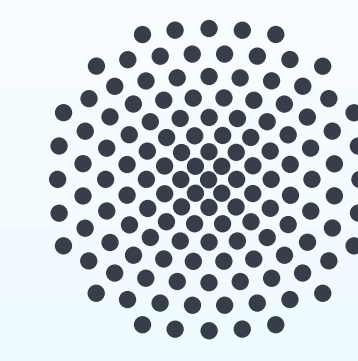
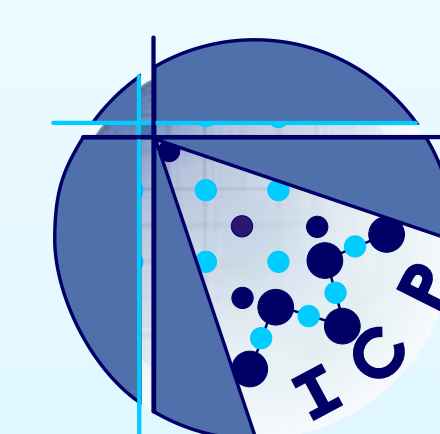


# Path Integral Molecular Dynamics Simulations Using ESPResSo



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## Motivation

- Often important to consider quantum and thermal effects  
⇒ e.g. superfluids, quantum gases, isotope effects in crystals, etc.
- Still may want to use more coarse-grained potentials rather than full electronic problem  
⇒ Path integrals provide an elegant formalism

## Path Integrals in Quantum Statistics

**Feynman path integral formalism** [1]:

- Transition amplitudes can be expressed as sum over paths:

$$\langle x_b t_b | x_a t_a \rangle = \sum_{\text{all paths } x(t)} \exp\left(\frac{i}{\hbar} S[x(t)]\right)$$

with action functional

$$S[x(t)] = \int_{t_a}^{t_b} dt L(x(t), \dot{x}(t), t)$$

- Follows from composition law of time evolution operator [2]

$$\begin{aligned} \langle x_b t_b | x_a t_a \rangle &= \langle x_b | \exp\left(-\frac{i}{\hbar}(t_b - t_a)H\right) | x_a \rangle = \langle x_b | U(t_b, t_a) | x_a \rangle \\ &= \langle x_b | U(t_b, t_N) U(t_N, t_{N-1}) \cdots U(t_1, t_a) | x_a \rangle \end{aligned}$$

and taking number of time slices  $N \rightarrow \infty$ :

$$\begin{aligned} \langle x_b t_b | x_a t_a \rangle &= \int_{x(t_a)=x_a}^{x(t_b)=x_b} \mathcal{D}x(t) \exp\left(\frac{i}{\hbar} S[x(t)]\right) \\ &\propto \lim_{N \rightarrow \infty} \prod_{n=1}^N \left[ \int_{-\infty}^{\infty} dx_n \right] \exp\left(\frac{i}{\hbar} S^N(x_1, \dots, x_N)\right) \end{aligned}$$

with time-sliced action  $S^N(x_1, \dots, x_N)$

**Wick rotation:**

- Analytical continuation to complex time:

$$t_b - t_a = -i\hbar\beta$$

- Transition amplitudes become matrix elements of density matrix:

$$\rho(x_a, x_b) = \langle x_b | \exp(-\beta H) | x_a \rangle = \int_{x(0)=x_a}^{x(\tau=\hbar\beta)=x_b} \mathcal{D}x(\tau) \exp\left(-\frac{1}{\hbar} S_e[x(\tau)]\right)$$

- Partition function as path integral over closed paths:

$$Z = \text{Tr} \exp(-\beta H) = \int_{-\infty}^{\infty} dx \rho(x, x) = \oint \mathcal{D}x(\tau) \exp\left(-\frac{1}{\hbar} S_e[x(\tau)]\right)$$

with "euclidean action"  $S_e$

## PIMD: Isomorphism with Classical Ring Polymers

- Consider 1D quantum system with Hamiltonian

$$H = \frac{p^2}{2m} + V(x)$$

- For finite  $N$ , partition function can be written as

$$Z \approx \text{const.} \times \prod_{n=1}^N \left[ \int_{-\infty}^{\infty} dx_n \right] \exp\left(-\beta \left( \frac{\kappa}{2} \sum_{n=1}^N (x_n - x_{n+1})^2 + \frac{1}{N} \sum_{n=1}^N V(x_n) \right)\right)$$

