Energy gap closure of crystalline molecular hydrogen with pressure

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Accueil de Chercheurs de Haut Niveau

Metallization of solid hydrogen under pressure

- At low pressure is an insulating molecular crystal
- Does metallisation with pressure occurs into the molecular phase or does it requires a structural transition to a monoatomic crystal ?

DECEMBER, 1935 JOURNAL OF CHEMICAL PHYSICS VOLUME 3

On the Possibility of a Metallic Modification of Hydrogen

E. WIGNER AND H. B. HUNTINGTON, *Princeton University*

(Received October 14, 1935)

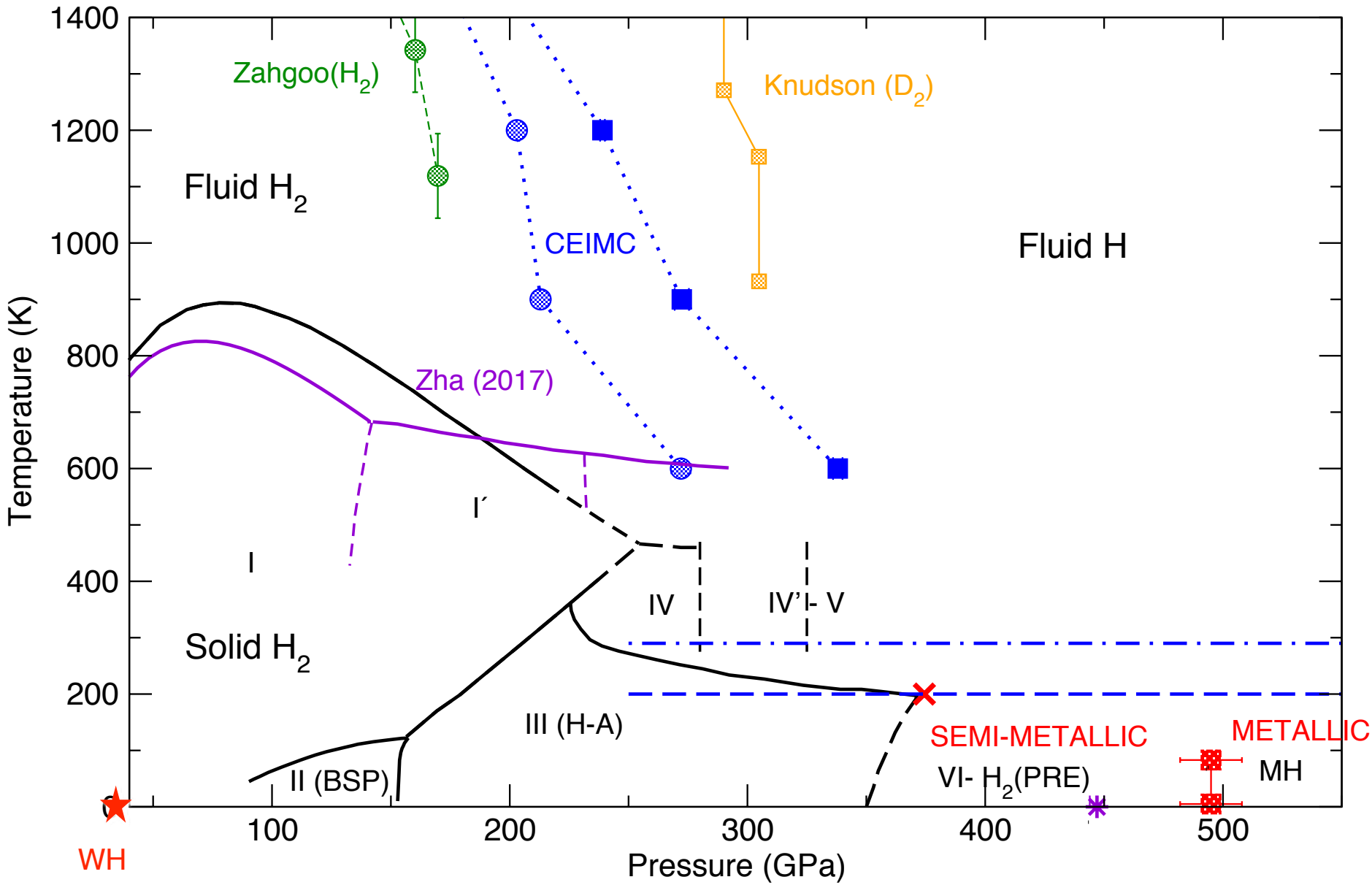
Any lattice in which the hydrogen atoms would be translationally identical (Bravais lattice) would have metallic properties. In the present paper the energy of a body-centered lattice of hydrogen is calculated as a function of the lattice constant. This energy is shown to assume its minimum value for a lattice constant which corresponds to a density many times higher than that of the ordinary, molecular lattice of solid hydrogen. This minimum—though negative—is much higher than that of the molecular form. The body-centered modification of hydrogen cannot be obtained with the present pressures, nor can the other simple metallic lattices. The chances are better, perhaps, for intermediate, layer-like lattices.

BCC could be stable for P>25GPa

layer-like structures might be stable at lower P

Still today open questions remains?

Hydrogen molecular crystals



G. Rillo, M.A. Morales, D.M. Ceperley and C. Pierleoni, *J. Chem. Phys.* 148, 102314 (2018).

the first announcement of experimental realisation of metallic hydrogen in 2017

HIGH-PRESSURE PHYSICS

Science **355**, 715–718 (2017) 17 February 2017

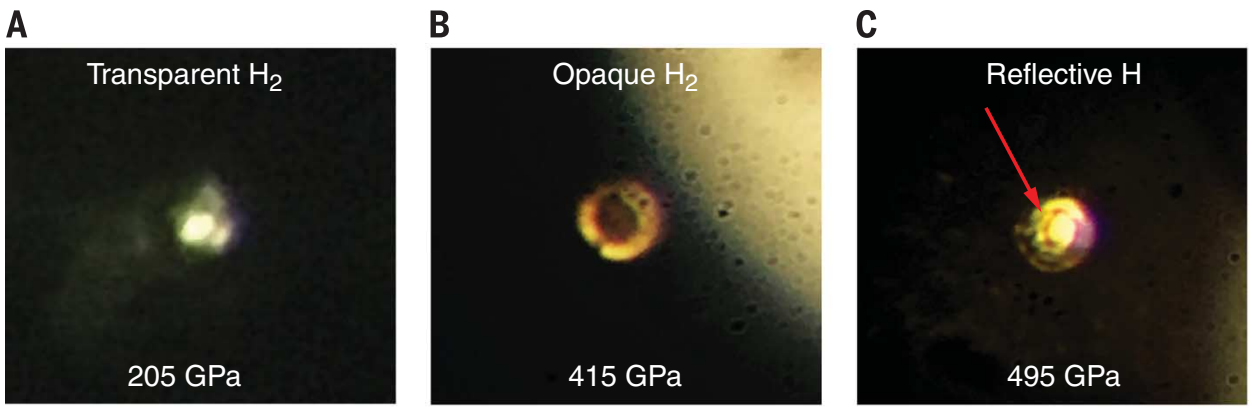
Observation of the Wigner-Huntington transition to metallic hydrogen

Detected by optical measurements

Ranga P. Dias and Isaac F. Silvera*

Producing metallic hydrogen has been a great challenge in condensed matter physics. Metallic hydrogen may be a room-temperature superconductor and metastable when the pressure is released and could have an important impact on energy and rocketry. We have studied solid molecular hydrogen under pressure at low temperatures. At a pressure of 495 gigapascals, hydrogen becomes metallic, with reflectivity as high as 0.91. We fit the reflectance using a Drude free-electron model to determine the plasma frequency of 32.5 ± 2.1 electron volts at a temperature of 5.5 kelvin, with a corresponding electron carrier density of 7.7 ± 1.1 × 10^{23} particles per cubic centimeter, which is consistent with theoretical estimates of the atomic density. The properties are those of an atomic metal. We have produced the Wigner-Huntington dissociative transition to atomic metallic hydrogen in the laboratory.

