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Theoretical study of the nuclear spin-molecular rotation coupling for relativistic electrons and non-relativistic nuclei. II. Quantitative results in HX (X=H,F,Cl,Br,I) compounds

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In the present work, numerical results of the nuclear spin-rotation (SR) tensor in the series of compounds HX (X=H,F,Cl,Br,I) within relativistic 4-component expressions obtained by Aucar *et al.* [J. Chem. Phys. **136**, 204119 (2012)] are presented. The SR tensors of both the H and X nuclei are discussed. Calculations were carried out within the relativistic Linear Response formalism at the Random Phase Approximation with the DIRAC program. For the halogen nucleus X, correlation effects on the non-relativistic values are shown to be of similar magnitude and opposite sign to relativistic effects. For the light H nucleus, by means of the linear response within the elimination of the small component approach it is shown that the whole relativistic effect is given by the spin-orbit operator combined with the Fermi contact operator. Comparison of "best estimate" calculated values with experimental results yield differences smaller than 2%–3% in all cases. The validity of "Flygare's relation" linking the SR tensor and the NMR nuclear magnetic shielding tensor in the present series of compounds is analyzed. © *2013 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4796461]

I. INTRODUCTION

The spin-rotation interaction induces a splitting in the rotational levels of molecules. This feature is originated in interactions which couple the nuclear spins and the rotational angular momentum of the system, and it is described by the spin-rotation (SR) tensor. The determination of the SR tensor is important in rotational spectrum measurements, as a tool for the analysis of molecular structure, and recently there have been several advances in the theoretical determination of this spectral parameter.[1–13]

The SR tensor is also relevant for NMR spectroscopy as it was first shown by Ramsey,[14] and extensively analyzed by Flygare,[15–17] that, in the non-relativistic (NR) domain, this property is related to the NMR nuclear magnetic shielding (NMS) tensor. Explicitly, the formal expression of its electronic contribution is equivalent to that of the so-called paramagnetic contribution to the absolute NMS tensor when it is calculated taking the molecular center of mass as gauge origin of the magnetic potential of the spectrometer magnetic field. This will be referred to as "Flygare's relation." This result is very relevant in the field of NMR spectroscopy because experimentally, only the chemical shift, i.e., the shielding with respect to a reference molecule, can be measured. Combination of the paramagnetic value deduced from experimental high resolution rotational spectroscopy, with a theoretical calculation of the much simpler and stable "diamagnetic" term in a

reference molecule allows to establish an absolute NMS scale for light nuclei.

The consideration of relativistic effects in the theoretical analysis of molecular properties in heavy atom containing compounds is nowadays a widespread field of research. These effects are important both to attain experimental accuracy in many cases, or even in the determination of qualitative aspects of experimental results in some other cases.[18] In particular, magnetic properties, such as NMR parameters, are particularly sensitive to relativistic effects as they probe the electronic density in the close vicinity of atomic nuclei, where such effects are of major importance for heavy atoms.[19–21] One interesting result which was anticipated long ago, is the fact that Flygare's relation would fail in the relativistic domain, due to differences in the 4-component operators that should describe the NMS and SR parameters.[22] In the early 2000, a relativistic expression of the closely related molecular g-tensor was analyzed.[23] Recently, a theoretical expression of the SR tensor at the equilibrium geometry of a molecular system in a 4-component framework was developed.[24] It is based on the analysis of the molecular Hamiltonian in the laboratory system, considering relativistic electrons and non-relativistic nuclei. The effects of moving nuclei were added to this Hamiltonian in the rigid rotor approximation. The term coupling the electron and nuclei dynamics in the context of the Born-Oppenheimer (BO)[25] approximation was considered. This approach allowed to obtain a formal expression of the SR tensor within a 4-component formalism for electrons. In the same work, a perturbative expansion of the obtained

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expression in the context of the linear response within the elimination of the small component (LRESC) approach[26] was carried out, which allowed to make a deep analysis of the relation between the SR tensor and the NMS tensor in the relativistic framework.

The formal expression of the SR tensor thus obtained needs to be tested against experimental results in order to analyze its suitability to describe the SR Hamiltonian in heavy atom containing compounds. To the authors' knowledge, at the moment there are no full relativistic results of the spin-rotation tensor. This is the aim of the present work. We have selected the set of hydrogen halides HX (X=H,F,Cl,Br,I) as model systems to make an analysis of relativistic effects as the atomic number increases along Group VII of the periodic table. Calculations were carried out with the DIRAC[27] code to obtain the SR tensor at the random phase approximation (RPA). The corresponding non-relativistic RPA values were calculated with the DALTON[28] program in order to evaluate the importance of relativistic effects. In order to compare the obtained results with experimental values of the bibliography,[29–32] an analysis of correlation effects is also carried out. These calculations allow to obtain different features of the HAHA (heavy atom-heavy atom) and HALA (heavy atom-light atom) effects.[33] Finally, by means of the LRESC expansion, the origin of different kinds of relativistic effects, the estimation of correlation on such relativistic effects, and interesting insight on the validity of Flygare's relation are discussed. In this way, to the authors opinion, deep insight into the study of relativistic effects on the SR tensor is obtained.

II. METHODS AND COMPUTATIONS

A. Relativistic 4-component expression of the spin-rotation tensor

In a molecular system, the interaction between the nuclear spin $\boldsymbol{I}_N$ of nucleus N and the orbital angular momentum of the molecule $\boldsymbol{L}$ produces a splitting of its rotational spectrum. This feature is described by the spin-rotation Hamiltonian[17]

$$H = -\hat{\boldsymbol{I}}_N \boldsymbol{M}_N \hat{\boldsymbol{L}}, \tag{1}$$

where $\boldsymbol{M}_N$ is the SR tensor.

