



Recent Developments in Absolute Shielding Scales for NMR Spectroscopy

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Abstract

The absolute value of the nuclear magnetic shielding tensor, σ , cannot be directly measured as such, though at the moment experimental devices are available to obtain them by extrapolation to zero-density limit. This is the reason why since the beginning of NMR spectroscopy to obtain the experimental values of this parameter required the interplay between theory and experiments.

Early this century it was experimentally probed that the Ramsey–Flygare model, largely used to obtain the most accurate semiexperimental values of shieldings, does not work well when heavy-atom containing molecules are considered. Then, the search for a relativistic relationship like Ramsey–Flygare became highly necessary. This search has taken some years for being successful.

Within the research programme that focused on such a goal, the first important breakthrough was the finding of the relativistic Hamiltonian for spin–rotations interactions. Once this crucial step was overcome it was possible to develop some relativistic models, being the most accurate the so-called M-V. We shall show here some of the most important steps that were given in the search for a relativistic relationship between σ and the spin–rotation tensor, \mathbf{M} . We will describe the bottom-up procedure that make it possible, together with relativistic (four-component) theories of shieldings and spin–rotations that were published recently.

Why it was important to find that new relationship? There are now experimental developments that permits direct measurements of absolute shieldings in gas-phase NMR spectroscopy, and so, to compare with. It is also possible to accurately calculate them by using four-component methodologies, from which very small effects like nuclear charge distribution, Breit/Gaunt electron–electron interactions and QED effects are included. All of them will be highlighted here in some detail.

Lastly we shall stress the new understandings that arise from these developments together with some new challenges.

Keywords: Spin–rotation, Relativistic effects, Ramsey–Flygare, Model M-V



1. INTRODUCTION

The absolute values of the components of the nuclear magnetic shielding tensor, σ , cannot usually be obtained by measurements. It was by the use of microwave spectroscopy that such parameters were usually obtained through a semiexperimental relationship between σ and the spin–rotation, SR, tensor, \mathbf{M} , until the last decade and especially, the last few years in which direct measurements were performed in gas-phase NMR [1]. The relationship between them was first proposed by Ramsey in 1950 [2, 3], who found theoretical grounds for the NMR spectroscopic parameters and its relationship with the microwave spectroscopy based on a

nonrelativistic, NR, framework. This relationship was extended by Willis Flygare to others than linear molecules and since then it is well known as the Ramsey–Flygare relationship [4].

After those theoretical developments, nobody was able to generalize them to a relativistic framework, until few years ago [5,6]. In 1999 Visscher and collaborators showed that such a relationship could not work well for calculation of shielding anisotropy in a relativistic framework, due to the paramagnetic contribution of the parallel component of σ in linear molecules is not zero as happens in an NR context [7]. More recently, Gómez and Aucar probed that there is a high difference, of about 35%, for the shielding of iodine in IF when comparing calculations performed either with four-component methods or with Ramsey–Flygare relationship [8]. But the urgency to find out another more fundamental relationship than that of Ramsey–Flygare was clearly put on the table by Wasylishen and collaborators in 2004 [9]. They studied the nuclear shielding of xenon difluoride by solid-state NMR spectroscopy and provided the first direct evidence that consideration of relativistic effects is important in interpreting xenon magnetic shielding tensors both, experimentally and theoretically. Jameson made an smart analysis of that findings in 2011 and stressed that the experiment itself, separately from any quantum mechanical calculations, reveals that the relativistic corrections to the shielding cannot be ignored in XeF₂ [10]. She also pointed out that what the experimental results establish about the internal consistency of the individual tensor components with the free Xe atom is itself at odds with all the previous relationships derived from NR theory.

Why it took so long (meaning more than six decades) for getting a relationship between σ and M that is valid within a relativistic domain? One of the reasons may be the fact that one should relate two observables whose perturbative Hamiltonians are not easily related each other within a relativistic framework. The theoretical relationship that relates σ with M has its roots in Larmor's theorem, which in an NR framework shows the equivalence between one-particle Hamiltonian in an external magnetic field (until first order in such field) and that of a particle in a uniformly rotating frame [11]. This relation is broken in a relativistic framework.

It was a big challenge to find out the right answers to the earlier mentioned inquiries. One had to develop new physical insights because they were not present in the old relationship. On the other hand, it was a good opportunity to search for a relationship that must be valid for molecular systems that do contain, or not, heavy atoms. Besides, the new relativistic relationship must fulfil the restriction that when c is scaled to infinity,

it should go to the well-known NR relationship. At the end one shall find a relationship that must be valid within both regimes, relativistic and NR. The new relativistic relationship between σ and \mathbf{M} is such that new terms are introduced for the first time and so it will take some time to understand them completely.

What would be the most appropriate way to generalize Ramsey–Flygare relationship? The first step in such a direction was performed by finding the proper relativistic perturbative Hamiltonian from which the SR tensor could be derived. This Hamiltonian was shown for the first time in 2012 by Ruiz de Azúa, during the REHE Conference in Argentina [12]. The next step was also quite difficult to do because it required to use a bottom-up instead of the NR top-down procedure. The new relativistic relationship is well established though there are still some theoretical subtleties that need to be worked out in order to further improve its accuracy.

The main aim of this chapter is to highlight some of the new insights that appear when both tensors, σ and \mathbf{M} , together with its relationship, are treated within a relativistic framework. Most of recent findings about the absolute value of σ were performed in this area of research. We shall stress theoretical developments and also its relation with experiments.

We start with a short introduction to both spectroscopies, NMR and rotational, in order to consider the spectroscopic parameters we are going to work with. Some of the old knowledge about theory are briefly discussed together with some of the newest experimental developments concerning the measurement of σ . Then we go through the main goal of this chapter, the latest developments about the theory of σ and \mathbf{M} within a relativistic framework. At the end some novel results will be given and analyzed.



2. NMR AND ROTATIONAL SPECTROSCOPIES

Here we will give few of the basic elements of NMR and rotational spectroscopies necessary for later considerations. We shall explain how are they related each other, and concentrate our presentation mainly on diatomic molecules because of its simplicity and the fact that we shall work on them in what follows.

2.1 Phenomenological Hamiltonians

Measurable spectroscopic quantities (known as parameters) are theoretically obtained from the relation between both phenomenological and theoretical Hamiltonians that contain terms that contribute to the description of the

phenomenon under study. Phenomenological Hamiltonians should have enough parameters to explain with them the corresponding spectra. On the other side, theoretical Hamiltonians should include the basic physics that are relevant to the studied spectroscopy.

There are some recent reviews which include in more detail the theoretical treatment most of the main parameters of both spectroscopies [13–15].

The overall theoretical Hamiltonian relevant to the rotational spectroscopy for a diatomic molecule that only include SR interactions is

$$H = H_{rot} + H_{SR} \quad (1)$$

where H_{rot} and H_{SR} represent the pure rotational and the SR terms, respectively. There are some other perturbative terms to account for nuclear quadrupole-couplings and spin–spin interactions, but we will not consider them here.

Taking a diatomic molecule as a rigid rotor, the theoretical Hamiltonian is

$$H_{rot} = \frac{1}{2} \left(\frac{J_x^2}{I_x} + \frac{J_y^2}{I_y} + \frac{J_z^2}{I_z} \right) \quad (2)$$

where J_i and I_i ($i = x, y, z$) are components of both, the angular momentum corresponding to molecular rotation, \mathbf{J} , and the moment of inertia, \mathbf{I} .

On the other side, if we consider the molecule as a semirigid rotor with centrifugal distortion, new terms shall be included and then the more general phenomenological Hamiltonian can be expressed as [14]

$$H_{rot} = \frac{1}{2} \sum_{\alpha, \beta} R_{\alpha, \beta}^e J_{\alpha} J_{\beta} + \frac{1}{4} \sum_{\alpha, \beta, \gamma, \delta} T_{\alpha, \beta, \gamma, \delta} J_{\alpha} J_{\beta} J_{\gamma} J_{\delta} + \dots \quad (3)$$

being the coefficient of the first term related with an effective inverse inertia tensor. The second and following terms add contributions that arise due to centrifugal distortion.

The perturbative nuclear SR Hamiltonian, H_{SR} , introduce the perturbation due to the coupling between the nuclear spin angular momentum and the rotational angular momentum

$$H_{SR} = -\frac{1}{\hbar^2} \sum_K \mathbf{I}_K \otimes \mathbf{M}_K \otimes \mathbf{J} \quad (4)$$

where the summation runs over all nuclei with nonvanishing spin. \mathbf{I}_K is the nuclear spin angular momentum of nucleus K , \mathbf{M}_K is its nuclear SR tensor and \hbar is the reduced Planck's constant.

From Eqs. (3) and (4) and for a diatomic molecule with only one isotope with nuclear spin different from zero (and equal to $1/2$), the total rotational energy levels, E_{Rot} , that include SR interactions and centrifugal distortion, and one of the transition frequencies between those energy levels, $\nu_{(J+1)\leftarrow J}$, are given by [14,15]

$$E_{rot} = E_J + E_{SR} \quad (5)$$

$$E_J = B_\nu J(J+1) - D_\nu [J(J+1)]^2 \quad (6)$$

$$\nu_{(J+1)\leftarrow J} = \nu_0 = 2B_\nu(J+1) - 4D_\nu(J+1)^3 \quad (7)$$

where B_ν is the rotational constant for vibrational level ν , and D_ν is a constant that introduce centrifugal distortions.

For a linear molecule, where due to symmetry reasons \mathbf{M}_K is characterized by only one constant ($M_{\perp, K}$), the hyperfine energy levels are given by

$$E_{SR}^K = -\frac{M_{\perp, K}}{2} [F(F+1) - I_K(I_K+1) - J(J+1)] \quad (8)$$

Therefore, for a rotational transition $J \rightarrow J+1$ we obtain (in frequency units) the transition frequencies that arise from them. They are

$$\begin{aligned} \nu_{(F+1)\leftarrow F} &= \nu_0 + M_{\perp, K}(J+1) - M_{\perp, K}(F+1) \\ \nu_{F\leftarrow F} &= \nu_0 + M_{\perp, K}(J+1) \\ \nu_{(F-1)\leftarrow F} &= \nu_0 + M_{\perp, K}(J+1) - M_{\perp, K}F \end{aligned} \quad (9)$$

where $\mathbf{F} = \mathbf{J} + \mathbf{I}_K$, and the selection rules are $\Delta F = 0, \pm 1$ and $\Delta I_K = 0$.

The last equations are used to analyze the experimentally observed splittings and shifts in the rotational energy levels, E_J , due to the nuclear SR interactions.

In what follows we shall not consider the contributions of both, centrifugal distortion ($D_\nu = 0$) and quadrupole hyperfine structure.

The complete Hamiltonian that includes the phenomenological one, for describing accurately the experimental NMR spectra, is [16]

$$H = H_0 + H_{NMR} \quad (10)$$

being H_0 the unperturbed Hamiltonian and

$$H_{\text{NMR}} = \sum_{KL} \boldsymbol{\mu}_K \otimes (\mathbf{D}_{KL} + \mathbf{J}_{KL}) \otimes \boldsymbol{\mu}_L + \sum_K \boldsymbol{\mu}_K \otimes (\mathbf{I} - \boldsymbol{\sigma}_K) \otimes \mathbf{B}_0 \quad (11)$$

where $\boldsymbol{\mu}_K$ is the nuclear dipole moment of nucleus K , \mathbf{D}_{KL} and \mathbf{J}_{KL} are the direct and indirect nuclear spin coupling tensors, respectively, $\boldsymbol{\sigma}_K$ the nuclear magnetic shielding of nucleus K and \mathbf{B}_0 the static external magnetic field. From these last equations it is clearly seen that when one wants to derive theoretical expressions for NMR spectroscopic parameters one should propose bilinear perturbative Hamiltonians depending on two different nuclear dipole moments or one nuclear dipole moment and the external magnetic field.

The interaction energy between nuclear spin \mathbf{I}_K and the external static magnetic field \mathbf{B}_0 that is oriented to direction z is

$$E_{\text{shield}}^K = -\mu_K^z (1 - \sigma_K) B_0 = -\hbar \gamma_K I_K^z (1 - \sigma_K) B_0 \quad (12)$$

Then, the nuclear resonance frequency for a nucleus of spin 1/2 is given by

$$\nu_K = \frac{\gamma_K B_0}{2\pi} (1 - \sigma_K) \quad (13)$$

One should highlight here the fact that the magnetogyric ration, γ_K , correspond to the “bare” unshielded nucleus. σ_K is the electronic shielding that modify the magnetic field at the site of nucleus K , when such nucleus is surrounded by electrons.

2.2 Response Property Calculations

Phenomenological perturbing Hamiltonians are used to describe experimental spectra accurately. In the case of perturbations of Eqs. (4) and (11), which arise from the molecular rotation and internal and external magnetic fields, the phenomenological expression of the energy for a closed-shell molecule is

$$E = E_0 - \frac{1}{\hbar^2} \sum_K \mathbf{I}_K \otimes \mathbf{M}_K \otimes \mathbf{J} - \sum_K \boldsymbol{\mu}_K \otimes (\mathbf{I} - \boldsymbol{\sigma}_K) \otimes \mathbf{B}_0 \quad (14)$$

From this expansion the set of two molecular tensors of interest are obtained as

$$\boldsymbol{\sigma}_K = \mathbf{1} + \left. \frac{\partial^2 E}{\partial \boldsymbol{\mu}_K \partial \mathbf{B}_0} \right|_{\boldsymbol{\mu}_K = \mathbf{B}_0 = 0} \quad (15)$$

$$\mathbf{M}_K = -\hbar^2 \frac{\partial^2 E}{\partial \mathbf{I}_K \partial \mathbf{J}} \Big|_{\mu_k=J=0} \quad (16)$$

On the other hand the molecular Hamiltonian can be separated into two terms: the unperturbed Hamiltonian, H_0 , plus a much smaller perturbative Hamiltonian, V

$$H = H_0 + V = H_0 + V_B + V_K + V_J \quad (17)$$

The perturbation terms are V_B (due to an external uniform magnetic field, \mathbf{B}_0), V_K (due to the spin magnetic moment of each nucleus of the molecule, μ_K) 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 above mentioned two response properties.

The calculation of response properties can be performed at different levels of approaches within wave-function-based, DFT-based or polarization propagator formalisms [17,18].

Using perturbation theory, σ and \mathbf{M} arise from second-order corrections to the electronic energy

$$E_{PQ}^{(2)} = \sum_{n \neq 0} \left\{ \frac{\langle 0 | H^P | n \rangle \langle n | H^Q | 0 \rangle}{E_0 - E_n} + c.c. \right\} \quad (18)$$

where *c.c.* stands for the complex conjugate of the preceding term, $|n\rangle$ stand for a complete set of eigenstates of H_0 . The unperturbed Hamiltonian belongs to one-component (Hartree–Fock) or four-component (Dirac–Fock) space when calculations are performed within NR or relativistic regimes, respectively. The perturbation Hamiltonians H^P and H^Q are any of the perturbative Hamiltonians of Eq. (17). Furthermore, any static second-order molecular property can be calculated by using polarization propagators as [19]

$$E_{PQ}^2 = \text{Re} \langle \langle H^P; H^Q \rangle \rangle_{E=0} \quad (19)$$

2.3 Chemical Shift vs Magnetic Shielding

The most important measured parameter of NMR spectroscopy is the chemical shift, δ . This parameter was discovered in 1950 [20,21] and is defined as the difference of the frequencies of resonance of the same nucleus though belonging to different molecules under the same external magnetic field,

$$\delta_K = \frac{\nu_K - \nu_K^{ref}}{\nu_K^{ref}} 10^6 = \frac{\sigma_K^{ref} - \sigma_K}{1 - \sigma_K^{ref}} 10^6 \approx (\sigma_K^{ref} - \sigma_K) 10^6 \quad (20)$$

There are several restrictions that arise when using chemical shifts to get absolute values of magnetic shieldings. Among them one can mention the fact that they show only the relative values of shieldings and also that there is no possibility for direct comparison of experimental and calculated results for shieldings. The diagram given in Fig. 1 shows five typical levels to extract information about chemical shifts. The first two (a and b) are only available by calculations. The last two are mostly obtainable by experiments.

The best molecular condition for fitting experimental values with theoretical calculations of magnetic shieldings is given by the third level, where one measures or calculates magnetic shieldings in isolated molecules at 300 K of temperature.

Levels (a) and (b) refer to the nuclear shieldings in isolated molecules at equilibrium geometries and their corrections due to zero-point vibration, ZPV, at 0 K, respectively. Level (c) considers corrections due to temperature and levels (d) and (e) refer to measurements in gases and vapours, and liquids, respectively. As mentioned, this last two levels are suitable for NMR measurements.

As seen, chemical shifts have an arbitrary nature due to they are secondary parameters. They are obtained by setting the chemical shift of a particular

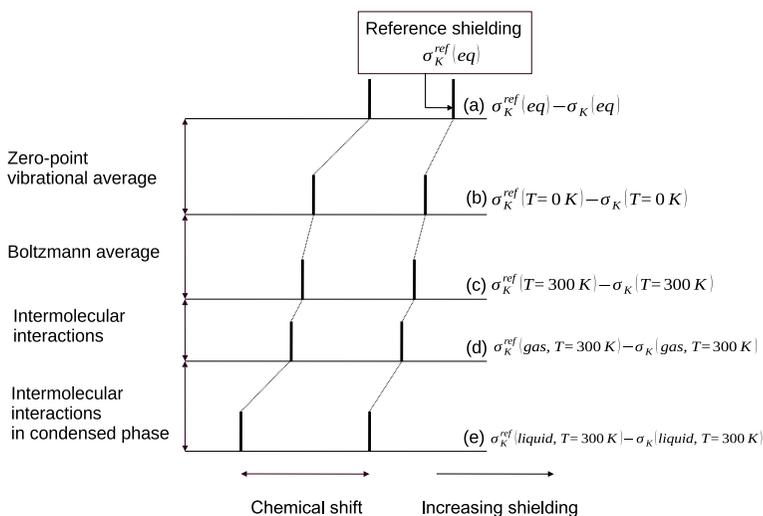


Fig. 1 Schematic relation between calculated and measured chemical shift.

peak, the reference, to a particular arbitrary value for convenience. Furthermore, each chemical shift is assigned to a given magnetic nuclide that has its own reference standard. Given that these references are different each other, there is no way to properly compare shieldings of different nuclides. Based on chemical shift one cannot define an absolute scale for all nuclides, or in other words, one obtains one absolute scale for each nuclide.

