# Formal relations connecting different approaches to calculate relativistic effects on molecular magnetic properties

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(Received 6 September 2005; accepted 7 December 2005; published online 1 February 2006)

In the present work a set of formal relations connecting different approaches to calculate relativistic effects on magnetic molecular properties are proven. The linear response (LR) within the elimination of the small component (ESC), Breit Pauli, and minimal-coupling approaches are compared. To this end, the leading order ESC reduction of operators within the minimal-coupling four-component approach is carried out. The equivalence of all three approaches within the ESC approximation is proven. It is numerically verified for the NMR nuclear-magnetic shielding tensor taking H$X$ and $CH_3X$ ($X$=Br,I) as model compounds. Formal relations proving the gauge origin invariance of the full relativistic effect on the NMR nuclear-magnetic shielding tensor within the LR-ESC approach are presented. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2162541]

## I. INTRODUCTION

Relativistic effects on nuclear-magnetic-resonance parameters have shown to be of major importance. In particular, the absolute nuclear-magnetic shielding tensors in heavy atom containing compounds are strongly affected by such effects. Within four-component linear-response theory at the random phase approximation (RPA) level a series of benchmark results were obtained.[1,2] The first ones[1] were obtained within the Sternheim approximation.[3] It has been shown formally[4,5] that the diamagnetic component of magnetic properties is only recovered in the nonrelativistic limit when electron-positron rotations are taken into account. Therefore in the four-component linear-response theory the paramagnetic term is identified with the linear-response related to electron-electron rotations, while the diamagnetic one is identified with the contribution associated to electron-positron rotations. Since the early results of Visscher *et al.*,[1] it has been recognized that electron-positron rotations must be taken into account beyond the Sternheim[3] approximation in order to obtain correct results[2] of the nuclear-magnetic shielding tensor. However there are different definitions of para- and diamagnetic contributions at the four-component level yielding the same para- and diamagnetic separation in the nonrelativistic limit. For instance, recently, Visscher[6] analyzed the implementation and numerical results of the nuclear-magnetic shielding within a method of "minimal coupling" of large and small components proposed by Kutzelnigg.[7] In this method a unitary transformation of the four-component Dirac Hamiltonian in the presence of a magnetic potential **A** is carried out. As a result, the magnetic perturbation is expressed as a sum of a linear and a quadratic term in **A**, which closely resemble the nonrelativistic operators (plus additional terms). Rather unexpectedly, however, numerical results of the usual linear-response approach and minimal-coupling approach show significant differences.[6] Even though differences in the paramagnetic and diamagnetic terms were to be expected, the total nuclear-magnetic shieldings should be in close agreement. It has been suggested[6] that it would be interesting to compare the individual terms in Kutzelnigg's approach to the outcome of the perturbative quadratic response by Manninen *et al.*[8] and Melo *et al.*[9,10]

Approximate two-component methods to calculate nuclear-magnetic shieldings also yield different decompositions into para- and diamagnetic components of magnetic properties.[8–16] Among them, in the linear response within the elimination of small component (LR-ESC) approach,[9] the separation into para- and diamagnetic terms is explicitly obtained by considering separately the contributions from electronic excited states on one hand, and contributions from electron-positron pair-creation terms on the other. This decomposition is therefore fully consistent with the one carried out in the four-component linear-response calculations[1,2] which considers separately the contributions from electronic and positronic states to a given positive-energy four-component spinor in order to define the paramagnetic and diamagnetic components. The Breit-Pauli approach, in which the magnetic vector potential **A** is added to the canonical momentum in the Breit-Pauli Hamiltonian, was first investigated by Fukui *et al.*,[17,18] and later expanded and completed by Manninen *et al.*[8] and Fukui *et al.*[18] However, it is interesting to remark the following point. It seems natural to identify the paramagnetic contribution as that originating in operators linear in **A**, and to identify the diamagnetic one with operators quadratic in **A**. This definition leads to a different

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separation into para- and diamagnetic components in the Breit-Pauli approach to those of the LR-ESC one. In fact, this definition applied to the Breit-Pauli approach does not correspond to a decomposition into electron excitations and electron-positron contributions at the four-component level. A formal relation connecting the Breit-Pauli and LR-ESC approaches was proven in Ref. 9. Kutzelnigg[16] developed two-component expressions of magnetic properties starting from the Dirac equation in the presence of a magnetic field and using direct perturbation theory. By carrying out a double perturbation expansion (both in $c^{-1}$ and the magnetic potential) he arrived at formal perturbative expressions based on the Lévy-Leblond Hamiltonian. In this way, some singularities of the Foldy-Wouthuysen transformation are avoided.

In the present work, different formal relations allowing to analyze different questions related to the leading-order ESC approach are discussed. The ESC reduction of Visscher's nuclear-magnetic shielding based on Kutzelnigg's minimal-coupling approach is carried out. In this way a comparison of the LR-ESC, Breit-Pauli, and ESC-reduced minimal-coupling approaches can be established. Formal relations connecting the different para- and diamagnetic contributions of each approach are explicitly proven. Numerical results based on calculations of Ref. 10 are presented in order to verify explicitly the fulfillment of such relations. H$X$ and $CH_3X$ ($X$=Br,I) are taken as model compounds. In a second section, the gauge origin invariance of the LR-ESC approach is analyzed. Formal relations connecting different contributions to the nuclear-magnetic shielding for different gauge origins are explicitly proven for all one-body operators of the LR-ESC formalism. Numerical results are presented for the calculation of the $H$ nuclear-magnetic shielding in H$X$ ($X$=Br,I), by considering a shift of the gauge origin from the $H$ nucleus to the $X$ nucleus. Results thus obtained fully explain differences found in previous works between the closely related operators of the LR-ESC (gauge origin at the $H$ nucleus)[10] and Breit-Pauli (gauge origin at the heavy nucleus)[8,19] approaches.

## II. THEORY

### A. Leading-order relativistic effects on molecular magnetic properties within the ESC approach

#### 1. Breit-Pauli approach

The Pauli Hamiltonian can be obtained as the leading-order ESC approximation of the Dirac Hamiltonian, i.e.,

$$c\sigma p\phi^S + V\phi^L = E\phi^L, \tag{1}$$

$$c\sigma p\phi^L + V\phi^S = (2mc^2 + E)\phi^S, \tag{2}$$

where $\phi^L$ and $\phi^S$ stand for the large and small components of a Dirac four-component spinor of positive energy $mc^2+E$, $\sigma$ stand for the $2\times 2$ Pauli matrices, $p$ is the momentum operator, and $V$ is the Coulomb potential of the nuclei. In the ESC scheme,

$$\phi^S = (2mc^2 + E - V)^{-1}c\sigma p\phi^L \tag{3}$$

and the leading-order relativistic approximation is

$$\phi^S = \left(1 - \frac{E-V}{2mc^2}\right)\frac{\sigma p}{2mc}\phi^L. \tag{4}$$

Inserting this relation in Eq. (1) the following equation for the large component is obtained that

$$\left[\sigma p\left(1 + \frac{V}{2mc^2}\right)\frac{\sigma p}{2m} + V\right]\phi^L = E\left(1 + \frac{\sigma p\sigma p}{4m^2c^2}\right)\phi^L. \tag{5}$$

Consistently up to order $c^{-2}$, this equation is transformed to an eigenvalue equation for the hermitian Pauli Hamiltonian by means of the following transformation:

$$\tilde{\phi} = \left(1 - \frac{\sigma p\sigma p}{8m^2c^2}\right)\phi^L \tag{6}$$

The one-body Pauli Hamiltonian takes the form,

$$H_0^P = \frac{\sigma p\sigma p}{2m} + V + \frac{1}{4m^2c^2}\sigma pV\sigma p - \frac{1}{8m^2c^2}\left\{\frac{\sigma p\sigma p}{2m} + V; \sigma p\sigma p\right\}, \tag{7}$$

where the curly brackets stand for the anticommutator. The first two terms yield the Schrödinger Hamiltonian $H$. Therefore, relativistic effects on molecular states can be obtained from Rayleigh-Schrödinger perturbation theory (RSPT) for the Hamiltonian,

$$H_0^P = H + H^R, \tag{8}$$

where $H^R$ gathers the well-known relativistic spin-orbit (SO), Darwin (Dw), and mass-velocity (MV) operators.

Two-body interaction terms in this approximation are obtained by considering the Coulomb and Breit interaction operators between positive-energy four-component spinors and carrying out the ESC procedure in order to express the leading-order contributions (up to order $c^{-2}$) in terms of Pauli two-component spinors $\tilde{\phi}$. This procedure yields the Breit-Pauli Hamiltonian (see, e.g., Ref. 20). In the present work we restrict ourselves to the analysis of one-body operators and therefore two-body operators are not presented explicitly.

