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Theoretical study of the nuclear spin-molecular rotation coupling for relativistic electrons and non-relativistic nuclei

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A theoretical study of the relation between the relativistic formulation of the nuclear magnetic shielding and spin-rotation tensors is presented. To this end a theoretical expression of the relativistic spin-rotation tensor is formulated, considering a molecular Hamiltonian of relativistic electrons and non-relativistic nuclei. Molecular rotation effects are introduced considering the terms of the Born-Oppenheimer decomposition, which couple the electrons and nuclei dynamics. The loss of the simple relation linking both spectral parameters in the non-relativistic formulation is further analyzed carrying out a perturbative expansion of relativistic effects by means of the linear response within the elimination of the small component approach. It is concluded that relativistic effects on the spin-rotation tensor are less important than those of the nuclear magnetic shielding tensor.

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I. INTRODUCTION

Nuclear magnetic resonance (NMR) spectroscopy is a powerful tool for the analysis of molecular structure and subtle intra- or intermolecular interactions. In particular, the nuclear magnetic shielding tensor is very sensitive to the characteristics of the electronic distribution in the close vicinity of the atomic nucleus of interest. From the theoretical point of view the study of NMR spectral parameters is a very interesting subject. Nuclear magnetic resonance parameters are particularly sensitive to correlation effects, chemical environment effects, etc., and therefore, precise quantitative values require the use of powerful theoretical quantum chemistry approaches.¹ In particular, relativistic effects are very relevant when heavy nuclei are present in the system under study. In fact these effects are relevant for elements beyond the fourth row of the periodic table. In the last decade, powerful relativistic quantum chemistry tools were developed to obtain the nuclear magnetic shielding and spin-spin coupling tensors in a relativistic framework.¹⁻³ In fact, relativistic effects have shown to have deep influence even in qualitative aspects of NMR spectra, as shown, e.g., in the remarkable Xe spectrum discussed in Ref. 4.

However, the relation between theoretical and experimental values of the NMR nuclear magnetic shielding can only be established for the relative shielding of a same nucleus in different chemical environments, i.e., the chemical shift. The absolute nuclear magnetic shielding cannot be obtained from a NMR spectrum, since the resonance line observed is associated to transitions of nuclear spin states in the effective magnetic field produced by the spectrometer and the surrounding electrons. The establishment of an absolute

nuclear shielding scale would require to carry out the same experiment for the “naked” nucleus, and this has not been feasible.⁵ In the early times of NMR spectroscopy, a shortcut towards the establishment of an absolute nuclear magnetic shielding scale was proposed.⁶⁻⁸ It was realized that the spin-rotation (SR) constant, which can be obtained from the rotational spectrum of the system, is closely related to the nuclear magnetic shielding tensor. The electronic contribution to the spin-rotation tensor has the same theoretical expression as the paramagnetic contribution to the nuclear magnetic shielding tensor (when the gauge origin is placed at the center of mass (CM) of the molecule). The accurate calculation of the diamagnetic contribution in a simple reference system yields, in principle, the possibility of obtaining an absolute nuclear shielding scale for a given nucleus. The spin-rotation tensor is also an interesting spectral parameter by itself in the analysis of molecular structure and recent advances have been published in the theoretical determination of this spectral parameter.⁹⁻¹⁹

The theoretical relation linking the nuclear magnetic shielding tensor and the spin-rotation tensor is based in Larmor’s theorem, which demonstrates the formal equivalence, in non-relativistic (NR) dynamics, of the Hamiltonian for a particle in a uniform magnetic field and in a uniformly rotating system, which holds up to first order in the field intensity.²⁰ However, in the presence of a heavy nucleus, relativistic dynamics must be applied in the study of the electronic distribution. In this context, the previously mentioned equivalence does not hold any longer, as pointed out earlier, as, e.g., in Ref. 21. Therefore, it is of great importance to critically re-analyze the relation between both molecular parameters in this case. The aim of the present work is to establish a theoretical expression of the spin-rotation tensor in the case of relativistic electrons and to analyze its relation with the (relativistic) nuclear magnetic shielding tensor. The method we follow

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is based on first order corrections to the Born-Oppenheimer (BO) approximation.²² We compare our result with other approaches of the bibliography.^{23,24} We carry out a perturbation theory expansion based on the use of Pauli spinors (linear response within the elimination of the small component (LRESC; Ref. 25)) in order to obtain the lowest order relativistic corrections which define the difference between both spectral parameters. The suitability of the found relation to obtain an absolute shielding scale in the relativistic case is discussed.

II. THEORY

The spin-rotation Hamiltonian couples the nuclear spin \vec{I}_N and the angular momentum \vec{L} of the nuclei by means of the spin-rotation tensor \vec{M}_N ,⁸

$$H^{SR}(\vec{I}_N, \vec{L}) = -\vec{I}_N \cdot \vec{M}_N \cdot \vec{L}. \quad (1)$$

H^{SR} is an operator in the subspace of rotational molecular states and yields a splitting of rotational energy levels. In order to obtain a theoretical expression of the spin-rotation tensor \vec{M}_N , it is necessary to identify those terms of the molecular Hamiltonian which couple \vec{I}_N and \vec{L} . Therefore, the molecular Hamiltonian must be extended to include electron-nucleus and nucleus-nucleus interactions of moving nuclei⁶⁻⁸ in the laboratory frame. Since the nuclear momenta are related to \vec{L} by the relation

$$\vec{L} = \sum_N \vec{r}_N \times \vec{p}_N, \quad (2)$$

only those terms linear in \vec{p}_N need to be retained. In the present work, we intend to extend previous work to consider relativistic electrons and non-relativistic nuclei. This last assumption is totally justified taking into account that the molecular kinetic energy in a rotational state is much smaller than its rest energy, i.e., the nuclei velocity satisfy the condition $v/c \ll 1$. Therefore, only the leading order terms (in $1/c$) in the nuclear momenta will be retained in what follows. In order to obtain the final result, the rigid rotor approximation for the nuclei dynamics will be assumed and the following relations hold:

$$\vec{p}_N = m_N \vec{\omega} \times \vec{r}_{N,CM}, \quad (3)$$

where $\vec{r}_{N,CM}$ is the nucleus N position with respect to the center of mass of the molecule, and

$$\vec{\omega} = \vec{I}^{-1} \vec{L}. \quad (4)$$

\vec{I} is the inertia tensor of the molecule with respect to the CM, for the equilibrium geometry.

A. The molecular Hamiltonian

In the present section, a molecular Hamiltonian for relativistic electrons and non-relativistic nuclei is introduced. In relativistic quantum chemistry, the electronic Hamiltonian for fixed nuclei is an effective Hamiltonian, containing the Dirac operator with the nuclei Coulomb potential (usually described as a finite charge distribution potential in actual applications)

as one-body Hamiltonian, and the Coulomb and Breit (CB) operators describing the two-body interaction. This interaction operator yields, in the lowest order relativistic approximation, the Coulomb potential and a whole series of terms which can be interpreted as magnetic interactions involving the orbital and spin magnetic moments of electrons.²⁶ On the other hand, in the present work, the dynamics of atomic nuclei is described in the non-relativistic limit, by means of the Schrödinger Hamiltonian. Magnetic interactions involving atomic nuclei can be included by perturbation theory considering their magnetic fields, and writing the relativistic magnetic interaction operators for electrons, and the non-relativistic ones for nucleus-nucleus magnetic interactions. We adopt Gaussian atomic units throughout this work. This choice for the system of units is justified by the fact that a more clear track of relative order in $1/c$ can be kept along the derivations.

