

## HYDROGEN UNDER EXTREME CONDITIONS

**Allocation:** Blue Waters Professor/0.24 Mnh  
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### EXECUTIVE SUMMARY:

We have completed a calculation of a first-order liquid-liquid transition in warm dense hydrogen using a quantum Monte Carlo method, Coupled-Electron Ion Monte Carlo. As hydrogen is compressed, it makes a sudden first-order transition between an insulating molecular liquid and a metallic atomic liquid. There are two conflicting experimental measurements for the transition of dense hydrogen that have been made during the past year. Our computational results lie between the two experiments.

### INTRODUCTION

Hydrogen accounts for much of the visible mass in the universe. The properties of hydrogen and helium are important 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 correlations are quantum and correlated. It has long been an open question how hydrogen makes a transition from a molecular insulating state to an atomic metallic state [1]. We have developed new Quantum Monte Carlo simulation methods to treat such systems and using these methods have studied molecular dissociation in liquid hydrogen and have observed clear evidence of an extra liquid-liquid phase transition [2]. During the past year, two experimental groups [3,4] have reported observations of the transition we predicted; however, the observations do not agree with each other, differing in pressure by a factor of two. This motivated us to repeat our earlier calculations on Blue Waters, to better control the convergence and use recent improvements in methodology.

### METHODS & RESULTS

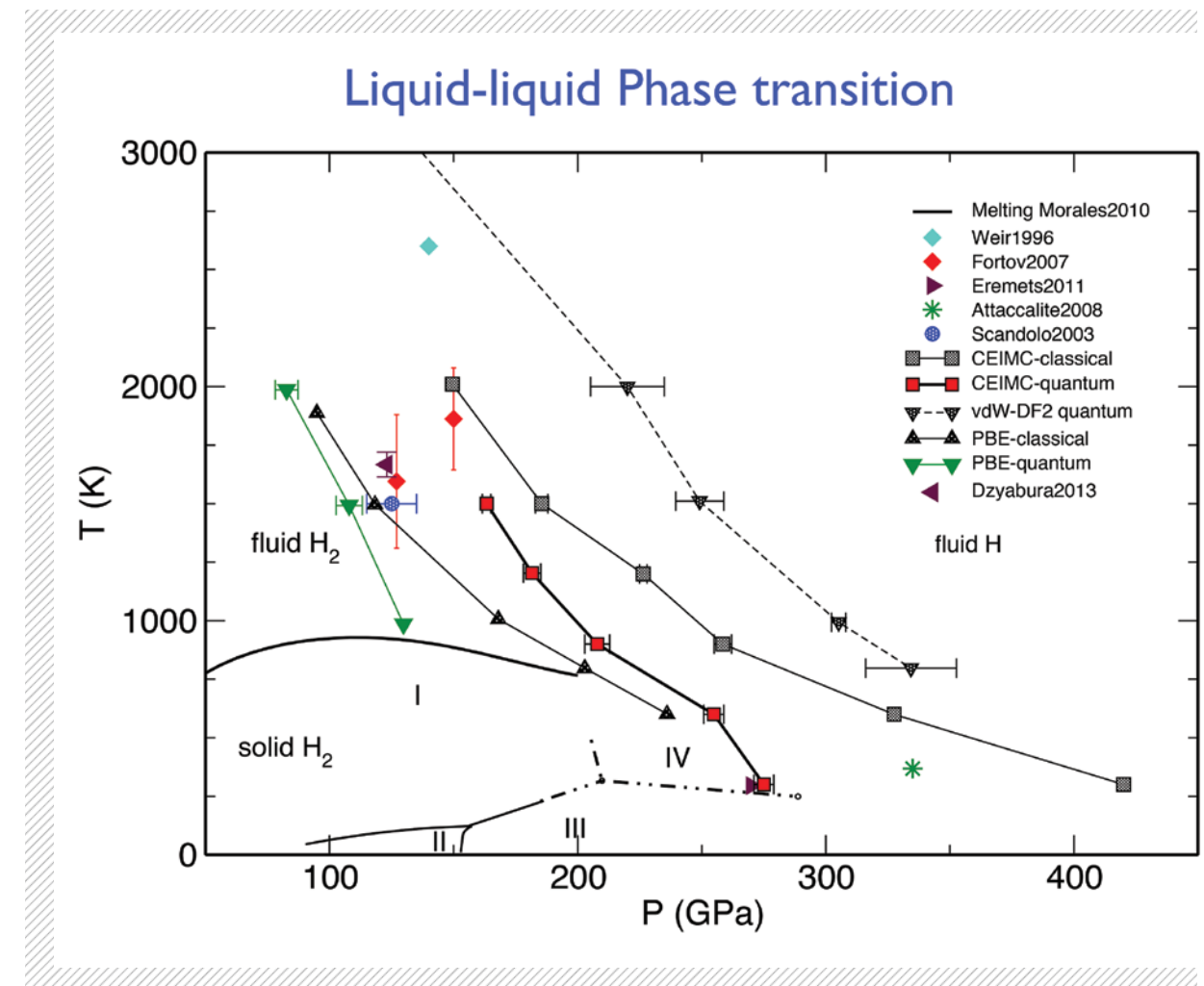
We use a quantum Monte Carlo method (Coupled Electron Ion Monte Carlo) where we start with the true interaction between the electrons and protons and treat both fully quantum mechanically. In contrast to density functional calculations, all effects of electronic correlation are explicitly included. This is particularly important in hydrogen because of possible self-interaction effects, difficulty in treating the hydrogen bond breaking, and the large van der Waals interactions. We model hydrogen with about 100 electrons and protons in a periodic cell. Special methods are used to extrapolate to the thermodynamic limit. With our method, we simulated hydrogen for temperatures in the range of 200K up to 5,000K, and at relevant pressures, 100GPa to 500GPa.

For temperatures below 2,000K we observe a first-order transition between an insulating molecular liquid and a more dense metallic atomic liquid. Our predicted transition pressure is intermediate between the two experimental observations [3,4]. Future work will be to perform further simulations and analysis to understand the divergent results of the experiments and of the unusual properties of the molecular and atomic liquid.

The present calculations are needed to validate both our computational method and the experimental measurement. It is essential for progress in the high-pressure community to resolve the difference between the experiments and computation. After validation, the method can be used with more confidence in modeling the wide variety of astrophysical objects being observed, composed largely of hydrogen and helium under extreme conditions.

### WHY BLUE WATERS

Without access to Blue Waters we would not have been able to perform this study because of the computational demands of the simultaneous treatment of quantum electrons and protons. With more resources we will be able to study systems containing elements heavier than hydrogen and helium, important not only in astrophysics but for materials.



**FIGURE 1:** The predicted phase diagram (temperature versus pressure) of dense hydrogen. The red squares show the results from the Blue Waters calculation. The other symbols show results of other calculations or experimental measurements.