Relativistic calculation of nuclear magnetic shielding tensor using the regular approximation to the normalized elimination of the small component. III. Introduction of gauge-including atomic orbitals and a finite-size nuclear model

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The relativistic calculation of nuclear magnetic shielding tensors in hydrogen halides is performed using the second-order regular approximation to the normalized elimination of the small component (SORA-NESC) method with the inclusion of the perturbation terms from the metric operator. This computational scheme is denoted as SORA-Met. The SORA-Met calculation yields anisotropies, $\Delta\sigma=\sigma_{\parallel}-\sigma_{\perp}$, for the halogen nuclei in hydrogen halides that are too small. In the NESC theory, the small component of the spinor is combined to the large component via the operator $\vec{\sigma}\cdot\vec{\pi}U/2c$, in which $\vec{\pi}=\vec{p}+\vec{A}$, U is a nonunitary transformation operator, and $c\cong 137.036$ a.u. is the velocity of light. The operator U depends on the vector potential $\vec{A}$ (i.e., the magnetic perturbations in the system) with the leading order c^{-2} and the magnetic perturbation terms of U contribute to the Hamiltonian and metric operators of the system in the leading order c^{-4}. It is shown that the small $\Delta\sigma$ for halogen nuclei found in our previous studies is related to the neglect of the $U^{(0,1)}$ perturbation operator of U, which is independent of the external magnetic field and of the first order with respect to the nuclear magnetic dipole moment. Introduction of gauge-including atomic orbitals and a finite-size nuclear model is also discussed. © *2008 American Institute of Physics*.
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I. INTRODUCTION

Evaluation of relativistic effects on molecular magnetic properties is one of the critical problems in heavy-atom-containing compounds. The methodology for relativistic calculation of molecular properties is divided into two categories, i.e., four-component (normally called fully relativistic)[1–5] and two-component (normally called quasirelativistic) methods. Furthermore, two-component approaches are divided into two groups: a unitary decoupling transformation method[6–10] and a method of eliminating the small component (ESC).[11–15] However, it has been demonstrated[16] that these two methods are mathematically equivalent.

At the four-component relativistic level, the perturbation Hamiltonian $D^{(1)}$ describing the magnetic interactions is given by $D^{(1)}=c\vec{\alpha}\cdot\vec{A}$ (in a.u.), and the whole magnetic property is formally presented by the sum-over-states (SOS) formulation. There is no close resemblance between the relativistic and nonrelativistic expressions for the diamagnetic shielding contribution. In the pioneering work by Visscher *et al.*,[17] the diamagnetic shielding term was evaluated as an expectation value, which was obtained by applying the Sternheim approximation[18] to the SOS type of expression over the negative-energy states. An alternative novel approach was proposed recently by Kutzelnigg,[5] in which the Dirac equation is unitary transformed to remove the $c\vec{\alpha}\cdot\vec{A}$ term from the transformed Dirac Hamiltonian $\tilde{D}$. The Kutzelnigg's new method leads to a separation of the perturbation Hamiltonian into the linear and quadratic operator parts, which are in close resemblance with the nonrelativistic counterparts. There are at least two basic problems in the four-component calculation of magnetic shieldings. One of them is the contribution of negative-energy states, although it is reduced greatly on account of the unitary transformation introduced by Kutzelnigg. The other is related to the completeness of the basis sets. Namely, in addition to the $\vec{\sigma}\cdot\vec{p}$ basis, the $\vec{\sigma}\cdot\vec{A}$ basis is also needed to expand the small components of the Dirac four spinors.[5,19] If we want to circumvent the use of $\vec{\sigma}\cdot\vec{A}$ basis for small component expansion, the magnetic balance condition must be imposed at the stage of formulation. In order to explicitly take into account the magnetic balance in the shielding formulation, Xiao and co-workers[20,21] proposed the orbital decomposition approach (ODA) and the full field-dependent unitary transformation method at the matrix level. It was shown that the incorporation of the magnetic balance largely suppresses the contribution of the negative-energy states. Komorovský *et al.*,[22] on the other hand, presented the method using a restricted magnetically balanced (RMB) basis set $\{\vec{\sigma}\cdot(\vec{p}+\vec{A}_0)\chi_{\mu}^{L}\}$ for small component expansion, in which $\vec{A}_0$ is the vector potential of a uniform external magnetic field $\vec{B}_0$ and χ_{μ}^{L}'s are basis functions used for expanding the large components. The RMB method is more exact than ODA in the treatment of magnetic

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balance. Aucar and co-workers[23,24] indicated that all of diamagnetic contributions to shielding arises from negative-energy states higher than $-4c^2$ and lower than $-2c^2$.

Due to the recent developments in four-component approaches, the warranty of two-component approaches may be undermined,[20] but we believe that the two-component methods have still some advantages. Above all, in the use of two-component approaches we are released from a yoke of negative-energy states. We have recently presented a theory that decouples a magnetically perturbed Dirac Hamiltonian correct to the third order of the vector potential in the energy, practically the exact degree for calculating the second-order properties.[25] This theory can yield exact magnetic properties for a one-electron system. However, the unitary decoupling transformation method has the disadvantage that the two-component Hamiltonian obtained is complicated and difficult to extend. For example, the unitary transformation scheme cannot be applied to gauge-including atomic orbitals (GIAOs).[26] On the other hand, the two-component ESC Hamiltonian is simple and easy to extend. We found that the method of normalized elimination of the small component (NESC)[27,28] is simple and flexible. The NESC method was proposed by Dyall[27,28] as the first exact two-component method to yield the same positive energy solutions as the Dirac equation. Filatov and Cremer[29] applied the regular approximation to the exact NESC theory by Dyall and obtained numerical stability in a quasivariational scheme. We introduced magnetic interactions into the regular approximation to the NESC theory and applied it to the relativistic calculation of nuclear magnetic shielding tensors in HX (X=F,Cl,Br,I) systems for comparison with the previously reported values.[30–32] However, a sophistication of the theory has not necessarily led to closer agreement with the fully relativistic Dirac–Hartree–Fock (DHF) results,[3] which are considered to be a benchmark. In particular, in our last paper,[32] which incorporated the contribution from the metric perturbation operators in the framework of the second-order regular approximation (SORA) to the NESC theory, a poor result was obtained for $\Delta\sigma=\sigma_{\parallel}-\sigma_{\perp}$ of the I nucleus in HI.

In order to further develop the theory and to search for the cause of the poor results for $\Delta\sigma$, we extend it to include GIAOs. If the basis sets used are insufficient, introduction of GIAOs may improve the $\Delta\sigma$ values. GIAOs were introduced into the calculation of shieldings at the Douglas–Kroll–Hess (DKH) level by Fukuda *et al.*[33] However, since the $\vec{\sigma}\cdot(\vec{p}+\vec{A})$ term is decomposed into $\vec{\sigma}\cdot\vec{p}$ and $\vec{\sigma}\cdot\vec{A}$ terms in their DKH Hamiltonian, the benefits to be obtained by using GIAOs will be lost. In the present work, the structure of $\vec{\sigma}\cdot(\vec{p}+\vec{A})$ is kept in the Hamiltonian. One of the difficult problems in the NESC calculation of nuclear magnetic properties is the production of a singular operator $V\vec{A}_M\cdot\vec{p}$ in which V is the nuclear attraction potential, $\vec{A}_M$ is the vector potential due to the nuclear point dipole $\vec{\mu}_M$ at the Mth nuclear position, and $\vec{p}$ is the momentum operator of an electron. This operator cannot be evaluated analytically. In our published papers,[30–32] we employed the resolution of the identity (RI) approximation to calculate the operator. However, the RI approximation is problematic. We therefore calculate the above operator numerically in the present study. Another difficult problem is inadequacy of the point nuclear model. We introduce a finite-size nuclear model[10,34–40] into the present work.

