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# Theoretical study of the relativistic molecular rotational g-tensor

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An original formulation of the relativistic molecular rotational g-tensor valid for heavy atom containing compounds is presented. In such formulation, the relevant terms of a molecular Hamiltonian for non-relativistic nuclei and relativistic electrons in the laboratory system are considered. Terms linear and bilinear in the nuclear rotation angular momentum and an external uniform magnetic field are considered within first and second order (relativistic) perturbation theory to obtain the rotational g-tensor. Relativistic effects are further analyzed by carrying out the linear response within the elimination of the small component expansion. Quantitative results for model systems HX (X=F, Cl, Br, I), XF (X=Cl, Br, I), and YH$^+$ (Y=Ne, Ar, Kr, Xe, Rn) are obtained both at the RPA and density functional theory levels of approximation. Relativistic effects are shown to be small for this molecular property. The relation between the rotational g-tensor and susceptibility tensor which is valid in the non-relativistic theory does not hold within the relativistic framework, and differences between both molecular parameters are analyzed for the model systems under study. It is found that the non-relativistic relation remains valid within 2% even for the heavy HI, IF, and XeH$^+$ systems. Only for the sixth-row Rn atom a significant deviation of this relation is found. © 2014 AIP Publishing LLC.
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## I. INTRODUCTION

The great development of *ab initio* relativistic quantum chemistry in the last decade allows present days routine calculations of many molecular properties in a relativistic context. In particular, spectroscopic parameters depending on the electronic distribution in the close vicinity of the molecule atomic nuclei are very sensitive to relativistic effects in heavy atom containing compounds. This is the case, for instance, of the NMR shielding-tensor (NMST) $\sigma$ and J couplings.[1,2] Theoretical details associated to finite nucleus effects, subtle quantum electrodynamics (QED) effects, Breit interaction effects, etc., have been analyzed in the recent literature.[3]

Despite these great advances, for the case of spectral parameters associated to molecular rotation effects, some crucial points have been unveiled only in the past few years.[4–7] The difficulty of coupling the effect of molecular rotation with a relativistic description of the electronic distribution was solved in a sound and clear framework in Ref. 4. The key aspect of this procedure was to consider non-relativistic dynamics for the description of molecular nuclei in rotational states coupled to relativistic electrons in a molecular Hamiltonian written entirely in the laboratory system.

This approach is largely justified taking into account the slow motion of nuclei in rotational states. In this context, a theoretical expression for the spin rotation (SR) tensor was derived. Numerical results[5,8–11] strongly support the correctness of this approach. In particular, it was possible to critically discuss the loss of the connection between the SR and the NMR shielding-tensor $\sigma$ valid in non-relativistic quantum dynamics. This property was anticipated long ago,[12] but a strict formal and numerical analysis of the differences between both spectral parameters was carried out for the first time in Ref. 5. Further developments in the relativistic theory of the SR tensor were also published by others.[6,7,13]

The excellent results obtained for the case of the SR tensor are a strong indication that the theoretical procedure developed in Ref. 4 is a sound approach, yielding results within 1%-2% of experimental values. Subtle effects, like electron-(moving)nucleus Breit interaction effects have shown to give only tiny contributions to the total SR tensor in the model systems considered until now.[8]

The formalism developed in Ref. 4 has shown to yield the key to correctly couple the electrons and nuclear dynamics in the case of relativistic electrons. In the present work, we apply it to the analysis of the molecular rotational g-tensor, which describes the response of the rotating molecule to an external uniform magnetic field. Even though formal expressions of the relativistic rotational g-tensor were obtained in the past,[14] it is interesting to re-discuss it in the present context.

Similar to the case of the NMR shielding $\sigma$ and SR tensors, in the non-relativistic theory there exists a formal relation connecting the rotational g-tensor and paramagnetic component of the molecular susceptibility tensor $\chi$.[15] It has

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been long recognised that this connection will fail to hold in the relativistic theory.[12] The susceptibility tensor within relativistic theory was analyzed in the past.[12,14,16] However, 4-component calculations of the susceptibility tensor were carried out as part of the present work for comparison purposes. In order to deepen the analysis of the relation between both parameters, we have carried out a perturbative expansion of relativistic effects based on the LRESC[17] (Linear Response within the Elimination of the Small Component) approach. Remarkable differences with the cases of the NMR shielding and the SR tensor are highlighted.

Benchmark numerical results of the molecular g-tensor carried out with the DIRAC program[18] are presented in a set of model systems containing increasingly heavy atoms: HX (X=F, Cl, Br, I), XF (X=Cl, Br, I), and YH$^+$ (Y=Ne, Ar, Kr, Xe, Rn). Linear response calculations were carried out at the RPA level,[12,19] and also with the LDA[20] and PBE0[21] approaches of density functional theory (DFT)[22,23] in order to estimate the importance of correlation effects. Both the g- and susceptibility tensors test the response of the electron density in terms of operators which are non-singular at the nuclear positions. Therefore, relativistic effects related to inner-shell electrons are expected to be less important in these cases than those of the $\sigma$ and SR tensors.

## II. METHODS AND COMPUTATIONS

### A. Relativistic 4-component expressions of the rotational g-tensor and magnetic susceptibility $\chi$ tensor

The rotational g-tensor is the molecular parameter describing the induced magnetic moment of a molecule due to rotation:

$$\boldsymbol{m} = \frac{\mu_N}{\hbar} \boldsymbol{g} \boldsymbol{L}, \tag{1}$$

where $\boldsymbol{m}$ is the molecule magnetic moment, $\mu_N$ the nuclear magneton, and $\boldsymbol{L}$ the rotational angular momentum of the molecule. In the present work, we consider only systems with no electronic contribution to the total molecular angular momentum, i.e., the rotational $\boldsymbol{L}$ angular momentum is given only by the rotational states of the nuclei of the system. Gaussian atomic units (a.u.) are adopted in the present work. In this system of units, easier track of relativistic effects can be kept, as the fine structure constant is directly given as $1/c$. The nuclear magneton is $\mu_N = 1/2M_p c$, where $M_p$ is the proton mass in a.u.

Formally, the molecular g-tensor can be obtained considering the Hamiltonian of a molecule in the presence of a uniform external magnetic field as

$$g_{ij} = -2M_p c \frac{\partial^2 E(\boldsymbol{B}, \boldsymbol{L})}{\partial L_j \partial B_i}\Big|_{B=L=0}, \tag{2}$$

where $E(\boldsymbol{B}, \boldsymbol{L})$ is the expectation value of the Hamiltonian. This means that terms linear and bilinear in the rotational angular momentum $\boldsymbol{L}$ and the external magnetic field intensity $\boldsymbol{B}$ must be retained in the molecular Hamiltonian in order to be able to evaluate all contributions to $E(\boldsymbol{B}, \boldsymbol{L})$ by first and second order perturbation theory.

The molecular magnetizability tensor $\boldsymbol{\chi}$ relates the response of the molecule to the presence of a uniform magnetic field with the corresponding field intensity $\boldsymbol{B}$. It can be formally obtained from a second order expansion of the molecular energy as

$$\chi_{ij} = -\frac{\partial^2 E(\boldsymbol{B})}{\partial B_i \partial B_j}\Big|_{B=0}. \tag{3}$$

Typical nuclear velocities in molecular rotational states are negligibly small compared to the speed of light. Therefore, nuclei can be described properly by a non-relativistic Hamiltonian, with the addition (when relevant) of relativistic corrections like magnetic and spin-orbit nuclear effects. But in the presence of heavy atoms, the electrons dynamics must be described within a relativistic theory. Under these assumptions a formal theoretical treatment of the molecular Hamiltonian for nuclei and electrons was obtained on Ref. 4, yielding the coupling between both in rotational states. Details of the formal derivation were extensively discussed in that work. Therefore, only a brief sketch of the formalism is presented here.

