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Relativistic effects on the nuclear magnetic shielding tensor

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A new approach for calculating relativistic corrections to the nuclear magnetic shieldings is presented. Starting from a full relativistic second order perturbation theory expression a two-component formalism is constructed by transforming matrix elements using the elimination of small component scheme and separating out the contributions from the no-virtual pair and the virtual pair part of the second order corrections to the energy. In this way we avoid a strong simplification used previously in the literature. We arrive at final expressions for the relativistic corrections which are equivalent to those of Fukui *et al.* [J. Chem Phys. **105**, 3175 (1996)] and at some other additional terms correcting both the paramagnetic and the diamagnetic part of the nuclear magnetic shielding. Results for some relativistic corrections to the shieldings of the heavy and light nuclei in HX and CH_3X (X=Br,I) at both random phase and second order polarization propagator approach levels are given. © *2003 American Institute of Physics.*
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I. INTRODUCTION

Relativistic effects on molecular properties were shown to be relevant from the earliest time of molecular quantum mechanics. In particular for properties which depend strongly on the electronic density in regions close to the nuclei, like nuclear magnetic resonance (NMR) parameters. In the last few years an ever increasing number of new formalisms and calculations for the evaluation of relativistic effects on molecular properties from four-, two-, or one-component response schemes or perturbation theory approaches have been published.[1–11] It was shown that the inclusion of such effects in the calculation of some molecular properties is mandatory when one wants to reproduce experimental trends.[4,10]

Relativistic spin–orbit (SO) effects on magnetic molecular properties were thought to be the most important ones until recent calculations of Visscher *et al.*[4] Numerical results for nuclear magnetic shieldings obtained by four-component calculations and their counterpart from Rayleigh–Schrödinger perturbation theory (RSPT) only match each other for the shielding of heavy atoms X in HX compounds when a new term different from SO is included. The so called mass-correction (MC) term was proposed for the first time by Fukui *et al.*[6] It was obtained within a formalism in which the external magnetic field is explicitly included in the Breit–Pauli Hamiltonian in order to get a gauge-invariant scheme up to order c^{-4}. The MC term is a second order expression containing the Fermi contact (FC) and the kinetic energy (p^2) operators. Nakatsuji *et al.*[7] had previously derived explicit expressions for nuclear magnetic shieldings within a finite perturbation theory (FPT) approach, where the MC term did not appear. This last scheme is not gauge-invariant.

In a four-component context all relativistic corrections are included per se. A few years ago a full-relativistic scheme developed to calculate magnetic molecular properties within response theory was presented by Aucar and Oddershede.[1] Their relativistic polarization propagator approach (RPPA) was shown to be a natural extension of its nonrelativistic counterpart. The nonrelativistic limit of a given molecular property is reached by considering the corresponding limit of the property matrix elements and the principal propagator separately. They explicitly applied this procedure to the magnetic field interaction operator. The four-component calculations of Visscher *et al.*[3,4] make use of this formalism within a fixed gauge origin approach.

The gauge-invariant two-component theory of Fukui *et al.*[6] starts from a positive energy Hamiltonian which includes the magnetic interaction potential. The new MC contribution to the nuclear magnetic shielding comes from Eq. (5) in Ref. 6. However, the authors apply a justified simplification and neglect other operators arising from Eq. (5), being the mass–velocity operator the most remarkable one. Their *N*-electron wave function is built up as a Slater determinant of one-electron unrestricted Hartree–Fock (UHF) spin–orbitals obtained from that two-component positive energy Hamiltonian. In such a case one important point to clear up is related to the above mentioned simplification in the theory of Fukui *et al.*[6] Given that the MC term is by far the largest one for relativistic corrections of shieldings on the

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heavy atom in compounds like HX, there could be some other terms that were neglected though they could have important contributions.

The use of perturbative approaches allowing the calculation of relativistic effects employing the Schrödinger molecular spectrum is attractive because such approaches can be implemented within any standard quantum chemistry computational program. In the present work we are presenting a two-component theory for shielding calculations starting from a four-component RSPT formalism. A set of operators entering the RSPT expressions in terms of the Schrödinger molecular spectrum are derived by expanding such four-component expression as a power series in c^{-1}. All formal expressions are retained, without neglecting any terms in the intermediate steps of our derivation. In doing so one of our main goals has been to obtain formal expressions for operators previously neglected by other authors, regardless of the actual difficulties which could arise in their numerical evaluation. At the end we arrive to expressions that are similar to those of Fukui *et al.*[6] though there are some other new terms. There are also some differences between closely related terms like the MC one which in our case has different constant factors and it also has anisotropic contributions. However, the existence of a sum rule connecting the present MC like operator and that one of Ref. 6 has been proven as part of the present work.

This paper is organized as follows: In Sec. II A the relativistic RSPT expression of magnetic properties in Dirac–Fock space is expanded as a power series in terms of c^{-1} in order to obtain expressions which are correct up to order c^{-4}. Consistently to this order, all quantities involved can be calculated in terms of solutions of the molecular Breit–Pauli Hamiltonian, which is briefly summarized in Sec. II B. Explicit expressions for the relativistic corrections to the magnetic shielding tensor are derived in Sec. II C. They consist of RSPT(1), RSPT(2), and RSPT(3) corrections to the Schrödinger molecular energy. The existence of a sum rule connecting the present results to those of Fukui *et al.*[6] is explicitly shown in Sec. II D. Numerical results for the magnetic shielding constants of the heavy and light nuclei in HX and CH_3X (X=Br,I) are presented in Sec. III. Concluding remarks are discussed in Sec. IV. Details of calculations are given in Appendices A, B, and C.

II. THEORETICAL APPROACH

A. Magnetic properties within the RSPT(2)

Within the relativistic framework magnetic molecular properties which are bilinear in the magnetic potential $V=\alpha\cdot A$ (in a.u.) such as the nuclear magnetic shielding tensor can be obtained from second order corrections to the relativistic molecular ground state energy. In the present work the unperturbed system Hamiltonian considered is the Breit Hamiltonian,[12–15]

$$H^B=h^D+V^C+V^B, \tag{1}$$

where h^D stands for the one-body Dirac Hamiltonian for a particle in the field of the (fixed) nuclei of the molecule, and V^C and V^B stand for the Coulomb and Breit two-body interaction operators in Dirac–Fock space. Introducing a complete set of eigenstates of H^B and subtracting the vacuum polarization term,[14,16] the second order correction to the energy, $E^{(2)}$, can be expressed as

$$E^{(2)}=\sum_{n\neq 0}\frac{\langle 0|V|n\rangle\langle n|V|0\rangle}{E_0-E_n}-\sum_{n\neq \overline{\text{vac}}}\frac{\langle\overline{\text{vac}}|V|n\rangle\langle n|V|\overline{\text{vac}}\rangle}{E_{\overline{\text{vac}}}-E_n}. \tag{2}$$

In Eq. (2), states $\{|n\rangle\}$ stand for all states in Dirac–Fock space that can be connected to $|0\rangle$($|\overline{\text{vac}}\rangle$ in the second term) by the magnetic interaction operator V. In the relativistic framework, the spectrum of states $\{|0\rangle,|n\rangle\}$ must have fixed charge $Q=-eN$ for an N electron system in the nonrelativistic limit. But they do not have fixed number of particles, as both V and H^B operators in principle contain pair creation and destruction operators. $|\overline{\text{vac}}\rangle$ stands for the vacuum state in the QED picture.[15]

In what follows, the nonrelativistic limit and the lowest order corrections in powers of c^{-1} to $E^{(2)}$ are given. To this end, the sum in Eq. (2) is splitted up according to the behavior of $(E_0-E_n)^{-1}$ in the nonrelativistic limit,

$$E^{(2)}=E_a+E_b. \tag{3}$$

E_a collects those terms such that $(E_0-E_n)^{-1}$ does not vanish in that limit. Hereafter, the intermediate states in E_a will be referred to as $\{|n_a\rangle\}$. In the nonrelativistic limit, these states correspond to the Schrödinger molecular spectrum. E_b collects terms where states $\{|n_b\rangle\}$ are such that $(E_0-E_n)^{-1}$ does vanish in the nonrelativistic limit, i.e., they contain at least one virtual electron–positron pair created on $|0\rangle$. The vacuum contribution is included in E_b. Therefore,

$$E_a=\sum_{n_a\neq 0}\frac{\langle 0|V|n_a\rangle\langle n_a|V|0\rangle}{E_0-E_{n_a}}, \tag{4}$$

$$E_b=\sum_{n_b}\frac{\langle 0|V|n_b\rangle\langle n_b|V|0\rangle}{E_0-E_{n_b}}-\sum_{n_b}\frac{\langle\overline{\text{vac}}|V|n_b\rangle\langle n_b|V|\overline{\text{vac}}\rangle}{E_{\overline{\text{vac}}}-E_{n_b}}. \tag{5}$$

Expansion of E_a up to order c^{-2} yields the nonrelativistic paramagnetic contribution to magnetic properties.[1] In agreement with Ref. 11, it will be shown that expansion of E_b up to order c^{-2} yields the diamagnetic contribution. The lowest order relativistic corrections to molecular magnetic properties arise to order c^{-4} in E_a and E_b. Consistently to this order, E_b can be approximated by expanding $(E_0-E_{n_b})^{-1}$ as follows:

$$(E_0-E_{n_b})^{-1}=-(2mc^2+\Delta_{n_b0})^{-1}\cong-\frac{1}{2mc^2}\left(2+\frac{E_0-E_{n_b}}{2mc^2}\right), \tag{6}$$

where $\Delta_{n_b0}=E_{n_b}-E_0-2mc^2$ is of order c^0 or lower.

Taking Eq. (6) into account, the following expression of E_b is valid up to order c^{-4}:

$$E_b = -\frac{1}{2mc^2}\sum_{n_b}\left\{2\langle 0|V|n_b\rangle\langle n_b|V|0\rangle + \frac{E_0 - E_{n_b}}{2mc^2}\langle 0|V|n_b\rangle\langle n_b|V|0\rangle\right\} + \frac{1}{2mc^2}\sum_{n_b}\left\{2\langle\overline{\text{vac}}|V|n_b\rangle\langle n_b|V|\overline{\text{vac}}\rangle + \frac{E_{\text{vac}} - E_{n_b}}{2mc^2}\langle\overline{\text{vac}}|V|n_b\rangle\langle n_b|V|\overline{\text{vac}}\rangle\right\}. \quad (7)$$

Considering that

$$(E_0 - E_{n_b})\langle 0|V|n_b\rangle = \langle 0|[H^B, V]|n_b\rangle, \quad (8)$$

Eq. (7) can be expressed as

$$E_b = -\frac{1}{2mc^2}\sum_{n_b}\left\{\langle 0|2V + \frac{1}{2mc^2}[H^B, V]|n_b\rangle\langle n_b|V|0\rangle\right\} + \frac{1}{2mc^2}\sum_{n_b}\left\{\langle\overline{\text{vac}}|2V + \frac{1}{2mc^2}[H^B, V]|n_b\rangle \times\langle n_b|V|\overline{\text{vac}}\rangle\right\}. \quad (9)$$

As a result, an expression of $E^{(2)}$ consistent up to order c^{-4} is obtained from which relativistic corrections to magnetic properties can be derived,

$$E^{(2)} = \sum_{n_a \neq 0}\frac{\langle 0|V|n_a\rangle\langle n_a|V|0\rangle}{E_0 - E_{n_a}} - \frac{1}{2mc^2}\times\sum_{n_b}\left\{\langle 0|2V + \frac{1}{2mc^2}[H^B, V]|n_b\rangle\langle n_b|V|0\rangle\right\} + \frac{1}{2mc^2}\sum_{n_b}\left\{\langle\overline{\text{vac}}|2V + \frac{1}{2mc^2}[H^B, V]|n_b\rangle \times\langle n_b|V|\overline{\text{vac}}\rangle\right\}. \quad (10)$$

The set of unperturbed relativistic molecular states $\{|n_a\rangle, |n_b\rangle\}$ in Eq. (10) is now considered. As mentioned above, they correspond to eigenstates of the Breit Hamiltonian H^B, in Dirac–Fock space. The complete space can be spanned in terms of the set of one-particle states obtained as solutions of the one-body Dirac-Hamiltonian h_1^D for a particle in the Coulomb field of the (fixed) nuclei in the molecular system.[13] Consistently with the QED picture, this procedure defines the set of ''electronic'' and ''positronic'' bispinors needed to span the Dirac–Fock space. The bare vacuum $|\text{vac}\rangle$ is defined as the state which does not contain neither electrons nor positrons. In terms of such one-particle states, molecular states $\{|n_a\rangle, |n_b\rangle\}$ do not have a fixed number of particles, due to the presence of virtual pair creation and destruction operators in the Coulomb and Breit interaction terms.

