

Relativistic calculation of nuclear magnetic shielding tensor using the regular approximation to the normalized elimination of the small component. II. Consideration of perturbations in the metric operator

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A previous relativistic shielding calculation theory based on the regular approximation to the normalized elimination of the small component approach is improved by the inclusion of the magnetic interaction term contained in the metric operator. In order to consider effects of the metric perturbation, the self-consistent perturbation theory is used for the case of perturbation-dependent overlap integrals. The calculation results show that the second-order regular approximation results obtained for the isotropic shielding constants of halogen nuclei are well improved by the inclusion of the metric perturbation to reproduce the fully relativistic four-component Dirac-Hartree-Fock results. However, it is shown that the metric perturbation hardly or does not affect the anisotropy of the halogen shielding tensors and the proton magnetic shieldings. © 2007 American Institute of Physics. [DOI: 10.1063/1.2733650]

I. INTRODUCTION

Evaluation of relativistic effects on molecular properties is one of the most important problems in quantum chemistry. The methodology for relativistic calculation of molecular properties is divided into two sets of methods, i.e., four-component (normally called fully relativistic) and two-component (normally called quasirelativistic) methods, and each set has merits and demerits, individually. Compared with four-component methods, two-component approaches are computationally much less demanding, but two-component approaches involve too complicated operators and are plagued by the so-called picture change problem. Although both sets are not complete, both sets have been applied to relativistic evaluation of molecular properties with considerable success in the last decade.

We have recently presented a theory for relativistically calculating nuclear magnetic shielding¹ based on the regular approximation^{2,3} to the method of normalized elimination of the small component (NESC).^{4,5} The NESC method was proposed by Dyall^{4,5} as the first exact two-component method which yields the positive energy solutions of the Dirac equation. Later, Filatov and Cremer⁶ applied the regular approximation to the exact NESC theory by Dyall and obtained numerical stability in a quasivariational scheme. Several variants of the NESC theory are proposed and discussed in the paper by Liu and Peng.⁷ We introduced magnetic interactions in the regular approximation to the NESC theory and used it to the relativistic calculation of nuclear magnetic shielding tensors in HX (X=F, Cl, Br, I) systems for comparison with previously reported values.⁸⁻¹¹ 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 tensors. We found that the NESC-SORA

results are slightly farther from the benchmark results⁹ obtained by using the fully relativistic four-component Dirac-Hartree-Fock (DHF) calculation than those of NESC-ZORA. This finding was unexpected.

In the previous NESC calculations¹ we ignored the relativistic two-electron contribution and the magnetic interaction term contained in the metric operator. All the neglected operators have the order of c^{-2} . In order to improve our regular approximation of NESC method, the two-electron spin-orbit (SO) interaction effect, neglected in Ref. 1, was added in the next publication.¹² This calculation method was dubbed as NESC-SORA+ J_{LL} . The calculation showed that inclusion of the two-electron SO term improves the results, especially the results for the proton shieldings in HX systems. However, it was shown that considerable differences still remain between our results and DHF results.⁹ In the present paper, we include in the theory the c^{-2} order magnetic perturbation term in the metric operator to improve our regular approximation of NESC calculation. The authors have already published a paper¹¹ developing a relativistic theory for molecular magnetic property calculation, in which infinite-order two-component (IOTC) theory by Barysz and Sadlej¹³ is used. The IOTC theory yields the exact decoupling of the positive and negative energy spectra of a one-electron system, but it includes a cumbersome problem of the so-called picture change error (PCE) for the two-electron interactions. The NESC theory is free from the PCE problem and may provide a simple formulation for introducing relativistic two-electron interactions into the theory. This is a motivation for us to develop the regular approximation of NESC method for calculating relativistic effects on molecular properties. In the following section, we survey the regular approximation to the NESC theory including the metric perturbation.

II. THEORY

A. A brief description of the regular approximation to NESC 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 M th nuclear position \mathbf{R}_M is given in a.u. ($\hbar=1$, $e=1$, $m_e=1$, and $4\pi\epsilon_0=1$. Therefore, $\mu_0/4\pi=c^{-2}$ and $c=137.035\,989\,5$) by

$$H_D\psi_{Di} = \varepsilon_i\psi_{Di}, \quad i = 1, 2, \dots, \quad (1)$$

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

$$\boldsymbol{\pi} = \mathbf{p} + \mathbf{A} = \mathbf{p} + \mathbf{A}_0 + \mathbf{A}_M, \quad (3)$$

$$\mathbf{A}_0 = \frac{1}{2}\mathbf{B}_0 \times \mathbf{r}_0, \quad \mathbf{r}_0 = \mathbf{r} - \mathbf{R}_0, \quad (4)$$

