


Absolute NMR shielding scales in methyl halides obtained from experimental and calculated nuclear spin-rotation constants

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The nonrelativistic “Ramsey-Flygare relationship” is the most used procedure to obtain semiexperimental nuclear magnetic resonance (NMR) absolute shieldings by a correspondence between NMR shieldings (σ) and nuclear spin-rotation constants (M). One of its generalizations to the relativistic framework is known as the M-V model, which was proposed few year ago by some of the authors of the present work and right now is only applied to linear molecules. This model includes terms that do not have nonrelativistic counterparts and also include the paramagnetic contribution to the NMR shielding of nuclei in free atoms. All this ensures that its results fit quite well with those of four-component (4c) calculations. The first application of the M-V model to nonlinear molecules, like methyl halides or CH_3X molecules ($X = \text{F}, \text{Cl}, \text{Br}, \text{and I}$), is given here. The analysis of each electronic mechanism of σ shows that most of their electron correlation effects are strongly related with the same effects in M . By including experimental data of M in the M-V model most of the correlation effects are accurately taken into account for the absolute values of σ . Calculations of M_Y and σ_Y ($Y = \text{H}, \text{C}, \text{and X}$) were carried out within the linear response formalism at the random-phase level of approach and density functional theory in both 4c and nonrelativistic frameworks. The best fits between calculations of M and experimental data are obtained from calculations at 4c-PBE0 level of theory in all cases, but not for $M_{\parallel, \text{Cl}}$, which suggests that a revision of the available experimental data may be necessary. There is an additional advantage of using the M-V model: one can indirectly calculate shieldings of open-shell free atoms, which cannot be obtained at the moment by applying 4c methods.

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I. INTRODUCTION

Nuclear spin-rotation (SR) tensors (M) are accurately measured by microwave spectroscopy. They have been extensively employed to validate many-electron structure calculations in a wide number of molecules and are quite useful in nuclear magnetic resonance (NMR) spectroscopy. The absolute values of NMR magnetic shieldings (σ), which are very difficult to measure, are obtainable from them by applying the widely known “Ramsey-Flygare relationship” [1,2]. This is a relationship between the paramagnetic contribution to the NMR shieldings and the electronic contribution to the SR constants within a nonrelativistic (NR) framework.

During the last decade several groups of research around the world have made contributions that improve the calculation of the absolute shieldings in heavy-atom-containing systems [3–13]. Four-component and two-component methodologies were applied to achieve this goal. One of the last one was the development of the M-V model, which was proposed by our research group [14–16]. There are still some doubts about which methodology gives both more insights on the physics behind the methodology and accurate results, given that one can use different strategies to generalize the Ramsey-Flygare relationship. On the other hand our model was only

applied to linear systems, and it is necessary to enlarge its application to nonlinear molecular systems in order to know whether such a model can be safely used in nongeometrically restricted molecular systems.

As mentioned, Flygare found an indirect way of obtaining absolute shielding constants by combining experimental SR data with some highly accurate calculations [17–19]. He assumed the following:

- (i) The paramagnetic contributions to the shielding constants of free-atom nuclei are null.
- (ii) The NMR shieldings and SR tensors for linear molecules have null elements on the symmetry axis of the molecule.
- (iii) For molecules, there is an equivalence between the perturbative Hamiltonian that describes the interaction of magnetic moments of nuclear spins with an external and uniform magnetic field and the perturbative Hamiltonian that describes electronic effects due to molecular rotation of the nuclei.

Since the earliest theoretical works that included relativistic effects on NMR shieldings, it is known that the first statement is not correct. Besides, it is known that in a relativistic framework the symmetry axis elements of the NMR shielding tensor of a linear molecule are not zero, which violates condition (ii) [20]. These findings together with some accurate experimental data collected by Wasylishen and collaborators suggested that the Ramsey-Flygare relationship is

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not valid when relativistic effects are not negligible [21]. More recently it was shown that the formal expressions of both properties—the NMR magnetic shielding and SR tensors—cannot be explicitly related to each other within the relativistic regime [22]. This means that it is not possible to obtain an exact theoretical relationship among them that would be valid within the relativistic framework. So, one of the abovementioned conditions, the third one, is not fulfilled any longer. Therefore, the Ramsey-Flygare relationship does not work in heavy-atom-containing molecules.

One of the straight ways to generalize it makes use of the *linear response within the elimination of small components* (LRESC) model [23,24]. The development of the M-V model was highly grounded on a bottom-up procedure whose first steps were worked out within the LRESC model. This procedure makes it so that, when the velocity of light, c , is scaled to infinity, the M-V model goes to the Ramsey-Flygare one [14,15,25]. It is also worth mentioning that, in addition to the M-V model, some other models were recently developed in order to extend the applicability of the Ramsey-Flygare relationship to heavy-atom-containing molecules [4,5].

All previous applications of the M-V model to the computation of NMR shieldings have shown that it gives very close results to the four-component (4c) ones for heavy-atom-containing linear molecules [15,16,26]. As a next step of our development of the model M-V we show here how accurate it is to reproduce magnetic shieldings in little more general molecules like the set CH_3X ($X = {}^{19}\text{F}$, ${}^{35}\text{Cl}$, ${}^{79}\text{Br}$, and ${}^{127}\text{I}$), meaning nonlinear compounds. For them we also studied the electronic origin of both electron correlation and relativistic effects on paramagneticlike (or $e-e$) and diamagneticlike (or $p-p$) contributions to both σ and M tensors.

The analysis of the SR constants of both nuclei X and H in CH_3X molecules ($X = \text{F}$, Cl, Br, and I) has been performed in several computational and experimental works. The earliest experimental works applied different techniques: (i) a molecular-beam electric resonance spectrometer to obtain radio-frequency spectra for CH_3F [27], (ii) a molecular-beam maser spectrometer to obtain high-resolution measurements of hyperfine structure on CH_3Cl [28], and (iii) a molecular-beam absorption spectrometer to obtain high-resolution microwave spectra for CH_3Cl [29], CH_3Br [30], and CH_3I [31]. Besides, rotational constants of CH_3Br and CH_3I were obtained with the highest accuracy by combining data taken from rotational spectra and pure quadrupole resonances [32]. The rotational spectra of CH_3I were also observed once more and analyzed in the submillimeter-wave region, being that these data were combined with the microwave and millimeter-wave measurements to determine with high accuracy its rotational constants [33]. Then, combining the data obtained with the Doppler-free double-resonance technique with that of previous Fourier-transform infrared spectroscopy, the molecular constants of CH_3I were again obtained [34]. At the same time the Ramsey-Flygare relationship given in Eq. (4) of Sec. II B of this work was applied to obtain semiexperimental values of NMR shieldings for F [27], Cl [29], Br [30], and I [31].

More recently, the microwave spectra of CH_3Cl were obtained using the Prague millimeter-wave semiconductor spectrometer [35], and furthermore the Lamb-dip technique

was exploited to obtain sub-Doppler resolution, enabling the determination of SR constants with an accuracy that rivals that obtained by molecular-beam electric resonance measurements on CH_3F [36].

Concerning the NMR spectroscopy, Jackowski and coworkers have developed a remarkable methodology to get experimentally based absolute shielding values. They obtained absolute shieldings of ${}^1\text{H}$ and ${}^{13}\text{C}$ in CH_3F [37], CH_3Br [38], and CH_3I [39]. A systematic study of this experimental setup can be found in Ref. [40].

On the theoretical side, relativistic effects on magnetic shieldings of methyl halides were first studied with different methodologies which only included spin-orbit (SO) interactions [41–46]. A more general though two-component perturbative approximation for including relativistic effects on magnetic properties, the LRESC model [23,24], was recently applied to calculate $\sigma({}^{127}\text{I})$, $\sigma({}^{79}\text{Br})$, $\sigma({}^{13}\text{C})$, and $\sigma({}^1\text{H})$ in CH_3Br and CH_3I [47]. This method allows for the consideration of a number of relativistic mechanisms others than the SO one. Another and related recent work was devoted to the study of $\sigma({}^1\text{H})$ and $\sigma({}^{13}\text{C})$ for the family of CH_3X ($X = \text{F}$, Cl, Br, and I) molecules. Quantum chemical calculations were carried out at both *ab initio* and density functional theory (DFT) levels of approach, where relativistic corrections were taken into account at the leading-order Breit-Pauli perturbation level of approach [48].

