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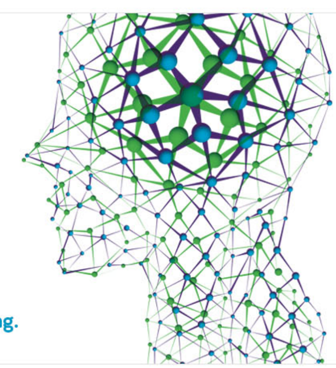

Mean field linear response within the elimination of the small component formalism to evaluate relativistic effects on magnetic properties

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The linear response within the elimination of the small component formalism is aimed at obtaining the leading order relativistic corrections to magnetic molecular properties in the context of the elimination of the small component approximation. In the present work we extend the method in order to include two-body effects in the form of a mean field one-body operator. To this end we consider the four-component Dirac-Hartree-Fock operator as the starting point in the evaluation of the second order relativistic expression of magnetic properties. The approach thus obtained is the fully consistent leading order approximation of the random phase approximation four-component formalism. The mean field effect on the relativistic corrections to both the diamagnetic and paramagnetic terms of magnetic properties taking into account both the Coulomb and Breit two-body interactions is considered. © *2006 American Institute of Physics*.
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I. INTRODUCTION

The correct evaluation of relativistic effects on magnetic molecular properties is a subject of major current interest.[1] This is particularly true for NMR spectroscopic parameters such as the nuclear magnetic shielding tensor and the (nuclear) spin-spin coupling tensor in molecules containing heavy atoms. At present theoretical methods have evolved in such a way that quantitative precision is becoming available in the study of these parameters. At the four-component level, theoretical methods based on the linear response random phase approximation (RPA) formalism[2–5] and direct perturbation theory approaches[6,7] were presented. Numerical results of the four-component approach[5] are taken as benchmark values to test the accuracy of two-component methods.

In fact, two-component methods are attractive from the computational point of view, since explicit construction of the "small component" of four-component spinors is avoided. This is the case of the zeroth order regular approximation[8,9] (ZORA) and related approaches, the Douglas-Kroll-Hess formalism[10–12] or Breit Pauli[13–17] two-component formalism. In most cases, these approaches are based on one-body operators only or make explicit use of the no-pair approximation to the Hamiltonian which contains the magnetic field interaction. The linear response within the elimination of the small component (LR-ESC) approach[18–20] is also aimed at obtaining the leading order relativistic effect within a two-component formalism. It is based in a four-component Rayleigh-Schrödinger perturbation theory expression in Dirac-Fock space. Since the unperturbed Hamiltonian does not contain the magnetic interaction, explicit electron-positron pair creation and destruction operators need be considered. The LR-ESC formalism is fully consistent up to order c^{-2} within a many-body approach.

The four-component RPA formalism contains the influence of two-body effects in the form of a one-body mean field operator. Therefore, strictly speaking, a two-component approach which may be compared to such four-component results should include a mean field description of two-body effects. In this line, spin-orbit (SO) mean field effects were considered in previous works.[21,22] In the present work we present a mean field LR-ESC approach based on the Dirac-Hartree-Fock Hamiltonian, including both the Coulomb and Breit terms of the interaction. We follow closely all steps of the derivation of the LR-ESC approach in this context. As a consequence, we obtain explicit mean field contributions to the leading order relativistic correction of magnetic properties. The theoretical approach is presented in Sec. II. The starting point is the four-component Dirac-Hartree-Fock Hamiltonian. Mean field corrections to the magnetically unperturbed molecular states are obtained defining two-component "mean field" Pauli spinors in Sec. II A. The mean field SO operator of Refs. 21 and 22 is obtained as a particular case. Mean field magnetic field dependent operators are also obtained in Sec. II B. Results obtained are discussed in Sec. III, together with a numerical evaluation of the Coulomb mean field correction to the diamagnetic term of the nuclear magnetic shielding constant. Concluding remarks are presented in Sec. IV.

II. THEORY

The starting point in the LR-ESC scheme is a fully relativistic second order Rayleigh-Schrödinger perturbation theory (RSPT2) expression of magnetic properties in Dirac-Fock space:[18]

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$$E^{(2)} = \sum_{n\neq 0} \frac{\langle 0|\alpha A|n\rangle\langle n|\alpha A|0\rangle}{E_0 - E_n} - \sum_n \frac{\langle \text{vac}|\alpha A|n\rangle\langle n|\alpha A|\text{vac}\rangle}{E_{\text{vac}} - E_n}, \quad (1)$$

where α stand for the 4×4 Dirac matrices and A stands for the vector potential of a static magnetic field; $\{|0\rangle, |n\rangle\}$ stand for stationary solutions of the Breit Hamiltonian in Dirac-Fock space:

$$H^B = h^D + U^C + U^B, \quad (2)$$

where

$$h^D = c\alpha p + \beta mc^2 + V_C \quad (3)$$

is the one-body Dirac Hamiltonian in the presence of the electrostatic potential of the nuclei V_C and the Coulomb and Breit interactions are given by

$$U^C = \frac{1}{r_{12}}, \quad (4)$$

$$U^B = \alpha_1 \cdot \overleftrightarrow{O}_{12} \cdot \alpha_2, \quad (5)$$

$$\overleftrightarrow{O}_{12} = -\frac{1}{2r_{12}}\left(\overleftrightarrow{1} + \frac{\mathbf{r}_{12}\cdot\mathbf{r}_{12}^t}{r_{12}^2}\right), \quad \mathbf{r}_{12} = \mathbf{r}_1 - \mathbf{r}_2. \quad (6)$$

Consistent with the QED picture, the Dirac-Fock space can be spanned by the solutions of the one-body Dirac Hamiltonian. Positive energy solutions are identified with electronic states, and negative energy solutions are reinterpreted as positive energy positronic states. The last term in Eq. (1) is a renormalization of the energy of the vacuum state $|\text{vac}\rangle$.[23]

In principle, an exact treatment of the Breit Hamiltonian should be independent of the choice of one-particle states used to span the Dirac-Fock space. However, when approximations are sought in which fixed particle number states are considered, this choice may be of major importance for the accuracy of the approximation. In the present work the one-particle electronic and positronic states considered in spanning the Dirac-Fock space are the solutions of the Dirac-Hartree-Fock (DHF) equations.[24] The DHF Hamiltonian is given by

$$F^{\text{DHF}} = h^D + V^{\text{DHF}}, \quad (7)$$

where V^{DHF} is the mean field interaction potential. It is defined self-consistently to contain the N lowest positive energy four-component DHF spinors taking into account both the Coulomb and Breit interactions. On the basis of the DHF Hamiltonian, the Breit Hamiltonian is now partitioned as

$$H^B = F^{\text{DHF}} + U^C + U^B - V^{\text{DHF}}, \quad (8)$$

i.e., the two-body terms are now given by the fluctuation potential. In this way, the one-particle solutions defining electronic and positronic states include the mean field effect of the interaction. The Breit Hamiltonian connects different particle number manifolds of the same charge $Q=-eN$ for a system with N electrons in the nonrelativistic limit.

