Tully Models revisited: The molecule is the limit?

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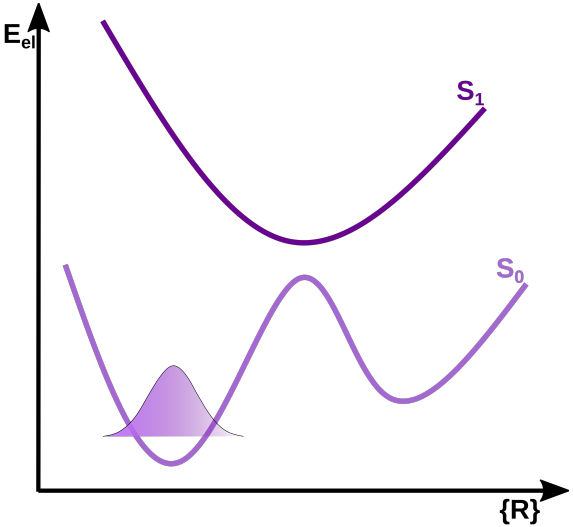
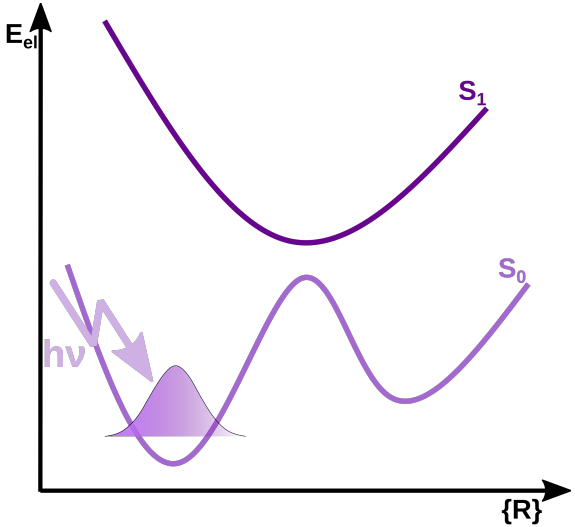
VISTA
October 22, 2020

In Silico Photochemistry



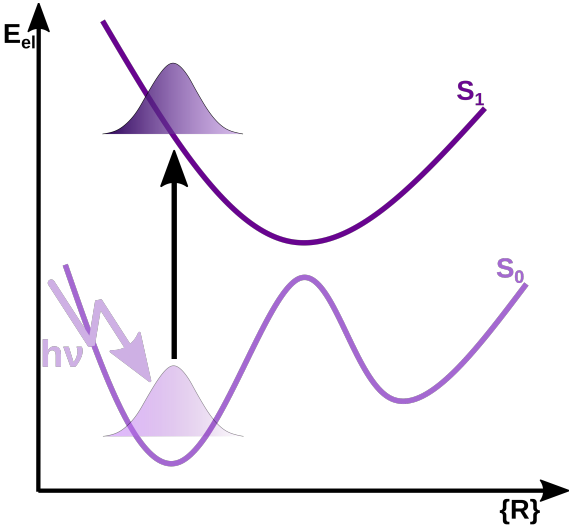
Molecule is in its ground state.

In Silico Photochemistry



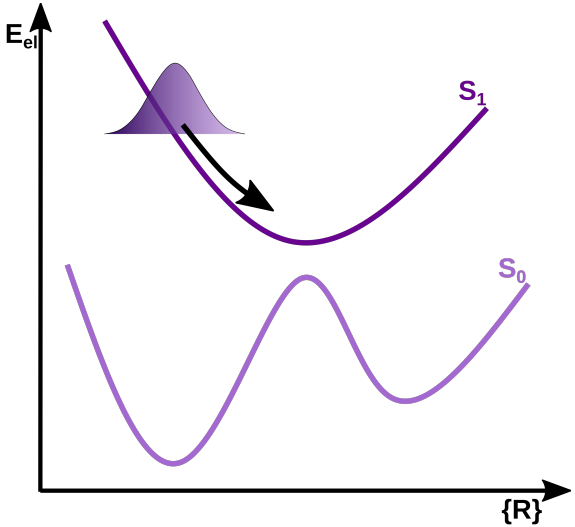
Molecule absorbs a photon...

