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

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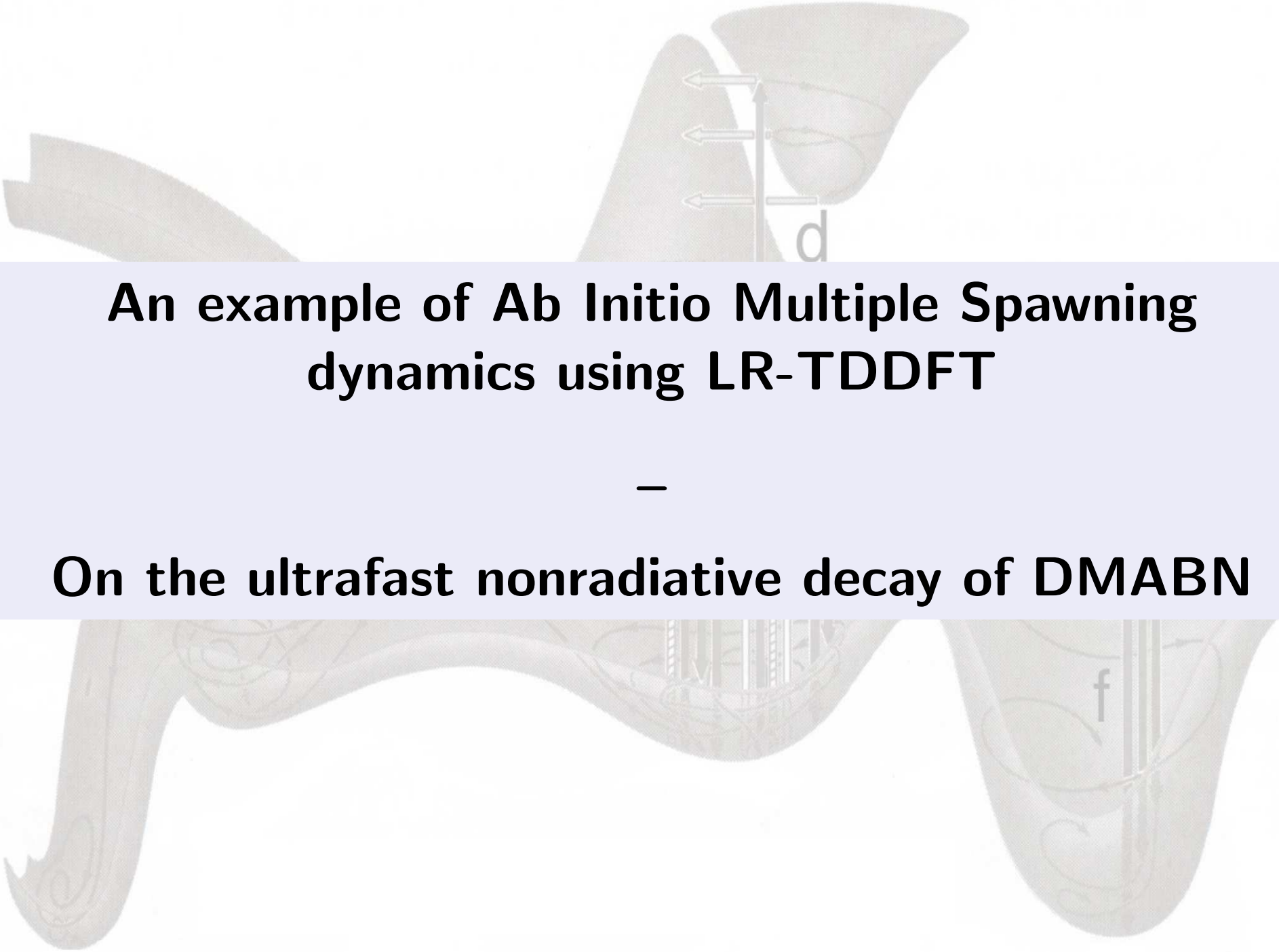
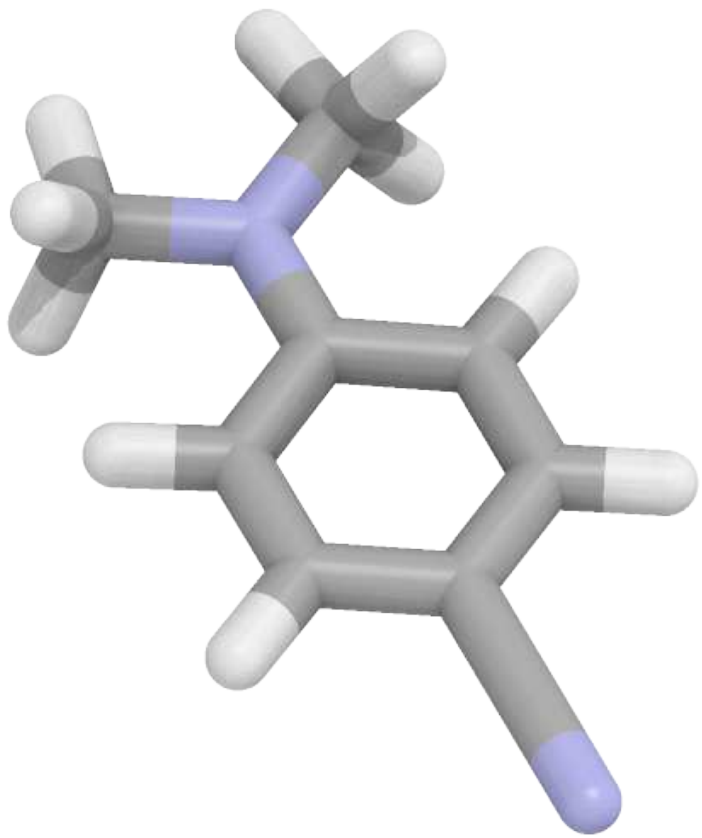
On the ultrafast nonradiative decay of DMABN