The moving nucleus N of charge Z_N and magnetic moment $\vec{\mu}_N$ has an associated total electromagnetic field given by the potentials $(\varphi; \vec{A})$ (Ref. 27)

$$\varphi(\vec{r}) = \frac{Z_N}{|\vec{r} - \vec{r}_N|} + \frac{\vec{p}_N}{m_N c} \cdot \vec{A}_N(\vec{r}), \quad (5)$$

$$\vec{A}(\vec{r}) = \vec{A}_N(\vec{r}) + \frac{Z_N \vec{p}_N}{m_N c |\vec{r} - \vec{r}_N|}, \quad (6)$$

where

$$\vec{A}_N(\vec{r}) = \frac{\vec{\mu}_N \times (\vec{r} - \vec{r}_N)}{|\vec{r} - \vec{r}_N|^3}, \quad (7)$$

m_N , \vec{r}_N and \vec{p}_N are the nucleus mass, position operator, and linear momentum operator, respectively. The electromagnetic operators appearing in Eqs. (5) and (6) are obtained considering the leading order Lorentz transformation of the static Coulomb and magnetic moment potentials of the nucleus. Taking into account that the nuclei are considered in the non-relativistic approximation, these leading order electromagnetic fields will be shown to be adequate to describe the spin-rotation tensor (see below). It is worthy to mention that an ambiguity regarding the second term of Eq. (6) arises in the quantum domain since \vec{p}_N and $\frac{1}{|\vec{r} - \vec{r}_N|}$ operators do not commute. Care must be taken to obtain final Hermitian well-defined operators in the interaction Hamiltonian.

Leaving aside the leading Coulomb term of Eq. (5), which is explicitly taken into account in the zeroth-order Hamiltonian, the electromagnetic interaction operator for relativistic electrons of charge $e = -1$ a.u. in the nucleus field has the form²⁶

$$\begin{aligned} h_{eN}^{(1)} &= -\varphi + \vec{\alpha} \cdot \vec{A} = -\vec{\beta}_N \cdot \vec{A}_N + \vec{\alpha} \cdot \vec{A}_N + \frac{\vec{\alpha} \cdot \vec{\beta}_N Z_N}{|\vec{r} - \vec{r}_N|} \\ &= (\vec{\alpha} - \vec{\beta}_N) \cdot \vec{A}_N + \frac{\vec{\alpha} \cdot \vec{\beta}_N Z_N}{|\vec{r} - \vec{r}_N|}, \end{aligned} \quad (8)$$

where for brevity

$$\vec{\beta}_N = \frac{\vec{p}_N}{m_N c}. \quad (9)$$

It is interesting to point out that the effect of taking into account the magnetic term in the scalar potential allows one to

rewrite the interaction in terms of $c(\vec{\alpha} - \vec{\beta}_N)$, which is the operator representing the relative velocity of the electron with respect to the nucleus. As mentioned above, there is an ambiguity in the definition of the second term. However, this kind of terms will be neglected in our final expression of the spin-rotation tensor, since they would give rise to higher order relativistic effects (see below).

The nucleus-nucleus interaction terms of the Hamiltonian are obtained taking into account that the moving nucleus M is a particle of charge Z_M and magnetic dipole moment $\vec{\mu}_M$ in its rest frame, and therefore it carries an extra associated electric dipole moment $\vec{d}_M = \vec{\beta}_M \times \vec{\mu}_M$ in the laboratory frame.²⁷ The interaction with the electric and magnetic fields of nucleus N given in Eqs. (5) and (6) is obtained considering the non-relativistic Hamiltonian of nucleus M in the presence of these external fields, which is

$$h_M = \frac{1}{2m_M} \left(\vec{p}_M - \frac{Z_M}{c} \vec{A}(\vec{r}_M) \right)^2 + Z_M \varphi(\vec{r}_M) - \vec{d}_M \cdot \vec{E}(\vec{r}_M) - \vec{\mu}_M \cdot \nabla_M \times \vec{A}, \quad (10)$$

where

$$\vec{E} = -\nabla\varphi. \quad (11)$$

The third term represents the interaction of the electric dipole associated to moving nucleus M with the electric field. It is the correct form of the electrostatic interaction for a particle bearing both a charge of value Z_M and a dipole moment \vec{d}_M .

Therefore, the N - M interaction terms are

$$h_{NM}^{(1)} = Z_M \varphi(\vec{r}_M) - \frac{1}{2} \{Z_M \vec{\beta}_M, \vec{A}(\vec{r}_M)\} - \vec{d}_M \cdot \vec{E}(\vec{r}_M) + \frac{Z_M^2}{2m_M c^2} A^2(\vec{r}_M) - \vec{\mu}_M \cdot (\nabla_M \times \vec{A}), \quad (12)$$

where $\{, \}$ stands for the anticommutator. Leaving aside the Coulomb term, and neglecting the diamagnetic term which yields terms of higher order in $1/c$ as well as terms bilinear in $\vec{\beta}_N, \vec{\beta}_M$ (only operators linear in the nuclei momenta need to be kept), it is obtained

$$h_{NM}^{(1)} = -Z_M (\vec{\beta}_M - \vec{\beta}_N) \cdot \vec{A}_N(\vec{r}_M) - \vec{\mu}_M \cdot (\nabla_M \times \vec{A}_N) - \vec{\mu}_M \cdot \left(\frac{Z_N \vec{\beta}_N \times (\vec{r}_M - \vec{r}_N)}{|\vec{r}_M - \vec{r}_N|^3} \right) + (\vec{\mu}_M \times \vec{\beta}_M) \cdot \left(Z_N \frac{(\vec{r}_M - \vec{r}_N)}{|\vec{r}_M - \vec{r}_N|^3} \right). \quad (13)$$

In the first term of Eq. (13), the magnetic interaction of the orbital motion of nucleus M with the magnetic moment of nucleus N and the interaction of the nucleus M charge with the scalar potential of nucleus N have been put together; the second term contains the magnetic interaction of the magnetic moments of both nuclei; the third term contains the interaction of the nucleus M magnetic moment with the orbital motion of nucleus N ; and the last term describes the electrostatic interaction of the electric dipole associated to the moving magnetic dipole of nucleus M (Ref. 27) with the Coulomb field of nucleus N (only the leading order term is kept). Both terms are

well-defined Hermitian operators. Rearrangement of terms allows to rewrite Eq. (13) as follows:

$$h_{NM}^{(1)} = -Z_M (\vec{\beta}_M - \vec{\beta}_N) \cdot \vec{A}_N(\vec{r}_M) - Z_N (\vec{\beta}_N - \vec{\beta}_M) \cdot \vec{A}_M(\vec{r}_N) - \vec{\mu}_M \cdot \nabla_M \times \vec{A}_N. \quad (14)$$

Considering that the last term is the direct dipole-dipole interaction, operator $h_{NM}^{(1)}$ in Eq. (14) is a Hermitian well-defined operator which is symmetric in N and M . Its physical interpretation is straightforward: each magnetic dipole has a magnetic interaction with the other nucleus moving relative to it, as shown by the appearance of the relative velocity in the first two terms; and the mutual direct magnetic dipole interaction of the last term.

In addition, it is also possible to include as a perturbation a spin-orbit operator associated to the nuclear spin, on the basis of the Thomas precession,²⁷ as suggested originally by Flygare.⁶ It has the form

$$h^{\text{SO}} = \frac{Z_N}{2m_N^2 c^2} \vec{I}_N \cdot (-\vec{E}(\vec{r}_N) \times \vec{p}_N), \quad (15)$$

where $\vec{E}(\vec{r}_N)$ stands for the total electrostatic field operator at the nucleus position, which is a sum of the fields of electrons and other nuclei. Therefore, this operator can be separated into an electron-nucleus operator

$$h_{eN}^{\text{SO}} = \frac{Z_N}{2m_N^2 c^2} \vec{I}_N \cdot \left(\frac{\vec{r} - \vec{r}_N}{|\vec{r} - \vec{r}_N|^3} \times \vec{p}_N \right) = \frac{Z_N}{2m_N c} \vec{\beta}_N \cdot \left(\vec{I}_N \times \frac{\vec{r} - \vec{r}_N}{|\vec{r} - \vec{r}_N|^3} \right) \quad (16)$$

and a nucleus-nucleus operator

$$h_{NM}^{\text{SO}} = -\frac{Z_M Z_N}{2m_N^2 c^2} \vec{I}_N \cdot \left(\frac{\vec{r}_M - \vec{r}_N}{|\vec{r}_M - \vec{r}_N|^3} \times \vec{p}_N \right) = -\frac{Z_M Z_N}{2m_N c} \vec{\beta}_N \cdot \left(\vec{I}_N \times \frac{\vec{r}_M - \vec{r}_N}{|\vec{r}_M - \vec{r}_N|^3} \right). \quad (17)$$

With the precedent discussion we have established the necessary Hamiltonian operators for the interactions of relativistic electrons and non-relativistic nuclei, including moving nuclei electromagnetic effects. In doing so we intend to carry out the full analysis of the spin-rotation tensor in terms of operators defined in the inertial laboratory frame, avoiding considerations about rotating systems. The coupling of the molecular rotation to the electronic distribution comes out as the consequence of “inertial” effects beyond the zeroth-order Born-Oppenheimer approximation, as it was suggested in the papers of Flygare⁶ and Van Vleck²⁸ on the spin-rotation tensor.

