Theoretical benchmarks of deep inelastic neutron scattering. From the kinetic energy to the full particle momentum distribution

Michele Ceriotti, COSMO

Neutron Matters, Rome, Nov. 2017

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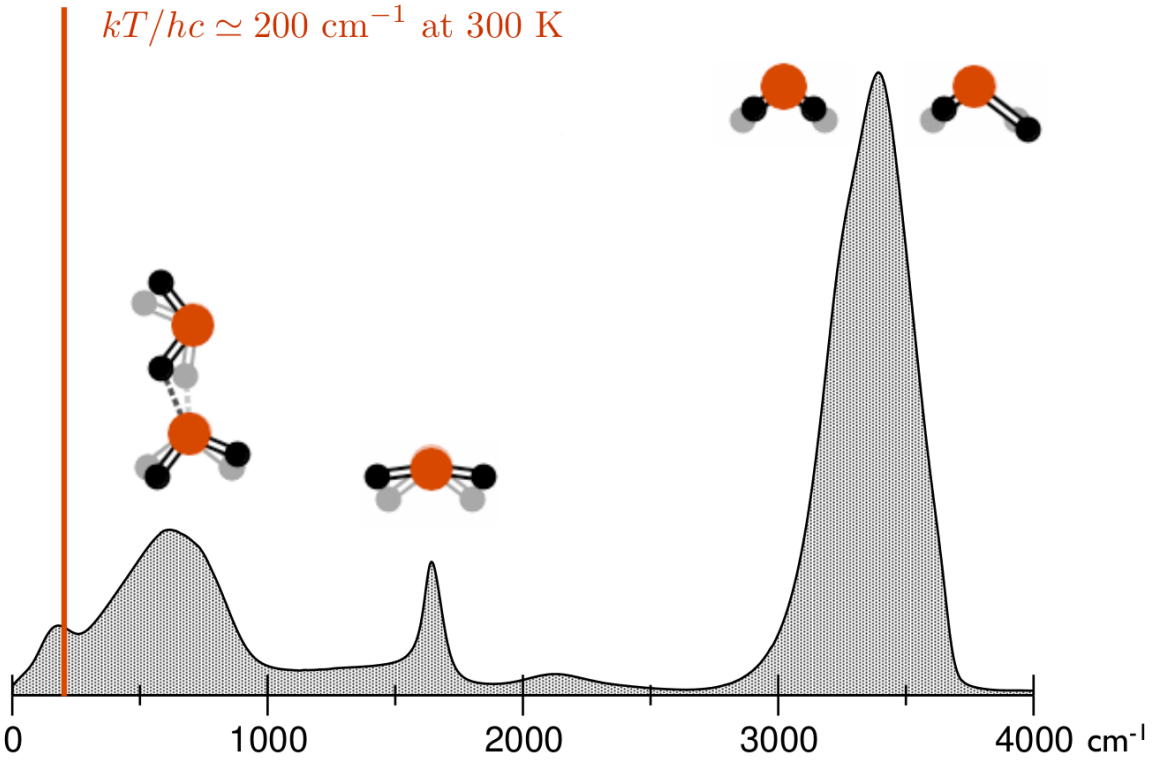
Nuclear quantum effects

- Light nuclei do not obey Newtonian mechanics
- Quantum nature of a vibrational mode of frequency ω becomes important when $\hbar\omega / k_B T > 1$.
  - Light nuclei have strong quantum behavior even at room temperature: $k_B T / \hbar \approx 200$ cm^{-1}!
  - Example: properties of isotopically-pure water



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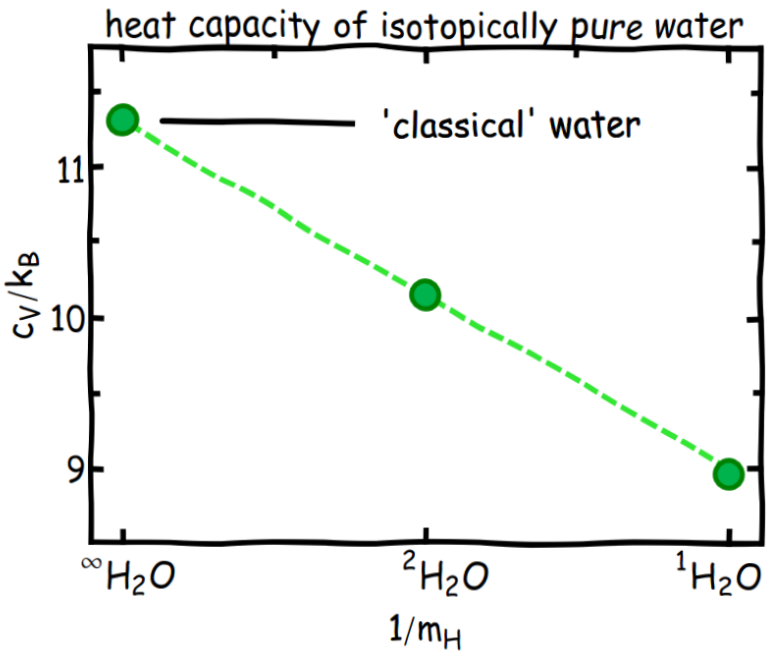

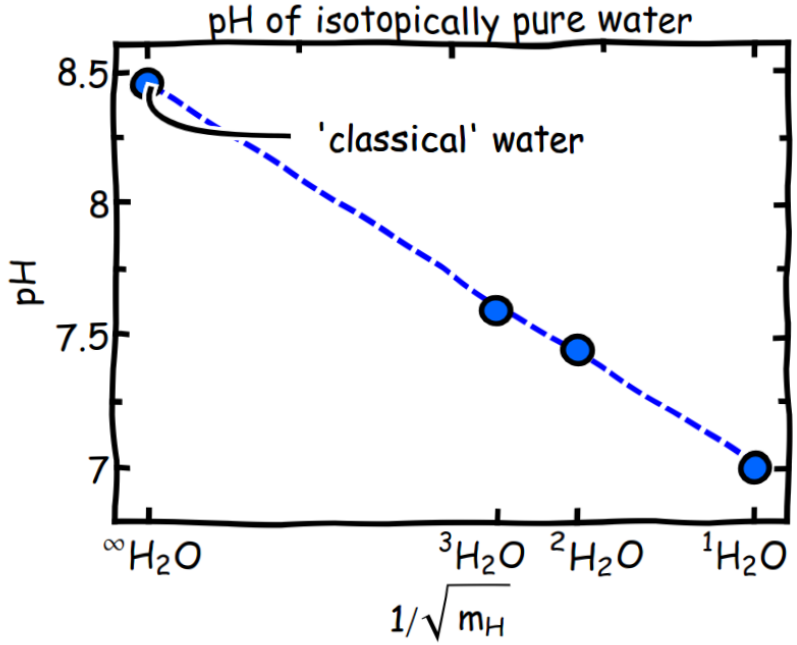

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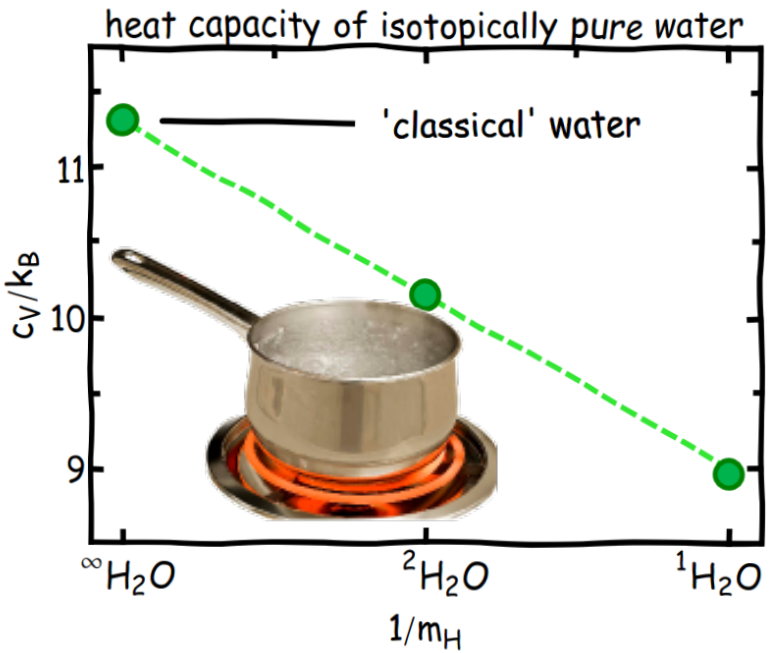
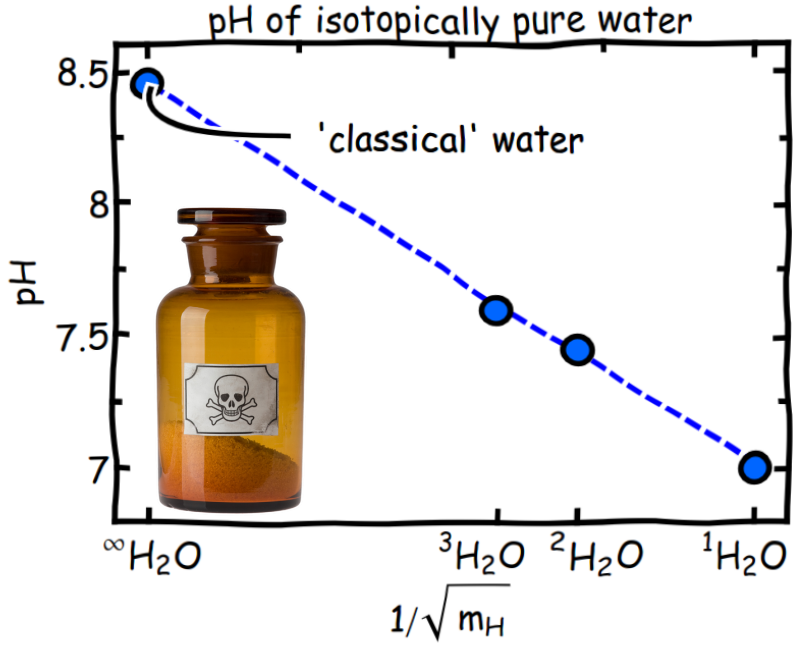


