Development of Local Hybrid Density Functionals by Systematic Large-Scale Optimization of Adjustable Parameters

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In Short

- Improved and more flexible local hybrid functionals that satisfy many physical constraints are developed.

- Systematic global and local optimizations of adjustable parameters by self-consistent Kohn-Sham computations using a multi-level, highly parallel computational protocol.

Local hybrid functionals (local hybrids, LHs) in Kohn-Sham density functional theory (DFT) vary the amount of exact exchange in real-space, using physically motivated local mixing functions (LMFs). (1) They combine an LMF with a semi-local and the exact exchange-energy density, some semi-local correlation functional and a calibration function (CF) to address the ambiguity of exchange-energy densities. The first-generation LSDA-based LHs lacked a CF and had at most two adjustable parameters, but with a "scaled t-LMF" ($g(r) = b \cdot \frac{\tau}{\tau_w}$) they nevertheless provided remarkable accuracy for a wide variety of properties. (1, 2)

With new types of more sophisticated LMFs that combine a t-LMF with a linear combination of further inhomogeneity parameters, we seek to extend flexibility and satisfy additional constraints lacking for a scaled t-LMF, to improve the accuracy of LHs for a wide variety of properties. To find the best-performing functional, we will combine these new

LMFs with GGA-based exchange (PBE and B88) and meta-GGA B95 correlation as well as the GGA-based pig2 CF. (3) We further have derived CFs also from PBE and will evaluate to what extent it is desirable to use a PBE-based CF in this context. We do now also have the formulas for a (pig3) CF based on PBE exchange (A. V. Arbuznikov, M. Kaupp, unpublished). This should allow an even more flexible treatment of the gauge problem of exchange-energy densities, and we will evaluate this as part of the optimizations.

For each of these functionals we need to perform full optimizations of adjustable parameters in self-consistent Kohn-Sham computations, which leads to the request for HPC resources. First the parameters in the LMFs and in the B95 correlation functional are optimized by minimization of the weighted mean absolute deviations of physicochemical data from published reference data. In a next step the adjustable parameters in the CF are optimized by minimizing measures of spurious non-dynamical correlation (3). In a further step the LMF is optimized by minimizing mean absolute deviations of core excitation reference data to improve the functionals for core-related properties. These three steps have to be repeated until convergence of the parameters is achived. For a fully optimized functional, dispersion corrections will be added, and the LHs will be evaluated for larger data sets.

The appreciable number of adjustable parameters and necessary Kohn-Sham calculations requires efficient methods for the optimization of the functional. Our optimization protocol, written in Python 3, contains a multi-layer single-linkage global optimization algorithm in combination with a BFGS local optimization algorithm using a numerical gradient. The time-determining step in the optimization procedure are the self-consistent Kohn-Sham computations for all test molecules/atoms per iteration of the algorithm, using our own local version of the Turbomole program package extended for local hybrids. (1) We thus parallelize the optimization on three levels: a) all points per iteration of the global as well as the local optimization are calculated in parallel, b) all Kohn-Sham calculations for one point are done simultaneously, and c) we run the most time-consuming Kohn-Sham calculations in MPI-parallelized form.
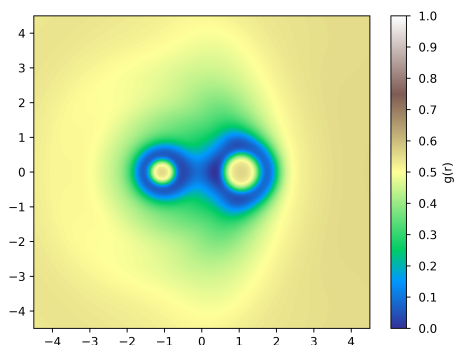

Figure 1: *Amount of exact-exchange admixture in a CO molecule using a scaled t-LMF.*

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More Information

[1] Maier, T. M.; Arbuznikov, A. V.; Kaupp, *M. Wiley Interdiscip. Rev. Comput. Mol.Sci.* **2019**, 9, e1378.

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[3] Maier, T. M.; Haasler, M.; Arbuznikov, A. V.; Kaupp, *M. Phys. Chem. Chem. Phys.* **2016**, 18, 21133-21144.