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Relativistic two-component geometric approximation of the electron-positron contribution to magnetic properties in terms of Breit–Pauli spinors

Daniel Zaccari,[1] Juan I. Melo,[2] Martín C. Ruiz de Azúa,[2,a)] and Claudia G. Giribet[2]
[1]*Departamento de Física, Facultad de Ciencias Exactas, Fisicoquímicas y Naturales, Universidad Nacional de Río Cuarto, Ruta 36, km 601, 5800 Río Cuarto, Córdoba, Argentina*
[2]*Departamento de Física, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Cdad. Universitaria, Pab. I, 1428 Buenos Aires, Argentina and CONICET*

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An alternative approach for the calculation of the electron-positron (e-p) contribution to magnetic properties based on two-component Breit–Pauli spinors is presented. In it, the elimination of the small component scheme is applied to the inverse propagator matrix of e-p pairs. The effect of the positronic manifold is expressed as an operator acting on Breit–Pauli spinors. The operator form thus obtained sums up the relativistic correction as a geometric series and as a result a totally different behavior in the vicinity of a nucleus is obtained as compared to the one of the linear response approximation. This feature has deep influence in numerical values of the e-p contribution to the nuclear magnetic shielding of heavy atoms. Numerical calculations carried out for Kr, Xe, and I show that with this approach, the e-p contributions to this property are in good agreement with those of four-component methods. © *2009 American Institute of Physics*.
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I. INTRODUCTION

Relativistic effects have proven to be of major importance on molecular magnetic properties of heavy atom containing compounds, especially for those involving the field of a magnetic nucleus, such as NMR parameters.[1,2] Significant advances have been achieved in recent years in the theoretical description of such effects, both within Dirac four-component spinors and quasirelativistic two-component approaches.[3–20,27–29] The question of the diamagnetic-paramagnetic separation of terms at the four-component level has also been a subject of discussion in several papers in the field.[4,17–20] In the particular case of the NMR nuclear magnetic shielding tensor, numerical results in model compounds within four-component approaches stand as benchmark values to decide the accuracy of computationally less expensive two-component approximations.

However, beyond the superiority of fully relativistic four-component approaches from a theoretical point of view, two-component approaches have shown to adequately describe qualitatively or even quantitatively different aspects of relativistic effects. In fact, quasirelativistic theories are nowadays available which are exactly equivalent to a four-component theory and very promising results were obtained in this context.[21–26] Other two-component approaches are also worthy to mention as they have shown to be very successful in practical applications. For instance, the zeroth order relativistic approximation (ZORA) has been widely applied for the study of both nuclear magnetic shieldings and spin spin couplings.[10–12] Approaches based on the Douglas–Kroll decomposition have received increasing attention in recent years.[27–30] Approaches based on the Breit–Pauli approximation are also in widespread use and produce particularly chemical shift results that are very competitive compared to other approaches available for both the light and heavy nuclei of a molecule.[2,6–9,31–36]

In the linear response within the elimination of the small component (LRESC) approach,[6] the elimination of the small component (ESC) reduction is applied directly to a four-component Rayleigh–Schrödinger perturbation theory (RSPT) expression of magnetic properties. In this sense, it is wholly consistent with the most direct relativistic theory of magnetic properties, as it is explicitly related to a perturbational treatment of the four-component magnetic interaction given by the operator $W=\alpha\cdot A$ in Dirac's equation. The equivalence of the total result of the usual Breit–Pauli and LRESC schemes was theoretically proven, although the particular operators involved are different.[37] The LRESC or Breit–Pauli schemes are interesting because they present several advantages compared to other approaches. First, from the physical point of view, they are based on the Schrödinger Hamiltonian and perturbation operators are amenable to physical interpretation in terms of usual nonrelativistic spin orbitals. Second, from the computational point of view, the problems of generating the small component of spinors and taking account of negative energy solutions are avoided, with great savings of computational resources. Such approaches are in widespread use currently and produce particularly chemical shift results that are very competitive as compared to other approaches available.[31–33] It is therefore of great interest to establish theoretically and numerically the reliability of results of such schemes for elements of different rows of the Periodic Table.

a)Electronic mail: azua@df.uba.ar.

One particular feature of the LRESC scheme is that proper track of contributions coming from electronic excitations and negative energy (i.e., positronic) states can be kept in the whole derivation in a way fully consistent with the usual four-component random phase approximation (RPA) scheme.[3,4] In numerical applications, large negative relativistic effects on the positronic contribution to the nuclear magnetic shielding of a heavy element are found.[7,43] Although this result is in line with the corresponding one in four-component calculations,[4] it seems to be somewhat overestimated. A separation into atomic orbital contributions shows that such effect is largely dominated by contributions from inner shell *s* atomic orbitals.[43] This fact suggests that such contributions are overestimated and it might be interesting to develop an alternative formulation which could correct this problem.

This is the aim of the present work. We present an alternative approach for considering the negative energy state (i.e., positronic) contributions to magnetic properties within the LRESC approach. We apply the ESC approximation to the inverse electron-positron (e-p) propagator matrix. However, we formally eliminate explicit evaluation of matrix elements involving positronic states and therefore we obtain a final expression which is evaluated in terms of Breit–Pauli spinors.[38] The propagator thus obtained adds up the relativistic correction as a geometric series. Although this improvement will have little effect on the calculated chemical shifts, which are very well reproduced at this theoretical level, we believe that it is of fundamental physical interest to introduce this improvement in the LRESC scheme, as the total absolute shielding results are largely affected. Numerical results are presented for selected model compounds. A very good agreement with four-component RPA results is recovered following such scheme. It is explicitly shown that linearization of the propagator yields precisely the LRESC expression of previous work.

II. THEORY

The LRESC scheme for the calculation of magnetic properties which are bilinear in the magnetic vector potential is based on a second order RSPT expression in Dirac–Fock space:[6]

$$E^{(2)} = \sum_{n\neq 0} \frac{\langle 0|\alpha\cdot\mathbf{A}|n\rangle\langle n|\alpha\cdot\mathbf{A}|0\rangle}{E_0 - E_n} - \sum_{n\neq \mathrm{vac}} \frac{\langle \mathrm{vac}|\alpha\cdot\mathbf{A}|n\rangle\langle n|\alpha\cdot\mathbf{A}|\mathrm{vac}\rangle}{E_{\mathrm{vac}} - E_n}, \tag{1}$$

where the last term accounts for the correction to the "vacuum" energy when adopting the quantum electrodynamics (QED) picture in which negative energy states are reinterpreted as positive energy states for positrons.[39] In this work, atomic units based on the Gaussian system of units for the electromagnetic field are adopted. Therefore, the magnetic susceptibility of vacuum and other factors are taken into account by a factor of c^{-1} accompanying the magnetic vector potential $\mathbf{A}$. Therefore, the mechanical momentum takes the form

$$\pi = \mathbf{p} + \frac{1}{c}\mathbf{A}. \tag{2}$$

Such c factor should not be confused with a relativistic correction factor.