This paper is organized as follows. In Sec. II the GIAO formalism for magnetic shielding tensor calculation within the SORA-NESC theory is presented. Furthermore, a finite-size nuclear model is incorporated into the theory. In Sec. III details of the implementation are provided and the calculated results are discussed. Concluding remarks are stated in Sec. IV.

II. THEORY

A. A GIAO formalism for the SORA-NESC calculation of magnetic shieldings

The Dirac equation for a one-electron system under an external magnetic flux density $\vec{B}_0$ and a nuclear magnetic moment $\vec{\mu}_M$ at the Mth nuclear position $\vec{R}_M$ is given in a.u. ($\hbar=1$, $e=1$, $m_e=1$, and $4\pi\varepsilon_0=1$. Therefore, $\mu_0/4\pi=c^{-2}$ and $c=137.035\ 989\ 5$) by

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

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

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

$$\vec{A}_0=\tfrac{1}{2}\vec{B}_0\times\vec{r}_0;\quad \vec{r}_0=\vec{r}-\vec{R}_0, \tag{4}$$

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

Here, $\vec{\alpha}$ and β are the usual 4×4 Dirac vector and scalar matrices, $V(\vec{r})$ is the nuclear attraction potential, and $\vec{R}_0$ is the position of the common gauge origin. Nucleus M at the position $\vec{R}_M$ is the target nucleus of the present nuclear magnetic shielding tensor calculation. The ith four-component wave function ψ_{Di} with the eigenvalue ε_i is written using the large two-component spinor ϕ_{Li} and the small two-component spinor ϕ_{Si}. In the NESC scheme, ϕ_{Si} is connected to ϕ_{Li} via the nonunitary transformation operator U,

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

Substituting Eq. (6) into Eq. (1), we obtain the one-electron equation for ϕ_{Li} as

$$H\phi_{Li}=\varepsilon_i M\phi_{Li}, \tag{7}$$

where

$$H=TU+U^{\dagger}T-U^{\dagger}TU+V+U^{\dagger}WU, \tag{8}$$

$$M=1+\frac{1}{2c^2}U^{\dagger}TU, \tag{9}$$

$$T=\tfrac{1}{2}(\vec{\sigma}\cdot\vec{\pi})^2, \tag{10}$$

and

$$W = \frac{1}{4c^2}\vec{\sigma}\cdot\vec{\pi}V\vec{\sigma}\cdot\vec{\pi}. \tag{11}$$

M is the metric operator and T is the kinetic energy operator. We demand that the transformation operator U has the same form for any ε_i and ϕ_{Li}. Using Eqs. (1) and (6), we obtain

$$\left[T + (W-T)U - \frac{1}{2c^2}TU\varepsilon_i\right]\phi_{Li} = 0. \tag{12}$$

Substituting $\varepsilon_i\phi_{Li} = M^{-1}H\phi_{Li}$, obtained from Eq. (7), into Eq. (12) yields

$$\left[T + (W-T)U - \frac{1}{2c^2}TUM^{-1}H\right]\phi_{Li} = 0. \tag{13}$$

If we compel U to satisfy Eq. (13) for any ϕ_{Li}, U is written as

$$U = (T-W)^{-1}T\left(1 - \frac{1}{2c^2}UM^{-1}H\right). \tag{14}$$

For a many-electron system, the Hamiltonian operator H in Eqs. (7) and (14) is replaced by the Fock operator F. The Fock operator F and the transformation operator U should be determined self-consistently for all occupied electronic orbitals. However, in the present calculation, we neglect the two-electron interactions including the small component spinors. In other words, we treat the two-electron interaction nonrelativistically. We found that neglecting the two-electron relativistic effects is not so bad an approximation, at least in hydrogen halide molecules.[31] The most important term in the two-electron relativistic effects seems to be the two-electron spin-orbit (SO2) interaction whose contribution was less than 100 ppm for the I nucleus in HI. Inclusion of the SO2 effect improved the proton shieldings in HI a little. Therefore, we neglect the two-electron relativistic effects in the present work. The Fock operator F is then simply given at the Hartree–Fock approximation level as $F=H+J_{LL}-K_{LL}$, in which J_{LL} and K_{LL} are the Coulomb and exchange operators due to all the occupied large-component spinors, respectively.

The large two-component molecular orbitals ϕ_{Li} $(i=1,2,\ldots,m)$ can be written as a linear combination of two-component GIAOs $\chi_1,\chi_2,\ldots,\chi_m$. We write χ_ν $(\nu=1,2,\ldots,m)$ as

$$\chi_\nu = f_\nu\omega_\nu, \tag{15}$$

where f_ν is the gauge factor defined by

$$f_\nu = \exp\left[-\frac{i}{2}\vec{B}_0\times(\vec{R}_\nu - \vec{R}_0)\cdot\vec{r}\right], \tag{16}$$

ω_ν $(\nu=1,2,\ldots,m)$ are normalized two-component Gaussian-type orbitals (GTOs), which are usually one-component GTOs multiplied by two-component spinors, $\binom{1}{0}$ or $\binom{0}{1}$, and $\vec{R}_\nu$ is the center position of the Gaussian function in ω_ν. For the gauge factor f_ν, we have the relation

$$(\vec{p} + \vec{A}_0)f_\nu = f_\nu(\vec{p} + \vec{A}_{0\nu}), \tag{17}$$

where

$$\vec{A}_{0\nu} = \tfrac{1}{2}\vec{B}_0\times\vec{r}_\nu, \quad \vec{r}_\nu = \vec{r} - \vec{R}_\nu. \tag{18}$$

We then have $\vec{\sigma}\cdot\vec{\pi}f_\nu = f_\nu\vec{\sigma}\cdot\vec{\pi}_\nu$, in which $\vec{\pi}_\nu = \vec{p} + \vec{A}_{0\nu} + \vec{A}_M$. The gauge origin $\vec{R}_0$ is removed from $\vec{A}_{0\nu}$ and $\vec{\pi}_\nu$. The NESC theory is appropriate for GIAO calculations because the momentum $\vec{p}$ and $\vec{A}_0$ always appear via the operator $\vec{\sigma}\cdot\vec{\pi}$ in the NESC theory. Keeping $(\vec{\sigma}\cdot\vec{\pi})$ intact is crucial for preserving gauge invariance.

