Assessing density functionals for π-electron molecules by using quantum Monte Carlo methods

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We applied our pure-sampling quantum Monte Carlo method [J. Chem. Phys 142(2):024114 (2015); 145, 026101 (2016)] to the ethylene molecule, for which the trial wave functions were generated from a variety of density functionals: BP86, TPSS, BLYP, PBE, M06-L, TPSSh, B3LYP, PBE0, M06, BHandH, M06-2X, and M06-HF. Given physically meaningful orbitals, the resulting energy provides an upper bound to the exact, Born-Oppenheimer, non-relativistic ground-state energy. This allows us to assess the quality of the underlying electron distributions. What the best functionals have in common is identified and discussed.