The Kohn-Sham calculations with Adiabatic Connection Models with Improved Treatment of the Strong-Interaction Limit

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Adiabatic connection models (ACMs), which interpolate between the limits of weak and strong interaction, are powerful tools to build accurate exchange-correlation functionals within Kohn-Sham Density Functional Theory (KS-DFT)[1]. If the exact weak-interaction expansion from second- order perturbation theory is included, a self-consistent implementation of these functionals is challenging and still absent in the literature. In this work [2] we fill this gap by presenting a fully self-consistent-field (SCF) implementation of some popular ACM functionals. While using second- order perturbation theory at weak interactions, we have also introduced new generalised gradient approximations (GGA's), beyond the usual point charge-plus-continuum model, for the first two leading terms at strong interactions, which are crucial to ensure robustness and reliability.

We then assess the SCF-ACM functionals for molecular systems and for prototypical strong-correlation problems (Hooke's atom, dissociation of H_2). We find that they perform well for both the total energy and the electronic density and that the impact of SCF orbitals is directly connected to the accuracy of the ACM functional form.

For the H_2 dissociation the SCF-ACM functionals yield significant improvements with respect to standard functionals, also thanks to the use of the new GGA's for the strong-coupling functionals.

[1] W. Kohn, L. J. Sham, Phys. Rev., **140** (1965), A1133.

[2] S. Śmiga, F. D. Sala, P. Gori-Giorgi, E. Fabiano, J. Chem. Theory Comput., **18** (2022), 5936-5947.