Selected Paper

Dirac–Hartree–Fock Perturbation Calculation of Magnetic Shielding Using the External Field-Dependent Restricted Magnetic Balance Condition

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A formulism for four-component Dirac–Hartree–Fock perturbation theory using the restricted magnetic balance (RMB) condition with gauge-including atomic orbitals (GIAOs) is derived at an ab initio level. In this formulation, the zeroth-order Dirac–Hartree–Fock equations are subject only to the usual restricted kinetic balance (RKB) condition, while the external field-dependent RMB condition is introduced in the calculation of the first-order magnetically perturbed orbitals. The magnetic shielding can be divided into a paramagnetic part and a diamagnetic part, as for nonrelativistic (NR) shielding. The present theory is applied to the calculation of hydrogen halide and molecular halogen shieldings.

The magnetic properties of compounds containing heavy elements are strongly influenced by relativistic effects. Such relativistic effects can be accounted for by applying a relativistic version of the Hartree–Fock (HF) approximation, known as the Dirac–Hartree–Fock (DHF) approximation.[1,2] In this treatment, an n-electron wave function $\Psi(1,2,\ldots,n)$ is constructed as a Slater determinant of one-electron Dirac orbitals $\psi_i(\vec{r})$ $(i = 1,2,\ldots,n)$, which are determined from the variational principle as follows:

$$\delta\langle\Psi|\mathcal{H}_{\mathrm{DC}}|\Psi\rangle = 0 \tag{1}$$

Here, $\mathcal{H}_{\mathrm{DC}}$ is the Dirac–Coulomb Hamiltonian defined by

$$\mathcal{H}_{\mathrm{DC}} = \sum_{i=1}^{n} \hat{h}_{\mathrm{D}}(i) + \sum_{i<j}^{n} \frac{1}{r_{ij}} \tag{2}$$

and

$$\hat{h}_{\mathrm{D}} = c\vec{\alpha}\cdot(\vec{p} + \vec{A}) + (\beta - 1)c^2 + V \tag{3}$$

where $\vec{A}$ is the vector potential and V is the nuclear attraction potential. In a magnetic shielding problem, $\vec{A}$ consists of two parts: the vector potential $\vec{A}_0$ due to an external magnetic flux density $\vec{B}_0$ and the vector potential $\vec{A}_{\mathrm{M}}$ due to a nuclear magnetic dipole moment $\vec{\mu}_{\mathrm{M}}$.

The Hamiltonian $\mathcal{H}_{\mathrm{DC}}$ was previously thought to have no eigenfunctions corresponding to bound states due to continuum dissolution (the Brown–Ravenhall disease[3,4]) and variational collapse. To circumvent these problems, the one-electron Dirac Hamiltonian $\hat{h}_{\mathrm{D}}$ is often converted to an effective Hamiltonian that operates only on a one-component or two-component wave function instead of on the full four-component wave function.[5–15] However, there has also been progress in the four-component approach toward overcoming these problems. The dissolution of bound electronic states into continuum states in molecular DHF calculations was solved by using the no-pair approach or hole theory. A variational collapse has been shown to arise when the large and small component basis sets are chosen independently without any relation in the finite basis representation of the Dirac wave function.[16–19] The proper relationship between the large and small component basis sets must be used as the kinetic balance (KB) condition.[19]

We recently presented two-component magnetic perturbation calculations[20–23] based on a regular approximation to the normalized elimination of the small component (NESC).[24,25] The NESC-based effective Hamiltonian includes a singular term that arises from the cross term between V and $\vec{A}_{\mathrm{M}}$ in the nonunitary transformation operator U, which connects the small component spinor with the large component spinor. This cross term contributes to the magnetically perturbed Hamiltonian in order c^{-4} while the nonrelativistic terms are of order c^0 and the leading terms of the relativistic effects are of order c^{-2}. However, if this term is neglected,[23] the $\Delta\sigma$ $(\sigma_{\parallel} - \sigma_{\perp})$ in HI molecule, for example, reduces to 66% of the reference value due to a DHF method.[26] If this cross term is included in the perturbation Hamiltonian, the $\Delta\sigma$ exhibits quasidivergent behavior, attaining 290% of the reference value with point charge nuclei. Although the quasidivergence of the $\Delta\sigma$ can be suppressed by introducing a finite-size nuclear model, $\Delta\sigma$ still presents 118% of the reference value. It was shown that the numerical instability of our NESC calculation arises from the Taylor expansion of the transformation operator U in terms of the magnetic perturbation parameters.

In the four-component magnetic perturbation calculation, two primary problems must be addressed: insufficiencies in the restricted kinetic balance (RKB) basis and the lack of a diamagnetic term. The RKB basis consists of the basis $\{f_\nu^{\mathrm{L}}\}$ for expanding the upper (large) component spinor φ^{L} of the Dirac bispinor $\psi = (\varphi^{\mathrm{L}}, \varphi^{\mathrm{S}})$, and the basis $\{f_\nu^{\mathrm{S}} = \vec{\sigma}\cdot\vec{\nabla}f_\nu^{\mathrm{L}}\}$ for expanding the lower (small) component spinor φ^{S}. In the unrestricted kinetic balance (UKB) basis, φ^{S} is expanded into separate functions of $\sigma_x\partial f_\nu^{\mathrm{L}}/\partial x$, $\sigma_y\partial f_\nu^{\mathrm{L}}/\partial y$, and $\sigma_z\partial f_\nu^{\mathrm{L}}/\partial z$ as a basis of threefold dimensionality. The use of the UKB basis thus provides enhanced flexibility, but at a higher computa-

