Relativistic calculation of nuclear magnetic shielding using normalized elimination of the small component

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The normalized elimination of the small component (NESC) theory, recently proposed by Filatov and Cremer [J. Chem. Phys. **122**, 064104 (2005)], is extended to include magnetic interactions and applied to the calculation of the nuclear magnetic shielding in HX (X=F,Cl,Br,I) systems. The NESC calculations are performed at the levels of the zeroth-order regular approximation (ZORA) and the second-order regular approximation (SORA). The calculations show that the NESC-ZORA results are very close to the NESC-SORA results, except for the shielding of the I nucleus. Both the NESC-ZORA and NESC-SORA calculations yield very similar results to the previously reported values obtained using the relativistic infinite-order two-component coupled Hartree-Fock method. The difference between NESC-ZORA and NESC-SORA results is significant for the shieldings of iodine. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2204606]

I. INTRODUCTION

The inclusion of the theory of special relativity is one of the most important problems in quantum chemistry. Although research on the inclusion into quantum mechanics started about 80 years ago,[1] developments are still being made. Among molecular properties, nuclear magnetic shielding is a sensitive probe for detecting relativistic effects, i.e., a kind of magnifying glass for observing relativistic effects.[2–5] Since nuclear magnetic shielding strongly depends on the electronic density and motion near the nuclei in a molecule, it severely reflects the relativistic effects on the electronic states produced by electrons in heavy atoms in the molecule. Fully relativistic treatments[6–11] based on the four-component spinor form of the one-electron wave function are still very costly, primarily due to the cost of a proper description of the small two-component spinor. In the four-component scheme, an accurate evaluation of the diamagnetic contribution to the nuclear magnetic shielding needs an explicit consideration of the negative energy states as virtual states. Thus, the development of an appropriate, less costly, two-component scheme is important. Many methods have been proposed to reduce the four-component Dirac equation to computationally much simpler two-component equations. Two groups of methods have been successful thus far: methods based on the Douglas-Kroll-Hess (DKH) approach[12–18] and methods based on the regular Hamiltonian approximation (RHA).[19–24]

In the DKH approach, the 4×4 Dirac Hamiltonian is block diagonalized by applying successive unitary transformations. The resultant transformed electronic wave function does not include the small two-component spinor. In the RHA approach, the small component is connected with the large component via a transformation operator. Since the small component does not disappear, the RHA method includes the small component contribution in the normalization condition of the wave function.

We have previously presented relativistic calculations of nuclear magnetic shielding in HX (X=F,Cl,Br,I) H_2X (X=O,S,Se,Te) and noble gas X (X=He,Ne,Ar,Kr,Xe) systems[25] using the relativistic infinite-order two-component coupled Hartree-Fock (IOTC-CHF) method proposed by Barysz and Sadlej.[15] The IOTC-CHF method is an infinite-order DKH (i.e., DKH∞) method. Our calculation results were compared with the previously reported values,[8,9,26–31] and it was shown that the IOTC-CHF results are consistent with the previously reported values.

Experimentally determined shielding anisotropies for $\Delta\sigma^{Xe}$ and $\Delta\sigma^{F}$ in XeF_2 have been reported recently.[32] In order to investigate the reliability of our IOTC-CHF calculation, we have performed IOTC-CHF calculations of $\Delta\sigma^{Xe}$ and $\Delta\sigma^{F}$ for XeF_2 and compared the results with the experimental values. It was shown that the IOTC-CHF results well reproduce the experimental values.[33] However, it is important to assess the reliability of our IOTC-CHF calculations by comparison with the results of another accurate and independent calculation method. Recently, Filatov and Cremer[34] proposed a new relativistic two-component equation, derived from the normalized elimination of the small component (NESC) theory. A similar fully relativistic two-component theory has been proposed by Kutzelnigg and Liu.[35] In the present paper, we extend the NESC theory to include magnetic interactions and apply it to the calculation of the nuclear magnetic shielding in HX (X=F,Cl,Br,I) systems for comparison with the previously reported values.

II. THEORY

A. One-electron systems

The Dirac equation for a one-electron system under an external magnetic flux density $\mathbf{B}_0$ and nuclear magnetic moment $\boldsymbol{\mu}_M$ at the Mth nuclear position $\mathbf{R}_M$ is given in atomic units ($\hbar=1$, $e=1$, $m_e=1$, $4\pi\varepsilon_0=1$, $c=137.035\ 989\ 5$) by

$$H_D\psi_{Di}=\varepsilon_i\psi_{Di},\quad i=1,2,\ldots, \tag{1}$$

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$$H_D = c\boldsymbol{\alpha}\cdot\boldsymbol{\pi} + (\beta-1)c^2 + V_n(\mathbf{r}), \tag{2}$$

$$\boldsymbol{\pi} = \mathbf{p} + \mathbf{A} = \mathbf{p} + \mathbf{A}_0 + \mathbf{A}_M, \tag{3}$$

$$\mathbf{A}_0 = \frac{1}{2}\mathbf{B}_0 \times \mathbf{r}_0, \quad \mathbf{r}_0 = \mathbf{r} - \mathbf{R}_0, \tag{4}$$

$$\mathbf{A}_M = c^{-2} r_M^{-3} \boldsymbol{\mu}_M \times \mathbf{r}_M, \quad \mathbf{r}_M = \mathbf{r} - \mathbf{R}_M. \tag{5}$$