Summing up, the molecular Hamiltonian of the present work defined in the tensorial product of Dirac-Fock space for electrons and Schrödinger state space for nuclei is written as

$$H_{\text{mol}} = H_1^D + V^{\text{CB}} + T_{\text{Nuc}} + V_{\text{Nuc}} + V_{e\text{Nuc}} + H_{e\text{Nuc}}^{(1)} + H_{\text{Nuc}}^{(1)} + H_{e\text{Nuc}}^{\text{SO}} + H_{\text{Nuc}}^{\text{SO}}, \quad (18)$$

where

$$H_1^D = c\vec{\alpha} \cdot \vec{p} + \beta m c^2, \quad (19)$$

$$V^{\text{CB}} = \frac{1}{r_{12}} - \frac{1}{2r_{12}} \left(\tilde{\alpha}_1 \tilde{\alpha}_2 + \left(\frac{(\tilde{\alpha}_1 \cdot \vec{r}_{12})(\tilde{\alpha}_2 \cdot \vec{r}_{12})}{r_{12}^2} \right) \right), \quad (20)$$

$$V_{eNuc} = - \sum_N \frac{Z_N}{|\vec{r} - \vec{r}_N|}, \quad (21)$$

$$T_{Nuc} = \sum_N \frac{p_N^2}{2m_N}, \quad (22)$$

$$V_{Nuc} = \frac{1}{2} \sum_N \sum_M \frac{Z_N Z_M}{|\vec{r}_N - \vec{r}_M|}, \quad (23)$$

$$H_{eNuc}^{(1)} = \sum_N h_{eN}^{(1)}, \quad (24)$$

$$H_{Nuc}^{(1)} = \frac{1}{2} \sum_N \sum_M h_{NM}^{(1)}, \quad (25)$$

$$H_{eNuc}^{\text{SO}} = \sum_N h_{eN}^{\text{SO}}, \quad (26)$$

$$H_{Nuc}^{\text{SO}} = \frac{1}{2} \sum_N \sum_M h_{NM}^{\text{SO}}, \quad (27)$$

where $(\beta, \tilde{\alpha})$ are the Dirac matrices, and all operators for electrons must be understood as operators defined in Dirac-Fock space. V^{CB} stands for the two-body Coulomb-Breit interaction defined in Dirac-Fock space.²⁹

B. The Born-Oppenheimer approximation and the coupling of the electronic state to molecular rotation

In order to obtain the spin-rotation Hamiltonian starting from the molecular Hamiltonian of Sec. II A, the Born-Oppenheimer decoupling is applied.²² The molecular wavefunction is split as follows:

$$\Psi_{\text{mol}}(x, X) = \psi_e(x, X) \phi_N(X), \quad (28)$$

where $\{x\}$ and $\{X\}$ are shorthand notations making reference to electronic and nuclei variables, respectively (both spatial coordinates and spin states). In the Born-Oppenheimer approximation, an electronic Hamiltonian at fixed nuclear variables is defined as

$$H_{el}(X) = H_1^D + V^{\text{CB}} + V_{eNuc}(X), \quad (29)$$

and the electronic part of the molecular wavefunction is an eigenstate of the electronic Hamiltonian for every nuclear configuration X

$$H_{el}(X) \psi_e(x, X) = E_{el}(X) \psi_e(x, X). \quad (30)$$

With this electronic state inserted in the molecular wavefunction, the action of T_{Nuc} on the molecular state can be split into two terms

$$T_{Nuc} \psi_e(x, X) \phi_N(X) = \psi_e(x, X) T_{Nuc} \phi_N(X) + T_N^{(1)} \psi_e(x, X) \phi_N(X), \quad (31)$$

where the last term collects all terms in which the nuclear momentum operator acts at least once on the nuclear variables of the electronic wavefunction. Neglecting this term in the kinetic energy operator an effective Hamiltonian for the nuclear state $\phi_N(X)$ is obtained

$$H_{Nuc}^{(0)} = T_{Nuc} + E_{el}(X) + V_{Nuc}(X). \quad (32)$$

This is the standard procedure followed to decouple the electronic and nuclear problems in the Born-Oppenheimer approximation. The terms gathered in $T_N^{(1)}$ couple the electronic and nuclear dynamics and can be taken into account by perturbation theory together with interaction operators of the molecular Hamiltonian of Eq. (18). Of course, the perturbation parameter is different in this case and the perturbation procedure must be understood as a two-parameter perturbation expansion.

The perturbation expansion carried out in order to define an effective spin-rotation Hamiltonian can be understood on the following grounds. The potential energy surface defining the nuclei dynamics depends on the electronic state via $E_{el}(X)$. For the n th electronic energy level, the corresponding energy can be labeled as $E_{el}^n(X)$. The large energy difference between molecular states of different potential energy surfaces (in the UV region of the electromagnetic spectrum) compared to the magnetic and rotational energies within the nuclei state space makes it possible to restrict the perturbation theory calculation of nuclear states to the subspace of rotational states at each different potential energy surface, provided a bound state exists on such energy surface. In particular, for the molecular ground state energy surface, the effective nuclear Hamiltonian needs only be considered in the subspace spanned by the rotational states at the molecular equilibrium geometry (and eventually consider the ground vibrational state correction).³⁰ This being the case, the rigid rotor Hamiltonian describes the spatial nuclear variables

$$H = T_{Nuc} = \frac{1}{2} \vec{\omega} \cdot \vec{L} = \frac{1}{2} \sum_{i,j=x,y,z} I_{ij}^{-1} L_i L_j, \quad (33)$$

where I_{ij} stands for the i,j component of the inertia tensor of the molecule at the ground state molecular geometry and L_i is i th component of the orbital angular momentum for the nuclear coordinates with respect to the molecular CM. If (x, y, z) in Eq. (33) refer to a reference system fixed to the molecule, the inertia tensor components are constant. Therefore, this is the appropriate form of operator $T_N^{(1)}$ in Eq. (31). In order to understand the action of such operator on the nuclear coordinates of the electronic part of the wavefunction $L_i \psi_e(x, X)$, it must be remembered that L_i is the generator of rotations of nuclear coordinates about the “ i ” axis. Taking into account that the electronic state is referred to a reference system fixed to the molecule, this infinitesimal rotation is equivalent to a rigid rotation of the electronic state as a whole in the *opposite* sense, which is described by the total angular momentum electronic operator (both orbital and spin) carrying a minus sign. The relativistic total angular momentum operator is^{29,31}

$$\vec{J}_e = \vec{r} \times \vec{p} + \frac{1}{2} \vec{\Sigma}, \quad (34)$$

where $\vec{\Sigma}$ is the four-component extension of the Pauli matrices $\vec{\sigma}$, i.e.,

$$\vec{\Sigma} = \begin{bmatrix} \vec{\sigma} & 0 \\ 0 & \vec{\sigma} \end{bmatrix}, \quad (35)$$

where the position operator must be defined with respect to the molecular center of mass.

