

# Nonadiabatic molecular dynamics coupled to time dependent external potentials

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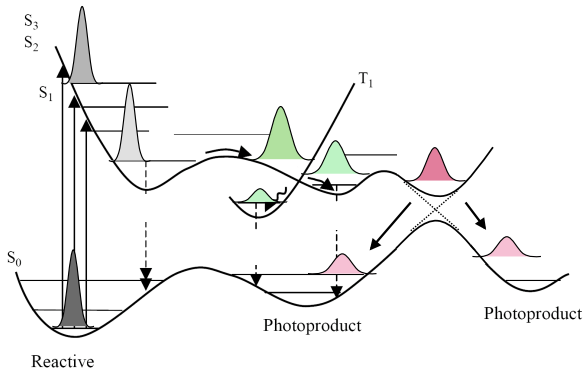
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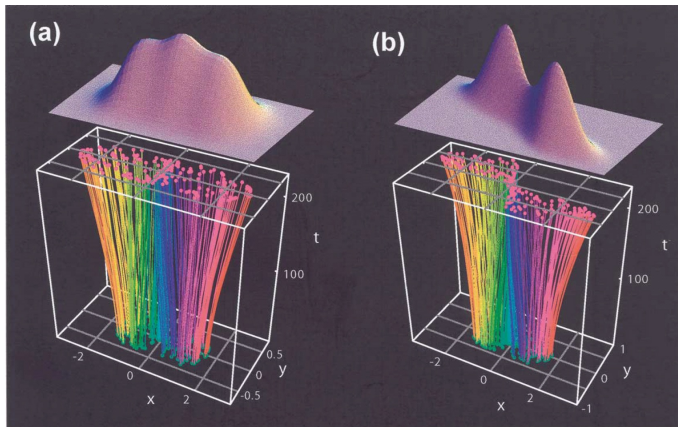
# Nonadiabatic effects requires quantum nuclear dynamics

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



Branching is crucial.

# Nonadiabatic dynamics: Multi-trajectory solutions



K. Na, R.E. Wyatt, *Physics Letters A* **306**, 97 (2002)



## Starting point

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

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

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

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

### Ansätze

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

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

$$\Psi(\mathbf{r}, \mathbf{R}, t) \xrightarrow[\text{decomp.}]{\text{Exact-}} \Phi(\mathbf{r}, t) \Omega(\mathbf{R}, t)$$

# On-the-fly nonadiabatic dynamics with trajectories

## a. Potential energy surfaces

Computed on-the-fly using linear response TDDFT

## b. Propagation of the nuclear wavepacket

The wavepacket dynamics is replaced by the time-propagation of a swarm of trajectories. We consider two options:

- Classical trajectories driven by forces computed as gradient of the TDDFT PESs
- Quantum (Bohmian) trajectories driven by classical and quantum potentials both computed within TDDFT

## c. Nonadiabatic couplings between the PESs

Transition between PESs governed by the nonadiabatic couplings derived from TDDFT

## d. Coupling with the environment

Coupling with external (static and time-dependent) fields at TDDFT level

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## LR-TDDFT - Energies and forces

- Using the linear response orbitals (perturbative solution: Sternheimer 1951)

$$\sum_{j=1}^N (H_0^\sigma \delta_{ij} - \epsilon_{ij}) |\phi'_{I,j\sigma}\rangle + Q^\sigma \delta v_I^{\sigma\text{SCF}} |\phi_{i\sigma}\rangle = \omega_I |\phi'_{I,i\sigma}\rangle$$

- Using the virtual Kohn-Sham orbital expansion (Casida formulation)

$$\begin{bmatrix} \mathcal{A}(\omega) & \mathcal{B}(\omega) \\ \mathcal{B}(\omega) & \mathcal{A}(\omega) \end{bmatrix} \begin{bmatrix} \mathbf{x}_I \\ \mathbf{y}_I \end{bmatrix} = \omega_I \begin{bmatrix} \mathcal{C} & 0 \\ 0 & -\mathcal{C} \end{bmatrix} \begin{bmatrix} \mathbf{x}_I \\ \mathbf{y}_I \end{bmatrix}$$

- Analytic excited state forces (using the Lagrange multiplier formalism)

$$\frac{dE_{\text{tot}}[c^{\{0\}}, x, y]}{d\eta} = \frac{dE_{\text{KS}}[c^{\{0\}}]}{d\eta} + \frac{d\omega[c^{\{0\}}, x, y]}{d\eta}$$

[J. Hutter, JCP, 118, 3928 (2003)]

- Solution always within the adiabatic approximation (no memory kernel)

## Trajectory based solution of the nuclear dynamics

In trajectory based solutions of the quantum dynamics we obtain a Newton-like equation of motion for the nuclei

$$M_{\beta} \frac{d^2 R_{\beta}}{(dt^J)^2} = -\nabla_{\beta} \left[ E_{el}^J(R) + Q_J(R, t) + \sum_I \mathcal{D}_{JI}(R, t) \right]$$

$Q_J(R, t)$ : adiabatic quantum potential

$\mathcal{D}_{JI}(R, t)$ : nonadiabatic couplings

1. NonAdiabatic Ehrenfest Dynamics (mean-field one-trajectory solution)
  2. NonAdiabatic Bohmian Dynamics (NABDY) provides an exact solution for the two extra terms:  $Q$  and  $\mathcal{D}_{JI}$ . [PCCP, 13, 3231 (2011)]
  3. Trajectory Surface Hopping Dynamics (TSH) is derived from the so called Independent Trajectory Approximation (ITA) together with [Tully, JCP, 1971]
    - $\hbar \rightarrow 0$  for the action (classical trajectories:  $Q = 0$ )
    - stochastic (*phenomenological*) description of the couplings
- $\mathcal{D}_{JI}$ : trajectory surface hopping algorithm.

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## The NABDY solution [B. Curchod]

Inserting  $\Psi(\mathbf{r}, \mathbf{R}, t) = \sum_I \Phi_I(\mathbf{r}, \mathbf{R}) \Omega_I(\mathbf{R}, t)$  in the time-dependent Schrödinger equation and multiply from the left by  $\Phi_J^*(\mathbf{r}; \mathbf{R})$  we get (integration over  $\mathbf{r}$ ),

$$i\hbar\dot{\Omega}_J(\mathbf{R}, t) = - \sum_{\gamma} \frac{\hbar^2}{2M_{\gamma}} \nabla_{\gamma}^2 \Omega_J(\mathbf{R}, t) + E_J^{el}(\mathbf{R}) \Omega_J(\mathbf{R}, t) \\ + \sum_{\gamma, I} \frac{\hbar^2}{2M_{\gamma}} D_{JI}^{\gamma}(\mathbf{R}) \Omega_I(\mathbf{R}, t) - \sum_{\gamma, I \neq J} \frac{\hbar^2}{M_{\gamma}} \mathbf{d}_{JI}^{\gamma}(\mathbf{R}) \nabla_{\gamma} \Omega_I(\mathbf{R}, t),$$

where

- $\mathbf{d}_{JI}^{\gamma}(\mathbf{R}) = \int \{ \Phi_J^*(\mathbf{r}; \mathbf{R}) [\nabla_{\gamma} \Phi_I(\mathbf{r}; \mathbf{R})] \} d\mathbf{r}$  are the first order nonadiabatic coupling elements (NACs)
- $D_{JI}^{\gamma}(\mathbf{R}) = \int \{ \Phi_J^*(\mathbf{r}; \mathbf{R}) [\nabla_{\gamma}^2 \Phi_I(\mathbf{r}; \mathbf{R})] \} d\mathbf{r}$  are the second order NACs.

The electrons are “static” (non explicit time-dependence in  $\Phi_I(\mathbf{r}, \mathbf{R})$ ).

