TDDFT in mixed quantum-classical dynamics

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

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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

1. **TDDFT-based trajectory surface hopping**
   - Nonadiabatic couplings in TDDFT

2. **TDDFT-TSH: Applications**
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   - Local control theory
   - LC of protontransfer: from gas-phase to solution
Tully’s surface hopping - On-the-fly dynamics

\[ i\hbar \dot{C}_k^\alpha (t) = \sum_j C_j^\alpha (t) (H_{kj} - i\hbar \dot{R}_k^\alpha \cdot d_{kj}^\alpha) \]

\[ M_l \ddot{R}_l = -\nabla_l E_k^e (R) \]

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

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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Tully’s surface hopping

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TDDFT in mixed quantum-classical dynamics
Tully’s surface hopping - On-the-fly dynamics

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TDDFT in mixed quantum-classical dynamics
Nonadiabatic coupling vectors are defined in terms of electronic wavefunctions:

\[ d_{kj} = \langle \Phi_k(R) | \nabla_R | \Phi_j(R) \rangle = \frac{\langle \Phi_k(R) | \nabla_R \hat{H}_{el} | \Phi_j(R) \rangle}{E_j(R) - E_k(R)} \]

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).

\[ d_{kj} \rightarrow d_{kj}[\rho] \]

Different approaches for the calculation of \( d_{0j}[\rho] \) are available.\(^1\)

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

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The density response SOS formula

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

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

with

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

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

\[
(\omega^2 \mathbb{I} - \Omega(\omega))^{-1} = \sum_n \frac{Z_n Z_n^\dagger}{\omega_n^2 - \omega^2}
\]

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

\[
\Omega Z_n = \omega_0^2 Z_n,
\]

Therefore

\[
\chi(\omega) = \sum_n \frac{S^{-1/2} Z_n Z_n^\dagger S^{-1/2}}{\omega_n^2 - \omega^2}
\]

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

\[
\delta \mathcal{O}^{TDDFT}(\omega) = \sum_n \sum_{ij,kl\tau} o_{ij\sigma} \frac{(S^{-1/2} Z_n)_{ik\sigma} (Z_n^\dagger S^{-1/2})_{kl\tau}}{\omega_n^2 - \omega^2} \nu_{kl\tau} E(\omega).
\]

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

$$\delta O^{MBPT}(\omega) = \sum_n \frac{2\omega_i 0 \langle \Psi_0 | \hat{O} | \Psi_n \rangle \langle \Psi_n | \hat{\nabla} E(\omega) | \Psi_0 \rangle}{\omega_{n0}^2 - \omega^2}$$

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

$$\langle \Psi_0 | \hat{O} | \Psi_n \rangle = \sum_{ij\sigma} \frac{1}{\sqrt{\omega_n}} o_{ij\sigma} (S^{-1/2} Z_n)_{ij\sigma}$$

For any one-body operator, $\hat{O}$, a mapping between MBPT and TDDFT quantities gives (for the moment, we only consider transitions from the ground state $\Psi_0$)

$$O^\dagger S^{-1/2} Z_n = \omega_{0n}^{1/2} \langle \Psi_0 | \hat{O} | \Psi_n \rangle$$

where the operator $\hat{O} = \sum_{i\sigma} o_{i\sigma} \hat{a}_{i\sigma}^\dagger \hat{a}_{i\sigma}$ has components $o_{i\sigma} = \langle \phi_{i\sigma} | \hat{O} | \psi_{a\sigma} \rangle$ 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 $\epsilon_{i\sigma}$.

$^3 \sum_{i\sigma} \text{ stands for } \sum_{i=1}^{N} \sum_{a=1}^{\infty} \sum_{\sigma \in \{\alpha, \beta\}}.$
The auxiliary wavefunction

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

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

with

$$c_{i\alpha\sigma}^k \equiv \sqrt{\frac{S_{i\alpha\sigma}^{-1}}{\omega_0} e_{i\alpha\sigma}^k}$$

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!)

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

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Nonadiabatic couplings

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

\[
\dot{\mathbf{R}} \cdot \mathbf{d}_{0k}|_{t+\delta t/2}[\{\phi,\}]=\left\langle \tilde{\Phi}_0(r; R(t)) \left| \nabla_R \left| \tilde{\Phi}_k(r; R(t)) \right\rangle \cdot \dot{\mathbf{R}} = \left\langle \tilde{\Phi}_0(r; R(t)) \left| \frac{\partial}{\partial t} \left| \tilde{\Phi}_k(r; R(t)) \right\rangle \right. \right| \\
\approx \frac{1}{2\delta t} \left[ \left\langle \tilde{\Phi}_0(r; R(t)) \left| \tilde{\Phi}_k(r; R(t+\delta t)) \right\rangle - \left\langle \tilde{\Phi}_0(r; R(t+\delta t)) \left| \tilde{\Phi}_k(r; R(t)) \right\rangle \right. \right] \]

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

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

- 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 $O(\delta \rho^3)$ in full response).
As always, the quality of the nonadiabatic couplings will depend on the xc-functional used...

\[ d_{kj}[\{\phi.\}] = \langle \tilde{\phi}_k(R) | \nabla R | \tilde{\phi}_j(R) \rangle \]

Protonated formaldimine: nonadiabatic coupling vectors \( d_{01} \) with LR-TDDFT/TDA.
Nonadiabatic couplings - examples

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\[
d_{kj}[\{\phi.\}] = \langle \tilde{\Phi}_k(R) | \nabla_R | \tilde{\Phi}_j(R) \rangle
\]

Protonated formaldimine: nonadiabatic coupling vectors \( d_{12} \) with LR-TDDFT/TDA.
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TDDFT in mixed quantum-classical dynamics
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 ~100 fs.

