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

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OUTLINE

- Motivation
- Hydrogen: the paradigmatic system
- Electronic structure methods: DFT vs QMC
- Ab-initio simulation methods: the CEIMC
- Trial wave function for hydrogen
- Liquid-liquid phase transition in hydrogen
- Crystalline molecular hydrogen: CEIMC vs PIMD predictions
- Conclusions & perspectives

Motivations

- *To contribute to develop First-Principles simulation methods to a predictive level*: standard first principle simulation methods are mostly based on Density Functional Theory, in practice a *mean-field theory*, with uncontrolled approximations. Our aim is to develop simulation methods where all approximations can be controlled and improved, hence switching from non-predictive to ***predictive methods***.

- *To study matter at extreme conditions beyond present experimental capabilities*: those methods will be able to provide reliable predictions even in absence of experimental results. Experiments at extreme conditions are difficult and extremely expensive, they often provide only partial information and different methods are often in disagreement. Predictive First Principle theories will greatly help our understanding and will reduce the cost of these activities.

- *Light elements like Hydrogen, Helium, Lithium are very fundamental:* their study under extreme conditions requires considering explicitly the ***electronic correlation,*** a fully ***quantum treatment of nuclei***

Hydrogen: the paradigmatic system

- 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 the equation of state of hydrogen, helium and their mixtures.

- Hydrogen is relevant for energy applications: nuclear fusion, etc.

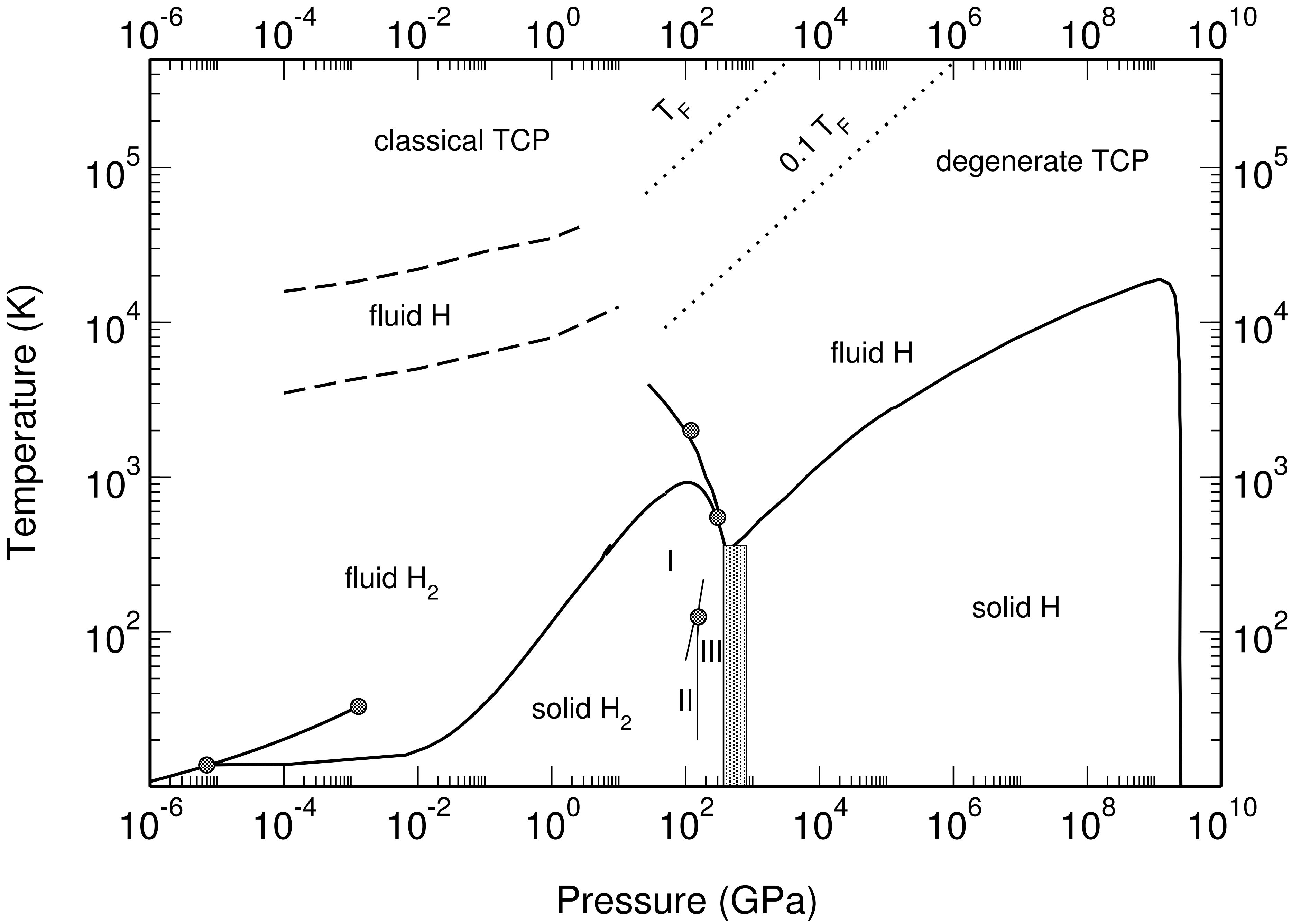
- The hydrogen atom and and the hydrogen molecule have been the prototype models in developing Quantum Mechanics. Hydrogen is the ***ideal playground to develop new theoretical approaches and methods***.

- Being the simplest element, it is desirable to be able to predict its properties from first-principle (the Hamiltonian is known and simple) from a theoretical perspective.

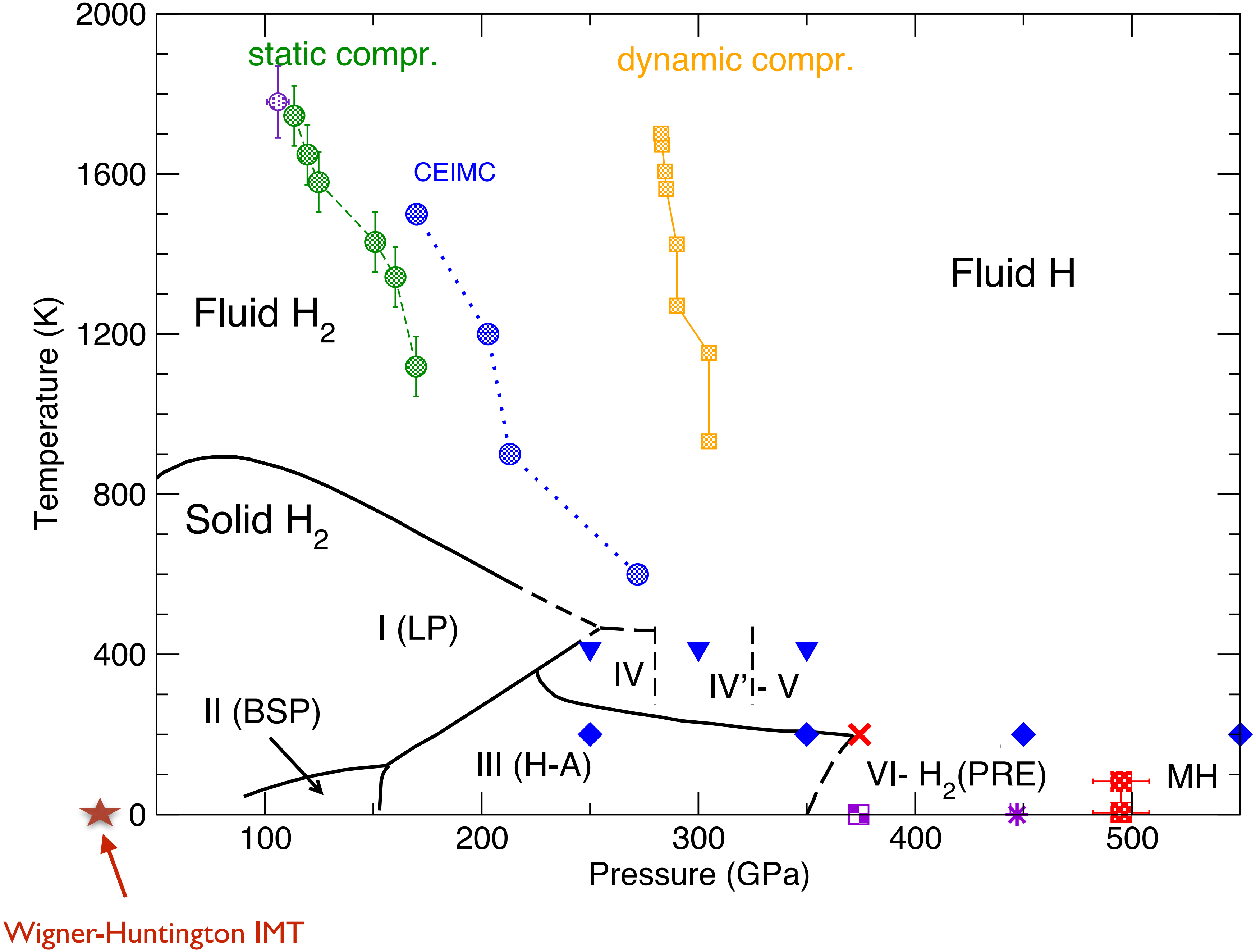
- Despite its simplicity Hydrogen under pressure presents a reach and difficult physics.

Hydrogen phase diagram

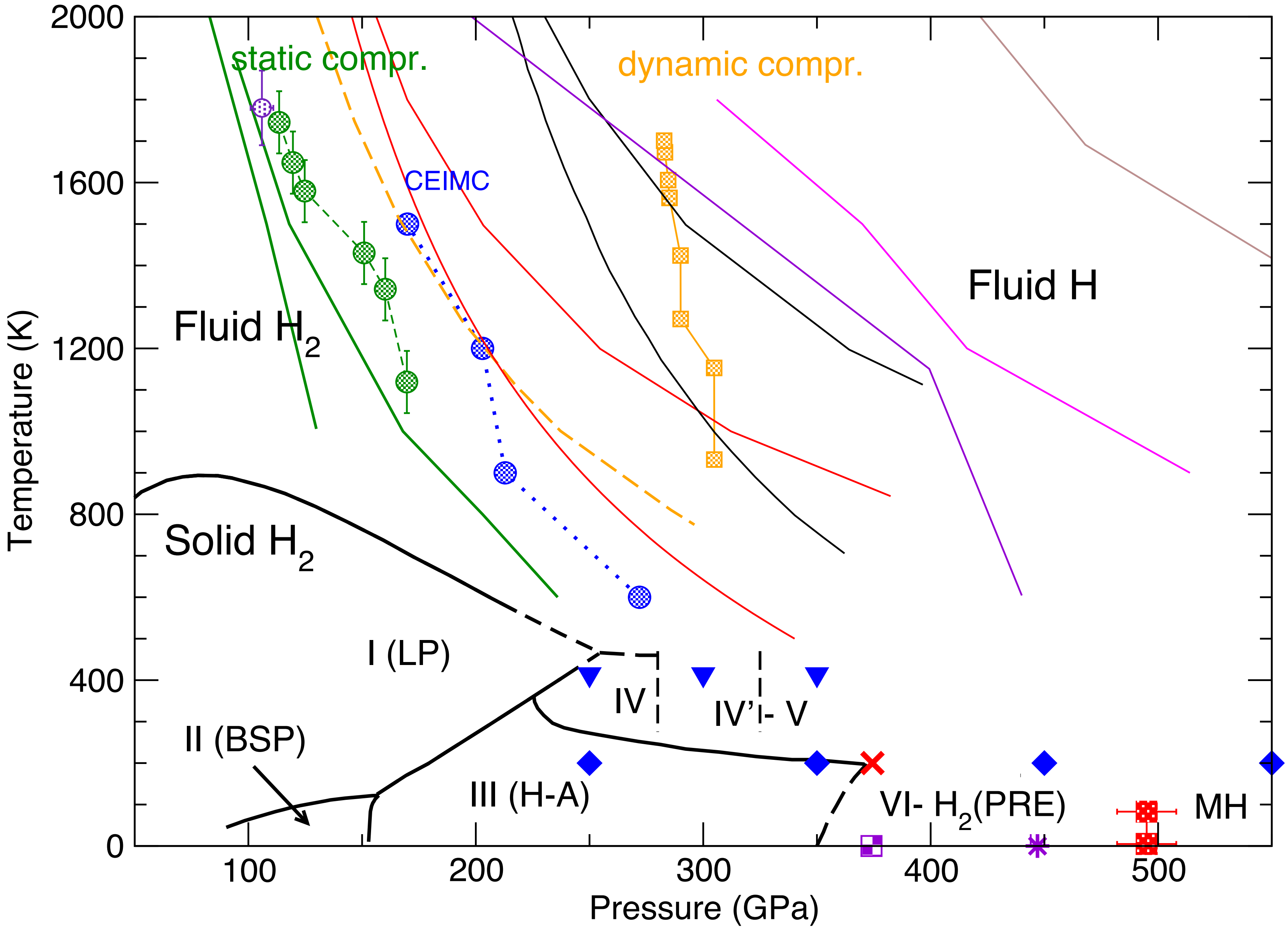
from J. McMahon, M.A. Morales, C. Pierleoni and D.M. Ceperley, Rev Mod Phys (2012)



Hydrogen phase diagram



Pierleoni, Morales, Rillo, Holzmann, Ceperley PNAS 113, 4953 (2016)



Pierleoni, Morales, Rillo, Holzmann, Ceperley PNAS 113, 4953 (2016)

First-principles theoretical methods

- first-principle methods based on ***Quantum Mechanics*** and ***Statistical Mechanics***.
- they treat ***nuclei and electrons explicitly*** and are unique methods to study systems in a large variety of chemical and physical states
- they assume the ***non-relativistic Hamiltonian*** of the system of nuclei and electrons in a volume Ω at temperature T *(in condensed phase)*
- Under rather general conditions, the energy scales for nuclei and electrons are widely separated: ***adiabatic approximation (Born-Oppenheimer)***

$$\begin{aligned}\hat{H} &= \hat{T}_n + \hat{H}_{el} = \hat{T}_n + \hat{T}_e + \hat{V}, \\ \hat{T}_n &= -\sum_{I=1}^{N_n} \lambda_I \hat{\nabla}_I^2, \quad \hat{T}_e = -\lambda_e \sum_{i=1}^{N_e} \hat{\nabla}_i^2, \\ \hat{V} &= \sum_{I<J} \frac{z_I z_J}{|\vec{R}_I - \vec{R}_J|} + \sum_{i<j} \frac{1}{|\vec{r}_i - \vec{r}_j|} - \sum_{i,I} \frac{z_I}{|\vec{r}_i - \vec{R}_I|},\end{aligned}$$

kinetic energies

Coulomb law

$$\lambda_e = 1/2, \quad \lambda_I = 1/(2M_I),$$

First principles

McMahon, Morales, Pierleoni, Ceperley, Rev. Mod. Phys. 84, 1607 (2012)

Electrons: solve the electronic problem at given nuclear positions

$$\hat{H}_{el} = \hat{K}_{el} + \hat{V}$$

ground state energy

nuclear coordinates ($3N_n$)

$$\boxed{\hat{H}_{el}\Phi_0(r|R) = E_0(R)\Phi_0(r|R)}$$

Schroedinger equation (SE)

electronic coordinates ($3N_e$)

ground state wave function

Density Functional Theory: maps the interacting electrons problem onto a single electron problem in a self-consistent effective potential.

