Approximate statistical properties of quantum nuclei via Generalised Langevin Dynamics

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Nuclear quantum effects are relevant to describe processes of experimental significance occurring at low temperature or high pressure, and even surprisingly close to ambient conditions, as in the case of reactions involving proton transfer. The simulation of these effects still poses a formidable numerical challenge due to the exponential scaling of exact methods with the number of degrees of freedom. In spite of a considerable amount of work in this area, no general, affordable, method has emerged. In this talk, two recently developed schemes to compute static and time-dependent quantum nuclear properties will be presented. The first approach improves on the *ad hoc* Quantum Thermal Bath dynamics [1-3] by providing a systematic criterion to gauge zero point energy leakage, a well-know and often fatal limitation of the approach, and proposes an adaptive scheme to balance the leakage on-the-fly by enforcing the quantum fluctuation-dissipation theorem. The second approach provides an asymptotically exact method to sample the Wigner thermal density, a key quantity in semiclassical approximation of quantum time-correlation functions, using Langevin dynamics. The performance of both methods will be demonstated on model and realistic systems of increasing complexity.

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