calculating schemes were applied for the calculation of shieldings and also of the spin-rotation constants.

All the results displayed in the tables and figures of this article correspond to the scheme of calculations named above as (i). Only after the full calculation was performed, the (e–e) and (e–p) parts of the linear response were split.

We have also solved the linear response equations considering separately the (e–e) and the (e–p) coupling terms. They give values which are very close to those corresponding to the coupled equations (scheme (i)); meaning that the error is very small when ignoring the coupling of the two kinds of coupling terms in the Hessian.<sup>41</sup> These results are in agreement with previous studies of shieldings.<sup>42</sup>

Quantitatively, the differences in the (e–e) part of  $\sigma_{\perp}$  are of 1.6% (in 36.34 ppm) for Br in HBr and less than 0.1% for all other nuclei in the whole set of compounds. For all calculations of  $\sigma_{\perp}^{(e-p)}$  the differences are less than 0.1%. For  $M_{\perp}^{(e-e)}$  the differences are also negligible, whereas its (e–p) part are vanishingly small in both cases.

## 4 Results and discussion

In order to show the accuracy of the results of calculations using the three models that are specified in Table 1, we start

with the analysis of how atomic are the electronic OZ-K, SZ-K and B-SO electronic mechanisms. In other words, the validity of replacing eqn (26) by eqn (28). Then we shall show the results of calculations of  $\sigma_{\perp}^{(e-e)}$  vs. different models, *e.g.* M-I, M-II and M-III as they are given in Table 1. We shall also show a comparison with NR values.  $M_{\perp}^{(e-e)}$  and  $\sigma_{\perp}^{(e-e)}$  were calculated by applying eqn (9) and (10). As highlighted above one interesting point is related to the importance of the contribution of the new SO-S mechanism. This will be addressed in Section 4.3.

The isotropic contributions are analyzed at the end of this general section. They are used by experimentalists. Furthermore, we emphasize that our analysis is performed for linear molecules.

### 4.1 Core-dependent electronic contributions

In eqn (26)  $M_{\perp}^{\text{elec-LRESC}}$  and  $\sigma_{\perp}^{(e-e)\text{-LRESC}}$  are related to each other by the appearance of four electronic mechanisms. It shows that some mechanisms that appear in a relativistic framework do not appear in Flygare's relation. Most of those mechanisms are core-dependent.

Given those new findings, we ask ourselves about the exactitude of the following relation

$$\sigma_{\perp}^{\text{atom}(e-e)\text{-LRESC}} \cong \sigma_{\perp,Y}^{\text{OZ-K}} + \sigma_{\perp,Y}^{\text{SZ-K}} + \sigma_{\perp,Y}^{\text{B-SO}}. \quad (33)$$

We consider the perpendicular components of the relation among  $\sigma$  and  $M$  because the parallel component of  $M$  is null.

We remind here that the rhs of eqn (33) refers to the shielding of the given atom in the molecule of interest, whereas the lhs refers to the isolated atom. If this eqn is valid within an error of less than 1% we shall assume that eqn (29) can be used with confidence. In other words, the assumption we used for getting eqn (28) from eqn (26) is well justified.

In Fig. 1 we show the addition of these three contributions, defined as

$$\sigma_{\perp,Y}^{\text{LRESC-core}} = \sigma_{\perp,Y}^{\text{OZ-K}} + \sigma_{\perp,Y}^{\text{SZ-K}} + \sigma_{\perp,Y}^{\text{B-SO}} \quad (34)$$

for different atoms in different environments. Then, how close are  $\sigma_{\perp}^{\text{atom}(e-e)\text{-LRESC}}$  and  $\sigma_{\perp,Y}^{\text{LRESC-core}}$  in the worst case? We found that, for iodine atoms they are 2161 ppm and 2167 ppm, respectively. For fluorine they are 8.70 ppm and 8.86 ppm, respectively. So, they are very close to each other.

We also depict the results of four-component calculations of the (e–e) part for each atom. As can be seen these four-component values are close to the LRESC contributions for a given atom in the whole set of molecules studied. Furthermore we show, in dashed lines, the behavior of the curves that match both types of points. In the case of LRESC-core points the dependence is such that  $\sigma_{\perp}^{\text{atom}(e-e)\text{-LRESC}} \simeq 8.706 \times 10^{-3} Z_Y^{3.129}$  ppm. On the other hand the four-component points fit with the following dependence,  $\sigma_{\perp}^{\text{atom}(e-e)} \simeq 7.935 \times 10^{-3} Z_Y^{3.125}$  ppm, which shows the agreement of the curves. It means that the leading terms of the LRESC model give results that are close to that of the four-component RPPA method. There are higher-order corrections that should be included in order to get closer results among these two- and four-component methods. It is



