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In this work, relativistic effects on the nuclear spin-rotation (SR) tensor originated in the electron-nucleus and electron-electron Breit interactions are analysed. To this end, four-component numerical calculations were carried out in model systems HX (X=H,F,Cl,Br,I). The electron-nucleus Breit interaction couples the electrons and nuclei dynamics giving rise to a purely relativistic contribution to the SR tensor. Its leading order in 1/c is of the same value as that of relativistic corrections on the usual second order expression of the SR tensor considered in previous work [I. A. Aucar, S. S. Gómez, J. I. Melo, C. G. Giribet, and M. C. Ruiz de Azúa, J. Chem. Phys. **138**, 134107 (2013)], and therefore it is absolutely necessary to establish its relative importance. For the sake of completeness, the corresponding effect originating in the electron-electron Breit interaction is also considered. It is verified that in all cases these Breit interactions yield only very small corrections to the SR tensors of both the X and H nuclei in the present series of compounds. Results of the present work strongly suggest that in order to achieve experimental accuracy in the theoretical study of the SR tensor both electron-nucleus and electron-electron Breit effects can be safely neglected. © 2013 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4819958]

I. INTRODUCTION

The interaction between nuclear magnetic moments and magnetic currents due to molecular rotation gives rise to hyperfine structure in rotational spectra. This coupling is described by the spin-rotation (SR) tensor,[1–4] which is a valuable spectral parameter in the analysis of molecular structure. Theoretical advances in this field aim at providing reliable calculated values as a complementary tool for spectroscopy. In this regard, use of London-type orbitals, large basis sets, and correlated calculations provide sound theoretical background in the study of light atom containing compounds. Moreover, in non-relativistic theory, a link relating the SR tensor and the nuclear magnetic resonance (NMR) shielding tensor holds: the second order electronic contribution to the SR tensor is formally equivalent to the paramagnetic contribution to the nuclear magnetic shielding (NMS) tensor (for equilibrium molecular geometry) when the molecular center of mass (CM) is used as gauge origin of the NMR spectrometer magnetic field.[1–4] The SR tensor can thus be used as a valuable complementary tool to establish absolute nuclear magnetic shielding scales.

For heavy atom containing compounds, relativistic effects become relevant both in the analysis of the SR and NMS tensors. Even though 4-component relativistic theory of NMR parameters was developed several years ago, only recently the relativistic theory of the SR tensor has been treated in detail by different authors.[5–7] In particular our re-

search group has developed a formal theory considering an approximation of non-relativistic nuclei and relativistic electrons, taking into account that nuclei in molecular bound states are by far much slower than the speed of light c (in the molecule center of mass system). The starting point is a molecular Hamiltonian defined entirely in the laboratory system. The "drift" of electrons in a given molecular rotational state is obtained by considering the inertia effect on the electronic distribution given by the terms of the nuclear kinetic energy operator that are neglected in the zeroth order Born-Oppenheimer (BO) approximation,[8] in a first-order perturbation theory procedure. Analysis of quantitative numerical results given by this theoretical approach was carried out in Ref. 7 for model systems HX (X=H,F,Cl,Br,I) in order to establish the importance of relativistic effects for increasing atomic number of the halogen atom. The same theoretical approach was implemented within density functional theory (DFT) by Malkina *et al.*[9] in order to discuss the absolute NMS scale of ^{119}Sn.

However, as it was stated on semi-classical grounds in Ref. 6 and explicitly presented in Ref. 7, the full consistency of this approach requires to take account of the interactions between moving electrons and moving nuclei, given by the Breit electron-nucleus interaction. This effect gives rise to a purely relativistic contribution to the SR tensor. Taking into account that nuclei are by far much slower than electrons, this kind of terms were completely neglected in numerical calculations presented in Ref. 7.

Both the Breit electron-nucleus (e-N) interaction and the Breit/Gaunt electron-electron (e-e) interaction yield

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relativistic corrections to the SR tensor with leading order in $1/c$ which is the same as those of relativistic effects given in Ref. 7. Therefore, it is really important to clarify and to obtain definite conclusions about the importance of such interactions in the analysis of the spin-rotation tensor within the theoretical formalism developed in Ref. 6. We present in this work numerical results of the corresponding contributions to the SR tensors of the series of compounds analysed in Ref. 7 HX (X=H,F,Cl,Br,I). Results of the e-N Breit and e-e Gaunt effects are presented and compared to 4-component calculations of Ref. 7 for the cases of both the light H nucleus and X nucleus SR tensors. The relative importance of both terms is, therefore, clearly established. Numerical results were obtained with the DIRAC[10] program.