T<100K

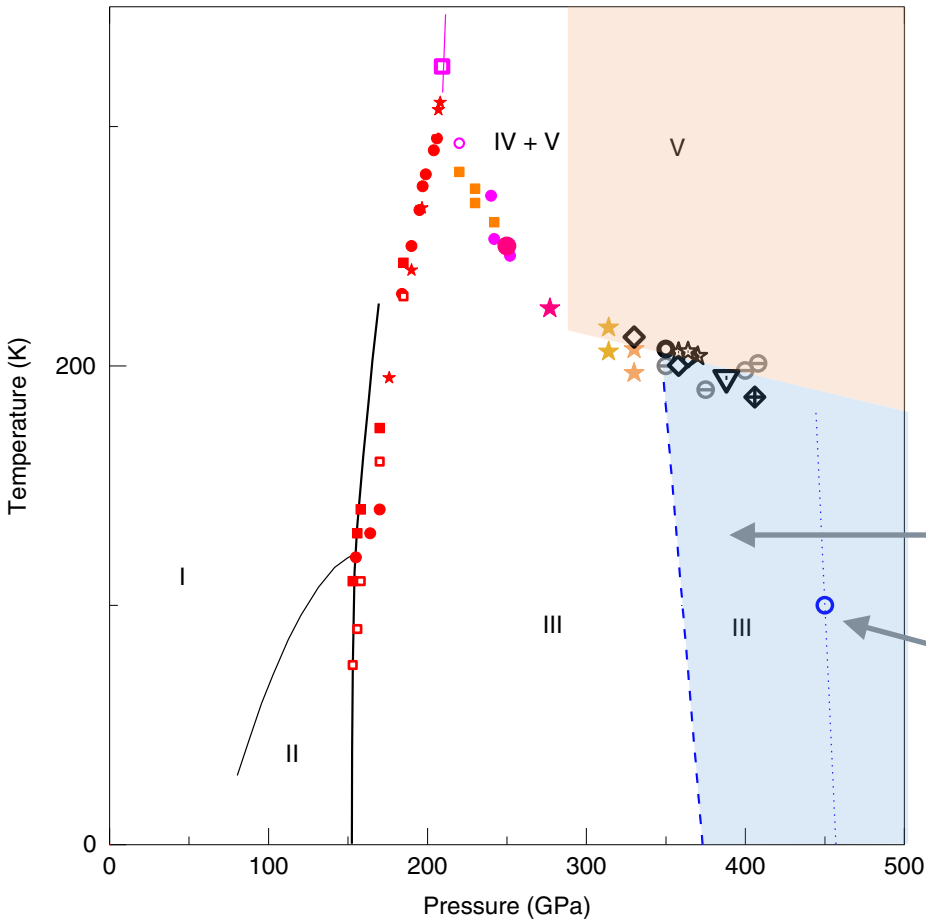


nature physics
LETTERS
https://doi.org/10.1038/s41567-019-0646-x

Semimetallic molecular hydrogen at pressure above 350 GPa

M. I. Eremets*, A. P. Drozdov, P. P. Kong and H. Wang

Nature Physics 2019



Semi-metallic domain of Phase III

vanishing of the molecular Raman signal: structural transition or direct gap closure?

Fig. 1 | Low-temperature part of the phase diagram of hydrogen. The domains of the different phases are indicated by Roman numerals (see ref. [12] for details). The black experimental points were obtained in the present work as described in Supplementary Fig. 5. The other points are from ref. [12]. The different colours and symbols indicate different experimental runs. The shaded blue region indicates the domain of the molecular but metallic (semimetallic) hydrogen in phase III; the shaded orange region indicates the domain of phase V. A point at ~450 GPa and 100 K indicates a possible boundary with the next non-molecular phase (or good metallic molecular state) as signatures of hydrogen molecules in the Raman spectra disappeared at higher pressures; the *P*,*T* boundary is tentatively outlined by the dotted line.

The strain in the anvil limits the pressure of the standard DAC to about 400GPa

New geometries (toroidal) allows to go up to ~1TPa …

ARTICLE

DOI: 10.1038/s41467-018-05294-2 OPEN NATURE COMMUNICATIONS | (2018)

Toroidal diamond anvil cell for detailed measurements under extreme static pressures

Agnès Dewaele[1], Paul Loubeyre[1], Florent Occelli[1], Olivier Marie[1] & Mohamed Mezouar[2]

… and the use of X-ray synchrotron radiation allow new investigations

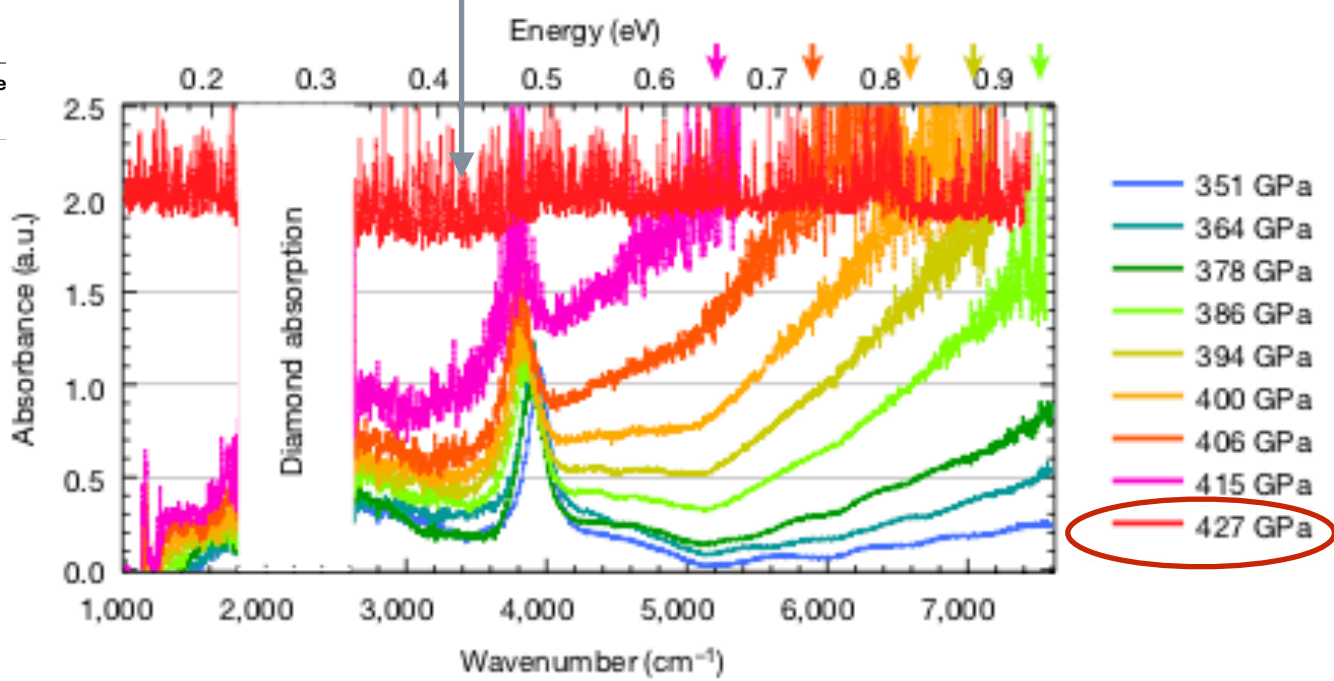
Synchrotron infrared spectroscopic evidence of the probable transition to metal hydrogen

https://doi.org/10.1038/s41586-019-1927-3

Received: 12 April 2019

Paul Loubeyre[1]*, Florent Occe

Full absorbance: direct gap closure



Problems for theory of hydrogen

1) Crystalline structures are unknown: they need to be guessed

2) DFT is the work-horse but its electronic solution is not really predictive. Different functionals need to be benchmarked against more fundamental theories like QMC.

3) We need to sample coupled electron-proton systems in a predictive way.

