

Mixed Quantum-Classical Dynamics:  
Foundations and Application to Photo-Biological Questions  
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## NEW DEVELOPMENTS IN MQCD

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# Mixed Quantum-Classical Dynamics (MQCD).

The MQCD methods, such as Surface Hopping, ...

- ... are simple, fast and easy to program.
- ... can be combined with on the fly calculations of PES and couplings
- ... yield results that can be easily interpreted in a mechanistic way.

But a mixed quantum/classical system does not exist in nature, therefore...

- ... different formulations are equally valid in principle
- ... none is fully satisfactory [1–10].

Examples: zero-point vibrational energy, momentum adjustment and frustrated hops, energy conservation.

We shall examine two problems:

- The quantum decoherence problem and the hopping algorithm
- The sampling of initial conditions

# Mixing quantum and classical dynamics

Nuclear motion: Newton equations

Electronic motion: Schrödinger equation

$$i \frac{d}{dt} |\psi_{el}(t)\rangle = \hat{\mathcal{H}}_{el} |\psi_{el}(t)\rangle$$

$$\hat{\mathcal{H}}_{el}(Q(t)) |\psi_K(Q(t))\rangle = U_K(Q(t)) |\psi_K(Q(t))\rangle$$

$$|\psi_{el}(t)\rangle = \sum_L A_L(t) e^{-i\gamma_L(t)} |\psi_L(Q(t))\rangle$$

$$\gamma_L(t) = \int_0^t U_L(Q(t')) dt'$$

$$\frac{d}{dt} |\psi_{el}(t)\rangle = \sum_L \left[ (\dot{A}_L - iA_L U_L) |\psi_L\rangle + A_L \left| \frac{d\psi_L}{dt} \right\rangle \right] e^{-i\gamma_L(t)} =$$

$$\sum_L \left[ (\dot{A}_L - iA_L U_L) |\psi_L\rangle + A_L \sum_r \left| \frac{\partial \psi_L}{\partial Q_r} \right\rangle \dot{Q}_r \right] e^{-i\gamma_L(t)}$$

$$\dot{A}_K = \sum_{L(\neq K)} A_L(t) e^{i(\gamma_K - \gamma_L)} \sum_r \dot{Q}_r g_{KL}^{(r)}$$

$$g_{KL}^{(r)} = \left\langle \psi_K \left| \frac{\partial}{\partial Q_r} \right| \psi_L \right\rangle$$

For each trajectory, we must know the forces (i.e. the potential energy functions  $U_K$ ) and the nonadiabatic couplings  $g_{KL}^{(r)}$ . Actually, it is sufficient to calculate the projection of the  $\mathbf{g}_{KL}$  vector on the velocity vector  $\dot{\mathbf{Q}}$ .

By integrating the system of differential equations for the coefficients  $A_K$ , we obtain the state probabilities:

$$P_K(t) = |A_K(t)|^2$$

that are specific of each trajectory.

## The forces acting on the nuclei.

$$V(Q) = \langle \psi(t) | \hat{\mathcal{H}}_{el} | \psi(t) \rangle = \sum_K |A_K|^2 U_K$$

Energy conservation:

$$\frac{d}{dt} [V(Q) + \frac{1}{2} \sum_r m_r \dot{Q}_r^2] = 0$$

$$\sum_r m_r \dot{Q}_r \ddot{Q}_r = - \sum_K \left[ |A_K|^2 \frac{\partial U_K}{\partial Q_r} \dot{Q}_r + (\dot{A}_K A_K^* + A_K \dot{A}_K^*) U_K \right]$$

$$\sum_r m_r \dot{Q}_r \ddot{Q}_r = - \sum_r \dot{Q}_r \sum_K \left[ |A_K|^2 \frac{\partial U_K}{\partial Q_r} + 2 \sum_{L(\neq K)} \Re (A_K^* A_L e^{i(\gamma_K - \gamma_L)}) U_K g_{KL}^{(r)} \right]$$

We equate  $m_r \ddot{Q}_r$  to the  $r$  component of the force in the mean-field (Ehrenfest) formulation. The last equation is satisfied for any  $\dot{\mathbf{Q}}$  if:

$$F_r = - \sum_K \left[ |A_K|^2 \frac{\partial U_K}{\partial Q_r} + 2 \sum_{L(\neq K)} \Re (A_K^* A_L e^{i(\gamma_K - \gamma_L)}) U_K g_{KL}^{(r)} \right] = F_r^{(1)} + F_r^{(2)}$$

As in quantum wavepacket dynamics, the nuclear motion is determined by two terms. The first one depends on the adiabatic potentials:

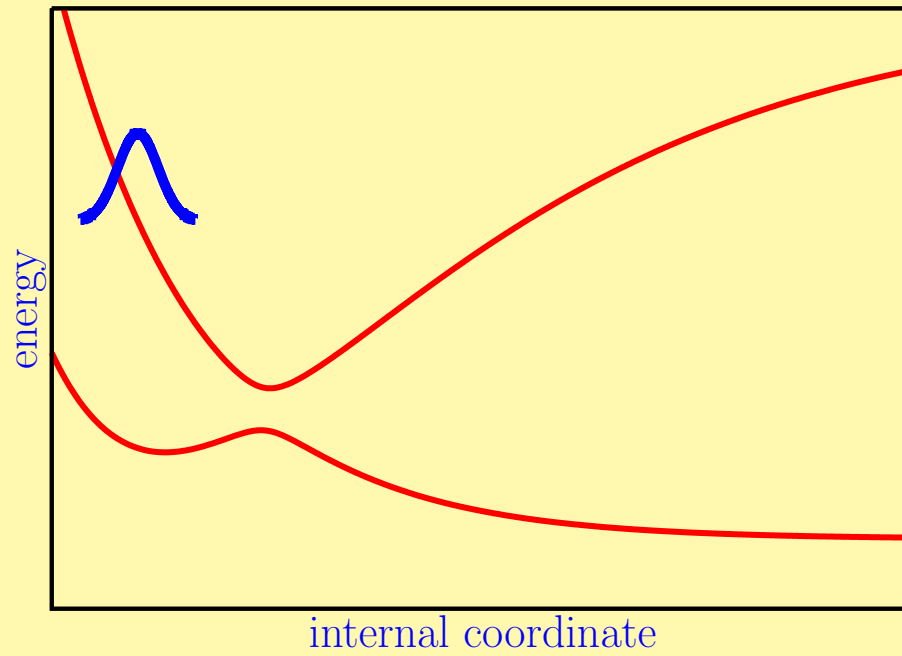
$$F_r^{(1)} = - \sum_K |A_K|^2 \frac{\partial U_K}{\partial Q_r}$$

