GA

TN

FS

# QUANTUM SIMULATIONS: PROPERTIES OF DENSE HYDROGEN

**Allocation:** Blue Waters Professor/200 Knh
**PI:** David Ceperley[1]
**Collaborator:** Carlo Pierleoni[2]

[1]University of Illinois at Urbana–Champaign
[2]University of L'Aquila

## EXECUTIVE SUMMARY

The research in this project on Blue Waters is related to the Materials Genome Initiative, the federally supported cross-agency program to develop computational tools for designing new materials. In the past year, the research group has been running calculations for dense hydrogen and lithium in order to make predictions that have been tested experimentally. In particular, the team performed coupled electron–ion quantum Monte Carlo calculations of the transition between molecular and atomic hydrogen to determine the changes in optical properties across the transition. During the past year, their prediction of a transition was verified by a new experiment.

## RESEARCH CHALLENGE

The phase diagram of high-pressure hydrogen is of great interest both for fundamental research, such as in astrophysics, and for energy applications such as high-temperature superconductivity in hydrides.

## METHODS & CODES

The team employs 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. The method is able to use Blue Waters effectively because there are several pathways to find parallel performance.

## RESULTS & IMPACT

The research group's recent computations on Blue Waters included the following two projects:

*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 in 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 the location of the phase transition. Theoretical results based on density functional theory are also very scattered. Before 2018, the research team 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 gigapascal 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 2016–17, the research team's prediction of a transition was verified by three separate experiments. In particular, a new experiment [1] verified the results of the team's calculation, which was covered by *The New York Times* [2].

Recently, the team has continued the calculations to control various computational approximations and quantify their errors. In the papers listed below, the researchers published additional information about dense hydrogen as the system changes from a molecular liquid to an atomic liquid. These findings are valuable in understanding and reconciling the different experiments.

*More accurate predictions of the Compton profile in liquid and solid lithium.* The research group has 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. For example, the team simulated both solid and liquid lithium at the experimental conditions of temperature and included core electrons in the simulation. They were able to agree with experiment on an order of magnitude better than previous calculations. The work will be published in 2019 together with the experimental data.

## WHY BLUE WATERS

Access to Blue Waters was necessary because of the computational demands of the calculation involving hydrogen and lithium. The systems typically had more than one hundred electrons treated as quantum particles and the ions (protons or lithium ions) were dynamic and disordered.

## PUBLICATIONS & DATA SETS

G. Rillo, M. A. Morales, D. M. Ceperley, and C. Pierleoni, "Optical properties of high-pressure fluid hydrogen across molecular dissociation," *Proc. Nat. Acad. Sci. U.S.A.*, vol. 116, no. 20, pp. 9770–9774, 2019.

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," *Contrib. Plasma Phys.*, vol. 59, no. 4–5, p. e201800185, 2019.

C. Pierleoni, G. Rillo, D. M. Ceperley, and M. Holzmann, "Electron localization properties in high pressure hydrogen at the liquid–liquid phase transition by coupled electron–ion Monte Carlo, *J. Phys.*, Conf. Ser. 1136, p. 012005, 2018.

C. Pierleoni, M. Holzmann, and D. M. Ceperley, "Local structure in dense hydrogen at the liquid–liquid phase transition by coupled electron–ion Monte Carlo, *Contrib. Plasma Phys.*, vol. 58, no. 2–3, pp. 99–106, 2018.