[B.F.E. Curchod, IT, U.Rothlisberger, **PCCP**, 13, 3231 (2011)]

With the polar representation:  $\Omega_J(\mathbf{R}, t) = A_J(\mathbf{R}, t)e^{i\hbar^{-1}S_J(\mathbf{R}, t)}$  we obtain, after separating real and imaginary parts (in the adiabatic representation),

$$-\frac{\partial S_J(\mathbf{R}, t)}{\partial t} = \sum_{\gamma} \frac{1}{2M_{\gamma}} (\nabla_{\gamma} S_J(\mathbf{R}, t))^2 + E_J^{el}(\mathbf{R}) - \sum_{\gamma} \frac{\hbar^2}{2M_{\gamma}} \frac{\nabla_{\gamma}^2 A_J(\mathbf{R}, t)}{A_J(\mathbf{R}, t)} + \sum_{\gamma, I} \frac{\hbar^2}{2M_{\gamma}} D_{JI}^{\gamma}(\mathbf{R}) \frac{A_I(\mathbf{R}, t)}{A_J(\mathbf{R}, t)} \Re [e^{i\phi}]$$

$$- \sum_{\gamma, I \neq J} \frac{\hbar^2}{M_{\gamma}} d_{JI}^{\gamma}(\mathbf{R}) \frac{\nabla_{\gamma} A_I(\mathbf{R}, t)}{A_J(\mathbf{R}, t)} \Re [e^{i\phi}] + \sum_{\gamma, I \neq J} \frac{\hbar}{M_{\gamma}} d_{JI}^{\gamma}(\mathbf{R}) \frac{A_I(\mathbf{R}, t)}{A_J(\mathbf{R}, t)} \nabla_{\gamma} S_I(\mathbf{R}, t) \Im [e^{i\phi}]$$

and

$$\frac{\partial A_J(\mathbf{R}, t)}{\partial t} = - \sum_{\gamma} \frac{1}{M_{\gamma}} \nabla_{\gamma} A_J(\mathbf{R}, t) \nabla_{\gamma} S_J(\mathbf{R}, t) - \sum_{\gamma} \frac{1}{2M_{\gamma}} A_J(\mathbf{R}, t) \nabla_{\gamma}^2 S_J(\mathbf{R}, t)$$

$$+ \sum_{\gamma, I} \frac{\hbar}{2M_{\gamma}} D_{JI}^{\gamma}(\mathbf{R}) A_I(\mathbf{R}, t) \Im [e^{i\phi}] - \sum_{\gamma, I \neq J} \frac{\hbar}{M_{\gamma}} d_{JI}^{\gamma}(\mathbf{R}) \nabla_{\gamma} A_I(\mathbf{R}, t) \Im [e^{i\phi}]$$

$$- \sum_{\gamma, I \neq J} \frac{1}{M_{\gamma}} d_{JI}^{\gamma}(\mathbf{R}) A_I(\mathbf{R}, t) \nabla_{\gamma} S_I(\mathbf{R}, t) \Re [e^{i\phi}],$$

where  $\phi = \frac{1}{\hbar}(S_I(\mathbf{R}, t) - S_J(\mathbf{R}, t))$ .

[R.E. Wyatt, C.L. Lopreore, G Parlant, JCP, 114, 5113 (2001) (diabatic representation);

J.C. Burant, J.C. Tully, JCP, 112, 6097 (2000) (classical limit)]

## Time evolution of $S_J(\mathbf{R}, t)$ (phase)

The phase ( $\sim$  classical action) evolves according to

$$-\frac{\partial S_J(\mathbf{R}, t)}{\partial t} = \sum_{\gamma} \frac{1}{2M_{\gamma}} (\nabla_{\gamma} S_J(\mathbf{R}, t))^2 + E_J^e(\mathbf{R}) - \sum_{\gamma} \frac{\hbar^2}{2M_{\gamma}} \frac{\nabla_{\gamma}^2 A_J(\mathbf{R}, t)}{A_J(\mathbf{R}, t)} + \sum_{\gamma I} \frac{\hbar^2}{2M_{\gamma}} D_{JI}^{\gamma}(\mathbf{R}) \frac{A_I(\mathbf{R}, t)}{A_J(\mathbf{R}, t)} \Re [e^{i\phi}]$$

$$- \sum_{\gamma, I \neq J} \frac{\hbar^2}{M_{\gamma}} d_{JI}^{\gamma}(\mathbf{R}) \frac{\nabla_{\gamma} A_I(\mathbf{R}, t)}{A_J(\mathbf{R}, t)} \Re [e^{i\phi}] + \sum_{\gamma, I \neq J} \frac{\hbar}{M_{\gamma}} d_{JI}^{\gamma}(\mathbf{R}) \frac{A_I(\mathbf{R}, t)}{A_J(\mathbf{R}, t)} \nabla_{\gamma} S_I(\mathbf{R}, t) \Im [e^{i\phi}]$$

This is the equivalent of the classical **Hamilton-Jacobi** equation (first two terms) for the action  $S(\mathbf{R}, t)$ , augmented with two additional parts of quantum nature of order  $\hbar$  and  $\hbar^2$ :

- **3<sup>rd</sup> term:** quantum potential  $Q_J(\mathbf{R}, t)$  describing all quantum effects within a state and introducing nonlocality.
- **4<sup>th</sup> to 6<sup>th</sup> term:** nonadiabatic quantum potential  $\mathcal{D}_{IJ}(\mathbf{R}, t)$  describing interstate contributions.



## Time evolution of $S_J(\mathbf{R}, t)$ (phase)

Applying the gradient with respect to the nucleus  $\beta$  on both sides we get

$$\nabla_{\beta} \frac{\partial S_J(\mathbf{R}, t)}{\partial t} + \sum_{\gamma} \left( \frac{1}{M_{\gamma}} \nabla_{\gamma} S_J(\mathbf{R}, t) \cdot \nabla_{\gamma} \right) \nabla_{\beta} S_J(\mathbf{R}, t) = -\nabla_{\beta} \left[ E_{el}^J(\mathbf{R}) + Q_J(\mathbf{R}, t) + \sum_I \mathcal{D}_{IJ}(\mathbf{R}, t) \right]$$

After moving to the Lagrangian frame and using the HJ definition of the momenta  $\nabla_{\beta} S_J(\mathbf{R}, t) = \mathbf{P}_{\beta}^J$ , we obtain a Newton-like equation of motion

$$M_{\beta} \frac{d^2 \mathbf{R}_{\beta}}{(dt^J)^2} = -\nabla_{\beta} \left[ E_{el}^J(\mathbf{R}) + Q_J(\mathbf{R}, t) + \sum_I \mathcal{D}_{IJ}(\mathbf{R}, t) \right]$$

describing the time evolution (trajectory) of the  $\mathbf{R}_{\beta}$  components of a fluid element with collective variable  $\mathbf{R}$ . ( $d/dt^J = \partial/\partial t + \sum_{\gamma} \nabla_{\gamma} S_J(\mathbf{R}, t)/M_{\gamma} \cdot \nabla_{\gamma}$ ).

# Time evolution of $A_J(\mathbf{R}, t)$ (amplitude)

The amplitudes evolve according to

$$\begin{aligned} \frac{\partial A_J(\mathbf{R}, t)}{\partial t} = & - \sum_{\gamma} \frac{1}{M_{\gamma}} \nabla_{\gamma} A_J(\mathbf{R}, t) \nabla_{\gamma} S_J(\mathbf{R}, t) - \sum_{\gamma} \frac{1}{2M_{\gamma}} A_J(\mathbf{R}, t) \nabla_{\gamma}^2 S_J(\mathbf{R}, t) \\ & + \sum_{\gamma I} \frac{\hbar}{2M_{\gamma}} D_{JI}^{\gamma}(\mathbf{R}) A_I(\mathbf{R}, t) \Im [e^{i\phi}] - \sum_{\gamma, I \neq J} \frac{\hbar}{M_{\gamma}} d_{JI}^{\gamma}(\mathbf{R}) \nabla_{\gamma} A_I(\mathbf{R}, t) \Im [e^{i\phi}] \\ & - \sum_{\gamma, I \neq J} \frac{1}{M_{\gamma}} d_{JI}^{\gamma}(\mathbf{R}) A_I(\mathbf{R}, t) \nabla_{\gamma} S_I(\mathbf{R}, t) \Re [e^{i\phi}], \end{aligned}$$

It corresponds to the **continuity equation for the density probability** on state  $J$ , augmented by **three nonadiabatic terms** describing the amplitude change of state  $J$  due to the coupling with the other states.

