Density-functional theory with σ-functionals for highly accurate energies and molecular properties

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σ-Functionals are a new type of functionals for the Kohn-Sham(KS) correlation energy based on the adiabatic-connection fluctuation-dissipation (ACFD) theorem [1-3]. σ-Functionals are closely related to the well-known direct random phase approximation (dRPA). In the dRPA a coupling constant and a frequency integration of a function of the eigenvalues of the dynamic KS response function is carried out. In σ-functionals the dRPA expression in this integral is replaced by a function motivated by perturbation theory along the adiabatic connection [4]. This function is optimized with respect to reference sets of reaction and interaction energies in order to correct the errors resulting from neglecting the exchange-correlation kernel in dRPA.

σ-Functionals are applied in a post-self-consistent way using input orbitals and eigenvalues from a previous conventional DFT calculation, e.g. with the PBE functional [1] or with hybrid functionals (PBE0, B3LYP) [2,3]. σ-Functionals based on the latter yield mean absolute errors around or below 1 kcal/mol for reaction energies, barrier heights, and non-covalent interactions, thus reach chemical accuracy, and were shown to even slightly outperform the double hybrid functional DSD-BLYP-D3(BJ) for main group chemistry [5].

In Ref. [5] three setups of basis set combinations were proposed, which offer a good compromise between accuracy and numerical efficiency. The evaluation of the post-SCF total energy in a RPA or σ-functional method requires less computational time than a preceding hybrid DFT method, and thus can be carried out routinely for systems of practical relevance.

Besides calculating accurate energies, σ-functionals have been used to compute many chemical properties, such as geometries and vibrational frequencies (using analytic gradients of σ-functionals [6]) as well as NMR shieldings [7]. Also singlet-triplet gaps have been reported [8]. Although none of these quantities were involved in their optimization, σ-functionals do not only outperform conventional DFT methods and the dRPA, but can compete with high level methods such as double hybrid functionals and even coupled-cluster theory.

σ-Functionals have been implemented in several popular quantum chemistry codes (Molpro, Turbomole, ADF, PySCF, FermiONs++, VASP).

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