【Grant-in-Aid for Scientific Research (S)】

Science and Engineering (Chemistry)

Title of Project : Nonadiabatic Electron Dynamics in Chemistry of Charge Separation, Proton Transfer, Electron Transmission, and Huge Electronic-State Fluctuation

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Research Project Number : 15H05752 Researcher Number : 70154797
Research Area : Theoretical Chemistry, Excited State Chemistry, Chemical Dynamics
Keyword : Nonadiabatic electron dynamics, Charge separation, Coupled proton-electron transfer

【Purpose and Background of the Research】

We define "Beyond-Born-Oppenheimer chemistry" as a research field for the phenomena that are far away from the framework of the so-called Born-Oppenheimer approximation, in which electronic states are described as stationary states. Through those studies, we explore chemistry that has not been studied before. In particular, our basic focus is placed on; (1) Time-dependent phenomena dominated by nonadiabatic electron dynamics, particularly the coupled dynamics with proton transfer, (2) Huge fluctuation of molecular electronic states induced by nonadiabatic interactions in densely quasi-degenerate electronic state, (3) Interaction of molecular electronic states with ultrafast and intensity laser fields. More precisely, typical phenomena we are interested in are; (A) Basic mechanism of fractional charge separation in the initial stages of photo-synthesis and water splitting in biological and/or organic systems, and relevant mechanism of proton relay and long-range electron transmittance, (B) Huge electronic state fluctuation in excited states of atomic clusters and its reactions and provided reaction fields, (C) Dynamical mechanism of electron exchange between atomic clusters and solvents to set a theoretical foundation of designing cluster electrodes, (D) Mechanism of one-way proton pumping through protein membrane and the relevant roles of proton-electron simultaneous dynamics (with Dr. Takefumi Yamashita), (E) Molecular electron dynamics in atto-second laser and/or intense pulse lasers to control chemical reactions, and (F) Quantization of non-Born-Oppenheimer paths arising from nonadiabatic transitions (with Dr. Satoshi Takahashi) .

【Research Methods】

We have been developing a theory of nonadiabatic electron wavepacket dynamics, in which electronic-state mixing and packet-branching undergo along branching nuclear paths, which we call the path-branching representation. We have established related algorithms for computer codes and applied to various chemical problems, such as excited state chemical reactions. All these computer programs can treat those nonadiabatic dynamics in the vector potentials of electromagnetic fields. We will further make these programs faster and larger to cope with more general molecular systems. We also plan to embed the nonadiabatic path-branching dynamics into statistical solvents.

【Expected Research Achievements and Scientific Significance】

We will thus develop a new field of theoretical chemistry and explore chemical phenomena that could not be studied before. The individual objectives we listed above are actually highly correlated with many cutting-edge experimental researches, and therefore we will collaborate with experimentalist in many ways anticipating possible feedbacks. The fields on which the present project may have impacts are cluster science, electrochemistry, photochemistry (photoinduced oxidation and reduction reactions in particular), biochemistry (energy metabolism in particular), molecular energy engineering, ultrafast chemical dynamics and atto-second electron dynamics

【Publications Relevant to the Project】

"Fundamental Approaches to Nonadiabaticity: Towards a Chemical Theory beyond the Born-Oppenheimer Paradigm", T. Yonehara, K. Hanasaki, K. Takatsuka, *Chem. Rev.* **112**, 499-542 (2012).
"Chemical Theory beyond the Born-Oppenheimer Paradigm: Nonadiabatic Electronic and Nuclear Dynamics in Chemical Reactions", K. Takatsuka, T. Yonehara, K. Hanasaki, and Y. Arasaki (World Scientific, Singapore, 2014)

【Term of Project】 FY2015-2019
【Budget Allocation】 126,800 Thousand Yen

【Homepage Address and Other Contact Information】

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