

Charge-transfer and the hydrogen bond: Spectroscopic and structural implications from electronic structure calculations.

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Abstract

The absolutely localized molecular orbital (ALMO) model is a fully variational approach which permits polarization of molecules interacting in a cluster while prohibiting charge transfer (or dative interactions) between individual molecules. The ALMO model can be applied within any density functional theory calculation – the B3LYP functional is employed in this work. ALMO DFT calculations of observables such as optimized geometry, vibrational frequencies and their intensities, and vertical detachment energies are performed for the water dimer, the chloride-water complex and the cyanide water complex. The vibrational spectra are obtained both within the harmonic approximation and by quasiclassical trajectory simulations. By comparing these ALMO DFT calculations with full DFT calculations using precisely the same functional and basis, the role of charge transfer on observables in these model hydrogen bonding systems can be assessed. The results can be further interpreted using ALMO-based energy decomposition analysis, which help to reveal the origin of sensitivity or insensitivity of observables to dative interactions. Analysis of the results also suggests that the B3LYP functional, while qualitatively adequate, appears to somewhat overestimate charge transfer effects.