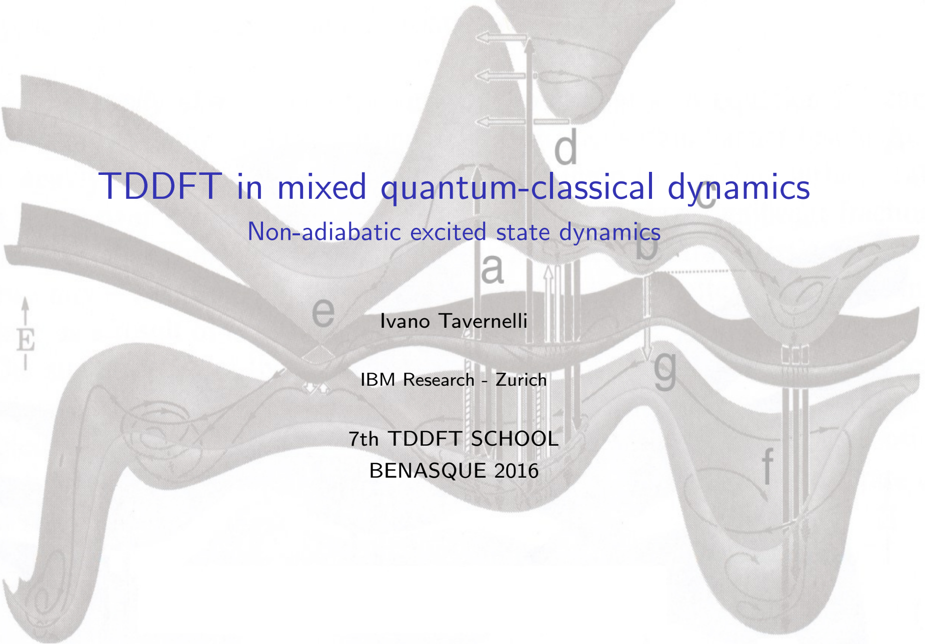


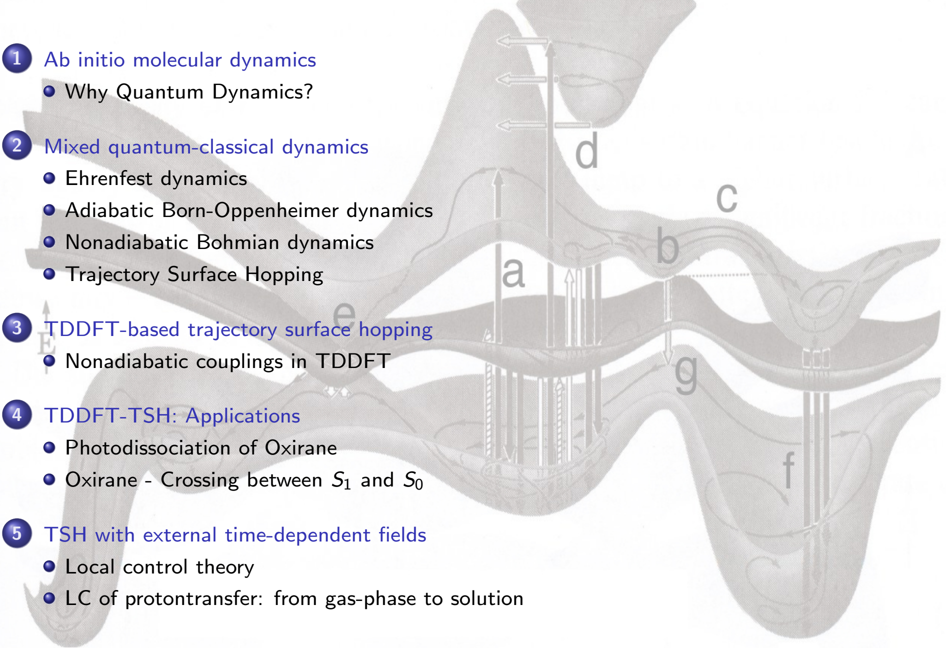
TDDFT in mixed quantum-classical dynamics

Non-adiabatic excited state dynamics

Ivano Tavernelli

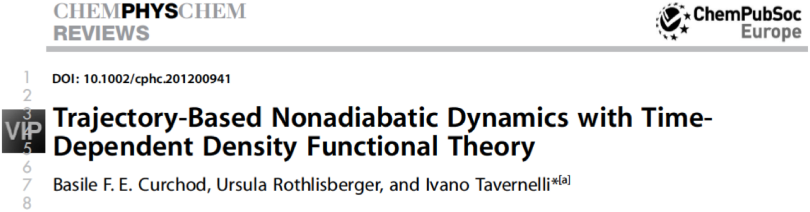
IBM Research - Zurich

7th TDDFT SCHOOL
BENASQUE 2016



1. Ab initio molecular dynamics
    - Why Quantum Dynamics?
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 theory
    - LC of protontransfer: from gas-phase to solution

Recent review on TDDFT-based nonadiabatic dynamics



CHEMPHYSCHEM
REVIEWS

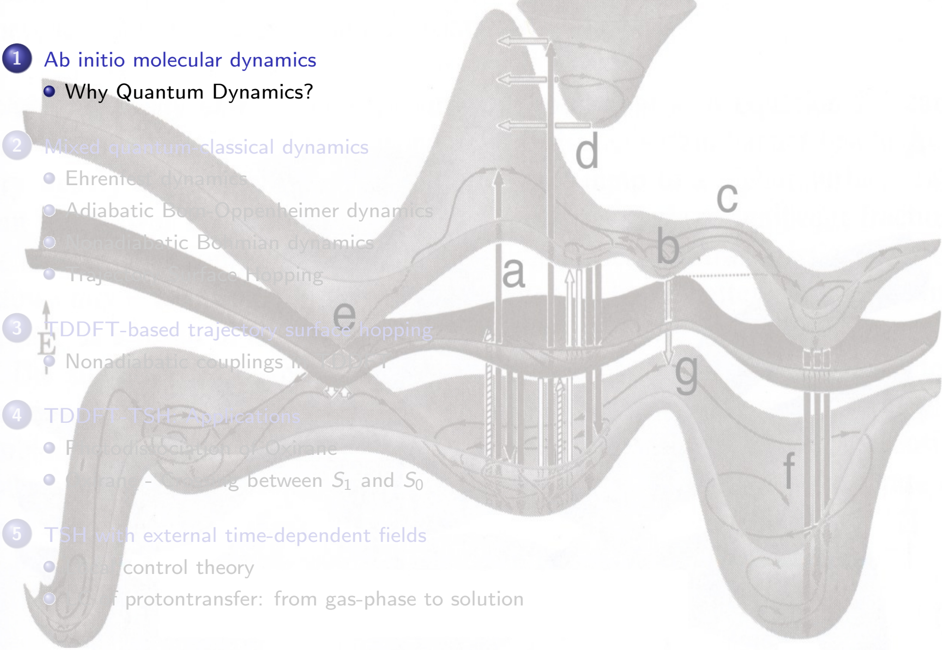
ChemPubSoc
Europe

DOI: 10.1002/cphc.201200941

Trajectory-Based Nonadiabatic Dynamics with Time-Dependent Density Functional Theory

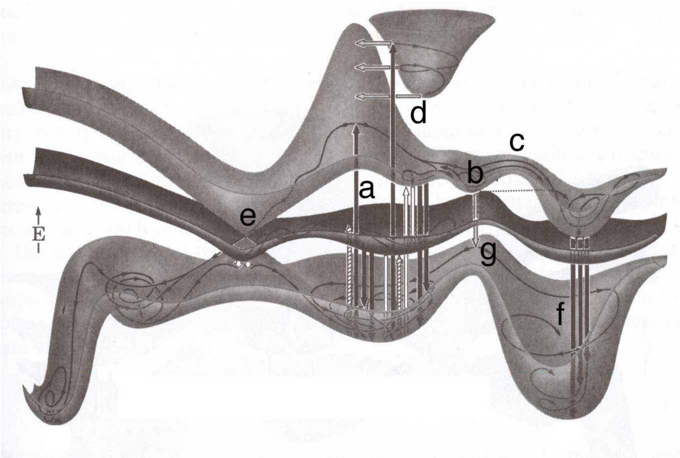
Basile F. E. Curchod, Ursula Rothlisberger, and Ivano Tavernelli*[a]

ChemPhysChem,**14**, 1314 (2013)



1. Ab initio molecular dynamics
    - Why Quantum Dynamics?
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 theory
    - LCT of protontransfer: from gas-phase to solution

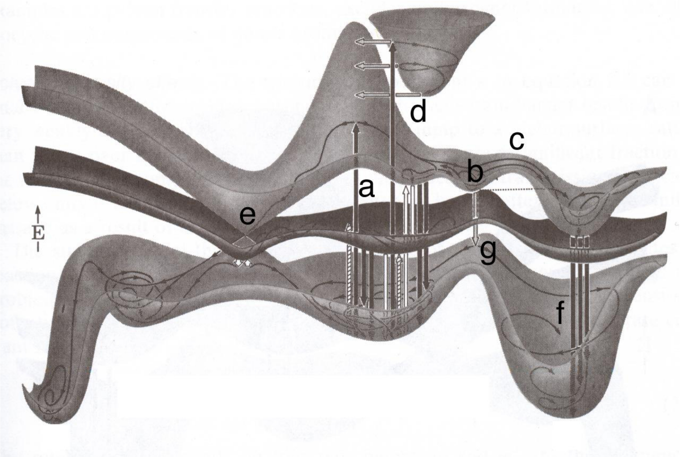
Reminder from last lecture: potential energy surfaces



We have electronic structure methods for electronic ground and excited states...

Now, we need to propagate the nuclei...

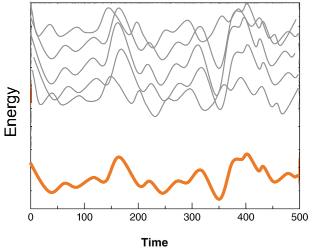
Reminder from last lecture: potential energy surfaces

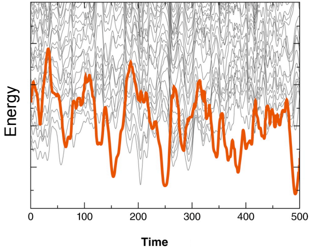


We have electronic structure methods for electronic ground and excited states...

Now, we need to propagate the nuclei...

Why Quantum dynamics?





GS adiabatic dynamics (BO vs. CP)

BO $M_I \ddot{\mathbf{R}}_I(t) = -\nabla \min_\rho E_{KS}(\{\phi_i[\rho]\})$

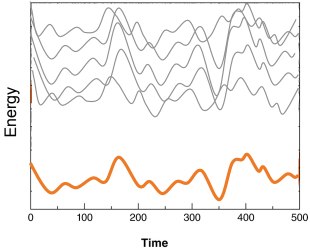
CP $\mu_i|\ddot{\phi}_i(t)\rangle = -\frac{\delta}{\delta\langle\phi_i|} E_{KS}(\{\phi_i(\mathbf{r})\}) + \frac{\delta}{\delta\langle\phi_i|}\{\text{constr.}\}$

$M_I \ddot{\mathbf{R}}_I(t) = -\nabla E_{KS}(\{\phi_i(t)\})$

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?

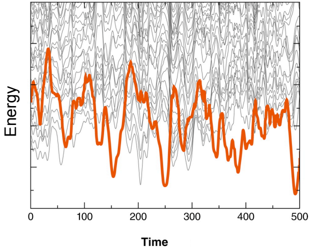


GS adiabatic dynamics

First principles Heaven

Ab initio MD with WF methods
Ab initio MD with DFT & TDDFT [CP]
classical MD
Coarse-grained MD
…

No principles World



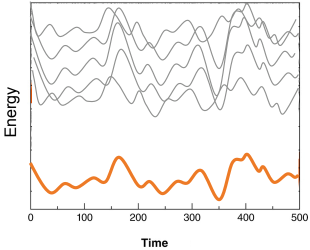
ES nonadiabatic quantum dynamics

First principles Heaven

Ab initio MD with WF methods
Ab initio MD with DFT & TDDFT [CP]
↓
Models
↓?

No principles World

Why Quantum dynamics?

