关于原子核的量子效应的模拟方法的介绍

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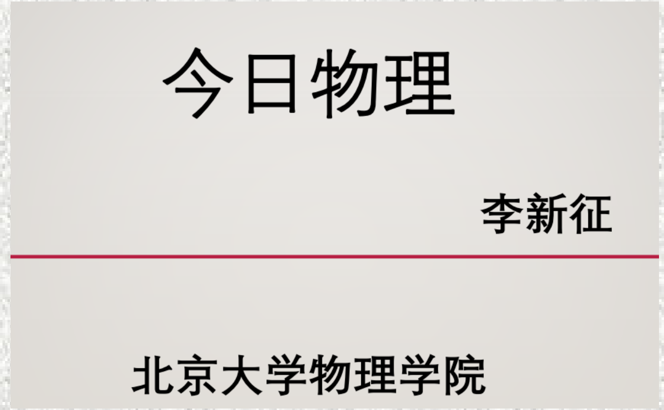
感谢高老师的邀请!

目 录

- 什么是原子核的量子效应?
- 模拟原子核量子效应的计算方法有哪些，它们的优缺点是什么?
- 几个例子，来感受相关研究。
- **Take-home Message.**

第一部分：什么是原子核的量子效应？

- 物理学的核心任务是思维范式的建立！



- ➢ 物理学的哲学属性；
- ➢ 物理学史；
- ➢ 今天的物理学。

今天也会用这个路子来介绍这个方向

- 出发点：上面那句话。

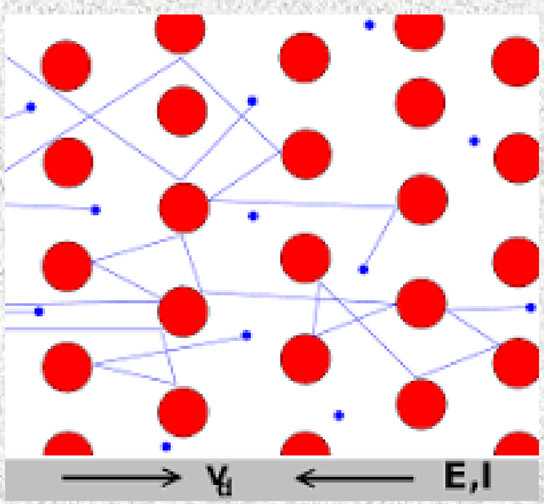
Apply to: 牛顿力学、热力学、电动力学、量子力学、统计力学、相对论力学等。

学完之后，我们脑子里面无非是有了一个理论框架，去描述相关问题（客观、有预测能力）

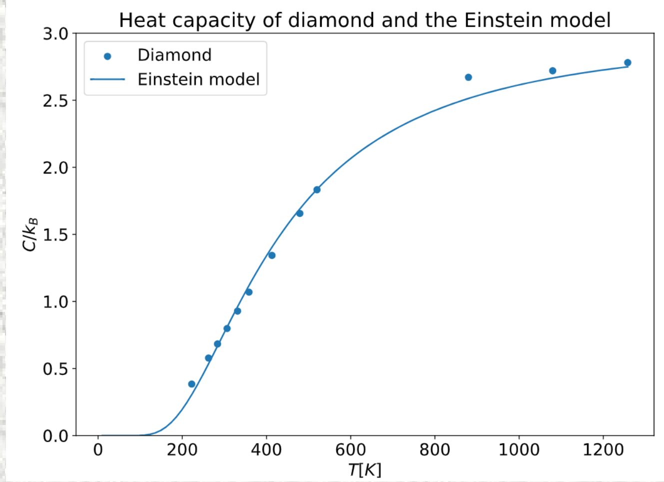
第一部分：什么是原子核的量子效应？

- 这个情况，同样apply to凝聚态物理

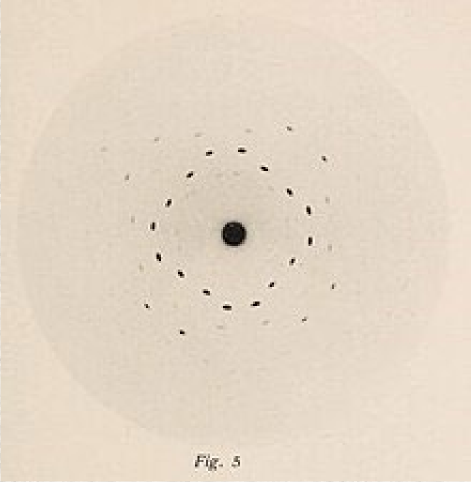
历史上，我们凝聚态物理的发展，一模一样走的就是这条路！



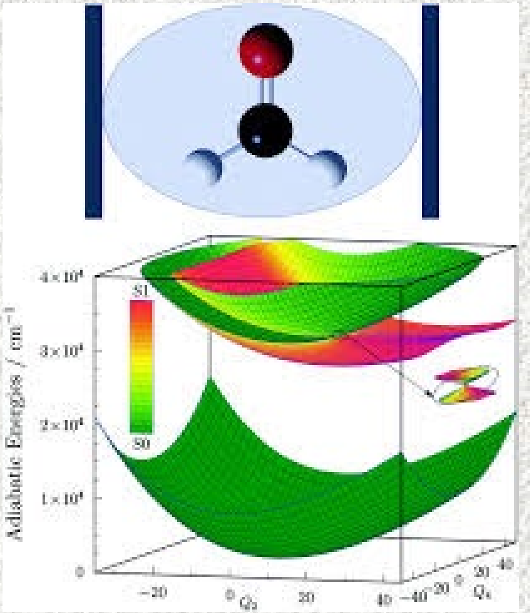
1900 Drude Model



1907 Einstein Model



1912 Laue X-ray

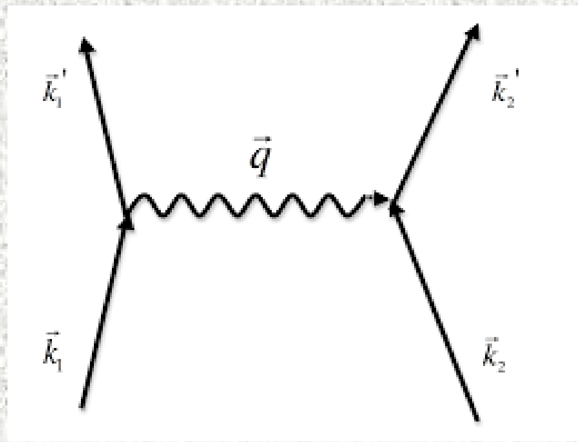


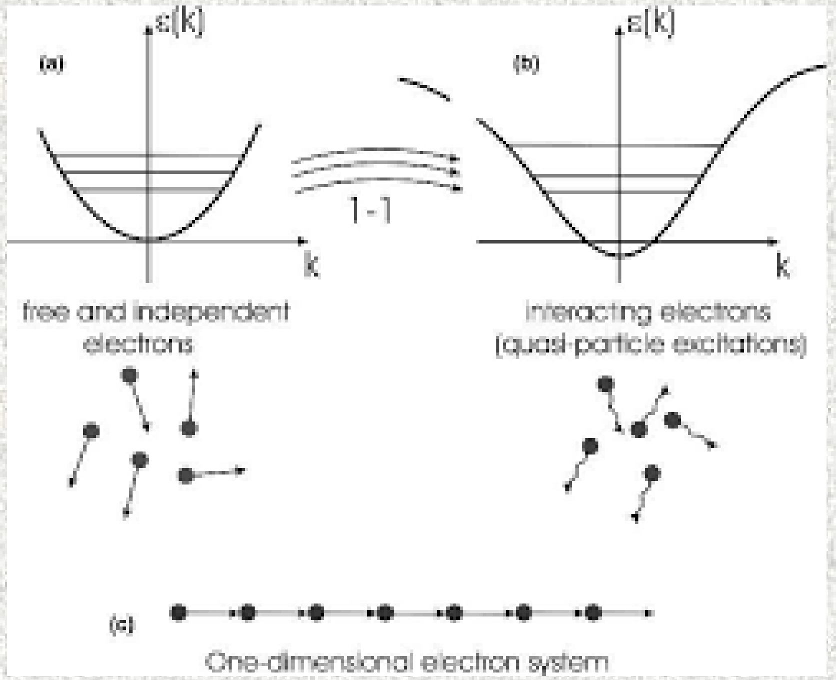
量子气体理论 ← Bloch波、周期性边界条件、简谐声子 + Quantum Mechanic & Born-Oppenheimer Approximation

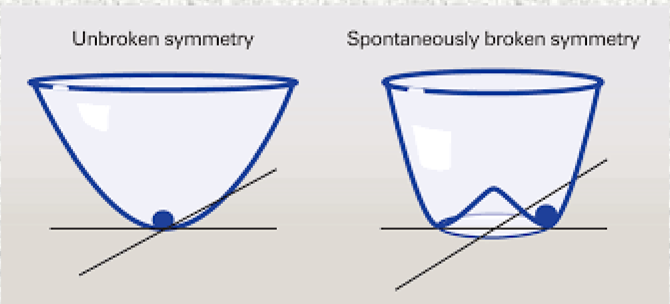
第一部分：什么是原子核的量子效应？

- 这个情况，同样apply to凝聚态物理

上世纪40年代开始，高潮是50、60年代，之后依然延展





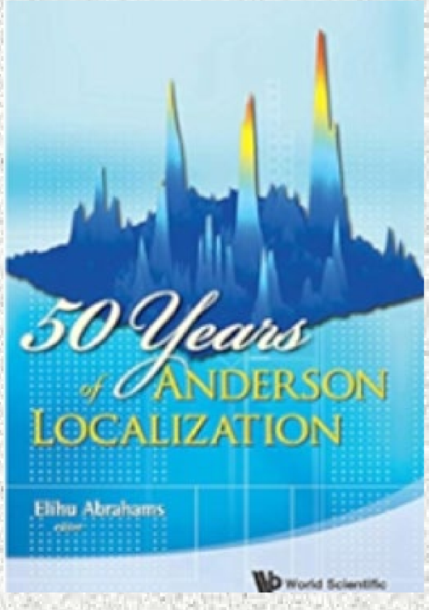


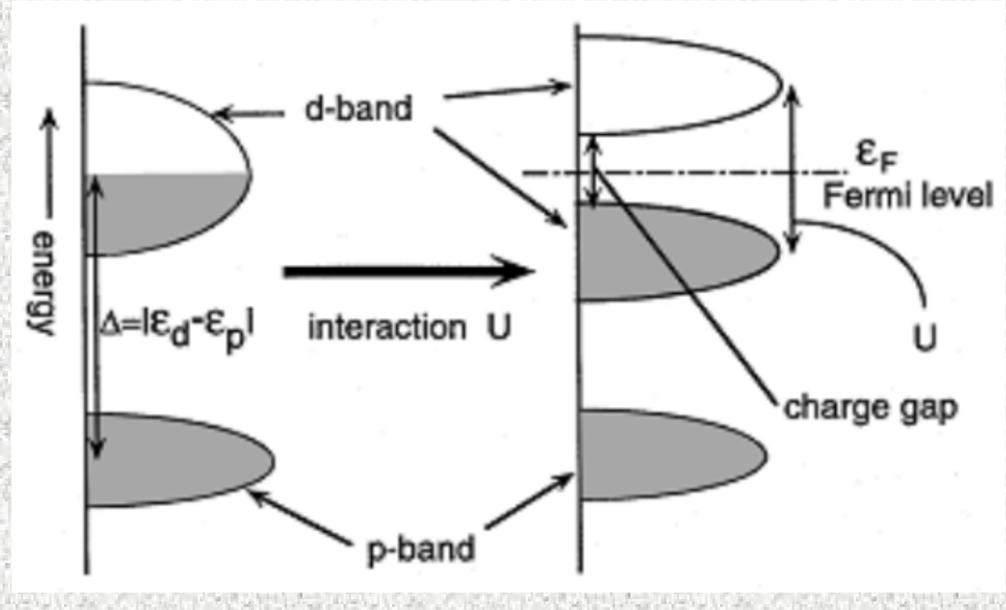
量子液体理论

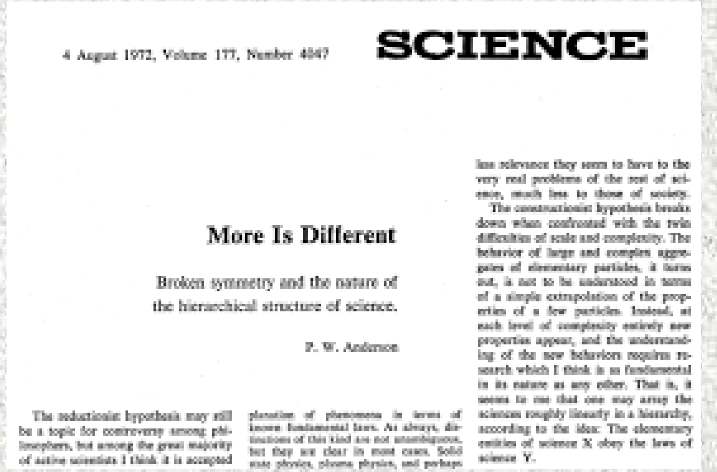
第一部分：什么是原子核的量子效应？

- 这个情况，同样apply to凝聚态物理

上世纪50年代开始，70年代喊出来







4 August 1972, Volume 177, Number 4047

SCIENCE

More Is Different

Broken symmetry and the nature of the hierarchical structure of science.

P. W. Anderson

The reductionist hypothesis may still be a topic for controversy among philosophers, but among the great majority of active scientists I think it is accepted ... planation of phenomena in terms of known fundamental laws. As always, distinctions of this kind are not unambiguous, but they are clear in most cases. Solid state physics, plasma physics, and perhaps ... less relevance they seem to have to the very real problems of the rest of science, much less to those of society.

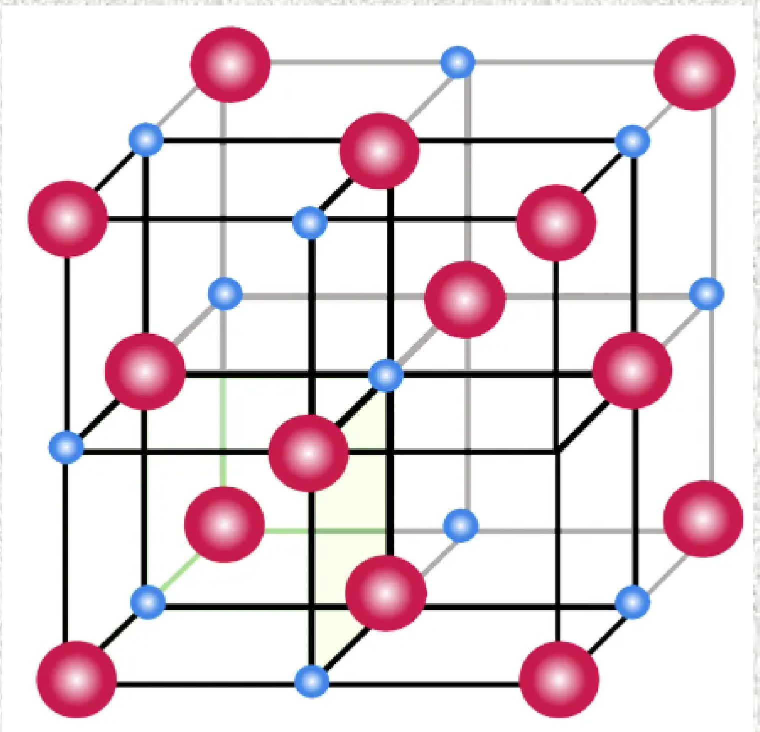
The constructionist hypothesis breaks down when confronted with the twin difficulties of scale and complexity. The behavior of large and complex aggregates of elementary particles, it turns out, is not to be understood in terms of a simple extrapolation of the properties of a few particles. Instead, at each level of complexity entirely new properties appear, and the understanding of the new behaviors requires research which I think is as fundamental in its nature as any other. That is, it seems to me that one may array the sciences roughly linearly in a hierarchy, according to the idea: The elementary entities of science X obey the laws of science Y.

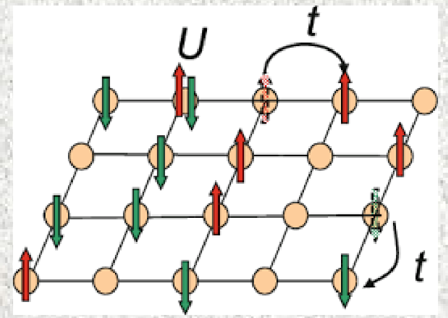
1958 Anderson Localization Mott (1949)-Hubbard (1963) Insulator

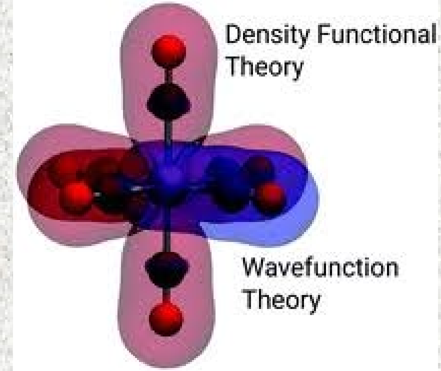
Emergent Phenomenon

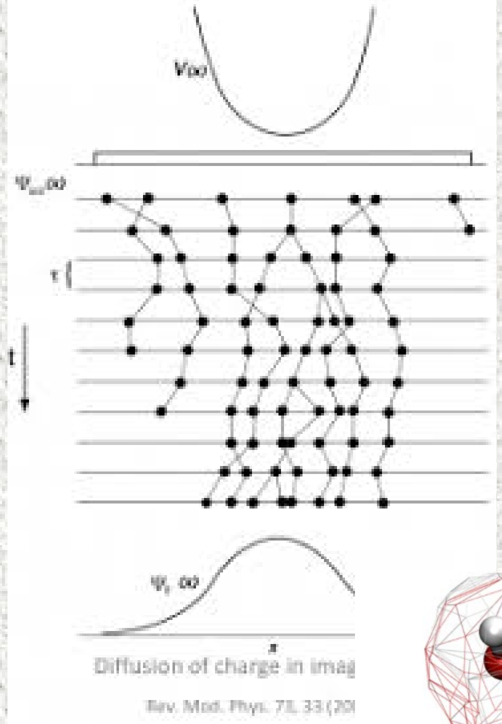
第一部分：什么是原子核的量子效应？

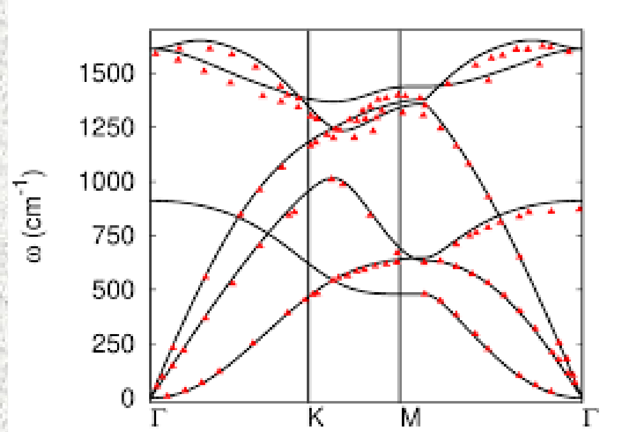
- 这个情况，同样apply to凝聚态物理

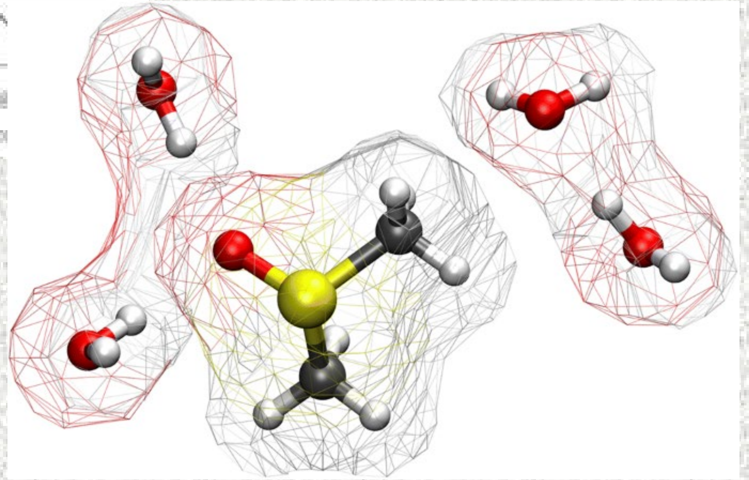








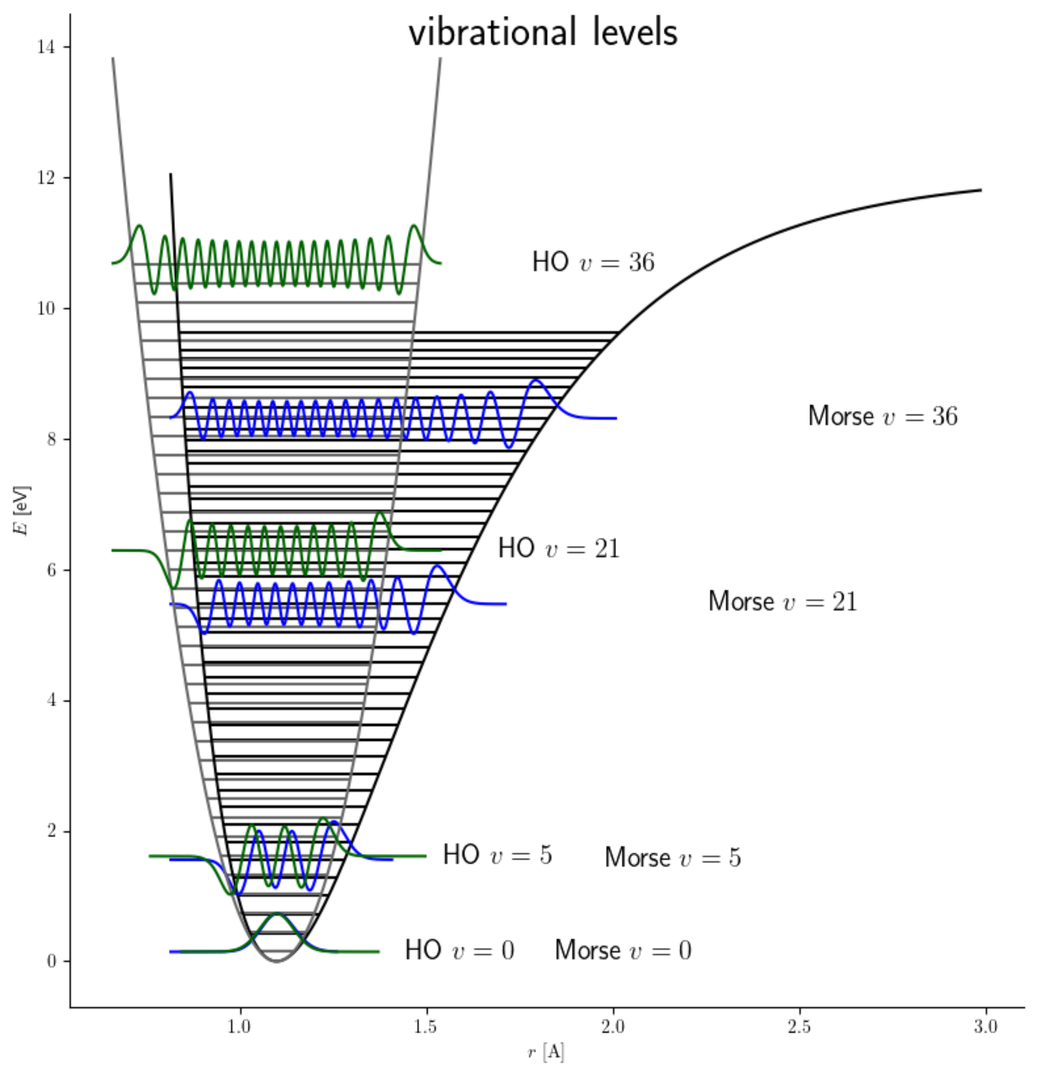


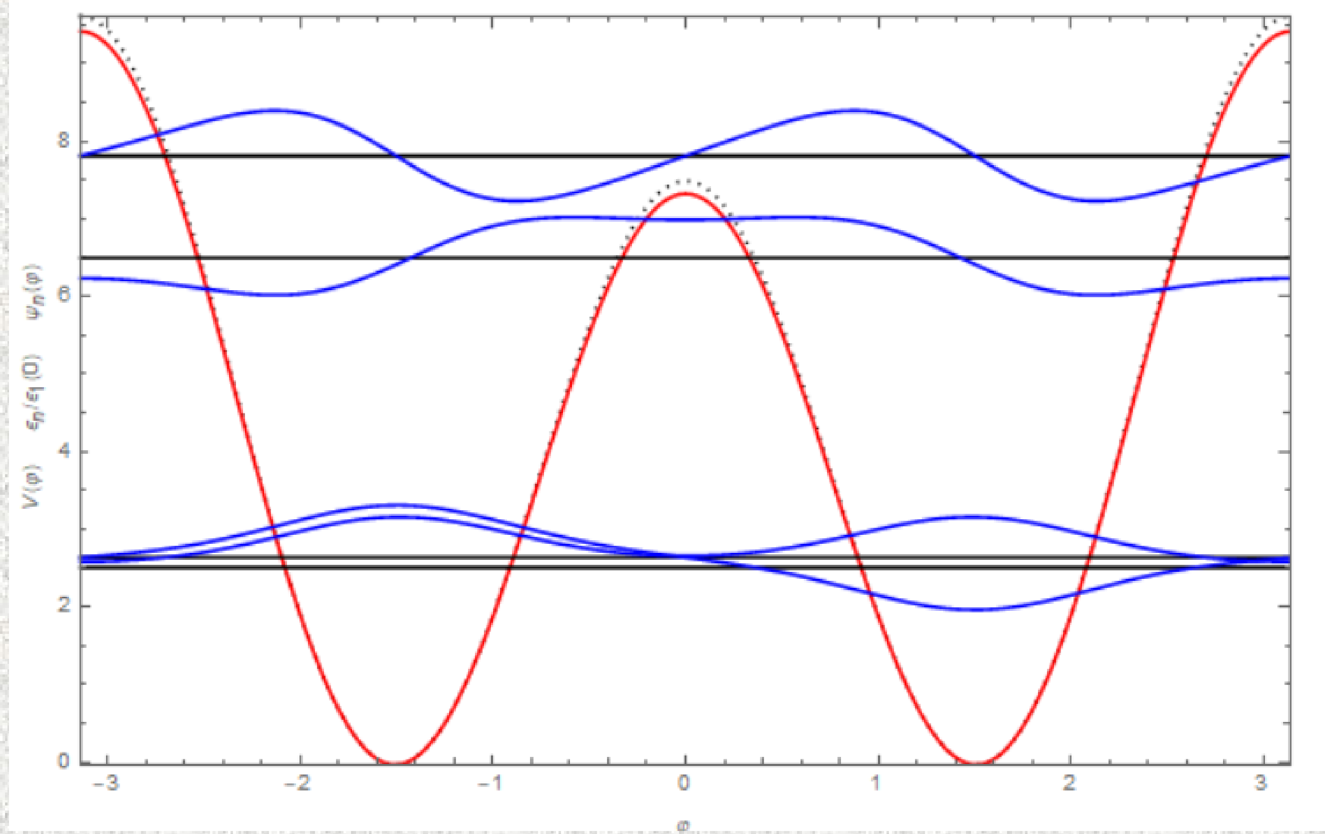


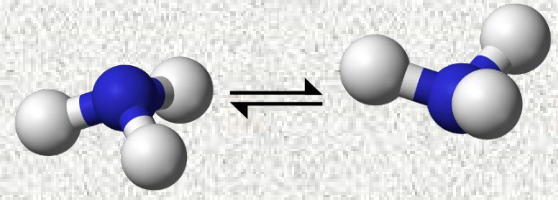
一个思维范式（很长，但可以说清）

第一部分：什么是原子核的量子效应?

