



# TDDFT in mixed quantum-classical dynamics

## (2) TDDFT-based non-adiabatic dynamics: the case of TSH

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8th TDDFT SCHOOL

BENASQUE 2018

## 1 TDDFT-based trajectory surface hopping

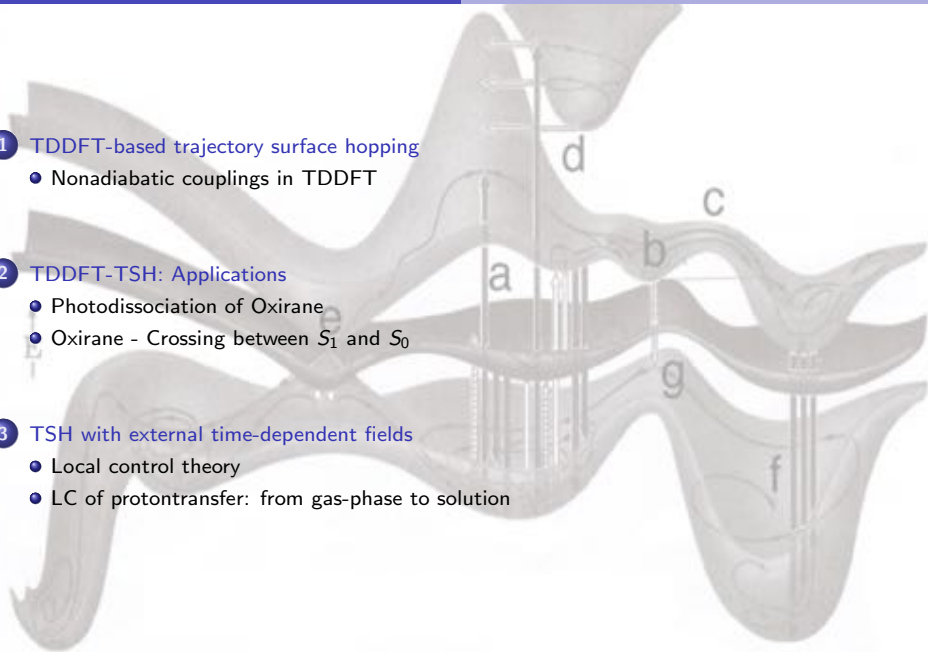
- Nonadiabatic couplings in TDDFT

## 2 TDDFT-TSH: Applications

- Photodissociation of Oxirane
- Oxirane - Crossing between  $S_1$  and  $S_0$

## 3 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



DOI: 10.1002/cphc.201200941

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VIP

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

Basile F. E. Curchod, Ursula Rothlisberger, and Ivano Tavernelli<sup>\*[a]</sup>

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

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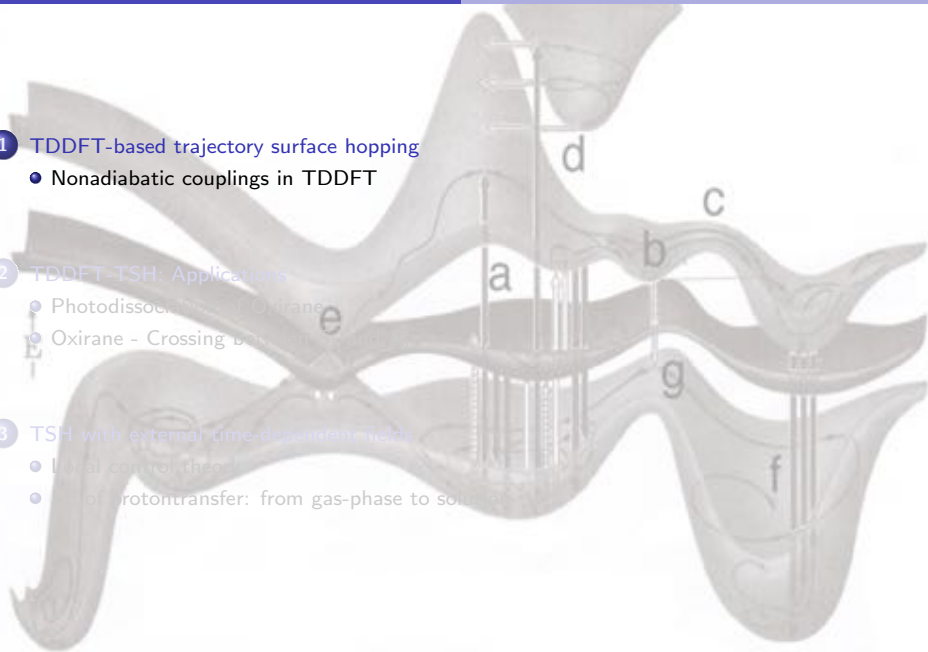
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# Tully's surface hopping - On-the-fly dynamics

## 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, ...

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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:

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

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>1</sup>.

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

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<sup>1</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).