In Eq. (1), states $|0\rangle$, $|n\rangle$ stand for eigenstates of the Dirac–Coulomb–Breit Hamiltonian in Dirac–Fock space. As a consequence, such states correspond to states with a well defined charge $Q=-eN$, where N is the number of electrons of the system in the nonrelativistic limit, but they do not have a fixed number of particles.[40] The consideration of such Hamiltonian within the subspace of fixed N particle states constitutes the no pair approximation.

In the presence of the magnetic perturbation $W=\alpha\cdot\mathbf{A}$, different particle number manifolds are connected even if the Coulomb–Breit interaction between particles is neglected. The aim of the present work is to analyze in detail the pair creation contribution to magnetic properties, which yields the diamagnetic term in the nonrelativistic limit.[41] Particle states used to span the Dirac–Fock space are the solutions of a one-body Hamiltonian. This Hamiltonian can be taken as the Dirac Hamiltonian for a particle in the field of the nuclei in the molecule or alternatively as that corresponding to the Dirac–Hartree–Fock approximation.[42] In the last case the interaction between particles is included in the mean-field approximation, and the (magnetically) nonperturbed Hamiltonian connects different particle number manifolds only through the "fluctuation" potential of the interaction. However, such terms will be neglected in the present work. In this approximation state $|0\rangle$ is an N particle state, and it may be connected to states $|n\rangle$ of different particle numbers only by the magnetic interaction.

Therefore, the RSPT expression of Eq. (1) can be separated into two terms according to the particle number of the excited states involved:[6]

$$E^2 = E^a + E^b, \tag{3}$$

where

$$E^a = \sum_{n_N\neq 0_N} \frac{\langle 0_N|\alpha\cdot\mathbf{A}|n_N\rangle\langle n_N|\alpha\cdot\mathbf{A}|0_N\rangle}{E_{0,N} - E_{n_N}}, \tag{4}$$

$$E^b = \sum_{n_{N+2}} \frac{\langle 0_N|\alpha\cdot\mathbf{A}|n_{N+2}\rangle\langle n_{N+2}|\alpha\cdot\mathbf{A}|0_N\rangle}{E_{0,N} - E_{n,N+2}} - \sum_{n=2} \frac{\langle \mathrm{vac}|\alpha\cdot\mathbf{A}|n_2\rangle\langle n_2|\alpha\cdot\mathbf{A}|\mathrm{vac}\rangle}{E_{\mathrm{vac}} - E_{n,2}}. \tag{5}$$

The vacuum correction is included in E^b, and in this term the number of particles of the "excited" states is $N=2$. If an e-p pair is created by the magnetic interaction, the same positron state must be destroyed to give a state overlapping with the ground state $|0\rangle$, but a different electronic state may be involved. As a result, it may be written as

$$E^b = \sum_{e,e'\,\mathrm{occ},p} \langle e|\alpha\cdot\mathbf{A}|p\rangle P_{ep,e'p}\langle p|\alpha\cdot\mathbf{A}|e'\rangle. \tag{6}$$

The sum runs over occupied electronic states only. P stands for the propagator of pair creation excitations of the system.

Taking into account that the Hamiltonian under consideration is a one-body Hamiltonian, the propagator has a straightforward expression in terms of the corresponding eigenstates and eigenvalues:

$$P^{-1}_{ep,e'p'} = \delta_{e,e'}\delta_{p,p'}(E_e + E_p). \tag{7}$$

In this case, E^b can be re-expressed as

$$E^b = \sum_{e\text{occ}} \sum_{p} \langle e|\alpha \cdot \mathbf{A}|p\rangle P_{ep,ep} \langle p|\alpha \cdot \mathbf{A}|e\rangle. \tag{8}$$

This is our starting point to obtain the nonrelativistic limit and the leading order relativistic correction coming from these terms. The Dirac (or Dirac–Fock) Hamiltonian for electrons and positrons can be expressed as

$$(H^D - mc^2)\psi_e = E'_e \psi_e, \tag{9}$$

$$-(H^D + mc^2)\psi_p = E'_p \psi_p. \tag{10}$$

The leading order in the energy E is given by the rest mass of the electron and positron, and the difference, represented by E', which depends strictly on the states involved, will be considered as a perturbation. As a consequence the propagator can be separated accordingly:

$$P^{-1}_{ep,e'p'} = P^{(0)-1}_{ep,e'p'} + P^{(1)-1}_{ep,e'p'}, \tag{11}$$

$$P^{(0)-1}_{ep,e'p'} = 2mc^2 \delta_{e,e'}\delta_{p,p'}, \tag{12}$$

$$P^{(1)-1}_{ep,e'p'} = \delta_{e,e'}\delta_{p,p'}(E'_e + E'_p) = P^{(0)-1}_{ep,e''p''} \cdot M_{e''p'',e'p'}, \tag{13}$$

$$M_{ep,e'p'} = \delta_{e,e'}\delta_{p,p'}\frac{E'_e + E'_p}{2mc^2}. \tag{14}$$

The definition of matrix $\mathbf{M}$ in Eq. (14) allows one to write the propagator as

$$\mathbf{P} = (1 + \mathbf{M})^{-1}\mathbf{P}^{(0)}. \tag{15}$$

Taking into account electronic states on one hand and positronic states on the other, it is possible to write

$$(1 + \mathbf{M})_{ep,e'p'} = \delta_{e,e'}(1 + \mathbf{M}(\mathbf{e}))_{p,p'}, \tag{16}$$

i.e., for each electronic state a corresponding matrix involving only positronic states can be defined. This matrix is different for each electronic state. This is clear as matrix $\mathbf{M}(\mathbf{e})$ contains the eigenvalue of the electronic state under consideration. The usefulness of such separation is given by the fact that the inverse matrix can be factorized in the same way, i.e.,

$$(1 + \mathbf{M})^{-1}_{ep,e'p'} = \delta_{e,e'}(1 + \mathbf{M}(\mathbf{e}))^{-1}_{p,p'}. \tag{17}$$