For the purposes of the present work, the set of states $\{|0\rangle, |n\rangle\}$ needs only be considered within the fixed particle number approximation. The ground state $|0_N\rangle$ is an N-particle state. Taking into account that the magnetic interaction may connect different particle number manifolds, the expression of $E^{(2)}$, Eq. (1), can be split as

$$E^{\text{para}} = \sum_{|n_N\rangle\neq|0_N\rangle} \frac{\langle 0_N|\alpha A|n_N\rangle\langle n_N|\alpha A|0_N\rangle}{E_{0,N} - E_{n,N}}, \quad (9)$$

$$E^{\text{dia}} = \sum_{n,N+2} \frac{\langle 0_N|\alpha A|n_{N+2}\rangle\langle n_{N+2}|\alpha A|0_N\rangle}{E_0 - E_{n,N+2}} - \sum_{n,N=2} \frac{\langle \text{vac}|\alpha A|n_{N=2}\rangle\langle n_{N=2}|\alpha A|\text{vac}\rangle}{E_{\text{vac}} - E_{n,N=2}}, \quad (10)$$

in agreement with Ref. 3. In the LR-ESC scheme presented in Ref. 18, different results depend heavily on the choice of one-particle states defining the fixed particle number manifolds of Dirac-Fock space. In the present work the LR-ESC lowest order relativistic effects on molecular properties are rederived taking into account the mean field one-particle states of the DHF approximation.

A. Leading order mean field ESC states

States $\{|0_N\rangle, |n_N\rangle\}$ are built up as configuration interaction (CI) expansions of Slater determinants of positive energy four-component DHF spinors:[24]

$$F^{\text{DHF}}|\phi^4\rangle = (mc^2 + E)|\phi^4\rangle, \quad (11)$$

where the mean field potential has the form

$$V^{\text{DHF}} = \sum_\mu J_\mu{}^{(4)} - K_\mu{}^{(4)}. \quad (12)$$

The direct and exchange mean field operators are defined by their corresponding matrix elements for the Coulomb and Breit operators:

$$\langle\phi^4|J_\mu{}^{(4)}|\phi'^4\rangle = \langle\phi^4\phi_\mu^4|U^C + U^B|\phi'^4\phi_\mu^4\rangle, \quad (13)$$

$$\langle\phi^4|K_\mu{}^{(4)}|\phi'^4\rangle = \langle\phi^4\phi_\mu^4|U^C + U^B|\phi_\mu^4\phi'^4\rangle. \quad (14)$$

Partitioning four-component spinors into large and small components, the mean field operator can be split as (see, e.g., Ref. 25)

$$V^{\text{DHF}} = \begin{bmatrix} V^{LL} & V^{LS} \\ V^{SL} & V^{SS} \end{bmatrix}. \quad (15)$$

In terms of such spinors, the leading order ESC approximation is obtained as follows:

$$(c\sigma p + V^{LS})|\phi^S\rangle + (V_C + V^{LL})|\phi^L\rangle = E|\phi^L\rangle, \quad (16)$$

$$(c\sigma p + V^{SL})|\phi^L\rangle + (V_C + V^{SS})|\phi^S\rangle = (E + 2mc^2)|\phi^S\rangle. \quad (17)$$

The small component can be expressed as the following function of the large one:

$$|\phi^S\rangle = (E + 2mc^2 - V_C - V^{SS})^{-1}(c\sigma p + V^{SL})|\phi^L\rangle, \tag{18}$$

and the leading order ESC approximation is

$$|\phi^S\rangle = \frac{1}{2mc^2}\left(1 - \frac{E - V_C - V^{SS}}{2mc^2}\right)(c\sigma p + V^{SL})|\phi^L\rangle. \tag{19}$$

Therefore, the mean field equation for the large component can be expressed as

$$\left[(c\sigma p + V^{LS})\frac{1}{2mc^2}\left(1 - \frac{E - V_C - V^{SS}}{2mc^2}\right)(c\sigma p + V^{SL}) + V_C + V^{LL}\right]|\phi^L\rangle = E|\phi^L\rangle. \tag{20}$$

In order to carry out a consistent approximation of order c^{-2}, it is necessary to specify the dependence of the mean field operators on this parameter. This analysis for both the Coulomb and Breit operators is carried out in Appendix A. The leading order of both V^{LL} and V^{SS} is c^0, and that of V^{LS} is c^{-1}. Therefore, consistent to order c^{-2}, the usual procedure leading to the Pauli Hamiltonian can be carried out in order to transform the previous equation into an eigenvalue problem for a Hermitian operator. We introduce the mean field Pauli spinor $|\phi\rangle$, which is related to the large component of the four-component spinor as indicated in Eq. (21):

$$|\phi^L\rangle = N|\phi\rangle, \tag{21}$$

where, consistent to order c^{-2}, N is given by

$$N = \left(1 - \frac{x^2}{2}\right) \tag{22}$$

and operator x is given by

$$x = \frac{\sigma p}{2mc}. \tag{23}$$

Equation (20) thus transforms into the following equation for a Hermitian operator yielding the mean field Pauli spinors:

$$N\left[\frac{p^2}{2m} + V_C + V^{LL} + xV^{SL} + V^{LS}x + x(V_C + V^{SS})x\right]N|\phi\rangle = E|\phi\rangle. \tag{24}$$

The zeroth order operator contains the Schrödinger Hamiltonian plus the zeroth order contribution of the mean field operator V^{LL}. The mean field operator up to order c^{-2} is

$$V^{\mathrm{mf}} = N[xV^{SL} + V^{LS}x + xV^{SS}x + V^{LL}]N = (N\ Nx)\begin{bmatrix} V^{LL} & V^{LL} \\ V^{SL} & V^{SS}\end{bmatrix}\begin{pmatrix} N \\ xN\end{pmatrix}. \tag{25}$$

