Non-adiabatic mixed quantum-classical dynamics using TDDFT

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Overview – the PES picture

Photochemistry and Photophysics

Photochemistry and photophysics are strongly dependent on the topology of the PESs.

grey: singlet states
dark: triplet state

a) singlet excitations  
b) energetic minimum  
c) saddle point  
d) avoided crossing  
e) conical intersection  
f) fluorescence  
g) phosphorescence
OVERVIEW

# Mixed Quantum-Classical Dynamics
  - Ehrenfest dynamics
  - Surface hopping

# TDDFT for PESs and molecular forces

# TDDFT based trajectory surface hopping
  - Non-adiabatic coupling vectors

# Approximations and implementation

# Applications
  - Protonated formaldimine: a test case
  - Photo-induced ring opening in oxirane
  - Intramolecular photo-induced proton transfer
Motivation

What are the requirements of an ab-initio method in order to have predictive power in:

Photophysics, photochemistry, photo-biology and photo-medicine?

1. Accurate energies (GS and excited states) and properties (for all relevant states)
   
   

2. Accurate topology of the potential energy surfaces (PES)

3. Accurate external potentials (including environment [QM/MM])

4. Sampling (statistical mechanics + molecular mechanics (MD))

5. Computational efficiency
Motivation

Spectroscopic properties of the Azurin

External potential effects

Sampling

Spin density

QM/MM-TDDFT spectra of Azurin
Averaged over 50 frames taken from a 20 ps production run at 300K.

Motivation

Hydrogen or proton transfer?

CIS/CASSCF for the in-plane geometry. Potential energy surfaces for GS, S_1 and S_2 along a reaction coordinate (fix C_5 symmetry).

\[ \text{(C.Tanner, C Manca, S. Leutwyler, Science, 302, 1736 (2003))} \]

TDDFT/PBE/TDA combined with non-adiabatic molecular dynamics.

Dynamics breaks symmetry.
The system remains in the \( \pi \pi^* \) state.
Proton transfer is observed (no hydrogen transfer).

Confirmed later by geometry optimizations at CASSCF/CASPT2 level:
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\[ \hbar \rightarrow 0 \]  for the nuclei only

(Does this limit exist?)
Mixed quantum-classical dynamics

Photochemistry and Photophysics
Mixed quantum-classical dynamics
Photochemistry and Photophysics

Mixed quantum-classical dynamics
Photochemistry and Photophysics

S₃
S₂
S₁
Absorption
Adiabatic photoreaction
Intersystem Crossing
T₁
Fluorescence
Fluorescence
Fluorescence
Phosphorescence
Photoproduct
Photoproduct
Small energy gap
Reactive
Mixed quantum-classical dynamics

Photochemistry and Photophysics

Diagram showing energy levels $S_0$, $S_1$, $S_2$, $S_3$ with transitions to $T_1$ and intersystem crossing, leading to absorption, fluorescence, phosphorescence, and reactive photoproducts. The diagram illustrates small energy gaps and adiabatic photoreactions.
Mixed quantum-classical dynamics

Photochemistry and Photophysics
Mixed quantum-classical dynamics

Photochemistry and Photophysics
Mixed quantum-classical dynamics

Photochemistry and Photophysics

How to look at this type of dynamics using classical trajectories?
Mixed quantum-classical dynamics

Multi-component wavefunction-based formulation

\{ r, m \}  \quad \text{fast degrees of freedom}
\{ \mathbf{R}, M_I \}  \quad \text{slow degrees of freedom}

- **Mean-field (Ehrenfest-type) dynamics**

\[
\Psi(\mathbf{r}, \mathbf{R}, t) = \Phi(\mathbf{r}, t) \Omega(\mathbf{R}, t) e^{i \frac{\hbar}{\mathcal{E}}} \int_{t_0}^{t} E_{el}(t') dt
\]

\[
E_{el}(t') = \int \int d\mathbf{r} d\mathbf{R} \; \Phi^{*}(\mathbf{r}, t) \Omega^{*}(\mathbf{R}, t) \mathcal{H}_{el} \Phi(\mathbf{r}, t) \Omega(\mathbf{R}, t)
\]