In Silico Photochemistry



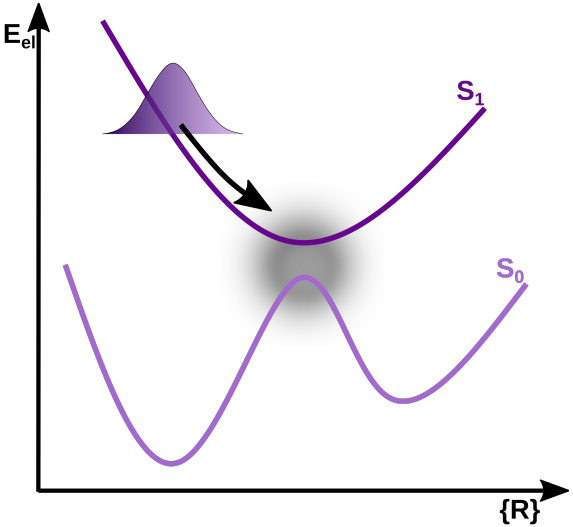
...and gets excited to e.g. S_1.

In Silico Photochemistry



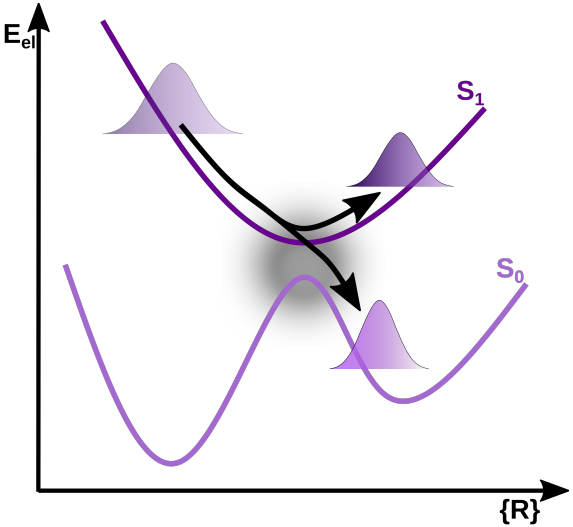
Evolution in S_1

In Silico Photochemistry



Nonadiabatic processes

In Silico Photochemistry

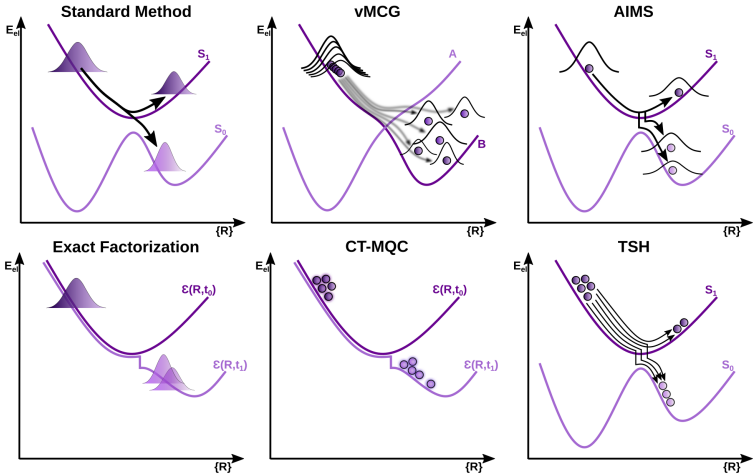


Splitting of wavepacket.

Challenge for computational chemistry:

- Electrons and nuclei coupled!
- Accurate electronic structure, valid at all times
- Nuclear dynamics

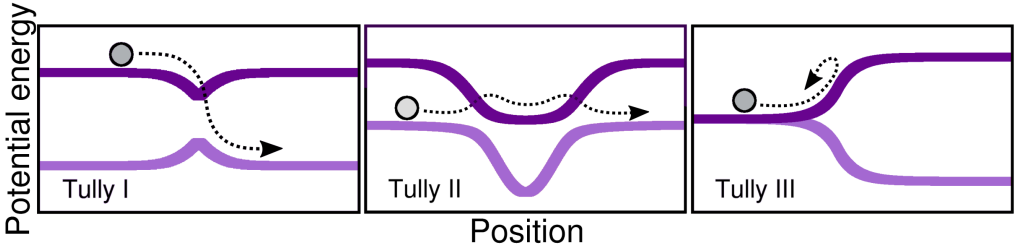
Nonadiabatic Dynamics Approaches



Countless different methods to describe photodynamics:

- different representation of nuclear wavefunction
- different level of approximations
- quantum or classical nuclei
- accounting for quantum effects
- *Any new method needs to be duly tested to understand its limitations*

Tully Models: A 1D Testbed

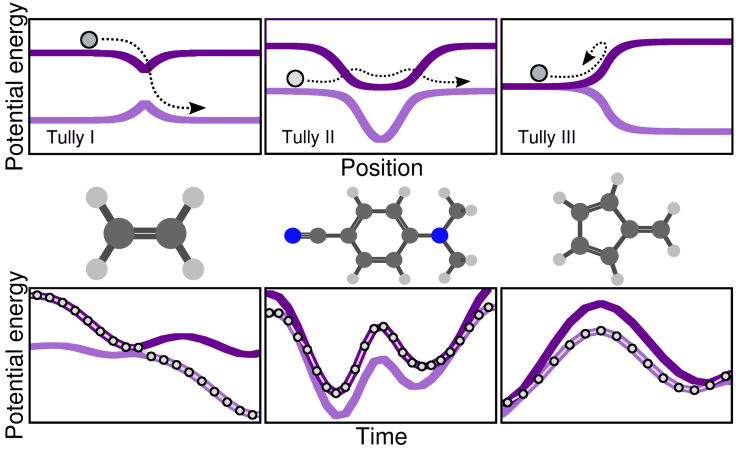


Used to test e.g.: full multiple spawning, semiclassical initial value representation, symmetrical quasi-classical windowing combined with Meyer-Miller mapping Hamiltonian, surface hopping Herman-Kluk semiclassical initial value representation method, semiclassical Monte-Carlo, dephasing representation of quantum fidelity, counter-propagating wave methods trajectories, Ehrenfest-Plus, coupled-trajectory mixed quantum/classical dynamics, quantum trajectory mean-field approach, iterative linearized approach to nonadiabatic dynamics, mean-field dynamics with stochastic decoherence, nonadiabatic Bohmian dynamics, mean-field molecular dynamics with surface hopping, non-Hermitian surface hopping, multi-state trajectory approach to nonadiabatic dynamics, partial linearized density matrix dynamics, ring polymer surface hopping, quantum trajectory surface hopping, consensus surface hopping, quasiclassical mapping Hamiltonian methods...

Tully, *J. Chem. Phys.* (**1990**), 93, 1061-1071

Test Set for Molecular Simulations

As we want to ultimately simulate dynamics of molecular in their full dimensionality:
Molecular Tully Models



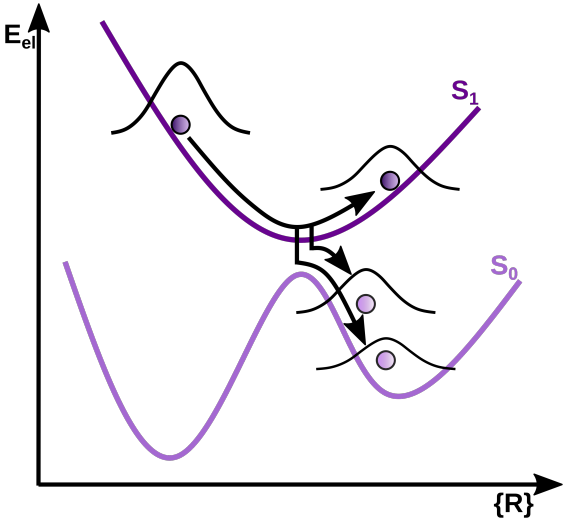
Highlighted challenges with *Ab Initio Multiple Spawning* and *(decoherence corrected) Trajectory Surface Hopping*

All initial conditions are available at
DOI:10.15128/r1qj72p715m

We want to provide a testset of real, full-dimensional, molecular systems for nonadiabatic dynamics!

