Phase Transitions in dense hydrogen
with Quantum Monte Carlo

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Recent Collaborators

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Carlo Pierleoni *L'Aquila, Italy*

AND many other collaborators over the years!

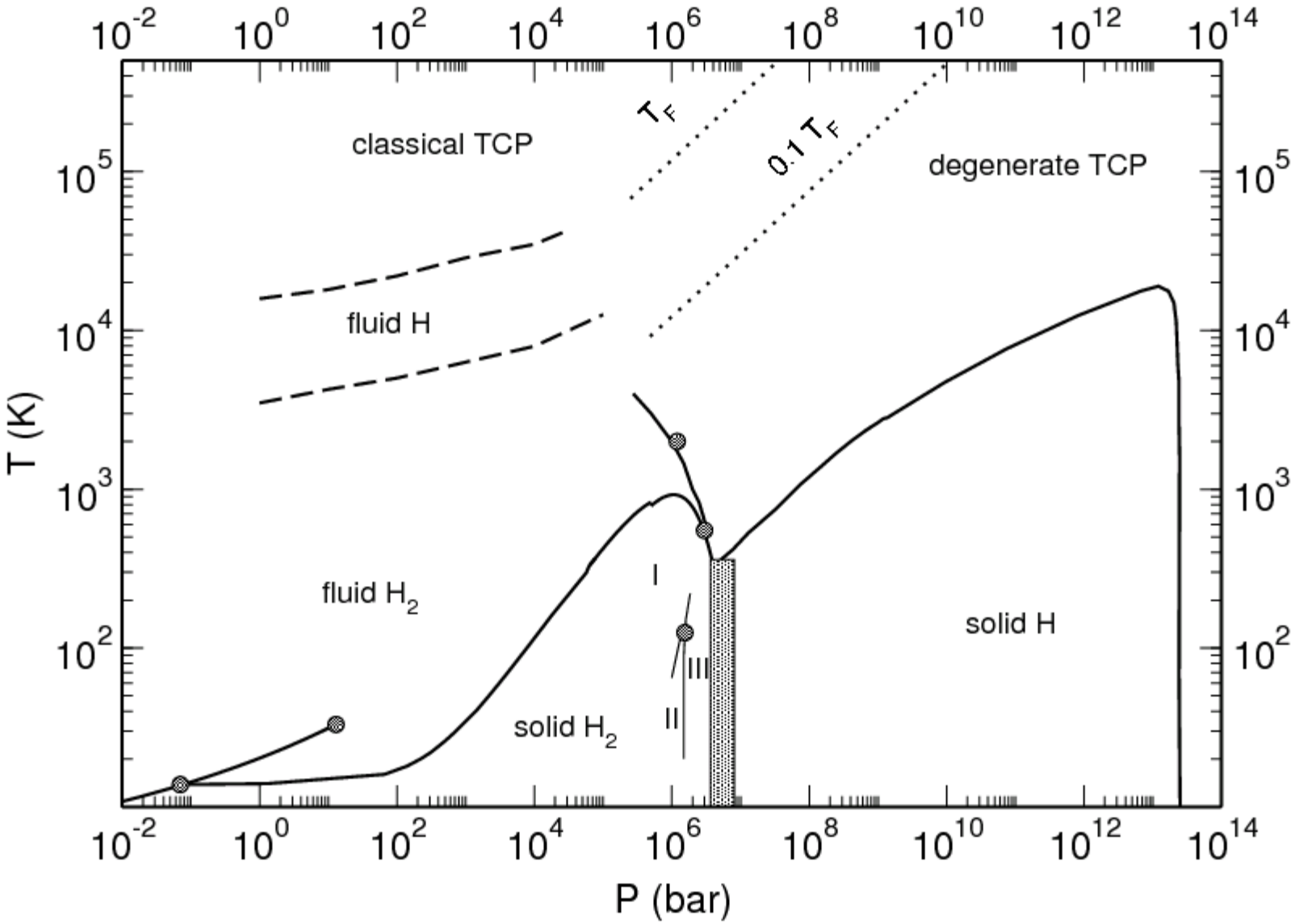
DOE-NNSA 0002911

INCITE & Blue Waters award of computer time

Why study dense Hydrogen?

- Applications:
  - Astrophysics: giant planets, exoplanets
  - Inertially confined fusion: NIF
- Fundamental physics:
  - What phases are stable?
  - Superfluid/ superconducting phases?
- Benchmark for simulation:
  - “Simple” electronic structure; no core states
  - But strong quantum effects from its nuclei

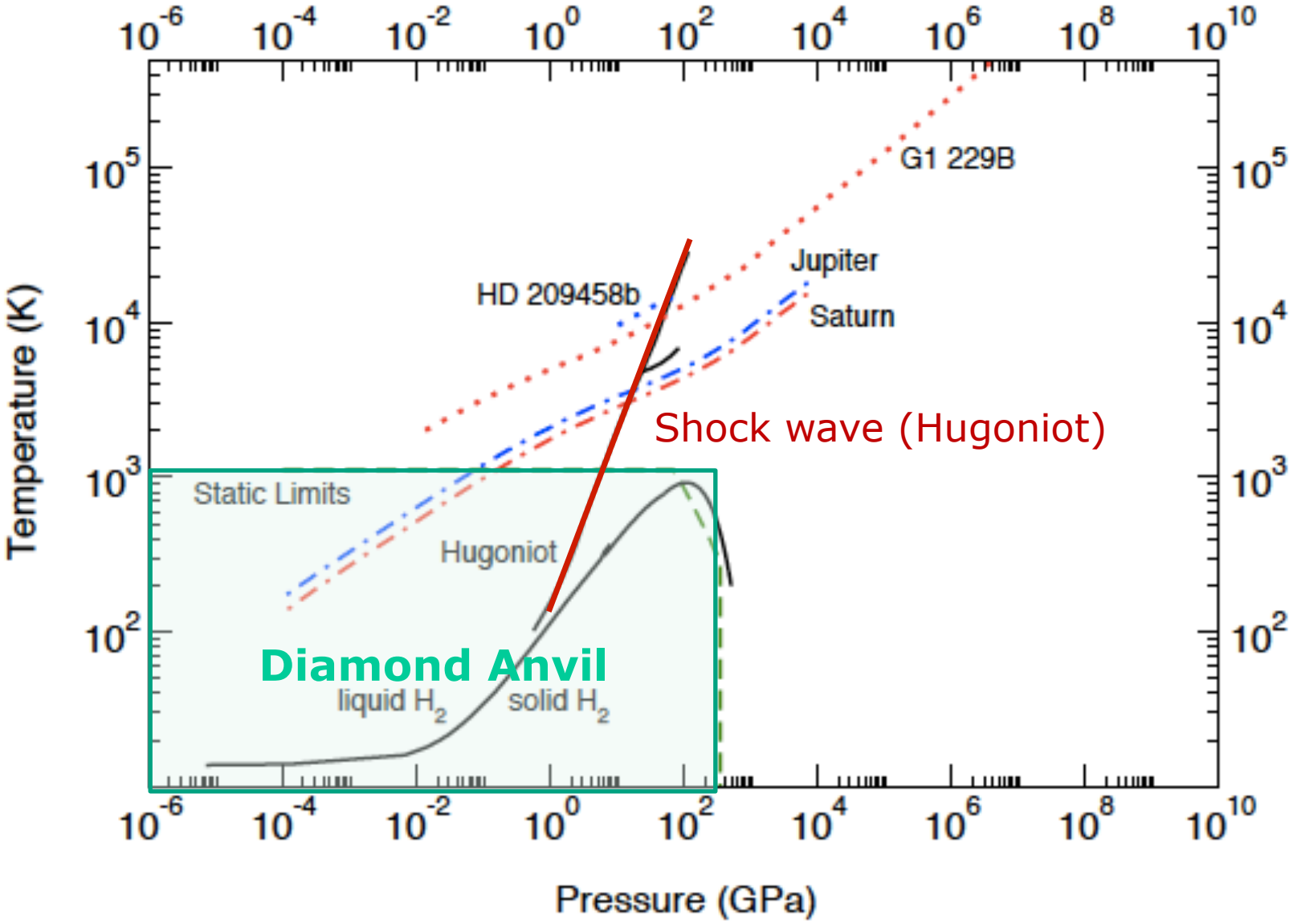
Simplified H Phase Diagram



Questions about the phase diagram of hydrogen

1. Is there a liquid-liquid transition in dense hydrogen?
2. How does the atomic/molecular or insulator/metal transition take place?
3. What are the crystal structures of solid H?
4. Could dense hydrogen be a quantum fluid? What is its melting temperature?
5. Are there superfluid/superconducting phases?
6. Is helium soluble in hydrogen?
7. What are its detailed properties under extreme conditions?