- **Surface hopping (SH)**

\[
\Psi(\mathbf{r}, \mathbf{R}, t) = \sum_{i} \Phi_{i}(\mathbf{r}; \mathbf{R}) \Omega_{i}(\mathbf{R}, t)  \quad \text{sum over states}
\]

\( \Phi_{i}(\mathbf{r}; \mathbf{R}) \quad \text{Solutions of the time-independent Schrödinger equation}
\]

\( \text{(depend only parametrically on nuclei positions)} \)
Mixed quantum-classical dynamics

The Hamilton-Jacobi formulation

\[ \mathcal{H}_{\text{tot}} = - \sum_i \frac{\hbar^2}{2M_i} \nabla_i^2 - \sum_i \frac{\hbar^2}{2m} \nabla_i^2 + V_{eN}(r, R) = - \sum_i \frac{\hbar^2}{2M_i} \nabla_i^2 + \mathcal{H}_{e}(r; R) \]

\[ \Psi(r, R, t) = \sum_i \Phi_i(r; R) \Omega_i(R, t) \] in the time-dependent Schrödinger equation gives:

> **Nuclei** \[ \Omega_i(R, t) = A_i(R, t) e^{i \frac{\hbar}{\theta} S_i(R, t)} \]

\[ \left\{ \begin{array}{l}
- \frac{\partial A_i}{\partial t} = F(A_j, \nabla_i A_j, S_j, \nabla_i S_j) + \sum_{i \neq j} A_j \left[ \sum_I \hat{\mathbf{r}} \cdot \mathbf{d}_{ji}^I + \frac{i}{\hbar} H_{ji} \right] e^{-\frac{\hbar}{\hbar} \int_{t_0}^{t} \mathcal{d} \tau (H_{ii} - H_{ji})} \\
- \frac{\partial S_j}{\partial t} = \sum_I \frac{1}{2M_i} (\nabla_i S_j)^2 + H_{ii} \end{array} \right. \] (Hamilton-Jacobi equation)

Motion evolves on each potential energy surface, with transport of flux between potential surfaces governed by the off-diagonal terms, \( \mathbf{d}_{ji}^I \) and \( H_{ji} \).

The exact solution for \( \# \) does not exist.

> **Electrons** are NOT dynamical: PESs computed on-the-fly.
Trajectory surface hopping: Tully’s scheme
Quantum trajectories solution of the HJ equations

Discretization of the nuclear wavefunction and evolution of the quantum trajectories

\[- \frac{\partial A_j}{\partial t} = F(A_j, \nabla_I A_j, S_j, \nabla_I S_j) + \sum_{i \neq j} A_j \left[ \sum_{l} \left( \dot{\mathbf{R}} \cdot \mathbf{d}_{ji}^l + \frac{i}{\hbar} H_{ji} \right) e^{-\frac{i}{\hbar} \int_{t_0}^{t} d\tau (H_{ii} - H_{jj})} \right] \]
**Trajectory surface hopping: Tully’s scheme**

**Independent trajectory approximation: ITA**

In the independent trajectory approximation each quantum trajectory is evolved independently from all the others (missing coherence/decoherence effects) and the amplitudes can only change through the coupling between different surfaces:

$$-\frac{\partial A_j}{\partial t} = F(A_j, \nabla A_j, S_j, \nabla S_j) + \sum_{i \neq j} A_j \left[ \sum_l \hat{R} \cdot \hat{d}_{ji}^l + \frac{i}{\hbar} H_{ji} \right] e^{-\frac{i}{\hbar} \int_{t_0}^t d\tau (H_{ii} - H_{jj})}$$

Tully has introduced a stochastic algorithm that (after taking the limit $\hbar \rightarrow 0$) decide about which surface should drag the “classical” nuclear dynamics at any instant of time.

Tully’s Surface Hopping probability:

$$P_{i,j}(t, dt) \approx -2 \int_t^{t+dt} d\tau \frac{\mathbb{R}[\tilde{A}_j(\tau)\tilde{A}_i^*(\tau)(\hat{R} \cdot \hat{d}_{ji})(\tau)]}{A_i(\tau)A_j(\tau)}$$

where

$$\hat{R} \cdot \hat{d}_{ij}^l(R) = \langle \Phi_i | \frac{\partial}{\partial t} \Phi_j \rangle = \frac{\partial \mathbb{R}_l}{\partial t} \langle \Phi_i | \frac{\partial}{\partial \mathbb{R}_l} \Phi_j \rangle$$

are the non-adiabatic coupling elements.