To our knowledge there are only three papers that contain 4c calculations of σ in methyl halides. In the first one, $\sigma({}^{13}\text{C})$ in CH_3I at 4c-DFT (using the KT3 functional) and random-phase approximation (RPA) levels of theory, and using the gauge-independent atomic orbital (GIAO) scheme, was studied. The authors also calculated $\sigma({}^{13}\text{C})$ with a hybrid method, mixing NR-MP2 and 4c-RPA calculations [49]. Then, in a second paper the same authors extended their work to the analysis of $\sigma({}^{13}\text{C})$ in 70 $\text{CX}_n\text{Y}_{4-n}$ halogenomethanes (with $n = 1, 2, 3$, and 4 and $X, Y = \text{H}, \text{F}, \text{Cl}, \text{Br}$, and I). They performed RPA and DFT 4c calculations (with the OPW91 functional) and also used two hybrid methods (NR-MP2 + 4c-RPA and NR-MP2 + 4c-OPW91) to calculate $\sigma({}^{13}\text{C})$ [50]. The third one is the most recent and is close to the present one. In this work, Uhlíková and Urban [13] have calculated $\sigma(\text{Br})$ and $\sigma(\text{I})$ in CH_3Br and CH_3I using a 4c Dirac-Coulomb Hamiltonian at DFT-BP86 and DFT-PBE levels of approach, together with their NR counterparts. They compared the results of calculations of shieldings and SR constants employing experimental and *ab initio* optimized equilibrium geometries, but then they applied the Ramsey-Flygare relationship to get σ , employing both NR and 4c methods. Another aim of our work is related with the analysis of the consequences that arise on the values of absolute shieldings when they are calculated in this way.

In the following section we treat the equations for NMR shielding and nuclear SR tensors derived within the 4c framework, as well as the relationship between them, both in NR and 4c levels of theory. In Sec. III the computational details for all calculations are given and Sec. IV starts with a comparison of calculated nuclear SR tensor elements with the corresponding experimental data. The accuracy of the M-V model for methyl halides is then analyzed and concluding remarks are given in Sec. V.

II. THEORY

The SR tensor of a nucleus Y , \mathbf{M}_Y , couples the magnetic dipole moment due to nuclear spin with the molecular rotational angular momentum [19,22]. On the other hand, the NMR shielding tensor of a nucleus Y , σ_Y , couples the nuclear magnetic dipole moment with an external uniform magnetic field.

A. Nuclear spin rotation and NMR shielding tensors

The tensor \mathbf{M}_Y in a molecule in equilibrium depends on both nuclear and electronic degrees of freedom: $\mathbf{M}_Y = \mathbf{M}_Y^{\text{nuc}} + \mathbf{M}_Y^{\text{elec}}$ [19,22]. In Gaussian atomic units, which are used throughout the present work, they are written as

$$\mathbf{M}_Y^{\text{nuc}} = \sum_{X \neq Y} \frac{g_Y Z_X}{2m_p c^2} \left[\mathbf{R}_{X,\text{CM}} \cdot \frac{\mathbf{R}_{XY}}{|\mathbf{R}_{XY}|^3} - \mathbf{R}_{X,\text{CM}} \frac{\mathbf{R}_{XY}}{|\mathbf{R}_{XY}|^3} \right] \otimes \mathbf{I}^{-1} \quad (1)$$

and

$$\mathbf{M}_Y^{\text{elec}} = \frac{g_Y}{2m_p c^2} \left\langle \left\langle \left(\frac{\mathbf{r} - \mathbf{R}_Y}{|\mathbf{r} - \mathbf{R}_Y|^3} \times c \boldsymbol{\alpha} \right); \mathbf{J}_e \right\rangle \right\rangle \otimes \mathbf{I}^{-1}. \quad (2)$$

Here, g_Y is the nuclear g value of nucleus Y , Z_X is the atomic number of nucleus X , m_p is the proton mass, c is the speed of light in vacuum, \mathbf{R}_{XY} and $\mathbf{R}_{X,\text{CM}}$ are the position vectors of nucleus X with respect to nucleus Y and the molecular center of mass, respectively, and \mathbf{I} is the molecular moment of inertia tensor in the equilibrium geometry with respect to its center of mass. Furthermore, $\langle \langle ; \rangle \rangle$ stands for the relativistic polarization propagator, $\boldsymbol{\alpha}$ is the Dirac operator, and $\mathbf{J}_e = (\mathbf{r} - \mathbf{R}_{\text{CM}}) \times \mathbf{p} + \frac{1}{2} \boldsymbol{\Sigma}$ is the relativistic electronic total angular momentum operator, which is the sum of the total orbital and spin angular momenta. The orbital angular momentum is taken with respect to the molecular center of mass, and $\boldsymbol{\Sigma}$ is the 4c extension of the Pauli matrices. Then, Eq. (2) can be written as $\mathbf{M}_Y^{\text{elec}} = \mathbf{M}_Y^L + \mathbf{M}_Y^S$.

On the other hand, within the 4c polarization propagator theory (4c-PolProp) σ_Y is written as

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

where \mathbf{R}_G represents the gauge origin position of the magnetic potential.

Working with the 4c-PolProp theory, tensors $\mathbf{M}_Y^{\text{elec}}$ and σ_Y can be approximated as the sum of two terms which contain the following transition moment matrix elements: one that is built between occupied positive-energy orbitals and unoccupied positive-energy orbitals (e - e contributions), and another one that is built between occupied positive-energy orbitals and unoccupied negative-energy orbitals (p - p contributions) [51,52].

B. Relationship between σ and \mathbf{M}

Ramsey and Flygare based their works on the Schrödinger representation. They found a reliable theoretical relationship between σ_Y and \mathbf{M}_Y which is still useful for obtaining absolute shieldings from measured SR constants [1,2,19]. Such a relation, the Ramsey-Flygare relationship, is valid when the

molecules do not contain heavy atoms and are considered as rigid rotors; it is written as

$$\begin{aligned} \sigma_Y &= \sigma_Y^{\text{NR-para}} + \sigma_Y^{\text{NR-dia}} \\ &\approx \frac{m_p}{g_Y} \mathbf{M}_Y^{\text{NR}} \otimes \mathbf{I} + \sigma_Y^{\text{FA,NR}}. \end{aligned} \quad (4)$$

The symbols $\sigma_Y^{\text{NR-para}}$ and $\sigma_Y^{\text{NR-dia}}$ stand for paramagnetic and diamagnetic contributions to the NR shielding, respectively, and $\sigma_Y^{\text{FA,NR}}$ is the shielding of a nucleus Y for a free atom (which has only diamagnetic contributions within the NR domain). Furthermore, results of calculations with the Ramsey-Flygare relationship are more accurate for isotropic values than for individual tensor elements [17–19].

Our main concern here is related with the application of the M-V model to nonlinear molecules. This model is the most accurate of the set of M- i ($i = \text{I to V}$) models whose theoretical grounds are given elsewhere [15,16]. In this model both properties are related as follows:

$$\sigma_Y^{\text{M-V}} = \sigma_Y^{\text{SR}} + \sigma_Y^{\text{FA}} + \frac{1}{2c} (\mathbf{v}_Y^S - \mathbf{v}_Y^{\text{FA,S}}), \quad (5)$$

where

$$\sigma_Y^{\text{SR}} = \frac{m_p}{g_Y} \mathbf{M}_Y \otimes \mathbf{I}, \quad (6)$$

σ_Y^{FA} is the 4c shielding tensor of nucleus Y for the free atom, and both \mathbf{v}_Y^S and $\mathbf{v}_Y^{\text{FA,S}}$ are terms without NR equivalents, where [15]

$$\frac{1}{2c} \mathbf{v}_Y^S = \frac{1}{2c^2} \left\langle \left\langle \left(\frac{\mathbf{r} - \mathbf{r}_Y}{|\mathbf{r} - \mathbf{r}_Y|^3} \times c \boldsymbol{\alpha} \right); \mathbf{S}_e \right\rangle \right\rangle = \frac{m_p}{g_Y} \mathbf{M}_Y^S \otimes \mathbf{I}, \quad (7)$$

being $\mathbf{S}_e = \frac{1}{2} \boldsymbol{\Sigma}$. Besides, $\mathbf{v}_Y^{\text{FA,S}}$ has the same expression as that of \mathbf{v}_Y^S , but refers to the free atom. In addition, the linear response on the right-hand side of Eq. (7) is formally the same as that of \mathbf{M}_Y^S .

