Annual Report for Blue Waters Allocation

- **Project Information**
  - Blue Water Professorship
  - So Hirata, University of Illinois at Urbana-Champaign
  - sohirata@illinois.edu

- **Executive summary (150 words)**

We develop and apply two highly scalable and systematically accurate electronic structure methods. One is the embedded-fragment method for various structural, thermodynamic, and spectroscopic properties of molecular crystals, amorphous solids, and liquids. The other is the Monte Carlo many-body perturbation and Green's function methods, running efficiently on thousands of CPUs or hundreds of GPUs or more. With Blue Waters, we perform grand-challenge large-scale applications of both methods.

- **Description of research activities and results**

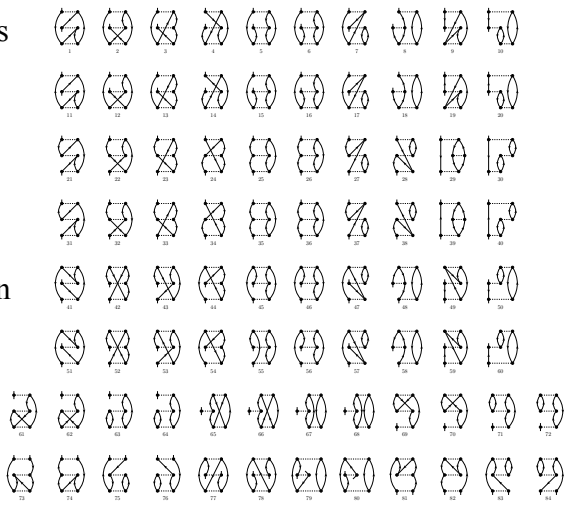
  - *Key Challenges:* Our group have made two breakthroughs in computational chemistry for large molecules, solids, and liquids. (1) One is the method that allows such high-level calculations to be applied to an infinitely extended molecular crystals, amorphous solids, and liquids, including nature's most important solids and liquids such as ice and liquid water. It divides them into fragments embedded in their electrostatic field and treat these fragments by well-developed molecular theories and software in a highly parallel algorithm. (2) 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 large molecules and solids. With Blue Waters, we aim to perform grand-challenge applications to demonstrate these methods' full capacity. The applications may include (1) computationally explaining the thermodynamic and phase properties of crystalline and amorphous ices as well as structural and spectroscopic properties of liquid water as well as (2) near-exact calculations of ionization energies and electron affinities of large conjugated molecules, important for advanced organic materials for optoelectronic devices.

  - *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 enhance the accuracy rather than enlarge the system size (which is already formally infinite). In electronic structure theory, this means switching from density-functional methods 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 and extremely expensive. The aforementioned combination of *ab initio* theories with quantum Monte Carlo and the embedded-fragment methods are among the few that may be realistically and usefully deployable on the large number of processors available on Blue Waters, enabling formerly unthinkable predictively accurate calculations for large systems.

- *Accomplishments:* Green's function theory provides ionization energies, electron affinities, and band gaps which are critical in the characterization of chemical and material processes. Providing benchmark quality energies with Green's function theory requires the inclusion of corrections beyond second-order. To address this, we have developed a stochastic implementation of third-order Green's function theory (MC-GF3), computer-generating 84 Goldstone diagrams (right figure) and the corresponding parallel computer codes. Furthermore, we extended the MC-GF framework (at both the second and third orders) to incorporate the off-diagonal and frequency-dependent effects, which had previously been neglected due to technical challenges but are nevertheless vital for the prediction of benchmark quality energies. These codes execute efficiently on hundreds of Blue Waters XE or XK nodes. On Blue Waters, the performance characteristics of MC-GF3 have been measured and the benchmark calculations on molecular systems as large as C_{60} have been performed. A manuscript reporting this work is being finalized for publication.



- **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."

S. Y. Willlow, M. A. Salim, K. S. Kim, and S. Hirata, *Scientific Reports* **5**, 14358 (2015) (14 pages), "*Ab initio* molecular dynamics of liquid water using embedded-fragment second-order many-body perturbation theory towards its accurate property prediction."

M. A. Salim, S. Y. Willow, and S. Hirata, *The Journal of Chemical Physics* **144**, 204503 (2016), "Ice Ih anomalies: Thermal contraction, anomalous volume isotope effect, and pressure-induced amorphization."

S. Hirata, K. Gilliard, X. He, M. Keçeli, J. Li, M. A. Salim, O. Sode, and K. Yagi, an invited book chapter in *Fragmentation: Toward Accurate Calculations on Complex Molecular Systems* edited by M. S. Gordon (Wiley, Chichester, 2017), "*Ab initio* ice, dry ice, and liquid water."

A. E. Doran and S. Hirata, *Journal of Chemical Theory and Computation* **12**, 4821-4932 (2016), "Monte Carlo MP2 on many graphical processing units."

C. M. Johnson, A. E. Doran, J. Zhang, E. F. Valeev, and S. Hirata, *The Journal of Chemical Physics* **145**, 154115 (2016), "Monte Carlo explicitly correlated second-order many-body perturbation theory."

C. M. Johnson, S. Hirata, and S. Ten-no, *Chemical Physics Letters* [A. H. Zewail Commemorative Issue] **683**, 247-252 (2017), "Correlation factors in explicitly correlated methods."

C. M. Johnson, A. E. Doran, S. Ten-no, and S. Hirata, *The Journal of Chemical Physics* **149**, 174112 (2018), "Monte Carlo explicitly correlated second-order many-body Green's function theory."

A. E. Doran and S. Hirata, "Stochastic evaluation of third-order Dyson self-energies," to be submitted (2019).

M. A. Salim and S. Hirata, "Ab initio phase diagram of ice Ih, II, III, V, VI, and IX," in preparation (2019).

M. A. Salim and S. Hirata, "Embedded-fragment VB theory," in preparation (2019).

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); Blue Waters Symposium (2014); Sanibel Symposium (2015); CECAM meeting (2015); Blue Waters Symposium (2015); RAEST (2015); Pacifichem 2015 (2015); Low-Scaling and Unconventional Electronic Structure Techniques Conference (2016); Molecular Quantum Mechanics 2016; International Symposium of Theoretical Chemical Physics (2016); Molecular Electronic Structure in Buenos Aires (2016); Southeast Regional ACS Meeting (2016); Seminar, Institute for Molecular Science (2016); Seminar, Kobe University (2016); Seminar, Waseda University (2016); Seminar, Keio University (2016); Sanibel Symposium (2017); ACS National Meeting in San Francisco (2017); Seminar, BU-Harvard-MIT (2017); Molecular Science of Ice Symposium (2017); Department of Energy Chemical Theory and Computation Meeting (2017); Canadian Society of Chemistry National Meeting (2017); ACS National Meeting in Washington DC (2017); WATOC (2017); Waterloo Chemical Physics Symposium (2017); XVI Reunion Mexicana de Fiscoquímica Téorica (2017); The Robert S. Mulliken Lecture, University of Georgia (2018).

- **Plan for next year**

We request 200,000 node-hours (100,000 node-hours on XE and 100,000 node-hours on XK).

Grand-challenge applications of MC-MP2, MC-MP3, and explicitly correlated MC-MP2 calculations will be performed for the C_{60} dimer with the 100,000 XK node-hours using the GPU-based algorithm developed in this project. This will be in a funded collaboration with Pacific Northwest National Laboratory to computationally predict a phase diagram of C_{60}.

We will use the 100,000 XE node-hours on the development and application of MC-MP2 and MC-GF2 for three-dimensional solids as well as the application of grid-based diffusion Monte Carlo without a fixed-node approximation.

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