Fully Quantum Dynamics of Proton Transfer in water and aqueous systems: the case study of the Zundel ion

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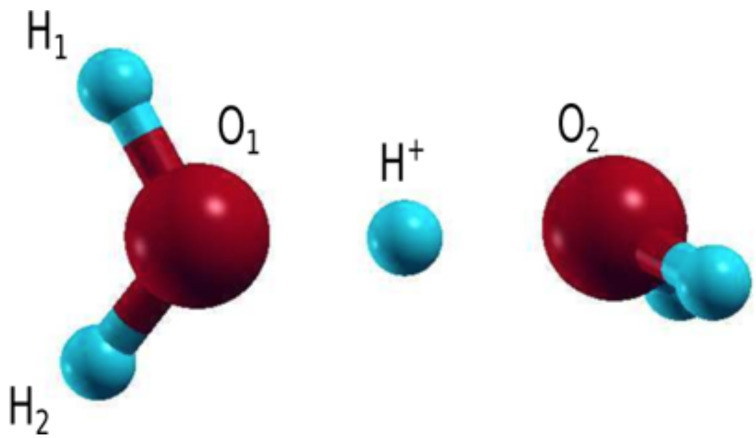
July, 8 2015

Introduction

- Water: liquid of life with many remarkable properties due to the hydrogen bond and proton hopping.
- **Problem:** what are the quantum/thermal effects on the mobility and the proton localization?
- Zundel ion $H_5O_2^+$: ideal reference system for the study of **proton transfer** in bulk liquid.



Methods

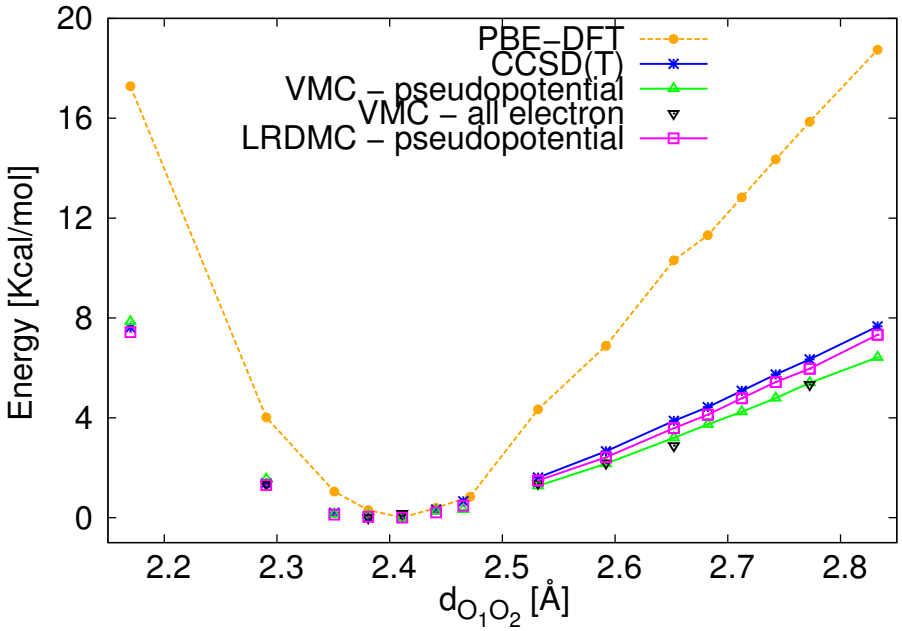
- **Numerical challenge**: gather the 3 ingredients which are necessary to describe quantitatively proton transfer in water.
  1. very accurate treatment of the electronic part.
  2. include thermal effects.
  3. deal with quantum effects for the nuclei.

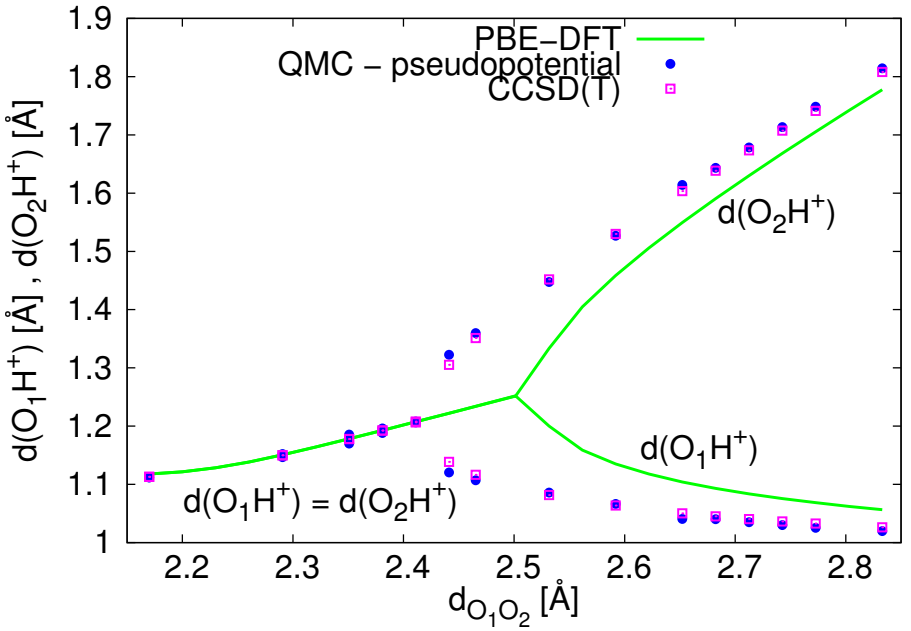
- *Electronic part* $\rightarrow$ Quantum Monte Carlo (QMC) is high accuracy method (results similar to CCSD(T) theory) with a favorable scaling.

- *Thermal effects* $\rightarrow$ Langevin Dynamics at finite temperature.

- *Nuclear quantum effects* $\rightarrow$ Path Integral + Langevin Dynamics (PILD).

Electronic part: previous QMC results at 0 K [2]





[2] M.Dagrada *et al.*, J. Chem. Theory Comput., 2014, **10**, pp.1980-1993.

- 2 regimes: symmetric for $d_{O_1O_2} \leq d_c$, otherwise asymmetric.
- PBE-DFT overestimates the slope of the PES $\rightarrow$ **electronic correlations** are essential to describe proton localization properly.
- QMC results are in excellent agreement with those obtained at CC level of theory.

Thermal effects: Langevin dynamics (1)

- **Goal of the project**: perform MD simulations at finite temperature T with ionic forces computed by VMC calculations.

- QMC forces are noisy: how to incorporate them in a MD framework and sample canonical distribution? $\rightarrow$ Langevin dynamics! [3]

[3] C.Attaccalite *et al.*, Phys. Rev. Lett., 2008, **100**, 114501.

