Ab initio photochemistry 2

“On-the-fly” non-adiabatic molecular dynamics

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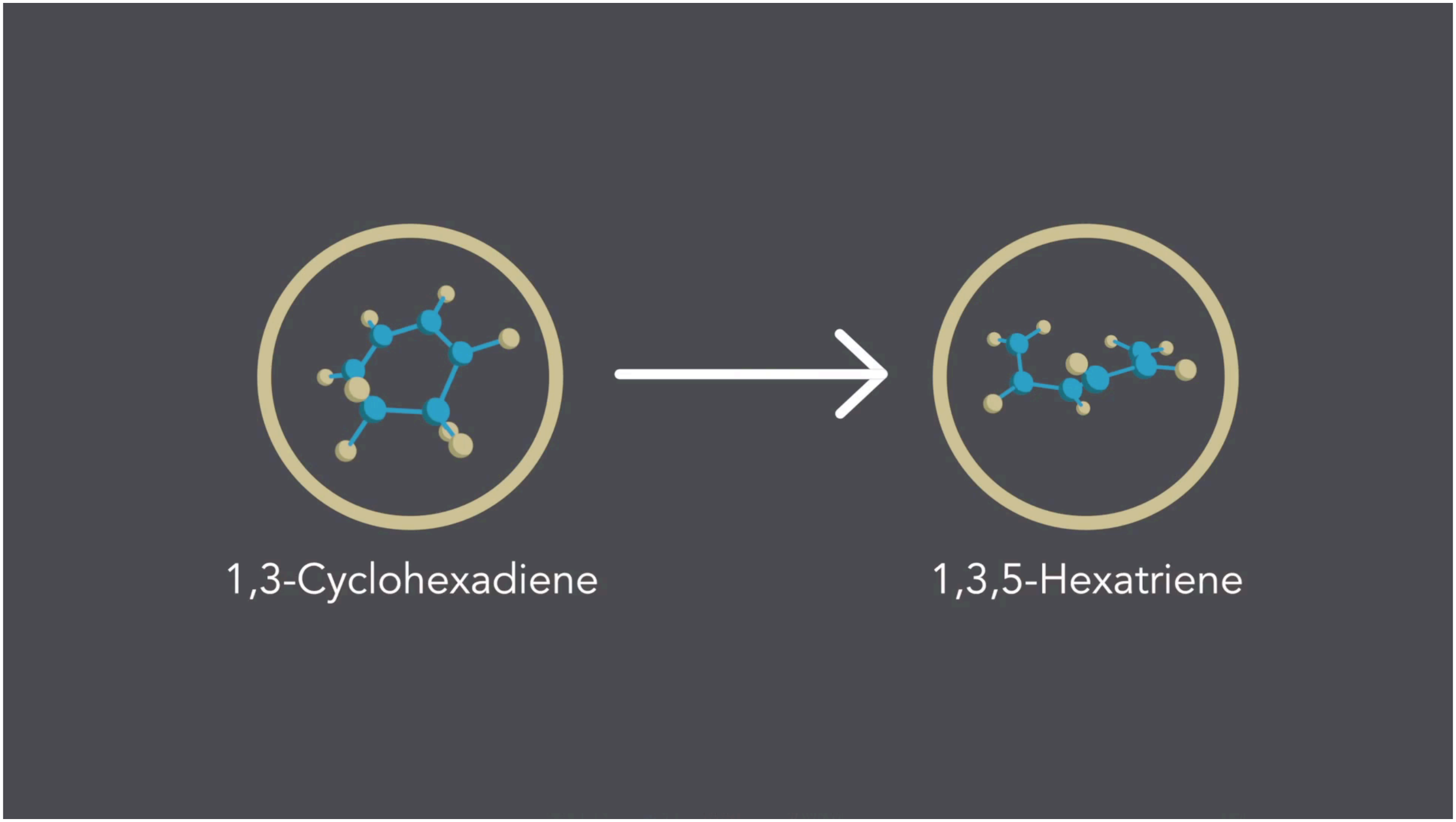
Outline

1. Motivation
2. Overview of the computational methods
3. Examples

1.Why molecular dynamics?



Minitti et al, *Phys. Rev. Lett.* (2015) **114**, 255501
https://www.chemistryworld.com/news/ultra-bright-x-rays-film-molecular-reaction/8675.article

2. How does a molecule move with time?

time-dependent Schrödinger equation $$i\hbar\frac{\partial\Psi}{\partial t} = \hat{H}\Psi$$

molecular Hamiltonian $$\hat{H}(R,r) = \hat{T}_n(R) + \hat{T}_e(r) + \hat{U}(R,r)$$

clampled-nucleus Hamiltonian $$\hat{H}_{el}(r;R) = \hat{T}_e(r) + \hat{U}(r;R)$$

For any given value of *R*, $$\hat{H}_{el}\Phi_i(r;R) = V_i(R)\Phi_i(r;R)$$

electronic eigenstates — electronic eigenvalues

Born representation: $$\Psi(R,r,t) = \sum_i^\infty \chi_i(R,t)\Phi_i(r;R)$$

nuclear function

non-adiabatic coupling $$\hat{\Lambda}_{ij} = \frac{1}{2M}(2F_{ij} + G_{ij})$$

$$i\hbar\frac{\partial\chi_j}{\partial t} = [\hat{T}_n + V_j]\chi_j - \sum_i^\infty \hat{\Lambda}_{ji}\chi_i$$

Worth and Cederbaum, *Annu. Rev. Phys. Chem.* (2004) **55**, 127:58

2. What approximations can we make?

- Born-Oppenheimer approximation:

$$\Psi(R,r) = \cancel{\sum_{i}^{\infty}} \chi_i(R)\Phi_i(r;R) \longrightarrow \Psi(R,r) = \chi(R)\Phi(r;R)$$

$$i\hbar\frac{\partial\chi_j}{\partial t} = [\hat{T}_n + V_j]\chi_j - \cancel{\sum_{i}^{\infty}} \hat{\Lambda}_{ji}\chi_i \longrightarrow i\hbar\frac{\partial\chi}{\partial t} = [\hat{T}_n + V - \cancel{\hat{\Lambda}}]\chi$$

- Adiabatic approximation:

$$\longrightarrow i\hbar\frac{\partial\chi}{\partial t} = [\hat{T}_n + V]\chi$$

- Group Born-Oppenheimer approximation:

$$\Psi(R,r) = \sum_{i\in\{g\}} \chi_i(R)\Phi_i(r;R) \quad i\hbar\frac{\partial\chi_j}{\partial t} = [\hat{T}_n + V_j]\chi_j - \sum_{i\in\{g\}} \hat{\Lambda}^{(g)}_{ji}\chi_i$$

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non-adiabatic coupling

$$\hat{\Lambda}_{ij} = \frac{1}{2M}(2F_{ij} + G_{ij}) \qquad F_{ij} = \langle\Phi_i|\nabla\Phi_j\rangle = \frac{\langle\Phi_i|(\nabla\hat{H}_{el})|\Phi_j\rangle}{V_j - V_i}$$

Worth and Cederbaum, *Annu. Rev. Phys. Chem.* (2004) **55**, 127:58

2. Which basis of electronic states should we use?

- Adiabatic basis

$$i\hbar\frac{\partial\chi_j}{\partial t} = [\hat{T}_n + V_j]\chi_j - \sum_i \hat{\Lambda}_{ji}\chi_i$$