It is readily seen that the lowest possible approximation to the propagator P of Eq. (15) is of order $1/c^2$, and only $\mathbf{P}^{(0)}$ is retained in this case. This yields the nonrelativistic diamagnetic term of magnetic properties. Expansion of $\mathbf{P}$ in terms of $1/c$ requires the linearization of the inverse matrix as $\mathbf{M}$ is of order $1/c^2$, and the proper definitions of the electronic and positronic manifolds in the one-particle state space. This was the way followed in previous work.[6] In the present work we intend to develop an approximation of order $1/c^2$ to the inverse polarization propagator (PP) matrix, keeping it in the denominator of Eq. (15). This procedure sums the relativistic effects as a geometric series of the first order correction, in close resemblance to the RPA approximation. Therefore, it is expected to bring calculated results closer to four-component RPA ones.

In what follows a fixed electronic state is assumed and the whole positronic contribution is added up. To this end we consider matrix $(1+\mathbf{M}(\mathbf{e}))$, Eq. (17). Consistently to order c^{-2} the eigenvalue E'_p can be replaced by the nonrelativistic limit of the Dirac equation for positrons. We start from

$$-(\mathbf{H^D} + mc^2 1)\psi_p = E'_p \psi_p. \tag{18}$$

Separating into upper (U) and lower (L) components, the following is obtained:

$$-((2mc^2 + V)\psi^U_p + c(\sigma \cdot p)\psi^L_p) = E'_p \psi^U_p, \tag{19}$$

$$-(c(\sigma \cdot p)\psi^U_p + V\psi^L_p) = E'_p \psi^L_p. \tag{20}$$

As it is seen, in this case ψ^U_p plays the role of the small component and ψ^L_p is the large one. Following the standard ESC scheme the following is obtained at the lowest order:

$$\psi^U_p = -\frac{\sigma \cdot p}{2mc}\psi^L_p, \tag{21}$$

and the following equation is obtained for ψ^L_p:

$$\left(\frac{p^2}{2m} - V\right)\psi^L_p = E'_p \psi^L_p, \tag{22}$$

which has the form of the Schrödinger equation for a particle in a repulsive potential. This is the only component that remains at the order c^0. As a consequence, consistently to the order c^{-2},

$$\mathbf{M}(\mathbf{e})_{p,p'} = \frac{1}{2mc^2}(E'_e \cdot 1 + \mathbf{H}^+)_{p,p'}, \tag{23}$$

where H^+ stands for the operator in Eq. (22). In order to obtain an explicit expression of this operator in four-component Dirac space, it is useful to introduce the projectors onto electronic and positronic state spaces and a unitary operator that expresses these projectors as diagonal operators.

The projectors onto the subspace of electronic states (P_e) and of positronic states (P_p) consistent with the ESC scheme up to order c^{-2} can be expressed as[38]

$$P_e = \begin{bmatrix} 1 - x^2 & x \\ x & x^2 \end{bmatrix} \tag{24}$$

and

$$P_p = \begin{bmatrix} x^2 & -x \\ -x & 1 - x^2 \end{bmatrix}, \tag{25}$$

where

$$x = \frac{\sigma \cdot p}{2mc}. \tag{26}$$

Neglecting terms of order higher than c^{-2} the transformation

$$U = \begin{bmatrix} 1 - \frac{x^2}{2} & -x \\ x & 1 - \frac{x^2}{2} \end{bmatrix} \tag{27}$$

is unitary and has the properties

$$U \begin{bmatrix} 1 & 0 \\ 0 & 0 \end{bmatrix} U^{\dagger} = P_e, \tag{28}$$

$$U \begin{bmatrix} 0 & 0 \\ 0 & 1 \end{bmatrix} U^{\dagger} = P_p, \tag{29}$$

i.e., this transformation yields a representation such that electronic states have nonzero amplitude only in the first two components of the corresponding 4-spinor. In fact, this amplitude is described by the Pauli two-component spinor $\tilde{\phi}_e$:

$$\begin{bmatrix} \psi_e^L \\ \psi_e^S \end{bmatrix} = U \cdot \begin{bmatrix} \tilde{\phi}_e \\ 0 \end{bmatrix}. \tag{30}$$

Positronic states have nonzero amplitude only in the last two components of the corresponding four-component spinor. This being the case, the projection of matrix $1 + \mathbf{M}(\mathbf{e})$ [Eq. (17)] onto the positronic manifold has the form

$$1 + \mathbf{M}(\mathbf{e}) = \begin{bmatrix} \mathbf{0} & \mathbf{0} \\ \mathbf{0} & 1 + \frac{1}{2mc^2}(E_e' 1 + \mathbf{H}^+) \end{bmatrix}. \tag{31}$$

The corresponding inverse is defined only for the lower 2×2 block, as needed. It is readily obtained as

$$(1 + \mathbf{M}(\mathbf{e}))^{-1} = \begin{bmatrix} \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \left(1 + \frac{1}{2mc^2}(E_e' 1 + \mathbf{H}^+)\right)^{-1} \end{bmatrix}. \tag{32}$$

As mentioned above, in this representation electronic states are described by the corresponding Pauli spinor. In order to evaluate the matrix element of Eq. (8) the magnetic interaction operator must be transformed to this representation:

$$(\alpha \cdot \mathbf{A})^T = U^{\dagger} \cdot \alpha \cdot \mathbf{A} \cdot U. \tag{33}$$

The following is obtained:

$$(\alpha \cdot \mathbf{A})^T = \begin{bmatrix} -(x(\sigma \cdot A)R + R(\sigma \cdot A)x) & R(\sigma \cdot A)R - x(\sigma \cdot A)x \\ R(\sigma \cdot A)R - x(\sigma \cdot A)x & R(\sigma \cdot A)x + x(\sigma \cdot A)R \end{bmatrix}, \tag{34}$$

where

$$R = 1 - \frac{x^2}{2}. \tag{35}$$

For the sake of brevity we define

$$\begin{aligned} a_1 &= -(x(\sigma \cdot A)R + R(\sigma \cdot A)x), \\ a_2 &= R(\sigma \cdot A)R - x(\sigma \cdot A)x, \end{aligned} \tag{36}$$

and thus

$$(\alpha \cdot \mathbf{A})^T = \begin{bmatrix} a_1 & a_2 \\ a_2 & -a_1 \end{bmatrix}. \tag{37}$$

