

凝聚态论坛，2012年4月5日

基于第一性原理电子结构计算的路径积分的分子动力学：方法及应用

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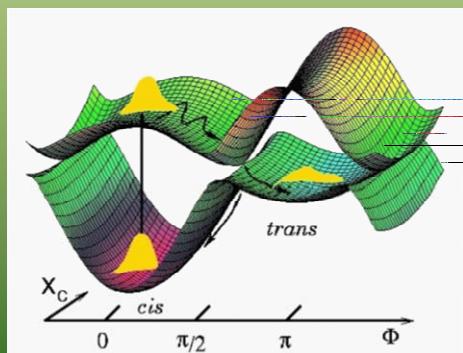
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- ◆ 理解材料性质时的关键概念
 - Born-Oppenheimer (BO) 近似
 - 实际系统在BO-势能面上运动
- ◆ 最为通行的方法: ab-initio MD

核量子效应

- ◆ 我们的目标：真实材料性质的全量子模拟。



Outline

◆ 方法的简介

◆ 实际问题:

- 金属与水的界面



- : :

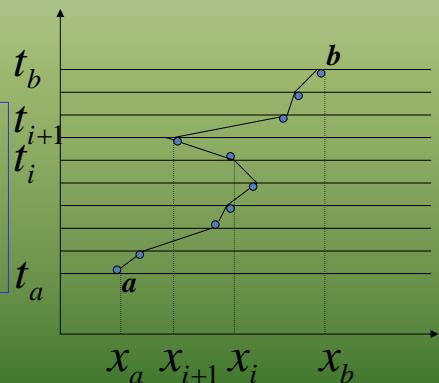
- Quantum mechanics: probability, propagator

$$(\langle \ , \ ; \ , \ \rangle) = \langle \langle \ , \ \rangle \rangle_j \langle \ , \ a \rangle \rangle^* e^{(i/\hbar) E_j(t_b - t_a)}$$

- Path-integral:

$$K(b, a) = \lim_{\varepsilon \rightarrow 0} \frac{1}{A} \int \int \dots \int e^{(i/\hbar) S[b, a]} \frac{dx_1}{A} \frac{dx_2}{A} \dots \frac{dx_{N-1}}{A}$$

$$\text{where } S[b, a] = \int_{t_a}^{t_b} L(\dot{x}, t) dt$$



:

□ $\rho(x_N, x_0; 1/k_B T) = \sum_j \phi_j^*(x_2) \phi_j(x_1) e^{-E_j/k_B T}$

$\hat{H}(x) = -\frac{d^2}{dx^2} + V(x)$

$K(x_N, t_N; x_0, t_0) = \sum_j \phi_j^*(x_N) \phi_j(x_0) e^{-(i/\eta) E_j (t_N - t_0)}$

$i(t_N - t_0)/\eta \rightarrow 1/k_B T$

□ Path-integral enters:

$\rho(x, x'; k_B T) = \sqrt{\frac{2\pi\eta}{mk_B TN}} \int_{x_0=x}^{x_{N+1}=x'} \left(\exp \left\{ -\frac{1}{k_B T} \sum_{i=0}^N \left[\frac{m(k_B T)^2 N}{2\eta} (x_{i+1} - x_i)^2 + \frac{1}{N} V(x_i) \right] \right\} \right) \prod_{i=1}^{N-1} dx_i$

Density matrix of a quantum system → **Density matrix of a classical polymer of N beads (images)**

:

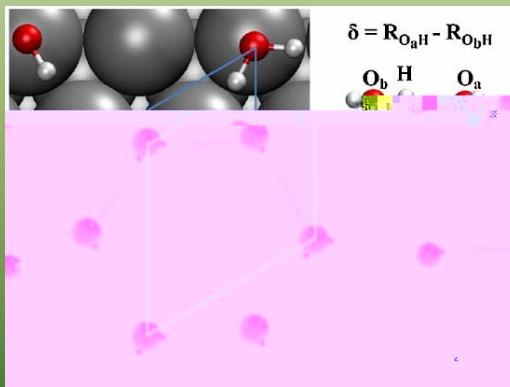
■ Path-integral enters:

