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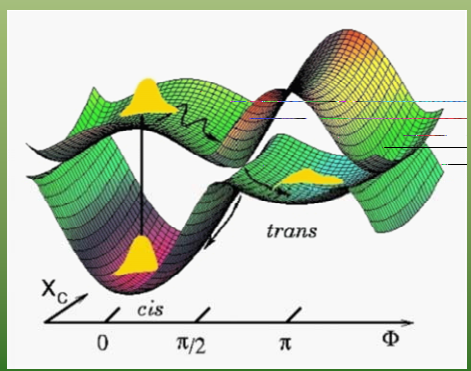
- 理解材料性质时的关键概念
  - Born-Oppenheimer (BO) 近似
  - 实际系统在BO-势能面上运动
- 最为通行的方法：ab-initio MD

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

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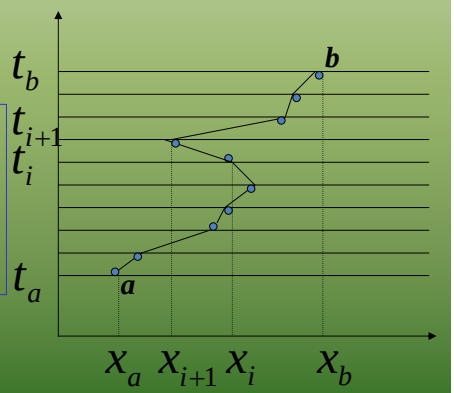
- :
  - **Quantum mechanics: probability, propagator**

(, ; ,) *( ) $_{j}$($_{a}$) (i/)$E_j(t_b \;\; t_a)$

  - **Path-integral:**

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

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



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

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

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

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

Path-integral enters:

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

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

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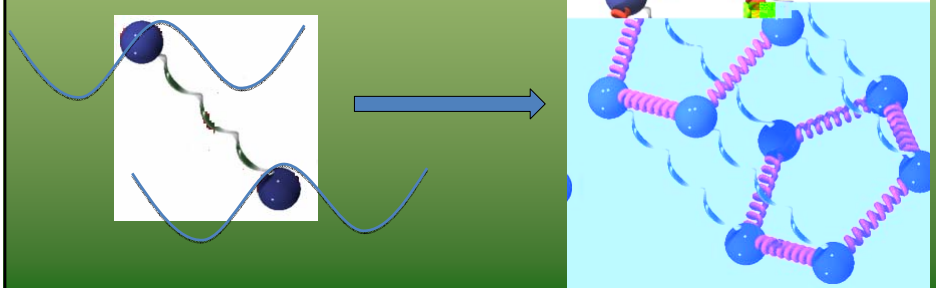
$$\rho(x; k_B T) = \sqrt{\frac{2\pi\eta}{mk_B TN}} \int_{x_0=x}^{x_{N+1}=x} \left(\exp\left\{ -\frac{1}{k_B T} \sum_{i=0}^{N-1} \left[\frac{m(k_B T)^2 N}{2\eta} (x_{i+1} - x_i)^2 + \frac{1}{N} V(x_i) \right] \right\} \right) \prod_{i=0}^{N-1} dx_i$$

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



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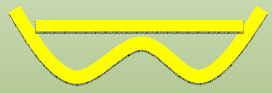
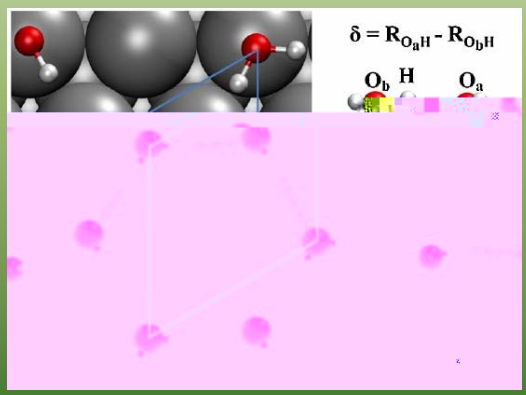
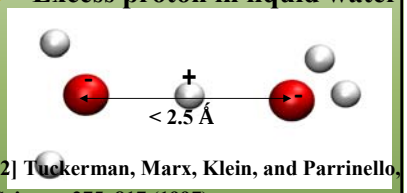
- Water-metal interface is an important issue at the core of several fields
  - Corrosion
  - Electrochemistry
  - Catalysis





