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Calculations of atomic magnetic nuclear shielding constants based on the two-component normalized elimination of the small component method

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A new method for calculating nuclear magnetic resonance shielding constants of relativistic atoms based on the two-component (2c), spin-orbit coupling including Dirac-exact NESC (Normalized Elimination of the Small Component) approach is developed where each term of the diamagnetic and paramagnetic contribution to the isotropic shielding constant σ_{iso} is expressed in terms of analytical energy derivatives with regard to the magnetic field **B** and the nuclear magnetic moment $\boldsymbol{\mu}$. The picture change caused by renormalization of the wave function is correctly described. 2c-NESC/HF (Hartree-Fock) results for the σ_{iso} values of 13 atoms with a closed shell ground state reveal a deviation from 4c-DHF (Dirac-HF) values by 0.01%–0.76%. Since the 2-electron part is effectively calculated using a modified screened nuclear shielding approach, the calculation is efficient and based on a series of matrix manipulations scaling with $(2M)^3$ (M: number of basis functions). *Published by AIP Publishing.* [http://dx.doi.org/10.1063/1.4979499]

I. INTRODUCTION

Nuclear magnetic properties such as the isotropic magnetic shielding constant σ_{iso} sensitively depend on the spin density distribution close to the nucleus as its magnetic moment interacts with the spin density induced by the external homogeneous magnetic field.[1,2] The shielding or deshielding effects of the induced electronic magnetic fields caused by the external magnetic field lead to an atom-specific σ_{iso} value in a given electronic environment. The exact nuclear magnetic resonance (NMR) measurement and analysis of σ_{iso} shieldings of heavy atoms with atomic numbers larger than 54 (Xe) are still a challenge, which can be eased by reliable quantum chemical calculations.[3–6]

The magnetic shielding constant of a nucleus is a second order response property and as such requires the calculation of a mixed Hessian, i.e., the energy derivatives are calculated with regard to the components of an external magnetic field **B** and the nuclear magnetic moments $\boldsymbol{\mu}$. The nuclear magnetic shielding constants are sensitive to the degree of electron correlation included in a calculation and the size of the basis set being used to describe the electronic wave function. Relativistic corrections are known to be essential for a correct calculation of the nuclear shielding constants of *relativistic* atoms. There are two major relativistic corrections that have to be considered, a scalar coupling and a spin-orbit coupling (SOC), which both increase with the atomic number.

Recently, we have developed an algorithm for the calculation of second order response properties with the help of analytical energy derivatives for a Dirac-exact two-component (2c) NESC (Normalized Elimination of the Small Component) method.[7] This work was based on Dyall's original work on NESC.[8,9] Furthermore, the development of a generally

applicable 2c-NESC method was already the second part of a longer research project aimed at developing a general purpose program for calculating molecular properties for relativistic Dirac-exact wave functions. In the first part of the project, the focus was on the spin-free methodology in form of 1c (one-component)-NESC and the programming of an algorithm for the rapid execution of NESC calculations.[10] After solving this problem, the applicability of 1c-NESC was systematically extended to the calculation of first order response properties (geometries,[11] electric dipole moments,[12] EPR hyperfine structure constants,[13] contact densities and Mössbauer isomer shifts,[14] and electric field gradients for nuclear quadrupole coupling constants[15]) and second order response properties (vibrational frequencies,[12,16] static electric polarizabilities,[12] and infrared intensities[12]). These methods were used to solve various chemical problems.[12,17–19]

In the second part of the project, we developed a 2c-NESC method that is based on a general Hartree-Fock (GHF) or, alternatively, general density functional theory (GDFT) wave function.[20] Once 2c-NESC was installed, it was possible to calculate SOC effects, which are essential for the understanding of the electronic structure of relativistic atoms and molecules.[2,21] The applicability of 2c-NESC was enlarged in a similar way as this was done for the 1c-NESC method. The routine calculation of geometries was made possible by deriving the analytical 2c-NESC gradient.[22] In follow-up work, we used the energy gradient algorithm to reliably determine SO-corrected electrical properties such as the molecular electrical moments[7] and to develop the 2c-NESC Hessian with regard to the components of the electric field for the calculation of the static electric dipole polarizability,[7] which required the use of coupled perturbed GHF (CPGHF)[23] and a coupled perturbed general Kohn-Sham (CPGKS) approach.[24–27]

Our work on NESC has to be seen on the background of a multi-pronged approach to obtain exact relativistic descriptions, which has involved several research groups. Best known is the Douglas-Kroll-Hess (DKH) method that has been worked out for lower orders n[28–32] as well as higher orders.[33,34] In continuation of this work, arbitrary order DKHn theory has been developed, which reproduces exact 4c-Dirac energies.[35–39] The DKHn theory suffers from slow convergence to the Dirac-exact result and difficulties when formulating higher orders of the DKHn perturbation approach. Arbitrary order theory offers in this regard an important improvement of DKH. Second, one has to mention the infinite-order two-component (IOTC) relativistic Hamiltonian approach of Barysz, Sadlej, and Snijders,[40] which triggered a number of developments based on this approach.[41–46] Iliaš and co-workers[47] also used matrix algebra to derive the IOTC Hamiltonian, which has led to substantial improvements of IOTC by Iliaš and Saue[48] and Barysz and co-workers[46] showing that IOTC can also provide exact 2c-energies. Kutzelnigg and Liu have classified quasi-relativistic methods as being operator-based or matrix-based and pointed out in this connection that the latter lead much easier to an exact quasi-relativistic presentation of 4c-Dirac theory.[49–51]

Filatov and Cremer worked out the prerequisites for correctly solving the NESC equations by starting with the regular approximation.[52,53] They developed the matrix representations of the ZORA (zeroth order regular approximation)[54] and IORA (infinite order regular approximation) Hamiltonians,[55–59] derived their relationship to an exact quasi-relativistic Hamiltonian,[60] and solved the gauge-dependence problem of ZORA and IORA.[61] Filatov and Cremer also pointed out that IORA[62,63] is a convenient starting point for an iterative solution of the NESC equations.[53]

Liu has argued that Dirac-exact relativistic 2c-methods, which use, in the one-electron part, the transformation from the Dirac picture to the Schrödinger picture, should be called X2C methods.[64] While such a term is useful to characterize relativistic methods from a more general point of view, it disguises differences that are essential for the practical realization of these methods. The term NESC is used in this and previous work to emphasize two aspects: (i) To honor Dyall's pioneering work who employed matrix algebra to reformulate the Dirac equation and to develop the foundation of NESC at a time when the major work on relativistic theory was based on operator algebra. (ii) NESC has been programmed to be generally applicable. Therefore it is based on an effective combination of one-step and iterative solutions of the NESC equation, the "First-Diagonalize-then-Contract" strategy to avoid or control variational or inverse variational collapse problems,[10,65] the use of the correct renormalization of the NESC wave function for the correct picture-change,[66] the exact calculation of the matrix $\mathbf{U}$ associated with the elimination of the small component as well as the exact calculation of its derivatives, the consequent use of a finite nucleus model, the compact and efficient programming of NESC response properties in terms of products of traces of matrices[65,67] to provide the possibility of a rapid calculation of first and second order 1c- or 2c-NESC response properties, and a program structure that makes it possible to run NESC with any (dynamical and/or

non-dynamical) correlation method available. These features distinguish (partly or in total) the current development of a Dirac-exact 1c- or 2c-relativistic methodology from other X1C and X2C methods and therefore it is justified to speak of NESC/X2C or simply 2c-NESC methods.[7]

The current work is embedded in the development of other relativistic methods to calculate magnetic properties. Komorovský and co-workers[68] showed that restricted magnetically balanced (RMB) basis sets are optimal for the calculation of the small component and for obtaining reliable nuclear shielding constants at the 4c-relativistic level. The 4c-RMB description is important to suppress the strong basis set dependence, especially when properly describing the diamagnetic term at the 4c level.[68,69] Cheng and co-workers[70] as well as Komorovský and co-workers[71] combined the RMB basis sets with the gauge including atomic orbital (GIAO) method[72–74] to obtain converged NMR values even with relatively small basis sets. In 2012, Olejniczak and co-workers[75] proposed an efficient 4c-relativistic method of NMR shielding constants based on RMB and unrestricted kinetic balance (UKB)[76] basis sets in combination with GIAOs. The authors coined in this connection the term *simple magnetic balance (sMB)* method.[75] Based on the RMB-GIAO or sMB-GIAO method, recently, some 4c-relativistic NMR calculations for relatively large molecules have been reported at the DFT level.[77–79]

