

# Nuclear quantum effects the colored way

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## A simple and robust generalized Langevin framework for molecular dynamics

Use a non-Markovian, generalized Langevin equation to modify the sampling properties of molecular dynamics.

$$\dot{q} = -p, \quad \dot{p} = -f(q) - \int_0^\infty K(s)p(t-s)ds + \zeta \quad (1)$$

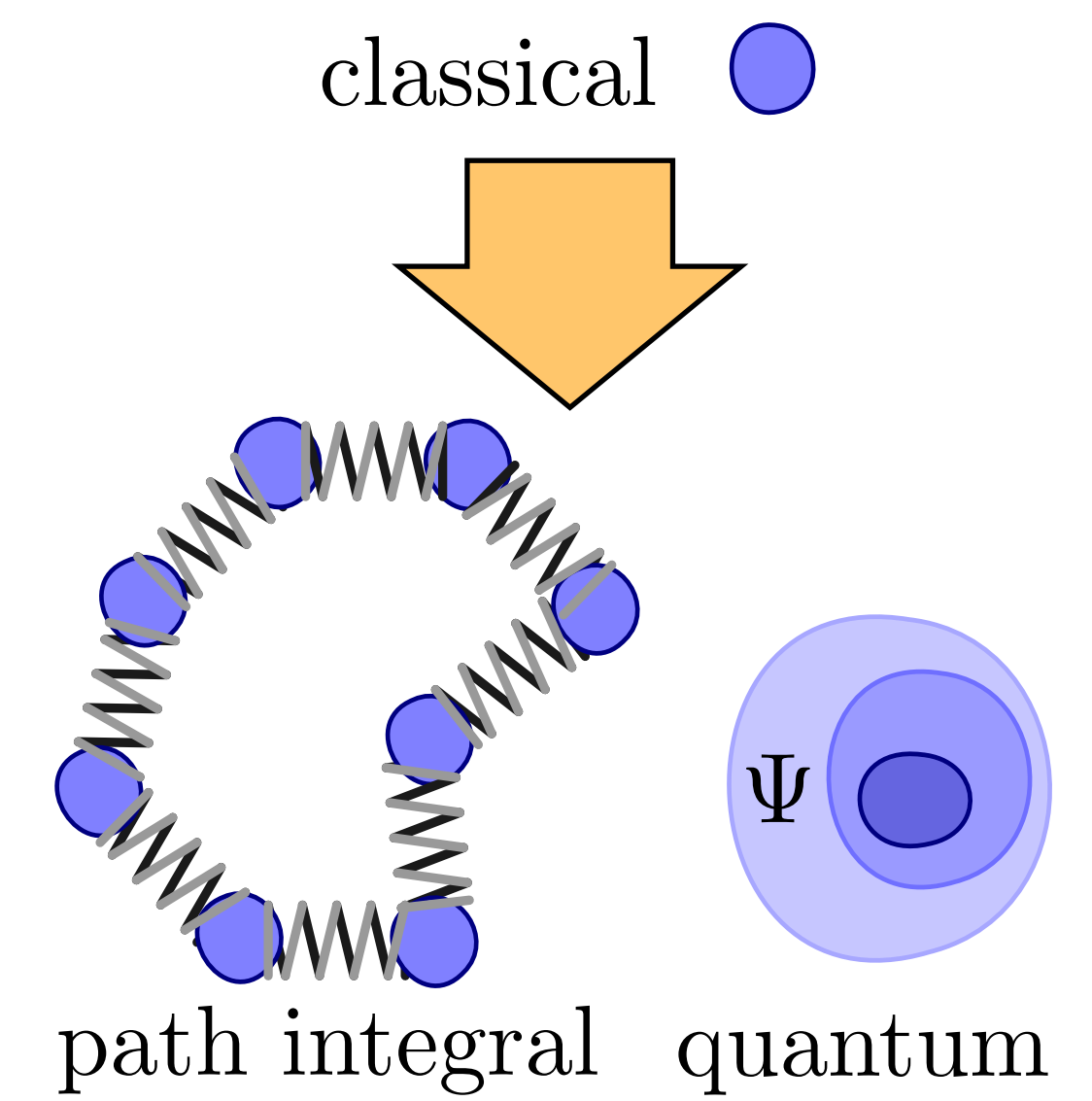
- Map the non-Markovian dynamics onto a Markovian stochastic differential equation in an extended phase space.

$$\dot{q} = -p, \quad \begin{pmatrix} \dot{p} \\ \dot{s} \end{pmatrix} = \begin{pmatrix} -f(q) \\ \mathbf{0} \end{pmatrix} - \begin{pmatrix} a_{pp} & \mathbf{a}_p^T \\ \bar{\mathbf{a}}_p & \mathbf{A} \end{pmatrix} \begin{pmatrix} p \\ s \end{pmatrix} + \mathbf{B}_p \xi \quad (2)$$

- This is fully **linear** in the harmonic limit: predict response properties analytically!
- The predicted response can be fitted to the optimal requirements for a given application.
- The thermostat “recognizes” the vibrational modes which are present, and automatically behaves according to predictions.