Solve the single electron SE as an ***eigenvalue problem in 3 dimensions***.

Mean field solution, introduces ***uncontrolled approximations***.

Quantum Monte Carlo: assumes an explicit form of the many-electrons wave function based on physical insight and exploits the *Variational Principle* to control the accuracy

$$E_0(R) \leq E_T(R) \equiv \frac{\int dr\ \Psi_T^*(r|R)\ \hat{H}_{el}\Psi_T(r|R)}{\int\ dr\ |\Psi_T(r|R)|^2}$$

trial wave function

$$0 \leq \sigma_T^2(R) \equiv \frac{\int\ dr\ \Psi_T^*(r|R)\ \left[\hat{H}_{el} - E_T(R)\right]^2\ \Psi_T(r|R)}{\int\ dr\ |\Psi_T(r|R)|^2}$$

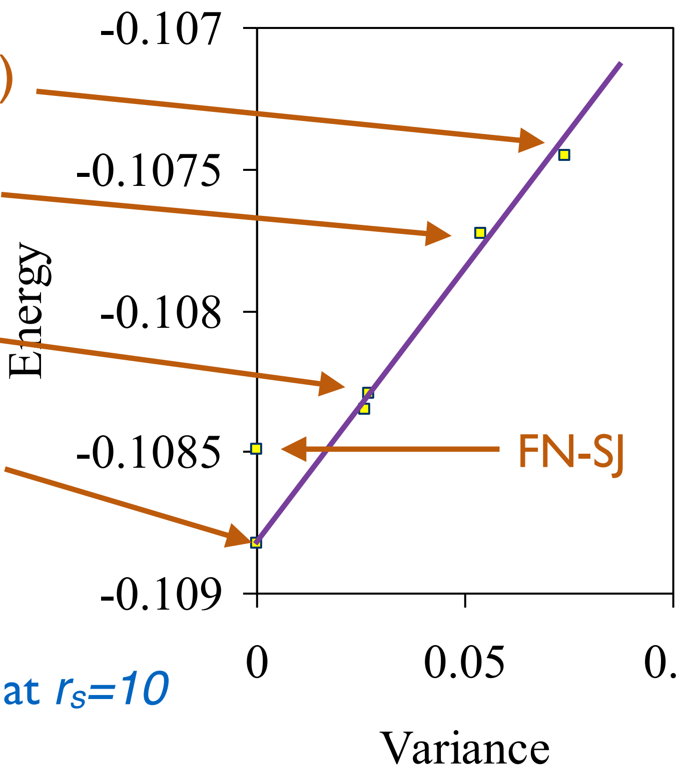
$\Psi_T(r|R)$ depends explicitly on some ***free parameters to be optimized*** using the variational principle: the lower the energy and the variance the better the quality of the solution.

The variational principle provides an ***internal consistency check*** when comparing various trial functions.

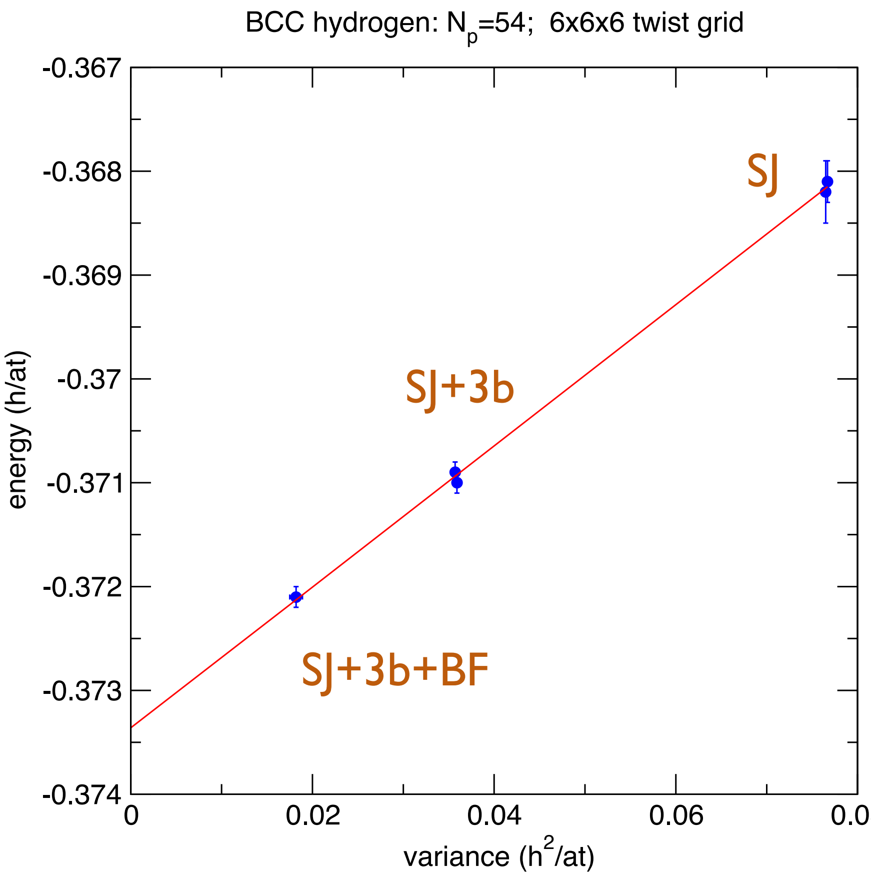
Imaginary time projection automatically optimizes but requires an approximation for fermions: the fixed node approximation but the method remain variational

$$\lim_{t\to\infty} e^{-t\hat{H}} \; |\Psi_T\rangle \propto |\Phi_0\rangle$$

- Slater-Jastrow (SJ)
- three-body (3b)
- backflow (BF)
- fixed-node (FN)



3D electron gas at r_s=10



DFT

Advantages:

- DFT is reasonably fast and accurate.
- it is far more transferrable than the effective potential approach.
- electronic dynamical properties can also be computed in the single-electron theory (optical spectra, transport properties….) (not fully justified).

Limitations:

- DFT misses an internal check on the accuracy of the various approximations
- assessment of accuracy based on comparison with experiments or more accurate theories (like QMC).
- dispersion interactions, band gaps and excited states are generally bad.
- the approximation is an extra variable to choose.

QMC

Advantages:

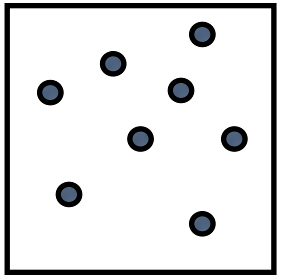
- electron correlation is explicitly put in the wave function.
- the accuracy can be assessed by the Variational Principle (internal check of the theory).
- efficient methods to compute properties other than the energy are available

Limitations:

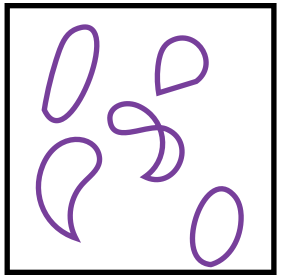
- projection introduces the fixed node approximation. But the method is still variational.
- it needs larger computer resources.
- electronic dynamics is more difficult but, to some extend, can be dealt with by CFQMC (see Li et al, PRL 2010)
- the development of community codes is much behind DFT, so the use of QMC much less spread.

Nuclear sampling: use the electronic energy (or forces) to sample the nuclear configurational space at physical temperature (Boltzmann):

classical nuclei are point particles (P=1)



quantum nuclei are paths in configuration space
(P>1, closed for diagonal observables)



$$\rho_n(R) \sim e^{-[K_n+E_T(R)]/k_B T} \qquad R \in \mathbb{R}^{3N_n P} \longrightarrow$$

Molecular Dynamics
or
Monte Carlo +
importance sampling

BOMD (CPMD): uses DFT forces and MD to sample nuclear configuration space

CEIMC: uses QMC energy and Metropolis MC for nuclear sampling
QMCMD: uses QMC forces and LD for nuclear sampling

Coupled Electron-Ion Monte Carlo (CEIMC):

an ab-initio simulation method with QMC accuracy

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 (VMC) & Reptation Quantum Monte Carlo (RQMC)
  - Twist Average Boundary Conditions (TABC) within CEIMC to reduce electronic (single particle) finite size effects.
  - Efficient energy difference method
  - Efficient RQMC algorithm: The bounce algorithm
- Finite temperature ions: Noisy Monte Carlo The Penalty Method
- Quantum Protons: Path Integral Monte Carlo (PIMC) within CEIMC
- Moving the nuclei: two level sampling

- The computational cost of CEIMC in the present implementation is quite higher than for BOMD (limited to small systems ~100 protons), but the scaling is the same ($\sim N^3$).

- *HPC Tier-0 systems are now available for this generation of calculations!*

Moving the ions

- In Metropolis MC we generate a Markov chain of ionic states S distributed according to Boltzmann

$$P(S) \propto \exp(-\beta E_{BO}(S))$$

$E_{BO}(S) =$ Born-Oppenheimer energy for the configuration S.

- Given an initial state S we propose a trial state S' with probability

$$T(S \to S') = T(S' \to S)$$

and we accept the move with probability

$$A(S \to S') = min\left[1, \exp\left\{-\beta[E_{BO}(S') - E_{BO}(S)]\right\}\right]$$

- After a finite number of moves the Markov chain is distributed with Boltzmann (if ergodicity holds).

- But $E_{BO}(S)$ from QMC is noisy $\Rightarrow$ use the penalty method

JOURNAL OF CHEMICAL PHYSICS VOLUME 110, NUMBER 20 22 MAY 1999

The penalty method for random walks with uncertain energies

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The Penalty Method

- Assume mean value and variance of the energy difference over the noise distribution $P(\delta|S,S')$ exist

$$\begin{aligned}\beta[E_{BO}(S') - E_{BO}(S)] &= <\delta(S,S')>= \Delta(S,S') \\ <(\delta-\Delta)^2> &= \sigma^2(S,S')\end{aligned}$$

We want to find the new acceptance probability $a(S \rightarrow S')$ such that we satisfy detailed balance on average:

$$T(S \rightarrow S') < a(S \rightarrow S') >= T(S' \rightarrow S) < a(S' \rightarrow S) > \exp[-\beta\Delta(S,S')]$$

$$< a(S \rightarrow S') >= \int_{-\infty}^{\infty} d\delta P(\delta|S,S') a(\delta|S,S')$$

Under general assumption one can show that

$$a(\delta|\sigma) = min\left[1, \exp\left(-\delta - \frac{\sigma^2}{2}\right)\right]$$

- **The noise always causes extra rejection !**

- In few simple examples the optimal noise level was found to be $s^2 = \sigma^2/n \approx 1$.
  In CEIMC other constraints imposes the noise level but as a rule of thumb we always try to stay around 1.
- $\sigma^2 \sim T^{-2}$: lowering the temperature requires smaller noise level, i.e. longer electronic runs

Quantum Protons in CEIMC

PIMC: we need to consider the thermal density matrix of the nuclei

$$\hat{\rho}(\beta) = e^{-\beta\mathcal{H}}$$

β is the physical inverse temperature

- for diagonal observables we map protons onto ring polymers
- we limit to distinguishable particles so far, but nuclear Bose or Fermi statistics could be considered.
- to minimize the time step error in the Trotter break-up, we introduce pairwise effective potentials between nuclei:

$$\hat{\rho}(\beta) = e^{-\beta\mathcal{H}} = e^{-\beta[\mathcal{K}_p+\mathcal{V}_{eff}+(\mathcal{H}_{el}-\mathcal{V}_{eff})]}$$

$$\rho(S,S'|\tau) \approx \langle S|e^{-\tau[\mathcal{K}_p+\mathcal{V}_{eff}]}|S'\rangle e^{-\frac{\tau}{2}\left[(E_{BO}-V_{eff})(S)+(E_{BO}-V_{eff})(S')\right]}$$

- we use the pair action approximation for the effective many body density matrix

$$\langle S|e^{-\tau[\mathcal{K}_p+\mathcal{V}_{eff}]}|S'\rangle \approx \prod_{ij}\rho^{(2)}(r_i,r_j;r'_i,r'_j|\tau) = \rho_0(S,S'|\tau)e^{-\sum_{ij}u(r_i,r_j;r'_i,r'_j|\tau)}$$

$$u = -log[\rho^{(2)}/\rho_0^{(2)}]$$

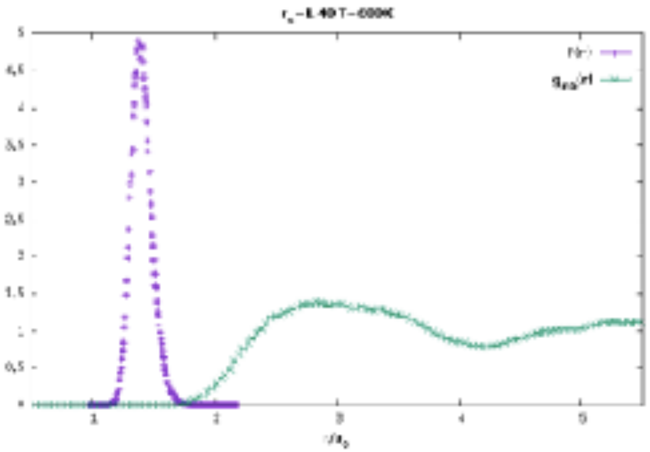
D.M. Ceperley, Rev.Mod.Phys. (1995)

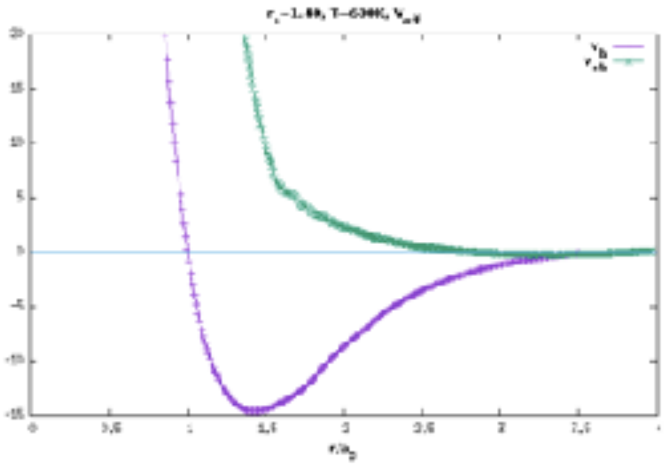
Quantum Protons in CEIMC

- for molecular state we use bonding and non-bonding effective potentials
- at molecular dissociation only non-bonding one.

$$V_{eff}(S) = \frac{1}{2}\sum_{i\neq j} v_{nb}(r_{ij}) + \sum_I v_b(d_I)$$

Potentials obtained at reference thermodynamic states by Boltzmann Inversion





Pair action obtained by the matrix squaring method, stored in numerical tables and used during the simulation.

$$\rho^{(2)}(r,r'|2\tau) = \int dr" \; \rho^{(2)}(r,r"|\tau)\rho^{(2)}(r",r'|\tau)$$

The form of the potential only affects the convergence with the number of proton slices, not the accuracy of the calculation!!!