- 这个情况，同样apply to凝聚态物理



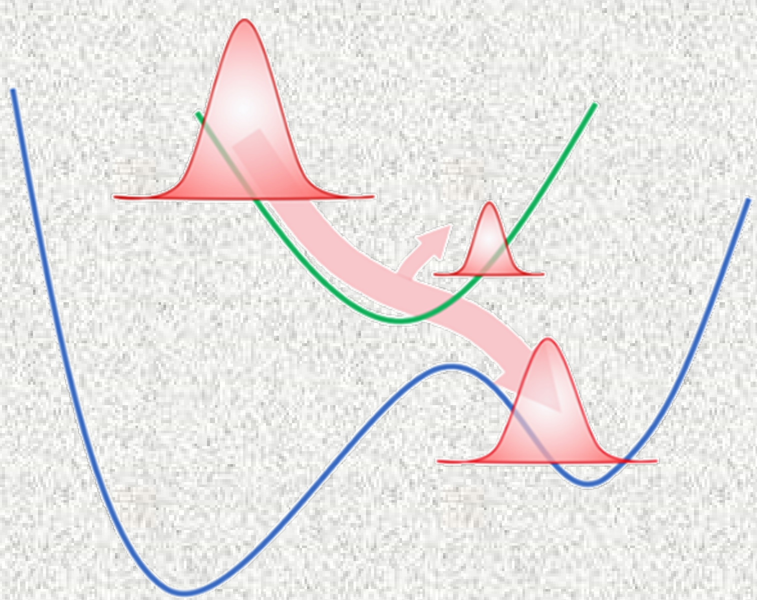




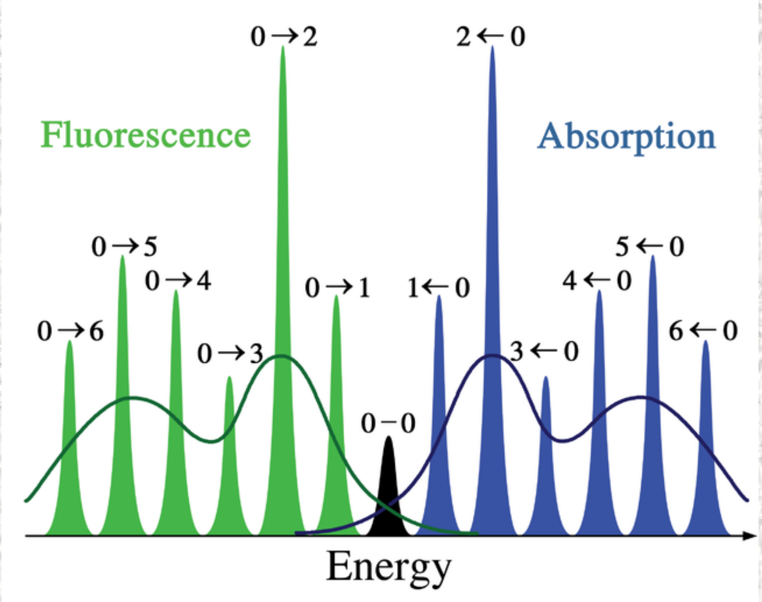
第一部分：什么是原子核的量子效应?

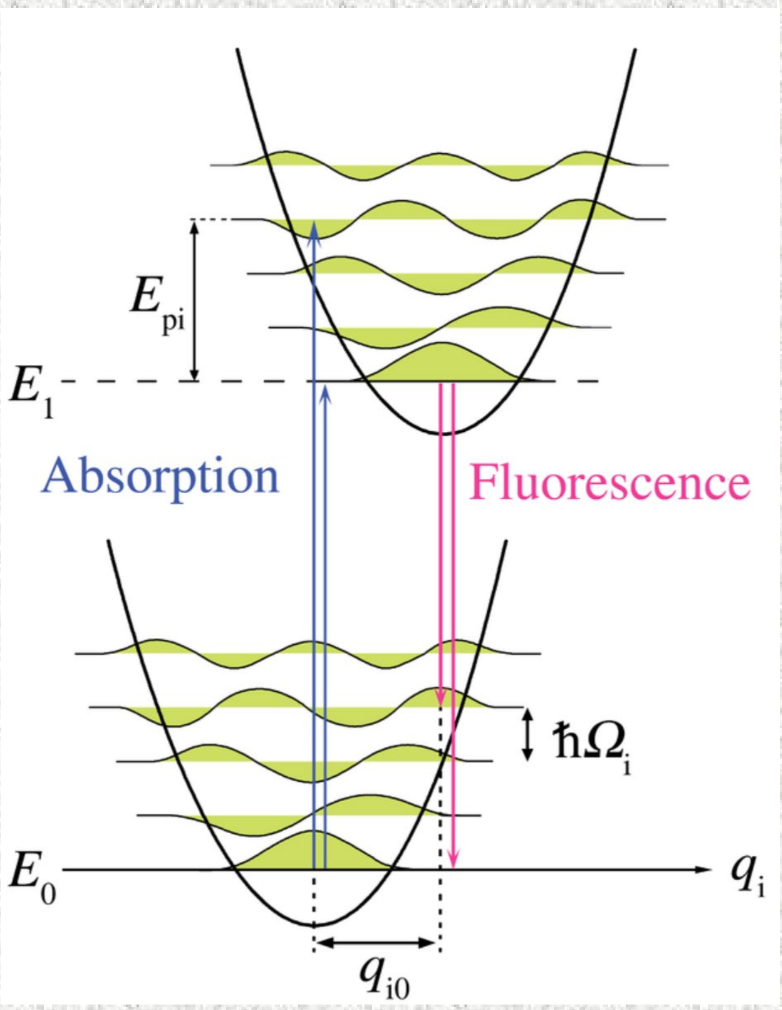
- 这个情况，同样apply to凝聚态物理

Coupled nuclear & electronic DOFs



Franck-Condon principle (1926)：





Clear: Quantum states of vibration contribute to the spectrum.
Unclear: how should the quantum state with nuclei be rigorously expressed?

第一部分：什么是原子核的量子效应?

- 这个情况，同样apply to凝聚态物理

Die Gültigkeitsgrenze der Theorie der idealen Kristalle und ihre Überwindung.

Von

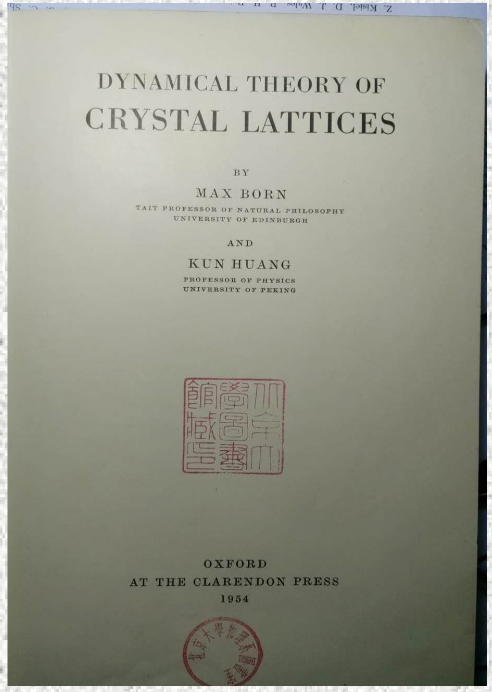
Max Born, F. R. S., Edinburgh.

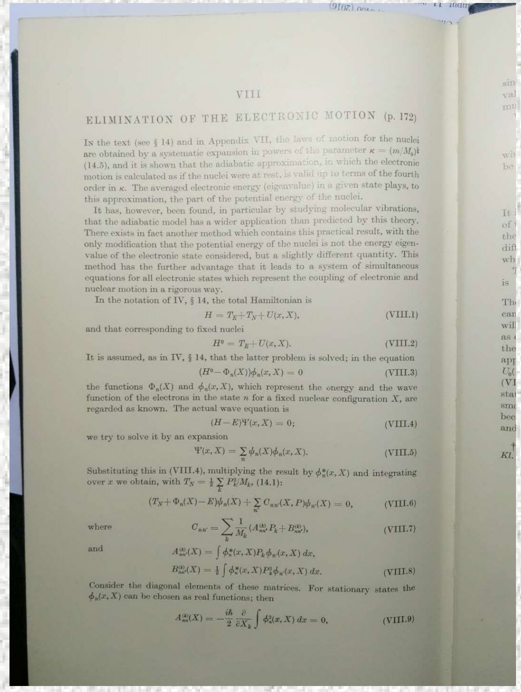
Einleitung.

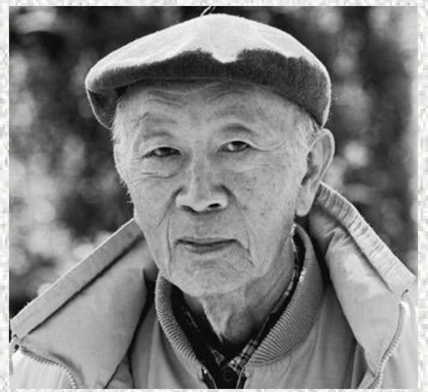
Die Theorie der idealen Kristalle, an der ich seit mehr als 40 Jahren gearbeitet habe, ist trotz mancher Erfolge weder logisch noch empirisch befriedigend. Die wichtigsten Einwände sind die folgenden:

M. Born, Nachr. Akad. Wiss. Göttingen, Math.-Phys. Klasse IIa, Math.-phys.-chem. Abt., S. Art. Nr. 6, 1 (1951)

(The validity limit of the theory of ideal crystals and their overcoming)







Born-Huang Expansion (1954)

第一部分：什么是原子核的量子效应？

- 这个情况，同样apply to凝聚态物理

$$\Psi(x, X, X^0) = \sum_n \psi_n(X, X^0)\, \varphi_n(x, X^0), \quad (2.5)$$

Born, 1951

$$\Psi(x, X) = \sum_n \psi_n(X)\phi_n(x, X). \quad (\text{VIII}.5)$$

Born & Huang, 1954

- **A time-dependent many-body wave function of electrons and nuclei:**

$$\Psi^j(\vec{r}, \vec{R}, t) = \sum_{n=1}^{\text{el}} \chi_n^j(\vec{R}, t)\Phi_n(\vec{r}, \vec{R})$$

$\Phi_n(\vec{r}, \vec{R})$ **n-th electronic state wave function with ionic potential defined by $\vec{R}$**

$\chi_n^j(\vec{R}, t)$ **Time-dependent wave packet of nuclei on the *n*-th electronic state, with contribution from different vibronic states included.**

理想世界。

原子核的量子效应、非绝热效应，取舍

目录

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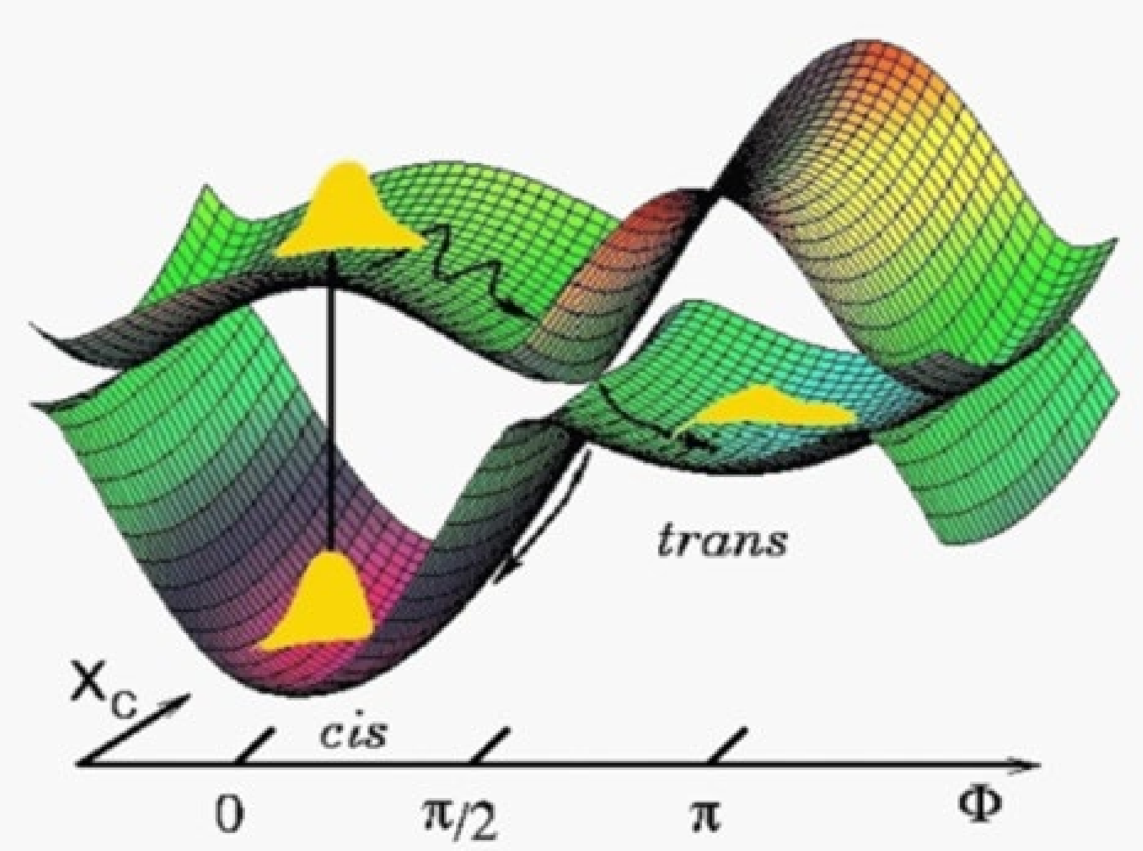
- 模拟原子核量子效应的计算方法有哪些，它们的优缺点是什么?
- 几个例子，来感受相关研究。
- **Take-home Message.**

第二部分：模拟方法、优缺点



$$\Psi^j(\vec{r},\vec{R},t)=\sum_{n=1}^{\mathrm{el}}\chi_n^j(\vec{R},t)\Phi_n(\vec{r},\vec{R})$$

绝热层面的核量子效应（统计层面、考虑动力学）、考虑了非绝热的核量子效应（统计层面、考虑动力学）

方法：

波函数方法、路径积分方法、半经典方法等。

第二部分：模拟方法、优缺点

- Physics behind: path-integral
  - Quantum mechanics: probability, propagator

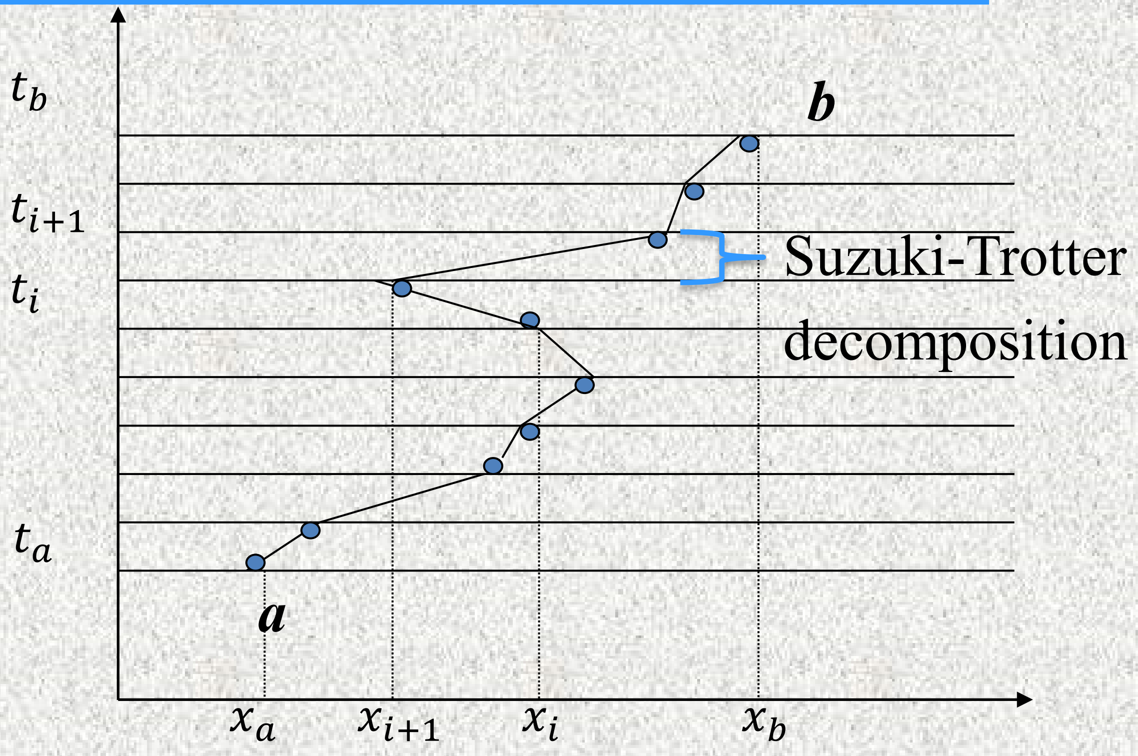
Schrodinger:

$$K(x_b,t_b;x_a,t_a)=\sum_j \varphi_j(x_b)\,\varphi_j^*(x_a)e^{-(i/\hbar)E_j(t_b-t_a)}$$

  - Path-integral

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

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



第二部分：模拟方法、优缺点

- Density matrix

$$\rho(x_N, x_0; 1/k_BT) = \sum_j \varphi_j(x_N)\,\varphi_j^*(x_0) e^{-E_j/k_BT}$$

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

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

$i(t_N - t_0)/\hbar$ → $1/k_BT$

- Path-integral enters

$$\rho(x, x'; k_BT) = \sqrt{\frac{2\pi\hbar}{mk_BTN}} \int_{x_0=x}^{x_N=x\prime} \left(\exp\left\{ -\frac{1}{k_BT} \sum_{i=0}^{N} \left[\frac{m(k_BT)^2 N}{2\hbar} (x_{i+1} - x_i)^2 + \frac{1}{N} V(x_i) \right] \right\} \right) \prod_{N-1}^{i=1} dx_i$$

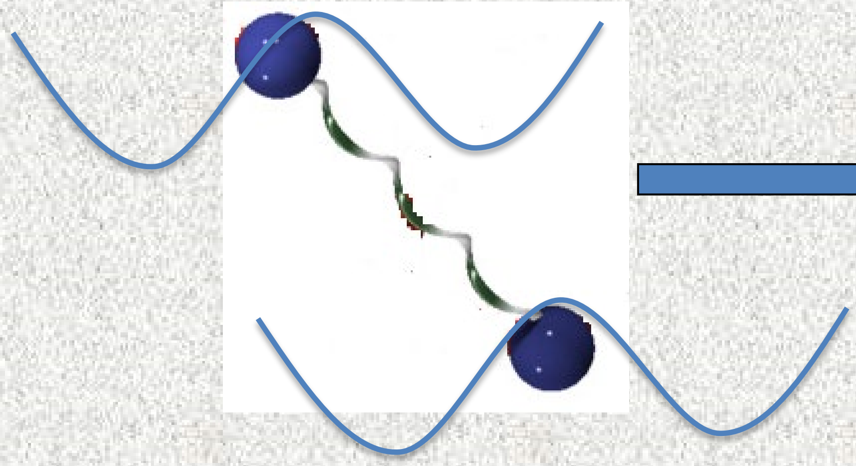
Density matrix of a quantum system → **Density matrix of a classical polymer of N beads (images)**

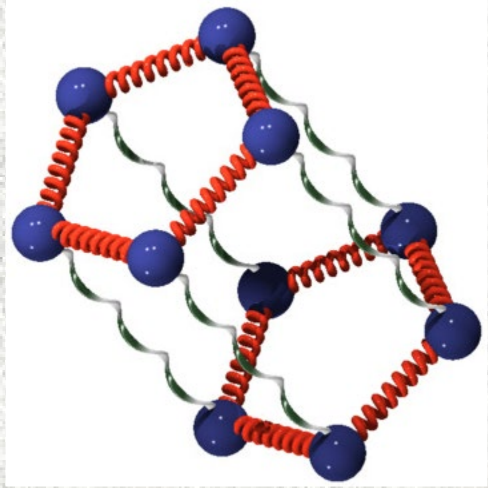
第二部分：模拟方法、优缺点

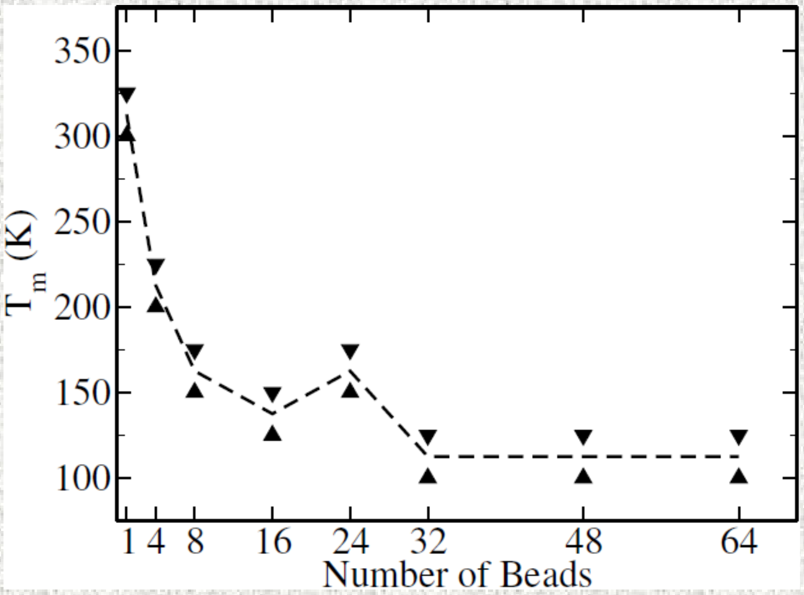
- Density function

$$\rho(x;k_BT)=\sqrt{\frac{2\pi\hbar}{mk_BTN}}\int_{x_0=x}^{x_{N+1}=x}\left(\exp\left\{-\frac{1}{k_BT}\sum_{i=0}^{N-1}\left[\frac{m(k_BT)^2N}{2\hbar}(x_{i+1}-x_i)^2+\frac{1}{N}V(x_i)\right]\right\}\right)\prod^{\substack{i=0\\N-1}}dx_i$$

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







第二部分：模拟方法、优缺点

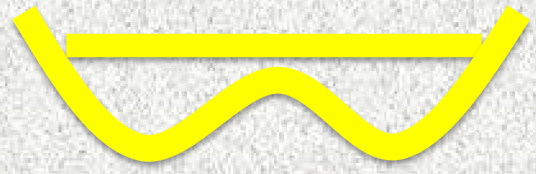
X.Z. Li, M. Probert, A. Alavi, and A. Michaelides, **Phys. Rev. Lett. 104**, 066102 (2010)

D. Chandler and P.G. Wolynes, **J. Chem. Phys. 74**, 4078 (1981)

B. J. Berne and D. Thirumalai, **Ann. Rev. Phys. Chem. 37**,401 (1986)

D. Marx and M. Parrinello, **Z. Phy. B: Condens. Matter 95**, 143 (1994)

M. E. Tuckerman, D. Marx, M. L. Klein, and M. Parrinello, **J. Chem. Phys. 104**, 5579 (1996)



第二部分：模拟方法、优缺点

- 理论框架的搭构：

[1] R. P. Feynman, **Phys. Rev. 76**, 769 (1949).
[2] R. P. Feynman, **Phys. Rev. 90**, 1116 (1953).
[3] R. P. Feynman, **Phys. Rev. 91**, 1291 (1953).
[4] R. P. Feynman, **Phys. Rev. 91**, 1301 (1953).
[5] R. P. Feynman and A. R. Hibbs, *Quantum Mechanics and Path Integrals* (McGraw-Hill Inc., 1965).

- 分子模拟中的早期尝试：

分子动力学采样

[1] D. Chandler and P. G. Wolynes, **J. Chem. Phys. 74**, 4078 (1981).
[2] M. Parrinello and A. Rahman, **J. Chem. Phys. 80**, 860 (1984).
[3] B. J. Berne and D. Thirumalai, **Annu. Rev. Phys. Chem. 37**, 401 (1986).

第二部分：模拟方法、优缺点

蒙特卡洛采样

[1] E. L. Pollock and D. M. Ceperley, **Phys. Rev. B 30**, 2555 (1984).
[2] D. M. Ceperley and E. L. Pollock, **Phys. Rev. Lett. 56**, 351 (1986).
[3] E. L. Pollock and D. M. Ceperley, **Phys. Rev. B 36**, 8343 (1987).
[4] D. M. Ceperley, **Rev. Mod. Phys. 67**, 279 (1995).

共同点：基于力场，无法描述化学键断裂这种有意思的现象

- 与第一性原理电子结构计算的结合：

[1] M. E. Tuckerman, D. Marx, M. L. Klein, and M. Parrinello, **J. Chem. Phys. 104**, 5579 (1996).
[2] D. Marx and M. Parrinello, **J. Chem. Phys. 104**, 4077 (1996).
[3] M. E. Tuckerman, D. Marx, M. L. Klein, and M. Parrinello, **Science 275**, 817 (1997).
[4] M. Benoit, D. Marx, and Parrinello, **Nature 392**, 258 (1998).
[5] D. Marx, M. E. Tuckerman, J. Hutter, and M. Parrinello, **Nature 397**, 601 (1999)……..

特点：**Car-Parrinello MD（BO-MD的一个近似）**

第二部分：模拟方法、优缺点

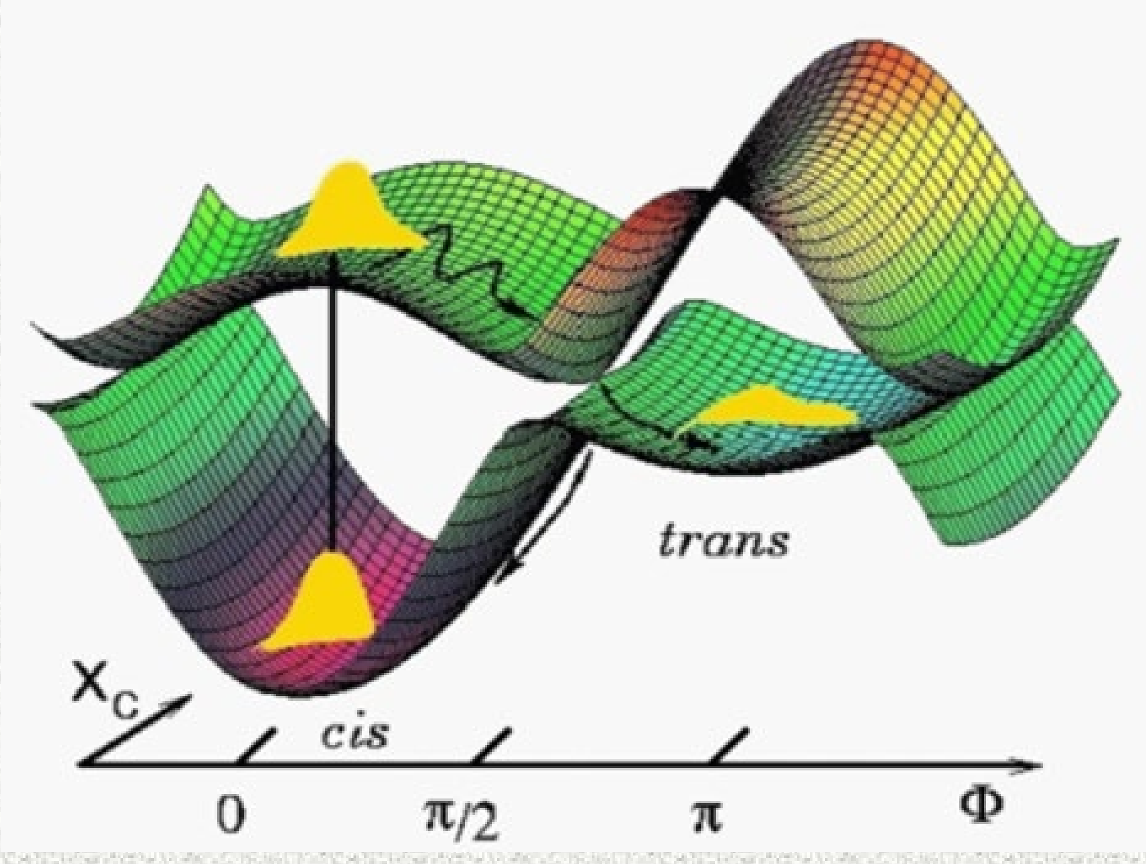
- **Born-Oppenheimer MD的引入与应用：**

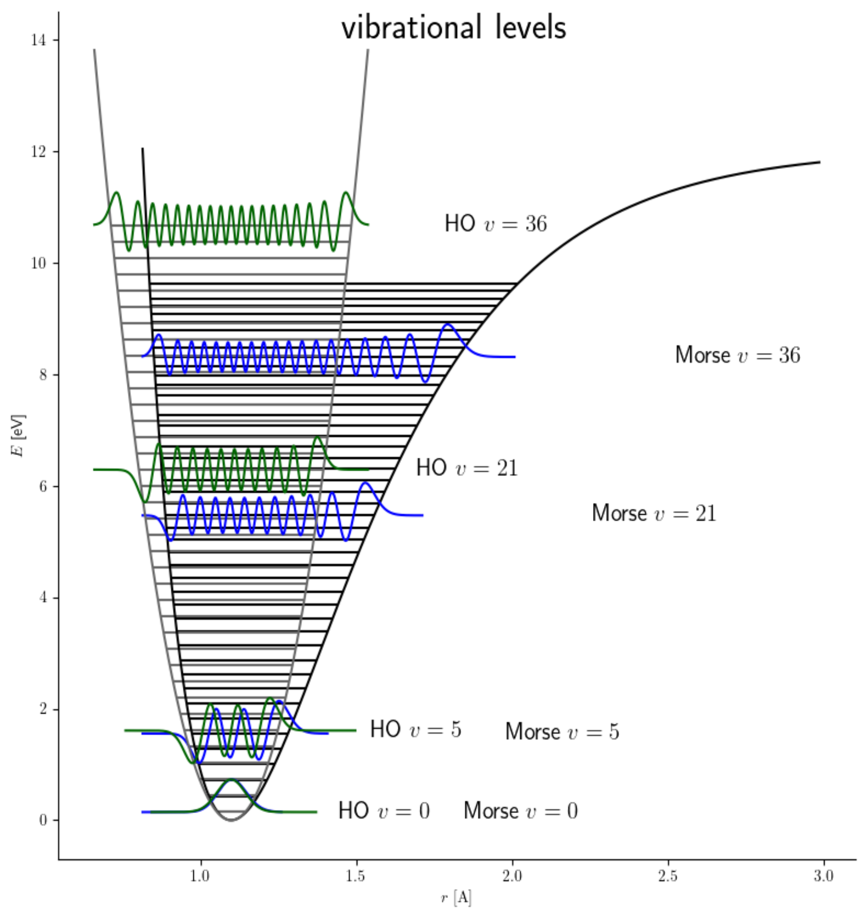
[1] M. Tachikawa ,et. al, **J. Am. Chem. Soc. 127**, 11908 (2005).
[2] A. Kaczmarek, et. al. **J. Phys. Chem. A 113**, 1985 (2009).
[3] X. Z. Li, M. Probert, et al., **Phys. Rev. Lett. 104**, 066102 (2010).
[4] X. Z. Li, B. Walker, and A. Michaelides, **PNAS 108**, 6369 (2011).
[5] J. Chen, X. Z. Li*, E. G. Wang*, et al., **Nat. Commun. 4**, 2064 (2013).