However, within perturbation theory in terms of the c^{-1} parameter, the set of states $\{|n_a\rangle\}$ consist of N-particle states plus small virtual pair creation contributions; and states $\{|n_b\rangle\}$ are $N\pm 2$ and $N\pm 4$ particle states with corresponding virtual pair corrections. In order to make clear this separation and easier the matrix element calculations involved in Eq. (10) we partition the second quantized form of the H^B Hamiltonian as[13]

$$H^B = H^{(0)} + H^{(\pm)}. \quad (11)$$

$H^{(0)}$ contains those terms of H^B which do not connect different particle number manifolds in Dirac–Fock space, i.e., it is the particle number conserving part of H^B. The corresponding spectrum consists of fixed particle number states. In particular, for a molecule of charge $Q=-eN$, solving $H^{(0)}$ within the N-particles manifold of Dirac–Fock space constitutes the no-pair approximation to molecular states. By construction, the one-body part, h_1^D, which contains terms of order c^2 is wholly included in $H^{(0)}$, since it has been diagonalized. $H^{(\pm)}$ gathers those terms of the Coulomb and Breit two-body operators that create or destroy one and two electron–positron pairs, i.e., connecting the N-particle manifold with both the $N\pm 2$ and $N\pm 4$ particle manifolds of the same charge Q. Matrix elements therein are of order c^0 or lower. As a consequence, the influence of $H^{(\pm)}$ can be taken into account by the application of perturbation theory with c^{-1} as perturbation parameter.

Taking into account the previous discussion, it is concluded that $E^{(2)}$ in Eq. (10) can be evaluated as a double perturbation series expansion in the magnetic interaction V and $H^{(\pm)}$. Within this approach the ''unperturbed'' Hamiltonian is $H^{(0)}$, i.e., the particle number conserving part of H^B. The fixed particle number spectrum of $H^{(0)}$ can be classified as follows. States of type $\{|n_a\rangle\}$ are N-particles states and they correspond to the no-pair approximation of the molecular spectrum. They are hereafter dubbed as $\{|n_a^{(0)}\rangle \equiv |n_N\rangle\}$. Eigenstates of $H^{(0)}$ of type $\{|n_b\rangle\}$ are $N\pm 2$ or $N\pm 4$ particles states and they are hereafter referred to as $\{|n_b^{(0)}\rangle \equiv |n_K\rangle, K = N\pm 2, N\pm 4\}$. Considering operators V and $H^{(\pm)}$, evaluation of $E^{(2)}$ from Eq. (10), can be separated into two terms: (1) a contribution obtained by considering the no-pair approximation to the spectrum of molecular states within the N-particle manifold of Dirac–Fock space, and (2) a contribution originating in one and two pair-creation effects.

1. No-pair approximation

When the no-pair approximation of unperturbed states is considered within the N-particle manifold of Dirac–Fock space in $E^{(2)}$, only the first term E_a in Eq. (10) yields a nonzero contribution. All quantities involved in it depend only on both the positive energy spectrum of the one-body relativistic Hamiltonian h_1^D and on the N-particles states $\{|0_N\rangle, |n_N\rangle\}$ which lead to the Schrödinger spectrum of states in the nonrelativistic limit. Such N-particle states contain only ''electronic'' bispinors, and they can be obtained consistently up to order c^{-2} applying perturbation theory to the nonrelativistic Schrödinger molecular spectrum via the Breit–Pauli Hamiltonian[12] (see Sec. II B for further details). Therefore, the E_a contribution to $E^{(2)}$, Eq. (10), within the no-pair approximation is

$$E_a^{\mathrm{NP}}=\sum_{n\neq 0}\frac{\langle 0_N|V|n_N\rangle\langle n_N|V|0_N\rangle}{E_{0_N}-E_{n_N}}. \tag{12}$$

Equation (12) is a suitable expression to obtain relativistic corrections as a power series in c^{-1} starting from the Schrödinger spectrum of states. To this end, matrix elements of the magnetic interaction involving ''electronic'' bispinors must be re-expressed in terms of their ''large'' components. The detailed calculation of these terms is presented in Sec. II C and Appendix A.

2. One and two virtual pair creation contributions

One and two virtual pair contributions to $E^{(2)}$, Eq. (10), are as follows: On the one hand, neglecting $H^{(\pm)}$, in E_b the magnetic interaction operator V connects the no-pair N-particle ground state with the manifold of $N+2$ particles states. This contribution is taken into account in E_b^{N+2},

$$\begin{aligned}E_b^{N+2}=&-\frac{1}{2mc^2}\sum_{n_{N+2}}\left\{\langle 0_N|2V\right.\\&\left.+\frac{1}{2mc^2}[H^B,V]|n_{N+2}\rangle\langle n_{N+2}|V|0_N\rangle\right\}\\&+\frac{1}{2mc^2}\sum_{n_2}\left\{\langle\mathrm{vac}|2V+\frac{1}{2mc^2}\right.\\&\left.\times[H^B,V]|n_2\rangle\langle n_2|V|\mathrm{vac}\rangle\right\},\end{aligned} \tag{13}$$

where the consistent $|\overline{\mathrm{vac}}\rangle$ state is the bare vacuum $|\mathrm{vac}\rangle$ in the Dirac–Fock space. The intermediate states in the first (second) term of E_b^{N+2} are $N+2$ (2) particle states. Therefore, the sums in Eq. (13) act as projectors onto the manifold of the corresponding number of particles in each case. Defining the projection operator P_K onto the K-particle manifold of the Dirac–Fock space as

$$P_K=\sum_{n_K}|n_K\rangle\langle n_K|, \tag{14}$$

E_b^{N+2} can be expressed as

$$\begin{aligned}E_b^{N+2}=&-\frac{1}{2mc^2}\langle 0_N|\left(2V+\frac{1}{2mc^2}[H^B,V]\right)P_{N+2}V|0_N\rangle\\&+\frac{1}{2mc^2}\langle\mathrm{vac}|\left(2V+\frac{1}{2mc^2}[H^B,V]\right)P_2V|\mathrm{vac}\rangle.\end{aligned} \tag{15}$$

In Sec. II C 2 explicit expressions are derived for each term in Eq. (15) as a function of the Schrödinger spectrum of states consistently up to order c^{-4}.

On the other hand, virtual pair creation contributions are also obtained when the effect of $H^{(\pm)}$ is taken into account into molecular states in E_a and E_b. These contributions can be introduced considering the first-order correction given by $H^{(\pm)}$ to the no-pair molecular states $\{|n_N\rangle\}$. Following Ref. 13, the leading term of this correction in the expansion parameter c^{-1} can be expressed as

$$E_{n_a}^{(1)}=\langle n_N|H^{(\pm)}|n_N\rangle=0, \tag{16}$$

$$\begin{aligned}|n_a^{(1)}\rangle=&\sum_m\frac{|m\rangle\langle m|H^{(\pm)}|n_N\rangle}{E_n-E_m}\\\cong&-\left(\frac{1}{4mc^2}P_{N+4}+\frac{1}{2mc^2}P_{N+2}\right)H^{(\pm)}|n_N\rangle.\end{aligned} \tag{17}$$

The result in Eq. (17) is based on the following grounds. Since $|n_N\rangle$ is an N-electron state, $H^{(\pm)}$ connects it with states $|m\rangle$ which contain $N+2$ or $N+4$ particles, i.e., one or two electron–positron pairs created on $|n_N\rangle$. The leading term in the energy differences (E_n-E_m) is $-2mc^2$ in first place, and $-4mc^2$ secondly. Keeping only these leading terms in the denominator the sum over intermediate states $|m\rangle$ acts as a projector onto the $N+2$ or $N+4$ particle manifolds, respectively, yielding the final result of Eq. (17). It is worth mentioning that $P_{N+4}H^{(\pm)}|n_N\rangle$ contains terms of order c^0 due to the Breit interaction operator, but $P_{N+2}H^{(\pm)}|n_N\rangle$ is of order c^{-1}, or lower.

Replacing Eqs. (16) and (17) in Eq. (10), and keeping terms up to order c^{-4}, the following corrections to $E^{(2)}$ due to one and two virtual pair creation contributions originating in $H^{(\pm)}$ are found:

$$\begin{aligned}E_a^{\mathrm{VP}}=&-\frac{1}{2mc^2}\\&\times\sum_{n\neq 0}\frac{\langle 0_N|H^{(\pm)}P_{N+2}V+VP_{N+2}H^{(\pm)}|n_N\rangle\langle n_N|V|0_N\rangle}{E_{0_N}-E_{n_N}}\\&+\frac{\langle 0_N|V|n_N\rangle\langle n_N|H^{(\pm)}P_{N+2}V+VP_{N+2}H^{(\pm)}|0_N\rangle}{E_{0_N}-E_{n_N}},\end{aligned} \tag{18a}$$

$$\begin{aligned}E_b^{N+4}=&\frac{1}{8m^2c^4}(\langle 0_N|H^{(\pm)}P_{N+4}VP_{N+2}V|0_N\rangle\\&+\langle 0_N|VP_{N+2}VP_{N+4}H^{(\pm)}|0_N\rangle)\\&-\frac{1}{8m^2c^4}(\langle\mathrm{vac}|H^{(\pm)}P_4VP_2V|\mathrm{vac}\rangle\\&+\langle\mathrm{vac}|VP_2VP_4H^{(\pm)}|\mathrm{vac}\rangle),\end{aligned} \tag{18b}$$

where it must be understood that in Eq. (18) all intermediate states correspond to fixed particle number states.

Taking into account results Eqs. (12), (13), (18a), and (18b), the second-order energy correction has been split up as

$$E^{(2)}=E_a^{\mathrm{NP}}+E_a^{\mathrm{VP}}+E_b^{N+2}+E_b^{N+4}. \tag{19}$$

B. Relationship between no-pair relativistic molecular states and Schrödinger molecular states: The Breit–Pauli Hamiltonian

In order to evaluate the different contributions to $E^{(2)}$ in Eq. (19) as a series expansion in powers of c^{-1} in terms of the Schrödinger spectrum of states, the relationship between relativistic molecular states $\{|0_N\rangle,|n_N\rangle\}$, i.e., the N-particle solutions to $H^{(0)}$, and the Schrödinger spectrum of states

must be established. This connection is readily provided by the Breit–Pauli Hamiltonian,[12,17] which is briefly summarized here.

