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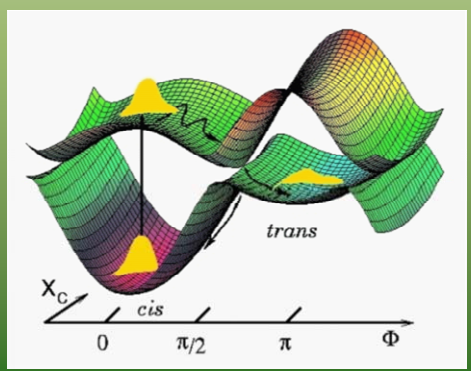
- ❖ 理解材料性质时的关键概念
  - Born-Oppenheimer (BO) 近似
  - 实际系统在BO-势能面上进动
- ❖ 最为通行的方法: ab-initio MD

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
  - 核量子效应对氢键强弱的影响
  - 氢的相图
- ❖进展中的工作

第一部分: 方法

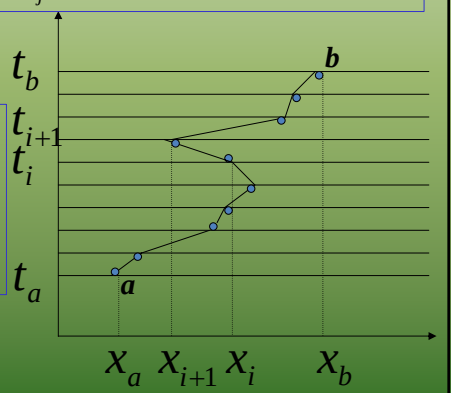
- 背后的物理: 路径积分
  - **Quantum mechanics: probability, propagator**

Schrodinger: $K(x_b,t_b;x_a,t_a)=\sum_j \phi_j^*(x_b)\phi_j(x_a)e^{-(i/\eta)E_j(t_b-t_a)}$

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



第一部分: 方法

- 热力学计算中的价值: 密度矩阵

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

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

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

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

- **Path-integral enters:**

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

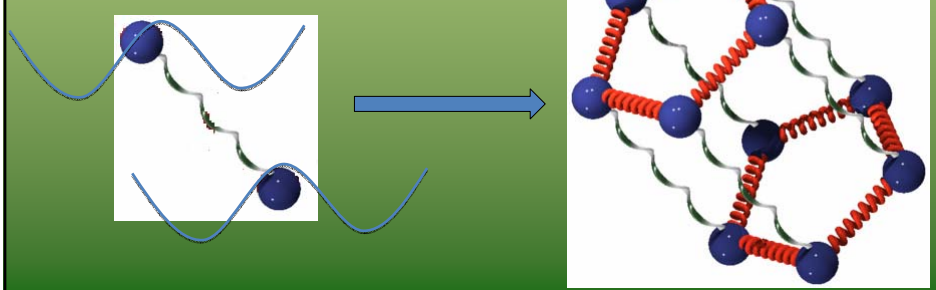
Density matrix of a quantum system ⇒ *Density matrix of a classical polymer of N beads (images)*

第一部分: 方法

- **Path-integral enters:**

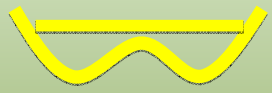
$$\rho(x; k_B T) = \sqrt{\frac{2\pi\eta}{mk_B TN}} \int_{x_0=x}^{x_{N+1}=x} \left(\exp\left\{ -\frac{1}{k_B T} \sum_{i=0}^{N-1} \left[\frac{m(k_B T)^2 N}{2\eta} (x_{i+1} - x_i)^2 + \frac{1}{N} V(x_i) \right] \right\} \right) \prod_{i=0}^{N-1} dx_i$$

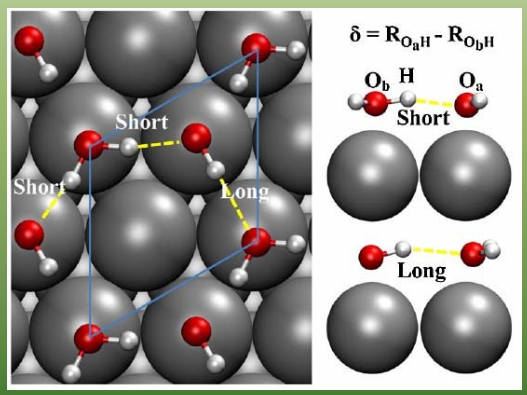
Density function of a quantum system ⇒ *Density function of a polymer of N beads (images)*



