Separation for Excitation

Optimization of Range-Separated Local Hybrid Functionals

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In Short

- implementation of range-separated local hybrids into the TURBOMOLE program package
- optimization of range-separated local hybrid functionals for ground state properties
- improved description of excited-state properties
- attenuation of self-interaction and delocalization errors
- appropriate description of intermolecular charge transfer

Within modern density functional theory (DFT) local hybrid (LH) functionals[1] generalize the concept of global hybrids. The exchange-correlation energy is expressed as sum of a semi-local correlation functional and a space dependent mixing of Hartree-Fock and semi-local exchange, controlled by a local mixing function (LMF). Because of this mixing and the ambiguity of energy densities local hybrids require a calibration of the chosen semi-local exchange-energy densities by a calibration function (CF)[2]. Range-separated hybrids provide an alternative description of the exchange energy based on separating the Coulomb-operator into a short- and long-range term. Figure 1 visualizes differences in hybrid models. The strength of DFT lies in computing ground state properties whereas excited states are best described by a time dependent theory approaching the dynamic density changes. Within the adiabatic approximation of linear-response time dependent density functional theory (TDDFT) most density functional approximations (DFAs) reproduce local excitations well, while range-separated hybrids better predict the usually significantly underestimated charge-transfer (CT) and Rydberg excitation energies. Range-separated local hybrids combine the concept of local hybrid functionals and range-separation by describing the exchange-correlation energy as sum of long-range HF exchange and local mixing of short-range HF exchange and short-range semi-local exchange-energy densities. Range-separated local hybrids promise to improve the prediction of charge-transfer excitations, conceivably even more than their global counterparts. An appropriate description of charge-transfer excitations is of special interest not only in material sciences when studying photo-induced charge-transfer processes in solar photocatalysis, but also for biological chromophores.

As part of this work, range-separated local hybrids have been implemented into the TURBOMOLE program package for electronic structure calculations to enable ground state DFT calculations, followed by a TDDFT implementation to enable the computation of excitation energies. A number of adjustable parameters have been determined empirically by an optimization of atomization energies and reaction barriers against reference data sets. The number of parameters for such an optimization depend on the choice of the LMF, the CF and the semi-local correlation functional and require efficient methods for the optimizations of the functionals. These optimizations have been performed by a Python 3 program using

	global	local
full	$aE_{x,ex}$	$\int a(r)\, e_{x,ex}(r)\, dr$
separated	$aE^{SR}_{x,ex} + E^{LR}_{x,ex}$	$E^{LR}_{x,ex} + \int a(r)\, e^{SR}_{x,ex}(r)\, dr$

***Figure 1:** Incorporation of the exact-exchange energy density for global and local hybrids with full and separated range.*

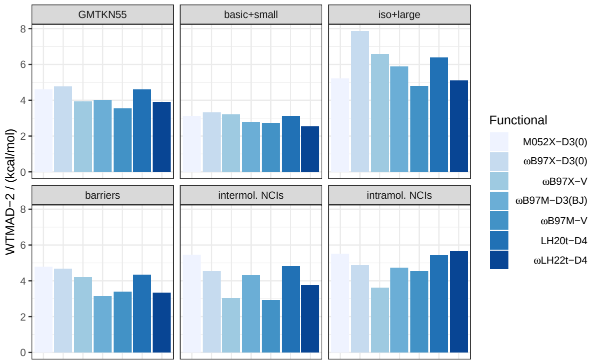

***Figure 2:** Performance of the ωLH22t for the GMTKN55 subgroups compared to the local hybrid LH20t and one of the best performing range-separated hybrids ωB97X-D.*

a multi-layer single-linkage (MLSL) global optimization algorithm, that minimizes the sum of weighted mean absolute deviation from test set calculations to published reference data. The global optimization executes a number of BFGS local optimizations using a numerical gradient. The HPC resources allow to parallelize the necessary test set calculations within the BFGS iterations to determine the value of the optimization function and its numerical gradient. The Kohn-Sham single point calculations within the test set calculations can be parallelized using the TURBOMOLE OpenMP implementation, that showed superlinear speedup in our test cases.