# Nonadiabatic Quantum Hydrodynamics

These are Quantum Hydrodynamic (nonadiabatic) equations (QHE)

$$\left\{ \begin{array}{l} \frac{d\rho_0}{dt} = -\rho_0 \nabla \cdot \mathbf{v}_0 + P_{0I} \\ \frac{dS_0}{dt} = \frac{1}{2} M v_0^2 - (V_0 + Q_0 + D_{0I}) \\ \frac{d\mathbf{r}_0}{dt} = \mathbf{v}_0 = \frac{1}{M} \nabla S_0 \end{array} \right. \quad \left\{ \begin{array}{l} \frac{d\rho_I}{dt} = -\rho_I \nabla \cdot \mathbf{v}_I + P_{I0} \\ \frac{dS_I}{dt} = \frac{1}{2} M v_I^2 - (V_I + Q_I + D_{I0}) \\ \frac{d\mathbf{r}_I}{dt} = \mathbf{v}_I = \frac{1}{M} \nabla S_I \end{array} \right.$$

where  $\rho_I(\mathbf{R}, t) = A_I^2(\mathbf{R}, t)$

$$Q_I(\mathbf{R}, t) = -\frac{\hbar^2}{2M} \frac{1}{A_I(\mathbf{R}, t)} \nabla^2 A_I(\mathbf{R}, t) \quad \text{the quantum potential}$$

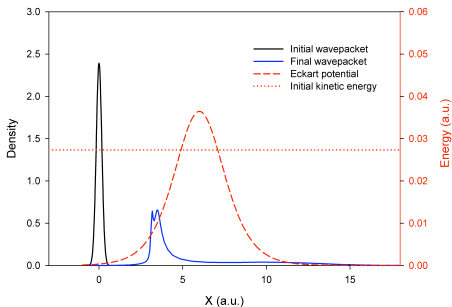
$P_{0I}$  Density coupling term

$D_{IJ}$  Phase coupling term

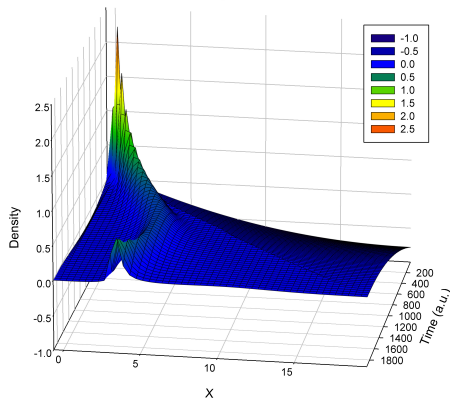
Solution by characteristics = Bohmian trajectories

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

Main picture of a QTM trajectory

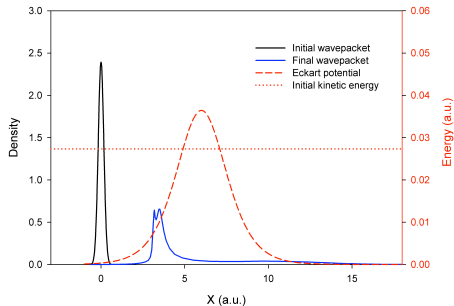


Density evolution

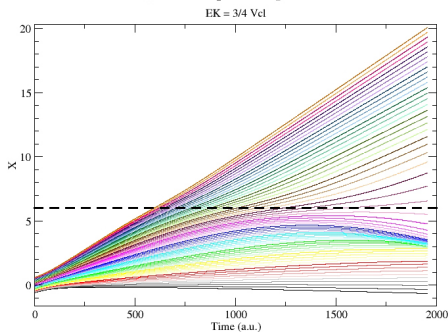


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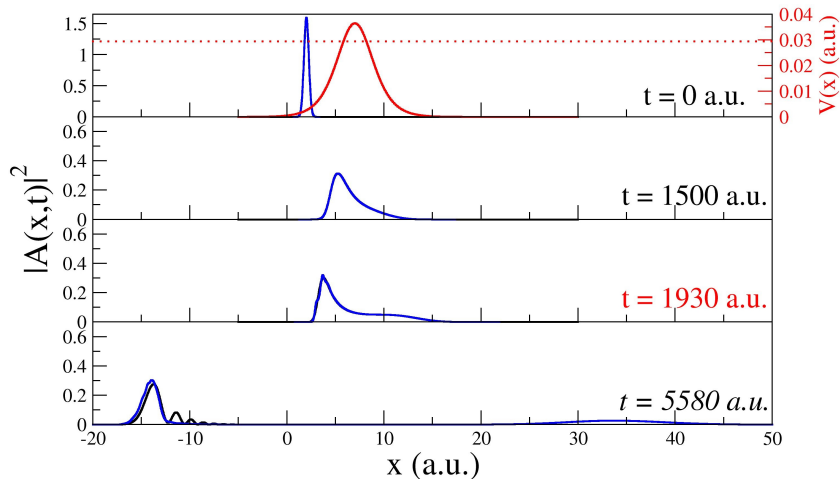
Main picture of a QTM trajectory



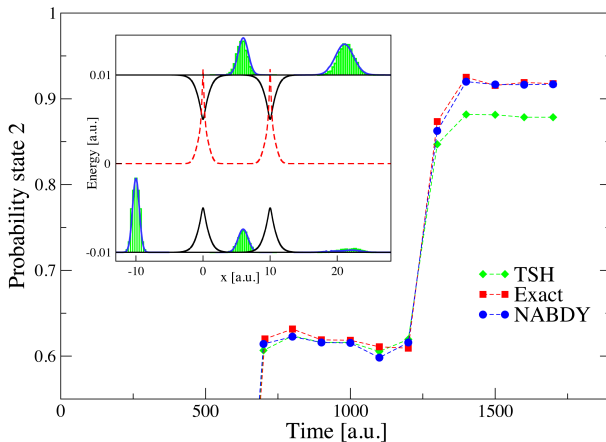
QTM with quantum potential



# Approximate solution to the node problem in 1D

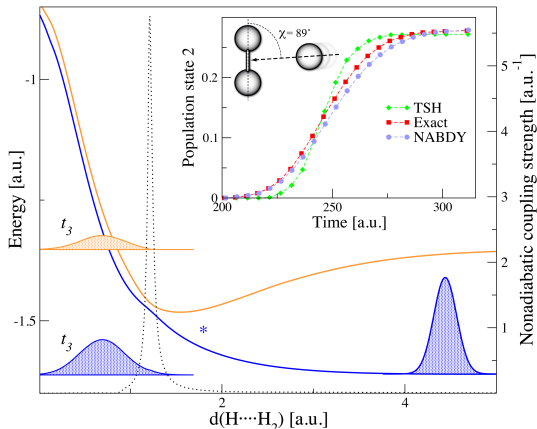


## Tully's model 1 (x2)



**Figure:** Population dynamics on the double well potential. We used 3112 trajectories for TSH, 314 for NABDY dynamics, and 8192 grid points for the exact propagation scheme ( $k = 32$  a.u. in all cases).

# Bohmian Quantum Hydrodynamics: $H_2 + H$ collision



Current and future developments of NABDY:

- ✓ Extension to higher dimensions (configuration space)
- ✓ Off-grid propagation of the amplitudes
- Implementation in CPMD

[B.F.E. Curchod, IT, U.Rothlisberger, PCCP, 13, 3231 (2011)]



# TSH nonadiabatic MD ( $\hbar \rightarrow 0$ for $\Omega_I(\mathbf{R}, t)$ and more)

[E. Tapavicza, B. Curchod]

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

- classical (*adiabatic*) time evolution of the nuclear trajectories on adiabatic states solution of the Schrödinger equation for the electronic sub-system
- propagation of a “quantum” amplitude,  $C_k^\alpha(t)$ , associated to each PES,  $k$

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

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

- transitions (hops) of the trajectories between electronic states according to a stochastic algorithm, which depends on the nonadiabatic couplings and the amplitudes  $C_k^\alpha(t)$

See also: J. Tully, *Faraday discussion*, **110**, 407 (1998) and B. Curchod, U. Rothlisberger, IT, in preparation.