### 1. Correction terms to the molecular Hamiltonian which take account of molecular rotation

The effect of rotation in molecular states is included in the molecular Hamiltonian considering leading order corrections to the Born-Oppenheimer (BO) approximation.[24] At zeroth order, the molecular wavefunction is expressed as a product of the solution of the electronic problem, with fixed nuclear positions, and the nuclear wavefunction is obtained considering an effective potential produced by the other nuclei and the electrons in their ground state

$$\Psi_{mol}(x, X) = \psi_e(x, X)\phi(X), \tag{4}$$

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 one corresponding to a purely rotating system around the molecular center of mass (CM) described by the rigid rotor Hamiltonian,[4,25]

$$H^R = \frac{1}{2}\hat{\boldsymbol{L}} \boldsymbol{I}^{-1} \hat{\boldsymbol{L}}, \tag{5}$$

where $\hat{\boldsymbol{L}}$ is the rotational angular momentum, and $\boldsymbol{I}$ is the molecular inertia tensor, both taken with respect to the CM of the system. 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 $\hat{\boldsymbol{J}}_e$,[4,25] taken with respect to the molecular CM. There are two such terms, one of them is quadratic

in $\hat{J}_e$, while the second term couples the electronic angular momentum $\hat{J}_e$ and the nuclear angular momentum $\hat{L}$

$$h_{BO}^{(1)} = -(I^{-1}\hat{L})\hat{J}_e. \tag{6}$$

$h_{BO}^{(1)}$ describes the "drift" of the electronic distribution due to molecular rotation as an operator linear in the nuclear angular momentum $\hat{L}$. In Eq. (6), operator $\hat{J}_e$ was moved to the right in order to highlight that it applies directly on the electronic wavefunction.

A second effect of molecular rotation on the electronic distribution comes out as a consequence of the electromagnetic interaction between electrons and moving nuclei. In addition to the electrostatic term, each moving nuclear charge $Z_N$ gives rise to magnetic and retardation effects. An appropriate derivation of this Hamiltonian is accomplished within the QED theory.[26–28] The correspondent expression is given by the Breit-like operator, replacing the velocity operator corresponding to one electron with its nuclear counterpart. Within this approximation, retardation effects are neglected. The formal expression (which is also linear in the nuclear velocity $\beta_N$[4]) is given by

$$h_{Breit}^{(1)} = \sum_N \frac{Z_N}{r_{eN}}(\alpha\beta_N) - \frac{Z_N}{2r_{eN}}\alpha\left(I - \hat{r}_{eN}{}^t\hat{r}_{eN}\right)\beta_N, \tag{7}$$

where $\alpha$ are the four-dimensional Dirac matrices, $\beta_N$ represents the nucleus velocity relative to c, and $\hat{r}_{eN}$ is the unit vector of the electron position with respect to nucleus N. The operator of Eq. (7) acting on the molecular wavefunction gives rise to operator terms which are linear in the rotational angular momentum $L$. This happens when operator $\beta_N$ in Eq. (7) acts on the nuclear variables of the nuclear state. Explicitly, this relation is given by

$$\beta_N = \frac{1}{c}(\omega) \times r_{N,CM} = \frac{1}{c}(I^{-1} \cdot L) \times r_{N,CM}, \tag{8}$$

where $r_{N,CM} = r_N - r_{CM}$ is the nuclear position with respect to the molecular center of mass.

### 2. Interactions with an external magnetic field

In the presence of a uniform magnetic field, the relativistic interaction of electrons is given by

$$h_B^{(1)} = \alpha \cdot A(r_{eG}), \tag{9}$$

where the magnetic potential is given by

$$A(r_{eG}) = \frac{1}{2}B \times (r_e - R_G). \tag{10}$$

$R_G$ stands for the vector position of the (arbitrary) gauge origin of the magnetic potential. For the purposes of the present work, it is convenient to take the CM of the molecule as gauge origin. Therefore, in what follows no explicit reference to the gauge origin will be necessary and the subindex "G" is dropped from all equations. The corresponding interaction with moving non-relativistic nuclei (the diamagnetic term in Eq. (11) is neglected since it is independent of the nuclear velocities) is given by

$$h_{\omega,B}^{(2)} = -\sum_N Z_N \beta_N \cdot A(r_N). \tag{11}$$

### 3. The relativistic rotational g- and magnetic susceptibility χ tensors

Taking into account the definition of the rotational g-tensor, Eq. (2), its formal expression is obtained by considering the perturbative Hamiltonians discussed above, and combining them in first and second order perturbation theory energy corrections yielding results bilinear in the magnetic field intensity $B$ and the rotational angular momentum $L$.

The nuclear contribution is given by the non-relativistic result

$$g_{nuc} = \sum_N Z_N M_p((r_{N,G} \cdot r_{N,CM})I^{-1} - (r_{N,G} \cdot I^{-1})r_{N,CM}). \tag{12}$$

The electronic part can be obtained within the linear response approach[12,19] considering operators $h_B^{(1)}$, Eq. (9) on one hand and operators $h_{BO}^{(1)}$, Eq. (6) and $h_{Breit}^{(1)}$, Eq. (7) on the other hand,

$$g^{el-R} = M_p c \langle\langle r_e \times \alpha \quad ; \quad I^{-1}J_e$$
$$- \sum_M (r_{M,CM} \times D_M\alpha)I^{-1}\rangle\rangle_{\omega=0}, \tag{13}$$

where the symmetric tensor operator $D_M$:

$$D_M = \frac{Z_M}{2c\,r_{eM}}\left(I + \hat{r}_{eN}{}^t\hat{r}_{eN}\right) \tag{14}$$

has been introduced to move operator $\alpha$ to the right in Eq. (13). The tensor components of $g^{el}$ in Eq. (13) are obtained by tensor product of the vector components of the r.h.s. and l.h.s. vector operators in the linear response expression. The Breit contribution is expected to be negligibly small and will not be considered further in the present work.[8]

The magnetic susceptibility tensor, which was defined in Eq. (3) also has both nuclear and electronic contributions, which were extensively worked out in the bibliography at the relativistic level.[12,14,16] We only report the formal expressions for comparison with those of the rotational g-tensor. Neglecting contributions quadratic in the nuclear velocities, the nuclear part is only diamagnetic

$$\chi_{nuc}^{dia} = -\frac{1}{8}\sum_N \frac{Z_N^2}{m_N c^2}\left(\hat{I}r_N^2 - r_N^t r_N\right). \tag{15}$$

The electronic contribution is obtained through second order perturbation theory

$$\chi^{el} = -\frac{1}{4}\langle\langle\alpha \times r_e \quad ; \quad \alpha \times r_e\rangle\rangle_{\omega=0}. \tag{16}$$

The calculation of the propagator in Eqs. (13) and (16) involves excitations to virtual electronic states (e-e excitations) and virtual positronic states (e-p excitations). The contribution from each kind of excitations can be separated with a decomposition of the propagator as indicated in Refs. 19 and 29. In the non-relativistic limit, the (e-e) part corresponds to the paramagnetic component of the magnetic property under study while the (e-p) part gives rise to the diamagnetic component.[29]

The theoretical expression of the relativistic g-tensor derived in the present work has differences with those of

previous works in the bibliography.[14] As it was anticipated in previous work,[12] the usual relation valid within the non-relativistic theory between the rotational g-tensor and the paramagnetic component of the susceptibility tensor is lost (compare Eqs. (13) and (16)). However, within the present approach, it can be shown that the "diamagnetic" component of the rotational g-tensor vanishes naturally in the non-relativistic limit. The non-relativistic formal equivalence is therefore recovered as a formal property of the theory. As it happens with the SR tensor (e-p) contributions will also give a zero result at the leading order relativistic correction (*vide infra*). In order to deepen the understanding of the relation between both molecular parameters, leading order relativistic effects given by the LRESC approach are discussed in Sec. II B.

## B. Leading relativistic corrections to molecular g- and susceptibility χ tensors within the LRESC approach

The LRESC approach[17] allows any second order relativistic property to be expanded in terms of the fine structure constant ($1/c$ in a.u.). The zeroth order term yields the non-relativistic expression of the property, and the leading order relativistic corrections are obtained in the context of the elimination of the small component (ESC) approach.[30]

In the present section, the LRESC expressions of the g and χ tensors are obtained. The kind of analysis allowed by the LRESC approach are mainly related to unveil the physical mechanisms of relativistic effects. In the present work, such analysis is also useful to establish the relation between the g- and magnetic susceptibility tensor. The situation has similarities but also interesting differences with the relation between the NMR shielding and nuclear spin-rotation tensors analyzed in previous work.[4] The details of the LRESC approach were extensively discussed in Refs. 17, 31, and 32. Therefore, only the main steps yielding the LRESC g-tensor and magnetic susceptibility tensors are worked out in the present section.