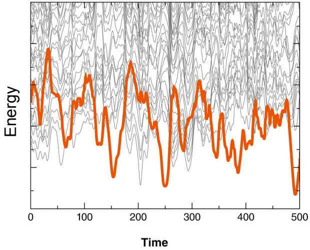


GS adiabatic dynamics

First principles Heaven

Ab initio MD with WF methods
Ab initio MD with DFT & TDDFT [CP]
classical MD
Coarse-grained MD
...

No principles World

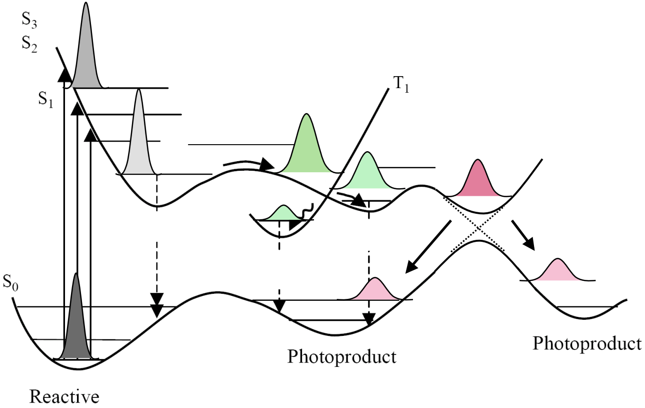


ES nonadiabatic quantum dynamics

(-) 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 ($< ps$)

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)



Why trajectory-based approaches?

W1 In "conventional" nuclear wavepacket propagation potential energy surfaces are needed.

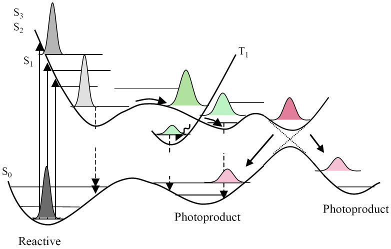
W2 Difficulty to obtain and fit potential energy surfaces for large molecules.

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 :

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

where $\hat{H}$ is the molecular time-independent Hamiltonian and $\Psi(\boldsymbol{r},\boldsymbol{R},t)$ 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 $\hbar \to 0$ for the nuclear wf).

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

$$\Psi(\boldsymbol{r},\boldsymbol{R},t) \xrightarrow[\text{Huang}]{\text{Born-}} \sum_{j}^{\infty} \Phi_j(\boldsymbol{r};\boldsymbol{R})\Omega_j(\boldsymbol{R},t)$$

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

$$\Psi(\boldsymbol{r},\boldsymbol{R},t) \xrightarrow{\text{Exact Factorization}} \Phi_{\boldsymbol{R}}(\boldsymbol{r},t)\Omega(\boldsymbol{R},t); \quad \text{with} \quad \int d\boldsymbol{r}\ \Phi_{\boldsymbol{R}}(\boldsymbol{r},t) = 1,\ \forall\boldsymbol{R}.$$

Tarjectory-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
  [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: $\Psi(\boldsymbol{r}, \boldsymbol{R}, t) = \Omega(\boldsymbol{R}, t)\Phi(\boldsymbol{r}, t)$.

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

Ehrenfest dynamics

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

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

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

where $\hat{V}(\boldsymbol{r},\boldsymbol{R}) = \sum_{i<j}\frac{e^2}{|\boldsymbol{r}_i-\boldsymbol{r}_j|} - \sum_{\gamma,i}\frac{e^2 Z_\gamma}{|\boldsymbol{R}_\gamma-\boldsymbol{r}_i|}$.
In a similar way, multiplying by $\Phi^*(\boldsymbol{r},t)$ and integrating over $\boldsymbol{r}$ we obtain

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

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 brakets). 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

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

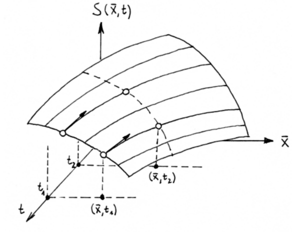
where the amplitude $A(\boldsymbol{R}, t)$ and the phase $S(\boldsymbol{R}, t)/\hbar$ are real functions.
Inserting this representation for $\Omega(\boldsymbol{R}, t)$ and separating the real and the imaginary parts one gets for the phase S in the classical limit $\hbar \to 0$

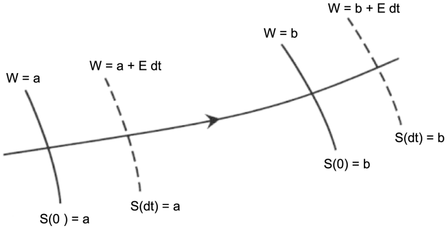
$$\frac{\partial S}{\partial t} = -\frac{1}{2} \sum_{\gamma} M_{\gamma}^{-1} \left(\nabla_{\gamma} S\right)^2 - \left[\int d\boldsymbol{r}\; \Phi^*(\boldsymbol{r}, t) \hat{\mathcal{H}}_{el}(\boldsymbol{r}, \boldsymbol{R}) \Phi(\boldsymbol{r}, t)\right]$$

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

Ehrenfest dynamics - the nuclear equation

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





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

Ehrenfest dynamics - the nuclear equation

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

$$\boldsymbol{P} = \nabla_{\boldsymbol{R}} S(\boldsymbol{R}).$$

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

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

Ehrenfest dynamics

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

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

Ehrenfest dynamics - the nuclear equation

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

$$\boldsymbol{P} = \nabla_{\boldsymbol{R}} S(\boldsymbol{R}).$$

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

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

Ehrenfest dynamics - Densityfunctionalization (ϕ_k: KS orbitals)

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

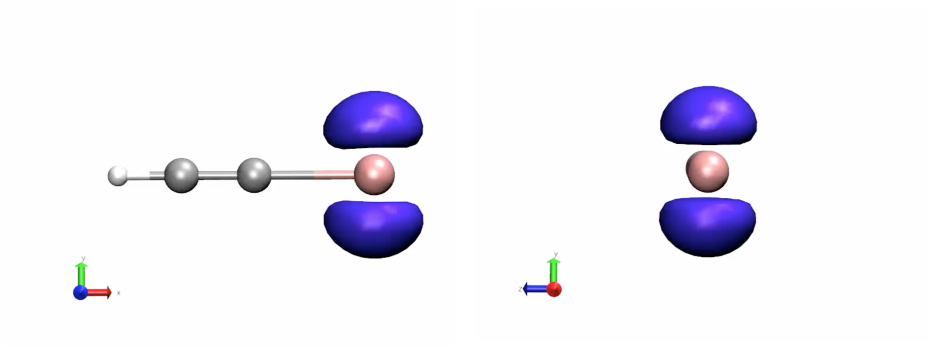
$$M_I \ddot{\mathbf{R}}_I = -\nabla_I E[\rho(\boldsymbol{r}, t)]$$

Ehrenfest dynamics - Example

Ehrenfest dynamics

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

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



Ehrenfest dynamics and mixing of electronic states

Ehrenfest dynamics

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

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

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

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

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

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

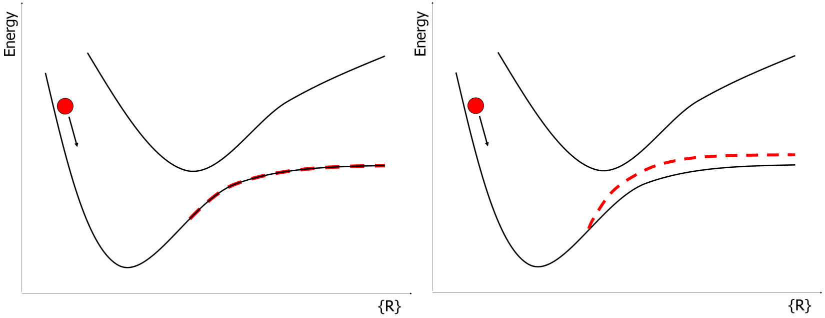
$$M_I\ddot{\mathbf{R}}_I = -\nabla_I\sum_{k=0}^{\infty}|c_k(t)|^2 E_k^{el}$$

where

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

Thus we incorporate directly nonadiabatic effects.

Ehrenfest dynamics: the mean-field potential



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

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

Tarjectory-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
  [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: $\Psi(\boldsymbol{r}, \boldsymbol{R}, t) = \Omega(\boldsymbol{R}, t)\Phi(\boldsymbol{r}, t)$.

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

Born-Oppenheimer approximation

$$\Psi(\boldsymbol{r}, \boldsymbol{R}, t) \xrightarrow[\text{Huang}]{\text{Born-}} \sum_{j}^{\infty} \Phi_j(\boldsymbol{r}; \boldsymbol{R}) \Omega_j(\boldsymbol{R}, t)$$

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

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

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

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

Born-Oppenheimer approximation

$$\Psi(\boldsymbol{r},\boldsymbol{R},t) \xrightarrow[\text{Huang}]{\text{Born-}} \sum_{j}^{\infty} \Phi_j(\boldsymbol{r};\boldsymbol{R})\Omega_j(\boldsymbol{R},t)$$

Electrons are *static*. Use your favourite electronic structure method.

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

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

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

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

Born-Oppenheimer approximation

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

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

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

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

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

Born-Oppenheimer approximation

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

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

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

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

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

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

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

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

$A_k(\boldsymbol{R},t)$ represents an amplitude and $S_k(\boldsymbol{R},t)/\hbar$ 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

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

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

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).

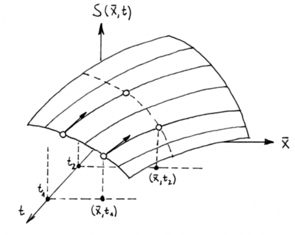
We have now a time-dependent equation for both the amplitude and the phase.
Since we are in the adiabatic case there is only one PES and the second equation becomes trivially a diffusion continuity equation.

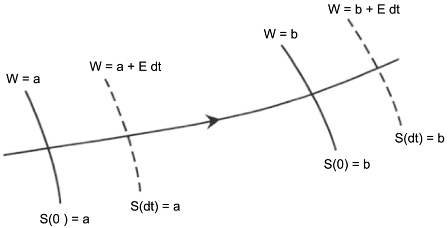
The nuclear dynamics is derived from the real part ($\frac{\partial S_k}{\partial t}$). This equation has again the form of a *classical* Hamilton-Jacobi equation.

Born-Oppenheimer approximation: the nuclear trajectories

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

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





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

Born-Oppenheimer approximation: the nuclear trajectories

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

The classical limit is obtained by taking[1]: $\hbar \to 0$

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

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

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

The momentum of a particle I is related to

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

---

[1] Caution! This classical limit is subject to controversy...

Born-Oppenheimer approximation: the nuclear trajectories

Therefore, taking the gradient,

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

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

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

In Summary:

Adiabatic BO MD

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

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

Mean-field vs. BO MD (adiabatic case)

Ehrenfest dynamics

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

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

Explicit time dependence of the electronic wavefunction.

Born-Oppenheimer dynamics

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

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

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

Mean-field vs. BO MD (adiabatic case)

Method	Born-Oppenheimer MD	Ehrenfest MD
	adiabatic MD (one PES)	nonadiabatic MD (mean-field)
	Efficient propagation of the nuclei	Get the "real" dynamics of the electrons
	Adiabatic nuclear propagation	Propagation of nuclei & electrons
	δt ∼10-20 a.u. (0.25-0.5 fs)	δt ∼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 $\hbar \to 0$?)