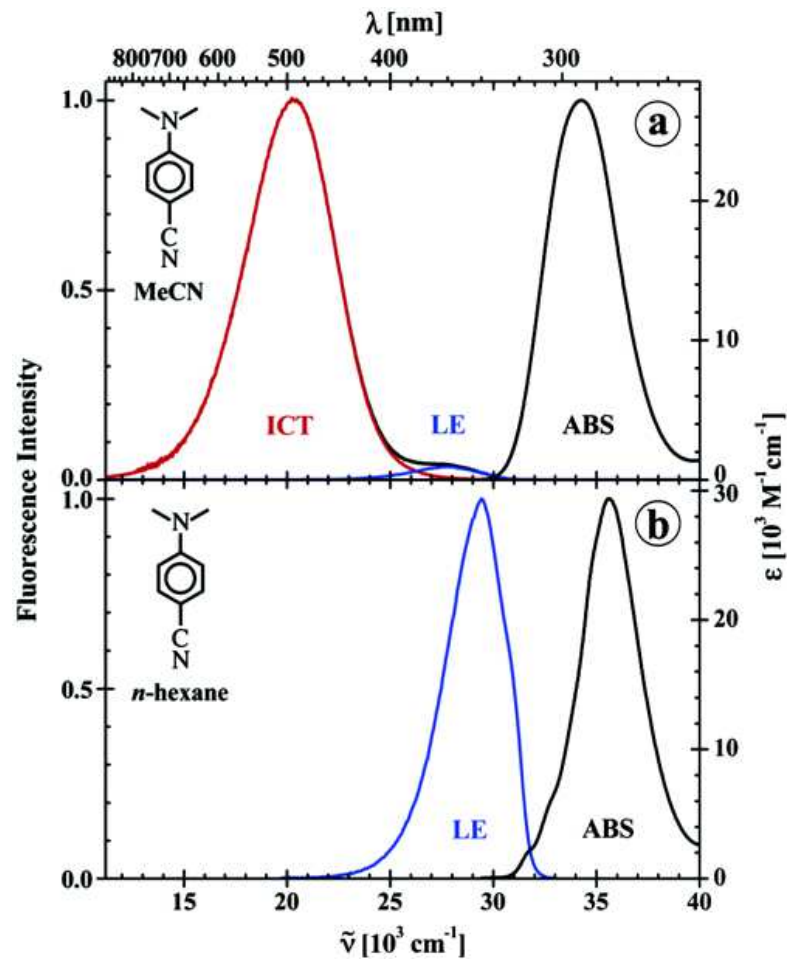


Credit: J. Michl and V. Bonacic-Koutecký, "Electronic Aspects of Organic Photochemistry". John Wiley and Sons, Inc., New York, 1990.

