Dynamical transition orbitals: Theoretical formulation and applications

We expand the concept of natural transition orbitals in the context of real-time time-dependent density functional theory (RT-TDDFT) and show its application in practical calculations. Kohn–Sham single-particle wavefunctions are propagated in RT-TDDFT simulation, and physical properties remain invariant under their unitary transformation. In this work, we exploit this gauge freedom and expand the concept of natural transition orbitals, which is widely used in linear-response TDDFT, for obtaining a particle–hole description in RT-TDDFT simulation. While linear-response TDDFT is widely used to study electronic excitation, RT-TDDFT can be employed more generally to simulate non-equilibrium electron dynamics. By constructing natural transition orbitals through projecting time-dependent Kohn–Sham wave functions onto occupied/unoccupied eigenstate subspaces, we prove that linear combinations of a pair of the resulting hole/particle orbitals form a new gauge, which we refer to as dynamical transition orbitals. We demonstrate the utility of this framework to analyse RT-TDDFT simulations of optical excitation, electronic stopping dynamics, and nonadiabatic Thouless pumping.

Reference:

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2. Zhou, R., Yost, D. C., & Kanai, Y. (2021). First-principles demonstration of nonadiabatic thouless pumping of electrons in a molecular system. *The Journal of Physical Chemistry Letters*, *12*(19), 4496-4503.