Building active spaces automatically and systematically from atomic valence orbitals

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Quantum chemical modelling of systems with strong electron-electron correlation usually requires a multiconfigurational and multireference treatment. A major challenge in applying these methods in practice is that a suitable active space needs to be chosen. The selection of the active space is accompanied by several problems, ranging from the necessity to manually select active orbitals to difficulties with clearly identifying molecular orbitals responsible for the principal chemical properties. In this work we describe a new method of constructing multireference active spaces automatically and systematically from a single-reference wavefunction and atomic valence orbitals, based on a linear transformation of the occupied and unoccupied orbital spaces. To demonstrate the capabilities of this approach, we performed calculations for a variety of transition metal complexes.