CMD® Studies and Special Lecture:
Path Integral Simulations

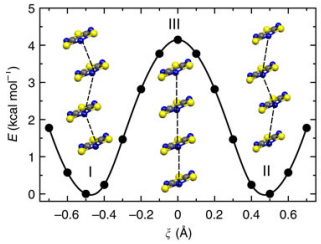
Motoyuki Shiga
(Japan Atomic Energy Agency)

CMD Workshop 2020
September 4, 2020, online

Self-Introduction:
Development and Applications of *Ab Initio* Simulations

Ab initio Molecular Dynamics
dynamics, thermodynamics

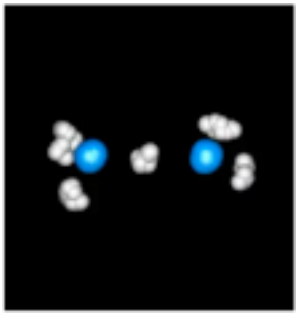
Nature Commun. 307, 393 (2014)



spin phase transition of TTTA

Path Integral Simulations
nuclear quantum effects

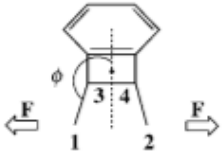
JCP. 115, 9149 (2001)
JACS 127, 11906 (2005)



protonated water clusters

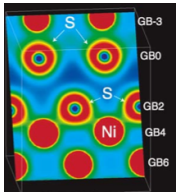
Electronic Structure Theory
molecular structures, electronic properties

Angew. Chem. 48, 4190 (2009)



mechanochemical ring opening reactions

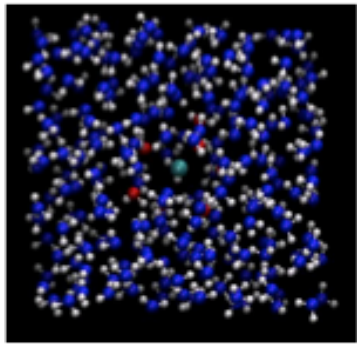
Science 307, 393 (2005)



grain boundary embrittlement of Ni

QM/MM
large molecules, condensed phases

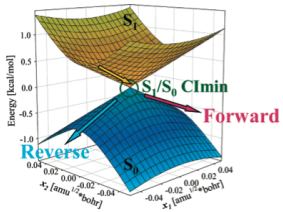
JCP 139, 033120 (2013)



aqueous solutions

Nonadiabatic Dynamics
photochemistry

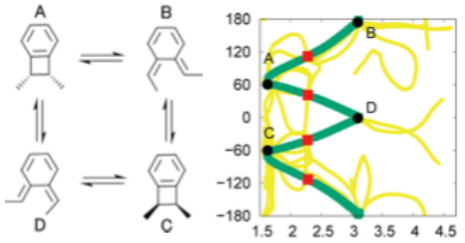
JACS 129, 6405 (2007)



ultrafast dynamics of phenol blue

Rare Event Sampling
chemical reactions

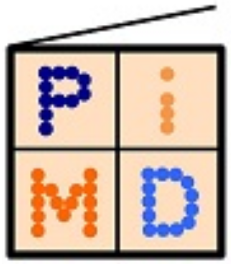
J. Phys. Chem. Lett. 9 6207 (2018)



reaction path search algorithem

Self-Introduction:
Software Development

PIMD - an open-source software for parallel molecular simulations



Language: MPI Fortran 90 (300,000 lines)

License: Apache 2.0 (for anyone, free of charge)

URL: https://ccse.jaea.go.jp/software/PIMD/index.en.html

Manual: https://ccse.jaea.go.jp/software/PIMD/doc/manual.pdf (235 pages)

Author: M. Shiga (JAEA)

Contributors:
K. Ishimura (IMS), Y. Kawashima (RIKEN),
H. Kimizuka (Osaka Univ.), **Y. Nagai (JAEA),** T. Morishita (AIST),
Y. Ota (RIST), S. Ruiz-Barragan (JAEA), **B. Thomsen (JAEA)**

Your contribution is also welcome!

Features of PIMD

Simulation methods

- **Statics:** Geometry optimization, phonon calculations
- **Reaction paths:** string method, steepest descent, gentlest ascent method
- **Classical mechanics:** molecular dynamics (MD), hybrid Monte Carlo
- **Classical statistics:** replica exchange method
- **Quantum statistics:** path integral MD
- **Semiclassical dynamics:** centroid and ring polymer MD
- **Nonadiabatic dynamics:** surface hopping, mean field dynamics
- **Free energies:** metadyamics, constrained MD, mean force dynamics

Statistical ensembles

- constant energy (*NVE*), constant temperature (*NVT*),
  constant pressure (*NPT*), constant stress (*N*t*T*)

Features of PIMD

Potentials

- **Ab initio quantum chemistry:** *SMASH (HF, B3LYP, MP2)*
- **Classical force fields:** *AMBER, CHARMM, OPLS, EAM*
- **Interface with other codes (ab initio):**

  CP2K, GAMESS, GAUSSIAN, MOLPRO, NTCHEM, ORCA,

  QUANTUM ESPRESSO, TURBOMOLE, VASP
- **Interface with other codes (semiempirical):** *DFTB+, MOPAC*
- **Multiscale methods:** *ONIOM, QM/MM*
- **Machine learning potentials:** *AENET*
- A subroutine intended for user-defined potentials.

Boundary conditions

- free boundary, periodic boundary (cubic cell, parallel-piped cell)

Features of PIMD

PHYSICAL REVIEW B **102**, 041124(R) (2020)

Rapid Communications

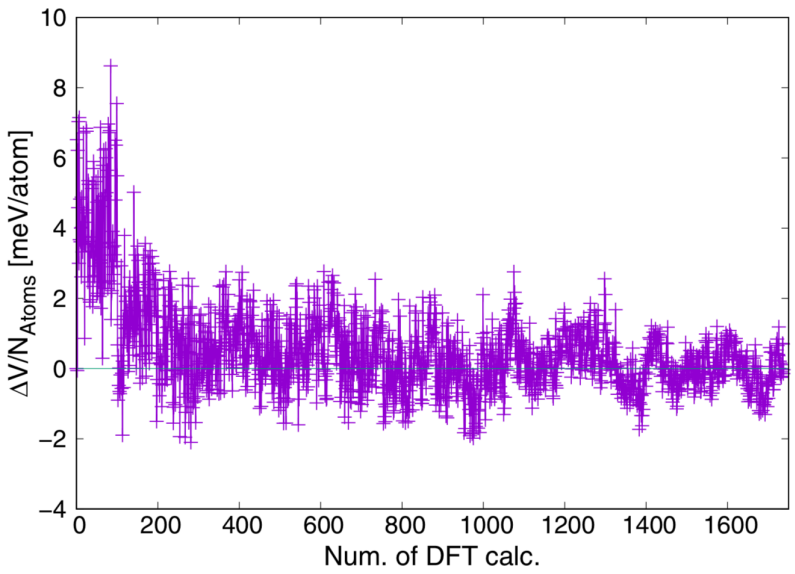
Self-learning hybrid Monte Carlo: A first-principles approach

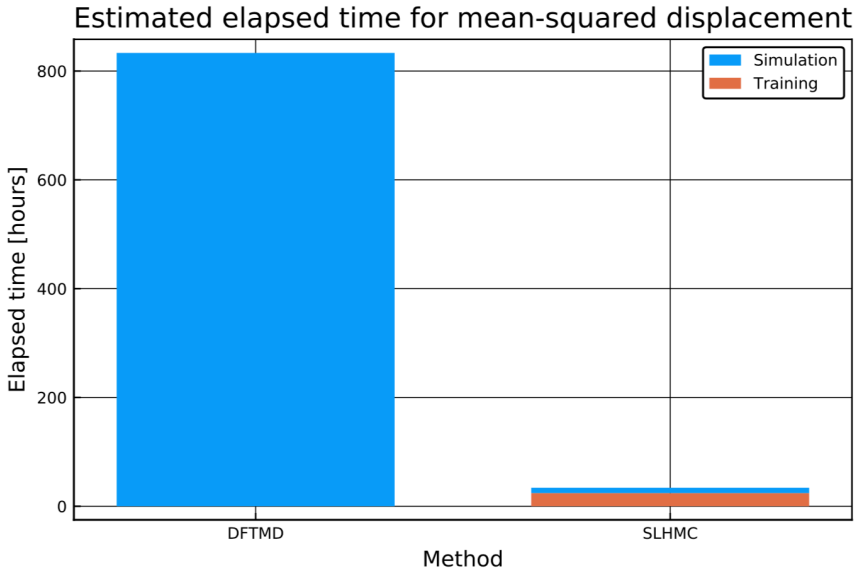
Yuki Nagai,[1,2,*] Masahiko Okumura,[1] Keita Kobayashi,[3] and Motoyuki Shiga[1,†]

[1]*CCSE, Japan Atomic Energy Agency, 178-4-4, Wakashiba, Kashiwa, Chiba, 277-0871, Japan*

[2]*Mathematical Science Team, RIKEN Center for Advanced Intelligence Project (AIP), 1-4-1 Nihonbashi, Chuo-ku, Tokyo 103-0027, Japan*

[3]*Research Organization for Information Science and Technology (RIST), 2-4, Shirakata, Tokai-mura, Ibaraki 319-1106, Japan*





Features of PIMD

THE JOURNAL OF PHYSICAL CHEMISTRY B

Article

Cite This: J. Phys. Chem. B 2019, 123, 1662−1671

pubs.acs.org/JPCB

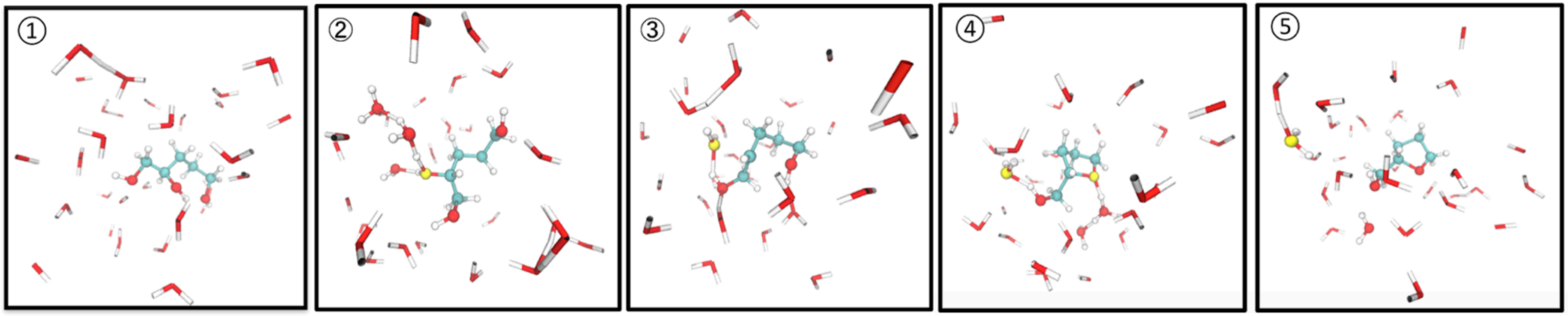
Understanding Competition of Polyalcohol Dehydration Reactions in Hot Water

Yong Lik Chang,[†] Takehiko Sasaki,[†] Jordi Ribas-Ariño,[‡] Masahiko Machida,[§] and Motoyuki Shiga*[,§]

[†]Department of Complexity Science and Engineering, Graduate School of Frontier Sciences, The University of Tokyo, 5-1-5, Kashiwanoha, Kashiwa 277-8561, Japan

[‡]Departament de Química-Física i CERQT, Universitat de Barcelona, Diagonal, 645, 08028 Barcelona, Spain

[§]Center for Computational Science and e-Systems, Japan Atomic Energy Agency, 178-4-4, Wakashiba, Kashiwa, Chiba 277-0871, Japan



Quantum Simulations

Quantum systems/phenomena	Methods
Electronic structures	First principles/ab initio methods
Quantum statistics, Semiclassical dynamics	Path integral simulations
Vibrational energy levels	Vibrational SCF
Nonadiabatic Dynamics	Surface hopping, mean field dynamics
Quantum wave packet dynamics	DVR method, MCTDH method
Ground state of strongly correlated systems	Variational/Diffusion Monte Carlo

Ab initio path integral simulations

Electronic structure calculations – Born-Oppenheimer approximation:

Schroedinger Eq. for electron-nucleus system with electrostatic interaction

$$H_{\mathbf{R}}(\hat{\mathbf{r}}, \hat{\mathbf{p}})\Psi_{\mathbf{R}}(\mathbf{r}) = E_{\mathbf{R}}\Psi_{\mathbf{R}}(\mathbf{r})$$

$\Psi_{\mathbf{R}}$: electronic ground state

$\mathbf{R}$: nuclei ... fixed

$\mathbf{r}, \mathbf{p}$: electrons

Ab initio molecular dynamics – classical trajectory:

$$M\ddot{\mathbf{R}} = -\nabla V(\mathbf{R}) \qquad \text{where} \qquad V(\mathbf{R}) = E_{\mathbf{R}}$$

Nuclear quantum effects (beyond AIMD):

$$H\left(\hat{\mathbf{R}}, \hat{\mathbf{P}}\right)\varphi_k(\mathbf{R}) = E_k\varphi_k(\mathbf{R}) \qquad \text{where} \qquad H\left(\hat{\mathbf{R}}, \hat{\mathbf{P}}\right) = \frac{\hat{\mathbf{P}}^2}{2M} + V\left(\hat{\mathbf{R}}\right)$$

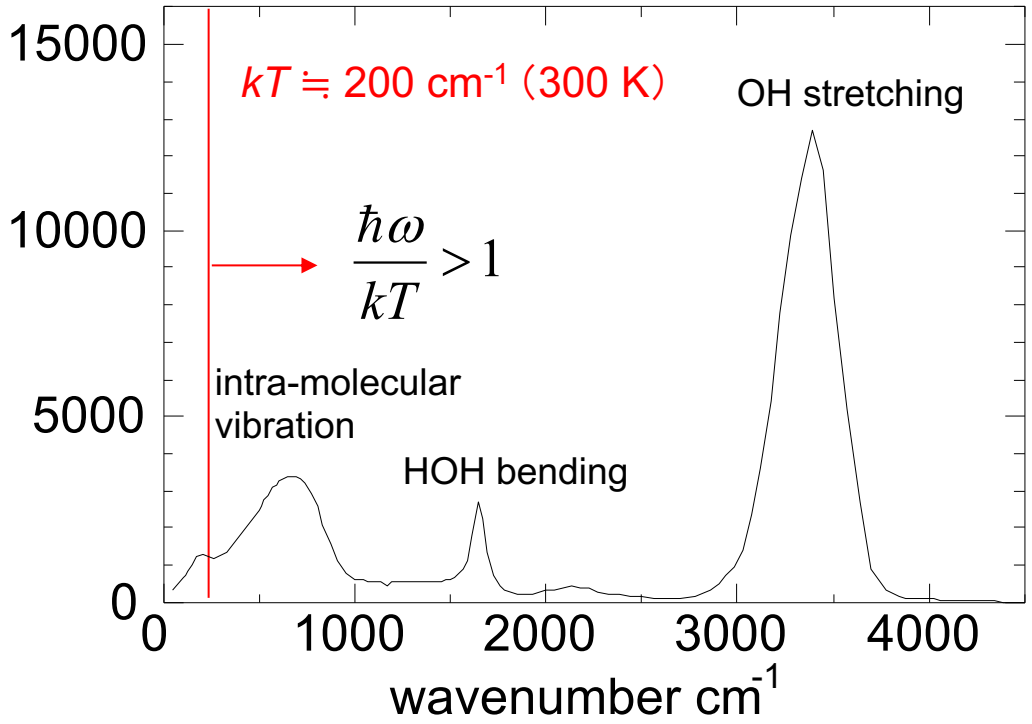
φ_k : rovibrational state

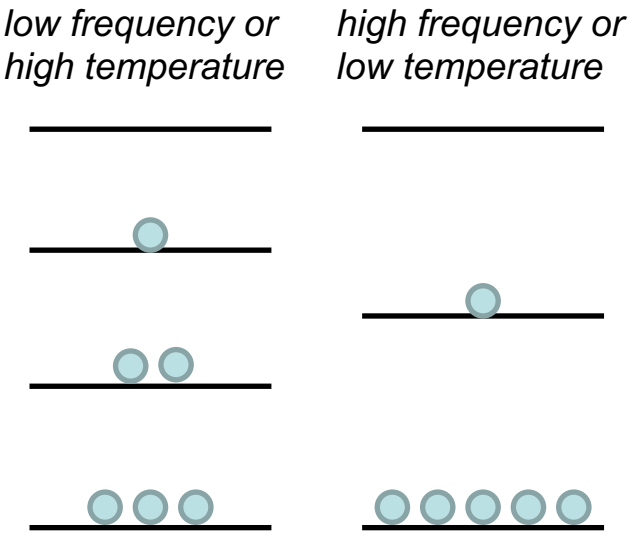
(However, NQE will be solved here in a different manner, via **path integrals**)

Nuclear Quantum Effects

Experiment Hale and Querry, *Appl. Opt.* **12**, 555 (1973).

