Relativistic range-separated density functional theory

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Résumé

Standard Kohn-Sham density-functional theory (DFT) with the usual approximations is a very efficient tool for calculating electronic properties of systems so long as they do not display near-degeneracy effects. It so happens that systems containing heavy elements usually display both strong correlation and relativistic effects.
An efficient scheme to deal with strong correlation is range-separated density functional theory (rs-DFT) where the electron-electron Coulomb interaction potential is being split into a short-range interaction to be treated in DFT and a complementary long-range interaction to be treated in wave-function theory (WFT). One can then use multiconfigurational WFT to account for the long-range static correlation, and consider the short-range dynamical correlation through a DFT functional. This scheme was later adapted to account for some relativistic effects by O. Kullie and T. Saue through the use of a relativistic four-component long-range MP2 scheme and a complementary non-relativistic short-range functional.
In order to take relativistic effects in account both in the long-range wave function and short-range density functional we started the construction of a four-component range-separated scheme starting from the Dirac equation with a relativistic electron-electron Coulomb-Breit interaction potential. The first step of this work was the construction of a relativistic short-range LDA exchange functional, followed by the implementation of a four-component rs-DFT plugin within the software Quantum Package in order to test it. The second step was the the construction of a relativistic short-range correlation functional, starting from the relativistic short-range RPA.

Mots-Clés: Relativistic chemistry, range, separation, functionals

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