Relativistic density functional theory with picture-change corrected electron density

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Because one-component (1c) relativistic density functional theory (RDFT) can be implemented easily by extending a program code of nonrelativistic(NR) DFT, it is a standard and practical scheme to perform an all-electron calculation including scalar relativistic effects. Although many quantum chemical program packages adopt such 1c DFT approach, the inconsistency of pictures of Hamiltonian and density are involved. Namely, despite the one-electron Dirac Hamiltonian and the two-electron Coulomb operator are transformed to eliminate the small components or to decouple the electronic and positronic components, the electron density, which is the fundamental variable to evaluate the exchange-correlation energy, is obtained by using the NR density operator. We have developed the picture-change corrected (PCC) RDFT that relies on a unitary-transformed density operator as well as a unitary-transformed Hamiltonian [1,2]. Furthermore, we have examined the techniques to reduce the computational cost to evaluate the PCC density. This approach has been implemented into the relativistic program package developed in the author's group, namely, Relativistic And Quantum Electronic Theory (RAQET) [3]. In the presentation, I will explain the theoretical aspects, implementation, and some numerical applications of the present approach.

References

1. T. Oyama, Y. Ikabata, S. Seino, and H. Nakai, *Chem. Phys. Lett.* **680** (2017) 37.
2. Y. Ikabata, T. Oyama, M. Hayami, J. Seino, and H. Nakai, *J. Chem. Phys.* **150** (2019) 164104.
3. M. Hayami, J. Seino, Y. Nakajima, M. Nakano, Y. Ikabata, T. Yoshikawa, T. Oyama, K. Hiraga, S. Hirata, and H. Nakai, *J. Comput. Chem.* **39** (2018) 2333.