Photophysics of DMABN - Ultrafast deactivation

Typical example of **dual emission**.



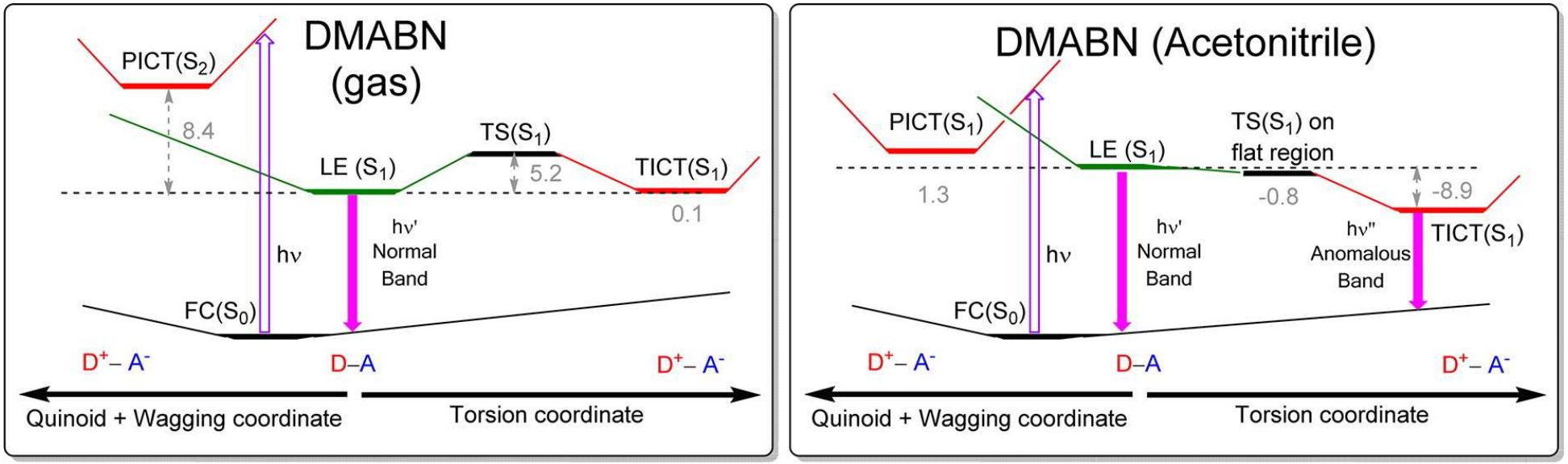


DMABN = 4-(*N*,*N*-dimethylamino)benzonitrile

S. I. Druzhinin, N. P. Ernsting, S. A. Kovalenko, L. P. Lustres, T. A. Senyushkina, K. A. Zachariasse, *J. Phys. Chem. A*, **110**, 2955 (2006).

