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Calculation of nuclear magnetic shieldings. XIII. Gauge-origin independent relativistic effects

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The gauge-origin independent expression for the relativistic nuclear magnetic shieldings was derived from the Douglas-Kroll transformation of the no-pair equation and the use of the gauge including atomic orbitals (GIAOs) proposed by London. Using our expression the relativistic spin free effect on the nuclear magnetic shieldings was evaluated for the four hydrogen halide molecules, HF, HCl, HBr, and HI, at the coupled Hartree-Fock (CHF) level with uncontracted Cartesian Gaussian-type basis sets. It was found that the GIAO-CHF results are very similar to the shielding values calculated with the fixed gauge origins at the halogen nuclei. The calculated results showed that the spin independent relativistic effect produces high-field shifts at both the halogen nuclei and protons in the hydrogen halides. However, the computed spin free effect was too small to interpret the very large upshield proton shifts observed in HBr and HI molecules. © *1999 American Institute of Physics.* [S0021-9606(99)31301-5]

I. INTRODUCTION

Many years ago Morishima *et al.*[1] emphasized great importance of the relativistic effects on the nuclear magnetic shieldings of heavy nuclei. Since the pioneering work of Morishima *et al.* there have been a large number of papers[2–12] treating this specific problem. There is currently a great deal of research interest in this field, but the problem is still far from being completely solved.

Recently we presented a formulation for the relativistic nuclear magnetic shieldings[13] in which the no-pair Hamiltonian[14,15] and its Douglas and Kroll (DK) transformation[16] were used. We calculated the relativistic spin free effects on the nuclear magnetic shieldings in the hydrogen halides at the coupled Hartree-Fock (CHF) level. Our calculation showed that the spin free effect increases the nuclear magnetic shieldings of the halogen nuclei in the hydrogen halides. The increments in the halogen shielding constants were proportional to the 3.5 power of the atomic numbers, Z's, of the halogen nuclei. This increase in the shieldings results from the so-called relativistic contraction effect[17] concentrating the electrons in the vicinity of the heavy nuclei.

Our calculation presented, on the other hand, a large gauge origin dependence in the relativistic effects on the proton shielding constants. The hydrogen iodide showed the largest gauge origin dependence in which the relativistic effects on the proton shielding constant were $+2.50$ ppm and -3.21 ppm for the gauge origins at the I and H nuclei, respectively. The relativistic effects were completely masked with the large gauge-origin dependence and we were not able to determine the relativistic effects on the proton shieldings. It is greatly important to get the gauge-origin independent relativistic effects.

The nuclear magnetic shielding of a nucleus M is equal to the electronic energy change of the system bilinear in the vector potential $\mathbf{A}_0$, due to the external magnetic flux density $\mathbf{B}_0$, and the vector potential $\mathbf{A}_M$, due to the nuclear magnetic moment $\boldsymbol{\mu}_M = \gamma_M \hbar \mathbf{I}_M$. The sum of the momentum $\mathbf{p}$ and the vector potential $\mathbf{A}_0$ multiplied by e (elementary charge) forms the gauge invariant mechanical momentum. The gauge invariance of the electronic energy will be kept only if we use a complete basis set and we treat the momentum $\mathbf{p}$ and the vector potential term $e\mathbf{A}_0$ to an equal order with respect to inverse powers of the velocity of light c.[18] Our previous theory[13] includes the expansion of the momentum $\mathbf{p}$ to the infinite order of the inverse light velocity c^{-1}, but it kept only the nonrelativistic term of the order of c^0 for the expansion of $e\mathbf{A}_0$. The legitimate strategy solving the gauge-origin dependence problem may be the full inclusion of the relativistic corrections to the vector potentials and the use of a complete basis set. However, this approach is difficult to carry out at present.

We have another approach which offers apparently gauge-origin independent results for the nuclear magnetic shielding calculations. It uses the gauge including atomic orbitals (GIAOs) proposed by London.[19] With the use of GIAOs the common gauge origin $\mathbf{R}_0$ is replaced by the local origin $\mathbf{R}_\nu$, the center position of basis function χ_ν, and the calculated results become independent of the used gauge origin $\mathbf{R}_0$.

It is the purpose of this article to present gauge-origin independent relativistic calculations of nuclear magnetic shieldings with GIAOs. In Sec. II we state our theory for the relativistic nuclear magnetic shielding with GIAOs. In Sec. III we present a numerical estimation for the spin independent relativistic effect on the nuclear magnetic shieldings in the four hydrogen halide molecules, HF, HCl, HBr, and HI.

II. THEORY

In our previous paper, Part XII,[13] we started with a no-pair Hamiltonian[14,15] employing the positive energy projection operator to an n electron system in the external fields

which consist of the electric field due to static point nuclear charges, a homogeneous external magnetic flux density $\mathbf{B}_0$, and the local magnetic field produced by a nuclear magnetic point dipole moment $\boldsymbol{\mu}_M$. In order to decouple the positive and negative components in the Dirac-type four-component wave function, we used the Douglas and Kroll (DK) transformations.[16] The first- and second-order DK transformations were performed on the no-pair equation to obtain the two-component Schrödinger-Pauli (SP) type wave equation which yields only the positive energy eigenvalues of the system. We write the SP type equation as

$$H_+\Psi_+ = E_+\Psi_+ . \tag{1}$$

E_+ is the positive electronic energy of the system, and the positive energy Hamiltonian H_+ is written as

$$H_+ = \sum_{j=1}^{n} \hat{h}^+(j) + \sum_{j<k}^{n} [\tilde{V}_{ee}(j,k) + \tilde{B}_{ee}(j,k)], \tag{2}$$

where

$$\hat{h}^+(j) = E_p(j) - m_e c^2 + \tilde{V}_n(j). \tag{3}$$

Here, the $\tilde{V}_n$, $\tilde{V}_{ee}$, and $\tilde{B}_{ee}$ terms mean the DK transformed operators of the nuclear attraction potential, the electron-electron Coulomb repulsion potential, and the Breit potential, respectively. These are given in our pervious paper.[13] The E_p is the DK transformed one-electron kinetic energy, that is, the relativistic kinetic energy of an electron in the magnetic fields.