Tarjectory-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)

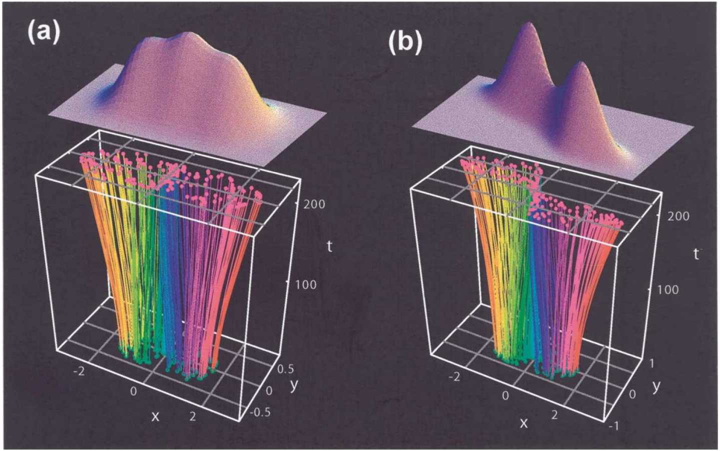
- Nonadiabatic Trajectory Surface Hopping (TSH) dynamics
  [ROKS: N. L. Doltsinis, D. Marx, *PRL*, **88**, 166402 (2002)]
  C. F. Craig, W. R. Duncan, and O. V. Prezhdo, *PRL*, **95**, 163001 (2005)
  E. Tapavicza, I. Tavernelli, U. Rothlisberger, *PRL*, **98**, 023001 (2007)

- Time dependent potential energy surface approach

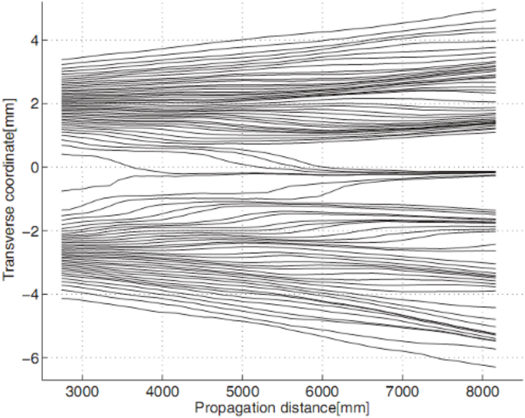
  based on the exact decomposition: $\Psi(\boldsymbol{r}, \boldsymbol{R}, t) = \Omega(\boldsymbol{R}, t)\Phi(\boldsymbol{r}, t)$.

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

Nonadiabatic dynamics: Multi-trajectory solutions



Nonadiabatic Bohmian dynamics



Pioneers in quantum hydrodynamics: D. Bohm, P. R. Holland, R. E. Wyatt, and many others.

NABDY: “exact” trajectory-based nonadiabatic dynamics

Using

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

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

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

and

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

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

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 $\nabla_\beta S_j(\boldsymbol{R}, t) = \boldsymbol{P}^j_\beta$)

$$M_\beta \frac{d^2 \boldsymbol{R}_\beta}{(dt^j)^2} = -\nabla_\beta \left[E^j_{el}(\boldsymbol{R}) + \mathcal{Q}_j(\boldsymbol{R}, t) + \sum\nolimits_i D_{ij}(\boldsymbol{R}, t) \right]$$

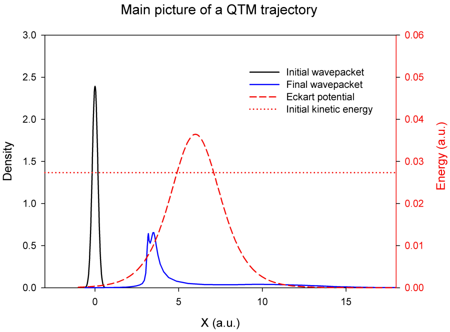
where $\mathcal{Q}_j(\boldsymbol{R}, t)$ is the quantum potential responsible for all coherence/decoherence "intrasurface" QM effects, and $\mathcal{D}_j(\boldsymbol{R}, t)$ is the *nonadiabatic* potential responsible for the amlpitude transfer among the different PESs.

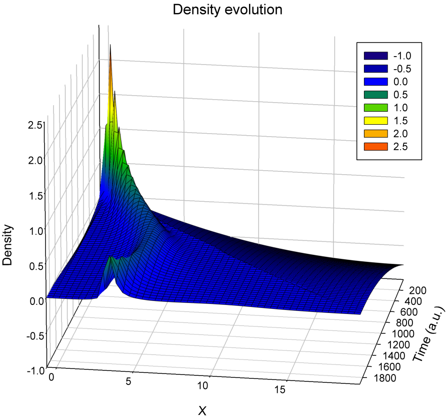
For more informations see:
B. Curchod, IT, U. Rothlisberger, *PCCP*, **13**, 3231 – 3236 (2011)

NABDY limitations

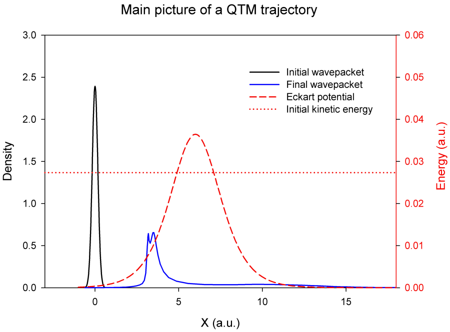
- Mainly numerical challenges
- Instabilities induced by the quantum potential
- Compute derivatives in the $3N$ dimensional($\mathbb{R}^{3N}$) configuration space

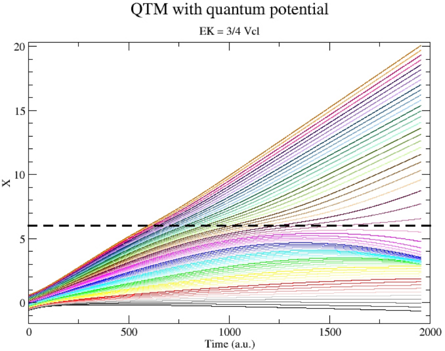
Gaussian wavepacket on an Eckart potential ($E_k = 3/4V$)

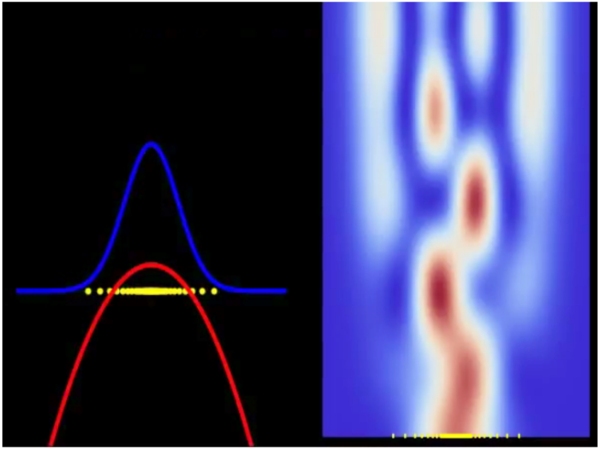




Gaussian wavepacket on an Eckart potential ($E_k = 3/4V$)







Tarjectory-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
  [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)

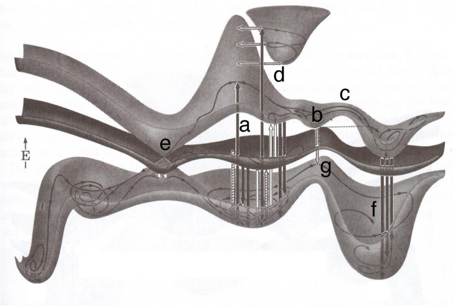
- Time dependent potential energy surface approach

  based on the exact decomposition: $\Psi(\boldsymbol{r}, \boldsymbol{R}, t) = \Omega(\boldsymbol{R}, t)\Phi(\boldsymbol{r}, t)$.

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

Applications in Photochemistry and Photophysics

Trajectory-based solutions of the “exact” nonadiabatic equations are still impractical.



Approximate solutions are available. Among the most popular is

Trajectory Surface Hopping (TSH)

The trajectory surface hopping dynamics (1)

TSH is a mixed quantum-classical theory

The classical component

- ensemble of classical trajectories following

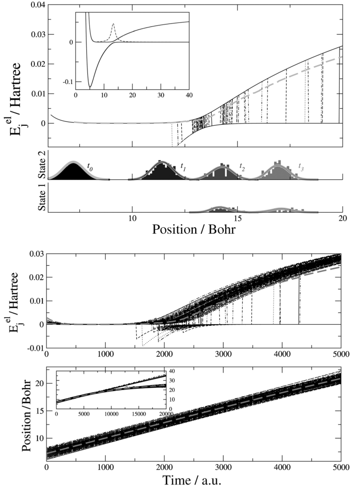
  Newton's equation of motion

$$\frac{d\boldsymbol{P}_j^{\beta}(t)}{dt^j} = -\nabla_{\beta} E_j^{el}(\boldsymbol{R}(t))$$

- trajectories are independent (ITA).

  No coherence
- density of trajectories $({}^{CL}\rho_j(\boldsymbol{R}(t), t))$ at each time step reproduces a 'classical distribution' on the different PESs.

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



The trajectory surface hopping dynamics (2)

The quantum component

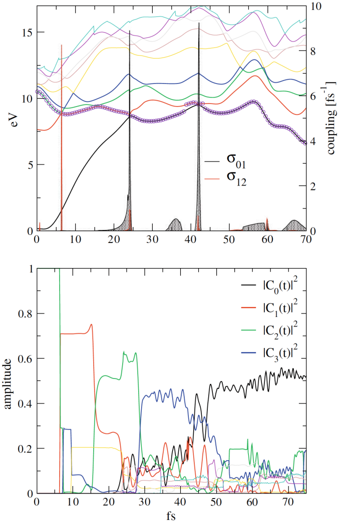
- To each trajectory there are quantum amplitudes ${}^{QM}C_j(\boldsymbol{R}(t),t)$ associated to each PES: $\{C_0(\boldsymbol{R}(t),t), C_1(\boldsymbol{R}(t),t), C_2(\boldsymbol{R}(t),t),\ldots\}$.
- They evolve according to

$$i\hbar\frac{dC_j}{dt} = C_j E_j^{el} - i\hbar\sum_i\left(\boldsymbol{d}_{ji}\cdot\dot{\boldsymbol{R}}C_i\right)$$

- ${}^{QM}C_j(\boldsymbol{R}(t),t)$ determine the surface hopping probabilities,

$$p^{[\alpha]}_{i\leftarrow j}(\Delta t) = -2\int_t^{t+\Delta t}\frac{\Re[C_i^{[\alpha]}(\tau)C_j^{[\alpha]*}(\tau)\dot{\boldsymbol{R}}(\tau)\cdot\boldsymbol{d}_{ij}(\boldsymbol{R}(\tau))]}{C_j^{[\alpha]}(\tau)C_j^{[\alpha]*}(\tau)}\,d\tau$$

so that: ${}^{QM}C_j^2(\boldsymbol{R}(t),t) \equiv {}^{CL}\rho_j(\boldsymbol{R}(t),t)$.



Tully's surface hopping - Summary

Tully's surface hopping

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

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

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

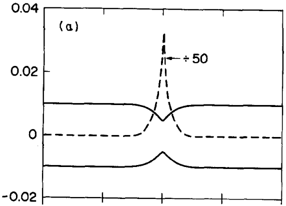
Some warnings:

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.

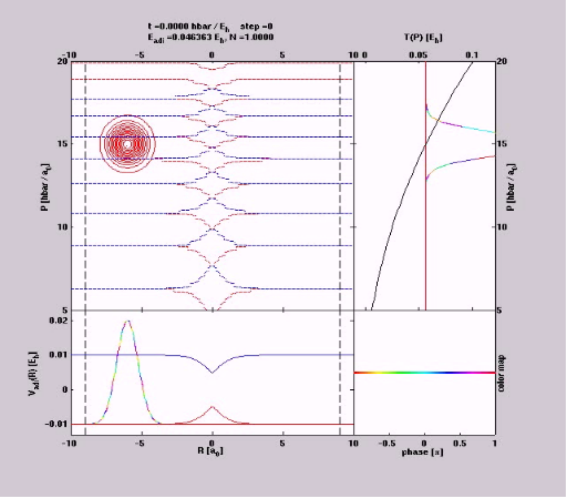
For more details (and warnings) about Tully's surface hopping, see G. Granucci and M. Persico, J Chem Phys 126, 134114 (2007).