From first principles considerations, the effect of rotation on the molecular system (nuclei and electrons) must be described. Since the typical velocity of the rotating molecular nuclei is small compared to the speed of light, it can be assumed that nuclei in the molecule are adequately described by non-relativistic dynamics. On the other hand, electrons must be treated with a Dirac equation in the presence of heavy nuclei (i.e., third row atoms or heavier). Under these assumptions, a formal theoretical expression of the SR tensor in a relativistic framework was developed in Ref. 24. Here, we sketch the main steps leading to the final theoretical expressions on which numerical results of the present work are based. The interested reader will find all details of the derivations in Ref. 24.

The SR tensor of nucleus N is obtained from terms of the molecular Hamiltonian which couple bilinearly the molecular orbital angular momentum $\hat{\boldsymbol{L}}$ and the N-nucleus spin $\hat{\boldsymbol{I}}_N$.

In order to analyze the effect of rotation in the molecular dynamics, the starting point is the molecular Hamiltonian within the BO approximation,[25] in which the wavefunction for electrons and nuclei is expressed as a product of the solution of the electronic problem, with fixed nuclear positions, and the nuclear wavefunction is the ground state of the nuclei in an effective potential produced by the other nuclei and the electrons in their ground state:

$$\Psi_{mol}(x, X) = \psi_e(x, X)\phi(X), \tag{2}$$

where x and X stand for the whole set of electron and nuclear variables of the system, respectively. Neglecting vibrational effects, the Hamiltonian for the nuclei is the corresponding to a purely rotating system described by the rigid rotor Hamiltonian,[24, 34]

$$H^R = \frac{1}{2}\hat{\boldsymbol{L}}\boldsymbol{I}^{-1}\hat{\boldsymbol{L}}, \tag{3}$$

where $\hat{\boldsymbol{L}}$ is the rotational angular momentum, and $\boldsymbol{I}$ is the molecular inertia tensor at its equilibrium geometry with respect to the center of mass. This angular momentum has an associated angular velocity $\boldsymbol{\omega} = \boldsymbol{I}^{-1}\hat{\boldsymbol{L}}$.

The effect of nuclear rotation on the electronic system can be included by considering the terms of the kinetic energy operator which affect the electronic part of the wavefunction, which are neglected in the zeroth-order BO approximation, that is those terms in which the nuclear angular momentum operator is applied to the electronic wavefunction. Since the electronic wavefunction is referred to a reference system fixed to the molecular frame, the action of the $\hat{\boldsymbol{L}}$ operator on the nuclear variables is equivalent to the action of (minus) the total 4-component relativistic angular momentum operator for electrons $\boldsymbol{J}_e$.[24, 34] There are two such terms:

$$V = \frac{1}{2}\hat{\boldsymbol{J}}_e \boldsymbol{I}^{-1}\hat{\boldsymbol{J}}_e - \hat{\boldsymbol{L}}\boldsymbol{I}^{-1}\hat{\boldsymbol{J}}_e. \tag{4}$$

The first term on the rhs of Eq. (4) is quadratic in $\boldsymbol{J}_e$. The second term couples the electronic angular momentum $\boldsymbol{J}_e$ and the nuclear angular velocity $\boldsymbol{\omega}$,

$$h_{BO}^{(1)} = -\boldsymbol{\omega}\hat{\boldsymbol{J}}_e. \tag{5}$$

The moving nuclear charge Z_N gives rise to a Hamiltonian term which is also linear in ω. This term was derived in a semiclassical way in Ref. 24, and it is more correctly given by the electron-nucleus Breit interaction:[35]

$$h_B = \sum_N \frac{Z_N}{r_{eN}}(\boldsymbol{\alpha}\boldsymbol{\beta}_N) - \frac{Z_N}{2r_{eN}}\boldsymbol{\alpha}(\boldsymbol{I} - \hat{\boldsymbol{r}}_{eN}^t\hat{\boldsymbol{r}}_{eN})\boldsymbol{\beta}_N, \tag{6}$$

where $\boldsymbol{\beta}_N$ represents the nucleus velocity relative to c, and $\hat{\boldsymbol{r}}_{eN}$ is the unit vector of the electron position with respect to nucleus N. However, as it was discussed in Ref. 24, this operator contains linearly the nucleus velocity relative to c, and the electron velocity relative to c. Taking into account that nuclei are by far much slower than electrons, this contribution can be expected to yield much smaller contributions to the SR tensor than relativistic effects originating in Eq. (5), even if at

first sight it carries a leading factor $1/c^2$. On this basis, as a first approach to the main relativistic effects on the SR tensor this term has been neglected in the present calculations.

The interaction Hamiltonian of electrons with the moving nucleus magnetic moment $\boldsymbol{\mu}_N$ is obtained by retaining those electromagnetic interactions containing the associated vector potential operator[24]

$$h_{\mu_N} = \left(\boldsymbol{\alpha} - \frac{\boldsymbol{p}_N}{m_N c} \right) \cdot \boldsymbol{A}_N(\boldsymbol{r}), \tag{7}$$

where the magnetic vector potential is given by

$$\boldsymbol{A}_N(\boldsymbol{r}) = \frac{\boldsymbol{\mu}_N \times (\boldsymbol{r} - \boldsymbol{r}_N)}{|\boldsymbol{r} - \boldsymbol{r}_N|^3}, \tag{8}$$

Here, $\boldsymbol{\mu}_N = g_N \mu_p \hbar \boldsymbol{I}_N$ is the nuclear magnetic moment, g_N its gyromagnetic factor, $\mu_p = 1/2m_p c$ (in cgs a.u., m_p is the proton mass) the nuclear magneton, m_N is the mass of nucleus N. Atomic gaussian units are used throughout this work, since in these units easier track of relativistic factors can be kept. It is interesting to observe that, at the leading order in $1/c$, this magnetic interaction involves the *relative* velocity of the electron with respect to the nucleus.[24]

On the other hand, the moving nuclei electric and magnetic fields give rise to electromagnetic interactions with the nuclear magnetic moments of other nuclei. These interactions are described at the non-relativistic level and, therefore, are coincident with the ones of previous work in the bibliography.[14, 16, 17] They are obtained with the minimal coupling $\boldsymbol{\pi} = \boldsymbol{p} - \frac{q}{c}\boldsymbol{A}$ prescription in the non-relativistic Hamiltonian. For the calculation of the SR tensor, only terms which are linear in $\boldsymbol{A}_N(\boldsymbol{r})$ must be retained[24]

$$h_{\omega,\mu_N}^{(2)nuc} = -\sum_M Z_M \left(\frac{\boldsymbol{p}_M}{m_M c} - \frac{\boldsymbol{p}_N}{m_N c} \right) \cdot \boldsymbol{A}_N(\boldsymbol{r}_M), \tag{9}$$

where, once again, the relevant interaction is given by the *relative* velocities of the interacting nuclei.

