Annual Report for Blue Waters Professor Project

January 2017

Project Information

- Title: Quantum Simulations
- PI: David Ceperley (Blue Waters Professor), Department of Physics, University of Illinois Urbana-Champaign
- Collaborators: Carlo Pierleoni (Rome, Italy), Markus Holzmann(Grenoble, France)
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Executive summary (150 words)

Much of our research on Blue Waters is related to the "Materials Genome Initiative," the federally supported cross-agency program to develop computational tools to design materials. We employ Quantum Monte Carlo calculations that provide nearly exact information on quantum many-body systems. This is the most accurate general method capable of treating electron correlation, thus it needs to be in the kernel of any materials design initiative. It is able to use Blue Waters effectively because there are several pathways to find parallel performance. Ceperley's group has a number of funded and proposed projects to use Blue Waters as listed below. In the past year, we have been running calculations for dense hydrogen in order to make predictions that can be tested experimentally. We have also been testing a new method that can be used to solve the fermion sign problem and to find dynamical properties of quantum systems.

Description of research activities and results

- *Key Challenges:* description of the science/engineering problem being addressed
- *Why it Matters*: description of the potential impact of solving this research problem, and, if appropriate, the educational outcomes. For exploratory allocations, indicate whether the results will be used to substantiate a future proposal.
- *Why Blue Waters:* explanation of why you need the unique scale and attributes of Blue Waters to address these challenges; if relevant, provide an assessment of code(s) performance on Blue Waters.
- *Accomplishments:* explanation of results you obtained

During the past year, the following 4 grants of which Ceperley is a PI or CoPI, and that involve Blue Waters usage, been active. Access to Blue Waters is crucial for success of these projects.

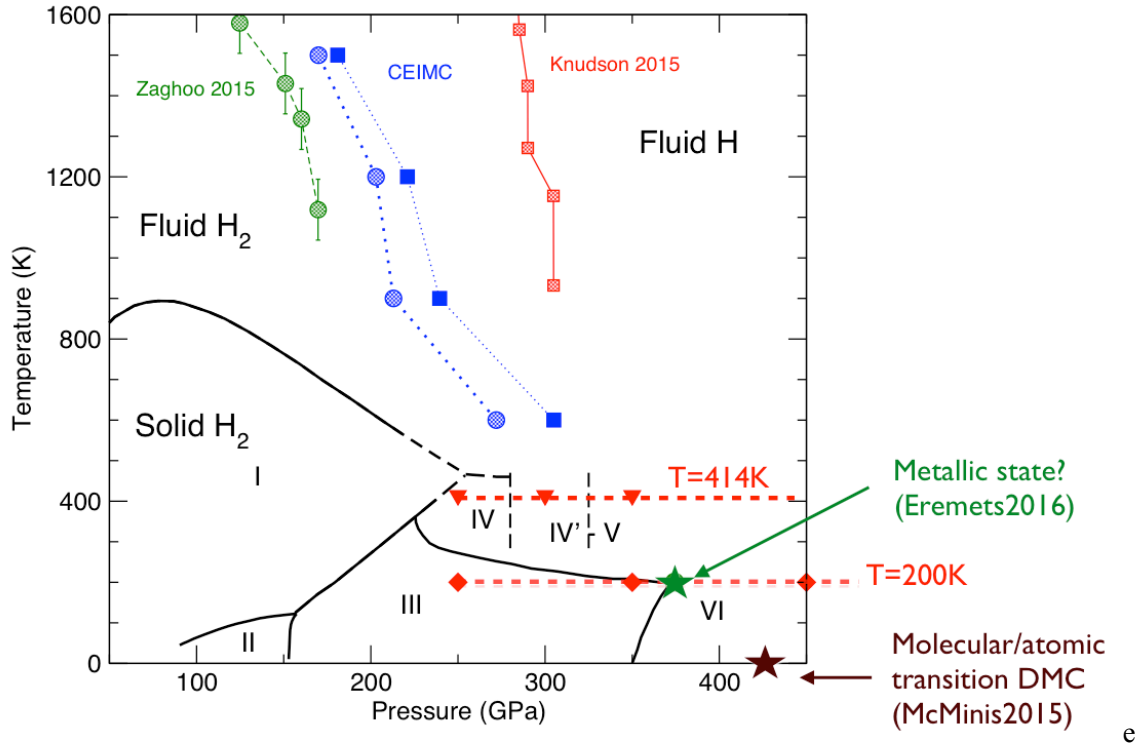
- "Warm dense matter"DE-NA0001789. Computation of properties of hydrogen and helium under extreme conditions of temperature and pressure. Ceperley is the sole PI.
- SCIDAC, Predictive Computing for Condensed Matter DE-SC0008692. So Hirata is the PI, involves 5 other UIUC faculty members.
- "Network for Ab Initio Many-body Methods" for the development of the QMC software, QMCPACK. Kent at Oak Ridge is the PI, involves scientists at 4 national labs as well as UIUC. As part of this grant we held a summer school at NCSA in June 2016 to teach the usage of QMCPACK.

