Non-Adiabatic Excited-State Time-Dependent *GW* Molecular Dynamics Satisfying Extended Koopmans' Theorem

Aaditya Manjanath[1]*, Ryoji Sahara[1], Kaoru Ohno[2], and Yoshiyuki Kawazoe[3]
[1] *Research Center for Structural Materials, National Institute for Materials Science, Tsukuba 305-0047, Japan*
[2] *Department of Physics, Yokohama National University, Yokohama 240-8501, Japan*
[3] *New Industry Creation Hatchery Center, Tohoku University, Sendai 980-8579, Japan*
[*] *E-mail: manjanath.aaditya@nims.go.jp*

Keywords: *GW*, excited-state molecular dynamics, TDDFT

Time-dependent density functional theory molecular dynamics (TDDFT-MD) [1] is the usual workhorse for studying excited-state (ES) dynamics in experimentally relevant systems, due to its reasonable computational cost. However, TDDFT-MD inevitably relies on the adiabatic local density approximation (ALDA) [2], which is valid only for the initial state being the ground state and not for any initially excited state such as in photochemical reactions. Therefore, the results obtained with TDDFT-MD based on ALDA may be unreliable.

The *GW* approximation (*GW*A) [3] is a reliable and accurate first-principles many-body approach in which electron exchange and correlation are described through the Green's function, G, the screened Coulomb interaction, W [4], and the resulting self-energy, $\Sigma = \mathrm{i}GW$. Conventional *GW*A defines quasiparticle (QP) energies for a ground-state electronic reference. Extended quasiparticle theory (EQPT) further shows that QP energies can be defined for electronically excited states [5] (Figure 1, left panel).

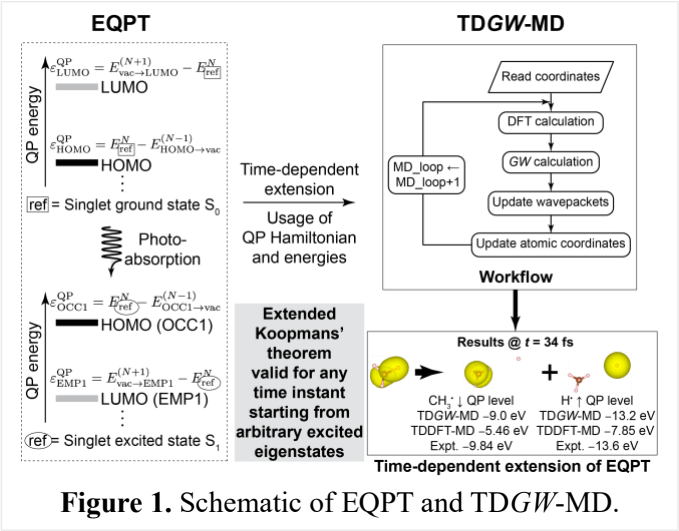

Figure 1. Schematic of EQPT and TD*GW*-MD.

Building on this foundation, we have recently developed non-adiabatic excited-state time-dependent *GW* molecular dynamics (NA-ES-TD*GW*-MD or TD*GW*-MD for short), a time-dependent extension of EQPT [6,7] (Figure 1, right panel). TD*GW*-MD follows correlated QP levels together with nuclear motion providing both reaction trajectories and experimentally interpretable electronic descriptions of bond breaking and product formation. It exactly satisfies extended Koopmans' theorem [8] and scales as ~O($N_B^{3\text{-}4}$), N_B - number of basis functions, which is distinctly advantageous to performing dynamics using configuration interaction. In this talk, I will show the mechanisms of important photochemical reactions using TD*GW*-MD, such as (a) the photo(cata)lysis of methane [6,7] as well as (b) the selective bond dissociation of partially deuterated water (HOD) via vibrationally mediated photodissociation, as a way to demonstrate how TD*GW*-MD can be a major step towards traversing the excited-state dynamical landscape accurately.

[1] E. Runge and E. K. U. Gross, *Phys. Rev. Lett.* **52**, 997–1000 (1984)
[2] M. Petersilka, U. J. Gossmann, and E. K. U. Gross, *Phys. Rev. Lett.* **76**, 1212–1215 (1996)
[3] M. S. Hybertsen and S. G. Louie, *Phys. Rev. B* **34**, 5390 (1986)
[4] L. Hedin, *Phys. Rev.* **139**, A796 (1965)
[5] K. Ohno, S. Ono, and T. Isobe, *J. Chem. Phys.* **146**, 084108 (2017)
[6] A. Manjanath, R. Sahara, K. Ohno, and Y. Kawazoe, *J. Chem. Phys.* **160**, 184102 (2024)
[7] A. Manjanath, R. Sahara, Y. Kawazoe, and K. Ohno, *Nanomaterials* **14**, 1775 (2024)
[8] D. W. Smith and O. W. Day, *J. Chem. Phys.* **62**, 113–114 (1975)