问题一: 金属与水的界面

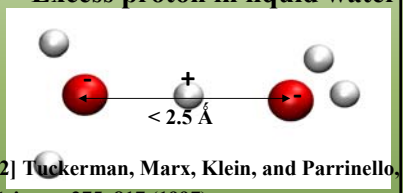
- Water-metal interface is an important issue at the core of several fields
  - Corrosion
  - Electrochemistry
  - Catalysis





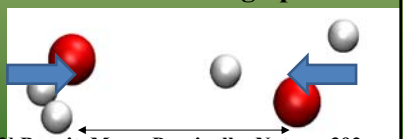
[1] Michaelides, and Hu, JACS, 123, 4235 (2001)

- Excess proton in liquid water



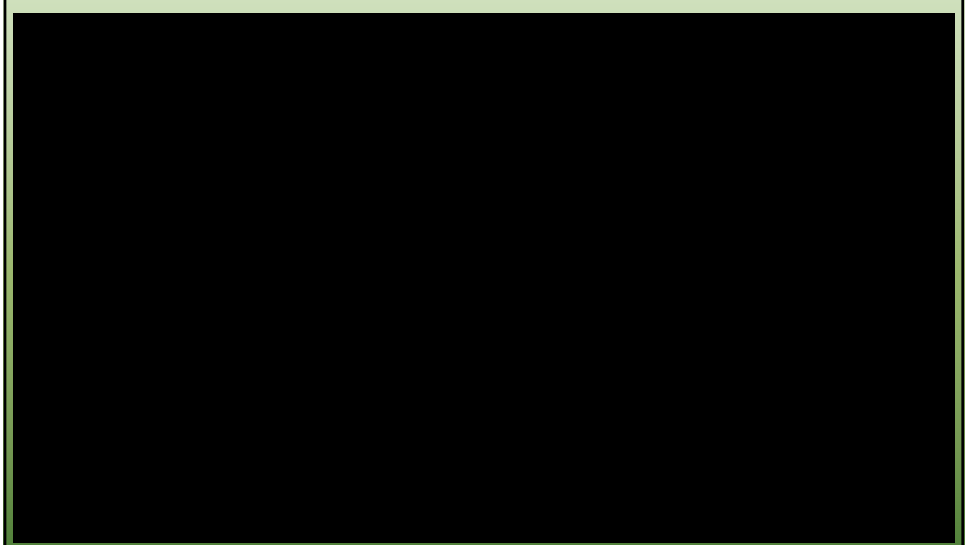
[2] Tuckerman, Marx, Klein, and Parrinello, Science, 275, 817 (1997)

- Bulk ice under high pressure



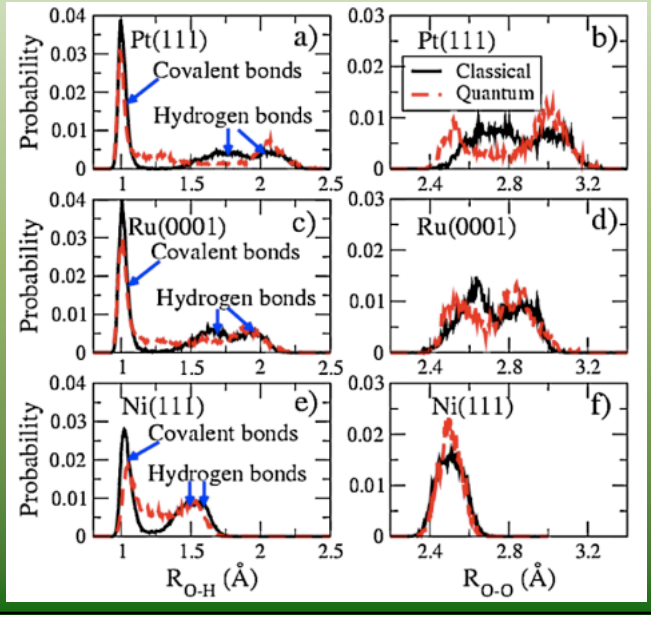
[3] Benoit, Marx, Parrinello, Nature, 392, 258(1998)