B. Magnetic perturbation expansion

The magnetic perturbation expansion of the electronic energy E is rather complicated in its use of GIAOs. In this subsection, we use the hat symbol to denote an operator in order to distinguish an operator from its matrix representation. On the other hand, we use round brackets for the matrix representation of an operator. We assume here that the used GIAO basis functions form a complete basis set. Using the RI approximation, the matrix representation of an operator product $\hat{A}\hat{B}$ $(\hat{A}\hat{B})$ is given by $(\hat{A}\hat{B}) = AS^{-1}B$, in which S is the overlap integral matrix between the specified GIAOs. Since $(\hat{1}) = S$, the matrix representation of an inverse operator $\hat{A}^{-1}$ $(\hat{A}^{-1})$ is represented by $SA^{-1}S$. Using the RI approximation, the matrix form for the transformation operator $\hat{U}$ $(\hat{U})$ is written as $S\tilde{U}$, where

$$\tilde{U} = (T-W)^{-1}T\left(1 - \frac{1}{2c^2}\tilde{U}M^{-1}F\right). \tag{19}$$

Similarly, the Fock matrix F and the metric matrix M are given by

$$F = (\hat{F}) = T\tilde{U} + \tilde{U}^\dagger T - \tilde{U}^\dagger T\tilde{U} + V + \tilde{U}^\dagger W\tilde{U} + J_{LL} - K_{LL} \tag{20}$$

and

$$M = (\hat{M}) = S + \frac{1}{2c^2}\tilde{U}^\dagger T\tilde{U}, \tag{21}$$

respectively. The Fock matrix F and the metric matrix M are expanded in terms of the perturbation parameters, B_{0t} $(t\in x, y, z)$ and $c^{-2}\mu_{Mu}$ $(u\in x, y, z)$. Specifically,

$$F = F^{(0)} + \sum_t B_{0t}F_t^{(1,0)} + c^{-2}\sum_u \mu_{Mu}F_u^{(0,1)} + c^{-2}\sum_{tu} B_{0t}\mu_{Mu}F_{tu}^{(1,1)} + \cdots \tag{22}$$

and

$$M = M^{(0)} + \sum_t B_{0t}M_t^{(1,0)} + c^{-2}\sum_u \mu_{Mu}M_u^{(0,1)} + c^{-2}\sum_{tu} B_{0t}\mu_{Mu}M_{tu}^{(1,1)} + \cdots. \tag{23}$$

From Eq. (19), we note that $\tilde{U} = 1 + \mathcal{O}(c^{-2}) + \cdots$. The magnetically perturbed part of $\tilde{U}$ (i.e., $\tilde{U}^{(1,0)}$, $\tilde{U}^{(0,1)}$, and $\tilde{U}^{(1,1)}$ matrices) has leading terms of c^{-2} with respect to c inverse. Because $\tilde{U}^{(0)} = 1 + \mathcal{O}(c^{-2}) + \cdots$, the perturbation terms of $\tilde{U}$ contribute to F and M only in order c^{-4} and higher orders of

c^{-1}. We may omit in F and M the magnetic perturbation terms with the order c^{-4} and higher-order relativistic effects. We therefore ignore the magnetic perturbations originating from $\tilde{U}$ in the calculation. We retain only the unperturbed transformation matrix $\tilde{U}^{(0)}$, i.e., $\tilde{U}=\tilde{U}^{(0)}$. Neglecting the perturbation terms of $\tilde{U}$ greatly simplifies the magnetic perturbation expansion of E. The perturbation expansions of F and M are then straightforwardly performed from the expansions of T, V, S, and W.

The (μ,ν) elements of the matrices of T, V, S, and W for GIAOs are given as follows:

$$T^{(0)}_{\mu\nu}=\langle\omega_\mu|-\tfrac{1}{2}\Delta|\omega_\nu\rangle, \tag{24}$$

$$T^{(1,0)}_{t\mu\nu}=\langle\omega_\mu|\frac{i}{2}(\vec{R}_{\mu\nu}\times\vec{r})_t\left(-\frac{1}{2}\Delta\right)|\omega_\nu\rangle + \frac{1}{4}\langle\omega_\mu|-i(\vec{r}_\nu\times\vec{\nabla})_t-\sigma_t\vec{r}_\nu\cdot\vec{\nabla}+\vec{\sigma}\cdot\vec{r}_\nu\nabla_t|\omega_\nu\rangle + \frac{1}{4}\langle\omega_\nu|-i(\vec{r}_\nu\times\vec{\nabla})_t-\sigma_t\vec{r}_\nu\cdot\vec{\nabla}+\vec{\sigma}\cdot\vec{r}_\nu\nabla_t|\omega_\mu\rangle^*, \tag{25}$$

$$T^{(0,1)}_{u\mu\nu}=\tfrac{1}{2}\langle\omega_\mu|r_M^{-3}[-i(\vec{r}_M\times\vec{\nabla})_u-\sigma_u\vec{r}_M\cdot\vec{\nabla}+\vec{\sigma}\cdot\vec{r}_M\nabla_u]|\omega_\nu\rangle + \text{Hermitian conjugate}, \tag{26}$$

$$T^{(1,1)}_{tu\mu\nu}=\frac{1}{2}\langle\omega_\mu|r_M^{-3}[\delta_{tu}\vec{r}_M\cdot\vec{r}_\nu-r_{Mt}r_{\nu u}]|\omega_\nu\rangle + \frac{i}{4}\langle\omega_\mu|(\vec{R}_{\mu\nu}\times\vec{r})_t r_M^{-3}[-i(\vec{r}_M\times\vec{\nabla})_u-\sigma_u\vec{r}_M\cdot\vec{\nabla} + \vec{\sigma}\cdot\vec{r}_M\nabla_u]|\omega_\nu\rangle-\frac{i}{4}\langle\omega_\nu|r_M^{-3}[-i(\vec{r}_M\times\vec{\nabla})_u - \sigma_u\vec{r}_M\cdot\vec{\nabla}+\vec{\sigma}\cdot\vec{r}_M\nabla_u](\vec{R}_{\nu\mu}\times\vec{r})_t|\omega_\mu\rangle^*, \tag{27}$$

$$V^{(0)}_{\mu\nu}=\sum_n\langle\omega_\mu|-Z_n/r_n|\omega_\nu\rangle, \tag{28}$$

$$V^{(1,0)}_{t\mu\nu}=\sum_n\langle\omega_\mu|\frac{i}{2}(\vec{R}_{\mu\nu}\times\vec{r})_t(-Z_n/r_n)|\omega_\nu\rangle, \tag{29}$$

$$V^{(0,1)}_{u\mu\nu}=0,\quad V^{(1,1)}_{tu\mu\nu}=0, \tag{30}$$

$$S^{(0)}_{\mu\nu}=\langle\omega_\mu|\omega_\nu\rangle, \tag{31}$$

$$S^{(1,0)}_{t\mu\nu}=\langle\omega_\mu|\frac{i}{2}(\vec{R}_{\mu\nu}\times\vec{r})_t|\omega_\nu\rangle, \tag{32}$$

$$S^{(0,1)}_{u\mu\nu}=0,\quad S^{(1,1)}_{tu\mu\nu}=0, \tag{33}$$

$$W^{(0)}_{\mu\nu}=\frac{1}{4c^2}\sum_n\langle\omega_\mu|Z_n\left[\vec{\nabla}\frac{1}{r_n}\cdot\vec{\nabla}+i\vec{\sigma}\cdot\left(\vec{\nabla}\frac{1}{r_n}\right)\times\vec{\nabla}\right]|\omega_\nu\rangle, \tag{34}$$