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Trajectory surface hopping: Tully’s scheme
Independent trajectory approximation: ITA

In the “independent trajectory approximation” of J. Tully, a SINGLE trajectory follows adiabatically a PES \((i)\) until a transition to a different surface \((j)\) is accepted with a given probability (Monte Carlo step).

A swarm of independent classical trajectories will then reproduce the approximate dynamics of the amplitude of the nuclear wavefunction.

The algorithm “guarantee” that at any instant in time for an ENSEMBLE of trajectories, the fraction of trajectories assigned to any PES is approximately equal to the relative population of the state \(|A_k(t)|^2\).

We replace nuclear wavefunctions with an ensemble of classical trajectories.

Trajectory surface hopping: Tully's scheme

Independent trajectory approximation: ITA
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The time dependent Kohn-Sham equations (Ehrenfest-type of dynamics)

The Runge-Gross theorem leads to following time dependent Kohn-Sham equations

\[
\left[ -\frac{1}{2} \nabla^2 + v_{\text{ext}}(r, t) + v_{\text{ions}}(R, t) + v_H(r, t) + v_{xc}(r, t) \right] \phi_i(r, t) = i \frac{\partial}{\partial t} \phi_i(r, t)
\]

which are related to the time density \( \rho(r, t) = \sum_i f_i |\phi_i(r, t)|^2 \)

The Kohn-Sham potential \( v_s(r, t) \) is defined by the requirement that it yields the same density as in the ‘real’ interacting system.

Applications to periodic systems:

- Dielectric constant of liquid water
  
  \textit{I.T., PRB 73, 094204 (2006)}

- Coulomb explosion in liquid water
  
  Time-Dependent Density Functional Theory Molecular Dynamics Simulations of Liquid Water Radiolysis

  \textit{CHEMPHYSCHEM in press (2008)}

**TDDFT based TSH**

**DFT and TDDFT potential energy surfaces**

TDDFT in the linear response approximation

\[
\rho'(r, \omega) = \int d^3r' \chi(r, r', \omega) \nu'(r, \omega)
\]

\[
\chi^{-1}(r, r', \omega) = \chi_{KS}^{-1}(r, r', \omega) - \frac{1}{|r - r'|} - f_{xc}(r, r', \omega)
\]

The poles of \( \chi^{-1}(r, r', \omega; R_I) \) are the excitation energies of the system. \( f_{xc}(r, r', \omega) \) is the TDDFT kernel and is known exactly for the HEG.

1. Casida equations

\[
\begin{bmatrix}
A(\omega) & B(\omega) \\
B(\omega) & A(\omega)
\end{bmatrix}
\begin{bmatrix}
\vec{X}_I \\
\vec{Y}_I
\end{bmatrix} = \omega_I \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \begin{bmatrix} \vec{X}_I \\ \vec{Y}_I \end{bmatrix}.
\]


\[
\phi_{i\sigma}(r, t) \to \phi_{i\sigma} + \lambda \phi_{i\sigma}^{\pm}(r, t) \quad \rho^{(1)}(r, t) = \sum_{i\sigma} \phi_{i\sigma}(r) \phi_{i\sigma}^{\pm}(r, t) + \phi_{i\sigma}(r, t) \phi_{i\sigma}^{\pm}(r)
\]

\[
\sum_{ij}^{N_o} (H_{KS} \delta_{ij} - \epsilon_{ij}) \phi_{j\sigma}^{\pm} + \delta \nu_{SCF}^{\pm}(\pm \omega) |\phi_i\rangle = \mp \omega_k |\phi_i^{\pm}\rangle
\]