## TSH nonadiabatic MD ( $\hbar \rightarrow 0$ for $\Omega_l(\mathbf{R}, t)$ and more)

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

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

Inserting

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

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

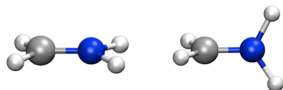
$$i\hbar \dot{C}_k^\alpha(t) = \sum_j C_j^\alpha(t) (H_{kj} - i\hbar \dot{\mathbf{R}}^\alpha \cdot \mathbf{d}_{kj}^\alpha)$$

with  $H_{kj} = \delta_{kj} \langle \Phi_k(\mathbf{r}; \mathbf{R}) | \hat{\mathcal{H}}_{el} | \Phi_j(\mathbf{r}; \mathbf{R}) \rangle \leftarrow$  **Densityfunctionalized (LR-TDDFT)**

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

## On-the-fly TDDFT/TSH: photo-excited $\text{CH}_2\text{NH}_2^+$

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

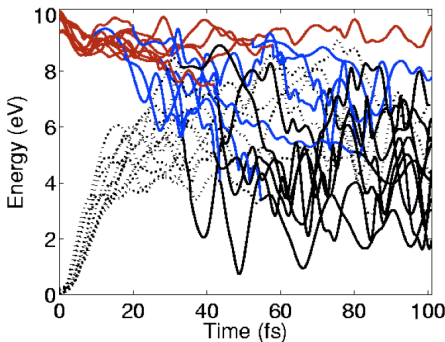


$\text{CH}_2\text{NH}_2^+$

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)]



## The quest for matrix elements $\langle \Phi | \mathcal{O} | \Psi \rangle$ in TDDFT

TDDFT **energies** and **forces** are available since a decade, but in order to perform nonadiabatic dynamics (TSH or Bohmian) one needs to express nonadiabatic coupling elements (NAC) and **nonadiabatic coupling vectors** (NACV)

$$d_{J0}^\gamma[\Phi_0, \Phi_J] = \frac{\langle \Phi_0 | \nabla \mathcal{H} | \Phi_J \rangle}{\Delta E_{J0}}$$

$$d_{J0}^\gamma[\rho, \delta\rho] = ?$$

as a functional of the electronic density  $\rho(r)$  or, equivalently, of the occupied Kohn-Sham orbitals  $\{\phi_i(r)\}$ .

Additional care is required for the case of matrix elements between **pairs of excited states**, which calculation goes beyond simple linear response theory

$$o_{JI}^\gamma(\tau) = \langle \Phi_I | \mathcal{O} | \Phi_J \rangle.$$

## Auxiliary wavefunctions for LR-TDDFT

It is possible to express linear response quantities within TDDFT using a set of auxiliary many-electron wavefunctions.

- I.T., E. Tapavicza, U. Rothlisberger, JCP, **130**, 124107 (2007)
- I.T., B. F. E. Curchod, U. Rothlisberger, JCP, **131**, 196101 (2009)
- I.T., B. F. E. Curchod, A. Laktionov, U. Rothlisberger, JCP, **133**, 194104 (2010)

They are given as a linear combination of singly excited Slater determinants

The auxiliary many-electron wavefunctions (AX WF)

$$\tilde{\psi}_I[\{\phi.\}] = \sum_{ia\sigma} c'_{ia\sigma} \hat{a}_{a\sigma}^\dagger \hat{a}_{i\sigma} \tilde{\psi}_0[\{\phi.\}]$$

with

$$c'_{ia\sigma} \equiv \sqrt{\frac{S_{ia\sigma}^{-1}}{\omega_{0I}}} e'_{ia\sigma}$$

where  $\tilde{\psi}_0[\{\phi.\}]$  is the Slater determinant of all occupied KS orbitals  $\{\phi_{i\sigma}\}_{i=1}^N$ , and  $\hat{a}_{a\sigma}^\dagger, \hat{a}_{i\sigma}$  are the creation (of virtual orbitals,  $\phi_{a\sigma}$ ) and annihilation operators.

## Applications of the AX WF

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

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

- The *nonadiabatic coupling vectors*

$$\mathbf{d}_{0I}[\{\phi.\}] = \langle \tilde{\psi}_0(\mathbf{R}) | \nabla_{\mathbf{R}} | \tilde{\psi}_I(\mathbf{R}) \rangle = \frac{\langle \tilde{\psi}_0(\mathbf{R}) | \nabla_{\mathbf{R}} \mathcal{H} | \tilde{\psi}_I(\mathbf{R}) \rangle}{E_I(\mathbf{R}) - E_0(\mathbf{R})}$$

- The *transition dipole matrix elements*

$$\boldsymbol{\mu}_{0I}[\{\phi.\}] = \langle \tilde{\psi}_0(\mathbf{R}) | \hat{\boldsymbol{\mu}} | \tilde{\psi}_I(\mathbf{R}) \rangle = -e\omega_{0I}^{-1/2} \mathbf{r}^\dagger \mathbf{S}^{-1/2} \mathbf{e}_I$$

# Matrix elements for pairs of excited states

THE JOURNAL OF CHEMICAL PHYSICS **133**, 194104 (2010)

## Nonadiabatic coupling vectors for excited states within time-dependent density functional theory in the Tamm–Dancoff approximation and beyond

Ivano Tavernelli,<sup>a)</sup> Basile F. E. Curchod, Andrey Laktionov, and Ursula Rothlisberger

The equations for the NACVs are obtained from the one-to-one (or residue-by-residue) mapping between

- ▷  $\beta_{MBPT}^{(\alpha\beta\gamma)}(\omega_1, \omega_2)[\Psi_0, \Psi_1, \Psi_2]$  : **MBPT second-order polarizability**
- ▷  $\beta_{TDDFT}^{(\alpha\beta\gamma)}(\omega_1, \omega_2)[\rho, \delta\rho]$  : **TDDFT second-order polarizability**.  
(SOS representation of  $\beta_{TDDFT}^{(\alpha\beta\gamma)}$  through **bosonization** (HA) of the KS excitation operators).

The same procedure used in the derivation of the matrix elements between ground and excited states can be followed for the calculation of the second order response matrix elements  $\langle \Psi_I | \hat{O} | \Psi_J \rangle$ , where both states  $\Psi_I$  and  $\Psi_J$  are linear response excited states.

## MBPT second-order polarizability

Within the many-body formulation of quantum mechanics in second quantization, the SOS second-order density-density response function is obtained using a perturbative approach applied to the molecular Hamiltonian and reads <sup>1</sup>

$$\beta_{MBPT}^{(\alpha\beta\gamma)}(\omega_1, \omega_2) = \frac{1}{2} \sum_{IJ=1}^M \sum_{\text{perm}(\omega_1, \omega_2)} \left[ \frac{\mu_J^{(\alpha)} \mu_{-JI}^{(\beta)} \mu_{-I}^{(\gamma)}}{(\Omega_J - \omega_1 - \omega_2)(\Omega_I - \omega_1)} + \frac{\mu_J^{(\alpha)} \mu_{-JI}^{(\beta)} \mu_{-I}^{(\gamma)}}{(\Omega_J + \omega_2)(\Omega_I + \omega_1 + \omega_2)} + \frac{\mu_{JI}^{(\alpha)} \mu_{-J}^{(\beta)} \mu_{-I}^{(\gamma)}}{(\Omega_J + \omega_2)(\Omega_I - \omega_1)} \right]$$

with  $\mu_J^{(\alpha)} = \langle \Psi_0 | \mu^{(\alpha)} | \Psi_J \rangle$  and  $\mu_{-JI}^{(\alpha)} = \langle \Psi_J | \mu^{(\alpha)} | \Psi_I \rangle$ .

<sup>1</sup>J. F. Ward, *Rev. Mod. Phys.* **37**, 1 (1965); B. J. Orr, J. F. Ward, *Mol. Phys.* **20**, 513 (1971).



## TDDFT second-order polarizability

The second-order TDDFT density response functions are given by <sup>2</sup>

$$\beta^{(2)}(\omega_1, \omega_2, r, r', r'') = \sum_{IJK} \frac{V''_{IJK} \mu_I(r) \mu_{-J}(r') \mu_{-K}(r'') s_I s_J s_K}{(\Omega_I - \omega_1 - \omega_2)(\Omega_J - \omega_1)(\Omega_K - \omega_2)} - \frac{1}{2} \sum_{IJ} \frac{\mu_{-IJ}(r) \mu_I(r') \mu_{-J}(r'') s_I s_J}{(\Omega_I - \omega_1 - \omega_2)(\Omega_J - \omega_1)}$$

$$- \frac{1}{2} \sum_{IJ} \frac{\mu_{-IJ}(r) \mu_I(r') \mu_{-J}(r'') s_I s_J}{(\Omega_I - \omega_1 - \omega_2)(\Omega_J - \omega_2)} - \frac{1}{2} \sum_{IJ} \frac{\mu_{IJ}(r) \mu_{-I}(r') \mu_{-J}(r'') s_I s_J}{(\Omega_I - \omega_1)(\Omega_J - \omega_2)}$$

where

- $s_I = \text{sign}(I)$ ,
- $I, J, K = \pm 1, \pm 2, \dots$ ,
- $V''_{IJK}$  are the second-order coupling terms between excited states
- $\xi_I$  are the eigenvectors of the LR-TDDFT eigenvalue equations

$$\mathcal{L} \xi_I = \Omega_I \xi_I.$$

<sup>2</sup>S. Tretiak and S. Mukamel, *Chem. Rev.*, **102**, 3171 (2002); S. Tretiak and V. Chernyak, *J Chem Phys*, **119**, 8809 (2003); I. T, B.F.E. Curchod, A. Laktionov, and U. Rothlisberger, *J. Chem. Phys.*, **133**, 194104 (2010)..

