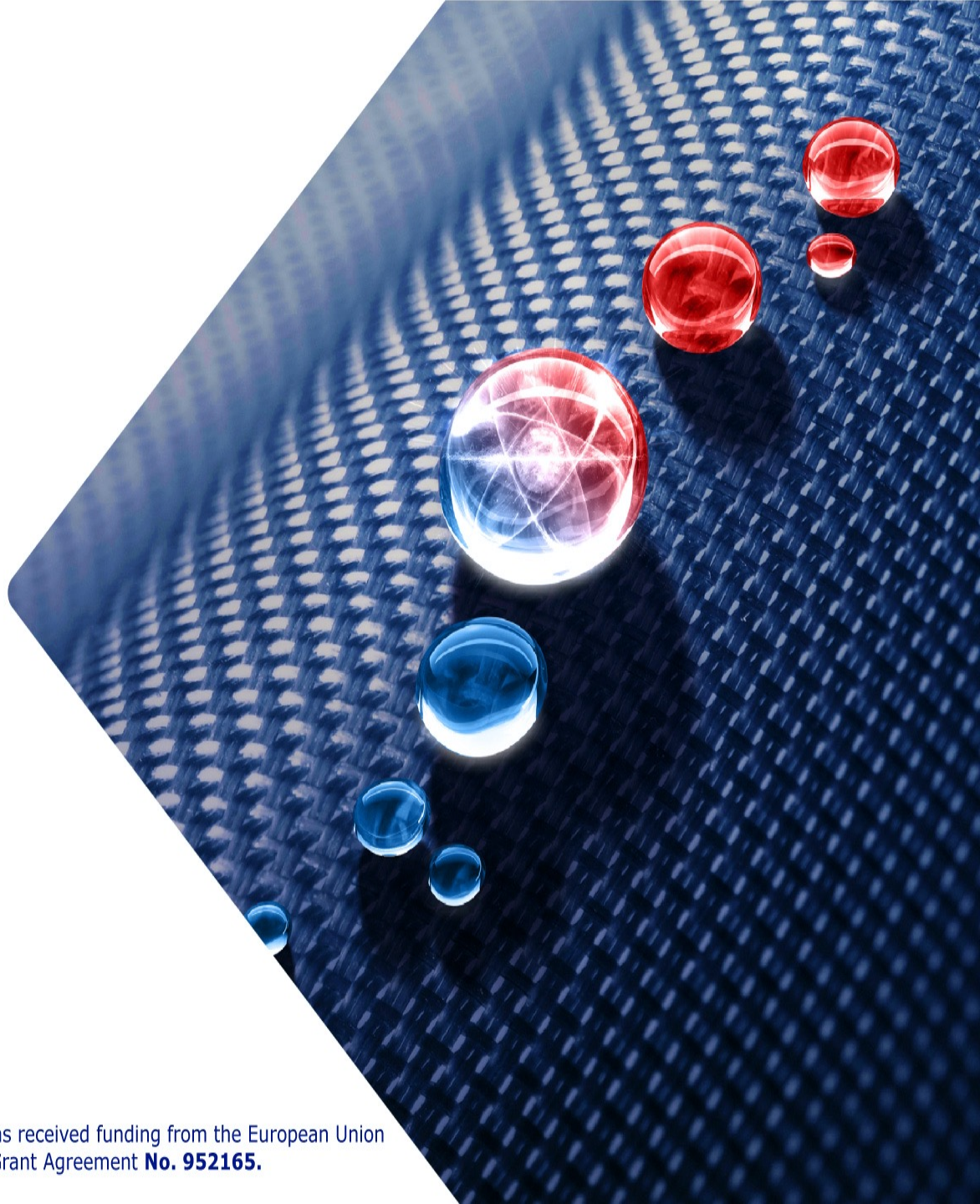
Targeting Real chemical accuracy at the EXascale



Demonstrations

Michele Casula

IMPMC, Sorbonne Université and CNRS

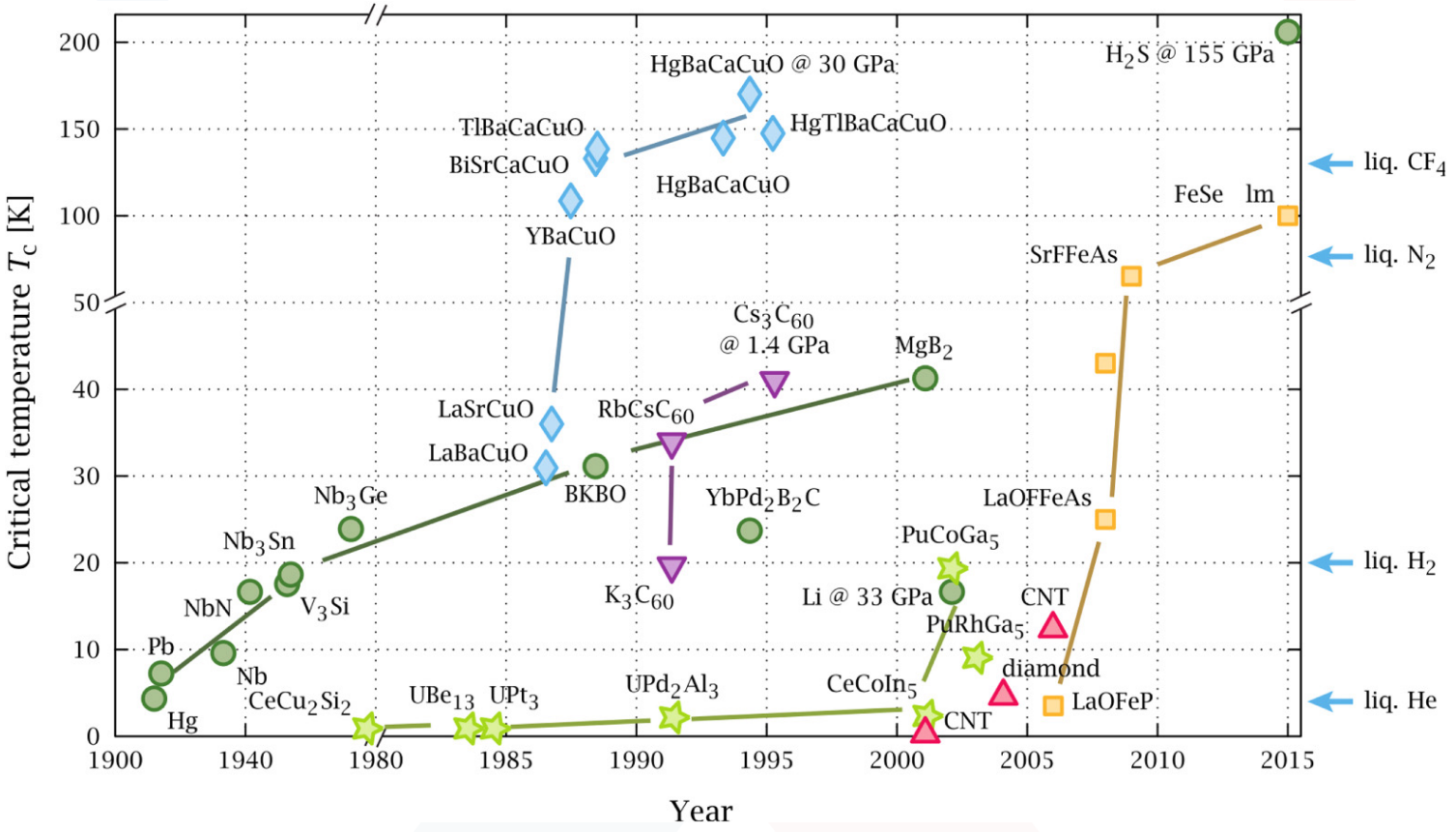
Targeting Real Chemical Accuracy at the Exascale project has received funding from the European Union Horizoon 2020 research and innovation programme under Grant Agreement **No. 952165.**

Outline

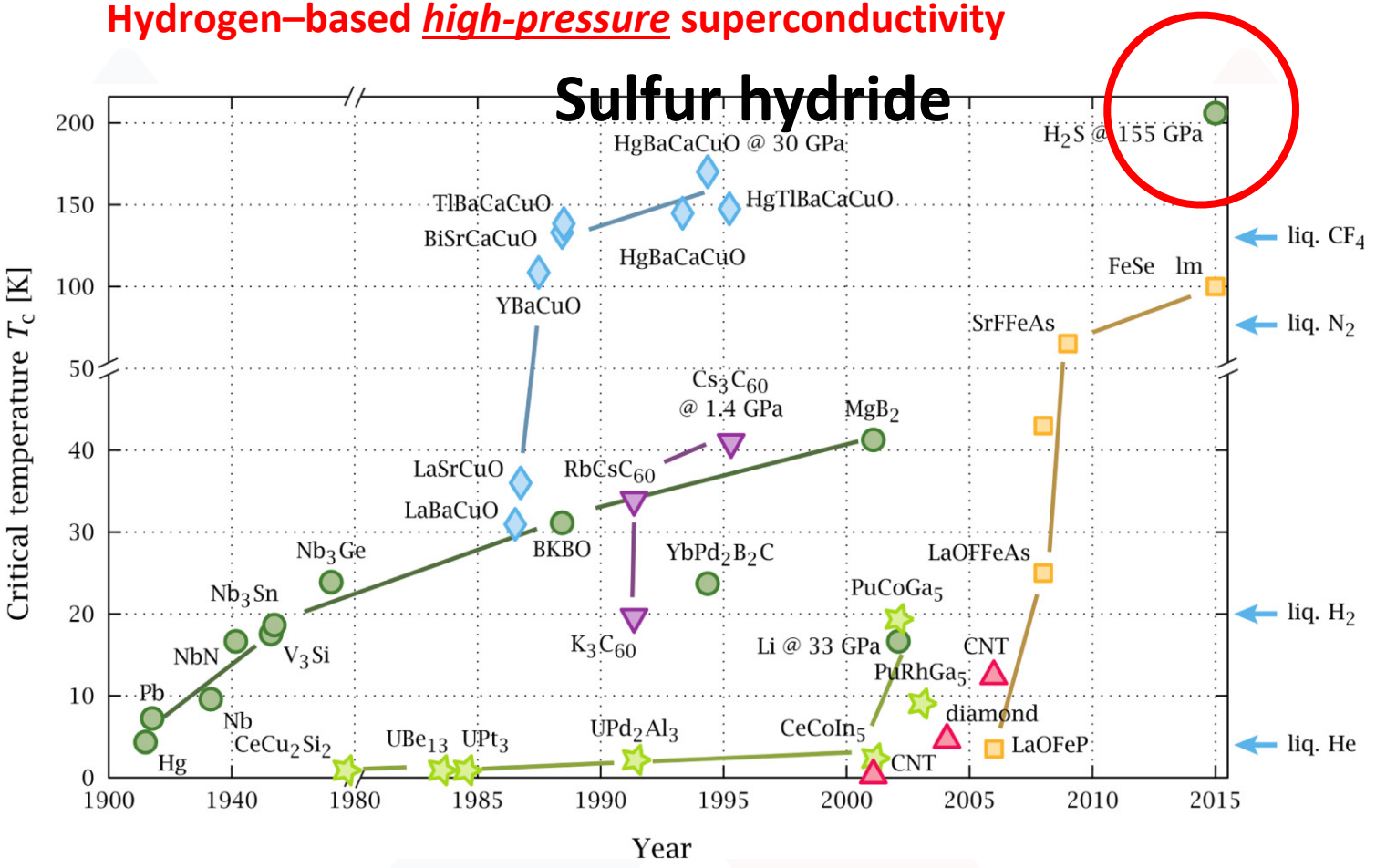
- Recent applications
  - Hydrogen
  - Protonated water clusters
- Perspectives

