# Liquid-liquid phase transition in high pressure hydrogen

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Quantum Monte Carlo in the Apuan Alps IX

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## Outline

- Hydrogen phase diagram: an overview and open problems
- many-electrons vs single electrons methods for hydrogen
  - Restricted Path Integrals
  - DFT-based Molecular Dynamics: BOMD
  - QMC-based methods: the Coupled-Electron Ion Monte Carlo
- Nuclear Quantum effects in FPMD
- benchmark of DFT via Quantum Monte Carlo
- Liquid-liquid Phase transition (LLPT)

# Why Hydrogen?

- Hydrogen is the simplest element, i.e. the element with the simplest electronic structure
- Hydrogen is the most abundant element in the Universe: the Giant gas planets are comprised by 70-90% of hydrogen, plus helium and other heavier elements. Developing accurate planetary models requires accurate acknowledge of hydrogen Equation of State (EOS).
- Hydrogen is relevant for energy applications: nuclear fusion etc.
- The hydrogen atom and molecule have been the prototype systems in developing Quantum Mechanics
- Hydrogen is the ideal playground to develop and test new theoretical approaches and methods
- Being the simplest element, it is desirable to be able to predict its properties in a wide range of physical parameters from first-principle.
- Hydrogen under pressure presents a reach and difficult physics.

## Hydrogen phase diagram

from J. McMahon, M.A. Morales, C. Pierleoni and D.M. Ceperley, Rev Mod Phys (2012)



- At ambient conditions it is molecular and at low temperature its phase diagram is dominated by the orto-para separation (Silvera '80).
- Metallization and molecular dissociation with pressure in the ground state was predicted long ago to be at P~25Gpa (Wigner 1935) but modern experiments up to 350GPa did not found a metallic state (Loubeyre '02).
- Three different insulating molecular crystal phases has been observed for increasing pressure. Recently a forth phase (IV) has been observed (<u>Howie</u> et al, 2012)
- The observed reentrant melting of the molecular crystal and the <u>molecular dissociation-metallization</u> in the fluid phase, together with the large zero point effect on the protons, have suggested the existence of a low temperature liquid phase which could separate the molecular crystal from the atomic crystal.
- Metallic hydrogen might be a new phase of matter: metallic supefluid and superconductor



#### Imaginary time path integral methods: restricted-PIMC

hydrogen (Pierleoni et al 1994, Militzer et al 2001) helium (Militzer 2006, 2008)

Limitations: only practical for high temperatures (T>10000K)

### Born-Oppenheimer based methods:

- solve the electronic Schroedinger equation (ground state only) at fixed nuclei
- compute the statistical mechanics (dynamics) of nuclei with the energy (forces) of the instantaneous electronic ground-state (Monte Carlo and Molecular Dynamics)

**BO Molecular Dynamics (BOMD)** (or Car-Parrinello MD): based on <u>Density Functional Theory (DFT)</u> solution of the electronic problem

Coupled Electron-Ion Monte Carlo (Pierleoni-Ceperley): uses electronic energies from Quantum Monte Carlo (QMC) to sample the nuclear configuration space. QMC-MD (Sorella): uses forces from QMC to sample nuclear configuration space.

## DFT

in <u>Kohn-Sham DFT</u> the electronic wave function is a Slater determinant of single-electron orbitals obtained as the self-consistent solution which minimizes the Kohn-Sham functional

$$E_{\text{KS}}[n] = -\frac{1}{2} \sum_{i=1}^{N} |\vec{\nabla}\psi_{i}(\vec{r})|^{2} + \int d^{3}\vec{r}n(\vec{r})V_{\text{ext}}(\vec{r}) + E_{H}[n] + E_{nn} + E_{\text{xc}}[n],$$

$$E_{H}[n] = \frac{1}{2} \int d^{3}\vec{r}d^{3}\vec{r}' \frac{n(\vec{r})n(\vec{r}')}{|\vec{r} - \vec{r}'|},$$

$$E_{KS}[n] = \sum_{i=1}^{N} |\psi_{i}(\vec{r})|^{2}.$$
Exchange-correlation functional unknown (approximation)

Approximated exchange-correlation functionals:

- Local density LDA:
- <u>Generalized-Gradient (GGA)</u>:
- Non-local functionals: to correct self-interaction errors and improve exchange
- Dispersion functionals: to treat dispersion interactions (van-der-Waals)
- A (too) long list of different options ......