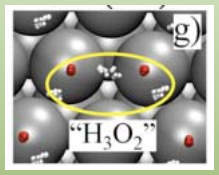
问题一: 金属与水的界面

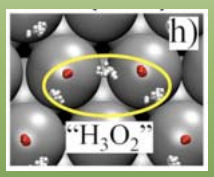


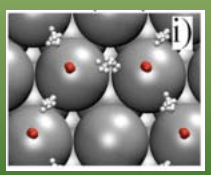
问题一: 金属与水的界面

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



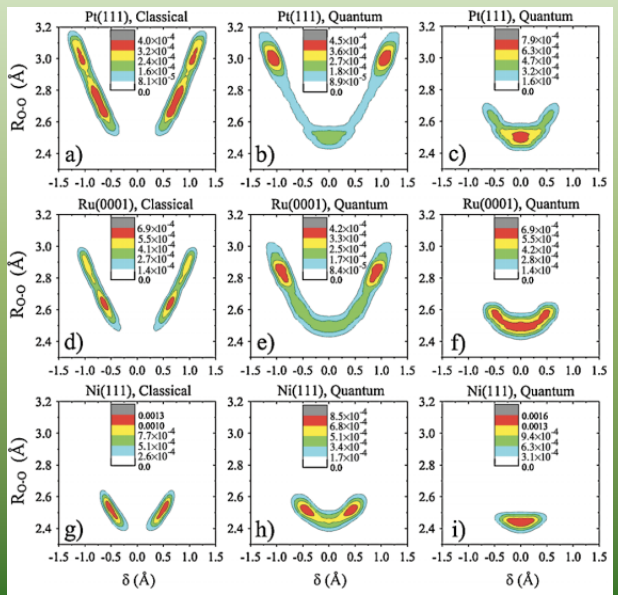


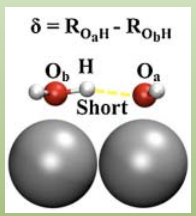




问题一: 金属与水的界面

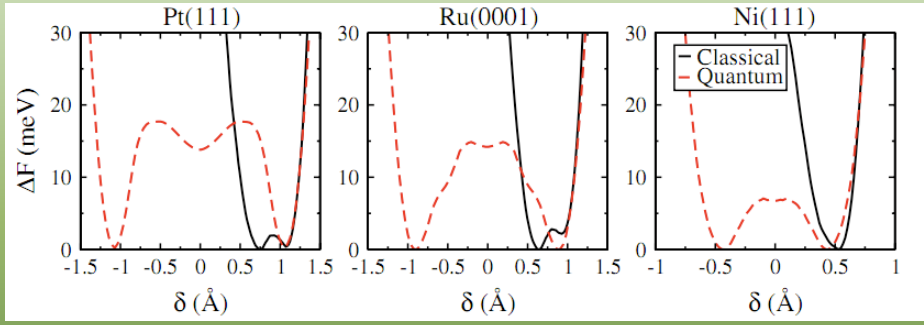
- **Correlate O-H and O-O**





问题一: 金属与水的界面

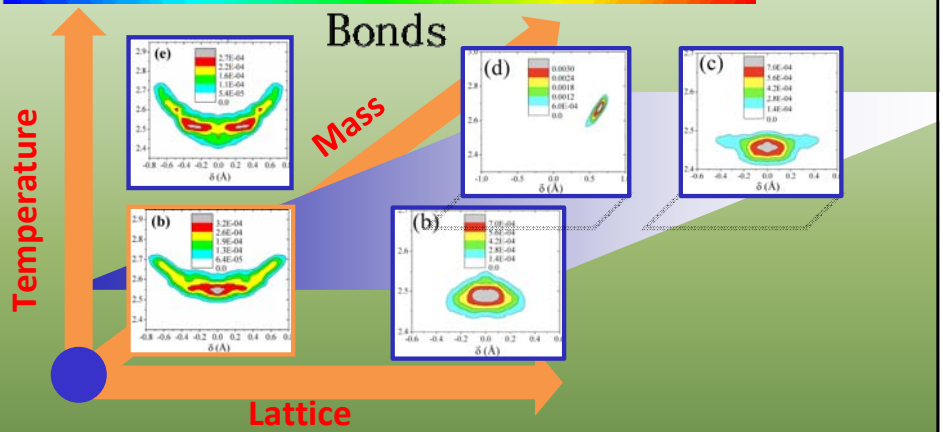
- **Focus on the proton transfer**



