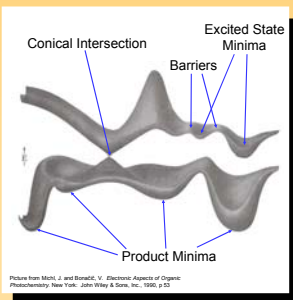


Double Excitations and Conical Intersections in Time-Dependent Density Functional Theory

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Studying Photochemistry

Vertical Excitation Energies are Only the Beginning



- We examine important features of the potential energy surface (PES) including excited state minima, conical intersections, and barriers. We also run dynamical simulations.
- States of many different characters are important (singly excited, doubly excited, etc).
- To study these systems we usually utilize multireference ab initio methods such as CASSCF, CASPT2, and MRCI. Accurate treatment of dynamical correlation is important, but very expensive.

TDDFT could provide an inexpensive, highly accurate alternative to multireference ab initio methods.

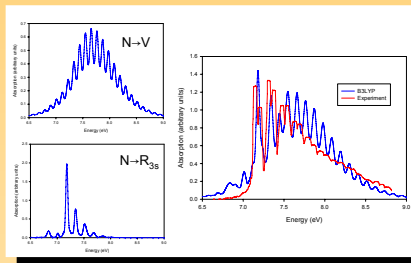
TDDFT in the Frank-Condon region

Ethylene Absorption Spectrum

- Absorption spectra are calculated from simulations of nuclear wavepacket dynamics.

$$\epsilon(\omega) = C \omega \int_0^{\infty} \langle \hat{\rho}(0) | \hat{\rho}(t) \rangle e^{i\omega t} dt$$

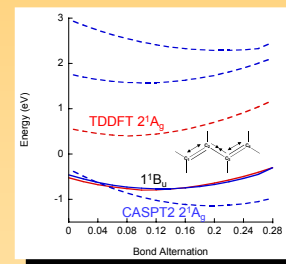
$$|\hat{\rho}\rangle = \mu |R\rangle |f\rangle; |\hat{\rho}(t)\rangle = \exp(-i\hat{H}t) |\hat{\rho}\rangle$$
- The PES is calculated 'on the fly' at the B3LYP/6-31+G level of theory.
- Results of runs on the valence (N-V) and 3s Rydberg (N-R_{3s}) states are shifted to match experimental excitation energies and summed according to their TDDFT oscillator strengths.



TDDFT can accurately reproduce the shape of singly excited potential energy surfaces in the Frank-Condon region.

Doubly Excited States of Butadiene

- The dark 2¹A_g state of butadiene is nearly degenerate to the bright 1¹B_u state at the Frank-Condon point.
- This dark state contains significant doubly excited character.

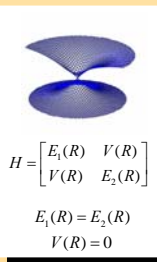


TDDFT does not capture the doubly excited character of this excited state.

TDDFT outside the Frank-Condon region

What is a Conical Intersection?

- A conical intersection is a point of true degeneracy between electronic states.
- Two conditions must be met for degeneracy therefore conical intersections exist not as single points but as N-2 dimensional seams (where N is the number of nuclear degrees of freedom).
- Normally we search for the minimum energy points along these seams (MECIs).



Searching for MECIs

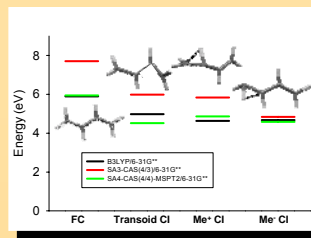
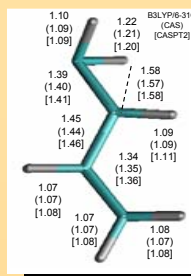
- Excited state energy is optimized subject to the constraint that the energy gap is zero.

$$g(Q, \lambda) = E_{ExcitedState}(Q) + \lambda \Delta E(Q)$$

$$\lambda = \text{Lagrange multiplier}$$
- Function is smoothed to allow numerical differentiation.