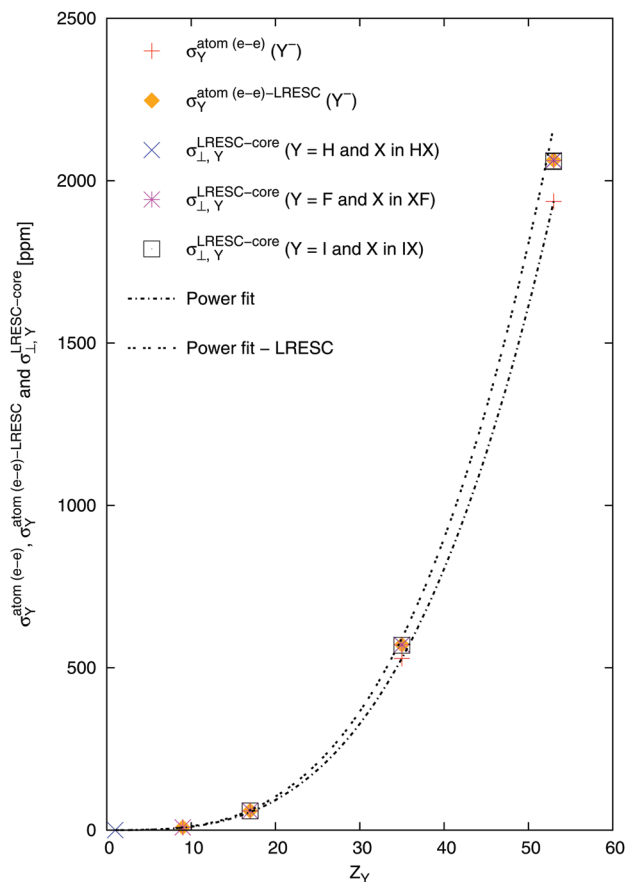


Fig. 1 Comparative values of  $\sigma_{\perp,Y}^{\text{atom}(e-e)}$ ,  $\sigma_{\perp,Y}^{\text{atom}(e-e)\text{-LRESC}}$  and  $\sigma_{\perp,Y}^{\text{LRESC-core}}$  for the family of compounds HX ( $X = \text{F, Cl, Br, I}$ ), XF and IX ( $X = \text{Cl, Br, I}$ ). In dashed lines approximate estimations for both kind of approximations are shown. All values are given in ppm.

interesting to see that the Mass Correction effect which corresponds to the SZ-K mechanism scales approximately as  $\sigma_Y^{\text{SZ-K}} \approx 11.3 \times 10^{-3} Z_Y^{3.1}$  ppm.<sup>43</sup>

We are now able to replace, with confidence, eqn (26) by eqn (28). Then, we do the next assumption: we assume the equivalence among LRESC atomic (e-p) terms and the four-component atomic terms. This fact will produce eqn (29).

#### 4.2 Analysis of models M-I, M-II and M-III

As was mentioned above the relation among nuclear spin-rotation and nuclear magnetic shielding constants, proposed by Ramsey and further developed by Flygare, breaks down within the relativistic regime.

We analyze here in some detail, the application of the three M-i models to the whole family of compounds selected for our studies. In all cases we only analyze the perpendicular component. As mentioned above we were searching first for new models that could relate the absolute values of  $\sigma^{(e-e)}$  to  $M$  constants. This takes us to the first model, M-I. It considers that there is no (e-e) contributions from free atoms, an assumption that is not valid any longer within the relativistic domain. Then we added such a contribution and the M-II model appears. Furthermore we realized that another term

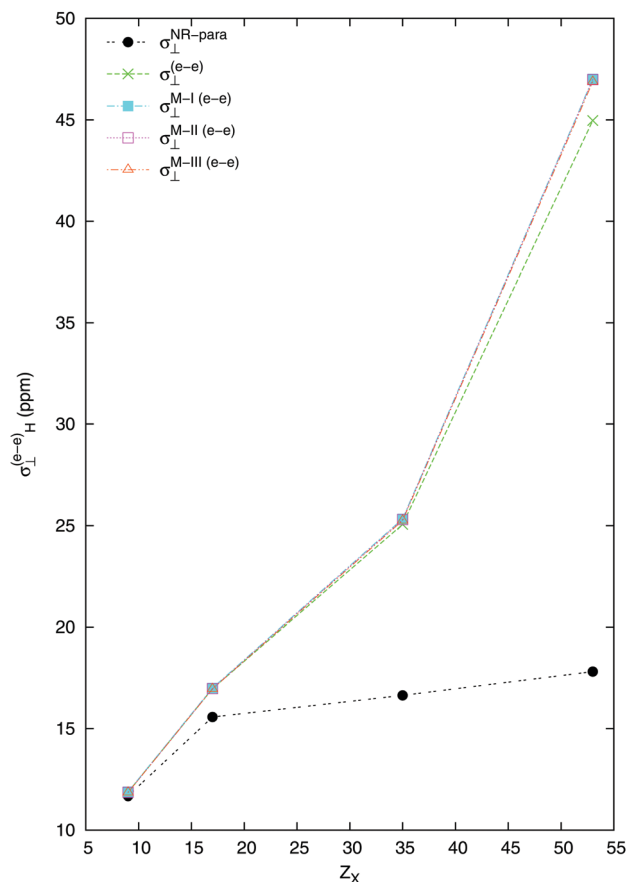


Fig. 2 Patterns of the dependence of  $\sigma_{\perp,H}^{(e-e)}$  in HX ( $X = \text{F, Cl, Br and I}$ ), the ones obtained with different models of Table 1, and Flygare's relation of eqn (2).  $\sigma_{\perp,H}^{\text{NR-para}}$  is also given. All values are in ppm.

should be included, meaning the SO-S term. It gives the best model we are presenting here, the M-III one.

As the benchmark numbers of  $\sigma_{\perp}^{(e-e)}$  we use results of four-component relativistic calculations.

In Fig. 2 we show the values of  $\sigma_{\perp,H}$  in hydrogen halides, HX ( $X = \text{F, Cl, Br, I}$ ). They correspond to the NR Flygare's relationship of eqn (2), our models M-i and the four-component  $\sigma_{\perp,H}^{(e-e)}$ .

The following comments are noteworthy. As stated previously, the main relativistic effect in  $\sigma_H$  of hydrogen halides is due to the SO-L mechanism.<sup>7,30</sup> This is included in both constants  $M$  and  $\sigma$  as shown in eqn (16) and (21). Therefore, as was shown in ref. 14, Flygare's relation is fulfilled in this particular case.