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tional cost, and is generally unnecessary for systems without magnetic perturbation.[27] Recently, it has been shown that UKB calculations are not more time-consuming than RKB calculations because the UKB prescription ensures convergence with smaller basis sets.[28] In a small basis $\{f_\nu^{\mathrm{L}}\}$, the use of $\{\vec{\sigma}\cdot\vec{\nabla}f_\nu^{\mathrm{L}}\}$ alone for the expansion of φ^{S} has been shown to be insufficient in magnetic problems; the inclusion of $\{\vec{\sigma}\cdot\vec{A}f_\nu^{\mathrm{L}}\}$ for the expansion of φ^{S} is considered to be necessary.[29] The latter problem, the lack of a diamagnetic term, is related to the fact that the magnetic perturbation operator $c\vec{\alpha}\cdot(\vec{A}_0+\vec{A}_{\mathrm{M}})$ in the Dirac Hamiltonian is linear in $\vec{A}_0$ and $\vec{A}_{\mathrm{M}}$. In the standard linear response theory (LRT),[30,31] a four-component perturbation approach, the first-order wave function is expanded directly in the full basis of the unperturbed wave functions subject only to the RKB condition. Although the perturbation operator $c\vec{\alpha}\cdot\vec{A}_{\mathrm{M}}$ behaves appropriately, even when using a point nuclear magnetic dipole moment, the operator $c\vec{\alpha}\cdot\vec{A}$ in eq 3 strongly couples the large and small components of Dirac spinors. The strong coupling between the large and small components of the Dirac spinors leads to a large contribution of negative energy states and hence the insufficiencies of the RKB basis may need large basis sets for the convergence of negative energy sum-over-states (SOS) calculations of the diamagnetic contribution to the shielding. An approach for realizing minimal coupling between the large and small components was proposed,[32] in which the coupling between the large and small components in the unitary-transformed Hamiltonian is reduced by a factor of c^{-2}. As a result, the contributions of the negative energy states are reduced by a factor of c^{-4}.[33] Although the unitary-transformed Hamiltonian includes singular operators when it is used with a magnetic point dipole model,[33,34] the individual divergences cancel when all the singular terms are summed.[34] Furthermore, it was shown that the singularity can be avoided in matrix level transformation.[33,35]

It is concluded that to compensate for the insufficiency of the RKB basis sets for expanding φ^{S} in the magnetically perturbed states, it is necessary to include $\{\vec{\sigma}\cdot\vec{A}f_\nu^{\mathrm{L}}\}$ for the expansion of φ^{S}. The vector potential $\vec{A}$ is the sum of $\vec{A}_0$ and $\vec{A}_{\mathrm{M}}$, but the inclusion of $\{\vec{\sigma}\cdot\vec{A}_{\mathrm{M}}f_\nu^{\mathrm{L}}\}$ produces singular integrals as $\langle g_\mu|Vr_{\mathrm{M}}^{-3}(\vec{r}_{\mathrm{M}}\times\vec{p})_u|g_\nu\rangle$ $(u\in x,y,z)$ in the perturbed *SS* type Hamiltonian matrix elements. Although the restricted magnetic balance (RMB) condition employing $\{\vec{\sigma}\cdot(\vec{p}+\vec{A}_{\mathrm{M}})f_\nu^{\mathrm{L}}\}$ has been successfully applied to the spin–spin coupling calculations[36] in the density functional theory (DFT) formalism, the presence of $\{\vec{\sigma}\cdot\vec{A}_{\mathrm{M}}f_\nu^{\mathrm{L}}\}$ basis functions may generate a quasidivergence or numerical instability problem. On the other hand, the $\{\vec{\sigma}\cdot\vec{A}_0f_\nu^{\mathrm{L}}\}$ type basis functions are regular for expanding the first-order perturbed orbitals. The reported RMB calculations for the shieldings[37–39] do not contain $\{\vec{\sigma}\cdot\vec{A}_{\mathrm{M}}f_\nu^{\mathrm{L}}\}$ functions. Although the RMB formulation by Komorovský et al.[37] includes $\frac{1}{2c}\vec{\sigma}\cdot\vec{A}_{\mathrm{M}}f_\nu^{\mathrm{L}}$ functions in the starting formula for f_ν^{S} (eq 14 in Ref. 37), the effect of inclusion of $\vec{\sigma}\cdot\vec{A}_{\mathrm{M}}f_u^{\mathrm{L}}$ functions on the perturbation expansion is not described. An ab initio formulation for the external field-dependent RMB condition using $\{\vec{\sigma}\cdot(\vec{p}+\vec{A}_0)f_\nu^{\mathrm{L}}\}$ is stated in the next section and the full field-dependent RMB formulation using $\{\vec{\sigma}\cdot(\vec{p}+\vec{A}_0+\vec{A}_{\mathrm{M}})f_\nu^{\mathrm{L}}\}$ is given in Appendix. In our formulation, gauge-including atomic orbital (GIAO) basis sets are used with the RMB condition. The form of $\vec{p}+\vec{A}_0$ is necessary to keep gauge invariance, in addition to the use of GIAOs.

Because of the linear form of the magnetic perturbation terms in the Dirac Hamiltonian, there is no resemblance between the relativistic and nonrelativistic expressions for the diamagnetic shielding contribution. However, under the RMB condition, the magnetic shielding tensor of nucleus M (denoted as σ^{M}) can be divided into a paramagnetic part (denoted as σ^{M} (para)) and a diamagnetic part (denoted as σ^{M} (dia)), as for the nonrelativistic shielding tensors. The external field-dependent RMB theory is applied to the shielding calculation for hydrogen halides and halogen molecules in the third section.