II. METHODS AND COMPUTATIONS

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

In a molecular system, the interaction between a given magnetic nucleus N and the "semitotal" molecular angular momentum produces a hyperfine splitting of its rotational spectrum. The semitotal angular momentum is given by the orbital and spin angular momenta of the electronic distribution and the rotational angular momentum of nuclei. This feature is described by the spin-rotation Hamiltonian.[1–4] In the case of molecules with a non-degenerate electronic ground state symmetric under time reversal, the "semitotal" angular momentum is given entirely by the orbital angular momentum of rotating nuclei. In such case the spin rotation Hamiltonian takes the form

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

where $\boldsymbol{L}$ is the rotational angular momentum of molecular nuclei with respect to the center of mass (CM) of the molecule (we reserve the symbol $\boldsymbol{J}$ for the total, orbital and spin electronic angular momentum operator, see below); $\boldsymbol{M}_N$ is the SR tensor; and $\boldsymbol{I}_N$ stands for the spin operator of nucleus N.

From first principles considerations, in order to describe de SR tensor, it is necessary to identify those terms of the molecular Hamiltonian which couple bilinearly the nuclei rotational angular momentum $\boldsymbol{L}$ and the N-nucleus spin $\boldsymbol{I}_N$. In Ref. 6, we developed a theoretical formalism based on first order corrections to the BO approximation.[8] The zeroth order molecular wave function is expressed as the product

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

where $\psi_e(x, X)$ stands for the (relativistic) electronic ground state for fixed nuclear configuration X and $\phi(X)$ is the eigenstate of an effective Hamiltonian for the nuclei where the electron nucleus interaction is replaced by the corresponding mean value over the electronic wave function at each nuclear configuration. Taking the equilibrium configuration as starting point and neglecting vibrational effects, the Hamiltonian for the nuclei is the one corresponding to a purely rotating system described by the rigid rotor Hamiltonian,[6, 11]

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

where $\boldsymbol{L}$ 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 $\boldsymbol{\omega} = \boldsymbol{I}^{-1}\boldsymbol{L}$.

The effect of nuclear rotation on the electronic system can be taken into account by considering the action of the nuclear kinetic energy operator on the nuclear coordinates of the electronic part of the molecular wave function. Such terms are neglected in the zeroth-order BO approximation. Since the electronic state is referred to a reference system fixed to the molecular frame, the action of the $\boldsymbol{L}$ operator on the nuclear variables is equivalent to the action of minus the total 4-component relativistic angular momentum operator for electrons $\boldsymbol{J}_e$,[6, 11] yielding the following operator which is linear in $\boldsymbol{\omega}$:

$$h_{BO}^{(1)} = -\boldsymbol{\omega}\boldsymbol{J}_e. \tag{4}$$

The moving nuclear charge Z_N gives rise to an electron-nucleus Hamiltonian containing magnetic and retardation effects. Such terms are also linear in the nuclear velocity (and therefore in ω), and they were derived in a semiclassical way in Ref. 6. However, only within the QED theory this magnetic effect is obtained correctly, as published previously for the particular case of electron nuclear interaction for a nucleus with one half spin[12] and with zero spin.[13] The expressions obtained in both cases are similar to those of the electron-electron Breit interaction considered in the context of the so called mass shift term or recoil effect,[14–17] replacing the velocity operator corresponding to one electron by its nuclear counterpart. It is worthy to note that in such Breit Hamiltonian retardation effects are neglected. The electron-nucleus Breit Hamiltonian has the form

$$h_B^{(1)} = \sum_N \frac{Z_N}{\hat{r}_{eN}}(\boldsymbol{\alpha}\boldsymbol{\beta}_N) - \frac{Z_N}{2\hat{r}_{eN}}\boldsymbol{\alpha}\left(1 - \hat{r}_{eN}^t \hat{r}_{eN}\right)\boldsymbol{\beta}_N, \tag{5}$$

where $\boldsymbol{\alpha}$ are the four dimensional Dirac matrices, $\boldsymbol{\beta}_N$ represents the nucleus velocity relative to c, and $\hat{r}_{eN}$ is the unit vector of the electron position with respect to nucleus N. Atomic Gaussian units are used throughout this work, since in these units easier track of relativistic factors can be kept. The operator of Eq. (5) acting on the molecular wavefunction also gives rise to operator terms which are linear in the molecular angular velocity $\boldsymbol{\omega}$. This happens when operator $\boldsymbol{\beta}_N$ in Eq. (5) acts on the nuclear variables of the nuclear state. Taking into account that the leading order of this operator is $1/c^2$, which is of the same order as the leading order corrections taken into account in Ref. 6, full consistency of our relativistic approach requires detailed discussion of this effect.