In the presence of a magnetic field described by a vector potential $\mathbf{A}$ the operator $p$ in the Dirac Hamiltonian is replaced by operator $\pi = p + (1/c)A$ (in a.u.). All steps of the previous derivation remain valid and the Pauli Hamiltonian in the presence of a magnetic field is obtained making the same replacement in Eq. (7). It is obtained that

$$H^P = H_0^P + O^1 + O^{\mathrm{Diam,NR}} + O^{3,\mathrm{BP}} + O^{\mathrm{Diam,BP}}, \tag{9}$$

where

$$O^1 = 1/2mc\{\sigma p, \sigma A\}, \tag{10}$$

$$O^{\mathrm{Diam,NR}} = \frac{1}{2mc^2}A^2, \tag{11}$$

are the "nonrelativistic" magnetic operators, and

$$O^{3,\mathrm{BP}} = -\frac{1}{4m^2c^2}\{p^2, O^1\} + \frac{1}{8m^2c^3}[[\sigma p, \sigma A], V], \tag{12}$$

$$O^{\mathrm{Diam,BP}} = -\frac{1}{8m^3c^4}(\{\sigma p,\sigma A\}^2 + \{p^2,A^2\}), \tag{13}$$

yield the leading-order relativistic field-dependent corrections. It is worthy to note that the commutator in Eq. (12) yields

$$\frac{1}{8m^2c^3}[[\sigma p,\sigma A],V] = \frac{1}{4m^2c^3}\sigma(\nabla V \times A), \tag{14}$$

i.e., it is the "field-induced" spin-orbit operator considered in different works.[8,17,21,22] As a consequence, relativistic effects on magnetic properties within the Breit-Pauli approximation can be expressed as first-, second-, and third-order RSPT corrections to the Schrödinger molecular energy.

### 2. Linear response (LR) within the ESC approach

Within the LR-ESC approach[9] the starting point is an RSPT (2)-like expression of the magnetic properties bilinear in the magnetic potential, based on the Breit Hamiltonian in the four-component Dirac-Fock space.[20,23] The perturbation operator is $W=\alpha\cdot A$ (where $\alpha$ are the $4\times4$ Dirac vector matrices). Within the no-pair approximation, the ground state $|0_N\rangle$ of an $N$-electron system can be expressed as a combination of determinants containing only "electronic" four-component spinors, i.e., positive-energy eigenvectors of the one-body Dirac Hamiltonian. The magnetic perturbation can connect such state with excited states of the same type, $\{|n_N\rangle\}$, and with states which have an electron-positron pair created on $|0_N\rangle$. Considering contributions from different particle number manifolds in Dirac-Fock space, the para ($E^{\mathrm{para}}$) and diamagnetic ($E^{\mathrm{dia}}$) contributions can be defined as[9]

$$E^{\mathrm{para}} = \sum_{n\neq0}\frac{\langle 0_N|\alpha\cdot A|n_N\rangle\langle n_N|\alpha\cdot A|0_N\rangle}{E_0-E_n}, \tag{15}$$

$$E^{\mathrm{dia}} = \sum_{n}\frac{\langle 0_N|\alpha\cdot A|n_{N+2}\rangle\langle n_{N+2}|\alpha\cdot A|0_N\rangle}{E_0-E_n} - \frac{\langle vac|\alpha\cdot 1|n_2\rangle\langle n_2|\alpha\cdot A|vac\rangle}{E_{\mathrm{vac}}-E_n}. \tag{16}$$

The last term in $E^{\mathrm{dia}}$ takes account of a renormalization of the vacuum energy due to the magnetic potential. This separation into para- and diamagnetic contributions is consistent with that of Refs. 1, 2, 4, and 5 in the context of the linear-response four-component (RPA) approach. In the LR-ESC approach the lowest-order relativistic corrections are obtained by applying the leading-order ESC approximation to all terms in Eqs. (15) and (16). As a result a set of operators describing relativistic effects on magnetic properties is obtained.[9,10] Magnetic-field-dependent operators entering the "paramagnetic" contribution, Eq. (15), are obtained when the matrix elements of the magnetic interaction between positive-energy four-component spinors are considered

$$\langle\phi_i^4|\alpha\cdot A|\phi_j^4\rangle = \langle\phi_i^L|c(\sigma\cdot p)R_i^{-1}(\sigma\cdot A) + (\sigma\cdot A)R_j^{-1}(c\sigma\cdot p)|\phi_j^L\rangle, \tag{17}$$

where, consistently in the leading-order ESC scheme it holds

$$R_i^{-1} \approx \frac{1}{2mc^2}\left[1+\frac{V-E_i}{2mc^2}\right], \tag{18}$$

and the relation between the large component and the two-component spinors of the unperturbed Pauli Hamiltonian is

$$|\phi_i^L\rangle = \left(1-\frac{p^2}{8m^2c^2}\right)|\tilde{\phi}_i\rangle. \tag{19}$$

Explicit third-order field-dependent operators were obtained in Ref. 9 from the relation Eq. (17). A brief account is given here. The following relation is correct up to order $c^{-3}$:

$$(V-E)(\sigma p)|\tilde{\phi}\rangle = (\sigma p)\left(\frac{-p^2}{2m}\right)|\tilde{\phi}\rangle - [(\sigma p),V]|\tilde{\phi}\rangle \tag{20}$$

Taking Eqs. (17)–(20) into account, the following operators can be defined as

$$O^1 = 1/2mc\{\sigma p,\sigma A\}, \tag{21}$$

$$O^{3,\mathrm{LR}} = \frac{-1}{8m^2c^2}\{p^2,O^1\} - \frac{1}{8m^3c^3}(\sigma A\sigma p p^2 + p^2\sigma p\sigma A) + \frac{1}{4m^2c^3}[[\sigma p,\sigma A],V], \tag{22}$$

where the superscript LR indicates that this is the form of the field-dependent operator in Ref. 9.

In addition to the nonrelativistic diamagnetic operator, the leading-order relativistic correction to the "diamagnetic" term was obtained by expressing the electron-positron contribution to magnetic properties, Eq. (16), in terms of Pauli two-component spinors consistently with the ESC approach. The detailed derivation of the resulting operators is presented in Ref. 9. A brief summary is presented in Appendix A. As a consequence, the following operator bilinear in the magnetic potential was obtained:

$$O^{\mathrm{Diam,LR}} = -\frac{1}{8m^3c^4}((\sigma p\sigma A)^2 + 2\sigma A p^2\sigma A + (\sigma A\sigma p)^2 + \{p^2,A^2\}), \tag{23}$$

where the superscript LR indicates that this is the form of the diamagnetic operator in the LR-ESC scheme.

### 3. Leading-order ESC-reduced "minimal-coupling" approach

Recently, a unitary transformation of the Dirac Hamiltonian in the presence of a magnetic potential yielding a minimal coupling between the large and small components of four-component spinors was proposed by Kutzelnigg.[7] The unitary operator:

$$U = \exp\left(\frac{\beta\alpha \cdot A}{2c^2}\right), \tag{24}$$

is applied to the Dirac one-body Hamiltonian in the presence of a magnetic potential **A**,

$$H^D = c\alpha p + \beta mc^2 + V + \alpha A, \tag{25}$$

in order to obtain the minimal-coupling-transformed Hamiltonian,

$$H^K = UH^D U^+. \tag{26}$$

It was shown in Ref. 7 that expansion of $H^K$ in powers of the magnetic potential up to second-order yields the following Hamiltonian:

$$H^K \cong H_0^D + D^{(1)} + D^{(2)}, \tag{27}$$

where $H_0^D$ is the unperturbed Dirac Hamiltonian [$A=0$ in Eq. (25)], and

$$D^{(1)} = \beta O^1, \tag{28}$$

$$D^{(2)} = \frac{1}{2mc^2}\beta A^2 - \frac{1}{4m^2c^3}\{\alpha A, pA\}. \tag{29}$$

In this way, the odd terms $\alpha A$ are removed from the Hamiltonian. Within this approach, magnetic properties bilinear in the magnetic potential are obtained from first- and second-order four-component perturbation theory considering operators $D^{(2)}$ and $D^{(1)}$, respectively, i.e.,

$$E^{(2)} = \langle\langle D^{(1)}; D^{(1)}\rangle\rangle + \langle 0|D^{(2)}|0\rangle, \tag{30}$$

where $\langle\langle A;B\rangle\rangle$ is a shorthand notation for a second-order correction to the molecular energy and the second term is an expectation value for the unperturbed molecular relativistic ground state. This approach was implemented by Visscher for the calculation of the magnetic shielding tensor[6] within the four-component linear-response RPA formalism.