Summing up, the relevant operators to be combined in first and second order perturbation theory expansions in order to obtain the spin-rotation tensor arising from the above Hamiltonians are (for more details see Ref. 24 and references therein)

$$h_{\mu_N}^{(1)} = \boldsymbol{\alpha} \cdot \boldsymbol{A}_N(\boldsymbol{r}), \tag{10}$$

which comes from Eq. (7),

$$h_{\omega}^{(1)} = -\boldsymbol{\omega} \cdot \hat{\boldsymbol{J}}_e, \tag{11}$$

which is strictly Eq. (5), and

$$h_{\omega,\mu_N}^{(2)e} = -\frac{\boldsymbol{p}_N}{m_N c} \cdot \boldsymbol{A}_N(\boldsymbol{r}), \tag{12}$$

which comes from the second term in Eq. (7), and finally the nucleus-nucleus interaction bilinear in the nuclei momenta and the N nucleus magnetic moment, Eq. (9). All quantities must be referenced to the center of mass system of the molecule. The first term is an electron-nucleus perturbation operator linear in the magnetic moment, the second one is an electron-nucleus perturbation, linear in the nuclei momenta, the third one is an electron-nucleus perturbation operator bi-

linear in the magnetic moment and momentum of nucleus N, and the term of Eq. (9) is the nuclear-nuclear term.

The spin-rotation tensor is obtained by carrying out a first and second order expansion of the electronic energy at fixed nuclear configuration, and adding to it the contribution coming from nucleus-nucleus interaction terms.

The second order electronic contribution can be obtained by means of the relativistic 4-component linear response (*lr*) theory[22] at zero frequency, as the propagator

$$\boldsymbol{M}_{N,i,j}^{lr} = \frac{\partial^2}{\partial I_{N,i} \partial L_j} \frac{g_N}{m_p c} \left\langle\!\!\left\langle \boldsymbol{I}_N \cdot \left(\frac{\boldsymbol{r} - \boldsymbol{r}_N}{|\boldsymbol{r} - \boldsymbol{r}_N|^3} \times \boldsymbol{\alpha} \right); \hat{\boldsymbol{L}} \boldsymbol{I}^{-1} \boldsymbol{J}_e \right\rangle\!\!\right\rangle_0. \tag{13}$$

The calculation of the propagator involves excitations to virtual electronic states (e-e excitations) and virtual positronic states (e-p excitations), which can be obtained separately with adequate decomposition of the corresponding blocks of the propagator.[36, 37]

The first order electronic contribution is obtained from an expectation value for the operator of Eq. (12),

$$E^{(1)} = \langle \psi_e | h_{\omega,\mu_N}^{(2)e} | \psi_e \rangle = \langle \psi_e | - \frac{\boldsymbol{p}_N}{m_N c} \cdot \left(\boldsymbol{\mu}_N \times \frac{(\boldsymbol{r} - \boldsymbol{r}_N)}{|\boldsymbol{r} - \boldsymbol{r}_N|^3} \right) | \psi_e \rangle. \tag{14}$$

This expectation value depends on the total electronic electric field at nucleus N, as it can be seen by reordering the previous expression, where we include the sum over all electrons of the system to make the assertion more clear

$$E^{(1)} = -\frac{\boldsymbol{p}_N}{m_N c} \cdot \left(\boldsymbol{\mu}_N \times \langle \psi_e | \sum_e \frac{(\boldsymbol{r} - \boldsymbol{r}_N)}{|\boldsymbol{r} - \boldsymbol{r}_N|^3} | \psi_e \rangle \right). \tag{15}$$

But within the rigid rotor approximation, the nuclei rest at their equilibrium positions so that the *total* electric field at the nuclei positions is zero. Therefore, the first order electronic contribution is cancelled by the similar expression coming from the nuclear contribution $h_{\omega,\mu_N}^{(2)nuc}$, so that the combined contributions from both terms can be resumed in just one nuclear contribution of the form[24]

$$M_{N,i,j}^{nuc} = \sum_{M \neq N} \frac{Z_M g_N}{2 m_p c^2} \left(\boldsymbol{I}_{i,j}^{-1} \frac{\boldsymbol{r}_{M,CM} \cdot (\boldsymbol{r}_M - \boldsymbol{r}_N)}{|\boldsymbol{r}_M - \boldsymbol{r}_N|^3} \right.$$
$$\left. - \frac{\boldsymbol{r}_{M,CM,i}((\boldsymbol{r}_M - \boldsymbol{r}_N) \cdot \boldsymbol{I}^{-1})_j}{|\boldsymbol{r}_M - \boldsymbol{r}_N|^3} \right). \tag{16}$$

Therefore, the final SR tensor is built up from two contributions: the linear response electronic term $\boldsymbol{M}_N^{lr}$, Eq. (13) and the nuclear term $\boldsymbol{M}_N^{nuc}$, Eq. (16).

B. Leading relativistic corrections of the spin-rotation tensor within the LRESC approach

Nowadays, 4-component calculations are carried out in a regular basis, for example, with the DIRAC program,[27] and the usefulness of expansion approximations such as LRESC are mainly of interest for analysis purposes. In the present work, the kind of analysis allowed by the LRESC approach is related to the physical mechanisms responsible of relativistic effects, the discussion of electron correlation in such

effects, and the relations between the SR tensor and the NMR nuclear magnetic shielding tensor, which are closely related in the non-relativistic approach by "Flygare's relation."[17] For these reasons, the explicit LRESC expressions for the SR tensor are quoted in the present work.