$\rho(x; k_B T) = \sqrt{\frac{2\pi\eta}{mk_B TN}} \int_{x_0=x}^{x_{N+1}=x} \left(\exp \left\{ -\frac{1}{k_B T} \sum_{i=0}^{N-1} \left[\frac{m(k_B T)^2 N}{2\eta} (x_{i+1} - x_i)^2 + \frac{1}{N} V(x_i) \right] \right\} \right) \prod_{i=0}^{N-1} dx_i$

Density function of a quantum system → **Density function of a polymer of N beads (images)**

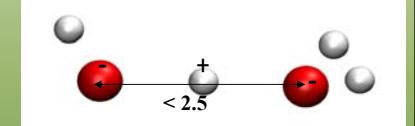
- Water-metal interface is an important issue at the core of several fields

- Corrosion
- Electrochemistry
- Catalysis



[1] Michaelides, and Hu, JACS, 123, 4235 (2001)

Excess proton in liquid water



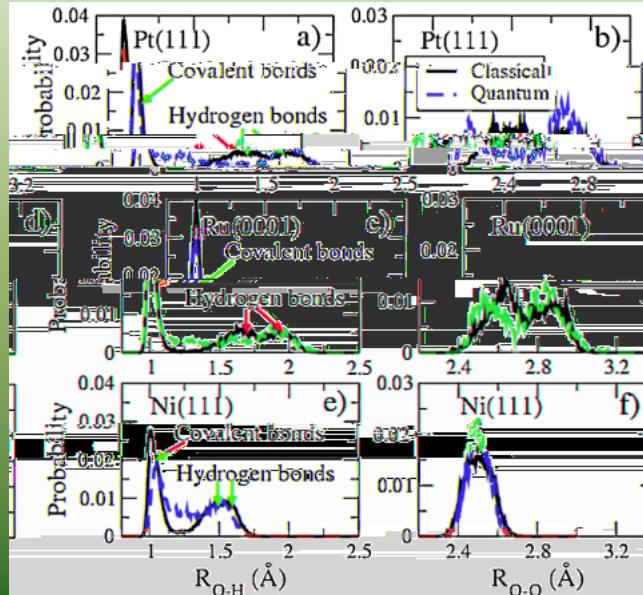
[2] Tuckerman, Marx, Klein, and Parrinello, Science, 275, 817 (1997)

Bulk ice under high pressure

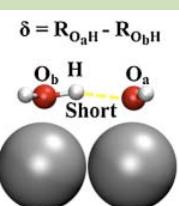
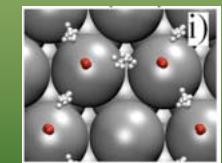
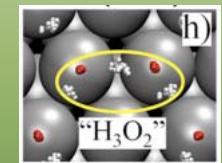
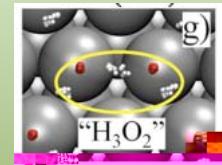
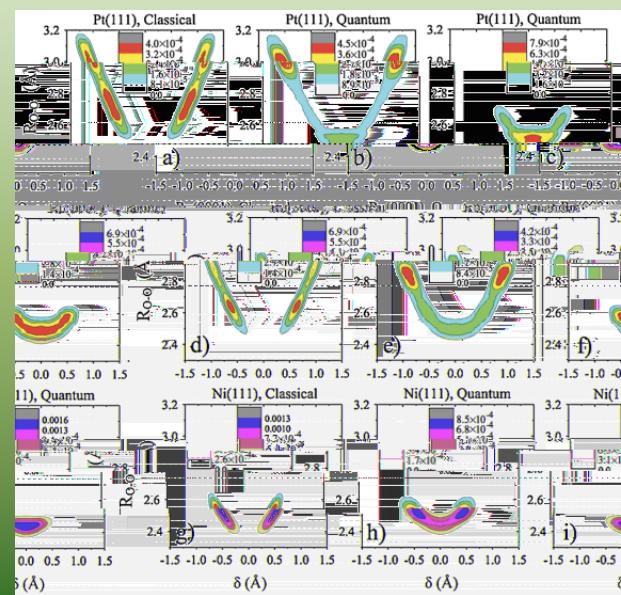


[3] 258(1998)

