Ab initio nonadiabatic molecular dynamics
TDDFT for ultrafast electronic dynamics

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TDDFT SCHOOL
BENASQUE 2014
1 Ab initio molecular dynamics
   - Why Quantum Dynamics?

2 Mixed quantum-classical dynamics
   - Ehrenfest dynamics
   - Adiabatic Born-Oppenheimer dynamics
   - Nonadiabatic Bohmian dynamics
   - Trajectory Surface Hopping

3 TDDFT-based trajectory surface hopping
   - Nonadiabatic couplings in TDDFT

4 TDDFT-TSH: Applications
   - Photodissociation of Oxirane
   - Oxirane - Crossing between $S_1$ and $S_0$

5 TSH with external time-dependent fields
Recent review on TDDFT-based nonadiabatic dynamics

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Ab initio molecular dynamics

Reminder from last lecture: potential energy surfaces

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

Now, we need to propagate the nuclei...
Reminder from last lecture: potential energy surfaces

We have electronic structure methods for electronic ground and excited states... Now, we need to propagate the nuclei...
GS adiabatic dynamics (BO vs. CP)

\[
M_i \ddot{R}_i(t) = -\nabla \min_\rho E_{KS}(\{\phi_i[\rho]\})
\]

\[
\mu_i |\dot{\phi}_i(t)\rangle = -\frac{\delta}{\delta |\phi_i\rangle} E_{KS}(\{\phi_i(r)\}) + \frac{\delta}{\delta |\phi_i\rangle} \{\text{constr.}\}
\]

\[
M_i \ddot{R}_i(t) = -\nabla E_{KS}(\{\phi_i(t)\})
\]

ES nonadiabatic quantum dynamics

- Wavepacket dynamics (MCTDH)
- Trajectory-based approaches
  - Tully’s trajectory surface hopping (TSH)
  - Bohmian dynamics (quantum hydrodyn.)
  - Semiclassical (WKB, DR)
  - Path integrals (Pechukas)
  - Mean-field solution (Ehrenfest dynamics)
- Density matrix, Liouvillian approaches, ...
Why Quantum dynamics?

GS adiabatic dynamics

First principles Heaven

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

No principles World

ES nonadiabatic quantum dynamics

First principles Heaven

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

No principles World
Why Quantum dynamics?

GS adiabatic dynamics

<table>
<thead>
<tr>
<th>First principles</th>
<th>Heaven</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ab initio MD with WF methods</td>
<td></td>
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<tr>
<td>Ab initio MD with DFT &amp; TDDFT [CP]</td>
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| No principles | World |

ES nonadiabatic quantum dynamics

(-) We cannot get read of electrons
(-) Nuclei keep some QM flavor
(-) Accuracy is an issue
(-) Size can be large (diffuse excitons)
(+ ) Time scales are usually short (< ps)
Nonadiabatic effects requires quantum nuclear dynamics

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

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

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

W3 Nuclear wavepacket dynamics is very expensive for large systems (6 degrees of freedom, 30 for MCTDH). Bad scaling.

T1 Trajectory based approaches can be run on-the-fly (no need to parametrize potential energy surfaces).

T2 Can handle large molecules in the full (unconstraint) configuration space.

T3 They offer a good compromise between accuracy and computational effort.
Mixed quantum-classical dynamics

Starting point

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

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

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

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

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

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

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

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

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

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

where \( \hat{V}(r, R) = \sum_{i<j} \frac{e^2}{|r_i - r_j|} - \sum_{\gamma,i} \frac{e^2 Z_\gamma}{|R_\gamma - r_i|} \).

In a similar way, multiplying by \( \Phi^*(r, t) \) and integrating over \( r \) we obtain

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

Conservation of energy has also to be imposed through the condition that \( d\langle \hat{H} \rangle / dt \equiv 0 \).