Theory

The gauge factor ω_ν for a one-component spin independent basis function g_ν is introduced as follows:

$$\omega_\nu=\exp\left[-\frac{1}{2}i\vec{B}_0\times(\vec{R}_\nu-\vec{R}_0)\cdot\vec{r}\right] \tag{4}$$

Here, $\vec{R}_\nu$ is the center position of the Gaussian function g_ν and $\vec{R}_0$ is the position of the common gauge origin for an external magnetic flux density $\vec{B}_0$. The vector potential $\vec{A}_0$ produced by $\vec{B}_0$ is then given by

$$\vec{A}_0=\frac{1}{2}\vec{B}_0\times\vec{r}_0;\quad \vec{r}_0=\vec{r}-\vec{R}_0 \tag{5}$$

The following two-component basis $\{f_\nu^{\mathrm{L}}\}$ is employed for expanding the upper (large) spinor component φ^{L}:

$$f_\nu^{\mathrm{L}}=\omega_\nu g_\nu[m_\nu];\quad m_\nu=1\text{ or }2;\quad \nu=1,2,\ldots,2K \tag{6}$$

where $[1]=\left[\begin{smallmatrix}1\\0\end{smallmatrix}\right]$, $[2]=\left[\begin{smallmatrix}0\\1\end{smallmatrix}\right]$ and K is the number of different Gaussian functions g_ν. Namely, $g_{2\alpha-1}=g_{2\alpha}$ and $\omega_{2\alpha-1}=\omega_{2\alpha}$. m_ν is 1 or 2 for odd or even numbers of ν, respectively. The corresponding two-component basis $\{f_\nu^{\mathrm{S}}\}$ for expanding the lower (small) component spinor φ^{S} is then given by[37]

$$f_\nu^{\mathrm{S}}=\frac{1}{2c}\vec{\sigma}\cdot(\vec{p}+\vec{A}_0)f_\nu^{\mathrm{L}} \tag{7}$$

For the gauge factor ω_ν, we have the relation

$$(\vec{p}+\vec{A}_0)\omega_\nu=\omega_\nu(\vec{p}+\vec{A}_{0\nu}) \tag{8}$$

where

$$\vec{A}_{0\nu}=\frac{1}{2}\vec{B}_0\times\vec{r}_\nu;\quad \vec{r}_\nu=\vec{r}-\vec{R}_\nu \tag{9}$$

Therefore, f_ν^{S} has the form $\frac{1}{2c}\omega_\nu\vec{\sigma}\cdot(\vec{p}+\vec{A}_{0\nu})g_\nu[m_\nu]$. The matrix elements used in the following theory are independent of $\vec{R}_0$. The pth X (X = L or S) two-component spinor φ_p^X of the pth Dirac bispinor ψ_p $(\varphi_p^{\mathrm{L}},\varphi_p^{\mathrm{S}})$ is expanded in $\{f_\nu^X\}$ as

$$\varphi_p^X=\sum_\nu c_{\nu p}^X f_\nu^X,\quad X=\mathrm{L}\text{ or }\mathrm{S} \tag{10}$$

In the following, the symbols i, j, k, and l are introduced to denote the occupied orbitals; a, b, c, and d denote the unoccupied orbitals including negative energy orbitals; and p, q, r, and s denote the general orbitals including both the occupied and unoccupied orbitals. The symbols μ, ν, λ, and σ indicate the basis functions. ψ, φ, and f are omitted for simplicity. The treatment begins with the approach of Dyall

et al.[40] for molecular DHF calculations. The Dirac–Fock electronic energy E in an n-electron system is expressed as

$$E = \sum_{j=1}^{n} \langle j|\hat{h}_{\mathrm{D}}|j\rangle + \frac{1}{2}\sum_{j,k=1}^{n}[\langle jk|r_{12}^{-1}|jk\rangle - \langle jk|r_{12}^{-1}|kj\rangle] \quad (11)$$

The one-electron Dirac Hamiltonian $\hat{h}_{\mathrm{D}}$ is given in eq 3, the vector potential $\vec{A}$ is given by the sum of $\vec{A}_0$ and $\vec{A}_{\mathrm{M}}$, and $\vec{A}_0$ is given in eq 5. The vector potential $\vec{A}_{\mathrm{M}}$ due to a nuclear magnetic dipole moment $\vec{\mu}_{\mathrm{M}}$ is explicitly expressed as

$$\vec{A}_{\mathrm{M}} = c^{-2} r_{\mathrm{M}}^{-3} \vec{\mu}_{\mathrm{M}} \times \vec{r}_{\mathrm{M}}; \quad \vec{r}_{\mathrm{M}} = \vec{r} - \vec{R}_{\mathrm{M}} \quad (12)$$

where $\vec{R}_{\mathrm{M}}$ is the position of the point dipole moment $\vec{\mu}_{\mathrm{M}}$ of nucleus M, which is the target nucleus of the present nuclear magnetic shielding tensor calculation theory.

The total electronic energy E is expanded in terms of the perturbation parameters B_{0t} ($t \in x, y, z$) and $c^{-2}\mu_{\mathrm{M}u}$ ($u \in x, y, z$) as follows:

$$E = E^{(0)} + \sum_t B_{0t} E_t^{(1,0)} + c^{-2}\sum_u \mu_{\mathrm{M}u} E_u^{(0,1)} + c^{-2}\sum_{tu} B_{0t}\mu_{\mathrm{M}u} E_{tu}^{(1,1)} + \ldots \quad (13)$$

For the magnetic shielding tensor component of nucleus M σ_{tu}^{M}, we have $\sigma_{tu}^{\mathrm{M}} = (\frac{\partial^2 E}{\partial B_{0t}\partial \mu_{\mathrm{M}u}})_{\vec{B}_0=0,\vec{\mu}_{\mathrm{M}}=0}$, which is equal to $c^{-2}E_{tu}^{(1,1)}$ in eq 13. σ_{tu}^{M} is given with the Fock matrix F^{XY} and the density matrix ρ^{XY} as

$$\sigma_{tu}^{\mathrm{M}} = c^{-2}\sum_{XY}\mathrm{Tr}(F^{XY(0)}\rho_{tu}^{YX(1,1)} + F_t^{XY(1,0)}\rho_u^{YX(0,1)} + H_{tu}^{XY(1,1)}\rho^{YX(0)} + H_u^{XY(0,1)}\rho_t^{YX(1,0)}) \quad (14)$$