This result is now inserted in Eq. (8), where the electronic state is represented by the corresponding Pauli spinor, denoted by $\tilde{\phi}_e$:

$$E^b = \sum_{e\text{occ}} \frac{1}{2mc^2} \langle \tilde{\phi}_e | a_2 \left(1 + \frac{1}{2mc^2}(E_e' 1 + \mathbf{H}^+)\right)^{-1} a_2 | \tilde{\phi}_e \rangle. \tag{38}$$

In order to separate explicitly the term containing the inverse matrix of the propagator, E^b can be splitted as

$$E^b = E^{b,NR} + E^{b,A} + E^{b,P}, \tag{39}$$

where

$$E^{b,NR} = \frac{1}{2mc^2} \sum_{e\text{occ}} \langle \phi_e | \mathbf{A}^2 | \phi_e \rangle, \tag{40}$$

$$E^{b,A} = \frac{1}{2mc^2} \sum_{e\text{occ}} \langle \phi_e | a_2^2 - A^2 | \phi_e \rangle + \frac{1}{2mc^2} E^{(2)}(H^{mv} + H^{Dw}; A^2), \tag{41}$$

$$E^{b,P} = \frac{1}{2mc^2} \sum_{e\text{occ}} \langle \phi_e | \mathbf{A} \left(\left(1 + \frac{1}{2mc^2}(E_e' 1 + \mathbf{H}^+)\right)^{-1} - 1 \right) \mathbf{A} | \phi_e \rangle, \tag{42}$$

where $|\phi_e\rangle$ are the Schrödinger spin orbitals; $E^{(2)}(A,B)$ stands for a second order RSPT expression for operators A, B:

$$E^{(2)}(A,B) = \sum_{n \neq 0} \frac{\langle 0|A|n\rangle\langle n|B|0\rangle + \langle 0|B|n\rangle\langle n|A|0\rangle}{E_0 - E_n}, \tag{43}$$

and the mass-velocity and Darwin operators are given by[38]

$$H^{mv} = -\frac{p^4}{8m^3c^2}, \tag{44}$$

$$H^{Dw} = \frac{\nabla^2 V_C}{4m^2c^2}. \tag{45}$$

In Eqs. (40)–(42) a singlet ground state is assumed and therefore triplet operators are excluded from the final expressions.

$E^{b,A}$ gathers relativistic effects originated in the c^{-2} expansion of the magnetic operators a_1 and a_2, Eq. (36), and on the molecular ground state (second term of Eq. (41). These corrections keep the form of previous work. $E^{b,P}$, on the other hand, contains relativistic corrections strictly originated in the e-p propagator, which are added up as a geometric series in the present work.

The expression of E^b, Eq. (38), is consistent to the order c^{-2}. The effect of the positronic manifold is wholly taken into account in this expression by means of operator H^+. This procedure sums the linear correction of previous work as a geometric series and therefore it will be referred to as the geometric ESC approximation (GESC). The lowest order approximation is obtained by setting $R=1$, neglecting the term of order c^{-2} in the denominator, and replacing the Pauli spinors by the Schrödinger ones. The nonrelativistic diamagnetic term of magnetic properties is thus obtained. In the relativistic result, it is seen that a different operator is defined for each electronic state. However, this dependence is only through the corresponding orbital energy. It can be taken out from the operator either by neglecting its value, as in the ZORA,[10–12] or by linearizing its contribution, leaving a unique operator for the positronic contribution for all electronic states. The full linearization of the operator yields the diamagnetic term of previous work,[6] as it will be explicitly shown in Sec. II A. It is worthy to note that from the computational point of view, in order to evaluate the diamagnetic term of Eq. (42), the matrix representation of $p^2/2m$ and V are required, which are readily included as part of any quantum chemistry program. Therefore, there is nearly no need of extra computational effort to carry out numerical calculations.

A. Linearization and LRESC expression of the diamagnetic contribution

The leading order of the relativistic correction to the diamagnetic contribution is now obtained by linearizing the propagator Eq. (38) to obtain

$$E^b = \sum_e \frac{1}{2mc^2}\langle\tilde{\phi}_e|a_2\left(1 - \frac{1}{2mc^2}(E_e 1 + \mathbf{H}^+)\right)a_2|\tilde{\phi}_e\rangle. \tag{46}$$

Due to the factor $1/(2mc^2)^2$, the last term must be evaluated for the nonrelativistic (i.e., Schrödinger) electronic state ϕ_e and the nonrelativistic approximation for a_2:

$$a_2^{(0)} = \sigma\cdot\mathbf{A}. \tag{47}$$

Therefore, the expectation value for each electronic state in the last term has the form

$$\langle\phi_e|\sigma\cdot\mathbf{A}(E'_e 1 + \mathbf{H}^+)\sigma\cdot\mathbf{A}|\phi_e\rangle, \tag{48}$$

where E'_e in the nonrelativistic limit is the Schrödinger eigenvalue for the electronic state under consideration. E'_e and $\sigma\cdot\mathbf{A}$ can be commuted to write

$$\langle\phi_e|\sigma\cdot\mathbf{A}(E'_e 1 + \mathbf{H}^+)\sigma\cdot\mathbf{A}|\phi_e\rangle = \langle\phi_e|\sigma\cdot\mathbf{A}(\sigma\cdot\mathbf{A}\mathbf{H}^- + \mathbf{H}^+\sigma\cdot\mathbf{A})|\phi_e\rangle, \tag{49}$$

where H^- stands for the Schrödinger Hamiltonian for the electronic state. Explicitly,

$$\sigma\cdot\mathbf{A}\mathbf{H}^- + \mathbf{H}^+\sigma\cdot\mathbf{A} = \sigma\cdot\mathbf{A}\left(\frac{p^2}{2m} + V\right) + \left(\frac{p^2}{2m} - V\right)\sigma\cdot\mathbf{A} = \left\{\sigma\cdot\mathbf{A}, \frac{p^2}{2m}\right\} \tag{50}$$

since V and $\sigma\cdot\mathbf{A}$ commute. { ,} stands for the anticommutator. The explicit dependence on the energy eigenvalue E'_e has been eliminated and the whole contribution can be expressed as an expectation value. The full result is

$$E^b = \frac{1}{2mc^2}\sum_e \langle\phi_e|\mathbf{A}^2|\phi_e\rangle + \frac{1}{2mc^2}E^{(2)}(H^{mv} + H^{Dw}; A^2) + \frac{1}{2mc^2}\sum_e \langle\phi_e|\mathbf{a}_2^2 - \mathbf{A}^2|\phi_e\rangle - \langle\phi_e|\mathbf{A}^2x^2 + \sigma\cdot\mathbf{A}x^2\sigma\cdot\mathbf{A}|\phi_e\rangle. \tag{51}$$

