A Dynamic Correlation Factor for Multiconfiguration Density Functional Theory

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The treatment of multireference systems in the Kohn-Sham (KS) formalism of density functional theory (DFT) is a controversial topic. While progress has been made in the last decade in this regard [1], it is evident that some problems are out of the reach of KS-DFT. Here, we present an attempt to address this issue in which we propose to extend the correlation factor recently developed in our group [2,3,4,5] to a multiconfigurational (MC) reference wave function. In this new approach, the exchange-correlation hole is written as a product of a dynamic correlation factor $f_c(\mathbf{r},u)$ (where $\mathbf{r}$ is the electron position vector and u is the interelectronic separation) and an exchange plus static correlation hole $\varrho_{XS}(\mathbf{r},u)$, which is constructed to reproduce the exchange-correlation energy of a MC wave function. We show that the proposed method for adding dynamic correlation provides results for properties such as barrier heights and atomization energies that are on par with state-of-the-art non-empirical functionals, while avoiding the size-consistency problem and space- and spin-symmetry dilemma of KS-DFT. This is achieved while keeping the linear computational scaling characteristic of density functional methods. Additionally, we discuss simplifications and efficient and self-consistent implementations of the method [6].

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