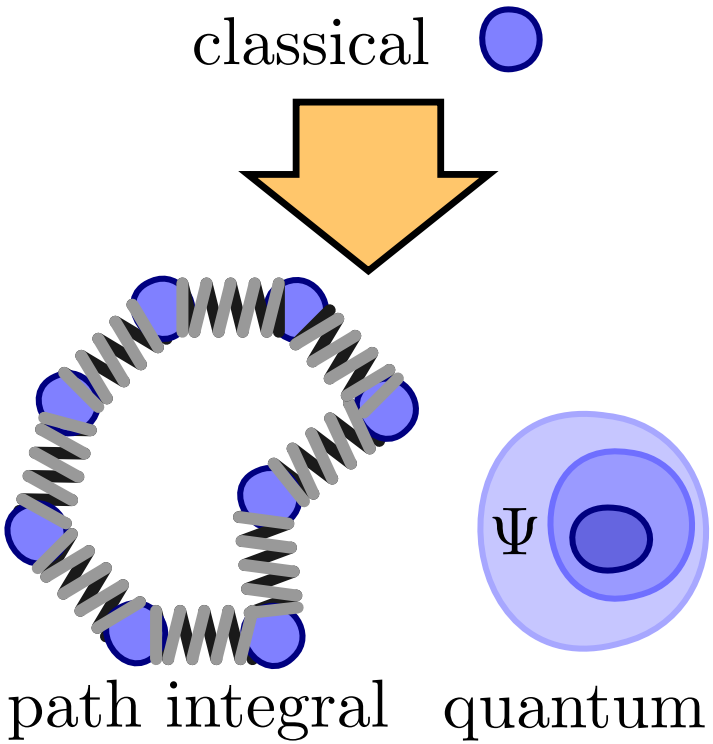


How to include NQEs in MD

- Solving the Schrödinger equation for the nuclei is impractical
- A connection exists between the statistical properties of a quantum system and those of a classical **ring polymer**

$$H_P = \sum_{i=1}^{P} \left[V(\mathbf{q}_i) + \frac{\mathbf{p}_i^2}{2m} + \frac{1}{2} m\omega_P^2 (\mathbf{q}_i - \mathbf{q}_{i-1})^2 \right]$$

  - Harmonic springs hold corresponding particles together
  - Convergence to quantum averages for $P \gg \hbar\omega / k_B T$



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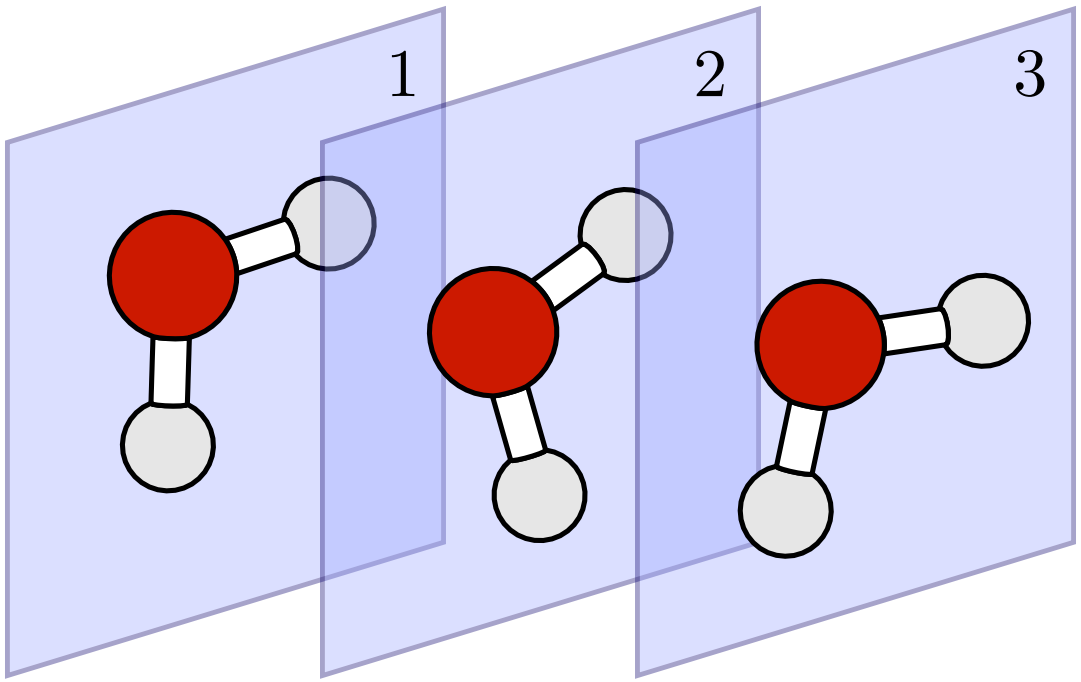

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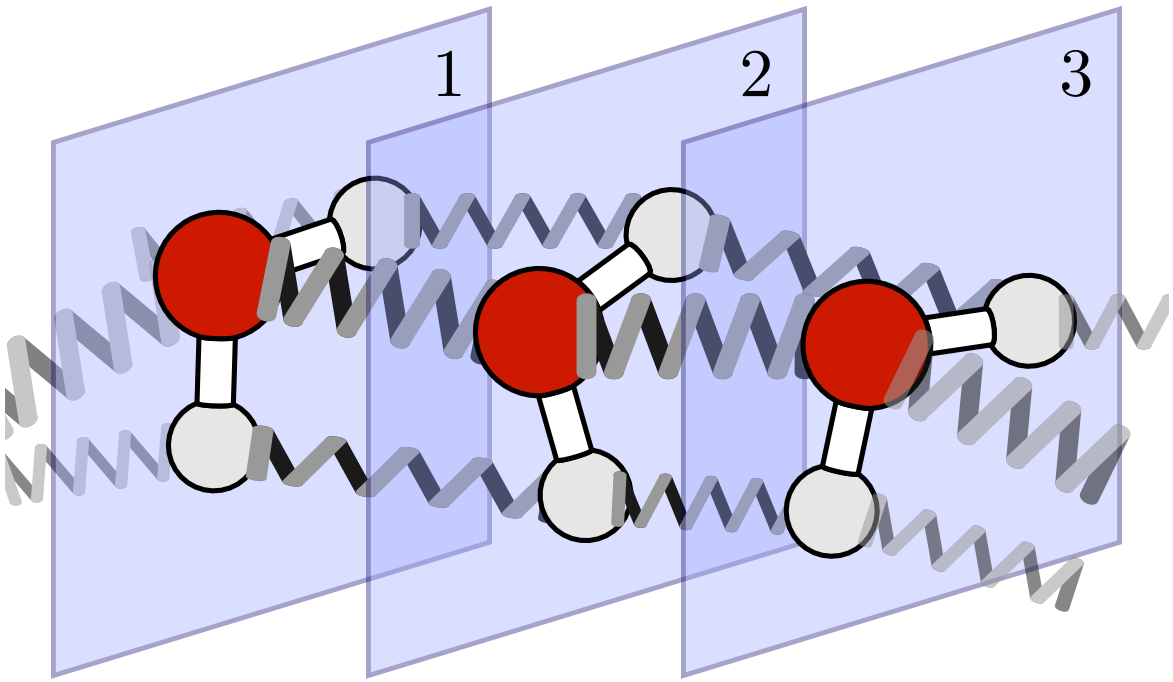