Here, the density matrix ρ^{XY} is defined by the expansion coefficients $\{c_{\nu j}^{X}\}$ in eq 10 as follows:

$$\rho_{\mu\nu}^{XY} = \sum_{j=1}^{n} c_{\mu j}^{X} c_{\nu j}^{Y*} \quad (15)$$

The perturbation expansion of ρ^{XY} in eq 15 in terms of B_{0t} and $c^{-2}\mu_{\mathrm{M}u}$ is obtained from the perturbation expansion of molecular orbital coefficients $\{c_{\nu j}^{X}\}$ in eq 10. The perturbed coefficients $c_{\nu p}^{X(\alpha,\beta)}$ ($\alpha, \beta \in 0, 1$) are then expanded in terms of the zeroth-order coefficients $\{c_{\nu q}^{X(0)}\}$ as follows:

$$c_{\nu p}^{X(\alpha,\beta)} = \sum_q d_{qp}^{(\alpha,\beta)} c_{\nu q}^{X(0)} \quad (\alpha, \beta \in 0, 1) \quad (16)$$

The relations among the $d_{qp,t}^{(1,0)}$, $d_{qp,u}^{(0,1)}$, and $d_{qp,tu}^{(1,1)}$ coefficients are obtained from the orthonormal condition of orbitals. Using the relations among $d_{qp,t}^{(1,0)}$, $d_{qp,u}^{(0,1)}$, and $d_{qp,tu}^{(1,1)}$, it can be shown that

$$\sum_{XY}\mathrm{Tr}(F^{XY(0)}\rho_{tu}^{YX(1,1)} + F_t^{XY(1,0)}\rho_u^{YX(0,1)}) = 0 \quad (17)$$

The shielding tensor component σ_{tu}^{M} can subsequently be given by

$$\sigma_{tu}^{\mathrm{M}} = c^{-2}\sum_{X\neq Y}\mathrm{Tr}(H_{tu}^{XY(1,1)}\rho^{YX(0)} + H_u^{XY(0,1)}\rho_t^{YX(1,0)}) \quad (18)$$

It is shown that the (0,1) and (1,1) perturbation terms come from the LS and SL parts only of the Hamiltonian. We have

$$H_{\mu\nu,u}^{XY(0,1)}(X \neq Y) = \langle \mu^{X(0)}|-cr_{\mathrm{M}}^{-3}(\vec{\sigma}\times\vec{r}_{\mathrm{M}})_u|\nu^{Y(0)}\rangle \quad (19a)$$

and

$$H_{\mu\nu,tu}^{XY(1,1)}(X \neq Y) = \langle \mu^{X(0)}|-cr_{\mathrm{M}}^{-3}(\vec{\sigma}\times\vec{r}_{\mathrm{M}})_u|\nu_{,t}^{Y(1,0)}\rangle + \langle \mu_{,t}^{X(1,0)}|-cr_{\mathrm{M}}^{-3}(\vec{\sigma}\times\vec{r}_{\mathrm{M}})_u|\nu^{Y(0)}\rangle \quad (19b)$$

Here,

$$|\nu_{,t}^{\mathrm{L}(1,0)}\rangle = -\frac{1}{2} i[(\vec{R}_\nu - \vec{R}_0)\times\vec{r}]_t g_\nu[m_\nu] \quad (20a)$$

and

$$|\nu_{,t}^{\mathrm{S}(1,0)}\rangle = -\frac{1}{4c}\{i[(\vec{R}_\nu - \vec{R}_0)\times\vec{r}]_t\vec{\sigma}\cdot\vec{p} + [\vec{\sigma}\times(\vec{r} - \vec{R}_\nu)]_t\}g_\nu[m_\nu] \quad (20b)$$

Equation 18 then leads to

$$\sigma_{tu}^{\mathrm{M}} = c^{-2}\sum_j\left[H_{jj,tu}^{(1,1)} - \sum_i S_{ij,t}^{(1,0)}H_{ji,u}^{(0,1)} + \sum_a(d_{aj,t}^{(1,0)}H_{aj,u}^{(0,1)*} + d_{aj,t}^{(1,0)*}H_{aj,u}^{(0,1)})\right] \quad (21)$$

where

$$H_{pq,u}^{(0,1)} = \sum_{X\neq Y}\sum_{\mu\nu} c_{\mu p}^{X(0)*} H_{\mu\nu,u}^{XY(0,1)} c_{\nu q}^{Y(0)} \quad (22a)$$

and

$$H_{pq,tu}^{(1,1)} = \sum_{X\neq Y}\sum_{\mu\nu} c_{\mu p}^{X(0)*} H_{\mu\nu,tu}^{XY(1,1)} c_{\nu q}^{Y(0)} \quad (22b)$$

The coefficients $d_{aj,t}{}^{(1,0)}$ can be derived from

$$d_{aj,t}^{(1,0)} = (\varepsilon_j^{(0)} - \varepsilon_a^{(0)})^{-1}(F_{aj,t}^{(1,0)} - \varepsilon_j^{(0)}S_{aj,t}^{(1,0)}) \quad (23)$$

Here,

$$F_{aj,t}^{(1,0)} = \sum_{XY}\sum_{\mu\nu} c_{\mu a}^{X(0)*} F_{\mu\nu,t}^{XY(1,0)} c_{\nu j}^{Y(0)} \quad (24)$$

and

$$S_{pq,t}^{(1,0)} = \sum_{X}\sum_{\mu\nu} c_{\mu p}^{X(0)*} S_{\mu\nu,t}^{XX(1,0)} c_{\nu q}^{X(0)} \quad (25)$$

In eq 24, $F^{XY(1,0)}$ is a function of two-electron integrals g and the density matrix ρ through the two-electron interaction energy $G^{XY(1,0)}$. Namely, we have

$$F^{XY(1,0)} = H^{XY(1,0)} + G^{XY(1,0)}(g^{(1,0)}, \rho^{(0)}) + G^{XY(1,0)}(g^{(0)}, \rho^{(1,0)}) \quad (26)$$

where $\rho^{(1,0)}$ also depends on $d^{(1,0)}$. Therefore, eq 23 has to be solved iteratively. $\rho^{(1,0)}$ is given by

$$\rho_{\mu\nu,t}^{XY(1,0)} = -\sum_{ij}^{\mathrm{occ}} S_{ij,t}^{(1,0)} c_{\mu i}^{X(0)} c_{\nu j}^{Y(0)*} + \sum_{a}^{\mathrm{unocc}}\sum_{j}^{\mathrm{occ}}(d_{aj,t}^{(1,0)} c_{\mu a}^{X(0)} c_{\nu j}^{Y(0)*} + d_{aj,t}^{(1,0)*} c_{\mu j}^{X(0)} c_{\nu a}^{Y(0)*}) \quad (27)$$