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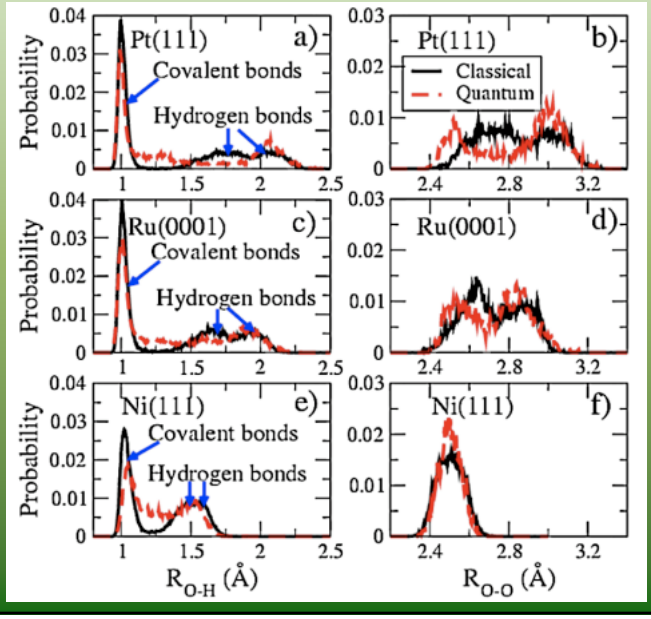
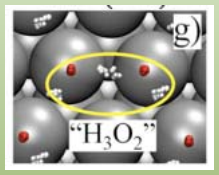
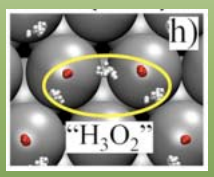
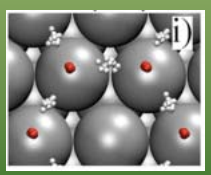
- **Structural properties of the overlayer at 160 K**









问题二: 核量子效应对氢键强弱的影响

➢ **Impact of quantum nuclear effects on H-bond strength?**

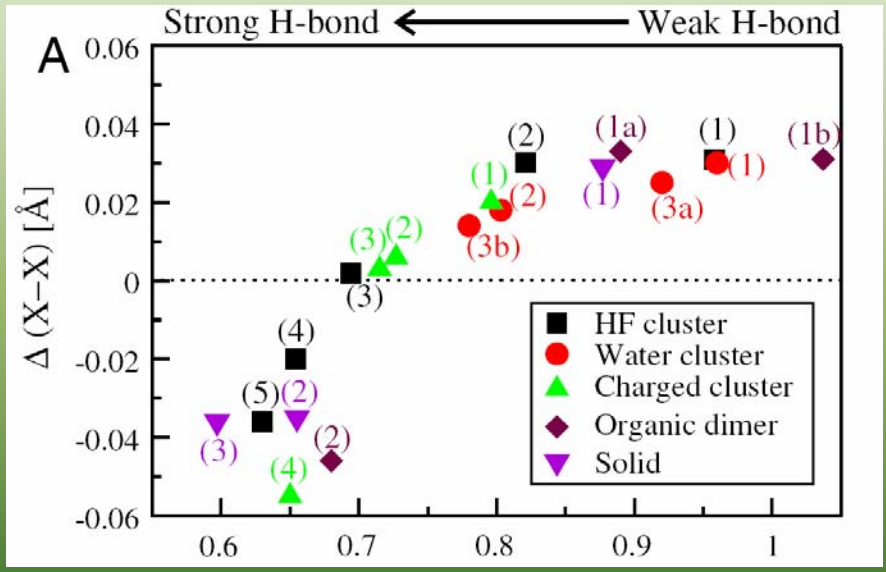
❑ **In 1950s, Ubbelohde effect (replace H with D) in H-bonded crystals.**