Ultrafast deactivation of DMABN - gas phase

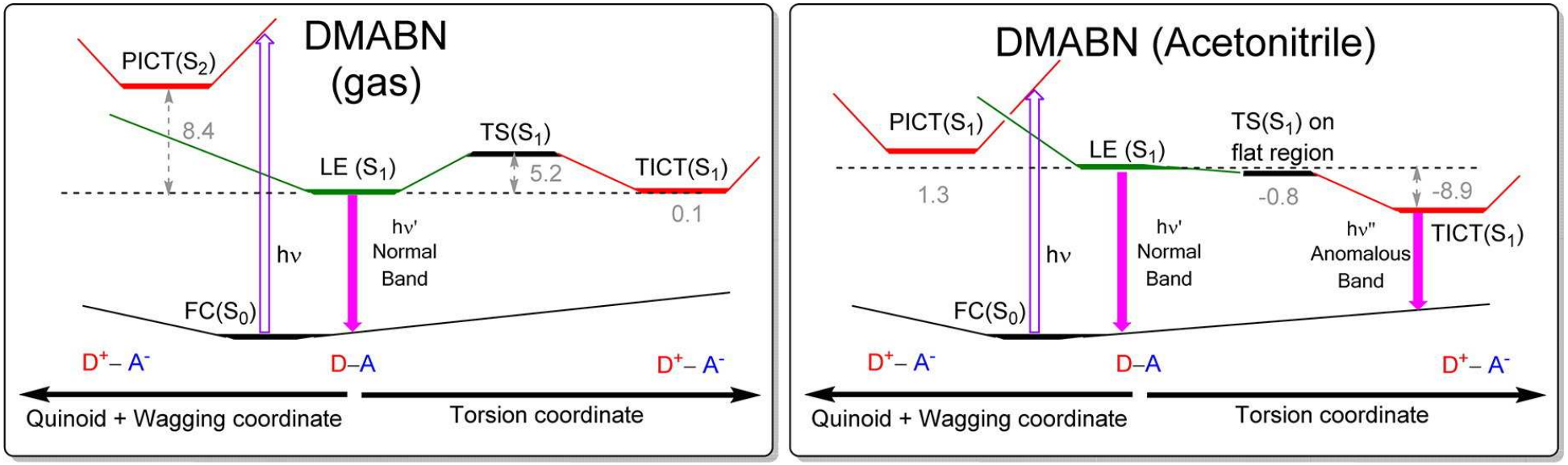
Explanation from quantum-chemical calculations:



CASPT2/CASSCF, *J. Phys. Chem. A*, **119**, 1983 (2015).

Ultrafast deactivation of DMABN - gas phase

Explanation from quantum-chemical calculations:



CASPT2/CASSCF, *J. Phys. Chem. A*, **119**, 1983 (2015).

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.

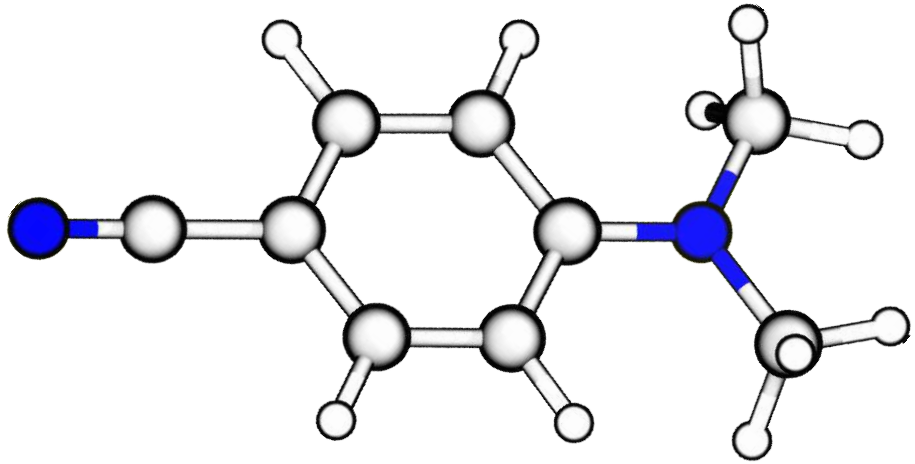
W. Fuß, K. K. Pushpa, W. Rettig, W. E. Schmid, and S. A. Trushin, *Photochem. Photobiol. Sci.*, **1**, 255 (2002).