Ibele and Curchod, *Phys. Chem. Chem. Phys.* (**2020**), 22, 15183-15196

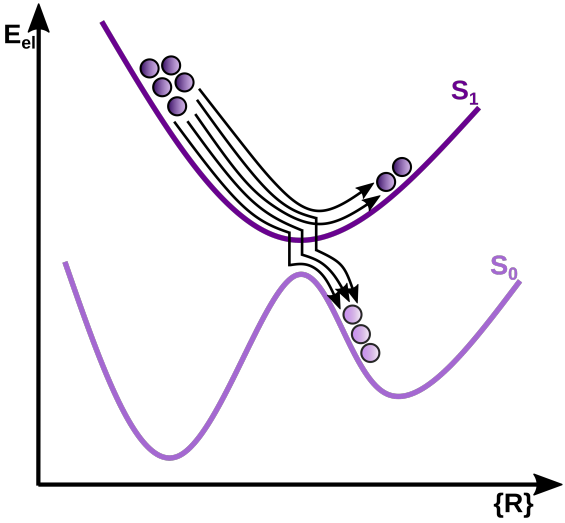
Ab Initio Multiple Spawning



- Nuclear wavefunction expressed in basis of *Gaussian trajectory basis functions (TBFs)*
- TBFs propagated classically, but are fully coupled
- Spawning allows to adapt the size of the basis in regions of high nonadiabaticity
- Full Multiple Spawning (FMS) *in principle* exact
- Ab Initio Multiple Spawning (AIMS) for molecules approximates couplings:
  - Saddle Point Approximation of order zero (SPA0)
  - Independent First Generation Approximation (IFGA)

Martínez et al., *J. Phys. Chem.* (**1996**), 100, 7884-7895;
Martínez et al., *Adv. Chem. Phys.* (**2002**), 121, 439-513

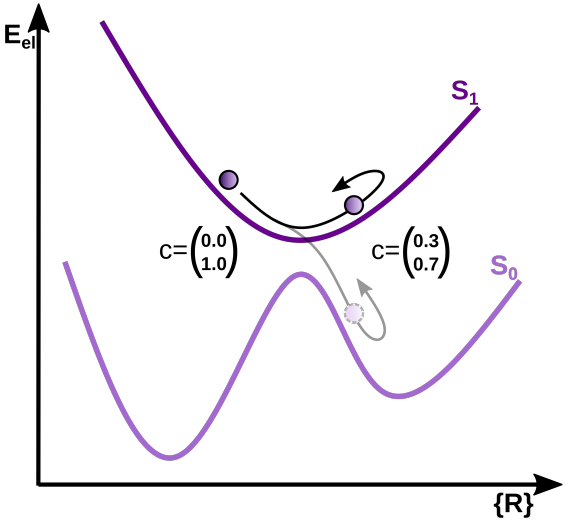
Trajectory Surface Hopping



- Applying an *Independent Trajectory Approximation (ITA)*
- Swarm of totally independent classical trajectories
- Associated amplitudes mimic a wavepacket
- Nonadiabatic effects:
  Hops between surfaces allow change of electronic states

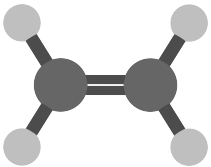
Tully, *J. Chem. Phys.* (**1990**), 93, 1061-1071;
Hammes-Schiffer and Tully, *J. Chem. Phys.* (**1994**), 101, 4657-4667

Trajectory Surface Hopping



- *TSH is overcoherent*
- All electronic population follows force of active state
- A variety of *ad hoc* corrections (dTSH), see e.g.:
  - Zhu et al., *J. Chem. Phys.* (**2004**) 121, 7658
  - Jasper and Truhlar, *J. Chem. Phys.* (**2007**), 127, 194306
  - Granucci and Persico, *J. Chem. Phys.* (**2007**), 126, 134114
  - Granucci et al., *J. Chem. Phys.* (**2010**), 133, 134111
  - Shenvi et al., *J. Chem. Phys.* (**2011**), 134, 144102
  - Jain et al., *J. Chem. Theory Comput.* (**2016**), 12, 11, 5256
  - Ha et al., *J. Phys. Chem. Lett.* (**2018**), 9, 1097
  - ...