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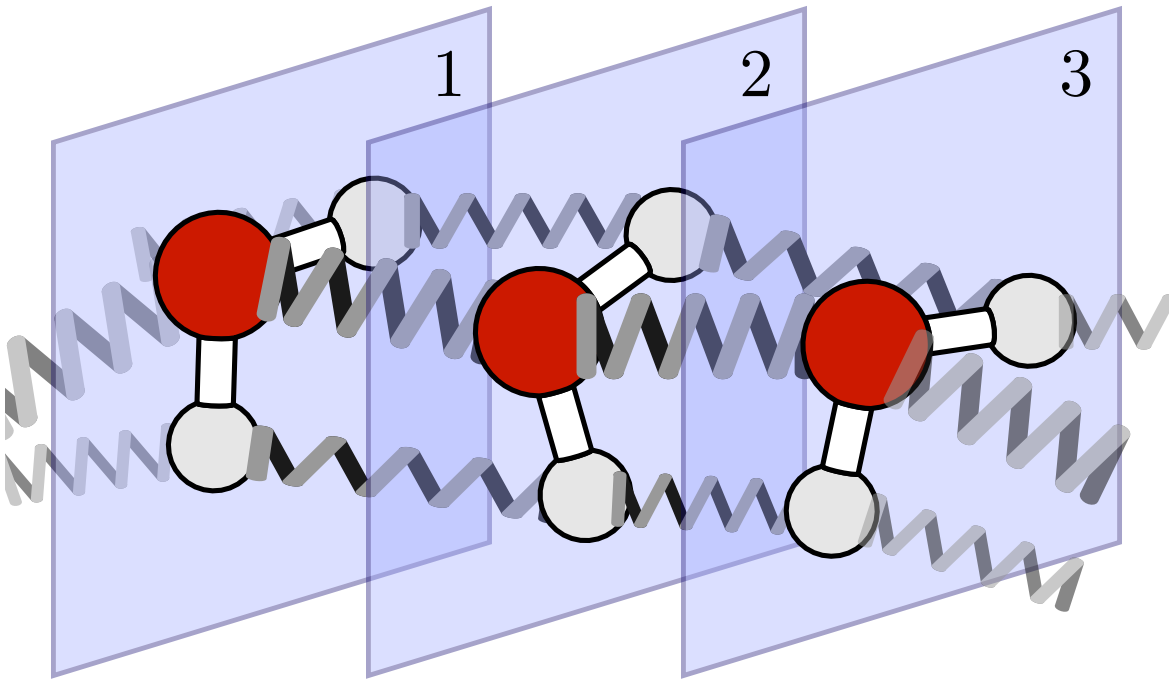
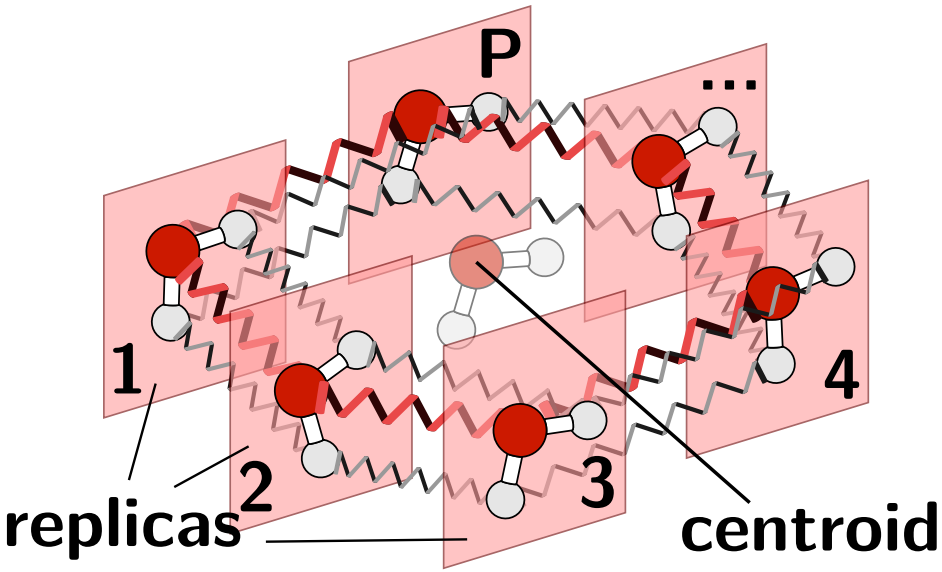
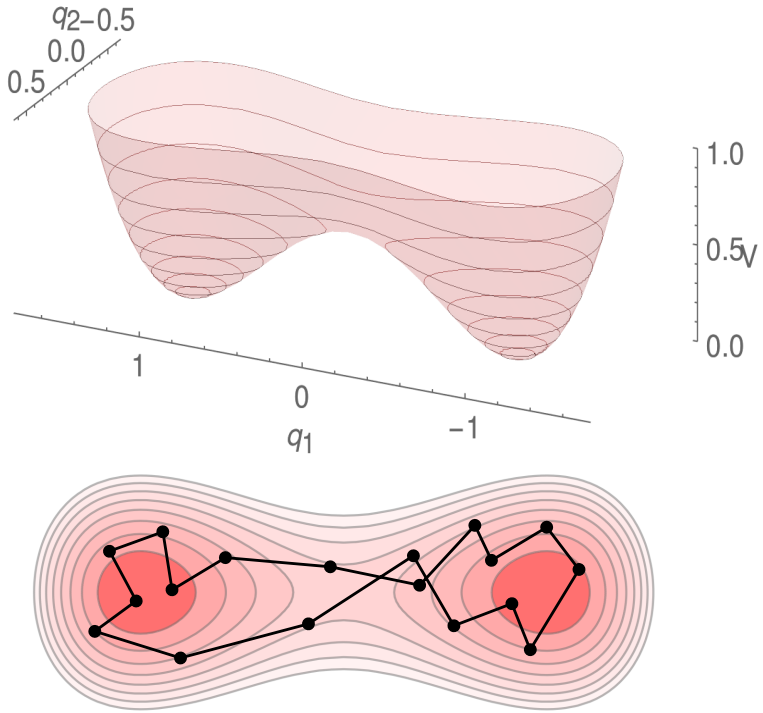


NQEs For The Masses

- Many techniques have been developed to reduce the cost of PIMD
  - Ring-polymer contraction (when slow & accurate/fast & cheap splitting of the potential is available)
  - High-order PI (by reweighting or finite-difference evaluations)
  - Colored-noise thermostats (personal favourite :-))
- All of this is readily available in i-PI





Markland, Ceriotti, Nature Review Chemistry, in press

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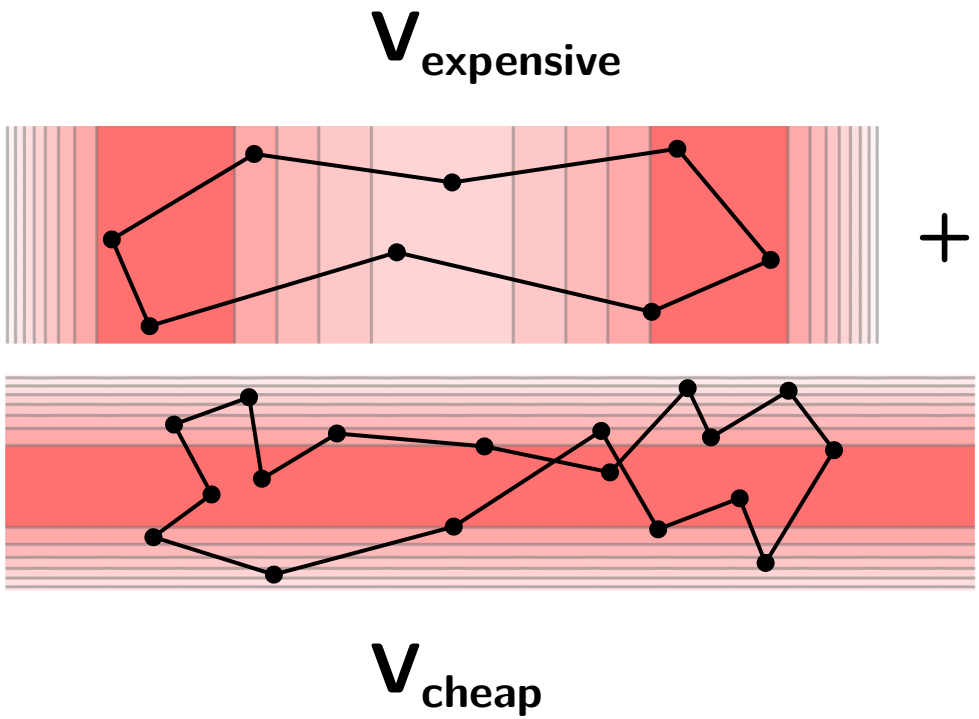

Markland, Manolopoulos, Chem. Phys. Lett. (2008); Kapil, VandeVondele, Ceriotti, J. Chem. Phys. (2016)

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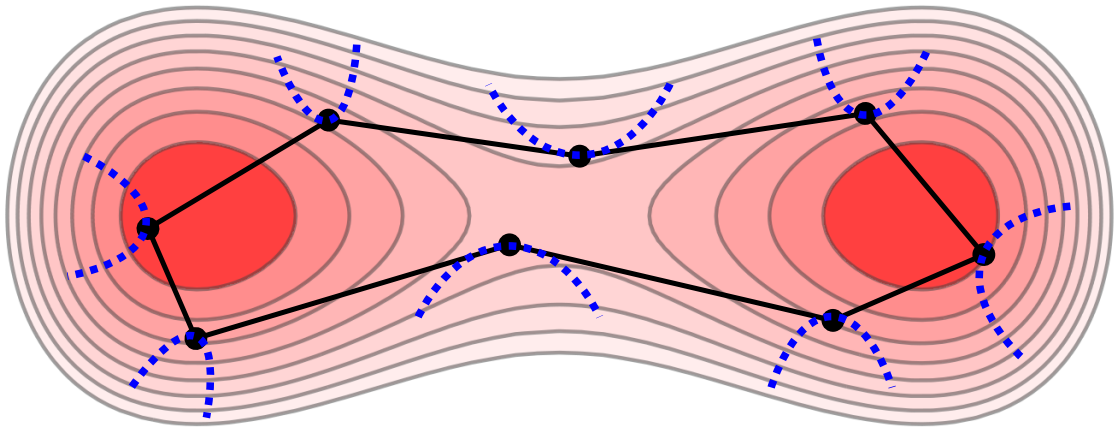
$$V_{sc} \sim V + |V'|^2$$



Jang, Voth, J. Chem. Phys. (2001); Kapil, Behler, Ceriotti, J. Chem. Phys. (2016)

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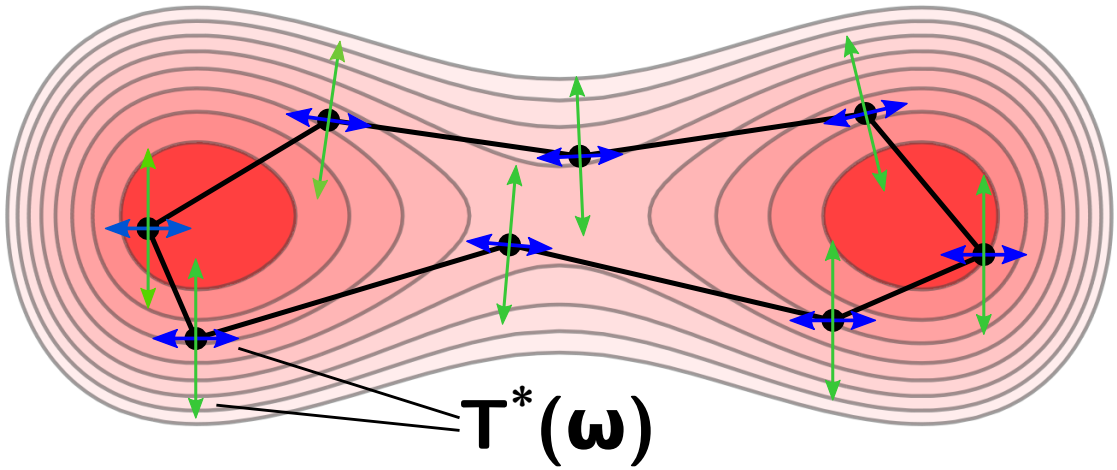

Ceriotti, Manolopoulos, Phys. Rev. Lett. (2012)