The interaction Hamiltonian of electrons with the moving nucleus magnetic moment $\boldsymbol{\mu}_N$ is obtained by retaining those electromagnetic interactions which contain the associated vector potential operator,[6]

$$h_{\mu_N} = \left(\boldsymbol{\alpha} - \frac{\boldsymbol{p}_N}{m_N c}\right) \cdot \boldsymbol{A}_N(\boldsymbol{r}), \tag{6}$$

where the magnetic vector potential is given by

$$\boldsymbol{A}_N(\boldsymbol{r}) = \frac{\boldsymbol{\mu}_N \times (\boldsymbol{r} - \boldsymbol{r}_N)}{|\boldsymbol{r} - \boldsymbol{r}_N|^3}. \tag{7}$$

$\boldsymbol{\mu}_N = g_N \mu_p \hbar \boldsymbol{I}_N$ is the nuclear magnetic moment, g_N is its gyromagnetic factor, $\mu_p = 1/2 m_p c$ (in cgs a.u., m_p is the proton mass) the nuclear magneton, m_N is the mass of nucleus N.

On the other hand, the moving nuclei electric and magnetic fields give rise to electromagnetic interactions with the nuclear magnetic moments of other nuclei. For the calculation of the SR tensor, only terms which are linear in $\boldsymbol{A}_N(\boldsymbol{r})$ must be retained:[6]

$$h_{\omega,\mu_N}^{(2)nuc} = -\sum_M Z_M \left(\frac{\boldsymbol{p}_M}{m_M c} - \frac{\boldsymbol{p}_N}{m_N c} \right) \cdot \boldsymbol{A}_N(\boldsymbol{r}_M). \quad (8)$$

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. 6 and references therein)

$$h_{\mu_N}^{(1)} = \boldsymbol{\alpha} \cdot \boldsymbol{A}_N(\boldsymbol{r}), \quad (9)$$

which comes from Eq. (6),

$$h_\omega^{(1)} = h_{BO}^{(1)} + h_B^{(1)} \quad (10)$$

and

$$h_{\omega,\mu_N}^{(2)e} = -\frac{\boldsymbol{p}_N}{m_N c} \cdot \boldsymbol{A}_N(\boldsymbol{r}). \quad (11)$$

The first term of Eq. (10) will be referred to as the Born-Oppenheimer ("BO") contribution, and the second one as the "Breit" contribution.

The second order electronic contribution can be obtained by means of the relativistic 4-component linear response (*lr*) theory[18] at zero frequency, as the propagator

$$E^{(2)} = \langle\langle h_{\mu_N}^{(1)}; h_{BO}^{(1)} + h_B^{(1)} \rangle\rangle_0. \quad (12)$$

Explicit expression of the BO term considered in Ref. 7 is given by

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

The new contribution explicitly considered in the present work is the Breit one, given by

$$M_{N,i,j}^{(B)} = -\frac{\partial^2}{\partial I_{N,i} \partial L_j} \frac{g_N}{m_p c} \left\langle\left\langle \boldsymbol{I}_N \cdot \left(\frac{\boldsymbol{r} - \boldsymbol{r}_N}{|\boldsymbol{r} - \boldsymbol{r}_N|^3} \times \boldsymbol{\alpha} \right); \right.\right.$$
$$\left.\left. \times \sum_M \left(\boldsymbol{r}_{M,CM} \times \boldsymbol{D}_M \boldsymbol{\alpha} \right) \right\rangle\right\rangle_0 \boldsymbol{I}^{-1} \hat{\boldsymbol{L}}, \quad (14)$$

where the symmetric character of the tensor operator $\boldsymbol{D}_M$,

$$\boldsymbol{D}_M = \frac{Z_M}{2 c r_{eM}} \left(\boldsymbol{I} + \hat{\boldsymbol{r}}_{eM}^{\ t} \hat{\boldsymbol{r}}_{eM} \right) \quad (15)$$

has been used to move operator $\boldsymbol{\alpha}$ to the right in Eq. (14). The calculation of the propagator involves excitations to virtual electronic states (e-e excitations) and virtual positronic states (e-p excitations). Both kinds of terms can be obtained separately with adequate decomposition of the corresponding

blocks of the propagator,[19,20] as implemented in the DIRAC[10] code.

