Rung 3.5 exchange-correlation functionals

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Abstract:

This work discusses a new class of approximate exchange-correlation (XC) functionals for Kohn-Sham density functional theory (DFT). The functionals employ the nonlocal one-particle density matrix of the noninteracting reference system, contracted with a model density matrix from a "semilocal" model exchange hole. The model density matrix automatically screens the nonlocal information, aiding evaluation in extended systems. Properties including molecular and organometallic thermochemistry, gas-phase reaction barriers, geometries, and vibrational frequencies are treated with accuracy approaching hybrid XC functionals. Preliminary results are presented for a real-space "Rung 3.5" model of nondynamical correlation extending that in A. D. Becke, J. Chem. Phys. 122, 064101 (2005). This model works towards rationalization of hybrid XC functionals' useful but nonsystematic simulation of left-right correlation in chemical bonds.