The kinetic energy E_p is given by

$$E_p = [m_e^2 c^4 + c^2(\boldsymbol{\sigma}\cdot\boldsymbol{\pi})^2]^{1/2}, \tag{4}$$

where

$$\boldsymbol{\pi} = \mathbf{p} + e\mathbf{A}_0 + e\mathbf{A}_M , \tag{5}$$

$$\mathbf{A}_0 = \mathbf{B}_0 \times \mathbf{r}_0/2, \quad \mathbf{r}_0 = \mathbf{r} - \mathbf{R}_0 , \tag{6}$$

and

$$\mathbf{A}_M = (\mu_0/4\pi) r_M^{-3} \boldsymbol{\mu}_M \times \mathbf{r}_M ,$$

$$\boldsymbol{\mu}_M = \gamma_M \hbar \mathbf{I}_M , \quad \mathbf{r}_M = \mathbf{r} - \mathbf{R}_M . \tag{7}$$

m_e and $-e$ are the rest mass and the electric charge of the electron, respectively. The $\mathbf{R}_0$ and $\mathbf{R}_M$ are the position vectors of the gauge origin and the point nuclear magnetic moment $\boldsymbol{\mu}_M$, respectively. μ_0 is the permeability of the vacuum, γ_M is the nuclear magnetogyric ratio, and $\hbar\mathbf{I}_M$ is the nuclear spin angular momentum. $\boldsymbol{\sigma}$ is the 2×2 Pauli spin matrix vector.

In order to allow gauge-origin independent calculations, we use GIAO functions $\{\phi_\nu\}$, which are defined by

$$\phi_\nu(\mathbf{B}_0) = f_\nu(\mathbf{B}_0)\chi_\nu , \tag{8}$$

where

$$f_\nu(\mathbf{B}_0) = \exp(-ie\mathbf{A}_\nu \cdot \mathbf{r}/\hbar) \tag{9}$$

and

$$\mathbf{A}_\nu = \mathbf{B}_0 \times (\mathbf{R}_\nu - \mathbf{R}_0)/2. \tag{10}$$

The function $f_\nu(\mathbf{B}_0)$ is the gauge factor for the real basis function (RBF) χ_ν and $\mathbf{R}_\nu$ is the center position of χ_ν. We have a following commutation relation between the canonical momentum $\boldsymbol{\pi}$ and the gauge factor f_ν:

$$\boldsymbol{\pi} f_\nu = f_\nu \boldsymbol{\pi}_\nu , \tag{11}$$

where

$$\boldsymbol{\pi}_\nu = \mathbf{p} + e\mathbf{A}_{0\nu} + e\mathbf{A}_M \tag{12}$$

and

$$\mathbf{A}_{0\nu} = \mathbf{B}_0 \times \mathbf{r}_\nu/2, \quad \mathbf{r}_\nu = \mathbf{r} - \mathbf{R}_\nu . \tag{13}$$

Therefore, we have

$$f_\mu^* [E_p - m_e c^2 + \tilde{V}_n] f_\nu = f_\mu^* f_\nu [E_{p\nu} - m_e c^2 + \tilde{V}_{n\nu}], \tag{14}$$

where

$$E_{p\nu} = [m_e^2 c^4 + c^2(\boldsymbol{\sigma}\cdot\boldsymbol{\pi}_\nu)^2]^{1/2}. \tag{15}$$

$\tilde{V}_{n\nu}$ is obtained from $\tilde{V}_n$ with the replacement of $\boldsymbol{\pi}$ by $\boldsymbol{\pi}_\nu$.

The nonrelativistic contribution $f_\mu^* f_\nu[(\boldsymbol{\sigma}\cdot\boldsymbol{\pi}_\nu)^2/2m_e + V_n]$ in Eq. (14) is written as

$$\begin{aligned} & f_\mu^* f_\nu [(\boldsymbol{\sigma}\cdot\boldsymbol{\pi}_\nu)^2/2m_e + V_n] \\ &= f_\mu^* f_\nu [(\boldsymbol{\pi}_\nu^2 + i\boldsymbol{\sigma}\cdot\boldsymbol{\pi}_\nu \times \boldsymbol{\pi}_\nu)/2m_e + V_n] \\ &= (-\hbar^2\Delta + e^2\mathbf{A}_{0\nu}^2 + e^2\mathbf{A}_M^2)/2m_e \\ &\quad + V_n + \hat{h}_{\mathrm{OZ}} + \hat{h}_V + \hat{h}_{\mathrm{SZ}} + \hat{h}_{\mathrm{OP}} + \hat{h}_{\mathrm{FC}} + \hat{h}_{\mathrm{SD}} + \hat{h}_{\mathrm{DS}}, \end{aligned} \tag{16}$$

where

$$V_n = \sum_a (-Z_a e^2/4\pi\varepsilon_0 r_a), \quad r_a = |\mathbf{r} - \mathbf{R}_a|, \tag{17}$$

$$\begin{aligned} & \hat{h}_{\mathrm{OZ}} = \mu_B[\mathbf{B}_0 \cdot \mathbf{l}_\nu - (i/2)\mathbf{B}_0 \cdot \mathbf{R}_{\mu\nu} \times \mathbf{r}\Delta], \\ & \mathbf{l}_\nu = -i\mathbf{r}_\nu \times \boldsymbol{\nabla}, \quad \mathbf{R}_{\mu\nu} = \mathbf{R}_\mu - \mathbf{R}_\nu , \end{aligned} \tag{18}$$

