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Non-Adiabatic Transition Path Sampling: Application to a Model Proton-Transfer Reaction LAURA J. KINNAMAN, Physics, U. of Notre Dame, STEVEN A. CORCELLI, Chemistry & Biochemistry, U. of Notre Dame, KATHIE E. NEWMAN, Physics, U. of Notre Dame — A new algorithmic method is discussed, Non-Adiabatic Path Sampling (NAPS), which combines features of transition path sampling (TPS) and molecular dynamics with quantum transitions (MDQT). The goal is to ultimately address problems which involve excited and coupled electronic states, as well as large systems and long timescales (*e.g.*, semiconductor photocatalysis). TPS focuses specifically on trajectories that take a system from reactants to products, which allows the study of chemical processes that are dominated by rare but important events whose timescales are outside the range of direct simulation. In the MDQT algorithm, the nuclear dynamics of the system do not occur on a single Born-Oppenheimer potential energy surface, but rather may involve non-adiabatic transitions between many coupled electronic states. The NAPS algorithm uses the statistical framework of TPS to analyze MDQT trajectories, using the advantages of each method to get results for otherwise inaccessible systems. The algorithm is tested on a simple model of proton transfer: A quantum-mechanical proton in a double-well quartic potential bi-linearly coupled to a thermal bath of classical harmonic oscillators. Results from the model are compared to numerically exact results available in the literature.

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