Already in the 90s, 2c-relativistic NMR calculations of shielding constants have been carried out using ZORA.[54,80] Interestingly, the idea of the RMB was already used in the ZORA-NMR method[80] with the help of the substitution $(\mathbf{p} \rightarrow \pi)$ based on the principle of minimal electromagnetic coupling.[81] In 2012, Sun and co-workers[27] developed an X2C method that included two-electron relativistic correction terms, which were derived from the Dirac-Fock matrix in the RMB-GIAO form[64,82] and obtained NMR shielding constants equivalent to the 4c-RMB-GIAO-NMR calculations. In 2013, Yoshizawa and Hada incorporated the RMB-GIAO method into the second-order DKH (DKH2) method[28–30] and calculated NMR values with relatively small basis sets.[83,84] Also, Cheng and co-workers[85] developed a spin-free X1C method based on RMB-GIAO to calculate NMR shielding constants in combination with the coupled-cluster single and double excitations (CCSD) method[86] and a perturbational treatment of the triple excitations leading to CCSD(T).[87]

In the present work, we extend the spin-free X1C-NMR method of Cheng and co-workers[85] to the 2c-relativistic level by using the 2c-NESC methodology developed in previous work.[11,12,16,22] To reduce the high cost of previous approaches including the relativistic two-electron terms,[27,88] we use the non-relativistic two-electron term of the GHF method.[7,89] As a result, we need the renormalization matrix $\mathbf{G}$[66] to transform the Dirac picture (with the 4c-relativistic metric) to the Schrödinger picture (with the 2c-relativistic metric). This has the disadvantage of calculating first and second derivatives of $\mathbf{G}$, which are not needed if the full NESC method including all two-electron terms is used.[8,27] However, we will demonstrate that the effective calculation of the $\mathbf{G}$ matrix and its derivatives combined with a cost-efficient description of the two-electron part of SOC[20] leads to reliable 2c-NESC nuclear magnetic

shieldings and therefore represents a cost-effective alternative to already existing methods.

The results of this work are presented in the following way. In Section II, the 2c-NESC theory in the presence of magnetic fields and the formulas for the calculation of the 2c-NESC nuclear magnetic shielding constants are developed. Section III gives some details on the implementation of the NMR shielding constant programs and their application. In Section IV, results of this work are discussed whereas in Sec. V the conclusions of this work are summarized.

II. THEORY

The one-electron Dirac equation in the matrix form based on the restricted kinetic balance (RKB)[90] is written as

$$\begin{pmatrix} \mathbf{V} & \mathbf{T} \\ \mathbf{T} & \mathbf{W} - \mathbf{T} \end{pmatrix} \begin{pmatrix} \mathbf{C}_-^L & \mathbf{C}_+^L \\ \mathbf{C}_-^S & \mathbf{C}_+^S \end{pmatrix}$$
$$= \begin{pmatrix} \mathbf{S} & \mathbf{0} \\ \mathbf{0} & \mathbf{T}/(2mc^2) \end{pmatrix} \begin{pmatrix} \mathbf{C}_-^L & \mathbf{C}_+^L \\ \mathbf{C}_-^S & \mathbf{C}_+^S \end{pmatrix} \begin{pmatrix} \boldsymbol{\epsilon}^- & \mathbf{0} \\ \mathbf{0} & \boldsymbol{\epsilon}^+ \end{pmatrix}, \quad (1)$$

where $\mathbf{T}$ denotes the kinetic energy matrix, $\mathbf{V}$ the potential energy matrix, and $\mathbf{S}$ the overlap matrix in the 2c framework (with dimension $2M \times 2M$; M: number of basis functions), whereas $\mathbf{W}$ is the matrix of the operator $(\boldsymbol{\sigma} \cdot \mathbf{p})V(\mathbf{r})(\boldsymbol{\sigma} \cdot \mathbf{p})/(4m^2c^2)$ with $\mathbf{p}$ being the momentum operator, $\boldsymbol{\sigma}$ the vector of the three Pauli spin matrices, $\mathbf{r}$ the position vector of the electron, and c the speed of light. Matrices $\mathbf{C}_-^L$ and $\mathbf{C}_-^S$ correspond to the large and the small components of the positronic states with eigenvalues $\boldsymbol{\epsilon}^-$ while $\mathbf{C}_+^L$ and $\mathbf{C}_+^S$ are the components of the electronic states with energies $\boldsymbol{\epsilon}^+$.

The 2c renormalized NESC one-electron Hamiltonian matrix $\mathbf{H}_{1e}$ is derived from Eq. (1),

$$\mathbf{H}_{1e} = \mathbf{G}^\dagger \tilde{\mathbf{L}} \mathbf{G}, \quad (2)$$

where the NESC matrix $\tilde{\mathbf{L}}$[8,10,49,91,92] and the renormalization matrix $\mathbf{G}$[66] are defined by

$$\tilde{\mathbf{L}} = \mathbf{U}^\dagger \mathbf{T} + \mathbf{T}\mathbf{U} - \mathbf{U}^\dagger (\mathbf{T} - \mathbf{W}) \mathbf{U} + \mathbf{V}, \quad (3)$$

$$\mathbf{G} = \mathbf{S}^{-1/2} \left(\mathbf{S}^{-1/2} \tilde{\mathbf{S}} \mathbf{S}^{-1/2} \right)^{-1/2} \mathbf{S}^{1/2}, \quad (4)$$

and $\tilde{\mathbf{S}}$ is given by

$$\tilde{\mathbf{S}} = \mathbf{S} + \frac{1}{2mc^2} \mathbf{U}^\dagger \mathbf{T} \mathbf{U}. \quad (5)$$

The matrix $\mathbf{U}$ connects the large component $\mathbf{C}_+^L$ and the small component $\mathbf{C}_+^S$ according to $\mathbf{C}_+^S = \mathbf{U}\mathbf{C}_+^L$.[8,10]

A. 2c-NESC Hamiltonian in the presence of a magnetic field

The one-electron Dirac equation in the presence of a magnetic field is written in matrix form by using the vector potential $\mathbf{A}$ and RMB-based GIAOs

$$\begin{pmatrix} \mathbf{V}_m & \boldsymbol{\Pi}^\dagger \\ \boldsymbol{\Pi} & \mathbf{W}_m - \mathbf{T}_m \end{pmatrix} \begin{pmatrix} \mathbf{C}_-^L & \mathbf{C}_+^L \\ \mathbf{C}_-^S & \mathbf{C}_+^S \end{pmatrix}$$
$$= \begin{pmatrix} \mathbf{S}_m & \mathbf{0} \\ \mathbf{0} & \mathbf{T}_m/(2mc^2) \end{pmatrix} \begin{pmatrix} \mathbf{C}_-^L & \mathbf{C}_+^L \\ \mathbf{C}_-^S & \mathbf{C}_+^S \end{pmatrix} \begin{pmatrix} \boldsymbol{\epsilon}^- & \mathbf{0} \\ \mathbf{0} & \boldsymbol{\epsilon}^+ \end{pmatrix}. \quad (6)$$

Here, the following definitions are used:

$$\mathbf{V}_m = \begin{pmatrix} \mathbf{V}'_m & \mathbf{0} \\ \mathbf{0} & \mathbf{V}'_m \end{pmatrix}, \quad (7)$$

$$\mathbf{S}_m = \begin{pmatrix} \mathbf{S}'_m & \mathbf{0} \\ \mathbf{0} & \mathbf{S}'_m \end{pmatrix}, \quad (8)$$

$$(\boldsymbol{\Pi})_{\mu\nu} = \frac{1}{2} (\mu | f_{\mu\nu}^* \boldsymbol{\sigma}(\mathbf{p} + \mathbf{A}_\nu^{10}) \boldsymbol{\sigma}(\mathbf{p} + \mathbf{A}_\nu) | \nu), \quad (9)$$

$$(\mathbf{W}_m)_{\mu\nu} = \frac{1}{4m^2c^2} (\mu | f_{\mu\nu}^* \boldsymbol{\sigma}(\mathbf{p} + \mathbf{A}_\nu^{10}) V \boldsymbol{\sigma}(\mathbf{p} + \mathbf{A}_\nu^{10}) | \nu), \quad (10)$$

$$(\mathbf{T}_m)_{\mu\nu} = \frac{1}{2} (\mu | f_{\mu\nu}^* \boldsymbol{\sigma}(\mathbf{p} + \mathbf{A}_\nu^{10}) \boldsymbol{\sigma}(\mathbf{p} + \mathbf{A}_\nu^{10}) | \nu), \quad (11)$$

where

$$(\mathbf{V}'_m)_{\mu\nu} = (\mu | f_{\mu\nu}^* V | \nu), \quad (12)$$

$$(\mathbf{S}'_m)_{\mu\nu} = (\mu | f_{\mu\nu}^* | \nu), \quad (13)$$

$$f_{\mu\nu}^* = \exp \left[\frac{i}{2} \left[\mathbf{B} \times \left(\mathbf{R}_\mu - \mathbf{R}_\nu \right) \right] \cdot \mathbf{r} \right]. \quad (14)$$

In these definitions, μ and ν are the indices of the non-GIAO-type basis functions (i.e., field-independent basis functions), $\mathbf{B}$ is the external magnetic field, and $\mathbf{R}_\mu$ is the position vector of atomic orbital χ_μ. The quantity $f_{\mu\nu}^*$ in Eq. (14) results from the field-dependent phase factor of the GIAO function. Also note that $\boldsymbol{\Pi} \neq \boldsymbol{\Pi}^\dagger$ in Eq. (6). In the present study, the vector potential $\mathbf{A}_\nu$ includes the vector potential $\mathbf{A}^{01}$ originating from the nuclear magnetic moment $\boldsymbol{\mu}_M$ of nucleus M as well as $\mathbf{A}_\nu^{10}$ originating from the external magnetic field $\mathbf{B}$,

$$\mathbf{A}_\nu = \mathbf{A}_\nu^{10} + \mathbf{A}^{01}, \quad (15)$$

$$\mathbf{A}_\nu^{10} = \frac{1}{2} (\mathbf{B} \times \mathbf{r}_\nu), \quad \mathbf{r}_\nu = \mathbf{r} - \mathbf{R}_\nu, \quad (16)$$

$$\mathbf{A}^{01} = \frac{1}{c^2} \left(\boldsymbol{\mu}_M \times \frac{\mathbf{r}_M}{r_M^3} \right), \quad \mathbf{r}_M = \mathbf{r} - \mathbf{R}_M, \quad (17)$$

where $\mathbf{R}_M$ is the position vector of nucleus M.