Consistently to the order c^{-2} and taking into account that x^2 and $\mathbf{A}^2$ can be commuted in the expectation value, the last two term contributions can be rewritten as the expectation value for the operator:

$$O^{\mathrm{diam},LR} = -\frac{1}{2mc^2}(\{\mathbf{A}^2, x^2\} + 2\sigma\cdot\mathbf{A}x^2\sigma\cdot\mathbf{A} + (x\sigma\cdot\mathbf{A})^2 + (\sigma\cdot\mathbf{A}x)^2), \tag{52}$$

which is exactly the expression found within the LRESC approximation of previous work for the relativistic correction of the diamagnetic contribution to magnetic properties.[6,37]

B. The electron-positron contribution to the nuclear magnetic shielding tensor

Relativistic effects gathered in $E^{b,A}$ are equivalent to those calculated in previous work. The corresponding expressions for the specific case of the nuclear magnetic shielding tensor are considered in this section. The nuclear magnetic shielding tensor of nucleus M can be obtained as

$$\sigma(M)_{i,j} = \frac{\partial^2 E}{\partial\mu_{M,i}\,\partial B_j}_{\mu_M=0,B=0}, \tag{53}$$

where E is the molecular energy in the presence of the magnetic fields of the nucleus and the uniform external field $\mathbf{B}_0$. For a point dipole nucleus M:

$$\mathbf{A}_M = \frac{\boldsymbol{\mu}_\mathbf{M}\times\mathbf{r}_M}{r_M^3}, \tag{54}$$

and for the external magnetic field $\mathbf{B}_0$:

$$\mathbf{A}_B = \tfrac{1}{2}\mathbf{B}_0 \times \mathbf{r}. \tag{55}$$

In what follows, the gauge origin is placed at the nucleus position, i.e., $\mathbf{r}_M = \mathbf{r}$. The explicit derivation of the final form of the operators involved in $E^{b,A}$ and LRESC $E^{b,P}$ was carried out in Ref. 6. A brief account is presented in the Appendix. The following is obtained:

$$E^{b,A} = -\frac{1}{8m^3c^4}\sum_{e\text{occ}} \langle \phi_e | \frac{20\pi}{3}(\mathbf{B}_0 \cdot \mu_\mathbf{M})\delta(\mathbf{r}_\mathbf{M}) + 4\left(\frac{\mu_\mathbf{M} \cdot \mathbf{L}}{r^3}\right)(\mathbf{B}_0 \cdot \mathbf{L}) + \mathbf{B}_0 \cdot \mathbf{B}_{M,\text{dip}} | \phi_e \rangle + \frac{1}{mc^2}E^{(2)}(H^{mv} + H^{Dw}; \mathbf{A}_M \cdot \mathbf{A}_B), \tag{56}$$

$$E^{b,P,\text{LRESC}} = -\frac{1}{8m^3c^4}\sum_{e\text{occ}} \langle \phi_e | \left(\frac{8\pi}{3}(\mathbf{B}_0 \cdot \mu_\mathbf{M})\delta(\mathbf{r}_\mathbf{M}) + + 4(\mathbf{A}_\mathbf{M} \cdot \mathbf{A}_\mathbf{B})\mathrm{p}^2 + \mathbf{B}_0 \cdot \mathbf{B}_{\mathbf{M},\text{dip}} \right) | \phi_e \rangle, \tag{57}$$

where

$$\mathbf{B}_{\mathbf{M},\text{dip}} = \frac{3(\mu_\mathbf{M} \cdot \mathbf{r}_\mathbf{M})\mathbf{r}_\mathbf{M} - \mu_\mathbf{M} r_M^2}{r_M^5} \tag{58}$$

is the dipole component of the nucleus magnetic field. Within the formalism developed in the present work, the expression of $E^{b,P}$ is given by

$$E^{b,P} = \frac{1}{2c^2}\sum_{e\text{occ}} \langle \phi_e | \left(\frac{\mu_\mathbf{M} \times \mathbf{r}}{r^3} \right) \times \left(\left(1 + \frac{1}{2mc^2}(E_e' 1 + \mathbf{H}^+) \right)^{-1} - 1 \right) \left(\frac{\mathbf{B}_0}{2} \times \mathbf{r} \right) | \phi_e \rangle. \tag{59}$$

The corresponding contributions to the magnetic shielding tensor $\sigma_\mathbf{M}$ obtained according to Eq. (53) will be referred to as $\sigma^{b,A}$ and $\sigma^{b,P}$, respectively.

III. METHOD OF CALCULATION

In order to carry out numerical calculations of the e-p contribution to the nuclear magnetic shielding tensor with the formalism of the previous section the following procedure was adopted. Contributions contained in $E^{b,A}$ involve operators for which explicit numerical results were obtained in previous works,[7–9,43] both with the DALTON (Ref. 44) and SYSMO (Ref. 45) programs. In order to calculate the newly developed term $E^{b,P}$ a computational program was implemented which works as a subroutine of the SYSMO program. The matrix representation of the inverse propagator of Eq. (59) is carried out in the molecular orbital (MO) basis set of a Hartree–Fock calculation. The eigenvalue of the electronic state E' of each term of Eq. (59) is replaced by the corresponding orbital energy of the involved MO. This is consistent with taking the Fock operator as the one-body Hamiltonian of the problem. Consistently, the matrix elements of operator H^+ were also defined on the basis of the Fock operator F in the following way:

$$H^+ = T - V^F = 2T - F, \tag{60}$$

where T is the kinetic energy operator and V^F stands for the Hartree–Fock potential. The corresponding matrix elements are obtained from the SYSMO program files. Once the matrix representation of the inverse propagator of Eq. (59) is obtained, the calculation of $E^{b,P}$ is carried out by inserting the matrix representations of the nuclear magnetic potential operator and the uniform magnetic field potential operator, which are included in the SYSMO program. For comparison purposes, the linearized LRESC propagator is obtained with the same procedure, i.e., as the matrix products of the linearized propagator and magnetic field operators. The calculated values can be splitted into individual MO contributions, allowing interesting insight into the obtained values. The nonrelativistic diamagnetic contribution is also obtained with the nonrelativistic propagator $P^{(0)}$, Eq. (13), and the same magnetic field operators. It is worthy to observe that both at the relativistic and nonrelativistic levels, it is necessary to enlarge the atomic basis set with higher angular momentum basis functions in order to obtain appropriate matrix representations of the vector operators involved.