# 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

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

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

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

Therefore <sup>2</sup>

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

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

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

<sup>2</sup>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,

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

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  $\Psi_0$ )

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

where the operator  $\hat{\mathcal{O}} = \sum_{ia\sigma} o_{ia\sigma} \hat{a}_{i\sigma}^\dagger \hat{a}_{a\sigma}$  has components  $o_{ia\sigma} = \langle \phi_{i\sigma} | \hat{\mathcal{O}} | \psi_{a\sigma} \rangle$ <sup>3</sup> 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  $\epsilon_{i\sigma}$ .

<sup>3</sup> $\sum_{ia\sigma}$  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<sup>4</sup> as a linear combination of singly excited Slater determinants

$$\tilde{\Phi}_k[\{\phi.\}] = \sum_{ia\sigma} c_{ia\sigma}^k \hat{a}_{a\sigma}^\dagger \hat{a}_{i\sigma} \tilde{\Phi}_0[\{\phi.\}],$$

with

$$c_{ia\sigma}^k \equiv \sqrt{\frac{S_{ia\sigma}^{-1}}{\omega_{0k}}} e_{ia\sigma}^k$$

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!)

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

<sup>4</sup>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

$$\begin{aligned} \dot{\mathbf{R}} \cdot \mathbf{d}_{0k}|_{t+\delta t/2}[\{\phi.\}] &= \langle \tilde{\Phi}_0(\mathbf{r}; \mathbf{R}(t)) | \nabla_{\mathbf{R}} | \tilde{\Phi}_k(\mathbf{r}; \mathbf{R}(t)) \rangle \cdot \dot{\mathbf{R}} = \langle \tilde{\Phi}_0(\mathbf{r}; \mathbf{R}(t)) | \frac{\partial}{\partial t} | \tilde{\Phi}_k(\mathbf{r}; \mathbf{R}(t)) \rangle \\ &\simeq \frac{1}{2\delta t} \left[ \langle \tilde{\Phi}_0(\mathbf{r}; \mathbf{R}(t)) | \tilde{\Phi}_k(\mathbf{r}; \mathbf{R}(t + \delta t)) \rangle - \langle \tilde{\Phi}_0(\mathbf{r}; \mathbf{R}(t + \delta t)) | \tilde{\Phi}_k(\mathbf{r}; \mathbf{R}(t)) \rangle \right] \end{aligned}$$

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

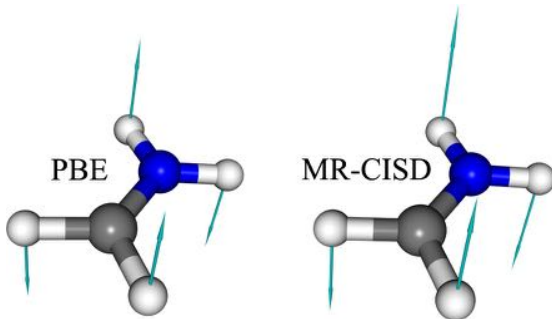
$$\mathbf{d}_{kj}[\{\phi.\}] = \frac{\langle \tilde{\Phi}_k(\mathbf{R}) | \nabla_{\mathbf{R}} \hat{\mathcal{H}}_{el} | \tilde{\Phi}_j(\mathbf{R}) \rangle}{E_j(\mathbf{R}) - E_k(\mathbf{R})}$$

- ▶ 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...

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

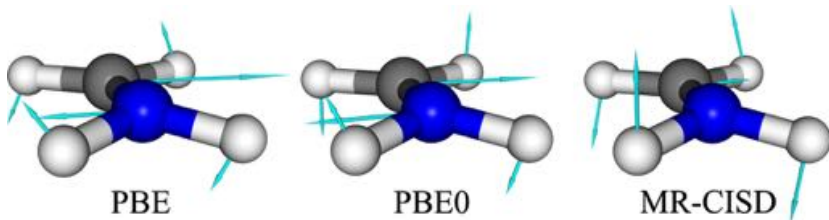


Protonated formalimine: nonadiabatic coupling vectors  $\mathbf{d}_{01}$  with LR-TDDFT/TDA.

