



Abstract

Nuclear Quantum Effect (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 Barrier Hydrogen Bonding (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]

	Weak	Medium	Strong
HB Strength (kcal/mol)	< 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 H₃O₂⁻

Hydroxyl ion transfer in aqueous solution
ΔE=0.2 kcal/mol (Low barrier height)

•HB ferroelectric materials

Tc(H) = 371K
Tc(D) = 516K

Tc(H) = --
Tc(D) = 85K

The Tc increases (more than 100K) by deuteration!

Where is LBHB?

•H₃(Cat-EDT-TTF)₂

Chemical structures of the molecules in test. (a) H₃Cat-EDT-TTF and H₃Cat-EDT-ST molecules. (b) A hydrogen-bonded molecular unit, κ-S and κ-D.

The phase transition is found only for κ-D

•PYP (Photo Yellow Protein)

Formation of LBHB in PYP by neutron crystallography

E46, Y42, pCA

The formation of LBHB is found in PYP by neutron crystallography

ab initio PIMD

-(N)-body quantum
 $\hat{H} = \sum_{i=1}^N \frac{p_i^2}{2m_i} + V(\{R_i\})$ V_0 : Potential

-(N X P)-body classical
 $Z = \int \prod_{i=1}^N dR_i e^{-\beta H}$ ← Partition function

•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)

$\hat{H}_{(e,p)} = \sum_{i=1}^N \frac{1}{2} \nabla_i^2 + \sum_{i=1}^N \sum_{j=1}^M \frac{1}{r_{ij}} - \sum_{i=1}^N \sum_{A=1}^M \sum_{a=1}^L \frac{Z_A}{r_{iAa}} + \sum_{a=1}^L \sum_{b=1}^L \frac{1}{r_{ab}}$

↑ Conventional DFT ↑ Quantum nuclei

• Kohn-Sham (KS) eq. for MC DFT **KS operator for MC DFT**

$f_{e,p}^{(KS)} \phi_i = \epsilon_i^{e,p} \phi_i^{e,p}$ Electron $f_e^{(KS)} = h_e + \sum_c \sum_p J_c - \sum_p J_p + V_{XC(e-e)}$ Quantum nuclei $f_p^{(KS)} = h_p + \sum_c \sum_p J_c - \sum_c J_c$

Nuclear quantum effect on H₃O₂⁻

•2D distribution with respect to δ_{OH}⁺ and R_{OO} [3]

50 K: $\langle R_{OO}^{(H)} \rangle = 2.494$ (Å), $\langle R_{OO}^{(D)} \rangle = 2.477$ (Å)

600 K: $\langle R_{OO}^{(H)} \rangle = 2.529$ (Å), $\langle R_{OO}^{(D)} \rangle = 2.501$ (Å)

• At 50K, average OO bond length of T₃O₂⁻ is **shorter** than that of H₃O₂⁻ due to the anharmonicity of the potential, which is a similar result of QMC.

• At 600K, average OO bond length of T₃O₂⁻ is **longer** than that of H₃O₂⁻, which is a similar result of our previous PIMD.

CPLB method

Combined Plane wave and Localized Basis-sets method is using MC_DFT at the cluster model around H/D.

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

•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]

•CH₄/CD₄ 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 C₆H₁₂/C₆D₁₂ 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 C₆H₁₂/C₆D₁₂ adsorption.

These results suggest CD₄ has a weaker interaction with the Rh(111) surface than CH₄.

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

Nuclear quantum and H/D isotope effect

•Photoactive Yellow Protein (PYP)

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

H-bonds in PYP

Arg52, Tyr42, pCA, Glu46

(para-coumaric acid; chromophore of PYP)

LBHB

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

•Enhanced Green Fluorescent Pr (EGFP)

✓ Special geometry of D2O and Hydrogen-bonding network in EGFP (C. Shibazaki et al., *J. Phys. Chem. Lett.*, **11**, 492-496, 2020)

[1] T. Isono, H. Kamo, A. Ueda, K. Takahashi, A. Nakao, R. Kumai, H. Nakao, K. Kobayashi, Y. Murakami, Y. Mori, *Nat. Commun.* **2013**, *4*, 1344 [2] A. Ueda, S. Yamada, T. Isono, H. Kamo, A. Nakao, R. Kumai, H. Nakao, Y. Murakami, Y. 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).