In the LRESC approach,[26] the second order correction to the energy involving a given four component operator V is re-expressed as an expansion in terms of $1/c$ (the fine structure constant in a.u.). The zeroth order approximation yields the non-relativistic result, and the lowest order relativistic corrections are obtained by the use of the elimination of the small component methodology. In order to carry out this expansion, contributions from the positive energy spectrum for electronic states yielding the "electron-electron" (e-e) corrections and those due to the negative energy spectrum yielding the "electron-positron" (e-p) corrections are treated separately.

In order to carry out the LRESC expansion of the e-e contributions to the energy, matrix elements of the 4-component operator V between positive energy 4-component spinors $|\phi_j^{(4)}\rangle$ are expanded by means of the elimination of the small component (ESC) approach so that at the end they are expressed as matrix elements of new operators acting in the space spanned by Pauli spinors $|\phi_j^P\rangle$, i.e.,

$$\langle \phi_i^{(4)} | V | \phi_j^{(4)} \rangle \approx \langle \phi_i^P | O(V) | \phi_j^P \rangle. \tag{17}$$

Explicitly, for the operators involved in the second-order expression of the SR tensor we have

$$O(\boldsymbol{\alpha} \cdot \boldsymbol{A}_N) = H^{PSO} + H^{FC/SD} + H^{PSO-K} + \cdots. \tag{18}$$

The lowest order terms are the usual paramagnetic (nuclear) spin-orbit (PSO), Fermi-contact (FC), and spin-dipolar (SD) operators. Relativistic corrections of next order in $1/c$ to these operators have been derived in different works.[24,26,38] Among them, here we only retain the one identified as H^{PSO-K} because it is the only one that is relevant for the SR tensor of closed shell molecules. This operator has the form

$$H^{PSO-K} = -\frac{1}{4m^2c^2} \{p^2; H^{PSO}\}, \tag{19}$$

where $\{,\}$ stands for the anticommutator of two operators.

When the same procedure is applied to the 4-component total angular momentum operator $\boldsymbol{J}_e^{(4)}$ it is obtained

$$O(\boldsymbol{J}_e^{(4)}) = \boldsymbol{J}_e^{(2)} \tag{20}$$

with no additional terms at the order $1/c^2$.

The second source of relativistic corrections are the spin-orbit, Darwin and mass-velocity effects on the Pauli spinors themselves. As a consequence, the leading order relativistic corrections for M_N^{el} originated in e-e excitations obtained with this methodology are

$$\boldsymbol{M}_N^{el} - \boldsymbol{M}_N^{NR} \simeq \frac{\partial^2}{\partial \boldsymbol{I}_N \partial \boldsymbol{L}} (E^{(2)}(H^{PSO-k}, -\boldsymbol{\omega} \cdot \boldsymbol{L}_e)$$
$$+ E^{(3)}(D; H^{PSO} + H^{FC/SD}, -\boldsymbol{\omega} \cdot \boldsymbol{J}_e)), \tag{21}$$

where M_N^{NR} is the non-relativistic expression of the SR tensor; $E^{(2)}$, $E^{(3)}$ stand for second and third order corrections to the energy within Rayleigh-Schrödinger perturbation theory

(RSPT); D is the sum of the mass velocity, Darwin and spin-orbit operators.[39] Operator $\boldsymbol{J}_e$ was replaced by operator $\boldsymbol{L}_e$ in the first term of the right-hand side because the spin part yields zero in the case of closed shell molecules. However, as it was thoroughly discussed in Ref. 40, the full $\boldsymbol{J}_e$ operator makes contributions to the third order term.

The contribution coming from e-p excitations to the second order correction to the energy for perturbation V is obtained following a similar procedure in the context of the QED picture, in which negative-energy solutions of the Dirac equation are reinterpreted as positive energy states for positrons.[26] Linearization of the corresponding second order correction to the energy then allows to re-express the full contribution as the following expectation value over the 4-component electronic ground state:

$$E^{(ep)} = \frac{1}{2mc^2} \langle \psi_e | V P_p X(V) | \psi_e \rangle, \tag{22}$$

where

$$X(V) = 2V + \frac{1}{2mc^2} [H^D, V], \tag{23}$$

where H^D is the Dirac Hamiltonian,[39] and P_p is a projector onto the subspace of positronic states. The detailed derivation of this expression can be found in Ref. 26. For the two operators involved in the SR tensor it is obtained[24]

$$X(\boldsymbol{J}^{(4)}) = \boldsymbol{J}^{(4)}, \tag{24}$$

$$X(\boldsymbol{\alpha} \cdot \boldsymbol{A}_N) = (2 + \beta)\boldsymbol{\alpha} \cdot \boldsymbol{A}_N, \tag{25}$$

where β is the Dirac matrix.[39] Inserting these expressions in Eq. (22) and retaining terms bilinear in $\boldsymbol{J}^{(4)}$ and $\boldsymbol{A}_N$ it is found

$$E^{(ep)} = \frac{1}{2mc^2} \langle \psi_e | -\boldsymbol{\omega} \cdot \boldsymbol{J}^{(4)} P_p X(\boldsymbol{\alpha} \cdot \boldsymbol{A}_N) | \psi_e \rangle$$
$$+ \frac{1}{2mc^2} \langle \psi_e | \boldsymbol{\alpha} \cdot \boldsymbol{A}_N P_p \cdot (-\boldsymbol{\omega}) \cdot X(\boldsymbol{J}^{(4)}) | \psi_e \rangle. \tag{26}$$

From this expression it is concluded that there is no zeroth order contribution, i.e., of the same order of the non-relativistic expression. Due to the factor $1/2mc^2$, the leading order relativistic correction arises by replacing all operators and electron states by their zeroth order approximation, i.e., by 4-component spinors with zero value in the lower components and Schrödinger spinors as upper components. But due to the presence of the P_p projector in such case the full expression is also zero. As a conclusion, it is found that the e-p contribution to the SR tensor must be zero at least up to order $1/c^2$.

