

論文の内容の要旨

論文題目 Theoretical Study on Real-Time Electron Dynamics in Nonadiabatic Processes
(非断熱過程における実時間電子ダイナミクスに関する理論的研究)

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1. Introduction

With the recent energy problems and increasing seriousness of environmental problems, it is very important to develop and improve new energy sources. The role of theoretical science in this global-scale project is considerable. If we can perfectly simulate the real-time coupled electron-nuclear dynamics of the system concerned, it must be enormously helpful in the development and improvement of energy devices because the simulation can produce all physical quantities needed. Therefore, the study of the real-time coupled electron nuclear dynamics has been considered a very important subject and there have been many studies. Most of these studies have focused on how to reproduce the nuclear dynamics, not the electron dynamics. Because the study of nuclear dynamics has recently come to result in success, the main problem now has become how to simulate the electron dynamics.

Real-time electron dynamics, especially of charge-transfer reactions, is very important and accurate simulation of it is in high demand. Charge-transfer reactions are ubiquitous among reactions occurring at surfaces or interfaces in the energy devices. These systems consist of innumerable adiabatic potential energy surfaces; thus, they are nonadiabatic processes. If we can simulate the real-time electron dynamics in such nonadiabatic processes, it will produce tremendously useful knowledge to develop and improve these devices. Furthermore, considering the recent developments in intense attosecond laser technology, there is significant demand to establish simulation theory that can simulate the real-time electron dynamics in such extreme nonadiabatic processes.

Therefore, this work, entitled “Theoretical Study on Real-Time Electron Dynamics in Nonadiabatic Processes,” completes a series of studies toward the establishment of an efficient simulation and control method for the real-time electron dynamics in nonadiabatic processes. For this purpose, I have devised a strategy consisting of four successive projects: (1) full inspection of the validity and limitations of previous electron dynamics simulation methods, the TDH and Ehrenfest methods, for charge-transfer reactions induced by nuclear motion, (2) practical application of the Ehrenfest method to study the real-time electron dynamics in a practical fuel cell system using TDDFT, and (3) development of the electron-nuclear correlation functional for the time-dependent multicomponent density functional theory (TDMCDFT)

toward the perfect description of coupled electron-nuclear dynamics, and (4) study of the mechanism of control of real-time electron dynamics in nonadiabatic processes.

2. The Validity of Time-Dependent Hartree and Ehrenfest Methods for Real-Time Electron Dynamics Simulation of Charge Transfer Reactions Induced by Nuclear Motion

The first project is the full inspection of the previous methods of simulating real-time electron dynamics. There have been two popular methods, the TDH and Ehrenfest methods. However, their validity in reproducing the real-time electron dynamics in nonadiabatic processes has never been examined. Therefore, elucidating of their validity is extremely important. With this knowledge, we will be able to choose a method that is appropriate for the situation.

Thus, I calculated the real-time electron dynamics of charge-transfer reactions induced by nuclear motion using the TDH and Ehrenfest methods, and compared them with the numerically exact results. Employing a two-electron system, I found that, as long as nuclei move as localized wave packets, the TDH and Ehrenfest methods can reproduce the exact electron dynamics qualitatively well, even when nonadiabatic transitions occur. On the other hand, I also studied cases where the electron dynamics of the TDH and Ehrenfest methods fail by using a one-electron transfer model. I found that, when the quantum nature of nuclei is crucial neither the TDH nor the Ehrenfest method could reproduce the exact electron dynamics well.

The results of this study show the validity of the TDH and Ehrenfest methods in simulating electron transfer dynamics coupled with nuclear motion to the extent that nuclear wave packets are localized. However, it also shows their limitations for electron dynamics where splitting or broadening of nuclear wave packets occur, indicating the importance of appropriate consideration of electron-nuclear correlations in such situations.

3. Real-Time Electron Dynamics Simulation of the Adsorption of an Oxygen Molecule on Pt and Au Clusters

In the first project, it is confirmed that, as long as nuclei move as localized wave packets, the TDH and Ehrenfest methods can reproduce the real-time electron dynamics in nonadiabatic processes sufficiently well. The second project of this thesis is the application of the Ehrenfest method to study the real-time electron dynamics induced by nuclear motion in charge-transfer reactions that occur in practical energy devices. Combining real-time TDDFT, the Ehrenfest method can be applied to large systems, but so far, there have been no such studies.