Note that both the electronic and nuclear parts evolve according to an average potential generated by the other component (in square brakets). These average potentials are time-dependent and are responsible for the feedback interaction between the electronic and nuclear components.
Ehrenfest dynamics - the nuclear equation

We start from the polar representation of the nuclear wavefunction

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

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

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

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

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

Instead of solving the field equation for $S(R, t)$, find the equation of motion for the corresponding trajectories (characteristics).
Ehrenfest dynamics - the nuclear equation

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

$$P = \nabla_R S(R).$$

The solutions of this Hamiltonian system are curves (characteristics) in the $(R, t)$-space, which are extrema of the action $S(R, t)$ for given initial conditions $R(t_0)$ and $P(t_0) = \nabla_R S(R)|_{R(t_0)}$.

Newton-like equation for the nuclear trajectories corresponding to the HJ equation

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

Ehrenfest dynamics

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

$$M_i \ddot{R}_i = -\nabla_i \langle \hat{H}_{el}(r; R) \rangle$$
Ehrenfest dynamics - the nuclear equation

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

\[
P = \nabla_{\mathbf{R}} S(\mathbf{R}).
\]

The solutions of this Hamiltonian system are curves (\textit{characteristics}) in the \((\mathbf{R}, t)\)-space, which are extrema of the action \( S(\mathbf{R}, t) \) for given initial conditions \( \mathbf{R}(t_0) \) and \( \mathbf{P}(t_0) = \nabla_{\mathbf{R}} S(\mathbf{R})|_{\mathbf{R}(t_0)}. \)

Newton-like equation for the nuclear trajectories corresponding to the HJ equation

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

Ehrenfest dynamics - Densityfunctionalization (\( \phi_k \): KS orbitals)

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

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

Ehrenfest dynamics

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

\[ M_I \ddot{R}_I = -\nabla_I \langle \hat{H}_{el}(r; R) \rangle \]

\[ \rho(r, t) - \rho_0^{\text{(no C}^4\text{+)}}(r) \]
Ehrenfest dynamics and mixing of electronic states

**Ehrenfest dynamics**

\[
i\hbar \frac{\partial \Phi(\mathbf{r}; \mathbf{R}, t)}{\partial t} = \hat{H}_{el}(\mathbf{r}; \mathbf{R})\Phi(\mathbf{r}; \mathbf{R}, t)
\]

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

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

\[
\Phi(\mathbf{r}; \mathbf{R}, t) = \sum_{k=0}^{\infty} c_k(t) \Phi_k(\mathbf{r}; \mathbf{R})
\]

The time-dependency is now on the set of coefficients \( \{ c_k(t) \} \) (\(|c_k(t)|^2\) is the population of state \( k \)). Inserting in the Ehrenfest’s equations...
Ehrenfest dynamics and mixing of electronic states

Ehrenfest dynamics

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

\[
M_I \ddot{\mathbf{R}}_I = -\nabla I \sum_{k=0}^{\infty} |c_k(t)|^2 E_k^{el}
\]

where

\[
D_{kj} = \langle \Phi_k | \frac{\partial}{\partial t} | \Phi_j \rangle = \langle \Phi_k | \frac{\partial \mathbf{R}}{\partial t} \frac{\partial}{\partial \mathbf{R}} | \Phi_j \rangle = \dot{\mathbf{R}} \langle \Phi_k | \nabla | \Phi_j \rangle = \dot{\mathbf{R}} \cdot d_{kj}
\]

Thus we incorporate directly nonadiabatic effects.
Ehrenfest dynamics: the mean-field potential

\[ i\hbar \dot{c}_k(t) = c_k(t)E_{El}^k - i\hbar \sum_j c_j(t)D_{kj} \]

\[ M_I \ddot{R}_I = -\nabla_I \sum_{k=0}^{\infty} |c_k(t)|^2 E_{El}^k \]
Tarjectory-based quantum and mixed QM-CL solutions

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

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- **Time dependent potential energy surface approach**
  - based on the exact decomposition: \( \Psi(r, R, t) = \Omega(R, t)\Phi(r, t) \).
In this equation, \( \{ \Phi_j(r; R) \} \) describes a complete basis of electronic states solution of the time-independent Schrödinger equation:

\[
\hat{H}_{el}(r; R)\Phi_j(r; R) = E_{el,j}(R)\Phi_j(r; R)
\]

\( R \) is taken as a parameter. Eigenfunctions of \( \hat{H}_{el}(r; R) \) are considered to be orthonormal, i.e. \( \langle \Phi_j | \Phi_i \rangle = \delta_{ij} \).
**Born-Oppenheimer approximation**

\[
\psi(r, R, t) \xrightarrow{\text{Born-Huang}} \sum_{j}^{\infty} \phi_j(r; R)\omega_j(R, t)
\]

Electrons are static. Use your favorite el. str. method.