The other one depends on the nonadiabatic couplings, and is less important whenever the Born-Oppenheimer approximation is valid:

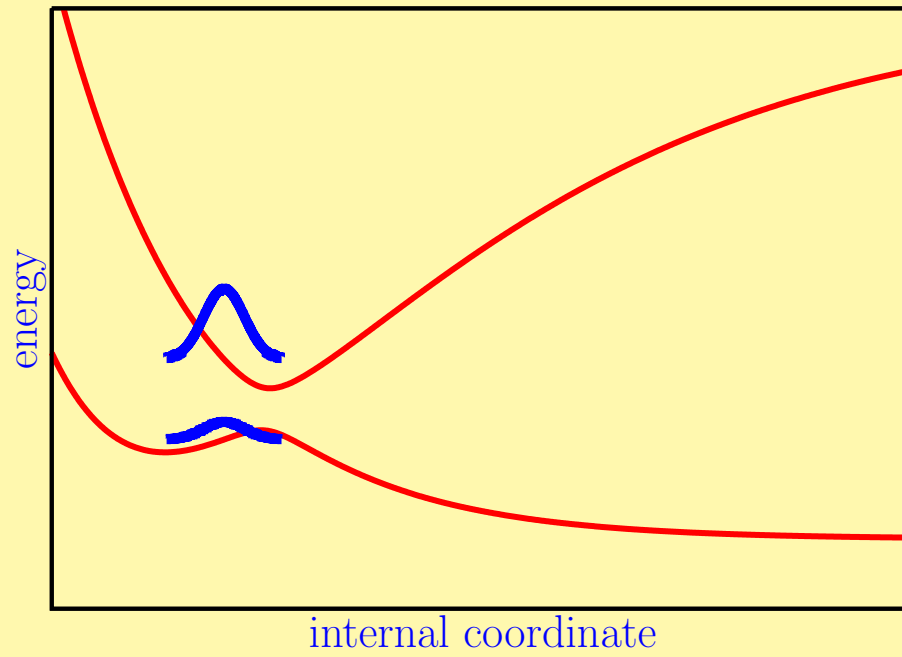
$$F_r^{(2)} = - \sum_K \sum_{L(\neq K)} \Re \left( A_K^* A_L e^{i(\gamma_K - \gamma_L)} \right) (U_K - U_L) g_{KL}^{(r)}$$

The main difference, with respect to quantum wavepacket dynamics, is that the representative point for the nuclear motion is the same for all the electronic states, so the force is a weighted average of all the  $U_K$  and  $g_{KL}$  contributions.

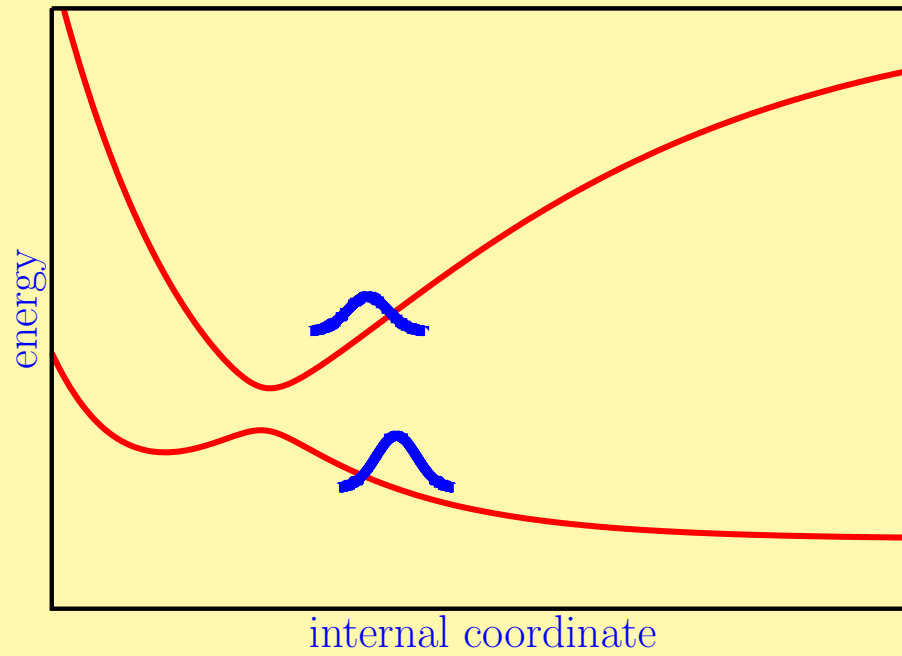
# Quantum wavepackets.