IR absorption spectrum of water





Most vibrational modes have quantum nature

Nuclear Quantum Effects

Theory

Classical averages

$$\langle A \rangle = \frac{\int A(R) \exp(-\beta V) dR}{\int \exp(-\beta V) dR}$$

mass-independent

Quantum averages

$$\langle A \rangle = \frac{\mathrm{Tr}\left(\hat{A} \exp\left(-\beta \hat{H}\right)\right)}{\mathrm{Tr}\left(\exp\left(-\beta \hat{H}\right)\right)}$$

mass-dependent

Classical energy

$$\langle H \rangle = \frac{3N}{2\beta} + \langle V \rangle$$

(principle of equipartition)

mass-independent

Quantum energy

$$\langle H \rangle = \left\langle \frac{\hat{P}^2}{2M} \right\rangle + \langle \hat{V} \rangle$$

mass-dependent

Classical free energy

$$F_B - F_A = -\beta^{-1} \log \frac{\int \exp(-\beta V_B) dR}{\int \exp(-\beta V_A) dR}$$

mass-independent

Quantum free energy

$$F_B - F_A = -\beta^{-1} \log \frac{\mathrm{Tr}\left(\exp\left(-\beta \hat{H}_A\right)\right)}{\mathrm{Tr}\left(\exp\left(-\beta \hat{H}_B\right)\right)}$$

mass-dependent

Isotope effects on thermal properties are mainly from nuclear quantum effects

Review of Quantum Mechanics

Quantum mechanics: Variables are expressed as operators

Position $r \longrightarrow$ Position operator $\hat{r}$

Momentum $p \longrightarrow$ Momentum operator $\hat{p} = -i\hbar \dfrac{\partial}{\partial r}$

Hamiltonian operator $\hat{H} = \dfrac{\hat{p}^2}{2m} + V(\hat{r}) = -\dfrac{\hbar^2}{2m}\dfrac{\partial^2}{\partial r^2} + V(\hat{r})$

When *A* is a function of position

$$A(\hat{r})|r\rangle = A(r)|r\rangle$$

When *A* is a function of momentum

$$A(\hat{p})|p\rangle = A(p)|p\rangle$$

Review of Quantum Mechanics

Closure relation for orthonormal basis functions:

$$\sum_i \left|\phi_i\right\rangle\left\langle\phi_i\right| = 1$$

r-representation

$$\int \left|r\right\rangle\left\langle r\right| dr = 1$$

p-representation

$$\frac{1}{2\pi\hbar}\int \left|p\right\rangle\left\langle p\right| dp = 1$$

p-basis functions are plane waves

$$\left\langle p\middle| r\right\rangle = \exp\left(-\frac{ipr}{\hbar}\right), \qquad \left\langle r\middle| p\right\rangle = \exp\left(\frac{ipr}{\hbar}\right), \qquad \left\langle r\middle| r'\right\rangle = \delta\left(r-r'\right)$$

Review of Quantum Mechanics

Time-dependent Schrödinger equation

$$i\hbar\frac{\partial}{\partial t}\left|\Psi\right\rangle = \hat{H}\left|\Psi\right\rangle$$

The formal solution is

$$\left|\Psi(t)\right\rangle = \exp\left(-\frac{i\hat{H}t}{\hbar}\right)\left|\Psi(0)\right\rangle$$

Time evolution operator

The matrix element in *r*-representation

$$G(r,r';t) = \left\langle r'\right|\exp\left(-\frac{i\hat{H}t}{\hbar}\right)\left|r\right\rangle$$

“Propagator” or “Green function”

Review of Quantum Mechanics

The formal solution

$$\left|\Psi(t)\right\rangle = \exp\left(-\frac{i\hat{H}t}{\hbar}\right)\left|\Psi(0)\right\rangle$$

Using the closure relation

$$\left\langle r'\middle|\Psi(t)\right\rangle = \int \left\langle r'\middle|\exp\left(-\frac{i\hat{H}t}{\hbar}\right)\middle| r\right\rangle \left\langle r\middle|\Psi(0)\right\rangle dr$$

Therefore

$$\Psi(r',t) = \int G(r,r';t)\Psi(r,0)dr$$

G has the full information: Ψ is obtained as a time-space function

G(*r”*,*r’*;*t*) is equal to Ψ(*r’*,*t*) when Ψ(*r*,*0*) = δ(*r*-*r”*)

Path Integral Theory

For a Hamiltonian operator of single particle

$$\hat{H} = \hat{T} + \hat{V} = \frac{\hat{p}^2}{2m} + V(\hat{r})$$

The propagator can be expressed as (Feynman, 1965)

$$G(r', r; t) = \lim_{P \to \infty} \left(\frac{m}{2\pi i \hbar \Delta t} \right)^{\frac{P}{2}} \int dr_2 \int dr_3 \ldots \int dr_P \exp(iS[r]/\hbar)$$

where we defined

$$\Delta t = \frac{t}{P}, \quad r_1 = r, \quad r_{P+1} = r'$$

and the action

$$S[r] = \sum_{s=1}^{P} \left[\frac{m}{2} \left(\frac{r_{s+1} - r_s}{\Delta t} \right)^2 - \frac{V(r_s) + V(r_{s+1})}{2} \right] \Delta t$$

Path Integral Theory

$$G(r,r';t)=\langle r'|\exp\left(-\frac{i\hat{H}t}{\hbar}\right)|r\rangle$$

$$\exp\left(-\frac{i\hat{H}t}{\hbar}\right)=\left(\exp\left(-\frac{i\hat{H}\Delta t}{\hbar}\right)\right)^{P}=\exp\left(-\frac{i\hat{H}\Delta t}{\hbar}\right)\times\cdots\times\exp\left(-\frac{i\hat{H}\Delta t}{\hbar}\right)$$

$$G(r,r';t)=\lim_{P\to\infty}\langle r'|\exp\left(-\frac{i\hat{H}\Delta t}{\hbar}\right)^{P}|r\rangle \qquad \Delta t=\frac{t}{P}$$

$$\int|r\rangle\langle r|dr=1$$

$$G(r,r';t)=\lim_{P\to\infty}\int dr_2\int dr_3\ldots\int dr_P\,\langle r'|\exp\left(-\frac{i\hat{H}\Delta t}{\hbar}\right)|r_P\rangle\times\langle r_P|\exp\left(-\frac{i\hat{H}\Delta t}{\hbar}\right)|r_{P-1}\rangle\times\cdots\times\langle r_2|\exp\left(-\frac{i\hat{H}\Delta t}{\hbar}\right)|r\rangle$$

Path Integral Theory

$$G(r,r';\Delta t)=\langle r'|\exp\left(-\frac{i\hat{H}\Delta t}{\hbar}\right)|r\rangle \approx \langle r'|\exp\left(-\frac{i\hat{V}\Delta t}{\hbar}\right)\exp\left(-\frac{i\hat{T}\Delta t}{\hbar}\right)\exp\left(-\frac{i\hat{V}\Delta t}{\hbar}\right)|r\rangle$$

$$=\left(\frac{1}{2\pi\hbar}\right)\int dp\,\langle r'|\exp\left(-\frac{i\hat{V}\Delta t}{2\hbar}\right)|p\rangle\langle p|\exp\left(-\frac{i\hat{T}\Delta t}{\hbar}\right)\exp\left(-\frac{i\hat{V}\Delta t}{2\hbar}\right)|r\rangle$$

$$1=\left(\frac{1}{2\pi\hbar}\right)\int dp\,|p\rangle\langle p|$$

$$=\left(\frac{1}{2\pi\hbar}\right)\int dp\,\exp\left(-\frac{iV(r')\Delta t}{2\hbar}\right)\langle r'|p\rangle\exp\left(-\frac{i\Delta t}{\hbar}\left(\frac{p^2}{2m}\right)\right)\langle p|r\rangle\exp\left(-\frac{iV(r)\Delta t}{2\hbar}\right)$$

$$\langle r|p\rangle=\exp\left(\frac{ipr}{\hbar}\right)$$

$$\langle p|r\rangle=\exp\left(-\frac{ipr}{\hbar}\right)$$

$$=\left(\frac{1}{2\pi\hbar}\right)\exp\left(-\frac{i(V(r')+V(r))\Delta t}{2\hbar}\right)\int dp\,\exp\left(-\frac{i\Delta t}{\hbar}\left(\frac{p^2}{2m}\right)\right)\exp\left(-\frac{i}{\hbar}p(r'-r)\right)$$

$$=\left(\frac{m}{2\pi\hbar i\Delta t}\right)^{\frac{1}{2}}\exp\left(-\frac{i}{\hbar}\left(\frac{m}{2}\left(\frac{r'-r}{\Delta t}\right)^2-\frac{V(r')+V(r)}{2}\right)\Delta t\right)$$

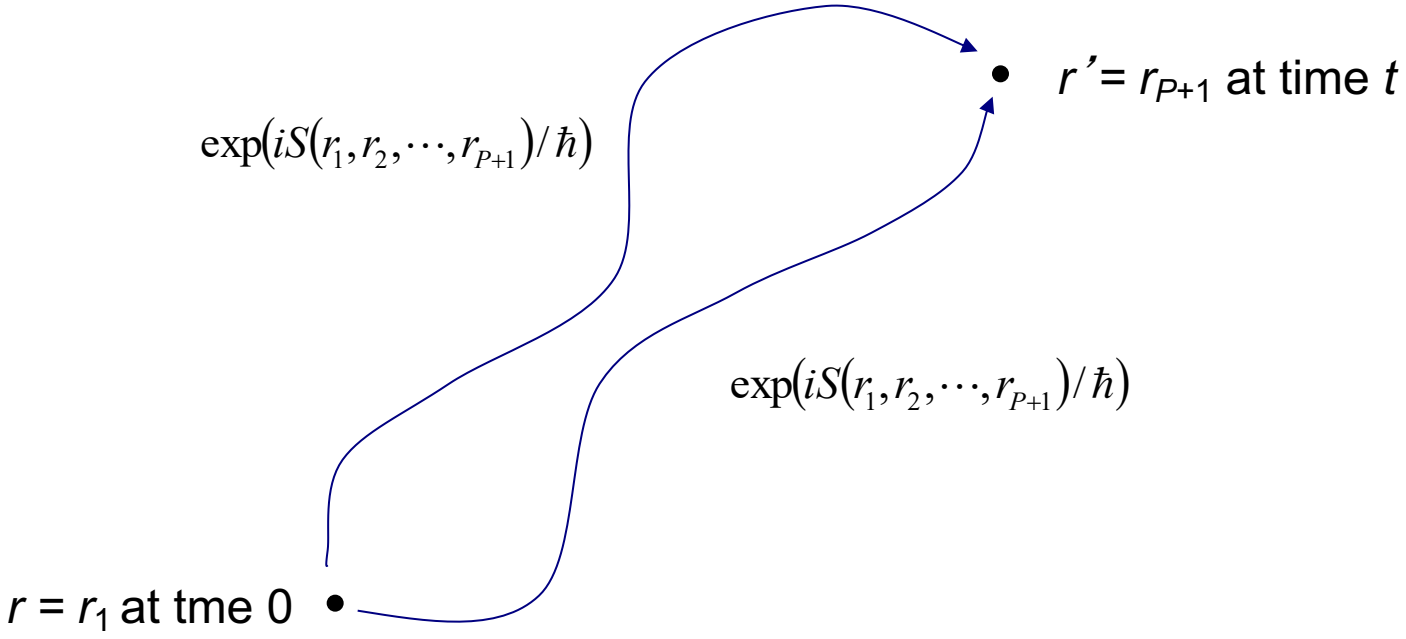
$$=\left(\frac{m}{2\pi\hbar i\Delta t}\right)^{\frac{1}{2}}\exp\left(-\frac{i}{\hbar}\times Lagrangian\times\Delta t\right)$$

2nd order Trotter expansion

Path Integral Theory

$$G(r,r';t) \propto \lim_{P\to\infty} \int dr_2 \int dr_3 \ldots \int dr_P \exp\left(iS(r_1,r_2,\cdots,r_{P+1})/\hbar\right)$$

