

# Trajectory-based nonadiabatic molecular dynamics

A TDDFT approach

Ivano Tavernelli

IBM -Research Zurich

Summer School of the  
Max-Planck-EPFL Center for Molecular Nanoscience & Technology

Trajectory-based nonadiabatic molecular dynamics

- 1 Ab initio molecular dynamics
  - Why Quantum Dynamics?
  - Nuclear quantum effects
- 2 Mixed quantum-classical dynamics
  - Ehrenfest dynamics
  - Adiabatic Born-Oppenheimer dynamics
  - Nonadiabatic Bohmian dynamics
  - Trajectory Surface Hopping
- 3 TDDFT-based trajectory surface hopping
  - Nonadiabatic couplings in TDDFT
- 4 TDDFT-TSH: Applications
  - Photodissociation of Oxirane
  - Oxirane - Crossing between  $S_1$  and  $S_0$
- 5 TSH with external time-dependent fields
  - Local control (LC) theory
  - Application of LCT

Trajectory-based nonadiabatic molecular dynamics

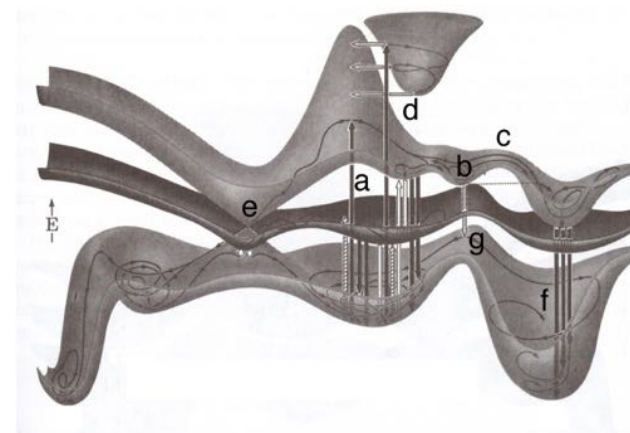
Ab initio molecular dynamics

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Ab initio molecular dynamics

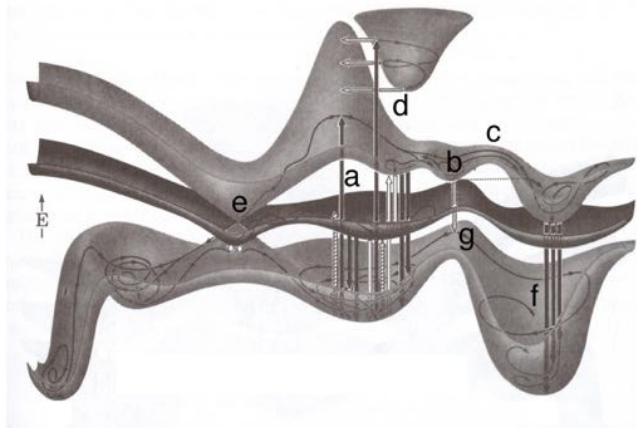
Reminder from last lecture: potential energy surfaces



We have electronic structure methods for electronic ground and excited states...  
Now, we need to propagate the nuclei...

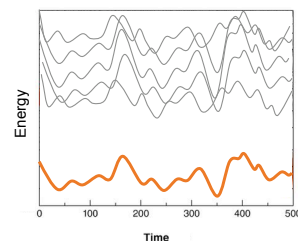
Trajectory-based nonadiabatic molecular dynamics

# Reminder from last lecture: potential energy surfaces



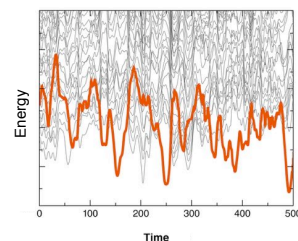
We have electronic structure methods for electronic ground and excited states...  
Now, we need to propagate the nuclei...

# Why Quantum dynamics?



GS adiabatic dynamics (BO vs. CP)

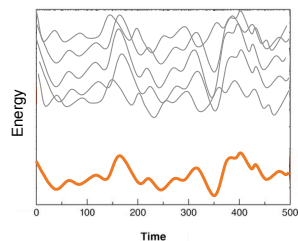
BO  $M_i \ddot{\mathbf{R}}_i(t) = -\nabla \min_{\rho} E_{KS}(\{\phi_i, [\rho]\})$   
 CP  $\mu_i |\ddot{\phi}_i(t)\rangle = -\frac{\delta}{\delta \langle \phi_i |} E_{KS}(\{\phi_i(\mathbf{r})\}) + \frac{\delta}{\delta \langle \phi_i |} \{\text{constr.}\}$   
 $M_i \ddot{\mathbf{R}}_i(t) = -\nabla E_{KS}(\{\phi_i(t)\})$



ES nonadiabatic quantum dynamics

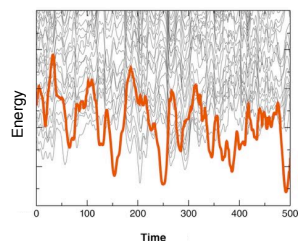
- Wavepacket dynamics (MCTDH)
- Trajectory-based approaches
  - Tully's trajectory surface hopping (TSH)
  - Bohmian dynamics (quantum hydrodyn.)
  - Semiclassical (WKB, DR)
  - Path integrals (Pechukas)
  - Mean-field solution (Ehrenfest dynamics)
- Density matrix, Liouvillian approaches, ...

# Why Quantum dynamics?



GS adiabatic dynamics

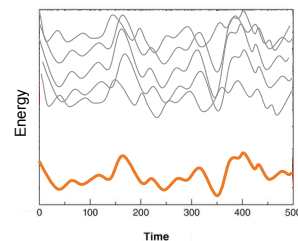
First principles Heaven
Ab initio MD with WF methods
Ab initio MD with DFT & TDDFT [CP]
classical MD
Coarse-grained MD
...
No principles World



ES nonadiabatic quantum dynamics

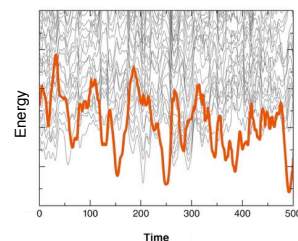
First principles Heaven
Ab initio MD with WF methods
Ab initio MD with DFT & TDDFT [CP]
↓
Models
↓ ?
No principles World

# Why Quantum dynamics?



GS adiabatic dynamics

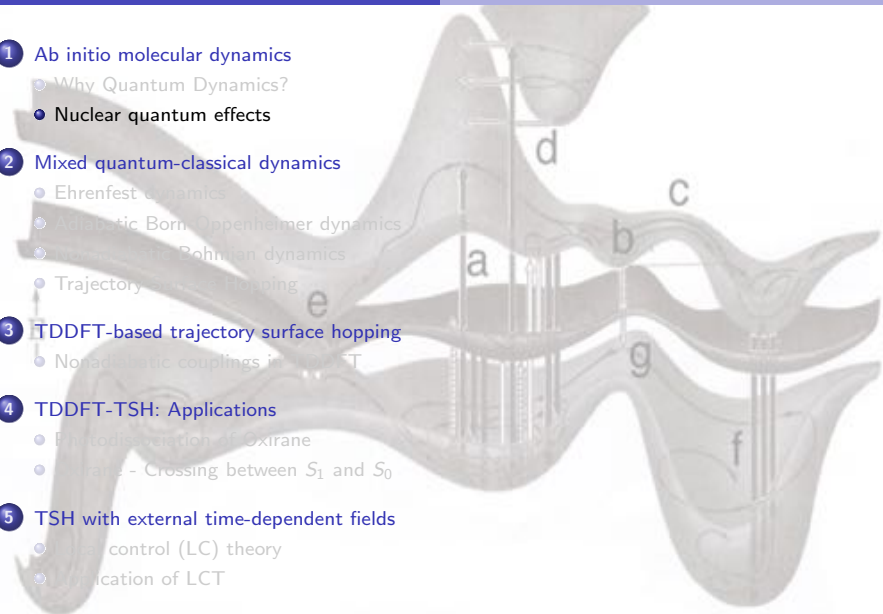
First principles Heaven
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ES nonadiabatic quantum dynamics

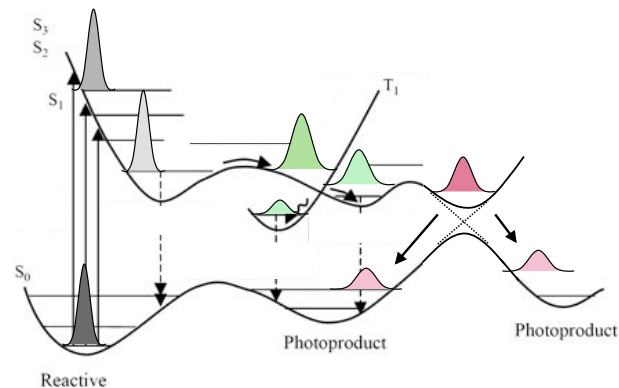
- (-) We cannot get read of electrons
- (-) Nuclei keep some QM flavor
- (-) Accuracy is an issue
- (-) Size can be large (diffuse excitons)
- (+) Time scales are usually short (< ps)

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## Nonadiabatic effects requires quantum nuclear dynamics

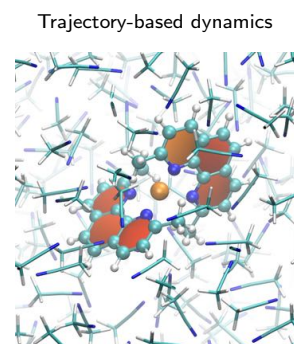
The nuclear dynamics cannot be described by a single classical trajectory (like in the ground state -adiabatically separated- case)



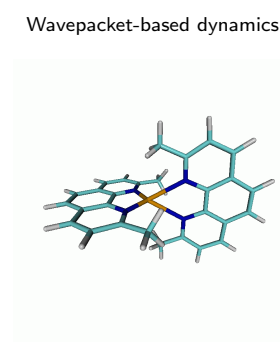
## Multi-trajectories vs. wavepacket

Trajectory-based dyn.	Wavepacket dyn.
dynamics in phase space $d=3N-6$ (unbiased)	reaction coordinates $d=1-10$ (knowledge based)
<i>on-the-fly</i> dynamics	pre-computed energy surfaces on a grid
good scaling (linear in $d$ )	scaling catastrophe ( $M^d$ )
coupling to real environment	coupling to harmonic bath
slow convergence	good convergence
approximate	'exact' in low dimensions

## Wavepacket-dynamics vs. trajectory-based QD



- Dynamics in **3N dimensions**
- **Approximated quantum dynamics** (trajectory ensemble)



- Dynamics in **8 dimensions**
- **'Exact' quantum dynamics** (nuclear wavepakets)

# Wavepacket dynamics with MCTDH

The multiconfiguration time-dependent Hartree, MCTDH, approach.

1) collecting variables:

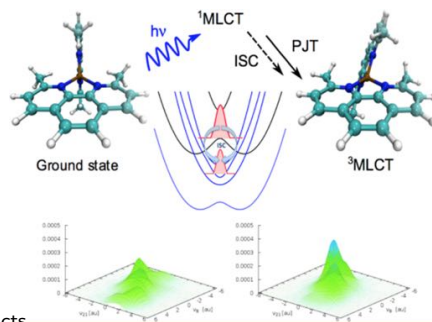
$$\Psi(\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_{3N}) \rightarrow \Psi(\mathbf{Q}_1, \dots, \mathbf{Q}_M)$$

with  $M \ll 3N$ , and

$$\mathbf{Q}_1(\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_{3N})$$

...

$$\mathbf{Q}_M(\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_{3N})$$



2) Ansatz: linear combination of Hartree products

$$\Psi(\mathbf{Q}_1, \mathbf{Q}_2, \dots, \mathbf{Q}_M) = \sum_{j_1=1}^{n_1} \dots \sum_{j_f=1}^{n_f} A_{j_1 \dots j_f}(t) \prod_{k=1}^f \phi_{j_k}^{(k)}(\mathbf{Q}_k, t)$$

3) EOF from Dirac-Frenkel variational principle:  $\langle \delta\Psi | \hat{H} - i \frac{\partial}{\partial t} | \Psi \rangle = 0$ .

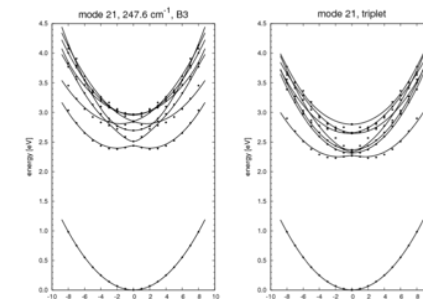
# Wavepacket dynamics with MCTDH

Precomputed TDDFT surfaces along selected modes (8).

Potential energy surfaces computed along 2 vibrational modes (Spin Orbit Coupling (SOC) described by the Breit-Pauli operator.)