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

\[
\hat{H}\psi(r, R, t) = i\hbar \frac{\partial}{\partial t}\psi(r, R, t)
\]

After left multiplication by \(\phi_k^*(r; R)\) and integration over \(r\), we obtain the following equation (we used \(\langle \phi_j | \phi_i \rangle = \delta_{ij}\)):

\[
\left[-\sum_l \frac{\hbar^2}{2M_l} \nabla_l^2 + E_{el, k}(R)\right] \omega_k(R, t) + \sum_{j}^{\infty} D_{kj}\omega_j(R, t) = i\hbar \frac{\partial}{\partial t}\omega_k(R, t)
\]
Born-Oppenheimer approximation

\[
\left[ -\sum_i \frac{\hbar^2}{2M_i} \nabla_i^2 + E_{el,k}(\mathbf{R}) \right] \Omega_k(\mathbf{R}, t) + \sum_j D_{kj} \Omega_j(\mathbf{R}, t) = i\hbar \frac{\partial}{\partial t} \Omega_k(\mathbf{R}, t)
\]

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

**Important additional term**: \( D_{kj} \) ! NONADIABATIC COUPLING TERMS

\[
D_{kj} = \int \Phi_k^*(\mathbf{r}; \mathbf{R}) \left[ \sum_i \frac{\hbar^2}{2M_i} \nabla_i^2 \right] \Phi_j(\mathbf{r}; \mathbf{R}) d\mathbf{r}
+ \sum_i \frac{1}{M_i} \left\{ \int \Phi_k^*(\mathbf{r}; \mathbf{R}) \left[ -i\hbar \nabla_i \right] \Phi_j(\mathbf{r}; \mathbf{R}) d\mathbf{r} \right\} \left[ -i\hbar \nabla_i \right]
\]
Born-Oppenheimer approximation

\[
D_{kj} = \int \Phi_k^*(r; R) \left[ \sum_I \frac{\hbar^2}{2M_I} \nabla_I^2 \right] \Phi_j(r; R) dr \\
+ \sum_I \frac{1}{M_I} \left\{ \int \Phi_k^*(r; R) \left[ -i\hbar \nabla_I \right] \Phi_j(r; R) dr \right\} \left[ -i\hbar \nabla_I \right]
\]

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

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

Mainly for ground state dynamics or for dynamics on states that do not couple with others.
(Back to nonadiabatic dynamics later).
Born-Oppenheimer approximation: the nuclear trajectories

\[
\left[ -\sum_{l} \frac{\hbar^2}{2M_l} \nabla_l^2 + E_{el,k}(\mathbf{R}) \right] \Omega_k(\mathbf{R}, t) = i\hbar \frac{\partial}{\partial t} \Omega_k(\mathbf{R}, t)
\]

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

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

\( A_k(\mathbf{R}, t) \) represents an amplitude and \( S_k(\mathbf{R}, t)/\hbar \) a phase.

Further: insert the polar representation into the equation above, do some algebra, and separate real and imaginary part, we obtain an interesting set of equations:
Born-Oppenheimer approximation: the nuclear trajectories

\[ \frac{\partial S_k}{\partial t} = \frac{\hbar^2}{2} \sum_{l} M_l^{-1} \frac{\nabla^2 A_k}{A_k} - \frac{1}{2} \sum_{l} M_l^{-1} (\nabla_l S_k)^2 - E_k \]

\[ \frac{\partial A_k}{\partial t} = -\sum_{l} M_l^{-1} \nabla_l A_k \nabla_l S_k - \frac{1}{2} \sum_{l} M_l^{-1} A_k \nabla^2_l S_k \]

Dependences of the functions \( S \) and \( A \) are omitted for clarity (\( k \) is a index for the electronic state; in principle there is only one state in the adiabatic case).

