論文の内容の要旨

論文題目：Method of simulating excited-state dynamics

(励起状態の動力学計算手法)

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In this thesis we develop methods to simulate excited-state dynamics; (A) an analytical expression for the excited-state force, (B) a method to compute the nonadiabatic couplings (NACs) between different electronic states, and (C) a many-body expression for the dissipative dynamics. The present study is motivated by the curiosity to investigate the excited state on which many important phenomena, such as desorption, structural changes, and catalysis, can occur more easily than on the ground state. To do the research, it is important in the first step to clarify the potential energy surface (PES) of the excited state. In the second step, it is important to clarify the coupling among PESs because the coupling becomes very large when they cross with each other or are located closely. When they cross with each other, dynamical effects such as the quantum interference are important, and moreover, the excited-state dynamics is easily affected by the environment. Therefore, it is important in the third step to understand the complex excited-state dynamics by performing a simulation. The simulation requires accurate and efficient methods for (A) the excited-state force, (B) NAC and (C) dissipative dynamics, which we develop in this thesis.

Former two quantities, (A) and (B), have been calculated using finite difference method, which is generally not accurate and efficient enough because of possible numerical round-off error and the required atomic displacements in all the directions. For the last one, (C), density matrix approach or stochastic approach have been used, but they are numerically very demanding in that it is difficult to achieve reasonable convergence. In this context, we develop analytical methods for (A) and (B) using the density functional perturbation theory (DFPT), and for (C), we derived a nonlinear Schrödinger equation to take into account the dissipative effect. We believe that these methods will advance the study on the excited-state dynamics from first principle.