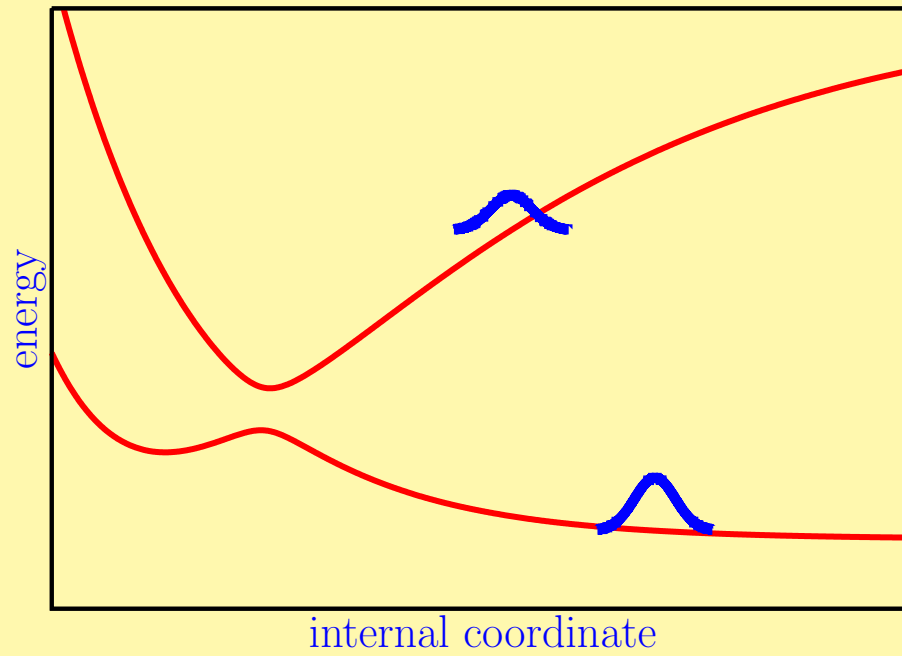
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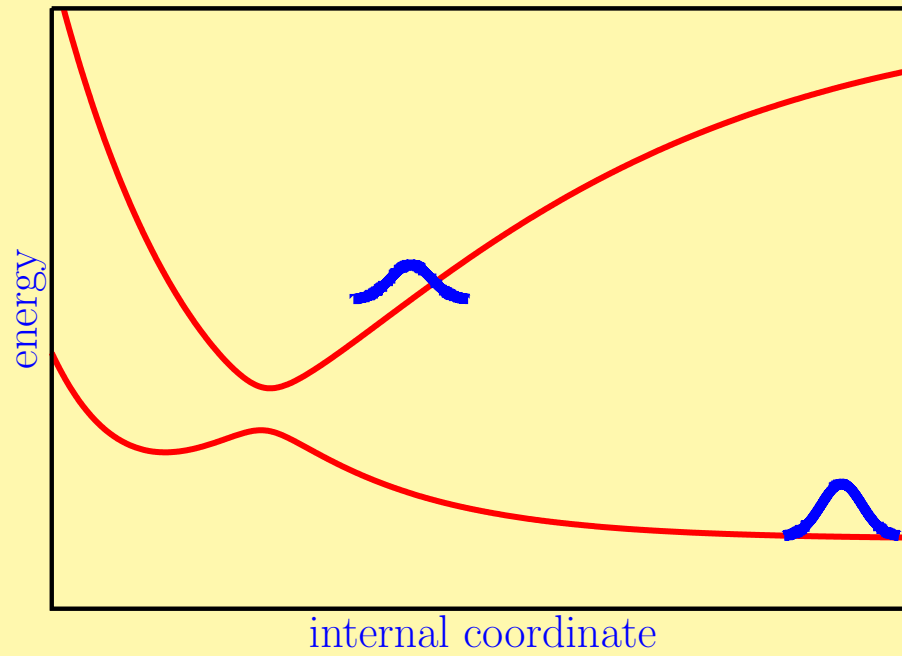
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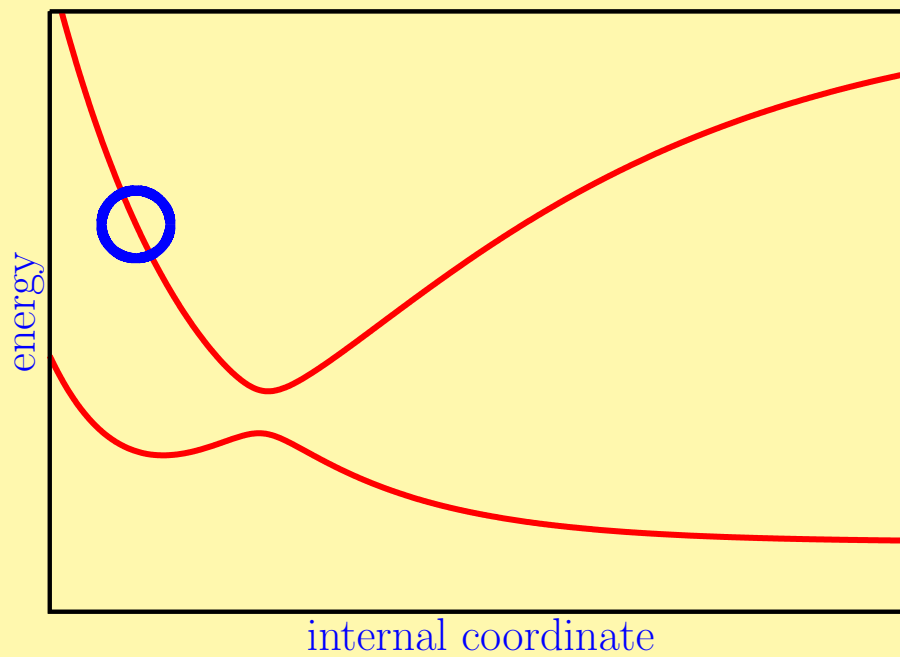
