

Ultrafast Molecular Dynamics in Excited States Using Mixed Quantum-Classical Approaches

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Vienna, July 8, 2008

General algorithm for MQCD methods

MQCD methods

$$(H_e - E_i)|i\rangle = 0$$

- 1 For a fixed nuclear geometry, solve time-independent Schrödinger Eq. for electrons. Get the energy gradient ∇E_i and the couplings $\mathbf{h}_{ik} = \langle i|\nabla k\rangle$.

$$-\nabla E_i = M_I \frac{d^2 \mathbf{R}_I^c}{dt^2}$$

- 2 Use the energy gradient to update the nuclear geometry according to the Newton's Eq.

$$\frac{\partial \chi_i(\mathbf{R}^c)}{\partial t} = -i\hbar \sum_{k=1}^{N_s} (\mathbf{v} \cdot \mathbf{h}_{ik} e^{-i\gamma_{ik}}) \chi_k(\mathbf{R}^c)$$

- 3 For the new nuclear geometry (only!), solve the SC-TDSE and correct classical solution by performing a hopping if necessary.

$$i) |\Phi\rangle = \sum \chi_k e^{i\gamma_k} |k\rangle$$

$$ii) O(\hbar^2) \rightarrow 0$$

$$iii) \chi_i(\mathbf{R}) \approx \chi_i(\mathbf{R}) \delta(\mathbf{R} - \mathbf{R}^c) = \chi_i(\mathbf{R}^c)$$

MQCD methods

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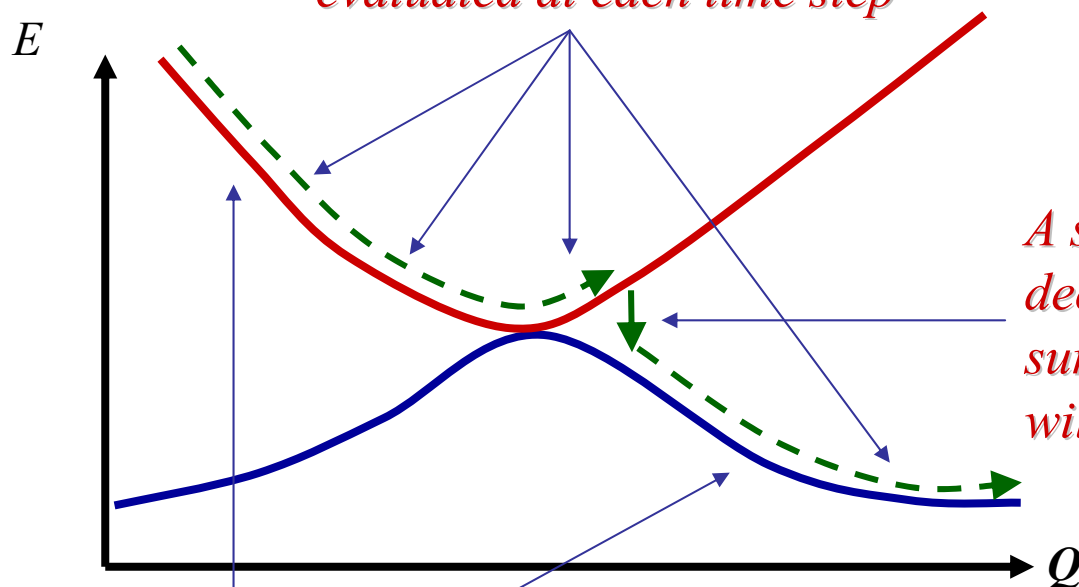
- 3** For the new nuclear geometry (only!), solve the SC-TDSE and correct classical solution by performing a hopping if necessary.

- 4** Go back to step **1** and repeat the procedure until the end of the trajectory.
- 5** Repeat procedure for a large number of trajectories to have the “classical wave packet”.

MQCD methods: surface hopping

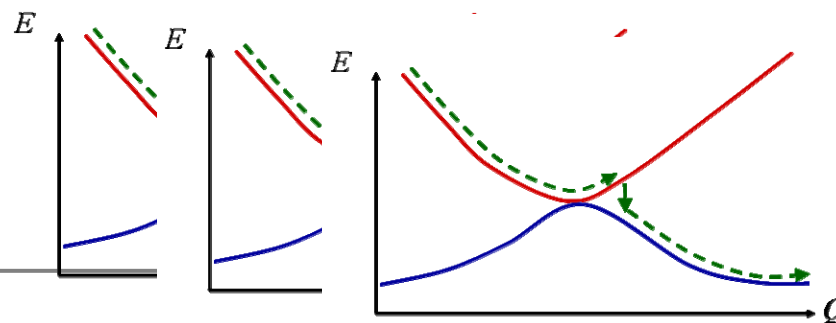
$$P_{k \rightarrow j} = -2|\chi_j|^{-2} \operatorname{Re}(\chi_k \chi_j^* e^{i\gamma_{kj}}) \mathbf{v} \cdot \mathbf{h}_{jk} \Delta t$$

Transition probability is evaluated at each time step



A stochastic algorithm decides on which surface the molecule will continue

Classical nuclear motion on the BO surface

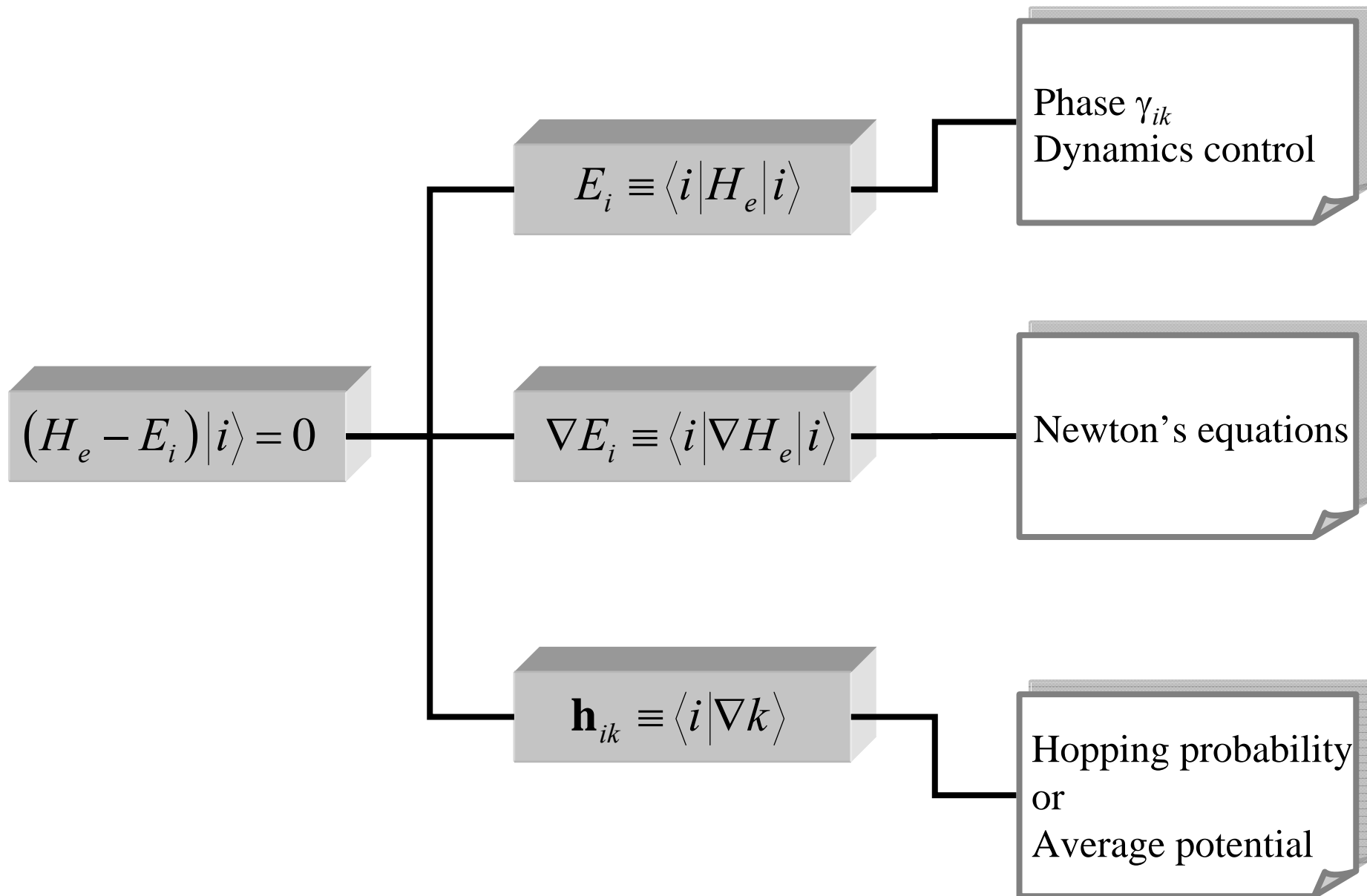


Tully, J. Chem. Phys. 93, 1061 (1990)

Barbatti et al., J. Photochem. Photobio. A **190**, 228 (2007)

The static problem: conventional quantum chemistry electronic structure methods

Quantum chemistry



Quantum chemistry methods: Present situation

Methods allowing the excited-state calculations:

Method	Single/Multi Reference	Analytical gradients	Coupling vectors	Computat. effort	Typical implementation
MR-CISD	MR	√	√		Columbus
EOM-CC	SR	√	√		Aces II
SAC-CI	SR	√	×		Gaussian
RI-CC2	SR	√	×		Turbomole
CASPT2	MR	√	×		Molpro
MRPT2	MR	×	×		Gamess
CISD/QCISD	SR	√	×		Molpro / Gaussian
MCSCF	MR	√	√		Columbus / Molpro
DFT/MRCI	MR	×	×		Grimme (Münster)
TD-DFT	SR	√	×		Turbomole
DFTB	SR	√	×		Elstner (Paderborn)
FOMO/AM1	MR	√	√		Mopac (Pisa)
OM2	MR	√	√		Thiel (Mülheim)

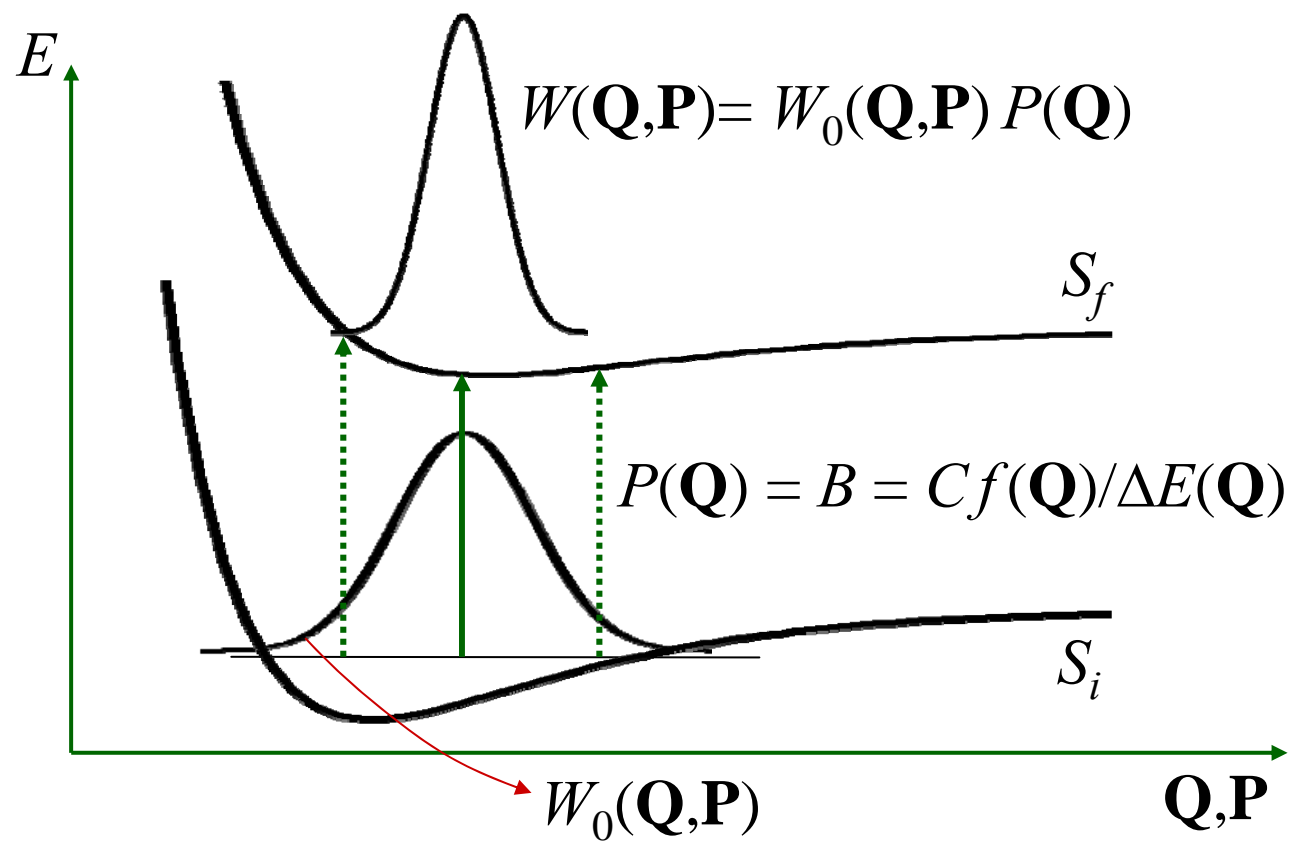
Quantum chemistry methods: Present situation

Methods allowing the non-adiabatic coupling calculations:

	Advantages	Disadvantages
MRCI	Ab initio Well defined hierarchy of approximations	Too expensive
MCSCF	Ab initio Well defined hierarchy of approximations	Still quite expensive Orbital rotations Bad vertical energies
TD-DFT	Low computational cost	Single reference
Semi-empirical	Low computational cost	Need for parameters

