Quantum Simulations for Dense Matter

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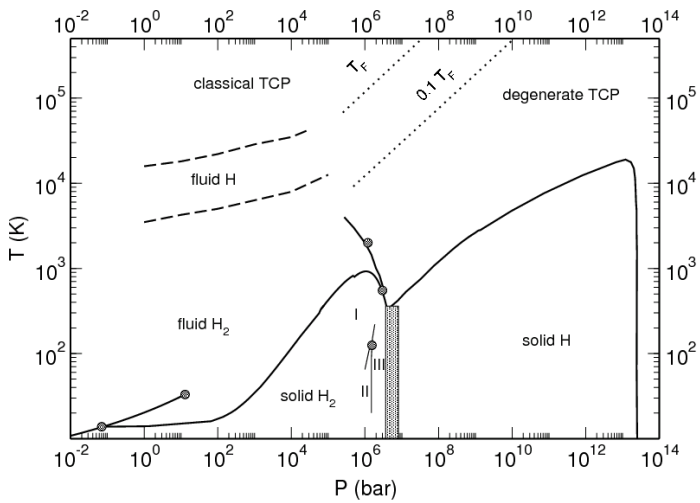
DOE DE-NA0001789 and DE-NA0002911



Collaborators

Norm Tubman	*Berkeley*
Jeff McMahon	*Washington State*
Miguel Morales	*Livermore*
*Ray Clay**	*U of Illinois*
Carlo Pierleoni	*L'Aquila, Italy*
Markus Holzmann	*Grenoble, France*

To develop and apply accurate Quantum Monte Carlo simulations for warm dense matter primarily low-Z elements

OUTLINE

- Liquid-liquid phase transition
- Melting of solid hydrogen
- Hydrogen Hugoniot
- Benchmarking DFT

Simulation Methods

Density Functional Theory

Molecular Dynamics

& Path Integral MD

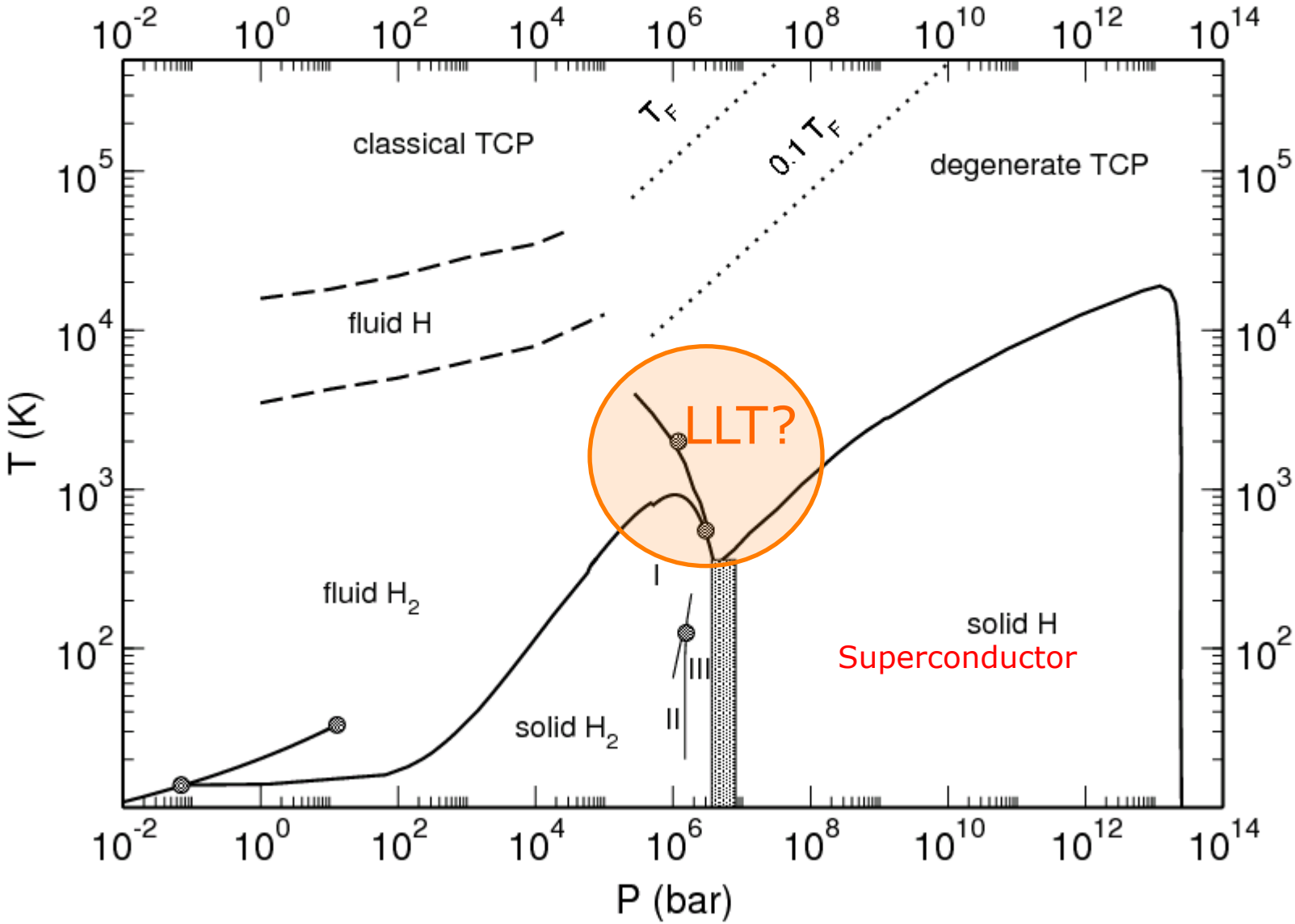
- Electron energy is an assumed functional of electron density
- Benchmark several functionals
- Born-Oppenheimer MD
- Norm-conserving pseudopotentials
- Up to 432 atoms

