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PROPERTIES OF DENSE HYDROGEN

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EXECUTIVE SUMMARY

The phase diagram of high-pressure hydrogen is of great interest for fundamental research, planetary physics, energy applications, and as a benchmark for computational quantum simulation methods. Using highly accurate coupled electron–ion Monte Carlo simulation methods, we predicted transitions between a molecular insulating fluid and a monoatomic metallic fluid. The existence and precise location of the transition line is relevant for planetary models. Experiments have reported contrasting results about the location of the transition; however, this year the most precise experiments have confirmed our predictions, validating the simulation methods for materials that cannot be measured in the laboratory. We have also explored the properties and structures of molecular and atomic solid hydrogen at lower temperatures.

RESEARCH CHALLENGE

The properties of hydrogen under extreme conditions of pressure and temperature are of great interest for fundamental research, planetary physics, and energy applications [1]. Hydrogen accounts for much of the visible mass in the universe. The properties of hydrogen and helium are needed for understanding the giant planets, Jupiter and Saturn, but experiments under the relevant conditions are challenging. Even though hydrogen is the first element in the periodic table, calculating its properties is not simple since both the electronic and protonic motions are quantum and correlated. Nonetheless, hydrogen is a valuable benchmark for computational quantum simulation methods.

It has long been an open question [1] how hydrogen makes a transition from a molecular insulating state to an atomic metallic state as pressure and temperature are increased. Previously, we predicted a first-order phase transition in the fluid phase between a molecular insulating fluid and a monoatomic metallic fluid [2]. Recent experiments [3,4] reported contrasting results regarding the location of the transition that differed by a factor of two in pressure. Theoretical results based on density functional theory are also very scattered, and hence, not predictive [5]. These findings motivated us to repeat our earlier calculations on Blue Waters to better control the convergence and utilize recent improvements in methodology. Our recent experiments have also probed the solid phase leading up to the atomic transition [7] and the melting temperature.

METHODS & CODES

Over the past decade we have developed new quantum Monte Carlo simulation methods to treat quantum systems at low temperature. The quantum Monte Carlo method we use (Coupled Electron–Ion Monte Carlo) works with the full interaction among the electrons and protons and treats both particles fully quantum mechanically. In contrast to density functional calculations, all effects of electronic correlation are explicitly included. This is particularly important in hydrogen because of possible self-interaction effects, as well as the difficulty in treating the hydrogen bond-breaking and the large van der Waals interactions. We model hydrogen with as many as 100 electrons and protons in a periodic cell and use special methods to extrapolate accurately to the thermodynamic limit. With our method, we simulated hydrogen for temperatures in the range of 200K up to 5000K, and at pressures of 100 GPa to 700 GPa.

RESULTS & IMPACT

For temperatures below 2000K we observed [5] a transition between an insulating molecular liquid and a more dense metallic atomic liquid. Our predicted transition pressures are intermediate between the two experimental observations [3,4]. Our work stimulated extensive experiments and further calculations on dense hydrogen. The most recent experiments confirm our predictions.

In work published in 2017 [7], we performed a detailed study of solid molecular hydrogen at temperatures between 200K and 414K and pressures between 180 GPa and 520 GPa to understand the detailed crystal structures, the melting temperature of the solid, and the changes in optical properties during the transitions. A controversial report, also published in 2017, concerns the experimental observation of this transition [6].

Our calculations are needed both to validate our computational method and to resolve the different experimental measurements. For progress in the high-pressure community to occur, it is essential to resolve this difference between experiments and computation. After validation, the method can be used with more confidence in modeling the wide variety of astrophysical objects being observed, which are composed largely of hydrogen and helium under extreme conditions. As a byproduct of our simulation, we are also judging the accuracy of various density functionals and force fields for the simulation of these systems.

WHY BLUE WATERS

Without access to Blue Waters we could not have performed this study because of the computational demands from the simultaneous treatment of quantum electrons and protons.

PUBLICATIONS & DATA SETS

Holzmann, M., et al., Theory of Finite Size Effects for Electronic Quantum Monte Carlo Calculations of Liquids and Solids. *Phys. Rev. B*, 94 (2016), DOI:10.1103/PhysRevB.94.035126.

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