The contributions to the molecular energy given in Eq. (30) are related to the second-order expression for the usual magnetic interaction,[1]

$$E^{(2)} = \langle\langle \alpha A; \alpha A\rangle\rangle. \tag{31}$$

by a formal relation provided by the proposed unitary transformation itself. At the four-component level, this relation is as follows:

$$\langle\langle \alpha \cdot A; [K, H_0^D]\rangle\rangle + \langle\langle [K, H_0^D]; \alpha \cdot A\rangle\rangle = -\langle 0|[K, \alpha \cdot A]|0\rangle, \tag{32}$$

where

$$K = \beta\alpha \cdot A/2c^2. \tag{33}$$

If the leading-order ESC approximation [Eqs. (17)–(20)] is applied to operators $D^{(1)}$ and $D^{(2)}$, the following linear and quadratic operators are found

$$O^{3,K} = -\frac{1}{8m^2c^2}\{p^2, O^1\} - \frac{1}{4m^2c^2}\sigma pO^1\sigma p, \tag{34}$$

$$O^{\mathrm{Diam},K} = -\frac{1}{8m^2c^4}((\sigma p\sigma A)^2 + (\sigma A\sigma p)^2 + 2\sigma pA^2\sigma p + \{p^2, A^2\}) \tag{35}$$

where the superscript $K$ indicates that these are the ESC-reduced operators of the minimal-coupling formalism. A brief derivation of these operators is presented in Appendix B, as a detailed account of leading-order effects can be found in Ref. 7.

### B. Relations connecting the Breit-Pauli, LR-ESC, and ESC-reduced minimal-coupling approaches

Within the leading-order ESC schemes presented in the previous sections, relativistic effects on magnetic properties which are bilinear in the magnetic potential can be expressed as first-, second-, and third-order RSPT corrections to the Schrödinger molecular energy. Two kinds of relativistic effects can be distinguished: (i) "passive" effects, in which relativistic corrections to the unperturbed molecular states are considered by means of the spin-orbit, Darwin, and mass-velocity operators in $H^R$, Eq. (8), and lowest-order magnetic operators $O^1$, and $O^{\mathrm{Diam,NR}}$ [Eqs. (10) and (11)]; and (ii) "active" effects, in which the explicit field-dependent operators $O^{3,X}$ and $O^{\mathrm{Diam},X}$ ($X$=BP, LR, or K) are considered. This terminology has become conventional in the bibliography,[8,19] and is therefore applied in the present work.

Passive effects are exactly the same in the Breit-Pauli, LR-ESC, and minimal-coupling formalisms. Active effects are obtained by considering, on one hand, second-order RSPT corrections to the molecular energy for operators $O^1$ and $O^{3,X}$,

$$E(O^1, O^{3,X}) = \sum_{n\neq 0} \frac{\langle 0|O^1(N)|n\rangle\langle n|O^{3,X}(N)|0\rangle}{E_0 - E_n} + \frac{\langle 0|O^{3,X}(N)|n\rangle\langle n|O^1(N)|0\rangle}{E_0 - E_n}, \tag{36}$$

where $O(N)$ stands for the one-body operator $A$ in the $N$ particles states space

$$O(N) = \sum_i O_i. \tag{37}$$

On the other hand, the relativistic active correction to the diamagnetic contribution within each formalism is obtained as a first-order RSPT energy correction for the corresponding $O^{\mathrm{Diam},X}$ operator, i.e.,

$$E^1 = \langle 0|O^{\mathrm{Diam},X}|0\rangle. \tag{38}$$

In order to analyze the relations between the different ESC approaches for the calculation of molecular magnetic properties, the commutator in Eq. (39) is considered

$$O^3(H) = \frac{1}{8m^2c^3}[[\sigma p, \sigma A], H], \tag{39}$$

where $H$ is the many-body Schrödinger Hamiltonian. The second-order RSPT correction to the molecular energy involving a commutator with $H$ can be reexpressed as

$$E(O^1;O^3(H)) = \frac{1}{8m^2c^3}\langle 0|[O^1,[\sigma p,\sigma A]]|0\rangle, \tag{40}$$

i.e., as an expectation value for an operator bilinear in the magnetic potential. Results Eqs. (39) and (40) show that by means of these formal relations, paramagnetic contributions to magnetic properties involving operator $O^3(H)$ can be transformed into diamagnetic contributions, i.e., contributions which are obtained as an expectation value for an operator bilinear in the magnetic potential.

Explicit relations among the different ESC formalisms are hereby proven.

By a simple rearrangement of terms in Eq. (22) $O^{3,\mathrm{LR}}$ can be expressed as

$$\begin{aligned} O^{3,\mathrm{LR}} &= -\frac{1}{4m^2c^2}\{p^2,O^1\} - \frac{1}{16m^3c^3}[p^2,[\sigma p,\sigma A]] \\ &\quad + \frac{1}{4m^2c^3}[[\sigma p,\sigma A],V] \\ &= -\frac{1}{4m^2c^2}\{p^2,O^1\} + \frac{1}{8m^2c^3}[[\sigma p,\sigma A],V] \\ &\quad + \frac{1}{8m^2c^3}\left[[\sigma p,\sigma A],\left(\frac{p^2}{2m}+V\right)\right], \end{aligned} \tag{41}$$

and, therefore,

$$\begin{aligned} O^{3,\mathrm{LR}} &= O^{3,\mathrm{BP}} - \frac{1}{8m^2c^3}[[\sigma p,\sigma A],U] \\ &\quad + \frac{1}{8m^2c^3}[[\sigma p,\sigma A],H], \end{aligned} \tag{42}$$

[see Eq. (12)] where $U$ stands for the two-body Coulomb interaction in the Schrödinger Hamiltonian. The second-order RSPT expression involving the third term in Eq. (42) can be taken into account as indicated in Eq. (40), yielding a modified diamagnetic operator of the form,

$$\begin{aligned} &\frac{1}{8m^2c^3}[O^1,[\sigma p,\sigma A]] + O^{\mathrm{Diam,LR}} \\ &\quad = -\frac{1}{8m^3c^4}(\{\sigma p,\sigma A\}^2 + \{p^2,A^2\}) \\ &\quad = O^{\mathrm{Diam,BP}}, \end{aligned} \tag{43}$$

i.e., the operator of the Breit-Pauli scheme, Eq. (13), is readily obtained. Therefore, we have obtained a formal expression relating the operators of the LR-ESC scheme and those of the Breit-Pauli one.[9] In Eq. (42) there is a two-body contribution which should be taken into account in order to make the relation between both approaches exact. Such contribution is neglected in the present work. It is seen that the separation into paramagnetic and diamagnetic contributions associating the linear operators to the first one and the quadratic to the second in the Breit-Pauli approach does not correspond to the separation into electronic excitations and electron-positron rotations, as does the LR-ESC scheme. In the present work the fulfillment of these relations is analyzed numerically taking HBr and HI as model examples.

The ESC-reduced minimal-coupling operators can also be obtained starting from the LR-ESC ones, Eqs. (22) and (23), and reexpressing them in a convenient way. The term containing V in $O^{3,\mathrm{LR}}$ in Eq. (22) can be replaced in terms of $O^3(H)$, Eq. (39), yielding the following formal expression:

$$\begin{aligned} O^{3,\mathrm{LR}} &= -\frac{1}{8m^2c^2}\{p^2,O^1\} - \frac{1}{8m^3c^3}(\sigma A\sigma pp^2 + p^2\sigma p\sigma A) \\ &\quad - \frac{1}{8m^3c^3}[[\sigma p,\sigma A],p^2] + \frac{1}{4m^2c^3}[[\sigma p,\sigma A],H] \\ &\quad - \frac{1}{4m^2c^3}[[\sigma p,\sigma A],U]. \end{aligned} \tag{44}$$

Taking into account that the second and third terms in Eq. (44) can be written as

$$\begin{aligned} &-\frac{1}{8m^3c^3}(\sigma A\sigma pp^2 + p^2\sigma p\sigma A) - \frac{1}{8m^2c^3}[[\sigma p,\sigma A],p^2] \\ &\quad = -\frac{1}{4m^2c^2}\sigma p\cdot O^1\cdot\sigma p, \end{aligned} \tag{45}$$

it is seen that

$$O^{3,\mathrm{LR}} = O^{3,K} + 2O^3(H) - 2O^3(U), \tag{46}$$

where $O^{3,K}$ is the ESC-reduced operator of Eq. (34). Once again, the contribution of the second term of Eq. (46) to the molecular energy can be reexpressed as an expectation value for the operator in Eq. (40). Therefore the form of the quadratic operator in this approach is

$$\frac{1}{4m^2c^3}[O^1,[\sigma p,\sigma A]] + O^{\mathrm{Diam,LR}} = O^{\mathrm{Diam},K}, \tag{47}$$

i.e., precisely the ESC-reduced operator of Kutzelnigg's formalism, Eq. (35). It is interesting to remark that in this context there are no operators involving the one-body Coulomb potential $V$.