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

Here, $\boldsymbol{\alpha}$ and β are the usual 4×4 Dirac vector and scalar matrices, $V_n(\mathbf{r})$ is the nuclear attraction 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 present nuclear magnetic shielding tensor calculation. The i th four-component wave function ψ_{Di} with the eigenvalue ε_i is written using the large two-component spinor ϕ_{Li} and the small two-component spinor ϕ_{Si} . In the NESC approach, ϕ_{Si} is connected with ϕ_{Li} via an energy-dependent nonunitary transformation operator $U(\varepsilon_i)$,

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

The transformation operator U implicitly depends on the energy eigenvalue ε_i . The energy dependence of U is given by a substitution of U into the Dirac equation.

For a many-electron system, the transformation operator U must be determined self-consistently. The large two-component wave function ϕ_{Li} ($i=1, 2, \dots$) are written as a linear combination of spin including basis functions, $\chi_1, \chi_2, \dots, \chi_m$. We write ϕ_{Li} ($i=1, 2, \dots, m$) as

$$\phi_{Li} = \sum_{\mu=1}^m a_{\mu i}\chi_{\mu}, \quad i = 1, 2, \dots, m. \quad (7)$$

The linear combination coefficients $a_{\mu i}$ and the orbital energies ε_i are written as matrices, and they are determined by solving the self-consistent field (SCF) equation

$$FA = SA\varepsilon, \quad (8)$$

where A is the matrix consisting of the coefficients $a_{\mu i}$ and ε is the diagonal matrix consisting of the eigenvalues ε_i . The Fock matrix F and the metric matrix S are computed using the operators

$$\begin{aligned} F &= TU + U^\dagger T - U^\dagger TU + V_n \\ &+ \frac{1}{4c^2}U^\dagger \boldsymbol{\sigma} \cdot \boldsymbol{\pi}(V_n + J_{LL})\boldsymbol{\sigma} \cdot \boldsymbol{\pi}U + J_{LL} \\ &- K_{LL} + H_A U + U^\dagger H_A - U^\dagger H_A U \end{aligned} \quad (9)$$

and

$$S = 1 + \frac{1}{2c^2}U^\dagger(T + H_A)U, \quad (10)$$

respectively. Here, $(1/2c^2)U^\dagger H_A U$ in S is the magnetic perturbation term in the metric operator which was neglected in the previous works. The kinetic energy operator T and the magnetic interaction operator H_A are defined as

$$T = \frac{1}{2}p^2 \quad (11)$$

and

$$H_A = \frac{1}{2}(\boldsymbol{\sigma} \cdot \boldsymbol{\pi})^2 - T, \quad (12)$$

respectively. The two-electron interaction operators J_{LL} and K_{LL} are given by

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

and

$$K_{LL} = \sum_j^{\text{occ}} \phi_{Lj}^\dagger(2) \frac{1}{r_{12}} \hat{P}_{12} \phi_{Lj}(2) d\tau_2, \quad (14)$$

respectively. \hat{P}_{12} is the operator interchanging the two electrons, labeled 1 and 2. Finally, the transformation matrix U is computed from the operator

$$U = \left[T - \frac{1}{4c^2} \boldsymbol{\sigma} \cdot \mathbf{p}(V_n + J_{LL})\boldsymbol{\sigma} \cdot \mathbf{p} \right]^{-1} \left[T - \frac{1}{2c^2} T U S^{-1} F \right]. \quad (15)$$

The matrix F in Eq. (15) yields the energy dependence of U . Since the transformation matrix U includes the Fock matrix F and J_{LL} , U must be determined iteratively, starting from the initial conditions of $U, F=0$ and $J_{LL}=0$.

B. Magnetic perturbation expansion

Since the metric operator S includes H_A , the magnetic perturbation expansion of the total electronic energy E of the system becomes rather cumbersome. This problem is stated in the present subsection. The nuclear magnetic shielding tensor component $\sigma_{\alpha\beta}^M(\boldsymbol{\alpha}, \boldsymbol{\beta} \in x, y, z)$ is equal to the second-order perturbation coefficient $E_{\alpha\beta}^{(1,1)}$ which yields the electronic energy bilinear in $B_{0\alpha}$ and $\mu_{M\beta}$. The formulation for $E_{\alpha\beta}^{(1,1)}$ is given in the Appendix. The Eq. (A18) for $E_{\alpha\beta}^{(1,1)}$ is mathematically equivalent to Eq. (38) in the paper by Dodds *et al.*¹⁴ when perturbation-independent basis functions are used. However, Eq. (38) by Dodds *et al.* is rather complicated and not transparent. We use Eq. (A18) for $E_{\alpha\beta}^{(1,1)}$.