The no-pair approximation to the Breit Hamiltonian of Eq. (20),[12,17]

$$H^B=\sum_{i=1}^{N} h_1^D(i)+\frac{1}{2}\sum_{i\neq j}^{N}\left\{\frac{1}{r_{ij}}-\frac{1}{2r_{ij}}\left[\alpha_i\alpha_j+\frac{(\alpha_i\cdot\mathbf{r}_{ij})(\alpha_j\cdot\mathbf{r}_{ij})}{r_{ij}^2}\right]\right\} \tag{20}$$

is obtained considering all possible configurations $|K^4\rangle=|\phi_{K_1}^4\cdots\phi_{K_N}^4\rangle$ of N positive-energy four-component spinors $|\phi_i^4\rangle$ which are solutions of the one-body Dirac Hamiltonian h_1^D, i.e.,

$$h_1^D=c\,\boldsymbol{\alpha}\mathbf{p}+mc^2\beta-\sum_A\frac{Z_A}{|r-R_A|}, \tag{21}$$

$$h_1^D|\phi_i^4\rangle=(mc^2+E_i)|\phi_i^4\rangle. \tag{22}$$

A given positive energy four-component spinor can be split in its large (L) and small (S) components,

$$|\phi_i^4\rangle=\begin{bmatrix}|\phi_i^L\rangle\\ |\phi_i^S\rangle\end{bmatrix}, \tag{23}$$

$$|\phi_i^S\rangle=R_i^{-1}c\cdot(\sigma p)|\phi_i^L\rangle, \tag{24}$$

$$R_i=(2mc^2-(V_C-E_i)), \tag{25}$$

where V_C stands for the one-body potential in Eq. (21) and σ stand for the two-dimensional Pauli matrices. Consistently to order c^{-4} R_i^{-1} can be written as

$$R_i^{-1}\approx\frac{1}{2mc^2}\left[1+\frac{V_C-E_i}{2mc^2}\right]. \tag{26}$$

Replacing Eq. (26) in Eq. (24) an expression for $|\phi_i^S\rangle$ which is exact up to order c^{-3} is obtained,

$$|\phi_i^S\rangle\approx\frac{1}{2mc}\left[1+\frac{V_C-E_i}{2mc^2}\right](\sigma p)|\phi_i^L\rangle \tag{27}$$

when the large component is exact up to order c^{-2}.

The differential equation for the large component $|\phi_i^L\rangle$ that arises from the Dirac Hamiltonian can be transformed into an eigenvalue problem with unit metric consistently up to order c^{-2} for a "normalized" spinor $|\tilde{\phi}_i\rangle$ with the following Pauli Hamiltonian:[17]

$$H^P=h^S+D_1, \tag{28}$$

where

$$|\phi_i^L\rangle=\left(1-\frac{p^2}{8m^2c^2}\right)|\tilde{\phi}_i\rangle, \tag{29}$$

h^S stands for the one-body Schrödinger Hamiltonian and D_1 is

$$D_1=\frac{1}{8m^3c^2}p^4+\frac{1}{8m^2c^2}(\nabla^2V_C)+\frac{1}{4m^2c^2}\sigma(\nabla V_C\times p), \tag{30}$$

where the familiar mass–velocity (MV), Darwin (DW) and spin–orbit (SO) terms are readily recognized. In an analogous way, the two-body interaction terms in H^B between configurations of positive energy bispinors $|K^4\rangle$ can be re-expressed in terms of configurations $|\tilde{K}\rangle$ of the corresponding "normalized" spinors $|\tilde{\phi}_i\rangle$. Consistently up to order c^{-2}, this procedure leads to the Breit–Pauli Hamiltonian, H^{BP},

$$\langle L^4|H^B|K^4\rangle\cong\langle\tilde{L}|H^{\mathrm{BP}}|\tilde{K}\rangle, \tag{31}$$

$$H^{\mathrm{BP}}=H^S+D, \tag{32}$$

where H^S stands for the N-electron Schrödinger Hamiltonian and D is given by

$$D=D_1+D_2, \tag{33}$$

with D_1 being the generalization of Eq. (30) to the N-particle state space and D_2 is

$$D_2=\frac{1}{2m^2c^2}\sum_{i\neq j}\left\{-\frac{1}{4}\frac{\mathbf{r}_{ij}^2\mathbf{p}_i\mathbf{p}_j+(\mathbf{r}_{ij}(\mathbf{r}_{ij}.\mathbf{p}_j).\mathbf{p}_i)}{\mathbf{r}_{ij}^3}-\pi\delta(\mathbf{r}_{ij})+\frac{\left(\frac{\sigma_i}{2}+\sigma_j\right).\mathbf{r}_{ij}\times\mathbf{p}_i}{\mathbf{r}_{ij}^3}-\frac{\pi}{3}(\sigma_i\cdot\sigma_j)\,\delta(\mathbf{r}_{ij})+\frac{1}{8}\frac{r_{ij}^2(\sigma_i\sigma_j)-3(\sigma_i\mathbf{r}_{ij})(\sigma_j\mathbf{r}_{ij})}{\mathbf{r}_{ij}^5}\right\}. \tag{34}$$

Different terms in D_2 can be identified as follows: The first term is the so-called orbit–orbit (OO) interaction, the second one is the two-body Darwin term [DW(2)], the third one represents the two-body spin orbit [SO(2)] and spin–other orbit (SOO) interactions and the fourth and fifth terms stand for the spin–spin interaction terms, both Fermi contact (FC-SS) and dipole–dipole (SD-SS) interactions.

Therefore, the energy eigenvalues and configuration coefficients $\{E_n,|n_N\rangle=\Sigma C_{n_K}|K^4\rangle\}$ corresponding to N-particles eigenstates $\{|n_N\rangle\}$ of H^B (i.e., within the no-pair approximation) can be obtained correctly up to order c^{-2} from the Breit–Pauli Hamiltonian. As a consequence, consistently to this order, both the expectation values and the RSPT expressions in Eqs. (12), (15), and (18), can be evaluated employing the H^{BP} spectrum of states. To this end, the reduction of matrix elements of a given Dirac-type operator W between configurations $\{|K^4\rangle\}$ to those of a new operator $O(W)$ between the corresponding configurations of "nor-

malized'' spinors $\{|\tilde{K}\rangle\}$ must be carried out consistently to the desired order,

$$\langle L^4|W|K^4\rangle \cong \langle \tilde{L}|O(W)|\tilde{K}\rangle. \tag{35}$$

Thus, hereafter use will be made of Eqs. (36) and (37),

$$\langle 0^4|W|0^4\rangle \cong \langle \tilde{0}|O(W)|\tilde{0}\rangle, \tag{36}$$

$$\sum_{n_N\neq 0} \frac{\langle 0_N^4|W|n_N^4\rangle\langle n_N^4|W|0_N^4\rangle}{E_0-E_{n_N}} \cong \sum_{\tilde{n}\neq 0} \frac{\langle \tilde{0}|O(W)|\tilde{n}\rangle\langle \tilde{n}|O(W)|\tilde{0}\rangle}{E_0-E_{\tilde{n}}}, \tag{37}$$

where the superscripts are written in order to emphasize that the l.h.s. of Eqs. (36) and (37) are evaluated in terms of configurations $\{|K^4\rangle\}$, whereas those of the r.h.s. are evaluated in terms of configurations $\{|\tilde{K}\rangle\}$.

In the r.h.s. of Eqs. (36) and (37) the unperturbed states correspond to eigenstates of the Breit–Pauli Hamiltonian H^{BP}. The usefulness of such expressions comes from the fact that relativistic effects in H^{BP} are introduced via operators D_1 and D_2 which can be thought of as perturbations to the Schrödinger molecular Hamiltonian. The first order RSPT corrections to the energy and molecular states yield results that are correct up to order c^{-2},

$$E_{\tilde{n}} = E_n^S + \langle n^S|(D_1+D_2)|n^S\rangle, \tag{38}$$

$$|\tilde{n}\rangle = |n^S\rangle + \sum_{n\neq n} \frac{\langle m^S|(D_1+D_2)|n^S\rangle}{E_n^S-E_m^S}|m^S\rangle, \tag{39}$$

where the superscript ''S'' identifies eigenstates of the Schrödinger molecular Hamiltonian, H^S.

C. Relativistic corrections to the nuclear magnetic shielding tensor

The nuclear magnetic shielding tensor for a nucleus M can be obtained as[18]

$$\sigma_{Mij} = \left(\frac{\partial^2 E}{\partial \boldsymbol{\mu}_{Mi}\partial \mathbf{B}_j}\right)_{\substack{\mathbf{B}=0\\ \boldsymbol{\mu}_M=0}}, \tag{40}$$

where E stands for the molecular electronic energy in the presence of both the external uniform and the nuclear magnetic fields. In order to express relativistic corrections to σ_M consistently up to order c^{-4} in terms of the Schrödinger molecular spectrum, all quantities defined in Sec. II A, i.e., E_a^{NP}, Eq. (12); E_a^{VP}, Eq. (18a); E_b^{N+2}, Eq. (15); and E_b^{N+4}, Eq. (18b), must be re-expressed according to results in Sec. II B, Eqs. (36)–(39). The corresponding expressions are obtained in the present section. Contributions that arise from E_a^{NP} and E_a^{VP} will be assigned to the paramagnetic term of σ_M, whereas those originating in E_b^{N+2} and E_b^{N+4} correspond to the diamagnetic term.

1. Paramagnetic term

a. Contribution from no virtual pair excitations to the paramagnetic term: In order to evaluate E_a^{NP} of Eq. (12), the reduction of matrix elements of the magnetic interaction operator $V=\alpha\cdot\mathbf{A}$ (atomic units are used throughout) between positive energy bispinor configurations to spinor configurations is readily obtained if such reduction is carried out for the positive-energy bispinors themselves according to the discussion in Sec. II B [see Eq. (35)], i.e.,

$$\langle \phi_i^4|\alpha\cdot\mathbf{A}|\phi_j^4\rangle = \langle \tilde{\phi}_i|O(\alpha\cdot\mathbf{A})|\tilde{\phi}_j\rangle. \tag{41}$$

Details of the derivation are presented in Appendix A. The resulting one-body operator O can be split up into a c^{-1} contribution (O^1), and a c^{-3} contribution (O^3). For the specific calculation of the nuclear magnetic shielding tensor one operator of this kind can be defined as a function of the uniform magnetic field B and another one as a function of the nuclear magnetic moment μ_M. These operators can still be re-expressed according to their singlet or triplet character. Explicit expressions are as follows. The first order singlet and triplet operators associated to the uniform magnetic field are

$$O^{1S}(B) = \frac{1}{2mc} L.B, \tag{42a}$$

$$O^{1T}(B) = \frac{1}{2mc} \sigma.B, \tag{42b}$$

which represent the orbital and spin Zeeman interactions which hereafter will be referred to with the acronyms ''OZ'' and ''SZ,'' respectively.

The first order singlet and triplet operators associated with the nuclear magnetic moment are

$$O^{1S}(\mu_M) = \frac{1}{mc}\frac{\mu_M.L_M}{r_M^3}, \tag{43a}$$

$$O^{1T}(\mu_M) = \frac{1}{2mc}\sigma.B_M, \tag{43b}$$

where

$$B_M = \left(\frac{8\pi}{3}\delta(r_M)\mu_M + \frac{3(\mu_M.r_M)r_M - r_M^2\mu_M}{r_M^5}\right). \tag{43c}$$

$O^{1S}(\mu_M)$ is the paramagnetic spin–orbit interaction operator (PSO) and $O^{1T}(\mu_M)$ contains the Fermi contact (FC) and spin-dipolar (SD) operators.