One can easily see that Eqs. (4) and (5) are expressed with some similar formal terms. The main difference is that the first one is written within the NR framework, meaning that it includes only scalar terms; instead, the M-V model has all its elements written within the relativistic framework.

We consider two different components of the σ tensors for carbon and halogen nuclei. They are the perpendicular and parallel components relative to the C- X molecular bond axis. Hence,

$$\begin{aligned} \sigma_{\perp(\parallel),Y}^{\text{M-V}(e-e)} &= \frac{m_p I_{\perp(\parallel)}}{g_Y} \mathbf{M}_{\perp(\parallel),Y}^{\text{elec}(e-e)} + \sigma_Y^{\text{FA}(e-e)} \\ &\quad + \frac{1}{2c} (\mathbf{v}_{\perp(\parallel),Y}^{S(e-e)} - \mathbf{v}_Y^{\text{FA},S(e-e)}) \end{aligned} \quad (8)$$

and

$$\begin{aligned} \sigma_{\perp(\parallel),Y}^{\text{M-V}(p-p)} &= \frac{m_p I_{\perp(\parallel)}}{g_Y} (\mathbf{M}_{\perp(\parallel),Y}^{\text{nuc}} + \mathbf{M}_{\perp(\parallel),Y}^{\text{elec}(p-p)}) + \sigma_Y^{\text{FA}(p-p)} \\ &\quad + \frac{1}{2c} (\mathbf{v}_{\perp(\parallel),Y}^{S(p-p)} - \mathbf{v}_Y^{\text{FA},S(p-p)}). \end{aligned} \quad (9)$$

Then, the isotropic shielding constants for H, C, and X nuclei are expressed as

$$\sigma_{\text{iso},Y}^{\text{M-V}} = \sigma_{\text{iso},Y}^{\text{SR}} + \sigma_Y^{\text{FA}} + \frac{1}{2c} (\mathbf{v}_{\text{iso},Y}^S - \mathbf{v}_Y^{\text{FA,S}}). \quad (10)$$

TABLE I. Equilibrium bond distances and angles for CH_3X ($X = {}^{19}\text{F}$, ${}^{35}\text{Cl}$, ${}^{79}\text{Br}$, and ${}^{127}\text{I}$) molecules.

	CH_3F	CH_3Cl	CH_3Br	CH_3I
C–H (in Å)	1.095	1.090	1.086	1.084
C–X (in Å)	1.382	1.785	1.933	2.132
$\theta(\text{HCH})$	110.45°	110.8°	111.2°	111.2°

III. COMPUTATIONAL DETAILS

Gas phase experimental geometries, determined by microwave and infrared spectroscopies and taken from Ref. [53], were considered for CH_3X ($X = {}^{19}\text{F}$, ${}^{35}\text{Cl}$, ${}^{79}\text{Br}$, and ${}^{127}\text{I}$) molecules. The equilibrium bond distances and angles are given in Table I.

Furthermore, calculations of SR constants were performed with values of nuclear g factors taken from Ref. [54]: 5.585 694 for ${}^1\text{H}$, 1.404 824 for ${}^{13}\text{C}$, 5.257 736 for ${}^{19}\text{F}$, 0.547 916 for ${}^{35}\text{Cl}$, 1.404 267 for ${}^{79}\text{Br}$, and 1.125 309 for ${}^{127}\text{I}$. Four-component calculations of σ , \mathbf{M} , and \mathbf{v}^S were performed with the DIRAC program package [55,56]. All of them were based on the Dirac-Coulomb Hamiltonian, employing the default choice for a Hamiltonian of the DIRAC code. It uses an energy correction to avoid the explicit calculation of $(\text{SS} | \text{SS})$ integrals [57].

In all calculations, Dyall's relativistic acv4z basis sets (dyall.acv4z) were employed for hydrogen [58], fluorine, carbon, chlorine [59], bromine, and iodine [60], together with uncontracted Gaussian basis sets and the common gauge-origin (CGO) approach (additional calculations employing GIAOs are given in the Supplemental Material [61]). The small component basis sets for relativistic calculations were generated by applying the unrestricted kinetic balance prescription [52]. In addition, the Gaussian nuclear charge distribution was used [62].

Most of response calculations have been carried out at the 4c-PolProp-RPA level of approach employing Dirac Hartree-Fock (DHF) wave functions. Nonrelativistic values of σ and \mathbf{M} (reported here as $\sigma^{\text{NR-para}}$, $\sigma^{\text{NR-dia}}$, and $\mathbf{M}^{\text{NR-elec}}$) were obtained scaling the speed of light to $c = 100c_0$. The value of the speed of light in vacuum used throughout all 4c calculations was $c_0 = 137.035\,999\,8$ a.u.

The gauge origin for the external magnetic potential was always placed at the molecular center of mass. Then a direct comparison with the SR results could be safely made. Furthermore, the values of σ^{FA} and $\mathbf{v}^{\text{FA},S}$ were calculated for the following anions: ${}^{19}\text{F}^-$, ${}^{35}\text{Cl}^-$, ${}^{79}\text{Br}^-$, and ${}^{127}\text{I}^-$, instead of the neutral atoms in order to consider closed-shell systems.

The influence of electron correlation effects was studied through Dirac Kohn-Sham DFT calculations performed employing the DIRAC code. DFT calculations were also based on the 4c Dirac-Coulomb Hamiltonian and were done using a variety of NR exchange-correlation functionals in the following categories: (i) the generalized-gradient-approximation functionals KT3 [63] and BP86 [64,65], and (ii) the hybrid functional PBE0 [66].

IV. RESULTS AND DISCUSSION

In this section, 4c calculations of SR constants at RPA and DFT levels of theory are compared with available experimental data for hydrogen and halogen atoms. Afterwards, each term of $\sigma_Y^{\text{M-V}}$ is analyzed separately in order to learn about the underlying physics that may be influencing both the paramagneticlike (e - e) and the diamagneticlike (p - p) contributions to σ_Y . In line with this, results of 4c calculations of the isotropic shieldings are compared with those obtained from the application of the M-V model. Then, an analysis of semiexperimental values of absolute shieldings is introduced, where experimental SR constants are included in the M-V model together with highly accurate calculations of σ_Y^{FA} and $\frac{1}{2c}(\mathbf{v}_{\text{iso},Y}^S - \mathbf{v}_Y^{\text{FA},S})$ to obtain values of $\sigma_{\text{iso},Y}^{\text{M-V}}$ (semiexpt). In the last subsection we give an analysis of the electronic origin of \mathbf{M}_C and σ_C for ${}^{13}\text{C}$.

A. Four component calculations of the tensor \mathbf{M}

Results of calculations of parallel and perpendicular components of \mathbf{M}_X , and the isotropic contribution to \mathbf{M}_H , are displayed in Table II. We start analyzing \mathbf{M}_X . As expected, relativistic effects in \mathbf{M}_X increase as Z_X becomes higher. Besides, those effects have opposite signs on the perpendicular and parallel tensor elements. This fact implies that relativistic effects on isotropic values of \mathbf{M}_X become smaller than the ones in each component.

Results of calculations at the 4c-PBE0 level of theory are, by far, the best fitting to experimental data. Those values are within error bars of experiments for both perpendicular and parallel components of the nuclear spin-rotation tensor and for all nuclei, but not for the chlorine nucleus in CH_3Cl . For this last case, a discrepancy between calculated and experimental values is found, even if the experimental error bar is particularly large. So it may be interesting to know whether new measurements can confirm which one of both numbers is the most accurate.

Furthermore, only 4c calculations reproduce in an adequate manner the experimental anisotropies of the SR tensor of halogens, i.e., the differences between $M_{\perp,X}$ and $M_{\parallel,X}$, as it can be seen from results given in Table II. In order to be more clear about this fact, we take the iodine nucleus as an example. The experimental value of its anisotropy is (-0.298 ± 0.097) kHz, whereas the NR-PBE0 and 4c-PBE0 calculations give -3.4299 and -0.2693 kHz, respectively.

Concerning electron correlations our results show that they are larger than the relativistic effects in all cases. These last ones are less than 1.6 kHz for $M_{\perp,X}$ and up to 3.0 kHz for $M_{\parallel,X}$. On the other hand, correlation effects are 6.0 kHz at most for both perpendicular and parallel components of \mathbf{M}_X .