The perturbation calculation of $E_{\alpha\beta}^{(1,1)}$ needs the following one-electron operators of $H_{\alpha}^{(1,0)}$, $H_{\beta}^{(0,1)}$, $H_{\alpha\beta}^{(1,1)}$, $S_{\alpha}^{(1,0)}$, $S_{\beta}^{(0,1)}$, and $S_{\alpha\beta}^{(1,1)}$. From Eq. (10), the metric perturbation term is equal to $U^{\dagger}H_A U/2c^2$. Therefore, the calculation of a shielding tensor component needs only the perturbation expansions for H_A and H . The one-electron Hamiltonian H of the system is given by

$$H = TU + U^{\dagger}T - U^{\dagger}TU + V_n + \frac{1}{4c^2}U^{\dagger}\boldsymbol{\sigma} \cdot \boldsymbol{\pi}V_n\boldsymbol{\sigma} \cdot \boldsymbol{\pi}U \\ + H_A U + U^{\dagger}H_A - U^{\dagger}H_A U. \quad (16)$$

The perturbation expansions for H_A and H are presented in our previous paper.¹

III. RESULTS AND DISCUSSION

The present calculation uses experimental atomic distances¹⁸ and a pointlike nuclear model. The common gauge origin \mathbf{R}_0 is placed on the halogen nuclei. We perform the shielding tensor calculation for HX (X=F, Cl, Br, I), systems at the three levels of approximation, i.e., NESC-ZORA, NESC-SORA, and NESC-SORA+ J_{LL} including the metric perturbation. The NESC-ZORA calculation neglects $(1/4c^2)U^{\dagger}\boldsymbol{\sigma} \cdot \boldsymbol{\pi}J_{LL}\boldsymbol{\sigma} \cdot \boldsymbol{\pi}U$ term in the F matrix and $-(1/4c^2)\boldsymbol{\sigma} \cdot \mathbf{p}J_{LL}\boldsymbol{\sigma} \cdot \mathbf{p}$ and $-(1/2c^2)TUS^{-1}F$ terms in the U matrix. The NESC-SORA calculation keeps $-(1/2c^2)TUS^{-1}F$ term in the transformation matrix U . The NESC-SORA+ J_{LL} calculation uses Eq. (9) for the F matrix and Eq. (15) for the U matrix without neglect. In the present calculation, the magnetic interaction term in the metric operator S , i.e., $(1/2c^2)U^{\dagger}H_A U$ is considered for comparison with our previous results neglecting the above magnetic term in the S matrix. The results obtained with and without inclusion of the metric perturbation are shown Table I. Moreover, the DHF values^{9,19} are presented as the benchmark and our previous IOTC results¹¹ are shown for comparison. The results including the metric perturbation are listed in Table I as the ZORA-Met, SORA-Met, and SORA+ J_{LL} -Met. The basis sets used in the present calculations are (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. 1.

Table I shows that the inclusion of the metric perturbation considerably improves the NESC-SORA results for the isotropic shielding constants of halogen nuclei. When the magnetic interaction in the metric is considered, the NESC-SORA-Met result for σ^{iso} (iodine) is much closer to the fully relativistic four-component DHF value than that of the NESC-ZORA-Met. The NESC-ZORA-Met result for σ^{iso} (iodine) becomes too low. The isotropic shielding constant of iodine, σ^{iso} (I), is lowered by about 300 ppm by the inclusion of the metric perturbation. The reduction of σ^{iso} is due to the paramagnetic contribution while the diamagnetic contribution is slightly raised by inclusion of the magnetic interaction in the metric. As a whole, the metric perturbation reduces the isotropic magnetic shielding constants of halogen nuclei. To the contrary, the inclusion of the metric perturbation hardly