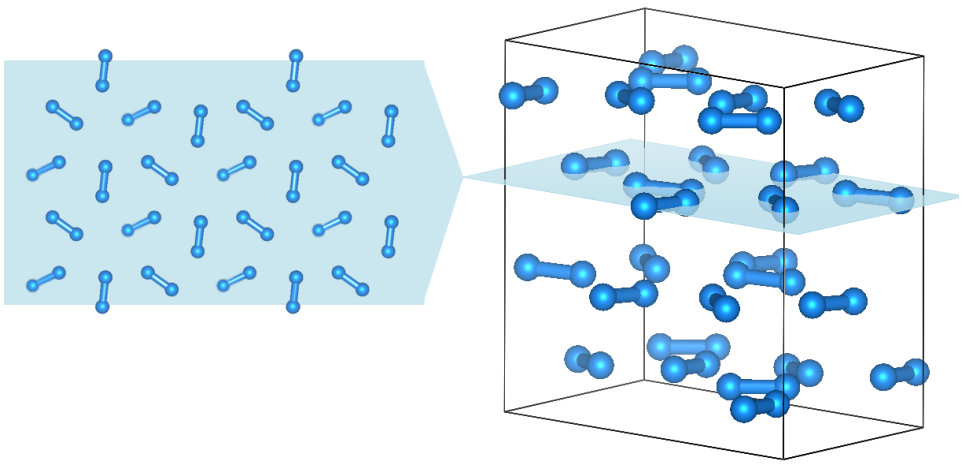
4) Nuclear Quantum effects are very large and need to be treated accurately.

5) We relay on BO approximation: is it appropriate?

6) We would like to have access not only to nuclear but also to electronic properties (like optical responses) with predictive accuracy.

Cristalline structures: Phases III - Metallic Hyd.

C_2/c-24



Best structures according to Ab-Initio Random Structure Search with GGA-PBE and zero point energy accounted by Self-consistent harmonic approximation

Pickard-Needs, Nature Physics 3, 473 (2007)
McMahon, Ceperley PRL 106, 165302 (2011)

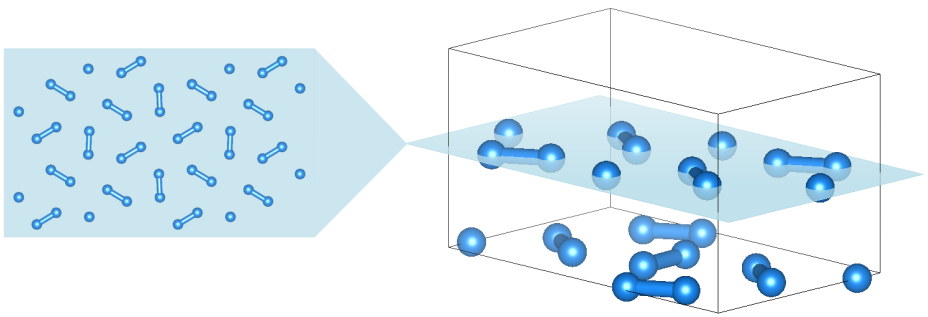
Ground State Prediction (QMC+DFTHA)

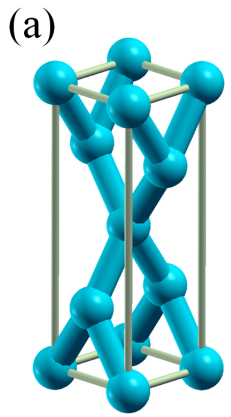
McMinis et al PRL, 2015:

P<450 GPa C_2/c

P>450GPa CsIV

Cmca12





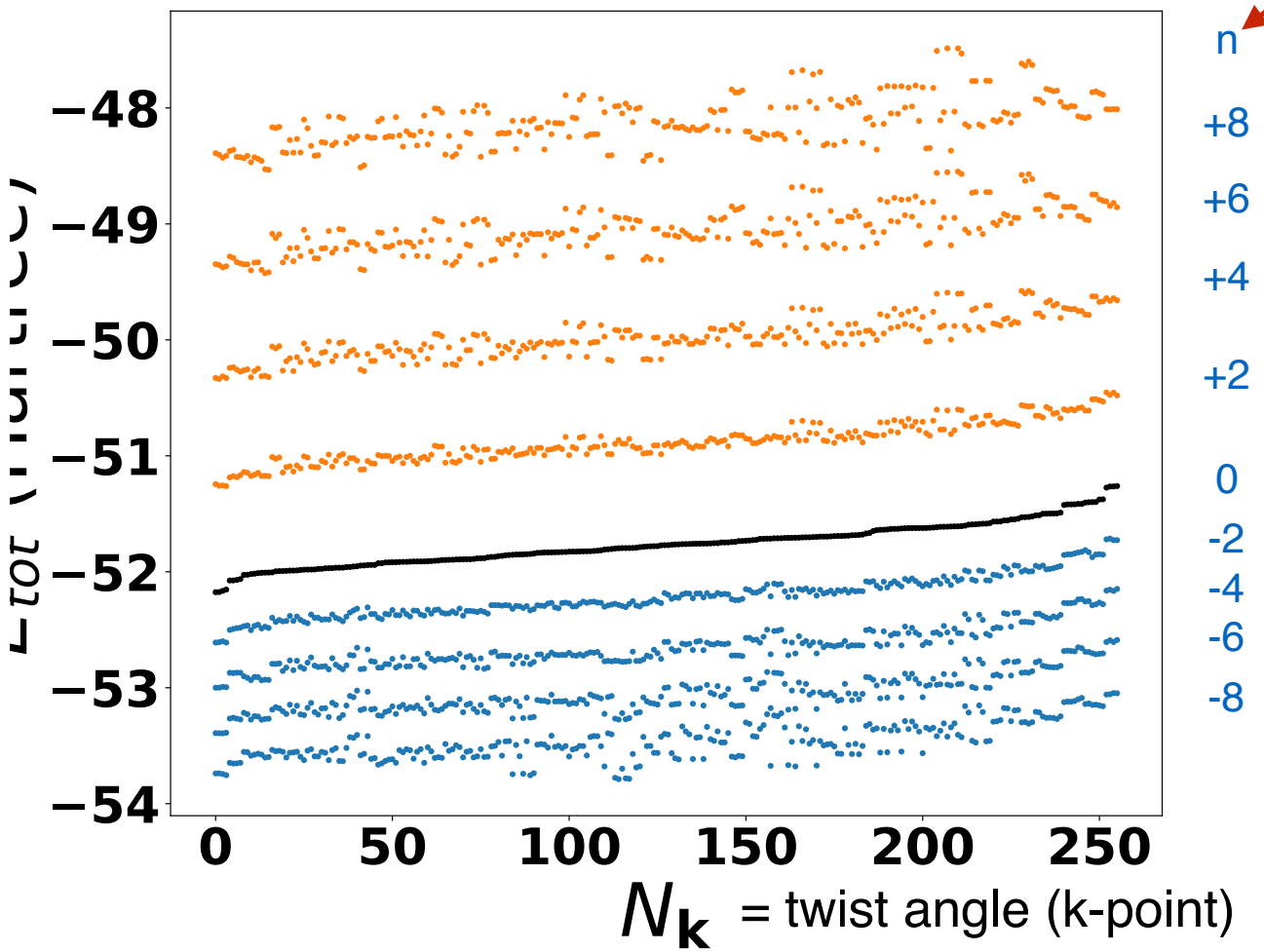
Cs-IV (up to 1200GPa)

Fundamental gap by QMC

fundamental gap: $$\Delta_{qp} = \lim_{N\to\infty} \{[E_0(N+1) - E_0(N)] - [E_0(N) + E_0(N-1)]\} = \mu^+ - \mu^-$$

Twisted-boundary Grand Canonical QMC analysis.

- For fixed nuclei we run RQMC/DMC electronic calculations with $N_e \in [N_p - n, N_p + n]$ electrons and a 3D regular grid of twist angles θ.