- EFRC: Center for Emergent Superconductivity. A very ambitious project to discover new superconducting materials using computation and experimental validation. This grant was funded in July 2014. The PI is Peter Johnson at Brookhaven National Lab and involves other faculty at UIUC.

The following projects are active on Blue Waters during 2016:

1. "Multiscale" approach. We want to use highly accurate energies from quantum Monte Carlo to treat larger systems at longer length scales. Atomistic simulations are widely used across many different scientific disciplines, including physics, material science, chemistry, and biology. Large-scale simulations and highly accurate simulations cannot generally be performed simultaneously since *ab initio* simulations are limited to small system sizes. Despite its cost, Quantum Monte Carlo is important, since high accuracy is needed. In high-pressure hydrogen simulations, we have recently shown that various density functionals differ significantly from benchmark quantum Monte Carlo simulations. At the end of 2016 we computed a database of hydrogen configurations and are now trying to construct a low cost force field to represent them. If this is successful we can generalize to other elements.

2. Liquid-liquid phase transition in hydrogen by Coupled Electron-Ion Monte Carlo Simulations. The phase diagram of high pressure hydrogen is of great interest both for fundamental research, such as planetary physics, and for energy applications. The existence and precise location of a phase transition in the liquid phase between a molecular insulating fluid and a monoatomic metallic fluid is relevant for planetary models. Recent experiments reported contrasting results about its location. Theoretical results based on Density Functional Theory are also very scattered. During 2015, we performed highly accurate Coupled Electron-Ion Monte Carlo calculations of this transition, finding results [1] that lie between the two experimental predictions, close to that measured in Diamond Anvil Cell experiments but at 25-30 GPa higher pressure. The transition along an isotherm is signaled by a discontinuity in the specific volume, a sudden dissociation of th

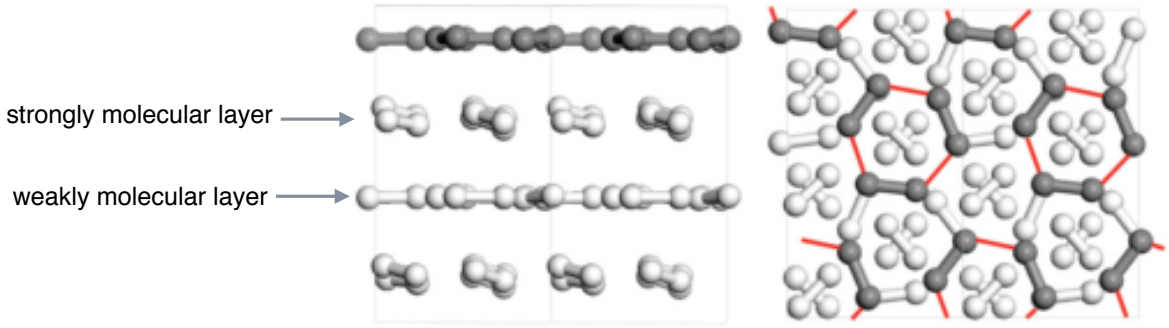


e molecules, a jump in electrical conductivity and in electron localization.

The hydrogen phase diagram with experimental liquid-liquid transition lines and CEIMC predictions. Black continuous lines

indicate the melting line as well as the transition lines between different experimentally detected crystalline phases: I to IV'. Blue circles and squares are CEIMC predictions for the liquid-liquid transition line in hydrogen and in deuterium, respectively. DAC experimental results for hydrogen are indicated by green circles and purple circles, while red squares indicate shock wave experimental data for deuterium.