Tully's surface hopping - Examples

1D systems

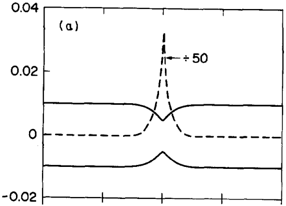


J.C. Tully, J. Chem. Phys. (1990), 93, 1061

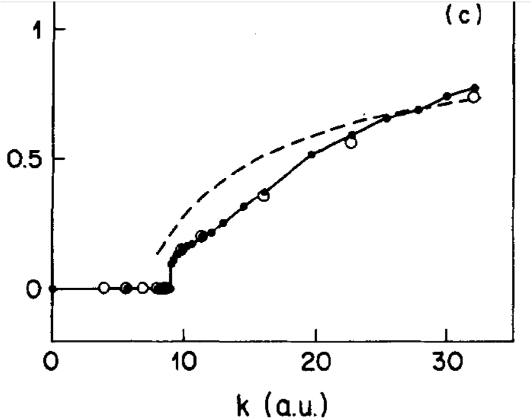


Tully's surface hopping - Examples

1D systems



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

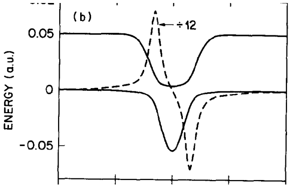


On the right: population of the upper state (k=mom)

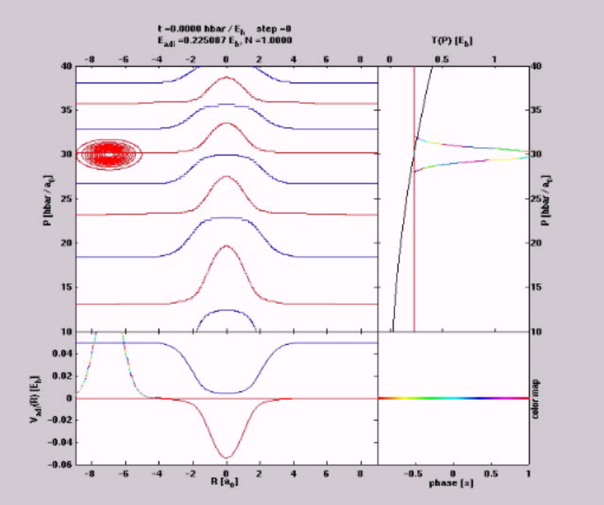
- ○ exact
- ● TSH
- – Landau-Zener

Tully's surface hopping - Examples

1D systems

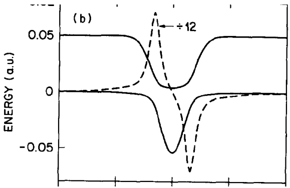


J.C. Tully, J. Chem. Phys. (1990), 93, 1061



Tully's surface hopping - Examples

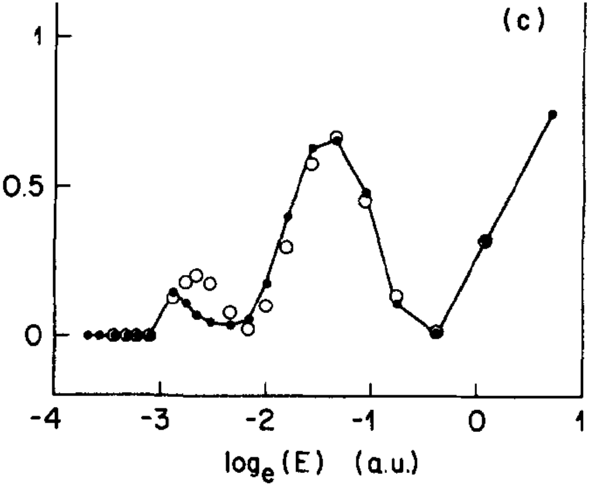
1D systems



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

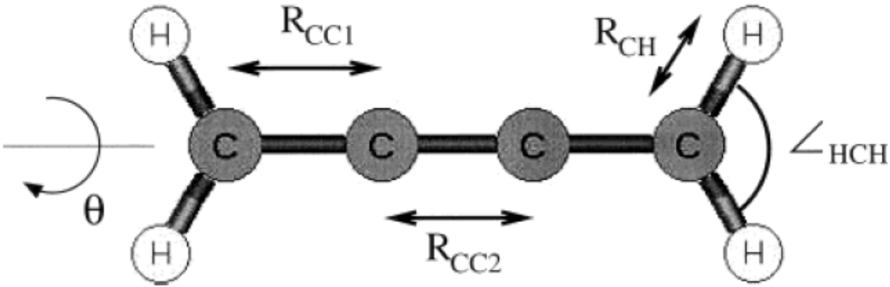
On the right: population of the upper state

- ○ exact
- ● TSH



Comparison with wavepacket dynamics

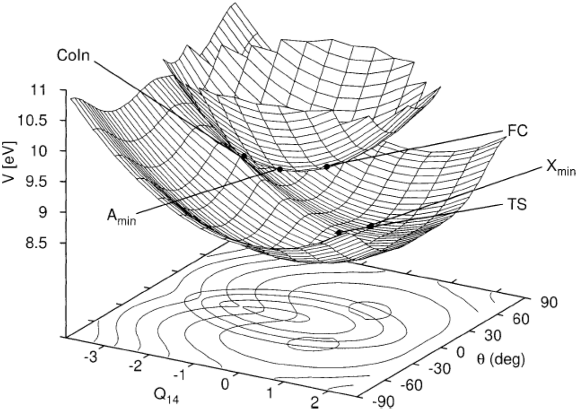
Butatriene molecule: dynamics of the radical cation in the first excited state.



JPCA,107,621 (2003)

Comparison with wavepacket dynamics

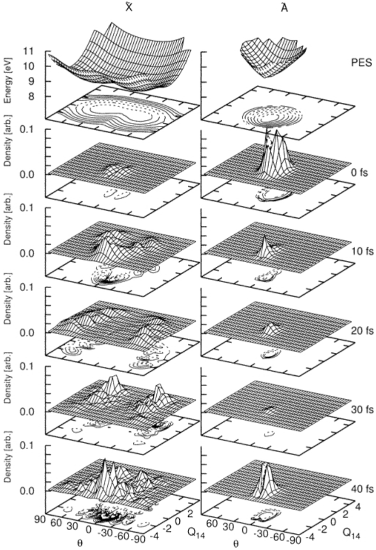
Butatriene molecule: dynamics of the radical cation in the first excited state.



JPCA,107,621 (2003)

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

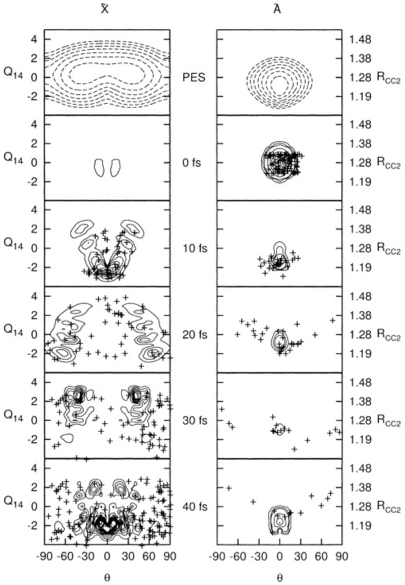
Comparison with wavepacket dynamics



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

JPCA,107,621 (2003)

Comparison with wavepacket dynamics



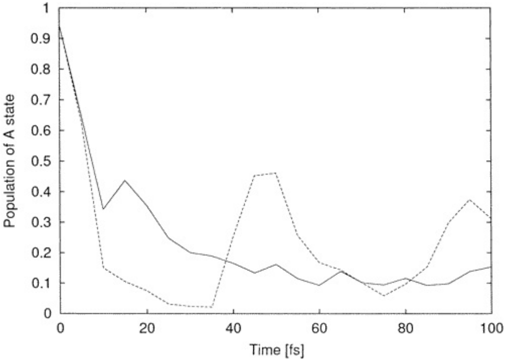
On-the-fly dynamics with 80 trajectories (crosses).

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)

Comparison with wavepacket dynamics

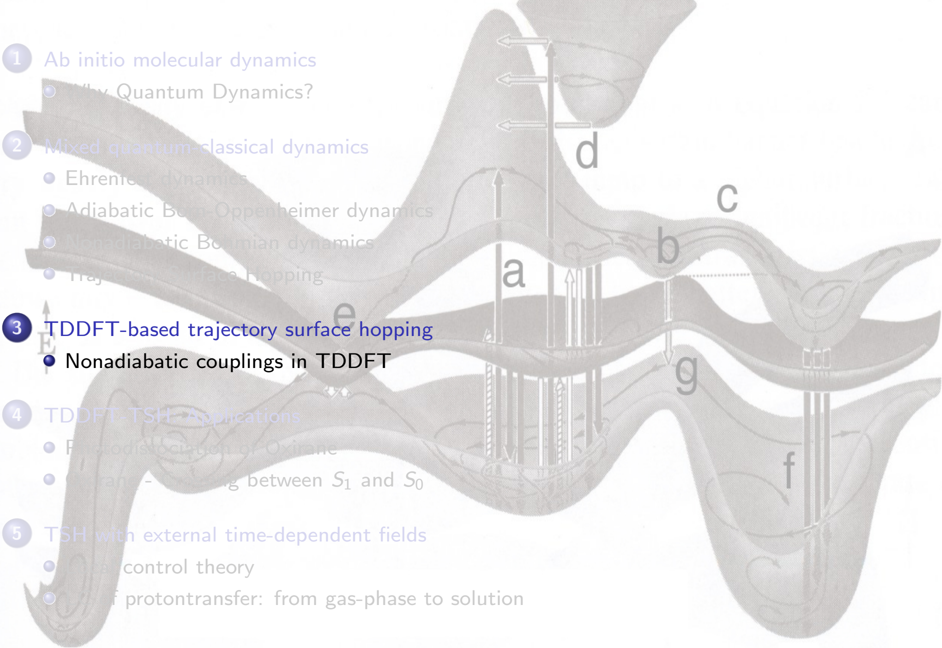


On-the-fly dynamics with 80 trajectories.

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)



1. Ab initio molecular dynamics
   - Why Quantum Dynamics?
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 theory
   - LC of protontransfer: from gas-phase to solution

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

Tully's surface hopping

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

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

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

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, ...

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

Tully's surface hopping

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

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

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

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, ...

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

Tully's surface hopping

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

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

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

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, ...

Nonadiabatic couplings with LR-TDDFT?

Nonadiabatic coupling vectors are defined in terms of electronic wavefunctions:

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

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).

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

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

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

---

[2] 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).

The density response SOS formula

In TDDFT the density response $\chi(\omega)$ is

$$\chi(\omega) = \mathbb{S}^{-1/2}(\omega^2\mathbb{I} - \Omega(\omega))^{-1}\mathbb{S}^{-1/2}$$

with

$$\Omega_{ij\sigma,kl\tau} = \delta_{\sigma\tau}\delta_{ik}\delta_{jl}(\epsilon_{l\tau} - \epsilon_{k\sigma})^2 + 2\sqrt{(f_{i\sigma} - f_{j\sigma})(\epsilon_{j\sigma} - \epsilon_{i\sigma})}K_{ij\sigma,kl\tau}\sqrt{(f_{k\tau} - f_{l\tau})(\epsilon_{l\tau} - \epsilon_{k\tau})}$$

Using the spectral representation of the $(\omega^2\mathbb{I} - \Omega(\omega))^{-1}$, we can write

$$(\omega^2\mathbb{I} - \Omega(\omega))^{-1} = \sum_n \frac{\boldsymbol{Z}_n\boldsymbol{Z}_n^\dagger}{\omega_n^2 - \omega^2}$$

where $\mathbf{Z}_n$ are the TDDFT eigenvectors of the pseudoeigenvalue equation, $(S_{ij\sigma,kl\tau} = \frac{\delta_{ik}\delta_{jl}\delta_{\sigma\tau}}{(f_{k\sigma}-f_{l\sigma})(\epsilon_{l\sigma}-\epsilon_{k\sigma})})$

$$\mathbf{\Omega}\mathbf{Z}_n = \omega_{0n}^2\mathbf{Z}_n \, ,$$

Therefore [3]

$$\chi(\omega) = \sum_n \frac{\mathbb{S}^{-1/2}\boldsymbol{Z}_n\boldsymbol{Z}_n^\dagger\mathbb{S}^{-1/2}}{\omega_n^2 - \omega^2}$$

and finally the perturbation of any observable $(\delta\mathcal{O}(\omega) = \sum_{ij\sigma} o_{ij\sigma}\delta P_{ij\sigma})$

$$\delta\mathcal{O}^{TDDFT}(\omega) = \sum_n \sum_{ij\sigma,kl\tau} o_{ij\sigma} \frac{(\mathbb{S}^{-1/2}\boldsymbol{Z}_n)_{ik\sigma}(\boldsymbol{Z}_n^\dagger\mathbb{S}^{-1/2})_{kl\tau}}{\omega_n^2 - \omega^2} v'_{kl\tau}E(\omega) \, .$$