$$\hat{h}_V = i(e/2\hbar)\mathbf{B}_0 \cdot \mathbf{R}_{\mu\nu} \times \mathbf{r} V_n , \tag{19}$$

$$\hat{h}_{\mathrm{SZ}} = \mu_B \mathbf{B}_0 \cdot \boldsymbol{\sigma}, \tag{20}$$

$$\hat{h}_{\mathrm{OP}} = 2(\mu_0/4\pi)\mu_B r_M^{-3} \boldsymbol{\mu}_M \cdot \mathbf{l}_M , \quad \mathbf{l}_M = -i\mathbf{r}_M \times \boldsymbol{\nabla}, \tag{21}$$

$$\hat{h}_{\mathrm{FC}} = (8\pi/3)(\mu_0/4\pi)\mu_B \delta(\mathbf{r}_M)\boldsymbol{\mu}_M \cdot \boldsymbol{\sigma}, \tag{22}$$

$$\begin{aligned} \hat{h}_{\mathrm{SD}} = (\mu_0/4\pi)\mu_B [& -r_M^{-3}\boldsymbol{\mu}_M \cdot \boldsymbol{\sigma} \\ & + 3r_M^{-5}(\boldsymbol{\mu}_M \cdot \mathbf{r}_M)(\mathbf{r}_M \cdot \boldsymbol{\sigma})], \end{aligned} \tag{23}$$

$$\begin{aligned} \hat{h}_{\mathrm{DS}} = (\mu_0/4\pi)(e^2/2m_e) r_M^{-3} [& (\mathbf{B}_0 \cdot \boldsymbol{\mu}_M)(\mathbf{r}_\nu \cdot \mathbf{r}_M) \\ & - (\mathbf{B}_0 \cdot \mathbf{r}_M)(\boldsymbol{\mu}_M \cdot \mathbf{r}_\nu)] + i(e/2\hbar)\mathbf{B}_0 \cdot \mathbf{R}_{\mu\nu} \\ & \times \mathbf{r}[\hat{h}_{\mathrm{OP}} + \hat{h}_{\mathrm{FC}} + \hat{h}_{\mathrm{SD}}], \end{aligned} \tag{24}$$

and

$$\mu_B = e\hbar/2m_e . \tag{25}$$

We have used here the identity

$$\begin{aligned} \nabla_t (r_u/r^3) = (4\pi/3)\delta(\mathbf{r})\delta_{tu} + \delta_{tu}/r^3 \\ - 3r_t r_u/r^5, \quad (t,u \in x,y,z). \end{aligned} \tag{26}$$

Here, V_n is the nonrelativistic nuclear attraction energy. Z_a is the atomic number of nucleus a located at $\mathbf{R}_a$. $\hat{h}_{\mathrm{OZ}}$ and $\hat{h}_{\mathrm{SZ}}$ are the orbital Zeeman (OZ) term and the spin Zeeman (SZ) term, respectively. $\hat{h}_{\mathrm{OP}}$, $\hat{h}_{\mathrm{FC}}$, and $\hat{h}_{\mathrm{SD}}$ are the orbital paramagnetic (OP) term, the Fermi-contact (FC) term, and the spin-dipole (SD) term, respectively. $\hat{h}_{\mathrm{DS}}$ is the diamagnetic shielding (DS) term. μ_B is the Bohr magneton.

If we treat the magnetic perturbations at the nonrelativistic level and ignore the $\mathbf{A}_{0\nu}^2$ and $\mathbf{A}_M^2$ terms, the GIAO integral of the one-electron Hamiltonian $\hat{h}_+$ in Eq. (3) is written as

$$\begin{aligned}\langle\phi_\mu|\hat{h}_+|\phi_\nu\rangle &= \langle\phi_\mu|E_p - m_e c^2 + \tilde{V}_n|\phi_\nu\rangle \\ &= \langle\chi_\mu|f_\mu^* f_\nu(E_{p\nu} - m_e c^2 + \tilde{V}_{n\nu})|\chi_\nu\rangle \\ &= \langle\chi_\mu|\hat{h}^0 + \hat{h}_{\mathrm{OZ}} + \hat{h}_V + \hat{h}_{\mathrm{SZ}} + \hat{h}_{\mathrm{OP}} \\ &\quad + \hat{h}_{\mathrm{FC}} + \hat{h}_{\mathrm{SD}} + \hat{h}_{\mathrm{DS}}|\chi_\nu\rangle \\ &= \langle\chi_\mu|\hat{h}_{\mu\nu}|\chi_\nu\rangle, \end{aligned} \tag{27}$$

where

$$\hat{h}^0 = E_p^0 - m_e c^2 + \tilde{V}_n^0 \tag{28}$$

and

$$E_p^0 = [m_e^2 c^4 + c^2 \mathbf{p}^2]^{1/2}. \tag{29}$$

$\tilde{V}_n^0$ in Eq. (28) is the field independent relativistic nuclear attraction potential given by Eq. (63) in Ref. 13.

III. RESULTS AND DISCUSSION

The t,u $(t,u \in x,y,z)$ element of the nuclear magnetic shielding tensor $\hat{\sigma}(M)$ of nucleus M is given by

$$\sigma_{tu}(M) = (\partial^2 E_+ / \partial B_{0t} \partial \mu_{Mu})_{\mathbf{B}_0 = 0, \boldsymbol{\mu}_M = 0}. \tag{30}$$

In order to simplify the wave equation (1) we introduce here the following approximations:

(i) We treat the electron-electron interaction nonrelativistically. So we replace $\tilde{V}_{ee}$ by the nonrelativistic Coulomb repulsion interaction V_{ee} $(=\Sigma_{j<k}^n (e^2/4\pi\varepsilon_0 r_{jk}))$. We discard the Breit potential $\tilde{B}_{ee}$ and all the relativistic effects coming from the DK transformation of V_{ee}.

