Non-adiabatic dynamics with external laser fields

Ivano Tavernelli

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1. **MQCD**
   - Mixed Quantum-Classical Dynamics
   - Quantum Dynamics with Trajectories

2. **Radiation Field**
   - Interaction Hamiltonian

3. **NAC**
   - NAC in DFT

4. **NAC computation**
   - Sternheimer
   - Implementation
   - Nearly equilateral $H_3$
   - Protonated formaldimine, $CH_2NH_2^+$

5. **Appl. $H_2^+$**
   - $H_2^+$

6. **Appl. LiF**
   - LiF

7. **Appl. Oxirane**
   - Oxirane
Definitions

- \{r, m\} fast (light) degrees of freedom
- \{R, M\} slow (heavy) degrees of freedom

Mean-field (Ehrenfest-type) dynamics

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

\[ E_{el}(t) = \int \int dr dR \Phi^*(r, t)\Omega^*(R, t)\mathcal{H}_{el}\Phi(r, t)\Omega(R, t) \]

Born-Oppenheimer (BO) and non-adiabatic BO

\[ \psi(r, R, t) = \sum_i \Phi_i(r, R)\Omega_i(R, t) \]

\( \Phi_i(r, R) \) Solution of the time-independent Schrödinger equation
(Only parametrically dependent on \( R \))

Other possible Ansätze
Molecular Hamiltonian

$$\mathcal{H}_{tot} = -\sum_{\gamma} \frac{\hbar^2}{2M_{\gamma}} \nabla^2_{\gamma} - \sum_{i} \frac{\hbar^2}{2m_i} \nabla^2_{i} + V_{eN}(r, R)$$

Inserting $\Psi(r, R, t) = \sum_{I} \Phi_{I}(r, R)\Omega_{I}(R, t)$ in the TDSE

- Nuclei $\Omega_{I}(R, t) = A_{I}(R, t)e^{\frac{i}{\hbar}S_{I}(R, t)}$ in the limit ($\hbar \rightarrow 0$)

\[
\begin{align*}
-\frac{\partial A_{J}}{\partial t} &= F(A_{J}, \nabla A_{J}, S_{J}, \nabla S_{J}) + \sum_{I \neq J} A_{J} \left[ \dot{R} \cdot d_{JI} + \frac{i}{\hbar} H_{IJ} \right] e^{-\frac{i}{\hbar} \int_{t_0}^{t} d\tau (H_{II} - H_{JJ})} \\
-\frac{\partial S_{J}}{\partial t} &= \sum_{\gamma} \frac{1}{2M_{\gamma}} (\nabla_{\gamma} S_{J})^2 + H_{II}
\end{align*}
\]

Motion evolves on each PES with transport of amplitude between PESs governed by the off-diagonal terms $d_{JI}$ and $H_{JI}$.

- Electrons are NOT dynamical. Define the PES computed on-the-fly
In the ITA each classical trajectory representing the nuclear wavepacket evolve independently from all the other (missing coherence/decoherence effects) and the amplitudes only change through the coupling terms between PESs.

\[-\frac{\partial A_J}{\partial t} = \sum_{l \neq J} A_J \left[ \dot{R} \cdot d_{JI} + \frac{i}{\hbar} H_{IJ} \right] e^{-i \frac{t-t_0}{\hbar} \int_{t_0}^{t} (H_{II} - H_{JJ})} \]

J. Tully\(^1\) has introduced a stochastic algorithm that (in the limit \(\hbar \to 0\)) decide about the surface that drags the "classical" nuclear dynamics.