---

[3] M. E. Casida, in Recent Advances in Density Functional Methods, edited by D. P. Chong, World Scientific, Singapore (1995), JCP, 130, 124107 (2007)

In MBPT the density response $\chi(\omega)$ is

$$\delta\mathcal{O}^{MBPT}(\omega) = \sum_n \frac{2\omega_{i0}\langle\Psi_0|\hat{\mathcal{O}}|\Psi_n\rangle\langle\Psi_n|\hat{v}'E(\omega)|\Psi_0\rangle}{\omega_{n0}^2 - \omega^2}$$

Equating $\delta\mathcal{O}^{TDDFT}(\omega)$ with $\delta\mathcal{O}^{MBPT}(\omega)$ residue-by-residue,

$$\langle\Psi_0|\hat{\mathcal{O}}|\Psi_n\rangle = \sum_{ij\sigma}^{(f_{i\sigma}-f_{j\sigma})>0} \frac{1}{\sqrt{\omega_n}} o_{ij\sigma}(\mathbb{S}^{-1/2}\boldsymbol{Z}_n)_{ij\sigma}$$

For any one-body operator, $\hat{\mathcal{O}}$, a mapping between MBPT and TDDFT quantities gives (for the moment, we only consider transitions from the ground state Ψ_0)

$$\mathbf{O}^\dagger\mathbb{S}^{-1/2}\mathbf{Z}_n = \omega_{0n}^{1/2}\langle\Psi_0|\hat{\mathcal{O}}|\Psi_n\rangle$$

where the operator $\hat{\mathcal{O}} = \sum_{ia\sigma} o_{ia\sigma}\hat{a}_{i\sigma}^\dagger\hat{a}_{a\sigma}$ has components $o_{ia\sigma} = \langle\phi_{i\sigma}|\hat{\mathcal{O}}|\psi_{a\sigma}\rangle$ [4] with $\omega_{0n} = E_n - E_0$. All matrices and vectors are given in the basis of KS orbitals $\{\phi_{i\sigma}\}$ with corresponding occupations $f_{i\sigma}$ and orbital energies $\epsilon_{i\sigma}$.

---

[4] $\sum_{ia\sigma}$ stands for $\sum_{i=1}^N\sum_{a=1}^\infty\sum_{\sigma\in\{\alpha,\beta\}}$.

The auxiliary wavefunction

For practical purposes we introduce the auxiliary linear-response many-electron wavefunctions [5] as a linear combination of singly excited Slater determinants

$$\tilde{\Phi}_k[\{\phi.\}] = \sum_{ia\sigma} c^k_{ia\sigma}\, \hat{a}^\dagger_{a\sigma}\hat{a}_{i\sigma}\tilde{\Phi}_0[\{\phi.\}]\,,$$

with

$$c^k_{ia\sigma} \equiv \sqrt{\frac{S^{-1}_{ia\sigma}}{\omega_{0k}}}\, e^k_{ia\sigma}$$

where $\tilde{\Phi}_0[\{\phi.\}]$ is the Slater determinant of all occupied KS orbitals $\{\phi_{i\sigma}\}_{i=1}^N$, which, at a turn, are promoted into a virtual (unoccupied) orbitals, $\psi_{a\sigma}$.

We therefore have (in linear response!)

$$\langle \Psi_0|\hat{\mathcal{O}}|\Psi_n\rangle = \langle \tilde{\Phi}_0|\hat{\mathcal{O}}|\tilde{\Phi}_n\rangle$$

---

[5] JCP, 130, 124107 (2007), JCP, 131, 196101 (2009).

Nonadiabatic couplings

- The *nonadiabatic coupling elements* at the mid step $t + \delta t/2$ of a LR-TDDFT AIMD can therefore be calculated as

$$\dot{\boldsymbol{R}} \cdot \boldsymbol{d}_{0k}|_{t+\delta t/2}[\{\phi_\cdot\}] = \left\langle \tilde{\Phi}_0(\boldsymbol{r}; \boldsymbol{R}(t)) \,\middle|\, \nabla_{\boldsymbol{R}} \,\middle|\, \tilde{\Phi}_k(\boldsymbol{r}; \boldsymbol{R}(t)) \right\rangle \cdot \dot{\boldsymbol{R}} = \left\langle \tilde{\Phi}_0(\boldsymbol{r}; \boldsymbol{R}(t)) \,\middle|\, \frac{\partial}{\partial t} \,\middle|\, \tilde{\Phi}_k(\mathbf{r}; \boldsymbol{R}(t)) \right\rangle$$
$$\simeq \frac{1}{2\delta t}\left[\langle \tilde{\Phi}_0(\boldsymbol{r}; \boldsymbol{R}(t)) | \tilde{\Phi}_k(\boldsymbol{r}; \boldsymbol{R}(t+\delta t))\rangle - \langle \tilde{\Phi}_0(\boldsymbol{r}; \boldsymbol{R}(t+\delta t)) | \tilde{\Phi}_k(\boldsymbol{r}; \boldsymbol{R}(t))\rangle\right]$$

- The *nonadiabatic coupling vectors* between **pairs of excites states** (second order response)

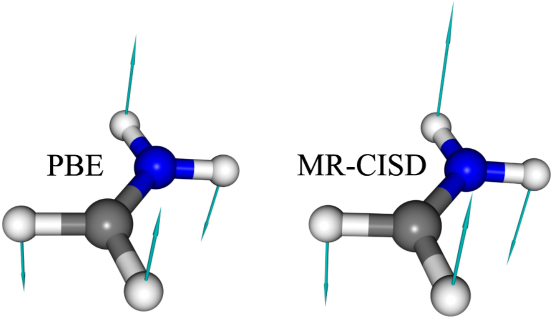
$$\mathbf{d}_{kj}[\{\phi_\cdot\}] = \frac{\langle \tilde{\Phi}_k(\boldsymbol{R}) | \nabla_{\boldsymbol{R}} \hat{\mathcal{H}}_{el} | \tilde{\Phi}_j(\boldsymbol{R})\rangle}{E_j(\boldsymbol{R}) - E_k(\boldsymbol{R})}$$

  - Auxiliary many-electron wavefunctions give exact couplings between ground state and any (singly) excited state.
  - Auxiliary many-electron wavefunctions give *high quality* couplings between pairs of (singly) excited states ("exact" in the TDA and up to $\mathcal{O}(\delta\rho^3)$ in full response).

Nonadiabatic couplings - examples

As always, the quality of the nonadiabatic couplings will depend on the *xc*-functional used...

$$\mathbf{d}_{kj}[\{\phi_\cdot\}] = \langle \tilde{\Phi}_k(\mathbf{R}) | \nabla_{\mathbf{R}} | \tilde{\Phi}_j(\mathbf{R}) \rangle$$

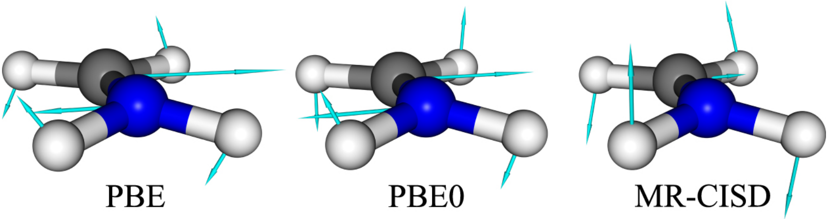


Protonated formaldimine: nonadiabatic coupling vectors $\mathbf{d}_{01}$ with LR-TDDFT/TDA.

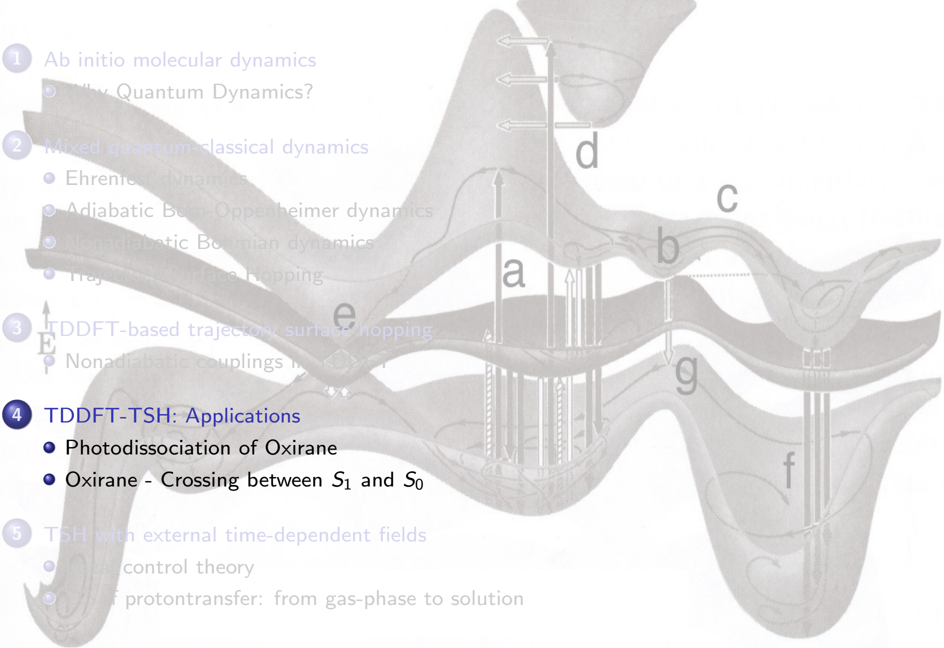
Nonadiabatic couplings - examples

As always, the quality of the nonadiabatic couplings will depend on the *xc*-functional used...

$$\mathbf{d}_{kj}[\{\phi.\}] = \langle \tilde{\Phi}_k(\mathbf{R}) | \nabla_{\mathbf{R}} | \tilde{\Phi}_j(\mathbf{R}) \rangle$$



Protonated formaldimine: nonadiabatic coupling vectors $\mathbf{d}_{12}$ with LR-TDDFT/TDA.



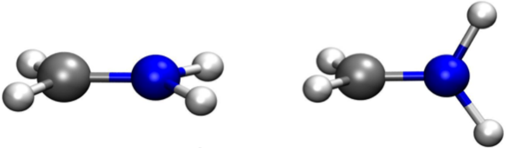
1. Ab initio molecular dynamics
   - Why Quantum Dynamics?
2. Mixed quantum-classical dynamics
   - Ehrenfest dynamics
   - Adiabatic Born-Oppenheimer dynamics
   - Nonadiabatic Bohmian dynamics
   - Trajectory Surface Hopping
3. TDDFT-based trajectory surface hopping
   - Nonadiabatic couplings in TDDFT
4. TDDFT-TSH: Applications
   - Photodissociation of Oxirane
   - Oxirane - Crossing between S_1 and S_0
5. TSH with external time-dependent fields
   - Optimal control theory
   - Control of protontransfer: from gas-phase to solution

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)

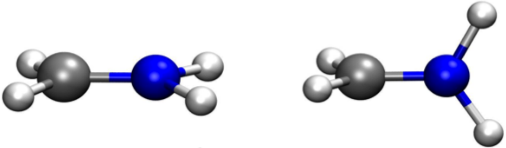


$CH_2NH_2^+$

Protonated formaldimine

Computational details

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

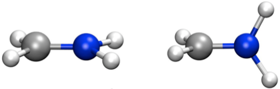


$CH_2NH_2^+$

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

Protonated formaldimine

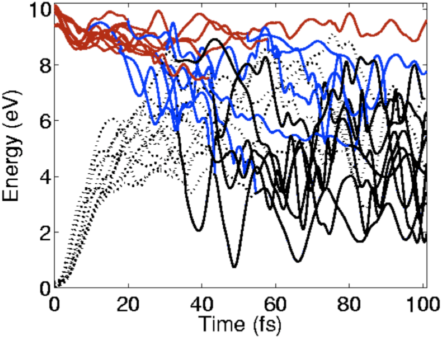
Protonated formaldimine as a model compound for the study of the isomerization of retinal.



$CH_2\,NH_2^+$

Photo-excitation promotes the system mainly into S_2.