Equation 23 can be solved without time consuming four-index transformations. Equation 21 is the same at the operator level as the nonrelativistic (NR) shielding formula using GIAOs.[41] The magnetic shielding can be divided into a paramagnetic part and a diamagnetic part, as for nonrelativistic shieldings. The paramagnetic part σ_{tu}^{M}(para) is given by

$$\sigma_{tu}^{\mathrm{M}}(\mathrm{para}) = c^{-2}\sum_{j}^{\mathrm{occ}}\Bigg[-\sum_{i}^{\mathrm{occ}} S_{ij,t}^{(1,0)} H_{ji,u}^{(0,1)} + \sum_{a}^{\mathrm{unocc}}\left(d_{aj,t}^{(1,0)} H_{aj,u}^{(0,1)*} + d_{aj,t}^{(1,0)*} H_{aj,u}^{(0,1)}\right)\Bigg] \quad (28)$$

and the diamagnetic part $\sigma_{tu}^{\mathrm{M}}(\mathrm{dia})$ is given by

$$\sigma_{tu}^{\mathrm{M}}(\mathrm{dia}) = c^{-2}\sum_{j}^{\mathrm{occ}} H_{jj,tu}^{(1,1)} \quad (29)$$

In eq 28, a includes negative energy orbitals in addition to positive unoccupied one-electron states.

Results and Discussion

To circumvent the production of singular terms, the external field-dependent RMB condition is used for the calculation. The most time consuming part of the process outlined above is the computation of $G^{\mathrm{SS}(1,0)}(g^{(1,0)}, \rho^{(0)})$ in eq 26. We employed an approximation where all two-center SS type differential overlaps included in two-electron integrals of (SS|SS) and (LL|SS) types in the zeroth and first-order calculations are neglected. Consequently, we have only two-center (SS|SS) integrals and three-center (LL|SS) integrals. This approximation is justified by the fact that the small-component density has a one-center character. Next, small perturbed first-order integrals $(\mathrm{SS}|\mathrm{SS})^{(1,0)}$ are discarded before computation by an approximate estimation of their magnitudes using overlap integrals of $\langle \mathrm{S}|\mathrm{S}\rangle^{(0)}$ and $\langle \mathrm{S}|\mathrm{S}\rangle^{(1,0)}$. As a result, the computational time is much reduced but there remain computational difficulties for a system of many basis functions. The computational time ratio for RMB-GIAO, NESC-GIAO, and NR-GIAO calculations for HI was 130:3:1. The perturbed $(\mathrm{SS}|\mathrm{SS})^{(1,0)}$ type integrals need much computational time. The computational time for an RMB-GIAO calculation increases rapidly as the number of basis functions used increases.

There are three important questions that we have to answer in the present work. First, does our RMB-GIAO method produce the σ(dia) parts of shielding similar to those of nonrelativistic SCF-GIAO calculations? Second, in our RMB theory, the negative energy orbital contributions enter into the σ(para) part alone in eq 28, so how large are the contributions of the negative energy states to σ(para)? Third, can the RMB-GIAO theory reproduce other reference values of DHF with point charge nuclei? In order to answer these questions, we compute the nuclear magnetic shielding of the hydrogen halide molecules HX (X = F, Cl, Br, and I) and the halogen molecules X_2 (X = F, Cl, Br, and I).

Hydrogen Halides. The present results for the hydrogen halide molecules HX (X = F, Cl, Br, and I) calculated by our RMB-GIAO method are shown in the fourth column of Table 1. The basis sets $\{g_\nu\}$ used are (F: 17s14p5d2f/H: 10s6p) for HF, (Cl: 19s16p7d2f/H: 10s6p) for HCl, (Br: 22s22p12d4f/H: 10s6p) for HBr, and (I: 25s25p14d6f/H: 12s10p) for HI. We used fully uncontracted Cartesian Gaussian functions as the basis sets and a point nuclear charge model. The Gaussian exponents are described in Ref. 20. All the calculations were carried out in experimental geometries.[42] For comparison, the present nonrelativistic SCF-GIAO and NESC-GIAO calculations results obtained with the same basis sets and molecular geometries as the RMB-GIAO calculation are shown in the fifth and sixth columns of Table 1, respectively. Other DHF results taken from Refs. 26, 37, and 39 are presented as reference values in the last column of Table 1. The numerical difference in the diamagnetic parts of shielding between the RMB-GIAO and nonrelativistic SCF-GIAO results may be ascribed to the relativistic effects. It is found that the diamagnetic parts of σ^{iso} and $\Delta\sigma$ for RMB-GIAO can reproduce the nonrelativistic diamagnetic shieldings. The NESC-GIAO results show the $\Delta\sigma$(para) being too small for I in HI. This problem was discussed in the first section.

The contributions of negative energy states to the paramagnetic shielding calculated from eq 28 are shown in parentheses in the fourth column of Table 1. The negative energy contribution is small for H, F, and Cl, but it is significant for Br and I. Especially, the contribution to σ^{iso} of I is considerable. The magnitude of the negative state contributions to proton shieldings is small and irregular. We can however see a regularity except for HF. In spite of the small basis sets, the RMB-GIAO calculation fairly well reproduces the DHF results of Ref. 26, though the anisotropies for Br and I are slightly different from those of Ref. 26. A part of this discrepancy may be due to the basis set insufficiency for Br and I in the RMB-GIAO calculation. The RMB-DFT calculation results taken from Refs. 37 and 39 show the rather small σ^{iso} values. Overall, the RMB-GIAO method exhibits fast basis set convergence. It was found that the ratio $\sigma(\mathrm{para})/\sigma(\mathrm{dia})$ depends on the basis set size but the sum, $\sigma(\mathrm{total}) = \sigma(\mathrm{para}) + \sigma(\mathrm{dia})$, converges smoothly. The magnitude of the negative state contributions in σ(para) showed a large basis set size dependence. The Ref. 39 yields a very small negative energy contribution for $\Delta\sigma$(I) in HI. This may be due to the use of a finite nuclear model in Ref. 39. The negative energy contribution arises from rotations between the positive- and negative-energy one-particle states due to the vector potential. The calculation of negative energy contribution needs analytical evaluation of shielding. The numerical calculation of shielding[43] yields the sum of paramagnetic and diamagnetic parts.

