ADIABATIC AND NONADIABATIC MOLECULAR DYNAMICS WITH CONDITIONAL WAVE FUNCTIONS

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I will present an exact trajectory-based scheme to decompose the coupled electron-nuclear motion in terms of conditional wave functions[1]. By projecting the time-dependent Schrödinger equation on the configuration of an ensemble of generally defined trajectories, nonunitary equations of motion for the nuclei (or electrons), that depend parametrically on the electronic (or nuclear) degrees of freedom are obtained. These equations do not rely on tracing-out degrees of freedom and no prior knowledge of Born-Oppenheimer potential-energy surfaces nor of nonadiabatic couplings is required. By choosing the trajectories to be Bohmian particles, the formulation acquires an additional interpretative value and the resulting propagation scheme does not require the computation of the unstable quantum potential[2]. The above formalism can be made specific for adiabatic dynamics: the evolution of the N-body nuclear wave function moving on a 3N-dimensional Born–Oppenheimer potential-energy hyper-surface is then rewritten in terms of single-nuclei wave functions evolving nonunitarily on a 3-dimensional potential-energy surface[3].

[1] Phys. Rev. Lett., 2014, 113, 083003.
[2] Phys. Chem. Chem. Phys. 2011, 13, 3231.
[3] J. Phys. Chem. Lett., 2015, 6, 1529.