- **与其它分子模拟手段的结合：**

[1] A. Perez and O. A. von Lilienfeld, **J. Chem. Theory Comput. 7**, 2358 (2011).
[2] R. Ramirez and C. P. Herrero, **J. Chem. Phys. 133**, 144511 (2010).
[3] Y. X. Feng, J. Chen, D. Alfe, X. Z. Li*, and E. G. Wang*, **J. Chem. Phys. 142**, 064506 (2015)

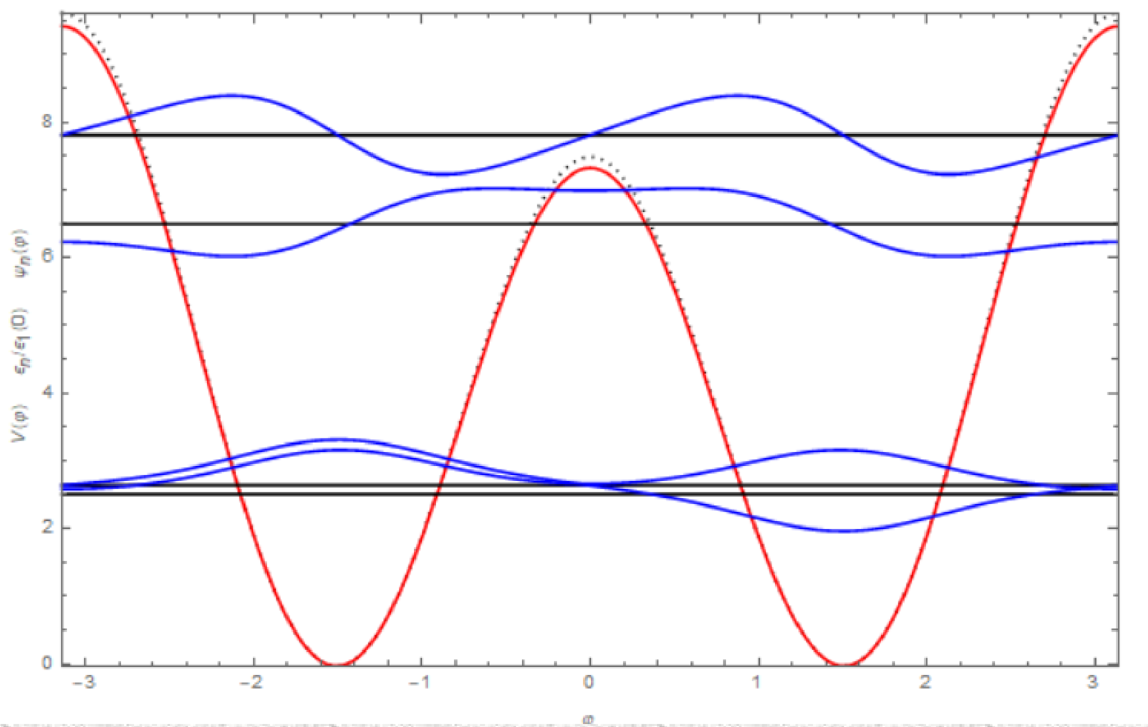
第二部分：模拟方法、优缺点



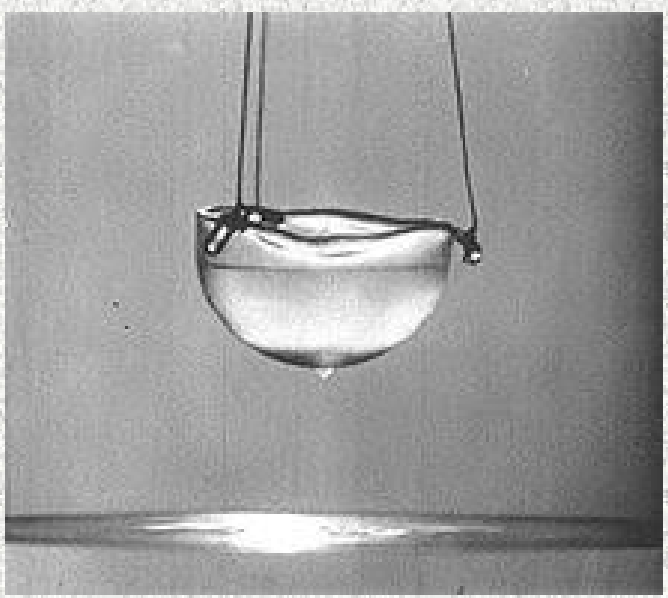


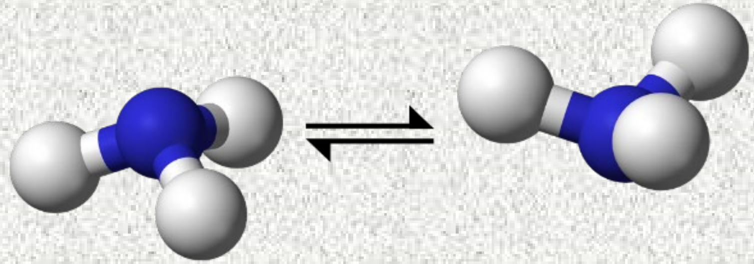
- 动力学信息，**Initial Value Representation**（我周四上午报告，曾嘉熙）

第二部分：模拟方法、优缺点



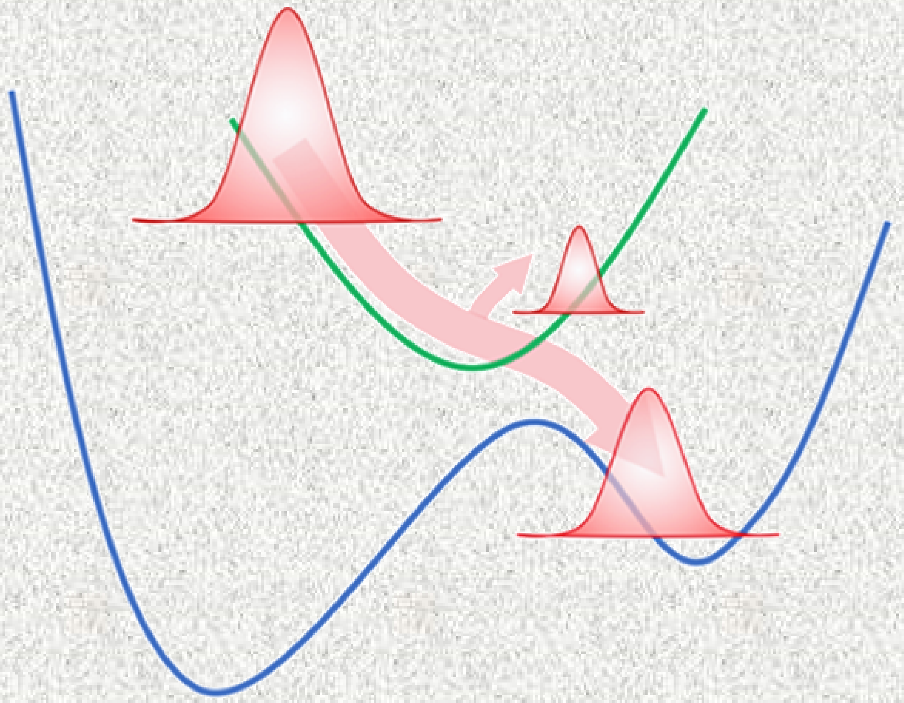
- 瞬子方法（方为，复旦大学；朱禹丞，北京大学）

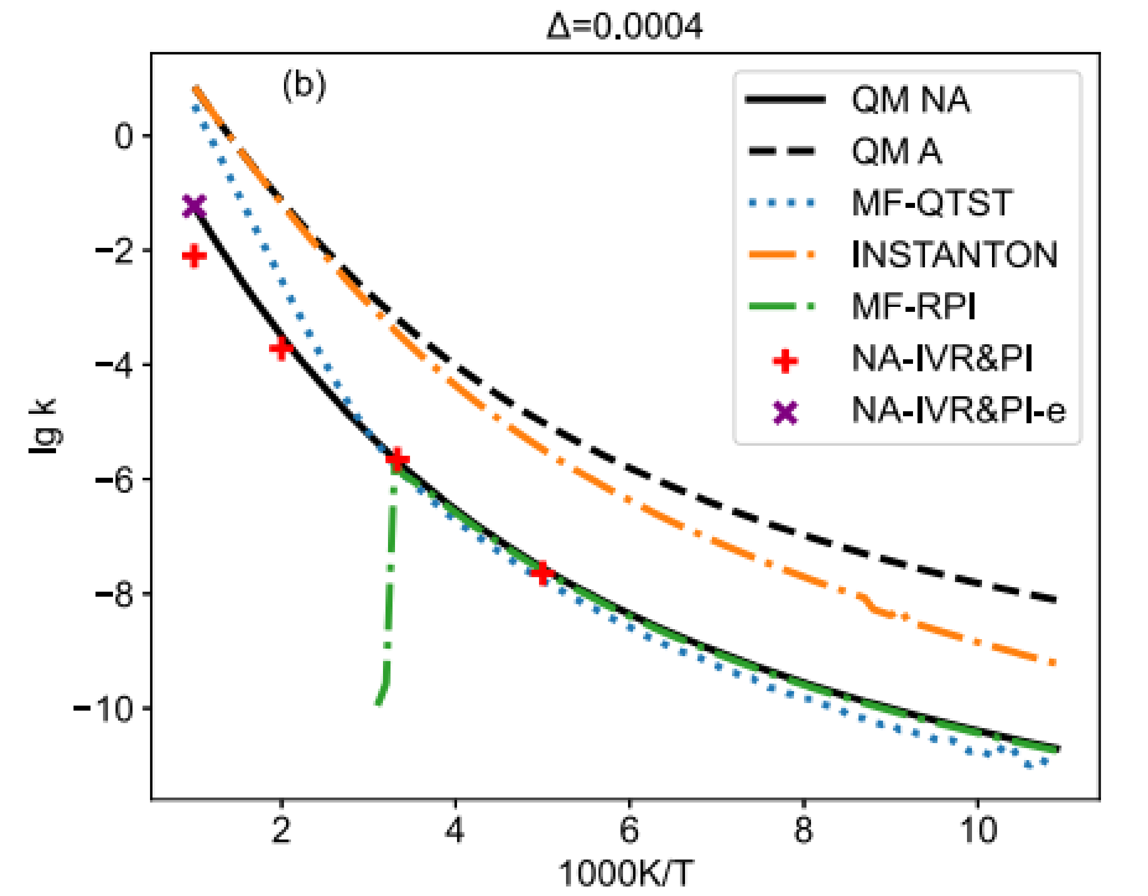




- 包含量子交换的路径积分方法（杨数、王聪、何染尘，北京大学）

第二部分：模拟方法、优缺点





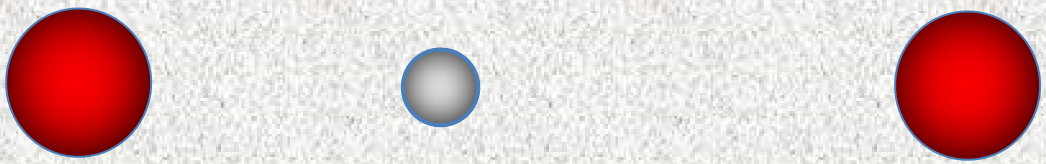
- 曾嘉熙，北京大学

目 录

- 什么是原子核的量子效应?
- 模拟原子核量子效应的计算方法有哪些，它们的优缺点是什么?
- 几个例子，来感受相关研究。
- **Take-home Message.**

第三部分：相关例子，感受研究

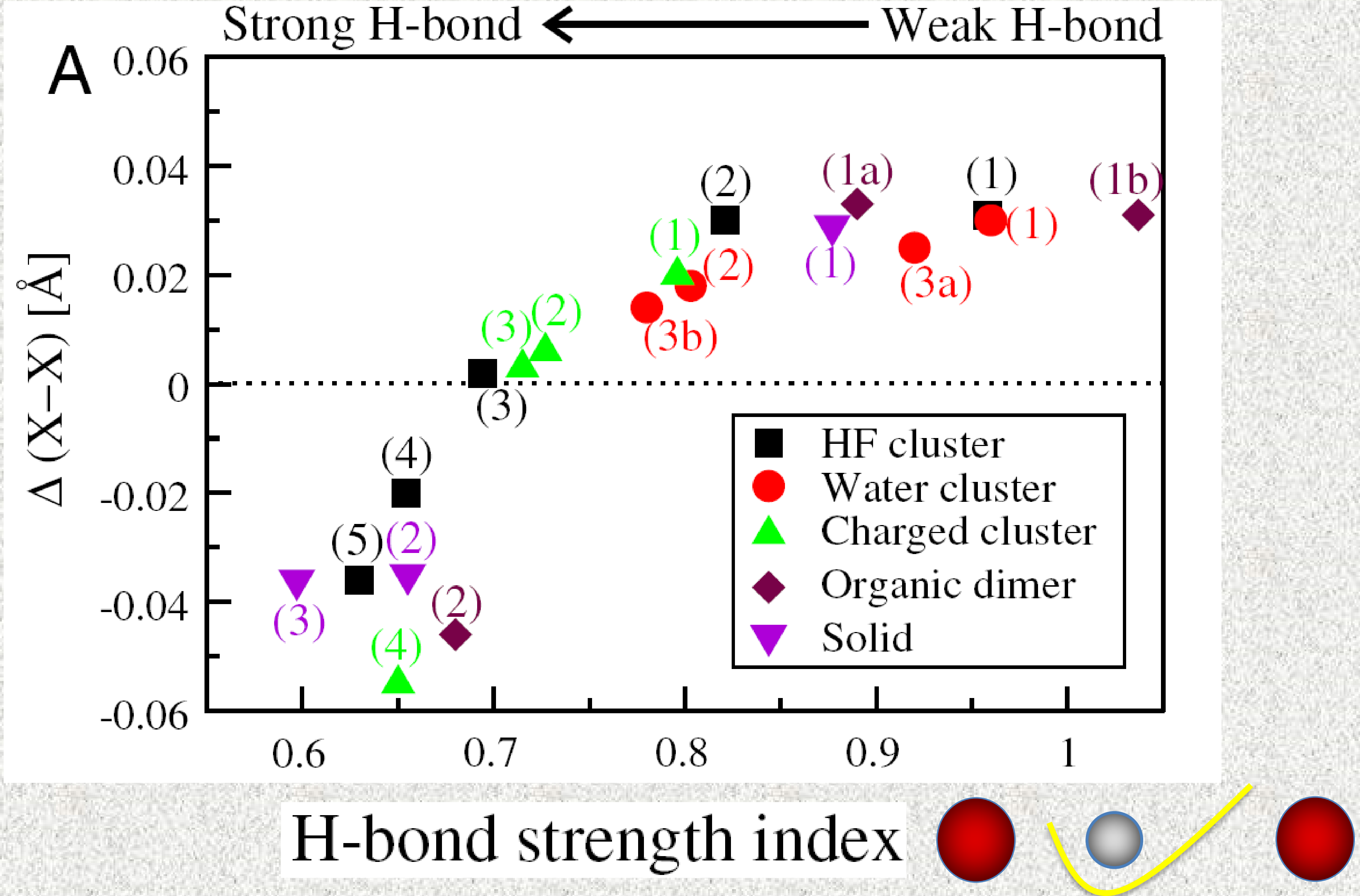
- Impact of quantum nuclear effects on H-bond strength?



- In 1950s, Ubbelohde effect (replace H with D) in H-bonded crystals.
- Liquids: water structure no consensus, and liquid HF is strengthened.
- Clusters: $(HF)_n$ with n > 4, strengthened, otherwise, weakened, $(H_2O)_n$ always weakened.

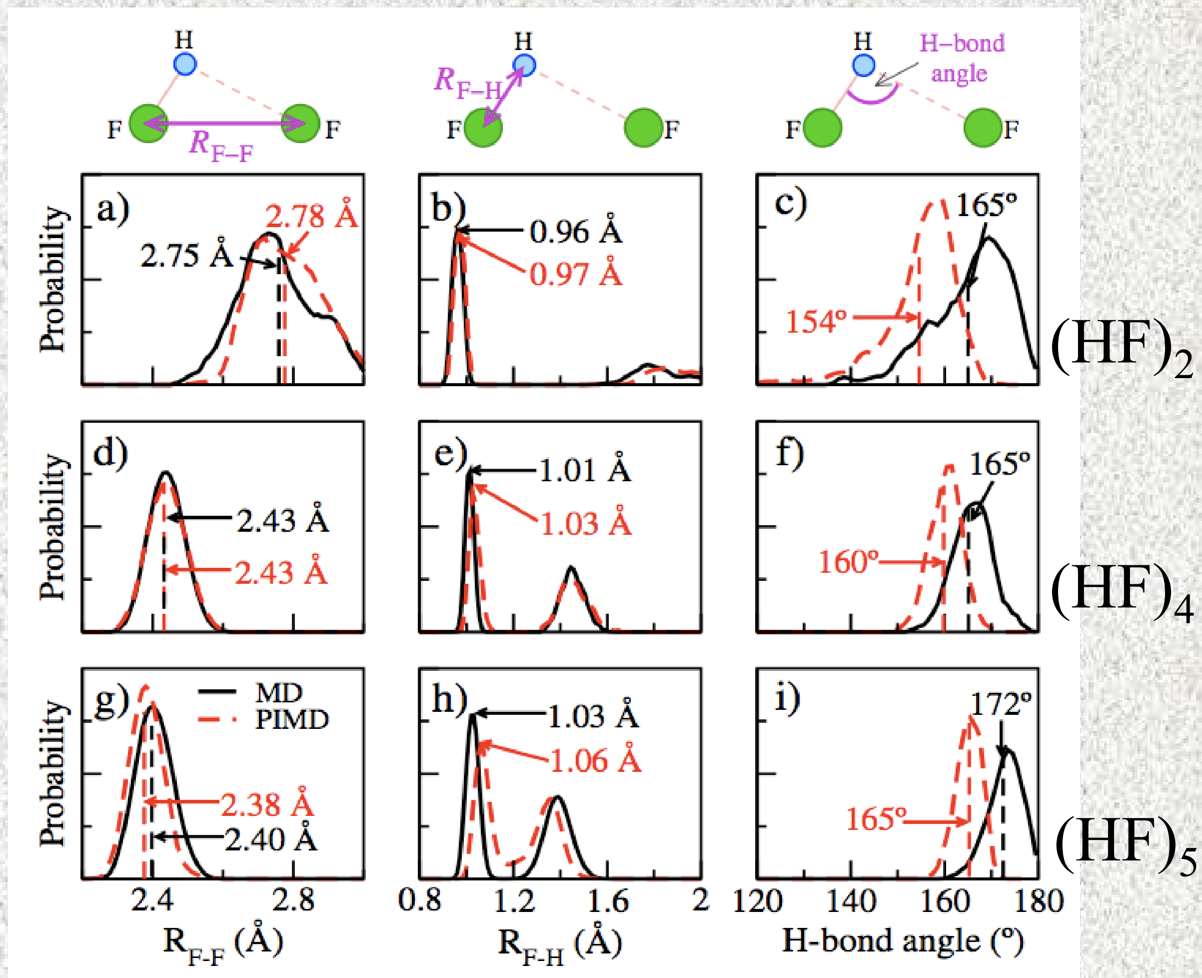
Question: is there a unified picture?

第三部分：相关例子，感受研究

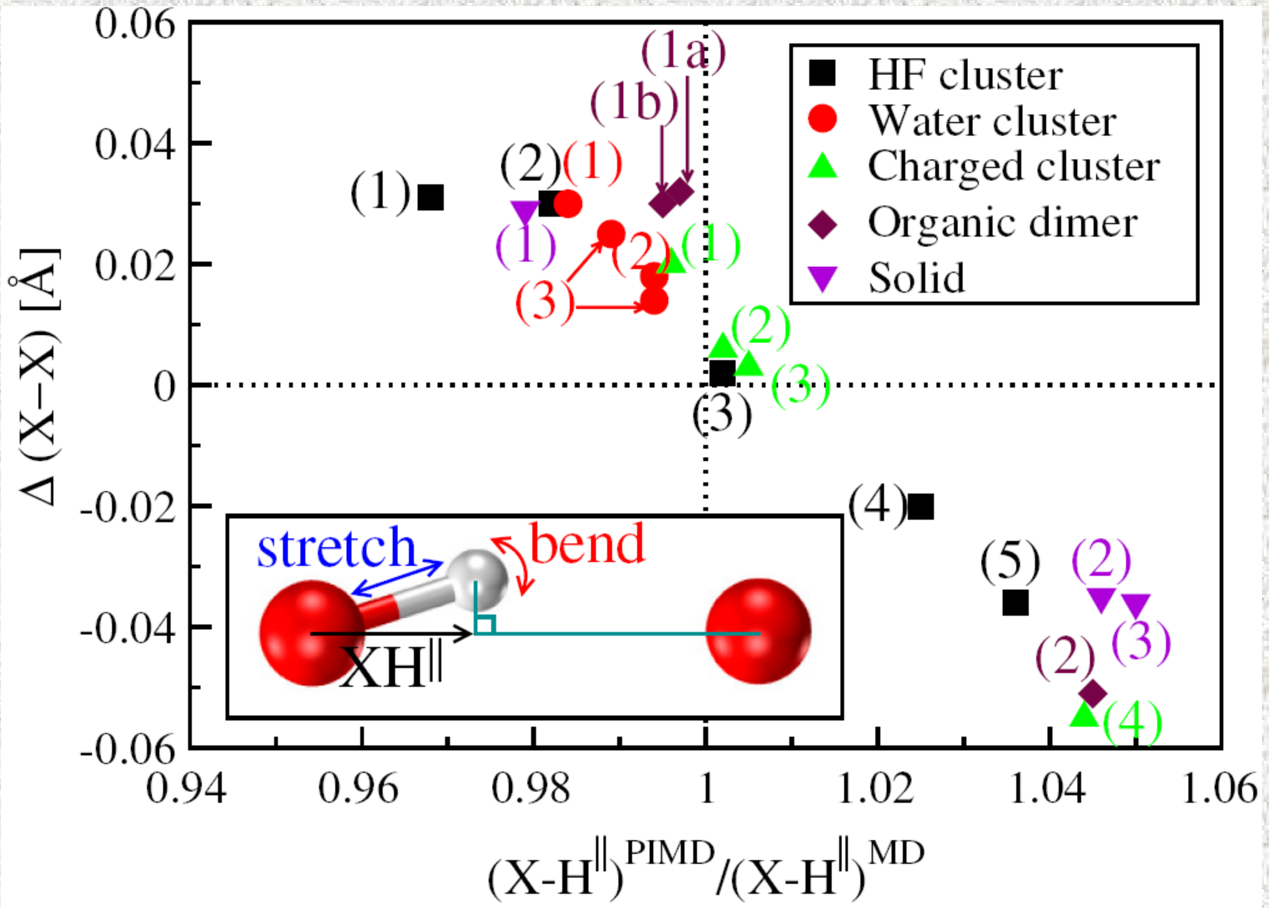


第三部分：相关例子，感受研究

- Why?



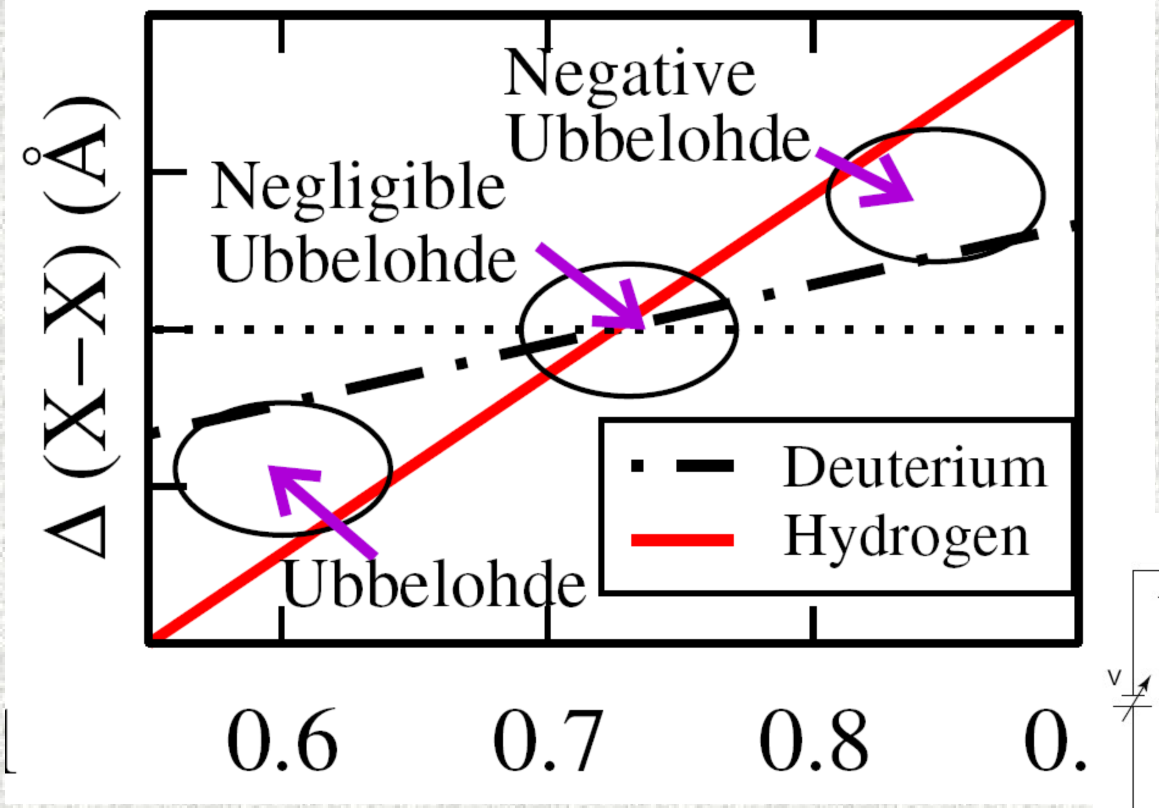
- Quantitative



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

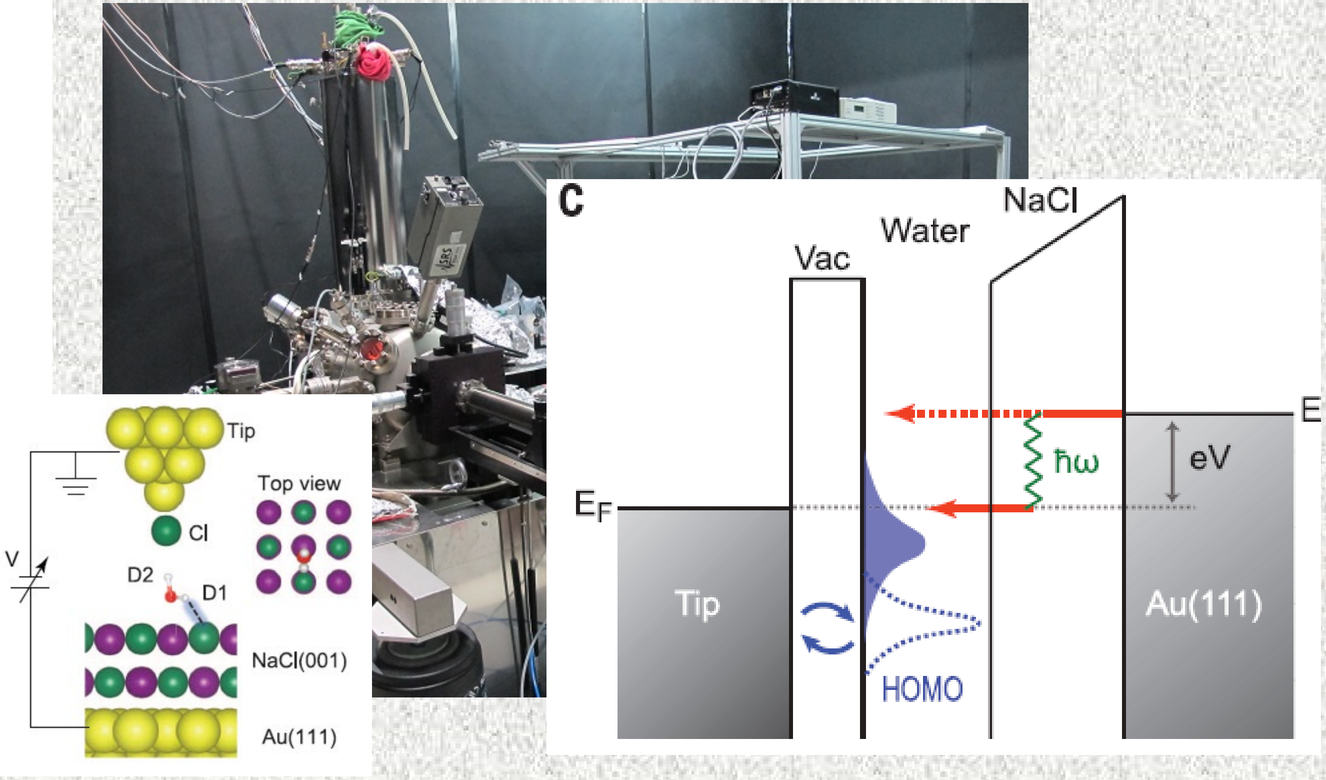
第三部分：相关例子，感受研究

- Isotope Substitution



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

- New Experiment (Inelastic electron tunneling spectroscopy, IETS):