## Nuclear quantum effects by colored noise

Nuclear quantum effects are important whenever light atoms are present. The standard simulation technique uses the imaginary-time path integral formulation. **×10 to ×100 overhead over conventional MD**: prohibitive when high accuracy methods are used for forces.



For the harmonic oscillator, the quantum distribution is the same as that of a classical oscillator with a different, **frequency-dependent** effective temperature,

$$T^*(\omega) = \frac{\hbar\omega}{2k_B} \coth \frac{\hbar\omega}{2k_B T} \quad (3)$$

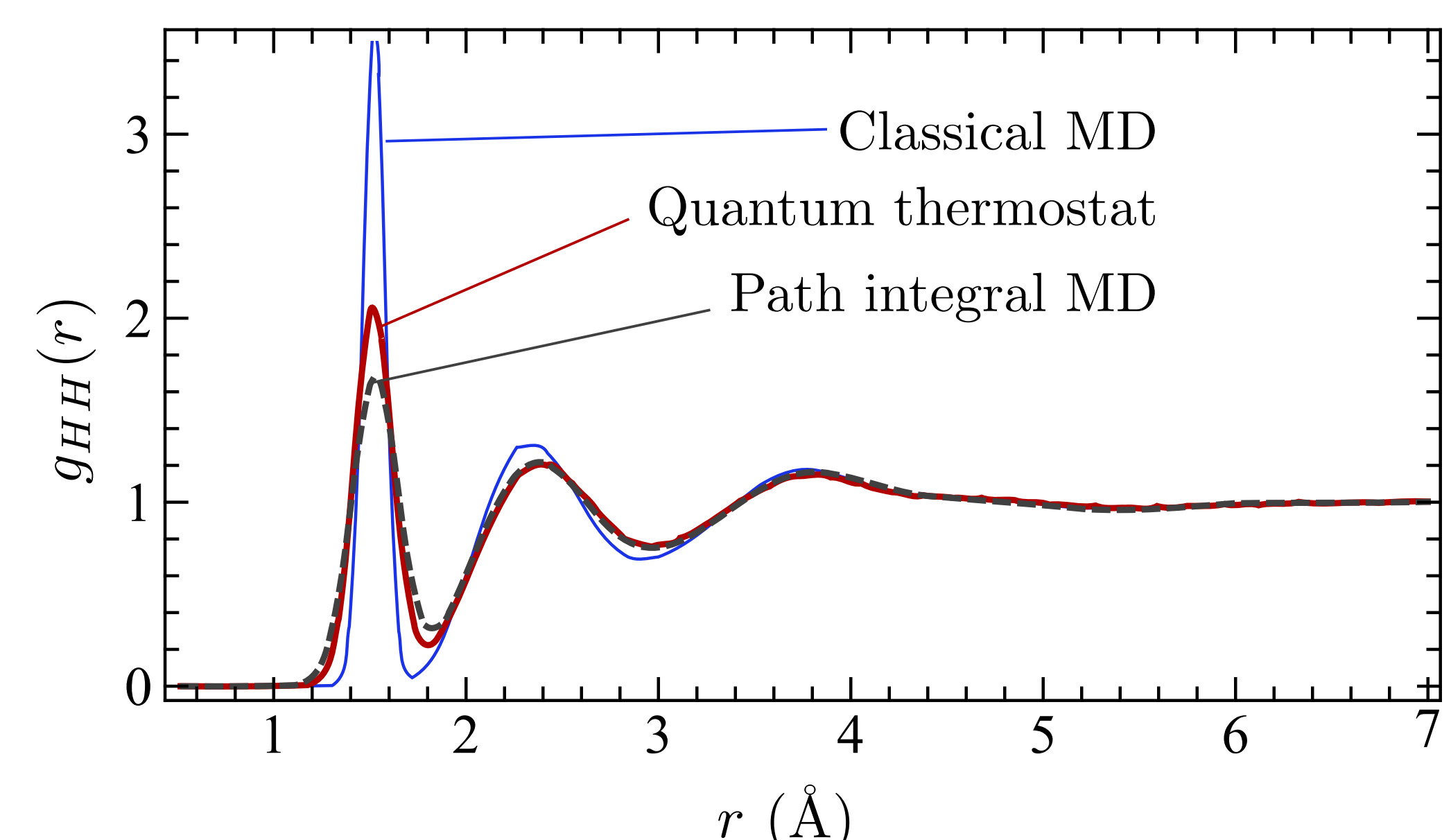
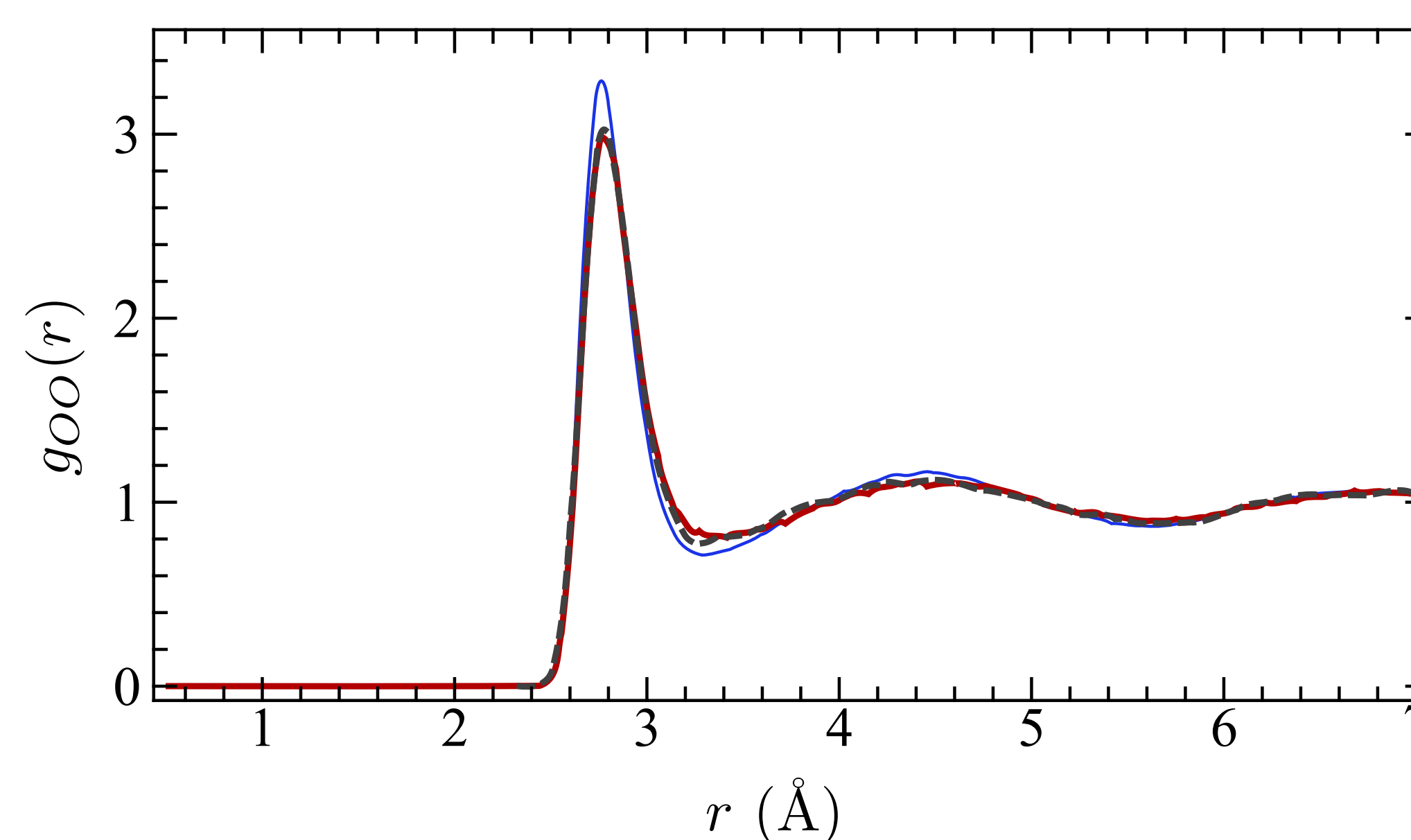
quantum = class.  $T^*$

$T^*(\omega)$  can be enforced automatically by an appropriate **non-equilibrium**, generalized Langevin equation!