or does not affect the anisotropy of the halogen shielding tensors and the proton magnetic shieldings. It is concluded that both the NESC-SORA-Met and NESC-SORA+ J_{LL} -Met approaches can reproduce the halogen shieldings of the fully relativistic DHF as a rule. The effects of the two-electron spin-orbit interaction, i.e., SO2 term are not so large in the halogen shieldings. However, as for the proton shieldings, the results of the NESC-SORA+ J_{LL} -Met are better than those of the NESC-SORA-Met. The inclusion of the two-electron SO interaction improves the proton shielding results. The small difference in the proton shieldings between the NESC-SORA+ J_{LL} -Met and DHF results may be reduced to the difference between the used basis set functions and the neglect of other c^{-2} order relativistic two-electron contributions to the F matrix than $(1/4c^2)U^{\dagger}\boldsymbol{\sigma} \cdot \boldsymbol{\pi}J_{LL}\boldsymbol{\sigma} \cdot \boldsymbol{\pi}U$. Unexpectedly, the inclusion of the two-electron SO interaction in the SORA+ J_{LL} -Met calculation worsens a little the results for σ^{iso} (I) and $\Delta\sigma$ (I). This may be due to the neglect of the other relativistic two-electron interactions coming from J_{LS} , J_{SL} , and J_{SS} terms. A fortuitous error cancellation may exist in the NESC-SORA-Met calculation. Finally, the comparison with the IOTC results shows that the qualities of the NESC-SORA+ J_{LL} -Met and IOTC calculations are comparable for the halogen and proton shieldings as a whole. For halogen nuclei, the IOTC method is a little better while for proton shieldings, the NESC-SORA+ J_{LL} -Met method is a little better. The IOTC method treats the two-electron interactions nonrelativistically. A fortuitous error cancellation may exist in the IOTC calculation of halogen shieldings.

IV. CONCLUSION

In order to consider the effects of the perturbation term contained in the metric operator S , we used the self-consistent perturbation theory for the case in which the overlap integrals are perturbation dependent. The calculation including the metric perturbation was performed for the nuclear magnetic shielding tensors in HX (X=F, Cl, Br, I) systems for comparison with our previously reported results neglecting the magnetic interaction term in the metric operator. The calculation results showed that the metric perturbation considerably lowers the isotropic shielding constants of halogen nuclei and the NESC-SORA results are so much improved. As a result of inclusion of the metric perturbation, the NESC-SORA results become much closer to the fully relativistic DHF results than those of the NESC-ZORA. It was shown that the metric perturbation strongly affects the isotropic shielding constants of halogen nuclei while the anisotropy of the halogen shielding tensors and the proton magnetic shieldings are hardly or not affected.

