

REVIEW

Foundations of the LRESC model for response properties and some applications

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Abstract

Accurate calculations of some response properties, like the NMR spectroscopic parameters, are quite exigent for the theoretical quantum chemistry models together with the computational codes that are written from them. They need to include a very good description of the electronic density in regions close to the nuclei. When heavy-atom containing systems are studied, those requirements become even higher. Given that relativistic effects must be included in one way or another on the calculation of response properties of heavy-atoms and heavy-atom containing molecules, different schemes were developed during the past decades to include them in as good as possible way. There are some four-component models, which include relativistic effects in a very compact way, although calculations have large time-consumption; one also needs to deal with new and unusual four-component operators. There are also two-component models, which in general may be less accurate, although their application to property calculations on medium-size and large-size molecules are feasible, and they maintain the application of usual operators. In this review, we give the fundamentals of the two-component linear response elimination of small component formalism, LRESC, together with some applications to few selected response properties. New physical insights do appear when the LRESC model is used to analyze the effect of the environment on magnetic shieldings, and when one search for the relativistic extension of well-known nonrelativistic relationships like Flygare's relation among the NMR magnetic shielding and the nuclear spin-rotation constant. A similar relationship is found for the g-tensor and the susceptibility tensor.

KEYWORDS

g-tensor, NMR, response properties, spin-rotation tensor, two-component methods

1 | INTRODUCTION

The strong influence of relativistic effects on atomic and molecular response properties of heavy-atom containing molecules was first shown few decades ago.^[1] Pyykkö included relativistic effects in the calculations of NMR spectroscopic parameters by applying a relativistic model that resemble Ramsey's theory^[2] and use relativistic molecular wave function of the relativistically parameterized extended Hückel method, REX.^[3] Other more elaborated semi-empirical methods and codes were later on used to improve those first results.^[4–6]

The importance of including relativistic effects on the calculation of response properties compelled the theoretical chemists to develop new specific relativistic theories and models. Several formalisms and models appeared in the literature from that time, whose implementations gave more accurate results than that obtained using previous schemes.^[7–12] We can split them into two broad groups: four-component methods and two-component methods.^[12–15]

Even though accurate calculations of response properties of medium-size molecules, meaning molecules containing more than 10 heavy atoms (belonging to the fourth row or below of the Periodic Table) cannot be actually performed using four-component ab initio methods, they provide

the best theoretical framework to do it. Conversely, they still have some sound theoretical difficulties about the interpretation of mechanisms and its electronic origin that will be mentioned below. One remarkable point that must be stressed is the fact that the four-component theoretical studies of magnetic properties using polarization propagators, one need to consider the contributions of the virtual pair creation/annihilation, to include what is known within the nonrelativistic (NR) regime as the diamagnetic contributions. This naturally arises within the relativistic regime, but it is not an easy task when the studies are performed with two-component methods.^[12,16]

Polarization propagators are among the most powerful methods to study response properties^[10,17–20] They can be used within both regimes, relativistic, and NR. The implementations of its four-component version^[21] does not include at the moment electron correlation til second-order of approach,^[22] which, at least within the NR regime must be used to get accurate results in the calculation of NMR magnetic properties.^[10,14] Still the four-component version of polarization propagators permit to get the paramagnetic and diamagnetic contributions by applying few well defined approximations shown in Ref. [23] In such a case, the NR paramagnetic contributions arises from the excitations to the positive-energy spectra and diamagnetic contributions by considering virtual pair creation/annihilation. We should mention that there is another recently developed scheme which permit the calculation of diamagnetic and paramagnetic relativistic terms for magnetic properties.^[24]

Taking into account these last findings, and the work of Fukui and coworkers^[25] who developed a gauge invariant scheme by including the external magnetic field in the Breit–Pauli Hamiltonian up to order c^{-4} , a new two-component formalism was derived by two argentinian groups.^[26,27] At almost the same time, another two-component formalism in which perturbation theory was applied to the Breit–Pauli Hamiltonian (Breit–Pauli perturbation theory, BPPT) although with different grounds was derived.^[28,29] The former model, known as linear response with elimination of small components, LRESC, was first applied to NMR magnetic shieldings, and then, recently, to other response properties.^[30–32]

In this review, we shall shortly explain the basic ideas that underlies to the LRESC model, and what physical insights do appears from its application. We shall explain it in a systematic way, and show how the leading relativistic corrections to the NR contributions of some response properties do appear, and shed some light about the electronic mechanisms that only appears within the LRESC model. We shall also explain how the LRESC models were used to get new relativistic relationships among few response properties, like among NMR magnetic shieldings and nuclear spin-rotation constants, and among g -factors and susceptibilities. The analysis of the main characteristic of the LRESC will be illustrated with results of calculations on molecular models and the following response properties: NMR magnetic shielding, nuclear spin-rotation tensor, g -tensor, and susceptibility.

2 | RESPONSE PROPERTIES

The study of spectroscopic parameters starts with the proposal of phenomenological perturbing Hamiltonians, from which experimental spectra are described accurately. In the case of perturbations that arise from internal or external magnetic fields and also from the molecular rotation, the phenomenological expression of the energy of a closed-shell molecule is

$$E = E_0 - \frac{1}{2} \mathbf{B} \otimes \boldsymbol{\chi} \otimes \mathbf{B} - \frac{1}{2m_p c} \mathbf{B} \otimes \mathbf{g} \otimes \mathbf{L} - \sum_K I_K \otimes \mathbf{M}_K \otimes \mathbf{L} - \sum_K \mathbf{B} \otimes (1 - \sigma_K) \otimes \boldsymbol{\mu}_K + \sum_{K>L} \boldsymbol{\mu}_K \otimes (\mathbf{D}_{KL} + \mathbf{J}_{KL}) \otimes \boldsymbol{\mu}_L \quad (1)$$

where \mathbf{L} is the rotational angular momentum (related to the system angular velocity $\boldsymbol{\omega} = \mathbf{I}^{-1} \otimes \mathbf{L}$, with \mathbf{I} the tensor of inertia). This momentum is given only by the rotational states of the nuclei of the system.^[32] In addition, \mathbf{B} is an external magnetic field, and $\boldsymbol{\mu}_N = \frac{g_N e}{2m_p c} I_N$ is the magnetic moment of nucleus N . g_N , e , m_p , and c are the g -factor of nucleus N , the electronic charge, nuclear mass and the speed of light in the vacuum, respectively. I_N is the spin angular momentum of nucleus N . Gaussian units are used throughout this work.

From this expansion, the set of molecular tensors are obtained as

$$\sigma_N = 1 + \left. \frac{\partial^2 E}{\partial \boldsymbol{\mu}_N \partial \mathbf{B}} \right|_{\boldsymbol{\mu}_N = \mathbf{B} = 0}; \quad \mathbf{J}_{NM} = \left. \frac{\partial^2 E}{\partial \boldsymbol{\mu}_N \partial \boldsymbol{\mu}_M} \right|_{\boldsymbol{\mu}_N = \boldsymbol{\mu}_M = 0} - \mathbf{D}_{NM} \quad (2)$$

$$\mathbf{M}_N = - \left. \frac{\partial^2 E}{\partial I_N \partial \mathbf{L}} \right|_{\boldsymbol{\mu}_N = \mathbf{L} = 0} \quad (3)$$

$$\boldsymbol{\chi} = -2 \left. \frac{\partial^2 E}{\partial \mathbf{B} \partial \mathbf{B}} \right|_{\mathbf{B} = 0}; \quad \mathbf{g} = -2m_p c \left. \frac{\partial^2 E}{\partial \mathbf{L} \partial \mathbf{B}} \right|_{\mathbf{B} = \mathbf{L} = 0} \quad (4)$$

where σ_N and \mathbf{J}_{NM} are the nuclear magnetic shielding and the indirect nuclear spin coupling tensors (both NMR spectroscopic parameters), respectively; \mathbf{M}_N the nuclear spin-rotation tensor; $\boldsymbol{\chi}$ the magnetic susceptibility tensor; and \mathbf{g} the rotational g -tensor. \mathbf{D}_{NM} is the direct nuclear spin coupling tensor which does not contribute to gas-phase and also to averaged liquid-phase spectra.

Conversely, the molecular Hamiltonian can be separated into two terms: the unperturbed Hamiltonian plus a much smaller perturbative Hamiltonian

$$H = H^{\text{DCB}} + V = H^{\text{DCB}} + V_B + V_N + V_J \quad (5)$$

where H^{DCB} is the Dirac–Coulomb–Breit Hamiltonian and the perturbation terms are: V_B (due to an external uniform magnetic field, \mathbf{B}), V_N (due to the magnetic moment of each nucleus of the molecule, μ_N), and V_J , due to the molecular rotation. There are several other perturbations that are not considered, here, because we restrict our theoretical analysis to the aforementioned five response properties.

When point nuclear models are used, the vector potentials that are the sources of V_B and V_N are given by

$$\mathbf{A}_N = \left(\mu_N \times \frac{\mathbf{r}_N}{r_N^3} \right) \quad (6)$$

$$\mathbf{A}_B = \mathbf{B} \times \frac{\mathbf{r}}{2} \quad (7)$$

where $\mathbf{r}_N = \mathbf{r} - \mathbf{R}_N$ refers to the electron position with respect to nucleus N , \mathbf{r} taken from the origin of coordinates.

It is worth to mention, here, that definitions given in Equations 2–4 are independent of the theoretical regime in which they are expressed.

3 | MODELS AND LEVELS OF APPROACH

To explore the behavior of response properties three different formalisms are mainly used: wave-function-based, DFT-based, and polarization propagators. The first two are widely known by the quantum chemistry community. The third one was developed in the early seventies of the 20th century within a NR framework, and some years later was successfully extended to the relativistic framework.^[21]

Polarization propagators give new insights on the way one realize which and how important are the electronic mechanisms involved in the theoretical description of response properties. It has some advantages: (i) their formal expressions are the same with independence of the regime where they are expressed, (ii) the relation among the formal expressions used to calculate properties in both frameworks, relativistic, and NR, arise naturally by scaling the velocity of light, c , and (iii) it appears quite clearly that paramagnetic and diamagnetic contributions as such are well defined only within the NR regime. This separation does not appear within the relativistic regime, even though one can obtain them starting from such regime and making $c \rightarrow \infty$. One of its main disadvantage may be on the introduction of four-component electron correlation which is at the moment only included at its first-order level of approach.

One should also mention that quite recently polarization propagators were written within the QED language giving new roads to include QED effects together with all other well-known effects.^[20] Furthermore, it was also shown that polarization propagators can be obtained from the path integral formalism, and this fact explains why they have the advantages aforementioned.

The application of four-component methods to the calculation of response properties is highly demanding of computer-power and time-consumption in ab initio methods when the study considers both, medium-size molecules and high accuracy. They are usually performed on top of accurate calculation of wave functions and energy spectra, for which the inclusion of electron correlation is usually mandatory.^[33–37] This is normally worked out within the no-pair approximation although a new scheme to go beyond the no-pair approximation was published.^[38,39] All the efforts performed for getting accurate wave functions and energy spectra are then translated to response property calculations.

Furthermore, the usual and well-known nonrelativistic electronic mechanisms, which were historically considered by spectroscopist and quantum chemist to analyze the physics underlying the whole set of spectroscopic parameters, do not appear explicitly in the actual four-component expressions. In line with this, it must also be mentioned the appearance of the negative-energy branch of the energy spectra which introduce another source of difficulties in the analysis of electronic mechanisms. So, two-component and scalar formalisms were proposed to reduce computational costs and continuous using the NR way of thinking about the physics behind response properties.

As mentioned in other recent reviews^[12,15,40] and chapter of books,^[41] there are several two-component models which were developed during the last decades. In this review, our main concern is related with two-component methods, and specifically with the LRESC one. So we shall give a broader explanation of its fundamentals together with its relation with polarization propagators as written in both regimes, relativistic, and NR.

3.1 | Four-component models

Some of the formally most accurate models to treat molecular properties of heavy-atom containing molecules are based on effective four-component Hamiltonians, which were built on the grounds of their NR equivalents. We specially mention here, due to its relation with magnetic properties, those developed by Malkin and coworkers,^[42–44] at four-component DFT level,^[45,46] the linear response theory at the four-component relativistic molecular Hartree–Fock level of Saue and Jensen,^[47] the theories and applications of Liu and coworkers^[48–50] and the relativistic polarization propagator formalism^[19] which were all implemented at four-component level.

We want to mention few of the four-component calculations of the response properties we are interested in. Calculations of shieldings and QED effects on water molecules,^[13] the first calculations of NMR shielding and indirect spin–spin coupling tensors in hydrogen halides,^[51] the gauge origin independent calculations of molecular magnetizabilities,^[52] and the calculation of the second-order magnetic properties of Bast and coworkers.^[53]

Within the relativistic regime, the perturbative four-component Hamiltonians used to obtain the response properties we are interested in, are the following

$$V_B = \alpha \cdot \mathbf{A}_B; \quad V_N = \alpha \cdot \mathbf{A}_N; \quad V_J = -\omega \cdot \mathbf{J}_e \quad (8)$$

where α are the Dirac matrices, and $\mathbf{J}_e = \mathbf{L}_e + 1/2\Sigma_e$ is the total angular momentum.

We shall now sketch the polarization propagators due to they can be separated, after an approximation, in two terms that are related with equivalent terms in the two-component formalism we are going to explain below in some detail.

3.1.1 | Polarization propagators

The general form of the four-component polarization propagator is given in a matrix form as

$$\langle\langle P; Q \rangle\rangle_E = \begin{pmatrix} \mathbf{P}_a^\dagger & \mathbf{P}_b^\dagger & \dots \end{pmatrix} \begin{pmatrix} \mathbf{W}_{aa} & \mathbf{W}_{ab} & \dots \\ \mathbf{W}_{ba} & \mathbf{W}_{bb} & \dots \\ \dots & \dots & \dots \end{pmatrix}^{-1} \begin{pmatrix} \mathbf{Q}_a \\ \mathbf{Q}_b \\ \dots \end{pmatrix}, \quad (9)$$

where

$$\mathbf{P}_a = (P | \mathbf{h}_a), \quad (10)$$

and

$$\mathbf{W}_{ab} = (\mathbf{h}_a | \hat{E} \hat{I} - \hat{H}_0 | \mathbf{h}_b). \quad (11)$$

In these expressions, \mathbf{h} is a manifold of excitation operators from which the complete set of excited states can be obtained. Besides, the operators P and Q are described in a basis of excitation operators. Equations 10 and 11 contain binary products defined as

$$(P|Q) = \langle 0 | [P^\dagger, Q] | 0 \rangle \quad (12)$$

We can write Equation 9 in a more compact way

$$\langle\langle P; Q \rangle\rangle_E = \mathbf{b}^P \mathbf{W}^{-1} \mathbf{b}^Q \quad (13)$$

The factor \mathbf{W}^{-1} of the rhs of Equation 9 is known as the *principal* propagator, while \mathbf{b}^P and \mathbf{b}^Q are the property matrix elements or, as they were called within the semi-empirical models, the *perturbators*.^[5] The principal propagator depends only on both the electronic molecular system as a whole and the spin (time-reversal within the relativistic regime) dependence of the perturbators, but it is independent of the particular response property. It gives the main streamlines for the transmission of the interaction between the external perturbations related with the property matrix elements, through the unperturbed electronic system. It means that the external perturbations intervene explicitly only on the perturbators.

In the exact case, the polarization propagators and the term linear in each of both external perturbations of the second-order corrections to the energy are equal, that is,

$$E_{PQ}^{(2)} = \text{Re} \langle\langle P; Q \rangle\rangle_{E=0} \quad (14)$$

When considering excitations from an occupied MO to both the positive- and negative-energy MOs one shall get an equivalent expression to that of Equation 9,

$$\langle\langle \hat{P}; \hat{Q} \rangle\rangle_E = \begin{pmatrix} \hat{\mathbf{P}}^{ee} & \hat{\mathbf{P}}^{ep} \end{pmatrix} \begin{pmatrix} \mathbf{W}^{ee,ee} & \mathbf{W}^{ee,ep} \\ \mathbf{W}^{ep,ee} & \mathbf{W}^{ep,ep} \end{pmatrix}^{-1} \begin{pmatrix} \mathbf{Q}^{ee} \\ \mathbf{Q}^{ep} \end{pmatrix} \quad (15)$$

where *ee* and *ep* means that only excitations to positive-energy and negative-energy electronic orbitals are allowed, respectively.

One very important property of this formulation is the fact that both, the relativistic *principal* propagators and *perturbators* go to their NR counterparts when the velocity of light is scaled to ∞ . This means that one can obtain the NR formal expressions and their results of calculations using this natural limit.

3.1.2 | (e-e) or paramagnetic-like and (p-p) or diamagnetic-like contributions

At first sight, the relativistic four-component expressions of magnetic response properties do not show, explicitly, purely diamagnetic or purely paramagnetic electronic mechanisms.^[21] They provide only one mechanism that is paramagnetic-like due to its formal relation with such type of usual NR electronic mechanisms. As an example, the full relativistic expressions of the NMR spectroscopic parameters are obtained as

$$\sigma_M = \frac{e^2}{c^2} \left\langle \left\langle \frac{c \alpha \times r_M}{r_M^3}; c \alpha \times r_G \right\rangle \right\rangle \quad (16)$$

and

$$\mathbf{J}_{MN} = \frac{e^2 \hbar^2}{hc^2} \gamma_M \gamma_N \left\langle \left\langle \frac{c \alpha \times r_M}{r_M^3}; \frac{c \alpha \times r_N}{r_N^3} \right\rangle \right\rangle \quad (17)$$

where r_G is the electronic position with respect to the Gauge origin. Constants γ_M and γ_N are the magnetogyric constants of nucleus M and N , respectively.

We may ask then: how the diamagnetic and paramagnetic NR mechanisms do appear? As was shown in Ref. [23] the off-diagonal contributions to the *principal* propagator are smaller than the diagonal ones. So, leading contributions will include only the diagonal terms, meaning that one can neglect the $\mathbf{W}^{ee,ep}$ and $\mathbf{W}^{ep,ee}$ matrices of Equation 15 in not very accurate calculations. In such a case, taking $P = Q = V$, Equation 15 can be rewritten as

$$\begin{aligned} \langle\langle V; V \rangle\rangle &\approx \langle\langle V; V \rangle\rangle^{(e-e)} + \langle\langle V; V \rangle\rangle^{(p-p)} \\ &= \mathbf{b}^{P,ee} (\mathbf{W}^{ee,ee})^{-1} \mathbf{b}^{Q,ee} + \mathbf{b}^{P,ep} (\mathbf{W}^{ep,ep})^{-1} \mathbf{b}^{Q,ep} \end{aligned} \quad (18)$$

From the last equation, it is seen that the $\langle\langle ; \rangle\rangle^{(e-e)}$ and $\langle\langle ; \rangle\rangle^{(p-p)}$ correspond to paramagnetic and the diamagnetic terms, respectively, of any response property within the NR domain. So, the so called $(e-e)$ and $(p-p)$ contributions to the four-component expressions of the four-component polarization propagators can be considered as paramagnetic-like and diamagnetic-like, respectively.

3.2 | Two-component models

The main advantages of the two-component models we want to stress are the following: (1) their less expensive use of computational resources, and (2) the possibility of using well-known electronic mechanisms to explain the behavior of atomic and molecular response properties. This last advantage refers to the elimination of the negative-energy branch of states and the application of the usual *NR way of thinking* about the physical world. When one include the virtual creation and annihilation of electron-positron pairs and four-component operators, one is facing with new interpretative difficulties about the physical mechanisms involved that are still far from being well understood.

Our main concern in this review is on the model coined LRESC, although we should mention few of the more representative two-component methods that were applied or are being applied to calculate and analyze response properties. They are the methods developed by Fukui and coworkers,^[25,54] Vaara and coworkers or BPPT,^[29] DKH,^[55–59] ZORA,^[60–62] 2c-NESC/HF,^[63] and the different X2C models.^[64–68]

Zaccari and coworkers^[69] published the formal relation that relate the BBPT (Breit–Pauli perturbation theory) approach and another one formulated by Kutzelnigg.^[70] These three proposals appeared almost at the same time and started from different grounds.

3.3 | The linear response within the elimination of small components model

In this section, we shall explain in some detail the theoretical grounds of the LRESC model, which was originally presented as a scheme to describe relativistic effects on the nuclear magnetic shielding tensor.^[26,27] At present it has already been extended to analyze some other response properties which will also be discussed in this review.

The overall procedure has two large steps:

- a Apply the Rayleigh–Schrödinger perturbation theory, RSPT, within the Fock space spanned first by H^{DCB} and then another one spanned by $H^{(0)}$. We consider explicitly the contribution of electronic states and positronic states. Afterwards a double perturbation theory is used to consider either operators that conserve the number of particles or operators that do not conserve the number of particles. Some tricky procedures are involved inside all this, and will be shown when necessary.
- b The four-component matrix elements are transformed in two-component matrix elements by using the elimination of small component scheme, ESC, to expand those matrix elements til order c^{-4} . All correcting terms will be expressed in the language of polarization propagators.

We start writing down the unperturbed four-component relativistic Hamiltonian for an N -electron atomic or molecular system, in an appropriate form

$$H^{\text{DCB}} = H^{\text{D}} + V^{\text{CB}} \quad (19)$$

or

$$H^{\text{DCB}} = H^{(0)} + H^{(\pm)} \quad (20)$$

H^D is the summation of one-body Dirac Hamiltonians of a particle in the Coulomb field of the nuclei; and V^{CB} stands for the Coulomb–Breit interactions. The eigensolutions of H^{DCB} span a Dirac–Fock space. Its elements have a definite number of particles, meaning $N, N + 2, N + 4, \dots$. The term $H^{(0)}$ does not connect states with different number of particles in the Dirac–Fock space, and $H^{(\pm)}$ gathers two-body operators that create or destroy one- and two- electron-positron virtual pairs. In a nutshell, H^{DCB} is a charge conserving operator although it does not conserve the number of particles.