Quantum Monte Carlo

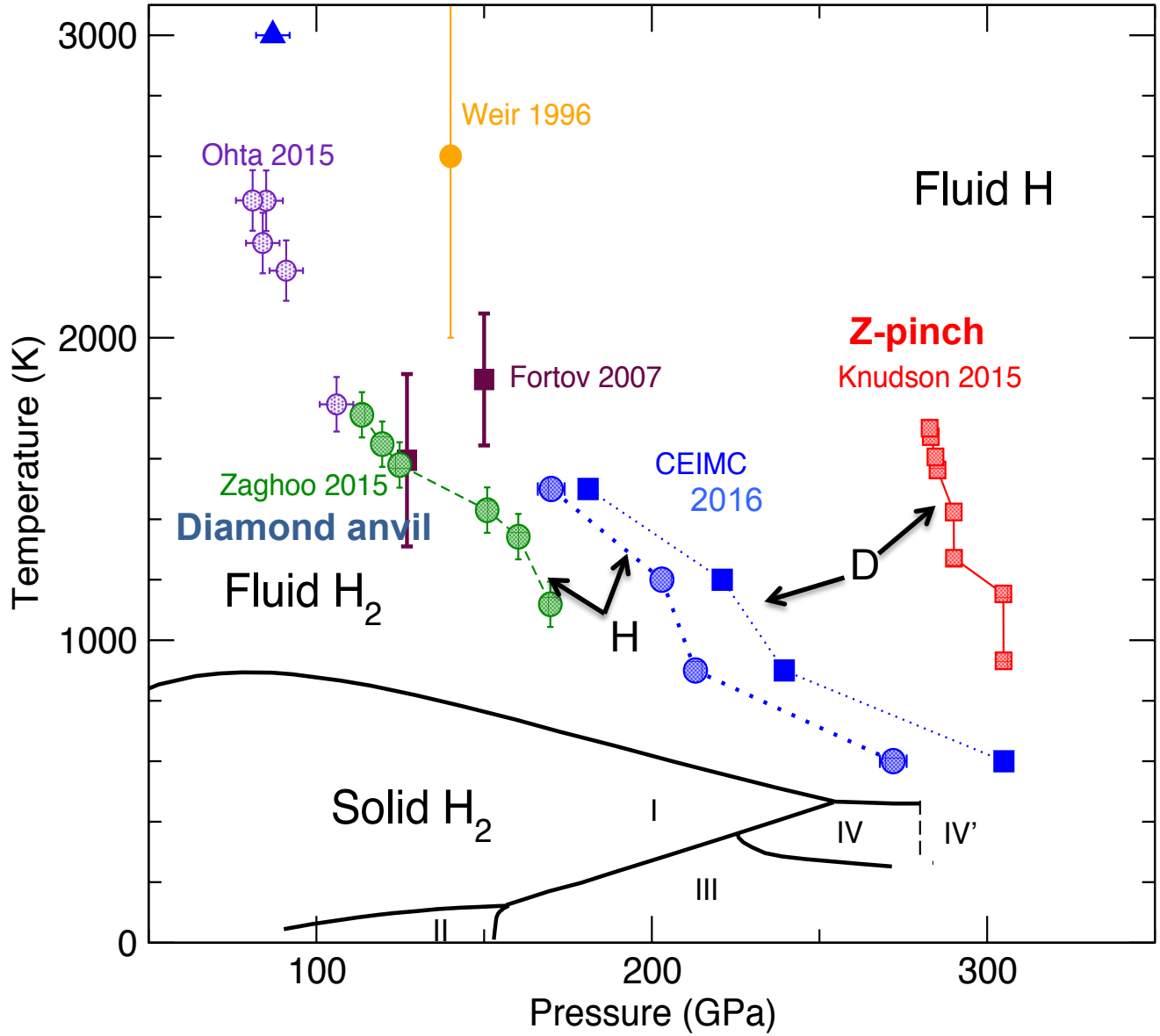
- Coupled Electron-Ion Monte Carlo
  - Electrons at T=0K with Reptation Quantum Monte Carlo
  - Path Integral MC for the ions
- 54/108 electrons
- Correlated trial wave functions with backflow.