In addition, the core contributions of  $\sigma_H^{\text{atom}(e-e)}$  arising from OZ-K, SZ-K and B-SO mechanisms are negligibly small. Then, the models M-II and M-III are equivalent so that they are able to describe  $\sigma_{\perp,H}^{(e-e)}$  with good accuracy. Their values are within 5% for iodine, which is the heaviest atom in the series.

In Fig. 3 we show the (e-e) values corresponding to the heavy atom X of hydrogen halides. It is seen that when the nucleus X becomes heavier, core relativistic effects become more important, and therefore the values obtained using the model M-I fail. It is observed that the values of  $\sigma_{\perp,X}^{\text{M-I}}$  are still close to the NR values  $\sigma_{\perp,X}^{\text{NR-para}}$  even when the atomic number of the nucleus X increases.

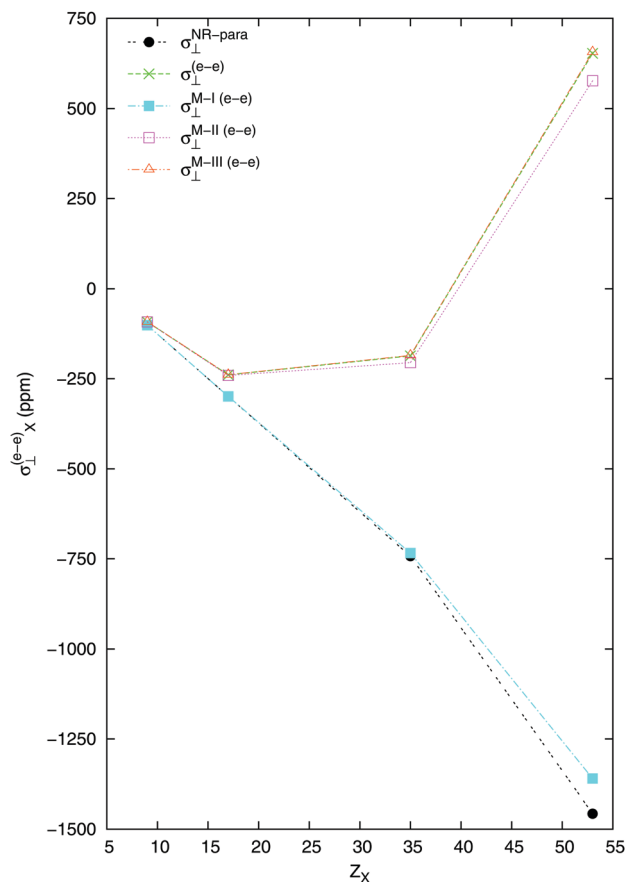


Fig. 3 Patterns of the dependence of  $\sigma_{\perp,X}^{(e-e)}$  in HX ( $X = \text{F, Cl, Br and I}$ ), the ones obtained with different models of Table 1, and Flygare's relation of eqn (2).  $\sigma_{\perp,X}^{\text{NR-para}}$  is also given. All values are in ppm.

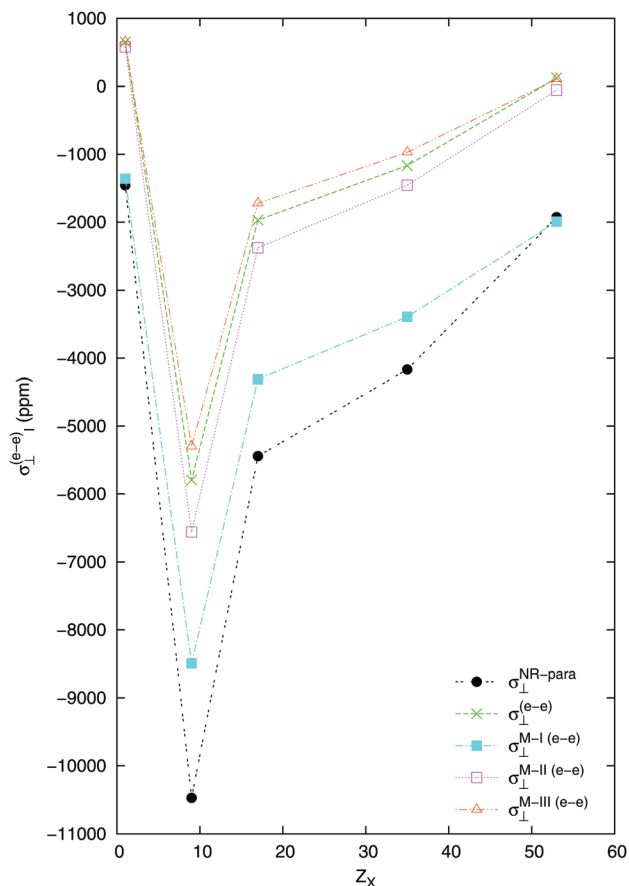


Fig. 4 Patterns of the dependence of  $\sigma_{\perp,I}^{(e-e)}$  in IX ( $X = \text{H, F, Cl, Br and I}$ ), the ones obtained with different models of Table 1, and Flygare's relation of eqn (2).  $\sigma_{\perp,I}^{\text{NR-para}}$  is also given. All values are in ppm.

On the other hand, by including the atomic value of  $\sigma_X^{\text{atom}(e-e)}$  we obtain a very good agreement between the results of four-component relativistic calculations and those of M-II and M-III models.