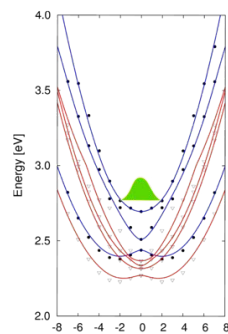
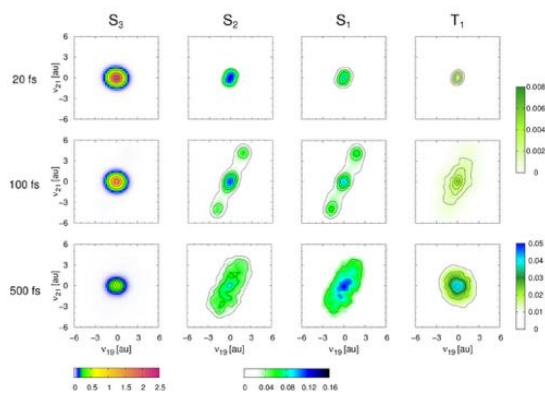
state	sym.	eV	f
S1	B3	2.43	0.0006
S2	A	2.51	0.0000
S3	B3	2.69	0.1608
S4	B1	2.83	0.0023

mode	cm <sup>-1</sup>	sym.	type
19	193.61	B3	Rocking
21	247.61	B3	Jahn Teller
31	420.77	B3	As. Stretching
41	502.65	B3	Rocking
55	704.75	B3	Rocking
58	790.76	B3	Rocking
25	270.85	A	Twisting



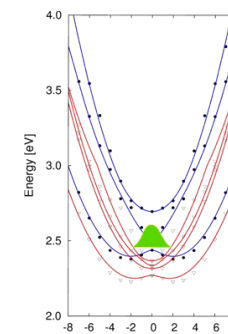
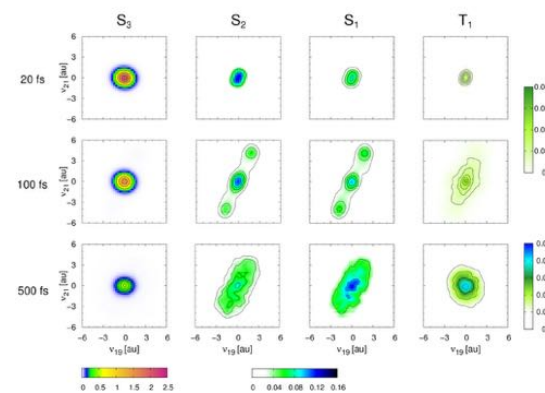
SOC at equilibrium:  
 $S_1/T_1 = 65 \text{ cm}^{-1}$ ;  $S_2/T_1 = 35 \text{ cm}^{-1}$   
 SOC at distorted geometry:  
 $S_1/T_1 = 30 \text{ cm}^{-1}$ ;  $S_2/T_1 = 30 \text{ cm}^{-1}$

# Wavepacket-dynamics of Cu-phenanthroline



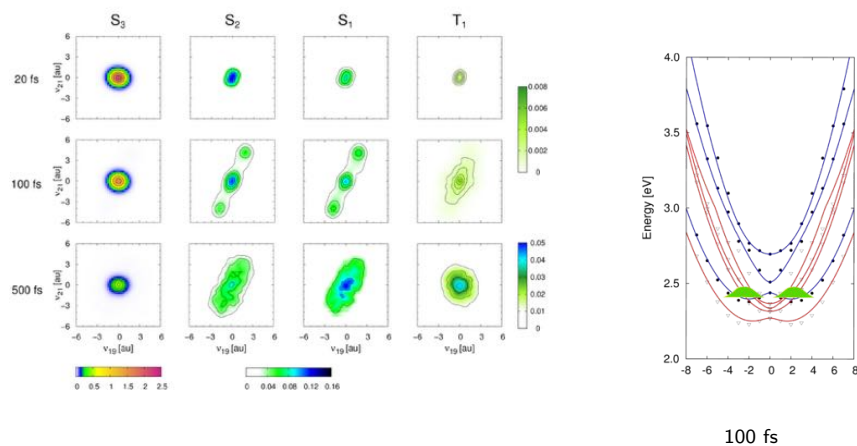
0 fs

# Wavepacket-dynamics of Cu-phenanthroline

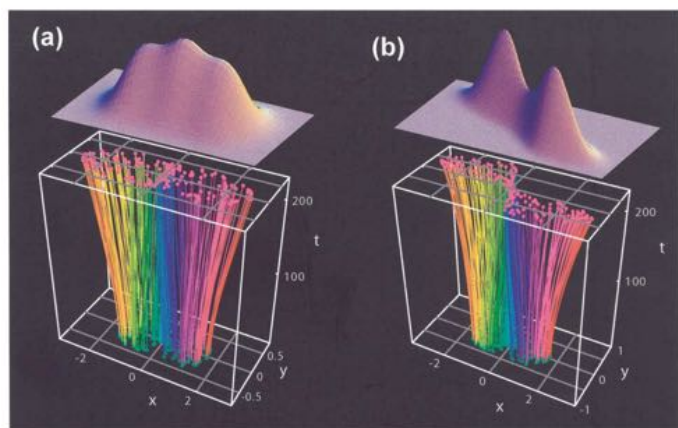


20 fs

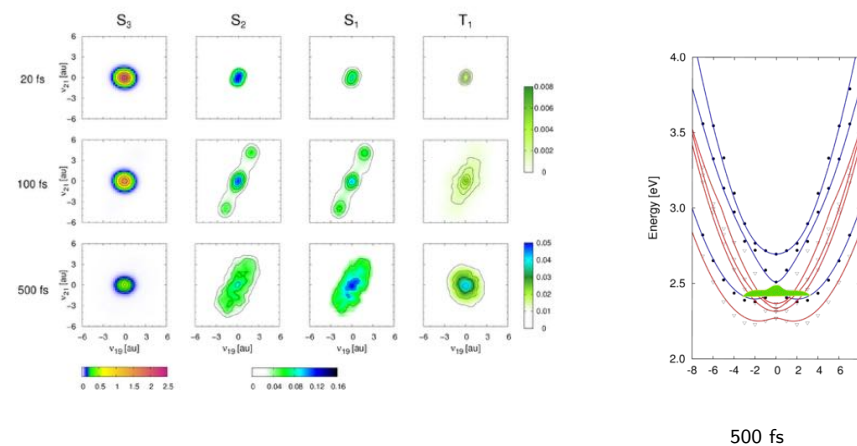
# Wavepacket-dynamics of Cu-phenanthroline



# Trajectory-based quantum dynamics

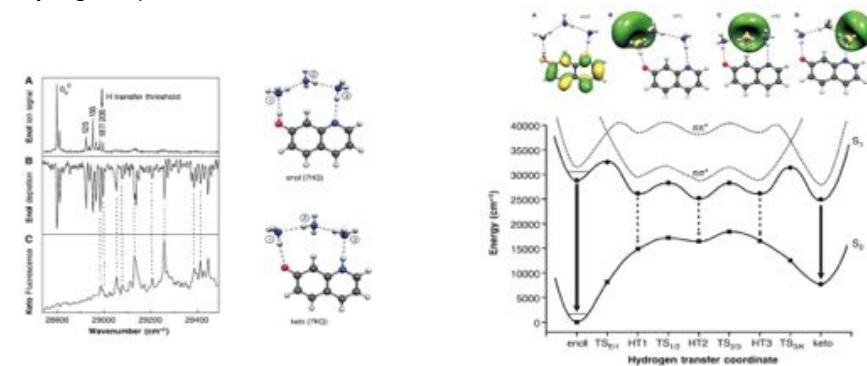


# Wavepacket-dynamics of Cu-phenanthroline



# Trajectory-based quantum dynamics: an example

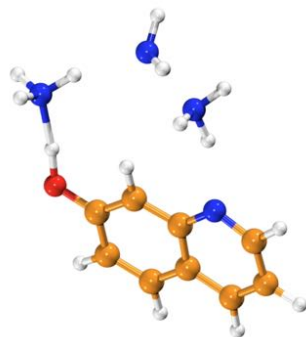
Ultrafast tautomerization of 4-hydroxyquinoline:(NH<sub>3</sub>)<sub>3</sub>  
Hydrogen or proton transfer?



CIS/CASSCF for the in-plane geometry  $\rightarrow \pi\pi^*/\pi\sigma^*$  crossing leads to a hydrogen atom transfer.  
S. Leutwyler *et al.*, Science, 302, 1736 (2003)

## Trajectory-based quantum dynamics: an example

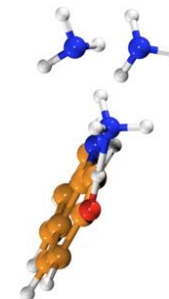
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What about TDDFT combined with nonadiabatic dynamics (1)?

## Trajectory-based quantum dynamics: an example

Ultrafast tautomerization of 4-hydroxyquinoline:(NH<sub>3</sub>)<sub>3</sub>  
Hydrogen or proton transfer?



What about TDDFT combined with nonadiabatic dynamics (2)?

## Trajectory-based quantum dynamics: an example

Ultrafast tautomerization of 4-hydroxyquinoline:(NH<sub>3</sub>)<sub>3</sub>  
Hydrogen or proton transfer?

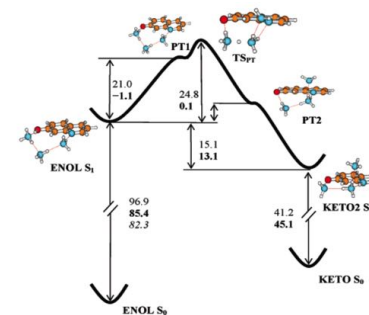
With TDDFT, we observe:

- Symmetry breaking.
- No crossing with the  $\pi\sigma^*$  state.
- Proton transfer instead of a hydrogen transfer.

Guglielmi *et al.*, PCCP, 11, 4549 (2009).

## Trajectory-based quantum dynamics: an example

Ultrafast tautomerization of 4-hydroxyquinoline:(NH<sub>3</sub>)<sub>3</sub>  
Hydrogen or proton transfer?  
Similar observations with CASPT2 calculations:



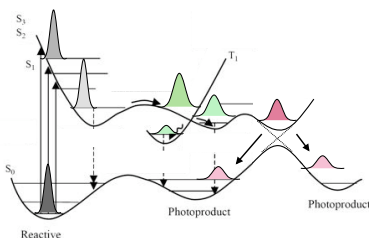
Forcing in-plane symmetry: hydrogen transfer.

Unconstrained geometry optimization leads to a proton transfer!

Fernandez-Ramos *et al.*, JPCA, 111, 5907 (2007).

## Summary: Why trajectory-based approaches?

- W1 In “conventional” nuclear wavepacket propagation potential energy surfaces are needed.
- W2 Difficulty to obtain and fit potential energy surfaces for large molecules.
- W3 Nuclear wavepacket dynamics is very expensive for large systems (6 degrees of freedom, 30 for MCTDH). Bad scaling.
- T1 Trajectory based approaches can be run *on-the-fly* (no need to parametrize potential energy surfaces).
- T2 Can handle large molecules in the full (unconstraint) configuration space.
- T3 They offer a good **compromise** between accuracy and computational effort.



## Starting point

The starting point is the molecular time-dependent Schrödinger equation:

$$i\hbar \frac{\partial}{\partial t} \Psi(\mathbf{r}, \mathbf{R}, t) = \hat{H} \Psi(\mathbf{r}, \mathbf{R}, t)$$

where  $\hat{H}$  is the molecular time-independent Hamiltonian and  $\Psi(\mathbf{r}, \mathbf{R}, t)$  the total wavefunction (nuclear + electronic) of our system.

In **mixed quantum-classical dynamics** the nuclear dynamics is described by a swarm of classical trajectories (taking a “partial” limit  $\hbar \rightarrow 0$  for the nuclear wf).