Here, $\boldsymbol{\alpha}$ and β are the usual 4×4 Dirac vector and scalar matrices, $V_n(\mathbf{r})$ is the bare nuclear potential, and $\mathbf{R}_0$ is the position of the common gauge origin. The nucleus M at the position $\mathbf{R}_M$ is considered to be the target nucleus of the calculation. In order to derive the two-component equation, the ith four-component wave function ψ_{Di} is written using the large two-component spinor ϕ_{Li} and the small two-component spinor ϕ_{Si}. Furthermore, we connect ϕ_{Si} with ϕ_{Li} by introducing a general nonunitary transformation operator U as[34]

$$|\phi_{Si}\rangle = \frac{\boldsymbol{\sigma}\cdot\boldsymbol{\pi}}{2c} U |\phi_{Li}\rangle. \tag{6}$$

The Dirac equation (1) leads to the following two-component equations[34]

$$\left[V_n + \tfrac{1}{2}(\boldsymbol{\sigma}\cdot\boldsymbol{\pi})^2 U\right]\phi_{Li} = \varepsilon_i \phi_{Li}, \tag{7a}$$

$$\left[\frac{1}{2}(\boldsymbol{\sigma}\cdot\boldsymbol{\pi})^2 + \frac{1}{4c^2}\boldsymbol{\sigma}\cdot\boldsymbol{\pi}V_n\boldsymbol{\sigma}\cdot\boldsymbol{\pi}U - \frac{1}{2}(\boldsymbol{\sigma}\cdot\boldsymbol{\pi})^2 U\right]\phi_{Li} = \frac{\varepsilon_i}{2c^2}\frac{1}{2}(\boldsymbol{\sigma}\cdot\boldsymbol{\pi})^2 U\phi_{Li}. \tag{7b}$$

We define here the usual kinetic energy operator T and the magnetic interaction operator H_A by

$$T = \frac{1}{2}p^2, \tag{8}$$

$$H_A = \frac{1}{2}(\boldsymbol{\sigma}\cdot\boldsymbol{\pi})^2 - T. \tag{9}$$

H_A is explicitly written as

$$H_A = \frac{1}{2}(\mathbf{A}_0\cdot\mathbf{p} + \mathbf{p}\cdot\mathbf{A}_0 + \mathbf{A}_M\cdot\mathbf{p} + \mathbf{p}\cdot\mathbf{A}_M) + \frac{1}{2}i\boldsymbol{\sigma}\cdot(\mathbf{p}\times\mathbf{A}_0 + \mathbf{A}_0\times\mathbf{p} + \mathbf{p}\times\mathbf{A}_M + \mathbf{A}_M\times\mathbf{p}) + \mathbf{A}_0\cdot\mathbf{A}_M. \tag{10}$$

In Eq. (10), A_0^2 and A_M^2 terms have been discarded because we are not concerned about them. Equations (7a) and (7b) are then written as

$$[V_n + (T+H_A)U]\phi_{Li} = \varepsilon_i\phi_{Li}, \tag{11a}$$

$$[T + H_A + (W_0 - T - H_A)U]\phi_{Li} = \frac{\varepsilon_i}{2c^2}(T+H_A)U\phi_{Li}, \tag{11b}$$

where

$$W_0 = \frac{1}{4c^2}\boldsymbol{\sigma}\cdot\boldsymbol{\pi}V_n\boldsymbol{\sigma}\cdot\boldsymbol{\pi}. \tag{12}$$

Equations (11a) and (11b) are exact and equivalent to the Dirac equation for the positive energy states.[36] Equation (11b) shows that the transformation operator U depends on the energy eigenvalues ε_i. From Eq. (11b) we get

$$U = \left[T + H_A - W_0 + \frac{\varepsilon_i}{2c^2}(T+H_A)\right]^{-1}(T+H_A). \tag{13}$$

The dependence of the transformation operator U on ε_i requires that a cumbersome iteration procedure be used to solve the two-component equations (11a) and (11b). However, we assume here that the dependence of U on the energy eigenvalues ε_i is rather weak and that the last term in the brackets of Eq. (13) can be neglected in the zeroth-order approximation. This assumption yields the zeroth-order regular approximation (ZORA) of the NESC scheme, i.e., the NESC-ZORA scheme. Using ZORA leads to

$$U = (T - W_0 + H_A)^{-1}(T + H_A). \tag{14}$$

Multiplying Eq. (11b) by $U^\dagger$ from the left and adding it to Eq. (11a), we obtain the large component equation,

$$H\phi_{Li} = \varepsilon_i S\phi_{Li}, \tag{15}$$

where

$$H = TU + U^\dagger T - U^\dagger TU + V_n + U^\dagger W_0 U + H_A U + U^\dagger H_A - U^\dagger H_A U, \tag{16}$$

$$S = 1 + \frac{1}{2c^2}U^\dagger(T+H_A)U. \tag{17}$$

The proper orthonormalization of the Dirac wave functions ψ_{Di} $(i=1,2,\ldots)$ is retained, i.e.,

$$\langle\psi_{Di}|\psi_{Dj}\rangle = \langle\phi_{Li}|\phi_{Lj}\rangle + \langle\phi_{Si}|\phi_{Sj}\rangle = \langle\phi_{Li}|S|\phi_{Lj}\rangle = \delta_{ij}. \tag{18}$$