Another set of molecules, namely IX ( $X = \text{H, F, Cl, Br, I}$ ), was studied performing calculations of  $\sigma$  and  $M$  constants for both the iodine and the  $X$  nuclei. Results corresponding to the three models M-I to M-III are compared with the values of reference  $\sigma_{\perp,I}^{(e-e)}$ . They are shown in Fig. 4 together with the NR values,  $\sigma_{\perp,I}^{\text{NR-para}}$ .

Since core effects for the shielding of iodine are close to the values of  $\sigma_I^{\text{atom}(e-e)}$  ( $\approx 1936$  ppm), a large difference between  $\sigma_{\perp,I}^{(e-e)}$  and  $\sigma_{\perp,I}^{\text{M-I}}$  is expected. This is what is observed in Fig. 4. Moreover, the larger the value of  $Z_X$ , more accurate the model M-II becomes. This allows us to conclude that also in this case, both models M-II and M-III improve relativistic Flygare's prescription.

Results of calculations for nucleus  $X$  in the IX family of compounds are shown in Fig. 5. Some observations are in place about what is shown in this figure. As  $Z_X$  increases, the values of  $\sigma_{\perp,X}^{\text{NR-para}}$  become closer to  $\sigma_{\perp,X}^{\text{M-I}}$ , than to the four-component  $\sigma_{\perp,X}^{(e-e)}$ . This fact indicates a huge failure in Flygare's relation. For iodine, the difference among the most accurate four-component value

and that of the M-III model is about 50 ppm, while that given by eqn (2) is larger than 2000 ppm.

The family XF of compounds is a special case. For these molecules the large electronegativity of the fluorine atom gives rise to large spin-orbit effects, which include both SO-L and SO-S. While the SO-L is already accounted for in Flygare's relation, the SO-S is neither atomic nor included in the Flygare's relation. This mechanism, which is not included in the models M-I and M-II, will be analyzed in the next subsection.

For the fluorine atoms the value of  $\sigma_F^{\text{atom}(e-e)}$  is approximately 10 ppm. On the other hand, as depicted in Fig. 6, the difference between  $\sigma_{\perp,F}^{\text{M-I}}$  and  $\sigma_{\perp,F}^{\text{NR-para}}$  in IF is close to 170 ppm, where the main relativistic effect is the SO-S contribution to the NSR constant; also higher-order effects play an important role. There is still a difference of 100 ppm with  $\sigma_{\perp,F}^{(e-e)}$  which is also associated with the SO-S mechanism.

### 4.3 Contributions from the SO-S mechanism

As shown in the previous section, although the model coined as M-II in Table 1 describes  $\sigma_{\perp}^{(e-e)}$  adequately, for most of the molecular systems studied here there are some molecules in which there exists an appreciable difference between these values. These systems have large spin-orbit effects in which

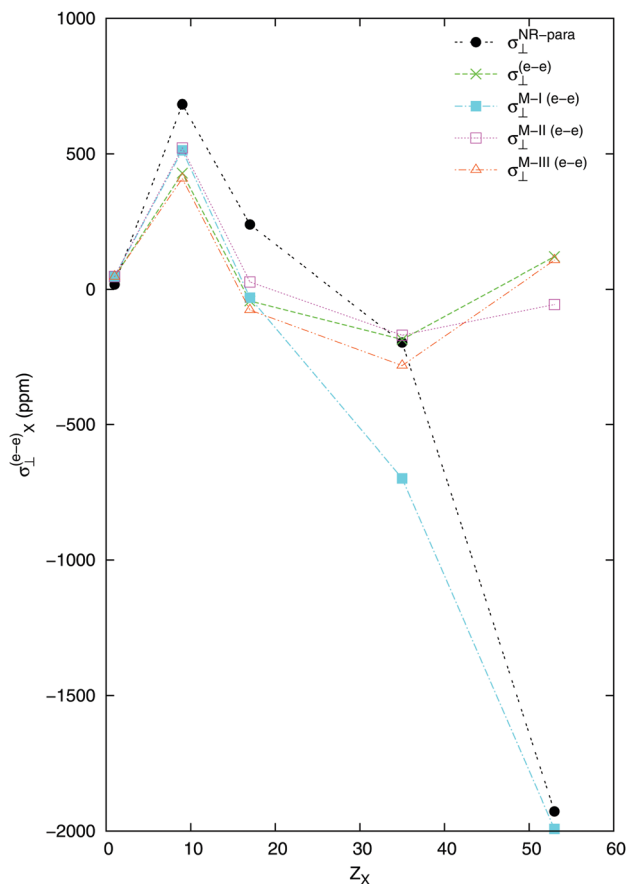


Fig. 5 Patterns of the dependence of  $\sigma_{\perp}^{(e-e)}_X$  in IX (X = H, F, Cl, Br and I), the ones obtained with different models of Table 1, and Flygare's relation of eqn (2).  $\sigma_{\perp,X}^{(NR-para)}$ . All values are in ppm.