3. Crystal searching. We have been using Blue Waters to run Coupled Electron-Ion Monte Carlo (CEIMC) simulations of molecular crystalline hydrogen along two isotherms, T=200K and T=414K, for several pressure from 200GPa up to 550GPa. The equilibrium crystalline structure of solid hydrogen at given temperature and pressure is unknown because X-ray scattering experiments are prevented by the small dimensions of the samples and by the very small cross-section of hydrogen. Therefore information is gathered by Infrared absorption spectra and Raman spectra. Inferring the crystalline structure from those spectra is not easy since it requires computing those spectra for several candidate structures. However, DFT-based simulation methods for hydrogen are not accurate enough, particularly near molecular dissociation and metallization and nuclear zero point effects require a fully ab-initio treatment of quantum protons. With CEIMC we have investigated a few different crystalline structures selected as the best candidates from a DFT random search and investigated along the T=0 isotherm by QMC [2]. In this first CEIMC investigation of solid hydrogen our aim was to test the dynamical stabilities of structures. Specifically we have investigated the C2/c and the Cmca-12 structures in Phase III at T=200K at four different pressures P=250GPa, 350GPa, 450GPa and 550GPa and the Pc48 structure for Phase IV (see figure 2) at T=414K and 250GPa, 300GPa and 350Gpa. The result of this study will be published soon. Moreover we are investigating the possibility of estimating the dynamic signal from high frequency nuclear modes from the imaginary time correlation functions of the nuclear path integrals.



Pc48 structure from AIRSS with GGA-PBE and zero point energy accounted by Self-consistent harmonic approximation

4. How do exact quantum Monte Carlo projection methods behave in the thermodynamic limit? The release-node procedure uses imaginary time projection of a trial wavefunction to obtain "in principle" exact properties of quantum systems. However, for general fermion systems, the signal to noise ratio decreases exponentially fast with respect to the imaginary time projection. We have done calculation on Blue Waters for charged bosons and fermions on the behavior of the projection versus the number of particles. Methods for finding better estimates of the exact energy of quantum systems in the thermodynamic limit have been discovered. This work has been reported on at conferences and will be published soon.

[1] C. Pierleoni, M.A. Morales, G. Rillo, M. Holzmann and D.M. Ceperley: “Liquid-liquid phase transition in hydrogen by coupled electron-ion Monte Carlo”, PNAS 113, 4953–4957 (2016).

[2] J. McMinis, R.C.Clay III, D. Lee and M.A. Morales, Phys Rev Lett. 114, 105305 (2015)

[3] R.C. Clay, J. McMinis, J.McMahon, C. Pierleoni, D.M. Ceperley and M. A. Morales, Phys. Rev B, **89**, 184106 (2014)
[4] G. Rillo, M.A.Morales, M.Holzmann, D.M. Cperley and C. Pierleoni, "Coupled Electron-Ion Monte Carlo investigation of Phases III and IV of solid hydrogen", in preparation

Talks by D. M. Ceperley on this research in 2016.

- "The liquid-liquid transition in dense hydrogen", Berkeley Statistical Mechanics Meeting, Berkeley CA.
- "Simulation of Dense Hydrogen" SSAP annual meeting, Washington DC
- "How can we find out what is inside Jupiter and Saturn?" Guelph-Waterloo Physics Institute, Guelph CA
- "Computational Methods for Dense Hydrogen" EOS in quantum many-body problems, Trento, Italy
- "Hydrogen under Extreme Conditions" Blue Waters Symposium, Bend OR
- "Computation of Dense Hydrogen" Gordon Research Conference, Holerness NH.

Talks by C. Pierleoni on this research on 2016.

- "Coupled Electron-Ion Monte Carlo study of hydrogen under extreme conditions" workshop on "Equation of state in quantum many-body systems", Trento Italy
- "Theory of liquid-liquid phase transition in hydrogen". 54th Eur. High Pressure, Bayreuth, Germany.

Plans for next year

As mentioned above we have several projects underway. Blue Waters capability is needed to take the research from the model level to realistic description of materials where electron correlation is important. Typical materials require simulation of a unit cell with at least one thousand electrons. Just holding the single-body orbitals in memory for a realistic material requires a multiprocessor computer. Relevant accuracy for materials design will definitely require petascale computational access.

We plan to continue the current project on hydrogen, in particular examining the phases at lower temperature, verifying results in conjunction with exciting new experimental results. We plan extensive calculations of liquid and solid hydrogen enabled by the newly developed hydrogen force-field. We expect to submit the results from the projects mentioned above within the next few months of 2017.

We request 240,000 node hours on Blue Waters, for the period Feb 2017-Jan 2018. We expect to be using the time uniformly throughout the year. The data transfer, data storage and access requirements should be similar to our usage in 2016.