B. Many-electron systems

For many-electron systems we start from the description of the Dirac-Fock (DF) operator F_D, which is given by

$$F_D = c\boldsymbol{\alpha}\cdot\boldsymbol{\pi} + (\beta-1)c^2 + V_n + \sum_j^{\text{occ}}\left[\int \psi_{Dj}^\dagger(2)\frac{1}{r_{12}}(1-\hat{P}_{12})\psi_{Dj}(2)d\tau_2\right], \tag{19}$$

where $\hat{P}_{12}$ is the operator interchanging two electrons, 1 and 2. In Eq. (19), the label for electron 1 is omitted for simplicity. The 4×4 matrix F_D is divided into the four 2×2 matrices, F_{11}, F_{12}, F_{21}, and F_{22}. Namely,

$$F_{11} = V_n + J_{11} - K_{11} + J_{22}, \tag{20a}$$

$$F_{12} = c\boldsymbol{\sigma}\cdot\boldsymbol{\pi} - K_{21}, \tag{20b}$$

$$F_{21} = c\boldsymbol{\sigma}\cdot\boldsymbol{\pi} - K_{12}, \tag{20c}$$

$$F_{22} = V_n - 2c^2 + J_{11} + J_{22} - K_{22}, \tag{20d}$$

where

$$J_{11} = \sum_{j}^{\text{occ}} \int \phi_{Lj}^{\dagger}(2) \frac{1}{r_{12}} \phi_{Lj}(2) d\tau_2, \tag{21a}$$

$$J_{22} = \sum_{j}^{\text{occ}} \int [\Pi(2)\phi_{Lj}(2)]^{\dagger} \frac{1}{r_{12}} [\Pi(2)\phi_{Lj}(2)] d\tau_2, \tag{21b}$$

$$K_{11} = \sum_{j}^{\text{occ}} \int \phi_{Lj}^{\dagger}(2) \frac{1}{r_{12}} \hat{P}_{12} \phi_{Lj}(2) d\tau_2, \tag{21c}$$

$$K_{12} = \sum_{j}^{\text{occ}} \int \phi_{Lj}^{\dagger}(2) \frac{1}{r_{12}} \hat{P}_{12} [\Pi(2)\phi_{Lj}(2)] d\tau_2, \tag{21d}$$

$$K_{21} = \sum_{j}^{\text{occ}} \int [\Pi(2)\phi_{Lj}(2)]^{\dagger} \frac{1}{r_{12}} \hat{P}_{12} \phi_{Lj}(2) d\tau_2, \tag{21e}$$

$$K_{22} = \sum_{j}^{\text{occ}} \int [\Pi(2)\phi_{Lj}(2)]^{\dagger} \frac{1}{r_{12}} \hat{P}_{12} [\Pi(2)\phi_{Lj}(2)] d\tau_2. \tag{21f}$$

Here, the operator Π is defined as

$$\Pi = \frac{\boldsymbol{\sigma} \cdot \boldsymbol{\pi}}{2c} U. \tag{22}$$

The two-component equations are derived from the DF equation,

$$\begin{bmatrix} F_{11} & F_{12} \\ F_{21} & F_{22} \end{bmatrix} \begin{bmatrix} \phi_{Li} \\ \Pi\phi_{Li} \end{bmatrix} = \varepsilon_i \begin{bmatrix} \phi_{Li} \\ \Pi\phi_{Li} \end{bmatrix}, \quad i = 1,2, \ldots . \tag{23}$$

Henceforth, we omit terms of the order of c^{-3} and smaller. The two-component equations for many-electron systems are thus

$$[V_n + J_{11} - K_{11} + J_{22} + (c\boldsymbol{\sigma} \cdot \boldsymbol{\pi} - K_{21})\Pi]\phi_{Li} = \varepsilon_i \phi_{Li}, \tag{24a}$$

$$[c\boldsymbol{\sigma} \cdot \boldsymbol{\pi} - K_{12} + (V_n - 2c^2 + J_{11})\Pi]\phi_{Li} = \varepsilon_i \Pi \phi_{Li}. \tag{24b}$$

Multiplying Eq. (24b) by $(1/2c)(\boldsymbol{\sigma} \cdot \boldsymbol{\pi})$ from the left, we obtain

$$\left[T + H_A - \frac{1}{2c} \boldsymbol{\sigma} \cdot \boldsymbol{\pi} K_{12} + \left(W_0 - T - H_A + \frac{1}{4c^2} \boldsymbol{\sigma} \cdot \boldsymbol{\pi} J_{11} \boldsymbol{\sigma} \cdot \boldsymbol{\pi} \right) U \right] \phi_{Li} = \frac{\varepsilon_i}{2c^2} (T + H_A) U \phi_{Li}. \tag{25}$$

