

Molecular orbital calculations of water clusters on counterpoise-corrected potential energy surfaces.,.

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Streszczenie

Water dimer and the cyclic trimer and tetramer are calculated using the Hartree–Fock (HF), second-order Møller–Plesset (MP2), and two density functional theory (DFT) methods, B3PW91 and B3LYP for a wide variety of different basis sets. The interaction energies and O...O distances as calculated on the normal and counterpoise (CP) corrected potential energy surfaces (PES) are compared as a function of basis set quality (as measured by the energies for optimized water monomer) for each of the four methods. The HF and DFT procedures lead to reasonably rapid convergence to the large basis set values for both interaction energies and O...O distances. Even moderate basis sets can be used to obtain results similar to the extrapolated values when optimizations are performed on the CP-corrected PES's. For MP2, these energies and distances converge to the extrapolated values much more slowly. Basis set superposition error (BSSE) remains significant even for the best basis sets used (aug-cc-pVQz and aug-cc-pVTZ). Nevertheless, the extrapolated MP2 interaction energies could also be reproduced with moderate sized basis sets on the CP-corrected PES, although the calculated O...O distances were less well reproduced with moderate sized basis sets. We calculated the CP using the procedure where each fragment is calculated in the basis of the entire aggregate. The results show this procedure to be well-behaved, as the normal and CP-optimized calculations converged systematically to the same values as the basis set improved for all four methods used. The advantages of this practice over a proposed hierarchical procedure for calculating the CP are discussed. A misconception about the supposed superiority of the latter procedure is remedied.

Słowa kluczowe

Basis sets, Chemical calculations, Energy, Interaction energies, Oligomers

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