Introducing a complete set of eigenstates of H^{DCB} in the Dirac–Fock space, the $E^{(2)}$ term can be written as

$$E^{(2)} = \sum_{n \neq 0} \frac{\langle 0|V|n\rangle \langle n|V|0\rangle}{E_0 - E_n} - \sum_{n \neq \text{vac}} \frac{\langle \text{vac}|V|n\rangle \langle n|V|\text{vac}\rangle}{E_{\text{vac}} - E_n} \quad (21)$$

where $|n\rangle$ are those states that can be connected with $|0\rangle$ (or $|\text{vac}\rangle$, in the second term) by the application of the perturbation V (that is divided in three terms) of Equation 5. The state $|\text{vac}\rangle$ stands for the vacuum state in the QED picture. The second term of the rhs of Equation 21 means the vacuum polarization contribution that arise 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 a term within the NR regime) and should be subtracted to properly account for the modifications that a magnetic field produce in an atomic or molecular electronic system.^[71,72] This procedure is similar to that proposed recently by Liu and Lindgren.^[38]

Then, starting from four-component matrix elements of Equation 21, and expanding them as a power series in c^{-1} up to order c^{-4} , one finally obtain the two-component LRESC model. To be coherent in the treatment of the rhs of Equation 21, we divided it in two terms which are defined according to their NR limits.

$$E^{(2)} = E_a + E_b \quad (22)$$

where the contributing terms to E_a fulfill $\lim_{c \rightarrow \infty} (E_0 - E_n)^{-1} \neq 0$ and $\{|n\rangle\} \rightarrow \{|n_a\rangle\}$. So, hereafter, they will represent those molecular states which generate the Schrödinger-type molecular spectrum and shall be explained in more detail below.

Conversely, E_b is built with those terms which fulfill a similar condition, for example, $\lim_{c \rightarrow \infty} (E_0 - E_n)^{-1} = 0$ and $|n\rangle \rightarrow |n_b\rangle$. They contain terms which have contributions from at least one virtual electron-positron pair. The vacuum polarization effects arises due to the presence of the external potential V and are included in E_b .

Within the relativistic regime, the four-component states $\{|0\rangle, |n\rangle\}$ do have a definite number of particles although they can be different because of the virtual pair creation/annihilation implicit in V and H^{DCB} . Conversely, the charge $Q = -eN$ is conserved in both regimes.

From Equations 21 and 22, the paramagnetic-like and diamagnetic-like contributions to the second-order energy are

$$E_a = \sum_{n_a \neq 0} \frac{\langle 0|V|n_a\rangle \langle n_a|V|0\rangle}{E_0 - E_{n_a}} \quad (23)$$

and

$$E_b = \sum_{n_b \neq 0} \frac{\langle 0|V|n_b\rangle \langle n_b|V|0\rangle}{E_0 - E_{n_b}} - \sum_{n_b \neq \text{vac}} \frac{\langle \text{vac}|V|n_b\rangle \langle n_b|V|\text{vac}\rangle}{E_{\text{vac}} - E_{n_b}} \quad (24)$$

Few considerations shall explicitly be given here:

1. The eigenstates $|n_a\rangle$ have a definite number of particles. The N -particle eigenstates of $H^{(0)}$ are written as $\{|n_a^{(0)}\rangle \equiv |n_N\rangle\}$,
2. We shall consider zeroth- and first-order contributions to eigenstates $|n_a\rangle$ ($|n_a\rangle = |n_a^{(0)}\rangle + |n_a^{(1)}\rangle$), being $|n_a^{(1)}\rangle = \sum_m \frac{|m\rangle \langle m|H^{(\pm)}|n_a^{(0)}\rangle}{E_{n_N} - E_m}$,
3. The eigenstates $\{|n_b\rangle\}$ of $H^{(0)}$ are states of $N \pm 2$ or $N \pm 4$ particles and will be written as $\{|n_b^{(0)}\rangle \equiv |n_K\rangle, K = N \pm 2, N \pm 4\}$.

Based on these considerations, only E_a has matrix elements with no virtual pair contributions, NP, and both, E_a and E_b , do have few contributions due to the effect of one- and two- virtual pairs.

$$E_a \simeq E_a^{\text{NP}} + E_a^{\text{VP}} \quad (25)$$

We want now to consider the Equation 24 because we proposed for it a tricky solution. Given that one should calculate matrix elements that contain positive and negative energy states, together with difference of energies that include the whole branch of negative-energy states, we adopted the proposal used previously in Ref. [23]: the inverse of the difference of energies can be approximated by

$$(E_0 - E_{n_b})^{-1} = -(2mc^2 + \Delta_{n_b 0})^{-1} \simeq -\frac{1}{2mc^2} \left(2 + \frac{E_0 - E_{n_b}}{2mc^2} \right) \quad (26)$$

where $\Delta_{n_b 0} = E_{n_b} - E_0 - 2mc^2$ is of order c^0 or lower so that $\frac{\Delta_{n_b 0}}{2mc^2}$ can be considered as an expansion parameter. We make use of the fact that, within the QED picture, negative energy solutions of the Dirac equation are re-interpreted as positive energy states for positrons.

Introducing this relationship in Equation 24

$$\begin{aligned}
 E_b \simeq & -\frac{1}{2mc^2} \sum_{n_b} \left(\left\langle 0 \left| 2V + \frac{1}{2mc^2} [H^{\text{DCB}}, V] \right| n_b \right\rangle \langle n_b | V | 0 \rangle \right) \\
 & + \frac{1}{2mc^2} \sum_{n_b} \left(\left\langle \text{vac} \left| 2V + \frac{1}{2mc^2} [H^{\text{DCB}}, V] \right| n_b \right\rangle \langle n_b | V | \text{vac} \rangle \right) \\
 & = E_b^{N+2} + E_b^{N+4}
 \end{aligned} \tag{27}$$

where we have used

$$(E_0 - E_n) \langle 0 | V | n_b \rangle = \langle 0 | [H^{\text{DCB}}, V] | n_b \rangle \tag{28}$$

Then Equation 22 do have the following four terms^[26]

$$E^{(2)} \simeq E_a^{\text{NP}} + E_a^{\text{VP}} + E_b^{N+2} + E_b^{N+4} \tag{29}$$

Each one of these four terms could have one-body and/or two-body contributions. They explicitly are

$$E_a^{\text{NP}} = E_a^{\text{NP}}(1) + E_a^{\text{NP}}(2) \tag{30}$$

$$E_a^{\text{VP}} = E_a^{\text{VP}}(2) \tag{31}$$

$$E_b^{N+2} = E_b^{N+2}(1) + E_b^{N+2}(2) \tag{32}$$

$$E_b^{N+4} = E_b^{N+4}(2) \tag{33}$$

When the contribution of positronic states is taken separated of that of electronic states, the addition of the first two terms give $E^{(e-e)}$, and equivalently, the addition of the last two terms give $E^{(p-p)}$. Furthermore, the lowest order of relativistic corrections of $E^{(e-e)}$ and $E^{(p-p)}$ is c^{-2} .

In the formalism of relativistic polarization propagators (see subsection 3.1.1), $E^{(e-e)}$ is related with the positive energy - positive energy coupling terms of the linear response functions. It yields the so-called “electron-electron” ($e-e$) rotations. The expansion of $E^{(e-e)}$ will lead to the paramagnetic term (NR) and its (relativistic) corrections, as shown below. $E^{(p-p)}$ is related with contributions from electronic–positronic coupling terms of the linear response functions, yielding the so-called “electron-positron” ($p-p$) corrections. From the $E^{(p-p)}$ energy correcting terms we shall get the usual diamagnetic contributions to magnetic properties at the NR limit, in addition to its relativistic corrections.

Now, we can go further and supply some details of the second large step, which consist in the application of the scheme of elimination of the small components to the matrix elements of Equations 23 and 27. In this way, the final expressions shall all be expressed in terms of positive-energy orbitals.

The four-component matrix elements are transformed to the Pauli space of spinors, $|\tilde{\phi}_i\rangle$ by applying the ESC method

$$\langle \phi_i^{(4)} | V | \phi_j^{(4)} \rangle \cong \langle \tilde{\phi}_i | O(V) | \tilde{\phi}_j \rangle. \tag{34}$$

Given that we are interested only in the leading order relativistic effects, we shall retain terms up to order c^{-2} , and so $O(V) \cong O^{\text{nr}}(V) + O^{(2)}(V)$, where $O^{\text{nr}}(V)$ is the NR operator and the remaining term is the leading order relativistic correction to operator V .

According to Refs. [26,28,73], the two-component operators that are actually used in the LRESC model

$$O(\boldsymbol{\alpha} \cdot \mathbf{A}_B) \quad O(\boldsymbol{\alpha} \cdot \mathbf{A}_N) \quad O(-\boldsymbol{\omega} \cdot \mathbf{J}_e) \tag{35}$$

are obtained when the Equation 34 is applied to the operators of Equation 8 (see Appendix). We shall consider that

$$|\phi_i^{(4)}\rangle = \begin{pmatrix} |\phi_i^L\rangle \\ |\phi_i^S\rangle \end{pmatrix} \tag{36}$$

together with the fact that the normalized wave-function is given by

$$|\phi_i^L\rangle = N |\tilde{\phi}_i\rangle = \left(1 - \frac{p^2}{8c^2} \right) |\tilde{\phi}_i\rangle, \tag{37}$$

and the usual ESC relationship among the small and large components

$$|\phi_i^S\rangle \simeq \frac{1}{2mc} \left[1 + \frac{V^C - E_i}{2mc^2} \right] (\boldsymbol{\sigma} \cdot \mathbf{p}) |\phi_i^L\rangle \tag{38}$$

being the large component exact up to order c^{-2} .

The two-component spinors that are solutions of the Breit–Pauli Hamiltonian are expanded in its base. Such a Hamiltonian is obtained from

$$\langle \phi_i^{(4)} | H^{\text{DCB}} | \phi_j^{(4)} \rangle \cong \langle \tilde{\phi}_i | H^{\text{BP}} | \tilde{\phi}_j \rangle. \tag{39}$$

where

$$H^{BP} = H^S + D, \quad (40)$$

H^S stand for the Schrödinger molecular Hamiltonian and the operator D do contain the generalized N -particle space operators of one-body, D_1 , and two-body, D_2 , terms.^[26] The complete one-body term is $D_1 = H^{Mv/Dw} + H^{SO(1)}$, where

$$H^{Mv} = -\frac{p^4}{8m^3c^2} \quad (41)$$

$$H^{Dw} = \frac{1}{8m^2c^2} \nabla^2 V^C \quad (42)$$

$$H^{SO(1)} = \frac{1}{4m^2c^2} \boldsymbol{\sigma} \cdot (\nabla V^C \times \mathbf{p}), \quad (43)$$

and V^C represent the electron-nucleus coulombic attraction. The two-body contribution to D is $D_2 = H^{Dw(2)} + H^{OO} + H^{FC-SS} + H^{SO(2)} + H^{SOO}$.

We are now able to show the final formal expressions for $E^{(e-e)}$ and $E^{(p-p)}$. So, for two perturbative operators, V_1 and V_2 , the $(e-e)$ contribution to the energy can be expressed as

$$E_a^{NP}(V_1, V_2) = E^{(2)}(O^{nr}(V_1), O^{nr}(V_2)) + E^{(2)}(O^{nr}(V_1), O^{(2)}(V_2)) + E^{(2)}(O^{(2)}(V_1), O^{nr}(V_2)) + E^{(3)}(O^{nr}(V_1), O^{nr}(V_2), D), \quad (44)$$

where $E^{(2)}$ and $E^{(3)}$ are the second- and third-order corrections to the (NR) energy:

$$E^{(2)}(A, B) = \sum_{n \neq 0} \frac{\langle 0|A|n\rangle \langle n|B|0\rangle}{E_0 - E_n} + c.c., \quad (45)$$

and

$$E^{(3)}(A, B, C) = \sum_{n,m \neq 0} \left\{ \frac{\langle 0|A|n\rangle \langle n|B-\langle B\rangle|m\rangle \langle m|C|0\rangle}{(E_0 - E_n)(E_0 - E_m)} + \frac{\langle 0|B|n\rangle \langle n|C-\langle C\rangle|m\rangle \langle m|A|0\rangle}{(E_0 - E_n)(E_0 - E_m)} + \frac{\langle 0|C|n\rangle \langle n|A-\langle A\rangle|m\rangle \langle m|B|0\rangle}{(E_0 - E_n)(E_0 - E_m)} \right\} + c.c., \quad (46)$$

$A, B, \gamma C$ are N -particle operators, $|0\rangle$ is the ground state, $c.c.$ indicate the complex conjugate of the preceding terms, and $\langle X \rangle$ is the ground-state expectation value of the operator X ($X = A, B, C$). When $A = B$, Equations 45 and 46 do not include the $c.c.$ terms.

To complete the explicit expressions of E_a we give E_a^{VP} as

$$E_a^{VP}(V) = -\frac{1}{2mc^2} \sum_{n \neq 0} \frac{\langle 0_N | H^{(\pm)} P_{N+2} V + V P_{N+2} H^{(\pm)} | n_N \rangle \langle n_N | V | 0_N \rangle}{E_{0_N} - E_{n_N}} - \frac{1}{2mc^2} \sum_{n \neq 0} \frac{\langle 0_N | V | n_N \rangle \langle n_N | H^{(\pm)} P_{N+2} V + V P_{N+2} H^{(\pm)} | 0_N \rangle}{E_{0_N} - E_{n_N}} \quad (47)$$

where $V = V_1 + V_2$.

Conversely, the actual expressions of E_b are found through some tricky procedures,^[26] although we shall sketch, here, the main ones. From Equation 27 we define the operator $X(V)$ as

$$X(V) = 2V + \frac{1}{2mc^2} [H^{DCB}, V] \quad (48)$$

This operator has two different terms: one-body or $X(V; 1)$ and two-body or $X(V; 2)$. They are

$$X(V; 1) = 2V + \frac{1}{2mc^2} [H^D, V] \quad (49)$$

and

$$X(V; 2) = 2V + \frac{1}{2mc^2} [V^B, V] \quad (50)$$

due to $[V^C, V] = 0$.

Furthermore, for the calculation of the response to two external fields, V should include both of them. Then, being $\sum |n_b\rangle \langle n_b| = P_p$ a projector onto positronic states, or making explicit that P_p is a projection onto the K -particle manifold of the Dirac-Fock space ($\sum |n_k\rangle \langle n_k| = P_k$) we can write both terms of Equation 27 as (For more details see eqs. 61, 62, and 70–75 of Ref. [26])

$$E_b^{N+2}(V) = -\frac{1}{2mc^2} \langle 0_N | X(V) P_{N+2} V | 0_N \rangle + \frac{1}{2mc^2} \langle \text{vac} | X(V) P_2 V | \text{vac} \rangle \quad (51)$$

and

$$E_b^{N+4}(V) = \frac{1}{8m^2c^4} \left(\langle 0_N | H^{(\pm)} P_{N+4} V P_{N+2} V | 0_N \rangle + \langle 0_N | V P_{N+2} V P_{N+4} H^{(\pm)} | 0_N \rangle \right) - \frac{1}{8m^2c^4} \left(\langle \text{vac} | H^{(\pm)} P_4 V P_2 V | \text{vac} \rangle + \langle \text{vac} | V P_2 V P_4 H^{(\pm)} | \text{vac} \rangle \right) \quad (52)$$

where $V = V_1 + V_2$. If we consider only those terms that involves the one-body part of H^{DCB} (see Equation 32), we get^[26]

$$E_b^{N+2}(1) = \frac{1}{2mc^2} \langle 0_N | V_1 P_p X(V_2; 1) + V_2 P_p X(V_1; 1) | 0_N \rangle \quad (53)$$

In the case of magnetic perturbations, the term E_b^{N+4} is canceled out with one of the different contributions to E_b^{N+2} , although it does not happens for other perturbative Hamiltonians.

At the end, the actual expressions usable to calculate the ($e-e$) and ($p-p$) contributions to atomic and molecular response properties are those of Equations 44 and 53, respectively.

We should mention that polarization propagators can be applied to calculate every second-order static molecular property at four- or two-component level of approach. This is apparent from the following equation

$$E_{V_1 V_2}^{(2)} = \text{Re} \langle \langle V_1; V_2 \rangle \rangle_{E=0}, \quad (54)$$

where V_1 and V_2 are the interaction Hamiltonians that consider external perturbations acting on the unperturbed system. $E_{V_1 V_2}^{(2)}$ stands for the second-order correction to the atomic or molecular electronic energy. Response properties are obtained from these expressions.^[19]

Within the LRESC model they have a form equivalent to Equation 54

$$E_{O(V_1)O(V_2)}^{(2)} = \text{Re} \langle \langle O(V_1); O(V_2) \rangle \rangle_{E=0}, \quad (55)$$

where $O(V_1)$ and $O(V_2)$ are the operators V_1 and V_2 written in the framework of the two-component LRESC model.

3.4 | Response properties within the LRESC model

The actual expressions, up to order c^{-2} , of the formal two-component operators mentioned in Equations 35, 44, and 55 are

$$O^{\text{nr}}(V_N) = H^{\text{PSO}} + H^{\text{FC/SD}} \quad (56)$$

$$O^{(2)}(V_N) = H^{\text{PSO-K}} + H^{\text{FC/SD-K}} \quad (57)$$

$$O^{\text{nr}}(V_B) = H^{\text{OZ}} + H^{\text{SZ}} \quad (58)$$

$$O^{(2)}(V_B) = H^{\text{OZ-K}} + H^{\text{SZ-K}} + H^{\text{B-SO}} \quad (59)$$

$$O^{\text{nr}}(V_J) = H^{\text{BO-L}} + H^{\text{BO-S}} = H^{\text{BO-J}} \quad (60)$$

$$O^{(2)}(V_J) = 0 \quad (61)$$

where all explicit expressions of perturbative Hamiltonians are given in the Appendix.

Then, combining two of the perturbative potentials we obtain all tensors we are interested in: V_N with V_B give the NMR magnetic shielding; V_N with V_J give the spin-rotation tensor; V_B with V_J give the g -tensor and V_B with V_B give the magnetizability. We should also mention that combining V_N with V_M we would obtain the J -coupling tensor, J_{NM} , which still have some problems to be worked out within the LRESC model. We should also mention that, combining V_J with V_J we obtain the operator X that gives the effective tensor of inertia, as mentioned in Ref. [74] but now including relativistic effects.

In the last set of equations, the NR perturbative Hamiltonians are the following: H^{PSO} is the *paramagnetic spin orbit*, $H^{\text{FC/SD}}$ is the *Fermi contact/spin dipolar*, H^{OZ} is the *orbital Zeeman*, and H^{SZ} is the *spin Zeeman*. They are originated in the electronic interactions with either, the magnetic moments of the nucleus N , μ_N , or with an external magnetic field \mathbf{B} . Conversely, $H^{\text{BO-L}}$ and $H^{\text{BO-S}}$ are the Born-Oppenheimer perturbations that appears due to the rotation of the nuclear system and is associated with the electronic orbital \mathbf{L} and electronic spin \mathbf{S} angular momenta, with respect to the center of mass, CM, of the molecule.

The leading order relativistic corrections are: $H^{\text{PSO-K}}$, the *Kinetic-paramagnetic spin orbit*, $H^{\text{FC/SD-K}}$, the *Kinetic-Fermi contact/spin dipolar*, $H^{\text{OZ-K}}$, the *Kinetic-orbital Zeeman*, $H^{\text{SZ-K}}$, the *Kinetic-spin Zeeman*, and $H^{\text{B-SO}}$, the so-called *magnetic field induced spin-orbit*.

T1 T2 In Tables 1 and 2, we show a summary of how the ($e-e$) contributions of properties are expressed within the LRESC model, up to order c^{-2} (see Equation 44). As usual $[\cdot, \cdot]$ and $\{\cdot, \cdot\}$ represent commutator and anticommutator operations, respectively.

Gaussian atomic units ($e=m=\hbar=1$ and $c=137.0359998$) are used from here.