The renormalized 2c-NESC Hamiltonian matrix $\mathbf{H}_m$ in the presence of a magnetic field,

$$\mathbf{H}_m = \mathbf{G}_m^\dagger \tilde{\mathbf{L}}_m \mathbf{G}_m, \quad (18)$$

is determined by $\tilde{\mathbf{L}}_m$ and $\mathbf{G}_m$,

$$\tilde{\mathbf{L}}_m = \mathbf{U}_m^\dagger \boldsymbol{\Pi} + \boldsymbol{\Pi}^\dagger \mathbf{U}_m - \mathbf{U}_m^\dagger (\mathbf{T}_m - \mathbf{W}_m) \mathbf{U}_m + \mathbf{V}_m, \quad (19)$$

$$\mathbf{G}_m = \mathbf{S}_m^{-1/2} \left(\mathbf{S}_m^{-1/2} \tilde{\mathbf{S}}_m \mathbf{S}_m^{-1/2} \right)^{-1/2} \mathbf{S}_m^{1/2}, \quad (20)$$

where the relativistic metric

$$\tilde{\mathbf{S}}_m = \mathbf{S}_m + \frac{1}{2mc^2} \mathbf{U}_m^\dagger \mathbf{T}_m \mathbf{U}_m \quad (21)$$

depends on matrix $\mathbf{U}_m$ that is obtained from $\mathbf{C}_+^S = \mathbf{U}_m \mathbf{C}_+^L$ by using the eigenvectors $\mathbf{C}_+^S$ and $\mathbf{C}_+^L$ of Eq. (6). Note that for $\mathbf{B} = \boldsymbol{\mu}_M = 0$, $\boldsymbol{\Pi} = \mathbf{T}$, $\mathbf{S}_m = \mathbf{S}$, etc.

B. NMR shielding tensor at the GHF level

The formula of the NMR shielding tensor σ_{tu} ($t, u = x, y, z$) at the GHF level is given by

$$\sigma_{tu} = \frac{\partial^2 E}{\partial B_t \partial \mu_{M,u}} \bigg|_{\mathbf{B} = \boldsymbol{\mu}_M = 0}$$
$$= tr \left[\mathbf{P} \left(\frac{\partial^2 \mathbf{H}_m}{\partial B_t \partial \mu_{M,u}} \right) \right]_{\mathbf{B} = \boldsymbol{\mu}_M = 0}$$
$$+ tr \left[\frac{\partial \mathbf{P}}{\partial B_t} \left(\frac{\partial \mathbf{H}_m}{\partial \mu_{M,u}} \right) \right]_{\mathbf{B} = \boldsymbol{\mu}_M = 0}, \quad (22)$$

where E denotes the total electronic energy, $\mathbf{P}$ the zeroth-order density matrix ($\mathbf{P} = \mathbf{CnC}^\dagger$ with $\mathbf{C}$ being the 2c spinor coefficient matrix), and the first-order density matrix ($\partial\mathbf{P}/\partial B_t$) is obtained by solving the GIAO-based CPGHF equations[84] for the perturbation ($\partial\mathbf{H}_m/\partial B_t)_{\mathbf{B}=\boldsymbol{\mu}_M=\mathbf{0}}$. In the following, we use subscript $\mathbf{0}$ to denote $\mathbf{B} = \boldsymbol{\mu}_M = \mathbf{0}$ and omit the subscripts t and u when their use is not important.

C. Deriving the first derivatives of the 2c-NESC magnetic Hamiltonian matrix

To calculate the NMR shielding constants by using Eq. (22), the three derivatives of the 2c-NESC magnetic Hamiltonian matrix of Eq. (18) are needed: $(\partial\mathbf{H}_m/\partial B)_{\mathbf{0}}$, $(\partial\mathbf{H}_m/\partial\mu_M)_{\mathbf{0}}$, and $(\partial^2\mathbf{H}_m/\partial B\partial\mu_M)_{\mathbf{0}}$.

The derivative $(\partial\mathbf{H}_m/\partial B)_{\mathbf{0}}$ is given by

$$\left(\frac{\partial\mathbf{H}_m}{\partial B}\right)_{\mathbf{0}} = \mathbf{G}^\dagger\left(\frac{\partial\tilde{\mathbf{L}}_m}{\partial B}\right)_{\mathbf{0}}\mathbf{G}$$
$$+ \left(\frac{\partial\mathbf{G}_m^\dagger}{\partial B}\right)_{\mathbf{0}}\tilde{\mathbf{L}}\mathbf{G} + \mathbf{G}^\dagger\tilde{\mathbf{L}}\left(\frac{\partial\mathbf{G}_m}{\partial B}\right)_{\mathbf{0}}, \quad (23)$$

where the derivative of $\tilde{\mathbf{L}}_m$ is determined according to

$$\left(\frac{\partial\tilde{\mathbf{L}}_m}{\partial B}\right)_{\mathbf{0}} = \left(\frac{\partial\mathbf{V}_m}{\partial B}\right)_{\mathbf{0}} + \mathbf{U}^\dagger\left[\left(\frac{\partial\mathbf{W}_m}{\partial B}\right)_{\mathbf{0}} - \left(\frac{\partial\mathbf{T}_m}{\partial B}\right)_{\mathbf{0}}\right]\mathbf{U}$$
$$+ \left[\mathbf{U}^\dagger\left(\frac{\partial\boldsymbol{\Pi}}{\partial B}\right)_{\mathbf{0}} + \left[\mathbf{T} - \mathbf{U}^\dagger(\mathbf{T} - \mathbf{W})\right]\left(\frac{\partial\mathbf{U}_m}{\partial B}\right)_{\mathbf{0}}\right]^\dagger$$
$$+ \mathbf{U}^\dagger\left(\frac{\partial\boldsymbol{\Pi}}{\partial B}\right)_{\mathbf{0}} + \left[\mathbf{T} - \mathbf{U}^\dagger(\mathbf{T} - \mathbf{W})\right]\left(\frac{\partial\mathbf{U}_m}{\partial B}\right)_{\mathbf{0}}. \quad (24)$$

Hence, the derivatives $(\partial\mathbf{G}_m/\partial B)_{\mathbf{0}}$ and $(\partial\mathbf{U}_m/\partial B)_{\mathbf{0}}$ are required to calculate $(\partial\mathbf{H}_m/\partial B)_{\mathbf{0}}$. Utilizing the relationship $\mathbf{G}_m^2 = \tilde{\mathbf{S}}_m^{-1}\mathbf{S}_m$ and solving the Sylvester equation $\mathbf{GX} + \mathbf{XG} = \mathbf{Q}$ (where $\mathbf{X} = (\partial\mathbf{G}_m/\partial B)_{\mathbf{0}}$ and $\mathbf{Q} = (\partial\tilde{\mathbf{S}}_m^{-1}\mathbf{S}_m/\partial B)_{\mathbf{0}}$), derivative $(\partial\mathbf{G}_m/\partial B)_{\mathbf{0}}$ can be written as

$$\left(\frac{\partial\mathbf{G}_m}{\partial B}\bigg|_{\mathbf{0}}\right)_{\mu\nu}$$
$$= \sum_{i,j}\frac{1}{g_i + g_j}(\mathbf{R}_G)_{\mu i}\left[\mathbf{R}_G^{-1}\left(\frac{\partial\mathbf{G}_m^2}{\partial B}\right)_{\mathbf{0}}\mathbf{R}_G\right]_{ij}\left(\mathbf{R}_G^{-1}\right)_{j\nu}, \quad (25)$$

