# A self-consistent systematic optimization of range-separated hybrid functionals from first principle

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Abstract

We represent a self-consistent systematic optimization procedure for the development of optimally tuned range-separated (RS) hybrid functionals from first principle. This has been inspired from our recent work published in J. Chem. Phys., 150, 064104, 2019, where we have pursued a purely numerical approach for efficient computation of the Hartree-Fock exchange contribution in the conventional global hybrid functionals using an optimally tuned RS technique through a Cartesian-grid based pseudopotential (Generalised) KS-DFT framework. Here, our well-established systematic grid-optimization procedure from Int. J. Quant. Chem., 118, e25708, 2018 has been redefined considering the size dependency of exchange-correlation energy which gives rise to a constraint on RS-parameter for a given system of interest. This has been manifested self-consistently by optimizing the total energy with respect to "grid parameters" which implicitly define the system's size. Now, we assert that our size dependency based *ansatz* for the optimally tuned RS-parameter can show superiority in predicting properties derived both from the frontier orbital energies and total energies than the default respective RS-hybrid functionals. To the best of our knowledge, this size dependency ansatz represents the first attempt to find optimized RS-parameter in a RS-hybrid functionals. For the sake of comparison, some preliminary results are provided here along with the behavior towards fractional occupation in atoms to demonstrate the deviation from the exact piecewise straight line. The first-step statistical analysis, then, reveals the viability and suitability of our approach for a given system of interest within the Cartesian-grid based pseudopotential KS-DFT framework.