- Diabatic basis

$$\tilde{\Phi} = S(R)\Phi$$

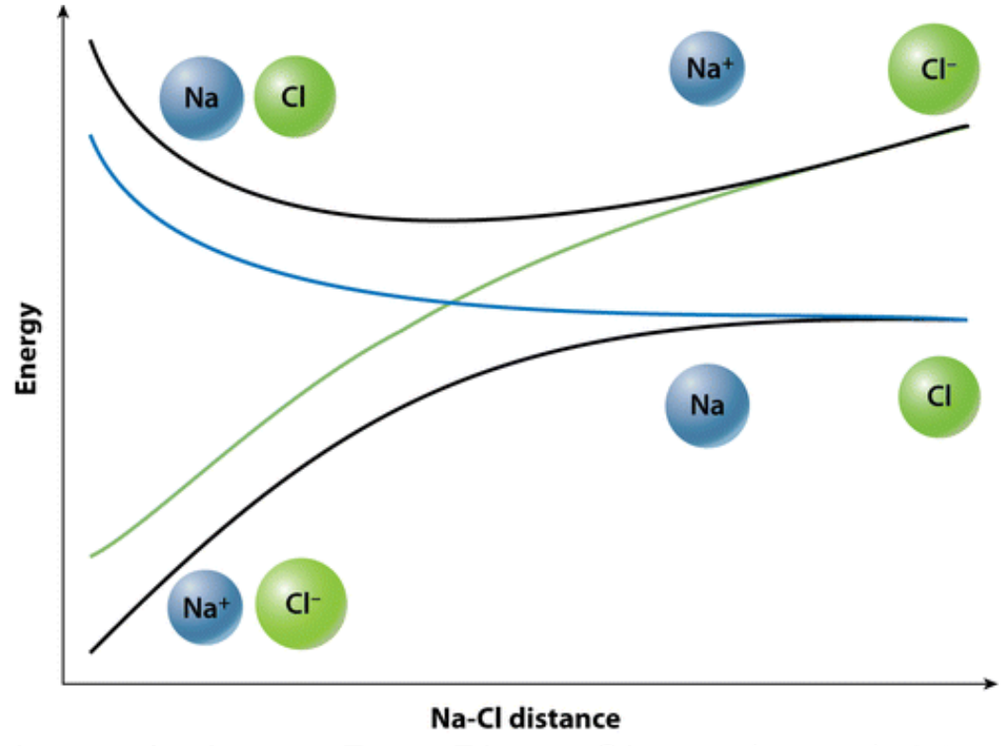
$$i\hbar\frac{\partial\tilde{\chi}_j}{\partial t} = \hat{T}_n\tilde{\chi}_j + \sum_i W_{ji}\tilde{\chi}_i$$

😊 no singularity of the derivative coupling

😓 how to find *S(R)* ?

😊 what comes out of standard quantum chemistry packages

😟 singularity of derivative coupling at conical intersection



Van Voorhis et al, *Annu. Rev. Phys. Chem.* (2010) **61**, 149

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non-adiabatic coupling

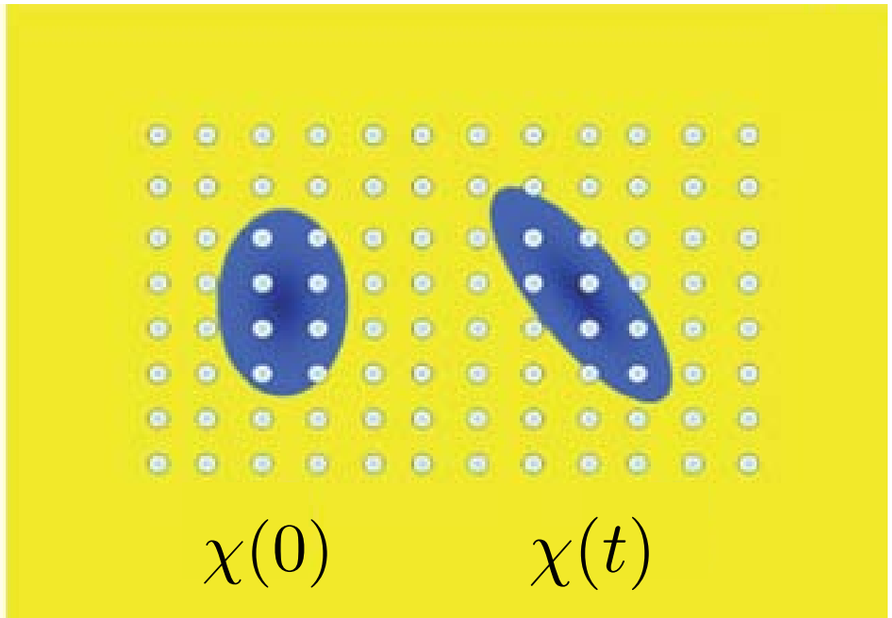
$$\hat{\Lambda}_{ij} = \frac{1}{2M}(2F_{ij} + G_{ij})$$

$$F_{ij} = \langle\Phi_i|\nabla\Phi_j\rangle = \frac{\langle\Phi_i|(\nabla\hat{H}_{el})|\Phi_j\rangle}{V_j - V_i}$$

Thiel et al, *JCP* (1999) **110**, 9371, Köppel et al, *JCP* (2001) **115**, 2377, Köppel et al, *Mol. Phys.* (2006) **104**, 1069

2. How to describe the nuclear functions?

Grid-based methods

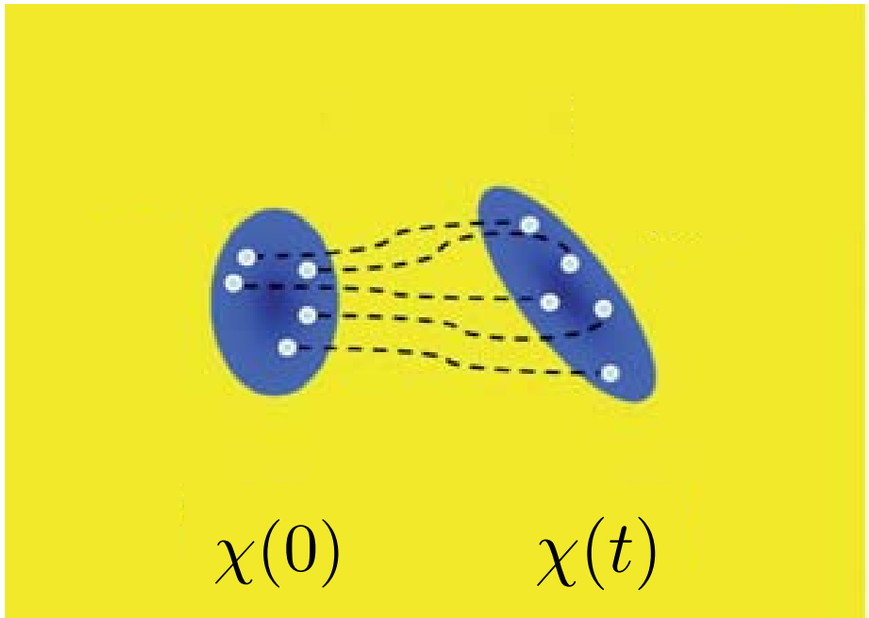


😊 numerical integration on a grid

😟 computation and fit of PES before any dynamics calculation

😭 p grid points per dimension, N dimensions: p^N grid points in total.
→ "exponential scaling" of the basis set with the number of degrees of freedom

Trajectory-based methods



😊 minimise the basis set size

😟 convergence with respect to the basis set size

😊 more intuitive picture

😊 local character of Gaussian function

→ generate the PES "on-the-fly"

Shalashilin, *Faraday Discuss.* (2011) **153**, 105-116

2. How to describe the nuclear functions?

$$\Psi(R,r,t) = \sum_i \chi_i(R,t)\Phi_i(r;R)$$

"multi-set" formalism $\{g_j^{(i)}(R,t)\}$

$$\Psi(R,r,t) = \sum_i \sum_j A_j^{(i)}(t) g_j^{(i)}(R,t)\Phi_i(r;R)$$

😊 GBF able to adapt better to the different electronic states

😟 need more basis functions

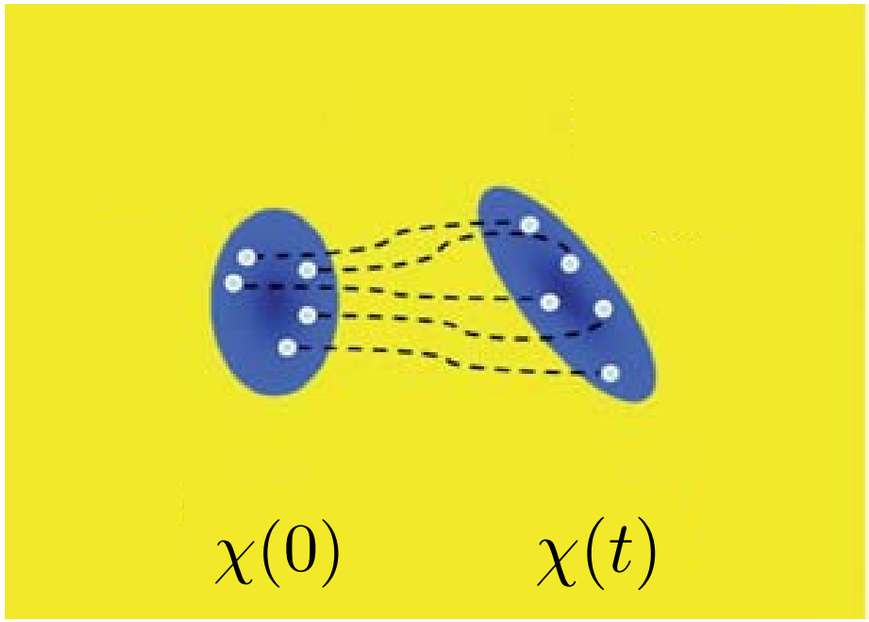
"single-set" formalism $\{g_j(R,t)\}$

$$\Psi(R,r,t) = \sum_i \sum_j A_j^{(i)}(t) g_j(R,t)\Phi_i(r;R)$$

😊 need less basis functions

😟 GBF constrained to move the same way for all electronic states

Trajectory-based methods



😊 minimise the basis set size

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😊 more intuitive picture

😊 local character of Gaussian function

→ generate the PES "on-the-fly"