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Adiabatic approximation (ALDA)

\[
v_{xc}^{ALDA}[n](r, t) = v_{xc}^{GS}[n](r)|_{n=n(r,t)} = \frac{\delta \varepsilon_{xc}[n]}{\delta n}|_{n=n(r,t)}
\]

\[
f_{xc}^{ALDA}[n](r, r', t-t') = \delta(r-r') \delta(t-t') f_{xc}^{GS}[n]|_{n=n(t)}
\]

Properties and failures of the TDDFT functionals

- Naturally the TDDFT functionals retain all the problems of the ground state functionals
- Especially important are the limitations introduced by the wrong asymptotic (charge transfer excitations) and the SIC correction (charge localization)
- Non-locality (in space) is needed to include retardation \( \omega \neq 0 \)
  
  Vignale and Kohn proved that non-locality (in space) can be circumvented using \textit{current density functional theory} (TDCDFT)
- Computational efficiency requires local kernels

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TDDFT based TSH
On-the-fly semi-classical Molecular Dynamics

For a given electronic state the forces on the ions can be computed from the Hellmann-Feynman Theorem

\[ F_I = -\nabla_I \langle \Psi_0 | \mathcal{H}_{el} | \Psi_0 \rangle = - \langle \nabla_I \Psi_0 | \mathcal{H}_{el} | \Psi_0 \rangle - \langle \Psi_0 | \nabla_I \mathcal{H}_{el} | \Psi_0 \rangle - \langle \Psi_0 | \mathcal{H}_{el} | \nabla_I \Psi_0 \rangle \]

within KS-DFT

\[ E = \frac{\langle \Psi_0 | \mathcal{H}_{el} | \Psi_0 \rangle}{\langle \Psi_0 \Psi_0 \rangle} = \left( \sum_i \frac{1}{2} \nabla_i^2 \right) + \left( \frac{1}{2} \sum_{i \neq j} \frac{1}{|r_i - r_j|} \right) + \int d^3r V_{\text{ext}}(r) n(r) + \frac{1}{2} \sum_{i \neq j} \frac{Z_i Z_j e^2}{|R_i - R_j|} \]

\[ F_I = -\nabla_I E = - \int d^3r n(r) \nabla_I V_{\text{ext}} - \nabla_I \left( \frac{1}{2} \sum_{i \neq j} \frac{Z_i Z_j e^2}{|R_i - R_j|} \right) \]

Within linear response TDDFT, ionic forces for excited potential energy surfaces can be computed using the extended Lagrangian formalism (J. Hutter, JCP, 118, 3928, 2003)

\[ F_I = \frac{dE_{GS}^{K_S}(\rho, \rho_1, R_I)}{dR_I} + \frac{d\omega(\rho, \rho_1, R_I)}{dR_I} + \sum_{\alpha \sigma} Z_{a \sigma} \frac{\partial H_{K_S}^\sigma}{\partial R_I \phi_0^\sigma} \]

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TDDFT based TSH

Literature on DFT/TDDFT based non-adiabatic coupling methods

- Density-matrix representation of nonadiabatic couplings in TDDFT
- Real time TDDFT
- Finite differences of 1 electron KS-orbitals, using Slater Transition State theory
- Non-adiabatic (memory effects in $f_{xc}$) TDDFT
- Fictitious electron dynamics of ROKS Car-Parrinello MD
- Finite differences of single Slater determinants
- Restricted open shell Kohn-Sham (ROKS)
- NAC vectors by LR-TDDFT
- Finite differences of linear combination of Slater determinants:

$\omega$: LR-TDDFT excited state energies
$F_j$: LR-TDDFT ionic forces
NAC: NACs computed from a reconstruction of a many body wavefunction (from LT-TDDFT quantities)
DFT/TDDFT based TSH
A multi-determinant expansion of the excited wavefunction

Outline of the derivation

Dynamic dipole polarizability:

In many-body theory

\[
\alpha_{xz}(\omega) = \sum_I \frac{2(E_I - E_0) \langle \Psi_0 | \hat{x} | \Psi_I \rangle \langle \Psi_I | \hat{x} | \Psi_0 \rangle}{(E_I - E_0)^2 - \omega^2}
\]