# Nonadiabatic couplings - examples

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



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

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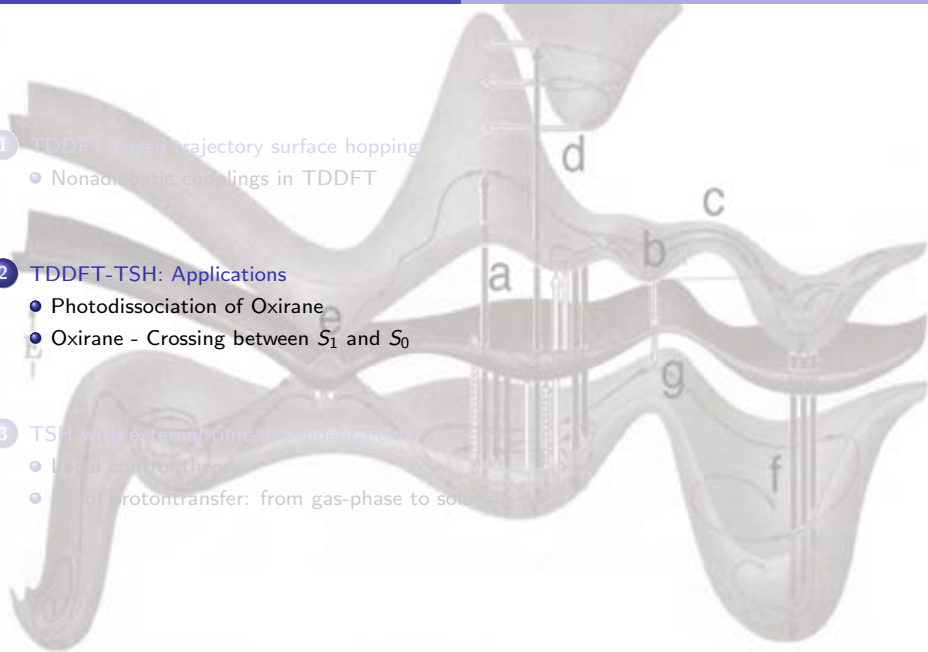
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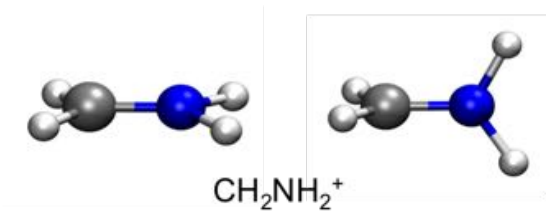


# Protonated formaldimine

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)

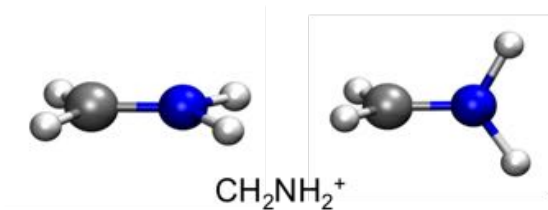




# Protonated formaldimine

## 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.

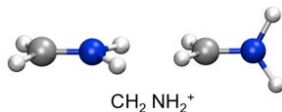
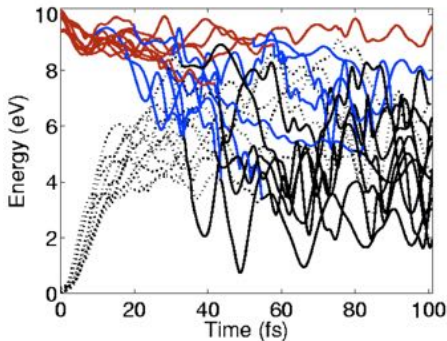


Photo-excitation promotes the system mainly into  $S_2$ .

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

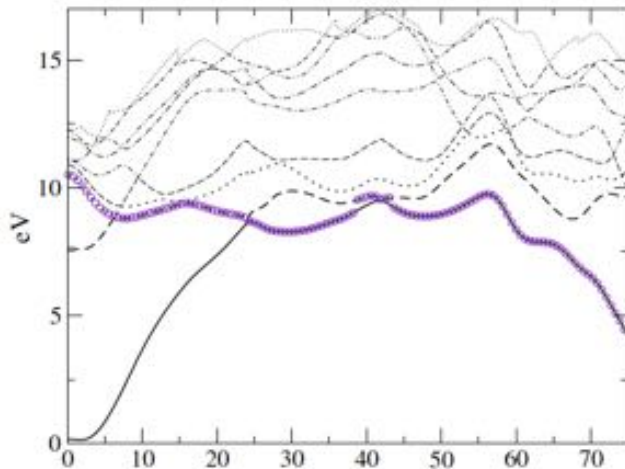



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[E. Tapavicza, I. T., U. Rothlisberger, PRL, **98**, 023001 (2007); THEOCHEM, **914**, 22 (2009)]