Ultrafast deactivation of DMABN - gas phase

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

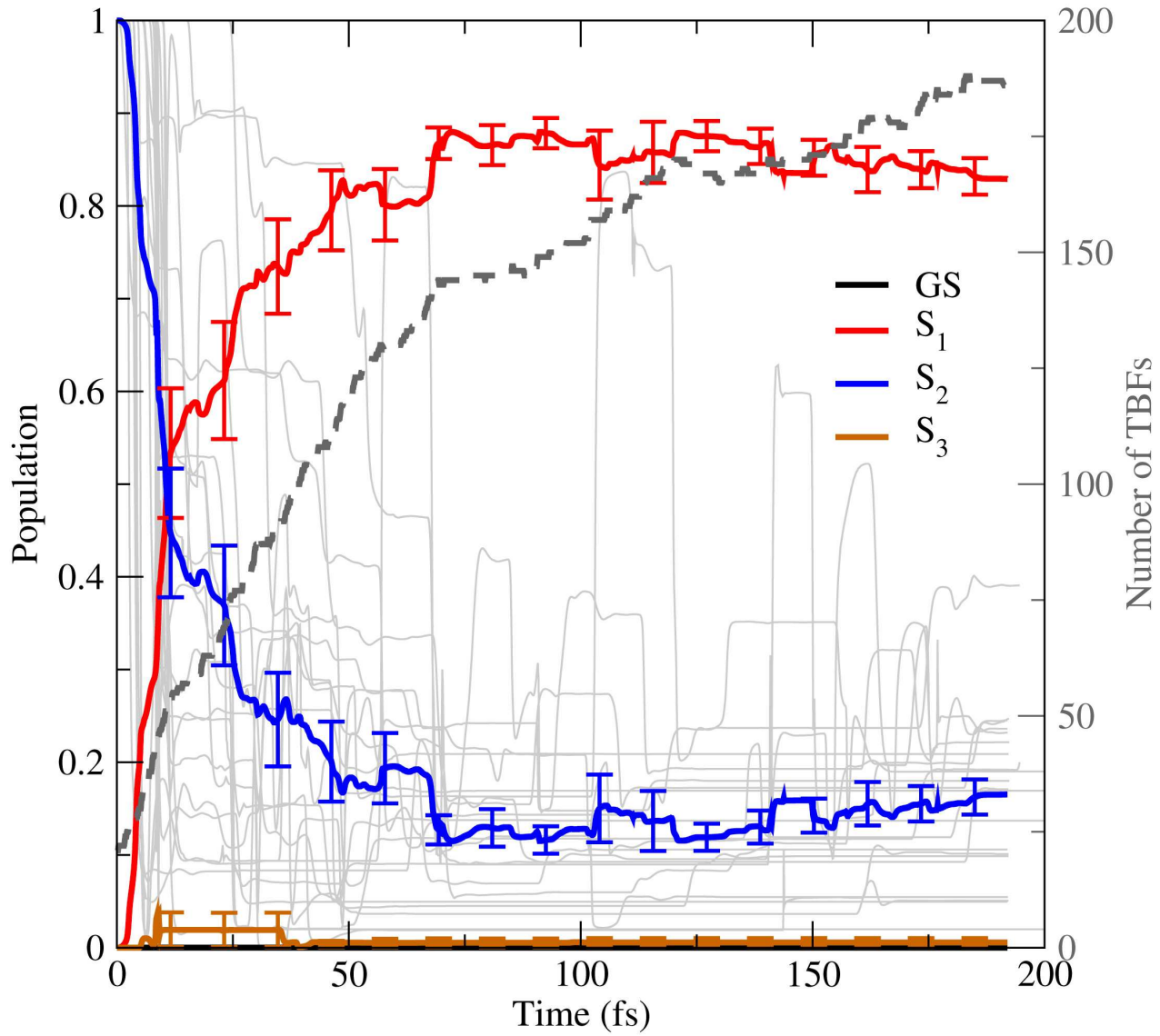
Does the twist of the dimethylamino group take place immediately upon photoexcitation?