where $\mathbf{R}_G$ and $\mathbf{g}$ are the eigenvector and eigenvalue of $\mathbf{G}$: $\mathbf{GR}_G = \mathbf{R}_G\mathbf{g}$. By using $\mathbf{G}_m^2 = \tilde{\mathbf{S}}_m^{-1}\mathbf{S}_m$, the derivative $(\partial\mathbf{G}_m^2/\partial B)_{\mathbf{0}}$ is obtained as

$$\left(\frac{\partial\mathbf{G}_m^2}{\partial B}\right)_{\mathbf{0}} = \tilde{\mathbf{S}}^{-1}\left(\frac{\partial\mathbf{S}_m}{\partial B}\right)_{\mathbf{0}} - \left[\tilde{\mathbf{S}}^{-1}\left(\frac{\partial\tilde{\mathbf{S}}_m}{\partial B}\right)_{\mathbf{0}}\tilde{\mathbf{S}}^{-1}\right]\mathbf{S}, \quad (26)$$

where

$$\left(\frac{\partial\tilde{\mathbf{S}}_m}{\partial B}\right)_{\mathbf{0}} = \left(\frac{\partial\mathbf{S}_m}{\partial B}\right)_{\mathbf{0}} + \frac{1}{2mc^2}\mathbf{U}^\dagger\left(\frac{\partial\mathbf{T}_m}{\partial B}\right)_{\mathbf{0}}\mathbf{U}$$
$$+ \frac{1}{2mc^2}\left[\left(\frac{\partial\mathbf{U}_m^\dagger}{\partial B}\right)_{\mathbf{0}}\mathbf{TU} + \mathbf{U}^\dagger\mathbf{T}\left(\frac{\partial\mathbf{U}_m}{\partial B}\right)_{\mathbf{0}}\right]. \quad (27)$$

The derivative $(\partial\mathbf{U}_m/\partial B)_{\mathbf{0}}$ is required for the calculation of $(\partial\mathbf{G}_m/\partial B)_{\mathbf{0}}$ (Eq. (25)) and $(\partial\tilde{\mathbf{L}}_m/\partial B)_{\mathbf{0}}$ (Eq. (24)). Ways to calculate the derivative of $\mathbf{U}$ were already suggested by Cheng and Gauss[93] as well as Filatov and co-workers[14] (see Eqs. (36) and (37) in Ref. 14). In the present study, the derivative $(\partial\mathbf{U}_m/\partial B)_{\mathbf{0}}$ is written as

$$\left(\frac{\partial\mathbf{U}_m}{\partial B}\right)_{\mathbf{0}} = \left(\mathbf{C}_-^S - \mathbf{U}\mathbf{C}_-^L\right)\left(\frac{\partial\mathbf{O}_{-+}}{\partial B}\right)_{\mathbf{0}}\mathbf{C}_+^{L\dagger}\tilde{\mathbf{S}}, \quad (28)$$

where $(\partial\mathbf{O}_{-+}/\partial B)_{\mathbf{0}}$ denotes the mixing coefficient matrix for describing the mixing of the spinors due to the magnetic perturbation

$$\begin{pmatrix}\partial\mathbf{C}_-^L/\partial B & \partial\mathbf{C}_+^L/\partial B\\\partial\mathbf{C}_-^S/\partial B & \partial\mathbf{C}_+^S/\partial B\end{pmatrix}$$
$$= \begin{pmatrix}\mathbf{C}_-^L & \mathbf{C}_+^L\\\mathbf{C}_-^S & \mathbf{C}_+^S\end{pmatrix}\begin{pmatrix}\partial\mathbf{O}_{--}/\partial B & \partial\mathbf{O}_{-+}/\partial B\\\partial\mathbf{O}_{+-}/\partial B & \partial\mathbf{O}_{++}/\partial B\end{pmatrix}. \quad (29)$$

By utilizing formulas from Refs. 12 and 14, the mixing coefficient matrix is given as

$$\left(\frac{\partial\mathbf{O}_{-+}}{\partial B}\bigg|_{\mathbf{0}}\right)_{ij} = \frac{1}{\epsilon_j^+ - \epsilon_i^-}\left[\mathbf{C}_-^{L\dagger}\left(\frac{\partial\mathbf{V}_m}{\partial B}\right)_{\mathbf{0}}\mathbf{C}_+^L\right.$$
$$+ \mathbf{C}_-^{L\dagger}\left(\frac{\partial\boldsymbol{\Pi}^\dagger}{\partial B}\right)_{\mathbf{0}}\mathbf{C}_+^S + \mathbf{C}_-^{S\dagger}\left(\frac{\partial\boldsymbol{\Pi}}{\partial B}\right)_{\mathbf{0}}\mathbf{C}_+^L$$
$$+ \mathbf{C}_-^{S\dagger}\left[\left(\frac{\partial\mathbf{W}_m}{\partial B}\right)_{\mathbf{0}} - \left(\frac{\partial\mathbf{T}_m}{\partial B}\right)_{\mathbf{0}}\right]\mathbf{C}_+^S\right]_{ij}$$
$$- \frac{\epsilon_j^+}{\epsilon_j^+ - \epsilon_i^-}\left[\mathbf{C}_-^{L\dagger}\left(\frac{\partial\mathbf{S}_m}{\partial B}\right)_{\mathbf{0}}\mathbf{C}_+^L\right.$$
$$\left.+ \frac{1}{2mc^2}\mathbf{C}_-^{S\dagger}\left(\frac{\partial\mathbf{T}_m}{\partial B}\right)_{\mathbf{0}}\mathbf{C}_+^S\right]_{ij}. \quad (30)$$

The derivative $(\partial\mathbf{H}_m/\partial\mu_M)_{\mathbf{0}}$ can be obtained similarly where only the terms containing $\partial\boldsymbol{\Pi}/\partial\mu_M$ are kept.

D. Deriving the second derivative of the 2c-NESC magnetic Hamiltonian matrix

In a previous paper, Zou and co-workers already derived the second derivatives of the spin-free NESC Hamiltonian.[16] According to the formulas given by these authors,[16] the second derivative $(\partial^2\mathbf{H}_m/\partial B\partial\mu_M)_{\mathbf{0}}$ can be written as

$$\left(\frac{\partial^2\mathbf{H}_m}{\partial B\partial\mu_M}\right)_{\mathbf{0}} = \mathbf{G}^\dagger\left(\frac{\partial^2\tilde{\mathbf{L}}_m}{\partial B\partial\mu_M}\right)_{\mathbf{0}}\mathbf{G} + \left\{\mathbf{G}^\dagger\tilde{\mathbf{L}}\left(\frac{\partial^2\mathbf{G}_m}{\partial B\partial\mu_M}\right)_{\mathbf{0}}\right\}^\dagger + \mathbf{G}^\dagger\tilde{\mathbf{L}}\left(\frac{\partial^2\mathbf{G}_m}{\partial B\partial\mu_M}\right)_{\mathbf{0}} + \left\{\mathbf{G}^\dagger\left[\left(\frac{\partial\tilde{\mathbf{L}}_m}{\partial\mu_M}\right)_{\mathbf{0}}\left(\frac{\partial\mathbf{G}_m}{\partial B}\right)_{\mathbf{0}} + \left(\frac{\partial\tilde{\mathbf{L}}_m}{\partial B}\right)_{\mathbf{0}}\left(\frac{\partial\mathbf{G}_m}{\partial\mu_M}\right)_{\mathbf{0}}\right]\right.$$
$$\left.+ \left(\frac{\partial\mathbf{G}_m^\dagger}{\partial B}\right)_{\mathbf{0}}\tilde{\mathbf{L}}\left(\frac{\partial\mathbf{G}_m}{\partial\mu_M}\right)_{\mathbf{0}}\right\}^\dagger + \mathbf{G}^\dagger\left[\left(\frac{\partial\tilde{\mathbf{L}}_m}{\partial\mu_M}\right)_{\mathbf{0}}\left(\frac{\partial\mathbf{G}_m}{\partial B}\right)_{\mathbf{0}} + \left(\frac{\partial\tilde{\mathbf{L}}_m}{\partial B}\right)_{\mathbf{0}}\left(\frac{\partial\mathbf{G}_m}{\partial\mu_M}\right)_{\mathbf{0}}\right] + \left(\frac{\partial\mathbf{G}_m^\dagger}{\partial B}\right)_{\mathbf{0}}\tilde{\mathbf{L}}\left(\frac{\partial\mathbf{G}_m}{\partial\mu_M}\right)_{\mathbf{0}}, \quad (31)$$