# DFT

#### Advantages:

- DFT is reasonably fast and accurate (often very accurate) in reproducing experimental data in many situations
- historically it was a major
   breakthrough in simulation to avoid
   effective potentials

• it is far more transferrable than the effective potential approach in particular in presence of changes of the chemical nature of the material (different hybridization)

• electronic dynamical properties can also be computed in the single-electron theory (optical spectra, transport properties....)

#### Limitations:

- DFT misses an internal check on the accuracy of the various functionals
- accuracy of the method is based on comparison with experiments or more accurate quantum methods on specific systems
- geometries are generally good (i.e. energy minima are ok) but band gaps are generally bad as well as energy barriers and excited states
- dispersion interactions are accounted in an approximated way only
- major problem at the metal-insulator transition
- the approximation is an extra variable to chose.

Until very recently the DFT paradigm for applications in dense hydrogen was GGA-PBE.

## Quantum Monte Carlo (QMC)

- In QMC an analytic form of the many-electron ground state wave function in terms of the electronic and nuclear coordinates is assumed and optimized based on the Variational Principle of QM (<u>Variational Monte Carlo</u>).
- Electronic correlation is explicitly put into the wave function and can be improved at will (with enough human effort!!).
- Further improvement can be obtained by projecting the optimized wave function onto the "exact" many-body ground state (<u>Projection Monte Carlo</u>).
- Projection QMC introduces the sign-problem for fermions: we adopt the fixed node approximation so that the method is variational with respect to the nodes.
- Dynamical properties (conductivity, etc) are not provided in QMC but can be obtained with <u>Correlation Functions QMC</u> (see Lin et al, PRL 103, 256401 (2009))

## CEIMC

CEIMC: Metropolis Monte Carlo for finite T ions. The BO energy in the Boltzmann distribution is obtained by a QMC calculation for ground state electrons.

- Ground state electrons:
  - Variation Monte Carlo (<u>VMC</u>) & Reptation Quantum Monte Carlo (RQMC)
  - Moving the electrons: <u>the bounce algorithm</u> for RQMC
  - <u>Energy difference methods</u>
  - Twist Average Boundary Conditions (<u>TABC</u>) within CEIMC to reduce electronic (single particle) finite size effects.
- Finite temperature ions: Noisy Monte Carlo <u>The Penalty Method</u>
- <u>Quantum Protons</u>: Path Integral Monte Carlo (PIMC) within CEIMC
- The computational cost of CEIMC (and QMC-MD) is quite higher than for BOMD (limited small systems ~100 protons).

# CEIMC: trial functions for hydrogen

- QMC for fermions exploits the fixed node approximation and the accuracy depends on the accuracy of the many body trial wave function.
- Slater-Jastrow form:  $\Psi_T(R|S) = \exp\left[-U(R|S)\right] \operatorname{Det}\left(\Sigma^{\uparrow}\right) \operatorname{Det}\left(\Sigma^{\downarrow}\right)$
- U(R|S) is a (two-body + three-body + ...) correlation factor (bosonic).
- $\Sigma$  is a Slater determinant of single electron orbitals
- The nodes are determined by the form of the orbitals only. They are the most important part of the trial function since the nodes are not optimized by projection.
- <u>Hydrogen trial function</u>
  - Single electron orbitals obtained from a DFT calculation (<u>with various approx</u>s) for each proton configuration.

 $\theta_k(\vec{x}_i, \sigma_i | S)$ 

- Analytical electron-electron and electron-proton backflow transformation (BF) to improve the nodes [Holzmann, Ceperley, Pierleoni, Esler PRE 68, 046707 (2003)].
- Analytical form for the single and 2-body Jastrow within RPA (Gaskell, 1967)
- Addition of numerical single, 2-body, 3-body jastrows and backflow terms (3-body ee is not-effective)
- <u>few variational parameters to be optimized</u> (on selected configurations).

## Hydrogen phase diagram



## Reentrant melting of phase I and crystalline molecular phases

from J. McMahon, M.A. Morales, C. Pierleoni and D.M. Ceperley, Rev Mod Phys (2012)



- GGA-PBE BOMD is accurate below ~200GPa
- PBE predicts band-gap closure beyond ~200GPa
- Experiments reported insulating state up to 350GPa (Loubeyre)
- Good agreement between theory (GGA-PBE) and experiments for melting line up to ~150GPa (large experimental error bars!)
- Inclusion of NQE is catastrophic !
- More advanced methods are needed to address the higher pressure region

GGA-PBE fails to reproduce the reflectivity from experiments across the metal-insulator transition (hugoniot of precompressed samples).



