

On the accuracy of density-functional theory exchange-correlation functionals for hydrogen bonds in water

Authors:

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Abstract:

Despite widespread application of density-functional theory (DFT) to the treatment of water in various environments, for example, liquid water, ice, adsorbed, and confined water, there are still question marks over how well DFT with exchange-correlation (xc) functionals such as PBE and BLYP describe hydrogen bonds between H₂O molecules. Here, we address this issue through a series of studies on water clusters. Such clusters are important in their own right (implicated in phenomena such as acid rain formation and ice nucleation) and, moreover, are amenable to treatment with explicitly correlated quantum chemistry methods and quantum Monte Carlo.

Using coupled cluster with single and double excitations plus a perturbative correction for connected triples [CCSD(T)] as a reference, we have considered how well a range of xc functionals perform in describing the energetics of water monomers and dimers extracted from DFT simulations of liquid water. A key observation is that both PBE and BLYP significantly overestimate the dissociation energies of water dimers extracted from the liquid, in marked contrast to how these functionals perform for water clusters in their equilibrium gas phase geometries. This is because PBE and BLYP incorrectly describe the cost to stretch the OH bonds of the water molecules to their distorted liquid water geometries. Thus we provide a possible explanation for the overstructured radial distribution functions routinely observed in BLYP and PBE simulations of liquid water.