## TDDFT second-order polarizability

Required quantities: <sup>3</sup>

$$V''_{IJK} = \frac{1}{2} \text{Tr}[(I - 2\rho_0)((\xi_J \xi_K + \xi_K \xi_J)V''(\xi_I) + (\xi_I \xi_J + \xi_J \xi_I)V''(\xi_K) + (\xi_I \xi_K + \xi_K \xi_I)V''(\xi_J))]$$

with

$$V''(\xi_I)(\mathbf{r})\xi_J = V'[\xi_I](\mathbf{r})\xi_J + V''_{nl}[\xi_I, \xi_J](\mathbf{r})\rho_0(\mathbf{r})$$

$$V'[\xi_I](\mathbf{r}) = \int d\mathbf{r}' f_{xc}[\rho](\mathbf{r}, \mathbf{r}')\xi_I(\mathbf{r}')$$

$$V''_{nl}[\xi_I, \xi_J](\mathbf{r}) = \int d\mathbf{r}' \int d\mathbf{r}'' g_{xc}[\rho](\mathbf{r}, \mathbf{r}', \mathbf{r}'')\xi_I(\mathbf{r}')\xi_J(\mathbf{r}'')$$

and

$$\rho_{I,JK}(\mathbf{r}) = -\xi_I(\xi_J \xi_K + \xi_K \xi_J)(\mathbf{r}).$$

<sup>3</sup>S. Tretiak and S. Mukamel, *Chem. Rev.*, **102**, 3171 (2002); S. Tretiak and V. Chernyak, *J Chem Phys*, **119**, 8809 (2003); I. T, B.F.E. Curchod, A. Laktionov, and U. Rothlisberger, *J. Chem. Phys.*, **133**, 194104 (2010)..

## TDDFT second-order polarizability

Using the following definition of the dipole matrices

$$\mu_I = \text{Tr}([\rho_0, \xi_I][\mu, \rho_0])$$

$$\mu_{IJ} = \text{Tr}([\rho_0, \xi_I][\mu, \xi_J])$$

the second-order polarizability within TDDFT becomes

$$\begin{aligned} \beta^{(\alpha\beta\gamma)}(\omega_1, \omega_2) = & - \sum_{IJK=-M}^M \frac{V''_{-IJK} \mu_I^{(\alpha)} \mu_{-J}^{(\beta)} \mu_{-K}^{(\gamma)} s_I s_J s_K}{(\Omega_I - \omega_1 - \omega_2)(\Omega_J - \omega_1)(\Omega_K - \omega_2)} + \frac{1}{2} \sum_{IJ=-M}^M \frac{\mu_{-IJ}^{(\beta)} \mu_I^{(\alpha)} \mu_{-J}^{(\gamma)} s_I s_J}{(\Omega_I - \omega_1 - \omega_2)(\Omega_J - \omega_1)} \\ & + \frac{1}{2} \sum_{IJ=-M}^M \frac{\mu_{-IJ}^{(\beta)} \mu_I^{(\alpha)} \mu_{-J}^{(\gamma)} s_I s_J}{(\Omega_I - \omega_1 - \omega_2)(\Omega_J - \omega_2)} + \frac{1}{2} \sum_{IJ=-M}^M \frac{\mu_{IJ}^{(\alpha)} \mu_{-I}^{(\beta)} \mu_{-J}^{(\gamma)} s_I s_J}{(\Omega_I - \omega_1)(\Omega_J - \omega_2)} \end{aligned}$$

where  $\alpha, \beta, \gamma \in \{x, y, z\}$ , and  $\mu_{-IJ}$  is the transition dipole between states  $I$  and  $J$  for which  $\mu_I = \mu_{-I}^*$  and  $\mu_{-IJ} = \mu_{-JI}^*$

However, this is NOT a SOS formula (coupling terms  $V''_{-IJK}$ ).

## Bosonization of the TDDFT second order response

Mukamel, Tretiak, Chernyak and Berman propose a classical system of coupled harmonic oscillators (bosons) that shares the same linear and second-order response properties of TDDFT.

$$\sum_{\sigma} \hat{c}_{r\sigma}^{\dagger} \hat{c}_{s\sigma} \longrightarrow \sum_{\sigma} \tilde{c}_{r\sigma}^{\dagger} \tilde{c}_{s\sigma}$$

Comparing term-by-term  $\beta_{MBPT}^{\text{SOS}}$  with  $\beta_{TDDFT}^{(B)\text{SOS}}$

$$\langle \Psi_0 | \sum_{\sigma} \hat{c}_{r\sigma}^{\dagger} \hat{c}_{s\sigma} | \Psi_0 \rangle = (\rho_0)_{rs}$$

$$\langle \Psi_0 | \sum_{\sigma} \hat{c}_{r\sigma}^{\dagger} \hat{c}_{s\sigma} | \Psi_I^{(1)} \rangle = (\xi_I)_{rs}$$

$$\langle \Psi_0 | \sum_{\sigma} \hat{c}_{r\sigma}^{\dagger} \hat{c}_{s\sigma} | \Psi_{IJ}^{(2)} \rangle = \frac{1}{\sqrt{1 + \delta_{IJ}}} \left[ ([[\xi_I, \rho_0], \xi_J])_{rs} + \sum_{K>0} \left( \frac{V''_{IJ-K}(\xi_K)_{rs}}{\Omega_I + \Omega_J - \Omega_K} - \frac{V''_{IJK}(\xi_K^{\dagger})_{rs}}{\Omega_I + \Omega_J + \Omega_K} \right) \right]$$

$$\langle \Psi_I^{(1)} | \sum_{\sigma} \hat{c}_{r\sigma}^{\dagger} \hat{c}_{s\sigma} | \Psi_J^{(1)} \rangle = (\rho_0)_{rs} \delta_{IJ} + ([[\xi_I^{\dagger}, \rho_0], \xi_J])_{rs} + \sum_{K>0} \left( \frac{V''_{-IJ-K}(\xi_K)_{rs}}{\Omega_J - \Omega_I - \Omega_K} - \frac{V''_{I-J-K}(\xi_K^{\dagger})_{rs}}{\Omega_J - \Omega_I + \Omega_K} \right)$$

where  $\xi_j^{\dagger} = \xi_{-j}$ .

## The auxiliary many-electron wavefunction approach

Considering only terms up to second order in  $\mathbf{Z}_I$  where ( $\mathbf{Z}_I \sim \mathbf{X}_I + \mathbf{Y}_I$ ) we compare results for  $\langle \Psi_J | \hat{O} | \Psi_I \rangle$  obtained using the “bosonization” (B) and the “auxiliary wavefunctions” (AX) schemes:

$$\begin{aligned} \langle \Psi_{ia}^J | \hat{O} | \Psi_{jb}^I \rangle_B &= -Tr_o(\mathbf{Y}_J^\dagger \mathcal{O}_o \mathbf{Y}_I) + Tr_v(\mathbf{X}_J \mathcal{O}_v \mathbf{X}_I^\dagger) - Tr_o(\mathbf{X}_I^\dagger \mathcal{O}_o \mathbf{X}_J) + Tr_v(\mathbf{Y}_I \mathcal{O}_v \mathbf{Y}_J^\dagger) \\ \langle \Psi_{ia}^J | \hat{O} | \Psi_{jb}^I \rangle_{AX} &= \sum_{ia} \sum_{jb} c_{ia}^{J\dagger} c_{jb}^I \langle \tilde{\Psi}_{ia}^J | \hat{O} | \tilde{\Psi}_{jb}^I \rangle \\ &= \left[ Tr_v(\mathbf{X}_\beta \mathcal{O}_v \mathbf{X}_I^\dagger) + Tr_v(\mathbf{Y}_\beta \mathcal{O}_v \mathbf{X}_I^\dagger) + Tr_v(\mathbf{X}_\beta \mathcal{O}_v \mathbf{Y}_I^\dagger) + Tr_v(\mathbf{Y}_\beta \mathcal{O}_v \mathbf{Y}_I^\dagger) \right] \\ &\quad - \left[ Tr_o(\mathbf{X}_I^\dagger \mathcal{O}_o \mathbf{X}_J) + Tr_o(\mathbf{X}_I^\dagger \mathcal{O}_o \mathbf{Y}_J) + Tr_o(\mathbf{Y}_I^\dagger \mathcal{O}_o \mathbf{X}_J) + Tr_o(\mathbf{Y}_I^\dagger \mathcal{O}_o \mathbf{Y}_J) \right]. \end{aligned}$$

The second solution is more symmetric with respect to the  $ph$  and  $hp$  transitions than the one obtained from the bosonization (AX contains terms of the form  $\mathbf{X}_I \mathcal{O} \mathbf{Y}_J$ ).