$$W^{(1,0)}_{t\mu\nu}=\frac{i}{8c^2}\sum_n\langle\omega_\mu|Z_n(\vec{R}_{\mu\nu}\times\vec{r})_t\left[\vec{\nabla}\frac{1}{r_n}\cdot\vec{\nabla}+i\vec{\sigma}\cdot\left(\vec{\nabla}\frac{1}{r_n}\right)\times\vec{\nabla}\right]|\omega_\nu\rangle + \frac{1}{8c^2}\sum_n\langle\omega_\mu|(-Z_n/r_n)[-i(\vec{r}_\nu\times\vec{\nabla})_t - \sigma_t\vec{r}_\nu\cdot\vec{\nabla}+\vec{\sigma}\cdot\vec{r}_\nu\nabla_t]|\omega_\nu\rangle + \frac{1}{8c^2}\sum_n\langle\omega_\nu|(-Z_n/r_n) \times[-i(\vec{r}_\nu\times\vec{\nabla})_t-\sigma_t\vec{r}_\nu\cdot\vec{\nabla}+\vec{\sigma}\cdot\vec{r}_\nu\nabla_t]|\omega_\mu\rangle^*, \tag{35}$$

$$W^{(0,1)}_{u\mu\nu}=\frac{1}{4c^2}\langle\omega_\mu|Vr_M^{-3}[-i(\vec{r}_M\times\vec{\nabla})_u-\sigma_u\vec{r}_M\cdot\vec{\nabla} + \vec{\sigma}\cdot\vec{r}_M\nabla_u]|\omega_\nu\rangle+\text{Hermitian conjugate}, \tag{36}$$

$$W^{(1,1)}_{tu\mu\nu}=\frac{1}{4c^2}\langle\omega_\mu|Vr_M^{-3}[\delta_{tu}\vec{r}_M\cdot\vec{r}_\nu-r_{Mt}r_{\nu u}]|\omega_\nu\rangle + \frac{i}{8c^2}\langle\omega_\mu|V(\vec{R}_{\mu\nu}\times\vec{r})_t r_M^{-3}[-i(\vec{r}_M\times\vec{\nabla})_u - \sigma_u\vec{r}_M\cdot\vec{\nabla}+\vec{\sigma}\cdot\vec{r}_M\nabla_u]|\omega_\nu\rangle-\frac{i}{8c^2}\langle\omega_\nu|Vr_M^{-3} \times[-i(\vec{r}_M\times\vec{\nabla})_u-\sigma_u\vec{r}_M\cdot\vec{\nabla}+\vec{\sigma}\cdot\vec{r}_M\nabla_u] \times(\vec{R}_{\nu\mu}\times\vec{r})_t|\omega_\mu\rangle^*, \tag{37}$$

where Z_n is the atomic number of the nth atom and

$$\vec{R}_{\mu\nu}=\vec{R}_\mu-\vec{R}_\nu. \tag{38}$$

r_n is the distance from nucleus n, and the parentheses in $(\vec{\nabla}1/r_n)$ mean that $\vec{\nabla}$ operates solely on $1/r_n$. The magnetic shielding tensor component σ^M_{tu} $(t,u\in x,y,z)$ is computed as $(\partial^2E/\partial B_{0t}\partial\mu_{Mu})$ at $\vec{B}_0=0$ and $\vec{\mu}_M=0$, where E is the total electronic energy of the system.

One of the difficult problems we encountered in our previous studies[30–32] was the evaluation of $W^{(0,1)}$ and $W^{(1,1)}$ matrices, which cannot be calculated analytically. In our previous studies, we employed the RI approximation for calculation of $W^{(1,0)}$, $W^{(0,1)}$, and $W^{(1,1)}$ matrices. However, the RI approximation is problematic. Therefore, in the present study we evaluate $W^{(1,0)}$ analytically, and $W^{(0,1)}$ and $W^{(1,1)}$ numerically using the Gauss–Legendre quadrature (GLQ). The nuclear attraction potential V in the point nuclear model is given by

$$V=-\sum_n Z_n/r_n. \tag{39}$$

We can apply a Singer transformation[41] to evaluate $W^{(0,1)}$ and $W^{(1,1)}$,

$$\frac{1}{r_n}=\frac{2}{\sqrt{\pi}}\int_0^\infty e^{-\eta^2r_n^2}d\eta. \tag{40}$$

The integrals contained in $W^{(0,1)}_{u\mu\nu}$ and $W^{(1,1)}_{tu\mu\nu}$ are evaluated using the formula

$$\langle \omega_\mu | r_n^{-1} r_M^{-3} r_{Mv} | \omega_\nu \rangle = \frac{2}{\sqrt{\pi}} \int_0^\infty \langle \omega_\mu | e^{-\eta^2 r_n^2} r_M^{-3} r_{Mv} | \omega_\nu \rangle d\eta; \quad v \in x,y,z. \quad (41)$$

The operator $Vr_M^{-3}r_{Mv}$ has a quasidivergent point at the position of nucleus M when $n=M$. The most severe integral for convergence is $\langle s_A | r_M^{-4} z_M | s_B \rangle$ in which s_A and s_B are both s-type GTOs and the A, B, and M centers lie on the molecular axis, which taken to be the z axis. It is shown in the Appendix that this type of integral converges.

C. A finite-size nuclear model

Another difficult problem is the inadequacy of the point nuclear model. The numerical instability, which is often observed in the shielding calculation by NESC, may originate from the singularity in the point nuclear model employed. In this subsection, we consider a finite-size nuclear model calculation for V, $\vec{A}_M$, and W. We introduce a charge density distribution function for the one nuclear positive charge for nucleus n, $w_n(\vec{r}_n)$, the integration of which is normalized to 1. We assume a normalized $1s$-type Gaussian function for $w_n(\vec{r}_n)$.[10,34–40] The function w_n is given by

$$w_n(\vec{r}_n) = (\alpha_n/\pi)^{3/2} e^{-\alpha_n r_n^2}, \quad r_n = |\vec{r} - \vec{R}_n|, \quad (42)$$

where $\vec{R}_n$ is the center position of nucleus n. α_n is related to the root-mean-square (rms) radius of nucleus n, $\langle r_n^2 \rangle^{1/2}$. Namely, $\alpha_n = 3/(2\langle r_n^2 \rangle)$. Experimental rms nuclear radius $\langle r_n^2 \rangle^{1/2}$ is a function of the nucleon number of nucleus n, A_n, and is given as[34–36,39,40]

$$\langle r_n^2 \rangle^{1/2} = 1.58 \times 10^{-5} A_n^{1/3} + 1.08 \times 10^{-5}. \quad (43)$$

The matrices of V and $\vec{A}_M$ in the Gaussian distribution of a finite-size nuclear charge are computed as below. The matrix elements of nuclear attraction potential V can be evaluated as

$$\langle \chi_\mu | V | \chi_\nu \rangle = \sum_n \left(-Z_n \int \chi_\mu^*(\vec{r}) \chi_\nu(\vec{r}) | \vec{r} - \vec{r}' |^{-1} w_n(\vec{r}') d^3r d^3r' \right). \quad (44)$$