The relativistic second order perturbation theory correction to the energy $E(V, W)$ for two 4-component operators $V$ and $W$ is split into two terms, one involving the positive energy spectrum of electronic states ((e-e) excitations) and a second term involving the negative energy spectrum, i.e., virtual electron-positron pairs in the QED picture (e-p excitations).

In order to carry out the LRESC expansion of the (e-e) contributions, on one hand one must apply the ESC approximation to matrix elements of the 4-component operator $V$ (and $W$ as well) involved between positive energy four-component spinors $|\phi_j^{(4)}\rangle$, 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.,[17]

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

Retaining up to the leading order relativistic effects ($1/c^2$), operator $O(V)$ can be split as

$$O(V) = O^{nr}(V) + O^{(2)}(V), \tag{18}$$

where $O^{nr}(V)$ is the non-relativistic (i.e., Schrödinger) expression of the operator and $O^{(2)}(V)$ the leading order relativistic correction.

The second source of relativistic corrections come out from the unperturbed Pauli Hamiltonian[30] (we consider only one-body relativistic effects in the present work)

$$H^P = H^{Sch} + D, \tag{19}$$

where $H^{Sch}$ is the non-relativistic Schrödinger molecular Hamiltonian, and

$$D = -\frac{p^4}{8c^2} + \frac{1}{8c^2}\nabla^2 V_C + \frac{1}{2c^2}\boldsymbol{S}\cdot(\nabla V_C \times \boldsymbol{p}) \tag{20}$$

are the Pauli mass-velocity $H^{Mv}$ (first term), Darwin $H^{Dw}$ (second term), and spin-orbit $H^{SO}$ (third term) perturbative relativistic corrections. $V_C$ stands for the Coulomb potential of the atomic nuclei.

The LRESC contribution to the energy coming from (e-e) excitations is therefore given by

$$\begin{aligned}
E^{(e-e)}(V, W) &= E^{(2)}(O^{nr}(V), O^{nr}(W)) \\
&\quad + E^{(2)}(O^{nr}(V), O^{(2)}(W)) \\
&\quad + E^{(2)}(O^{(2)}(V), O^{nr}(W)) \\
&\quad + E^{(3)}(O^{nr}(V), O^{nr}(W), D), \tag{21}
\end{aligned}$$

where $E^{(2)}$, $E^{(3)}$ stand for second and third order corrections to the energy within (non-relativistic) Rayleigh-Schrödinger perturbation theory (RSPT).

Contributions coming from e-p excitations are now considered. Taking into account that within the QED picture, negative-energy solutions of the Dirac equation are reinterpreted as positive energy states for positrons, the non-relativistic and lower order contributions to $E^{(e-p)}(V, W)$ can be obtained starting with the following expansion of the energy differences between the relativistic ground state and a state carrying an extra electron-positron pair:

$$E_n - E_0 = 2c^2 + \Delta_{n,o} = 2c^2\left(1 + \frac{\Delta_{n,0}}{2c^2}\right), \tag{22}$$

where $\Delta_{n,0}$ is of order $c^0$ or lower, and therefore the term $\frac{\Delta_{n,0}}{2c^2}$ can be used as expansion parameter.

A key result derived in Ref. 17 is to show that up to the leading order in this expansion parameter the overall (e-p) contribution to the energy can be obtained from the 4-component expression

$$\begin{aligned}
E^{(e-p)}(V, W) &= \frac{1}{2c^2}(\langle\Psi_0|V P_p X(W)|\Psi_0\rangle \\
&\quad + \langle\Psi_0|W P_p X(V)|\Psi_0\rangle), \tag{23}
\end{aligned}$$

where $|\psi_0\rangle$ stands for the relativistic ground state of the Dirac Hartree-Fock approximation and, for brevity, it was defined

$$X(V) = 2V + \frac{1}{2c^2}[H, V], \tag{24}$$

where $H$ is the relativistic unperturbed Hamiltonian, and $P_p$ in Eq. (23) is the projector onto "positronic" states. Neglecting two-body terms in the final result, consistently to the lowest

order in $1/c^2$ it holds

$$X(V) \approx 2V + \frac{1}{2}[\beta, V], \qquad (25)$$

where $\beta$ is the scalar 4-dimensional Dirac matrix. Taking into account that $P_p$ is the complement of the projector onto the subspace of positive energy 4-spinors, the full $E^{(e-p)}$ expression of Eq. (23) can be expanded in terms of the ESC approximation. As a consequence, the non-relativistic limit and leading order relativistic corrections originated in (e-p) terms can be obtained.[17] Explicit expressions are worked out for the case of the rotational g-tensor.

### 1. The LRESC expression of the rotational g-tensor

The rotational g-tensor involves operators $V = \boldsymbol{\alpha} \cdot \boldsymbol{A}$ and $W = -\boldsymbol{\omega} \cdot \boldsymbol{J}_e^{(4)}$. The corresponding expansion defined in Eq. (18) for the magnetic interaction has been worked out extensively by different authors, and therefore only the final expression is presented here[17,33,34]

$$O(\boldsymbol{\alpha} \cdot \boldsymbol{A}) = \frac{1}{2c}(\boldsymbol{L}_e + 2\boldsymbol{S}) \cdot \boldsymbol{B} + (\boldsymbol{V}^{OZ-K}$$
$$+ \boldsymbol{V}^{SZ-K} + \boldsymbol{V}^{B-SO}) \cdot \boldsymbol{B}, \qquad (26)$$

where now $\boldsymbol{L}_e$, $\boldsymbol{S}$ are the non-relativistic electronic orbital and spin angular momentum operators. The lowest order terms in Eq. (26) are the Orbital- and Spin-Zeeman operators (OZ and SZ, respectively). The leading order relativistic effects are described by operators

$$\boldsymbol{V}^{OZ-K} = -\frac{1}{8c^3}\{p^2; \boldsymbol{L}_e\}, \qquad (27)$$

$$\boldsymbol{V}^{SZ-K} = -\frac{1}{4c^3}(3\boldsymbol{S}p^2 - (\boldsymbol{S} \cdot \boldsymbol{p})\boldsymbol{p}), \qquad (28)$$

and the so-called "magnetic external field induced spin-orbit" (B-SO) operator,

$$\boldsymbol{V}^{B-SO} = \frac{1}{2c^3}[(\boldsymbol{r} \cdot \nabla V_C)\boldsymbol{S} - (\boldsymbol{r} \cdot \boldsymbol{S})\nabla V_C]. \qquad (29)$$

In Eq. (27), the curly brackets stand for the anticommutator of operators $p^2$ and $\boldsymbol{L}_e$.

On the other hand, the LRESC expansion of matrix elements of the 4-component $\boldsymbol{J}_e^{(4)}$ operator was worked out in detail in Ref. 4 and it holds

$$O(\boldsymbol{J}_e^{(4)}) = \boldsymbol{J}_e^{(2)} = \boldsymbol{L}_e + \boldsymbol{S}. \qquad (30)$$

As it is seen in Eq. (30) no additional terms, up to order $1/c^2$, contribute to the 4-component total angular momentum operator $\boldsymbol{J}_e^{(4)}$ expansion.