The results of the RMB-GIAO calculation are numerically stable and have no sign of quasidivergence. We removed the $\vec{\sigma}\cdot\vec{A}_{\mathrm{M}}$ term from the small component basis to avoid a quasidivergency similar to that creating difficulty in the NESC method. The removal of the $\vec{\sigma}\cdot\vec{A}_{\mathrm{M}}$ term corresponds to a change from the FFUT (full field-dependent unitary transformation) to the EFUT (external field-dependent unitary transformation) in the four-component unitary transformation scheme by Xiao et al.[33] The FFUT calculation showed numerical instability, while the EFUT was stable.[33]

There has been considerable effort to restore the diamagnetic part of shielding in four-component schemes, for example, the Sternheim diamagnetic approximation,[44] the Gordon decomposition,[45,46] the minimal coupling,[32] the ODA (orbital decomposition approach),[47] and the EFUT.[33] It is found that the external field-dependent RMB-GIAO method is an effective approach for restoring the diamagnetic part of shielding in the four-component scheme.[39]

Halogen Molecules. The present results for the halogen molecules X_2 (X = F, Cl, Br, and I) calculated by the RMB-GIAO method are shown in the fourth column of Table 2. The

Table 1. Calculated Nuclear Magnetic Shielding Tensor Components (in ppm) in HX (X = F, Cl, Br, and I) Systems[a)]

Molecule	Nucleus	Property[b)]	RMB-GIAO[c)]	NR-GIAO[d)]	NESC-GIAO[e)]	Other results
HF	F	σ^{iso}(para)	−48.2 (−1.7)	−52.5	−46.4	
		σ^{iso}(dia)	466.4	466.1	465.7	
		σ^{iso}(total)	418.1	413.7	419.3	418.4[f)], 411.4[g)], 415.4[h)]
		$\Delta\sigma$(para)	78.0 (0.1)	78.7	76.3	
		$\Delta\sigma$(dia)	23.3	23.4	23.3	
		$\Delta\sigma$(total)	101.3	102.0	99.6	100.7[f)]
	H	σ^{iso}(para)	1.78 (0.36)	1.43	1.61	
		σ^{iso}(dia)	26.77	26.98	26.94	
		σ^{iso}(total)	28.55	28.41	28.56	28.03[f)]
		$\Delta\sigma$(para)	−2.67 (−0.54)	−2.15	−2.43	
		$\Delta\sigma$(dia)	25.91	25.63	25.59	
		$\Delta\sigma$(total)	23.25	23.48	23.16	23.80[f)]
HCl	Cl	σ^{iso}(para)	−165.6 (−11.1)	−195.4	−152.9	
		σ^{iso}(dia)	1147.3	1144.9	1141.7	
		σ^{iso}(total)	981.8	949.4	988.8	984.5[f)], 936.3[g)], 975.4[h)]
		$\Delta\sigma$(para)	288.0 (1.0)	293.1	276.0	
		$\Delta\sigma$(dia)	5.1	6.0	6.0	
		$\Delta\sigma$(total)	293.1	299.1	282.0	288.2[f)]
	H	σ^{iso}(para)	1.46 (0.08)	0.49	1.59	
		σ^{iso}(dia)	30.08	30.14	30.01	
		σ^{iso}(total)	31.55	30.63	31.61	31.18[f)]
		$\Delta\sigma$(para)	−2.21 (−0.13)	−0.73	−2.40	
		$\Delta\sigma$(dia)	23.12	23.10	23.04	
		$\Delta\sigma$(total)	20.91	22.37	20.64	21.32[f)]
HBr	Br	σ^{iso}(para)	−175.7 (−75.8)	−473.3	−76.9	
		σ^{iso}(dia)	3142.3	3117.3	3090.4	
		σ^{iso}(total)	2966.6	2644.0	3013.5	2959.4[f)], 2887.9[g)], 2881.8[h)]
		$\Delta\sigma$(para)	647.6 (7.0)	710.0	540.0	
		$\Delta\sigma$(dia)	6.8	13.7	13.4	
		$\Delta\sigma$(total)	654.4	723.7	553.4	664.0[f)]
	H	σ^{iso}(para)	4.89 (0.29)	−0.65	5.13	
		σ^{iso}(dia)	31.50	31.83	31.27	
		σ^{iso}(total)	36.39	31.18	36.41	35.86[f)]
		$\Delta\sigma$(para)	−7.83 (−0.44)	0.97	−8.34	
		$\Delta\sigma$(dia)	26.40	26.31	26.00	
		$\Delta\sigma$(total)	18.58	27.28	17.66	18.11[f)]
HI	I	σ^{iso}(para)	299.1 (−199.5)	−964.5	154.9	
		σ^{iso}(dia)	5607.3	5501.9	5408.7	
		σ^{iso}(total)	5906.3	4537.4	5563.6	5913.7[f)], 5705.1[g)], 5691.0 (−165.4)[h)]
		$\Delta\sigma$(para)	1071.4 (33.9)	1446.7	687.7	
		$\Delta\sigma$(dia)	−29.2	4.4	4.3	
		$\Delta\sigma$(total)	1042.2	1451.2	691.9	1025.2[f)], 1316.2 (−0.1)[h)]
	H	σ^{iso}(para)	17.27 (0.98)	−0.56	17.62	
		σ^{iso}(dia)	30.78	31.99	30.69	
		σ^{iso}(total)	48.05	31.43	48.31	47.05[f)]
		$\Delta\sigma$(para)	−31.13 (−1.49)	0.84	−32.65	
		$\Delta\sigma$(dia)	31.11	30.21	29.56	
		$\Delta\sigma$(total)	−0.02	31.05	−3.09	0.39[f)]

