Advances in local hybrid exchange-correlation functionals: From thermochemistry to response properties

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Our progress in the construction and validation of local hybrid functionals, [1] attained during the last years within the DFG SPP-1145 is reviewed. Local hybrids provide a very promising new generation of exchange-correlation functionals for the simultaneous accurate description of various properties within Kohn-Sham DFT. Compared to traditional (global) hybrids (e.g., B3LYP, PBE0, TPSSh) local hybrids exhibit larger flexibility, due to the replacement of a constant exact-exchange admixture by a position-dependent one. The latter is governed by a so-called *local mixing function* (LMF), and this is the crucial quantity which controls the overall performance of local hybrids.

The most successful LMFs have been derived partially in a semi-empirical way, based on a physically justified balance between the elimination of Coulomb self-interaction and efficient simulation of nondynamical correlation. Such LMFs may be built of the dimensionless density gradient [2], the ratio of von Weizsäcker kinetic energy density to local kinetic energy density [1,3], spin polarization [4], etc. On the other hand, LMFs can be derived within a purely *ab initio* approach based, for instance, on the adiabatic connection (AC) formalism [5] that provides valuable insights into the performance and limits of various local hybrids while being less practically successful than a semi-empirical approach.

Our best local hybrids include a minimal number of adjustable parameters (one or two) and turn out to be superior in the description of atomization energies, reaction barrier heights [2-4,6], NMR chemical shifts [7], EPR g tensors [8], and electric response properties (polarizabilities and hyperpolarizabilities) compared to traditional hybrids that often suffer from being overparametrized. Important implementation aspects (nonlocal vs. localized exchange-correlation potentials) and an outlook on the further improvement of local hybrid functionals, and their extension to computation of other properties are discussed as well.

Literature:

[1] J. Jaramillo, G. E. Scuseria, M. Ernzerhof, *J. Chem. Phys.* **118** (2003) 1068.
[2] A. V. Arbuznikov, M. Kaupp, *Chem. Phys. Lett.* **440** (2007) 160.
[3] H. Bahmann, A. Rodenberg, A. V. Arbuznikov, M. Kaupp *J. Chem. Phys.* **126** (2007) 011103.
[4] A. V. Arbuznikov, H. Bahmann, M. Kaupp, *J. Phys. Chem. A*, **113** (2009) 11898.
[5] A. V. Arbuznikov, M. Kaupp, *J. Chem. Phys.* **128** (2008) 214107.
[6] M. Kaupp, H. Bahmann, A. V. Arbuznikov, *J. Chem. Phys.*, **127** (2007) 194102.
[7] A. V. Arbuznikov, M. Kaupp, *Chem. Phys. Lett.* **442** (2007) 496.
[8] A. V. Arbuznikov, M. Kaupp, *J. Chem. Theory Comput.* **5** (2009) 2985.