To try to overcome these disadvantages new experimental devices were designed to obtain unknown magnetic shieldings by using the knowledge of a given shielding parameter, like $\sigma(\text{He})$ and two appropriate nuclear magnetic moments, e.g., one of the He atom and the other one of the nucleus with unknown magnetic shielding. In other words, as will be mentioned in [Section 4](#), there is a new method to measure directly the shielding of a given nucleus when an isolated helium-3 atom is used as the universal reference standard [22].



3. NONRELATIVISTIC THEORIES FOR NMR AND SPIN-ROTATION TENSORS

At the beginning of NMR spectroscopy, Ramsey was interested in finding the way to both, calculate and measure the NMR spectroscopic parameters. He was able to introduce the first approach to the electronic mechanisms that underlies the nucleus–electron interactions for describing the experimental outputs. He also found the electronic mechanisms that are involved in the rotational spectroscopy, and then he was able to relate both spectroscopies as much as possible by theory [23].

In this section we shall shortly expose the basic physics used within an NR framework for describing those spectroscopies, the mathematical tools used to calculate and analyze their spectroscopic parameters and the relationship between those two spectroscopies that is only valid within this framework. This way of thinking must be overpassed in order to get more accurate values of all spectroscopic parameters, and a deeper understanding on the physics that is really involved in them. This fact becomes more evident when heavy elements are involved. The required description of the physics within a relativistic framework will be given in [Section 5](#).

3.1 The Nonrelativistic Framework

From the beginning of rotational and NMR spectroscopies, their spectroscopic parameters were defined within the NR framework [3,24]. The Hamiltonian describing the interaction of the nuclear magnetic dipole of

a nucleus K with the effective field at that nucleus due to the rotation of the molecule, for molecules in equilibrium, do have two terms: one that depends on nuclear coordinates and the other one that depends on electronic coordinates. Then, the tensor \mathbf{M}_K of the second term of the rhs of Eq. (14) can be written as $\mathbf{M}_K = \mathbf{M}_K^{nuc} + \mathbf{M}_K^{elec}$, where the electronic part is calculated applying perturbation theory or linear response theory as

$$\begin{aligned} \mathbf{M}_K^{NR-elec} &= \frac{e^2 \hbar^2}{2 m_e m_p c^2} g_K \left[\sum_{n \neq 0} \frac{\langle 0 | \sum_j \frac{\mathbf{r}_{jK} \times \mathbf{p}_j}{|\mathbf{r}_{jK}|^3} |n\rangle \langle n | \sum_j \mathbf{r}_{j,CM} \times \mathbf{p}_j |0\rangle}{E_0 - E_n} + c.c. \right] \otimes \mathbf{I}^{-1} \\ &= \frac{e^2 \hbar^2}{2 m_e m_p c^2} g_K \left\langle \left\langle \frac{\mathbf{r}_K \times \mathbf{p}}{|\mathbf{r}_K|^3}; \mathbf{r}_{CM} \times \mathbf{p} \right\rangle \right\rangle \otimes \mathbf{I}^{-1} \end{aligned} \quad (21)$$

where e and m_e are the electronic charge and mass, respectively; m_p is the proton mass; c is the speed of light in vacuum; g_K is the g -factor of nucleus K and \mathbf{I}^{-1} is the inverse molecular moment of inertia around the molecular centre of mass (CM). In addition, $\mathbf{r}_{jK} = \mathbf{r}_j - \mathbf{R}_K$ is the j electron position with respect to the K nucleus, and $\mathbf{r}_{j,CM} = \mathbf{r}_j - \mathbf{R}_{CM}$ is the position of electron j with respect to the molecular CM.

Within the NR framework, magnetic shielding tensors of Eq. (11) arise from two electronic mechanisms [3,16], so that $\sigma_K^{NR} = \sigma_K^{NR-dia} + \sigma_K^{NR-para}$. The contribution of the first mechanism (the diamagnetic term) depends on the ground state of the molecule, so that it can actually be calculated accurately.

The paramagnetic contribution arises as a response property

$$\begin{aligned} \sigma_K^{NR-para} &= \frac{e^2}{2 m_e^2 c^2} \left[\sum_{n \neq 0} \frac{\langle 0 | \sum_j \frac{\mathbf{r}_{jK} \times \mathbf{p}_j}{|\mathbf{r}_{jK}|^3} |n\rangle \langle n | \sum_j \mathbf{r}_{j,G} \times \mathbf{p}_j |0\rangle}{E_0 - E_n} + c.c. \right] \\ &= \frac{e^2}{2 m_e^2 c^2} \left\langle \left\langle \frac{\mathbf{r}_K \times \mathbf{p}}{|\mathbf{r}_K|^3}; \mathbf{r}_G \times \mathbf{p} \right\rangle \right\rangle \end{aligned} \quad (22)$$

where $\mathbf{r}_{j,G} = \mathbf{r}_j - \mathbf{R}_G$ is the position of electron j with respect to the gauge origin (GO) of the magnetic potential.

For diatomic molecules, the tensor elements of M_K^{NR} and $\sigma_K^{\text{NR-para}}$ along their molecular bond axis are null, i.e., $M_{\parallel,K}^{\text{NR}} = \sigma_{\parallel,K}^{\text{NR-para}} = 0$.

3.2 Corrections to $\sigma(eq)$ for Comparison With Experiments

Theoretical calculations are performed first considering the equilibrium geometry of a given molecule. Such geometry could be theoretically calculated or taken from experiments. Equilibrium values of the nuclear shieldings, $\sigma(eq)$, are obtained by including electron correlation and relativistic effects. All these calculations should be performed with the best level of theory available for them [17].

Values of σ at equilibrium geometry cannot be compared with experiments. One should include the influence of the changes in the molecular geometry due to the ZPV and temperature effects. Relativistic effects should also be considered because they could modify the molecular equilibrium geometry and the value of the shielding for a given geometry.

The ZPV contribution is calculated as

$$\sigma_K = \sigma_K(eq) + \sum_i \frac{\partial \sigma_K}{\partial Q_i} \langle Q_i \rangle + \frac{1}{2} \sum_{ij} \frac{\partial^2 \sigma_K}{\partial Q_i \partial Q_j} \langle Q_i Q_j \rangle \quad (23)$$

where $\langle Q_i \rangle$ is the average value of the normal coordinate Q_i in the particular ro-vibrational state.

Temperature and ro-vibrational effects are then introduced and so, level (c) of Fig. 1 is obtained.

$$\begin{aligned} \sigma_{K,iso}(T) = & \sigma_{K,iso}(eq) + \frac{B_e}{\omega_e} \left[\left(\frac{\partial^2 \sigma_{K,iso}}{\partial \xi^2} \right)_{\xi=0} - 3a \left(\frac{\partial \sigma_{K,iso}}{\partial \xi} \right)_{\xi=0} \right] \left[\frac{1}{2} + \frac{\exp[-hc\omega_e/(kT)]}{1 - \exp[-hc\omega_e/(kT)]} \right] \\ & + \frac{4kT}{hcB_e} \left(\frac{B_e}{\omega_e} \right)^2 \left(\frac{\partial \sigma_{K,iso}}{\partial \xi} \right)_{\xi=0} \end{aligned} \quad (24)$$

where ξ is the bond displacement

$$\xi = \frac{(r - r_{eq})}{r_{eq}} \quad (25)$$

B_e can be calculated from rotational constants and ω_e is obtained from vibrational spectroscopy [15].

3.3 The Nonrelativistic Ramsey–Flygare Model

As mentioned in Section 2, chemical shifts are the main spectroscopic parameters that are usually measured. This parameter is defined as the difference among two absolute magnetic shieldings (see Eq. (20)). Then, in order to get absolute magnetic shieldings by experiments one should find the way to obtain σ_K^{ref} .

Ramsey was the first to propose a clever solution to this dilemma. From a theoretical relationship between the electronic part of the SR tensor and one of the terms of the magnetic shielding tensor, its paramagnetic contribution, and adding then its diamagnetic term by using theoretical calculations he found the way to obtain mixed experimental/theoretical values of absolute magnetic shieldings. After the pioneering works of Ramsey, Flygare extended them to more general molecules and also added new terms [4,23,25–27].

The Ramsey–Flygare relationship links the paramagnetic contribution to σ_K and the electronic contribution to \mathbf{M}_K according to

$$\begin{aligned}\sigma_K^{NR\text{-para}} &= \frac{m_p}{g_K} \mathbf{M}_K^{NR\text{-elec}} \otimes \mathbf{I} \\ &= \frac{m_p}{g_K} (\mathbf{M}_K^{NR} - \mathbf{M}_K^{nuc}) \otimes \mathbf{I}\end{aligned}\quad (26)$$

Gaussian atomic units were used in the last expression and shall be used throughout this chapter. Eq. (26) explicitly shows that \mathbf{M}_K^{NR} can be expressed as the sum of $\mathbf{M}_K^{NR\text{-elec}}$ and $\mathbf{M}_K^{NR\text{-nuc}}$. As it was shown in Eq. (21), $\mathbf{M}_K^{NR\text{-elec}}$ is the linear response that takes account of two external potentials originated in: (i) the total electronic orbital angular momentum centred in the molecular CM, and (ii) the spin magnetic moment of nucleus K . Besides, Eq. (26) is valid only when the GO of the magnetic potential is located at the molecular CM.

Another finding of Flygare and coworkers was a relationship between the diamagnetic contribution to σ of a nucleus in a molecule, $\sigma_K^{NR\text{-dia}}$, when the GO is placed at the position of nucleus K , and the shielding of that nucleus in the corresponding free atom, $\sigma_K^{atom,NR}$ (which has only diamagnetic contributions within the NR domain). They first found that $\sigma_K^{NR\text{-dia}}$ can be approximated as the sum of $\sigma_K^{atom,NR}$ and another tensor that only depends on the nuclear positions at equilibrium (the first term in equation (6) of Ref. [4], which includes our \mathbf{M}_K^{nuc} as part of it; see Ref. [28]) [4,25]. Applying this relation they found that the average (isotropic) values are more accurately reproduced by this sum than the individual tensor elements of $\sigma_K^{NR\text{-dia}}$. In further works, they improved the last relation by using an atom

dipole model, including other two terms: a dipole one—in general quite small—and a quadrupole term [26,27].

It is important to stress that, even though Flygare found this relation taking the position of nucleus K as the GO in the shielding tensor [4], it is also valid when the CM is taken as the GO for the magnetic potential. The latter assumption is taken for the GO throughout this chapter. The Flygare's diamagnetic approach (following the arguments of Ref. [28]) can be expressed as $\sigma_K^{\text{NR-dia}} \cong \sigma_K^{\text{atom,NR}} + \frac{m_p}{g_K} \mathbf{M}_K^{\text{mic}} \otimes \mathbf{I}$.

As the Flygare's quadrupole term appears only for individual tensor elements of $\sigma_K^{\text{NR-dia}}$ (it does not contribute to the isotropic diamagnetic shielding), ignoring this term may introduce significant errors in the approximation of the tensor elements of $\sigma_K^{\text{NR-dia}}$. So, the isotropic diamagnetic shielding can accurately be reproduced as the sum of $\sigma_K^{\text{atom,NR}}$ and $M_{\text{iso},K}^{\text{mic}}$ (in ppm), whereas only fair estimations will be obtained for the individual tensor elements if the quadrupole term is ignored [26].

From these considerations one obtains the well-known Ramsey–Flygare relationship

$$\begin{aligned} \sigma_K &= \sigma_K^{\text{NR-para}} + \sigma_K^{\text{NR-dia}} \\ &\approx \frac{m_p}{g_K} \mathbf{M}_K^{\text{NR}} \otimes \mathbf{I} + \sigma_K^{\text{atom,NR}} \end{aligned} \quad (27)$$

which is restricted to rigid rotor molecules in their equilibrium geometries. As it was stated, the approximation is in general more accurate for the isotropic than for each individual tensor elements.

One can obtain the semiexperimental values of σ following the scheme of Fig. 2, first suggested by Hindermann and Cornwell [29].

If an experimental value of the perpendicular component of \mathbf{M}_K is reported for a particular vibrational and rotational state, $M_{\perp,K}(\nu, J)$, then the equilibrium value, $M_{\perp,K}(eq)$, is found including ro-vibrational corrections to the experimentally obtained $M_{\perp,K}(\nu, J)$. Ro-vibrational corrections are given by [15]

$$\begin{aligned} M_{\perp,K}(eq) &= M_{\perp,K}(\nu, J) - \left(\nu + \frac{1}{2} \right) \frac{B_e}{\omega_e} \left[\left(\frac{\partial^2 M_{\perp,K}}{\partial \xi^2} \right)_{\xi=0} - 3a \left(\frac{\partial M_{\perp,K}}{\partial \xi} \right)_{\xi=0} \right] \\ &\quad - 4(J^2 + J) \left(\frac{B_e}{\omega_e} \right)^2 \left(\frac{\partial M_{\perp,K}}{\partial \xi} \right)_{\xi=0} \end{aligned} \quad (28)$$

where first and second derivatives are taken from theoretical calculations.

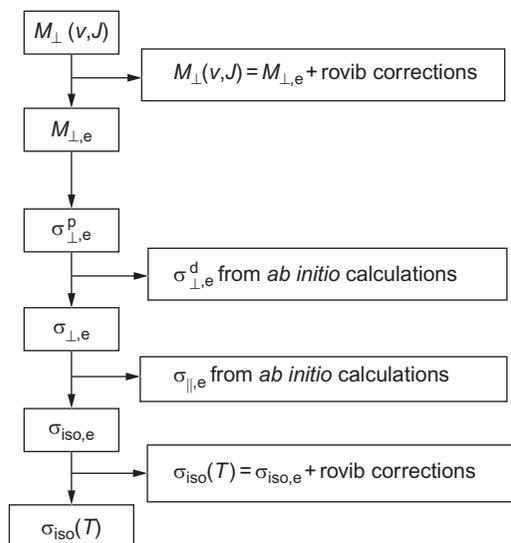


Fig. 2 Scheme to theoretically obtain the Isotropic magnetic shielding from experimental spin-rotation constant, adding temperature and rovibrational corrections. *Reprinted and adapted with permission from M. Gee, R.E. Wasylshen, and A. Laaksonen, A more reliable absolute shielding scale for chlorine: combined experimental and theoretical approach, J. Phys. Chem. A 103 (50) (1999) 10805–10812. Copyright 1999 American Chemical Society.*



4. RECENT EXPERIMENTAL DEVELOPMENTS

Chemical shift is the parameter that is routinely measured in NMR spectroscopy. What is usually performed is the chemical shift measurement on samples in its liquid or gas phase. Getting δ in those phases makes difficult its comparison with theoretical calculations.

As mentioned above, the Ramsey–Flygare model was extensively applied to obtain semiexperimental values of σ . They were found not to give accurate values when heavy-atom containing molecules are under study. Then one may try to generalize the Ramsey–Flygare model or try to get σ directly by experiments, or try to do both. The last option seems to be the best.

4.1 Direct Measurement of NMR Shieldings

There were few recent experimental proposals for measuring magnetic shieldings directly instead of chemical shifts [1]. They first started considering that a given nuclear dipole magnetic moment is related with its nuclear spin, i.e., $\boldsymbol{\mu}_K = \hbar\gamma_K\mathbf{I}_K$.

The NMR frequency of resonance is given by

$$\hbar\nu_K = \Delta\mu_K^z(1 - \sigma_K)B_0 = \mu_K \frac{\Delta I_K^z}{I_K}(1 - \sigma_K)B_0 \quad (29)$$

Then, by using the same expression for two different nuclides, one obtain a relation between the frequency of resonance, the nuclear magnetic moments and the shieldings of both nuclides:

$$\sigma_K = 1 - \frac{\nu_K \mu_L}{\nu_L \mu_K}(1 - \sigma_L) \quad (30)$$

One should know in advance the accurate values of nuclear magnetic moments of the nuclides involved. If one can measure the frequencies of resonances of nuclides K and L , and the shielding of nucleus L , the shielding of nucleus K is obtained.

Jackowski and collaborators had shown that Eq. (30) can be applied to obtain absolute shieldings of few nuclei, like ^1H , ^{13}C , ^{15}N and others, using ^3He as the universal primary reference standard of nuclear magnetic shielding [22,30]. The magnetic shielding of ^3He is well known from accurate calculations [31] and therefore it is the best choice for a primary reference of σ . This method is available for gases and liquids (isotropic species) on standard NMR spectrometer.

Eq. (30) permits the measurement of observable shieldings even in liquid samples. The value of absolute shielding can be transferred from ^3He to pure liquid deuterated solvents which are used for the stabilization of the external magnetic field [1].

4.2 Magnetic Shielding in Gas-Phase NMR Experiments

In the case of NMR experiments with low density gases, σ_K can be expanded in powers of the density, ρ [30,32,33]. If the density dependence is linear,

$$\sigma_K = \sigma_{0,K} + \sigma_{1,K} \rho \quad (31)$$

being $\sigma_{0,K}$ the shielding for an isolated molecule and $\sigma_{1,K}$ a measure of the effect on the nuclear shielding due to binary collisions.