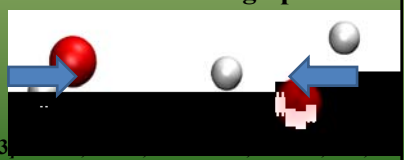
[1] Michaelides, and Hu, JACS, 123, 4235 (2001)

- Excess proton in liquid water



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

- Bulk ice under high pressure



[3] 258(1998)

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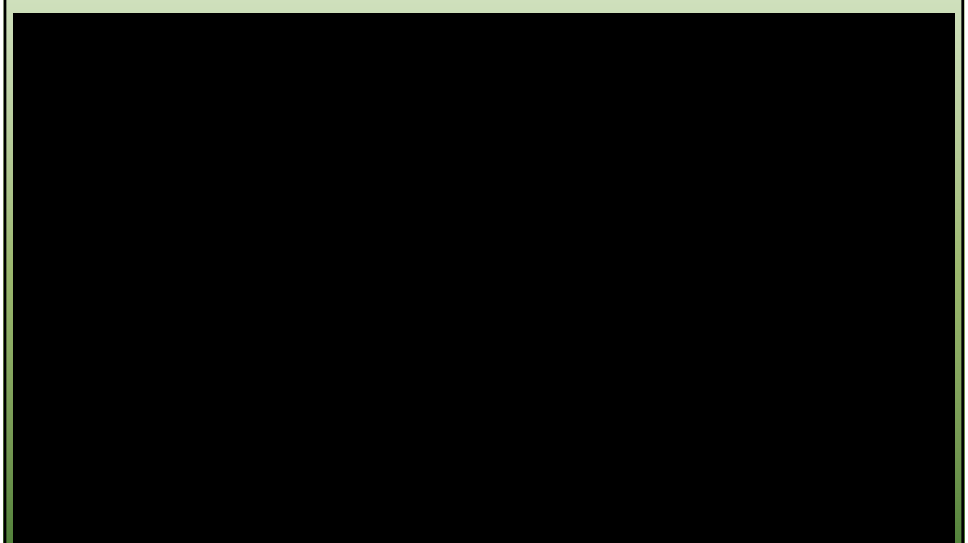

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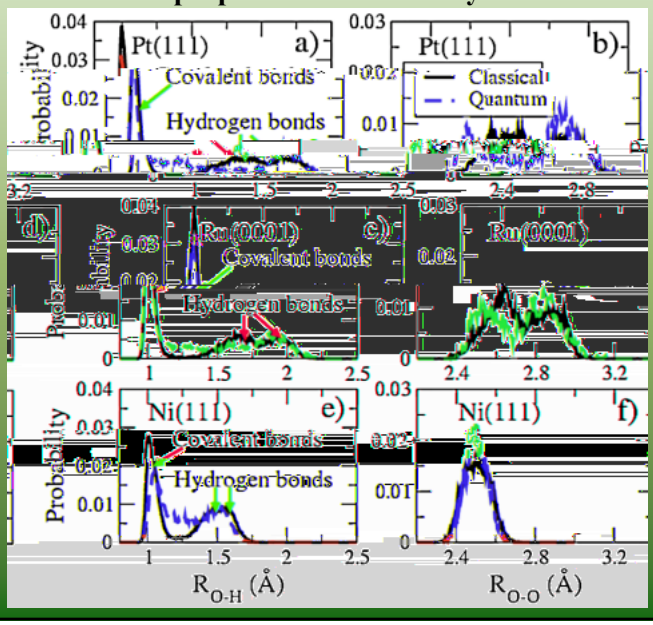
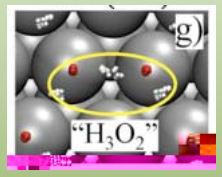
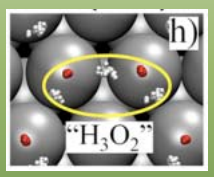
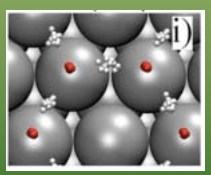
- **Structural properties of the overlayer at 160 K**