- **Classical Langevin equation:**

$$m_i \dot{v}_i = F_i^{QMC} \underbrace{-m_i \gamma v_i}_{\text{friction}} + \underbrace{\eta_i}_{\text{random force}}$$

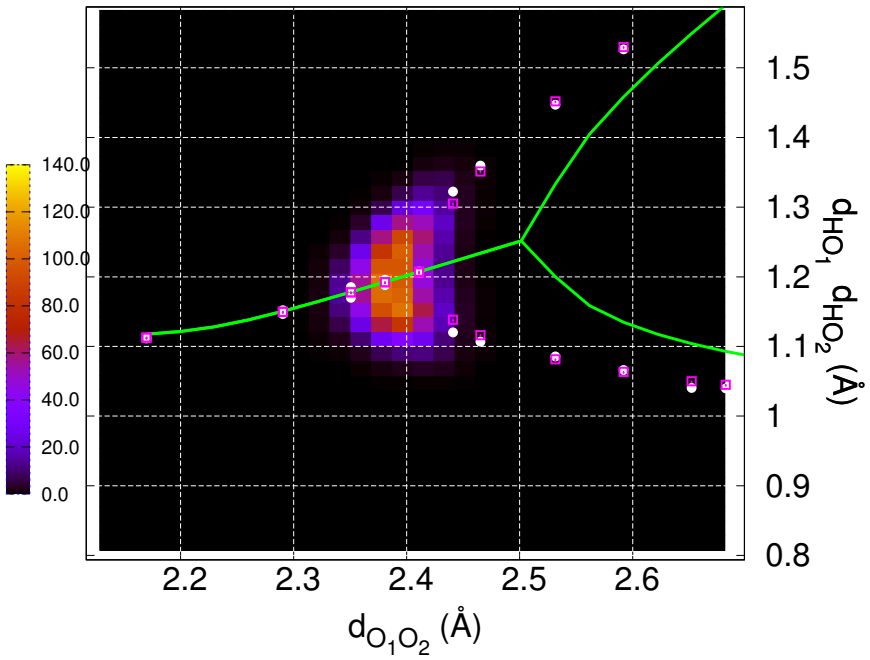
with $\langle \eta_i(t) \eta_j(0) \rangle = 2 k_B T \gamma \delta(t) = \alpha_{ij} \delta(t)$

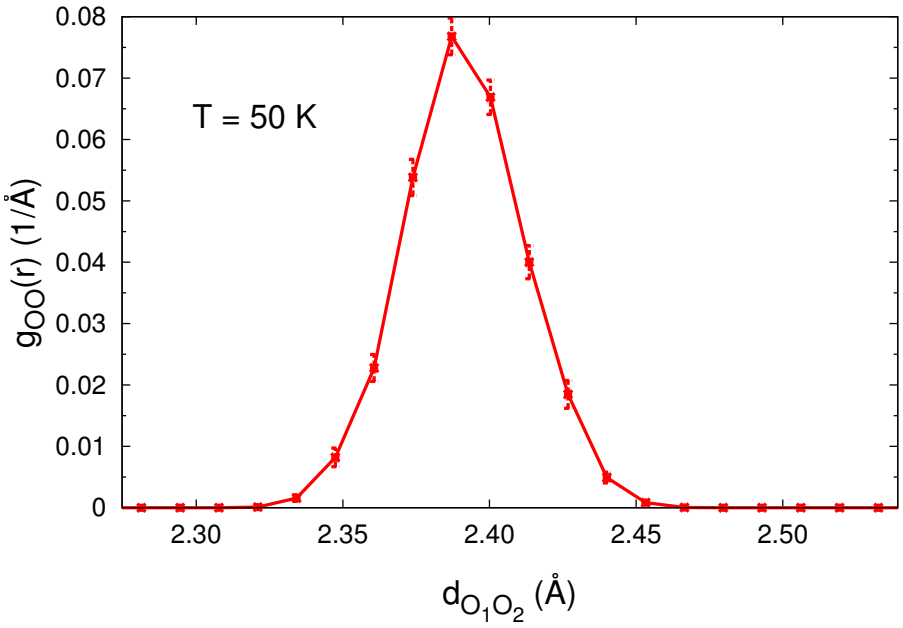
α_{ij} is the *QMC force covariance matrix* which controls the temperature of the system via the generalized fluctuation-dissipation theorem.

Thermal effects: Langevin dynamics (2)

- Integration of the equations of motion is standard.
- **Key step:** optimize the wave function after each ionic move until we are close to the Born-Oppenheimer (BO) surface.
- Compromise between the accuracy of the electronic part and the length of the ions dynamics at fixed number of QMC generations.

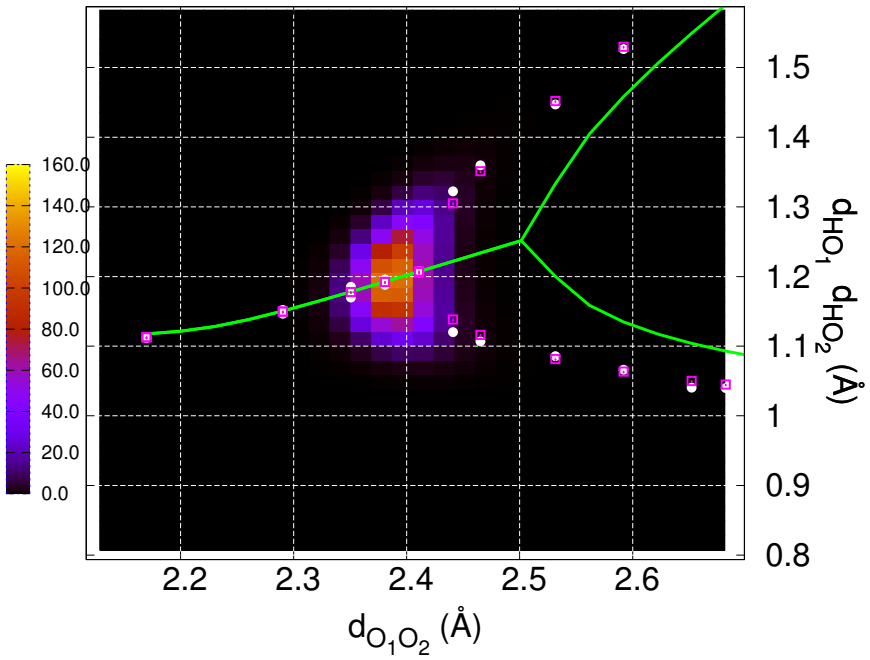
Results at 50K: QMC forces

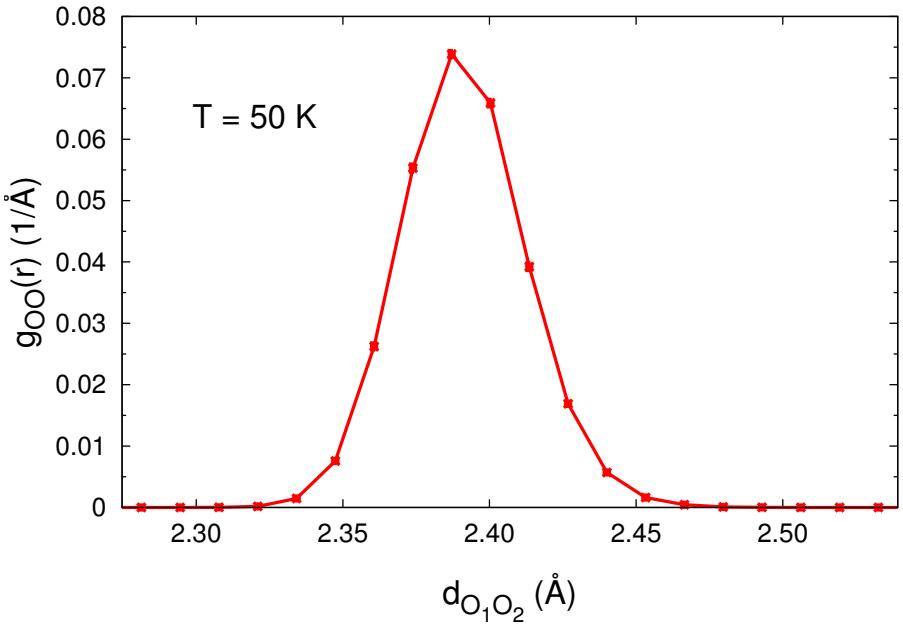




- Low temperature regime: the proton remains **localized**.
- Symmetric configuration: no proton hopping.
- Ionic forces are noisy because QMC is a **stochastic** method.
  $\rightarrow$ How to validate them?

