Decoupling of the Dirac equation correct to the third order for the magnetic perturbation

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(Received 7 May 2007; accepted 20 June 2007; published online 31 August 2007)

A two-component relativistic theory accurately decoupling the positive and negative states of the Dirac Hamiltonian that includes magnetic perturbations is derived. The derived theory eliminates all of the odd terms originating from the nuclear attraction potential V and the first-order odd terms originating from the magnetic vector potential $\mathbf{A}$, which connect the positive states to the negative states. The electronic energy obtained by the decoupling is correct to the third order with respect to $\mathbf{A}$ due to the $(2n+1)$ rule. The decoupling is exact for the magnetic shielding calculation. However, the calculation of the diamagnetic property requires both the positive and negative states of the unperturbed $(\mathbf{A}=0)$ Hamiltonian. The derived theory is applied to the relativistic calculation of nuclear magnetic shielding tensors of HX $(\mathrm{X}=\mathrm{F},\mathrm{Cl},\mathrm{Br},\mathrm{I})$ systems at the Hartree-Fock level. The results indicate that such a substantially exact decoupling calculation well reproduces the four-component Dirac-Hartree-Fock results. © *2007 American Institute of Physics*.
[DOI: 10.1063/1.2759199]

I. INTRODUCTION

Due to recent developments in the relativistic quantum theory and its applications, the accuracy of the quasirelativistic theory, i.e., the two-component Hamiltonian method for calculating the relativistic effects on molecular properties, has greatly increased.[1–13] There are two approaches to incorporate relativistic effects on the molecular properties in the two-component framework. One approach is a treatment using nonrelativistic wave functions and incorporating relativistic effects as passive or active perturbations, which are obtained from the Breit-Pauli Hamiltonian.[1–7] The other approach is a variational treatment that involves calculating the stationary states of a quasirelativistic Hamiltonian.[8–13] The latter approach is separated into a unitary decoupling transformation method based on the Douglas-Kroll-Hess (DKH) transformation[8–10] and a method of eliminating the small component (ESC),[11–15] which sometimes uses the regular approximation.[16–21] Recently, Ilias and Saue[22] reported that the above two methods of DKH and ESC are mathematically equivalent at the limit of exact quasirelativistic (XQR) theory. Kutzelnigg and Liu[23] proposed five different iteration schemes by which to calculate the exact coupling matrix between the large and small components, which lead to the XQR theory. Liu and Peng[24] extended the theory of Kutzelnigg and Liu to the one-particle Kohn-Sham scheme of the density functional theory.

There are only two basic types of properties that might occur within a four-component Hamiltonian. Electric or electric-field-like properties are generally described by an even, i.e., diagonal block, perturbation Hamiltonian $H_{\mathcal{E}}$. In contrast to the electric properties, the magnetic or magnetic-field-like properties are described by an odd, i.e., off-diagonal block, perturbation Hamiltonian $H_{\mathcal{O}}$. Recently, Wolf and Reiher[25,26] presented a theory by which to evaluate the expectation value $\langle H_M \rangle$ for a molecular property M described with an even or odd perturbation Hamiltonian ($H_{\mathcal{E}}$ or $H_{\mathcal{O}}$) using the perturbation-independent DKH transformation, which is correct up to an arbitrary order with respect to the instantaneous electron-nuclei Coulomb interaction energy V. However, the diamagnetic part of a nuclear magnetic shielding tensor cannot be calculated in the two-component framework as the expectation value of the magnetic perturbation Hamiltonian obtained by the perturbation-independent unitary transformation. In order to evaluate the diamagnetic part of a magnetic shielding tensor in the two-component scheme, the four-component interaction Hamiltonian has to be magnetically decoupled and a quadratic operator with respect to the vector potential $\mathbf{A}$ has to be obtained. In the four-component scheme, the diamagnetic contributions are obtained by a summation over negative-energy states.[27,28] Kutzelnigg[29] proposed a unitary transformation of the Dirac Hamiltonian that removes the off-diagonal operator $c\boldsymbol{\alpha}\cdot\mathbf{A}$ but keeps $c\boldsymbol{\alpha}\cdot\mathbf{p}$ in the off-diagonal block. The transformed Hamiltonian appears to simplify the evaluation of magnetic properties because the diamagnetic contributions are obtained as the expectation values of the unperturbed $(\mathbf{A}=0)$ wave function.

In the present study, we extend the theory by Wolf and Reiher[25] to include an application to diamagnetic shielding calculations. The authors have already extended the infinite-order two-component (IOTC) theory reported by Barysz and Sadlej[30] to the calculation of a nuclear magnetic shielding tensor.[10] In our previous study, the nuclear attraction potential V is completely decoupled, but the decoupling of the vector potential $\mathbf{A}$ is incomplete. An odd term of the first order with respect to $\mathbf{A}$ remains in the unitary transformed Hamiltonian and contributes to the electronic energy of the second order with respect to $\mathbf{A}$. In the present study, we derive a theory to decouple all of the scalar potential terms of V and the first-order vector potential term of $\mathbf{A}$. The decou-

pling will yield a substantially exact magnetic energy that is correct to the third order with respect to **A** due to the $(2n+1)$ rule. In order to perform an exact decoupling of the Dirac equation, including magnetic perturbations, we are sometimes tempted to remove the $c\boldsymbol{\alpha}\cdot\mathbf{p}$ and $c\boldsymbol{\alpha}\cdot\mathbf{A}$ terms at the same time.[31,32] However, doing so would lead to a very complicated analytical differentiation of the electronic energy of the system, E, with respect to magnetic perturbations. Therefore, in the present theory, we decouple the $c\boldsymbol{\alpha}\cdot\mathbf{p}$, V, and $c\boldsymbol{\alpha}\cdot\mathbf{A}$ terms successively, and the magnetic shielding tensor components are easily computed via an analytical differentiation of the electronic energy of the system.

