

**Simulations of nonadiabatic dynamics
by on-the-fly semiempirical and QM/MM
methods.**

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Semiclassical simulations of photochemistry: our options.

- The nuclear dynamics is represented by a swarm of classical trajectories; each trajectory runs on a given adiabatic PES, but it may jump to another PES at any time (surface hopping).
- The electronic wavefunction $|\Psi(t)\rangle$ evolves in time according to the TDSE:
$$i\frac{d}{dt} |\Psi(t)\rangle = \hat{\mathcal{H}}_{el}(t) |\Psi(t)\rangle$$
- $|\Psi(t)\rangle$ is expanded in the basis of the N lowest adiabatic states ψ_K :
$$|\Psi(t)\rangle = \sum_K A_K(t) |\psi_K(t)\rangle$$
and $P_K(t) = |A_K|^2$ are the adiabatic probabilities.
- Switching from an adiabatic surface to another depends on the $P_K(t)$ probabilities, according to Tully's surface hopping algorithm.
- Initial coords. and momenta in the ground state are sampled according to Wigner or Boltzmann distributions; each trajectory starts with a vertical excitation.
- Observables are computed as averages over many trajectories.

The “direct” strategy.

- The adiabatic electronic states $|\psi_K\rangle$ and energies E_K are computed at each step of the trajectory by a semiempirical NDO method.
- CI wavefunctions are built with MO's obtained by floating occupation SCF.
- The semiempirical parameters are optimized so as to reproduce ab initio or empirical data.
- The TDSE is integrated by expansion on a “locally diabatic” basis, i.e. a set of electronic states $|\eta_I\rangle$ such as to annihilate the projection of the dynamical couplings along the nuclear velocity vector:

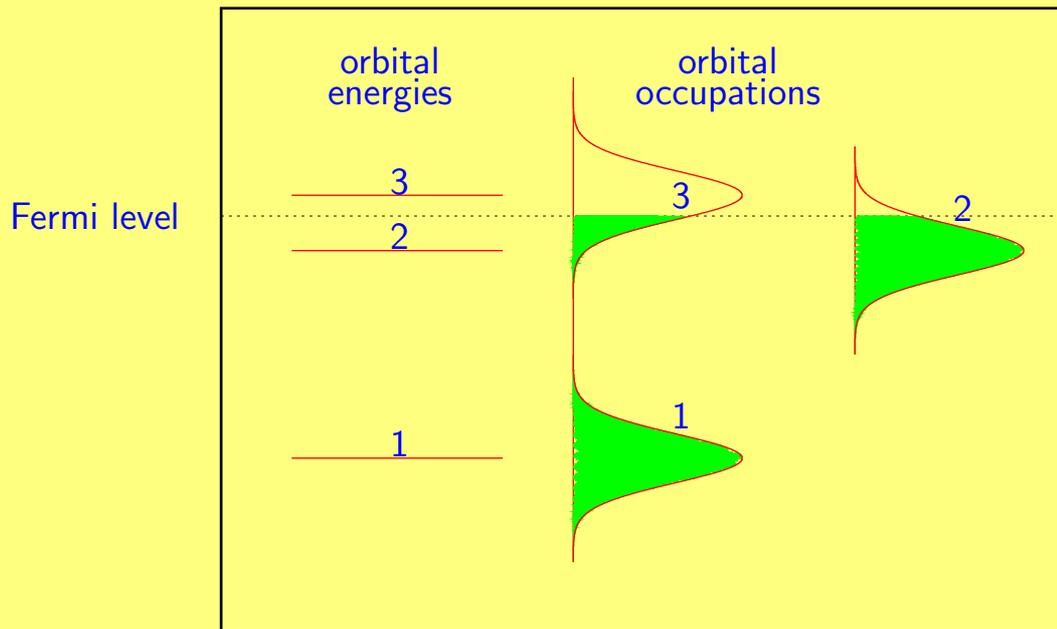
$$\sum_{\alpha} \langle \eta_I | \frac{d}{dQ_{\alpha}} | \eta_J \rangle \cdot \dot{Q}_{\alpha} = \langle \eta_I | \frac{d}{dt} | \eta_J \rangle = 0.$$

The diabatic states are obtained by rotation of the adiabatic basis, according to the overlaps $\langle \psi_K(t) | \psi_K(t + \Delta) \rangle$, computed across a time-step: they are diabatic only with regard to a given trajectory.

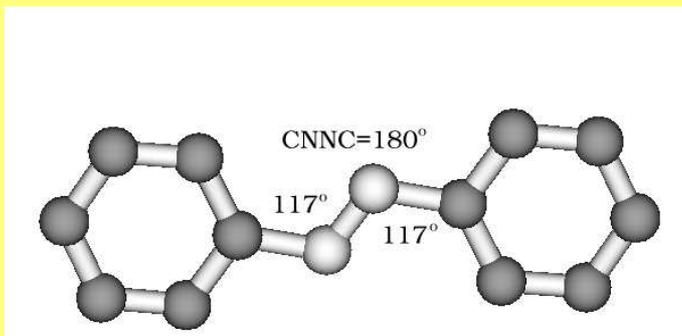
See: Granucci and Toniolo, Chem. Phys. Lett. **325**, 79 (2000);

Granucci, Persico and Toniolo, J. Chem. Phys. **114**, 10608 (2001)