For the equilibrium molecular geometry, the first order electronic contribution and the nuclear contribution $h_{\omega,\mu_N}^{(2)nuc}$ can be gathered together in the simple (nuclear) term

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

In relativistic quantum chemistry, the interaction Hamiltonian of electrons taking full account of relativistic exchange of one photon between two "positive energy" electrons should contain both the Coulomb term and the Breit correction

$$U(1,2) = \frac{1}{r_{12}} - \frac{\boldsymbol{\alpha}_1 . \boldsymbol{\alpha}_2}{r_{12}} + \frac{\boldsymbol{\alpha}_1 \left(\hat{\boldsymbol{I}} - \hat{\boldsymbol{r}}_{12}^{\ t} \hat{\boldsymbol{r}}_{12} \right) \boldsymbol{\alpha}_2}{2 r_{12}}. \quad (17)$$

In Eq. (17), the second term is the Gaunt term and, together with the third term, the full correction to the Coulomb potential is the Breit operator. Consistency of relativistic calculations requires the inclusion of such terms, as their leading order is $1/c^2$, i.e., the same order as all leading order relativistic corrections. However, as it is computationally demanding and yields only small corrections, this term is usually neglected in 4-component calculations of magnetic properties.

The e-e Breit interaction will also yield a relativistic correction to the SR tensor in a given rotational molecular state. In fact, there must be an electronic analogue of the e-N Breit effect. It can be rationalized on the following grounds. The molecular rotation "drift" of the electronic state is obtained as a response to the $h_{BO}^{(1)}$ "inertia" operator, yielding a first order electronic state which is linear in ω. The corresponding change in the e-e Breit interaction for this perturbed electronic state reflects the change in the electrons velocities due to nuclear rotation and it is the electronic analogue of the e-N Breit interaction. The effect of this modification of the e-e interaction on the SR tensor could be obtained by evaluating the interaction with the chosen nucleus N magnetic dipole moment by means of third order perturbation theory. However, in DIRAC[10] code the Gaunt e-e interaction can be chosen to be included as part of the *un*perturbed Hamiltonian and the above mentioned effect on the SR tensor will be implicitly taken into account in the linear response calculation of the SR tensor with the usual expression of Eq. (13). Both the e-N Breit and the e-e Gaunt effects are analysed quantitatively in the present work in order to establish their relative importance in the relativistic calculation of the SR tensor in the set of model systems HX (X=H,F,Cl,Br,I).

B. Computational details

In the present work, Eq. (14) is used to obtain full-relativistic calculations of the electron nucleus Breit interaction contribution to the spin-rotation constant in model systems HX (X=H,F,Cl,Br,I) and compare their relative importance to the BO contribution of Eq. (13), the total value and

experimental results. The sign convention for the SR tensor is that of Refs. 1–4, although in modern literature it is usual to refer to the "c_N" tensor, which carries an opposite sign. Care must, therefore, be taken about this sign convention.

Relativistic calculations of spin-rotation constants were performed at the random phase approximation (RPA) level of polarization propagator formalism with the Dirac Coulomb Hartree-Fock (DCHF) and Dirac Coulomb-Gaunt approaches in order to investigate the importance of the Gaunt e-e interaction, as implemented in the DIRAC code.[10]

The basis sets used for H, F, and Cl atoms were the aug-cc-pV5Z basis set.[21,22] For Br and I we used the dyall.cv3z[23] basis set.

Experimental geometrical parameters[24] of HX (X=H,F,Cl,Br,I) compounds were considered. 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).

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 the "spin rotation (SR) constant" M_N (N=X,H).