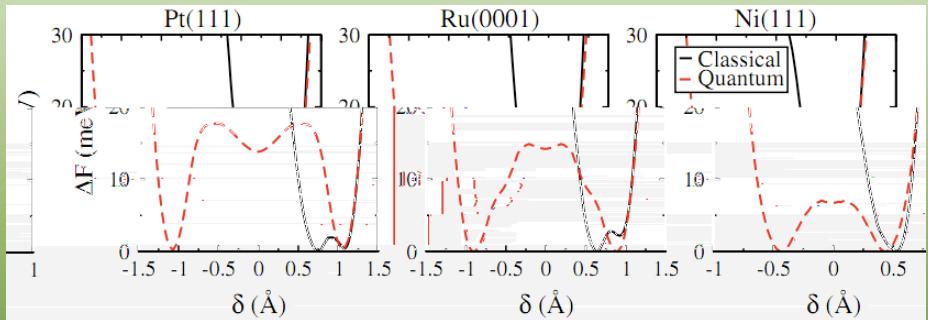
Structural properties of the overlayer at 160 K



Correlate O-H and O-O

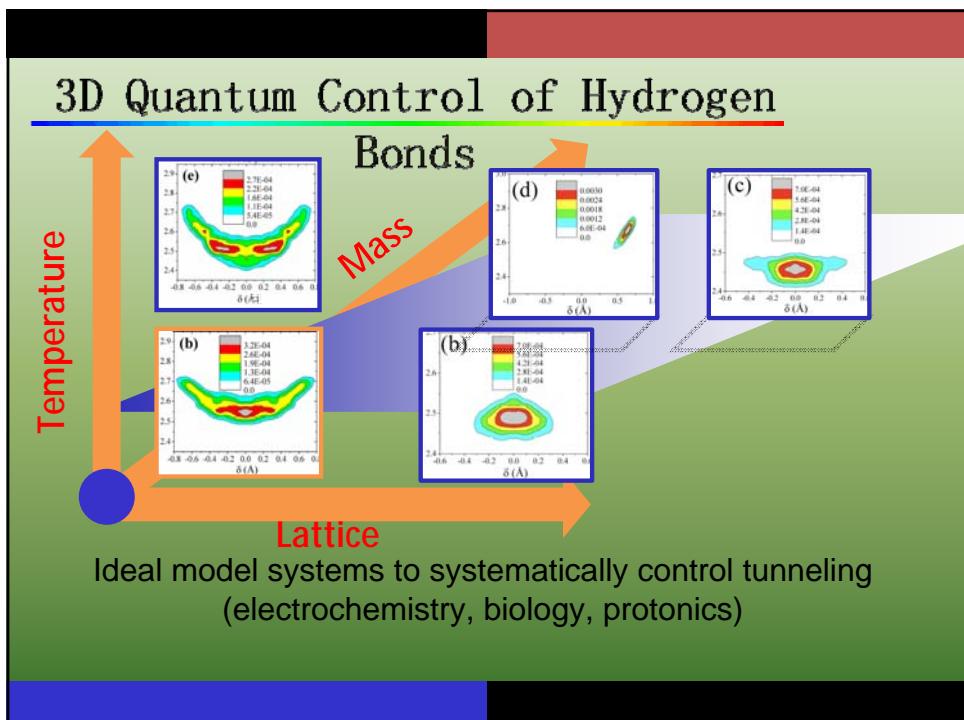


■ Focus on the proton transfer

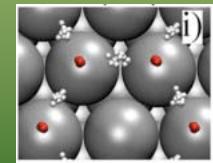
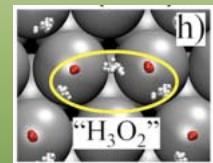
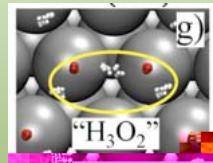
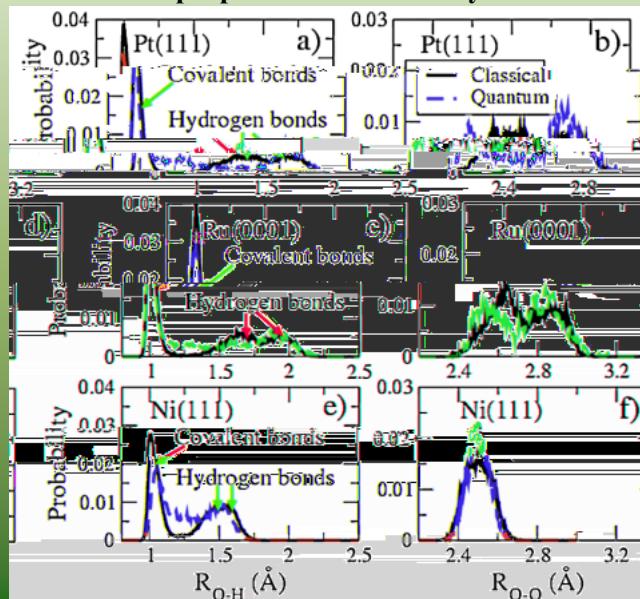


