Electron dynamics described by real-time TDHF/TDDFT calculation: Application to the dissociative recombination reaction

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Electron dynamics is an ultrafast phenomenon occurring in attoseconds, which was recently observed by experiments and has attracted much attention. Electron dynamics is caused by change of external field of the intriguing system, such as light or collision of molecules and electrons. Therefore, electron dynamics should play an important role in reaction of interstellar matters which is sometimes concerned with electronically excited states. To elucidate mechanism of electron dynamics, theoretical calculation would be a powerful tool. Real-time propagation (RT) of time-dependent theories, such as time-dependent Hartree-Fock (TDHF) method and time-dependent density functional theory (TDDFT), have been applied to describing electron dynamics.

The dissociative recombination (DR) reaction is a combination of an electron and a positive molecular ion, followed by the dissociation into several neutral fragments ($XY + e^- \rightarrow [XY]^* \rightarrow X + Y$). The DR reaction proceeds via the direct process or the indirect process. In the direct process, the molecular system directly hops to the dissociative excited state of neutral molecule after capturing an electron, while in the indirect process, this transition proceeds via Rydberg states. In the previous studies for DR reactions, AIMD calculation was performed for the direct process [1] and the indirect process [2,3], although the electron capture process was not considered explicitly.

In this study, we applied RT-TDHF/TDDFT calculation describing electron dynamics to the indirect process of the DR reaction. The electron capturing process ($XY + e^- \rightarrow [XY]^*$) of the indirect process was approximately described by the electron dynamics calculation using RT-TDHF/TDDFT, starting with the initial condition that an electron added to the Rydberg orbital of the ground state of the cation. To analyze this calculation and obtain the distribution to the excited states (including Rydberg and dissociative states), Fourier transform analysis was applied to time evolution of polarization vector and density matrix elements.

References
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