In "TDA" ( $\mathbb{B} = 0$ ) the two solutions coincide.

## Nonadiabatic couplings between excited states

The (AX) representation of the matrix elements  $\langle \Psi_{ia}^J | \hat{O} | \Psi_{jb}^I \rangle$  is used to compute nonadiabatic coupling vectors between excited states along nonadiabatic trajectories.<sup>4</sup>

$$\begin{aligned} \langle \Psi_{ia}^J | \nabla_R \hat{\mathcal{H}} | \Psi_{jb}^I \rangle &= \sum_{ab} (X_J^\dagger X_I + X_J^\dagger Y_I + Y_J^\dagger X_I + Y_J^\dagger Y_I)_{ab} \langle \phi_b | \nabla_R \hat{\mathcal{H}} | \phi_a \rangle \\ &\quad - \sum_{ij} (X_I X_J^\dagger + Y_I X_J^\dagger + X_I Y_J^\dagger + Y_I Y_J^\dagger)_{ji} \langle \phi_i | \nabla_R \hat{\mathcal{H}} | \phi_j \rangle. \end{aligned}$$

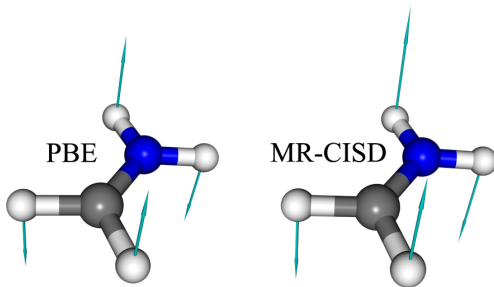
The numerical evaluation of the matrix elements  $\langle \phi_b | \nabla_R \hat{\mathcal{H}} | \phi_a \rangle$  is done as in the case of couplings with the ground state.

<sup>4</sup>I.T., E. Tapavicza, U. Rothlisberger, *J. Chem. Phys.* **130**, 124107 (2009); I. T, B.F.E. Curchod, A. Laktionov, and U. Rothlisberger, *J. Chem. Phys.*, **133**, 194104 (2010).

## Nonadiabatic couplings - examples

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

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

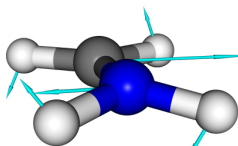


Protonated formaldimine: nonadiabatic coupling vectors  $\mathbf{d}_{01}$  with LR-TDDFT/TDA.

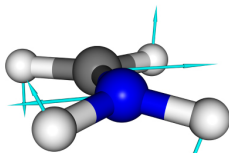
## Nonadiabatic couplings - examples

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

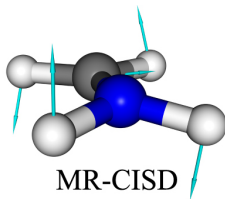
$$\mathbf{d}_{kj}[\{\phi.\}] = \langle \tilde{\Phi}_k(\mathbf{R}) | \nabla_{\mathbf{R}} | \tilde{\Phi}_j(\mathbf{R}) \rangle$$



PBE



PBE0



MR-CISD

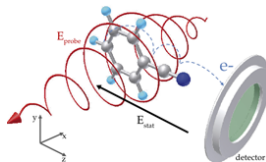
Protonated formalimine:  
TDDFT/TDA.

nonadiabatic coupling vectors  $\mathbf{d}_{12}$  with LR-

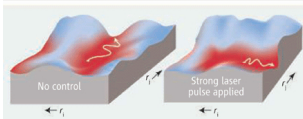
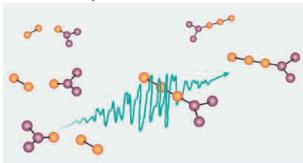


## Coupling with the environment

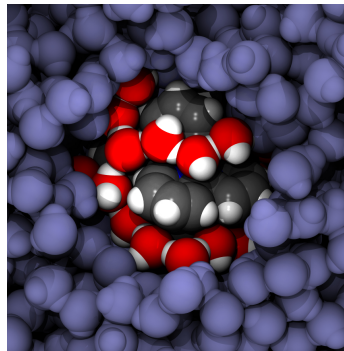
Explicit (time-dependent) laser fields



... optimal control ...



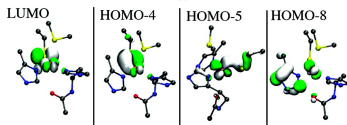
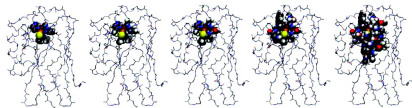
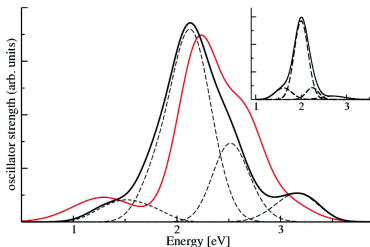
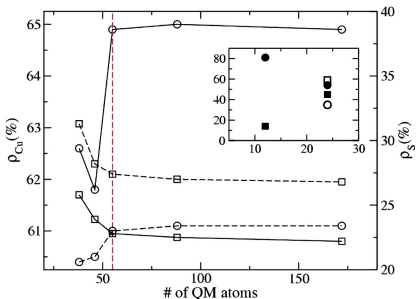
QM/MM static coupling with liquid and solid phases



[A. Laio, J. VandeVondele, and U. Rothlisberger, J. Chem. Phys. 116, 6941 (2002); A. Laio, J. VandeVondele, and U. Rothlisberger, J. Phys. Chem. B, 106, 7300, (2002); M. Colombo et al. CHIMIA 56, 11 (2002)].

## Environment (QM/MM) and sampling is crucial

Calculation of the QM/MM coupling using  $\delta\rho^{LR-TDDFT}(\mathbf{r})$ :  
 IT, B. Curchod, U. Rothlisberger, *Chem. Phys.* **391**, 101 (2011).



M. Casella, M.A. Cuendet, I.T., U. Rothlisberger, *JPC B*, **111**, 10248 (2007)

## Coupling with td electric fields [B. Curchod]

### The Interaction Hamiltonian

In the Born-Oppenheimer approximation for the separation of electronic and nuclear degrees of freedom (which is assumed in Tully's dynamics), the total (non relativistic) Hamiltonian is given by

$$H_{tot} = H_{mol} + H_{rad} + H_{int}$$

where the interaction Hamiltonian (with no spin-magnetic field contributions) is obtained from the standard prescription  $\mathbf{p} \rightarrow \mathbf{p} - e\mathbf{A}/c$ ,

$$H_{int} = \sum_i \left[ -\frac{e}{2mc} (\mathbf{p}_i \cdot \mathbf{A}(\mathbf{r}_i, t) + \mathbf{A}(\mathbf{r}_i, t) \cdot \mathbf{p}_i) + \frac{e^2}{2mc^2} \mathbf{A}(\mathbf{r}_i, t) \mathbf{A}(\mathbf{r}_i, t) \right].$$

The vector potential is of the form  $\mathbf{A} = A_0 \epsilon^\lambda e^{-ik \cdot \mathbf{r} + i\omega t}$

In the *dipole approximation*, the TSH equations

$$i\hbar\dot{C}_J = \sum_I C_I (H_{JI} - i\hbar\dot{\mathbf{R}} \cdot \mathbf{d}_{JI})$$

become

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

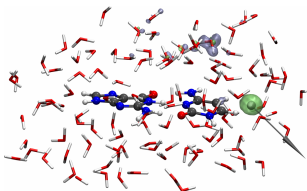
In addition, a classical electrostatic interaction term of the form

$$E^{nucl}(\mathbf{R}^\alpha) = - \sum_K Z_K \mathbf{R}_K \cdot \mathbf{E}(t),$$

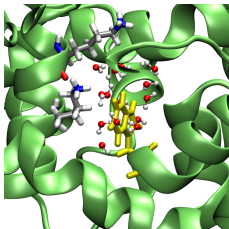
with  $\mathbf{E}(t) = -\frac{1}{c} \frac{\partial}{\partial t} \mathbf{A}(t)$  is added to the potential energy of the nuclei, which, according to Tully's scheme, follow a "classical" trajectory on a single PES with possible surface hops according to the hopping probability  $g_{JI}$ .

