

Abstract Submitted  
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**Accurate path integral molecular dynamics simulation of ab-initio water at near-zero added cost**<sup>1</sup> DANIEL ELTON, Stony Brook University, MICHELLE FRITZ, JOS SOLER, Universidad Autonoma de Madrid, MARIVI FERNANDEZ-SERRA, Stony Brook University — It is now established that nuclear quantum motion plays an important role in determining water's structure and dynamics. These effects are important to consider when evaluating DFT functionals and attempting to develop better ones for water. The standard way of treating nuclear quantum effects, path integral molecular dynamics (PIMD), multiplies the number of energy/force calculations by the number of beads, which is typically 32. Here we introduce a method whereby PIMD can be incorporated into a DFT molecular dynamics simulation at virtually zero cost. The method is based on the cluster (many body) expansion of the energy. We first subtract the DFT monomer energies, using a custom DFT-based monomer potential energy surface. The evolution of the PIMD beads is then performed using only the more-accurate Partridge-Schwenke monomer energy surface. The DFT calculations are done using the centroid positions. Various bead thermostats can be employed to speed up the sampling of the quantum ensemble. The method bears some resemblance to multiple timestep algorithms and other schemes used to speed up PIMD with classical force fields. We show that our method correctly captures some of key effects of nuclear quantum motion on both the structure and dynamics of water.

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