Compressing multireference character of wave functions via fermionic mode optimization

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The aim of the localization of orbitals in quantum chemistry is twofold. On the one hand, localization leads to chemically intuitive orbitals for rationalizing electronic structure of molecular systems. On the other hand, localized molecular orbitals has proven to be useful in making the high-level correlated quantum chemical methods more tractable computationally. These methods usually involve the optimization of the expectation value of specific physical quantities (e.g., radial extent or charge of the orbitals).

A brief overview of the orbital optimization is presented within the framework of tensor network state (TNS) methods, and demonstrate that it has the potential to compress the multireference character of the wave functions after finding optimal molecular orbitals (modes), based on entanglement minimization. This is the quantum chemical application of the more general fermionic mode transformation [1], which is a joint optimization approach that optimizes both the tensors and the modes simultaneously. This strategy is expected to lead to a routine application of TNS methods for strongly correlated multireference problems.

Numerical simulations have been performed for the nitrogen dimer in the cc-pVDZ orbital set for the equilibrium and for stretched geometries [2].

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