Sum of all possible paths



Imaginary Time Path Integral Theory

Quantum Statistical Mechanics

For Canonical Ensemble

Partition function

$$Z = \mathrm{Tr}\,\exp\left(-\beta\hat{H}\right)$$
$$= \int \left\langle r\left|\exp\left(-\beta\hat{H}\right)\right|r\right\rangle dr$$
$$= \int G\left(r,r;\text{-}i\beta\hbar\right)dr$$

$$t \rightarrow \text{-}i\beta\hbar$$

Statistical Average

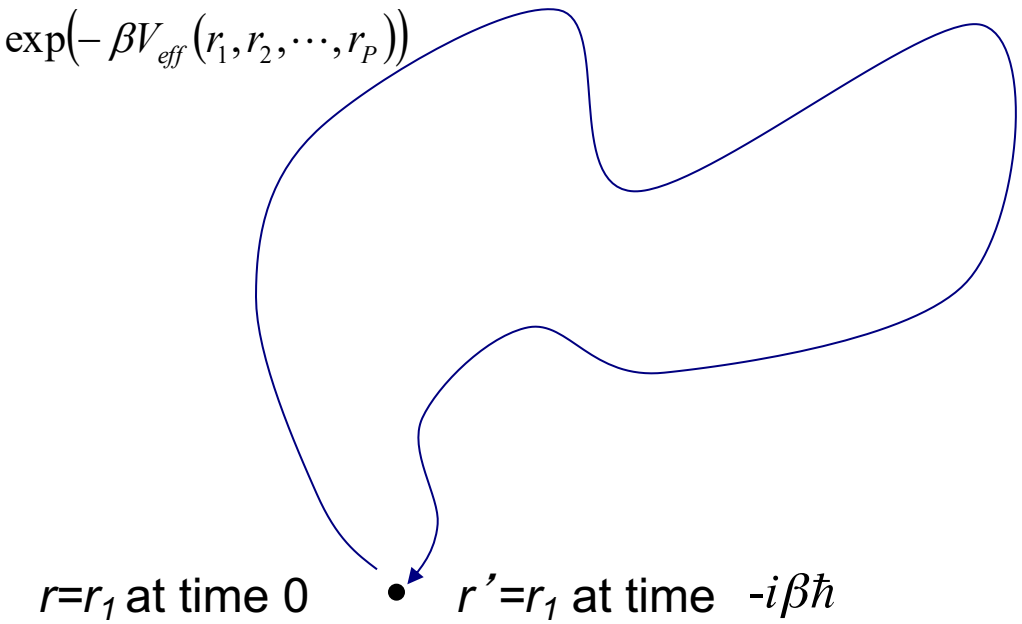
$$\left\langle A\left(\hat{r}\right)\right\rangle = Z^{-1}\mathrm{Tr}\; A\left(\hat{r}\right)\exp\left(-\beta\hat{H}\right)$$
$$= Z^{-1}\int \left\langle r\left|A\left(\hat{r}\right)\exp\left(-\beta\hat{H}\right)\right|r\right\rangle dr$$
$$= Z^{-1}\int A\left(r\right)\left\langle r\left|\exp\left(-\beta\hat{H}\right)\right|r\right\rangle dr$$
$$= Z^{-1}\int A\left(r\right)G\left(r,r;\text{-}i\beta\hbar\right)dr$$

Propagator in imaginary time $G\left(r,r;\text{-}i\beta\hbar\right) = \left\langle r\left|\exp\left(-\beta\hat{H}\right)\right|r\right\rangle$

Imaginary Time Path Integral Theory

$$G\left(r,r';-i\beta\hbar\right) \propto \lim_{P\to\infty} \int dr_2 \int dr_3 \ldots \int dr_P \exp\left(-\beta V_{eff}\left(r_1,r_2,\cdots,r_P\right)\right)$$

Sum of all possible paths

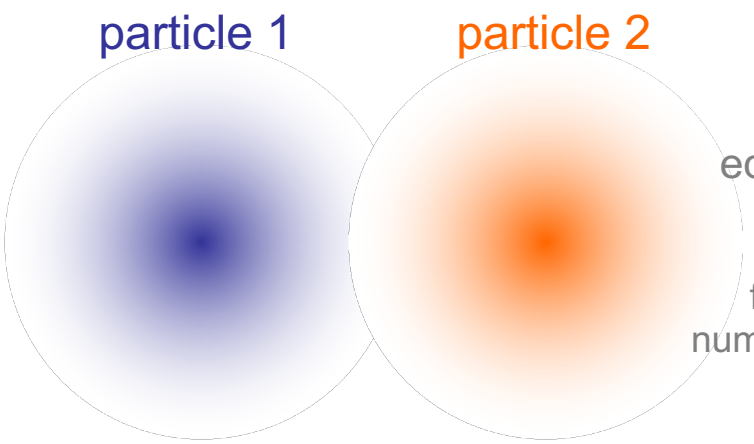


Path Integral Simulations

Imaginary time path integral theory - quantum statistical mechanics

Application to molecular systems: Chandler, Wolynes, *J. Chem. Phys.* **74**, 4078 (1981).

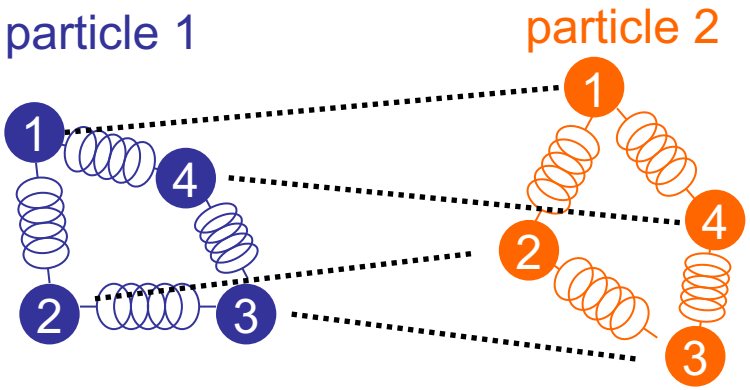
Density of two particles (nuclei)



equivalent

for infinite number of beads

"Ring polymer connected by beads"



Uncertainty principle: spread of polymer

Path integral molecular dynamics: MD sampling using forces on each bead

Ab initio PIMD uses Born-Oppenheimer forces: Quantum many electron-nuclei systems

Marx, Parrinello, *J. Chem. Phys.* **104**, 4077, (1996). **CPMD**

Shiga, Tachikawa, Miura, *J. Chem. Phys.* **115**, 9149 (2001) **BOMD**

Shiga, "Path Integral Simulations", *Reference Module in Chemistry, Elsevier* (2018).

Path Integral Simulations

Partition function of single-particle system

$$Z = \mathrm{Tr}\exp\left(-\beta\hat{H}\right) \quad \text{where} \quad \hat{H} = \hat{T} + \hat{V} = \frac{\hat{p}^2}{2M} + V(\hat{r})$$

The path integral representation

$$Z = \lim_{P\to\infty}\left(\frac{MP}{2\pi\beta\hbar^2}\right)^{\frac{P}{2}} \int dR_1 \int dR_2 \ldots \int dR_P \exp\left(-\beta\left(\sum_{s=1}^{P}\frac{M}{2}\omega_P^2\left(R_s - R_{s-1}\right)^2 + \frac{1}{P}\sum_{s=1}^{P}V(R_s)\right)\right) \quad \text{with} \quad \omega_P \equiv \frac{\sqrt{P}}{\hbar\beta}$$

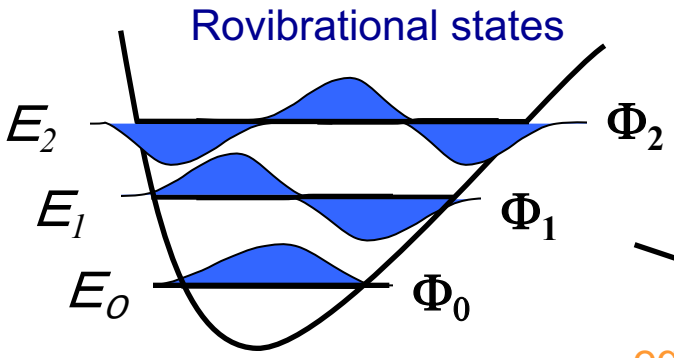
is isomorph to classical partition function of interacting *P*-particle system (ring polymer)

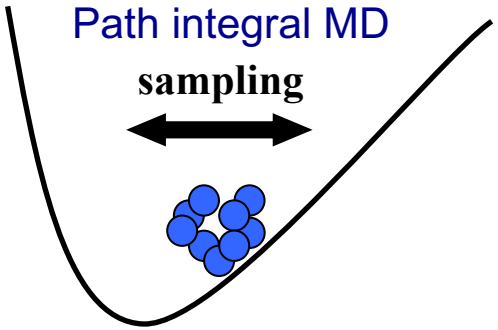
$$Q = N\int dR_1 \int dR_2 \ldots \int dR_P \exp\left(-\beta V_{eff}\left(R_1, \cdots, R_P\right)\right)$$

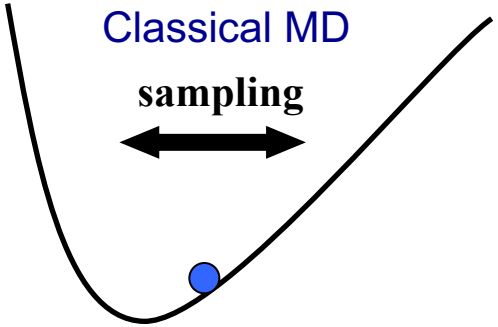
where the effective potential is $V_{eff}\left(R_1, \cdots, R_P\right) = \sum_{s=1}^{P}\frac{M}{2}\omega_P^2\left(R_s - R_{s-1}\right)^2 + \frac{1}{P}\sum_{s=1}^{P}V(R_s)$

Classical MD of *NP* particle system effective potential V_{eff}
→ Classical statistics of *NP* particle system
→ Quantum statistics of *N* particle system

Path Integral vs Wavefunction Calculations





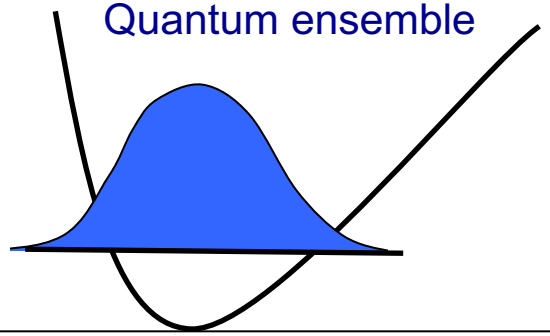


equivalent !

Distribution $\rho(x) = Z^{-1} \sum_i \left|\Phi_i(x)\right|^2 \exp(-\beta E_i)$

Energy $\langle H \rangle = Z^{-1} \sum_i E_i \exp(-\beta E_i)$

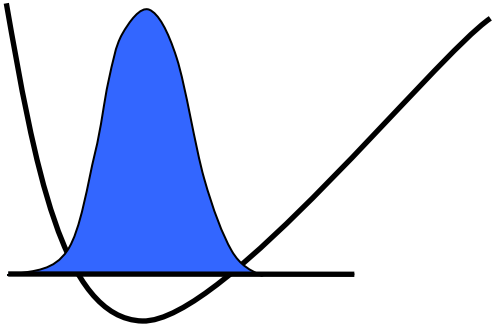
Quantum ensemble



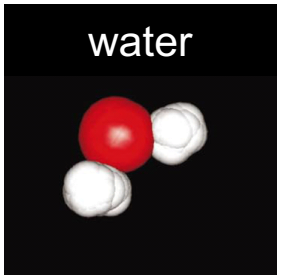
Distribution $\rho(x) = Z^{-1}\mathrm{Tr}\left[\exp(-\beta H)\ \delta(r-x)\right]$

Energy $\langle H \rangle = Z^{-1}\mathrm{Tr}\left[\exp(-\beta H) H\right]$

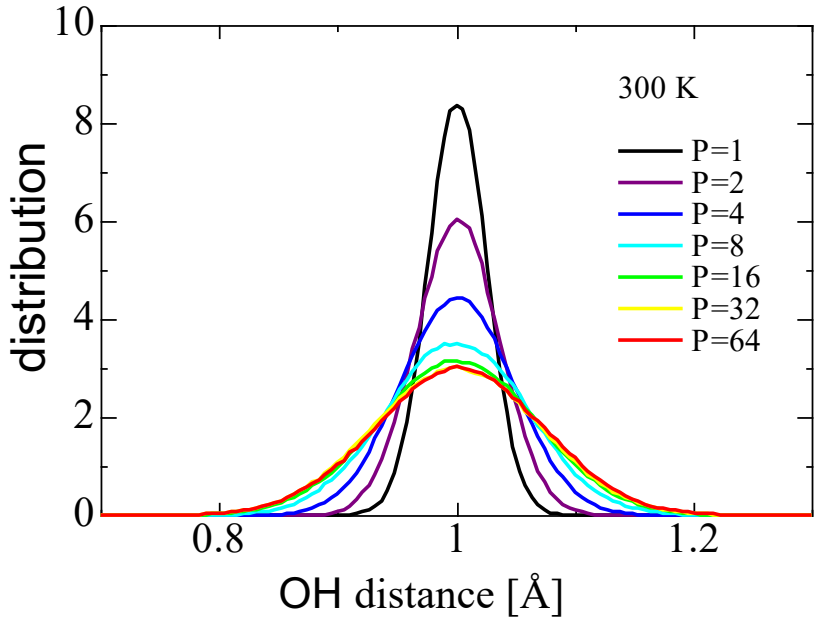
Classical ensemble

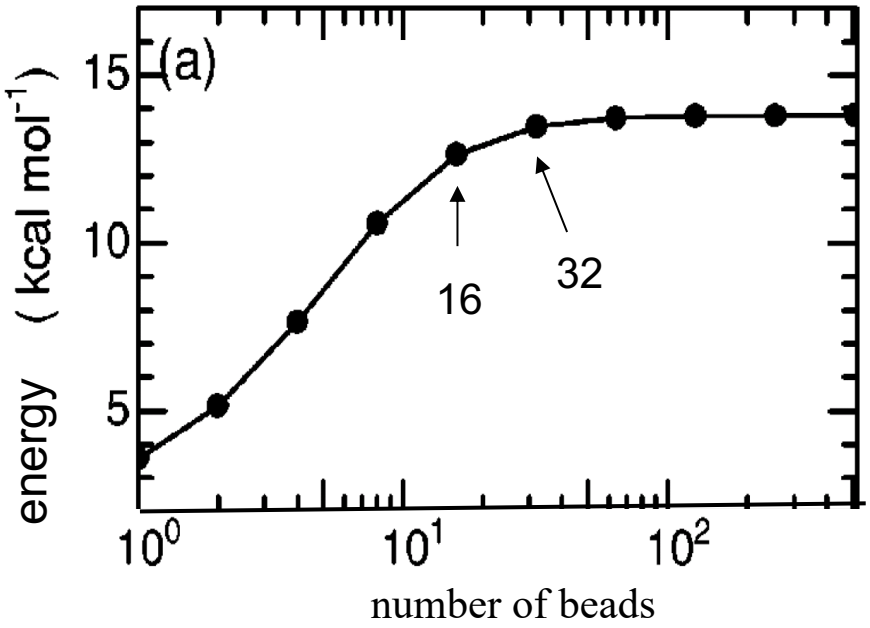


Bead Convergence



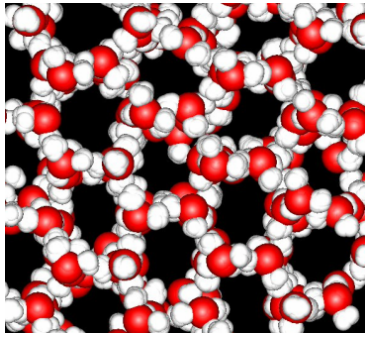
- Inversely proportional to temperature
- Proportional to the highest frequency in the system
- Independent of system size
- 16-32 beads at the ambient temperature for water



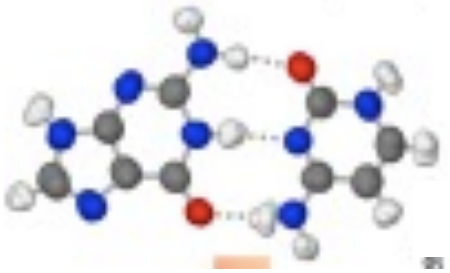


Shinoda, Shiga, *Phys. Rev. E* **71**, 041204 (2005).

