A BSSE-free second-order perturbation theory from Hermitian CHA-SCF Canonic Orbitals

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Abstract

We present an alternative perturbational approach free of basis set superposition error (BSSE) within the framework of the Chemical Hamiltonian Approach (CHA). The new formulation (CHA-S-MP2) is based on canonic (and orthogonal) CHA orbitals obtained from a hermitized CHA Fock operator. The final expression shows a considerable simplification of the method as compared to the previous CHA-MP2 formalism. In the present formulation only two four-index transformations are necessary so that the computational cost of the CHA-S-MP2 calculation is just twice that of a conventional uncorrected MP2 calculation. Also, contrary to the counterpoise method, the computational cost doesn't depend on the number of interacting fragments. Numerical full geometry optimizations of water and hydrogen fluoride dimers and potential energy surfaces for helium and argon dimers for several basis sets are presented. The present method is compared to both the counterpoise and previous CHA-MP2 BSSE correction schemes, showing a remarkable agreement between all three methods. However, the wrong behavior using the aug-cc-pVDZ basis set indicates that the present method is not as robust as the original non-hermitian CHA-MP2 formulation.

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