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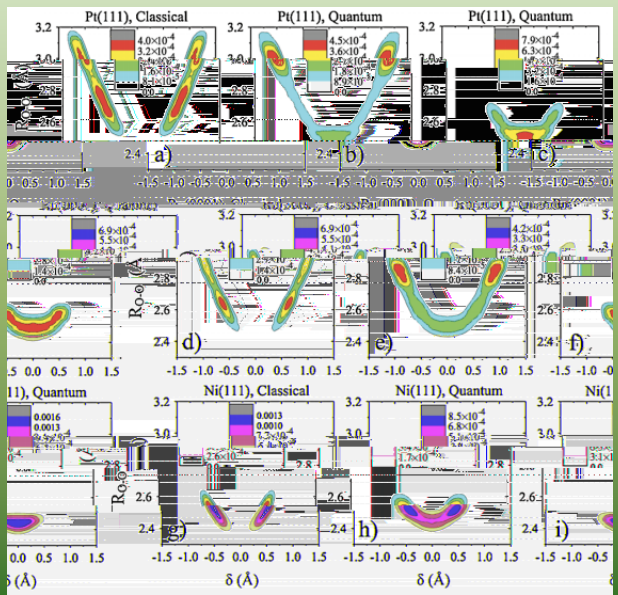
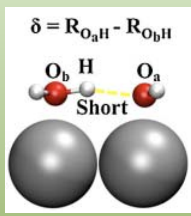
- **Correlate O-H and O-O**





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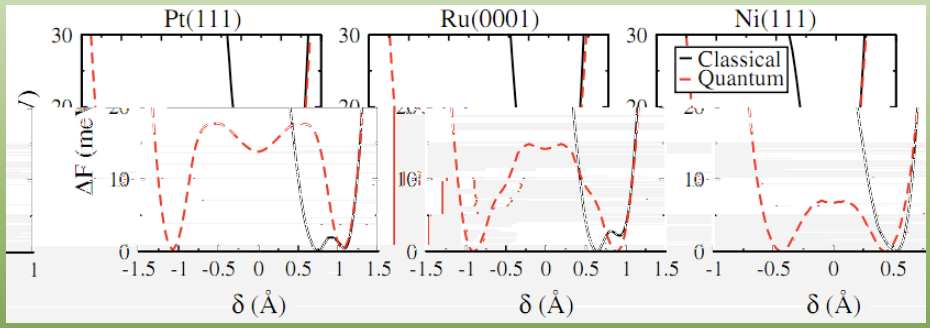
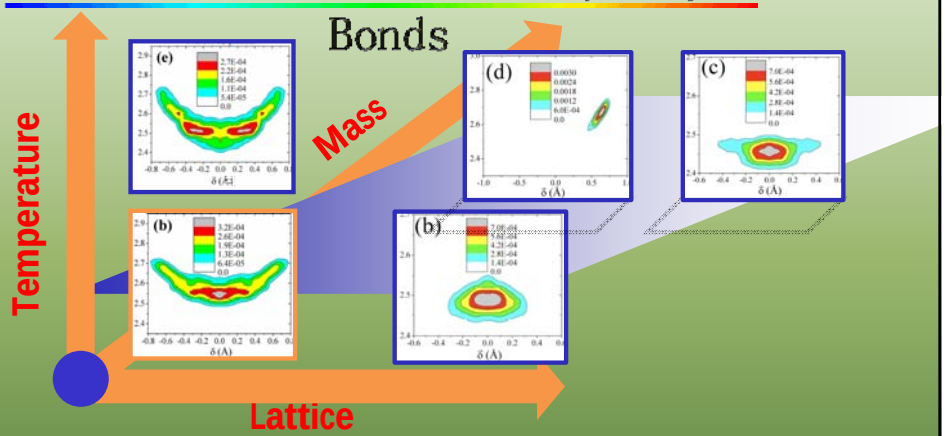
- **Focus on the proton transfer**