Richings et al, *Int. Rev. Phys. Chem.* (2015) **34**(2):269 and Vacher et al, *Theor. Chem. Acc.* (2016) **135**, 187

2. How do the nuclear functions move?

$$\Psi(R,r,t) = \sum_i \sum_j A_j^{(i)}(t) g_j(R,t) \Phi_i(r;R)$$

Dirac-Frenkel variational principle:

→ equation of motion for the expansion coefficients

$$i\hbar \dot{A}_j^{(i)} = \sum_{l,m} [S^{-1}]_{jl} \left[(H_{lm}^{(ii)} - i\hbar\tau_{lm}) A_m^{(i)} + \sum_{i' \neq i} H_{lm}^{(ii')} A_m^{(i')} \right]$$

→ equation of motion for the frozen-width Gaussian basis function parameters (position and momentum) $\{\lambda_j(t)\}$

$$i\hbar \sum_{l\beta} C_{j\alpha,l\beta} \dot{\lambda}_{l\beta} = Y_{j\alpha}$$

(Direct-dynamics) variational multi-configuration Gaussian method
DD-vMCG

Richings et al, *Int. Rev. Phys. Chem.* (2015) **34**(2):269 and Vacher et al, *Theor. Chem. Acc.* (2016) **135**, 187

2. What approximations can we make?

multi-set

DD-vMCG

single-set

classical trajectories

FMS/ AIMS

independent trajectories

Surface Hoping

$$i\hbar \sum_{l\beta} C_{j\alpha,l\beta}\dot{\lambda}_{l\beta} = Y_{j\alpha}$$

Newton's Equation of motion

$$i\hbar\dot{A}_j^{(i)} = \sum_{l,m}[S^{-1}]_{jl}\left[(H_{lm}^{(ii)} - i\hbar\dot{T}_{lm})A_m^{(i)} + \sum_{i'\neq i} H_{lm}^{(ii')}A_m^{(i')}\right]$$

$A_j^{(i)}$ only coupled to $A_j^{(i')}$

classical trajectories

CCS/ MCE

independent trajectories

Ehrenfest

😐 not necessarily more expensive

😊 does converge to the quantum mechanical result!

😊 not much more expensive

😊 does converge to the quantum mechanical result!

😟 "purely" quantum effects not well described

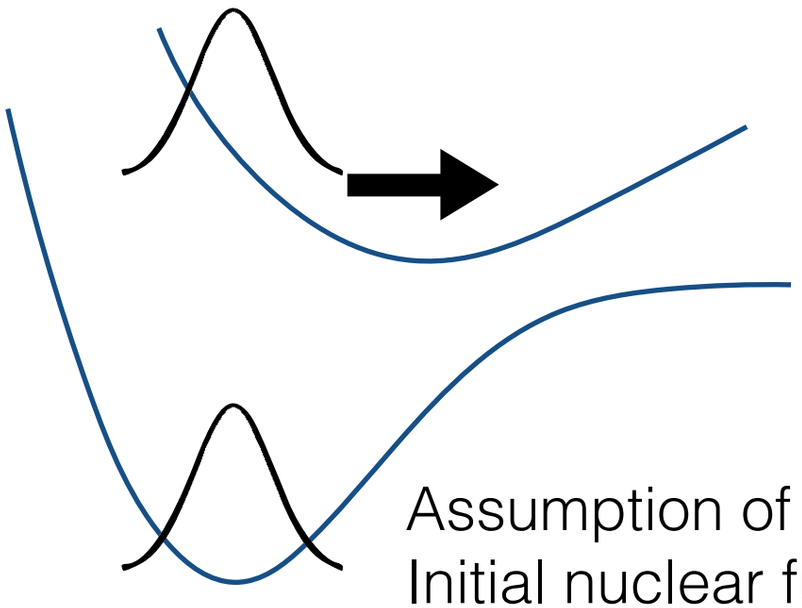
😊 "cheap"

😟 does not converge to the quantum mechanical result!

DD-vMCG (direct dynamics variational multi-configuration Gaussian)
FMS (full multiple spawning) and AIMS (ab initio multiple spawning)
CCS (coupled-coherent states) and MCE (multi-configurational Ehrenfest)

Vacher et al, *Theor. Chem. Acc.* (2016) **135**, 187

2. How to describe the initial nuclear function?

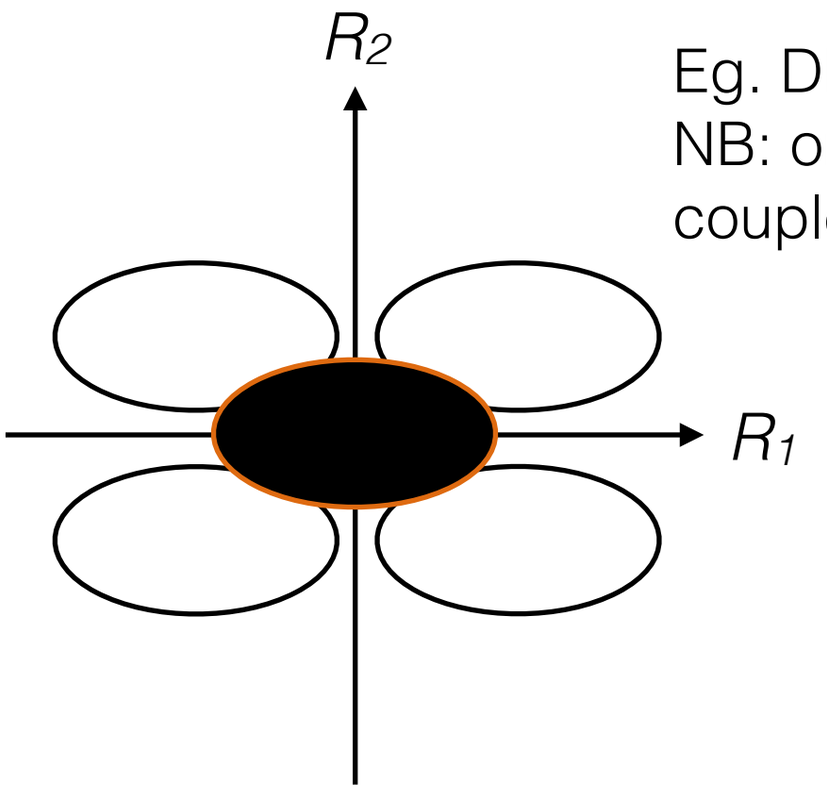


$$\Psi(R, r, t=0) = \sum_i \sum_j A_j^{(i)}(t=0)\, g_j(R, t=0)\, \Phi_i(r; R)$$

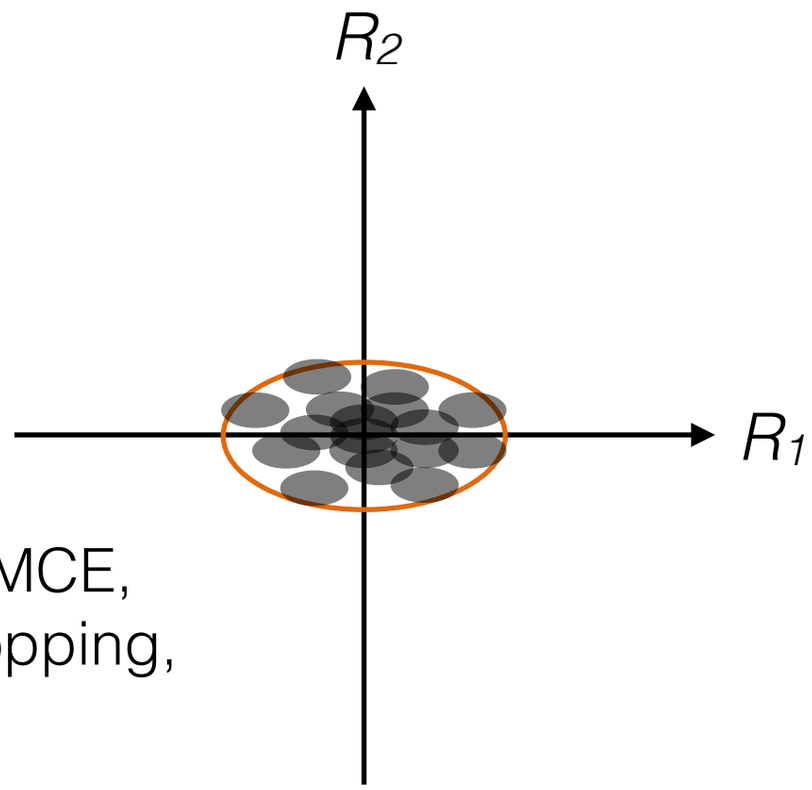
amplitude coefficients?

positions? momenta?
widths of the GBF?