8 slices at T=600K and at molecular dissociation are enough for convergence.

Sampling the nuclear paths in CEIMC

- we want to displace all protons simultaneously because any nuclear move changes the wave function.
- we employ a 2-level Metropolis scheme to pre-screen proposed configurations before performing the VMC calculation.
- Splitting of the Hamiltonian:

$$\hat{H}_p = \hat{K}_p + \hat{E}_{qmc} = [\hat{K}_p + \hat{V}_{eff}] + [\hat{E}_{dft} - \hat{V}_{eff}] + [\hat{E}_{qmc} - \hat{E}_{dft}]$$

- pair action
- primitive approximation 1st Metropolis test
- primitive approximation 2nd Metropolis test

Propose the new configuration by a drifted random walk

$$\vec{S}' = \vec{S} + h\vec{F} + \vec{\xi} \qquad \vec{F} = \vec{F}_{kin} + \vec{F}_u + \vec{F}_{dft} - \vec{F}_{eff} \qquad < \xi_i \xi_j >= 2hk_B T \delta_{ij}$$

$\vec{F}_{kin}$ Force from kinetic action (spring term)

$\vec{F}_u = -\nabla U \qquad U = \sum_{i<j} u_{ij}$ pair action

$$\vec{F}_{eff} = -\nabla V_{eff}$$

Sampling the nuclear paths in CEIMC

1st Metropolis test (noiseless)

$$A_1(\vec{S} \to \vec{S}') = \min\left[1, q_1(\vec{S} \to \vec{S}')\right] \qquad q_1(\vec{S} \to \vec{S}') = \frac{G(\vec{S} \to \vec{S}')\rho_{eff}(S'|\beta)e^{-\beta\left[E_{dft}(S')-V_{eff}(S')\right]}}{G(\vec{S}' \to \vec{S})\rho_{eff}(S|\beta)e^{-\beta[E_{dft}(S)-V_{eff}(S)]}}$$

$$G(\vec{S} \to \vec{S}') \propto \exp\left[-\frac{\left(\vec{S}' - \vec{S} - h\vec{F}(S)\right)^2}{2\sigma^2}\right]$$

2nd Metropolis test with penalty (only if the first step is passed)

$$A_2(\vec{S} \to \vec{S}') = min\left[1, q_2(\vec{S} \to \vec{S}')\right] \qquad q_2(\vec{S} \to \vec{S}') = \frac{e^{-\beta\left[E_{qmc}(S')-E_{dft}(S')\right]}}{e^{-\beta[E_{qmc}(S)-E_{dft}(S)]}} \quad e^{-\beta^2\chi^2(S,S')}$$

This scheme is implemented in the normal mode basis of the path (kinetic action) to decouple the amplitude of the centroid move (q=0) from the amplitude of the internal modes (q>0) moves and to adjust them according to their order for an optimal sampling (Cao-Berne, Tuckerman).

With this scheme we can sample systems of 100 protons with paths of 32 beads with no major problems.

in CEIMC quantum nuclei are not more expensive than classical nuclei !!

In the penalty method we need to run QMC calculations to reduce the noise on the energy difference to an acceptable level. We do this by running many independent QMC calculations with different twisted boundary conditions to reduce the size effects.

Suppose we run classical ions with a given noise level $(\beta\sigma_{cl})^2$.

Consider now representing the quantum ions by *P* slices. To have a comparable extra-rejection we need a noise level per slice given by

$(\beta\sigma_{cl})^2 \approx P(\beta\sigma_q/P)^2$ which provides: $\sigma_q^2 \approx \sigma_{cl}^2/P$.

We can allow the noise P times larger on each slice, i.e. consider P times less independent estimates of the energy difference per slice.
However we need to run P different calculations one for each time slice, so that the amount of computing for a fixed global noise level is the same as for classical ions.

With TABC, we replicate all twists for each time slices: optimal for parallel computers.

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: $\Psi_T(R|S) = \exp\left[-U(R|S)\right] \mathrm{Det}\left(\Sigma^{\uparrow}\right) \mathrm{Det}\left(\Sigma^{\downarrow}\right)$
- U(R|S) is a (two-body + three-body + ...) correlation factor (bosonic).
- Σ is a Slater determinant of single electron orbitals $\theta_k(\vec{x}_i, \sigma_i|S)$
- 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.
- Hydrogen trial function
  - Single electron orbitals obtained from a DFT calculation (with various approxs) for each proton configuration.
  - 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 1-body, 2-body, 3-body Jastrows and backflow terms (3-body e-e is not-effective)
  - few variational parameters to be optimized (on selected configurations only).

13 variational parameters only ! effect of optimization: ~1 mH/at on the energy
~40% on the variance

Backflow-3Body trial function

Holzmann et al, Phys. Rev. E 68, 046707 (2003)
Pierleoni et al, Comp. Phys. Comm. 179, 89–97 (2008).

$$\Psi_T(\vec{R}|\vec{S}) = det[\theta_k(\vec{x}_i|\vec{S})] \exp\left(-\sum_{i=1}^{N_e}\left[\frac{1}{2}\sum_{j\neq i}^{N_e}\tilde{u}_{ee}(r_{ij}) - \sum_{I=1}^{N_p}\tilde{u}_{ep}(|r_i - S_I|) - \frac{1}{2}|\vec{G}_i|^2\right]\right)$$

2-body

$$\tilde{u}_\alpha(r) = u_\alpha^{RPA}(r) + \lambda_{2b}^\alpha \exp[-(r/w_{2b}^\alpha)^2] \qquad \alpha = (ee, ep)$$

backflow

$$\vec{x}_i = \vec{r}_i + \sum_{j\neq i}^{N_e}\left[y_{ee}^{RPA}(r_{ij}) + \eta_{ee}(r_{ij})(\vec{r}_i - \vec{r}_j)\right]$$

$$+ \sum_{I=1}^{N_P}\left[y_{ep}^{RPA}(|r_i - S_I|) + \eta_{ep}(|r_i - S_I|)(\vec{r}_i - \vec{S}_I)\right]$$

$$\eta_\alpha(r) = \lambda_b^\alpha \exp[-((r - r_b^\alpha)/w_b^\alpha)^2] \qquad \alpha = (ee, ep)$$

Backflow-3Body trial function

Holzmann et al, Phys. Rev. E 68, 046707 (2003)
Pierleoni et al, Comp. Phys. Comm. 179, 89–97 (2008).

3-body

$$\vec{G}_i = \sum_{j\neq i}^{N_e} \left[\xi_{ee}^{RPA}(r_{ij}) + \xi_{ee}(r_{ij})\right](\vec{r}_i - \vec{r}_j) + \sum_{I=1}^{N_p} \left[\xi_{ep}^{RPA}(|r_i - S_I|) + \xi_{ep}(|r_i - S_I|)\right](\vec{r}_i - \vec{S}_I)$$

$$\xi_\alpha(r) = \lambda_{3b}^{\alpha} \exp[-((r - r_{3b}^{\alpha})/w_{3b}^{\alpha})^2] \qquad \alpha = (ee, ep)$$

Backflow-3Body trial function

Holzmann et al, Phys. Rev. E 68, 046707 (2003)
Pierleoni et al, Comp. Phys. Comm. 179, 89–97 (2008).

3-body

$$\vec{G}_i = \sum_{j\neq i}^{N_e} \xcancel{\left[\xi_{ee}^{RPA}(r_{ij}) + \xi_{ee}(r_{ij})\right]} (\vec{r}_i - \vec{r}_j)$$

$$+ \sum_{I=1}^{N_p} \left[\xi_{ep}^{RPA}(|r_i - S_I|) + \xi_{ep}(|r_i - S_I|)\right] (\vec{r}_i - \vec{S}_I)$$

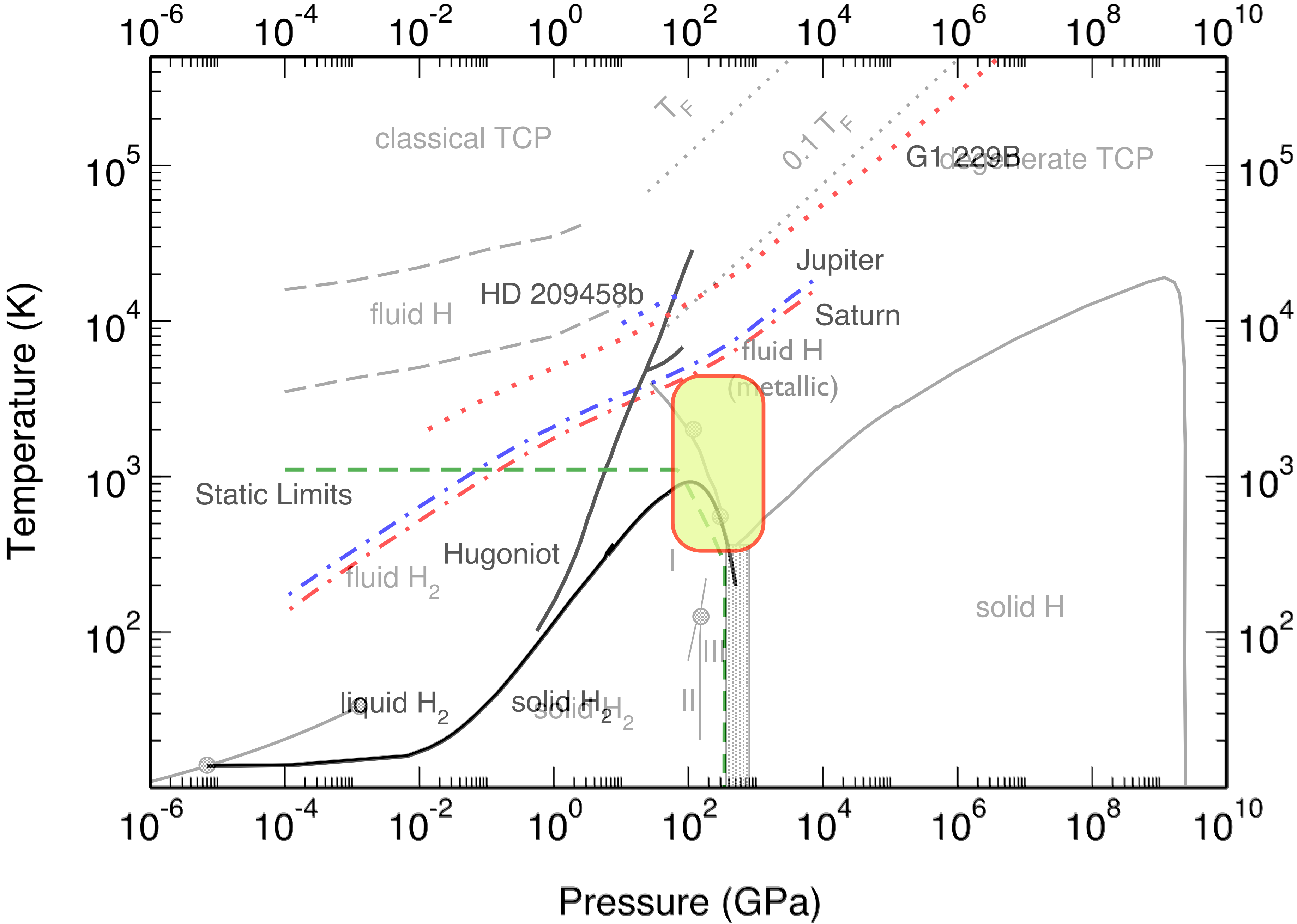
$$\xi_\alpha(r) = \lambda_{3b}^\alpha \exp[-((r - r_{3b}^\alpha)/w_{3b}^\alpha)^2] \qquad \alpha = (ee, ep)$$

13 variational parameters only !
effect of optimization: ~1 mH/at on the energy
~40% on the variance

Optimizing each newly proposed nuclear configuration prior its acceptance is a major bottleneck for the efficiency of the method