The operators needed to obtain the $E^{(e-p)}$ contribution in the LRESC expansion are now considered

$$X(\boldsymbol{\alpha} \cdot \boldsymbol{A}) = 2\boldsymbol{\alpha} \cdot \boldsymbol{A} + \frac{1}{2}[\beta, \boldsymbol{\alpha} \cdot \boldsymbol{A}] = (2 + \beta)\boldsymbol{\alpha} \cdot \boldsymbol{A}; \quad (31)$$

$$X(\boldsymbol{J}_e^{(4)}) = 2\boldsymbol{J}_e^{(4)} + \frac{1}{2}[\beta, \boldsymbol{J}_e^{(4)}] = 2\boldsymbol{J}_e^{(4)}. \qquad (32)$$

Taking into account Eqs. (26) and (30), the non-relativistic limit of the (e-e) contribution to the rotational g-tensor yields

naturally the expression of the non-relativistic theory

$$\boldsymbol{g}^{el-NR} = M_p E^{(2)}(\boldsymbol{L}_e; \boldsymbol{L}_e)\boldsymbol{I}^{-1}. \qquad (33)$$

The leading order LRESC relativistic corrections to the g-tensor

$$\boldsymbol{g}^{(2)} \simeq \boldsymbol{g}^{el-R} - \boldsymbol{g}^{el-NR}, \qquad (34)$$

in the case of closed shell molecules (i.e., with a non-relativistic ground state with $S = 0$), $\boldsymbol{g}^{(2)}$ is given by

$$\boldsymbol{g}^{(2)} = (-2M_p c)\left[ E^{(2)}(\boldsymbol{V}^{OZ-K}, -\boldsymbol{I}^{-1}\boldsymbol{L}_e) + \frac{1}{2c}E^{(3)}(D; \boldsymbol{L}_e \right.$$
$$\left. + 2\boldsymbol{S}; -\boldsymbol{I}^{-1}\boldsymbol{J}_e) \right] + \boldsymbol{g}^{(e-p)} \qquad (35)$$

(the nuclear contribution is neglected since it is the same in both cases, as in the present approach nuclei are treated within a non-relativistic approach). Operator $\boldsymbol{J}_e$ was replaced by operator $\boldsymbol{L}_e$ in the first term of the right hand side of Eq. (35) because the spin part yields zero in the case of closed shell molecules. In principle, this gives rise to four mechanisms in the (e-e) excitation part

$$\boldsymbol{g}^{OZ-K} = -\frac{M_p}{4c^2}E^{(2)}(\{\boldsymbol{L}_e, p^2\}, \boldsymbol{L}_e)\boldsymbol{I}^{-1}, \qquad (36)$$

and

$$\boldsymbol{g}^{Mv} = M_p E^{(3)}(H^{Mv}, \boldsymbol{L}_e, \boldsymbol{L}_e)\boldsymbol{I}^{-1}, \qquad (37)$$

$$\boldsymbol{g}^{Dw} = M_p E^{(3)}(H^{Dw}, \boldsymbol{L}_e, \boldsymbol{L}_e)\boldsymbol{I}^{-1}, \qquad (38)$$

$$\boldsymbol{g}^{SO} = 3M_p E^{(3)}(H^{SO}, \boldsymbol{L}_e, \boldsymbol{S})\boldsymbol{I}^{-1}. \qquad (39)$$

These four mechanisms are analogous to those found for the SR tensor,[4] but the magnetic field of an atomic nucleus is replaced by a uniform magnetic field. However, unlike the case of the SR tensor, here the last term, $\boldsymbol{g}^{(SO)}$ vanishes identically.

The (e-p) term, $\boldsymbol{g}^{(e-p)}$ is now considered. To this end, the approximate expression of the (e-p) contribution to the energy in Eq. (23) is expanded considering the ESC scheme

$$E^{(e-p)} = \frac{1}{2c^2}\big(\langle\Psi_0|(\boldsymbol{\alpha} \cdot \boldsymbol{A})P_p X(-\boldsymbol{\omega} \cdot \boldsymbol{J}_e^{(4)})|\Psi_0\rangle$$
$$+ \langle\Psi_0|(-\boldsymbol{\omega} \cdot \boldsymbol{J}_e^{(4)})P_p X(\boldsymbol{\alpha} \cdot \boldsymbol{A})|\Psi_0\rangle\big). \qquad (40)$$

Taking into account that the non-relativistic rotational g-tensor carries no factors of $1/c$, it is immediately concluded that there is no non-relativistic contribution, and that the lowest order term is itself a relativistic effect. In order to calculate such leading order correction, the expectation value in Eq. (40) must be evaluated up to order $c^{-3}$. By explicit calculation, it can be shown that such contribution is also identically zero.

Therefore, it is verified that both, the non-relativistic and the leading order LRESC relativistic correction to $E^{(e-p)}$ yield a zero for the rotational g-tensor, i.e.,

$$\boldsymbol{g}^{(e-p)} = 0. \qquad (41)$$

This behaviour is totally similar to that found for the spin-rotation tensor.[4]

### 2. LRESC expansion of the magnetic susceptibility tensor

The magnetic susceptibility tensor involves twice the magnetic field interaction operator ($\boldsymbol{\alpha} \cdot \boldsymbol{A}$). The component coming from excitations to excited electronic states $\chi^{(e-e)}$ is first considered. From the first term in Eq. (26), it is readily seen that in the non-relativistic limit the paramagnetic component of the (non-relativistic) magnetic susceptibility tensor is obtained

$$\chi^{(e-e)NR} = -\frac{1}{4c^2} E^{(2)}(\boldsymbol{L}_e, \boldsymbol{L}_e) = \chi^{p-NR}. \quad (42)$$

The leading order relativistic corrections $\chi^{(e-e)(2)}$ within the LRESC scheme are

$$\chi^{(e-e)(2)} = -\left[\frac{1}{c} E^{(2)}(\boldsymbol{V}^{OZ-K}, \boldsymbol{L}_e) \right.$$
$$\left. + \frac{1}{4c^2} E^{(3)}(D; \boldsymbol{L}_e + 2\boldsymbol{S}; \boldsymbol{L}_e + 2\boldsymbol{S})\right], \quad (43)$$

with $\chi^{(e-e)(2)} \simeq \chi^{(e-e)} - \chi^{(e-e)NR}$. For the case of closed shell molecules, the last term in Eq. (43) gives rise to the same type of mechanism found for $\boldsymbol{g}^{(2)}$. But the first, OZ-K correction carries a different factor, originating a deviation of the LRESC theory of the susceptibility tensor. In fact, this is the only source of differences between the "paramagnetic" component of the susceptibility tensor and the rotational g-tensor within the LRESC approach.

For the (e-p) contribution, we consider again Eq. (23),

$$E^{(e-p)} = \frac{1}{2c^2}(\langle \Psi_0 | (\boldsymbol{\alpha} \cdot \boldsymbol{A}) P_p (2 + \beta)(\boldsymbol{\alpha} \cdot \boldsymbol{A}) | \Psi_0 \rangle). \quad (44)$$

From this expression, the diamagnetic component of the susceptibility is obtained in the non-relativistic limit and leading order relativistic effects may be obtained as well. Since no explicit use of these expressions are needed for the purposes of the present work, they are not worked out further here.

### C. Computational details

Following Eqs. (12) and (13), relativistic four-component calculations of the molecular g-tensor were carried out in model systems HX (X=F, Cl, Br, I), XF (X=Cl,Br,I), and YH$^+$ (Y=Ne, Ar, Kr, Xe, Rn). Due to molecular symmetry, the rotational g-tensor is defined by only one component perpendicular to the molecular axis of symmetry. This component will be referred to as the rotational g-factor. In addition, an analysis of relativistic corrections was done using LRESC expressions according to Eqs. (35) and (43).

Relativistic calculations were performed with the DIRAC13 code,[18] both within the RPA[12,19] and DFT[22,23] response schemes. DFT results were obtained within the LDA[20] and PBE0[21] functionals, in order to estimate correlation effects in these properties. LRESC calculations were performed with the DALTON2013 program;[35,36] in this case, linear and quadratic response calculations were carried out at the RPA level.

