### Active Orbital Space Selection Based on Density Matrices

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**INTRODUCTION**

- The selection of active orbitals is crucial for any quantum-chemical multi-configurational method.
- A poor choice of this subset of orbitals can lead to even qualitatively wrong results.
- Currently, these active orbitals are chosen based on empirical rules (see e.g., [1]) or natural orbital occupation numbers from preceding calculations (see e.g., [2,3]).
- These selection procedures often include a preliminary phase of trial and error and are therefore only be applied by experienced experts.
- Objective selection criteria that culminate in an automated active orbital selection are highly desirable.

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**PRINCIPLES OF THE METHOD**

- We exploit the following benefits of the density matrix renormalization group (DMRG) [4]:
  - Handle active spaces with up to 100 orbitals.
  - Analyze partially converged wave functions with respect to orbital entanglement.
  - Statically correlated orbitals have to be included in the active space, which can be identified by their entanglement [5].
  - The single-orbital entropy $S_1$, the two-orbital entropy $S_2$, and the mutual information $I_{ij}$ are suitable entanglement measures.
  - $S_1 = \frac{1}{2} \sum_i \ln \lambda_i$, $S_2 = \frac{1}{2} \sum_{ij} \ln \lambda_i \lambda_j$, $I_{ij} = \frac{1}{2} \sum_i \sum_j \ln \frac{\lambda_i \lambda_j}{\lambda_i + \lambda_j}$, $\lambda_i$ and $\lambda_{ij}$ are the eigenvalues of the one- and two-orbital reduced density matrices for orbital $i$ and orbitals $i$ and $j$, respectively.
  - $\alpha$ labels the four possible occupations in a spatial orbital basis.

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**RESULTS FOR THE PERMANGANATE ION, OXO-MN(SALEN) AND CuO₂²⁺ [4]**

- A large active orbital space including 44 orbitals around the Fermi level was analyzed with respect to the orbital entanglement for the singlet, triplet, and quintet state.

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**AUTOMATIC SELECTION PROTOCOL**

- Initial calculation is performed for a very large active space.
- Consistency tests ensure stability of the method.
- Molecular independence is achieved by defining thresholds for each individual calculation.
- Recommended settings involve CI-DEAS start guess [6] for the initial DMRG calculation.
- Final calculation can be performed with DMRG or traditional methods.
- Single-configuration cases are identified.
- Automation is implemented with Python scripts.
- Solely the generation of starting orbitals is not automated.

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**REFERENCES**


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