Turning now to the analysis of the isotropic values of \mathbf{M}_H we want first to highlight that both effects, relativistic and electron correlation, are very small. This behavior is different from the one observed in hydrogen halides. In these last molecules the HALA effects (due to the inclusion of relativity in the calculations) strongly contribute to \mathbf{M}_H [67]. This means that, for methyl halides, heavy-atom effects are not efficiently transmitted through two-bonds. Again electron correlation effects are higher than the relativistic ones. On the

TABLE II. Results (in kHz) of NR and 4c calculations of $M_{\perp}(X)$, $M_{\parallel}(X)$, and $M_{\text{iso}}(H)$ for CH_3X molecules ($X = \text{F, Cl, Br, and I}$).

Molec	Nuc	Comp	NR				4c				Expt.
			RPA	BP86	PBE0	KT3	RPA	BP86	PBE0	KT3	
CH ₃ F	F	⊥	6.2594	2.4380	3.7170	0.0005	6.2557	2.4360	3.7149	-0.0134	4.50 ± 0.58 ^a
	F	∥	-45.0782	-65.0642	-57.4576	-63.7227	-45.2198	-65.2510	-57.6251	-63.9125	-55.7 ± 1.2 ^a
	H	iso	5.6462	5.2498	5.3795	5.3746	5.6603	5.2676	5.3957	5.3933	
CH ₃ Cl	Cl	⊥	-1.8819	-2.6344	-2.3548	-2.5833	-1.8772	-2.6332	-2.3525	-2.5854	-2.150 ± 0.063 ^b
	Cl	∥	-3.6698	-5.0344	-4.5309	-4.9215	-3.7069	-5.0948	-4.5833	-4.9827	-7.0 ± 1.6 ^c
	H	iso	5.6034	5.3640	5.4383	5.4873	5.6209	5.3881	5.4601	5.4874	
CH ₃ Br	Br	⊥	-10.1826	-14.5261	-12.9952	-14.2724	-9.8760	-14.4345	-12.8472	-14.2405	-12.63 ± 0.10 ^d
	Br	∥	-14.3106	-19.9670	-17.9759	-19.9978	-15.0453	-21.2517	-19.0814	-21.2982	-18.8 ± 1.7 ^d
	H	iso	5.5808	5.3708	5.4342	5.4653	5.6241	5.4388	5.4952	5.5365	
CH ₃ I	I	⊥	-14.8484	-19.9219	-18.0681	-19.5614	-13.2497	-19.5386	-17.4197	-19.2467	-17.398 ± 0.0475 ^e
	I	∥	-11.5564	-16.1591	-14.6382	-16.4485	-13.0986	-19.0835	-17.1504	-19.4188	-17.10 ± 0.085 ^e
	H	iso	5.6514	5.5083	5.5236	5.5599	5.6915	5.5702	5.6111	5.6652	

^aTaken from Ref. [36].

^bTaken from Ref. [35].

^cTaken from Ref. [29].

^dTaken from Ref. [30].

^eTaken from Ref. [34]. Standard deviations are computed as one half of the reported errors.

other hand, electron correlation effects grow up in the opposite direction as compared to the relativistic effects, meaning from CH₃I to CH₃F.

B. Accuracy of the M-V model

Since 2016, the M-V model was successfully applied to a few sets of linear molecules which include the following dihalogen molecules: XY ($X, Y = \text{H, F, Cl, Br, I, and At}$) [15], and some others like UV ($U = \text{Li, Na, K, Rb, Cs, Cu, Ag, Au, H, F, Cl, Br, and I}$; $V = \text{H and I}$), and AgZ and CsZ ($Z = \text{H, F, Cl, Br, and I}$) [16]. In those cases, NMR shielding constants were accurately reproduced. So, if the same happens also for methyl halides it would mean that our model could also be safely applied to some nonlinear molecules.

In Table III perpendicular and parallel tensor elements of σ_X , in terms of ($e-e$) and ($p-p$) contributions, are given.

TABLE III. Calculated values (in ppm) of \perp and \parallel components of σ_X and $\sigma_X^{\text{M-V}}$ in terms of their ($e-e$) and ($p-p$) contributions. Four-component calculations were performed at the RPA level of approach.

	$\sigma_X^{(e-e)}$	$\sigma_X^{\text{M-V}(e-e)}$	$\Delta^{(e-e)}$	$\sigma_X^{(p-p)}$	$\sigma_X^{\text{M-V}(p-p)}$	$\Delta^{(p-p)}$
	X = F					
⊥	6.14	6.40	-0.26	505.19	519.11	-13.92
∥	-48.31	-48.18	-0.13	489.33	479.41	9.92
	X = Cl					
⊥	-222.18	-221.79	-0.39	1157.30	1166.89	-9.59
∥	9.66	9.76	-0.10	1129.47	1125.35	4.12
	X = Br					
⊥	-173.30	-172.34	-0.96	2956.06	2963.95	-7.89
∥	411.54	411.78	-0.24	2920.03	2916.75	3.28
	X = I					
⊥	516.04	517.64	-1.60	4932.43	4939.19	-6.76
∥	1599.67	1600.09	-0.42	4894.33	4892.44	1.89

The same occurs with $\sigma_X^{\text{M-V}}$. The differences among the ($e-e$) contributions to σ_X and $\sigma_X^{\text{M-V}}$ increase as Z_X grows, whereas the opposite trend is found for the differences between their ($p-p$) contributions. They are less than 1.6 ppm (in absolute values) for all halogen atoms. Besides, the M-V model better reproduces the values of $\sigma_{\parallel,X}^{(e-e)}$ than those of $\sigma_{\perp,X}^{(e-e)}$. Furthermore, in agreement with earlier works [17,18], the differences in the ($p-p$) contributions of both components, i.e., $\sigma_{\perp,X}^{(p-p)} - \sigma_{\perp,X}^{\text{M-V}(p-p)}$ and $\sigma_{\parallel,X}^{(p-p)} - \sigma_{\parallel,X}^{\text{M-V}(p-p)}$, have opposite signs. Then, the M-V model reproduces $\sigma_{\text{iso},X}^{(p-p)}$ better than their individual tensor elements. The same behavior is found in the NR Ramsey-Flygare relationship [14,17–19]. The behaviors of the ($e-e$) contributions to σ_X and to each one of the three terms of the right-hand side of Eq. (5) are shown in Fig. 1. According to the Ramsey-Flygare relationship, the NR limit of $\sigma_X^{(e-e)}$ (which is equal to $\sigma_X^{\text{NR-para}}$) is such that the last two terms of that equation are zero. This fact allows us to realize that relativistic effects in $M_X^{(e-e)}$ are much smaller than those in $\sigma_X^{(e-e)}$ (see Fig. 1). The highest relativistic effects (in percentage) appear for $M_{\parallel,I}^{(e-e)}$ (12.8%) followed by $M_{\perp,I}^{(e-e)}$ (10.4%). Besides, for all cases other than iodine the relativistic effects in $M_{\perp,X}^{(e-e)}$ and $M_{\parallel,X}^{(e-e)}$ are smaller than 5%.

In addition, it is clearly seen that relativistic effects in $\sigma_X^{(e-e)}$ grow up from fluorine to iodine, and this occurs for both perpendicular and parallel tensor components. In particular, relativistic effects in $\sigma_{\parallel,I}^{(e-e)}$ contribute around 1662.00 ppm. According to the M-V model, this quite large value (its NR limit is $\sigma_{\parallel,I}^{\text{NR-para}} = -62.55$ ppm) is mainly due to the core contribution of $\sigma_{I-}^{\text{FA}(e-e)}$, whose NR limit is equal to zero.