- No density functional
- No energy cutoff
- No pseudopotentials
- Twist Averaged Boundary Conditions: 4x4x4 grids
- Quantum protons/deuterons

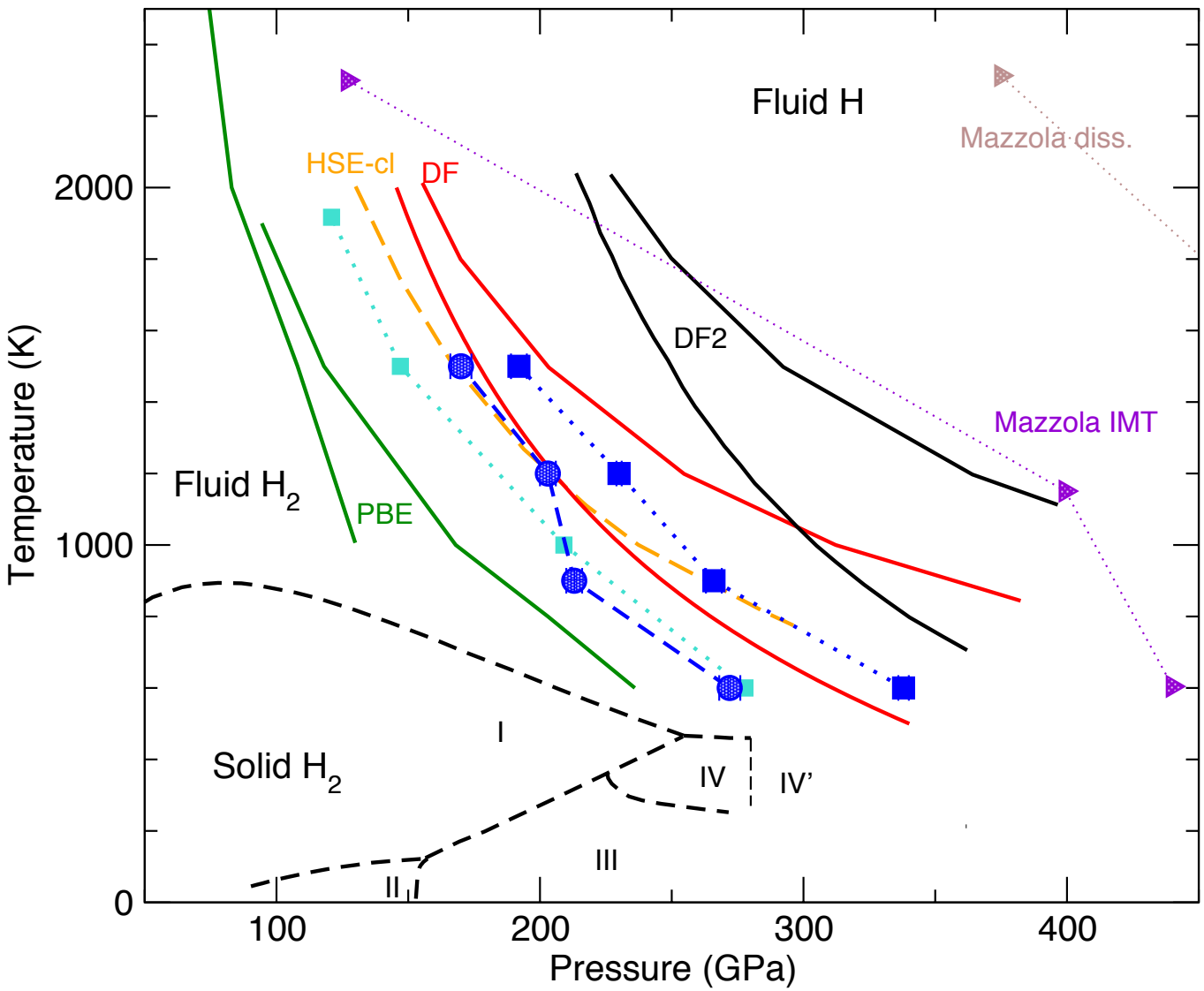
Liquid-Liquid transition observed



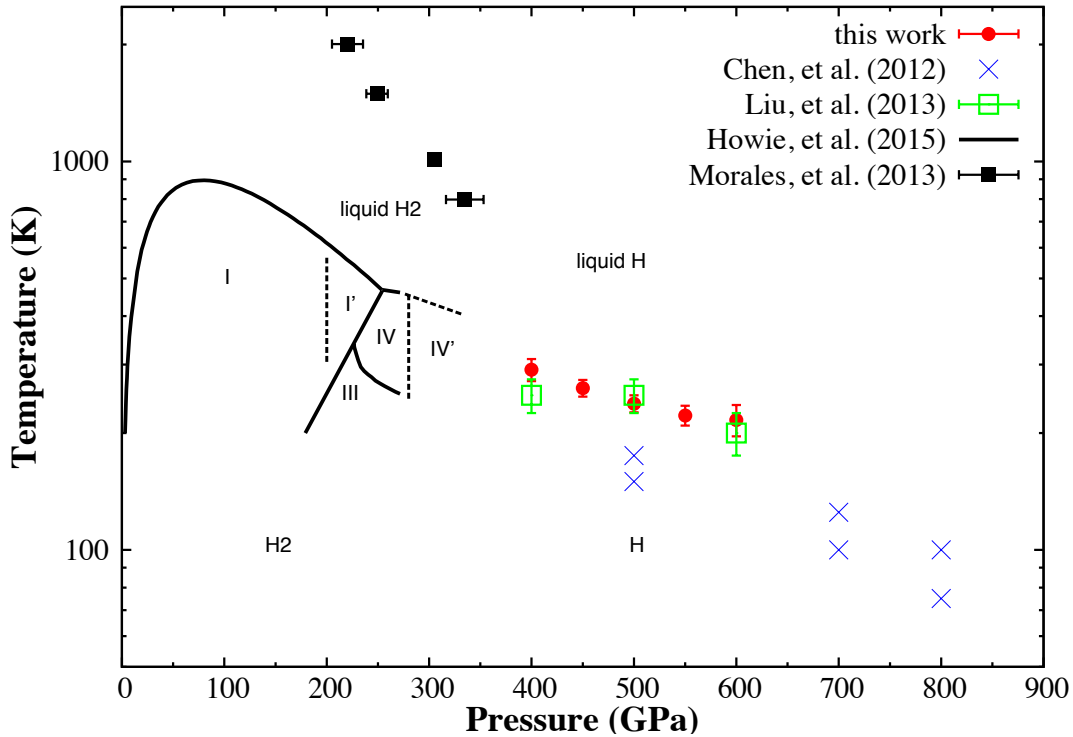
Experimental results vs. CEIMC



QMC vs. DFT


Fluid H
Mazzola diss.
HSE-cl
DF
DF2
Mazzola IMT
Fluid H_2
PBE
Solid H_2
I
II
III
IV
IV'
Temperature (K)
Pressure (GPa)
0
1000
2000
100
200
300
400

Melting temperatures of solid H