Experiments on hydrogen



Atomic/Molecular Simulations

accuracy ↓

–Hard sphere MD/MC ~1953 (Metropolis, Alder)

–Empirical potentials (e.g. Lennard-Jones) ~1960 (Verlet, Rahman)

–Local density functional theory ~1985 (Car-Parrinello)

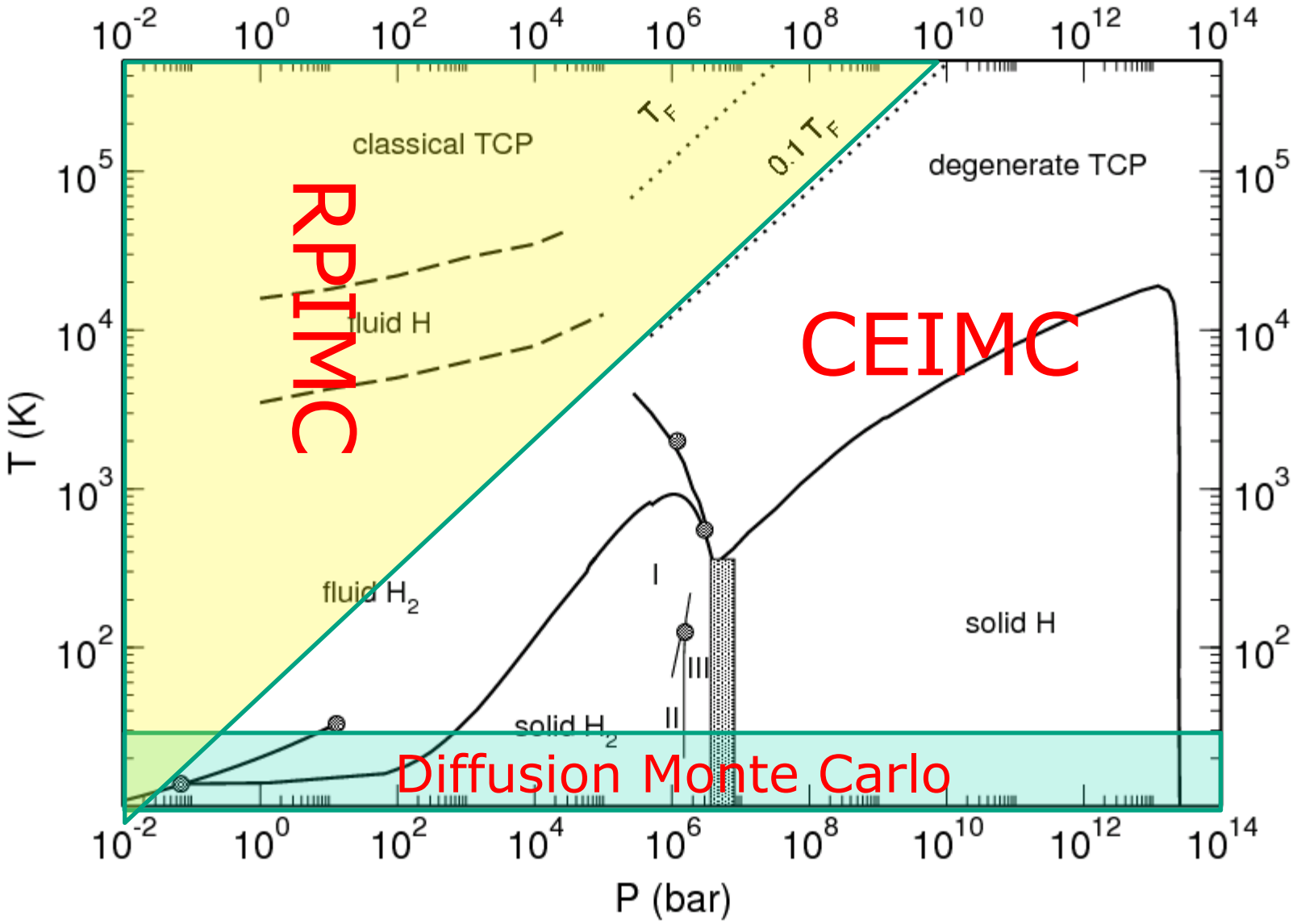
–Quantum Monte Carlo: VMC/DMC 1980, PIMC 1990 CEIMC 2000

- Initial simulations used interatomic potentials based on experiment. But are they accurate enough.
- Much progress with "ab initio" molecular dynamics simulations where the effects of electrons are solved for each step.
- Progress is limited by the accuracy of the DFT exchange and correlation functionals for hydrogen
- The most accurate approach is to simulate both the electrons and ions

Quantum Monte Carlo

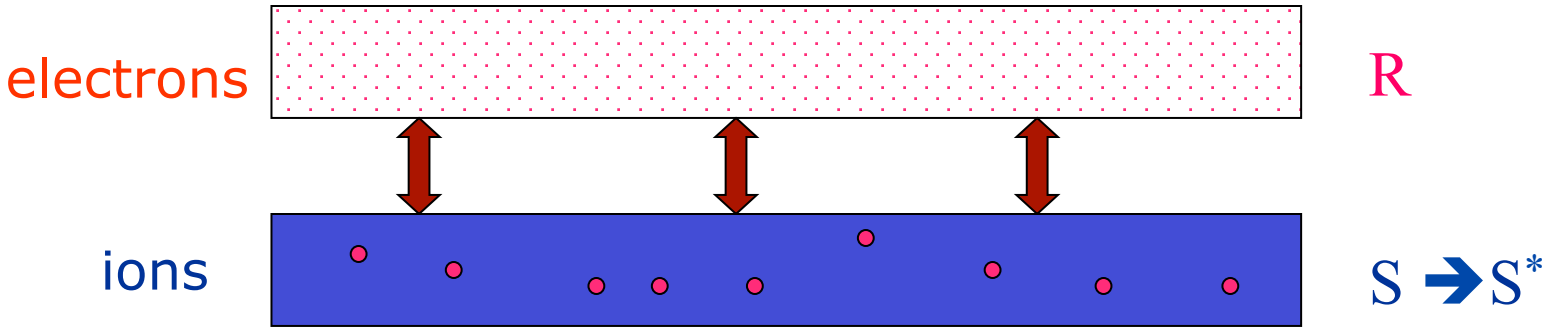
- Premise: we need to use simulation techniques to "solve" many-body quantum problems just as you need them classically.
- Both the wavefunction and expectation values are determined by the simulations. Correlation built in from the start.
- Primarily based on Feynman's imaginary time path integrals.
- QMC gives most accurate method for general quantum many-body systems.
- QMC determined electronic energy is the standard for approximate LDA calculations. (but fermion sign problem!)
- Path Integral Methods provide a exact way to include effects of ionic zero point motion (include all anharmonic effects)
- A variety of stochastic QMC methods:
  - **Variational Monte Carlo VMC (T=0)**
  - **Projector Monte Carlo (T=0)**
    - **Diffusion MC (DMC)**
    - **Reptation MC (RQMC)**
  - **Path Integral Monte Carlo (PIMC) (T>0)**
  - **Coupled Electron-Ion Monte Carlo (CEIMC)**