TABLE 1 LRESC contributions to the no-pair ($e-e$) part of four-component expressions

Property	$O(V_1)$	$O(V_2)$	D	LRESC contributions to E_a^{NPa}
$\sigma_N^{(e-e)}$	$O^{nr}(V_N)$	$O^{nr}(V_B)$	-	$\langle\langle H_N^{PSO}; H^{OZ} \rangle\rangle$
	$O^{nr}(V_N)$	$O^{(2)}(V_B)$	-	$\langle\langle H_N^{PSO}; H^{OZ-K} \rangle\rangle + \langle\langle H_N^{FC/SD}; H^{SZ-K} \rangle\rangle$ $+ \langle\langle H_N^{FC/SD}; H^{B-SO} \rangle\rangle$
	$O^{(2)}(V_N)$	$O^{nr}(V_B)$	-	$\langle\langle H_N^{PSO-K}; H^{OZ} \rangle\rangle$
	$O^{nr}(V_N)$	$O^{nr}(V_B)$	D_1	$\langle\langle H_N^{PSO}; H^{Mv/Dw}; H^{OZ} \rangle\rangle$ $+ \langle\langle H_N^{FC/SD}; H^{SO(1)}; H^{OZ} \rangle\rangle + \langle\langle H_N^{FC/SD}; H^{SO(1)}; H^{SZ} \rangle\rangle$
	$O^{nr}(V_N)$	$O^{nr}(V_B)$	D_2	$\langle\langle H_N^{PSO}; H^{Dw(2)}; H^{OZ} \rangle\rangle + \langle\langle H_N^{PSO}; H^{OO}; H^{OZ} \rangle\rangle$ $+ \langle\langle H_N^{PSO}; H^{FC-SS}; H^{OZ} \rangle\rangle$ $+ \langle\langle H_N^{FC/SD}; H^{SO(2)}; H^{OZ} \rangle\rangle + \langle\langle H_N^{FC/SD}; H^{SO(2)}; H^{SZ} \rangle\rangle$ $+ \langle\langle H_N^{FC/SD}; H^{SOO}; H^{OZ} \rangle\rangle + \langle\langle H_N^{FC/SD}; H^{SOO}; H^{SZ} \rangle\rangle$
$M_N^{elec(e-e)}$	$O^{nr}(V_N)$	$O^{nr}(V_J)$	-	$\langle\langle H_N^{PSO}; H^{BO-L} \rangle\rangle$
	$O^{nr}(V_N)$	$O^{(2)}(V_J)$	-	-
	$O^{(2)}(V_N)$	$O^{nr}(V_J)$	-	$\langle\langle H_N^{PSO-K}; H^{BO-L} \rangle\rangle$
	$O^{nr}(V_N)$	$O^{nr}(V_J)$	D_1	$\langle\langle H_N^{PSO}; H^{Mv/Dw}; H^{BO-L} \rangle\rangle$ $+ \langle\langle H_N^{FC/SD}; H^{SO(1)}; H^{BO-L} \rangle\rangle + \langle\langle H_N^{FC/SD}; H^{SO(1)}; H^{BO-S} \rangle\rangle$
	$O^{nr}(V_N)$	$O^{nr}(V_J)$	D_2	$\langle\langle H_N^{PSO}; H^{Dw(2)}; H^{BO-L} \rangle\rangle + \langle\langle H_N^{PSO}; H^{OO}; H^{BO-L} \rangle\rangle$ $+ \langle\langle H_N^{PSO}; H^{FC-SS}; H^{BO-L} \rangle\rangle$ $+ \langle\langle H_N^{FC/SD}; H^{SO(2)}; H^{BO-L} \rangle\rangle + \langle\langle H_N^{FC/SD}; H^{SO(2)}; H^{BO-S} \rangle\rangle$ $+ \langle\langle H_N^{FC/SD}; H^{SOO}; H^{BO-L} \rangle\rangle + \langle\langle H_N^{FC/SD}; H^{SOO}; H^{BO-S} \rangle\rangle$
$J_{NM}^{(e-e)}$	$O^{nr}(V_N)$	$O^{nr}(V_M)$	-	$\langle\langle H_N^{PSO}; H_M^{PSO} \rangle\rangle + \langle\langle H_N^{FC+SD}; H_M^{FC+SD} \rangle\rangle$
	$O^{nr}(V_N)$	$O^{(2)}(V_M)$	-	$\langle\langle H_N^{PSO}; H_M^{PSO-K} \rangle\rangle + \langle\langle H_N^{FC/SD}; H_M^{FC/SD-K} \rangle\rangle$
	$O^{(2)}(V_N)$	$O^{nr}(V_M)$	-	$\langle\langle H_N^{PSO-K}; H_M^{PSO} \rangle\rangle + \langle\langle H_N^{FC/SD-K}; H_M^{FC/SD} \rangle\rangle$
	$O^{nr}(V_N)$	$O^{nr}(V_M)$	D_1	$\langle\langle H_N^{PSO}; H_M^{Mv/Dw}; H_M^{PSO} \rangle\rangle$ $+ \langle\langle H_N^{PSO}; H^{SO(1)}; H_M^{FC/SD} \rangle\rangle + \langle\langle H_N^{PSO}; H^{SO(1)}; H_M^{FC/SD} \rangle\rangle$ $+ \langle\langle H_N^{FC/SD}; H_M^{Mv/Dw}; H_M^{FC/SD} \rangle\rangle + \langle\langle H_N^{FC/SD}; H^{SO(1)}; H_M^{FC/SD} \rangle\rangle$
	$O^{nr}(V_N)$	$O^{nr}(V_M)$	D_2	$\langle\langle H_N^{PSO}; H^{Dw(2)} + H^{OO} + H^{FC-SS}; H_M^{PSO} \rangle\rangle$ $+ \langle\langle H_N^{PSO}; H^{SO(2)} + H^{SOO}; H_M^{FC/SD} \rangle\rangle$ $+ \langle\langle H_M^{PSO}; H^{SO(2)} + H^{SOO}; H_N^{FC/SD} \rangle\rangle$ $+ \langle\langle H_N^{FC/SD}; H^{Dw(2)} + H^{OO} + H^{FC-SS}; H_M^{FC/SD} \rangle\rangle$ $+ \langle\langle H_N^{FC/SD}; H^{SO(2)} + H^{SOO}; H_M^{FC/SD} \rangle\rangle$

^aElectronic contributions to the molecular energy (NR linear and quadratic responses).

3.4.1 | The NMR magnetic shielding tensor

We now give a brief account of the leading order LRESC corrections to the shielding tensor, σ . The correcting terms are summarized in Table 1 where the whole branch of one-body and two-body operators is displayed. In the calculations only one-body operators will be considered.

The whole set of leading relativistic corrections had been clustered in different ways: (i) taking into account their spin character, as singlet or triplet; (ii) taking into account their response order in perturbation theory, namely first-, second-, or third-order; and (iii) regarding the historical classification of paramagnetic and diamagnetic terms. We should mention that Vaara and coworkers proposed also to cluster the corrections as “passive” and “active.”^[28]

T3 T4 In Tables 3 and 4, we show all corrections grouped as paramagnetic and diamagnetic, together with their correcting terms. The operators involved in both Tables are corrections to the Schrödinger Hamiltonian of singlet-type, that is, Mass velocity (H^{Mv}) and Darwin (H^{Dw}) operators; and of triplet-type as is the case of Spin-orbit ($H^{SO(1)}$) operator.

Regarding the diamagnetic corrections that appears in Table 4, both are of singlet type, although one is of zeroth order and the other one of first order.

From Equation 53, the ($p-p$) contribution to the shielding tensor can be obtained making $V_1=V_N$ and $V_2=V_B$. With this replacement, the contributions of Table 4 can be expressed as

$$E^{\sigma(p-p)}(V_N, V_B) = \langle 0 | H^{Dia} | 0 \rangle - \frac{1}{4c^4} \langle 0 | H^{Dia-K} | 0 \rangle + E^{(2)}(H^{Dia}, H^{Mv/Dw}) \quad (62)$$

where

TABLE 2 LRESC contributions to the no-pair ($e-e$) part of four-component expressions

Property	$O(V_1)$	$O(V_2)$	D	LRESC contributions to E_a^{NPa}
$g^{\text{elec}(e-e)}$	$O^{\text{nr}}(V_B)$	$O^{\text{nr}}(V_J)$	-	$\langle\langle H^{\text{OZ}}; H^{\text{BO-L}} \rangle\rangle$
	$O^{\text{nr}}(V_B)$	$O^{(2)}(V_J)$	-	-
	$O^2(V_B)$	$O^{\text{nr}}(V_J)$	-	$\langle\langle H^{\text{OZ-K}}; H^{\text{BO-L}} \rangle\rangle$
	$O^{\text{nr}}(V_B)$	$O^{\text{nr}}(V_J)$	D_1	$\langle\langle H^{\text{OZ}}; H^{\text{Mv/Dw}}; H^{\text{BO-L}} \rangle\rangle$
	$O^{\text{nr}}(V_B)$	$O^{\text{nr}}(V_J)$	D_2	$\langle\langle H^{\text{OZ}}; H^{\text{Dw}(2)}; H^{\text{BO-L}} \rangle\rangle + \langle\langle H^{\text{OZ}}; H^{\text{OO}}; H^{\text{BO-L}} \rangle\rangle + \langle\langle H^{\text{OZ}}; H^{\text{FC-SS}}; H^{\text{BO-L}} \rangle\rangle$
$\chi^{\text{elec}(e-e)}$	$O^{\text{nr}}(V_B)$	$O^{\text{nr}}(V_B)$	-	$\frac{1}{2} \langle\langle H^{\text{OZ}}; H^{\text{OZ}} \rangle\rangle$
	$O^{\text{nr}}(V_B)$	$O^{(2)}(V_B)$	-	$\frac{1}{2} \langle\langle H^{\text{OZ}}; H^{\text{OZ-K}} \rangle\rangle$
	$O^{(2)}(V_B)$	$O^{\text{nr}}(V_B)$	-	$\frac{1}{2} \langle\langle H^{\text{OZ-K}}; H^{\text{OZ}} \rangle\rangle$
	$O^{\text{nr}}(V_B)$	$O^{\text{nr}}(V_B)$	D_1	$\frac{1}{2} \langle\langle H^{\text{OZ}}; H^{\text{Mv/Dw}}; H^{\text{OZ}} \rangle\rangle$
	$O^{\text{nr}}(V_B)$	$O^{\text{nr}}(V_B)$	D_2	$\frac{1}{2} \langle\langle H^{\text{OZ}}; H^{\text{Dw}(2)}; H^{\text{OZ}} \rangle\rangle + \frac{1}{2} \langle\langle H^{\text{OZ}}; H^{\text{OO}}; H^{\text{OZ}} \rangle\rangle + \frac{1}{2} \langle\langle H^{\text{OZ}}; H^{\text{FC-SS}}; H^{\text{OZ}} \rangle\rangle$
$\chi^{(e-e)}$	$O^{\text{nr}}(V_J)$	$O^{\text{nr}}(V_J)$	-	$\frac{1}{2} \langle\langle H^{\text{BO-L}}; H^{\text{BO-L}} \rangle\rangle$
	$O^{\text{nr}}(V_J)$	$O^{(2)}(V_J)$	-	-
	$O^{(2)}(V_J)$	$O^{\text{nr}}(V_J)$	-	-
	$O^{\text{nr}}(V_J)$	$O^{\text{nr}}(V_J)$	D_1	$\frac{1}{2} \langle\langle H^{\text{BO-L}}; H^{\text{Mv/Dw}}; H^{\text{BO-L}} \rangle\rangle$
	$O^{\text{nr}}(V_J)$	$O^{\text{nr}}(V_J)$	D_2	$\frac{1}{2} \langle\langle H^{\text{BO-L}}; H^{\text{Dw}(2)}; H^{\text{BO-L}} \rangle\rangle + \frac{1}{2} \langle\langle H^{\text{BO-L}}; H^{\text{OO}}; H^{\text{BO-L}} \rangle\rangle + \frac{1}{2} \langle\langle H^{\text{BO-L}}; H^{\text{FC-SS}}; H^{\text{BO-L}} \rangle\rangle$

^aElectronic contributions to the molecular energy (NR linear and quadratic responses).

$$H^{\text{Dia}} = \mathbf{A}_N \cdot \mathbf{A}_B \tag{63}$$

$$H^{\text{Dia-K}} = -\frac{1}{4c^4} \left[2 \left(\frac{\boldsymbol{\mu}_N \cdot \mathbf{L}_N}{r_N^3} \right) (\mathbf{B} \cdot \mathbf{L}_N) + \mathbf{B} \cdot \mathbf{B}_N + 2(\mathbf{A}_N \cdot \mathbf{A}_B) p^2 + 2\pi(\boldsymbol{\mu}_N \cdot \mathbf{B}) \delta(r_N) \right] \tag{64}$$

with $\mathbf{B} = \nabla \times \mathbf{A}_B$, the external magnetic field, and $\mathbf{B}_N = \nabla \times \mathbf{A}_N$. In addition, $\mathbf{L}_N = (\mathbf{r} - r\mathbf{N}) \times \mathbf{p}$ is the electronic angular momentum with respect to the nucleus N .

All the details concerning the derivation of the leading order relativistic corrections to $E^{\sigma(p-p)}(V_N, V_B)$ are given elsewhere.^[26]

We can then express the ($e-e$) contribution of Equation 44 within the LRESC model as (see Table 1)

$$E^{\sigma(e-e)}(V_N, V_B) = E^{(2)}(H^{\text{PSO}}, H^{\text{OZ}}) + E^{(2)}(H^{\text{PSO-K}}, H^{\text{OZ}}) + E^{(2)}(H^{\text{PSO}}, H^{\text{OZ-K}}) + E^{(2)}(H^{\text{FC/SD}}, H^{\text{SZ-K}} + H^{\text{B-SO}}) + E^{(3)}(H^{\text{PSO}}, H^{\text{Mv/Dw}}, H^{\text{OZ}}) + E^{(3)}(H^{\text{FC/SD}}, H^{\text{SO}(1)}, H^{\text{OZ}}) + E^{(3)}(H^{\text{FC/SD}}, H^{\text{SO}(1)}, H^{\text{SZ}}). \tag{65}$$

where the one-electron operator D_1 do contain the relativistic corrections to the Schrödinger Hamiltonian, $H^{\text{Mv/Dw}}$ and $H^{\text{SO}(1)}$.

3.4.2 | The nuclear spin-rotation tensor

Few years ago a new relativistic formalism was developed to obtain the spin-rotation tensor.^[30,75] Such a tensor do have a nuclear in addition to an electronic contribution. This last one is also divided in two terms: ($e-e$) and ($p-p$) contributing terms. A little later Liu and coworkers proposed another formalism, based on a body-fixed relativistic molecular Hamiltonian.^[49,76] The formulation of the SR tensor within the LRESC formalism requires the knowledge of two terms of the second-order corrections to the energy: $E^{M(e-e)}$ and $E^{M(p-p)}$. Hereafter, only E_a^{NP} is considered to obtain $E^{M(e-e)}$, whereas for $E^{M(p-p)}$ only the $E_b^{\text{N}+2}(1)$ will be taken into account. The first term is

TABLE 3 LRESC corrections to the paramagnetic term on nuclear magnetic shielding tensor

Paramagnetic corrections	$\sigma^{\text{SZ-K}} + \sigma^{\text{B-SO}}$	$\sigma^{\text{OZ-K}} + \sigma^{\text{PSO-K}}$	σ^{SO}	$\sigma^{\text{para-Mv/Dw}}$
Character	First-order triplet (P1T)	First-order singlet (P1S)	Third-order triplet (P3T)	Third-order singlet(P3S)
Response functions	$\langle\langle H^{\text{FC/SD}}; H^{\text{SZ-K}} \rangle\rangle + \langle\langle H^{\text{FC/SD}}; H^{\text{B-SO}} \rangle\rangle$	$\langle\langle H^{\text{PSO}}; H^{\text{OZ-K}} \rangle\rangle + \langle\langle H^{\text{PSO-K}}; H^{\text{OZ}} \rangle\rangle$	$\langle\langle H^{\text{OZ}}; H^{\text{FC/SD}}; H^{\text{SO}(1)} \rangle\rangle$	$\langle\langle H^{\text{OZ}}; H^{\text{PSO}}; H^{\text{Mv/Dw}} \rangle\rangle$

TABLE 4 LRESC corrections to the diamagnetic term on nuclear magnetic shielding tensor

Diamagnetic corrections	$\sigma^{\text{Dia-Mv/Dw}}$	$\sigma^{\text{Dia-K}}$
Character	First-order singlet (D1S)	Zeroth-order singlet (DOS)
Response functions	$\langle\langle H^{\text{Dia}}; H^{\text{Mv/Dw}} \rangle\rangle$	$\langle H^{\text{Dia-K}} \rangle$

$$\begin{aligned}
 E^{M(e-e)}(V_N, V_J) &= \langle\langle H^{\text{PSO}} + H^{\text{FC/SD}} + H^{\text{PSO-K}} + H^{\text{FC/SD-K}}; -\omega \cdot J_e^{(2)} \rangle\rangle \\
 &+ \langle\langle H^{\text{PSO}} + H^{\text{FC/SD}}; D; -\omega \cdot J_e^{(2)} \rangle\rangle \\
 &= \langle\langle H^{\text{PSO}}; -\omega \cdot L_e \rangle\rangle + \langle\langle H^{\text{PSO-K}}; -\omega \cdot L_e \rangle\rangle \\
 &+ \langle\langle H^{\text{PSO}} + H^{\text{FC/SD}}; D; -\omega \cdot J_e^{(2)} \rangle\rangle,
 \end{aligned} \tag{66}$$

Given that we shall deal with the ground-state of closed-shell systems, the operator $J_e^{(2)}$ can be replaced by L_e in the first two terms. The first term of Equation 66 is the well-known NR expression of the spin-rotation energy, whereas all the other terms are its relativistic corrections.

It must be stressed that the operator $O(-\omega \cdot J_e)$ do not contribute to the relativistic corrections of the energy, up to order $1/c^2$ (see Equation 61).

We shall now analyze separately the LRESC expansion of both parts of $E^{M(e-e)}(\alpha \cdot A_N, -\omega \cdot J_e^{(4)})$. They are

$$\begin{aligned}
 E^{M(e-e)}(\alpha \cdot A_N, -\omega \cdot L_e^{(4)}) &= \langle\langle H^{\text{PSO}}; -\omega \cdot L_e \rangle\rangle \\
 &+ \langle\langle H^{\text{PSO-K}}; -\omega \cdot L_e \rangle\rangle \\
 &+ \langle\langle H^{\text{FC/SD}}; -\frac{1}{4c^2} \omega \cdot (\sigma p^2 - (\sigma \cdot p)p) \rangle\rangle \\
 &+ \langle\langle H^{\text{PSO}} + H^{\text{FC/SD}}; D; -\omega \cdot L_e \rangle\rangle,
 \end{aligned} \tag{67}$$

and

$$\begin{aligned}
 E^{M(e-e)}(\alpha \cdot A_N, -\omega \cdot S^{(4)}) &= \langle\langle H^{\text{FC/SD}}; \frac{1}{4c^2} \omega \cdot (\sigma p^2 - (\sigma \cdot p)p) \rangle\rangle \\
 &+ \langle\langle H^{\text{PSO}} + H^{\text{FC/SD}}; D; -\omega \cdot S \rangle\rangle.
 \end{aligned} \tag{68}$$

The third term of Equation 67 is canceled by the first term of Equation 68. In addition, expanding the fourth term of Equation 67 and the second one in Equation 68, and also using arguments of symmetry it is obtained (retaining only one-body terms, that is, considering $E^{M(e-e)} = E_a^{\text{NP}}(1)$) that

$$\begin{aligned}
 E^{M(e-e)}(\alpha \cdot A_N, -\omega \cdot J_e^{(4)}) &= \langle\langle H^{\text{PSO}}; -\omega \cdot L_e \rangle\rangle \\
 &+ \langle\langle H^{\text{PSO-K}}; -\omega \cdot L_e \rangle\rangle \\
 &+ \langle\langle H^{\text{PSO}}; H^{\text{Mv/Dw}}; -\omega \cdot L_e \rangle\rangle \\
 &+ \langle\langle H^{\text{FC/SD}}; H^{\text{SO}(1)}; -\omega \cdot L_e \rangle\rangle \\
 &+ \langle\langle H^{\text{FC/SD}}; H^{\text{SO}(1)}; -\omega \cdot S \rangle\rangle.
 \end{aligned} \tag{69}$$

One of the important features of the $(e-e)$ contribution to E^M is the fact that the lowest order term of $E^{M(e-e)}(\alpha \cdot A_N, -\omega \cdot S^{(4)})$ is of order $1/c^2$, whereas the lowest order correcting term to $E^{M(e-e)}(\alpha \cdot A_N, -\omega \cdot L^{(4)})$ is of order c^0 . Nevertheless, the former is non-negligible with respect to the last one.

Therefore, the LRESC expansion of the electronic $(e-e)$ part of the spin-rotation, SR, constant of a nucleus N can be written as^[77]

$$\begin{aligned}
 M_N^{\text{elec}(e-e)} &= -\frac{\partial^2}{\partial I_N \partial L} E^{M(e-e)}(\alpha \cdot A_N, -\omega \cdot J_e) \\
 &= M_N^{\text{NR-elec}} \\
 &+ M_N^{\text{PSO-K}} + M_N^{\text{para-Mv/Dw}} + M_N^{\text{SO-L}} + M_N^{\text{SO-S}},
 \end{aligned} \tag{70}$$

where $M_N^{\text{NR-elec}}$ is the NR electronic contribution to M_N , $M_N^{\text{PSO-K}}$ is a second-order RSPT relativistic correction, and the remaining three terms are third-order corrections.

We shall now turn to obtain the one-body LRESC contributions to $M_N^{\text{elec}(p-p)}$. They arise from the evaluation of the electronic excitations to negative-energy states, in which case the projector is written as $P_p = 1 - P_e = 1 - |n_a\rangle\langle n_a|$. Then, according to Equation 53 we have

$$E^{M(p-p)}(V_N, V_J) = \frac{1}{2c^2} (\langle 0_N | V_N P_p X(V_J; 1) | 0_N \rangle + \langle 0_N | V_J P_p X(V_N; 1) | 0_N \rangle), \tag{71}$$

where

$$X(V_N; 1) = 2\alpha \cdot A_N + \frac{1}{2c^2} [H^D, \alpha \cdot A_N], \quad (72)$$

$$X(V_J; 1) = -2\omega \cdot J_e - \frac{1}{2c^2} [H^D, \omega \cdot J_e]. \quad (73)$$

The analysis of the dependence of the energy of Equation 71 with c^{-1} shows that $E^{M(p-p)}(V_N, V_J)$ is at least of order $\frac{h\nu}{c^2}$ ($V_N = \alpha \cdot A_N$ is proportional to μ_N). As it has been shown that the NR limit of $E^{M(e-e)}(V_N, V_J)$ is of order $\frac{h\nu}{c}$, it is easily deduced that the NR limit of $E^{M(p-p)}(V_N, V_J)$ is zero.