Thus, as the second step of this thesis, I applied the Ehrenfest TDDFT method to simulate the real-time electron dynamics of the oxygen reduction reaction on platinum surfaces. The time correlation between electron dynamics and nuclear dynamics during dissociative adsorption of

oxygen molecules on a platinum cluster was investigated. The results were compared with those on a gold cluster. It was observed that dissociative adsorption of O₂ occurred on the Pt(001) surface but not on the Au(001) surface, reproducing the difference in catalytic activity between these surfaces. An analysis of the correlation between the time evolution of the O₂-surface distances and the number of electrons transferred showed that electron transfer occurred more easily from the Pt(001) surface to O₂ than from the Au(001) surface. It was shown that, by the time O₂ approached within approximately 1.6 Å of the Pt(001) surface, one electron had already finished transferring from Pt to the O₂ π* antibonding orbital; thus, it could approach the surface more closely and more electrons transferred to it, which was the critical factor for dissociative adsorption.

4. Towards the Development of the Time-Dependent Effective Nuclear Potential for Time-Dependent Multicomponent Density Functional Theory

As the third project of this thesis, I attempted to develop simulation theory for real-time electron dynamics in systems where the quantum nature of nuclei is crucial. For this purpose, I aimed to establish TDMCDFT, as a suitable candidate for coupled electron-nuclear dynamics. It will provide a numerically tractable scheme that can treat both electron and nuclear dynamics quantum mechanically. However, as an electron-nuclear interaction potential functional, a key factor of this theory, had not been established, I attempted to develop one.

According to the results in the first project, I concluded that it is adequate to start with the development of time-dependent (TD) effective nuclear potentials to establish TDMCDFT and I proceeded using this strategy.

For this purpose, I focused on the concept of exact factorization of the time-dependent Schrödinger equation and the exact TDPEs that was proposed recently. I found that the exactly factorized nuclear equation is nothing but the TDMCKS nuclear equation. I prepared two model systems where strong nonadiabatic transitions and splitting of the nuclear wave packets occur, and analyzed the curvature of the exact TDPEs. One exact TDPE was indeed found to reproduce the nonadiabatic transition that induces splitting of the nuclear wave packet, and at that time, the discontinuous step between the two Born-Oppenheimer potential energy surfaces appears on the exact TDPEs. Then, I investigated the TDPEs using the time-dependent linear combination of atomic orbital (TD LCAO) ansatz approach that is considered to be a good starting point to develop the TDMCDFT. I compared this TDPEs with the exact TDPEs and the TDPEs obtained using the TDH method, and elucidated how well this method works. Such a TDPEs comparison will be very important for improving the TD LCAO approach and establishing the TDMCDFT scheme.

5. Exact time-dependent potential energy surface on electron excitation and localization in the dissociation of H_2^+

Finally, as the fourth project of this thesis, I addressed the ultimate application that results from the study of real-time electron dynamics in nonadiabatic processes, i.e., the control of electron localization using ultrashort pulse lasers. The control of electron dynamics and the control of chemical reactions by controlling electron dynamics should be a dream for all scientists because, if such technology exists, it will bring us a powerful tool to produce all desired reactions including the reactions of new energy devices.

To develop this technology and realize the dream, full theoretical elucidation of its mechanism is required. In particular, elucidation of the correlation between the electron motion and nuclear motion in such highly nonadiabatic processes is extremely important, because the dynamics affect each other in a very complex way and, without knowing the mechanism, arbitrary control of those dynamics will never be achieved.

Therefore, I aimed to reveal the electron-nuclear correlation in the electron excitation and localization during dissociation of H_2^+ by two sequential ultrashort laser pulses. I treated a one-dimensional H_2^+ model system and a UV pulse laser that generated electronic excitation to only the first excited state. By varying the time delay between pulses, I calculated the change of population with time for each BO state and also the exact TDPES, and evaluated the induced effect of electron localization on nuclear motion.

As a result, I revealed that the exact TDPES is a very efficient tool for analyzing the induced effect of electron localization on nuclear motion, because it produces a very clear intuitive picture of the potential the nucleus feels in real time during such a process. It can clearly explain how the dissociation dynamics is affected by the electron localization. It was found that the electron localization affects the exact TDPES in a very complex way.

In total, this work presents an important step toward the establishment of a simulation method for real-time electron dynamics in nonadiabatic processes. I conclude that the Ehrenfest TDDFT method is a very efficient method of simulating real-time electron dynamics in nonadiabatic processes as long as nuclei move as localized wave packets. Considering that TDDFT will be developed further in the future, this Ehrenfest TDDFT method will become more important and should be used more extensively. On the other hand, for the situation where the quantum nature of nuclei is crucial, such as surface reactions of small molecules or reactions in an intense laser field, the establishment of TDMCDFT is high demand. Analyzing the exact TDPES and improving the TD LCAO ansatz approach is considered a most promising direction toward this goal. Furthermore, it is considered that the exact TDPES will serve as a promising tool toward the ultimate technology of controlling real-time electron dynamics in nonadiabatic processes, and further studies are expected to be devoted to this project.