II. THEORY

In our previous IOTC scheme, the transformed Hamiltonian was obtained by (1) an initial free-particle Foldy-Wouthuysen (fpFW) transformation followed by (2) the elimination of the leading odd term linear in the vector potential **A** by an exponential-type unitary operator,[33] and finally (3) infinite-order decoupling with respect to the scalar potential V. However, after the second step, the transformed Hamiltonian includes an odd term bilinear in **A** and V, which is neglected in the final decoupling. The neglected term will lead to an error of electronic energy of second order with respect to **A**. Computed diamagnetic properties are incorrect. In the present theory, steps (2) and (3) are reversed. The first-order odd terms with respect to **A** are accurately eliminated. The leading odd term, which is neglected, is of the second order with respect to **A**. Neglecting this term will give rise to an error of $\mathbf{A}^4$, which does not contribute to the magnetic shielding tensor. The electronic energy obtained by the decoupling is correct to the third order in the magnetic perturbation. The decoupling presented below is *exact* for calculating nuclear magnetic shielding tensors.

A. Exact decoupling of the nuclear Coulomb potential part

We consider the Dirac equation for a one-electron system under a nuclear attraction potential V and a vector potential **A**.

$$H_D\psi_i=\varepsilon_i\psi_i;\quad i=1,2,3,\cdots, \tag{1}$$

$$H_D=H_D^{(0)}+H_D^{(1)}, \tag{2}$$

$$H_D^{(0)}=c\boldsymbol{\alpha}\cdot\mathbf{p}+(\beta-1)c^2+V=\begin{bmatrix} V & c\boldsymbol{\sigma}\cdot\mathbf{p} \\ c\boldsymbol{\sigma}\cdot\mathbf{p} & V-2c^2 \end{bmatrix}, \tag{3}$$

$$H_D^{(1)}=c\boldsymbol{\alpha}\cdot\mathbf{A}=\begin{bmatrix} 0 & c\boldsymbol{\sigma}\cdot\mathbf{A} \\ c\boldsymbol{\sigma}\cdot\mathbf{A} & 0 \end{bmatrix}. \tag{4}$$

Throughout the present paper, we use atomic units, i.e., $\hbar=1$, $e=1$, $m_e=1$, $4\pi\varepsilon_0=1$, and $c=137.0359895$. The first step is an application of the fpFW transformation to the Dirac equation. The fpFW unitary operator U_0 is given as

$$U_0=\left(1+\frac{\boldsymbol{\alpha}\cdot\mathbf{p}}{e_p+c}\beta\right)R, \tag{5}$$

$$R=\left[\frac{e_p+c}{2e_p}\right]^{1/2}, \tag{6}$$

and

$$e_p=(c^2+p^2)^{1/2}. \tag{7}$$

The fpFW transformation of the Dirac Hamiltonian is given as

$$U_0^\dagger H_D^{(0)}U_0=\begin{bmatrix} h_{LL}^V & 0 \\ 0 & h_{SS}^V \end{bmatrix}+\begin{bmatrix} 0 & h_{LS}^V \\ h_{SL}^V & 0 \end{bmatrix}$$
$$=-c^2+ce_p\beta+V_{\mathcal{E}}+V_{\mathcal{O}}, \tag{8}$$

$$V_{\mathcal{E}}=RVR+Q\boldsymbol{\alpha}\cdot\mathbf{p}V\boldsymbol{\alpha}\cdot\mathbf{p}Q, \tag{9}$$

$$V_{\mathcal{O}}=\beta(Q\boldsymbol{\alpha}\cdot\mathbf{p}VR-RV\boldsymbol{\alpha}\cdot\mathbf{p}Q), \tag{10}$$

$$U_0^\dagger H_D^{(1)}U_0=\begin{bmatrix} h_{LL}^A & 0 \\ 0 & h_{SS}^A \end{bmatrix}+\begin{bmatrix} 0 & h_{LS}^A \\ h_{SL}^A & 0 \end{bmatrix}=A_{\mathcal{E}}+A_{\mathcal{O}}, \tag{11}$$

$$A_{\mathcal{E}}=c\beta(R\boldsymbol{\alpha}\cdot\mathbf{A}\boldsymbol{\alpha}\cdot\mathbf{p}Q+Q\boldsymbol{\alpha}\cdot\mathbf{p}\boldsymbol{\alpha}\cdot\mathbf{A}R), \tag{12}$$

$$A_{\mathcal{O}}=c(R\boldsymbol{\alpha}\cdot\mathbf{A}R-Q\boldsymbol{\alpha}\cdot\mathbf{p}\boldsymbol{\alpha}\cdot\mathbf{A}\boldsymbol{\alpha}\cdot\mathbf{p}Q), \tag{13}$$

where

$$Q=\frac{R}{e_p+c}=[2e_p(e_p+c)]^{-1/2}. \tag{14}$$

Here, $h_{SL}^V=h_{LS}^{V\dagger}$ and $h_{SL}^A=h_{LS}^{A\dagger}$.

The second step is the complete decoupling of $U_0^\dagger H_D^{(0)}U_0$ using the IOTC theory. We write the unitary operator of IOTC as U_{BS}. U_{BS} is given as[30]

$$U_{BS}=\begin{bmatrix} \dfrac{1}{\sqrt{1+X^\dagger X}} & -X^\dagger\dfrac{1}{\sqrt{1+XX^\dagger}} \\ X\dfrac{1}{\sqrt{1+X^\dagger X}} & \dfrac{1}{\sqrt{1+XX^\dagger}} \end{bmatrix}, \tag{15}$$

where the two-component operator X must satisfy the condition

$$X=(h_{SS}^V)^{-1}[-h_{SL}^V+Xh_{LL}^V+Xh_{LS}^VX]. \tag{16}$$

The two-component operators h_{LL}^V, h_{LS}^V, h_{SL}^V, and h_{SS}^V are defined in Eq. (8). The results of the transformation by U_{BS} are given as[34]

$$\tilde{H}_D^{(0)}=U_{BS}^\dagger U_0^\dagger H_D^{(0)}U_0U_{BS}=\begin{bmatrix} h_{++}^V & 0 \\ 0 & h_{--}^V \end{bmatrix}, \tag{17}$$

$$h_{++}^V=\sqrt{1+X^\dagger X}[h_{LL}^V+h_{LS}^VX]\frac{1}{\sqrt{1+X^\dagger X}}, \tag{18}$$

$$h_{--}^V=\frac{1}{\sqrt{1+XX^\dagger}}[h_{SS}^V-Xh_{LS}^V]\sqrt{1+XX^\dagger}, \tag{19}$$