In order to highlight the accuracy of our model we performed a deeper analysis of the shielding of the iodine nucleus in methyl iodide. Calculations of $\frac{m_p I}{g_I} (M_{\perp,I}^{(e-e)} - M_{\perp,I}^{\text{NR-elec}})$, $\sigma_{I-}^{\text{FA}(e-e)}$, and $\frac{1}{2c} (v_{\perp,I}^{S(e-e)} - v_{I-}^{\text{FA},S(e-e)})$ at the RPA level of approach give [as shown in Fig. 1(a)] 171.73, 1913.47, and 81.81 ppm, respectively. The addition of all of them gives 2167.01

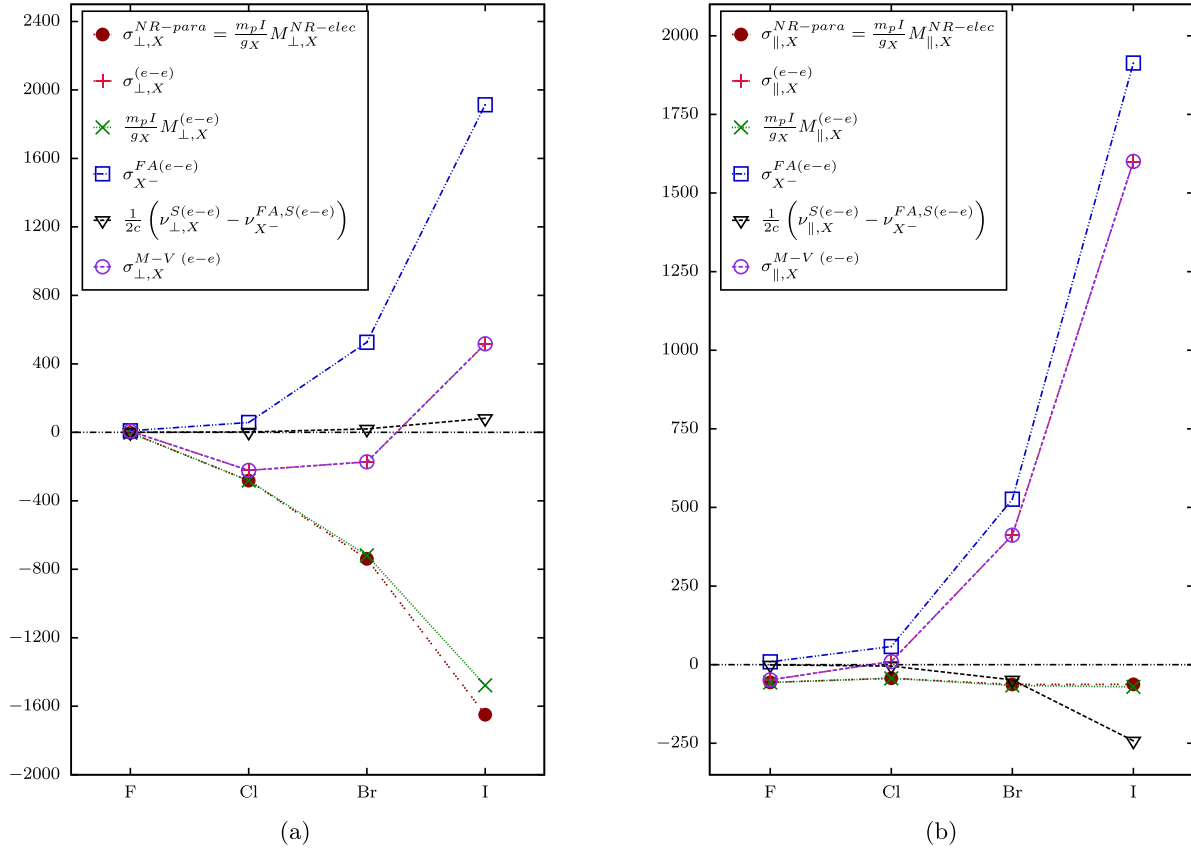


FIG. 1. (a) Perpendicular ($e-e$) and (b) parallel ($e-e$) tensor contributions (in ppm) to $\sigma_X^{(e-e)}$, $M_X^{(e-e)}$, $\sigma_X^{FA(e-e)}$, and $\nu_X^{S(e-e)} - \nu_X^{FA,S(e-e)}$ for the X nuclei in CH_3X molecules ($X = \text{F}, \text{Cl}, \text{Br}, \text{and I}$). Calculations were performed at the relativistic RPA level of approach. Values of $\sigma_X^{NR-para}$ are also displayed.

ppm, and the relativistic effect in $\sigma_{\perp, I}^{(e-e)}$ (i.e., $\sigma_{\perp, I}^{(e-e)} - \sigma_{\perp, I}^{NR-para}$) is 2165.41 ppm. Therefore, the difference between relativistic effects of $\sigma_{\perp, I}^{(e-e)}$ and $\sigma_{\perp, I}^{M-V(e-e)}$ amount to only -1.60 ppm, meaning that it is less than 0.1% (as seen in Table III). Then, it can safely be stated that the M-V model accurately reproduces the relativistic effects for $\sigma_{\perp, I}^{(e-e)}$.

Furthermore, the application of our model to the study of $\sigma_{\parallel, I}^{(e-e)}$ gives even better results. In Eq. (8) it is seen that relativistic effects arise from the following three factors: $\frac{m_p I}{g_I} (M_{\parallel, I}^{(e-e)} - M_{\parallel, I}^{NR-elec})$, $\sigma_{I-}^{FA(e-e)}$, and $\frac{1}{2c} (\nu_{\parallel, I}^{S(e-e)} - \nu_{I-}^{FA,S(e-e)})$. Their 4c-RPA values are -8.25 , 1913.47 , and -242.80 ppm, respectively [see Fig. 1(b)], being the addition of the three equal to 1662.42 ppm, while $\sigma_{\parallel, I}^{(e-e)} - \sigma_{\parallel, I}^{NR-para} = 1662.00$ ppm. So, in this case the difference between them is -0.42 ppm (as reported in Table III).

Concerning the ($p-p$) contributions [see Eq. (9)], we observe that relativistic contributions to $\sigma_{\perp, Y}^{(p-p)}$ are mainly given by those of $\sigma_Y^{FA(p-p)}$. In the special case of iodine we found that there is an accurate matching between 4c and the M-V values at the RPA level of approach (see Table III). Besides, $\sigma_{I-}^{FA(p-p)} = 4890.21$ ppm, $\sigma_{\perp, I}^{(p-p)} = 4932.43$ ppm, and $\sigma_{\parallel, I}^{(p-p)} = 4894.33$ ppm, so that almost the whole contribution to $\sigma_{\perp, Y}^{(p-p)}$ is of an atomic nature. Therefore, we note that ($p-p$) contributions to shieldings are such that (i) they are almost completely described by $\sigma_Y^{FA(p-p)}$ and (ii) the parallel and perpendicular

tensor elements have values of $\sigma^{(p-p)} - \sigma^{M-V(p-p)}$ with opposite signs (see Table III). Then the value of $\sigma_{iso}^{(p-p)} - \sigma_{iso}^{M-V(p-p)}$ is highly reduced, as happens when calculations are performed within the NR regime [17,18].

An additional point must be raised here. The error introduced by including NMR shieldings of anions instead of the shielding of neutral free atoms, as it should be, can be estimated working within the NR regime. As an example, for iodine such a difference is found to be between -5.3 and -5.1 ppm, according to the level of theory employed (see Supplemental Material [61]). Even though such differences (calculation of anions instead of neutral atoms) do not change the main statements pointed out above, they do contribute to a better reproduction of isotropic values by employing the M-V model.

C. Isotropic shieldings and spans of halogens

The application of the M-V model gives new and powerful tools to the analysis of the electronic origin of the relativistic effects on $\sigma_{iso, X}$. As we did above, we analyze now the ($e-e$) and ($p-p$) contributions to it.

First of all we should highlight here that $\sigma_{iso, X}^{(e-e)}$ represents only up to 15% of the total shielding for iodine (7% for bromine, 23% for chlorine, and 10% for fluorine). This means that the ($p-p$) term gives the largest contribution, being its

$M_{\text{iso},X}^{(p-p)}$ values are almost zero in all cases, as expected [22,67]. Besides, as stated recently in Ref. [15], the differences $\nu_{\text{iso},X}^{S(p-p)} - \nu_X^{\text{FA},S(p-p)}$ are also vanishingly small. Therefore, $\sigma_{\text{iso},X}^{\text{M-V}(p-p)} \approx \frac{m_p}{3g_X} \text{Tr}(\mathbf{M}_X^{\text{nuc}} \otimes \mathbf{I}) + \sigma_X^{\text{FA}(p-p)}$, being that this expression is close to the Ramsey-Flygare relationship for $\sigma_{\text{iso},X}^{\text{NR,dia}}$ [17,18]. Furthermore, almost all (more than 99%) of the relativistic effects of $\sigma_{\text{iso},X}^{(p-p)}$ come from the relativistic effects of $\sigma_X^{\text{FA}(p-p)}$. These effects become larger as Z_X increases, being less than 13% in the case of iodine.