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

Molecule	Nucleus	Property	ZORA ^a	SORA ^b	SORA+ J_{LL} ^c	ZORA-Met ^d	SORA-Met ^e	SORA+ J_{LL} -Met ^f	DHF ^g	IOTC ^h
HF	F	σ_{\perp} (para)	-92.4	-92.5		-93.9	-94.0	-94.6		-91.4
		σ_{\perp} (dia)	480.4	480.4		480.7	480.7	480.9		475.4
		σ_{\perp} (total)	388.0	387.9	387.5	386.8	386.7	386.3	384.9	384.0
		σ_{\parallel} (para)	7.5	7.4		6.0	5.9	5.4		8.4
		σ_{\parallel} (dia)	479.6	479.6		479.8	479.8	480.0		474.6
		σ_{\parallel} (total)	487.1	487.0	486.7	485.8	485.7	485.4	485.6	483.0
		σ^{iso} (total) ⁱ	421.0	421.0	420.6	419.8	419.7	419.3	418.4	417.0
	$\Delta\sigma$ (total) ^j	99.0	99.0	99.2	99.0	99.0	99.2	100.7	99.0	
	H	σ_{\perp} (para)	18.89	18.89		18.89	18.89	18.85		18.92
		σ_{\perp} (dia)	1.34	1.34		1.34	1.34	1.35		0.01
		σ_{\perp} (total)	20.24	20.24	20.20	20.24	20.24	20.20	20.10	18.93
		σ_{\parallel} (para)	0.00	0.00		-0.01	-0.01	0.00		0.01
		σ_{\parallel} (dia)	44.04	44.04		44.04	44.04	44.07		42.89
		σ_{\parallel} (total)	44.04	44.04	44.07	44.04	44.04	44.07	43.90	42.89
σ^{iso} (total) ⁱ		28.17	28.17	28.15	28.17	28.17	28.16	28.03	26.92	
$\Delta\sigma$ (total) ^j	23.80	23.80	23.88	23.80	23.80	23.88	23.80	23.96		
HCl	Cl	σ_{\perp} (para)	-237.4	-237.4		-247.7	-247.8	-250.6		-232.0
		σ_{\perp} (dia)	1136.3	1136.2		1138.0	1137.9	1139.1		1124.6
		σ_{\perp} (total)	898.9	898.8	897.1	890.3	890.2	888.5	888.5	892.6
		σ_{\parallel} (para)	52.1	52.1		41.8	41.8	39.4		56.4
		σ_{\parallel} (dia)	1133.5	1133.4		1135.2	1135.1	1136.3		1121.8
		σ_{\parallel} (total)	1185.6	1185.5	1184.3	1177.1	1176.9	1175.7	1176.7	1178.3
		σ^{iso} (total) ⁱ	994.4	994.3	992.8	985.9	985.7	984.3	984.5	987.8
	$\Delta\sigma$ (total) ^j	286.7	286.7	287.2	286.7	286.7	287.2	288.2	285.7	
	H	σ_{\perp} (para)	22.49	22.49		22.49	22.49	22.32		22.51
		σ_{\perp} (dia)	1.89	1.89		1.89	1.89	1.90		1.05
		σ_{\perp} (total)	24.38	24.38	24.22	24.38	24.38	24.22	24.07	23.56
		σ_{\parallel} (para)	-0.01	-0.01		-0.01	-0.01	0.00		0.01
		σ_{\parallel} (dia)	45.36	45.37		45.37	45.37	45.42		44.40
		σ_{\parallel} (total)	45.35	45.36	45.42	45.35	45.35	45.42	45.39	44.41
σ^{iso} (total) ⁱ		31.37	31.37	31.29	31.37	31.37	31.29	31.18	30.51	
$\Delta\sigma$ (total) ^j	20.97	20.97	21.20	20.97	20.97	21.20	21.32	20.85		
HBr	Br	σ_{\perp} (para)	-192.0	-176.1		-281.8	-271.3	-288.7		-171.2
		σ_{\perp} (dia)	2987.6	2983.5		3005.4	3001.7	3010.2		2929.6
		σ_{\perp} (total)	2795.6	2807.3	2796.7	2723.5	2730.4	2721.5	2738.1	2758.3
		σ_{\parallel} (para)	458.8	474.7		368.5	379.9	365.0		472.1
		σ_{\parallel} (dia)	2984.6	2980.4		3002.3	2998.7	3007.1		2927.9
		σ_{\parallel} (total)	3443.4	3455.1	3447.4	3370.9	3378.5	3372.1	3402.1	3400.0
		σ^{iso} (total) ⁱ	3011.5	3023.3	3013.6	2939.3	2946.4	2938.3	2959.4	2972.2
	$\Delta\sigma$ (total) ^j	647.8	647.8	650.8	647.3	648.1	650.6	664.0	641.7	
	H	σ_{\perp} (para)	30.12	30.12		30.12	30.12	29.53		30.04
		σ_{\perp} (dia)	-0.01	-0.01		-0.01	-0.01	0.00		-0.79
		σ_{\perp} (total)	30.12	30.12	29.53	30.11	30.11	29.53	29.82	29.26
		σ_{\parallel} (para)	-0.45	-0.45		-0.45	-0.45	-0.37		-0.38
		σ_{\parallel} (dia)	48.50	48.50		48.50	48.50	48.65		48.23
		σ_{\parallel} (total)	48.05	48.05	48.28	48.05	48.05	48.28	47.93	47.85
σ^{iso} (total) ⁱ		36.10	36.10	35.78	36.09	36.09	35.78	35.86	35.46	
$\Delta\sigma$ (total) ^j	17.93	17.93	18.74	17.94	17.94	18.75	18.11	18.59		
HI	I	σ_{\perp} (para)	578.8	879.8		267.5	509.2	449.6		708.0
		σ_{\perp} (dia)	5001.2	4967.9		5067.8	5037.9	5063.6		4870.7
		σ_{\perp} (total)	5580.0	5847.8	5810.5	5335.3	5547.2	5513.2	5571.9	5578.7
		σ_{\parallel} (para)	1615.7	1917.1		1306.8	1547.0	1507.1		1691.0
		σ_{\parallel} (dia)	4997.9	4964.6		5064.4	5034.6	5060.2		4868.7
		σ_{\parallel} (total)	6613.6	6881.7	6863.1	6371.3	6581.6	6567.3	6597.1	6559.7
		σ^{iso} (total) ⁱ	5924.5	6192.4	6161.4	5680.6	5892.0	5864.6	5913.7	5905.7
	$\Delta\sigma$ (total) ^j	1033.5	1033.9	1052.4	1036.0	1034.4	1054.2	1025.2	981.0	
	H	σ_{\perp} (para)	50.94	50.95		50.94	50.95	49.44		50.00
		σ_{\perp} (dia)	-1.76	-1.80		-1.76	-1.80	-1.79		-1.61
		σ_{\perp} (total)	49.18	49.15	47.65	49.18	49.15	47.65	46.92	48.39
		σ_{\parallel} (para)	-4.32	-4.32		-4.32	-4.32	-3.88		-3.95

TABLE I. (Continued.)