- *Quantum* materials / *quantum* crystals:
  - Both electrons and nuclei are **quantum particles**
  - **Nuclear quantum effects (NQE) strongly affect materials' properties**
  - **Light mass → nuclear delocalization:**
    nuclei are **not point-like** but have a **significant "spread"**
  - **Hydrogen and Hydrogen-rich materials belong to this family**
  - **Remarkable properties**

Towards room temperature superconductivity

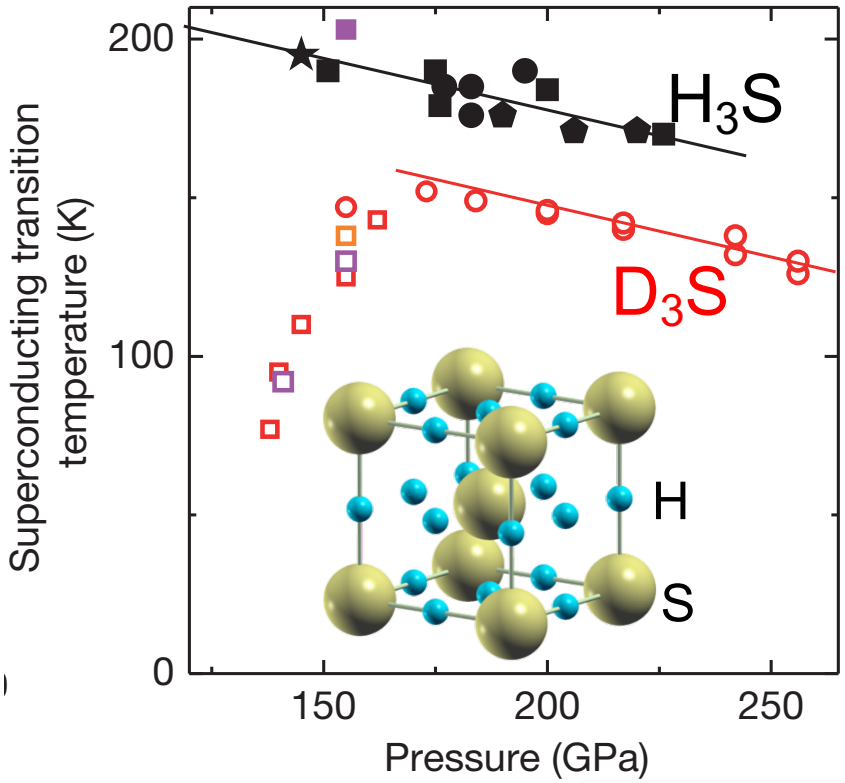


Hydrogen–based *high-pressure* superconductivity



Hydrogen–based *high-pressure* superconductivity

Sulfur hydride



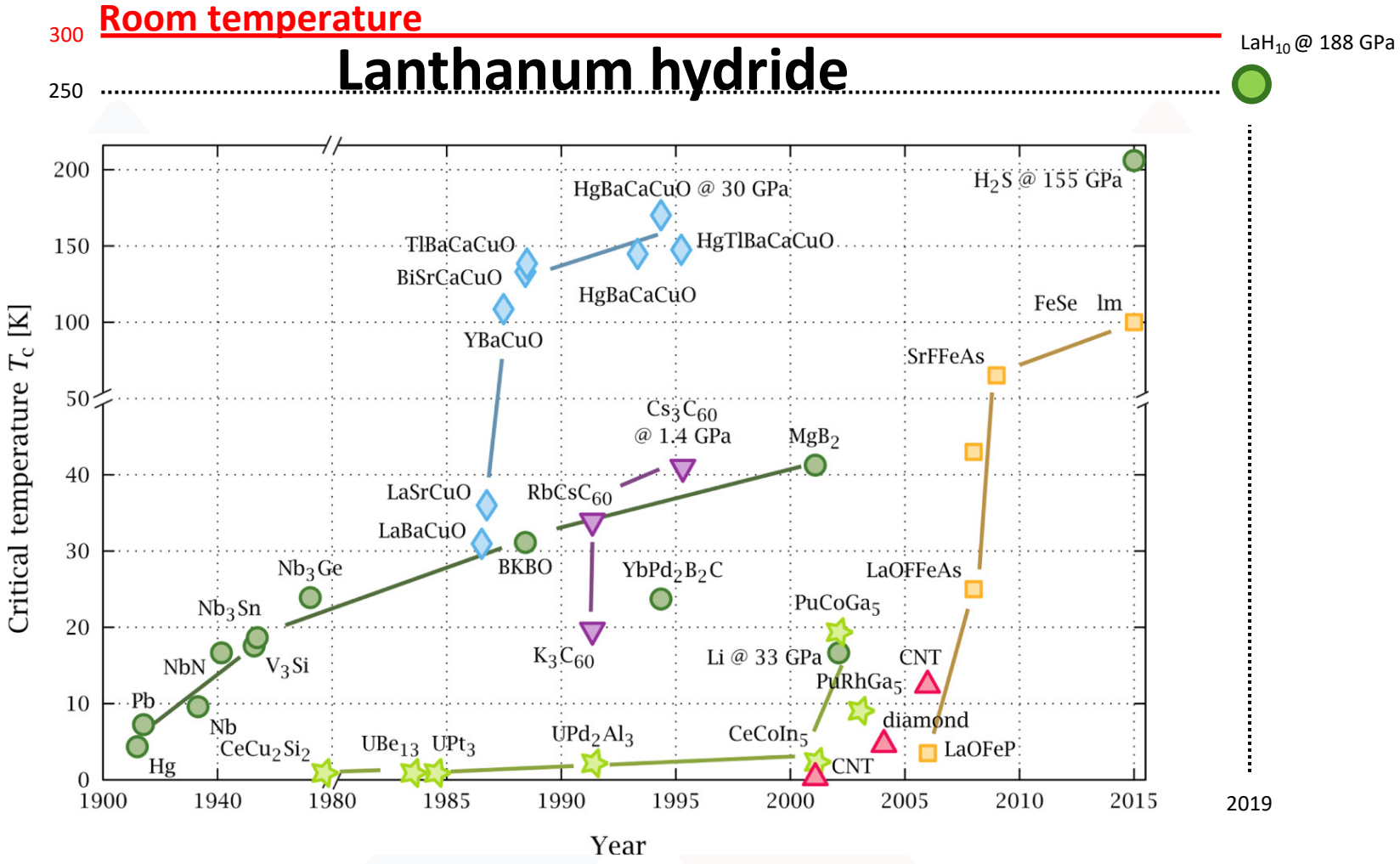
2015: superconductivity

at 203 K and 150 GPa in H_3S

(Nature 525, 73)

Critical temperature

higher than Hg-based cuprates!


Room temperature
300
250
Lanthanum hydride
LaH10 @ 188 GPa
2019
Critical temperature Tc [K]
Year
200
150
100
50
40
30
20
10
0
1900
1940
1980
1985
1990
1995
2000
2005
2010
2015
HgBaCaCuO @ 30 GPa
H2S @ 155 GPa
TlBaCaCuO
HgTlBaCaCuO
BiSrCaCuO
HgBaCaCuO
YBaCuO
FeSe
lm
SrFFeAs
Cs3C60 @ 1.4 GPa
MgB2
LaSrCuO
RbCsC60
LaBaCuO
BKBO
Nb3Ge
YbPd2B2C
LaOFFeAs
Nb3Sn
PuCoGa5
K3C60
Li @ 33 GPa
CNT
NbN
V3Si
PuRhGa5
Pb
Nb
diamond
CeCu2Si2
UBe13
UPt3
UPd2Al3
CeCoIn5
LaOFeP
Hg
CNT

300 **Room temperature**

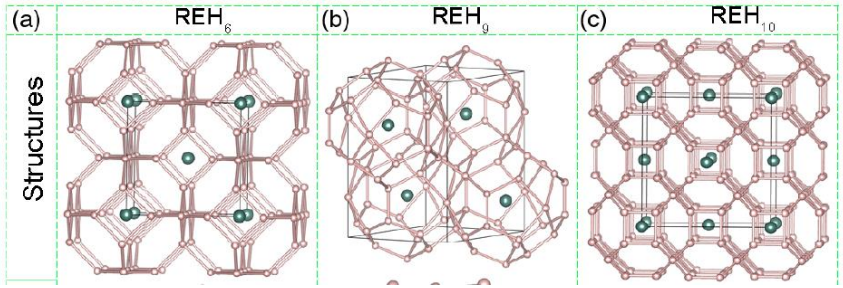
250

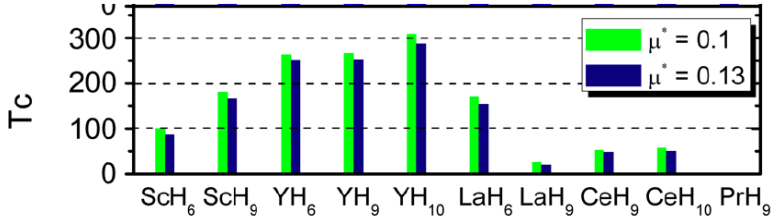
Lanthanum hydride

LaH_{10} @ 188 GPa

PRL 119, 107001 (2017) PHYSICAL REVIEW LETTERS week ending 8 SEPTEMBER 2017

Hydrogen Clathrate Structures in Rare Earth Hydrides at High Pressures: Possible Route to Room-Temperature Superconductivity





Rare earth hydrides (2017) → discovery 2019

2019

Superconductivity at 255 K and 188 GPa in LaH_{10} *(PRL 122, 027001)*

Highest ever measured critical temperature

Almost room temperature!

Hydrogen as conventional high-T superconductor

Three Bardeen-Cooper-Schrieffer (BCS) golden rules to maximize

$$\Delta = 2\hbar\omega_{\text{cut}}\ e^{-1/N(\epsilon_F)V}$$

1. **large nuclear vibrations**
2. **high electronic density of states at the Fermi level**
3. **strong coupling between phonons and electrons**

VOLUME 21, NUMBER 26 PHYSICAL REVIEW LETTERS 23 DECEMBER 1968

METALLIC HYDROGEN: A HIGH-TEMPERATURE SUPERCONDUCTOR?