The singlet and triplet operators to the third order in c^{-1} associated to the uniform magnetic field B are

$$O^{3S}(B) = -\frac{1}{8m^3c^3}\{L.B,p^2\}, \tag{44a}$$

$$O^{3T}(B) = -\frac{1}{8m^3c^3}(3(\sigma.B)p^2 - (\sigma.p)(p.B) - 4m\sigma.\nabla V_C\times A_B), \tag{44b}$$

where the curly brackets stand for the anticommutator and V_C for the one-body Coulomb potential in the Pauli Hamiltonian. $O^{3S}(B)$ will be identified by the acronym OZ-K. The first two terms in $O^{3T}(B)$ will be identified altogether by the acronym SZ-K and the third term will be called B-SO (magnetic external field induced spin–orbit term).

Singlet and triplet operators to the third order in c^{-1} associated with the nuclear magnetic moment are

$$O^{3S}(\mu_M) = -\frac{1}{4m^3c^3}\left\{\frac{\mu_M.L_M}{r_M^3}, p^2\right\}, \tag{45a}$$

$$O^{3T}(\mu_M) = -\frac{1}{8m^3c^3}\left(\frac{3}{2}p^2(\sigma.B_M) + \frac{1}{2}(\sigma.B_M)p^2 + i\sigma.[A_M\times p, p^2] - 4m\sigma.\nabla V_C\times A_M\right). \tag{45b}$$

$O^{3S}(\mu_M)$ will be referred to as the PSO-K term. The first, second, and third terms in $O^{3T}(\mu_M)$ will be identified altogether by the acronym SZ-B_M-K and the last one by B_M-SO (nuclear magnetic field-induced spin–orbit term).

Considering Eqs. (42)–(45) the expression of E_a^{NP} can be evaluated first at the lowest possible order in the parameter c^{-1}. In this case, the unperturbed molecular spectrum corresponds to the H^S spectrum and the perturbation operators are $O^1(\mu_M)$ and $O^1(B)$. For a system with a singlet ground state it is found

$$E^{(\mathrm{para,NR})} = E(O^{1S}(\mu_M), O^{1S}(B)), \tag{46}$$

where the shorthand notation for a second order RSPT expression of Eq. (47) has been introduced,

$$E(A,B) = \sum_{n\neq 0}\left\{\frac{\langle 0|A(N)|n\rangle\langle n|B(N)|0\rangle}{E_0 - E_n} + \frac{\langle 0|B(N)|n\rangle\langle n|A(N)|0\rangle}{E_0 - E_n}\right\}, \tag{47}$$

where $A(N)$ stands for the one-body operator A in the N-particle state space,

$$A(N) = \sum_i A_i. \tag{48}$$

Result of Eq. (46) yields the nonrelativistic paramagnetic contribution to σ_M. Triplet operators do not contribute to Eq. (46) because for a singlet ground state Eq. (49) holds,

$$O^{1T}(B)|0\rangle = 0. \tag{49}$$

Two classes of relativistic corrections to E_a^{para} originating in E_a^{NP} do appear up to order c^{-4}. Within the first class of terms, a third-order operator O^3 is included in a second-order RSPT expression,

$$E^{(\mathrm{para,2})} = E(O^{1S}(\mu_M), O^{3S}(B)) + E(O^{1T}(\mu_M), O^{3T}(B)) + E(O^{3S}(\mu_M), O^{1S}(B)). \tag{50}$$

We do not consider $O^{3T}(\mu_N)$ due to the result of Eq. (49).

The second class of terms are those in which an O^1 operator enters twice and the unperturbed molecular spectrum contains relativistic corrections via operator $D = D_1 + D_2$ defined in Sec. II B, Eq. (33). These combinations yield third order RSPT expressions. Introducing the short-hand notation,

$$E(A,B,C) = \sum_{n\neq 0}\frac{\langle 0|A(N)|n\rangle\langle n|B(N) - \langle B(N)\rangle|m\rangle\langle m|C(N)|0\rangle}{(E_0 - E_n)(E_0 - E_m)} + \frac{\langle 0|B(N)|n\rangle\langle n|C(N) - \langle C(N)\rangle|m\rangle\langle m|A(N)|0\rangle}{(E_0 - E_n)(E_0 - E_m)} + \frac{\langle 0|C(N)|n\rangle\langle n|A(N) - \langle A(N)\rangle|m\rangle\langle m|B(N)|0\rangle}{(E_0 - E_n)(E_0 - E_m)}, \tag{51}$$

where $\langle X(N)\rangle = \langle 0|X(N)|0\rangle$, the following terms are found for a system with a singlet ground state (taking spin symmetry into account):

$$E^{(\mathrm{para,3})} = E(O^{1S}(\mu_M), O^{1S}(B), D^S) + E(O^{1T}(\mu_M), O^{1S}(B), D^T) + E(O^{1T}(\mu_M), O^{1T}(B), D^T), \tag{52}$$

where the operator D has been separated into tensor components of rank 0 (singlet), D^S; 1 (triplet), D^T; and 2 (quintuplet), D^Q, in spin-space. The singlet D_1^S term corresponds both to the Darwin (DW) and mass–velocity (MV) operators and the triplet D_1^T term corresponds to the spin–orbit (SO) term. The singlet terms in D_2 are OO, DW(2), and FC-SS defined in Sec. II B. The triplet ones are the two-body SO(2) and SOO terms and the quintuplet one is SD-SS. For a system with a singlet ground state, there is no contribution from the SD-SS operator in Eq. (52), due to the result in Eq. (49). In Table I all possible contributions originating in Eqs. (50) and (52) are presented. The total contribution to $E^{(2)}$ which comes from E_a^{NP} is thus

$$E_a^{\mathrm{NP}} = E^{(\mathrm{para,NR})} + E^{(\mathrm{para,2})} + E^{(\mathrm{para,3})}. \tag{53}$$

b. One and two virtual pair contributions to the paramagnetic term: Turning the attention now to the operators in E_a^{VP}, Eq. (18a), it is observed that due to the factor $1/2mc^2$ and to the fact that the magnetic interaction operator V between N particles states yields matrix elements of order c^{-1} or lower, only terms of order c^{-1} of the remainder operators should be calculated. To this end, the corresponding reduction from bispinor configurations to the spinor configurations representation of the operator W defined in Eq. (54) must be carried out,

$$W = P_N(H^{(\pm)}P_{N+2}V + VP_{N+2}H^{(\pm)})P_N. \tag{54}$$

Considering the second quantized form of the operators involved and both the Coulomb and Breit interaction terms in $H^{(\pm)}$, the final form of the operator reduced to spinors configurations according to Eq. (35) (see Appendix C for details), $O(W)$ is

$$O(W) = -\sum_{i\neq j}\left\{O_i^1, \frac{1}{r_{ij}}\right\} - \frac{1}{mc}\sum_{i\neq j}\left[\{p_i, \vec{O}_{ij}A_j\} - \left(\sigma_j\times\frac{r_{ij}}{r_{ij}^3}\right).A_i\right], \tag{55}$$

TABLE I. Relativistic corrections to the paramagnetic contribution of the nuclear magnetic shielding tensor arising from Eqs. (50) and (52).

$O(\mu_M)$	$O(B)$	D	Term[a] $\sigma_M^p(A,B)$ or $\sigma_M^p(A,B,C)$
PSO	OZ-K	⋯	(PSO,OZ-K)
PSO-K	OZ		(PSO-K,OZ)
FC, SD	SZ-K, B-SO		(FC,SZ-K) (SD,SZ-K)
			(FC,B-SO) (SD,B-SO)
PSO	OZ	DW, MV	(PSO,OZ,DW) (PSO,OZ,MV)
		DW(2), OO, FC-SS	(PSO,OZ,DW(2))
			(PSO,OZ,OO)
			(PSO,OZ,FC-SS)
FC,SD	OZ	SO	(FC,OZ,SO) (SD,OZ,SO)
		(=SO(1)+SO(2))	(FC,OZ,SOO) (SD,OZ,SOO)
FC,SD	SZ	SO	(FC,SZ,SO) (SD,SZ,SO)
		(=SO(1)+SO(2))	(FC,SZ,SOO) (SD,SZ,SOO)

[a]See text for the definitions of the acronyms identifying the different involved operators.

where O_i^1 stands for the first order magnetic operator defined in Eqs. (42) and (43), the curly brackets stand for the anticommutator; the two-body tensor operator $\vec{\vec{O}}_{ij}$ is defined as

$$\vec{\vec{O}}_{ij} = -\frac{1}{2r_{ij}}\left(\vec{\vec{I}} + \frac{r_{ij}.r_{ij}^t}{r_{ij}^2}\right), \tag{56}$$

where r_{ij}^t is the transpose of r_{ij}. An operator $O(W)$, Eq. (55), can be defined for the uniform magnetic field, $O(W_B)$, and another one for the nuclear magnetic moment $O(W_{\mu_M})$. In order to obtain contributions to σ_M correct to order c^{-4} originating in E_a^{VP}, operators $O(W)$ must be combined with operators O^1 [Eqs. (42) and (43)] in second order RSPT expressions based on the Schrödinger molecular unperturbed spectrum, i.e.,

$$E_a^{\mathrm{VP}} = -\frac{1}{2mc^2}\{E(O(W_B),O^1(\mu_M)) + E(O(W_{\mu_M}),O^1(B))\}, \tag{57}$$

where the shorthand notation of Eq. (47) has been used.

2. Diamagnetic term

The contribution to $E^{(2)}$ which arises from E_b^{N+2}, Eq. (15), is

$$E^{\mathrm{diam}} = -\frac{1}{2mc^2}\langle 0_N|\left(2V + \frac{1}{2mc^2}\lfloor H^B,V\rfloor\right)P_{N+2}V|0_N\rangle + \frac{1}{2mc^2}\langle \mathrm{vac}|\left(2V + \frac{1}{2mc^2}[H^B,V]\right)P_2V|\mathrm{vac}\rangle. \tag{58}$$

The reduction of matrix elements in Eq. (58) from bispinors configurations to spinor configurations according to results in Sec. II B [Eqs. (36)–(39)] is now considered. To this end we define operator X,

$$X = 2V + \frac{1}{2mc^2}[H^B,V], \tag{59}$$

which can be separated into two terms. The first one involves the one-body part of H^B and the second one the two-body part,

$$X(1) = 2V + \frac{1}{2mc^2}[h^D,V], \qquad X(2) = \frac{1}{2mc^2}[V^C + V^B,V]. \tag{60}$$

V^C, V^B stand for the two-body Coulomb and Breit operators, Eq. (1). The commutator $\lfloor V^C,V\rfloor$ vanishes and therefore only the Breit interaction must be taken into account in $X(2)$.

Let us first analyze the contributions to E_b^{N+2} originating from $X(1)$, which is a one-body operator. The corresponding term is dubbed $E^{\mathrm{diam}}(1)$,

$$E^{\mathrm{diam}}(1) = -\frac{1}{2mc^2}\langle 0_N|X(1)P_{N+2}V|0_N\rangle + \frac{1}{2mc^2}\langle \mathrm{vac}|X(1)P_2V|\mathrm{vac}\rangle. \tag{61}$$

Due to the factor $1/2mc^2$ the expectation values in Eq. (61) should be expanded up to order c^{-2}. A more compact form for $E^{\mathrm{diam}}(1)$ can be found considering the second quantized form of the operators involved in it and also Eqs. (36)–(37). After rearrangement of terms (see Appendix B for details) it is found,

$$E^{\mathrm{diam}}(1) = \frac{1}{2mc^2}\langle\tilde{0}|\sum_i A^2(i)|\tilde{0}\rangle - \frac{1}{8m^3c^4} \times \langle\tilde{0}|\sum_i (\{\sigma p,\sigma A\}^2 + (\sigma A)p^2(\sigma A) - (\sigma p)A^2(\sigma p) + \{p^2,A^2\} + \tfrac{1}{2}[A^2,p^2])(i)|\tilde{0}\rangle. \tag{62}$$

In Eq. (62) it is explicitly seen that, up to order c^{-2}, only the first term remains and $|\tilde{0}\rangle$ must be replaced by the Schrödinger molecular ground state $|0\rangle$. The nonrelativistic dia-

magnetic contribution to magnetic properties is thus obtained, in accordance to Ref. 11. In order to obtain a result which is exact up to order c^{-4}, in the first term $|\tilde{0}\rangle$ must include relativistic corrections via the operator D, but, due to the factor $1/8m^3c^4$, the last expectation value must be calculated with the Schrödinger molecular ground state.