Therefore, the terms in Eq. (31) involving $T_N^{(1)}$ can be expressed as

$$\begin{aligned} T_N^{(1)} \psi_{el} \phi_N &= \sum_{i,j=x,y,z} I_{ij}^{-1} (L_i \psi_{el})(L_j \phi_N) + \frac{1}{2} \sum_{i,j=x,y,z} I_{ij}^{-1} \phi_N (L_i L_j \psi_{el}) \\ &= - \sum_{i,j=x,y,z} I_{ij}^{-1} (J_{ei} \psi_{el})(L_j \phi_N) + \frac{1}{2} \sum_{i,j=x,y,z} I_{ij}^{-1} \phi_N (J_{ei} J_{ej} \psi_{el}). \end{aligned} \quad (36)$$

The first term couples the electronic angular momentum and the nuclear rotation and the second term can be interpreted as a centrifugal potential on the electronic state due to molecular rotation. Only the first one needs to be considered in the analysis of the spin-rotation tensor. The appropriate form of the perturbative Hamiltonian originated in the Born-Oppenheimer coupling terms is therefore

$$H_{BO}^{(1)} = - \sum_{i,j=x,y,z} I_{ij}^{-1} J_{ei} L_j, \quad (37)$$

where use has been made of the symmetry property of the inertia tensor and it must be remembered that \vec{L} applies only on the nuclear wavefunction. In terms of $\vec{\omega}$, Eq. (4), operator $H_{BO}^{(1)}$ takes the simple expression

$$H_{BO}^{(1)} = -\vec{\omega} \cdot \vec{J}_e. \quad (38)$$

The present derivation follows exactly the same steps as those implied in the spin-rotation Hamiltonian obtained in the non-relativistic limit.^{6,7} It is interesting to point out that in the non-relativistic approach the operator coupling the molecular rotation and electronic state is also the total electronic angular momentum. In those works, the spin part is neglected explicitly because applications envisaged apply to closed shell molecules. The difference of the relativistic and non-relativistic spin-rotation operators is due to the different relation of the linear momentum operator \vec{p} and the velocity operator $[\vec{r}, H]$ in relativistic and non-relativistic dynamics.

C. The spin-rotation Hamiltonian

In this section, the perturbation theory analysis of all operators of the molecular Hamiltonian describing nuclear spin and molecular rotation effects is carried out. The perturbation operators of Eqs. (24)–(27) and (37) are considered by means of first and second order perturbation theory. It is worthy to note that the particular perturbation theory technique applied is not relevant for the purpose of the present work, which is to specifically identify the operators involved in first and second order perturbation theory calculations. The perturbation theory technique of Ref. 21 would be quite adequate. Here, we

follow the procedure proposed in Ref. 25. Its key aspects are as follows:

- An unperturbed relativistic molecular state within the no-pair approximation is considered as starting point. This state $|\Psi_0\rangle$ is defined in the subspace of Dirac-Fock state space spanned by Slater determinants containing N “electronic” solutions, i.e., made up of positive energy solutions of a starting one-particle Dirac Hamiltonian,³² e.g., that for a particle in the Coulomb potential of the atomic nuclei. It can be a correlated N-particles state in this manifold of Dirac-Fock space. No effects of electron-positron terms are considered.
- Within the QED picture, negative energy solutions of the starting one-particle Dirac Hamiltonian are reinterpreted as positive energy states for positrons. A one-body perturbation V applied to $|\Psi_0\rangle$ yields non-zero matrix elements with the whole spectrum of excited states within the same N-particles manifold and with all states of the N+2-particles manifold containing an extra electron-positron pair.
- The proposal in Ref. 25 which is inspired in Ref. 32 is to restrict the perturbation theory analysis to the manifold of N- and N+2-particles, neglecting pair creation effects of the Coulomb Breit interaction. Since within the QED picture the energy is referred to the energy of the “vacuum” state, the effect of the perturbation on the vacuum state must also be included. This can be formally expressed as a perturbation theory expression onto the N = 2 particles manifold (one electron-positron pair).

As a consequence, it holds

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

where

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

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

and the first and second order Rayleigh-Schrödinger like corrections to the energy are

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

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

The expression of $E^{(2)}(V, V)$ can be splitted into a term E_a involving only excited states within the N-particles states manifold, and a term E_b containing the electron-positron effects

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

$$\begin{aligned} E_b &= \sum_n \frac{\langle \psi_0 | V | \psi_n(N+2) \rangle \langle \psi_n(N+2) | V | \psi_0 \rangle}{E_0 - E_n} \\ &\quad - \sum_n \frac{\langle vac | V | \psi_n(2) \rangle \langle \psi_n(2) | V | vac \rangle}{E_{vac} - E_n}. \end{aligned} \quad (44)$$

It is important to emphasize that in E_b , each individual term is divergent and only the total sum of both terms is a well-defined quantity.

In the case that V is a combination of two perturbation operators

$$V = A + B, \quad (45)$$

the linearity of the first order correction to the energy ensures

$$E^{(1)}(V) = E^{(1)}(A) + E^{(1)}(B), \quad (46)$$

and the bilinearity of the second order expression ensures

$$E^{(2)}(V, V) = E^{(2)}(A, A) + E^{(2)}(A, B) + E^{(2)}(B, A) + E^{(2)}(B, B). \quad (47)$$

so that the energy term involving linearly operators A and B is

$$E_{AB}^{(2)} = E^{(2)}(A, B) + E^{(2)}(B, A), \quad (48)$$

which is the energy expression needed in the present work.

For the purpose of obtaining the spin-rotation tensor, the perturbative operators involving linearly the nuclei momenta (rotational state) and those involving linearly the N nucleus spin, as well as those which are bilinear in the same variables must be inserted in the perturbation theory procedure. In particular, however, for the latter the result comes up as an expectation value for the molecule ground state. In such case, the operators in Eqs. (26) and (27) are the electronic and nuclear contributions to the total electric field at the position of nucleus N , as indicated in Eq. (15). But it can be anticipated that for the equilibrium geometry of the molecule, the total electric field at each nucleus position is zero. Therefore, the operators of Eqs. (26) and (27) yield no contribution at all to the spin-rotation Hamiltonian and they are not considered further in the present discussion.

Explicitly, the relevant operators, written in the corresponding state space can be classified as follows.

–Electron-nucleus perturbation operators linear in the N nucleus magnetic moment

$$h_{\mu_N}^{(1)} = \vec{\alpha} \cdot \vec{A}_N. \quad (49)$$

–Electron-nucleus perturbation operators which are linear in the nuclei momenta

$$h_{\omega}^{(1)} = - \sum_{i,j=x,y,z} I_{ij}^{-1} J_{ei} L_j + \frac{Z_N \vec{\alpha} \cdot \vec{\beta}_N}{|\vec{r} - \vec{r}_N|}. \quad (50)$$

As it was already mentioned, the first term of Eq. (50) is the “inertia” effect coupling the electronic and nuclear dynamics, and it is proportional to the electrons and nuclear angular momenta. The second term is a magnetic effect of the moving nucleus, and it depends on $\vec{\alpha}$ and $\vec{\beta}_N$, which represent the particles velocities relative to c . Consequently, its expression carries an extra factor c^{-2} as compared to the first one. In particular, operator $\vec{\alpha}$ couples large and small components of 4-component spinors, yielding a $1/c$ factor in each matrix element. Therefore, this term is neglected in the present analysis.

–Electron-nucleus perturbation operator bilinear in the N nucleus magnetic moment and momentum

$$h_{\mu_N, \omega}^{(2)} = -\vec{\beta}_N \cdot \vec{A}_N. \quad (51)$$

–Nucleus N -nucleus M perturbation operator bilinear in the N nucleus magnetic moment and nuclei linear momenta

$$h_{\mu_N, \omega}^{(2)}]_{M, N} = -Z_M (\vec{\beta}_M - \vec{\beta}_N) \cdot \vec{A}_N(\vec{r}_M). \quad (52)$$

The spin-rotation Hamiltonian is obtained by carrying out, in first place, a first and second order expansion of the electronic energy at fixed $\{X\}$ nuclear configuration. The first order result is

$$\begin{aligned} E^{(1)}(\vec{I}_N, \vec{L})(X) &= \langle \psi_{el}(X) | \sum_e -\vec{\beta}_N \cdot \vec{A}_N(\vec{r}) | \psi_{el}(X) \rangle \\ &= \frac{-g_N}{2m_p c^2} \langle \psi_{el}(X) | \sum_e \left(\vec{I}_N \times \frac{\vec{r} - \vec{r}_N}{|\vec{r} - \vec{r}_N|^3} \right) | \psi_{el}(X) \rangle \cdot (\vec{\omega} \times \vec{r}_{N,CM}), \end{aligned} \quad (53)$$

where the nuclear velocity has been replaced by the relation

$$\vec{\beta}_N = \frac{1}{c} \vec{\omega} \times \vec{r}_{N,CM} = \frac{1}{c} (\vec{I}^{-1} \vec{L}) \times \vec{r}_{N,CM}. \quad (54)$$

g_N is the gyromagnetic factor of nucleus N and m_p is the proton mass.

