



Challenges Associated with the Development of Electron-Correlated Methods for Excited State Structure and Dynamics

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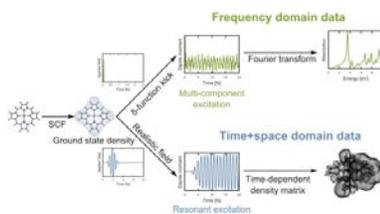
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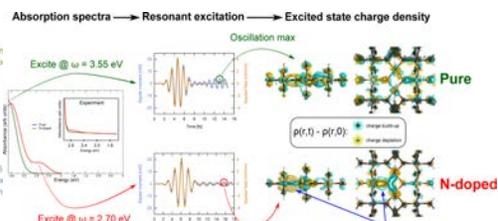
Challenges with Excited States

Real-time TDDFT in a nutshell

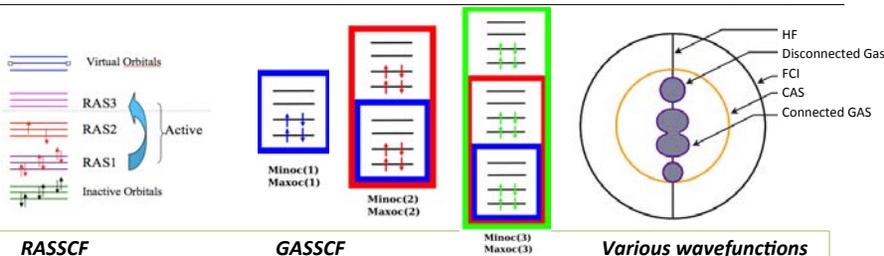


- ◆ Full response beyond perturbation limit
- ◆ Real-time, real-space → full dynamical information
- ◆ Insight into ultrafast and nonlinear processes

Real-Time TDDFT Calculations



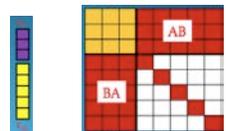
Multiconfigurational QM: New Developments



RASSCF

GASSCF

Various wavefunctions



How to solve the system of Secular Equations?

$$\sum_{n=1}^N (H_{mn} - E\delta_{mn})c_n = 0 \quad m = 1, 2, \dots, N$$

$$\begin{cases} \sum_n (U_{mn} - E\delta_{mn})c_n = 0 & m \in (A) \\ c_m = \sum_n \frac{U_{mn}}{E - H_{mm}} c_n & m \in (B) \end{cases}$$

No Configurations neglected!

$$\begin{pmatrix} H^{AA} & H^{AB} \\ H^{BA} & H^{BB} \end{pmatrix} \rightarrow \begin{pmatrix} U^{AA} \end{pmatrix}$$

$$U_{mn} = H_{mn} + \sum_{\alpha} \frac{H'_{m\alpha} H'_{\alpha n}}{E - H_{\alpha\alpha}} + \sum_{\alpha} \sum_{\beta} \frac{H'_{m\alpha} H'_{\alpha\beta} H'_{\beta n}}{(E - H_{\alpha\alpha})(E - H_{\beta\beta})} + \{\dots\}$$



Esmond Ng

Why NWChem?

- DOE's Premier computational chemistry software
- Scalable with respect to scientific challenge and compute platforms
- From molecules and nanoparticles to solid state and biomolecular systems
- Open-source (ECL 2.0)

Electronically nonadiabatic and ultrafast dynamics

ANT (Adiabatic and Nonadiabatic Trajectories) program
Two methods for non-Born-Oppenheimer dynamics:
FSTU: surface hopping by fewest switches with time uncertainty
CSDM: coherent switches with time-uncertainty

Tuned and balanced (smeared) redistributed charge schemes in (QM/MM)



Implement FSTU with decoherence into NWChem

Mathematical issue: Is it physically correct to add decoherence onto FSTU?
Scientific issue: How accurate is FSTU with decoherence?
Algorithmic Issue: What is the most efficient way to integrate the coupled differential equations?

Challenge: Polar bonds across the the QM/MM boundary.

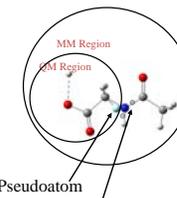
Method:

Charge Balancing: Adjust the MM charges to conserve the total charge of the entire QM/MM system.

Charge Redistribution: Move the charges that are close to the boundary away from the boundary.

Charge Smearing: Place the redistributed charges in Slater-type orbitals.

Tuned Pseudoatom: Use Fluorine as the link atom but add a pseudopotential $U(r)$ to it to mimic the original MM atom.



Tuned Pseudoatom
Balanced (Smeared) Redistributed Charges

Multiscale approaches for explicit local solvation environments and conformational sampling of chromophores

Automatic generation of a large number of uncorrelated explicit-solvent configurations and chromophore conformations

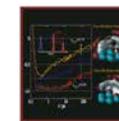
Development of a fitness function to measure whether a subset of these configurations/conformations is representative of the entire ensemble

Monte Carlo simulated annealing/genetic evolution algorithm for pruning of subsets



NWChem program

Computation of ground- and excited-state wave functions and convergence control



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