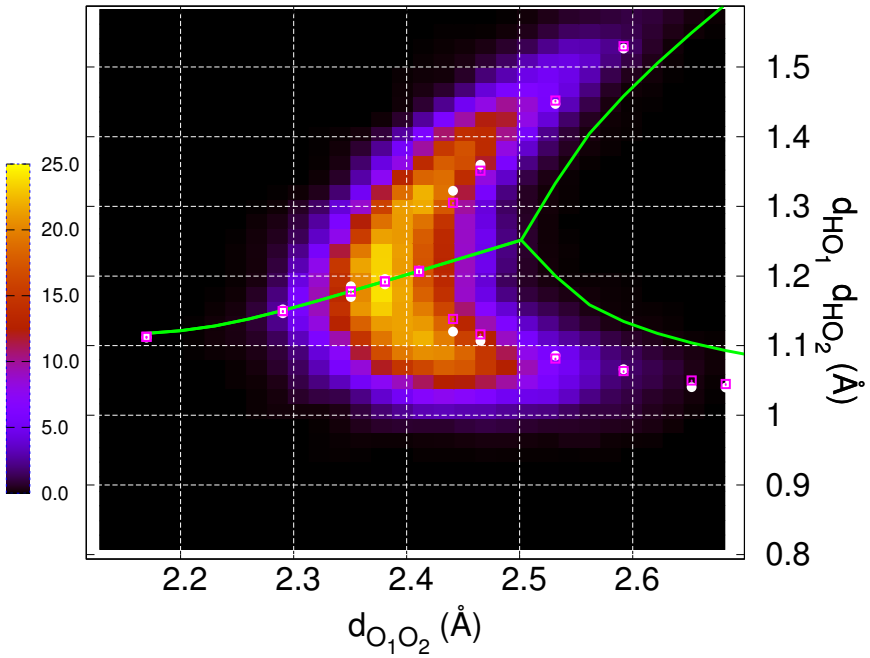
Results at 50K: CC forces

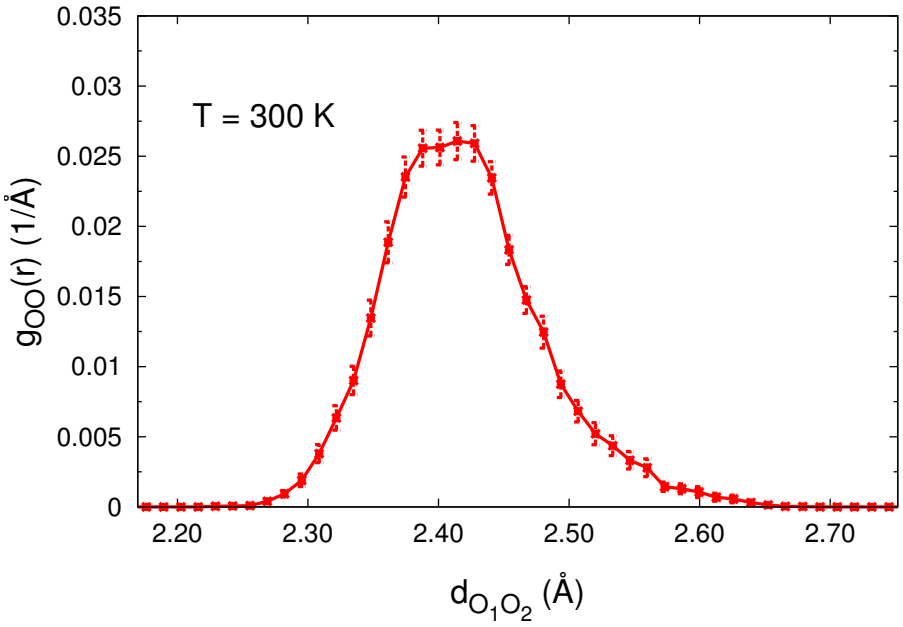




- Analytic forces computed by finite differences of the CC PES.
- **Same distributions** obtained with 'exact' forces → validates QMC forces!

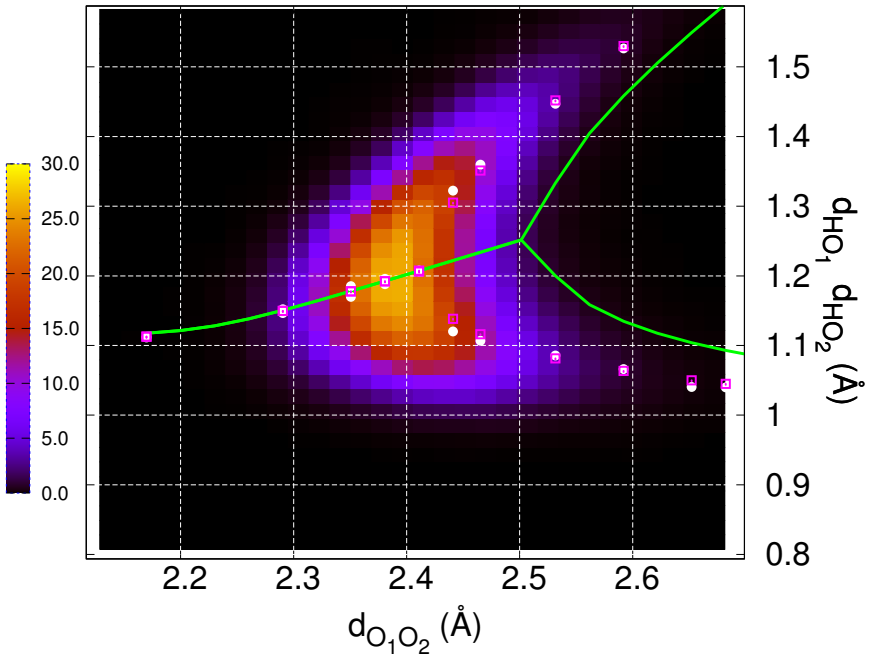
Results at 300K: QMC forces

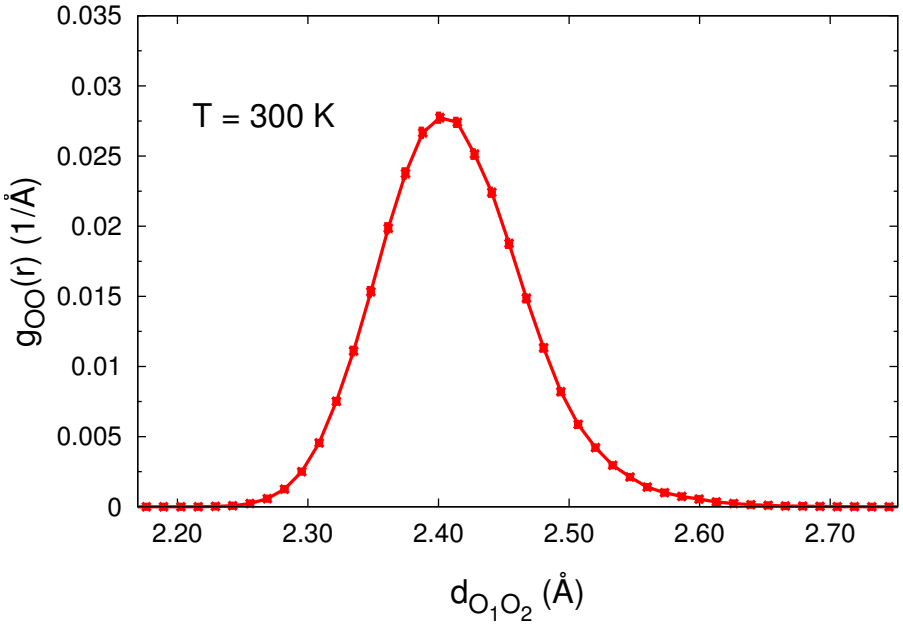




- Room temperature regime: more **molecular vibrations**.
- Symmetric configuration with larger $\langle d_{O_1O_2} \rangle$: proton can hop.