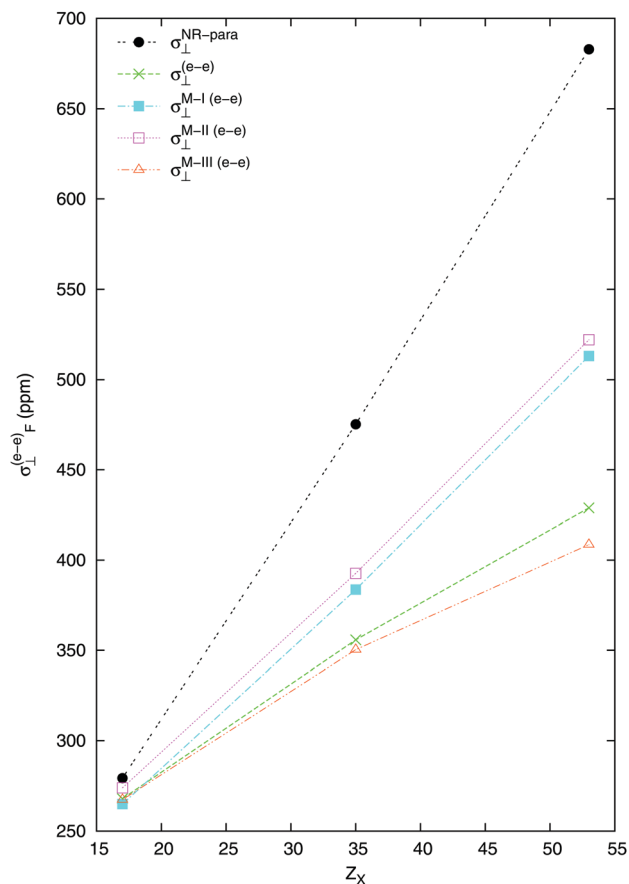


Fig. 6 Patterns of the dependence of  $\sigma_{\perp}^{(e-e)}_F$  in XF (X = Cl, Br and I), the ones obtained with different models of Table 1, and Flygare's relation of eqn (2).  $\sigma_{\perp,F}^{(NR-para)}$ . All values are in ppm.

case the model M-II does not work properly. In the third column of Table 2 we show results of the differences between the perpendicular (e-e) component of the shielding and the values of  $\sigma_{\perp}^{M-II}$ . This difference was calculated as

$$\Delta\sigma_{\perp,Y}^{II} = \sigma_{\perp,Y}^{(e-e)} - \sigma_{\perp,Y}^{M-II} \quad (35)$$

The contributions of the SO-S mechanism are given in the fourth column of Table 2. For the heavier atoms in the family of HX compounds, the SO-S mechanism accounts for the error in the model M-II, with an agreement that is within 25% for chloride, 7% for bromine and 5% for iodine. Although for Hydrogen the SO-S mechanism does not describe adequately the difference within the errors defined above, this difference is always smaller than 5%. On the other hand, for XF compounds the errors are larger, especially for iodine in IF with a difference between  $\sigma_{\perp,I}^{SO-S}$  and  $\Delta\sigma_{\perp,I}^{II}$  that is close to 500 ppm, as shown in Fig. 7.

In Fig. 8 we show the importance of the SO-S contribution, depending on how heavy the atom is the studied molecule. For light systems  $\Delta\sigma^{II}$  is small, but it increases dramatically when the atoms become heavier. In the case of IX systems one must include the contributions of the SO-S mechanism in order to get closer results to the four-component calculations.

Table 2 Results of calculations using eqn (35) and the contribution of  $\sigma_{\perp,Y}^{SO-S}$  from the LRESP formalism for comparison. In the second column an atomic index is given for each atom. This is the order shown in Fig. 8 in the abscissa

Molecule	Y(index)	$\Delta\sigma_{\perp,Y}^{II}$	$\frac{1}{2}\sigma_{\perp,Y}^{SO-S}$
HF	F (1)	0.1229	0.4047
	H (2)	0.0056	-0.007
HCl	Cl (3)	1.7835	2.2359
	H (4)	-0.0002	-0.0162
HBr	Br (5)	18.8324	20.2157
	H (6)	-0.2479	-0.0555
HI	I (7)	76.0476	79.7705
	H (8)	-2.0068	-0.1082
ClF	Cl (9)	19.1046	22.8714
	F (10)	-6.0071	-6.5715
BrF	Br (11)	203.1594	262.9432
	F (12)	-36.8840	-42.3210
IF	I (13)	761.1004	1258.1374
	F (14)	-93.1288	-113.4171
ICl	I (15)	405.6070	652.6087
	Cl (16)	-70.2610	-103.8723
IBr	I (17)	289.0529	483.3305
	Br (18)	-15.7822	-112.1212
I <sub>2</sub>	I (19)	175.9080	162.9558

**Table 3** Isotropic contributions to the nuclear shielding of linear molecules. The last column contains the results of four-component calculations. Results obtained using the gaussian-type nuclear model (with and without London atomic orbitals), and values taken from other authors are given between parentheses. Available experimental values of SRC are given between brackets. All values are in ppm