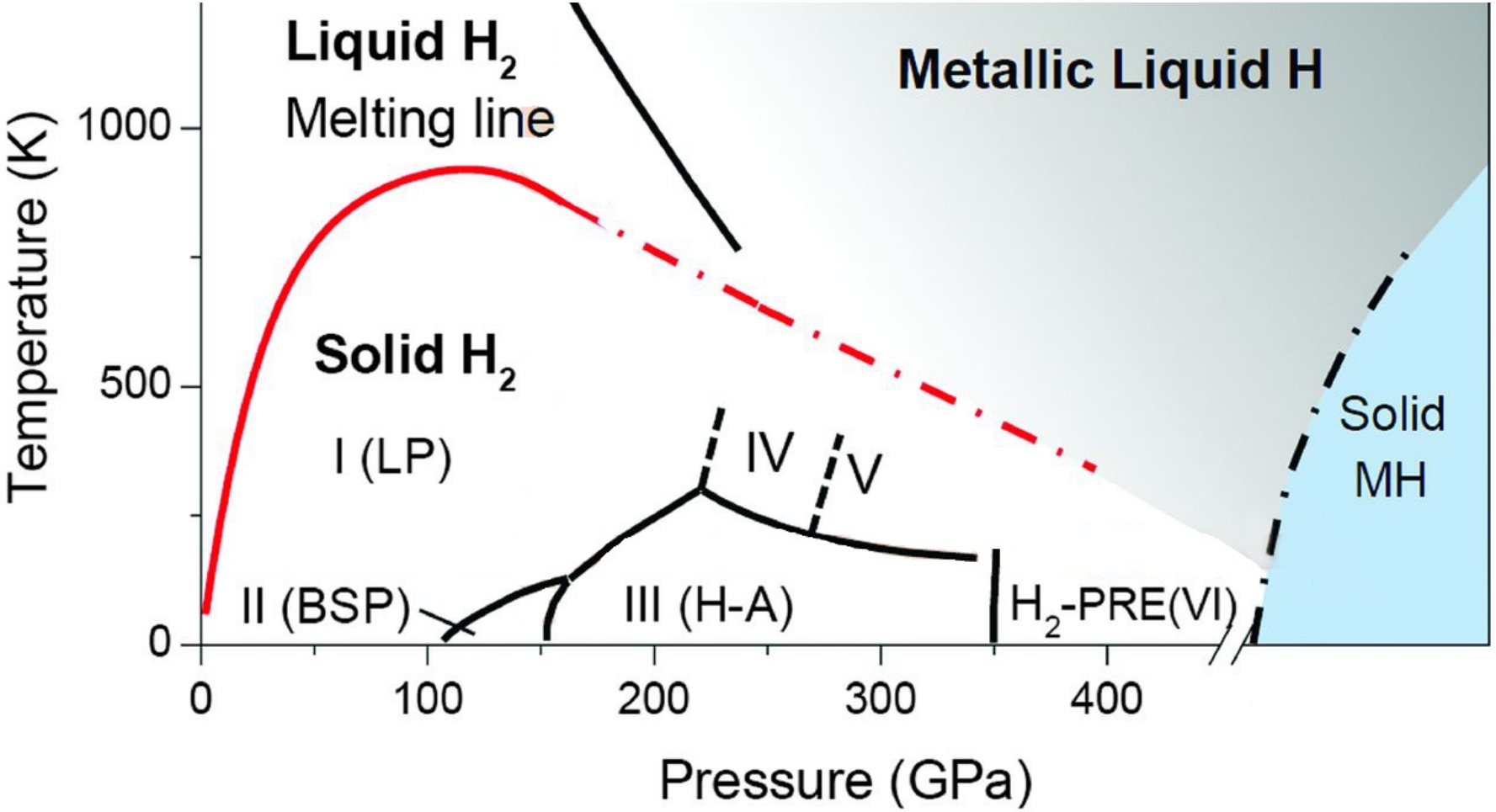
N. W. Ashcroft
Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, New York 14850
(Received 3 May 1968)

Application of the BCS theory to the proposed metallic modification of hydrogen suggests that it will be a high-temperature superconductor. This prediction has interesting astrophysical consequences, as well as implications for the possible development of a superconductor for use at elevated temperatures.

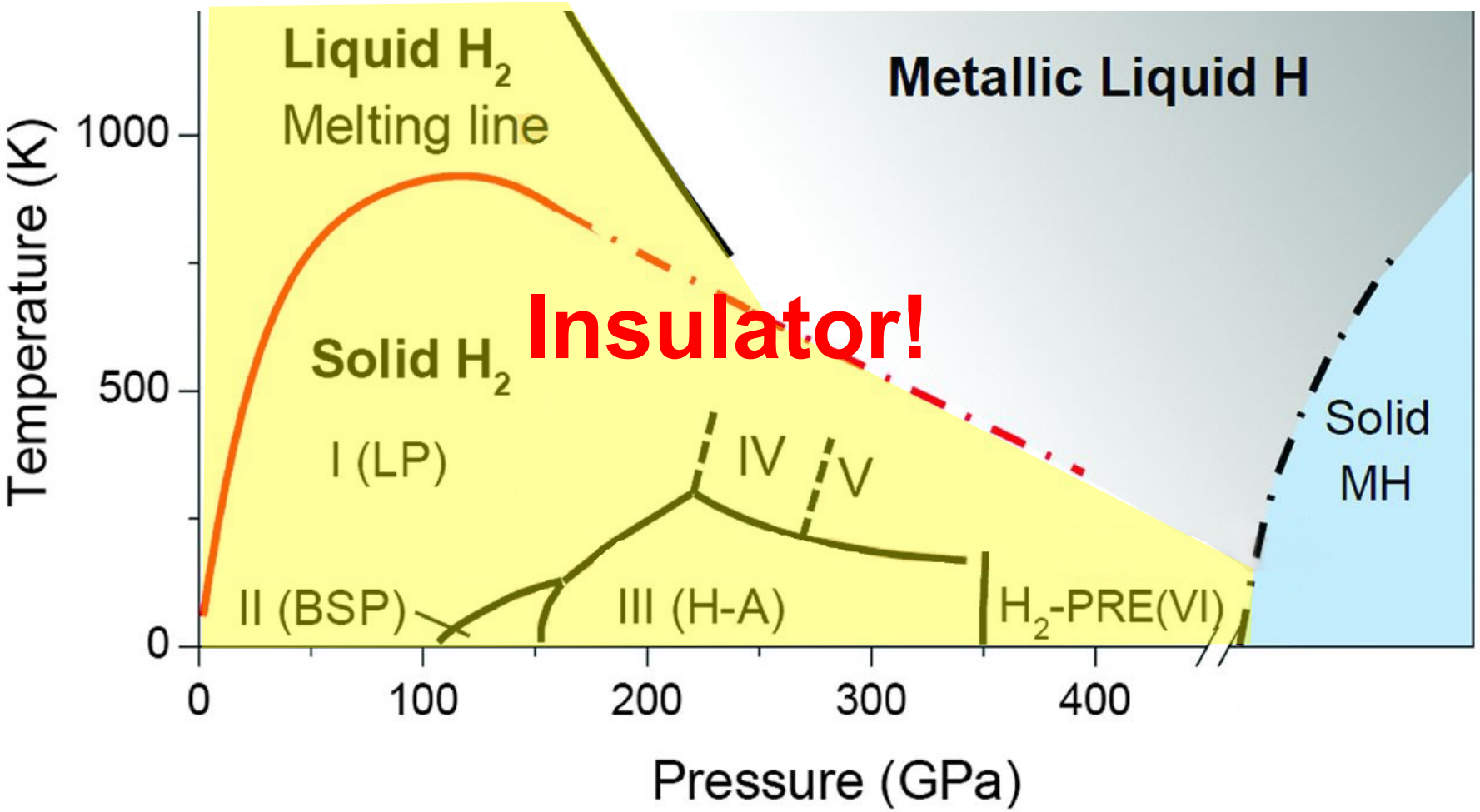
Hydrogen will meet the above requirements thanks to its light mass

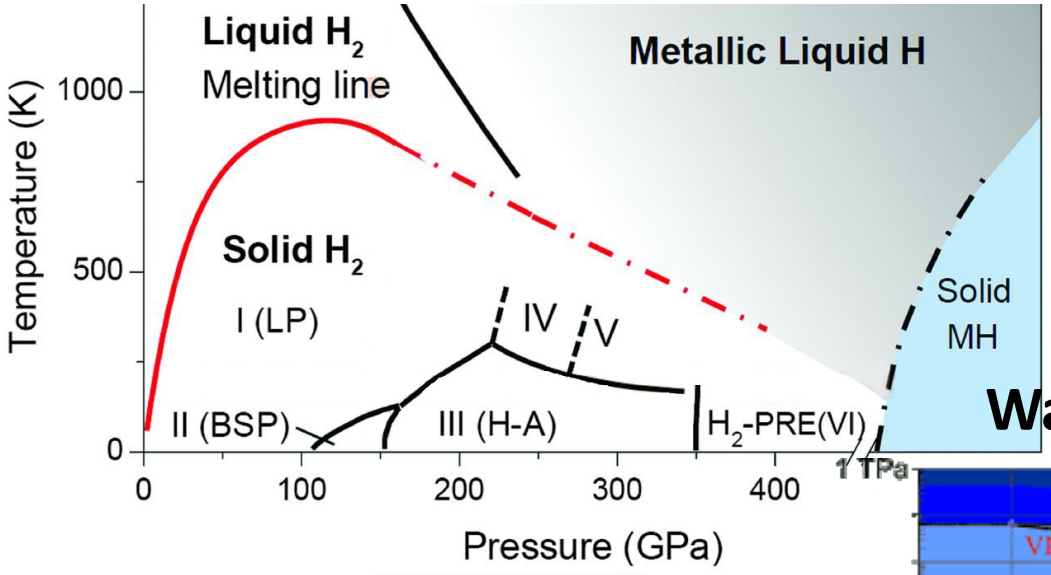
But first it needs to become a metal!