The NR limits of both $\sigma_{\text{iso},X}^{(e-e)}$ and $M_{\text{iso},X}^{L(e-e)}$ fulfill the Ramsey-Flygare relationship but their corresponding relativistic effects have opposite signs. This is what underlies the breakdown of that well-known relation when heavy atoms are involved. On the other hand, the values of $\sigma_{\text{iso},X}^{\text{M-V}(e-e)}$ have a very good agreement with those of $\sigma_{\text{iso},X}^{(e-e)}$. This is so because the M-V model includes the contributions (from largest to smallest) of $\sigma_X^{\text{FA}(e-e)}$, $M_{\text{iso},X}^{S(e-e)}$, and $\nu_{\text{iso},X}^{S(e-e)} - \nu_X^{\text{FA},S(e-e)}$, which are all zero in the NR limit. It is worth stressing that all of them are important in order to get the values of $\sigma_{\text{iso},X}^{\text{M-V}(e-e)}$ close to $\sigma_{\text{iso},X}^{(e-e)}$ (see Supplemental Material [61]). In the case of iodine, for instance, when $\sigma_X^{\text{FA}(e-e)}$ and $\nu_{\text{iso},X}^{S(e-e)} - \nu_X^{\text{FA},S(e-e)}$ are neglected, 95% of the relativistic effects of $\sigma_{\text{iso},I}^{(e-e)}$ are not included. This means that the relativistic effects of $M_{\text{iso},I}^{(e-e)}$ represent only around 5% of the relativistic effects of $\sigma_{\text{iso},I}^{(e-e)}$. Therefore, the inadequate replacement of $M_{\text{iso},X}^{\text{NR-para}}$ by $M_{\text{iso},X}^{(e-e)}$ as equivalent to the NR Ramsey-Flygare relationship (a proposal recently adopted in several works) gives incomplete and, therefore, wrong results [4,6,9,13].

We start now the analysis of correlation effects in $\sigma_{\text{iso},X}$ employing the M-V model. Among 97.0% and 101.5% of the correlation effects on both $\sigma_{\text{iso},X}^{(e-e)}$ and $M_{\text{iso},X}^{L(e-e)}$ have a similar electronic origin (see Supplemental Material [61]).

This means that when electron correlation effects are accurately included in $M_X^{(e-e)}$, much of these effects will be included in $\sigma_{\text{iso},X}^{(e-e)}$. On the other hand, correlation effects for $\sigma_X^{\text{FA}(p-p)}$, which are the main contributions to $\sigma_{\text{iso},X}^{(p-p)}$, are smaller than 0.5% (see Supplemental Material [61]).

All these findings can be summarized as follows: (i) relativistic effects in $M_{\text{iso},X}^{(e-e)}$ represent only a small fraction of its contributions to $\sigma_{\text{iso},X}^{(e-e)}$, whereas most of them are due to $\sigma_X^{\text{FA}(e-e)}$; (ii) correlation effects are almost of the same value for $\frac{m_p}{3g_X} \text{Tr}(\mathbf{M}_X^{(e-e)} \otimes \mathbf{I})$ and $\sigma_{\text{iso},X}^{(e-e)}$; (iii) $\sigma_{\text{iso},X}^{(p-p)}$ is mostly independent of electronic correlation effects, and (iv) relativistic effects on $\sigma_{\text{iso},X}^{(p-p)}$ are smaller than 13%. Then, one can estimate the accuracy of the M-V model to reproduce the total values of isotropic shieldings of halogen atoms in methyl halides by knowing that $\frac{\sigma_{\text{iso},X}^{\text{M-V}} - \sigma_{\text{iso},X}^{(e-e)}}{\sigma_{\text{iso},X}^{(e-e)}}$ is smaller than 0.013 for fluorine, 0.006 for chlorine, 0.002 for bromine, and 0.001 for iodine.

The analysis of the anisotropy of the shielding can be performed from the span (Ω) of the halogen nuclei in methyl halides (i.e., $\Omega_X = \sigma_{\perp,X} - \sigma_{\parallel,X}$) employing the M-V model. In Fig. 2 the accuracy of this model in reproducing the 4c values of the shielding's span is observed. The small differences between them are almost completely given by their (p-p) contributions, as can be seen in Table III.

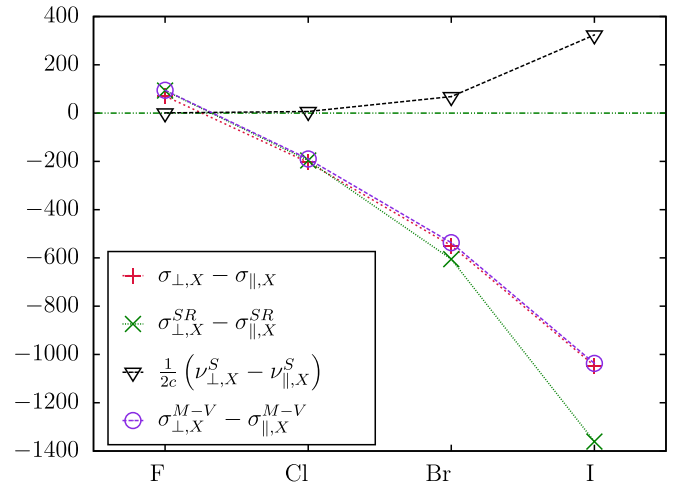


FIG. 2. 4c RPA values of the spans of NMR shielding, SR tensors, and results using the M-V model (i.e., perpendicular minus parallel contributions to σ_X , M_X , and $\sigma_X^{\text{M-V}}$) in CH_3X molecules ($X = \text{F}, \text{Cl}, \text{Br}, \text{and I}$). All values are given in ppm.

Another fact that Fig. 2 highlights is the crucial role that ν_X^S plays in the reproduction of the 4c values of Ω_X . The 4c-RPA value of $\frac{1}{2c}(\nu_{\perp,I}^S - \nu_{\parallel,I}^S)$ in methyl iodide is 323.87 ppm, whereas $\Omega_I = -1045.53$ ppm for this molecule. This not only indicates how important the relativistic effects are for accurately reproducing the values of spans (because ν^S is always zero in the NR limit), but even more important is that it confirms that ν^S cannot be neglected to accurately reproduce the complete NMR shielding tensor from its relation with the SR tensor.

D. New semiexperimental absolute values of σ_X

From the three terms of Eq. (10) only one, the first one, can be taken either from calculations or from experiments. Including its values from experiments, semiexperimental values of $\sigma_{\text{iso},X}$ are obtained and given in Table IV. The main differences among theoretical and experimental values of $\sigma_{\text{iso},X}^{\text{SR}}$ [see Eq. (6)], shown in the second column of Table IV, are mainly due to the discrepancies between experimental data and the calculated values of $M_{\perp,X}$ (and not $M_{\parallel,X}$, because $I_{\perp} > I_{\parallel}$). As observed in Table II the best agreement between $M_{\perp,X}^{\text{expt}}$ and their calculated counterparts is found for iodine in CH_3I at the DFT-PBE0 level of theory, being the same behavior observed in Table IV.

On the other hand, the second term of Eq. (10) cannot be directly obtainable employing the DIRAC code because linear response calculations for open-shell electronic structures (as halogens are) are not currently implemented in it. Then, they can be estimated as the sum of two terms: (i) the shielding of the ionized closed-shell atom instead of the neutral atom, i.e., $\sigma_{X^-}^{\text{FA}}$, and (ii) the NR correction given by $\Delta\sigma_X^{\text{FA,NR}} = \sigma_X^{\text{FA,NR}} - \sigma_{X^-}^{\text{FA,NR}}$, where $\sigma_X^{\text{FA,NR}}$ is calculated as a NR electronic ground-state expectation value.

Concerning how important are electron correlation effects on the absolute values of the shieldings, one should first realize that the correlation effects are naturally included in

TABLE IV. Semiexperimental values of $\sigma_{\text{iso},X}$ obtained from experimental values of SR constants taken from Table II and 4c-DFT-PBE0 calculations of σ_X^{FA} , $\nu_{\text{iso},X}^S$, and $\nu_X^{\text{FA},S}$ for halogens in methyl halides. Results are in ppm.