Adiabatic proton transfer: general importance in water-metal interfaces

detail: X.Z Li *et al.* Phys. Rev. Lett. 104, 066102 (2010)



□ Structural properties of the overlayer at 160 K

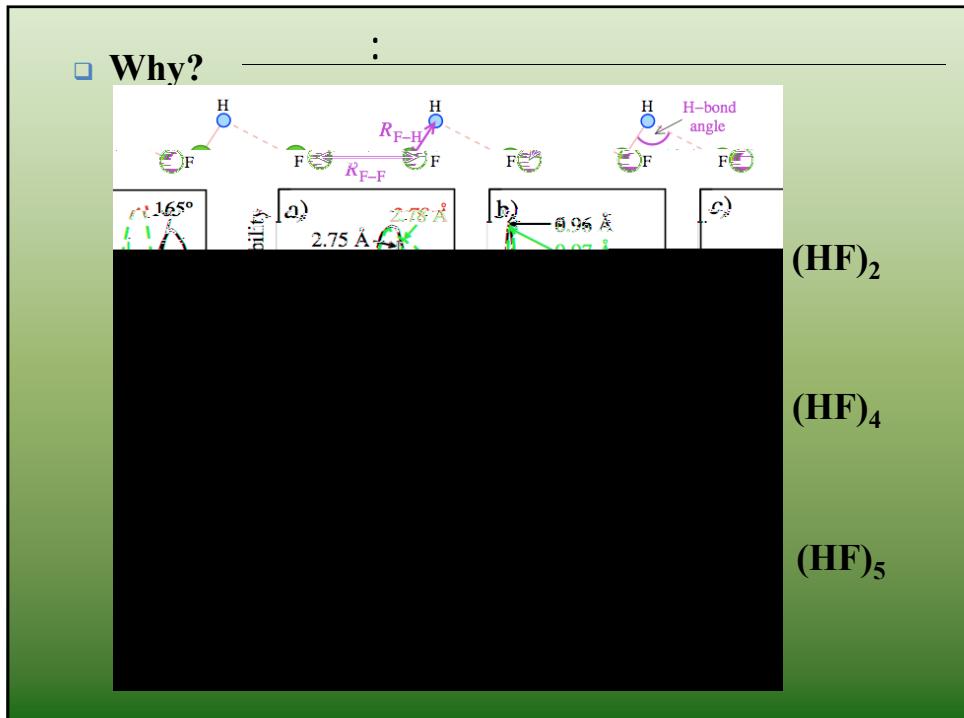
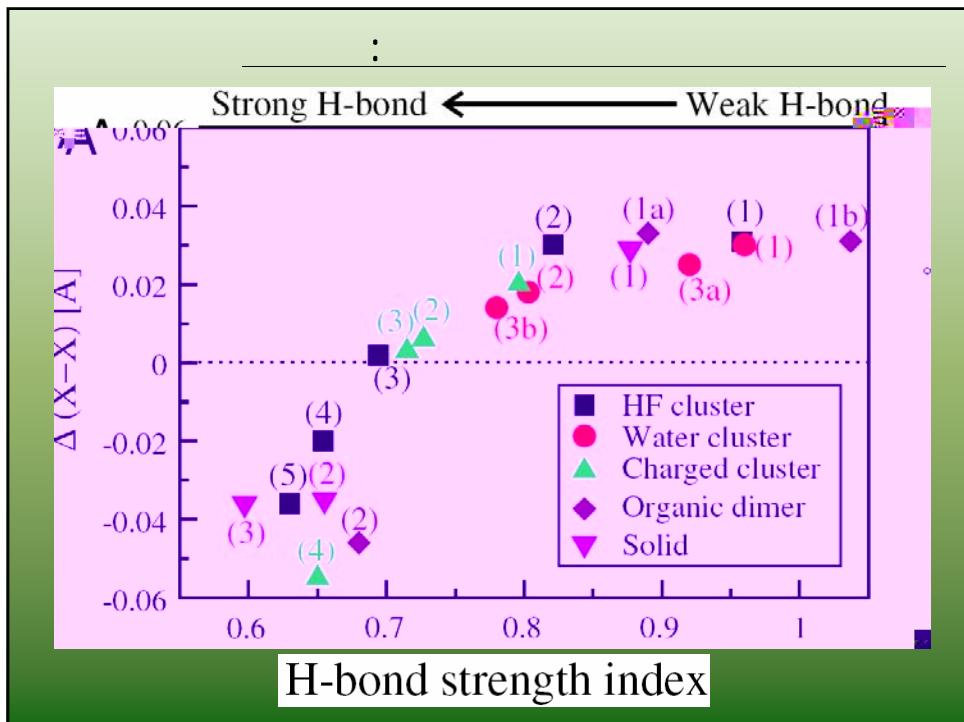