where the second derivatives of $\tilde{\mathbf{L}}_m$ take the form

$$\left(\frac{\partial^2 \tilde{\mathbf{L}}_m}{\partial B \partial \mu_{\mathrm{M}}}\right)_0 = \left[\mathbf{U}^\dagger \left(\frac{\partial^2 \mathbf{\Pi}}{\partial B \partial \mu_{\mathrm{M}}}\right)_0\right]^\dagger + \mathbf{U}^\dagger \left(\frac{\partial^2 \mathbf{\Pi}}{\partial B \partial \mu_{\mathrm{M}}}\right)_0 + \left[\left[\mathbf{T} - \mathbf{U}^\dagger (\mathbf{T} - \mathbf{W})\right]\left(\frac{\partial^2 \mathbf{U}_m}{\partial B \partial \mu_{\mathrm{M}}}\right)_0\right]^\dagger + \left[\mathbf{T} - \mathbf{U}^\dagger (\mathbf{T} - \mathbf{W})\right]\left(\frac{\partial^2 \mathbf{U}_m}{\partial B \partial \mu_{\mathrm{M}}}\right)_0$$

$$+ \left[\left(\frac{\partial \mathbf{U}_m^\dagger}{\partial \mu_{\mathrm{M}}}\right)_0 \left(\frac{\partial \mathbf{\Pi}}{\partial B}\right)_0 + \left(\frac{\partial \mathbf{U}_m^\dagger}{\partial B}\right)_0 \left(\frac{\partial \mathbf{\Pi}}{\partial \mu_{\mathrm{M}}}\right)_0\right]^\dagger + \left(\frac{\partial \mathbf{U}_m^\dagger}{\partial \mu_{\mathrm{M}}}\right)_0 \left(\frac{\partial \mathbf{\Pi}}{\partial B}\right)_0$$

$$+ \left(\frac{\partial \mathbf{U}_m^\dagger}{\partial B}\right)_0 \left(\frac{\partial \mathbf{\Pi}}{\partial \mu_{\mathrm{M}}}\right)_0 - \left[\mathbf{U}^\dagger \left[\left(\frac{\partial \mathbf{T}_m}{\partial B}\right)_0 - \left(\frac{\partial \mathbf{W}_m}{\partial B}\right)_0\right]\left(\frac{\partial \mathbf{U}_m}{\partial \mu_{\mathrm{M}}}\right)_0\right]^\dagger - \mathbf{U}^\dagger \left[\left(\frac{\partial \mathbf{T}_m}{\partial B}\right)_0\right.$$

$$- \left.\left(\frac{\partial \mathbf{W}_m}{\partial B}\right)_0\right]\left(\frac{\partial \mathbf{U}_m}{\partial \mu_{\mathrm{M}}}\right)_0 - \left[\left(\frac{\partial \mathbf{U}_m^\dagger}{\partial \mu_{\mathrm{M}}}\right)_0 (\mathbf{T} - \mathbf{W})\left(\frac{\partial \mathbf{U}_m}{\partial B}\right)_0\right]^\dagger - \left(\frac{\partial \mathbf{U}_m^\dagger}{\partial \mu_{\mathrm{M}}}\right)_0 (\mathbf{T} - \mathbf{W})\left(\frac{\partial \mathbf{U}_m}{\partial B}\right)_0. \quad (32)$$

Matrices $(\partial^2 \mathbf{G}_m/\partial B \partial \mu_{\mathrm{M}})_0$ and $(\partial^2 \mathbf{U}_m/\partial B \partial \mu_{\mathrm{M}})_0$ are required to calculate $(\partial^2 \mathbf{H}_m/\partial B \partial \mu_{\mathrm{M}})_0$. Solving the Sylvester equation,

$$\left(\frac{\partial^2 \mathbf{G}_m}{\partial B \partial \mu_{\mathrm{M}}}\right)_0 \mathbf{G} + \mathbf{G}\left(\frac{\partial^2 \mathbf{G}_m}{\partial B \partial \mu_{\mathrm{M}}}\right)_0 = \left(\frac{\partial^2 \tilde{\mathbf{S}}_m^{-1} \mathbf{S}_m}{\partial B \partial \mu_{\mathrm{M}}}\right)_0$$
$$- \left(\frac{\partial \mathbf{G}_m}{\partial \mu_{\mathrm{M}}}\right)_0 \left(\frac{\partial \mathbf{G}_m}{\partial B}\right)_0 - \left(\frac{\partial \mathbf{G}_m}{\partial B}\right)_0 \left(\frac{\partial \mathbf{G}_m}{\partial \mu_{\mathrm{M}}}\right)_0, \quad (33)$$

one obtains the following formula for the second derivatives of $\mathbf{G}_m$:

$$\left(\frac{\partial^2 \mathbf{G}_m}{\partial B \partial \mu_{\mathrm{M}}}\bigg|_0\right)_{\mu\nu}$$
$$= \sum_{i,j} \frac{1}{g_i + g_j} (\mathbf{R}_G)_{\mu i} \left[\mathbf{R}_G^{-1}\left(\frac{\partial^2 \mathbf{G}_m^2}{\partial B \partial \mu_{\mathrm{M}}}\right)_0 \mathbf{R}_G\right]_{ij} \left(\mathbf{R}_G^{-1}\right)_{j\nu} \quad (34)$$

with

$$\left(\frac{\partial^2 \mathbf{G}_m^2}{\partial B \partial \mu_{\mathrm{M}}}\right)_0 = -\tilde{\mathbf{S}}^{-1}\left\{\left(\frac{\partial^2 \tilde{\mathbf{S}}_m}{\partial B \partial \mu_{\mathrm{M}}}\right)_0 \mathbf{G}\mathbf{G}\right.$$
$$+ \left(\frac{\partial \tilde{\mathbf{S}}_m}{\partial B}\right)_0 \left[\left(\frac{\partial \mathbf{G}_m}{\partial \mu_{\mathrm{M}}}\right)_0 \mathbf{G} + \mathbf{G}\left(\frac{\partial \mathbf{G}_m}{\partial \mu_{\mathrm{M}}}\right)_0\right]$$
$$+ \left.\left(\frac{\partial \tilde{\mathbf{S}}_m}{\partial \mu_{\mathrm{M}}}\right)_0 \left[\left(\frac{\partial \mathbf{G}_m}{\partial B}\right)_0 \mathbf{G} + \mathbf{G}\left(\frac{\partial \mathbf{G}_m}{\partial B}\right)_0\right]\right\}$$
$$- \left(\frac{\partial \mathbf{G}_m}{\partial \mu_{\mathrm{M}}}\right)_0 \left(\frac{\partial \mathbf{G}_m}{\partial B}\right)_0 - \left(\frac{\partial \mathbf{G}_m}{\partial B}\right)_0 \left(\frac{\partial \mathbf{G}_m}{\partial \mu_{\mathrm{M}}}\right)_0, \quad (35)$$

where the second derivative of $\tilde{\mathbf{S}}_m$ in Eq. (35) is given by

$$\left(\frac{\partial^2 \tilde{\mathbf{S}}_m}{\partial B \partial \mu_{\mathrm{M}}}\right)_0 = \frac{1}{2mc^2}\left\{\left[\left(\frac{\partial \mathbf{U}_m^\dagger}{\partial B}\right)_0 \mathbf{T}\left(\frac{\partial \mathbf{U}_m}{\partial \mu_{\mathrm{M}}}\right)_0\right.\right.$$
$$+ \mathbf{U}^\dagger \left(\frac{\partial \mathbf{T}_m}{\partial B}\right)_0 \left(\frac{\partial \mathbf{U}_m}{\partial \mu_{\mathrm{M}}}\right)_0 + \left.\mathbf{U}^\dagger \mathbf{T}\left(\frac{\partial^2 \mathbf{U}_m}{\partial B \partial \mu_{\mathrm{M}}}\right)_0\right]^\dagger$$
$$+ \left(\frac{\partial \mathbf{U}_m^\dagger}{\partial B}\right)_0 \mathbf{T}\left(\frac{\partial \mathbf{U}_m}{\partial \mu_{\mathrm{M}}}\right)_0 + \mathbf{U}^\dagger \left(\frac{\partial \mathbf{T}_m}{\partial B}\right)_0 \left(\frac{\partial \mathbf{U}_m}{\partial \mu_{\mathrm{M}}}\right)_0$$
$$+ \left.\mathbf{U}^\dagger \mathbf{T}\left(\frac{\partial^2 \mathbf{U}_m}{\partial B \partial \mu_{\mathrm{M}}}\right)_0\right\}. \quad (36)$$

In Eqs. (32) and (36), the second derivate $(\partial^2 \mathbf{U}_m/\partial B \partial \mu_{\mathrm{M}})_0$ is required, which will be derived in Subsection II E.