Consistent to the order c^{-2}, only the leading term of the small component of a given occupied spinor as a function of the corresponding mean field Pauli spinor is needed to define V^{mf}. To that order, this relation is the same as in the usual Pauli scheme (there are no extra terms from the mean field operator). As a consequence, the operator in Eq. (25) is precisely the one needed to obtain from the Coulomb and Breit interaction potentials the direct and exchange contributions of the two-body terms of the Pauli Hamiltonian (see, e.g., Ref. 26):

$$V^{\mathrm{mf}} = \sum_\mu J_\mu - K_\mu, \tag{26}$$

where the operators act now on two-component mean field Pauli spinors in the following way:

$$\langle\phi|J_\mu|\phi'\rangle = \langle\phi\phi_\mu|D^{(2)}|\phi'\phi_\mu\rangle \tag{27}$$

$$\langle\phi|K_\mu|\phi'\rangle = \langle\phi\phi_\mu|D^{(2)}|\phi_\mu\phi'\rangle \tag{28}$$

for the operator[26]

$$D^{(2)} = \frac{1}{r_{12}} - \frac{1}{2m^2c^2}\frac{r_{12}^2(p_1p_2) + (r_{12}(r_{12}\cdot p_2)p_1)}{r_{12}^3} - \frac{\pi}{m^2c^2}\delta(r_{12}) - \frac{1}{4m^2c^2}(\sigma_1\cdot(r_{12}\times p_1) - \sigma_2\cdot(r_{12}\times p_2)) + \frac{1}{2m^2c^2}(\sigma_1\cdot(r_{12}\times p_2) - \sigma_2\cdot(r_{12}\times p_1)) - \frac{2\pi}{3m^2c^2}(\sigma_1\cdot\sigma_2)\delta(r_{12}) + \frac{1}{4m^2c^2}\frac{r_{12}^2(\sigma\cdot 1\sigma_2) - 3(\sigma_1 r_{12})(\sigma_2 r_{12})}{r_{12}^5}. \tag{29}$$

The first term is the zeroth order Coulomb interaction, the second and third ones are the so-called orbit-orbit (OO) interaction and two-body Darwin term, the fourth term is the spin-same-orbit interaction, the fifth one contains the spin-other-orbit interactions, and the remaining terms describe spin-spin interactions, both Fermi contact (FC) and spin dipolar (SD). The equation for the two-component mean field Pauli spinors has thus the form

$$[H^P + V^{\mathrm{mf}}]|\phi\rangle = E|\phi\rangle, \tag{30}$$

where H^P is the one-body Pauli Hamiltonian:

$$H^P = H^{\mathrm{Sch}} + H^R, \tag{31}$$

where H^{Sch} is the one-body Schrödinger Hamiltonian and H^R gathers the relativistic spin-orbit (SO), mass-velocity (Mv), and Darwin (Dw) corrections:

$$H^R = \frac{1}{4m^2c^2}\sigma\cdot(\nabla V_C \times p) - \frac{1}{8m^3c^2}p^4 + \frac{1}{4m^2c^2}\nabla^2 V_C. \quad (32)$$

It is thus seen that the leading order ESC scheme applied to the DHF Hamiltonian leads naturally to a mean field approximation of the Breit-Pauli Hamiltonian.

In order to obtain relativistic effects perturbatively in $1/c$, it is useful to separate the mean field operator as

$$V^{\mathrm{mf}} = V^{\mathrm{mf}(0)} + V^{\mathrm{mf}(2)}, \quad (33)$$

where $V^{\mathrm{mf}(0)}$ contains the Coulomb and exchange interactions and $V^{\mathrm{mf}(2)}$ the relativistic effects of $D^{(2)}$. The nonrelativistic limit of Eq. (30) is first considered. These are the standard Hartree-Fock equations for nonrelativistic spin-orbitals, obtained self-consistently.

The leading order relativistic correction is obtained by introducing the leading order operators of the Pauli one-body Hamiltonian and the leading order corrections to the mean field operators. Due to the factor $1/c^2$ in $V^{\mathrm{mf}(2)}$, only the nonrelativistic occupied spin-orbitals are involved in the construction of this operator. It is interesting to note that, as a consequence, $V^{\mathrm{mf}(2)}$ behaves strictly as a one-body operator in this approximation. Unlike $V^{\mathrm{mf}(0)}$ it has not to be self-consistently corrected in terms of the relativistically modified spin-orbitals. The set of equations is therefore standard coupled Hartree-Fock equations for a one-body operator of the form

$$H^{R,\mathrm{mf}} = H^R + V^{\mathrm{mf}(2)}. \quad (34)$$

Within the terms which are obtained in $V^{\mathrm{mf}(2)}$, one can readily recognize the mean field spin-orbit (SO) operator of Refs. 21 and 22, and mean field Darwin, orbit-orbit, and spin-spin operators as well, in the form of direct and exchange operators.

B. Leading order magnetic field dependent operators

1. Paramagnetic term

In the paramagnetic term, Eq. (9), matrix elements of the magnetic perturbation between different positive energy four-component spinors have to be evaluated. They must be reexpressed in terms of mean field Pauli spinors up to order c^{-3} in order to obtain the leading order magnetic field dependent relativistic corrections. Such matrix elements connect the large and small components of a given four-component spinor:

$$\langle \phi^4|\alpha A|\phi'^4\rangle = \langle \phi^L|\sigma A|\phi'^S\rangle + \langle \phi^S|\sigma A|\phi'^L\rangle. \quad (35)$$

Consider, for instance, the first term in Eq. (35):

$$\begin{aligned}\langle \phi^L|\sigma A|\phi'^S\rangle &= \langle \phi^L|\sigma A\left(\frac{\sigma p}{2mc} - \frac{(E'-V_C-V^{SS})(\sigma p)}{4m^2c^3} + \frac{V^{SL}}{2mc^2}\right)|\phi'^L\rangle \\ &= \langle \phi|N\sigma A\left(\frac{\sigma p}{2mc}N - \frac{(E'-V_C-V^{SS})\sigma p}{4m^2c^3} + \frac{V^{SL}}{2mc^2}\right)|\phi'\rangle, \end{aligned} \quad (36)$$

where we have used Eq. (19). Consistent up to order c^{-3}, the "normalization" operator N, Eq. (22), needs only be introduced in the first term, and the two last terms need only be calculated for nonrelativistic mean field spinors. The mean field contributions to the small component are collected in the terms

$$\frac{1}{4m^2c^3}(V^{SS}\sigma p + 2mcV^{SL}). \quad (37)$$

Due to the factor c^{-3}, the operators in brackets need only be evaluated to the order c^0. We consider separately the Coulomb and Breit contributions to these terms. For the Coulomb operator it holds (details of this derivation are presented in Appendix A)

$$V^{SS} = J, \quad (38)$$

$$V^{SL} = -\frac{\sigma p}{2mc}K + \frac{i}{2mc}\sigma\cdot K\left(\frac{\mathbf{r}_{12}}{r_{12}^3}\right), \quad (39)$$

where J and K stand for the nonrelativistic Coulomb and exchange operators and $K(\mathbf{r}_{12}/r_{12}^3)$ stands for an exchange operator defined by means of the corresponding matrix elements:

$$\langle \phi_m|K\left(\frac{r_{12}}{r_{12}^3}\right)|\phi_n\rangle = \sum_\mu \langle \phi_m\phi_\mu|\frac{r_{12}}{r_{12}^3}|\phi_\mu\phi_n\rangle. \quad (40)$$

For the Breit contribution it holds that

$$V^{SS}\sigma p + 2mcV^{SL} = \sigma\cdot\mathbf{V}^B(1), \quad (41)$$

where $\mathbf{V}^B(1)$ is a one-body mean field Breit operator defined as

$$\begin{aligned}\langle m|\mathbf{V}^B(1)|n\rangle &= \sum_\mu \langle m\phi_\mu|\mathbf{V}^B(1,2)|n\phi_\mu\rangle \\ &\quad - \langle m\phi_\mu|\mathbf{V}^B(1,2)|\phi_\mu n\rangle \end{aligned} \quad (42)$$

for the two-body operator:

$$\mathbf{V}^B(1,2) = 2\overleftrightarrow{O}_{12}\cdot p_2 - \sigma_2 \times \frac{\mathbf{r}_{12}}{r_{12}^3}. \tag{43}$$

Details of this result are given in Appendix B.