If one has a binary mixture of gas A and gas B, and the former contain the nucleus K whose shielding is being observed, the shielding of nucleus K belonging to gas A can be expanded as a series [34]

$$\sigma_K^A = \sigma_{0,K}^A + \sigma_{1,K}^{AA} \rho_A + \sigma_{1,K}^{AB} \rho_B \quad (32)$$

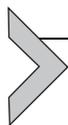
where only the first expansion terms were here included.

If the density of A is kept very low the A–A molecular interaction can be eliminated and so

$$\sigma_K^A = \sigma_{0,K}^A + \sigma_{1,K}^{AB} \rho_B \quad (33)$$

This permits the determination of magnetic shielding for an isolated molecule after linear extrapolation of the results to the zero-density point. $\sigma_{1,K}^{AB}$ includes the bulk susceptibility correction as well as the term describing all the intermolecular interactions between molecules A and B. This expression was successfully applied to investigate magnetic shieldings of hydrogen isotopomers in gas phase. A linear dependence of $\sigma(^1\text{H})$ and $\sigma(^2\text{H})$ in gaseous mixture with He, Ne and Ar as diluting rare gases was observed. The shielding parameters σ_H and σ_D free from intermolecular interactions were obtained at room temperature [30,35]. Higher order terms of Eq. (32) were included by Jackowski and collaborators in a recent study of σ_N in a sample of nitrogen with synthetic air, pressurized up to 300 bar [36]. They found that the binary $\text{N}_2\text{--O}_2$ interactions contribute to the shielding an order of magnitude larger than the $\text{N}_2\text{--N}_2$ pairs.

This methodology was also applied to obtain extrapolated experimental gas-phase results for the shielding of Pb, C and H for $\text{Pb}(\text{CH}_3)_4$ with diluting gases of SF_6 and Xe [37].



5. RELATIVISTIC THEORIES FOR SHIELDING AND SPIN-ROTATION TENSORS

When heavy elements are involved in theoretical calculations of response properties, one should consider relativistic effects. They are usually small for atoms with $Z < 36$ though not vanishingly small to neglect them in accurate calculations [38,39]. There are also molecular systems with non-heavy elements for which relativistic effects on NMR spectroscopic parameters are as large as, or even larger, than the NR values [40–43].

In addition to the quantification of relativistic effects, we should also be aware about the huge conceptual changes introduced by relativity in quantum chemistry. There are several new understandings that need to be highlighted in the current literature [44,45]. Specially, the fact that the well-known electronic mechanisms that underlie response properties within the NR regime are fully modified when treated within the relativistic framework [46–50]. Relativistic formalisms introduce completely new physical insights that shall take some time to be fully understood.

We shall concentrate in this section on some of the new understandings that arise within the relativistic regime for the treatment of both, magnetic shieldings and SR tensors. Besides we shall try to shed some light on the way they are related each other. In this sense we should mention that, during more than 60 years there was a huge improvement on the accuracy of calculations of those properties, together with its use to get more reliable semi-experimental values of σ using the Ramsey–Flygare relationship. At the same time, there were clear indications that such a relationship did not work well for heavy–element containing molecules, but it was not easy to find the way to solve it.

The generalization of the paramagnetic contribution to σ was addressed during the 1980s, but the generalization of the SR tensor took more than 20 years after that decade. Why it was so long? One of the main problems was to find the way to describe response properties of rotating quantum systems within a relativistic framework. Once the relativistic expression of tensor \mathbf{M} was found, the next challenging step was to generalize, if possible, the Ramsey–Flygare relationship. Here the main difficulty was related to the fact that, at first sight, any likely relationship between theoretical expressions of both tensors within the new regime were not available.

5.1 The Relativistic Framework

Changing the regime within which response properties are expressed means changing the basic framework. So, scalar operators are now expressed as four–dimensional matrix operators and scalar wave–functions become four–component wave–functions.

The fundamental dynamical wave–function equations shall be modified in order to fulfil relativistic requirements, though the way response properties are theoretically obtained is mainly the same in both regimes. Still it happens that the appearance of the negative–energy branch of the energy spectra introduce additional difficulties to calculations and interpretations. One of the main characteristics of the new relativistic framework is the splitting of the energy spectra in two branches. Then perturbation theory must take care of this. The appearance of negative–energy states has deep consequences and quantum chemist are not used to treat with them.

The introduction of relativistic effects through four–component methodologies gave a good platform to the next step: quantum electrodynamics [51–53]. It also permitted the estimation of other very small effects, like the nuclear charge distribution effects and the Breit electron–electron interactions [54,55].

As happens within the NR regime, there are basically three different formalisms for the treatment of response properties within the relativistic regime. What all of them have in common is the increase of complexity in calculations and interpretations.

The treatment of response properties within any of both regimes do have the additional difficulty of matching both of them when light atoms are involved, or when the condition of $c \rightarrow \infty$ is assumed. There is a formalism that can consider the last condition in a straightforward way: polarization propagators.

Given that we will apply this last method in few of the following sections, we shall sketch it after the introduction of relativistic perturbative Hamiltonians for nuclear magnetic shieldings. Then we shall highlight recent theoretical treatments of magnetic shieldings and SR tensors within the relativistic regime.

5.2 Relativistic Theory of NMR Shieldings

There are new features that appear when one extend NR concepts to the relativistic domain. In the case of NMR spectroscopic parameters we should mention here that Ramsey's formulation introduced perturbative Hamiltonians as ad hoc Hamiltonians. He considered all interactions that contribute to NMR spectroscopic parameters based on a phenomenological and NR point of view [2,3,56–58]. Within the relativistic domain they do not appear as such, but they naturally arises from the proper perturbative Hamiltonian. The NR mechanisms must then appears as $c \rightarrow \infty$.

Pyykkö and Pyper were the first to publish four-component relativistic theories of NMR shieldings based on the sum-over-states formalism. It is worth to mention that they titled their articles as “theories on chemical shifts” [59,60]. Ten years later Aucar and Oddershede developed the relativistic theory of polarization propagators from which any response property can be calculated [61].

The interaction of an N-electron system with an external magnetic field is accounted for by the minimal coupling prescription. Its explicit expression is $\mathbf{p} \rightarrow \mathbf{p} + \frac{e}{c}\mathbf{A}$, leading to the introduction of the perturbative Hamiltonian

$$H_1 = e\boldsymbol{\alpha} \cdot \mathbf{A} \quad (34)$$

where $\boldsymbol{\alpha}$ is the Dirac matrix operator of dimension 4, and $\mathbf{A} = \mathbf{A}_K + \mathbf{A}_B$ is the sum of the nuclear and the external vector potentials

$$\mathbf{A}_K = \frac{\boldsymbol{\mu}_K \times \mathbf{r}_K}{r_K^3} \quad (35)$$

and

$$\mathbf{A}_B = \frac{1}{2} \mathbf{B} \times \mathbf{r}_G \quad (36)$$

where $\mathbf{r}_G = \mathbf{r} - \mathbf{R}_G$ and $\mathbf{r}_K = \mathbf{r} - \mathbf{R}_K$; \mathbf{r} , \mathbf{R}_G and \mathbf{R}_K are the coordinates of the positions of the electron, the GO of the magnetic potential and the nucleus K, respectively. Then Eq (34) can be written as

$$\begin{aligned} H_{1,K} &= e\boldsymbol{\alpha} \cdot \left\{ \frac{\boldsymbol{\mu}_K \times \mathbf{r}_K}{r_K^3} + \frac{1}{2} \mathbf{B} \times \mathbf{r}_G \right\} \\ &= -e\hbar\gamma_K \mathbf{I}_K \cdot \left(\frac{\boldsymbol{\alpha} \times \mathbf{r}_K}{r_K^3} \right) - \frac{e}{2} \mathbf{B} \cdot (\boldsymbol{\alpha} \times \mathbf{r}_G) \end{aligned} \quad (37)$$

where $\boldsymbol{\mu}_K = \hbar\gamma_K \mathbf{I}_K$.

Once the appropriate four-component perturbative Hamiltonian is well defined, one can apply four-component relativistic methods to obtain nuclear magnetic shieldings from perturbation theory. By considering Eqs. (14) and (15), and applying the second-order perturbative correction to the energy

$$E_{PQ}^{(2)} = \sum_{n \neq 0} \left\{ \frac{\langle 0 | H^P | n \rangle \langle n | H^Q | 0 \rangle}{E_0 - E_n} + c.c. \right\} \quad (38)$$

where *c.c.* stand for complex conjugate, the excitation energies are both, positive- and negative-energy states, and perturbative Hamiltonians H^P and H^Q are replaced by $H_{1,K}$, we are able to obtain the relativistic expression of σ .

There are three basic different four-component methods: wave-function-based, DFT-based and polarization propagators [62], and also two-component and scalar relativistic methods [17]. We shall sketch some of the four-component methods in the following sections.

In order to properly apply Eq. (38) within the relativistic regime, one should be very careful with the treatment of the virtual electron–positron pair creation and annihilation [41]. One should precisely define the way to include, in the ground-state and excited state wave-functions, the number of electrons together with the number of pairs. To be as explicit as possible we use here the method given in Ref. [63]. There the following considerations were introduced

- The unperturbed reference state is built within the *no-pair* approximation. This state is well defined within the N-electron subspace of

Dirac–Fock states expanded as Slater determinants built each of them from one-electron positive-energy states [64]. This means that the effects of electron–positron pairs are not considered in the unperturbed N -electron state.

- The one-particle negative-energy electronic states are related with positive-energy positronic states. Then when one-particle perturbative operator V acts on the reference N -electron state, it will produce matrix elements between this state and N -electron excited states and also, with states of $(N + 2)$ particles which contain one electron–positron virtual pair.
- The application of perturbation theory is restricted to (N) - and $(N + 2)$ -particle states, and also neglecting the effects of pair creation/annihilation due to the Coulomb–Breit interactions. Furthermore, given that within QED the energy should be related with the vacuum, one must consider perturbative effects on the vacuum. So this can be expressed as a perturbation on the $(N = 2)$ -particle state (states with only one electron–positron pair).

From these considerations the first-order correction to wave-functions is

$$|\psi^{(1)}\rangle = |\psi^{(1)}(N)\rangle + |\psi^{(1)}(N + 2)\rangle, \quad (39)$$

where

$$|\psi^{(1)}(N)\rangle = \sum_{n \neq 0} |\psi_n(N)\rangle \frac{\langle \psi_n(N) | V | \psi_0 \rangle}{E_0 - E_n}, \quad (40)$$

$$|\psi^{(1)}(N + 2)\rangle = \sum_n |\psi_n(N + 2)\rangle \frac{\langle \psi_n(N + 2) | V | \psi_0 \rangle}{E_0 - E_n},$$

and the Rayleigh–Schrödinger corrections to the energy are

$$E^{(1)} = \langle \psi_0 | V | \psi_0 \rangle, \quad (41)$$

$$E^{(2)} = [\langle \psi_0 | V | \psi^{(1)} \rangle - \langle vac | V | vac^{(1)} \rangle] + c.c., \quad (42)$$

being $|vac\rangle$ the vacuum state.

The second-order energy correction can be divided in two terms: one that contains excitations to N -particle states, and another one that include the electron–positron virtual pairs. They are

$$E^{(e-e)} = \sum_{n \neq 0} \frac{\langle \psi_0 | V | \psi_n(N) \rangle \langle \psi_n(N) | V | \psi_0 \rangle}{E_0 - E_n}, \quad (43)$$

$$E^{(p-p)} = \sum_n \frac{\langle \psi_0 | V | \psi_n(N+2) \rangle \langle \psi_n(N+2) | V | \psi_0 \rangle}{E_0 - E_n} - \sum_n \frac{\langle vac | V | \psi_n(2) \rangle \langle \psi_n(2) | V | vac \rangle}{E_{vac} - E_n}. \quad (44)$$

One should be aware that only the total value of $E^{(p-p)}$ is well defined; each one of both of its terms does not converge when taken alone.

5.2.1 Relativistic and Nonrelativistic Polarization Propagators

The matricial form of polarization propagators is given by [61,65]

$$\langle\langle P; Q \rangle\rangle_E = \left(\mathbf{P}_a^\dagger, \mathbf{P}_b^\dagger, \dots \right) \begin{pmatrix} \mathbf{W}_{aa} & \mathbf{W}_{ab} & \dots \\ \mathbf{W}_{ba} & \mathbf{W}_{bb} & \dots \\ \dots & \dots & \dots \end{pmatrix}^{-1} \begin{pmatrix} \mathbf{Q}_a \\ \mathbf{Q}_b \\ \dots \end{pmatrix}, \quad (45)$$

where

$$\mathbf{P}_a = (P | \mathbf{h}_a), \quad (46)$$

and

$$\mathbf{W}_{ab} = \left(\mathbf{h}_a | E\hat{I} - \hat{H}_0 | \tilde{\mathbf{h}}_b \right). \quad (47)$$

In those expressions, \mathbf{h} stands for the manifold of excitation operators from which the complete set of excited states can be obtained. Besides, operators P and Q are described in a basis of excitation operators. Besides, the binary products of Eqs. (46) and (47) are defined as

$$(P | Q) = \langle 0 | [P^\dagger, Q] | 0 \rangle \quad (48)$$

Eq. (45) can be written in a more compact way as

$$\langle\langle P; Q \rangle\rangle_E = \mathbf{b}^P \mathbf{W}^{-1} \mathbf{b}^Q \quad (49)$$

The matrix \mathbf{W}^{-1} of the rhs of Eq. (45) is known as the *principal propagator matrix*, while \mathbf{b}^P and \mathbf{b}^Q are the property matrices or, as they were called by Contreras group, the *perturbators* [65,66]. 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. Furthermore, in the exact case, Eqs. (38) and (49) are equal.

The relativistic generalization of polarization propagators appeared 20 years after the publication of their NR theory (first published in 1993). It was just clear at that time that if only the positive-energy branch of the Dirac's spectra is considered, the diamagnetic terms do not appear.

Then, the special term of the second-order correction to the energy related with relativistic polarization propagators for calculation of shieldings is written as,

$$E^{(2)} = \frac{1}{2} \text{Re} \langle \langle H_1; H_1 \rangle \rangle = \frac{e^2 \hbar}{2c^2} \sum_K \gamma_K \mathbf{I}_K \cdot \text{Re} \left\langle \left\langle \frac{c \boldsymbol{\alpha} \times \mathbf{r}_K}{r_K^3}; c \boldsymbol{\alpha} \times \mathbf{r}_G \right\rangle \right\rangle \cdot \mathbf{B}$$

So, the full relativistic expression of the NMR shielding tensor is

$$\sigma_K = \frac{e^2}{2c^2} \left\langle \left\langle \frac{c \boldsymbol{\alpha} \times \mathbf{r}_K}{r_K^3}; c \boldsymbol{\alpha} \times \mathbf{r}_G \right\rangle \right\rangle \quad (50)$$

where \mathbf{r}_G is the electronic position with respect to the GO. Constant γ_K is the magnetogyric constants of nucleus K .

From these equations one observes that only one electronic mechanism is involved. There is no formal distinction between dia- and paramagnetic terms [41], even though one can recover what is well known within the NR regime applying a proper approximation, meaning $c \rightarrow \infty$. This fact is completely new and its explanation gave us the opportunity to get new insights on the electronic origin of molecular magnetic properties.

When considering excitations from an occupied MO to both the positive- and negative-energy MOs one shall get an equivalent expression to that of Eq. (45), i.e.,

$$\langle \langle \hat{P}; \hat{Q} \rangle \rangle_E = \left(\tilde{\mathbf{P}}^{ee}, \tilde{\mathbf{P}}^{ep} \right) \begin{pmatrix} \mathbf{W}^{ee, ee} & \mathbf{W}^{ee, ep} \\ \mathbf{W}^{ep, ee} & \mathbf{W}^{ep, ep} \end{pmatrix}^{-1} \begin{pmatrix} \mathbf{Q}^{ee} \\ \mathbf{Q}^{ep} \end{pmatrix} \quad (51)$$

where ee and ep means that excitations are allowed to connect occupied electronic orbitals with either positive-energy or negative-energy electronic virtual orbitals, respectively.

One very important property of this formulation is the fact that both relativistic matrix operators, the *principal* propagator and *perturbators*, go to their NR counterparts when the velocity of light is scaled to ∞ [41,61]. This means that one can obtain the NR limit of formal expressions, and calculations, applying the procedure previously used in classical physics.

5.2.2 (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 [61]. They provide only one mechanism that is paramagnetic-like due to its formal relation with such type of usual NR electronic mechanisms.

We may then ask to ourselves: how the well-known NR diamagnetic and paramagnetic mechanisms do appear? As was shown in Ref. [41] 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 $\mathbf{W}^{ee,ep}$ and $\mathbf{W}^{ep,ee}$ matrix elements of Eq. (51) for not very accurate calculations. In such a case, considering $P = Q = V$, Eq. (51) can be rewritten as

$$\begin{aligned} \langle\langle V; V \rangle\rangle &\approx \langle\langle V; V \rangle\rangle^{(e-e)} + \langle\langle V; V \rangle\rangle^{(p-p)} \\ &= \mathbf{b}^{P,ee} (\mathbf{W}^{ee,ee})^{-1} \mathbf{b}^{Q,ee} + \mathbf{b}^{P,ep} (\mathbf{W}^{ep,ep})^{-1} \mathbf{b}^{Q,ep} \end{aligned} \quad (52)$$

From this last equation it is seen that the $\langle\langle \cdot; \cdot \rangle\rangle^{(e-e)}$ and $\langle\langle \cdot; \cdot \rangle\rangle^{(p-p)}$ correspond to paramagnetic and diamagnetic terms, respectively, of any response property within the NR domain. Then, 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.

