

# Accurate ab initio quantum chemistry for large molecules. New developments and future opportunities

Frank Neese

Max-Planck-Institut für Chemische Energiekonversion, Stiftstraße 34-36,  
45470 Mülheim an der Ruhr, Germany

The coupled cluster method has been proven to be robust, accurate and size consistent. It hence is an ideal tool for computational chemistry. The overwhelming problem in applying coupled cluster theory in a large scale (e.g. comparable to the use of density functional theory) is its high computational cost and its unfavorable scaling with system size. Many variants of low order scaling coupled cluster methods have been proposed over the years. Our contribution to this field was to realize that highly efficient and accurate local coupled cluster methods can be based on the concept of pair natural orbitals (PNOs). The original local pair natural orbital coupled cluster method with single- and double excitations (LPNO-CCSD) has been proposed in 2009 and has since been proven to be reliable, efficient and accurate. A drawback of this method was the expansion of the PNOs in the virtual MO basis which led to some higher order scaling steps (up to  $O(N^5)$ ). We have previously succeeded to reformulate this method in a fashion that is near linear scaling while retaining the accuracy and all the outstanding features of the original LPNO-CCSD method. The new method is termed "domain based LPNO-CCSD(T)" (DLPNO-CCSD(T)) and is based on the idea to expand the PNOs (which are local in nature) in projected atomic orbitals (PAOs) that belong to domains.[1,2] The domains are chosen to be large (typically between 10 and 20 atoms) such that an accurate expansion of the PNOs is possible. The original DLPNO-CCSD method had only three cut-off parameters. Any additional truncation in DLPNO-CCSD is based on these three cut-offs, such that the method fully retains its robust black box character. Calculations with more than 450 atoms and 8900 basis functions have been successfully carried out with this methodology. The talk will discuss this method together with other recent developments in the area.

[1] Riplinger, C., Neese, F., *J. Chem. Phys.* 138, 034106 2013.

[2] Riplinger, C.; Sandhoefer, B.; Hansen, A.; Neese, F. *J. Chem. Phys.*, 134101, 2013.