In both relativistic and non-relativistic calculations, the electrostatic electron-nucleus interaction was modeled using a finite nucleus with Gaussian charge distribution. The gauge origin of the magnetic potential is set at the molecular CM, as this condition is necessary for the formal equivalence between $\chi^p$ and $\boldsymbol{g}$ to hold in the non-relativistic theory. Even though in relativistic calculations gauge origin invariance can be achieved by the use of appropriate generalization of London orbitals,[16] the separate values of the (e-e) and (e-p) contributions to $\chi$ do depend on the choice of gauge origin. In fact, London-type orbitals were defined within the non-relativistic theory of the spin-rotation and rotational g-tensor[37] in order to ensure fast convergence of results. In the present work, overall gauge origin invariance was controlled through the use of large and converged basis sets, and taking into account previous work in the bibliography in the study of the magnetic susceptibility tensor (Refs. 14 and 16 and references therein). The Breit contribution (Eq. (7)) is neglected in the present work, mostly based on the fact that it is expected to be a negligibly small effect.[8]

The same basis set was used for non-relativistic and for the large component of relativistic 4-spinors of relativistic calculations. In the latter case, the small component basis was generated using restricted kinetic balance (RKB). For H, F, Ne, Cl, and Ar atoms, the aug-cc-pCV5Z basis set[38–42] was used, while for Br, Kr, I, Xe, and Rn the dyall.acv4z[43] basis set was employed. In all cases, basis sets were fully uncontracted.

Experimental geometrical parameters of HX (X=F, Cl, Br, I),[44] XF (X=Cl,[44] Br,[44] I[45]), and YH$^+$ (Y=Ne,[46] Ar,[47] Kr,[47] Xe,[48] Rn[14]) compounds were used. The equilibrium bond distances in Angstroms are: 0.9170 (HF), 0.9912 (NeH$^+$), 1.2746 (HCl), 1.28037 (ArH$^+$), 1.6283 (ClF), 1.4145 (HBr), 1.421190 (KrH$^+$), 1.7590 (BrF), 1.6090 (HI), 1.60281 (XeH$^+$), 1.9098 (IF), and 1.7020 (RnH$^+$).

## III. RESULTS AND DISCUSSION

### A. Relativistic 4-component results of the rotational g-factor

In Table I, non-relativistic RPA, as well as relativistic RPA and DFT results of the rotational g-factor in model systems HX (X=F, Cl, Br, I), XF (X=Cl, Br, I), and YH$^+$ (Y=Ne, Ar, Kr, Xe, Rn) are presented. When available, experimental values are quoted for comparison. The g-factor is composed by a nuclear and an electronic contribution. It should be kept in mind that the nuclear values for all HX and YH$^+$ systems range between 0.973 and 0.997. The value 1.00 would correspond to the H nucleus rotating around a fixed origin. As a consequence, the smaller g values in HX and YH$^+$ along the series of increasing atomic number Z of the X or Y atoms reflect an increasingly negative electronic contribution.

As it might be anticipated, relativistic effects are much smaller (in a relative scale) in the case of the g-factor than they were in the case of the SR tensor. Correlation effects are of similar order of magnitude in most cases. Correlation and relativistic effects follow opposite trends in the case of the heavier HX systems (X=Br, I), nearly cancelling each other. For the series YH$^+$, they both yield negative corrections. As a consequence, correlated relativistic effects bring the total

TABLE I. Relativistic values of rotational g-factor for HX (X=F, Cl, Br, I), XF (X=Cl, Br, I), and YH$^+$ (Y=Ne, Ar, Kr, Xe, Rn) molecules, calculated at the RPA Dirac Fock, and DFT (LDA and PBE0) levels of approximation. Experimental values are quoted when available.

| Mol. | Method | $g^{NR}$ | $g^R$ | $\Delta g^R$ | $\Delta g^{corr, NR}$ | $\Delta g^{corr, R}$ | $g^{exp}$ |
|---|---|---|---|---|---|---|---|
| H$^{19}$F | RPA | 0.7623 | 0.7617 | $-0.0007$ | ... | ... | 0.741599(5)[49] |
| | LDA | 0.7515 | 0.7508 | $-0.0007$ | $-0.0109$ | $-0.0109$ | |
| | PBE0 | 0.7434 | 0.7427 | $-0.0007$ | $-0.0189$ | $-0.0190$ | |
| H$^{35}$Cl | RPA | 0.4552 | 0.4535 | $-0.0017$ | ... | ... | 0.4594[50] |
| | LDA | 0.4875 | 0.4858 | $-0.0017$ | 0.0323 | 0.0323 | |
| | PBE0 | 0.4670 | 0.4653 | $-0.0017$ | 0.0117 | 0.0118 | |
| H$^{81}$Br | RPA | 0.3740 | 0.3682 | $-0.0058$ | | | 0.37122(8)[51] |
| | LDA | 0.4055 | 0.3968 | $-0.0087$ | 0.0315 | 0.0286 | |
| | PBE0 | 0.3814 | 0.3730 | $-0.0084$ | 0.0074 | 0.0048 | |
| H$^{127}$I | RPA | 0.1838 | 0.1648 | $-0.0190$ | | | ... |
| | LDA | 0.2438 | 0.2140 | $-0.0298$ | 0.0600 | 0.0492 | |
| | PBE0 | 0.2090 | 0.1805 | $-0.0285$ | 0.0252 | 0.0157 | |
| $^{20}$NeH$^+$ | RPA | 0.8790 | 0.8787 | $-0.0003$ | | | ... |
| | LDA | 0.8528 | 0.8524 | $-0.0004$ | $-0.0262$ | $-0.0263$ | |
| | PBE0 | 0.8547 | 0.8543 | $-0.0004$ | $-0.0243$ | $-0.0244$ | |
| $^{40}$ArH$^+$ | RPA | 0.6841 | 0.6832 | $-0.0009$ | | | 0.6638(34)[52] |
| | LDA | 0.6757 | 0.6747 | $-0.0010$ | $-0.0084$ | $-0.0085$ | |
| | PBE0 | 0.6687 | 0.6678 | $-0.0010$ | $-0.0154$ | $-0.0154$ | |
| $^{84}$KrH$^+$ | RPA | 0.6009 | 0.5989 | $-0.0021$ | | | 0.5545[53] |
| | LDA | 0.5939 | 0.5889 | $-0.0050$ | $-0.0071$ | $-0.0100$ | |
| | PBE0 | 0.5828 | 0.5782 | $-0.0046$ | $-0.0182$ | $-0.0207$ | |
| $^{132}$XeH$^+$ | RPA | 0.4297 | 0.4202 | $-0.0094$ | | | ... |
| | LDA | 0.4436 | 0.4236 | $-0.0200$ | 0.0139 | 0.0033 | |
| | PBE0 | 0.4235 | 0.4048 | $-0.0187$ | $-0.0062$ | $-0.0154$ | |
| $^{222}$RnH$^+$ | RPA | 0.3361 | 0.1979 | $-0.1381$ | | | ... |
| | LDA | 0.3590 | 0.2060 | $-0.1530$ | 0.0229 | 0.0081 | |
| | PBE0 | 0.3341 | 0.1748 | $-0.1594$ | $-0.0019$ | $-0.0232$ | |
| $^{35}$ClF | RPA | $-0.1072$ | $-0.1077$ | $-0.0004$ | | | ... |
| | LDA | $-0.1222$ | $-0.1227$ | $-0.0005$ | $-0.0150$ | $-0.0151$ | |
| | PBE0 | $-0.1135$ | $-0.1140$ | $-0.0005$ | $-0.0063$ | $-0.0063$ | |
| $^{81}$BrF | RPA | $-0.1036$ | $-0.1076$ | $-0.0040$ | | | ... |
| | LDA | $-0.1135$ | $-0.1164$ | $-0.0030$ | $-0.0099$ | $-0.0089$ | |
| | PBE0 | $-0.1066$ | $-0.1097$ | $-0.0031$ | $-0.0030$ | $-0.0022$ | |
| $^{127}$IF | RPA | $-0.1250$ | $-0.1468$ | $-0.0218$ | | | ... |
| | LDA | $-0.1329$ | $-0.1457$ | $-0.0128$ | $-0.0079$ | 0.0011 | |
| | PBE0 | $-0.1260$ | $-0.1411$ | $-0.0150$ | $-0.0010$ | 0.0058 | |

values closer to experiment in the cases Y=Ar, Kr. It is interesting to point out that experimental values are determined with high precision in such cases. It is necessary to go down to the sixth row of the periodic table to obtain really significant relativistic effects: in the case Y=Rn, the relativistic effect is by far more important than correlation effects as described by both DFT functionals.