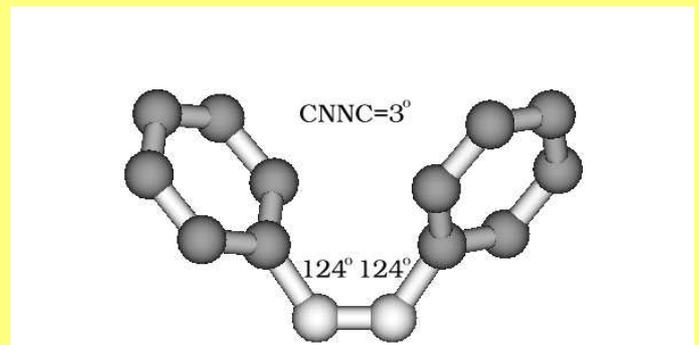
Floating occupation SCF



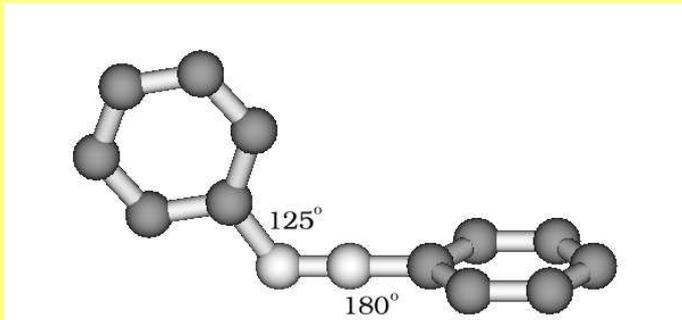
Example: azobenzene photochemistry.



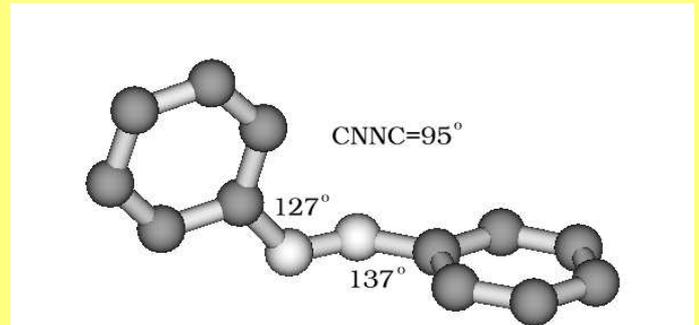
trans-azobenzene (TAB), S_0



cis-azobenzene (CAB), S_0



perpendicular invertomer, S_0



rotamer, S_1

See: Ciminelli, Granucci and Persico, Chem. Eur. J. 10, 2327 (2004)

Azobenzene, vertical excitation energies (eV).

method	TAB			CAB		
	S_1	S_2	S_3	S_1	S_2	S_3
semiemp. (this work)	2.94	4.28	4.80	3.23	5.03	5.00
CIPSI ^a	2.81	4.55	4.61	2.94	4.82	4.86
CASSCF 6e ⁻ /5MO	3.48	6.26	6.37	4.53	6.80	6.37
MRSDCI ^b	3.11	5.39	6.56	3.95	6.12	5.56
CASSCF 10e ⁻ /10MO ^c	3.11	5.56	5.66			
CASPT2 ^c	2.34	4.74	4.81			
CASSCF 14e ⁻ /12MO ^d	3.18			3.38		
CASPT2 ^e	2.70	3.95	4.12			
experimental ^f	2.80	3.94		2.86	4.38	

^a Multireference perturbation theory with selected zero-order space; reduced 6-31G basis set with polarization functions on N.

^b Multireference singles and doubles CI; split-valence basis set with

polarization functions on N.

^c 6-31G basis set.

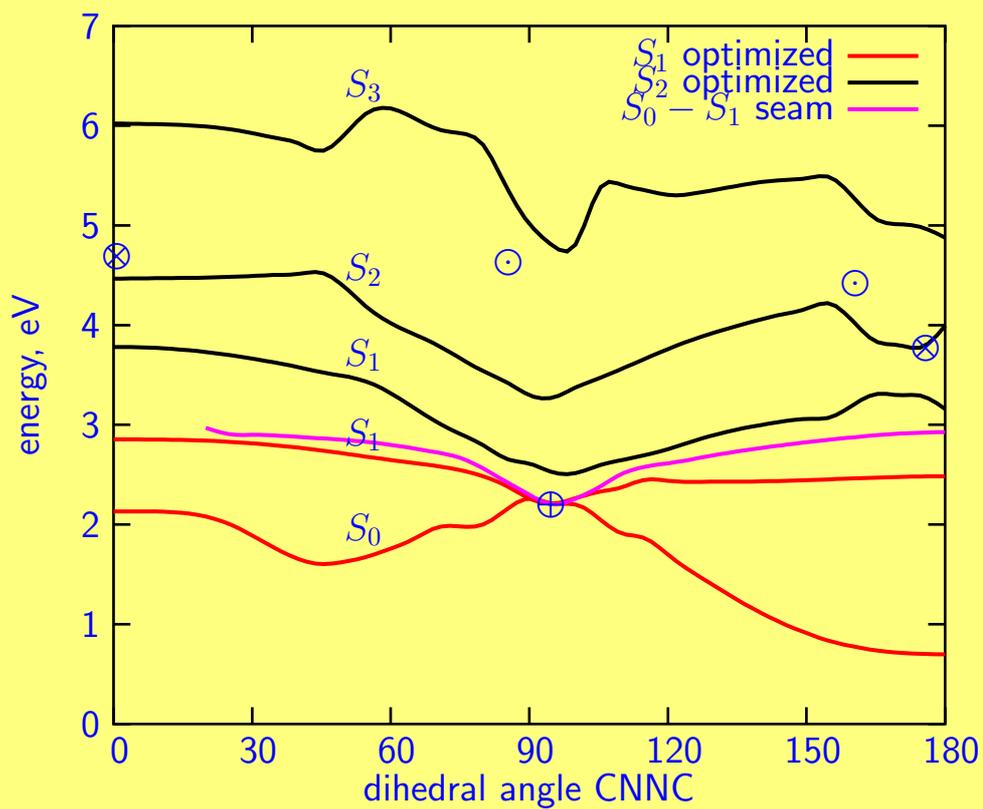
^d 6-31G* basis set.