In order to simplify Eq. (62) it is useful to observe that

$$\langle 0|\sum_i [p_i^2,A_i^2]|0\rangle=\langle 0|\left[\sum_i p_i^2,\sum_j A_j^2\right]|0\rangle$$
$$=2m\langle 0|\left[H^{\mathrm{Sch}},\sum_j A_j^2\right]|0\rangle=0, \quad (63)$$

and, therefore, collecting terms bilinear in the magnetic potential of the external uniform field A_B and of the nuclear magnetic field A_M, Eq. (62) can be expressed as

$$E^{\mathrm{diam}}(1)=\frac{1}{mc^2}\langle\tilde{0}|\sum_i A_B.A_M(i)|\tilde{0}\rangle$$
$$-\frac{1}{8m^3c^4}\langle 0|\sum_i W_i+W_i^+|0\rangle, \quad (64)$$

where

$$W=4(A_Mp)(A_Bp)+2(\sigma B_M)(A_Bp)+2(A_Mp)(\sigma B)$$
$$+(\sigma B_M)(\sigma B)+(\sigma A_M)(p^2\sigma A_B)$$
$$-(\sigma p)(A_B.A_M)(\sigma p)+2(A_B.A_M)p^2. \quad (65)$$

Taking into account that

$$\langle 0|\sum_i W_i+W_i^+|0\rangle=2\,\mathrm{Re}\langle 0|\sum_i W_i|0\rangle \quad (66)$$

for a molecule with a real singlet ground state only those terms of W which do not contain the Pauli matrices or imaginary operators (in coordinates representation) can give nonzero contributions. The overall result in this case, including relativistic corrections to $|\tilde{0}\rangle$, can be expressed as

$$E^{\mathrm{diam}}(1)=\frac{1}{mc^2}\langle 0|A_B.A_M|0\rangle+E\left(\frac{1}{mc^2}A_B.A_M,D^S\right)$$
$$-\frac{1}{4m^3c^4}\langle 0|\sum_i W_i'|0\rangle,$$
$$W'=4(A_Mp)(A_Bp)+B.B_M+A_Mp^2A_B$$
$$-p(A_B.A_M)p+2(A_B.A_M)p^2, \quad (67)$$

where the shorthand notation of Eq. (47) is used to indicate a second-order RSPT contribution. After a few algebraic steps, W' can be re-expressed as

$$W'=W_1'+W_2',$$
$$W_1'=\sum_{i,j=x,y,z}4A_{Mi}A_{Bj}p_ip_j+2(A_B.A_M)p^2, \quad (68)$$
$$W_2'=\tfrac{1}{2}A_B.(\nabla\times B_M).$$

If the gauge origin of the external uniform magnetic potential is placed at the position r_M of the nucleus M, Eq. (69) holds,

$$W_2'=2\pi(\mu_M.B)\delta(r_M). \quad (69)$$

The contribution to E_b^{N+2} originating in $X(2)$ is now considered. It will be referred to as $E^{\mathrm{diam}}(2)$,

$$E^{\mathrm{diam}}(2)=\frac{-1}{2mc^2}(\langle 0_N|X(2)P_{N+2}V|0_N\rangle$$
$$-\langle\mathrm{vac}|X(2)P_2|\mathrm{vac}\rangle)$$
$$=\frac{-1}{(2mc^2)^2}(\langle 0_N|[V^B,V]P_{N+2}V|0_N\rangle$$
$$-\langle\mathrm{vac}|[V^B,V]P_2V|\mathrm{vac}\rangle). \quad (70)$$

Consistently to order c^{-4}, only the c^0 contribution to the expectation value in Eq. (70) must be calculated. For the magnetic interaction operator V only terms creating or destroying one electron–positron pair are of order c^0. For the Breit interaction operator, matrix elements of order c^0 are those creating two electron–positron pairs, destroying two such pairs or containing one creation and one destruction electron–positron pair operator. Therefore, the contributions of order c^0 to the expectation value for the ground state $|0_N\rangle$ can be expressed as

$$\langle 0_N|[V^B,V]P_{N+2}V|0_N\rangle=\langle 0_N|V^BP_{N+4}VP_{N+2}V|0_N\rangle$$
$$+\langle 0_N|V^BP_NVP_{N+2}V|0_N\rangle$$
$$-\langle 0_N|VP_{N+2}V^BP_{N+2}V|0_N\rangle$$
$$-\langle 0_N|VP_{N-2}V^BP_{N+2}V|0_N\rangle. \quad (71)$$

A similar expression holds for the expectation value for the $|\mathrm{vac}\rangle$ state. Consistently to order c^0 the first term in Eq. (71) is exactly cancelled by E_b^{N+4} in Eq. (18b) (see Sec. II A). The second and fourth terms vanish because of the presence in V^B of positron destruction operators. Therefore, the unique nonvanishing contribution originates in the third term,

$$E^{\mathrm{diam}}(2)=\frac{1}{(2mc^2)^2}(\langle 0_N|VP_{N+2}V^BP_{N+2}V|0_N\rangle$$
$$-\langle\mathrm{vac}|VP_2V^BP_2V^BP_2V|\mathrm{vac}\rangle). \quad (72)$$

Finally, the Breit interaction operator is expressed as

$$V^B=\tfrac{1}{2}\sum_{i\neq j}\alpha_i\vec{\vec{O}}_{ij}\alpha_j, \quad (73)$$

where $\vec{\vec{O}}_{ij}$ was defined in Eq. (56). Reduction of Eq. (72) from bispinor configurations to spinor configurations is better carried out considering the second quantized form of the operators involved in it. The final result is (see Appendix C for details)

$$E^{\mathrm{diam}}(2)=\frac{1}{(2mc^2)^2}\langle 0|\sum_{i\neq j}A_i.\vec{\vec{O}}_{ij}.A_j$$
$$+(\sigma_i\times A_i).\vec{\vec{O}}_{ij}.(\sigma_j\times A_j)|0\rangle, \quad (74)$$

where $|0\rangle$ is the Schrödinger molecular ground state. Considering the external uniform magnetic field contribution to the

magnetic potential, A_B, and the nuclear magnetic potential, A_M, and retaining only terms bilinear in B and μ_M it is found that

$$E^{\mathrm{diam}}(2)=\frac{2}{(2mc^2)^2}\langle 0|\sum_{i\neq j} A_{Bi}.\vec{O}_{ij}.A_{Mj} + (\sigma_i\times A_{Bi}).\vec{O}_{ij}.(\sigma_j\times A_{Mj})|0\rangle. \quad (75)$$

Summing up, the total contribution originating in E_b of Eq. (5) has been expressed as

$$E_b=E^{\mathrm{diam}}(1)+E^{\mathrm{diam}}(2). \quad (76)$$

D. Sum rules and alternative expressions for $E^{(\mathrm{para},2)}$ and $E^{\mathrm{diam}}(1)$

In Sec. II C two operators were defined containing corrections of order c^{-3} to matrix elements of the magnetic interaction, i.e., $O^{3T}(B)$ of Eq. (44), and $O^{3T}(\mu_M)$ of Eq. (45). According to the discussion in Sec. II C [see Eq. (50)], only the first one yields relativistic corrections to the magnetic shielding tensor for a singlet ground state molecule in a second order RSPT contribution, that is,

$$E(O^{1T}(\mu_M),O^{3T}(B)). \quad (77)$$

An alternative expression for the contribution to the molecular energy originating in $O^{3T}(B)$ can be obtained by re-expressing this operator in a different way. Applying the results of Appendix A, Eq. (A26), to the triplet operator $O^{3T}(B)$ associated with the uniform magnetic field within the N-particle state space, Eq. (78) is obtained,

$$O^{3T}(B)=O'^{3T}(B)+O''^{3T}(B), \quad (78)$$

where

$$O'^{3T}(B)=-\frac{1}{8m^2c^3}\sum_i 2(\sigma_i.B)p_i^2-2m\sigma_i.(\nabla_i V_C\times A_{Bi})+\frac{1}{8m^2c^3}\sum_{i\neq j}\left[\frac{1}{r_{ij}},[\sigma p,\sigma A_B](i)\right], \quad (79)$$

$$O''^{3T}(B)=-\frac{1}{8m^2c^3}\left[H^{\mathrm{Sch}},\sum_i [\sigma p,\sigma A_B](i)\right]. \quad (80)$$

The potential V_C in Eq. (79) stands for the one-body Coulomb potential of the nuclei in the Schrödinger Hamiltonian. The last term in Eq. (79) is now a two-body operator which can be expressed as

$$\frac{1}{8m^2c^3}\sum_{i\neq j}\left[\frac{1}{r_{ij}},[\sigma p,\sigma A_B](i)\right]=-\frac{1}{4m^2c^3}\sum_{i\neq j}(\sigma_i\times A_{Bi}).\frac{r_{ij}}{r_{ij}^3}. \quad (81)$$

This expression corresponds to the ''field induced'' two-body spin–orbit contribution of Refs. 6 and 9.

The contribution to the molecular energy due to $O^{3T}(B)$ is now splitted up into

(1) a second order RSPT expression containing $O'^{3T}(B)$, i.e.,

$$E(O^{1T}(\mu_M),O'^{3T}(B)) \quad (82)$$

and

(2) one contribution due to $O''^{3T}(B)$ which can be re-expressed as

$$E(O''^{3T}(B),O^{1T}(\mu_M))=-\frac{1}{8m^2c^3}\sum_n\frac{\langle 0|[H^{\mathrm{Sch}},\Sigma_i[\sigma p,\sigma A](i)]|n\rangle\langle n|O^{1T}(\mu_M)|0\rangle}{E_0-E_n}-\frac{1}{8m^2c^3}\sum_n\frac{\langle 0|O^{1T}(\mu_M)|n\rangle\langle n|[H^{\mathrm{Sch}},\Sigma_i[\sigma p,\sigma A](i)]|0\rangle}{E_0-E_n}=\frac{1}{8m^2c^3}\langle 0|-\sum_i [\sigma p,\sigma A_B]O^{1T}(\mu_M)(i)+\sum_i O^{1T}(\mu_M)[\sigma p,\sigma A_B](i)|0\rangle. \quad (83)$$

Inserting the explicit expression of $O^{1T}(\mu_M)$ of Eq. (43) into Eq. (83) the final result is

$$E(O''^{3T}(B),O^{1T}(\mu_M))=\frac{1}{16m^3c^4}\langle 0|\sum_i [\sigma.B_M,[\sigma p,\sigma A]](i)|0\rangle=\frac{1}{8m^3c^4}\langle 0|\sum_i (A_B.(\nabla\times B_M))(i)|0\rangle. \quad (84)$$

This means that it can be expressed as a first-order correction to the molecular energy. It is worth noting that this contribution cancels exactly that originating in $\langle 0|W_2'|0\rangle$ in the diamagnetic component, Eqs. (68) and (69).