# Protonated formaldimine

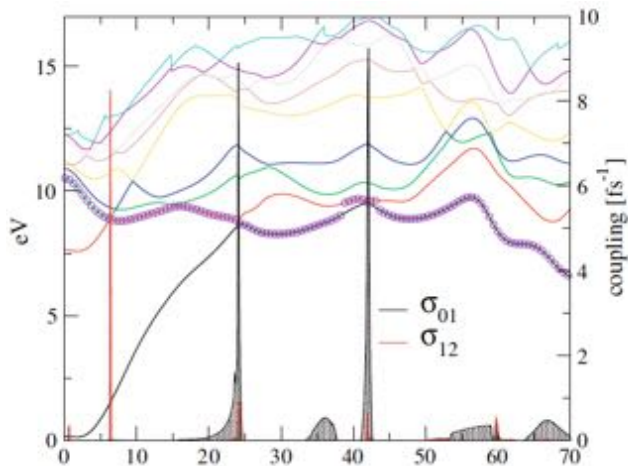
## Typical trajectory



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

# Protonated formaldimine

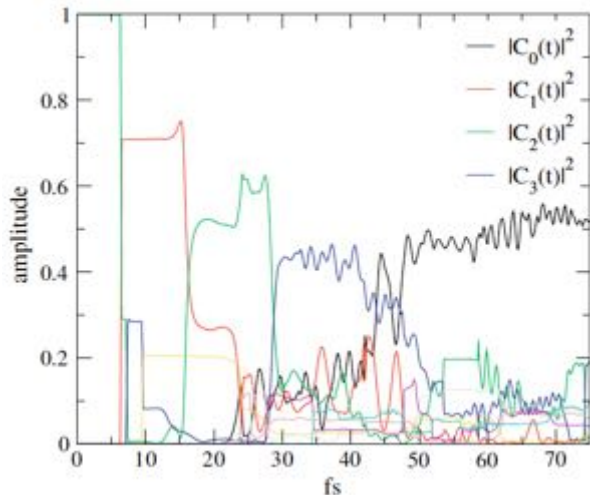
Nonadiabatic couplings  $\sigma_{kj} = \dot{\mathbf{R}}^\alpha \cdot \mathbf{d}_{kj}^\alpha$



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

# Protonated formaldimine

## States population

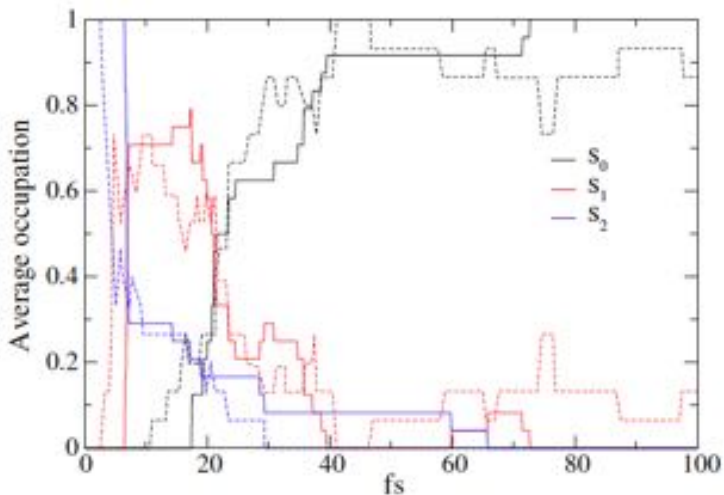


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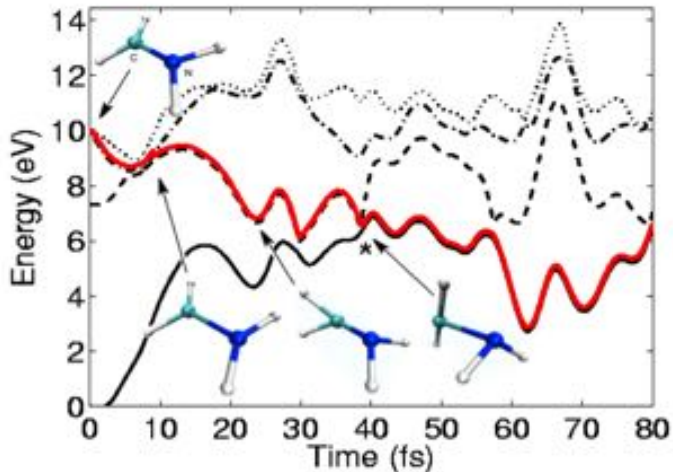
States population - **Average over many trajectories.**

Dashed line = CASSCF result.



# Protonated formaldimine

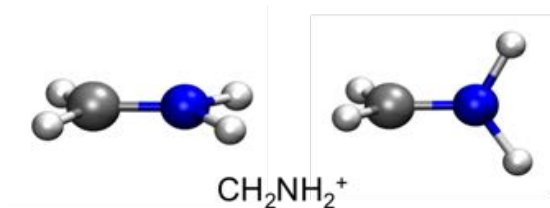
## Geometrical modifications



# Protonated formaldimine

## Comparison with experiment and model calculations

- In addition to the isomerization channel, intra-molecular proton transfer reactions was observed (formation of  $\text{CH}_3\text{NH}^+$ ).
- $\text{H}_2$  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.

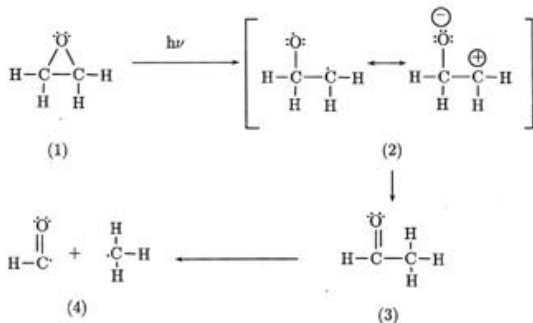


Figure: Mechanism proposed by Gomer and Noyes

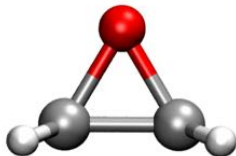
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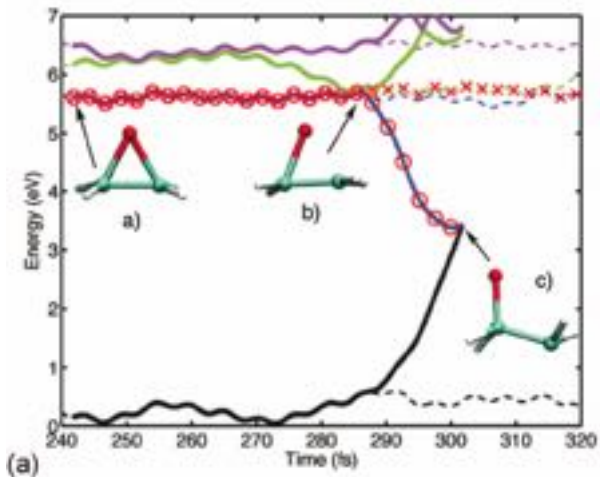
- Isolated system
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- 30 trajectories (NVT) each of  $\sim 100$  fs.