^e ANO basis

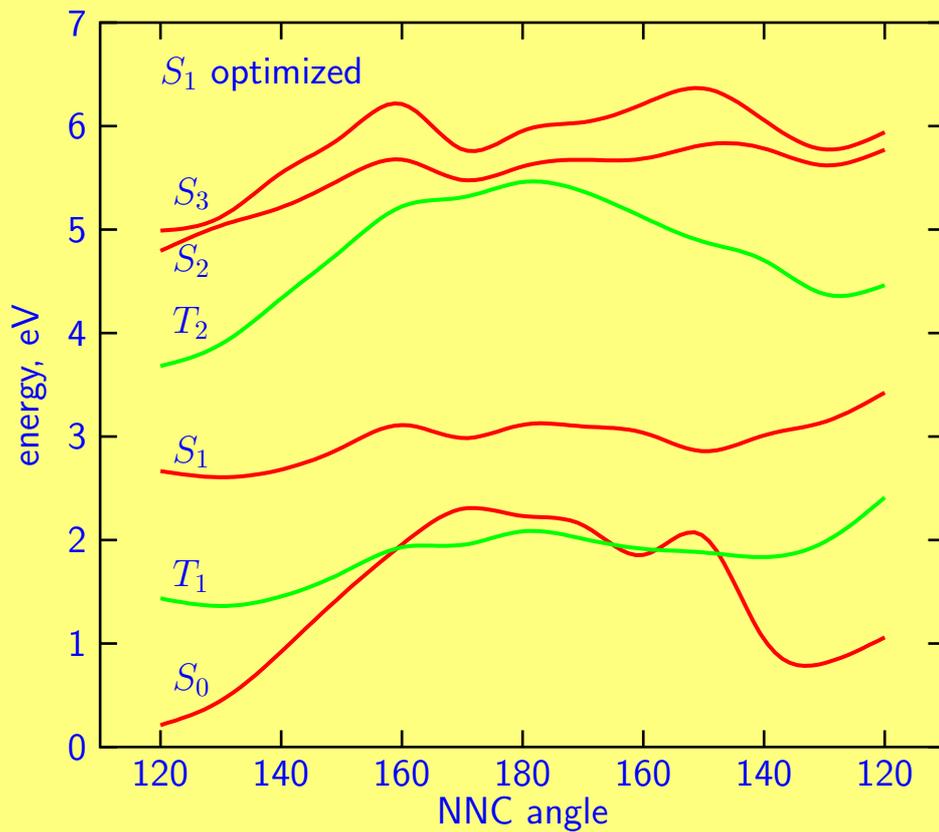
set, $3s2p1d$ for C and N, $2s1p$ for H. Based on 14e⁻/12MO CASSCF

^f Absorption maxima.

Potential energy curves of azobenzene: torsion.



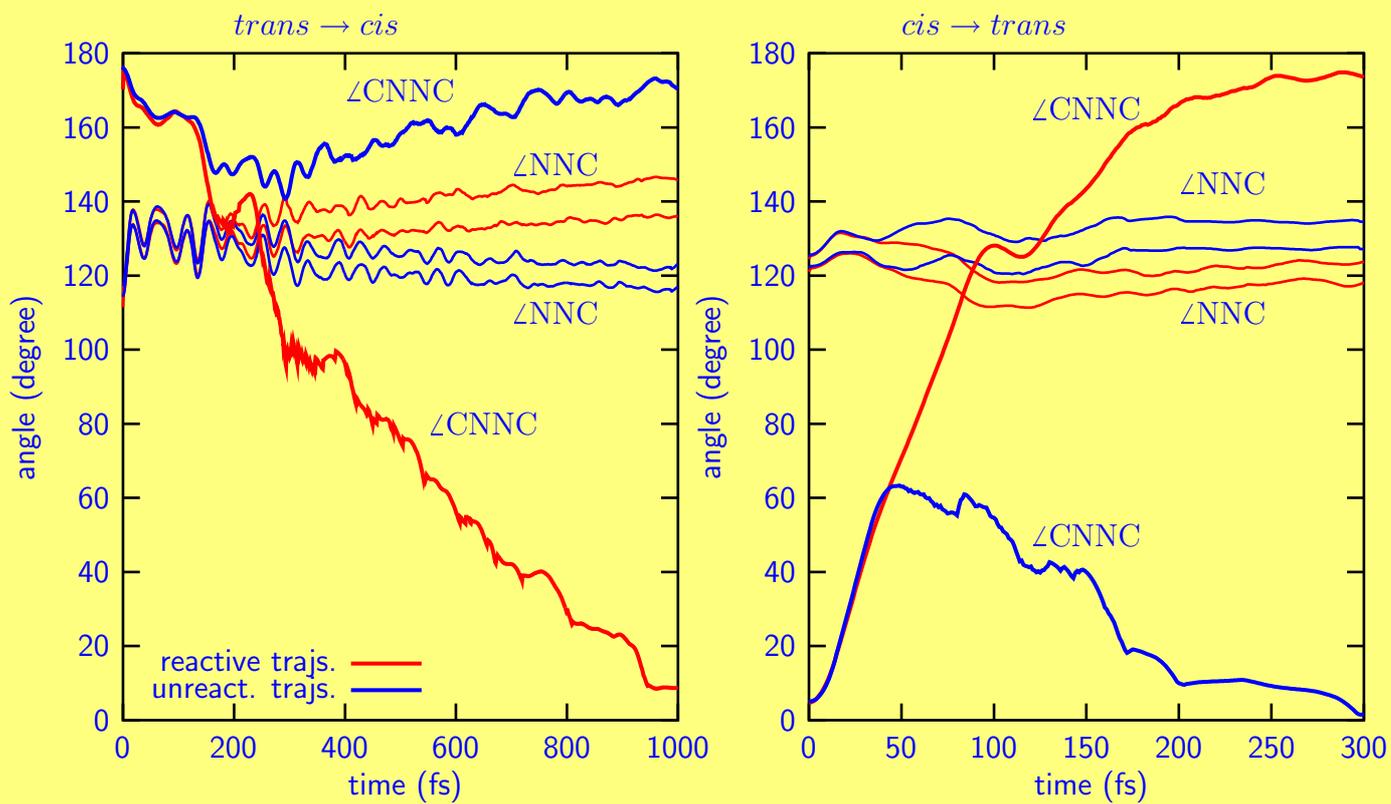
Potential energy curves of azobenzene: inversion.