III. RESULTS AND DISCUSSION

A. Electron-nucleus Breit and electron-electron Gaunt contributions to the SR tensor

In Table I, we present 4-component RPA numerical results of the electron-nucleus Breit contribution to the SR tensors of the X and H nuclei in HX (X=F,Cl,Br,I) systems, together with the corresponding values of the total "linear response" contribution arising from the BO term, Eq. (4) of Ref. 7, the corresponding relativistic correction, and the

experimental uncertainty of experimental values quoted in Ref. 7. In all cases where relativistic effects are meaningful, the e-N Breit correction is a very small portion of the relativistic effect, even though at first sight its leading order contribution is of order $1/c^2$ with respect to the non-relativistic expression, i.e., the same leading order as the BO correction itself. This is verified in the cases X=Cl,Br, and I. In such cases, the Breit e-N contribution is negligibly small in a relative scale both for M_X and M_H, and below uncertainty in the experimental value by approximately one order of magnitude. As it was expected from a series expansion in $1/c$, only for non-relativistic electrons the Breit e-N contribution is of a similar magnitude as the BO one, but in such case the whole relativistic correction is negligibly small. This is the case of H_2, where relativistic corrections are within numerical error of calculated values.

From first principles, the electron-electron Breit interaction also yields relativistic effects with a leading order contribution of $1/c^2$ as compared to non-relativistic dynamics in the electronic Hamiltonian. Therefore, a consistent approach including the e-N Breit effect should also include such e-e Breit interaction in the Dirac-Coulomb-Breit Hamiltonian. Unfortunately, the DIRAC code allows only to take account of the Gaunt e-e interaction instead of the full Breit interaction. However, we believe it is very interesting to present the effect of including such Gaunt interaction in calculations of the SR tensor in the present series of molecules. This allows to obtain qualitative insight on the relative importance of such terms as compared to the e-N Breit effect. Numerical results are presented in Table II for the heavier X=Cl, Br, and I halogen hydrides.

In all cases, the e-N Breit and e-e Gaunt effects are negligibly small but of similar magnitude for the halogen nucleus X. But in the case of M_H, the e-e Gaunt effect is much larger than the e-N Breit effect, and it is of increasing importance in the series Cl, Br, I. The largest contribution of −0.43 kHz for M_H in HI is certainly a non-negligible contribution to the full SR tensor, despite it being only 2% as compared to the BO relativistic effect of Table I. It is interesting to remark that these findings are consistent with previous results on the NMR shielding (NMS) tensor. The so-called two-body spin-orbit effect on magnetic properties comes out precisely from carrying out the elimination of the small component (ESC) procedure in the electron-electron Breit interaction.[25,26] This two-body spin-orbit effect was numerically estimated in the case of the NMS tensor in Ref. 18 and within a mean-field approach in Ref. 27. The obtained value of −1.3 ppm[27] as

TABLE I. "Best estimate" linear response M_{lr} contribution to spin-rotation constants M_N (in kHz) for HX molecules (X=H,F,Cl,Br,I) obtained for the BO term in Ref. 7, relativistic effect given as the difference with the correlated non-relativistic values, $\Delta^R M_{lr}$, RPA linear response contribution given by the electron-nucleus Breit interaction, M_{lr}^B, and experimental results.

Molecule	N	M_{lr}	$\Delta^R M_{lr}$	M_{lr}^B	M_N^{exp} [a]
H_2	^{1}H	11.01	0.02	0.0110	11.09 (<0.001)[b]
HF	^{19}F	−357.57	−0.67	−0.029	−360.11(0.02)[c]
HCl	^{35}Cl	−56.54	−0.04	−0.004	−55.88(0.05)[d]
HBr	^{79}Br	−294.80	3.09	−0.027	−294.65(0.08)[e]
HI	^{127}I	−349.03	22.19	−0.029	−353.18(0.3)[f]
HF	^{1}H	50.77	1.03	−0.0087	48.47(0.02)[c]
HCl	^{1}H	33.96	2.12	−0.005	32.24(0.14)[d]
HBr	^{1}H	35.56	8.95	−0.003	35.00(0.31)[e]
HI	^{1}H	43.85	21.49	−0.006	45.18(0.22)[f]

[a] The M_N tensor is defined here according to the sign convention of Flygare.[4] Modern literature usually makes reference to the opposite "c_N" tensor. The nuclear contribution has been subtracted from the experimental value. In the case of H_2 the vibrational correction was also subtracted.
[b] Taken from Ref. 29.
[c] Taken from Ref. 30.
[d] Taken from Ref. 31.
[e] Taken from Ref. 32.
[f] Taken from Ref. 33.