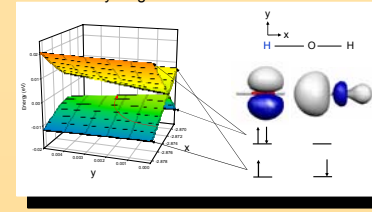
$$h(Q, \lambda) = E_{ExcitedState}(Q) + \left(\frac{1}{2} + \lambda\right) \frac{\Delta E(Q)^2}{(\Delta E(Q) + \alpha)} - \frac{1}{2} \Delta E(Q)$$

$$\alpha = \text{smoothing parameter}$$
- Function optimized with conjugate gradient method.
- Intersections are optimized at the trusted MS-CASPT2 level and compared with TDDFT results.



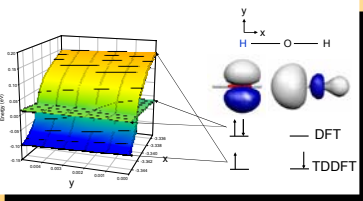
TDDFT can accurately predict the location and energy of conical intersections.

Linear Water Intersection – CASSCF – Everything an intersection should be



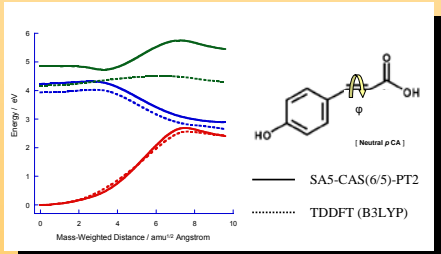
- Degeneracy is lifted in two independent directions.
- State characters mix as molecule moves 'around' intersection (follows red arrow).
- Energy gap varies linearly in region surrounding intersection.

Linear Water Intersection - TDDFT



- Degeneracy is lifted only in one direction. $V(R)=0$ for all geometries because Brillouin's theorem applies to the coupling between the DFT ground state and TDDFT excited states.)
- State characters cannot mix.
- Energy gap changes dramatically and nonlinearly in region surrounding intersection.

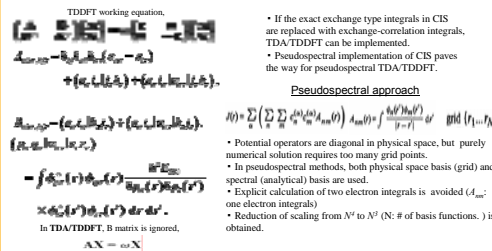
Torsional Coordinate Driving Curve for the model chromophore of Photoactive Yellow Protein (PYP)



- The isomerizable double bond dihedral angle ϕ was driven while the rest of geometrical parameters were optimized with respect to S₁ energy at state-averaged CASSCF(6-31G*) level of theory. CASPT2 was done at these geometries.
- After crossing the isomerization barrier on S₁, S₂ has significant double excitation character.

TDDFT for Large Molecules/Condensed Phases: Pseudospectral Implementation of Configuration Interaction Singles

- Tamm-Dancoff approximation (TDA) TDDFT and Configuration Interaction Singles (CIS)



Conclusions

- TDDFT accurately predicts the shape of the PES of singly excited states in the Frank-Condon region.
- TDDFT fails to accurately describe states with significant doubly excited character.
- TDDFT does predict the existence of intersections between states where they exist according to high level ab initio calculations.
- The dimensionality and shape of intersections between the DFT ground state and TDDFT excited states are pathological.

Future Work

- Investigate possible extensions and alternatives to TDDFT as accurate and low cost electronic structure method for the study of photochemistry.

Acknowledgement

TDDFT fails to produce correctly shaped PESs in the region surrounding intersections involving DFT ground states.

TDDFT agrees very well with multi-reference perturbation theory if the states are *not* of double excitation character