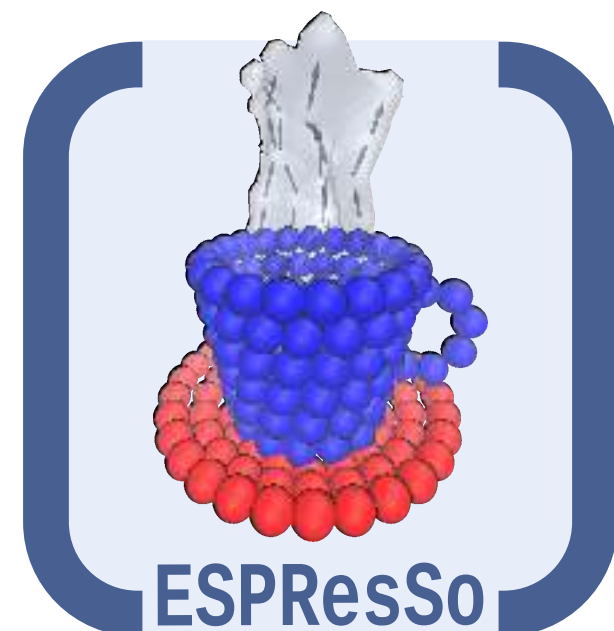
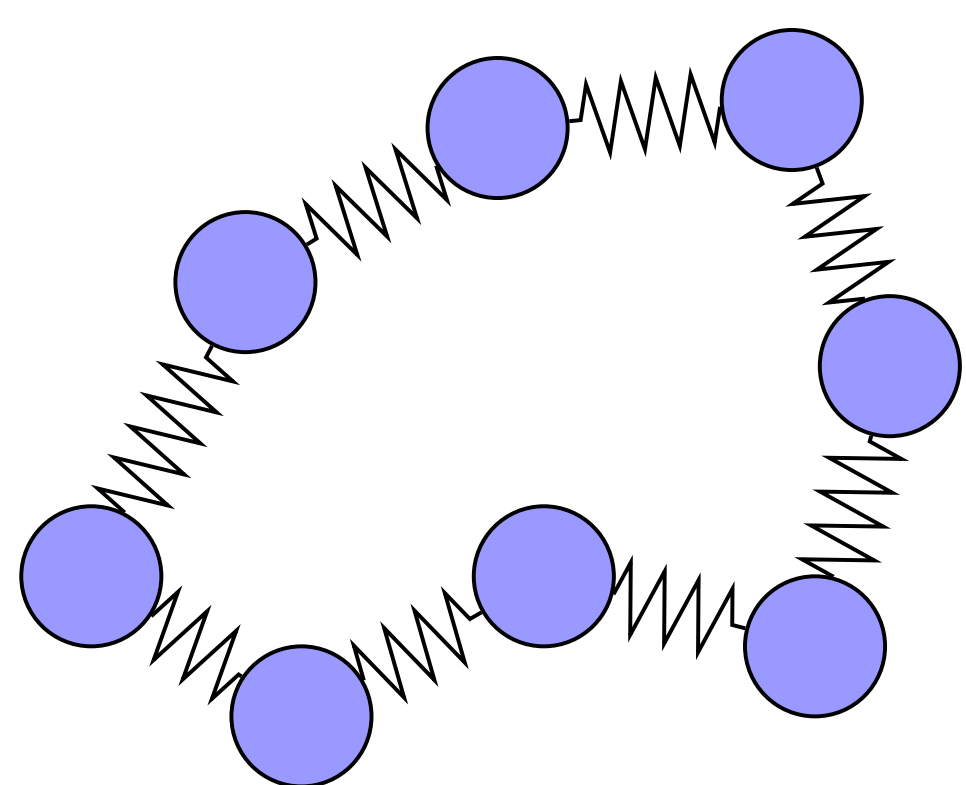
with PBC  $x_{N+1} = x_1$

⇒ discretized euclidean action looks like Hamiltonian of classical ring polymer with harmonic bonds

$$V_{\text{bonded}}(x_n, x_{n+1}) = \frac{\kappa}{2} (x_n - x_{n+1})^2$$

in external potential  $V(x)$

- Path Integral Molecular Dynamics (PIMD):** use classical canonical MD to sample equilibrium distribution of ring polymer  
⇒ here: use ESPResSo and Langevin dynamics