Besides, the leading order relativistic corrections are obtained retaining only terms of order $\frac{h\nu}{c}$ in the expectation values of Equation 71. Therefore, for simplicity (with no loss of precision) it can be taken that

$$X(V_N; 1) \simeq 2\alpha \cdot A_N + \frac{1}{2} [\beta, \alpha \cdot A_N] = 2\alpha \cdot A_N + \beta \alpha \cdot A_N, \quad (74)$$

$$X(V_J; 1) \simeq -2\omega \cdot J_e - \frac{1}{2} [\beta, \omega \cdot J_e] = -2\omega \cdot J_e. \quad (75)$$

Given that the projection operator over the negative-energy electronic states, $P_p = 1 - P_e$, up to order c^{-1} , is expressed as the following 4×4 matrix of spinors components

$$P_p = \begin{pmatrix} 0 & -\frac{\sigma \cdot p}{2c} \\ -\frac{\sigma \cdot p}{2c} & 1 \end{pmatrix}, \quad (76)$$

the operators in Equation 71 shall be written as

$$V_N P_p X(V_J; 1) = (\alpha \cdot A_N) P_p X(-\omega \cdot J_e^{(4)}; 1) = -2 \begin{pmatrix} -\sigma \cdot A_N \frac{\sigma \cdot p}{2c} & \sigma \cdot A_N \\ 0 & -\sigma \cdot A_N \frac{\sigma \cdot p}{2c} \end{pmatrix} \omega \cdot J_e, \quad (77)$$

and

$$V_J P_p X(V_N; 1) = (-\omega \cdot J_e^{(4)}) P_p X(\alpha \cdot A_N; 1) = \omega \cdot J_e \begin{pmatrix} \frac{\sigma \cdot p}{2c} \sigma \cdot A_N & 0 \\ -\sigma \cdot A_N & 3 \frac{\sigma \cdot p}{2c} \sigma \cdot A_N \end{pmatrix}. \quad (78)$$

Then, Equation 71 can be rewritten as

$$E^{M(p-p)}(V_N, V_J) = \frac{1}{2c^2} \langle 0_N^L | \langle 0_N^S | \left[-2 \begin{pmatrix} -\sigma \cdot A_N \frac{\sigma \cdot p}{2c} & \sigma \cdot A_N \\ 0 & -\sigma \cdot A_N \frac{\sigma \cdot p}{2c} \end{pmatrix} \omega \cdot J_e + \omega \cdot J_e \begin{pmatrix} \frac{\sigma \cdot p}{2c} \sigma \cdot A_N & 0 \\ -\sigma \cdot A_N & 3 \frac{\sigma \cdot p}{2c} \sigma \cdot A_N \end{pmatrix} \right] \begin{pmatrix} |0_N^L\rangle \\ |0_N^S\rangle \end{pmatrix}, \quad (79)$$

or

$$E^{M(p-p)}(V_N, V_J) = \frac{1}{4c^3} \langle 0_N^L | \langle 0_N^S | (\omega \cdot J_e \sigma \cdot p \sigma \cdot A_N + 2\sigma \cdot A_N \sigma \cdot p \omega \cdot J_e - 2\sigma \cdot A_N \omega \cdot J_e \sigma \cdot p - \sigma \cdot p \omega \cdot J_e \sigma \cdot A_N) | 0_N^L \rangle.$$

This expression can be reduced to

$$E^{M(p-p)}(V_N, V_J) = \frac{1}{4c^3} \langle 0_N^L | \langle 0_N^S | ([\omega \cdot J_e, \sigma \cdot p] \sigma \cdot A_N + 2\sigma \cdot A_N [\sigma \cdot p, \omega \cdot J_e]) | 0_N^L \rangle. \quad (80)$$

As the relativistic leading order corrections to $E^{M(e-e)}$ have a factor $\frac{h\nu}{c^3}$, which is the same as the factor appearing in Equation 80, $E^{M(p-p)}$ will not have NR contributions. So, Equation 80 gives the lowest order relativistic correction to $E^{M(p-p)}$. Furthermore, given that $[\sigma \cdot p, \omega \cdot J_e] = 0$, then $E^{M(p-p)} = 0$ up to this order.

Therefore, the LRESC model explicitly shows that both, the NR and the lowest order relativistic correction to $E^{M(p-p)}$ are zero. It means that, up to order $1/c^2$

$$E^{M(p-p)}(V_N, V_J) = 0 \Rightarrow M_N^{\text{elec}(p-p)} = 0. \quad (81)$$

3.4.3 | The relativistic relationship between the NMR shielding and the spin-rotation constants

Within the relativistic regime there is no immediate relationship among the NMR magnetic shielding and the SR tensors. This is apparent when we consider the second-order corrections to the energy that are used to obtain the relativistic NMR shielding tensor, and spin-rotation tensor

TABLE 5 LRESC core and ligand corrections

First-order triplet	First-order singlet	Third-order triplet	Third-order singlet	Zeroth-order singlet	First-order singlet
P1T	P1S	P3T	P3S	DOS	D1S
core		ligand		core	
$\sigma^{\text{SZ-K}} + \sigma^{\text{B-SO}}$		$\sigma^{\text{OZ-K}} + \sigma^{\text{PSO-K}} + \sigma^{\text{SO}} + \sigma^{\text{para-Mv/Dw}}$		$\sigma^{\text{Dia-K}} + \sigma^{\text{Dia-Mv/Dw}}$	

$$E^{(2)}(I_N, \mathbf{B}) = \frac{g_N}{2m_p c} I_N \cdot \left\langle \left\langle \frac{(\mathbf{r}-\mathbf{r}_N) \times \boldsymbol{\alpha}}{|\mathbf{r}-\mathbf{r}_N|^3}; [(\mathbf{r}-\mathbf{r}_G) \times \boldsymbol{\alpha}] \right\rangle \right\rangle \cdot \mathbf{B}, \quad (82)$$

and

$$\begin{aligned} E^{(2)}(I_N, \mathbf{L}) &= -\frac{g_N}{2m_p c} I_N \cdot \left\langle \left\langle \frac{(\mathbf{r}-\mathbf{r}_N) \times \boldsymbol{\alpha}}{|\mathbf{r}-\mathbf{r}_N|^3}; \mathbf{J}_e \right\rangle \right\rangle \times I^{-1} \cdot \mathbf{L} \\ &= -\frac{g_N}{2m_p c} I_N \cdot \left\langle \left\langle \frac{(\mathbf{r}-\mathbf{r}_N) \times \boldsymbol{\alpha}}{|\mathbf{r}-\mathbf{r}_N|^3}; \left[(\mathbf{r}-\mathbf{r}_{CM}) \times \mathbf{p} + \frac{1}{2} \boldsymbol{\Sigma} \right] \right\rangle \right\rangle \times I^{-1} \cdot \mathbf{L}. \end{aligned} \quad (83)$$

where $\boldsymbol{\mu}_N = \frac{g_N}{2m_p c} I_N$ is the magnetic moment of nucleus N, I_N is its nuclear spin, and g_N is its g-factor.

From our LRESC model we can get a deeper insight on why the NR relationship, known as Flygare relationship,^[74,78] breakdown.^[75] Considering the LRESC expressions of the (e-e) contribution to E^σ and E^M , both can be related each other, up to order $1/c^2$, in the following manner

$$\begin{aligned} 2c \frac{\partial}{\partial B_i} E^{\sigma(e-e)}(\boldsymbol{\alpha} \cdot \mathbf{A}_N, \boldsymbol{\alpha} \cdot \mathbf{A}_B) &= -\frac{\partial}{\partial \omega_j} E^{M(e-e)}(\boldsymbol{\alpha} \cdot \mathbf{A}_N, -\boldsymbol{\omega} \cdot \mathbf{J}_e) \\ &+ \left\langle \left\langle H^{\text{PSO}}; -\frac{1}{4c^2} \{p^2, L_i\} \right\rangle \right\rangle \\ &+ \left\langle \left\langle H^{\text{FC/SD}}; -\frac{1}{2c^2} [3S_i p^2 - (\mathbf{S} \cdot \mathbf{p}) p_i] \right\rangle \right\rangle \\ &+ \left\langle \left\langle H^{\text{FC/SD}}; \frac{1}{c^2} [(\mathbf{r} \cdot \nabla) V_C S_i - (\mathbf{r} \cdot \mathbf{S}) \nabla_i V_C] \right\rangle \right\rangle \\ &+ \left\langle \left\langle H^{\text{FC/SD}}; H^{\text{SO}(1)}; S_i \right\rangle \right\rangle. \end{aligned} \quad (84)$$

From the definitions of NMR shielding and SR tensors, we can rewrite this relationship as

$$\begin{aligned} \sigma_N^{(e-e)\text{LRESC}} &= \frac{m_p}{g_N} \mathbf{M}_N^{(e-e)\text{LRESC}} \otimes \mathbf{I} \\ &+ \sigma_N^{\text{OZ-K}} + \sigma_N^{\text{SZ-K}} + \sigma_N^{\text{B-SO}} + \frac{1}{2} \sigma_N^{\text{SO-S}}. \end{aligned} \quad (85)$$

where $\mathbf{M}_N^{(e-e)\text{LRESC}}$ is given by the Equation 70. We can see that the NR Flygare's relation

$$\sigma_N^{\text{NR-para}} = \frac{m_p}{g_N} \mathbf{M}_N^{\text{NR-elec}} \otimes \mathbf{I}, \quad (86)$$

is fulfilled,^[74,78] together with the following relationships,^[77]

$$\sigma_N^X = \frac{m_p}{g_N} \mathbf{M}_N^X \otimes \mathbf{I} \quad (87)$$

being $X = \text{PSO-K, para-Mv/Dw, and SO-L}$. The SO-S contribution has a similar relationship although with an extra factor 2,

$$\sigma_N^{\text{SO-S}} = 2 \frac{m_p}{g_N} \mathbf{M}_N^{\text{SO-S}} \otimes \mathbf{I}. \quad (88)$$

T6 Table 6 gives a representation of the LRESC contributions shared among the relativistic $\sigma_N^{(e-e)}$ and $\mathbf{M}_N^{\text{elec}(e-e)}$ tensors. It shows schematically which of the LRESC contributions to the shielding constants are also found in the SR tensor.

We should now introduce an analysis of the system of units used to relate both properties. We should take care of the fact that throughout the whole of this article the Gaussian cgs atomic system of units is used, and the fact that the NMR shielding is a dimensionless magnitude expressed in parts per million (ppm). So, the expression of the SR tensor, M_N shall be expressed as dimensionless. Given that atomic units were used in the derivation of this last property, the SR tensor shall be expressed at the end in Hartrees. As kHz are the units used in their measurements, they have to be transformed using the fact that 1 Hartree = $6.579683920729 \times 10^{12}$ kHz (Taken from Ref. [79]).

It is worth to highlight the fact that all relativistic corrections of the SR constants (up to order $1/c^2$) are included in the relativistic corrections of the NMR shieldings, but they have additional terms related with operators $H^{\text{OZ-K}}$, $H^{\text{SZ-K}}$, and $H^{\text{B-SO}}$. In addition to that, there is a factor 2 of difference between the SO due to spin contribution to both properties.

TABLE 6 LRESC (*e-e*) contributions shared among relativistic σ_N and M_N tensors

$\sigma_N^{(e-e)\text{-LRESC}}$		
$\sigma_N^{\text{NR-para}} + \sigma_N^{\text{PSO-K}} + \sigma_N^{\text{para-Mv/Dw}} + \sigma_N^{\text{SO-L}} + \frac{1}{2}\sigma_N^{\text{SO-S}}$	$\frac{1}{2}\sigma_N^{\text{SO-S}}$	$\sigma_N^{\text{OZ-K}} + \sigma_N^{\text{SZ-K}} + \sigma_N^{\text{B-SO}}$
$= \left(\frac{m_p}{g_N}\right) M_N^{(e-e)\text{-LRESC}} \otimes I$	$= \frac{1}{2}\sigma_N^{\text{SO-S}}$	$\cong \sigma_N^{\text{atom}(e-e)\text{-LRESC}}$
$= \left(\frac{m_p}{g_N}\right) \times \left(M_N^{\text{NR-elec}} + M_N^{\text{PSO-K}} + M_N^{\text{para-Mv/Dw}} + M_N^{\text{SO-L}} + M_N^{\text{SO-S}}\right) \otimes I$	$= \frac{1}{2}\sigma_N^{\text{SO-S}}$	$= \sigma_N^{\text{atom-OZ-K}} + \sigma_N^{\text{atom-SZ-K}} + \sigma_N^{\text{atom-B-SO}}$

During the last few years several works were published containing studies related with the breakdown of the NR relationship among σ_N and M_N .^[44,80–88] They applied the formalism given in Ref. [30] on heavy atom containing systems, using the NR relation from which the electronic contribution to the SR constant can be transformed to units of magnetic shielding. Comparison of their results with four-component calculations show large differences among σ_N and M_N within the relativistic regime if one use the NR Flygare's model.

Recently, based on the fact that the OZ-K, SZ-K, and B-SO mechanisms are core-dependent, an extension of the Flygare's relationship was proposed, in which the shielding tensor can be obtained from the SR tensor employing the new *M-i* (*i*=I, II, III, IV, V) models.^[77,89] The *M-III* model was the best model proposed in Ref. [77] and it is expressed as:

$$\sigma_N^{M-III} = \frac{m_p}{g_N} M_N \otimes I + \sigma_N^{\text{atom}} + \frac{1}{2}\sigma_N^{\text{SO-S}} \tag{89}$$

It is still possible to propose a better model,^[89] which must include all spin-dependent contributions in the last term of the model given in Equation 89. If we do this we arrive to

$$\sigma_N^{M-V} = \frac{m_p}{g_N} M_N \otimes I + \sigma_N^{\text{atom}} + \frac{1}{2c} \left(v_N^S - v_N^{\text{atom},S} \right) \tag{90}$$

where

$$v_N^S = \left\langle \left(\frac{(\mathbf{r}-\mathbf{r}_N) \times \boldsymbol{\alpha}}{|\mathbf{r}-\mathbf{r}_N|^3} ; \mathbf{S}^{(4)} \right) \right\rangle. \tag{91}$$

The new term $\frac{1}{2c} \left(v_N^S - v_N^{\text{atom},S} \right)$ is a generalization of $\frac{1}{2}\sigma_N^{\text{SO-S}}$, which represent now its lowest order contribution.

First, applications of the new relationship of Equation 90 show that they are much accurate than the previous attempts to obtain a relativistic generalization of Flygare's model.^[89]

3.4.4 | The rotational g-tensor and the magnetic susceptibility tensor

As shown in Equation 4, the rotational g-tensor involves the operators $V_B = \boldsymbol{\alpha} \cdot \mathbf{A}_B$ and $V_J = -\boldsymbol{\omega} \cdot \mathbf{J}_e$, and the susceptibility tensor has a bilinear dependence of the operator V_B .

In the case of the g-tensor, we should mention that the action of the operator \mathbf{L} on the nuclear variables of the electronic wavefunction is equivalent to (minus) the action of the total electronic four-component angular momentum operator.^[32] This is the reason why the g-tensor depends on $\mathbf{J}_e^{(4)}$.

Both tensors can be written as a sum of two terms: one nuclear and one electronic. The electronic terms are obtained in both cases through the linear response approach.^[51,90] This can also be done for spin-rotation tensors. In our case they are

$$g_N = \sum_N Z_N m_p \left[(\mathbf{r}_{N,G} \cdot \mathbf{r}_{N,CM}) \mathbf{I}^{-1} - (\mathbf{r}_{N,G} \cdot \mathbf{I}^{-1}) \mathbf{r}_{N,CM} \right] + m_p c \left\langle \left(\mathbf{r}_{e,CM} \times \boldsymbol{\alpha} ; \mathbf{J}_e \right) \right\rangle_{\omega=0} \otimes \mathbf{I}^{-1}. \tag{92}$$

and

$$\chi_N = -\frac{1}{8} \sum_N \frac{Z_N^2}{m_N c^2} \left(\hat{r}_N^2 - r_N^t r_N \right) - \frac{1}{4} \left\langle \left(\boldsymbol{\alpha} \times \mathbf{r}_{e,G} ; \boldsymbol{\alpha} \times \mathbf{r}_{e,G} \right) \right\rangle_{\omega=0}. \tag{93}$$

As happens for all relativistic polarization propagators,^[19] the ones of Equations 92 and 93 involves excitations to positive-energy electronic states (*e-e* rotations) and negative-energy electronic states (*p-p* rotations), which after few approximations can be expressed as two separated terms.^[23] The NR limit of the (*e-e*) and (*p-p*) contributions of both properties corresponds to their paramagnetic and diamagnetic terms, respectively.

As it was previously suggested^[51] and explicitly demonstrated few years ago,^[32] the NR relationship between the electronic part of the rotational g-tensor and the paramagnetic component of the susceptibility tensor is lost within the relativistic regime (see Equations 92 and 93). Besides, in the NR limit the Flygare's equivalence^[74] is recovered.

Again, the application of the LRESC model allows us to get a deeper understanding of the relation between both properties within a relativistic framework.

The expansion for the magnetic interaction has been worked out above and it was extensively discussed by different authors.^[26,28,73] It has the form (see Equations 58 and 59):

$$O(\boldsymbol{\alpha} \cdot \mathbf{A}_B) = H^{OZ} + H^{SZ} + H^{OZ-K} + H^{SZ-K} + H^{B-SO} \quad (94)$$

Following the same arguments used in the LRESC expansion of the matrix elements of the four-component operator $J_e^{(4)}$ for the SR tensor we can write (see Equations 60 and 61)

$$O(-\boldsymbol{\omega} \cdot \mathbf{J}_e^{(4)}) = H^{BO-L} + H^{BO-S}. \quad (95)$$

From this equation, we observe that no terms of order $1/c^2$ contribute to the four-component total angular momentum operator $J_e^{(4)}$.

Considering the last two equations, the energy expansion (up to order $1/c^2$) can be written as

$$E^{g(e-e)}(V_B, V_J) = \langle\langle (H^{OZ} + H^{SZ} + H^{OZ-K} + H^{SZ-K} + H^{B-SO}); (H^{BO-L} + H^{BO-S}) \rangle\rangle + \langle\langle (H^{OZ} + H^{SZ}); D; (H^{BO-L} + H^{BO-S}) \rangle\rangle \quad (96)$$

We shall mention again that if closed shell electronic structures are considered, then the one-body corrections belonging to $E^{g(e-e)}$ are

$$E^{g(e-e)}(V_B, V_J) = \langle\langle H^{OZ}; H^{BO-L} \rangle\rangle + \langle\langle H^{OZ-K}; H^{BO-L} \rangle\rangle + \langle\langle H^{OZ}; H^{Mv/Dw}; H^{BO-L} \rangle\rangle + \langle\langle H^{OZ}; H^{SO(1)}; H^{BO-S} \rangle\rangle + \langle\langle H^{SZ}; H^{SO(1)}; H^{BO-L} \rangle\rangle. \quad (97)$$

or

$$E^{g(e-e)}(\boldsymbol{\alpha} \cdot \mathbf{A}_B, -\boldsymbol{\omega} \cdot \mathbf{J}_e) = \langle\langle H^{OZ}; -\boldsymbol{\omega} \cdot \mathbf{L}_e \rangle\rangle + \langle\langle H^{OZ-K}; -\boldsymbol{\omega} \cdot \mathbf{L}_e \rangle\rangle + \langle\langle H^{OZ}; H^{Mv/Dw}; -\boldsymbol{\omega} \cdot \mathbf{L}_e \rangle\rangle, \quad (98)$$

From this expression, the g-tensor (see Table 2) is

$$\mathbf{g}^{\text{elec}(e-e)} = m_p \langle\langle \mathbf{L}_e; \mathbf{L}_e \rangle\rangle \otimes I^{-1} - \frac{m_p}{4c^2} \langle\langle \{p^2, \mathbf{L}_e\}; \mathbf{L}_e \rangle\rangle \otimes I^{-1} + m_p \langle\langle \mathbf{L}_e; H^{Mv/Dw}; \mathbf{L}_e \rangle\rangle \otimes I^{-1}. \quad (99)$$

The first term of Equation 99 is the NR paramagnetic contribution to the g-tensor,^[74] whereas the other two are the mechanisms of the leading order relativistic effects of $\mathbf{g}^{(e-e)}$. In this way, the LRESC model applied to the g-tensor give the following results

$$\mathbf{g}^{\text{elec}(e-e)} = -2m_p c \frac{\partial^2}{\partial \mathbf{B} \partial \mathbf{L}} E^{g(e-e)}(\boldsymbol{\alpha} \cdot \mathbf{A}_B, -\boldsymbol{\omega} \cdot \mathbf{J}_e) = \mathbf{g}^{\text{NR-elec}} + \mathbf{g}^{\text{OZ-K}} + \mathbf{g}^{\text{Mv/Dw}}, \quad (100)$$

These mechanisms are analogous to those of the nuclear SR tensor.^[30] In the case of the g-tensor, unlike for the SR tensor, the spin-orbit contribution vanishes identically.

