

# Is valence CCSD(T) enough for the binding of water clusters? The isomers of $(\text{H}_2\text{O})_6$ and $(\text{H}_2\text{O})_{20}$ as a case study

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Benchmark calculations on noncovalent interactions typically exclude correlation effects beyond valence CCSD(T) owing to their steep computational cost scaling. In this work, we consider their importance for water clusters, specifically, eight isomers of  $(\text{H}_2\text{O})_6$  and four Wales-Hodges isomers of  $(\text{H}_2\text{O})_{20}$ . Higher order connected triple excitations,  $T_3\text{-(T)}$ , destabilize  $(\text{H}_2\text{O})_{20}$  isomers by about  $-0.4$  kcal/mol, but this is more than compensated by an stabilization of up to  $0.85$  kcal/mol due to connected quadruple excitations. In general, higher-order correlation effects favor more compact isomers over more ‘spread-out’ ones. We also consider additional small effects for balance: scalar relativistics destabilize  $(\text{H}_2\text{O})_{20}$  by ca.  $-0.4$  kcal/mol, which is fortuitously compensated by the ca.  $0.55$  kcal/mol diagonal Born-Oppenheimer correction. Core-valence correlation has the greatest impact, at ca.  $1.3$  kcal/mol for the icosamer. In all, contributions beyond valence CCSD(T) need to be considered if cohesive energies of water clusters are to be accurate to better than 1%.

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