

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
- improved description of ground- and excited-state properties

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. 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 to be determined empirically by an optimization of atomization energies and reaction barriers against reference data sets. The number of parameters depends 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 will be performed by a Python 3 program using 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.

The resulting functionals will be evaluated using further benchmark data sets, especially for excitation energies.

WWW

<https://www.quantenchemie.tu-berlin.de>

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

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

Figure 1: Amount of exact exchange in different hybrid models.

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