❑ **Liquids: water structure is weakened, and liquid HF is strengthened**

❑ **Clusters: $(HF)_n$ when n > 4, strengthened, otherwise, weakened; $(H_2O)_n$ always weakened**

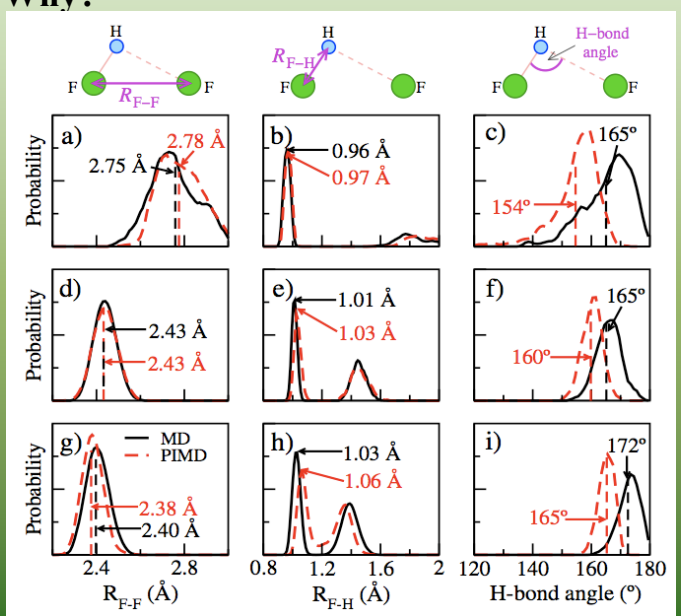
Biggest question: is there a unified picture?

问题二: 核量子效应对氢键强弱的影响



问题二: 核量子效应对氢键强弱的影响

- Why?