a) The contributions of negative energy states to the paramagnetic part are given in parentheses. b) $\sigma^{iso} = \frac{1}{3}(2\sigma_{\perp} + \sigma_{\parallel})$ and $\Delta\sigma = \sigma_{\parallel} - \sigma_{\perp}$. c) Present results calculated by using the external field-dependent restricted magnetic balance theory with GIAOs. d) Present results calculated by using the nonrelativistic SCF-GIAO theory with the same basis sets and molecular geometries as the RMB-GIAO calculation. e) Present results calculated by using NESC-GIAO theory with the same basis sets and molecular geometries as the RMB-GIAO calculation. f) Four-component linear response theory results taken from Ref. 26. g) RMB-DFT results taken from Ref. 37. h) RMB-DFT results taken from Ref. 39. The finite Gaussian nuclear model is employed for the nuclear charge distribution. The figure in parentheses is the contribution of negative energy states.

Table 2. Calculated Nuclear Magnetic Shielding Tensor Components (in ppm) in X_2 (X = F, Cl, Br, and I) Systems[a)]

Molecule	Nucleus	Property[b)]	RMB-GIAO[c)]	NR-GIAO[d)]	NESC-GIAO[e)]	Other results
F_2	F	σ^{iso}(para)	−648.4 (−1.6)	−653.5	−649.8	
		σ^{iso}(dia)	463.9	463.6	463.2	
		σ^{iso}(total)	−184.6	−189.9	−186.6	−140.7[f)], −182.1[g)]
		$\Delta\sigma$(para)	974.5 (0.0)	980.3	975.7	
		$\Delta\sigma$(dia)	37.3	37.4	37.3	
		$\Delta\sigma$(total)	1011.8	1017.7	1013.0	
Cl_2	Cl	σ^{iso}(para)	−266.8 (−10.1)	−297.4	−260.9	
		σ^{iso}(dia)	1145.9	1144.0	1140.8	
		σ^{iso}(total)	879.1	846.6	879.9	
		$\Delta\sigma$(para)	436.7 (0.1)	446.1	433.3	
		$\Delta\sigma$(dia)	20.1	20.2	20.2	
		$\Delta\sigma$(total)	456.8	466.4	453.5	
Br_2	Br	σ^{iso}(para)	−719.4 (−65.4)	−1003.9	−727.8	
		σ^{iso}(dia)	3140.8	3119.7	3092.8	
		σ^{iso}(total)	2421.4	2115.8	2364.9	
		$\Delta\sigma$(para)	1350.8 (2.7)	1505.9	1375.6	
		$\Delta\sigma$(dia)	19.9	21.0	20.5	
		$\Delta\sigma$(total)	1370.7	1526.9	1378.1	
I_2	I	σ^{iso}(para)	118.3 (−179.6)	−1148.0	−105.1	
		σ^{iso}(dia)	5586.3	5501.9	5408.5	
		σ^{iso}(total)	5704.7	4353.8	5303.4	4754.8 (0.0)[h)]
		$\Delta\sigma$(para)	771.6 (72.2)	1722.0	1025.1	
		$\Delta\sigma$(dia)	15.0	17.5	16.6	
		$\Delta\sigma$(total)	786.5	1739.5	1041.7	893.7 (−0.2)[h)]

a) The contributions of negative energy states to the paramagnetic part are given in parentheses. b) $\sigma^{iso} = \frac{1}{3}(2\sigma_\perp + \sigma_\parallel)$ and $\Delta\sigma = \sigma_\parallel - \sigma_\perp$. c) Present results calculated by using the external field-dependent restricted magnetic balance theory with GIAOs. d) Present results calculated by using the nonrelativistic SCF-GIAO theory with the same basis sets and molecular geometries as the RMB-GIAO calculation. e) Present results calculated by using NESC-GIAO theory with the same basis sets and molecular geometries as the RMB-GIAO calculation. f) Nonrelativistic MP2/cc-pVTZ results taken from Ref. 48. g) Nonrelativistic CCSD(T)/cc-pVQZ results taken from Ref. 48. h) RMB-DFT results taken from Ref. 39. The finite Gaussian nuclear model is employed for the nuclear charge distribution. The figure in parentheses is the contribution of negative energy states.

basis sets used for halogen atoms in the HX systems are too expensive for the X_2 systems. The basis sets used for the X_2 systems are (15s12p5d) for F, (17s14p6d) for Cl, (19s16p7d3f) for Br, and (22s19p8d4f) for I.[20] All the calculations were performed in experimental geometries[42] with a point nuclear charge model. The results of the present nonrelativistic SCF-GIAO and NESC-GIAO calculations obtained with the same basis sets and molecular geometries as the RMB-GIAO calculation are shown in the fifth and sixth columns of Table 2, respectively. Other nonrelativistic correlated calculation results for F_2[48] and RMB-DFT results for I_2[39] are presented as reference values in the last column of Table 2. To our knowledge, reference data of shieldings for Cl_2 and Br_2 are not available. The contributions of negative energy states to the paramagnetic shielding are shown in parentheses in the fourth column of Table 2.