IV. RESULTS AND DISCUSSION

In order to carry out numerical calculations the noble gas atoms Kr and Xe and the hydrogen halide IH were taken as model compounds. The main reason for this choice is the existence of a large amount of benchmark numerical results for these systems in the current bibliography. The basis sets used in the calculations are based on Faegri's basis sets[46] for Kr and Xe and aug-ccpVTZ basis[47–49] for I, enlarged in different ways until saturation of results was achieved. On one hand, tight functions were added in order to have flexibility in the vicinity of the heavy nucleus. On the other, higher angular momentum basis functions were added in order to be able to reproduce the action of the vector operators involved in Eq. (59). In the latter case, it was verified that the nonrelativistic value obtained with Eq. (59) in the limit $c \to \infty$ is coincident with the result of the diamagnetic operator. The final results make use of uncontracted basis sets of quality: $(17s24p18d8f)$ for Kr, $(22s21p15d15f)$ for Xe, $(23s18p13d13f)$ for I, and $(6s4p3d)$ for H.

Results for the noble gas atoms Kr and Xe are presented in Tables I and II, respectively. Values obtained with the formalism developed in the present work are indicated as "GESC" to indicate that the geometric approximation of the propagator is used. Values of the LRESC approach are also quoted for comparison. Contributions from individual converged occupied orbitals are listed. As it was shown in previous work,[50] the total relativistic effect is defined to a large extent by contributions from the inner shell s-type orbitals. It is seen that for these contributions the GESC and linearized LRESC values differ significantly. As a consequence, contribution $\sigma^{b,P}$ to the relativistic effect on e-p rotations is reduced in absolute value by a factor of nearly 2 in both Kr and Xe. The difference between both approaches becomes less

TABLE I. Atomic orbital contributions to relativistic effects on the nuclear magnetic shielding constant of Kr for the isolated atom arising from e-p rotations given by Eq. (59). LRESC, GESC, and difference between both. Values in ppm.

		$\sigma^{b,P}$		
AO	NR	GESC	LRESC	Difference
1*s*	1260.13	−121.27	−208.73	87.45
2*s*	281.11	−13.64	−23.91	10.27
2*P* (×3)	279.32	−3.09	−3.21	0.12
3*s*	93.63	−2.28	−3.09	1.62
3*p* (×3)	89.56	−0.53	−0.54	0.02
3*d* (×5)	80.83	−0.17	−0.17	0.001
4*s*	28.55	−0.24	−0.83	0.59
4*p* (×3)	23.29	−0.04	0.07	−0.11
Total	3244.08	−149.26	−249.28	100.02

important as orbitals with zero density at the nucleus are considered. It is worthy to note a significant difference in the stability and reliability of results of the GESC and LRESC calculated values as obtained in the present work. As the basis set is enlarged with tight *s*-type functions, the linearized propagator shows numerical problems, which are due to the $1/r$ dependence of H^+. This difficulty is only overcome when the operator form of Eq. (52) based in the elimination of the potential V in Eq. (50) is considered. On the contrary, in the GESC expressions, inclusion of tight *s* functions does not have a significant influence in the propagator matrix, as in this case the large effect of the $1/r$ dependence is in the denominator. This is a situation in which the linearization in terms of c^{-2} yields an operator expression which is singular in the vicinity of the nucleus. This singularity is spurious and does not correspond to a good description of the relativistic effect. The GESC propagator overcomes this problem in a way similar to that of the ZORA[10–12] approach.

In Table III the total e-p contribution and the total absolute value of the relativistic nuclear magnetic shielding constants of the isolated Kr and Xe atoms and of I in IH obtained in the present work are compared to four-component and previous Breit–Pauli and LRESC two-component results of the bibliography. In order to obtain the full e-p values of Table III, the contributions arising from $E^{b,A}$, Eq. (56), must be computed. As it is shown in the Appendix, the corresponding values can be obtained by adequate rescaling of numerical data taken from Refs. 7 and 43 or Refs. 8 and 9. It is seen that the GESC result comes much closer to the four-component ones than the LRESC/BPPT values in all cases. The differences in the cases of Xe and I are within 1% of the total absolute shielding.

TABLE II. Atomic orbital contributions to relativistic effects on the nuclear magnetic shielding constant of Xe for the isolated atom arising from e-p rotations given by Eq. (59). LRESC, GESC, and difference between both. Values in ppm.

		$\sigma^{b,P}$		
AO	NR	GESC	LRESC	Difference
1*s*	1898.06	−324.70	−618.91	294.20
2*s*	436.98	−39.39	−63.39	24.01
2*p* (×3)	436.28	−11.06	−12.10	1.03
3*s*	160.71	−8.24	−16.80	8.56
3*p* (×3)	157.76	−2.48	−2.71	0.24
3*d* (×5)	152.80	−1.017	−1.035	0.017
4*s*	65.41	−1.75	−5.23	3.48
4*p* (×3)	61.82	−0.504	−0.546	0.042
4*d* (×5)	53.56	−0.170	−0.173	0.003
5*s*	23.00	−0.218	−0.304	0.086
5*p* (×3)	19.47	−0.059	−0.026	−0.033
Total	5641.98	−422.56	−756.82	334.27

V. CONCLUDING REMARKS

An alternative approach for the calculation of the e-p contribution to magnetic properties within the LRESC scheme was developed. Its main features are as follows. The ESC approximation is applied to the inverse propagator matrix in such a way that the relativistic effect is now summed up as a geometric series. However, no explicit evaluation of positronic states is needed and the final form is expressed in terms of Breit–Pauli spinors corresponding to electronic states only. Due to the presence of operator H^+ in the denominator, a singularity in the vicinity of the nucleus is avoided, yielding a better description of the sought relativistic effect. This feature has a deep influence in numerical results of the nuclear magnetic shielding tensor, especially on those contributions corresponding to inner shell tight orbitals. In fact, numerical results presented in this work show that with the GESC approximation, the inner shell *s*-type orbitals yield a smaller contribution in absolute value as compared to the LRESC scheme. As a consequence, the total nuclear shielding of the heavy nucleus is in close agreement with results of four-component approaches for atomic numbers of the order $Z=50$, i.e., in the fifth row of the Periodic Table.

