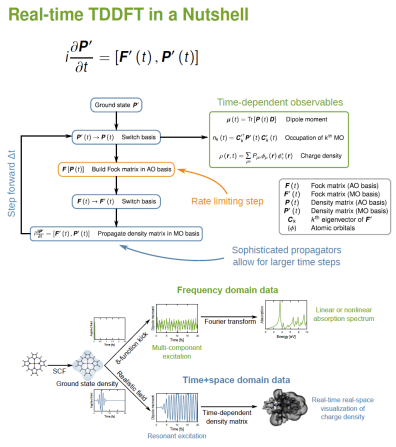
Excited State Absorption from Real-Time Time-Dependent Density Functional Theory

Sean Fischer[1], Niri Govind[1], Chris Cramer[2]

Real-Time (RT) TDDFT

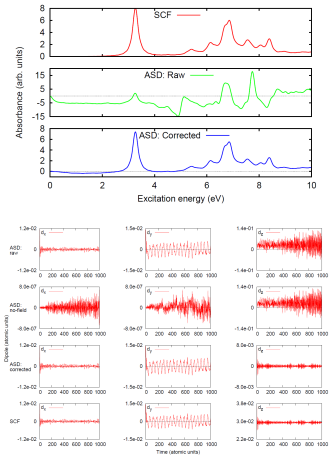


- Full response beyond perturbation limit
- Real-time, real-space → full dynamical information
- Insight into ultrafast and nonlinear processes
- High harmonic generation
- Valence, core, and now excited state excitations
- Compatible with all XC functionals in NWChem

Excited State Absorption

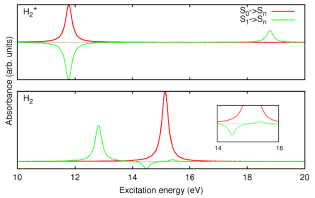
- QR-TDDFT
  - Excited state energies obtained from LR-TDDFT
  - Transition moments between excited states obtained from second order residues of the QR function
  - Straightforward assignment of states
  - Can be cumbersome and costly for excited state absorption spectrum of a large molecule
- RT-TDDFT
  - Obtain excited state absorption spectrum by propagating excited state density (linear response of excited state)
  - Excited state density obtained from LR-TDDFT gradients calculation
  - Scales favorably with system size
  - Assignment of states not straightforward

Signal Processing



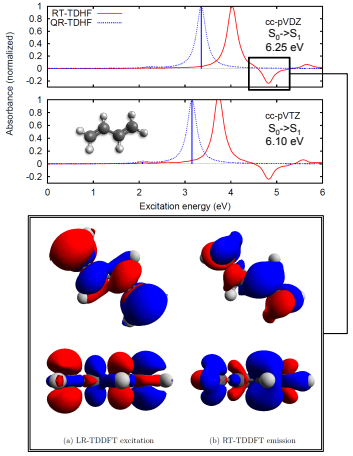
- Non-stationary state
  - Due to approximations in exchange-correlation functional, initial excited state is not stationary
  - Can (mostly) account for non-stationary initial state by creating a moving reference
  - Dipole moment with applied field referenced to simulation without applied field

H_2^+ and H_2 ESA

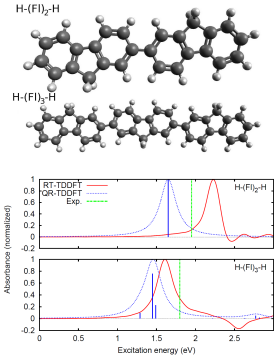


- RT-TDHF/6-31G
  - HF is exact for one-electron case
  - Emission is natural part of approach
  - Different reference state leads to different transition frequencies/intensities for inexact theories

RT-TDDFT vs QR-TDDFT

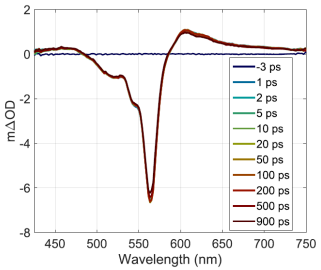


- Butadiene
  - RT-TDHF and QR-TDHF give similar results
  - Transition density from RT-TDHF for negative feature qualitatively agrees with transition density from LR-TDHF, indicating emission in the RT-TDHF simulation

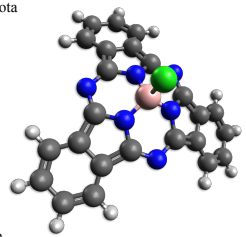


- Oligofluorenes: B3LYP/6-31G
  - RT-TDDFT shows slightly better performance than QR-TDDFT relative to experiment

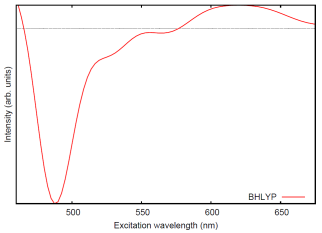
Transient Absorption



- Boron subphthalocyanine chloride
  - Transient absorption spectra
  - Measurement from lab of Prof. David Blank, University of Minnesota



- Simulation
  - B3LYP/6-31G* optimized ground state geometry
  - RT-TDDFT with BHLYP/6-31G*
  - Simulated transient spectrum obtained from subtracting the ground state spectrum from the excited state spectrum



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[1]Pacific Northwest National Laboratory
[2]University of Minnesota