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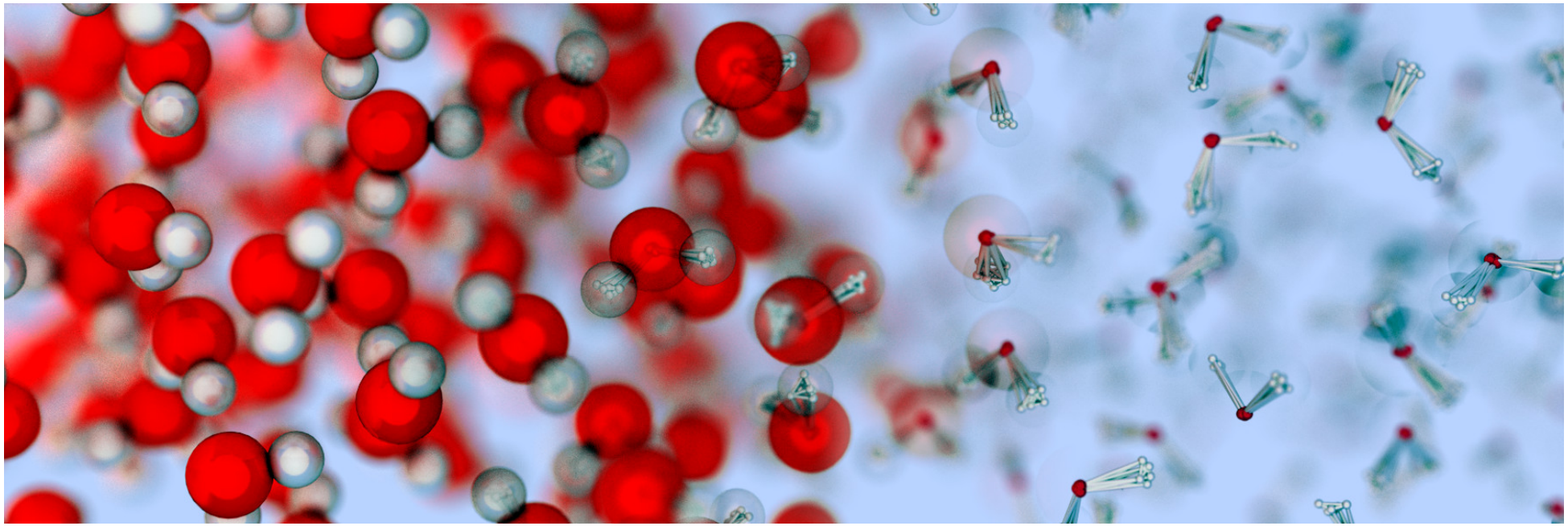
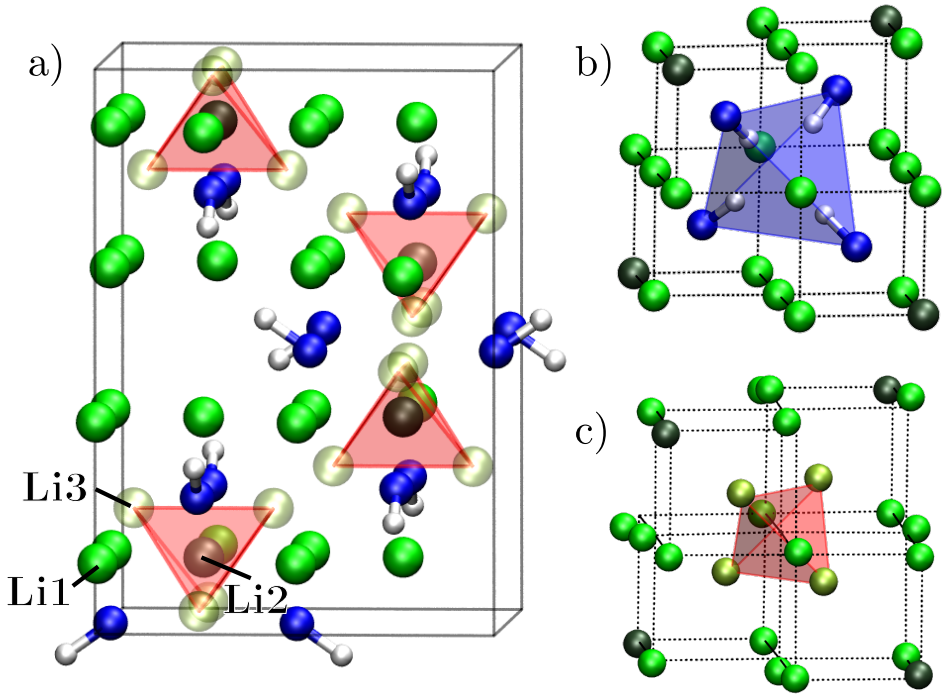


Ceriotti, More, Manolopoulos, Comp. Phys. Comm. (2014); **http://ipi-code.org**

Lithium Imide: a DINS story

- Partially disordered structure with fractional occupations.
- Strongly anharmonic system
  - Librations of NH groups.
  - Quasi-harmonic description is inadequate
  - Pronounced quantum effects on hydrogens
- Quantum effects are dramatic in the proton momentum distribution



Ceriotti et al., Phys. Rev. B (2010)
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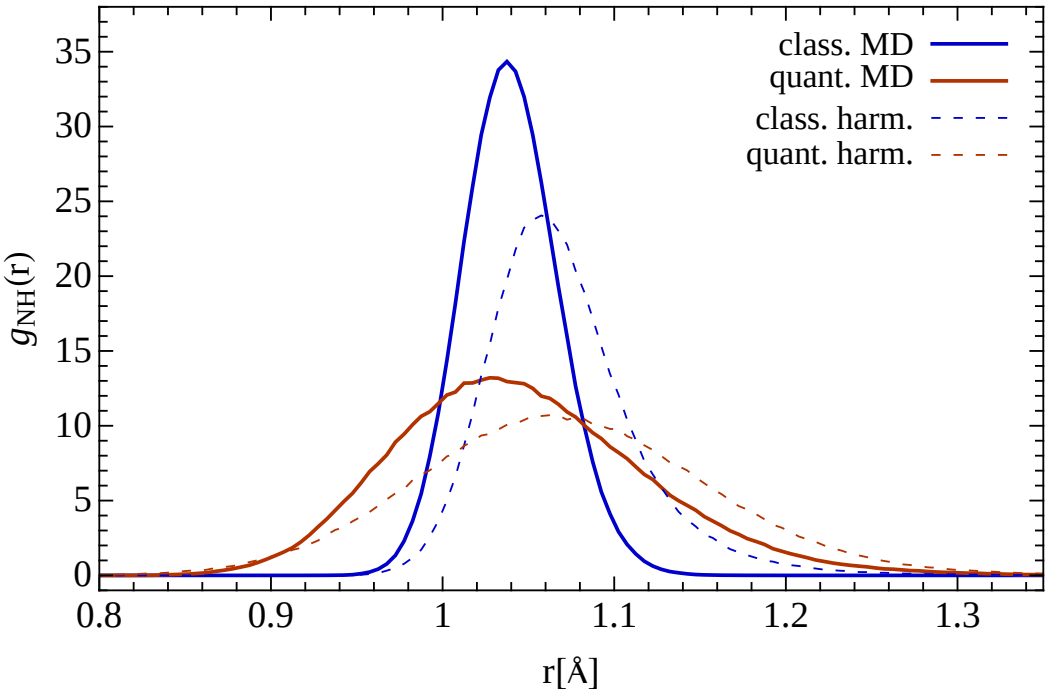

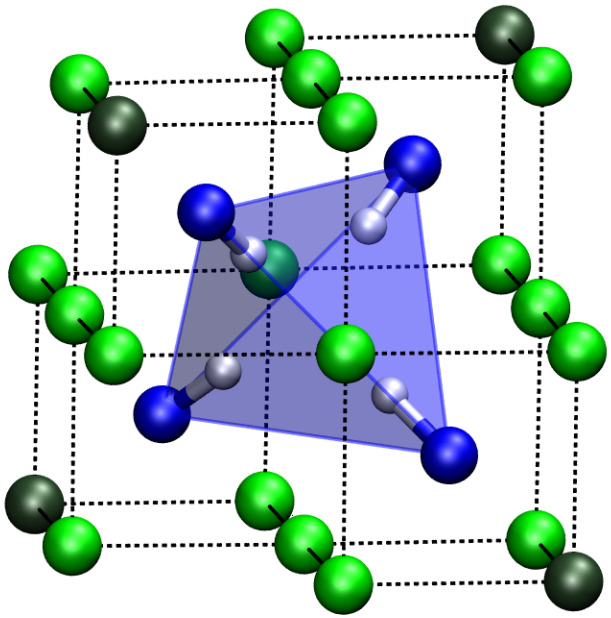

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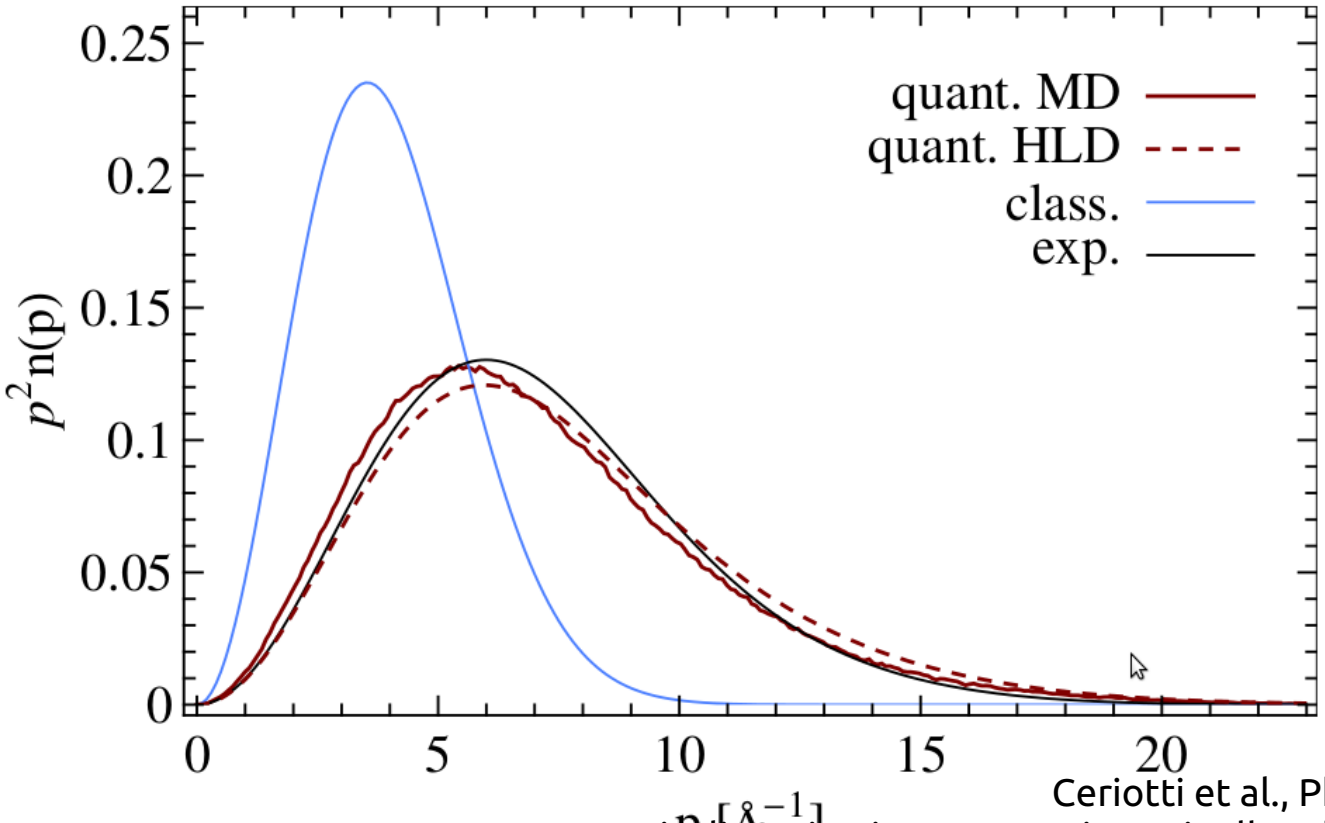

