Fragment-based quantum subspace diagonalization methods for strongly correlated systems

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Strongly correlated systems, as interesting and as-yet unsolved problems in quantum chemistry, may benefit from the advantages of quantum computers over classical computers. To tackle the high computational cost of methods designed to simulate such systems, fragmentation schemes have been used widely in classical quantum chemistry with encouraging results. One such method is the localized active space self-consistent field (LASSCF) method [J. Chem. Theory Comput. 16(8): 4923–4937 (2020)], which provides a good approximation to complete active space self-consistent field (CASSCF) while significantly reducing the computational cost by breaking the large active space into smaller fragment active spaces. However, correlation between fragments is not considered, and to obtain accurate results for systems with a higher degree of inter-fragment correlation on a classical computer, we would need to move once again towards the factorial scaling associated with CASSCF. Instead, we can leverage the unique structure of a quantum computer to simulate these inter-fragment pieces at relatively lower cost. To that end, we have developed a novel quantum-classical algorithm for multireference systems, by combining the LASSCF algorithm with a Krylov-subspace diagonalization method on quantum computers. The simulation uses information from a LASSCF calculation to prepare an initial state, and then performs a quantum Krylov subspace diagonalization (QKSD) to obtain the ground state energy of the system, giving us the LAS-QKSD method. The QKSD algorithm provides high accuracy with fewer calls to the quantum computer than methods such as quantum phase estimation (QPE), while providing guarantees of convergence, unlike the variational quantum eigensolver (VQE). Fragmentation has the benefit of fewer Slater determinants on the classical side of the algorithm as well as a lowered cost of state preparation on the quantum side. We show that the LAS-QKSD method is a viable alternative to highly expensive CASSCF calculations on molecules requiring large active spaces, using the unique advantages of a quantum computer.