JCP, 129, 124108 (2009).



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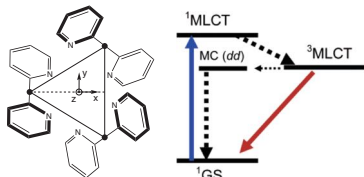
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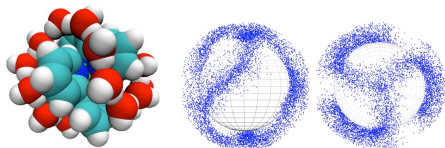
JCP, 129, 124108 (2009).

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

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



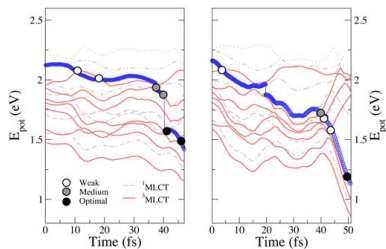
$[\text{Ru}(\text{bpy})_3]^{2+}$  dye: Solvent structure



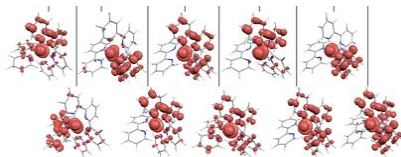
[M.E. Moret, I.T., U. Rothlisberger, *JPC B*, **113**, 7737 (2009); IT, B.

Curchod, U. Rothlisberger, *Chem.Phys.*, **391**, 101 (2011)]

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



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



# 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:  $\Psi(\mathbf{r}, \mathbf{R}, t) = \Omega(\mathbf{R}, t)\Phi(\mathbf{r}, t)$ .

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

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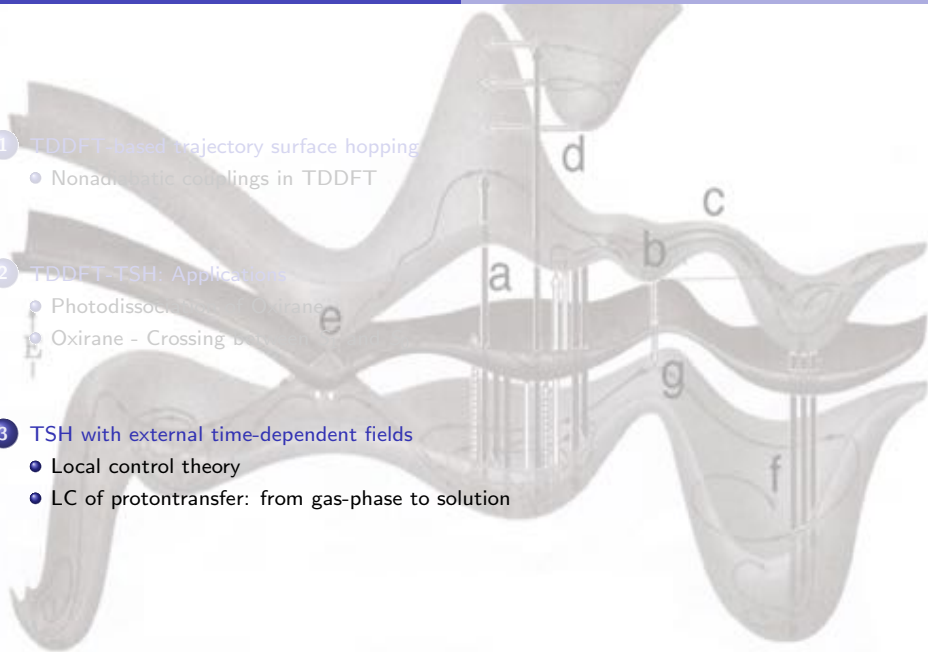
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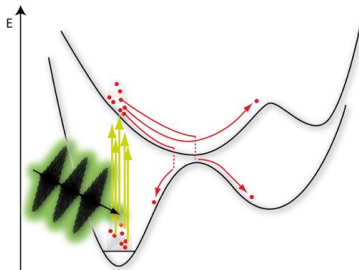
### 3 TSH with external time-dependent fields

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# 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)