The transformation operator U for many-electron systems can be written as

$$U = \left[T - W_0 - \frac{1}{4c^2} \boldsymbol{\sigma} \cdot \boldsymbol{\pi} J_{11} \boldsymbol{\sigma} \cdot \boldsymbol{\pi} + H_A + \frac{\varepsilon_i}{2c^2} (T + H_A) \right]^{-1} \left(T - \frac{1}{2c} \boldsymbol{\sigma} \cdot \boldsymbol{\pi} K_{12} + H_A \right). \tag{26}$$

Multiplying Eq. (25) by $U^{\dagger}$ from the left and adding it to Eq. (24a), we obtain the large component self-consistent field (SCF) equation for many-electron systems:

$$F\phi_{Li} = \varepsilon_i S \phi_{Li}, \tag{27}$$

where

$$F = H + J_{11} - K_{11} + J_{22} - \frac{1}{2c} K_{21} \boldsymbol{\sigma} \cdot \boldsymbol{\pi} U - \frac{1}{2c} U^{\dagger} \boldsymbol{\sigma} \cdot \boldsymbol{\pi} K_{12} + \frac{1}{4c^2} U^{\dagger} \boldsymbol{\sigma} \cdot \boldsymbol{\pi} J_{11} \boldsymbol{\sigma} \cdot \boldsymbol{\pi} U. \tag{28}$$

The core Hamiltonian operator H and the metric operator S are given by Eqs. (16) and (17), respectively.

According to conventional molecular orbital theory, the large component wave function ϕ_{Li} can be expanded in the spin including basis functions, $\chi_1, \chi_2, \ldots, \chi_m$. We write ϕ_{Li} $(i = 1,2,\ldots,m)$ as

$$\phi_{Li} = \sum_{\mu=1}^{m} a_{\mu i} \chi_{\mu}; \quad i = 1,2, \ldots, m. \tag{29}$$

We introduce the matrix A with the coefficients $a_{\mu i}$ as the (μ, i) element and the diagonal matrix $\mathcal{E}$ including the eigenvalues ε_i as diagonal elements. The SCF eigenvalue equation Eq. (27) can then be rewritten as

$$FA = SA\mathcal{E}, \tag{30}$$

where we have used the same notation for the operator and matrix. Equation (25), which determines the transformation matrix U, is rewritten as

$$T + H_A - \frac{1}{2c} \boldsymbol{\sigma} \cdot \boldsymbol{\pi} K_{12} + \left(W_0 - T - H_A + \frac{1}{4c^2} \boldsymbol{\sigma} \cdot \boldsymbol{\pi} J_{11} \boldsymbol{\sigma} \cdot \boldsymbol{\pi} \right) U = \frac{1}{2c^2} (T + H_A) U A \mathcal{E} A^{-1}. \tag{31}$$

The orthonormal condition Eq. (18) becomes

$$A^{\dagger} S A = I. \tag{32}$$

Using Eq. (30), we obtain

$$A \mathcal{E} A^{-1} = S^{-1} F. \tag{33}$$

The transformation matrix U can be determined self-consistently according to the equation

$$U = \left(T - W_0 - \frac{1}{4c^2} \boldsymbol{\sigma} \cdot \boldsymbol{\pi} J_{11} \boldsymbol{\sigma} \cdot \boldsymbol{\pi} + H_A \right)^{-1} \times \left[T + H_A - \frac{1}{2c} \boldsymbol{\sigma} \cdot \boldsymbol{\pi} K_{12} - \frac{1}{2c^2} (T + H_A) U S^{-1} F \right]. \tag{34}$$

Equation (34) corresponds to Eq. (31) in the paper by Filatov and Cremer.[34] However, Eq. (31) of that paper contains an error, the last term contains $\cdots S^{-1}H$, rather than $\cdots S^{-1}F$ as in Eq. (34) above. Because of this error, the second-order regular approximation (SORA) equation in the earlier paper is incorrect. Equations (28) and (34) constitute the first accurate formulation for the NESC approach. However, Eqs. (28) and (34) are too complicated to apply to a real system. Therefore, all c^{-2} order electron-electron interaction operators and the

c^{-2} order magnetic interaction operators in the transformation operator U and the metric operator S should be neglected. We then have for F and U,

$$F = H + J_{11} - K_{11}, \tag{35}$$

$$U = (T - W_0^{(0)} + H_A)^{-1}\left(T + H_A - \frac{1}{2c^2}TUS^{-1}F\right), \tag{36}$$

where

$$W_0^{(0)} = \frac{1}{4c^2}\boldsymbol{\sigma}\cdot\mathbf{p}V_n\boldsymbol{\sigma}\cdot\mathbf{p}. \tag{37}$$

