Quantum dynamics and spectroscopy of ab initio aqueous solutions: the interplay of nuclear and electronic quantum effects

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Describing the structure and dynamics of aqueous solutions requires the accurate treatment of their electronic structure and nuclear quantum effects, such as zero-point energy and tunneling. Path integral simulations, combined with an ab initio evaluation of interactions using electronic structure theory, incorporate the quantum mechanical nature of both the electrons and nuclei. However, for aqueous systems, even at ambient temperatures, the computational cost of these ab initio path integral simulations has traditionally been at least two orders of magnitude greater than treating the nuclei classically, making them prohibitively costly for most applications. Our recent work that extends the ring polymer contraction method to ab initio molecular dynamics simulations and combines it with a multiple time stepping scheme brings the cost of nuclear quantum effects below that of a typical classical ab initio molecular dynamics simulation. This approach has allowed us to elucidate the interplay of nuclear and electronic quantum effects that give rise to the structure, dynamics and vibrational spectroscopy of liquid water and reactive aqueous defects, such as highly concentrated acids, and provides near quantitative agreement with experiment.