Regimes for Quantum Monte Carlo



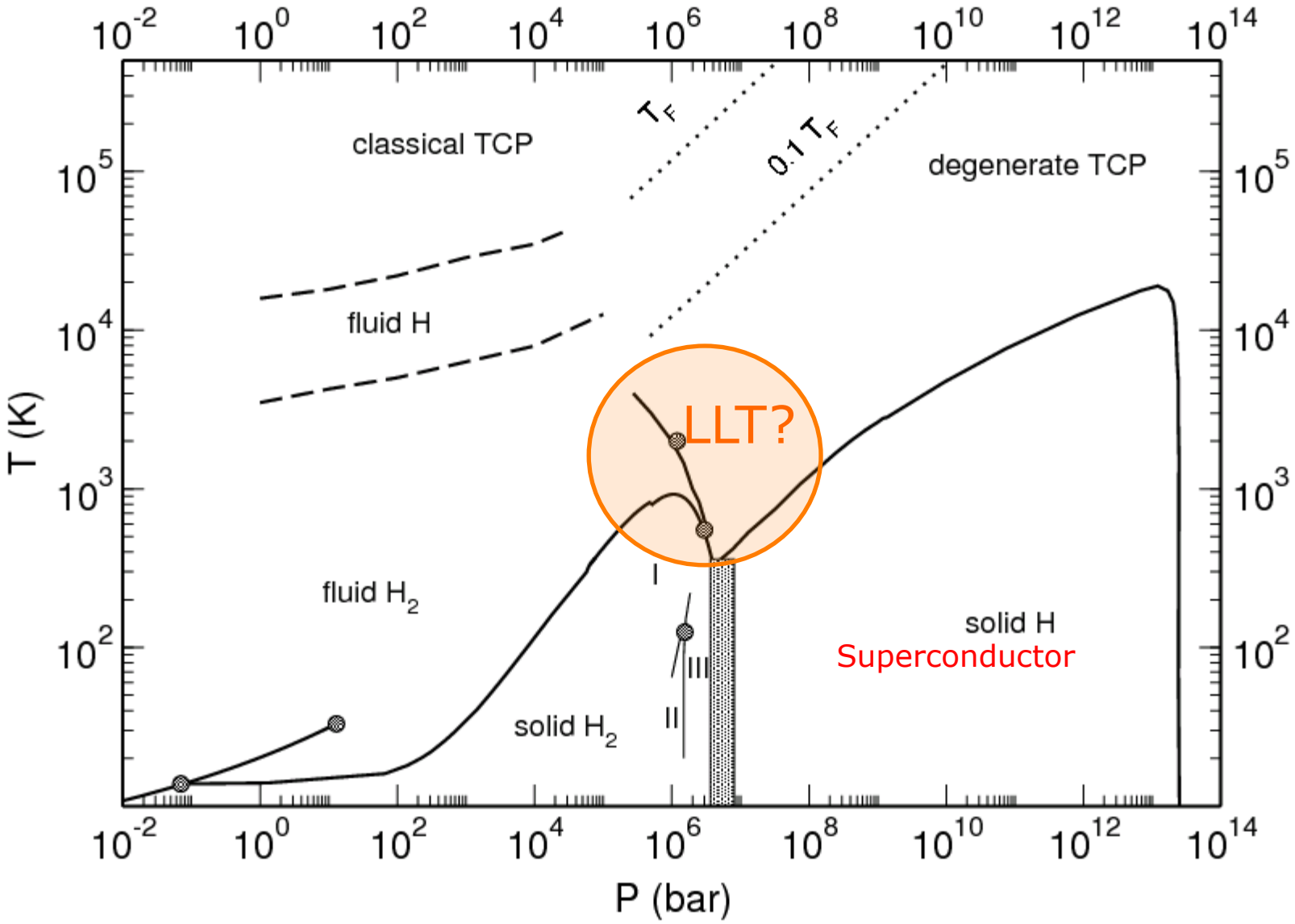
Coupled Electron-Ionic Monte Carlo:CEIMC

1. Do Path Integrals for the ions at T>0.
2. Let electrons be at zero temperature, a reasonable approximation for $T<<E_F$.
3. Use Metropolis MC to accept/reject moves based on QMC computation of electronic energy



The "noise" coming from electronic energy can be treated without approximation using the penalty method.

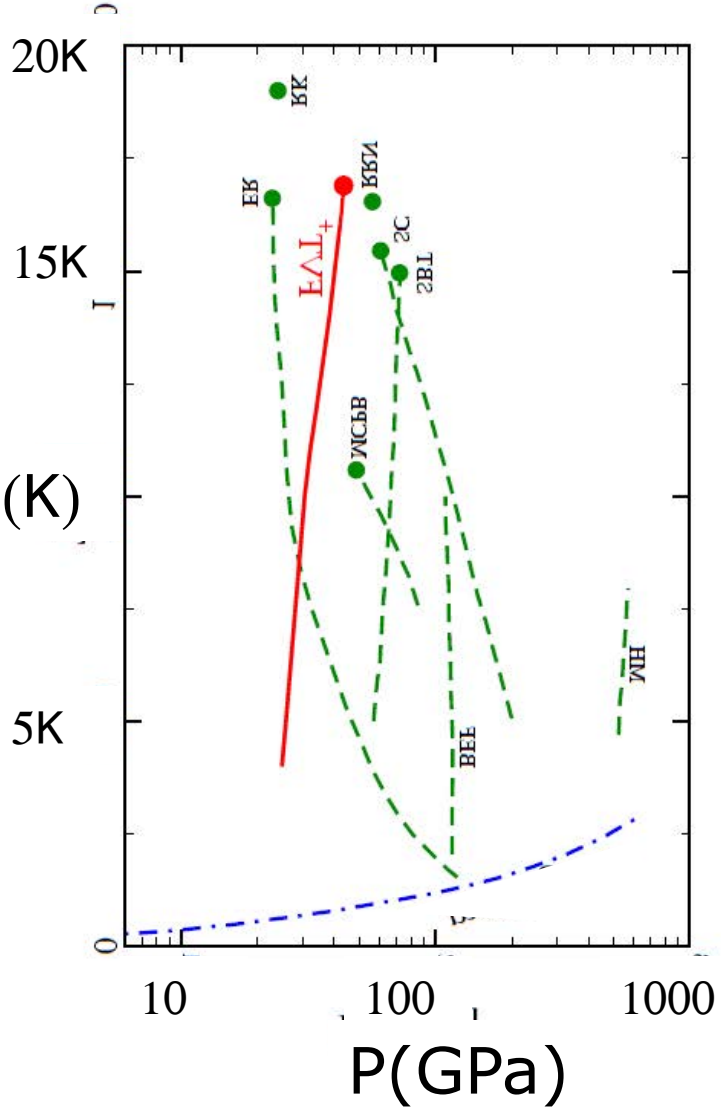
Liquid-Liquid transition?



