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NMR 遮蔽テンソルの４成分計算

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Abstract: A formulism for four-component Dirac-Hartree-Fock perturbation theory using gauge-including atomic orbitals (GIAOs) and the restricted magnetic balance (RMB) condition is derived. In this formulation, the zeroth-order Dirac-Hartree-Fock equation is subject to the usual restricted kinetic balance (RKB) condition, but the external field-dependent RMB condition is introduced in the calculation of first-order magnetically perturbed orbitals. The obtained formula is the same at the operator level as the nonrelativistic shielding formula using GIAOs. The magnetic shielding can be divided into the paramagnetic part and the diamagnetic part like nonrelativistic shieldings. The present theory is applied to the calculation of hydrogen halide shieldings with a good performance.

The magnetic properties of compounds containing heavy elements are strongly influenced by relativistic effects. The present authors recently presented two-component magnetic perturbation calculations [1]-[4] based on a regular approximation to the normalized elimination of the small component (NESC) [5], [6]. The NESC-based effective Hamiltonian includes a singular term that arises from the cross term between the nuclear attraction potential V and the vector potential $\vec{A}_M$ due to the nuclear magnetic dipole moment $\vec{\mu}_M$. In nuclear magnetic shielding calculations for HI by the NESC approach, the iodine nucleus exhibits quasidivergent behavior [4]. Although the quasidivergence produced in the NESC calculations can be suppressed by the introduction of a finite-size nuclear model, the causative numerical instability remains. Numerical instability appears to be inherent in the two-component magnetic perturbation calculations, suggesting that a four-component scheme is necessary.

In the four-component magnetic perturbation calculation, a primary problem must be addressed; insufficiencies of the restricted kinetic balance (RKB) basis. The RKB basis consists of the basis $\left\{f_\nu^L\right\}$ for expansion of the upper (large) component spinor φ^L of the Dirac bispinor $\psi = \left(\varphi^L, \varphi^S\right)$, and the basis $\left\{f_\nu^S = \vec{\sigma} \cdot \vec{\nabla} f_\nu^L\right\}$ for the lower (small) component spinor φ^S. In not so large basis $\left\{f_\nu^L\right\}$, the use of $\left\{\vec{\sigma} \cdot \vec{\nabla} f_\nu^L\right\}$ alone for the expansion of φ^S has been shown to be insufficient [7], with the inclusion of $\left\{\vec{\sigma} \cdot \vec{A} f_\nu^L\right\}$ for the expansion of φ^S considered to be necessary for the systems including vector potentials

$\vec{A}$. In order to compensate insufficiency of the RKB basis sets for expanding φ^S in the magnetically perturbed states, the inclusion of $\left\{\vec{\sigma} \cdot \vec{A} f_\nu^L\right\}$ is necessary for the expansion of φ^S. The vector potential $\vec{A}$ is the sum of $\vec{A}_0$ due to an external magnetic flux density $\vec{B}_0$ and $\vec{A}_M$ due to the magnetic dipole moment $\vec{\mu}_M$. The inclusion of $\left\{\vec{\sigma} \cdot \vec{A}_M f_\nu^L\right\}$ will produce a singular term $V \vec{A}_M \cdot \vec{p}$ in the perturbed SS type Hamiltonian matrix. On the other hand, the $\left\{\vec{\sigma} \cdot \vec{A}_0 f_\nu^L\right\}$ type basis functions are important and regular for expanding the first-order perturbed orbitals. In order to circumvent the production of singular terms, the external field-dependent restricted magnetic balance (RMB) condition using $\left\{\vec{\sigma} \cdot \left(\vec{p} + \vec{A}_0\right) f_\nu^L\right\}$ is proposed in the present study. Furthermore, the use of gauge-including atomic orbital (GIAO) basis sets is effective with the RMB condition, because both the form of $\vec{p}+\vec{A}_0$ and the use of GIAOs are necessary for keeping gauge invariance. The magnetic perturbation operator $c\vec{\alpha} \cdot \left(\vec{A}_0 + \vec{A}_M\right)$ in the Dirac Hamiltonian is linear in $\vec{A}_0$ and $\vec{A}_M$. There is no resemblance between the relativistic and nonrelativistic expressions for the diamagnetic shielding contribution. However, in the use of RMB condition, the magnetic shielding of nucleus M, σ^M, can be divided into the paramagnetic part $\sigma^M(\text{para})$ and the diamagnetic part $\sigma^M(\text{dia})$ like the nonrelativistic shieldings. The external field-dependent RMB theory was successfully applied to the calculation of hydrogen halide shieldings. The results showed no sign of quasidivergence.

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