The second order result is

$$\begin{aligned} E^{(2)}(\vec{I}_N, \vec{L})(X) &= -2 \sum_{n \neq 0} \frac{\langle \psi_{el}^0 | \vec{\alpha} \cdot \vec{A}_N | \psi_{el}^n \rangle \langle \psi_{el}^n | \sum_{i,j=x,y,z} I_{ij}^{-1} J_{ei} L_j | \psi_{el}^0 \rangle}{E_{el}^0 - E_{el}^n}. \end{aligned} \quad (55)$$

This second order expression of the electronic energy must be understood in the sense discussed in Eqs. (39)–(48).

With these results, the effective spin-rotation Hamiltonian is obtained adding the nucleus-nucleus contributions of Eq. (52)

$$\begin{aligned} H_N^{SR} &= E^{(1)}(\vec{I}_N, \vec{L}) + E^{(2)}(\vec{I}_N, \vec{L}) + \sum_{M \neq N} \left(\vec{I}_N \times \frac{\vec{r}_M - \vec{r}_N}{|\vec{r}_M - \vec{r}_N|^3} \right) \\ &\quad \cdot \left(\vec{\omega} \times \left(\frac{Z_M g_N}{2m_p c^2} (\vec{r}_N - \vec{r}_M) \right) \right). \end{aligned} \quad (56)$$

But it can be shown that

$$\begin{aligned} E^{(1)}(\vec{I}_N, \vec{L}) + \sum_{M \neq N} \left(\vec{I}_N \times \frac{\vec{r}_M - \vec{r}_N}{|\vec{r}_M - \vec{r}_N|^3} \right) \cdot \left(\vec{\omega} \times \left(\frac{Z_M g_N}{2m_p c^2} \vec{r}_{N,CM} \right) \right) \\ = \frac{g_N}{2m_p c^2} (\vec{I}_N \times \langle -\vec{E}(\vec{r}_N) \rangle) \cdot (\vec{\omega} \times (\vec{r}_{N,CM})) = 0 \end{aligned} \quad (57)$$

because the total electric field at a nucleus position is zero for the equilibrium geometry of the molecule. Summing up, the

spin-rotation Hamiltonian may be written as

$$H_N^{\text{SR}} = E^{(2)}(\vec{I}_N, \vec{L}) - \sum_{M \neq N} \frac{Z_M g_N}{2m_p c^2} \left(\vec{I}_N \times \frac{\vec{r}_M - \vec{r}_N}{|\vec{r}_M - \vec{r}_N|^3} \right) \cdot (\vec{\omega} \times \vec{r}_{M,\text{CM}}). \quad (58)$$

The components of the spin rotation tensor \vec{M}_N are obtained by factoring out the components of the nuclear spin \vec{I}_N to the left and those of the rotational angular momentum \vec{L} to the right (and take account of the minus sign in Eq. (1)). For the second order term it is obtained

$$M_{N,i,j}^{(2)} = \frac{g_N}{m_p c} \sum_{n \neq 0} \left(\frac{1}{E_{el}^0 - E_{el}^n} \right) \langle \psi_{el}^0 | \varepsilon_{i,l,m} \times \frac{(r_l - r_{N,l})}{|\vec{r} - r_N|^3} \alpha_m | \psi_{el}^n \rangle \langle \psi_{el}^n | J_{ek} | \psi_{el}^0 \rangle I_{kj}^{-1}, \quad (59)$$

where Einstein's convention of sum of repeated indices is implied and $\varepsilon_{i,l,m}$ is the Levy Civita tensor. For the second nuclear term it is found

$$M_{N,i,j}^{(\text{nuc})} = \sum_{M \neq N} \frac{Z_M g_N}{2m_p c^2} \left(\delta_{i,k} \frac{\vec{r}_{M,\text{CM}} \cdot (\vec{r}_M - \vec{r}_N)}{|\vec{r}_M - \vec{r}_N|^3} - \frac{r_{M,\text{CM},i}(r_{M,k} - r_{N,k})}{|\vec{r}_M - \vec{r}_N|^3} \right) I_{k,j}^{-1}. \quad (60)$$

D. Formal relations between the relativistic expressions of the spin-rotation tensor and the nuclear magnetic shielding tensor

The NMR nuclear magnetic shielding tensor describes the effect of the electronic distribution on the magnetic interaction between a magnetic nucleus and a uniform magnetic field. The formal expression of the relativistic nuclear magnetic shielding tensor is a second order Rayleigh Schrödinger perturbation theory (RSPT)-like relativistic expression containing the magnetic interaction of the electronic distribution with the nucleus magnetic moment and the uniform magnetic field, at fixed nuclei positions at the equilibrium molecular geometry.^{21,25} The first is the same interaction as the one in Eq. (49) entering the RSPT expression of the spin-rotation tensor, and the second one, considering the magnetic potential of the uniform magnetic field

$$\vec{A}_B = \frac{1}{2} \vec{B} \times \vec{r} \quad (61)$$

is given by

$$h_B^{(1)} = \vec{\alpha} \cdot \vec{A}_B = \frac{1}{2} \vec{\alpha} \cdot (\vec{B} \times \vec{r}) = \frac{1}{2} \vec{B} \cdot (\vec{r} \times \vec{\alpha}). \quad (62)$$

The relativistic RSPT-like expression is therefore given by

$$E^{(2)}(\vec{I}_N, \vec{B}) = 2 \sum_{n \neq 0} \frac{\langle \psi_{el}^0 | \vec{\alpha} \cdot \vec{A}_N | \psi_{el}^n \rangle \langle \psi_{el}^n | \frac{1}{2} \vec{B} \cdot (\vec{r} \times \vec{\alpha}) | \psi_{el}^0 \rangle}{E_{el}^0 - E_{el}^n}. \quad (63)$$

Comparison with Eq. (55) is better established taking into account that $\vec{\omega} = \vec{I}^{-1} \vec{L}$ and therefore

$$E^{(2)}(\vec{I}_N, \vec{\omega})(X) = 2 \sum_{n \neq 0} \frac{\langle \psi_{el}^0 | \vec{\alpha} \cdot \vec{A}_N | \psi_{el}^n \rangle \langle \psi_{el}^n | -\vec{\omega} \cdot \vec{J}_e | \psi_{el}^0 \rangle}{E_{el}^0 - E_{el}^n}. \quad (64)$$

It is therefore explicitly shown that in relativistic quantum chemistry the formal expressions of both spectroscopic parameters are very different. The coupling of the electronic distribution to the magnetic field is described by the vector product of the position and velocity operator, $c(\vec{r} \times \vec{\alpha})$, while the coupling of the electronic state and the rotational state is described, as it should, by the total angular momentum operator \vec{J}_e . Both quantities are simply related at the non-relativistic limit, but the difference between them in relativistic quantum mechanics has deep consequences on the quantitative values of both spectroscopic parameters. In particular, it is interesting to point out that operator $(\vec{r} \times \vec{\alpha})$ couples the upper and lower components of 4-component spinors, while operator \vec{J}_e couples upper (lower) components to upper (lower) components. In order to make explicit the differences that hold when relativistic effects are taken into account, a series expansion taking the fine structure constant as perturbation parameter is carried out in Sec. III for the spin-rotation tensor, on the basis of the LRESC approach.

III. LEADING RELATIVISTIC CORRECTION OBTAINED BY THE LINEAR RESPONSE WITHIN THE ELIMINATION OF THE SMALL COMPONENT APPROACH

The LRESC approach²⁵ is a general formalism allowing any second order relativistic property to be expanded in terms of the fine structure constant ($1/c$ in a.u.). The zeroth-order term is the non-relativistic approximation based on the Schrödinger Hamiltonian, and the lowest order relativistic corrections are obtained in the framework of the ESC approach. A detailed account of the LRESC method is given in Ref. 25, and therefore only a brief derivation of its main results for the spin-rotation tensor is carried out in the present work. In the case of the spin-rotation tensor, the second order expression of Eq. (64) needs to be considered. The LRESC approach is based on the analysis of the non-relativistic limit and leading order relativistic corrections to the perturbation theory expressions of Eqs. (39)–(48). In the non-relativistic limit, E_a , Eq. (43) becomes the usual RSPT(2) expression containing the Schrödinger eigenstates of the unperturbed system and the non-relativistic perturbation operator. States $\{|\psi_n(N+2)\rangle\}$ in E_b , Eq. (44), stand for molecular states containing an electron-positron (virtual) pair. In the lowest order relativistic limit, due to the energy differences in the denominator, the corresponding contribution carries a factor $1/2mc^2$.

