Spectroscopic observables from DFT and TDDFT: limitations and hopes

Stephan Kümmel

Theoretical Physics IV, University of Bayreuth, Bayreuth, Germany

Present day density functionals serve many purposes, but most of them also suffer from systematic limitations. The insufficient accuracy in describing localization effects, the tremendous overestimation of long-range charge transfers, and the limited interpretability of the Kohn-Sham eigenvalues are prominent examples. This talk will show that many of these problems are inherently linked to one-electron self-interaction and can be significantly reduced with a self-interaction correction based on the Optimized Effective Potential [1]. It will further be discussed that range-separated hybrid functionals can achieve similar effects in a different way. Pros and cons of both type of approaches will be pointed out [2,3]. Final remarks will address the hopes that one may pin on new types of semi-local functionals which capture important features of exact exchange in their semi-local potential [4].

[1]
D. Hofmann, T. Körzdörfer, S. Kümmel,
"Kohn-Sham Self-Interaction Correction in Real Time",
Physical Review Letters 108, 146401 (2012).

[2]
A. Karolewski, L. Kronik, S. Kümmel,
"Using optimally tuned range separated hybrid functionals in ground-state calculations: Consequences and caveats",
J. Chem. Phys. 138, 204115 (2013)

[3]
Thiago B. de Queiroz, S. Kümmel,
"Charge-transfer excitations in low-gap systems under the influence of solvation and conformational disorder: Exploring rang-separation tuning",
Journal of Chemical Physics 141, 084303 (2014)

[4]
R. Armiento, S. Kümmel,
"Orbital Localization, Charge Transfer, and Band Gaps in Semilocal Density-Functional Theory",
Physical Review Letters 111, 036402 (2013)