Ab Initio Multiple Spawning with Informed Stochastic Selections

AIMSWISS

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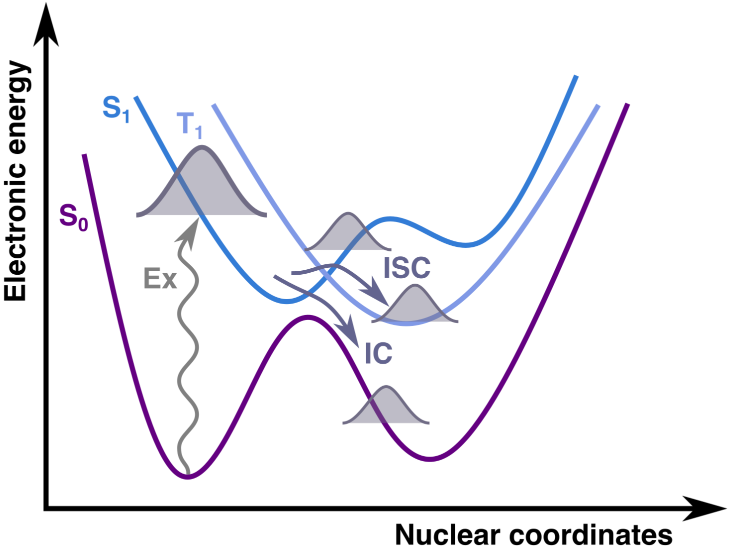
VISTA Seminar 27

11.11.2021

IN SILICO PHOTOCHEMISTRY GROUP

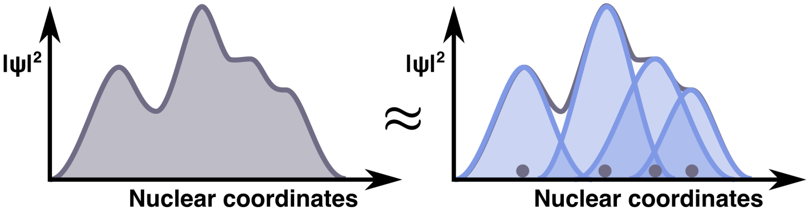
Durham University

Standard Model of Photochemistry



The Threefold Way of Multiple Spawning

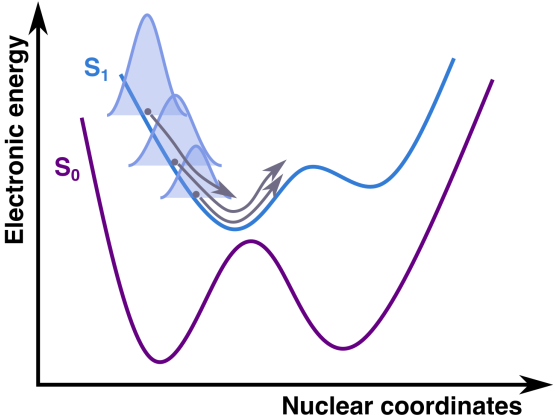
1. Expand nuclear wavefunctions in a basis set of frozen Gaussians



T. J. Martinez, M. Ben-Nun and R. D. Levine, J. Phys. Chem. 1996, **100** (19), 7884–7895.

The Threefold Way of Multiple Spawning

1. Expand nuclear wavefunctions in a basis set of <u>frozen</u> Gaussians
2. Propagate phase space centres of Gaussians classically on single adiabatic surfaces ⇔ trajectory basis functions (TBFs)



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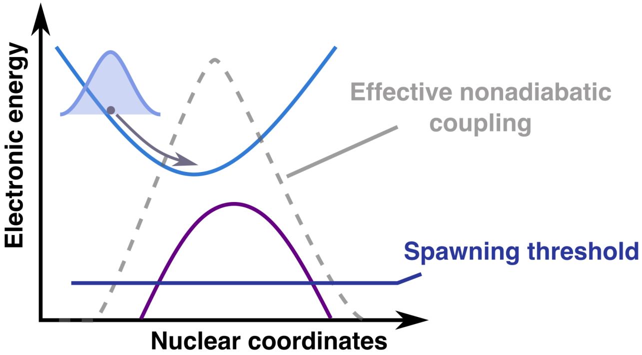
3. Grow basis set size when nonadiabatic events are imminent

t_{entry}:



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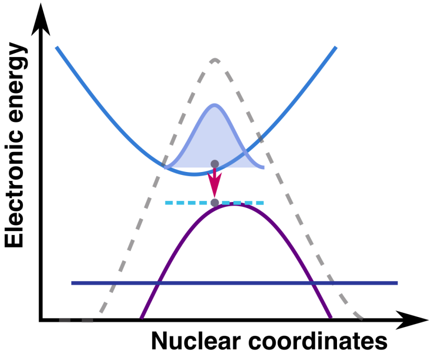

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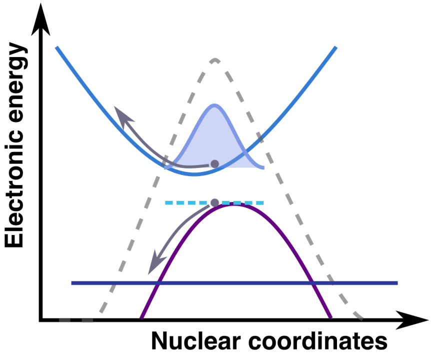

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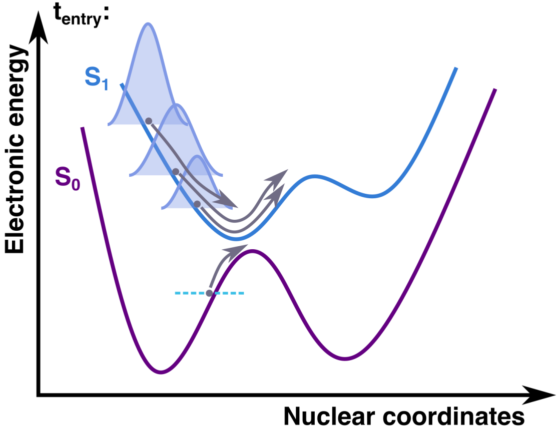
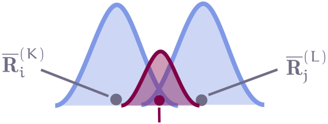


Ab Initio Multiple Spawning

- Multiple spawning is in principle exact, but in practice intractable
- Two approximations are made to arrive at ab initio multiple spawning (AIMS):
    1. Saddle-point approximation of zeroth order:

$$\langle \chi_i^{(K)} | \Theta^{(KL)}(\mathbf{R}) | \chi_j^{(L)} \rangle_{\mathbf{R}} \approx \Theta^{(KL)}(\overline{\mathbf{R}}_{ij}^{(KL)}) \langle \chi_i^{(K)} | \chi_j^{(L)} \rangle_{\mathbf{R}}$$



$$\overline{\mathbf{R}}_{ij}^{(KL)} = (\overline{\mathbf{R}}_i^{(K)} + \overline{\mathbf{R}}_j^{(L)})/2$$

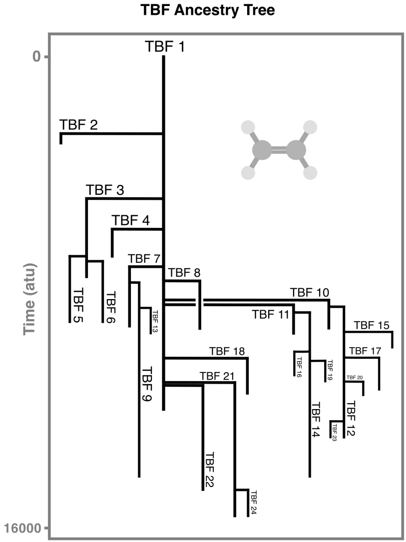
Complexity of dynamics is then: $O(N_{TBF}^2)$

2. Independent first generation approximation (IFGA)

B. Mignolet and B. F. E. Curchod, J. Chem. Phys. 2018, **148**, 134110.

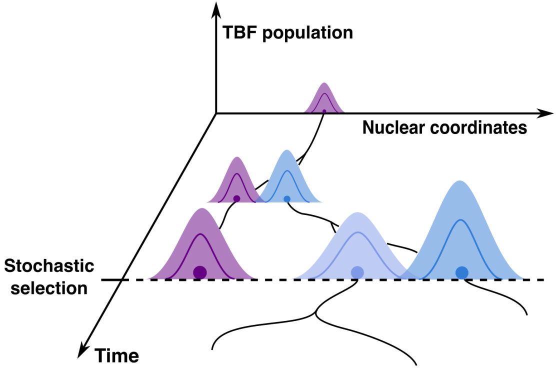
L. M. Ibele and B. F. E. Curchod, J. Chem. Phys. 2021 **155**, 174119

