Relativistic calculation of nuclear magnetic shielding tensor including two-electron spin-orbit interactions

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A relativistic calculation of nuclear magnetic shielding tensor including two-electron spin-orbit interactions is performed. In order to reduce the computational load in evaluating the two-electron relativistic integrals, the charge density is approximated by a linear combination of the squares of *s*-type spatial basis functions. Including the two-electron spin-orbit interaction effect is found to improve the calculation results. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2361292]

I. INTRODUCTION

An electron in a heavy atom can be considered an observer of relativistic phenomena. Especially, it is known that nuclear magnetic resonance (NMR) chemical shielding tensor is a sensitive probe for detecting relativistic effects.[1–7] Since the relativistic electronic structures of molecules are expressed by the four-component Dirac equation, it is natural to use four-component wave functions for theoretical calculations of NMR chemical shielding tensors. Although *ab initio* four-component relativistic calculations of NMR chemical shieldings have been performed,[8–11] the two-component theory is still important and effective. The main difficulties in four-component calculations of NMR chemical shieldings are the severe requirements on the small-component wave function calculation and the necessity of performing negative continuum state calculation for evaluation of the diamagnetic component.[12–14]

We have recently presented a relativistic theory for calculating nuclear magnetic shielding[15] based on the regular approximation to the method of normalized elimination of the small component (NESC).[16–18] The NESC method was first proposed by Dyall[16,17] as the exact two-component method which yields the positive-energy solutions of the Dirac equation. The NESC method has essentially variational stability. Dyall considered in Ref. 17 an approximation to the NESC method, but it did not produce variationally stable solutions. Filatov and Cremer[18] applied the regular approximation to the exact NESC theory by Dyall and obtained numerical stability in a quasivariational scheme. We introduced magnetic interactions in the regular approximation to the NESC theory and used it to the calculation of nuclear magnetic shielding in H*X* (*X*=F,Cl,Br,I) systems for comparison with previously reported values.[10,11,19,20] We used two levels of approximation, the zeroth-order regular approximation (NESC-ZORA) and the second-order regular approximation (NESC-SORA), in our calculation of the nuclear magnetic shielding. We found that the NESC-SORA results are slightly farther from the benchmark results obtained by using the four-component fully relativistic Dirac-Hartree-Fock (DHF) calculation than those of NESC-ZORA. This finding was unexpected.

In our previous NESC calculations we ignored the two-electron relativistic contributions. It is likely that the most important neglected contribution was the two-electron spin-orbit (SO) effect. This effect attenuates the one-electron SO effect of the bare nuclear charges, and hence neglecting the two-electron SO effect will lead to an overestimation of the SO effect in the nuclear magnetic shielding.[21] In the present paper, we evaluate the two-electron SO effect on nuclear magnetic shielding in hydrogen halide molecules. In the following section, we survey the theory.

II. THEORY

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

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

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

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

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

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

Here, $\boldsymbol{\alpha}$ and β are the usual 4×4 Dirac vector and scalar matrices, $V_n(\mathbf{r})$ is the bare nuclear potential, and $\mathbf{R}_0$ is the position of the common gauge origin. The nucleus M at the position $\mathbf{R}_M$ is the target nucleus of the nuclear magnetic shielding calculations. In order to derive the two-component equation, the ith four-component wave function ψ_{Di} is written using the large two-component spinor ϕ_{Li} and the small two-component spinor ϕ_{Si}. In the NESC scheme, ϕ_{Si} is connected with ϕ_{Li} via a general nonunitary transformation operator U,

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

The transformation operator U can be self-consistently determined for many-electron systems, as presented in our previous paper,[15]

$$U = \left[T - \frac{1}{4c^2}\boldsymbol{\sigma}\cdot\boldsymbol{\pi}(V_n + J_{LL})\boldsymbol{\sigma}\cdot\boldsymbol{\pi} + H_A\right]^{-1} \times\left[T - \frac{1}{4c^2}\boldsymbol{\sigma}\cdot\boldsymbol{\pi}K_{LS} - \frac{1}{2c^2}(T+H_A)US^{-1}F + H_A\right], \tag{7}$$

where

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

and

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

S is the metric operator that provides the proper orthonormal relation between large-component wave functions, that is,

$$\langle\psi_{Di}|\psi_{Dj}\rangle = \langle\phi_{Li}|S|\phi_{Lj}\rangle = \delta_{ij}. \tag{10}$$