Assumption of vertical excitation:
Initial nuclear function = nuclear function on the electronic ground state



Eg. DD-vMCG
NB: only possible with coupled trajectories



Eg. AIMS, MCE, Surface Hopping, Ehrenfest

2. What is our target distribution?

- "Quantum" sampling

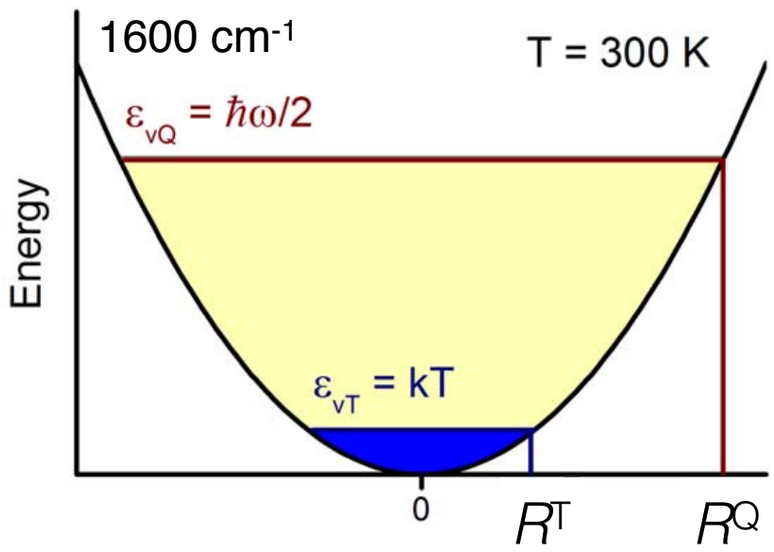
→ reproduce the distribution of positions and momenta in the quantum vibrational ground state (at the zero-point energy)

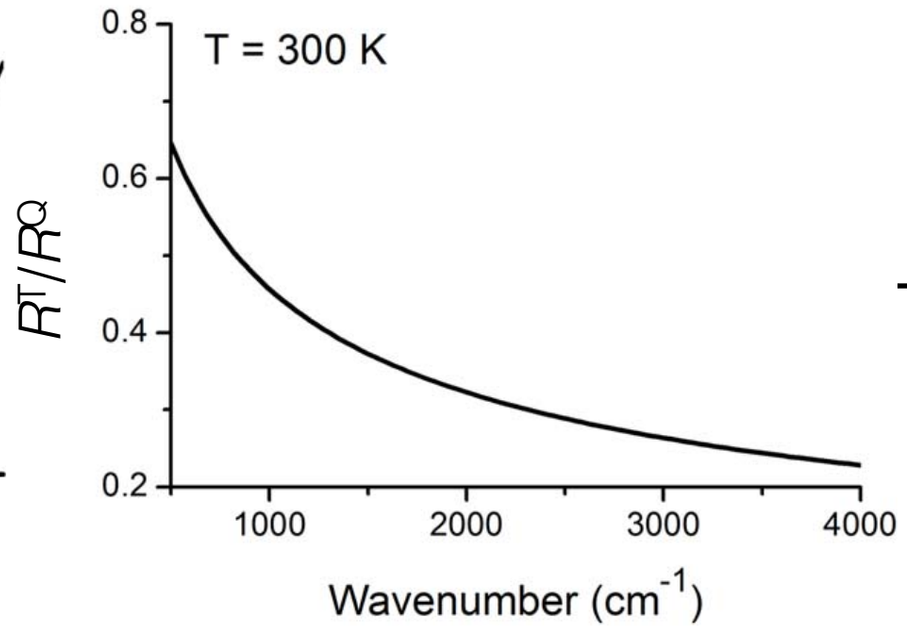
Wigner distribution function: $W^{(n=0)}(R,P) = \frac{1}{\pi\hbar}\exp^{-\omega R^2/\hbar}\exp^{-P^2/\omega\hbar}$

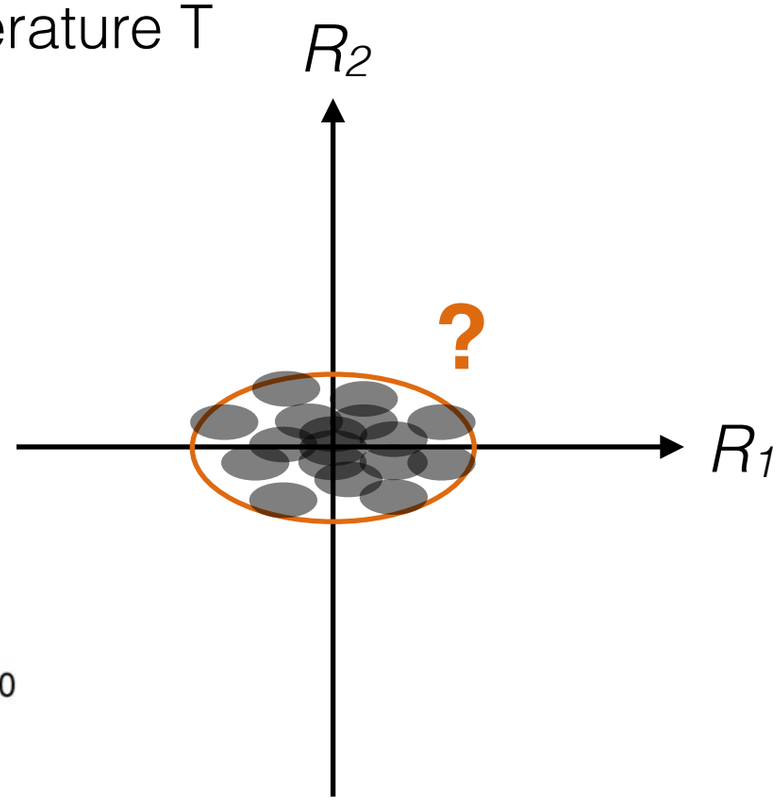
$$W^{(n=0)}(E) = \frac{1}{\pi\hbar\nu}\exp^{-2E/\omega\hbar} \longrightarrow \langle E\rangle = \int_0^\infty E\ W^{(n=0)}(E)dE = \hbar\omega/2$$