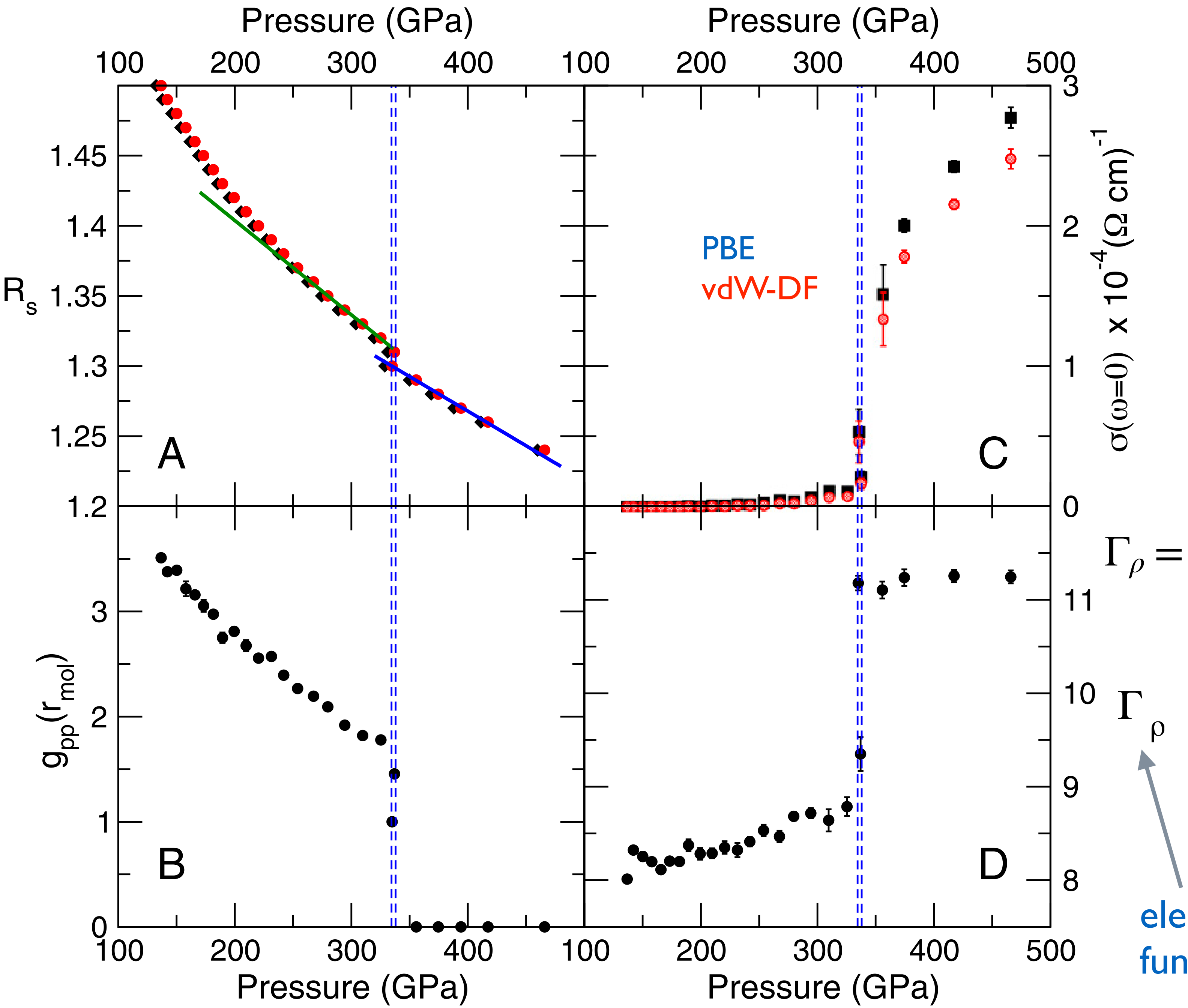
Liquid-liquid phase transition (LLPT)

Morales, Pierleoni, Schwegler, Ceperley PNAS 108, 12799 (2010)
Morales, McMahon, Pierleoni, Ceperley PRL 110, 065702 (2013)
Pierleoni, Morales, Rillo, Holzmann, Ceperley PNAS 113, 4953 (2016)



CEIMC: T=600K classical

Pierleoni, Morales, Rillo, Holzmann, Ceperley PNAS 113, 4953 (2016)

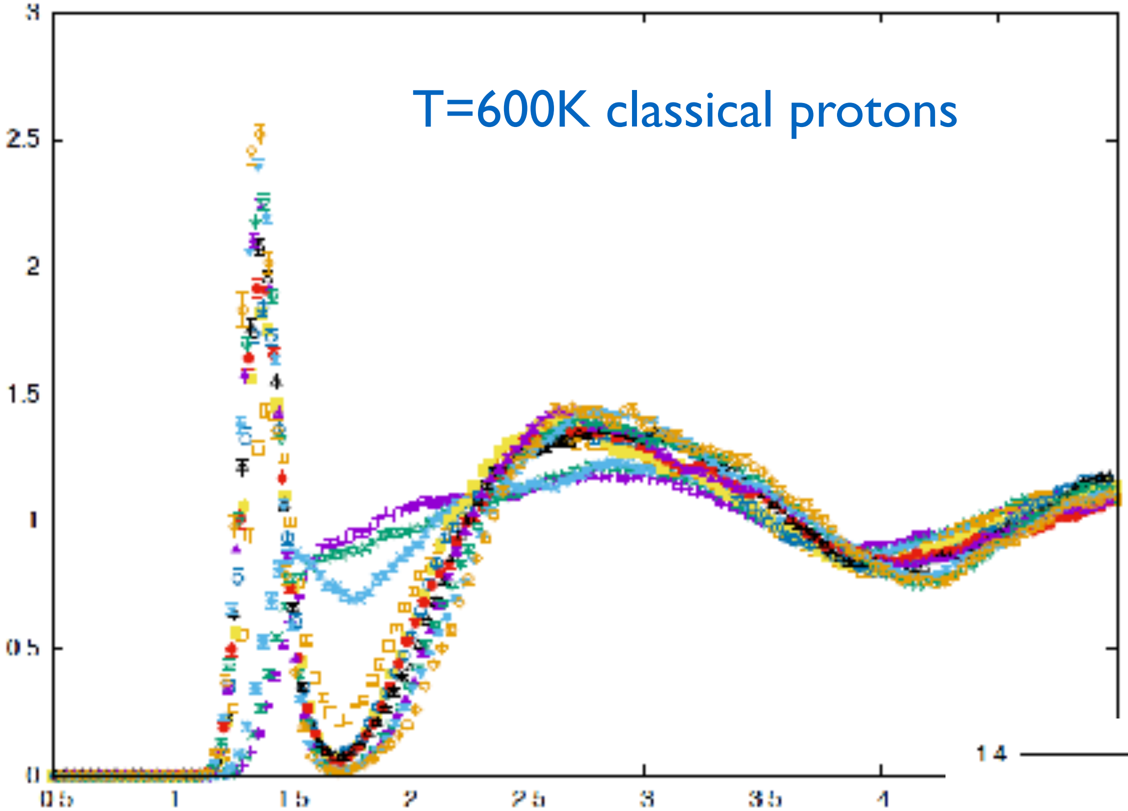


- absence of hysteresis allows to detect the transition pressure directly
- Electrical conductivity from Kubo-Greenwood with DFT on nuclear configurations from CEIMC

$$\Gamma_\rho = \frac{1}{N}\int_V \frac{d\mathbf{r}d\mathbf{r}'}{V}\left|\rho^{(1)}(\mathbf{r},\mathbf{r}')\right|,$$

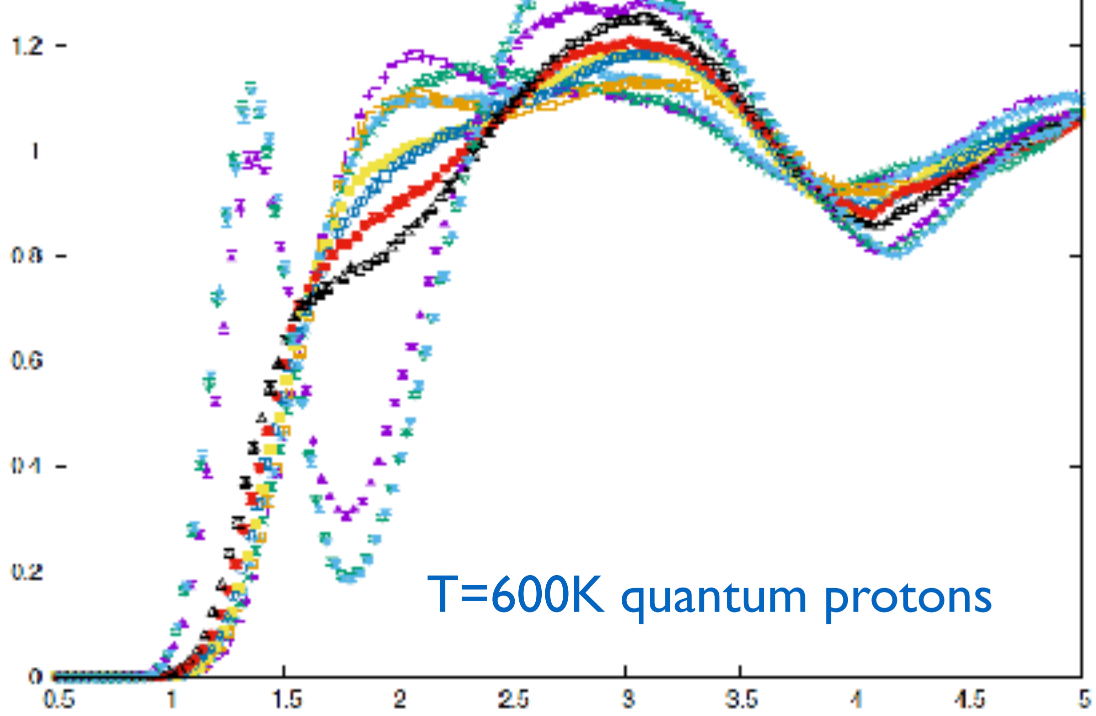
single electron density matrix

electron localization function


T=600K classical protons

molecular dissociation is abrupt
at variance with DFT predictions

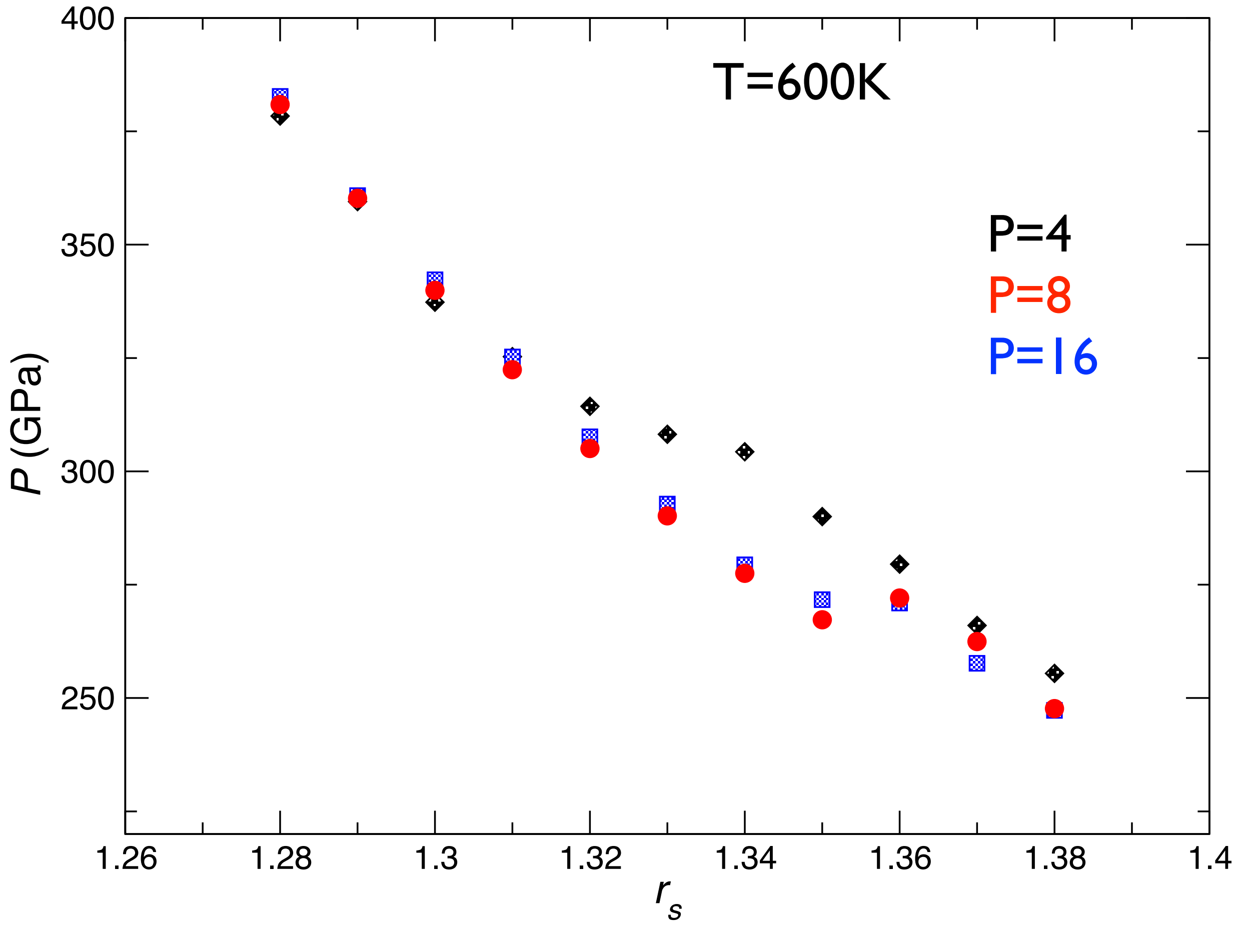
Δr_s=0.01
$\Delta n \sim 0.001\ a_0^{-3}$