The matrix elements of $r_M^{-3} x_M$ in $\vec{A}_M$ can be calculated using integration by parts,

$$\begin{aligned} \langle \chi_\mu | r_M^{-3} x_M | \chi_\nu \rangle &= \int \chi_\mu^*(\vec{r}) \chi_\nu(\vec{r}) | \vec{r} - \vec{r}' |^{-3} \times (x - x') w_M(\vec{r}') d^3r d^3r' \\ &= -\int \chi_\mu^*(\vec{r}) \chi_\nu(\vec{r}) | \vec{r} - \vec{r}' |^{-1} \left[\frac{\partial}{\partial x'} w_M(\vec{r}') \right] d^3r d^3r'. \end{aligned} \quad (45)$$

The integrations of Eqs. (44) and (45) are performed using a conventional two-electron integration program. Since the distribution of nuclear magnetic moment is less established, we assume the same distribution function for the magnetic moment as that for the nuclear charge.[40]

The matrices of $W^{(0,1)}$ and $W^{(1,1)}$ can be evaluated with the method that is used for calculating $\langle \chi_\mu | r_n^{-1} | \chi_\nu \rangle$ and $\langle \chi_\mu | r_M^{-3} x_M | \chi_\nu \rangle$ unless n equals M. When $n=M$, however, it is difficult to calculate $W^{(0,1)}$ and $W^{(1,1)}$ with the finite-size nuclear model of the Gaussian function for a nuclear charge distribution. For $n=M$ we instead assume a spherically symmetric uniform charge distribution for a nuclear charge. The nuclear attraction potential V_n due to the nucleus n of the atomic number Z_n is then given by

$$V_n(r_n) = \begin{cases} -Z_n/r_n & \text{for } r_n \geq a_n \\ -Z_n \left[\frac{3}{2} \frac{1}{a_n} - \frac{1}{2} \frac{r_n^2}{a_n^3} \right] & \text{for } r_n \leq a_n, \end{cases} \quad (46)$$

where a_n is the nuclear radius of nucleus n and r_n is the distance of an electron from the center position of nucleus n. The most singular terms in $W^{(0,1)}$ and $W^{(1,1)}$ will arise when $n=M$. The dipolar potential due to the magnetic dipole moment $\vec{\mu}_M$ is $r_M^{-3} r_{Mu}$ $(u \in x,y,z)$ in the point dipole model. We notice that for the point dipole moment $\vec{\mu}_M$

$$r_M^{-3} r_{Mu} = \frac{\partial}{\partial r_u} \left(\frac{-1}{|\vec{r} - \vec{R}_M|} \right) = \frac{\partial}{\partial r_u} \frac{V_M}{Z_M}. \quad (47)$$

Here we propose the following function for the dipolar potential F_{Mu} due to the finite-size nuclear magnetic dipole moment $\vec{\mu}_M$, i.e.,

$$F_{Mu}(r_M) = \frac{\partial}{\partial r_u} \frac{V_M}{Z_M} = \begin{cases} r_M^{-3} r_{Mu} & \text{for } r_M \geq a_M \\ a_M^{-3} r_{Mu} & \text{for } r_M \leq a_M. \end{cases} \quad (48)$$

Using Eqs. (46) and (48), we can replace the most singular operator, $W_{Mu} = -Z_M r_M^{-4} r_{Mu}$, in the point nuclear dipole model for $W^{(0,1)}$ and $W^{(1,1)}$ by

$$W_{Mu}(r_M) = V_M F_{Mu} = \begin{cases} -Z_M r_M^{-4} r_{Mu} & \text{for } r_M \geq a_M \\ -Z_M \left[\frac{3}{2} \frac{1}{a_M} - \frac{1}{2} \frac{r_M^2}{a_M^3} \right] a_M^{-3} r_{Mu} & \text{for } r_M \leq a_M. \end{cases} \quad (49)$$

It is interesting to note that W_{Mu} is zero at $r_M=0$. We may assume that $W_{Mu}(r_M)=0$ for $r_M \leq a_M$. a_M is given by $\sqrt{5/3}\langle r_M^2 \rangle^{1/2}$.[39]

III. RESULTS AND DISCUSSION

All of the present calculations use the SORA-NESC theory including the magnetic perturbations from the metric operator M. We denote this scheme as SORA-Met. We investigate in this section the cause of the poor results of anisotropy of shielding tensor $\Delta\sigma$ obtained using the SORA-Met approach. Although the hydrogen halide system may not be the most appropriate system for probing the importance of the various approximations introduced, the hydrogen halide system is one of the most examined systems for relativistic effects on the shieldings. We have an accumu-

lation of data of relativistic effects on the hydrogen halide shieldings. We test the approximations introduced using hydrogen halide molecules as the probe.

In our previous calculation of the magnetic shielding tensors in HX (X=F,Cl,Br,I) systems,[32] the RI approximation was used to evaluate the $W^{(1,0)}$, $W^{(0,1)}$, and $W^{(1,1)}$ matrices. Our previous results are presented in the fourth column of Table I as SORA-Met-RI. The SORA-Met-RI results yield too small anisotropies, $\Delta\sigma=\sigma_{\parallel}-\sigma_{\perp}$, for the halogen nuclei, especially for I, compared to the DHF results[3,4] presented in the last column, which are considered to be benchmarks. The RI approximation is problematic. In order to search and to determine the cause of our small $\Delta\sigma$ values for halogen nuclei, we next evaluate $W^{(1,0)}$ analytically, and $W^{(0,1)}$ and $W^{(1,1)}$ numerically using GLQ. For Gaussian exponent functions, which are not so large, we used a Singer transformation[41] presented in Eq. (40). When the sum of the two Gaussian exponents, α_{μ} and α_{ν}, used for two Gaussian-type basis functions, ω_{μ} and ω_{ν}, is less than 10^3, we employed Eq. (41) to evaluate $W^{(0,1)}$ and $W^{(1,1)}$. On the other hand, if $\alpha_{\mu}+\alpha_{\nu}\geq 10^3$, we employed the twofold numerical integration of GLQ to evaluate the integrals of $r_M^{-4}r_{Mv}$ ($v\in x, y, z$). The integration for $r_n^{-1}r_M^{-3}r_{Mu}$ ($n\neq M$) is evaluated using the Taylor expansion of r_n^{-1} or $r_M^{-3}r_{Mu}$. The numerical integration results for $W^{(0,1)}$ and $W^{(1,1)}$ matrices are presented in the fifth column of Table I (labeled as SORA-Met-GLQ). The SORA-Met-GLQ results yield shielding tensor values similar to those of SORA-Met-RI. The SORA-Met-GLQ gives a value of σ^{iso} for I that is 89.7 ppm smaller than that of SORA-Met-RI, and the $\Delta\sigma$ value of I increases slightly. It is concluded that the RI approximation is a reasonable approximation and the small $\Delta\sigma$ values of halogen nuclei do not originate from the RI approximation.

In our previous calculation and the present SORA-Met-GLQ calculation, the common gauge origins were selected to be on the halogen nuclei. If the basis sets[32] used are inadequate, the GIAO calculation will yield tensor components that differ greatly from the common gauge origin results. The GIAO calculation results are presented in the sixth column of Table I (labeled as SORA-Met-GIAO). The results of SORA-Met-GIAO are very similar to those of SORA-Met-GLQ. Both calculations give the same values for $\sigma_{\parallel}$, as can be showed mathematically. The $\Delta\sigma$ values of F and Cl are improved but those of Br and I remain unchanged. It is concluded that the basis sets used are not so inadequate and that the origin of the small $\Delta\sigma$ of halogen nuclei is not the inadequacy of the basis sets.