Hydrogen Ideal crystal
C2/c-24 P=248GPa,
$N_p = 96$

Total energy (hartrees): each point is a different RQMC calculation

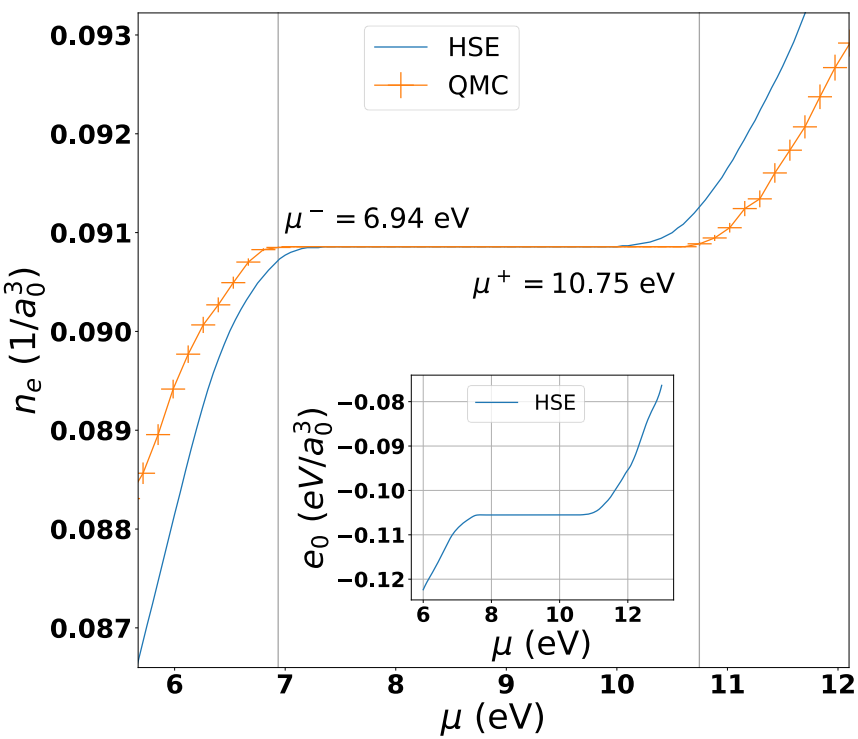
In the Grand-Canonical ensemble at T=0K, the equilibrium state corresponds to

$$\Omega(\mu,\theta) = \min_n \left[E(N+n,\theta) - \mu(N+n)\right]$$

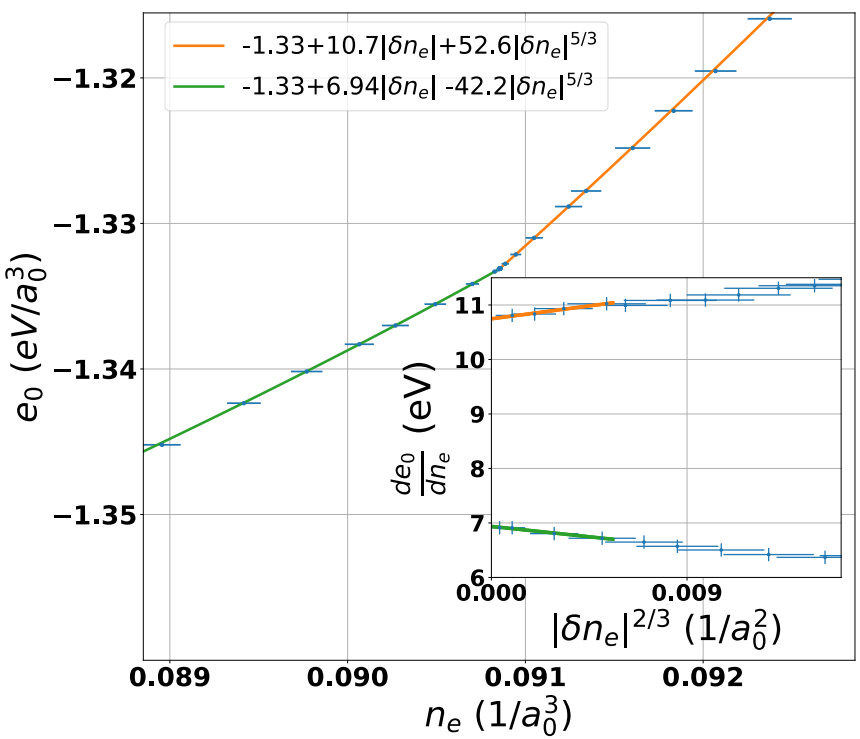
At fixed μ, it implies that the optimal number of electrons depends on the twist: $\bar{n}(\theta,\mu) \Longrightarrow E(N+\bar{n},\theta)$

Averaging over twists ($\langle \ldots \rangle_\theta$) at fixed μ and inverting the relation between $\langle \bar{n} \rangle_\theta$ and μ the gap is

$$\Delta_{qp} = \mu^+ - \mu^- \simeq \left.\frac{d\langle E\rangle_\theta}{d\langle \bar{n}\rangle_\theta}\right|_{0+} - \left.\frac{d\langle E\rangle_\theta}{d\langle \bar{n}\rangle_\theta}\right|_{0-}$$



(a)



(b)

Y. Yubo, V. Gorelov, Pierleoni, Ceperley, Holzmann, Electronic band gaps from Quantum Monte Carlo methods, PRB 101, 085115 (2020).

V. Gorelov, M. Holzmann, DM Ceperley and C. Pierleoni, Energy gap closure of crystalline molecular hydrogen with pressure , PRL (2020).

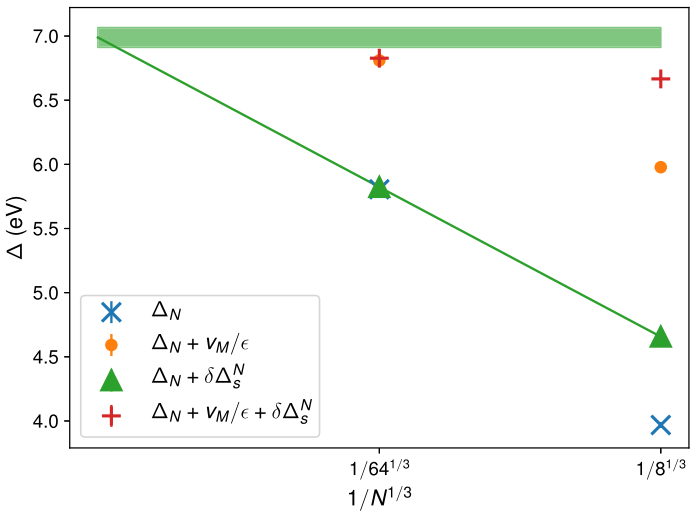
Correcting finite size effects is crucial for accurate predictions

PHYSICAL REVIEW B **101**, 085115 (2020)

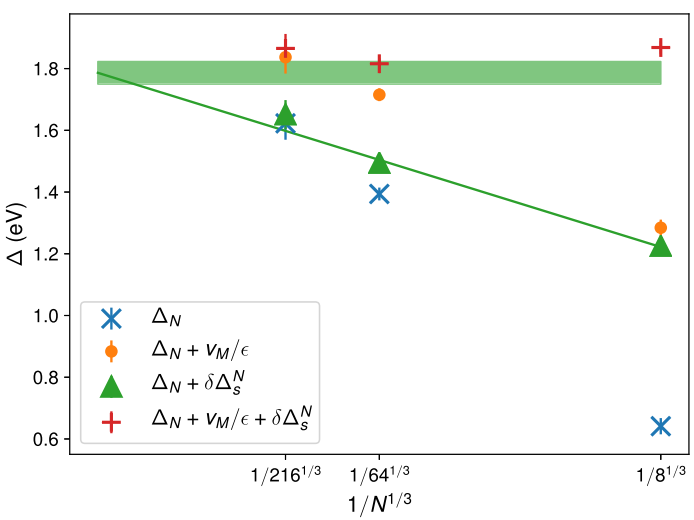
Editors' Suggestion

Electronic band gaps from quantum Monte Carlo methods

Yubo Yang (杨煜波),[1] Vitaly Gorelov,[2] Carlo Pierleoni,[2,3] David M. Ceperley,[1] and Markus Holzmann[4,5]