5.2.3 Recent Four-Component and Effective Models

Ilias and coauthors developed the theory and its implementation of the four-component London atomic orbital, LAO, and published it in 2009 [67]. Their calculations were based on the four-component Dirac–Coulomb Hamiltonian. The introduction of LAOs in the relativistic domain provides atomic magnetic balance for the calculation of molecular properties. This development is an extension of the previously published four-component linear response method [68]. They found that calculations performed by this method on hydrogen iodine give reliable values for magnetic shieldings with standard basis sets. Its extension to molecular magnetizability calculations was recently published [69].

Within the group lead by Malkin, in Bratislava, it was developed a method that was then implemented in a code named as relativistic spectroscopy, ReSpect, which permits the estimation of relativistic effects on the

NMR shielding and SR constants [70,71]. The restricted magnetic balance is included in it [72,73].

The method named matrix Dirac–Kohn–Sham Restricted Magnetic Balance, mDKS–RMB, was extended to include the gauge including atomic orbitals, GIAO approach. The combined method eliminates a strong dependence of the results, calculated with a finite basis set, on the choice of the GO for the magnetic potential of a uniform external magnetic field [74]. They have shown calculations for xenon dimer and the HX series ($X = \text{F, Cl, Br, I}$), where it is known that the heavy-atom effect on light-atom, HALA, effects affect the hydrogen shieldings. They also showed that the shieldings calculated at the four-component level with a common gauge, highly depend on its choice.

As a continuation of these developments, a new calculation scheme was recently published [75]. In it relativistic effects were included as the differences between four-component values obtained at the DFT level with the PBE functional [76], and the corresponding NR values. Some other functionals were used in more recent calculations [37]: BP86 [77,78] and B3LYP [79–81]. Several studies were published studying absolute magnetic shieldings of tin in SnH_4 , $\text{Sn}(\text{CH}_3)_4$ and SnCl_4 [82], H and Cl in HCl [75], F and $X = \text{S, Se, Te, Mo}$ and W in XF_6 [83], $X = \text{B, Al, Ga, In}$ and Tl in XF , [84] O and S in H_2O , CO and H_2S [85], C, O and $X = \text{Ni, Pd}$ and Pt in XCO [86], H and $X = \text{F, Cl, Br, I, At, O, S, Se, Te, Po, N, P, As, Sb, Bi, C, Si, Ge, Sn, Pb, B, Al, Ga, In, Tl}$ in XH_n ($n = 1, 4$) [87], Lu, Au and $X = \text{F, Cl, Br}$ and I in LuX and AuX [88] and XSe and XTe ($X = \text{Si, Ge, Sn}$ and Pb) [89].

In most of those calculations electron correlation was taken within the NR framework at the CCSD(T) level of approach [90]. A short description of some of these studies is given in Ref. [90]. In Ref. [82] the authors raised some new inquires, together with the statement that absolute shielding constant of ^{119}Sn must be re-evaluated by 1000 ppm. They found that ZORA provides reliable estimates for the chemical shifts, but not for absolute shielding constant [91], and put forward a question mark about the validity of some known absolute shielding scales, given that Ramsey–Flygare does not work well for heavy atoms.

In the search for a procedure to get reliable absolute values for magnetic shieldings, Maldonado and Aucar proposed a procedure that consisted in mixing accurate experimental chemical shifts and theoretical magnetic shieldings [92]. They calculated $\sigma(\text{Sn})$ and $\sigma(\text{Pb})$ in a family of heavy-halogen-containing molecules. They found out that $\sigma^{ref}[\text{Sn}; \text{Sn}(\text{CH}_3)_4]$

in gas phase should be close to 3864.11 ± 20.05 ppm. For Pb atom, $\sigma^{ref}[\text{Pb}; \text{Pb}(\text{CH}_3)_4]$ should be close to $14,475.1 \pm 500.7$ ppm. Such theoretical values correspond to calculations with the relativistic polarization propagator method, RelPPA, at the RPA level of approach. They are closer to experimental values as compared to those obtained applying few different functionals. They studied tin and lead shieldings in the family of compounds XY_{4n}Z_n ($X = \text{Sn}, \text{Pb}$; $Y, Z = \text{H}, \text{F}, \text{Cl}, \text{Br}, \text{I}$) and $\text{PbH}_{4n}\text{I}_n$ ($n = 0, 1, 2, 3, 4$) with four-component functionals as implemented in the DIRAC code [93].

A similar method was applied to get reference values for $\sigma(\text{Si})$ and $\sigma(\text{Ge})$ in tetramethyl silane and tetramethyl germanium [94]. It was found that $\sigma^{ref}[\text{Si}; \text{Si}(\text{CH}_3)_4]$ in gas phase should be close to 410.49 ± 6.77 ppm and $\sigma^{ref}[\text{Ge}; \text{Ge}(\text{CH}_3)_4]$ should be close to 1705.29 ± 19.51 ppm.

More recent theoretical/experimental studies were published about the absolute shielding scale of ^{207}Pb on an isolated tetramethyllead $\text{Pb}(\text{CH}_3)_4$ molecule. The assignment of the experimental resonance frequency from the gas-phase NMR spectra of $\text{Pb}(\text{CH}_3)_4$ in a binary mixture with SF_6 or Xe was extrapolated to zero density of the buffer gas to obtain the result for an isolated molecule. The computed ^{207}Pb shielding constant was $10,790 \pm 600$ ppm for the isolated molecule, leading to a shielding of $10,799.7$ ppm for liquid $\text{Pb}(\text{CH}_3)_4$. On the other hand, the fully hydrated Pb^{2+} ion in water solution has, according to their measurements, a much larger shielding of $13,657.2$ ppm.

5.2.4 The Orbital-Decomposition-Based and X2C Methods

In Ref. [95] Xiao et al. gave an account of various of their own four-component formulations that can be unified in terms of the idea of “orbital decomposition”. They are completely equivalent and differ only in the partitioning of the relativistic paramagnetic-like and diamagnetic-like terms. The magnetic balance, MB, condition plays an essential role, both conceptually and computationally, in their formulations and also the ansatz of “gauge-including atomic orbitals”, GIAO, at both the mean-field and correlated levels [49]. A comprehensive presentation about these models and also the concept of body-fixed molecular Hamiltonian is given in Ref. [96]

The orbital decomposition is strongly related with the fact that the Dirac operator is linear with respect to the vector potential, and so, the perturbative Hamiltonian from which one obtains the diamagnetic contribution within the NR domain is lost in the relativistic framework [41,61]. Several methods are able to include such a contribution. One of them is the polarization propagator. Another one is the decomposition of the orbitals [97,98].

The so-called exact two-component methods, X2C, were first developed for the calculation of the energy spectra [48,99]. The group lead by Liu have presented their own version of X2C methodology to calculate NMR parameters [100,101].

Another development of X2C type was performed by Yoshizawa and Hada [102]. Being found the analytic formulas based on the two-component normalized elimination of the small component (2c-NESC) method [103], it was recently developed the computer code for the restricted magnetic balance, RMB-2c-NESC method to calculate NMR shielding tensors of molecules containing heavy elements. They have given results for HX ($X = \text{I, At}$), H_2X ($X = \text{Te, Po}$), and HXeCCH . In addition, at the HF level, they have demonstrated that for X_2 ($X = \text{Ne, Ar, Kr, Xe}$) and HgL_2 ($L = \text{CH}_3, \text{Cl, Br, I}$) molecules the RMB-2c-NESC method reproduces the four-component relativistic NMR shielding constants within errors of 0.12% and 0.31%, respectively, of the four-component relativistic results [93]. Besides, the X ($X = \text{Ne, Ar, Kr, Xe}$) and Hg chemical shifts are in good agreement with the four-component results. They also found by calculations that for several molecules the RMB-GIAO-based 2c-NESC method provides gauge-origin independent NMR shielding values.

5.3 Relativistic Theory of Spin–Rotation Tensor

A relativistic relationship between nuclear shieldings and SR tensors should start with a proper definition of both properties within a relativistic framework. The relativistic theory for SR tensor was very recently found, more than 30 years after its nuclear shielding counterpart. We should remember that the relativistic theory of nuclear shieldings was first given in 1983 in an SOS context [59,60] and then in 1993 within the linear response theory [61].

5.3.1 First Attempt Proposed by Ruiz de Azúa et al. in 2012

The nuclear SR Hamiltonian describes the coupling of the nuclear spin of nucleus K , \mathbf{I}_K , and the rotational angular momentum of a molecule, \mathbf{L} , by means of the nuclear SR tensor \mathbf{M}_K [4,104,105],

$$H^{\text{SR}} = -\frac{1}{\hbar^2} \mathbf{I}_K \cdot \mathbf{M}_K \cdot \mathbf{L}. \quad (53)$$

Their eigenvalues belong to the subspace of molecular rotational states, giving rise to splittings in their energy levels.

To obtain a theoretical expression of \mathbf{M}_K it is necessary to identify those terms of the Hamiltonian that involve the nuclear spin and the molecular

rotational angular momentum operators. For the latter, it means that those terms involving the nuclear rotational angular momentum, in the laboratory framework, must be retained [4,27,106].

As the linear momentum of the nuclei are related to \mathbf{L} by mean of the relation

$$\mathbf{L} = \sum_K \mathbf{R}_{K,CM} \times \mathbf{P}_K, \quad (54)$$

where $\mathbf{R}_{K,CM}$ is the position of nucleus K relative to the molecular CM. We must retain those terms of the Hamiltonian, linear in the nuclear momentum \mathbf{P}_K . In Ref. [28] an extension of the work of Van Vleck and Flygare is presented [27,105], but considering the electronic dynamic from a relativistic perspective, while the nucleus are analyzed in a semirelativistic way. This last assumption is based on the fact that the kinetic molecular energy in a rotational state is much smaller than its rest energy, i.e., the nuclear velocities fulfill the relation $\frac{v}{c} \ll 1$. As in previous NR works, the rigid rotor model is employed to describe the nuclear dynamic, and therefore

$$\mathbf{P}_K = m_K \boldsymbol{\omega} \times \mathbf{R}_{K,CM}, \quad (55)$$

where m_K is the mass of nucleus K , $\boldsymbol{\omega} = \mathbf{I}^{-1} \otimes \mathbf{L}$ is the molecular angular velocity, and \mathbf{I}^{-1} is the inverse molecular inertia tensor with respect to the molecular CM, in the equilibrium geometry.

The theoretical expression of the nuclear SR tensor is obtained from the perturbative potentials linear in the nuclear rotational angular momenta, linear in the nuclear spin angular momentum and bilinear in both operators. They will give rise to first- and second-order perturbation energy corrections.

As it was derived in 2012 [28], there are few perturbative terms simultaneously bilinear in both operators, the nuclear rotational angular momenta (\mathbf{L}) and the nucleus K spin angular momentum (\mathbf{I}_K). They will give rise to one of the contributions to \mathbf{M}_K , which is obtained from the mean value of these terms in the molecular ground state. They can be splitted in terms that do not depend on the electronic dynamics ($H_{NN}^{(2)}$), and those that do depend on them ($H_{eN}^{(2)}$):

$$H_{K,NN}^{(2)} = \sum_{M \neq K} \frac{Z_M g_K}{2m_p c} |\mathbf{R}_{MK}|^{-3} \left[\left(1 - \frac{Z_K m_p}{m_K g_K} \right) \boldsymbol{\beta}_K - \boldsymbol{\beta}_M \right] \cdot (\mathbf{I}_K \times \mathbf{R}_{MK}) \quad (56)$$

$$H_{K,eN}^{(2)} = -\frac{g_K}{2m_p c} \left(1 - \frac{Z_K m_p}{m_K g_K} \right) \boldsymbol{\beta}_K \cdot \left(\mathbf{I}_K \times \frac{\mathbf{r}_K}{|\mathbf{r}_K|^3} \right) \quad (57)$$

where $\mathbf{R}_{MK} = \mathbf{R}_M - \mathbf{R}_K$ and $\mathbf{r}_K = \mathbf{r} - \mathbf{R}_K$.

It must be highlighted that the rigid rotor model was assumed for the nuclear dynamic, and then

$$\boldsymbol{\beta}_M = \frac{1}{c} (\mathbf{I}^{-1} \otimes \mathbf{L}) \times \mathbf{R}_{M,CM}. \quad (58)$$

In addition, the relation between the nuclear magnetic moment and the spin angular momentum is given by $\boldsymbol{\mu}_K = \frac{g_K}{2m_p c} \mathbf{I}_K$ (where m_p is the proton mass).

It can be shown that the sum of both previous equations gives rise to $-\sum_{M \neq K} Z_M \boldsymbol{\beta}_M \cdot \mathbf{A}_K(\mathbf{r}_M)$, because the sum of all other terms equals the total electric field at the nucleus K position, which is exactly zero when the molecule is in its equilibrium geometry.

On the other hand, there are perturbative terms in the Hamiltonian, linear in \mathbf{L} or linear in \mathbf{I}_K , which will be treated employing second-order perturbation theory. They are the electron–nucleus interaction linear in the magnetic moment of nucleus K ,

$$H_{\mu_K}^{(1)} = \boldsymbol{\alpha} \cdot \mathbf{A}_K, \quad (59)$$

and the electron–nucleus potential, linear in the rotational nuclear momentum,

$$H_{\omega}^{(1)} = -\boldsymbol{\omega} \cdot \mathbf{J}_e + \sum_N \left\{ \frac{Z_N}{r_{eN}} (\boldsymbol{\alpha} \cdot \boldsymbol{\beta}_N) - \frac{Z_N}{2r_{eN}} \boldsymbol{\alpha} \cdot \left(\frac{\mathbf{I} r_{eN}^2 - \mathbf{r}_{eN} \mathbf{r}_{eN}}{r_{eN}^2} \right) \cdot \boldsymbol{\beta}_N \right\}. \quad (60)$$

The first term of Eq. (60) couples *inertially* both the electronic and the nuclear dynamics, and it is proportional to the rotational angular momentum. The second term comes from a magnetic effect due to the movement of the nuclei (with magnetic spin moment $\boldsymbol{\mu}_K$). This expression is of order c^{-2} with respect to the previous term.

The nuclear SR Hamiltonian is obtained by means of a first- and second-order expansion of the electronic energy, for a given fixed nuclear configuration.

By one side, the sum of the nuclear terms and the first-order electronic energy contribution gives

$$\begin{aligned}
E^{(1)}(\mathbf{I}_K, \mathbf{L})(X) + E^{nuc}(\mathbf{I}_K, \mathbf{L}) = & -\frac{g_K}{2Z_K m_p c} \left(1 - \frac{Z_K m_p}{m_K g_K}\right) \boldsymbol{\beta}_K \cdot \\
& \left[\mathbf{I}_K \times \left(\langle \psi_{el}(X) | \sum_i \mathbf{E}_i(\mathbf{R}_K) | \psi_{el}(X) \rangle + \sum_{M \neq K} \mathbf{E}_M(\mathbf{R}_K) \right) \right] \\
& - \sum_{M \neq K} Z_M \boldsymbol{\beta}_M \cdot \mathbf{A}_K(\mathbf{R}_M).
\end{aligned} \tag{61}$$

where $\mathbf{E}_i(\mathbf{R}_K)$ and $\mathbf{E}_M(\mathbf{R}_K)$ are the electric field at the K nuclear position due to the electron i and nucleus M , respectively.

As the electric field at each nuclear position is zero when the molecule is in its equilibrium position, we have

$$\begin{aligned}
E^{(1)}(\mathbf{I}_K, \mathbf{L})(X) + E^{nuc}(\mathbf{I}_K, \mathbf{L}) = & - \sum_{M \neq N} Z_M \boldsymbol{\beta}_M \cdot \mathbf{A}_K(\mathbf{R}_M) \\
= & -\frac{g_K}{2m_p c^2} \sum_{M \neq N} Z_M (\mathbf{I}^{-1} \otimes \mathbf{L} \times \mathbf{R}_{M,CM}) \cdot \frac{\mathbf{I}_K \times \mathbf{R}_{MN}}{R_{MN}^3} \\
= & \mathbf{I}_K \cdot \sum_{M \neq N} \frac{Z_M g_K}{2m_p c^2} \left[\mathbf{R}_{M,CM} \frac{\mathbf{R}_{MN}}{R_{MN}^3} - \mathbf{I} \right. \\
& \left. \left(\mathbf{R}_{M,CM} \cdot \frac{\mathbf{R}_{MN}}{R_{MN}^3} \right) \right] \cdot \mathbf{I}^{-1} \otimes \mathbf{L}.
\end{aligned} \tag{62}$$

On the other hand, the second-order electronic energy contribution is

$$\begin{aligned}
E^{(2)}(\mathbf{I}_K, \mathbf{L}) = & \sum_{n \neq 0} \frac{\langle \psi_{el}^0 | \boldsymbol{\alpha} \cdot \mathbf{A}_K(\mathbf{r}) | \psi_{el}^n \rangle \langle \psi_{el}^n | (-\boldsymbol{\omega} \cdot \mathbf{J}_e) | \psi_{el}^0 \rangle}{E_{el}^0 - E_{el}^n} + c.c. \\
= & -\frac{g_K}{2m_p c} \mathbf{I}_K \cdot \left[\sum_{n \neq 0} \frac{\langle \psi_{el}^0 | \frac{\mathbf{r}_K \times \boldsymbol{\alpha}}{|\mathbf{r}_K|^3} | \psi_{el}^n \rangle \langle \psi_{el}^n | \mathbf{J}_e | \psi_{el}^0 \rangle}{E_{el}^0 - E_{el}^n} + c.c. \right] \cdot \mathbf{I}^{-1} \otimes \mathbf{L}.
\end{aligned} \tag{63}$$

This expression must be taken in the sense of Eqs. (38) and (19).