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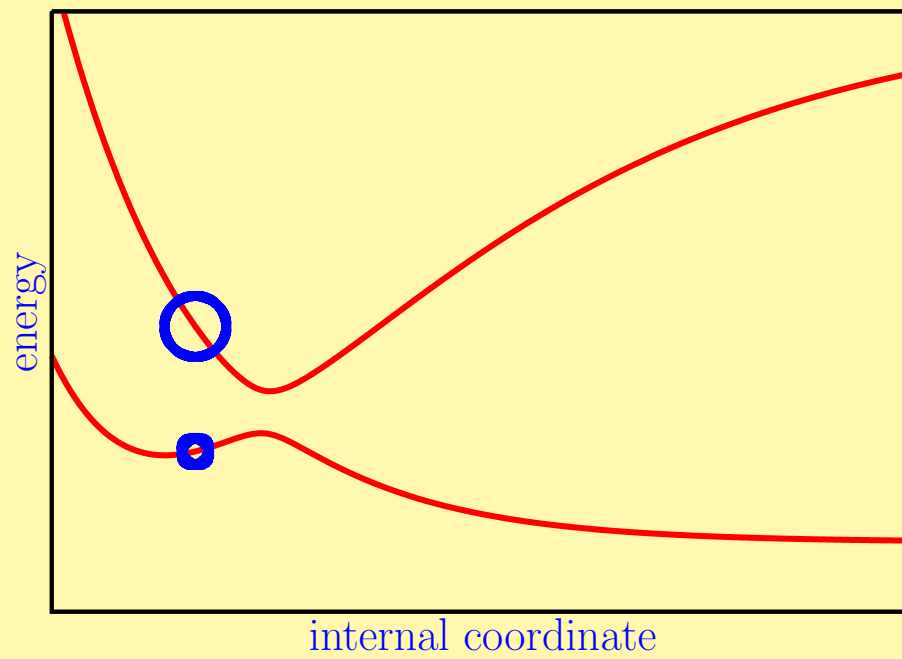
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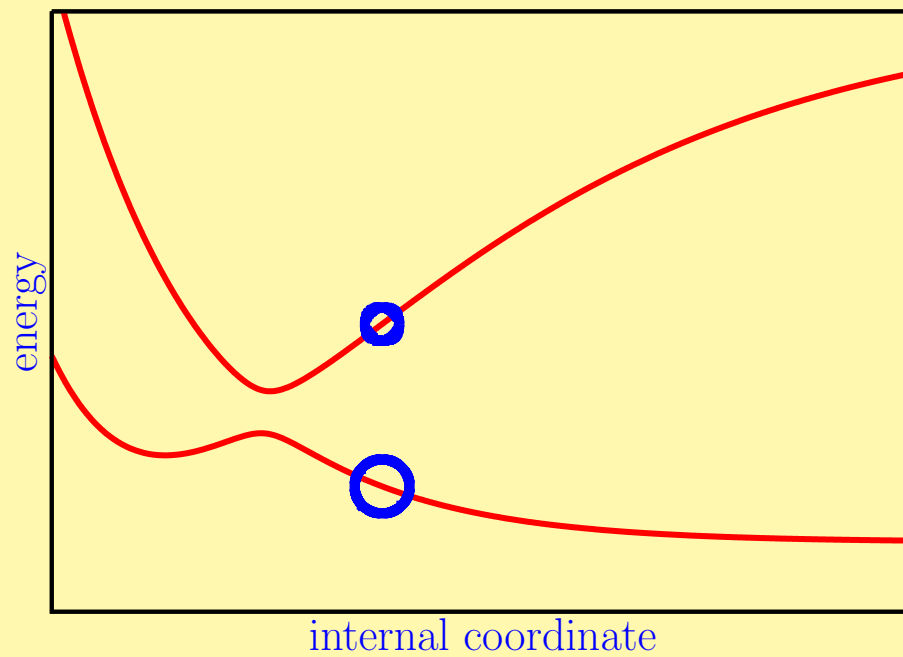
# MQC treatment: mean-field.