In order to search for the cause of our small $\Delta\sigma$ for halogen nuclei, we investigate the effects of the magnetic perturbation terms originating from the transformation matrix $\tilde{U}$ presented in Eq. (19). The magnetic perturbation terms of $\tilde{U}$ (i.e., $\tilde{U}^{(1,0)}$, $\tilde{U}^{(0,1)}$, and $\tilde{U}^{(1,1)}$) contribute to F and M matrices only in the order of c^{-4} and smaller. We expand $\tilde{U}$ in the magnetic perturbation parameter λ as

$$\tilde{U}=\tilde{U}^{(0)}+\lambda\tilde{U}^{(1)}+\lambda^2\tilde{U}^{(2)}+\cdots, \tag{50}$$

where λ means collectively B_{0t}, $c^{-2}\mu_{Mu}$, and $c^{-2}B_{0t}\mu_{Mu}$. Using the Taylor expansion, we obtain

$$\begin{aligned}\tilde{U}^{(1)}=&(T^{(0)}-W^{(0)})^{-1}W^{(1)}-(T^{(0)}-W^{(0)})^{-1}T^{(1)}(T^{(0)}\\&-W^{(0)})^{-1}W^{(0)}-\frac{1}{2c^2}\\&\times(T^{(0)}-W^{(0)})^{-1}T^{(0)}\tilde{U}^{(0)}M^{(0)-1}F^{(1)}\\&+(T^{(0)}-W^{(0)})^{-1}W^{(1)}(T^{(0)}-W^{(0)})^{-1}W^{(0)}\end{aligned} \tag{51}$$

and

$$\begin{aligned}\tilde{U}^{(2)}=&[(T^{(0)}-W^{(0)})^{-1}T^{(1)}]^2(T^{(0)}-W^{(0)})^{-1}W^{(0)}\\&-(T^{(0)}-W^{(0)})^{-1}T^{(1)}(T^{(0)}-W^{(0)})^{-1}W^{(1)}.\end{aligned} \tag{52}$$

In the above expansion, we retain only the c^{-2} order perturbations except the last term in Eq. (51). Owing to the $r_M^{-3}r_{Mv}$ ($v\in x, y, z$) operator originating from the point dipolar field, $\tilde{U}^{(0,1)}$ may have non-negligible effects on the paramagnetic parts of $\sigma_{\perp}$ and $\sigma_{\parallel}$ of iodine. The last term in Eq. (51) is of the order of c^{-4} but it may be significant in $\tilde{U}^{(0,1)}$ because of the inclusion of both $W^{(0,1)}$ and $W^{(0)}$. Table I shows that the small $\Delta\sigma$ values of halogen nuclei may be due to the values of $\sigma_{\parallel}$ (para) being too small. We obtained $\tilde{U}_u^{(0,1)}$ from Eq. (51) with $\lambda=c^{-2}\mu_{Mu}$. We add only the $\tilde{U}_u^{(0,1)}$ ($u\in x, y, z$) perturbation contributions to the perturbed Fock $F_u^{(0,1)}$ and metric $M_u^{(0,1)}$ matrices and calculated the shielding tensors with the SORA-Met-GLQ method. The results are presented in the fourth column of Table II (labeled as SORA-Met-$\tilde{U}^{(0,1)}$). The results of SORA-Met-$\tilde{U}^{(0,1)}$ exhibit a quasidivergent behavior for iodine nucleus. The $\tilde{U}^{(0,1)}$ terms exert a surprisingly large effect on the $\sigma_{\perp}$ (para) and $\sigma_{\parallel}$ (para) of iodine, which is an unexpected result. Although the $\Delta\sigma$ for I is too large, the direction of change is correct. The $\Delta\sigma$ for Br is significantly improved but it is still too small.

The divergence caused by the inclusion of $\tilde{U}^{(0,1)}$ may come from the point nuclear model. In order to prevent this divergence, we introduce a finite-size nuclear model to the SORA-Met-$\tilde{U}^{(0,1)}$ calculation. The results of finite-size nuclei are presented in the fifth column of Table II (labeled as SORA-Met-$\tilde{U}^{(0,1)}$-Fn). The results for SORA-Met-$\tilde{U}^{(0,1)}$-Fn show a convergent and mild behavior for the $\sigma_{\perp}$ (para) and $\sigma_{\parallel}$ (para) values of iodine but the $\Delta\sigma$ value of I is still rather large. However, the $\Delta\sigma$ value of Br obtained by SORA-Met-$\tilde{U}^{(0,1)}$-Fn is rather small in comparison with the DHF value. Our preliminary calculations showed that introduction of the finite-size nuclear model to the SORA-Met schemes, without the $\tilde{U}^{(0,1)}$ perturbation, hardly changes $\Delta\sigma$ values. The $\Delta\sigma$ (I) in HI was slightly reduced with the finite-size nuclear model alone by several ppm. It is therefore concluded that the small $\Delta\sigma$ values for halogen nuclei are due to the neglect of the $\tilde{U}^{(0,1)}$ perturbation terms. Furthermore, the use of a more sophisticated finite-size nuclear model may be essential to accurately reproduce the $\Delta\sigma$ values of DHF.[36,38] In the four-component scheme, similarly, the calculation of the nuclear hyperfine terms, $\vec{A}_M\cdot\vec{p}$ and $(\vec{p}\times\vec{A}_M)$, is a subtle problem.[42]

TABLE I. Calculated nuclear magnetic shielding tensor components (in ppm) in HX (X=F,Cl,Br,I) systems.