$$\tilde{H}_D^{(1)} = U_{BS}^{\dagger} U_0^{\dagger} H_D^{(1)} U_0 U_{BS} = \begin{bmatrix} h_{++}^A & 0 \\ 0 & h_{--}^A \end{bmatrix} + \begin{bmatrix} 0 & h_{+-}^A \\ h_{-+}^A & 0 \end{bmatrix} = \tilde{H}_{\mathcal{E}}^{(1)} + \tilde{H}_{\mathcal{O}}^{(1)}, \tag{20}$$

$$h_{++}^A = \frac{1}{\sqrt{1+X^{\dagger}X}}[h_{LL}^A + h_{LS}^A X + X^{\dagger} h_{SL}^A + X^{\dagger} h_{SS}^A X] \frac{1}{\sqrt{1+X^{\dagger}X}}, \tag{21}$$

$$h_{--}^A = \frac{1}{\sqrt{1+XX^{\dagger}}}[h_{SS}^A - h_{SL}^A X^{\dagger} - X h_{LS}^A + X h_{LL}^A X^{\dagger}] \frac{1}{\sqrt{1+XX^{\dagger}}}, \tag{22}$$

$$h_{+-}^A = \frac{1}{\sqrt{1+X^{\dagger}X}}[h_{LS}^A - h_{LL}^A X^{\dagger} + X^{\dagger} h_{SS}^A - X^{\dagger} h_{SL}^A X^{\dagger}] \frac{1}{\sqrt{1+XX^{\dagger}}}, \tag{23}$$

and

$$h_{-+}^A = \frac{1}{\sqrt{1+XX^{\dagger}}}[h_{SL}^A + h_{SS}^A X - X h_{LL}^A - X h_{LS}^A X] \frac{1}{\sqrt{1+X^{\dagger}X}}. \tag{24}$$

Here, we have the relation of $h_{-+}^A = (h_{+-}^A)^{\dagger}$. h_{++}^V and h_{--}^V are both Hermitian.[22]

The final step of the decoupling is the elimination of the first-order odd Hamiltonian $\tilde{H}_{\mathcal{O}}^{(1)}$. We apply the unitary transformation using an exponential-type unitary operator proposed by Nakajima and Hirao[33] to the sum of $\tilde{H}_D^{(0)}$ and $\tilde{H}_D^{(1)}$ Hamiltonians. The result of the unitary transformation is

$$\exp(W_1^A)(\tilde{H}_D^{(0)} + \tilde{H}_D^{(1)})\exp(-W_1^A) = \tilde{H}_D^{(0)} + \tilde{H}_{\mathcal{E}}^{(1)} + \tilde{H}_{\mathcal{O}}^{(1)} + [W_1^A, \tilde{H}_D^{(0)}] + [W_1^A, \tilde{H}_{\mathcal{O}}^{(1)}] + \tfrac{1}{2}[W_1^A, [W_1^A, \tilde{H}_D^{(0)}]] + [W_1^A, \tilde{H}_{\mathcal{E}}^{(1)}] + \tfrac{1}{2}[W_1^A, [W_1^A, \tilde{H}_{\mathcal{E}}^{(1)}]] + \cdots. \tag{25}$$

If we can obtain the odd operator W_1^A satisfying the equation

$$[W_1^A, \tilde{H}_D^{(0)}] = -\tilde{H}_{\mathcal{O}}^{(1)}, \tag{26}$$

then the (LL) part of Eq. (25) will yield an electronic energy correct to the third order with respect to the vector potential $\mathbf{A}$ due to the $(2n+1)$ rule. Using Eqs. (25) and (26), we then obtain

$$\exp(W_1^A)(\tilde{H}_D^{(0)} + \tilde{H}_D^{(1)})\exp(-W_1^A) = \tilde{H}_D^{(0)} + \tilde{H}_{\mathcal{E}}^{(1)} + \tfrac{1}{2}[W_1^A, \tilde{H}_{\mathcal{O}}^{(1)}] + [W_1^A, \tilde{H}_{\mathcal{E}}^{(1)}] + \tfrac{1}{2}[W_1^A, [W_1^A, \tilde{H}_{\mathcal{E}}^{(1)}]] + \cdots. \tag{27}$$

The second-order odd term of $[W_1^A, \tilde{H}_{\mathcal{E}}^{(1)}]$ in Eq. (27) can be ignored because it will lead to an electronic energy proportional to $\mathbf{A}^4$ and does not contribute to the magnetic shieldings. Similarly, the third-order even term of $(1/2)\times[W_1^A,[W_1^A,\tilde{H}_{\mathcal{E}}^{(1)}]]$ can be neglected. Since only the first three terms in the right-hand side of Eq. (27) are necessary for the calculation of the nuclear magnetic shielding tensor, we define the two-component positive Hamiltonian h_+ as the (LL) part of these three terms. Namely,

$$h_+ = h_{++}^V + h_{++}^A + \tfrac{1}{2}[W_1^A, \tilde{H}_{\mathcal{O}}^{(1)}]_{LL} = h_+(\mathrm{I}) + h_+(\mathrm{II}) + h_+(\mathrm{III}). \tag{28}$$

h_{++}^A corresponds to the exact molecular property operator $X_{DKH\infty}^{LL}$ defined in the theory presented by Wolf and Reiher.[25] The magnetically quadratic term of $(1/2)[W_1^A, \tilde{H}_{\mathcal{O}}^{(1)}]_{LL}$ in Eq. (28) arises from the magnetically induced mixing between the positive and negative states of $\tilde{H}_D^{(0)}$ via the W_1^A operator.

B. First-order decoupling of the vector potential part

In order to eliminate the first-order odd terms with respect to the vector potential $\mathbf{A}$, we have to solve Eq. (26). We first diagonalize the $\tilde{H}_D^{(0)}$ matrix. We assume that $\tilde{H}_D^{(0)}$ is diagonalized to $\Lambda_D^{(0)}$ using the unitary matrix U. Namely,

$$U^{\dagger} \tilde{H}_D^{(0)} U = \Lambda_D^{(0)} = \begin{bmatrix} \lambda_+^{(0)} & 0 \\ 0 & \lambda_-^{(0)} \end{bmatrix}. \tag{29}$$