Applications of Path Integral Simulations

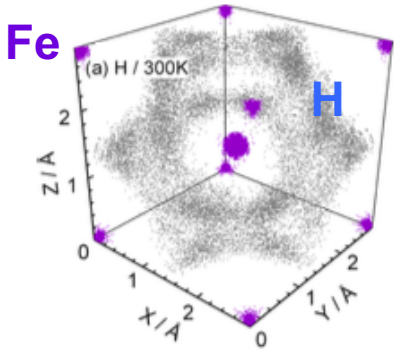


Water & Ice
PRE **71**, 041204 (2005).

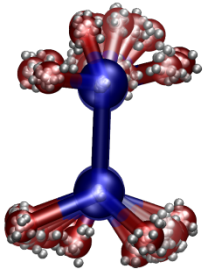


Guanine-Cytosine

H-bonds in biomoleules
CPL **625**, 174 (2015).



Hydrogen in metals
JPCC **116**, 23113 (2012).

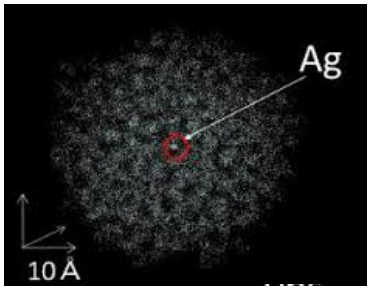


N_2H_4

Floppy molecules
JPCA **113**, 1985 (2009).

NH_4^+ BeH_2

Dihydrogen bonds
JCP **125**, 204310 (2006).



Ag^+ in He

Helium droplet
PCCP **19**, 13798 (2017).

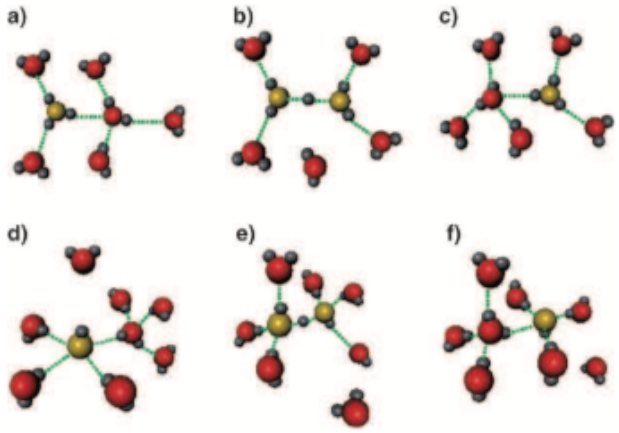
Proton Transfer in Water

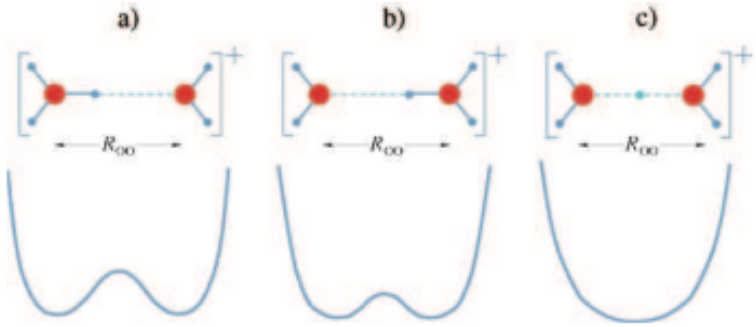
DOI: 10.1002/cphc.200600128

Proton Transfer 200 Years after von Grotthuss: Insights from Ab Initio Simulations**

Dominik Marx*[a]

In the last decade, ab initio simulations and especially Car–Parrinello molecular dynamics have significantly contributed to the improvement of our understanding of both the physical and chemical properties of water, ice, and hydrogen-bonded systems in general. At the heart of this family of in silico techniques lies the crucial idea of computing the many-body interactions by solving the electronic structure problem "on the fly" as the simulation proceeds, which circumvents the need for pre-parameterized potential models. In particular, the field of proton transfer in hydrogen-bonded networks greatly benefits from these technical advances. Here, several systems of seemingly quite different nature and of increasing complexity, such as Grotthuss diffusion in water, excited-state proton-transfer in solution, phase transitions in ice, and protonated water networks in the membrane protein bacteriorhodopsin, are discussed in the realms of a unifying viewpoint.



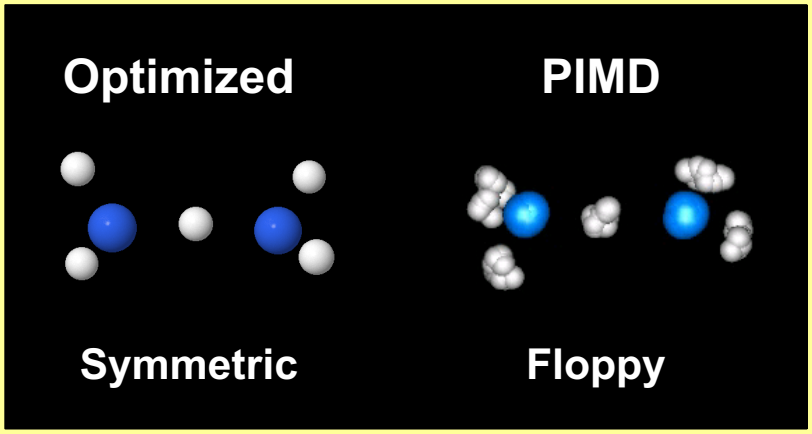


Marx, *ChemPhysChem,* **7**, 1848 (2006)

Nature of Protons in Water Clusters

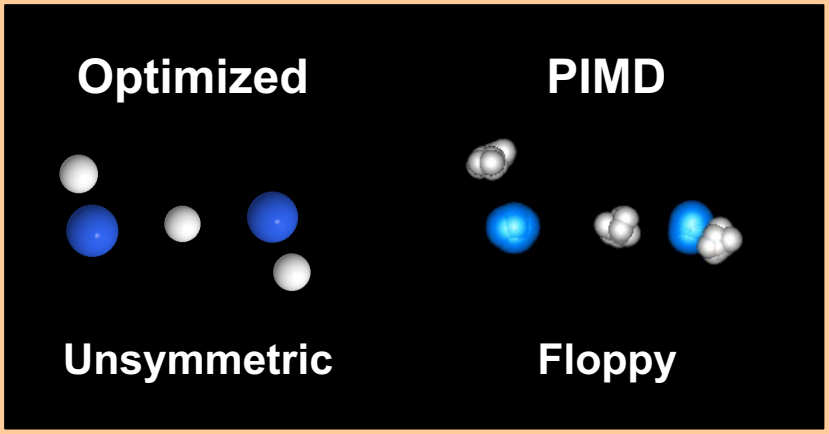
$H_5O_2^+$

Protonated water dimer



$H_3O_2^-$

Deprotonated water dimer



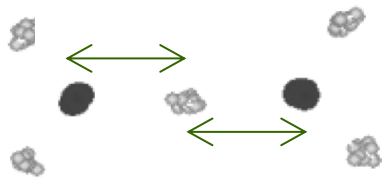
No fixed shape due to large quantum fluctuations
(zero-point vibrations / tunnel effects)

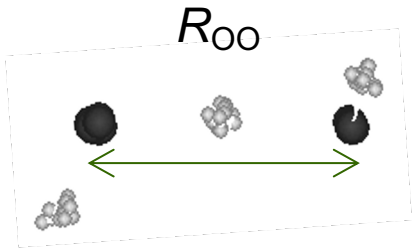
Tachikawa, Shiga, *J. Amer. Chem. Soc.* **127**, 11908 (2005).
Suzuki, Tachikawa, Shiga, *J. Chem. Phys.* **138**, 184307 (2013).

Nature of Protons in Water Clusters

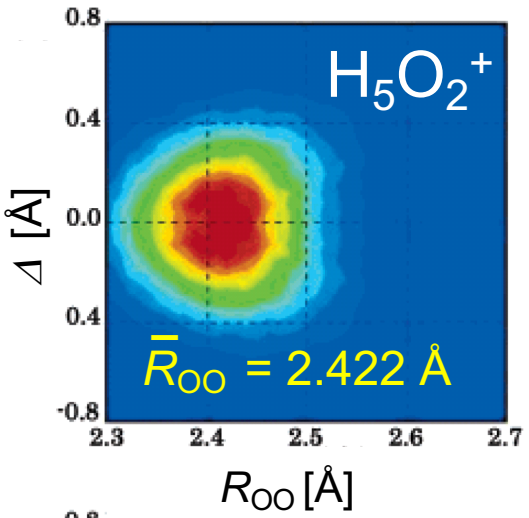
2D distributions R_{OO}, Δ

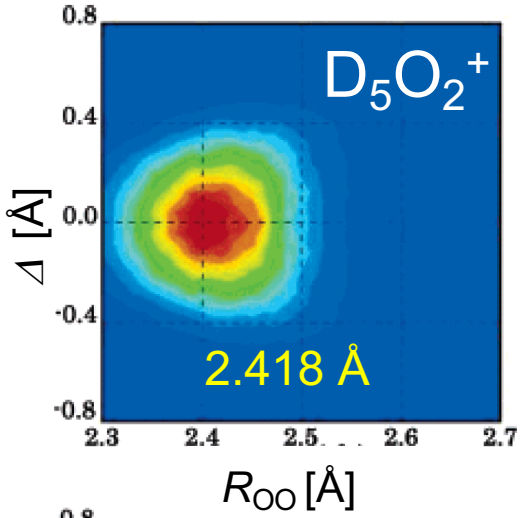
$\Delta = R_{OH^*} - R_{H^*O}$

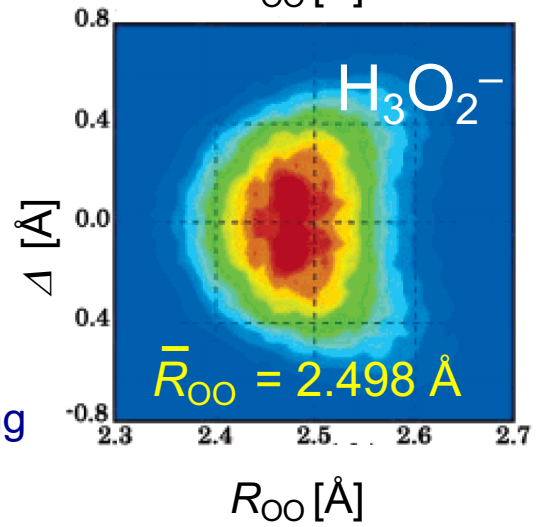


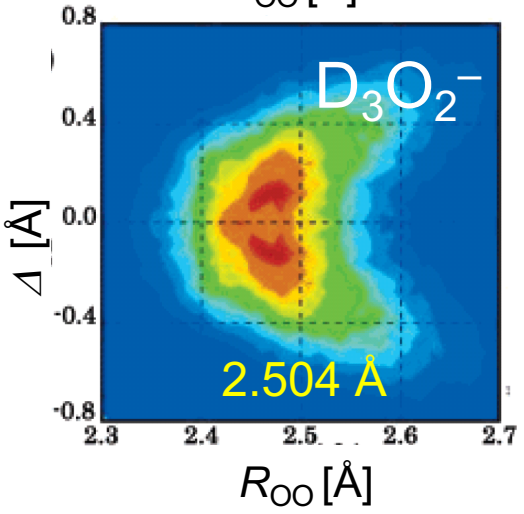


Geometric isotope effects:
Competing effects of
zero-point vibration and tunneling



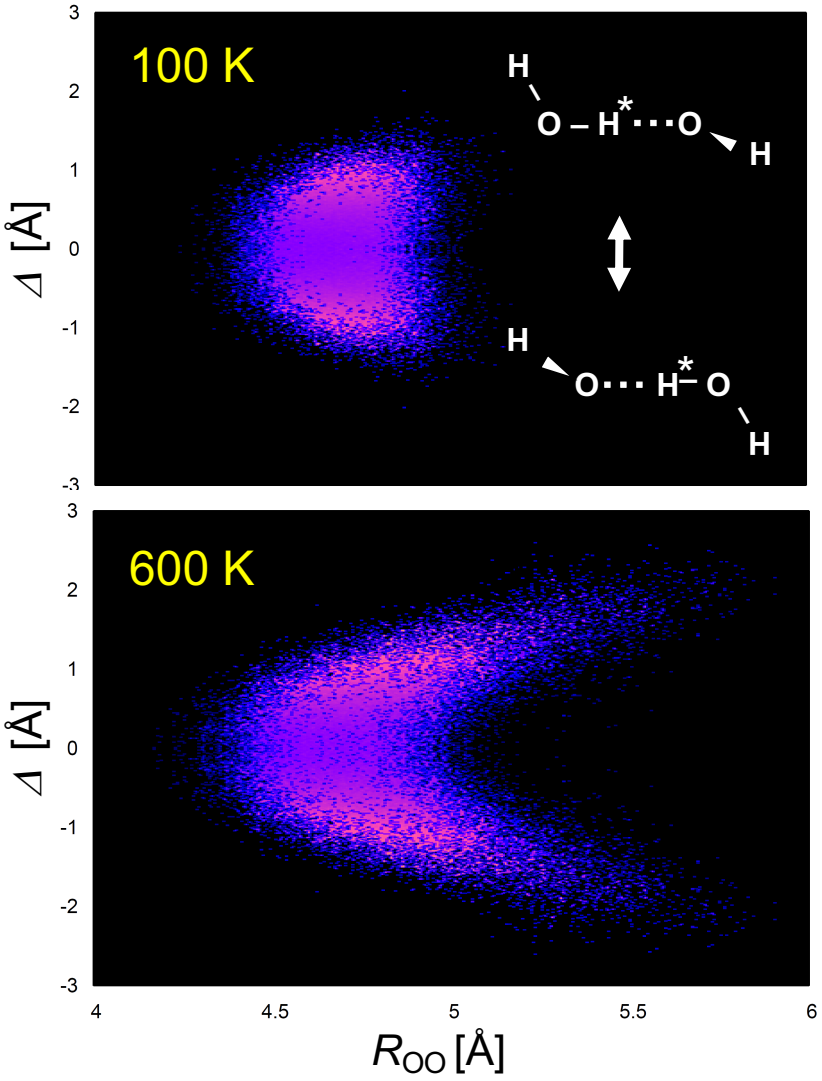


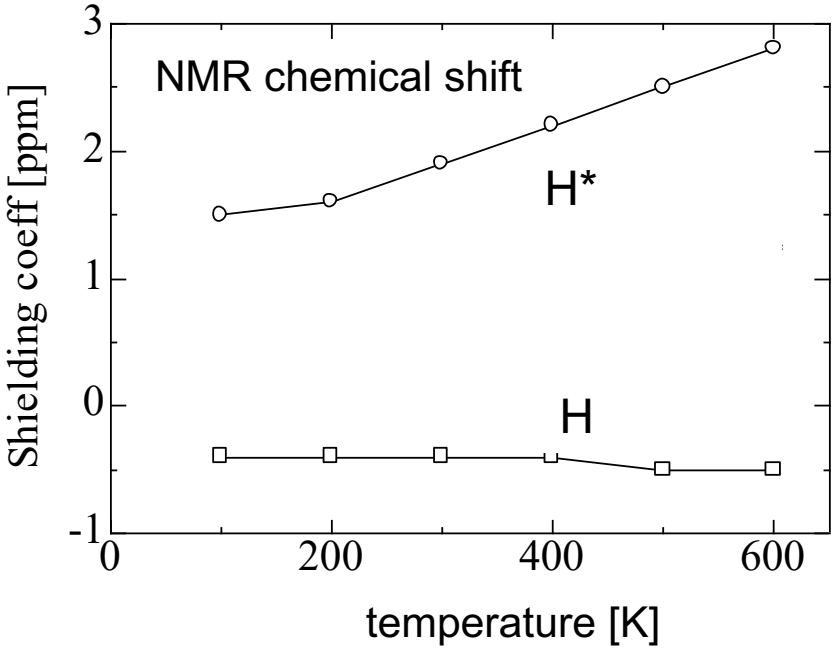




Tachikawa, Shiga, *J. Amer. Chem. Soc.* **127**, 11908 (2005).