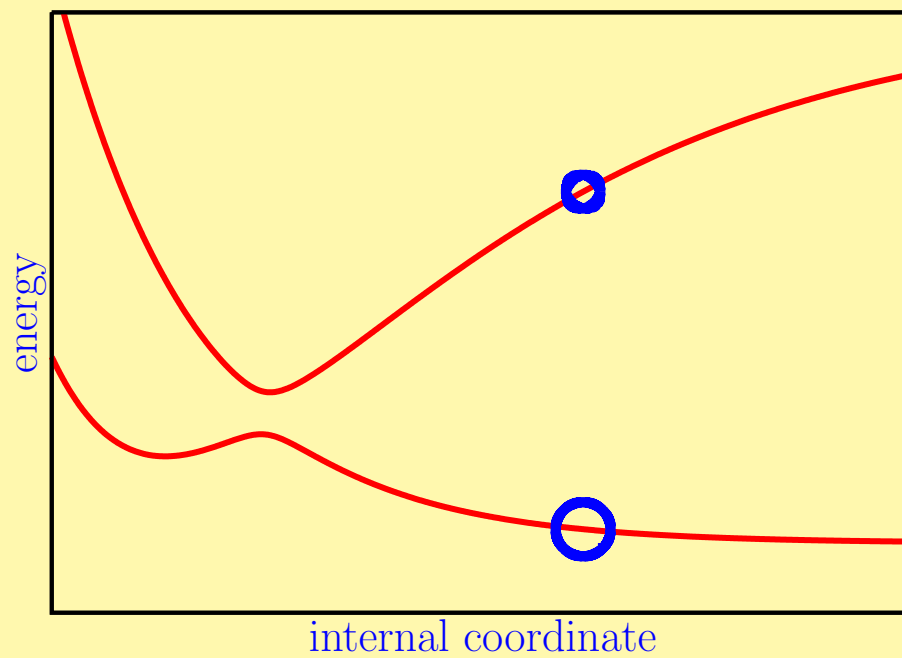
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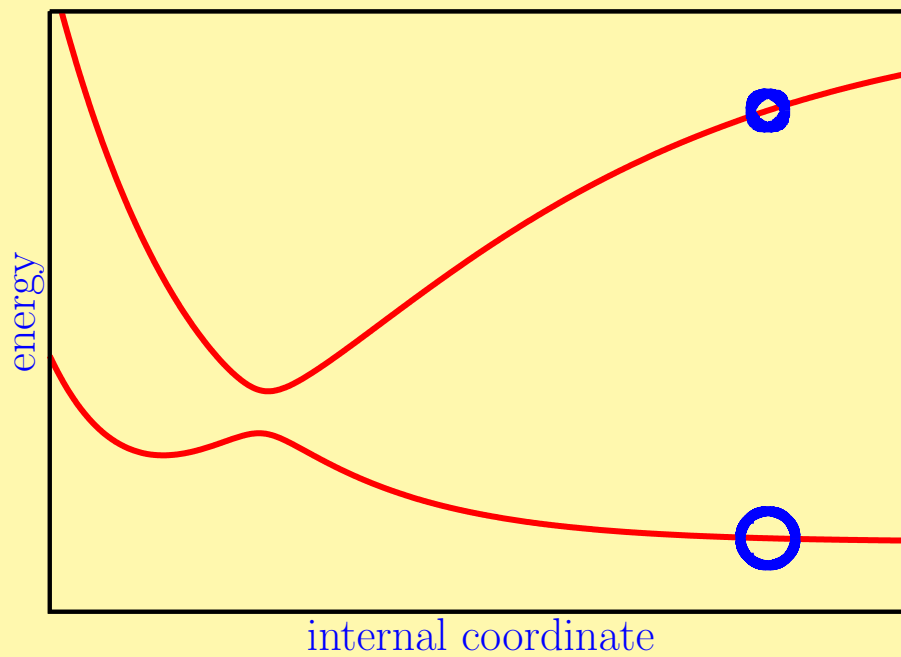
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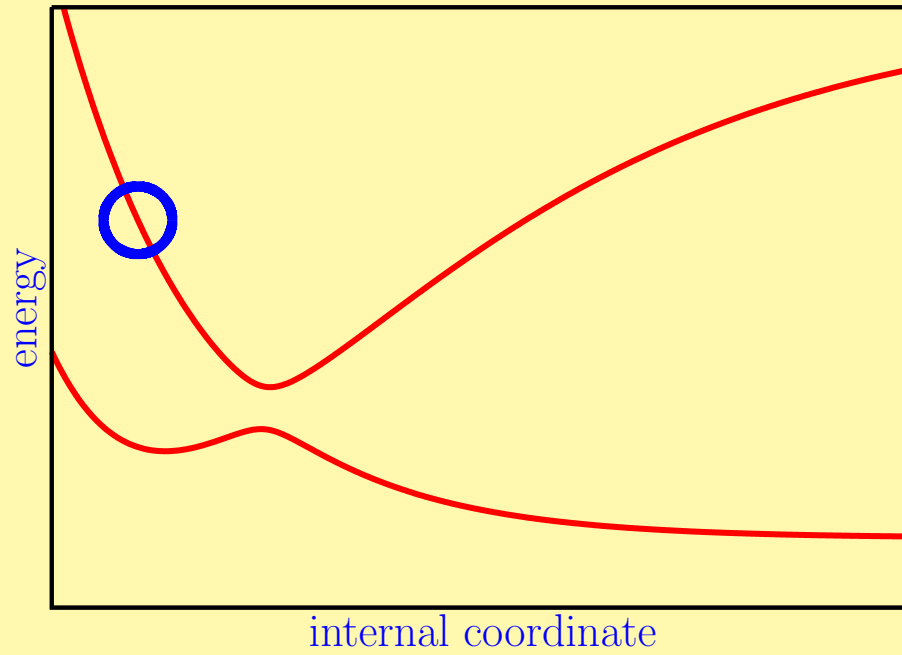