The unitary matrix U is written in terms of the two half-size matrices of u_+ and u_- in diagonal-block form. We write the unitary transformation of Eq. (26) as

$$\bar{W}_1^A \Lambda_D^{(0)} - \Lambda_D^{(0)} \bar{W}_1^A = -\bar{H}_{\mathcal{O}}^{(1)}, \tag{30}$$

where $\bar{W}_1^A = U^{\dagger} W_1^A U$ and $\bar{H}_{\mathcal{O}}^{(1)} = U^{\dagger} \tilde{H}_{\mathcal{O}}^{(1)} U$. We write $\bar{W}_1^A$ and $\bar{H}_{\mathcal{O}}^{(1)}$ in terms of the half-size matrices as follows:

$$\bar{W}_1^A = \begin{bmatrix} 0 & \bar{w}_{+-}^A \\ \bar{w}_{-+}^A & 0 \end{bmatrix} \tag{31}$$

and

$$\bar{H}_{\mathcal{O}}^{(1)} = \begin{bmatrix} 0 & \bar{h}_{+-}^A \\ \bar{h}_{-+}^A & 0 \end{bmatrix}. \tag{32}$$

Here, $\bar{w}_{-+}^A = -(\bar{w}_{+-}^A)^{\dagger}$ and $\bar{h}_{-+}^A = (\bar{h}_{+-}^A)^{\dagger}$. Equation (30) is written in terms of the half-size matrices. Then, the (μ,ν) element in the $\bar{w}_{+-}^A$ matrix can be obtained as

$$(\bar{w}_{+-}^A)_{\mu\nu} = \frac{(\bar{h}_{+-}^A)_{\mu\nu}}{(\lambda_+^{(0)})_{\mu} - (\lambda_-^{(0)})_{\nu}}. \tag{33}$$

Equation (33) means that $\bar{h}_{+-}^A$ produces the excitation from the positive states to the negative states of $\tilde{H}_D^{(0)}$. The anti-Hermitian operator W_1^A used in Eq. (28) can be obtained from $\bar{W}_1^A$ using the inverse unitary transformation.

In order to evaluate $\Lambda_D^{(0)}$, we have to calculate the $\tilde{H}_D^{(0)}$ matrix. Since it is desirable to eliminate the linear terms in $\boldsymbol{\sigma}\cdot\mathbf{p}$ from h_{++}^V, a new two-component operator Y is introduced, as defined by[30,35]

$$X = p^{-1}\boldsymbol{\sigma}\cdot\mathbf{p}Y, \tag{34}$$

where $p=(p^2)^{1/2}$. Y is explicitly presented in Refs. 10 and 30. $h_+(\mathrm{I})=h_{++}^V$ is rewritten using Y as

$$h_+(\mathrm{I}) = h_{++}^V = \sqrt{1+Y^\dagger Y}[-c^2 + ce_p + RVR + QV_SQ + (QV_SRp^{-1} - RVQp)Y]\frac{1}{\sqrt{1+Y^\dagger Y}}, \tag{35}$$

where

$$V_S = \boldsymbol{\sigma}\cdot\mathbf{p}V\boldsymbol{\sigma}\cdot\mathbf{p}. \tag{36}$$

h_{++}^V is diagonalized to $\lambda_+^{(0)}$ using the unitary matrix u_+. Namely, $u_+^\dagger h_{++}^V u_+ = \lambda_+^{(0)}$.

In order to eliminate the linear terms in $\boldsymbol{\sigma}\cdot\mathbf{p}$ from h_{--}^V, another new two-component operator Z is introduced, as defined by

$$X = Z\boldsymbol{\sigma}\cdot\mathbf{p}p^{-1}. \tag{37}$$

Z satisfies the equation

$$c(e_pZ + Ze_p) = RVQp - QV_SRp^{-1} + (RVR + QV_SQ)Z - Z(p^{-1}RV_SRp^{-1} + pQVQp) + Z(p^{-1}RV_SQ - pQVR)Z. \tag{38}$$

Similarly, h_{--}^V is rewritten using Z as

$$h_{--}^V = \frac{1}{\sqrt{1+ZZ^\dagger}}[-c^2 - ce_p + RVR + QV_SQ + Z(p^{-1}RV_SQ - pQVR)]\sqrt{1+ZZ^\dagger}. \tag{39}$$

h_{--}^V is diagonalized to $\lambda_-^{(0)}$ using the unitary matrix u_-. Namely, $u_-^\dagger h_{--}^V u_- = \lambda_-^{(0)}$. The anti-Hermitian matrix W_1^A is obtained inversely from $\bar{W}_1^A$ and U as $U\bar{W}_1^A U^\dagger$. Therefore, $h_+(\mathrm{III})$ is given by

$$h_+(\mathrm{III}) = \tfrac{1}{2}[W_1^A, \tilde{H}_O^{(1)}]_{LL} = \tfrac{1}{2}[u_+\bar{w}_{+-}^A u_-^\dagger (h_{+-}^A)^\dagger + \text{Hermitian conjugate}]. \tag{40}$$

Here, the relation of $h_{-+}^A=(h_{+-}^A)^\dagger$ has been used. Finally, we rewrite $h_+(\mathrm{II})=h_{++}^A$ and h_{+-}^A using Y and Z as follows:

$$h_+(\mathrm{II}) = h_{++}^A = \frac{c}{\sqrt{1+Y^\dagger Y}}[RH_AQ + QH_A^\dagger R + (RH_ARp^{-1}Y - QH_A^\dagger QpY) + (RH_ARp^{-1}Y - QH_A^\dagger QpY)^\dagger - Y^\dagger(p^{-1}RH_A^\dagger Qp + pQH_ARp^{-1})Y]\frac{1}{\sqrt{1+Y^\dagger Y}} \tag{41}$$

and

$$h_{+-}^A = \frac{c}{\sqrt{1+Y^\dagger Y}}[R\boldsymbol{\sigma}\cdot\mathbf{A}R - Q\boldsymbol{\sigma}\cdot\mathbf{p}\boldsymbol{\sigma}\cdot\mathbf{A}\boldsymbol{\sigma}\cdot\mathbf{p}Q - (R\boldsymbol{\sigma}\cdot\mathbf{A}Qp + Q\boldsymbol{\sigma}\cdot\mathbf{p}\boldsymbol{\sigma}\cdot\mathbf{A}\boldsymbol{\sigma}\cdot\mathbf{p}Rp^{-1})Z^\dagger - Y^\dagger(pQ\boldsymbol{\sigma}\cdot\mathbf{A}R + p^{-1}R\boldsymbol{\sigma}\cdot\mathbf{p}\boldsymbol{\sigma}\cdot\mathbf{A}\boldsymbol{\sigma}\cdot\mathbf{p}Q) + Y^\dagger(pQ\boldsymbol{\sigma}\cdot\mathbf{A}Qp - p^{-1}R\boldsymbol{\sigma}\cdot\mathbf{p}\boldsymbol{\sigma}\cdot\mathbf{A}\boldsymbol{\sigma}\cdot\mathbf{p}Rp^{-1})Z^\dagger]\frac{1}{\sqrt{1+ZZ^\dagger}}. \tag{42}$$

Here, we introduced $H_A=\boldsymbol{\sigma}\cdot\mathbf{A}\boldsymbol{\sigma}\cdot\mathbf{p}$. In order calculate $\bar{w}_{+-}^A$ from Eq. (33), we need $\bar{h}_{+-}^A$, which is given by $\bar{h}_{+-}^A = u_+^\dagger h_{+-}^A u_-$.