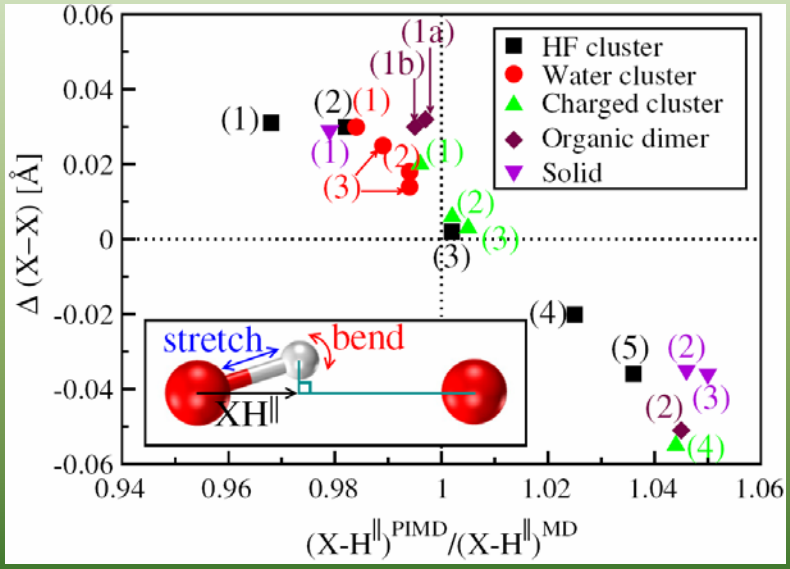
$(HF)_2$

$(HF)_4$

$(HF)_5$

问题二: 核量子效应对氢键强弱的影响

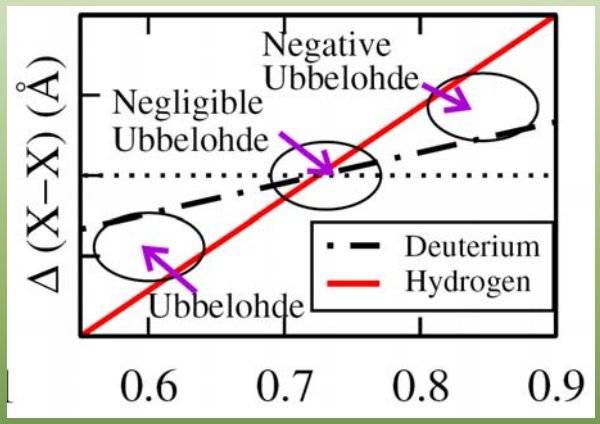
- **Quantitative**



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

问题二: 核量子效应对氢键强弱的影响

- **Rule of Thumb**

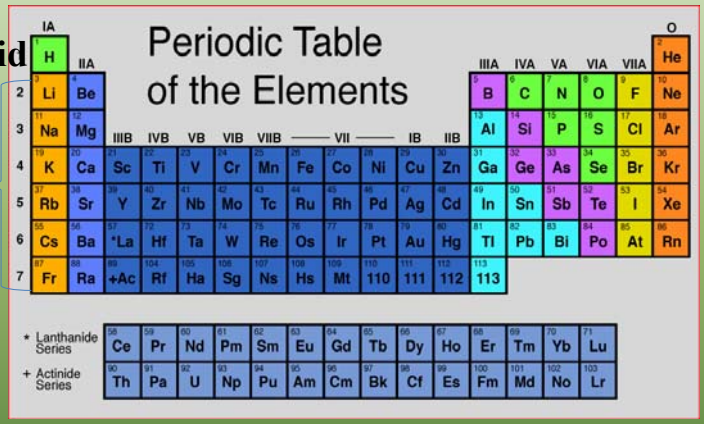


- **Flexible monomer with anharmonic potential must be used if one want to use force-field method in PIMD simulations**

问题三: 氢的相图

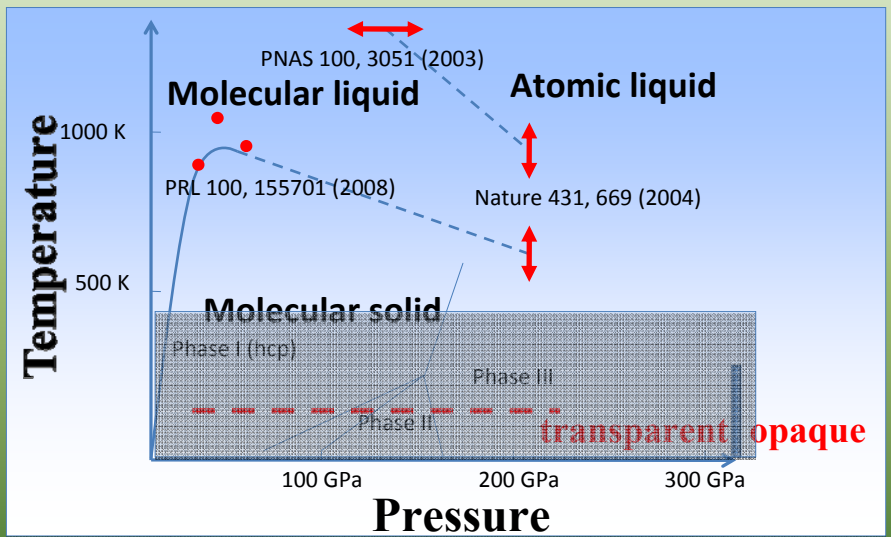
Molecular solid

Alkali metal: atomic solid



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

问题三: 氢的相图



1) Phase I: free rotating molecular hcp phase
2) Phase II, III: molecular feature kept
3) Phase boundary: spectrum changes
4) I/II isotope dependent, II/III not.
5) Turns opaque at 300 GPa, completely dark at 320 GPa.