# 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 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.

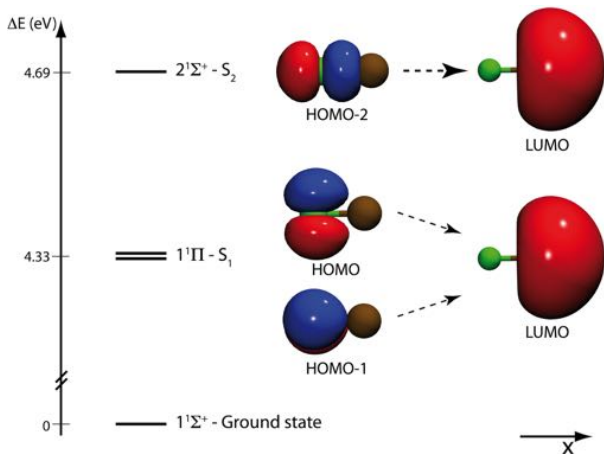
IT, B. Curchod, U. Rothlisberger, Phys. Rec. A **81**, 052508 (2010)

# Effect of an electromagnetic field - Lithium fluoride

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

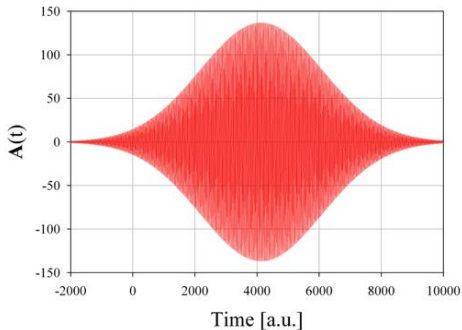
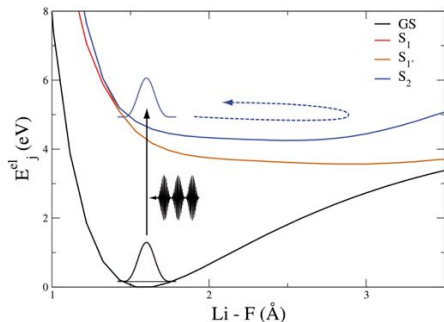
## Electronic structure of LiF