S is written as

$$S = 1 + \frac{1}{2c^2}U^\dagger(T+H_A)U. \tag{11}$$

F is the two-component Fock operator, written as

$$F = TU + U^\dagger T - U^\dagger TU + V_n + \frac{1}{4c^2}U^\dagger\boldsymbol{\sigma}\cdot\boldsymbol{\pi}(V_n + J_{LL})\boldsymbol{\sigma}\cdot\boldsymbol{\pi}U + J_{LL} - K_{LL} + \frac{1}{4c^2}J_{SS} - \frac{1}{4c^2}K_{SL}\boldsymbol{\sigma}\cdot\boldsymbol{\pi}U - \frac{1}{4c^2}U^\dagger\boldsymbol{\sigma}\cdot\boldsymbol{\pi}K_{LS} + H_AU + U^\dagger H_A - U^\dagger H_AU. \tag{12}$$

The two-electron operators J_{LL}, J_{SS}, K_{LL}, K_{LS}, and K_{SL} are defined as follows:

$$J_{LL} = \sum_j^{\text{occ}}\int \phi_{Lj}^\dagger(2)\frac{1}{r_{12}}\phi_{Lj}(2)d\tau_2, \tag{13}$$

$$J_{SS} = \sum_j^{\text{occ}}\int [\Pi(2)\phi_{Lj}(2)]^\dagger\frac{1}{r_{12}}[\Pi(2)\phi_{Lj}(2)]d\tau_2, \tag{14}$$

$$K_{LL} = \sum_j^{\text{occ}}\int \phi_{Lj}^\dagger(2)\frac{1}{r_{12}}\hat{P}_{12}\phi_{Lj}(2)d\tau_2, \tag{15}$$

$$K_{LS} = \sum_j^{\text{occ}}\int \phi_{Lj}^\dagger(2)\frac{1}{r_{12}}\hat{P}_{12}[\Pi(2)\phi_{Lj}(2)]d\tau_2, \tag{16}$$

$$K_{SL} = \sum_j^{\text{occ}}\int [\Pi(2)\phi_{Lj}(2)]^\dagger\frac{1}{r_{12}}\hat{P}_{12}\phi_{Lj}(2)d\tau_2. \tag{17}$$

Here, $\Pi = \boldsymbol{\sigma}\cdot\boldsymbol{\pi}U$ and $\hat{P}_{12}$ is the operator interchanging the two electrons, labeled 1 and 2. $\int d\tau_2$ represents two-component integration with respect to electron 2. The large two-component wave functions ϕ_{Li} $(i=1,2,\ldots)$ are determined self-consistently as the solutions of the eigenvalue equations

$$F\phi_{Li} = \varepsilon_i S\phi_{Li}, \quad i = 1,2,\ldots. \tag{18}$$

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

$$\phi_{Li} = \sum_{\mu=1}^{m} a_{\mu i}\chi_\mu; \quad i = 1,2,\ldots,m. \tag{19}$$

To satisfy Eq. (18), the coefficient $a_{\mu i}$ is determined by the equation

$$FA = SA\mathcal{E}, \tag{20}$$

where A is the matrix of the coefficients $a_{\mu i}$ $(\mu=1,2,\ldots,m;$ $i=1,2,\ldots,m)$ and $\mathcal{E}$ is a diagonal matrix that includes the eigenvalues ε_i as diagonal elements.

III. RESULTS AND DISCUSSION

In our previous paper, we simplified the matrices U, F, and S as follows.

(i) All c^{-2} order two-electron operators, i.e., J_{LL}, J_{SS}, K_{SL}, and K_{LS} terms multiplied by $1/4c^2$, were neglected from U and F. However, the nonrelativistic two-electron part in F, i.e., $J_{LL}-K_{LL}$, was retained in Eqs. (7) and (12).

(ii) H_A and all magnetic operators arising from $\boldsymbol{\sigma}\cdot\boldsymbol{\pi}$ were neglected from U because they contribute to F and S in the order of c^{-4}.

(iii) The H_A term in S was neglected for simplicity though it contributes to S in the order of c^{-2}.