In order to eliminate the eigenvalue E' in Eq. (36) and obtain a spinor independent operator, the following zeroth order commutator is introduced:

$$\begin{aligned}(E' - V_C - J)\sigma p &= \sigma p(E' - V_C - J) + [(E' - V_C - J), \sigma p] \\ &= \sigma p(E' - V_C - J) - i\sigma \cdot \nabla(V_C + J).\end{aligned} \tag{44}$$

Taking into account Eqs. (38)–(41) and (44), the matrix element in Eq. (36) can be expressed as

$$\begin{aligned}&\left\langle \phi \middle| N\sigma A\left(\frac{\sigma p}{2mc}N - \frac{(E' - V_C - V^{SS})\sigma p}{4m^2c^3} + \frac{V^{SL}}{2mc^2}\right)\middle|\phi'\right\rangle \\ &= \left\langle \phi \middle| N\sigma A\frac{\sigma p}{2mc}N\middle|\phi'\right\rangle + \left\langle \phi \middle| \sigma A\left(-\frac{1}{4m^2c^3}\sigma p(E' - V_C - J + K) + \frac{i\sigma}{4m^2c^3}\cdot\left(\nabla V_C + \nabla J + K\left(\frac{\mathbf{r}_{12}}{r_{12}^3}\right) - i\mathbf{V}^B(1)\right)\right)\middle|\phi'\right\rangle.\end{aligned} \tag{45}$$

The nonrelativistic Hartree-Fock equation can now be used to eliminate the state dependent eigenvalue:

$$(E' - V_C - J + K)|\phi'\rangle = \frac{p^2}{2m}|\phi'\rangle. \tag{46}$$

As a consequence, in agreement with the notation of Ref. 18, the following magnetic field dependent operators are found:

$$O^1 = \frac{1}{2mc}\{\sigma p, \sigma A\}, \tag{47}$$

$$O^3 = -\frac{1}{8mc^2}\{O^1, p^2\} - \frac{1}{8m^3c^3}(\sigma A\sigma p p^2 + p^2\sigma p\sigma A) + \frac{i\sigma}{2m^2c^3}\cdot\left(\nabla(V_C + J) + K\left(\frac{r_{12}}{r_{12}^3}\right) - i\mathbf{V}^B(1)\right). \tag{48}$$

Explicitly, the mean field contribution to the relativistic operator O^3 is given by

$$O^{3,\mathrm{mf}} = \frac{i\sigma}{2m^2c^3}\cdot\left(\nabla J + K\left(\frac{r_{12}}{r_{12}^3}\right) - i\mathbf{V}^B(1)\right). \tag{49}$$

The paramagnetic term E^{para} expanded up to order c^{-4} is thus

$$E^{\mathrm{para}} = E(O^1;O^1) + E(O^1;O^3) + E(O^1;O^1;H^{R,\mathrm{mf}}), \tag{50}$$

where $E(A;B)$ stands for a second order Rayleigh-Schrödinger perturbation theory expression based on the Schrödinger Hamiltonian,

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

and $E(A;B;C)$ stands for a third order Rayleigh-Schrödinger perturbation theory expression:

$$\begin{aligned}E(A;B;C) = \sum_{n,m\neq 0}&\frac{\langle 0|A|n\rangle\langle n|B - \langle B\rangle|m\rangle\langle m|C|0\rangle}{(E_0 - E_n)(E_0 - E_m)} \\ &+ \frac{\langle 0|B|n\rangle\langle n|C - \langle C\rangle|m\rangle\langle m|A|0\rangle}{(E_0 - E_n)(E_0 - E_m)} \\ &+ \frac{\langle 0|C|n\rangle\langle n|A - \langle A\rangle|m\rangle\langle m|B|0\rangle}{(E_0 - E_n)(E_0 - E_m)} + \mathrm{c.c.}\end{aligned} \tag{52}$$

In Eq. (50), the first term is the nonrelativistic expression of the paramagnetic term of magnetic properties, the second term contains the so-called active relativistic effects on the paramagnetic term, as it involves explicitly field dependent relativistic operators, and the third one gathers the so-called passive effects, i.e., those originating in relativistic effects on the magnetically unperturbed molecular states. Explicitly, the mean field contribution is given by

$$E^{\mathrm{para,mf}} = E(O^1;O^{3,\mathrm{mf}}) + E(O^1;O^1;V^{\mathrm{mf}(2)}). \tag{53}$$

2. Diamagnetic term

The starting point is the pair creation contribution E^{dia}; Eq. (10). Consistent up to order c^{-4}, the following approximation holds:[18]

$$\begin{aligned}\frac{\langle n_{N+2}|\alpha A|0_N\rangle}{E_{0,N} - E_{n,N+2}} &\cong -\frac{1}{2mc^2}\left(1 - \frac{E_{n,N+2} - E_{0,N} - 2mc^2}{2mc^2}\right)\times\langle n_{N+2}|\alpha A|0_N\rangle \\ &= -\frac{1}{2mc^2}\langle n_{N+2}|\alpha A|0_N\rangle + \frac{1}{4m^2c^4}\langle n_{N+2}|([H^B, \alpha A] - 2mc^2\alpha A)|0_N\rangle,\end{aligned} \tag{54}$$

with similar expressions for the term involving the vacuum state in Eq. (10). In Eq. (54) the first (second) term is of order $c^{-2}(c^{-4})$ or lower. H^B stands for the Breit Hamiltonian in Dirac-Fock space. In the context of the present work, the Dirac-Fock space is defined by the solutions of the one-body Dirac-Hartree-Fock operator. Therefore, in order to obtain the mean field approximation, H^B can be replaced by the one-body Dirac-Hartree-Fock operator and we have

$$\begin{aligned}X(1) &= \frac{1}{2mc^2}([F^{\mathrm{DHF}}, \alpha A] - 2mc^2\alpha A) \\ &= (\beta - 1)\alpha A + \frac{1}{2mc}[\alpha p, \alpha A] + \frac{1}{2mc^2}[V^{\mathrm{DHF}}, \alpha A]\end{aligned} \tag{55}$$

and

$$[V^{\mathrm{DHF}},\alpha A]=\begin{bmatrix} 0 & V^{LL}\sigma A-\sigma A V^{SS} \\ V^{SS}\sigma A-\sigma A V^{LL} & 0 \end{bmatrix} \quad (56)$$