### C. The nuclear-magnetic shielding tensor in the Breit-Pauli, LR-ESC, and ESC-reduced minimal-coupling approaches

The NMR nuclear-magnetic shielding tensor can be calculated as

$$\sigma_{N,ij} = \left.\frac{\partial^2 E}{\partial\mu_{N,i}\partial B_j}\right|_{\mu_N,B=0}, \tag{48}$$

where $E$ is the molecular energy in the presence of the magnetic moment of nucleus $N$, $\mu_N$, and a uniform magnetic field $B$. The lowest-order relativistic corrections to the magnetic shielding tensor of nucleus $N$ arising from passive operators are the same for all approaches, as they involve the nonrelativistic magnetic operators and relativistic effects are only included in the molecular magnetically unperturbed states. Relativistic corrections due to active operators within the different approaches considered are obtained from the RSPT expressions bilinear in $\mu_N$ and $B$, i.e.,

$$E^{(2)} = E(O^1(\mu_N); O^{3X}(B)) + E(O^1(B); O^{3X}(\mu_N)) + \langle O^{\mathrm{Diam},X}(\mu_N; B)\rangle, \tag{49}$$

where the last term represents an expectation value for the Schrödinger molecular ground state, $X$ stands for the Breit-Pauli ($X$=BP), LR-ESC ($X$=LR), or minimal-coupling ($X=K$) approach, and

$$O^1(\mu_N) = \frac{L_N \mu_N}{m c r_N^3} + \frac{\sigma}{2mc} B_N \tag{50}$$

gathers the paramagnetic (nuclear) spin-orbit (PSO) and Fermi contact (FC) and spin-dipolar (SD) operators,

$$B_N = \nabla \times A_N, \tag{51}$$

$$A_N = \frac{\mu_N \times r_N}{r_N^3}, \tag{52}$$

where $r_N$ is the electron position with respect to nucleus $N$; and

$$O^1(B) = \frac{1}{2mc} L \cdot B + \frac{\sigma}{2mc} B \tag{53}$$

contains the orbital Zeeman (OZ) and spin Zeeman (SZ) operators,

$$B = \nabla \times A_B = \nabla \times \left(\tfrac{1}{2} B \times r\right). \tag{54}$$

In this section, LR-ESC operators will be considered in first place. The only third-order operators contributing to the nuclear-magnetic shielding tensor are

$$O^{3S,\mathrm{LR}}(\mu_N) = -\frac{1}{4m^2c^3}\left\{p^2, \frac{L_N \mu_N}{r_N^3}\right\}, \tag{55}$$

hereafter identified as PSO-$K$ (it combines the PSO and kinetic-energy operators)

$$O^{3S,\mathrm{LR}}(B) = -\frac{1}{4m^2c^3} p^2 B \cdot L, \tag{56}$$

identified as OZ-$K$, and

$$O^{3T,\mathrm{LR}}(B) = -\frac{3}{8m^2c^3} p^2(\sigma \cdot B) + \frac{1}{8m^2c^3}(\sigma \cdot p)(B \cdot p) + \frac{\sigma}{2m^2c^3}(\nabla V \times A_B), \tag{57}$$

where the first two terms are dubbed SZ-$K$ and the last one is dubbed BSO (field-induced spin-orbit). The superscript $S$ and $T$ in Eqs. (55)–(57) stand for singlet and triplet operators, respectively. As indicated in Sec. II B the relation between different approaches is based in the subtraction of a term proportional to $O^3(h)$ to the LR-ESC operators (where $h$ stands for the one-body part of the Schrödinger Hamiltonian). $O^3(h)$ is a purely triplet operator, and therefore the different approaches yield different expressions for operator $O^{3T}(B)$, while all other operators Eqs. (50), (53), (55), and (56) remain unchanged. Explicitly, we have

$$O^3(h,B) = -\frac{1}{8m^3c^3} p^2(\sigma \cdot B) + \frac{1}{8m^3c^3}(\sigma \cdot p)(B \cdot p) - \frac{\sigma}{4m^2c^3}(\nabla V \times A_B), \tag{58}$$

where $O^3(h,B)$ is the commutator of Eq. (39) specialized to the case of the uniform magnetic field. Consistently with results in Eq. (40), it holds

$$E(O^1(\mu_N), O^3(h,B)) = \frac{1}{8m^2c^3}\langle [O^1(\mu_N), [\sigma \cdot p, \sigma \cdot A_B]]\rangle - E(O^1(\mu_N), O^3(U,B)), \tag{59}$$

where $O^3(U,B)$ is the commutator Eq. (39) with the two-body Coulomb potential $U$ and the uniform magnetic-field vector potential, and

$$\langle [O^1(\mu_N), [\sigma \cdot p, \sigma \cdot A_B]]\rangle = \frac{1}{mc}\langle A_B(\nabla \times B_N)\rangle. \tag{60}$$

On the other hand, $O^{\mathrm{Diam}}(\mu_N; B)$ collects terms bilinear in $\mu_N$ and $B$ from the quadratic operator $O^{\mathrm{Diam}}$. Within the LR-ESC approach it is obtained that

$$O^{\mathrm{Diam,LR}}(\mu_N; B) = -\frac{1}{4m^3c^4}\left(4(A_N \cdot p)(A_B \cdot p) + B \cdot B_N + \frac{1}{2} A_B(\nabla \times B_N) + 2(A_N \cdot A_B)p^2\right). \tag{61}$$

For the sake of clarity, each term in Eq. (61) will be referred to as $W_i^{\mathrm{LR}}$ ($i$=1,4), respectively, in order to be able to identify each contribution separately. For a real ground state (in coordinate representation) it holds

$$\langle A_B(\nabla \times B_N)\rangle = 4\pi\langle(\mu_N \cdot B\,\delta(r_N) + iA_B(R_N) \times \delta(r_N)(\mu_N \times p))\rangle, \tag{62}$$

where $A_B(R_N)$ is the vector potential of the uniform magnetic field at the position of nucleus $N$ and vanishes if the gauge origin is placed at the nucleus site. The expectation value in Eq. (59) contains exactly the operator Eq. (62).

In Table I we present a summary of the contributions of active operators to both the paramagnetic and diamagnetic terms of the nuclear-magnetic shielding tensor in the LR-ESC, Breit-Pauli, and ESC-reduced minimal-coupling approaches. The numerical factors indicate the scaling of a given term with respect to its value in the LR-ESC method. Second-order contributions are identified by the two operators combined in $E(A,B)$ and first-order ones are separated into two terms: $\sigma_1(\mathrm{Dia}-K)$ collects those terms containing a delta-type operator at nucleus $N$ [$W_2$ and $W_3$ in Eq. (61)]; and $\sigma_2(\mathrm{Dia}-K)$ contains contributions from $W_1$ and $W_4$ of Eq. (61).

In Table II numerical results are presented taking HI as model compound. Relativistic corrections to the magnetic shielding constant of the I nucleus are presented. Numerical values are taken from Ref. 10 and rescaled according to factors in Table I to yield the values corresponding to different approaches. The gauge origin is placed at the I nucleus position.

TABLE I. Second-order (paramagnetic) $E^X(A,B)$ and first-order (diamagnetic) $\sigma_i^X(\mathrm{Dia}-K)$ $(i=1,2)$ contributions to the nuclear-magnetic shielding tensor in the LR-ESC ($X$=LR), Breit-Pauli ($X$=BP), and ESC-minimal-coupling ($X$=K) approaches, originating in active (i.e., field-dependent) operators.

| | A[a] | B$^{X}$ [b] | $X$=LR−ESC | $X$=BP | $X$=K |
|---|---|---|---|---|---|
| Paramagnetic terms $E(A,B^X)$ | OZ | PSO−$K$ | 1 | 1 | 1 |
| | PSO | OZ−$K$ | 1 | 1 | 1 |
| | FC | SZ−$K^X$ | 1 | 3/4 | 1/2 |
| | SD | SZ−$K^X$ | 1 | 0 | −1 |
| | FC | BSO$^X$ | 1 | 1/2 | 0 |
| | SD | BSO$^X$ | 1 | 1/2 | 0 |
| Diamagnetic terms[c] | $\sigma_1^X(\mathrm{Dia}-K)=W_2^X+W_3^X$ | | 1 | 4/7 | 1/7 |
| | $\sigma_2^X(\mathrm{Dia}-K)=W_1^X+W_4^X$ | | 1 | 1 | 1 |

[a]PSO: paramagnetic (nuclear) spin-orbit; FC: Fermi contact; SD: spin-dipolar [Eq. (50)]. OZ: orbital Zeeman; SZ: spin Zeeman [Eq. (53)].
[b]$K$ indicates combination of a magnetic operator with the kinetic-energy operator. PSO−$K$: Eq. (55); OZ−$K$: Eq. (56); SZ−$K$ and BSO: Eq. (57).
[c]Operators $W_1^X$ are defined after Eq. (61).