Nature of Protons in Water Clusters



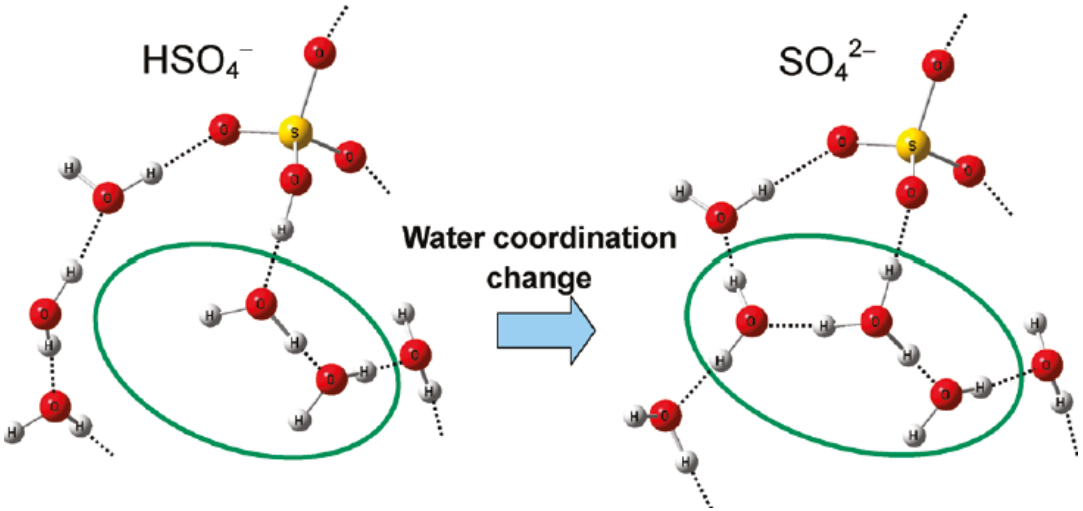


Proton distribution
→electrons on protons
→chemical shift

Shiga, Suzuki, Tachikawa,
J. Chem. Phys. **132**, 114104 (2010).

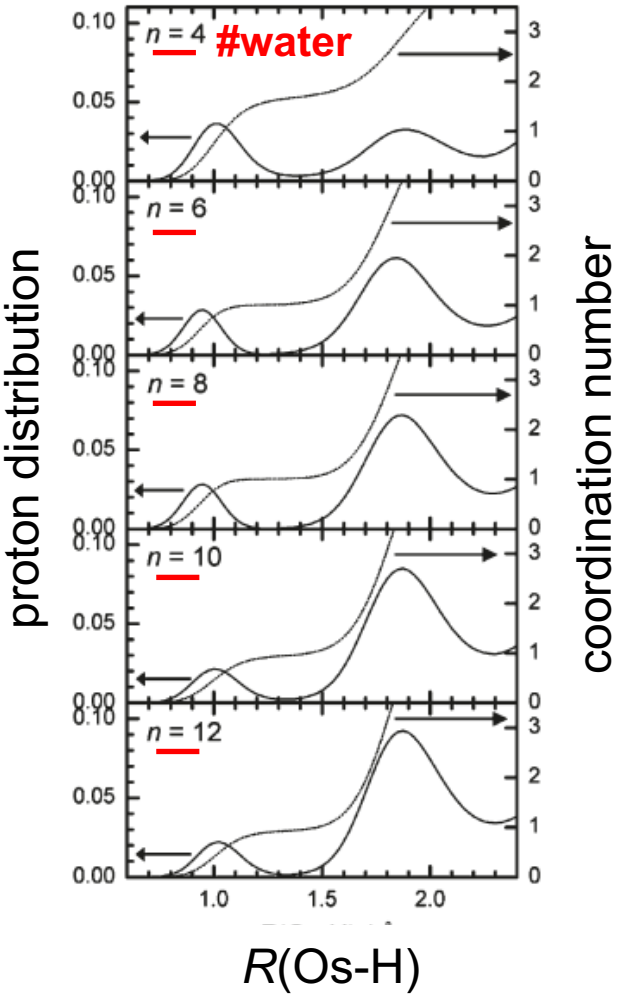
Nature of Protons in Water Clusters

sulfuric acid clusters



existence ratio

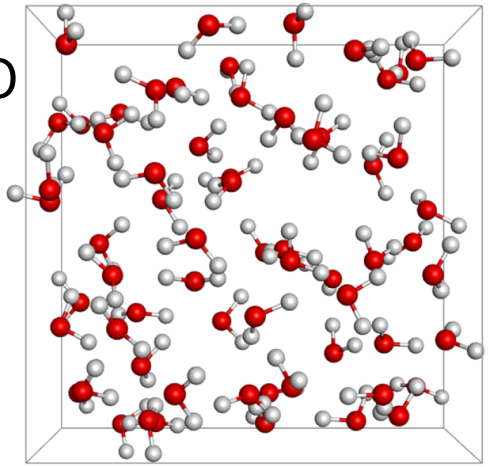
n #water	H_2SO_4	HSO_4^-	SO_4^{2-}
4	0.62	0.38	0.00
6	0.01	0.99	0.00
8	0.00	1.00	0.00
10	0.00	0.92	0.08
12	0.00	0.91	0.09

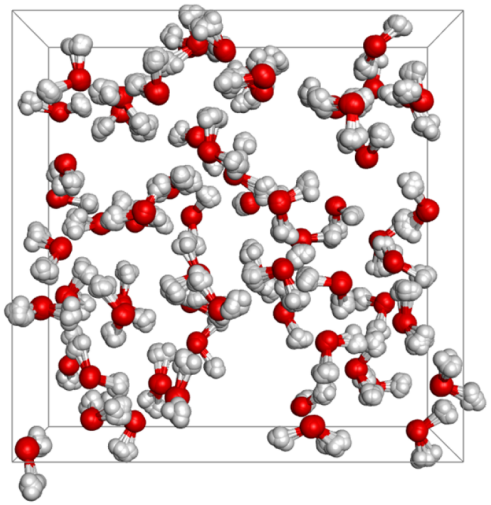


Sugawara, Yoshikawa, Takayanagi, Shiga, Tachikawa. *J. Phys. Chem. B.* **115**, 11486 (2009).

Liquid water at ambient condition

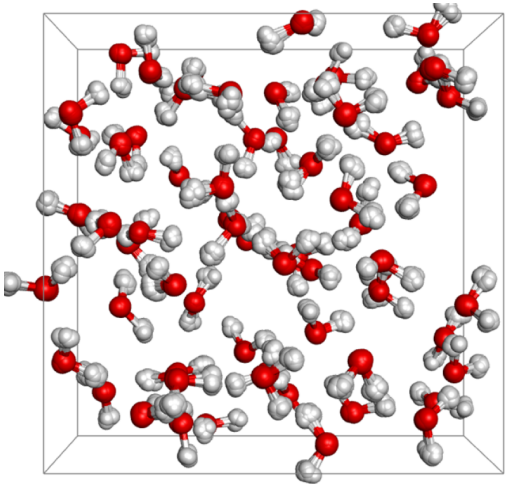
$H_2O/D_2O/T_2O$
(古典論)

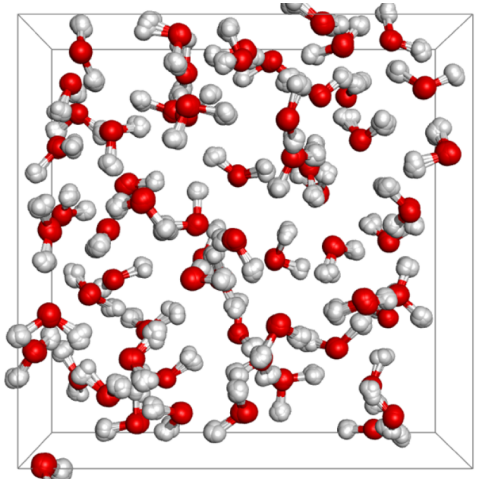




H_2O
(量子論)

D_2O
(量子論)



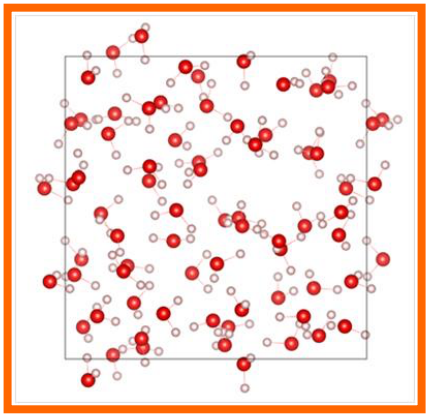


T_2O
(量子論)

Machida, Kato, Shiga, *J. Chem. Phys.* **148**, 102324 (2018).

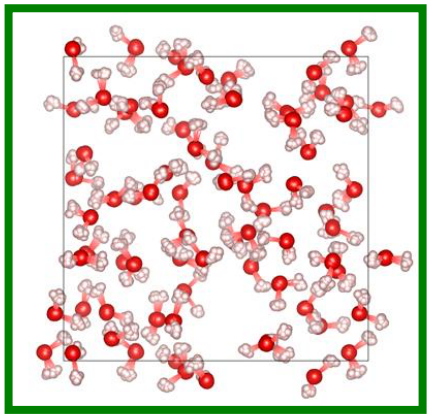
Liquid water at ambient condition

First-principles BOMD [BLYP-D2 functional, PAW, $(H_2O)_{64}$, periodic boundary]

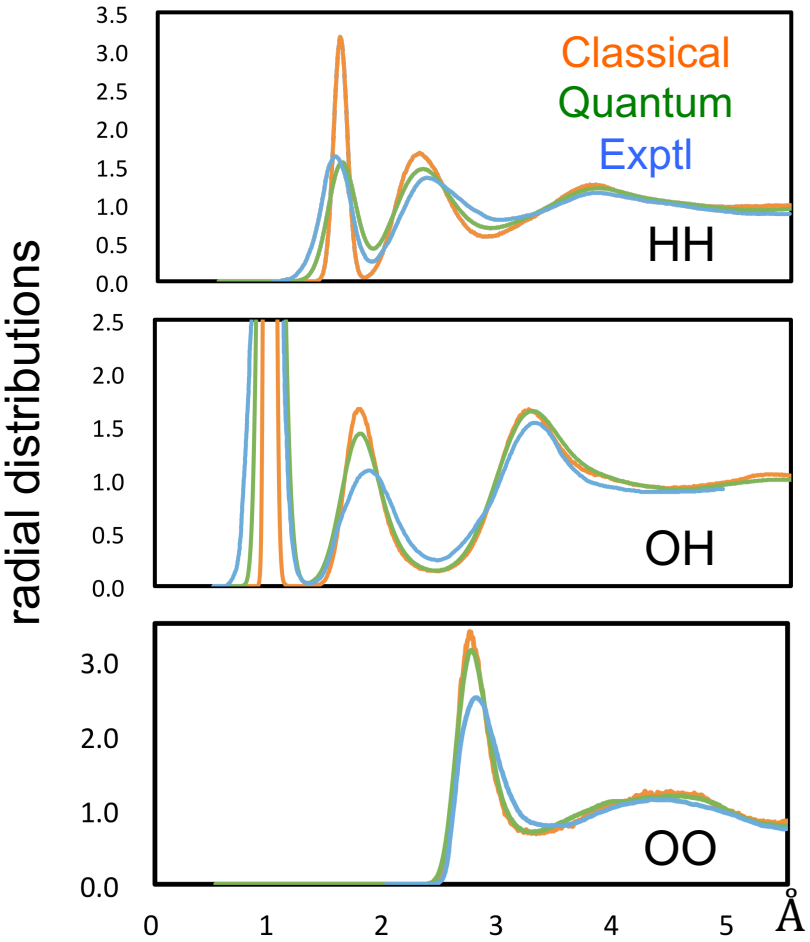


classical MD H_2O

sampling
15 ps



quantum PIMD H_2O



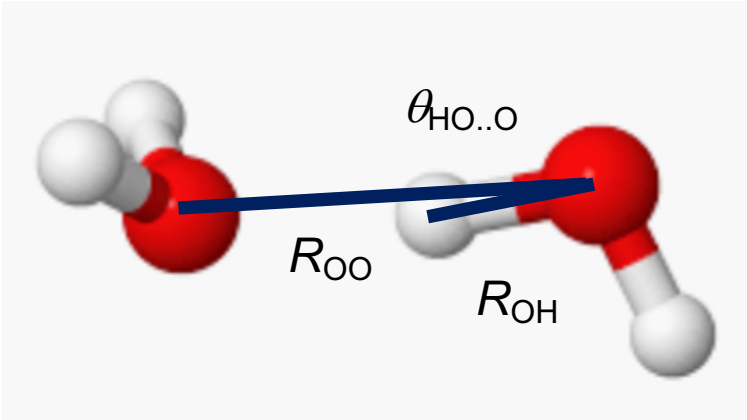
Machida, Kato, Shiga, *J. Chem. Phys.* **148**, 102324 (2018).

