Title:

Coupled Electron-Ion Monte Carlo study of hydrogen under extreme conditions

Author:

Carlo Pierleoni

Affiliations:

1) Department of Physical and Chemical Sciences, University of L'Aquila, Italy

2) Maison de la Simulation, CEA-Saclay, France.

Abstract:

The phase diagram of high pressure hydrogen is of great interest for fundamental research, planetary physics, and energy applications[1]. Laboratory experiments to reach the appropriate thermodynamics conditions are difficult and extremely expensive, therefore ab-initio theory has played a crucial role in developing the field. The accuracy of Density Functional based calculations is however limited and often non-predictive. We have developed a quantitative methodology based on Quantum Monte Carlo to study hydrogen in extreme conditions: the Coupled Electron-Ion Monte Carlo (CEIMC). We will report results for a number of studies we have recently performed.

The first application of CEIMC is in computing the principal Hugoniot of deuterium[2]. We find that the maximum compression along the Hugoniot is ~5% higher than with DFT and ~15% higher than most accurate experimental data[3].

A second application is to tracing the liquid-liquid transition line. A first-order phase transition in the fluid phase between a molecular insulating fluid and a monoatomic metallic fluid has been predicted[4-6]. The existence and precise location of the transition line is relevant for planetary models. Recent experiments reported contrasting results about the location of the transition[7-9]. Theoretical results based on density functional theory are also very scattered[8]. We report highly accurate coupled electron-ion Monte Carlo calculations of this transition finding results 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 the molecules, a jump in electrical conductivity and loss of electron localization[10]. We discuss the difference observed with respect to the predictions of a different Quantum Monte Carlo method [11,12].

Finally a third application of CEIMC is to study the stability of the various crystalline molecular phases of hydrogen. We have performed calculations along the T=200K isotherm in the phase III and along the T=414K isotherm in the phase IV. We report a preliminary comparison between CEIMC results and DFT based results and discuss the electronic character of the various phases[13].

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