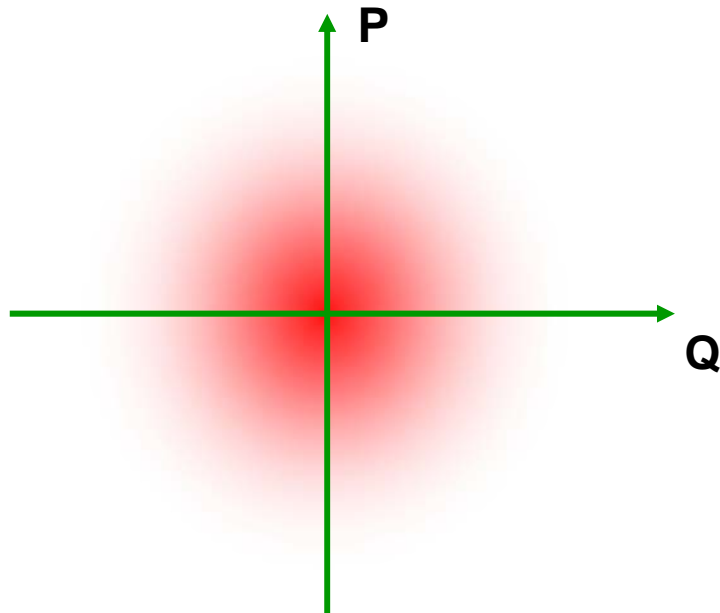
Initial conditions

Generating initial conditions

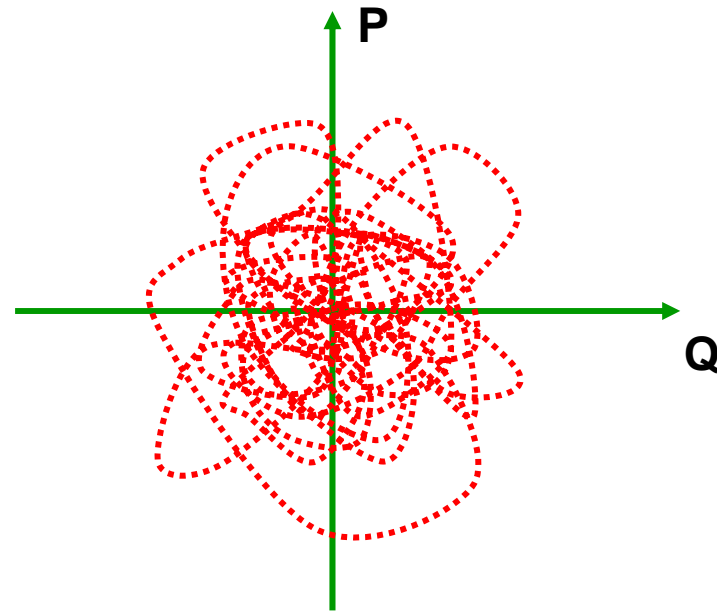


Ergodic hypothesis

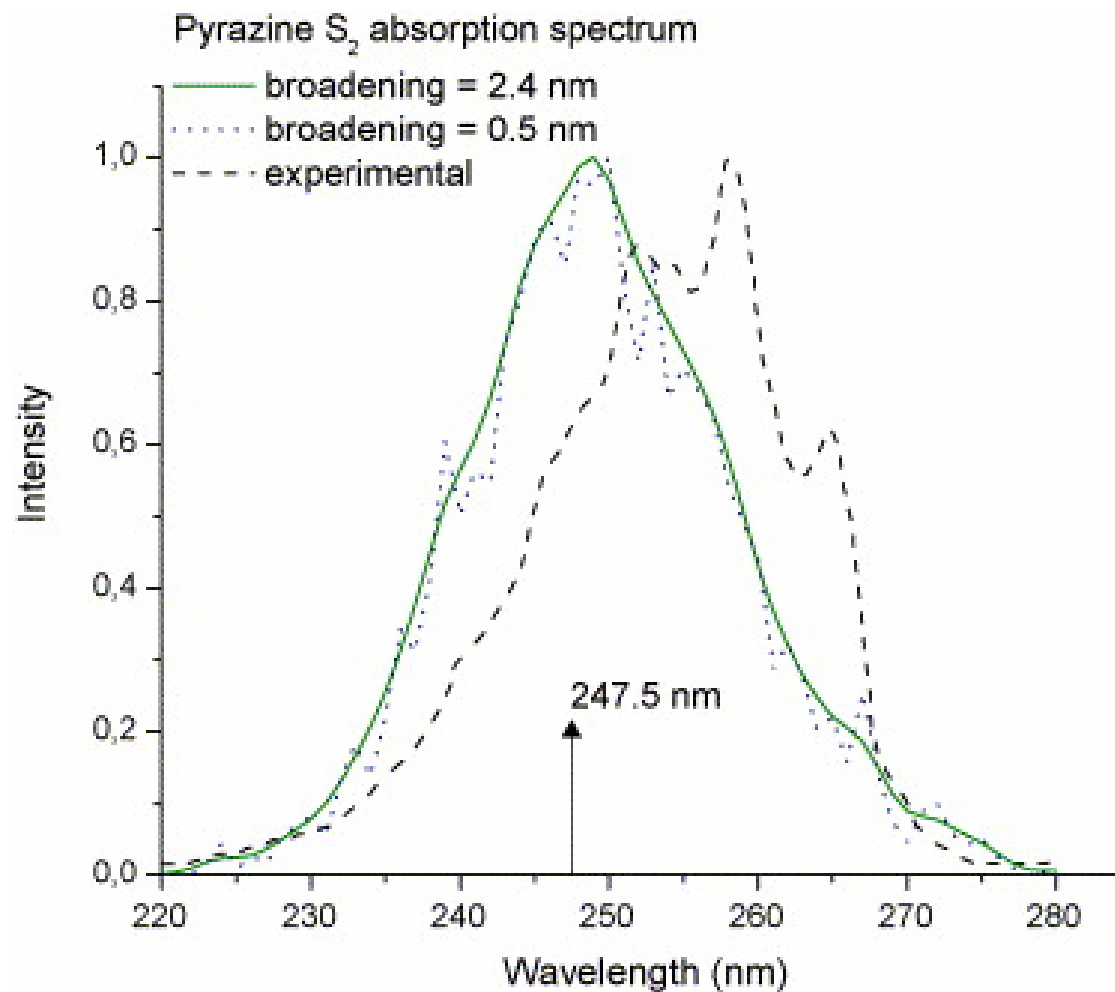
$W_0(\mathbf{Q}, \mathbf{P})$ from distribution



$W_0(\mathbf{Q}, \mathbf{P})$ from trajectory



Spectrum simulation: Pyrazine



2000 single point calculations
SA-3-CAS(10,8)/6-31G*

The classical problem:
integrating the Newton's equations

Classical equations: Velocity Verlet Algorithm

For each nucleus I :

$$\mathbf{a}_I(t) = -\frac{1}{M_I} \nabla E[\mathbf{R}_I(t)]$$

$$\mathbf{R}_I(t + \Delta t) = \mathbf{R}_I(t) + \mathbf{v}_I(t)\Delta t + \frac{1}{2}\mathbf{a}_I(t)\Delta t^2$$

$$\mathbf{v}_I\left(t + \frac{\Delta t}{2}\right) = \mathbf{v}_I(t) + \frac{1}{2}\mathbf{a}_I(t)\Delta t$$

$$\mathbf{a}_I(t + \Delta t) = -\frac{1}{M_I} \nabla E[\mathbf{R}_I(t + \Delta t)]$$

$$\mathbf{v}_I(t + \Delta t) = \mathbf{v}_I\left(t + \frac{\Delta t}{2}\right) + \frac{1}{2}\mathbf{a}_I(t + \Delta t)\Delta t$$

Time step: Classical equations

Table 1 Some typical vibrational modes^a

Vibrational mode	Wavelength of absorption [cm ⁻¹] (1/λ)	Absorption frequency [s ⁻¹] (ν = c/λ)	Period [fs] (1/ν)	Period/π [fs]
{ O-H stretch N-H stretch C-H stretch	3200–3600	1.0 × 10 ¹⁴	9.8	3.1
	3000	9.0 × 10 ¹³	11.1	3.5
	O–C–O asymmetric stretch	2400	7.2 × 10 ¹³	13.9
C≡C, C≡N stretch	2100	6.3 × 10 ¹³	15.9	5.1
C=O (carbonyl) stretch	1700	5.1 × 10 ¹³	19.6	6.2
C=C stretch				
H–O–H bend	1600	4.8 × 10 ¹³	20.8	6.4
C–N–H bend	1500	4.5 × 10 ¹³	22.2	7.1
H–N–H bend				
C=C (aromatic) stretch				
C–N stretch (amines)	1250	3.8 × 10 ¹³	26.2	8.4
Water Libration (rocking)	800	2.4 × 10 ¹³	41.7	13
O–C–O bending	700	2.1 × 10 ¹³	47.6	15
C=C–H bending (alkenes)				
C=C–H bending (aromatic)				

^aAll values are approximate; a range is associated with each motion depending on the system. The value of $c = 3.00 \times 10^{10}$ cm s⁻¹. The last column indicates the timestep limit for leap-frog stability for a harmonic oscillator: $\Delta t < 2/\omega = 2/(2\pi\nu)$.

Time step: Classical equations

Table 1 Some typical vibrational modes^a

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{ O-H stretch N-H stretch C-H stretch	3200–3600	1.0×10^{14}	9.8	3.1
	3000	9.0×10^{13}	11.1	3.5

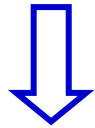
Time step should not be larger than 1 fs ($1/10\nu$).

$\Delta t = 0.5$ fs assures a good level of conservation of energy most of time.

The (quasi) quantum problem:
Integrating the time-dependent
Schrödinger equations

TDSE

$$\Phi(\mathbf{r}, \mathbf{R}, t) = \sum_k \chi_k(\mathbf{R}, t) \exp\left[-i\hbar^{-1} \int_0^t E_k dt\right] \psi_k(\mathbf{R}; \mathbf{r}, t)$$



$$\left[i\hbar \frac{\partial \psi}{\partial t} - H \right] \Phi = 0 \quad \text{with } O(\hbar^2) \rightarrow 0$$



$$\frac{\partial \chi_i}{\partial t} = -i\hbar \sum_{i \neq k} \chi_k \exp\left[-i\hbar^{-1} \int_0^t E_{ik} dt\right] d_{ki}(t) \quad (\text{adiabatic basis})$$

$$d_{ik} \equiv \left\langle \psi_i \left| \frac{\partial}{\partial t} \psi_k \right. \right\rangle = \mathbf{v} \cdot \left\langle \psi_i \left| \nabla \psi_k \right. \right\rangle + \frac{1}{2} v^2 \left\langle \psi_i \left| \nabla^2 \psi_k \right. \right\rangle dt \approx \mathbf{v} \cdot \mathbf{h}_{ik}$$