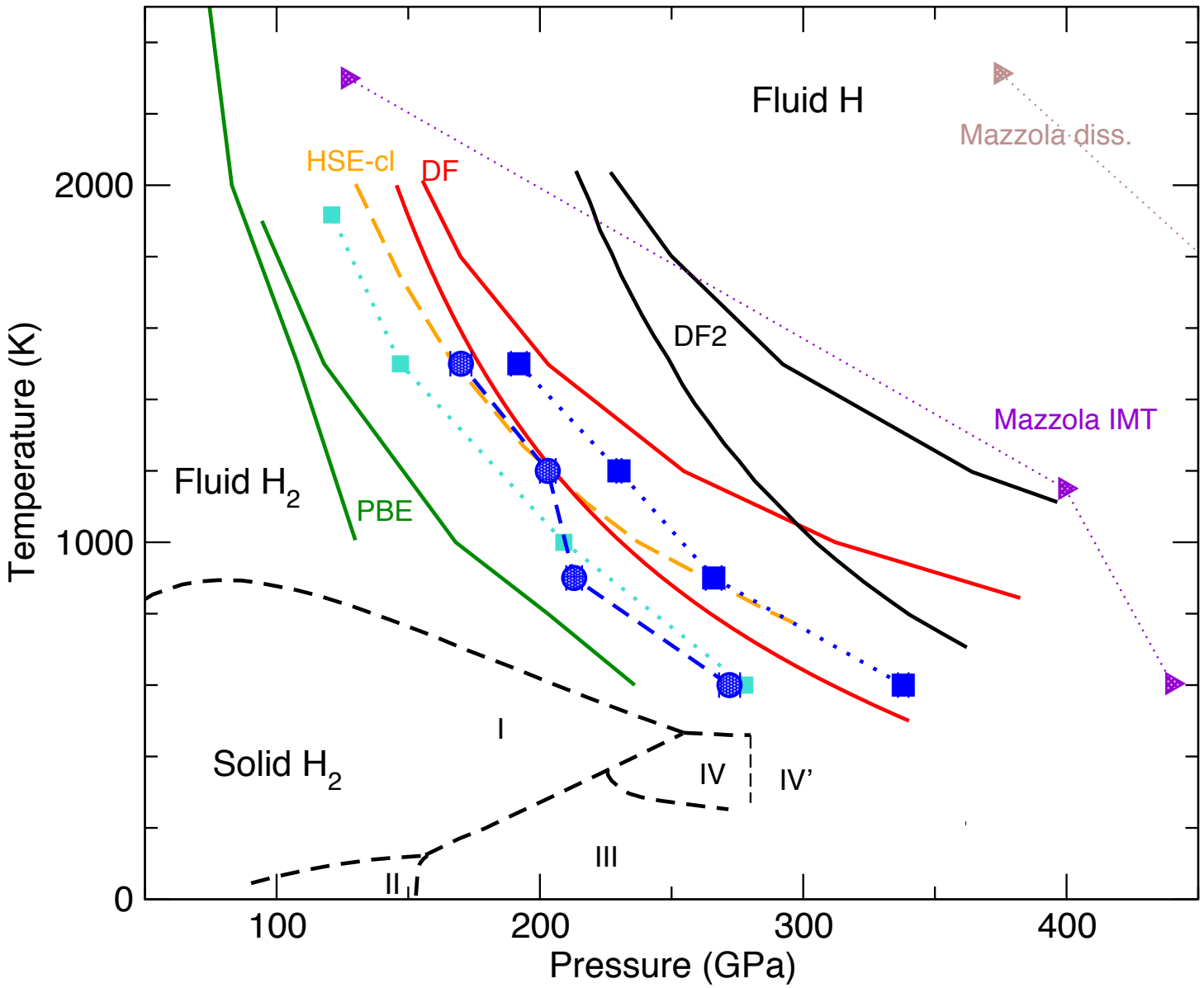
Liquid-Liquid transition

aka "Plasma Phase transition"

- How does an insulating molecular liquid become a metallic atomic liquid? Either a
  - Continuous transition or
  - First order transition with a critical point
- Zeldovitch and Landau (1944) *"a phase transition with a discontinuous change of the electrical conductivity, volume and other properties must take place"*
- Chemical models are predisposed to have a transition since it is difficult to have an smooth crossover between 2 models (e.g. in the Saumon-Chabrier hydrogen EOS)



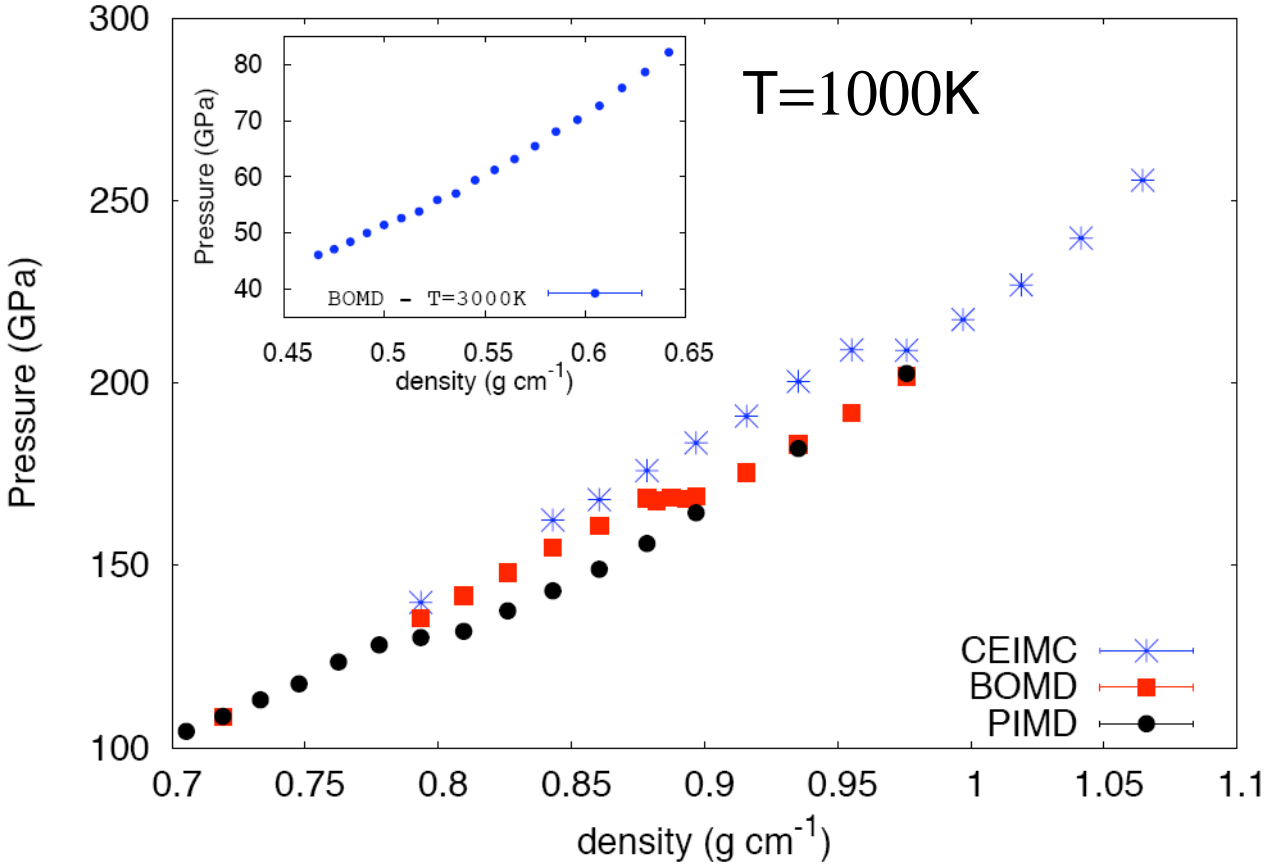
DFT calculations are not very predictive