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

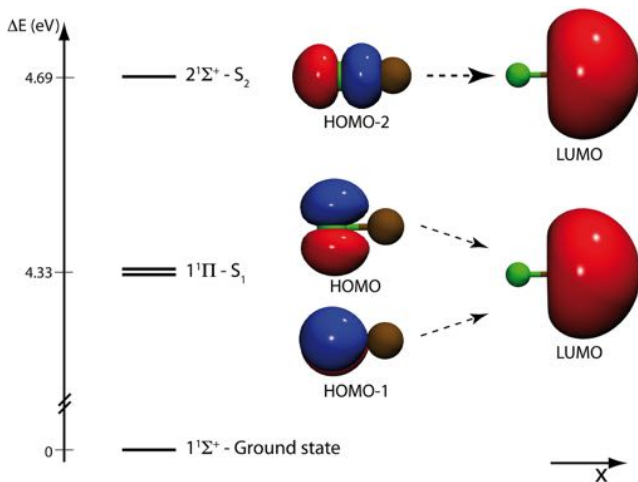


# Effect of an electromagnetic field - Lithium fluoride

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

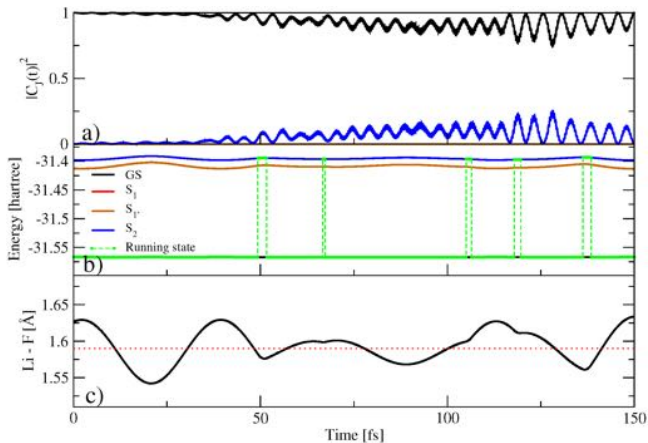


## Effect of an electromagnetic field - Lithium fluoride

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

# Effect of an electromagnetic field - Lithium fluoride

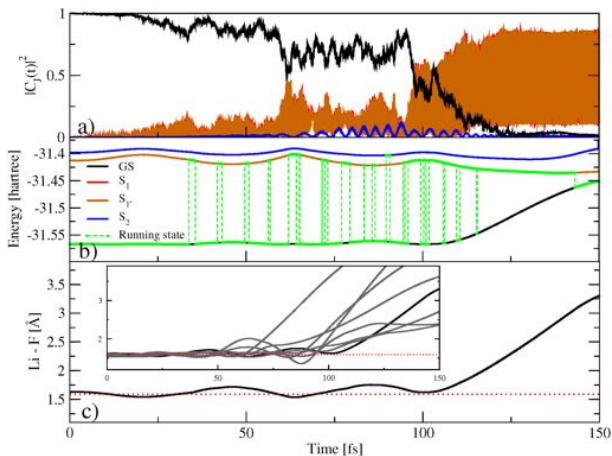
$$\epsilon^\lambda = (1, 0, 0)$$



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

## Effect of an electromagnetic field - Lithium fluoride

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



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

# Local control theory

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

Using the TSH for the total molecular wavefunction

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

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

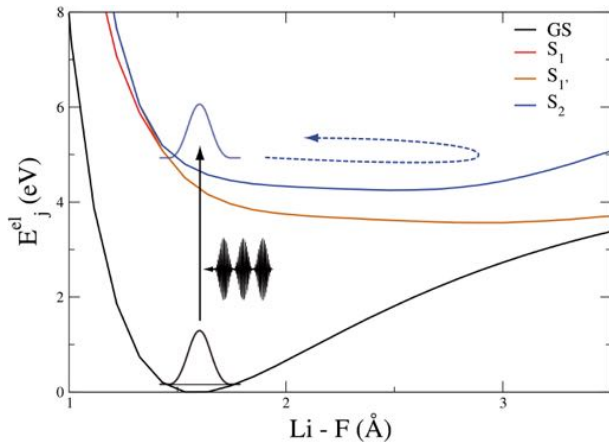
$$\mathbf{E}(t) = -\lambda \sum_J \Im[C_I^\alpha(t) C_J^{\alpha*} \boldsymbol{\mu}_{IJ}]$$

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

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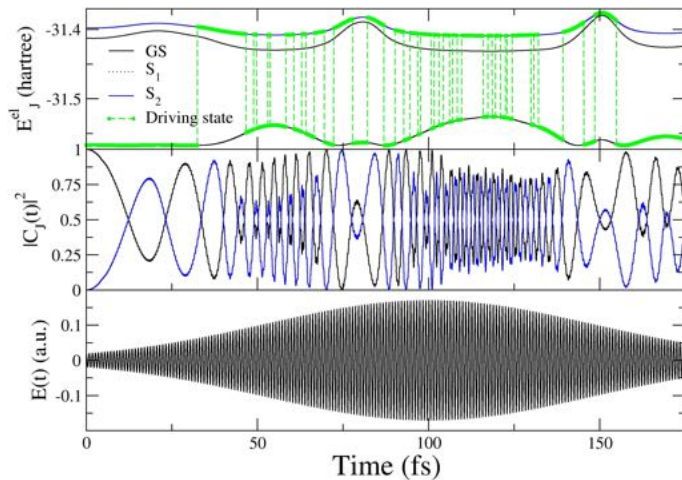
T. J. Penfold, G. A. Worth, C. Meier, *Phys. Chem. Chem. Phys.* **12**, 15616 (2010).

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

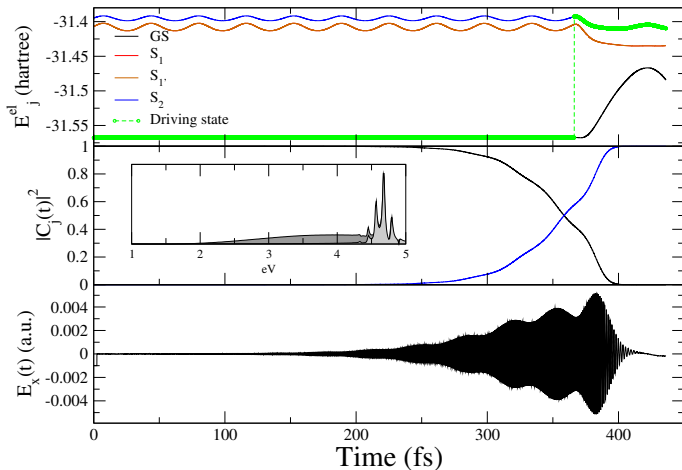
Application: Photoexcitation of LiF in the bound state  $S_2$ 



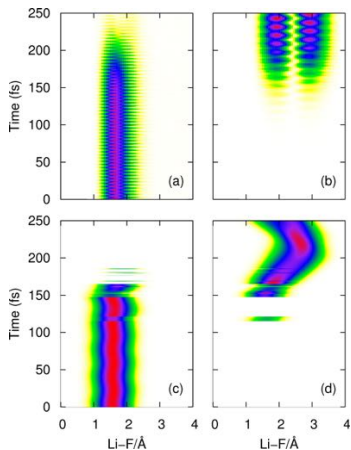
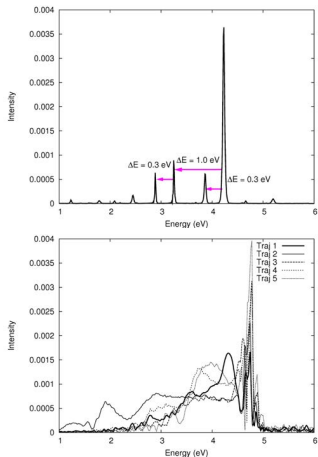
# Effect of a generic polarized pulse



# LC pulse: efficient population transfer and stable excitation



# Comparison with wavepacket propagation (MCTDH)

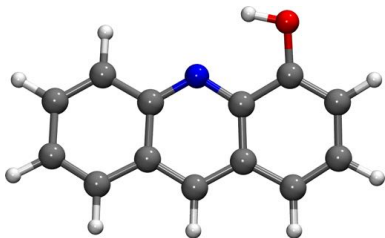


B.F.E Curchod, T. Penfold, U. Rothlisberger, IT, *PRA*, **84**, 042507 (2011)