Molecule	Nucleus	Property	ZORA ^a	SORA ^b	SORA+ J_{LL} ^c	ZORA-Met ^d	SORA-Met ^e	SORA+ J_{LL} -Met ^f	DHF ^g	IOTC ^h
		$\sigma_{\parallel}(\text{dia})$	50.30	50.28		50.30	50.28	50.54		50.16
		$\sigma_{\parallel}(\text{total})$	45.98	45.95	46.66	45.98	45.95	46.66	47.31	46.21
		$\sigma^{\text{iso}}(\text{total})^i$	48.11	48.08	47.32 ^k	48.11	48.08	47.32	47.05	47.66
		$\Delta\sigma(\text{total})^j$	-3.19	-3.20	-1.00	-3.19	-3.20	-0.99	0.39	-2.18

^aNESC-ZORA results taken from Ref. 1.^bNESC-SORA results taken from Ref. 1.^cNESC-SORA+ J_{LL} results taken from Ref. 12.^dPresent NESC-ZORA results including the magnetic interaction term in the metric operator.^ePresent NESC-SORA results including the magnetic interaction term in the metric operator.^fPresent NESC-SORA+ J_{LL} results including the magnetic interaction term in the metric operator.^gDirac-Hartree-Fock results taken from Refs. 9 and 19.^hInfinite-order two-component calculation results taken from Ref. 11.ⁱ $\sigma^{\text{iso}} = (1/3)(2\sigma_{\perp} + \sigma_{\parallel})$.^j $\Delta\sigma = \sigma_{\parallel} - \sigma_{\perp}$.^kThe value of 46.99 in Ref. 12 should be corrected to 47.32.

APPENDIX: SELF-CONSISTENT THEORY INCLUDING THE METRIC PERTURBATION

A self-consistent perturbation theory for perturbation-dependent overlap integrals has already been derived by Dodds *et al.*¹⁴ However, we present a simpler formula for calculating the second-order perturbation energy for the case of perturbation-dependent metric operator. The total electronic energy E is given by

$$E = \text{Tr} \left(H + \frac{1}{2}G \right) \rho, \quad (\text{A1})$$

where ρ is the density matrix, H is the one-electron Hamiltonian matrix, and G is a matrix defined by

$$G_{\mu\nu} = \sum_{\lambda\sigma} g_{\mu\nu,\lambda\sigma} \rho_{\sigma\lambda}, \quad (\text{A2})$$

$$\begin{aligned} g_{\mu\nu,\lambda\sigma} &= \langle \chi_{\mu} \chi_{\lambda} | \chi_{\nu} \chi_{\sigma} \rangle - \langle \chi_{\mu} \chi_{\lambda} | \chi_{\sigma} \chi_{\nu} \rangle \\ &= (\chi_{\mu} \chi_{\nu} | \chi_{\lambda} \chi_{\sigma}) - (\chi_{\mu} \chi_{\sigma} | \chi_{\lambda} \chi_{\nu}). \end{aligned} \quad (\text{A3})$$

The one-electron Hamiltonian operator H is given in the text. The density matrix ρ is related to the expansion coefficients of the occupied large two-component spinors ϕ_{Li} by the equation

$$\rho_{\mu\nu} = \sum_i^{\text{occ}} a_{\mu i} a_{\nu i}^*. \quad (\text{A4})$$

We use from now the suffixes i, j, k for occupied orbitals, u, v, w for virtual orbitals, and p, q, r for occupied or virtual unspecified orbitals. There are two kinds of perturbations, i.e., α ($\alpha \in x, y, z$) component of the external magnetic flux density, $B_{0\alpha}$, and the β ($\beta \in x, y, z$) component of the nuclear magnetic moment, $\mu_{M\beta}$. The perturbation term of the m th order with respect to \mathbf{B}_0 and the n th order with respect to $\boldsymbol{\mu}_M$ is denoted as (m, n) . Our aim is to derive the total electronic energy change $E_{\alpha\beta}^{(1,1)} B_{0\alpha} \mu_{M\beta}$ which is bilinear in $B_{0\alpha}$ and $\mu_{M\beta}$. The orbital coefficient a_{vi} is expanded as

