Electron correlation effects on first-order intermolecular interaction energies from Brueckner orbitals

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Intramonomer electron correlation plays a crucial role for the determination of first-order electrostatic and exchange intermolecular interaction energies. We investigate to which extent a single determinant description using Brueckner orbitals from a Brueckner Coupled-Cluster Doubles calculation is able to account for intramonomer correlation effects on their long- and short-range contributions. First it is shown that dipole moments, quadrupole moments and radial expectation values compare quite well with BCCD finite-field results for a test selection of nine molecules enclosing HF, H_2O, NH_3, CO, N_2, NO^+, HCN, CuH and CH_3OH and three rare gas atoms, He, Ne and Ar. Then short-range electrostatic and exchange interaction energies calculated with a Brueckner reference determinant description of the monomers will be compared to results from correlated symmetry-adapted perturbation theory calculations for some rare-gas, hydrogen-bonded and mixed dimers. It is found that in general the results improve significantly upon the Hartree-Fock determinant description in those cases, where electron correlation is important. Finally, it is discussed whether a Kohn-Sham determinant could also be used to efficiently calculate correlated first-order interaction energies.