Parameter-free global hybrids: an efficient tool for DFT electronic structure calculations

Pietro Cortona

Laboratoire SPMS, Université Paris-Saclay, CentraleSupélec, CNRS UMR 8580, Grande Voie des Vignes, Châtenay-Malabry, F-92295 France

Global hybrid exchange-correlation density functionals are known to substantially increase the accuracy with respect to results obtained by generalized-gradient approximations (GGA). They are nowadays the standard tool for density functional molecular calculations and their use for solid-state system is rapidly growing, despite the difficulties of their implementation in periodic electronic-structure codes. Almost all hybrid functionals contain parameters determined by fitting some training datasets. However, starting from a parameter-free semi-local exchange-correlation functional, it is possible to derive a non-fitted global hybrid by using theoretical considerations in order to determine the relative weight of the Hartree-Fock and DFT exchanges. The first theoretical arguments aiming to fix this relative weight, were given by Perdew, Ernzerhof, and Burke [1], who recommended using 25% of Hartree-Fock exchange. This suggestion was very successful when the global hybrid was based on the PBE GGA [2] (obtaining the so-called PBE0 functional [3,4]), while the results were not particularly good when the PW91 GGA was used instead of PBE. Recently, it has been shown that others mixing coefficients can be theoretically justified [5] and used to construct parameter-free global hybrids. Indeed, it turns out that even basing the hybrid on PBE, the accuracy of the results for many properties is increased by using one of the new coefficients (1/3) instead of 0.25 [6]. In this communication, the arguments supporting the use of the new coefficients will be recalled and two parameter-free global hybrids (PBE0-1/3 [6] and hAPBE [7]) will be presented and their performances will be analyzed by a wide set of benchmarks.

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