The metric operator S becomes

$$S = 1 + \frac{1}{2c^2}U^\dagger TU. \tag{38}$$

C. Magnetic perturbation expansion

The operator W_0 is explicitly written as

$$W_0 = W_0^{(0)} + \frac{1}{4c^2}[V_n\boldsymbol{\sigma}\cdot\mathbf{A}\boldsymbol{\sigma}\cdot\mathbf{p} + (V_n\boldsymbol{\sigma}\cdot\mathbf{A}\boldsymbol{\sigma}\cdot\mathbf{p})^\dagger + 2V_n\mathbf{A}_0\cdot\mathbf{A}_M], \tag{39}$$

where $\mathbf{A}=\mathbf{A}_0+\mathbf{A}_M$. To start our formulation, we adopt the zeroth-order regular approximation to U, i.e., the NESC-ZORA scheme. In this case, U is given by Eq. (36) assuming $F=0$. The transformation matrix U is expanded in H_A as

$$U = (T - W_0^{(0)} + H_A)^{-1}(T + H_A) = (T - W_0^{(0)})^{-1}T - T^{-1}H_AT^{-1}W_0^{(0)} + O(H_A^2) + \cdots. \tag{40}$$

The first-order contribution of H_A is itself of the order of c^{-2}, and it does not contribute to F and S in the order of c^{-2}. Therefore, we may neglect the H_A term in U. For the NESC-ZORA we use

$$U = (T - W_0^{(0)})^{-1}T. \tag{41}$$

In the NESC-ZORA approach, the Fock operator F and the metric operator S are given by Eqs. (35) and (38), respectively, using the U of Eq. (41).

The magnetic interaction operator H_A can be expanded in B_{0t} $(t\in x,y,z)$ and μ_{Mu} $(\mathrm{u}\in x,y,z)$. Namely,

$$H_A = \sum_t B_{0t}H_{At}^{(1,0)} + \sum_u \mu_{Mu}H_{Au}^{(0,1)} + \sum_{tu} B_{0t}\mu_{Mu}H_{Atu}^{(1,1)}. \tag{42}$$

Using Eq. (10), $H_{At}^{(1,0)}$, $H_{Au}^{(0,1)}$, and $H_{Atu}^{(1,1)}$ are given as

$$H_{At}^{(1,0)} = -\frac{1}{4}i(\mathbf{r}_0\times\boldsymbol{\nabla})_t + \frac{1}{4}(-\sigma_t\mathbf{r}_0\cdot\boldsymbol{\nabla} + \boldsymbol{\sigma}\cdot\mathbf{r}_0\nabla_t) + \text{Hermitian conjugate}, \tag{43}$$

$$H_{Au}^{(0,1)} = -\frac{1}{2c^2}ir_M^{-3}(\mathbf{r}_M\times\boldsymbol{\nabla})_u + \frac{1}{2c^2}r_M^{-3}(-\sigma_u\mathbf{r}_M\cdot\boldsymbol{\nabla} + \boldsymbol{\sigma}\cdot\mathbf{r}_M\nabla_u) + \text{Hermitian conjugate}, \tag{44}$$

$$H_{Atu}^{(1,1)} = (2c^2r_M^3)^{-1}[\mathbf{r}_0\cdot\mathbf{r}_M\delta_{tu} - r_{0u}r_{Mt}]. \tag{45}$$

The core Hamiltonian H is written as

$$H = TU + U^\dagger T - U^\dagger TU + V_n + U^\dagger W_0^{(0)}U + H_AU + U^\dagger H_A - U^\dagger H_AU + \frac{1}{4c^2}[U^\dagger V_n\boldsymbol{\sigma}\cdot\mathbf{A}\boldsymbol{\sigma}\cdot\mathbf{p}U + (U^\dagger V_n\boldsymbol{\sigma}\cdot\mathbf{A}\boldsymbol{\sigma}\cdot\mathbf{p}U)^\dagger + 2U^\dagger V_n\mathbf{A}_0\cdot\mathbf{A}_MU]. \tag{46}$$

H and the total electronic energy E are expanded likewise in B_{0t} and μ_{Mu} as

$$H = H^{(0)} + \sum_t B_{0t}H_t^{(1,0)} + \sum_u \mu_{Mu}H_u^{(0,1)} + \sum_{tu} B_{0t}\mu_{Mu}H_{tu}^{(1,1)}, \tag{47}$$

$$E = E^{(0)} + \sum_t B_{0t}E_t^{(1,0)} + \sum_u \mu_{Mu}E_u^{(0,1)} + \sum_{tu} B_{0t}\mu_{Mu}E_{tu}^{(1,1)} + \cdots. \tag{48}$$

The nuclear magnetic shielding tensor component σ_{tu}^M is equal to $E_{tu}^{(1,1)}$ because σ_{tu}^M is defined as

$$\sigma_{tu}^M = \left(\frac{\partial^2 E}{\partial B_{0t}\partial\mu_{Mu}}\right)_{\mathbf{B}_0=0,\boldsymbol{\mu}_M=0}. \tag{49}$$

The perturbation energy $E_{tu}^{(1,1)}$ is given by Dodds *et al.*[37] as

$$\sigma_{tu}^M = E_{tu}^{(1,1)} = \mathrm{Tr}(H_{tu}^{(1,1)}R^{(0)} + H_u^{(0,1)}R_t^{(1,0)}), \tag{50}$$

where the density matrix R is defined as

$$R_{\mu\nu} = \sum_i^{\mathrm{occ}} a_{\mu i}a_{\nu i}^*. \tag{51}$$

The computation of $R_t^{(1,0)}$ is described elsewhere.[38] The first term in the right-hand side (rhs) of Eq. (50) yields the diamagnetic contribution (σ^{dia}) to the σ_{tu}^M, while the second term produces the paramagnetic contribution (σ^{para}). The dia- and paramagnetic contributions individually depend on the gauge origin, but the sum of them σ_{tu}^M does not depend on the gauge origin when a complete basis set is used.