The \mathbf{M}_K tensor will be obtained factorizing the nuclear spin \mathbf{I}_K and the angular momentum \mathbf{L} , taking account of the minus sign in Eqs. (4) and (16), in such a way that

$$\mathbf{M}_K = \mathbf{M}_K^{nuclear} + \mathbf{M}_K^{(1)} + \mathbf{M}_K^{(2)}. \quad (64)$$

The two first terms of Eq. (64) come from Eq. (61). They are

$$\begin{aligned} \mathbf{M}_K^{nuclear} + \mathbf{M}_K^{(1)}(\mathbf{X}) &= \frac{g_K}{2m_p c^2} \left(1 - \frac{Z_K m_p}{m_K g_K} \right) \left[\left(\mathbf{R}_{K,CM} \cdot \left\langle \frac{\mathbf{r}_K}{|\mathbf{r}_K|^3} \right\rangle \right) \mathbf{1} - \left\langle \frac{\mathbf{r}_K}{|\mathbf{r}_K|^3} \right\rangle \mathbf{R}_{K,CM} \right] \otimes \mathbf{I}^{-1} \\ &\quad + \frac{g_K}{2m_p c^2} \sum_{M \neq K} Z_M |\mathbf{R}_{MK}|^{-3} \\ &\quad \left[\left(\left\{ \mathbf{R}_{M,CM} - \left(1 - \frac{Z_K m_p}{m_K g_K} \right) \mathbf{R}_{K,CM} \right\} \cdot \mathbf{R}_{MK} \right) \mathbf{1} \right. \\ &\quad \left. - \left\{ \mathbf{R}_{M,CM} - \left(1 - \frac{Z_K m_p}{m_K g_K} \right) \mathbf{R}_{K,CM} \right\} \mathbf{R}_{MK} \right] \otimes \mathbf{I}^{-1}. \end{aligned} \quad (65)$$

For molecules in equilibrium positions, the last sum will give rise to one term, which depends exclusively on nuclear variables:

$$\begin{aligned} \mathbf{M}_K^{nuc} &= \mathbf{M}_K^{nuclear}(eq) + \mathbf{M}_K^{(1)}(eq) \\ &= \sum_{M \neq K} \frac{Z_M g_K}{2m_p c^2} \left[\mathbf{R}_{M,CM} \cdot \frac{\mathbf{R}_{MK}}{|\mathbf{R}_{MK}|^3} - \mathbf{R}_{M,CM} \frac{\mathbf{R}_{MK}}{|\mathbf{R}_{MK}|^3} \right] \otimes \mathbf{I}^{-1}, \end{aligned} \quad (66)$$

In this way, for molecules in equilibrium geometries, the only one contribution to \mathbf{M}_K linked to electronic operators is $\mathbf{M}_K^{(2)}(eq)$, which in this particular case will be called \mathbf{M}_K^{elec} , and

$$\mathbf{M}_K^{elec} = \frac{g_K}{2m_p c^2} \left[\sum_{n \neq 0} \frac{\langle \psi_{el}^0 | \frac{\mathbf{r}_K \times c \boldsymbol{\alpha}}{|\mathbf{r}_K|^3} | \psi_{el}^n \rangle \langle \psi_{el}^n | \mathbf{J}_e | \psi_{el}^0 \rangle}{E_{el}^0 - E_{el}^n} + c.c. \right] \otimes \mathbf{I}^{-1}, \quad (67)$$

and, according to the four-component linear response theory at zero frequency [7], it can be written as:

$$\mathbf{M}_K^{elec} = \frac{g_K}{2m_p c^2} \left\langle \left\langle \frac{\mathbf{r}_K \times c \boldsymbol{\alpha}}{|\mathbf{r}_K|^3}; \mathbf{J}_e \right\rangle \right\rangle_{\omega=0} \otimes \mathbf{I}^{-1}. \quad (68)$$

The total electronic angular momentum operator \mathbf{J}_e is defined in terms of the orbital and spin angular momentum as $\mathbf{J}_e = (\mathbf{r} - \mathbf{R}_{CM}) \times \mathbf{p} + \frac{1}{2} \boldsymbol{\Sigma}$.

The second-order energy correction due to the Breit interactions between electrons and nuclei is written as

$$E^{(2)} = \langle\langle H_{\mu_K}^{(1)} ; H_{BO}^{(1)} + H_B^{(1)} \rangle\rangle_{\omega=0}. \quad (69)$$

The electron–nuclei Breit interaction contribution to \mathbf{M}_K can be derived from the second term of Eq. (69). It is given by

$$\mathbf{M}_K^{\text{Breit}} = -\frac{g_K}{2m_p c^2} \left\langle\left\langle \left(\frac{\mathbf{r}_K}{|\mathbf{r}_K|^3} \times c\boldsymbol{\alpha} \right); \sum_M (\mathbf{R}_{M,\text{CM}} \times \mathbf{D}_M c\boldsymbol{\alpha}) \right\rangle\right\rangle_{\omega=0} \otimes \mathbf{I}^{-1}, \quad (70)$$

where symmetry of operator \mathbf{D}_M was used,

$$\mathbf{D}_M = \frac{Z_M}{2c^2 r_M^3} (\mathbf{r}_M \cdot \mathbf{r}_M + \mathbf{r}_M \mathbf{r}_M), \quad (71)$$

to move operator $\boldsymbol{\alpha}$ to the right in Eq. (70).

In relativistic quantum chemistry, the interaction Hamiltonian of electrons taking account of relativistic exchange of one photon between two “positive-energy” electrons should contain both the Coulomb and the Breit terms:

$$U(1,2) = \frac{1}{r_{12}} - \frac{(c\boldsymbol{\alpha}_1) \cdot (c\boldsymbol{\alpha}_2)}{c^2 r_{12}} + \frac{(c\boldsymbol{\alpha}_1) \cdot (\mathbf{r}_{12} \cdot \mathbf{r}_{12} - \mathbf{r}_{12} \mathbf{r}_{12}) \cdot (c\boldsymbol{\alpha}_2)}{2c^2 r_{12}^3}. \quad (72)$$

In Eq. (72) the second term is the Gaunt term and, together with the third term, they correspond to the Breit operator, which is the correction to the Coulomb potential. Theoretical consistency requires the inclusion of such terms, as their leading order is $1/c^2$, i.e., the same order as all leading order relativistic corrections. However, as it is computationally demanding and yields only small corrections, this term is usually neglected in four-component calculations of magnetic properties.

The electron–electron Breit interaction will also yield a relativistic correction to \mathbf{M}_K in a given rotational molecular state. In fact, there must be an electronic analogue of the electron–nucleus Breit effect. It can be rationalized on the following grounds. The molecular rotation “drift” of the electronic state is obtained as a response to the $H_{BO}^{(1)}$ “inertia” operator, yielding a first-order electronic state which is linear in $\boldsymbol{\omega}$. The corresponding change in the electron–electron Breit interaction for this perturbed electronic state reflects the change in the electron velocities due to nuclear rotation and it is the electronic analogue of the electron–nucleus Breit interaction. The effect of this modification of the electron–electron interaction on \mathbf{M}_K could be obtained

by evaluating the interaction with the chosen nucleus K magnetic dipole moment by means of third-order perturbation theory.

The first SR constants calculations employing the pioneer relativistic formalism [28] were presented at the 10th REHE International Conference in 2012 (Corrientes, Argentina) [107]. Then, two articles were almost simultaneously published with calculations of M_{\perp} , performed at the relativistic four-component Dirac–Kohn–Sham [82] and Dirac–Hartree–Fock RPA levels of theory [108].

Four-component relativistic calculations of shielding and SR tensor elements presented for the first time in this chapter were performed using a locally modified developer version of the DIRAC17 program package [93].

The linear molecules were displayed along the z axis. For symmetry reasons, only diagonal components of shielding and SR tensors are non null. In the case of \mathbf{M} , in both relativistic and NR domains only its perpendicular components are nonzero and are equal each other. These tensor elements are usually known as the spin–rotation constant M . On the other side, within the relativistic domain the shielding tensor has nonzero parallel component ($\sigma_{\parallel} = \sigma_{zz}$).

Four-component calculations are based on the Dirac–Coulomb Hamiltonian, employing an energy correction to avoid the explicit calculation of (SS|SS) integrals, i.e., two-electron integrals containing only small component basis functions [40].

Most of response calculations were performed within the Dirac–Hartree–Fock–Coulomb relativistic polarization propagator approach at the random phase level of approach (RPA).

Nonrelativistic RPA values of σ and \mathbf{M} (reported as $\sigma^{\text{NR-para}}$, $\sigma^{\text{NR-dia}}$, and $\mathbf{M}^{\text{NR-elec}}$) were obtained taking the speed of light scaled to $c = 30c_0$. The value of the speed of light in vacuum used throughout all four-component calculations was $c_0 = 137.0359998$ a.u.

The gauge origin of the external magnetic potential was placed at the molecular center of mass in all NMR shielding calculations. By this choice of the gauge origin a direct comparison with SR results can be safely made. Furthermore, in order to calculate shieldings of nuclei in closed shell free atoms using the DIRAC code (this feature is not implemented for open shell systems), an electron was added to the halogen free atoms.

The nuclear g -factor values were taken from Ref. [109] for calculations of SR constants. Available experimental bond distances of free molecules in gas phase were used. They were extracted from Ref. [110], except for AuF, AuCl, AuBr, and AuI, which were taken from Refs [111–113].

Dyall's relativistic acv4z basis sets (dyall.acv4z) were employed for H (K.G. Dyall, unpublished), F, Cl [114], Br, and I [115]; for all other atoms (Li, Na [114], K, Rb, Cs [116], Cu (K.G. Dyall and A.S.P. Gomes, unpublished), Ag and Au [117]) Dyall's cv4z basis sets (dyall.cv4z) were used. In all cases, the uncontracted Gaussian basis sets were used with the common gauge-origin (CGO) approach. The small component basis sets for relativistic calculations were generated by applying the unrestricted kinetic balance prescription (UKB).

A finite nuclear model—modeled by Gaussian charge distributions—was employed in all calculations, as implemented in the DIRAC code. The importance of the nuclear charge distribution effects was recently analyzed in SR and shielding constants [118].

In order to include correlation effects, not only RPA, but also Kohn–Sham–DFT calculations were performed employing the DIRAC code. DFT calculations are based on the four-component Dirac–Coulomb Hamiltonian, and have been done using a variety of NR exchange–correlation functionals in several categories: (i) The local density approximation (LDA) functional [119,120]; (ii) the generalized gradient approximation (GGAs) functionals: PBE [76], KT2 [121], KT3 [122], and BP86 [77,78]; and (iii) the hybrid functional PBE0 [123].

When stated, SOPPA–CCSD calculations were performed employing the DALTON2016 code [124].

In Table 1 four-component relativistic RPA values of $M_{\perp,H}$ and $M_{\perp,X}$ are displayed for HX compounds ($X = \text{H, F, Cl, Br, I}$) [108,135]; the corresponding ($e-e$) and ($p-p$) contributions are shown, together with the nuclear contribution; in addition, their NR limits and experimental values are also displayed.

For Br and I, the relativistic calculations predict a positive relativistic effect which increases substantially from Br to I (from *ca.* 3 to 23 kHz). This effect is much smaller than the NR value, and at first sight it seems to fail to improve the NR result as compared to experimental values. The relativistic effect in I is *ca.* 7% of the NR result, which is rather small in a relative scale, as compared, e.g., with the case of the nuclear magnetic shielding constant, where the relativistic effect is *ca.* 30% [131–134].

On the other hand, $M_{\perp,H}$ present significant relativistic effects in all compounds, which are particularly large for HBr and HI. Deeper insight on the origin of this large relativistic effect can be obtained using the *linear response within the elimination of small components* (LRESC) model. As it is the case for the shielding of the H nucleus in HX compounds, the spin–orbit (SO) effect is also by far the dominant relativistic correction for $M_{\perp,H}$.

Table 1 Relativistic Calculations of $M_{\perp,K}$ at RPA Level of Theory for HX Molecules ($X = \text{H, F, Cl, Br, I}$)

	K	$M_{\perp,K}^{\text{nuc}}$	$M_{\perp,K}^{\text{elec}}$				$M_{\perp,K}$	$M_{\perp,K}^{\text{NR}}$	$M_{\perp,K}^{\text{exp}}$
			$M_{\perp,K}^{\text{elec}(e-e)}$		$M_{\perp,K}^{\text{elec}(p-p)}$				
			L	S	L	S			
H ₂	¹ H	104.487	10.558	0.027	0.012	-0.012	115.072	115.074	113.904 ^{a,b}
HF	¹ H	22.661	45.433	-0.060	0.002	-0.002	68.034	67.119	71.128(24) ^c
	¹⁹ F	52.457	-377.287	12.157	3.782	-3.769	-312.660	-312.173	-307.637(20) ^c
HCl	¹ H	9.432	32.895	-0.058	0.001	-0.001	42.269	39.478	41.877(139) ^d
	³⁵ Cl	2.036	-60.787	4.057	1.063	-1.059	-54.689	-54.729	-53.829(53) ^d
HBr	¹ H	6.285	39.571	-0.451	0.001	-0.001	45.405	32.094	41.27(31) ^e
	⁷⁹ Br	3.819	-362.331	77.231	18.246	-18.198	-281.233	-284.508	-290.83(8) ^e
HI	¹ H	4.056	58.270	-2.443	0.001	-0.001	59.884	25.429	49.22(22) ^f
	¹²⁷ I	2.079	-505.103	179.112	31.348	-31.260	-323.824	-346.597	-351.1(3) ^f

The third column shows the nuclear contribution, while $M_{\perp,K}^{\text{elec}}$ is the linear response of Eq. (68). In addition, $(e-e)$ and $(p-p)$ parts of $M_{\perp,K}^L$ and $M_{\perp,K}^S$ are displayed. Finally, nonrelativistic and experimental results are given. Values in kHz.

^aTaken from Ref. [125].

^bRo-vibrational effects have a value of -1.56 kHz [126].

^cTaken from Ref. [127].

^dTaken from Ref. [128].

^eTaken from Ref. [129].

^fTaken from Ref. [130].

Regarding the $(e-e)$ and $(p-p)$ contributions, it is interesting to highlight the strong cancellation of the $(p-p)$ results for all $M_{\perp,K}$ from the terms involving the \mathbf{L}_e and \mathbf{S} relativistic angular momentum operators ($M_{\perp,K}^L$ and $M_{\perp,K}^S$, respectively). This feature was anticipated on the basis of the LRESC analysis of relativistic effects on \mathbf{M}_K : it was found that both the NR limit and the leading order relativistic correction of $(p-p)$ contributions are zero.

In the NR limit, only $M_{\perp,K}^{muc}$ and part of $M_{\perp,K}^L$ should remain nonvanishing in the case of closed-shell molecules. Therefore, the $M_{\perp,K}^S$ contribution is wholly relativistic. This contribution is increasingly important for $M_{\perp,X}$.

In addition, there seems to be large cancellation between relativistic effects on both $M_{\perp,K}^L$ and $M_{\perp,K}^S$ terms. Once more, this feature is based on the way the relativistic \mathbf{J}_e operator behaves. The LRESC model shows that the leading order relativistic effects of $M_{\perp,K}^{L(e-e)}$ and $M_{\perp,K}^{S(e-e)}$ have a common contribution, each with opposite sign [135,136]. This fact explains that partial cancellation.

To compare the relative importance of relativistic and correlation effects, an analysis based on RPA NR values of $M_{\perp,K}$ was presented [108]. NR calculations at the SOPPA level of approach (with CCSD based wavefunctions) were performed to analyze correlation effects.

For $M_{\perp,H}$, correlation effects on the NR values are negligibly small in all cases. From previous experience on shielding [137], it is known that correlation effects may be of major importance in considering the SO effect on a light nucleus in the vicinity of a heavy one (HALA effect). From the different terms giving rise to SO effects, the Fermi-contact one (FC-SO) effect is by far the largest one in the case of $M_{\perp,H}$ in HX.

In Ref. [108] it is shown that the total relativistic effect at the RPA level of approach and the total LRESC are very similar each other for $M_{\perp,H}$, and the FC-SO is almost equal to them. Then, correlated calculations of this particular term were used [137] to see that the correlation effects are really important in this term and it was thus predicted that relativistic corrections to $M_{\perp,H}$ is smaller than those given by four-component RPA results.

In order to discuss the adequacy of the relativistic theory of \mathbf{M}_K developed in Ref. [28], Table 2 shows four-component RPA, “best estimate” and experimental values of \mathbf{M}_K in HCl, HBr and HI, given in Refs. [108,135]. The “best estimate” value for $M_{\perp,X}$ was obtained as the sum of the SOPPA-CCSD NR value and the relativistic correction as given by the difference of

Table 2 Nonrelativistic RPA Results of $M_{\perp,K}^{\text{NR}}$, Relativistic Corrections at RPA Level of Theory, $\Delta^R M_{\perp,K}$; NR Electronic Correlation Effets, $\Delta^{\text{corr}} M_{\perp,K}^{\text{NR}}$, *best estimation*, and Experimental Values of M_K for HCl, HBr and HI (in kHz)

X	K	$M_{\perp,K}^{\text{NR}}$ (RPA)	$\Delta^R M_{\perp,K}$ ^a	$\Delta^{\text{corr}} M_{\perp,K}^{\text{NR}}$ ^b	<i>Best Estimation</i> ^c	M_N^{exp}
Cl	¹ H	39.478	2.790 (2.22)	0.739	43.008 (42.438)	41.877(139) ^d
	³⁵ Cl	-54.729	0.040	-0.100	-54.789	-53.829(53) ^d
Br	¹ H	32.094	13.311 (9.19)	0.790	46.195 (42.074)	41.27(31) ^e
	⁷⁹ Br	-284.508	3.275	-11.927	-293.161	-290.83(8) ^e
I	¹ H	25.429	34.455 (21.14)	0.516	60.400 (47.084)	49.22(22) ^f
	¹²⁷ I	-346.597	22.773	-27.166	-350.990	-351.1(3) ^f

^aDifference between RPA relativistic and NR calculations.