➤ Impact of quantum nuclear effects on H-bond strength?

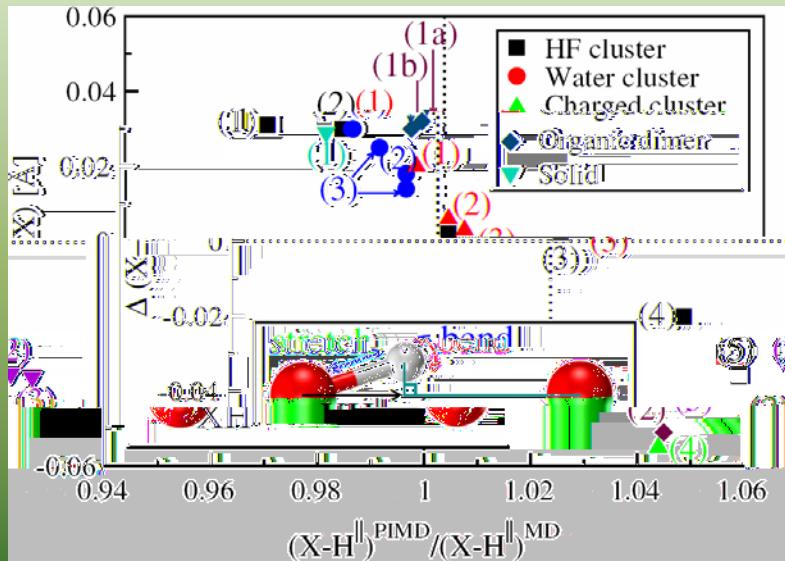


- In 1950s, Ubbelohde effect (replace H with D) in H-bonded crystals.
- Liquids: water structure is weakened, and liquid HF is strengthened
- Clusters: $(HF)_n$ when $n > 4$, strengthened, otherwise, weakened; $(H_2O)_n$ always weakened

Biggest question: is there a unified picture?

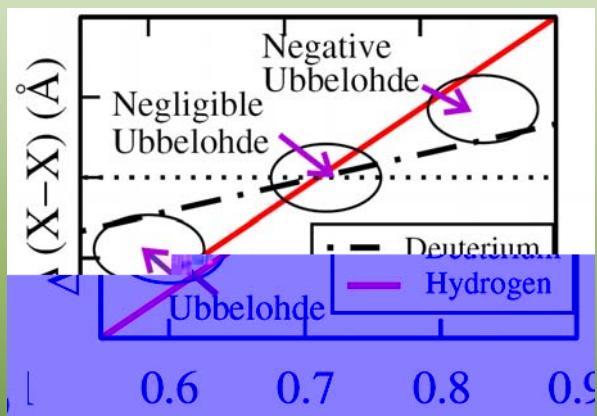


□ Quantitative



detail: X.Z Li *et al.* Proc. Natl. Acad. Sci. USA 108, 6369 (2011)