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

The nuclear dynamics is derived from the real part \( \left( \frac{\partial S_k}{\partial t} \right) \). This equation has again the form of a classical Hamilton-Jacobi equation.
Born-Oppenheimer approximation: the nuclear trajectories

\[
\frac{\partial S_k}{\partial t} = \frac{\hbar^2}{2} \sum_I M_I^{-1} \frac{\nabla^2 I A_k}{A_k} - \frac{1}{2} \sum_I M_I^{-1} (\nabla I S_k)^2 - E_k
\]

\[
\frac{\partial A_k}{\partial t} = - \sum_I M_I^{-1} \nabla I A_k \nabla I S_k - \frac{1}{2} \sum_I M_I^{-1} A_k \nabla^2 I S_k
\]

Instead of solving the field equation for \( S(\mathbf{R}, t) \), find the equation of motion for the corresponding trajectories (characteristics).
Born-Oppenheimer approximation: the nuclear trajectories

\[
\frac{\partial S_k}{\partial t} = \frac{\hbar^2}{2} \sum_l M_l^{-1} \frac{\nabla_l^2 A_k}{A_k} - \frac{1}{2} \sum_l M_l^{-1} (\nabla_l S_k)^2 - E_k
\]

The classical limit is obtained by taking\(^1\): \(\hbar \to 0\)

\[
\frac{\partial S_k}{\partial t} = -\frac{1}{2} \sum_l M_l^{-1} (\nabla_l S_k)^2 - E_k
\]

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

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

The momentum of a particle \(l\) is related to

\[
\nabla_l S = p_l = \frac{v_l}{M_l}
\]

\(^1\)Caution! This classical limit is subject to controversy...
Born-Oppenheimer approximation: the nuclear trajectories

Therefore, taking the gradient,

\[-\nabla J \frac{\partial S_k}{\partial t} = \frac{1}{2} \nabla J \sum_l M_l^{-1} (\nabla_l S_k)^2 + \nabla J E_k\]

and rearranging this equation using \(\nabla J S_k / M_J = v^k_j\), we obtain the (familiar) Newton equation:

\[M_J \frac{d}{dt} v^k_j = -\nabla J E_k\]

In Summary:

**Adiabatic BO MD**

\[\hat{H}_{el}(\mathbf{r}; \mathbf{R})\Phi_k(\mathbf{r}; \mathbf{R}) = E_{el}^k(\mathbf{R})\Phi_k(\mathbf{r}; \mathbf{R})\]

\[M_l \ddot{R}_l = -\nabla_l E_{el}^k(\mathbf{R}) = -\nabla_l \langle \Phi_k | \hat{H}_{el} | \Phi_k \rangle_{min\Phi_k}\]
Mean-field vs. BO MD (adiabatic case)

Ehrenfest dynamics

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

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

Explicit time dependence of the electronic wavefunction.

Born-Oppenheimer dynamics

\[ \hat{\mathcal{H}}_{el}(r; R)\Phi_k(r; R) = E^el_k(R)\Phi_k(r; R) \]

\[ M_I \ddot{R}_I = -\nabla_I E^el_k(R) = -\nabla_I \langle \Phi_k | \hat{\mathcal{H}}_{el} | \Phi_k \rangle \]

The electronic wavefunction are static (only implicit time-dependence.)
### Mean-field vs. BO MD (adiabatic case)

<table>
<thead>
<tr>
<th>Method</th>
<th>Born-Oppenheimer MD</th>
<th>Ehrenfest MD</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td><em>adiabatic</em> MD (one PES)</td>
<td><em>nonadiabatic</em> MD (mean-field)</td>
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<tr>
<td>Efficient propagation of the nuclei</td>
<td>Adiabatic nuclear propagation</td>
<td>Get the “real” dynamics of the electrons</td>
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<td>$\delta t \sim 10-20$ a.u. (0.25-0.5 fs)</td>
<td>Propagation of nuclei &amp; electrons</td>
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<td>Simple algorithm</td>
<td>$\delta t \sim 0.01$ a.u. (0.25 as)</td>
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<td>Common propagation of the nuclei and the electrons implies more sophisticated algorithms</td>
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### Exact quantum dynamics?