C. Magnetic perturbation expansion of the two-component Hamiltonian

The two-component electronic Hamiltonian h_+ defined in Eq. (28) can be easily expanded in terms of the external magnetic flux density component $B_{0t}(t\in x,y,z)$ and the nuclear magnetic moment component $\mu_{Mu}(u\in x,y,z)$ as follows:

$$h_+ = h_+^{(0,0)} + \sum_t B_{0t}h_{+t}^{(1,0)} + \sum_u \mu_{Mu}h_{+u}^{(0,1)} + \sum_{tu} B_{0t}\mu_{Mu}h_{+tu}^{(1,1)}. \tag{43}$$

Obviously, $h_+(\mathrm{I})$ does not include any magnetic perturbations and is equal to $h_+^{(0,0)}$. $h_+(\mathrm{II})$ is of the first order with respect to $\mathbf{A}$ and yields the $h_+^{(1,0)}$ and $h_+^{(0,1)}$ perturbation Hamiltonians, i.e., the paramagnetic shielding contribution. $h_+(\mathrm{III})$ is quadratic with respect to $\mathbf{A}$ and yields the $h_+^{(1,1)}$ perturbation Hamiltonian, i.e., the diamagnetic shielding contribution. The vector potential $\mathbf{A}$ is the sum of two vector potentials, $\mathbf{A}^{(1,0)}$ and $\mathbf{A}^{(0,1)}$, which are written explicitly as follows:

$$\mathbf{A}^{(1,0)} = \tfrac{1}{2}\mathbf{B}_0\times\mathbf{r}_0, \quad \mathbf{r}_0 = \mathbf{r}-\mathbf{R_0} \tag{44a}$$

and

$$\mathbf{A}^{(0,1)} = c^{-2}r_M^{-3}\boldsymbol{\mu}_\mathbf{M}\times\mathbf{r}_M, \quad \mathbf{r}_M = \mathbf{r}-\mathbf{R}_M. \tag{44b}$$

Here, $\mathbf{R}_0$ is the position of the common gauge origin and $\mathbf{R}_M$ is the position of the nucleus M, which is considered to be the target nucleus of the shielding calculation. We use the pointlike nuclear magnetic dipole model. Corresponding to $\mathbf{A}^{(1,0)}$ and $\mathbf{A}^{(0,1)}$, we define $H_A^{(1,0)}$ and $H_A^{(0,1)}$ as

$$H_A^{(1,0)} = \boldsymbol{\sigma}\cdot\mathbf{A}^{(1,0)}\boldsymbol{\sigma}\cdot\mathbf{p} = \sum_t B_{0t}H_{At}^{(1,0)} = \sum_t B_{0t}\tfrac{1}{2}[-i(\mathbf{r_0}\times\boldsymbol{\nabla})_t - \sigma_t\mathbf{r_0}\cdot\boldsymbol{\nabla} + \boldsymbol{\sigma}\cdot\mathbf{r_0}\nabla_t] \tag{45a}$$

and

$$H_A^{(0,1)} = \boldsymbol{\sigma}\cdot\mathbf{A}^{(0,1)}\boldsymbol{\sigma}\cdot\mathbf{p} = \sum_u \mu_{Mu}H_{Au}^{(0,1)} = \sum_u \mu_{Mu}c^{-2}r_M^{-3}[-i(\mathbf{r_M}\times\boldsymbol{\nabla})_u - \sigma_u\mathbf{r_M}\cdot\boldsymbol{\nabla} + \boldsymbol{\sigma}\cdot\mathbf{r_M}\nabla_u], \tag{45b}$$

respectively. H_A is the sum of $H_A^{(1,0)}$ and $H_A^{(0,1)}$. $h_{+t}^{(1,0)}$ and $h_{+u}^{(0,1)}$ are obtained by replacing H_A in $h_+(\mathrm{II})$ with $H_{At}^{(1,0)}$ or $H_{Au}^{(0,1)}$, respectively.

The evaluation of $h_{+tu}^{(1,1)}$ requires the perturbation expansion of the h_{+-}^A Hamiltonian. h_{+-}^A includes $\boldsymbol{\sigma}\cdot\mathbf{A}$ and $\boldsymbol{\sigma}\cdot\mathbf{p}\boldsymbol{\sigma}\cdot\mathbf{A}\boldsymbol{\sigma}\cdot\mathbf{p}$ as magnetic perturbation operators. The expansion of $\boldsymbol{\sigma}\cdot\mathbf{A}$ is trivial. $\boldsymbol{\sigma}\cdot\mathbf{p}\boldsymbol{\sigma}\cdot\mathbf{A}\boldsymbol{\sigma}\cdot\mathbf{p}$ is expanded as follows.

