Quantum optimization through path-integral molecular dynamics

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1. Introduction

- **Motivation**
  Global optimization of atomic degrees of freedom is a key problem in physics whenever the number of candidate structures (local minima) is combinatorially large: cluster physics, polymer folding, interfaces...
- **The idea**
  Novel implementation of **Quantum Annealing** (QA) using **Path-Integral Molecular Dynamics** (PIMD), labeled QA-PIMD. While **Classical Annealing** (CA) involves melting the system and then slowly cooling it through a temperature schedule, QA relies on quantum delocalization.

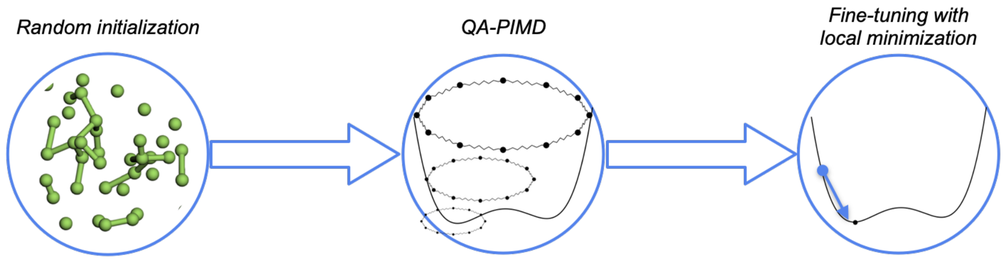


Figure: Summary of the workflow

2. Methods

QA-PIMD is obtained by combining two powerful methods:

- **Quantum annealing: exploration through quantum delocalization**

$$\hat{H}(t) = -\alpha(t) \sum_{i=1}^{N} \frac{\hbar^2}{2m_i}\nabla^2 + U(\hat{\mathbf{x}}_1, \ldots, \hat{\mathbf{x}}_N)$$

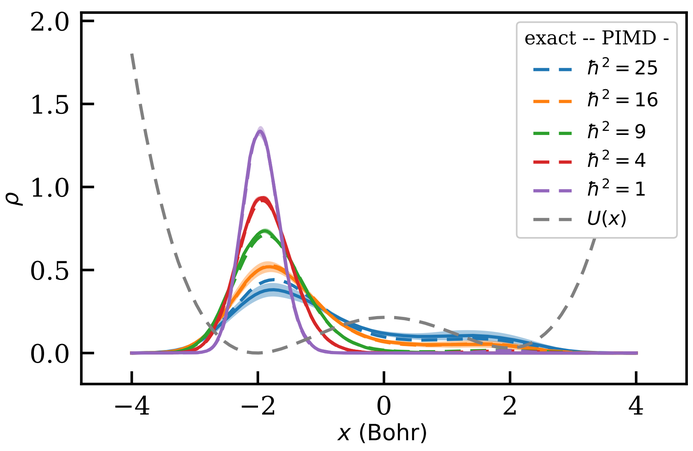
  - $\alpha(t=0) \gg 1$, $\alpha(t_{\text{max}}) \ll 1$
  - $\lim_{t_{\text{max}}\to\infty} \text{Tr}[\rho(t_{\text{max}})U] = \min U$
- **Path-Integral Molecular Dynamics**
  Equilibrium nuclear quantum effects (NQEs) from P classical simulations ($P \sim 10-100$).

$$H_P = \sum_{i=1}^{N}\sum_{j=1}^{P}\left[\frac{1}{2m_i}|\mathbf{p}_i^{(j)}|^2 + \frac{1}{2}m_i\omega_P^2\,|\mathbf{x}_i^{(j)} - \mathbf{x}_i^{(j+1)}|^2\right] + \sum_{j=1}^{P} U(\mathbf{x}_1^{(j)}, \ldots, \mathbf{x}_N^{(j)}),$$

$$\omega_P = \frac{Pk_BT}{\hbar}$$

3. Benchmark: asymmetric double well

The local density from 200-ps PIMD simulations follows the exact instantaneous quantum density adiabatically. $T = 100$ K.



4.1 Lennard-Jones clusters

LJ clusters: millions of estimated local minima with only a few tens of atoms!

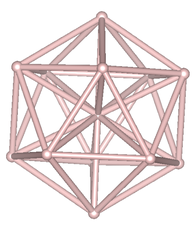


Figure: Global minimum of an LJ cluster with $N = 13$.

4.2 LJ clusters: classical vs quantum

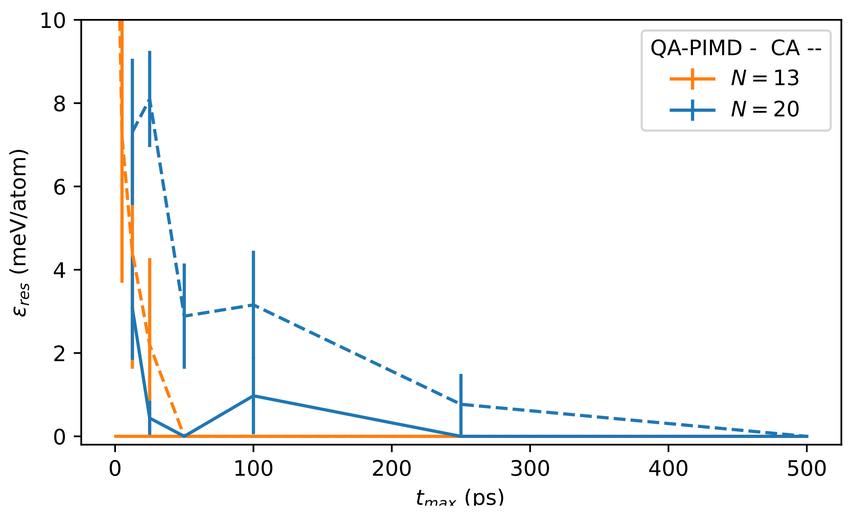


Figure: Comparison of QA and CA residual energies as a function of annealing time, for two LJ cluster sizes.