Can we derive “exact” quantum equations of motion for the nuclei? (without taking the classical limit $\hbar \to 0$?)
Tarjectory-based quantum and mixed QM-CL solutions

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

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

Pioneers in quantum hydrodynamics: D. Bohm, P. R. Holland, R. E. Wyatt, and many others.
NABDY: “exact” trajectory-based nonadiabatic dynamics

Using

\[ \Psi(r, R, t) = \sum_{j}^{\infty} \Phi_j(r; R) \Omega_j(R, t) \]

\[ \Omega_j(R, t) = A_j(R, t) \exp \left[ \frac{i}{\hbar} S_j(R, t) \right] \]

in the exact time-dependent Schrodinger equation for the nuclear wavefunction we get

\[ -\frac{\partial S_j(R, t)}{\partial t} = \sum_{\gamma} \frac{1}{2M_{\gamma}} \left( \nabla_{\gamma} S_j(R, t) \right)^2 + E_j^e(R) - \sum_{\gamma} \frac{\hbar^2}{2M_{\gamma}} \frac{\nabla_{\gamma}^2 A_j(R, t)}{A_j(R, t)} \]

\[ + \sum_{\gamma i} \frac{\hbar^2}{2M_{\gamma}} D_{ji}^\gamma(R) \frac{A_i(R, t)}{A_j(R, t)} \Re \left[ e^{i\phi} \right] - \sum_{\gamma, i \neq j} \frac{\hbar^2}{M_{\gamma}} d_{ji}^\gamma(R) \nabla_{\gamma} A_j(R, t) \Re \left[ e^{i\phi} \right] \]

\[ + \sum_{\gamma, i \neq j} \frac{\hbar}{M_{\gamma}} d_{ji}^\gamma(R) \frac{A_i(R, t)}{A_j(R, t)} \nabla_{\gamma} S_i(R, t) \Im \left[ e^{i\phi} \right] \]

and

\[ \frac{\partial A_j(R, t)}{\partial t} = -\sum_{\gamma} \frac{1}{M_{\gamma}} \nabla_{\gamma} A_j(R, t) \nabla_{\gamma} S_j(R, t) - \sum_{\gamma} \frac{1}{2M_{\gamma}} A_j(R, t) \nabla_{\gamma}^2 S_j(R, t) \]

\[ + \sum_{\gamma i} \frac{\hbar}{2M_{\gamma}} D_{ji}^\gamma(R) A_i(R, t) \Im \left[ e^{i\phi} \right] - \sum_{\gamma, i \neq j} \frac{\hbar}{M_{\gamma}} d_{ji}^\gamma(R) \nabla_{\gamma} A_i(R, t) \Im \left[ e^{i\phi} \right] \]

\[ - \sum_{\gamma, i \neq j} \frac{1}{M_{\gamma}} d_{ji}^\gamma(R) A_i(R, t) \nabla_{\gamma} S_j(R, t) \Re \left[ e^{i\phi} \right] \]

where both \( S_j(R, t) \) and \( A_j(R, t) \) are real fields and \( \phi = \frac{1}{\hbar} (S_i(R, t) - S_j(R, t)) \).
NABDY: “exact” trajectory-based nonadiabatic dynamics

From the NABDY equations we can obtain a Newton-like equation of motion (using the HJ definition of the momenta $\nabla_\beta S_j(R, t) = P^j_\beta$)

$$M_\beta \frac{d^2 R_\beta}{(dt^j)^2} = -\nabla_\beta \left[ E^{el}_j(R) + Q_j(R, t) + \sum_i D_{ij}(R, t) \right]$$

where $Q_j(R, t)$ is the quantum potential responsible for all coherence/decoherence “intrasurface” QM effects, and $D_{ij}(R, t)$ is the nonadiabatic potential responsible for the amplitude transfer among the different PESs.

