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Nonadiabatic Molecular Dynamics with Trajectories

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In the mixed quantum-classical description of molecular systems, only the quantum character of the electronic degrees of freedom is considered while the nuclear motion is treated at a classical level. In the adiabatic case, this picture corresponds to the Born-Oppenheimer limit where the nuclei move as point charges on the potential energy surface (PES) associated with a given electronic state. Despite the success of this approximation, many physical and chemical processes do not fall in the regime where nuclei and electrons can be considered decoupled. In particular, most photoreactions pass through regions of the PES in which electron-nuclear quantum interference effects are sizeable and often crucial for a correct description of the phenomena. Recently, we have developed a trajectory-based nonadiabatic molecular dynamics scheme that describes the nuclear wavepacket as an ensemble of particles following classical trajectories on PESs derived from time-dependent density functional theory (TDDFT) [1]. The method is based on Tully's fewest switches trajectories surface hopping (TSH) where the nonadiabatic coupling elements between the different potential energy surfaces are computed *on-the-fly* as functionals of the ground state electron density or, equivalently, of the corresponding Kohn-Sham orbitals [2]. Here, we present the theoretical fundamentals of our approach together with an extension that allows for the direct coupling of the dynamics to an external electromagnetic field [3] as well as to the external potential generated by the environment (solvent effects) [4]. The method is applied to the study of the photodissociation dynamics of simple molecules in gas phase and to the description of the fast excited state dynamics of molecules in solution (in particular Ruthenium (II) tris(bipyridine) in water).

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