Mol	$Z_Y$	$\frac{2}{3} \frac{m_p I}{g_Y} M_Y$	$\sigma_Y^{\text{atom}}$	$\frac{2}{3} \frac{m_p I}{g_Y} M_Y + \sigma_Y^{\text{atom}}$	$\sigma_Y^{\text{iso}}$
HF	9	-57.95 [-57.01] <sup>f</sup>	480.38	422.43	415.84 (415.84) <sup>a</sup> (415.98) <sup>b</sup> (418.36) <sup>c</sup> (416.2) <sup>d</sup>
HCl	17	-192.38 [-189.35] <sup>g</sup>	1132.22	939.84	934.18 (934.17) <sup>a</sup> (934.00) <sup>b</sup> (973.9) <sup>d</sup>
HBr	35	-482.78 [-499.39] <sup>h</sup>	3357.02	2874.23	2867.10 (2865.24) <sup>a</sup> (2865.51) <sup>b</sup> (2945.66) <sup>c</sup> (2899.4) <sup>d</sup>
HI	53	-900.50 [-978.12] <sup>i</sup>	6424.24	5523.74	5488.83 (5469.77) <sup>a</sup> (5469.93) <sup>b</sup> (5860.34) <sup>c</sup> (5716.3) <sup>d</sup>
ClF	9	210.96 [168.48] <sup>j</sup>	480.38	691.34	683.91 (683.91) <sup>a</sup> (684.30) <sup>b</sup> (640.4) <sup>e</sup>
BrF	9	291.93 [263.76] <sup>k</sup>	480.38	772.31	756.73 (756.72) <sup>a</sup> (756.86) <sup>b</sup> (666.2) <sup>e</sup>
IF	9	375.82 [386.64] <sup>k</sup>	480.38	856.20	790.75 (790.75) <sup>a</sup> (787.28) <sup>b</sup> (747.3) <sup>e</sup>
ClF	17	-1598.31 [-1559.00] <sup>j</sup>	1132.22	-466.10	-473.76 (-473.78) <sup>a</sup> (-473.88) <sup>b</sup> (-617.5) <sup>e</sup>
BrF	35	-3568.06 [-3638.56] <sup>k</sup>	3357.02	-211.04	-255.50 (-258.18) <sup>a</sup> (-258.03) <sup>b</sup> (-221.7) <sup>e</sup>
IF	53	-5621.35 [-6108.51] <sup>k</sup>	6424.24	802.90	531.00 (507.57) <sup>a</sup> (507.74) <sup>b</sup> (366.2) <sup>e</sup>
ICl	53	-2819.73	6424.24	3604.51	3348.58 (3326.03) <sup>a</sup> (3326.48) <sup>b</sup>
IBr	53	-2177.63	6424.24	4246.61	4006.37 (3984.55) <sup>a</sup> (3984.96) <sup>b</sup>
I <sub>2</sub>	53	-1234.44	6424.24	5189.80	5132.57 (5112.98) <sup>a</sup> (5103.90) <sup>b</sup>
ICl	17	25.75	1132.22	1157.97	1129.35 (1129.32) <sup>a</sup> (1124.49) <sup>b</sup>
IBr	35	-388.30	3357.02	2968.72	2984.86 (2983.12) <sup>a</sup> (2974.95) <sup>b</sup>

<sup>a</sup> Calculations using the gaussian nuclear model and conventional orbitals. <sup>b</sup> Calculations using the gaussian nuclear model and London atomic orbitals. <sup>c</sup> Taken from ref. 11. <sup>d</sup> Taken from ref. 44. <sup>e</sup> Taken from ref. 45. <sup>f</sup> Experimental value of  $M_Y$  taken from ref. 46. <sup>g</sup> Experimental value of  $M_Y$  taken from ref. 47. <sup>h</sup> Experimental value of  $M_Y$  taken from ref. 48. <sup>i</sup> Experimental value of  $M_Y$  taken from ref. 49. <sup>j</sup> Experimental value of  $M_Y$  taken from ref. 50. <sup>k</sup> Experimental value of  $M_Y$  taken from ref. 51.

#### 4.4 Isotropic values of $\sigma$

In this subsection we shall analyze the accuracy of the results of calculations with our models as compared with the results of calculations of  $\sigma^{\text{iso}}$  performed with four-component relativistic polarization propagators. As mentioned at the end of Section 1 we obtain the total value of  $\sigma$  through the calculation of two independent terms, meaning (e-e) and (e-p). Each one of them does have different accuracies.

Even though the SO-S mechanism is quite important for heavier systems, it does not contribute to the isotropic parameters for linear molecules, as shown in eqn (32). It is worth mentioning that the formal expressions of models M-II and M-III are the same for linear molecules.

In Table 3 we show the contributions of each different term of the rhs of eqn (32), their addition and the value of four-component calculation of isotropic shieldings. We include also the values of  $\sigma^{\text{iso}}$  using gaussian-type nuclear models as implemented in the DIRAC code, showing that almost all results are close to those obtained using a point-type nuclear model. An exception is the shielding of iodine in all compounds, where a systematic nuclear size effect contribution of 20 ppm is obtained. This indicates that this effect is very local and of atomic nature. In addition, we display values of isotropic shieldings using London atomic orbitals (with gaussian-type nuclear model), and show that our results are quite good; meaning that our basis sets are of such a quality that the total values obtained with them are close (less than 0.4% of difference in all cases) to that obtained with London orbitals.

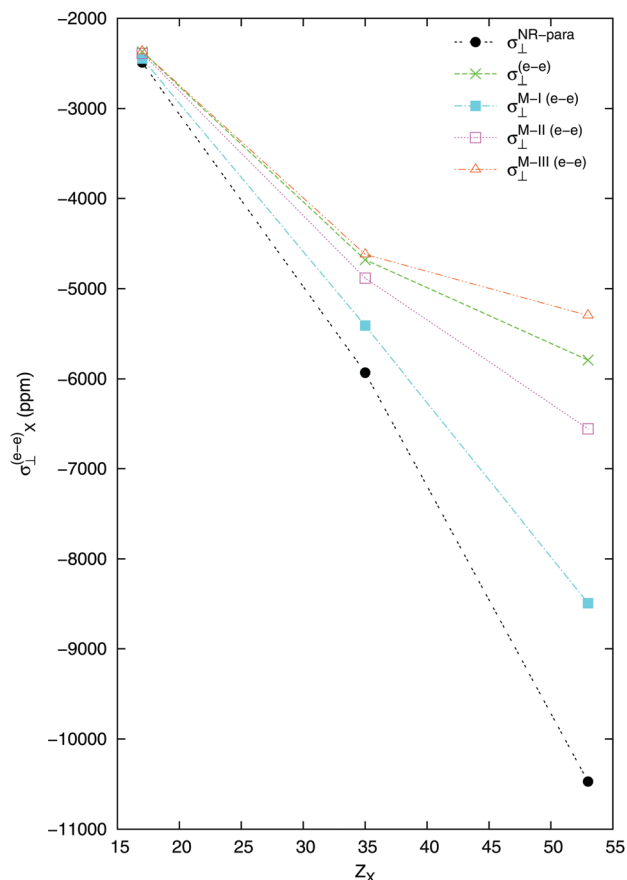


Fig. 7 Patterns of the dependence of  $\sigma_{\perp}^{(e-e)}_X$  in the set of molecules XF (X = Cl, Br and I), the ones obtained with different models of Table 1, and Flygare's relation of eqn (2).  $\sigma_{\perp}^{(NR-para)}$ . All values are in ppm.