- "Thermal" sampling

→ snapshots of classical ground state dynamics at temperature T





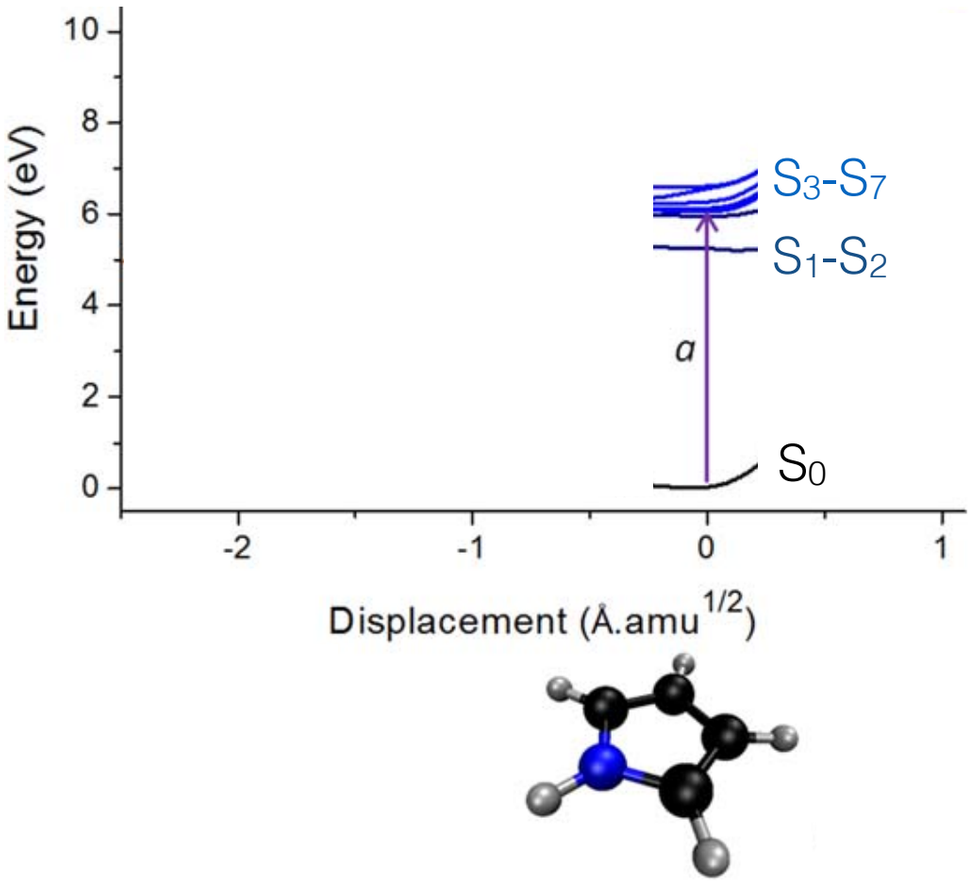


Barbatti et al, *Int. J. Quant. Chem.* (2015) **116**, 762-771

3. Example: Pyrrole
“Quantum” sampling vs “thermal” sampling?

Non-adiabatic dynamics in pyrrole molecule upon excitation with a 6.1eV photon:

- S_3-S_7 manifold initially populated
- surface hopping method
- ADC2 for electronic structure
- 100 trajectories
- “quantum” sampling versus “thermal” sampling at T=300K



$$i\hbar\frac{\partial A^{(i)}}{\partial t} = V_i A^{(i)} - i\hbar\sum_{i'}\dot{R}\cdot F_{ii'}A^{(i')}$$

$$\frac{dP}{dt} = -\frac{dV_i}{dR}$$

Fewest switches algorithm:

$$\mathrm{Proba}_{i\to i'}(t) = -\frac{1}{|A_i|^2}\frac{d|A_i|^2}{dt}\Delta t$$

→ stochastic procedure
(“classically frustrated” hops)

Barbatti et al, *Int. J. Quant. Chem.* (2015) **116**, 762-771

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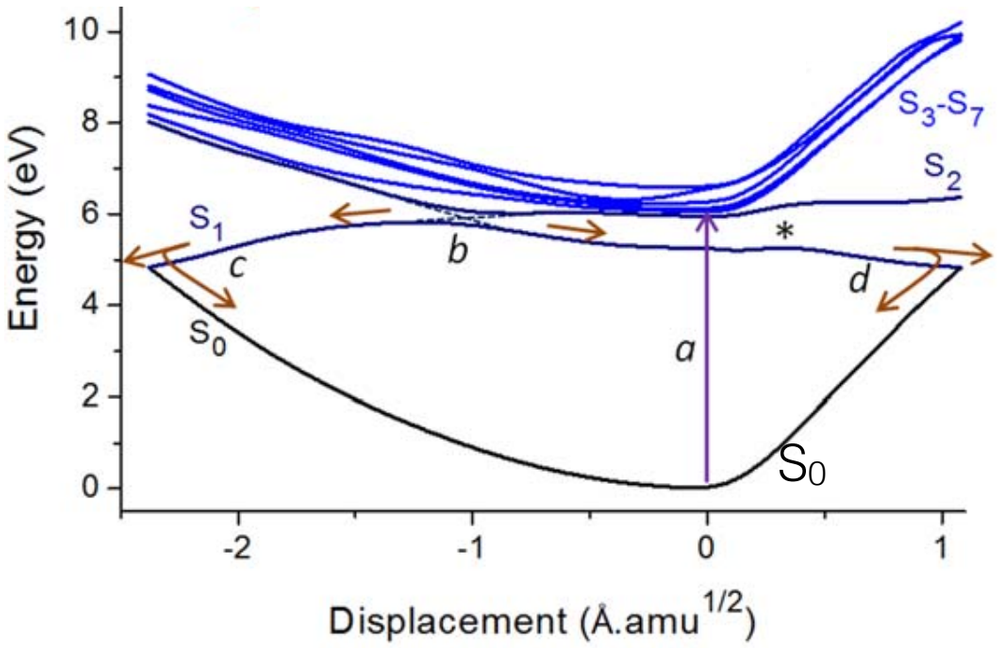
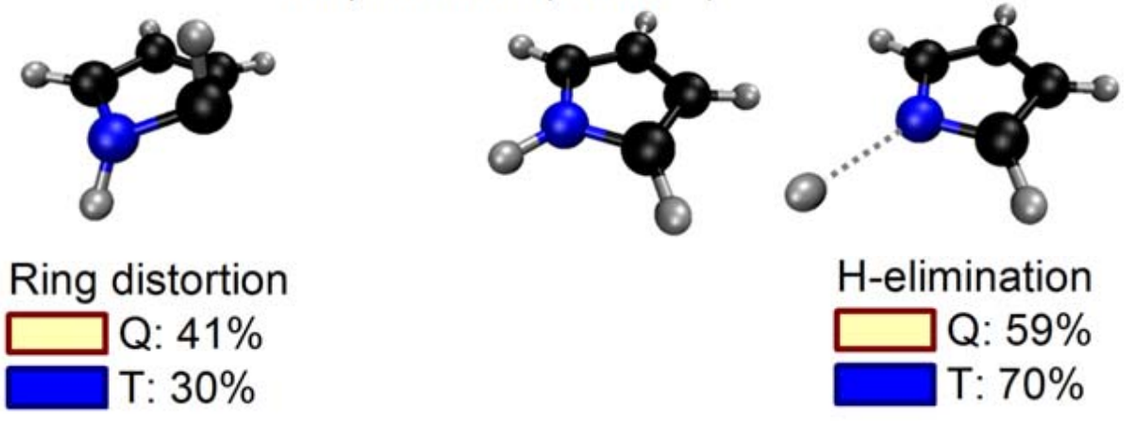
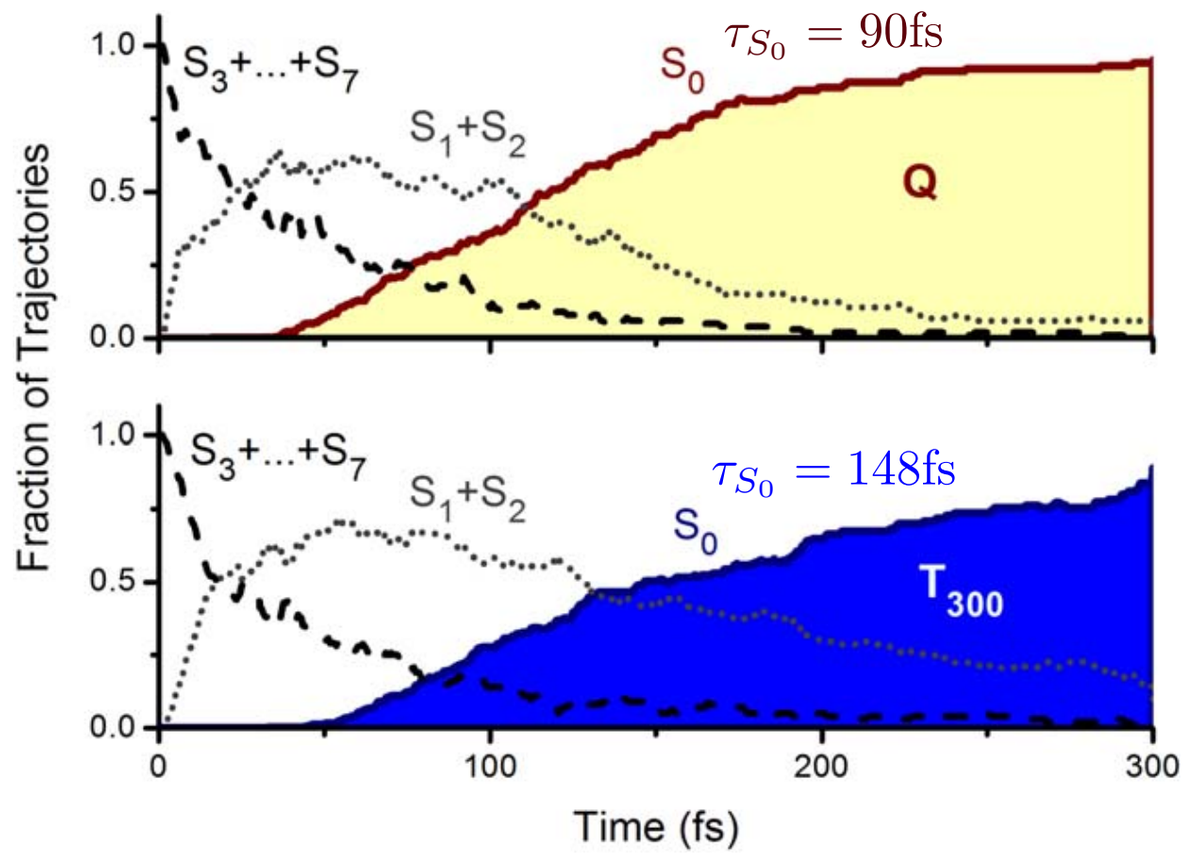






