Femtosecond electron-ion dynamics in excited nano-materials

Real-time propagation based on the time-dependent density functional theory

Yoshiyuki Miyamoto

Fundamental and Environmental Research Labs., NEC, 34 Miyukigaoka, Tsukuba,305-8501 Japan

y-miyamoto@ce.jp.nec.com

Electronic excitations induce very fast phenomena like as photo-induced chemical reactions, energy shake up by ion impacts, decay of hot-carriers, and so on. Such fast dynamics typically take few hundreds femtoseconds (fs = 10^{-15} seconds), where the application of conventional Fermi-Golden rule and Boltzmann transport equation are no longer valid. Yet such fast phenomena play crucial roles in current nano-technology where precise control and design of materials are highly demanded. To challenge such very fast phenomena, direct treatment of time-propagation of electron wave functions is made being coupled with the molecular dynamics (MD) simulation. This is an alternative approach to conventional first-principles MD simulation where the diagonalization of the Hamiltonian is performed to obtain electronic steady state.

In this paper, I will discuss first-principles approach being applied to such fast dynamics. The basic ideas of the first-principles approach are the following two. The first is obtaining an approximated excited state within constraint density functional theory (DFT), in which artificial promotion of occupation numbers of electrons is made throughout the self-consistent field (SCF) iteration in diagonalizing the Kohn-Sham Hamiltonian. The second is to perform electron ion dynamics respectively based on the time-dependent DFT (TDDFT) [1] and on classical Newton's equations for ions starting from the approximated excited state. In solving the time-dependent Kohn-Sham equations, the Suzuki-Trotter split operator method [2], which conserves orthonormality of time-evolving wave functions and guarantees higher order of accuracy with respect to the interval of simulation-time-step, is applied. The numerical stability throughout long-time TDDFT and molecular dynamics (MD) simulations has been achieved by using the computer code FPSEID (First-Principles Simulation tool for Electron Ion Dynamics) [3].

Validation of this TDDFT-MD approach is guaranteed when the simulation follows a particular adiabatic potential energy surface (PES) since the Hellmann-Feynman theorem can be explicitly applied in computing forces on ions. On the other hand, in case of non-adiabatic transition, the simulation shows us appearance of off-diagonal elements of the time-dependent Kohn-Sham Hamiltonian with respect to the time-dependent Kohn-Sham wave functions. At this moment, we have an ambiguity in obtaining the forces on ions. I will discuss this problem in cases of molecules and condensed matters. An important note is that the famous approach of 'surface-hopping' [4] is basically not valid for DFT-based theories.

The displayed figure expresses one of applications of TDDFT-MD method: hot-carrier decay in photo-excited carbon nanotube which demonstrates the benefit of solving the time-evolution of many wave functions for tracing one particular PES even when the level crossing among the state with different electronic occupation occurs. This figure shows time-evolution of single-particle energy levels for excited electron and hole under lattice motions initiated at the room temperature. Rapid reduction of electron-hole energy gap can be seen, denoting non-radiative decay of hot-carrier in carbon nanotube within sub-picosecond time-constant.

References:

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[2] M. Suzuki, J. Phys. Soc. Jpn, **61** (1992) L3015.
[3] O. Sugino, Y. Miyamoto, Phys. Rev. B**59** (1999) 2579; ibid, Phys. Rev. B**66** (2002) 89901(E).
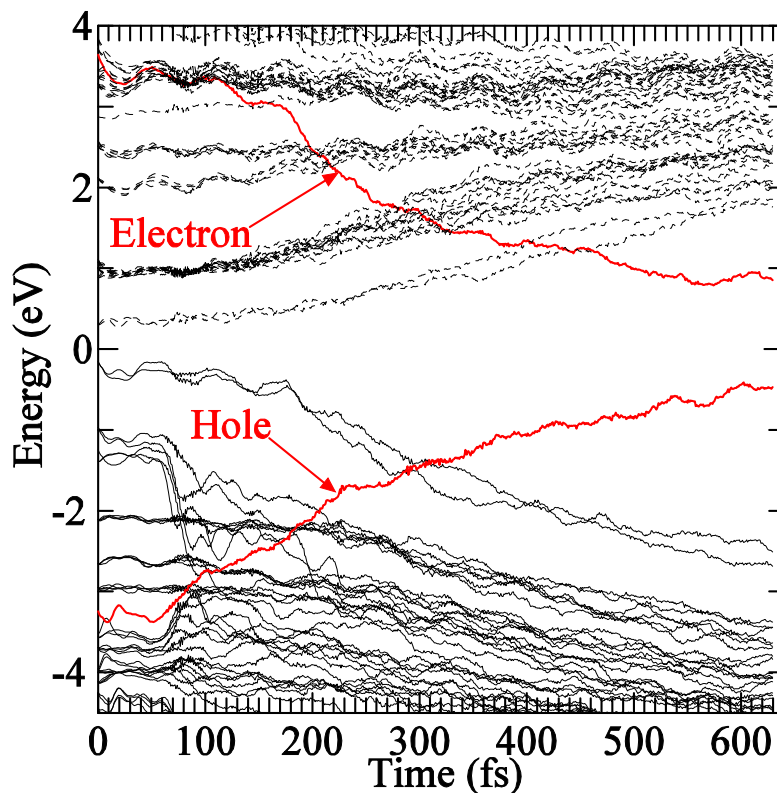[4] J. C. Tully, and R. L. Preston, J. Chem. Phys., **55** (1971) 217.

Figures:

Figure 1. Time evolution of hot-carrier in a (3,3) carbon nanotube. Excited electron and hole states are indicated by arrows. Solid and dotted lines are valence and conduction bands, respectively. This plot is for a Γ point with use of a supercell as eight-times longer than that of primitive cell of the (3,3) nanotube.