Adding dynamic correlation to DMRG via adiabatic connection

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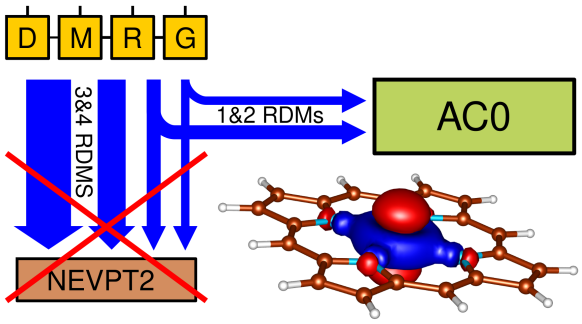

For multireference calculations, CASSCF is the method of choice. Due to exponential scaling, CASSCF is limited to around 20 strongly correlated orbitals in the active space. With the DMRG method, we can push this limit to more than 50 orbitals without losing much accuracy. However, the orbitals outside of the active space are not correlated and to make accurate predictions, we also need to capture the weaker dynamic correlation outside of the active space. Most state-of-the-art methods for multireference dynamic correlation treatment (NEVPT2 for example) use up to 4 particle reduced density matrices (RDMs) from the active space, which leads to an unfavorable scaling with the active space size. While this is not an issue with canonical CASSCF, as the imposed limit is close to the limits of CASSCF itself, it completely prohibits the use of these methods with the large active spaces typical for DMRG-CASSCF.

In this talk we present the new Adiabatic Connection (AC) method of Kasia Pernal, which needs only 1&2 RDMs from the active space, which in combination with DMRG-CASSCF allows us to perform accurate multireference calculations with huge active spaces. We illustrate the usefulness of this approach on several challenging systems.

[1] K. Pernal, Phys. Rev. Lett., **120** (2018), 013001.

[2] P. Beran, M. Matoušek, M. Hapka, K. Pernal, L. Veis, J. Chem. Theory Comput., **17** (2021), 7575–7585.