In order to obtain the leading order relativistic terms of Eqs. (43) and (44), it is necessary to expand both the starting point positive energy 4-component spinors and the relativistic V operator in terms of the fine structure constant $1/c$. This is accomplished by considering the Breit Pauli approximation of the Hamiltonian.²⁶ Only key results for the present derivation are discussed. A positive energy 4-component spinor $|\phi_i^{(4)}\rangle$

is related to the corresponding Pauli spinor by the following relations:

$$|\phi_i^{(4)}\rangle = \begin{bmatrix} |\phi_i^L\rangle \\ |\phi_i^S\rangle \end{bmatrix}, \quad (65)$$

$$\begin{aligned} |\phi_i^S\rangle &= (2mc^2 - (V_C - E_i))^{-1} c \cdot (\sigma p) |\phi_i^L\rangle \\ &\cong \frac{1}{2mc} \left[1 + \frac{V_C - E_i}{2mc^2} \right] \sigma p |\phi_i^L\rangle, \end{aligned} \quad (66)$$

where V_C stands for the one-body potential of the Hamiltonian

$$|\phi_i^L\rangle = N |\tilde{\phi}_i\rangle, \quad (67)$$

$$N = \left(1 - \frac{p^2}{8m^2c^2} \right), \quad (68)$$

and the Pauli two-component spinors $|\tilde{\phi}_i\rangle$ span the two-component spinors space to solve the Breit Pauli Hamiltonian

$$H^{\text{BP}} = H^S + D, \quad (69)$$

where H^S stands for the unperturbed Schrödinger molecular Hamiltonian, and D contains the leading order relativistic one-body (mass-velocity, Darwin, and spin-orbit) and two-body effects.²⁶

A. LRESC expansion of E_a term of the spin-rotation tensor

The matrix elements needed to compute E_a are matrix elements of an operator V between two N -particles states which are combinations of Slater determinants containing N “electronic” spinors. Therefore, for V a one-body operator the result is a combination of matrix elements of operator V between such positive energy 4-component spinors themselves. The non-relativistic and leading relativistic corrections are obtained by transforming them to matrix elements of a new operator between the corresponding Pauli 2-component spinors

$$\langle \phi_i^{(4)} | V | \phi_j^{(4)} \rangle \cong \langle \tilde{\phi}_i | O(V) | \tilde{\phi}_j \rangle. \quad (70)$$

The perturbation operators to be considered in the present case are

$$V_N = \vec{\alpha} \cdot \vec{A}_N \quad (71)$$

and

$$V_J = -\vec{\omega} \cdot \vec{J}. \quad (72)$$

Making use of Eqs. (65)–(68) the matrix elements of V_N can be worked out as follows:²⁵

$$\begin{aligned} \langle \phi_i^{(4)} | \vec{\alpha} \cdot \vec{A}_N | \phi_j^{(4)} \rangle &\cong \langle \tilde{\phi}_i | N \left(\frac{\vec{\sigma} \cdot \vec{p}}{2mc} \right) \left(1 + \frac{V - E_i}{2mc^2} \right) \vec{\sigma} \cdot \vec{A}_N N \\ &+ N \vec{\sigma} \cdot \vec{A}_N \left(1 + \frac{V - E_j}{2mc^2} \right) \left(\frac{\vec{\sigma} \cdot \vec{p}}{2mc} \right) N | \tilde{\phi}_j \rangle. \end{aligned} \quad (73)$$

After a few algebraic manipulations (see the Appendix), Eq. (73) can be expressed as matrix elements of the operator²⁵

$$O(\vec{\alpha} \cdot \vec{A}_N) = H^{\text{PSO}} + H^{\text{FC/SD}} + H^{\text{PSO-K}} + H^{\text{FC/SD-K}}, \quad (74)$$

$$H^{\text{PSO}} = \frac{1}{mc} \vec{\mu}_N \cdot \frac{\vec{L}_N}{r_N^3}, \quad (75)$$

$$H^{\text{FC/SD}} = \frac{\vec{\sigma}}{2mc} \cdot \nabla \times \vec{A}_N, \quad (76)$$

$$H^{\text{PSO-K}} = -\frac{1}{4m^2c^2} \{p^2, H^{\text{PSO}}\}, \quad (77)$$

$$\begin{aligned} H^{\text{FC/SD-K}} &= -\frac{1}{8m^2c^2} \{p^2, H^{\text{FC/SD}}\} + \frac{1}{2m^2c^3} \vec{\sigma} \cdot (\vec{\nabla} V \times \vec{A}_N) \\ &- \frac{1}{8m^3c^3} [p^2, i\vec{\sigma} \cdot (\vec{p} \times \vec{A}_N)], \end{aligned} \quad (78)$$

where $\{, \}$ stands for the anticommutator and $[,]$ stands for the commutator of two operators. As it will be shown below only H^{PSO} , $H^{\text{FC/SD}}$, and $H^{\text{PSO-K}}$ need to be considered in the present work.

The matrix elements of V_J must be worked out similarly

$$\begin{aligned} \langle \phi_i^{(4)} | \vec{\omega} \cdot \vec{J} | \phi_j^{(4)} \rangle &\cong \langle \tilde{\phi}_i | N \vec{\omega} \cdot \vec{J}^{(2)} N + N \left(\frac{\vec{\sigma} \cdot \vec{p}}{2mc} \right) \left(1 + \frac{V - E_i}{2mc^2} \right) \\ &\times \vec{\omega} \cdot \vec{J}^{(2)} \left(1 + \frac{V - E_j}{2mc^2} \right) \left(\frac{\vec{\sigma} \cdot \vec{p}}{2mc} \right) N | \tilde{\phi}_j \rangle, \end{aligned} \quad (79)$$

where the total angular momentum in the space of two-component spinors is

$$\vec{J}^{(2)} = \vec{r} \times \vec{p} + \frac{1}{2} \vec{\sigma}, \quad (80)$$

where $\vec{\sigma}$ are the standard Pauli matrices. The leading term is of order c^0 and the leading relativistic correction is of order c^{-2} . The terms containing $\frac{V-E}{2mc^2}$ can be neglected, since they give rise to higher order effects, and the leading order correction is given by

$$\begin{aligned} \langle \phi_i^{(4)} | \vec{\omega} \cdot \vec{J} | \phi_j^{(4)} \rangle &\cong \langle \tilde{\phi}_i | N \vec{\omega} \cdot \vec{J}^{(2)} N + N \left(\frac{\vec{\sigma} \cdot \vec{p}}{2mc} \right) \vec{\omega} \cdot \vec{J}^{(2)} \left(\frac{\vec{\sigma} \cdot \vec{p}}{2mc} \right) N | \tilde{\phi}_j \rangle. \end{aligned} \quad (81)$$

Taking into account that $\vec{J}^{(2)}$ is the generator of rotations, it holds

$$\left[\frac{\vec{\sigma} \cdot \vec{p}}{2mc}, \vec{J}^{(2)} \right] = 0 \quad (82)$$

and correct up to order $1/c^2$ we find

$$O(-\vec{\omega} \cdot \vec{J}^{(4)}) = -\vec{\omega} \cdot \vec{J}^{(2)}. \quad (83)$$

Summing up, when the RSPT energy correction E_a is expanded in terms of Pauli spinors, the NR limit is re-obtained and two kinds of relativistic corrections to the spin-rotation tensor are found

$$\begin{aligned} E_a &\cong E^{(2)}(H^{\text{PSO}}; -\vec{\omega} \cdot \vec{L}) + E^{(2)}(H^{\text{PSO-K}}; -\vec{\omega} \cdot \vec{L}) \\ &+ E^{(3)}(D; H^{\text{PSO}} + H^{\text{FC/SD}}; -\vec{\omega} \cdot \vec{J}). \end{aligned} \quad (84)$$

