Annual Report for Blue Waters Allocation

- **Project Information**
  - Blue Water Professorship
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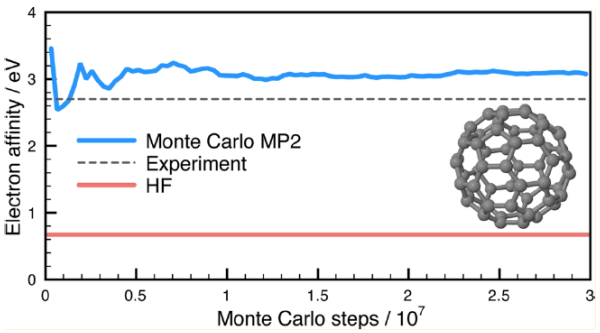
- **Executive summary (150 words)**

Two breakthroughs in the algorithms of *ab initio* electronic structure theory developed recently by the PI's group are deployed on Blue Waters to perform predictively accurate calculations for the optoelectronic properties of large conjugated molecules used in advanced materials and for structures of nature's most important crystals such as ice and dry ice and liquids such as water, all from first principles. These *ab initio* methods go beyond the usual workhorse of solid-state calculations (density-functional approximations) in the fidelity of simulations that can be achieved and also uses novel stochastic algorithm, embedded-fragment algorithm, or both to realize unprecedented scalability with respect to both system and computer sizes.

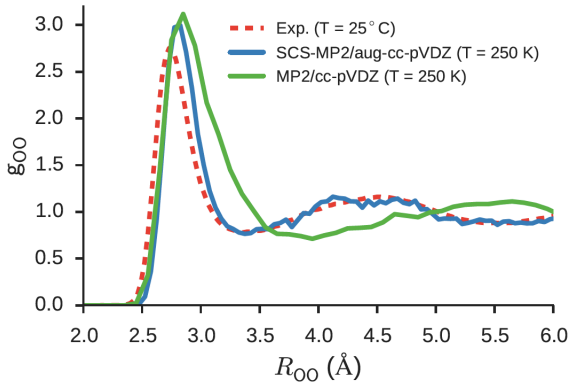
- **Description of research activities and results**
  - *Key Challenges:* Our group has recently made two breakthroughs in computational chemistry for large molecules, solids, and liquids. One is the method that allows such high-level calculations to be applied to an infinitely extended molecular crystals and molecular liquids, including nature's most important solids and liquids such as ice and liquid water. It divides these crystals and liquids into fragments embedded in their electrostatic field and treat these fragments by well-developed molecular theories and software in a highly parallel algorithm. The other weds systematic (i.e., *ab initio*) many-body electronic structure methods with quantum Monte Carlo, enabling massively parallel, systematically accurate electronic structure calculations for larger molecules and solids. With these, (1) we plan to predict a variety of properties of all known molecular phases of ice and dry ice to construct *ab initio* phase diagrams of these important solids as well as of liquid water using *ab initio* Born-Oppenheimer molecular dynamics. (2) We will also apply the novel quantum Monte Carlo method to predict the stacking interaction energies (important for morphology and thus functions) and optoelectronic parameters (ionization and electron attachment energies, band gaps) of conjugated organic molecular solids and supramolecular assemblies.
  - *Why it Matters*: Project (1) advances geochemistry, astrophysics, and planetary science where probing high-pressure phases of ices of atmospheric species on Earth or other planets are important but experimentally difficult and expensive. The systems studied by project (2) include solids that serve as bases of advanced materials such as bulk heterojunction organic solar cells, batteries, sensors, smart windows, field-effect transistors, and light emitting diodes. The optoelectronic parameters are the quantities of prime importance determining the solids

performance and functions, but the usual density-functional approximations are known to be poor for these properties. Here, our new method is uniquely useful and accurate. The impact of this research is broadly in the area of energy science and technology.