According to these simplifications U is considerably simplified to

$$U = \left[T - \frac{1}{4c^2}\boldsymbol{\sigma}\cdot\mathbf{p}V_n\boldsymbol{\sigma}\cdot\mathbf{p}\right]^{-1}\left[T - \frac{1}{2c^2}TUS^{-1}F\right], \tag{21}$$

where F is the Fock operator simplified due to (i).

We introduce in the present work $(1/4c^2)\boldsymbol{\sigma}\cdot\mathbf{p}J_{LL}\boldsymbol{\sigma}\cdot\mathbf{p}$ in U and $(1/4c^2)U^\dagger\boldsymbol{\sigma}\cdot\boldsymbol{\pi}J_{LL}\boldsymbol{\sigma}\cdot\boldsymbol{\pi}U$ in F, both of which were neglected in our previous calculation. However, it is still necessary to avoid a significant computational load in evaluating the matrices which include the operator J_{LL}. Hence we approximate the charge density $\Sigma_j^{\text{occ}}\phi_{Li}^\dagger\phi_{Li}$ in Eq. (13) by a linear combination of the squares of the real and spin-independent s-type spatial basis functions, $(g_k^s)^2$ $(k=1,2,\ldots)$.

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

Molecule	Nucleus	Property	NR[a]	SORA[b]	SORA+J_{LL}[c]	DHF[d]
HF	F	$\sigma_\perp$	378.5	387.9	387.5	384.9
		$\sigma_\parallel$	478.8	487.0	486.7	485.6
		σ^{iso}[e]	412.0	421.0	420.6	418.4
		$\Delta\sigma$[f]	100.3	99.0	99.2	100.7
	H	$\sigma_\perp$	18.63	20.24	20.20	20.10
		$\sigma_\parallel$	42.91	44.04	44.07	43.90
		σ^{iso}[e]	26.72	28.17	28.15	28.03
		$\Delta\sigma$[f]	24.28	23.80	23.88	23.80
HCl	Cl	$\sigma_\perp$	857.4	898.8	897.1	888.5
		$\sigma_\parallel$	1144.6	1185.5	1184.3	1176.7
		σ^{iso}[e]	953.1	994.3	992.8	984.5
		$\Delta\sigma$[f]	287.2	286.7	287.2	288.2
	H	$\sigma_\perp$	22.81	24.38	24.22	24.07
		$\sigma_\parallel$	44.54	45.36	45.42	45.39
		σ^{iso}[e]	30.05	31.37	31.29	31.18
		$\Delta\sigma$[f]	21.73	20.97	21.20	21.32
HBr	Br	$\sigma_\perp$	2375.0	2807.3	2796.7	2738.1
		$\sigma_\parallel$	3097.6	3455.1	3447.4	3402.1
		σ^{iso}[e]	2615.9	3023.3	3013.6	2959.4
		$\Delta\sigma$[f]	722.6	647.8	650.8	664.0
	H	$\sigma_\perp$	20.31	30.12	29.53	29.82
		$\sigma_\parallel$	48.50	48.05	48.28	47.93
		σ^{iso}[e]	29.70	36.10	35.78	35.86
		$\Delta\sigma$[f]	28.20	17.93	18.74	18.11
HI	I	$\sigma_\perp$	3880.9	5847.8	5810.5	5571.9
		$\sigma_\parallel$	5332.9	6881.7	6863.1	6597.1
		σ^{iso}[e]	4364.9	6192.4	6161.4	5913.7
		$\Delta\sigma$[f]	1451.9	1033.9	1052.4	1025.2
	H	$\sigma_\perp$	19.28	49.15	47.65	46.92
		$\sigma_\parallel$	50.74	45.95	46.66	47.31
		σ^{iso}[e]	29.76	48.08	46.99	47.05
		$\Delta\sigma$[f]	31.49	−3.20	−1.00	0.39

[a]Nonrelativistic results taken from Ref. 19.
[b]NESC-SORA results taken from Ref. 15.
[c]Present NESC-SORA results including the operator $\boldsymbol{\sigma}\cdot\boldsymbol{\pi}J_{LL}\boldsymbol{\sigma}\cdot\boldsymbol{\pi}/4c^2$.
[d]Dirac-Hartree-Fock calculation results taken from Ref. 11.
[e]$\sigma^{\mathrm{iso}}=\frac{1}{3}(2\sigma_\parallel+\sigma_\perp)$.
[f]$\Delta\sigma=\sigma_\parallel-\sigma_\perp$.

