

Two- and three-body energies from the DLPNO-CCSD(T) method

M. Krzyżowska and R. Podeszwa

Institute of Chemistry, University of Silesia, Szkolna 9, 40-006 Katowice, Poland
rafal.podeszwa@us.edu.pl

Domain-based local pair natural orbital coupled cluster theory with single, double, and perturbative triple excitations [DLPNO-CCSD(T)] method [1] was applied to calculations of two- and three-body intermolecular interactions energies of several van der Waals complexes. The results were compared with the coupled cluster method with single, double and non-iterative triples excitations with the complete basis set extrapolation [CCSD(T)/CBS] benchmarks and several density functional theory plus dispersion approaches (DFT-D) [2,3]. The accuracy of the DLPNO-CCSD(T) method for two-body interaction energies was tested with several local cutoff thresholds with both orbital basis sets and with explicitly correlated DLPNO-MP2-F12 method [4] used with a DLPNO-CCSD(T) correction. The large computational speed-up of the DLPNO-CCSD(T) method compared to the canonical CCSD(T) method is followed by decrease of the accuracy but the the quality of the two-body energies was found to be competitive with the DFT-D methods. For three-body non-additive energies, the DLPNO-CCSD(T) offers similar overall accuracy to the MP2 method, a rather disappointing result considering the lack of non-additive dispersion in the supermolecular MP2 approach. On the other hand, for three-body energies, the DFT-D methods do not work, either [5]. Overall, DLPNO-CCSD(T) can be to some extent used for intermolecular interactions after careful selection of cutoffs and basis sets.

References

1. C. Riplinger, B. Sandhoefer, A. Hansen, F. Neese, *J. Chem. Phys.*, **139** 134101 (2013).
2. D. E. Taylor, J.G. ngyn, *et al.*, *J. Chem. Phys.*, **145** 124105 (2016).
3. J. Řezáč, Y. Huang, P. Hobza, G. J. Beran, *Journal of Chemical Theory and Computation*, **11** 3065-3079 (2015).
4. F. Pavoevi, P. Pinski, *et al.*, *J. Chem. Phys.*, **144** 144109 (2016).
5. W. Jankiewicz, R. Podeszwa, and H. A. Witek, *J. Chem. Theory Comput.*, **14**, 5079–5089 (2018).