Selection of active orbitals for strong electron correlation

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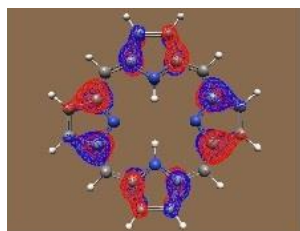
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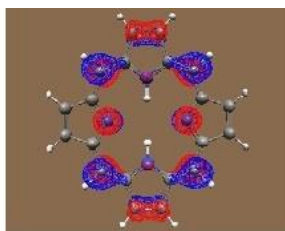
Strong electron correlation is still a major problem in quantum chemistry. It occurs in transition states where bonds are broken, large conjugated systems, transition metal compounds and virtually all excited states. Density functional theory can treat only moderately strong correlation. The best wavefunction methods use a multiconfigurational (usually CAS) reference function augmented by dynamical correlation. They require the definition of initial active orbitals, preferably by an inexpensive black-box method. Chemical intuition works only rarely. There was much recent interest in this field, and several methods were proposed. For ground states these utilize spontaneous symmetry breaking, preliminary Density Matrix Renormalization Group calculations, high temperature SCF, and identification of a conceptual minimum AO basis. For excited states, preliminary UHF and CIS calculations were proposed. Some of these methods are expensive, same still rely on chemical intuition, others identify only the frontier orbitals, disregarding the essential exchange terms. We will show that the simplest (and oldest) criterion, using Unrestricted Natural Orbital (UNO) occupation numbers, yields the correct active space in all ground-state examples we could verify using high-level methods (mainly DMRG). It is largely black box, inexpensive, and allows the definition of a minimal active space. In view of the factorial scaling of the computational effort with the size of the CAS space, the latter is important. Other spontaneous symmetry breakings explored recently (e.g., Complex and General Hartree-Fock) are not expected to change the results qualitatively. Although UHF is inexpensive, finding symmetry breaking solutions is often difficult and requires a recently developed analytical method (Tóth and PP, JCP **2016**, *145*, 164102). Examples shown include simpler cases like polyenes and polyacenes, and more difficult systems like free base porphine, Thiele's hydrocarbon, C_{60}, transition states of pericyclic reactions, and transition metal compounds like $[Fe(CO)_3NO]^-$ and ferrocene.

Unrestricted Natural Orbital Occupation numbers of the four most strongly correlated (Gouterman) orbitals in free base porphine (out of 18)
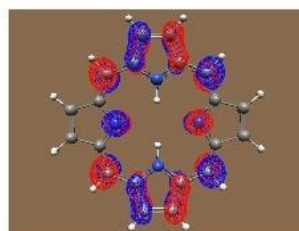
1.558	1.488	0.512	0.442