In the same table we show the results of previous calculations, which are close to ours in most compounds.

We also observe that the closeness of the results obtained with our models, compared with those of four-component relativistic methods, depends on the type of compounds and also with the type of atoms. The closest is found for Br in HBr, where the difference is of 0.25%. In the whole family of hydrogen halides the largest difference is of 1.58% for  $\sigma_F$ . For the other family of compounds, meaning that of the XY type (X and Y = F, Cl, Br, I), the closeness varies quite a lot, being among 51% for  $\sigma_I$  in IF till 0.54% for  $\sigma_{Br}$  in IBr. There is a large difference for Br in BrF (17.4%). All other results are close to or less than 8%. Calculations with models M-i (i = I, II and III) in the XF family of compounds give the worst results.

Why do we find such a difference in the performance of our models? In Table 4 we show the results of calculations for both terms, (e-e) and (e-p), of eqn (32) though considering each component as given in eqn (30) and (31). Then it is possible to get an indication about how good are the (e-e) and (e-p) terms of our models to reproduce the four-component equivalent terms.

It is important to highlight the fact that the (e-e) contribution to the atomic shielding increase with the nuclear charge. This is one of the reasons why Flygare's NR relationship fails within the relativistic framework because it considers that this contribution

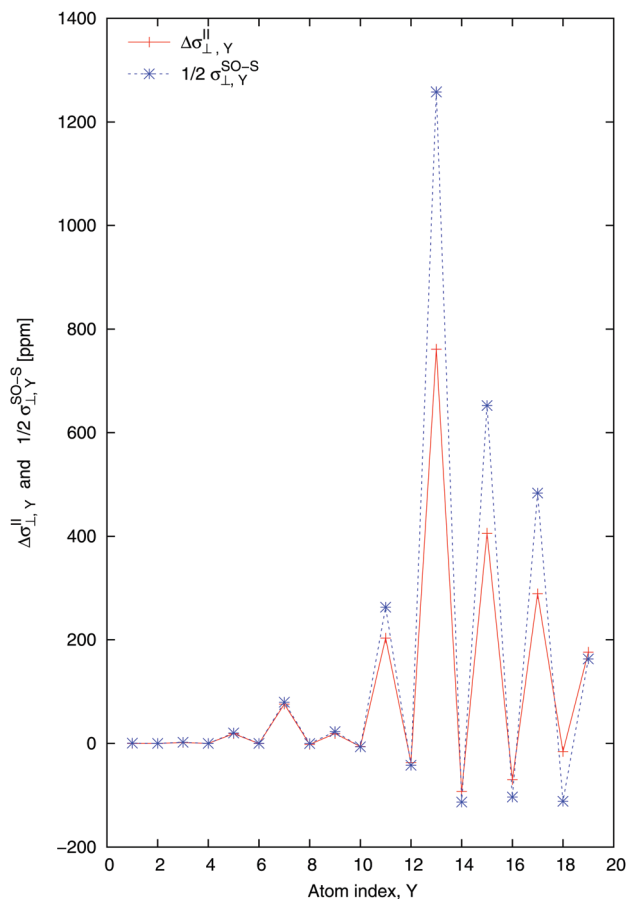


Fig. 8  $\Delta\sigma_{\perp,Y}^{II}$  and  $\frac{1}{2}\sigma_{\perp,Y}^{SO-S}$  as a function of the atomic index defined on Table 2.

Table 4 Isotropic values of shieldings in ppm. The last two columns show results of four-component relativistic calculations

Mol	$Z_Y$	$\frac{2}{3} \frac{m_p I}{g_Y} M_Y^{(e-e)}$	$\sigma_Y^{atom(e-e)}$	$\frac{2}{3} \frac{m_p I}{g_Y} M_Y^{nuc}$	$\sigma_Y^{atom(e-p)}$	$\sigma_Y^{(e-e)}$	$\sigma_Y^{(e-p)}$
HF	9	-67.67	9.04	9.72	471.34	-58.81	474.65
HCl	17	-199.54	58.08	7.16	1074.13	-141.69	1075.87
HBr	35	-489.34	528.71	6.56	2828.31	36.34	2830.76
HI	53	-906.30	1936.39	5.79	4487.86	998.97	4489.86
ClF	9	176.52	9.04	34.43	471.34	185.13	498.78
BrF	9	255.77	9.04	36.16	471.34	255.78	500.95
IF	9	341.95	9.04	33.87	471.34	292.66	498.09
ClF	17	-1631.93	58.08	33.62	1074.13	-1574.86	1101.10
BrF	35	-3606.79	528.71	38.73	2828.31	-3118.05	2862.54
IF	53	-5659.89	1936.39	38.54	4487.86	-3992.59	4523.58
ICl	53	-2873.74	1936.39	54.01	4487.86	-1190.05	4538.63
IBr	53	-2259.83	1936.39	82.21	4487.86	-560.47	4566.84
I <sub>2</sub>	53	-1327.90	1936.39	93.45	4487.86	557.66	4574.91
ICl	17	-20.60	58.08	46.35	1074.13	16.00	1113.35
IBr	35	-465.62	528.71	77.32	2828.31	86.10	2898.76

is zero. At the four-component level the atomic shielding,  $\sigma_Y^{atom}$ , arises as the addition of both  $\sigma_Y^{atom(e-e)}$  and  $\sigma_Y^{atom(e-p)}$ .

