

Exploring short-range DFT energy corrections to multiconfigurational wave functions

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Abstract

Electron correlation is a pivotal concept in quantum chemistry. Commonly, strong correlation effects are dealt with multiconfigurational wave function theories (WFT), while density functional theory (DFT) approximations efficiently recover instantaneous electron-electron interactions, i.e., dynamic correlation. Therefore, a variety of methodologies aim to take advantage of the distinct strengths of these two nearly antagonistic theories [1]. One of these strategies lies on merging WFT with DFT through the range separation of the Coulomb operator [2], in which DFT functionals evaluate the short-distance region, while long-range inter-electronic interactions are quantified by WFT (WFT-*sr*DFT). During my presentation, I will try to uncover the limitations of WFT-*sr*DFT in the characterization of close and open-shell systems. In particular, I will discuss the importance of spin polarization effects in the (short-range) DFT exchange energy and I will show their importance in order to provide a balanced description between closed and open-shell configurations. I will introduce different strategies to account for spin polarization in the short range based on the definition of a spin polarized electron density and with the use of short-range exact exchange. The performance of these energy functionals will be tested in the dissociation of single bonds, the calculation of energy gaps in spin-triplet atoms and molecular diradicals, and the characterization of low-lying excited states [3,4].

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