

論文内容の要旨

論文題目: Non-Adiabatic Molecular Dynamics Simulations using Time-Dependent Density Functional Theory

(時間依存密度汎関数法を用いた非断熱分子動力学シミュレーション)

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The first-principles molecular dynamics (FPMD) simulation has been established as a standard tool to study chemical and physical processes in molecular sciences and condensed matter physics. Because of its reasonable accuracy and moderate computational demand, density functional theory (DFT) is currently most preferred electronic structure method for FPMD simulation. But its application is limited to the electronic ground-state because DFT is a ground-state theory in its original formulation. Recently, the study of excited-state have also become possible by the development of the time-dependent density functional theory (TD-DFT), which is an exact reformulation for time-dependent systems.

However, most of those simulations were based on the Born-Oppenheimer (adiabatic) approximation. This approximation has been the keystone to the visualization of chemical processes. By separating the electronic and nuclear motion, it enables us to picture molecules as a set of nuclei moving over a potential energy surface provided by the electrons. Whereas the validity of this approximation for the vast majority of chemistry and physics is not in doubt, it is now clear that this approximation breaks down and non-adiabatic effect becomes significant when those surfaces are at or near the degeneracy, namely when the crossing or avoided crossing point is closely located. Occurrence of such degeneracy is not a rare event: it appears in many physical and chemical, as well as biological systems, and the non-adiabatic processes play a crucial role in the transfer and recombination dynamics of carriers in the bulk and at the surfaces/interfaces. All metal systems are entirely non-adiabatic where the electronic states are always degenerate. In metals, it is well known that a dominant source of nuclear energy dissipation is through the excitation of the electrons of the metals, which can not be described within the Born-Oppenheimer approximation. Hence, it is important to extend the simulation to include non-adiabatic

effect. These non-adiabatic phenomena can not be accessed by DFT method because computation of the electronic excited state is necessary for these systems. Therefore TD-DFT is the most promising candidate for the first-principle non-adiabatic molecular dynamics (FPNAMD) simulations.

We have developed and implemented the schemes for FPNAMD simulation on the basis of TD-DFT within the adiabatic local density approximation (ALDA). The methods include full quantum wavepacket dynamics simulations as well as semi-classical simulations, such as the surface hopping and the Ehrenfest dynamics. For the computation of non-adiabatic coupling, which plays key roles in the surface hopping and wavepacket approaches, we formulated an efficient method within the framework of TD-DFT in frequency domain (Casida formalism). For the computation of the NAC vector and excited-state force, we implemented the method using planewave basis and pseudopotential. For the Ehrenfest dynamics, we used the real-space finite difference method and Watanabe's time-propagation scheme. These methods have been applied to the several types of the non-adiabatic systems. In these studies, the most suited non-adiabatic simulation methods were used in the each system.

Firstly the surface hopping method was applied to photo-isomerization dynamics of a formalimine molecule. We found that the inversion motion was induced initially after the photo-excitation, and when the twisting motion was subsequently induced, the non-adiabatic transition occurred. And we found the details of the dynamics were importantly affected by the environment, suggesting that more sophisticated treatment of the environments is required to elucidate the non-adiabatic dynamics truly from first-principles.

Next we studied the non-adiabatic diffusion process of hydrogen from BC site to T site in the n-type silicon using the wavepacket dynamics method. We confirmed the existence of the avoided crossing along the path. Analysis of the Casida vector and Kohn-Sham orbitals shows that the origin of the avoided crossing is the charge transfer of the excess electron. Our wavepacket dynamics simulation revealed that the Born-Oppenheimer approximation can be valid for hydrogen and deuterium as far as the momentums are not very large, but for muonium, the Born-Oppenheimer approximation can not be valid in all the range of the momentum.

Finally, we showed the results of TD-DFT Ehrenfest molecular dynamics simulation for the vibrational relaxation of hydrogen atom on metal surface using the Jellium model. We found that we should use the system with sufficiently large number of electrons to simulate the non-adiabatic dynamics of metal system. And we found the recurrence effect was caused by the finite-sizeness of the electron system. To circumvent the recurrence problem, we developed the dissipative Ehrenfest dynamics method using the Doebner-Goldin equation and artificial orthogonalization. And it was found that the recurrence problem can be successfully avoided by this scheme.

The relatively low computational costs of these methods allowed the study of relatively large systems and multiple trajectories. These methods are expected to be useful tool for the study of the photochemistry and the other non-adiabatic systems.