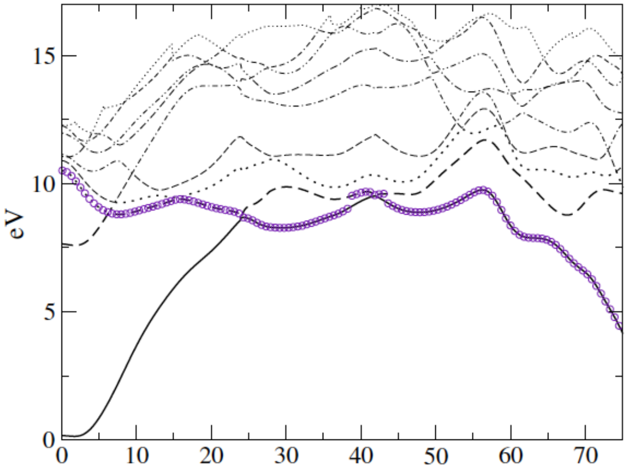
Relaxation involves at least 3 states:
S_0 (GS), S_1 and S_2.



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

Protonated formaldimine

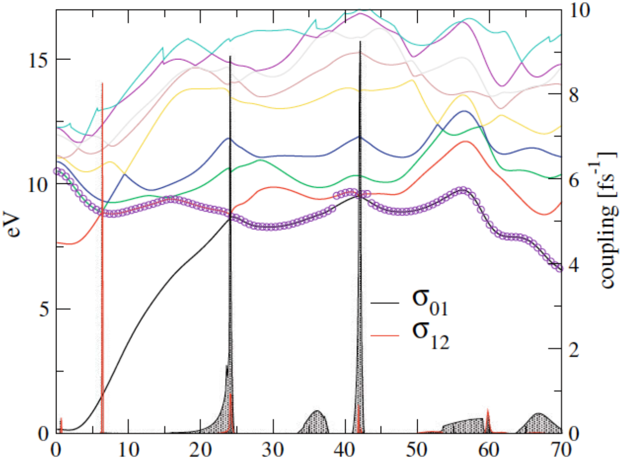
Typical trajectory



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

Protonated formaldimine

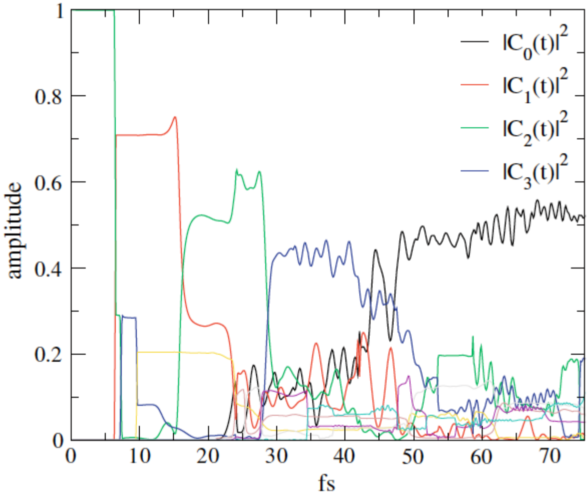
Nonadiabatic couplings $\sigma_{kj} = \dot{\boldsymbol{R}}^{\alpha} \cdot \boldsymbol{d}^{\alpha}_{kj}$



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

Protonated formaldimine

States population

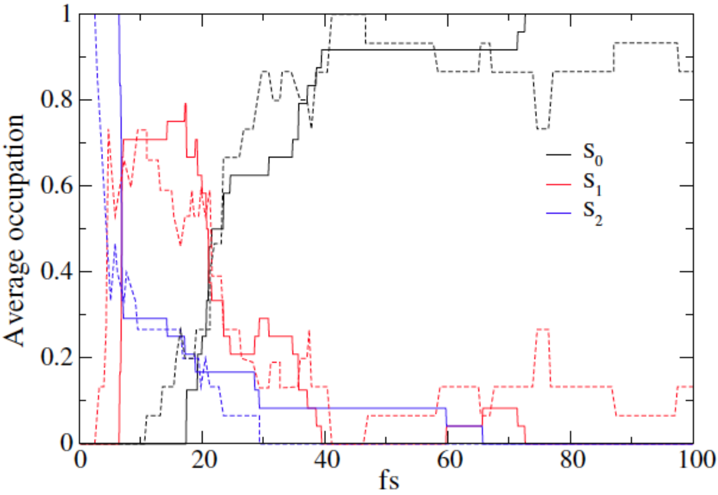


PRL, 98, 023001 (2007); THEOCHEM, 914, 22 (2009).

Protonated formaldimine

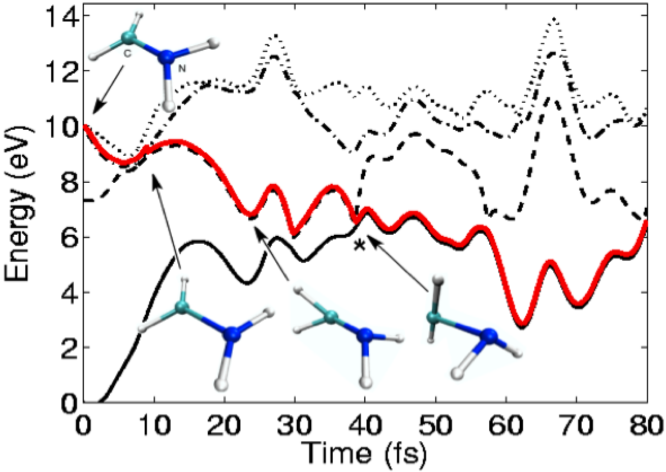
States population - **Average over many trajectories**.

Dashed line = CASSCF result.



Protonated formaldimine

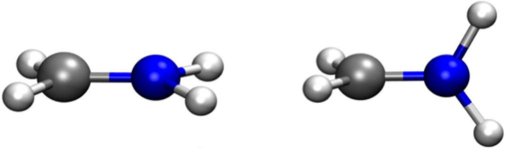
Geometrical modifications



Protonated formaldimine

Comparison with experiment and model calculations

- In addition to the isomerization channel, intra-molecular proton transfer reactions was observed (formation of CH_3NH^+).
- 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.



$CH_2NH_2^+$

Oxirane

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

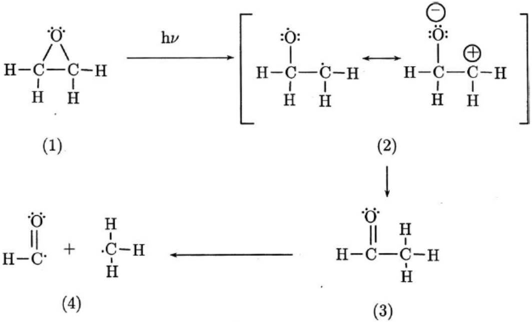


Figure: Mechanism proposed by Gomer and Noyes

Oxirane

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

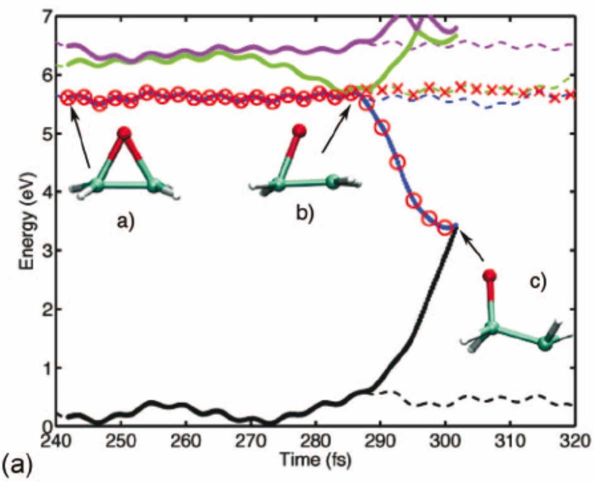
Computational details

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

JCP, 129, 124108 (2009).

Oxirane

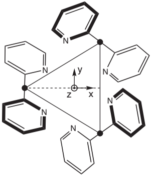
Oxirane has interesting non-radiative decay channels, during which ring opening and dissociation can occur.

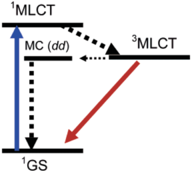


JCP, 129, 124108 (2009).

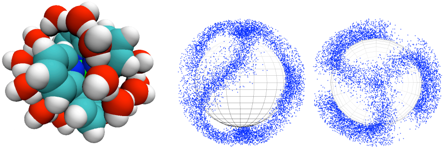
The photophysics of solvated Ruthenium(II) tris-bipyridine

$[Ru(bpy)_3)]^{2+}$ dye: photophysics



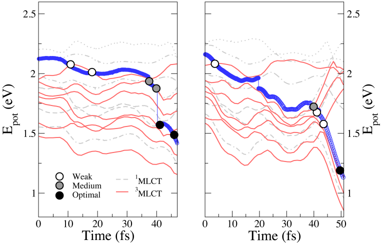


$[Ru(bpy)_3)]^{2+}$ dye: Solvent structure

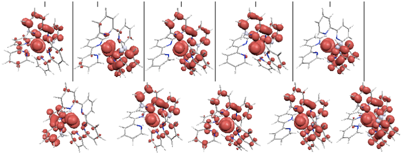


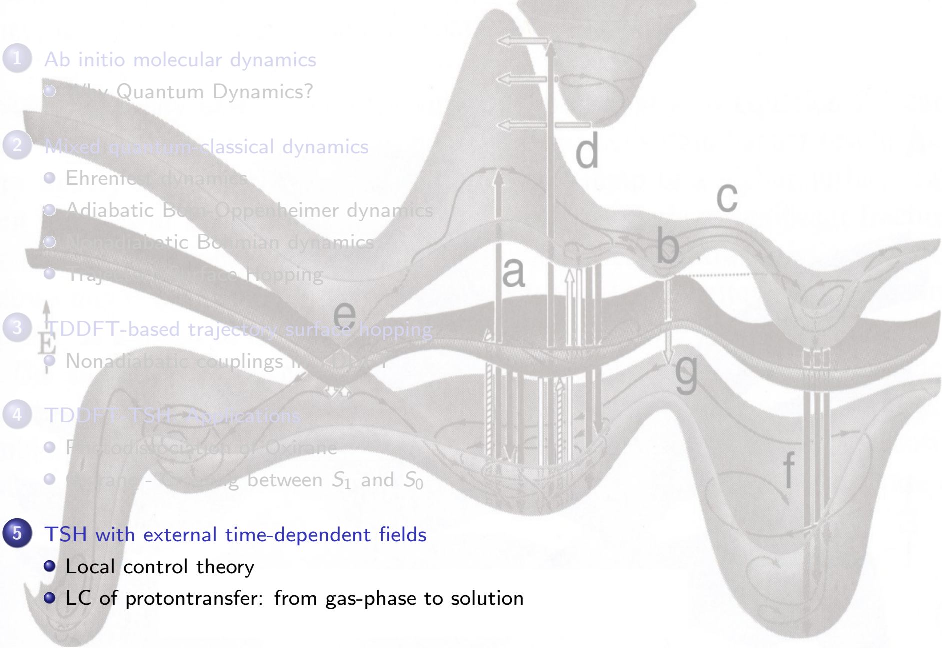
[M.E. Moret, I.T., U. Rothlisberger, *JPC B*, **113**, 7737 (2009); IT, B. Curchod, U. Rothlisberger, *Chem.Phys.*, **391**, 101 (2011)]

$[Ru(bpy)_3)]^{2+}$ dye: Singlet state dynamics



$[Ru(bpy)_3)]^{2+}$ dye: triplet state dynamics

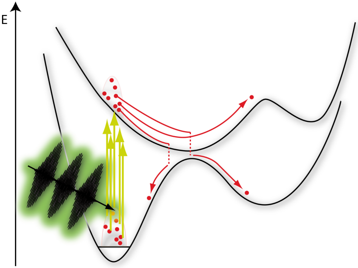




1. Ab initio molecular dynamics
   - Why Quantum Dynamics?
2. Mixed quantum-classical dynamics
   - Ehrenfest dynamics
   - Adiabatic Born-Oppenheimer dynamics
   - Nonadiabatic Bohmian dynamics
   - Trajectory Surface Hopping
3. TDDFT-based trajectory surface hopping
   - Nonadiabatic couplings in TDDFT
4. TDDFT-TSH: Applications
   - Photodissociation of Oxirane
   - Oxirane - Crossing between S_1 and S_0
5. TSH with external time-dependent fields
   - Local control theory
   - LC of protontransfer: from gas-phase to solution

TSH with external time-dependent fields

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



Startegy

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)

TSH with external time-dependent fields

Short summary of the theory

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

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

where $\boldsymbol{A}(\boldsymbol{r}, t)$ is the (classical) vector potential of the electromagnetic field, $\hat{\boldsymbol{p}}_i$ 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 TDCDFT.

