We introduce an atomistic, all-electron, black-box electronic structure code to simulate transient absorption (TA) spectra and apply it to simulate pyrazole and a GFP-chromophore derivative1. The method is an application of OSCF2, our dissipative extension of time-dependent density-functional theory. We compare our simulated spectra directly with recent ultra-fast spectroscopic experiments. We identify features in the TA spectra to Pauli-blocking which may be missed without a first-principles model. An important ingredient in this method is the stationary-TDDFT correction scheme recently put forwards by Fischer, Govind, and Cramer which allows us to overcome a limitation of adiabatic TDDFT. We demonstrate that OSCF2 is able to reproduce the energies of bleaches and induced absorptions, as well as the decay of the transient spectrum, with only the molecular structure as input. We show that the treatment of electron correlation is the biggest hurdle for TA simulations, which motivates the second half of the talk a new method for realtime electron correlation.

We continue to derive and propagate self-consistent electronic dynamics. Extending our derivation of OSCF2 to include electron correlation we obtain a non-linear correlated one-body equation of motion which corrects TDHF. Similar equations are known in quantum kinetic theory, but rare in electronic structure. We introduce approximations that stabilize the theory and reduce its computational cost. We compare the resulting dynamics with well-known exact and approximate theories showing improvements over TDHF. When propagated EE2 changes occupation numbers like exact theory, an important feature missing from TDHF or TDDFT. We introduce a rotating wave approximation to reduce the scaling of the model to $O(N^4)$, and enable propagation on realistically large systems. The equation-of-motion does not rely on a pure-state model for the electronic state, and could be used to study the relationship between electron correlation and relaxation/dephasing or as a non-adiabatic kernel for TDDFT. We show that a quasi-thermal Fermi-Dirac population of one-particle states is a stationary state of the method reached as the endpoint of propagation in some limits. We discuss this ‘thermalization’ of an isolated quantum many-body system in the context of the eigenstate thermalization hypothesis.