In this lecture we will discuss two main approximate solutions based on the following Ansätze for the total wavefunction

$$\Psi(\mathbf{r}, \mathbf{R}, t) \xrightarrow[\text{Huang}]{\text{Born-}} \sum_j \Phi_j(\mathbf{r}; \mathbf{R}) \Omega_j(\mathbf{R}, t)$$

$$\Psi(\mathbf{r}, \mathbf{R}, t) \xrightarrow{\text{Ehrenfest}} \Phi(\mathbf{r}, t) \Omega(\mathbf{R}, t) \exp \left[ \frac{i}{\hbar} \int_{t_0}^t E_{el}(t') dt' \right]$$

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## Tarjectory-based quantum and mixed QM-CL solutions

We can “derive” the following trajectory-based solutions:

- **Nonadiabatic Ehrenfest dynamics**  
I. Tavernelli et al., *Mol. Phys.*, **103**, 963981 (2005).
- **Adiabatic Born-Oppenheimer MD equations**
- **Nonadiabatic Bohmian Dynamics (NABDY)**  
B. Curchod, IT, U. Rothlisberger, *PCCP*, **13**, 32313236 (2011)
- **Nonadiabatic Trajectory Surface Hopping (TSH) dynamics**  
[ROKS: N. L. Doltsinis, D. Marx, *PRL*, **88**, 166402 (2002)]  
C. F. Craig, W. R. Duncan, and O. V. Prezhdo, *PRL*, **95**, 163001 (2005)  
E. Tapavicza, I. Tavernelli, U. Rothlisberger, *PRL*, **98**, 023001 (2007)
- **Time dependent potential energy surface approach**  
based on the exact decomposition:  $\Psi(\mathbf{r}, \mathbf{R}, t) = \Omega(\mathbf{R}, t) \Phi(\mathbf{r}, t)$ .  
A. Abedi, N. T. Maitra, E. K. U. Gross, *PRL*, **105**, 123002 (2010)

## Ehrenfest dynamics

$$\Psi(\mathbf{r}, \mathbf{R}, t) \xrightarrow{\text{Ehrenfest}} \Phi(\mathbf{r}, t) \Omega(\mathbf{R}, t) \exp \left[ \frac{i}{\hbar} \int_{t_0}^t E_{el}(t') dt' \right]$$

Inserting this representation of the total wavefunction into the molecular td Schrödinger equation and multiplying from the left-hand side by  $\Omega^*(\mathbf{R}, t)$  and integrating over  $\mathbf{R}$  we get

$$i\hbar \frac{\partial \Phi(\mathbf{r}, t)}{\partial t} = -\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 \Phi(\mathbf{r}, t) + \left[ \int d\mathbf{R} \Omega^*(\mathbf{R}, t) \hat{V}(\mathbf{r}, \mathbf{R}) \Omega(\mathbf{R}, t) \right] \Phi(\mathbf{r}, t)$$

$$\text{where } \hat{V}(\mathbf{r}, \mathbf{R}) = \sum_{i < j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{\gamma, i} \frac{e^2 Z_\gamma}{|\mathbf{R}_\gamma - \mathbf{r}_i|}$$

In a similar way, multiplying by  $\Phi^*(\mathbf{r}, t)$  and integrating over  $\mathbf{r}$  we obtain

$$i\hbar \frac{\partial \Omega(\mathbf{R}, t)}{\partial t} = -\frac{\hbar^2}{2} \sum_\gamma M_\gamma^{-1} \nabla_\gamma^2 \Omega(\mathbf{R}, t) + \left[ \int d\mathbf{r} \Phi^*(\mathbf{r}, t) \hat{\mathcal{H}}_{el}(\mathbf{r}, \mathbf{R}) \Phi(\mathbf{r}, t) \right] \Omega(\mathbf{R}, t)$$

Conservation of energy has also to be imposed through the condition that  $d\langle \hat{H} \rangle / dt \equiv 0$ .

Note that both the electronic and nuclear parts evolve according to an average potential generated by the other component (in square brackets). These average potentials are time-dependent and are responsible for the feedback interaction between the electronic and nuclear components.

## Ehrenfest dynamics - the nuclear equation

We start from the polar representation of the nuclear wavefunction

$$\Omega(\mathbf{R}, t) = A(\mathbf{R}, t) \exp \left[ \frac{i}{\hbar} S(\mathbf{R}, t) \right]$$

where the amplitude  $A(\mathbf{R}, t)$  and the phase  $S(\mathbf{R}, t)/\hbar$  are real functions.

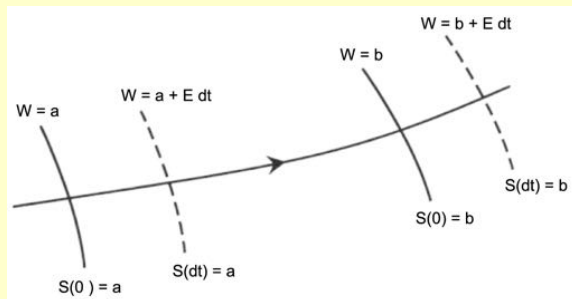
Inserting this representation for  $\Omega(\mathbf{R}, t)$  and separating the real and the imaginary parts one gets for the phase  $S$  in the **classical limit**  $\hbar \rightarrow 0$

$$\frac{\partial S}{\partial t} = -\frac{1}{2} \sum_\gamma M_\gamma^{-1} (\nabla_\gamma S)^2 - \left[ \int d\mathbf{r} \Phi^*(\mathbf{r}, t) \hat{\mathcal{H}}_{el}(\mathbf{r}, \mathbf{R}) \Phi(\mathbf{r}, t) \right]$$

This has the form of the "**Hamilton-Jacobi**" (HJ) equation of classical mechanics, which establishes a relation between the partial differential equation for  $S(\mathbf{R}, t)$  in configuration space and the trajectories of the corresponding (quantum) mechanical systems.

## Ehrenfest dynamics - the nuclear equation

$$\frac{\partial S}{\partial t} = -\frac{1}{2} \sum_\gamma M_\gamma^{-1} (\nabla_\gamma S)^2 - \left[ \int d\mathbf{r} \Phi^*(\mathbf{r}, t) \hat{\mathcal{H}}_{el}(\mathbf{r}, \mathbf{R}) \Phi(\mathbf{r}, t) \right]$$



Instead of solving the field equation for  $S(\mathbf{R}, t)$ , find the equation of motion for the corresponding trajectories (*characteristics*).

## Ehrenfest dynamics - the nuclear equation

The identification of  $S(\mathbf{R}, t)$  with the "classical" action, defines a point-particle dynamics with Hamiltonian,  $H_{cl}$  and momenta

$$\mathbf{P} = \nabla_{\mathbf{R}} S(\mathbf{R}, t)$$

The solutions of this Hamiltonian system are curves (*characteristics*) in the  $(\mathbf{R}, t)$ -space, which are extrema of the action  $S(\mathbf{R}, t)$  for given initial conditions  $\mathbf{R}(t_0)$  and  $\mathbf{P}(t_0) = \nabla_{\mathbf{R}} S(\mathbf{R})|_{\mathbf{R}(t_0)}$ . Newton-like equation for the nuclear trajectories corresponding to the HJ equation

$$\frac{d\mathbf{P}_\gamma}{dt} = -\nabla_\gamma \left[ \int d\mathbf{r} \Phi^*(\mathbf{r}, t) \hat{\mathcal{H}}_{el}(\mathbf{r}, \mathbf{R}) \Phi(\mathbf{r}, t) \right]$$

## Ehrenfest dynamics

$$i\hbar \frac{\partial \Phi(\mathbf{r}; \mathbf{R}, t)}{\partial t} = \hat{\mathcal{H}}_{el}(\mathbf{r}; \mathbf{R}) \Phi(\mathbf{r}; \mathbf{R}, t)$$

$$M_I \ddot{\mathbf{R}}_I = -\nabla_I \langle \hat{\mathcal{H}}_{el}(\mathbf{r}; \mathbf{R}) \rangle$$



## Ehrenfest dynamics - the nuclear equation

The identification of  $S(\mathbf{R}, t)$  with the "classical" action, defines a point-particle dynamics with Hamiltonian,  $H_{cl}$  and momenta

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$$\frac{d\mathbf{P}_\gamma}{dt} = -\nabla_\gamma \left[ \int d\mathbf{r} \Phi^*(\mathbf{r}, t) \hat{\mathcal{H}}_{el}(\mathbf{r}, \mathbf{R}) \Phi(\mathbf{r}, t) \right]$$

Ehrenfest dynamics - Densityfunctionalization ( $\phi_k$ : KS orbitals)

$$i\hbar \frac{\partial}{\partial t} \phi_k(\mathbf{r}, t) = -\frac{1}{2m_e} \nabla_{\mathbf{r}}^2 \phi_k(\mathbf{r}, t) + v_{\text{eff}}[\rho, \Phi_0](\mathbf{r}, t) \phi_k(\mathbf{r}, t)$$

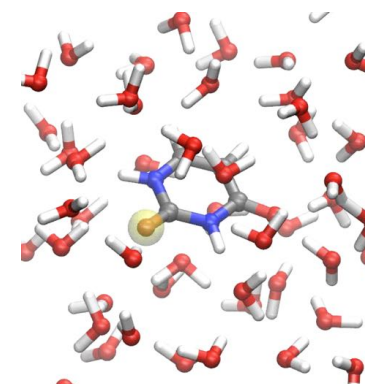
$$M_I \ddot{\mathbf{R}}_I = -\nabla_I E[\rho(\mathbf{r}, t)]$$

## Ehrenfest dynamics - Example

## Ehrenfest dynamics

$$i\hbar \frac{\partial}{\partial t} \phi_k(\mathbf{r}, t) = -\frac{1}{2m_e} \nabla_{\mathbf{r}}^2 \phi_k(\mathbf{r}, t) + v_{\text{eff}}[\rho, \Phi_0](\mathbf{r}, t) \phi_k(\mathbf{r}, t)$$

$$M_I \ddot{\mathbf{R}}_I = -\nabla_I \langle \hat{\mathcal{H}}_{el}(\mathbf{r}; \mathbf{R}) \rangle$$



## Ehrenfest dynamics and mixing of electronic states

## Ehrenfest dynamics

$$i\hbar \frac{\partial \Phi(\mathbf{r}; \mathbf{R}, t)}{\partial t} = \hat{\mathcal{H}}_{el}(\mathbf{r}; \mathbf{R}) \Phi(\mathbf{r}; \mathbf{R}, t)$$

$$M_I \ddot{\mathbf{R}}_I = -\nabla_I \langle \hat{\mathcal{H}}_{el}(\mathbf{r}; \mathbf{R}) \rangle$$

Consider the following expansion of  $\Phi(\mathbf{r}; \mathbf{R}, t)$  in the *static* basis of electronic wavefunctions  $\{\Phi_k(\mathbf{r}; \mathbf{R})\}$

$$\Phi(\mathbf{r}; \mathbf{R}, t) = \sum_{k=0}^{\infty} c_k(t) \Phi_k(\mathbf{r}; \mathbf{R})$$

The time-dependency is now on the set of coefficients  $\{c_k(t)\}$  ( $|c_k(t)|^2$  is the population of state  $k$ ). Inserting in the Ehrenfest's equations...

## Ehrenfest dynamics and mixing of electronic states

## Ehrenfest dynamics

$$i\hbar \dot{c}_k(t) = c_k(t) E_k^{el} - i\hbar \sum_j c_j(t) D_{kj}$$

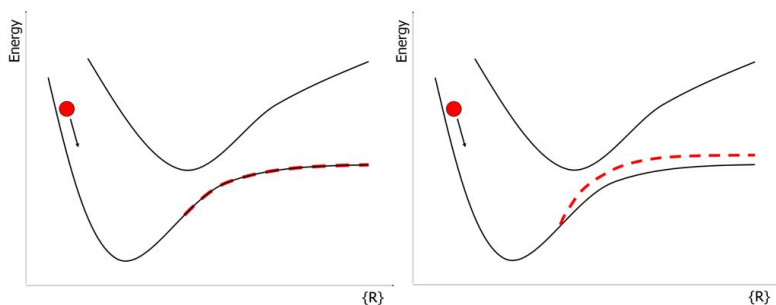
$$M_I \ddot{\mathbf{R}}_I = -\nabla_I \sum_{k=0}^{\infty} |c_k(t)|^2 E_k^{el}$$

where

$$D_{kj} = \langle \Phi_k | \frac{\partial}{\partial \mathbf{t}} | \Phi_j \rangle = \langle \Phi_k | \frac{\partial \mathbf{R}}{\partial \mathbf{t}} \frac{\partial}{\partial \mathbf{R}} | \Phi_j \rangle = \dot{\mathbf{R}} \langle \Phi_k | \nabla | \Phi_j \rangle = \dot{\mathbf{R}} \cdot \mathbf{d}_{kj}$$

Thus we incorporate directly nonadiabatic effects.

## Ehrenfest dynamics: the mean-field potential



$$i\hbar\dot{c}_k(t) = c_k(t)E_k^{el} - i\hbar\sum_j c_j(t)D_{kj}$$

$$M_I\ddot{\mathbf{R}}_I = -\nabla_I\sum_{k=0}^{\infty}|c_k(t)|^2E_k^{el}$$

Trajectory-based nonadiabatic molecular dynamics

## Born-Oppenheimer approximation

$$\Psi(\mathbf{r}, \mathbf{R}, t) \xrightarrow{\text{Born-Huang}} \sum_j \Phi_j(\mathbf{r}; \mathbf{R})\Omega_j(\mathbf{R}, t)$$

In this equation,  $\{\Phi_j(\mathbf{r}; \mathbf{R})\}$  describes a **complete basis** of electronic states solution of the time-independent Schrödinger equation:

$$\hat{H}_{el}(\mathbf{r}; \mathbf{R})\Phi_j(\mathbf{r}; \mathbf{R}) = E_{el,j}(\mathbf{R})\Phi_j(\mathbf{r}; \mathbf{R})$$

$\mathbf{R}$  is taken as a parameter.

Eigenfunctions of  $\hat{H}_{el}(\mathbf{r}; \mathbf{R})$  are considered to be orthonormal, i.e.  $\langle\Phi_j|\Phi_i\rangle = \delta_{ij}$ .