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

Molecule	Nucleus	Property	NR[a]	IOTC[b]	MIOTC[c]	DHF[d]	NESC-SORA-Met[e]
HF	F	$\sigma_{\perp}$(para)	−101.2	−91.4	−91.3		−94.0
	F	$\sigma_{\perp}$(dia)	479.7	475.4	478.0		480.7
	F	$\sigma_{\perp}$(total)	378.5	384.0	386.7	384.9	386.7
	F	$\sigma_{\parallel}$(para)	0.0	8.4	8.4		5.9
	F	$\sigma_{\parallel}$(dia)	478.9	474.6	477.1		479.8
	F	$\sigma_{\parallel}$(total)	478.8	483.0	485.6	485.6	485.7
	F	σ^{iso}(total)[f]	412.0	417.0	419.6	418.4	419.7
	F	$\Delta\sigma$(total)[g]	100.3	99.0	98.9	100.7	99.0
	H	$\sigma_{\perp}$(para)	18.63	18.92	18.92		18.89
	H	$\sigma_{\perp}$(dia)	0.00	0.01	1.30		1.34
	H	$\sigma_{\perp}$(total)	18.63	18.93	20.22	20.10	20.24
	H	$\sigma_{\parallel}$(para)	0.00	0.01	0.01		−0.01
	H	$\sigma_{\parallel}$(dia)	42.91	42.89	43.96		44.04
	H	$\sigma_{\parallel}$(total)	42.91	42.89	43.97	43.90	44.04
	H	σ^{iso}(total)[f]	26.72	26.92	28.13	28.03	28.17
	H	$\Delta\sigma$(total)[g]	24.28	23.96	23.75	23.80	23.80
HCl	Cl	$\sigma_{\perp}$(para)	−292.7	−232.0	−231.5		−247.8
	Cl	$\sigma_{\perp}$(dia)	1150.1	1124.6	1122.5		1137.9
	Cl	$\sigma_{\perp}$(total)	857.4	892.6	891.0	888.5	890.2
	Cl	$\sigma_{\parallel}$(para)	−2.7	56.4	56.9		41.8
	Cl	$\sigma_{\parallel}$(dia)	1147.3	1121.8	1119.8		1135.1
	Cl	$\sigma_{\parallel}$(total)	1144.6	1178.3	1176.7	1176.7	1176.9
	Cl	σ^{iso}(total)[f]	953.1	987.8	986.2	984.5	985.7
	Cl	$\Delta\sigma$(total)[g]	287.2	285.7	285.7	288.2	286.7
	H	$\sigma_{\perp}$(para)	21.69	22.51	22.51		22.49
	H	$\sigma_{\perp}$(dia)	1.13	1.05	1.98		1.89
	H	$\sigma_{\perp}$(total)	22.81	23.56	24.49	24.07	24.38
	H	$\sigma_{\parallel}$(para)	0.02	0.01	0.01		−0.01
	H	$\sigma_{\parallel}$(dia)	44.52	44.40	45.44		45.37
	H	$\sigma_{\parallel}$(total)	44.54	44.41	45.45	45.39	45.35
	H	σ^{iso}(total)[f]	30.05	30.51	31.47	31.18	31.37
	H	$\Delta\sigma$(total)[g]	21.73	20.85	20.97	21.32	20.97
HBr	Br	$\sigma_{\perp}$(para)	−725.0	−171.2	−165.0		−271.3
	Br	$\sigma_{\perp}$(dia)	3100.0	2929.6	2918.1		3001.7
	Br	$\sigma_{\perp}$(total)	2375.0	2758.3	2753.1	2738.1	2730.4
	Br	$\sigma_{\parallel}$(para)	−0.7	472.1	479.0		379.9
	Br	$\sigma_{\parallel}$(dia)	3098.3	2927.9	2915.0		2998.7
	Br	$\sigma_{\parallel}$(total)	3097.6	3400.0	3394.0	3402.1	3378.5
	Br	σ^{iso}(total)[f]	2615.9	2972.2	2966.7	2959.4	2946.4
	Br	$\Delta\sigma$(total)[g]	722.6	641.7	640.9	664.0	648.1
	H	$\sigma_{\perp}$(para)	21.13	30.04	30.04		30.12
	H	$\sigma_{\perp}$(dia)	−0.82	−0.79	0.57		−0.01
	H	$\sigma_{\perp}$(total)	20.31	29.26	30.61	29.82	30.11
	H	$\sigma_{\parallel}$(para)	0.00	−0.38	−0.38		−0.45
	H	$\sigma_{\parallel}$(dia)	48.49	48.23	48.97		48.50
	H	$\sigma_{\parallel}$(total)	48.50	47.85	48.59	47.93	48.05
	H	σ^{iso}(total)[f]	29.70	35.46	36.61	35.86	36.09
	H	$\Delta\sigma$(total)[g]	28.19	18.59	17.98	18.11	17.94
HI	I	$\sigma_{\perp}$(para)	−1454.2[h]	707.5[i]	706.4		509.2
	I	$\sigma_{\perp}$(dia)	5509.0[h]	5018.6[i]	4888.9	5037.9	
	I	$\sigma_{\perp}$(total)	4054.9[h]	5726.1[i]	5595.3	5571.9	5547.2
	I	$\sigma_{\parallel}$(para)	0.0[h]	1693.7[i]	1705.8		1547.0
	I	$\sigma_{\parallel}$(dia)	5505.4[h]	5016.6[i]	4885.4		5034.6
	I	$\sigma_{\parallel}$(total)	5505.4[h]	6710.4[i]	6591.2	6597.1	6581.6
	I	σ^{iso}(total)[f]	4538.4[h]	6054.2[i]	5927.3	5913.7	5892.0
	I	$\Delta\sigma$(total)[g]	1450.6[h]	984.2[i]	995.9	1025.2	1034.4
	H	$\sigma_{\perp}$(para)	20.96[h]	49.91[i]	49.91		50.95
	H	$\sigma_{\perp}$(dia)	−0.43[h]	−1.80[i]	−0.29		−1.80
	H	$\sigma_{\perp}$(total)	20.53[h]	48.11[i]	49.62	46.92	49.15

TABLE I. (*Continued.*)

Molecule	Nucleus	Property	NR[a]	IOTC[b]	MIOTC[c]	DHF[d]	NESC-SORA-Met[e]
	H	$\sigma_{\parallel}$(para)	0.00[h]	−3.92[i]	−3.92		−4.32
	H	$\sigma_{\parallel}$(dia)	52.00[h]	50.64[i]	51.40		50.28
	H	$\sigma_{\parallel}$(total)	52.00[h]	46.73[i]	47.49	47.31	45.95
	H	σ^{iso}(total)[f]	31.02[h]	47.65[i]	48.91	47.05	48.08
	H	$\Delta\sigma$(total)[g]	31.48[h]	−1.38[i]	−2.13	0.39	−3.20