□ Rule of Thumb

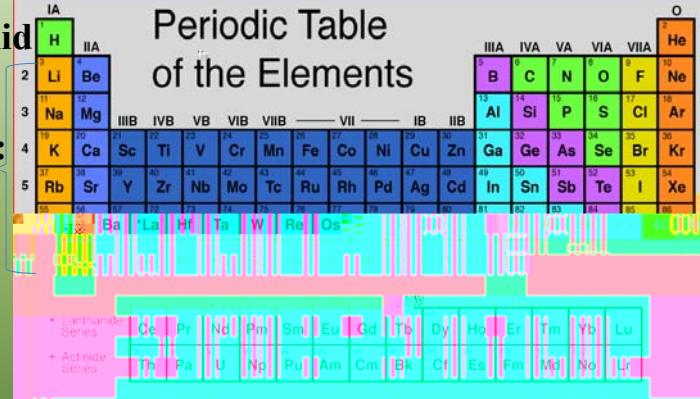


- ❖ Flexible monomer with anharmonic potential must be used if one want to use force-field method in PIMD simulations

Molecular solid

Alkali metal:
atomic solid

Periodic Table of the Elements

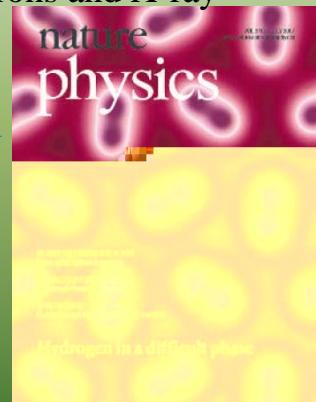


IA	IIA											O
H	Be											He
2 Li	3 Be											
3 Na	4 Mg	5 Al	6 Si	7 P	8 S	9 Cl	10 Ar					
4 K	5 Ca	6 Sc	7 Ti	8 V	9 Cr	10 Mn	11 Fe	12 Co	13 Ni	14 Cu	15 Zn	16 Ga