Molecular Tully I: Ethylene



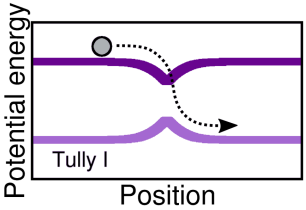
Single avoided crossing

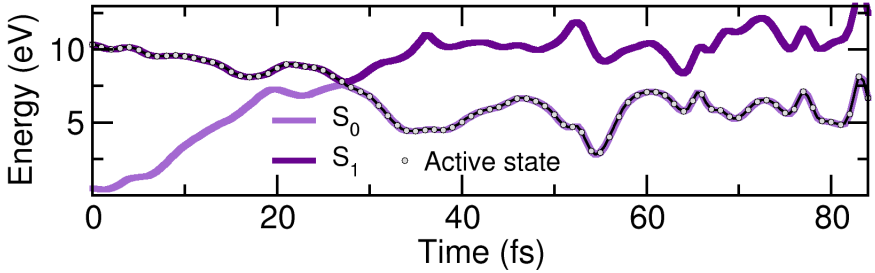
SA(3)-CASSCF(2/2)/6-31G* (MOLPRO)

66 Initial Conditions

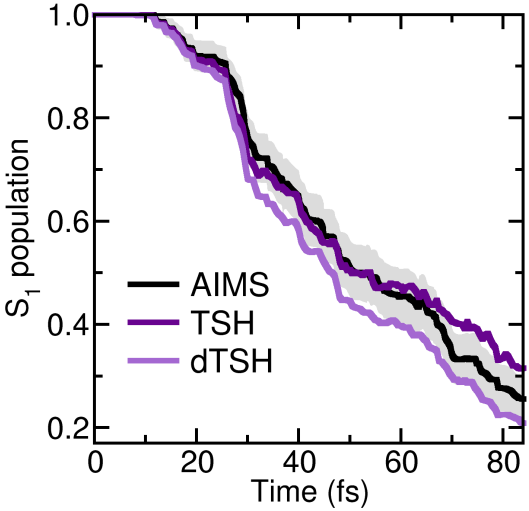
(d)TSH repeated with 10 random numbers with SHARC

AIMS with FMS90 in Molpro

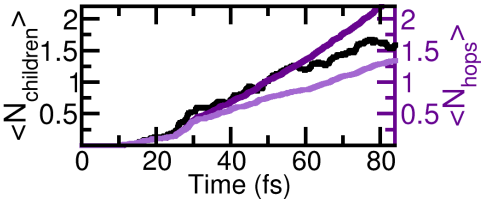




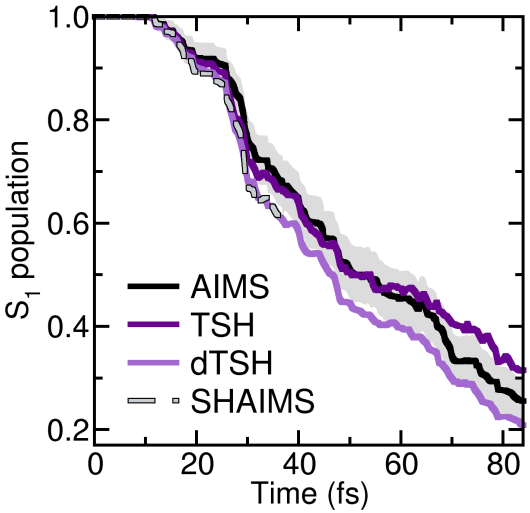
Molecular Tully I: Ethylene



AIMS: rapid decay, on average below 2 spawns
TSH: similar decay, number of hops rises above two
dTSH: significantly slower decay than AIMS
In TSH larger number of back hops – slower deactivation artifact of overcoherence



Molecular Tully I: Ethylene

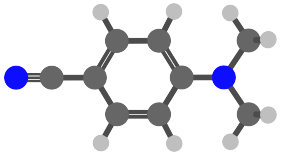


Surface **H**opping approach to **AIMS**:
Approximates AIMS equations of motion to ressemble TSH:

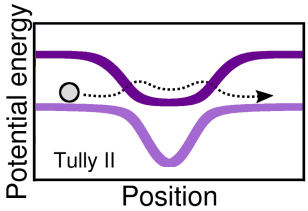
- remove all intrastate couplings
- force overlap=1 between TBFs on different states
- place the TBFs on the same position
- only consider the NACV of parent TBF

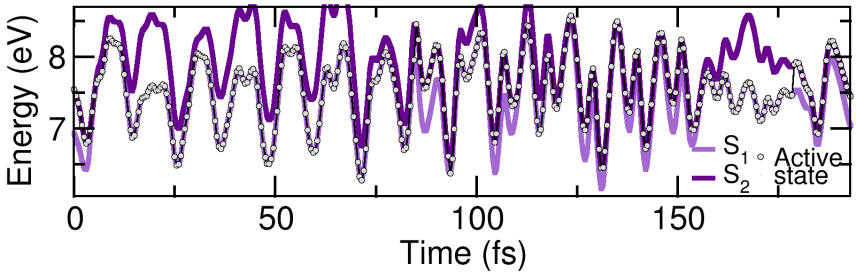
Reproduces dTSH perfectly – differences due to ITA inherent to TSH

