# Investigation of DLPNO-CCSD(T) for Noncovalently Bonded Systems

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Domain based local pair natural orbital coupled cluster method with single-, double-, and perturbative triple excitations (DLPNO-CCSD(T)), is a relatively new quantum chemical method that can compute energies in a fraction of the time compared to canonical CCSD(T). It is also nearly linear scaling, making it applicable for molecules with hundreds of atoms. This makes it an intriguing option for computational chemists, however some accuracy is lost in the process. We investigated the performance of this method compared to the canonical CCSD(T) for noncovalently bonded systems by looking at the computational timing, number of pair-natural orbitals (PNOs) included, absolute energies, binding energies, and conformational energies. We studied water clusters with 1-10 waters and the S22 data set, using def2-TZVP, aVDZ, aVTZ, and aVQZ basis sets. The three default, “black box” cutoff criteria for the DLPNO-CCSD(T) method; ‘loose’, ‘normal’, and ‘tight’, were used as well as our own ‘verytight’ and ‘veryverytight’ cutoffs based on error analysis performed by Liakos et al.[1] Different types of extrapolation were done, including commonly used basis set extrapolation as well as unique PNO extrapolation. Some of the extrapolation results were promising but others were not impressive. It was determined that it is very important to use tight enough cutoffs to ensure accurate energies. It is also worthy to note that the method’s accuracy varies based on the on system; performing better for the water clusters, but less so for certain molecules in the S22 database. Overall, DLPNO-CCSD(T) saves a huge amount of time, especially for larger systems, however tight enough cutoffs are needed to achieve desired accuracy.

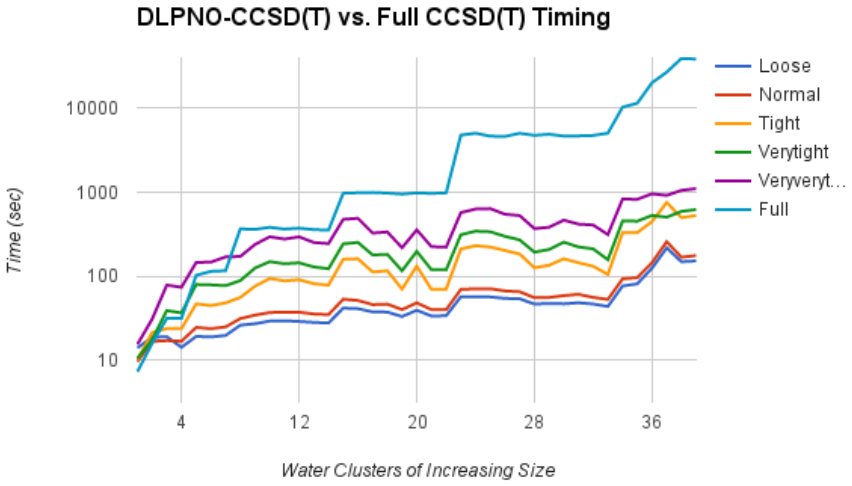


Figure 1. The timing/scaling of the different DLPNO-CCSD(T) cutoff criteria compared to the full CCSD(T) method for water clusters with 1-10 waters.

[1] J. Chem. Theory Comput. 2015, 11, 1525−1539