Quantum Monte Carlo Study of High-pressure solid hydrogen

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Quantum Monte Carlo in the Apuan Alps VIII July2013





Motivation for studying dense hydrogen:

I - The most abundant element in the universe, 70%-95% the mass of Jupiter and Saturn:



10¹⁰

10⁵ Ξ

'10⁴

10³

10² ∃

Ξ

Ξ

10¹⁰

10⁸

10⁶

G1 229B

10⁶

10⁸

L HUI

 10^{2}

 10^{2}

10⁴

1 1111

10⁴

Jupiter

Saturn



II. Understanding and predicting the properties of simplest element in the periodic table:

superconductor for use at elevated temperatures.

letallic Solid Hydrogen

DECEMBER, 1935

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On the Possibility of a Metallic Modification of Hydrogen

E. WIGNER AND H. B. HUNTINGTON, *Princelon University* (Received October 14, 1935)

At very high pressure solid molecular hydrogen would dissociate and form an atomic solid that is metallic

High-Temperature Superconductivity

Volume 21, Number 26	PHYSICAL REVIEW L	ETTERS	23 December 1968
METALLIC	HYDROGEN: A HIGH-TEMPERAT	URE SUPERCO	ONDUCTOR?
Laboratory of Ato	N. W. Ashcroft omic and Solid State Physics, Cornell Ur (Received 3 May 1968)	niversity, Ithaca	, New York 14850
Application of gests that it wil astrophysical co	the BCS theory to the proposed metallic l be a high-temperature superconductor onsequences, as well as implications for) modification of . This predictio r the possible de	hydrogen sug- n has interesting velopment of a





letters to nature

A superconductor to superfluid phase transition in liquid metallic hydrogen

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at high (but experimentally accessible) pressures, compressed hydrogen will adopt a liquid state, even at low temperatures. In reaching this phase, hydrogen is also projected to pass through an insulator-to-metal transition. This raises the possibility of new state of matter: a near ground-state liquid metal, and its ordered states in the quantum domain.



Phase III (P > 150 Gpa): At 150 GPa, a large low-temperature <u>discontinuity in</u> <u>the frequency of the Raman</u> and a <u>strong rise in</u> <u>the IR molecular vibrons</u> mark the appearance of Phase III.



Phase I (P < 110 Gpa): freely rotating H₂ molecules whose centers of mass are arranged in an *hcp* structure.

Phase II (110 < P < 150 GPa): Also known as the broken symmetry phase. DFT calculations predict orthorhombic Cmc2₁, Pca2₁, and P2₁/C structures. Characterized by changes in the low-frequency region of the Raman and IR spectra.



Recent Experimental Contradiction:

Above 220 Gpa, hydrogen became opaque and electrically conductive. At 260–270 GPa, hydrogen transformed into a metal as the conductance of hydrogen sharply increased and changed little on further pressurizing up to 300 GPa or cooling to at least 30 K; and the sample reflected light well.

The metallic phase transformed back at 295 K into molecular hydrogen at 200 GPa. This significant hysteresis indicates that the transformation of molecular hydrogen into a metal is accompanied by a first-order structural transition presumably in to a montomic liquid state (PhaseIV ?!).



Eremets, Nature Materials December 2011



The persistence of the strong infrared absorption of the vibron characteristic of phase III indicates the stability of the paired state of hydrogen. There is no evidence for the predicted Metallic state (up to 360 Gpa) over these conditions, in contrast to recent reports, but electronic properties consistent with semimetallic behavior are observed. Measurements show no evidence

for the optical conductivity

expected for a metal over the entire range of temperatures to the highest pressures explored, and no signatures of an atomic liquid are observed.

Hemley group, PRL, April 2012





III. Developing and testing computer simulation methods:



The lack of accurate and trustworthy experimental results increases the importance of theoretical calculations in the study of solid hydrogen; it is hard to think of a research area in which theory and simulation have more to offer

No core electrons, the atomic structure is simple and the errors from the pseudopotential approximation, often employed to increase computational efficiency, are rather small or absent

The nuclei are so light, they too behave as quantum particles. This effect has such a strong influence that even the most basic properties of hydrogen are affected, such as relative stabilities of atomic structures. Thus, both electrons and ions have to be treated using rigorous quantum mechanics in order to make definitive predictions.

If the modern computational techniques, such as those based on density functional theory (DFT) and quantum Monte Carlo (QMC) calculations, are not accurate for hydrogen then there may be serious problems in trusting them for heavier elements.

Main Questions:

What are the crystal structures of phases II and III of solid hydrogen?

Finding the most stable arrangements of atoms in solids and molecules is and will remain a very difficult task, but significant progress has been made over the past few years, *e.g* methods based on simulated annealing, metadynamics, random sampling, evolutionary algorithms, basin hopping, minima hopping, and data mining, ...

What is the metallization mechanism/pressure of solid hydrogen?

Band-gap closure Atomization Structural transformation

To what extent can the protons be treated as classical, as opposed to quantum mechanical, particles?