^bDifference between SOPPA-CCSD and RPA NR calculations.

^cDefinition of *best estimation* in the text. Values between parenthesis correspond to CAS-MCSCF calculations of the FC-SO contribution to $M_{\perp,K}$.

^dTaken from Ref. [128].

^eTaken from Ref. [129].

^fTaken from Ref. [130].

the four-component and NR RPA values. The “best estimate” for $M_{\perp,H}$ was taken as the sum of the correlated NR value and the correlated SO correction.

Comparison of experimental and “best estimate” results in Table 2 shows that the effect of relativity on M_K is adequately taken into account by the theory developed in Ref. [28], with differences from 1% until 4%. It is interesting to remark that in the case of $M_{\perp,X}$, correlation effects on the NR results need be considered to obtain a good estimate of the final value, as seen in Fig. 3.

Even if correlated relativistic corrections would certainly improve the final result, the opposite trends in Fig. 3 explain the fact that the NR RPA values are very close to experimental values.

On the opposite side, for $M_{\perp,H}$ correlation effects on the NR values are negligibly small. The RPA relativistic value gives a correction in the right direction, but it is largely overestimated. It is interesting to emphasize the insight allowed by the LRESC expansion in this case: the correlated SO correction brings the total value of $M_{\perp,H}$ quite close to the experimental one for HBr and HI.

The good agreement between calculated and experimental results obtained in Table 2 is a strong indication that the major part of relativistic

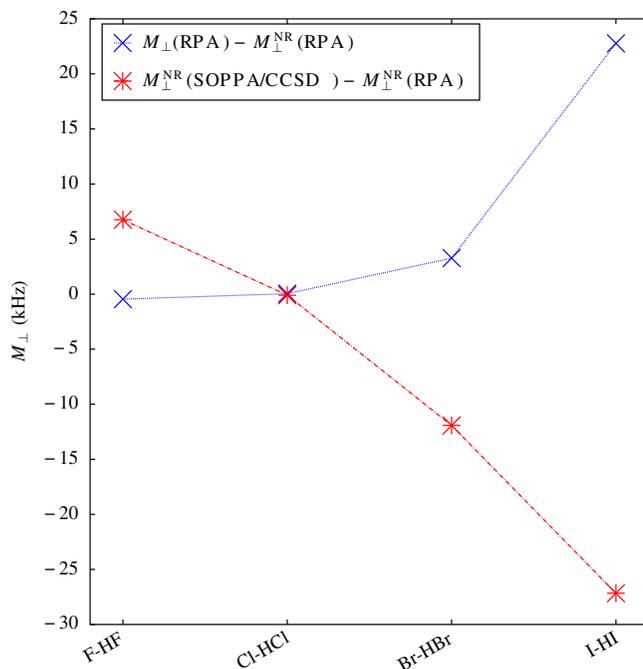


Fig. 3 Relativistic effects (blue points) and correlation effects (red points) for $M_{\perp,X}$ on HX ($X = \text{F, Cl, Br}$ and I). There is a partial cancellation between both effects.

effects are adequately described by the present approach. On the basis of these results it can be concluded that all remaining effects: vibrational, nuclear charge distribution [118], electron–nucleus and electron–electron Breit/Gaunt [54], between others should altogether account for only a small part of the total value.

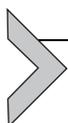
5.3.2 Few Recent Applications From Other Schemes

Some publications appeared recently with applications based on the new relativistic theory of SR [28,108,138,139].

Ruud and coauthors studied XF_6 molecules ($X = \text{S, Se, Te, Mo, W}$) [83] and XF ($X = \text{B, Al, Ga, In}$ and Tl) molecules [84]. Their calculations were based on ab initio coupled cluster and four-component relativistic density–functional. The results show that the relativistic contributions to the SR are large both for the heavy elements as well as for the fluorine nuclei. The analysis was performed on the isotropic SR constants and their anisotropic components. They assumed that correlation and relativistic effects are

approximately additive. Thus, the computed relativistic corrections were added to the best NR coupled-cluster results.

A similar study was performed on LuX and AuX ($X = \text{F, Cl, Br, I}$) molecules. They were calculated at the NR (CCSD(T) and DFT) and four-component relativistic DFT levels of theory [88]. It is worth to stress that for the LuF and LuCl molecules, Demissie and coauthors found that the CCSD(T) SR constants are in good agreement with the experimental values, but adding the DFT-calculated relativistic corrections to these results deteriorates the agreement. On the contrary, for all the AuX molecules, the final calculated nuclear SR constants are in quite good agreement with the corresponding available experimental data. In the case of metal carbonyls XCO ($X = \text{Ni, Pd, Pt}$) molecules a good agreement between theoretical calculations and experimental values was found [86].



6. TOWARDS A MORE FUNDAMENTAL RELATIONSHIP BETWEEN σ AND M

Since more than one decade ago it is clear that one must improve the NR relationship between tensors σ and M . How to do it? How to generalize the Ramsey–Flygare relationship of Eq. (27)?

Working within the relativistic domain, it is not possible to follow the same procedure used by Flygare [4]. It is so because when both tensors are written within the relativistic domain they do not have theoretical expressions that can be related between them. Then one should follow a bottom-up procedure instead of the top-down. Very recently such a procedure was successfully developed, ending in the model coined as M-V [6].

In this section we will show why the Ramsey–Flygare relationship is not valid when relativistic effects are considered, and develop in some detail two new relativistic relationships between σ and M [6,140].

6.1 Relativistic Corrections to the Ramsey–Flygare Relationship

The relativistic four-component expressions of the NMR shielding and nuclear SR tensors of a nucleus K , for molecules in equilibrium, are obtained as

$$\sigma_K = \frac{1}{2c^2} \left\langle \left\langle \frac{\mathbf{r}_K \times c\boldsymbol{\alpha}}{r_K^3}; \mathbf{r}_G \times c\boldsymbol{\alpha} \right\rangle \right\rangle \quad (73)$$

and

$$\begin{aligned} \mathbf{M}_K &= \mathbf{M}_K^{nuc} + \mathbf{M}_K^{elec} \\ &= \mathbf{M}_K^{nuc} + \frac{g_K}{2m_p c^2} \left\langle \left\langle \frac{\mathbf{r}_K \times c \boldsymbol{\alpha}}{r_K^3} ; \left(\mathbf{r}_{CM} \times \mathbf{p} + \frac{1}{2} \boldsymbol{\Sigma} \right) \right\rangle \right\rangle \otimes \mathbf{I}^{-1} \end{aligned} \quad (74)$$

It is explicitly shown that the formal expressions of both spectroscopic parameters are very different in relativistic quantum chemistry. The coupling of the electronic distribution to the magnetic field is described by the vector product of the position and velocity operator, $\mathbf{r}_K \times c \boldsymbol{\alpha}$, while the coupling of the electronic state and the rotational state is described, as it should, by the total angular momentum operator $\mathbf{J}_e = \mathbf{r}_{CM} \times \mathbf{p} + \frac{1}{2} \boldsymbol{\Sigma}$ [28].

The differences between both relativistic expressions are the first indication that Ramsey–Flygare relationship is broken within the relativistic regime. As shown in Eq. (26), within the NR framework the electronic contribution to the SR constant is equivalent to the paramagnetic term of the shielding constant when the GO is located in the molecular CM.

Both tensors are related in a simple way in the NR regime, but the difference between them in relativistic quantum mechanics has deep consequences on their quantitative values. It is interesting to point out that operator $\mathbf{r}_K \times c \boldsymbol{\alpha}$ couples the upper to lower components of four-component spinors, while operator \mathbf{J}_e couples upper (lower) components to upper (lower) components.

6.1.1 Lowest Order Relativistic Relationships Between $\boldsymbol{\sigma}$ and \mathbf{M}

It is worth to start analyzing the relativistic contributions to both response properties by applying the LRESC model [63,136]. By this model one is able to introduce relativistic effects at lower order and see why the Ramsey–Flygare relationship is valid in few special cases.

According to the LRESC series expansion, the leading order relativistic corrections to \mathbf{M}_K^{elec} that appear from ($e-e$) and ($p-p$) excitations are [5,28,135]

$$\begin{aligned} \mathbf{M}_K^{elec(e-e)}(\text{LRESC}) &= \mathbf{M}_K^{\text{NR-elec}} + \mathbf{M}_K^{\text{PSO-K}} + \mathbf{M}_K^{\text{para-Mv/Dw}} + \mathbf{M}_K^{\text{SO-L}} + \mathbf{M}_K^{\text{SO-S}} \\ \mathbf{M}_K^{elec(p-p)}(\text{LRESC}) &= 0 \end{aligned} \quad (75)$$

where $\mathbf{M}_K^{\text{NR-elec}}$ is the NR electronic contribution to \mathbf{M}_K [4,28]. The other contributions were largely discussed in previous works. On the other hand,

the expansion of the ($e-e$) and ($p-p$) contributions to σ_K within the LRESC model is written as [63,136,141]:

$$\begin{aligned}\sigma_K^{(e-e)}(\text{LRESC}) &= \sigma_K^{\text{NR-para}} + \sigma_K^{\text{PSO-K}} + \sigma_K^{\text{para-Mv/Dw}} + \sigma_K^{\text{SO-L}} + \sigma_K^{\text{SO-S}} \\ &\quad + \sigma_K^{\text{OZ-K}} + \sigma_K^{\text{SZ-K}} + \sigma_K^{\text{B-SO}} \\ \sigma_K^{(p-p)}(\text{LRESC}) &= \sigma_K^{\text{NR-dia}} + \sigma_K^{\text{dia-K}} + \sigma_K^{\text{dia-Mv/Dw}}\end{aligned}\quad (76)$$

In Eqs. (75) and (76) different leading order relativistic mechanisms involved in σ_K and M_K are given. The zeroth order ($e-e$) contributions to both properties give rise to the well-known formal NR relationship between both properties (see Eq. (26)) [3,4,27]. This close relation can be ascribed to the simple link between the velocity and momentum electronic operators, $m\hat{v} = \hat{p}$, because the NR limit of the mean value of the Dirac operator $c\alpha$ gives the velocity of the particle.

The series expansion of the studied spectroscopic properties in Eqs. (75) and (76) allows to distinguish the common relativistic effects from those that appear in σ_K but not in M_K .

Both properties have terms due to the relativistic contributions to the Hamiltonian in the absence of magnetic fields: Darwin (H^{Dw}), mass-velocity (H^{Mv}) and spin-orbit (H^{SO}). In addition, both have also terms originated in the relativistic effects linked to the matrix elements of the nuclear magnetic potential. They give rise to the kinetic Fermi-contact, kinetic spin dipolar and kinetic paramagnetic SO operators ($H^{\text{FC/SD-K}}$ and $H^{\text{PSO-K}}$, respectively).

On the other hand, relativistic corrections arising from operators $\mathbf{r} \times \boldsymbol{\alpha}$ and \mathbf{J}_e are different. The first one contains the orbital- and spin-Zeeman operators ($H^{\text{OZ-K}}$ and $H^{\text{SZ-K}}$, respectively) and the field-induced SO term ($H^{\text{B-SO}}$) [63,136]. The operator \mathbf{J}_e does not give relativistic corrections on the same order of approximation, according to the LRESC model. Therefore, M_K will be less affected by relativistic effects than σ_K , because it contains less number of relativistic electronic mechanisms [28].

In other words, the ($e-e$) contributions to both properties have similarities and differences. Their NR limits fulfil the Ramsey-Flygare relationship, as also happens to the PSO-K, para-Mv/Dw and SO-L terms. Nevertheless, the OZ-K, SZ-K and B-SO terms only appear in the expression of magnetic shieldings. Finally, the SO-S contribution does appear in both expressions, but there is a factor 2 of difference that partially breaks the Ramsey-Flygare type relationship.

The LRESC model is able to accurately reproduce all relativistic effects that modify the SR constant of hydrogen in the HX ($X = \text{H, F, Cl, Br, I}$) family of compounds, and shows that the spin–orbit effect is the largest one [108].

Given that a similar behaviour is found for the shielding of hydrogen for the same molecular family [131,137,141], one can think, at first sight, that relativistic effects on both properties arises from similar mechanisms. On the other hand, one cannot expect that relativistic corrections will be the same due to the SO correcting operators involved are different. Within the LRESC model, the nuclear magnetic shielding depends on the operator $\mathbf{L}_e + 2\mathbf{S}$ that arises from the electronic interaction with the external magnetic field ($H^{\text{OZ}} + H^{\text{SZ}}$). Besides the SO correction to SR constants is related with the total angular momentum operator, $\mathbf{L}_e + \mathbf{S}$, which is related with the rotational effects of the molecule on the electronic distribution ($H^{\text{BO-L}} + H^{\text{BO-S}}$) [5,135,136]. So, there is a different factor 2 on the spin operators of those properties.

It is worth to analyze the mechanisms that contribute to the relativistic effects on $M_{\perp,X}$ and $M_{\perp,H}$ for the mentioned HX family of compounds. In the case of $M_{\perp,H}$ the SO contributions give almost the total relativistic corrections though for $M_{\perp,X}$ they are only one of several others. For $M_{\perp,H}$ in HI the contribution of the SO term which contain the spin operator is close to -0.1 kHz, being the total SO contribution of 34.7 kHz. The same behaviour is found for the other linear molecules. This means that the Ramsey–Flygare relationship between $M_{\perp,H}$ and $\sigma_{\perp,H}$ does continue being valid in these cases even though some of the systems have heavy atoms. On the contrary, such a relationship does not continue being valid if the contribution of the spin to the SO effects ($M_{\perp,K}^{\text{SO-S}}$ and $\sigma_{\perp,K}^{\text{SO-S}}$) become relevant [108].

For the heavy atoms of the HX family of compounds, the three relativistic correcting terms that appear within the LRESC model (e.g., $\sigma_K^{\text{OZ-K}}$, $\sigma_K^{\text{SZ-K}}$ and $\sigma_K^{\text{B-SO}}$) do contribute to one but not to the other of σ and \mathbf{M} in such a way that the differences between both properties are not vanishingly small.

Again one can analyze what happens with the Ramsey–Flygare relationship in the hydrogen iodine. The relativistic paramagnetic-like (i.e., $(e-e)$) corrections to $\sigma_{\perp,I}$ arise as the difference between the relativistic value $\sigma_{\perp,I}^{(e-e)} = 631.77$ ppm and the corresponding NR value $\sigma_{\perp,I}^{\text{NR-para}} = -1456.89$ ppm. This shows that relativistic effects on the $(e-e)$ part of $\sigma_{\perp,I}$ are 2088.66 ppm. On the other hand, relativistic effects on the SR constant of iodine in the same molecule are 22.77 kHz.

If the value of $\sigma_{\perp,I}^{\text{NR-para}}$ is converted to SR units by using Eq. (26) one obtains -348.68 kHz, which is, as expected, the value of $M_{\perp,I}^{\text{NR-elec}}$. On the other hand, if one uses again Eq. (26) to convert $\sigma_{\perp,I}^{(e-e)}$ in units of SR one obtains 151.20 kHz. This result is far away of the -325.99 kHz obtained from the four-component value of $M_{\perp,I}^{(e-e)}$. There is a difference of 477.19 kHz, which clearly shows that the Ramsey–Flygare’s relationship is broken in this case.

If the Ramsey–Flygare’s relationship would be valid for heavy atoms, the relativistic correction to $\sigma_{\perp,I}^{(e-e)}$ (for I in HI) would be 499.88 kHz (obtained by transforming 2088.66 ppm to units of SR employing Eq. (26)). This result is the difference between the transformed values of $\sigma_{\perp,I}^{(e-e)}$ and $\sigma_{\perp,I}^{\text{NR-para}}$, or 151.20 kHz $-$ (-348.68 kHz). The four-component relativistic correction to the SR constant of iodine, on the other hand, is 22.77 kHz. This means that, within the LRESC model, such a difference is due to the presence of perturbative relativistic operators in the nuclear shielding tensor that are not being part of the SR tensor.

6.2 The Four-Component Ramsey–Flygare Relationship

There were several implementations and calculations using the same formal expression of Eq. (27) but considering both M_K and σ_K within the relativistic domain.

Recently, few works were published where the breaking off of the NR Ramsey–Flygare’s relationship was studied. Based on the theoretical developments of the SR constant made by Aucar et al. in 2012 [28], some research groups have applied it to different heavy-atom containing molecular systems. The NR relationship was employed to transform the electronic contribution to the relativistic SR constants to shielding units; then, they were compared with four-component calculations of shieldings, analyzing the cases where the Ramsey–Flygare’s relation is still valid, and the cases where it is not [75,82–88].

6.3 The Generalization Proposed by Xiao et al. in 2013/2014

Xiao and Liu published the relativistic molecular Hamiltonian written in a body-fixed frame of reference. By means of that Hamiltonian they introduced nuclear vibrations and rotations in the calculation of spectroscopic parameters. With such a Hamiltonian they describe electrons

relativistically and nuclei quasi-relativistically for semirigid nonlinear and linear molecules [138,139].

They employ the relativistic mapping between magnetic shieldings and nuclear SR to derive absolute shielding constants for H and X in HX molecules ($X = \text{F, Cl, Br and I}$). Their results are more accurate than the values that were based on the well-known NR mapping [140].

They consider the following three terms: Δ_A , which is close to the relativistic effect on the paramagnetic-like mapping; Δ_B , the relativistic effect on the (p - p) or diamagnetic-like shielding and Δ_C , which gives the relativistic effects on the nuclear contribution to M_K , when the molecules are in their equilibrium position. It is important to state that Δ_C is negligibly small and corresponds to the slight difference in the molecular geometry due to the inclusion of relativistic considerations.