E. Derivation of the second derivative of the matrix $\mathbf{U}_m$

The second derivative of $\mathbf{U}$ (or $\mathbf{U}_m$) with respect to general perturbation parameters (here B and μ) has been derived in a previous paper by Zou and co-workers (there, Eq. (B19))[16]

$$\mathbf{U}^{B\mu} = \left(\mathbf{C}_-^S - \mathbf{U}\mathbf{C}_-^L\right)\left(\mathbf{O}_2^{B\mu} - \mathbf{O}_2^B\mathbf{O}_4^\mu - \mathbf{O}_2^\mu\mathbf{O}_4^B\right.$$
$$\left. - \mathbf{O}_2^B\mathbf{C}_+^{L\dagger}\tilde{\mathbf{S}}\mathbf{C}_-^L\mathbf{O}_2^\mu - \mathbf{O}_2^\mu\mathbf{C}_+^{L\dagger}\tilde{\mathbf{S}}\mathbf{C}_-^L\mathbf{O}_2^B\right)\mathbf{C}_+^{L\dagger}\tilde{\mathbf{S}}. \quad (37)$$

As shown in Appendix B in Ref. 16, when simplifying the one-electron Dirac equation of Eq. (6) according to

$$\tilde{\mathbf{D}}\mathbf{\Phi} = \tilde{\mathbf{M}}\mathbf{\Phi}\epsilon \quad (38)$$

and using the identities $\mathbf{\Phi}^\dagger \tilde{\mathbf{M}}\mathbf{\Phi} = \mathbf{I}$ and $\mathbf{\Phi}^\dagger \tilde{\mathbf{D}}\mathbf{\Phi} = \epsilon$, the first- and second-order mixing coefficient matrices $\mathbf{O}^\lambda$ ($\lambda = B, \mu, B\mu$) are determined by the following first- and second-order coupled-perturbed one-electron Dirac equations:

$$[\mathbf{O}^\lambda, \epsilon] = \mathbf{N}^\lambda - \epsilon^\lambda, \quad (39)$$

where $[\mathbf{a}, \mathbf{b}] = \mathbf{a}\mathbf{b} - \mathbf{b}\mathbf{a}, \mathbf{N}^\lambda = \mathbf{\Phi}^\dagger \tilde{\mathbf{D}}^\lambda \mathbf{\Phi} - \mathbf{\Phi}^\dagger \tilde{\mathbf{M}}^\lambda \mathbf{\Phi}\epsilon$ with $\lambda = B$ or μ, and

$$[\mathbf{O}^{B\mu}, \epsilon] = \mathbf{\Phi}^\dagger \tilde{\mathbf{D}}^{B\mu} \mathbf{\Phi} - \mathbf{\Phi}^\dagger \tilde{\mathbf{M}}^{B\mu}\mathbf{\Phi}\epsilon - \epsilon^{B\mu}$$
$$+ \mathbf{O}^B[\mathbf{O}^\mu, \epsilon] + \mathbf{O}^\mu[\mathbf{O}^B, \epsilon]$$
$$+ \mathbf{O}^{\dagger B}\mathbf{N}^\mu + \mathbf{N}^\mu\mathbf{O}^B + \mathbf{O}^{\dagger\mu}\mathbf{N}^B + \mathbf{N}^B\mathbf{O}^\mu \quad (40)$$

with the following relations:

$$\mathbf{\Phi}^\lambda = \mathbf{\Phi}\mathbf{O}^\lambda \text{ and } \mathbf{\Phi}^{B\lambda} = \mathbf{\Phi}\mathbf{O}^{B\lambda}. \quad (41)$$

The above Eq. (40) is equivalent to Eq. (B20) in Ref. 16 (however the last three signs in Eq. (B20) being +, +, and −) by introducing $\mathbf{O}^{\dagger\lambda} = -\mathbf{\Phi}^\dagger \tilde{\mathbf{M}}^\lambda \mathbf{\Phi} - \mathbf{O}^\lambda$, which can be obtained by deriving the identity $\mathbf{\Phi}^\dagger \tilde{\mathbf{M}}\mathbf{\Phi} = \mathbf{I}$.

Since one can write the relationship between the derivative of 4c-spinor and the mixing coefficient matrix as

$$\mathbf{C}_{\mu q}^\lambda = \sum_r^{\mathrm{MO}} \mathbf{C}_{\mu r}\mathbf{O}_{rq}^\lambda, \quad (42)$$

the mixing coefficient matrix $\mathbf{O}^\lambda$ has the following structure in the 4c relativistic framework:

$$\mathbf{O}^\lambda = \begin{pmatrix} \mathbf{O}^\lambda_{--}(p,p) & \mathbf{O}^\lambda_{-+}(p,o) & \mathbf{O}^\lambda_{-+}(p,v) \\ \mathbf{O}^\lambda_{+-}(o,p) & \mathbf{O}^\lambda_{++}(o,o) & \mathbf{O}^\lambda_{++}(o,v) \\ \mathbf{O}^\lambda_{+-}(v,p) & \mathbf{O}^\lambda_{++}(v,o) & \mathbf{O}^\lambda_{++}(v,v) \end{pmatrix}$$

$$= \begin{pmatrix} \mathbf{O}^\lambda_1(p,p) & \mathbf{O}^\lambda_2(p,o) & \mathbf{O}^\lambda_2(p,v) \\ \mathbf{O}^\lambda_3(o,p) & \mathbf{O}_{4\lambda}(o,o) & \mathbf{O}^\lambda_4(o,v) \\ \mathbf{O}^\lambda_3(v,p) & \mathbf{O}^\lambda_4(v,o) & \mathbf{O}^\lambda_4(v,v) \end{pmatrix}. \qquad (43)$$

Hereafter p and e denote 4c-spinors of positronic or electronic states, respectively, and the latter are specified as being an occupied spinor (o) or a virtual spinor (v). For reasons of simplicity, we use in the following the subscripts of 1, 2, 3, and 4 for $--$, $-+$, $+-$, and $++$, respectively. The first-order mixing coefficient matrix $\mathbf{O}^\lambda$ of Eq. (43) is fully defined by the following contributions:

$$\mathbf{O}^\lambda_k(i,i) = -\frac{1}{2}\left(\mathbf{\Phi}^\dagger \tilde{\mathbf{M}}^\lambda \mathbf{\Phi}\right)_{ii} \qquad (44)$$

with $i = p$ for $k = 1$ and $i = o$ or v for $k = 4$, and

$$\mathbf{O}^\lambda_k(i,j) = \frac{\left(\mathbf{\Phi}^\dagger \tilde{\mathbf{D}}^\lambda \mathbf{\Phi}\right)_{ij} - \left(\mathbf{\Phi}^\dagger \tilde{\mathbf{M}}^\lambda \mathbf{\Phi}\right)_{ij}\epsilon^+_j}{\epsilon^+_j - \epsilon^-_i} \qquad (45)$$

with $(i,j) = (p,e)$ for $k = 2$, $(i,j) = (e,p)$ for $k = 3$, and $(i,j) = (v,o)$ or (o,v) for $k = 4$. The second-order mixing coefficient matrix

$\mathbf{O}^{B\mu}_2$ in Eq. (37) is obtained by using Eq. (40),

$$\left(\mathbf{O}^{B\mu}_2\right)_{pe} = \frac{1}{\epsilon^+_e - \epsilon^-_p}\left\{\left(\mathbf{\Phi}^\dagger \tilde{\mathbf{D}}^{B\mu}\mathbf{\Phi}\right)_{pe} - \left(\mathbf{\Phi}^\dagger \tilde{\mathbf{M}}^{B\mu}\mathbf{\Phi}\right)_{pe}\epsilon^+_e \right.$$
$$+ \left(\mathbf{O}^B\mathbf{O}^\mu + \mathbf{O}^\mu\mathbf{O}^B\right)_{pe}\epsilon^+_e - \left(\mathbf{O}^B\boldsymbol{\epsilon}\mathbf{O}^\mu + \mathbf{O}^\mu\boldsymbol{\epsilon}\mathbf{O}^B\right)_{pe}$$
$$\left. + \left(\mathbf{O}^{\dagger B}\mathbf{N}^\mu + \mathbf{N}^\mu\mathbf{O}^B + \mathbf{O}^{\dagger\mu}\mathbf{N}^B + \mathbf{N}^B\mathbf{O}^\mu\right)_{pe}\right\}, \quad (46)$$

which, after some algebraic manipulations, leads to the needed second derivatives of $\mathbf{U}_m$,

$$\left(\frac{\partial^2 \mathbf{U}_m}{\partial B \partial \mu_{\mathrm{M}}}\right)_0 = \left(\mathbf{C}^S_- - \mathbf{U}\mathbf{C}^L_-\right)\left[\left(\frac{\partial^2 \mathbf{O}_2}{\partial B \partial \mu_{\mathrm{M}}}\right)_0\right.$$
$$- \left(\frac{\partial \mathbf{O}_2}{\partial B}\right)_0\left(\frac{\partial \mathbf{O}_4}{\partial \mu_{\mathrm{M}}}\right)_0 - \left(\frac{\partial \mathbf{O}_2}{\partial \mu_{\mathrm{M}}}\right)_0\left(\frac{\partial \mathbf{O}_4}{\partial B}\right)_0$$
$$- \left(\frac{\partial \mathbf{O}_2}{\partial B}\right)_0\mathbf{C}^{L\dagger}_+\tilde{\mathbf{S}}\mathbf{C}^L_-\left(\frac{\partial \mathbf{O}_2}{\partial \mu_{\mathrm{M}}}\right)_0$$
$$\left. - \left(\frac{\partial \mathbf{O}_2}{\partial \mu_{\mathrm{M}}}\right)_0\mathbf{C}^{L\dagger}_+\tilde{\mathbf{S}}\mathbf{C}^L_-\left(\frac{\partial \mathbf{O}_2}{\partial B}\right)_0\right]\mathbf{C}^{L\dagger}_+\tilde{\mathbf{S}}, \quad (47)$$