In TDDFT

\[
\alpha_{xz}(\omega) = 2 \sum_I x^I S^{-1/2} \frac{e^I e^I}{\omega_I^2 - \omega^2} S^{-1/2} z
\]

\[
\langle \Phi_0 | \hat{a}_{i\sigma}^+ \hat{a}_{a\sigma} | \Psi_I \rangle = \sqrt{\frac{\varepsilon_{a\sigma} - \varepsilon_{i\sigma}}{\omega_I}} e^I e^I_{a\sigma} \equiv c^I_{ia}
\]

\[
|\Psi_I \rangle = \sum_{ia} c^I_{ia} \hat{a}_{a\sigma}^+ \hat{a}_{i\sigma} |\Phi_0 \rangle
\]

|\Phi_0 \rangle is a Slater determinant made of occupied KS states.

|\Psi_I \rangle is a linear combination of singly excited Slater determinants.

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The excited many-electrons wavefunctions can now be approximated as:

$$|\Phi_0\rangle = \frac{1}{\sqrt{N_e!}} \sum_P (-1)^P P\phi_{\alpha_1}(1) \ldots \phi_{\alpha_N}(N)$$

The ground state many-electrons wavefunction can be approximated using a single Slater determinant made of occupied KS-orbitals

$$|\Phi(t)\rangle = A_0(t)|\Phi_0\rangle + \sum_{i=1}^{\text{far all excited states}} A_i(t)|\Psi_i(r; R)\rangle$$

The excited many-electrons wavefunctions can now be approximated as:

$$|\Psi_i(r; R)\rangle \approx \sum_{\alpha=1}^{N_o} \sum_{v=N_o+1}^{N_o+N_v} c^i_{ov} \hat{a}^\dagger_v \hat{a}_\alpha |\Phi_0(r; R)\rangle = \sum_{\alpha=1}^{N_o} \sum_{v=N_o+1}^{N_o+N_v} c^i_{ov} |\Phi^v_\alpha(r; R)\rangle$$

$$c^A_{ov} = \sqrt{\frac{\epsilon_{vv} - \epsilon_{oo}}{\omega_A}} \langle \phi^+_v | \phi^\alpha_o \rangle$$

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DFT/TDDFT based TSH
A summary

**LR-TDDFT equations**

\[
\sum_{ij}^{N_o} (H^{KS}_{ij} \delta_{ij} - \epsilon_{ij}) |\phi_j^{\pm}\rangle + \delta V^{SCF} (\pm \omega) |\phi_i\rangle = \mp \omega k |\phi_i^{\pm}\rangle
\]

Ansatz for excited many-electrons state vectors:

\[
|\Phi(t)\rangle = A_0(t)|\Phi_0\rangle + \sum_{i=1}^{N_o} A_i(t)|\Psi_A(r; R)\rangle = \sum_{o=1}^{N_o} \sum_{v=N_o+1}^{N_o+N_v} c_{ov}^A (\{\phi^{\pm}_o\}) |\Phi^v_o(r; R)\rangle
\]

In the ITA we obtained the TD equation for the occupation amplitudes

\[
i\hbar \dddot{A}_k(t) = \ddot{A}_k(t)\omega_k - i\hbar \sum_{j=0}^{N_{ad}} \ddot{A}_j(t) \dot{R} \cdot d_{kj}
\]

and the switching probability

\[
P_{i,j}(t, dt) \approx -2 \int_t^{t+dt} d\tau \frac{\Re[\dddot{A}_j(\tau) \ddot{A}_i^*(\tau) (\dot{R} \cdot d_{ji})(\tau)]}{A_A(\tau) A_j(\tau)}
\]

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Non adiabatic TDDFT coupling vectors

\[
\langle \psi_j | \nabla_{R_I} | \psi_k \rangle = \frac{\langle \psi_k | \nabla_{R_I} \hat{H}(R_I) | \psi_j \rangle}{\varepsilon_i - \varepsilon_k}
\]

\[
\nabla_R \hat{H}_{KS}[\rho](R) = \frac{\partial \hat{H}_{KS}[\rho](R)}{\partial R} \bigg|_{\rho} + \int d\mathbf{r} \frac{\delta \hat{H}_{KS}[\rho](R)}{\delta \rho(\mathbf{r})} \frac{\partial \rho(\mathbf{r})}{\partial R}
\]