Hydrogen phase diagram



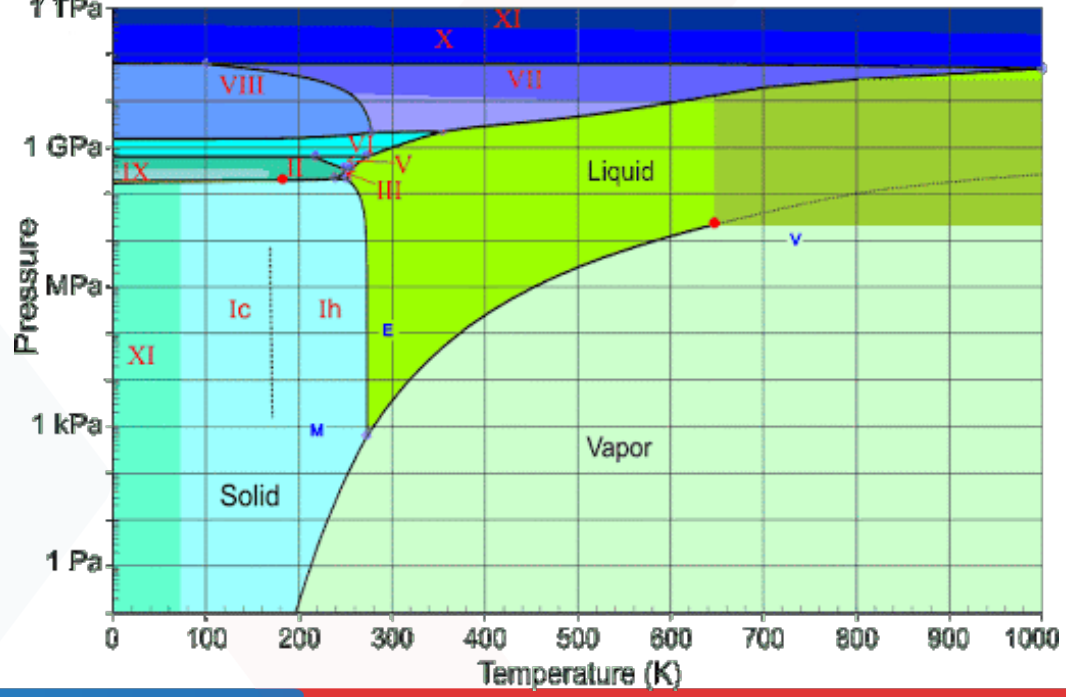
Hydrogen phase diagram

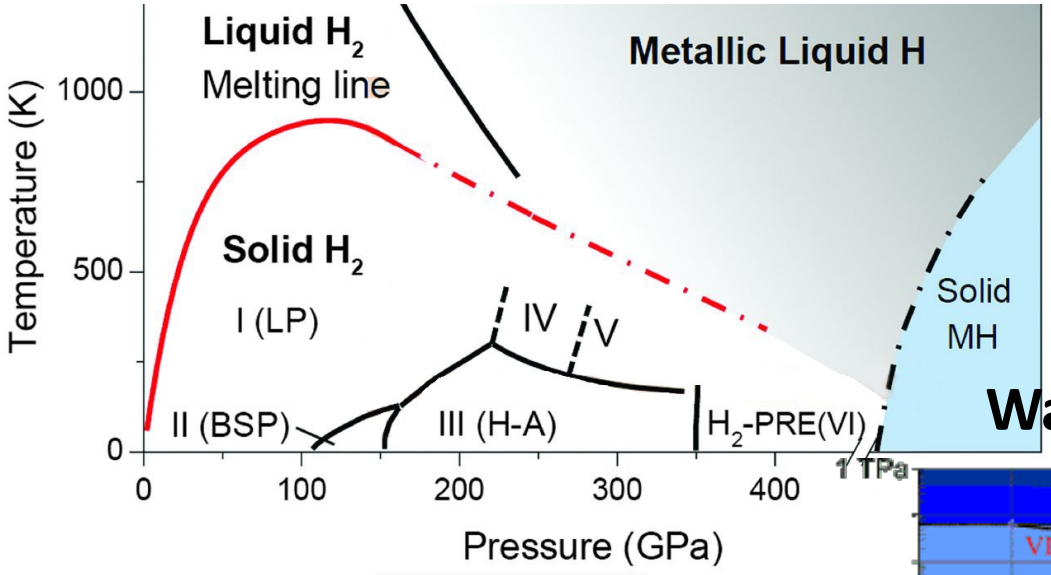




Hydrogen

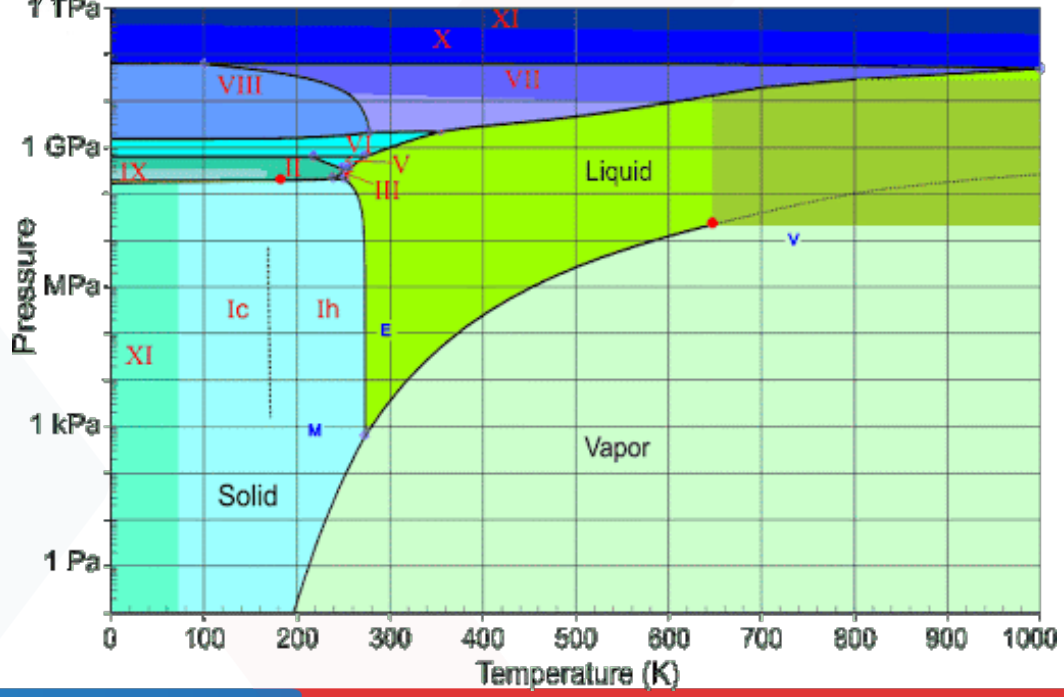
Water (H-bonded network)



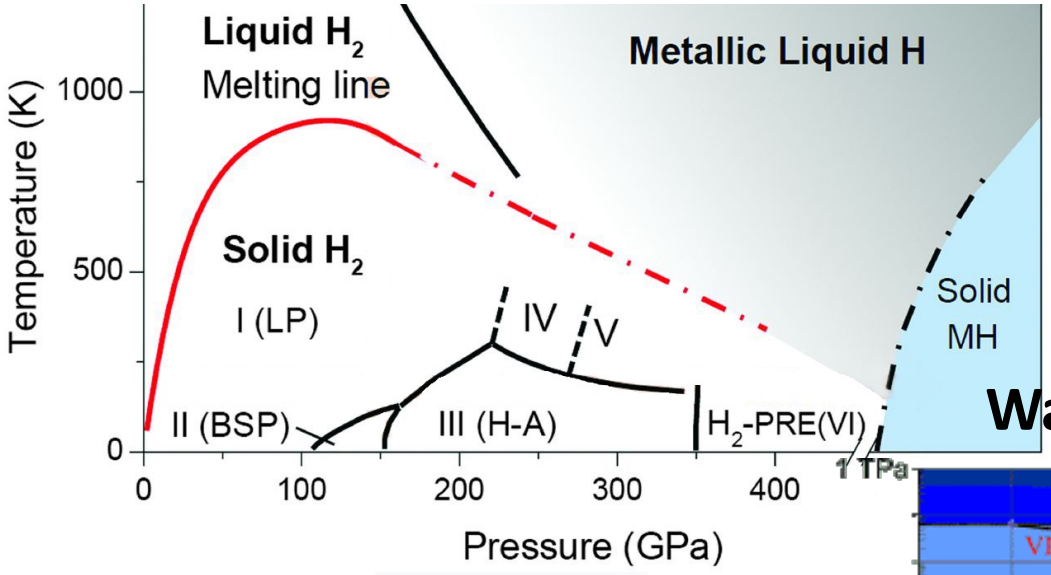


Hydrogen

Water (H-bonded network)

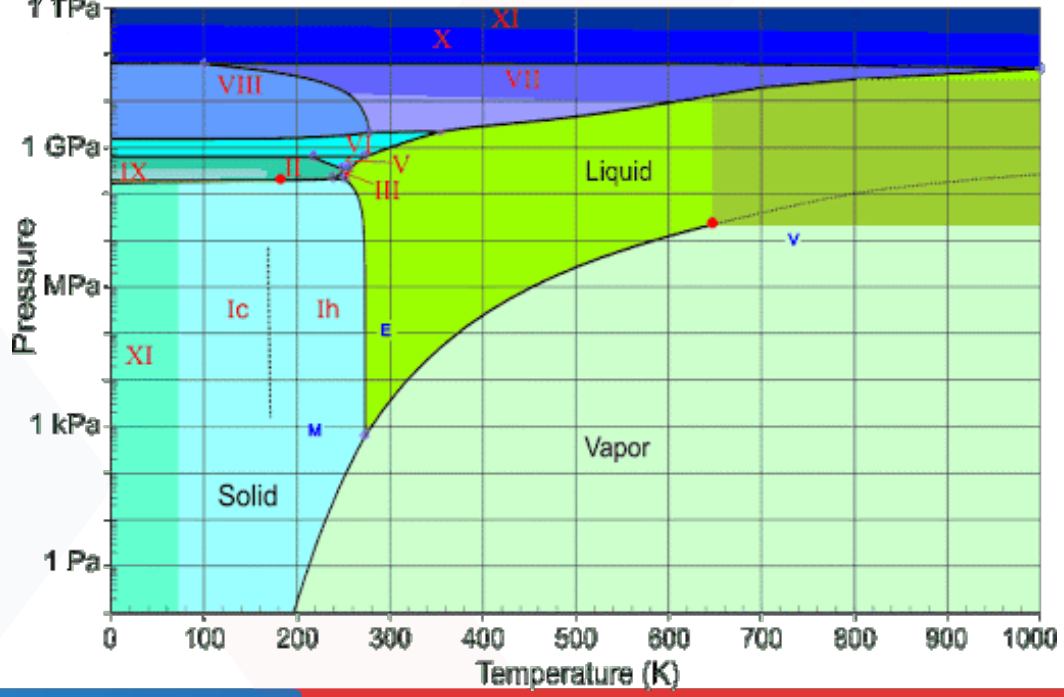


Quantum matter:
Very complex and rich phase diagrams



Hydrogen

Water (H-bonded network)



<u>Quantum matter</u>:
Very complex and rich phase diagrams

Competition/interplay between *internal (electronic)* and *vibrational (nuclear)* energies

Theoretical/computational challenges

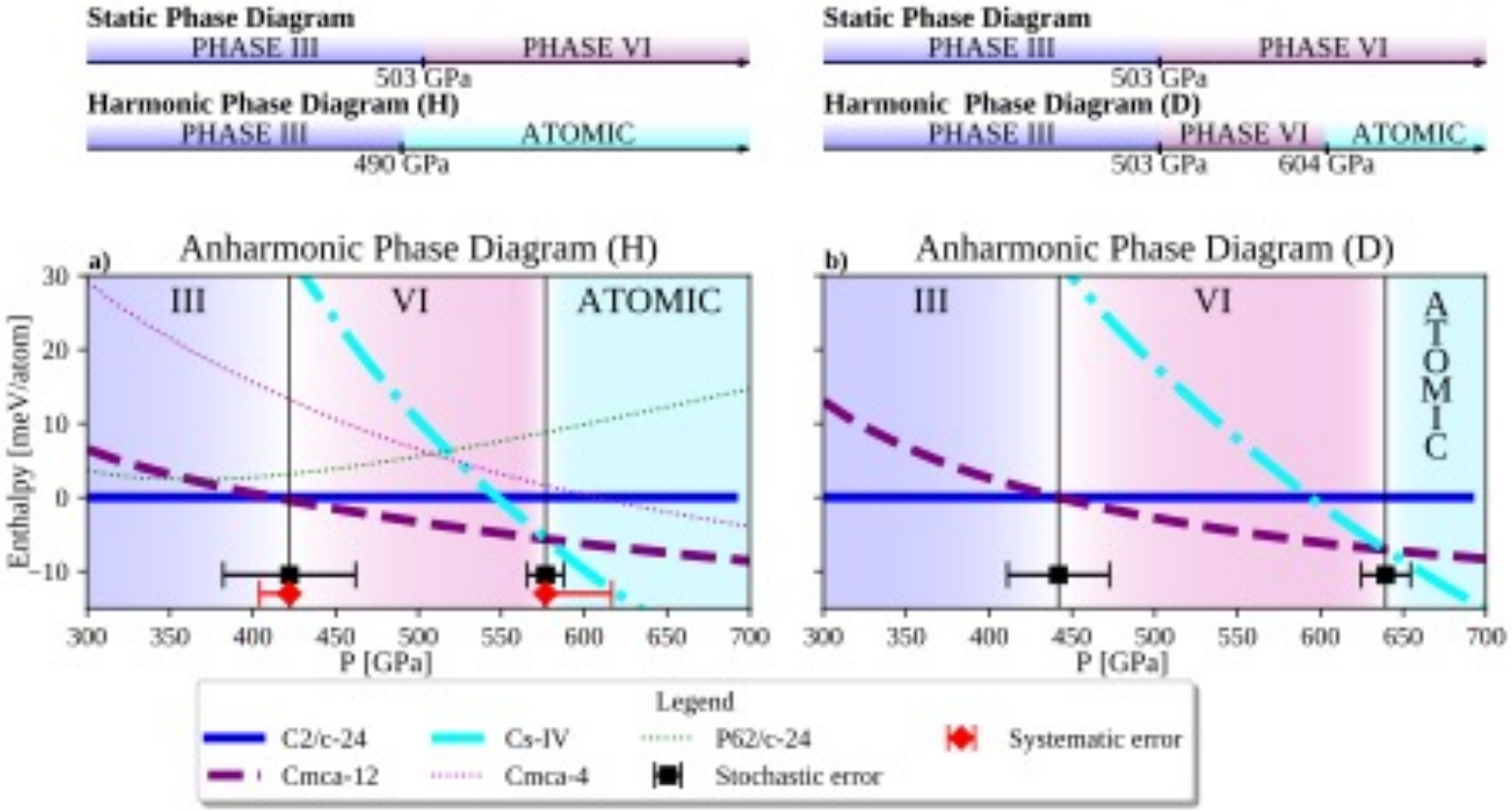
- Accurate evaluation of **electronic internal energies**
  (i.e. full account of *electronic correlation*)