In Ref. 48, a crude estimation of the experimental value of the g-factor in XeH$^+$ is quoted, of $\approx$0.30(5). The present calculations do not support this finding. The general trend of relativistic effects in YH$^+$ shows smaller values than those of HX, and correlation effects are not significant neither. Therefore, we predict the correct value of the g-factor in XeH$^+$ to be close to that of our present calculations.

Numerical results by other authors were obtained considering a different formal approach.[14] In these previous works, the g-factor formal expression is considered to be identically

proportional to the (e-e) part of the magnetic susceptibility. Therefore, comparison of the present approach with previous ones is better carried out in Subsection III C of this work.

Summing up, unlike the case of the SR tensor, the g-factor is only affected by subtle relativistic effects. This might be anticipated on qualitative grounds: the operators involved in the SR tensor probe the electronic distribution in the close vicinity of the atomic nuclei, where relativistic effects are very relevant for large Z, whereas those involved in the g-factor affect mostly valence electrons, for which relativistic effects are subtle. Regarding correlation effects, results of the LDA and PBE0 approaches give a general estimate of their relative importance in the present set of model compounds. However, more precise calculations should be carried out to obtain definite quantitative correlated values. Taking into account that correlation effects are not very important, we make only reference to the RPA values for analysis purposes in what follows.

TABLE II. Relativistic RPA values of rotational g-factor for HX (X=F, Cl, Br, I), YH$^+$ (Y=Ne, Ar, Kr, Xe, Rn), and XF (X=Cl, Br, I) molecules: nuclear contribution g$_{nuc}$, and electronic contribution g$^{el}$ split into its component originating in electron-electron excitations g$^{(e-e)}$ and the one involving electron-positron excitations g$^{(e-p)}$. In each case, the value given by the $L_e$ and $S$ terms of the total angular momentum operator $J_e$ are quoted separately.

| | | g$^{el}$ | | | | |
| | | g$^{(e-e)}$ | | g$^{(e-p)}$ | | |
| | g$_{nuc}$ | L | S | L | S | g$^{total}$ |
|---|---|---|---|---|---|---|
| H$^{19}$F | 0.97315 | − 0.21149 | − 0.000006 | 0.000092 | − 0.000092 | 0.76165 |
| H$^{35}$Cl | 0.98518 | − 0.53161 | − 0.000061 | 0.000084 | − 0.000084 | 0.45350 |
| H$^{81}$Br | 0.99252 | − 0.62305 | − 0.00129 | 0.00013 | − 0.00013 | 0.36818 |
| H$^{127}$I | 0.99490 | − 0.82169 | − 0.00840 | 0.00014 | − 0.00014 | 0.16481 |
| $^{20}$NeH$^+$ | 0.97567 | − 0.09698 | − 0.000004 | 0.000079 | − 0.000079 | 0.87869 |
| $^{40}$ArH$^+$ | 0.98603 | − 0.30280 | − 0.00005 | 0.000083 | − 0.000083 | 0.68318 |
| $^{84}$KrH$^+$ | 0.99272 | − 0.39289 | − 0.00095 | 0.00013 | − 0.00013 | 0.59888 |
| $^{132}$XeH$^+$ | 0.99501 | − 0.56848 | − 0.00630 | 0.00014 | − 0.00014 | 0.42023 |
| $^{222}$RnH$^+$ | 0.99670 | − 0.74625 | − 0.05255 | 0.000189 | − 0.000188 | 0.19790 |
| $^{35}$Cl$^{19}$F | 0.48158 | − 0.5892 | − 0.00006 | 0.0000072 | − 0.0000059 | − 0.10768 |
| $^{81}$Br$^{19}$F | 0.46928 | − 0.5753 | − 0.001569 | 0.000010 | − 0.000007 | − 0.10758 |
| $^{127}$I$^{19}$F | 0.46981 | − 0.60512 | − 0.01154 | 0.000014 | − 0.000007 | − 0.14683 |

In Table II, the nuclear part, and the 4-component relativistic RPA values of the electronic part of the g-factor, separated into (e-e) and (e-p) contributions are presented for the three series of compounds HX, XF, and YH$^+$. The decomposition into (e-e) and (e-p) contributions was done as implemented in DIRAC[18] code: g$^{(e-e)}$ is obtained as a response calculation involving only virtual excitations to positive energy spinors, and g$^{(e-p)}$ is obtained as the difference between the full response result and g$^{(e-e)}$.[19] Each contribution is further decomposed in Table II considering separately the orbital $L_e$ and spin $S$ angular momenta in the $J_e$ operator.

Results in Table II show interesting features. On one hand, it is verified that the (e-p) contribution is negligibly small in all cases, as it was anticipated by the LRESC analysis and the full result is practically given just by g$^{(e-e)}$. In fact, the $L_e$ and $S$ (mutually cancelling) contributions to g$^{(e-p)}$ are much smaller than those of g$^{(e-e)}$ when considered separately as well.

Looking to the orbital and spin terms of g(e-e) an interesting trend is found: the relative importance of the $S$ term in the full relativistic correction is negligibly small for the lighter atoms, but it increases sharply with Z, up to nearly 50% of the complete correction in the cases X=I, Y=Xe, Rn. This rather unexpected trend cannot be explained from the LRESC expansion, as no spin containing contributions appear within the LRESC theory of the g-factor of closed shell molecules. This subject deserves further discussion.

## B. Relativistic effects on the g-factor as a power series in 1/c: Leading and higher order effects

The LRESC approach is based on the idea of retaining the leading order relativistic effects on molecular properties within the ESC scheme. Within such approximation it was anticipated that the g(e-p) contribution is zero up to the leading order in 1/c, and no spin-dependent contributions to g(e-e) are found. LRESC relativistic effects are all given by "scalar"

operators: mass velocity, Darwin and the so-called "OZ-K" term of Eq. (36).

In order to investigate the LRESC results of g$^{(e-e)}$, in Table III numerical results of g$^{OZ-K}$ and the sum of g$^{Mv}$ and g$^{Dw}$ are presented for all HX, XF, and YH$^+$ compounds, together with the full 4-component relativistic effect. It is observed that the LRESC values fail to describe adequately the relativistic effects for the cases of X, Y atoms beyond the third row. The discrepancy could be due to missing spin-dependent terms in the LRESC expansion, or to the existence of higher order contributions.

Since the LRESC scheme is conceived as a power series in the fine structure constant 1/c (in a.u.) we could artificially vary the value of the speed of light in the four component calculation of the g-factor in order to obtain a power expansion in 1/c. This feature is included in the DIRAC program. In this way, it is possible to analyse the dependence of the 4-component g-factor setting the inverse of the speed of light as

TABLE III. Comparison of relativistic 4-component RPA corrections g$^{el}$−g$^{el-NR}$, and LRESC corrections g$^{OZ-K}$ Eq. (36) and g$^{Mv/Dw}$ Eqs. (37) and (38) to the rotational g-factor in HX (X=F, Cl, Br, I), YH$^+$ (Y = Ne, Ar, Kr, Xe, Rn), and XF (X=Cl, Br, I) molecules.

| Molecule | g$^{el}$ -g$^{el-NR}$ ($\times 10^{-3}$) | g$^{OZ-K}$ ($\times 10^{-3}$) | g$^{Mv/Dw}$ ($\times 10^{-3}$) |
|---|---|---|---|
| H$^{19}$F | − 0.680 | 0.009 | − 0.630 |
| H$^{35}$Cl | − 1.727 | − 0.012 | − 0.888 |
| H$^{81}$Br | − 5.805 | 0.0144 | − 1.888 |
| H$^{127}$I | − 18.966 | 0.0160 | 8.728 |
| $^{20}$NeH$^+$ | − 0.261 | 0.007 | − 0.308 |
| $^{40}$ArH$^+$ | − 0.949 | 0.009 | − 0.149 |
| $^{84}$KrH$^+$ | − 2.061 | 0.012 | − 1.018 |
| $^{132}$XeH$^+$ | − 9.447 | 0.014 | 13.48 |
| $^{222}$RnH$^+$ | − 138.15 | 0.017 | 57.35 |
| $^{35}$Cl$^{19}$F | − 0.449 | 0.092033 | − 1.015 |
| $^{81}$Br$^{19}$F | − 3.980 | 0.11942 | − 1.234 |
| $^{127}$I$^{19}$F | − 21.792 | 0.12368 | 0.696 |