Liquid-Liquid Transition

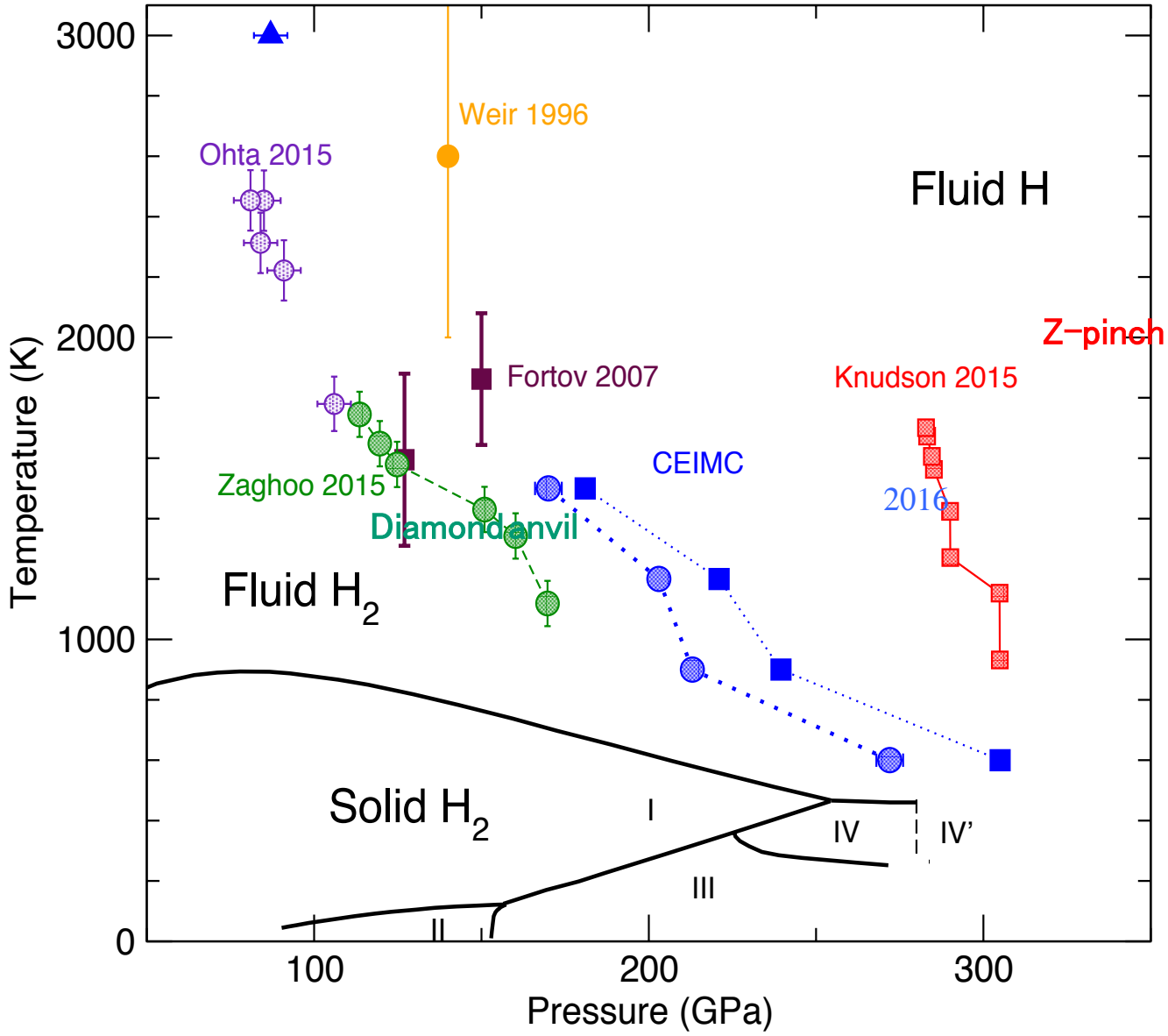
Morales,Pierleoni, Schwegler,DMC, PNAS 2010.

- Pressure plateau at low temperatures (T<2000K)- signature of a 1st order phase transition
- Seen in CEIMC and BOMD at different densities
- Finite size effects are very important
- Narrow transition (~2% width in V)
- Low critical temperature
- Small energy differences



Three experimental confirmations since 2015!!

Experimental results differ by a factor 2!!
CEIMC is in the middle.



Settling Arguments About Hydrogen With 168 Giant Lasers

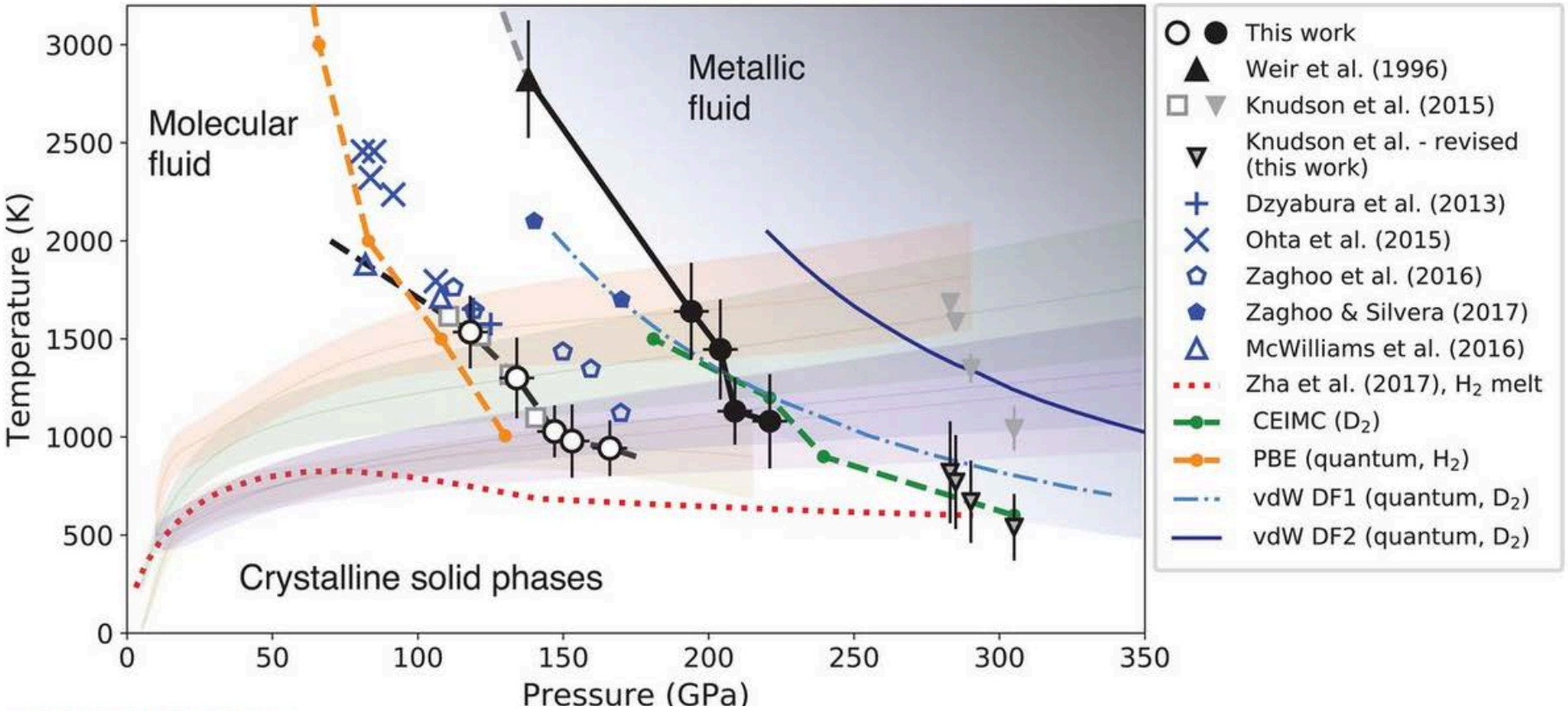
Scientists at Lawrence Livermore National Laboratory said they were "converging on the truth" in an experiment to understand hydrogen in its liquid metallic state.