The charge density ρ is written as

$$\rho=\sum_{j}^{\mathrm{occ}}\phi_{Lj}^{\dagger}\phi_{Lj}=\rho_{\alpha\alpha}\alpha^{\dagger}\alpha+\rho_{\beta\beta}\beta^{\dagger}\beta+\rho_{\alpha\beta}\alpha^{\dagger}\beta+\rho_{\beta\alpha}\beta^{\dagger}\alpha. \tag{22}$$

In our scheme, $\rho_{\alpha\alpha}+\rho_{\beta\beta}$ is approximated as

$$\rho_{\alpha\alpha}+\rho_{\beta\beta}\cong\sum_{k}D_k(g_k^s)^2. \tag{23}$$

Then,

$$J_{LL}=\sum_{k}D_k\int g_k^s(2)\frac{1}{r_{12}}g_k^s(2)d\mathbf{r}_2. \tag{24}$$

The coefficients D_k are determined by the least square method. As an example, in our calculation of the HI molecule, the large-component wave function ϕ_{Lj} (j=1,2,…) was made up of a linear combination of 814 spin-included basis functions χ_μ while $\rho_{\alpha\alpha}+\rho_{\beta\beta}$ was approximated by the linear combination of the squares of only 37 s-type spatial basis functions $(g_k^s)^2$. The approximation of Eq. (23) therefore reduces the computational load considerably. The matrix elements of

$$\langle\chi_\mu|\boldsymbol{\sigma}\cdot\mathbf{p}J_{LL}\boldsymbol{\sigma}\cdot\mathbf{p}|\chi_\nu\rangle$$

and

$$\langle\chi_\mu|U^{\dagger}\boldsymbol{\sigma}\cdot\boldsymbol{\pi}J_{LL}\boldsymbol{\sigma}\cdot\boldsymbol{\pi}U|\chi_\nu\rangle$$

can be evaluated using Eq. (24) and the resolution of the identity (RI).[18] Furthermore, the integrals

$$\langle \chi_\mu | \boldsymbol{\sigma} \cdot \mathbf{p} J_{LL} \boldsymbol{\sigma} \cdot \mathbf{p} | \chi_\nu \rangle$$

are easily computed using integration by parts.

We have confirmed the reliability of the approximation of Eq. (23), finding that the errors due to the approximation of Eq. (23) are less than 0.1% for both $\langle \chi_\mu | J_{LL} | \chi_\nu \rangle$ and $\langle \chi_\mu | p_t J_{LL} p_u | \chi_\nu \rangle$ $(t,u \in x,y,z)$.

The results of calculations of nuclear magnetic shielding tensor components (in ppm) for HX (X=F,Cl,Br,I) systems are presented in Table I. In the table, σ^{iso} is $(2\sigma_\perp + \sigma_\parallel)/3$ and $\Delta\sigma$ is defined as $\sigma_\parallel - \sigma_\perp$. The results of the present calculations, including the operator $\boldsymbol{\sigma} \cdot \boldsymbol{\pi} J_{LL} \boldsymbol{\sigma} \cdot \boldsymbol{\pi}$, are shown in the SORA+$J_{LL}$ column. The table compares the present SORA +J_{LL} values with nonrelativistic (NR) values,[19] NESC-SORA values,[15] and DHF values.[11] The present SORA+J_{LL}, previous NESC-SORA, and NR calculations use experimental atomic distances[22] and a pointlike nuclear model. The basis set functions used for SORA+J_{LL} are the same as for the previous SORA calculations. The common gauge origin $\mathbf{R}_0$ is placed on the halogen nuclei.

Table I shows that the SORA+J_{LL} results are closer to the benchmark results of DHF than those of SORA. The proton shielding results are especially improved, due to the fact that relativistic effects on the proton shielding in HX systems are mainly due to the spin-orbit interaction.[23] For the halogen shielding, however, considerable differences still remain between the SORA+J_{LL} and DHF results. The exchange terms of K_{LS} and K_{SL} are neglected in the present SORA+J_{LL} calculation as they seem to be much smaller than the J_{LL} terms. The neglected J_{SS} term may have a larger effect on the shielding than the exchange terms, but it cannot be evaluated simply. Another possible source of error in the shielding calculation is the neglect of the $(1/2c^2)U^\dagger H_A U$ term in the metric operator S in Eq. (11).

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