Adiabatic proton transfer: general importance in water-metal interfaces

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

3D Quantum Control of Hydrogen Bonds



Ideal model systems to systematically control tunneling (electrochemistry, biology, protonics)

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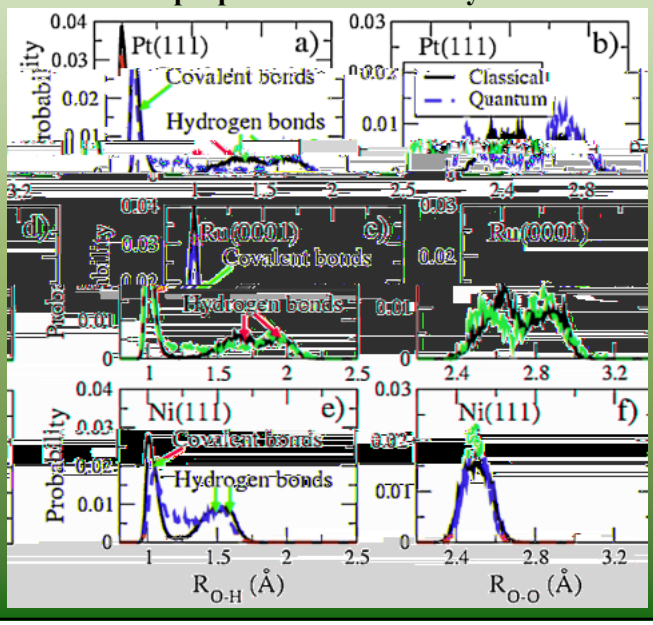
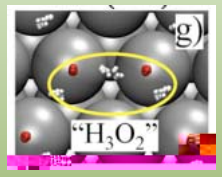
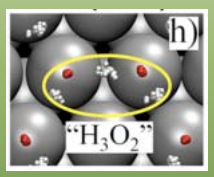
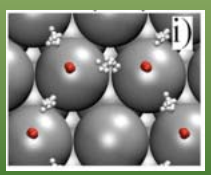
- **Structural properties of the overlayer at 160 K**









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➢ **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?

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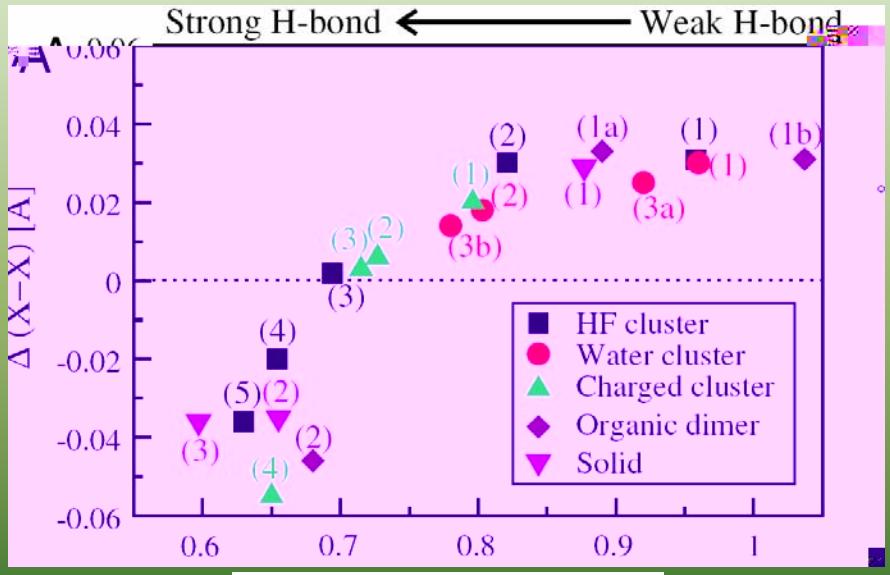