D. Second-order regular approximation

The next step is to obtain a more accurate solution for the NESC equations using Eqs. (35) and (36). The accurate solution is determined iteratively starting from the NESC-ZORA solution. We write U in the ith iteration as $U(i)$. Because we can neglect the magnetic interaction terms of $O(c^{-4})$, H_A can be discarded from Eq. (36). We write Eqs. (36) and (38) as

$$U(i) = (T - W_0^{(0)})^{-1}\left[T - \frac{1}{2c^2}TU(i-1)S^{-1}(i-1)F(i-1)\right], \tag{52}$$

$$S(i) = 1 + \frac{1}{2c^2}U^\dagger(i)TU(i), \tag{53}$$

respectively. The initial condition for the iteration is $U(0)=0$. Therefore, $U(1)=(T-W_0^{(0)})^{-1}T$, as in Eq. (41). Therefore,

TABLE I. The used parameters a, b, and k in atomic units. The parameters a, b, and k are defined in text.

Atom	a	b	k
H	0.072 79	3.424 470 870	7
F	0.257 332 589 13	3.038 706 664	12
Cl	0.181 968 700 61	2.946 425 155	14
Br	0.166 133 770 99	2.559 929 038	16
I	0.119 331 9	2.947 019 359	14

in the first iteration step, the SCF solution yields the NESC-ZORA solution. Here, the matrix $F(i)$ in each iterative step is determined self-consistently by Eq. (35) and $U(i)$. The SCF equation (30) using $F(i)$ and $S(i)$ is also solved self-consistently. The solution in the second iteration step with $U(2)$ corresponds to the second-order regular approximation solution of the NESC scheme, i.e., the NESC-SORA solution, because the Fock matrix F is correct to the second order with respect to the eigenvalues ε_i.[34]

III. RESULTS AND DISCUSSION

A. Basis functions

We now apply the NESC-ZORA and NESC-SORA methods to the calculation of the nuclear magnetic shielding tensors of HX (X=F,Cl,Br,I) systems. The basis functions used in the present work are uncontracted Cartesian-Gaussian-type orbitals with equal Gaussian exponents for all s-, p-, d-, f-, and g-type atomic orbital functions to reduce the gauge origin dependence of the magnetic shielding tensors computed with a fixed gauge origin.[25] The ith Gaussian exponent α_i is given by the formula $\alpha_i = ab(i)$. The rule for a and $b(i)$ used in our basis functions is as follows, in atomic units. For zero and negative integers i, $b(i)=4.0^i$ are used always. For zero and positive integers i, $b(i)=b^i$ for $0 \leqslant i \leqslant k$ and $b(i)=b^k \times 4.0^{i-k}$ for $i \geqslant k$. The constants a, b, and k vary with atoms. The used constants a, b, and k are listed in Table I. The sizes of the used basis sets and the ranges of i for the used exponents α_i are listed in Table II.

B. Calculation of shielding

In the present calculation, a pointlike nuclear model is used. Prior to the start of calculation, we must consider the singularity of the operator $U^\dagger W_0 U$ at the nuclear position $\mathbf{R}_M$. The function $r_M^{-1}\boldsymbol{\sigma}\cdot\mathbf{A}_M\boldsymbol{\sigma}\cdot\mathbf{p}|\chi_{1S}^M\rangle$ has a singularity of r_M^{-3} at $\mathbf{R}_M$ for Slater-type $1s$ orbital functions centered at $\mathbf{R}_M$, χ_{1s}^M and the integrals of W_0 diverge.[39] In another formulation, the operator W_0 includes the divergence terms at $\mathbf{R}_M$, such as $r_M^{-1}\delta(\mathbf{r}_M)$. However, the integral $\langle\chi_{1S}^M|U^\dagger W_0 U|\chi_{1S}^M\rangle$ converges because $U=(T-W_0^{(0)})^{-1}T$ and $U^\dagger$ go to zero at $\mathbf{R}_M$ like r_M.

The calculated nuclear magnetic shielding tensor components are shown in Table III. The NESC-ZORA and NESC-SORA results are shown in the fourth and fifth columns, respectively. Previously reported Breit-Pauli (BP) Hamiltonian perturbation,[10] four-component relativistic random-phase approximation (4-RPA),[8] Dirac-Hartree-Fock (DHF),[10] IOTC-CHF,[25] and DKH[27] calculation results are also shown in Table III. The present ZORA and SORA results are quite similar each other except I shieldings and consistent with the previously reported results. For HF and HCl, both give the same results within the computational precision. For the Br shielding components, there is only a slight difference between the ZORA and SORA results. However, for the I nucleus, there are large differences of about 300 ppm in $\sigma_\perp^{\mathrm{I}}$(para) and $\sigma_\parallel^{\mathrm{I}}$(para) between the ZORA and SORA calculations. The σ^{iso}(I) obtained with SORA is larger than that by ZORA. The results of ZORA are closer to the IOTC-CHF results than those of SORA. It is interesting to improve the SORA calculation by adding the contributions from H_A in the metric operator S and the relativistic two-electron term $\boldsymbol{\sigma}\cdot\boldsymbol{\pi}J_{11}\boldsymbol{\sigma}\cdot\boldsymbol{\pi}/4c^2$, which are both neglected in the present calculations.