- Free energy calculations using PIMD & DFT (GGA) in liquid & crystal.
- Only Cs-IV structure for atomic H is dynamically stable, and only at low temperatures.
- If we find a better structure, that must *increase* melting temperature.
- Melting temperature decreases with pressure.

Raman spectroscopy of hot hydrogen above 200 GPa

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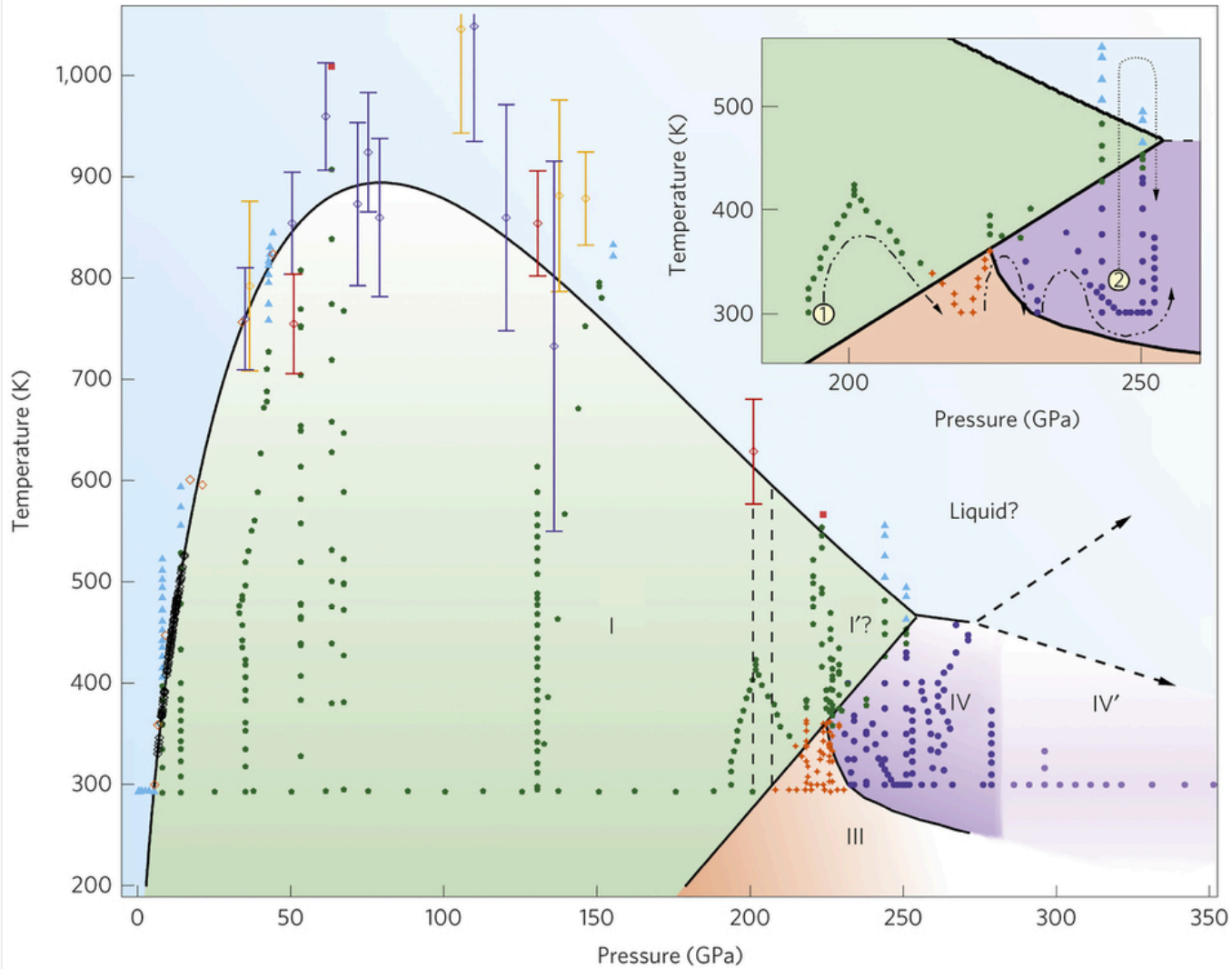
Nature Materials (2015) | doi:10.1038/nmat4213