[Ref: IT, BFE Curchod, U. Rothlisberger, *PRA*, 81, 052508 (2010)]

### Radiation damage in DNA



### Photostability of proteins

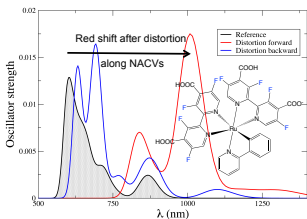


### Protein/DNA interaction

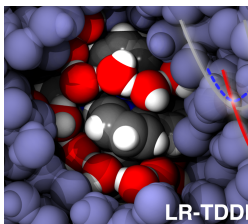


AAG-DNA (1EWN)

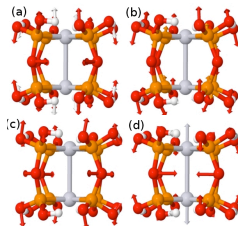
### NACV in design of new dyes



### Ultrafast spectroscopy



### Excited states vibr. dynamics



Collaboration: T. Penfold and M. Chergui

# Quantum optimal control theory

Optimal control theory can be formulated in the framework of **Ehrenfest mean-field** and **semiclassical** approaches.

Like in the solution of the semiclassical path-integral equations (Pechukas), QOCT requires the self-consistent solution of forward and backward propagation of Schrödinger-like equations:

$$\begin{aligned}
 i \frac{\partial}{\partial t} \psi(t) &= [H_0 - \mu \epsilon(t)] \psi(t), \quad \text{i.c.} \quad \psi(0) = \psi_0 \\
 i \frac{\partial}{\partial t} \chi(t) &= [H_0 - \mu \epsilon(t)] \chi(t), \quad \text{i.c.} \quad \chi(T) = \frac{\partial \mathcal{O}}{\partial \psi^*(T)} \\
 \alpha(t) \epsilon(t) &= -\text{Im} \langle \chi(t) | \mu | \psi_t \rangle
 \end{aligned}$$

where  $\mathcal{O}$  is the to-be-optimized quantity,  $\psi(\mathbf{r})$  is the system wavefunction,  $\epsilon(t)$  is the shaped laser field,  $\alpha(t)$  is a "switching function", and  $\chi(\mathbf{r}, t)$  is an auxiliary wavefunction.

## Local control theory [B. Curchod, T. Penfold]

Local control, is formulated in the framework of **Trajectory Surface Hopping** (TSH).

The time evolution of the expectation value of an arbitrary operator  $\hat{O}$  (Heisenberg representation) is given by

$$\begin{aligned} \dot{O}(t) = & \frac{i}{\hbar} \int \Psi^*(\mathbf{r}, \mathbf{R}, t) [\hat{H}_0, \hat{O}] \Psi(\mathbf{r}, \mathbf{R}, t) d\mathbf{r} d\mathbf{R} \\ & + \frac{i}{\hbar} \int \Psi^*(\mathbf{r}, \mathbf{R}, t) [\hat{H}_{int}, \hat{O}] \Psi(\mathbf{r}, \mathbf{R}, t) d\mathbf{r} d\mathbf{R} \end{aligned}$$

The evolution of the state population operator  $\hat{P}_I = |I\rangle\langle I|$  in a time dependent electric field  $\mathbf{E}(t)$  is then (assuming  $[\hat{H}_0, \hat{\mu}] = 0$ )

$$\dot{P}_I(t) = -\mathbf{E}(t) \frac{i}{\hbar} \Im \left[ \int \Psi^*(\mathbf{r}, \mathbf{R}, t) [\hat{\mu}, \hat{P}_I] \Psi(\mathbf{r}, \mathbf{R}, t) d\mathbf{r} d\mathbf{R} \right].$$

## 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

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

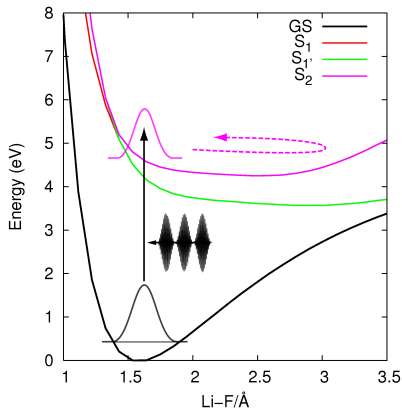
will ensure that  $\mathcal{P}_I(t)$  always increases in time.

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)

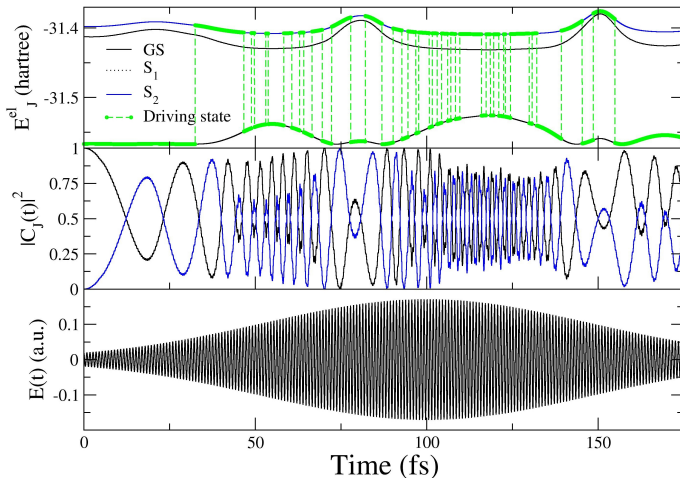


## Application: Photoexcitation of LiF in the bound state $S_2$

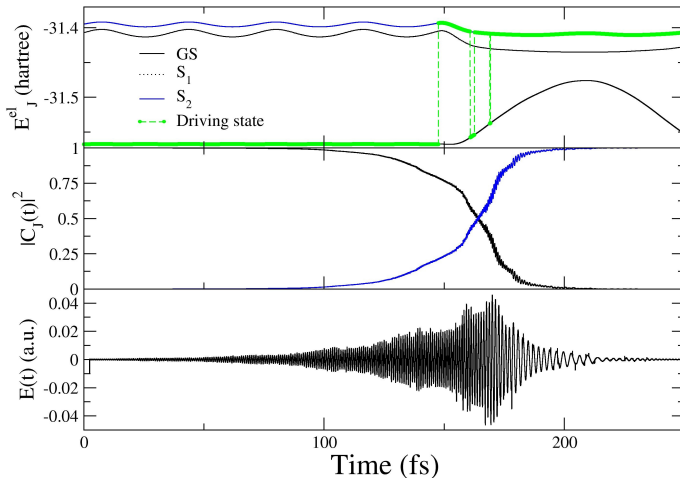


B.F.E Curchod, T. Penfold, U. Rothlisberger, IT, *PRA*, **84**, 042507 (2011)