TABLE II. The sizes of the used basis sets and the ranges of i for the used exponents α_i

Atom	Basis set	Orbital	Range
H	$(12s10p2d)$	s	$i=-2\sim9$
		p	$i=-2\sim7$ or $i=-1\sim8$
		d	$i=1, 2$
F	$(15s15p10d4f)$	s	$i=0\sim14$
		p	$i=0\sim14$
		d	$i=0\sim9$
		f	$i=1\sim4$
Cl	$(17s17p12d8f)$	s	$i=0\sim16$
		p	$i=0\sim16$
		d	$i=0\sim11$
		f	$i=0\sim7$
Br	$(21s21p12d8f2g)$	s	$i=-2\sim18$
		p	$i=-2\sim18$
		d	$i=-1\sim10$
		f	$i=1\sim8$
		g	$i=4, 5$
I	$(25s25p18d10f3g)$	s	$i=-2\sim22$
		p	$i=-2\sim22$
		d	$i=-2\sim15$
		f	$i=0\sim9$
		g	$i=3\sim5$

IV. CONCLUSION

We have extended the NESC theory proposed by Filatov and Cremer to include magnetic interactions and have applied it to the calculation of the nuclear magnetic shielding in HX (X=F,Cl,Br,I) systems. The transformation operator U connecting the small component with the large component depends on the eigenvalues of the one-electron wave functions, ε_i ($i=1,2,3,\ldots$). The exact transformation matrix U may be obtained with a complete set of basis functions $\{\chi\}$ by an iterative procedure determining U and $\mathcal{E}$ consistently. When the contribution of ε_i to U is neglected, the NESC theory yields the NESC-ZORA method. Inserting the ε_i values determined by the NESC-ZORA into U gives the NESC-SORA method in which the Fock matrix F is correct to $(\varepsilon_i/c^2)^2$. Both the NESC-ZORA and NESC-SORA results were very similar to previously reported values. The differ-

TABLE III. Calculated of nuclear magnetic shielding tensor components (in ppm) in H*X* (*X*=F, Cl, Br, I) systems by the NESC-ZORA and NESC-SORA methods.