Molecule	Nucleus	Property	SORA-Met-RI[a]	SORA-Met-GLQ[b]	SORA-Met-GIAO[c]	DHF[d]
		$\sigma_{\perp}$(para)	−94.0	−94.0	−71.8	
		$\sigma_{\perp}$(dia)	482.1	482.1	455.6	
		$\sigma_{\perp}$(total)	388.1	388.1	383.8	384.9
		$\sigma_{\parallel}$(para)	4.6	4.6	4.6	
		$\sigma_{\parallel}$(dia)	481.2	481.2	481.2	
		$\sigma_{\parallel}$(total)	485.8	485.8	485.8	485.6
		σ^{iso}(total)	420.7	420.6	417.8	418.4
	F	$\Delta\sigma$(total)	97.7	97.7	101.9	100.7
		$\sigma_{\perp}$(para)	18.89	18.89	3.77	
		$\sigma_{\perp}$(dia)	1.34	1.34	16.83	
		$\sigma_{\perp}$(total)	20.24	20.24	20.60	20.10
		$\sigma_{\parallel}$(para)	−0.01	−0.01	−0.01	
		$\sigma_{\parallel}$(dia)	44.05	44.05	44.05	
		$\sigma_{\parallel}$(total)	44.05	44.05	44.05	43.90
		σ^{iso}(total)	28.17	28.17	28.41	28.03
HF	H	$\Delta\sigma$(total)	23.81	23.81	23.45	23.80
		$\sigma_{\perp}$(para)	−247.7	−247.9	−243.6	
		$\sigma_{\perp}$(dia)	1148.4	1148.4	1138.0	
		$\sigma_{\perp}$(total)	900.7	900.5	894.3	888.5
		$\sigma_{\parallel}$(para)	31.9	31.6	31.6	
		$\sigma_{\parallel}$(dia)	1145.6	1145.6	1145.6	
		$\sigma_{\parallel}$(total)	1177.5	1177.3	1177.3	1176.7
		σ^{iso}(total)	993.0	992.7	988.6	984.5
	Cl	$\Delta\sigma$(total)	276.8	276.8	282.9	288.2
		$\sigma_{\perp}$(para)	22.49	22.49	-2.73	
		$\sigma_{\perp}$(dia)	1.89	1.89	27.33	
		$\sigma_{\perp}$(total)	24.38	24.38	24.60	24.07
		$\sigma_{\parallel}$(para)	−0.01	−0.02	−0.02	
		$\sigma_{\parallel}$(dia)	45.38	45.38	45.38	
		$\sigma_{\parallel}$(total)	45.37	45.37	45.37	45.39
		σ^{iso}(total)	31.38	31.38	31.52	31.18
HCl	H	$\Delta\sigma$(total)	20.99	20.98	20.77	21.32
		$\sigma_{\perp}$(para)	−267.0	−276.9	−254.5	
		$\sigma_{\perp}$(dia)	3102.5	3102.1	3084.1	
		$\sigma_{\perp}$(total)	2835.4	2825.2	2829.6	2738.1
		$\sigma_{\parallel}$(para)	286.9	278.2	278.1	
		$\sigma_{\parallel}$(dia)	3099.4	3099.1	3099.1	
		$\sigma_{\parallel}$(total)	3386.3	3377.2	3377.2	3402.1
		σ^{iso}(total)	3019.1	3009.2	3012.1	2959.4
	Br	$\Delta\sigma$(total)	550.9	552.0	547.6	664.0
		$\sigma_{\perp}$(para)	30.12	30.12	8.34	
		$\sigma_{\perp}$(dia)	−0.02	−0.02	21.96	
		$\sigma_{\perp}$(total)	30.10	30.10	30.29	29.82
		$\sigma_{\parallel}$(para)	−0.46	−0.46	−0.46	
		$\sigma_{\parallel}$(dia)	48.53	48.53	48.53	
		$\sigma_{\parallel}$(total)	48.07	48.07	48.07	47.93
		σ^{iso}(total)	36.09	36.09	36.22	35.86
HBr	H	$\Delta\sigma$(total)	17.97	17.97	17.78	18.11
		$\sigma_{\perp}$(para)	537.5	440.4	449.6	
		$\sigma_{\perp}$(dia)	5415.4	5415.3	5405.4	
		$\sigma_{\perp}$(total)	5952.9	5855.7	5855.1	5571.9
		$\sigma_{\parallel}$(para)	1197.1	1122.7	1122.7	
		$\sigma_{\parallel}$(dia)	5412.1	5411.9	5411.9	
		$\sigma_{\parallel}$(total)	6609.2	6534.6	6534.6	6597.1
		σ^{iso}(total)	6171.7	6082.0	6081.6	5913.7
	I	$\Delta\sigma$(total)	656.2	678.9	679.5	1025.2
		$\sigma_{\perp}$(para)	50.95	50.95	30.28	
		$\sigma_{\perp}$(dia)	−1.82	−1.82	19.04	
		$\sigma_{\perp}$(total)	49.14	49.14	49.32	46.92
		$\sigma_{\parallel}$(para)	−4.33	−4.33	−4.33	
		$\sigma_{\parallel}$(dia)	50.32	50.32	50.32	
		$\sigma_{\parallel}$(total)	45.99	45.99	45.99	47.31
		σ^{iso}(total)	48.09	48.09	48.21	47.05
HI	H	$\Delta\sigma$(total)	−3.15	−3.15	−3.33	0.39

[a]Previous results calculated by using the RI approximation for $W^{(1,0)}$, $W^{(0,1)}$, and $W^{(1,1)}$, which are taken from Ref. 32.
[b]Present results obtained by calculating $W^{(1,0)}$ analytically, and $W^{(0,1)}$ and $W^{(1,1)}$ numerically.
[c]Present results calculated by using GIAOs. The calculations of $W^{(1,0)}$, $W^{(0,1)}$, and $W^{(1,1)}$ are the same as for SORA-Met-GLQ.
[d]DHF results taken from Refs. 3 and 4.

TABLE II. Calculated nuclear magnetic shielding tensor components (in ppm) in HX (X=F,Cl,Br,I) systems.

Molecule	Nucleus	Property	SORA-Met-$\tilde{U}^{(0,1)}$[a]	SORA-Met-$\tilde{U}^{(0,1)}$-Fn[b]	DHF[c]
		$\sigma_\perp$(para)	−94.1	−94.1	
		$\sigma_\perp$(dia)	482.1	482.1	
		$\sigma_\perp$(total)	388.0	388.0	384.9
		$\sigma_\parallel$(para)	4.6	4.6	
		$\sigma_\parallel$(dia)	481.2	481.2	
		$\sigma_\parallel$(total)	485.8	485.8	485.6
		σ^{iso}(total)	420.6	420.6	418.4
	F	$\Delta\sigma$(total)	97.8	97.8	100.7
		$\sigma_\perp$(para)	18.89	18.89	
		$\sigma_\perp$(dia)	1.34	1.34	
		$\sigma_\perp$(total)	20.24	20.24	20.10
		$\sigma_\parallel$(para)	−0.01	−0.01	
		$\sigma_\parallel$(dia)	44.05	44.05	
		$\sigma_\parallel$(total)	44.05	44.05	43.90
		σ^{iso}(total)	28.17	28.17	28.03
HF	H	$\Delta\sigma$(total)	23.81	23.81	23.80
		$\sigma_\perp$(para)	−249.8	−249.5	
		$\sigma_\perp$(dia)	1148.4	1148.4	
		$\sigma_\perp$(total)	898.6	898.9	888.5
		$\sigma_\parallel$(para)	31.6	32.6	
		$\sigma_\parallel$(dia)	1145.6	1145.6	
		$\sigma_\parallel$(total)	1177.2	1178.3	1176.7
		σ^{iso}(total)	991.5	992.0	984.5
	Cl	$\Delta\sigma$(total)	278.6	279.3	288.2
		$\sigma_\perp$(para)	22.49	22.49	
		$\sigma_\perp$(dia)	1.89	1.89	
		$\sigma_\perp$(total)	24.38	24.38	24.07
		$\sigma_\parallel$(para)	−0.02	−0.02	
		$\sigma_\parallel$(dia)	45.38	45.38	
		$\sigma_\parallel$(total)	45.37	45.37	45.39
		σ^{iso}(total)	31.38	31.38	31.18
HCl	H	$\Delta\sigma$(total)	20.98	20.98	21.32
		$\sigma_\perp$(para)	−320.3	−311.5	
		$\sigma_\perp$(dia)	3102.1	3102.7	
		$\sigma_\perp$(total)	2781.8	2791.2	2738.1
		$\sigma_\parallel$(para)	280.3	311.8	
		$\sigma_\parallel$(dia)	3099.1	3099.7	
		$\sigma_\parallel$(total)	3379.3	3411.5	3402.1
		σ^{iso}(total)	2981.0	2997.9	2959.4
	Br	$\Delta\sigma$(total)	597.5	620.3	664.0
		$\sigma_\perp$(para)	30.12	30.12	
		$\sigma_\perp$(dia)	−0.02	−0.02	
		$\sigma_\perp$(total)	30.10	30.10	29.82
		$\sigma_\parallel$(para)	−0.46	−0.46	
		$\sigma_\parallel$(dia)	48.53	48.53	
		$\sigma_\parallel$(total)	48.07	48.07	47.93
		σ^{iso}(total)	36.09	36.09	35.86
HBr	H	$\Delta\sigma$(total)	17.97	17.97	18.11
		$\sigma_\perp$(para)	−1394.7	128.0	
		$\sigma_\perp$(dia)	5415.3	5419.5	
		$\sigma_\perp$(total)	4020.6	5547.4	5571.9
		$\sigma_\parallel$(para)	1582.8	1343.9	
		$\sigma_\parallel$(dia)	5411.9	5416.1	
		$\sigma_\parallel$(total)	6994.8	6760.1	6597.1
		σ^{iso}(total)	5012.0	5951.7	5913.7
	I	$\Delta\sigma$(total)	2974.2	1212.6	1025.2
		$\sigma_\perp$(para)	50.95	50.95	
		$\sigma_\perp$(dia)	−1.82	−1.82	
		$\sigma_\perp$(total)	49.14	49.13	46.92
		$\sigma_\parallel$(para)	−4.33	−4.33	
		$\sigma_\parallel$(dia)	50.32	50.32	
		$\sigma_\parallel$(total)	45.99	45.99	47.31
		σ^{iso}(total)	48.09	48.09	47.05
HI	H	$\Delta\sigma$(total)	−3.15	−3.14	0.39