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



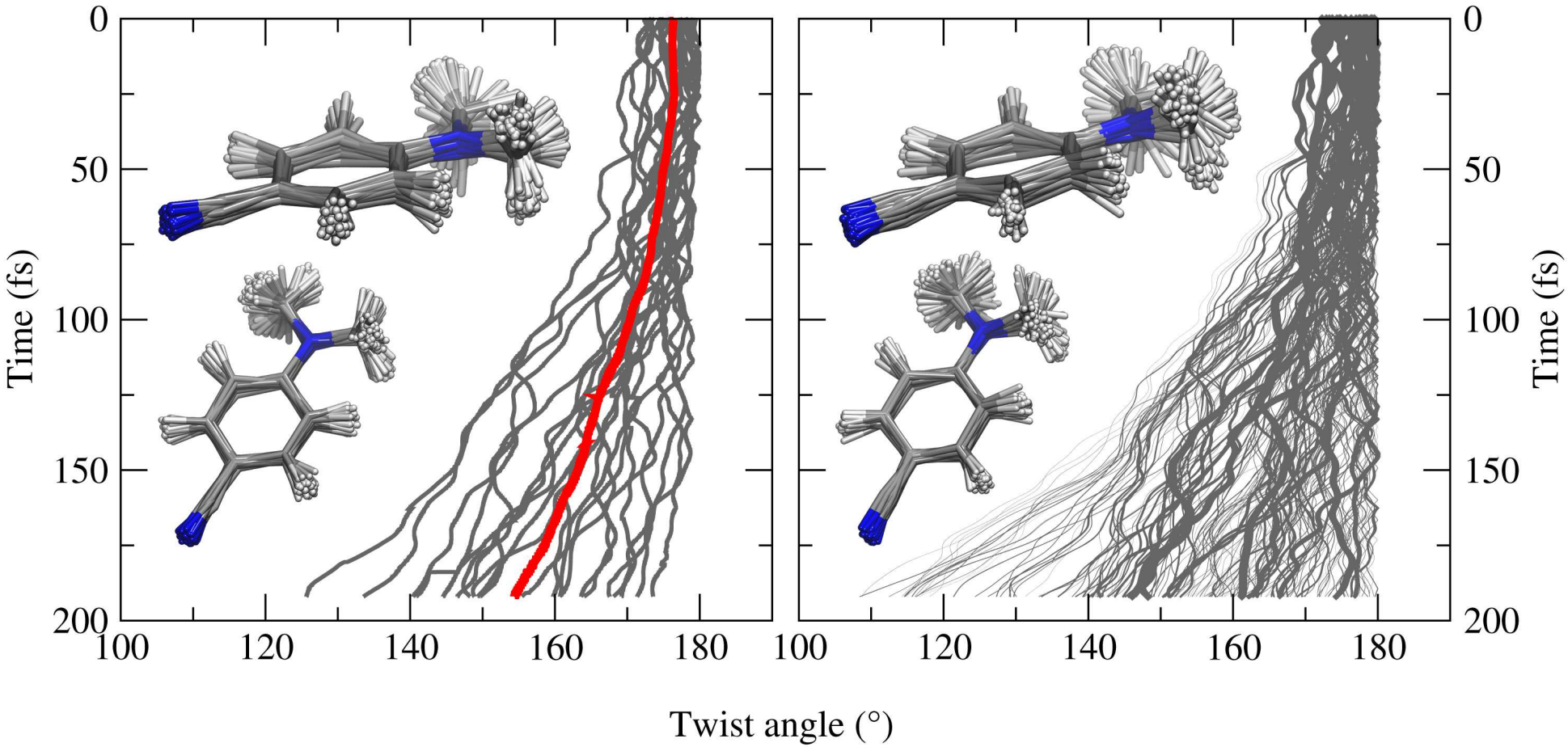
Computational details: AIMS/ωPBE(0.3)/6-31G (21 ICs), Tamm-Dancoff and adiabatic approximation. Validation with CC2 and ADC(2).

Excited-state population transfer



Ultrafast relaxation of DMABN from S_2 to S_1.