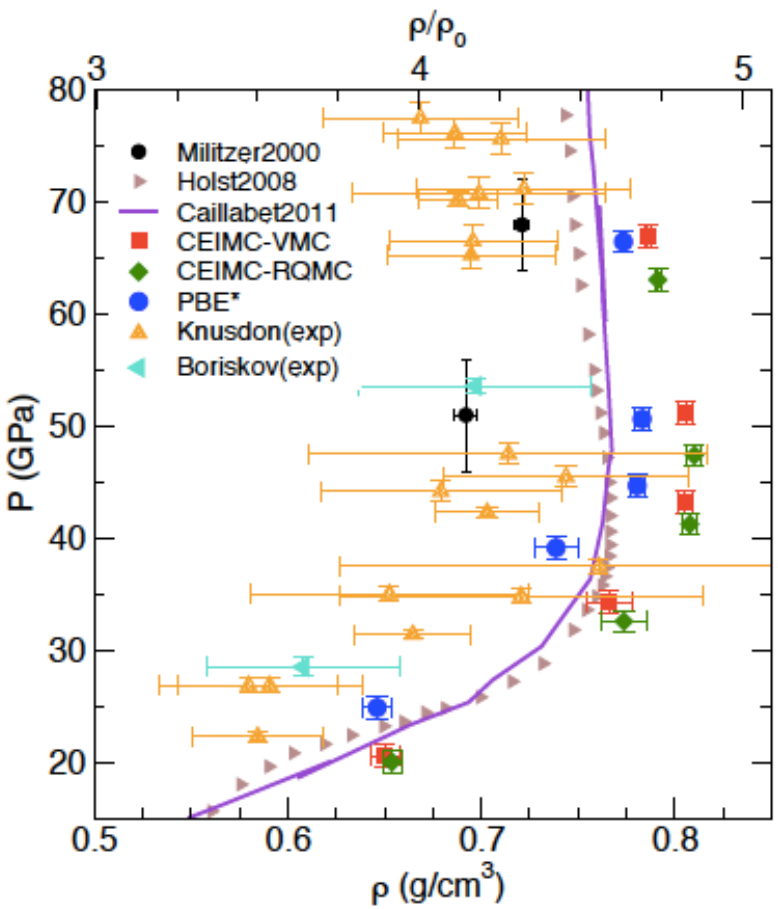
Received 07 August 2014 | Accepted 09 January 2015 | Published online 23 February 2015