\(^{1}\) J.C. Tully, R.K. Preston, JCP, 55, 562 (1971)
Quantum Dynamics with Trajectories

Tully’s Surface Hopping

In Tully’s dynamics, the classical trajectories evolve adiabatically according to Born-Oppenheimer dynamics until a *hop* between two potential energy surfaces \((H_{II} \text{ and } H_{JJ})\) occurs according to a Monte Carlo-type procedure. In the "fewest switches" algorithm, the transition probability from state \(I\) to state \(J\) in the time interval \([t, t + dt]\) is

\[
g_{IJ}(t, t + dt) \approx 2 \int_{t}^{t + dt} d\tau \frac{\text{Im}[A_J(\tau)A_I^*(\tau)H_{II}(\tau)] - \text{Re}[A_J(\tau)A_I^*(\tau)\Xi_{JI}(\tau)]}{A_I(\tau)A_I^*(\tau)}, \tag{1}
\]

where \(\Xi_{JI}(\tau) = \sum_\gamma \dot{R}_\gamma \cdot d_{JI}^\gamma(\tau) = \sum_\gamma \frac{\partial R_\gamma}{\partial t} \langle \Phi_I | \frac{\partial}{\partial R_\gamma} \Phi_J \rangle\), and a hop occurs if and only if

\[
\sum_{K \leq i - 1} g_{JK} < \zeta < \sum_{K \leq i} g_{JK}, \tag{2}
\]

where \(\zeta\) is generated randomly in the interval \([0, 1]\).
In the ITA a **single** trajectory follows adiabatically a PES ($I$) until a transition to a different PES ($J$) is accepted with a given probability $g(A_{IJ})$. The amplitudes $A_I$ evolve according to

$$i\hbar \dot{A}_J = \sum_I A_I (H_{JI} - i\hbar \dot{R} \cdot d_{JI})$$

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

**Tully’s claim**

The algorithm "guarantee" that at any instant of time for the ENSEMBLE of trajectories the fraction of trajectories assigned to any PES is approximately equal to the relative population of the state $|A_I(t)|^2$. 
Protonated formaldimine is a model compound for the study of isomerization in rhodopsin chromophore retinal.

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 $S_2$. 

![Diagram showing energy vs time](image-url)
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 $p \rightarrow p - eA/c$,

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

The vector potential is of the form $A = A_0 e^{\lambda} e^{-ik \cdot r + i\omega t}$.
In a typical molecular transition in the optical region, the wavelength of the interacting photon is much greater than the linear dimension of the molecule, \( \lambda = 2\omega/k \gg r_{\text{molecule}} \) and therefore

\[
e^{-ik \cdot r} = 1 - ik \cdot r + O(k \cdot r)^2
\]

can be replaced by the leading term, 1.

The radiation field coupling matrix element becomes (using \( A_0 = A_0 e^{\lambda} \))

\[
\langle H^{\text{int}} \rangle_{Jl} = i\omega_{Jl} \frac{A_0}{c} \cdot \mu_{Jl} e^{i\omega t}
\]

where

\[
\mu_{Jl} = -e \langle \Phi_J | \sum_{\alpha} r_\alpha | \Phi_I \rangle
\]

is the the transition dipole vector, and \( \omega_{Jl} = (E_J - E_I)/\hbar \).
Tully’s differential equations for the state amplitudes

\[ i\hbar \dot{A}_J = \sum_I A_I (H_{JI} - i\hbar \dot{R} \cdot d_{JI}) \]

become

\[ i\hbar \dot{A}_J = \sum_I A_I (H_{JI} - i\hbar \dot{R} \cdot d_{JI} + i\omega_{JI} \frac{A_0}{c} \cdot \mu_{JI} e^{i\omega t}) \]

In addition, a classical electrostatic interaction term of the form

\[ E^{nucl}(R^\alpha) = - \sum_\gamma Z_\gamma R_\gamma \cdot E(t) \]

with \( E(t) = \frac{1}{c} \frac{\partial}{\partial t} A(t) \) 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 \( g_{JI} \).
NAC in DFT

