

Molecular fragmentation techniques and intermolecular interaction energies

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Molecular fragmentation (MF) techniques have been developed over an extended period of time with aim to tackle large molecules, parallelly to other methods devoted to the same purpose, like local correlation or method-of-increments approaches. From several MF methods available in the literature, the systematic MF (SMF) [1] has been selected by us and modified to handle branched molecules in a more symmetric way [2]. It is well known that molecular properties other than total energies are often more sensible to the applied approximations, therefore, in this study we apply the SMF approach for intermolecular interaction energies, which up to the second order in terms of the intermolecular interaction operator, depend on first- and second-order properties of monomers (i.e. interacting molecules in the complex). Our investigation shows that the dispersion energy (which in the supermolecular approach corresponds to the electron-correlated part of the interaction energy) is well reproduced by fragmentation techniques. On the other hand, the remaining Hartree-Fock (HF) contribution is reproduced with a much worse accuracy, especially in the asymptotic region. Therefore, the MF techniques can be applied for the calculation of the electron-correlated part of the intermolecular interaction energy, while for the case of the HF energy either larger fragments should be used, or the monomers should be left unfragmented in order to obtain this part of the interaction energy without introducing considerable errors dependent on intermolecular distances [3]. Since the scaling of electron-correlated methods with the molecular size is much more steep than the HF scaling, such a hybrid method is expected to be useful in many applications. The proposed approach has been tested on various sample systems and on several real-life complexes, like calixarenes with amino acids.

References

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