Trajectory-based nonadiabatic molecular dynamics

## Trajectory-based quantum and mixed QM-CL solutions

We can “derive” the following trajectory-based solutions:

- Nonadiabatic Ehrenfest dynamics dynamics  
I. Tavernelli et al., *Mol. Phys.*, **103**, 963981 (2005).
- Adiabatic Born-Oppenheimer MD equations
- Nonadiabatic Bohmian Dynamics (NABDY)  
B. Curchod, IT, U. Rothlisberger, *PCCP*, **13**, 32313236 (2011)
- Nonadiabatic Trajectory Surface Hopping (TSH) dynamics  
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A. Abedi, N. T. Maitra, E. K. U. Gross, *PRL*, **105**, 123002 (2010)

Trajectory-based nonadiabatic molecular dynamics

## Born-Oppenheimer approximation

$$\Psi(\mathbf{r}, \mathbf{R}, t) \xrightarrow{\text{Born-Huang}} \sum_j \Phi_j(\mathbf{r}; \mathbf{R})\Omega_j(\mathbf{R}, t)$$

**Electrons** are *static*. Use your favorite el. str. method.

For the **nuclei**, insert this *Ansatz* into the molecular time-dependent Schrödinger equation

$$\hat{H}\Psi(\mathbf{r}, \mathbf{R}, t) = i\hbar\frac{\partial}{\partial t}\Psi(\mathbf{r}, \mathbf{R}, t)$$

After left multiplication by  $\Phi_k^*(\mathbf{r}; \mathbf{R})$  and integration over  $\mathbf{r}$ , we obtain the following equation (we used  $\langle\Phi_j|\Phi_i\rangle = \delta_{ij}$ ):

$$\left[-\sum_I\frac{\hbar^2}{2M_I}\nabla_I^2 + E_{el,k}(\mathbf{R})\right]\Omega_k(\mathbf{R}, t) + \sum_j D_{kj}\Omega_j(\mathbf{R}, t) = i\hbar\frac{\partial}{\partial t}\Omega_k(\mathbf{R}, t)$$

Trajectory-based nonadiabatic molecular dynamics

## Born-Oppenheimer approximation

$$\left[ -\sum_I \frac{\hbar^2}{2M_I} \nabla_I^2 + E_{el,k}(\mathbf{R}) \right] \Omega_k(\mathbf{R}, t) + \sum_j D_{kj} \Omega_j(\mathbf{R}, t) = i\hbar \frac{\partial}{\partial t} \Omega_k(\mathbf{R}, t)$$

- Equation for the nuclear "wavepacket",  $\Omega(\mathbf{R}, t)$ , dynamics.
- $E_{el,k}(\mathbf{R})$  represents a potential energy surface for the nuclei.

Important additional term :  $D_{kj}$  ! NONADIABATIC COUPLING TERMS

$$D_{kj} = \int \Phi_k^*(\mathbf{r}; \mathbf{R}) \left[ \sum_I \frac{\hbar^2}{2M_I} \nabla_I^2 \right] \Phi_j(\mathbf{r}; \mathbf{R}) d\mathbf{r} + \sum_I \frac{1}{M_I} \left\{ \int \Phi_k^*(\mathbf{r}; \mathbf{R}) [-i\hbar \nabla_I] \Phi_j(\mathbf{r}; \mathbf{R}) d\mathbf{r} \right\} [-i\hbar \nabla_I]$$

## Born-Oppenheimer approximation

$$D_{kj} = \int \Phi_k^*(\mathbf{r}; \mathbf{R}) \left[ \sum_I \frac{\hbar^2}{2M_I} \nabla_I^2 \right] \Phi_j(\mathbf{r}; \mathbf{R}) d\mathbf{r} + \sum_I \frac{1}{M_I} \left\{ \int \Phi_k^*(\mathbf{r}; \mathbf{R}) [-i\hbar \nabla_I] \Phi_j(\mathbf{r}; \mathbf{R}) d\mathbf{r} \right\} [-i\hbar \nabla_I]$$

If we neglect **all** the  $D_{kj}$  terms (diagonal and off-diagonal), we have the **Born-Oppenheimer approximation**.

$$\left[ -\sum_I \frac{\hbar^2}{2M_I} \nabla_I^2 + E_{el,k}(\mathbf{R}) \right] \Omega_k(\mathbf{R}, t) = i\hbar \frac{\partial}{\partial t} \Omega_k(\mathbf{R}, t)$$

Mainly for **ground state dynamics** or for dynamics on states that do not couple with others. (Back to nonadiabatic dynamics later).

## Born-Oppenheimer approximation: the nuclear trajectories

$$\left[ -\sum_I \frac{\hbar^2}{2M_I} \nabla_I^2 + E_{el,k}(\mathbf{R}) \right] \Omega_k(\mathbf{R}, t) = i\hbar \frac{\partial}{\partial t} \Omega_k(\mathbf{R}, t)$$

Using a polar expansion for  $\Omega_k(\mathbf{R}, t)$ , we may find a way to obtain classical equation of motions for the nuclei.

$$\Omega_k(\mathbf{R}, t) = A_k(\mathbf{R}, t) \exp \left[ \frac{i}{\hbar} S_k(\mathbf{R}, t) \right].$$

$A_k(\mathbf{R}, t)$  represents an amplitude and  $S_k(\mathbf{R}, t)/\hbar$  a phase.

Further: insert the polar representation into the equation above, do some algebra, and separate real and imaginary part, we obtain an interesting set of equations:

## Born-Oppenheimer approximation: the nuclear trajectories

$$\frac{\partial S_k}{\partial t} = \frac{\hbar^2}{2} \sum_I M_I^{-1} \frac{\nabla_I^2 A_k}{A_k} - \frac{1}{2} \sum_I M_I^{-1} (\nabla_I S_k)^2 - E_k$$

$$\frac{\partial A_k}{\partial t} = - \sum_I M_I^{-1} \nabla_I A_k \nabla_I S_k - \frac{1}{2} \sum_I M_I^{-1} A_k \nabla_I^2 S_k$$

Dependences of the functions  $S$  and  $A$  are omitted for clarity ( $k$  is a index for the electronic state; in principle there is only one state in the adiabatic case).

We have now a time-dependent equation for both the amplitude and the phase.

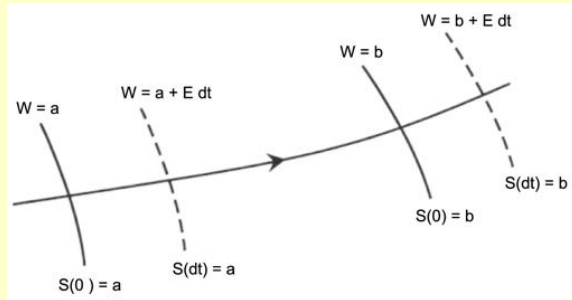
Since we are in the adiabatic case there is only one PES and the second equation becomes trivially a diffusion continuity equation.

The nuclear dynamics is derived from the real part ( $\frac{\partial S_k}{\partial t}$ ). This equation has again the form of a **classical Hamilton-Jacobi equation**.

## Born-Oppenheimer approximation: the nuclear trajectories

$$\frac{\partial S_k}{\partial t} = \frac{\hbar^2}{2} \sum_I M_I^{-1} \frac{\nabla_I^2 A_k}{A_k} - \frac{1}{2} \sum_I M_I^{-1} (\nabla_I S_k)^2 - E_k$$

$$\frac{\partial A_k}{\partial t} = - \sum_I M_I^{-1} \nabla_I A_k \nabla_I S_k - \frac{1}{2} \sum_I M_I^{-1} A_k \nabla_I^2 S_k$$



Instead of solving the field equation for  $S(\mathbf{R}, t)$ , find the equation of motion for the corresponding trajectories (*characteristics*).

## Born-Oppenheimer approximation: the nuclear trajectories

$$\frac{\partial S_k}{\partial t} = \frac{\hbar^2}{2} \sum_I M_I^{-1} \frac{\nabla_I^2 A_k}{A_k} - \frac{1}{2} \sum_I M_I^{-1} (\nabla_I S_k)^2 - E_k$$

The **classical limit** is obtained by taking<sup>1</sup>:  $\hbar \rightarrow 0$

$$\frac{\partial S_k}{\partial t} = - \frac{1}{2} \sum_I M_I^{-1} (\nabla_I S_k)^2 - E_k$$

These are the classical Hamilton-Jacobi equation and  $S$  is the classical action related to a particle.

$$S(t) = \int_{t_0}^t L(t') dt' = \int_{t_0}^t [E_{kin}(t') - E_{pot}(t')] dt'$$

The momentum of a particle  $I$  is related to

$$\nabla_I S = \mathbf{p}_I = \frac{\mathbf{v}_I}{M_I}$$

<sup>1</sup>Caution! This classical limit is subject to controversy...

## Born-Oppenheimer approximation: the nuclear trajectories

Therefore, taking the gradient,

$$-\nabla_J \frac{\partial S_k}{\partial t} = \frac{1}{2} \nabla_J \sum_I M_I^{-1} (\nabla_I S_k)^2 + \nabla_J E_k$$

and rearranging this equation using  $\nabla_J S_k / M_J = \mathbf{v}_J^k$ , we obtain the (familiar) Newton equation:

$$M_J \frac{d}{dt} \mathbf{v}_J^k = -\nabla_J E_k$$

In Summary:

Adiabatic BO MD

$$\hat{\mathcal{H}}_{el}(\mathbf{r}; \mathbf{R}) \Phi_k(\mathbf{r}; \mathbf{R}) = E_k^{el}(\mathbf{R}) \Phi_k(\mathbf{r}; \mathbf{R})$$

$$M_I \ddot{\mathbf{R}}_I = -\nabla_I E_k^{el}(\mathbf{R}) = - \nabla_I \langle \Phi_k | \hat{\mathcal{H}}_{el} | \Phi_k \rangle_{\min \Phi_k}$$

## Mean-field vs. BO MD (adiabatic case)

Ehrenfest dynamics

$$i\hbar \frac{\partial \Phi(\mathbf{r}; \mathbf{R}, t)}{\partial t} = \hat{\mathcal{H}}_{el}(\mathbf{r}; \mathbf{R}) \Phi(\mathbf{r}; \mathbf{R}, t)$$

$$M_I \ddot{\mathbf{R}}_I = -\nabla_I \langle \hat{\mathcal{H}}_{el}(\mathbf{r}; \mathbf{R}) \rangle$$

Explicit time dependence of the electronic wavefunction.

Born-Oppenheimer dynamics

$$\hat{\mathcal{H}}_{el}(\mathbf{r}; \mathbf{R}) \Phi_k(\mathbf{r}; \mathbf{R}) = E_k^{el}(\mathbf{R}) \Phi_k(\mathbf{r}; \mathbf{R})$$

$$M_I \ddot{\mathbf{R}}_I = -\nabla_I E_k^{el}(\mathbf{R}) = - \nabla_I \langle \Phi_k | \hat{\mathcal{H}}_{el} | \Phi_k \rangle_{\min \Phi_k}$$

The electronic wavefunction are *static* (only implicit time-dependence).

## Mean-field vs. BO MD (adiabatic case)

Method	Born-Oppenheimer MD	Ehrenfest MD
	<b>adiabatic</b> MD (one PES)	<b>nonadiabatic</b> MD (mean-field)
	Efficient propagation of the nuclei	Get the "real" dynamics of the electrons
	Adiabatic nuclear propagation	Propagation of nuclei & electrons
	$\delta t \sim 10\text{-}20$ a.u. (0.25-0.5 fs)	$\delta t \sim 0.01$ a.u. (0.25 as)
	Simple algorithm	Common propagation of the nuclei and the electrons implies more sophisticated algorithms

## Exact quantum dynamics?

Can we derive "exact" quantum equations of motion for the nuclei?  
(without taking the classical limit  $\hbar \rightarrow 0$ ?)

## NABDY: "exact" trajectory-based nonadiabatic dynamics

Using

- $\Psi(\mathbf{r}, \mathbf{R}, t) = \sum_j^\infty \phi_j(\mathbf{r}; \mathbf{R}) \Omega_j(\mathbf{R}, t)$
- $\Omega_j(\mathbf{R}, t) = A_j(\mathbf{R}, t) \exp\left[\frac{i}{\hbar} S_j(\mathbf{R}, t)\right]$

in the exact time-dependent Schrödinger equation for the nuclear wavefunction we get

$$\begin{aligned}
 -\frac{\partial S_j(\mathbf{R}, t)}{\partial t} &= \sum_\gamma \frac{1}{2M_\gamma} (\nabla_\gamma S_j(\mathbf{R}, t))^2 + E_{el}^j(\mathbf{R}) - \sum_\gamma \frac{\hbar^2}{2M_\gamma} \frac{\nabla_\gamma^2 A_j(\mathbf{R}, t)}{A_j(\mathbf{R}, t)} \\
 &+ \sum_{\gamma i} \frac{\hbar^2}{2M_\gamma} D_{ji}^{\gamma\gamma}(\mathbf{R}) \frac{A_i(\mathbf{R}, t)}{A_j(\mathbf{R}, t)} \Re[e^{i\phi}] - \sum_{\gamma, i \neq j} \frac{\hbar^2}{M_\gamma} d_{ji}^{\gamma\gamma}(\mathbf{R}) \frac{\nabla_\gamma A_i(\mathbf{R}, t)}{A_j(\mathbf{R}, t)} \Re[e^{i\phi}] \\
 &+ \sum_{\gamma, i \neq j} \frac{\hbar}{M_\gamma} d_{ji}^{\gamma\gamma}(\mathbf{R}) \frac{A_i(\mathbf{R}, t)}{A_j(\mathbf{R}, t)} \nabla_\gamma S_j(\mathbf{R}, t) \Im[e^{i\phi}]
 \end{aligned}$$

and

$$\begin{aligned}
 \frac{\partial A_j(\mathbf{R}, t)}{\partial t} &= - \sum_\gamma \frac{1}{M_\gamma} \nabla_\gamma A_j(\mathbf{R}, t) \nabla_\gamma S_j(\mathbf{R}, t) - \sum_\gamma \frac{1}{2M_\gamma} A_j(\mathbf{R}, t) \nabla_\gamma^2 S_j(\mathbf{R}, t) \\
 &+ \sum_{\gamma i} \frac{\hbar}{2M_\gamma} D_{ji}^{\gamma\gamma}(\mathbf{R}) A_i(\mathbf{R}, t) \Im[e^{i\phi}] - \sum_{\gamma, i \neq j} \frac{\hbar}{M_\gamma} d_{ji}^{\gamma\gamma}(\mathbf{R}) \nabla_\gamma A_i(\mathbf{R}, t) \Im[e^{i\phi}] \\
 &- \sum_{\gamma, i \neq j} \frac{1}{M_\gamma} d_{ji}^{\gamma\gamma}(\mathbf{R}) A_i(\mathbf{R}, t) \nabla_\gamma S_j(\mathbf{R}, t) \Im[e^{i\phi}],
 \end{aligned}$$

where both  $S_j(\mathbf{R}, t)$  and  $A_j(\mathbf{R}, t)$  are real fields and  $\phi = \frac{1}{\hbar}(S_i(\mathbf{R}, t) - S_j(\mathbf{R}, t))$ .