Results at 300K: CC forces

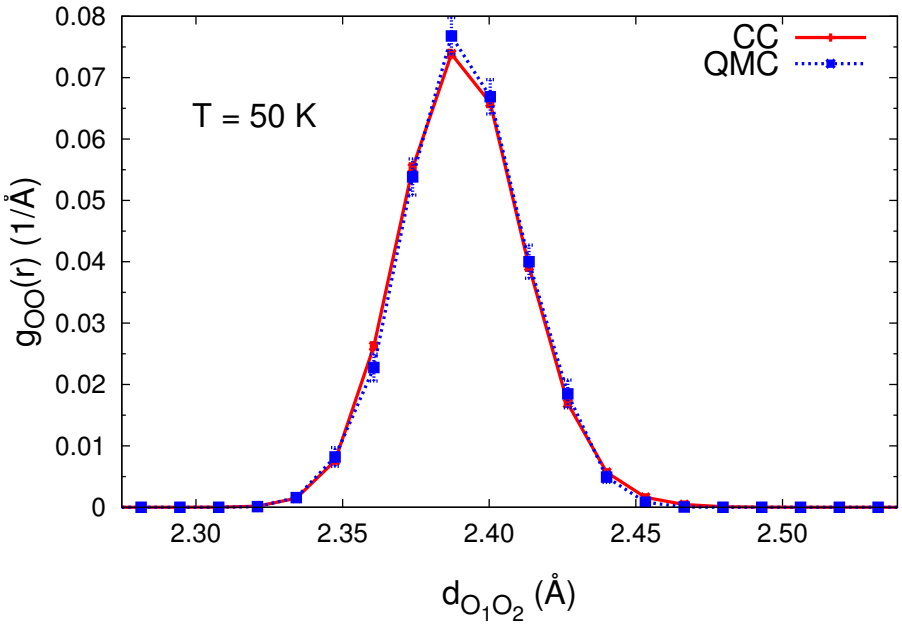




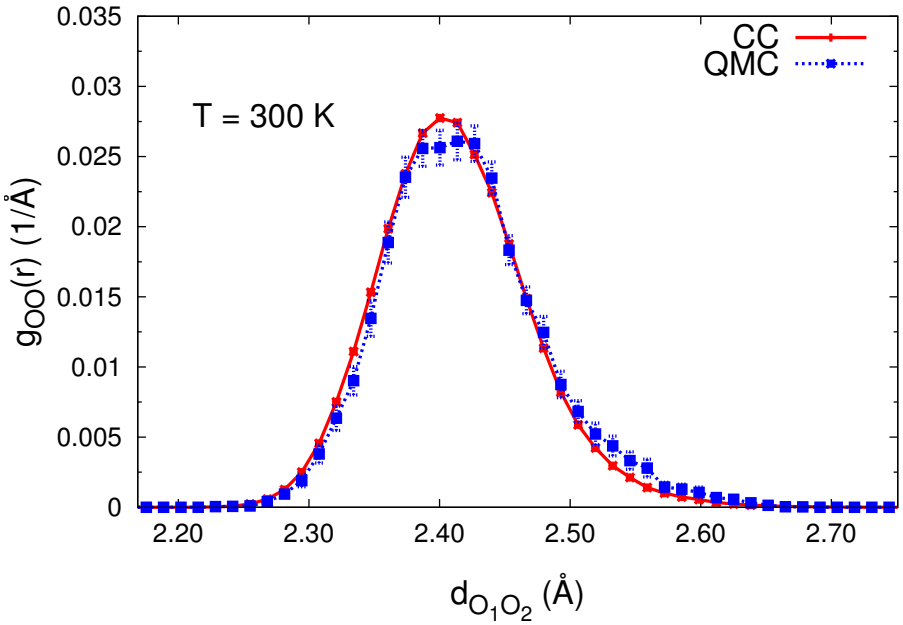
- Higher proton mobility at room temperature is confirmed.
- Tiny differences in the obtained distributions → thermalization + ergodic sampling of the system.

Comparison between QMC and CC forces

Blue: QMC forces ; **Red**: CC forces



Low temperature



Room temperature

- Excellent agreement which validates our method.
- More difficult to converge the OH distances properly.

Quantum effects: the Path Integral formalism

- Light mass of hydrogen $\rightarrow$ important Nuclear Quantum Effects (NQE) which are **essential** to describe properly proton transfer in water [6].

  [6] Tuckerman M. *et al.*, Science, 1997, 275(**5301**):817-20.

- NQE are included within the Path Integral (PI) framework.

- In PI approach: quantum particles are replaced by a collection of M beads connected to each other by a harmonic force.

$$\hat{H} = \sum_{i=1}^{M} \left[\frac{p_i^2}{2m_i} + \frac{1}{2} m\omega_M (x_{i+1} - x_i)^2 + \frac{1}{M} U(x_i) \right]$$

with the ring boundary condition: $x_{M+1} = x_1$ and $\omega_M = \frac{\sqrt{M}}{\beta\hbar}$.

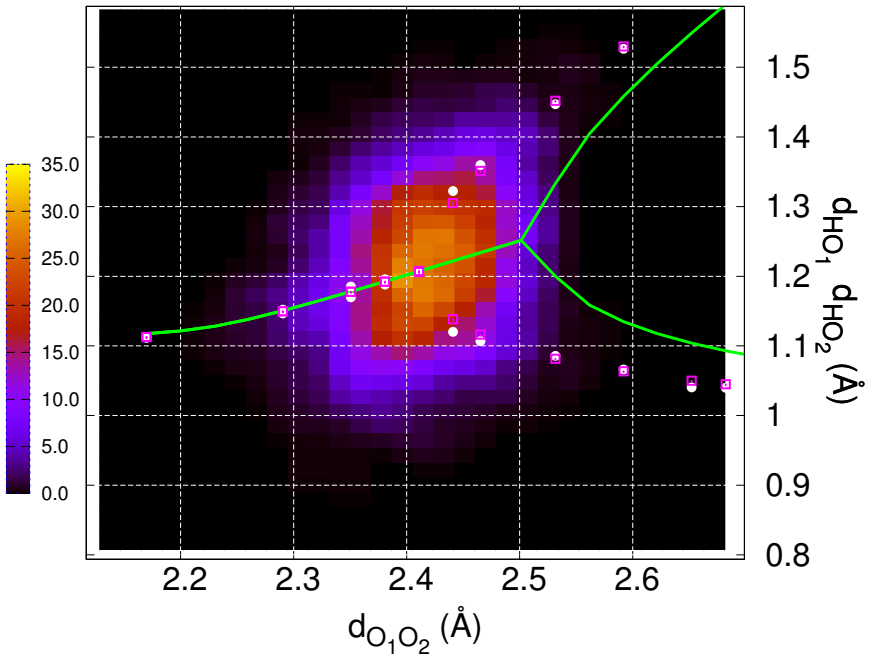
Path Integral Langevin Dynamics (PILD)