It is interesting to compare results in Sec. II C to those of the present section. In the first case, $O^{3T}(B)$ enters in a second-order RSPT expression and the diamagnetic term contains the term $\langle 0|W_2'|0\rangle$ of Eq. (68), which is the same as that of Eq. (84) with opposite sign. Both operators involved are one-body operators. It has been explicitly shown that this procedure is equivalent to consider operator $O'^{3T}(B)$ in a second-order RSPT expression and to cancel the contribution $\langle 0|W_2'|0\rangle$ to the diamagnetic term. In $O'^{3T}(B)$, Eq. (79), the different operators involved have the same expressions as those found in previous works. In Eq. (79) the MVEF-FC contribution of Refs. 6 and 4, the field induced spin–orbit term of Refs. 6 and 9, and the two-body field induced spin–

TABLE II. Relativistic corrections $\sigma_M^p(\mathrm{FC,SZ}\text{-}K)$ [Eqs. (44) and (50)] and $\sigma_M^d(W_2')$ [Eq. (68)] to the isotropic nuclear magnetic shielding constant in HX and CH_3X. Values in ppm.

Molecule	Nucleus	Basis set[a]	$\sigma_M^p(\mathrm{FC,SZ}\text{-}K)$ RPA	$\sigma_M^p(\mathrm{FC,SZ}\text{-}K)$ SOPPA	$\sigma_M^d(W_2')$ HF	$\sigma_M^d(W_2')$ MP2
HBr	Br	I	729.44		−131.25	
		II	729.24	729.06	−131.25	−131.25
		b	724.24			
CH_3Br	Br	II	729.30		−131.25	
HI	I	I	2554.71		−465.01	
		II	2554.22	2553.98	−465.01	−465.02
		b	2558.8			
CH_3I	I	II	2554.30		−465.01	
HBr	H	I	−0.022		...[c]	
		II	−0.020	−0.016	...[c]	
		b	−0.026		...[c]	
HI	H	I	−0.024		...[c]	
		II	−0.024	−0.017	...[c]	
		b	−0.026		...[c]	
CH_3Br	C	II	3.24		−0.54	
CH_3I	C	II	3.23		−0.54	
CH_3Br	H	II	...[c]		...[c]	
CH_3I	H	II	...[c]		...[c]	

[a]Basis set I: fully uncontracted sp-aug-ccpVTZ basis set of Ref. 21. Basis set II: same basis set but only *s* and *p*-type AOs are fully uncontracted.
[b]The MVEF-FC value of Ref. 4 is rescaled by a factor 4/3; see text for details.
[c]Absolute value smaller than 0.01 ppm.

orbit term of Refs. 6 and 9 are found. However, from the computational point of view, the first way of carrying out the calculations is preferred, since all these contributions (one- and two-body) are readily taken into account in terms of one-body operators.

III. RESULTS AND DISCUSSION

Among the different relativistic corrections to the nuclear magnetic shielding tensor obtained in Sec. II C, the one combining the SZ-*K* operator of $O^{3T}(B)$ in Eq. (44) together with the FC operator and dubbed $\sigma_M^p(\mathrm{FC,SZ}\text{-}K)$ in Table I is closely related to the term previously obtained by Fukui *et al.*[6] and quantitatively analyzed by Visscher *et al.* and dubbed "MVEF-FC" in Ref. 4. The differences between those terms are that operator SZ-*K* in Eq. (44) carries different constant factors and has an anisotropic contribution, while the MVEF-FC term is isotropic. As it was explicitly shown in Sec. II D the addition of contributions originating in $E(O^{1T}(\mu_M),O^{3T}(B))$ and $\langle W_2' \rangle$ [see Eqs. (68) and (69)] is equivalent to the sum of the MVEF-FC, the "field induced" one-body spin–orbit and the "field induced" two-body spin–orbit contributions of Refs. 6 and 9 (the "field induced" spin–other orbit term is not included). It is important to emphasize here that, within the present approach, the "field induced" two-body spin–orbit contribution is obtained from a calculation involving only one-body operators.

In the present section numerical results are presented. They correspond to the $\sigma_M^p(\mathrm{FC,SZ}\text{-}K)$ contribution defined in Table I, and to the contribution originated in W_2', which will be referred to as $\sigma_M^d(W_2')$. HX and CH_3X (X=Br,I) were taken as model compounds. Calculations were carried out with the DALTON code[19] for both the heavy and the light nuclei in each compound. $\sigma_M^p(\mathrm{FC,SZ}\text{-}K)$ values were obtained at the RPA and SOPPA levels for HX, and at the RPA level for CH_3X. $\sigma_M^d(W_2')$ values were calculated for the HF and MP2 molecular ground state. Geometric structures were taken from Ref. 20. The gauge origin was placed at the nucleus position in each case and therefore Eq. (69) holds. For HX the fully uncontracted sp-aug-ccpVTZ basis set of Ref. 21 was used. It will be referred to hereafter as basis set I. For CH_3X, the same basis set was used, but only the *s* and *p*-type atomic orbitals (AOs) were uncontracted, and it will be referred to as basis set II.

Results are displayed in Table II. For the isotropic nuclear magnetic shielding constant, the $\sigma_M^p(\mathrm{FC,SZ}\text{-}K)$ contribution is exactly 4/3 times the MVEF-FC one in Ref. 4. The corresponding values are included for comparison. There is excellent agreement between those values and the ones of the present work. In Table II it is seen that for the heavy nuclei X=Br, I the contributions $\sigma_M^p(\mathrm{FC,SZ}\text{-}K)$ and $\sigma_M^d(W_2')$ are large and have an opposite sign. It is also interesting to observe that the corresponding values in HX and CH_3X are very similar, i.e., these contributions are only slightly sensitive to the change in chemical environment from HX to CH_3X. The insensitivity of the $\sigma_M^d(W_2')$ term can be explained taking into account that this term is proportional to the electronic density at the nucleus site, Eq. (69). For the heavy nuclei this density is hardly affected by the change in chemical environment. The observed insensitivity of the $\sigma_M^p(\mathrm{FC,SZ}\text{-}K)$ term could be understood by the presence of p^2 in the SZ-*K* operator. The kinetic energy of the inner-shell electrons is larger than that of the valence electrons and therefore the main contribution to $\sigma_M^p(\mathrm{FC,SZ}\text{-}K)$ could be due to the behavior of the inner shell electrons of the heavy atom, which are almost insensitive to the change in chemical environment. However a deeper study needs to be

carried out in order to obtain definite conclusions on the origin of these relativistic effects.

The contributions $\sigma_M^p(\mathrm{FC,SZ}\text{-}K)$ and $\sigma_M^d(W_2')$ to the magnetic shielding constant of the H nuclei displayed in Table II are negligibly small, for both the H directly bonded to the heavy nucleus in HX and for the H nucleus two bonds away in CH_3X. However, for the C nucleus directly bonded to the heavy atom in CH_3X, the overall value of about 2.70 ppm (X=Br,I) is not negligible in comparison to the spin–orbit contribution of about 12–14 ppm (X=Br) and 20–40 ppm (X=I).[8,22]

SOPPA values of $\sigma_M^p(\mathrm{FC,SZ}\text{-}K)$ for the heavy and light nuclei carried out with basis set II are also displayed in Table II, as well as the MP2 values of $\sigma_M^d(W_2')$. Comparing these values with the respective RPA and HF ones, it is concluded that correlation effects yield only very small contributions to the calculated $\sigma_M^p(\mathrm{FC,SZ}\text{-}K)$ and $\sigma_M^d(W_2')$ relativistic corrections to the nuclear magnetic shielding constant in this case.

IV. CONCLUDING REMARKS

Within the approach followed in this work in order to obtain relativistic corrections to the nuclear magnetic shielding tensor, different contributions consisting of first, second, and third order RSPT expressions were found.

On the one hand, contributions originating in the Darwin, mass–velocity and spin–orbit corrections to the ground state wave function are obtained in agreement with previous works.[22,23] It is interesting to point out that in previous calculations of relativistic corrections to the nuclear magnetic shielding tensor, the Darwin and mass–velocity scalar effects were included within the ''unperturbed'' molecular Hamiltonian.[22,23] An alternative approach based on the zeroth order regular approximation (ZORA) was presented by Wolff *et al.*[24]

On the other hand, in agreement with Ref. 6, further contributions are found when the effect of the small component of the electronic bispinors is included in the corresponding large component in the presence of the magnetic potential. This is the case, for example, of the ''field induced'' spin–orbit contributions, also discussed previously by Vaara *et al.*,[9] and of the MVEF-FC term of Fukui *et al.*[6] which was quantitatively analyzed by Visscher *et al.*[4] However, additional contributions, not previously considered in the bibliography, are obtained within the present approach. These are the ones indicated as OZ-*K* and PSO-*K* in Table I and contributions W' to the diamagnetic term, Eq. (68). These novel contributions need careful quantitative analysis and work along this line is presently being carried out by our group. It is also interesting to emphasize that within the present approach one and two virtual pair corrections to the unperturbed molecular states were included and the corresponding contributions to the nuclear magnetic shielding tensor were obtained. Explicit calculations of the $\sigma_M^p(\mathrm{FC,SZ}\text{-}K)$ and $\sigma_M^d(W_2')$ contributions in HX and CH_3X were carried out. Even though the corresponding contributions to the absolute value of the nuclear magnetic shielding constant of the heavy nucleus are very large, they are almost insensitive to the change of chemical environment from HX to CH_3X. Electronic correlation effects were shown to be very small for these relativistic corrections in all the cases analyzed in this work.

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APPENDIX A: TRANSFORMATION OF MAGNETIC INTERACTION MATRIX ELEMENTS FROM POSITIVE ENERGY BISPINOR CONFIGURATIONS TO SPINOR CONFIGURATIONS

For $V=\alpha\cdot\mathbf{A}$ ($e=+1$, in a.u.) a one body-operator, the transformation of matrix elements from bispinor configurations to spinor configurations is readily obtained if such reduction is carried out for the positive-energy bispinors themselves, considering results in Sec. II B, Eqs. (21)–(29). The matrix elements of the magnetic interaction operator between positive-energy bispinors are considered in such a way that they are approximated by spinor matrix elements, i.e.,

$$\langle\phi_i^4|\alpha\cdot\mathbf{A}|\phi_j^4\rangle\cong\langle\tilde{\phi}_i|O(\alpha\cdot\mathbf{A})|\tilde{\phi}_j\rangle. \tag{A1}$$

First, the elimination of the small component is carried out. According to Eq. (27),

$$\langle\phi_i^4|\alpha\cdot\mathbf{A}|\phi_j^4\rangle=\langle\phi_i^L|c(\sigma.p)R_i^{-1}(\sigma.A)+(\sigma.A)R_j^{-1}(c\sigma.p)|\phi_j^L\rangle. \tag{A2}$$

Second, the large component is written in terms of the ''normalized'' spinors of Eq. (29). Expansion through order c^{-3} yields

$$\langle\phi_i^4|\alpha\cdot\mathbf{A}|\phi_j^4\rangle\cong O_{ij}^1+O_{ij}^3. \tag{A3}$$

The first term is of order c^{-1},

$$O_{ij}^1=\langle\tilde{\phi}_i|O^1|\tilde{\phi}_j\rangle, \tag{A4}$$

where operator O^1 is defined as

$$O^1=\frac{1}{2mc}\{\sigma p,\sigma A\}. \tag{A5}$$

The curly brackets stand for the anticommutator. On the other hand, the third-order contribution is

$$O_{ij}^3=\langle\tilde{\phi}_i|\frac{1}{2mc}(\sigma p)\left(\frac{V_C-E_i}{2mc^2}\right)(\sigma A)+\frac{1}{2mc}(\sigma A)\times\left(\frac{V_C-E_j}{2mc^2}\right)(\sigma p)-\frac{1}{8m^2c^2}\{p^2,O^1\}|\tilde{\phi}_j\rangle. \tag{A6}$$

