Picture-Change Corrected Relativistic Density Functional Theory

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Many of standard quantum chemical programs can perform one-component (1c) or scalar relativistic density functional theory (RDFT) calculations, which are implemented by extending a program code of nonrelativistic (NR) DFT. However, such straightforward extension brings about the inconsistency of pictures of Hamiltonian and density. Namely, the electron density, i.e., the fundamental variable to evaluate the exchange-correlation energy, is obtained by using the NR density operator, 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. 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, based on the local unitary transformation (LUT) technique [3,4]. In the presentation, I will explain the theoretical aspects and some numerical applications of the present approach.

References

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