C. Computational details

In the present work, Eqs. (13) and (16) were used to obtain full-relativistic calculations of the spin-rotation constant in model systems HX (X=H, F, Cl, Br, I) and compare them with experimental results. On the other hand, LRESC analysis of relativistic corrections were carried out according to Eq. (21).

Relativistic calculations of spin-rotation constants were performed at RPA level of polarization propagator formalism

TABLE I. Relativistic RPA values of spin-rotation constants M_N (in kHz) for HX molecules (X=F,Cl,Br,I). Third column corresponds to the nuclear contribution, while column M_{rl} is the calculation of the linear response Eq. (13). The e-e and e-p contributions of L and S operators are also shown.

| Molecule | N | M_{nuc} | M(e-e) | | M_N^{rl} M(e-p) | | M_N | M_{exp} |
			L	S	L	S		
H_2	^{1}H	105.478	10.557	0.027	0.0124	-0.0124	116.063	113.904[a,b]
HF	^{1}H	26.425	45.456	-0.060	0.0023	-0.0023	71.821	71.128(24)[c]
	^{19}F	52.511	-376.065	11.313	2.9063	-2.9064	-312.242	$-307.637(20)$[c]
HCl	^{1}H	10.085	33.998	-0.058	0.0015	-0.0014	44.025	41.877(139)[d]
	^{35}Cl	2.037	-60.392	3.930	-0.8835	0.8835	-54.426	$-53.829(53)$[e]
HBr	^{1}H	6.730	39.702	-0.451	0.0009	-0.0006	45.982	41.27(31)[e]
	^{79}Br	3.819	-359.169	75.503	16.5924	-16.5926	-279.847	$-290.83(8)$[d]
HI	^{1}H	4.307	58.556	-2.426	0.0010	-0.0005	60.437	49.22(22)[f]
	^{127}I	2.079	-502.793	178.099	30.5104	-30.5106	-322.615	$-351.1(3)$[f]

[a]Taken from Ref. 55.
[b]The rovibrational and Thomas precession effects yield -1.56 kHz.[1]
[c]Taken from Ref. 29.
[d]Taken from Ref. 56.
[e]Taken from Ref. 31.
[f]Taken from Ref. 32.

with Dirac Hartree Fock wavefunctions as implemented in the DIRAC code.[27] The non-relativistic calculations were performed with DALTON program,[28] at both RPA and correlated second order polarization propagator approach-coupled cluster singles and doubles (SOPPA-CCSD)[41,42] approximations for molecular properties.

The basis sets used for H, F, and Cl atoms were the aug-cc-pV5Z basis set.[43,44] For I and Br, we used the dyall.cv3z[45] basis set.

We have tested the convergence of the values of M_N by increasing the size of the basis set with tight and diffuse functions added with an even tempered criterion, and we did not find significant differences with results of the basis sets described above. For LRESC calculations, the basis set aug-cc-pVTZ-Jun3[44,46] was used for H, F, and Cl atoms.

Experimental geometrical parameters[47] of HX (X=H,F,Cl,Br,I) compounds were used. The HX bond distances in Å are: 0.7414 (X=H); 0.9169 (X=F); 1.2746 (X=Cl); 1.4145 (X=Br); 1.6090 (X=I).

III. RESULTS AND DISCUSSION

A. Relativistic 4-component results at the RPA level

In linear molecules, there is only one relevant element of the spin-rotation tensor $\boldsymbol{M}_N$ determining the corresponding spectrum, this is the component with respect to any axis perpendicular to the molecular axis, due to rotation symmetry. We refer to this component simply as M_N (N=X,H) and we refer to it simply as the "spin rotation constant."

In Table I, we present 4-component relativistic RPA values of the spin rotation constants M_H and M_X in HX compounds (X=H,F,Cl,Br,I), the corresponding e-e and e-p contributions, the nuclear contribution and experimental values. The decomposition into e-e and e-p contributions was done as implemented in DIRAC[48] code :$M_N(e-e)$ is obtained as a response calculation involving only virtual excitations to positive energy spinors, and $M_N(e-p)$ is obtained as the dif-

ference between the full response result and $M_N(e-e)$.[37] To our knowledge, these are the first relativistic calculations of the spin-rotation tensor in a 4-component framework. In Figures 1(a) and 1(b), the obtained values are presented
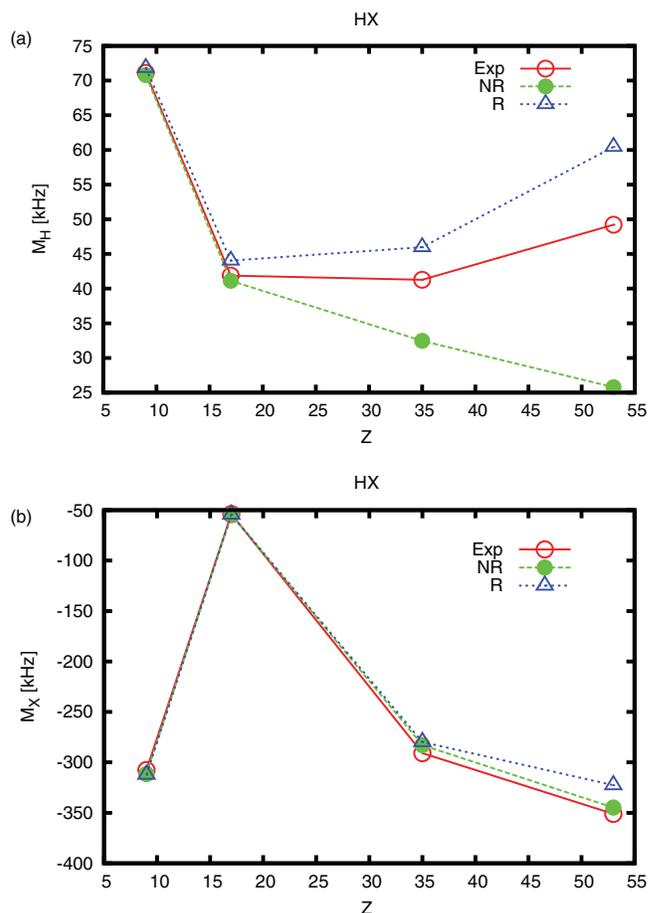