TABLE IV. Coefficients of the fitting curve of the g-factor as a function of parameter $\alpha^2$ (Eq. (45)) up to order $\alpha^4$, non-relativistic electronic value $g^{el-NR}$, and LRESC correction as given in Eq. (35) in model systems HBr (Fig. 1) and HI (Fig. 2).

|           | $g^{(0)}$ | $g^{(2)}$ | $g^{(4)}$ | $g^{el-NR}$ | $g^{OZ-K} + g^{Mv/Dw}$ |
|-----------|-----------|-----------|-----------|-------------|------------------------|
| $H^{81}Br$  | $-0.6182$ | $-0.00178$ | $-0.00382$ | $-0.6185$ | $-0.00187$ |
| $H^{127}I$  | $-0.8110$ | $0.00894$ | $-0.02527$ | $-0.8111$ | $0.00874$ |

$\alpha/c$ ($c = 137.0359998$ a.u.). Therefore, the value $\alpha = 0$ corresponds to the non-relativistic limit and $\alpha = 1$ corresponds to the true relativistic value,

$$g^{el}(\alpha) = g^{(0)} + g^{(2)}\alpha^2 + g^{(4)}\alpha^4 + \cdots \qquad (45)$$

so that $g^{(2)}$ ($g^{(4)}$) will be the relativistic correction up to order 2 (4) in the expansion of the g-factor. In a least-squares fit of the resulting curve, $g^{(0)}$ should agree with the non-relativistic value.

In Table IV, we show the expansion coefficients of the fitting of $g^{el}(\alpha)$ as a quadratic polynomial in $\alpha^2$ for the cases HBr and HI. The values $g^{el-NR}$, and LRESC results are also included for comparison. The resulting curves are shown in Fig. 1 for the case of HBr and in Fig. 2 for the case of HI. The obtained results are really interesting. The zeroth order constant $g^{(0)}$ matches very well the non-relativistic values (within less than 0.1%); the leading order correction $g^{(2)}$ is consistent with the LRESC result within 5%. But the coefficient $g^{(4)}$ confirms the existence of significant contributions scaling as $(1/c)^4$. In fact, such $g^{(4)}$ contribution is the dominant one in both HBr and HI. This result is wholly consistent with the appearance of the spin-dependent contribution discussed in Sec. III A, which was negligibly small for the lighter F, Cl atoms, but significant for atoms beyond the fourth row of the periodic table. From Figs. 1 and 2 it is also seen that higher order terms ($\alpha^6$) are not fully negligible in the full relativistic result, as the value given by the fitting curve of order $\alpha^4$ at $\alpha = 1$ is smaller than the relativistic one by about 10%.

## C. Relation of g-factor and magnetic susceptibility $\chi$ in the relativistic formalism

Within the 4-component formalism presented in this work the theoretical expressions of the rotational g-tensor, Eq. (13), and the magnetic susceptibility tensor, Eq. (16), are defined in terms of different operators. Therefore, there is no direct formal relation linking both parameters, as it is the case in the non-relativistic theory. By application of the LRESC expansion it was verified that the relativistic expressions lead naturally to the non-relativistic theory of both parameters in the limit $c \to \infty$: in such limit, the g-tensor and the paramagnetic component of the magnetic susceptibility tensor, $\chi^{p-NR}$, are defined in terms of the same operators (provided the molecular CM is taken as gauge origin of the magnetic potential) (see Eqs. (33) and (42)). Therefore, it holds
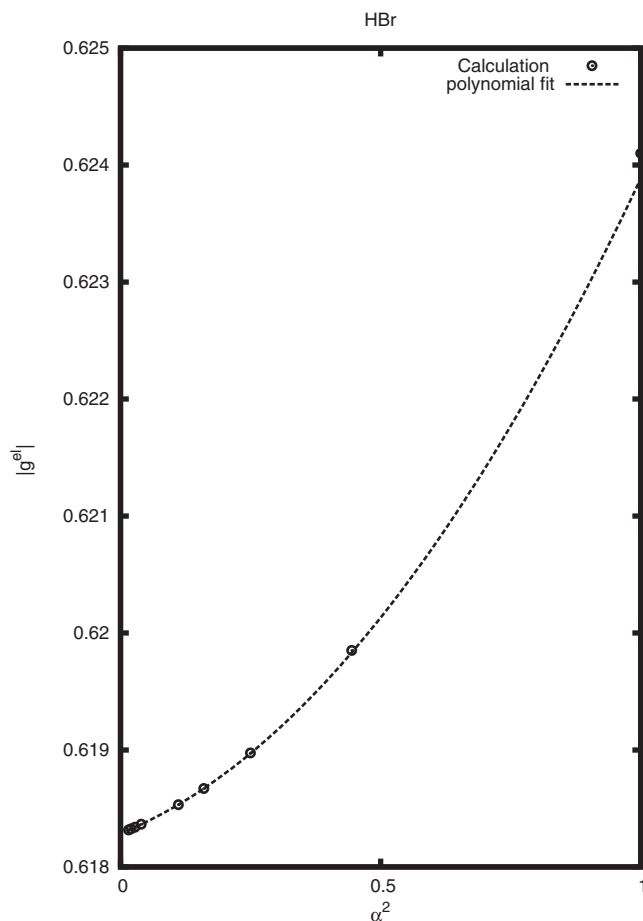
$$I g^{el-NR} = -4M_p c^2 \chi^{p-NR}. \qquad (46)$$



FIG. 1. Electronic contribution to the relativistic rotational g-factor for HBr (in absolute value) as a function of the parameter $\alpha^2$, where $\alpha/c$ is the fine structure constant in a.u. The polynomial fit of Eq. (46) is shown as a dotted line.

Furthermore, the LRESC expansion allows to explore the differences between both parameters by comparing the leading order relativistic corrections to the g-tensor and to the (e-e) contribution of the magnetic susceptibility, $\chi^{(e-e)}$. On one hand, "scalar" relativistic effects (Mv) and (Dw) do satisfy Eq. (46), while the SO effect is zero at this level of approximation for both tensors. On the other hand, the OZ-K correction appears only once in the LRESC expansion of the rotational g-tensor, but it appears twice in that of the susceptibility tensor,

$$2I g^{OZ-K} = -4M_p c^2 \chi^{OZ-K}. \qquad (47)$$

Therefore, in the leading order LRESC approximation, the only source for a deviation of the non-relativistic relation Eq. (46) comes out from the OZ-K term. But as shown in Table III, on one hand, the OZ-K correction is negligibly small in all cases, and on the other hand the LRESC result fails to reproduce correctly the full relativistic values of the g-factors of molecules containing atoms below the fourth row of the periodic table. Therefore, in order to deepen the analysis of the deviation of the relation Eq. (46) for heavy atom containing compounds from a quantitative point of view, relativistic calculations of the magnetic susceptibility tensor were carried out as part of the present work for the series of
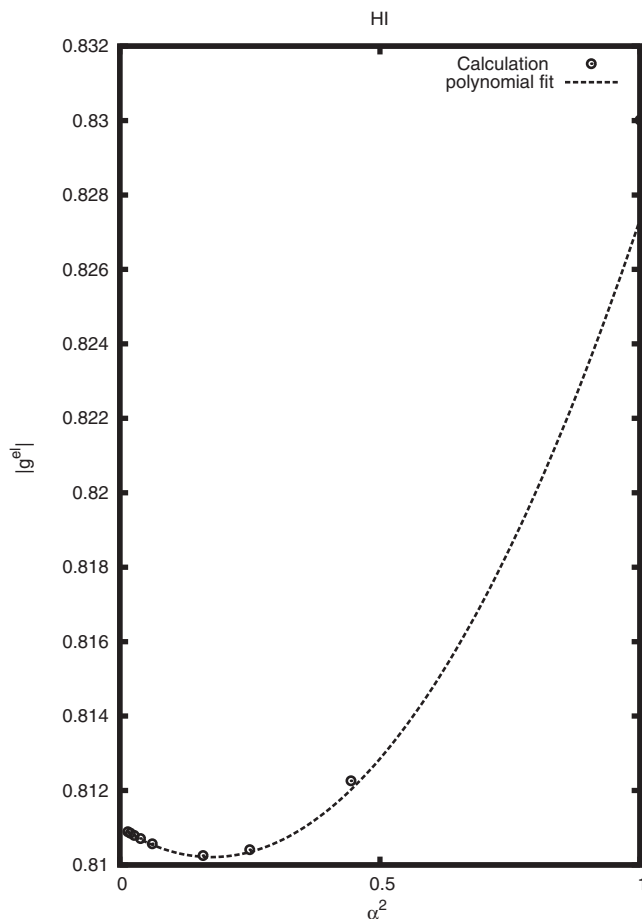
HI