where

$$\left(\frac{\partial^2 \mathbf{O}_2}{\partial B \partial \mu_{\mathrm{M}}}\bigg|_0\right)_{pe} = \frac{1}{\epsilon^+_e - \epsilon^-_p}\left\{\left[\mathbf{C}^{L\dagger}_-\left(\frac{\partial^2 \mathbf{\Pi}^\dagger}{\partial B \partial \mu_{\mathrm{M}}}\right)_0\mathbf{C}^S_+ + \mathbf{C}^{S\dagger}_-\left(\frac{\partial^2 \mathbf{\Pi}}{\partial B \partial \mu_{\mathrm{M}}}\right)_0\mathbf{C}^L_+\right]_{pe} + \left[\left(\frac{\partial \mathbf{O}_1}{\partial B}\right)_0\left(\frac{\partial \mathbf{O}_2}{\partial \mu_{\mathrm{M}}}\right)_0 + \left(\frac{\partial \mathbf{O}_2}{\partial B}\right)_0\left(\frac{\partial \mathbf{O}_4}{\partial \mu_{\mathrm{M}}}\right)_0\right.\right.$$
$$+ \left(\frac{\partial \mathbf{O}_2}{\partial \mu_{\mathrm{M}}}\right)_0\left(\frac{\partial \mathbf{O}_4}{\partial B}\right)_0\bigg]_{pe}\epsilon^+_e - \left[\left(\frac{\partial \mathbf{O}_1}{\partial B}\right)_0\epsilon^-_p\left(\frac{\partial \mathbf{O}_2}{\partial \mu_{\mathrm{M}}}\right)_0 + \left(\frac{\partial \mathbf{O}_2}{\partial B}\right)_0\epsilon^+_e\left(\frac{\partial \mathbf{O}_4}{\partial \mu_{\mathrm{M}}}\right)_0 + \left(\frac{\partial \mathbf{O}_2}{\partial \mu_{\mathrm{M}}}\right)_0\epsilon^+_e\left(\frac{\partial \mathbf{O}_4}{\partial B}\right)_0\bigg]_{pe}$$
$$+ \left[\left(\frac{\partial \mathbf{O}_3}{\partial B}\right)^\dagger_0\left(\frac{\partial \mathbf{d}_4}{\partial \mu_{\mathrm{M}}}\right)_0 + \left(\frac{\partial \mathbf{d}_1}{\partial \mu_{\mathrm{M}}}\right)_0\left(\frac{\partial \mathbf{O}_2}{\partial B}\right)_0 + \left(\frac{\partial \mathbf{O}_1}{\partial B}\right)^\dagger_0\left(\frac{\partial \mathbf{d}_2}{\partial \mu_{\mathrm{M}}}\right)_0 + \left(\frac{\partial \mathbf{d}_2}{\partial \mu_{\mathrm{M}}}\right)_0\left(\frac{\partial \mathbf{O}_4}{\partial B}\right)_0\right]_{pe}$$
$$+ \left[\left(\frac{\partial \mathbf{O}_3}{\partial \mu_{\mathrm{M}}}\right)^\dagger_0\left(\left(\frac{\partial \mathbf{d}_4}{\partial B}\right)_0 - \left(\frac{\partial \mathbf{m}_4}{\partial B}\right)_0\epsilon^+_e\right) + \left(\left(\frac{\partial \mathbf{d}_1}{\partial B}\right)_0 - \left(\frac{\partial \mathbf{m}_1}{\partial B}\right)_0\epsilon^-_p\right)\left(\frac{\partial \mathbf{O}_2}{\partial \mu_{\mathrm{M}}}\right)_0\right.$$
$$\left.\left. + \left(\left(\frac{\partial \mathbf{d}_2}{\partial B}\right)_0 - \left(\frac{\partial \mathbf{m}_2}{\partial B}\right)_0\epsilon^+_e\right)\left(\frac{\partial \mathbf{O}_4}{\partial \mu_{\mathrm{M}}}\right)_0\right]_{pe}\right\}. \qquad (48)$$

In Eq. (48), the derivatives $\mathbf{d}^\lambda_n$ ($\lambda = B$ and μ_{M}) or $\mathbf{m}^B_n$ ($n = 1$, 2, 3, 4) are defined as follows:

$$\begin{pmatrix} \mathbf{d}^\lambda_1 & \mathbf{d}^\lambda_2 \\ \mathbf{d}^\lambda_3 & \mathbf{d}^\lambda_4 \end{pmatrix}_0 := \mathbf{\Phi}^\dagger\left(\frac{\partial \tilde{\mathbf{D}}}{\partial \lambda}\right)_0\mathbf{\Phi}, \qquad (49)$$

$$\begin{pmatrix} \mathbf{m}^B_1 & \mathbf{m}^B_2 \\ \mathbf{m}^B_3 & \mathbf{m}^B_4 \end{pmatrix}_0 := \mathbf{\Phi}^\dagger\left(\frac{\partial \tilde{\mathbf{M}}}{\partial B}\right)_0\mathbf{\Phi}. \qquad (50)$$

Terms for calculating Eqs. (47) and (48) are given in the supplementary material.

III. COMPUTATIONAL DETAILS

The 2c-NESC formulas derived in Sec. II for calculating NMR shielding constants were implemented into the NESC program of the *ab initio* package COLOGNE2016.[94] The corresponding programs were tested in three different ways: (i) Both at 1c- and 2c-NESC level, it was verified that for

$c \to \infty$ non-relativistic NMR shielding values were recovered. (ii) The 1c-NESC nuclear magnetic shielding constants were compared with already published values.[85] (iii) The corresponding 2c-NESC values were compared with 4c-sMB calculations (see Table I).

Atomic NMR shielding constants were calculated at the GHF level to compare 1c-NESC and 2c-NESC values with the corresponding 4c-sMB results. For this purpose, uncontracted Dyall valence double zeta basis sets[95–100] were used for Kr, Xe, Rn, Cd, Hg, Ca, Sr, Ba, and Ra whereas for Ne, Ar, Zn, Be, and Mg uncontracted Dunning aug-cc-pVDZ basis sets[101–104] were applied. The modified screened-nuclear-spin-orbit (mSNSO) approach was employed to approximate the influence of the two-electron spin-orbit terms.[20,22]

The finite (F) model of the nucleus based on a Gaussian charge distribution[105] was used. For reasons of comparison, calculations with a point (P) charge model of the nucleus were

TABLE I. Calculated atomic NMR shielding constants (ppm) obtained with 1c- and 2c-NESC/HF and 4c-sMB/HF methods. The finite (F) and point (P) nuclear models were used.[a]

Nuclear model	Atom	State	1c-NESC	2c-NESC	4c-sMB	Δ(4c-1c)	Δ(4c-2c)	$\Delta(4c-2c)$/4c (%)
F	Ne	$^1S_0$	551.7	557.1	557.3	5.6	0.2	0.03
	Ar	$^1S_0$	1 239.1	1 271.8	1 270.5	31.4	−1.3	−0.11
	Kr	$^1S_0$	3 273.4	3 570.0	3 572.6	299.2	2.6	0.07
	Xe	$^1S_0$	5 774.2	6 968.5	6 993.7	1219.5	25.2	0.36
	Rn	$^1S_0$	11 549.5	19 447.1	19 595.5	8046.0	148.4	0.76
	Zn	$^1S_0$	2 536.1	2 701.7	2 709.7	173.6	8.0	0.29
	Cd	$^1S_0$	4 897.0	5 682.6	5 697.8	800.8	15.2	0.27
	Hg	$^1S_0$	10 362.4	15 952.7	15 983.7	5621.3	31.0	0.19
	Mg	$^1S_0$	708.8	718.2	720.5	11.7	2.3	0.32
	Ca	$^1S_0$	1 425.4	1 471.4	1 471.7	46.3	0.3	0.02
	Sr	$^1S_0$	3 523.4	3 880.8	3 880.4	357.0	−0.4	−0.01
	Ba	$^1S_0$	6 071.1	7 428.1	7 456.2	1385.1	28.1	0.38
	Ra	$^1S_0$	11 967.7	20 620.4	20 766.9	8799.2	146.5	0.71
P	Ne	$^1S_0$	551.7	557.1	557.3	5.6	0.2	0.03
	Ar	$^1S_0$	1 239.1	1 271.8	1 270.5	31.4	−1.3	−0.11
	Kr	$^1S_0$	3 273.4	3 570.5	3 573.1	299.7	2.6	0.07
	Xe	$^1S_0$	5 774.5	6 985.2	7 002.7	1228.2	17.5	0.25
	Rn	$^1S_0$	11 554.6	20 048.7	20 194.3	8639.7	145.6	0.72
	Zn	$^1S_0$	2 536.2	2 701.9	2 709.9	173.7	8.0	0.29
	Cd	$^1S_0$	4 897.1	5 690.3	5 709.7	812.6	19.4	0.34
	Hg	$^1S_0$	10 365.2	16 266.0	16 297.8	5932.6	31.8	0.20
	Mg	$^1S_0$	708.8	718.2	720.5	11.7	2.3	0.32
	Ca	$^1S_0$	1 425.4	1 471.4	1 471.7	46.3	0.3	0.02
	Sr	$^1S_0$	3 523.5	3 882.4	3 881.9	358.4	−0.5	−0.01
	Ba	$^1S_0$	6 071.4	7 450.7	7 479.0	1407.6	28.3	0.38
	Ra	$^1S_0$	12 010.2	21 353.6	21 491.6	9481.4	138.0	0.64

