Nonadiabatic theory in electron wavepacket dynamics

Kazuo Takatsuka,

Graduate School of Arts and Sciences, The University of Tokyo, Japan

Nonadiabatic transition is one of the most important and interesting quantum effects in chemical dynamics, in which sudden change in electronic states takes place. There have been proposed so many theoretical methods to treat such nonadiabatic transitions ranging from the very classic theories of Landau, Zener, Stueckelberg to state-of-the-art theories such as Zhu-Nakamura, the fewest switch surface hopping method and natural decay of mixing, and indeed their contributions to the progress of elementary dynamical processes of chemical reactions have been enormous. Yet, due to the rapid progress of experimental studies, we quite often face complicated and difficult experimental situations that have not been studied before. For instance, we are often interested in systems of densely degenerated electronic states, in which the concept of Born-Oppenheimer adiabatic potential energy surface (PES) can make only a weak sense due to the energy-time uncertainty relation. In those cases the nonadiabatic theories based on an assumption of transition among a few (mostly two) PESs at a time should be accordingly reformulated. Furthermore, advances in laser technology now make it possible to modify native molecular electronic states with an intense electromagnetic vector potential, which can induce novel nonadiabatic coupling in addition to the native one. Such nonadiabatic chemistry in intense laser field clearly constitutes a strong driving force to establish new theories of nonadiabatic transition.

In this talk, we report our recent theory of nonadiabatic transition from the view point of electron wavepaket dynamics [1]. In particular, we discuss the fundamental features of nonadiabaticity and quantum entanglement in electron-nucleus dynamics. We also discuss the interaction of molecular nonadiabatic states with intense laser fields [2]. It is also stressed that even without laser fields the dynamical electron theory can offer a useful tool to analyze and conceptualize chemical reactions. The present theory may be regarded as a general theory of mixed quantum-classical dynamics in which quantum and classical subsystems kinematically contact each other, letting the quantum mechanical entanglement survive in the classical subsystem.

[1] “Exploring dynamical electron theory beyond the Born-Oppenheimer framework: From chemical reactivity to non-adiabatically coupled electronic and nuclear wavepackets on-the-fly under laser field.” Kazuo Takatsuka and Tahehiro Yonehara, Phys. Chem. Chem. Phys. (Perspective) **13**, 4987-5016**.**

[2] “Nonadiabatic chemical dynamics in intermediate and intense laser fields“, Kazuo Takatsuka and Takehiro Yonehara, Adv. Chem. Phys. **144**, 93-156, (2009).