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ユニタリ変換法による核磁気遮蔽テンソルの相対論的計算

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Abstract: A two-component relativistic theory accurately decoupling the positive and negative states of the Dirac Hamiltonian is derived. The derived theory eliminates all of the odd terms originating from the nuclear attraction potential V and the first-order odd terms originating from the magnetic vector potential $\vec{A}$, which connect the positive states to the negative states. The decoupling is exact for the magnetic shielding calculation. The calculation of the diamagnetic property requires both the positive and negative states of the unperturbed ($\vec{A} = 0$) Hamiltonian. The derived theory is applied to the relativistic calculation of nuclear magnetic shielding tensors of HX (X=F, Cl, Br, I) systems at the Hartree-Fock level. The results indicate that such an exact decoupling calculation well reproduces the four-component Dirac-Hartree-Fock results.

Due to recent developments in the relativistic quantum theory and its applications, the accuracy of the quasirelativistic theory, i.e., the two-component Hamiltonian method for calculating the relativistic effects on molecular properties, has greatly increased. There are two approaches to incorporate relativistic effects on the molecular properties in the two-component framework. One approach is a treatment using nonrelativistic wave functions and incorporating relativistic effects as passive or active perturbations, which are obtained from the Breit-Pauli Hamiltonian. The other approach is a variational treatment that involves calculating the stationary states of a quasirelativistic Hamiltonian. The latter approach is separated into a unitary decoupling transformation method based on the Douglas-Kroll-Hess (DKH) transformation [1] and a method of eliminating the small component (ESC) [2]-[4], which sometimes uses the regular approximation.

There are only two basic types of properties that might occur within a four-component Hamiltonian. Electric or electric-field-like properties are generally described by an even, i.e., diagonal block, perturbation Hamiltonian $H_{\mathcal{E}}$. In contrast to the electric properties, the magnetic or magnetic-field-like properties are described by an odd, i.e., off-diagonal block, perturbation Hamiltonian $H_{\mathcal{O}}$. The relativistic treatment for magnetic properties is more difficult than for electric properties. For example, in order to evaluate the diamagnetic part of a magnetic shielding tensor in the two-component scheme, the four-component interaction Hamiltonian has to be magnetically decoupled and a quadratic operator with respect to the vector potential $\vec{A}$ has to be obtained. In our previous infinite-order DKH (DKH∞) study[1], the nuclear attraction potential V is completely decoupled, but the decoupling of the vector potential $\vec{A}$ is incomplete. An odd term of the first order with respect to $\vec{A}$ remains in the unitary transformed Hamiltonian and the neglected odd term will lead to an error of electronic energy of second order with respect to $\vec{A}$. In the present study, we derived a theory to decouple all of the scalar potential terms of V and the first-order vector potential term of $\vec{A}$. The obtained positive even block of Hamiltonian is correct to the third order with respect to $\vec{A}$ due to the (2n+1) rule. Therefore, the decoupling will yield an exact magnetic energy for the calculation of magnetic shieldings. The magnetic shielding tensor components are easily computed via an analytical differentiation of the electronic energy of the system.

The present calculation used experimental atomic distances [5] and a point-like nuclear model. We performed the shielding tensor calculation for HX (X=F, Cl, Br, I) systems at the Hartree-Fock level. The common gauge origin $\vec{R}_0$ was placed on the halogen nuclei. The used basis sets are as follows: (12s10p2d) for H, (15s15p10d4f) for F, (17s17p12d8f) for Cl, (21s21p12d8f2g) for Br, and (25s25p18d10f3g) for I. The obtained results were compared with other calculation results, that is, the DKH∞ results taken from Ref. [1], the four-component Dirac-Hartree-Fock (DHF) results taken from Refs. [6], and the normalized elimination of the small component calculation results at the level of the second-order regular approximation (NESC-SORA), taken from Ref. [4]. The present results agree better with the DHF values as the benchmark than the DKH∞ results do. However, somewhat larger differences remained between the present results and DHF values for the proton shieldings than for the halogen shieldings. This may arise from the fact that the present calculation treats the two-electron interactions nonrelativistically. The two-electron spin-orbit (SO2) interaction effects, which are important in the proton shieldings [3], are neglected in the present calculation.

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References

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

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

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

[4] H. Maeda, Y. Ootani, and H. Fukui, J. Chem. Phys. **126**, 174102 (2007).

[5] *Tables of Interatomic Distances and Configuration in Molecules and Ions, Supplement* (The Chemical Society, London, 1965).

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