Now we analyze the worst cases: IF and BrF. For  $\sigma_F$  in the BrF molecule, the reproduction of the (e-e) part has a 3.53% of



difference with respect to the four-component relativistic shielding calculation though it is of 1.31% for the (e-p) part. In the case of  $\sigma_{\text{Br}}$  in the same molecule the differences in both (e-e) and (e-p) parts are 1.28% and 0.16%, respectively. For  $\sigma_{\text{F}}$  in IF the (e-e) part has a difference of 20% while for the (e-p) part such a difference is of 1.4%. In the case of  $\sigma_{\text{I}}$  such differences are of 6.7% and less than 0.1%, respectively. One can conclude that the differences among the results using four-component relativistic methods and our M-II or M-III models arise from both parts, (e-e) and (e-p). In the case of BrF and IF, the contributions of both of them are of opposite sign and of equivalent magnitude. Then, the errors in each of them are added to give larger values. On the other hand, the errors in the (e-p) part are smaller than in the other part. So, when the contributions of the (e-p) part are much larger than the (e-e) part, the error in the total values is the smallest.

On the other side, our models may be considered the natural extension of Flygare's prescription, because they allow us to obtain absolute shielding values from experimental nuclear spin-rotation data combined with atomic calculations, which can be obtained to a high level of accuracy.

## 5 Conclusions

Absolute NMR magnetic shieldings can usually not be extracted from experiments. In order to get "experimental" values, what was broadly applied by experimentalists was a relationship proposed a long time ago by Ramsey and then extended by Flygare. It gives quite good values when molecular systems do not contain heavy atoms. Otherwise it breaks down. For heavy-atom containing molecules one should look for new ways of getting a relationship among nuclear spin-rotation and magnetic shielding constants,  $M$  and  $\sigma$ , respectively, that should be valid within a relativistic framework.

One of the goals of this work is to offer new models that generalize that of Flygare. We developed three, *e.g.* M-*i* (*i* = I, II and III) the best one being the M-III. Our models can be used to obtain "experimental" as well as theoretical values of shieldings. They consider the new relativistic relationship among magnetic shieldings and spin-rotation tensors developed recently by some of the present authors, and also accurate four-component calculations of the shielding of free atoms.

To get our new models we first performed a two-component relativistic analysis of the relationship among  $M$  and  $\sigma$ . From this analysis we were able to introduce the following two assumptions:

- There should be an equivalent relationship among  $M$  and  $\sigma$  that is valid within both relativistic formalisms, *i.e.* the four-component relativistic polarization propagator and the two-component LRESC model

- The core-dependent part of such a relationship is such that it can be replaced by summing the contributions (e-e) and (e-p) to the shielding of free atoms. Its most accurate value is obtained applying four-component relativistic methods.

Given these two assumptions and the fact that the spin-rotation tensor does not contain (e-p) contributions within the LRESC model (meaning that only very small contributions are

likely obtainable for these terms within a relativistic regime), we took one step further and proposed three models of which the most accurate is given by eqn (29), or

$$\sigma_{\text{Y}} \cong \frac{m_{\text{p}}I}{g_{\text{Y}}}M_{\text{Y}} + \sigma_{\text{Y}}^{\text{atom}} + \frac{1}{2}\sigma_{\text{Y}}^{\text{SO-S}}. \quad (36)$$

It is worth highlighting here that a new term coined as SO-S must be considered. One should include this term in order to get results that may match the most accurate ones, *i.e.* that of the four-component calculations.

The isotropic shielding for linear molecules is obtained from the last expression as

$$\sigma_{\text{Y}}^{\text{iso}} \cong \frac{2}{3} \frac{m_{\text{p}}I}{g_{\text{Y}}}M_{\text{Y}} + \sigma_{\text{Y}}^{\text{atom}}. \quad (37)$$

This expression has the same formal appearance as that of eqn (3). In other words it is the natural relativistic generalization of the famous Flygare relationship among NMR shieldings and spin-rotation constants.

Another important finding is that reliable (e-e) contributions for free atoms can be obtained as  $\sigma_{\text{Y}}^{\text{atom(e-e)}} \cong 7.935 \times 10^{-3} Z_{\text{Y}}^{3.125}$  ppm.

The magnetic shieldings of a set of halogen containing diatomic molecules were calculated applying the three models. The perpendicular component of the shieldings was analyzed because such a component is the most sensible to the relationship among tensors  $M$  and  $\sigma$ .

When the results obtained applying our models were compared with those of the relativistic formalism of polarization propagators, it was found that for the total shielding constants, the best agreement was found for hydrogen halides. In this case the largest difference was less than 0.7%. For the other set of molecules, *e.g.* XY (*X* and *Y* = F, Cl, Br and I), we also obtained close results together with some exceptions. The largest errors appear when the contributions of the two different terms of eqn (29) have different sign and similar absolute values. This happens for di-halogen molecules.

## Acknowledgements

Our models were named M-*i* (*i* = I, II and III) as a thankful recognition of the excellent work of Martín Ruiz de Azúa who passed away in 2014. We miss him. We thank the comments of referees that improved the manuscript. We gratefully acknowledge partial support from Secretaría General de Ciencia y Técnica (SGCyT-UNNE), the Argentinian National Research Council for Science and Technology (CONICET) and the Argentinian Agency for Promotion of Science and Technology (Grant PICT2012-1214).

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