The present expression is valid for molecules with a singlet ground state. For this reason, operator \vec{J} is replaced by operator \vec{L} in the first two terms. In the first term, the second order non-relativistic expression of the spin-rotation energy is recovered. In the second term, relativistic effects originating in relativistic corrections to the interaction operator $O(V_N)$ are considered in second order RSPT expressions (it must be remembered that $O(V_J)$ does not yield relativistic corrections). In the third term, relativistic effects originating in the mass velocity, spin-orbit, and Darwin terms of the Pauli Hamiltonian are considered. The second order RSPT expression is given by

$$E^{(2)}(A, B) = \sum_{n \neq 0} \left\{ \frac{\langle 0 | A | n \rangle \langle n | B | 0 \rangle}{E_0 - E_n} + \frac{\langle 0 | B | n \rangle \langle n | A | 0 \rangle}{E_0 - E_n} \right\}, \quad (85)$$

where A, B represent the extension of the necessary operators to the N -particle state space, and the zeroth-order Hamiltonian is the molecular Schrödinger Hamiltonian. The third order RSPT energy correction is given by

$$\begin{aligned} E^{(3)}(A, B, C) &= \sum_{n \neq 0} \frac{\langle 0 | A | n \rangle \langle n | B - \langle B \rangle | m \rangle \langle m | C | 0 \rangle}{(E_0 - E_n)(E_0 - E_m)} \\ &+ \frac{\langle 0 | B | n \rangle \langle n | C - \langle C \rangle | m \rangle \langle m | A | 0 \rangle}{(E_0 - E_n)(E_0 - E_m)} \\ &+ \frac{\langle 0 | C | n \rangle \langle n | A - \langle A \rangle | m \rangle \langle m | B | 0 \rangle}{(E_0 - E_n)(E_0 - E_m)} + \text{c.c.}, \quad (86) \end{aligned}$$

where c.c. stands for the complex conjugate of the previous expression, and $\langle A \rangle$ stands for the ground state expectation value of operator A .

B. LRESC expansion of E_b term of the spin-rotation tensor

The term of the relativistic RSPT expression of $E^{(2)}$ involving positronic states is now considered. Taking into account that within the QED picture, negative energy solutions of the Dirac equation are re-interpreted as positive energy states for positrons,^{29,31} the non-relativistic and lower order contributions to E_b , Eq. (44), can be obtained starting with the following expansion of the energy differences:

$$(E_0 - E_n)^{-1} = -(2mc^2 + \Delta_{n0})^{-1} \cong -\frac{1}{2mc^2} \left(2 + \frac{E_0 - E_n}{2mc^2} \right), \quad (87)$$

where $\Delta_{n0} = E_n - E_0 - 2mc^2$ is of order c^0 or lower. Inserting Eq. (87) as our approximation to the inverse of energy differences in Eq. (44), the energy differences of the second term can be absorbed into the matrix elements of the perturbation operator V

$$(E_0 - E_n) \langle \psi_0 | V | \psi_n(N+2) \rangle = \langle \psi_0(N) | [H_{el}, V] | \psi_n(N+2) \rangle, \quad (88)$$

where H_{el} is the Breit Hamiltonian, Eq. (29). As a consequence, the sum on “excited” states $\{|\psi_n(N+2)\rangle\}$ in the first (second) term of Eq. (44) acts as a projector onto the sub-

space of Dirac-Fock space of $N+2$ (2) particles. A key result derived in Ref. 25 is to show that the overall E_b term can be expressed as

$$E_b = \frac{1}{2mc^2} \langle \psi_0 | V P_p X | \psi_0 \rangle, \quad (89)$$

where for brevity, it was defined

$$X = 2V + \frac{1}{2mc^2} [H_{el}, V] \quad (90)$$

and P_p is the projector on “positronic” states. Neglecting two-body terms in H_{el} , consistently to the sought order in $1/c$ it holds

$$X = 2V + \frac{1}{2mc^2} [H_{el}, V] \cong 2V + \frac{1}{2} [\beta, V]. \quad (91)$$

Considering both operators involved, the E_b term is

$$E_b = \frac{1}{2mc^2} (\langle \psi_0 | V_J P_p X_N | \psi_0 \rangle + \langle \psi_0 | V_N P_p X_J | \psi_0 \rangle), \quad (92)$$

where

$$X_J = -2\vec{\omega} \cdot \vec{J} - \frac{1}{2} [\beta, \vec{\omega} \cdot \vec{J}] = -2\vec{\omega} \cdot \vec{J}, \quad (93)$$

$$X_N = 2\vec{\alpha} \cdot \vec{A}_N + \frac{1}{2} [\beta, \vec{\alpha} \cdot \vec{A}_N] \cong (2 + \beta) \vec{\alpha} \cdot \vec{A}_N. \quad (94)$$

This expression is especially well suited to carry out the non-relativistic limit and to obtain the leading order relativistic correction. In order to obtain the leading order term, the non-relativistic limit of the expectation values in Eq. (92) must be considered. It is readily seen that such term carries a factor μ_N/c^3 . Taking into account that the non-relativistic spin-rotation tensor $E^{(2)}(H^{\text{PSO}}; -\vec{\omega} \cdot \vec{L})$ of Eq. (84) carries a factor μ_N/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 the expectation values in the non-relativistic limit, it must be taken into account that in such case the 4-component spinor carries only a large component given by the corresponding Schrödinger spinor. But the projector onto the subspace of “positronic” states, expressed as a 4×4 matrix of spinor components, is

$$P_p = \begin{bmatrix} 0 & 0 \\ 0 & 1 \end{bmatrix} \quad (95)$$

and so the final result at the order μ_N/c^3 is

$$E_b = \frac{1}{2mc^2} (\langle \psi_0 | V_J P_p X_N | \psi_0 \rangle + \langle \psi_0 | V_N P_p X_J | \psi_0 \rangle) = 0 \quad (96)$$

because V_J, X_J do not connect “electronic” states contained in $|\psi_0\rangle$ to the subspace of “positronic” states, i.e., the P_p projector makes the whole result to be zero. Therefore, it is verified that both the non-relativistic and the leading order relativistic correction to E_b yield a zero for the spin-rotation energy.

IV. DISCUSSION

In Sec. II C, a formal expression for the spin-rotation tensor for the case of relativistic electrons and non-relativistic nuclei was established, Eqs. (59) and (60). For this reason

perturbative operators which can be associated to relativistic corrections to the nuclei dynamics were explicitly neglected. It is interesting to remark that the final expression of Eq. (58) has a rather simple physical interpretation: the first term depends on the electron velocity $c\vec{\alpha}$ of the perturbed electronic state, i.e., for the corrected state which takes account of the inertia effect of the moving nuclei. The state is no more symmetric under time reversal and therefore the interaction with the nucleus magnetic moment field is non-zero. The second term simply describes the non-relativistic interaction of the (other) nuclei orbital rotation with the nucleus N magnetic dipole.

It is interesting to focus in the relation between the nuclear magnetic shielding tensor and the spin-rotation tensor. The LRESC expression of Sec. III is illuminating on this respect. First, due to the difference of the $\vec{r} \times \vec{\alpha}$ and \vec{J}_e operators, the leading (i.e., “non-relativistic”) “E_a” term of both tensors yield values of order μ_N/c^2 and of order μ_N/c , respectively. The equivalence of the formal expressions of both quantities is recovered in this case (an overall constant factor relates both quantities). This equivalence can be traced to the fact that the velocity and momentum operators are simply related by $m\vec{v} = \vec{p}$ in the zeroth-order Hamiltonian in such limit. But whereas the “E_b” term of the nuclear magnetic shielding tensor has a leading term of the same order μ_N/c^2 which corresponds to the diamagnetic contribution to the shielding, in the case of the spin-rotation tensor the “E_b” term yields no contribution of order μ_N/c , i.e., at the non-relativistic limit there is no contribution from this term, as it is known to happen.⁶⁻⁸

When the leading order relativistic correction of the spin-rotation tensor is analyzed with the LRESC approach, it is found that the corresponding expressions are also closely related to those obtained for the nuclear magnetic shielding tensor in Ref. 25. First, Darwin, mass-velocity, and spin-orbit corrections to the spin-rotation tensor have exactly the same formal expressions as the corresponding ones of the paramagnetic component of the nuclear magnetic shielding tensor (with the gauge origin at the center of mass of the molecule). Second, relativistic effects associated to matrix elements of the nucleus magnetic potential take obviously the same expressions for both tensors, giving rise to the $H^{\text{FC/SD-K}}$ and $H^{\text{PSO-K}}$ operators. On the contrary, relativistic corrections associated to operator $\vec{r} \times \vec{\alpha}$ in the nuclear magnetic shielding tensor²⁵ on one hand, and those of the inertia term \vec{J}_e on the other hand behave in a totally different way: in fact, there are no relativistic corrections at the LRESC level associated to the \vec{J}_e operator. As a consequence, there are no further corrections to the second order term of the spin-rotation tensor, and the leading order relativistic correction coming from E_b is also zero. It is thus explicitly shown that the spin-rotation tensor is less affected by relativistic effects than the nuclear magnetic shielding tensor.

