Coupled cluster studies. III. Comparison of the numerical behavior of coupled cluster doubles with configuration interaction and perturbation theory. Basis set and geometry optimizations. Forner, Wolfgang; Pylypow, Laura; Cizek, Jiri

Abstract

In the Be atom most of the valence electron correlation energy can be obtained with only 3 equiv. excitations. This is possible also with only one primitive set of p-type gaussians, provided their exponent is carefully optimized. Moller-Plesset (MP) perturbation theory gives less correlation energy than coupled cluster doubles (CCD) in these cases but the same optimum exponent for the set of p functions. For the mols. CO and CO2 where MP2 is known to overestimate the correlation energy in comparison to CCD the convergence properties of MP are studied up to fourth order. The results of MP4(DQ) and CCD are very similar also in these cases. For comparison results for C2H4 are also discussed. Due to size consistency CCD is superior over CI with double excitations (CID). Equil. properties computed with CCD and MP4(DQ) are as reliable as those given by CID, although the variational theorem does not hold for CCD and MP4(DQ). The effect of single excitations turned out to be negligible in these cases. In basis set optimizations all correlation methods studied worked out similar.