

ABSTRACT

This doctoral thesis examines the role of electron correlation in exchange–correlation (XC) approximations of Kohn–Sham (KS) Density Functional Theory (DFT). Since XC functionals have historically been evaluated almost exclusively on the basis of energy and energy-derived benchmarks, the thesis addresses this bias by benchmarking existing hybrid XC functionals, and by constructing a new one, against the KS XC potential, the electron density, and the ionization potentials, using highly accurate reference data obtained from wavefunction *ab initio* methods (FCI, CCSD(T), EOM CCSD).

To make such an assessment, we have tested the reliability of existing Kohn–Sham inversion schemes and developed strategies to overcome existing challenges in computing accurate KS XC potentials from hybrid KS and reference *ab initio* densities. Finally, the Wu–Yang inversion procedure was chosen and employed to compute the XC potentials.

We evaluated 155 hybrid density functionals from the LIBXC library, comparing the XC potentials obtained by inverting each hybrid’s self-consistent KS density against reference potentials obtained by inverting the FCI and CCSD(T) electron densities. A clear hierarchy in the error metrics emerged, with total energy errors being the smallest, followed by density errors, ionization potential errors, and, finally, XC potential errors, which were three to four orders of magnitude larger than the energy errors. The quality of the XC potential was found to be directly correlated with the accuracy of the ionization potentials, and the decomposition of the total energy error into density and functional-driven parts depicted a dominant functional-driven contribution.

Our key observation is that the main qualitative features of the correlation potential and the correlated density in hybrid functionals arise not from the semi-local correlation functional but from the difference between the semi-local and the exact (Hartree–Fock) exchange. Based on this insight and on the adiabatic connection formalism, we developed a new procedure to optimize the global hybrid functional. As a result, the UMK26 functional was defined, with its single parameter obtained by a line search that minimizes the ionization-potential discrepancy against the EOM-CCSD ionization potentials from a 16-system benchmark set.

Compared with conventional global hybrids, UMK26 improves the description of the correlation potential, the correlated density, the HOMO and valence ionization potentials (401 reference values over 63 systems), and the charge transfer excitation energies, reaching the level of dedicated range-separated hybrids; it also reduces the self-interaction error, as demonstrated on the SIE4x4 test set and in the dissociation curves of charged species. Although UMK26 does not deliver a uniform gain across thermochemical benchmarks, its simple, physically transparent construction provides a route toward future XC functional design, including range-separated and machine learning variants.

The doctoral dissertation is based on two publications:

1. Vignesh Balaji Kumar, Szymon Śmiga, Ireneusz Grabowski; A Critical Evaluation of the Hybrid KS DFT Functionals Based on the KS Exchange-Correlation Potentials. *J. Phys. Chem. Lett.* 10 October 2024; 15 (40): 10219–10229.

<https://doi.org/10.1021/acs.jpcllett.4c01979>

2. Vignesh Balaji Kumar, Szymon Śmiga, Rodrigo Araújo Mendes, Bogumiła Jezierska, Rodney Bartlett, and Ireneusz Grabowski, “On the Primary Role of Semi-Local and Exact-Exchange Difference in the Description of Correlation Effects in Hybrid Functionals” (*J. Chem. Theory Comput.* XXX, 2026),

<https://doi.org/10.1021/acs.jctc.6c00843>