5 Rb	6 Sr	7 Y	8 Zr	9 Nb	10 Mo	11 Tc	12 Ru	13 Rh	14 Pd	15 Ag	16 Cd	17 In
6 Cs	7 Ba	8 La	9 Ce	10 Pr	11 Nd	12 Pm	13 Sm	14 Eu	15 Gd	16 Tb	17 Dy	18 Ho
7 Fr	8 Ra	9 Lu	10 Pa	11 U	12 Np	13 Pu	14 Am	15 Cm	16 Bk	17 Cf	18 Es	19 Fm
8	9	10	11	12	13	14	15	16	17	18	19	20
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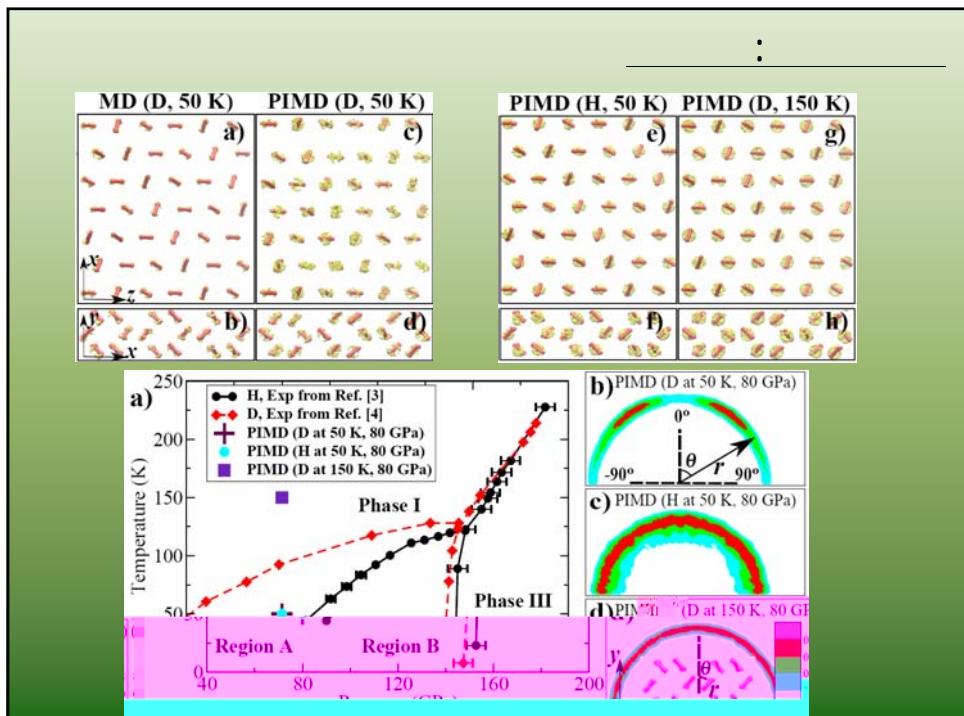
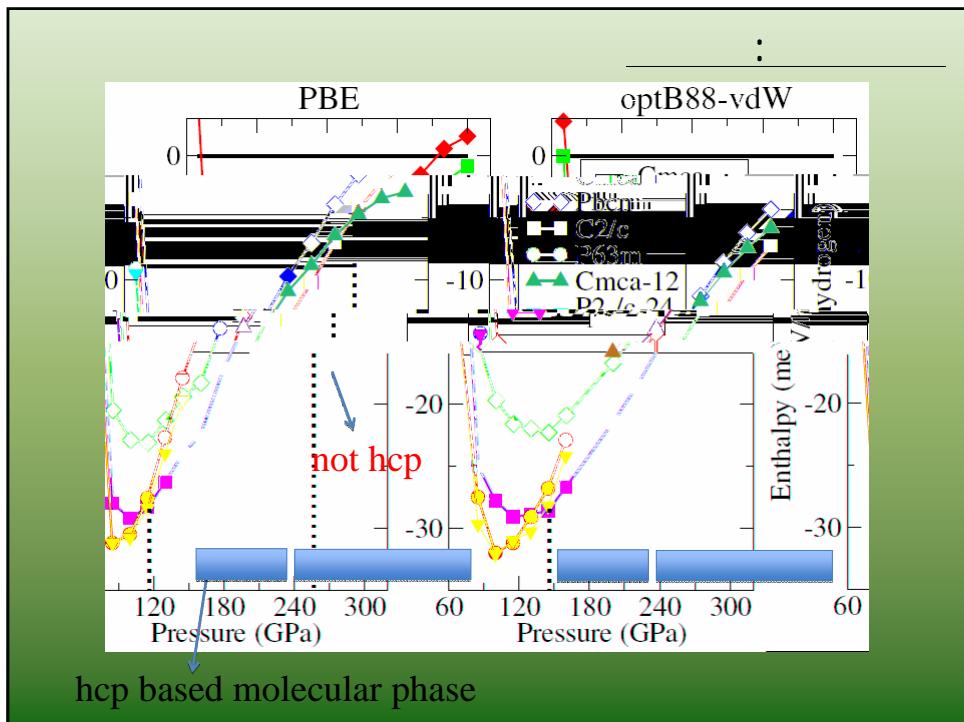
Wigner and Huntington (1935): Under high pressure, will H₂ become bcc solid?