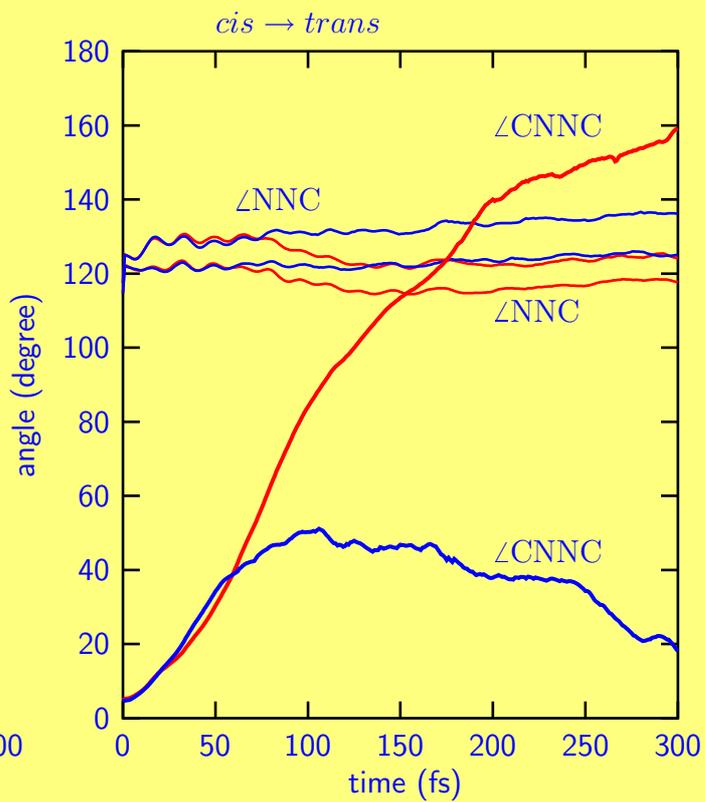
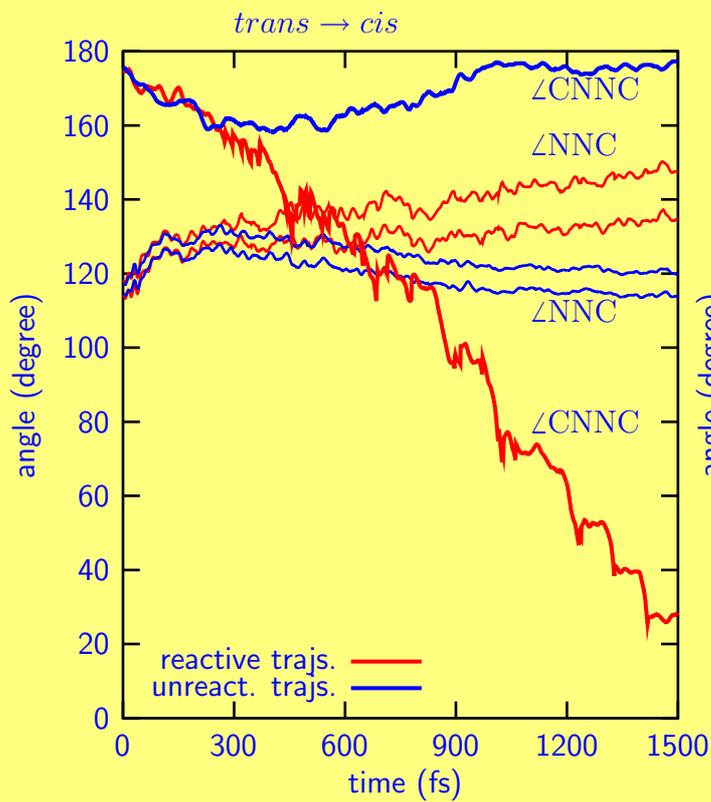
Azobenzene photoisomerization quantum yields.