## MQC treatment: surface hopping

- We calculate many trajectories
- At any time, each trajectory runs on one state,  $K$
- The force is given by the potential  $U_K$
- A trajectory can hop from state  $K$  to  $L$ , according to the computed state probabilities  $P_K(t)$  and  $P_L(t)$ , with a stochastic algorithm [1, 3, 4, 11]

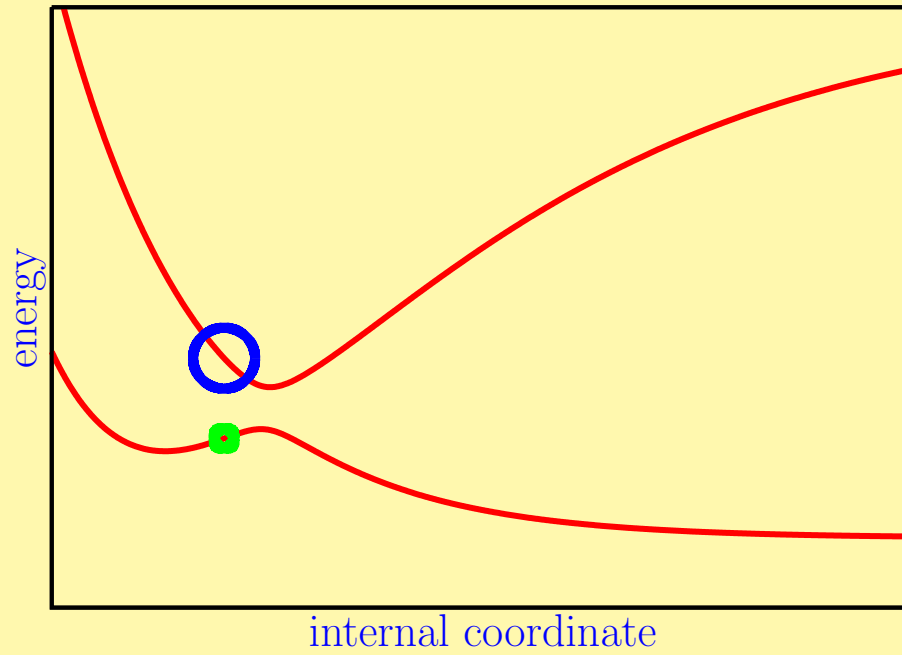
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A hop occurs