	$\sigma_{\text{iso},X}^{\text{SR}}(\text{expt})^a$	σ_X^{FA}	$\Delta\sigma_X^{\text{FA,NR}^b}$	$\Delta\nu_X^S{}^c$	$\sigma_{\text{iso},X}^{\text{M-V}}(\text{semiexpt})$
F	-0.60 ± 1.91 [−4.86] ^d	481.68	−9.62	−0.01	471.45 ± 1.91 [471.64] ^e [470.98] ^f
Cl	-205.64 ± 6.85 [−213.96] ^d	1179.41	−6.77	−0.07	966.93 ± 6.85 [960.21] ^e
Br	-596.28 ± 3.98 [−606.43] ^d	3439.70	−6.08	−2.73	2834.61 ± 3.98 [2825.92] ^e [2460.2] ^g
I	-1280.21 ± 2.42 [−1281.90] ^d	6800.30	−5.28	−25.69	5489.12 ± 2.42 [5487.96] ^e [4261.3] ^g

^aObtained as $\frac{m_p}{3g_X} \text{Tr}(\mathbf{M}_X^{\text{expt}} \otimes \mathbf{I})$, where $\mathbf{M}_X^{\text{expt}}$ are taken from the last column of Table II.

^b $\Delta\sigma_X^{\text{FA,NR}} = \sigma_X^{\text{FA,NR}} - \sigma_X^{\text{FA}}$ is the difference between NR-PBE0 shielding of neutral and ionized atoms (see Supplemental Material [61]).

^c $\Delta\nu_X^S = \frac{1}{2c}(\nu_{\text{iso},X}^S - \nu_X^{\text{FA},S})$.

^dFour-component PBE0 calculation (see Supplemental Material [61]).

^eFour-component PBE0 calculation of $\sigma_{\text{iso},X}$ (see Supplemental Material [61]).

^fExperimental value taken from Ref. [37].

^gFour-component BP86 calculation of $\sigma_X^{\text{dia}} + \sigma_X^{\text{SR}}$. Taken from Ref. [13].

experimental data. So, the semiexperimental values of absolute NMR shieldings given in Table IV do include most of such effects.

The way to include relativistic effects requires a special analysis. This will also shed some light on the reasons for the differences between our results and the ones recently published by Uhlířková and Urban [13]. In order to find the absolute isotropic shielding constants of bromine and iodine, they calculated $\sigma_{\text{iso},X}^{(e-e)}$, $\sigma_{\text{iso},X}^{(p-p)}$, and $\frac{m_p}{3g_X} \text{Tr}(\mathbf{M}_X^{\text{elec}} \otimes \mathbf{I})$ (in their work, σ^{para} , σ^{dia} , and σ^{SR} , respectively) at the 4c-DFT-BP86 level of theory and employed *ab initio* optimized geometries. They also obtained NR values by scaling the speed of light 100 times its real value. Even though their results were obtained using geometries and basis sets other than those employed in the present work, an appropriate comparison with ours is still valid. In their Table 5, they compare calculations of $\sigma_{\text{iso},X}$ (i.e., $\sigma_{\text{iso},X}^{(e-e)} + \sigma_{\text{iso},X}^{(p-p)}$) and $\frac{m_p}{3g_X} \text{Tr}(\mathbf{M}_X^{\text{elec}} \otimes \mathbf{I}) + \sigma_{\text{iso},X}^{(p-p)}$ with values of shieldings mentioned as “experimental,” being those obtained by the application of the NR Ramsey-Flygare relationship [our Eq. (4)] and including experimental SR constants [30,31]. They stated that Eq. (4) “can be used to determine the absolute nuclear shielding using a specific correction value, which will depend on the position of an element in the periodic table” [13]. Such a correction value should be related to $\sigma_{\text{iso},X}^{(e-e)} - \frac{m_p}{3g_X} \text{Tr}(\mathbf{M}_X^{\text{elec}} \otimes \mathbf{I})$, and following Eq. (8) of our model, this is equal to $\sigma_X^{\text{FA}(e-e)} + \frac{1}{2c}(\nu_{\text{iso},X}^{S(e-e)} - \nu_X^{\text{FA},S(e-e)})$ (note that according to Ref. [22], $\mathbf{M}_X^{\text{elec}(p-p)}$ is almost negligible in all cases). Then, this “specific correcting value” should be related to an atomic contribution ($\sigma_X^{\text{FA}(e-e)} - \frac{1}{2c}\nu_X^{\text{FA},S(e-e)}$) together with another term that depends on the environment ($\frac{1}{2c}\nu_{\text{iso},X}^{S(e-e)}$) [15,16,26].

The calculated values of $\frac{m_p}{3g_X} \text{Tr}(\mathbf{M}_X^{\text{elec}} \otimes \mathbf{I}) + \sigma_{\text{iso},X}^{(p-p)}$ published in Ref. [13] are closer to the experimental values of $\sigma_{\text{iso},X}^{\text{exp}}$ published a long time ago in Refs. [30,31] than to those of $\sigma_{\text{iso},X}^{(e-e)} + \sigma_{\text{iso},X}^{(p-p)}$. Nevertheless, this is in contrast with our findings because our calculated values of $\sigma_{\text{iso},X}$ are in very good agreement with $\sigma_{\text{iso},X}^{\text{M-V}}(\text{semiexpt})$ and far from

$\frac{m_p}{3g_X} \text{Tr}(\mathbf{M}_X^{\text{elec}} \otimes \mathbf{I}) + \sigma_{\text{iso},X}^{(p-p)}$ (see Table IV and Supplemental Material [61]).

According to this analysis the M-V model is useful not only for obtaining semiexperimental absolute values of NMR shieldings but also for learning more about the physics that is behind such a magnetic property.

E. Absolute shieldings of ^{13}C

First of all we consider the dependence on the shielding of carbon atoms when the isotope ^{13}C replaces that of ^{12}C in our calculations.

One difference may arise by the modification of the gauge origin position [see Eq. (3)]. In the present work, the gauge origin was placed at the molecular center of mass, which will change only a bit with the switch from ^{12}C to ^{13}C . Then, the shielding values are almost the same independently of which carbon isotope is used. Furthermore, when the GIAO approach is used instead of the CGO one, the gauge origin dependence for the NMR shieldings disappears and so they do not depend on which carbon’s isotope is employed. Besides, the substitution of ^{12}C by ^{13}C will slightly change the values reported above for the tensor \mathbf{M} of halogen and hydrogen atoms. Such differences are expected to happen because of the small displacement of the position of the molecular center of mass due to the isotope switch. The mentioned isotopic dependence clearly appears in both \mathbf{M}^{nuc} and \mathbf{M}^{elec} [see Eqs. (1) and (2)].

On the other hand, relativistic effects for both, (e-e) and (p-p) contributions to the shielding of carbons in methyl halides are almost independent of the amount of electron correlation involved. When relativistic effects are computed at the RPA level of approach for $\sigma_{\text{iso},C}^{(e-e)}$, their results (34.85 ppm) are close to those computed at the KT3, BP86, and PBE0 levels (33.04, 30.81, and 29.97 ppm, respectively). In addition, relativistic effects for $\sigma_{\text{iso},C}^{(p-p)}$ at the RPA level of approach (−1.51 ppm for CH_3I) are almost the same as those obtained within the DFT approach (between −1.54 and −1.50 ppm).