Taking into account that O_{ij}^3 is of order c^{-3}, the zeroth order relation,

$$(V_C-E)|\tilde{\phi}\rangle=\frac{-p^2}{2m}|\tilde{\phi}\rangle \tag{A7}$$

can be used to obtain

$$(V_C-E)(\sigma p)|\tilde{\phi}\rangle=(\sigma p)\left(\frac{-p^2}{2m}\right)|\tilde{\phi}\rangle-[(\sigma p),(V_C-E_i)]|\tilde{\phi}\rangle$$
$$=\left((\sigma p)\left(\frac{-p^2}{2m}\right)+i\sigma.\nabla V_C\right)|\tilde{\phi}\rangle. \quad \text{(A8)}$$

Applying Eq. (A8), O^3_{ij} can be re-expressed as

$$O^3_{ij}=\frac{-1}{8m^3c^3}\langle\tilde{\phi}_i|\{(\sigma p)p^2,(\sigma A)\}+2mi[\sigma.\nabla V_C,(\sigma A)]$$
$$+\tfrac{1}{2}\{p^2,\{\sigma p,\sigma A\}\}|\tilde{\phi}_j\rangle$$
$$=\frac{-1}{16m^3c^3}\langle\tilde{\phi}_i|2\{p^2,\{\sigma p,\sigma A\}\}+[p^2,[\sigma p,\sigma A]]$$
$$-8m\sigma.(\nabla V_C\times A)|\tilde{\phi}_j\rangle. \quad \text{(A9)}$$

It is observed that a new operator O^3 is defined in Eq. (A9) from which the third-order matrix elements can be obtained. It is convenient to split O^3 as follows:

$$O^3=A^{3A}+O^{3B}+O^{3C},$$
$$O^{3A}=-\frac{1}{8m^3c^3}\{p^2,\{\sigma p,\sigma A\}\},$$
$$O^{3B}=-\frac{1}{16m^3c^3}[p^2,[\sigma p,\sigma A]], \quad \text{(A10)}$$
$$O^{3C}=\frac{1}{2m^2c^3}\sigma.(\nabla V_C\times A).$$

Within the Coulomb gauge, results in Eq. (A11) hold,

$$\{\sigma p,\sigma A\}=2Ap+\sigma B_T,$$
$$[\sigma p,\sigma A]=\sigma B_T-2i\sigma.(A\times p), \quad \text{(A11)}$$

where B_T stands for the total magnetic field.

Taking Eq. (A11) into account it is seen that O^1 and O^{3A} have singlet and triplet components but O^{3B} and O^{3C} are triplet operators, i.e.,

$$O^1=O^{1S}+O^{1T}, \quad \text{(A12)}$$
$$O^3=O^{3S}+O^{3T}, \quad \text{(A13)}$$
$$O^{1S}=\frac{1}{mc}Ap, \quad \text{(A14)}$$
$$O^{1T}=\frac{1}{2mc}\sigma\cdot B_T, \quad \text{(A15)}$$
$$O^{3S}=O^{3AS}=\frac{-1}{4m^3c^3}\{p^2,Ap\}, \quad \text{(A16)}$$
$$O^{3T}=O^{3AT}+O^{3B}+O^{3C},$$
$$O^{3AT}=\frac{-1}{8m^3c^3}\{p^2,\sigma.B_T\}. \quad \text{(A17)}$$

The superscripts S and T stand for singlet and triplet operators.

The magnetic potential to be considered in order to obtain the nuclear magnetic shielding tensor is

$$A=A_M+A_B,$$
$$A_B=\tfrac{1}{2}B\times r, \quad \text{(A18)}$$
$$A_M=\frac{\mu_M\times r_M}{r_M^3}.$$

Explicit expressions can be derived for O^1 and O^3 corresponding to each of these fields. Inserting the corresponding magnetic potentials in Eqs. (A14)–(A15) the first order operators in Eqs. (42) and (43) are obtained straightforwardly. In order to obtain explicit expressions for the third order operators associated to the uniform magnetic field, the commutator in O^{3B} is explicitly evaluated using Eq. (A11),

$$[p^2,[\sigma p,\sigma A_B]]=2(\sigma.B)p^2-2(\sigma.p)(p.B). \quad \text{(A19)}$$

Therefore,

$$O^{3S}(B)=-\frac{1}{8m^3c^3}\{B.L,p^2\},$$
$$O^{3T}(B)=-\frac{1}{8m^3c^3}(3(\sigma.B)p^2-(\sigma.p)(p.B) \quad \text{(A20)}$$
$$-4m\sigma.\nabla V_C\times A_B).$$

The third-order operators associated to the nuclear magnetic field can be expressed as

$$O^{3S}(\mu_M)=-\frac{1}{4m^3c^3}\left\{\frac{\mu_M.L_M}{r_M^3},p^2\right\},$$
$$O^{3T}(\mu_M)=-\frac{1}{8m^3c^3}\left(\frac{3}{2}p^2(\sigma.B_M)+\frac{1}{2}(\sigma.B_M)p^2\right. \quad \text{(A21)}$$
$$\left.+i\sigma.[A_M\times p,p^2]-4m\sigma.\nabla V_C\times A_M\right).$$

As a final point, it is interesting to show that operator O^{3B} of Eq. (A10), can be worked out in a different way,

$$O^{3B}=-\frac{1}{16m^3c^3}\lfloor p^2,[\sigma p,\sigma A]\rfloor$$
$$=-\frac{1}{8m^2c^3}[h-V_C,[\sigma p,\sigma A]]$$
$$=-\frac{1}{8m^2c^3}[h,[\sigma p,\sigma A]]+\frac{1}{8m^2c^3}[V_C,[\sigma p,\sigma A]], \quad \text{(A22)}$$

where h and V_C stand for the one-body Hamiltonian and potential from which the zeroth order normalized spin–orbitals are obtained. The second term in Eq. (A22) can be expressed as

$$\frac{1}{8m^2c^3}[V_C,[\sigma p,\sigma A]]=-\frac{1}{4m^2c^3}\sigma.(\nabla V_C\times A)$$
$$=-\tfrac{1}{2}O^{3C} \quad \text{(A23)}$$

and included in the field induced spin–orbit term. When the operator defined in the first term,

$$O^{3B}(h) = -\frac{1}{8m^2c^3}[h,[\sigma p,\sigma A]], \tag{A24}$$

is extended to the N-particle state space, it can be expressed as

$$\begin{aligned} O_{3B}(h) &= -\frac{1}{8m^2c^3}\left[\sum_i h(i), \sum_j [\sigma p,\sigma A](j)\right] \\ &= -\frac{1}{8m^2c^3}\left[H^{\mathrm{Sch}} - U, \sum_j [\sigma p,\sigma A](j)\right] \\ &= O^{3B}(H^{\mathrm{Sch}}) - O^{3B}(U), \end{aligned} \tag{A25}$$

where U stands for the Coulomb interaction between electrons in the many-electron Schrödinger equation. Therefore,

$$\begin{aligned} &O^3 = O'^3 + O''^3, \\ &O'^3 = O^{3A} + \tfrac{1}{2}O^{3C} - O^{3B}(U), \\ &O''^3 = O^{3B}(H) = -\frac{1}{8m^2c^3}\left[H^{\mathrm{Sch}}, \sum_j [\sigma p,\sigma A](j)\right]. \end{aligned} \tag{A26}$$

APPENDIX B: REDUCTION OF MATRIX ELEMENTS IN EQ. (61) TO SPINOR CONFIGURATIONS

In order to evaluate the corresponding matrix elements in Eq. (61), the set of creation and destruction operators $\{e_\alpha^+, e_\beta; p_\alpha^+, p_\beta\}$ for electrons and positrons is introduced. This set and the reference vacuum state $|\mathrm{vac}\rangle$ is obtained from solutions of the one-body Dirac Hamiltonian h_1^D for the Coulomb field of the (fixed) nuclei in the molecular system. Alternatively, they can be thought of as originating in the Dirac–Hartree–Fock scheme. Following the QED picture, one-body operators are defined introducing normal ordered products of creation and destruction operators,[16,25]

$$\begin{aligned} Z = \sum_{\alpha,\beta} &\langle e_\alpha|Z|e_\beta\rangle e_\alpha^+ e_\beta + \langle e_\alpha|Z|p_\beta\rangle e_\alpha^+ p_\beta^+ \\ &+ \langle p_\alpha|Z|e_\beta\rangle p_\alpha e_\beta - \langle p_\alpha|Z|p_\beta\rangle p_\beta^+ p_\alpha . \end{aligned} \tag{B1}$$

In Eq. (61) the terms of V that need be considered are those creating an electron–positron pair when acting on $|0_N\rangle$ (and on $|\mathrm{vac}\rangle$ for the second term). As a consequence, the only terms of $X(1)$ to be included are those destroying an electron–positron pair. Therefore, Eq. (61) yields

$$\begin{aligned} E^{\mathrm{diam}}(1) = -\frac{1}{2mc^2}\sum_{\substack{\alpha,\beta \\ \mu,\nu}} &\langle p_\alpha|X|e_\beta\rangle\langle e_\mu|V|p_\nu\rangle \\ &\times(\langle 0_N|p_\alpha e_\beta e_\mu^+ p_\nu^+|0_N\rangle \\ &-\langle \mathrm{vac}|p_\alpha e_\beta e_\mu^+ p_\nu^+|\mathrm{vac}\rangle). \end{aligned} \tag{B2}$$

Taking into account that

$$\begin{aligned} &\langle 0|p_\alpha e_\beta e_\mu^+ p_\nu^+|0\rangle - \langle \mathrm{vac}|p_\alpha e_\beta e_\mu^+ p_\nu^+|\mathrm{vac}\rangle \\ &\quad = -\langle 0_N|e_\mu^+ e_\beta|0_N\rangle \delta_{\alpha,\nu}, \end{aligned} \tag{B3}$$

it follows that

$$E^{\mathrm{diam}}(1) = \frac{1}{2mc^2}\langle 0_N|M|0_N\rangle, \tag{B4}$$

being $M = VP_pX(1) = V(1-P_e)X(1)$ where P_p stands for a projector onto "positronic" states and P_e for a projector onto "electronic" states. Operator M in Eq. (B4) is a one-body operator.

The projector onto "electronic" states can be expressed, up to order c^{-2}, as

$$\begin{aligned} P_e &= \sum_e |\phi_e^4\rangle\langle\phi_e^4| \\ &= \begin{bmatrix} \sum_e |\phi_e^L\rangle\langle\phi_e^L| & \sum_e |\phi_e^L\rangle\langle\phi_e^S| \\ \sum_e |\phi_e^S\rangle\langle\phi_e^L| & \sum_e |\phi_e^S\rangle\langle\phi_e^S| \end{bmatrix} \\ &= \begin{bmatrix} \left(1 - \dfrac{p^2}{4m^2c^2}\right) & \dfrac{\sigma p}{2mc} \\ \dfrac{\sigma p}{2mc} & \dfrac{p^2}{4m^2c^2} \end{bmatrix}. \end{aligned} \tag{B5}$$

The operator $X(1)$ of Eq. (60) is

$$\begin{aligned} X(1) &= \frac{1}{2mc}[\sigma p,\sigma A] + (\beta+2)V \\ &= \begin{bmatrix} \dfrac{1}{2mc}[\sigma p,\sigma A] & 3\sigma A \\ \sigma A & \dfrac{1}{2mc}[\sigma p,\sigma A] \end{bmatrix}. \end{aligned} \tag{B6}$$

Taking into account results from Eqs. (B5) and (B6) the operator M in Eq. (B4) can be split in terms of the following components:

$$\begin{aligned} M_{LL} &= A^2 - (\sigma A)\frac{p^2}{(2mc)^2}(\sigma A) - \frac{1}{(2mc)^2}(\sigma A)(\sigma p) \\ &\quad \times[(\sigma p),(\sigma A)], \\ M_{LS} &= -2(\sigma A)\left(\frac{\sigma p}{2mc}\right)(\sigma A) - A^2\left(\frac{\sigma p}{2mc}\right), \\ M_{SL} &= -(\sigma A)\left(\frac{\sigma p}{2mc}\right)(\sigma A), \\ M_{SS} &= 2(\sigma A)\left(\frac{\sigma p}{2mc}\right)(\sigma A) - A^2\left(\frac{\sigma p}{2mc}\right). \end{aligned} \tag{B7}$$

Due to the factor $1/2mc^2$ in $E^{\mathrm{diam}}(1)$, only terms of order up to c^{-2} are retained in Eq. (B7).