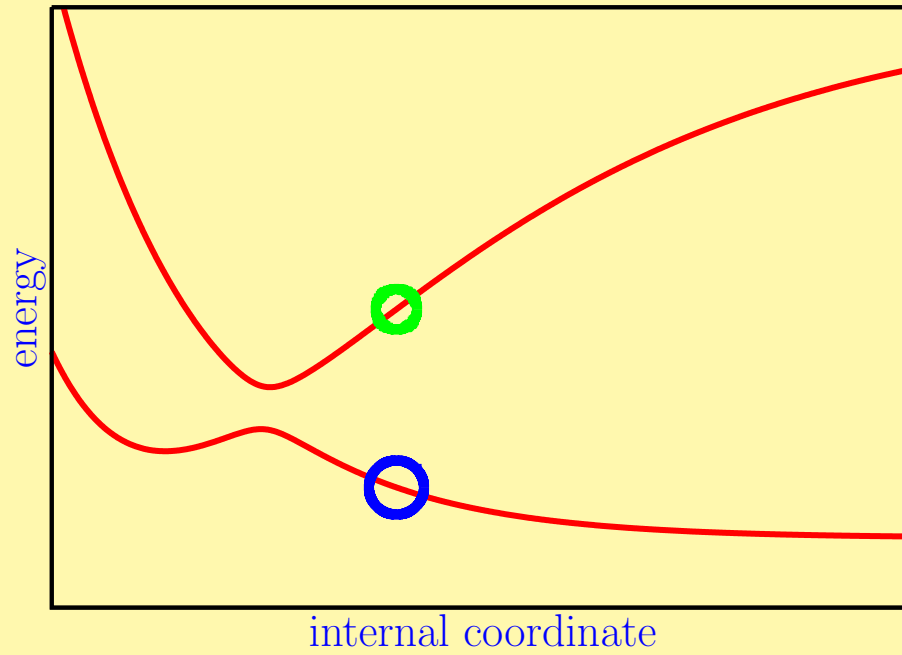
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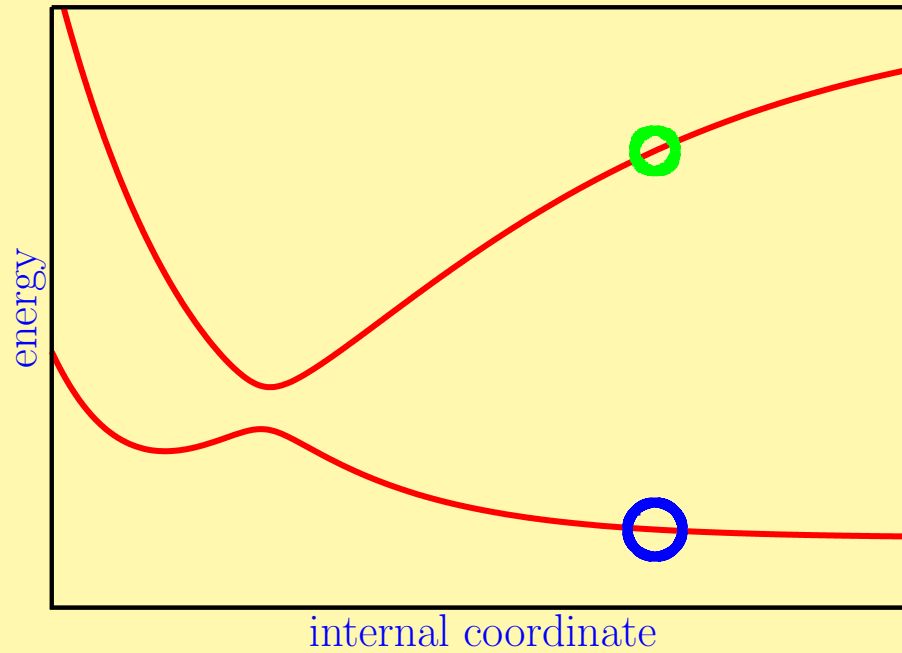
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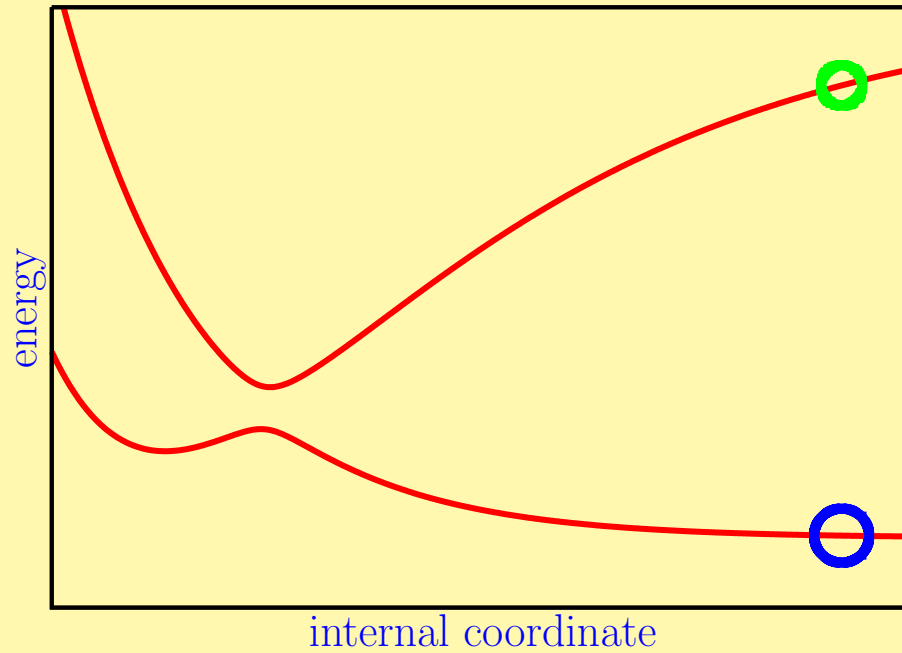
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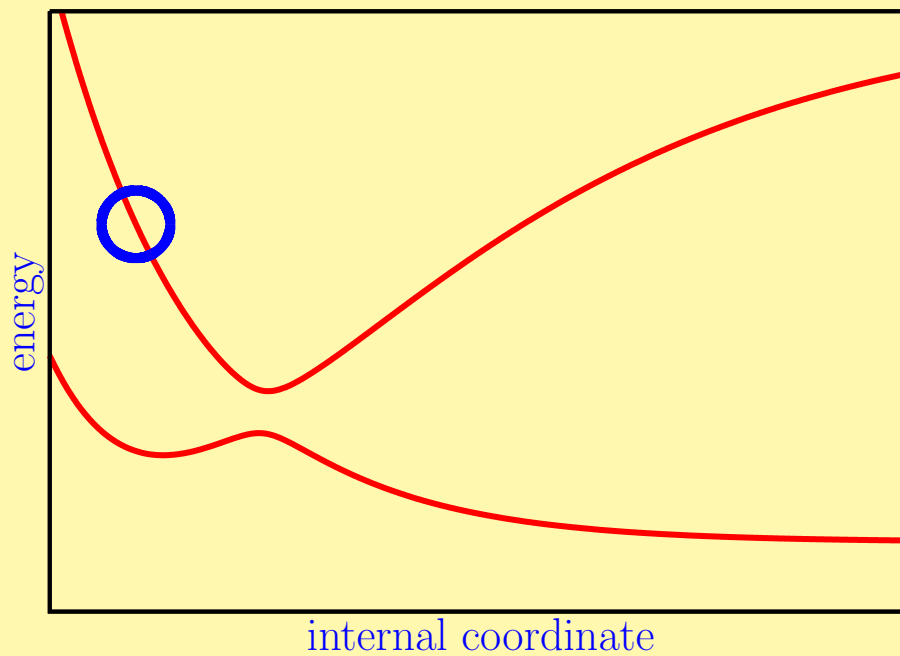
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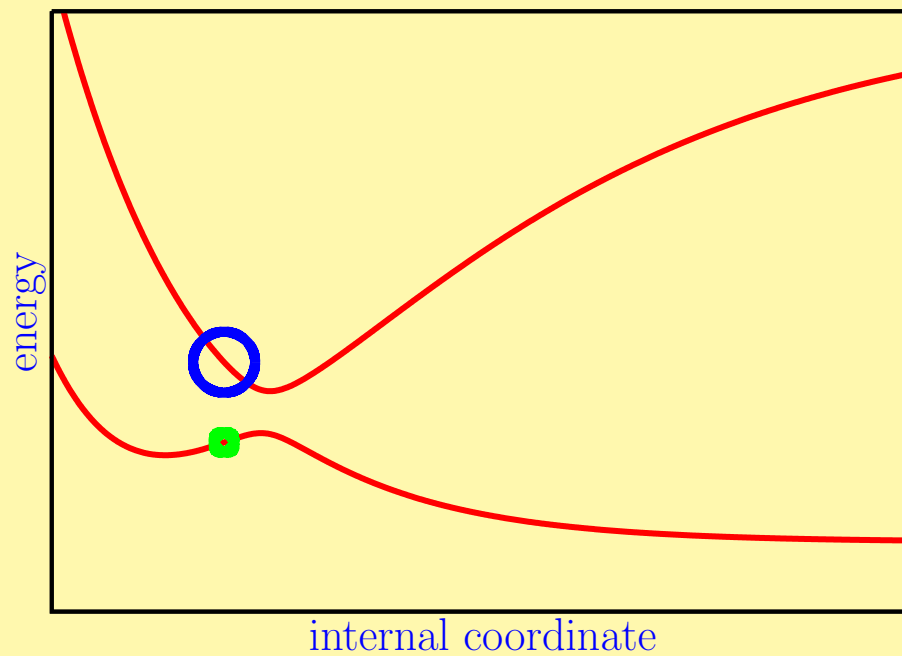
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No hop