(ii) We use the coupled Hartree-Fock (CHF) approximation for the wave function calculation in which Ψ_+ is given by a doubly-occupied single Slater determinant.

(iii) We treat the vector potentials $\mathbf{A}_{0\nu}$ and $\mathbf{A}_M$ nonrelativistically and ignore all the relativistic corrections to the $\mathbf{A}_{0\nu}$ and $\mathbf{A}_M$. The discarded c^{-2} corrections to the field perturbations are presented in the Appendix.

(iv) We consider only the spin independent perturbations and discard all the spin dependent terms such as the spin-orbit effect.

The CHF equation is written as

$$\sum_\nu F_{\mu\nu} C_{\nu j} = \varepsilon_j \sum_\nu S_{\mu\nu} C_{\nu j}. \tag{31}$$

The Fock matrix element $F_{\mu\nu}$ is given by

$$F_{\mu\nu} = H_{\mu\nu} + \sum_{\lambda\sigma} P_{\lambda\sigma}[G_{\mu\nu\lambda\sigma} - (1/2)G_{\mu\sigma\lambda\nu}], \tag{32}$$

where

$$H_{\mu\nu} = \langle\chi_\mu|\hat{h}_{\mu\nu}|\chi_\nu\rangle, \tag{33}$$

$$P_{\lambda\sigma} = 2\sum_{j=1}^n C_{\lambda j}^* C_{\sigma j}, \tag{34}$$

and

$$\begin{aligned} G_{\mu\nu\lambda\sigma} = \int \phi_\mu^*(1)\phi_\nu(1) \\ \times (e^2/4\pi\varepsilon_0 r_{12})\phi_\lambda^*(2)\phi_\sigma(2) d\tau_1 d\tau_2. \end{aligned} \tag{35}$$

Here $\hat{h}_{\mu\nu}$ and $G_{\mu\nu\lambda\sigma}$ are expanded in the field perturbations B_{0t} and μ_{Mu} as

$$\hat{h}_{\mu\nu} = \hat{h}^0 + B_{0t}\hat{h}_{\mu\nu,t}^{(1,0)} + \mu_{Mu}\hat{h}_{\mu\nu,u}^{(0,1)} + B_{0t}\mu_{Mu}\hat{h}_{\mu\nu,tu}^{(1,1)} + \cdots \tag{36}$$

and

$$G_{\mu\nu\lambda\sigma} = G_{\mu\nu\lambda\sigma}^0 + B_{0t}G_{\mu\nu\lambda\sigma,t}^{(1,0)} + \cdots, \tag{37}$$

where

$$\begin{aligned} \hat{h}_{\mu\nu,t}^{(1,0)} &= \mu_B[l_{\nu t} - (i/2)(\mathbf{R}_{\mu\nu}\times\mathbf{r})_t\Delta] \\ &\quad + i(e/2\hbar)(\mathbf{R}_{\mu\nu}\times\mathbf{r})_t V_n, \end{aligned} \tag{38}$$

$$\hat{h}_{\mu\nu,u}^{(0,1)} = 2(\mu_0/4\pi)\mu_B r_M^{-3} l_{Mu}, \tag{39}$$

$$\begin{aligned} \hat{h}_{\mu\nu,tu}^{(1,1)} &= (\mu_0/4\pi)(e^2/2m_e) r_M^{-3}[(\mathbf{r}_\nu\cdot\mathbf{r}_M)\delta_{tu} - r_{Mt}r_{\nu u}] \\ &\quad + i(e/2\hbar)(\mathbf{R}_{\mu\nu}\times\mathbf{r})_t \hat{h}_{\mu\nu,u}^{(0,1)}. \end{aligned} \tag{40}$$

$$G_{\mu\nu\lambda\sigma}^0 = \int \chi_\mu(1)\chi_\nu(e^2/4\pi\varepsilon_0 r_{12})\chi_\lambda(2)\chi_\sigma(2) d\tau_1 d\tau_2, \tag{41}$$

and

$$\begin{aligned} G_{\mu\nu\lambda\sigma,t}^{(1,0)} = i(e/2\hbar)\Big[&\int \chi_\mu(1)\chi_\nu(1)(\mathbf{R}_{\mu\nu}\times\mathbf{r}_1)_t \\ &\times (e^2/4\pi\varepsilon_0 r_{12})\chi_\lambda(2)\chi_\sigma(2) d\tau_1 d\tau_2 \\ &+ \int \chi_\mu(1)\chi_\nu(1)(e^2/4\pi\varepsilon_0 r_{12})\chi_\lambda(2)\chi_\sigma(2) \\ &\times (\mathbf{R}_{\lambda\sigma}\times\mathbf{r}_2)_t d\tau_1 d\tau_2 \Big]. \end{aligned} \tag{42}$$

We used in Eqs. (36) and (37) the Einstein summation convention over the repeated indices t and u.