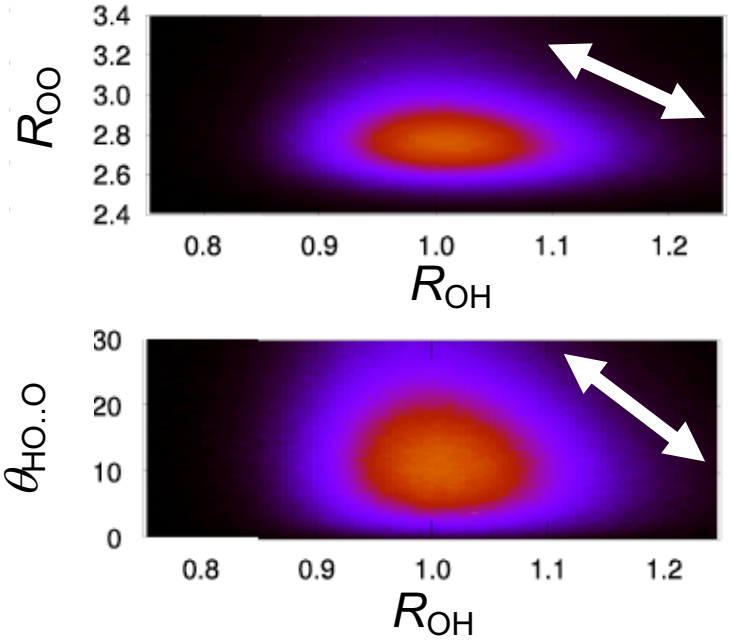
Liquid water at ambient condition

Evaporation energy [kcal/mol]	H_2O	D_2O	T_2O
Classical MD	11.9	11.9	11.9
Quantum PIMD	11.2	11.5	11.8
Exptl	10.0	10.4	

cf. D_2O m.p. 3.82 °C, b.p. 101.43 °C

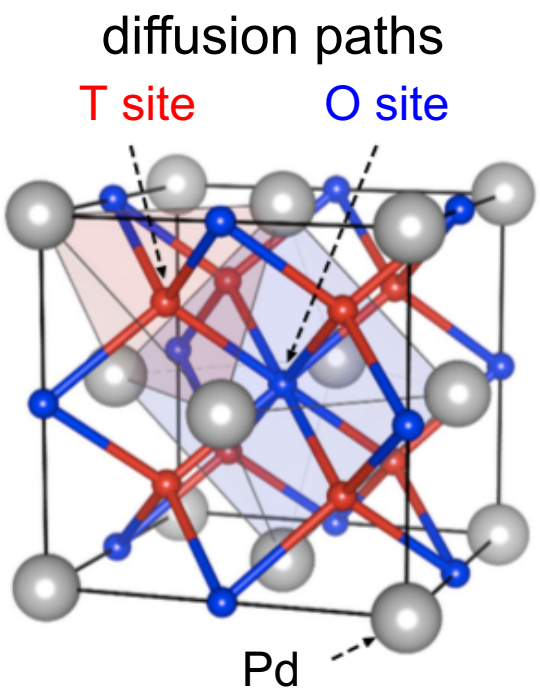
H-bond parameter correlations:
Effects of H-bonding



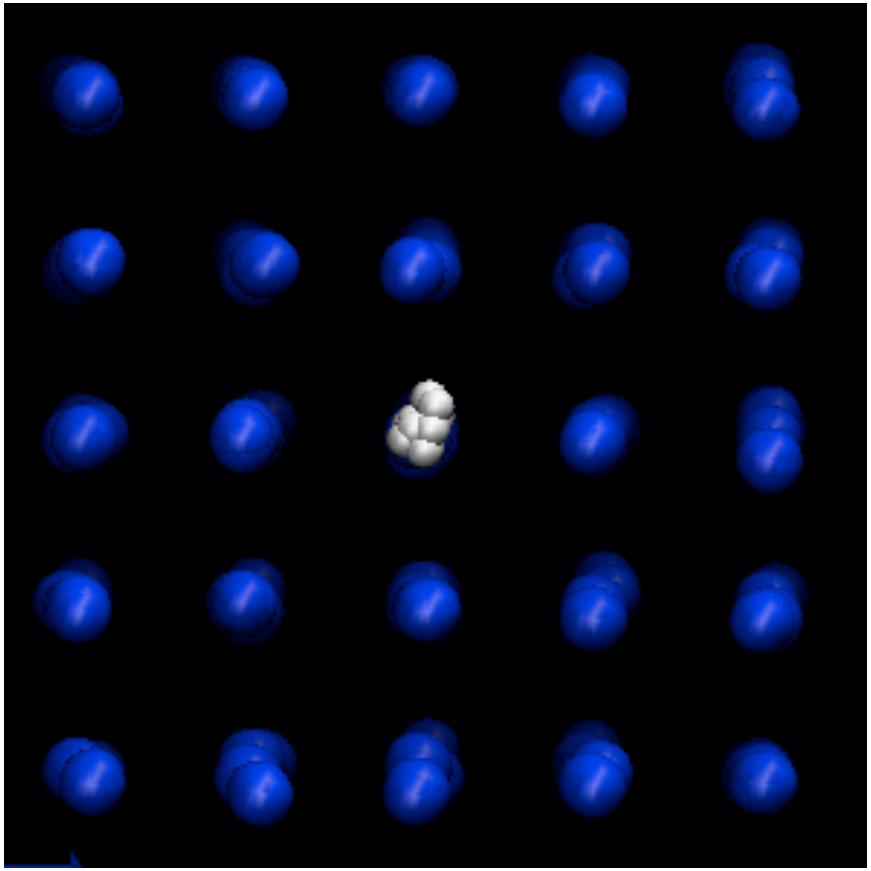


Machida, Kato, Shiga, *J. Chem. Phys.* **148**, 102324 (2018).

Hydrogen in Pd



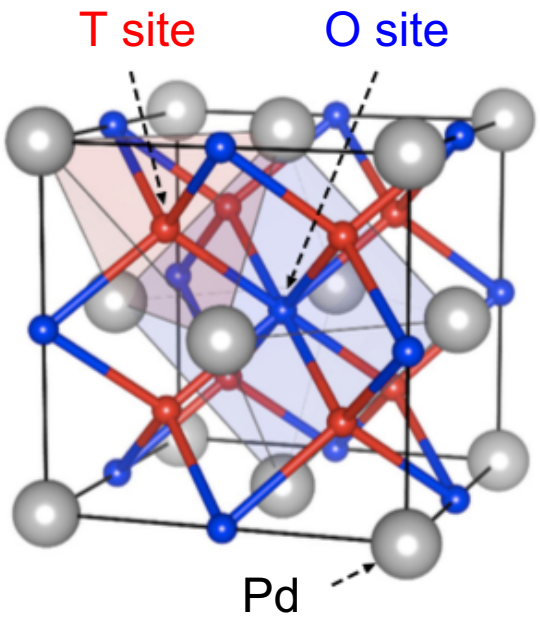
fcc lattice



Kimizuka, Ogata, Shiga, *Phys. Rev. B* **97**, 014102 (2018)
Kimizuka, Ogata, Shiga, *Phys. Rev. B* **100**, 024104 (2019).

Hydrogen in Pd

diffusion paths



fcc lattice

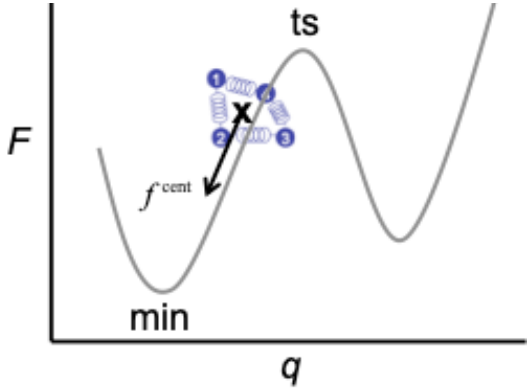
Quantum Transition State Theory:

Gillan, *Phys. Rev. Lett.* **58**, 563 (1987).

free energy calculations from ring polymer

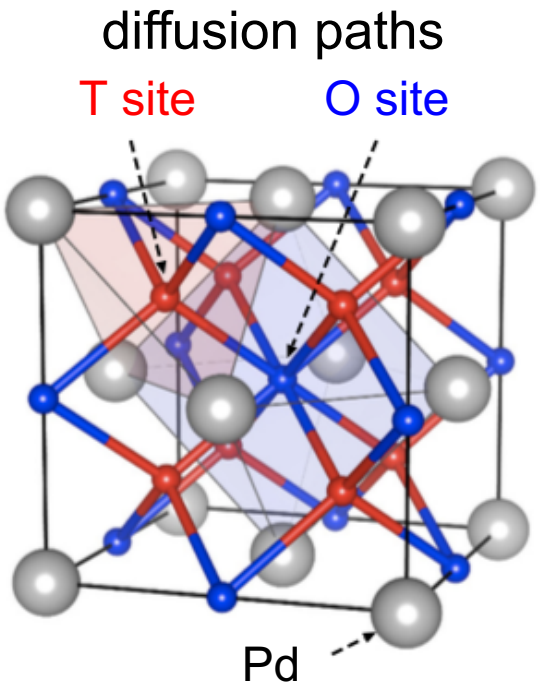
$$F(q) \equiv -\int dq \frac{\left\langle f^{\mathrm{cent}}(r)\,\delta\left(r^{\mathrm{cent}}-q\right)\right\rangle_{\mathrm{PI}}}{\left\langle \delta\left(r^{\mathrm{cent}}-q\right)\right\rangle_{\mathrm{PI}}}$$

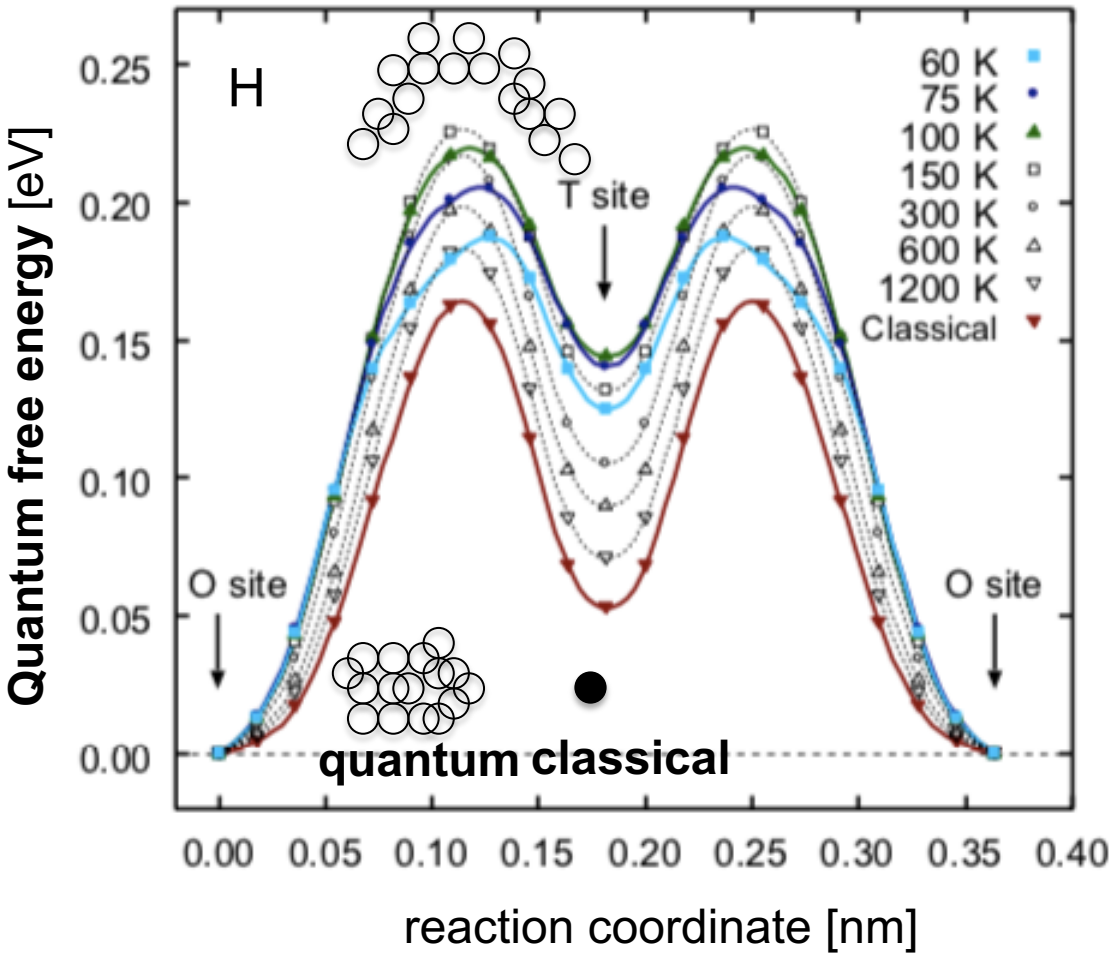
f^{cent} **:** force on the ring polymer centroids



Kimizuka, Ogata, Shiga, *Phys. Rev. B* **97**, 014102 (2018)
Kimizuka, Ogata, Shiga, *Phys. Rev. B* **100**, 024104 (2019).

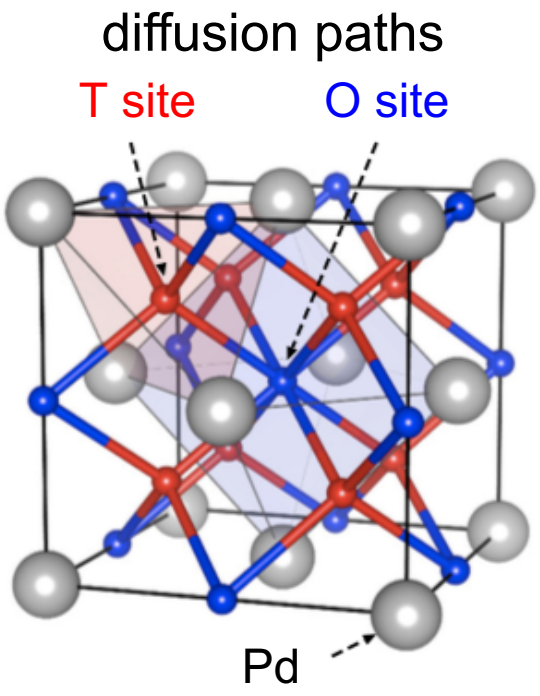
Hydrogen in Pd



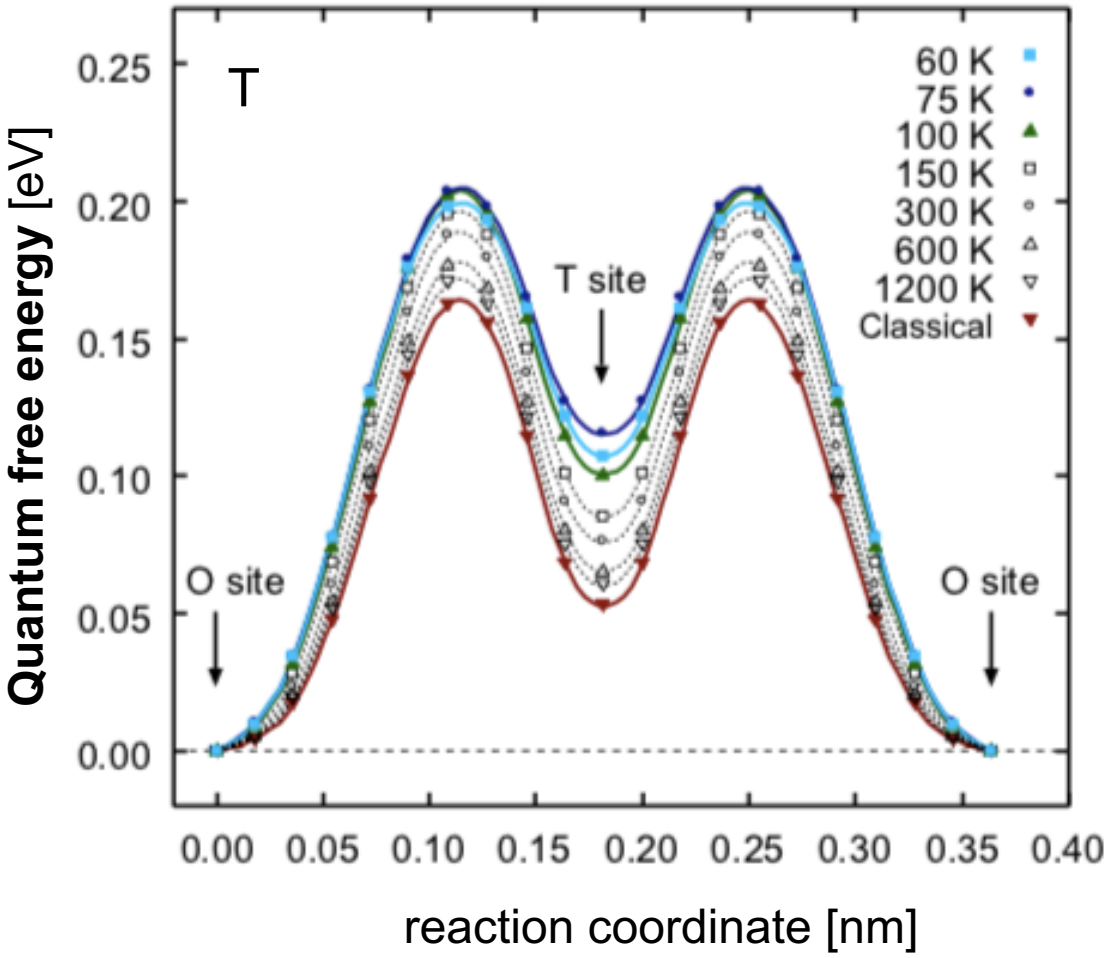


Kimizuka, Ogata, Shiga, *Phys. Rev. B* **97**, 014102 (2018)