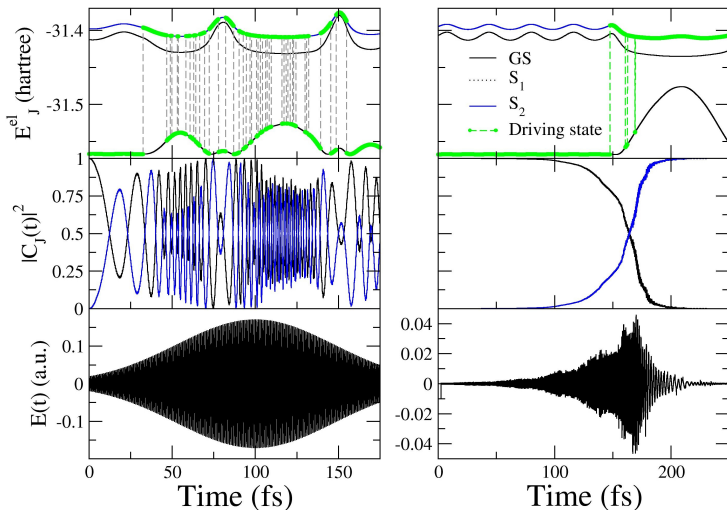
## Effect of a generic polarized pulse



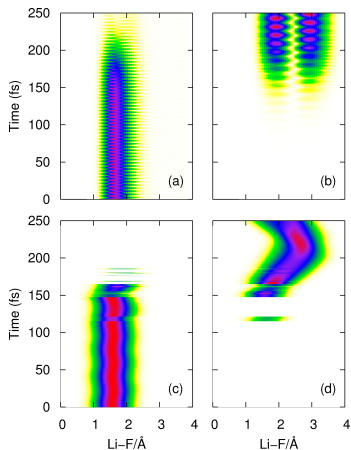
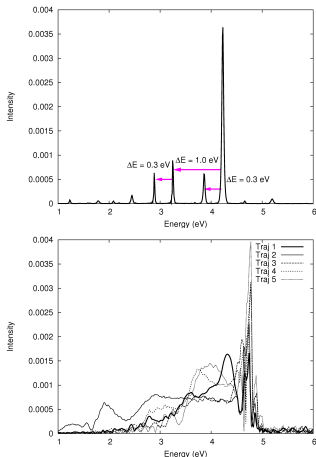
## LC pulse: efficient population transfer and stable excitation



## $\Pi$ pulse vs. optimized pulse (LC)

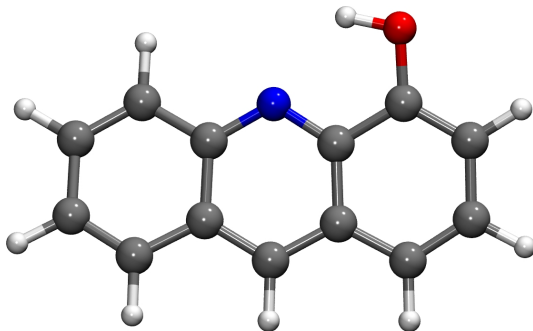


# Comparison with wavepacket propagation (MCTDH)

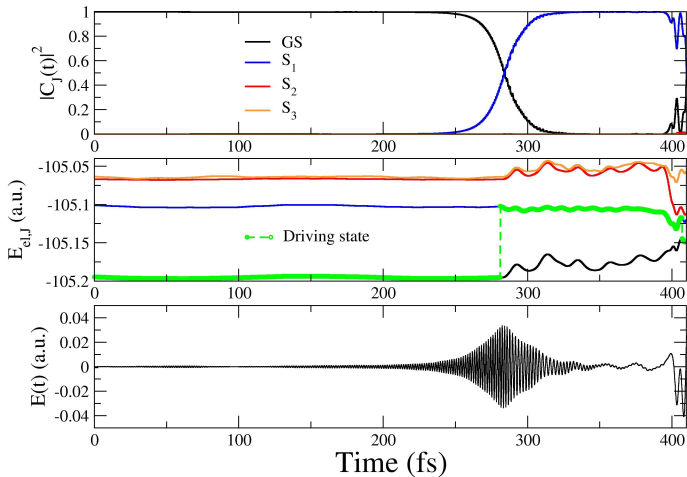


B.F.E Curchod, T. Penfold, U. Rothlisberger, *IT, PRA*, 84, 042507 (2011)

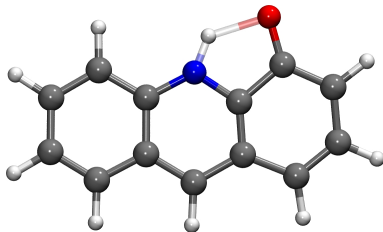
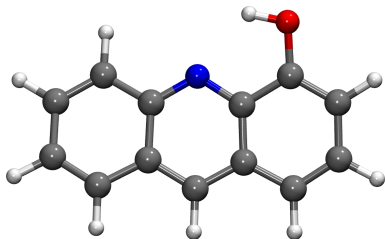
## Local control on proton transfer (in gas phase)



## Local control on proton transfer

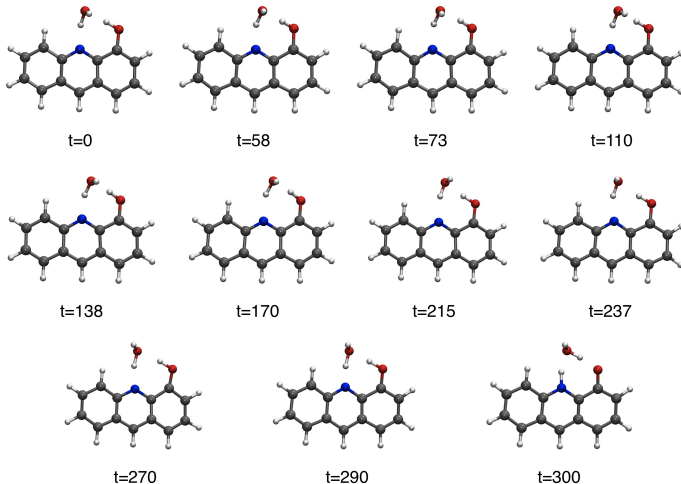


## Local control on proton transfer

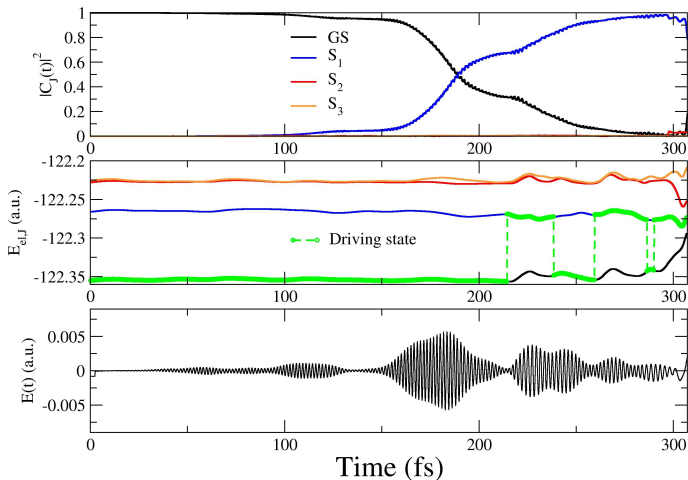




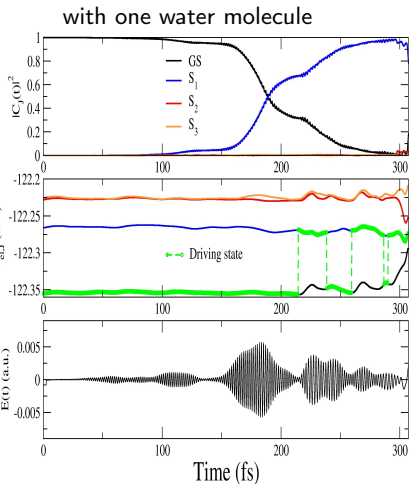
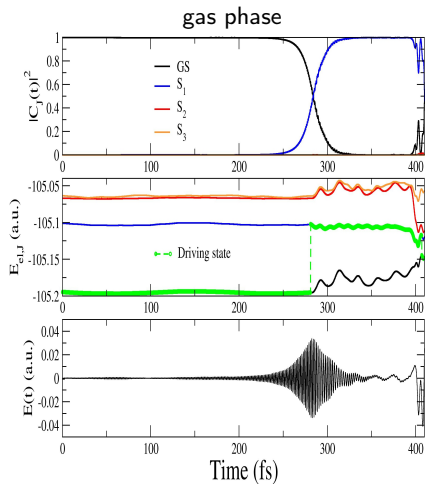
# Local control on proton transfer (with one water molecule)



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



# Local control on proton transfer (comparison)



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## Former group members

- Enrico Tapavicza (UC Irvine)
- Marc Etienne Moret (Caltech)

## Implementations & documentation

CPMD TDDFT/TSH (QM/MM + external EM field) available free of charge (for academics) from [www.cpmd.org](http://www.cpmd.org)



Turbomol Version by Vlasta Bonacic-Koutecky

Turbomol Implementation in the group of F. Furche (by Enrico Tapavicza). Soon available in the official release of the code.

CP2K Hopefully in the near future.

PetaChem Collaboration with Todd Martinez

Thank you for your attention