Liquid metallic hydrogen does not occur naturally on Earth, except possibly at the core, but scientists believe the interiors of Jupiter and Saturn are awash in hydrogen in that state.
NASA/Reuters

By Kenneth Chang

Aug. 16, 2018

Possible resolution (Livermore, 2018)



HIGH-PRESSURE PHYSICS

Insulator-metal transition in dense fluid deuterium

Science **361**, 677–682 (2018)

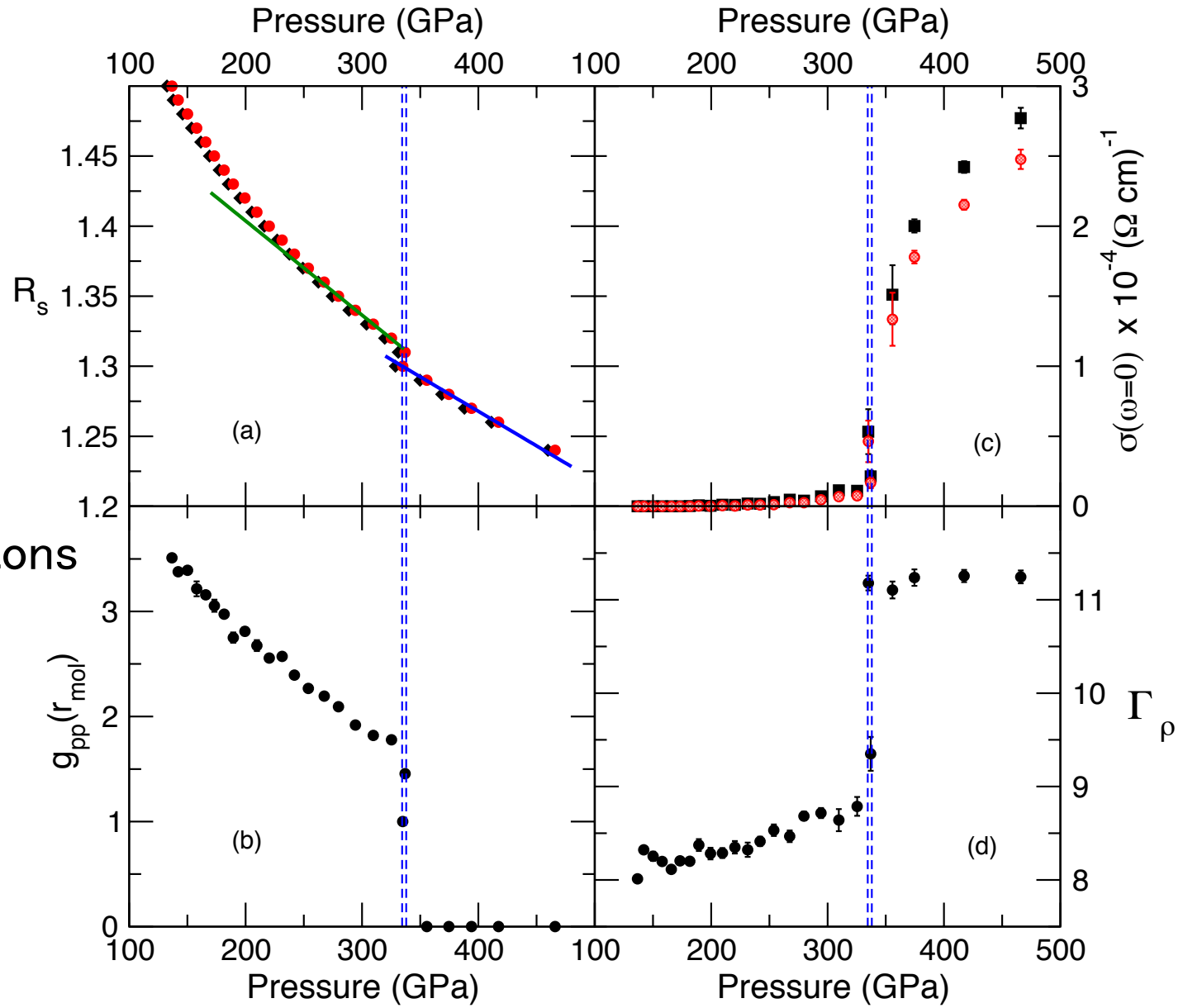
Peter M. Celliers[1*], Marius Millot[1], Stephanie Brygoo[2], R. Stewart McWilliams[3], Dayne E. Fratanduono[1], J. Ryan Rygg[1,4], Alexander F. Goncharov[5], Paul Loubeyre[2], Jon H. Eggert[1], J. Luc Peterson[1], Nathan B. Meezan[1], Sebastien Le Pape[1], Gilbert W. Collins[1,4], Raymond Jeanloz[6], Russell J. Hemley[7]

