

Approaching CCSD(T)/CBS energies for molecules of up to 1000 atoms: method development and benchmark applications

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Recent optimization efforts [1-3] and extensive benchmark applications [4-5] are presented illustrating the accuracy and efficiency of the local natural orbital (LNO) coupled-cluster (CC) with single-, double-, and perturbative triple excitations [LNO-CCSD(T)] method.

The accuracy of the local approximations can be systematically improved via a single parameter in a black box manner. The complete basis set (CBS) limit of LNO-CCSD(T) is reliably approached by extrapolating from augmented triple- and quadruple-zeta basis sets [CBS(T/Q)], since the quasi-linear dependence of the AO basis emerging in large molecules is also handled. [4]

Compared to canonical CCSD(T) references computed for molecules of up to 63 atoms the average LNO-CCSD(T) correlation and reaction energy errors with Normal settings are below 0.07% and 0.34 kcal/mol, respectively. [1] The same errors drop down by a factor of 3 when using the Tight truncation thresholds.[4] Further benchmarking performed on systems of 60-130 atoms revealed systematic convergence with Loose, Normal, Tight, etc. truncation thresholds, which can also be exploited to determine error estimates with respect to CCSD(T). Even for particularly complicated cases with up to about 100 atoms LNO-CCSD(T)/CBS(T,Q) results agree within 1-2 kJ/mol with recent, explicitly correlated local CCSD(T) reaction and interaction energies. [4]

An LNO-CCSD(T)/CBS(T,Q) energy evaluation usually takes less than an order of magnitude more time than DF-HF/CBS(T,Q), even in the range of a few hundred atoms. Parallel execution can further decrease wall times to the range of hours. Thus LNO-CCSD(T)/CBS(T,Q) is not the rate limiting if applied in computational protocols involving geometry optimization or frequency evaluation with DFAs above rung three. The low minimal memory requirement (few tens of GBs) and the negligible disk use of the method makes it routinely applicable for the majority of closed-shell molecules appearing in modern chemistry even with easily accessible, single CPU workstations.

The capabilities of the current LNO-CCSD(T) implementation are demonstrated on large, three-dimensional examples, such as protein-ligand binding.[5] An LNO-CCSD(T)/CBS(T,Q) correlation energy calculation is feasible for more than 1000 atoms and almost 50000 atomic orbitals using an 8-core processor and 120 GB memory (see Figure.).

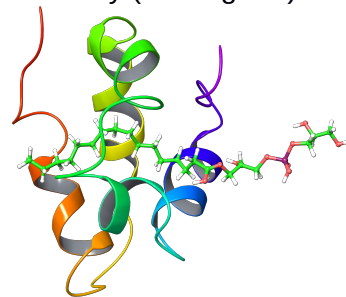


Figure 1: Lipid transfer protein, 1023 atoms,
LNO-CCSD(T)/def2-QZVPPD (49656 AOs) takes ~ 4 weeks on 8 cores.

References:

- [1] P. R. Nagy, G. Samu, M. Kállay, *J. Chem. Theory Comput.* **14** (2018), 4193
- [2] P. R. Nagy, G. Samu, M. Kállay, *J. Chem. Theory Comput.* **12** (2016), 4897
- [3] P. R. Nagy, M. Kállay, *J. Chem. Phys.* **146** (2017), 214106
- [4] P. R. Nagy, M. Kállay, submitted to JCTC (2019)
- [5] P. R. Nagy, M. Kállay, (2019) in preparation