Orbital-Dependent Functionals in Kohn-Sham DFT - Practical Realization of *ab initio* KS-DFT

Ireneusz Grabowski

Institute of Physics, Faculty of Physics, Astronomy and Informatics, Nicolaus Copernicus University, Grudziadzka 5, 87-100 Torun, Poland

An overview and assessment of several applications of correlated optimized effective potential (OEP) method in the context of KS-DFT is presented. We have performed a systematic and broad study of the performance of the different *ab initio* KS-DFT methods e.g. OEP2-sc [1], OEP-GL2 for closed-shell and spin-polarized systems. To analyse different correlation effects in standard KS-DFT functionals and *ab initio* KS-DFT methods we employ direct comparison of several quantities generated from those methods, and from *ab initio* WFT.

We have found then the KS correlation potentials, energies and densities generated from correlated OEP2 and from WFT methods - Coupled Cluster and MBPT2 show very similar and systematic behavior, reconfirming the correctness of the ab initio KS-DFT methods [2,3]. In a contrast it has been demonstrated that the VWN5 and LYP and other correlation functionals do not represent any substantial correlation effects on the KS-correlation potentials [3,4] and electron density [2,3], whereas these effects are well represented by the orbital dependent OEP correlation functionals.

An extension of OEP2 methods by using the spin resolved second-order correlation energy (SCS-MP2) is also presented. The effect of scaling the same- and opposite- spin components is investigated in detail to determine optimal scaling coefficients for different properties in proposed scaled-opposite–spin OEP functional OEP2-SOS [4] which is the most advantageous from a computational point of view (O(N^4) scaling).

We also introduce an orbital-optimized double-hybrid (DH) scheme using the OEP method. The orbitals are optimized using a local potential corresponding to the complete exchange-correlation energy expression including the MP2 correlation contribution. [5] Next we extend the range-separated double hybrid RSH+MP2 method, combining long-range HF exchange and MP2 correlation with a short-range density functional, to a fully self-consistent version using OEP technique in which the orbitals are obtained from a local potential including the long-range HF and MP2 contributions. [6]

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