Results in Table II deserve several comments. It is seen that results of the Breit-Pauli approach as obtained from the LR-ESC ones by applying the sum rule Eq. (40) are in excellent agreement with those of Refs. 8 and 19. For instance the $\sigma_1^{\mathrm{BP}}(\mathrm{Dia}-K)$ term in the second column of Table II must be compared to the one dubbed $\sigma^{\mathrm{con}}$ in Ref. 19. The agreement between both calculated values is excellent, despite the use of the "resolution of the identity" approximation in Ref. 10. The only exception occurs for $E(\mathrm{OZ},\mathrm{PSO}-K^{\mathrm{BP}})$. The present value nearly doubles that of Ref. 19 (63.63 ppm). This last value should be preferred. Comparison of the present ESC-minimal-coupling results in Table II to four-component ones of Visscher[6] is only possible for the full relativistic correction, as the individual contributions of Ref. 6 are not related to the ones in Table II in a simple way (not even the dia- and paramagnetic separation refer to the same terms). The minimum coupling of large and small components in Kutzelnigg's approach yields the smaller (in absolute value) paramagnetic and diamagnetic relativistic corrections. The problem of the inconsistency between the four-component calculations based on the standard RPA formalism[1,2] and Kutzelnigg's minimal-coupling one is not present at this level of approximation and confirms the suspicion that the difficulties are related to the positron rotation terms as considered in the four-component RPA calculations.

TABLE II. Relativistic corrections to the nuclear-magnetic shielding constant $\sigma$(I) in HI. $E(A,B^X)$: RSPT(2) expressions involving operators $A$ and $B^X$; $W_i^X$ $(i=1,4)$: expectation values for operators $O^{\mathrm{Diam},X}$. Values obtained by the LR-ESC ($X$=LR), Breit-Pauli ($X$=BP), and ESC minimal-coupling ($X$=K) approaches (Numerical values taken from Ref. 10 and rescaled according to numerical factors in Table I). Gauge origin at I. Values in ppm.

| | $X$=LR | $X$=BP | $X$=K |
|---|---|---|---|
| $E(\mathrm{OZ};\mathrm{PSO}-K^X)$[a] | 142.16 | 142.16 | 142.16 |
| $E(\mathrm{PSO};\mathrm{OZ}-K^X)$ | 112.59 | 112.59 | 112.59 |
| $E(\mathrm{FC};\mathrm{SZ}-K^X)$ | 2579.32 | 1934.49 | 1289.66 |
| $E(\mathrm{SD};\mathrm{SZ}-K^X)$ | 70.08 | 0 | −70.08 |
| $E(\mathrm{FC},\mathrm{BSO}^X)$ | −661.97 | −330.99 | 0 |
| $E(\mathrm{SD},\mathrm{BSO}^X)$ | 111.50 | 55.75 | 0 |
| Passive | −105.92 | −105.92 | −105.92 |
| Total paramagnetic correction | 2247.76 | 1808.08 | 1368.41 |
| $\sigma_1^X(\mathrm{Dia}-K)$ | −1092.90 | −624.51 | −156.13 |
| $\sigma_2^X(\mathrm{Dia}-K)$ | −564.51 | −564.51 | −564.51 |
| Passive | 415.68 | 415.68 | 415.68 |
| Total diamagnetic correction | −1241.73 | −773.34 | −304.96 |
| Total relativistic effect | 1006.03 | 1034.74 | 1063.45 |
| Total shielding | 5548.72 | 5577.43 | 5606.14 |

[a]See footnote to Table I for operators acronyms.

As it can be seen in Tables I and II the equivalence between the different methods relies on the following identity, extracted from Eq. (40)

$$-\frac{1}{4}E(\mathrm{FC};\mathrm{SZ}-K^{\mathrm{LR}})-E(\mathrm{SD};\mathrm{SZ}-K^{\mathrm{LR}})-\frac{1}{2}E(\mathrm{FC}+\mathrm{SD};\mathrm{BSO}^{\mathrm{LR}})=\frac{3}{7}\sigma_1^{\mathrm{LR}}(\mathrm{Dia}-K)+E(O^1(\mu_N);O^{3^{\mathrm{LR}}}(U,B)). \quad (63)$$

It is seen that in the right-hand side (rhs) of Eq. (63) there is a two-body contribution, which is automatically taken into account in the left-hand side (lhs) in terms of one-body operators only. Such two-body contribution must be present in the context of the Breit-Pauli approach. It represents the two-body part of the second-order spin-orbit operator found in Refs. 17 and 22. Unfortunately, no numerical estimates of this two-body term are found in the bibliography for the systems under study in the present work. It is interesting to emphasize that such contribution is automatically contained in the LR-ESC approach as part of calculations involving only one-body operators. As it is seen in Eq. (63), such contribution is needed to make the identity exact. Therefore, the difference in the total relativistic correction calculated with the LR-ESC, Breit-Pauli, and ESC-minimal-coupling approaches retaining only one-body operators has

TABLE III. Numerical verification of relations connecting the LR-ESC, Breit-Pauli, and ESC-minimal-coupling formalisms. As a consequence of such relation the numerical values of the lhs and rhs of Eq. (63) must be equivalent, except for a two-body contribution. All values in ppm.

| | | lhs of Eq. (63) | rhs of Eq. (63) | Difference |
|---|---|---|---|---|
| BrH | Br | −122.03 | −131.84 | 9.81 |
| $CH_3Br$ | Br | −122.05 | −131.84 | 9.79 |
| IH | I | −439.68 | −468.39 | 28.71 |
| $CH_3I$ | I | −439.70 | −468.39 | 28.69 |
| $CH_3Br$ | C | −0.45 | −0.56 | 0.11 |
| $CH_3I$ | C | −0.56 | −0.56 | 0.00 |

two sources: on one hand, the lack of the two-body term just mentioned and, on the other hand, differences due to the incompleteness of the basis set. The difference of 28.71 ppm found for I in HI between different approaches arises from these sources of error, and it can be considered very small compared to the total relativistic effect of ca. 1000 ppm.

In Table III the verification of the identity Eq. (63) is explicitly checked for $X$ in H$X$ and $X$ and C in $CH_3X$ ($X$ =Br,I). Values presented correspond to the right-hand side of Eq. (63) compared to those of the left-hand side of Eq. (63), neglecting the two-body contribution. Numerical values are taken from Ref. 10.

The fact that the difference is larger for the heaviest nucleus, I, significant for Br, and negligibly small for C could be an indication that it is really a measure of the importance of the two-body term and basis set incompleteness errors are negligibly small.

### D. Gauge origin invariance of the LR-ESC approach

When considering magnetic molecular properties, the problem of the gauge origin of the vector potential of the uniform magnetic field must be addressed, as quantities of physical significance must be gauge origin invariant. In non relativistic theory, the numerical values of the paramagnetic and diamagnetic terms of molecular properties depend on the gauge origin considered, but the total value of the magnetic property under study is gauge origin independent. The cancellation of the change in the paramagnetic and diamagnetic terms is demonstrated formally proving the existence of a formal relation connecting the contribution to the energy of operators containing the shift from one gauge origin to the other.

In the present section the gauge origin invariance of the LR-ESC nuclear-magnetic shielding is analyzed. All one-body operators yielding both active and passive corrections are considered. The superindex LR is dropped from all operators for brevity. Two-body terms are not taken into account, as no actual calculations have been carried out for them. Active relativistic corrections are summarized in Eq. (49). Passive relativistic effects are obtained by considering relativistic corrections to the unperturbed molecular states in the presence of the nonrelativistic magnetic operators, i.e.,

$$E^{\text{passive}} = E(O^1(\mu_N);O^1(B);H^R) + E\left(\frac{1}{mc^2}A_N \cdot A_B;H^R\right) \tag{64}$$

where $E(A;B;C)$ represents a third-order RSPT energy correction,

$$E(A;B;C) = \sum_{n\neq 0} \frac{\langle 0|A|n\rangle\langle n|B-\langle B\rangle|m\rangle\langle m|C|0\rangle}{(E_0-E_n)(E_0-E_m)} + \frac{\langle 0|B|n\rangle\langle n|C-\langle C\rangle|m\rangle\langle m|A|0\rangle}{(E_0-E_n)(E_0-E_m)} + \frac{\langle 0|C|n\rangle\langle n|A-\langle A\rangle|m\rangle\langle m|B|0\rangle}{(E_0-E_n)(E_0-E_m)} + \text{c.c.}, \tag{65}$$

and $H^R$ represents the relativistic corrections to the Schrödinger Hamiltonian as given in the Pauli Hamiltonian,

$$H^R = -\frac{1}{8m^3c^2}p^4 + \frac{1}{8m^2c^2}(\nabla^2 V) + \frac{1}{4m^2c^2}\sigma(\nabla V \times p) \tag{66}$$

The first term is the mass-velocity operator (MV), the second one is the Darwin operator (Dw), and the third one is the spin-orbit operator (SO). In Eq. (66), only the one-body terms of $H^R$ are retained, in order to be consistent with the purpose of obtaining connections between one-body operators only.