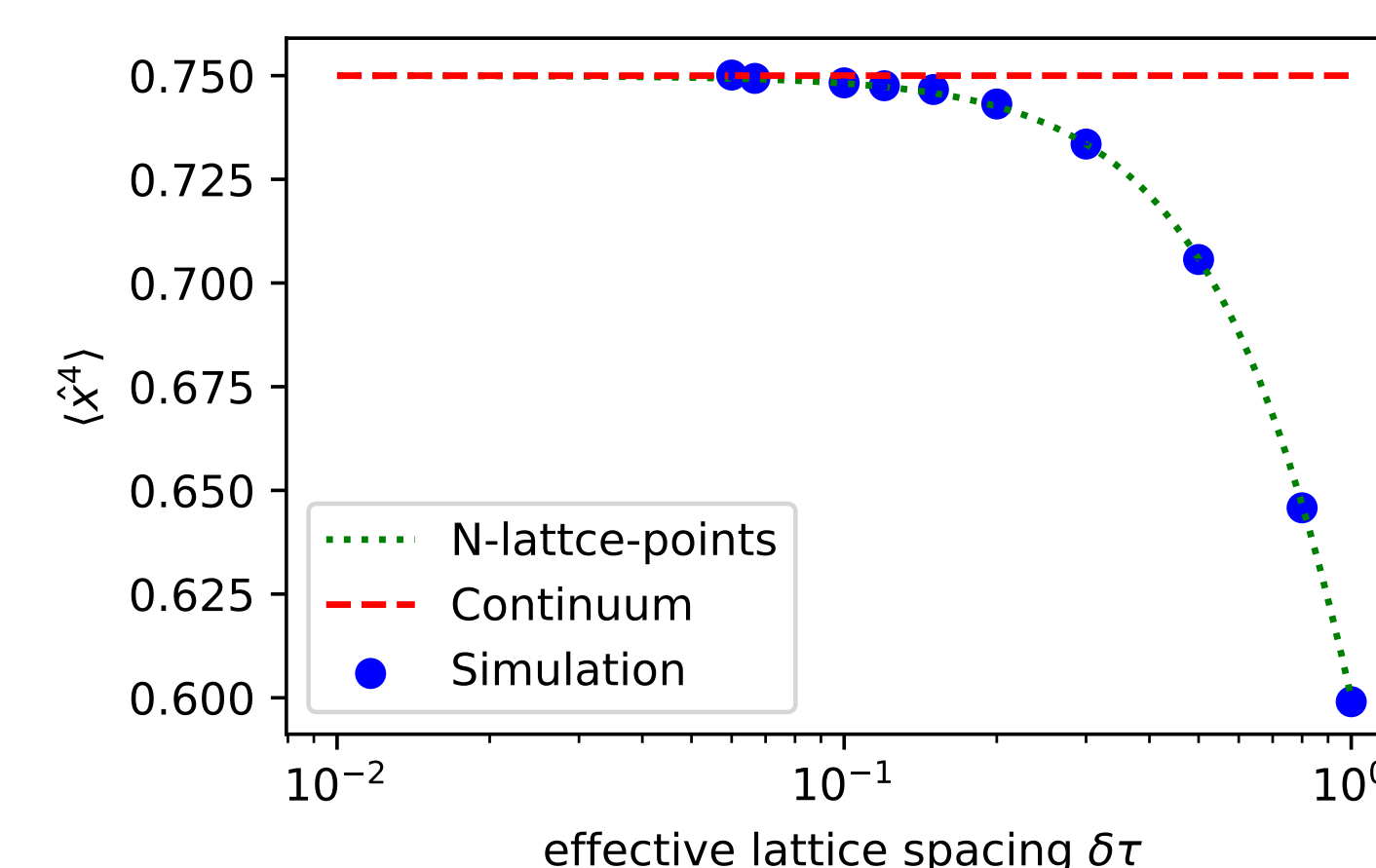


## Reaching the Continuum Limit

- Model system – 1D harmonic oscillator:

