Active Space Selection based on 1st order perturbation Theory (ASS1ST)

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Efficient and robust approximations to the full configuration interaction (Full-CI) method such as the density matrix renormalization group (DMRG) and the Full-CI quantum Monte-Carlo (FCIQMC) algorithm allow for multi-configurational self-consistent field (MC-SCF) calculations with large active spaces. This opens up the possibility to treat large and complex systems that were previously untractable but at the same time it calls for an efficient and reliable active space selection as the choice of how many electrons and orbitals enter the active space is critical for any multireference calculation. In this work we propose an Active Space Selection based on 1st order perturbation Theory (ASS1ST)[1] that follows a 'bottom-up' strategy and utilizes a set of quasi-natural orbitals together with sensible thresholds for their occupation numbers. The required quasi-natural orbitals are generated by diagonalizing the virtual and internal part of the one-electron reduced density matrix that is obtained from strongly contracted n-electron valence perturbation theory (SC-NEVPT2) on top of a minimal active space calculation. Self consistent results can be obtained when the proposed selection scheme is applied iteratively. Here we present the initial applications on some benchmark systems indicate the capabilities of ASS1ST and the strengths and limitations are critically discussed.

References

1. Abhishek Khedkar and Michael Roemelt. *J. Chem. Theory Comput.* **15(6)** (2019), 3522-3536.