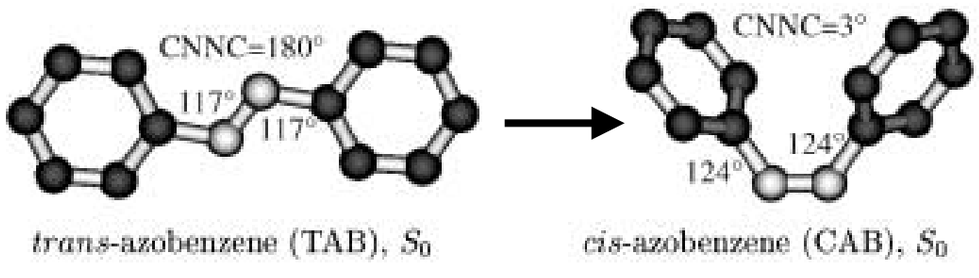
Q	T	exp
$\tau_* = 64$fs	100fs	57fs

Barbatti et al, *Int. J. Quant. Chem.* (2015) **116**, 762-771

3. Example: Isomerisation of azobenzene
Surface hopping vs FMS?

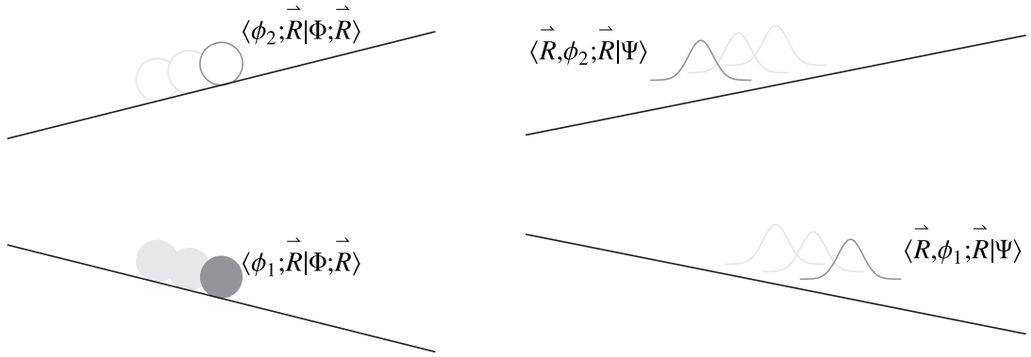
Non-adiabatic dynamics in azobenzene molecule upon n → pi* excitation:

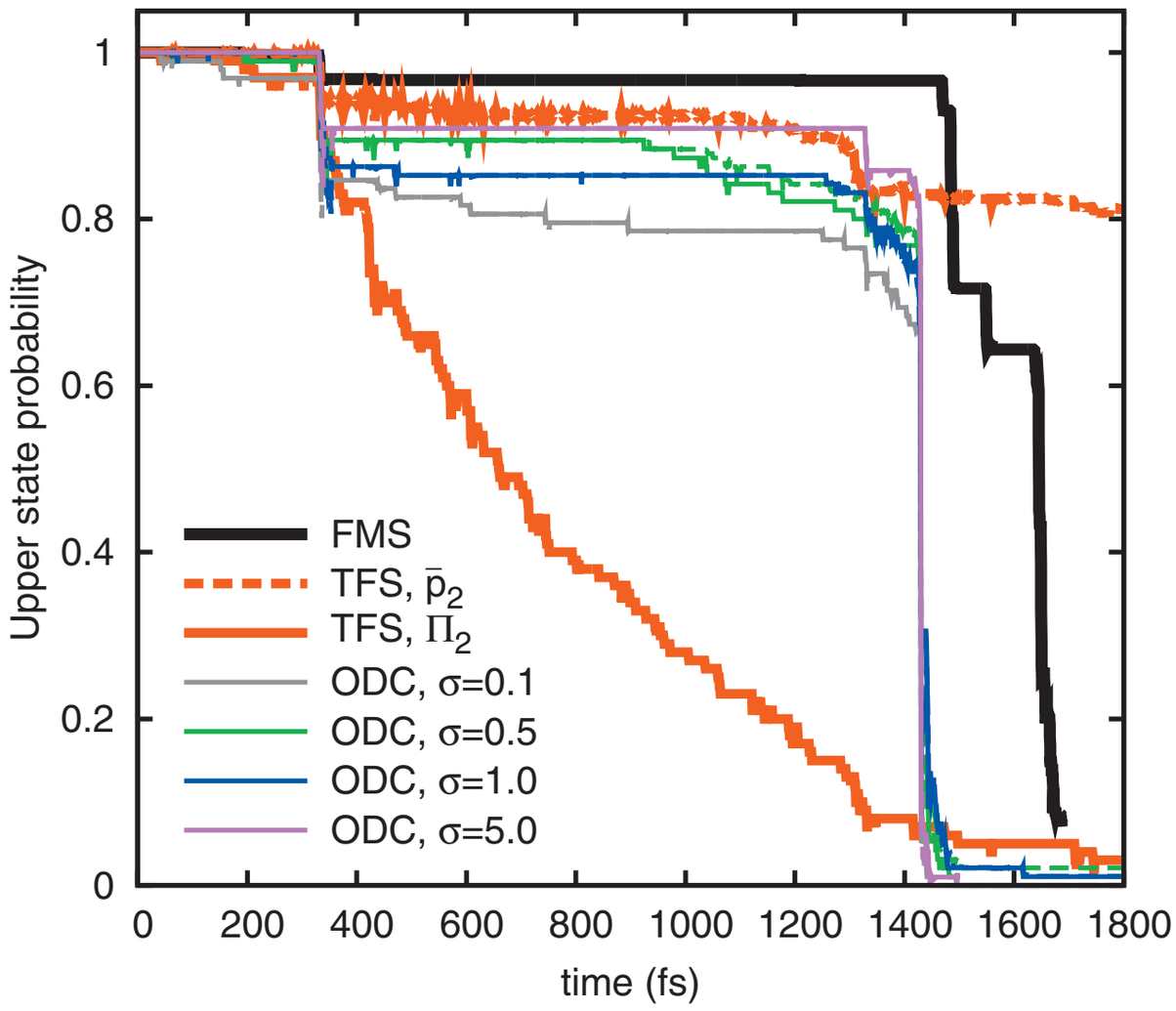
- S_1 state initially populated
- surface hopping method vs FMS, 100 trajectories
- AM1 and CAS-CI for electronic structure
- initial conditions of the slow decaying FMS wave packet from a Boltzmann distribution



trans-azobenzene (TAB), S_0 *cis*-azobenzene (CAB), S_0

Lack of decoherence in TSH:



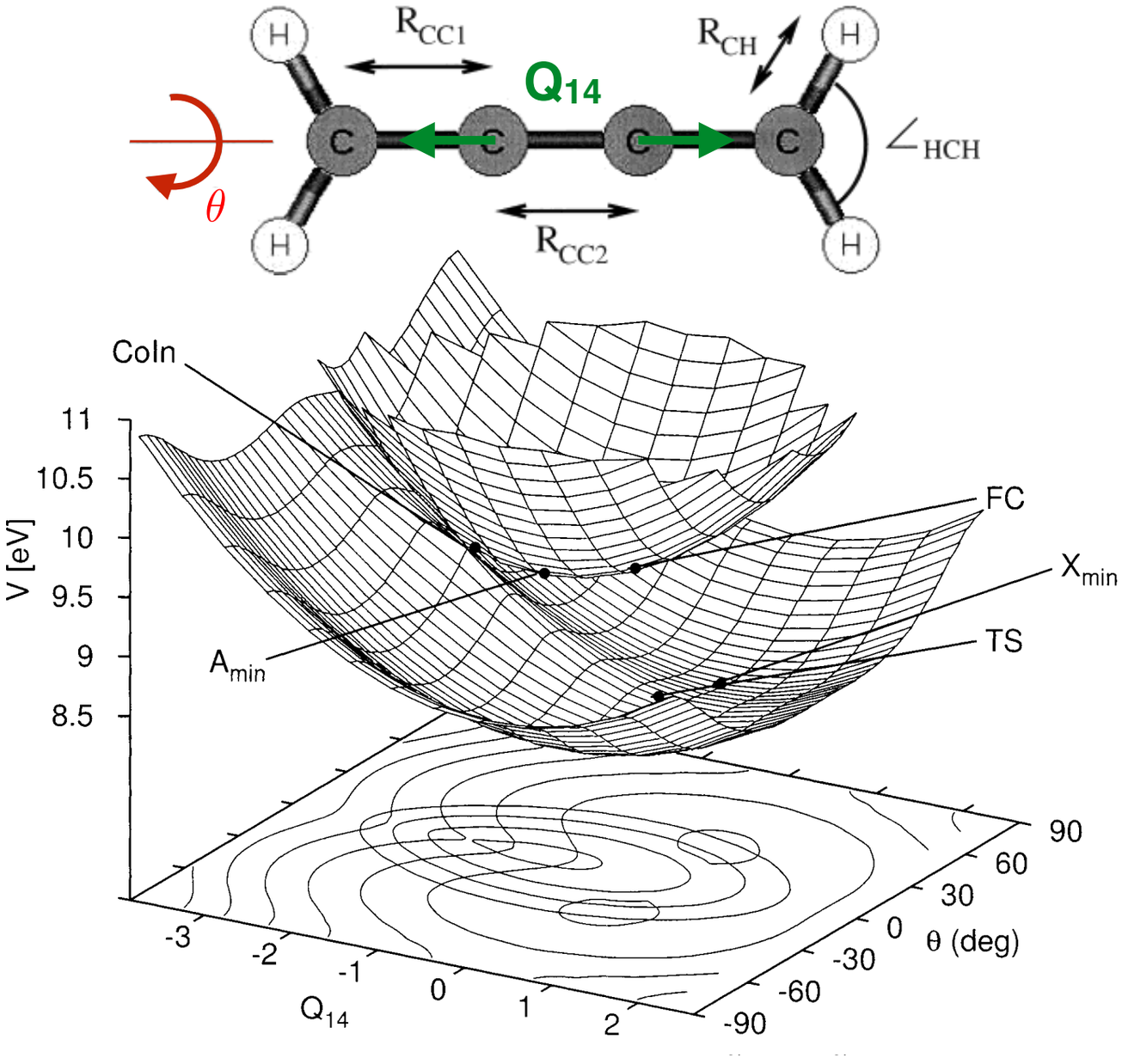


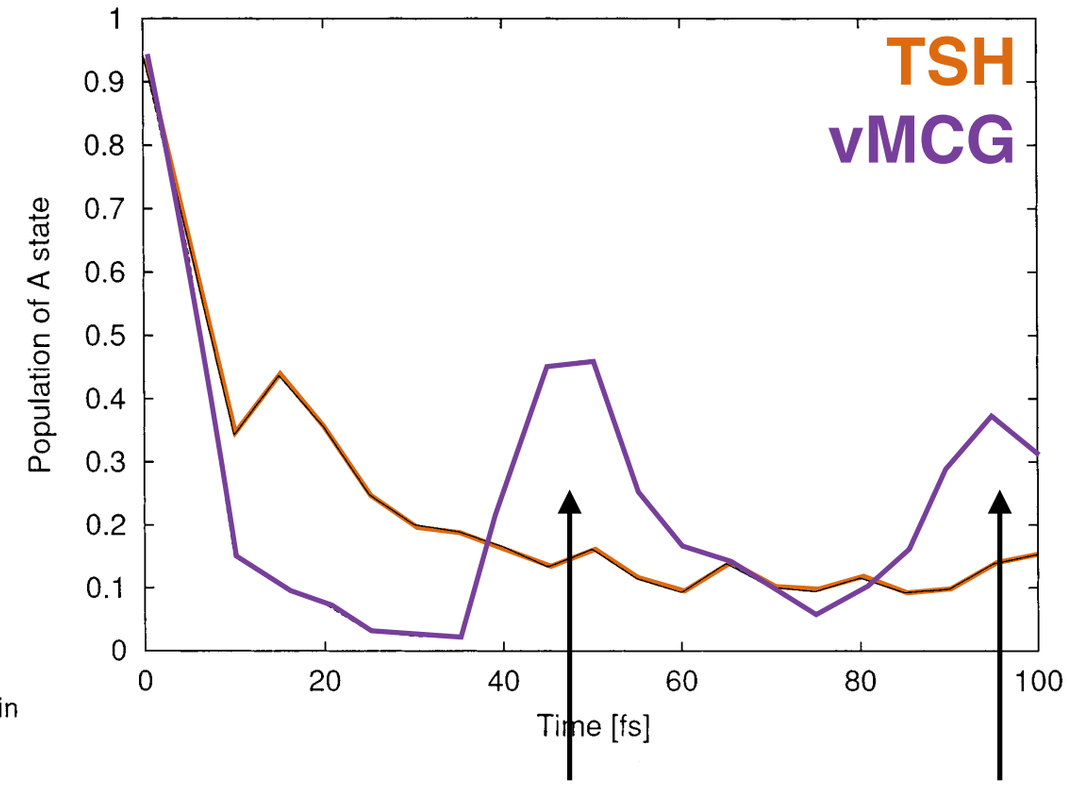
Malhado et al, *Frontiers in Chem.* (2014) **2**, 97 and Granucci et al, *J. Chem. Phys.* (2010) **133**, 134111

3. Example: Butatriene cation
Surface hopping vs vMCG?

Non-adiabatic dynamics in butatriene molecule upon ionisation:

- first cationic excited state “A state” initially populated
- surface hopping method with 80 trajectories vs vMCG (16 GBF)
- CASSCF for electronic structure





revivals of population on the upper state

Computational costs:

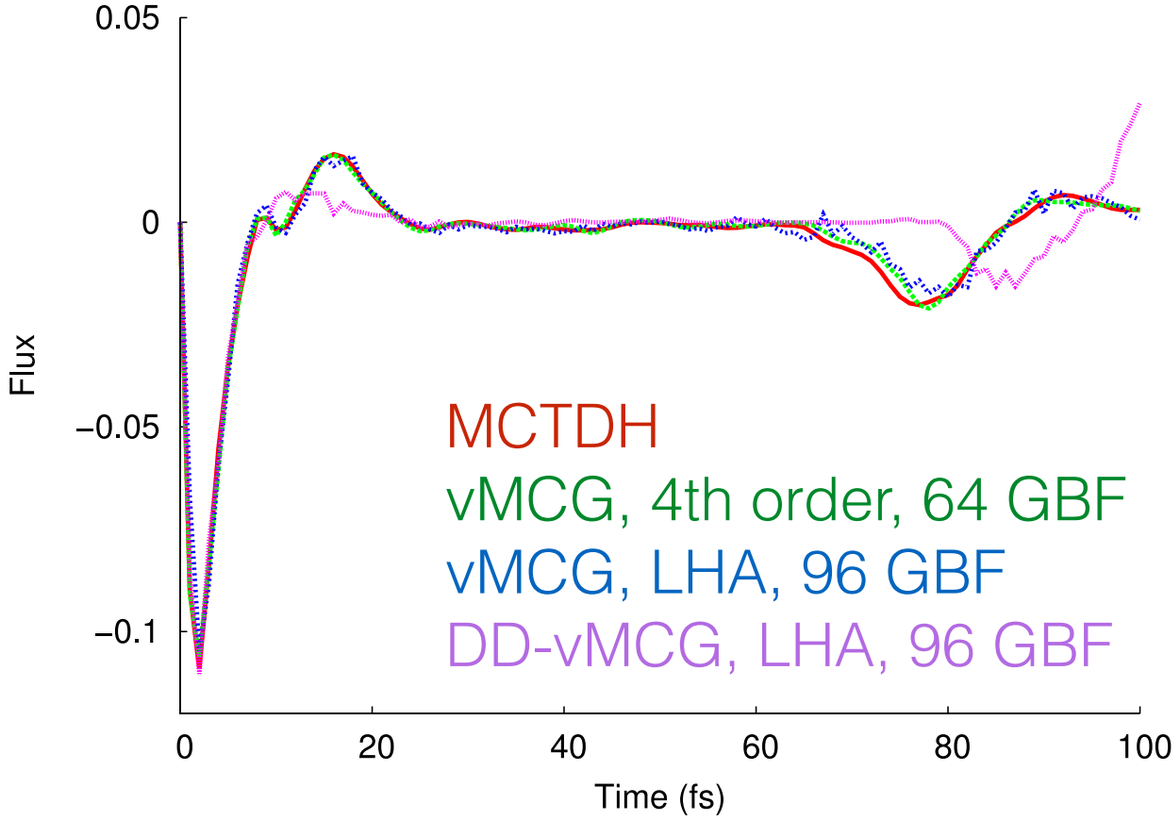
- 10h per TSH traj = 800h for TSH
- 100h for vMCG (16 GBF)

