Theory of Chemistry beyond the Born-Oppenheimer concept

Kazuo TAKATSUKA

(The University of Tokyo, Graduate School of Arts and Sciences, Professor)

【Outline of survey】

Theory and experiment for ultra-fast chemical reaction dynamics now enable to map the wave-packet of nuclear motions in the time scale of femto-second (10-15s). However, it has been mostly assumed in the former studies that the electronic and nuclear motions can be treated separately due to the large difference in masses and time-scales of them (the Born-Oppenheimer approximation). In the present research project will we create and develop a theory of electron wave-packet dynamics that couples with relevant nuclear motions, lifting the Born-Oppenheimer separation. Electron transfer dynamics associated with proton transfer is such an example, which is of fundamental importance not only in chemistry but also in biological and material oriented physical sciences. Another typical example is a possible control of chemical reactions through the laser manipulation of molecular electronic states. A molecule placed in an extremely intense vector field, which can now provide an electronic field that is as strong as the natural Coulombic interactions among the consisting nuclei and electrons, undergoes a strong induced (non-local) nonadiadiabatic coupling. It is therefore obvious that we should study molecules and reactions in this deeper stage of dynamical hierarchy.

【Expected results】

Many key and puzzling phenomena in contemporary physical chemistry can be analyzed, to my belief, from the above electron dynamics coupled with nuclear motions. We therefore will study some of them by appropriately picking the representative phenomena. However, the major outcome we expect is to establish a new filed of chemical research in which the concept of "potential energy surface" based on the Born-Oppenheimer approximation breaks down. We hope to find new properties and aspects of molecules that could not be appreciated before within the previous paradigm.

【References by the principal researcher】

“Non-Born-Oppenheimer paths in anti-Hermitian dynamics for nonadiabatic transitions.” Kazuo Takatsuka, J. Chem. Phys. **124**, 064111 (2006).

“Nonadiabatic chemical dynamics in an intense laser field: Electronic wavepacket coupled with classical nuclear motions.” Kiyoshi Yagi and Kazuo Takatsuka, J. Chem. Phys. **123**, 224103 (2005).

【Term of project】 FY2006－2010	【Budget allocation】17,800,000 yen

【Homepage address】 http://mns2.c.u-tokyo.ac.jp/index-e.html