Twist angle

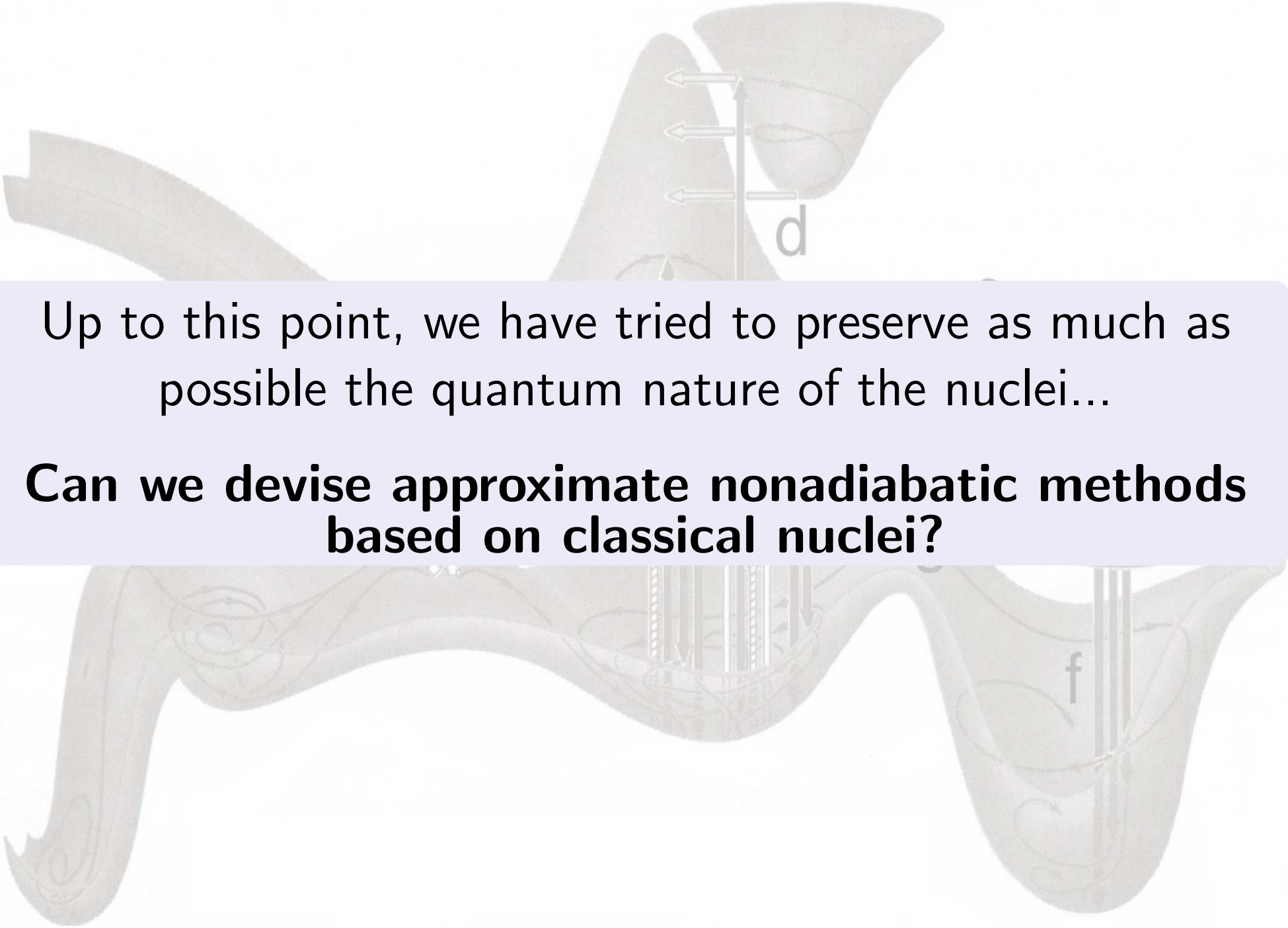


Population transfer takes place without a twist of the dimethylamino group.