FIG. 10. (Color online) Reflectivity versus temperature along the principal Hugoniot. The black lines are the calculations of the reflectivity at 808 nm and 404 nm from Collins *et al.* (Ref. 9) and Holst *et al.* (Ref. 10). The yellow symbols and dashed line represent the experimental data at 532 nm and their fit. venerdì 1 agosto 2014



# CEIMC vs. BOMD-GGA(PBE)



FIG. 4: Comparison of radial distribution functions between BOMD (blue) and CEIMC (red).

Morales, Pierleoni Ceperley, PRE 2010

## • CEIMC:

- 54 protons with 64-96 twist angles.
- Proton quantum effects are negligible
   (T>2000K)

## • BOMD:

- 250 protons in PBC.
- GGA-PBE xc functional, Hamann type pseudo-potential ( $r_c=0.3$  a.u.)
- energy cutoff of 90-130Ry.

• Correction to the pressure for static confs. with a 4x4x4 grid of k-points and 300Ry of energy cut-off.

Free energy calculations with CCI from a reference state of known free energy.

## **CEIMC vs BOMD-GGA(PBE)**



FIG. 6: (Color Online) Comparison of pressure as a function of density computed with SCVH, BOMD and CEIMC at T=6000 K. In the lower panel, the pressure is divided by  $\rho^2$  to emphasize the differences.

#### Morales, Pierleoni Ceperley, PRE 2010

- Classical nuclei only.
- GGA-PBE works extremey well except at low density near molecular formation
- Need for better functionals to describe the dissociation process
- Important physical ingredient missing in PBE are the Van der Waals forces
- Also Nuclear Quantum effects are expected to be large at molecular dissociation

## Liquid-liquid phase transition (LLPT) & Nuclear Quantum effects (NQE)



GGA-PBE fails to reproduce the reflectivity from experiments across the metalinsulator transition but vdW-DF2 approximation works better.



Molecular stability is the important element, more than the kind of orbitals used for optical calculations.

two different experiments with different initial densities (Loubeyre 2004)

Morales et al. PRL 110, 065702 (2013)

## Liquid-Liquid Phase Transition (LLPT) and Nuclear Quantum Effects (NQE)



from g(r): intramolecular NQE are relevant intermolecular NQE are less relevant

## LLPT: structure and DC conductivity





PPT is elusive on the basis of the molecular fraction but is very clear on the basis of the DC conductivity (in the single-electron theory)

- PPT is a first order phase transition below  $T_c \sim 1000-1500 K$
- Molecular dissociation is driven by metalization function of pressure calculated using the Kubo-Greenwood
- $\bullet$  Above  $T_c$  the metalization and the molecular dissociation are continuous processes

FIG. 4: The DC electronic conductivity of hydrogen as a function of pressure calculated using the Kubo-Greenwood formula and DFT. The black, red and blue points correspond to averages over protonic configurations sampled from the BOMD, CEIMC and PIMD simulations, respectively.

Clay et al, Phys. Rev B 89, 184106 (2014).

K OT I



 sets of 100 DFT-generated (VdW-DF2) configurations for 54 quantum protons at 1000K.

• three densities across the dissociationmetallization region

$$\langle |\widetilde{\delta e^{DF}}| \rangle = \frac{1}{M} \sum_{i} |e^{DF}(i) - e^{DMC}(i) - \alpha^{DF}|$$

$$\langle |\delta P^{DF}| \rangle = \frac{1}{M} \sum_{i} |P^{DF}(i) - P^{DMC}(i)|$$

 energy dispersion is the smallest with vdW-DF functional

• pressure absolute difference is larger with vdW-DF's functionals

## CEIMC:T=600K isotherm, Np=54, raw data

T=600K isotherm 400  $\mathbf{X}$ 380 Classical quantum P=8 -quantum P=16 326Gpa 360 329GPa 265Gpa 270GPa 340 Pressure (Gpa) 320 X 300 280 260 240 220 1.05 1.1 1.15 1.2 1.25 1.3 1 density (gr/cc)

From VMC but <u>RQMC corrections</u> are small (~5GPa, see Liberatore et al Mol Phys 2012)

## T=600K: pressure relaxation of the systems with P=8



## T=600K: proton-proton correlation functions



Quality of the wf across LLPT (T=1200K, classical)



Quality of the wf across LLPT (T=900K,  $r_s$ =1.34, classical)



#### Finite size effects

Runs with N<sub>p</sub>=128 for few test cases

Single-body and two-body corrections from the small-k behaviour of Sqq(k) (Chiesa et al, Drummond et al.)