up to order c^0, as we need because of the factor $1/2mc^2$ in the last term of Eq. (55). Within the approximation Eq. (54), the intermediate states in E^{dia} act as a projection operator on the $N+2$ particle state space P_{N+2} (and two-particle states for the term involving the vacuum, P_2):

$$P_{N+2}=\sum_n |n_{N+2}\rangle\langle n_{N+2}|. \quad (57)$$

Therefore it is obtained that

$$\begin{aligned} E^{\mathrm{dia}} &= -\frac{1}{2mc^2}\langle 0_N|\alpha A P_{N+2}\alpha A|0_N\rangle \\ &+\frac{1}{2mc^2}\langle 0_N|\alpha A P_{N+2}X|0_N\rangle \\ &+\frac{1}{2mc^2}\langle \mathrm{vac}|\alpha A P_2\alpha A|\mathrm{vac}\rangle \\ &-\frac{1}{2mc^2}\langle \mathrm{vac}|\alpha A P_2 X|\mathrm{vac}\rangle. \end{aligned} \quad (58)$$

These expectation values can be evaluated as follows:

$$\begin{aligned} &\langle 0_N|\alpha A P_{N+2}\alpha A|0_N\rangle-\langle \mathrm{vac}|\alpha A P_2\alpha A|\mathrm{vac}\rangle \\ &=\sum_{e,p,e',p'}(\alpha A)_{p'e'}(\alpha A)_{ep}(\langle 0_N|p'e'e^+p^+|0_N\rangle \\ &\quad-\langle \mathrm{vac}|p'e'e^+p^+|\mathrm{vac}\rangle) \\ &=\sum_{e,p,e',p'}(\alpha A)_{p'e'}(\alpha A)_{ep}\delta_{pp'}(\langle 0_N|\delta_{e'e}-e^+e'|0_N\rangle \\ &\quad-\delta_{e'e}) \\ &=-\Big\langle 0_N\Big|\sum_{e,e'}(\alpha A P_p\alpha A)_{e,e'}e^+e'\Big|0_N\Big\rangle, \end{aligned} \quad (59)$$

where the second quantized forms of the operators were 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. (58). It is concluded that E^{dia} can be expressed as an expectation value for the following one-body operators:

$$E^{\mathrm{dia}}=\frac{1}{2mc^2}\langle 0_N|\alpha A P_p\alpha A|0_N\rangle-\frac{1}{2mc^2}\langle 0_N|XP_p\alpha A|0_N\rangle, \quad (60)$$

where the first term yields the diamagnetic term in the nonrelativistic limit. In order to carry out the leading order ESC reduction of Eq. (60) in terms of mean field Pauli spinors, the projector P_p in the space of four-component Dirac spinors (split into 2×2 blocks) needs be expanded to the order c^{-2}. It can be written as

$$P_p=\begin{bmatrix} x^2 & -x \\ -x & 1-x^2 \end{bmatrix}, \quad (61)$$

where $x=\sigma p/2mc$, which is the same expression as for usual Pauli spinors. Therefore

$$\alpha A P_p\alpha A=\begin{bmatrix} \sigma A(1-x^2)\sigma A & -\sigma A x\sigma A \\ -\sigma A x\sigma A & \sigma A x^2\sigma A \end{bmatrix} \quad (62)$$

and

$$\begin{aligned} XP_p\alpha A &= \begin{bmatrix} -[x,\sigma A]x\sigma A & 0 \\ 2\sigma A x\sigma A+[x,\sigma A]\sigma A & 0 \end{bmatrix} \\ &+\frac{1}{2mc^2}\begin{bmatrix} (V^{LL}\sigma A-\sigma A V^{SS})\sigma A & 0 \\ 0 & 0 \end{bmatrix}, \end{aligned} \quad (63)$$

where we have separated explicitly the new contribution due to the mean field operator. In the present work we evaluate explicitly this term only, as the remainder operators must be worked out exactly as in Ref. 18. Due to the factor $1/2mc^2$, the operators in the second term must be evaluated only to the order c^0. Taking into account that

$$V^{LL(0)}=J-K^C, \quad (64)$$

$$V^{SS(0)}=J-K^B, \quad (65)$$

(where K^C and K^B are exchange operators of the Coulomb and Breit interactions respectively), the mean field contribution to the diamagnetic term is found to be

$$E^{\mathrm{dia,mf}}=\frac{1}{4m^2c^4}\langle 0|(K^C\sigma A-\sigma A K^B)\sigma A|0\rangle, \quad (66)$$

where $|0\rangle$ is the Schrödinger ground state. For a singlet real ground state it is obtained that

$$\langle 0|K^C\sigma A\sigma A|0\rangle=\langle 0|K^C A^2|0\rangle=\sum_{i,\mu}\Big\langle \phi_i\phi_\mu\Big|\frac{A^2(1)}{r_{12}}\Big|\phi_\mu\phi_i\Big\rangle, \quad (67)$$

$$\langle 0|\sigma A\cdot K^B\cdot\sigma A|0\rangle=-2\sum_{i,\mu}\Big\langle \phi_i\phi_\mu\Big|\frac{\mathbf{A}(1)\cdot\mathbf{A}(2)}{r_{12}}\Big|\phi_\mu\phi_i\Big\rangle. \quad (68)$$

Details of this last expression are given in Appendix C.

The full diamagnetic term of the mean field LR-ESC approach is

$$\begin{aligned} E^{\mathrm{dia}} &= \frac{1}{2mc^2}\langle 0|A^2|0\rangle+E\left(\frac{1}{2mc^2}A^2;H^{R,\mathrm{mf}}\right)+\langle 0|O^{\mathrm{dia},LR}|0\rangle \\ &+E^{\mathrm{dia,mf}}, \end{aligned} \quad (69)$$

where

$$\begin{aligned} O^{\mathrm{dia},LR} &= -\frac{1}{8m^3c^4}((\sigma p\sigma A)^2+2\sigma A p^2\sigma A+(\sigma A\sigma p)^2 \\ &+\{p^2,A^2\}) \end{aligned} \quad (70)$$

was obtained in Ref. 18. In Eq. (69), the first term is the nonrelativistic diamagnetic term of magnetic properties; the second collects passive effects on the diamagnetic term, i.e., those due to relativistic corrections to the magnetically unperturbed molecular states. It now contains mean field two-body effects given by $V^{\mathrm{mf}(2)}$. The third term gathers active one-body effects, and the fourth term is the newly found mean field active operator for the diamagnetic term. Due to the factor c^{-4}, the expectation value of the last two terms must be carried out for the nonrelativistic (i.e., Schrödinger) ground state.

