Annual Report for Blue Waters Professor Project

December 2019

Project Information

- Title: Quantum Simulations
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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 several projects to use Blue Waters. In the past year, we have been running calculations for dense hydrogen and lithium in order to make predictions that have been tested experimentally. In the next year we propose to use Blue Waters to develop new models applicable for macroscopic systems.

Description of research activities and results

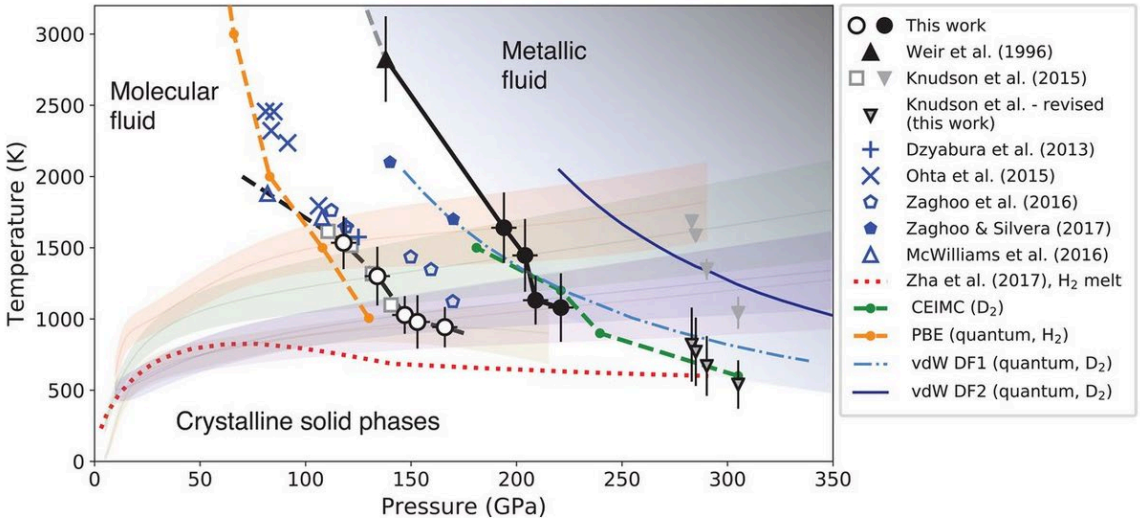
During the past year, the following grants that involve Blue Waters usage, have been active. Access to Blue Waters was crucial for their success:

- "Warm dense matter"DE-NA0001789. Computation of properties of hydrogen and helium under extreme conditions of temperature and pressure. Ceperley is the sole PI.
- "From sccurate correlated quantum simulations to mesoscopic scales" DOE DE-SC0020177. Ceperley is a PI and director of the grant (total of 6 Pis)

Our activity on Blue Waters during 2019 consisted of the following projects:

1. 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. In previous years, we performed highly accurate Coupled Electron-Ion Monte Carlo calculations of this transition, finding results that lay 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 the molecules, a jump in electrical conductivity and in electron localization.

During 2019 we have continued the calculations to control various computational approximations and quantify their errors. In refs. [1-5] we published additional information about dense hydrogen as the system changes from a molecular liquid to an atomic liquid, in particular the optical properties. These are valuable in understanding experiment.



The hydrogen phase diagram with experimental liquid-liquid transition lines and CEIMC predictions. The green dashed line shows the prediction from Blue Waters calculations in 2016. The Black circles are from the latest experiment. Other symbols are earlier measurements and calculations. See P. M. Celliers et al., *Science* **361**, 677 (2018) for references and more details.

2. 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 limited by the small dimensions of the samples and by the 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. 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 at T=414K and 250GPa, 300GPa and 350Gpa.

3. We have begun constructing a data base of hydrogen forces that will be used to determine a "force-field" that can be used to examine the properties of hydrogen at a longer length scale and longer times. So far several thousand snapshots of liquid hydrogen configurations each with 64 protons have been computed using QMCPACK.

4. More accurate predictions of the Compton Profile in liquid and solid Lithium. We have performed very accurate calculations of the momentum distribution of electrons in liquid and solid lithium to compare with new scattering experiments done on the latest experimental "light source". These calculations removed many of the assumptions and approximations of earlier calculations and were able to agree with experiment an order of magnitude better. The work will be published together with experiments in 2019 [6]

Publications during 2019

1. C. Pierleoni, G. Rillo, D. M. Ceperley, M. Holzmann, Electron localization properties in high pressure hydrogen at the liquid-liquid phase transition by Coupled Electron-Ion Monte Carlo in proceedings of the CCP2017. ArXiv 1712.00392
2. G. Rillo, M. A. Morales, D. M. Ceperley, and C. Pierleoni, Optical Properties of Liquid Hydrogen across the Molecular Dissociation, Proc. Nat. Acad. Science, 1818897116, 2019. arXiv 1810.08131
3. V. Gorelov, C. Pierleoni and D. M. Ceperley, Benchmarking vdW-DF first principle predictions against Coupled Electron-Ion Monte Carlo for high pressure liquid hydrogen, Contributions to Plasma Physics (2019). arXiv:1812.07818.
4. Vitaly Gorelov, Markus Holzmann, David M. Ceperley, Carlo Pierleoni "Energy gap closure of crystalline molecular hydrogen with pressure" arXiv:1911.06135
5. Yubo Yang, Vitaly Gorelov, Carlo Pierleoni, Markus Holzmann and David Ceperley, "Electronic band gaps from Quantum Monte Carlo methods" submitted to Phys. Rev. B (2019)
6. N. Hiraoka, Y. Yang, T. Hagiya, A. Niozu, K. Matsuda,3 S. Huotari, M. Holzmann, and D. M. Ceperley, Direct observation of the momentum distribution and renormalization factor in lithium, to be submitted to Phys. Rev. Letts. (2019).

Talks by D. M. Ceperley on this research in 2019

- Invited Talk, Livermore National Laboratory, Livermore CA (March 2019)
- Invited Talk, Blue Waters Symposium, Bend OR (June 2019)

• Plans for next year

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, in particular prediction of the melting transition for solid hydrogen. We have several publications in the pipeline at the present time concerning the electronic gap of molecular hydrogen.

We were awarded a DOE proposal in the spring of 2019 that proposed to use massively parallel computational tools based on Quantum Monte Carlo to construct a data-base of energies, forces and electronic matrix elements in order to make effective models of materials that can be used to accurately model materials for longer length and time scales. We need Blue Waters calculations to prototype these tools for our proposal.

We request 200,000 node hours on Blue Waters, for the period Jan 2020-Dec 2020. 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 2019.