Time derivative
coupling

Non-adiabatic
coupling vector \mathbf{h}_{ik}

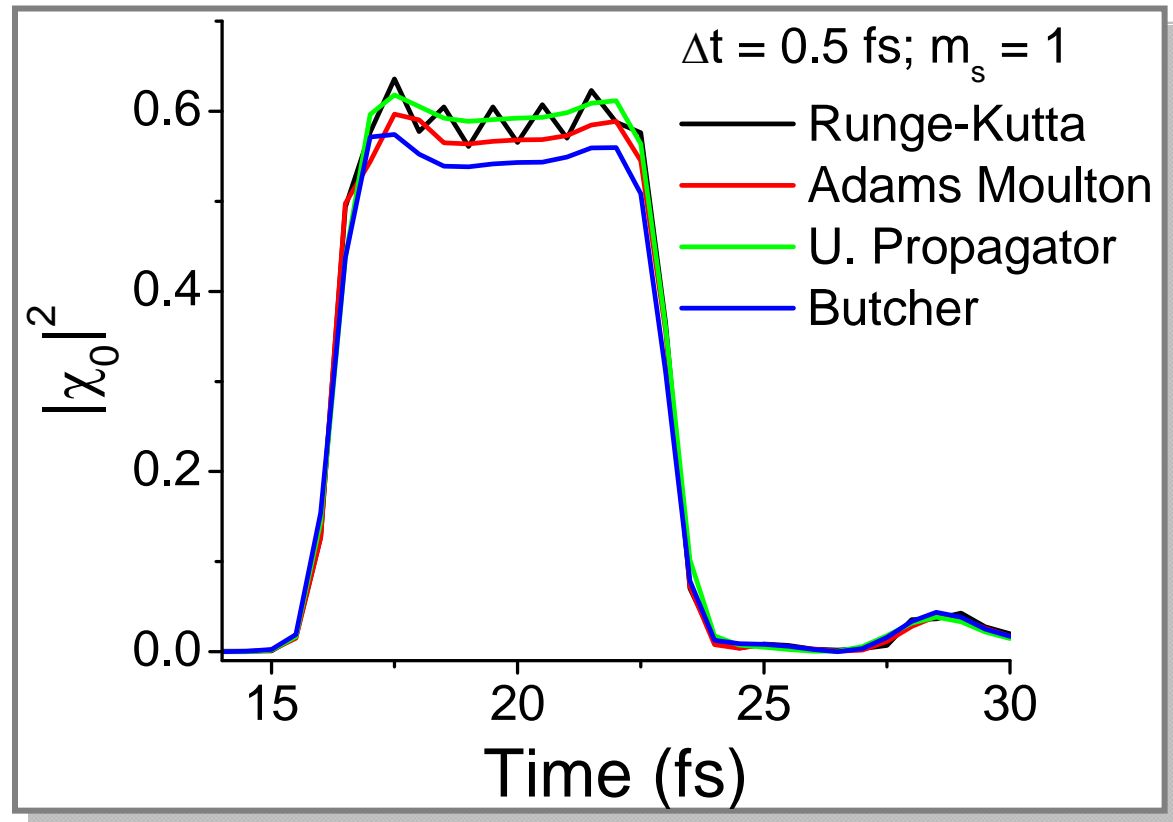
Non-adiabatic
scalar coupling

Semi-classical time-dependent Schrödinger equation

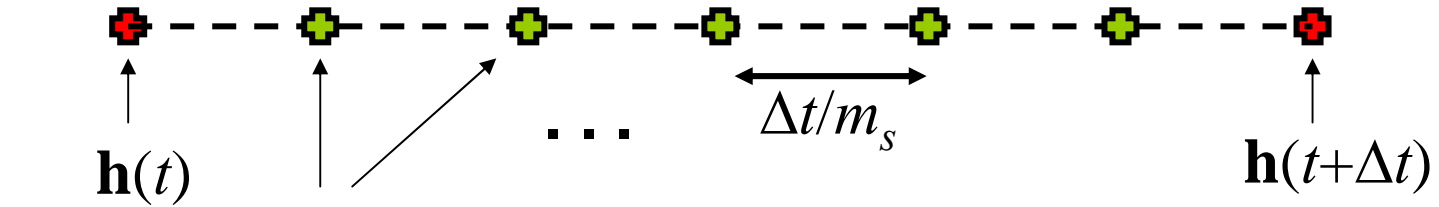
$$\frac{\partial \chi_i(\mathbf{R}_c)}{\partial t} = -i\hbar \sum_{k=1}^{N_s} (\mathbf{v}_c \cdot \mathbf{h}_{ik}) \chi_k(\mathbf{R}_c) \exp[-i\gamma_{ik}] \quad \text{SC-TDSE}$$

\mathbf{R}_c is the classical Newtonian geometry

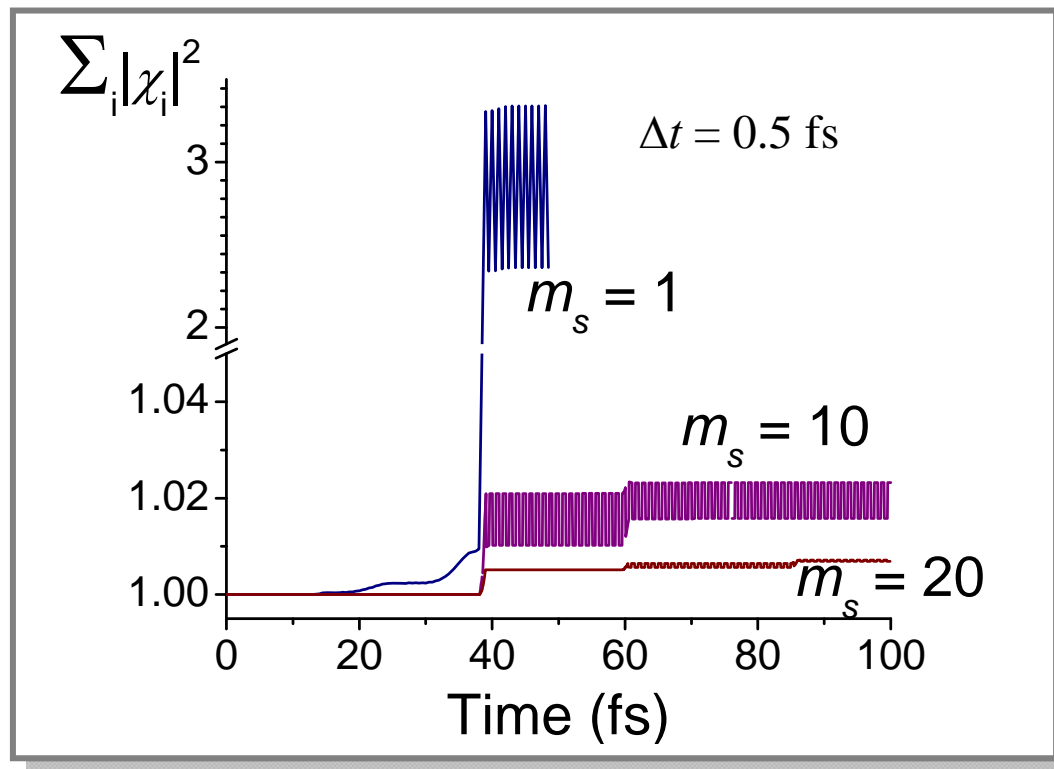
The SC-TDSE is solved by standard high-order integration methods.



Time-step: SC-TDSE



$$\mathbf{h}\left(t+\Delta t\left(1-\frac{n}{m_s}\right)\right) = \mathbf{h}(t) + \frac{n}{m_s}(\mathbf{h}(t+\Delta t) - \mathbf{h}(t)) \quad (n=1..m_s-1)$$



Alternative way to deal with the SC-TDSE

$$d_{ik} \equiv \langle \psi_i | \frac{\partial}{\partial t} \psi_k \rangle = \mathbf{v} \cdot \langle \psi_i | \nabla \psi_k \rangle + \frac{1}{2} v^2 \langle \psi_i | \nabla^2 \psi_k \rangle dt \approx \mathbf{v} \cdot \mathbf{h}_{ik}$$

Time derivative coupling Non-adiabatic coupling vector \mathbf{h}_{ik} Non-adiabatic scalar coupling

When using methods for which \mathbf{h} is not available, it is possible to compute the time-derivative coupling numerically.

Is to compute the time-derivative coupling numerically faster than to compute the non-adiabatic coupling vector analytically?

Is d_{ik} really comparable to $\mathbf{v} \cdot \mathbf{h}_{ik}$?

Alternative way to deal with the SC-TDSE

$$d_{ik} \equiv \langle \psi_i | \frac{\partial}{\partial t} \psi_k \rangle = \mathbf{v} \cdot \langle \psi_i | \nabla \psi_k \rangle + \frac{1}{2} v^2 \langle \psi_i | \nabla^2 \psi_k \rangle dt \approx \mathbf{v} \cdot \mathbf{h}_{ik}$$

Crude approximation by finite difference:

$$d_{ij}(t) \approx \frac{-1}{\Delta t} \langle \psi_i(t) | \psi_j(t - \Delta t) \rangle$$

A more sophisticated approximation:

$$d_{ij}(t) \approx \frac{1}{2} [3\sigma_1 - \sigma_0]$$

$$\sigma_0 = \frac{1}{2\Delta t} \left[\langle \psi_i(t - 2\Delta t) | \psi_j(t - \Delta t) \rangle - \langle \psi_i(t - \Delta t) | \psi_j(t - 2\Delta t) \rangle \right]$$

$$\sigma_1 = \frac{1}{2\Delta t} \left[\langle \psi_i(t - \Delta t) | \psi_j(t) \rangle - \langle \psi_i(t) | \psi_j(t - \Delta t) \rangle \right]$$