## Quantum effects in liquid water

Water exhibits very strong nuclear quantum effects. Our technique performs a fitting assuming harmonic behavior, hence a liquid is a very stringent test because of the strong anharmonicity. Accuracy can be greatly enhanced by tuning the **coupling strength**.

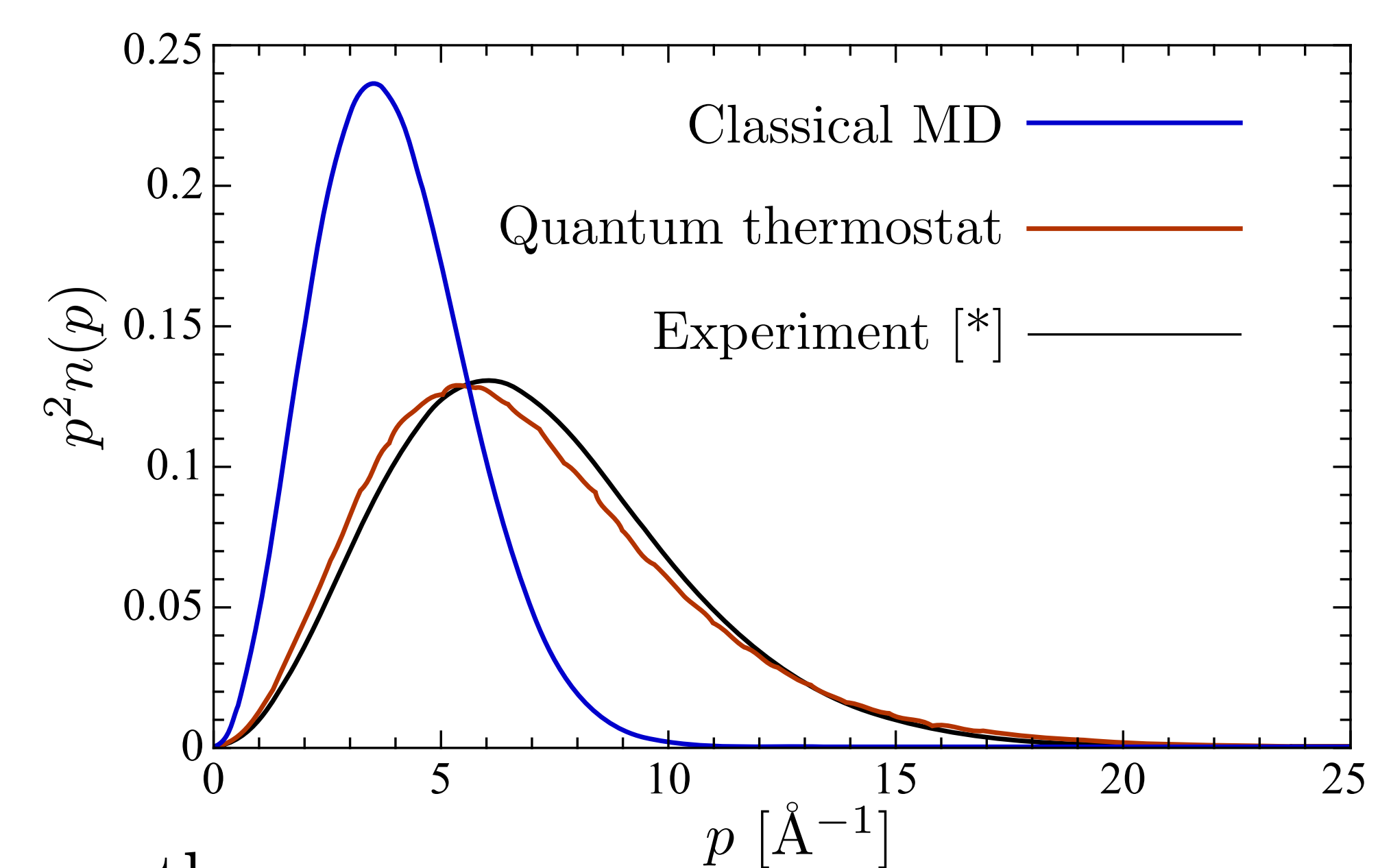
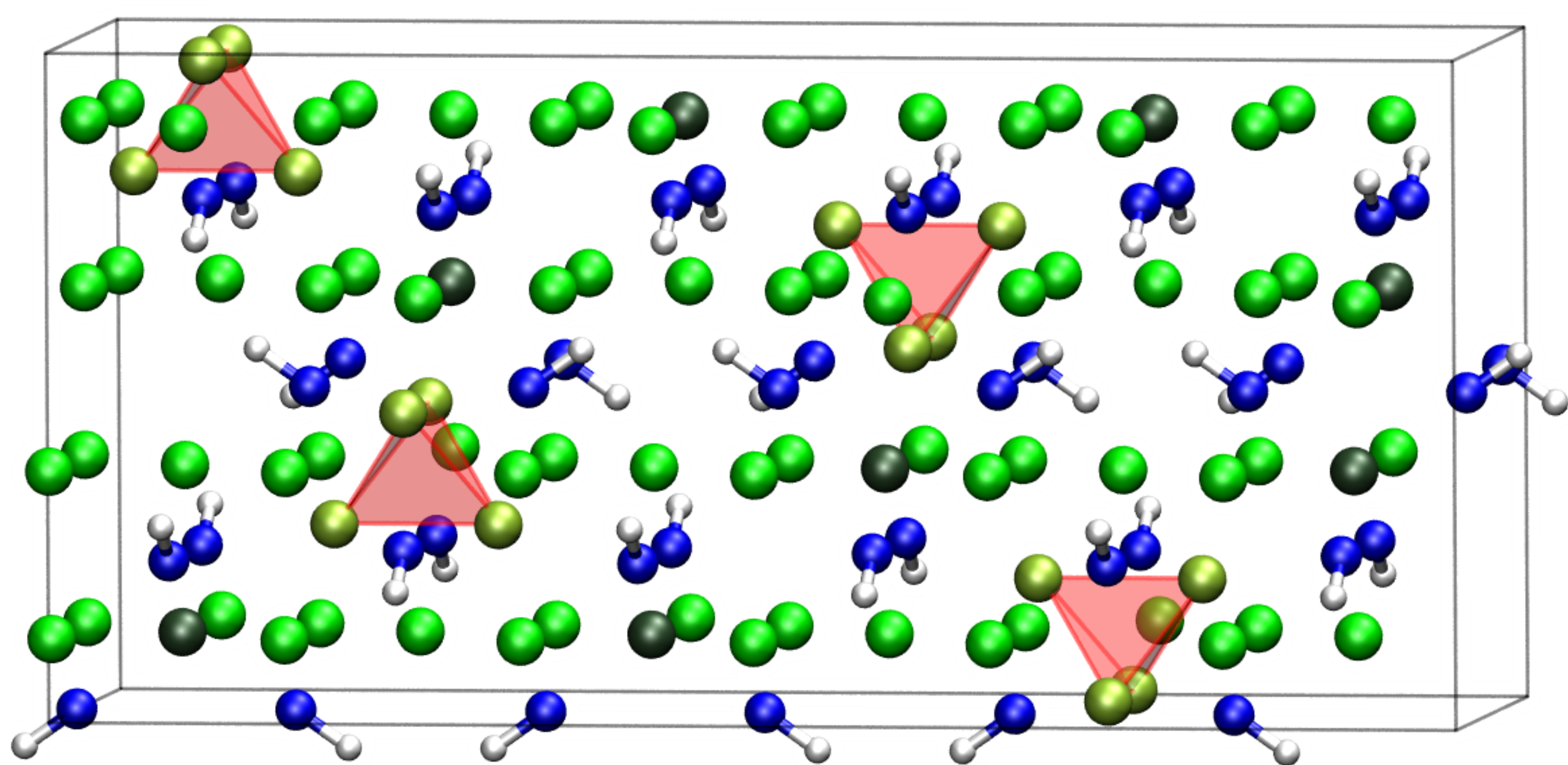
Radial distribution functions for a MD simulation at 300 K, using a force field[\*] fitted for path integral calculations.



