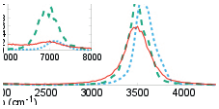

The adaptive quantum thermal bath for a quantum treatment of atomic nuclei

When modeling matter at the atomic scale, the behavior of electrons is described by the laws of quantum mechanics, but atomic nuclei, being heavier, are often treated as classical objects, obeying Newton's laws. This approximation greatly simplifies simulations, but it can lead to non-negligible errors, especially when light atoms such as hydrogen are involved. Some phenomena, such as isotope effects, even escape the classical description of atomic nuclei entirely. Researchers from the «Low-dimensional oxides» group at INSP, in collaboration with the Theoretical Chemistry Laboratory of Sorbonne Université, improved a recently developed method, the adaptive quantum thermal bath (QTB), which allows for a quantum treatment of the nuclei at a computational cost close to that of classical simulations. They show that the adaptive QTB is able to capture the subtle quantum effects at play in liquid water, which opens up promising perspectives, especially for the quantum modeling of hydrogen bonds in biological matter.

The most relevant quantum effect for the properties of atomic nuclei is the existence of a zero point energy: in addition to thermal fluctuations, nuclei are subject to quantum fluctuations that delocalize them and increase their average energy, with respect to that of classical particles under the same conditions. This effect can have great influence on the interatomic bond strength and consequently on the structure of molecules and materials. To capture zero point energy effects, simulation methods have been developed that use a quantum thermal bath (QTB), aiming to impose different effective temperatures to the different degrees of freedom that constitute the system. Thereby, high-frequency molecular vibration modes are associated with high effective temperatures. But these methods are affected by the zero point energy leakage error: the additional energy provided to high frequency modes tends to be transferred erroneously to low frequency modes. This problem is particularly marked for hydrogen-bonded systems such as water, where zero point energy leakage can cause strong structural distortions and invalidate the simulation results.

The innovation of this study is the use of adaptive QTB. This approach exploits a fundamental result of statistical physics, the fluctuation-dissipation theorem, to quantify zero point energy leakage precisely, and correct it efficiently. Although tested on simple models, the ability of adaptive QTB to describe realistic systems with large numbers of atoms remained to be demonstrated. We proposed several improvements that extend the field of application of the method and implement it to simulate liquid water. The equilibrium thermodynamic properties simulated via adaptive QTB are very close to those obtained by the reference method (based on Feynman path integrals[1]), but at a significantly lower calculation cost. Indeed, this cost is comparable to that of a classical or standard (non-adaptive) QTB simulations, the latter method being however strongly affected by zero point energy leakage which makes it unusable in practice (see figure). In addition, the adaptive QTB captures remarkably well the vibrational spectra, that are an essential element for the confrontation between simulations and experimental results.

1 In the path integrals method, each atom is replace d by P replicas (P = 32 for liquid water at room temperature), multiplying the simulation time by approximately the same factor compared to a classical simulation. Advanced techniques allow reducing the number P of replicas, but this reference method generally remain s much more complex to implement than classical or QTB molecular dynamics.

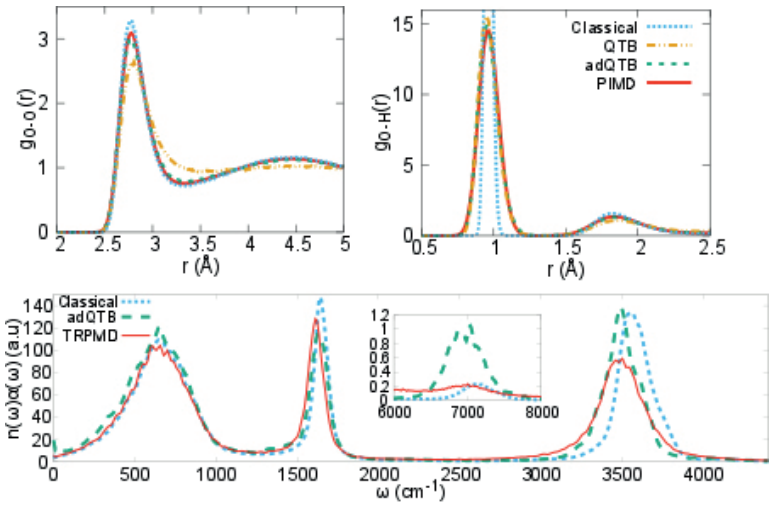

Figure - *Liquid watersimulations*

Top: radial distribution functions obtained by different molecular dynamics methods, classical or quantum. Adaptive QTB (adQTB) coincides with the quantum reference result (path integrals, PIMD), which is not the case of either classical or standard QTB simulations.
Bottom: Corresponding infrared absorption spectra. The inset shows an anharmonic resonance that only the adQTB is able to correctly describe, whereas classical and TRPMD (path-integral based) simulations greatly underestimate its amplitude.

This work paves the way towards a wider use of adaptive QTB to describe complex hydrogen-bonded systems, in particular for the study of biological processes, a field where, though the influence of nuclear quantum effects is suspected, only few theoretical studies have yet been carried out, largely due to the technical complexity of path integral methods.

Reference

« Nuclear Quantum Effects in Liquid Water at Near Classical Computational Cost Using the Adaptive Quantum Thermal Bath »
Nastasia Mauger, **Thomas Plé**, Louis Lagardère, Sara Bonella, **Étienne Mangaud**, Jean-Philip Piquemal, **Simon Huppert**
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