

Electron dynamics described by real-time time-dependent Hartree-Fock and/or time-dependent density functional theory (RT-TDHF/TDDFT) calculation

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Electron dynamics, which is an ultrafast phenomenon occurring in attoseconds or femtoseconds, 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,.

In previous studies, electron dynamics described by RT-TDHF/TDDFT calculations was analyzed by the Fourier transform technique to obtain frequency-domain properties and directly through time evolution of molecular properties. In this study, we proposed short-time Fourier transform (STFT) analysis for electron dynamics [1]. STFT is a time-frequency analysis technique to provide time evolution of spectrum, which is called spectrogram. Figure 1 shows absorption spectrograms obtained by STFT analysis of RT-TDHF calculation of formaldehyde dimer as a model system. The STFT analysis of RT-TDHF calculation enables us to directly observe the electron dynamics associated with the excited states.

Furthermore, the RT-TDHF/TDDFT approaches have limited applications because evaluation of the time evolution operator is computationally demanding. In this study, we developed an efficient time evolution method based on three-term recurrence relation (3TRR) [2]. 3TRR is derived by introducing transformation of the operator in time-dependent equation, such as Hamiltonian. The 3TRR method achieved efficiency that is about four times faster than conventional fourth-order Runge-Kutta method.

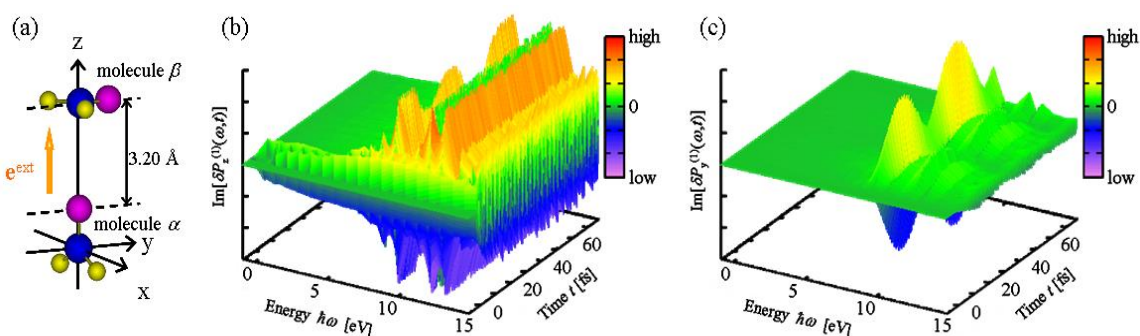


Figure 1: (a) Formaldehyde dimer model, in which two molecules are vertically arranged; (b) Absorption spectrogram for z direction; (c) Absorption spectrogram for y direction.

References

- [1] T. Akama & H. Nakai, 2010, JCP 132, 054104.
- [2] T. Akama, O. Kobayashi, & S. Nanbu, 2015, JCP 142, 204104.