T=600K quantum protons

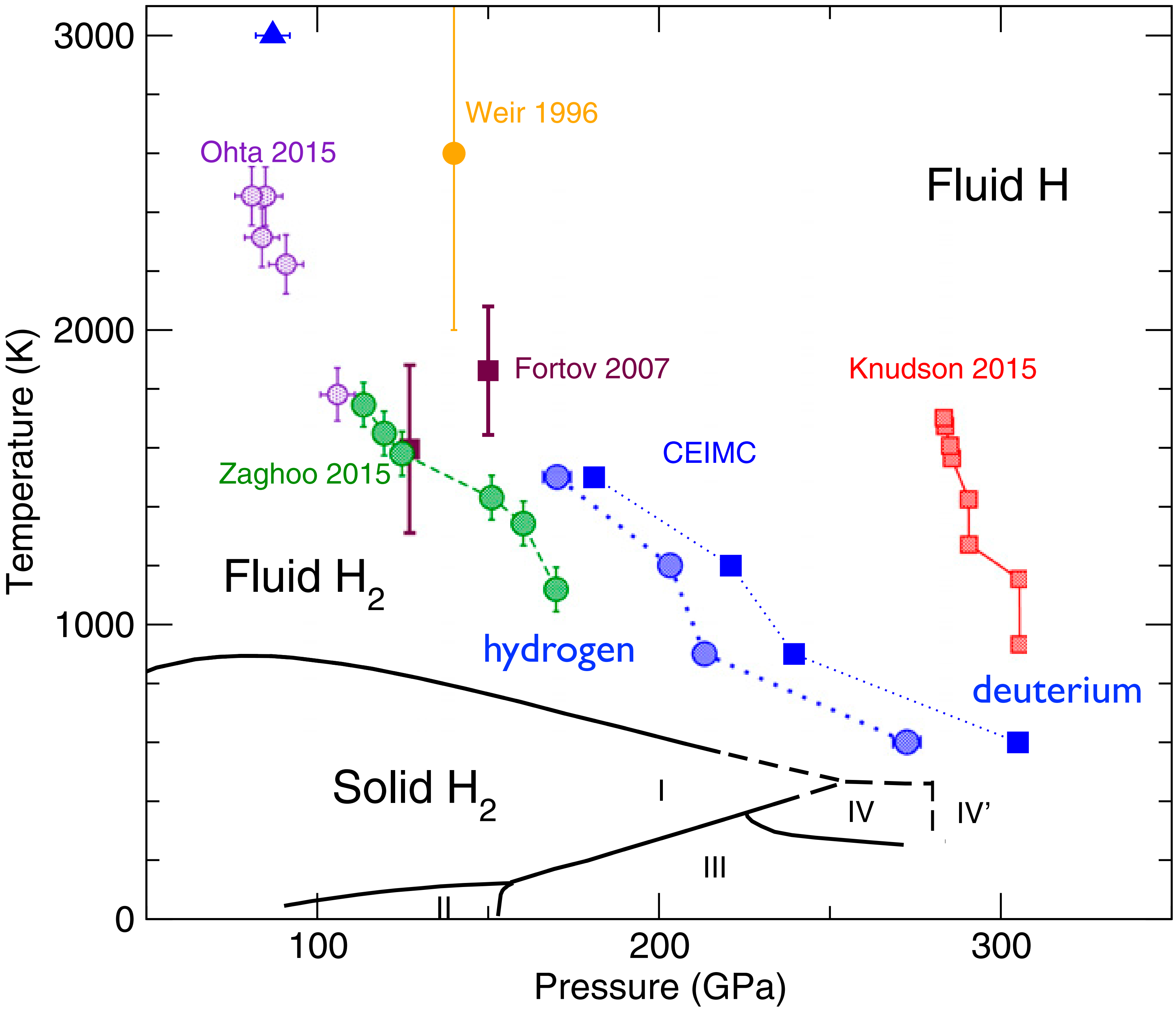
Convergence of the nuclear PI : we assume an effective pair interaction V_e and use pair action

$$\begin{aligned}\rho_P(S,S'|\tau_p) &= \langle\, S|e^{-\tau_p[\hat{H}_e+(\hat{E}_{BO}-\hat{V}_e)]}|S'\,\rangle \\ &\approx \langle\, S|e^{-\tau_p\hat{H}_e}|S'\,\rangle\; e^{-\frac{\tau_p}{2}[E_{BO}(S)-V_e(S)]+[E_{BO}(S')-V_e(S')]} \qquad (92)\end{aligned}$$

$$\langle S|e^{-\tau_p\hat{H}_e}|S'\rangle \approx \prod_{ij}^{N_p}\langle s_i,s_j|\hat{\rho}_e^{(2)}(\tau_p)|s_i',s_j'\rangle = \rho_0(S,S'|\tau_p)e^{-\sum_{ij}u_e(\boldsymbol{s}_{ij},\boldsymbol{s}_{ij}'|\tau_p)}$$

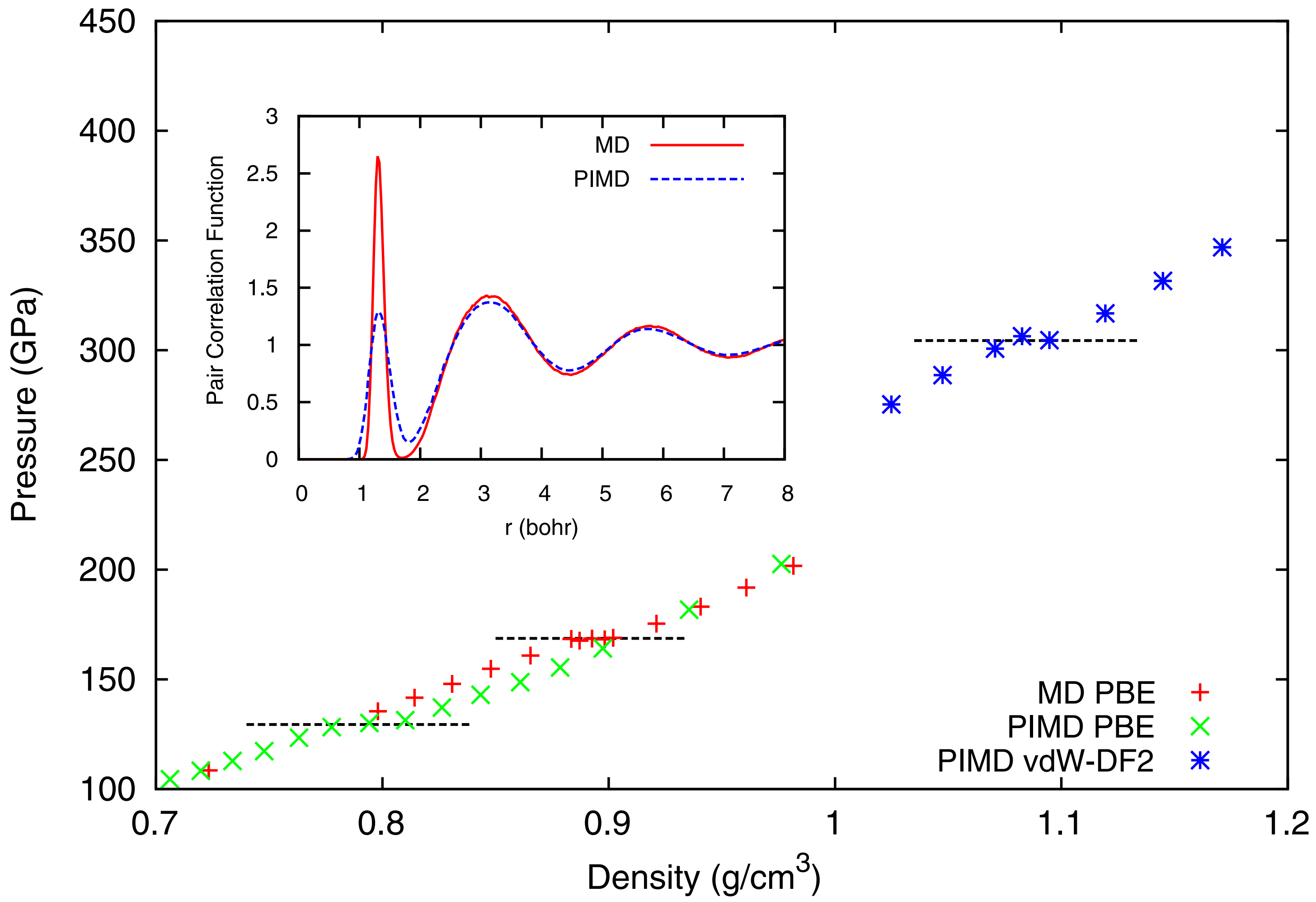


Pierleoni, Morales, Rillo, Holzmann, Ceperley PNAS 113, 4953 (2016)



Nuclear Quantum Effects (NQE) in DFT

Morales, McMahon, Pierleoni, Ceperley PRL 110, 065702 (2013)



Isotherm at
T=1000K

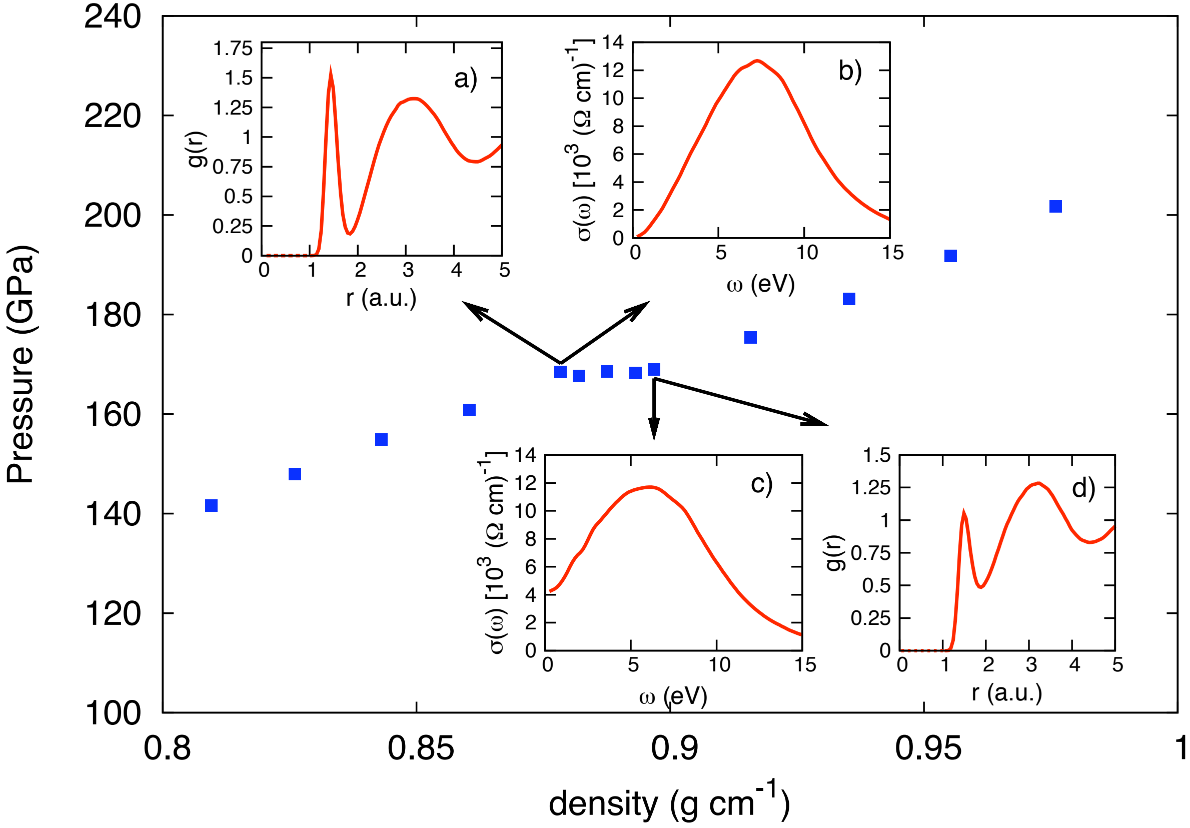
PBE < vdW-DF2

PIMD < BOMD

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

LLPT by DFT: structure and DC conductivity

Morales, Pierleoni, Schwegler, Ceperley PNAS 108, 12799 (2010)



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

- PPT is a first order phase transition below T_c~1000-1500K
- Molecular dissociation is driven by metallization
- Above T_c the metallization and the molecular dissociation are continuous processes

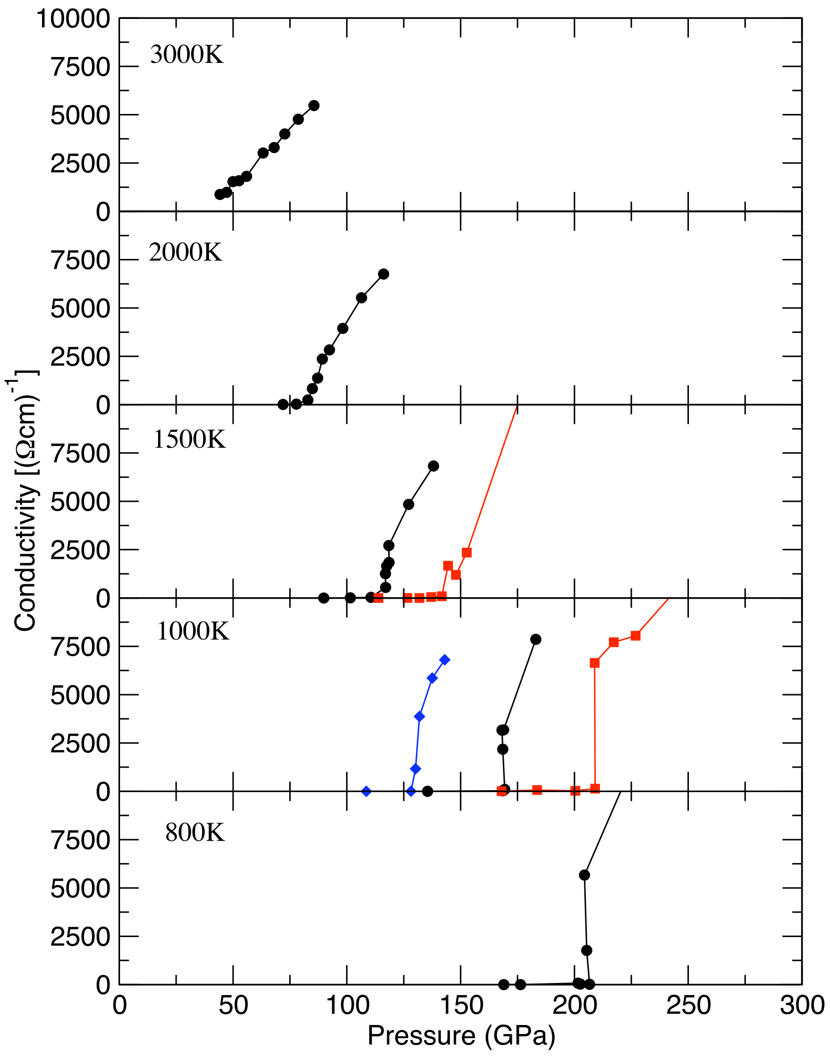


FIG. 4: The DC electronic conductivity of hydrogen as a function of pressure calculated using the Kubo-Greenwood formula and DFT. The black, red and blue points correspond to averages over protonic configurations sampled from the BOMD, CEIMC and PIMD simulations, respectively.