If a change of gauge origin of the uniform magnetic potential is carried out, given by a displacement vector $R_G$, the change in the individual contributions of Eqs. (49) and (64) can be expressed in terms of the change in $A_B$,

$$\delta A_B = \tfrac{1}{2}B \times R_G, \tag{67}$$

$$\delta O^1(B) = \frac{1}{mc}\delta A_B \cdot p = \frac{i}{c}[h, \delta A_B \cdot r], \tag{68}$$

where $h$ is the one-body Schrödinger Hamiltonian,

$$\delta O^3(B) = -\frac{1}{2mc^2}p^2\delta O^1(B) + \frac{\sigma}{2m^2c^3}(\nabla V \times \delta A_B). \tag{69}$$

The difference in the contribution of each term can be expressed as

$$\Delta E(O^1(\mu_N);O^3(B)) = E(O^1(\mu_N);\delta O^3(B)), \tag{70}$$

$$\Delta E(O^1(B);O^3(\mu_N)) = E(\delta O^1(B);O^3(\mu_N)), \tag{71}$$

$$\Delta\langle O^{\text{Diam,LR}}(\mu_N;B)\rangle = -\frac{1}{4m^3c^4}\langle (4(A_N \cdot p)(\delta A_B \cdot p) + \tfrac{1}{2}\delta A_B(\nabla \times B_N) + 2(A_N \cdot \delta A_B)p^2)\rangle. \tag{72}$$

Changes in the diamagnetic contributions $W_i$ of Eq. (61) indicated in Eq. (72) are dubbed $\Delta W_i$. It is readily seen that $\Delta W_2 = 0$. For passive contributions it is obtained that

$$\Delta E(O^1(\mu_N);O^1(B);H^R) = E(O^1(\mu_N);\delta O^1(B);H^R) \tag{73}$$

$$\Delta E\left(\frac{1}{mc^2}A_N\cdot A_B;H^R\right)=E\left(\frac{1}{mc^2}A_N\cdot \delta A_B;H^R\right). \tag{74}$$

In order to establish a connection among the changes of different terms, it is worthy to note that

$$E(A;[B,H])=\langle[A,B]\rangle, \tag{75}$$

$$E(A;[B,H];C)=E([A,B];C)-E(A;[B,C]), \tag{76}$$

where $H$ stands for the full (i.e., many-body) Schrödinger Hamiltonian.

In Eqs. (71) and (73) the commutator of Eq. (68) is involved. In order to make use of Eqs. (75) and (76), the one-body Hamiltonian $h$ should be replaced by the many-body Hamiltonian $H$. This can be done without the appearence of extra two-body terms, because the operator $\mathbf{r}$ in Eq. (68) commutes with the two-body Coulomb interaction operator. Therefore, making use of Eqs. (75) and (76) the following relations are found to hold exactly.

In the case of Eq. (71) it is obtained that

$$\begin{aligned}\Delta E(O^1(B);O^3(\mu_N))&=\frac{1}{4m^3c^4}\langle 4(A_N\cdot p)(\delta A_B\cdot p)\\&\quad+2(\delta A_B\cdot A_N)p^2\rangle\\&=-\Delta W_1-\Delta W_4.\end{aligned} \tag{77}$$

Details of the derivation are presented in Appendix C (identity 1). In the case of Eq. (73), it is useful to separate it into two terms: one, $H^{R,S}$, containing the scalar relativistic mass-velocity and Darwin operators, and a second one, $H^{R,T}$, containing the spin-orbit one (SO) (see Appendix C, identities 3 and 4),

$$\begin{aligned}\Delta E(O^1(\mu_N);O^1(B);H^{R,S})&=-E\left(\frac{1}{mc^2}A_N\cdot\delta A_B;H^{R,S}\right)\\&\quad-\Delta E(O^1(\mu_N);O^{3S}(B)),\end{aligned} \tag{78}$$

$$\begin{aligned}\Delta E(O^1(\mu_N);O^1(B);H^{R,T})&=-\frac{1}{8m^3c^4}\langle\delta A_B\cdot\nabla\times B_N\rangle\\&=\Delta W_3\end{aligned} \tag{79}$$

In the rhs of Eq. (78) the change in the contribution from singlet operators of Eq. (69), Eq. (70), is already included. Therefore, only the term containing triplet operators in Eq. (70) must be considered explicitly. To this end it is useful to observe that the triplet operator in Eq. (69) can be expressed as the following commutator:

$$\frac{\sigma}{2m^2c^3}\nabla V\times\delta A_B=-\frac{i}{2m^2c^3}[\sigma(p\times\delta A_B),h]. \tag{80}$$

In order to apply Eq. (75), the one-body Hamiltonian $h$ must be replaced by the many-body Hamiltonian $H$. The difference between them is given by the two-body Coulomb interaction and leads to a two-body contribution to Eq. (70). Such term is neglected in the present work. Therefore, application of Eq. (75) yields (see Appendix C, identity 2)

TABLE IV. Relations among the gauge origin dependence of different terms yielding the relativistic correction to the nuclear-magnetic shielding tensor in the LR-ESC approach. The cancellation of all terms in the last column shows the (formal) gauge origin independence of the (one-body) total result.

| | Equation number | Change $\Delta$ of | Equivalent change |
|---|---|---|---|
| Passive[a] | (78) | $E$(PSO;OZ;MV+Dw) | $-E$(Dia;MV+Dw)<br>$-E$(PSO,OZ$-K$) |
| | (79) | $E$(FC+SD;OZ;SO) | $\Delta W_3$ |
| | ⋯ | $E$(Dia;MV+Dw) | $E$(Dia;MV+Dw) |
| Active[b] | (77) | $E$(OZ;PSO$-K$) | $-(\Delta W_1+\Delta W_4)$ |
| | ⋯ | $E$(PSO;OZ$-K$) | $E$(PSO;OZ$-K$) |
| | (81) | $E$(FC+SD;BSO) | $-2\Delta W_3$ |
| | (72) | $O^{\mathrm{Diam}}(\mu_N;B)$ | $\Delta W_1+\Delta W_3+\Delta W_4$[c] |
| Total change | | $\Delta E$ | 0 |

[a]Equation (64).
[b]Equation (49).
[c]$\Delta W_2=0$.

$$\Delta E(O^1(\mu_N);O^{3T}(B))=\frac{1}{4m^3c^4}\langle\delta A_B\cdot\nabla\times B_N\rangle=-2\Delta W_3. \tag{81}$$

In Table IV the changes in different contributions and the cancellation of all terms showing the gauge origin invariance of the full one-body relativistic correction to the nuclear-magnetic shielding are summarized.

In numerical results of relativistic corrections to the nuclear-magnetic shielding within different approaches, different gauge origins were used for the calculation of the nuclear-magnetic shielding of the $H$ nucleus in H$X$ compounds.[8,10,19] It is thus interesting to compare numerically the fulfillment of the formal relations found in the present work connecting results with different gauge origins. We present numerical values taken from Ref. 10. As the formal fulfillment of such relations was proven, two sources of error can be expected. On one hand, numerical errors due to incompleteness of the basis sets used in the calculations, or numerical errors introduced due to the approximate procedure used to calculate matrix elements of some operators in Ref. 10. On the other hand, differences may also be expected whenever the fulfillment of a given formal relation depends on contributions from two-body operators. This is the case of Eq. (81). Numerical results are presented in Table V for HBr and in Table VI for HI.

From Tables V and VI the following conclusions can be obtained. All relations are fulfilled to a large extent in both cases. When small differences are found, they are surely due to basis set incompleteness errors, as they are of the same order of magnitude as the differences found in final results obtained with different basis sets in Ref. 10. The relation in Eq. (81) holds almost exactly. This feature indicates that two-body effects are really small in these calculations. When the gauge origin is changed from the $X$ center to the $H$ one in the calculation of the $H$ nuclear magnetic shielding, the largest changes are found for the scalar third order, the OZ-$K$, the PSO-$K$, and "active" diamagnetic terms $W_i$. All these terms yield negligibly small results when the gauge origin is placed at the $X$ nucleus.[8,19] When the gauge origin is placed

TABLE V. Gauge origin dependence of the LR-ESC relativistic corrections to the nuclear-magnetic shielding of H nucleus in HBr. Numerical values correspond to the difference in a given contribution when the gauge origin is shifted from the Br nucleus to the H nucleus.

| Change Δ of | | Equivalent change | |
|---|---|---|---|
| $E$(PSO,OZ;MV+Dw) | −1.62 | $-E$(Dia;MV+Dw) $-E$(PSO,OZ−$K$) Eq. (78) | −1.43 |
| $E$(FC+SD;OZ;SO) | −0.02 | $\Delta W_3$ Eq. (79) | 0.0 |
| $E$(Dia;MV−Dw) | 0.08 | $E$(Dia;MV+Dw) | 0.08 |
| $E$(OZ;PSO−$K$) | 1.34 | $-(\Delta W_1+\Delta W_4)$ Eq. (77) | 1.55 |
| $E$(PSO;OZ−$K$) | 1.35 | $E$(PSO;OZ−$K$) | 1.35 |
| $E$(FC+SD;BSO) | 0.02 | $-2\Delta W_3$ Eq. (81) | 0.01 |
| $O^{\mathrm{Diam}}(\mu_N;B)$ | −1.52 | $\Delta W_1+\Delta W_3+\Delta W_4$ Eq. (72) | −1.52 |
| $\Delta E$ | −0.36 | 0 | 0.0 |

at the $H$ nucleus, all these terms take non-negligible values that cancel each other, confirming the importance of taking them all into account in a consistent way.

