A. Project Summary.

Many-body computational methods for electronic structure of clusters and molecular nanosystems

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Quantum Monte Carlo (QMC) is one of the most promising many-body computational approaches for electronic and atomic structures of real materials. QMC combines analytical insights, computational results from other methods and stochastic techniques into a powerful tool for investigation of many-body quantum systems. Explicitly correlated wave functions and accurate solutions of the Schrödinger equation offer both new physical insights and valuable practical results. The QMC method possesses clear advantages in the direct and accurate treatment of correlation effects, favorable scaling in the number of particles when compared with other wave function approaches, scalability on parallel architectures and wide range of applicability. QMC is gradually becoming *a method of choice and a new alternative* whenever traditional approaches are not useful either because of approximations involved (Density Functional methods) or because of computational limits for larger systems (post-Hartree-Fock methods).

The vision for further development of QMC methods is based on the experience from a series of successful projects over the last few years. What is needed the most are quantities other than energies such as forces between ions, more systematic treatment of excitations and responses to external fields. The goals of this project are three-fold:

- To significantly expand the capabilities of QMC, in particular, for calculations of:
  - Born-Oppenheimer forces on ions
  - excited states and optical absorption
  - impact of zero point motion on excitations in systems with light atoms.
- To apply these developments to molecular nanosystems and clusters with high potential for scientific discoveries and applications. The systems of interest include:
  - thiolate derivatives which are being explored as prototypes for molecular devices
  - silicon Si_nH_m and $Si_nO_lH_m$ nanocrystals which are promising candidates for ultrabright luminofors.
- To train under- and graduate students in advanced electronic structure methods and in efficient use of parallel and distributed computational platforms at national supercomputing facilities.

Results from previous projects suggest that QMC is capable of solving research problems in *a combination of system sizes, fidelity to quantum principles and practical accuracy* which is out of reach of traditional methods. The planned method development will significantly expand this potential and provide a genuine many-body framework for accurate calculations of geometries and excitations, a long-standing computational challenge. The QMC developments will be applied to a number of interesting and unexplained phenomena in two classes of promising new nanomaterials.