Following the arguments in Sec. II B [see Eq. (35)] the expectation value of the one-body operator M for the molecular ground state is

$$\begin{aligned} &\langle 0_N|\sum_i M_i|0_N\rangle \cong \langle\tilde{0}|\sum_i O_i(M)|\tilde{0}\rangle, \\ &O(M) = M_{LL} - \frac{1}{8m^2c^2}\{p^2, M_{LL}\} + M_{LS}\frac{\sigma p}{2mc} \\ &\qquad + \frac{\sigma p}{2mc}M_{SL} + \frac{\sigma p}{2mc}M_{SS}\frac{\sigma p}{2mc}, \end{aligned} \tag{B8}$$

where it must be recalled that $|0_N\rangle$ stands for the no-pair solution to the Breit Hamiltonian and $|\tilde{0}\rangle$ for the corresponding solution to the Breit–Pauli Hamiltonian. Equation (B8) can be re-expressed to yield Eq. (62),

$$E^{\mathrm{diam}}(1)=\frac{1}{2mc^2}\langle 0_N|\sum_i M_i|0_N\rangle$$
$$\cong\frac{1}{2mc^2}\langle\tilde{0}|\sum_i O_i(M)|\tilde{0}\rangle$$
$$=\frac{1}{2mc^2}\langle\tilde{0}|\sum_i A_i^2|\tilde{0}\rangle$$
$$-\frac{1}{8m^3c^4}\langle\tilde{0}|\sum_i W_i|\tilde{0}\rangle, \tag{B9}$$

$$W=\{\sigma p,\sigma A\}^2+(\sigma A)p^2(\sigma A)-(\sigma p)A^2(\sigma p)$$
$$+\{p^2,A^2\}+\tfrac{1}{2}[A^2,p^2].$$

APPENDIX C: TRANSFORMATION OF MATRIX ELEMENTS BETWEEN BISPINOR CONFIGURATIONS TO SPINOR CONFIGURATIONS IN EQS. (54) AND (72)

The c^{-1} contribution to the operator shown in Eq. (54) can be obtained as follows. The magnetic interaction operator connecting the N particles manifold to the $(N+2)$-particles manifold contains matrix elements of order c^0,

$$P_{N+2}VP_N=\sum_{\mu,\nu}\langle e_\mu|V|p_\nu\rangle e_\mu^+p_\nu^+. \tag{C1}$$

In order to evaluate Eq. (54) consistently to order c^{-1}, the Coulomb and Breit two-body operators in $H^{(\pm)}$ connecting the $N+2$ particles manifold to the N particles manifold must contain one pair destruction operator and one electron excitation,

$$P_NH^{(\pm)}P_{N+2}=\sum_{\alpha\beta\gamma\delta}\langle p_\alpha e_\beta|H^{(\pm)}|e_\gamma e_\delta\rangle N(p_\alpha e_\beta^+e_\delta e_\gamma), \tag{C2}$$

where the symmetry of indices has been employed to eliminate a factor of $\frac{1}{2}$ and to write only one type of term in Eq. (C2). The product of operators shown in Eqs. (C1) and (C2) acting on an N-particle state leads to products of creation and destruction operators which, according to the QED picture must be evaluated as follows:[25]

$$N(p_\alpha e_\beta^+e_\delta e_\gamma)e_\mu^+p_\nu^+=N(e_\beta^+e_\delta e_\gamma e_\mu^+)\delta_{\alpha\nu}, \tag{C3}$$

where the normal ordered product of electronic operators ensures the correct elimination of contributions from the vacuum state.[16,25] The resulting operator can thus be expressed as

$$P_NH^{(\pm)}P_{N+2}VP_N=\sum_{\mu\beta\gamma\delta}C_{\mu\beta\gamma\delta}e_\mu^+e_\beta^+e_\delta e_\gamma, \tag{C4}$$

where

$$C_{\mu\beta\gamma\delta}=-\sum_\alpha\langle e_\mu|V|p_\alpha\rangle\langle p_\alpha e_\beta|H^{(\pm)}|e_\gamma e_\delta\rangle$$
$$=-\langle\Psi_\mu e_\beta|H^{(\pm)}|e_\gamma e_\delta\rangle,$$
$$|\Psi_\mu\rangle=P_pV|e_\mu\rangle, \tag{C5}$$

where P_p stands for the projector onto "positronic" states in the one-particle state space. Following a similar procedure to that carried out in Appendix B in order to transform matrix elements in Eq. (C5) from bispinors configurations to spinors configurations consistently to order c^{-1}, the result in Eq. (55) is obtained.

In order to reduce Eq. (72) from bispinors configurations to spinors configurations consistently to order c^0, the Breit operator within the $(N+2)$-particles manifold must be considered. There is only one c^0 contribution. It is the one containing one pair creation and one pair destruction operator, Eq. (C6),

$$P_{N+2}V^BP_{N+2}=\sum_{\mu,\nu}\langle p_\alpha e_\beta|V^B|e_\gamma p_\delta\rangle N(p_\alpha e_\beta^+p_\delta^+e_\gamma), \tag{C6}$$

where the symmetry of indices has been employed to eliminate a factor of $\frac{1}{2}$ and to write only one type of term. In Eq. (72) a product of three operators needs to be calculated. The third operator is the magnetic interaction operator connecting the $N+2$ particles manifold to the N particles manifold. This operator is just the adjoint of that in Eq. (C1). The product of creation and destruction operators involved in Eq. (72) is thus

$$p_\lambda e_\sigma N(p_\alpha e_\beta^+p_\delta^+e_\gamma)e_\mu^+p_\nu^+=N(e_\sigma e_\beta^+e_\gamma e_\mu^+)\delta_{\lambda\delta}\delta_{\alpha\nu}, \tag{C7}$$

and, therefore, the resulting operator within the N particles state space can be expressed as

$$P_NVP_{N+2}V^BP_{N+2}VP_N=\sum_{\beta\gamma\mu\sigma}C'_{\beta\mu\sigma\gamma}e_\beta^+e_\mu^+e_\gamma e_\sigma,$$
$$C'_{\beta\mu\sigma\gamma}=\sum_{\alpha;\lambda}\langle e_\mu|V|p_\alpha\rangle\langle p_\alpha e_\beta|V^B|e_\gamma p_\lambda\rangle\langle p_\lambda|V|e_\sigma\rangle$$
$$=\langle\Psi_\mu e_\beta|V^B|e_\gamma\Psi_\sigma\rangle,$$
$$|\Psi_\mu\rangle=P_pV|e_\mu\rangle,$$
$$|\Psi_\sigma\rangle=P_pV|e_\sigma\rangle, \tag{C8}$$

where P_p stands for the projector onto "positronic" states in the one-particle state space. Following a similar procedure to that carried out in Appendix B in order to reduce matrix elements in Eq. (C8) from bispinor configurations to spinor configurations consistently to order c^0, the result in Eq. (74) is obtained.

[1] G. A. Aucar and J. Oddershede, Int. J. Quantum Chem. **47**, 425 (1993).
[2] S. Kirpekar, H. J. Aa. Jensen, and J. Oddershede, Theor. Chem. Acc. **95**, 35 (1997).
[3] L. Visscher, T. Enevoldsen, T. Saue, and J. Oddershede, J. Chem. Phys. **109**, 9677 (1998).

[4] L. Visscher, T. Enevoldsen, T. Saue, J. A. Jensen, and J. Oddershede, J. Comput. Chem. **20**, 1262 (1999).
[5] Y. Ishikawa, T. Nakajima, M. Hada, and H. Nakatsuji, Chem. Phys. Lett. **283**, 119 (1998).
[6] H. Fukui, T. Baba, and H. Inomata, J. Chem. Phys. **105**, 3175 (1996).
[7] H. Nakatsuji, H. Takashima, and M. Hada, Chem. Phys. Lett. **233**, 95 (1995).
[8] J. Vaara, K. Ruud, O. Vahtras, H. Ågren, and J. Jokisaari, J. Chem. Phys. **109**, 1212 (1998).
[9] J. Vaara, K. Ruud, and O. Vahtras, J. Chem. Phys. **111**, 2900 (1999).
[10] J. Vaara, O. L. Malkina, H. Stoll, V. G. Malkin, and M. Kaupp, J. Chem. Phys. **114**, 61 (2001).
[11] G. A. Aucar, T. Saue, L. Visscher, and H. J. Aa. Jensen, J. Chem. Phys. **110**, 6208 (1999).
[12] R. E. Moss, *Advanced Molecular Quantum Mechanics* (Chapman and Hall, London, 1973).
[13] C. Cohen-Tannoudji, J. Dupont-Roc, and G. Grynberg, *Photons and Atoms* (Wiley, New York, 1997).
[14] H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One and Two Electron Atoms* (Plenum, New York, 1977).
[15] K. G. Dyall, Lecture notes: ''Introduction to Relativistic Quantum Chemistry,'' II Instituto de Física Molecular del MERCOSUR, Universidad Nacional del Nordeste, Corrientes Aregentina, February 2000.
[16] J. D. Bjorken and S. D. Drell, *Relativistic Quantum Mechanics*, in *International Series in Pure and Applied Physics*, edited by L. E. Schiff (McGraw–Hill, New York, 1964).
[17] R. Mc. Weeny, *Methods of Molecular Quantum Mechanics*, 2nd ed. (Academic, London, 1996).
[18] I. Ando and G. A. Webb, *Theory of NMR Parameters* (Academic, London, 1983).
[19] DALTON, a Molecular Electronic Structure Program, Release 1.2 (2001), written by T. Helgaker, H. J. Aa. Jensen, P. Jørgensen *et al.*
[20] *Tables of Interatomic Distances and Configurations in Molecules and Ions*, Scientific Editor, L. E. Sutton (The Chemical Society, London, 1958); *ibid.*, Supplement, 1965.
[21] L. Visscher and K. G. Dyall, J. Chem. Phys. **104**, 9040 (1996); L. Visscher, J. Styszinski, and W. C. Nieuwpoort, *ibid.* **105**, 1987 (1996).
[22] S. K. Wolff and T. Ziegler, J. Chem. Phys. **109**, 895 (1998).
[23] H. Nakatsuji, M. Hada, H. Kaneko, and C. C. Ballard, Chem. Phys. Lett. **255**, 195 (1996).
[24] S. K. Wolff, T. Ziegler, E. van Lenthe, and E. J. Baerends, J. Chem. Phys. **110**, 7689 (1999).
[25] F. Mand and G. Shaw, in *Quantum Field Theory* (Wiley, Great Britain, 1984).