- 1 TDDFT-based trajectory surface hopping
  - Nonadiabatic couplings in TDDFT
- 2 TDDFT-TSH: Applications
  - Photodissociation of Oxirane
  - Oxirane - Crossing between  $S_1$  and  $S_0$
- 3 TSH with external time-dependent fields
  - Local control theory
  - LC of protontransfer: from gas-phase to solution

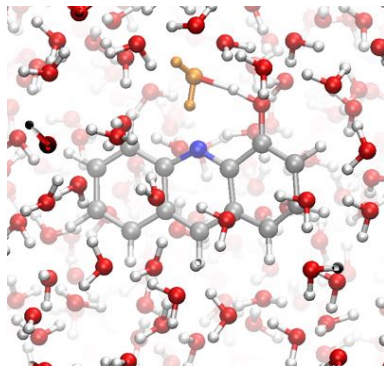
LR-TDDFT

# Local control of proton transfer: gas phase to solution



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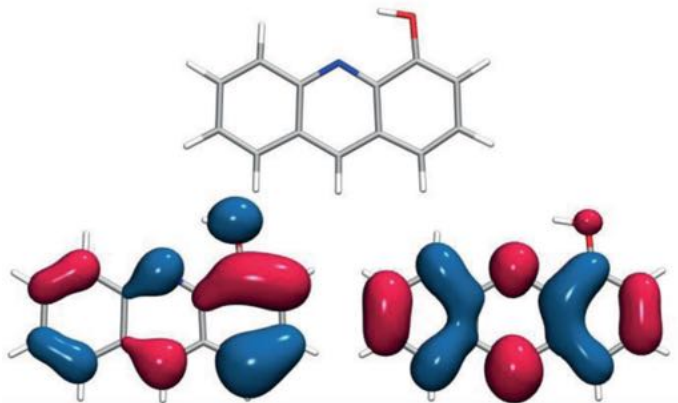
*ChemPhysChem*, 10, 2026 (2015)



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(in preparation)

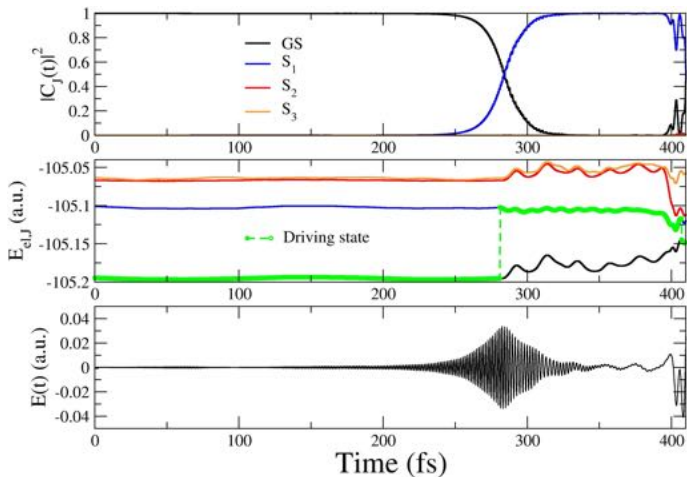
# Local control of proton transfer in gas phase



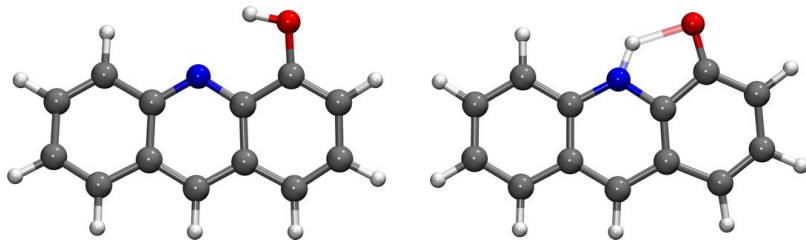
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*ChemPhysChem*, **10**, 2026 (2015)

# Local control of proton transfer

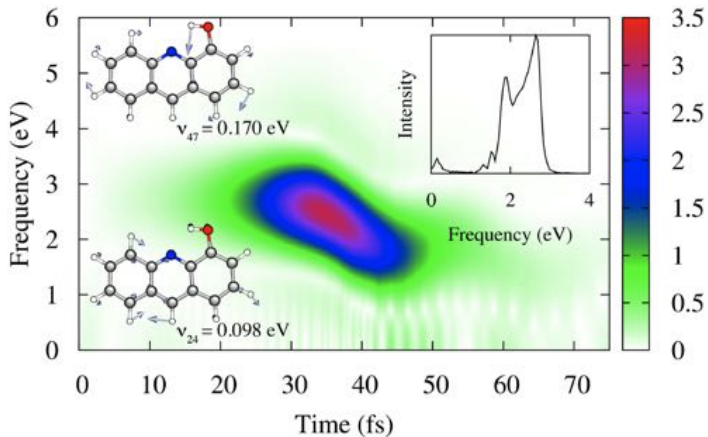


# Local control of proton transfer





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



## Local control of proton transfer. Average over 6 traj