Jing Guo, Jingtao Lü, Yexin Feng, Ji Chen, …, Xin-Zheng Li*, Enge Wang*, Ying Jiang*, **Science 352**, 321 (2016)

第三部分：相关例子，感受研究

- DNA base pair

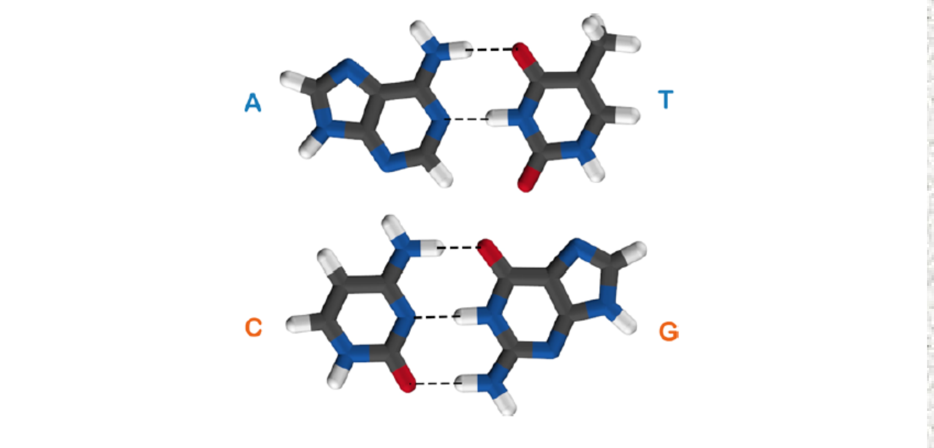
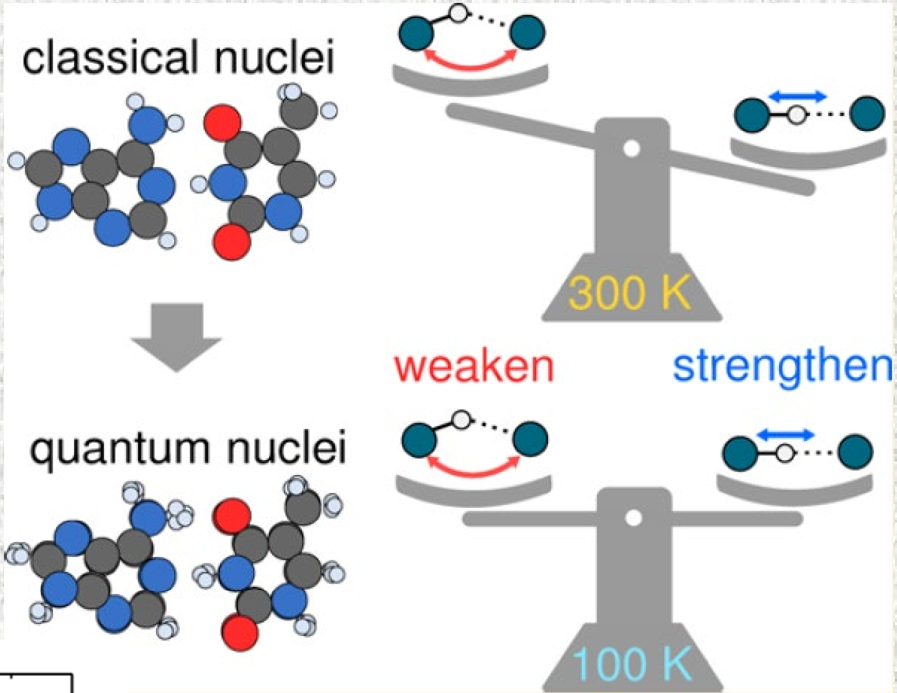
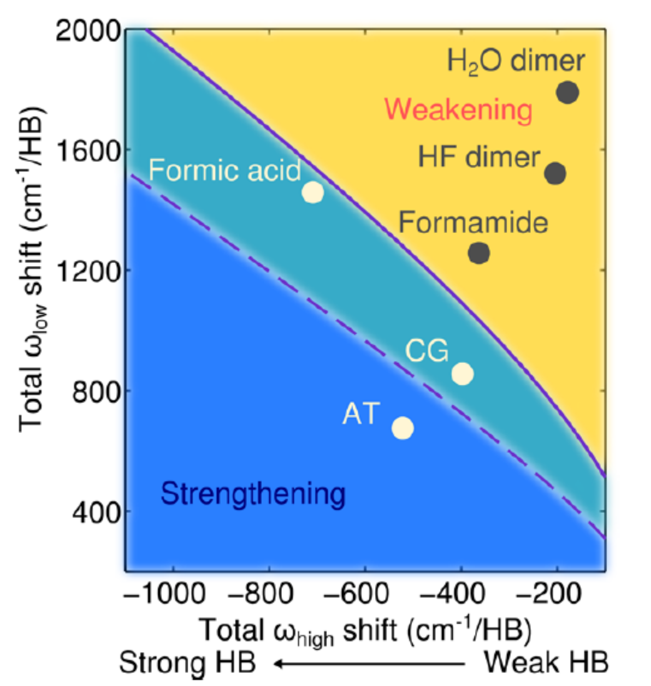
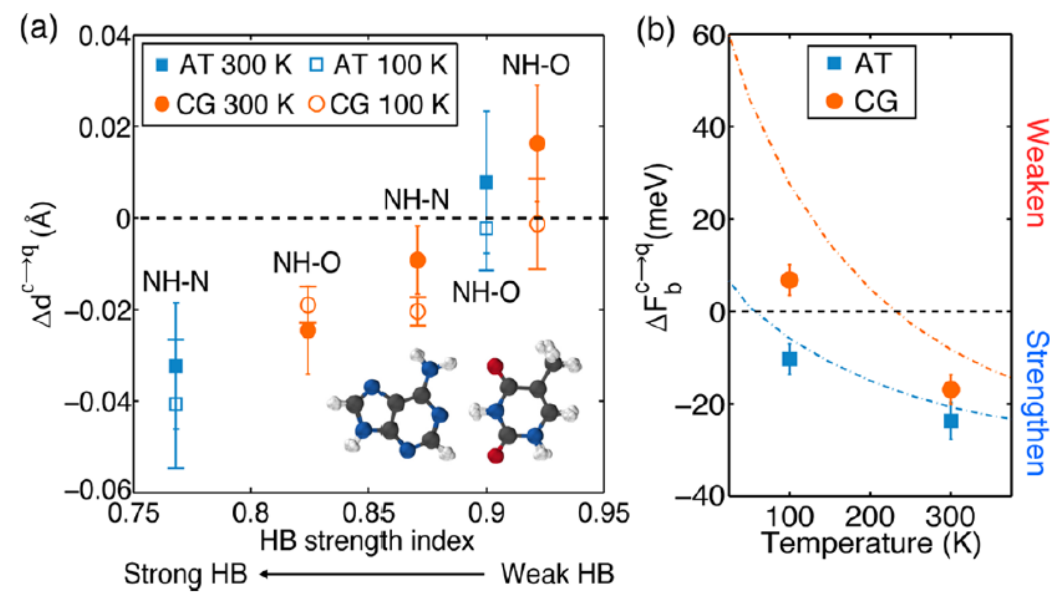


Figure 1. Structures of the Watson−Crick AT and CG base pairs. Black: carbon; red: oxygen; blue: nitrogen; white: hydrogen.







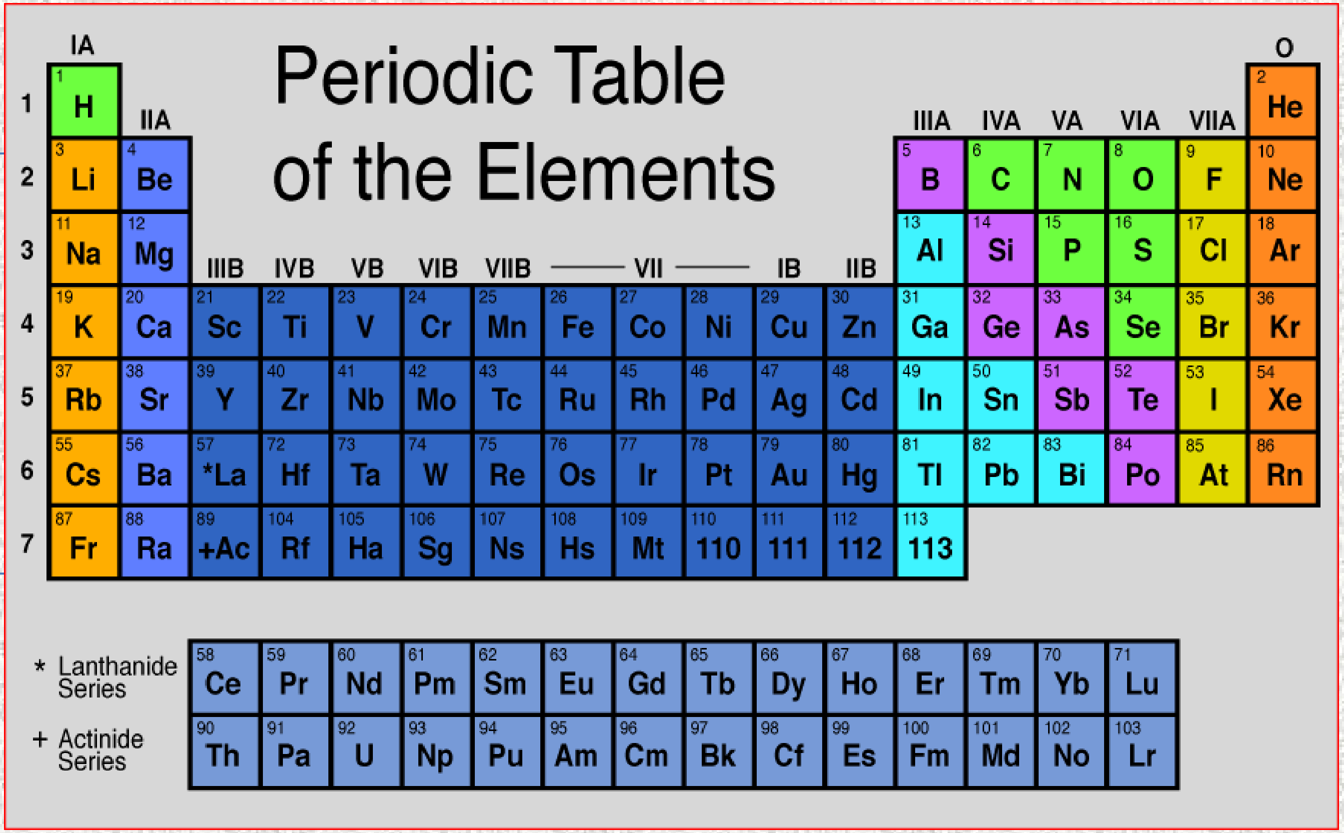
Wei Fang, Ji Chen, Mariana Rossi, Yexin Feng, Xin-Zheng Li*, and Angelos Michaelides*, **J. Phys. Chem. Lett. 7**, 2125 (2016)

第三部分：相关例子，感受研究

- The quantum nature of high pressure hydrogen

Molecular solid

Alkali metal: atomic solid

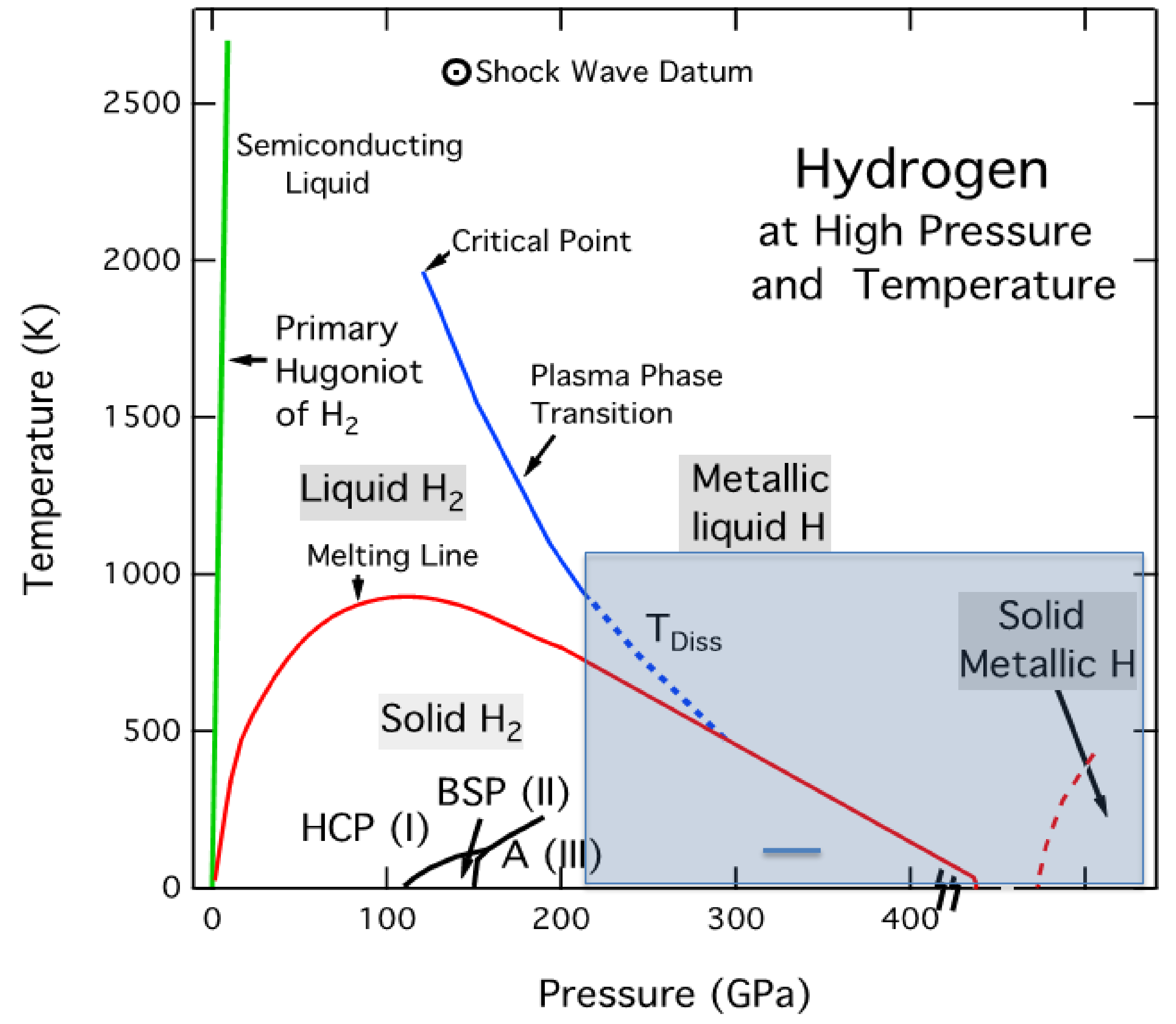


1). Wigner & Huntington, JCP(1935): Under high pressure (25 GPa), will H_2 become bcc solid?

2). Ashcroft , JPCM (2000): There will be a low-T liquid phase whose origin is due to QNEs.

第三部分：相关例子，感受研究

- The quantum nature of high pressure hydrogen



A. Alavi, M. Parrinello, and D. Frenkel, **Science 269**, 1252 (1995)

S. A. Bonev, E. Schwegler, T. Ogitu, G. Galli, **Nature 431**, 669 (2004)

……

Isaac Silvera, PNAS 107, 12743 (2010)

第三部分：相关例子，感受研究

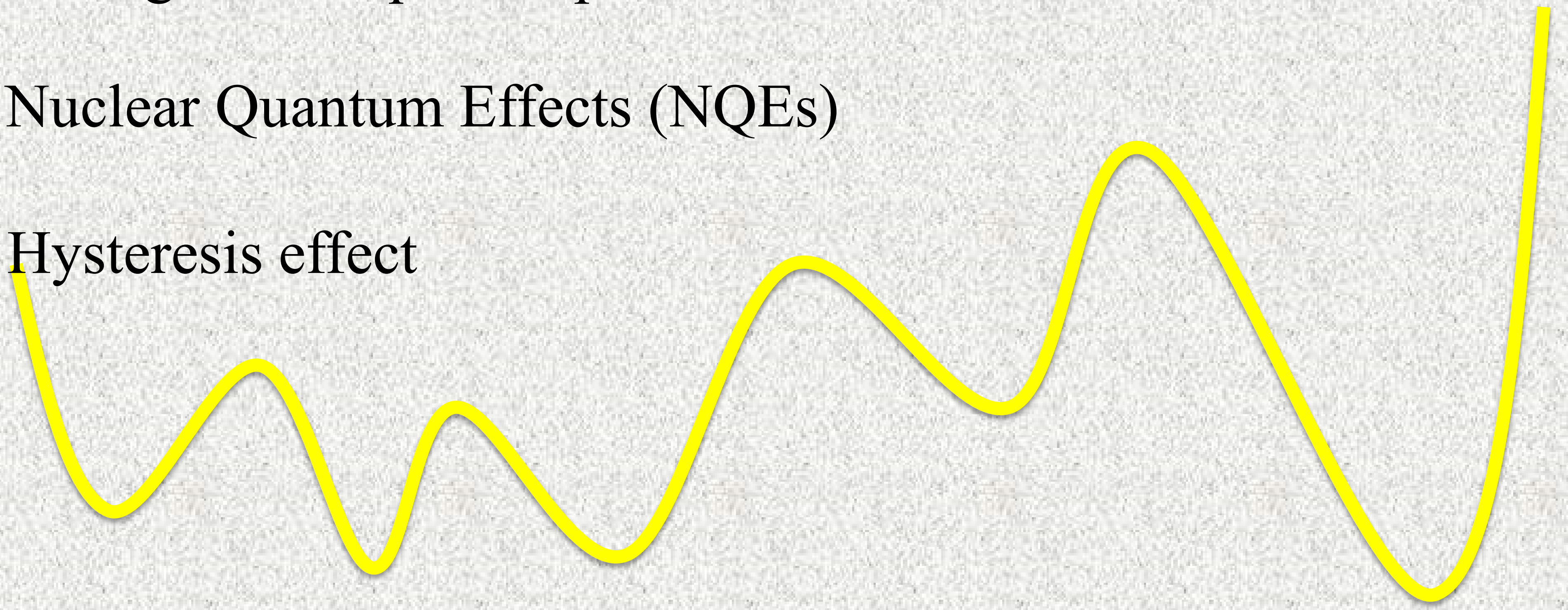
- The quantum nature of high pressure hydrogen
  - How do we tackle this problem:

    1) Electronic structure

    2) Configuration space explored

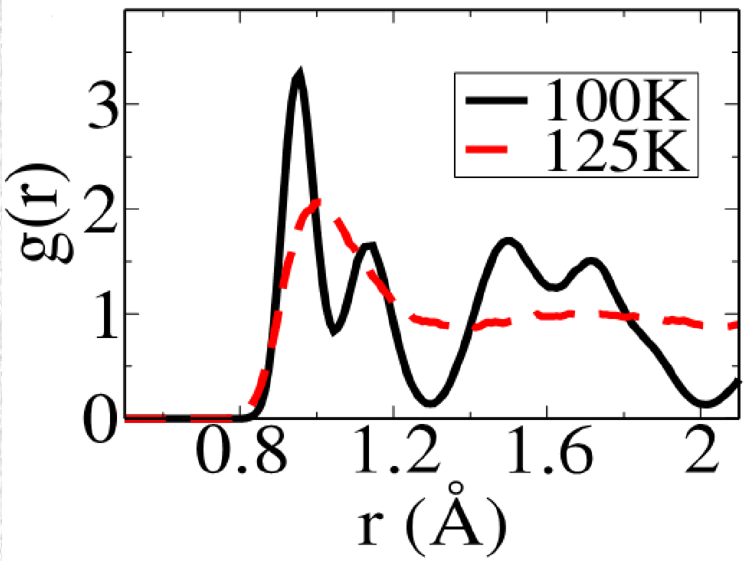
    3) Nuclear Quantum Effects (NQEs)

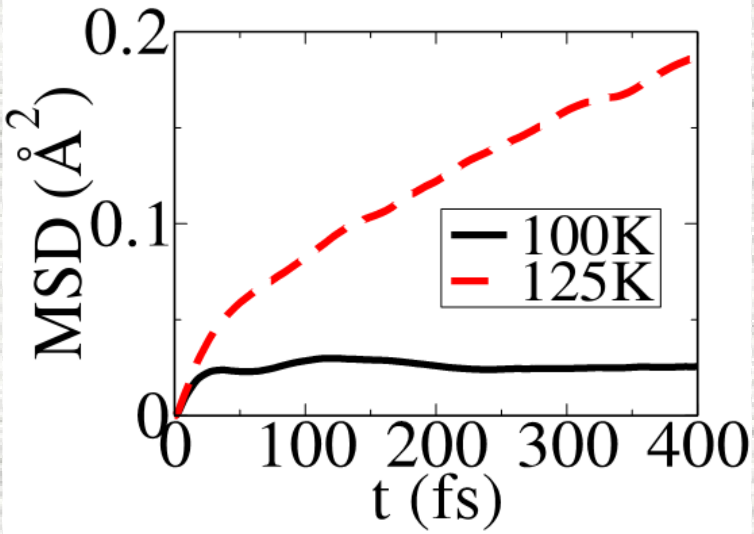
    4) Hysteresis effect



第三部分：相关例子，感受研究

- The quantum nature of high pressure hydrogen





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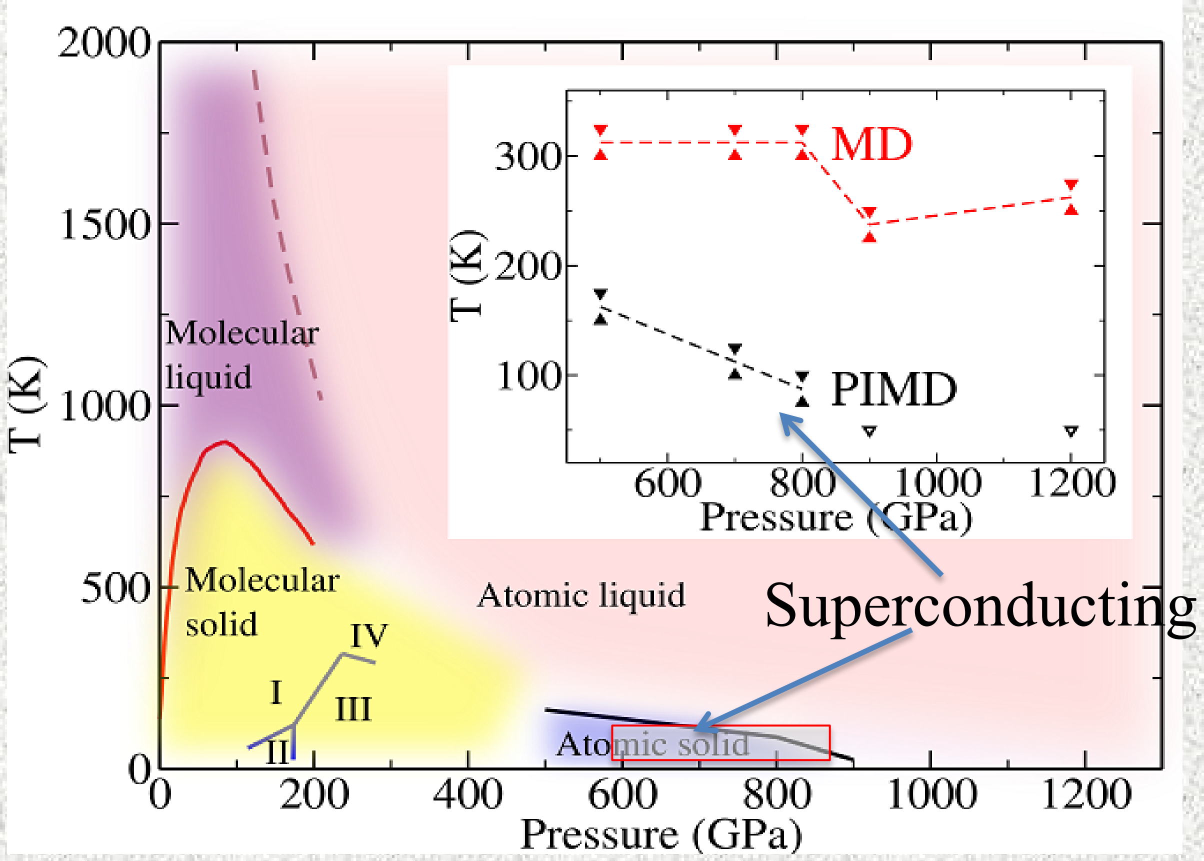
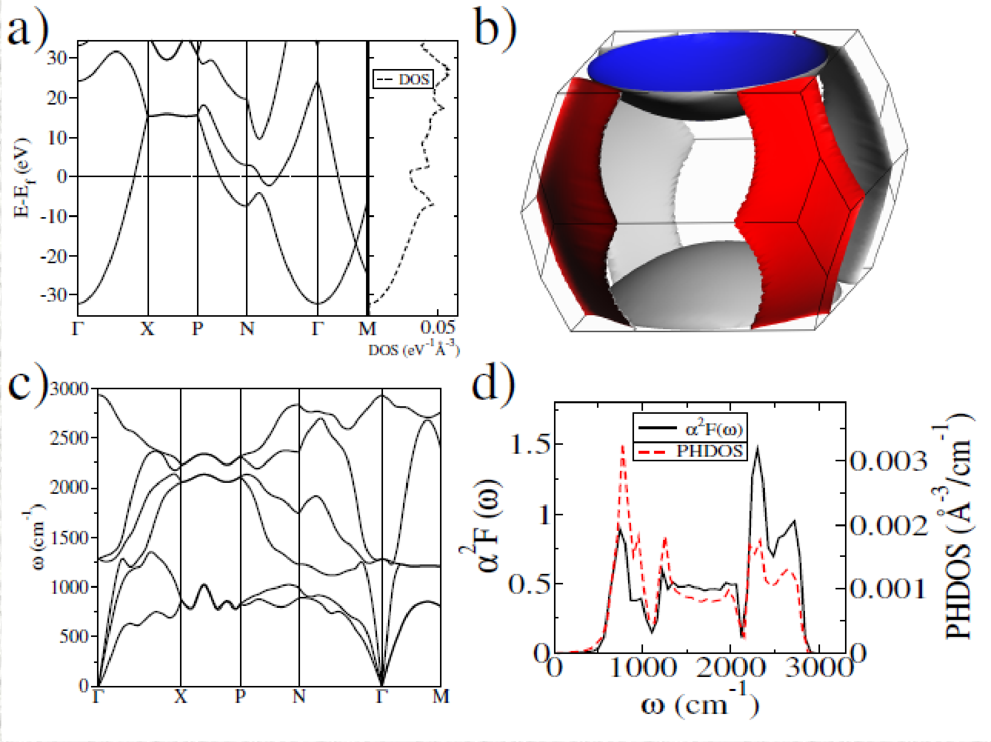
- The quantum nature of high pressure hydrogen