$$\begin{aligned} a_{vi} &= a_{vi}^{(0)} + \sum_{\alpha} a_{vi\alpha}^{(1,0)} B_{0\alpha} + \sum_{\beta} a_{vi\beta}^{(0,1)} \mu_{M\beta} + \sum_{\alpha\beta} a_{vi\alpha\beta}^{(1,1)} B_{0\alpha} \mu_{M\beta} \\ &+ \dots, \end{aligned} \quad (\text{A5})$$

where $a_{vi}^{(0)} = a_{vi}^{(0,0)}$. $\rho_{\mu\nu}$ is expanded similarly. From the definition of the density matrix, element of $\rho_{\alpha}^{(1,0)}$ is written as

$$\rho_{\mu\nu\alpha}^{(1,0)} = \sum_i^{\text{occ}} (a_{\mu i\alpha}^{(1,0)} a_{\nu i}^{(0)*} + a_{\mu i}^{(0)} a_{\nu i\alpha}^{(1,0)*}). \quad (\text{A6})$$

We assume that the first-order orbital $\phi_{Li\alpha}^{(1,0)}$ is expanded in terms of the zeroth-order orbitals $\phi_{Lp}^{(0)}$ using the orbital projection coefficients $d_{pi\alpha}^{(1,0)}$.

$$a_{\mu i\alpha}^{(1,0)} = \sum_p d_{pi\alpha}^{(1,0)} a_{\mu p}^{(0)}. \quad (\text{A7})$$

The orbital projection coefficients $d_{pi\alpha}^{(1,0)}$ are divided into the two parts of the occupied orbital coefficients $d_{pi\alpha}^{(1,0)}$ and the virtual orbital coefficients $d_{ui\alpha}^{(1,0)}$. The coefficients $d_{ji\alpha}^{(1,0)}$ can be determined from the orbital normalization condition. We have

$$d_{ji\alpha}^{(1,0)} = -\frac{1}{2} S_{ji\alpha}^{(1,0)}. \quad (\text{A8})$$

The coefficients $d_{ui\alpha}^{(1,0)}$ can be determined from the first-order perturbed SCF equation for ϕ_{Li} . We obtain

$$d_{ui\alpha}^{(1,0)} = (\varepsilon_i^{(0)} - \varepsilon_u^{(0)})^{-1} [F_{ui\alpha}^{(1,0)} - \varepsilon_i^{(0)} S_{ui\alpha}^{(1,0)}]. \quad (\text{A9})$$

Equations (A6)–(A9) yield the formula for $\rho_{\alpha}^{(1,0)}$. The similar formula is obtained for $\rho_{\beta}^{(0,1)}$.

The total electronic energy E is expanded into the series similar to Eq. (A5),

$$\begin{aligned} E &= E^{(0)} + \sum_{\alpha} E_{\alpha}^{(1,0)} B_{0\alpha} + \sum_{\beta} E_{\beta}^{(0,1)} \mu_{M\beta} + \sum_{\alpha\beta} E_{\alpha\beta}^{(1,1)} B_{0\alpha} \mu_{M\beta} \\ &+ \dots \end{aligned} \quad (\text{A10})$$

Using Eq. (A1), the second-order perturbation energy bilinear in $B_{0\alpha}$ and $\mu_{M\beta}$ is given by

$$\begin{aligned}
E_{\alpha\beta}^{(1,1)} = & \text{Tr}(H^{(0)}\rho_{\alpha\beta}^{(1,1)} + H_{\alpha}^{(1,0)}\rho_{\beta}^{(0,1)} + H_{\beta}^{(0,1)}\rho_{\alpha}^{(1,0)} + H_{\alpha\beta}^{(1,1)}\rho^{(0)}) \\
& + \frac{1}{2}G^{(0)}\rho_{\alpha\beta}^{(1,1)} + \frac{1}{2}G_{\alpha}^{(1,0)}\rho_{\beta}^{(0,1)} + \frac{1}{2}G_{\beta}^{(0,1)}\rho_{\alpha}^{(1,0)} \\
& + \frac{1}{2}G_{\alpha\beta}^{(1,1)}\rho^{(0)}. \quad (\text{A11})
\end{aligned}$$

