

# Nonadiabatic molecular dynamics at surfaces and interfaces

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Nonadiabatic molecular dynamics is a fundamental problem related to breakdown of the usual timescale separation between electron and nuclear dynamics. It plays an important role in many processes from chemistry and photochemistry to spectroscopy and nonradiative electronic relaxation and from electron and proton transfer to coherent control and photo-induced energy transfer. The significance of the problem stems from both the complexity of its fundamental theoretical description and applicational importance for development of optoelectronic and optomechanical molecular devices.

A crucial part of formulating nuclear dynamics at surfaces and interfaces is the definition of nuclear forces induced by the electronics subsystem. We present general first-principles derivation of the expression for current-induced forces. The expression is applicable in nonequilibrium molecular systems with arbitrary intramolecular interactions and for any form and strength of electron-nuclei coupling. It provides a controlled consistent way to account for quantum effects of nuclear motion around a classical trajectory, accounts for electronic non-Markov character of the electronic friction tensor, and suggests a method for treatment beyond strictly adiabatic approximation. Results of previous considerations are obtained from our general expression as particular limiting cases. We discuss effective ways to evaluate electronic friction tensor using recently introduced by us nonequilibrium Hubbard diagrammatic technique. The discussion is illustrated with numerical simulations employing a generic junction model.

Because full quantum mechanical solution of electron-nuclear dynamics is prohibitively expensive, one has to rely on quasi-classical approximations. Two most popular approaches are the Ehrenfest dynamics and the fewest switches surface hopping (SH) method. While the former can be obtained as expansion around classical solution, the latter is formulated in an ad hoc manner. We argue that one can overcome difficulties in derivation of the SH by employing a many-body flavor of the nonequilibrium Green's function technique. We derive a set of equations which reproduce the SH formulation in the limit of small metal-molecule coupling and the Ehrenfest dynamic when information on different charging states is traced out. This provides, for the first time, a theoretical basis for the surface hopping method as a limiting case of an exact equation of motion.

[1] F.Chen, K.Miwa, and M.Galperin, *J. Phys. Chem. A* 123, 693-701 (2019).

[2] M.Galperin and A.Nitzan. *J. Phys. Chem. Lett.* 6, 4898-4903 (2015).