

Nuclear Quantum Effects from the Analysis of Filtered Trajectories

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Nuclear quantum effects (NQE) have significant contribution to thermodynamic quantities and structural properties, furthermore expensive methods are necessary for their accurate calculations such as path-integral molecular dynamics (PIMD)[1]. Because of this, in most calculations NQEs are simply neglected or only taken into account within the quantum harmonic oscillator approximation.

Herein we present a new method, Generalized Smoothed Trajectory Analysis (GSTA) to determine NQEs from molecular dynamics simulations. To obtain quantum corrected data the time dependent variables of simulations such as coordinates, forces and velocities are filtered with a kernel function derived from the partition function of the harmonic oscillator. GSTA gives the exact zero point energy for harmonic oscillator, and also leads to the correct heat capacities in the high temperature limit, even for anharmonic systems. One of the main advantage of GSTA is that the different motions, like rotation, translation, vibration etc., do not need to be separated. As a post-processing analysis of classical simulations, our technique can be paralleled with the two-phase thermodynamic (2PT) method[2], but the expected field of application can be similar to that of the PIMD simulations.

The broad applicability is demonstrated on examples of harmonic oscillator and different states of water. Born-Oppenheimer Molecular Dynamics (BOMD) simulations have been performed for ideal gas at B3PW91/6-311g(d,p) level of theory up to the temperature of 5000 K.

Classical molecular dynamics have been carried out with SPC/Fw water model for Ih ice, liquid water and vapor. Respect to the experimental heat capacity, GSTA outperforms previous calculations from the literature in a very wide temperature range at much smaller computational cost than PIMD. Nuclear quantum effects on the structure of liquid water are also reproduced (Figure 1).

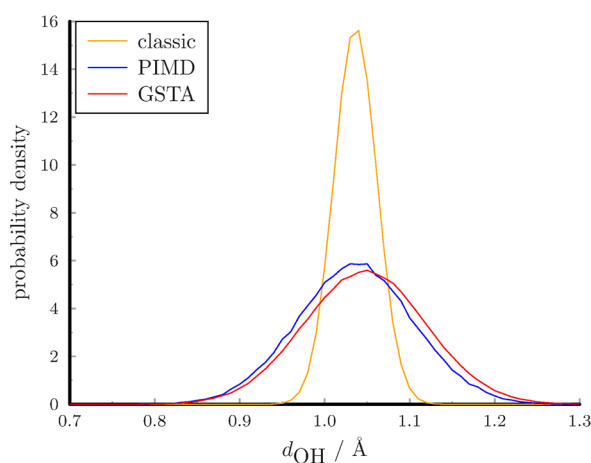


Figure 1: probability distribution functions of intramolecular O-H distance.

References

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2. S.-T. Lin, M. Blanco and W. A. Goddard, *J. Chem. Phys.* **119** (2003), 11792.