(a) carbon



(b) silicon

- The main correction to total energy is encoded into S(k)
- The main correction to the fundamental gap is encoded in

$$\lim_{k\to 0} S_k^{\pm} = \alpha_{\pm} + \mathcal{O}(k^2), \tag{11}$$

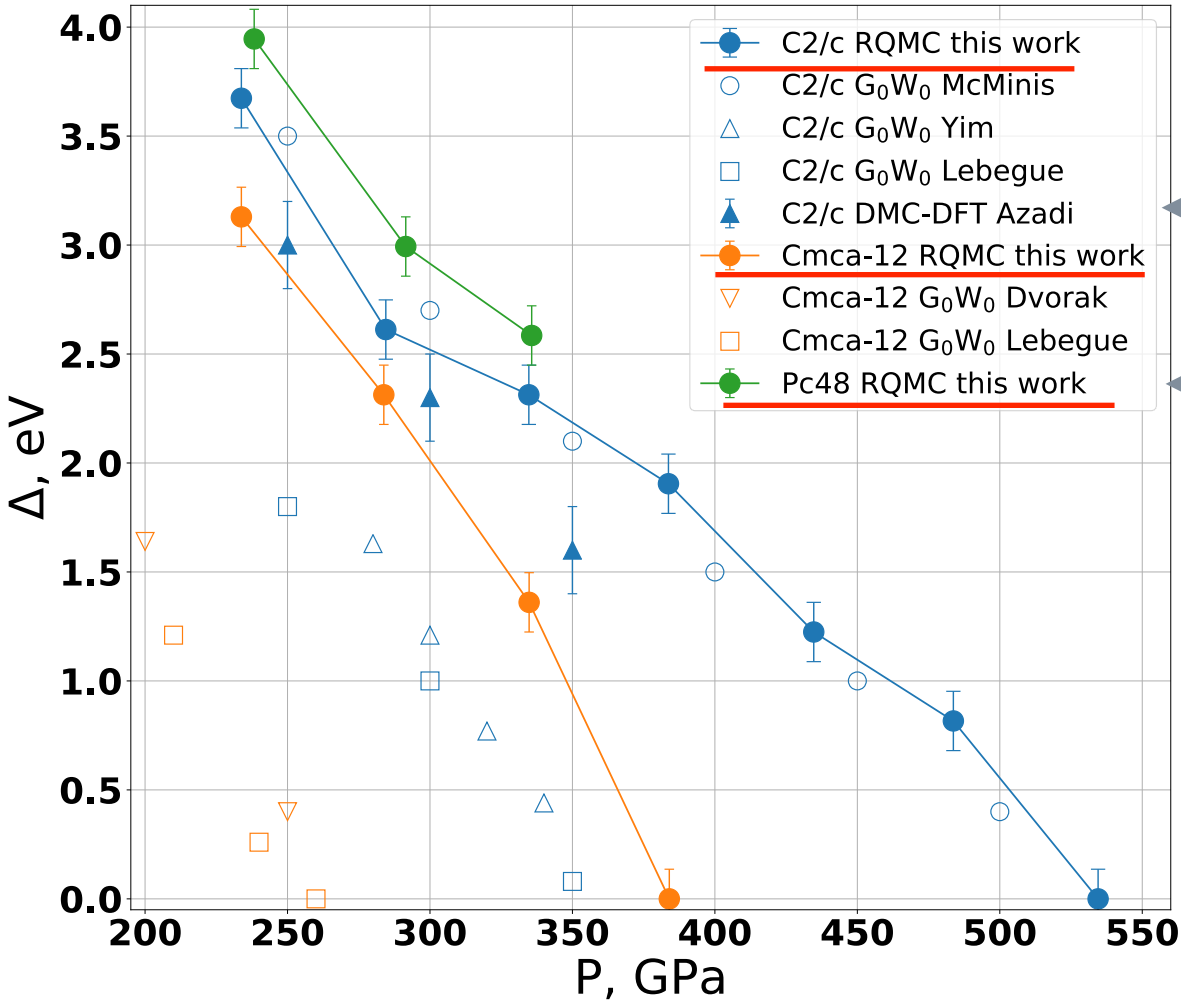
$$S_k^{\pm} \equiv (N_e \pm 1)S_{N_e\pm 1}(k) - N_e S_{N_e}(k), \tag{12}$$

comparison with experiments

	Δ_{BF}	AE - PP	e-ph	exp
C	6.6(2)	−0.26 (G_0W_0) [54]	−0.6 (GW) [56]	5.48 [67]
Si	1.7(1)	−0.25 (G_0W_0)[54]	−0.06 (DFT) [57]	1.17 [67]

Hydrogen fundamental gap for ideal structures

V. Gorelov, M. Holzmann, DM Ceperley and C. Pierleoni, PRL (2020).



(structures optimized with vdW-DF)

Phase III

QMC+scissor correction (2018)

Phase IV

RQMC calculation for a 96 protons supercell and size corrections to extrapolate to the TL

- Excellent agreement with GW gaps from McMinis (same structures)
- Good agreement with previous QMC estimates (Azadi et al, PRB 2017) but …
- other GW calculations predict smaller gap (1-2 eV smaller) but use different structures.

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

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

- ***HPC Tier-0 systems are now available for this generation of calculations and will be even more so in the near future (exascale).***

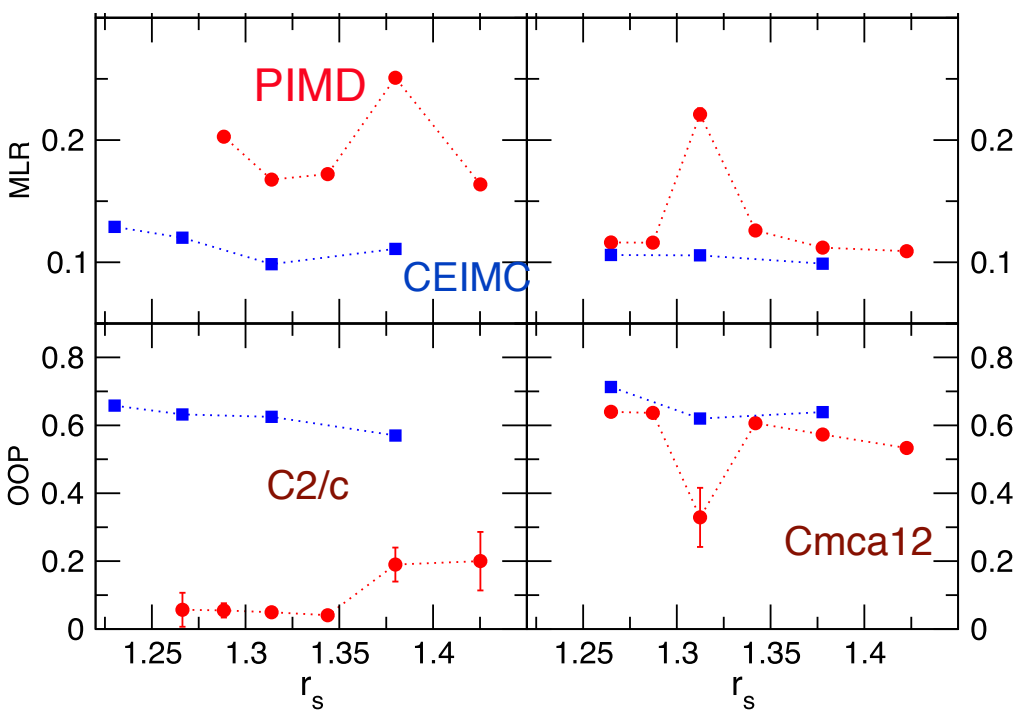
Pierleoni & Ceperley,
Lect Notes Phys. 703, 641 (2006)

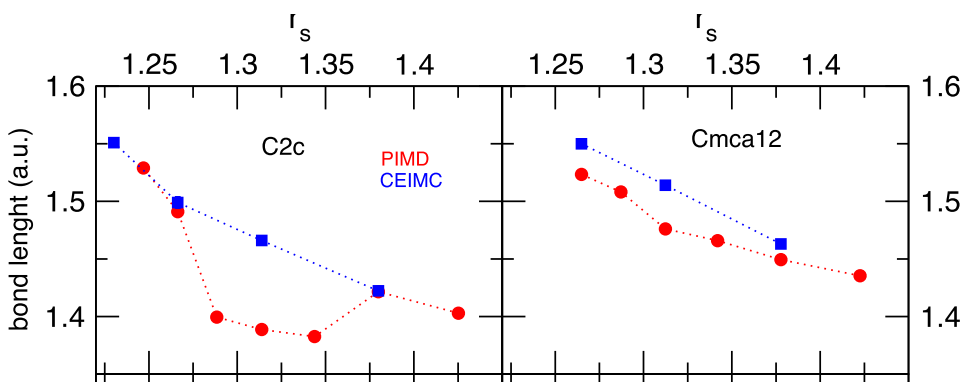
Coupled electron-ion Monte Carlo simulation of hydrogen molecular crystals

Giovanni Rillo,[1] Miguel A. Morales,[2] David M. Ceperley,[3] and Carlo Pierleoni[4,5,a)]

- CEIMC vs PIMD-vdW-DF1: PES from vdW-DF1 is less structured than the one from QMC

- higher proton mobility from PIMD than from CEIMC
- the comparison depends on the structures
- DFT has smaller barriers for molecular rotation and between different structures, hence exhibits different temperature effects.
- DFT provides larger molecular vibration (librations and MSD) and longer bonds.