For more informations see:

NABDY limitations
- Mainly numerical challenges
- Instabilities induced by the quantum potential
- Compute derivatives in the $3N$ dimensional($\mathbb{R}^{3N}$) configuration space
NABDY: “exact” trajectory-based nonadiabatic dynamics

Figure: NABDY: sketch of the dynamics
Gaussian wavepacket on an Eckart potential \((E_k = 3/4V)\)
Gaussian wavepacket on an Eckart potential \((E_k = 3/4V)\)
Mixed quantum-classical dynamics
Nonadiabatic Bohmian dynamics
Ab initio nonadiabatic molecular dynamics
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: \( \Psi(\mathbf{r}, \mathbf{R}, t) = \Omega(\mathbf{R}, t)\Phi(\mathbf{r}, t) \).
Applications in Photochemistry and Photophysics

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

Approximate solutions are available. Among the most popular is

**Trajectory Surface Hopping (TSH)**
TSH nonadiabatic MD

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

- propagation of a “quantum” amplitude, $C_k^\alpha(t)$, associated to each PES, $I$

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

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

- classical (adiabatic) time evolution of the nuclear trajectories on adiabatic states solution of the Schrödinger equation for the electronic sub-system.

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

Tully’s surface hopping - How does it work?

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

\[ \rho^{CL}_k(R^\alpha, t^\alpha) = \frac{N_k^\alpha(R^\alpha, dV, t^\alpha)}{N_{tot}} \frac{1}{dV} \sim |\Omega_k(R^\alpha, t^\alpha)|^2 \sim |C^\alpha_{k, R^\alpha, t^\alpha}|^2 \]

Inserting

\[ \Psi^\alpha(r, R, t) = \sum_k \infty C^\alpha_k(t) \Phi_k(r; R) \]

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

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

with \( H_{kj} = \langle \Phi_k(r; R) | \hat{H}_{el} | \Phi_j(r; R) \rangle \).

In the adiabatic representation, we have \( H_{kk} = E_{k}^{el} \) and \( H_{kj} = 0 \).
Tully’s surface hopping - How does it work?

Equation of motion for the amplitudes:

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

Switching algorithm:

In the fewest switches algorithm, the transition probability from state j to state k in the time interval \([t, t + dt]\) is given by:

\[ g_{jk}^\alpha(t, t + dt) \approx 2 \int_t^{t+dt} d\tau \mathcal{S}\left[ C_k^\alpha(\tau) C_j^{\alpha*}(\tau) H_{kj}(\tau) \right] - \mathcal{R}\left[ C_k^\alpha(\tau) C_j^{\alpha*}(\tau) \Xi_{kj}(\tau) \right] \]

\[ C_j^\alpha(\tau) C_j^{\alpha*}(\tau) \]

where \( \Xi_{kj}(\tau) = \dot{R}_j^\alpha \cdot d_{kj}^\alpha(\tau) \). A hop occurs between j and k if

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

where \( \zeta \) is generated randomly in the interval \([0, 1]\).
Tully’s surface hopping - Summary

Tully’s surface hopping

\[
\begin{align*}
  i\hbar \dot{C}_k^\alpha (t) &= \sum_j C_j^\alpha (t) \left( H_{kj} - i\hbar \dot{R}_j^\alpha \cdot d_{kj}^\alpha \right) \\

  \sum_{l \leq k-1} g_{jl}^\alpha &< \zeta < \sum_{l \leq k} g_{jl}^\alpha ,
\end{align*}
\]

Some warnings:

1. Evolution of classical trajectories (no QM effects – such as tunneling – are possible).
2. Rescaling of the nuclei velocities after a surface hop (to ensure energy conservation) is still a matter of debate.
3. Depending on the system studied, many trajectories could be needed to obtain a complete statistical description of the non-radiative channels.

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

1. Initialization of the classical variables (positions and velocities) according to the classical ensemble distribution corresponding to the target temperature (for example using an adiabatic MD simulation coupled to a thermostat).

2. Calculation of the electronic adiabatic states using LR-TDDFT and the corresponding forces on the nuclei.

3. Propagation of the classical variables for the desired timestep \( \Delta t \) using the velocity Verlet algorithm.

4. Reconstruction of the TDDFT excited wave functions using eq. (2.10) and calculation of the NAC \( \{\alpha_{ij}\} \) according to equation (2.6).

5. Propagation of the electronic expansion coefficients \( \{C_j\} \) according to eq. (2.4) for the time interval \( \Delta t \) using the 4th order Runge-Kutta algorithm. Store all quantities necessary for the next iteration.

