Explanation of a new density functional (SSB-D)

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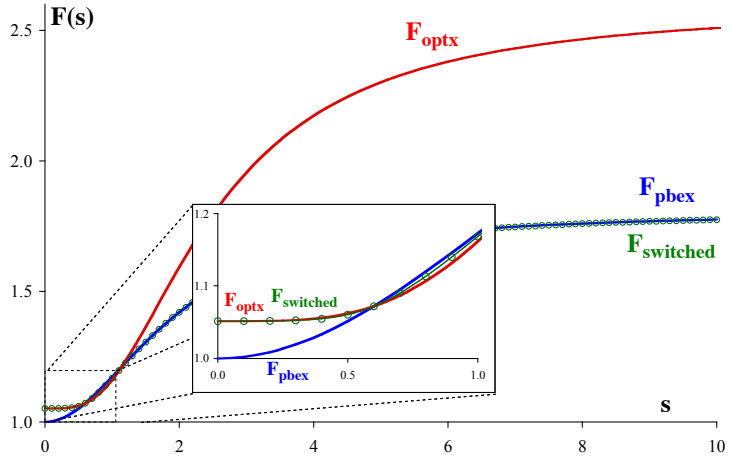
We recently reported a study into what causes the dramatic differences between OPBE and PBE for reaction barriers, spin-state energies, hydrogen-bonding and π-π stacking energies. [1] It was achieved by smoothly switching from OPBE to PBE at a predefined point P of the reduced density gradient *s*. By letting the point P run as function of the reduced density gradient *s*, with values from *s*=0.1 to *s*=10, we could determine which part of the exchange functional determines its behavior for the different interactions. Based on the thus obtained results, we created a new exchange functional that showed the good results of OPBE for reaction barriers and spin-state energies, and combined it with the good (H-bonds) and reasonable (π-stacking) results of PBE for weak interactions. In other words, it combined the best of OPBE with the best of PBE.

Encouraged by these good results, we have further improved the new exchange functional and fine-tuned its parameters. [2] Similar to the switched functional from ref. [1], our new SSB-D functional [2] works well for both S_N2 barriers (see e.g. ref. [3]), spin states and H-bonding interactions. Moreover, by including Grimme's dispersion corrections it also works well for π-π stacking interactions. [2]



In summary, we have constructed a new GGA exchange functional that when combined with the sPBE correlation functional [4] gives the correct spin ground-state of iron complexes, and small deviations for S_N2 barriers (2.6 kcal·mol^{-1}), geometries (0.006 Å), H-bond distances (0.012 Å), weak interactions (S22 set, 0.5 kcal·mol^{-1}), and transition-metal ligand distances (0.008 Å).

Keywords: S_N2 barriers, weak interactions, spin states

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[1] M. Swart, M. Solà, and F.M. Bickelhaupt, *J. Comp. Meth. Sci. Engin.*, **9**, 69 (2009)
[2] M. Swart, M. Solà, and F.M. Bickelhaupt, *J. Chem. Phys.*, **131**, 094103 (2009)
[3] M. Swart, M. Solà, and F.M. Bickelhaupt, *J. Comput. Chem.*, **28**, 1551 (2007)
[4] M. Swart, M. Solà, and F.M. Bickelhaupt, *"Constraining optimized exchange",* in "Handbook of Computational Chemistry", F. Columbus (Ed.), Nova Science: Hauptpage, USA, *in press* (2009)