

Dispersion-corrected r^2 SCAN based double-hybrid functionals

LUKAS WITTMANN¹, HAGEN NEUGEBAUER¹, STEFAN GRIMME¹, AND MARKUS BURSCH²

¹MULLIKEN CENTER FOR THEORETICAL CHEMISTRY, BERINGSTRASSE 4,
D-53115 BONN, GERMANY

²MAX-PLANCK-INSTITUT FÜR KOHLENFORSCHUNG, KAISER-WILHELM-PLATZ
1, D-45470 MÜLHEIM AN DER RUHR, GERMANY

April 15, 2024

ABSTRACT

We present an extension of the regularized and restored semi-local meta-generalized gradient approximation (meta-GGA) exchange-correlation functional r^2 SCAN [1] to adiabatic-connection-derived global double-hybrid functionals employing spin-opposite-scaled MP2 [2]. The 0-DH, CIDH, QIDH, and 0-2 type [3–7] double-hybrid schemes are created as a starting point for further modification. Variants with 50% and 69% Hartree–Fock exchange (HFX) are empirically optimized, resulting in $\text{Pr}^2\text{SCAN}50$ and $\text{Pr}^2\text{SCAN}69$. Additionally, the effect of MP2-regularization [8] ($\kappa\text{Pr}^2\text{SCAN}50$) and range-separated HFX ($\omega\text{Pr}^2\text{SCAN}50$) is evaluated for the parent $\text{Pr}^2\text{SCAN}50$. All functionals are combined with the state-of-the-art London dispersion corrections DFT-D4 and -NL. The resulting functionals are tested comprehensively for their performance on main-group and metal-organic thermochemistry on 90 different benchmark sets containing 25800 data points. These include the GMTKN55 [9] database, additional sets for main-group chemistry, and multiple sets covering transition-metal chemistry including the ROST61, MOR41, and MOBH35 [10–12]. Since the main goal of this study is to develop a broadly applicable, robust functional with low empiricism, special emphasis is put on variants with moderate amounts of HFX (50%) which are compared to the so far successful PWPB95-D4 (50% HFX, 20% MP2 correlation) functional [13]. The overall best variant, $\omega\text{Pr}^2\text{SCAN}50\text{-D4}$, performs well on main-group and metal-organic thermochemistry, followed by the $\text{Pr}^2\text{SCAN}69\text{-D4}$ that offers a slight edge for metal-organic thermochemistry, and by the low HFX global double-hybrid $\text{Pr}^2\text{SCAN}50\text{-D4}$ that performs robustly across all tested sets. All four optimized functionals, $\text{Pr}^2\text{SCAN}69\text{-D4}$, $\text{Pr}^2\text{SCAN}50\text{-D4}$, $\kappa\text{Pr}^2\text{SCAN}50\text{-D4}$, and $\omega\text{Pr}^2\text{SCAN}50\text{-D4}$ outperform the PWPB95-D4 functional.

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