$$H = \frac{p^2}{2m} + \frac{m\omega^2 x^2}{2}$$

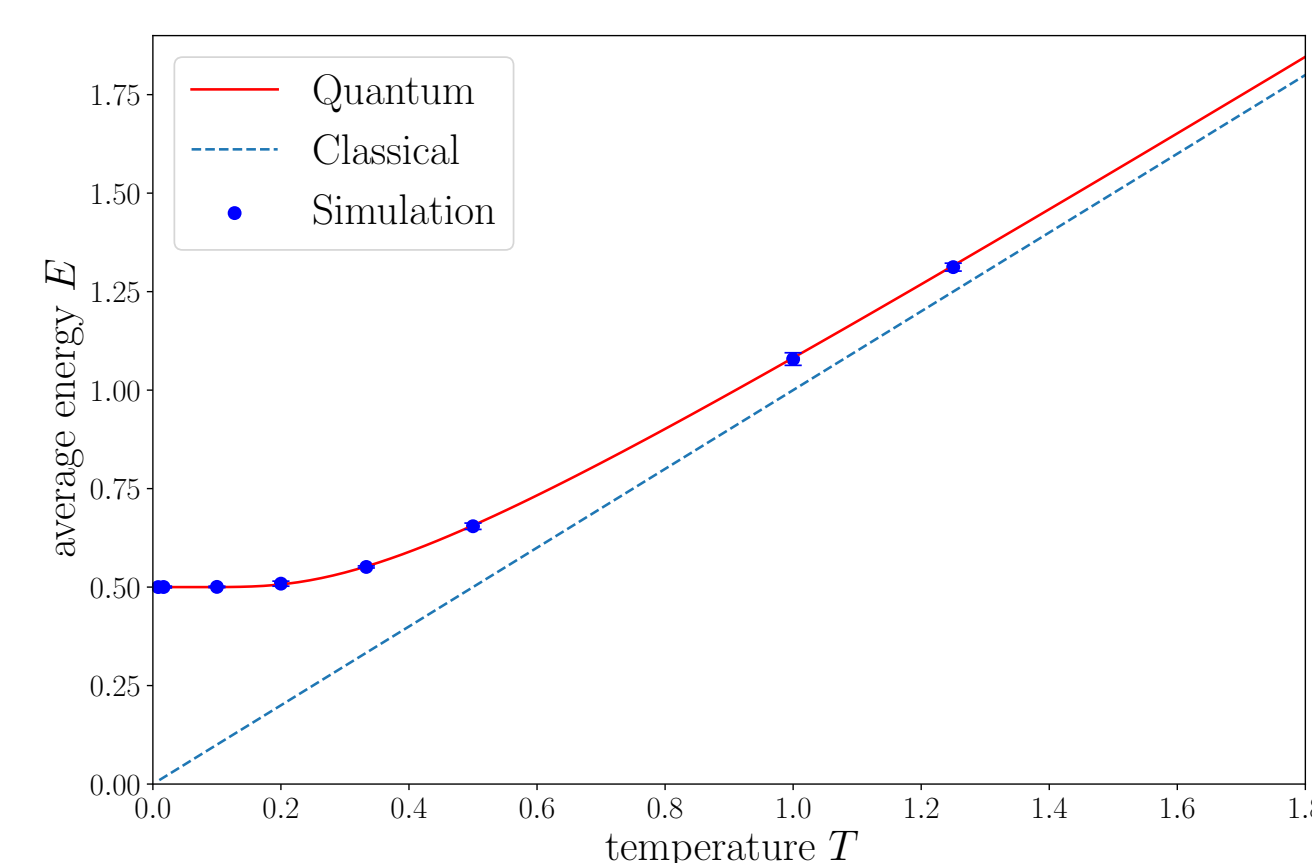
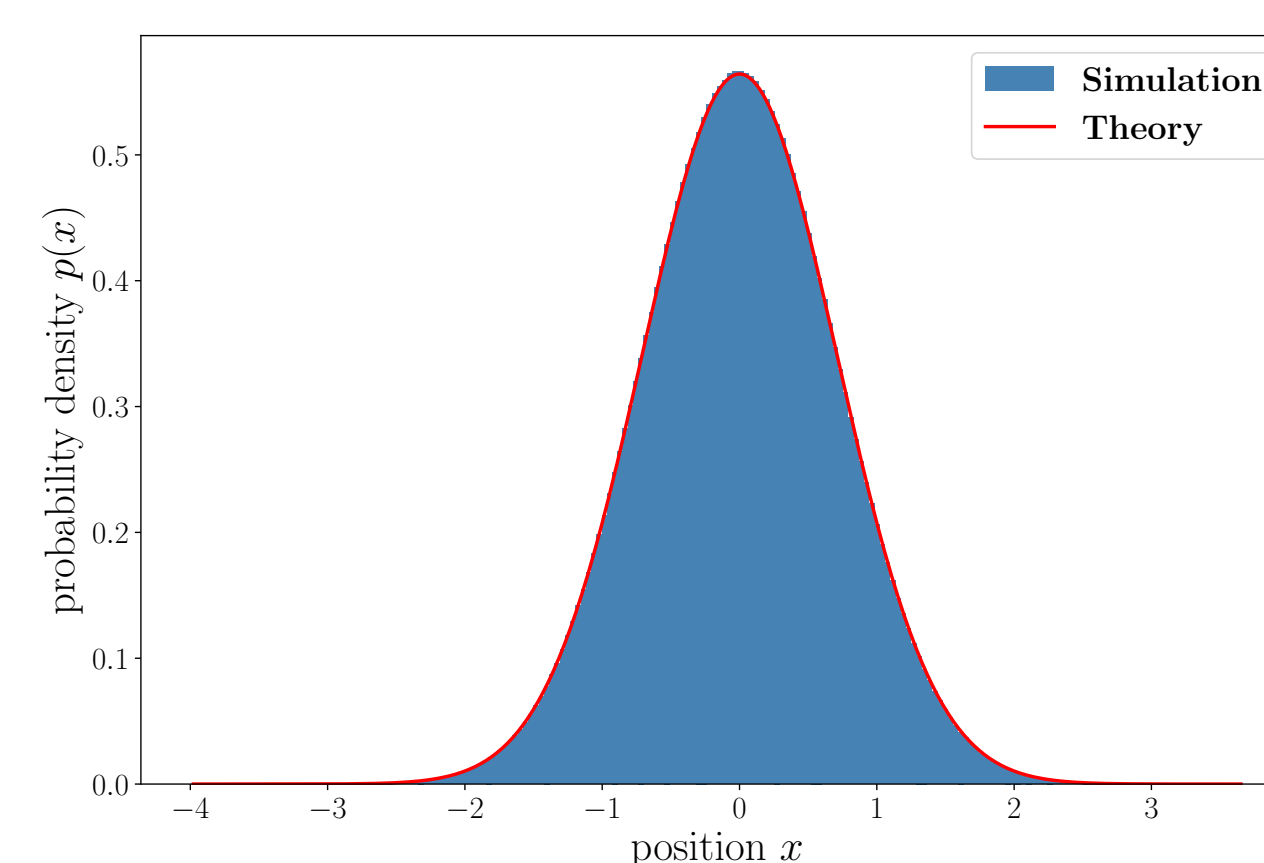
- Mapping to classical ring polymers only exact in the limit  $N \rightarrow \infty$   
⇒ need to extrapolate by performing simulations for different  $N$
- Results for different lattice spacings  $\delta\tau \propto 1/N$ :