Hydrogen gap for thermal crystals

V. Gorelov, M. Holzmann, DM Ceperley and C. Pierleoni, PRL (2020), arXiv:1911.06135

The fundamental gap is defined now in terms of the free Helmholtz energy

$$\Delta_{gc} = \mu_+ - \mu_- = \left.\frac{df}{dn_e}\right|_{n_p^+} - \left.\frac{df}{dn_e}\right|_{n_p^-} . \qquad (13)$$

which with very good accuracy can be estimated as

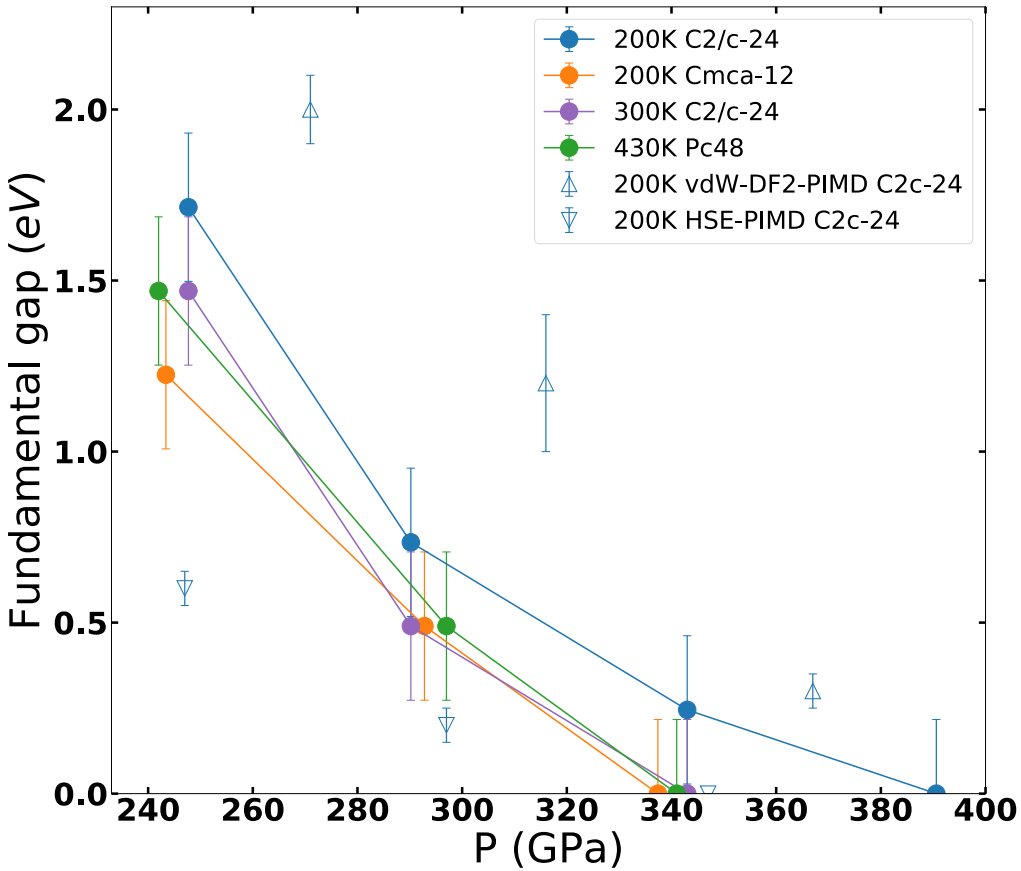
$$\Delta_{gc} = \mu_+ - \mu_- \simeq \left.\frac{d\langle e(n_e(\mu))\rangle_{N_p}}{dn_e}\right|_{n_p^+} - \left.\frac{d\langle e(n_e(\mu))\rangle_{N_p}}{dn_e}\right|_{n_p^-} \qquad (18)$$

where $\langle \ldots \rangle_{N_p}$ indicates an average performed over the BO surface with $N_e = N_p$ electrons.

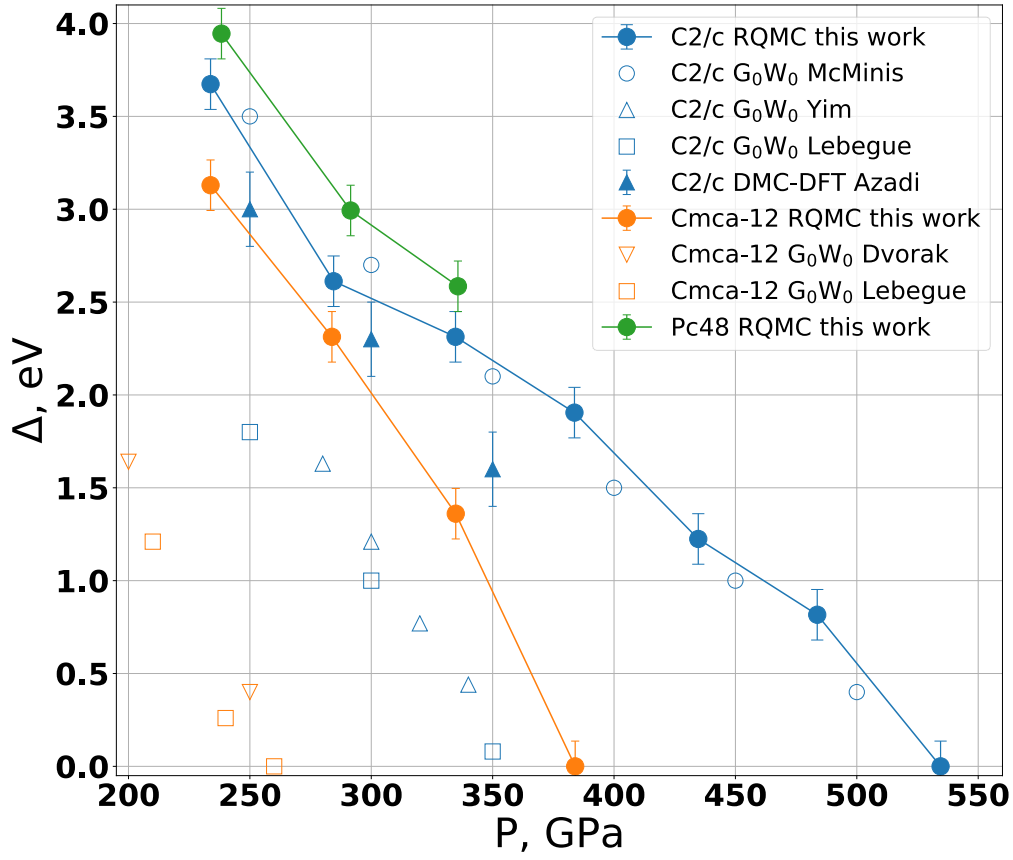
WARNING: this is not equivalent of taking the nuclear averages of the derivatives !!