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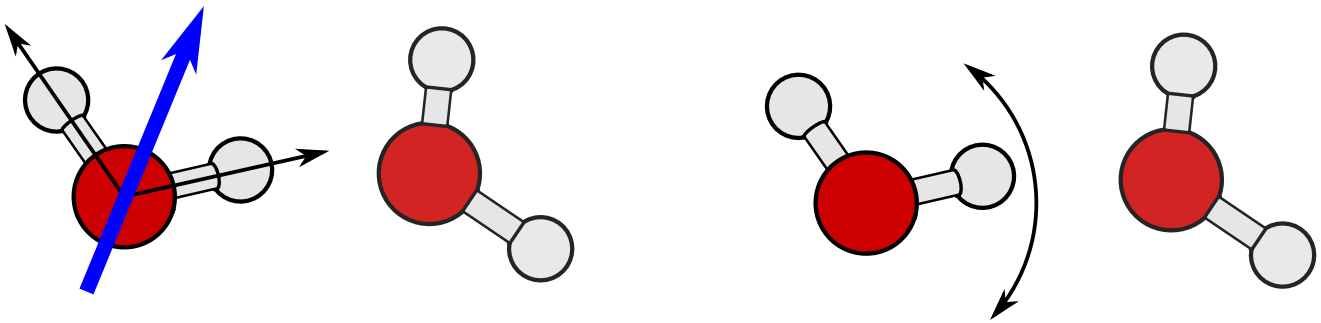
Competing quantum effects in water

- If nuclear quantum effects are so important, how comes that the melting point of H_2O and D_2O differ by "just" 4 K?
  - Growing theoretical evidence supports a **competition** between inter and intra molecular NQE
- The particle momentum distribution in water is strongly quantized: $\gg k_B T/2$ ($\approx$ 12meV) and **anisotropic**
- Compare with DINS to get **direct experimental evidence** of competing quantum effects in heavy water!



Habershon et al. JCP 2009; Li et al. PNAS 2011;
Markland, Berne PNAS 2012; Liu et al. JPCC 2013

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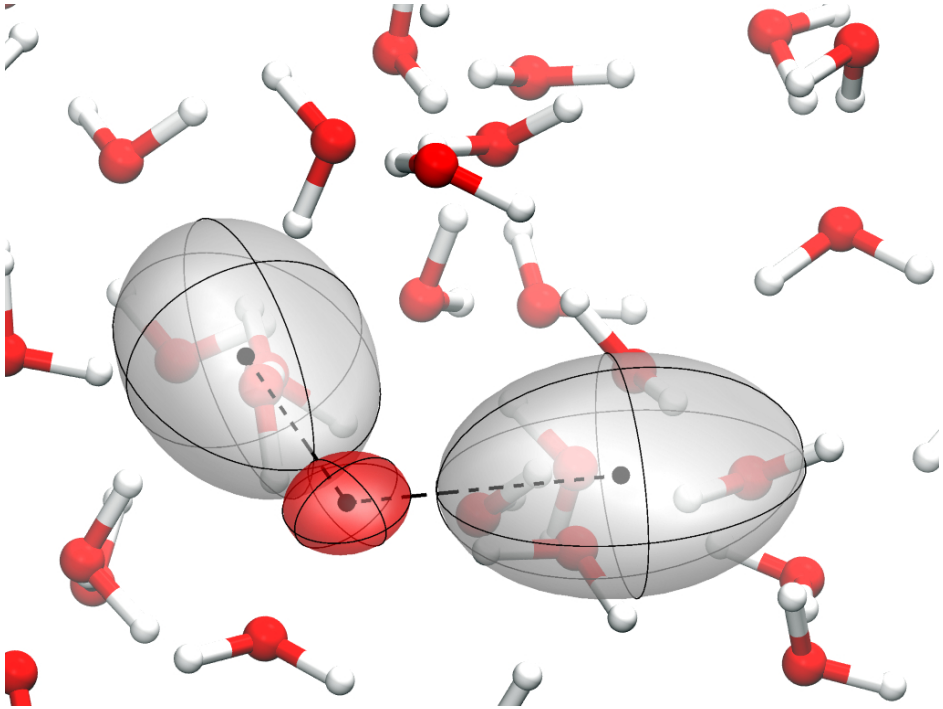
BLYP functional, DZVP basis, GTH PP, CP2K, PIGLET (6 beads)

Anisotropic PMD
in liquid water
Ceriotti & Manolopoulos PRL
2012



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D_2O, 280K	15.8	31.1	61.8	108.7

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exp/th (meV)	E_x	E_y	E_z	E_K
Liquid, 280K	**18.8**/15.8	**38.6**/31.1	**54.2**/61.8	**110**/108.7
Ice, 274K	**22.5**/17.0$\uparrow$	**37.4**/30.9$\downarrow$	**48.1**/60.4$\downarrow$	**108**/108.3

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Isotope Fractionation in Water

- Different phases in equilibrium contain different fractions of light and heavy isotopes

$$\mathrm{H}_{phase1} + \mathrm{D}_{phase2} \overset{\Delta G}{\rightleftharpoons} \mathrm{D}_{phase1} + \mathrm{H}_{phase2}$$

  - Very useful for geochemistry and atmospheric sciences: extremely accurate experimental data available
  - Very demanding calculations, but can be made cheaper with a few tricks

$$\Delta G \propto \int_{m_\mathrm{H}}^{m_\mathrm{D}} \frac{T_1(\mu)}{\mu} - \frac{T_2(\mu)}{\mu} \mathrm{d}\mu$$

- Purely quantum mechanical effect, would be zero for classical nuclei – Ideal test of the quality of DFT functionals
  - Because of quantum fluctuations, the simulations probe different regions of the potential energy surface

Ceriotti & Markland, JCP (2013); Cheng & Ceriotti, JCP (2014)

A comparison of different functionals

- Comparison of fractionation ratios with different functionals
  - Break down in different contributions give more insight
  - Comparison of (virtually) exact results in the gas phase, infer reference value for ΔA_l (CCSD(T) PES for the monomer)
- Temperature dependence for BLYP – qualitatively predicts inversion
- Fractionation can be linked to particle KE using the gas-phase molecule as reference

$$K_l(H) - K_g(H) \approx k_B T \ln \alpha_{l-g} / \left(2 - 2\sqrt{m_H/m_D}\right)$$

	PBE	BLYP	BLYP-D3	PBE0	B3LYP	B3LYP-D3	**Exp**
$-10^3 \Delta G / k_B T$	-17	62	48	90	102	95	**73**
O-H	-409	-292	-272	-241	-199	-205	-
Plane	114	104	90	99	88	87	-
Orthogonal	278	250	230	232	213	213	-

Partridge & Schwenke, JCP 1997;
Wang, Ceriotti & Markland, JCP 2014

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(meV)	PBE	BLYP	BLYP-D3	PBE0	B3LYP	B3LYP-D3	**Exact**
K_v	147.1	145.6	145.8	152.3	149.5	149.5	**151.1**
ΔA_v	-88.1	-87.2	-87.3	-91.1	-89.6	-89.6	**-90.4**
K_l	146.7	148.3	147.5	155.6	153.7	153.3	**-**
ΔA_l	-87.7	-88.8	-88.5	-93.4	-92.3	-92.1	**-92.3**

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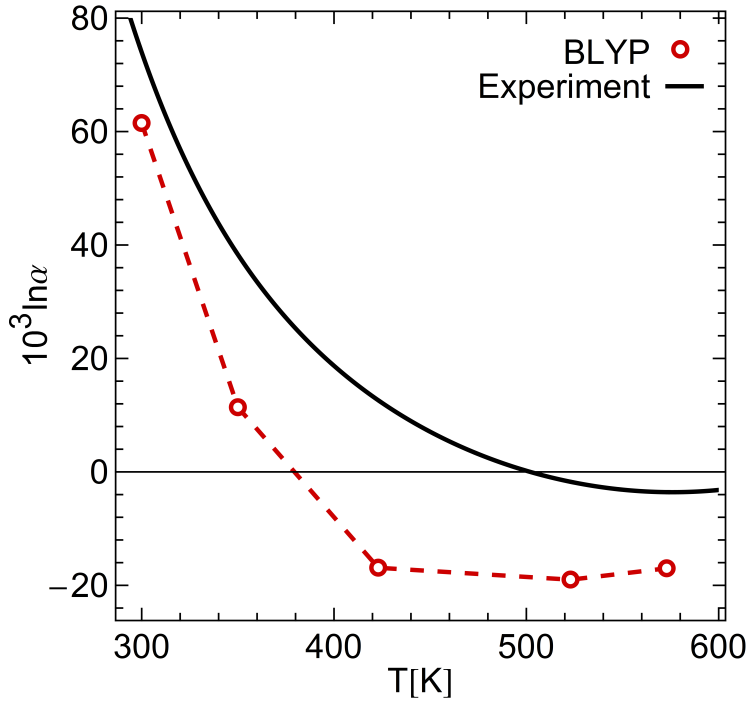