H-bond strength index

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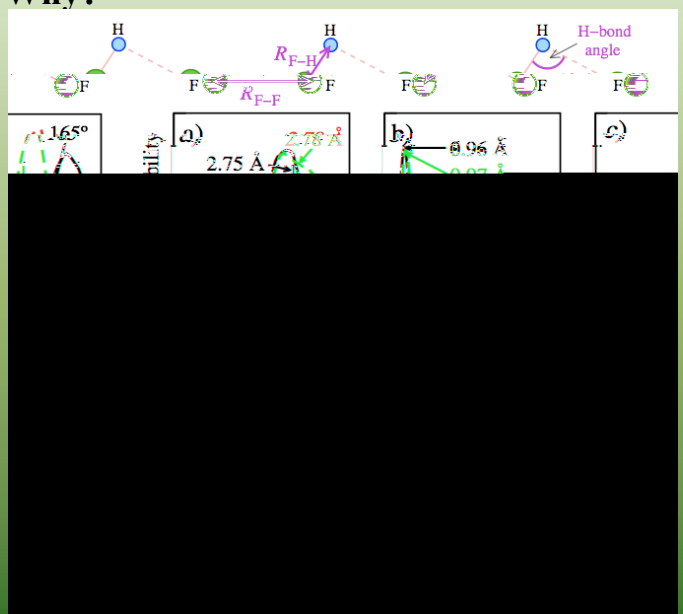
- **Why?**



$(HF)_2$

$(HF)_4$

$(HF)_5$

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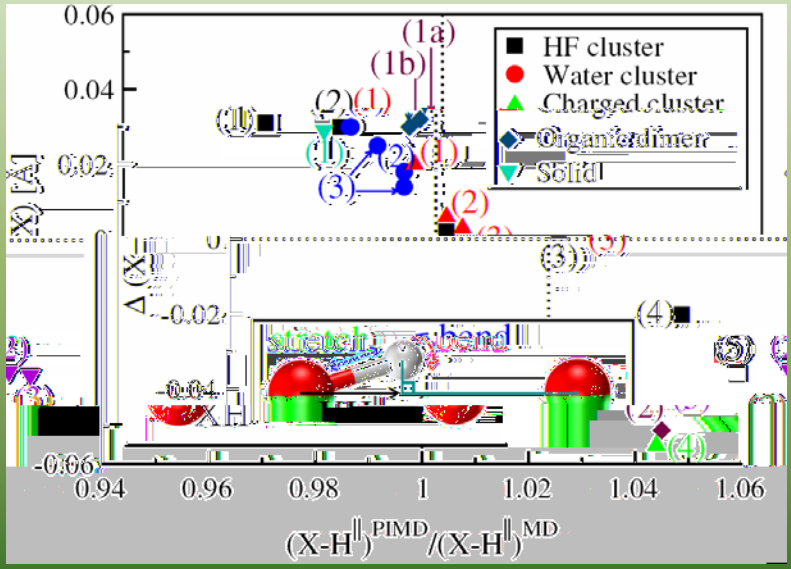
- **Quantitative**



