How black is the DFT black box?

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Methods rooted in Density Functional Theory are nowadays widely used in Chemistry for their very favorable accuracy/cost ratio. Indeed, they allow the modeling of an increasing number of chemical properties with an accuracy comparable to those obtained by the experiments (the so-called chemical accuracy). Among them, we can list thermochemistry, kinetics, molecular structures, ionization potentials, absorption and emission spectra, just to mention a few.

This effort towards more and more accurate DFT methods is based on the development of new exchange-correlation functionals, that reproduce the missing energy term in the Kohn-Sham formalism. It is common practice that new exchange-correlation functionals are systematically tested (benchmarked in DFT terminology) against reference data, in order to estimate the typical error on the property of interest. The numerical results then indicate the optimal functional to be used for the specific chemical application.

Here we question this procedure, suggesting that "real" Chemistry might be more complex than what is represented by standard benchmarks. This gap between test and real cases could not only affect the computational error on the chemical property of interest, but also lead to a theoretical picture where the Chemistry is functional-dependent.