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Main Accomplishments

The auxiliary field quantum Monte Carlo (AFQMC) method invented by the PIs has been shown to provide the most accurate description of strongly correlated electronic systems, from molecules to solids. Unlike other explicitly many-body approaches, quantum Monte Carlo (QMC) methods scale as a low order polynomial of systems size, similar to mean-field methods such as density functional theory (DFT). However, the AFQMC algorithm has the form of an entangled ensemble of mean-field calculations, and so it is significantly more expensive than traditional DFT calculations. This creates a bottleneck for applications to extended systems, such as large molecules and solids. Throughout the project, the AFQMC method has been further developed to overcome these bottlenecks, and benchmarked.

One outcome of the project has been the development of new AFQMC computational strategies to achieve improved scaling with system size, using downfolding and localization schemes, without sacrificing the predictive power of the calculations. A local embedding and effective downfolding scheme have been developed and implemented within the AFQMC method. In this approach a local cluster in which electrons are fully correlated is defined, and the frozen orbital method is used on the remainder of the system to construct an effective Hamiltonian, which operates within the local cluster. This allows to greatly increase the system size which can be feasibly treated given that only a single local cluster is explicitly correlated at the AFQMC level of theory. The approximation is controlled by the separate choice of the spatial size of the active occupied region and active virtual region.

An array of additional technical advances have been made that led to higher speed and accuracy of AFQMC calculations: low-rank tensor decomposition; computation of inter-atomic forces and geometry optimization; correlated sampling for excited states and energy differences; better pseudopotentials and frozen-core for treating core electrons.

An important advance has been the inclusion of the explicit, non-perturbative, treatment of spin-orbit coupling into ab initio auxiliary-field quantum Monte Carlo (AFQMC) calculations. The approach allows a general computational framework for molecular and bulk systems in which materials specificity, electron correlation, and spin-orbit coupling effects can be captured accurately and on equal footing, with favorable computational scaling versus system size.

The accurate computation of forces and other energy derivatives has been a long-standing challenge for quantum Monte Carlo methods. A number of technical obstacles contribute to this challenge. One of the outcomes of the project was to show how these obstacles can be removed with the AFQMC approach. The resulting approach allows applications of full geometry optimizations in bulk materials and paves the way for many-body computations of the phonon spectrum in solids.

A significant outcome of the project has been to extend the reach of AFQMC to calculate excited states. This was done by first building the necessary “computational infrastructure” by implementing quantum chemistry localization methods in both the occupied and virtual sectors. The methods were then deployed to study the chemistry of two- dimensional systems with transition metal atoms, which have possible applications for spintronic devices.

The strategies developed in the course of the project were applied successfully to different test cases. By implementing these strategies the AFQMC method was shown to provide highly accurate descriptions of strongly correlated electronic systems, from molecules to solids, while maintaining better computational scaling with system size, N [$O(N^3 - N^4)$], than most quantum chemistry many-body methods. Multiple challenging applications of the method were studied, including to various transition metal molecules and single-molecule magnets, systems of great interest for quantum information science (QIS) applications.

The theoretical capabilities developed in the course of the project have had cross-cutting impacts beyond specific systems, with the potential to deliver breakthrough science, given that the techniques and codes developed are very general and applicable to many other problems, for example strongly correlated transition metal oxides and materials with lanthanide and actinide elements. By establishing highly accurate benchmark calculations, the results have also allowed the validation of less computer intensive methods. The capability of the tools developed will allow a new level of prediction and understanding of materials.

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