- Accurate treatment of **the nuclear degrees of freedom by a quantum description**
  (i.e. full account of *nuclear quantum effects*)

- Non-trivial **interplay** between the two

Calculation of high-pressure hydrogen phase-diagram

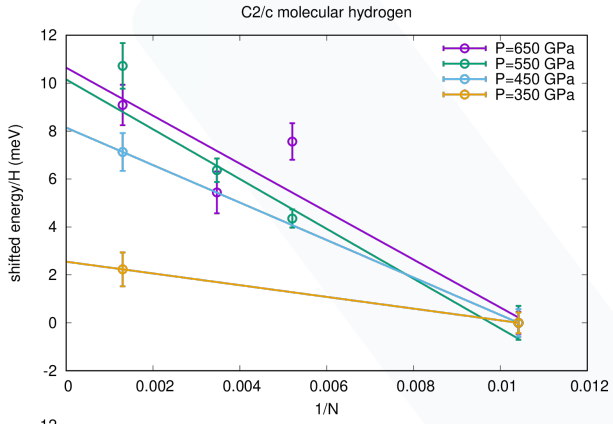
arXiv: 2202.05740: Lorenzo Monacelli, Michele Casula, Kosuke Nakano, Sandro Sorella, Francesco Mauri

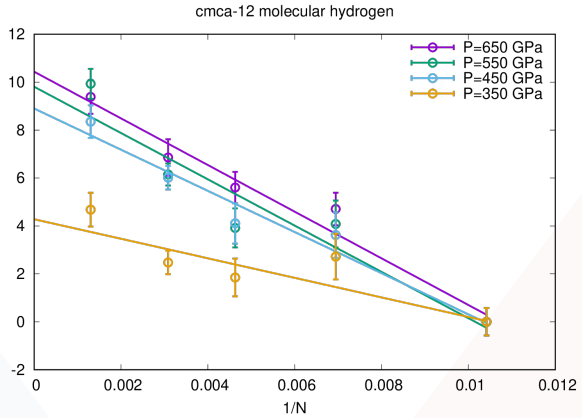


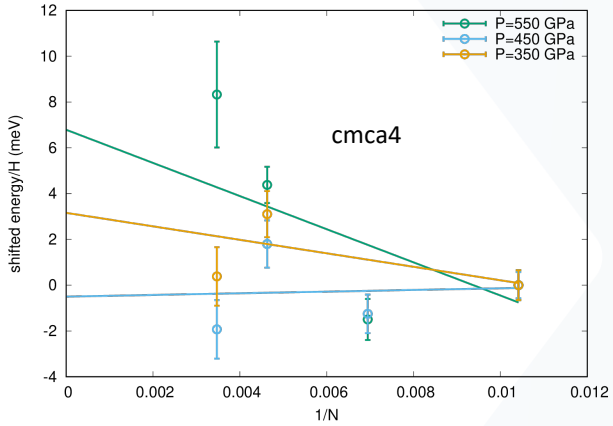
Calculation of high-pressure hydrogen phase-diagram

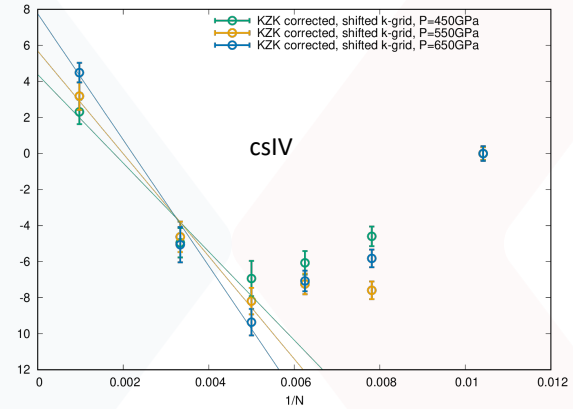
arXiv: 2202.05740: Lorenzo Monacelli, Michele Casula, Kosuke Nakano, Sandro Sorella, Francesco Mauri

Electronic part: DMC
Nuclear part: Stochastic self-consistent harmonic approximation using BLYP









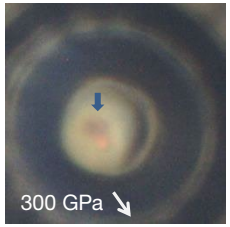
Up to 1024 atoms

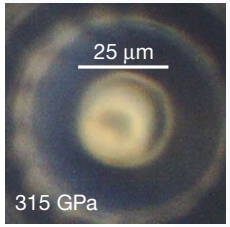
1-2 kcal/mol accuracy

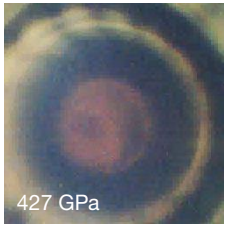
Color from first-principles (reflectivity)

Color from theory

Rendering by Mitsuba2

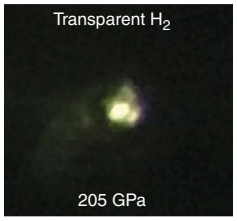


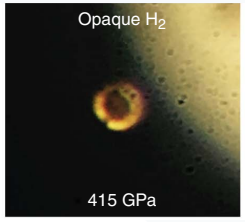


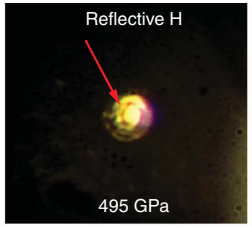


Color from experiment

Loubeyre, Ocelli, Dumas
Nature **577**, 631 (2020)







Color from experiment

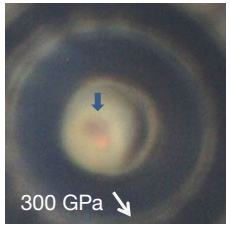
Dias, Silvera
Science **355**, 715 (2017)

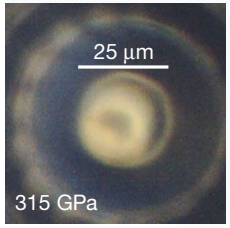
Pressure increase

Color from first-principles (reflectivity)

Color from theory

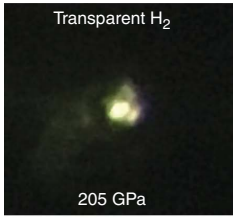
Rendering by Mitsuba2

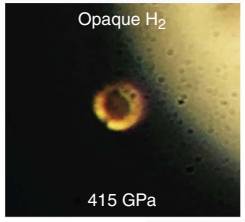


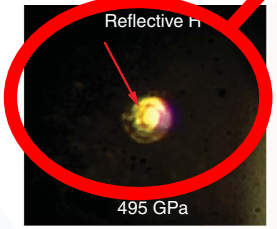


Color from experiment

Loubeyre, Ocelli, Dumas
Nature **577**, 631 (2020)







Color from experiment

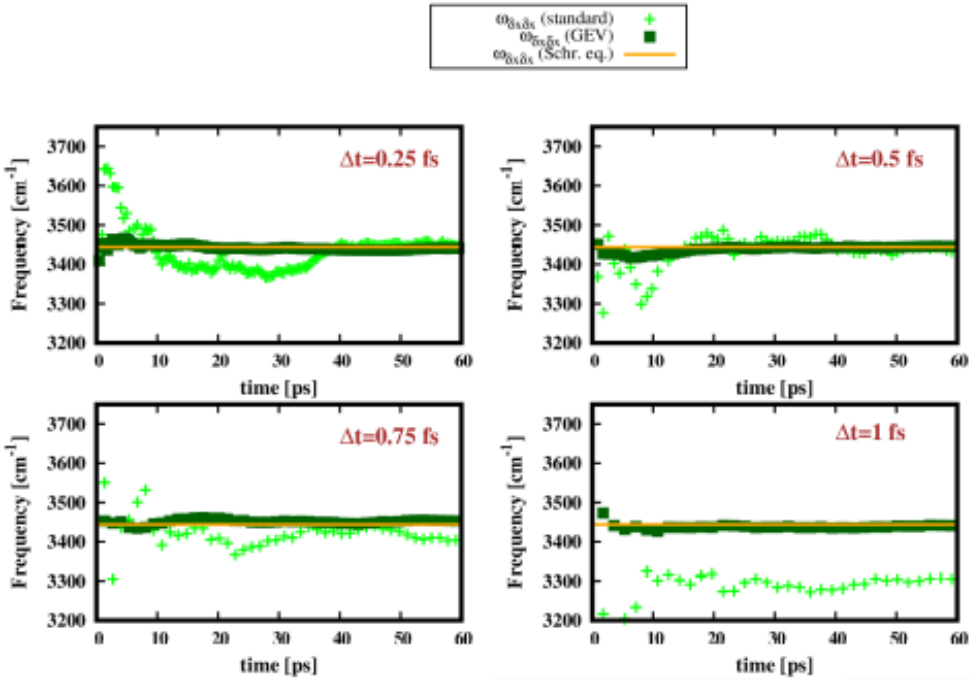
Dias, Silvera
Science **355**, 715 (2017)

Pressure increase

Phonons with quantum anharmonicity

JCP 154, 224108 (2021): Tommaso Morresi, Lorenzo Paulatto, Rodolphe Vuilleumier, Michele Casula

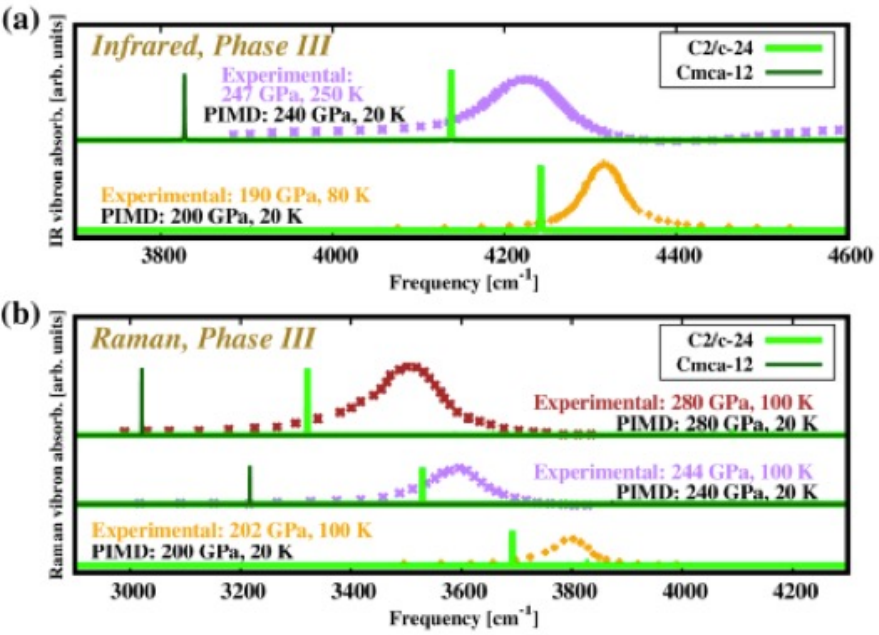
Electronic part: DFT
Nuclear part: Path-integral molecular dynamics (Langevin thermostat)
Phonons by “quantum correlators” (static limit of Matsubara Green’s function)