Now, we look for the electronic mechanisms that underlies the $\mathbf{g}^{(p-p)}$ term. Following the same arguments exposed above for the LRESC expansion of $E^{(p-p)}$, in this case, we have that the one-body ($p-p$) contributions are

$$E^{g(p-p)}(V_B, V_J) = \frac{1}{2c^2} (\langle\langle 0_N | V_B P_p X(V_J; 1) | 0_N \rangle\rangle + \langle\langle 0_N | V_J P_p X(V_B; 1) | 0_N \rangle\rangle), \quad (101)$$

where

$$X(V_B; 1) = 2\boldsymbol{\alpha} \cdot \mathbf{A}_B + \frac{1}{2} [\boldsymbol{\beta}, \boldsymbol{\alpha} \cdot \mathbf{A}_B] = 2\boldsymbol{\alpha} \cdot \mathbf{A}_B + \boldsymbol{\beta} \boldsymbol{\alpha} \cdot \mathbf{A}_B, \quad (102)$$

$$X(V_J; 1) = -2\boldsymbol{\omega} \cdot \mathbf{J}_e - \frac{1}{2} [\boldsymbol{\beta}, \boldsymbol{\omega} \cdot \mathbf{J}_e] = -2\boldsymbol{\omega} \cdot \mathbf{J}_e. \quad (103)$$

Expanding the operators of Equation 101 (with P_p up to order $1/c$) and applying the kinetic balance prescription to write Equation 101 in terms only of $|0_N^L\rangle$, and retaining terms up to order $1/c^3$, we obtain

$$E^{g(p-p)}(V_B, V_J) = \frac{1}{4c^3} \langle\langle 0_N^L | ([\boldsymbol{\omega} \cdot \mathbf{J}_e, \boldsymbol{\sigma} \cdot \mathbf{p}] \boldsymbol{\sigma} \cdot \mathbf{A}_B + 2\boldsymbol{\sigma} \cdot \mathbf{A}_B [\boldsymbol{\sigma} \cdot \mathbf{p}, \boldsymbol{\omega} \cdot \mathbf{J}_e]) | 0_N^L \rangle\rangle. \quad (104)$$

As happens for the SR tensor, the relativistic correction is also zero. Then, the lowest order contribution to the $(p-p)$ part of the energy is zero. It means that, on the grounds of the LRESC model, the following expression is valid up to order $1/c^2$:

$$E^{\beta(p-p)}(\boldsymbol{\alpha} \cdot \mathbf{A}_B, -\boldsymbol{\omega} \cdot \mathbf{J}_e) = 0 \Rightarrow \mathbf{g}^{\text{elec}(p-p)} = 0. \quad (105)$$

Now, we turn to the magnetic susceptibility tensor. Applying Equation 94, and including terms with the dependence on c up to order $1/c^2$

$$\begin{aligned} E^{\chi(e-e)}(\mathbf{V}_B, \mathbf{V}_B) &= \langle\langle H^{\text{OZ}} + H^{\text{SZ}}; H^{\text{OZ}} + H^{\text{SZ}} \rangle\rangle \\ &+ \langle\langle H^{\text{OZ}} + H^{\text{SZ}}; H^{\text{OZ-K}} + H^{\text{SZ-K}} + H^{\text{B-SO}} \rangle\rangle \\ &+ \langle\langle H^{\text{OZ-K}} + H^{\text{SZ-K}} + H^{\text{B-SO}}; H^{\text{OZ}} + H^{\text{SZ}} \rangle\rangle \\ &+ \langle\langle H^{\text{OZ}} + H^{\text{SZ}}; D; H^{\text{OZ}} + H^{\text{SZ}} \rangle\rangle \\ &= \langle\langle H^{\text{OZ}}; H^{\text{OZ}} \rangle\rangle + 2 \langle\langle H^{\text{OZ-K}}; H^{\text{OZ}} \rangle\rangle \\ &+ \langle\langle H^{\text{OZ}}; H^{\text{Mv/Dw}}; H^{\text{OZ}} \rangle\rangle. \end{aligned} \quad (106)$$

As for the g -tensor, the SO terms ($\langle\langle H^{\text{OZ}}; H^{\text{SO}(1)}; H^{\text{SZ}} \rangle\rangle$) are zero when closed shell electronic structures are considered. Therefore, the corresponding $(e-e)$ part of the energy will be given by the following three terms (see Table 2):

$$\begin{aligned} E^{\chi(e-e)}(\boldsymbol{\alpha} \cdot \mathbf{A}_B, \boldsymbol{\alpha} \cdot \mathbf{A}_B) &= \langle\langle H^{\text{OZ}}; \frac{1}{2c} \mathbf{L}_e \cdot \mathbf{B} \rangle\rangle + 2 \langle\langle H^{\text{OZ-K}}; \frac{1}{2c} \mathbf{L}_e \cdot \mathbf{B} \rangle\rangle \\ &+ \langle\langle H^{\text{OZ}}; H^{\text{Mv/Dw}}; \frac{1}{2c} \mathbf{L}_e \cdot \mathbf{B} \rangle\rangle, \end{aligned} \quad (107)$$

The first of them is the NR paramagnetic contribution to the magnetic susceptibility, whereas the remaining two terms are the leading order relativistic contributions originated in the operator $H^{\text{OZ-K}}$ and in the scalar correction to the Schrödinger Hamiltonian, $H^{\text{Mv/Dw}}$.

Therefore, according to the LRESC model, $\chi^{\text{elec}(e-e)}$ can be expanded (up to order $1/c^2$) as

$$\begin{aligned} \chi^{\text{elec}(e-e)} &= -\frac{\partial^2}{\partial \mathbf{B} \partial \mathbf{B}} E^{\chi(e-e)}(\boldsymbol{\alpha} \cdot \mathbf{A}_B, \boldsymbol{\alpha} \cdot \mathbf{A}_B) \\ &= \chi^{\text{NR-para}} \\ &+ \chi^{\text{OZ-K}} + \chi^{\text{para-Mv/Dw}}, \end{aligned} \quad (108)$$

When closed shell electronic structures are considered, the relativistic mechanisms appearing in Equation 108 are of the same type as those mechanisms found for $\mathbf{g}^{\text{LRESC}(e-e)}$. Nevertheless, the OZ-K correction carries a different factor. In fact, within the LRESC approach this is the unique difference between the $(e-e)$ contribution to the susceptibility tensor and the rotational g -tensor.

For the $(p-p)$ contribution we proceed as we did above,

$$E^{(p-p)} = \frac{1}{2c^2} (\langle\langle \Psi_0 | (\boldsymbol{\alpha} \cdot \mathbf{A}_B) P_p (2 + \beta) (\boldsymbol{\alpha} \cdot \mathbf{A}_B) | \Psi_0 \rangle\rangle). \quad (109)$$

From this equation, the diamagnetic component of the susceptibility tensor is obtained in the NR limit, together with the leading order relativistic contributions.

3.4.5 | The relativistic relationship among the g -tensor and the χ -tensor

From a theoretical point of view the relativistic magnetic susceptibility arises as a second-order correction to the energy due to the interaction among the electronic system and an external and uniform magnetic field.

According to the LRESC model, its electronic $(e-e)$ contributions can be expressed as in Equation 107. Conversely, the rotational g -tensor arises from induced molecular magnetic moment due to its rotational motion. In this case, according to the LRESC model, its $(e-e)$ electronic contribution is given by Equation 98. Then, a straightforward relationship between both expressions is immediately obtained,

$$\begin{aligned} 2c \frac{\partial}{\partial B_j} E^{\chi(e-e)}(\boldsymbol{\alpha} \cdot \mathbf{A}_B, \boldsymbol{\alpha} \cdot \mathbf{A}_B) &= -\frac{\partial}{\partial \omega_j} E^{\beta(e-e)}(\boldsymbol{\alpha} \cdot \mathbf{A}_B, -\boldsymbol{\omega} \cdot \mathbf{J}_e) \\ &+ \langle\langle H^{\text{OZ-K}}; L_j \rangle\rangle, \end{aligned} \quad (110)$$

which, in terms of the properties, is equivalent to

$$\chi^{(e-e)\text{LRESC}} = -\frac{1}{4m_p c^2} \mathbf{g}^{(e-e)\text{LRESC}} \otimes \mathbf{I} + \frac{1}{2} \chi^{\text{OZ-K}} \quad (111)$$

From here, the NR Flygare's relation is naturally recovered taking the NR limit. Within the relativistic framework, there is a factor 2 in the OZ-K contribution that formally breaks down such a relationship, when considering relativistic effects up to order $1/c^2$.

4 | APPLICATIONS OF THE LRESC MODEL

In this section, we are going to show some of the more relevant applications of the LRESC model. We start with the analysis of the nuclear magnetic shieldings, and then the spin-rotation constants. We will show the performance of our two-component model on the reproduction of four-component calculations together with the analysis of the electronic origin of the different contributions to the relativistic corrections. All calculations were performed considering only mono-electronic contributions, in such a way that $E^{(e-e)} = E_a^{\text{NP}}(1)$ and $E^{(p-p)} = E_b^{\text{N}+2}(1)$ is taken hereafter (see Equations 29–33), because the remaining two-body terms are not yet implemented in the DALTON code.^[91,92]

4.1 | Nuclear magnetic shielding constant

The LRESC model was first developed to analyze relativistic effects on the NMR magnetic shieldings. Then, historically it was this property the most analyzed using the LRESC.

4.1.1 | LRESC theoretical performance and few selected applications

Earliest results of calculations of magnetic shielding tensor applying the LRESC model were published in Refs. [26,27,93,94]. There, all one-body correcting terms to the shielding constants of HX and CH₃X (X = F, Br, I) were presented as benchmark calculations. It is worth to highlight, here, that, in four-component RPA calculations, two-body effects arising from the Coulomb interaction are included within the mean field approach. When these contributions are taking into account, even though they are small, the overall results with the LRESC method become excellent, as stated in Ref. [27].

In Ref. [93], results for the so-called scalar field dependent terms $\sigma^{\text{Dia-K}}$ (see Table 4) and $\sigma^{\text{OZ-K}} + \sigma^{\text{PSO-K}}$ (see Table 3) were presented. The analysis of the orbital contribution to each correcting term of atomic ions X⁻ and HX (X = F, Cl, Br, I), have shown that the inner shells were responsible for almost the total value of these corrections. One interesting finding was that $\sigma^{\text{Dia-K}}$ and $\sigma^{\text{OZ-K}} + \sigma^{\text{PSO-K}}$ are not sensitive to the changes of the molecular orbitals of the valence shell. Also, $\sigma^{\text{PSO-K}}$ vanishes for symmetric spherical electronic distributions (see Table 3), and its value in HX molecules is originated in the p-type lone pairs of the atom X.

Another study of contributions using localized orbitals was published by Gomez et al. in Ref. [94]. In that paper, relativistic corrections to the diamagnetic term of the shielding constant were evaluated in terms of localized molecular orbitals. The relative importance of the contributions of the inner core and the valence shell molecular orbitals was clearly exposed. For noble gases, the difference $\sigma^{\text{4comp}} - \sigma^{\text{nr}}$ for diamagnetic contribution was compared with the same difference in the LRESC context, $\sigma^{\text{LRESC}} - \sigma^{\text{nr}}$. It was found that the description of the diamagnetic terms with the LRESC scheme was very good, except for Radon atom. In this last case, the LRESC method does not reproduce accurately all the relativistic effects. This fact is under study in our research group.

To assess the completeness of LRESC regarding its theoretical grounds, in Ref. [69], Zaccari et al. focused on the formal relations that shows the gauge invariance of the LRESC method, and compared this scheme with two other similar descriptions for shielding constants, namely the Breit–Pauli approximation presented by Vaara and coworkers^[28] and the approach proposed by Kutzelnigg in Ref. [95]. It was shown, by the formal expressions and by calculations, that the LRESC model is gauge invariant for shielding constants. The HX and CH₃X (X = Br, I) model compounds were used. It was formally shown how different LRESC correcting terms compensate each other to give an overall gauge invariance of the shielding constant. The consistency among the LRESC, Breit–Pauli, and ESC-minimal-coupling approaches was also shown.

Roura et al. applied the LRESC formalism but using the molecular Hartree–Fock Hamiltonian.^[96] They obtained relations involving the Coulomb, *J*, and exchange, *K*, operators for LRESC shielding corrections. The mean field effects that arise from direct Coulombic contributions were obtained. Resulting in all cases by adding the Coulombic part of the HF operator to the external Coulomb field in the one-body LRESC expressions. Both exchange and different terms from the Breit operator are also consistently included. Regarding the diamagnetic term it includes a mean field correction depending on the exchange operator without a one-body counterpart. Roura et al., claims this term to lead a small contribution to the nuclear magnetic shielding constant. In this framework, the mean field spin orbit^[97,98] corrections are recovered, as well as the mean field counterpart of two-body effects. The contribution of mean field effects on diamagnetic term was estimated (in ppm) as: $\frac{1}{32\pi} \left(\frac{Z}{mc^2}\right)^2 (10^6)$ (see eq. 74 of Ref. [96]), yielding around 0.08 ppm for Xe atom.

Diamagnetic terms were also studied in more details. A better description of the shielding constants of sixth row atoms were published in Ref. [99]. An alternative approach to the electron-positron contribution to magnetic properties, based on two-component Breit–Pauli spinors, was presented there. It was coined as geometric elimination of small component (GESC). In the presence of a magnetic perturbation, the manifolds of different particle number operators are connected. This occurs even if the Coulomb–Breit interaction in the molecular Hamiltonian is neglected. The effect of the positronic manifold is wholly taken into account by means of the positronic Hamiltonian (*H*⁺), expressed as a geometric series (see Ref. [99]). Numerical results were presented for noble atomic gases and the HI molecule. For Xe atom the performance of GESC was quite good and provided an extra contribution of 334.27 ppm. GESC versus four-component calculations at RPA level of approach are 7052.8 ppm versus 7011 ppm, respectively (see table 3 on Ref. [99]). Total BPPT values of constant for Xe were reported as 6718.5 ppm (Refs. [73,100]) and 6747.2 ppm (Ref. [101]).

TABLE 7 Basis set convergence on $\sigma(\text{Sn})$ for all LRESC mechanisms. Uncontracted basis set were used in all cases

Sn	F	H	NR	SZ-K	B-SO	OZ-K + PSO-K	SO-L	para-Mv/Dw	Dia	LRESC
[21s15p11d2f]	[10s5p1d]	[4s1p] ^a	3084.5	2169.8	-513.8	296.8	16.9	-342.1	-791.6	3920.5
[23s20p16d5f]	[15s9p6d2f]	[10s3p2d] ^b	3103.7	2217.9	-460.1	303.2	15.0	-346.7	-792.6	4040.4
[25s21p16d5f]	[15s9p6d2f]	[10s3p2d] ^c	3100.8	2220.4	-460.6	304.0	15.0	-347.2	-792.7	4039.7

^adyall.cv2z for Sn and cc-pCVDZ for F, H.^bMMA-lresc.^caug-cc-pVTZ-lresc.

4.1.2 | Basis set analysis and gauge independence

T7 We studied the convergence of basis sets for calculations of σ^{NR} , as well as for the different LRESC relativistic corrections. In Table 7, we show the basis set used for the SnH_2F_2 molecule, in which case converged results were obtained. A similar behavior was obtained for all other molecular systems that contain Hydrogen, Halogen, group-11, and group-14 nuclei.

It can be seen in Table 7 that the convergence of calculations using different basis sets is obtained with the MMA-lresc basis set, which is a smaller version of aug-cc-pVTZ-lresc basis set and was named aug-Jun1 basis set in earlier works.^[102-104] The differences in the values of the total shielding, obtained as the addition of the NR shielding constant with all relativistic corrections, is smaller than 1 ppm compared with the values obtained using the larger basis set (aug-cc-pVTZ-lresc). Hereafter, we will consider all calculations of the shielding constant and their relativistic corrections as calculated with the MMA-lresc basis set, unless otherwise is specified.

T8 To show the gauge origin independence we carried out calculations of the relativistic corrections in the SnF_2H_2 molecule. The gauge origin was placed at both positions, the fluorine atom and the tin atom. Results of calculations are shown in Table 8.

We found that the quality of the basis set used in those calculations is such that there is no significant difference when the gauge origin is placed at the nucleus of interest or in a vicinal atom.

4.1.3 | Nuclear magnetic shielding with the LRESC scheme

LRESC for nuclear magnetic shielding constants was first tested on HX (X = F, Cl, Br, I) molecular systems, taken as benchmark compounds. This was done in the papers where the theoretical formalism was presented.^[26,27] To have a complete sight of LRESC, heavy atom containing molecular systems were studied. We also aim to have an insight on each correcting term, and finally on 2014 we proposed an overview to treat relativistic corrections grouped in two terms. We named those terms as core- and ligand-dependent.^[102] We present in this section a brief account of LRESC achievements in describing heavy atom containing molecular systems.

The nuclear magnetic shielding of the nucleus *N* given by the LRESC formalism can be written as

$$\sigma_N^{\text{LRESC}} = \sigma_N^{\text{NR}} + \sigma_N^{\text{corr}} \quad (112)$$

where σ^{NR} is the NR shielding value and σ^{corr} represents the relativistic corrections coming from the different electronic mechanisms of the LRESC scheme as it was described in section 3.

Melo and coworkers have shown in several works that the magnetic shielding calculated with LRESC scheme are in very good agreement with those obtained with four-component methods for atoms up to the fifth row of the Periodic Table.^[26,27,102,103,105] For medium-size molecular systems the differences among four-component and LRESC values are, in general, close to 2% and for heavier molecular systems, like SnI_4 , such a difference is close to 5%. However, for atoms belonging to the sixth row of the Periodic Table, like Au, Hg, Pb, and At, the differences reach values that are between 15% and 20% lower than the relativistic values.^[103,105,106]

In terms of the chemical environment of a heavy atom, Maldonado et al. studied in Ref. [105] the effects on the nuclear magnetic shielding constant of the surrounding atoms to central Sn and Pb in SnH_2XY and PbH_2XY (X, Y = F, Cl, Br, I) molecular systems. The electronic origin of the relativistic effects were discussed applying the LRESC model. It gave a 16% composition of HAVHA (heavy atom effect on vicinal heavy atom^[107]) type on $\sigma(\text{Sn})$ at SnH_2I_2 . It was found that the HAVHA type effect is due to the appearance of contributions that are different of $\sigma^{\text{SO-L}}$. With LRESC

TABLE 8 Gauge origin dependence for LRESC calculations on SnH_2F_2 with MMA-lresc basis set

SnH_2F_2	Atom	NR	SZ-K	B-SO	OZ-K + PSO-K	SO-L	Para-Mv/Dw	Dia	LRESC
Gauge on Sn	Sn	3103.7	2217.9	-460.1	303.2	15.0	-346.7	-792.6	4040.4
Gauge on F	Sn	3103.7	2217.9	-460.9	301.2	15.2	-345.2	-792.2	4039.7
Gauge on F	F	450.2	12.2	-3.0	1.5	2.5	-4.7	-6.6	452.0
Gauge on Sn	F	450.2	12.2	-3.1	0.2	2.5	-3.3	-5.2	453.5

plus an estimation of GESC correction to the heavy atom, shielding constants were compared to four-component RPA benchmark calculations. The LRESC model had an excellent performance when diamagnetic terms were corrected via GESC. For this case, most of relativistic correcting terms were not sensitive to the chemical environment. The ones which did change when substitutes changed were: $\sigma^{\text{SO-L}}$, $\sigma^{\text{OZ-K}} + \sigma^{\text{PSO-K}}$, and $\sigma^{\text{para-Mv/Dw}}$, only one of them being of SO-type. The other two reflect the enhancement of the PSO electronic mechanism due to a kinetic energy correcting term and angular momentum. The last term is always negative and opposite to the OZ-K + PSO-K. Then, its contributions are attenuated although when added to the SO-FC it gives a fine tuning for reproducing the total relativistic corrections to the shieldings of central and substituent atoms.

Regarding the spin-Zeeman operator of the spin-orbit contribution to shielding tensor, Ruiz de Azúa et al. critically discussed in Ref. [108] the assessment of the LRESC model on properties of linear molecules. They have shown that this correction yields no contribution to the isotropic shielding constant of linear molecules, but it has higher importance when individual tensor components are evaluated. Specially, when studying the anisotropy of the shielding tensor. In that paper it was found an interesting relation between SZ and OZ contributions to SO effects. Numerical examples were provided, showing that the individual shielding tensor components and the anisotropy of the tensor are in good agreement with results obtained with other methods, in particular with DHF approach.

Ruiz de Azúa and coworkers reported for Xe atom in XeF₂: $\sigma_{zz}(\text{Xe}) = 6143.5$ (6477.8) ppm with LRESC (GESC) scheme and the chemical shift $\delta\sigma = 4597.2$ ppm (LRESC). They compared the results with DFH values taken from Ref. [109]: $\sigma_{zz}(\text{Xe}) = 6418.3$ and 6380.0 ppm; $\delta\sigma(\text{Xe}) = 4268.0$ and 4479.9 ppm. Also comparison with experimental results were made: $\delta\sigma(\text{Xe}) = 4722$ and 4260 ppm; both measures in liquid CNH solvent^[110] and solid phase.^[111]

An interesting study of magnetic properties of Hg containing compounds, is the work published by Arcisauskaitė et al.^[106] They studied how important are relativistic effects on NMR shielding constants and chemical shifts of linear HgX₂ (X = Cl, Br, I, CH₃) compounds applying three different methods. Calculations performed with LRESC, ZORA and four component approaches were compared. Both, LRESC and ZORA are good enough to reproduce carbon shielding constants in Hg(CH₃)₂ within 6 ppm. In the case of chemical shifts, the LRESC fails to reproduce the tendency of ZORA and four component, even though ZORA underestimates the absolute shielding constant of mercury by 2100 ppm. Also a gaussian nucleus model for the Coulomb potentials was studied, reducing the shielding constant on Hg by 100–500 ppm and chemical shifts by 1–143 ppm when compared with point nuclear model. No effects were found on shielding constants for the lighter nuclei (C, Cl, Br, I). It is worth to mention that LRESC results lack in this case of the GESC correction, which inclusion might have reproduce in a better way chemical shifts.

To evaluate all LRESC corrections, one has to take into account 15 terms which can be divided in second- and third-order, and also of singlet and triplet type, as stated in Tables 3 and 4. Historically this way of showing LRESC results was useful to compare it with other theoretical schemes, as BPPT and minimal coupling. On the contrary this way of showing results is not quite useful to get insight on the overall shielding behavior, in terms of the molecular electronic origin of relativistic effects. To overcome this drawback two papers were written with a new proposal of grouping the leading relativistic corrections in terms of which molecular environment is the main source for those corrections.^[102,103] They can be divided in terms of core- and ligand-dependence, and they are explained in Table 5. “Core” corrections correspond to those LRESC corrections which do not change their absolute values when the environment of the studied nucleus is changed. Conversely, “ligand” corrections are those which have a strong dependence on each specific molecular environment.