Energy vs 1/N, rs=1.44 T=1200K, E<sub>0</sub>=-0.531(1)



#### Finite size effects:T=1200K classical



- NQE decreases the transition pressure by ~ 80GPa at T=600K (CEIMC)
- PIMD with DFT-PBE predicts dissociation and melting of phase I not in agreement with experiments
- optical properties (reflectivity) are also much larger (100%) than in experiments
- Partially compensating effects:
  - PBE favor dissociation
  - the use of classical nuclei un-favor dissociation resulting in a reasonable agreement with experiments
- PBE+quantum nuclei (PI) must be avoided near molecular dissociation !
- vdW-DF2 predicts a much stronger molecular character.
- vdW-DF2 predicts a much larger dissociation pressure ( $\Delta P \gtrsim 150$ GPa)
- vdW-DF2 appears to somehow overbind molecules (vs CEIMC)

# LLPT and melting: details

- CEIMC: (BOPIMC)
  - 54 protons with 64 twists (4x4x4)
  - Slater-Jastrow wfs with DFT orbitals + BF
  - VMC with RQMC corrections (small ~5Gpa, yet to be included)
  - Size corrections on the transition line are also small (~10Gpa, to be included)
  - PIMC with 8 slices at 600K (smart MC normal-mode sampling)
- BOMD: (VASP & QuantumESPRESSO)
  - PBE xc functional with a Troullier-Martins non-loc pseudopot. (rc=0.5a.u.)
  - PAW with VASP (HSE)
  - energy cutoff of 90 Ry
  - 432 protons at the Γ point for PPT (strong size effects in DFT!!!)
  - 432 protons in the liquid and 360 protons in the solid for the melting line calculation
- PIMD: imaginary time step  $\tau = (8000 \text{ K})^{-1}$  providing a 8 slice paths at T=1000K

Melting line determination via calculation of solid and liquid free energies. (classical nuclei with PBE)

Morales, Pierleoni, Schwegler, Ceperley PNAS 108, 12799 (2010) Morales, McMahon, Pierleoni, Ceperley PRL 110, 065702 (2013) Pierleoni, Morales, Holzmann, Ceperley, to be published (2014)

# Comparision with QMC-MD method

Mazzola, Yonuki, Sorella, Nature Comm (2013)



quality of the wave function is an obvious reasons for the discrepancy but we need a deeper investigation.

#### energy comparison on single confs for Np=54 at the $\Gamma$ point

r <sub>s</sub>	$E_{vmc}$	Erqmc	J=2s, det=2s	J=2s. det=6s5p1d	Δ	character
1,24	-0.52564(2)	-0.52638(3)	-0,5143	-0,5230	16 mH/at	atomic
1,44	-0.55605(2)	-0.5572(1)	-0,5412	-0,5542	15mH/at	molec.

# Conclusions

- BOMD based on GGA-PBE is accurate in a large region of the phase space
- GGA-PBE breaks down near metallization and molecular dissociation in hydrogen.
- Nuclear quantum effects are large at the molecular dissociation and for T<1000K and must be considered properly in a quantitative theory.</li>
- This requires to use different approximation in DFT.
- Which functional suits best is still an open question and useful benckmark can be obtained by QMC.
- Hydrogen metallization and dissociation in the liquid phase occurs through a weakly first order phase transition.
- The precise location of the transition line and of the critical point depend on the level of theory, the CEIMC's ones being intermediate between PBE and vdW-DF2.
- We are waiting for experimental validations.
- Major problem to be investigated: disagreement with QMC-MD

# Perspectives

• Hydrogen metallization at lower temperature is still elusive mainly because of the missing information on the crystalline structure of the molecular system.

- NQE are crucial at such low temperature as shown by CEIMC.
- CEIMC can provide useful information in this region and benchmark DFT approximations at finite nuclear temperature.
- Apply CEIMC in studying the stability of the "many" candidates crystalline structures for phase III and phase IV (in progress)
- Melting of phase I and phase IV (in progress)