III. DISCUSSION

The mean field LR-ESC expressions obtained in the present work are the consistent two-component approximation of the Dirac-Hartree-Fock and four-component RPA formalisms. It is interesting to realize that within a four-component approach, the N-particle manifolds of charge $Q=-eN$ of Dirac-Fock space spanned by solutions of the one-particle Dirac Hamiltonian h^D and by solutions of the DHF equations are not the same, in principle. This is so because positive energy solutions of the DHF equations are not linear combinations of positive energy solutions of h^D only. It is therefore interesting to analyze the way two-body effects are included in the mean field expressions.

In the leading order two-component mean field Pauli approach, the relation of the small and large components of a given four-component spinor carry a mean field contribution of order c^{-3} [Eq. (19)]. As a consequence, it was found that the relativistic mean field effect described by $V^{\mathrm{mf}(2)}$ acts strictly as a one-body operator defined only in terms of the zeroth order spinors, i.e., nonrelativistic Hartree-Fock spin-orbitals. This mean field potential contains both direct and exchange contributions. It is interesting to note that while the zeroth order V^{LL} operator contains both Coulomb and exchange HF potentials, V^{SS} contains only the Coulomb term (and a Breit zeroth order correction). As a consequence, it can be expected that a significant portion of two-body relativistic effects is included in such magnetically unperturbed spinors.

It is also interesting to analyze the way magnetic field dependent operators describing relativistic effects are modified. Such kind of effects were dubbed active effects in recent work.[15,19] In particular, due to the way V^{SS} and V^{LS} are combined, the Hartree-Fock relation is recovered in Eq. (46). As a consequence, the kinetic energy operator can be introduced and only the last term of O^3, Eq. (48), contains mean field dependent terms.

Rather unexpectedly, a mean field effect does correct explicitly the active diamagnetic operator, Eq. (66). This term has no one-body counterpart and contains only exchange mean field effects. In numerical calculations of the active diamagnetic contribution to the nuclear magnetic shielding tensor, it was found that such term is largely dominated by contributions from the innermost $1s$ atomic orbitals.[27,28] It can be expected that the mean field contribution will also be dominated by such orbitals because of the maximum Coulomb repulsion at this region and the dependence of the diamagnetic operator on the relative distance to the nucleus.[28] Therefore, in order to obtain a qualitative estimate of the mean field Coulomb correction of this new term, an explicit calculation involving $1s$ hydrogenic atomic orbitals in a nucleus of charge Z was carried out. The diamagnetic operator to be introduced in Eq. (67) is

$$2\mathbf{A}_N \cdot \mathbf{A}_B, \tag{71}$$

where

$$\mathbf{A}_N = \frac{\mu_N \times r_N}{r_N^3}, \tag{72}$$

$$\mathbf{A}_B = \tfrac{1}{2} B \times r \tag{73}$$

are the magnetic potential of the nucleus magnetic moment μ_N and of a static uniform magnetic field B, r_N is the electron position with respect to nucleus N, and r is the electron position with respect to the gauge origin of the uniform magnetic field. If it is chosen to be at the nucleus position and the isotropic part of the shielding σ^{dia} is sought, it is obtained that

$$\begin{aligned}\sigma^{\mathrm{dia,mf}} &= \frac{1}{4m^2c^4}\langle \phi_s | K_{1s}\left(\frac{2}{3r_N}\right) | \phi_s \rangle (10^6) \\ &= \frac{1}{32\pi}\left(\frac{Z}{mc^2}\right)^2 (10^6),\end{aligned} \tag{74}$$

where the factor 10^6 is introduced in order to give the result in ppm. The numerical value found for $Z=54$ (Xe) is ca. 0.08 ppm, yielding a tiny contribution of such two-body effects at a heavy atom.

IV. CONCLUDING REMARKS

A detailed derivation of mean field two-body effects on relativistic corrections to magnetic molecular properties consistent with the LR-ESC scheme has been presented. The mean field effects contain direct and exchange contributions. Coulomb direct contributions are in all cases described by adding the Coulomb HF operator to the external Coulomb field of the nuclei to the one-body expressions of previous work. Exchange contributions are also consistently included, as well as different terms coming from the Breit operator. The diamagnetic term carries a mean field correction which depends only on the exchange operator which has no one-body counterpart. However, such term is expected to yield a negligibly small contribution to the nuclear magnetic shielding constant.

It is interesting to remark that the mean field spin-orbit operator of Refs. 21 and 22 was recovered, as well as a mean field expression for all two-body effects. Additional two-body corrections depend on the "fluctuation" potential of the two-body interaction and can therefore be expected to yield much smaller quantitative contributions to magnetic properties.

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APPENDIX A: ORDER ANALYSIS OF MEAN FIELD OPERATORS

The order in the parameter c^{-1} of the mean field operators of Eq. (20) is here considered. To this end the matrix element between positive energy four-component spinors is calculated. For V^{LL} it holds that

$$V^{LL}=\sum_{\mu} J^{LL}_{C,\mu}+J^{LL}_{B,\mu}-K^{LL}_{C,\mu}-K^{LL}_{B,\mu}, \tag{A1}$$

where we have separated the Coulomb and Breit terms explicitly. V^{LL} connects the large components of two four-component spinors. An order analysis is carried out for each operator in Eq. (A1) in terms of mean field Pauli spinors:

$$\begin{aligned}\langle \phi^L|J^{LL}_{C,\mu}|\phi'^L\rangle &= \left\langle \phi^L\phi^4_\mu\right|\frac{1}{r_{12}}\left|\phi'^L\phi^4_\mu\right\rangle\\ &= \left\langle \phi^L\phi^L_\mu\right|\frac{1}{r_{12}}\left|\phi'^L\phi^L_\mu\right\rangle + \left\langle \phi^L\phi^S_\mu\right|\frac{1}{r_{12}}\left|\phi'^L\phi^S_\mu\right\rangle\\ &= \int\int d1d2(N\phi)^+(1)\left\{(N\phi_\mu)^+(2)\frac{1}{r_{12}}(N\phi_\mu(2))\right.\\ &\quad \left.+(x\phi_\mu)^+(2)\frac{1}{r_{12}}(x\phi_\mu(2))\right\}(N\phi')(1),\end{aligned} \tag{A2}$$

where ϕ, ϕ', and ϕ_μ stand for two-component mean field Pauli spinors. Consistent to order c^{-2}, only the leading order approximation of the small component is needed, given by operator x in Eq. (23). Operator N was defined in Eq. (22). It is worthy to note that the order of the operator will be defined considering only the role played by spinors explicitly contained in the operator. Taking into account that every mean field Pauli spinor ϕ_μ carries a zeroth order contribution, given by the mean field Hartree-Fock spin-orbital $\phi^{(0)}_\mu$, plus second order corrections, dubbed here as $\phi^{(2)}_\mu$, as well as the second order term contained in operator N, Eq. (A2) can be rewritten as

$$\begin{aligned}\langle \phi^L|J^{LL}_{C,\mu}|\phi'^L\rangle &= \int\int d1d2(N\phi)^+(1)\left\{(\phi^{(0)}_\mu)^+(2)\frac{1}{r_{12}}(\phi^{(0)}_\mu(2))\right\}(N\phi')(1)\\ &\quad+\int\int d1d2(N\phi)^+(1)\left\{\left(\phi^{(2)}_\mu-\frac{x^2}{2}\phi^{(0)}_\mu\right)^+(2)\frac{1}{r_{12}}\phi^{(0)}_\mu(2)+\phi^{(0)+}_\mu(2)\frac{1}{r_{12}}\left(\phi^{(2)}_\mu-\frac{x^2}{2}\phi^{(0)}_\mu\right)(2)\right\}(N\phi')(1)\\ &\quad+\int\int d1d2(N\phi)^+(1)\left\{(x\phi^{(0)}_\mu)^+(2)\frac{1}{r_{12}}(x\phi^{(0)}_\mu(2))\right\}(N\phi')(1).\end{aligned} \tag{A3}$$