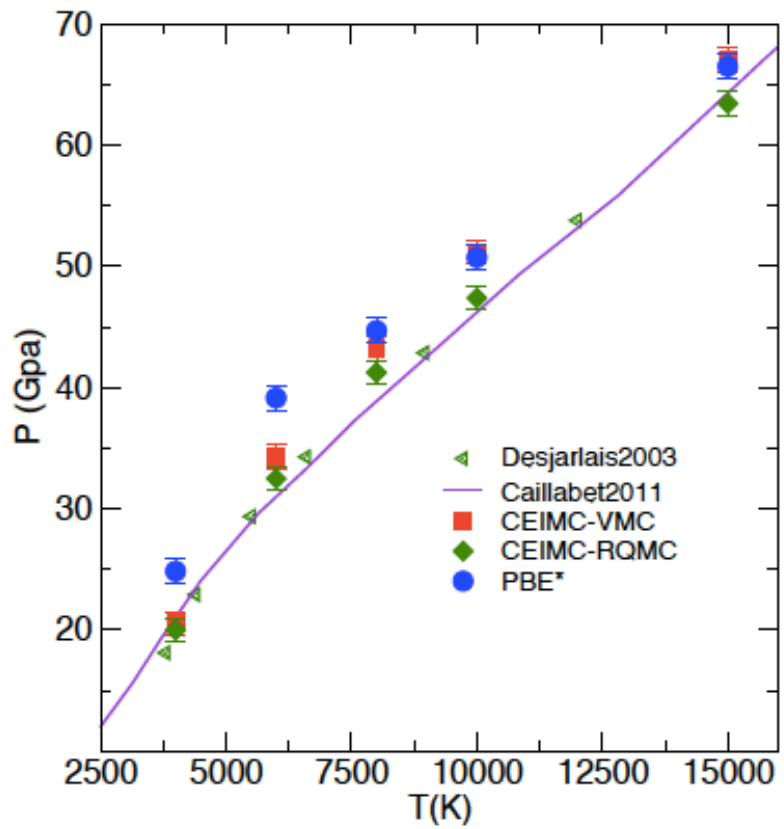


The inset shows the *P*–*T* paths (1 and 2) taken during temperature cycles. The melting curve is a Kechin fit[5] to the data points obtained here and in our previous study. Previous data are overlaid with different colour hollow diamonds: purple, ref. 8; yellow, ref. 7; orange, ref. 6; red, ref. 9; black, ref. 4. The phase lines between phases I, III and IV and the new phase (liquid) are from this study and refs 13, 14. The red squares show where the H_2 rapidly diffused from the sample chamber. The vertical dashed lines at around 190 GPa indicate the pressure region in which $(dv/dT)_P$ in phase I changes sign. The dashed lines ending with arrows are possible continuations of the transformation line (or melting curve). The lines between the phases have an error bar of about ±10 GPa but are consistent with our other studies[13, 14].

Deuterium Hugoniot

- Experimental data from Sandia (Knudson)
- Errors in DFT (PBE) seem to come from Pressure

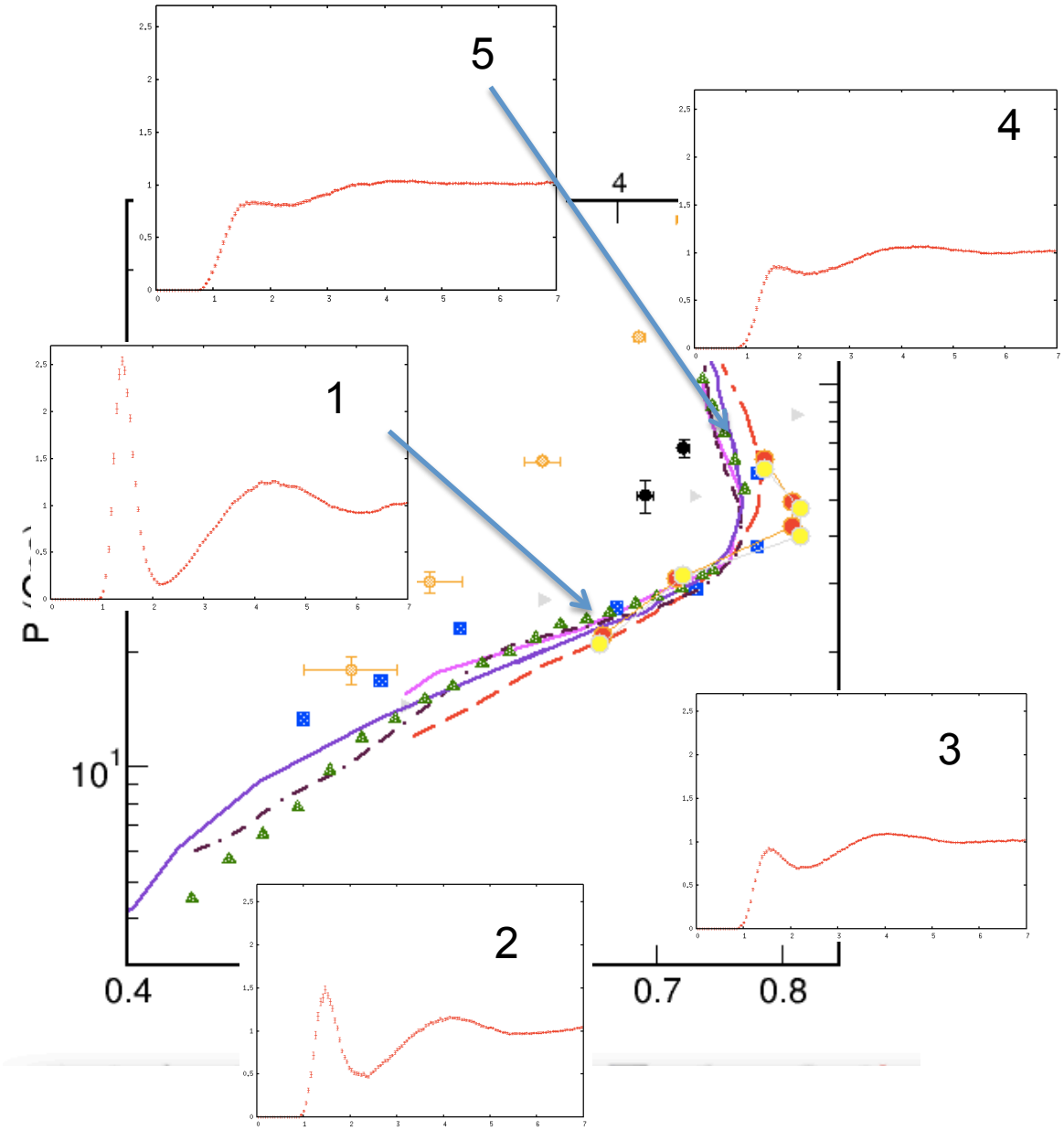




-Molecular to monoatomic phase transition observed, corresponding to the kink in the Hugoniot

- Density functional theory is significantly differences from QMC when bond breaking becomes important