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

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

$$i\hbar\dot{C}_J^\alpha(t) = \sum_I C_I^\alpha(t)(H_{JI} - i\hbar\dot{\mathbf{R}}^\alpha \cdot \mathbf{d}_{JI}^\alpha + i\omega_{JI}\frac{A_0}{c}\boldsymbol{\epsilon}^\lambda \cdot \boldsymbol{\mu}_{JI}^\alpha e^{-i\omega t})$$

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 $\mathbf{A}_0(t) = A_0\boldsymbol{\epsilon}^\lambda e^{-i\omega t}$ 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.

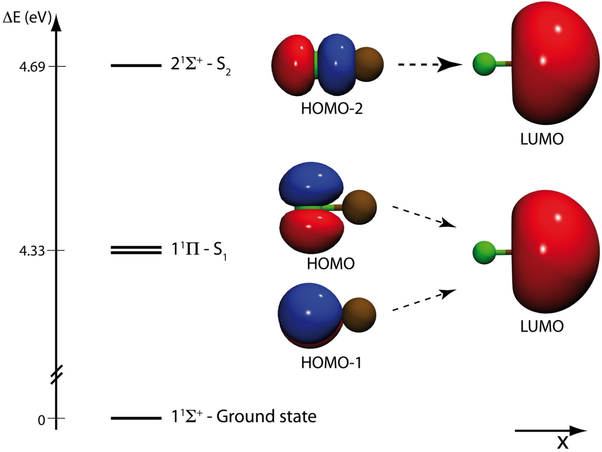
IT, B. Curchod, U. Rothlisberger, Phys. Rec. A **81**, 052508 (2010)

Effect of an electromagnetic field - Lithium fluoride

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

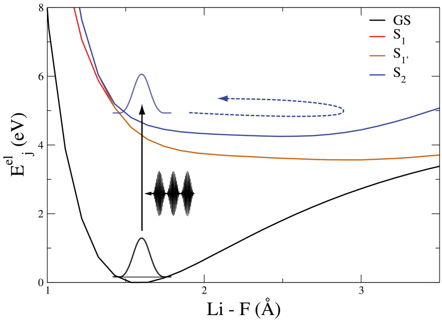
Electronic structure of LiF

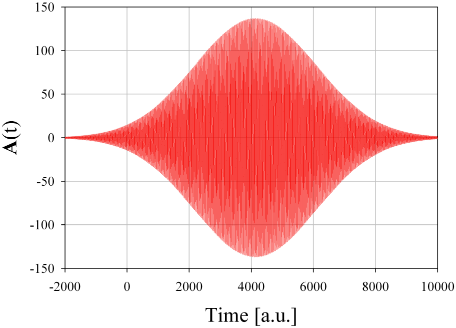
- Ground state - Σ symmetry (GS) .
- First excited state (doubly degenerate) - Π symmetry (S_1) .
- Second excited state - Σ symmetry (S_2) .
- Avoided crossing between GS and S_2



Effect of an electromagnetic field - Lithium fluoride

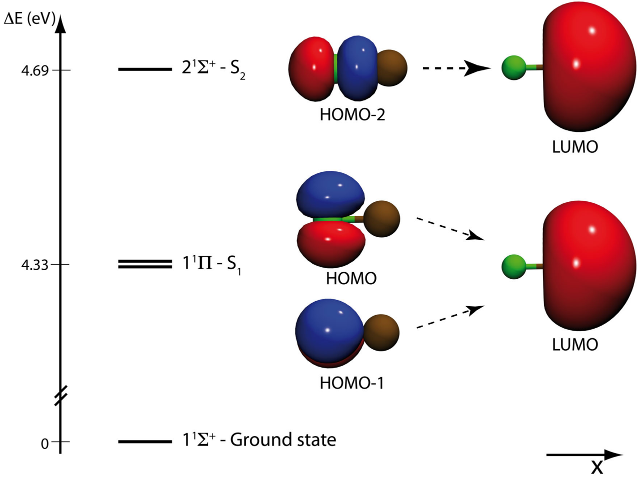
Pulse: $\boldsymbol{A}(t) = -A_0 \boldsymbol{\epsilon}^{\lambda} \exp\left(-\frac{(t-t_0)^2}{T^2}\right) \sin(\omega t)$





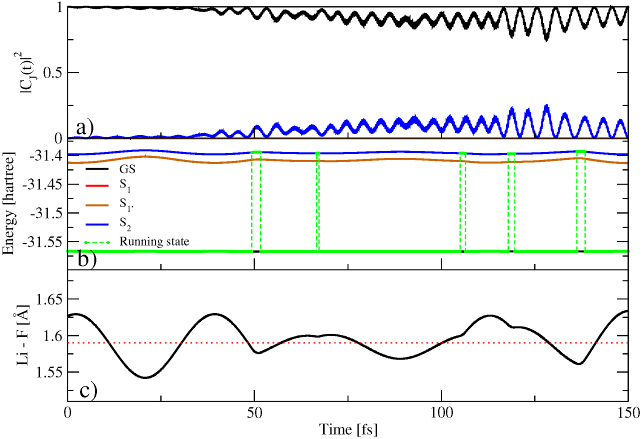
Effect of an electromagnetic field - Lithium fluoride

x-polarized pulse: $\epsilon^{\lambda} = (1, 0, 0)$



Effect of an electromagnetic field - Lithium fluoride

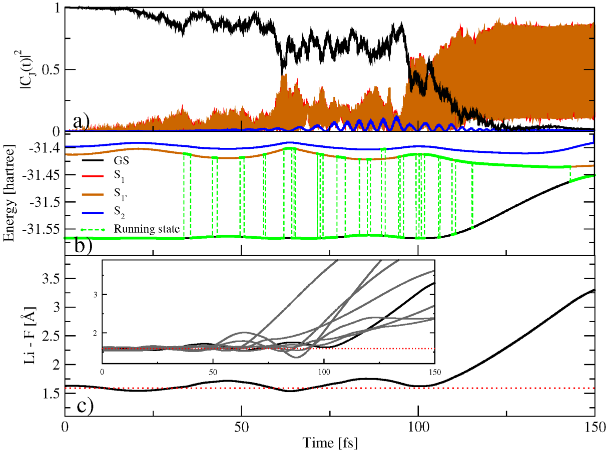
$\epsilon^\lambda = (1, 0, 0)$



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

Effect of an electromagnetic field - Lithium fluoride

$\boldsymbol{\epsilon}^{\lambda} = \frac{1}{\sqrt{3}}(1, 1, 1)$



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

Local control theory

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

Using the TSH for the total molecular wavefunction

$$\Psi^{\alpha}(\boldsymbol{r},\boldsymbol{R},t)=\sum_{J}^{\infty}C_J^{\alpha}(t)\Phi_J(\boldsymbol{r};\boldsymbol{R})$$

for a given trajectory α, the population time evolution simplifies to

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

It is now evident that choosing a field of the form

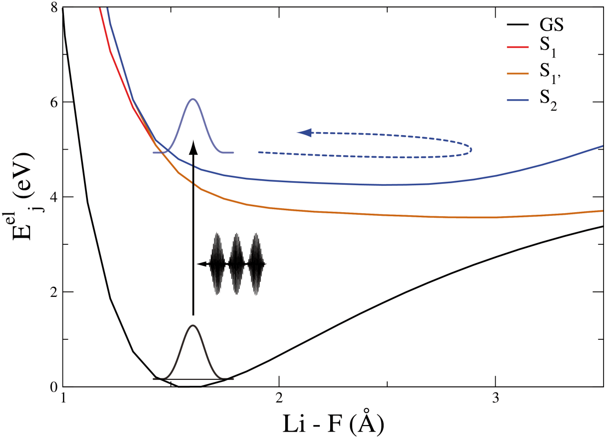
$$\boldsymbol{E}(t)=-\lambda\sum_J\Im\left[C_I^{\alpha}(t)C_J^{\alpha*}\boldsymbol{\mu}_{IJ})\right]$$

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).

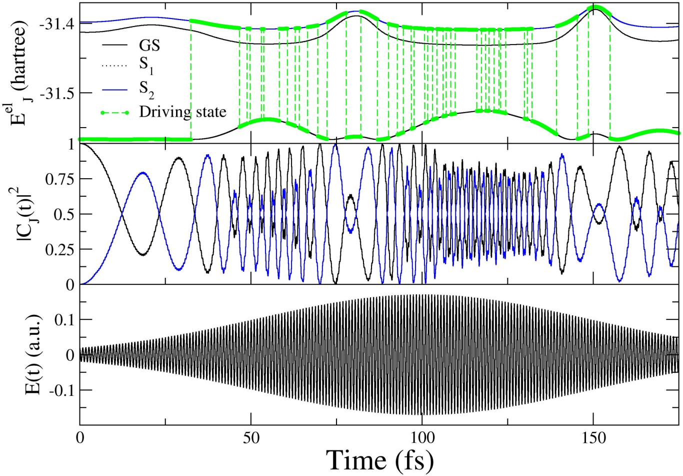
B.F.E Curchod, T. Penfold, U. Rothlisberger, IT, *PRA*, **84**, 042507 (2011)

Application: Photoexcitation of LiF in the bound state S_2

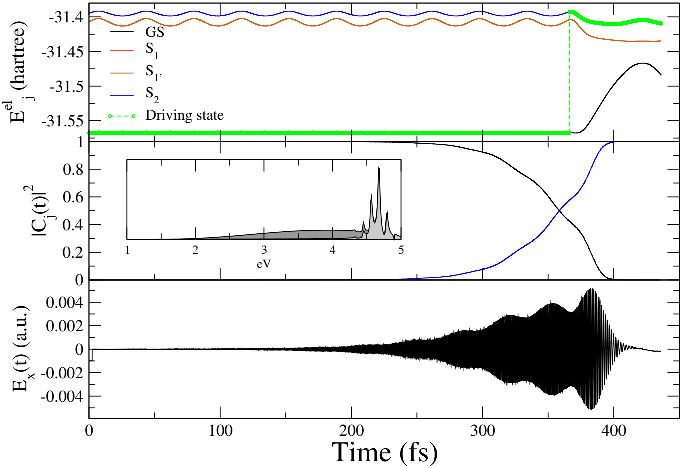


B.F.E Curchod, T. Penfold, U. Rothlisberger, IT, *PRA*, **84**, 042507 (2011)

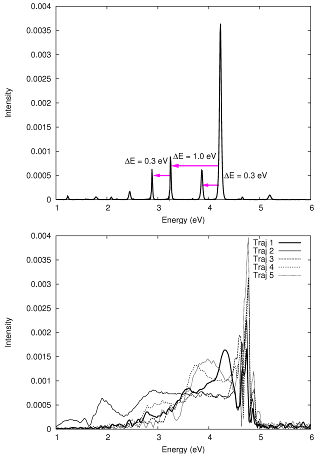
Effect of a generic polarized pulse

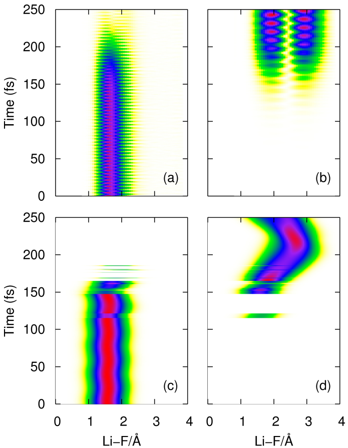


LC pulse: efficient population transfer and stable excitation



Comparison with wavepacket propagation (MCTDH)