Pierleoni, Morales, Rillo, Holzmann, Ceperley PNAS 113, 4953 (2016)

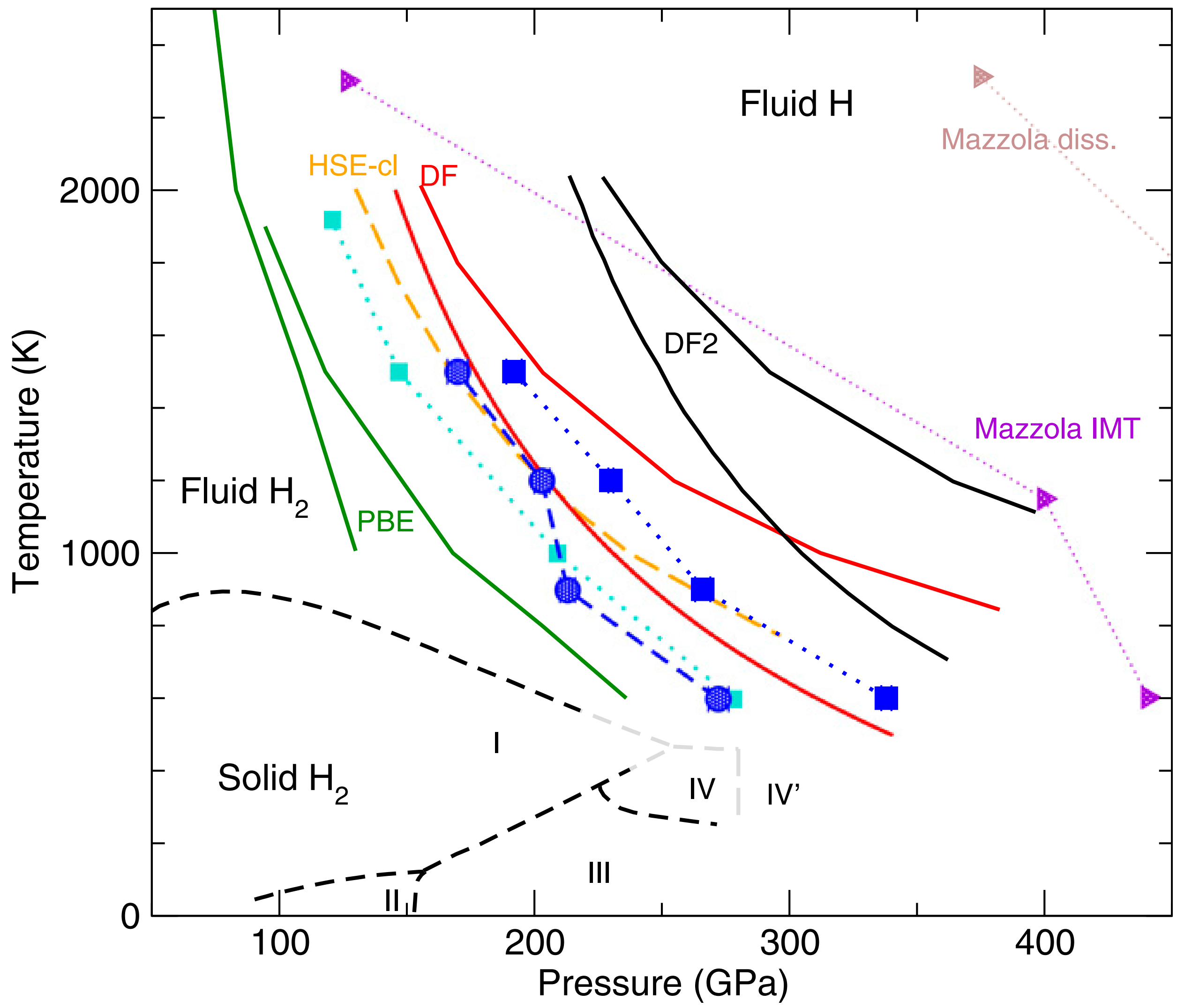


Fig. 3. Comparison of CEIMC results for the transition line with previous theoretical predictions. Blue circles and squares are CEIMC transition pressures for hydrogen and systems with classical protons, respectively. Continuous lines are predictions from FPMD with different X-C approximations: vdW-DF2 (black lines), vdW-DF (red lines), GGA-PBE (green lines), HSE (orange dashed line). For each approximation, except HSE, the line at lower pressure corresponds to quantum protons whereas the line at higher pressure corresponds to classical protons. For HSE only the classical protons line

- NQE decreases the transition pressure by ~ 80GPa at T=600K (CEIMC)

- best functionals are HSE and vdW-DF, but the quality depends on temperature!! (see also R. Clay et al, PRB 2014)

- HSE is too expensive to be routinely used

- 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 (Morales et al PRL 2013)

- vdW-DF2 tends to overbind molecules and predicts a larger dissociation pressure (by ~150GPa).

computational details

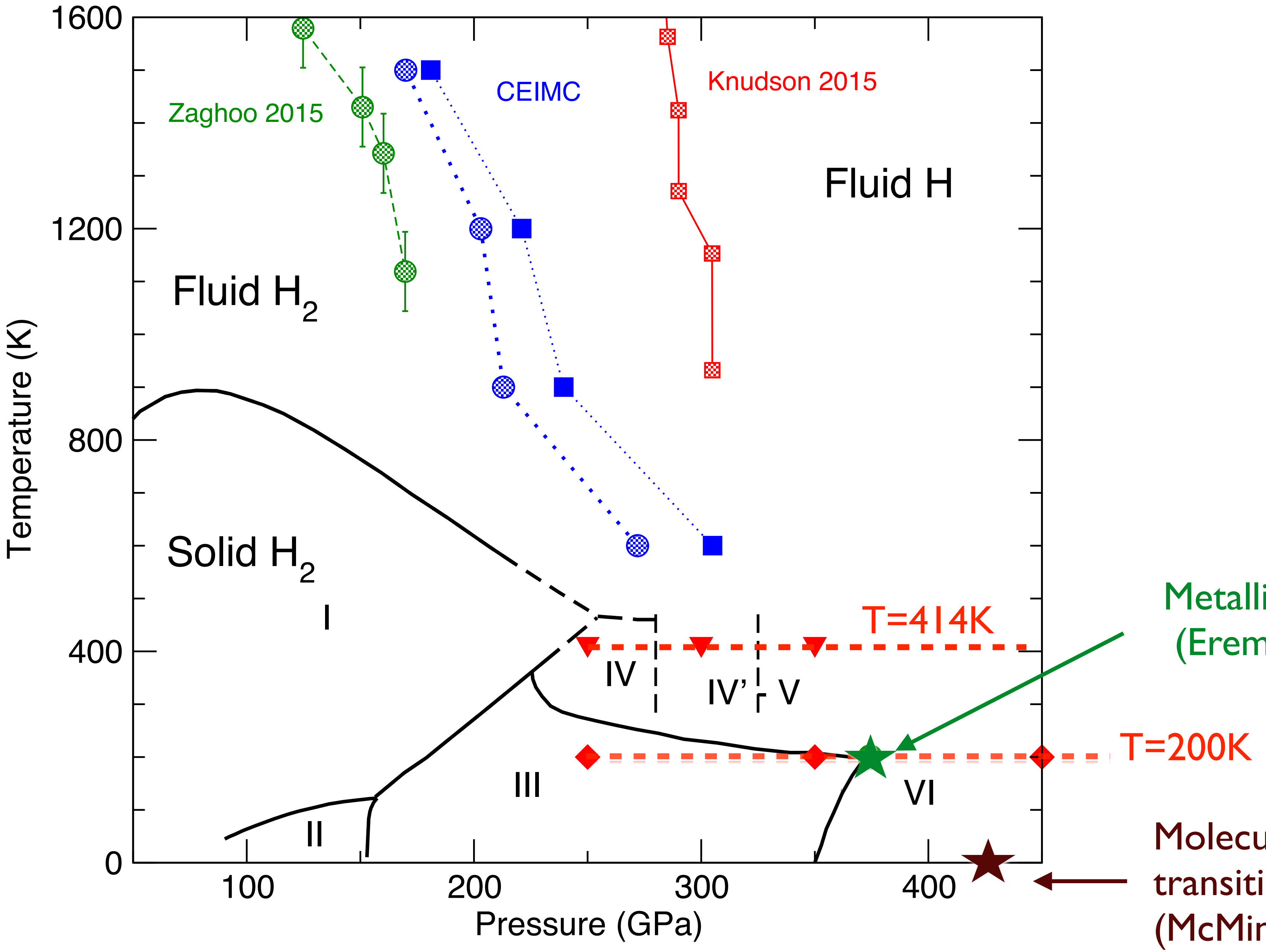
- CEIMC: (BOPIMC)
  - 54-128 protons with 64 twists (4x4x4)
  - Slater-Jastrow wfs with DFT orbitals + BF
  - VMC with RQMC corrections (small ~5Gpa)
  - Size corrections on the transition line are also small (~10Gpa)
  - PIMC with 8 slices at 600K (smart MC with DFT forces for normal-mode sampling)
  - We have checked all main biases

- BOMD: (VASP & QuantumESPRESSO)
  - PBE xc functional with a Troullier-Martins pseudopot. (r_c=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 τ=(4800 K)$^{-1}$ providing a 8 slice paths at T=600K

Morales, Pierleoni, Schwegler, Ceperley PNAS 108, 12799 (2010)
Morales, McMahon, Pierleoni, Ceperley PRL 110, 065702 (2013)
Pierleoni, Morales, Rillo, Holzmann, Ceperley, PNAS 113, 4953 (2016)

molecular crystalline phases



Metallic state?
(Eremets2016)

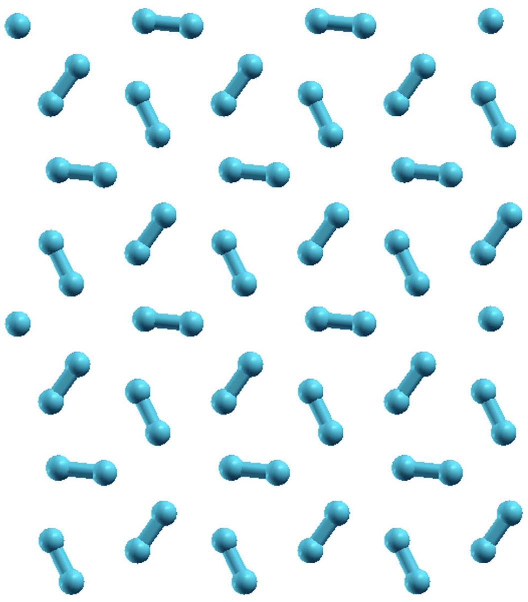
T=414K

T=200K

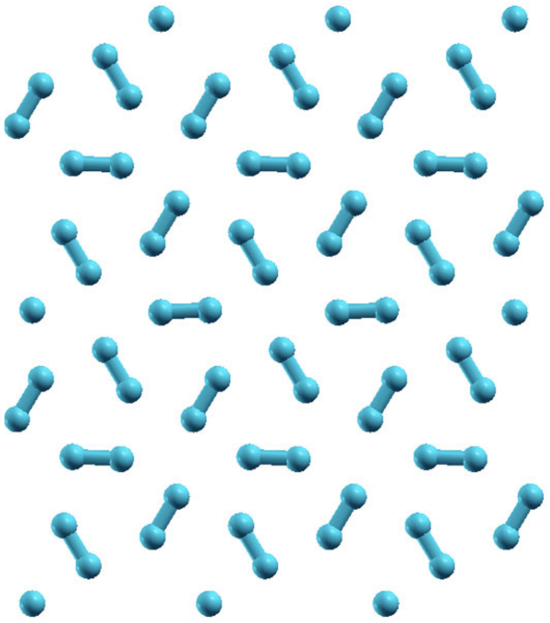
Molecular/atomic transition DMC (McMinis2015)

T=200K: Phase III and VI(?)

C_2/c

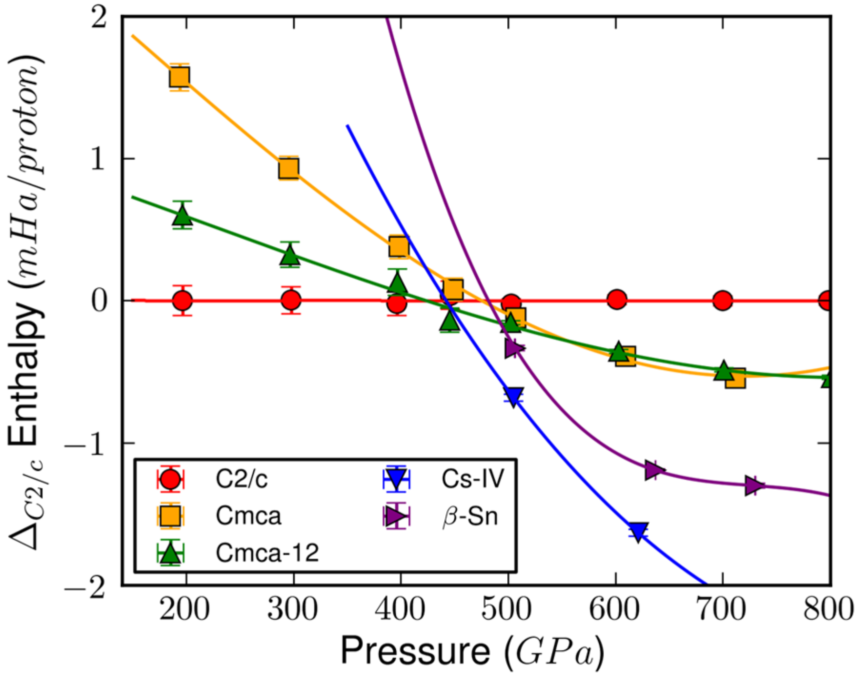


Cmca12



Most favorable structures according to AIRSS with GGA-PBE and zero point energy accounted by Self-consistent harmonic approximation

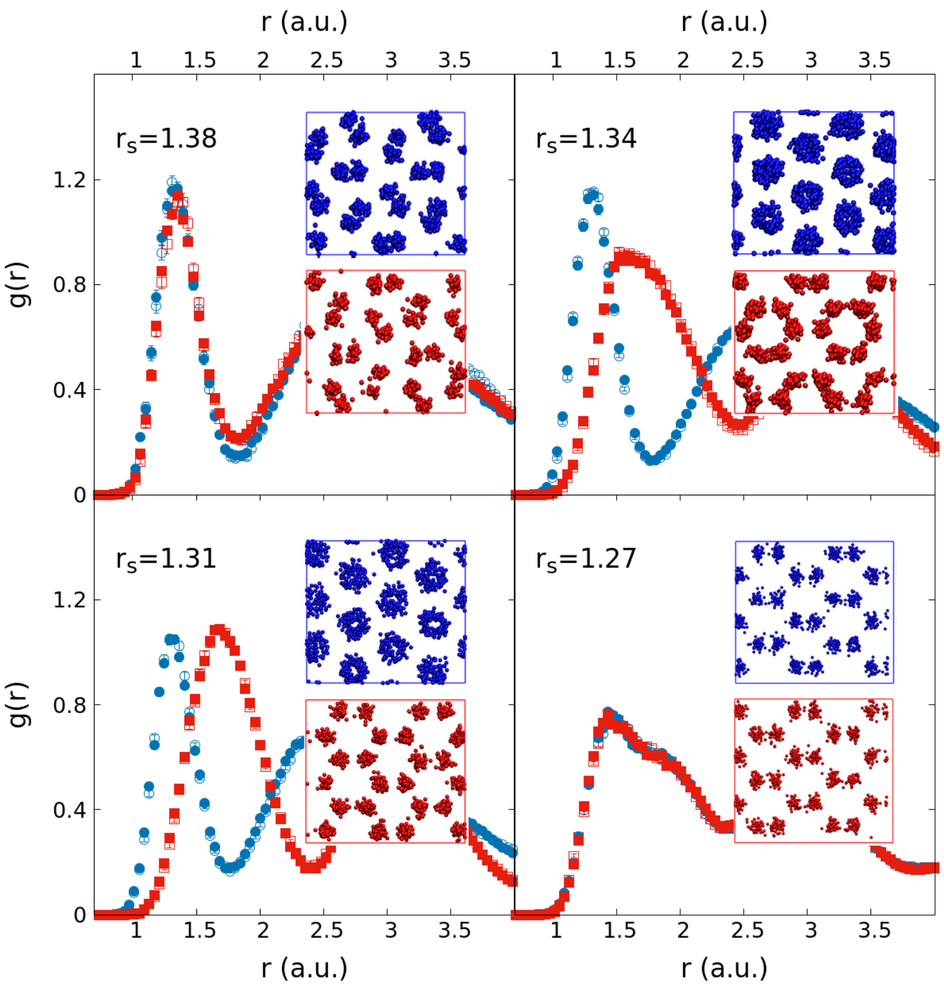
Pickard-Needs, Nature Physics 3, 473 (2007)