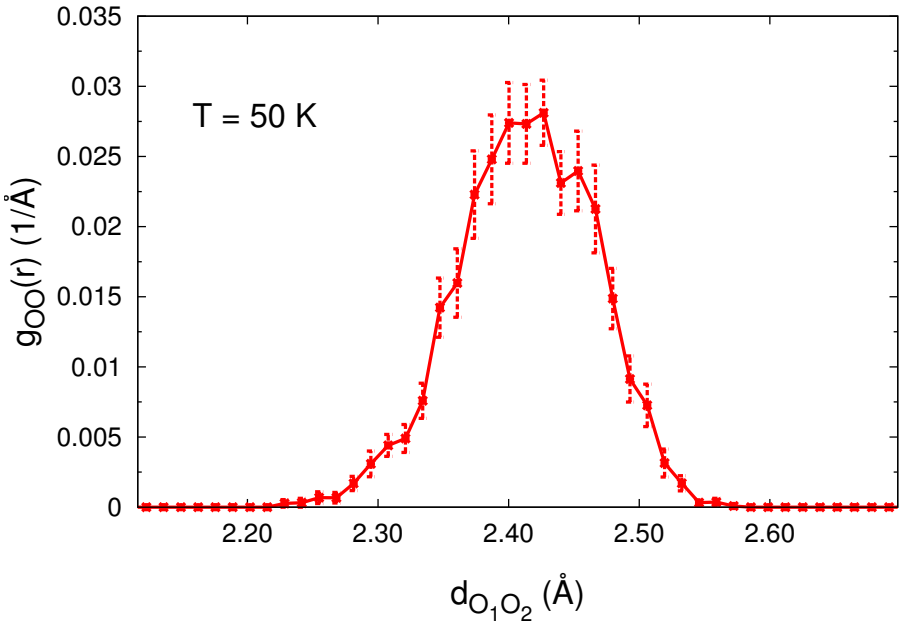
- Combination of the two previous approaches: PI + LD.
- Additional harmonic force in the Langevin equation:

$$m_i \dot{v}_i = F_i^{QMC} - m_i \gamma v_i + \eta_i + \underbrace{F_i^{harm}}_{\text{harmonic force}}$$

- Development and implementation of a **novel algorithm** to integrate exactly and efficiently the E.O.M working in the eigenmodes of the beads.
- **Trick:** making the approximation the wavefunction is locally the same for all the beads, we can use the whole QMC statistic to calculate the ionic forces $\rightarrow$ quantum FOR FREE for the electronic part!

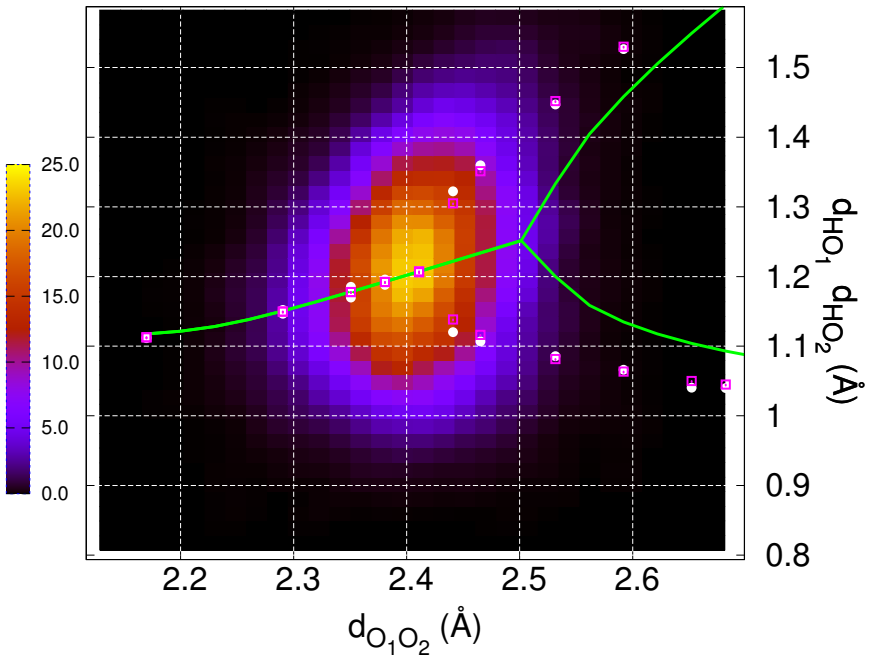
Results at 50K: QMC forces

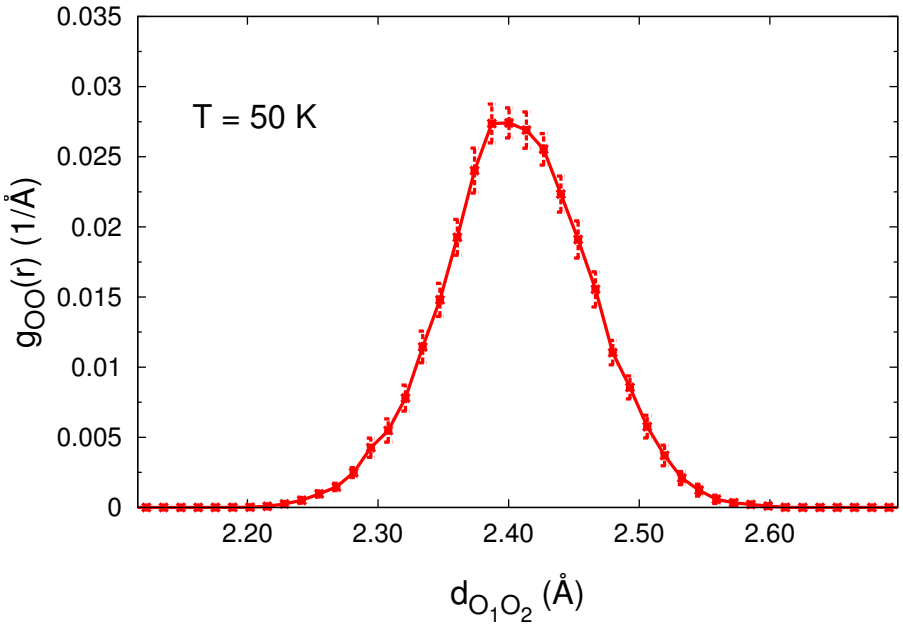




- **NQE** are very important at low temperature: delocalized proton.
- Quantum tunneling gives rise to a greater proton mobility.