[a]Nonrelativistic results taken from Ref. 10.
[b]Infinite-order two-component calculation results taken from Ref. 10.
[c]Present modified infinite-order two-component method results.
[d]Four-component Dirac-Hartree-Fock results taken from Refs. 2 and 37.
[e]Normalized elimination of the small component calculation results at the level of the second-order regular approximation and the inclusion of the metric perturbation, taken from Ref. 15.
[f]$\sigma^{\mathrm{iso}}=(1/3)(2\sigma_{\perp}+\sigma_{\parallel})$.
[g]$\Delta\sigma=\sigma_{\parallel}-\sigma_{\perp}$.
[h]Nonrelativistic calculation results obtained with the basis set of $(25s25p18d10f3g)$ for I. The nonrelativistic values are computed using the modified infinite-order two-component method program with 10^3 c as the velocity of light.
[i]Infinite-order two-component calculation results obtained with the basis set of $(25s25p18d10f3g)$ for I.

$$\boldsymbol{\sigma}\cdot\mathbf{p}\boldsymbol{\sigma}\cdot\mathbf{A}\boldsymbol{\sigma}\cdot\mathbf{p}=\boldsymbol{\sigma}\cdot\mathbf{p}\boldsymbol{\sigma}\cdot\mathbf{A}^{(1,0)}\boldsymbol{\sigma}\cdot\mathbf{p}+\boldsymbol{\sigma}\cdot\mathbf{p}\boldsymbol{\sigma}\cdot\mathbf{A}^{(0,1)}\boldsymbol{\sigma}\cdot\mathbf{p}, \tag{46}$$

$$\boldsymbol{\sigma}\cdot\mathbf{p}\boldsymbol{\sigma}\cdot\mathbf{A}^{(1,0)}\boldsymbol{\sigma}\cdot\mathbf{p}=\sum_t B_{0t}\tfrac{1}{2}[-\boldsymbol{\sigma}\cdot\boldsymbol{\nabla}(\mathbf{r_0}\times\boldsymbol{\nabla})_t+(\boldsymbol{\nabla}\times\mathbf{r_0})_t\boldsymbol{\sigma}\cdot\boldsymbol{\nabla}+i\nabla_t\mathbf{r_0}\cdot\boldsymbol{\nabla}-i\,\boldsymbol{\nabla}\cdot\mathbf{r_0}\nabla_t+\boldsymbol{\nabla}(\mathbf{r_0}\times\boldsymbol{\sigma})_t\cdot\boldsymbol{\nabla}], \tag{47}$$

$$\boldsymbol{\sigma}\cdot\mathbf{p}\boldsymbol{\sigma}\cdot\mathbf{A}^{(0,1)}\boldsymbol{\sigma}\cdot\mathbf{p}=\sum_u \mu_{Mu}c^{-2}[-\boldsymbol{\sigma}\cdot\boldsymbol{\nabla}r_M^{-3}(\mathbf{r_M}\times\boldsymbol{\nabla})_u+(\boldsymbol{\nabla}\times r_M^{-3}\mathbf{r_M})_u\boldsymbol{\sigma}\cdot\boldsymbol{\nabla}+i\nabla_u r_M^{-3}\mathbf{r_M}\cdot\boldsymbol{\nabla}-i\,\boldsymbol{\nabla}\cdot r_M^{-3}\mathbf{r_M}\nabla_u+\boldsymbol{\nabla}r_M^{-3}(\mathbf{r_M}\times\boldsymbol{\sigma})_u\cdot\boldsymbol{\nabla}]. \tag{48}$$

Equation (42) produces $h_{+-}^{A(1,0)}$ and $h_{+-}^{A(0,1)}$ depending on $\mathbf{A}^{(1,0)}$ or $\mathbf{A}^{(0,1)}$ in $\boldsymbol{\sigma}\cdot\mathbf{A}$ and $\boldsymbol{\sigma}\cdot\mathbf{p}\boldsymbol{\sigma}\cdot\mathbf{A}\boldsymbol{\sigma}\cdot\mathbf{p}$ operators. Namely, $h_{+-}^{A}=h_{+-}^{A(1,0)}+h_{+-}^{A(0,1)}$. Similarly, $\bar{w}_{+-}^{A}=\bar{w}_{+-}^{A(1,0)}+\bar{w}_{+-}^{A(0,1)}$. Expanding Eq. (40), $h_{+tu}^{(\tilde{1},1)}$ is given as

$$h_{+tu}^{(1,1)}=\tfrac{1}{2}[u_+\bar{w}_{+-t}^{A(1,0)}u_-^{\dagger}(h_{+-u}^{A(0,1)})^{\dagger}+u_+\bar{w}_{+-u}^{A(0,1)}u_-^{\dagger}(h_{+-t}^{A(1,0)})^{\dagger}]+\text{Hermitian conjugate}. \tag{49}$$

The calculation of the diamagnetic part requires both the positive and negative states of $\tilde{H}_D^{(0)}$.

III. RESULTS AND DISCUSSION

The present calculation uses experimental atomic distances[36] and a pointlike nuclear model. We perform the shielding tensor calculation for HX (X=F,Cl,Br,I) systems at the Hartree-Fock level. The common gauge origin $\mathbf{R}_0$ is placed on the halogen nuclei. The used basis sets are as follows: $(12s10p2d)$ for H, $(15s15p10d4f)$ for F, $(17s17p12d8f)$ for Cl, $(21s21p12d8f2g)$ for Br, and $(25s25p18d10f3g)$ for I. The Gaussian exponents of the basis functions are described in Ref. 13. The obtained results are shown in Table I. The present decoupling calculation results are shown in the sixth column of Table I as the modified infinite-order two-component (MIOTC) values. The MIOTC results are compared with other calculation results in Table I. The nonrelativistic (NR) results in the fourth column and the IOTC results in the fifth column are both taken from Ref. 10. However, for the HI molecule, both results were recalculated with the larger basis of $(25s25p18d10f3g)$ for I than that used in Ref. 10. The NR values for HI were obtained using the MIOTC program with 10^3c as the velocity of light. The four-component Dirac-Hartree-Fock (DHF) results taken from Refs. 2 and 37 are shown in the seventh column as the benchmark. Finally, the normalized elimination of the small component calculation results at the level of the second-order regular approximation and the inclusion of the metric perturbation (NESC-SORA-Met), taken from Ref. 15, are listed in the last column in Table I.