The Problem with Spawning



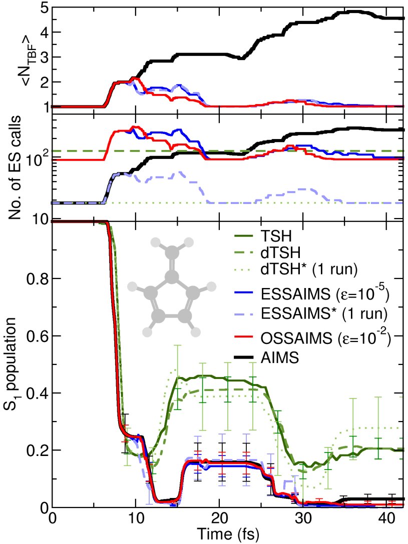
Stochastic selection: A solution

- Systematically remove TBFs from the simulation as soon as they become separated in phase space.
  $\Rightarrow$ Coupling determined by $|H_{ij}^{KL}|$ (ESSAIMS) or $|S_{ij}^{KL}|$ (OSSAIMS).
- If coupling falls $< \epsilon$ for any two groups of TBFs, pick one at random and renormalize remaining TBF populations.



B. F. E. Curchod, W. J. Glover and T. J. Martínez, J. Phys. Chem. A 2020, **124**, 6133–6143.

It actually works (and is performant)



- SA(2)-CASSCF(6,6)
- 18 initial conditions (Wigner)
- 5 (7) runs per initial condition SSAIMS (dTSH)
- Number of ES calls:
  - (d)TSH: $n_{\rm run} \times N_{\rm IC}$
  - (E/OSS)AIMS:

$$\sum_{j=1}^{n_{\rm run}} \sum_{k=1}^{N_{\rm IC}} N_{\rm TBF}^{j,k}(t) \times (N_{\rm TBF}^{j,k}(t)+1)/2$$

(worst case)

L. M. Ibele, Y. Lassmann, T. J. Martínez and B. F. E. Curchod, J. Chem. Phys. **154**, 104110 (2021).

Can we do better?

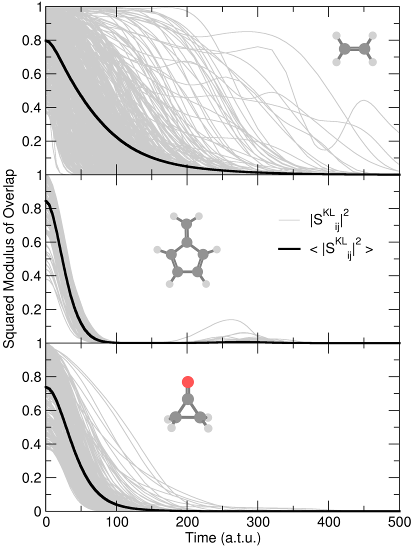
- SSAIMS performs well but relies on user defined thresholds, making it even less of a black box
- Is there some way to remove the selection threshold?
- Overlap of two frozen Gaussians with identical initial conditions should (approximately) decay as a Gaussian in time[1] with

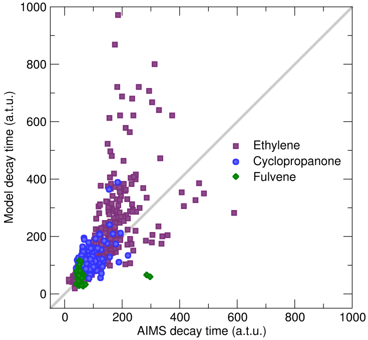
$$\tau_{\mathrm{D}} = \left[\frac{1}{4} \left(\mathbf{F}_{i,0}^{(K)} - \mathbf{F}_{j,0}^{(L)} \right)^{T} \alpha^{-1} \left(\mathbf{F}_{i,0}^{(K)} - \mathbf{F}_{j,0}^{(L)} \right) \right]^{-1/2} .$$

- It should consequently also apply to parent-child TBF pairs.