The overlap integral $S_{\mu\nu}$ is also expanded as

$$S_{\mu\nu} = S_{\mu\nu}^0 + B_{0t}S_{\mu\nu,t}^{(1,0)} + \cdots, \tag{43}$$

where

$$S_{\mu\nu}^0 = \langle\chi_\mu|\chi_\nu\rangle \tag{44}$$

and

$$S_{\mu\nu,t}^{(1,0)} = i(e/2\hbar)\langle\chi_\mu|(\mathbf{R}_{\mu\nu}\times\mathbf{r})_t|\chi_\nu\rangle. \tag{45}$$

The density matrix expansion is found from the perturbation expansion of the occupied orbital coefficients $C_{\nu j}$,

$$C_{\nu j}=C^0_{\nu j}+B_{0t}C^{(1,0)}_{\nu j,t}+\mu_{Mu}C^{(0,1)}_{\nu j,u}+B_{0t}\mu_{Mu}C^{(1,1)}_{\nu j,tu}+\cdots . \tag{46}$$

The electronic energy of the system E_+ is presented by

$$E_+=\sum_{\mu\nu}\left[H_{\mu\nu}+1/2\sum_{\lambda\sigma}P_{\lambda\sigma}(G_{\mu\nu\lambda\sigma}-(1/2)G_{\mu\sigma\lambda\nu})\right]P_{\mu\nu}. \tag{47}$$

The electronic energy of the system is expanded as

$$E_+=E^0_+ +B_{0t}E^{(1,0)}_{+,t}+\mu_{Mu}E^{(0,1)}_{+,u}+B_{0t}\mu_{Mu}E^{(1,1)}_{+,tu}+\cdots . \tag{48}$$

Equation (30) means that $E^{(1,1)}_{+,tu}$ is equal to the nuclear magnetic shielding tensor component $\sigma_{tu}(M)$. Dodds *et al.*[20] showed that the nuclear magnetic shielding tensor component $\sigma_{tu}(M)$ is given by

$$\sigma_{tu}(M)=\sum_{\mu\nu}(H^{(1,1)}_{\mu\nu,tu}P^0_{\mu\nu}+H^{(0,1)}_{\mu\nu,u}P^{(1,0)}_{\mu\nu,t}). \tag{49}$$

The density matrix element $P^{(1,0)}_{\mu\nu,t}$ is given by[20]

$$\begin{aligned}P^{(1,0)}_{\mu\nu,t}=&-1/2\sum_{\lambda\sigma}P^0_{\mu\lambda}S^{(1,0)}_{\lambda\sigma,t}P^0_{\sigma\nu}\\&+2\sum_{j}^{\mathrm{occ}}\sum_{a}^{\mathrm{unocc}}(\varepsilon^0_j-\varepsilon^0_a)^{-1}(C^0_{\mu j}C^0_{\nu a}-C^0_{\mu a}C^0_{\nu j})\\&\times\sum_{\lambda\sigma}C^0_{\lambda j}(F^{(1,0)}_{\lambda\sigma,t}-\varepsilon^0_j S^{(1,0)}_{\lambda\sigma,t})C^0_{\sigma a},\end{aligned} \tag{50}$$

where ε^0_j and ε^0_a are the field independent orbital energies of occupied orbital j and unoccupied orbital a, respectively. Since the $F^{(1,0)}_{\mu\nu,t}$ is written as

$$\begin{aligned}F^{(1,0)}_{\mu\nu,t}=&H^{(1,0)}_{\mu\nu,t}+\sum_{\lambda\sigma}[P^{(1,0)}_{\lambda\sigma,t}(G^0_{\mu\nu\lambda\sigma}-(1/2)G^0_{\mu\sigma\lambda\nu})\\&+P^0_{\lambda\sigma}(G^{(1,0)}_{\mu\nu\lambda\sigma,t}-(1/2)G^{(1,0)}_{\mu\sigma\lambda\nu,t})],\end{aligned} \tag{51}$$

we have to solve Eq. (50) iteratively to get $P^{(1,0)}_{\mu\nu,t}$. The most attractive feature of Eq. (51) is the avoidance of the transformation of two-electron integrals from the GIAO base to the MO base.

At the limit of $c\to\infty$ Eq. (49) presents the nonrelativistic GIAO-CHF shielding values. Therefore we refer to the shielding value given by Eq. (49) as the spin independent relativistic GIAO-CHF shielding. We computed the relativistic and nonrelativistic nuclear magnetic shieldings in the four hydrogen halide molecules, HF, HCl, HBr, and HI, with uncontracted Cartesian Gaussian-type basis sets. The calculated results are presented in Table I. The used bond lengths and Gaussian exponents are given in our previous paper.[13] We divided the shielding component $\sigma_{tu}(M)$ given by Eq. (49) into the two parts, that is, $\sigma^d_{tu}(M)$ and $\sigma^p_{tu}(M)$. Those are defined as

$$\sigma^d_{tu}(M)=\sum_{\mu\nu}H^{(1,1)}_{\mu\nu,tu}P^0_{\mu\nu} \tag{52}$$

and

$$\sigma^p_{tu}(M)=\sum_{\mu\nu}H^{(0,1)}_{\mu\nu,u}P^{(1,0)}_{\mu\nu,t}, \tag{53}$$

respectively. It is shown that $\sigma^p_{\|}$ is zero.

It is interesting to compare the present results of the GIAO-CHF calculation with the fixed gauge-origin CHF results in our previous paper.[13] Table I shows that the GIAO-CHF results are quite similar to the shielding values calculated with the fixed gauge origins at the halogen nuclei. The present GIAO-CHF calculation indicates that the relativistic effects on the proton shielding constants are positive. The relativistic spin free effect on the proton shielding constant in the hydrogen iodide is $+2.41$ ppm, which is very close to the $+2.50$ ppm value obtained with the fixed gauge origin at the I nucleus.