As shown in Table I, the MIOTC results agree better with the DHF values than the IOTC results do. However, somewhat larger differences remain between the MIOTC and DHF values for the proton shieldings than for the halogen shieldings. This may arise from the fact that the present MIOTC calculation treats the two-electron interactions nonrelativistically. The two-electron spin-orbit interaction effects, which are important in the proton shieldings,[14] are neglected in the MIOTC calculation. In other words, the present MIOTC results include the picture change error for the two-electron interactions. Based on Table I, the MIOTC and NESC-SORA-Met results are thought to have a comparable quality for calculating the relativistic effects on nuclear magnetic shielding tensors.

IV. CONCLUSION

A two-component theory for solving the Dirac equation that includes magnetic perturbations was derived. The obtained theory eliminates all of the odd nuclear attraction potential terms and the first-order odd magnetic vector potential terms connecting the positive states to the negative states. The obtained electronic energy is correct to the third order with respect to $\mathbf{A}$ as a result of the $(2n+1)$ rule. The decou-

pling is exact for the magnetic shielding calculation. However, the calculation of the diamagnetic part of the nuclear magnetic shielding tensor requires both the positive and negative states of the unperturbed ($\mathbf{A}=0$) Hamiltonian. The obtained theory was dubbed as the modified infinite-order two-component (MIOTC) theory. The MIOTC theory was applied to the relativistic calculation of the nuclear magnetic shielding tensors of HX (X=F, Cl, Br, I) systems at the Hartree-Fock level. The results show that the MIOTC calculation reproduces better the Dirac-Hartree-Fock results than the previous infinite-order two-component calculation does.

ACKNOWLEDGMENTS

This study was supported in part by the Japanese Ministry of Education, Science, Sports, and Culture of Japan (Grant No. 18550003).

[1] P. Manninen, P. Lantto, J. Vaara, and K. Ruud, J. Chem. Phys. **119**, 2623 (2003).
[2] P. Manninen, K. Ruud, P. Lantto, and J. Vaara, J. Chem. Phys. **122**, 114107 (2005); **124**, 149901(E) (2006).
[3] P. Lantto, R. H. Romero, S. S. Gómez, G. A. Aucar, and J. Vaara, J. Chem. Phys. **125**, 184113 (2006).
[4] J. I. Melo, M. C. Ruiz de Azúa, C. G. Giribet, G. A. Aucar, and R. H. Romero, J. Chem. Phys. **118**, 471 (2003).
[5] J. I. Melo, M. C. Ruiz de Azúa, C. G. Giribet, G. A. Aucar, and P. F. Provasi, J. Chem. Phys. **121**, 6798 (2004).
[6] D. G. Zaccari, M. C. Ruiz de Azúa, J. I. Melo, and C. G. Giribet, J. Chem. Phys. **124**, 054103 (2006).
[7] P. G. Roura, J. I. Melo, M. C. Ruiz de Azúa, and C. G. Giribet, J. Chem. Phys. **125**, 064107 (2006).
[8] R. Fukuda, M. Hada, and H. Nakatsuji, J. Chem. Phys. **118**, 1015 (2003).
[9] R. Fukuda, M. Hada, and H. Nakatsuji, J. Chem. Phys. **118**, 1027 (2003).
[10] K. Kudo and H. Fukui, J. Chem. Phys. **123**, 114102 (2005); **124**, 209901(E) (2006).
[11] K. G. Dyall, J. Chem. Phys. **106**, 9618 (1997).
[12] K. G. Dyall, J. Chem. Phys. **109**, 4201 (1998).
[13] K. Kudo, H. Maeda, T. Kawakubo, Y. Ootani, M. Funaki, and H. Fukui, J. Chem. Phys. **124**, 224106 (2006).
[14] Y. Ootani, H. Yamaguti, H. Maeda, and H. Fukui, J. Chem. Phys. **125**, 164106 (2006).
[15] H. Maeda, Y. Ootani, and H. Fukui, J. Chem. Phys. **126**, 174102 (2007).
[16] E. van Lenthe, E. J. Baerends, and J. G. Snijders, J. Chem. Phys. **99**, 4597 (1993).
[17] R. van Leeuwen, E. van Lenthe, E. J. Baerends, and J. G. Snijders, J. Chem. Phys. **101**, 1272 (1994).
[18] E. van Lenthe, E. J. Baerends, and J. G. Snijders, J. Chem. Phys. **101**, 9783 (1994).
[19] E. van Lenthe, R. van Leeuwen, E. J. Baerends, and J. G. Snijders, Int. J. Quantum Chem. **57**, 281 (1996).
[20] K. G. Dyall and E. van Lenthe, J. Chem. Phys. **111**, 1366 (1999).
[21] M. Filatov and D. Kremer, J. Chem. Phys. **122**, 064104 (2005).
[22] M. Ilias and T. Saue, J. Chem. Phys. **126**, 064102 (2007).
[23] W. Kutzelnigg and W. Liu, J. Chem. Phys. **123**, 241102 (2005).
[24] W. Liu and D. Peng, J. Chem. Phys. **125**, 044102 (2006); **125**, 149901(E) (2006).
[25] A. Wolf and M. Reiher, J. Chem. Phys. **124**, 064102 (2006).
[26] A. Wolf and M. Reiher, J. Chem. Phys. **124**, 064103 (2006).
[27] P. Pyykkö, Chem. Phys. **22**, 289 (1977).
[28] P. Pyykkö, Chem. Phys. **74**, 1 (1983).
[29] W. Kutzelnigg, Phys. Rev. A **67**, 032109 (2003).
[30] M. Barysz and A. J. Sadlej, J. Chem. Phys. **116**, 2696 (2002).
[31] K. G. Dyall, Int. J. Quantum Chem. **78**, 412 (2000).
[32] H. Fukui, T. Baba, Y. Shiraishi, S. Imanishi, K. Kudo, K. Mori, and M. Shimoji, Mol. Phys. **102**, 641 (2004).
[33] T. Nakajima and K. Hirao, J. Chem. Phys. **113**, 7786 (2000).
[34] The simple equations for h_{++}^{V} and h_{--}^{V}, shown in Eqs. (18) and (19), were suggested by one of the referees. The same simplification is presented in Ref. 22.
[35] D. Kedziera and M. Barysz, J. Chem. Phys. **121**, 6719 (2004).
[36] *Tables of Interatomic Distances and Configuration in Molecules and Ions, Supplement* (The Chemical Society, London, 1965).
[37] P. Manninen and J. Vaara, J. Chem. Phys. **124**, 137101 (2006).