[a]Present results obtained by adding $\tilde{U}^{(0,1)}$ perturbation terms to the calculation of SORA-Met-GLQ.

[b]Present results obtained by applying a finite-size nuclear model to the calculation of SORA-Met-$\tilde{U}^{(0,1)}$.

[c]DHF results taken from Refs. 3 and 4.

IV. CONCLUSION

The SORA-Met calculation, which applies the second-order regular approximation to the normalized elimination of the small component method and includes the magnetic perturbation terms from the metric operator, yields anisotropies, $\Delta\sigma=\sigma_{\parallel}-\sigma_{\perp}$, for halogen nuclei in hydrogen halides that are too small. In order to determine the cause of the small $\Delta\sigma$ values for halogen nuclei, the $r_n^{-1}r_M^{-3}r_{Mv}$ ($n=M$ or $n\neq M$, $v\in x, y, z$) type integrals were evaluated more precisely using the GLQ instead of the RI approximation used in our previous studies. The results demonstrate that the small $\Delta\sigma$ values do not originate from the RI approximation. The shielding calculation was performed using the GIAOs instead of using the usual Gaussian-type basis functions with the common gauge origins, which were selected to be on the halogen nuclei. The results showed no improvement in the $\Delta\sigma$ values for Br and I but showed an improvement in the $\Delta\sigma$'s of F and Cl. It is concluded that the small $\Delta\sigma$ values do not originate from an inadequacy of the basis sets. The transformation matrix for the small components $\tilde{U}$ was expanded in terms of the perturbation parameter $c^{-2}\mu_{Mu}$ ($u\in x, y, z$). The introduction of the first-order perturbation matrix of $\tilde{U}_u^{(0,1)}$ into the perturbed Fock $F_u^{(0,1)}$ and metric $M_u^{(0,1)}$ matrices unexpectedly yielded a $\Delta\sigma$ value for iodine that was too large. Finally, a finite-size nuclear model was introduced into the shielding calculation including the $\tilde{U}^{(0,1)}$. A $\Delta\sigma$ value for iodine that was acceptable, although still rather large, was obtained. It is concluded that too small $\Delta\sigma$ values for halogen nuclei obtained in our previous studies are a result of the neglect of the $\tilde{U}^{(0,1)}$ perturbation terms in the SORA-Met calculation.

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APPENDIX: INTEGRAL OF $\langle s_A|r_M^{-4}z_M|s_B\rangle$

We assume that s_A and s_B are $1s$-type Gaussian orbital functions centered on atoms A and B, respectively. We write s_A and s_B as

$$s_A=N_Ae^{-\alpha_Ar_A^2};\quad s_B=N_Be^{-\alpha_Br_B^2}. \tag{A1}$$

Here, N_A and N_B are normalization constants for s_A and s_B, respectively. For the integration, we use spherical polar coordinates with the origin located at the nuclear position M. We assume that A, B, and M all lie on the z axis. r_A^2 and r_B^2 are expressed in the polar coordinates of $\vec{r}_M$ as

$$r_A^2=r_M^2+Z_{AM}^2+2Z_{AM}r_M\cos\theta \tag{A2}$$

and

$$r_B^2=r_M^2+Z_{BM}^2+2Z_{BM}r_M\cos\theta, \tag{A3}$$

respectively. Here,

$$Z_{AM}=Z_M-Z_A,\quad Z_{BM}=Z_M-Z_B, \tag{A4}$$

where θ is the angle between $\vec{r}_M$ and the positive z direction. The integral $\langle s_A|r_M^{-4}z_M|s_B\rangle$ is given by

$$I=\langle s_A|r_M^{-4}z_M|s_B\rangle = 2\pi N_AN_Be^{-(\alpha_AZ_{AM}^2+\alpha_BZ_{BM}^2)}\int_0^{\infty}e^{-(\alpha_A+\alpha_B)r_M^2}[J(r_M)/r_M]dr_M, \tag{A5}$$

where

$$J(r_M)=\int_{-1}^{+1}ze^{-ar_Mz}dz. \tag{A6}$$

In Eq. (A6)

$$a=2(\alpha_AZ_{AM}+\alpha_BZ_{BM}). \tag{A7}$$

Integrating Eq. (A6) yields

$$J(r_M)=-\frac{1}{ar_M}(e^{ar_M}+e^{-ar_M})+\frac{1}{(ar_M)^2}(e^{ar_M}-e^{-ar_M}). \tag{A8}$$

It is impossible to obtain a closed analytical expression for the integral I, but we can prove that the integral I converges at $r_M=0$. The Taylor expansion of $J(r_M)$ leads to

$$J(r_M)/r_M=-\tfrac{2}{3}a-\tfrac{1}{15}a^3r_M^2+\cdots. \tag{A9}$$

Equation (A9) shows that the integral I converges. The integral I is expanded in terms of $[a^2/(\alpha_A+\alpha_B)]$ as

$$I=\langle s_A|r_M^{-4}z_M|s_B\rangle = -2\pi N_AN_Be^{-(\alpha_AZ_{AM}^2+\alpha_BZ_{BM}^2)}\times\sqrt{\frac{\pi a^2}{\alpha_A+\alpha_B}}\left[\frac{1}{3}+\frac{1}{60}\frac{a^2}{\alpha_A+\alpha_B}+\cdots\right]. \tag{A10}$$

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