V. CONCLUSIONS

The formal expression of the spin-rotation tensor for relativistic electrons and non-relativistic nuclei was established

considering the inertia effect given by the first order correction to the Born-Oppenheimer approximation coupling the electrons and nuclei dynamics. Due to the slow molecular rotation the approximation proposed in this work is considered to be quite suitable for a good quantitative description of this spectral parameter. In fact, a relativistic framework for electrons is mandatory when considering applications to heavy atom containing compounds. Numerical calculations within the present approach would be very interesting in order to establish the importance of relativistic effects in quantitative applications. Work along this line is under progress in our research group. The differences in the formal expressions of relativistic nuclear magnetic shielding and spin-rotation tensors anticipate that the simple relation linking both tensors valid within the non-relativistic theory is no longer valid in the relativistic regime. The LRESC expansion carried out in the present work is useful to obtain approximate expressions of the relativistic spin-rotation tensor on one hand, and on the other hand to carry out a deep analysis of the relations linking the relativistic spin-rotation and nuclear magnetic shielding tensors.

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APPENDIX: ESC EXPANSION OF MATRIX ELEMENTS OF THE MAGNETIC ELECTRON-NUCLEUS INTERACTION

$$\begin{aligned} \langle \phi_i^{(4)} | \vec{\alpha} \cdot \vec{A}_N | \phi_j^{(4)} \rangle &\cong \langle \tilde{\phi}_i | N \left(\frac{\vec{\sigma} \cdot \vec{p}}{2mc} \right) \left(1 + \frac{V - E_i}{2mc^2} \right) \vec{\sigma} \cdot \vec{A}_N N \\ &+ N \vec{\sigma} \cdot \vec{A}_N \left(1 + \frac{V - E_j}{2mc^2} \right) \left(\frac{\vec{\sigma} \cdot \vec{p}}{2mc} \right) N | \tilde{\phi}_j \rangle. \end{aligned} \quad (\text{A1})$$

In the “non-relativistic” term, $N = 1$ and the operator to be evaluated between Schrödinger spinors is

$$\begin{aligned} O(\vec{\alpha} \cdot \vec{A}_N)^{(1)} &= \left(\frac{\vec{\sigma} \cdot \vec{p}}{2mc} \right) \vec{\sigma} \cdot \vec{A}_N + \vec{\sigma} \cdot \vec{A}_N \left(\frac{\vec{\sigma} \cdot \vec{p}}{2mc} \right) = \frac{1}{mc} \vec{p} \cdot \vec{A}_N \\ &+ \frac{1}{2mc} \vec{\sigma} \cdot (\nabla \times \vec{A}_N). \end{aligned} \quad (\text{A2})$$

The last two terms define the paramagnetic spin-orbit (PSO) and Fermi contact (FC) and spin-dipolar (SD) operators

$$H^{\text{PSO}} = \frac{1}{mc} \vec{p} \cdot \vec{A}_N = \frac{1}{mc} \vec{\mu}_N \cdot \frac{\vec{L}_N}{r_N^3}, \quad (\text{A3})$$

$$H^{\text{FC/SD}} = \frac{1}{2mc} \vec{\sigma} \cdot (\nabla \times \vec{A}_N). \quad (\text{A4})$$

Leading order relativistic corrections come out from different sources. On one hand, spin-orbit, Darwin, and mass-velocity

corrections in Pauli spinors were taken into account in a separate, third order term, in Eq. (84). On the other hand, relativistic effects on the magnetic interaction matrix elements must be considered explicitly. From the N operator, Eq. (68), it is obtained

$$\left\{ \frac{-p^2}{8m^2c^2}, \left(\frac{\vec{\sigma} \cdot \vec{p}}{2mc} \right) \vec{\sigma} \cdot \vec{A}_N + \vec{\sigma} \cdot \vec{A}_N \left(\frac{\vec{\sigma} \cdot \vec{p}}{2mc} \right) \right\} = -\frac{1}{8m^2c^2} \{p^2, H^{\text{PSO}} + H^{\text{FC/SD}}\}. \quad (\text{A5})$$

Now we consider the terms corresponding to the $\frac{V-E_i}{2mc^2}$ corrections. To this end, we introduce the commutator

$$\left[\frac{\vec{\sigma} \cdot \vec{p}}{2mc}, \frac{V-E_i}{2mc^2} \right] = \frac{-i}{4m^2c^3} \vec{\sigma} \cdot \vec{\nabla} V \quad (\text{A6})$$

and the non-relativistic relation

$$(V-E_i)|\phi_i\rangle = -\frac{p^2}{2m}|\phi_i\rangle \quad (\text{A7})$$

to rewrite the corresponding terms in Eq. (A1) as

$$\begin{aligned} & \langle \phi_i | \left(\frac{\vec{\sigma} \cdot \vec{p}}{2mc} \right) \left(\frac{V-E_i}{2mc^2} \right) \vec{\sigma} \cdot \vec{A}_N + \vec{\sigma} \cdot \vec{A}_N \left(\frac{V-E_j}{2mc^2} \right) \left(\frac{\vec{\sigma} \cdot \vec{p}}{2mc} \right) | \phi_j \rangle \\ &= \langle \phi_i | \left(\frac{-i}{4m^2c^3} \vec{\sigma} \cdot \vec{\nabla} V - \frac{p^2}{4m^2c^2} \left(\frac{\vec{\sigma} \cdot \vec{p}}{2mc} \right) \right) \vec{\sigma} \cdot \vec{A}_N + \vec{\sigma} \cdot \vec{A}_N \left(\frac{+i}{4m^2c^3} \vec{\sigma} \cdot \vec{\nabla} V - \left(\frac{\vec{\sigma} \cdot \vec{p}}{2mc} \right) \frac{p^2}{4m^2c^2} \right) | \phi_j \rangle \\ &= \langle \phi_i | \frac{1}{2m^2c^3} \vec{\sigma} \cdot (\vec{\nabla} V \times \vec{A}_N) - \frac{p^2}{8m^3c^3} (\vec{p} \cdot \vec{A}_N + i\vec{\sigma} \cdot \vec{p} \times \vec{A}_N) - (\vec{p} \cdot \vec{A}_N - i\vec{\sigma} \cdot \vec{p} \times \vec{A}_N) \frac{p^2}{8m^3c^3} | \phi_j \rangle \\ &= \langle \phi_i | \frac{1}{2m^2c^3} \vec{\sigma} \cdot (\vec{\nabla} V \times \vec{A}_N) - \frac{1}{8m^2c^2} \left\{ p^2, \frac{\vec{p}}{mc} \cdot \vec{A}_N \right\} - \frac{1}{8m^3c^3} [p^2, i\vec{\sigma} \cdot \vec{p} \times \vec{A}_N] | \phi_j \rangle. \end{aligned} \quad (\text{A8})$$

Gathering the results of Eqs. (A5) and (A8) into a singlet and a triplet operator it is obtained

$$H^{\text{PSO-K}} = -\frac{1}{4m^2c^2} \{p^2, H^{\text{PSO}}\}, \quad (\text{A9})$$

$$\begin{aligned} H^{\text{FC/SD-K}} &= -\frac{1}{8m^2c^2} \{p^2, H^{\text{FC/SD}}\} + \frac{1}{2m^2c^3} \vec{\sigma} \cdot (\vec{\nabla} V \times \vec{A}_N) \\ &\quad - \frac{1}{8m^3c^3} [p^2, i\vec{\sigma} \cdot (\vec{p} \times \vec{A}_N)] \end{aligned} \quad (\text{A10})$$

The last operator $H^{\text{FC/SD-K}}$ is not worked out further since for the case of singlet ground state molecules there are no relativistic corrections involving it.

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