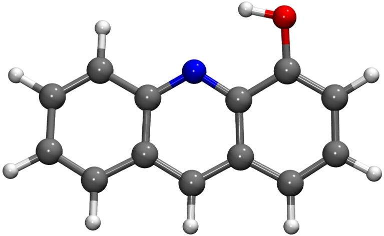




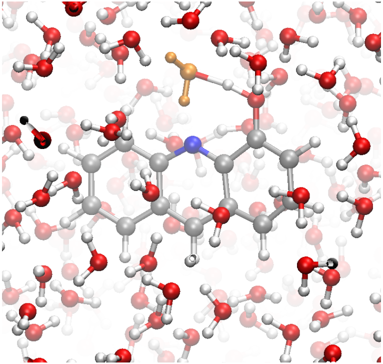
B.F.E Curchod, T. Penfold, U. Rothlisberger, IT, *PRA*, **84**, 042507 (2011)

1. Ab initio molecular dynamics
   - Why Quantum Dynamics?
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 theory
   - LC of protontransfer: from gas-phase to solution

Local control of proton transfer: gas phase to solution

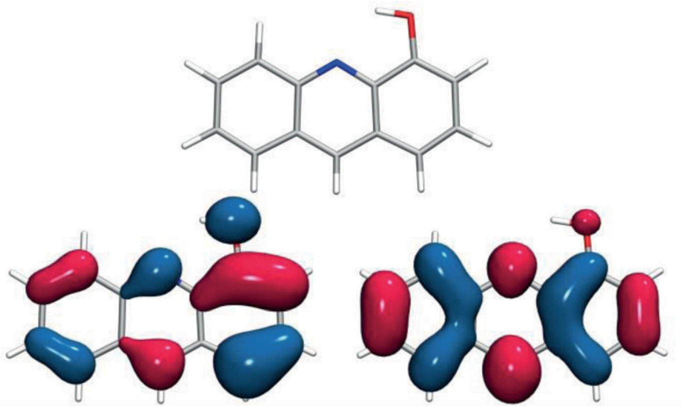


ChemPhysChem, **10**, 2026 (2015)



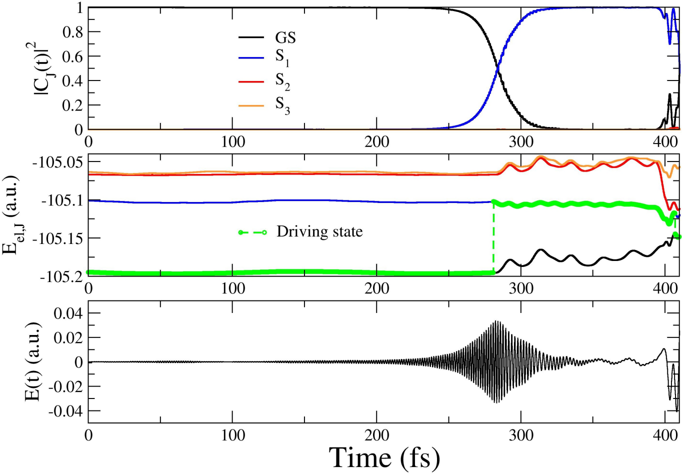
(in preparation)

Local control of proton transfer in gas phase



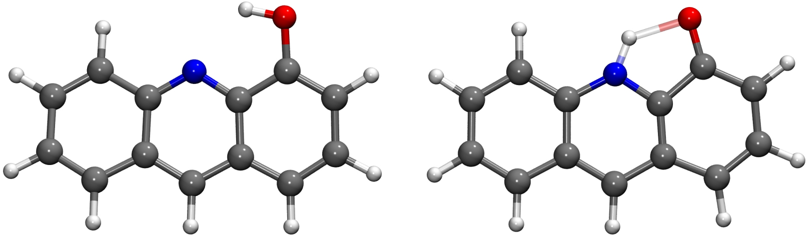
ChemPhysChem, **10**, 2026 (2015)

Local control of proton transfer

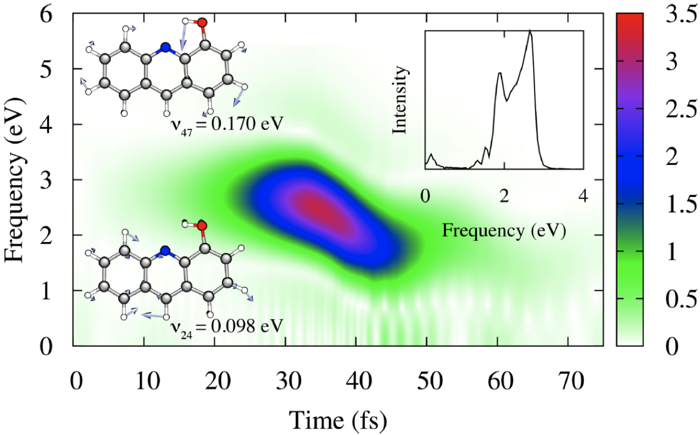


ChemPhysChem, **10**, 2026 (2015)

Local control of proton transfer

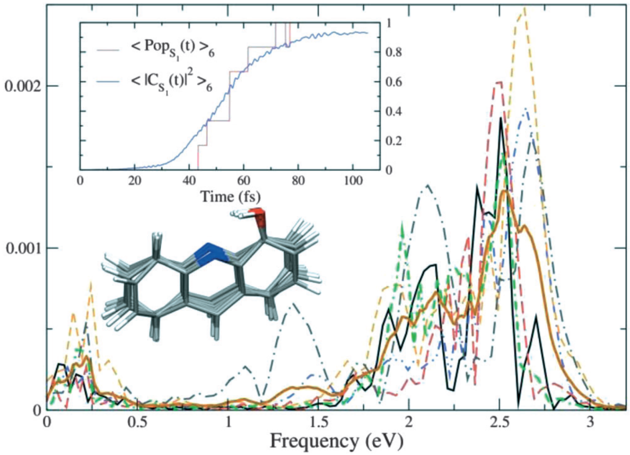


Local control of proton transfer (freq. vs. time)



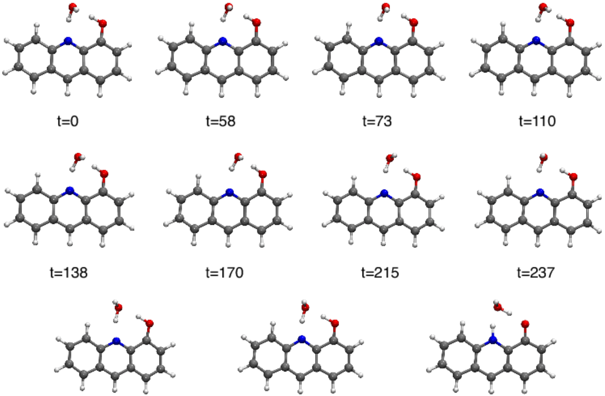
ChemPhysChem, **10**, 2026 (2015)

Local control of proton transfer. Average over 6 trajs



ChemPhysChem, **10**, 2026 (2015)

Local control of proton transfer (microsolvated)

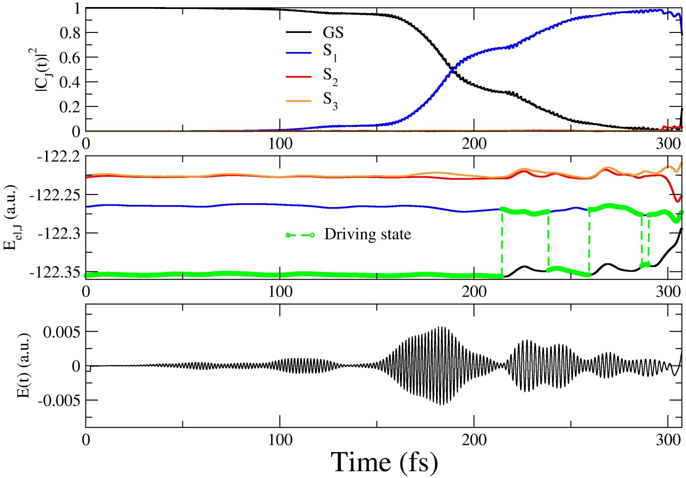


t=0 t=58 t=73 t=110

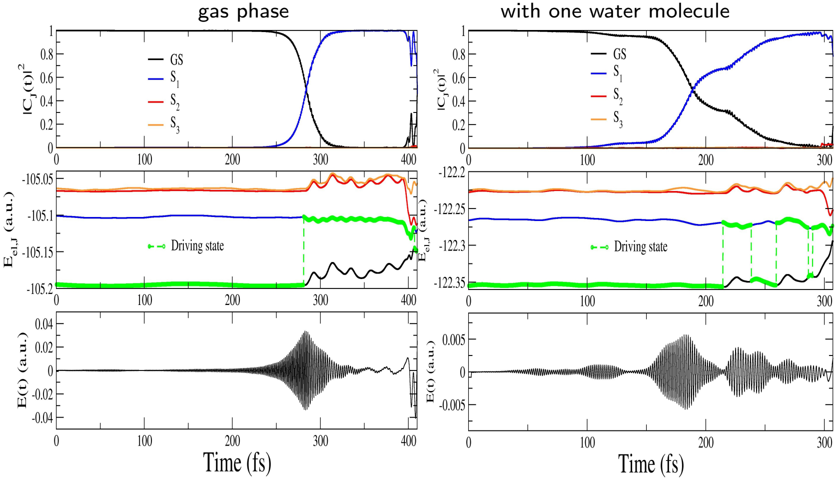
t=138 t=170 t=215 t=237

t=270 t=290 t=300

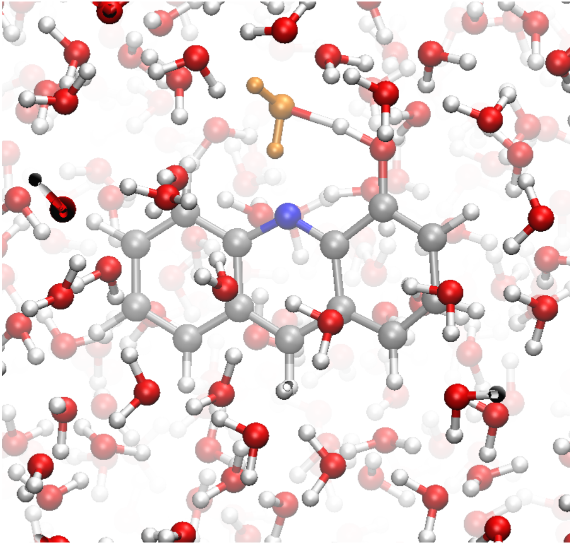
Local control on proton transfer (with one water molecule)



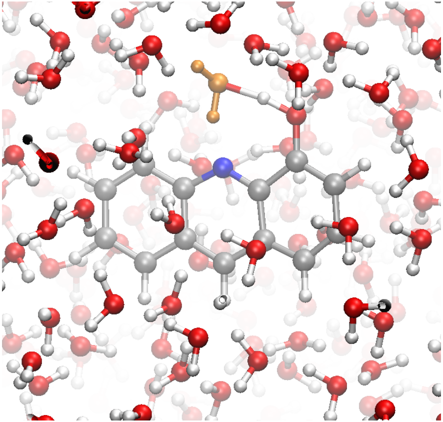
Local control of proton transfer (comparison)



LCT in explicit solvent: TDDFT/MM

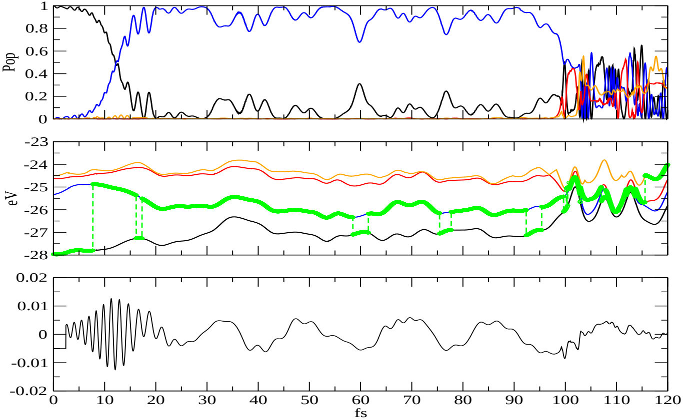


LCT in explicit solvent: TDDFT/MM



In preparation

LCT in explicit solvent: TDDFT/MM



In preparation