Molecule	Nucleus	Property	NESC-ZORA[a]	NESC-SORA[b]	BP[c]	Four component calculation		IOTC-CHF[d]	DKH[e]
HF	F	$\sigma_\perp$ (dia)	480.4	480.4				475.4	
		$\sigma_\perp$ (para)	−92.4	−92.5				−91.4	
		$\sigma_\perp$ (total)	388.0	387.9	384.2	390.0[f]	384.9[g]	384.0	
		$\sigma_\parallel$ (dia)	479.6	479.6				474.6	
		$\sigma_\parallel$ (para)	7.5	7.4				8.4	
		$\sigma_\parallel$ (total)	487.1	487.0	487.4	490.0[f]	485.6[g]	483.0	
		σ^{ISO} (total)	421.0	421.0	418.56	423.3[f]	418.43[g]	417.0	423.4
		$\Delta\sigma$ (total)	99.0	99.0	103.2	100.0[f]	100.7[g]	99.0	
	H	$\sigma_\perp$ (dia)	1.34	1.34				0.01	
		$\sigma_\perp$ (para)	18.89	18.89				18.92	
		$\sigma_\perp$ (total)	20.24	20.24	20.89	19.77[f]	20.10[g]	18.93	
		$\sigma_\parallel$ (dia)	44.04	44.04				42.89	
		$\sigma_\parallel$ (para)	0.00	0.00				0.01	
		$\sigma_\parallel$ (total)	44.04	44.04	44.03	44.08[f]	43.90[g]	42.89	
		σ^{ISO} (total)	28.17	28.17	28.60	27.87[f]	28.03[g]	26.92	28.34
		$\Delta\sigma$ (total)	23.80	23.80	23.14	24.31[f]	23.80[g]	23.96	
HCl	Cl	$\sigma_\perp$ (dia)	1136.3	1136.2				1124.6	
		$\sigma_\perp$ (para)	−237.4	−237.4				−232.0	
		$\sigma_\perp$ (total)	898.9	898.8	877.0	926.2[f]	888.5[g]	892.6	
		$\sigma_\parallel$ (dia)	1133.5	1133.4				1121.8	
		$\sigma_\parallel$ (para)	52.1	52.1				56.4	
		$\sigma_\parallel$ (total)	1185.6	1185.5	1187.1	1207.8[f]	1176.7[g]	1178.3	
		σ^{ISO} (total)	994.4	994.3	980.39	1020.1[f]	984.53[g]	987.8	1018.9
		$\Delta\sigma$ (total)	286.7	286.7	310.1	281.6[f]	288.2[g]	285.7	
	H	$\sigma_\perp$ (dia)	1.89	1.89				1.05	
		$\sigma_\perp$ (para)	22.49	22.49				22.51	
		$\sigma_\perp$ (total)	24.38	24.38	24.94	23.79[f]	24.07[g]	23.56	
		$\sigma_\parallel$ (dia)	45.36	45.37				44.40	
		$\sigma_\parallel$ (para)	−0.01	−0.01				0.01	
		$\sigma_\parallel$ (total)	45.35	45.36	45.46	45.42[f]	45.39[g]	44.41	
		σ^{ISO} (total)	31.37	31.37	31.78	31.00[f]	31.18[g]	30.51	31.56
		$\Delta\sigma$ (total)	20.97	20.97	20.52	21.63[f]	21.32[g]	20.85	
HBr	Br	$\sigma_\perp$ (dia)	2987.6	2983.5				2929.6	
		$\sigma_\perp$ (para)	−192.0	−176.1				−171.2	
		$\sigma_\perp$ (total)	2795.6	2807.3	2681.6	3003.3[f]	2738.1[g]	2758.3	
		$\sigma_\parallel$ (dia)	2984.6	2980.4				2927.9	
		$\sigma_\parallel$ (para)	458.8	474.7				472.1	
		$\sigma_\parallel$ (total)	3443.4	3455.1	3495.4	3667.1[f]	3402.1[g]	3400.0	
		σ^{ISO} (total)	3011.5	3023.3	2952.88	3224.6[f]	2959.41[g]	2972.2	3164.9
		$\Delta\sigma$ (total)	647.8	647.8	813.8	663.8[f]	664.0[g]	641.7	
	H	$\sigma_\perp$ (dia)	−0.01	−0.01				−0.79	
		$\sigma_\perp$ (para)	30.12	30.12				30.04	
		$\sigma_\perp$ (total)	30.12	30.12	31.11	29.97[f]	29.82[g]	29.26	
		$\sigma_\parallel$ (dia)	48.50	48.50				48.23	
		$\sigma_\parallel$ (para)	−0.45	−0.45				−0.38	
		$\sigma_\parallel$ (total)	48.05	48.05	48.57	48.30[f]	47.93[g]	47.85	
		σ^{ISO} (total)	36.10	36.10	36.93	36.08[f]	35.86[g]	35.46	37.15
		$\Delta\sigma$ (total)	17.93	17.93	17.46	18.33[f]	18.11[g]	18.59	
HI	I	$\sigma_\perp$ (dia)	5001.2	4967.9				4870.7	
		$\sigma_\perp$ (para)	578.8	879.8				708.0	
		$\sigma_\perp$ (total)	5580.0	5847.8	5123.5	6424.3[f]	5571.9[g]	5578.7	
		$\sigma_\parallel$ (dia)	4997.9	4964.6				4868.7	
		$\sigma_\parallel$ (para)	1615.7	1917.1				1691.0	
		$\sigma_\parallel$ (total)	6613.6	6881.7	6853.0	7456.6[f]	6597.1[g]	6559.7	
		σ^{ISO} (total)	5924.5	6192.4	5700.00	6768.4[f]	5913.65[g]	5905.7	6508.5
		$\Delta\sigma$ (total)	1033.5	1033.9	1729.5	1032.3[f]	1025.2[g]	981.0	
	H	$\sigma_\perp$ (dia)	−1.76	−1.80				−1.61	

TABLE III. (*Continued.*)

Molecule	Nucleus	Property	NESC-ZORA[a]	NESC-SORA[b]	BP[c]	Four component calculation		IOTC-CHF[d]	DKH[e]
		$\sigma_{\perp}$ (para)	50.94	50.95				50.00	
		$\sigma_{\perp}$ (total)	49.18	49.15	50.24	48.02[f]	46.92[g]	48.39	
		$\sigma_{\parallel}$ (dia)	50.30	50.28				50.16	
		$\sigma_{\parallel}$ (para)	−4.32	−4.32				−3.95	
		$\sigma_{\parallel}$ (total)	45.98	45.95	51.46	47.89[f]	47.31[g]	46.21	
		σ^{ISO} (total)	48.11	48.08	50.65	47.98[f]	47.05[g]	47.66	49.72
		$\Delta\sigma$ (total)	−3.19	−3.20	1.22	−0.13[f]	0.39[g]	−2.18	

[a]Present NESC-ZORA results.
[b]Present NESC-SORA results.
[c]Hartree-Fock self-consistent field response calculation results, in which all the leading-order relativistic one-electron contributions from the Breit-Pauli Hamiltonian are included as perturbational corrections, taken from Ref. 10.
[d]Relativistic infinite-order two-component coupled Hartree-Fock calculation results taken from Ref. 25. The results of hydrogen iodide are taken from Erratum of Ref. 25.
[e]Douglas-Kroll-Hess transformation results taken from Ref. 27.
[f]Four-component relativistic random-phase approximation results taken from Ref. 8. The Sternheim approximation (i.e., the diamagnetic approximation) is used.
[g]Dirac-Hartree-Fock calculation results taken from Ref. 10.

ences between the NESC-ZORA and NESC-SORA results were negligibly small, except for σ(para) for the I nucleus. The σ(para) determined by SORA was larger than that by ZORA by about 300 ppm.

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