jh260011

水素関連ナノ材料の量子動力学計算基盤の構築

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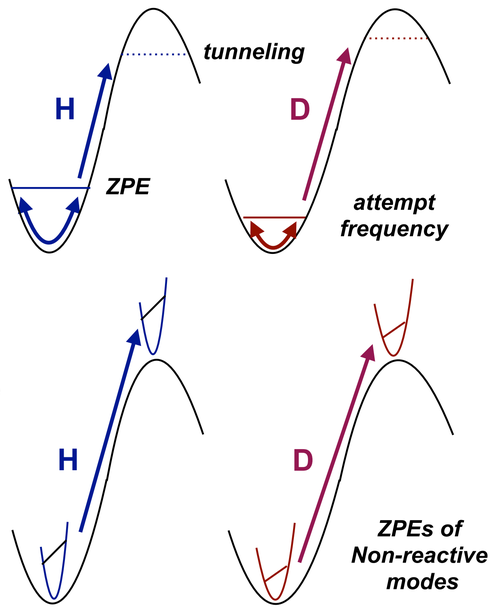
Nuclear Quantum Effects

Effects arising from the wave-like nature of light nuclei

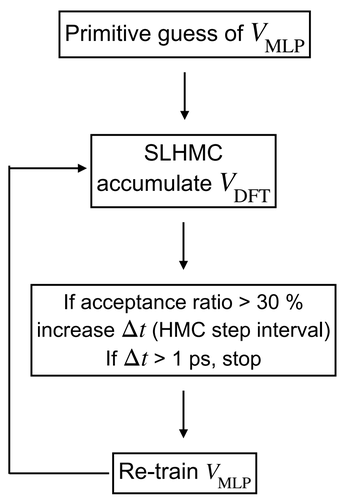
Isotope effects

- H/D substitution changes the structures, thermodynamic properties, reaction rates
- The effect arise from differences in the nuclei (not the electronic structure)
- Experimental evidence of the contribution from nuclear quantum effects

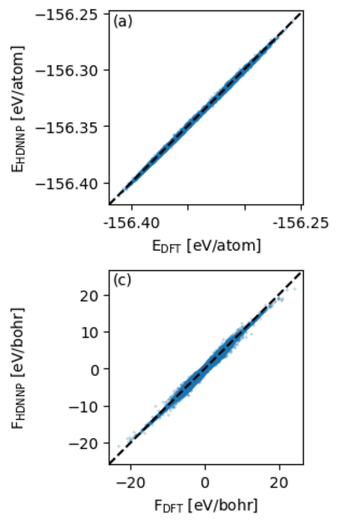


Active MLP training: Self-Learning hybrid Monte Carlo

Typical workflow



Liquid water, revPBE0-D3



Path Integral Molecular Dynamics

Chandler, Wolynes, *J. Chem. Phys.* **74**, 4078 (1981).

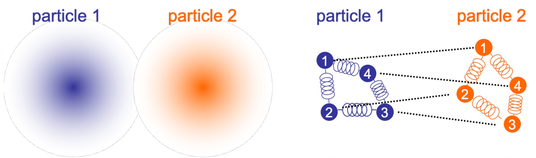
Quantum statistics of a particle = Classical statistics of replicated particles (beads)

$$Z = \mathrm{Tr}\exp\left(-\beta\left(\frac{\hat{p}^2}{2m} + \hat{V}(x)\right)\right) \propto \lim_{P\to\infty}\int dx_1 \int dx_2 \cdots \int dx_P \exp\left(-\beta V_{\mathrm{eff}}\left(x_1, \cdots, x_P\right)\right) \propto Z_{\mathrm{eff}}$$

The effective potential: $V_{\mathrm{eff}} = \sum_{s=1}^{P} \frac{mP}{2\beta^2\hbar^2}\left(x_{s+1} - x_s\right)^2 + \frac{1}{P}\sum_{s=1}^{P} V\left(x_s\right)$