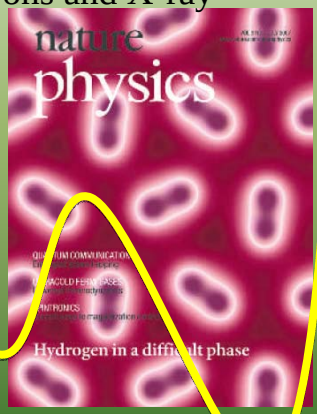
问题三: 氢的相图

❑ 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



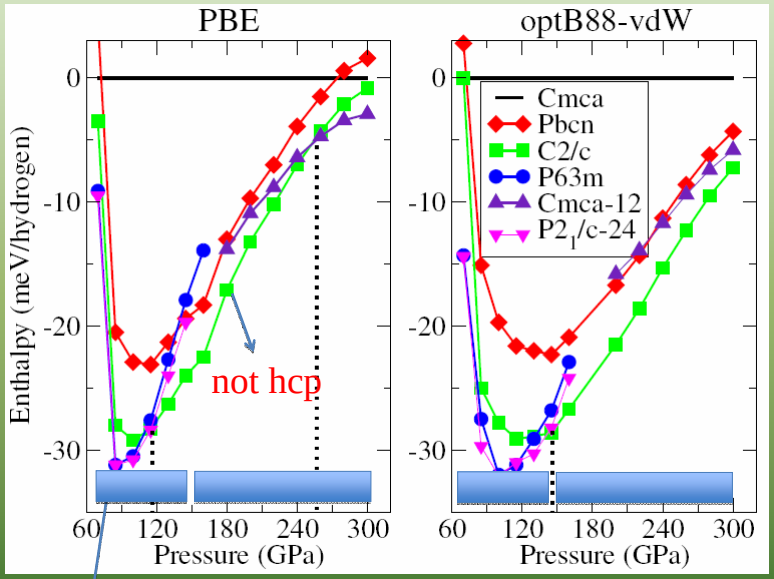
Pickard and Needs, 2007

问题三: 氢的相图

❑ Theoretically:

1) Electronic structure accurate: PBE + DF-vdW
2) Configuration space explored: AIRSS
3) Quantum nature of hydrogen ： ab initio PIMD addressed accurately
4) Optical property properly described: GW, hybrid functional, IR, X-ray diffraction, and Raman

问题三: 氢的相图



hcp based molecular phase

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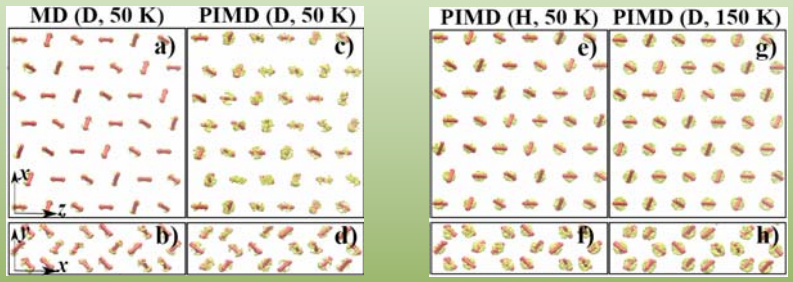