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

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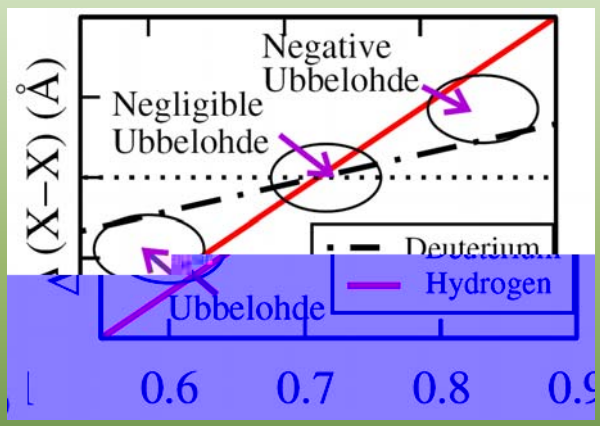
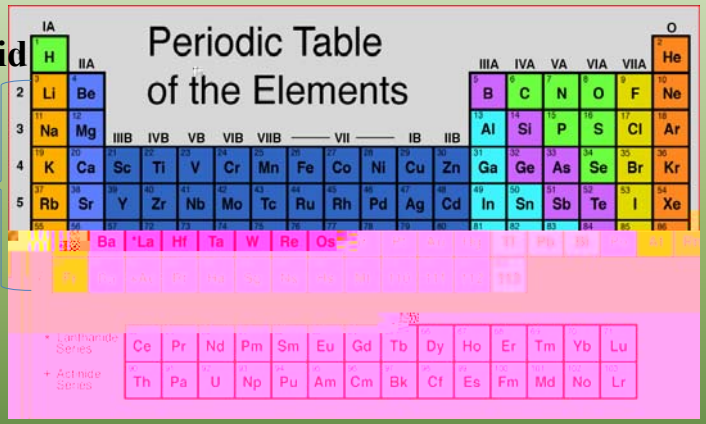
- **Rule of Thumb**



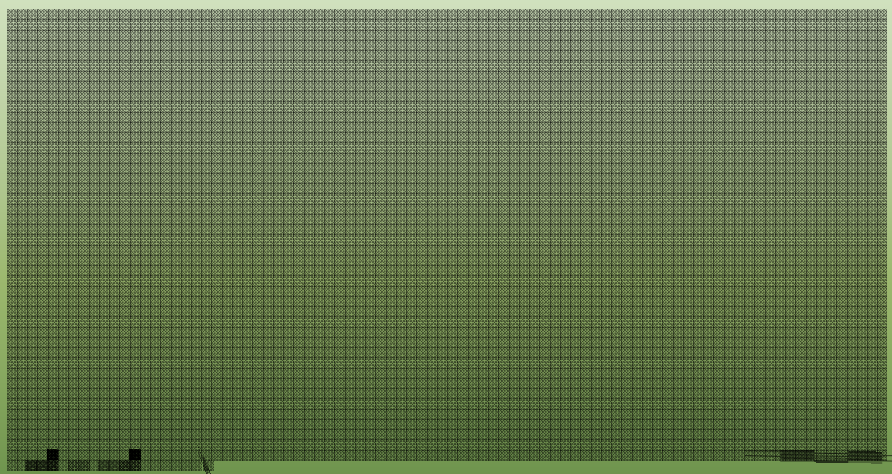
- **Flexible monomer with anharmonic potential must be used if one want to use force-field method in PIMD simulations**

Molecular solid

Alkali metal: atomic solid



Wigner* and *Huntington (1935): Under high pressure, will H_2 become bcc solid?

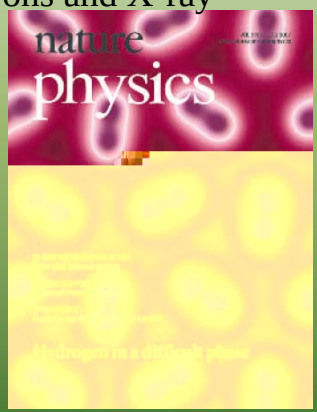


❑ Why do people know so little?