## Trajectory-based quantum and mixed QM-CL solutions

We can "derive" the following trajectory-based solutions:

- Nonadiabatic Ehrenfest dynamics dynamics  
I. Tavernelli et al., *Mol. Phys.*, **103**, 963981 (2005).
- Adiabatic Born-Oppenheimer MD equations
- **Nonadiabatic Bohmian Dynamics (NABDY)**  
B. Curchod, IT\*, U. Rothlisberger, *PCCP*, **13**, 32313236 (2011)
- Trajectory Surface Hopping (TSH) dynamics  
[ROKS: N. L. Doltsinis, D. Marx, *PRL*, **88**, 166402 (2002)]  
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E. Tapavicza, I. Tavernelli, U. Rothlisberger, *PRL*, **98**, 023001 (2007)
- Time dependent potential energy surface approach  
based on the exact decomposition:  $\Psi(\mathbf{r}, \mathbf{R}, t) = \Omega(\mathbf{R}, t)\Phi(\mathbf{r}, t)$ .  
A. Abedi, N. T. Maitra, E. K. U. Gross, *PRL*, **105**, 123002 (2010)

## NABDY: "exact" trajectory-based nonadiabatic dynamics

From the NABDY equations we can obtain a Newton-like equation of motion (using the HJ definition of the momenta  $\nabla_\beta S_j(\mathbf{R}, t) = \mathbf{P}_\beta^j$ )

$$M_\beta \frac{d^2 \mathbf{R}_\beta}{(dt)^2} = -\nabla_\beta \left[ E_{el}^j(\mathbf{R}) + Q_j(\mathbf{R}, t) + \sum_i D_{ij}(\mathbf{R}, t) \right]$$

where  $Q_j(\mathbf{R}, t)$  is the quantum potential responsible for all coherence/decoherence "intrasurface" QM effects, and  $D_j(\mathbf{R}, t)$  is the *nonadiabatic* potential responsible for the amplitude transfer among the different PESs.

For more informations see:

B. Curchod, IT, U. Rothlisberger, *PCCP*, **13**, 3231 – 3236 (2011)

## NABDY limitations

- Many numerical challenges
- Instabilities induced by the quantum potential
- Compute derivatives in the  $3N$  dimensional ( $\mathbb{R}^{3N}$ ) configuration space

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A. Abedi, N. T. Maitra, E. K. U. Gross, *PRL*, **105**, 123002 (2010)

Trajectory-based nonadiabatic molecular dynamics

## Tully's surface hopping - How does it work?

The main claim of TSH is that, the collection of a large enough set of **independent trajectories** gives an accurate representation of the nuclear wave packet

$$\rho_k^{CL}(\mathbf{R}^\alpha, t^\alpha) = \frac{N_k^\alpha(\mathbf{R}^\alpha, dV, t^\alpha)}{N_{tot}} \frac{1}{dV} \sim |\Omega_k(\mathbf{R}^\alpha, t^\alpha)|^2 \sim |C_{k, \mathbf{R}^\alpha, t^\alpha}^\alpha|^2$$

Inserting

$$\Psi^\alpha(\mathbf{r}, \mathbf{R}, t) = \sum_k C_k^\alpha(t) \Phi_k(\mathbf{r}; \mathbf{R})$$

into the molecular time-dependent Schrödinger equation and after some rearrangement, we obtain:

$$i\hbar \dot{C}_k^\alpha(t) = \sum_j C_j^\alpha(t) (H_{kj} - i\hbar \dot{\mathbf{R}}^\alpha \cdot \mathbf{d}_{kj}^\alpha)$$

with  $H_{kj} = \langle \Phi_k(\mathbf{r}; \mathbf{R}) | \hat{H}_{el} | \Phi_j(\mathbf{r}; \mathbf{R}) \rangle$ .

In the **adiabatic** representation, we have  $H_{kk} = E_k^{el}$  and  $H_{kj} = 0$ .

Trajectory-based nonadiabatic molecular dynamics

## TSH nonadiabatic MD

There is no derivation of TSH dynamics. The fundamental hypothesis beyond TSH is that it is possible to design a dynamics that consists of:

- propagation of a “quantum” amplitude,  $C_k^\alpha(t)$ , associated to each PES,  $k$

$$\Psi^\alpha(\mathbf{r}, \mathbf{R}, t) = \sum_k C_k^\alpha(t) \Phi_k(\mathbf{r}; \mathbf{R})$$

(the label  $\alpha$  is to recall that we have a different contribution from each different trajectory).

- classical (*adiabatic*) time evolution of the nuclear trajectories on adiabatic states solution of the Schrödinger equation for the electronic sub-system. Each trajectory  $\alpha$  carries a phase,  $C_k^\alpha(t)$ , associated to each surface  $k$ .
- transitions (hops) of the trajectories between electronic states according to a stochastic algorithm, which depends on the nonadiabatic couplings and the amplitudes  $C_k^\alpha(t)$ .

See also: J. Tully, *Faraday discussion*, **110**, 407 (1998).

Trajectory-based nonadiabatic molecular dynamics

## Tully's surface hopping - How does it work?

Equation of motion for the amplitudes:

$$i\hbar \dot{C}_k^\alpha(t) = \sum_j C_j^\alpha(t) (H_{kj} - i\hbar \dot{\mathbf{R}}^\alpha \cdot \mathbf{d}_{kj}^\alpha)$$

Switching algorithm:

In the fewest switches algorithm, the transition probability from state  $j$  to state  $k$  in the time interval  $[t, t + dt]$  is given by:

$$g_{jk}^\alpha(t, t + dt) \approx 2 \int_t^{t+dt} d\tau \frac{\Im[C_k^\alpha(\tau) C_j^{\alpha*}(\tau) H_{kj}(\tau)] - \Re[C_k^\alpha(\tau) C_j^{\alpha*}(\tau) \Xi_{kj}^\alpha(\tau)]}{C_j^\alpha(\tau) C_j^{\alpha*}(\tau)}$$

where  $\Xi_{kj}^\alpha(\tau) = \dot{\mathbf{R}}^\alpha \cdot \mathbf{d}_{kj}^\alpha(\tau)$ . A hop occurs between  $j$  and  $k$  if

$$\sum_{l \leq k-1} g_{jl}^\alpha < \zeta < \sum_{l \leq k} g_{jl}^\alpha,$$

where  $\zeta$  is generated randomly in the interval  $[0, 1]$ .

Trajectory-based nonadiabatic molecular dynamics

# Tully's surface hopping - Summary

## Tully's surface hopping

$$i\hbar\dot{C}_k^\alpha(t) = \sum_j C_j^\alpha(t)(H_{kj} - i\hbar\dot{\mathbf{R}}^\alpha \cdot \mathbf{d}_{kj}^\alpha)$$

$$M_I\ddot{\mathbf{R}}_I = -\nabla_I E_k^{\text{el}}(\mathbf{R})$$

$$\sum_{l \leq k-1} g_{jl}^\alpha < \zeta < \sum_{l \leq k} g_{jl}^\alpha,$$

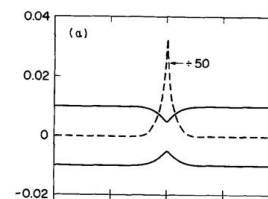
### Some warnings:

- 1 Evolution of classical trajectories (no QM effects – such as tunneling – are possible).
- 2 Rescaling of the nuclei velocities after a surface hop (to ensure energy conservation) is still a matter of debate.
- 3 Depending on the system studied, **many** trajectories could be needed to obtain a complete statistical description of the non-radiative channels.

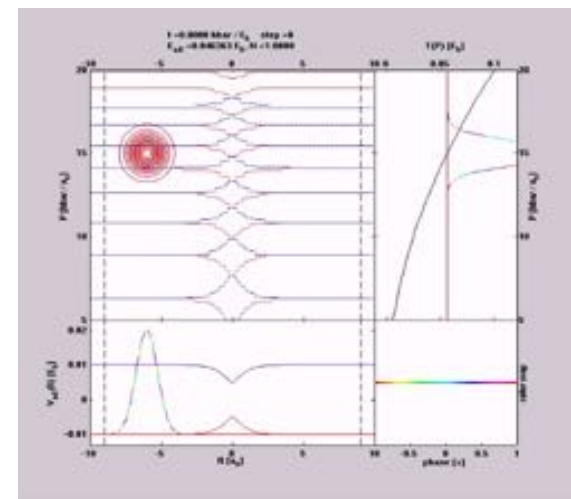
For more details (and warnings) about Tully's surface hopping, see G. Granucci and M. Persico, J Chem Phys 126, 134114 (2007).

# Tully's surface hopping - Examples

## 1D systems

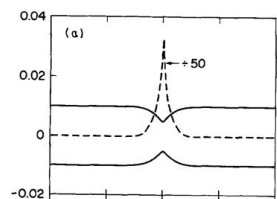


J.C. Tully, J. Chem. Phys. (1990), 93, 1061



# Tully's surface hopping - Examples

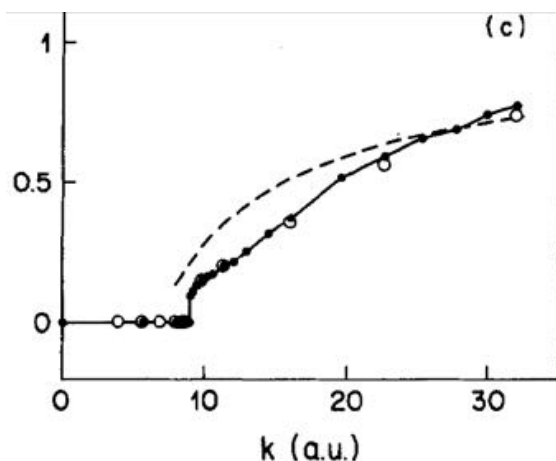
## 1D systems



J.C. Tully, J. Chem. Phys. (1990), 93, 1061

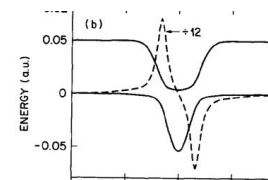
On the right: population of the upper state (k=mom)

- exact
- TSH
- Landau-Zener

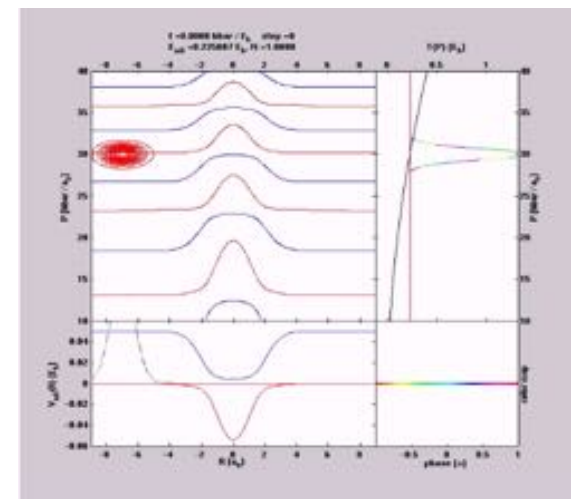


# Tully's surface hopping - Examples

## 1D systems

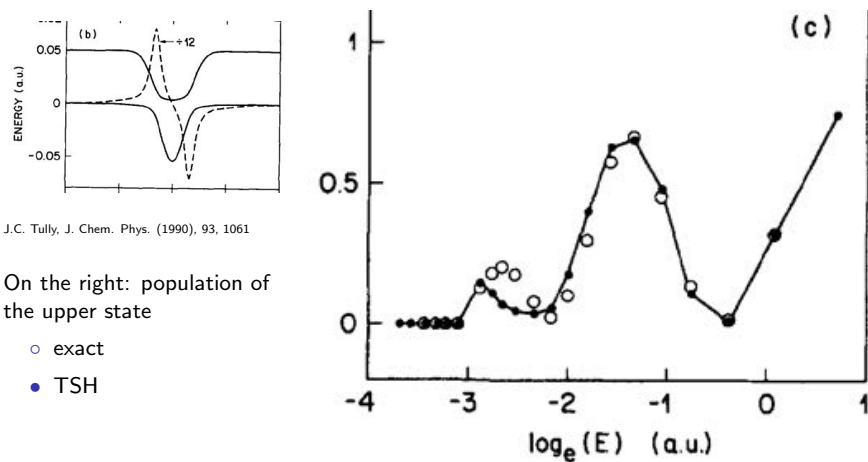


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## Tully's surface hopping - Examples

1D systems



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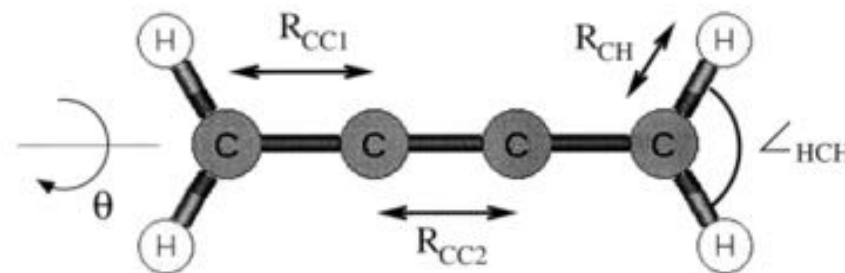
On the right: population of the upper state

- exact
- TSH

Trajectory-based nonadiabatic molecular dynamics

## Comparison with wavepacket dynamics

Butatriene molecule: dynamics of the radical cation in the first excited state.