First (explicit) term: 1. electrostatic interaction electrons-electrons, electrons-nuclei
2. local and non-local terms of the pseudopotentials for core-electrons

Second (implicit) term: zero for variational ground state
non-zero in general

Solutions

First (explicit) term: analytic derivatives

Second (implicit) term: density functional perturbation theory (DFPT)

Non adiabatic TDDFT coupling vectors

The ground state many-electrons wavefunction can be approximated using a single Slater determinant made of occupied KS-orbitals

$$|\Phi_0\rangle = \frac{1}{\sqrt{N_e!}} \sum_P (-1)^P P \phi_{\alpha_1}(1) \cdots \phi_{\alpha_N}(N)$$

The excited many-electrons wavefunctions are approximated with

$$|\Psi(t)\rangle = A_0(t)|\Phi_0\rangle + \sum_{k=1}^{N_e} A_k(t)|\Phi_k(r; R)\rangle$$

$$|\Phi_k(r; R)\rangle \approx \sum_{\alpha=1}^{N_o} \sum_{v=N_o+1}^{N_o+N_v} c_{\alpha v}^{k \dagger} \hat{a}_{\alpha} \hat{a}_{v} |\Phi_0(r; R)\rangle = \sum_{\alpha=1}^{N_o} \sum_{v=N_o+1}^{N_o+N_v} c_{\alpha v}^{k} |\Phi_{\alpha}^{0}(r; R)\rangle$$

$$c_{\alpha v}^{k} = \sqrt{\frac{\epsilon_{uv} - \epsilon_{\alpha 0}}{\omega_f}} \langle \phi_{\alpha}^{-} | \phi_{v} \rangle$$

Non adiabatic coupling vectors computed from the RHS of

$$\langle \Psi_j | \nabla R_f | \Psi_k \rangle = \frac{\langle \Psi_k | \nabla R_f \hat{H}(R_f) | \Psi_j \rangle}{\epsilon_i - \epsilon_k}$$

I.T., E. Tapavicza, U. Roethlisberger, in preparation
Non adiabatic TDDFT coupling vectors

Preliminary results: comparison with the ROKS (and CASSCF) results\(^{(1)}\)

\[ \begin{align*}
\text{NO}_2 & \quad \text{ROKS: singlet state} \\
\text{retinal} & \quad \text{TDDFT: mixed state} \\
\end{align*} \]

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Approximations

> The wavefunction expansion is valid to linear order

\[ |\Psi(t)\rangle = A_0(t)|\Phi_0\rangle + \sum_{i=1} A_i(t)|\Psi_A(r; R)\rangle = \sum_{o=1}^{N_o} \sum_{v=N_o+1}^{N_o+N_v} c_{ov}^A(\phi_\pm) |\Phi_o^v(r; R)\rangle \]

> The "scalar" non-adiabatic couplings are computed using a finite difference scheme

\[ \dot{R} \cdot d_{AB}|_{t+\Delta/2} = \frac{1}{2\Delta} \left[ \langle \Psi_A(r; R(t))|\hat{H}_{MBT}|\Psi_B(r; R(t+\Delta))\rangle - \langle \Psi_A(r; R(t+\Delta))|\Psi_B(r; R(t))\rangle \right] \]

> In the derivation of the differential equations for the coefficients \( A_k(t) \) we assumed that

\[ V_{AB} = \langle \Psi_A(r; R)|\hat{H}_{MBT}|\Psi_B(r; R)\rangle \approx \delta_{AB} \langle \Psi_A(r; R)|\hat{H}_{MBT}|\Psi_B(r; R)\rangle \]

and that

\[ \dot{V}_{AA} \equiv V_{AA} - \langle \Phi_0(r; R)|\hat{H}_{MBT}|\Phi_0(r; R)\rangle \approx \omega_{LR-TDDFT}^A \]

> Redistribution of the excess energy after a surface hop isotropically to all nuclear DoF

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Preparation of the initial conditions \( \{ \mathbf{R}_I, \dot{\mathbf{R}}_I \} \) of classical system according to the classical ensemble. Quantum system prepared in a pure state or in a coherent mixed state.

Calculation of the adiabatic eigenstates using LR-TDDFT.