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APPENDIX: EXPLICIT FORM OF LRESC OPERATORS FOR THE E-P CONTRIBUTION TO THE MAGNETIC SHIELDING TENSOR

The first term of Eq. (56) is worked out as follows:[6,37]

$$E_1^{b,A} = \frac{1}{2c^2}\sum_{eocc}\langle\phi_e|a_2^2 - A^2|\phi_e\rangle$$

$$= \frac{1}{2c^2}\sum_{eocc}\langle\phi_e|(N(\sigma\,.\,A)N - x(\sigma\,.\,A)x)^2 - A^2|\phi_e\rangle$$

$$= \frac{-1}{8c^4}\sum_{eocc}\langle\phi_e|\frac{1}{2}p^2A^2 + \mathbf{A}p^2\mathbf{A} + (\sigma\cdot A\sigma\cdot p)^2$$

$$+ \frac{1}{2}\sigma\cdot Ap^2\sigma\cdot A + \frac{1}{2}A^2p^2 + (\sigma\cdot A\sigma\cdot p)^2|\phi_e\rangle, \quad \text{(A1)}$$

where x and N were defined in Eqs. (26) and (35) and terms

TABLE III. Comparison of e-p contributions and total values of the nuclear magnetic shielding constant of Kr, Xe, and I obtained with present work GESC formalism, LRESC, and four-component methods. Values in ppm.

Nucleus	Kr	Xe	I
NR	3244.08, 3245.67[a]	5641.98, 5642.30[b]	5505.40[b]
$\sigma^{b,Ac}$	−124.51	−420.48	−385.72
$\sigma^{b,P}$ LRESC	−249.28, −251.12[c]	−756.82, −882.57[c]	−819.05
$\sigma^{b,P}$ GESC	−149.26	−422.56	−400.61
Total e-p LRESC	2868.45	4338.93	4300.63
Total e-p GESC	2968.5	4798.94	4719.07
Four-component e-p	2990[a]	4992.8,[b] 4905[a]	4889.1[b]
LRESC e-e[d]	685.3	1379.6	1242.9
Total LRESC/BPPT	3553.8[e]	6718.5,[e] 6747.2[f]	5543.5[g]
Total GESC	3653.8	7052.8	5962.0
Total four component	3598,[h] 3525.5,[i] 3572.6,[j] 3577.3,[a] 3593.4[k]	7040,[h] 6660.9,[i] 6982.2,[j] 6938,[a] 7011.6,[b] 7017.5,[k] 7019.8[f]	5855.3,[b] 5913.7[e]

[a]Reference 4.
[b]Reference 5.
[c]Reference 43. Rescaled as indicated in the Appendix.
[d]Calculated as the difference of the total LRESC/BPPT value and present LRESC e-p contributions.
[e]Reference 9.
[f]Reference 31.
[g]Reference 7.
[h]Reference 52 (RRPA).
[i]Reference 51. FPT-DF calculation with finite nucleus.
[j]Reference 13.
[k]Reference 20.

of order higher than c^{-4} have been neglected. The following relations hold:

$$\langle \phi_e | p^2 A^2 | \phi_e \rangle = \langle \phi_e | A^2 p^2 | \phi_e \rangle \tag{A2}$$

for $|\phi_e\rangle$ a real wave function,

$$\begin{aligned}((\sigma\cdot p)(\sigma\cdot A))^2 + ((\sigma\cdot A)(\sigma\cdot p))^2 \\ = ((\sigma\cdot p)(\sigma\cdot A) + (\sigma\cdot A)(\sigma\cdot p))^2 - (\sigma\cdot p)A^2(\sigma\cdot p) \\ - (\sigma\cdot A)p^2(\sigma\cdot A)\end{aligned} \tag{A3}$$

in the Coulomb gauge,

$$(\sigma\cdot p)(\sigma\cdot A) + (\sigma\cdot A)(\sigma\cdot p) = 2\mathbf{p}\cdot\mathbf{A} + \sigma\cdot B, \tag{A4}$$

$$\mathbf{p}A^2\mathbf{p} = (\mathbf{p}A^2)\cdot\mathbf{p} + A^2p^2, \tag{A5}$$

where the brackets indicate that $\mathbf{p}$ acts only on A^2.

Considering a singlet ground state wave function and therefore neglecting spin-dependent operators, Eq. (A1) can be re-expressed as

$$E_1^{b,A} = -\frac{1}{8c^4}\sum_{e\text{occ}} \langle \phi_e | 4(\mathbf{p}\cdot\mathbf{A})^2 + B^2 - (\mathbf{p}A^2)\cdot\mathbf{p} | \phi_e \rangle, \tag{A6}$$

$$\begin{aligned}\langle \phi_e | (\mathbf{p}A^2)\cdot\mathbf{p} | \phi_e \rangle &= \tfrac{1}{2}\langle \phi_e | \nabla^2 A^2 | \phi_e \rangle \\ &= \langle \phi_e | (\mathbf{A}\cdot\nabla^2\mathbf{A}) + (\partial_i A_j)(\partial_i A_j) | \phi_e \rangle,\end{aligned} \tag{A7}$$

where i,j stand for Cartesian components and Einstein's convention of sum of repeated indices is applied.