Up to now we chose a quite simple t-LMF for the local mixing of short-range HF exchange and short-range semi-local exchange-energy densities. The resulting functional ωLH22t has been evaluated on the GMTKN55 testset and proved to be one of the best performing rung 4 functionals according to the measures proposed by the authors of the GMTKN55 publication. Figure 2 shows the performance of the ωLH22t, compared to other functionals. The concept of range-separation promises an appropriate description of intermolecular charge-transfer excitations. The Mulliken rule describes a theoretical lower bound to the exact charge-transfer excitation energies in dependence of the intermolecular distance. Typical DFA functionals tend to underestimate those energies. Figure 3 shows how the ωLH22t improves the situation for the ethylene-tetrafluoroethylene dimer compared to the normal local hybrid LH20t [3] and the global range-separated hybrid ωB97X-D. Self-interaction and delocalisation errors can be evaluated by computing dissociation curves of charged noble gas dimers. Contemporary DFA functionals tend to undershoot the dissociation energies and approach an energy barrier with increasing atomic distance. Figure 4 shows how the situation improves with ωLH22t for the neon dimer Ne_2^+ compared to the non-separated local hybrid LH20t and the range-separated global hybrid ωB97X-D. To improve the success of range-separated local hybrids even more, we plan to replace the simple t-LMF based mixing of the short-ranged exact and semi-local energy densities by a more complex mixing, that requires the optimization of four additional parameters. In addition to atomization energies and reaction barriers as before, the optimization procedure for the new range-separated local hybrid functionals will also involve the consideration of core excitations.

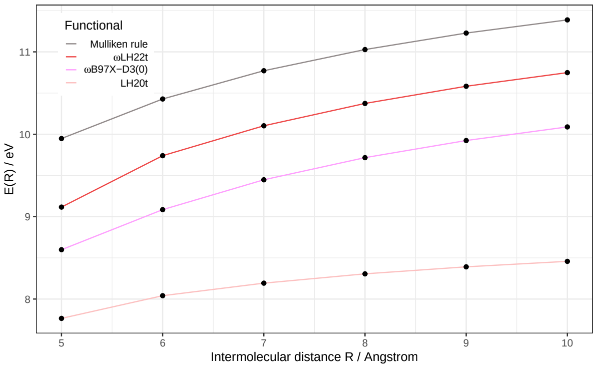

Figure 3: *Charge-transfer excitation energies for the ethylen-tetrafluoroethylene dimer in dependence of the intramolecular distance.*

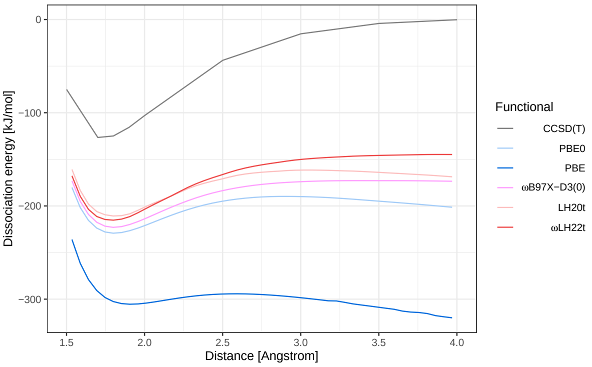

Figure 4: *Dissociation curves of the charged neon dimer* Ne_2^+.

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More Information

[1] Maier, T. M.; Arbuznikov, A. V.; Kaupp, M. *Wiley Interdiscip. Rev. Comput. Mol.Sci*. **2019**, 9, e1378. doi:10.1002/wcms.1378

[2] Maier, T. M.; Haasler, M.; Arbuznikov, A. V.; Kaupp, M. *Phys. Chem. Chem. Phys*. **2016**, 18, 21133-21144.doi:10.1039/C6CP00990E

[3] Haasler, M.; Maier, T. M.; Grotjahn R.; GÃ¼ckel S.; Arbuznikov, A. V.; Kaupp, M. *J. Chem. Theory Comput.*. **2020**, 16, 9, 5645-5657.doi:10.1021/acs.jctc.0c00498