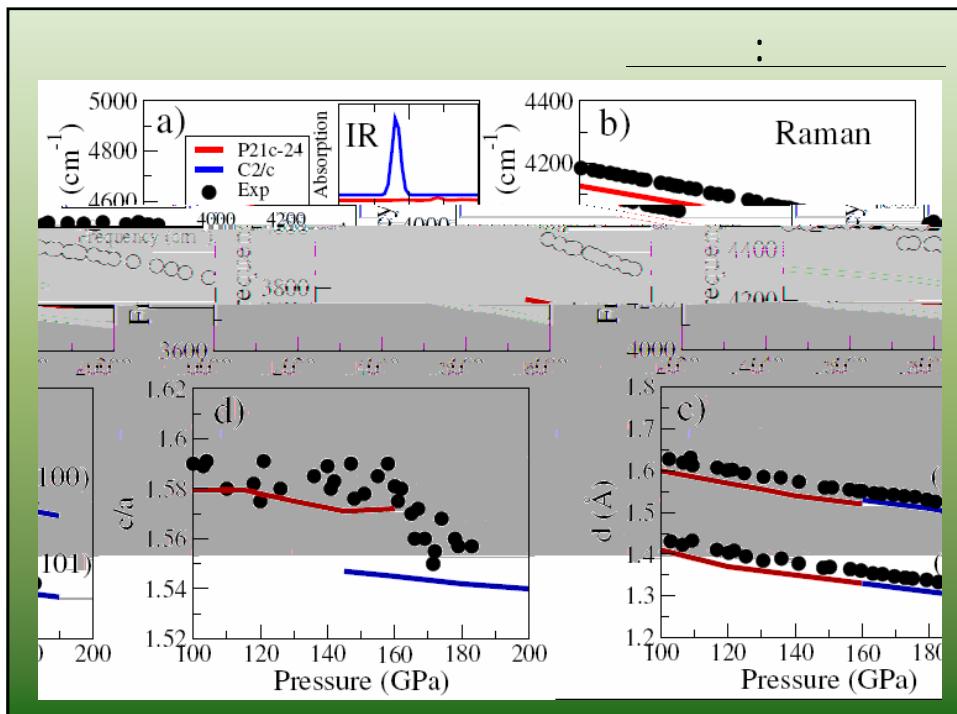
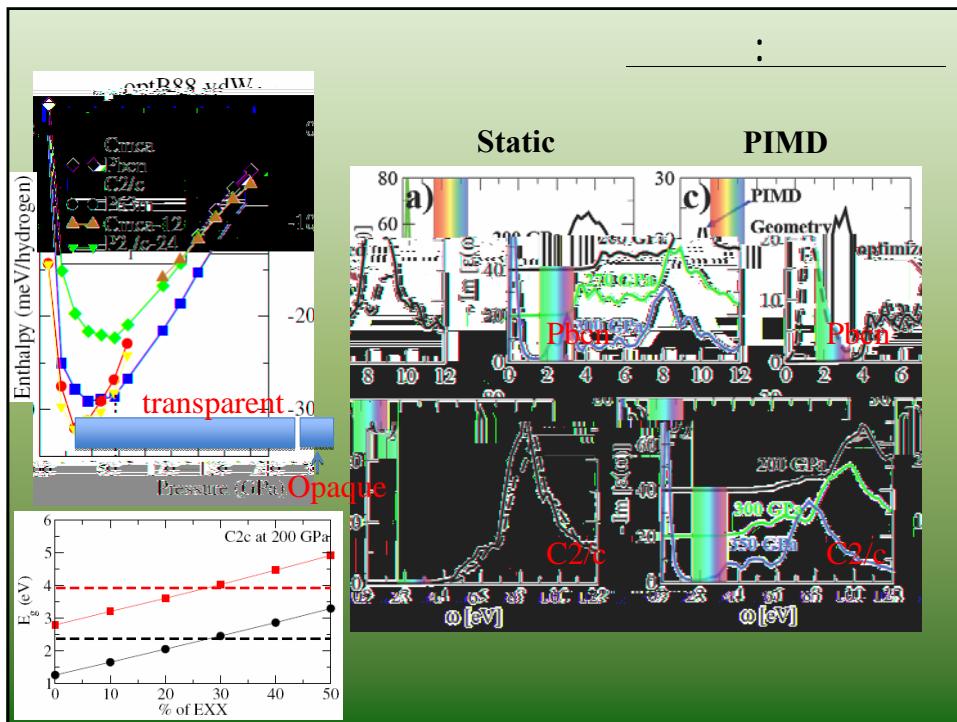
□ Why do people know so little?

- Experimentally, hard to probe, hydrogen has a very small scattering cross section for electrons and X-ray
- Theoretically:
 - 1) Electronic structure accurate
 - 2) Configuration space explored
 - 3) Quantum nature of hydrogen addressed accurately
 - 4) Optical property properly described



Pickard and Needs, 2007





➤ :

- ❑ Proton transport along 1D water chain
- ❑ Higher pressure hydrogen phase (>5Mbar)
- ❑ Soft Phonon
- ❑ Thermal Conductivity

➤ : FHI-aims

➤ : CMD, RPMD

!



Brent Walker



Mat Probert



Ali Alavi



Chris Pickard



Richard Needs



Angelos Michaelides

...

Name a few reasons:

1. Different melting, boiling point of H₂O and D₂O
2. D₂O is toxic if you keep drinking it
3. Phase transition between ice VII and VIII
4. Phase diagram of hydrogen under pressure

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