Nuclear quantum and thermal effects

thermal crystals



Ideal crystals

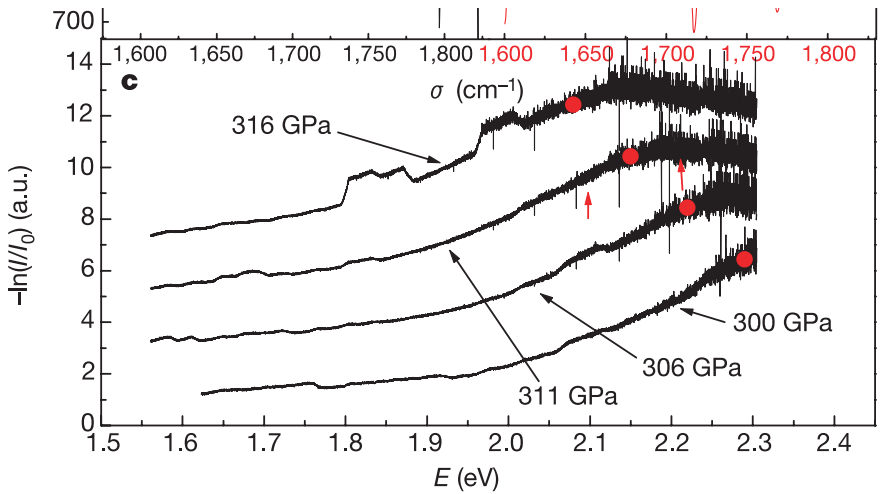


- The fundamental gap closes between 340GPa and 380GPa, depending on structure and temperature (temperature dependence is small).
- The gap reduction (~2-2.5eV) mainly comes from nuclear quantum effects.
- Agreement with recent experimental finding of semi-metal at 360GPa (Eremets 2019).
- PIMD-vdW-DF2 is less “metallic” than QMC, while PIMD-HSE is more “metallic”(Morales 2013).

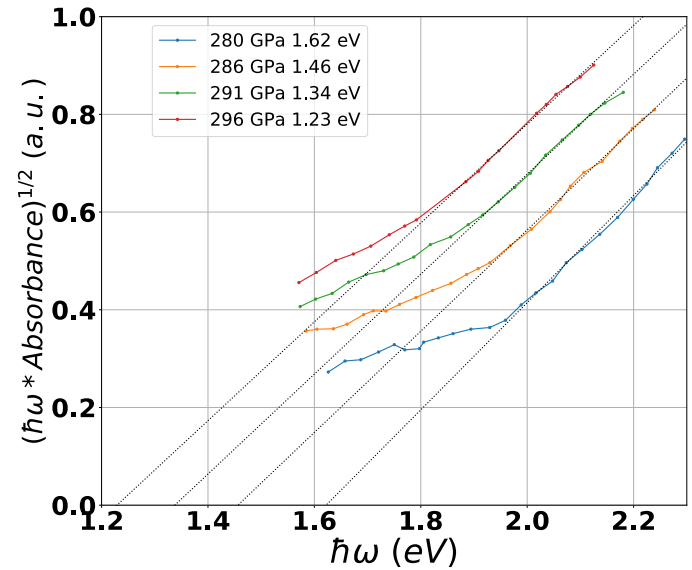
Optical studies of solid hydrogen to 320 GPa and evidence for black hydrogen

Paul Loubeyre*, Florent Occelli* & René LeToullec*†

NATURE | VOL 416 | 11 APRIL 2002 | www.nature.com



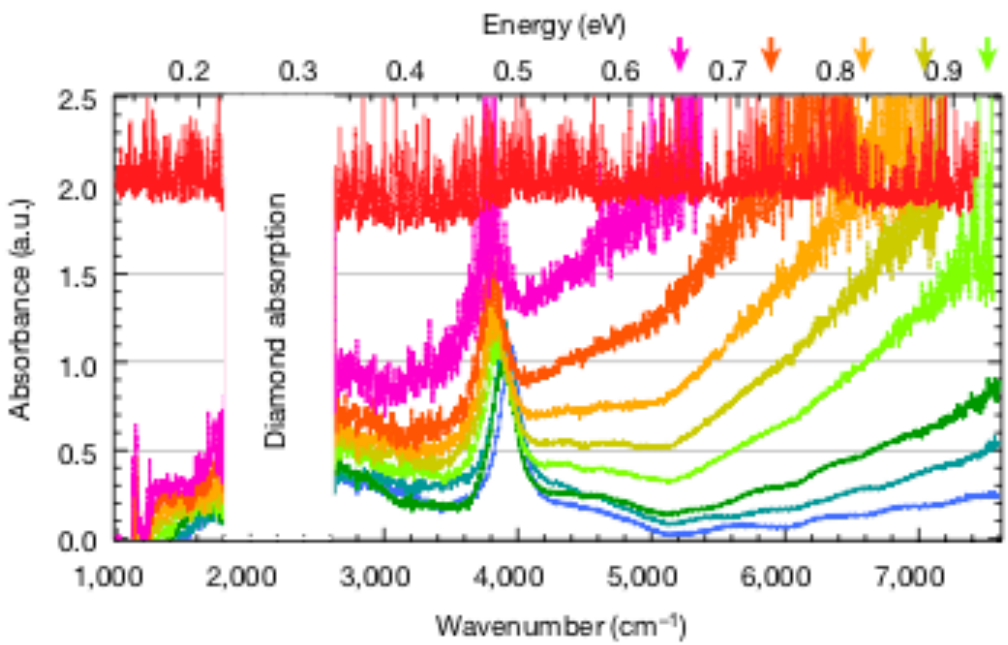
Tauc analysis for indirect gap

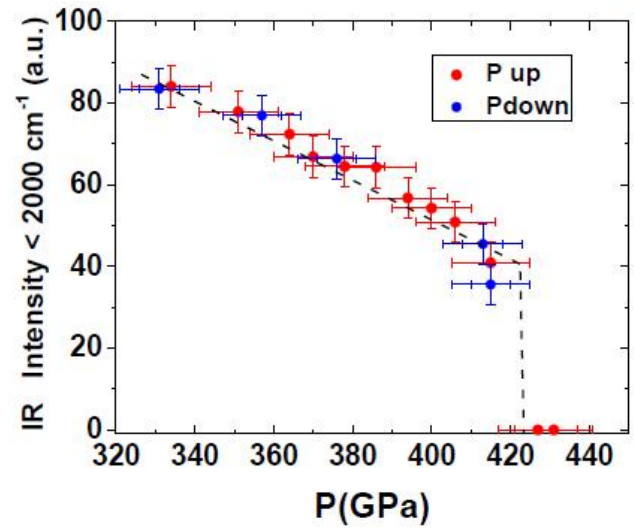


Synchrotron infrared spectroscopic evidence of the probable transition to metal hydrogen

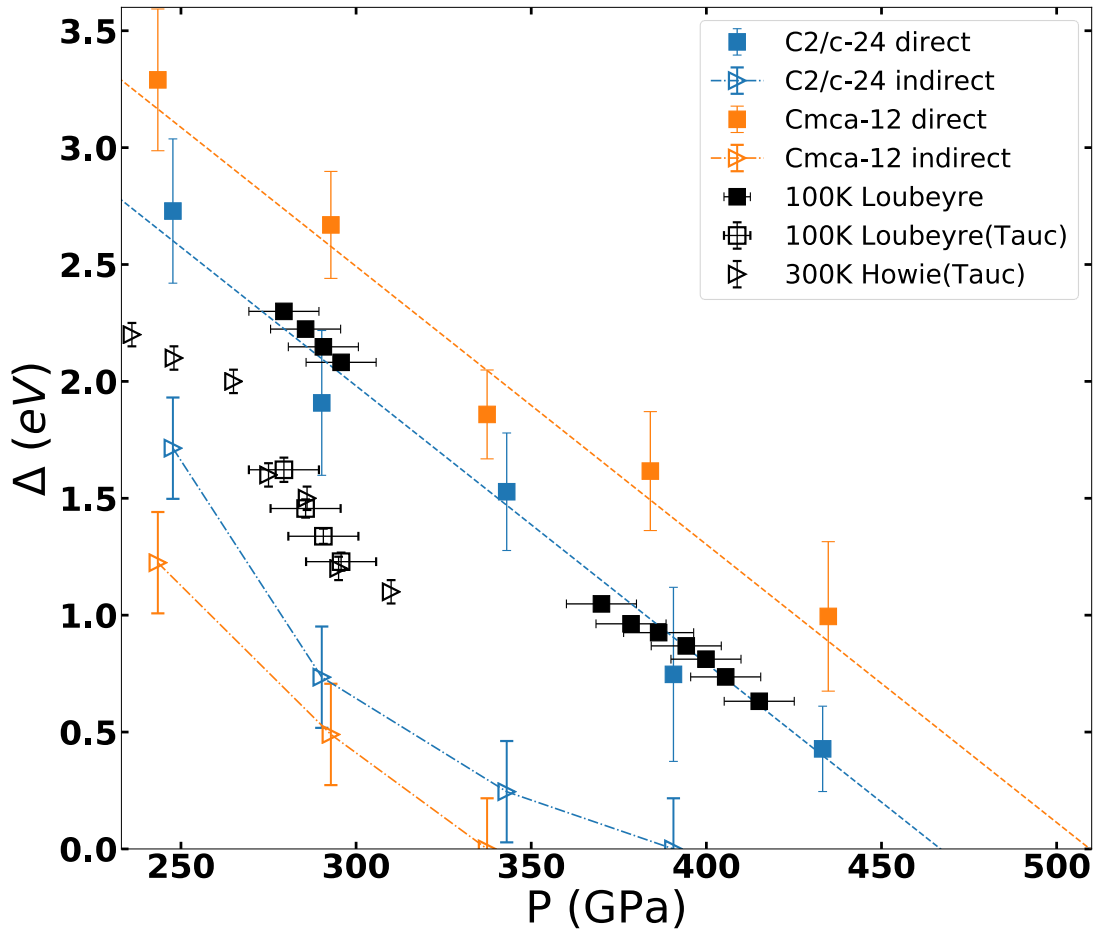
Paul Loubeyre[1]*, Florent Occelli[1] & Paul Dumas[1,2]