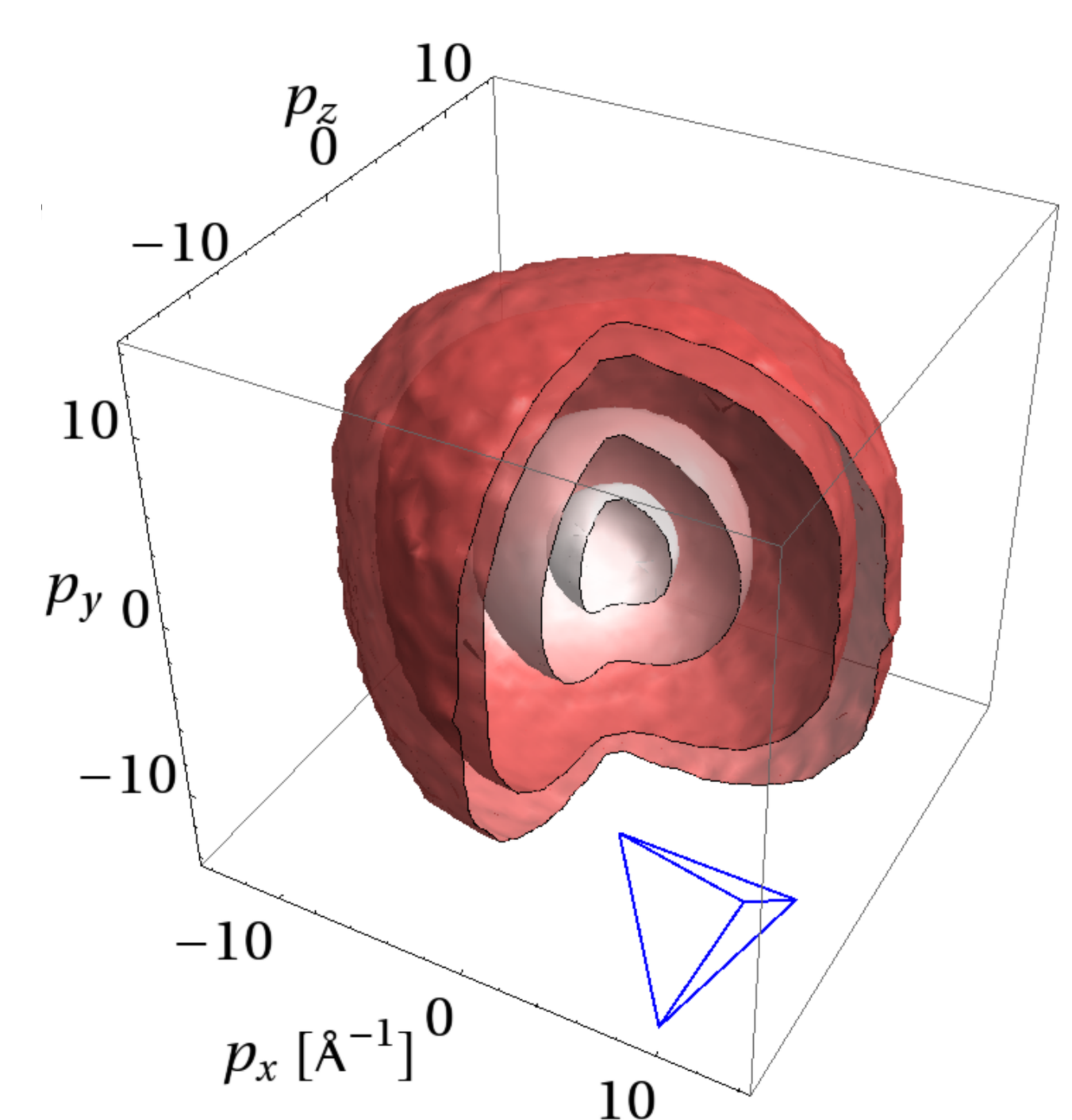
[\*] Habershon *et al.*, JCP 2010

## Proton momentum distribution in lithium imide

$\text{Li}_2\text{NH}$  has a **complex structure**, and a DFT treatment is required, as no empirical FF is available. This is a challenging example to apply the quantum thermostat. Nuclear quantum effects are important: when no fitting is used to model interactions, they would be completely ignored in the modelling. Quasi-harmonic approximation is problematic, because of the presence of anharmonic wagging modes of the imide groups. **A path integral treatment would be prohibitively expensive!**



It is possible to recover the proton momentum distribution by **inelastic neutron scattering** experiments. PMD contains information on the local environment of hydrogen atoms. Computing momentum distributions by path integral methods is complex and expensive. The quantum thermostats allows to extract the **anisotropic** distribution simply and inexpensively. The radial average agrees nicely with experiments.



[\*] A. Pietropaolo, private comm.

[1] M. Ceriotti, G. Bussi, and M. Parrinello, J. Chem. Theory Comput. 6, 1170 (2010)

[2] M. Ceriotti, G. Bussi, and M. Parrinello, Phys. Rev. Lett. 103, 030603 (2009)

[3] M. Ceriotti, G. Bussi, and M. Parrinello, Phys. Rev. Lett. 102, 020601 (2009)