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Converged Nuclear Quantum Statistics from Semi-Classical Path Integrals IGOR POLTAVSKYI, ALEXANDRE TKATCHENKO, Dr. — The quantum nature of nuclear motions plays a vital role in the structure, stability, and thermodynamics of molecular systems. The standard approach to take nuclear quantum effects (NQE) into account is the Feynman-Kac imaginary-time path-integral molecular dynamics (PIMD). Conventional PIMD simulations require exceedingly large number of classical subsystems (beads) to accurately capture NQE, resulting in considerable computational cost even at room temperature due to the rather high internal vibrational frequencies of many molecules of interest. We propose a novel parameter-free form for the PI partition function and estimators to calculate converged thermodynamic averages. Our approach requires the same ingredients as the conventional PIMD simulations, but decreases the number of required beads by roughly an order of magnitude. This greatly extends the applicability of *ab initio* PIMD for realistic molecular systems. The developed method has been applied to study the thermodynamics of N_2, H_2O, CO_2, and C_6H_6 molecules. For all of the considered systems at room temperature, 4 to 8 beads are enough to recover the NQE contribution to the total energy within 2% of the fully converged quantum result.

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