[1] B. J. Schwartz, E. R. Bittner, O. V. Prezhdo, and P. J. Rossky, J. Chem. Phys. **104**, 5942 (1996).

Yes we can!

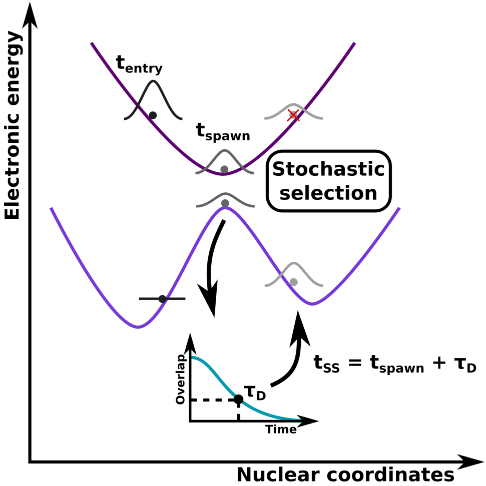




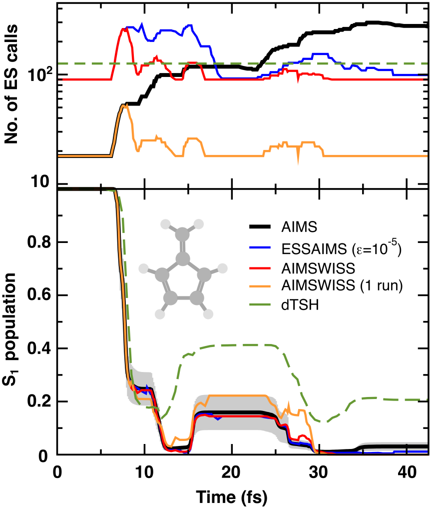
Y. Lassmann and B. F. E. Curchod, J. Chem. Phys. **154**, 211106 (2021)

Introducing AIMSWISS

Use the Schwartz decoherence time to predict when to perform stochastic selection.



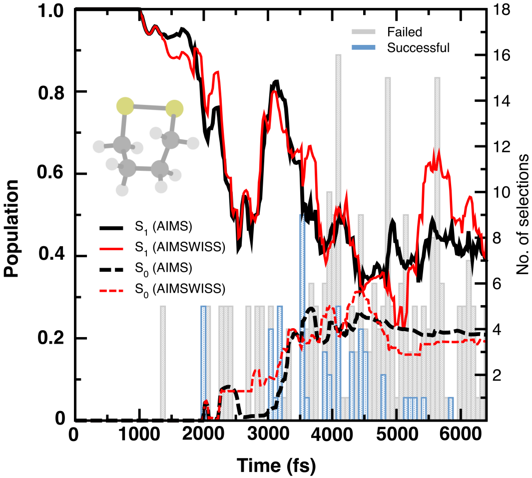
Back to Fulvene again



Y. Lassmann and B. F. E. Curchod, J. Chem. Phys. **154**, 211106 (2021)

AIMSWISS warning feature

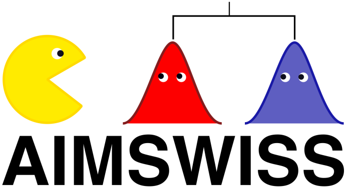
It is possible to notify the user, whenever the main assumption of AIMSWISS is not valid. E.g, for dithiane (unpublished work):



- SA(3)-CASSCF(6,4)
- 14 initial conditions (Wigner)
- 5 runs per initial condition

Conclusion & open questions

- The stochastic selection idea allows us to get AIMS quality dynamics at the computational cost of TSH
- AIMSWISS is the greediest version of SSAIMS possible
- However, a diagnostic is implemented that gauges the trustworthiness of the method.
- We envision AIMSWISS to be used as a
  - cheap benchmark of mixed quantum/classical dynamics methods
  - first step in an application of the multiple spawning methodology



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- How does stochastic selection affect other expectation values?
- Does it still work for low-dimensional systems?
- How far can we go when it comes to system size?

That's all folks!

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