Ji Chen, Xin-Zheng Li*, Qianfan Zhang, Matthew I. J. Probert, Chris J. Pickard, Richard J. Needs, Angelos Michaelides, and Enge Wang*, **Nat. Commun. 4**, 2064 (2013)

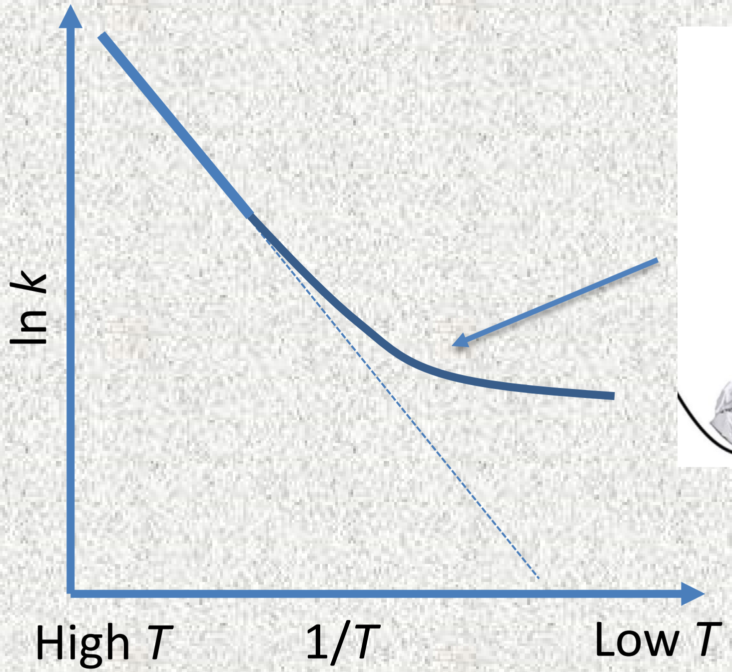


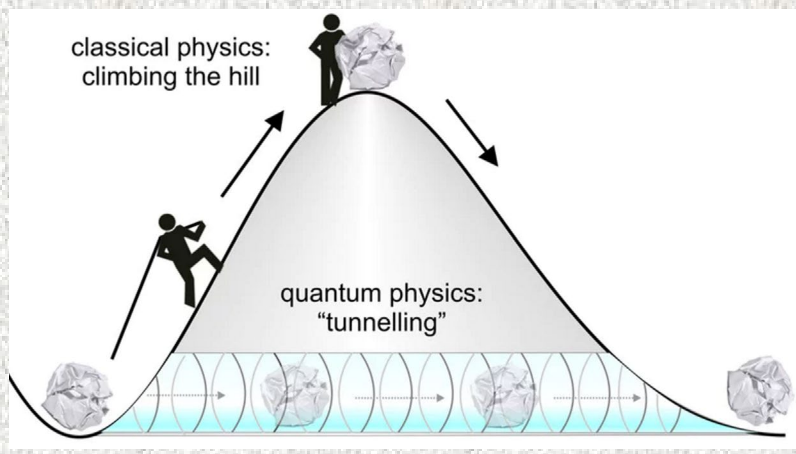
J. M. McMahon and D. M. Ceperley, **Phys. Rev. B. 84**, 144515 (2011)

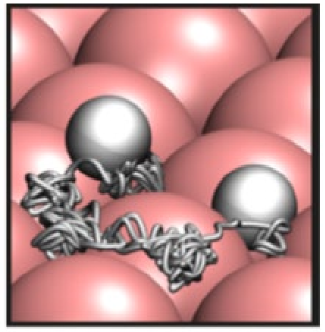
P. Cudazzo, et al., **Phys. Rev. Lett. 100**, 257001 (2008)

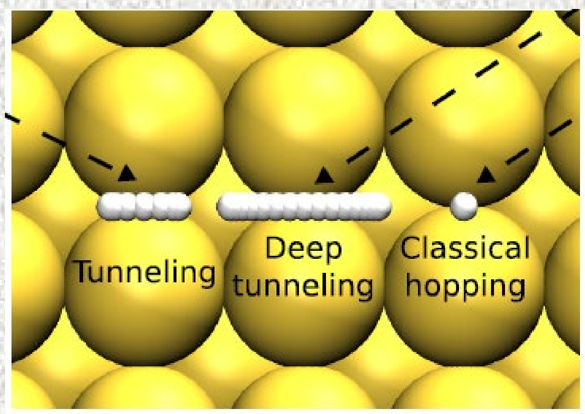
第三部分：相关例子，感受研究

- Tunneling of hydrogen & water molecules

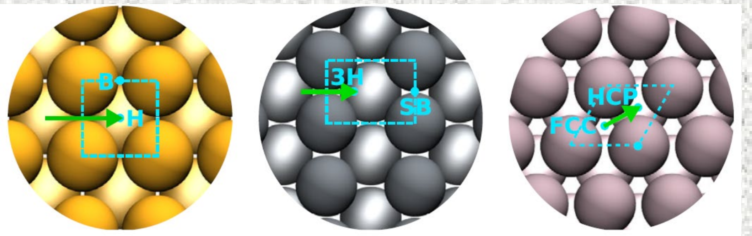




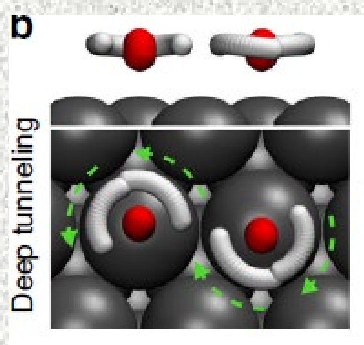




Path-Integral based method like Instanton: Allows the determination of the chemical reaction rate using the Euclidean action of the polymer, instead of the classical free-energy.



$$k_{\mathrm{inst}} Z_r(\beta) = (2\pi\hbar)^{-\frac{1}{2}} \left| \frac{\mathrm{d}^2 S[\mathbf{x}(\tau)]}{\mathrm{d}\tau^2} \right|^{\frac{1}{2}} Z^{\ddagger}(\beta) e^{-S[\mathbf{x}(\tau)]/\hbar}$$



Quantum tunneling can be addressed in an *ab initio* manner.

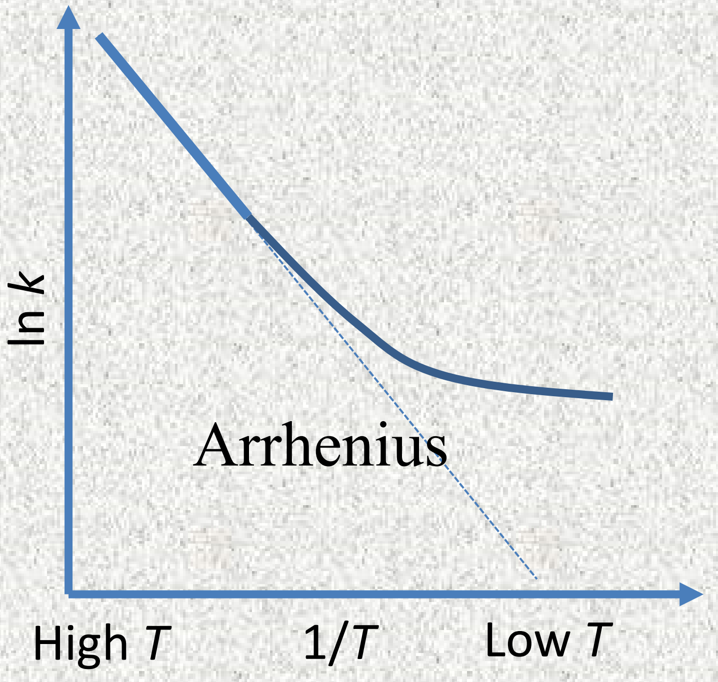
第三部分：相关例子，感受研究

Tunneling of hydrogen & water molecules

- Experimental Technique: Field Emission Microscopy (FEM), Laser Optical Diffraction (LOD), Scanning Tunneling Microscopy (STM), and Helium Spin Echo (HeSE).

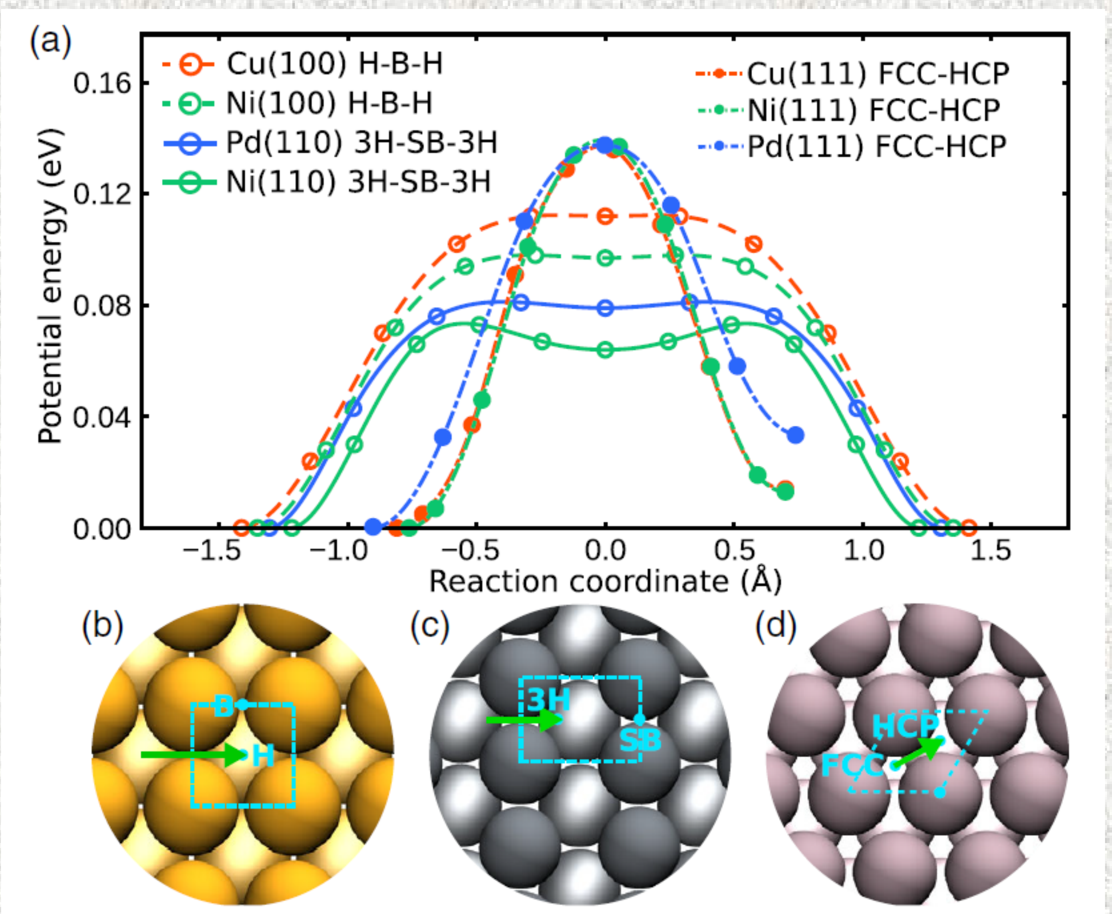
- Different transition curves has been reported, but why are they different is unclear.

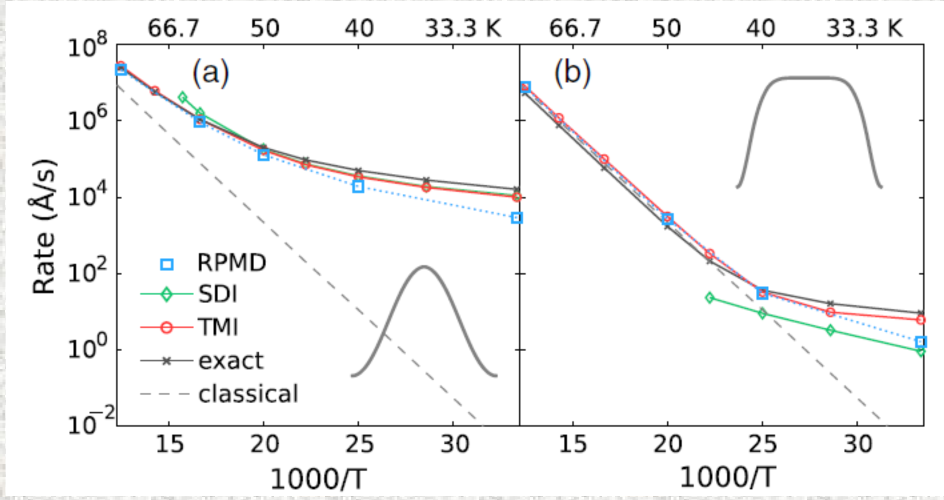
- For example, on Ru(0001), a gradual transition from Arrhenius behavior to a T-independent regime has been reported. However, on Ni(100) and Cu(100), diffusion rates suddenly become T independent below a certain T, indicating a sharp classical-to-quantum transition.

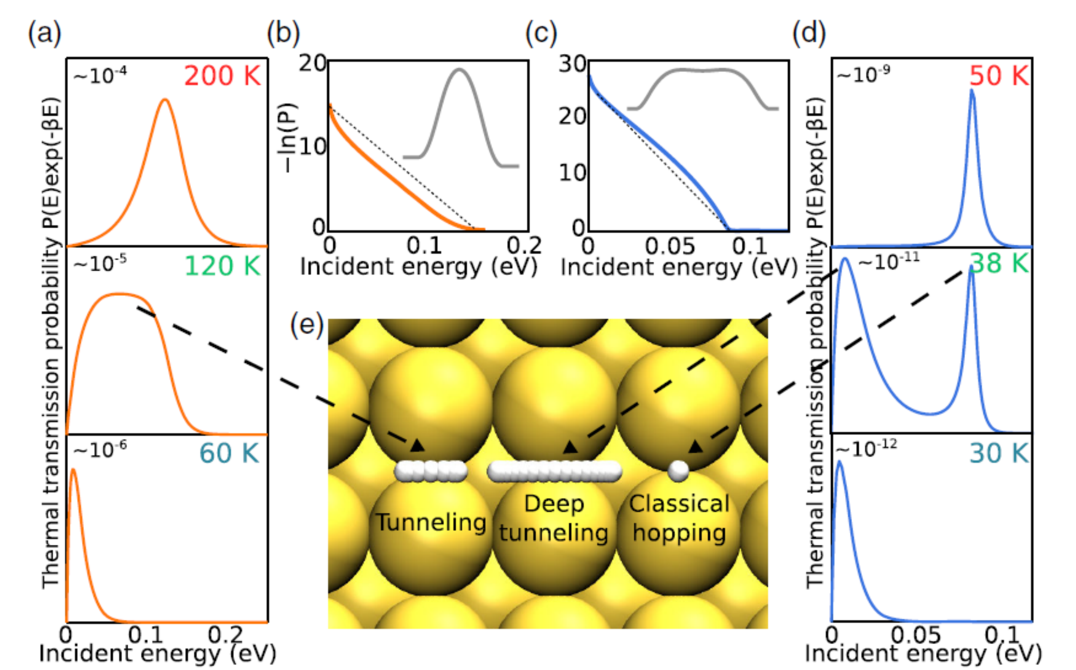


第三部分：相关例子，感受研究

- Tunneling of hydrogen & water molecules







Wei Fang, Jeremy O. Richardson*, Ji Chen, Xin-Zheng Li*, and Angelos Michaelides*, **Phys. Rev. Lett. 119**, 126001 (2017)

第三部分：相关例子，感受研究

- Tunneling of hydrogen & water molecules

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MEMBRANES   1 JANUARY 2016 • VOL 351 ISSUE 6268

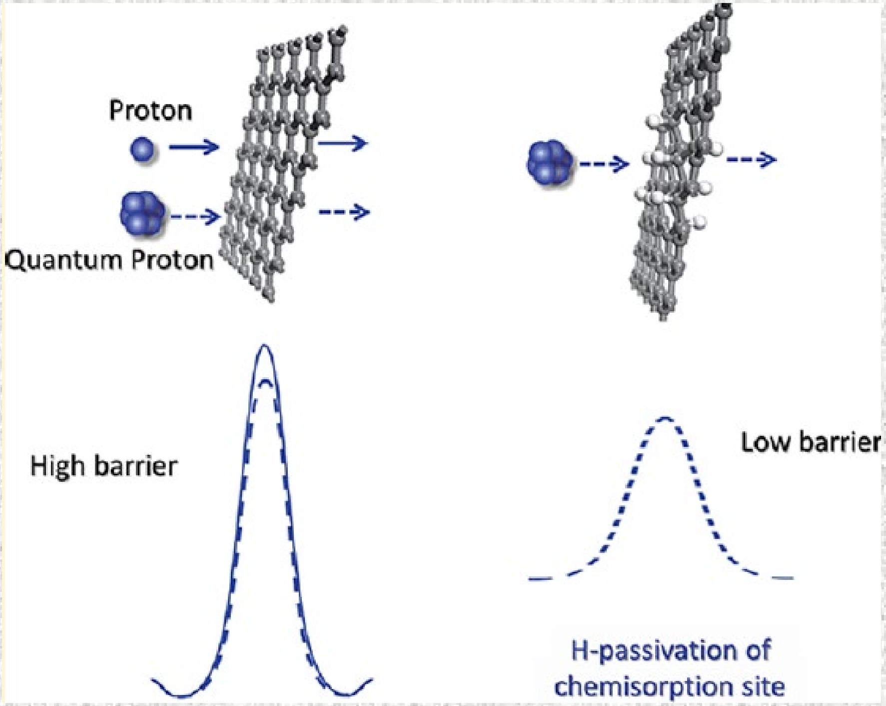
Sieving hydrogen isotopes through two-dimensional crystals

M. Lozada-Hidalgo,[1*†] S. Hu,[1†] O. Marshall,[1] A. Mishchenko,[1] A. N. Grigorenko,[1] R. A. W. Dryfe,[2] B. Radha,[1] I. V. Grigorieva,[1] A. K. Geim[1*]

One-atom-thick crystals are impermeable to atoms and molecules, but hydrogen ions (thermal protons) penetrate through them. We show that monolayers of graphene and boron nitride can be used to separate hydrogen ion isotopes. Using electrical measurements and mass spectrometry, we found that deuterons permeate through these crystals much slower than protons, resulting in a separation factor of ≈10 at room temperature. The isotope effect is attributed to a difference of ≈60 milli–electron volts between zero-point energies of incident protons and deuterons, which translates into the equivalent difference in the activation barriers posed by two-dimensional crystals. In addition to providing insight into the proton transport mechanism, the demonstrated approach offers a competitive and scalable way for hydrogen isotope enrichment.

Table 1. Calculated cNEB Barrier, ZPE Corrections (ΔE_{ZPE}) and Corrected Barrier (Barrier) for Proton Transfer Across Pristine and Hydrogenated Graphene and h-BN Sheets[a]

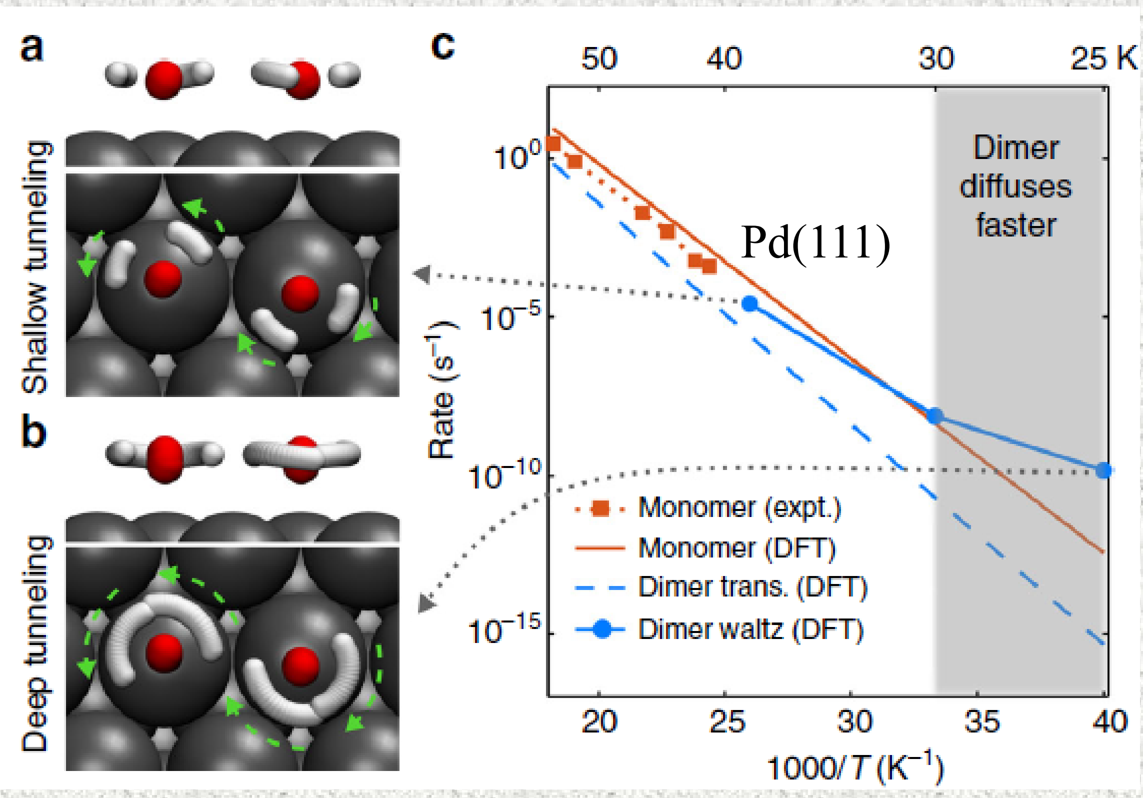
	cNEB Barrier	ΔE_{ZPE}	barrier
$G_{pristine}$	3.65	−0.26	3.39
$G_{chair\text{-}H}$	1.08	−0.07	1.06
$G_{boat\text{-}H}$	0.88	−0.12	0.76
$G_{disordered\text{-}H}$	0.79	−0.18	**0.61**

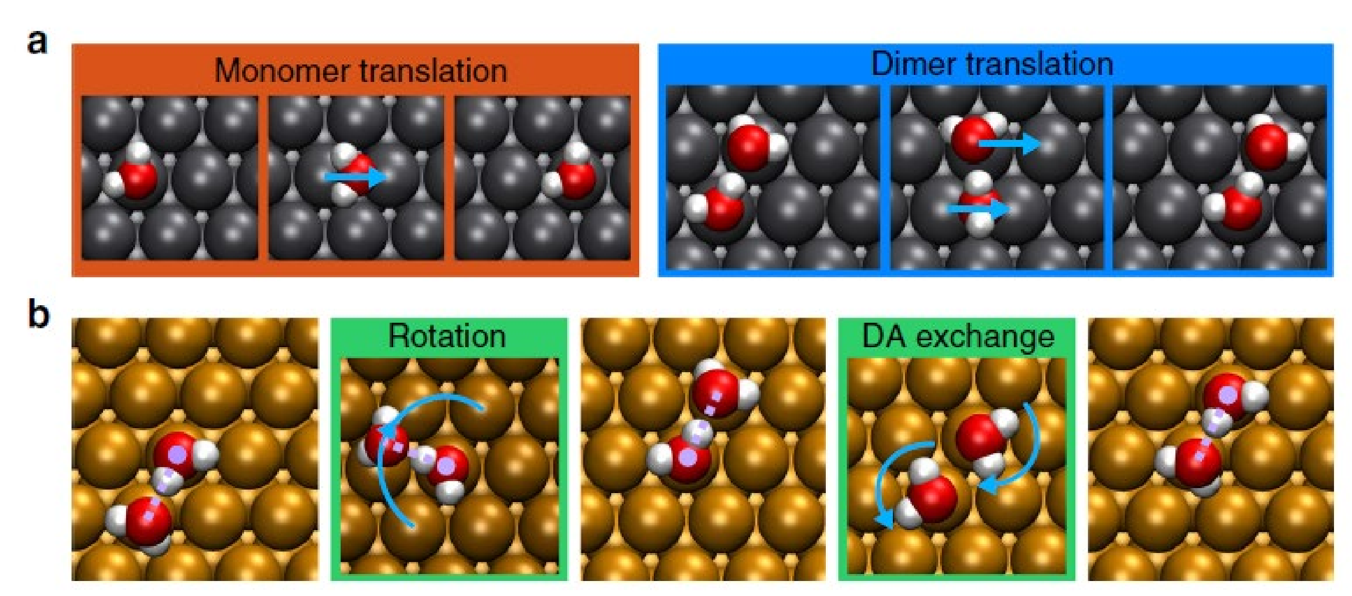


Yexin Feng, Ji Chen, Wei Fang, Enge Wang, Angelos Michaelides*, and Xin-Zheng Li*, **J. Phys. Chem. Lett. 8**, 6009 (2017)

第三部分：相关例子，感受研究

- Tunneling of hydrogen & water molecules



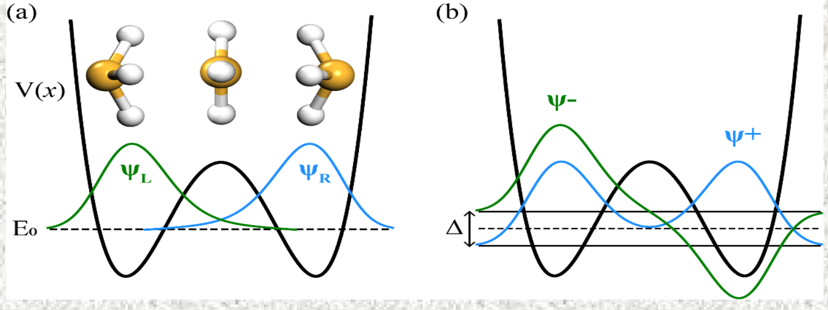


Wei Fang, Ji Chen, Philipp Pedevilla, Xin-Zheng Li*, Jeremy O. Richardson*, and Angelos Michaelides*, **Nat. Commun. 11**, 1689 (2020)