Therefore, it is seen that

$$J^{LL}_{C,\mu}=J^{LL(0)}_{C,\mu}+J^{LL(2)}_{C,\mu}, \tag{A4}$$

where the first term refers to the first term of Eq. (A3) and the second gathers the second and third terms of Eq. (A3).

The Breit operator connects the large components to the small ones, and it is obtained as

$$\langle \phi^L|J^{LL}_{B,\mu}|\phi'^L\rangle=\langle \phi^L\phi^4_\mu|U_B|\phi'^L\phi^4_\mu\rangle=0. \tag{A5}$$

For the exchange operators it is obtained that

$$\begin{aligned}\langle \phi^L|K^{LL}_{C,\mu}|\phi'^L\rangle &= \left\langle \phi^L\phi^4_\mu\right|\frac{1}{r_{12}}\left|\phi^4_\mu\phi'^L\right\rangle\\ &= \left\langle \phi^L\phi^L_\mu\right|\frac{1}{r_{12}}\left|\phi^L_\mu\phi'^L\right\rangle\\ &= \int\int d1d2(N\phi)^+(1)(N\phi_\mu)^+(2)\frac{1}{r_{12}}(N\phi_\mu)\\ &\quad\times(1)(N\phi')(2).\end{aligned} \tag{A6}$$

Equation (A6) can be worked out in a way similar to that of Eq. (A2), and it is obtained that

$$\begin{aligned}\langle \phi^L|K^{LL}_{C,\mu}|\phi'^L\rangle &= \int\int d1d2(N\phi)^+(1)(\phi^{(0)}_\mu)^+(2)\frac{1}{r_{12}}(\phi^{(0)}_\mu)\\ &\quad\times(1)(N\phi')(2)+\int\int d1d2(N\phi)^+(1)\\ &\quad\times\left(\phi^{(2)}_\mu-\frac{x^2}{2}\phi^{(0)}_\mu\right)^+(2)\frac{1}{r_{12}}(\phi^{(0)}_\mu)(1)(N\phi')\\ &\quad\times(2)+\int\int d1d2(N\phi)^+(1)\\ &\quad\times(\phi^{(0)}_\mu)^+(2)\frac{1}{r_{12}}\left(\phi^{(2)}_\mu-\frac{x^2}{2}\phi^{(0)}_\mu\right)\\ &\quad\times(1)(N\phi')(2).\end{aligned} \tag{A7}$$

In this case there is also a zeroth order contribution (first term), and relativistic effects are given by the normalization operator and the relativistic effects on the mean field Pauli spinors (second and third terms). Therefore we define

$$K_{C,\mu}^{LL} = K_{C,\mu}^{LL(0)} + K_{C,\mu}^{LL(2)}. \quad \text{(A8)}$$

Following a similar procedure, the exchange Breit operator is considered:

$$\begin{aligned}\langle \phi^L | K_{B,\mu}^{LL} | \phi'^L \rangle &= \langle \phi^L \phi_\mu^4 | U_B | \phi_\mu^4 \phi'^L \rangle \\ &= \langle \phi^L \phi_\mu^S | \sigma_1 \cdot O_{12} \cdot \sigma_2 | \phi_\mu^S \phi'^L \rangle \\ &= \int\int d1d2 (N\phi)^+(1) \\ &\quad \times (Nx\phi_\mu)^+(2) \sigma_1 \cdot O_{12} \cdot \sigma_2 (Nx\phi_\mu)(1) \\ &\quad \times (Nx\phi')(2). \end{aligned} \quad \text{(A9)}$$

In this case the small component of ϕ_μ^4 is involved twice, and therefore the lowest order contribution is of order c^{-2}. Explicitly, consistent to that order, it may be written as

$$\begin{aligned}\langle \phi^L | K_{B,\mu}^{LL} | \phi'^L \rangle &= \int\int d1d2 (N\phi)^+(1) \\ &\quad \times (x\phi_x^{(0)})^+(2) \sigma_1 \cdot O_{12} \cdot \sigma_2 (x\phi_\mu^{(0)})(1) \\ &\quad \times (Nx\phi')(2), \end{aligned} \quad \text{(A10)}$$

and, therefore, this operators yields only terms of order c^{-2}:

$$K_{B,\mu}^{LL} = K_{B,\mu}^{LL(2)}. \quad \text{(A11)}$$

It is thus seen that the leading order of each operator is defined by the component (large or small) of ϕ_μ^4 involved. Taking into account the spinors dependence of the Coulomb and Breit operators, it is straightforward to generalize the previous results to obtain

$$V^{LS} = \sum_\mu J_{B,\mu}^{LS,(1)} - K_{C,\mu}^{LS(1)} - K_{B,\mu}^{LS,(1)}, \quad \text{(A12)}$$

$$V^{SL} = V^{LS+}, \quad \text{(A13)}$$

$$V^{SS} = \sum_\mu J_{C,\mu}^{SS,(0)} + J_{C,\mu}^{SS,(2)} - K_{C,\mu}^{SS,(2)} - K_{B,\mu}^{SS(0)} - K_{B,\mu}^{SS(2)}. \quad \text{(A14)}$$

Therefore, the leading order of V^{LL} and V^{SS} is c^0, and that of V^{LS} is c^{-1}. Explicitly, the zeroth order mean field operators are as follows. For the Coulomb operator it is obtained that

$$V^{LL(0)} = \sum_{\mu\text{occ}} J_{C,\mu}^{LL,(0)} - K_{C,\mu}^{LL,(0)} \equiv J - K^C, \quad \text{(A15)}$$

$$V^{SS(0)} = \sum_{\mu\text{occ}} J_{C,\mu}^{LL,(0)} \equiv J. \quad \text{(A16)}$$

The exchange term is absent in $V^{SS(0)}$. For the Breit operator it is obtained that

$$V^{SS(0)} = -\sum_{\mu\text{occ}} K_{B,\mu}^{SS,(0)} \equiv -K^B. \quad \text{(A17)}$$