Molecular Tully II: DMABN



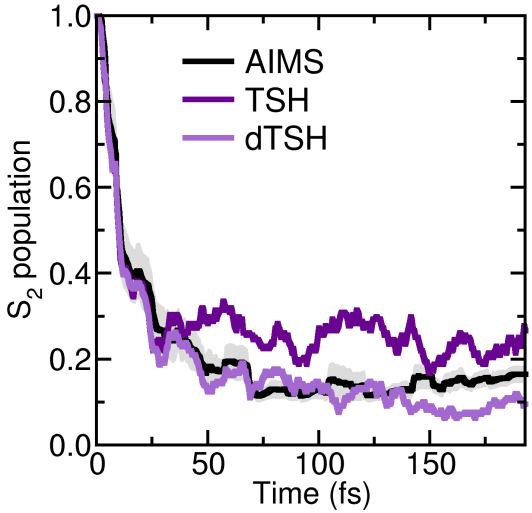
Dual avoided crossing
TDA-LC-PBA/6-31G
21 Initial Conditions
(d)TSH repeated with 10 random numbers
with Gaussian09/SHARC
AIMS with FMS90 in TeraChem from [a]





[a] Curchod et al., *J. Phys. Chem. A* (**2017**), 121, 1, 265-276

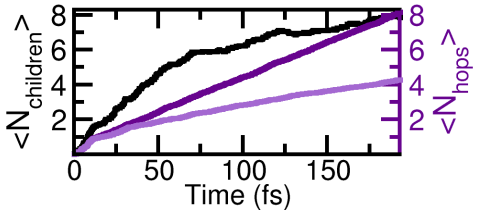
Molecular Tully II: DMABN



AIMS:[a] rapid decay, after 50 fs oscillations in the population, large number of spawns

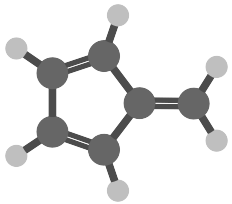
TSH: similar initial decay, deviations after 25 fs, total comparable number of hops

dTSH: great agreement with AIMS, much smaller number of hops



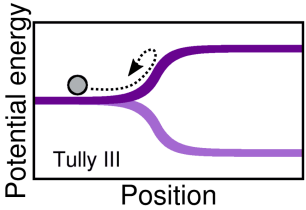
[a] Curchod et al., *J. Phys. Chem. A* (**2017**), 121, 1, 265-276

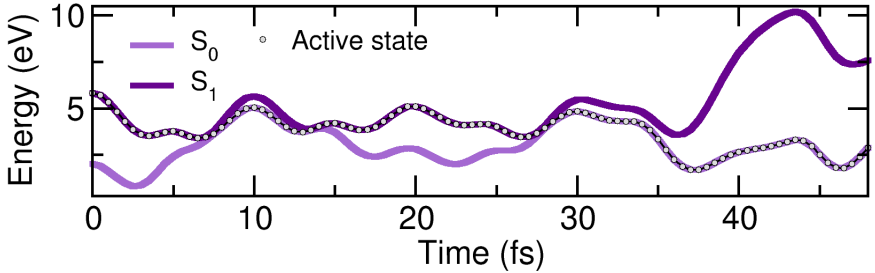
Molecular Tully III: Fulvene



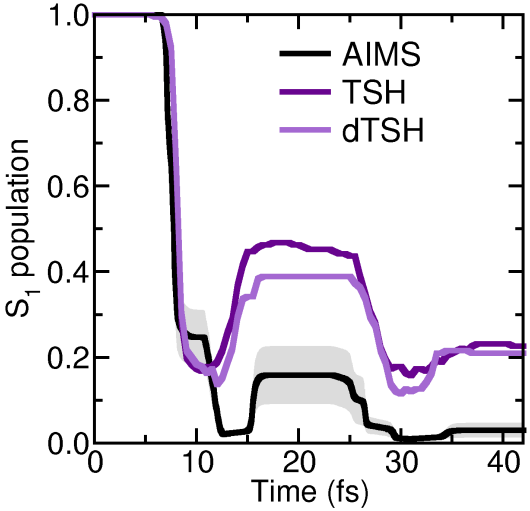
Extended coupling with reflection

SA(3)-CASSCF(6/6)/6-31G* (MOLPRO)
18 Initial Conditions (momenta set to zero)
(d)TSH repeated with 10 random numbers
with SHARC
AIMS with FMS90 in Molpro