Table 2 shows that the electron-correlation contributions are much larger than the relativistic effects for the F_2 shielding. On the other hand, the I_2 shielding has very large relativistic effects in both σ^{iso} and $\Delta\sigma$. The F_2 shielding presents a large $\Delta\sigma$(para) value. The diamagnetic contribution in the RMB-GIAO is very similar to that in the nonrelativistic SCF-GIAO except σ^{iso}(I) in I_2. The negative energy contribution is small for F and Cl, significant for Br, and considerable for I. The RMB-GIAO and NESC-GIAO calculation results agree for F_2 and Cl_2, but they show a considerable difference for I_2. The RMB-DFT results[39] yield a much smaller σ^{iso} value than the RMB-GIAO (DHF) results. Furthermore, the contribution of negative energy states for I_2 is almost zero in the RMB-DFT calculation,[39] which also differs greatly from the RMB-GIAO (DHF) results. The origin of these large differences is uncertain, but a main part of these discrepancies may be due to the use of the finite nuclear model in Ref. 39.

Conclusion

We have formulated the relativistic four-component calculation of shielding using the external field-dependent and full field-dependent RMB conditions with GIAOs. The magnetic perturbation operators are linear in the vector potentials of $\vec{A}_0$ and $\vec{A}_M$ in the Dirac Hamiltonian, while they are quadratic in the Schrödinger Hamiltonian. Therefore, there is no resemblance between the relativistic and nonrelativistic expressions for the diamagnetic shielding. The four-component calculation is made difficult because of the large and strongly basis-

set-dependent contribution of the negative energy states to the diamagnetic shielding. The use of the RMB condition eliminates the negative energy orbital contribution from the diamagnetic shielding and restores the diamagnetic shielding term similar to the nonrelativistic diamagnetic part. The RMB-GIAO magnetic shielding formula is the same at the operator level as the nonrelativistic shielding formula using GIAOs. The external field-dependent RMB-GIAO method was applied to the calculation of magnetic shielding in hydrogen halide molecules and halogen molecules, and compared with the nonrelativistic SCF-GIAO and NESC-GIAO results, and other 4-component reference values. The diamagnetic parts of shielding in RMB-GIAO were close to those in nonrelativistic SCF-GIAO. The RMB-GIAO computation showed a fast basis set convergence. The external field-dependent RMB-GIAO method was found to be effective and useful.

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Appendix

Full Field-Dependent RMB Theory. The corresponding two-component basis functions for the small component spinor φ^{S} is then given by

$$f_{\nu}^{\mathrm{S}} = \frac{1}{2c}\vec{\sigma}\cdot(\vec{p}+\vec{A}_0+\vec{A}_{\mathrm{M}})f_{\nu}^{\mathrm{L}} \tag{A-1}$$

In this case, eq 17 is changed to

$$\begin{aligned}
&\sum_{XY}\mathrm{Tr}(F^{XY(0)}\rho_{tu}^{YX(1,1)} + F_t^{XY(1,0)}\rho_u^{YX(0,1)}) \\
&\quad = -\sum_j\Bigg[\varepsilon_{j,t}^{(1,0)}S_{jj,u}^{(0,1)} \\
&\qquad + \varepsilon_j^{(0)}\Bigg\{S_{jj,tu}^{(1,1)} + \sum_q(d_{qj,t}^{(1,0)}S_{qj,u}^{(0,1)*} + d_{qj,t}^{(1,0)*}S_{qj,u}^{(0,1)})\Bigg\}\Bigg]
\end{aligned} \tag{A-2}$$

In the external field-dependent RMB theory, $S^{(0,1)} = S^{(1,1)} = 0$, and eq 17 is satisfied. σ_{tu}^{M} is given as follows.

$$\begin{aligned}
\sigma_{tu}^{\mathrm{M}} &= c^{-2}\sum_{XY}\mathrm{Tr}(F^{XY(0)}\rho_{tu}^{YX(1,1)} + F_t^{XY(1,0)}\rho_u^{YX(0,1)} \\
&\quad + H_{tu}^{XY(1,1)}\rho^{YX(0)} + H_u^{XY(0,1)}\rho_t^{YX(1,0)} \\
&\quad + \frac{1}{2}g_{tu}^{XY,X'Y'(1,1)}\rho^{Y'X'(0)}\rho^{YX(0)} \\
&\quad + g_u^{XY,X'Y'(0,1)}\rho^{Y'X'(0)}\rho_t^{YX(1,0)}) \\
&= -c^{-2}\sum_j\Bigg[\varepsilon_{j,t}^{(1,0)}S_{jj,u}^{(0,1)} + \varepsilon_j^{(0)}\Bigg\{S_{jj,tu}^{(1,1)} - \sum_i S_{ij,t}^{(1,0)}S_{ji,u}^{(0,1)} \\
&\quad + \sum_a(d_{aj,t}^{(1,0)}S_{aj,u}^{(0,1)*} + d_{aj,t}^{(1,0)*}S_{aj,u}^{(0,1)})\Bigg\}\Bigg] \\
&\quad + c^{-2}\sum_{XYX'Y'}\Bigg[\frac{1}{2}g_{tu}^{XY,X'Y'(1,1)}\rho^{Y'X'(0)}\rho^{YX(0)} \\
&\quad + g_u^{XY,X'Y'(0,1)}\rho^{Y'X'(0)}\rho_t^{YX(1,0)}\Bigg] \\
&\quad + c^{-2}\sum_j\Bigg[H_{jj,tu}^{(1,1)} - \sum_i S_{ij,t}^{(1,0)}H_{ji,u}^{(0,1)} \\
&\quad + \sum_a(d_{aj,t}^{(1,0)}H_{aj,u}^{(0,1)*} + d_{aj,t}^{(1,0)*}H_{aj,u}^{(0,1)})\Bigg]
\end{aligned} \tag{A-3}$$

$\varepsilon_{j,t}^{(1,0)}$ in eq A-3 can be replaced by $(F_{jj,t}^{(1,0)} - \varepsilon_j^{(0)}S_{jj,t}^{(1,0)})$. The reported RMB theory for the shielding[37–39] uses the Dalgarno's interchange theorem[49] and does not consider the (0,1) and (1,1) order perturbation contributions coming from the $\{\frac{1}{2c}\vec{\sigma}\cdot\vec{A}_{\mathrm{M}}f_{\nu}^{\mathrm{L}}\}$ functions. Equation A-3 is the first exact formula for the shielding in the full field-dependent RMB condition.

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