Signatures of the transition

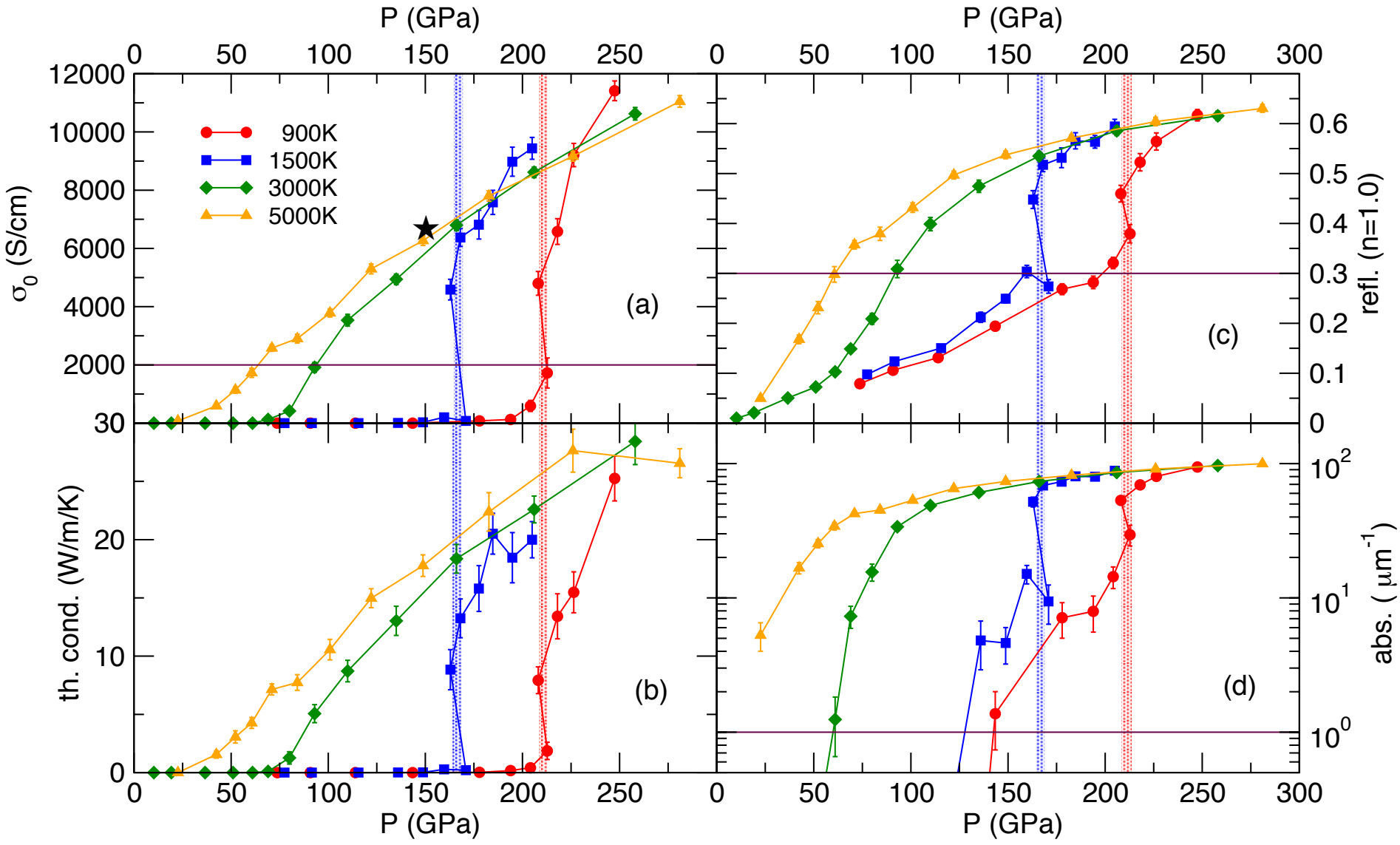
atomic-molecular & metal-insulator

T=600K

Classical protons



Properties across the transition

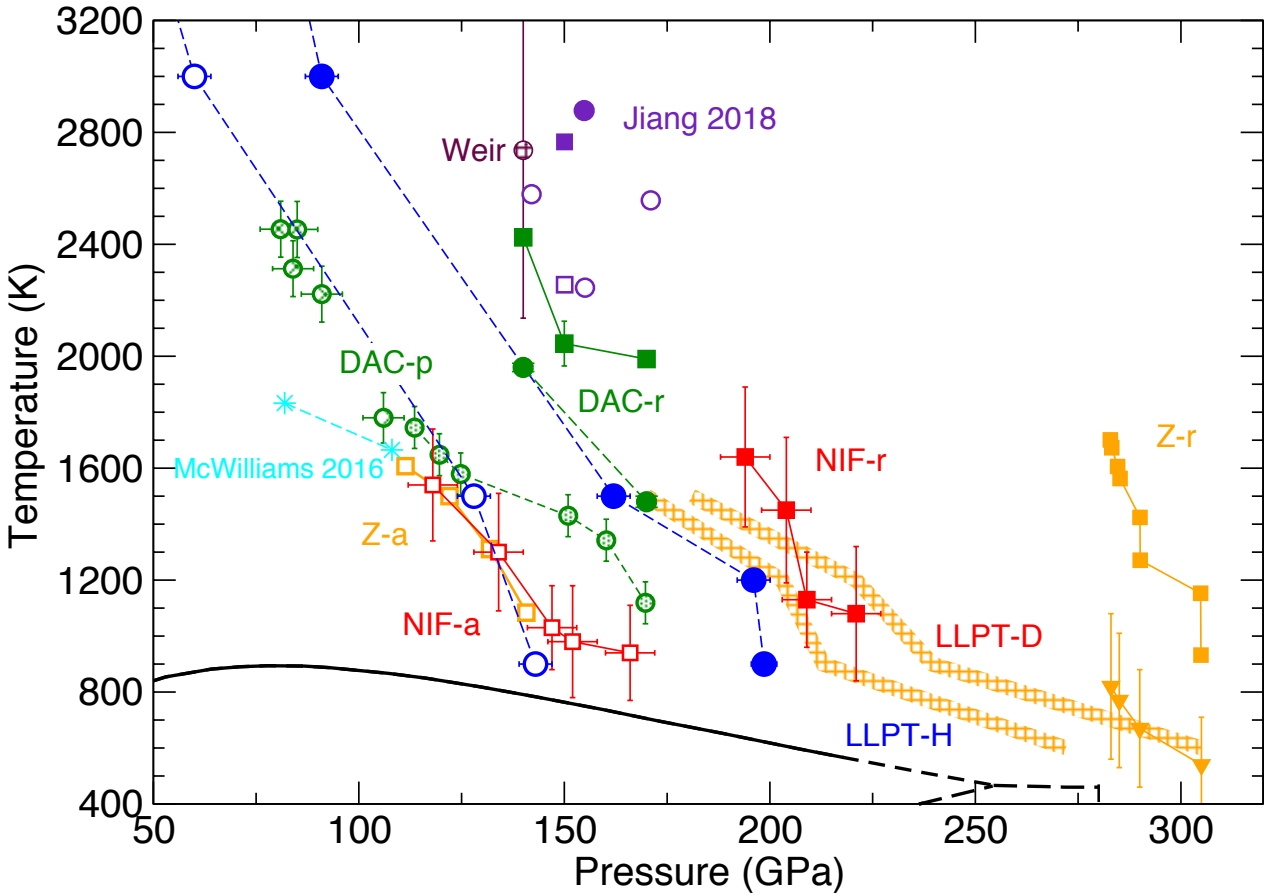


Rillo, Morales, DMC, Pierleoni, PNAS (2019)

Comparison of optical properties

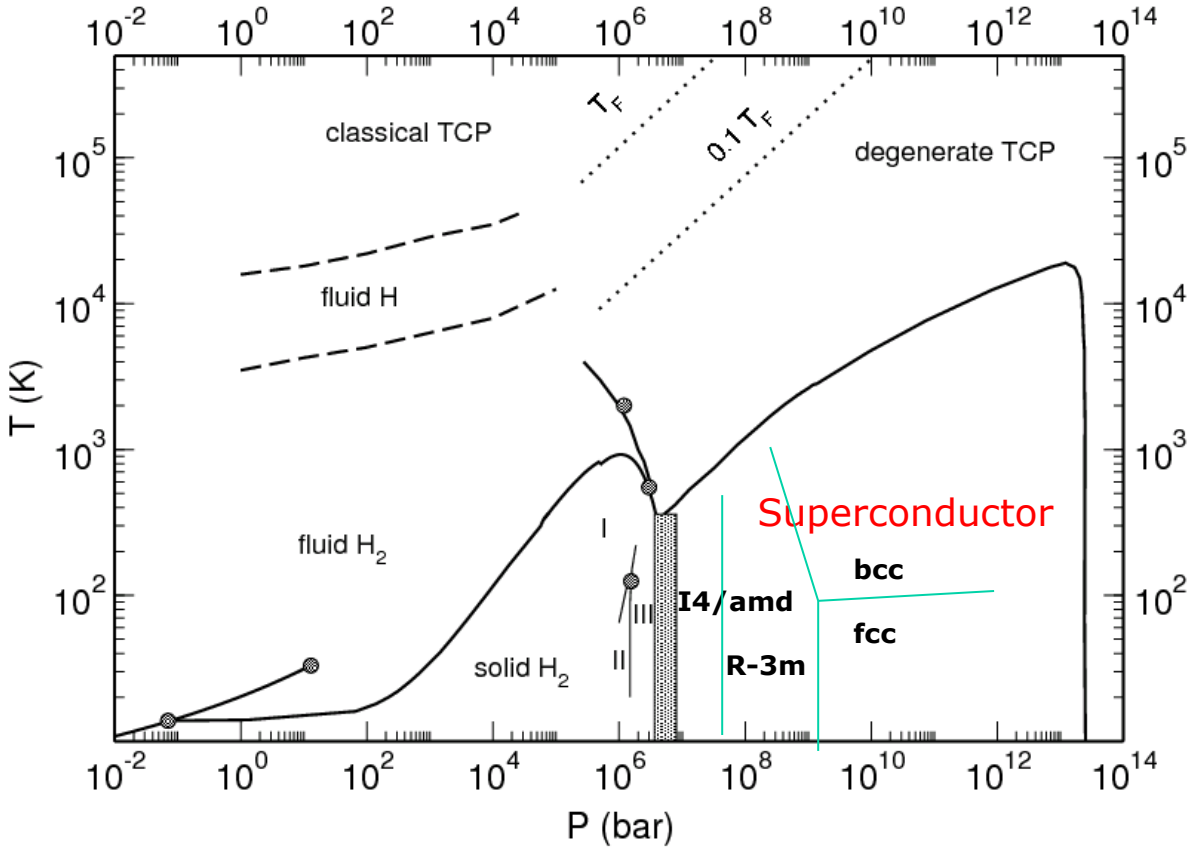
"a" adsorption
"r" reflectance
"p" plateau

○ Hydrogen
■ Deuterium



Rillo, Morales, DMC, Pierleoni, PNAS(2019).