Proton zero point energy (ZPE) Unharmonicity



Theoretical and computational methods:

- Path-integral Monte Carlo approach
- QMC-based first-principles simulations
- Ground-state quantum Monte Carlo methods
- Coupled electron-ion Monte Carlo method
- DFT-based first-principles simulations
- Density functional theory
- Born-Oppenheimer molecular dynamics
- Car-Parrinello molecular dynamics
- Path-integral molecular dynamics



Density Functional Theory (DFT) phase diagram:



Within the static-lattice approximation, the most stable phases are P63/m (<105 GPa), C2/c (105–270 GPa), Cmca-12 (270–385 GPa) and Cmca (385–490 GPa), followed by I41/amd. Of these phases, only Cmca and I41/amd were known previously. When ZP effects are included, C2/c becomes stable below 240 GPa and Cmca-12 above.

Pickard and Needs, Nature (2007)







The challenges of DFT :



DFT band-gap:







Hybrid functional metallization pressures are larger than GW ones ~ 50 GPa

GW predicts metallization should happen before 400 Gpa



Hybrid DFT phase diagram:

Hybrid DFT: DFT + small fraction of Hartree-Fock exchange

Typically yields much improved **band gap** that are often in close agreement with experiment





No Metallization, No structure transition !

The lower the energy The wider the band-gap Hemley, PRL **67** 1138 (1991)

Why DFT is unable to reproduce the phase diagram of high-pressure solid hydrogen ?

Two reasons:

One is caused by the very small enthalpy differences of a few meV per proton between phases. Exhaustive tests for molecules, where accurate results can be obtained using quantum chemical methods, have shown that no current XC functional is consistently capable of achieving such accuracy.

The second is the many-body self-interaction (XC-SI) error present in the XC functionals used here. A systematic investigation found the XC-SI errors of the LDA, GGA, and BLYP total energies of a single H_2 molecule to be **1.264**, -**0.126**, and **0.0846** eV, respectively. These values are more than two orders of magnitude larger than the DFT enthalpy differences between the crystal structures of high-pressure solid hydrogen.



Phonon spectra:





Proton Zero Point Energy:





If we had considered a wider range of structures, we would have seen qualitative as well as quantitative differences between the phase diagrams calculated using different XC functionals

DFT is probably not accurate enough to allow reliable comparisons of the stabilities of the insulating, semimetallic, and metallic phases of solid molecular hydrogen. Indeed, since simple DFT calculations fail to describe van der Waals interactions and severely underestimate band gaps, it would be unreasonably optimistic to expect such comparisons to be reliable.

S. Azadi and T. Kuhne, JETP LETT (2012), arXiv:1108.6190 S. Azadi and M. Foulkes, Phys. Rev .B , in press (2013) , arXiv:1307.1351





Effect of single particle slater determinant:



TABLE I. VMC and DMC energies of the $P6_3/m$ phase using PBE and PBE0 single particle orbitals. Energies and pressures are in eV per proton and GPa, respectively.

Pressure	PBE-VMC	PBE0-VMC	PBE-DMC	PBE0-DMC
100	-15.1335(4)	-15.1397(4)	-15.2327(3)	-15.2338(3)
200	-14.5898(4)	-14.5979(4)	-14.6856(3)	-14.6867(3)
300	-14.0473(4)	-14.0524(4)	-14.2184(3)	-14.2193(3)

This demonstrates that, in the case of solid molecular hydrogen, DMC energies calculated using PBE and PBE0 orbitals differ negligibly, even though the change of functional has a large effect on the DFT phase diagram. This contrasts with the case of 3d transition metal compounds [Phys. Rev. B 82 115108 (2010)], where changing the functional does affect the DMC results.

QMC+DFT to calculate FS correction:

Contrary to standard DFT methods, QMC calculations have to be performed on a super-cell. Therefore, finite-size (FS) effects can be a relevant source of error in QMC calculations.

One-body term (independent particle source), arises from the kinetic and Hartree term

Two-body term related to the FS effects of exchange and correlation

DMC -TABC: *Twist averaging* means taking the average of expectation values over all simulation-cell Bloch vectors \mathbf{k}_s in the first Brillouin zone of the simulation cell, i.e., over all offsets to the grid of \mathbf{k} vectors

KZK functional: the exchange and correlation energy functional is replaced by the LDA functional parameterized for a finite system, which keeps an explicit dependence on the number of particles (Phys. Rev. Lett. 100, 126404 (2008))



$$E^{QMC}(\infty) = E^{QMC}_{TAV}(L) + \Delta E^{FS}_{TAV}(L)$$

where

$$\Delta E_{TAV}^{FS}(L) = E^{DFT,LDA}(\infty) - E_{TAV}^{DFT,FS}(L)$$
$$E_{TAV}^{QMC}(L) = \frac{1}{N_{twist}} \sum_{\mathbf{k}_s}^{N_{twist}} E^{QMC}(L, \mathbf{k}_s)$$
$$E_{TAV}^{DFT,FS}(L) = \frac{1}{N_{twist}} \sum_{\mathbf{k}_s}^{N_{twist}} E^{DFT,FS}(L, \mathbf{k}_s)$$

Ν	$E^{EWA}(L)$	$E^{MPC}(L)$	$E^{QMC}(\infty)$
64	-14.3172(9)	-14.2021(9)	-14.2038(8)
96	-14.2651(5)	-14.1820(5)	-14.2134(6)
128	-14.2368(4)	-14.1685(4)	-14.2133(4)
144	-14.2535(4)	-14.1958(4)	-14.2109(4)







Thank you for your attention



