

Analysis and comparative study of intermolecular interactions using dimers from the S22 database

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Fourteen geometric points along the line of the center of masses and based on the published equilibrium geometries of the S22 dimers have been created for the purpose of comparative analysis and future methodological developments. Accurate MP2 and CCSD(T) Complete Basis Set (CBS) interaction energies has been obtained and analytical Morse and Rydberg curves have been fitted. The magnitude and the effect of the Basis Set Superposition Error (BSSE) have been carefully investigated. We found that going up to double and triple zeta Dunning basis sets are enough to obtain accurate CBS MP2 energies when BSSE corrected values are used but triple zeta and quadruple zeta basis sets are needed when the BSSE uncorrected total energies are used in CBS extrapolations. MP2 interaction energies with smaller like 6-31G* basis sets does not have dispersion energy components and the source of the attractive dispersion interactions are almost entirely due to BSSE. MP2 and CCSD(T) CBS interaction energies are always very close to each other if no aromatic system involved. Comparative analysis has been performed for widely used semi-empirical and *ab initio* methods using 6-31G* basis set that is moderate in size and affordable for larger and biologically interesting molecular sizes. The new M06-2x and M06-L DFT functionals found to be the most accurate ones compared to all methods we tested so far. Interaction energy curves by using SG1 grid show discontinuity for several dimers but they disappear when larger DFT grids are used.