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核磁気遮蔽テンソルの相対論的計算

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Abstract: The relativistic calculation of nuclear magnetic shielding tensors in hydrogen halides is performed using the second-order regular approximation to the normalized elimination of the small component (SORA-NESC) method with the inclusion of the perturbation terms from the metric operator. This computational scheme is denoted as SORA-Met. The SORA-Met calculation yields anisotropies, $\Delta\sigma = \sigma_{\parallel} - \sigma_{\perp}$, for the halogen nuclei in hydrogen halides that are too small. In the NESC theory, the small component of the spinor is combined to the large component via the operator $\vec{\sigma}\cdot\vec{\pi}U/2c$, in which $\vec{\pi} = \vec{p} + \vec{A}$, U is a nonunitary transformation operator, and $c \cong 137.036$ a.u. is the velocity of light. The operator U depends on the vector potential $\vec{A}$ (i.e., the magnetic perturbations in the system) with the leading order c^{-2} and the magnetic perturbation terms of U contribute to the Hamiltonian and metric operators of the system in the leading order c^{-4}. It is shown that the small $\Delta\sigma$ for halogen nuclei found in our previous studies is related to the neglect of the $U^{(0,1)}$ perturbation operator of U, which is independent of the external magnetic field and of the first order with respect to the nuclear magnetic dipole moment. Introduction of gauge-including atomic orbitals (GIAOs) and a finite-size nuclear model is also discussed.

RESULTS AND DISCUSSION

It was concluded that neither the resolution of identity (IR) approximation nor the inadequancy of the basis sets is the cause of the small $\Delta\sigma$ values of halogen nuclei. In order to search for the cause of our small $\Delta\sigma$ for halogen nuclei, we investigate the effects of the magnetic perturbation terms originating from the transformation matrix $\tilde{U}$. The magnetic perturbation terms of $\tilde{U}$ (i.e., $\tilde{U}^{(1,0)}$, $\tilde{U}^{(0,1)}$, and $\tilde{U}^{(1,1)}$) contribute to F and M matrices only in the order of c^{-4} and smaller. We expand $\tilde{U}$ in the magnetic perturbation parameter $c^{-2}\mu_{Mu}$ ($u \in x, y, z$) as

$$\tilde{U} = \tilde{U}^{(0)} + c^{-2}\sum_{u}\mu_{Mu}\tilde{U}_{u}^{(0,1)} + \cdots .$$

We add the $\tilde{U}_{u}^{(0,1)}$ ($u \in x, y, z$) perturbation terms to the perturbed Fock $F_{u}^{(0,1)}$ and metric $M_{u}^{(0,1)}$ matrices. The results are presented in the fourth column of Table I (labeled SORA-Met-$\tilde{U}^{(0,1)}$). The results of SORA-Met-$\tilde{U}^{(0,1)}$ exhibit a quasi-divergent behavior for iodine nucleus. The $\tilde{U}^{(0,1)}$ terms exert a surprisingly large effect on the $\sigma_{\perp}$(para) and $\sigma_{\parallel}$(para) of iodine, which is an unexpected result. Although the $\Delta\sigma$ for I is too large, the direction of change is correct. The $\Delta\sigma$ for Br is improved.

The divergence caused by the inclusion of $\tilde{U}^{(0,1)}$ may come from the point nuclear model. In order to prevent this divergence, we introduce a finite-size nuclear model to the SORA-Met-$\tilde{U}^{(0,1)}$ calculation. The results of finite-size nuclei are presented in the fifth column of Table I (labeled SORA-Met-$\tilde{U}^{(0,1)}$-Fn). The results for SORA-Met-$\tilde{U}^{(0,1)}$-Fn show a convergent and mild behavior for the $\sigma_{\perp}$(para) and $\sigma_{\parallel}$(para) values of iodine, but the $\Delta\sigma$ value of I is still too large. However, the $\Delta\sigma$ value of Br obtained by SORA-Met-$\tilde{U}^{(0,1)}$-Fn agrees well with the DHF (Dirac-Hartree-Fock) value. It is concluded that the small $\Delta\sigma$ values for halogen nuclei is due to neglecting the $\tilde{U}^{(0,1)}$ perturbation terms and that the use of a more sophisticated finite-size nuclear model is essential to accurately reproduce the $\Delta\sigma$ values of DHF.

TABLE I. Calculated nuclear magnetic shielding tensor components (in ppm) in HBr and HI systems.

Molecule	Nucleus	Property	SORA-Met-$\tilde{U}^{(0,1)}$[a]	SORA-Met-$\tilde{U}^{(0,1)}$-Fn[b]	DHF[c]
HBr	Br	$\sigma_\perp$(para)	−335.6	−327.5	
		$\sigma_\perp$(dia)	3102.1	3102.6	
		$\sigma_\perp$(total)	2766.5	2775.1	2738.1
		$\sigma_\parallel$(para)	315.9	336.7	
		$\sigma_\parallel$(dia)	3099.1	3099.5	
		$\sigma_\parallel$(total)	3415.0	3436.2	3402.1
		$\sigma^{\rm iso}$(total)	2982.6	2995.4	2959.4
		$\Delta\sigma$(total)	648.6	661.1	664.0
	H	$\sigma_\perp$(para)	30.12	30.12	
		$\sigma_\perp$(dia)	−0.02	−0.02	
		$\sigma_\perp$(total)	30.10	30.10	29.82
		$\sigma_\parallel$(para)	−0.46	−0.46	
		$\sigma_\parallel$(dia)	48.53	48.53	
		$\sigma_\parallel$(total)	48.07	48.07	47.93
		$\sigma^{\rm iso}$(total)	36.09	36.09	35.86
		$\Delta\sigma$(total)	17.97	17.97	18.11
HI	I	$\sigma_\perp$(para)	−6931.5	−207.4	
		$\sigma_\perp$(dia)	5415.3	5418.5	
		$\sigma_\perp$(total)	−1516.2	5211.1	5571.9
		$\sigma_\parallel$(para)	12036.2	1791.3	
		$\sigma_\parallel$(dia)	5411.9	5415.1	
		$\sigma_\parallel$(total)	17448.2	7206.4	6597.1
		$\sigma^{\rm iso}$(total)	4805.2	5876.2	5913.7
		$\Delta\sigma$(total)	18964.4	1995.3	1025.2
	H	$\sigma_\perp$(para)	50.95	50.95	
		$\sigma_\perp$(dia)	−1.82	−1.82	
		$\sigma_\perp$(total)	49.14	49.13	46.92
		$\sigma_\parallel$(para)	−4.33	−4.33	
		$\sigma_\parallel$(dia)	50.32	50.32	
		$\sigma_\parallel$(total)	45.99	45.99	47.31
		$\sigma^{\rm iso}$(total)	48.09	48.09	47.05
		$\Delta\sigma$(total)	−3.15	−3.14	0.39

[a] Present results obtained by adding $\tilde{U}^{(0,1)}$ perturbation terms to the perturbed Fock and metric matrices.
[b] Present results obtained by applying a finite-size nuclear model to the calculation of SORA-Met-$\tilde{U}^{(0,1)}$.
[c] Dirac-Hartree-Fock results taken from Refs. [1] and [2].

References

[1] P. Manninen, K. Rund, P. Lantto, and J. Vaara, J. Chem. Phys. **122**, 114107 (2005); **124**, 149901 (E) (2006).

[2] P. Manninen and J. Vaara, J. Chem. Phys. **124**, 137101 (2006).