Hydrogen in Pd



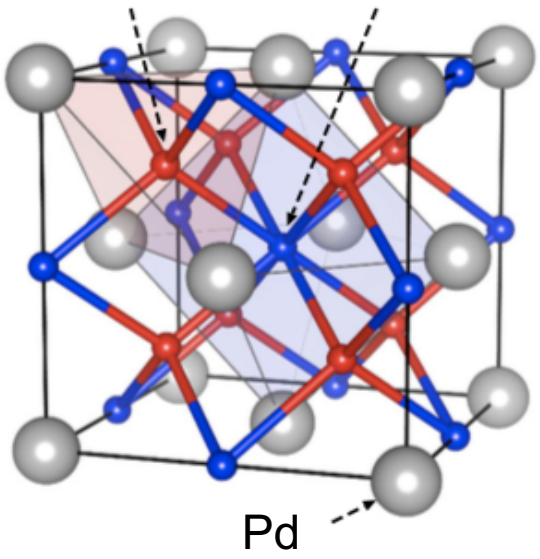
fcc lattice



Kimizuka, Ogata, Shiga, *Phys. Rev. B* **97**, 014102 (2018)

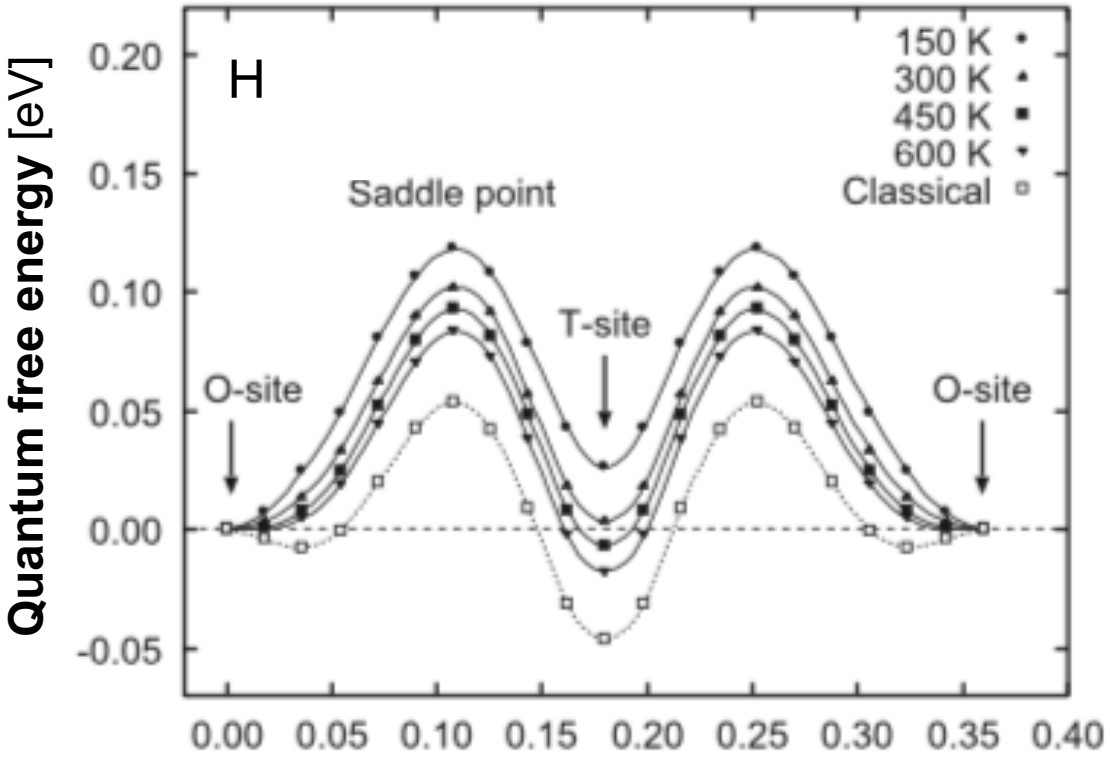
Hydrogen in Pd

diffusion paths



fcc lattice

With lattice expansion of 2.4%



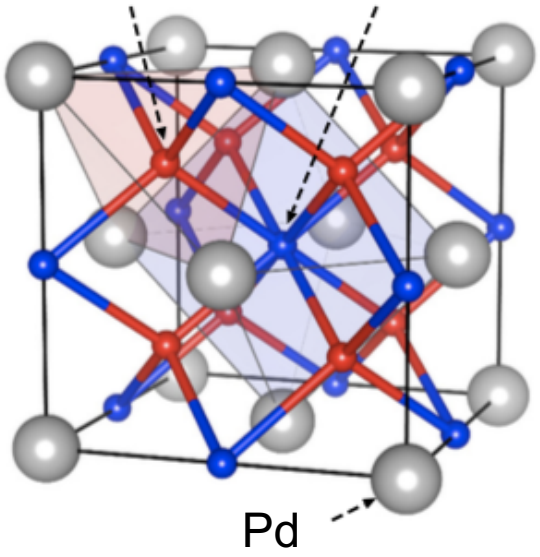
cf: **Nanoparticle expt. by** Kofu, Yamamuro, et al., *Phys. Rev. B* **94**, 064303 (2016)

Kimizuka, Ogata, Shiga, *Phys. Rev. B* **97**, 014102 (2018)

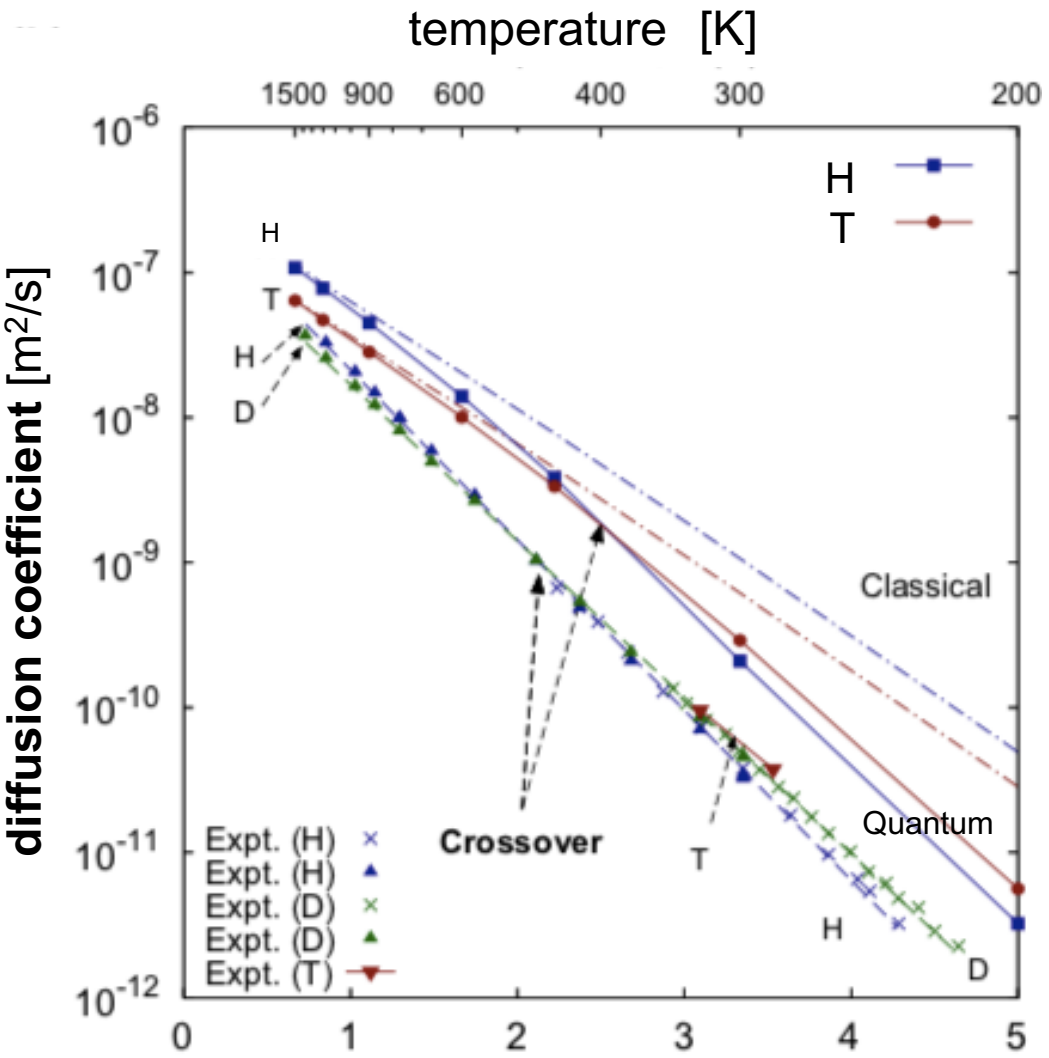
Hydrogen in Pd

diffusion paths

T site O site

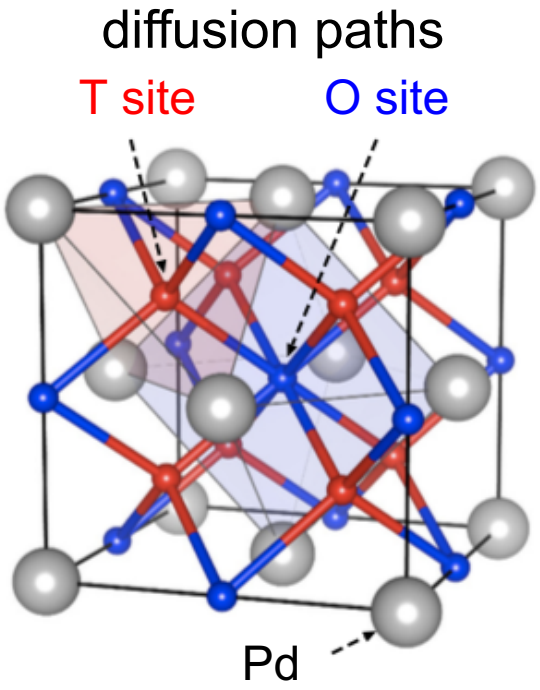


fcc lattice

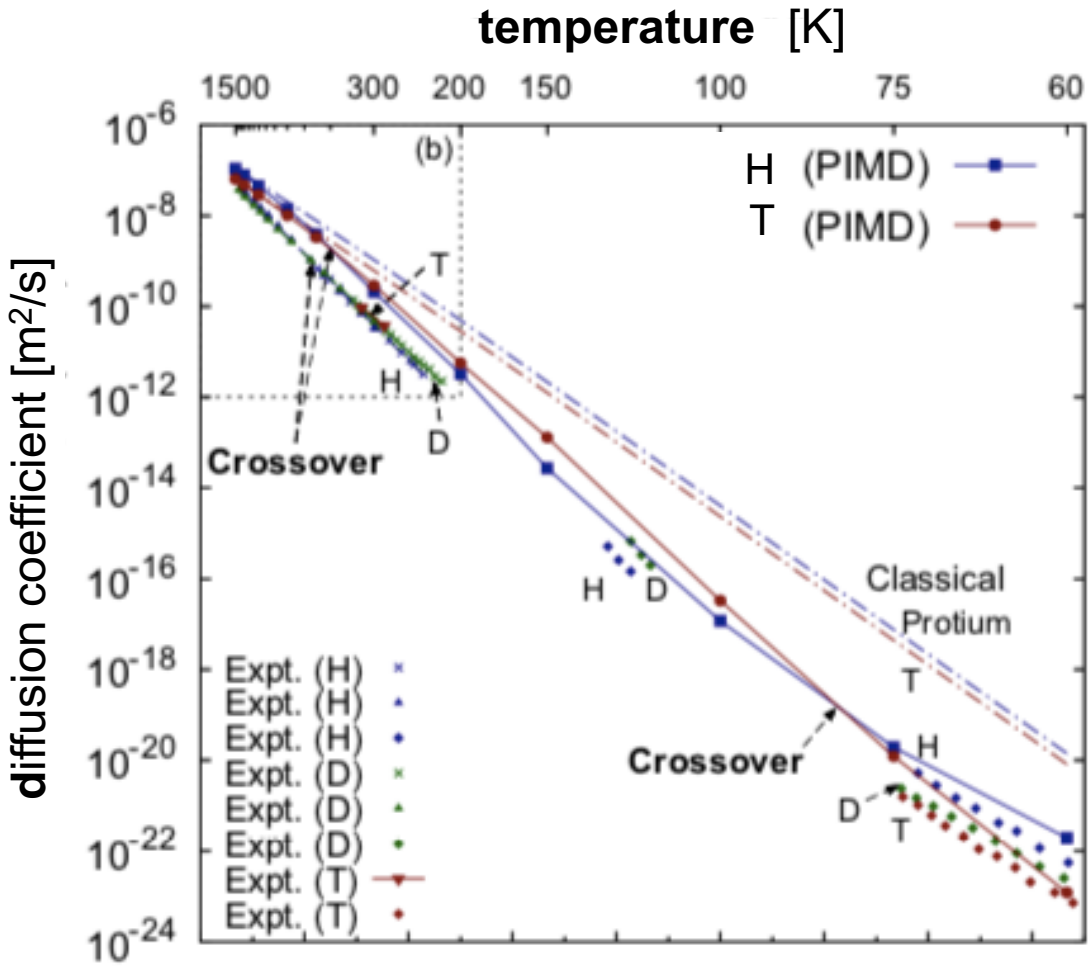


Kimizuka, Ogata, Shiga, *Phys. Rev. B* **100**, 024104 (2019).