6. Evaluation of the switching probability using eq. (2.8): Switch \( \psi \rightarrow \psi' \)?

   - **No**
     - Continue with step 5.

   - **Yes**
     - Change of the driving surface for the classical nuclei, and redistribution of the excess energy among the classical degrees of freedom.
Tully’s surface hopping - Examples

1D systems

Tully’s surface hopping - Examples

1D systems

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

- exact
- TSH
- Landau-Zener


Ab initio nonadiabatic molecular dynamics
Tully’s surface hopping - Examples

1D systems

Tully’s surface hopping - Examples

1D systems

On the right: population of the upper state
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Comparison with wavepacket dynamics

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

JPCA, 107, 621 (2003)
Comparison with wavepacket dynamics

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

CASSCF PESs for the radical cation ($Q_{14}$: symmetric stretch, $\theta$: torsional angle).
Comparison with wavepacket dynamics

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

JPCA,107,621 (2003)
Comparison with wavepacket dynamics

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

Trajectories are not coming back close to the conical intersection.

What is the reason for this discrepancy? The independent trajectory approximation?, i.e. the fact that trajectories are not correlated? (Or it has to do with differences in the PESs?)

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JPCA,107,621 (2003)
1. Ab initio molecular dynamics
   - Why Quantum Dynamics?

2. Mixed quantum-classical dynamics
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Ab initio nonadiabatic molecular dynamics
Tully’s surface hopping - On-the-fly dynamics

**Tully’s surface hopping**

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

\[ M_l \ddot{R}_l = -\nabla_l E_{el}^l(R) \]

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

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, ...

*Ab initio nonadiabatic molecular dynamics*
Tully’s surface hopping - On-the-fly dynamics

Tully’s surface hopping

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

\[ M_I \ddot{R}_I = -\nabla_I E^e_k (R) \]

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

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Ab initio nonadiabatic molecular dynamics
Tully’s surface hopping - On-the-fly dynamics

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- Forces on the nuclei \( \rightarrow \) MR-CISD, LR-TDDFT, semiempirical methods, ...
- Nonadiabatic coupling terms \( \rightarrow \) MR-CISD, LR-TDDFT (?), semiempirical methods, ...

Ab initio nonadiabatic molecular dynamics
Nonadiabatic coupling vectors are defined in terms of electronic wavefunctions:

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

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).

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

Different approaches for the calculation of \( d_{0j}[\rho] \) are available. Here we will use the method based on the auxiliary many-electron wavefunctions.

---

The density response SOS formula

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

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

where $Z_n$ are the TDDFT eigenvectors of the pseudoeigenvalue equation,

$$
S_{ij\sigma,kl\tau} = \frac{\delta_{ik}\delta_{jl}\delta_{\sigma\tau}}{(f_{k\sigma} - f_{l\sigma})(\epsilon_{l\sigma} - \epsilon_{k\sigma})}
$$

$$
\Omega Z_n = \omega_n^2 Z_n,
$$

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 $(\omega^2 I - \Omega(\omega))^{-1}$, we can write

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

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 ($\delta O(\omega) = \sum_{ij\sigma} o_{ij\sigma} \delta P_{ij\sigma}$)

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

---

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

$$\delta O^{MBPT}(\omega) = \sum_n \frac{2\omega_{i0} \langle \psi_0 | \hat{O} | \psi_n \rangle \langle \psi_n | \hat{\gamma}' E(\omega) | \psi_0 \rangle}{\omega_{n0}^2 - \omega^2}$$

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 $\psi_0$)

$$O^\dagger S^{-1/2} Z_n = \omega_0^{1/2} \langle \psi_0 | \hat{O} | \psi_n \rangle$$

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

\[\footnote{4} \sum_{ia \sigma} \text{ stands for } \sum_{i=1}^N \sum_{a=1}^\infty \sum_{\sigma \in \{\alpha, \beta\}} \cdot \]\n
Ab initio nonadiabatic molecular dynamics
The auxiliary wavefunction