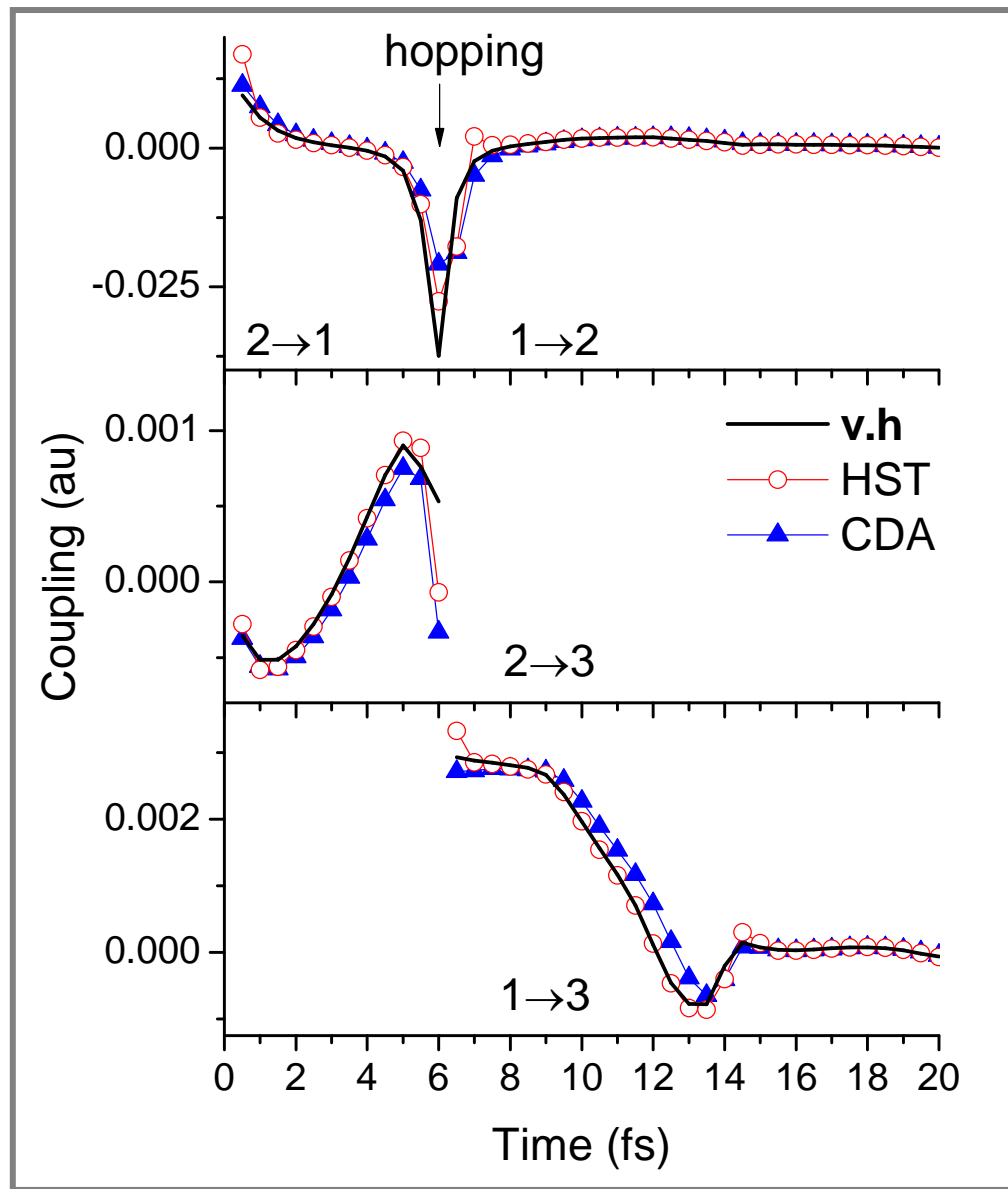
Hammes-Schiffer and Tully, J. Chem. Phys. **101**, 4657 (1994)

Tapavicza et al., Phys. Rev. Lett. **98**, 023001 (2007)

Werner et al., Chem. Phys. **349**, 319 (2008)

Fabiano et al. Chem. Phys. **351**, 111 (2008)

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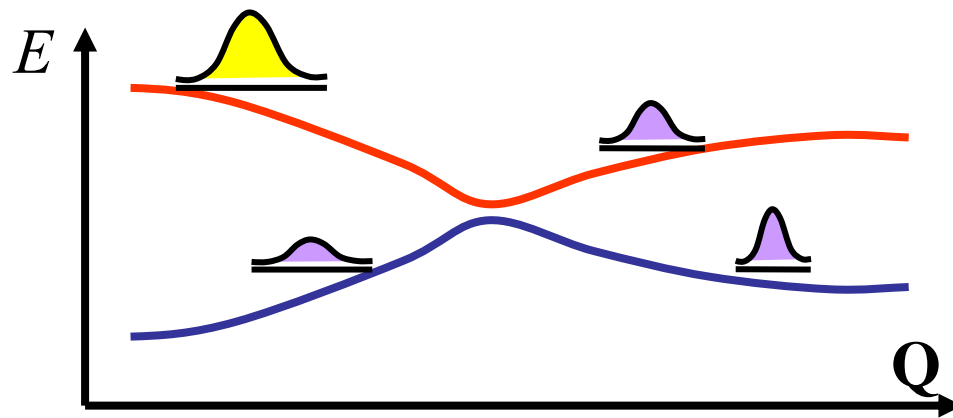


Alternative way to deal with the SC-TDSE

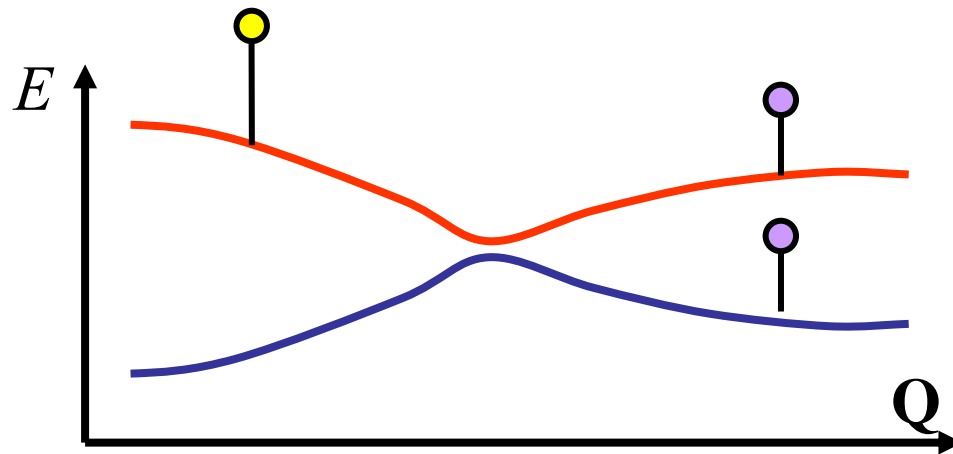
System	Level	CSFs	CI overlap	Conventional	Ratio
CH_2NH_2^+	CAS(12,8)	336	8	16	0.5
Imidazole	CAS(8,9)	5292	2280	2520	0.9

Decoherence

Because in the SC-TDSE the “wave-packet” split among the several electronic surface is kept correlated by the coordinate \mathbf{R}_c , the time propagation is fully coherent.



TDSE



SC-TDSE

Decoherence

Decoherence is introduced ad hoc by correcting the time dependent coefficients:

$$\chi_k' = \chi_k \exp(-\Delta t / \tau_{ki})$$

$$\chi_i = \chi_i \left[|\chi_i|^2 \left(1 - \sum_{k \neq i} |\chi_k'|^2 \right) \right]^{1/2}$$

$$\tau_{ki} = \frac{\hbar}{|E_k - E_i|} \left(1 + \frac{C}{E_{kin}} \right)$$

$$C = 0.1 \text{ hartree}$$

MQCD: surface hopping

Fewest switches probabilities

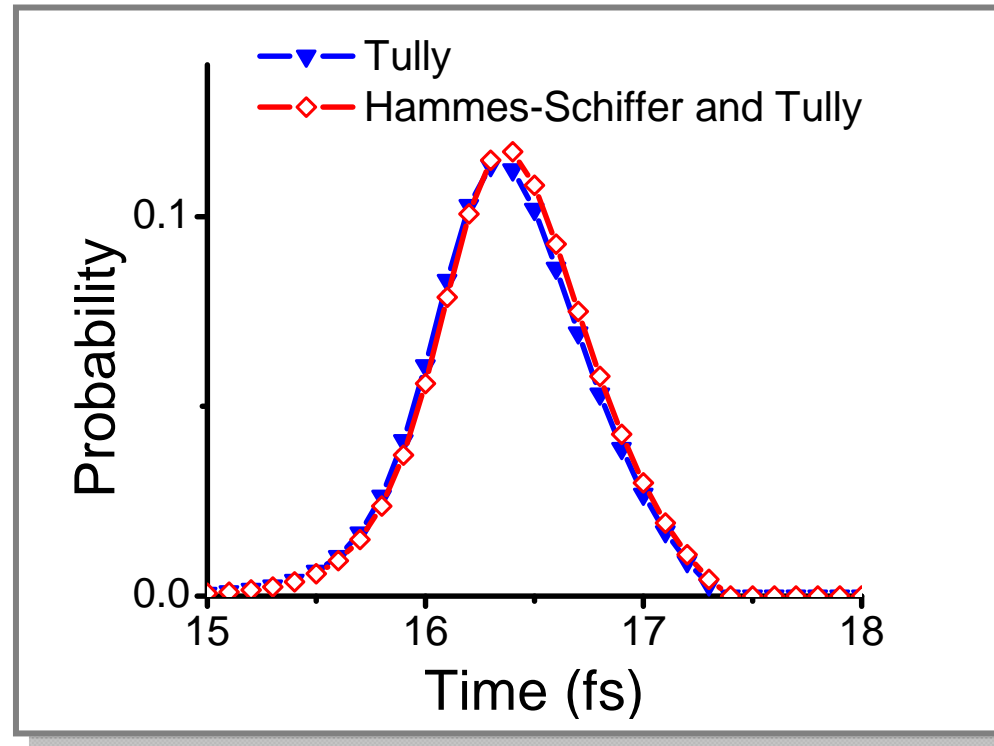
$$b_{jk} = -2 \operatorname{Re}(\chi_k \chi_j^* e^{i\gamma_{jk}}) \mathbf{v} \cdot \mathbf{h}_{jk}$$

Tully:

$$P_{k \rightarrow j} = \frac{b_{jk}}{|\chi_j|^2} \Delta t$$

Hammes-Schiffer and Tully:

$$P_{k \rightarrow j} = \frac{1}{|\chi_j|^2} \int_t^{t+\Delta t} b_{jk}(t') \Delta t'$$