**NAC evaluation**

For any one-body operator, $\hat{O}$, a mapping between MBPT and TDDFT quantities gives (we only consider transitions from the ground state $\Phi_0$)

$$\hat{O}^\dagger S^{-1/2} e_I = \omega_{0I}^{1/2} \langle \Phi_0 | \hat{O} | \Phi_I \rangle$$

where the operator $\hat{O} = \sum_{i\sigma} o_{i\sigma} \hat{a}_{a\sigma}^\dagger \hat{a}_{i\sigma}$ has components $o_{i\sigma} = \langle \phi_i | \hat{O} | \psi_{a\sigma} \rangle^2$ with $\omega_{0I} = E_I - E_0$ and

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

$e_I$ are the TDDFT eigenvectors of the pseudoeigenvalue equation,

$$\Omega e_I = \omega_{0I}^2 e_I,$$

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

$K$ is the matrix form of the TDDFT kernel

$\sum_{ia\sigma}$ stands for $\sum_{i=1}^N \sum_{a=1}^\infty \sum_{\sigma \in \{\alpha,\beta\}}$.
The operator $\hat{O}$ can be the position operator, $\hat{r}$ or the gradient $\nabla_R \hat{H}_{ee}$, or any other one-body operator of interest, and may depend parametrically on the atomic positions, $R$. 3

For practical purposes we introduce the auxiliary linear-response many-electron wavefunctions 4 as a linear combination of singly excited Slater determinants

$$\tilde{\Phi}_I[\{\phi_i\}] = \sum_{ia\sigma} c_{ia\sigma}^I \hat{a}_a^{\dagger} \hat{a}_i \hat{\Phi}_0[\{\phi_i\}],$$

with

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

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, $\psi_{a\sigma}$.

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4 IT, E. Tapavicza, U. Rothlisberger, JCP, 130, 124107 (2007); JCP, 131, 196101 (2009)
The non-adiabatic coupling elements at the mid step $t + \delta t/2$ of a TDDFT MD dynamics can therefore be calculated as

$$\dot{\mathbf{R}} \cdot d_{0l}|_{t+\delta t/2} = \left\langle \tilde{\Phi}_0(r; R(t)) \big| \nabla_R \big| \tilde{\Phi}_I(r; R(t)) \right\rangle \cdot \dot{\mathbf{R}} = \left\langle \tilde{\Phi}_0(r; R(t)) \big| \frac{\partial}{\partial t} \big| \tilde{\Phi}_I(r; R(t)) \right\rangle$$

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

The non-adiabatic coupling vectors

$$\Omega_{0l} = -\left\langle \tilde{\Phi}_I(R) | \nabla_R \tilde{\Phi}_0(R) \right\rangle = \frac{-\left\langle \tilde{\Phi}_I(R) | \nabla_R \mathcal{H} \tilde{\Phi}_0(R) \right\rangle}{E_I(R) - E_0(R)}$$

In second quantization, $\hat{r} = \sum_{ia} r_{ia} \hat{a}^{\dagger}_{a\sigma} \hat{a}_{i\sigma}$, and $\mathbf{r}$ is the vector with elements $r_{ia} = \langle \phi_a | \hat{r} | \psi_a \rangle$ in the basis of the KS orbitals.

The transition dipole matrix elements

$$\mu_{0l} = -e \omega_{0l}^{-1/2} r^{\dagger} S^{-1/2} e_l$$
Implementation

Linear response perturbative TDDFT equations (Sternheimer 1951)

\[
\sum_{j=1}^{N} (H^0_\sigma \delta_{ij} - \epsilon_{ij}) |\phi'_{l,j}\sigma> + Q^\sigma \delta v^\sigma_{\text{SCF}} |\phi_{i}\sigma> = \omega_l |\phi'_{l,i}\sigma>
\]

where \(Q^\sigma = 1 - \sum_{i=1}^{N} |\phi_{i}\sigma><\phi_{i}\sigma|\), \(H^0_\sigma\) is the Kohn-Sham Hamiltonian, \(\epsilon_{ij}\) is a Lagrangian multiplier ensuring the orthogonality of the ground state orbitals, 

\[
\delta v^\sigma_{\text{SCF}} (r, \omega) = \int d^3 r' \left( \frac{1}{|r - r'|} + \frac{\delta^2 E_{xc}}{\delta \rho_\sigma (r) \delta \rho_\sigma (r')} \bigg|_{\rho = \rho_0} \right) \rho'_{l,i}(r', \omega)
\]

(using ALDA) with \(\rho'_{l,i}(r, t) = \sum_i \phi_{i}\sigma(r) \phi'^*_{l,i}\sigma(r, t) + \phi'_{l,i}(r, t) \phi^*_{i}\sigma(r)\).