Results at 50K: CC forces





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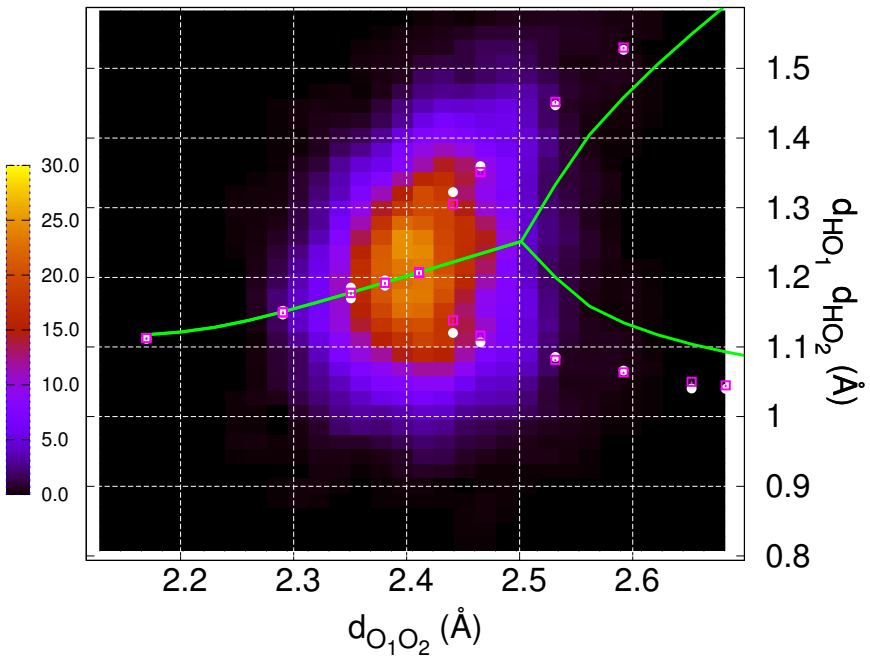
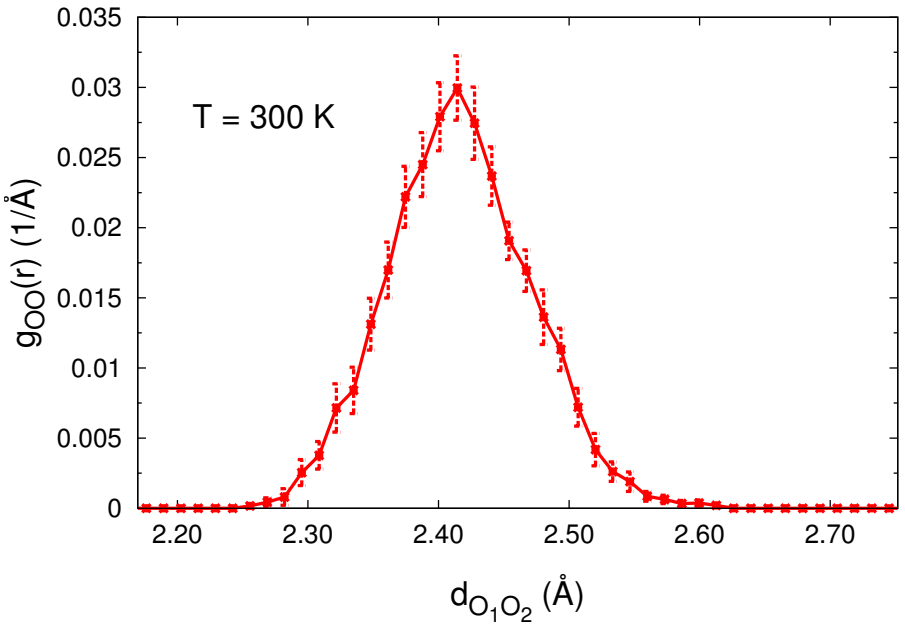
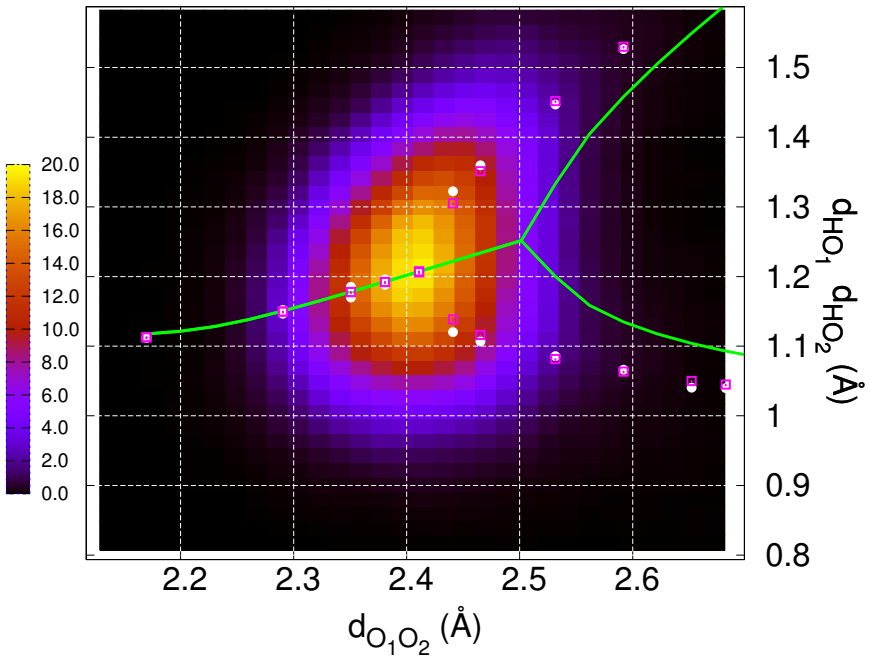
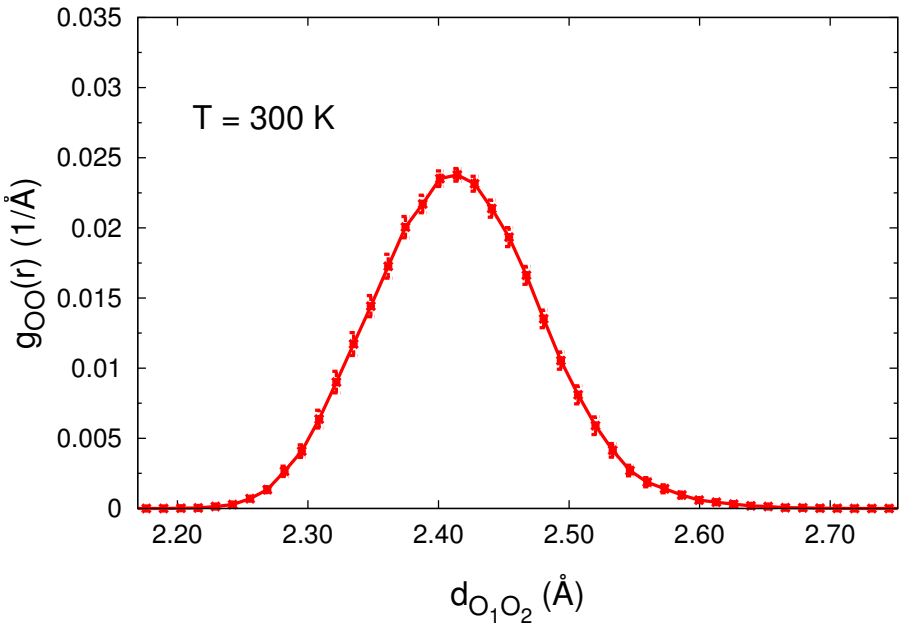




- QMC statistics is rather poor: one needs to improve the sampling of the phase space.
- One cannot neglect **NQE** at room temperature!