5.1 Missing hydrogen sites

Many experimental structures lack hydrogen sites.
We reconstruct 10 H-compounds using QA-PIMD with a foundational MLIP (MACE).

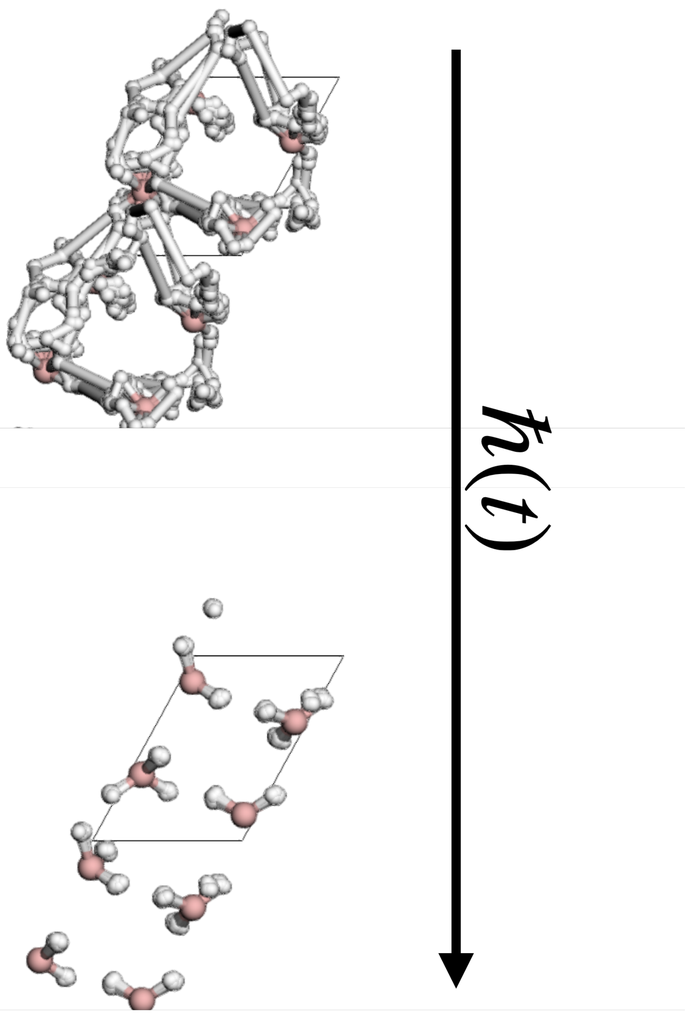


Figure: Example of identifying hydrogen sites in B_4H_{12} through QA-PIMD. Check the QR code for the video!

5.2 Results: missing hydrogen problem

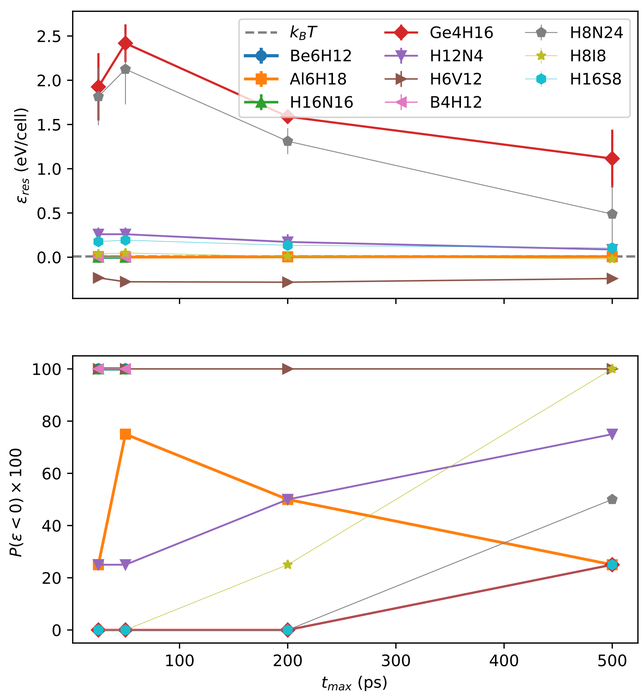


Figure: Top: residual energy with respect to the MC3D database as a function of annealing time. Bottom: probability of finding an equal or lower energy.

6. Conclusion

- QA-PIMD is a novel, unbiased, and general global optimization algorithm using quantum fluctuations.
- It can outperform classical annealing; e.g., shorter annealing times are sufficient for LJ clusters.
- Material discovery: identifies new candidate stable crystals from the MC3D database.

Open questions and challenges:

- Small but **finite** temperature — not a ground-state method.
- PIMD time evolution is not exactly quantum; dynamically, $\text{QA}-\text{PIMD} \neq \text{QA}$.

7. References

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8. Acknowledgements

We thank S. Baroni, L. Vojáček, A. Carta, V. Sanella, and S. Schären for insightful discussions. Financial support was provided by the NCCR MARVEL, a National Centre of Competence in Research funded by the Swiss National Science Foundation (grant number 205602).