第三部分：相关例子，感受研究

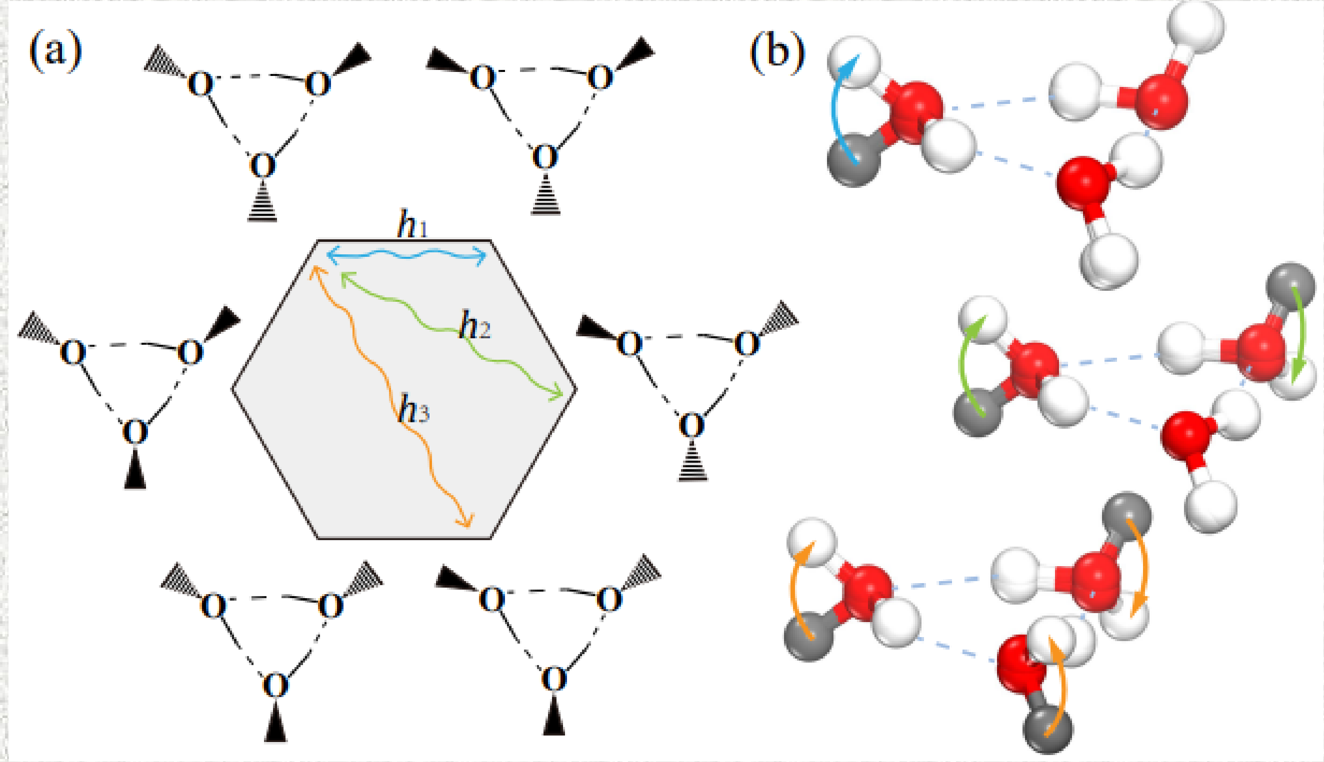
- Tunneling splitting of water clusters

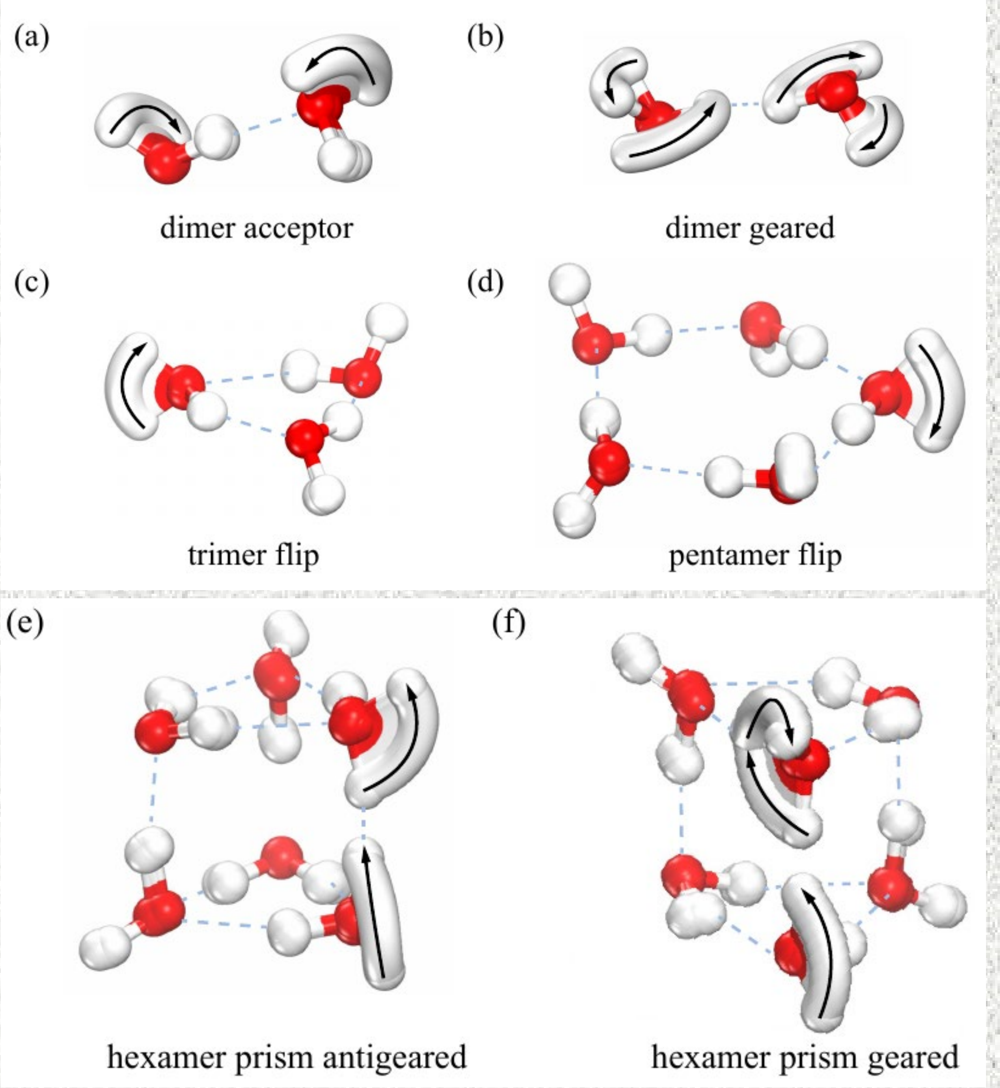
R. G. Dickinson, , R. T. Dillon, and F. Rasetti, **Phys. Rev. 34**, 582 (1929) (Caltech)



$$\hat{H} = \begin{pmatrix} E_0 & \Delta/2 \\ \Delta/2 & E_0 \end{pmatrix}$$

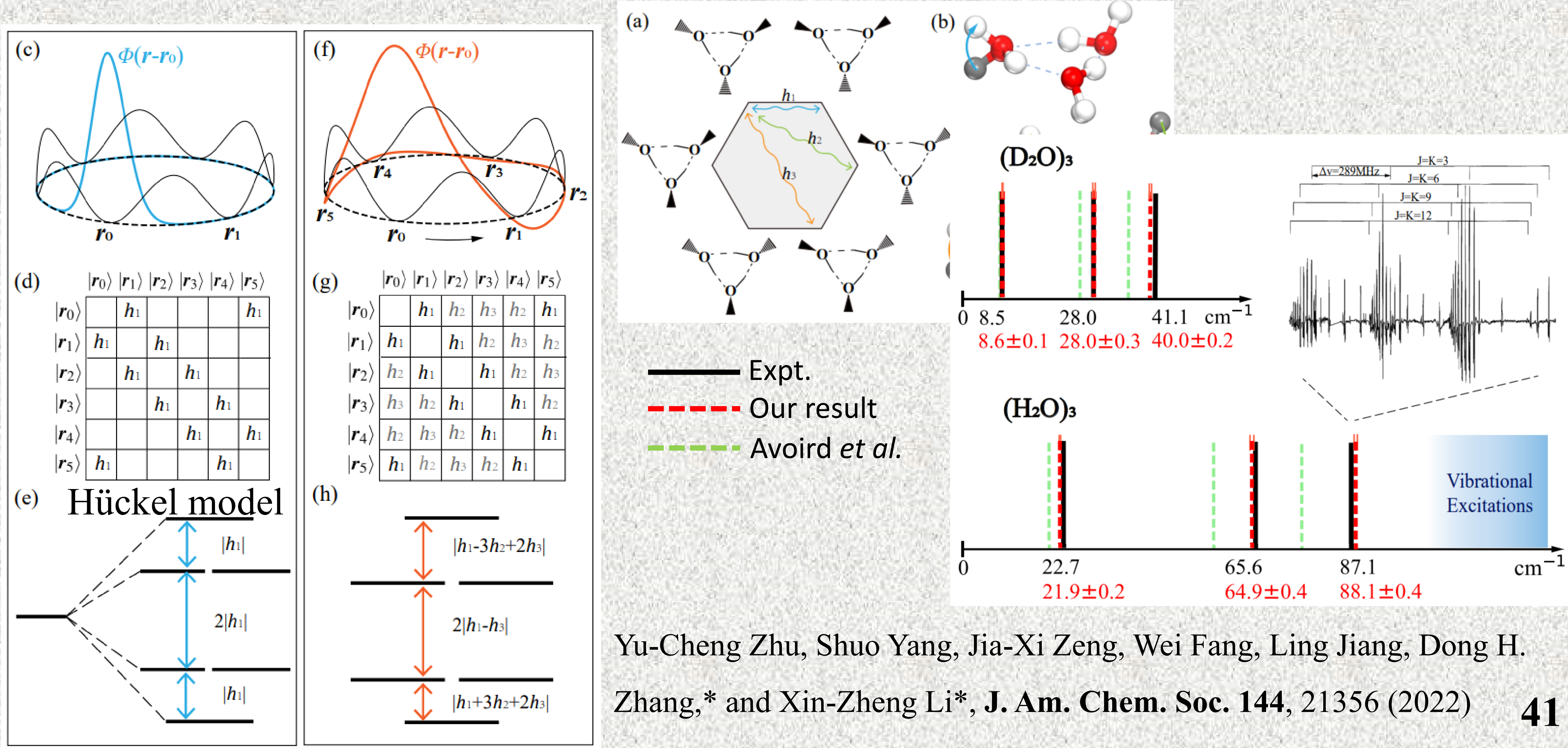
$$\psi^+ = (|\psi_L> + |\psi_R>)/\sqrt{2}$$
$$\psi^- = (|\psi_L> - |\psi_R>)/\sqrt{2}$$





第三部分：相关例子，感受研究

- Tunneling splitting of water clusters



(d)

	$\|r_0\rangle$	$\|r_1\rangle$	$\|r_2\rangle$	$\|r_3\rangle$	$\|r_4\rangle$	$\|r_5\rangle$
$\|r_0\rangle$		h_1				h_1
$\|r_1\rangle$	h_1		h_1			
$\|r_2\rangle$		h_1		h_1		
$\|r_3\rangle$			h_1		h_1	
$\|r_4\rangle$				h_1		h_1
$\|r_5\rangle$	h_1				h_1	

(g)

	$\|r_0\rangle$	$\|r_1\rangle$	$\|r_2\rangle$	$\|r_3\rangle$	$\|r_4\rangle$	$\|r_5\rangle$
$\|r_0\rangle$		h_1	h_2	h_3	h_2	h_1
$\|r_1\rangle$	h_1		h_1	h_2	h_3	h_2
$\|r_2\rangle$	h_2	h_1		h_1	h_2	h_3
$\|r_3\rangle$	h_3	h_2	h_1		h_1	h_2
$\|r_4\rangle$	h_2	h_3	h_2	h_1		h_1
$\|r_5\rangle$	h_1	h_2	h_3	h_2	h_1	

Yu-Cheng Zhu, Shuo Yang, Jia-Xi Zeng, Wei Fang, Ling Jiang, Dong H. Zhang,* and Xin-Zheng Li*, **J. Am. Chem. Soc. 144**, 21356 (2022)

目 录

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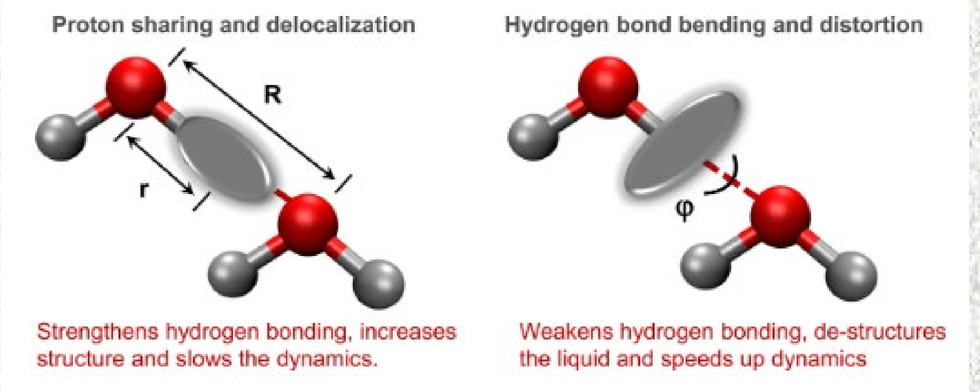
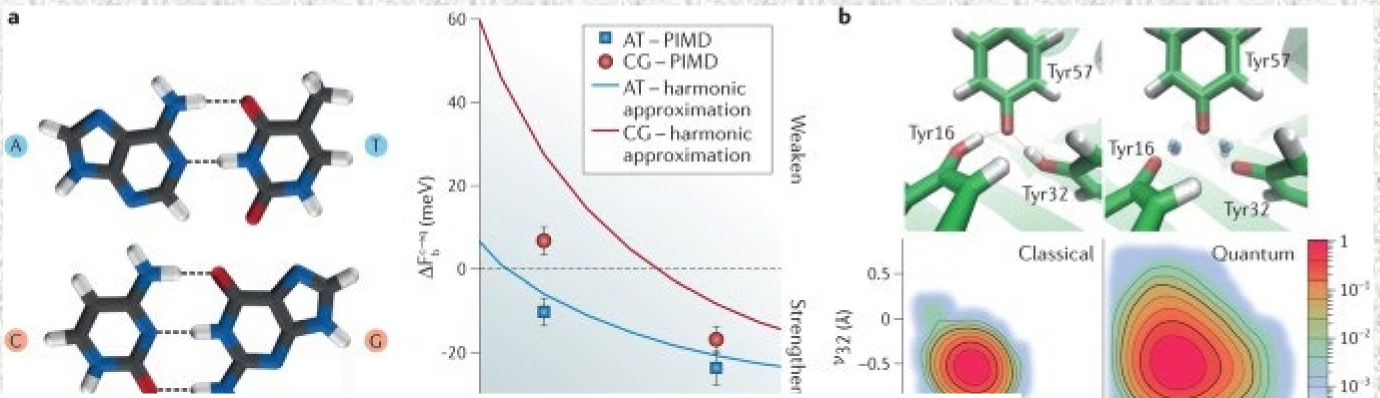
- Take-home Message.

第四部分: Take-home message





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Nuclear Quantum Effects in Water and Aqueous Systems: Experiment, Theory, and Current Challenges

Michele Ceriotti[†], Wei Fang[‡], Peter G. Kusalik[§], Ross H. McKenzie[∥], Angelos Michaelides[‡], Miguel A. Morales[⊥], and Thomas E. Markland[*#]

View Author Information

Cite this: *Chem. Rev.* 2016, 116, 13, 7529–7550
Publication Date: April 6, 2016
https://doi.org/10.1021/acs.chemrev.5b00674

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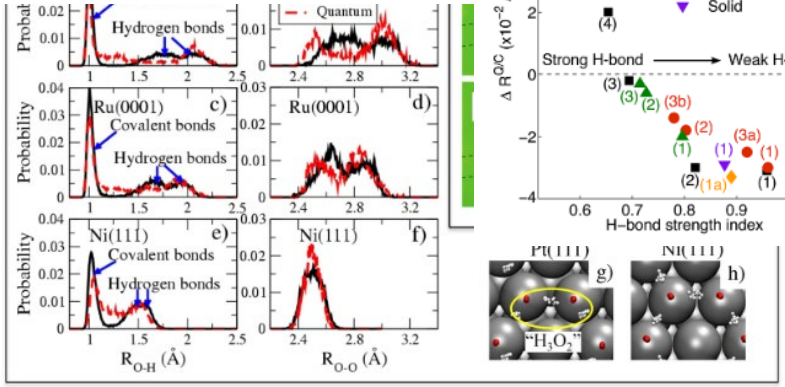

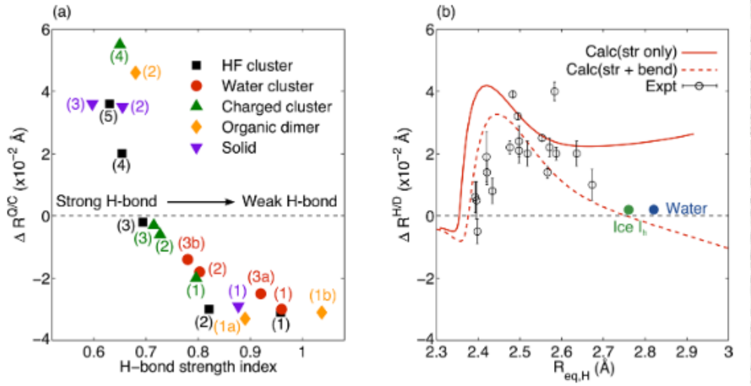

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Thomas E. Markland & Michele Ceriotti

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Acknowledgement

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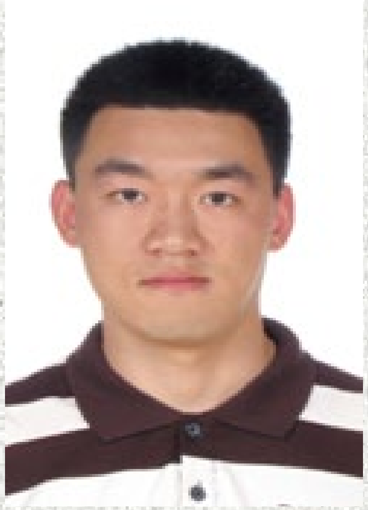

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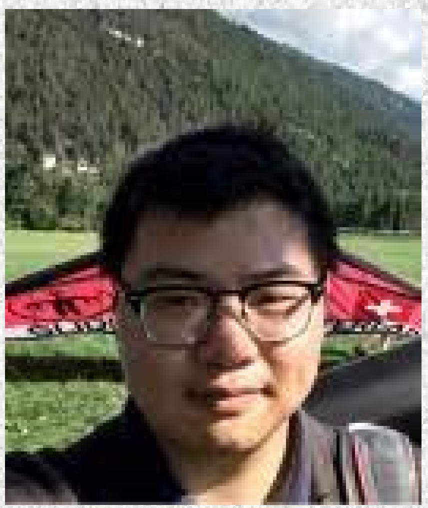
Yexin Feng (HNU)



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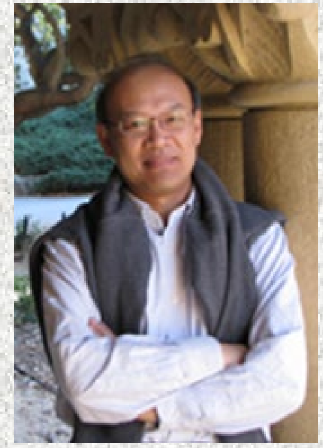


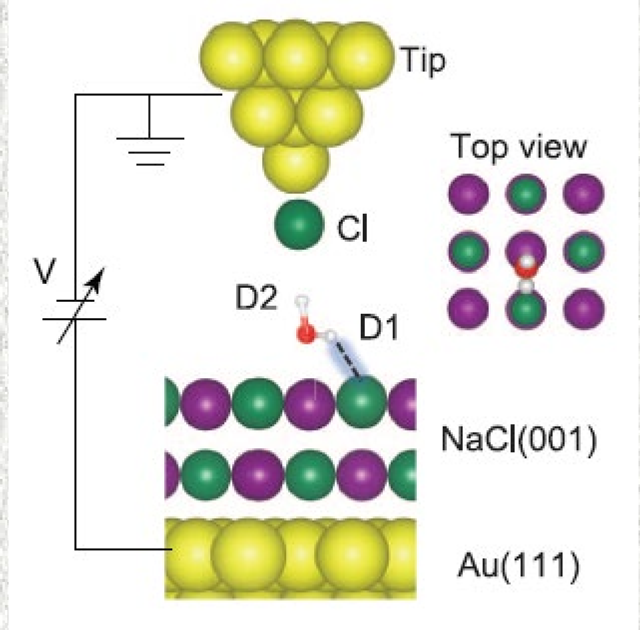
Enge Wang

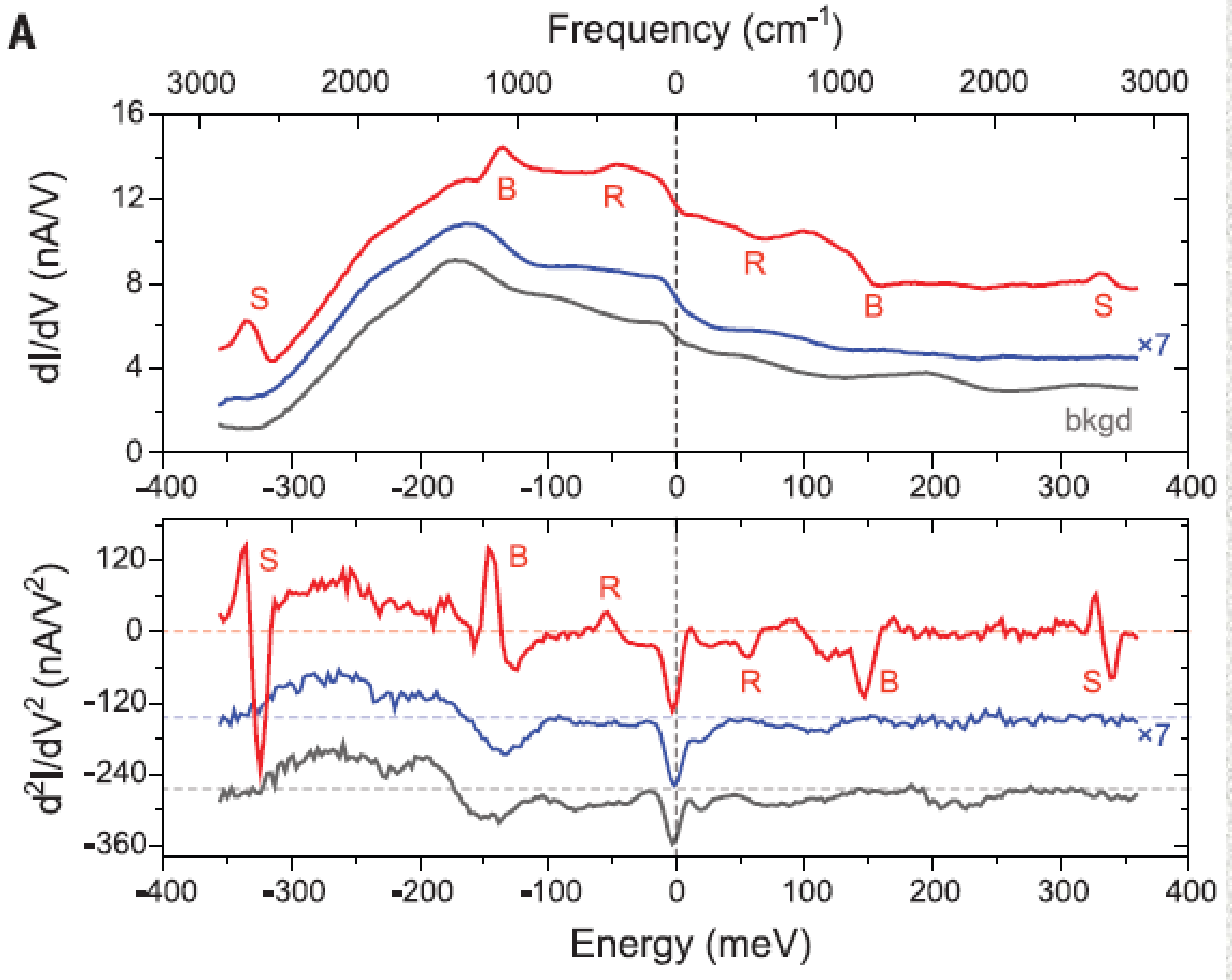
Guangshan Tian

Thank you ! ! !

Part III: Quantum Nature of Hydrogen Bond

- New Experiment (Inelastic tunneling spectroscopy, IETS):





Part III: Quantum Nature of Hydrogen Bond

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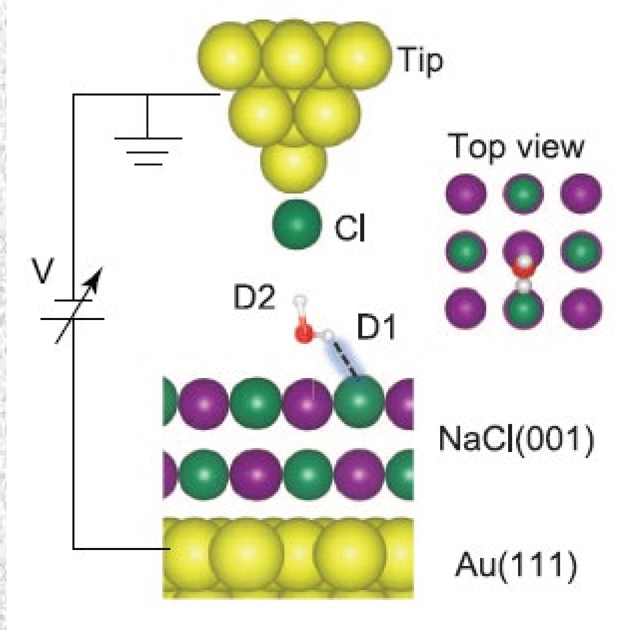
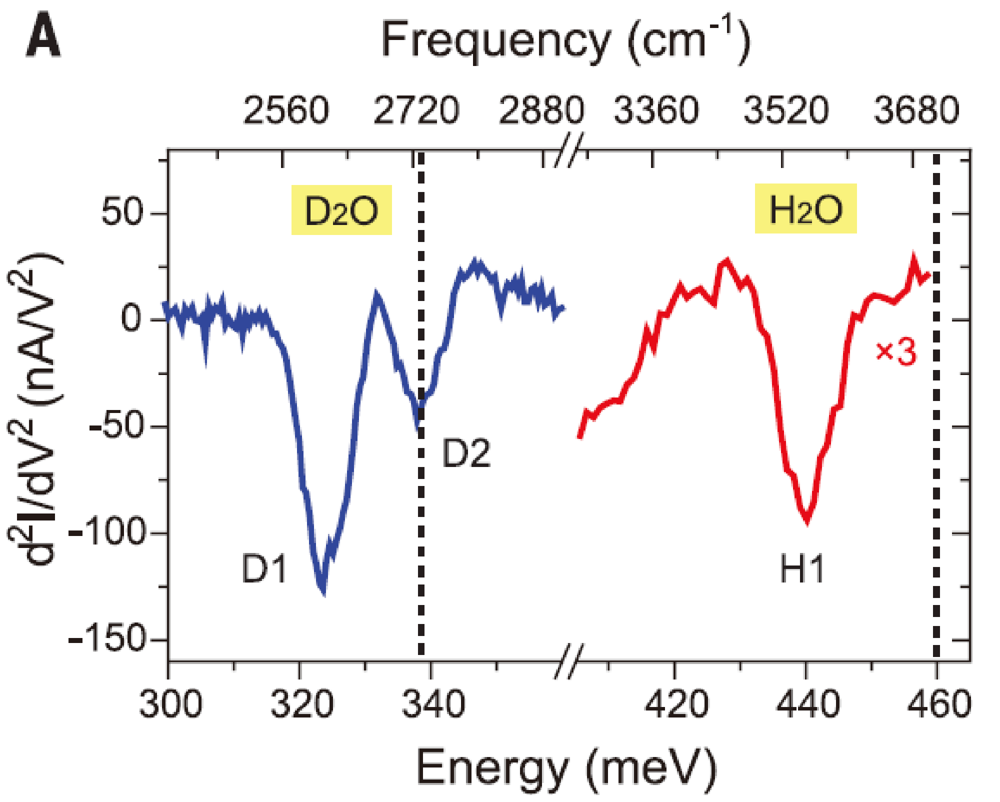
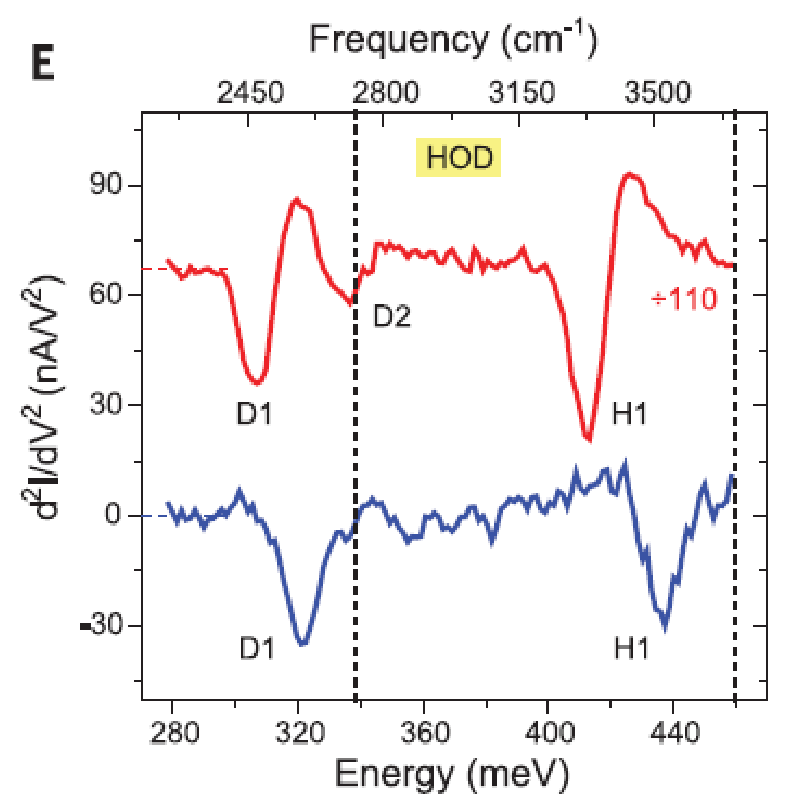
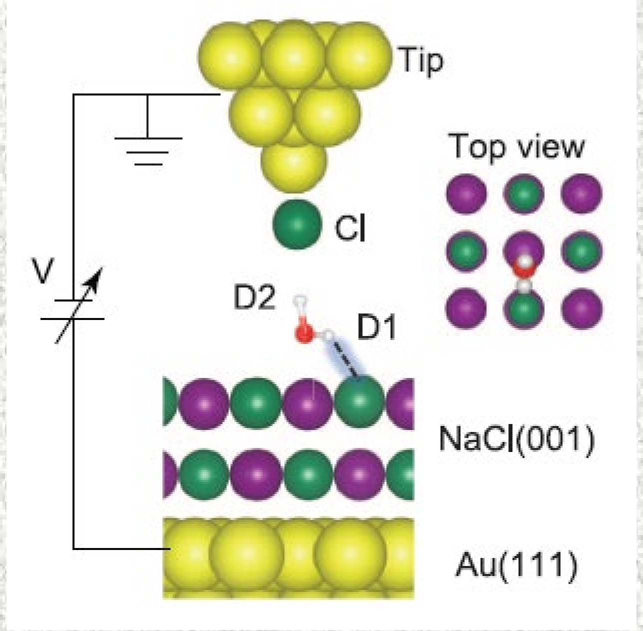


