Calculation of intermolecular interaction energies using explicitly correlated coupled-cluster methods

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The CCSD(T)-F12a method is used to compute highly accurate interaction energies of molecular dimers. Comparison with extrapolated conventional CCSD(T) calculations for the S22 benchmark set shows excellent agreement. Using augmented triple zeta basis sets the CCSD(T)-F12 interaction energies agree within 0.02 kcal with the estimate complete basis set (CBS) values. Furthermore, a dispersion weighted variant of spin component scaling MP2-F12 (DW-MP2-F12) is employed to correct approximately for higher-order correlation effects in intermolecular interactions. In this method a weighted average of the MP2-F12 and SCS-MP2-F12 correlation energies is used, and the weight factors are determined on the basis of the Hartree-Fock and MP2-F12 correlation contributions to the interaction energies. This yields good agreement with CCSD(T)-F12a results of the same basis set quality for the description of all types of weak interactions. For the S22 set, the maximum deviation from the CCSD(T)-F12a results is reduced from 3.27 kcal/mol (MP2-F12/aug-cc-pVDZ) to 0.41 kcal/mol (DW-SCS-MP2-F12/aug-cc-pVDZ). This allows computing interaction energies of near CCSD(T)/CBS quality for much larger clusters than can be treated with CCSD(T). Furthermore, DW-MP2-F12 optimized geometry properties are compared with CCSD(T) results.

Literature:

[1] H.-J. Werner, T. B. Adler, and F.R. Manby, J. Chem. Phys. **126**, 164102 (2007).
[2] T. B. Adler, G. Knizia and H.-J. Werner, J. Chem. Phys. **127**, 221106 (2007).
[3] G. Knizia, T. B. Adler, and H.-J. Werner, J. Chem. Phys., submitted (2008).
[4] O. Marchetti and H.-J. Werner, Phys. Chem. Chem. Phys., DOI:10.1039/B804334E (2008).
[5] P. Jurečka, J. Černy, J. Šponer, and P. Hobza, Phys. Chem. Chem. Phys. **8**, 1985 (2006).
[6] O. Marchetti and H.-J. Werner, J. Phys. Chem. A **113**, 11580 (2009).