Nuclear quantum effects in water: a study in position and momentum space

Joseph Morrone
Columbia University
New York, USA

The importance of nuclear quantum effects in hydrogen bonded systems has been underlined by recent experimental measurements of the proton momentum distribution. In this work, we utilize open path integral Car-Parrinello molecular dynamics simulations in order to compute the proton momentum distribution and assess the impact of nuclear quantum effects in several phases of water. We find that our results are in good agreement with the experimental momentum distributions measured in liquid water and hexagonal ice. It is also found that the inclusion of nuclear quantum effects systematically improves the agreement of first-principles simulations of liquid water with experiment. In addition, we study phases of high-pressure ice that exhibit symmetric hydrogen bonds and quantum tunneling. The symmetric hydrogen bonded phase possesses a narrowed momentum distribution as compared with a covalently bonded phase, in agreement with recent experimental findings. The signatures of tunneling that we observe are a narrowed distribution in the low-to-intermediate momentum region, with a tail that extends to match the result of the covalently bonded state. The transition to tunneling behavior shows similarity to features observed in recent experiments performed on confined water.