Time-dependent *GW* molecular dynamics – a new possible paradigm for an accurate description of dynamics of photochemical reactions

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Time-dependent density functional theory molecular dynamics $(TDDFT-MD)^{1}$ is the usual workhorse for studying excited-state (ES) dynamics, since it is computationally inexpensive. However, TDDFT-MD inevitably relies on adiabatic local density approximation (ALDA)², which is not valid for any initially ES such as in photochemical reactions. Therefore, the results obtained with TDDFT-MD based on ALDA may be unreliable. On the other hand, extended quasiparticle theory (EQPT)³ has been shown to guarantee the applicability of the GW approximation to any excited state as the initial reference state, contrary to conventional wisdom in the GW community. We have recently developed for the first time, a non-adiabatic dynamics methodology based on EQPT known as time-dependent GW molecular dynamics (TDGW-MD) to overcome the problem of ALDA for ES dynamics⁴. TDGW-MD exactly satisfies extended Koopmans' theorem⁵ and scales as $\sim O(N_B^{3-4})$, 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 TDGW-MD, such as (a) the photolysis of methane^{4,6} as well as (b) the interbase proton transfer in DNA base pairs in a step towards understanding ultraviolet-mediated mutations.

References

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