PRL, 98, 023001 (2007); THEOCHEM, 914, 22 (2009).
Protonated formaldimine as a model compound for the study of the isomerization of retinal.

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

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

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

Typical trajectory

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

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

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

States population

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

States population - **Average over many trajectories**.
Dashed line = CASSCF result.
Protonated formaldimine

Geometrical modifications
Protonated formaldimine

Comparison with experiment and model calculations

- In addition to the isomerization channel, intra-molecular proton transfer reactions was observed (formation of CH$_3$NH$^+$).
- 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
Oxirane

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

**Computational details**

- Isolated system
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JCP, 129, 124108 (2009).
Oxirane

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

JCP, 129, 124108 (2009).
The photophysics of solvated Ruthenium(II) tris-bipyridine

\[ \text{[Ru(bpy)\textsubscript{3}]\textsuperscript{2+}} \] dye: photophysics

\[ ^1\text{MLCT} \]

\[ ^1\text{GS} \]

\[ \text{MC (dd)} \]

\[ ^3\text{MLCT} \]

\[ \text{[Ru(bpy)\textsubscript{3}]\textsuperscript{2+}} \] dye: Solvent structure

\[ \text{[Ru(bpy)\textsubscript{3}]\textsuperscript{2+}} \] dye: Singlet state dynamics

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Tarjectory-based quantum and mixed QM-CL solutions

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

- **Nonadiabatic Ehrenfest dynamics**

- **Adiabatic Born-Oppenheimer MD equations**

- **Nonadiabatic Bohmian Dynamics (NABDY)**

- **Nonadiabatic Trajectory Surface Hopping (TSH) dynamics**

- **Time dependent potential energy surface approach**
  based on the *exact decomposition*: \( \Psi(r, R, t) = \Omega(R, t)\Phi(r, t) \).
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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.

Short summary of the theory

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

\[ \hat{H}_{\text{int}} = -\frac{e}{2m_e c} \sum_i A(r_i, t) \cdot \hat{p}_i \]

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

\[ i\hbar \dot{C}_j^\alpha (t) = \sum_l C_l^\alpha (t)(H_{jl} - i\hbar \dot{R}_l^\alpha \cdot d_{jl}^\alpha + i\omega_{jl} \frac{A_0}{c} \epsilon^\lambda \cdot \mu_{jl} e^{-i\omega t}) \]

with

\[ i\omega_{jl} \frac{A_0(t)}{c} \cdot \mu_{jl} = \langle \Phi_j | \hat{H}_{\text{int}} | \Phi_l \rangle \]

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

\[ \mu_{jl} = -e \langle \Phi_j | \sum_i \hat{r}_i | \Phi_l \rangle \]

is the the transition dipole vector, and \( \omega_{jl} = (E_j - E_l)/\hbar \).

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

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: \( A(t) = -A_0 \epsilon^\lambda \exp\left(-\frac{(t-t_0)^2}{T^2}\right) \sin(\omega t) \)
Effect of an electromagnetic field - Lithium fluoride

$\epsilon^x = (1, 0, 0)$
Effect of an electromagnetic field - Lithium fluoride

\[ \epsilon^\lambda = (1, 0, 0) \]

Effect of an electromagnetic field - Lithium fluoride

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

Local control theory

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

Using the TSH for the total molecular wavefunction

$$\Psi^\alpha(r, R, t) = \sum_{j=1}^{\infty} C_j^\alpha(t) \Phi_J(r; R)$$

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

$$\dot{P}_I(t) = -2E^\alpha(t) \sum_J \Im [C_j^\alpha* \mu_{jj} C_j^\alpha(t)]$$

It is now evident that choosing a field of the form

$$E(t) = -\lambda \sum_J \Im [C_i^\alpha(t) C_j^\alpha* \mu_{jj}]$$

will ensure that $P_I(t)$ always increases in time.


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

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

TDDFT in mixed quantum-classical dynamics
Effect of a generic polarized pulse
LC pulse: efficient population transfer and stable excitation

TDDFT in mixed quantum-classical dynamics
Comparison with wavepacket propagation (MCTDH)

B.F.E Curchod, T. Penfold, U. Rothlisberger, IT, PRA, 84, 042507 (2011)
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Local control of proton transfer: gas phase to solution

*ChemPhysChem, 10, 2026 (2015)*

(in preparation)
Local control of proton transfer in gas phase

Local control of proton transfer

Local control of proton transfer

TDDFT in mixed quantum-classical dynamics
Local control of proton transfer (freq. vs. time)

Local control of proton transfer. Average over 6 trajs