Final report

1) DOE Award #: DE-FG02-07ER46366
Recipient: College of William & Mary

2) Project Title: "Predictive Capability for Strongly Correlated Systems: Mott Transition in MnO, Multielectron Magnetic Moments, and Dynamics Effects in Correlated Materials"
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4) Abstract

There are classes of materials that are important to DOE and to the science and technology community, generically referred to as strongly correlated electron systems (SCES), which have proven very difficult to understand and to simulate in a material-specific manner. These range from actinides, which are central to the DOE mission, to transition metal oxides, which include the most promising components of new spin electronics applications as well as the high temperature superconductors, to intermetallic compounds whose heavy fermion characteristics and quantum critical behavior has given rise to some of the most active areas in condensed matter theory. The objective of the CMSN cooperative research team was to focus on the application of these new methodologies to the specific issue of Mott transitions, multi-electron magnetic moments, and dynamical properties correlated materials. Working towards this goal, the W&M team extended its first-principles phaseless auxiliary-field quantum Monte Carlo (AFQMC) method to accurately calculate structural phase transitions and excited states.

5) Brief description of accomplishments:

Significant progress was achieved in developing and applying our phaseless auxiliary-field quantum Monte Carlo (AFQMC) method. The following papers cite this DOE grant:

1. "Eliminating spin contamination in auxiliary-field quantum Monte Carlo: realistic potential energy curve of F_2," W. Purwanto, W. A. Al-Saidi, H. Krakauer, and S. Zhang, *Journal of Chemical Physics* **128**, 114309 (2009).

   Introduced a method to eliminate spin-contamination in AFQMC calculations. Most correlated electronic structure methods rely on the use of an approximate reference state wave function Ψ_r, which is often spin-contaminated. This may break the spin symmetry of spin-independent Hamiltonians and can result in significant errors, especially when bonds are stretched or broken. Our paper introduced a simple spin-projection method for AF QMC, which yields spin-contamination-free results, even with a spin-contaminated Ψ_r.

2. "Excited state calculations using phaseless auxiliary-field quantum Monte Carlo: potential energy curves of low lying C_2 singlet states," W. Purwanto, S. Zhang, and H. Krakauer, *Journal of Chemical Physics* **130**, 094107 (2009).

We showed that AFQMC can be used for the difficult task of calculating many-body excited states. For excited states, we showed how to prevent of collapse into the ground state, at the same time controlling Fermion sign/phase problem. Using the challenging C2 molecule as a test case, we calculated the potential energy curves of the ground and two low-lying singlet excited states and obtained good agreement with experimental spectroscopic constants for both ground and excited states.

3. "Pressure-induced diamond to beta-tin transition in bulk silicon: A quantum Monte Carlo study," W. Purwanto, H. Krakauer, and S. Zhang, *Physical Review B* **80**, 214116 (2009).

The pressure-induced structural phase transition from diamond to beta-tin structure in silicon is an excellent test for theoretical total-energy methods. The transition pressure provides a sensitive measure of small relative energy changes between the two phases (one a semiconductor and the other a semimetal). Density-functional results exhibit sensitivity to the particular form of the exchange-correlation functional. Even the generally much more accurate diffusion Monte Carlo method has shown a noticeable fixed-node error. We used our phaseless AFQMC method to calculate the relative energy differences in the two phases. In this method, all but the error due to the phaseless constraint can be controlled systematically and driven to zero. In both structural phases we were able to benchmark the error of the phaseless constraint by carrying out exact unconstrained AFQMC calculations for small supercells. Comparison between the two shows that the systematic error in the absolute total energies due to the phaseless constraint is well within 0.5 mEh /atom. Consistent with these internal benchmarks, the transition pressure obtained by the phaseless AFQMC from large supercells is in very good agreement with experiment.