Summary - nonadiabatic dynamics of DMABN

- **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.**

B. F. E. Curchod, A. Sisto, T. J. Martínez, *J. Phys. Chem. A*, **121**, 265 (2017)



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

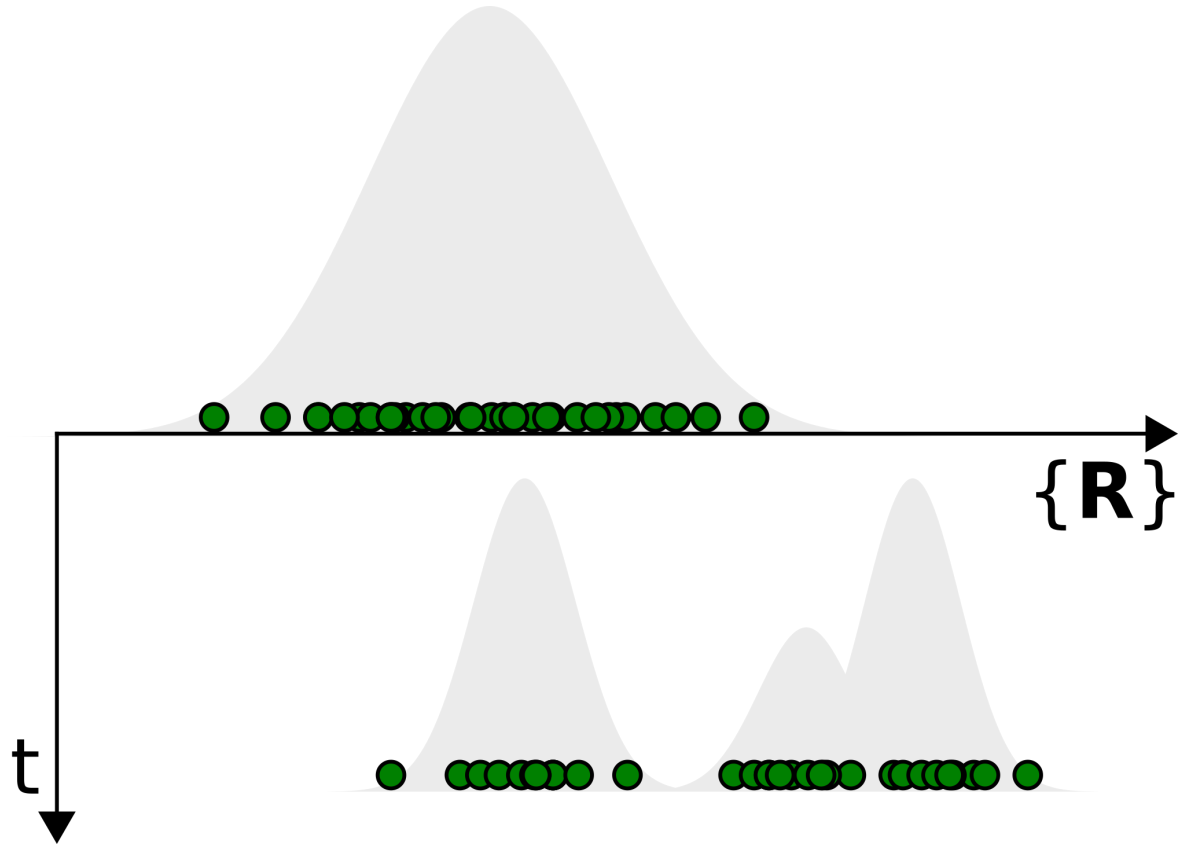
Can we devise approximate nonadiabatic methods based on classical nuclei?

Credit: J. Michl and V. Bonacic-Koutecký, "Electronic Aspects of Organic Photochemistry". John Wiley and Sons, Inc., New York, 1990.

Approximate methods based on classical nuclei

Dynamics of the nuclear density represented by trajectories

$$|\chi_I(\mathbf{R},t)|^2 = \frac{1}{N_{traj}} \sum_{\alpha}^{N_{traj}} \delta(\mathbf{R}_I^{\alpha}(t) - \mathbf{R})$$



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 α.

Time-dependent electronic Schrödinger equation

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

Newton equation

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

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**.

[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:

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

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

Time-dependent electronic Schrödinger equation in an electronic basis

$$i\hbar \dot{c}_I^\alpha(t) = \sum_J c_J^\alpha(t) \left(E_J^{el}(\mathbf{R}^\alpha(t)) \delta_{IJ} - i\hbar \dot{\mathbf{R}}^\alpha \cdot \mathbf{d}_{IJ}(\mathbf{R}^\alpha(t)) \right)$$

In this form, one recognizes the electronic energies $E_I^{el}(\mathbf{R}^\alpha(t))$ and the nonadiabatic coupling vectors $\mathbf{d}_{IJ}(\mathbf{R}^\alpha(t))$ 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 α.

Time-dependent electronic Schrödinger equation in an electronic basis

$$i\hbar\dot{c}_I^\alpha(t) = \sum_J c_J^\alpha(t)\left(E_J^{el}(\mathbf{R}^\alpha(t))\delta_{IJ} - i\hbar\dot{\mathbf{R}}^\alpha \cdot \mathbf{d}_{IJ}(\mathbf{R}^\alpha(t))\right)$$

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