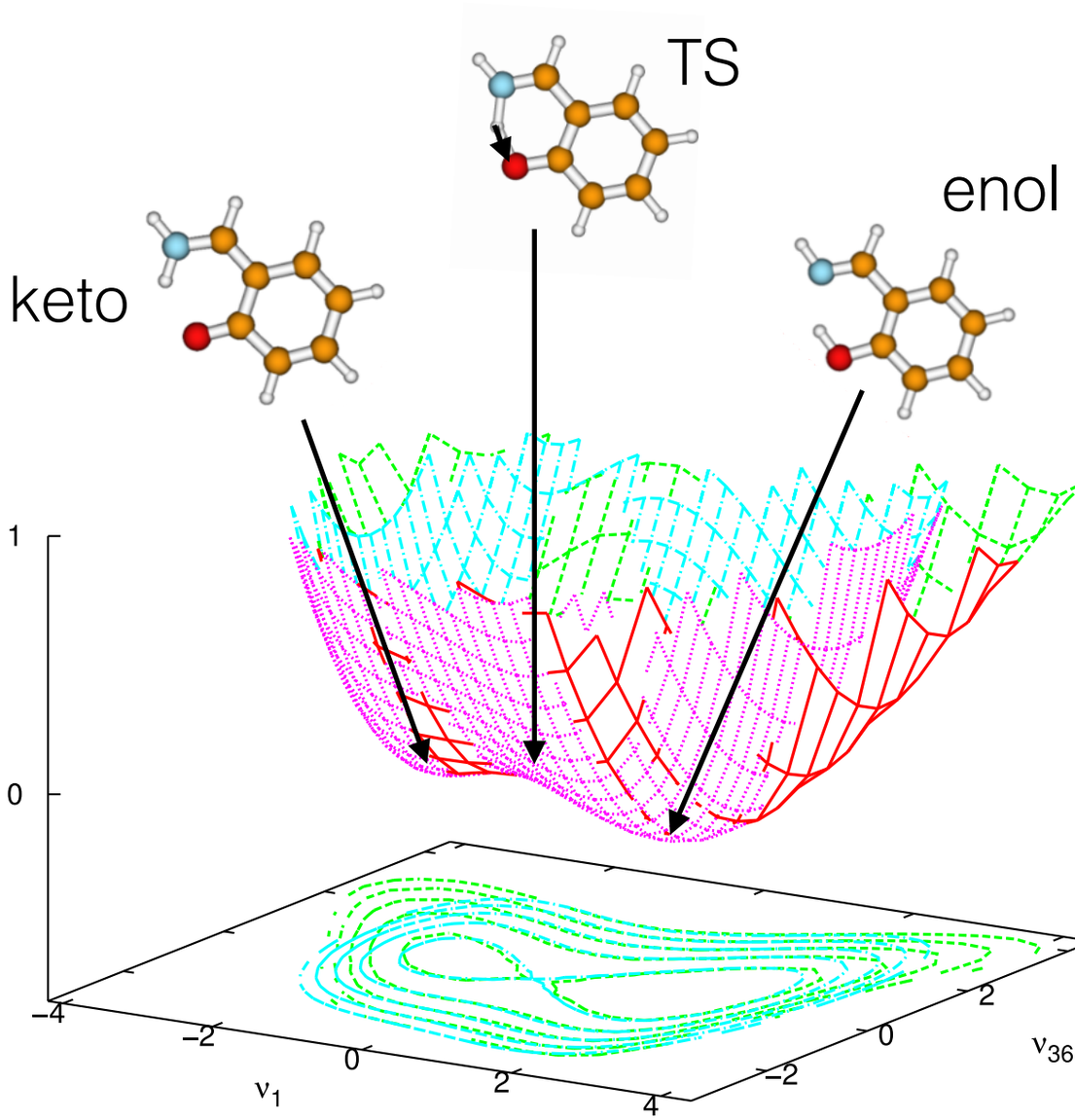
Worth et al, *J. Phys. Chem. A* (2003) **107**, 5 and Worth et al, *Faraday Discuss.* (2004) **127**, 307-323

3. Example: Salicylaldimine Tunnelling with vMCG?

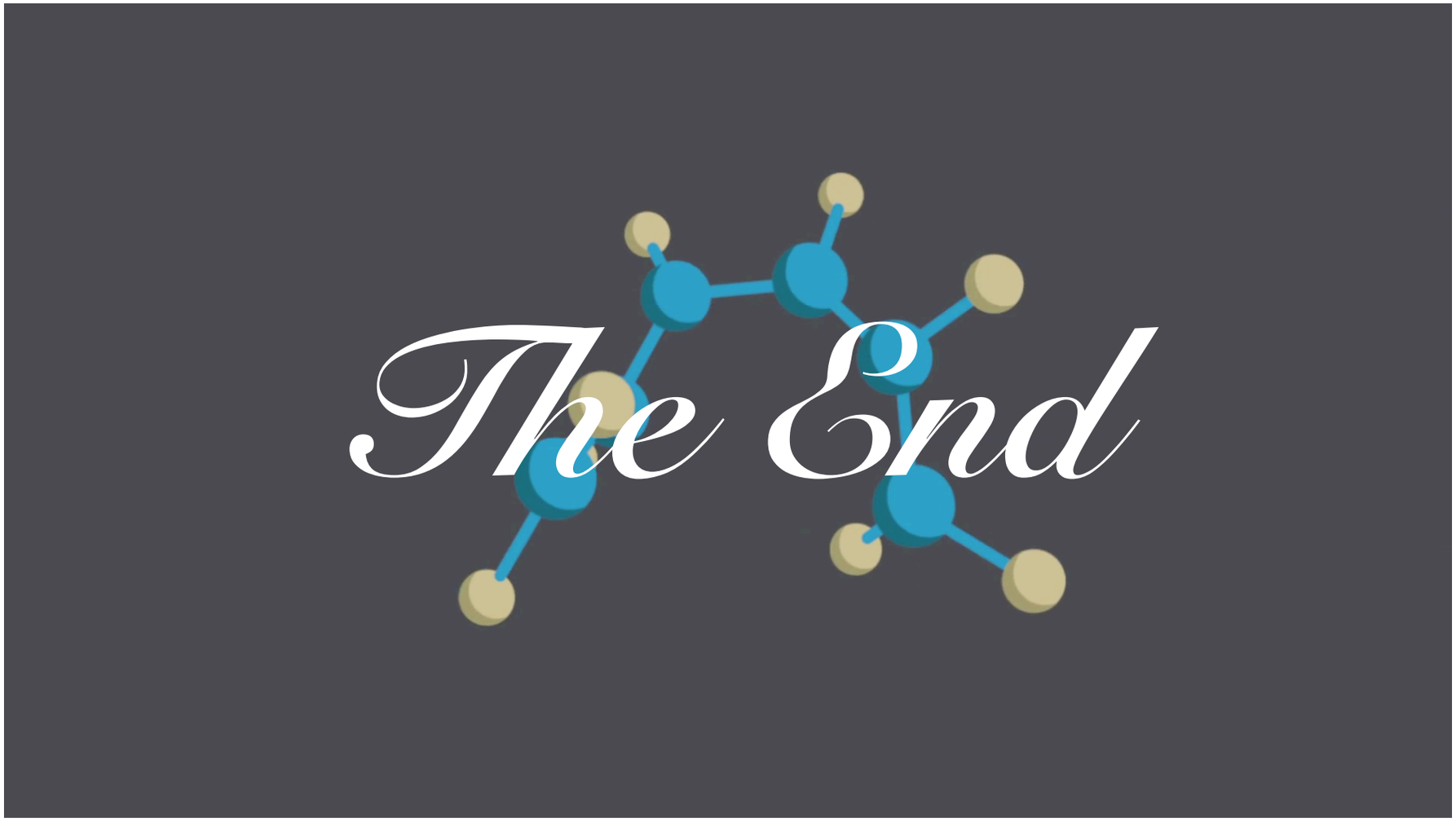
Ground state dynamics in salicylaldimine molecule:

- ground state initially populated
- nuclear wave packet slightly displaced from the keto conformation
- zero initial momentum (below the barrier)
- MCTDH vs (DD-)vMCG in 13D
- HF for electronic structure





Polyak et al, *J. Phys. Chem. A* (2015) **143**, 084121



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