		$n \rightarrow \pi^*$ excitation	$\pi \rightarrow \pi^*$ excitation
$trans \rightarrow cis$	computed	0.33 ± 0.03	0.15 ± 0.02
	experim.	0.20-0.36	0.09-0.20
$cis \rightarrow trans$	computed	0.61 ± 0.03	0.48 ± 0.03
	experim.	0.40-0.75	0.27-0.44

Isomerization mechanism, $n \rightarrow \pi^*$ excitation.



Isomerization mechanism, $\pi \rightarrow \pi^*$ excitation.



Torsion angle $\theta = \angle\text{CNNC}$ and surface hopping.

units: degrees and fs

trans \rightarrow *cis*

initial $\langle\theta\rangle$

$\langle\theta\rangle$ at first hop $S_1 \rightarrow S_0$

$\langle d\theta/dt \rangle$ at first hop $S_1 \rightarrow S_0$

$\langle\theta\rangle$ at last hop $S_1 \rightarrow S_0$

$\langle d\theta/dt \rangle$ at last hop $S_1 \rightarrow S_0$

cis \rightarrow *trans*

initial $\theta = \angle\text{CNNC}$

$\langle\theta\rangle$ at first hop $S_1 \rightarrow S_0$

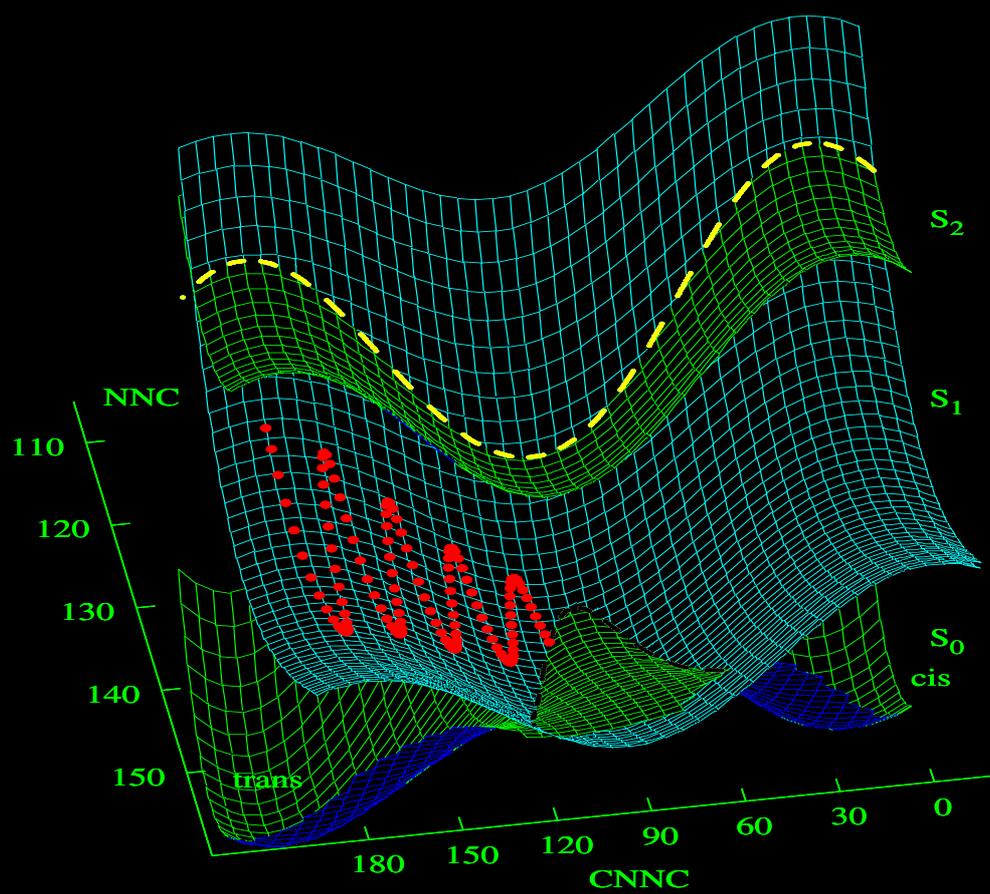
$\langle d\theta/dt \rangle$ at first hop $S_1 \rightarrow S_0$