Inserting the magnetic potentials of the uniform and nucleus fields and retaining terms bilinear in μ and $\mathbf{B}_0$ the following is obtained:

$$\langle \phi_e | 2(\partial_i A_{N,j})(\partial_i A_{B,j}) | \phi_e \rangle = \langle \phi_e | \mathbf{B}_0\cdot\mathbf{B}_\mathbf{N} | \phi_e \rangle, \tag{A8}$$

$$\langle \phi_e | -\mathbf{A}_\mathbf{B}\nabla^2\mathbf{A}_\mathbf{N} | \phi_e \rangle = 4\pi\langle \phi_e | \mathbf{A}_\mathbf{B}\cdot(\nabla\times\mu\delta(\mathbf{r}_\mathbf{N})) | \phi_e \rangle, \tag{A9}$$

$$\langle \phi_e | \mathbf{A}_\mathbf{B}\cdot(\nabla\times\mu\delta(\mathbf{r})) | \phi_e \rangle = \langle \phi_e | \mu\cdot\mathbf{B}_0\delta(\mathbf{r}_\mathbf{N}) | \phi_e \rangle, \tag{A10}$$

and, therefore,

$$\begin{aligned}E_1^{b,A} = \frac{-1}{8c^4}\sum_{e\text{occ}} \langle \phi_e | 4\left(\frac{\mu\cdot\mathbf{L}_\mathbf{N}}{r_N^3}\right)(\mathbf{B}_0\cdot\mathbf{L}) + \mathbf{B}_0\cdot\mathbf{B}_\mathbf{N} \\ + 4\pi\mu\cdot\mathbf{B}_0\delta(\mathbf{r}_\mathbf{N}) | \phi_e \rangle.\end{aligned} \tag{A11}$$

Separating explicitly the Fermi contact term of the nucleus magnetic field the following is obtained:

$$\begin{aligned}E_1^{b,A} = -\frac{1}{8c^4}\sum_{e\text{occ}} \langle \phi_e | 4\left(\frac{\mu\cdot\mathbf{L}_\mathbf{N}}{r_n^3}\right)(\mathbf{B}_0\cdot\mathbf{L}) + \mathbf{B}_0\cdot\mathbf{B}_{\mathbf{N,dip}} \\ + \frac{20\pi}{3}\mu\cdot\mathbf{B}_0\delta(\mathbf{r}) | \phi_e \rangle.\end{aligned} \tag{A12}$$

The $E^{b,P,\text{LRESC}}$ contribution contains the following matrix elements:

$$\begin{aligned}\langle \phi_e | (\sigma\cdot A)((\sigma\cdot A)p^2 + p^2(\sigma\cdot A)) | \phi_e \rangle \\ = \langle \phi_e | A^2p^2 + \mathbf{A}p^2\cdot\mathbf{A} | \phi_e \rangle,\end{aligned} \tag{A13}$$

where only spin-independent operators are retained as a singlet ground state wave function is assumed. Since

$$p^2\mathbf{A} = (p^2\mathbf{A}) + 2(p_i\mathbf{A})p_i + \mathbf{A}p^2, \tag{A14}$$

$$2\mathbf{A}\cdot(p_i\mathbf{A})p_i = (\mathbf{p}A^2)\cdot\mathbf{p}, \tag{A15}$$

where once again brackets are used to indicate that operator $\mathbf{p}$ acts only on functions contained in it and making use of Eq. (A7) the following is obtained:

$$\langle\phi_e|\mathbf{A}p^2\cdot\mathbf{A}|\phi_e\rangle = \langle\phi_e|(\partial_i A_j)(\partial_i A_j) + A^2p^2|\phi_e\rangle. \tag{A16}$$

As a consequence, Eq. (A13) can be expressed as

$$\langle\phi_e|A^2p^2 + \mathbf{A}p^2\cdot\mathbf{A}|\phi_e\rangle = \langle\phi_e|2A^2p^2 + (\partial_i A_j)(\partial_i A_j)|\phi_e\rangle. \tag{A17}$$

Inserting the magnetic potentials of the uniform and nucleus magnetic fields and retaining terms bilinear in μ and $\mathbf{B}_0$ the following is obtained:

$$E^{b,P,\mathrm{LRESC}} = -\frac{1}{8c^4}\sum_{e\mathrm{occ}}\langle\phi_e|4(\mathbf{A_B}\cdot\mathbf{A_N})p^2 + \frac{8\pi}{3}(\mu\cdot\mathbf{B}_0\delta(\mathbf{r_N}) + \mathbf{B}_0\cdot\mathbf{B_{N,dip}}\ |\phi_e\rangle. \tag{A18}$$

In Refs. 8, 9, and 43 numerical values for the relativistic corrections of the diamagnetic term are classified as σ^{cont}, $\sigma^{d\text{-KE}}$, $\sigma^{L\text{-PSO}}$ and σ^{dip}, which are obtained from the following energy expressions:

$$E^{\mathrm{cont}} = -\frac{2\pi}{3c^4}\sum_{e\mathrm{occ}}\langle\phi_e|(\mu\cdot\mathbf{B}_0\delta(\mathbf{r_N})\ |\phi_e\rangle, \tag{A19}$$

$$E^{d\text{-KE}} = -\frac{1}{2c^4}\sum_{e\mathrm{occ}}\langle\phi_e|4(\mathbf{A_B}\cdot\mathbf{A_N})p^2|\phi_e\rangle, \tag{A20}$$

$$E^{L\text{-PSO}} = -\frac{1}{2c^4}\sum_{e\mathrm{occ}}\langle\phi_e|4\left(\frac{\mu\cdot\mathbf{L_N}}{r_n^3}\right)(\mathbf{B}_0\cdot\mathbf{L})|\phi_e\rangle, \tag{A21}$$

$$E^{\mathrm{dip}} = -\frac{1}{4c^4}\sum_{e\mathrm{occ}}\langle\phi_e|\mathbf{B}_0\cdot\mathbf{B_{N,dip}}|\phi_e\rangle. \tag{A22}$$

This last term makes no contribution to the isotropic shielding for the systems under study in the present work.

Explicitly, the relations applied in order to obtain numerical results from Ref. 43 are

$$E_1^{b,A} = \tfrac{5}{4}E^{\mathrm{cont}} + E^{L\text{-PSO}} + \tfrac{1}{2}E^{\mathrm{dip}}, \tag{A23}$$

$$E^{b,P,\mathrm{LRESC}} = \tfrac{1}{2}E^{\mathrm{cont}} + E^{d\text{-KE}} + \tfrac{1}{2}E^{\mathrm{dip}}. \tag{A24}$$

[1] See, e.g., *Calculation of NMR and EPR Parameters: Theory and Applications*, edited by M. Kaupp, M. Bühl, and V. G. Malkin (Wiley-VCH, Weinheim, 2004).
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