An example of Ab Initio Multiple Spawning dynamics using LR-TDDFT

On the ultrafast nonradiative decay of DMABN
Photophysics of DMABN - Ultrafast deactivation

Typical example of dual emission.

\[ \text{DMABN} = 4-(N,N\text{-dimethylamino})\text{benzonitrile} \]

Ultrafast deactivation of DMABN - gas phase

Explanation from quantum-chemical calculations:

Ultrafast deactivation of DMABN - gas phase

Explanation from quantum-chemical calculations:


What about the ultrafast relaxation from $S_2$ to $S_1$ after photoexcitation?

Experimental result: $S_2$ to $S_1$ relaxation is potentially linked to a twist of the dimethylamino group.

Ultrafast deactivation of DMABN - gas phase

What about the ultrafast relaxation from $S_2$ to $S_1$ after photoexcitation?

Does the twist of the dimethylamino group take place immediately upon photoexcitation?

Use Ab Initio Multiple Spawning coupled with LR-TDDFT (GPUs) to investigate the $S_2/S_1$ ultrafast relaxation of DMABN.

Computational details: AIMS/ωPBE(0.3)/6-31G (21 ICs), Tamm-Dancoff and adiabatic approximation. Validation with CC2 and ADC(2).
Excited-state population transfer

Ultrafast relaxation of DMABN from $S_2$ to $S_1$. 
Twist angle

Population transfer takes place without a twist of the dimethylamino group.
Nonadiabatic relaxation from $S_2$ to $S_1$ in 50fs, with an ultrafast decay in the first 10fs.

Twist of the dimethylamino group only happens after the first 50fs.

Nuclear wavepacket rapidly acquires a dominant LE character.

Up to this point, we have tried to preserve as much as possible the quantum nature of the nuclei...

Can we devise approximate nonadiabatic methods based on classical nuclei?
Approximate methods based on classical nuclei

Dynamics of the nuclear density represented by trajectories

\[ \left| \chi_I(R, t) \right|^2 = \frac{1}{N_{\text{traj}}} \sum_{\alpha}^{N_{\text{traj}}} \delta(R_{i\alpha}(t) - R) \]

Mixed quantum/classical methods: the dynamics of the nuclear wavepacket(s) can be approximated by a swarm of classically-evolving trajectories.
Mixed quantum/classical approaches – main idea

The nuclei of the molecule of interest will evolve according to Newton’s law of motion\(^1\), and a time-dependent Schrödinger equation is propagated on the support of this trajectory \(\alpha\).

**Time-dependent electronic Schrödinger equation**

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

**Newton equation**

\[
F^\alpha = -\nabla_{\mathbf{R}} \epsilon(\mathbf{R})\big|_{\mathbf{R} = \mathbf{R}^\alpha(t)}
\]

The prescription for the the potential energy \(\epsilon(\mathbf{R})\) used to propagate the classical nuclei gives rise to two methods: **Ehrenfest dynamics** and **Trajectory Surface Hopping**.

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\(^1\)A link between the time-dependent Schrödinger equation for the nuclei and the Newton equation can be performed using a polar representation of the nuclear wavefunction. See for example *ChemPhysChem*, **14**, 1314 (2013).
Mixed quantum/classical approaches – main idea

The electronic wavefunction is often expanded in a basis of adiabatic electronic states:

$$\tilde{\Phi}(r; R^\alpha(t), t) = \sum_J c_j^\alpha(t) \Phi_J(r; R^\alpha(t)).$$

Upon insertion into the time-dependent electronic Schrödinger equation, we obtain:

**Time-dependent electronic Schrödinger equation in an electronic basis**

$$i\hbar \dot{c}_j^\alpha(t) = \sum_J c_j^\alpha(t) \left( E_J^\text{el}(R^\alpha(t)) \delta_{JJ} - i\hbar \dot{R}_j^\alpha \cdot d_{IJ}(R^\alpha(t)) \right)$$

In this form, one recognizes the electronic energies $E_J^\text{el}(R^\alpha(t))$ and the nonadiabatic coupling vectors $d_{IJ}(R^\alpha(t))$ described previously.

The propagation of the time-dependent electronic wavefunction on the support of the classical trajectory provides a measure of nonadiabatic effects.
Mixed quantum/classical approaches

The nuclei of the molecule of interest will evolve according to Newton’s law of motion\(^2\), and a time-dependent Schrödinger equation is propagated on the support of this trajectory \(\alpha\).

### Time-dependent electronic Schrödinger equation in an electronic basis

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### Newton equation

\[
F^\alpha = -\nabla_R \epsilon(R)|_{R=R^\alpha(t)}
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The prescription for the potential energy \(\epsilon(R)\) used to propagate the classical nuclei gives rise to two methods:

**Ehrenfest dynamics** and **Trajectory Surface Hopping**.

\(^2\)A link between the time-dependent Schrödinger equation for the nuclei and the Newton equation can be obtained by using a polar representation of the nuclear wavefunction. See for example *ChemPhysChem*, **14**, 1314 (2013).