Electrostatic interactions between molecules from relaxed one-electron density matrices of the coupled cluster singles and doubles model

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The influence of the electron correlation on the electrostatic interaction between closed-shell molecules is studied using the relaxed electron densities of the coupled cluster singles and doubles model (CCSD). The corresponding CCSD one-electron density matrices are efficiently computed without full four-index transformation by employing the generalized exchange and Coulomb operator technique. Using several representative van der Waals and hydrogen-bonded complexes we found that in most cases the convergence of the Møller-Plesset expansion of the electrostatic energy, restricted to single, double and quadruple excitations, is quite satisfactory and the fourth-order triple excitation term is more important than the sum of the fifth- and higher-order contributions from the CCSD theory. The relaxation contribution to the CCSD electrostatic energy is of the same order as the triple excitation correction and thus cannot be neglected in any accurate application. The importance of the CCSD correlation correction to the electrostatic energy was gauged by comparison of the total interaction energy computed by the symmetry-adapted perturbation theory (SAPT) and by the supermolecular CCSD(T) approach (coupled cluster singles and doubles model with a noniterative inclusion of triple excitations). Except for the CO and N_2 dimers very good agreement between the two sets of results is observed. For the difficult case of the CO dimer the difference between the SAPT and CCSD(T) results can be explained by the truncation of the SAPT expansion for the dispersion energy at the second order in the intramonomer correlation operator.