As it will be seen in the next section, the addition of two terms, $\sigma_K^{atom(e-e)}$ (which is of pure relativistic nature) and $\frac{1}{2c}(\nu_K^S - \nu_K^{atom,S})$ (which will be introduced in the next section) is related with Δ_A . This is because $M_K^{(p-p)}$ (which is also included formally in Δ_A) is completely negligible, as it was shown theoretically and in few applications [5,28,108,140].

Lastly, Δ_B can be approximated as $\sigma_K^{atom(p-p)} - \sigma_K^{atom,NR}$, in the same spirit as the original Ramsey–Flygare relationship, where the diamagnetic shielding of a free atom serves as an approximation for the diamagnetic component of the shielding of a nucleus in its molecular environment.

In a nutshell, the model presented by Xiao and Liu starts from the following identity between experimental and theoretical terms [140,142]:

$$\sigma_{eq}^K(exp) + \frac{I_K}{2g_K\mu_n} M_{eq}^K(exp) = \sigma_{eq}^K(theo) + \frac{I_K}{2g_K\mu_n} M_{eq}^K(theo) \quad (77)$$

From this last equation one can write the “experimental” expression for the nuclear shielding as,

$$\sigma_{eq}^K(exp) = \sigma_{eq}^{K,d}(theo) - \frac{I_K}{2g_K\mu_n} \left[M_{eq}^K(exp) - M_{eq}^{K,d}(theo) \right] + \Delta_{eq}^{K,p}(theo) \quad (78)$$

where $\Delta_{eq}^{K,p}(theo) = \sigma_{eq}^{K,p}(theo) + \frac{I_K}{2g_K\mu_n} M_{eq}^{K,p}(theo)$.

As mentioned, Xiao and Liu introduced relativistic corrections by means of four-component definition of both properties and calculations with the best level of theory available. They find experimental values of the nuclear shielding by applying the identity of Eq. (77).

6.4 Models M- i ($i = I-V$)

In this section we will show another model that resembles as much as possible Ramsey–Flygare criteria of getting an absolute scale from accurate experimental measurements of SR tensor, together with state-of-the-art atomic calculations.

We want to show few of the most important physical insights that underlies the models coined as M- i ($i = I-V$) [5,6,136]. This name is to honour Profs. Ruiz de Azúa who was one of the leading scientists of our group of research.

The research programme whose latest step was the output of model M-V started by looking for an appropriate procedure to generalize the old Ramsey–Flygare relationship. The crudest way to do it is to consider that relativistic expressions relating \mathbf{M}_K with $\boldsymbol{\sigma}_K$ may have the same formal appearance as that of the NR regime. If this formal relationship does not fulfil what is found by applying four-component calculations of both tensors, one should include some other relativistic corrections. How to do it? Which would be the starting point? We decided to start using one of the well-known two-component formalisms that include the leading relativistic corrections to response properties, e.g., the LRESC formalism [136]. We also considered the splitting of both tensors, \mathbf{M}_K and $\boldsymbol{\sigma}_K$ in the ($e-e$) and ($p-p$) terms and introduced the following three assumptions:

- There is an equivalent relationship between \mathbf{M}_K and $\boldsymbol{\sigma}_K$, which is valid within both relativistic formalisms, i.e., the four-component relativistic polarization propagator and the two-component LRESC model.
- The core-dependent part of such a relationship is such that it can be replaced by the addition of the ($e-e$) and ($p-p$) contributions to the shielding of free atoms. Its most accurate value is obtained applying four-component relativistic methods.
- The SR tensor does not contain ($p-p$) contributions within the LRESC model (meaning that only very small contributions are likely obtainable for these terms within a relativistic regime).

6.4.1 The First Three Models: M-I to M-III

In addition to the well-known Ramsey–Flygare’s relationship of Eq. (26), there is a close relationship between some contributions to $\mathbf{M}_K^{(e-e)\text{-LRESC}}$ and $\boldsymbol{\sigma}_K^{(e-e)\text{-LRESC}}$ (see Eqs. (75) and (76)) [5]. They are given by

$$\boldsymbol{\sigma}_K^u = \frac{m_p}{g_K} \mathbf{M}_K^u \otimes \mathbf{I} \quad (79)$$

where the superscript u stands for the PSO-K, para-Mv/Dw and SO-L mechanisms. Although the SO-S term fulfil a similar relation, a factor 2 of difference does appear

$$\sigma_K^{\text{SO-S}} = 2 \frac{m_p}{g_K} \mathbf{M}_K^{\text{SO-S}} \otimes \mathbf{I} \quad (80)$$

Once these expressions are found, it is possible to state a new relationship that links both tensors, σ_K and \mathbf{M}_K , in a two-component relativistic domain:

$$\sigma_K^{(e-e)\text{-LRESC}} = \frac{m_p}{g_K} \mathbf{M}_K^{(e-e)\text{-LRESC}} \otimes \mathbf{I} + \frac{1}{2} \sigma_K^{\text{SO-S}} + \sigma_K^{\text{OZ-K}} + \sigma_K^{\text{SZ-K}} + \sigma_K^{\text{B-SO}} \quad (81)$$

This last equation clearly shows that there are several relativistic mechanisms that can restrict the fulfilment of Ramsey–Flygare’s relationship within the relativistic regime. In addition, two important remarks shall be made

- The usual (orbital) spin–orbit mechanism (SO-L), which is the main responsible for the HALA effect [143–145], follows the Ramsey–Flygare’s relationship. Therefore, one should expect that for light elements placed in an environment containing heavy atoms (where all other contributions are close to zero) this relation will still be fulfilled [108].
- The OZ-K, SZ-K and B-SO mechanisms are core-dependent and belong to what is known as heavy-atom effect on heavy atoms, HAAA [143–145]. They are not much influenced by the environment. As a result, these contributions may be introduced by means of atomic calculations.

Furthermore, due to the spherical symmetry of isolated atoms, there can only be few nonzero contributions to the $(e-e)$ component of shieldings within the LRESC model. They are [5]

$$\sigma_K^{\text{atom}(e-e)\text{-LRESC}} = \sigma_K^{\text{atom-OZ-K}} + \sigma_K^{\text{atom-SZ-K}} + \sigma_K^{\text{atom-B-SO}} \quad (82)$$

Given that the OZ-K, SZ-K and B-SO mechanisms are core-dependent, their contributions must be almost equal to its corresponding atomic counterparts. So we can rewrite Eq. (81) as

$$\begin{aligned} \sigma_K^{(e-e)\text{-LRESC}} &\cong \frac{m_p}{g_K} \mathbf{M}_K^{(e-e)\text{-LRESC}} \otimes \mathbf{I} \\ &+ \sigma_K^{\text{atom}(e-e)\text{-LRESC}} + \frac{1}{2} \sigma_K^{\text{SO-S}} \end{aligned} \quad (83)$$

As mentioned above, one can replace the core-dependent molecular contributions by atomic calculations. The last equation is in line with such proposal.

The Eq. (83) shows a two-component relationship between both tensors, though only for the ($e-e$) part. The consideration of the ($p-p$) part on both tensors and within the relativistic domain is straightforward.

We should stress at this stage that Ramsey–Flygare relationship includes the atomic contribution plus \mathbf{M}_K^{nuc} and some other terms that are usually neglected [25]. So, we can conjecture a relativistic generalization of Ramsey–Flygare relationship that start from Eq. (83).

If we assume that the LRESC model adequately reproduces the leading relativistic corrections on both, ($e-e$) and ($p-p$) terms of molecular properties, we can consider that the diamagnetic-like terms of the atomic shielding in the molecule is approximately equal to equivalent terms though taken from the free atom, in addition to \mathbf{M}_K^{nuc} . In other words, when the molecular CM is taken as the GO of the magnetic potential, $\sigma_K^{(p-p)} \cong \sigma_K^{atom(p-p)} + \frac{m_p}{g_K} \mathbf{M}_K^{nuc} \otimes \mathbf{I}$.

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

$$\sigma_K \cong \sigma_K^{M-III} = \frac{m_p}{g_K} \mathbf{M}_K \otimes \mathbf{I} + \sigma_K^{atom} + \frac{1}{2} \sigma_K^{SO-S} \quad (84)$$

This new relationship seems to be one of the likely relativistic generalization of Ramsey–Flygare’s model and was coined as the M-III model [5]. We can see that the NR model is recovered when c scales to infinity. One important point to be stressed is the appearance of the last term, the SO-S one, which is a two-component correction. This term should be included in order to get results that match the most accurate ones, i.e., that of the four-component calculations.

From the tensorial relationship of Eq. (84), taking into account that the isotropic contribution to σ_K^{SO-S} in linear molecules vanishes identically [146], we can obtain the isotropic nuclear shielding for linear molecules as

$$\sigma_{iso,K} \cong \sigma_{iso,K}^{M-III} = \frac{2m_p I}{3g_K} M_{\perp,K} + \sigma_K^{atom} \quad (85)$$

This expression is formally the same as that of Eq. (27).

6.4.2 The More Accurate M-IV and M-V Models

One may expect that the model M-III shall fail when higher order effects are not vanishingly small. So, when the SO-S term is replaced by its proper four-component counterpart a more accurate model must appear.

In Ref. [5] the accuracy of the M-III model was studied. With such an aim the $(e-e)$ part of the perpendicular components of σ_K^{M-III} of Eq. (84) was analyzed. The closeness of $\frac{1}{2}\sigma_{\perp,K}^{SO-S}$ and $\sigma_{\perp,K}^{(e-e)} - \frac{m_p I}{g_K} M_{\perp,K}^{(e-e)} - \sigma_K^{atom(e-e)}$ in a series of linear molecules was studied. The differences observed were considered as due to relativistic higher order terms, not included in the SO-S one.

The next step was, then, to search for the way to get such terms. We started from the definition of the relativistic electronic contribution to tensor \mathbf{M}_K [28]. It is known that

$$\begin{aligned}
 \mathbf{M}_K^{elec} &= \mathbf{M}_K^L + \mathbf{M}_K^S \\
 &= \frac{g_K}{2m_p c^2} \left\langle \left\langle \frac{\mathbf{r}_K \times c \boldsymbol{\alpha}}{|\mathbf{r}_K|^3}; \mathbf{r}_{CM} \times \mathbf{p} \right\rangle \right\rangle \otimes \mathbf{I}^{-1} \\
 &\quad + \frac{g_K}{2m_p c^2} \left\langle \left\langle \frac{\mathbf{r}_K \times c \boldsymbol{\alpha}}{|\mathbf{r}_K|^3}; \mathbf{S}^{(4)} \right\rangle \right\rangle \otimes \mathbf{I}^{-1} \\
 &= \frac{g_K}{m_p} \left[\frac{1}{2c} (\boldsymbol{\nu}_K^L + \boldsymbol{\nu}_K^S) \right] \otimes \mathbf{I}^{-1}
 \end{aligned} \tag{86}$$

The linear responses $\boldsymbol{\nu}_K^L$ and $\boldsymbol{\nu}_K^S$ are associated with \mathbf{M}_K^L and \mathbf{M}_K^S , respectively, and the SO-S mechanism arises from $\mathbf{M}_K^{S(e-e)}$ [5].

In order to find the four-component counterpart to the SO-S term, the same methodology used previously in Ref. [8] was applied. This theoretical scheme is related to Dyall's formalism [147], in which the Dirac-Coulomb-Breit Hamiltonian is splitted into two Hamiltonians, i.e., one that is spin-free, SF, and another one that is SO-dependent. From this separation we were able to define a four-component SO-like mechanism for σ_K

$$\sigma_K^{SD} = \sigma_K - \sigma_K^{SF} \tag{87}$$

where σ_K^{SF} is the shielding tensor obtained when considering the SF Hamiltonian.

A similar definition can be applied to the linear response $\boldsymbol{\nu}_K^S$ of the second term of Eq. (86),

$$\boldsymbol{\nu}_K^{S-SD} = \boldsymbol{\nu}_K^S - \boldsymbol{\nu}_K^{S-SF} \tag{88}$$

Replacing $\frac{1}{2}\sigma_K^{SO-S}$ by $\frac{1}{2c}\boldsymbol{\nu}_K^{S-SD(e-e)}$ into Eq. (84), we obtain

$$\sigma_K^{\text{M-IV}} = \frac{m_p}{g_K} \mathbf{M}_K \otimes \mathbf{I} + \sigma_K^{\text{atom}} + \frac{1}{2c} \nu_K^{\text{S-SD}(e-e)} \quad (89)$$

where only ($e-e$) rotations were considered in $\nu_K^{\text{S-SD}}$, because they (and not the ($p-p$) ones) give rise to the SO-S term as leading order corrections [135]. We should also mention that, for linear molecules, the first term has no parallel contributions.

The replacement of $\frac{1}{2}\sigma_{\perp,K}^{\text{SO-S}}$ by $\frac{1}{2c}\nu_{\perp,K}^{\text{S-SD}(e-e)}$ greatly improves the behaviour of the M-III model. The remaining difference seems to be of atomic nature.

After the analysis of the remaining small differences among the model M-IV and four-component results, we have been able to propose a new model that is, until now, the best one of the M- i type:

$$\sigma_K^{\text{M-V}} = \frac{m_p}{g_K} \mathbf{M}_K \otimes \mathbf{I} + \sigma_K^{\text{atom}} + \frac{1}{2c} (\nu_K^{\text{S}} - \nu_K^{\text{atom,S}}) \quad (90)$$

where

$$\nu_K^{\text{S}} = \frac{1}{c} \left\langle \left\langle \frac{\mathbf{r}_K \times c \boldsymbol{\alpha}}{|\mathbf{r}_K|^3}; \mathbf{S}^{(4)} \right\rangle \right\rangle. \quad (91)$$

For linear molecules, perpendicular and parallel components of the shielding tensor are written as

$$\sigma_{\perp,K}^{\text{M-V}} = \frac{m_p I}{g_K} M_{\perp,K} + \sigma_K^{\text{atom}} + \frac{1}{2c} (\nu_{\perp,K}^{\text{S}} - \nu_K^{\text{atom,S}}) \quad (92)$$

$$\sigma_{\parallel,K}^{\text{M-V}} = \sigma_K^{\text{atom}} + \frac{1}{2c} (\nu_{\parallel,K}^{\text{S}} - \nu_K^{\text{atom,S}}) \quad (93)$$

In Fig. 4 it is shown the accuracy of models M-III, M-IV and M-V. One can see that the accuracy do increase from model M-III until model M-V. When including $\nu_K^{\text{S-SD}(e-e)}$ (model M-IV) there is still at least one point that is far away, but when including $\nu_K^{\text{S}} - \nu_K^{\text{atom,S}}$ (model M-V) all of them give results that are very close to the four-component calculations.

On the other hand, the perpendicular component of the shielding is more sensitive. This is the only one which contain the relation between σ and \mathbf{M} for linear molecules. The differences between our models and the four-component methods are larger though corrected by model M-V.

There are few important advantages introduced by the M-V model [5,6]

- The restrictions of considering only the SD and ($e-e$) parts of ν_K^{S} are not needed any more.

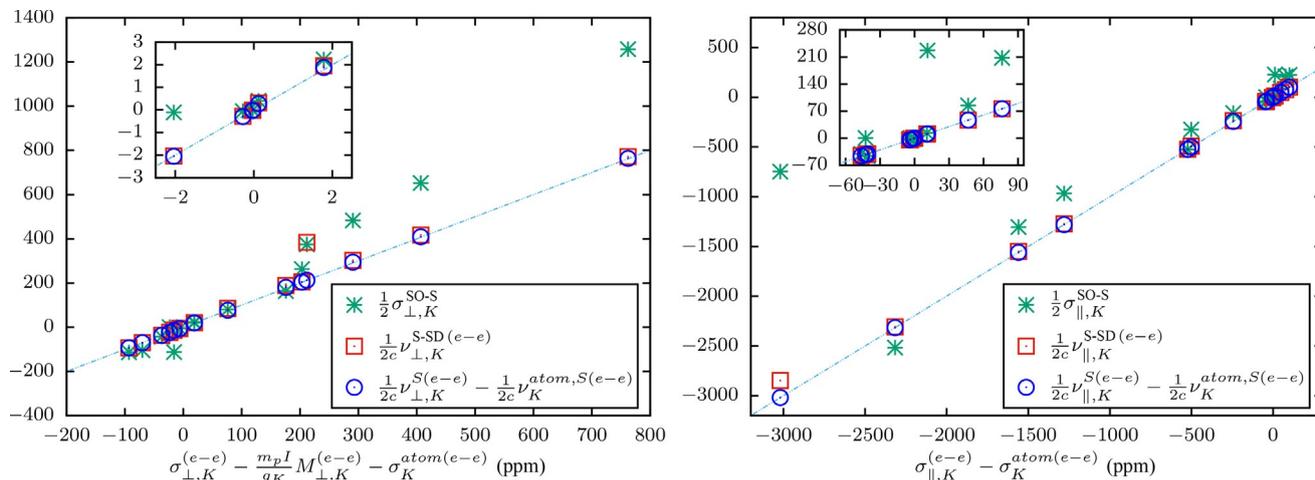


Fig. 4 Accuracy of different models M-*i* for perpendicular and parallel components of σ for HX ($X = \text{F, Cl, Br, I, At}$), XF ($X = \text{Cl, Br, I}$) and IX ($X = \text{Cl, Br, I}$) molecules. All calculations were performed at four-component RPA level of approach.

- From calculations we find that $\nu_K^{S(p-p)} \cong \nu_K^{atom, S(p-p)}$ and $\nu_K^{S-SF(e-e)} \cong \nu_K^{atom, S-SF(e-e)}$. Therefore, $\nu_K^S - \nu_K^{atom, S} \cong \nu_K^{S-SD(e-e)} - \nu_K^{atom, S-SD(e-e)}$.
- The application of the LRESC model to $\frac{1}{2c}(\nu_K^S - \nu_K^{atom, S})$ gives, as the leading order contribution, $\frac{1}{2}\sigma_K^{SO-S}$.