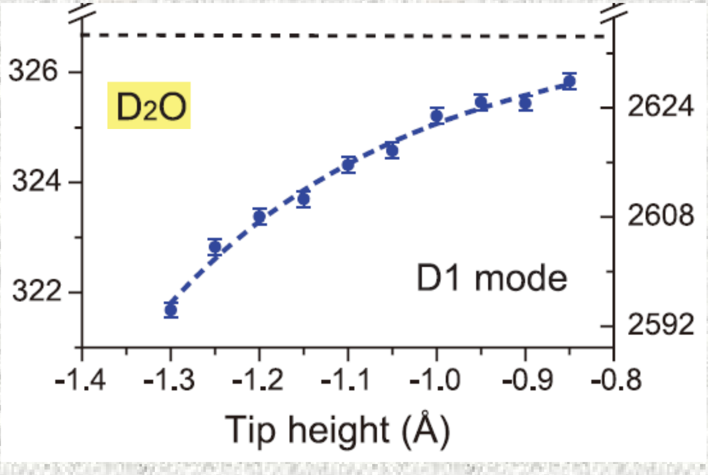


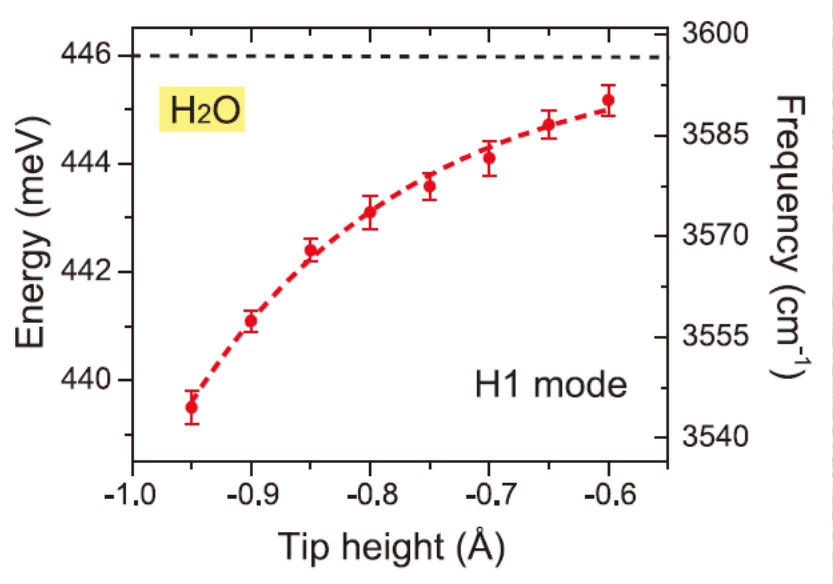


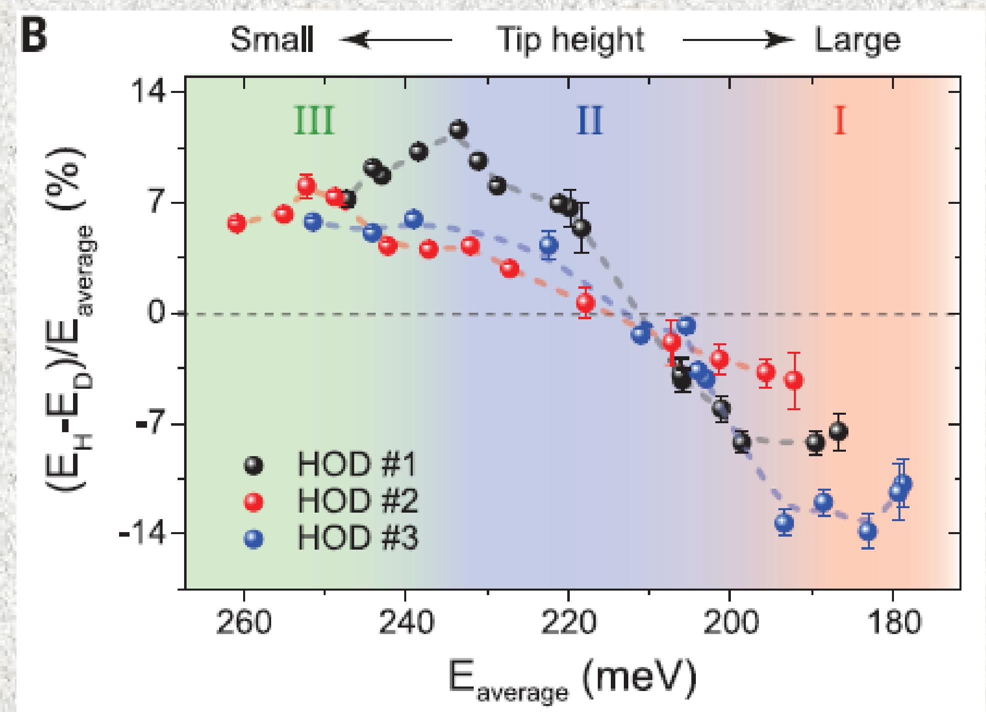
Part III: Quantum Nature of Hydrogen Bond

- New Experiment (Inelastic tunneling spectroscopy, IETS):



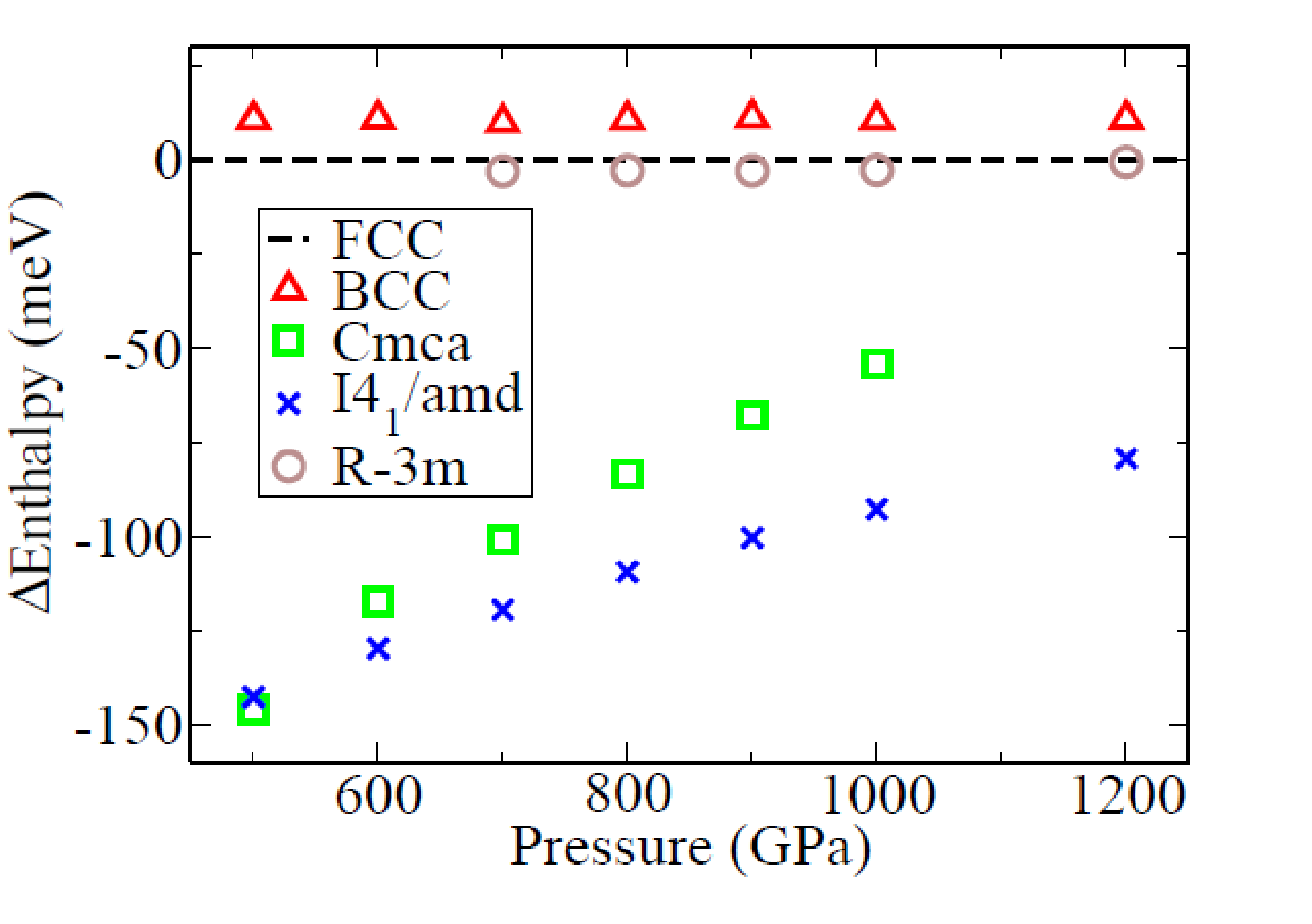


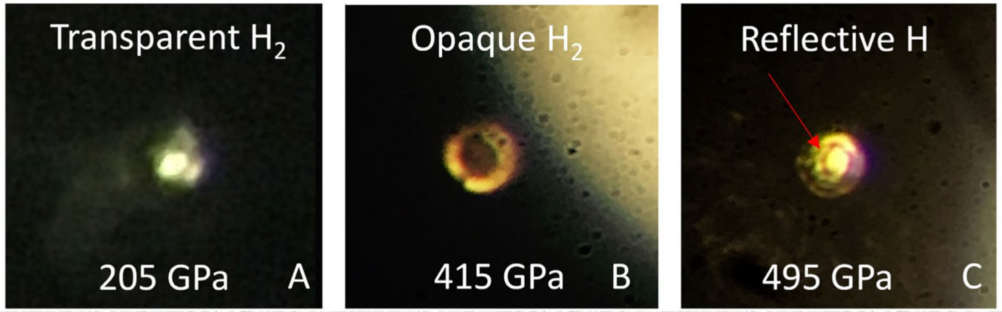


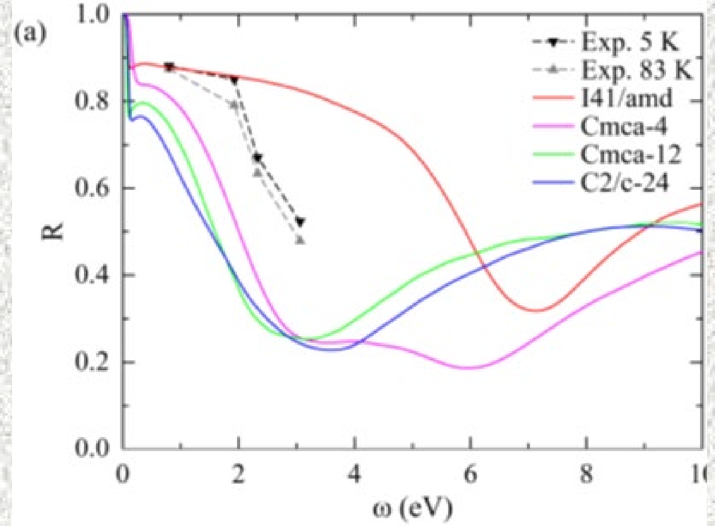


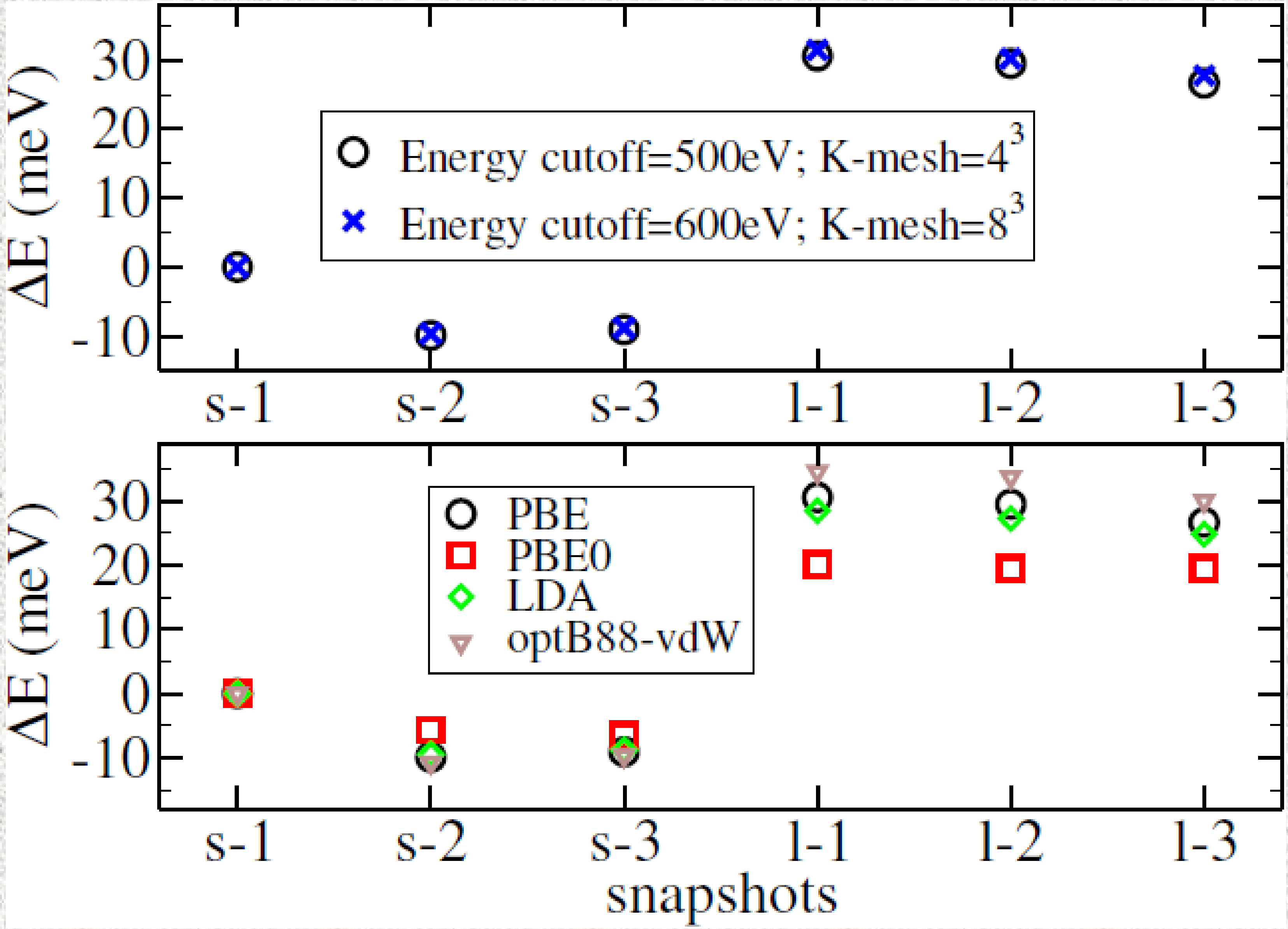
$$\Delta H = 1.3 \times \sqrt{\Delta \nu}$$

$$\nu(OH)/\nu(OD) = 1.3612$$

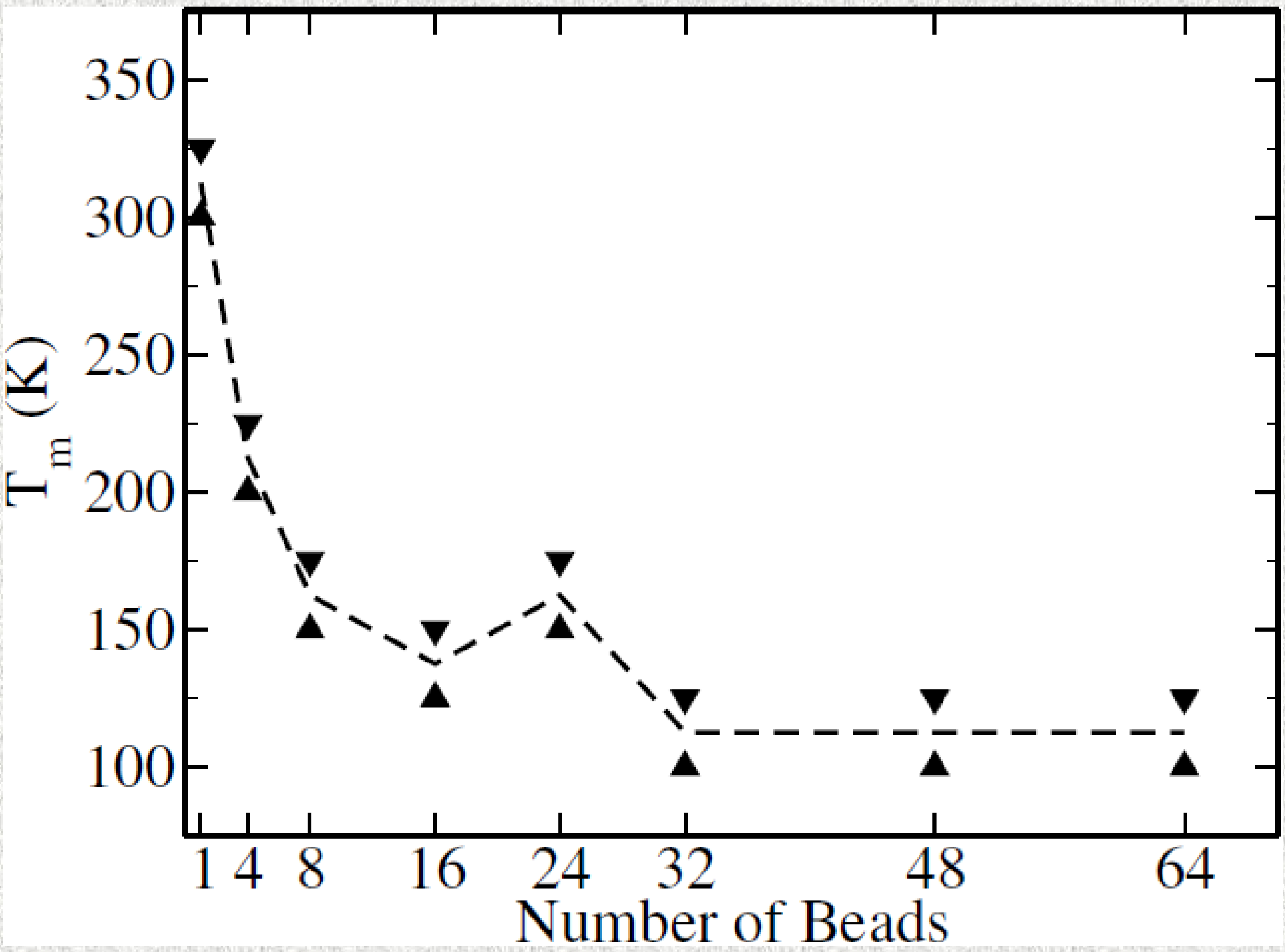

ΔEnthalpy (meV)
Pressure (GPa)
FCC
BCC
Cmca
I4₁/amd
R-3m
0
-50
-100
-150
600
800
1000
1200


Transparent H_2
205 GPa
A
Opaque H_2
415 GPa
B
Reflective H
495 GPa
C

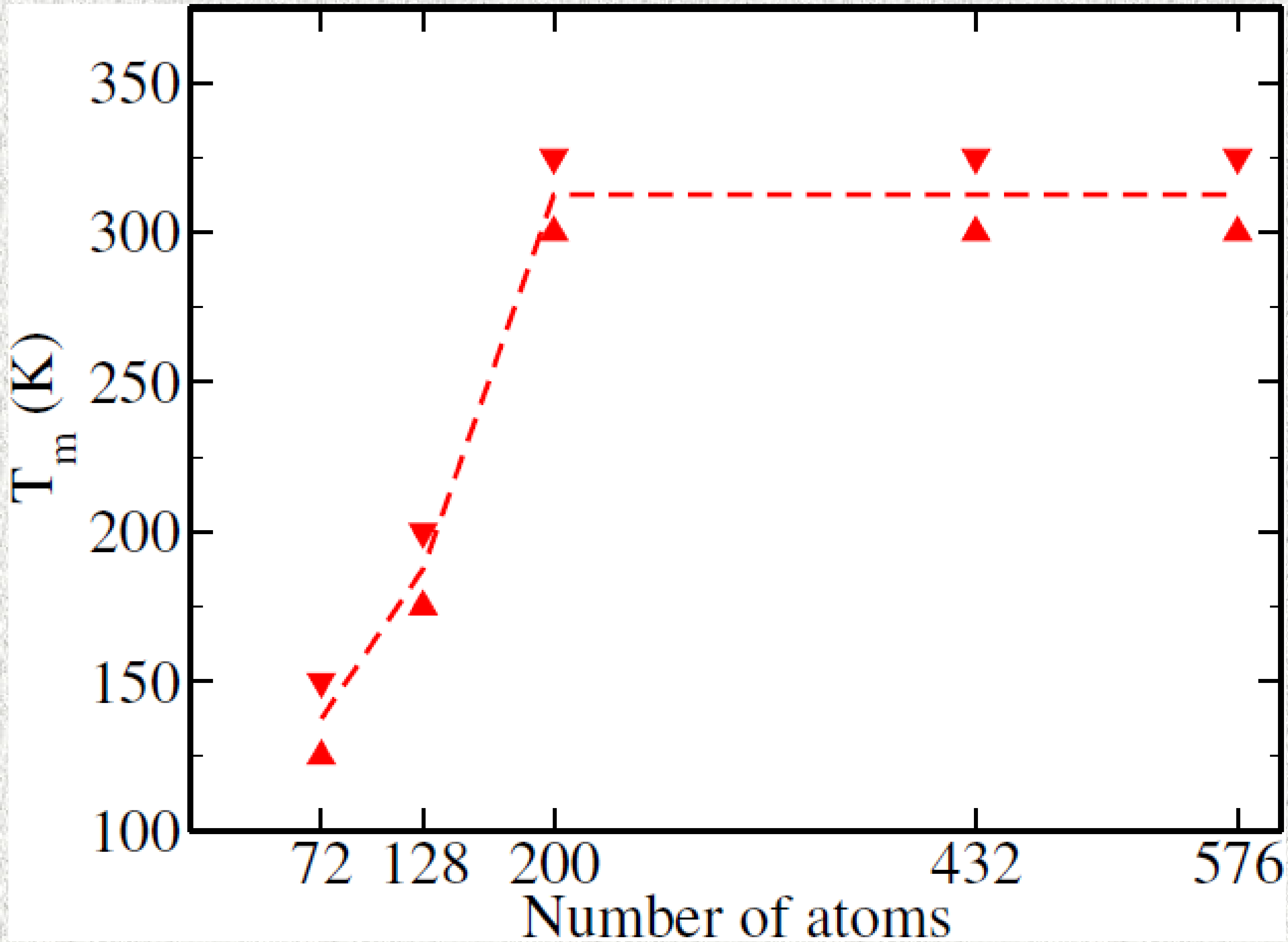

(a)
R
ω (eV)
Exp. 5 K
Exp. 83 K
I41/amd
Cmca-4
Cmca-12
C2/c-24
1.0
0.8
0.6
0.4
0.2
0.0
0
2
4
6
8



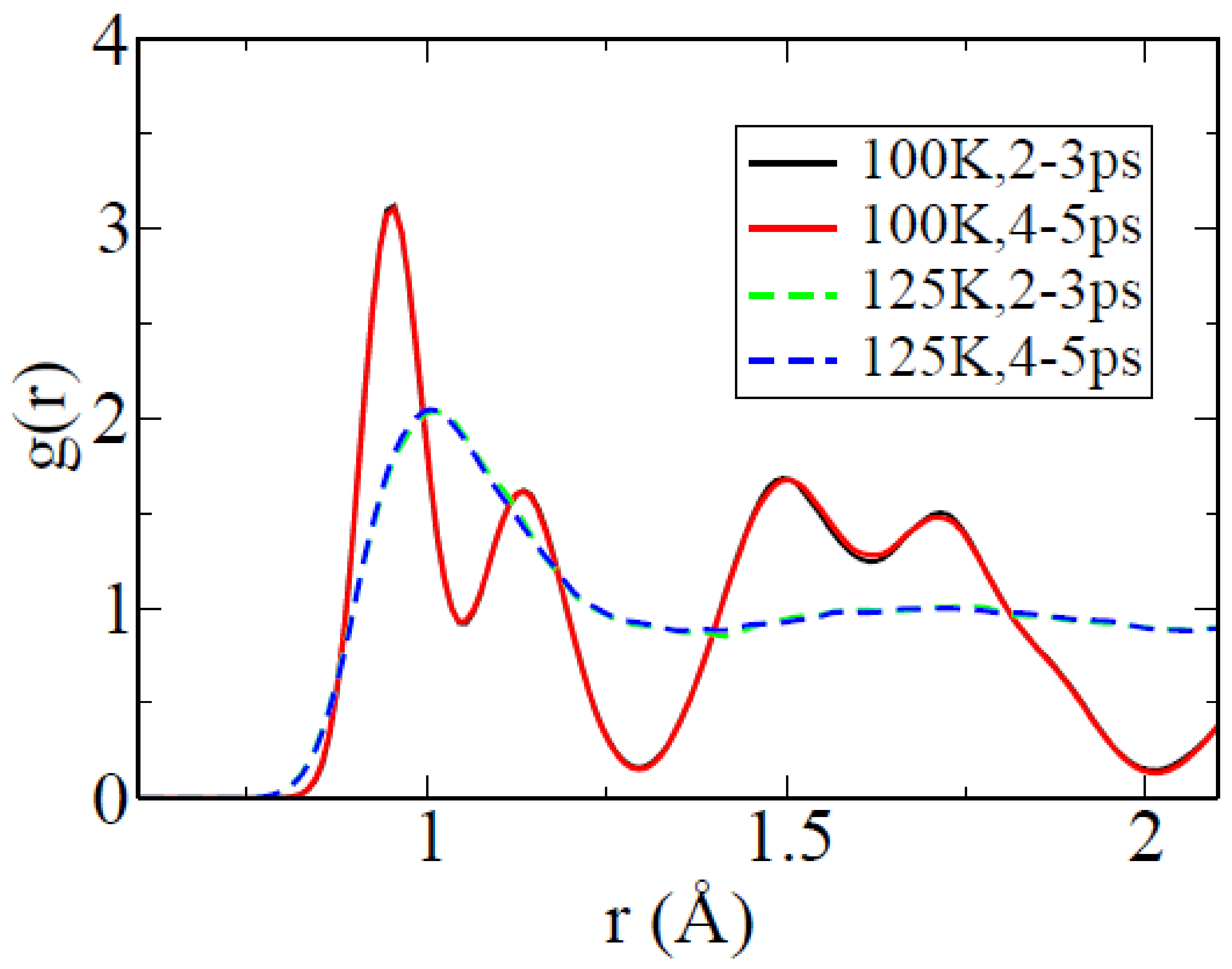
ΔE (meV)
30
20
10
0
-10
Energy cutoff=500eV; K-mesh=4^3
Energy cutoff=600eV; K-mesh=8^3
s-1
s-2
s-3
l-1
l-2
l-3
ΔE (meV)
PBE
PBE0
LDA
optB88-vdW
snapshots