Results at 300K: CC forces





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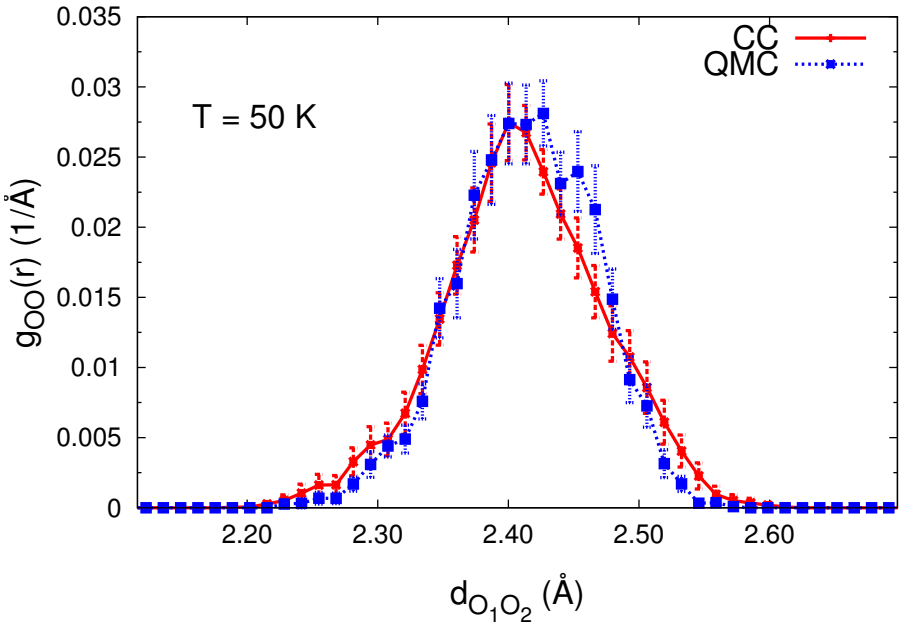
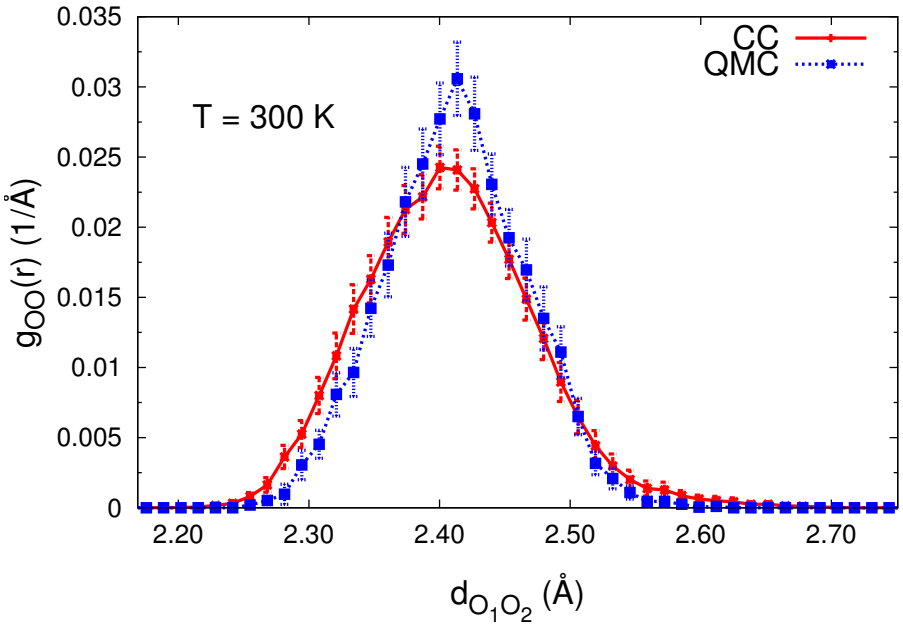


Low temperature

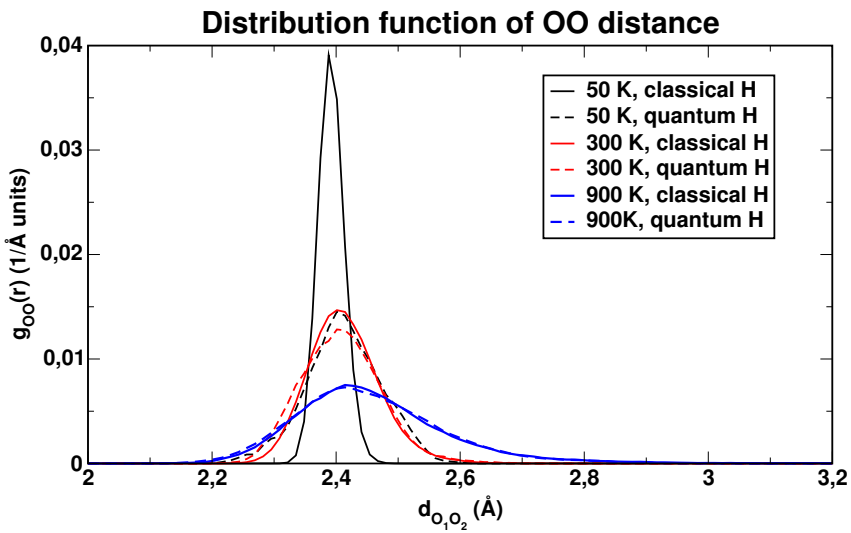


Room temperature

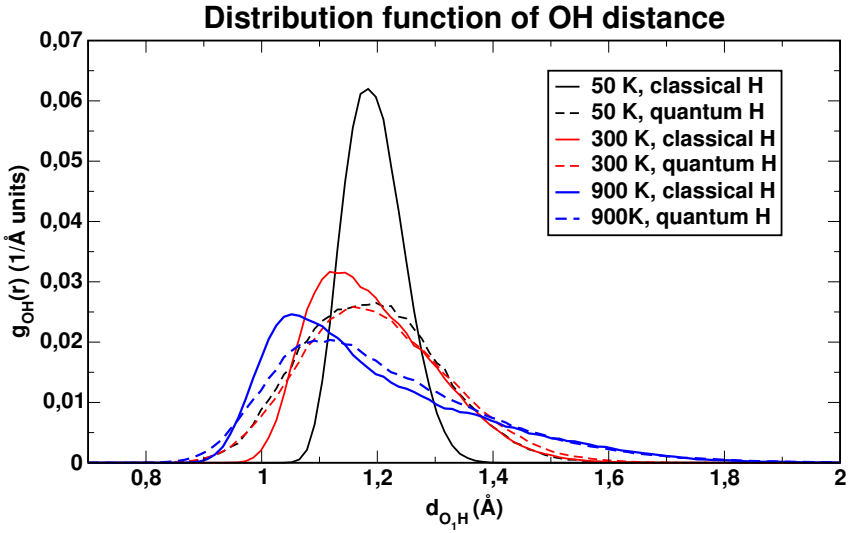
- Good agreement (within the error bars) which validates our method.
- At least up to room temperature, quantum effects prevail over thermal effects.

Quantum versus thermal effects

At room temperature, **NQE are essential** to describe properly proton transfer in the Zundel ion.



$g_{OO}(r)$



$g_{OH}(r)$

- Quantum tunneling of proton prevails over thermal fluctuations and molecular motion $\rightarrow$ weak thermal effects up to 300 K.
- Only at 900 K, thermal effects start to take over.

Conclusion and outlooks

Conclusion:

- Implementation and validation of a novel approach: **Path Integral + Langevin dynamics** (PILD) to describe properly quantum and thermal effects on proton transfer within QMC framework.
- Powerful tool to perform QMC-MD simulations of aqueous systems with noisy forces.
- NQE are indeed essential, even **at room temperature!**

Outlooks:

- Taking into account solvation effects studying larger ions.
  $\rightarrow H_9O_4^+$, $H_{13}O_6^+$ systems and $H_{11}O_6^-$ systems.
- Study of charge rearrangement in neutral and charged **water clusters**.