In this formulation:

\[
\tilde{\Phi}_l[\{\phi\}, \{\phi'\}, \{\phi''\}] = \sum_{\sigma} \hat{r}^\dagger_{l,i\sigma} \hat{a}_{i\sigma} \tilde{\Phi}_0[\{\phi\}]
\]

where \(\hat{r}^\dagger_{l,i\sigma}\) is the creator operator for the linear response orbital \(\phi'_{l,i\sigma}\).
The gradient of the Hamiltonian operator in

$$\Omega_{IJ} = -\langle \Phi_I(R) | \nabla_R | \Phi_J(R) \rangle = -\frac{\langle \Phi_I(R) | \nabla_R \hat{H} | \Phi_J(R) \rangle}{E_I(R) - E_J(R)}$$

is split into the *explicit* and the *implicit* terms,

$$\nabla_R \hat{H}[\rho](R) = \frac{\partial \hat{H}[\rho](R)}{\partial R} |_{\rho} + \int dR \frac{\partial \hat{H}[\rho](R)}{\partial \rho(r)} \frac{\partial \rho(r)}{\partial R},$$

- The first one can be computed analytically and describes the contribution from the electrostatic interaction between nuclei and electrons, and from the local and nonlocal parts of the pseudopotentials.
- The second term instead adds the contribution from the Hartree and exchange-correlation potentials.
There are two possible solutions of the implicit term:

- Using finite differences. Costly because there are $3 \times M$ nuclear displacements ($M$ is the number of atoms).
- Using Density Functional Perturbation Theory (DFPT) with perturbing functional

$$E_{\gamma}^{\text{pert}}[\rho] = \int d\mathbf{r} \rho(\mathbf{r}) \frac{\partial V_{\text{ions,el}}(\mathbf{r})}{\partial R_{\gamma}}$$

where the perturbation is described by an infinitesimal nuclear displacement, $\lambda \mathbf{e}_{A\mu}$, along the cartesian axis centered on each atom.

The index $A$ labels the ions and $\mu$ the cartesian coordinates along which the displacements occur ($\mu = 1, 2, 3$). We use the collective index $\gamma$ for both indices $A$ and $\mu$.

$$\delta \rho_{\gamma}(\mathbf{r}) = \sum_{i\sigma} \phi_{i\sigma}(\mathbf{r}) \delta \phi_{\gamma,i\sigma}^{*}(\mathbf{r}) + \delta \phi_{\gamma,i\sigma}(\mathbf{r}) \phi_{i\sigma}^{*}(\mathbf{r})$$
The linear response-density is then used to compute the matrix elements of the *implicit* term of $\nabla_R \hat{H}[\rho](R)$ according to

$$\langle \tilde{\Phi}_I | \sum_\sigma \int dr \frac{\partial \hat{H}[\rho](R)}{\partial \rho_\sigma(r)} \frac{\partial \rho_\sigma(r)}{\partial R} | \tilde{\Phi}_J \rangle = \langle \tilde{\Phi}_I | \sum_\gamma e_\gamma \sum_\sigma \int dr \frac{\partial \hat{H}[\rho](R)}{\partial \rho_\sigma(r)} \rho'_{\gamma\sigma}(r) | \tilde{\Phi}_J \rangle$$

where $| \tilde{\Phi}_J \rangle$ is either the ground state wavefunction ($J = 0$) or $^5$

$$| \tilde{\Phi}_J \rangle = \sum_{i=1}^N \sum_\sigma \hat{r}_{J,i\sigma}^\dagger \hat{a}_{J,i\sigma} | \tilde{\Phi}_0 \rangle$$

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$^5$ IT, E. Tapavicza, U. Rothlisberger, JCP, 130, 124001 (2009)
Nearly equilateral $H_3$

**Upper panel:** Adiabatic potential energy surfaces of the ground state and first singlet excited state of $H_3$ calculated along the path depicted here above. Solid lines: TDDFT/ALDA; Dashed lines: reference.

