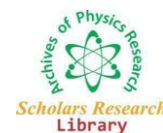




Extended Abstract

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Excited state, non-adiabatic dynamics of large photoswitchable molecules using a chemically transferable machine learning potential

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Light-induced chemical processes are ubiquitous in nature and have widespread technological applications. For example, the photoisomerization of azobenzene allows a drug with an azo scaffold to be activated with light. In principle, photoswitches with useful reactive properties, such as high isomerization yields, can be identified through virtual screening with reactive simulations. In practice these simulations are rarely used for screening, since they require hundreds of trajectories and expensive quantum chemical methods to account for non-adiabatic excited state effects. Here we introduce a neural network potential to accelerate such simulations for azobenzene derivatives. The model, which is based on diabatic states, is called the diabatic artificial neural network (DANN). The network is six orders of magnitude faster than the quantum chemistry method used for training. DANN is transferable to molecules outside the training set, predicting quantum yields for unseen species that are correlated with experiment. We use the model to virtually screen 3,100 hypothetical molecules, and identify several species with extremely high quantum yields. Our results pave the way for fast and accurate virtual screening of photoactive compounds.

Ab initio molecular dynamics (MD) simulation methods provide a universal tool to model materials at the atomistic scale directly from the first principles of quantum mechanics. As a rule, MD techniques that include electronic excited-state effects in a non-equilibrium regime should invoke solutions of Schrödinger's equation on-the-fly for the electronic levels and the molecular forces (interatomic potentials). Here, a manifold of electronically excited states in a prototypical molecular system is a function of multidimensional coordinates, R , spanning the space of vibrational (nuclear) degrees of freedom. Excited states are usually (but not necessarily) separated by a gap from the ground state. The potential energy surfaces (PESs) of these states are topologically complex and frequently cross each other, and perhaps even the ground state, as a function of R . Since the excited-state PESs are generally not known, their modeling requires elaborate quantum chemical techniques. The underlying model electronic structure can span the range from high accuracy wavefunction approaches, to density functional theory (DFT) and to effective reduced Hamiltonian methods. Excited-state processes such as photophysics and photochemistry in molecular and solid-state materials of practical interest necessarily involve multiple, and frequently dense, electronic states. For example, an initial non-equilibrium state (or an electronically excited wavepacket, can be created by optical excitation, by charge injection, or by shock means. This electron-vibrational (or vibronic) excitation evolves across the excited-state manifold, gradually losing its electronic energy into molecular vibrations (or heat), a process called internal conversion or non-radiative relaxation. In such a case, the excited-state molecular dynamics (ESMD) is non-adiabatic and occurs beyond the Born–Oppenheimer (BO) regime. Within the BO framework, electrons and nuclei evolve on significantly different time scales, allowing the system Hamiltonian to be split into “fast” (electrons) and “slow” (nuclei) degrees of freedom. Indeed, in the BO picture, all manybody electronic states are orthogonal to each other and there is no physically allowed way for the system to decay to a lower state unless electrons couple to nuclear motions, thus allowing for energy dissipation and a change of excited-state identity. In fact, such non-radiative relaxation is a very common process in materials that provide channeling of electronic energy into heat, which leads, for example, to Kasha's rule which states that molecules typically fluoresce from the lowest singlet excited electronic state. The non-adiabatic process occurs in the regions where excited states get close to each other or cross. The outcome of the dynamics can be a return to the equilibrium ground state (or quenching), i.e., a complete loss of the initial electronic energy into heat. Alternative scenarios with specific products emphasizing useful electronic functionalities of the material. For example, light emission require formation of a low-lying fluorescent state, frequently described by a bound electron–hole pair (or exciton). Light harvesting usually includes spatial electronic energy (exciton) transfer followed by charge

Bottom Note: This work is partly presented at 8th International Conference on Physical and Theoretical Chemistry