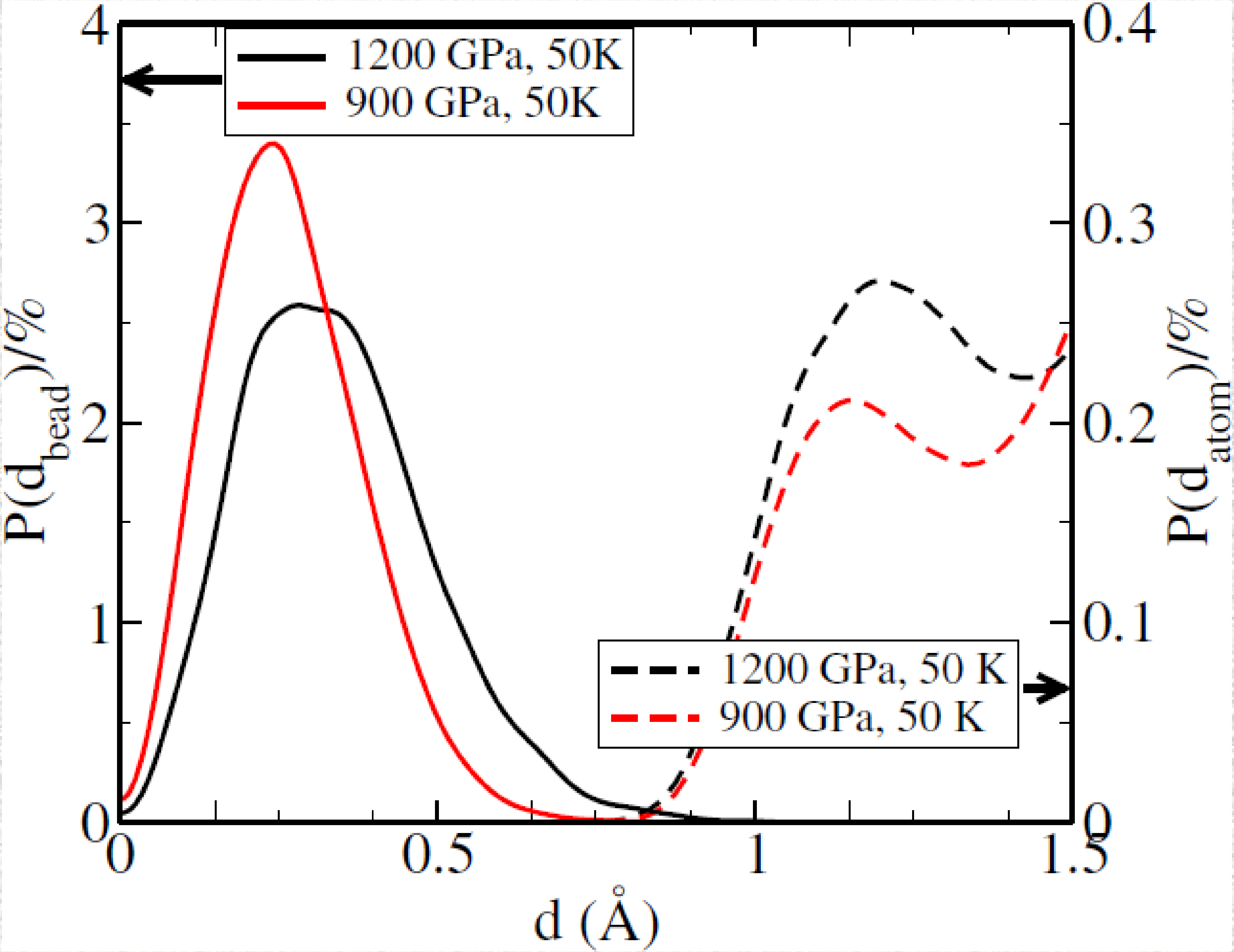
350
300
250
200
150
100
T_m (K)
1
4
8
16
24
32
48
64
Number of Beads



350
300
250
200
150
100
T m (K)
72
128
200
432
576
Number of atoms

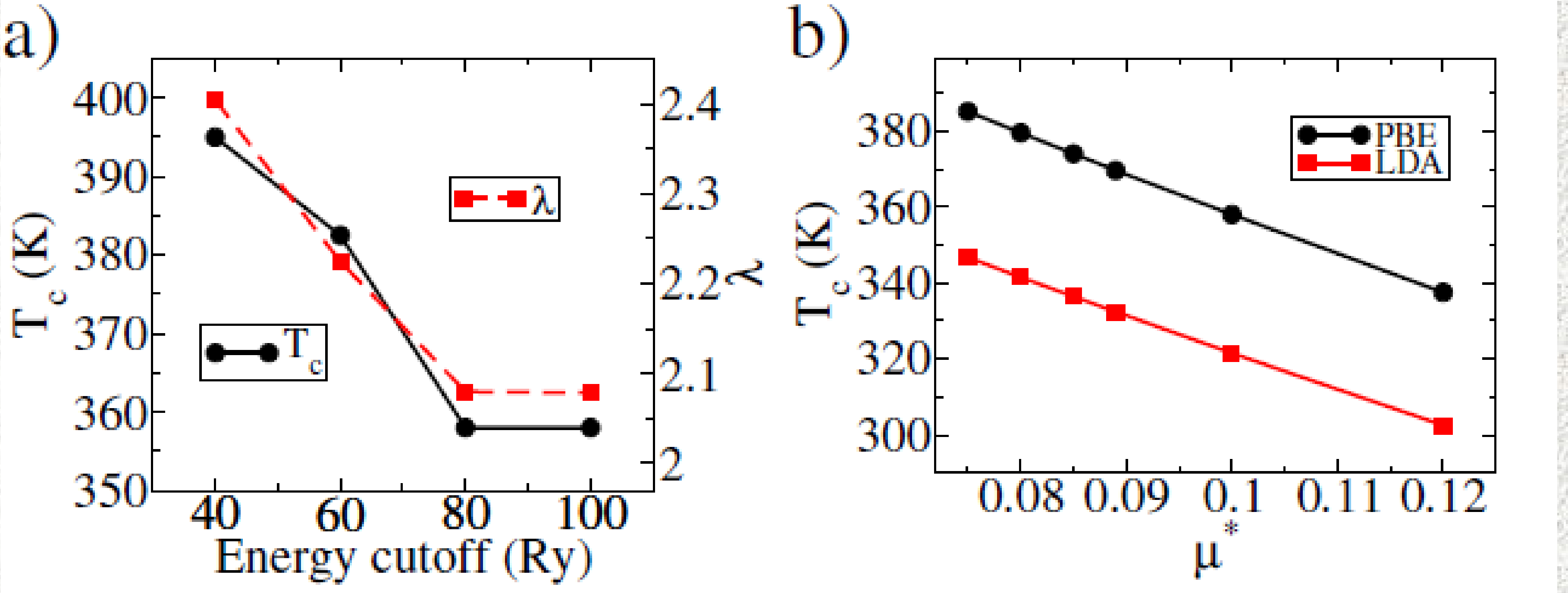


4
3
2
1
0
g(r)
1
1.5
2
r (Å)
100K,2-3ps
100K,4-5ps
125K,2-3ps
125K,4-5ps



1200 GPa, 50K
900 GPa, 50K
1200 GPa, 50 K
900 GPa, 50 K
P(d_bead)/%
P(d_atom)/%
d (Å)
0
0.5
1
1.5
1
2
3
4
0.1
0.2
0.3
0.4

Part II: Low-T metallic liquid hydrogen



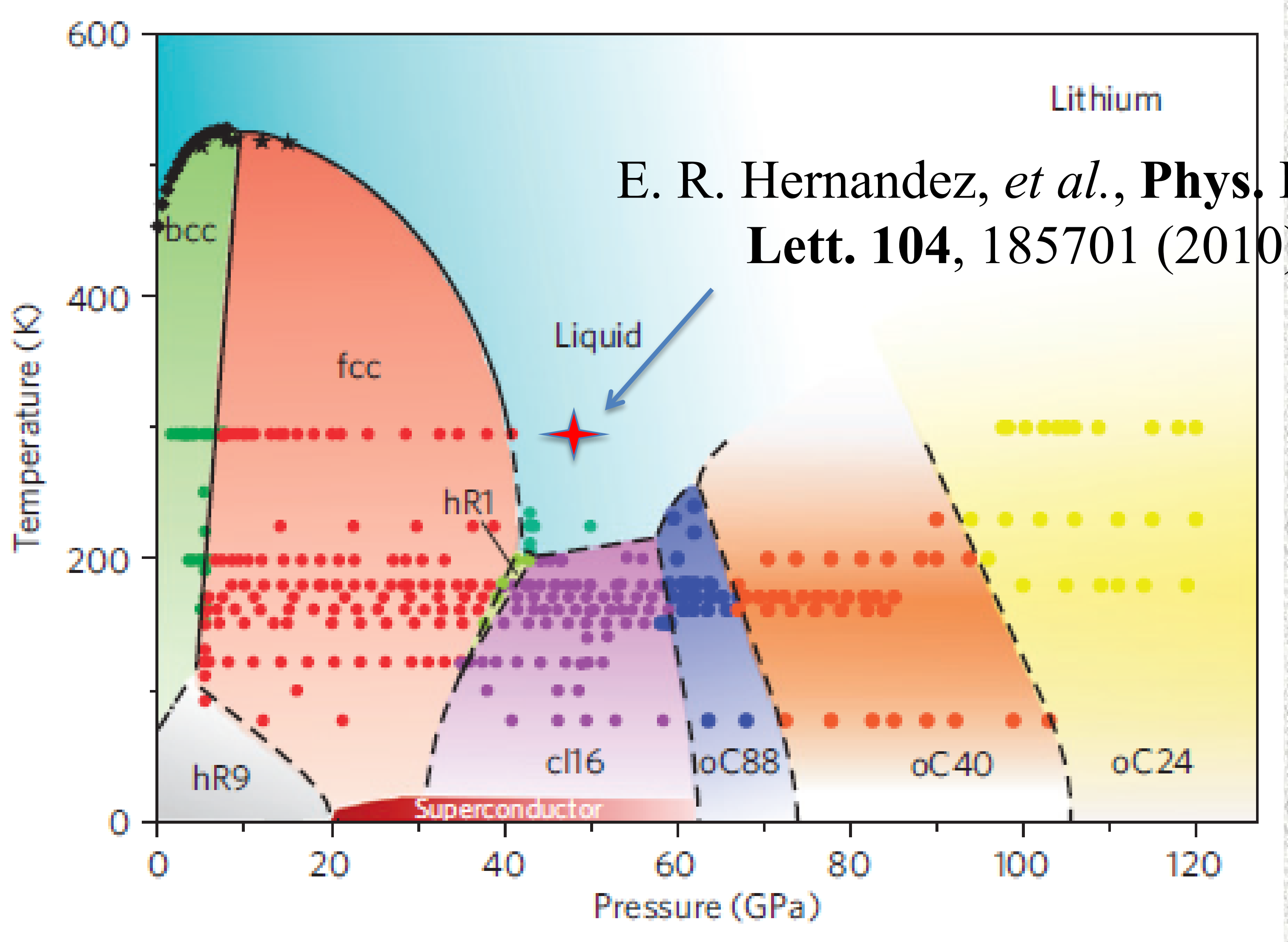
Parameters in the Allen-Dynes equation

Consistent with:

J. M. McMahon and D. M. Ceperley, **Phys. Rev. B. 84**, 144515 (2011)

P. Cudazzo, et al., **Phys. Rev. Lett. 100**, 257001 (2008)

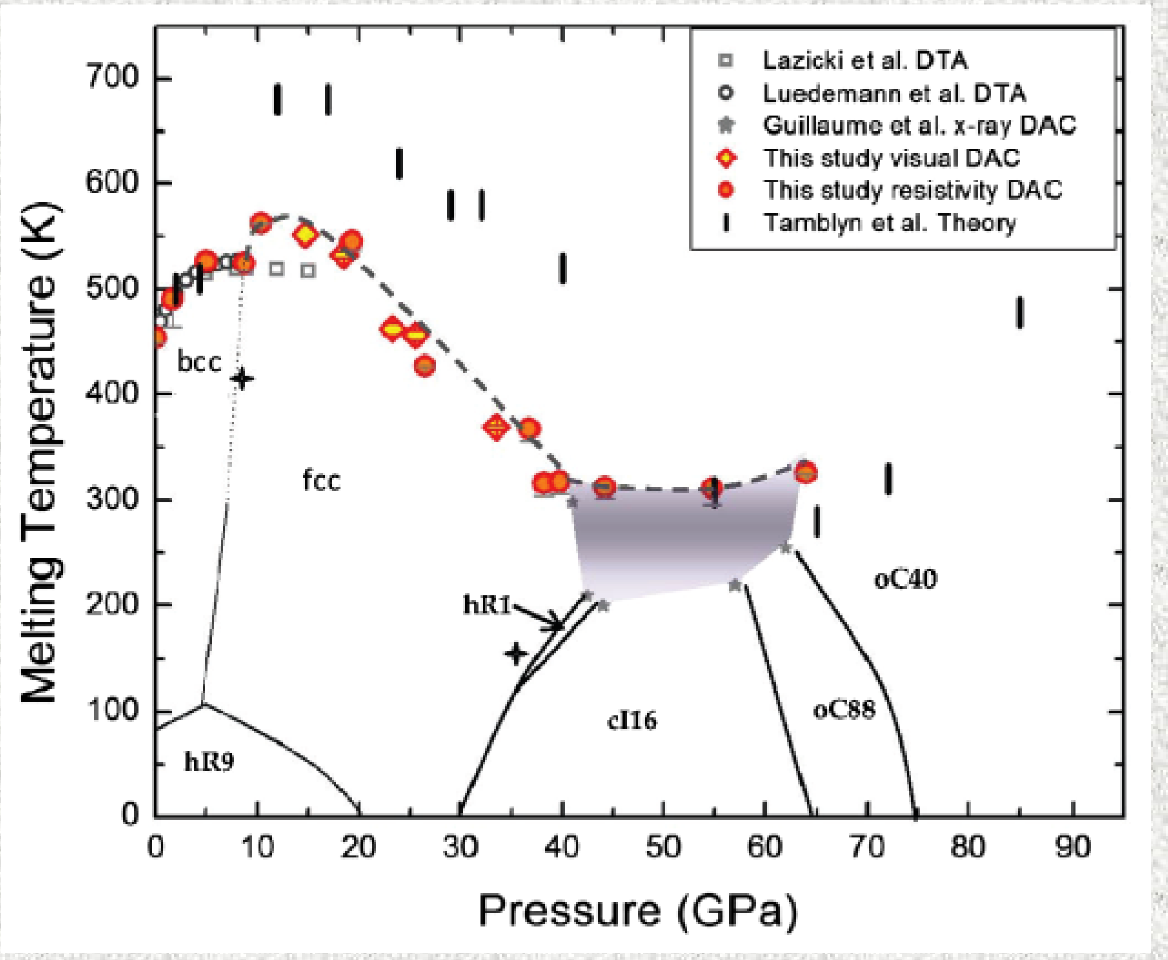
Part III: NQEs on the melting of lithium



E. R. Hernandez, *et al.*, **Phys. Rev. Lett. 104**, 185701 (2010)

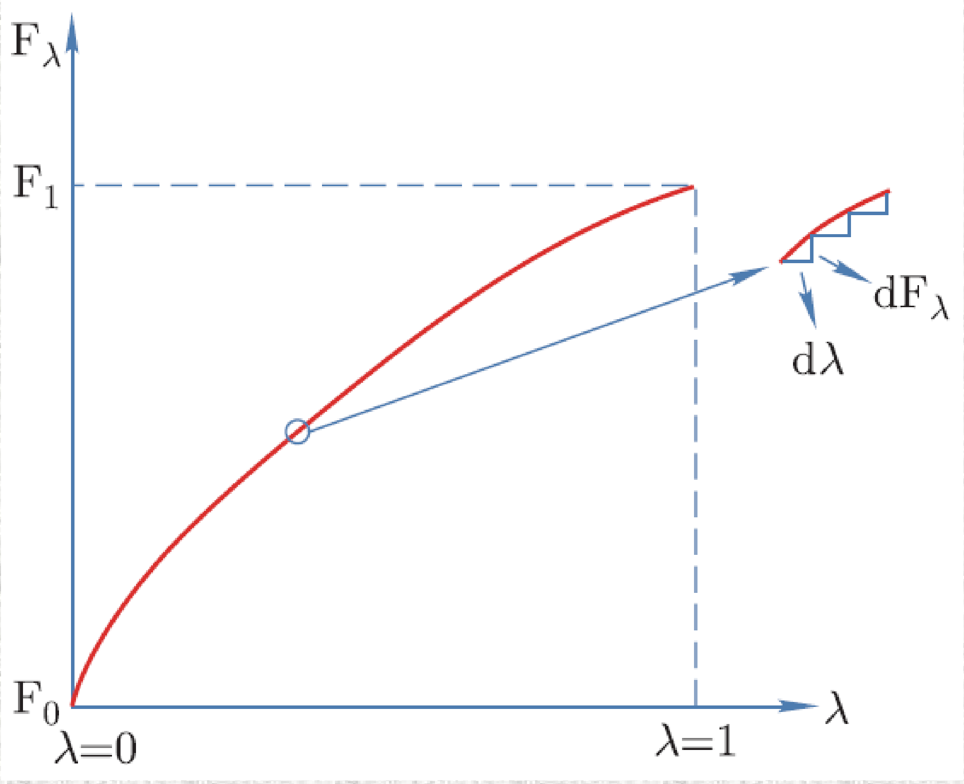
C. L. Guillaume *et al.*, **Nat. Phys. 7**, 211 (2011)

Part III: NQEs on the melting of lithium



A. M. J. Schaeffer *et al.*, Phys. Rev. Lett. 109, 185702 (2012)

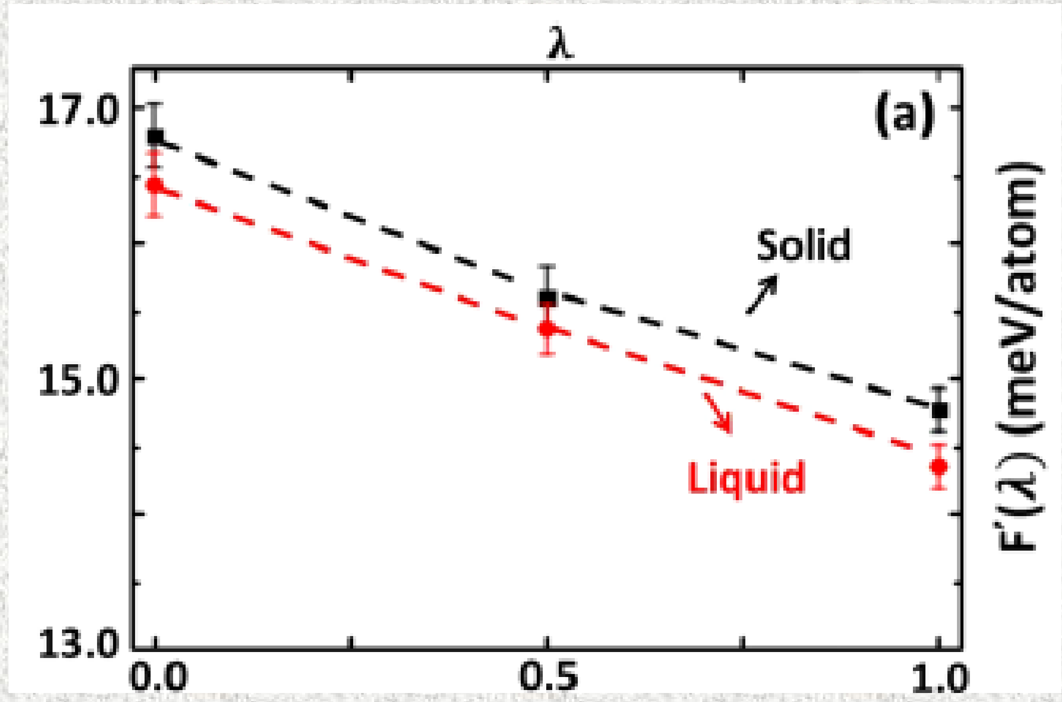
Part III: NQEs on the melting of lithium

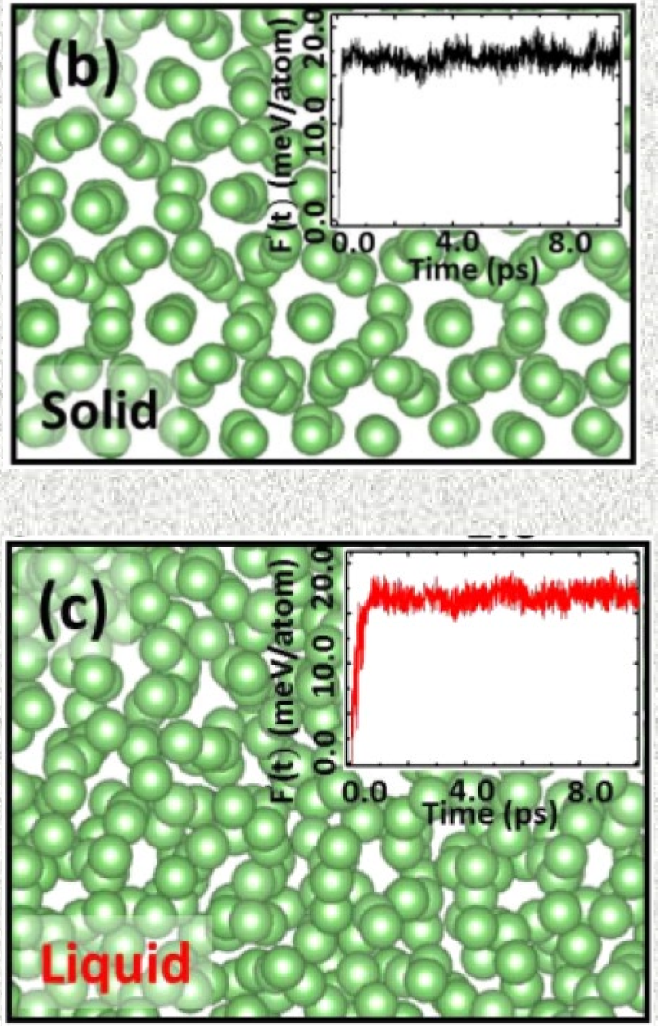


$$\Delta F = F(1) - F(0) = \int_0^1 \mathrm{d}\lambda F'(\lambda)$$

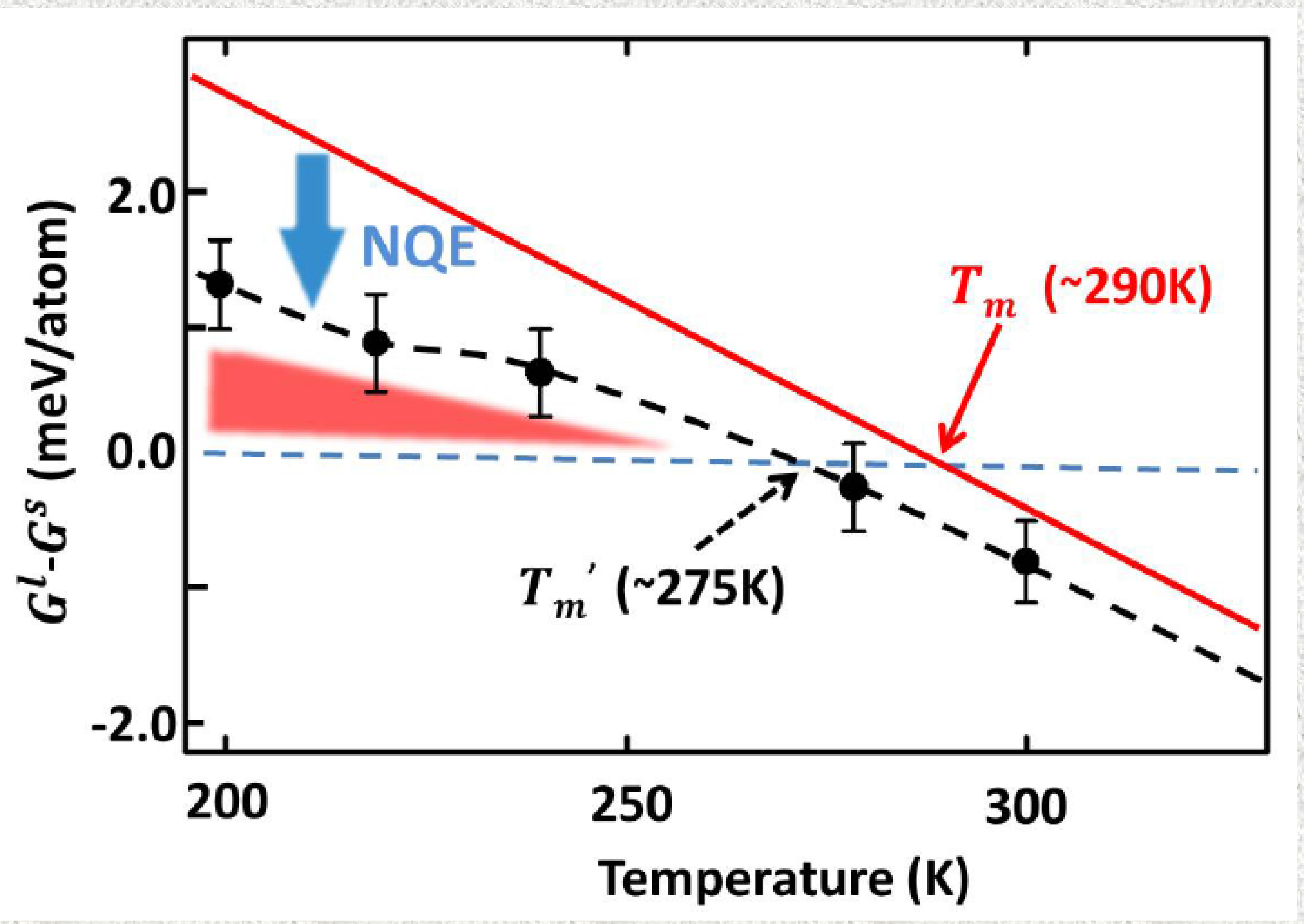
$$F'(\lambda) = \left\langle \frac{1}{P}\sum_{i=1}^{P}\left[V(\mathbf{x}_i^1,\cdots,\mathbf{x}_i^N) - V(\mathbf{x}_c^1,\cdots,\mathbf{x}_c^N)\right]\right\rangle_{V^{\mathrm{eff}}(\lambda)}$$

Part III: NQEs on the melting of lithium





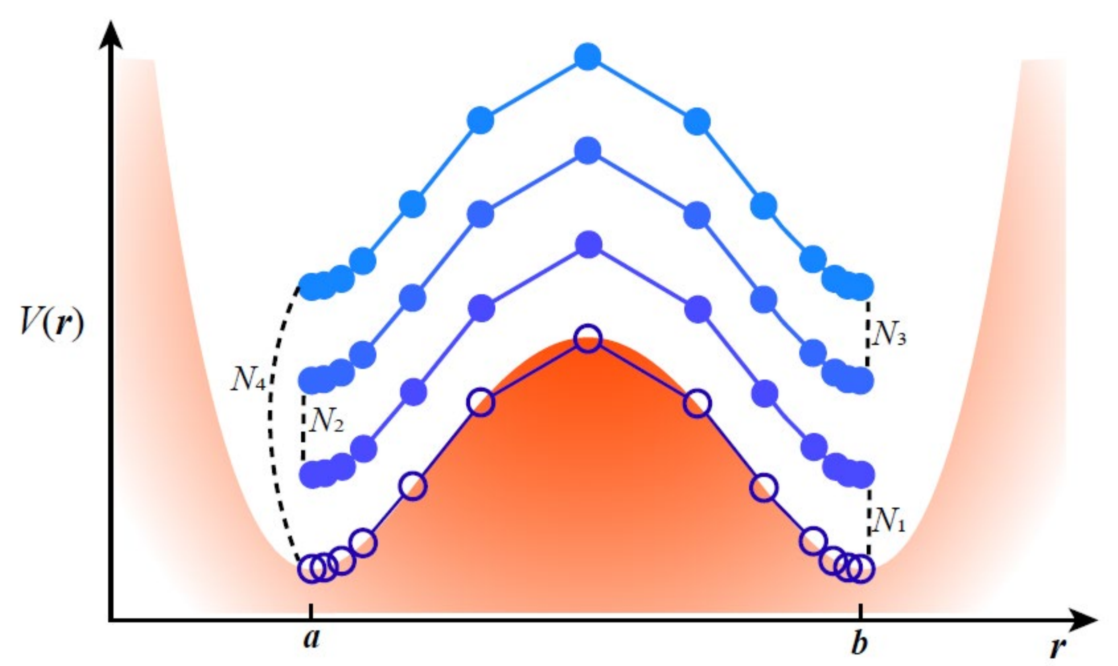
Part III: NQEs on the melting of lithium



Y. X. Feng *et al.*, J. Chem. Phys. 142, 064506 (2015)

Part III: NQEs on the melting of lithium

$$\lim_{\beta\to\infty}\frac{Q(\beta)}{2Q_0(\beta)} \approx \frac{e^{-\beta(E_0-\Delta/2)}+e^{-\beta(E_0+\Delta/2)}}{2e^{-\beta E_0}} = \cosh\left(\frac{\beta\Delta}{2}\right),$$



$Q_0(\beta)$ is easy to evaluate. Applying the steepest-descent approximation, it corresponds to the situation of a collapsed ring-polymer in the bottom of one of the wells. This results in a simple harmonic vibrational partition function. With $\beta_N = \beta/N$, N being the number of beads, one has

$$Q_0(\beta) \simeq \prod_k \frac{1}{\beta_N\hbar\omega_k} = \left(\frac{1}{\beta_N\hbar}\right)^N \frac{1}{\sqrt{\det\mathbf{G}_0}}. \quad (2)$$

ω_k^2 are the eigenvalues of the mass-weighted Hessian of the collapsed ring-polymer, the elements of which are

$$(\mathbf{G}_0)_{ii'} = \frac{2\delta_{ii'}-\delta_{ii'-1}-\delta_{ii'+1}}{(\beta_N\hbar)^2}+\omega_s^2\delta_{ii'}. \quad (3)$$

$$Q(\beta) = \sum_{n=0,\mathrm{even}}^{\infty}\frac{2N^n}{n!}Q_n(\beta)$$

Yucheng Zhu, Shuo Yang, Jiaxi Zeng, Wei Fang, Ling Jiang, Donghui Zhang, and Xin-Zheng Li, **J. Chem. Phys. 158**, 220901 (2023)