Many years ago Schneider, Bernstein, and Pople[21] reported that the proton chemical shift of hydrogen halides, HX, shows the abnormal high-field resonance when X=Br or I. Table II presents the calculated and observed proton chemical shifts of hydrogen halides relative to the HF proton shielding constant. Our spin free relativistic calculation partly reproduces the upshield proton shifts in HCl, HBr, and HI molecules. However, the calculated spin independent relativistic effects are too small to interpret the observed large upshield proton shifts. It seems that the abnormal high-field proton shifts observed in hydrogen halides mainly come from the spin-orbit effect.[8,9,22,23] The calculation of relativistic spin dependent effects such as the spin-orbit effect on the magnetic shieldings will be presented in our future paper.

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APPENDIX

In this appendix we derive the field perturbation Hamiltonians which are correct to the c^{-2} order. Keeping all the terms to the lowest relativistic order c^{-2} with respect to the vector potentials we expand the kinetic energy as follows:

$$\begin{aligned}E_p=&E^0_p+B_{0t}E^{(1,0)}_{pt}+\mu_{Mu}E^{(0,1)}_{pu}\\&+B_{0t}\mu_{Mu}B^{(1,1)}_{ptu},\quad (t,u\in x,y,z),\end{aligned} \tag{A1}$$

where

$$\begin{aligned}&E^{(1,0)}_{pt}=\mu_B(l_{0t}+\sigma_t)+(e\hbar^3/8m^3_ec^2)[l_{0t}+\sigma_t,\Delta]_+,\\&\mathbf{l}_0=-i\mathbf{r}_0\times\boldsymbol{\nabla},\quad \mathbf{r}_0=\mathbf{r}-\mathbf{R}_0,\end{aligned} \tag{A2}$$

$$\begin{aligned}E^{(0,1)}_{pu}=&(\mu_0/4\pi)\mu_B[2r^{-3}_M l_{Mu}+(8\pi/3)\delta(\mathbf{r}_M)\sigma_u-r^{-3}_M\sigma_u\\&+3r^{-5}_M(\boldsymbol{\sigma}\cdot\mathbf{r}_M)r_{Mu}]+(\mu_0/4\pi)(e\hbar^3/8m^3_ec^2)\\&\times[2r^{-3}_M l_{Mu}+(8\pi/3)\delta(\mathbf{r}_M)\sigma_u-r^{-3}_M\sigma_u\\&+3r^{-5}_M(\boldsymbol{\sigma}\cdot\mathbf{r}_M)r_{Mu},\Delta]_+,\end{aligned} \tag{A3}$$

and

TABLE I. Relativistic and nonrelativistic nuclear magnetic shieldings (in ppm) in the four hydrogen halides of HF, HCl, HBr, and HI.

Molecule[a]	Basis set[b]	Nucleus		Nonrela.	Rela.	Rela.-Nonrela.
HF	$(13s8p3d/7s2p)$	F	$\sigma_{\perp}^{d}$	461.1	464.5	3.4
			$\sigma_{\perp}^{p}$	−81.7	−83.5	−1.7
			$\sigma_{\perp}$	379.3	381.0	1.7
			$\sigma_{\parallel}$	481.9	485.5	3.5
			σ_{iso}	413.5	415.8	2.3
		H	$\sigma_{\perp}^{d}$	18.94	18.97	0.02
			$\sigma_{\perp}^{p}$	1.96	2.06	0.10
			$\sigma_{\perp}$	20.91	21.03	0.13
			$\sigma_{\parallel}$	44.08	44.08	0.00
			σ_{iso}	28.63	28.72	0.08
HCl	$(15s12p6d/7s2p)$	Cl	$\sigma_{\perp}^{d}$	1144.2	1172.3	28.1
			$\sigma_{\perp}^{p}$	−293.6	−307.2	−13.7
			$\sigma_{\perp}$	850.6	865.0	14.4
			$\sigma_{\parallel}$	1149.1	1177.2	28.1
			σ_{iso}	950.1	969.1	19.0
		H	$\sigma_{\perp}^{d}$	22.28	22.32	0.04
			$\sigma_{\perp}^{p}$	1.01	1.23	0.22
			$\sigma_{\perp}$	23.30	23.56	0.26
			$\sigma_{\parallel}$	45.56	45.53	−0.02
			σ_{iso}	30.72	30.88	0.17
HBr	$(17s13p8d4f/7s2p)$	Br	$\sigma_{\perp}^{d}$	3119.5	3455.1	335.6
			$\sigma_{\perp}^{p}$	−717.7	−890.6	−172.9
			$\sigma_{\perp}$	2401.8	2564.5	162.7
			$\sigma_{\parallel}$	3126.2	3462.3	336.1
			σ_{iso}	2643.2	2863.8	220.5
		H	$\sigma_{\perp}^{d}$	18.03	18.20	0.17
			$\sigma_{\perp}^{p}$	3.83	4.87	1.04
			$\sigma_{\perp}$	21.86	23.07	1.21
			$\sigma_{\parallel}$	49.36	49.20	−0.16
			σ_{iso}	31.03	31.78	0.75
HI	$(19s15p12d8f/7s2p)$	I	$\sigma_{\perp}^{d}$	5502.2	7479.0	1976.7
			$\sigma_{\perp}^{p}$	−1447.3	−2648.6	−1201.3
			$\sigma_{\perp}$	4055.0	4830.4	775.5
			$\sigma_{\parallel}$	5504.6	7481.8	1977.1
			σ_{iso}	4538.2	5714.2	1176.0
		H	$\sigma_{\perp}^{d}$	16.68	17.09	0.41
			$\sigma_{\perp}^{p}$	4.13	7.43	3.30
			$\sigma_{\perp}$	20.81	24.53	3.71
			$\sigma_{\parallel}$	52.14	51.94	−0.19
			σ_{iso}	31.25	33.66	2.41

[a]Used bond lengths are given in Ref. 13.
[b]Uncontracted basis sets are used. The Gaussian exponents are presented in Ref. 13.