[a]Symbols Δ(4c-1c) and Δ(4c-2c) denoted the differences between 4c-sMB and 1c-NESC or 2c-NESC values. Δ(4c-2c)/4c gives the relative deviation of 2c-NESC values from the 4c-sMB result in percentages.

also performed. A value of 137.035 999 070(98) was used for the velocity of light c.[106] The DIRAC12 program package[107] was employed to obtain 4c-sMB NMR shielding constants.

IV. RESULTS AND DISCUSSION

NMR magnetic shieldings obtained in this work at the 1c- or 2c-NESC level are compared in Table I with the corresponding 4c-sMB-values. In Figure 1, two correlations provide
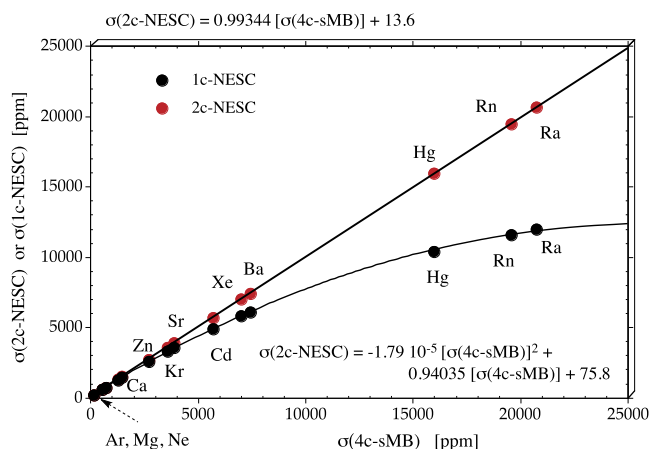

FIG. 1. Comparison of 1c-NESC and 2c-NESC magnetic shieldings with the corresponding 4c-sMB values for atoms with a closed shell electron configurations. R^2 = 1.000 in both cases.

a graphical comparison of 1c-NESC and 2c-NESC magnetic shieldings with 4c-sMB results.

The nuclear magnetic shieldings calculated in this work vary between 557 ppm (Ne, $^1S_0$) and 20 767 ppm (Ra, $^1S_0$, 4c-sMB values, Table I). Both the inspection of individual values in Table I and the general trends reflected by Figure 1 reveal that the 1c-NESC magnetic shieldings deviate for increasing atomic number more and more from the 4c-sMB values. There is a power relationship, which reflects the general trend observed for 1c-NESC magnetic nuclear shieldings σ_{iso}: SOC, which is not included in the spin-free representation, is of utmost importance for the correct description of the σ_{iso} values as is reflected by errors as large as 42% (Ra, error: 8799 ppm, Table I). Useful 1c-NESC σ_{iso} values can only be obtained for atomic numbers smaller than that of Kr when errors are reduced to ≤10%. But even for these atoms, SOC plays a role as it is responsible for deviations as large as 299 ppm (Kr). In the case of Ne, there is a 5.6 ppm deviation, which results from SOC. Already small SOC effects change the interaction mechanism between the nuclear magnetic moment and the applied external magnetic field, which leads even for nonrelativistic atoms to a sizable change of σ_{iso}. For other atomic properties such as the total energy, SOC comes only into play for closed shell atoms if high accuracy results are required. In so far, SOC makes the nuclear shielding a *relativistic property*.

2c-NESC nuclear magnetic shieldings reasonably agree with 4c-sMB values as are reflected by the linear relationship

in Figure 1. Relative errors are all smaller than 0.8% (Table I). The slope of the linear relationship is 0.993 and the R^2 coefficient is 1.000 ppm. There is a 13.6 ppm deviation at the origin, which results from a deviation up to 148 ppm for Rn (0.76%). If the calculated 2c-NESC values are fitted with the help of a quadratic or even cubic relationship, the value at the origin decreases to 1 ppm. The values obtained for Ne, Ar, Ca, and Sr are 0.2, −1.3, 0.3, and −0.4 ppm confirming an influence of SOC and the ability of 2c-NESC to reproduce the nuclear magnetic shielding of non-relativistic atoms. Similar curves as shown in Figure 1 are obtained when using the P nuclear model.

It is interesting to analyze the effect of using a P nuclear model or the more realistic F nuclear model. P values of σ are linearly related to those obtained with the F nuclear model (R^2: 1.000) at the 1c-NESC, 2c-NESC, and 4c-sMB levels of theory. Inspection of the relative deviation of the 2c-NESC values from the corresponding 4c-sMB results (last column in Table I) reveals that there are fine differences, for example, with regard to the nuclear magnetic shielding of Cd and Xe, which deviate more or less at the F level whereas at the P level the differences are reversed but remain ≤0.4% in these cases (Table I).

The difference between the F and P values of σ_{iso} increases with increasing atomic number. The influence of a finite nucleus is small for the spin-free 1c-NESC nuclear magnetic shielding constants (Hg, P nucleus: 10 362.4 + 2.8 ppm; Ra, P nucleus: 11 967.7 + 42.5 ppm; the second number gives the increase in σ_{iso} for reverting to the P model; Table I), which suggests that the scalar relativistic effects are hardly affected by using the finite size of a nucleus in the formulas for the nuclear magnetic shielding constant.

By including SOC as in 4c-sMB and 2c-NESC, a distinct dependence of the calculated σ_{iso} values on the nuclear charge is observed. As in the case of the 1c-NESC shieldings, the P model always leads to larger values. It is well known that the finite size of the nucleus affects the Fermi contact term, which is a result of the interaction of the nuclear magnetic moment and the spin polarization as induced by SOC.[108,109] The Fermi contact term vanishes if for closed-shell systems the spin-orbit interaction is switched off. Accordingly, the finite size of the nucleus has little impact on the nuclear magnetic shielding constant for a non-relativistic calculation.

V. CONCLUSIONS

A method has been worked out to calculate nuclear magnetic shielding constants from analytical second derivatives of the energy with regard to the perturbation caused by an external magnetic field and the nuclear magnetic moment where the energy is the 2c-NESC energy based on a GHF wave function. The diamagnetic and paramagnetic contributions to the nuclear magnetic shielding constant are first developed at the spin-free level of NESC and then extended to the 2c-NESC level to include SOC effects. For 13 closed shell atoms, the σ_{iso} value has been calculated and compared with the corresponding 4c-sMB reference values also determined in this work. 1c-NESC values show relatively large (up to 42%) deviations from the reference values. However, the 2c-NESC

nuclear magnetic shieldings are in excellent agreement with the 4c-sMB values, which is documented by relative errors <0.8% and a perfect correlation between the two sets of data (R^2 = 1.00, Figure 1). The improvement of the 2c-NESC nuclear magnetic shielding constants relative to the 1c-NESC values reflects the strong influence of SOC effects on σ_{iso}, which increases with increasing atomic charge and can be as large as 8653 ppm (Ra). The necessity of using a finite nucleus was also demonstrated.

Noteworthy is that the 2c-NESC-based method for calculating nuclear magnetic shielding constants does not have the difficulties of the corresponding 2c-BSS (Barysz, Sadlej, and Snijders)-based or 2c-DKH2-based formulations[27,83,84,110] when combining the 2c-approach with the RMB-GIAO method. Since the BSS or DKH2 operators are calculated in the momentum (or $\mathbf{p}^2$) space, it is difficult for these methods to derive useful magnetic operator matrices.[84] From another point of view, this difficulty is related to the commutation relation between $\mathbf{p}$ and $\mathbf{A}$ because it is not easy to extend the $\mathbf{p}^2$ space to the $\boldsymbol{\pi}^2$ space. Consequently, the NESC method is more favorable than the BSS and DKH2 methods for magnetic property calculations.

SUPPLEMENTARY MATERIAL

See supplementary material for calculating the various terms of Eqs. (47) and (48) and the one-electron integrals for determining the second order derivatives of the NESC Hamiltonian.

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