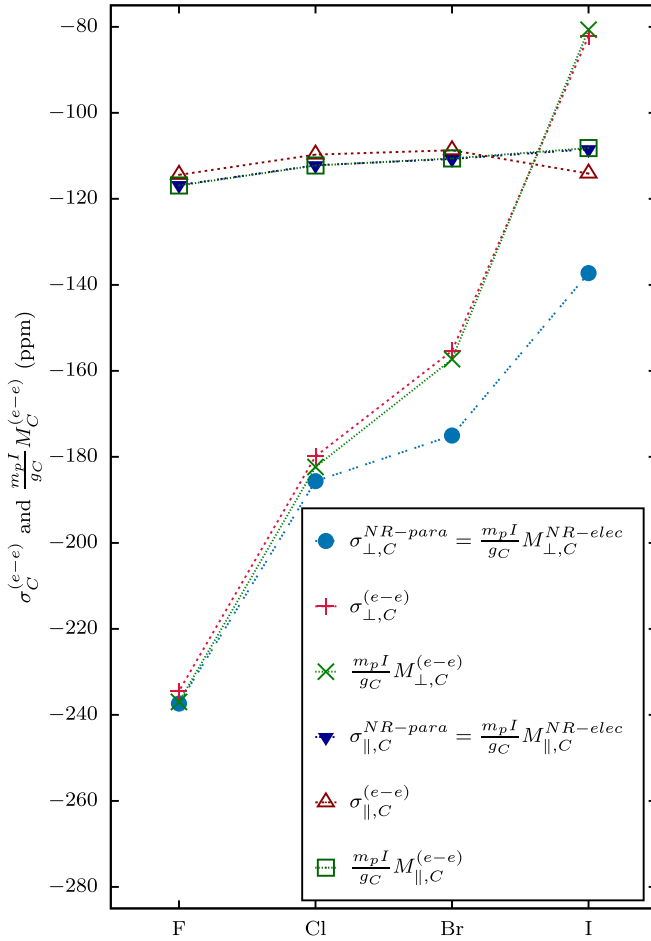


FIG. 3. Relativistic RPA values of the perpendicular and parallel contributions to $\sigma_C^{(e-e)}$ and $M_C^{(e-e)}$ in CH_3X molecules ($X = \text{F}, \text{Cl}, \text{Br}$, and I), together with their NR limits. Values are given in ppm.

Furthermore, as observed in Fig. 3 almost all relativistic effects on σ_C and M_C arise from $\sigma_{\perp,C}^{(e-e)}$ and $M_{\perp,C}^{(e-e)}$. Considering the RPA level of approach, relativistic effects in $\sigma_{\perp,C}^{(e-e)}$ for methyl iodide represent -65.7% of its total value. That proportion goes down as the halogen atom becomes lighter: -12.5% for CH_3Br , -3.2% for CH_3Cl , and -1.2% for CH_3F . From here it appears evident that those relativistic effects grow up as Z_X increases.

There is another feature that one can realize by observing Fig. 3: $\sigma_{\perp,C}^{(e-e)}$ and $\frac{m_p I}{g_C} M_{\perp,C}^{(e-e)}$ are close each other. Then, they almost fulfill the NR Ramsey-Flygare relationship. This trend indicates that the addition of the following terms, $\sigma_C^{\text{FA}(e-e)} + \frac{1}{2c}(\nu_{\perp,C}^{S(e-e)} - \nu_C^{\text{FA},S(e-e)})$, has a small contribution in methyl halides. So, the values of the difference $\sigma_{\perp,C}^{(e-e)} - \frac{m_p I}{g_C} M_{\perp,C}^{(e-e)}$ are always between -1.6 and 2.5 ppm.

Given that linear response calculations for open-shell systems (as a carbon atom is) are not implemented in the DIRAC code, one can estimate σ_C^{FA} from its NR value. Then, the way to calculate $\sigma_C^{\text{FA,NR}}$ is through the NR limit of $\frac{1}{3c_0} \langle 0 | \frac{1}{|r-R_C|} | 0 \rangle$, where $|0\rangle$ denotes the electronic DHF ground state of the atom. For getting such expectation value the NSTDAMAGNETIC keyword of the DIRAC program must be

used. In the present work the NR limit was reached by considering $c = 100c_0$, and doing this we found that $\sigma_C^{\text{FA,NR}} = 260.53$ ppm. Furthermore, the paramagnetic contributions to $\sigma_C^{\text{FA,NR}}$ are zero within the NR regime, being that such contributions are obtained as the NR limit of $\sigma_C^{\text{FA}(e-e)}$.

Concerning the addition of electron correlation and relativistic effects on the $(p-p)$ contribution to the carbon shieldings, it can be shown [see Eqs. (9) and (10)] that calculations of

$$\Delta_{\text{iso},C}^{(p-p)} = \sigma_{\text{iso},C}^{(p-p)} - \frac{m_p}{3g_C} \text{Tr}[(M_C^{\text{nuc}} + M_C^{(p-p)}) \otimes I] - \frac{1}{2c} \nu_{\text{iso},C}^{S(p-p)}$$

give results that belong to the range (261.4 ± 2.7) ppm for all methyl halides and all methods (see Supplemental Material [61]). In addition to that it was shown in Ref. [15] that $\frac{1}{2c} \nu_{\text{iso},C}^{\text{FA},S(p-p)}$ is almost equal to $\frac{1}{2c} \nu_{\text{iso},C}^{S(p-p)}$. As $\frac{1}{2c} \nu_{\text{iso},C}^{S(p-p)} = -0.35$ ppm for all methyl halides at both RPA and DFT levels of approach, this means that, according to the M-V model, $\sigma_C^{\text{FA}(p-p)}$ values should belong to the range (261.0 ± 2.7) ppm. Therefore, comparing the latter results with those of $\sigma_C^{\text{FA,NR}}$ ($= 260.53$ ppm), we found that the combined electron correlation and relativistic effects in $\sigma_C^{\text{FA}(p-p)}$ are smaller than 3.2 ppm.

All this shows an additional advantage of using the M-V model. It gives another way to estimate relativistic effects for shieldings of nuclei in free atoms with high accuracy, i.e., from molecular calculations of σ and M . Some time ago few attempts were made to calculate shieldings of free atoms [68–70], but given that 4c linear response calculations for open-shell electronic structures are not still implemented in relativistic codes, only shieldings of neutral noble gases were obtained, as well as shieldings of ionized atoms with closed-shell structures. The M-V model allows for accurate estimations of NMR shieldings for all kind of neutral atoms.

V. CONCLUDING REMARKS

Some of our previous theoretical works were focused on the development of formalisms aimed to best calculate absolute shielding scales by extending the well-known nonrelativistic Ramsey-Flygare rule to the relativistic regime. Its first and successful applications were made on linear molecules. In this work we went one step further by applying that formalism to nonlinear systems.

Systematic and highly accurate four-component (4c) calculations of spin-rotation (SR) tensors and NMR magnetic shieldings were performed at RPA and DFT levels of theory for all nuclei of methyl halides. A comparison with experimental values of the SR tensor shows that theoretical expressions proposed in Ref. [22] accurately describe this spectroscopic parameter. It was found that, even though the electron correlation and relativistic effects in SR tensors are not of the same order of magnitude, both effects must be introduced simultaneously to accurately describe the behavior of the experimental data.

Some of the most important findings of this work are the following.

(i) Experimental measurements of spin-rotation tensors of nuclei that belong to methyl halides can be accurately reproduced by theoretical calculations.

(ii) The M-V model reproduces 4c calculations of shieldings of H, C, F, Cl, Br, and I with high accuracy (at both levels of approach, RPA and DFT). This includes the 4c calculation of SR constants, σ^{FA} and $\nu^{\text{S}} - \nu^{\text{FA,S}}$. Then, this model can be safely employed to obtain semiexperimental values of σ by the combination of experimental SR data with the calculation of σ^{FA} and $\nu^{\text{S}} - \nu^{\text{FA,S}}$. These last values are more accurate for the heaviest atoms.

(iii) Most of the electron correlation effects for the shieldings of halogen nuclei, taken as the difference between DFT and RPA calculations, are strongly related with those effects in SR constants. Therefore, when experimental data for SR are used, many of these effects in shieldings are accurately taken into account.

(iv) Relativistic effects of both properties M and σ are negligibly small for hydrogen nuclei in methyl halides.

(v) A comparison between experimental values and 4c calculations of $M_{\parallel, \text{Cl}}$ at different levels of approach shows that available experimental data for this parameter need to be revisited.

(vi) We found a different procedure to estimate the free atom NMR shieldings. This procedure requires the calcu-

lation of M and σ of the given atom in a set of different molecules.

Another important finding is the fact that the results of previous models (see, for instance, Refs. [4,6,9,13]), which consider the sSR constants and the calculation of (p - p) contributions to the shieldings (its diamagneticlike contributions), should be taken with caution. They usually do not take into account the contributions of $\sigma^{\text{FA}(e-e)}$ and $\nu^{\text{S}} - \nu^{\text{FA,S}}$, which may be so large that they must be included. In addition, it should be pointed out that their proposal of an atomic correction may not be correct, because ν^{S} depends on the symmetry of the molecule and it can be not negligible at all.

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