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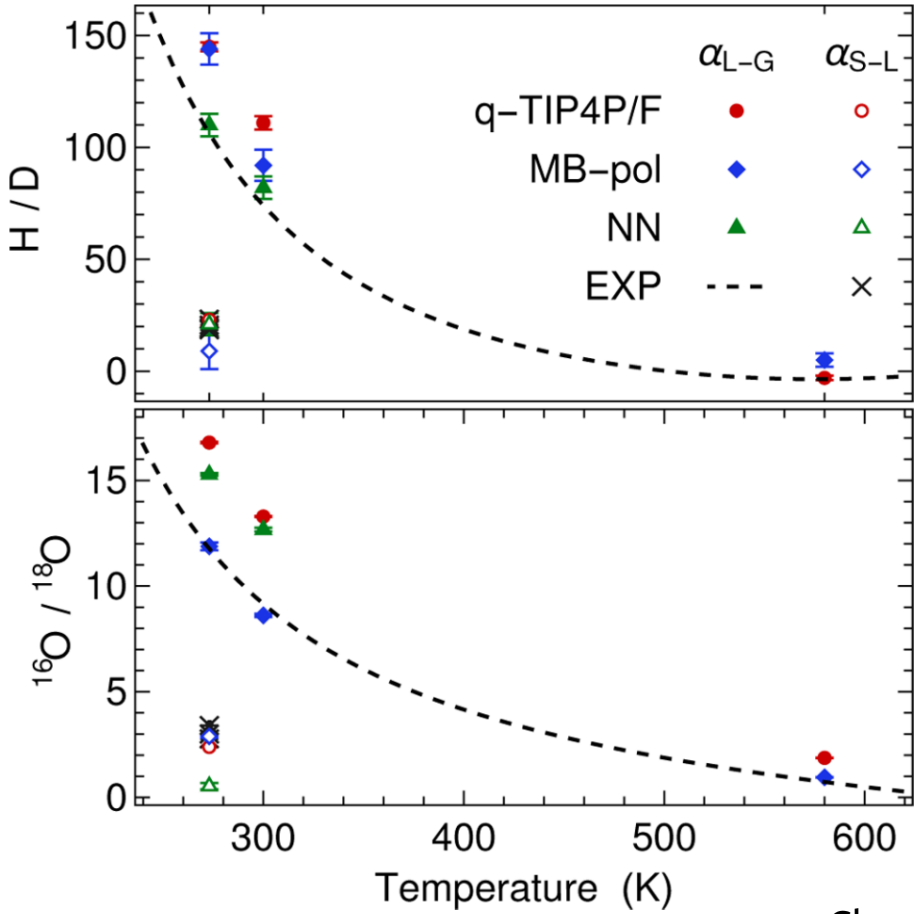
(meV)	273K	300K	580K
K_l from α&K_g	151.7	153.6	172.3
K_l from DINS	150±2 (BJP)	143±3 (PRL08)	172±5 (PRL08)

Colognesi, Phys. B 2011; Cheng, Behler, Ceriotti, JPCL 2016

A Benchmark: QKE at The Triple Point

- Comparison of Q-TIP4P/f, MB-POL, B3LYP+D3-NN
- Excellent results on isotope fractionation testify accuracy of the methods
- Very consistent results on QKE. $P = 64$ is mandatory
- OK match with DINS for K_l (156±2 meV @271K) & K_s (157±2 meV @271K). Puzzling discrepancy @300K (DINS: 146±3 meV, MB-POL: 155 ± 2meV)



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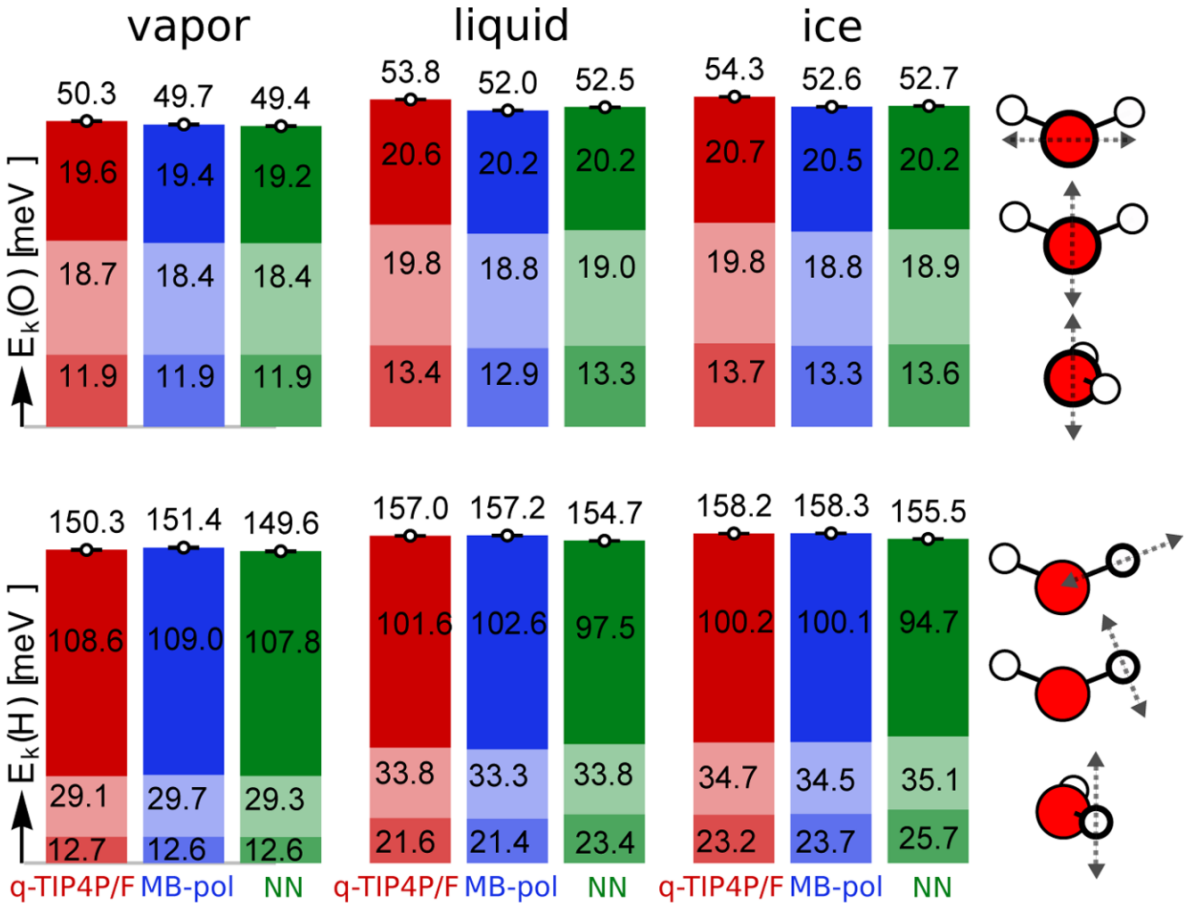

