大規模電子状態シミュレーションを用いた結晶系における水素量子効果の研究

Yokohama City Univ.（横浜市立大学）
**Masanori Tachikawa (立川仁典)**

Abstract

Nuclear **Q**uantum **E**ffect (**NQE**), such as zero-point vibrational energy, tunneling, and its H/D isotope effect, is quite important in various systems from small molecules to material or biochemical complex species. Especially, in the case of "Low **B**arrier **H**ydrogen **B**onding (**LBHB**) systems", NQE of proton (or deuteron) is indispensable. To elucidate such hydrogen-functional mechanism, we will develop some ab initio approaches for multi-component systems including both electrons and nuclei quantum-mechanically: (I) Multi-component density functional theory (**MC_DFT**) and (II) *ab initio* path integral molecular dynamics (**PIMD**) methods.

What is LBHB (Low Barrier Hydrogen Bonding)?

- HB patterns by Jefferey [1]

HB Strength (kcal/mol)	Weak	Medium	Strong
	< 4	4 - 15	15 - 40 (Ionic HB)
Example (X-H…A)	C-H……O	O-H….O	O-H…O⁻ F-H-F⁻
Geometric Isotope Effect (R_{XA})	Longer	Longer	?? Shorter
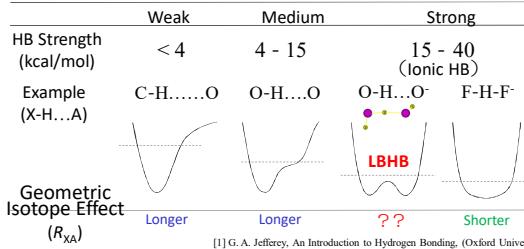
[1] G. A. Jefferey, An Introduction to Hydrogen Bonding, (Oxford University Press 1997).

- **Zundel structure of $H_3O_2^-$**
Hydroxyl ion transfer in aqueous solution
ΔE=0.2 kcal/mol (Low barrier height)

- **HB ferroelectric materials**
Tc(H) = 371K   Tc(H) = --
Tc(D) = 516K   Tc(D) = 85K
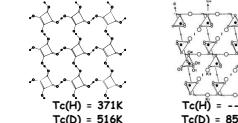
The Tc increases (more than 100K) by deuteration!

Where is LBHB?

- **H_3(Cat-EDT-TTF)$_2$**

The phase transition is found only for κ-D

- **PYP (Photo Yellow Protein)**

The formation of LBHB is found in PYP by neutron crystallography

ab initio PIMD

- Marx and Parrinello (1994)
- Cheng, Barnett, and Landman (1995)
- Schulte, Bohm, and Ramirez (1996)
- Kitamura, Tsuneyuki, Ogitsu, and Miyake (2000)

- **Potential:** *ab initio* MO
N(=2) × P(=8)

Full quantum treatment !! ➡ **Path integral for nucleus**
Ab initio MO for electron

- M. Shiga, M. Tachikawa, and S. Miura, *J. Chem. Phys.* **115**, 9149 (2001).
- M. Tachikawa and M. Shiga, *J. Am. Chem. Soc.* **127**, 11908 (2005).

ab initio MC_DFT

- Hamiltonian for Multi-Component system

(Electron: N, Classical nuclei: M, Quantum nuclei: L)

$$\hat{H}_{(e+p)} = \left[-\sum_{i=1}^{N}\frac{1}{2}\nabla_i^2 + \sum_{i=1}^{N}\sum_{j>i}^{N}\frac{1}{r_{ij}} - \sum_{i=1}^{N}\sum_{A=1}^{M}\frac{Z_A}{r_{iA}} \right] + \left[-\sum_{a=1}^{L}\frac{1}{2m_a}\nabla_a^2 - \sum_{a=1}^{L}\sum_{i=1}^{N}\frac{1}{r_{ia}} + \sum_{a=1}^{L}\sum_{A=1}^{M}\frac{Z_A}{r_{aA}} + \sum_{a=1}^{L}\sum_{b>a}^{L}\frac{1}{r_{ab}} \right]$$

↑Conventional DFT   ↑Quantum nuclei

- Kohn-Sham (KS) eq. for MC_DFT

$$f_{e,p}^{(KS)}\phi_i = \varepsilon_i^{e,p}\phi_i^{e,p}$$

- KS operator for MC_DFT

Electron
$$f_e^{(KS)} = h_e + \sum_e J_e - \sum_p J_p + V_{XC(e-e)}$$

Quantum nuclei
$$f_p^{(KS)} = h_p + \sum_p J_p - \sum_e J_e$$

Nuclear quantum effect on $H_3O_2^-$

- **2D distribution with respect to δ_{OH^*} and R_{OO} [3]**
$\delta_{OH^*} = r_1 - r_2$

50 K
$\langle R_{OO}^{(H)}\rangle$ = 2.484 (Å) $\langle R_{OO}^{(T)}\rangle$ = 2.477 (Å)

600 K
$\langle R_{OO}^{(H)}\rangle$ = 2.529 (Å) $\langle R_{OO}^{(T)}\rangle$ = 2.551 (Å)

- At 50K, average OO bond length of $T_3O_2^-$ is _shorter_ than that of $H_3O_2^-$ due to the anharmonicity of the potential, which is a similar result of QMC.