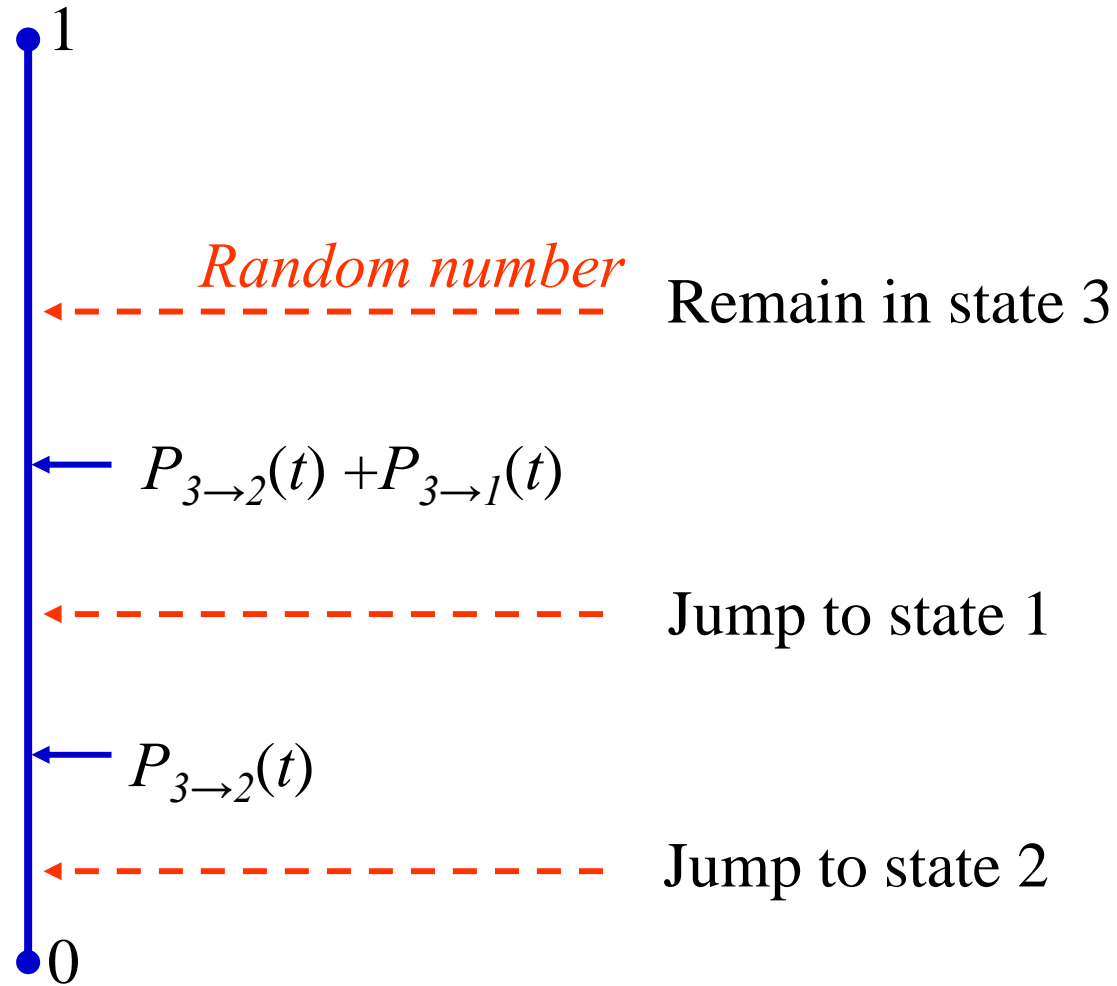


Tully, J. Chem. Phys. **93**, 1061 (1990)

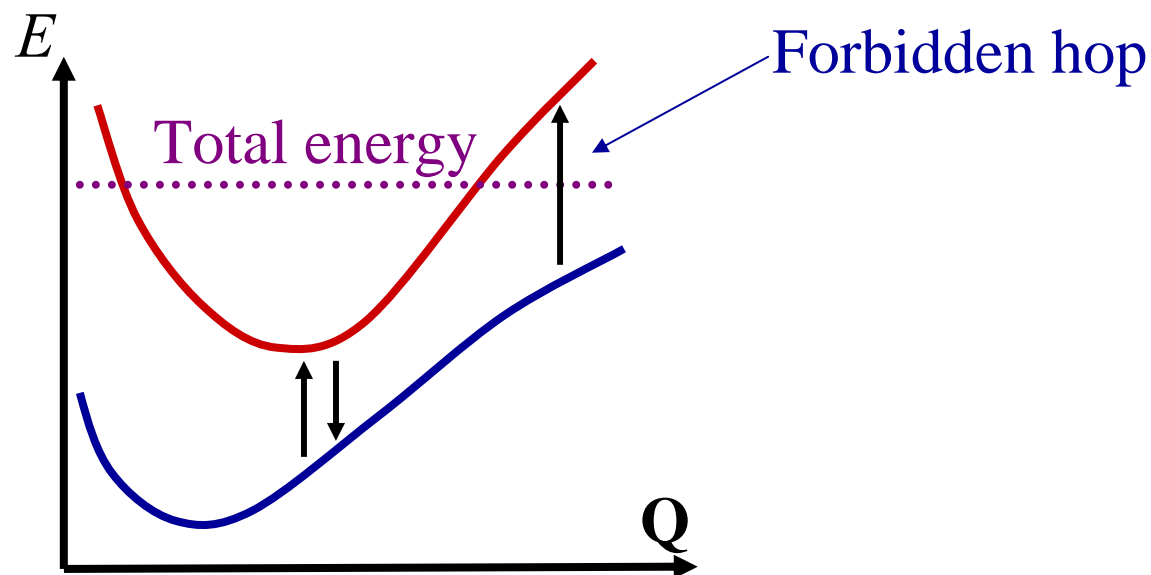
Hammes-Schiffer and Tully, J. Chem. Phys. **101**, 4657 (1994)

Hopping probabilities: example 3 states

Suppose molecule in state 3 at time t .



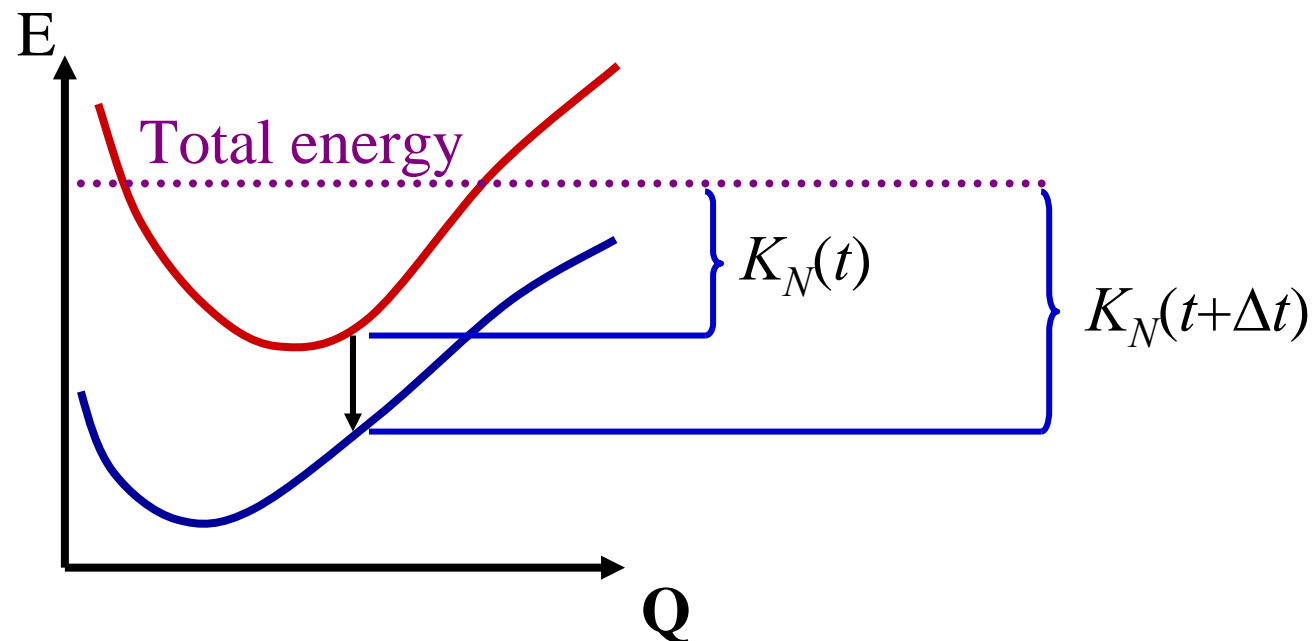
Forbidden hoppings



How to treat them:

- **Reject all classically forbidden hop and keep the momentum.**
- Reject all classically forbidden hop and **invert** the momentum.
- Use the time uncertainty to search for a point in which the hop is allowed.

Adjustment of momentum after hopping



After hop, what are the new nuclear velocities?