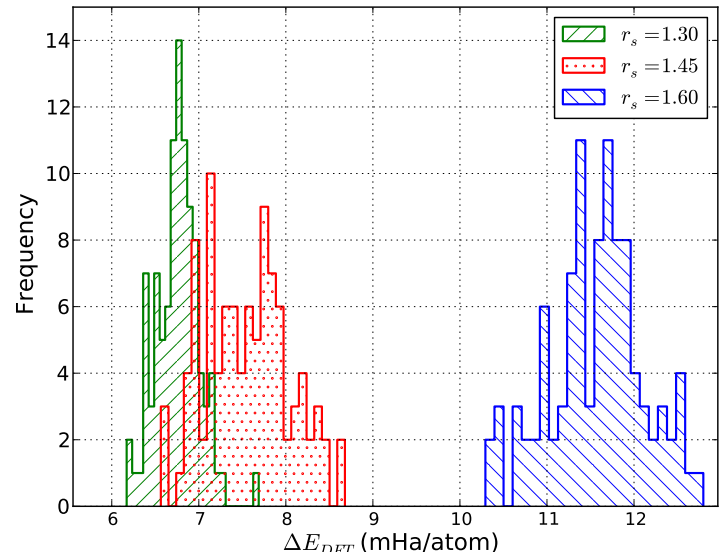
-VMC and DMC show similar results because of the highly optimized wave functions.

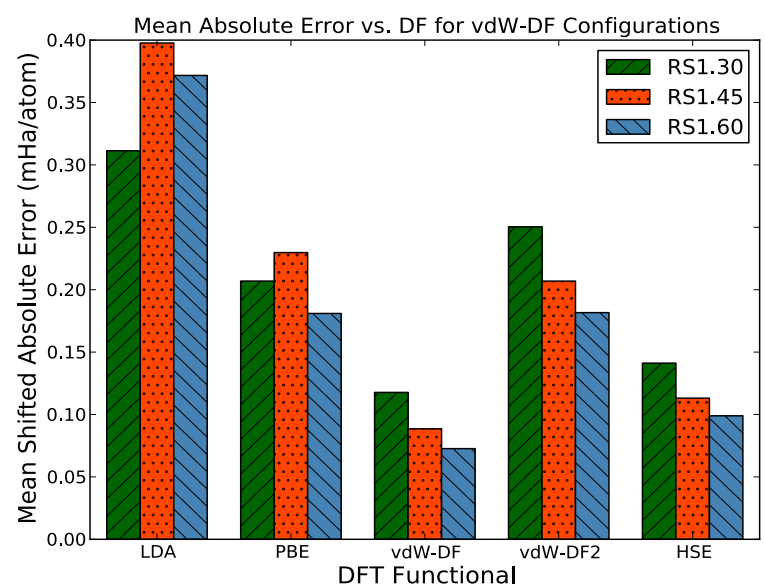


Use QMC to find the most accurate DFT functional.

- Generate 100's of 54-96 atom configurations of both liquids and solids.
- Determine accurate energies (better than 0.1mH/atom) with DMC.
- LDA and PBE functionals do poorly in the molecular phase.