## Density Matrix and Energy Levels

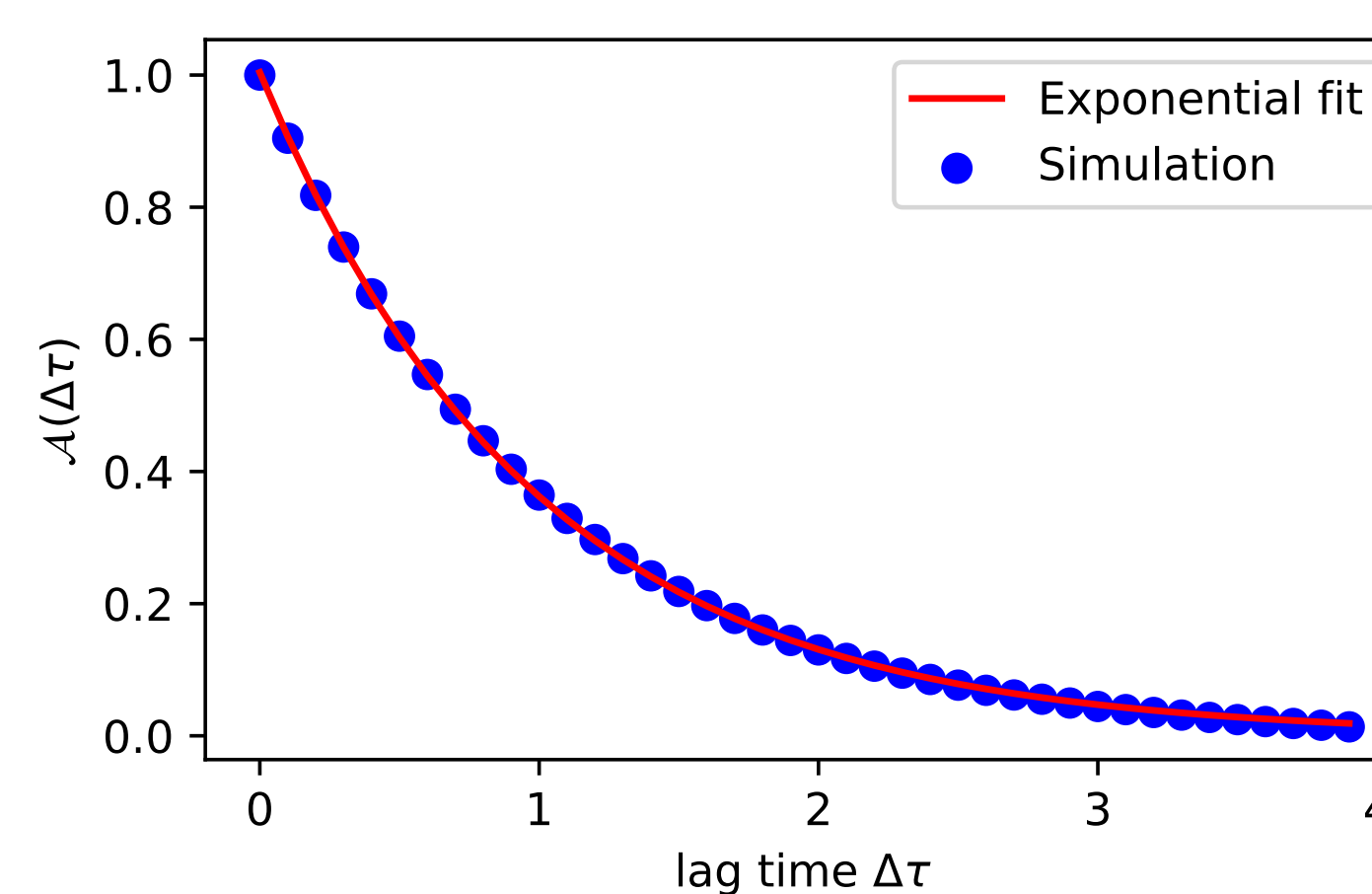
- Diagonal  $\rho(x, x)$  of density matrix can be directly obtained as histogram of monomer positions
- Mean energy can be obtained using virial estimator:

$$U_v = \frac{1}{2N} \sum_{n=1}^N x_n V'(x_n) + \frac{1}{N} \sum_{n=1}^N V(x_n)$$



- Energy-levels can be obtained using imaginary-time correlation functions, e.g.

$$\mathcal{A}(\Delta\tau) = \langle \hat{x}(\tau) \hat{x}(\tau + \Delta\tau) \rangle = e^{-(E_1 - E_0)\Delta\tau} \mathcal{A}(0)$$



	$E_n - E_0$	Error
2 point	1.01947	0.04
4 point	2.00502	0.07

## Conclusion and Outlook

- PIMD in ESPResSo allows to reproduce analytical results for quantum harmonic oscillator
- Next step: include permutation moves to correctly model Bose-Einstein statistics in many-body systems

## References

- [1] RICHARD FEYNMAN, *Space-Time Approach to Non-Relativistic Quantum Mechanics*, Rev. Mod. Phys., vol. 20, 1948.
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- [3] DAVID CEPERLEY, *Path integrals in the theory of condensed helium*, Rev. Mod. Phys., vol. 67, 1995.
- [4] MARISE WESTBROEK et al., *User's guide to Monte Carlo methods for evaluating path integrals*, Am. J. Phys., vol. 86, 2018.