Fully Consistent Density Functional Theory Determination of the Insulator-to-Metal Transition Boundary in Warm Dense Hydrogen

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The liquid–liquid insulator-to-metal transition (IMT) of warm dense hydrogen isotopes is a crucial phenomenon for giant planet structure and dynamics. Because hydrogen has the highest relative abundance in the universe, accurate determination of the IMT is key to modeling the interior dynamics and evolution of these Jovian-like planets.[1] An essential prerequisite for quantitative models is an accurate equation of state (EOS) that correctly describes both the onset and character of the IMT.[2] Independent of planetary physics, an accurate EOS for hydrogen and its isotopes is also essential for progress in inertial confinement fusion research.[3]

Despite its importance, accurate determination of the IMT boundary remains an experimental and theoretical/computational challenge. In this work we make a major step forward on the theory/computation side by providing a single, conceptually consistent density functional theory (DFT) treatment, with the best-balanced modern approximate exchange-correlation (XC) functional, namely SCAN-L with the nonlocal correlation correction rVV10. We provide results both with and without nuclear quantum effects (NQE's) that are mostly consistent with experimental findings and with best-available combinations of DFT and stochastic methods.

With the use of quantum molecular dynamic simulations, we probe warm dense fluid hydrogen from 60 to 320 GPa across a temperature range of 600 to 3000 K. Both classical nuclei, within the Born–Oppenheimer approximation, and quantum nuclei, as treated within the path integral formalism, are considered. In all cases the electrons are treated quantum mechanically within the finite temperature extension of DFT. The bulk system of fluid hydrogen is approximated with the use of a 256-atom system in a periodic cubic supercell maintained in a canonical ensemble with fixed particle number, temperature, and volume.

Analysis of the dc conductivity and reflectivity, calculated via the Kubo–Greenwood formalism, along with the extraction of the indirect band gap and ionic pair correlation function, shows concurrent abrupt changes at the onset of a minimum metallic behavior of 2000 S/cm. With the inclusion of nuclear quantum effects, the molecular character of the system is significantly diminished prior to the onset of metallization. This in turn sharpens the abrupt changes in the aforementioned properties and produces a shift in excess of 250 K in the IMT boundary location. Furthermore, the inclusion of NQE's produces an explicit isotope effect in the form of clear splitting in the hydrogen and deuterium IMT boundaries (see Fig. 1).

In summary, we have re-examined the problem of determining the IMT boundary of warm dense fluid hydrogen with consistent use of what is arguably the best approximate XC functional currently available for treating both molecular and condensed phase systems evenhandedly. The resulting hydrogen IMT boundary is in good agreement with experimental measurements across a wide range of pressures and temperatures. Our analysis supports the notion of a metallic transition driven by an abrupt band-gap closure associated with the dissociation of molecular to atom hydrogen.
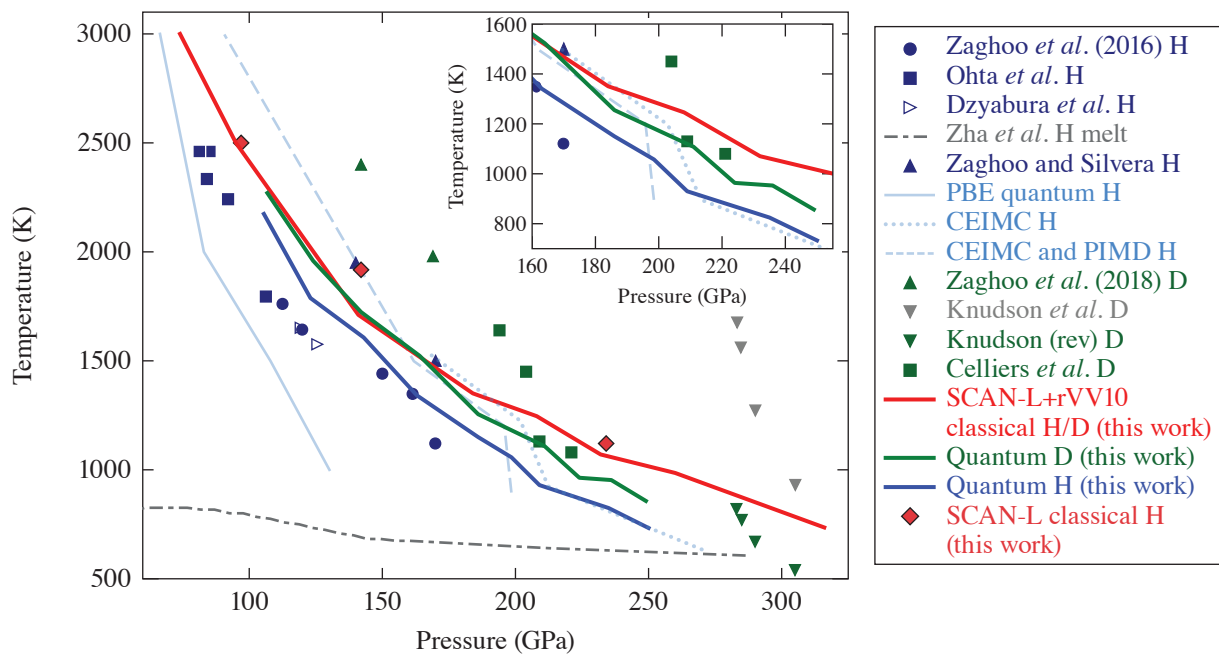
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Figure 1

Emerging picture of the hydrogen and deuterium IMT. Blue symbols show experimental results for hydrogen.[2–5] Upright blue triangles are the IMT from measured reflectivities.[5] All others are from the laser-heating curve plateau. Green symbols show reflectivity results for deuterium.[6–8] The dashed–dotted gray curve is the melt line based on Ref. 9. All other solid IMT curves are theoretical predictions. The red curve is the SCAN-L + rVV10 prediction with classical nuclei, and the red diamonds are three of the same classical nuclei predictions without the rVV10 correction. The corresponding blue and green curves are the predictions with NQE's for hydrogen and deuterium, respectively. Inset: With NQE inclusion, an apparent step in the IMT boundary appears. This feature has not been seen previously in DFT studies. Further analysis is required to ascertain the underlying cause of that feature.

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