- At 600K, average OO bond length of $T_3O_2^-$ is _longer_ than that of $H_3O_2^-$, which is a similar result of our previous PIMD.
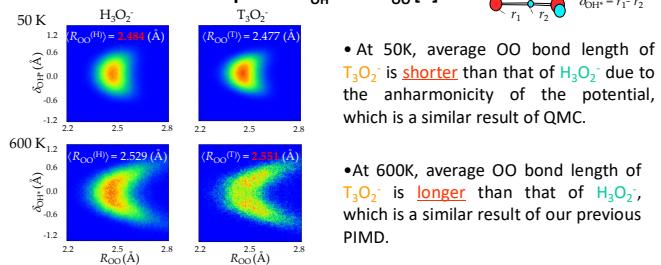
- **Muoniated acetone radical (Mu-ACE)**

HFCC (MHz)   Mu-ACE   H-ACE

improvement

Exptl. *in water*: 8.6 / 0.9
PIMD *in vacuo*: 32.1 / 4.0
Conventional DFT [5] *in vacuo*: -5.8 / -5.8

Our HFCC using PIMD qualitatively reproduced experimental HFCC.

CPLB method

Combined **P**lane wave and **L**ocalized **B**asis-sets method is using MC_DFT at the cluster model around H/D.

$$E_{CPLB, surface} = E_{Plane\ wave, surface} - E_{Plane\ wave, cluster} + E_{MC\_DFT, cluster}$$

Plane wave, cluster   MC_DFT, cluster   metal   Plane wave, surface

- H/D atom adsorption on Pd(111) surface

$r_{H-surface}$=0.800 Å > $r_{D-surface}$=0.785 Å
$E_{ads}(H)$=2.683 eV < $E_{ads}(D)$=2.698 eV
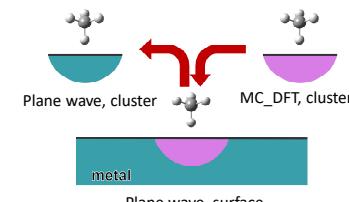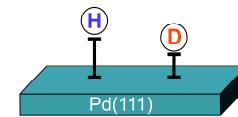
Adsorption distance $r_{H-surface}$ is _longer_ than of $r_{D-surface}$. Although no direct observations of this geometrical difference surface have been reported, this result expects due to the anharmonicity of the potential.
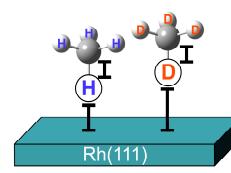
Adsorption energy $E_{ads}(H)$ is _lower_ than $E_{ads}(D)$, which result corresponds to the experimentally trend.[6]

- CH_4/CD_4 molecular adsorption on Rh(111) surface

r_{H-C}=1.119 Å > r_{D-C}=1.113 Å
$r_{H-surface}$=2.071 Å < $r_{D-surface}$=2.107 Å
$E_{ads}(CH_4)$=0.399 eV > $E_{ads}(CD_4)$=0.330 eV

Adsorption energy $E_{ads}(CH_4)$ is _higher_ than $E_{ads}(CD_4)$ due to the anharmonicity of the potential, which is similar trend as observed C_6H_{12}/C_6D_{12} adsorption.[7]

Adsorption distance $r_{H-surface}$ is _shorter_ than $r_{D-surface}$. And bond length r_{H-C} is longer than r_{D-C}. which is also similar trend as C_6H_{12}/C_6D_{12} adsorption.

0.002-0.003 Å
$r_{ad}(C_6H_{12}) > r_{ad}(C_6D_{12})$
0.084 eV
$E_{ads}(C_6H_{12}) < E_{ads}(C_6D_{12})$

[7]
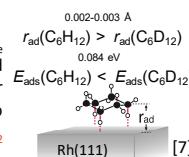
These results suggest CD_4 has a weaker interaction with the Rh(111) surface than CH_4.

Our CPLB method is expected to be an effective tool for analysing H/D on metal surfaces.

Nuclear quantum effect on PYP

Photoactive Yellow Protein (PYP)

✓ Neutron crystallography demonstrated the formation of LBHB in PYP, which was assumed to play the important role in photosencing process.[4]

OH bond lengths of Glu46

MC_DFT: DH / HH / DD / HD / Conv. DFT

R_{OH} [Å]: DA gas / DA ONIOM / DA ONIOM/PCM / exptl.[4]

H-bonds in PYP

Arg52   Tyr42   Glu46   LBHB
Z = H (PA) or null (DA)
pCA (*para*-coumaric acid; chromophore of PYP)

R_{OH} (Tyr42): 1.02 Å
R_{OH} (Glu46): 1.21 Å

➜ **The significant elongation of OH bond is possible when Arg52 is deprotonated.**

[1] T. Isono, H. Kamo, A. Ueda, K. Takahashi, A. Nakao, R. Kumai, H. Nakao, K. Kobayashi, Y. Murakami and H. Mori, *Nat. Commun.* **2013**, 4, 1344 [2] A. Ueda, S. Yamada, T. Isono, H. Kamo, A.Nakao, R. Kumai, H. Nakao, Y. Murakami, . Yamamoto, Y. Nishio and Hatsumi Mori, *J. Am. Chem. Soc.* **2014**, 136, 12184–12192 [3] T. Udagawa, M. Tachikawa, *J. Chem. Phys.*, **2006**, 125, 244105 [4] S. Yamaguchi, H. Kamikubo, et al., *Proc. Natl. Acad. Sci.*, **106**, 440 (2009). [5] R. M. Macrae, et al., *Physica B*, **326** 81 (2003). [6] Y. Jin, *et al., J. Alloys Compd.*, 340, 207 (2002). [7] T. Koitaya, *et al., J. Chem. Phys.*, **136**, 214705 (2012).