Effects of quantum motion of nuclei on reactivity of hydrocarbons studied in the approximate quantum trajectory framework

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- Quantum-mechanical nature of nuclei, in particular of protons, is essential for understanding of chemical reactions in condensed phase, such as enzyme environment, nano-scale carbon structures or membranes. The dominant quantum-mechanical effects, present even in large molecular systems, are tunneling, internal energy flow and nonadiabatic dynamics involving excited electronic states. We focus on the development and applications of trajectory dynamics with quantum corrections for selected nuclei scalable to large molecular systems.
- We have developed the following framework: for a system comprised of light (hydrogen) and heavy (carbon) nuclei the quantum correction is included only for the light particles, while a wavefunction description of a system is retained for all nuclei. The quantum correction on dynamics comes as “quantum” force acting in addition to the classical force.
- Efficient scaling with the system size has been achieved by defining the quantum force in the reduced dimensionality space of light nuclei. The accuracy of the approximation has been improved by making the quantum force parametrically-dependent on the configurations of the heavy nuclei.
- Current applications include carbon systems interacting with atomic and molecular hydrogen, based on the quantum trajectory code interfaced with the Density Functional Tight Binding method of electronic structure. For example, the zero-point energy of the CH bond has been captured, as follows from the spectrum of wavefunction autocorrelation function computed with trajectories (figure). Reactive systems of about hundred atoms will be studied in the future.