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Competing Nuclear Quantum Effects and van der Waals Interactions in Water JEFFREY MCMAHON, Department of Physics, University of Illinois, Urbana-Champaign, IL 61801, MIGUEL MORALES, Lawrence Livermore National Laboratory, Livermore, California 94550, USA, DAVID CEPERLEY, Department of Physics, University of Illinois, Urbana-Champaign, IL 61801 — Water plays a central role in many scientific disciplines, and a number of studies have been performed to understand its properties. However, providing an accurate ab initio description is a significant challenge, and because of this, many of water's properties remain elusive. In particular, the description of hydrogen bonding and the importance of van der Waals (vdW) interactions and nuclear quantum effects are still matters of debate. Recent computational advancements have been made that allow for the accurate and efficient modeling of such effects. We present results from path integral molecular dynamics simulations based on density functional theory employing exchange and correlation functionals capable of accounting for vdW interactions (so-called vdW-DF, vdW-DF2, and optB88-vdW). We demonstrate that, contrary to expectation, the interaction between nuclear quantum effects and vdW interactions hardens the structure of water. These results suggest that ad hoc methods to account for these effects, such as temperature rescaling of simulations employing classical nuclei, are insufficient to describe water, and that fully ab initio calculations must be performed. We discuss the implications of these results for understanding the local structure and hydrogen bonding in water.

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