APPENDIX B: MEAN FIELD BREIT CONTRIBUTION TO THE RELATION OF LARGE AND SMALL COMPONENTS OF MEAN FIELD PAULI SPINORS

We consider a matrix element of the operator in Eq. (41),

$$\begin{aligned}&\langle m | V^{SS} \sigma p + 2mc V^{SL} | n \rangle \\ &= \sum_\mu -\langle m\phi_\mu^L | \sigma_1 \cdot \overleftrightarrow{O}_{12} \cdot \sigma_2 | \phi_\mu^L (\sigma p n) \rangle + \langle m(\sigma p \phi_\mu) \\ &\quad \times | \sigma_1 \cdot \overleftrightarrow{O}_{12} \cdot \sigma_2 | n \phi_\mu^L \rangle + \langle m\phi_\mu^L | \sigma_1 \cdot \overleftrightarrow{O}_{12} \cdot \sigma_2 | n(\sigma p \phi_\mu) \rangle \\ &\quad - \langle m(\sigma p \phi_\mu) | \sigma_1 \cdot \overleftrightarrow{O}_{12} \cdot \sigma_2 | \phi_\mu^L n \rangle. \end{aligned} \quad \text{(B1)}$$

These are combinations of direct and exchange matrix elements of the following operator:

$$\begin{aligned}&(\sigma_2 p_2)(\sigma_1 \cdot \overleftrightarrow{O}_{12} \cdot \sigma_2) + (\sigma_1 \cdot \overleftrightarrow{O}_{12} \cdot \sigma_2)(\sigma_2 p_2) \\ &= p_2 \cdot \overleftrightarrow{O}_{12} \cdot \sigma_1 + i\sigma_2 \cdot (p_2 \times (\sigma_1 \cdot \overleftrightarrow{O}_{12})) + \sigma_1 \cdot \overleftrightarrow{O}_{12} \cdot p_2 \\ &\quad + i\sigma_2 \cdot ((\sigma_1 \cdot \overleftrightarrow{O}_{12}) \times p_2). \end{aligned} \quad \text{(B2)}$$

In order to simplify this expression we observe that

$$|p_2, \sigma_1 \cdot \overleftrightarrow{O}_{12}| = -i\sigma_{1l} \partial_{2k} O_{lk} = 0 \quad \text{(B3)}$$

and

$$\begin{aligned}&+ i\sigma_2 \cdot (p_2 \times (\sigma_1 \cdot \overleftrightarrow{O}_{12})) + i\sigma_2 \cdot ((\sigma_1 \cdot \overleftrightarrow{O}_{12}) \times p_2) \\ &= \sigma_2 \cdot (\nabla_2 \times (\sigma_1 \cdot \overleftrightarrow{O}_{12})) = -\sigma_1 \cdot \left(\sigma_2 \times \frac{r_{12}}{r_{12}^3} \right), \end{aligned} \quad \text{(B4)}$$

and, therefore,

$$\begin{aligned}&(\sigma_2 p_2)(\sigma_1 \cdot \overleftrightarrow{O}_{12} \cdot \sigma_2) + (\sigma_1 \cdot \overleftrightarrow{O}_{12} \cdot \sigma_2)(\sigma_2 p_2) \\ &= \sigma_1 \cdot \left(2\overleftrightarrow{O}_{12} \cdot p_2 - \sigma_2 \times \frac{r_{12}}{r_{12}^3} \right) \end{aligned} \quad \text{(B5)}$$

as indicated in Eq. (43).

APPENDIX C: MEAN FIELD BREIT CONTRIBUTION TO THE DIAMAGNETIC TERM

We consider a matrix element of the mean field operator of Eq. (68):

$$\begin{aligned}\langle \phi_m | \sigma A \cdot K^B \cdot \sigma A | \phi_n \rangle &= \sum_\mu \langle \phi_m \phi_\mu | (\sigma_1 A_1)(\sigma_1 O_{12} \sigma_2) \\ &\quad \times (\sigma_2 A_2) | \phi_\mu \phi_n \rangle, \end{aligned} \quad \text{(C1)}$$

where the subscripts indicate the particle on which each operator acts. In the mean field operator it must be taken into account that each orbital is contained twice, with both α and β spin states. First it is seen that

$$\begin{aligned}(\sigma_1 A_1)(\sigma_1 O_{12} \sigma_2)(\sigma_2 A_2) &= A_1 O_{12} A_2 + i\sigma_1 \cdot (A_1 \times O_{12} A_2) \\ &\quad + i\sigma_2 \cdot (A_1 O_{12} \times A_2) + (\sigma_1 \\ &\quad \times A_1) O_{12} (\sigma_2 \times A_2). \end{aligned} \quad \text{(C2)}$$

The second and third terms will give vanishing contributions for a real singlet ground state. The last term is explicitly evaluated as

$$(\sigma_1 \times A_1) O_{12} (\sigma_2 \times A_2) = \varepsilon_{ijk} \varepsilon_{lmn} \sigma_{1j} A_{1k} O_{12,il} \sigma_{2m} A_{2n}. \quad \text{(C3)}$$

The spin part of the matrix elements, for a singlet ground state, yields

$$\langle s_m\alpha|\sigma_{1j}\sigma_{2m}|\alpha s_n\rangle + \langle s_m\beta|\sigma_{1j}\sigma_{2m}|\beta s_n\rangle$$
$$= \langle s_m|\sigma_j(|\alpha\rangle\langle\alpha| + |\beta\rangle\langle\beta|)\sigma_m|s_n\rangle$$
$$= \langle s_m|\sigma_f\sigma_m|s_n\rangle$$
$$= \langle s_m|\delta_{jm} + i\sigma\cdot(\hat{j}\times\hat{m})|s_n\rangle. \quad \text{(C4)}$$

Only the first term will give nonvanishing contributions. As a consequence, the spin independent operator to be evaluated is

$$\varepsilon_{ijk}\varepsilon_{lmn}\delta_{jm}A_{1k}O_{12,il}A_{2n} = A_{1k}O_{12,ll}A_{2k} - A_{1k}O_{12,ik}A_i. \quad \text{(C5)}$$

The second term cancels the first one in Eq. (C2). The trace of O_{12} is given by

$$O_{12,ll} = -\frac{1}{2}\left(\frac{3}{r_{12}} + \frac{r_{12}^2}{r_{12}^3}\right) = -\frac{2}{r_{12}}, \quad \text{(C6)}$$

and, therefore, it is obtained that

$$\langle 0|\sigma A K^B \sigma A|0\rangle = -2\sum_{i,\mu}\left\langle \phi_i\phi_\mu\right|\frac{\mathbf{A}_1\mathbf{A}_2}{r_{12}}\left|\phi_\mu\phi_i\right\rangle \quad \text{(C7)}$$

as indicated in Eq. (68).

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