## III. CONCLUDING REMARKS

In this work a series of formal relations connecting different approaches to calculate relativistic effects at the leading-order ESC level of approximation were proven. In addition, the gauge origin invariance of the LR-ESC theory has been established. It is worthy to mention that although the main goal has been to establish these relations theoretically, numerical results are also presented in order to verify their fulfillment explicitly in practical applications. As a consequence several aspects of the relativistic calculation of nuclear-magnetic shieldings at the ESC level have been clarified. In particular, differences in numerical results of the LR-ESC and Breit-Pauli approaches in HI are explained for both the heavy and $H$ nuclei. Full consistency between the LR-ESC, Breit-Pauli, and ESC-minimal-coupling approaches was found. Differences in numerical values found at the four-component level are not present within the ESC approximation. A deeper comparison between the LR-ESC and minimal-coupling methods would be possible by carrying out explicitly the ESC reduction of each individual contribution of the nuclear-magnetic shielding in Ref. 6. A comparison with Kutzelnigg's direct perturbation-theory approach[16] would also be very interesting, as final expressions of such formalism are very different to ESC ones. Work along these lines is being carried out by our research group.

TABLE VI. Gauge origin dependence of the LR-ESC relativistic corrections to the nuclear-magnetic shielding of H nucleus in HI. Numerical values correspond to the difference in a given contribution when the gauge origin is shifted from the I nucleus to the H nucleus.

| Change Δ of | | Equivalent change | |
|---|---|---|---|
| $E$(PSO,OZ;MV+Dw) | −3.75 | $-E$(Dia;MV+Dw) $-E$(PSO,OZ−$K$) Eq. (78) | −3.20 |
| $E$(FC+SD;OZ;SO) | −0.07 | $\Delta W_3$ Eq. (79) | 0.0 |
| $E$(Dia;MV+Dw) | 0.20 | $E$(Dia;MV−Dw) | 0.20 |
| $E$(OZ;PSO−$K$) | 2.98 | $-(\Delta W_1+\Delta W_4)$ Eq. (77) | 3.23 |
| $E$(PSO;OZ−$K$) | 3.00 | $E$(PSO;OZ−$K$) | 3.00 |
| $E$(FC+SD;BSO) | 0.04 | $-2\Delta W_3$ Eq. (81) | 0.0 |
| $O^{\mathrm{Diam}}(\mu_N;B)$ | −3.23 | $\Delta W_1+\Delta W_3+\Delta W_4$ Eq. (72) | −3.23 |
| $\Delta E$ | −0.83 | 0 | 0.0 |

## ACKNOWLEDGMENTS

Financial support from UBACYT (Project No. X222) and CONICET (Project Nos. PEI 6217 and PIP 5119) is gratefully acknowledged. Two of the authors (M.C.R.J.A. and C.G.G.) are members of "Carrera del Investigador," CONICET. One of the authors (J.I.M.) has a fellowship grant from Universidad de Buenos Aires.

## APPENDIX A: THE DIAMAGNETIC TERM IN THE LR-ESC APPROACH

The starting point is the pair-creation contribution $E^{\mathrm{dia}}$, Eq. (16). Consistently up to order $c^{-4}$, the following approximation holds

$$\begin{aligned}\frac{\langle n_{N+2}|\alpha A|0_N\rangle}{E_{0,N}-E_{n,N+2}} &\cong -\frac{1}{2mc^2}\left(1-\frac{E_{n,N+2}-E_{0,N}-2mc^2}{2mc^2}\right)\\ &\quad\times\langle n_{N+2}|\alpha A|0_N\rangle\\ &= -\frac{1}{2mc^2}\langle n_{N+2}|\alpha A|0_N\rangle\\ &\quad+\frac{1}{4m^2c^4}\langle n_{N+2}|([H^B,\alpha A]-2mc^2\alpha A)|0_N\rangle,\end{aligned} \tag{A1}$$

with similar expressions for the term involving the vacuum state in Eq. (16). In Eq. (A1) the first (second) term is of order $c^{-2}$ ($c^{-4}$) or lower. $H^B$ stands for the Breit Hamiltonian in the Dirac-Fock space. For the purpose of the present work, $H^B$ can be replaced by the one-body Dirac hamiltonian $H_0^D$ and we have

$$\begin{aligned}X(1) &= \frac{1}{2mc^2}([H_0^D,\alpha A]-2mc^2\alpha A)\\ &= (\beta-1)\alpha A+\frac{1}{2mc}[\alpha p,\alpha A].\end{aligned} \tag{A2}$$

Within the approximation Eq. (A1), the intermediate states in $E^{\mathrm{dia}}$ act as a projection operator on the $N+2$ particles state space $P_{N+2}$ (and two-particle states for the term involving the vacuum, $P_2$). Therefore it is obtained that

$$E^{\mathrm{dia}} = -\frac{1}{2mc^2}\langle 0_N|\alpha A P_{N+2}\alpha A|0_N\rangle + \frac{1}{2mc^2}\langle 0_N|\alpha A P_{N+2} X|0_N\rangle + \frac{1}{2mc^2}\langle \mathrm{vac}|\alpha A P_2 \alpha A|\mathrm{vac}\rangle - \frac{1}{2mc^2}\langle \mathrm{vac}|\alpha A P_{N+2} X|\mathrm{vac}\rangle. \quad \text{(A3)}$$

These expectation values can be evaluated as follows:

$$\begin{aligned}&\langle 0_N|\alpha A P_{N+2}\alpha A|0_N\rangle - \langle \mathrm{vac}|\alpha A P_{N+2}\alpha A|\mathrm{vac}\rangle \\ &= \sum_{e,p,e',p'} (\alpha A)_{p'e'}(\alpha A)_{ep}(\langle 0_N|p'e'e^+p^+|0_N\rangle - \langle \mathrm{vac}|p'e'e^+p^+|\mathrm{vac}\rangle) \\ &= \sum_{e,p,e',p'} (\alpha A)_{p'e'}(\alpha A)_{ep}\delta_{pp'}(\langle 0_N|\delta_{e'e} - e^+e'|0_N\rangle - \delta_{e'e}) = -\langle 0_N|\sum_{e,e'} (\alpha A P_p \alpha A)_{e,e'} e^+e'|0_N\rangle, \end{aligned} \quad \text{(A4)}$$

where the second-quantized forms of the operators was used, $e(p)$ stand for "electronic" (positronic) four-component Dirac spinors, and $O_{ep}=\langle e|O|p\rangle$ represent matrix elements of one-body operator $O$. Similar steps can be carried out for the second and fourth terms in Eq. (A2). It is concluded that $E^{\mathrm{dia}}$ can be expressed as an expectation value for the following one-body operators:

$$E^{\mathrm{dia}} = \frac{1}{2mc^2}\langle 0_N|\alpha A P_p \alpha A|0_N\rangle - \frac{1}{2mc^2}\langle 0_N|X P_p \alpha A|0_N\rangle, \quad \text{(A5)}$$

where the first term yields the diamagnetic term in the nonrelativistic limit. In order to carry out the leading-order ESC reduction of Eq. (A5), the projector $P_p$ in the space of four-component Dirac spinors (splitted into $2\times 2$ blocks) can be written as

$$P_p = \begin{bmatrix} x^2 & -x \\ -x & 1-x^2 \end{bmatrix}, \quad \text{(A6)}$$

where $x=\sigma p/2mc$. Therefore

$$\alpha A P_p \alpha A = \begin{bmatrix} \sigma A(1-x^2)\sigma A & -\sigma A x \sigma A \\ -\sigma A x \sigma A & \sigma A x^2 \sigma A \end{bmatrix} \quad \text{(A7)}$$

and

$$X P_p \alpha A = \begin{bmatrix} -[x,\sigma A]x\sigma A & 0 \\ 2\sigma A x \sigma A + [x,\sigma A]\sigma A & 0 \end{bmatrix}, \quad \text{(A8)}$$

where only terms up to quadratic in $x$ were retained. In order to evaluate the expectation values in Eq. (A5) it is necessary to consider expectation values of all operators between positive-energy four-component spinors,

$$\begin{aligned}\langle \phi^4|O|\phi^4\rangle &= \langle \phi^L|O^{LL}|\phi^L\rangle + \langle \phi^L|O^{LS}|\phi^S\rangle + \langle \phi^S|O^{SL}|\phi^L\rangle + \langle \phi^S|O(1)|\phi^S\rangle \\ &= \langle \tilde{\phi}|O^{LL} - \left\{O^{LL}, \frac{x^2}{2}\right\} + O^{LS}x + xO^{SL} + xO^{SS}x|\tilde{\phi}\rangle, \end{aligned} \quad \text{(A9)}$$

where only terms up to order $x^2$ need be retained, and the expectation values are now to be carried out for the two-component Breit-Pauli spinors. Summing up, Eq. (A5) is re-expressed as

$$E^{\mathrm{dia}} = \frac{1}{2mc^2}\langle \tilde{0}|A^2|\tilde{0}\rangle + \langle \tilde{0}|O^{\mathrm{Diam,LR}}|\tilde{0}\rangle, \quad \text{(A10)}$$

where

$$O^{\mathrm{Diam,LR}} = -\frac{1}{8m^3c^4}((\sigma p\sigma A)^2 + 2\sigma A p^2 \sigma A + (\sigma A \sigma p)^2 + \{p^2, A^2\}), \quad \text{(A11)}$$

as indicated in Eq. (23). Due to the factor $c^{-4}$, the corresponding expectation value must be carried out for the nonrelativistic (i.e., Schrödinger) ground state.