• 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

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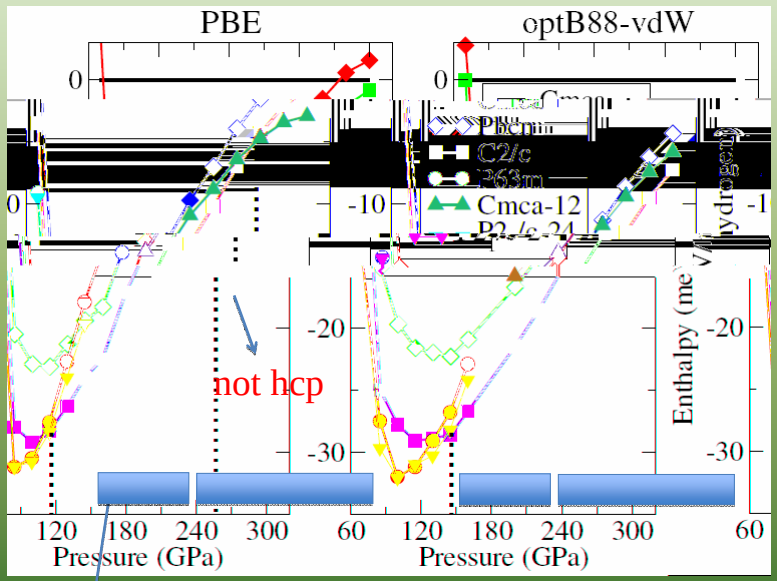

hcp based molecular phase

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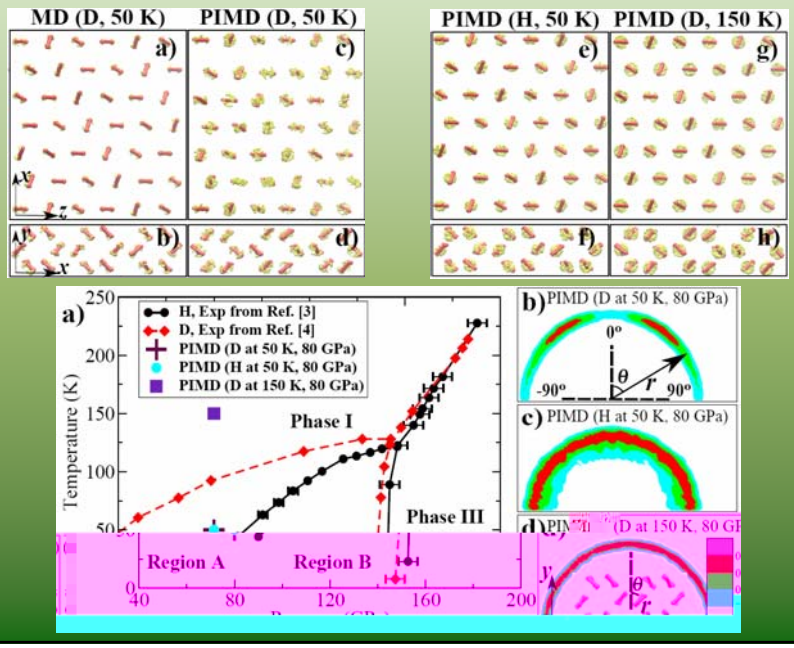