$\langle\theta\rangle$ at last hop $S_1 \rightarrow S_0$

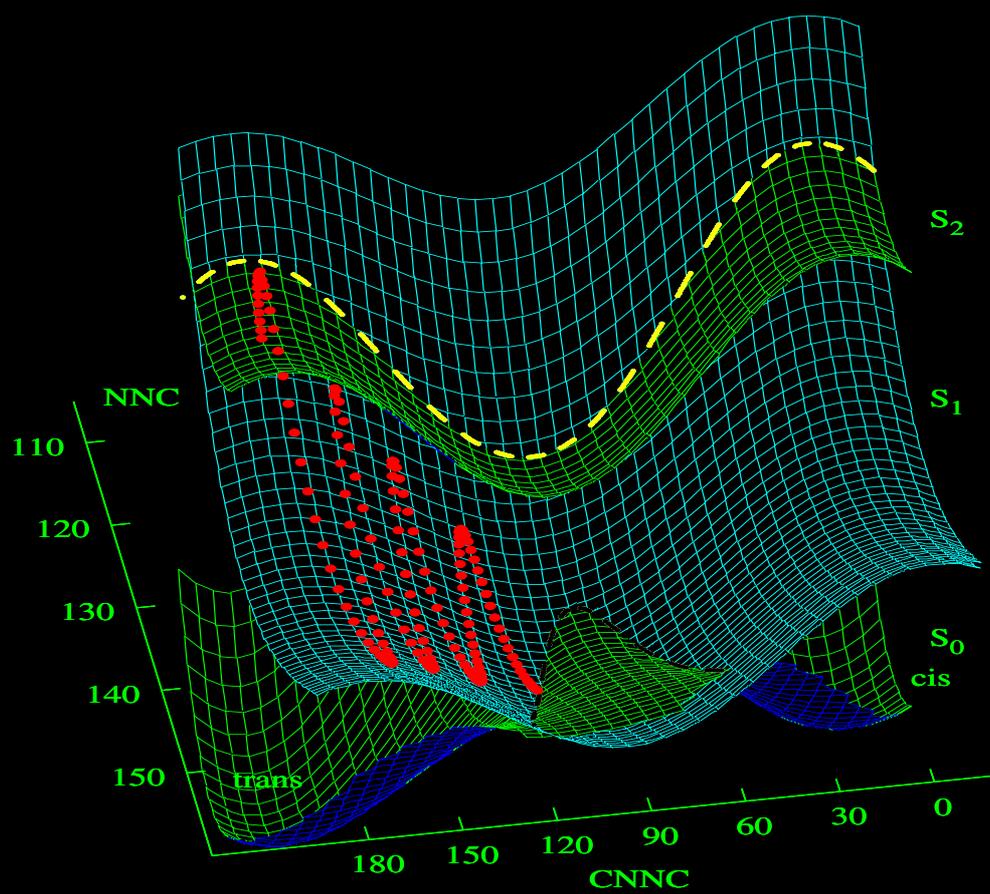
$\langle d\theta/dt \rangle$ at last hop $S_1 \rightarrow S_0$

	$n \rightarrow \pi^*$ excitation (S_1)			$\pi \rightarrow \pi^*$ excitation (S_2/S_3)		
	reactive	unreact.	total	reactive	unreact.	total
initial $\langle\theta\rangle$	175	176	176	175	176	176
$\langle\theta\rangle$ at first hop $S_1 \rightarrow S_0$	104	113	110	111	134	130
$\langle d\theta/dt \rangle$ at first hop $S_1 \rightarrow S_0$	-2.0	-0.3	-0.8	-1.7	-0.3	-0.6
$\langle\theta\rangle$ at last hop $S_1 \rightarrow S_0$	99	121	114	95	134	128
$\langle d\theta/dt \rangle$ at last hop $S_1 \rightarrow S_0$	-2.4	0.2	-0.6	-1.7	0.1	-0.2
	reactive	unreact.	total	reactive	unreact.	total
initial $\theta = \angle\text{CNNC}$	5	5	5	5	5	5
$\langle\theta\rangle$ at first hop $S_1 \rightarrow S_0$	82	81	82	82	79	80
$\langle d\theta/dt \rangle$ at first hop $S_1 \rightarrow S_0$	1.8	0.2	1.2	1.7	0.1	0.9
$\langle\theta\rangle$ at last hop $S_1 \rightarrow S_0$	88	81	85	108	80	93
$\langle d\theta/dt \rangle$ at last hop $S_1 \rightarrow S_0$	1.7	-0.6	0.8	0.8	-0.9	-0.1

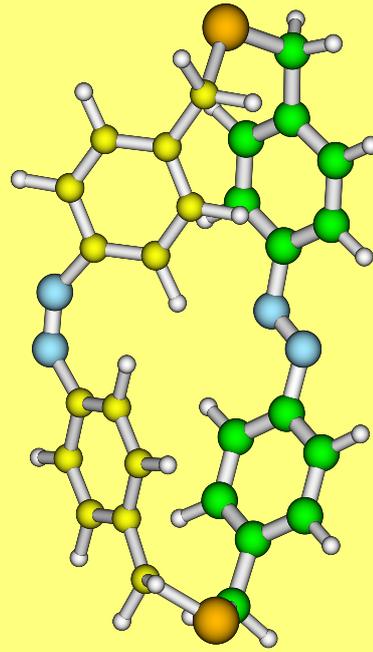
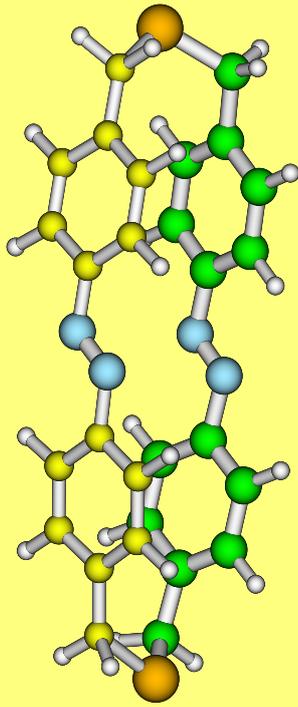
Typical *trans* \rightarrow *cis* trajectory starting in S_1 .



Typical *trans* \rightarrow *cis* trajectory starting in S_2 .



Azobenzophane *trans-trans* and *cis-trans* structures.



QM/MM strategy.

- The reactive portion of the system (“QM subsystem”) is treated quantum-mechanically at semiempirical level as before.
- The “MM subsystem” is treated by a force-field: it may be a solvent, a solid surface, a polymeric matrix... whatever takes part in the dynamics without undergoing bond breaking or getting electronically excited.
- The interaction between the two subsystems consists of Lennard-Jones and electrostatic terms:

$$\hat{\mathcal{H}}_{LJ} = \sum_{\alpha} \sum_{\beta} \frac{A_{\alpha\beta}}{R_{\alpha\beta}^{12}} - \frac{B_{\alpha\beta}}{R_{\alpha\beta}^6}$$

$$\hat{\mathcal{H}}_{elec} = \sum_{\alpha} \sum_{\beta} \frac{q_{\alpha}q_{\beta}}{R_{\alpha\beta}} - \sum_i \sum_{\beta} \frac{q_{\beta}}{R_{i\beta}}$$

where $\alpha =$ QM nucleus, $\beta =$ MM nucleus, $i =$ QM electron.