TABLE II. e-N Breit and e-e Gaunt contributions to M_X and M_H in HX (X=Cl,Br,I) given by 4 component RPA approach, and total combined effects. Values in kHz.

Molecule	N	M_{lr}^B	M_{lr}^G	$M_{lr}^G + M_{lr}^B$
HCl	^{35}Cl	−0.004	0.0026	−0.00172
HBr	^{79}Br	−0.027	0.0182	−0.0089
HI	^{127}I	−0.029	−0.080	−0.109
HCl	^{1}H	−0.005	−0.117	−0.122
HBr	^{1}H	−0.003	−0.245	−0.248
HI	^{1}H	−0.006	−0.424	−0.430

TABLE III. Decomposition of the e-N Breit contribution to M_X and M_H in HX (X=H,F,Cl,Br,I) into "electron excitation" terms (ee) and "electron-positron excitation" terms (ep) as given by 4 component RPA calculations. Values in kHz.

Molecule	N	M_{ee}^B	M_{ep}^B	M_{lr}^B
H_2	^{1}H	0.0133	−0.0023	0.011
HF	^{19}F	−0.0130	−0.0163	−0.0293
HCl	^{35}Cl	−0.0031	−0.0013	−0.0044
HBr	^{79}Br	−0.0186	−0.0085	−0.0271
HI	^{127}I	−0.0214	−0.0075	−0.0289
HF	^{1}H	0.0047	−0.0134	−0.0087
HCl	^{1}H	0.0117	−0.0163	−0.0046
HBr	^{1}H	0.0316	−0.0346	−0.0030
HI	^{1}H	0.0316	−0.0377	−0.0061

compared to the full relativistic effect of ~18.41 ppm[26] for the NMS constant of the H nucleus in HI reflects a relative contribution of about 7% in the case of this NMR parameter.

As a final remark we quote separately contributions from "electronic excitations" (ee) terms (i.e., positive energy states) and from "electron-positron excitations" (ep) terms (i.e., contributions from negative-energy states in the Dirac Hartree-Fock scheme) as given in DIRAC program.[10] Results are presented in Table III. It is seen that for the heavy nucleus X the (ee) contribution becomes larger in magnitude than the (ep) one for increasing atomic number, but the total value is of similar order of magnitude than individual terms. On the other hand, for the light H nucleus it is observed that for heavier X the contributions from (ee) and (ep) excitations are of similar magnitude and nearly cancel each other to give a total value one order of magnitude smaller than individual terms. It is interesting to remark that from first principles, the e-N Breit interaction is an approximate way to take account of the exchange of one virtual photon between positive-energy particles within quantum electrodynamics theory.[28] A more careful analysis would lead to improved results. However, as mentioned above, these contributions are smaller than or within experimental precision, and therefore estimates of the present work can be considered quite satisfactory to yield an idea of its relative importance in the calculation of the relativistic SR tensor.

IV. CONCLUDING REMARKS

The importance of the e-N Breit interaction in relativistic calculations of the SR tensor has been quantitatively analysed taking systems HX (X=H,F,Cl,Br,I) as model compounds. Results obtained fully confirm the assumptions made in Refs. 6 and 7 about the relative importance of such contributions as compared to the "BO" one discussed in those works. The e-e Gaunt effect was also analysed. Taking into account the corresponding values these contributions are by far much smaller than relativistic effects given within the 4 component theory of the BO contribution. It is concluded that in order to reach experimental accuracy in theoretical calculations of the SR tensor in heavy atom containing compounds, other relevant effects must be accurately calculated on such BO term. It is interesting to remark on this regard that unlike the case

of NMR, where the absolute NMS tensor cannot be measured in experiments, S.S.G. the SR tensor is precisely determined from experiments. Therefore, this spectroscopic parameter is a really tough probe for theoretical calculations. For instance, it was recognized in Ref. 7 that correlation effects are very relevant to yield quantitative values of the SR tensor in this series of compounds. Therefore, detailed calculations with different methods for taking account of correlation effects, and particularly inner-shell correlations can be tested by carrying out numerical studies of the SR tensor in different compounds. In order to improve further the accuracy of numerical values nuclear charge distribution effects might also be of importance, as well as vibrational corrections. Work along these lines is being carried out in our research group.

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