Evolution of the classical variables through a timestep \( \Delta t \)

Evolution of the quantum expansion coefficients \( A_i(t) \) with a timestep \( dt \) \((<< \Delta t)\) in the classical time interval \( \Delta t \)

Reconstruction of the TDDFT excited wavefunctions and calculation of the hopping probabilities \( P_{ij}(t, \Delta t) \)

no

Monte Carlo step \( i \rightarrow j \) ?

yes

Change of the driving surface for the classical nuclei. Redistribution of the excess energy \( E_i(\mathbf{R}) - E_j(\mathbf{R}) \) among the classical DoF.
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The protonated formaldimine is a model compound for the study of isomerization in rhodopsin chromophore retinal.

\( S_1: \sigma \rightarrow \pi^* \) transition (low oscillator strength)
\( S_2: \pi \rightarrow \pi^* \) transition (high oscillator strength)

Photo-excitation promotes the system mainly into \( S_2 \) and therefore the relaxation occurring in the excited states involves at least 3 states:
\( S_0 \) (GS), \( S_1 \) and \( S_2 \)

Method
- Isolated system
- LR-TDDFT/PBE/TDA and ALDA
- SH-AIMD

Simulation of an ensemble of 50 trajectories (NVT) each of \(~100\) fs.
Statistical interpretation of the branching ratio.

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DFT/TDDFT based TSH - Applications

Isomerization of protonated formaldimine

Results

- Structures and life times are in good agreement with reference calculations performed using high level wavefunction based methods (MCSCF).

- In addition to the isomerization channel, we also observed intra-molecular proton transfer reactions with the formation of

\[ \text{CH}_2\text{NH}_2^+ \rightarrow \text{CH}_3\text{NH}^+ \]

followed by proton back-transfer and isomerization after relaxation in \( S_0 \).

- H2 abstraction is also observed in some cases (suppressed when head dissipation is enhanced)

The different reaction channels have been experimentally observed.

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  - Intramolecular photo-induced proton transfer
DFT/TDDFT based TSH - Applications

Oxirane: excited state ring opening reaction

A textbook explanation based on symmetry arguments

But in the reality the situation can be much more complicated …


DFT/TDDFT based TSH – Applications

Oxirane: excited state ring opening reaction

Topology of the recombination and dissociation of Oxirane:
Complexity of the configurational space of a 7 atoms molecule.

DFT/TDDFT based TSH - Applications

Oxirane: excited state ring opening reaction

Product distribution from mass spectrometry:

\[
\begin{align*}
\text{Product} & \quad \text{Relative Abundance} \\
\text{CH}_3 + \text{CHO} & \quad 1 \\
\text{O} + \text{C}_2\text{H}_4(\text{C}_2\text{H}_2 + \text{H}_2) & \quad 0.7 \\
\text{H}_2 + (\text{CH}_2\text{CO}) & \quad 0.1 \\
\text{CH}_3\text{CHO} & \quad 0.2 \\
\text{CH}_2 + \text{HCHO} & \quad 0.2 \\
\end{align*}
\]

\[M. \text{ Kawasaki et al., J. Chem. Phys., 59, 2076 (1973)}\]

Proposed mechanism in 1950:

\[\text{Oxirane} \xrightarrow{\lambda} \text{Product} \]

\[\text{1. Gomer-Noyes mechanism} \]

\[\text{2. Reaction} \]

\[\text{3. Reaction} \]

\[\text{4. Reaction} \]

KS-orbitals obtained using the PBE functional:

a) HOMO (b₁, n)  
b) LUMO (a₁, 3s)  
c) LUMO+1 (a₁, 3p₂)  
d) LUMO+2 (b₂, σ*)

Different reaction pathways can be explained from the bonding/antibonding nature of the involved KS states.

