4P080

小成分消去法による核磁気しゃへいテンソルの相対論的計算

（北見工業大学）○前田倫，大谷優介，福井洋之

Abstract: 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.

We have recently presented a theory for relativistically calculating nuclear magnetic shielding based on the regular approximation to the method of normalized elimination of the small component (NESC). The NESC method was proposed by Dyall [1] as the first exact two-component method which yields the positive-energy solutions of the Dirac equation. Later, Filatov and Cremer [2] 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 [3]. 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 [4]. 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 results obtained by using the fully relativistic four-component Dirac-Hartree-Fock (DHF) calculation than those of NESC-ZORA. The NESC-SORA results for I shielding were too high. This finding was unexpected.

In the previous NESC calculations 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 (SO2) interaction effect, neglected in Ref. [4], was added in the next publication [5]. This calculation method was dubbed as NESC-SORA+J_{LL}. The calculation showed that inclusion of the SO2 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. In the present work, we included 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 paper [6] developing a relativistic theory for molecular magnetic property calculation, in which infinite-order two-component (IOTC) theory by Barysz and Sadlej [7] 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.

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.

ACKNOWLEDGMENT

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

References

[1] K. G. Dyall, J. Chem. Phys. **106**, 9618 (1997).

[2] M. Filatov and D. Cremer, J. Chem. Phys. **122**, 064104 (2005).

[3] W. Liu and D. Peng, J. Chem. Phys. **125**, 044102 (2006).

[4] K. Kudo, H. Maeda, T. Kawakubo, Y. Ootani, M. Funaki, and H. Fukui, J. Chem. Phys. **124**, 224106 (2006).

[5] Y. Ootani, H. Yamaguti, H. Maeda, and H. Fukui, J. Chem. Phys. **125**, 164106 (2006).

[6] K. Kudo and H. Fukui, J. Chem. Phys. **123**, 114102 (2005); **124**, 209901 (E) (2006).

[7] M. Barysz and A. J. Sadlej, J. Chem. Phys. **116**, 2696 (2002).