What is the behaviour of the M-V model in the NR limit?

- For all studied systems, the SD values of σ_K , σ_K^{atom} , M_K^L , M_K^S (and therefore also ν_K^L and ν_K^S) and $\nu_K^{atom, S}$ scale to zero as c scales to ∞ . This behaviour is fine because they arise only within the relativistic domain.
 - The SF contributions to M_K^S , ν_K^S and $\nu_K^{atom, S}$ also scale to zero as $c \rightarrow \infty$.
- The application of the M-V model to the special case of XeF₂ explains the origin of the well-known differences between $\sigma_{\parallel, K}$ in the molecule and σ_K^{atom} , for $K = \text{Xe}$ and F [9]. The finding of such differences was a clear indication that Ramsey–Flygare’s relationship is broken when heavy atoms are considered. Ramsey–Flygare’s relationship states that, for a nucleus K in a linear molecule, $\sigma_{\parallel, K}^{NR\text{-para}}$ is zero and $\sigma_K^{atom, NR\text{-para}}$ is also zero. Furthermore, it also holds that $\sigma_{\parallel, K}^{NR\text{-dia}} \cong \sigma_K^{atom, NR\text{-dia}} = \sigma_K^{atom, NR}$. All this is valid within the NR domain, but what happens within the relativistic domain?

We shall include here the analysis published in Ref. [6]. The calculation of the $(p-p)$ part at RPA level gives: $\sigma_{\parallel}^{(p-p)}(\text{Xe}; \text{XeF}_2) = 4599.7948$ ppm, whereas $\sigma^{atom(p-p)}(\text{Xe}) = 4593.3768$ ppm. It is seen that there is only a small difference between them. For fluorine such a difference is 18.9435 ppm. In both cases the differences are very likely due to quadrupole terms [26].

Besides, the relativistic $(e-e)$ contribution has a large difference with its NR counterpart. Within the relativistic regime $\sigma_K^{atom(e-e)}$ and $\sigma_{\parallel, K}^{(e-e)}$ are both different from zero. In the case of Xe, $\sigma_{\parallel}^{(e-e)}(\text{Xe}; \text{XeF}_2) = 1388.2505$ ppm while $\sigma^{atom(e-e)}(\text{Xe}) = 2026.0618$ ppm, being its difference of -637.8113 ppm.

If one assumes that the mechanism responsible for such a difference is related with $\nu_{\parallel}^{S(e-e)} - \nu^{atom, S(e-e)}$, one find that its RPA value for Xe in XeF₂ is -637.8190 ppm which is quite close to the value shown above. For fluorine in the same molecule, the difference among $\sigma_{\parallel}^{(e-e)}(\text{F})$ and $\sigma^{atom(e-e)}(\text{F}^-)$ is 19.3646 ppm, whereas $\frac{1}{2c}\nu_{\parallel}^{S(e-e)}(\text{F}; \text{XeF}_2) - \frac{1}{2c}\nu^{atom, S(e-e)}(\text{F}^-)$ is 19.5146 ppm.

Therefore, $\sigma_{\parallel} - \sigma^{atom} \cong \nu_{\parallel}^{S(e-e)} - \nu^{atom, S(e-e)}$. This occurs because the $(p-p)$ parts of $\sigma_{\parallel}^{(p-p)}$ and $\sigma^{atom(p-p)}$ are very close each other.

Concerning the search for the origin of the large difference between the parallel component of the NMR shielding tensor of Xe in XeF_2 and the shielding of the free Xe atom, first shown in 2004 by the work of Wasylishen and coauthors, it is now possible to explain it by including the newest term, $\nu_{K'}^S$, in the relationship between \mathbf{M}_K and $\boldsymbol{\sigma}_K$. Its physical origin and interpretation is still unknown.

The most recent calculations of $\boldsymbol{\sigma}$ show that the differences between four-component calculations and those with the M-V model are less than 1% different. We show in Figs. 5–8 new results of calculations at different levels of theory, for a family of linear molecules. In all cases, but not for

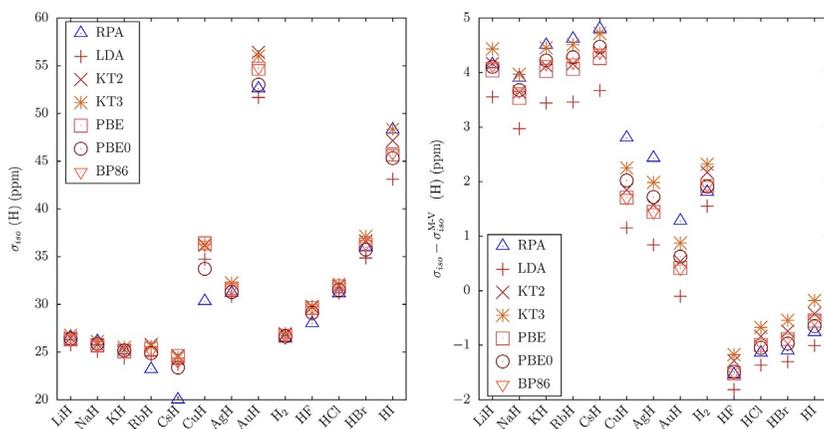


Fig. 5 Absolute values of shielding constant and accuracy of M-V model for H. All calculations were performed at different levels of DFT theory and RPA.

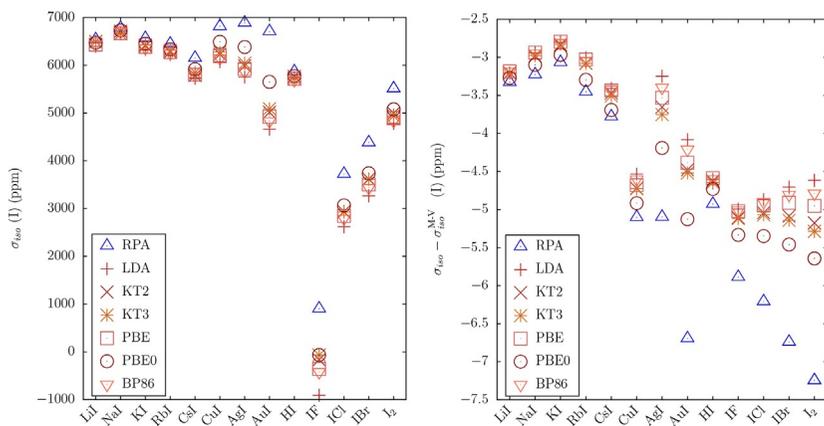


Fig. 6 Absolute values of shielding constant and accuracy of M-V model for I. All calculations were performed at different levels of DFT theory and RPA.

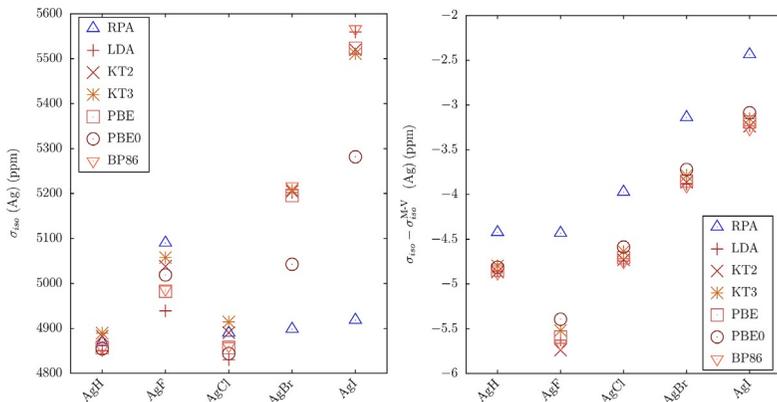


Fig. 7 Absolute values of shielding constant and accuracy of M-V model for Ag. All calculations were performed at different levels of DFT theory and RPA.

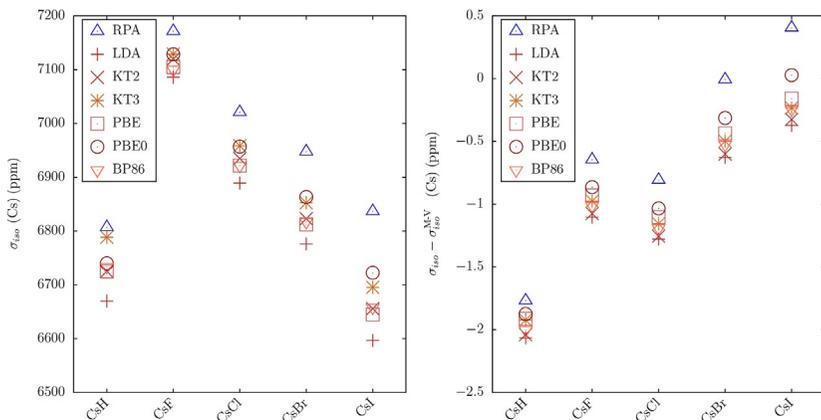


Fig. 8 Absolute values of shielding constant and accuracy of M-V model for Cs. All calculations were performed at different levels of DFT theory and RPA.

H, the accuracy of M-V model is close to 0.1%. One should also remark that there is a small dispersion of DFT values, though in some cases it is not so.

The accuracy in percentage of model M-V for H is the lowest one. This may be due to the fact that the absolute values of $\sigma(\text{H})$ are also the lowest. Relativistic effects are positive and increase $\sigma(\text{H})$. Even though its magnitude for AuH and HI are the largest, in both cases the relative difference between results of four-component and M-V model is the lowest. As will be mentioned below, this may be an indication that model M-V model could be improved including more NR effects, but not only that.

In the case of $\sigma(\text{I})$, we observe that correlation effects are important for IX systems, with $X = \text{F, Cl, Br, I}$ and Au. It is also observed that the dispersion between the DFT values using the model M-V is also a large one.

In the case of the shielding of silver, it is observed that both, relativistic and electron correlation effects are both very important, and they continues to be so for the M-V model. On the contrary, for cesium there is a deshielding when the substituent becomes heavier, though the accuracy of M-V is also increased with the increment of relativistic effects.

6.5 What Is Next?

Is it possible to improve the M-V model? How could it be done? There is no possibility to start from a deep mathematical–physics formalism and then make approximations. We must appeal to a bottom-up type procedure, as was used to obtain model M-V. For doing it one should consider in more details some of the behaviors of previous models.

In Fig. 9 we see that Ramsey–Flygare and M-V models have almost the same behaviour when one consider σ^{NR} for Ramsey–Flygare and the relativistic value of σ for the M-V model. One realize that the Ramsey–Flygare relationship is well defined and coherent when treated completely within the NR domain, and it happens the same when the M-V model is treated completely within the relativistic regime.

When including the comparison of Ramsey–Flygare and M-IV model with the four-component σ some differences do appear. It is observed that $(\nu_K^S - \nu_K^{\text{atom},S})$ is important when heavy elements are involved.

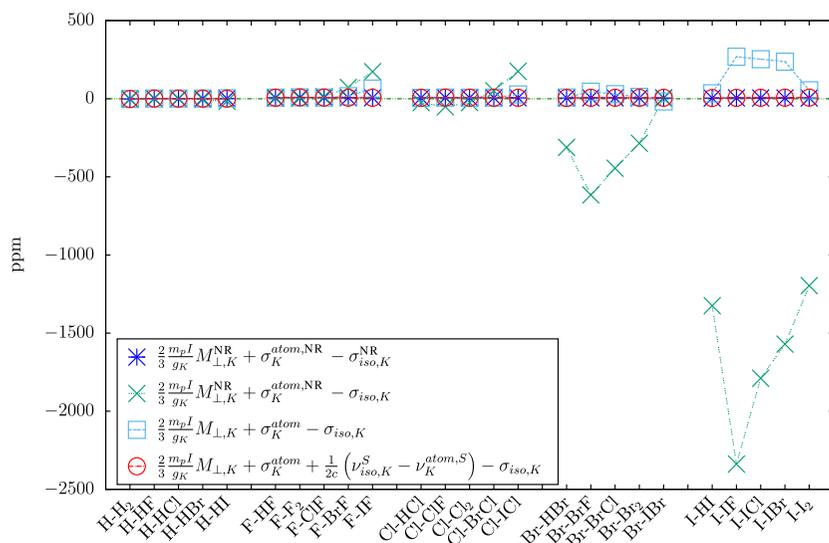


Fig. 9 Accuracy of different relationship between relativistic and NR models. All values at four-component RPA level of approach. The NR values were obtained scaling c to 100 c_0 .

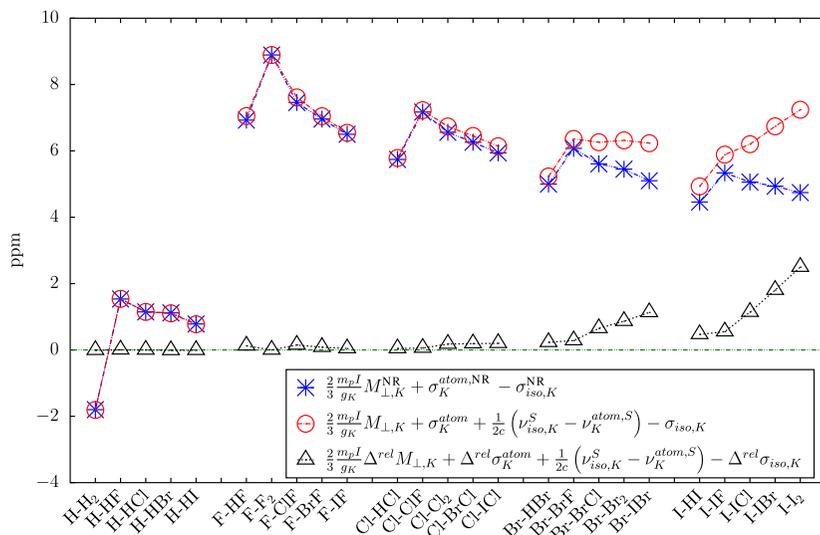


Fig. 10 Accuracy of different relationship between M-V and Ramsey-Flygare models. All values at four-component RPA level of approach. The NR values were obtained scaling c to $100 c_0$.

We claimed above that the improvement of the accuracy of M-V model depends on NR mechanisms, but not only that. In Fig. 10 one observes that there are NR effects that should be introduced but also some new relativistic effects. These relativistic effects do not have an atomic character as observed to the right of such figure. They are close to 2 ppm for I in I_2 being the difference of four-component and M-V model between 5 and 7 ppm for I in the IX series ($X = H, F, Cl, Br, I$).

7. CONCLUDING REMARKS

The two main NMR spectroscopic parameters are such that the indirect spin-spin coupling, J , is difficult to calculate and the nuclear shielding, σ is difficult to measure. At its earliest time theoretical developments were based on the NR framework. On the other hand, results of experiments are relativistic by its nature. It took more than five decades until theoretical and experimental results started to show large differences, specially when heavy-atom containing molecules were studied.

Ramsey was one of the scientists that lead in the beginning theoretical developments in this area of research. His first papers on the theory of J and σ are between the most cited in the history of spectroscopy. He also gave the main models about how to get semiexperimental values of shielding

constants. Flygare applied his ideas to different molecular geometries and then appear the well-known Ramsey–Flygare relationship. It express magnetic shieldings (theoretical/experimental) in terms of SR tensors (theoretical/experimental) in addition to theoretical calculations. In this way one can get theoretical or experimental values of σ .

Once relativistic effects started to be included in reliable calculations of magnetic shieldings, the Ramsey–Flygare relationship was found not to give good enough results. This meant that experimental values of magnetic shieldings could not be based on such a relationship. Then, it started to be necessary to find another model for getting more accurate experimental values. At the same time direct measurement of magnetic shielding started to be routinely available, though for a restricted number of compounds.

Given that most of recent developments on the absolute value of magnetic shieldings were mainly taken by theorist, we have focused on the largest part of this chapter, in the latest theoretical developments. They ended up in a relationship between magnetic shieldings and SR that is valid within the relativistic regime. This is more accurate and coherent than the previous one, and also it works for almost all molecular systems (having them heavy atoms or not).

Four-component (relativistic) theoretical calculations can be performed by using state-of-the-art methodologies that are wave-function-based or DFT-based or polarization propagators. Most of the electronic effects involved (electron correlation, nuclear charge distribution, Breit interactions and QED) and technicalities (converged basis set, kinetic or magnetic balance, gauge origin dependence) are now well established and can be included in usual calculations. What is still unaffordable is the consideration of all this in medium-size heavy-atom containing systems.

The old Ramsey–Flygare relationship state that magnetic shieldings are related with SR tensors, together with the calculation of atomic shieldings. Its relativistic generalization should be such that one must recover its NR expressions when the velocity of light scales to infinity. The first step in the process of generalizing Ramsey–Flygare was the development of the theory to express SR tensors within a relativistic framework. This was fulfilled between the years 2012 and 2013. At that stage, one could consider that the old NR relationship could be replaced by formally identical expressions, but fully relativistic. The main difficulty that was necessary to overcome was the fact that there were no exact perturbative Hamiltonians from which one could relate both spectroscopic properties. In other words, there are no top-down procedure available, and so, a bottom-up one was selected as necessary by some researchers. By applying this kind of procedure it was shown that in addition to formally the same expressions of the NR

case one should include a new relativistic term that does not exist within the NR framework.

In short, one has at hand at the moment accurate four-component methods to calculate magnetic shieldings of heavy-atom containing molecules, and a generalized relationship between magnetic shieldings and SR tensors to obtain semi experimental values of shieldings, and also the possibility to make direct measurement in gas-phase NMR for some special compounds. The precision of calculations is such that one can get theoretical results that are within the error bars of experiments.

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