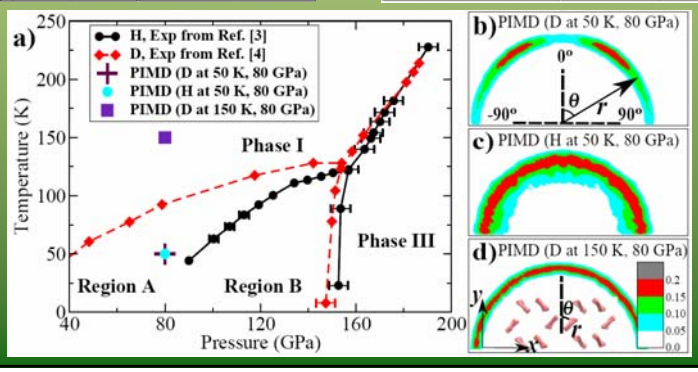

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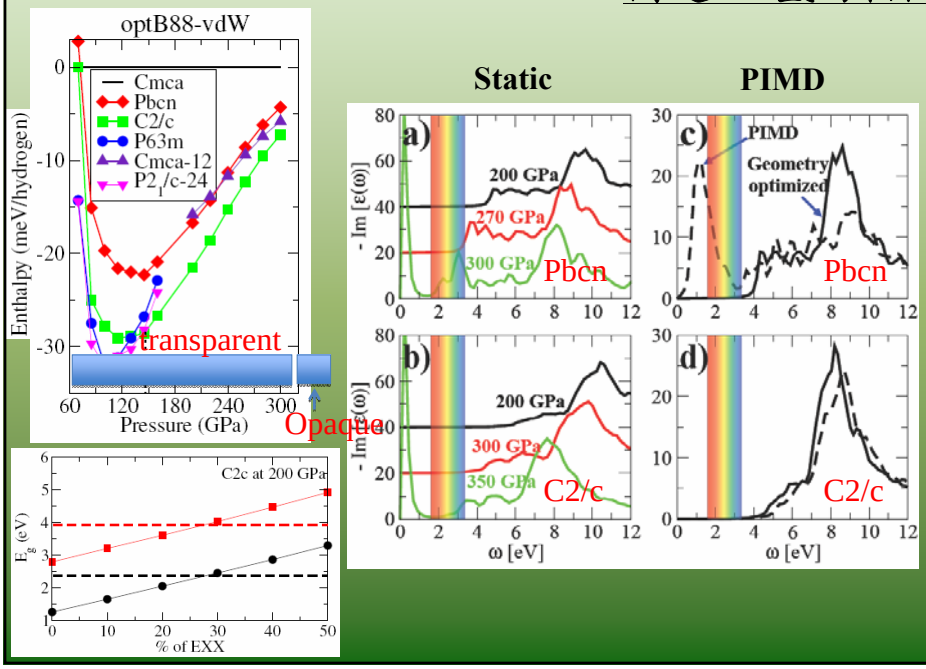

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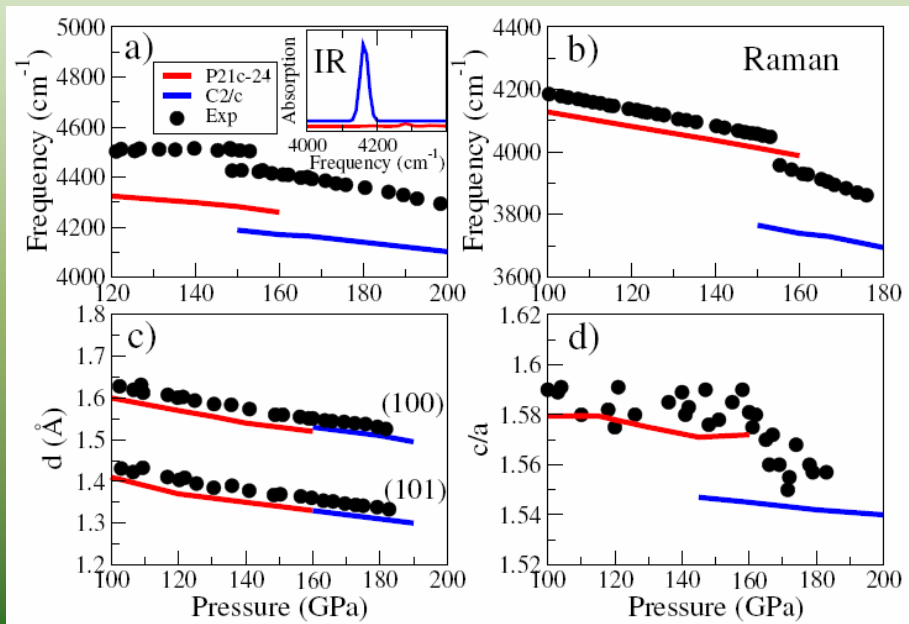

进行中的工作

- 现有程序基础上:
  - Proton transport along 1D water chain
  - Higher pressure hydrogen phase (>5Mbar)
  - Soft Phonon
  - Thermal Conductivity ….
- 新的程序: FHI-aims
- 实时进动: CMD, RPMD

谢谢!


Brent Walker


Mat Probert


Ali Alavi


Chris Pickard


Richard Needs


Angelos Michaelides

… 凝聚态所的各位老师

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**

…….