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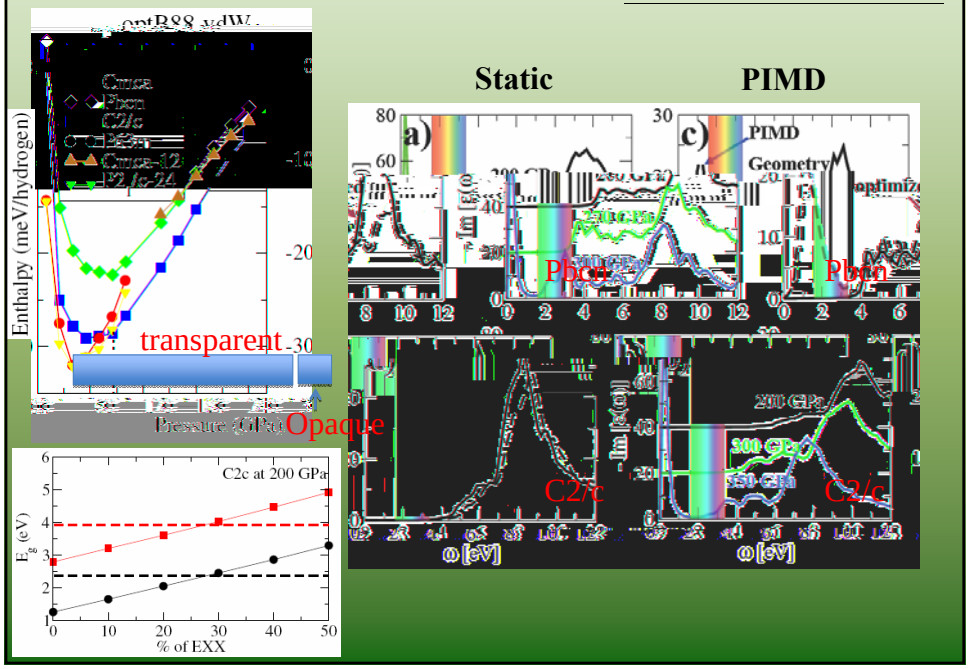
Static
PIMD
Enthalpy (meV/hydrogen)
transparent
Opaque
Pressure (GPa)
C2c at 200 GPa
% of EXX
PIMD
Geometry
Pbcn
Pbcn
C2/c
C2/c
200 GPa
300 GPa
ω [eV]
ω [eV]

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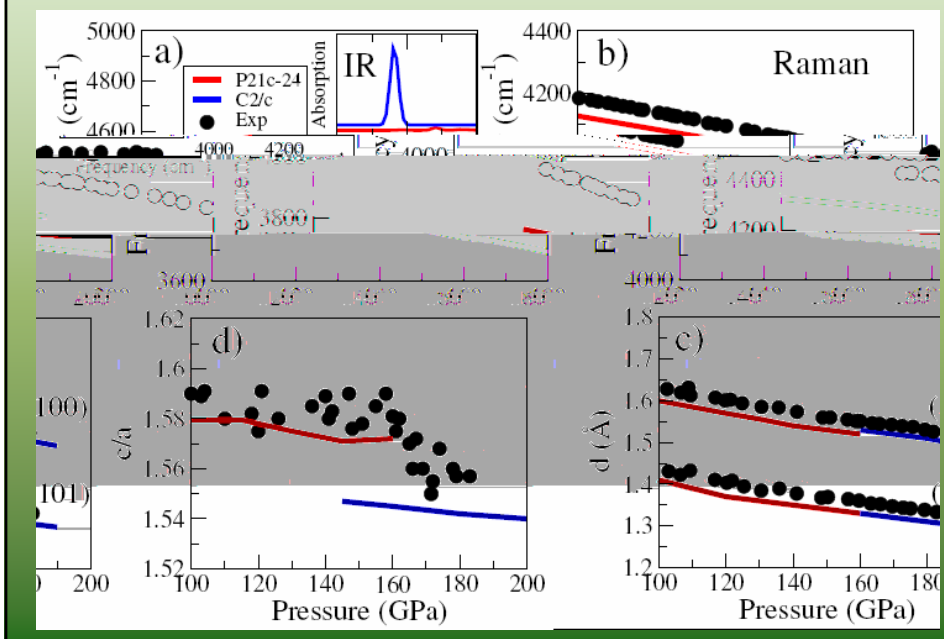
a)
P21c-24
C2/c
Exp
IR
Absorption
b)
Raman
d)
c)
c/a
d (Å)
Pressure (GPa)
Pressure (GPa)

➢ :

- ❑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 H_2O and D_2O**
2. **D_2O 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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