Local explicitly correlated coupled cluster methods: DF-LCCSD(T)-F12

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Recent developments in the DF-LCCSD(T)-F12x (x=a,b) methods [8] will be presented. For the first time ever the energies of large molecules with up to 100 light atoms can be calculated with an accuracy near the CCSD(T) basis set limit. It will be shown that neither the pair nor the domain approximations spoil the accuracy of the DF-LCCSD(T)-F12 methods significantly. Especially the domain error, which in severe cases could cause errors of several kcal/mol in DF-LCCSD(T), is efficiently cured by the local formulation of the strong orthogonality projector intrinsic in F12 theory [4,7]. The new local approximations of the additional F12x terms will be discussed in detail. These make it possible to achieve low order scaling of the computational resources (CPU, memory, and disk space) for the F12x terms. The DF-LCCSD(T)-F12x program relies on the linear scaling DF-LCCSD(T) program [1,2,3] and a linear scaling DF-LMP2-F12 program [5,6,7] developed in Stuttgart. Reaction energies of small, medium size and large molecules are studied. Enthalpies of a reaction set comprising 47 reactions are compared to experimental data and to the basis set limit. A QM/MM application will be presented.

Literature:

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