- *Why Blue Waters:* Today's workhorse computational methods for solids (density-functional methods) and liquids (classical molecular dynamics) are routine on a small computer cluster, but with limited accuracy. Therefore, the most meaningful use of Blue Waters in this area is to fundamentally improve the accuracy rather than system size (which is already formally infinite). In electronic structure theory, this means switching from density-functional methods or classical and empirical force fields to *ab initio* theories, which solve the fundamental equation of motion of chemistry rigorously and in systematic approximations with controlled errors. However, conventional matrix-algebra algorithms of *ab initio* theories are fundamentally non-scalable. The aforementioned combination of *ab initio* theories with quantum Monte Carlo and the fragment methods are among the few that may be realistically and usefully deployable on the large number of processors available on Blue Waters. Such calculations, in turn, can potentially directly address or answer some outstanding scientific questions of solids, liquids, or large optoelectronic materials purely computationally with sufficient accuracy.
- *Accomplishments:* There are four main accomplishments this year, in all of which Blue Waters has played an essential role: (1) *Parallel Monte Carlo second-order perturbation theory.* We have developed scalable Metropolis-Monte-Carlo algorithm for *ab initio* second-order many-body perturbation theory. It can compute correlation energies and correlation-corrected ionization and electron-attachment energies directly without the sign problem. In this work, we have evaluated the correlated electron affinity of C_{60} using 320 processors of Blue Waters (**figure**), whose derivatives serve as an electron acceptor material in many organic bulk heterojunction solar cells. (2) *GPU-based parallel Monte Carlo second-order perturbation theory.* The aforementioned method has been enhanced to execute on Blue Waters' CPU-GPU heterogeneous platform efficiently using CUDA. (3) *Ab initio calculation of thermal expansion in ice Ih.* Ice Ih, the most common form of water ice, has unusual thermal behavior: its volume initially contracts then expands with temperature. With the parallel fragment *ab initio* second-order many-body perturbation method running on Blue Waters, we have determined the structures and phonon frequencies of ice Ih under various pressures and simulated its thermal expansion coefficient in the entire temperature range of



the phase's existence. The calculation has reproduced the sign change in the thermal expansion coefficient correctly. (4) *Ab initio molecular dynamics simulation of water.* We have implemented Born-Oppenheimer molecular dynamics method using atomic forces calculated by an *ab initio* fragment method. Running parallel on Blue Waters, this calculation has reproduced the radial distribution function (**figure**), infrared absorption, and Raman scattering spectra as well as self-diffusion coefficients in liquid water completely from first principles. This study has revealed the counterintuitive relationship between the water-water interaction strengths and melting temperature.



- **List of publications and presentations associated with this work**

S. Y. Willow, M. R. Hermes, K. S. Kim, and S. Hirata, *Journal of Chemical Theory and Computation* **9**, 4396-4402 (2013), "Convergence acceleration of parallel Monte Carlo second-order many-body perturbation calculations using redundant walkers."

R. Brewster, S. Y. Willow, and S. Hirata, (in preparation, 2014), "GPU parallelism of Monte Carlo second-order many-body perturbation method."

M. Salim, S. Y. Willow, and S. Hirata, (in preparation, 2014), "Second-order many-body perturbation study of thermal expansion in ice Ih."

S. Y. Willlow, M. Salim, K. S. Kim, and S. Hirata, (in preparation, 2014), "Born-Oppenheimer molecular dynamics simulation of liquid water with the generalized embedded-fragment second-order many-body perturbation method."

Work benefitted from Blue Waters has been highlighted in invited talks by the PI in the following conferences and university seminars: American Conference on Theoretical Chemistry (2014); Low-Scaling and Unconventional Electronic Structure Techniques Conference (2014); International Symposium on "Quantum Chemistry for Extended Systems" in honor of Professor Jean-Marie André (2014); Seminar, Department of Chemistry and Biochemistry, University of Arkansas (2014); Seminar, Department of Chemistry, Virginia Tech (2014).

- **Plan for next year**

We request 150,000 node-hours (100,000 node-hours on XE and 50,000 node-hours on XK). (1) The Monte Carlo perturbation method can run on either XE or XK and

its typical production run may use a few hundred nodes for 10 hours, which may need to be repeated to reduce the statistical errors (the calculation is open-ended and can be terminated and restarted any time). The memory usage is minimal and disk usage is essentially null. There will be an MPI_REDUCE operation every 200 Monte Carlo steps and I/O to record tiny current data to the output files. We plan to run such calculations on a number of conjugated polymers, graphene sheet, carbon nanotubes, nanoribbons, and spheres, totaling in 50,000 node hours of usage, on XK whenever possible. (2) The fragment method can run on XE and uses modified NWChem as a backend. Each node or processor performs *ab initio* electronic structure (energy gradient) calculation using NWChem for a fragment (water dimer in the case of ice or liquid water) and synchronization occurs when all gradient calculations are complete. Its typical run can be parallelized up to the number of fragments, which is on the order of a thousand in nonperiodic crystals such as ice Ih or in liquid. In a geometry optimization of a crystal, one energy gradient calculation needs to be run tens to hundreds of times. In a molecular dynamics of a liquid, one energy gradient calculation needs to be run on the order of 10,000 times. These cost 100,000 node-hours. Unmodified NWChem has significant disk I/O and has had difficulty running on Blue Waters until we modified it to run on incore memory only. Hence, it has significant local memory access, but limited or no remote memory access. It also has nearly no disk I/O.

The usage schedule is, Q1: 25%, Q2: 25%, Q3: 25%, Q4: 25%.