## APPENDIX B: ESC REDUCTION OF OPERATORS OF THE MINIMAL-COUPLING APPROACH

The ESC reduction of operators of the minimal-coupling approach is as follows. In the case of the linear operator Eq. (28), matrix elements between different four-component spinors are considered

$$\langle \phi_i^4|\beta O^1|\phi_j^4\rangle \cong \langle \phi_i^L|O^1|\phi_j^L\rangle - \langle \phi_i^S|O^1|\phi_j^S\rangle. \quad \text{(B1)}$$

Consistently to order $c^{-3}$, making use of Eqs. (17)–(19), Eq. (B1) can be expressed as

$$\begin{aligned}&\langle \phi_i^L|O^1|\phi_j^L\rangle - \langle \phi_i^S|O^1|\phi_j^S\rangle \\ &\cong \langle \tilde{\phi}_i|\left(1-\frac{p^2}{8m^2c^2}\right)O^1\left(1-\frac{p^2}{8m^2c^2}\right)|\tilde{\phi}_j\rangle - \langle \tilde{\phi}_i|\frac{\sigma p}{2mc}O^1\frac{\sigma p}{2mc}|\tilde{\phi}_j\rangle \\ &\cong \langle \tilde{\phi}_i|O^1 - \left\{\frac{p^2}{8m^2c^2}, O^1\right\} - \frac{1}{4m^2c^2}\sigma p\cdot O^1\cdot \sigma p|\tilde{\phi}_j\rangle, \end{aligned} \quad \text{(B2)}$$

yielding the final result, Eq. (34).

In the case of the bilinear operator Eq. (29), the expectation value is considered.

$$\begin{aligned}&\langle \phi^4|\frac{1}{2mc^2}\beta A^2 - \frac{1}{4m^2c^3}\{\alpha A, pA\}|\phi^4\rangle \\ &= \langle \phi^L|\frac{1}{2}A^2|\phi^L\rangle - \langle \phi^S|\frac{1}{2}A^2|\phi^S\rangle - \frac{1}{4m^2c^3}(\langle \phi^L|\{\sigma p, \sigma A\}|\phi^S\rangle + \langle \phi^S|\{\sigma p, \sigma A\}|\phi^L\rangle), \end{aligned} \quad \text{(B3)}$$

where we have used that

$$pA = \tfrac{1}{2}(\{\sigma p, \sigma A\} - \sigma B), \quad \text{(B4)}$$

$$A \cdot B = 0. \tag{B5}$$

Inserting the relation of the small and large components with the Pauli two-spinors, Eqs. (17)–(19) consistently to the order $c^{-3}$ the operator Eq. (35) is obtained.

## APPENDIX C: FORMAL RELATIONS PROVING THE GAUGE ORIGIN INVARIANCE OF THE LR-ESC APPROACH

Formal relations for gauge invariance are hereby proven.

(a) Identity 1:

$$\begin{aligned}\Delta E(O^1(B);O^3(\mu_N)) &= E\left(\frac{1}{mc}\delta A_B \cdot p; O^3(\mu_N)\right)\\ &= \frac{1}{c}\delta A_{B,\alpha} E(i[H,r_\alpha];O^3(\mu_N))\\ &= \frac{i}{c}\delta A_{B,\alpha}\langle [r_\alpha;O^{3S}(\mu_N)]\rangle, \end{aligned}\tag{C1}$$

where the Greek indices refer to Cartesian components and a sum over repeated indices is implied in all expressions. The commutator,

$$\begin{aligned}\left[r_\alpha; p^2 \frac{\mu_N \cdot L_N}{r_N^3}\right] &= p^2\left[r_\alpha; \frac{(\mu_N \times r_N)\cdot p}{r_N^3}\right]\\ &\quad + [r_\alpha;p^2]\frac{\mu_N \cdot L_N}{r_N^3}\\ &= ip^2 A_{N,\alpha} + 2ip_\alpha (A_N \cdot p), \end{aligned}\tag{C2}$$

can be used to obtain

$$\begin{aligned}\frac{i}{c}\delta A_{B,\alpha}\langle [r_\alpha;O^{3S}(\mu_N)]\rangle &= \frac{1}{4m^3c^4}\langle 4(\delta A_B \cdot p)(A_N \cdot p)\\ &\quad + 2(\delta A_B \cdot A_N)p^2\rangle, \end{aligned}\tag{C3}$$

as given in Eq. (77).

(b) Identity 2:

$$\begin{aligned}\Delta E(O^{1T}(\mu_N);O^{3T}(B)) &= \frac{1}{2m^2c^3}E(O^{1T}(\mu_N);\sigma(\nabla V_C\\ &\quad \times \delta A_B)). \end{aligned}\tag{C4}$$

The second operator can be rewritten as

$$\begin{aligned}\sigma(\nabla V_C \times \delta A_B) &= \sigma([p,V_C]\times \delta A_B)\\ &= \sigma([p,H]\times \delta A_B)\\ &= [\delta A_B(\sigma \times p);H]. \end{aligned}\tag{C5}$$

Applying Eq. (75), it is obtained that

$$\begin{aligned}\Delta E(O^{1T}(\mu_N);O^{3T}(B)) &= \frac{i}{2m^2c^3}\langle [O^{1T}(\mu_N);\delta A_B(\sigma \times p)]\rangle\\ &= \frac{i}{4m^3c^4}\langle [\sigma \cdot B_N;\sigma(p\times \delta A_B)]\rangle\\ &= \frac{i}{4m^3c^4}\langle [B_{N,\alpha};(p\times \delta A_B)_\alpha]\rangle\\ &= \frac{1}{4m^3c^4}\langle \delta A_B \cdot \nabla \times B_N\rangle = -2\Delta W_3, \end{aligned}\tag{C6}$$

as given in Eq. (81).

(c) Identity 3:

$$\begin{aligned}&\Delta E(O^{1T}(\mu_N);O^{1S}(B);H^{R,T})\\ &= \frac{1}{mc}E(O^{1T}(\mu_N);\delta A_B \cdot p;H^{R,T})\\ &= -iE([O^{1T}(\mu_N),\delta A_B \cdot r];H^{R,T})\\ &\quad + iE(O^{1T}(\mu_N);[\delta A_B \cdot r,H^{R,T}]). \end{aligned}\tag{C7}$$

Now taking into account that

$$[O^{1T}(\mu_N),r] = 0, \tag{C8}$$

$$[r,H^{R,T}] = -\frac{1}{4m^2c^2}[\sigma \times p,H], \tag{C9}$$

it is finally obtained [see Eq. (A11)]

$$\begin{aligned}\Delta E(O^{1T}(\mu_N);O^{1S}(B);D^T) &= -\frac{1}{8m^3c^4}\langle \delta A_B \cdot \nabla \times B_N\rangle\\ &= \Delta W_3, \end{aligned}\tag{C10}$$

as indicated in Eq. (79).

(d) Identity 4:

$$\begin{aligned}&\Delta E(O^{1S}(\mu_N);O^{1S}(B);H^{R,S})\\ &= \frac{1}{mc}E(O^{1S}(\mu_N);\delta A_B \cdot p;H^{R,S})\\ &= -\frac{i}{c}E([O^{1S}(\mu_N),\delta A_B \cdot r];H^{R,S})\\ &\quad + \frac{i}{c}E(O^{1S}(\mu_N);[\delta A_B \cdot r,H^{RS}]). \end{aligned}\tag{C11}$$

Taking into account that

$$[O^{1S}(\mu_N),r] = \frac{1}{mc}[A_N \cdot p,r] = -\frac{i}{mc}A_N, \tag{C12}$$

$$[r_\alpha,H^{R,S}] = -\frac{i}{2m^3c^2}p^2 p_\alpha, \tag{C13}$$

it is obtained that

$$\begin{aligned}&\Delta E(O^{1S}(\mu_N);O^{1S}(B);D^S)\\ &= -\frac{1}{mc^2}E(\delta A_B \cdot A_N;D^S)\\ &\quad + \frac{1}{2m^3c^3}E(O^{1S}(\mu_N);p^2(p\cdot \delta A_B))\\ &= -\frac{1}{mc^2}E(\delta A_B \cdot A_N;D^S)\\ &\quad - \Delta E(O^{1S}(\mu_N);O^{3S}(B)), \end{aligned}\tag{C14}$$

which is the result Eq. (78).

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