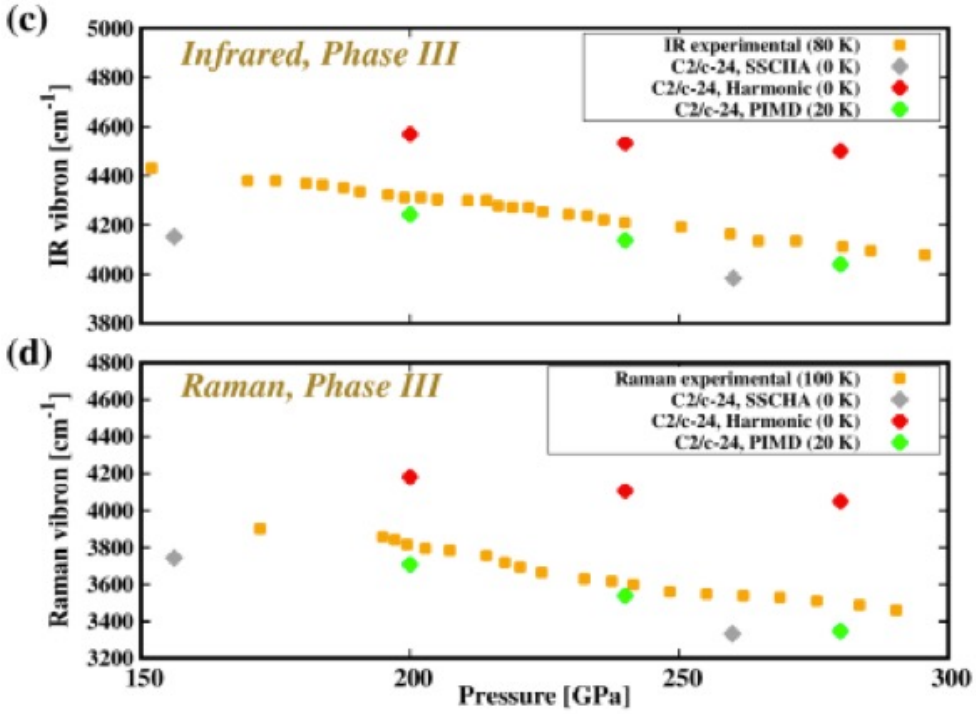


One-order-of-magnitude speedup

Phonons (vibrons) of hydrogen phase III

Ready to be submitted: Tommaso Morresi, Rodolphe Vuilleumier, Michele Casula





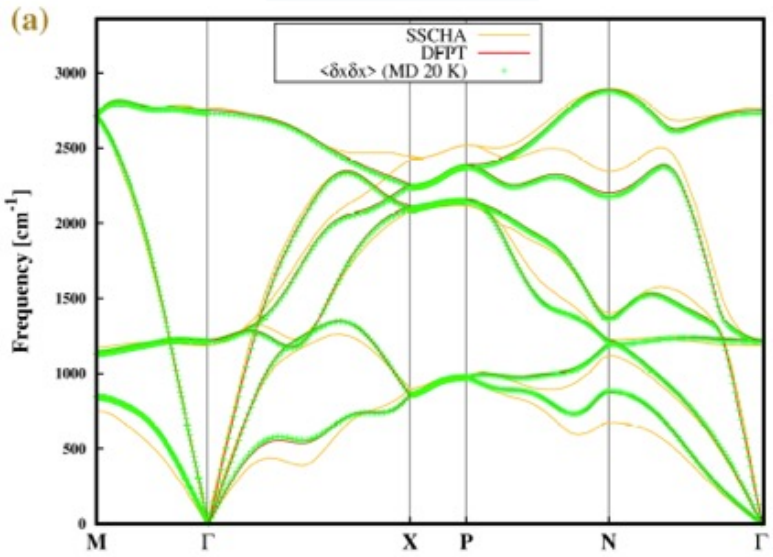
We can reproduce the temperature dependence of the vibron frequency!

Phonons in metallic phase of hydrogen

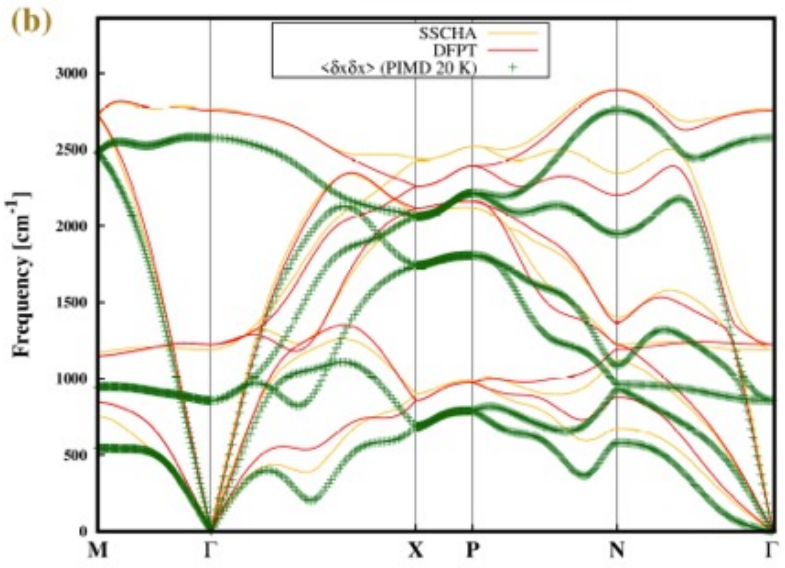
JCP 154, 224108 (2021): Tommaso Morresi, Lorenzo Paulatto, Rodolphe Vuilleumier, Michele Casula

Supercell made by 3 x 3 x 3 unit cells (54 H atoms);
DFT-PBE exchange-correlation functional

Classical MD phonon dispersion *(20 K)*



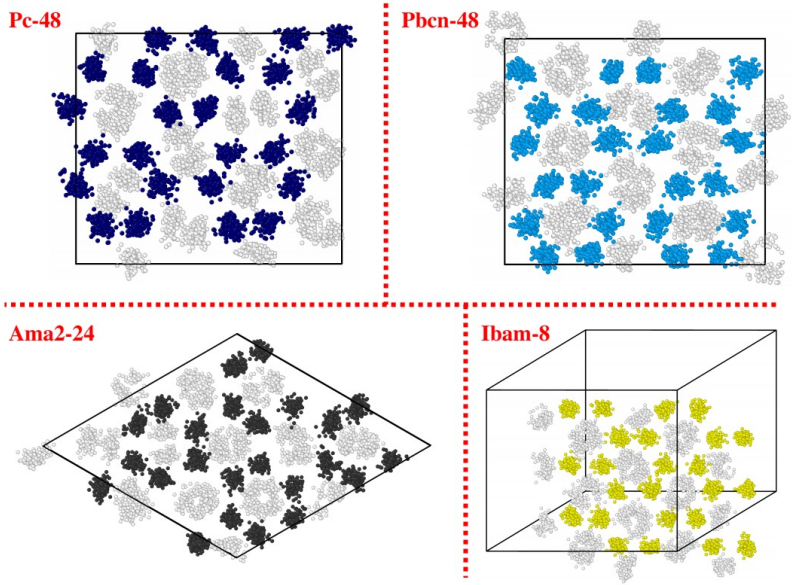
PIMD phonon dispersion *(120 beads; 20 K)*

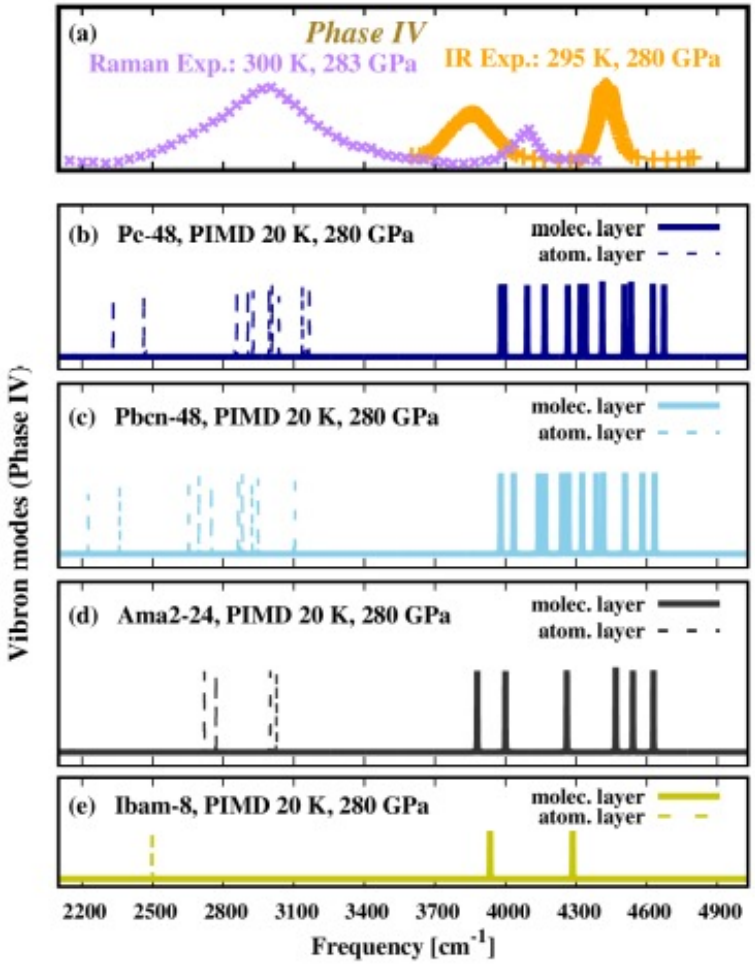


Large quantum effects!!

Phonons (vibrons) of hydrogen phase IV

Ready to be submitted: Tommaso Morresi, Rodolphe Vuilleumier, Michele Casula





Based on the vibron frequency matching with experiment:
Ama2-24 → phase IV

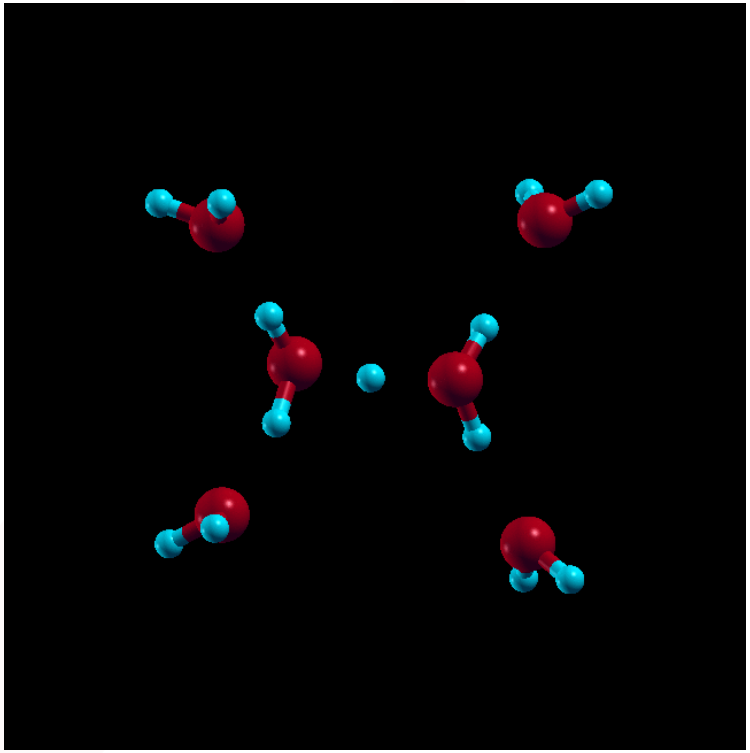
QMC-driven molecular dynamics: protonated water hexamer