4.1.4 | Core- and ligand-dependent corrections

The core-dependent contributions are given by all diamagnetic and one paramagnetic like corrections: mean values of diamagnetic singlet corrections ($\sigma_d^{S(0)}$); first-order diamagnetic singlet corrections ($\sigma_d^{S(1)}$) and first-order paramagnetic triplet corrections ($\sigma_p^{T(1)}$).

$$\sigma^{\text{core}} = \sigma_d^{S(0)} + \sigma_d^{S(1)} + \sigma_p^{T(1)} \quad (113)$$

Ligand-dependent contributions are given by the rest of the leading LRESC paramagnetic like corrections: first-order paramagnetic singlet corrections ($\sigma_p^{S(1)}$); third-order paramagnetic singlet corrections ($\sigma_p^{S(3)}$); and third-order paramagnetic triplet corrections ($\sigma_p^{T(3)}$).

$$\sigma^{\text{ligand}} = \sigma_p^{S(1)} + \sigma_p^{S(3)} + \sigma_p^{T(3)} \quad (114)$$

In Table 9, we show results of the calculations of NR magnetic shieldings and the whole set of relativistic corrections coming from the LRESC scheme in several model compounds, like IX, AgX, GeH₃X, and SnX₄ (X = H, F, Cl, Br, I) and the addition of all terms grouped as core- and ligand-dependent. Nonrelativistic calculations were performed with the DALTON suite of programs.^[91]

As aforementioned, the core-dependent corrections were rearranged in three specific terms: $\sigma_d^{S(0)}$, $\sigma_d^{S(1)}$, and $\sigma_p^{T(1)}$. Each one of them must be analyzed separately, because they arise from different electronic mechanisms, have different behavior, different signs, and they are not of the same order of magnitude. Two of them modify the diamagnetic component of the nuclear magnetic shielding (*p-p* part), and the third one modifies the paramagnetic component (*e-e* part).

For heavy central atom in tetrahedral compounds, like Sn, $\sigma_p^{T(1)}$ represents a large percentage of the σ^{nr} value. When the substituent halogen atom becomes heavier, such a percentage do increases because the NR value is smaller; for SnI₄ such a percentage reaches 66%. This correction is strongly core-dependent, and, for heavy atoms, it is of the same order of magnitude as σ^{nr} , as shown in Table 9. For light and not so heavy atoms,

TABLE 9 Leading relativistic corrections obtained with the LRESC model to magnetic shielding for Ag and I nuclei in AgX and IX linear molecules, and for Ge and Sn nuclei in GeH₃X and SnX₄ tetrahedral compounds (X = H, F, Cl, Br, I)

Molecules	σ^{nr}	Core			Ligand			Core	Ligand	LRESC	4-comp
		$\sigma_d^{S(0)}$	$\sigma_d^{S(1)}$	$\sigma_p^{T(1)}$	$\sigma_p^{S(1)}$	$\sigma_p^{S(3)}$	$\sigma_p^{T(3)}$				
AgH	4157.66	-940.72	283.45	1458.70	142.59	-69.02	-75.85	801.43	-2.28	4956.81	4803.55
AgF	4229.29	-940.69	283.35	1458.67	123.75	-67.67	52.02	801.32	108.10	5138.71	5019.70
AgCl	4087.53	-940.79	283.40	1458.69	141.45	-83.41	-2.44	801.30	53.15	4941.98	4827.98
AgBr	4076.90	-941.27	283.43	1458.88	143.25	-71.90	-13.72	801.03	57.63	4935.56	4841.57
AgI	4037.13	-942.19	283.47	1459.10	150.58	-54.92	-6.25	800.38	89.41	4926.92	4845.26
IH	4539.80	-1361.89	415.69	2098.97	279.71	-266.20	157.55	1152.77	171.06	5863.62	5885.47
IF	-1478.73	-1361.94	415.68	2101.72	1153.72	-1852.01	2460.07	1155.47	1761.79	1438.53	927.08
ICl	1923.10	-1362.02	415.68	2100.53	659.56	-992.04	1357.95	1154.19	1025.47	4102.76	3745.18
IBr	2799.68	-1362.52	415.68	2100.19	523.67	-809.94	1061.69	1153.36	784.42	4737.46	4403.04
I ₂	4290.44	-1363.37	415.70	2099.85	317.54	-495.61	273.59	1152.18	95.52	5538.14	5532.36
GeH ₄	1765.68	-287.85	83.75	450.81	66.61	-65.05	-9.30	246.71	-7.73	2004.66	1979.67
GeH ₃ F	1561.10	-287.87	83.74	450.83	74.47	-82.12	0.47	246.70	-7.19	1800.61	1756.47
GeH ₃ Cl	1601.30	-287.96	83.75	450.87	73.38	-79.38	3.84	246.65	-2.16	1845.79	1802.71
GeH ₃ Br	1614.55	-288.47	83.75	451.01	74.34	-81.33	29.80	246.29	22.81	1883.65	1850.29
GeH ₃ I	1655.51	-289.36	83.75	451.10	75.02	-85.24	99.26	245.49	89.04	1990.04	1954.32
SnH ₄	3270.26	-1137.66	345.16	1757.93	298.83	-304.29	-38.33	965.43	-43.79	4191.91	4126.14
SnF ₄	3453.94	-1137.69	345.03	1757.41	260.64	-291.25	20.00	964.76	-10.62	4408.08	4364.52
SnCl ₄	2929.16	-1138.06	345.15	1757.93	322.65	-401.14	91.62	965.02	13.13	3907.31	3988.53
SnBr ₄	2819.86	-1139.89	345.23	1759.50	347.81	-450.95	579.22	964.83	476.07	4260.76	4480.72
SnI ₄	2672.93	-1141.24	345.26	1760.75	372.94	-507.85	1715.75	962.98	1580.84	5216.74	5512.86

like germanium, such contributions are smaller when they are compared with the NR shielding value (smaller than 30%). The behavior of $\sigma_d^{S(0)}$ is similar to that of $\sigma_p^{T(1)}$, although it is less important than the latter and it has also opposite sign. The highest variations appear for tin atoms when they are in the center of the molecule, and such corrections are among 32.9% and 42.6% of σ^{nr} . The third core-dependent correction is $\sigma_d^{S(1)}$, although its contribution is smaller than the other ones. The variation with respect to the NR shielding constant is among 10.1% and 12.9% for tin containing molecules.

For the light central atoms, the total core-dependent contributions are not so important; but for molecules containing tin atoms they are almost of the same order of magnitude as σ^{nr} . Such contributions are between 27.9% and 36.0% of $\sigma^{nr}(\text{Sn})$, but the variation comes from the different NR shielding values. As an example, the total core-dependent contribution to $\sigma(\text{Sn})$ in SnF₄ is 964.76 ppm and for SnI₄ it is 964.77 ppm. However, $\sigma^{nr}(\text{Sn})$ is 3455.42 ppm in the former case and 2676.59 ppm in the latter, giving rise to different percentages.

When the chemical shifts ($\delta(\text{Sn})$) are calculated with respect to a reference system, the core-dependent contributions are almost completely canceled each other and the final value arises from the differences among the NR values, together with the ligand-dependent corrections.

F1 Figure 1 shows the relationship between the core-dependent contributions and the atomic number of the nucleus whose magnetic shielding is calculated. Two different fitting dependence can be proposed through quadratic and potential functions. Both functions give excellent fittings: $\sigma^{\text{core}}(Z) = 0.77Z^2 - 23.11Z + 194.27$ (ppm) and $\sigma^{\text{core}}(Z) = 0.0056Z^{3.083}$ (ppm).

Regarding ligand-dependent corrections, the $\sigma_p^{S(1)}$ term increases its value when the central atom becomes heavier, but it does not change very much when the environment is modified, even when the central atom is surrounded by several heavy atoms. Their contributions are close to 10% of the corresponding σ^{nr} values. Conversely, the contributions of $\sigma_p^{S(3)}$ are larger than $\sigma_p^{S(1)}$ reaching values close to 20% of σ^{nr} . Both contributions have opposite signs, giving a total contribution less than 10% (negative) for the heaviest molecular system and decreasing the total shielding value, $\sigma(\text{Sn})$. In some of the lighter molecular systems, both contributions almost cancel each other.

The most important of the whole set of ligand-dependent relativistic corrections is $\sigma_p^{T(3)}$, which is responsible of many relativistic effects. Such a correction includes the FC and SD contributions as can be seen in Table 5. The FC term has a very large range of variation when the weight of the molecule grows up and it can be of the same order of magnitude as the NR value. For light systems $\sigma_p^{T(3)}$ is negative because the contributing

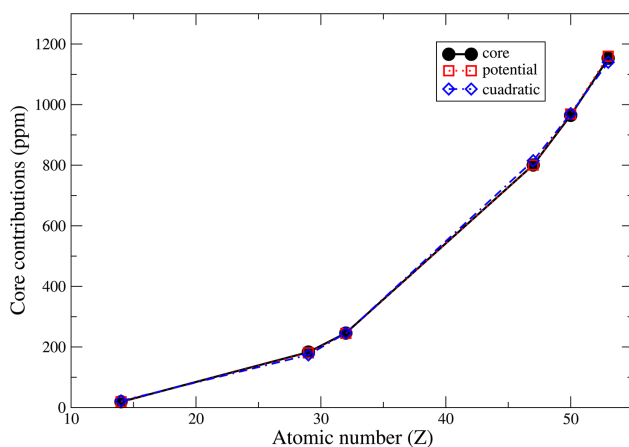


FIGURE 1 Relationship between core-dependent corrections on σ and the atomic number of nuclei

SD term are larger than the FC one (in absolute value). For medium-size systems both values are almost the same so they cancel each other, and then the total value is close to zero; but for heavy molecular systems the FC correcting term increases its value considerably and at the same time the SD term becomes not very important. For SnI_4 molecule, $\sigma^{\text{nr}}(\text{Sn}) = 2672.93$ ppm and $\sigma_p^{T(3)}(\text{Sn}) = 1715.75$ ppm representing 64.2% being the largest contribution.

F2

The total core- and ligand-dependent corrections are shown in Figure 2 for germanium and tin atom-containing molecules, in GeH_3X and SnX_4 ($\text{X} = \text{H}, \text{F}, \text{Cl}, \text{Br}, \text{I}$) model compounds. It can be seen in this Figure that for germanium atom, the main relativistic corrections are of core-dependent type. When the weight of the central atom grows up the most important corrections come from the ligand-dependent type, but only for heavy halogen substituent atom like Br and I.

The analysis given above shows a compensation among core- and ligand-dependent contributions. The addition of core-dependent and two of the three ligand-dependent corrections (excluding $\sigma_p^{T(3)}$) gives a very small contributions for light systems, and for the heaviest molecular system, SnI_4 , it reaches the largest absolute value, 26.4%. Conversely, only $\sigma_p^{T(3)}$ correction has a very different behavior and this is the reason why it was considered the main electronic mechanism responsible of ligand relativistic effects. However, this is true only for light or not so heavy molecules, since for heavy ones $\sigma_p^{T(3)}$ does not reproduce the total relativistic effect for the nuclear magnetic shielding. The other relativistic corrections do increase their contribution, especially those that are core-dependent. As a consequence, the addition of σ^{nr} plus $\sigma_p^{T(3)}$ does not give good enough reproduction of the relativistic value for heavy atoms because the others contributions become important.

For linear molecules, like AgX and IX ($\text{X} = \text{H}, \text{F}, \text{Cl}, \text{Br}, \text{I}$), the behavior of the relativistic contributions are different from those of the tetrahedral geometry, as can be seen in Table 9. The performance of the LRESC is not good enough for IX molecules, like IF , where the difference with the four-component value is large. The main relativistic corrections to the total magnetic shielding for the whole set of studied linear molecules are of core-dependent type. They have a different behavior when we compare them with the magnetic shielding of central atoms in tetrahedral compounds. The ligand-dependent corrections to σ have a small dependence with the type of the substituent for silver atom, but for a heavier nucleus like iodine, such contributions are larger. When iodine atom is bounded to fluorine atom, the most important ligand-dependent contributions do

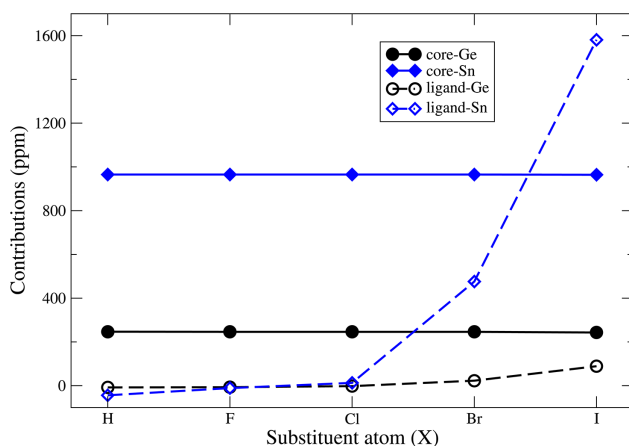


FIGURE 2 Core- and ligand-dependent corrections on $\sigma(\text{Ge})$ and $\sigma(\text{Sn})$ in GeH_3X and SnX_4 ($\text{X} = \text{H}, \text{F}, \text{Cl}, \text{Br}, \text{I}$) model compounds

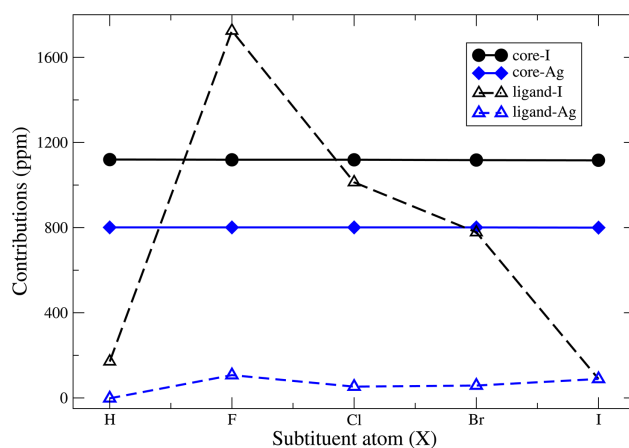


FIGURE 3 Core- and ligand-dependent contributions to magnetic shielding in linear model compounds AgX and IX (X = H, F, Cl, Br, I)

appear, being larger than the core-dependent ones. This seems to be the source of the difference with four-component value where the higher order corrections may be important.

F3

Figure 3 shows core and ligand-dependent contributions for AgX and IX molecules. Within the set of these corrections, the SO is the main one. Such SO effects are more positive in the whole set of molecular systems when the halogen is X = F. Furthermore, when the weight of the molecule increases few other important electronic mechanisms do become important.

4.2 | Nuclear spin-rotation constants

As seen in subsection 3.4.3, the SR and shielding tensors have some common mechanisms according to the LRESC model. Here, we analyze how accurately the LRESC model reproduces the four-component results of SR constants in the molecule series IX (X = H, F, Cl, Br, I) also analyzed in subsection 4.1, and we study how they are related with the shielding constants.

Nonrelativistic and relativistic calculations were performed at the RPA level of approach of the polarization propagator formalism with Hartree-Fock and Dirac-Hartree-Fock wave functions, respectively, as implemented in the DALTON^[91,92] and DIRAC program packages.^[22]

In all calculations, we employed the nonrelativistic Dunning's augmented correlation-consistent aug-cc-pCV5Z basis set for H, F, and Cl atoms.^[112] For Br and I, we used the relativistic acv4z basis sets of Dyall, dyall.acv4z.^[113] The small component basis sets of relativistic calculations were obtained by applying unrestricted kinetic balance (UKB) prescription. Uncontracted gaussian basis sets were used with the common gauge-origin (CGO) approach in all calculations. Experimental geometric distances in gaseous phase compounds were used for the IX (X = H,^[114] F,^[115] Cl,^[114] Br,^[114] I^[114]) series. The same geometries were used both in the NR and relativistic calculations. The bond distances in Å are: 1.6090 (HI), 1.9098 (IF), 2.3210 (ICI), 2.4691 (IBr), and 2.6663 (I₂). To describe the coulombic electron-nucleus interaction, a point nuclear model was employed

TABLE 10 Nuclear spin-rotation constants of nuclei of the IX (X = H, F, Cl, Br, I) systems obtained applying both four-component and LRESC methodologies

X	N	$\frac{m_p I}{g_N} [\text{ppm/kHz}]$	$\frac{m_p I}{g_N} M_{\perp, N}^{\text{nuc}}$	$\frac{m_p I}{g_N} M_{\perp, N}^{\text{elec}(e-e)}$		$\frac{m_p I}{g_N} M_{\perp, N}^{\text{elec}(p-p)}$	
				LRESC	4-comp	LRESC	4-comp
H	¹²⁷ I	4.18	8.69	-1415.56	-1359.89	0.00	0.38
	¹ H	0.84	3.41	47.16	47.00	0.00	0.00
F	¹²⁷ I	97.30	57.81	-8099.91	-8493.62	0.00	2.85
	¹⁹ F	20.82	50.80	568.57	512.96	0.00	-0.02
Cl	¹²⁷ I	238.41	81.01	-4137.22	-4312.62	0.00	1.53
	³⁵ Cl	489.63	69.53	-32.12	-30.86	0.00	-0.02
Br	¹²⁷ I	478.88	123.31	-3214.04	-3391.31	0.00	1.20
	⁷⁹ Br	383.77	115.98	-774.61	-698.21	0.00	-0.04
I	¹²⁷ I	728.20	140.18	-2006.02	-1992.33	0.00	0.51

Results are multiplied by the factor $\frac{m_p I}{g_N}$, to obtain their values in ppm. Nuclear and electronic values of SR constants are displayed separately, and the latter are splitted into their (e-e) and (p-p) contributions.

COLOR

TABLE 11 Individual LRESC contributions to the SR constants of both nuclei in IX (X = H, F, Cl, Br, I) systems.

X	N	$\frac{m_p}{3N} \times$						$\frac{m_p}{3N} M_{\perp,N}^{\text{LRESC}(e-e)}$
		$M_{\perp,N}^{\text{NR-elec}}$	$M_{\perp,N}^{\text{PSO-K}}$	$M_{\perp,N}^{\text{para-Mv/Dw}}$	$M_{\perp,N}^{\text{SO-L}}$	$M_{\perp,N}^{\text{SO-S}}$		
H	^{127}I	-1457.05	205.75	-400.04	156.00	79.77	-1415.56	
	^1H	17.81	0.04	0.04	29.38	-0.11	47.16	
F	^{127}I	-10 473.16	1507.93	-2754.20	2361.38	1258.14	-8099.91	
	^{19}F	682.79	-1.29	8.32	-7.83	-113.42	568.57	
Cl	^{127}I	-5442.91	771.75	-1478.90	1360.22	652.61	-4137.22	
	^{35}Cl	238.89	-3.03	-37.65	-126.45	-103.87	-32.12	
Br	^{127}I	-4168.70	580.29	-1206.95	1097.99	483.33	-3214.04	
	^{79}Br	-196.80	3.79	-136.39	-333.10	-112.12	-774.61	
I	^{127}I	-1927.55	253.46	-732.10	237.21	162.96	-2006.02	

Results are multiplied by the factor $\frac{m_p}{3N}$, to obtain values in ppm.

in all calculations, because it was the nuclear model used in the derivation of all the LRESC operators. Nuclear size effects were not considered in this work; they do not affect at all the main conclusions of the present work.

The diagonal tensor elements of properties are labeled in such a way that \perp refers to the xx and yy tensor elements, for linear molecules along the z axis.

T10 In Table 10, we see that $M_{\perp,N}^{\text{elec}(e-e)}$ (N = I, X) are well reproduced by the LRESC method, obtaining differences of less than 5% with respect to four-component results. There are two reasons to explain this behavior: (i) two-body operators were not included in the LRESC calculations of this work, as stated previously, and (ii) differences due to higher order effects (higher than those of order $\frac{1}{c^2}$) are not included in the current LRESC development. In addition, the (p-p) contributions are exactly zero according to the LRESC theory, whereas the four-component values are of a few ppm, fully corresponding to higher order corrections (of order $1/c^4$ and higher).

T11 In Table 11, each one of the LRESC contribution to the SR constants of I and X nuclei in IX (X = H, F, Cl, Br, I) systems is shown. It must be taken into account that such results do not include two-body contributions. A comparison of Tables 11 and 12 shows the full equivalence of the NR contributions of SR and shielding constants, but also of the PSO-K, para-Mv/Dw and SO-L mechanisms. A factor 2 distinguish the SO-S contributions to both properties.^[77]

F4 As stated in Ref. [77], the OZ-K, SZ-K, and B-SO values are in agreement with the homologous contributions of the shielding of free atoms. In Figure 4, it is clearly seen that $M_{\perp,N}^{\text{elec}(e-e)}$ is better reproduced by the LRESC model than $\sigma_{\perp,N}^{\text{elec}(e-e)}$ for iodine in the IX series. Following the arguments given in Refs. [77,89], and taking into account the recently proposed relationships between SR and shielding constants, some explanation of this behavior can be made.

An analysis of the models given in Equations 89 and 90, and their application to Figure 4, shows that the differences between four-component and LRESC values of the shielding of iodine includes the homologous differences for the SR constants, but they also includes the differences

TABLE 12 Individual LRESC contributions to the perpendicular (e-e) contributions to the shielding tensor of both nuclei in IX (X = H, F, Cl, Br, I) systems

X	N	$\sigma_{\perp,N}^{\text{NR-elec}}$	$\sigma_{\perp,N}^{\text{PSO-K}}$	$\sigma_{\perp,N}^{\text{para-Mv/Dw}}$	$\sigma_{\perp,N}^{\text{SO-L}}$	$\sigma_{\perp,N}^{\text{SO-S}}$	$\sigma_{\perp,N}^{\text{OZ-K}}$	$\sigma_{\perp,N}^{\text{SZ-K}}$	$\sigma_{\perp,N}^{\text{B-SO}}$	$\sigma_{\perp,N}^{\text{LRESC}(e-e)}$
H	^{127}I	-1457.05	205.75	-400.04	156.00	159.54	143.00	2552.76	-528.60	831.37
	^1H	17.81	0.04	0.04	29.38	-0.22	0.03	0.00	0.00	47.09
F	^{127}I	-10 473.16	1507.93	-2754.20	2361.38	2516.27	142.41	2552.83	-529.37	-4675.90
	^{19}F	682.79	-1.29	8.32	-7.83	-226.83	0.75	10.74	-2.63	464.01
Cl	^{127}I	-5442.91	771.75	-1478.89	1360.22	1305.22	141.71	2552.81	-529.99	-1320.09
	^{35}Cl	238.89	-3.03	-37.65	-126.45	-207.74	3.01	76.57	-19.32	-75.73
Br	^{127}I	-4168.70	580.29	-1206.95	1097.99	966.66	141.14	2552.81	-531.20	-567.96
	^{79}Br	-196.80	3.79	-136.39	-333.10	-224.24	34.92	714.98	-160.29	-297.13
I	^{127}I	-1927.55	253.46	-732.10	237.21	325.91	141.06	2552.80	-532.06	318.74

Results are given in ppm.