Acknowledgments

Supervisors:

- Michele Casula (IMPMC - CNRS) - Paris
- A. Marco Saitta (IMPMC - UPMC) - Paris

Collaborators:

- Rodolphe Vuilleumier (ENS - UPMC) - Paris
- Sandro Sorella (SISSA) - Trieste (Italy)

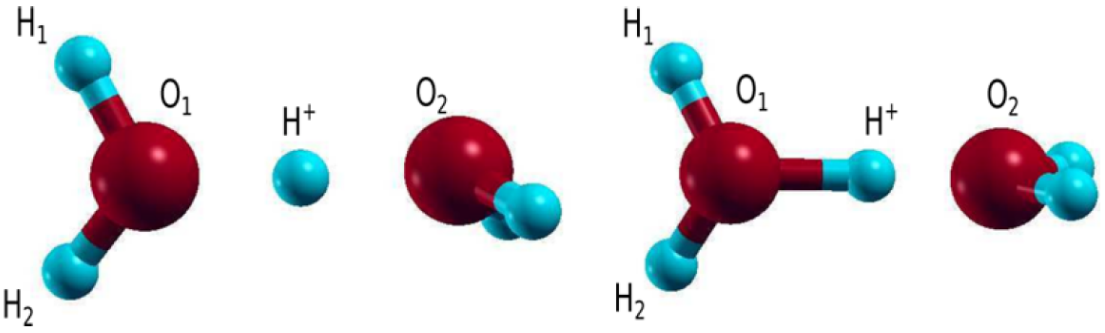
Thank you for your attention!

Zundel cation: short presentation

- Simplest system possible to describe proton transfer in solution.
- Extremely accurate Potential Energy Surface (PES) known from Coupled Cluster (CC) calculations at 0 K [1].

  [1] X.Huang *et al.*, J. Chem. Phys., 2005, **122**, 044308.

- Minimum geometry $\rightarrow$ symmetric configuration C_2.



Left: symmetric C_2 **Right**: asymmetric C_s

- *Reaction coordinates* are:
  1. oxygen-oxygen distance $d_{O_1O_2}$.
  2. hydrogen-oxygen distances d_{O_1H} and d_{O_2H}.
- **Limit of this model**: solvation effects are not taken into account!

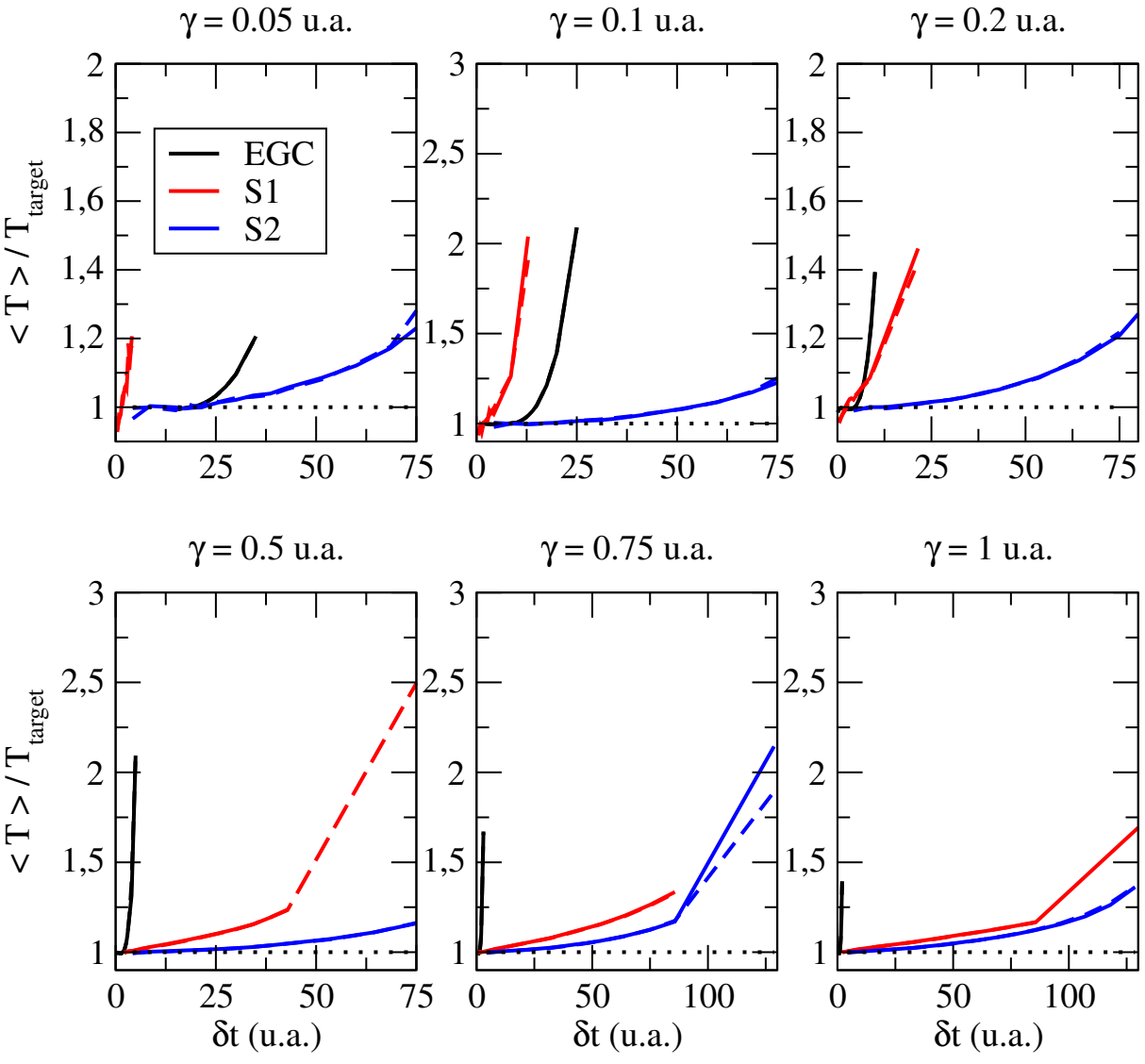
QMC versus CC scaling laws [2]

# of water molecules	total wall time (h) on 512 CPUs	
	VMC	LRDMC
1	0.05	0.15
2	0.24	2.13
6	6.49	164.35

[2] M.Dagrada *et al.*, J. Chem. Theory Comput., 2014, **10**, pp.1980-1993.

- VMC scales as N^3 where as LRDMC scales as N^4 and the theoretical scaling of the CCSD(T) theory is N^7.
- ... but **LARGE prefactor** for QMC simulations (to reduce statistical error) $\rightarrow$ for the 6 H_2O cluster, VMC and CC approaches are numerically equivalent.
- To perform Molecular Dynamics (MD) simulations of larger systems (bulk water), QMC approach must be privilegied.

Numerical stability study



EGC: 2^{nd} order integration for both velocities and positions. [4]

[4] E.Vanden-Eijnden *et al.*, Chem. Phys. Lett.,2006, **429**, pp 310-316.

S1: Exact integration for velocities + 1^{st} order integration for positions. [3]

[3] C.Attaccalite *et al.*, Phys. Rev. Lett., 2008, **100**, 114501.

S2: Exact integration for velocities + 2^{nd} order integration for positions. [5]

[5] A.Zen *et al.*, J. Chem. Phys., 2015, **142**, 144111.

S2 is the most efficient algorithm!