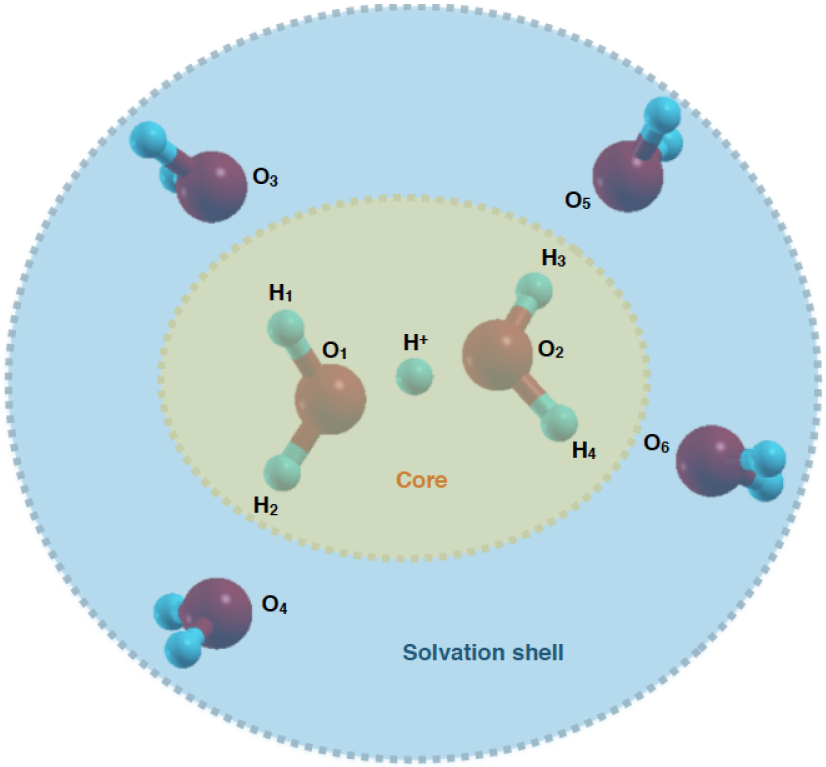
First **path integral molecular dynamics**
of **protonated water hexamer**
driven by **QMC ionic forces**

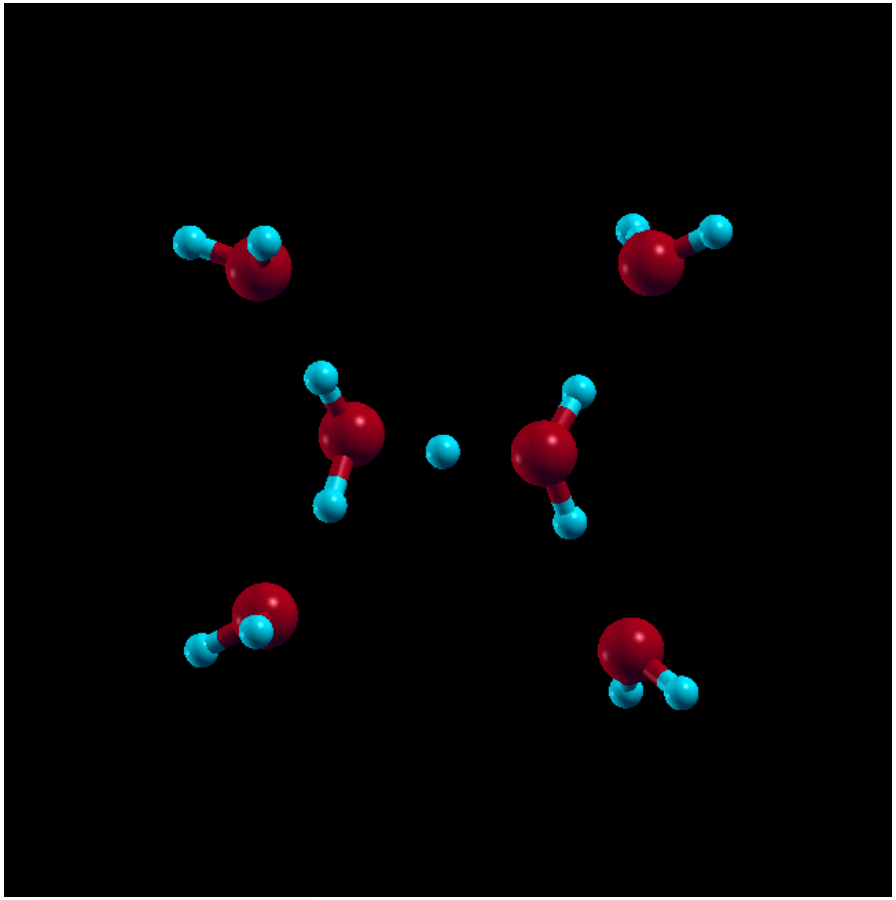
Both ions and electrons are treated quantum!

Hints on the **dynamics of hydrated proton in a correlated framework**

Casula et al. in preparation

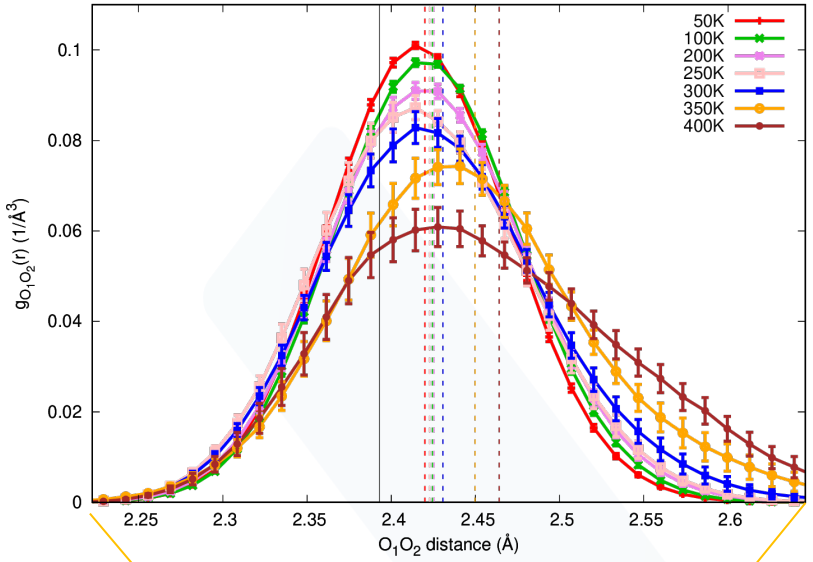


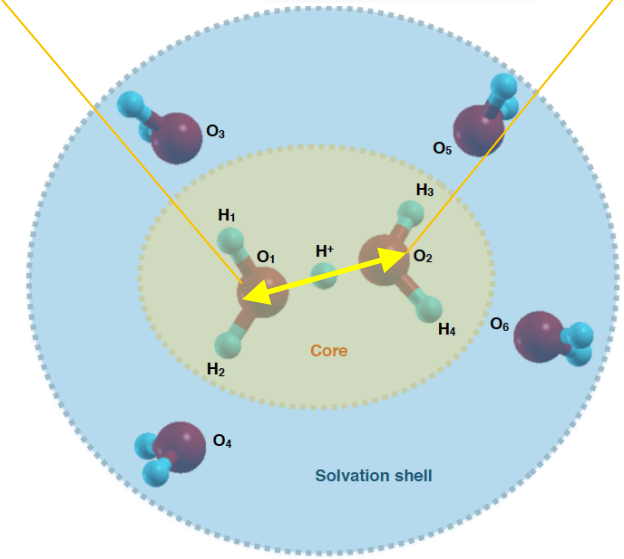




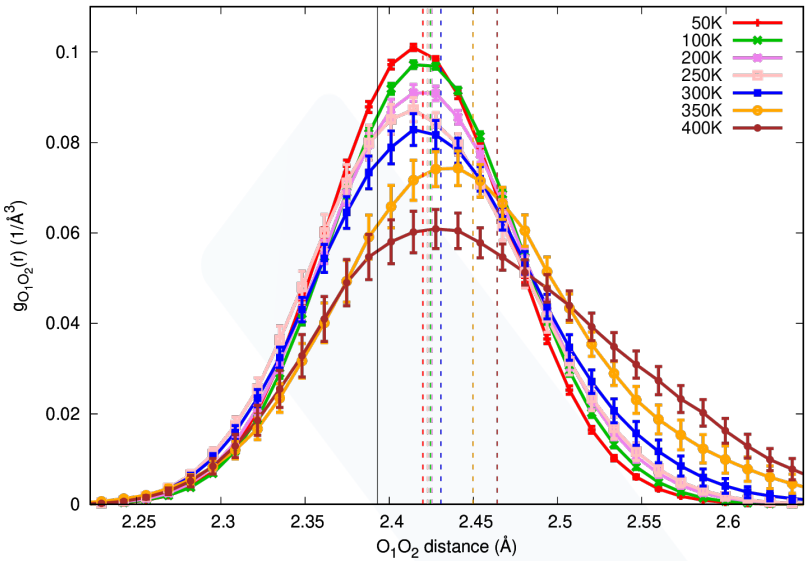
protonated water hexamer $H_{13}O_6^+$ as "realistic" playground to study H-bond and proton hopping