- Adjust velocities components in the direction of the momentum
- Adjust velocities components in the direction of the nonadiabatic coupling vector \mathbf{h}_{12}
- Adjust velocities components in the direction of the difference gradient vector \mathbf{g}_{12}
- Adjust velocities in the direction $\hat{\mathbf{e}} = \hat{\mathbf{h}}_{kl} \sin \theta + \hat{\mathbf{g}}_{kl} \cos \theta$

**NEWTON-X: a package for Newtonian
dynamics close to the crossing seam**

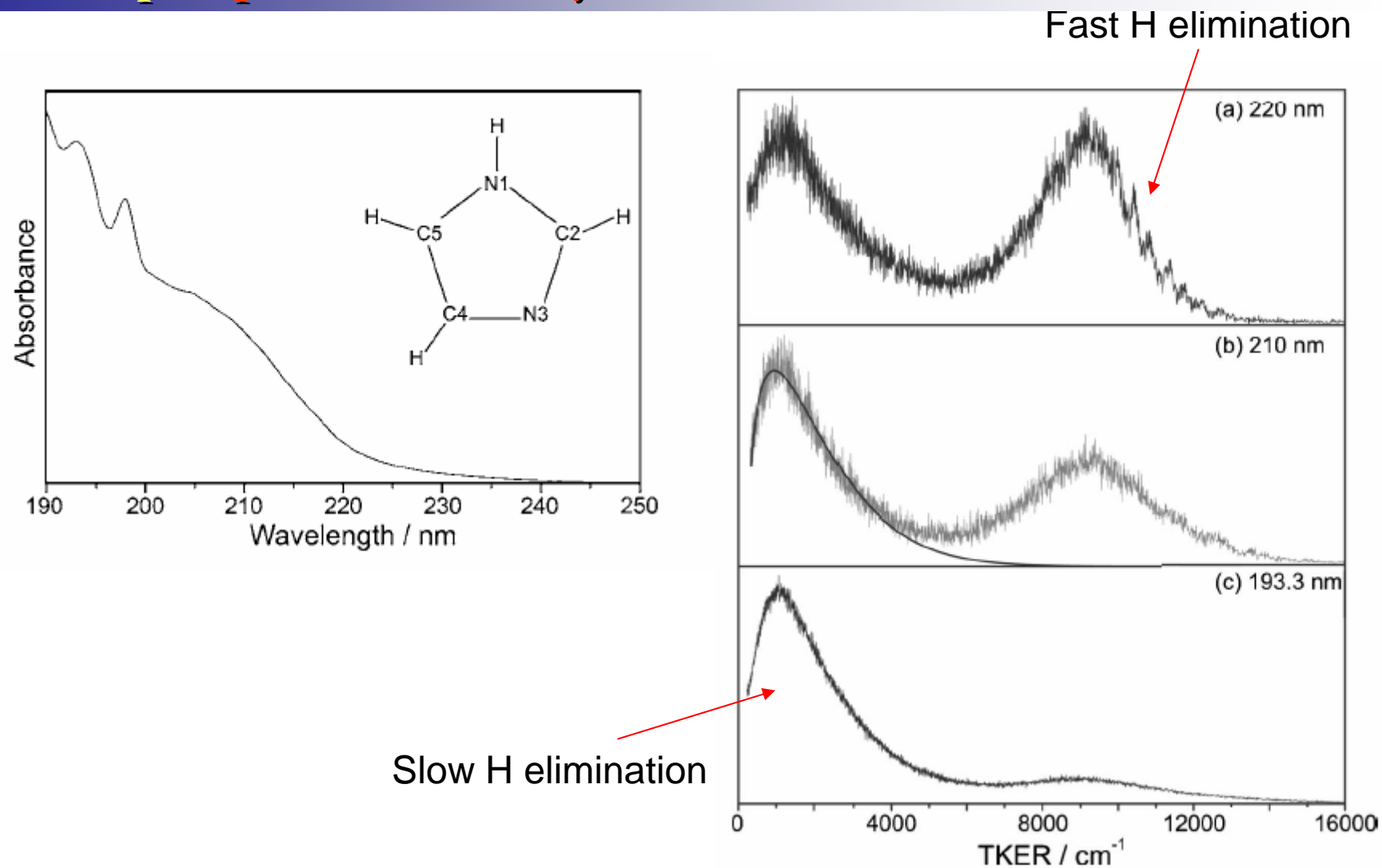
**Barbatti, Granucci, Ruckenbauer,
Pittner, Persico, and Lischka, v. 0.16c (2008)**

NEWTON-X

- **Easy and practical of using:** just make the inputs and start the simulations; monitor partial results on-the-fly; get relevant summary of results at the end;
- **Robust:** if the input is right, the job will run: in case of error, messages must guide the user to fix the problem;
- **Flexible:** some different case to study or new method to implement? It should be easy to change the code;
- **Open source:** NX is the first MQCD-oriented program freely available and opened to the community.