- The electrostatic QM/MM interaction is added to the semiempirical hamiltonian (state-specific treatment of environmental effects).

See: Persico, Granucci, Inglesse, Laino and Toniolo, THEOCHEM 621, 119 (2003)

Connection atom approach to covalent QM/MM interactions.

- The CA is part of the QM subsystem: it owns one electron and carries one basis function ($2s$ or $3s$). Therefore, it makes a single bond with the nearest QM atom.
- The CA also participates of the MM force field. This ensures the correct dependence of the potential on the bond lengths, angles and dihedrals involving the CA, the MM atoms and the closest QM atoms.
- The core charge of the CA is $q_{CA} = Q + 1 - \sum_{\beta} q_{\beta}$, where Q is the total charge (but $q_{CA} = 1$ when computing 1-2 and 1-3 Coulomb terms).

See: Toniolo, Ciminelli, Granucci, Laino and Persico, Theoret. Chem. Acc. **93**, 270 (2004)

Model compound for connection atom optimization.

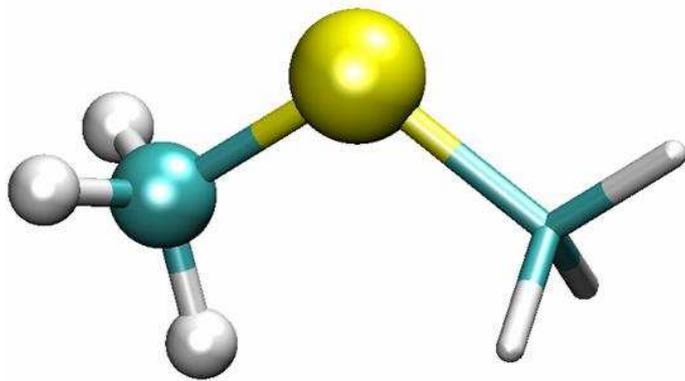
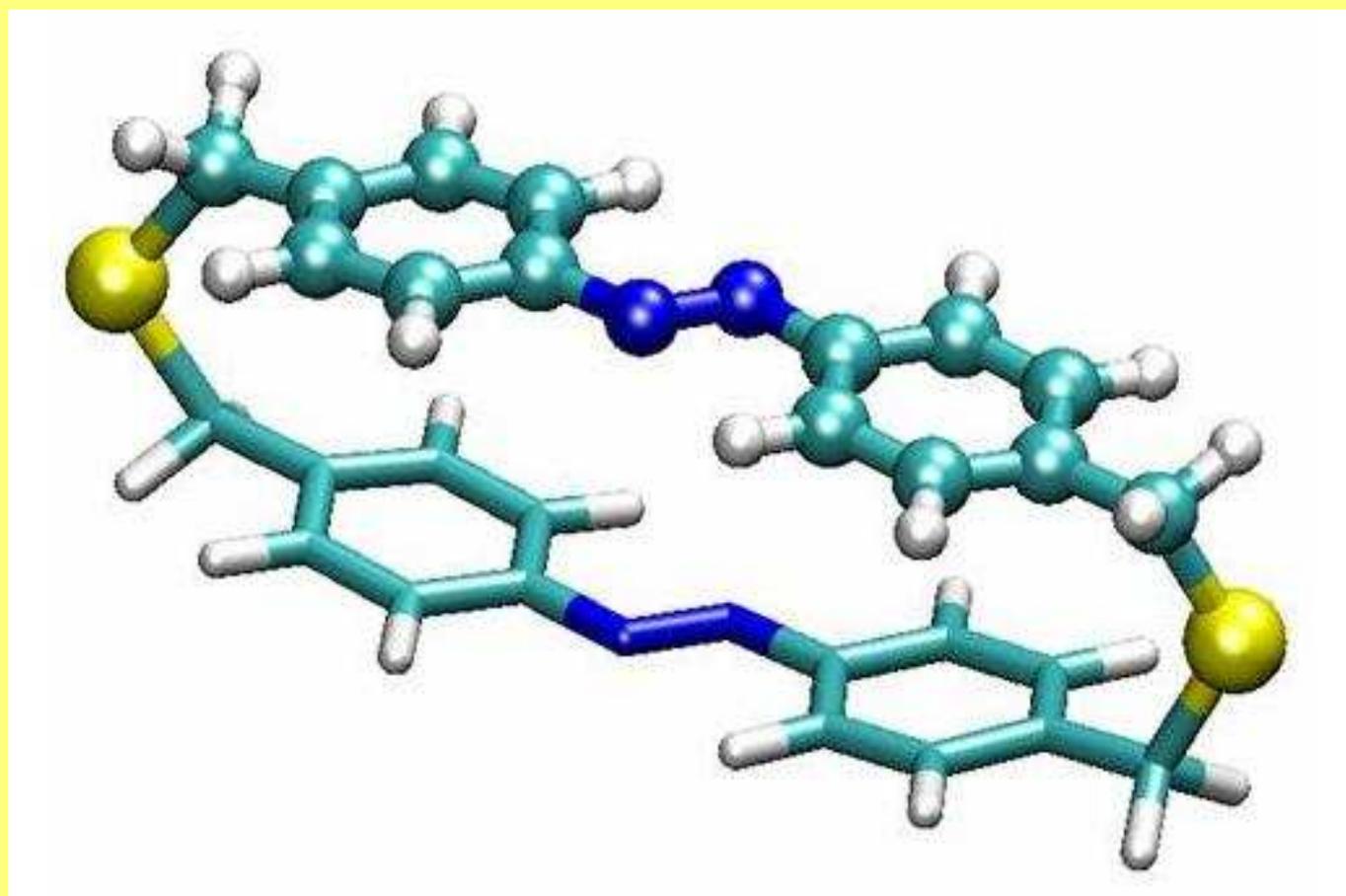
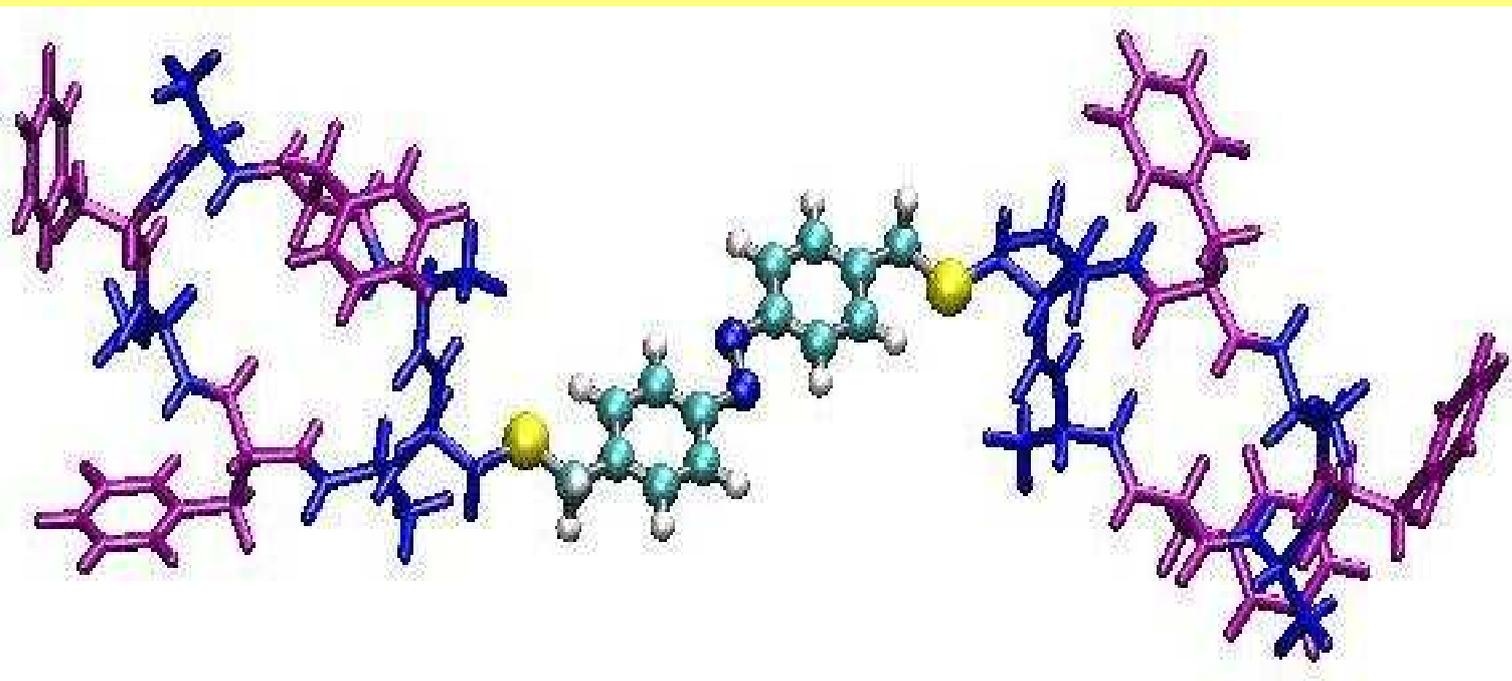


Figure 1

QM/MM calculation for the azobenzenophane.



Work in progress.



Conclusions.

- Experiments and/or potential energy surfaces are not always sufficient to fully understand the mechanism of photochemical reactions: simulations of the nonadiabatic dynamics are needed.
- The direct strategy is the most practical way to run simulations. Semiclassical dynamics, because of its local character, is most easily coupled with “on the fly” calculations of electronic quantities, but also certain quantum dynamics methods can be adapted in the same way (“Full Multiple Spawning” by T. J. Martínez, Urbana-Champaign).
- The QM/MM approach makes possible to simulate supramolecular systems (solvent effects, biological matrices, solid state photochemistry, supramolecular devices etc).

More about the Pisa research unit...

Treatment of solvent effects by a Polarizable Continuum Model (PCM). Benedetta Mennucci and coworkers.

- The hamiltonian of the solute includes the reaction field generated by the solvent.
- The solute cavity is of arbitrary shape and the solvent response is computed in terms of an apparent charge spread on the cavity surface.
- Geometry optimization of the solute molecules can be done for many kinds of ab initio wavefunctions, with analytical gradients.
- Many static and dynamic properties of solutes can be computed.
- Excited state energies and wavefunctions can be determined, taking into account solvent reorganization.
- Probabilities of excitation energy transfer between solvated chromophores can be evaluated.