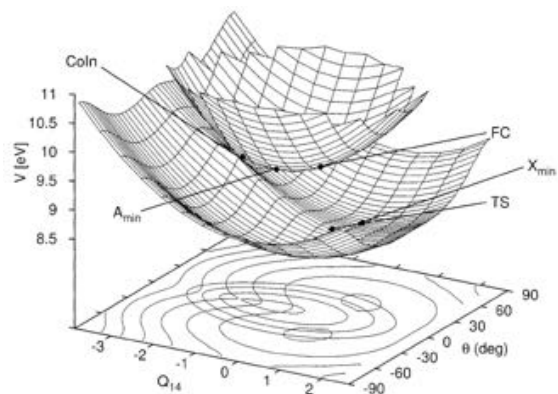


JPCA,107,621 (2003)

Trajectory-based nonadiabatic molecular dynamics

## Comparison with wavepacket dynamics

Butatriene molecule: dynamics of the radical cation in the first excited state.

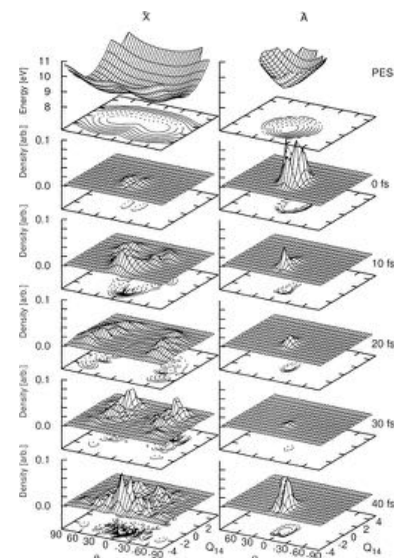


JPCA,107,621 (2003)

CASSCF PESs for the radical cation ( $Q_{14}$ : symmetric stretch,  $\theta$ : torsional angle).

Trajectory-based nonadiabatic molecular dynamics

## Comparison with wavepacket dynamics

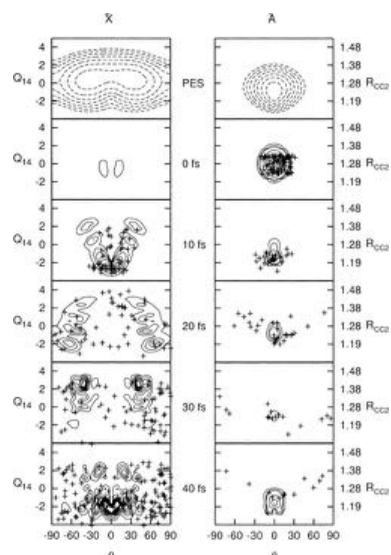
Nuclear wavepacket dynamics on fitted potential energy surfaces (using MCTDH with 5 modes). Reappearing of the wavepacket in  $S_1$  after  $\sim 40$ fs.

JPCA,107,621 (2003)

Trajectory-based nonadiabatic molecular dynamics



## Comparison with wavepacket dynamics



On-the-fly dynamics with 80 trajectories (crosses).

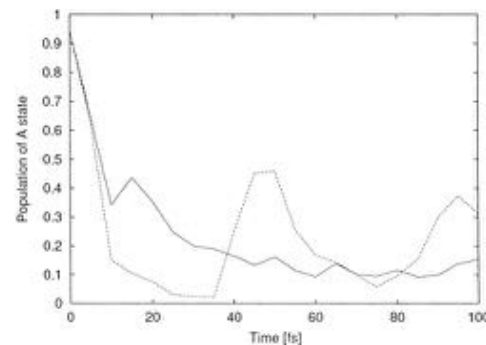
Trajectories are not coming back close to the conical intersection.

What is the reason for this discrepancy? The independent trajectory approximation?, i.e. the fact that trajectories are not correlated? (Or it has to do with differences in the PESs?)

JPCA.107.621 (2003)

Trajectory-based nonadiabatic molecular dynamics

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JPCA.107.621 (2003)

Trajectory-based nonadiabatic molecular dynamics

## TDDFT-based trajectory surface hopping

- 1 Ab initio molecular dynamics
  - Why Quantum Dynamics?
  - Nuclear quantum effects
- 2 Mixed quantum-classical dynamics
  - Ehrenfest dynamics
  - Adiabatic Born-Oppenheimer dynamics
  - Wavepacket on the Bohmian dynamics
  - Trajectory surface hopping
- 3 TDDFT-based trajectory surface hopping
  - Nonadiabatic couplings in TDDFT
- 4 TDDFT-TSH: Applications
  - Photoisomerization of Oxirane
  - Photoisomerization - Crossing between  $S_1$  and  $S_0$
- 5 TSH with external time-dependent fields
  - Control theory
  - Application of LCT

Trajectory-based nonadiabatic molecular dynamics

## TDDFT-based trajectory surface hopping

## Tully's surface hopping - On-the-fly dynamics

## Tully's surface hopping

$$i\hbar\dot{C}_k^\alpha(t) = \sum_j C_j^\alpha(t)(H_{kj} - i\hbar\dot{\mathbf{R}}^\alpha \cdot \mathbf{d}_{kj}^\alpha)$$

$$M_I \ddot{\mathbf{R}}_I = -\nabla_I E_k^{el}(\mathbf{R})$$

$$\sum_{l \leq k-1} g_{jl}^\alpha < \zeta < \sum_{l \leq k} g_{jl}^\alpha,$$

What about the electronic structure method for on-the-fly dynamics? We need:

- Potential energy surfaces → MR-CISD, LR-TDDFT, semiempirical, ...
- Forces on the nuclei → MR-CISD, LR-TDDFT, semiempirical methods, ...
- Nonadiabatic coupling terms → MR-CISD, LR-TDDFT (?), semiempirical methods, ...

Trajectory-based nonadiabatic molecular dynamics

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- **Nonadiabatic coupling terms** → MR-CISD, LR-TDDFT (?), semiempirical methods, ...

## Nonadiabatic couplings with LR-TDDFT?

**Nonadiabatic coupling vectors** are defined in terms of electronic wavefunctions:

$$\mathbf{d}_{kj} = \langle \Phi_k(\mathbf{R}) | \nabla_{\mathbf{R}} | \Phi_j(\mathbf{R}) \rangle = \frac{\langle \Phi_k(\mathbf{R}) | \nabla_{\mathbf{R}} \hat{H}_{el} | \Phi_j(\mathbf{R}) \rangle}{E_j(\mathbf{R}) - E_k(\mathbf{R})}$$

The main challenge is to compute all these quantities as a **functional** of the ground state electronic density (or equivalently, of the occupied Kohn-Sham orbitals).

$$\mathbf{d}_{kj} \rightarrow \mathbf{d}_{kj}[\rho]$$

Different approaches for the calculation of  $\mathbf{d}_{0j}[\rho]$  are available<sup>2</sup>.

Here we will use the method based on the **auxiliary many-electron wavefunctions**.

<sup>2</sup>V. Chernyak and S. Mukamel, J. Chem. Phys. 112, 3572 (2000); R. Baer, Chem. Phys. Lett. 364, 75 (2002); E. Tapavicza, I. Tavernelli, and U. Rothlisberger, Phys. Rev. Lett. 98, 023001 (2007); C. P. Hu, H. Hirai, and O. Sugino, J. Chem. Phys. 127, 064103 (2007).

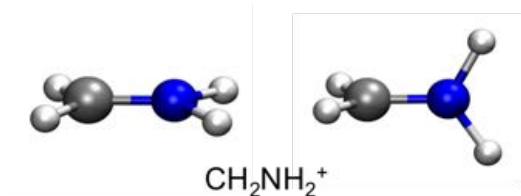
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## Protonated formaldimine

The protonated formaldimine is a model compound for the study of isomerization in rhodopsin chromophore retinal.

In addition to the ground state (GS), two excited electronic states are of interest:

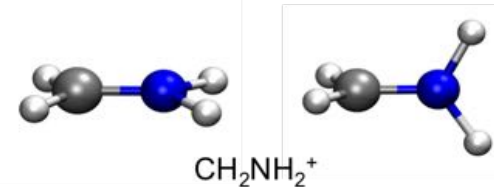
- 1  $S_1$  :  $\sigma \rightarrow \pi^*$  (low oscillator strength)
- 2  $S_2$  :  $\pi \rightarrow \pi^*$  (high oscillator strength)



## Protonated formaldimine

### Computational details

- Isolated system
- LR-TDDFT/PBE/TDA
- SH-AIMD
- 50 trajectories (NVT) each of  $\sim 100$  fs.



PRL, 98, 023001 (2007); THEOCHEM, 914, 22 (2009).

## Protonated formaldimine

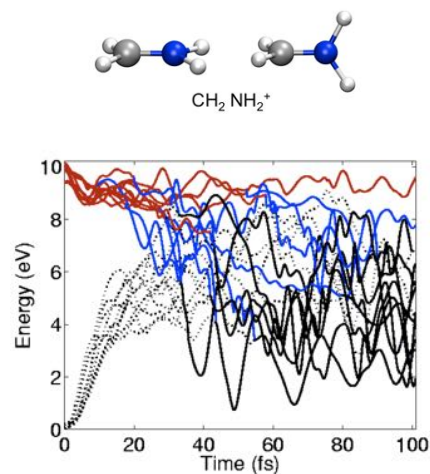
Protonated formaldimine as a model compound for the study of the isomerization of retinal.

Photo-excitation promotes the system mainly into  $S_2$ .

Relaxation involves at least 3 states:

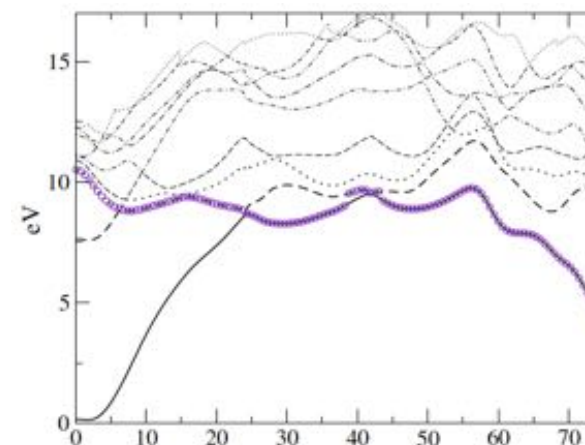
$S_0$  (GS),  $S_1$  and  $S_2$ .

[E. Tapavicza, I. T., U. Rothlisberger, PRL, 98, 023001 (2007); THEOCHEM, 914, 22 (2009)]



## Protonated formaldimine

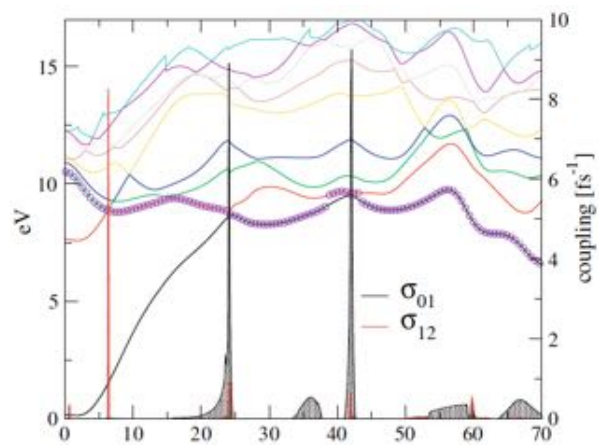
### Typical trajectory



PRL, 98, 023001 (2007); THEOCHEM, 914, 22 (2009).