Hydrogen in Pd



fcc lattice



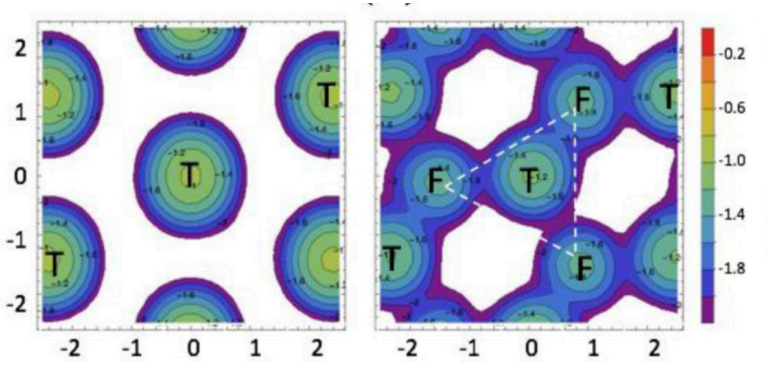
cf: **low temperature expt by** Fukutani's group

Kimizuka, Ogata, Shiga, *Phys. Rev. B* **100**, 024104 (2019).

Hydrogen adsorption on Pt(111) surface

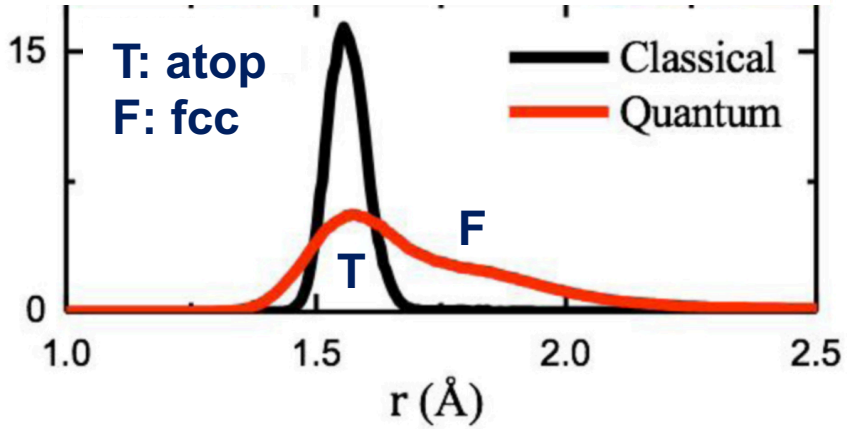
Full coverage

H distribution

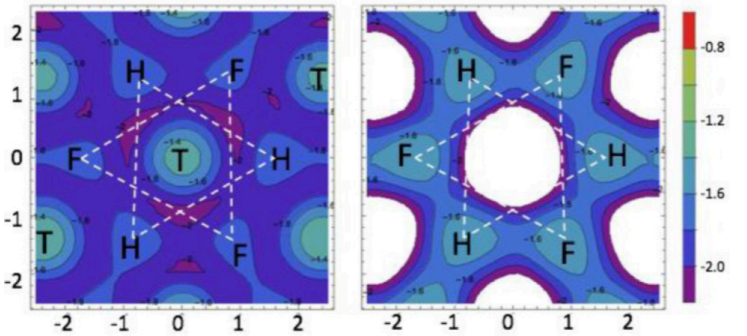


Classical Quantum

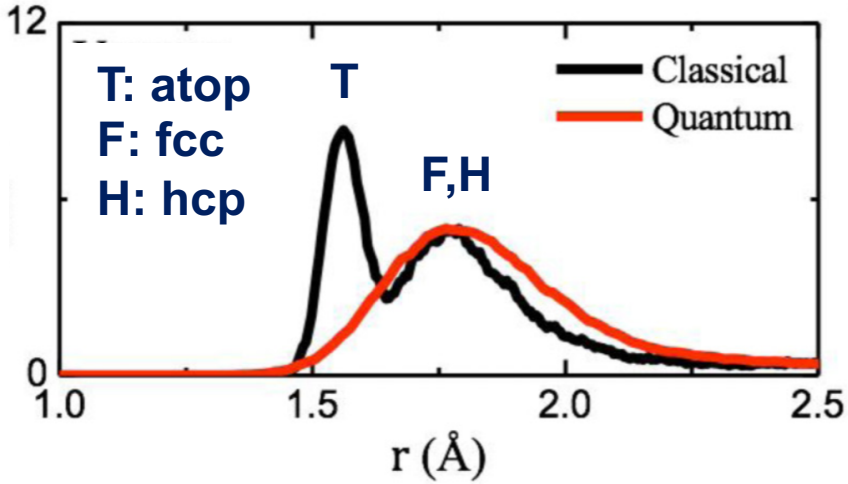
Pt-H distribution



2/3 coverage



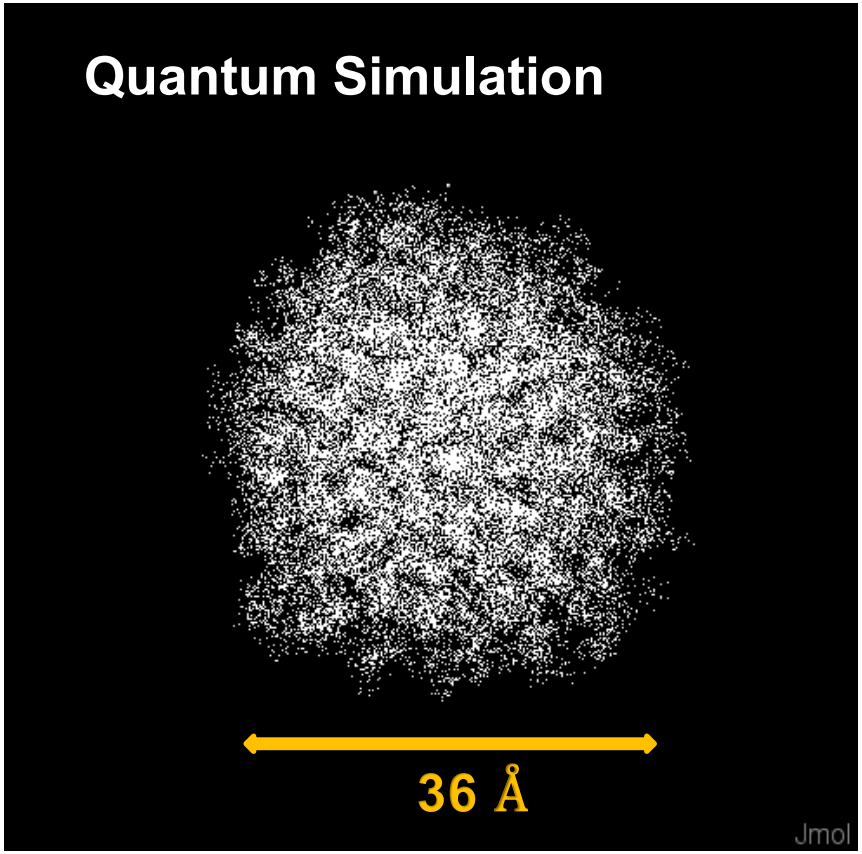
Classical Quantum

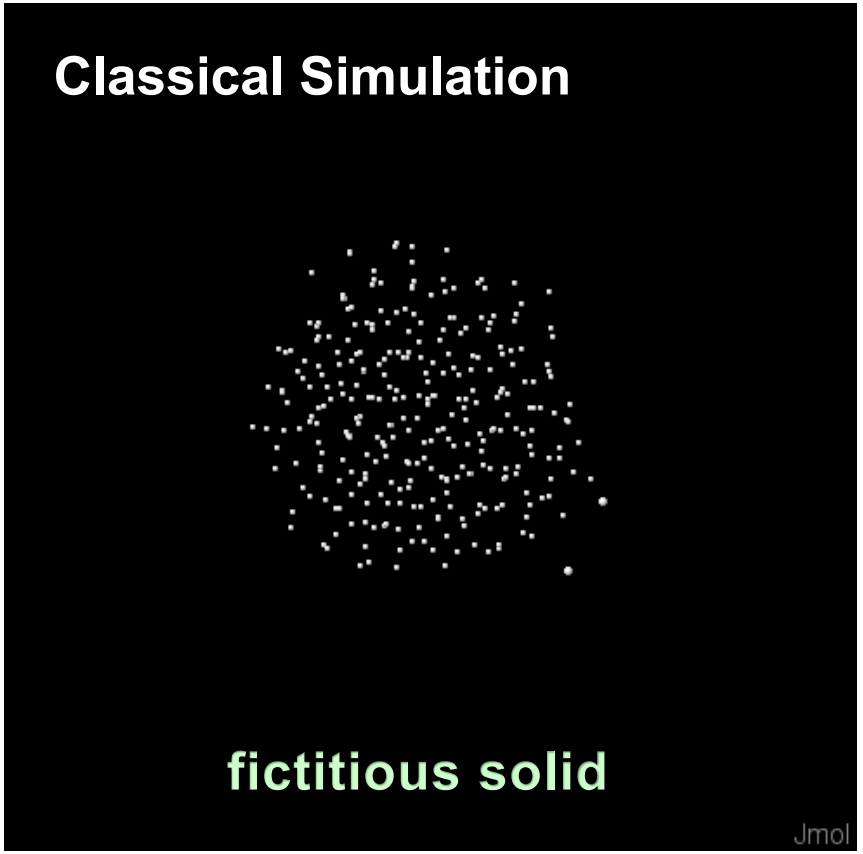


Yan, Yamamoto, Shiga, Sugino, *Phys. Rev. B* **101**, 165414 (2020).

Low Temperature Helium Droplet

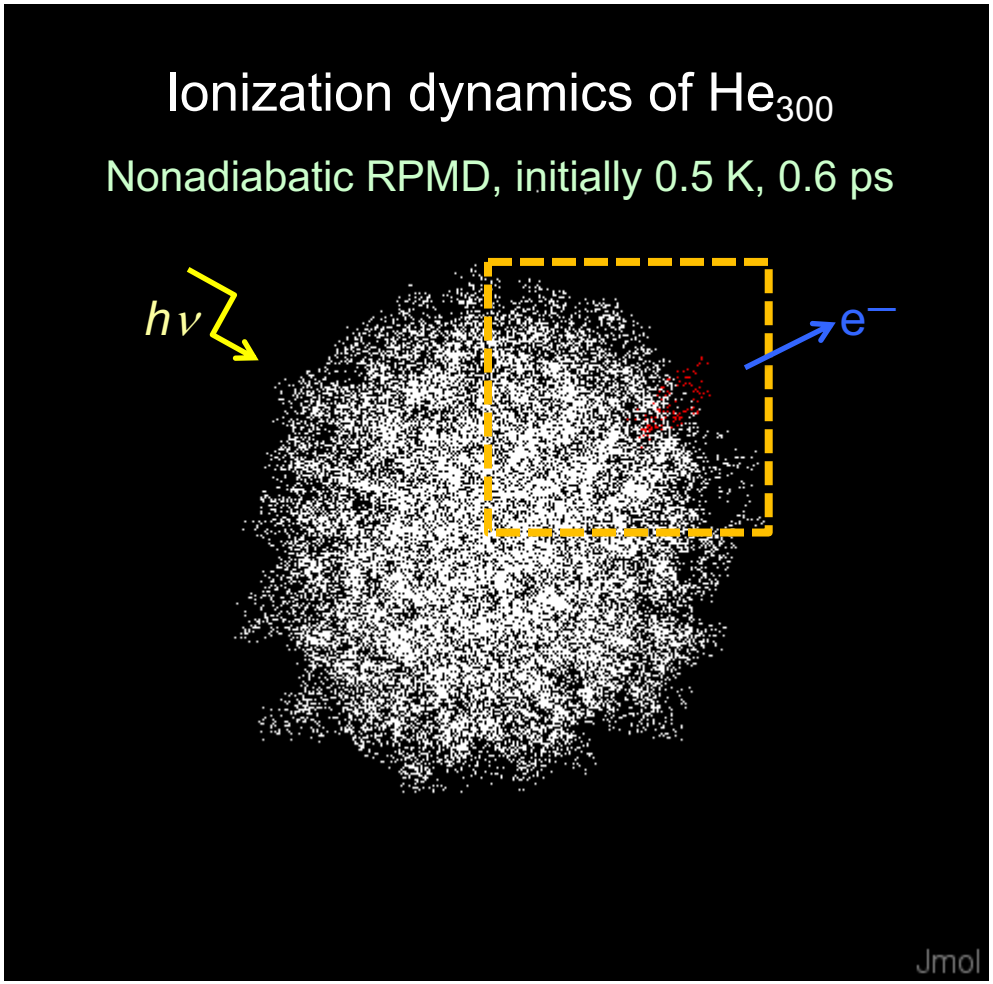
He_{300} cluster at 0.5 K

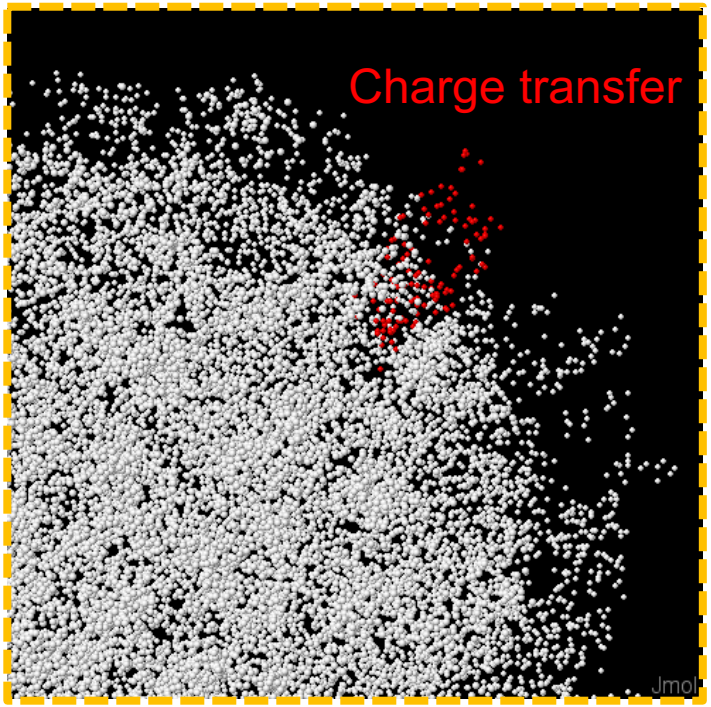




Suzuki, Miyazaki, Takayanagi, Shiga, *Phys. Chem. Chem. Phys.* **20**, 26489 (2018).

Low Temperature Helium Droplet





Suzuki, Miyazaki, Takayanagi, Shiga, *Phys. Chem. Chem. Phys.* **20**, 26489 (2018).

Acknowledgement

Water:

- Prof. M. Tachikawa (Yokohama City Univ)
- Dr. M. Machida (JAEA), Dr. K. Kato (Kyushu Univ)

Helium droplets:

- Prof. T. Takayanagi (Saitama Univ)

Hydrogen diffusion in Pd:

- Prof. H. Kimizuka (Nagoya University)
- Prof. S. Ogata (Osaka University)

Hydrogen adsopption on Pt(111):

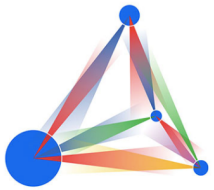
- Prof. O. Sugino, Dr. L. Yan, Dr. Y. Yamamoto (Univ of Tokyo)

PIMD:

- Dr. B. Thomsen, Dr. Y. Nagai (JAEA)

JSPS KAKENHI

- 18H05519, 18H01693, 18K05208, 16K05675



Hydrogenomics