FIG. 1. Spin rotation constants for H(a) and X(b) nuclei in the HX series. Open circles: experimental values; dotted lines with triangles: 4-c RPA relativistic calculations; and dashed line with filled circles: non-relativistic RPA calculations.

together with non-relativistic RPA values and experimental values and experimental values as a function of Z_X, the atomic number of the halogen atom involved. The following comments are noteworthy.

As expected, for X=F,Cl the relativistic effects on M_X are very small (less than 1 kHz). For Br and I, the relativistic calculations predict a positive relativistic effect which increases substantially from Br to I (from ca. 3 kHz to 22 kHz). This effect is much smaller than the non-relativistic (NR) value, and at first sight it seems to fail to improve the non-relativistic result as compared to experimental values. The relativistic effect in I is ca. 7% of the non-relativistic 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% considering the latest 4-component results.[49–52]

M_H constants present significant relativistic effects, which are particularly large for the cases X=Br, I, as it can be seen from Figure 1(a). While the non-relativistic values predict a decrease in M_H from Br to I, the experimental results show an increase, which is well reproduced by the relativistic RPA calculations. The relativistic effect is much larger in this case than in the previous one on a relative scale. In fact, the relativistic effect on the SR tensor M_H of IH is 135% of the non-relativistic value. Deeper insight into the origin of this large relativistic effect can be obtained from the LRESC expansion. It is seen that, as it is the case for the NMS of the H nucleus in HX compounds, for the spin-rotation tensor of the H nucleus the SO effect is also by far the dominant relativistic correction (see below).

Regarding the e-e and e-p contributions, it is interesting to highlight the strong cancellation of the e-p results for M_N from the terms involving the L_e and S operators in *all* cases. This feature was anticipated on the basis of the LRESC analysis of relativistic effects on the SR tensor: it was found that both the non-relativistic limit and the leading order relativistic correction of e-p contributions are zero according to the LRESC expansion. The obtained results nicely reproduce this feature: even for the heavier I nucleus the whole e-p contribution is ca. 5×10^{-4} kHz. E-e contributions define the whole value of the linear response part of the tensor, and except for the case of H_2, it is by far the dominating contribution. In the non-relativistic limit only the L_e part should remain in the present case of closed shell molecules. Therefore, the S contribution is wholly relativistic. This contribution is increasingly important for M_X. However, there seems to be large cancellation between relativistic effects on both terms, as the overall relativistic effect in the case of the heaviest I nucleus analyzed is ca. 22 kHz. Once more, this partial cancellation is based on the way the relativistic J_e operator behaves. As clearly shown by the LRESC expansion, Eq. (21) the leading order relativistic effects come only from relativistic corrections to the magnetic nuclear moment field, and mass-velocity, Darwin and spin-orbit terms of 4-component positive energy Dirac spinors. No term is directly associated with the J_e operator, which reduces smoothly to the L_e operator of the non-relativistic theory. In the case of M_H, the S contribution remains much smaller than the L_e one in all cases.

TABLE II. Correlation effects on the NR values of M_X and M_H in HX (X=H,F,Cl,Br,I). Values in kHz.

X	N	M_N^{NR} (RPA)	M_N^{NR} (SOPPA-CCSD)	ΔM_N^{NR} (corr)
H	^{1}H	116.046	115.362	-0.685
F	^{1}H	70.784	72.395	1.611
	^{19}F	-311.573	-304.431	7.142
Cl	^{1}H	41.124	41.303	0.179
	^{35}Cl	-54.388	-54.459	-0.071
Br	^{1}H	32.473	32.881	0.408
	^{79}Br	-282.940	-294.068	-11.128
I	^{1}H	25.793	26.407	0.613
	^{127}I	-344.811	-369.146	-24.335

B. Correlation vs. relativistic effects

In the present section, we compare the relative importance of relativistic and correlation effects on the RPA non-relativistic values of the spin rotation tensor. To this end, we have carried out SOPPA-CCSD calculations of the NR values for both M_X and M_H in the present series of compounds. Correlation effects on the leading relativistic corrections are analyzed on the basis of the LRESC approach.

Results are displayed in Table II. In the case of M_X, correlation effects are small for F and Cl, but they are increasingly important for Br and I. Negative values of ca. -11 kHz and -24 kHz are found, respectively, for these nuclei. Comparison of relativistic and correlation effects in Fig. 2 and Table II shows that both effects are of opposite signs and similar magnitudes, nearly cancelling each other. As a consequence, the final result is quite similar to the non-relativistic RPA value.

For M_H correlation effects on the non-relativistic values are negligibly small in all cases.