harmonic interaction between the "beads" — *bead average of physical potential*

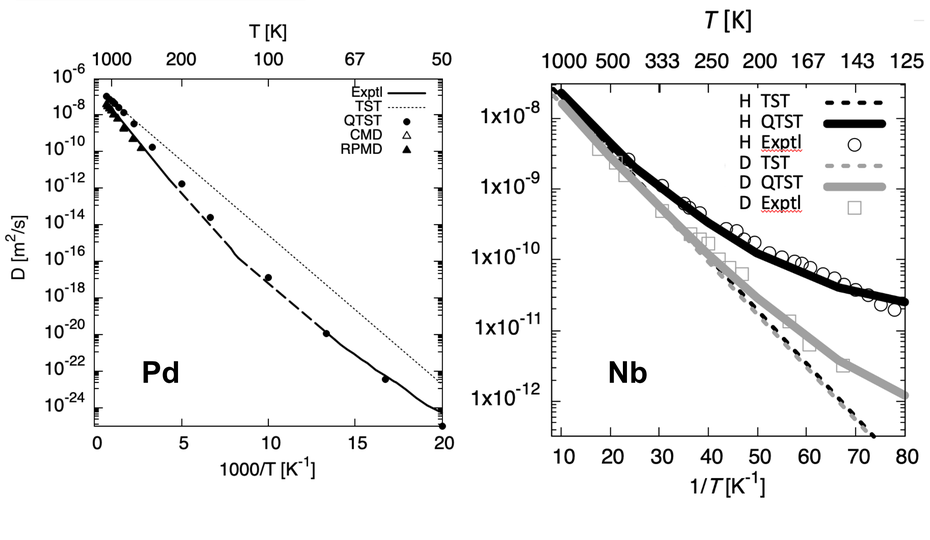
Description of diatomic molecule (for distinguishable atoms)



Ab initio PIMD: $V\left(x_s\right)$ is computed from electronic structure theory

CPMD — Marx, Parrinello, *JCP* **104**, 4077 (1996).
BOMD — Shiga, Tachikawa, Miura, *CPL* **332**, 396 (2000); *JCP* **115**, 9149 (2001).

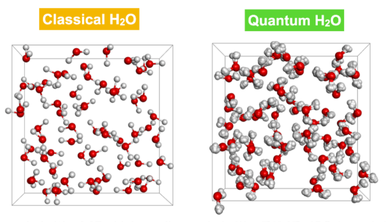
H diffusion in bulk metals



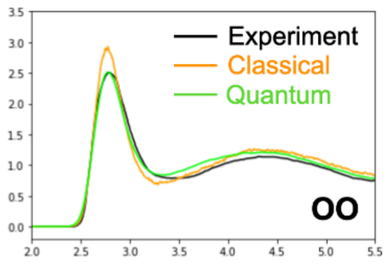
Kimizuka, Ogata, Thomsen, Shiga, *J. Phys. Condens. Matter*, **37**, 193001 (2025).
Kwon, Shiga, Kimizuka, Oda, *Acta Mater.* **247**, 118739 (2023).

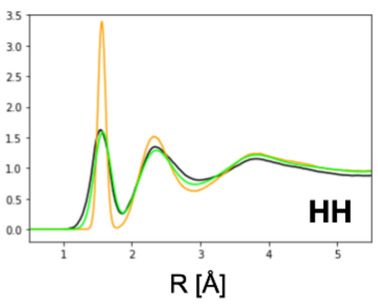
Liquid water

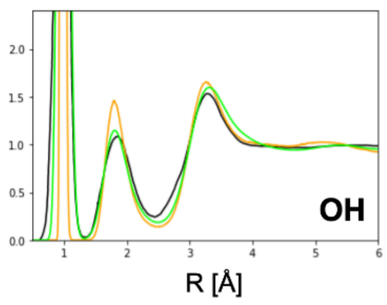
Radial distributions at ambient condition (RPBE+D3)



ab initio MD (1 bead) *ab initio PIMD (32 beads)*







Thomsen, Shiga, *J. Chem. Phys.* **155**, 194107 (2021).

Inelastic Neutron Scattering of H in Pd

Shiga, Thomsen, Kimizuka, *PRB* **109**, 054303 (2024).