1. Nuclear forces in S₁ (HOMO→LUMO) are similar to the ground state ones.  
   > S₁ is not a reactive channel.

2. The HOMO → LUMO+2 excitation has a vanishing small oscillator strength.  
   > No direct excitation  
   > Negligible coupling with the other states

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DFT/TDDFT based TSH - Applications

Oxirane: excited state ring opening reaction

dynamics starting in $S_1$

dynamics starting in $S_2$

DFT/TDDFT based TSH - Applications

Oxirane: excited state ring opening reaction

dynamics starting in $S_1$

dynamics starting in $S_2$

DFT/TDDFT based TSH - Applications

Oxirane: excited state ring opening reaction

Swarm of 10 trajectories showing the different possible reaction pathways

DFT/TDDFT based TSH - Applications

Oxirane: excited state ring opening reaction

Once the system reaches the ground state the dynamics is continued on $S_0$ and the different photoproducts are identified. Due to the conversion of the photon energy into kinetic energy, the photoproducts are in general very hot (1000-5000 K) and produce a rich chemistry. The results are compared with thermal decomposition studies (Joshi et al.).

With our calculations we identified many different reaction pathways:

- Gomer-Noyes
- CH$_4$ + CO
- O abstraction

State specific information about the reaction mechanism:

- Oxirane: excited state ring opening reaction

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DFT/TDDFT based TSH - Applications

Quality of the potential energy surfaces

PBE/TDA/TDDFT vs. CC2-aug-cc-pVTZ potential energy surfaces
DFT/TDDFT based TSH - Applications

Quality of the potential energy surfaces

S₀-S₁ energy gap

Cl or not Cl?

FIG. 19: Energy gap between S₀ and S₁ computed by CIS/aug-cc-pVTZ. Reaction coordinates are defined in caption of Fig. 15.

SA-CASSCF(4,5)/6-311G**

TDPBE/TDA/aug-cc-pVTZ

DFT/TDDFT based TSH - Applications

Oxirane: representative trajectory after excitation in $S_2$

Method
- Isolated system
- LR-TDDFT/PBE/TDA and ALDA
- SH-AIMD
- NVE ensemble
- Time step of 0.24 fs

Movie
Ground state BO dynamics
Excitation ($S_0$ to $S_2$)
TDDFT run of about 500 fs

> C-O bond rupture
> H transfer
OVERVIEW

# Mixed Quantum-Classical Dynamics
- Ehrenfest dynamics
- Surface hopping

# TDDFT for PESs and molecular forces

# TDDFT based trajectory surface hopping
- Non-adiabatic coupling vectors

# Approximations and implementation

# Applications
- Protonated formaldimine: a test case
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Intramolecular proton/hydrogen transfer

Hydrogen or proton transfer?

Experimental and theoretical evidences for an hydrogen transfer mechanism.

(C. Tanner, C. Manca, S. Leutwyler, Science, 302, 1736 (2003))

CIS/CASSCF for the in-plane geometry.
Potential energy surfaces for GS, S₁ and S₂ along a reaction coordinate (fix C₅ symmetry).
Intramolecular proton/hydrogen transfer

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CIS/CASSCF for the in-plane geometry. Potential energy surfaces for GS, S₁, and S₂ along a reaction coordinate (fix Cₛ symmetry).
**Intramolecular proton/hydrogen transfer**

Hydrogen or proton transfer?

TDDFT/PBE/TDA combined with non-adiabatic molecular dynamics. Move to a reaction coordinate free description of the mechanism. (PW basis set)

We observe:

- Symmetry breaking (strong out of plane displacement)
- No crossing with the $\pi\sigma^*$ state
- Proton transfer instead of hydrogen transfer

Experimental and theoretical evidences of an hydrogen transfer mechanism.

(C.Tanner, C Manca, S. Leutwyler, Science, 302, 1736 (2003))
Hydrogen or proton transfer?

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TDDFT/PBE/TDA combined with non-adiabatic molecular dynamics. Move to a reaction coordinate free description of the mechanism. (PW basis set)
Forcing in-plane ($C_s$) symmetry gives a qualitatively similar energy profile like in the CIS study. Hydrogen transfer can occur.

“Unconstrained” geometry optimization produces a completely different picture: The ammonia move out of plane and the $\pi\sigma^*$ remains high in energy and never gets populated. Proton transfer is observed.

With CASSCF: high barriers along the $\pi\sigma^*$ path.

At CASSCF/CASPT2 level of theory the proton transfer occurs almost barrierless.
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Thank you for your attention