From previous experience on the nuclear magnetic shielding,[38] 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). There are different terms giving rise to the SO effect, (cf. Eq. (21)). In each one, the SO operator is combined in third order corrections to
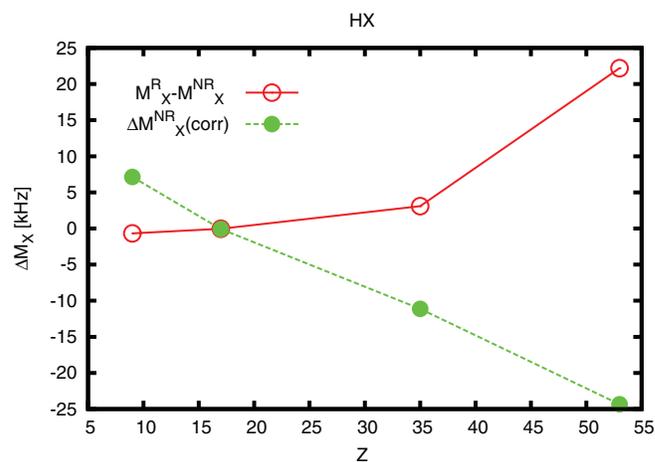

FIG. 2. Comparison between RPA relativistic effects (solid line with open circles) and SOPPA-CCSD non-relativistic correlation effects (dashed line with filled circles) for the spin rotation constants M_X in the HX series.

TABLE III. Comparison of relativistic RPA corrections, LRESC (Eq. (21)) corrections and SO corrections to the spin-rotation constants M_N for HX molecules (X=F,Cl,Br,I).

Molecule	N	$M_N^R - M_N^{NR}$	ΔM_N^{LRESC}	ΔM_N^{SO}
H_2	^{1}H	0.02	0.00	0.00
HF	^{1}H	1.04	1.22	1.11
	^{19}F	-0.67	0.87	2.26
HCl	^{1}H	2.90	3.34	3.18 (2.12)[a]
	^{35}Cl	-0.04	0.59	0.51
HBr	^{1}H	13.51	13.92	14.44 (8.95)[a]
	^{79}Br	3.09	5.88	16.77
HI	^{1}H	34.64	35.40	34.50 (21.48)[a]
	^{127}I	22.20	16.09	39.72

[a]LRESC FC-SO correction within CAS MCSCF approach following Ref. 38.

the energy with the following operators: the FC and SD operators in combination with the orbital angular momentum L_e; and the SD operator combined with the total S operator. From these, the FC-SO effect is by far the largest one in the case of M_H in the present series of compounds. This assertion is supported by calculated results presented in Table III. The total relativistic effect at the RPA level, the total LRESC correction and the FC-SO term are displayed. We have recalculated the LRESC SO correction within complete active space (CAS) MCSCF approach following Ref. 38 for the cases of HCl, HBr, and HI, for the slightly smaller uncontracted aug-J[53] basis set. Results obtained are also displayed in Table III. As it is seen, correlation effects are really important and it is thus predicted that relativistic corrections to M_H should be smaller than those given by 4-component RPA results.

In order to discuss the adequacy of the relativistic theory of the spin-rotation tensor developed in Ref. 24, in Table IV we present 4-component RPA, "best estimate" and

TABLE IV. HX Non-relativistic RPA M_N^{NR}, relativistic correction $\Delta^R M_N$, correlation effects $\Delta^{corr} M_N^{NR}$, "best estimate" and experimental values of the SR tensors in HX (in kHz).

X	N	M_N^{NR} (RPA)	$\Delta^R M_N$[a]	$\Delta^{corr} M_N^{NR}$[b]	Best estimate[c]	M_N^{exp}
H	^{1}H	116.05	0.02	-0.69	115.38	113.904[d,e]
F	^{1}H	70.79	1.04	1.61	73.43	71.128(24)[f]
	^{19}F	-311.57	-0.67	7.14	-305.10	$-307.637(20)$[f]
Cl	^{1}H	41.12	2.12	0.18	43.42	41.877(139)[g]
	^{35}Cl	-54.39	-0.04	-0.07	-54.50	$-53.829(53)$[g]
Br	^{1}H	32.47	8.95	0.41	41.83	41.27(31)[h]
	^{79}Br	-282.94	3.09	-11.13	-290.98	$-290.83(8)$[h]
I	^{1}H	25.79	21.48	0.61	47.89	49.22(22)[i]
	^{127}I	-344.81	22.20	-24.33	-346.95	$-351.1(3)$[i]

[a]Difference between 4-component and non-relativistic RPA results.
[b]Difference between non-relativstic SOPPA-CCSD and RPA values.
[c]See text for the definition of "best estimate" values.
[d]Taken from Ref. 55.
[e]The rovibrational and Thomas precession effects yield -1.56 kHz.[1]
[f]Taken from Ref. 29.
[g]Taken from Ref. 56.
[h]Taken from Ref. 31.
[i]Taken from Ref. 32.

experimental values of the SR constants in HX. The "best estimate" value for M_X is obtained as the sum of the correlated SOPPA-CCSD value and the relativistic correction as given by the difference of the 4-component and NR RPA values. The "best estimate" for M_H is taken as the sum of the correlated NR value and the correlated SO correction of Table III.

Comparison of experimental and "best estimate" results in Table IV shows that the effect of relativity on the spin-rotation tensor is adequately taken into account by the theory developed in Ref. 24, with differences smaller than 2%–3%. It is interesting to remark that in the case of M_X, correlation effects on the NR results need to be considered to obtain a good estimate of the final value. Even if correlated relativistic corrections would certainly improve the final result, the opposite trends shown by correlation and relativistic effects explain the fact that the NR RPA value is very close to experiment in this case. On the opposite side, for M_H it is concluded that correlation effects on the NR value 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_H quite close to the experimental one in HBr and HI.

The good agreement between calculated and experimental results obtained in Table IV is a strong indication that the major part of relativistic effects are adequately described by the present approach. On the basis of these results it can be concluded that all remaining effects: vibrational, nuclear size, electron-nucleus Breit, etc., should altogether account for only a small part of the total value. This finding strongly supports the validity of the approximation made by neglecting the Breit interaction, Eq. (6), as compared to the "inertia" effect of $h_{BO}^{(1)}$, Eq. (5), at least in those cases in which the relativistic correction is large. This is particularly so in the cases of M_H of X=Br and X=I. The calculated relativistic corrections are large and make the final values of M_H to be very close to experimental ones. In the case of M_X, despite the good agreement obtained between experimental and calculated results, the partial cancellation of correlation and relativistic effects makes it difficult to obtain definite conclusions, and further investigations would be of much interest.