Nature | Vol 577 | 30 January 2020 | **631**



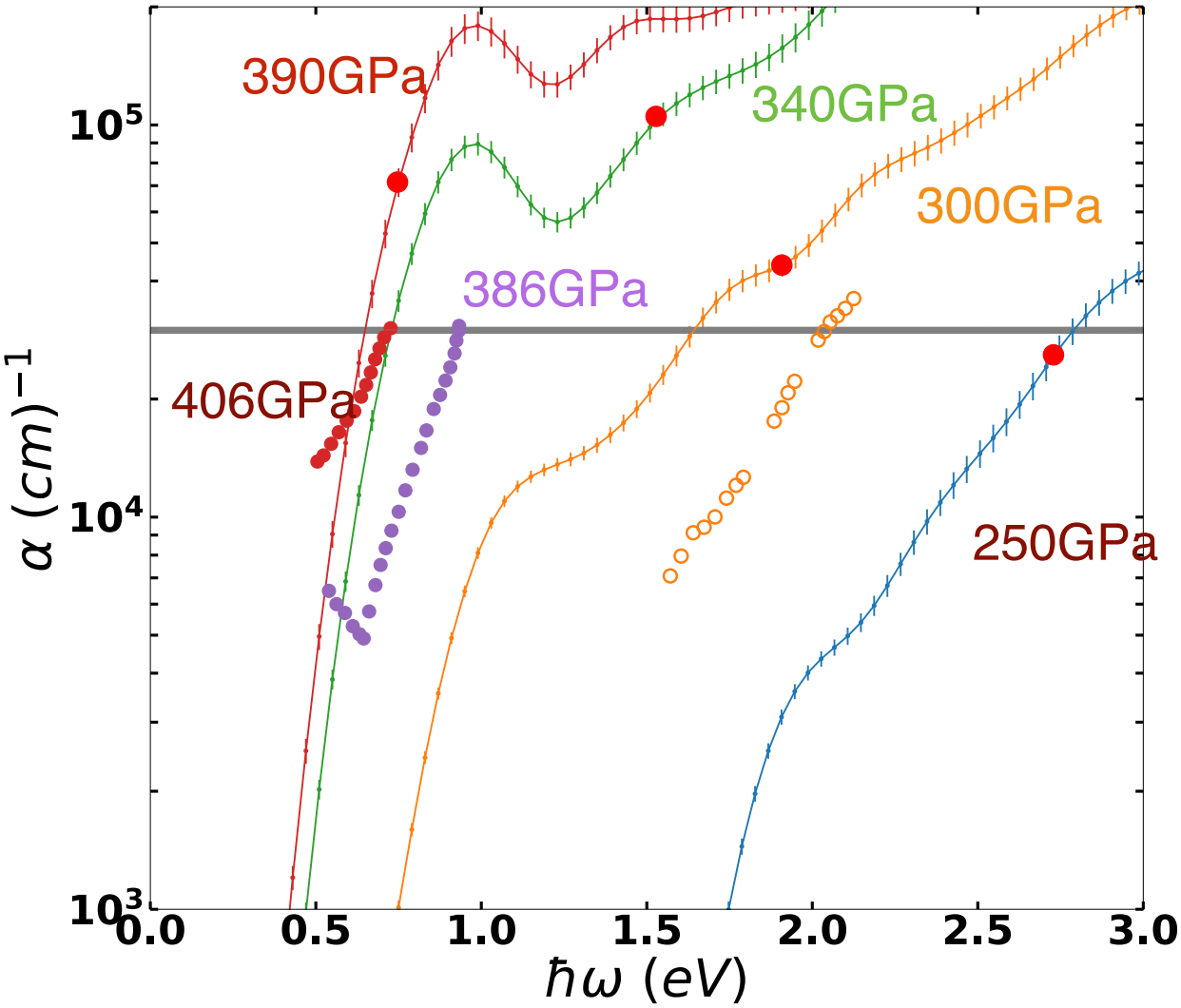


QMC gaps: comparison with experiments



- The experiment claims an abrupt collapse of the gap at 425GPa which is reversible upon releasing pressure.
- We cannot discuss this since our structures are dynamically stable.
- Excellent agreement for the direct gap, however ….

… the absorption spectra do not match (Kubo-Greenwood with KS orbitals)



- at each pressure 40 configurations and optical properties from Kubo-Greenwood with HSE Kohn-Sham spectrum
- WL semiclassical procedure to treat phonons does not provide sensible results
- an alternative way of averaging over configurations is more consistent but still differs from experiments

● direct gap value

the absorption at the energy of the direct gap does not correspond to the experimental threshold (30000 cm-1)

Conclusions

- CEIMC allows to investigate crystalline molecular hydrogen at metallization and molecular dissociation avoiding the XC approximation of DFT.
- We developed a new method to compute energy-gaps based on GC-QMC calculations.
- In hydrogen the fundamental gap is strongly reduced (>2eV) by nuclear quantum effects and closes around 360GPa (details depend on the structure).
- The *density of states at the Fermi level* fills progressively with pressure which has strong implications for the metallic character of the system.
- Direct gap values from QMC energies are in agreement with experiments.
- KG optical properties, for CEIMC generated configurations, with HSE KS spectrum shifted to match the QMC gap are not in agreement with experimental profiles.

- Our results suggest semi-metal behavior in the molecular phase between 360 and 450GPa, in qualitative agreement with Eremets *et al.* 2019, before transforming to the good metal phase.
- Whether the molecular dissociation occurs before the complete closure of the gap in the molecular crystal remains to be established.

Collaborators:

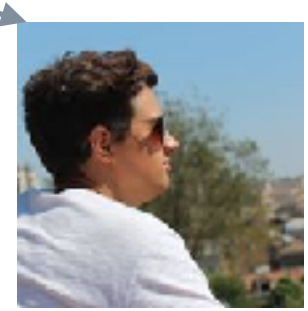
David Ceperley, UIUC USA

Markus Holzmann, CNRS Grenoble

Vitaly Gorelov, CEA Saclay

Yubo (Paul) Yang, Illinois

Michele Ruggeri, CEA



past:

Miguel Morales, LLNL (USA)

Giovanni Rillo, Sapienza Rome University

Elisa Liberatore, Sapienza Rome University

Raymond Clay, UIUC, Illinois

Financial support:

IIT-Seed (Italy)

NSF&DOE (USA)

CNRS (France)

ANR(France)

Conclusions

- CEIMC allows to investigate crystalline molecular hydrogen at metallization and molecular d
- W C c
- I d c
- T i
- k
  -
  -
  -
- C 4 c phase.
- Whether the molecular dissociation occurs before the complete closure of the gap in the molecular crystal remains to be established.

THANK YOU FOR YOUR ATTENTION !