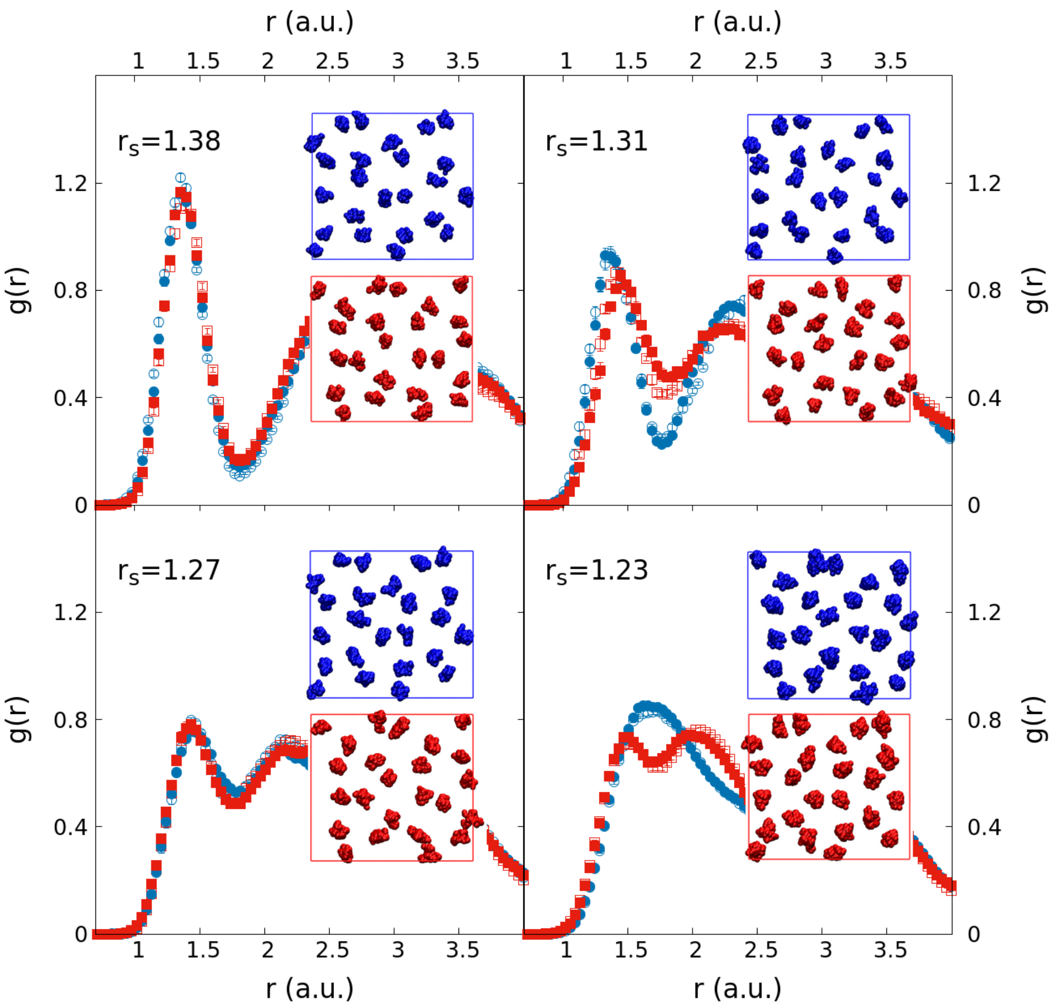
C2/c is favored in the QMC ground state with ZPE (SCHA) until the atomic phase with Cs-IV structure is reached.

McMinis et al. PRL 2015.

vdW-DF-PIMD



CEIMC-PIMC



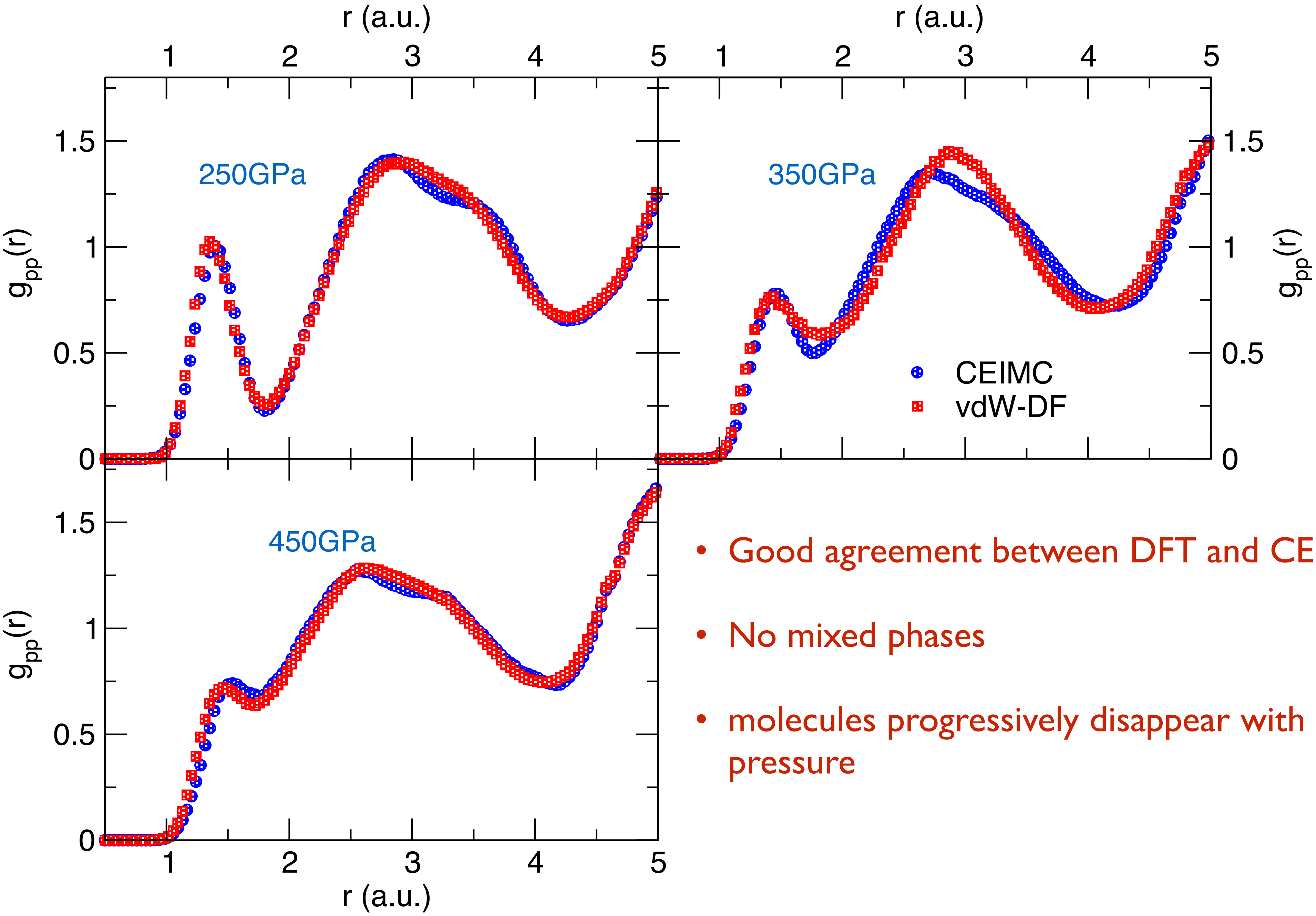
Initial configurations relaxed at constant pressure with DFT

with DFT-vdW-DF, C2/c is dynamical unstable towards:

- layered structures at intermediate densities
- metallic Cmca-4 structure at rs=1.27

with CEIMC no instabilities are seen, molecules progressively disappear with pressure

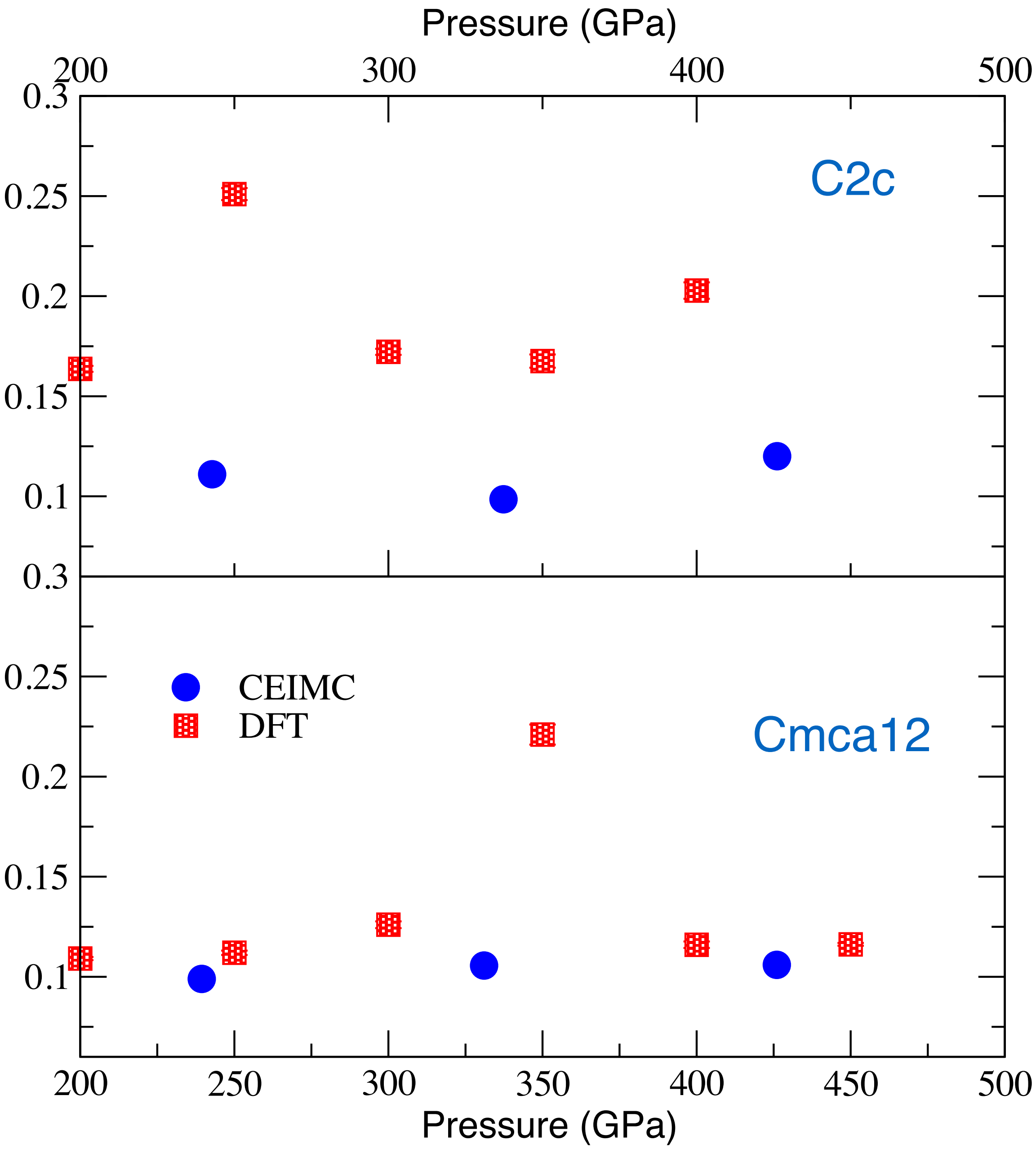
Cmca-12: CEIMC vs vdW-DF



- Good agreement between DFT and CEIMC
- No mixed phases
- molecules progressively disappear with pressure