**Lower panel:** Corresponding z-component of the NACVs on the approaching $H$ atom. The ALDA/TDDFT results (circles) are shown together with some reference data. Un-rescaled TDDFT/ALDA z components of the NACVs are also shown (crosses).

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Protonated formaldimine, $CH_2NH_2^+$

Time evolution of the potential energy surfaces (upper panel) $S_0$ (solid line), $S_1$ (dashed line), $S_2$ (dash dotted line), and $S_3$ (dotted line). The state that drives the dynamics is shown in red. The main structural change in $S_2$ during the first 10 fs is a CN bond elongation. The middle and lower panel show the corresponding time series of the absolute value of the NACVs of the carbon (black) and nitrogen (red) atoms computed for the pair of states $S_0/S_1$ and $S_1/S_2$, respectively.
Photoinduced excitation of $H_2^+$

\[ H_2^+ \]

Rabi oscillations

H$_2^+$

Non-adiabatic dynamics with external laser fields
**H$_2^+$ DFT BLYP**

![Graph showing energy as a function of internuclear distance and evolution of wavefunctions over time](image)

- Energy [a.u.]
- r [Å]
- fs

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**Non-adiabatic dynamics with external laser fields**
H$_2^+$ DFT BLYP

Energy [a.u.]

|c$_0$|$^2$

|c$_1$|$^2$

fs

H$_2$ Non-adiabatic dynamics with external laser fields

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Non-adiabatic dynamics with external laser fields

$H_2^+$ - HF

Energy [a.u.] vs. $r$ [Å]

$|C_0|^2$ and $|C_1|^2$ vs. time [fs]

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Non-adiabatic dynamics with external laser fields
Photoinduced excitation of LiF

E [eV]

2\textsuperscript{2}\Sigma^+ - S\textsubscript{2}

1\textsuperscript{1}\Pi - S\textsubscript{1}

1\textsuperscript{1}\Sigma^+ - Ground state

HOMO-2

LUMO

HOMO

LUMO

HOMO-1

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Non-adiabatic dynamics with external laser fields
LiF

(1,0,0) - Without hops

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LiF

Pulse (1,0,0) - High intensity

Li-F [Ångstrom]

Time [fs]

C(t)^2

Non-adiabatic dynamics with external laser fields
Non-adiabatic dynamics with external laser fields
LiF

Pulse (1,1,1)

Energy [hartree]

Time [fs]

LiF
Non-adiabatic dynamics with external laser fields
LiF

Pulse (1,1,1) - High intensity - Out of phase (omega = 0.005 a.u.)

Time [fs]

|C(t)|²

Li-F [Å]

Non-adiabatic dynamics with external laser fields
Photoinduced excitation of Oxirane

Disrotatory Mechanism

Conrotatory Mechanism

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Non-adiabatic dynamics with external laser fields
<table>
<thead>
<tr>
<th>Outline</th>
<th>MQCD</th>
<th>Radiation Field</th>
<th>NAC</th>
<th>NAC computation</th>
<th>Appl. H₂⁺</th>
<th>Appl. LiF</th>
<th>Appl. Oxirane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxirane</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

XXX
Oxirane

Succession of short pulses

|C(t)|

Energy [hartree]

A(t)

Time [fs]
Dr. Enrico Tapavicza (University of California Irvine)
Basile Curchod (EPFL)
Ursula Roethlisberger (EPFL)

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