## Protonated formalimine

Nonadiabatic couplings  $\sigma_{kj} = \dot{\mathbf{R}}^\alpha \cdot \mathbf{d}_{kj}^\alpha$

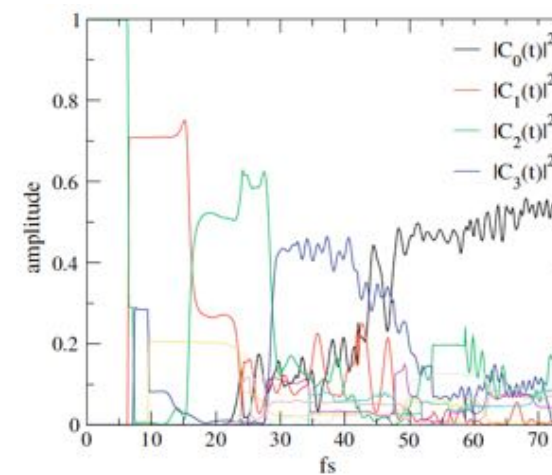


PRL, 98, 023001 (2007); THEOCHEM, 914, 22 (2009).

Trajectory-based nonadiabatic molecular dynamics

## Protonated formalimine

States population



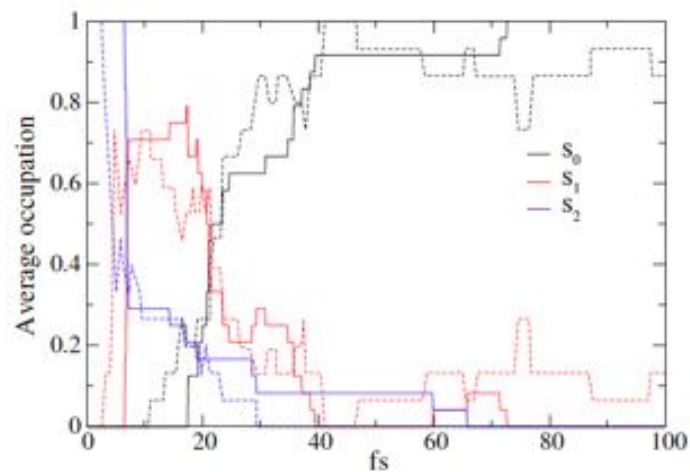
PRL, 98, 023001 (2007); THEOCHEM, 914, 22 (2009).

Trajectory-based nonadiabatic molecular dynamics

## Protonated formalimine

States population - Average over many trajectories.

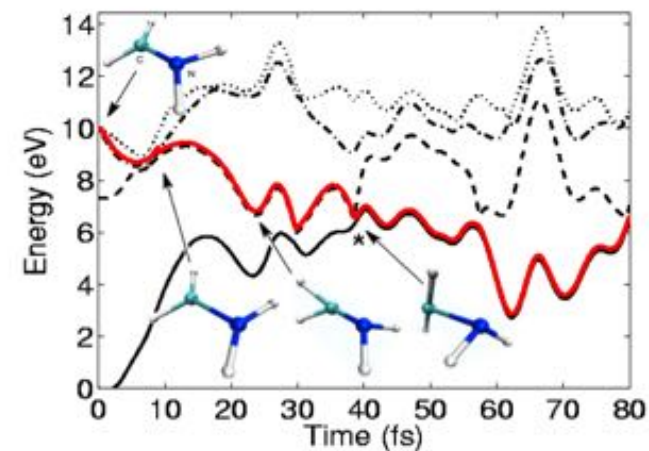
Dashed line = CASSCF result.



Trajectory-based nonadiabatic molecular dynamics

## Protonated formalimine

Geometrical modifications

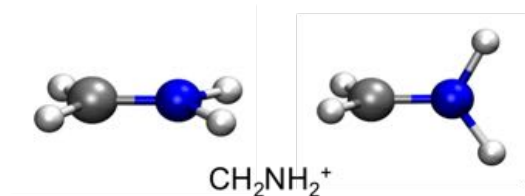


Trajectory-based nonadiabatic molecular dynamics

## Protonated formaldimine

### Comparison with experiment and model calculations

- In addition to the isomerization channel, intra-molecular proton transfer reactions was observed (formation of  $\text{CH}_3\text{NH}^+$ ).
- $\text{H}_2$  abstraction is also observed in some cases.
- Structures and life times are in good agreement with reference calculations performed using high level wavefunction based methods.

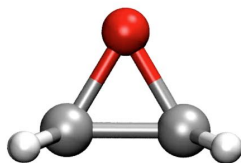


## Oxirane

Oxirane has interesting non-radiative decay channels, during which ring opening and dissociation can occur.

### Computational details

- Isolated system
- LR-TDDFT/PBE/TDA
- SH-AIMD
- 30 trajectories (NVT) each of  $\sim 100$  fs.



## Oxirane

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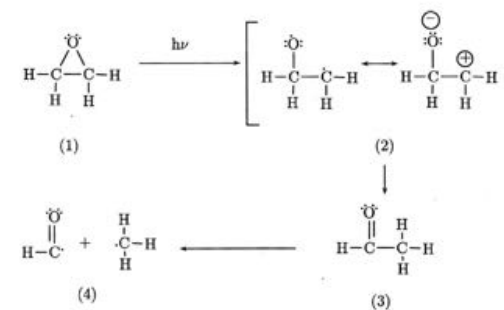
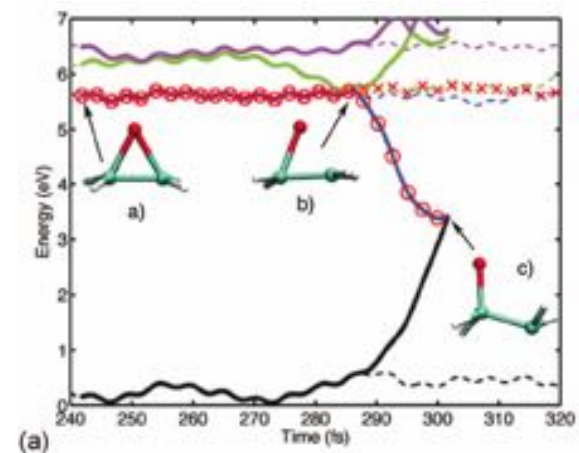


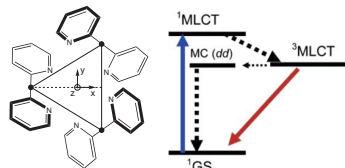
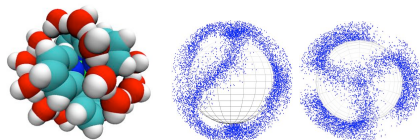
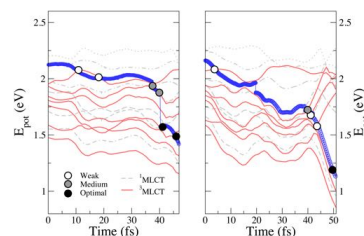
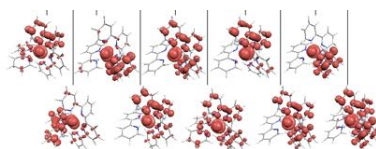
Figure: Mechanism proposed by Gomer and Noyes

## Oxirane

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## The photophysics of solvated Ruthenium(II) tris-bipyridine

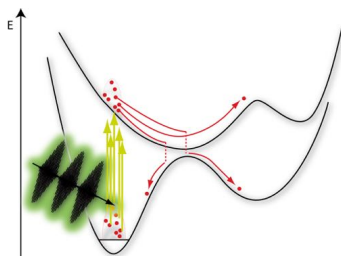
[Ru(bpy)<sub>3</sub>]<sup>2+</sup> dye: photophysics[Ru(bpy)<sub>3</sub>]<sup>2+</sup> dye: Solvent structure[Ru(bpy)<sub>3</sub>]<sup>2+</sup> dye: Singlet state dynamics[Ru(bpy)<sub>3</sub>]<sup>2+</sup> dye: triplet state dynamics[M.E. Moret, I.T., U. Rothlisberger, *JPC B*, 113, 7737 (2009); IT, B.Curchod, U. Rothlisberger, *Chem.Phys.*, 391, 101 (2011)]

Trajectory-based nonadiabatic molecular dynamics

TSH with external time-dependent fields

## TSH with external time-dependent fields

Addition of an external field within the equations of motion of TSH:



## Strategy

The idea is to induce electronic excitations through the direct interaction with the time-dependent (td) electric field instead of "artificially" promote the system into one of its excited states.

**Method:** extended TSH nonadiabatic dynamics.

IT, B. Curchod, U. Rothlisberger, *Phys. Rec. A* **81**, 052508 (2010)

Trajectory-based nonadiabatic molecular dynamics

TSH with external time-dependent fields

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Trajectory-based nonadiabatic molecular dynamics

TSH with external time-dependent fields

## TSH with external time-dependent fields

## Short summary of the theory

The interaction Hamiltonian between the electrons and the td electric field is

$$\hat{H}_{int} = -\frac{e}{2m_e c} \sum_i \mathbf{A}(\mathbf{r}_i, t) \cdot \hat{\mathbf{p}}_i$$

where  $\mathbf{A}(\mathbf{r}, t)$  is the (classical) vector potential of the electromagnetic field,  $\hat{\mathbf{p}}_i$  is the momentum operator of electron  $i$ ,  $e$  is the electron charge,  $m_e$  is the electron mass, and  $c$  is the speed of light.

## Remark

We are in the *dipole approximation* and therefore we do not need TDCDF.

IT, B. Curchod, U. Rothlisberger, *Phys. Rec. A* **81**, 052508 (2010)

Trajectory-based nonadiabatic molecular dynamics

## External field within TSH

It can be shown (Phys. Rev. A **81** 052508 (2010)) that through the coupling with the td electric field, Tully's propagation equations acquire an additional term

$$i\hbar\dot{C}_J^\alpha(t) = \sum_I C_I^\alpha(t)(H_{JI} - i\hbar\dot{\mathbf{R}}^\alpha \cdot \mathbf{d}_{JI}^\alpha + i\omega_{JI}\frac{\mathbf{A}_0}{c} \cdot \boldsymbol{\mu}_{JI}^\alpha e^{-i\omega t})$$

with

$$i\omega_{JI}\frac{\mathbf{A}_0(t)}{c} \cdot \boldsymbol{\mu}_{JI} = \langle \Phi_J | \hat{H}_{int} | \Phi_I \rangle$$

and where  $\mathbf{A}_0(t) = A_0 e^{\lambda} e^{-i\omega t}$  is the vector potential of the external td electric field,

$$\boldsymbol{\mu}_{JI} = -e \langle \Phi_J | \sum_i \hat{\mathbf{r}}_i | \Phi_I \rangle$$

is the the transition dipole vector, and  $\omega_{JI} = (E_J - E_I)/\hbar$ .

Note that Tully's hops probability should be modified accordingly.

IT, B. Curchod, U. Rothlisberger, Phys. Rec. A **81**, 052508 (2010)

## Local control theory

Control is achieved by tuning the temporal evolution of  $\mathbf{E}(t)$  in a way to maximize the population of a target state.

Using the TSH for the total molecular wavefunction

$$\Psi^\alpha(\mathbf{r}, \mathbf{R}, t) = \sum_J C_J^\alpha(t) \Phi_J(\mathbf{r}; \mathbf{R})$$

for a given trajectory  $\alpha$ , the population time evolution simplifies to

$$\dot{\mathcal{P}}_I(t) = -2\mathbf{E}^\alpha(t) \sum_J \Im[C_J^{\alpha*} \boldsymbol{\mu}_{JI} C_I^\alpha(t)]$$

It is now evident that choosing a field of the form

$$\mathbf{E}(t) = -\lambda \sum_J \Im[C_I^\alpha(t) C_J^{\alpha*} \boldsymbol{\mu}_{IJ}]$$

will ensure that  $\mathcal{P}_I(t)$  always increases in time.

T. J. Penfold, G. A. Worth, C. Meier, Phys. Chem. Chem. Phys. **12**, 15616 (2010).

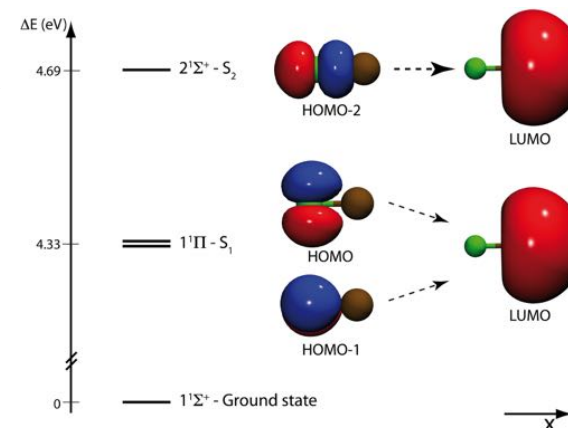
B.F.E Curchod, T. Penfold, U. Rothlisberger, IT, PRA, **84**, 042507 (2011)

## Effect of an electromagnetic field - Lithium fluoride

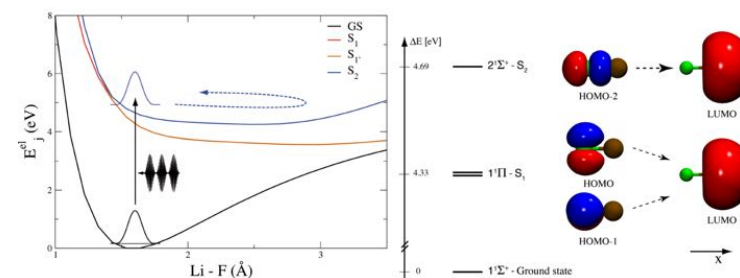
Different excitations can be obtained, depending on the polarization vector of the laser pulse.