Histogram of errors in PBE at 3 densities

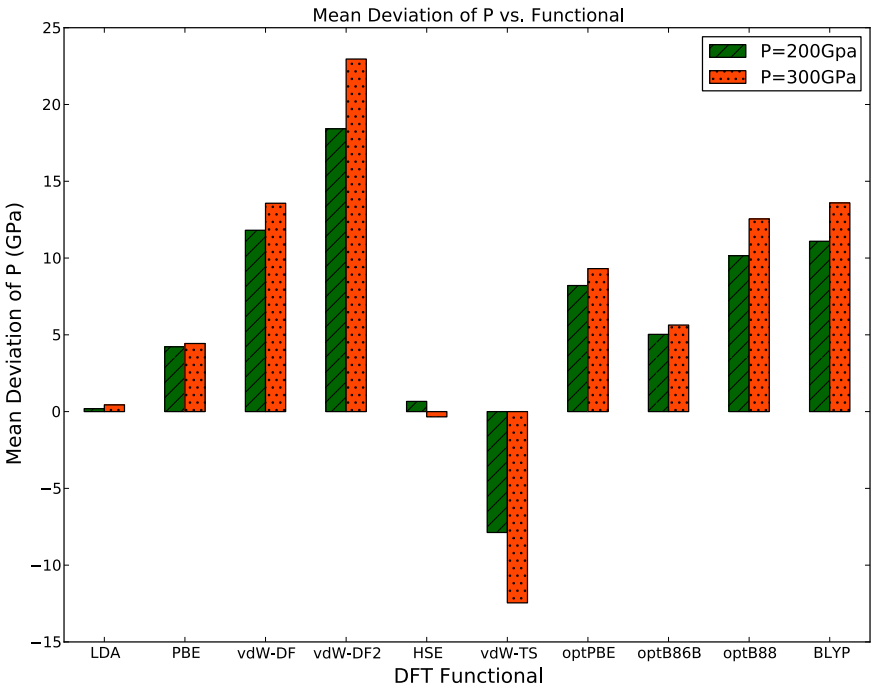




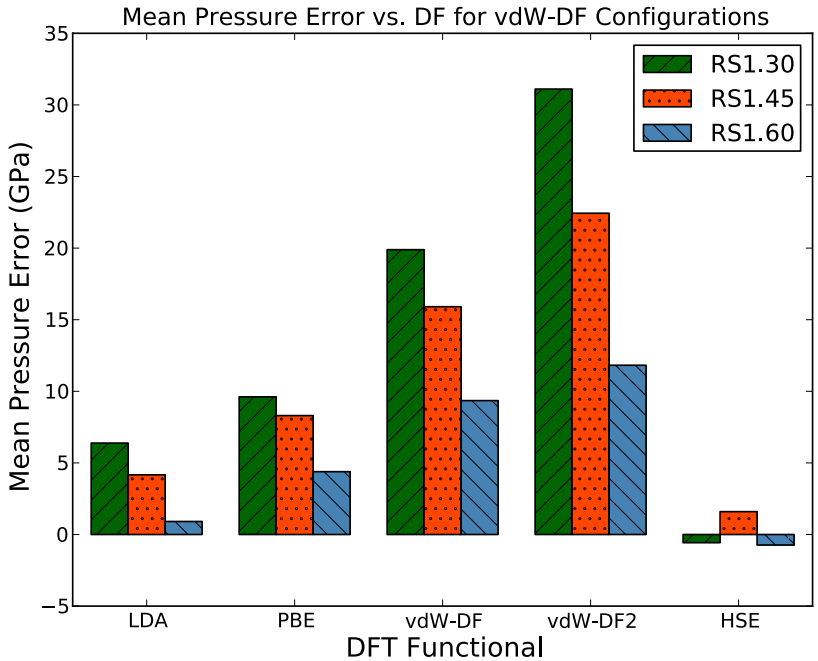
Average errors vs functional and density

Pressure errors

solids



liquid

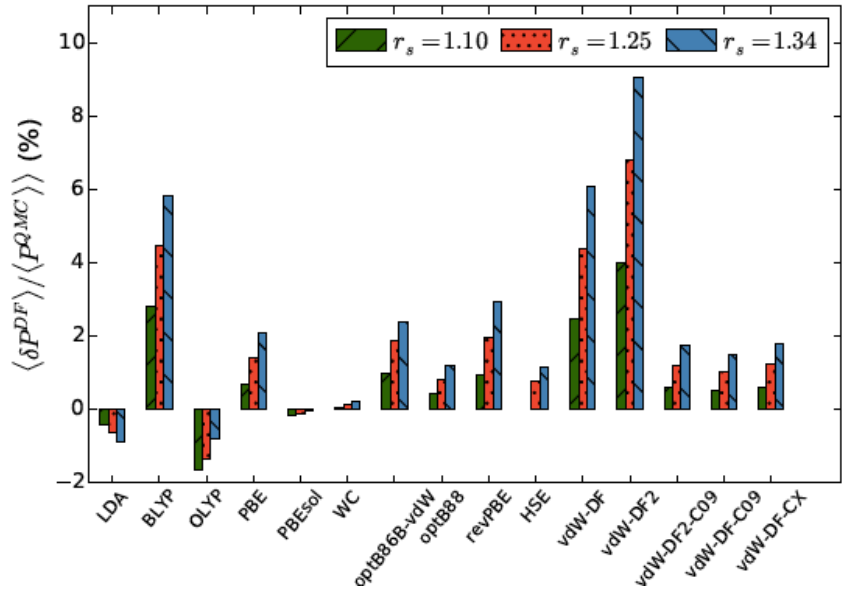


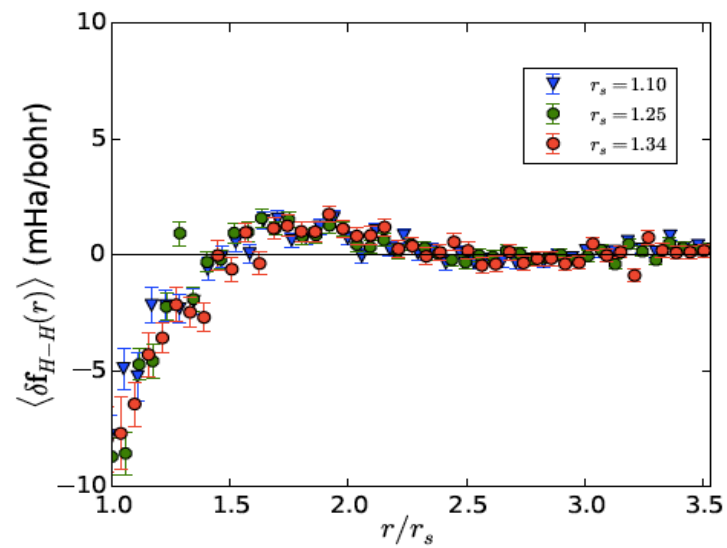
- LDA and HSE determine the pressure most accurately
- Use vdW-DF to simulate a structure, recalibrate pressure with QMC or LDA.

- Benchmark calculation of H-He mixtures. Comparison of DFT functionals
- Construction of potentials for dense hydrogen and helium using QMC forces.

CURRENT WORK

- Stability of hydrogen structures with CEIMC
- New methods to compute conductivity in dense hydrogen
- Examination of properties of dense hydrogen liquid





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