Quantum Information-Assisted Complete Active Space Optimization (QICAS)

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Automated active space selection is arguably one of the most challenging and essential aspects of multiconfigurational methods. If accomplished, it would elevate active space methods such as CASSCF to complete black-box machineries. As it turns out, this may be systematically achieved, by using precise quantum information tools for electronic structure analysis [1-5]. In particular, based on a preceding low-cost calculation, suitable active orbitals can be selected in an *ab initio* manner based on their unique high entanglement profile [4].

In this work we take these promising ideas to the next level by proposing a quantum information-assisted complete active space optimization method (QICAS) [6]. Instead of just selecting active orbitals as the most entangled Hartree-Fock orbitals, we *transform* the active space by minimizing the entanglement of the complementary inactive orbitals, which results in remarkably accurate optimal active orbitals. For instance, for C_2, the energy of a post-QICAS CASCI calculation matches nearly exactly with the CASSCF one.

Accordingly, our study reveals and validates for the first time a profound empirical statement: the optimal inactive space contains the least entanglement. This in turns inspires an energy-free orbital optimization method which places most of the correlation within the optimal active space. For challenging systems, QICAS offers an ideal starting point, from which the number of expensive CASSCF iterations needed for chemical accuracy is greatly reduced.
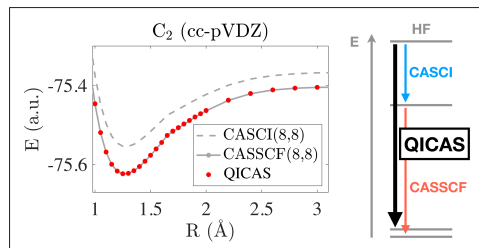

Figure 1: i-CAS energy compared to CASCI and CASSCF energies for C_2 in cc-pVDZ basis.

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