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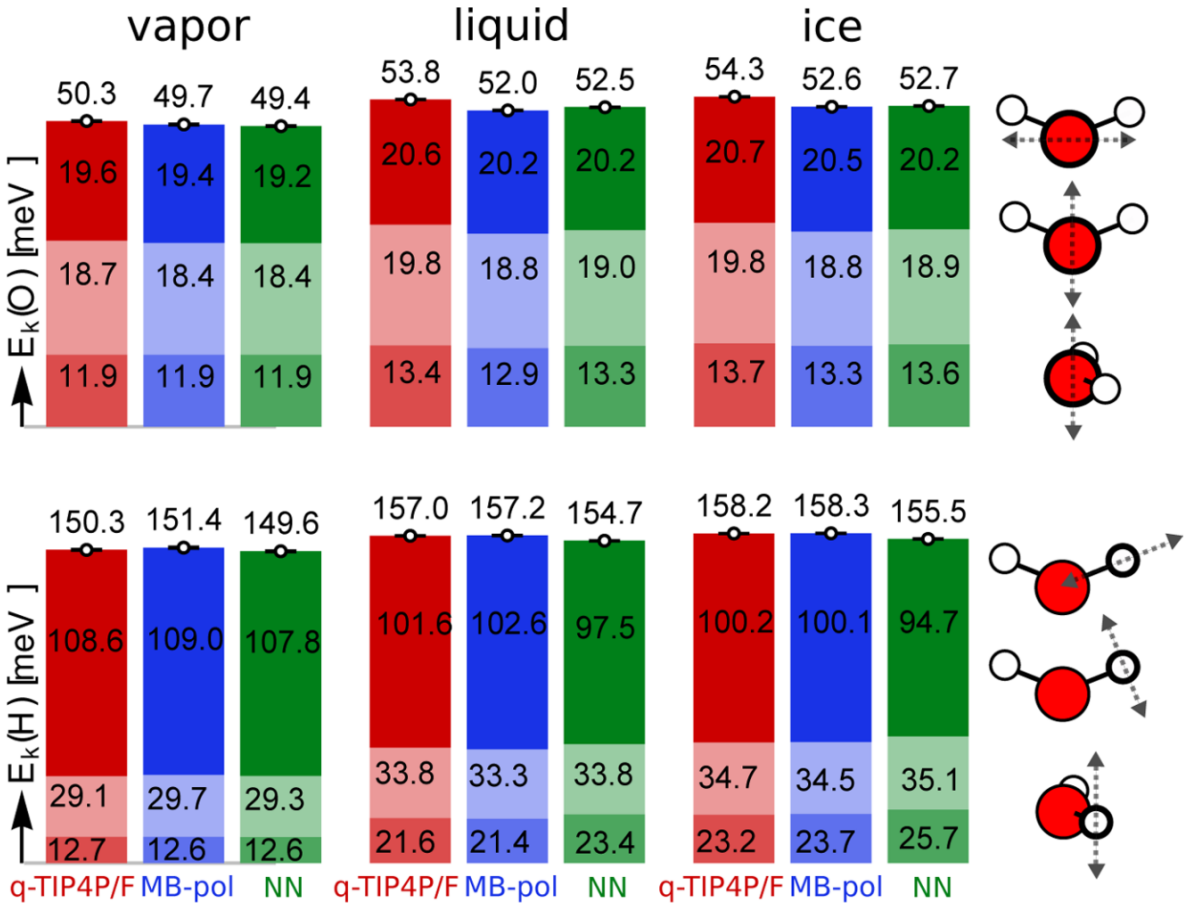
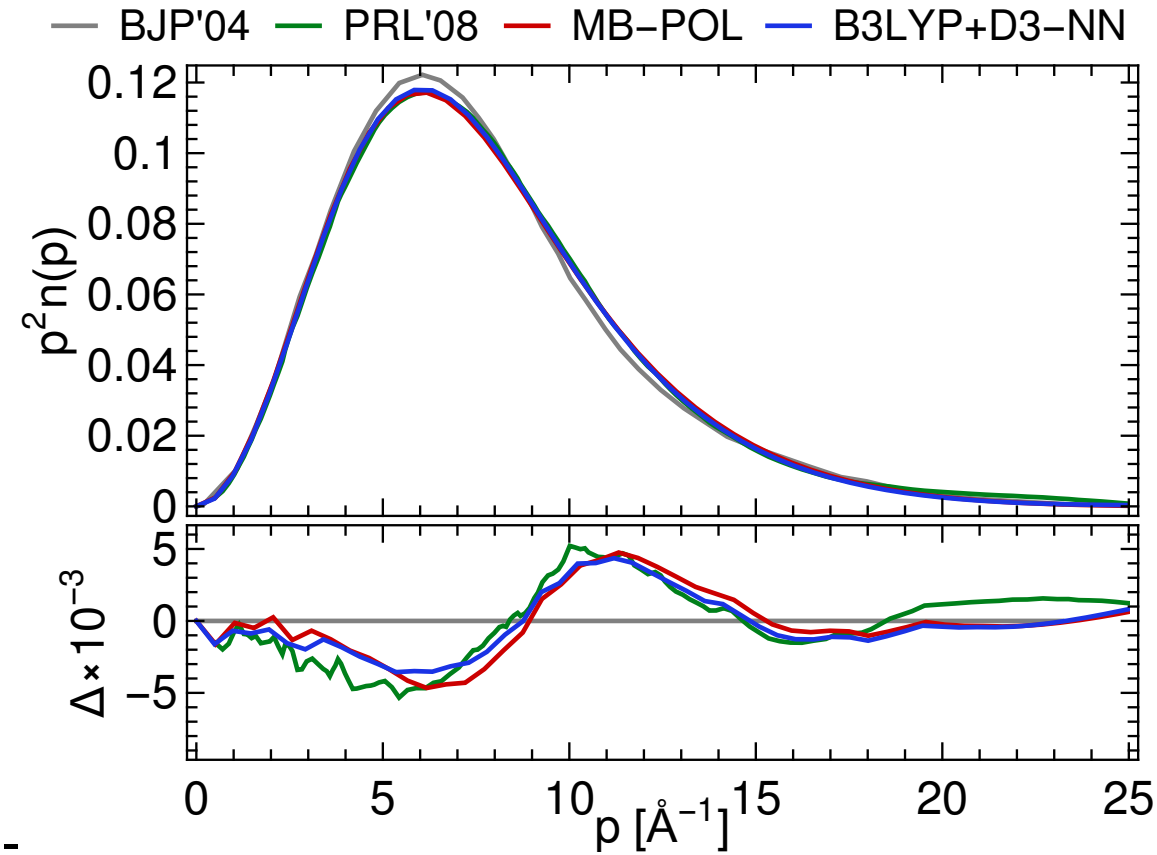


Andreani, Romanelli, Senesi, JPCL 2016

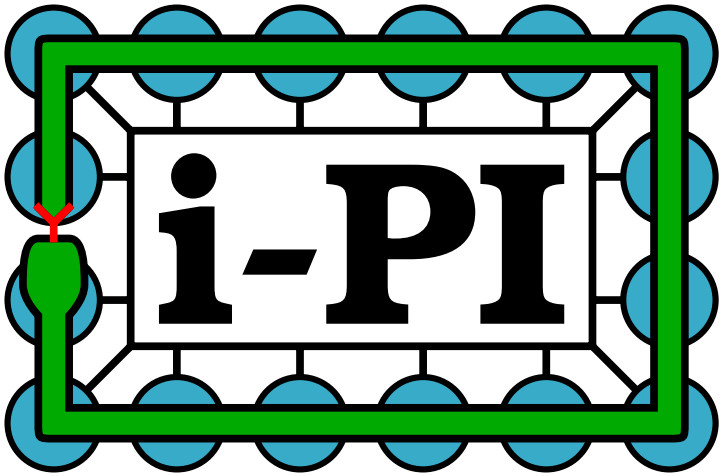
Is there more than p^2 in the PMD?

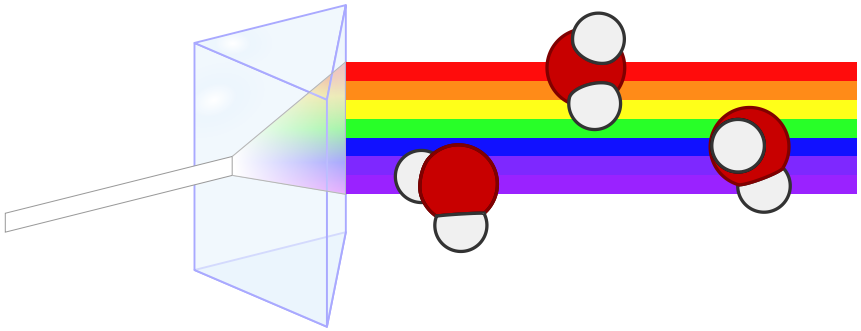
- Finally, open path integrals are coded into i-PI. We can easily compute PMD for different potentials: MB-POL and B3LYP+D3 are remarkably similar
- The discrepancy with DINS is significant. The spherically-averaged $n(p)$ is rather featureless: anisotropic Gaussian fit is the best one can extract with current accuracy of DINS



Conclusions & Outlook

- Proper modelling of NQEs is now affordable and requires no implementation effort. Open paths and $n(p)$ now available in i-PI
- Kinetic energy properties (isotope fractionation, DINS measurement) give direct theoretical & experimental probe into quantum fluctuations
- Theoretical and experimental estimates of $n(p)$ for water are converging. Still weird discrepancy at ~300K, should work together to resolve it
- How can we get more information out of DINS experiments?

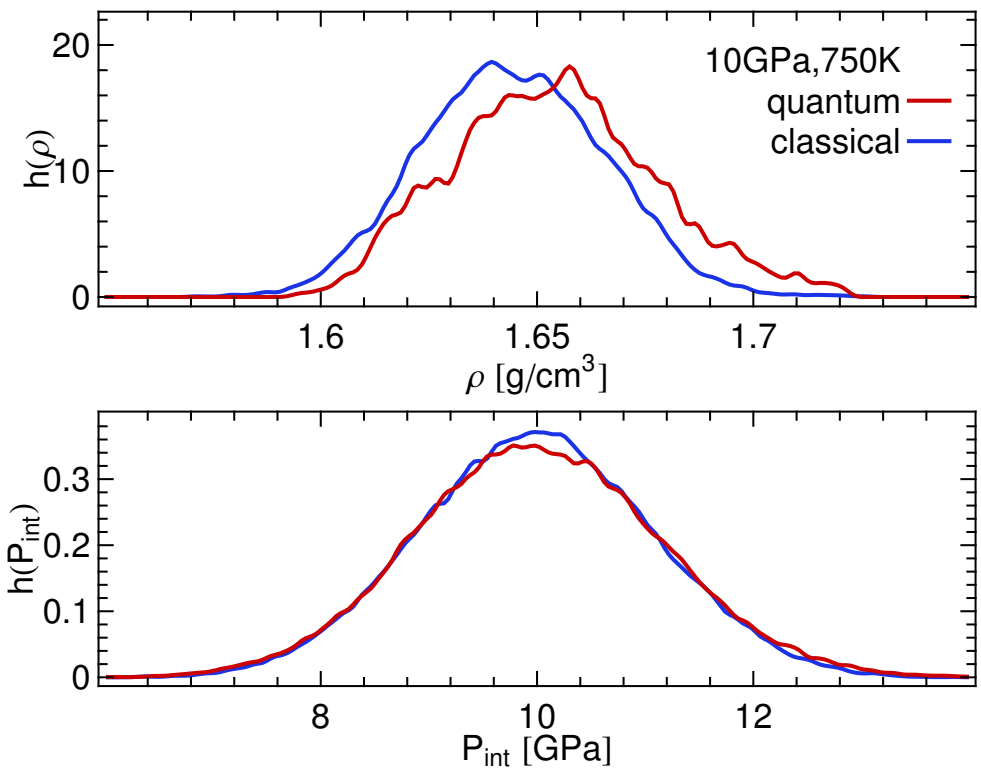




http://gle4md.org/

Self dissociation at 10GPa

- Quantum effects have a small (but noticeable) effect on density
- Pressure promotes water dissociation. Presence of a large concentration of charged species, particularly with NQEs



