Spin-free SC-NEVPT2 Method for the Quantum Embedding of the Open-Shell Systems

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High-level electronic structure models are essential for the correct description of molecular systems. These methods, however, suffer from unfavorable scaling with respect to system size, which limits their applicability. On the other hand, in many cases, such as the molecular recognition problem and the exploration of the chemical reaction mechanisms, only a small region of the large system is important for the process of interest. In those cases, it is usually sufficient to apply the high-level model on the relevant fragment only, while the rest of the system can be described with the low-level mean-field approaches. Quantum embedding methods, such as projection-based embedding [1], density matrix embedding theory [2], and bootstrap embedding [3], exploit this principle and have been successfully used to model large scale systems.

Embedding methods can yield fragments with significant multiconfigurational character, for which adequate electronic structure models, such as active space approaches, must be used. Density matrix renormalization group (DMRG) with the *N*-electron valence state perturbation theory (NEVPT2) has emerged as a go-to method for these cases [4]. In the case of systems with local open-shell regions, embedding methods can yield different effective potentials for the embedded α and β electrons, which is incompatible with the spin-free implementations of NEVPT2. Spin-free variant, however, has a more favorable scaling with respect to the active space size. We therefore developed an extension of the spin-free strongly contracted NEVPT2 method that treats the spin-difference term as a perturbation and works out-of-the-box with the commonly used spin-free DMRG software [5]. We present the results obtained by applying this method to the selected systems of interest to demonstrate its efficiency and accuracy.

References:

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