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

\[
\tilde{\Phi}_k[\{\phi_i\}] = \sum_{i\alpha\sigma} c_{i\alpha\sigma}^k \hat{a}^\dagger_{\alpha\sigma} \hat{a}_{i\sigma} \tilde{\Phi}_0[\{\phi_i\}],
\]

with

\[
c_{i\alpha\sigma}^k \equiv \sqrt{\frac{S_{i\alpha\sigma}^{-1}}{\omega_{0k}}} e_{i\alpha\sigma}^k
\]

where \( \tilde{\Phi}_0[\{\phi_i\}] \) 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!)

\[
\langle \Psi_0|\hat{O}|\Psi_n \rangle = \langle \tilde{\Phi}_0|\hat{O}|\tilde{\Phi}_n \rangle
\]
Nonadiabatic couplings

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

\[
\dot{R} \cdot d_{0k}|_{t+\delta t/2}[\{\phi\}] = \left\langle \tilde{\Phi}_0(r; R(t)) \bigg| \nabla_R \bigg| \tilde{\Phi}_k(r; R(t)) \right\rangle \cdot \dot{R} = \left\langle \tilde{\Phi}_0(r; R(t)) \bigg| \frac{\partial}{\partial t} \bigg| \tilde{\Phi}_k(r; R(t)) \right\rangle
\]

\[
\simeq \frac{1}{2\delta t} \left[ \left\langle \tilde{\Phi}_0(r; R(t)) \big| \tilde{\Phi}_k(r; R(t + \delta t)) \right\rangle - \left\langle \tilde{\Phi}_0(r; R(t + \delta t)) \big| \tilde{\Phi}_k(r; R(t)) \right\rangle \right]
\]

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

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

- 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).
Nonadiabatic couplings - examples

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

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

\[ d_{kj}[[\phi_\cdot]] = \langle \Phi_k(R) | \nabla R | \Phi_j(R) \rangle \]

Protonated formaldimine: nonadiabatic coupling vectors $d_{12}$ with LR-TDDFT/TDA.
1. Ab initio molecular dynamics
   - Why Quantum Dynamics?

2. Mixed quantum-classical dynamics
   - Ehrenfest dynamics
   - Adiabatic Born-Oppenheimer dynamics
   - Nonadiabatic Bohmian dynamics
   - Trajectory Surface Hopping

3. TDDFT-based trajectory surface hopping
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4. TDDFT-TSH: Applications
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5. TSH with external time-dependent fields
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.

CH$_2$NH$_2^+$

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

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

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 \( \sigma_{kj} = \dot{R}^\alpha \cdot d_{kj}^\alpha \)

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 $\text{CH}_3\text{NH}^+$).
- $\text{H}_2$ 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.

$\text{CH}_2\text{NH}_2^+$
Oxirane has interesting non-radiative decay channels, during which ring opening and dissociation can occur.

Figure: Mechanism proposed by Gomer and Noyes
Oxirane

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

Computational details

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

JCP, 129, 124108 (2009).
Oxirane

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

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

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

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

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

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

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

2. Mixed quantum-classical dynamics
   - Ehrenfest dynamics
   - Adiabatic Born-Oppenheimer dynamics
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5. TSH with external time-dependent fields
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.

TSH with external time-dependent fields

Short summary of the theory

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

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

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.

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

\[
i\hbar \dot{C}_j^\alpha(t) = \sum_I C_I^\alpha(t)(H_{JI} - i\hbar \dot{R}_I^\alpha \cdot d_{JI}^\alpha + i\omega_{JI} \frac{A_0}{c} \epsilon^\lambda \cdot \mu_{JI} e^{-i\omega t})
\]

with

\[
i\omega_{JI} \frac{A_0(t)}{c} \cdot \mu_{JI} = \langle \Phi_J | \hat{H}_{int} | \Phi_I \rangle
\]

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

\[
\mu_{JI} = -e \langle \Phi_J | \sum_i \hat{r}_i | \Phi_I \rangle
\]

is the the transition dipole vector, and \( \omega_{JI} = (E_J - E_I)/\hbar \).

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

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

$x$-polarized pulse: $\epsilon^x = (1, 0, 0)$
TSH with external time-dependent fields

Effect of an electromagnetic field - Lithium fluoride

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

Effect of an electromagnetic field - Lithium fluoride

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