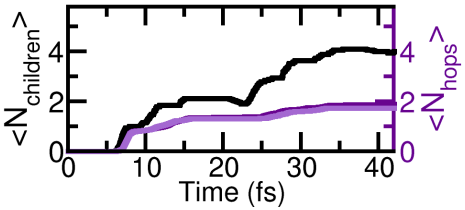
Molecular Tully III: Fulvene



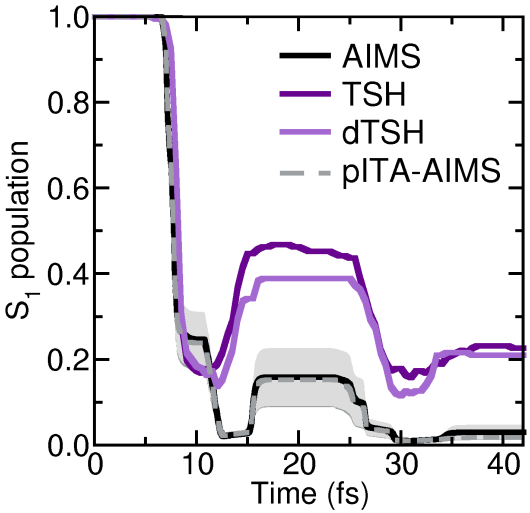
AIMS: almost complete inital decay, ~18% of reflection

TSH: less decay, stronger reflection (~48%)

dTSH: similar to TSH

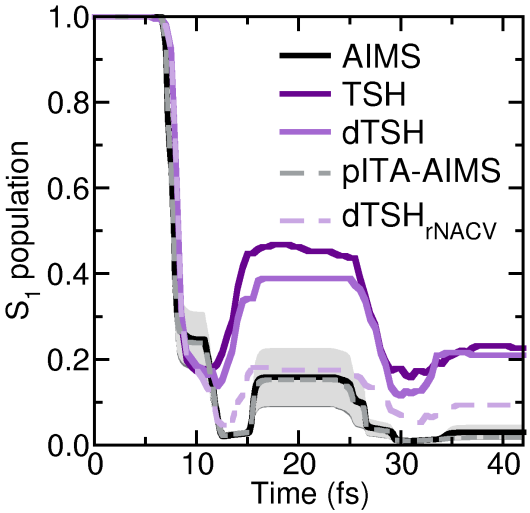


Molecular Tully III: Fulvene



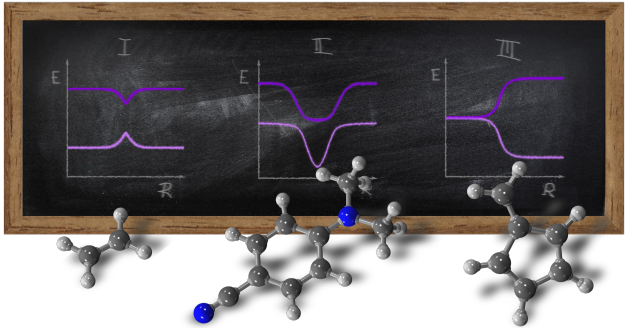
pseudo **I**ndependent **T**rajectory **A**pproximation in **AIMS**:
removes all direct intrastate couplings between TBFs in AIMS
→ close agreement with AIMS – interstate couplings stronger effect

Molecular Tully III: Fulvene



In TSH different scheme for the rescaling of the velocity after hops:
Often default: isotropically along the velocity vector
Alternatively parallel to the NACV – strong influence on the result.
(Similar different rescalings after spawns in AIMS have no influence)

Summary



Test your new nonadiabatic methods on a testset of real, full dimensional molecules!
All initial conditions are available at **DOI:10.15128/r1qj72p715m**

Acknowledgements

IN SILICO PHOTOCHEMISTRY GROUP

Durham University

EPSRC
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