Using a symmetry of the two-electron interaction integrals

$$g_{\mu\nu,\lambda\sigma} = g_{\lambda\sigma,\mu\nu} \quad (\text{A12})$$

and the relation

$$F = H + G, \quad (\text{A13})$$

$E_{\alpha\beta}^{(1,1)}$ is written with a simpler formula

$$\begin{aligned}
E_{\alpha\beta}^{(1,1)} = & \text{Tr}(F^{(0)}\rho_{\alpha\beta}^{(1,1)} + F_{\alpha}^{(1,0)}\rho_{\beta}^{(0,1)} + H_{\beta}^{(0,1)}\rho_{\alpha}^{(1,0)}) \\
& + H_{\alpha\beta}^{(1,1)}\rho^{(0)}. \quad (\text{A14})
\end{aligned}$$

The second-order orbitals $\phi_{Li\alpha\beta}^{(1,1)}$ is likewise expanded in terms of the zeroth-order orbitals $\phi_{Lp}^{(0)}$. We obtain

$$\begin{aligned}
\text{Tr}(F^{(0)}\rho_{\alpha\beta}^{(1,1)}) = & \sum_i \varepsilon_i^{(0)}(d_{ii\alpha\beta}^{(1,1)} + d_{ii\alpha\beta}^{(1,1)*}) \\
& + \sum_i \sum_p \varepsilon_p^{(0)}(d_{pi\alpha}^{(1,0)}d_{pi\beta}^{(0,1)*} + d_{pi\alpha}^{(1,0)*}d_{pi\beta}^{(0,1)}). \quad (\text{A15})
\end{aligned}$$

It is known that knowledge of all the orbital perturbations up to the n th order is sufficient to determine all the electronic energy perturbations up to the order $(2n+1)$.^{15,16} Furthermore, Dalgarno's interchange theorem^{16,17} makes it possible to express $E_{\alpha\beta}^{(1,1)}$ by using $d_{\alpha}^{(1,0)}$ or $d_{\beta}^{(0,1)}$ alone. According to the $(2n+1)$ rule, $d^{(1,1)}$ terms are eliminated and we obtain

$$\begin{aligned}
\text{Tr}(F^{(0)}\rho_{\alpha\beta}^{(1,1)}) = & \sum_i [(\varepsilon_i^{(0)}S_{ii\alpha}^{(1,0)} - F_{ii\alpha}^{(1,0)})S_{ii\beta}^{(0,1)} - \varepsilon_i^{(0)}S_{ii\alpha\beta}^{(1,0)}] \\
& - \sum_i \sum_p [d_{pi\beta}^{(0,1)*}F_{pi\alpha}^{(1,0)} + d_{pi\beta}^{(0,1)}F_{pi\alpha}^{(1,0)*} \\
& + \varepsilon_i^{(0)}(d_{pi\alpha}^{(1,0)*}S_{pi\beta}^{(0,1)} + d_{pi\alpha}^{(1,0)}S_{pi\beta}^{(0,1)*})]. \quad (\text{A16})
\end{aligned}$$

The second contribution for $E_{\alpha\beta}^{(1,1)}$ in Eq. (A14) is

$$\text{Tr}(F_{\alpha}^{(1,0)}\rho_{\beta}^{(0,1)}) = \sum_i \sum_p (d_{pi\beta}^{(0,1)*}F_{pi\alpha}^{(1,0)} + d_{pi\beta}^{(0,1)}F_{pi\alpha}^{(1,0)*}). \quad (\text{A17})$$

Equation (A14) gives us the final formula for $E_{\alpha\beta}^{(1,1)}$,

$$\begin{aligned}
E_{\alpha\beta}^{(1,1)} = & \sum_i [(\varepsilon_i^{(0)}S_{ii\alpha}^{(1,0)} - F_{ii\alpha}^{(1,0)})S_{ii\beta}^{(0,1)} - \varepsilon_i^{(0)}S_{ii\alpha\beta}^{(1,1)} + H_{ii\alpha\beta}^{(1,1)}] \\
& + \sum_i \sum_p [H_{pi\beta}^{(0,1)*}d_{pi\alpha}^{(1,0)} + H_{pi\beta}^{(0,1)}d_{pi\alpha}^{(1,0)*} \\
& - \varepsilon_i^{(0)}(S_{pi\beta}^{(0,1)*}d_{pi\alpha}^{(1,0)} + S_{pi\beta}^{(0,1)}d_{pi\alpha}^{(1,0)*})]. \quad (\text{A18})
\end{aligned}$$

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