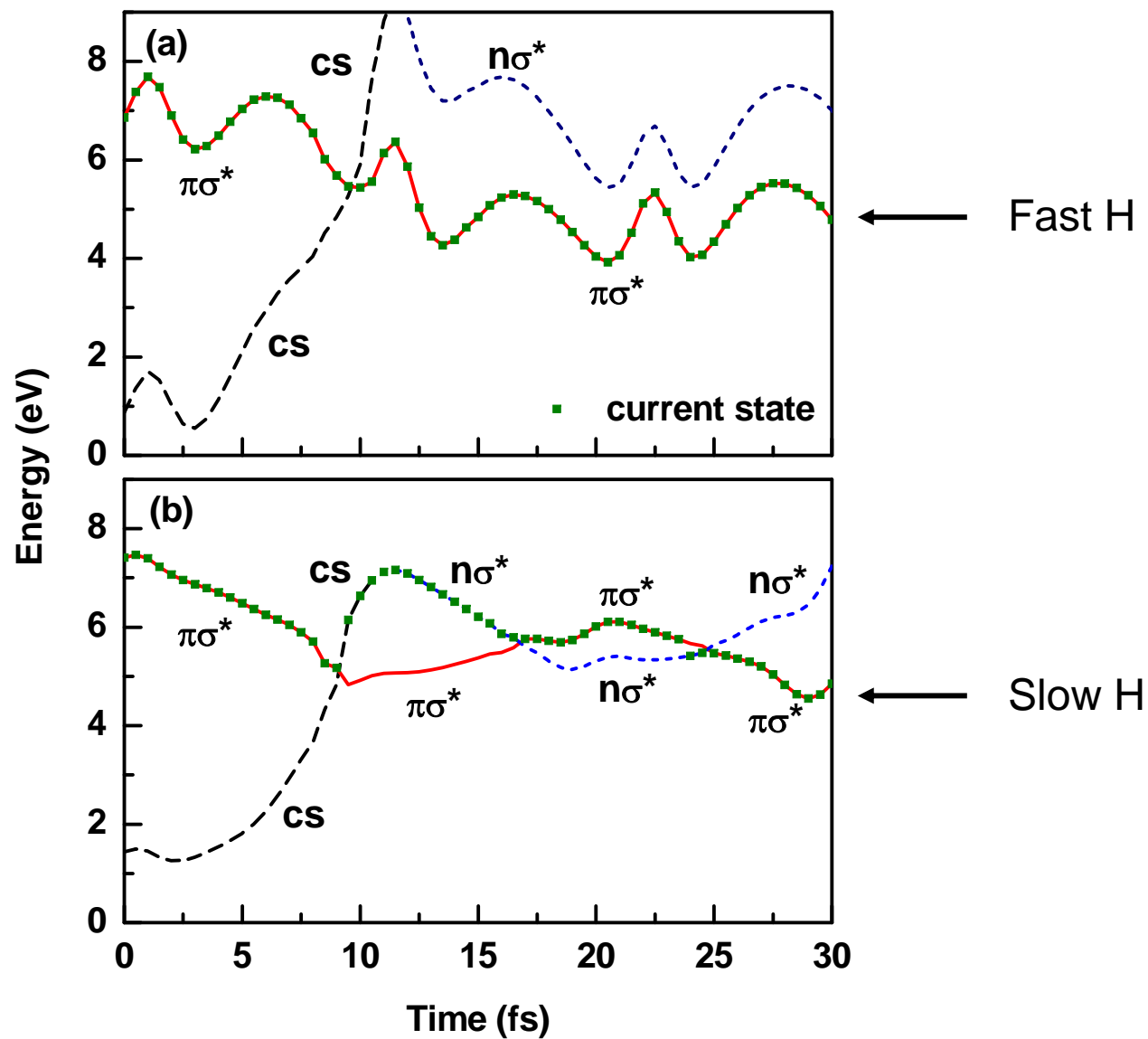
Example

Example: photochemistry of imidazole

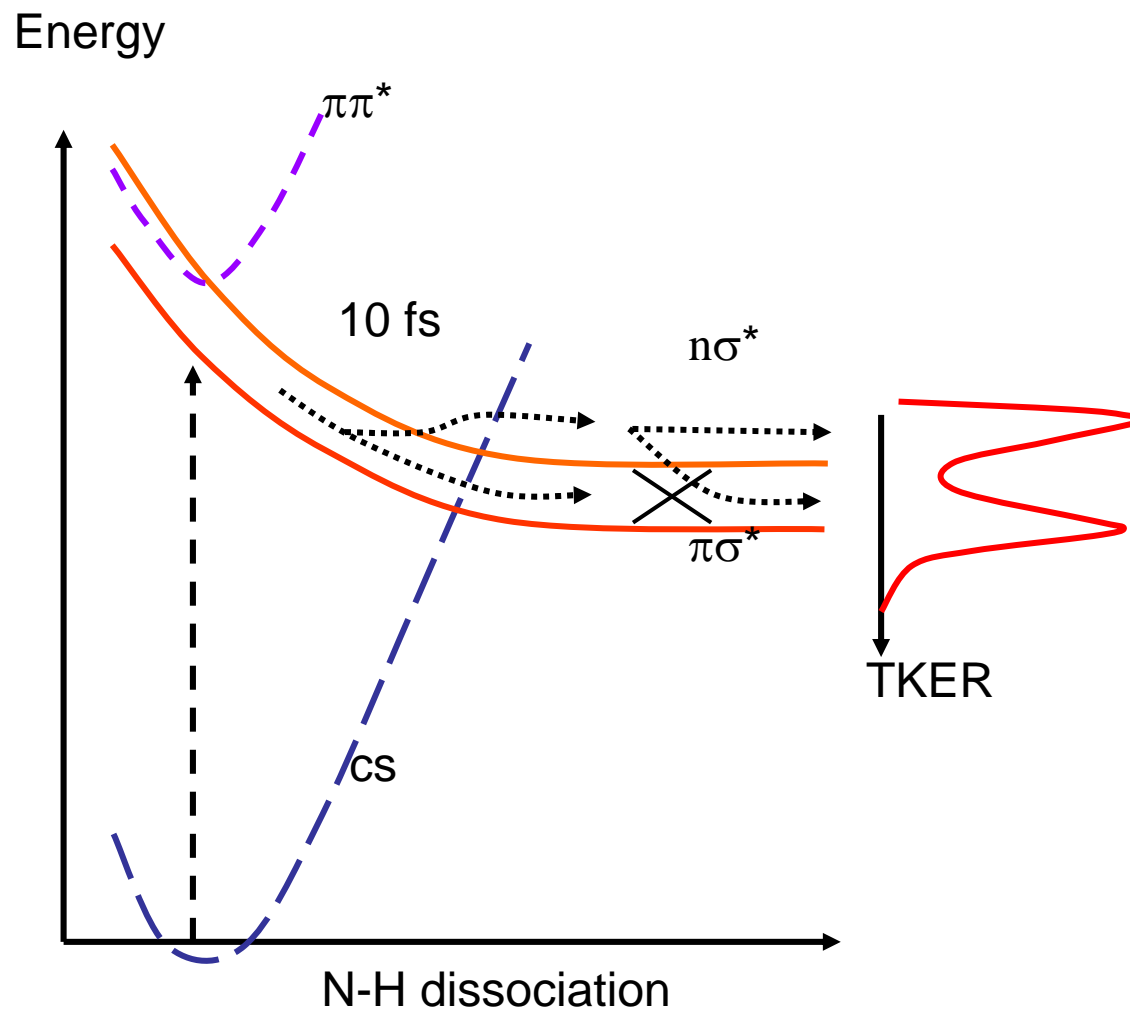


Devine et al. J. Chem. Phys. **125**, 184302 (2006)

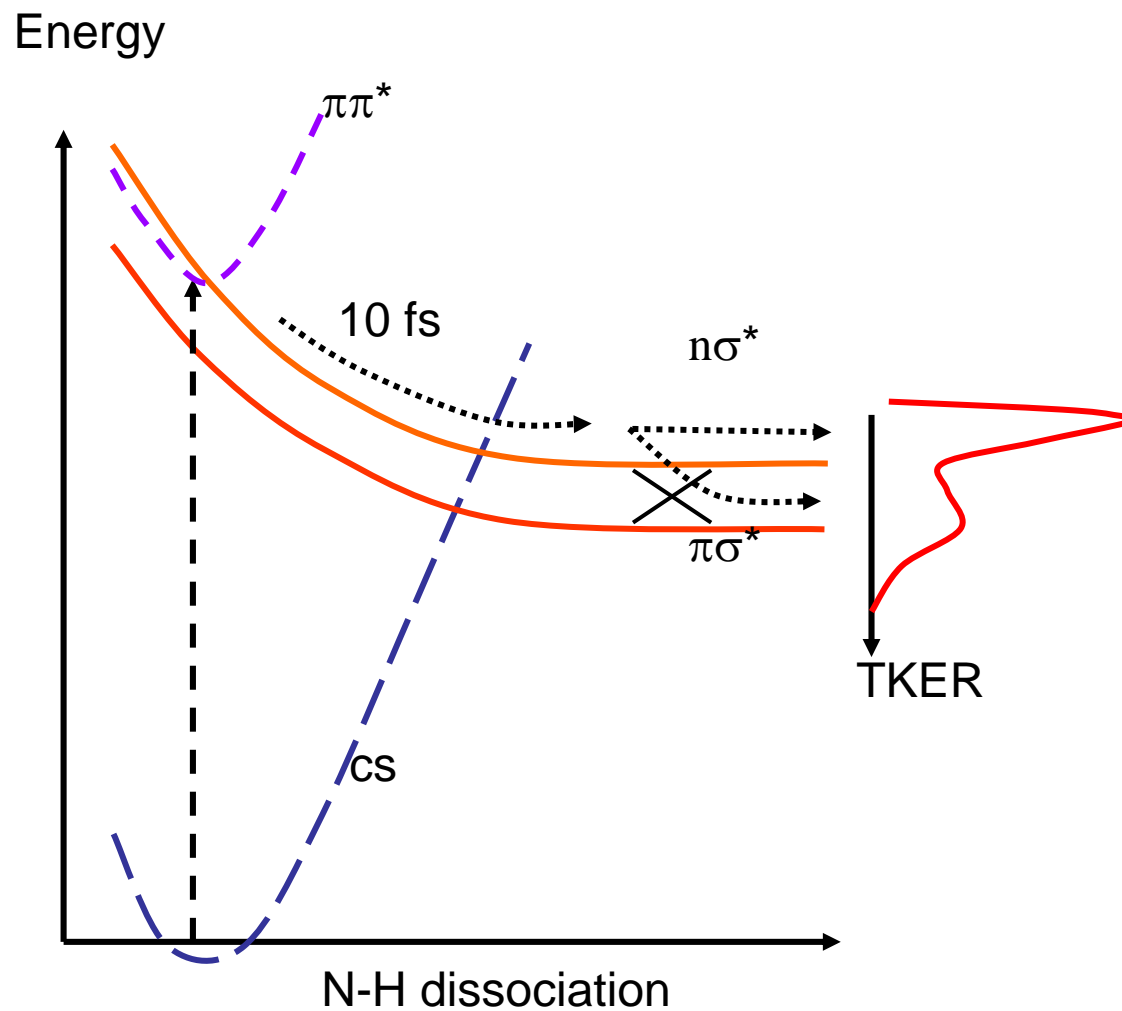
Example: photochemistry of imidazole



Example: photochemistry of imidazole



Example: photochemistry of imidazole



Conclusions

About the methods

- MQCD simulations at multireference level start to be feasible for molecules with about 10 heavy atoms with the current computational capabilities.
- They are still a new field being explored by few groups around the world.

About the methods

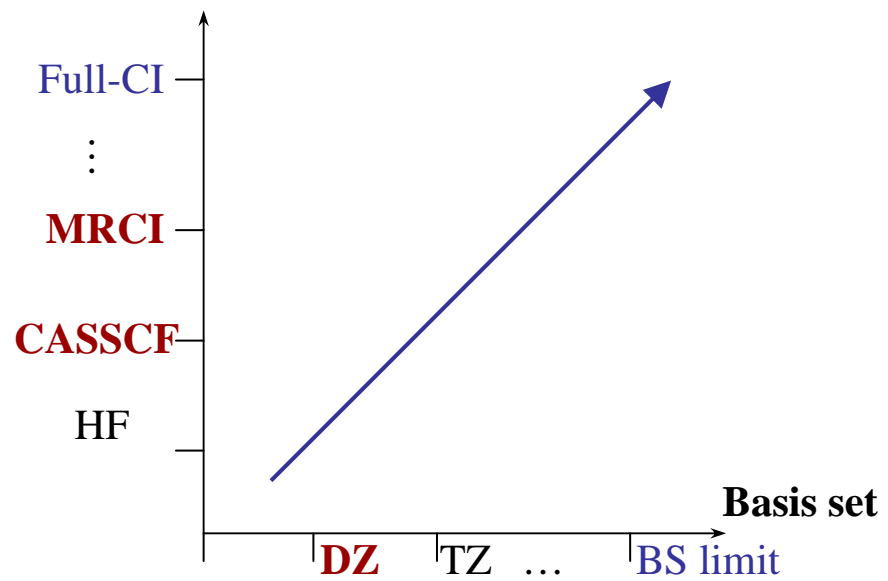
- MQCD simulations are not a substitute for the conventional quantum-chemistry calculations, but a complementary tool to be used carefully given their high computational costs.
- They can be specially useful to test specific hypothesis raised either by experimental analysis or conventional calculations.

New methods and interfaces being implemented:

- **Time-derivative couplings (Pittner)**
- **MQCD with QM/MM (Ruckenbauer)**
- **Essential dynamics/normal mode analysis (Plasser)**
- **Optimization of MCSCF integration (Plasser)**
- **Interfaces to ACES2 and GAUSSIAN (Tajti)**

Conclusions

Correlation Method



Conclusions