### Electronic structure of LiF

- Ground state -  $\Sigma$  symmetry (GS).
- First excited state (doubly degenerate) -  $\Pi$  symmetry ( $S_1$ ).
- Second excited state -  $\Sigma$  symmetry ( $S_2$ ).
- Avoided crossing between GS and  $S_2$



## Application: Photoexcitation of LiF in the bound state $S_2$



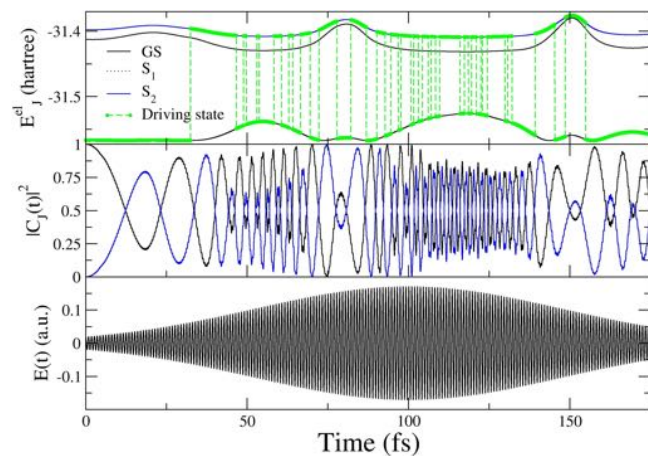
Test system: LiF.

The aim is to excite the molecule selectively into the  $S_2$  bound-excited-state starting from the ground state.

The dynamics is initiated in the ground state and the population is transferred from the GS into  $S_2$  through direct coupling with an electron magnetic pulse (pi-pulse or local controlled pulse).

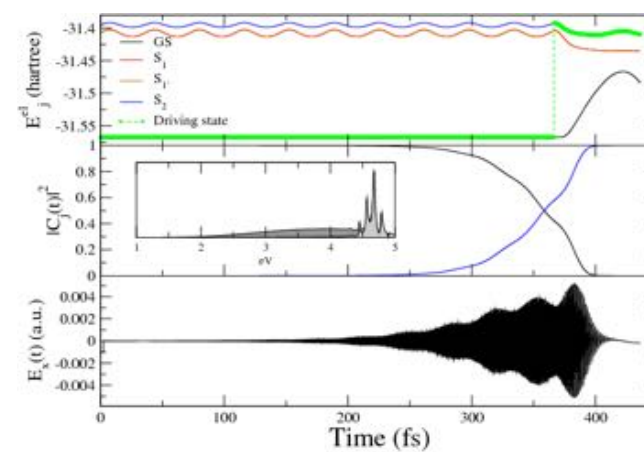
B.F.E Curchod, T. Penfold, U. Rothlisberger, IT, PRA, **84**, 042507 (2011)

## Effect of a generic polarized pulse



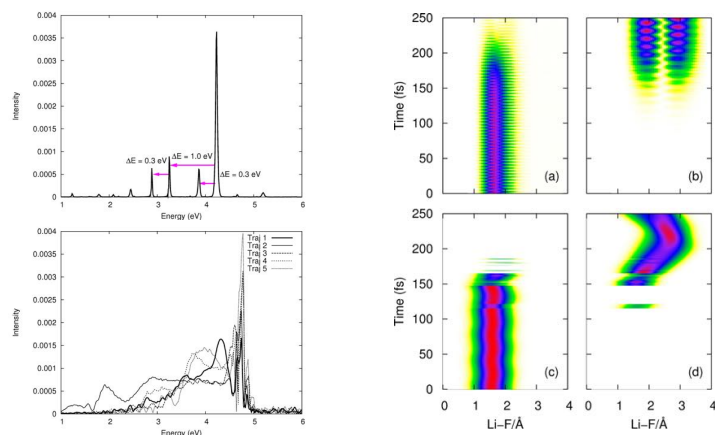
Trajectory-based nonadiabatic molecular dynamics

## LC pulse: efficient population transfer and stable excitation



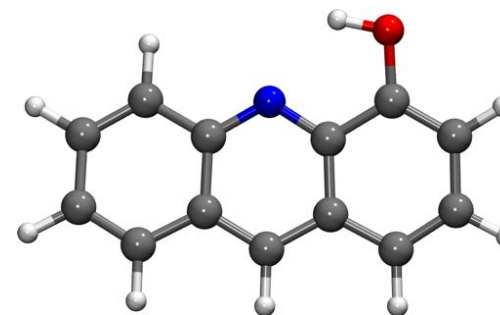
Trajectory-based nonadiabatic molecular dynamics

## Comparison with wavepacket propagation (MCTDH)

B.F.E Curchod, T. Penfold, U. Rothlisberger, *IT, PRA*, **84**, 042507 (2011)

Trajectory-based nonadiabatic molecular dynamics

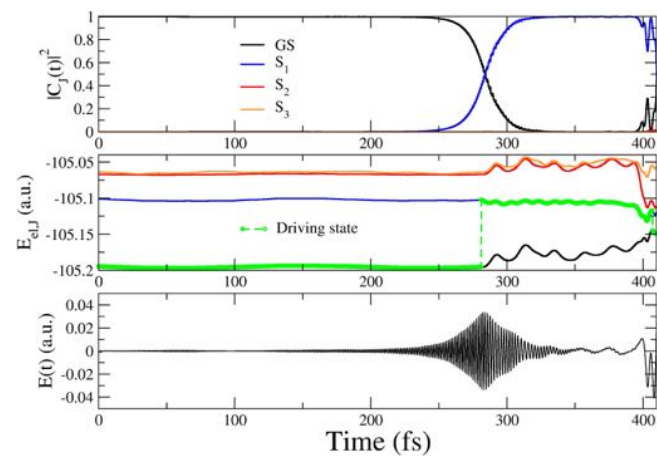
## Local control on proton transfer (in gas phase)



Trajectory-based nonadiabatic molecular dynamics

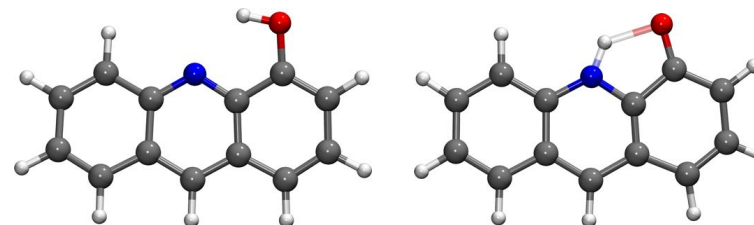


## Local control on proton transfer



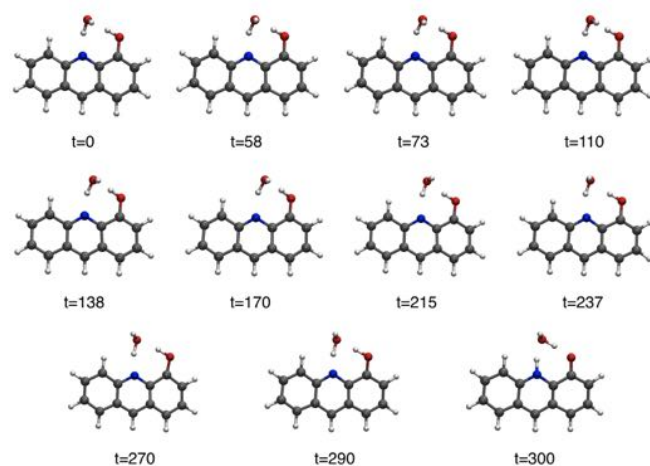
Trajectory-based nonadiabatic molecular dynamics

## Local control on proton transfer



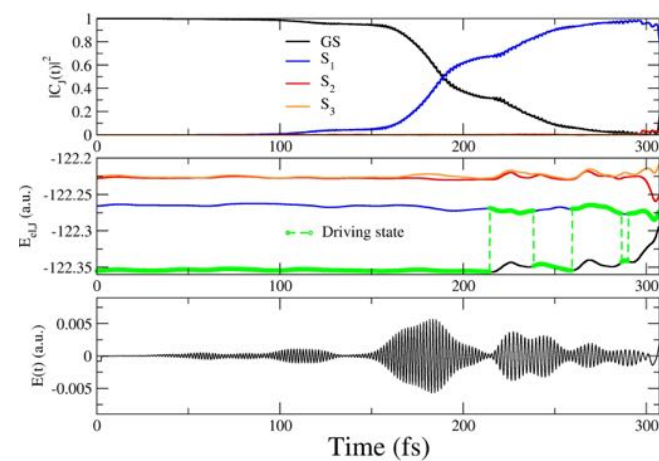
Trajectory-based nonadiabatic molecular dynamics

## Local control on proton transfer (with one water molecule)



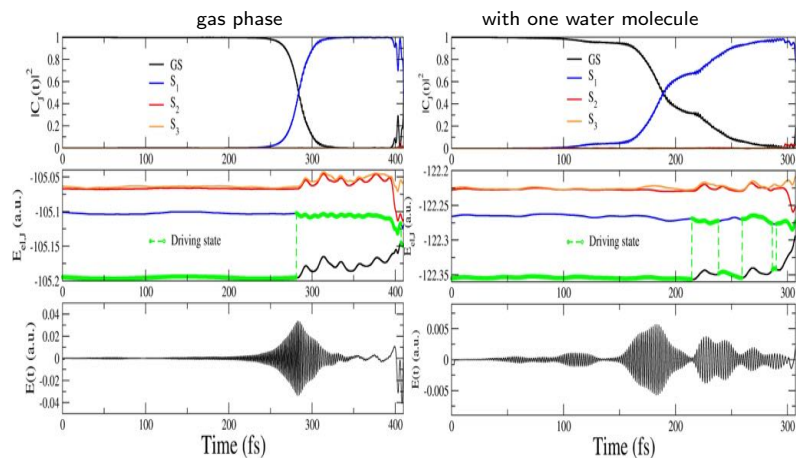
Trajectory-based nonadiabatic molecular dynamics

## Local control on proton transfer (with one water molecule)



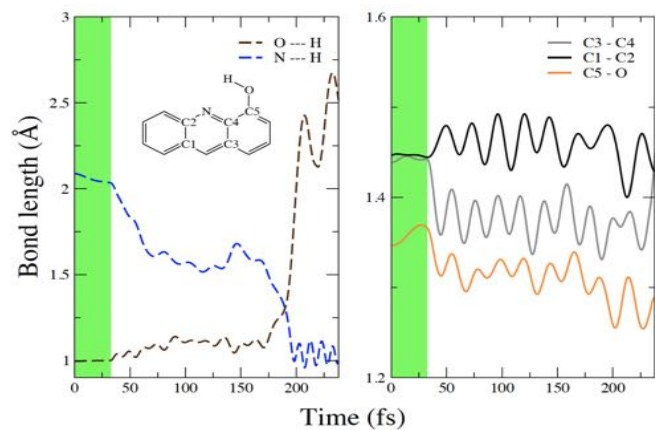
Trajectory-based nonadiabatic molecular dynamics

## Local control on proton transfer (comparison)



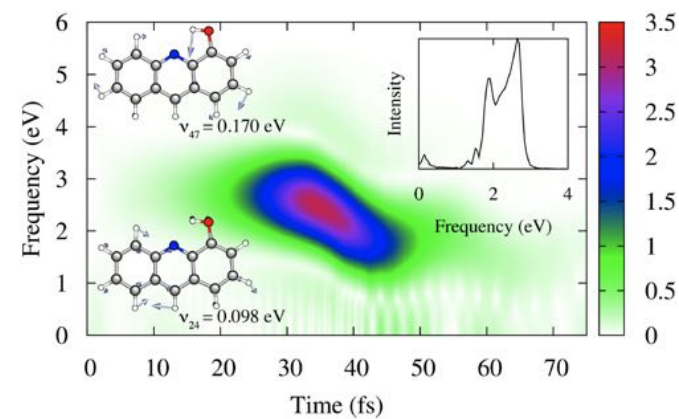
Trajectory-based nonadiabatic molecular dynamics

## Local control on proton transfer (mode analysis)



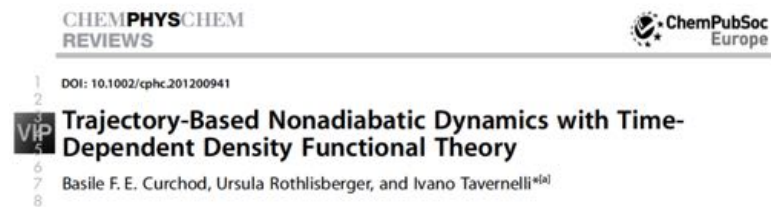
Trajectory-based nonadiabatic molecular dynamics

## Local control on proton transfer (freq. vs. time)



Trajectory-based nonadiabatic molecular dynamics

## Recent review on TDDFT-based nonadiabatic dynamics



ChemPhysChem, 14, 1314 (2013)

Trajectory-based nonadiabatic molecular dynamics