C. Discussion: Relativistic corrections, LRESC expansion, and Flygare relations

The aim of the present section is to establish a comparison of relativistic effects on the SR constant and the nuclear magnetic shielding (NMS) constant on the basis of the LRESC expansion. The separate analysis of different types of relativistic effects allows to discuss the validity of Flygare's relation between the NMS and SR tensors in the relativistic case. This relation establishes the equivalence of the SR tensor and the paramagnetic contribution to the NMS tensor when the gauge origin is placed at the center of mass of the molecule, and holds exactly in the frame of the non-relativistic theory of both spectroscopic parameters. The non-equivalence of the relativistic theories of the NMS tensor and SR tensors anticipates the failure of Flygare's relation in the

relativistic case.[22,24] However, as it is shown in the present series of compounds, in some cases, depending on the physical mechanism defining the relativistic effect, the relation may hold anyway.

In Table III results of the relativistic effects for M_N in HX (X=H,F,Cl,Br,I) compounds are presented, together with the LRESC value. The corresponding spin-orbit contribution is shown in a separate column.

In the case of M_X, there is qualitatively good agreement between the LRESC results and the four component calculation, especially taking into account the smallness of the total relativistic effect in a relative scale.

On the other hand, as discussed in Sec. III B, the relativistic correction on the light atom (HALA effect) is well reproduced by the LRESC approximation, and almost entirely originated in the FC-SO effect. This is also the case of the nuclear magnetic shielding constant $\sigma(H)$ in this series of compounds.[38,46,49]

These findings are consistent with the fact that the LRESC approach is not expected to give quantitatively good results for properties which depend on the very relativistic inner-shell electrons of heavy nuclei (as is the case of M_X or the absolute nuclear magnetic shielding), whereas very good results are found for properties depending on valence shell electrons, which are moderately affected by relativity. This seems to be the case of M_H, as it is also the case for the nuclear magnetic "chemical shift," as it was thoroughly discussed in Refs. 38, 49, 50, and 54.

The above result for M_H could suggest that the HALA effect on the nuclear magnetic shielding $\sigma(N)$ and the spin-rotation constant M_N in a light atom in the vicinity of a heavy atom are described by the same mechanism. However, an equivalence is not to be expected in the general case because the SO corrections in both parameters involve different operators in the third order RSPT expression. While in the shielding the SO corrections involve the operator $L_e + 2S$ of the magnetic interaction with the uniform external field, in M_N we have $J_e = L_e + S$, i.e., the operator of general rotations. Therefore, although the spin-orbit mechanism describes properly the relativistic HALA effects in $\sigma(N)$ and M_N, there is a difference arising from the factor 2 in the spin part.

For instance, in the case of M_H in HI, the SO correction involving the spin operator is about -0.1 kHz against 34 kHz of the total relativistic correction. This implies that in HX, the relation proposed by Flygare between M_H and $\sigma(H)$ holds. But this will not be the case if the spin part is important in the SO effect in a given compound.[40]

It is concluded that in molecules containing atoms of the fourth row or heavier, Flygare's relation for the light atom is an approximation which is only valid for particular examples as Hydrogen in HX compounds.

The relativistic corrections on M_X on the heavy atom are not described by only one mechanism. Each contribution defined in Eq. (21) is important to obtain the total value. As shown in Table III there is a large difference between the relativistic effect and the spin-orbit contribution. However, in these particular examples there is a curiosity. Due to partial cancellation of relativistic and correlation effects, the non-relativistic RPA value of the SR constant M_X is quite close to the experimental one as shown in Table IV, and of course it is coincident with the value of the non-relativistic theory of the NMS tensor! This feature might also be misleading with respect to the validity of Flygare's relation in the case of M_X. In order to show clearly the large difference between both spectroscopic parameters, we have calculated the relativistic electron-electron contributions to the NMS tensor as given by the LRESC approach[26,38] and transformed to SR tensor units as would suggest Flygare's relation: the relativistic *correction* for Br in HBr is of ca. 257 kHz and that for I in HI is ca. 571 kHz! These large differences are due to operators which describe relativistic effects on the magnetic interaction with the uniform spectrometer field in the NMS tensor which do not appear in the case of the SR tensor. In this way, we see the power of the LRESC expansion to obtain insight into the differences between the NMS and the SR tensors in the general case.

IV. CONCLUDING REMARKS

Numerical results of the relativistic SR tensor obtained in the present work for HX compounds show that the theoretical expressions proposed in Ref. 24 are adequate for the theoretical description of this spectral parameter in this series of heavy atom containing compounds. However, in the case of M_X, as it was anticipated in Ref. 24, the relativistic effect is rather small. In fact, it is of the same order of magnitude and opposite to correlation effects on the non-relativistic values. The overall agreement within a few % between theoretical and experimental values is worthy to note. In order to extract definite conclusions about the accuracy of theoretical values, correlated relativistic calculations should be carried out. Of course, in order to obtain experimental accuracy vibrational corrections, as well as the consideration of finite nucleus size corrections should be included. In particular, the relativistic contribution still lacks careful analysis of the electron-nucleus Breit interaction. Work along this line is being carried out in our research group. In the case of M_H relativistic effects are very large in a relative scale, and correctly reproduced by the theoretical formalism of Ref. 24. The LRESC analysis has shown that in this case the relativistic effect is largely dominated by the FC-SO correction, as it is also the case for the NMS tensor $\sigma(H)$. Therefore, Flygare's relation is shown to hold for the HALA effect on M_H and $\sigma(H)$. However, from a theoretical point of view, the spin contribution to the SO effect is different in the case of both spectral parameters, and therefore differences should be expected in the general case. The large differences in relativistic effects on M_X and $\sigma(X)$ of the heavy atom are due to the larger relativistic corrections needed to describe properly the interaction with the uniform spectrometer magnetic field in the case of the NMS tensor, as compared to the J_e angular momentum operator of the SR tensor.

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