Ceriotti, More, Manolopoulos, Comp. Phys. Comm. 2014

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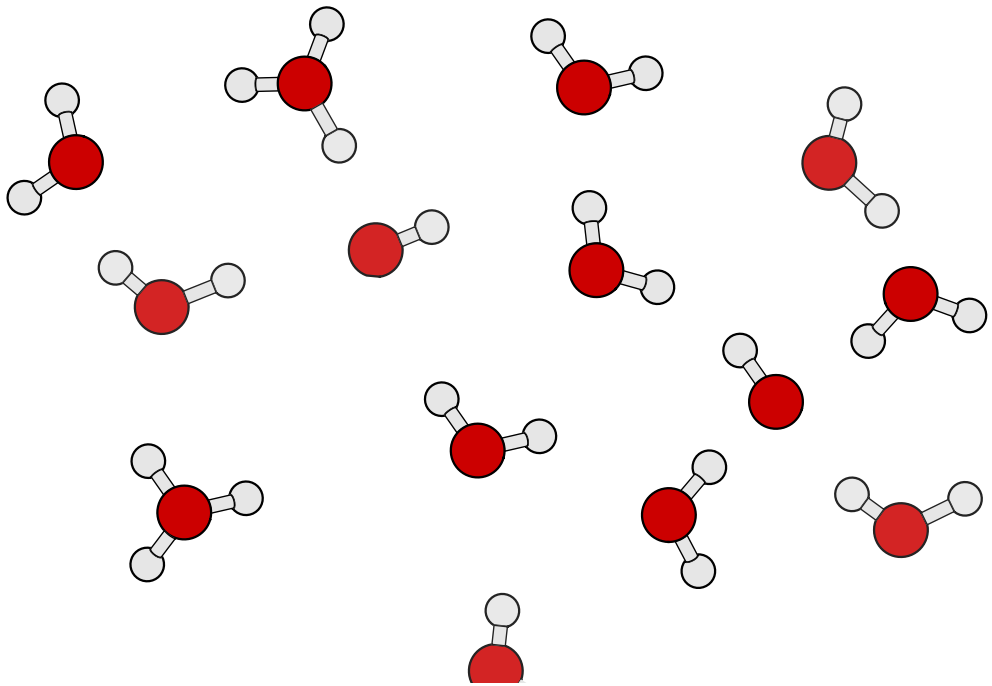

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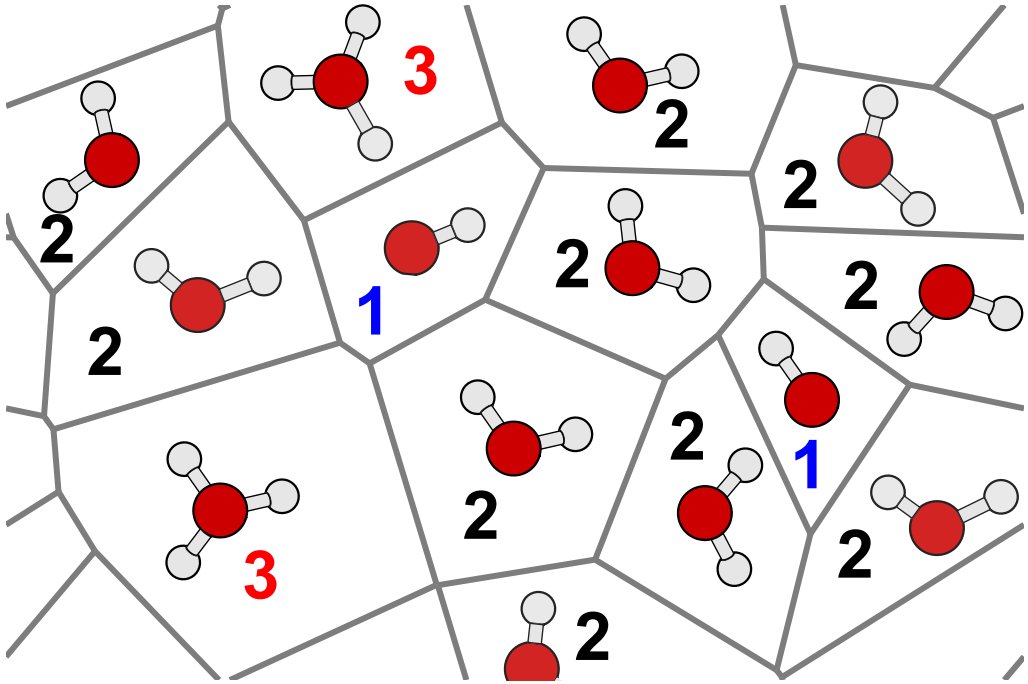

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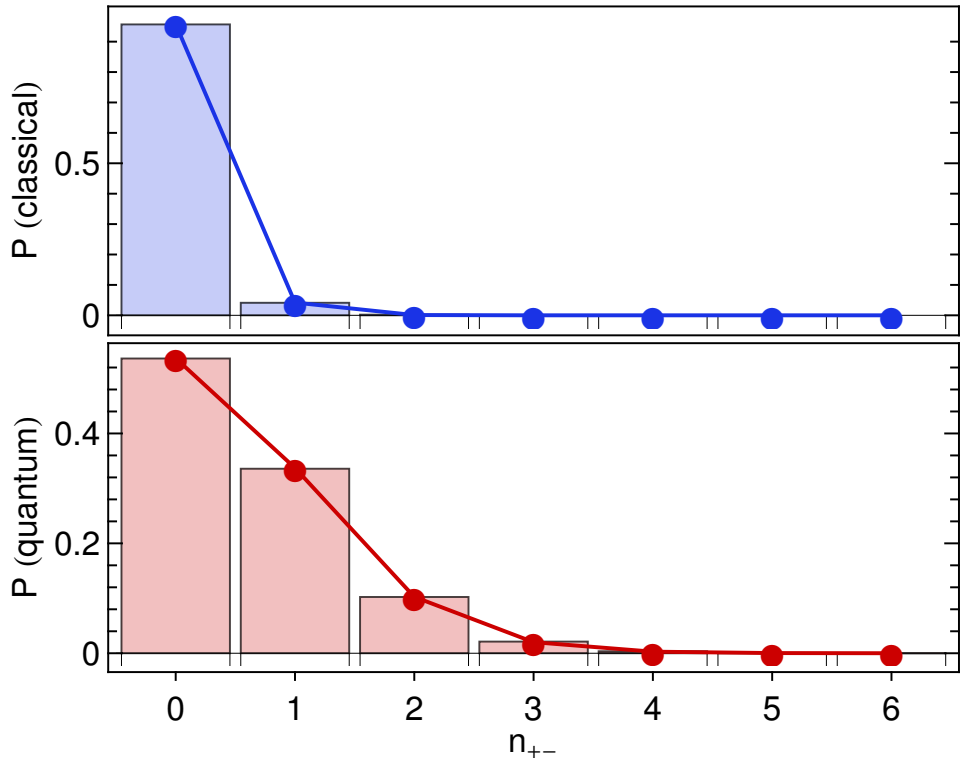
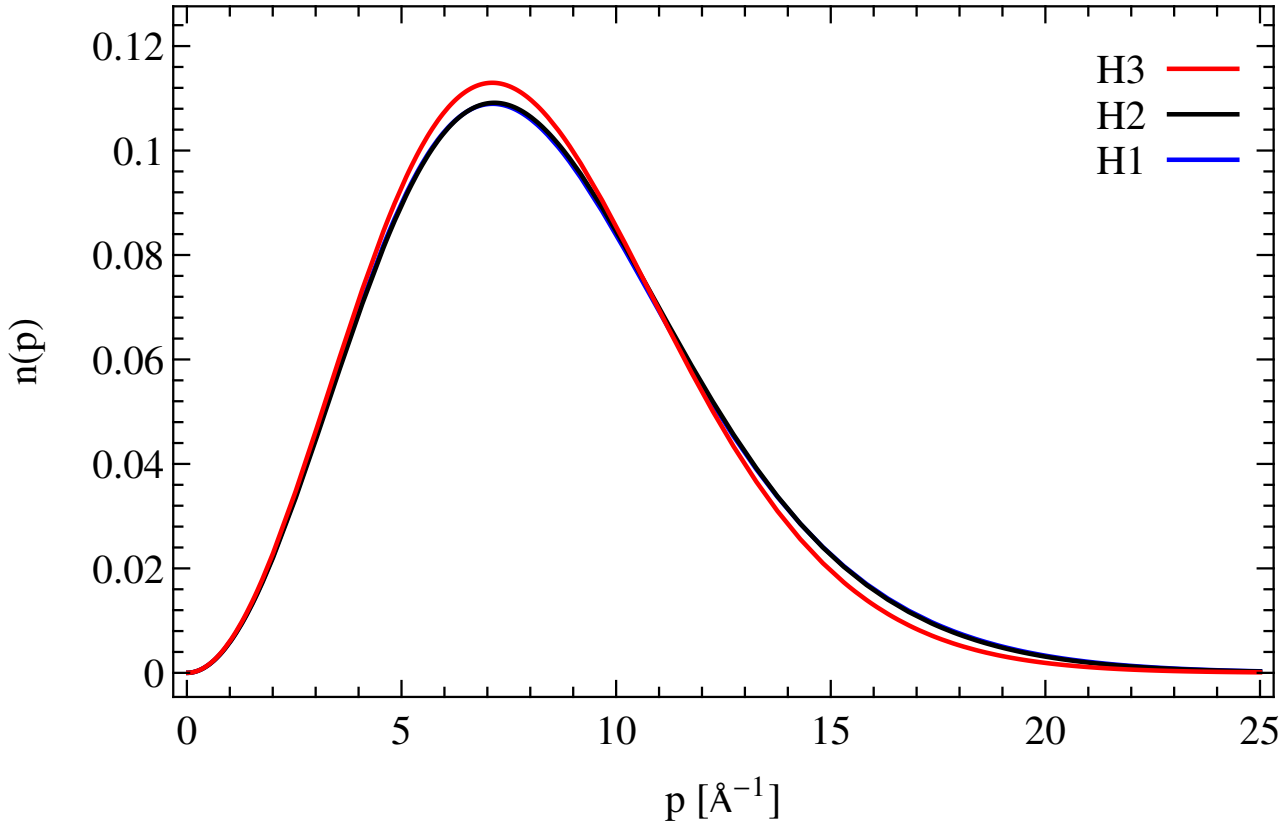


Ceriotti, More, Manolopoulos, Comp. Phys. Comm. 2014

Inhomogeneity and PMD

- How much different are the kinetic energies of different species?
- "Protonic" H3 has much smaller K_z, *but there is too little of it (1.6%) to make a real difference*
- Even if the mix was 1:1 H2:H3, it is impossible to tell the difference between a mixture and a best-fit "mean proton" scenario!



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Kinetic energy [meV]; TAG, $\Delta = 25$ fs. $k_B T/2 = 32.3$meV

	H1	H2	H3	*H*	O1	O2	O3	*O*
K_x	36.8	37.2	39.7	*37.2*	32.5	32.2	32.8	*32.5*
K_y	42.9	44.8	46.7	*44.8*	35.1	35.8	36.1	*35.8*
K_z	99.1	96.2	**80.5**	*96.0*	39.6	40.6	40.6	*40.6*
K	178.8	178.2	**166.9**	*178.0*	107.1	108.6	109.5	*108.6*

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