$$E_{ptu}^{(1,1)}=(\mu_0/4\pi)(e^2/2m_e)r_M^{-3}(\mathbf{r}_0\cdot\mathbf{r}_M\delta_{tu}-r_{0u}r_{Mt})$$
$$+(\mu_0/4\pi)(e^2\hbar^2/8m_e^3c^2)$$
$$\times\{[r_M^{-3}(\mathbf{r}_0\cdot\mathbf{r}_M\delta_{tu}-r_{0u}r_{Mt}),\Delta]_+$$
$$-[l_{0t}+\sigma_t,2r_M^{-3}l_{Mu}+(8\pi/3)\delta(\mathbf{r}_M)\sigma_u-r_M^{-3}\sigma_u$$
$$+3r_M^{-5}(\boldsymbol{\sigma}\cdot\mathbf{r}_M)r_{Mu}]_+\}. \quad \text{(A4)}$$

We used here the fixed gauge origin $\mathbf{R}_0$. $[A,B]_+$ means $AB+BA$.

We separate $\tilde{V}_n$ into the two part, $\tilde{V}_{n1}$ and $\tilde{V}_{n2}$, which are presented in Ref. 13. Since the leading term of $\tilde{V}_{n2}$ is of the order of c^{-4}, we can ignore the vector potential contribution coming from the $\tilde{V}_{n2}$ term. We only consider the vector potentials in the $\tilde{V}_{n1}$ term. We expand $\tilde{V}_n$ as

$$\tilde{V}_n=\tilde{V}_n^0+B_{0t}\tilde{V}_{nt}^{(1,0)}+\mu_{Mu}\tilde{V}_{nu}^{(0,1)}+B_{0t}\mu_{Mu}\tilde{V}_{ntu}^{(1,1)}, \quad \text{(A5)}$$

where $\tilde{V}_n^0$ is given by Eq. (63) in our previous paper.[13] The $\tilde{V}_{nt}^{(1,0)}$, $\tilde{V}_{nu}^{(0,1)}$, and $\tilde{V}_{ntu}^{(1,1)}$ terms are written as follows:

$$\tilde{V}_{nt}^{(1,0)}=(e\hbar/8m_e^2c^2)\boldsymbol{\sigma}\cdot(\boldsymbol{\nabla}V_n)\times(\hat{t}\times\mathbf{r}_0), \quad \text{(A6)}$$

$$\tilde{V}_{nu}^{(0,1)}=(\mu_0/4\pi)(e\hbar/4m_e^2c^2r_M^3)\boldsymbol{\sigma}\cdot(\boldsymbol{\nabla}V_n)\times(\hat{u}\times\mathbf{r}_M), \quad \text{(A7)}$$

TABLE II. The proton chemical shifts (in ppm) of hydrogen halides relative to the HF proton shielding constant. The positive sign of the chemical shifts indicates a low-field shift.

	HCl	HBr	HI
Nonrela. calc.	−2.08	−2.39	−2.62
Rela. calc.	−2.17	−3.06	−4.95
Observed[a]	−2.95	−6.85	−15.75

[a]Reference 21.

and

$$\tilde{V}_{ntu}^{(1,1)}=0. \tag{A8}$$

$\hat{t}$ and $\hat{u}$ are the unit vectors with the t and u directions, respectively. The parentheses in (∇V_n) indicate that ∇ operates solely on V_n.

The direct use of DK transformed electron-electron interaction is not realistic. Our previous paper expanded the DK transformed electron-electron interaction in the power series of the inverse light velocity and ignored the terms higher then c^{-2}. Keeping terms to the lowest relativistic order of c^{-2} we expand the DK transformed electron-electron interaction as follows:

$$\sum_{j<k}^{n}[\tilde{V}_{ee}(j,k)+\tilde{B}_{ee}(j,k)] =\sum_{j<k}^{n}V_{ee}(j,k)+H^{(r)}+B_{0t}H_{eet}^{(1,0)} +\mu_{Mu}H_{eeu}^{(0,1)}+B_{0t}\mu_{Mu}H_{eetu}^{(1,1)}, \tag{A9}$$

where

$$V_{ee}(j,k)=e^2/4\pi\varepsilon_0 r_{jk}. \tag{A10}$$

Here V_{ee} is the nonrelativistic electron-electron interaction and $H^{(r)}$ is the field independent relativistic correction to the electron-electron interaction. The relativistic perturbation $H^{(r)}$ is given by rows (68)–(72) in our previous paper.[13] The field dependent relativistic perturbation terms $H_{eet}^{(1,0)}$, $H_{eeu}^{(0,1)}$, and $H_{eetu}^{(1,1)}$ are obtain by substituting $\boldsymbol{\pi}=\mathbf{p}+e\mathbf{A}_0+e\mathbf{A}_M$ for $\mathbf{p}$ in $H^{(r)}$. The field dependent electron-electron interaction terms are written as follows:

$$\begin{aligned}H_{eet}^{(1,0)}=\sum_{j<k}^{n}[&(e^3\hbar/32\pi\varepsilon_0 m_e^2c^2r_{jk}^3)(2\boldsymbol{\sigma}_j\cdot\mathbf{r}_{jk}\times(\hat{t}\times\mathbf{r}_{k0})\\ &-2\sigma_k\cdot\mathbf{r}_{jk}\times(\hat{t}\times\mathbf{r}_{j0})-\boldsymbol{\sigma}_j\cdot\mathbf{r}_{jk}\times(\hat{t}\times\mathbf{r}_{j0})\\ &+\boldsymbol{\sigma}_k\cdot\mathbf{r}_{jk}\times(\hat{t}\times\mathbf{r}_{k0}))-(e^3/16\pi\varepsilon_0 m_e^2c^2)\\ &\times(\mathbf{p}_j\cdot r_{jk}^{-1}\hat{t}\times\mathbf{r}_{k0}+\hat{t}\times\mathbf{r}_{j0}\cdot r_{jk}^{-1}\mathbf{p}_k+\mathbf{p}_j\cdot\mathbf{r}_{jk}r_{jk}^{-3}\mathbf{r}_{jk}\cdot\mathbf{t}\\ &\times\mathbf{r}_{k0}+\hat{t}\times\mathbf{r}_{j0}\cdot\mathbf{r}_{jk}r_{jk}^{-3}\mathbf{r}_{jk}\cdot\mathbf{p}_k)],\end{aligned}$$