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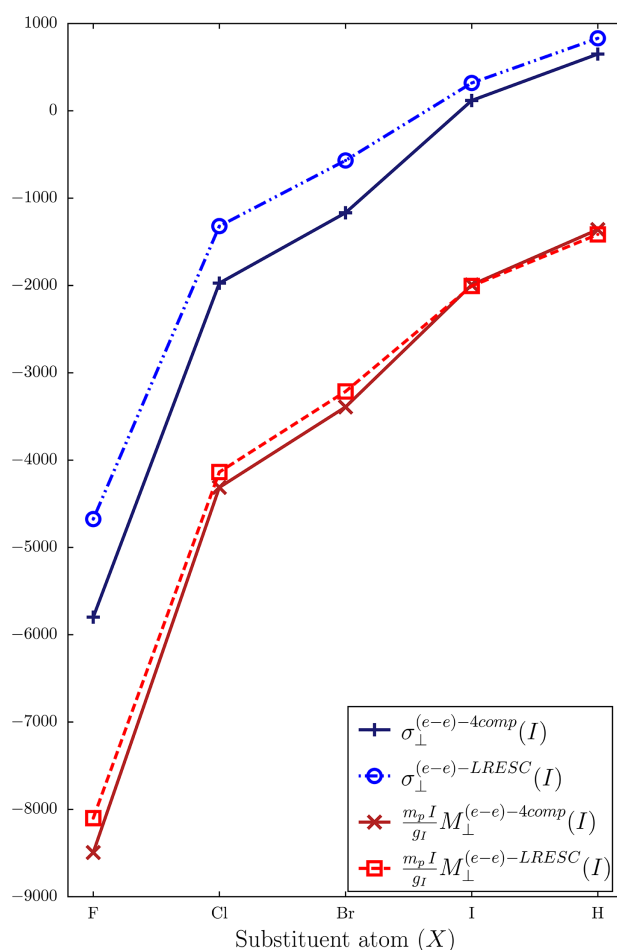


FIGURE 4 4c and LRESO perpendicular (e-e) components of shielding and spin-rotation (in ppm) tensors of iodine in IX (X = H, F, Cl, Br, I) systems

between four-component and LRESO values of the shielding of the free iodine atom and higher order effects corresponding to the SO-S contribution. In other words, according to Equations 89 and 90, and following Refs. [77,89], it can be showed that

$$\sigma_N^{4c} - \sigma_N^{LRESO} \cong \frac{m_p}{g_N} (M_N^{4c} - M_N^{LRESO}) \otimes I + (\sigma_N^{atom-4c} - \sigma_N^{atom-LRESO}) + \left[\frac{1}{2c} (v_N^S - v_N^{atom,S}) - \frac{1}{2} \sigma_N^{SO-S} \right]. \quad (115)$$

In Equation 115, it is shown that we can analyze the origin of “post-LRESO” contributions to shielding constants. In our current study, they have two origins, as we have mentioned: (i) the two-body terms not included in our LRESO calculations; and (ii) the effects of orders higher than $\frac{1}{2c}$.

Following Equation 115, it is seen that $\frac{m_p}{g_N} (M_{\perp,N}^{4c(e-e)} - M_{\perp,N}^{LRESO(e-e)})$ is included as part of $(\sigma_{\perp,N}^{4comp(e-e)} - \sigma_{\perp,N}^{LRESO(e-e)})$. According to Figure 4, the second and third term of the rhs of Equation 115 must be taken into account, because they play an important role.

TABLE 13 Differences between four-component and LRESO values of calculated perpendicular (e-e) contributions to shielding and spin-rotation tensors of iodine in IX compounds

Molecule	$\frac{m_p}{g_I} \Delta M_{\perp}^{(e-e)}(I)^a$	$\Delta \sigma^{atom(e-e)}(I^-)^a$	$\frac{1}{2c} \Delta v_{\perp}^{S(e-e)}(I)^b$	$\Delta \sigma_{\perp}^{(e-e)}(I)^a$
HI	55.66	-232.76	-3.26	-180.81
IF	-393.71	-232.76	-495.87	-1122.47
ICI	-175.40	-232.76	-243.46	-652.67
IBr	-177.27	-232.76	-189.23	-599.99
I ₂	13.69	-232.76	16.82	-200.79

Values of shielding of free ionized iodine are also displayed. All values are given in ppm.

^a Δ indicates the difference between four-component and LRESO values of the corresponding magnitude.

$$^b \frac{1}{2c} \Delta v_{\perp}^{S(e-e)}(I) = \frac{1}{2c} (v_{\perp}^{S(e-e)}(I) - v_{\perp}^{atom,S(e-e)}(I^-)) - \frac{1}{2} \sigma_{\perp}^{SO-S}(I).$$

From calculations of the shielding of free iodine atom simply ionized, we found that $(\sigma_{\perp}^{4\text{comp}(e-e)}(I^{-}) - \sigma_{\perp}^{\text{LRESC}(e-e)}(I^{-})) = 1934.46 \text{ ppm} - 2167.22 \text{ ppm} = -232.76 \text{ ppm}$. This difference indicates that higher order effects must be considered also for free shielding constants.

T13 In the particular cases of iodine in HI and I₂, the agreement between LRESC and four-component values of $M_{\perp}^{(e-e)}(I)$ is excellent (55.66 and 13.69 ppm of difference, respectively; see Figure 4 and Table 13), whereas for $\sigma_{\perp}^{(e-e)}(I)$ the differences are not negligible, but are the smallest of this set of molecules. As shown in Table 13, the main origin of the LRESC versus four-component differences in $\sigma_{\perp}^{(e-e)}(I)$, for HI and I₂, are the higher order effects of the shielding of free iodine atom.

For the remaining systems (IF, ICl, and IBr), the differences between four-component and LRESC calculations of $\sigma_{\perp}^{(e-e)}(I)$ are due not only to higher order effects of $\sigma^{\text{atom}(e-e)}(I^{-})$ (as in the case of HI and I₂), but also they are due to higher order effects on $M_{\perp}^{(e-e)}(I)$ and on $v_{\perp}^{S(e-e)}(I) - v^{\text{atom},S(e-e)}(I^{-})$ (the third term in the rhs of Equation 115).

Therefore, Table 13 allows one to deeply understand Figure 4, and particularly to know the origin of the differences between four-component and LRESC result of calculations. Work along this line of research is currently in progress in our laboratory.

5 | CONCLUSIONS

There are several two-component methods that introduce relativistic effects as perturbative corrections. They were first developed to accurately reproduce the four-component energy spectra.

The two-component linear response elimination of small component, LRESC, model was developed in the beginning to reproduce magnetic response properties, but then it was used to reproduce any of the response atomic and molecular properties.

In this review, we have given the fundamentals and the basic assumptions used to obtain the explicit expressions of the LRESC model. They are: (i) One should start working with the Rayleigh–Schrödinger perturbation theory, and divide the second-order correction to the energy into two terms, each depending on its behavior when c goes to infinity. There appears what we call the $(e-e)$ or paramagnetic-like terms and the $(p-p)$ or diamagnetic-like terms; (ii) the last term can be obtained making a transformation of the inverse of the difference of energies that consider negative-energy electronic states. This transformation is one of the key points of the model; (iii) once this transformation is made, the next step is to transform the four-component matrix elements into two-component matrix elements using the elimination of small component technique.

There is a second key assumption related with the vacuum. Given that the ground state is considered with respect to the vacuum, one need to consider also the effect of the perturbation on the vacuum to get the correct effect of the perturbation on the electronic states (both branch of energy states). Then, the $(p-p)$ contributions do contain a term which introduce the polarization of the vacuum due to the presence of the external perturbation.

We also analyzed the different relativistic correcting terms that appears in the LRESC model. One interesting physical insight arises due to the fact that there are correcting terms which depends on the core alone, and other terms that depends on the environment, named as core-dependent and ligand-dependent terms, respectively. Using this separation one can get specific patterns of variations of relativistic effects on NMR magnetic shieldings of different families of compounds.

Another very important finding shown in this review is related with the relativistic generalization of some of the well-known NR relationships, like Flygare's relation among SR and shielding constants. The LRESC model allows for the comparison of equivalent terms that arises in the different response properties. Being them exactly the same, one can find the way to generalize their NR relationship with the introduction of some new assumptions. In our case, we have shown how to construct the relativistic relationship among the NMR magnetic shielding and the spin-rotation constants, and also, among the g -tensors and susceptibilities. When the velocity of light is scaled to infinity these two relationships recover its NR expressions.

The separation of the theoretical expressions of response properties in terms of their perpendicular and parallel components, together with their $(e-e)$ and $(p-p)$ parts, give new insights about which are the main electronic mechanism involved when including relativistic correcting terms to the NR expressions, and how to understand and treat them. We are also able to have a look on the origin of the differences among the LRESC and the four-component results.

There are some molecular systems for which the LRESC model does not accurately reproduce the four-component results, but there are now clear indications on why it happens and how this difference can be overcome.

In short, we have shown, here, how powerful the LRESC model is for: (i) reproducing four-component values of response properties of atomic and molecular systems; (ii) the analysis based on known NR operators of the electronic mechanisms that underlies the different relativistic effects that appears in the response properties; and (iii) the search of the relativistic generalization of the likely relationships among properties that arises due to similar external perturbations. We probed it for the relationship among NMR shielding and spin-rotation constants, and the g -tensor and the susceptibility tensor.

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REFERENCES

- [1] P. Pyykkö, *Adv. Quantum Chem.* **1978**, *11*, 353.
- [2] P. Pyykkö, *Chem. Phys.* **1977**, *22*, 289.
- [3] L. L. J. Lohr and P. Pyykkö, *Chem. Phys. Lett.* **1979**, *62*, 333.
- [4] G. A. Aucar and R. H. Contreras, *J. Magn. Reson.* **1991**, *93*, 413.
- [5] R. H. Contreras, M. C. Ruiz de Azúa, C. G. Giribet, G. A. Aucar, and R. M. Lobayan de Bonczok, *J. Molec. Struct. (Theochem)* **1993**, *284*, 249.
- [6] R. M. Lobayan and G. A. Aucar, *J. Molec. Struct. (Theochem)* **1998**, *452*, 1.
- [7] M. Iliáš, V. Kello, and M. Urban, *Phys. Slov. Rev. Tut.* **2010**, *60*, 259.
- [8] T. Fleig, *Chem. Phys.* **2012a**, *395*, 2.
- [9] P. Pyykkö, *Chem. Rev.* **2012**, *112*, 371.
- [10] Y. Y. Rusakov and L. B. Krivdin, *Russ. Chem. Rev.* **2013**, *82*, 99.
- [11] J. Autschbach, *Phil. Trans. R. Soc. A* **2014**, *372*, 20120489.
- [12] W. Liu, *Phys. Rep.* **2014**, *537*, 59.
- [13] H. H. Quiney, H. Skaane, and I. P. Grant, *Chem. Phys. Lett.* **1998**, *290*, 473.
- [14] T. Helgaker, M. Jaszuński, and M. Pecul, *Prog. in NMR Spect.* **2008**, *53*, 249.
- [15] T. Saue, *ChemPhysChem.* **2011**, *12*, 3077.
- [16] J. Autschbach, *J. Chem. Theory Comput.* **2017**, *13*, 710.
- [17] J. Oddershede, *Adv. Quantum. Chem.* **1978**, *11*, 257.
- [18] J. Oddershede, P. Jorgensen, and D. L. Yeager, *Comp. Phys. Rep.* **1984**, *2*, 33.
- [19] G. A. Aucar, R. H. Romero, and A. F. Maldonado, *Int. Rev. Phys. Chem.* **2010**, *29*, 1.
- [20] G. A. Aucar, *Phys. Chem. Chem. Phys.* **2014**, *16*, 4420.
- [21] G. A. Aucar and J. Oddershede, *Int. J. Quantum Chem.* **1993**, *47*, 425.
- [22] DIRAC, a Relativistic Ab Initio Electronic Structure Program, Release DIRAC16 (2016), written by H. J. Aa. Jensen, R. Bast, T. Saue, and L. Visscher, with contributions from V. Bakken, K. G. Dyall, S. Dubillard, U. Ekström, E. Eliav, T. Enevoldsen, E. Fasshauer, T. Fleig, O. Fossgaard, A. S. P. Gomes, T. Helgaker, J. Henriksson, M. Iliáš, Ch. R. Jacob, S. Knecht, S. Komorovsky, O. Kullie, J. K. Lærdahl, C. V. Larsen, Y. S. Lee, H. S. Nataraj, M. K. Nayak, P. Norman, G. Olejniczak, J. Olsen, Y. C. Park, J. K. Pedersen, M. Pernpointner, R. Di Remigio, K. Ruud, P. Satek, B. Schimmelpfennig, J. Sikkema, A. J. Thorvaldsen, J. Thyssen, J. van Stralen, S. Villaume, O. Visser, T. Winther, and S. Yamamoto (see <http://www.diracprogram.org>).
- [23] G. A. Aucar, T. Saue, L. Visscher, and H. J. Aa. Jensen, *J. Chem. Phys.* **1999**, *110*, 6208.
- [24] Y. Xiao, W. Liu, and K. Ruud, *Relativistic Theory of Nuclear Spin-Rotation Tensor* (Springer Berlin Heidelberg, Berlin, Heidelberg, **2017**), pp. 693–723.
- [25] H. Fukui, T. Baba, and H. Inomata, *J. Chem. Phys.* **1996**, *105*, 3175.
- [26] J. I. Melo, M. C. Ruiz de Azúa, C. G. Giribet, G. A. Aucar, and R. H. Romero, *J. Chem. Phys.* **2003**, *118*, 471.
- [27] J. I. Melo, M. C. Ruiz de Azúa, C. G. Giribet, G. A. Aucar, and P. F. Provasi, *J. Chem. Phys.* **2004**, *121*, 6798.
- [28] P. Manninen, P. Lantto, J. Vaara, and K. Ruud, *J. Chem. Phys.* **2003**, *119*, 2623.
- [29] J. Vaara, *Phys. Chem. Chem. Phys.* **2007**, *9*, 5399.
- [30] I. A. Aucar, S. S. Gomez, M. C. Ruiz de Azúa, and C. G. Giribet, *J. Chem. Phys.* **2012**, *136*, 204119.
- [31] I. A. Aucar, S. S. Gomez, J. I. Melo, C. G. Giribet, and M. C. Ruiz de Azúa, *J. Chem. Phys.* **2013**, *138*, 134107.
- [32] I. A. Aucar, S. S. Gomez, C. G. Giribet, and M. C. Ruiz de Azúa, *J. Chem. Phys.* **2014**, *141*, 194103.
- [33] H. J. Aa. Jensen, K. G. Dyall, T. Saue, and K. Fægri (Jr.), *J. Chem. Phys.* **1996**, *104*, 4083.
- [34] M. Abe, T. Nakajima, and K. Hirao, *J. Chem. Phys.* **2006**, *125*, 234110.
- [35] S. Knecht, Ö. Legeza, and M. Reiher, *J. Chem. Phys.* **2014**, *140*, 041101.
- [36] J. Bieroń, C. F. Fischer, S. Fritzsche, G. Gaigalas, I. P. Grant, P. Indelicato, P. Jönsson, and P. Pyykkö, *Physica Scripta* **2015**, *90*, 054011.
- [37] A. Almoukhalalati, S. Knecht, H. J. Aa. Jensen, K. G. Dyall, and T. Saue, *J. Chem. Phys.* **2016**, *145*, 074104.
- [38] W. Liu and I. Lindgren, *J. Chem. Phys.* **2013**, *139*, 014108.
- [39] W. Liu, *Nat. Sci. Rev.* **2016**, *3*, 204.
- [40] T. Fleig, *Chem. Phys.* **395**, 2 (2012b), ISSN 0301-0104, recent Advances and Applications of Relativistic Quantum Chemistry.

- [41] M. Repisky, S. Komorovsky, R. Bast, and K. Ruud, in *Gas Phase NMR* (The Royal Society of Chemistry, 2016), pp. 267–303.
- [42] ReSpect, version 3.2, 2012; Relativistic Spectroscopy DFT Program of Authors Repisky, M., Komorovsky, S., Malkin, V. G., Malkina, O. L., Ruud, K., Kaupp, M., with contributions from Arbuznikov, A. V., Bast, R., Ekström, U., Malkin, I., Malkin, E.
- [43] S. Komorovsky, M. Repisky, O. L. Malkina, V. G. Malkin, O. I. Malkin, and M. Kaupp, *J. Chem. Phys.* **2008**, *128*, 104101.
- [44] S. Komorovsky, M. Repisky, E. Malkin, T. B. Demissie, and K. Ruud, *J. Chem. Theory Comput.* **2015a**, *11*, 3729.
- [45] T. Saue and T. Helgaker, *J. Comput. Chem.* **2002**, *23*, 814.
- [46] O. Fossgaard, O. Gropen, M. C. Valero, and T. Saue, *J. Chem. Phys.* **2003**, *118*, 10418.
- [47] T. Saue and H. J. Aa. Jensen, *J. Chem. Phys.* **2003**, *118*, 522.
- [48] L. Cheng, Y. Xiao, and W. Liu, *J. Chem. Phys.* **2009**, *130*, 144102.
- [49] Y. Xiao and W. Liu, *J. Chem. Phys.* **2013a**, *138*, 134104.
- [50] Y. Xiao, Y. Zhang, and W. Liu, *J. Chem. Phys.* **2014**, *141*, 164110.
- [51] L. Visscher, T. Enevoldsen, T. Saue, H. J. Aa. Jensen, and J. Oddershede, *J. Comput. Chem.* **1999**, *20*, 1262.
- [52] M. Iliáš, H. J. Aa. Jensen, R. Bast, and T. Saue, *Mol. Phys.* **2013**, *111*, 1373.
- [53] M. Olejniczak, R. Bast, and A. S. Pereira Gomes, *Phys. Chem. Chem. Phys.* **2017**, *19*, 8400.
- [54] K. Kudo, H. Maeda, T. Kawakubo, Y. Ootani, M. Funaki, and H. Fukui, *J. Chem. Phys.* **2006**, *124*, 224106.
- [55] M. Douglas and N. M. Kroll, *Ann. Phys.* **1974**, *82*, 89.
- [56] B. Hess, *Phys. Rev. A* **1985**, *32*, 756.
- [57] B. Hess, *Phys. Rev. A* **1986**, *33*, 3742.
- [58] M. Reiher and A. Wolf, *J. Chem. Phys.* **2004**, *121*, 2037.
- [59] J. Sikkema, L. Visscher, T. Saue, and M. Iliáš, *J. Chem. Phys.* **2009**, *131*, 124116.
- [60] C. Chang, M. Pelissier, and M. Durand, *Phys. Scr.* **1986**, *34*, 394.
- [61] E. van Lenthe, E. J. Baerends, and J. G. Snijders, *J. Chem. Phys.* **1993a**, *101*, 9783.
- [62] E. van Lenthe, E. J. Baerends, and J. G. Snijders, *J. Chem. Phys.* **1993b**, *99*, 4597.
- [63] T. Yoshizawa, W. Zou, and D. Cremer, *J. Chem. Phys.* **2017**, *146*, 134109.
- [64] M. Iliáš, H. J. Aa. Jensen, V. Kellö, B. O. Roos, and M. Urban, *Chem. Phys. Lett.* **2005**, *408*, 210.
- [65] W. Kutzelnigg and W. Liu, *J. Chem. Phys.* **2005**, *123*, 241102.
- [66] M. Iliáš and T. Saue, *J. Chem. Phys.* **2007**, *126*, 064102.
- [67] W. Liu, *Molec. Phys.* **2010**, *108*, 1679.
- [68] D. Peng and M. Reiher, *Theor. Chem. Acc.* **2012**, *131*, 1081.
- [69] D. Zaccari, M. C. Ruiz de Azúa, J. I. Melo, and C. G. Giribet, *J. Chem. Phys.* **2006**, *124*, 054103.
- [70] W. Kutzelnigg, *Phys. Rev. A* **2003**, *67*, 032109.
- [71] H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One- and Two- Electron Atoms* (Plenum Press, New York, 1977), 1st ed.
- [72] L. N. Labzowsky, G. L. Klimchirskaya, and Y. Y. Dmitriev, *Relativistic Effects in the Spectra of Atomic Systems* (IOP, Philadelphia, 1993), 1st ed.
- [73] P. Manninen, K. Ruud, P. Lantto, and J. Vaara, *J. Chem. Phys.* **2005**, *122*, 114107.
- [74] W. H. Flygare, *Chem. Rev.* **1974**, *74*, 653.
- [75] I. A. Aucar, Ph.D. thesis, Universidad Nacional del Nordeste, Argentina **2015**.
- [76] Y. Xiao and W. Liu, *J. Chem. Phys.* **2013b**, *139*, 034113.
- [77] I. A. Aucar, S. S. Gomez, C. G. Giribet, and G. A. Aucar, *Phys. Chem. Chem. Phys.* **2016a**, *18*, 23572.
- [78] W. H. Flygare, *J. Chem. Phys.* **1964**, *41*, 793.
- [79] P. J. Mohr, B. N. Taylor, and D. B. Newell, *J. Phys. Chem. Ref. Data* **2012**, *41*, 043109.
- [80] E. Malkin, S. Komorovsky, M. Repisky, T. B. Demissie, and K. Ruud, *J. Phys. Chem. Lett.* **2013**, *4*, 459.
- [81] M. Jaszuński, M. Repisky, T. B. Demissie, S. Komorovsky, E. Malkin, K. Ruud, P. Garbacz, K. Jackowski, and W. Makulski, *J. Chem. Phys.* **2013**, *139*, 234302.
- [82] M. Jaszuński, T. B. Demissie, and K. Ruud, *J. Phys. Chem. A* **2014**, *118*, 9588.
- [83] K. Ruud, T. B. Demissie, and M. Jaszuński, *J. Chem. Phys.* **2014**, *140*, 194308.
- [84] S. Komorovsky, M. Repisky, E. Malkin, K. Ruud, and J. Gauss, *J. Chem. Phys.* **2015b**, *142*, 091102.
- [85] T. B. Demissie, M. Jaszuński, E. Malkin, S. Komorovsky, and K. Ruud, *Molecular Physics* **2015a**, *113*, 1576.
- [86] T. B. Demissie, M. Jaszuński, S. Komorovsky, M. Repisky, and K. Ruud, *J. Chem. Phys.* **2015b**, *143*, 164311.
- [87] T. B. Demissie, *Phys. Chem. Chem. Phys.* **2015**, *18*, 3112.
- [88] B. Adrjan, W. Makulski, Jackowski, T. B. Demissie, K. Ruud, A. Antusek, and M. Jaszuński, *Phys. Chem. Chem. Phys.* **2016**, *18*, 16483.
- [89] I. A. Aucar, S. S. Gomez, C. G. Giribet, and G. A. Aucar, *J. Phys. Chem. Lett.* **2016b**, *7*, 5188.