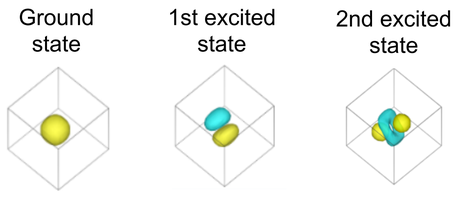
Dynamic structure factor (incoherent part):

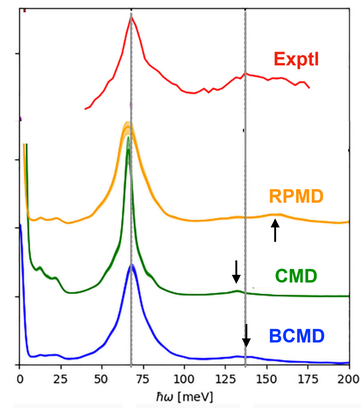
$$S_{\mathrm{inc}}(\mathbf{k},\omega) = \frac{\beta\hbar\omega}{1-\exp(-\beta\hbar\omega)} \times \frac{1}{2\pi}\int_{-\infty}^{\infty} \langle \overline{A}(\mathbf{k},0)\overline{A}^*(\mathbf{k},t)\rangle e^{-i\omega t}dt$$

with the bead average

$$\overline{A}(\mathbf{k},t) = \frac{1}{P}\sum_{s=1}^{P} e^{-i\mathbf{k}\cdot\mathbf{R}_{\mathrm{H}}^{(s)}}$$

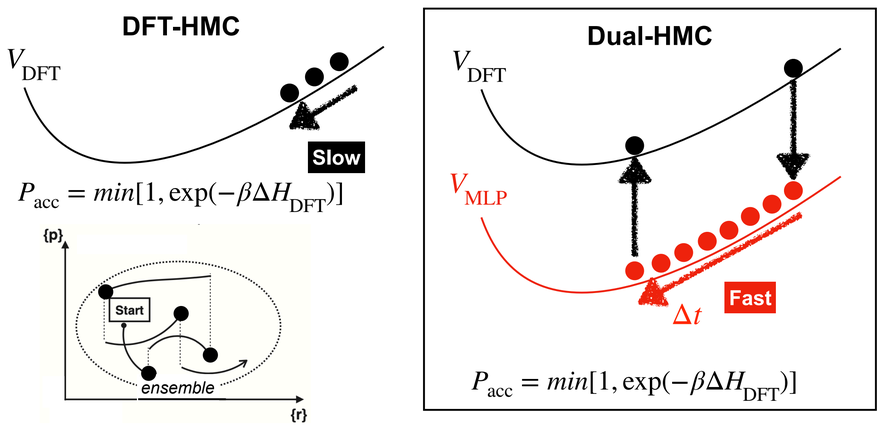
Ground state — 1st excited state — 2nd excited state





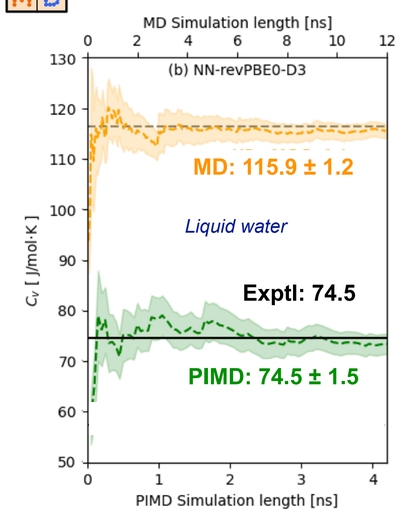
Active MLP training: Self-Learning hybrid Monte Carlo

Nagai, Okumura, Kobayashi, Shiga. *Phys. Rev. B* **102**, 041124(R) (2020)
Kobayashi, Nagai, Itakura, Shiga, *J. Chem. Phys.* **155**, 034106 (2021)



- *Canonical ensemble generator:* $P(\mathbf{r}) \propto \exp(-\beta V_{\mathrm{DFT}}(\mathbf{r}))$
- *Better acceptance as* V_{MLP} *is improved*
- *Trial trajectory made longer as it proceeds*

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



Shiga, Elsner, Behler, Thomsen,
J. Chem. Phys. **163**, 134119 (2025).
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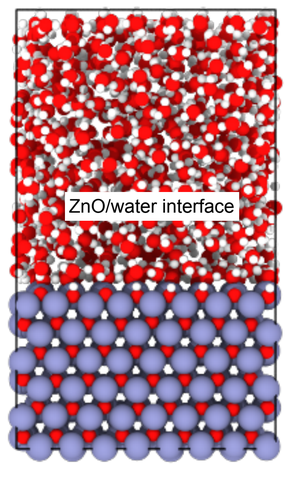

Elsner, Behler,
German Physical Society Meeting (2026)