FIG. 2. Electronic contribution to the relativistic rotational g-factor for HI (in absolute value) as a function of the parameter $\alpha^2$, where $\alpha/c$ is the fine structure constant in a.u. The polynomial fit of Eq. (46) is shown as a dotted line.

compounds HX (X=F, Cl, Br, I), XF (X=Cl, Br, I), and YH$^+$ (Y=Ne, Ar, Kr, Xe, Rn). Calculations were carried out at the RPA level. The corresponding results, divided into (e-e) and (e-p) components, are presented in Table V.

The component of the magnetic susceptibility yielding the paramagnetic component of the non-relativistic theory in

TABLE V. Relativistic RPA values of the magnetic susceptibility for HX (X=F, Cl, Br, I), YH$^+$ (Y=Ne, Ar, Kr, Xe, Rn), and XF (X=Cl, Br, I) molecules. The e-e and e-p contributions (corresponding to paramagnetic and diamagnetic contributions in the non-relativistic limit) are also shown.

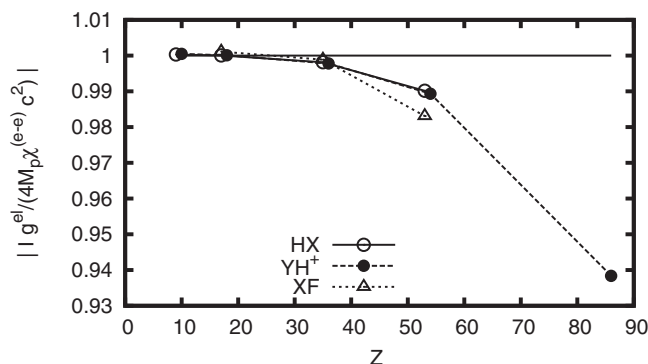| | $\chi^{(e-e)}$ ($10^{-4}$ a.u.) | $\chi^{(e-p)}$ ($10^{-4}$ a.u.) |
|---|---|---|
| H$^{19}$F | 0.080310 | −1.2230 |
| H$^{35}$Cl | 0.39933 | −3.0461 |
| H$^{81}$Br | 0.58800 | −4.2844 |
| H$^{127}$I | 1.0243 | −6.4627 |
| $^{20}$NeH$^+$ | 0.043104 | −0.83997 |
| $^{40}$ArH$^+$ | 0.23021 | −2.3060 |
| $^{84}$KrH$^+$ | 0.37451 | −3.4653 |
| $^{132}$XeH$^+$ | 0.70418 | −5.4463 |
| $^{222}$RnH$^+$ | 1.1670 | −6.8379 |
| $^{35}$Cl$^{19}$F | 9.0674 | −10.592 |
| $^{81}$Br$^{19}$F | 12.976 | −14.830 |
| $^{127}$I$^{19}$F | 17.843 | −19.559 |



FIG. 3. Quotient given in Eq. (46) relating the rotational g-factor and the magnetic susceptibility for the series of molecules HX (X=F, Cl, Br, I ), XF (X=Cl, Br, I), and YH$^+$ (Y=Ne, Ar, Kr, Xe, Rn).

the non-relativistic limit is $\chi^{(e-e)}$. Therefore, the deviation of the relation (46) when relativistic effects are relevant can be analysed by comparing the relativistic results of $g^{el}$ and $\chi^{(e-e)}$. In fact, in previous work,[14] the relativistic g-factor was defined as being proportional to $\chi^{(e-e)}$ and it is interesting to evaluate the differences with the theoretical expression of the present work. Results are presented in Fig. 3, where the quotient $-Ig^{el}/4M_p c^2 \chi^{(e-e)}$ is evaluated as a function of the atomic number Z of the X, Y atoms in the analyzed compounds. The value of 1 corresponds to full equivalence of the two values. It is seen that the quotient becomes smaller to 1 as a function of Z, indicating a larger $\chi^{(e-e)}$ as compared to the case of the non-relativistic theory. However, the deviation is negligibly small up to the fourth row (differences are of the order of 0.5%) and in the fifth row it is ∼2%. Therefore, the standard non-relativistic relation can be considered to hold within a 2% precision for moderately heavy atom containing compounds. Only for the very heavy Rn atom the difference is shown to be significant (≈6%).

## IV. CONCLUDING REMARKS

In the present work, an original formulation of the molecular rotational g-tensor in a relativistic context is presented. It is based on the analysis of a molecular Hamiltonian defined in the laboratory system which considers non-relativistic dynamics for nuclei and relativistic quantum theory for electrons.[4] Within the present approach, in the non-relativistic limit, the non-relativistic theory of the rotational g-tensor is obtained in a natural way. The relation with the susceptibility tensor valid in the non-relativistic context is lost at the relativistic level, as it was anticipated in the bibliography long ago.[12] Quantitative RPA and DFT results in model systems HX, XF, and YH$^+$ allowed the analysis of interesting features. First, contributions from electron-positron excitations show to be negligibly small along the whole series. The full relativistic g-factor is largely dominated by the $g^{(e-e)}$ contribution, i.e., the part given by excitations to "electronic" excited states of the system. Unlike the case of the SR tensor, relativistic effects on the rotational g-factor are shown to be small. Only for the sixth-row Rn atom a large relativistic correction is found. Relativistic effects on $g^{(e-e)}$ are not well reproduced by the LRESC approximation for compounds

containing atoms beyond the fourth row of the periodic table a significant portion of the relativistic effect originates in spin-dependent higher-order terms.

Comparison of the rotational g-tensor and the susceptibility tensor expressions shows that the relation linking both parameters valid in the non-relativistic theory, Eq. (46), breaks down in the relativistic regime. However, differences remain very small (up to 2% for X=I, Y=Xe), and only for the heavier Rn atom it becomes significant. Once more it is verified that even though at the LRESC approximation the OZ-K term enters differently in the relativistic correction to both parameters, this contribution does not explain the general trend, as the corresponding values are shown to be negligibly small in all cases. Higher order contributions must be responsible for the deviation of the relation (46) in heavy atom containing compounds.

These conclusions have similarities but also interesting differences with the case of the relation between the SR tensor M(N) and NMR shielding-tensor $\sigma$(N).[4,5] In that case, the LRESC expansion showed that while the OZ-K term is present in the LRESC expansion of the $\sigma$ tensor, it does not appear in the case of the SR tensor. But the main differences between both was shown in the different factors giving rise to SO effects, which are non-zero: the rotational operator carries the spin operator $S$, but the magnetic interaction operator carries a factor $g_e S$, where $g_e$ is the electron gyromagnetic factor. Due to this difference, the deviation of the non-relativistic relation between both parameters is significant in all cases where the SO effect is relevant, as there is a difference of a factor of $\approx 2$ in the spin-contribution to this effect. These differences may be important even in the case of moderately heavy atoms. In contrast, in the present case the SO term is zero at the LRESC level for both parameters, as it was discussed above. However, higher order spin-dependent effects will also carry different constant factors for the g-tensor as compared to the case of $\chi^{(e-e)}$: this is the source of the different behaviour of both parameters for heavy atom containing compounds.

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