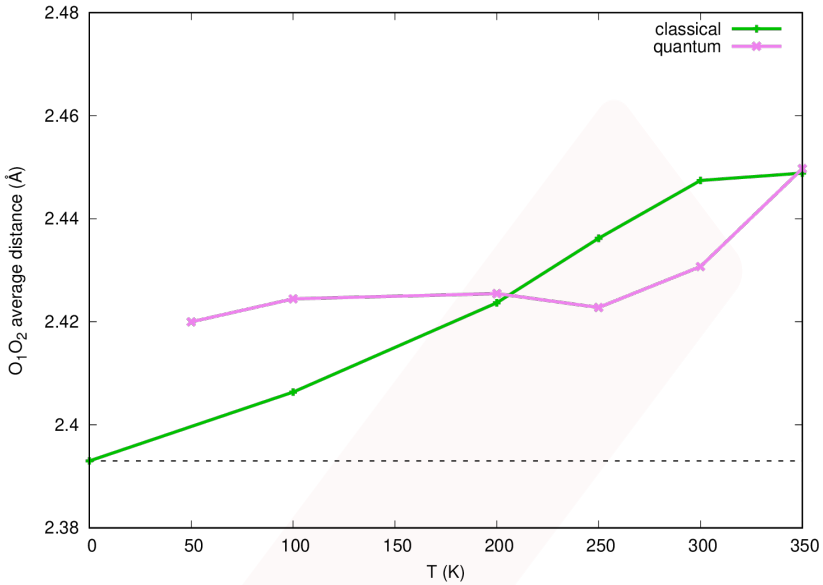
Nuclear quantum effects + temperature



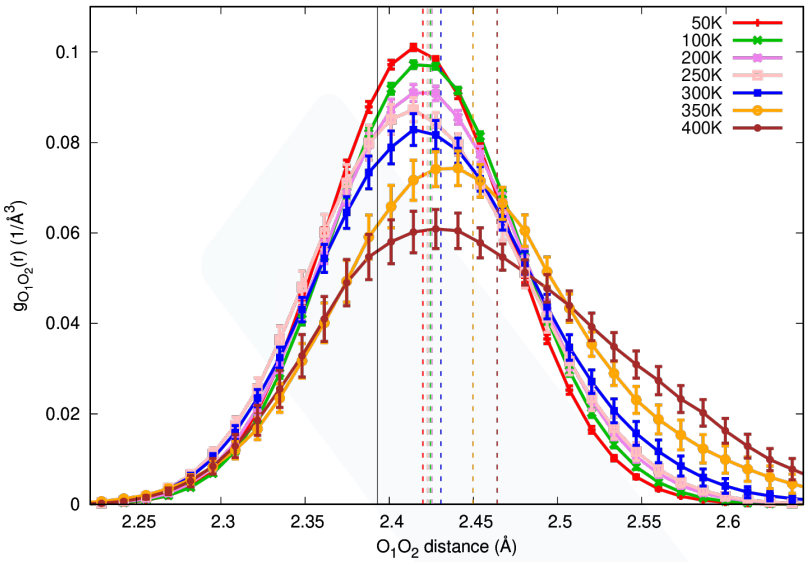


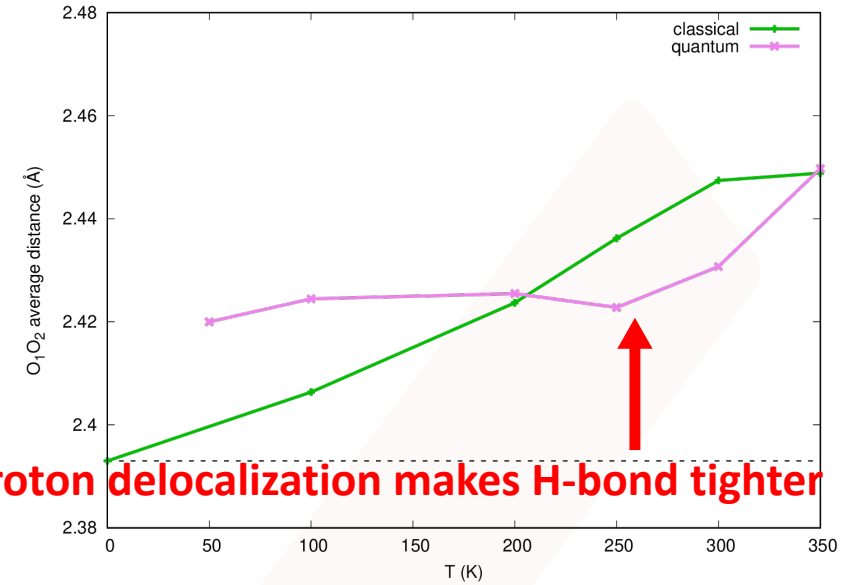
Nuclear quantum effects + temperature





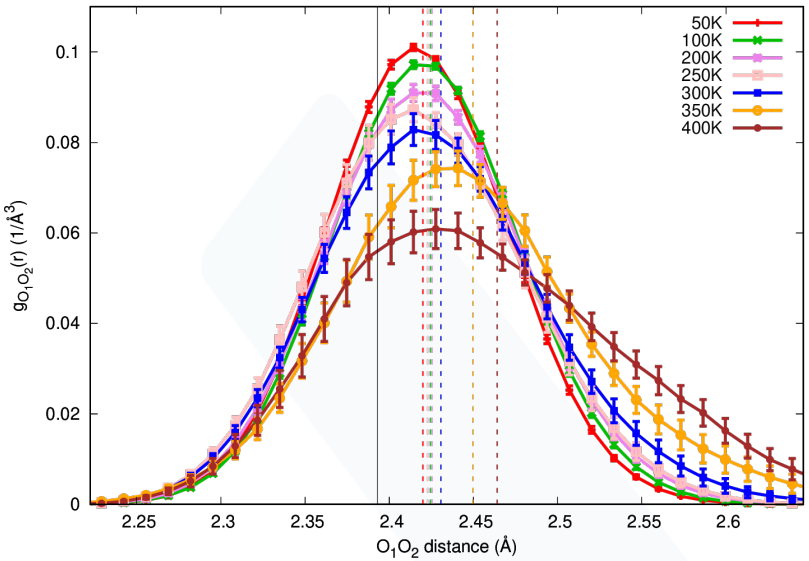
Nuclear quantum effects + temperature

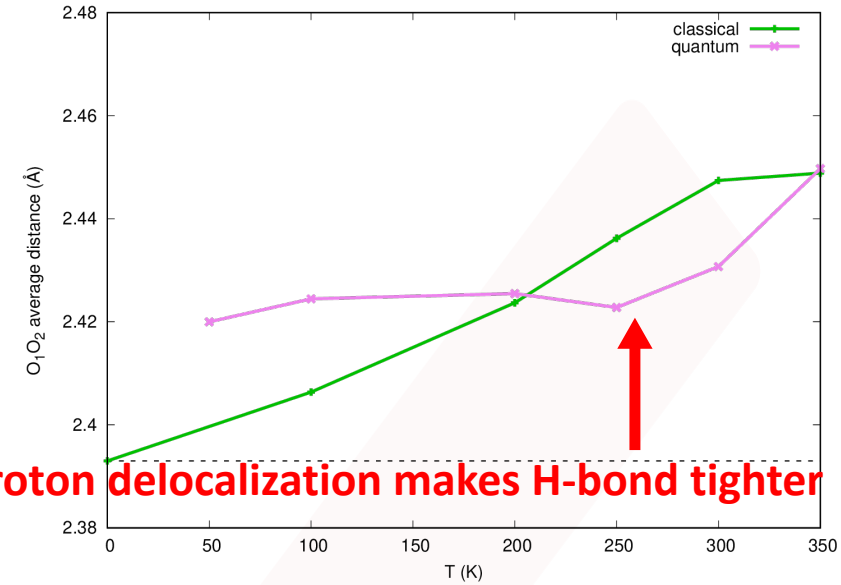




Proton delocalization makes H-bond tighter

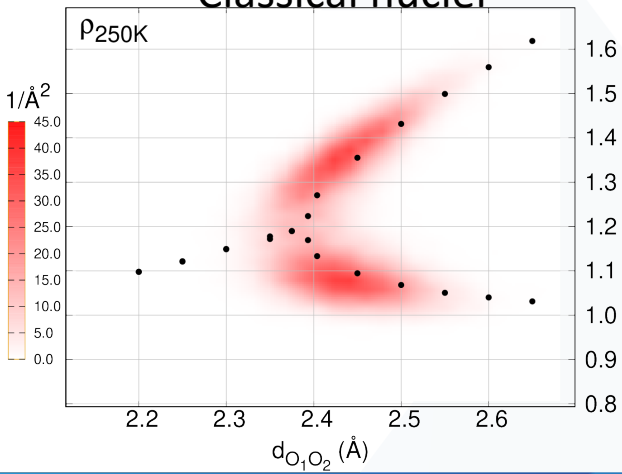
Nuclear quantum effects + temperature



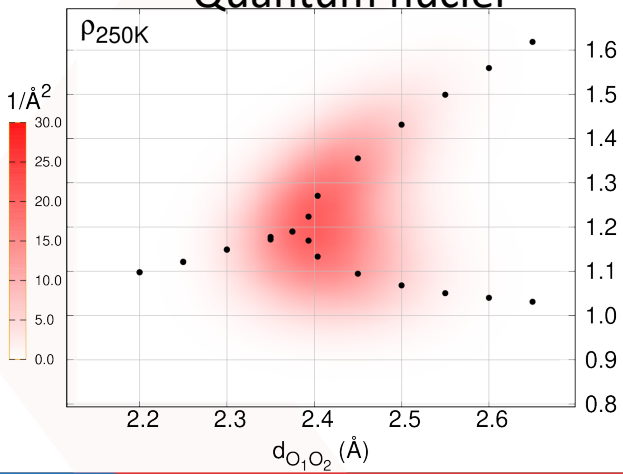


Proton delocalization makes H-bond tighter

Classical nuclei



Quantum nuclei

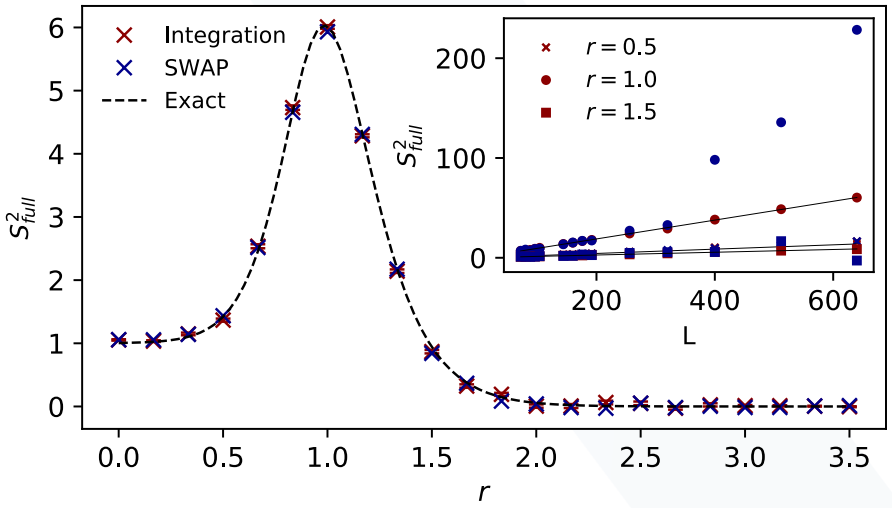


Proton entanglement via Renyi entropy

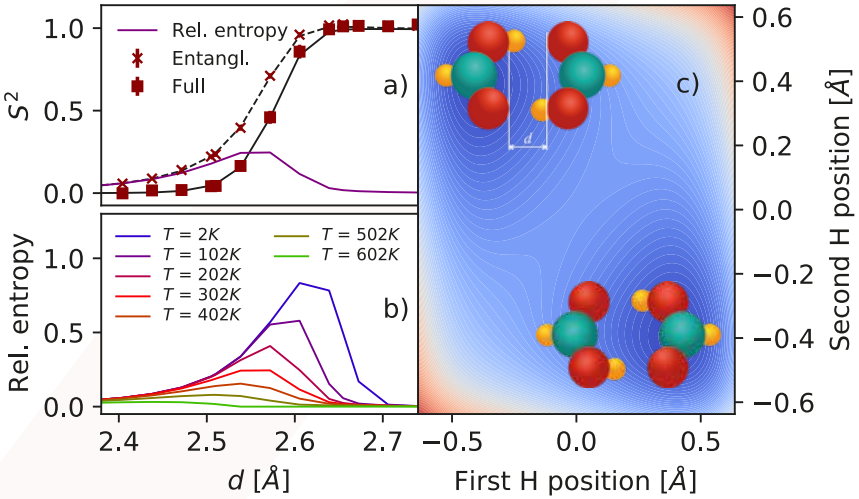
arXiv: 2202.05740: Miha Srdinsek, Michele Casula, Rodolphe Vuilleumier

Thermodynamic integration scheme to compute entanglement in realistic complex systems

$$H = \sum_i \sigma_i^z \sigma_{i+1}^z + r\sigma_i^x$$



Formic acid dimer



Nuclear quantum effects from QMC-based Machine Learning potential energy surfaces:

- Accurate phonon calculations in superconducting hydrides
- From water clusters to bulk water and ice

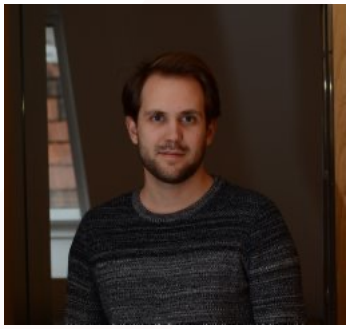
Development of a non-adiabatic electron-nucleus wave function:

- Quantum anharmonicity naturally included in the wave function
- Nuclear forces more easy to compute
- Electron-phonon coupling

Thanks

Romain Taureau

Tommaso Morresi



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