Hydrogen Phase Diagram



Based on the BCS theory estimates, we expect entire atomic solid to be superconducting at high T

But at high pressure!

How can we use QMC to enable calculations for larger systems at longer times?

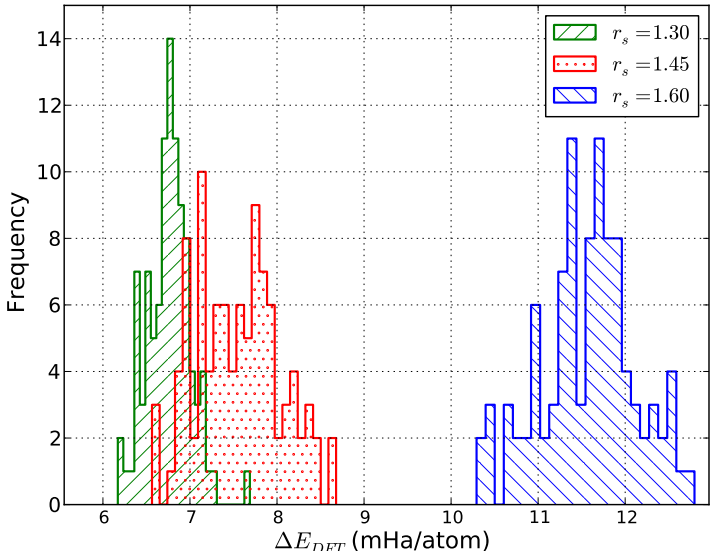
- Find better DFT functionals
- Find better “semi-empirical” potentials

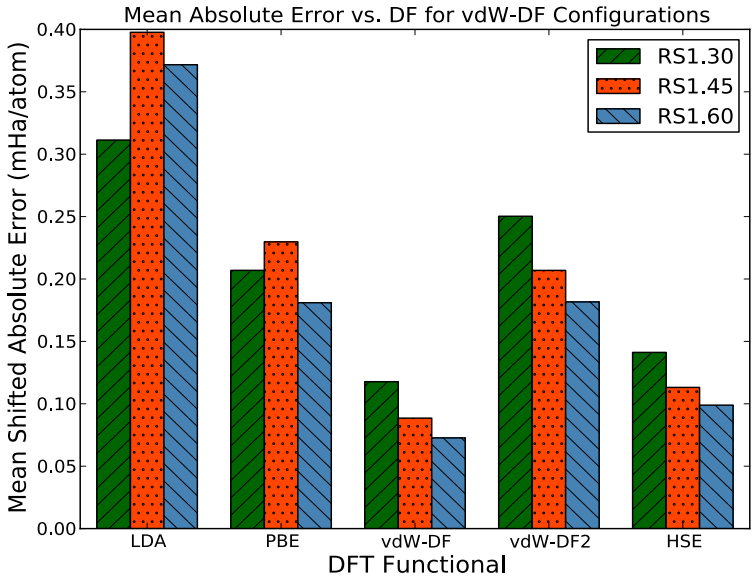
Use QMC to find the most accurate DFT functional.

- 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.

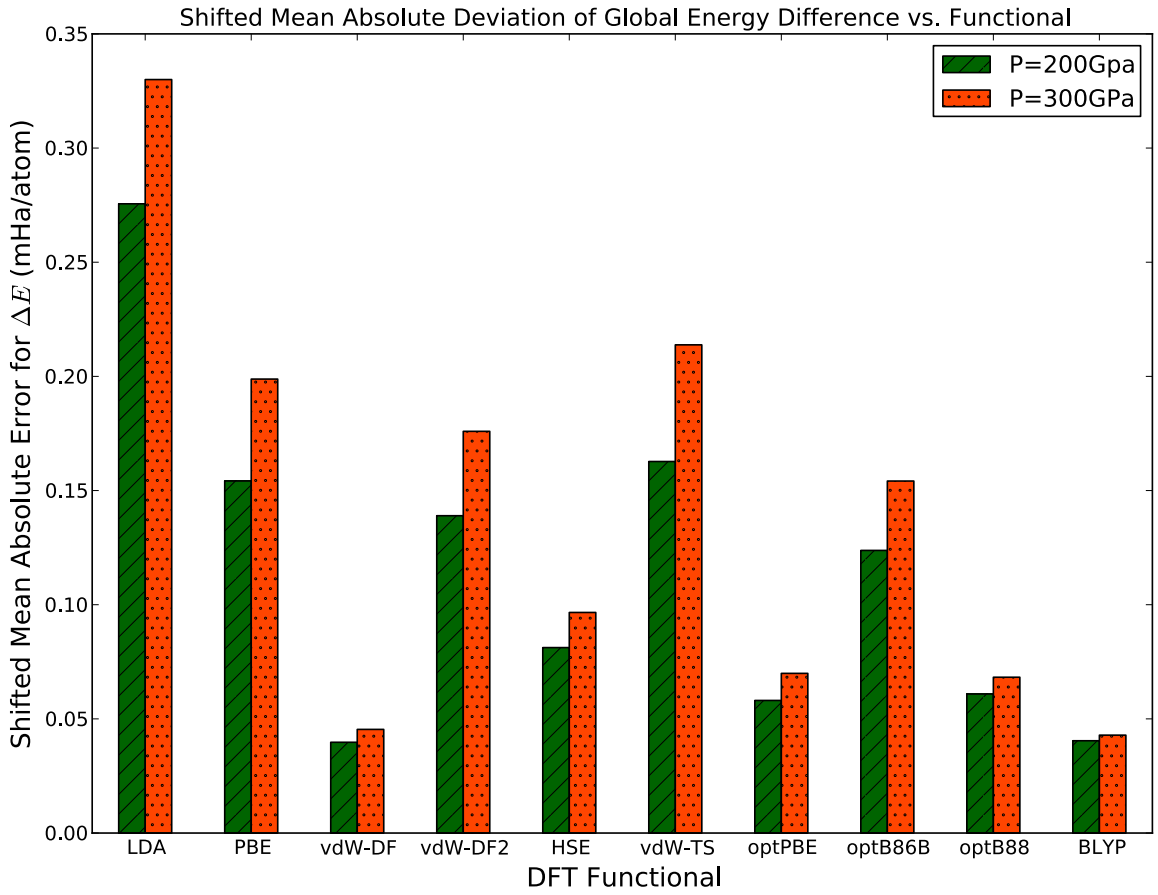
Average errors vs functional and density

Histogram of errors in PBE at 3 densities





In one solid structure find dispersion of errors.
Then average over solid structures
vdW-DF is most accurate.



Concluding Remarks

QMC is arguably the most accurate computational method to make predictions about properties of hydrogen under extreme conditions.

- DFT functionals give differing results especially near the phase transitions.
- DMC is most accurate for the ground state.
- CEIMC allows one access to disordered $T>0$ systems with control of correlation effects

There are many open questions with hydrogen:

- The sequence of molecular and atomic crystal structures
- Mechanism of metallization in the solid
- High temperature superconductivity in LaH_{10} and SH_3.

Future work is to study these with effective potentials learned from QMC energetics.