

Assessing the Performance of Density-Functional and Wavefunction Quantum Chemical Methods for Noncovalent Interactions

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Very high quality benchmark data, from CCSD(T) and high-order symmetry-adapted perturbation theory (SAPT), has been obtained for a significant collection of van der Waals dimers (469 high-quality single-point energies, and growing). This data is allowing for a thorough assessment of the quality of various wavefunction-based and modified DFT methods for noncovalent interactions. We have examined various DFT-D methods, Becke and Johnson's exchange dipole moment (XDM) method, various double-hybrids (ω B97X-D, XYG3), the Minnesota functionals (M05-2X, M06-2X), MP2C, and wavefunction-based methods such as lower-order SAPT, spin-component-scaled MP2, spin-component-scaled CCSD, and MP2.5. Results are analyzed for various classes of noncovalent interactions (hydrogen-bonded, dispersion-dominated, and mixed systems). Basis set effects are examined. We also explore how the quality of results is expected to behave as one moves to larger noncovalent complexes, and we consider the nature of noncovalent interactions in large systems.

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