$$\mathbf{r}_{j0}=\mathbf{r}_j-\mathbf{R}_0,\quad \mathbf{r}_{jk}=\mathbf{r}_j-\mathbf{r}_k, \tag{A11}$$

$$\begin{aligned}H_{eeu}^{(0,1)}=\sum_{j<k}^{n}[&(\mu_0/4\pi)(e^3\hbar/16\pi\varepsilon_0 m_e^2c^2r_{jk}^3)(2\boldsymbol{\sigma}_j\cdot\mathbf{r}_{jk}(\hat{u}\times\mathbf{r}_{kM})r_{kM}^{-3}-2\boldsymbol{\sigma}_k\cdot\mathbf{r}_{jk}(\hat{u}\times\mathbf{r}_{jM})r_{jM}^{-3}\\ &-\boldsymbol{\sigma}_j\cdot\mathbf{r}_{jk}(\hat{u}\times\mathbf{r}_{jM})r_{jM}^{-3}+\boldsymbol{\sigma}_k\cdot\mathbf{r}_{jk}\times(\hat{u}\times\mathbf{r}_{kM})r_{kM}^{-3})-(\mu_0/4\pi)(e^3/8\pi\varepsilon_0 m_e^2c^2)(\mathbf{p}_j\cdot r_{jk}^{-1}\hat{u}\times\mathbf{r}_{kM}r_{kM}^{-3}\\ &+r_{jM}^{-3}\hat{u}\times\mathbf{r}_{jM}\cdot r_{jk}^{-1}\mathbf{p}_k+\mathbf{p}_j\cdot\mathbf{r}_{jk}r_{jk}^{-3}\mathbf{r}_{jk}\cdot\hat{u}\times\mathbf{r}_{kM}r_{kM}^{-3}+r_{jM}^{-3}\hat{u}\\ &\times\mathbf{r}_{jM}\cdot\mathbf{r}_{jk}r_{jk}^{-3}\mathbf{r}_{jk}\cdot\mathbf{p}_k)],\quad \mathbf{r}_{jM}=\mathbf{r}_j-\mathbf{R}_M,\end{aligned} \tag{A12}$$

and

$$\begin{aligned}H_{eetu}^{(1,1)}=&-(\mu_0/4\pi)(e^4/16\pi\varepsilon_0 m_e^2c^2)\\ &\times\sum_{j<k}^{n}[\hat{t}\times\mathbf{r}_{j0}\cdot r_{jk}^{-1}\hat{u}\times\mathbf{r}_{kM}r_{kM}^{-3}\\ &+\hat{t}\times\mathbf{r}_{k0}\cdot r_{jk}^{-1}\hat{u}\times\mathbf{r}_{jM}r_{jM}^{-3}+\hat{t}\times\mathbf{r}_{j0}\cdot\mathbf{r}_{jk}r_{jk}^{-3}\mathbf{r}_{jk}\cdot\hat{u}\\ &\times\mathbf{r}_{kM}r_{kM}^{-3}+\hat{t}\times\mathbf{r}_{k0}\cdot\mathbf{r}_{jk}r_{jk}^{-3}\mathbf{r}_{jk}\cdot\hat{u}\times\mathbf{r}_{jM}r_{jM}^{-3}].\end{aligned} \tag{A13}$$

The E_p^0, $\tilde{V}_n^0$, and V_{ee} constitute the unperturbed eigenvalue equation, and $H^{(r)}$ and the field dependent terms form the perturbation Hamiltonians for the system. We write the full positive energy Hamiltonian H_+ as follows:

$$H_+=H^0+H^{(r)}+B_{0t}H_t^{(1,0)}+\mu_{Mu}H_u^{(0,1)}+B_{0t}\mu_{Mu}H_{tu}^{(1,1)}, \tag{A14}$$

where

$$H^0=\sum_{j=1}^{n}[E_p^0(j)-m_ec^2+\tilde{V}_n^0(j)]+\sum_{j<k}^{n}(e^2/4\pi\varepsilon_0 r_{jk}), \tag{A15}$$

$$H_t^{(1,0)}=\sum_{j=1}^{n}[E_{pt}^{(1,0)}(j)+\tilde{V}_{nt}^{(1,0)}(j)]+H_{eet}^{(1,0)}, \tag{A16}$$

$$H_u^{(0,1)}=\sum_{j=1}^{n}[E_{pu}^{(0,1)}(j)+\tilde{V}_{nu}^{(0,1)}(j)]+H_{eeu}^{(0,1)}, \tag{A17}$$

and

$$H_{tu}^{(1,1)}=\sum_{j=1}^{n}E_{ptu}^{(1,1)}(j)+H_{eetu}^{(1,1)}. \tag{A18}$$

Using GIAO basis functions we can shift the gauge origin from the fixed origin $\mathbf{R}_0$ to the center of the GIAO basis function $\mathbf{R}_\nu$. The effect on the Hamiltonian H^+ of introducing the gauge factor f_ν is not presented here.

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