Molecular Lindemann ratio

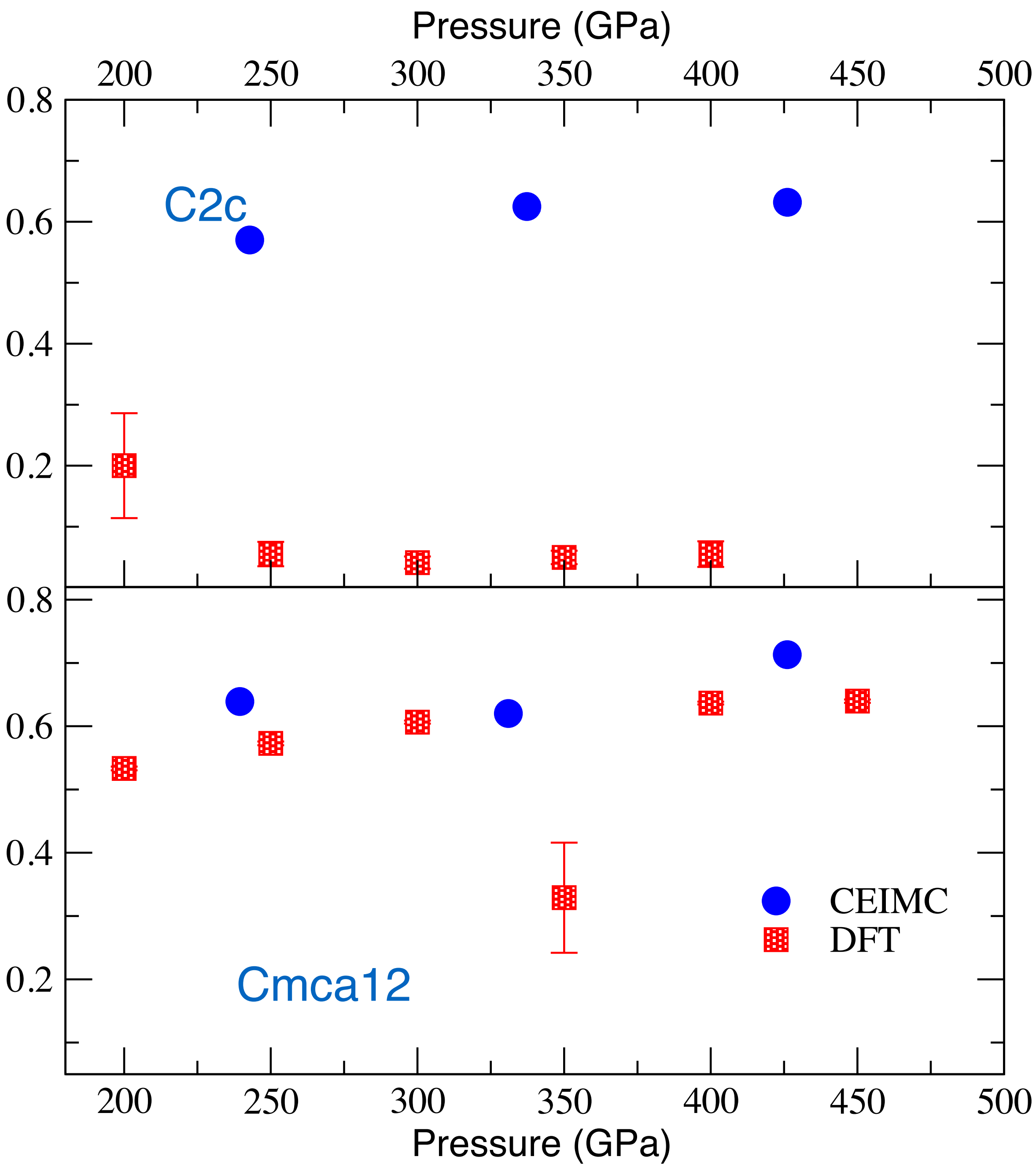
$$\hat{L} = \frac{\sqrt{\Delta^2}}{d}, \Delta^2 = \frac{1}{N}\sum_{i=1}^{N}(\mathbf{r}_i - \mathbf{r}_{i0})^2$$



Classical melting ~ 0.15

Quantum melting ~ 0.3

Molecular Orientation Order

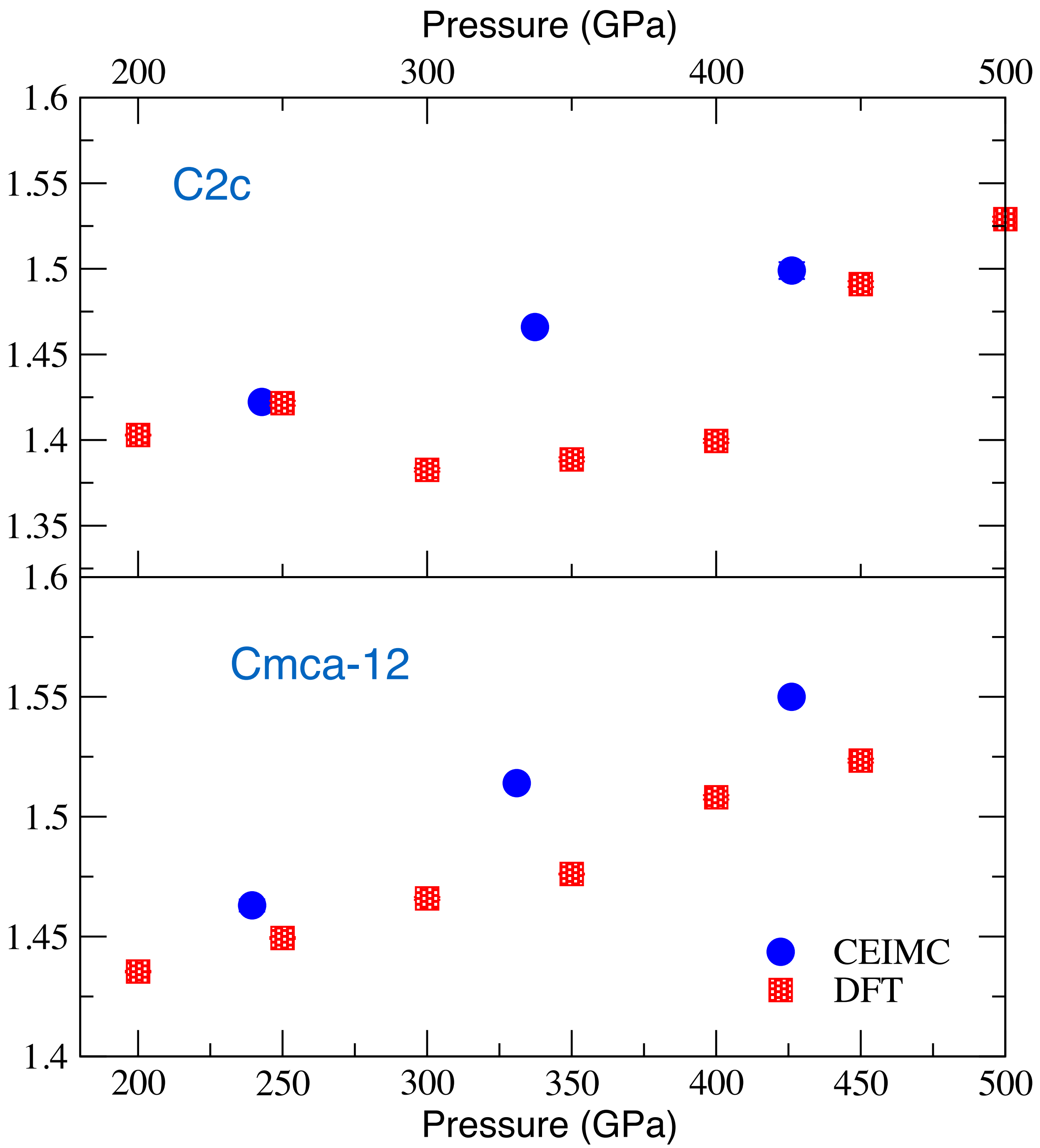


$$\hat{O} = \left[\frac{1}{N}\sum_{i=1}^{N} P_2(\hat{\Omega}_i \cdot \hat{e}_i)\right]^2$$

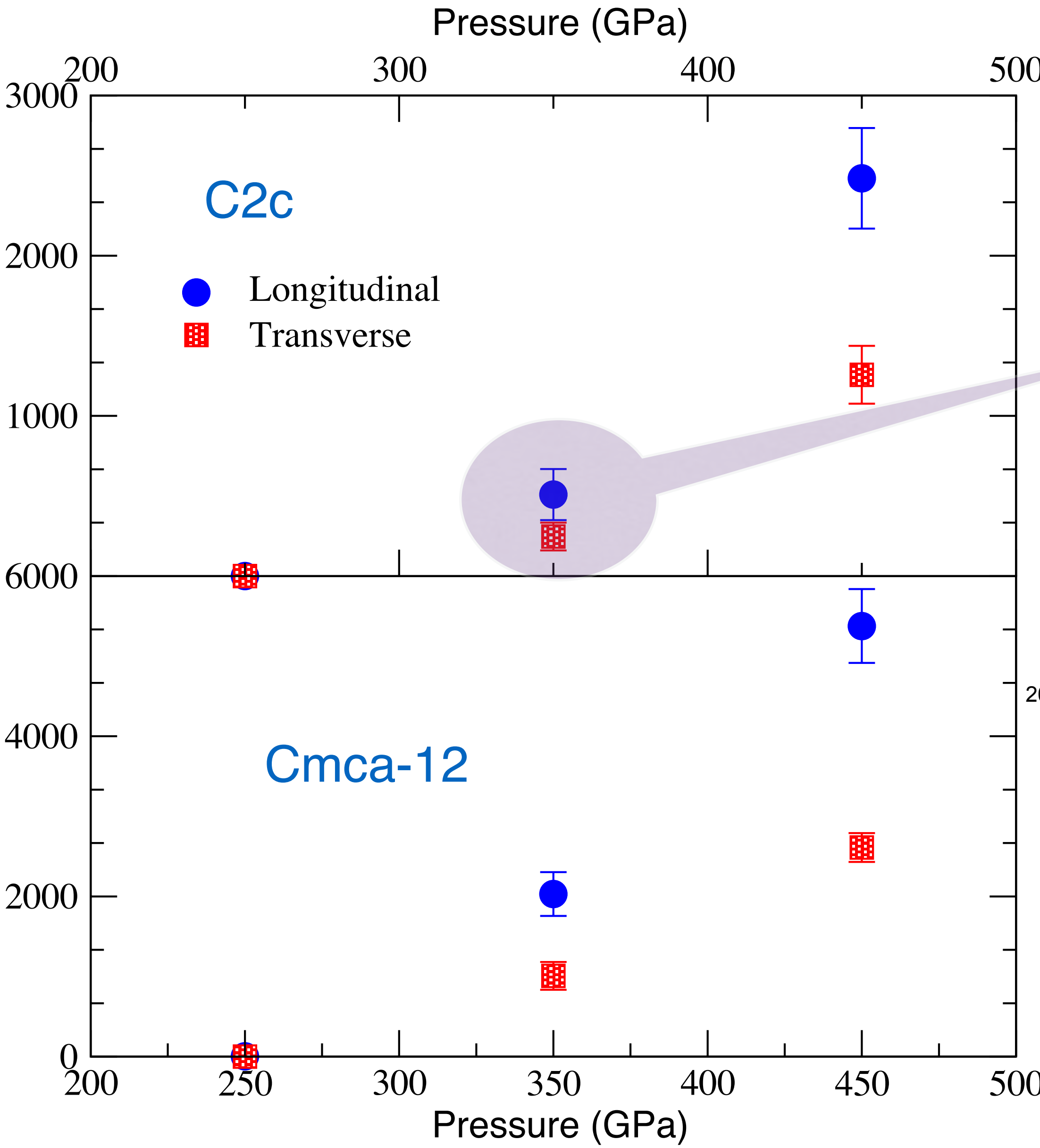
<O>=1 perfect alignment

<O>=0 no alignment

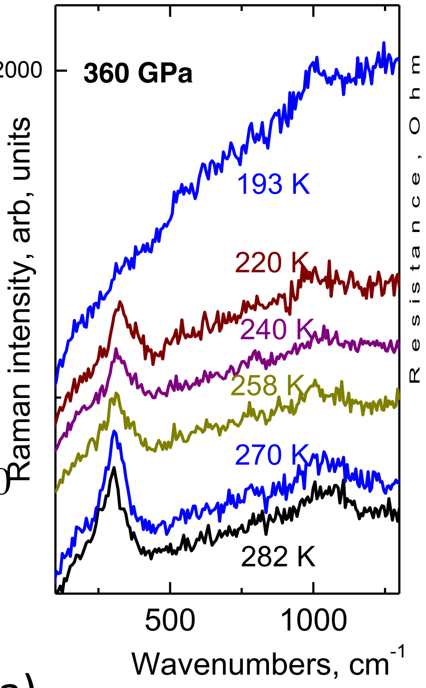
Molecular bond length



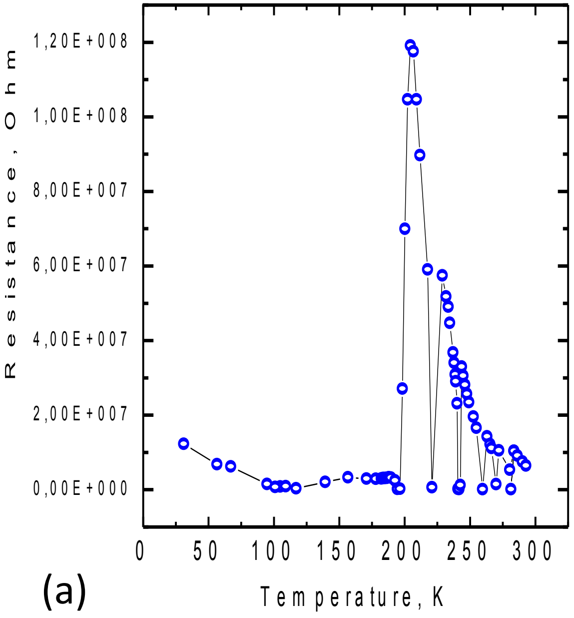
Electrical conductivity $(\Omega cm)^{-1}$



- Cmca12 more "conductive" than C2/c
- C2/c at 350GPa at the edge of the conductive behavior in qualitative agreement with recent experiments
- Eremets2016: arXiv:1601.04479



(a)



(a)

Conclusions

- BOMD is reasonably accurate in a large region of the thermodynamic space but breaks down near metallization and molecular dissociation in hydrogen.
- Hydrogen metallization and dissociation in the liquid phase occur simultaneously through a weakly first order phase transition below some critical temperature (T_c~2000K ?).
- 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. Different experiments are also in disagreement. We are closer (but at slightly higher pressure) to the static compression experiments (Silvera) than to the dynamic compression experiments (Knudson).
- <u>Molecular crystalline structures</u>: PE surface from CEIMC seems to be more structured than from DFT-vdW-DF1. DFT accuracy seems to depend on the specific structure.

Conclusions

- Hydrogen remains a very interesting system with many open questions in its high pressure regime
  - the structure of crystalline molecular phases (from II to VI) in the insulating molecular crystal
  - the mechanism of metallization at low temperature and its interplay with molecular dissociation and melting (recent claim of metallization at 500GPa and 80K)

- Hydrogen has confirmed itself as the ideal system for method development:
  - how to deal with quantum nuclei in DFT?
  - QMC benchmark of DFT functionals
  - what about hydrogen in more complex systems (water)?

- CEIMC is a method to perform ab-initio simulation with QMC accuracy
  - It is suitable to investigate systems (heavier elements?) around the MIT
  - It is unique in its ability to treat quantum protons without a major computational bottleneck
  - It is the obvious method to study hydrogen at intermediate temperature (T>100K)
  - How to treat nuclear statistics efficiently ?

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ANR(France)

PRACE

NCSA
National Centre for Supercomputing Applications

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INCITE
Leadership Computing

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THANK YOU FOR YOUR ATTENTION !

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