- [90] J. Vaara and P. Pyykkö, *J. Chem. Phys.* **2003**, *118*, 2973.
- [91] Dalton, a molecular electronic structure program, Release Dalton2016.1 **2015**, <http://daltonprogram.org>
- [92] K. Aidas, C. Angeli, K. L. Bak, V. Bakken, R. Bast, L. Boman, O. Christiansen, R. Cimирaglia, S. Coriani, P. Dahle, E. K. Dalskov, U. Ekström, T. Enevoldsen, J. J. Eriksen, P. Ettenhuber, B. Fernández, L. Ferrighi, H. Flieg, L. Frediani, K. Hald, A. Halkier, C. Hättig, H. Heiberg, T. Helgaker, A. C. Hennum, H. Hettema, E. Hjertenæs, S. Høst, I.-M. Høyvik, M. F. Izzi, B. Jansik, H. J. Aa. Jensen, D. Jonsson, P. Jørgensen, J. Kauczor, S. Kirpekar, T. Kjærgaard, W. Klopper, S. Knecht, R. Kobayashi, H. Koch, J. Kongsted, A. Krapp, K. Kristensen, A. Ligabue, O. B. Lutnæs, J. I. Melo, K. V. Mikkelsen, R. H. Myhre, C. Neiss, C. B. Nielsen, P. Norman, J. Olsen, J. M. H. Olsen, A. Osted, M. J. Packer, F. Pawłowski, T. B. Pedersen, P. F. Provasi, S. Reine, Z. Rinkevicius, T. A. Ruden, K. Ruud, V. Rybkin, P. Salek, C. C. M. Samson, A. Sánchez de Merás, T. Saue, S. P. A. Sauer, B. Schimmelpfennig, K. Sneskov, A. H. Stein-dal, K. O. Sylvester-Hvid, P. R. Taylor, A. M. Teale, E. I. Tellgren, D. P. Tew, A. J. Thorvaldsen, L. Thøgersen, O. Vahtras, M. A. Watson, D. J. D. Wilson, M. Ziolkowski, and H. Ågren, The Dalton quantum chemistry program system, *Wiley Interdiscip. Rev.: Comput. Mol. Sci.*, **2014**, *4*, 269.
- [93] M. C. Ruiz de Azúa, J. I. Melo, and C. G. Giribet, *Mol. Phys.* **2003**, *101*, 3103.
- [94] S. Gomez, J. I. Melo, R. H. Romero, G. A. Aucar, and M. C. Ruiz de Azúa, *J. Chem. Phys.* **2005**, *122*, 064103.
- [95] W. Kutzelnigg, *J. Comput. Chem.* **1999**, *20*, 1199.
- [96] P. G. Roura, J. I. Melo, M. C. Ruiz de Azúa, and C. G. Giribet, *J. Chem. Phys.* **2006**, *125*, 064107.
- [97] B. A. Hess, C. M. Marian, U. Wahlgren, and O. Grospen, *Chem. Phys. Lett.* **1996**, *251*, 365.
- [98] O. L. Malkina, B. Schimmelpfennig, M. Kaupp, B. Hess, P. Chandra, U. Wahlgren, and V. G. Malkin, *Chem. Phys. Lett.* **1998**, *296*, 93.
- [99] D. Zaccari, J. I. Melo, M. C. Ruiz de Azúa, and C. G. Giribet, *J. Chem. Phys.* **2009**, *130*, 084102.
- [100] P. Manninen, K. Ruud, P. Lantto, and J. Vaara, *J. Chem. Phys.* **2006**, *124*, 149901.
- [101] M. Hanni, P. Lantto, M. Iliáš, H. J. Aa. Jensen, and J. Vaara, *J. Chem. Phys.* **2007**, *127*, 164313.
- [102] A. F. Maldonado, G. A. Aucar, and J. I. Melo, *J. Mol. Model* **2014**, *20*, 2417.
- [103] A. F. Maldonado, J. I. Melo, and G. A. Aucar, *Phys. Chem. Chem. Phys.* **2015**, *17*, 25516.
- [104] E. Florez, A. F. Maldonado, G. A. Aucar, J. David, and A. Restrepo, *Phys. Chem. Chem. Phys.* **2016**, *18*, 1537.
- [105] J. I. Melo, A. F. Maldonado, and G. A. Aucar, *Theor. Chem. Acc.* **2011**, *129*, 483.
- [106] V. Arcisauskaitė, J. I. Melo, L. Hemmingsen, and S. P. A. Sauer, *J. Chem. Phys.* **2011**, *135*, 044306.
- [107] A. F. Maldonado and G. A. Aucar, *Phys. Chem. Chem. Phys.* **2009**, *11*, 5615.
- [108] M. C. Ruiz de Azúa, C. G. Giribet, and J. I. Melo, *J. Chem. Phys.* **2011**, *134*, 034123.
- [109] A. Antusek, M. Pecul, and J. Sadlej, *Chem. Phys. Lett.* **2006**, *281*, 427.
- [110] L. P. Ingman, J. Jokisaari, K. Oikarinen, and R. Seydoux, *J. Magn. Reson., Ser. A* **1994**, *111*, 155.
- [111] M. A. M. Forgeron, R. E. Wasylishen, and G. H. Penner, *J. Phys. Chem. A* **2004**, *108*, 4751.
- [112] T. H. Dunning, *J. Chem. Phys.* **1989**, *90*, 1007.
- [113] K. G. Dyall, *Theor. Chem. Acc.* **2006**, *115*, 441.
- [114] *Handbook of Chemistry*, vol. II (The Chemical Society of Japan Kagaku Benran (Maruzen Company, Tokyo), **1984**), 3rd ed.
- [115] K. P. Huber and G. Herzberg, *Constants of Diatomic Molecules* (Nostrand Reinhold, New York, **1979**).

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APPENDIX

We include, here, the techniques used to obtain the two-component operators used in the LRESC model and its actual expressions. The four-component operators that need to be transformed are $\alpha \cdot \mathbf{A}$ and $\omega \cdot \mathbf{J}_e$

The operator $\alpha \cdot \mathbf{A}$

Let us start with the four-component matrix element of the operator $\alpha \cdot \mathbf{A}$

$$\langle \phi_i^{(4)} | \alpha \cdot \mathbf{A} | \phi_j^{(4)} \rangle \cong \langle \tilde{\phi}_i | \left[N \left(\frac{\boldsymbol{\sigma} \cdot \mathbf{p}}{2c} \right) \left(1 + \frac{V - E_i}{2c^2} \right) \boldsymbol{\sigma} \cdot \mathbf{A} N + N \boldsymbol{\sigma} \cdot \mathbf{A} \left(1 + \frac{V - E_j}{2c^2} \right) \left(\frac{\boldsymbol{\sigma} \cdot \mathbf{p}}{2c} \right) N \right] | \tilde{\phi}_j \rangle. \quad (\text{A1})$$

where $N = \left(1 - \frac{p^2}{8c^2} \right)$ stands for the normalization constant of the wavefunction.

The NR correcting terms are then obtained when only terms of lower order in $1/c$ are considered

$$\begin{aligned} O(\alpha \cdot \mathbf{A})(0) &= \left(\frac{\boldsymbol{\sigma} \cdot \mathbf{p}}{2c} \right) \boldsymbol{\sigma} \cdot \mathbf{A} + \boldsymbol{\sigma} \cdot \mathbf{A} \left(\frac{\boldsymbol{\sigma} \cdot \mathbf{p}}{2c} \right) \\ &= \frac{1}{c} \mathbf{p} \cdot \mathbf{A} + \frac{1}{2c} \boldsymbol{\sigma} \cdot (\nabla \times \mathbf{A}). \end{aligned} \quad (\text{A2})$$

When $\mathbf{A} = \mathbf{A}_N$ the paramagnetic Spin-orbit, PSO, the Fermi-contact, FC, and the spin-dipolar, SD operators appear:

$$H^{\text{PSO}} = \frac{1}{c} \mathbf{p} \cdot \mathbf{A}_N = \frac{1}{c} \mu_N \cdot \frac{\mathbf{L}_N}{r_N^3}, \quad (\text{A3})$$

$$H^{\text{FC/SD}} = \frac{1}{2c} \boldsymbol{\sigma} \cdot (\nabla \times \mathbf{A}_N) = \frac{1}{2c} \boldsymbol{\sigma} \cdot \nabla \times \mathbf{A}_N, \quad (\text{A4})$$

although when $\mathbf{A} = \mathbf{A}_B$ the orbital Zeeman, OZ, and spin-Zeeman, SZ operators appear.

$$H^{\text{OZ}} = \frac{1}{c} \mathbf{p} \cdot \mathbf{A}_B = \frac{1}{2c} \mathbf{L} \cdot \mathbf{B}, \quad (\text{A5})$$

$$H^{\text{SZ}} = \frac{1}{2c} \boldsymbol{\sigma} \cdot (\nabla \times \mathbf{A}_B) = \frac{1}{c} \mathbf{S} \cdot \mathbf{B}. \quad (\text{A6})$$

Relativistic corrections to the matrix elements of magnetic interactions arise when the different magnetic potentials are considered. In the case of $\mathbf{A} = \mathbf{A}_N$

$$\left\{ -\frac{p^2}{8c^2}, \left(\frac{\sigma \cdot p}{2c}\right) \sigma \cdot A_N + \sigma \cdot A_N \left(\frac{\sigma \cdot p}{2c}\right) \right\} = -\frac{1}{8c^2} \{p^2, H^{\text{PSO}} + H^{\text{FC/SD}}\}. \quad (\text{A7})$$

On the other side, we shall consider terms that comes from $\frac{V-E_i}{2c^2}$. In this case, we introduce the commutator

$$\left[\frac{\sigma \cdot p}{2c}, \frac{V-E_i}{2c^2} \right] = -\frac{i}{4c^3} \sigma \cdot \nabla V, \quad (\text{A8})$$

and the relation

$$(V-E_i)|\phi_i\rangle = -\frac{p^2}{2} |\phi_i\rangle \quad (\text{A9})$$

to rewrite the corresponding terms of Equation A1 as

$$\begin{aligned} & \langle \tilde{\phi}_i | \left[\left(\frac{\sigma \cdot p}{2c}\right) \left(\frac{V-E_i}{2c^2}\right) \sigma \cdot A + \sigma \cdot A \left(\frac{V-E_i}{2c^2}\right) \left(\frac{\sigma \cdot p}{2c}\right) \right] | \tilde{\phi}_j \rangle \\ &= \langle \tilde{\phi}_i | \left(-\frac{i}{4c^3} \sigma \cdot \nabla V - \frac{p^2}{4c^2} \left(\frac{\sigma \cdot p}{2c}\right) \right) \sigma \cdot A \\ &+ \sigma \cdot A \left(\frac{i}{4c^3} \sigma \cdot \nabla V - \left(\frac{\sigma \cdot p}{2c}\right) \frac{p^2}{4c^2} \right) | \tilde{\phi}_j \rangle \\ &= \langle \tilde{\phi}_i | \frac{1}{2c^3} \sigma \cdot (\nabla V \times A) \\ &- \frac{p^2}{8c^3} (\sigma \cdot A + i\sigma \cdot p \times A) - (\sigma \cdot A - i\sigma \cdot p \times A) \frac{p^2}{8c^3} | \tilde{\phi}_j \rangle \\ &= \langle \tilde{\phi}_i | \frac{1}{2c^3} \sigma \cdot (\nabla V \times A) \\ &- \frac{1}{8c^2} \left\{ p^2, \frac{p}{c} \cdot A \right\} - \frac{1}{8c^3} [p^2, i\sigma \cdot p \times A] | \tilde{\phi}_j \rangle. \end{aligned} \quad (\text{A10})$$

In short, we get for the potential V_N the following relativistic operators

$$H^{\text{PSO-K}} = -\frac{1}{4c^2} \{p^2, H^{\text{PSO}}\}, \quad (\text{A11})$$

$$\begin{aligned} H^{\text{FC/SD-K}} &= -\frac{1}{8c^2} \{p^2, H^{\text{FC/SD}}\} + \frac{1}{2c^3} \sigma \cdot \nabla V \times A_N \\ &- \frac{1}{8c^3} [p^2, i\sigma \cdot p \times A_N]. \end{aligned} \quad (\text{A12})$$

In the case of $A = A_B$, by following again the same procedure as in the case of $A = A_N$, we obtain the lower order relativistic corrections when $V = V_B$

$$H^{\text{OZ-K}} = -\frac{1}{4c^2} \{p^2, H^{\text{OZ}}\}, \quad (\text{A13})$$

$$H^{\text{SZ-K}} = -\frac{1}{4c^3} [3Sp^2 - (S \cdot p)p] \cdot B, \quad (\text{A14})$$

$$H^{\text{B-SO}} = \frac{1}{2c^3} [(r \cdot \nabla) V_c S - (r \cdot S) \nabla V_c] \cdot B. \quad (\text{A15})$$

The operator $\omega \cdot J_e$

The matrix elements of V_N were analyzed above (together with those of V_B , for shielding). Therefore, we focus our attention now to the expansion of the matrix elements of V_J . Applying the same arguments used for shieldings, we obtain:

$$\langle \phi_j^{(4)} | (-\omega \cdot J_e) | \phi_j^{(4)} \rangle \cong -\langle \tilde{\phi}_i | \left[N\omega \cdot J_e^{(2)} N + N \left(\frac{\sigma \cdot p}{2c}\right) \left(1 + \frac{V-E_j}{2c^2}\right) \omega \cdot J_e^{(2)} \left(1 + \frac{V-E_j}{2c^2}\right) \left(\frac{\sigma \cdot p}{2c}\right) N \right] | \tilde{\phi}_j \rangle, \quad (\text{A16})$$

where $N = 1 - \frac{p^2}{8c^2}$ is the wave function normalization factor. The NR electronic total angular momentum operator $J_e^{(2)}$ is given by the addition of the two NR angular momentum operators, the orbital and the spin. So $J_e^{(2)} = r \times p + \frac{1}{2} \sigma$, where σ are the Pauli matrices.

The lowest order terms are of order c^0 , whereas the leading order relativistic effects are given by those terms of order c^{-2} . Considering that the terms involving $\frac{v-F}{2c^2}$ are of order c^{-4} and c^{-6} , the leading order expansion of the matrix elements of Equation A16 are

$$\langle \phi_i^{(4)} | (-\boldsymbol{\omega} \cdot \mathbf{J}_e) | \phi_j^{(4)} \rangle \cong -\langle \tilde{\phi}_i | \left[N \boldsymbol{\omega} \cdot \mathbf{J}_e^{(2)} N + \left(\frac{\boldsymbol{\sigma} \cdot \mathbf{p}}{2c} \right) \boldsymbol{\omega} \cdot \mathbf{J}_e^{(2)} \left(\frac{\boldsymbol{\sigma} \cdot \mathbf{p}}{2c} \right) \right] | \tilde{\phi}_j \rangle. \quad (\text{A17})$$

As the electronic total angular momentum operator is a rotation generator, it is fulfilled that it commutes with $\boldsymbol{\sigma} \cdot \mathbf{p}$, or

$$\left[\frac{\boldsymbol{\sigma} \cdot \mathbf{p}}{2c}, \mathbf{J}_e^{(2)} \right] = 0, \quad (\text{A18})$$

and, therefore, there are NR corrections of order c^{-2} . Then, Equation A17 gives rise to

$$\langle \phi_i^{(4)} | (-\boldsymbol{\omega} \cdot \mathbf{J}_e) | \phi_j^{(4)} \rangle = \langle \tilde{\phi}_i | (-\boldsymbol{\omega} \cdot \mathbf{J}_e^{(2)}) | \tilde{\phi}_j \rangle, \quad (\text{A19})$$

which is equivalent to state

$$O(-\boldsymbol{\omega} \cdot \mathbf{J}_e^{(4)}) = H^{\text{BO-J}} = H^{\text{BO-L}} + H^{\text{BO-S}}, \quad (\text{A20})$$

where

$$H^{\text{BO-J}} = -\boldsymbol{\omega} \cdot \mathbf{J}_e^{(2)}, \quad (\text{A21})$$

$$H^{\text{BO-L}} = -\boldsymbol{\omega} \cdot \mathbf{L}_e, \quad (\text{A22})$$

$$H^{\text{BO-S}} = -\boldsymbol{\omega} \cdot \mathbf{S}_e. \quad (\text{A23})$$

A complete development of Equation A17 will give us an insight on how we can split the orbital and the spin angular momentum operators. It can be rewritten as

$$\begin{aligned} \boldsymbol{\omega} \cdot \langle \phi_i^{(4)} | \mathbf{J}_e | \phi_j^{(4)} \rangle &\simeq \boldsymbol{\omega} \cdot \langle \tilde{\phi}_i | (\mathbf{L}_e + \mathbf{S}) | \tilde{\phi}_j \rangle + \\ \boldsymbol{\omega} \cdot \langle \tilde{\phi}_i | \left[-\frac{1}{8c^2} \{p^2, (\mathbf{L}_e + \mathbf{S})\} + \frac{1}{4c^2} \boldsymbol{\sigma} \cdot \mathbf{p} (\mathbf{L}_e + \mathbf{S}) \boldsymbol{\sigma} \cdot \mathbf{p} \right] | \tilde{\phi}_j \rangle. \end{aligned} \quad (\text{A24})$$

and, as a consequence of Equation A18, we have

$$\boldsymbol{\sigma} \cdot \mathbf{p} (\mathbf{L}_e + \mathbf{S}) \boldsymbol{\sigma} \cdot \mathbf{p} = (\mathbf{L}_e + \mathbf{S}) p^2 = \frac{1}{2} \{(\mathbf{L}_e + \mathbf{S}), p^2\}. \quad (\text{A25})$$

Then, it is explicitly shown that there are no relativistic corrections, up to order c^{-2} , related to the operator $\mathbf{J}_e^{(4)}$,

$$\boldsymbol{\omega} \cdot \langle \phi_i^{(4)} | \mathbf{J}_e^{(4)} | \phi_j^{(4)} \rangle \simeq \boldsymbol{\omega} \cdot \langle \tilde{\phi}_i | (\mathbf{L}_e + \mathbf{S}) | \tilde{\phi}_j \rangle. \quad (\text{A26})$$

Nevertheless, it is important to highlight that a different behavior is found for the individual $\mathbf{L}_e^{(4)}$ and $\mathbf{S}^{(4)}$ operators, where

$$\boldsymbol{\omega} \cdot \langle \phi_i^{(4)} | \mathbf{L}_e^{(4)} | \phi_j^{(4)} \rangle \neq \boldsymbol{\omega} \cdot \langle \tilde{\phi}_i | \mathbf{L}_e | \tilde{\phi}_j \rangle, \quad (\text{A27})$$

$$\boldsymbol{\omega} \cdot \langle \phi_i^{(4)} | \mathbf{S}^{(4)} | \phi_j^{(4)} \rangle \neq \boldsymbol{\omega} \cdot \langle \tilde{\phi}_i | \mathbf{S} | \tilde{\phi}_j \rangle. \quad (\text{A28})$$

It is clear that this occurs because of the noncommutativity of operators \mathbf{L}_e and \mathbf{S} with $\boldsymbol{\sigma} \cdot \mathbf{p}$. Only the addition of both satisfies the commutation relation.

The matrix elements found for that operators are, then,

$$\boldsymbol{\omega} \cdot \langle \phi_i^{(4)} | \mathbf{L}_e^{(4)} | \phi_j^{(4)} \rangle = \boldsymbol{\omega} \cdot \langle \tilde{\phi}_i | \mathbf{L}_e + \frac{1}{4c^2} (\boldsymbol{\sigma} p^2 - (\boldsymbol{\sigma} \cdot \mathbf{p}) \mathbf{p}) | \tilde{\phi}_j \rangle, \quad (\text{A29})$$

$$\boldsymbol{\omega} \cdot \langle \phi_i^{(4)} | \mathbf{S}^{(4)} | \phi_j^{(4)} \rangle = \boldsymbol{\omega} \cdot \langle \tilde{\phi}_i | \mathbf{S} - \frac{1}{4c^2} (\boldsymbol{\sigma} p^2 - (\boldsymbol{\sigma} \cdot \mathbf{p}) \mathbf{p}) | \tilde{\phi}_j \rangle. \quad (\text{A30})$$

In the last equation, the matrix elements involving the spin operator, $\langle \tilde{\phi}_i | \mathbf{S} | \tilde{\phi}_j \rangle$ will be zero if $|\tilde{\phi}_i\rangle$ or $|\tilde{\phi}_j\rangle$ are the ground state electronic wave function. In addition, it is seen that the relativistic corrections to both operators (up to order $1/c^2$) are equal and have opposite signs.