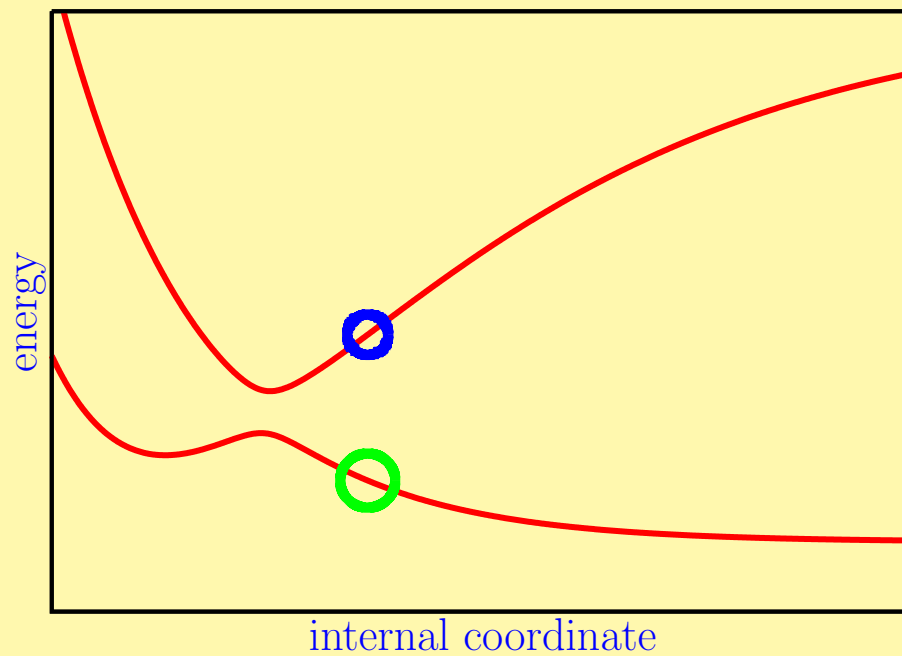
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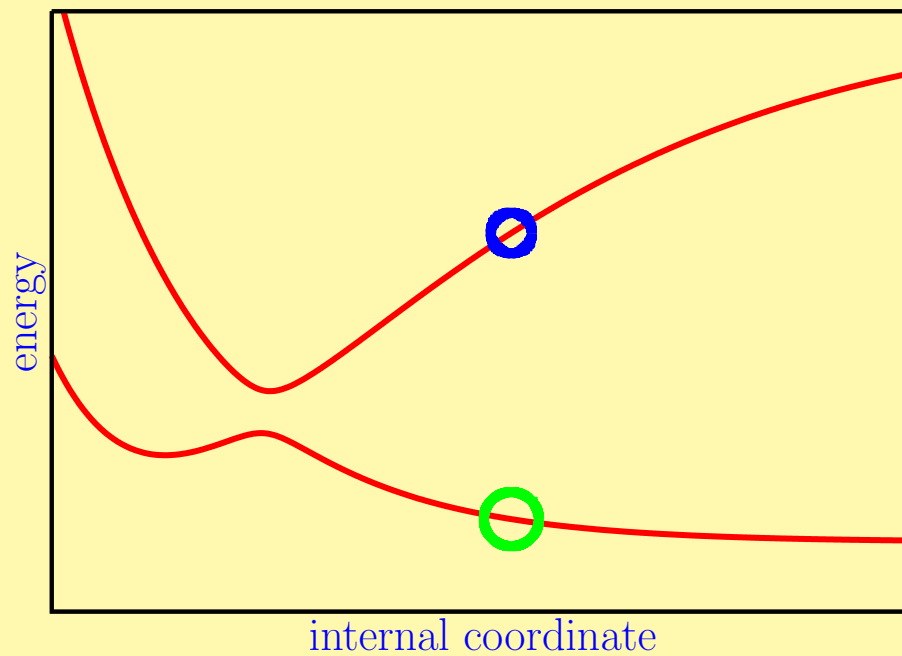
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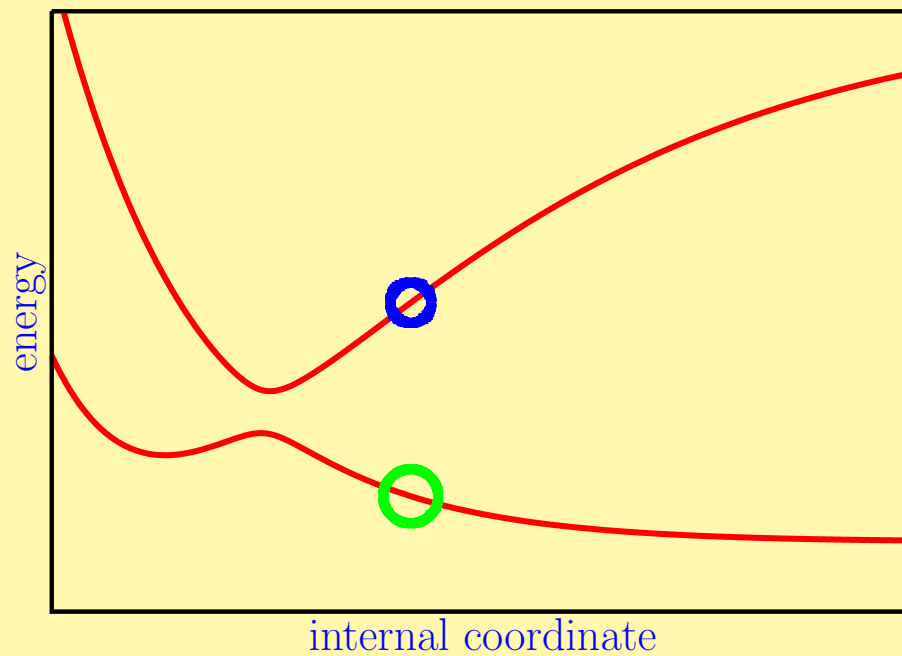
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No hop



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No hop



# Internal consistency of surface hopping

Definitions:

$P_K(t)$  = single trajectory computed probability of state  $K$

$\bar{P}_K(t)$  = average over all traj. of  $P_K(t)$

$\Pi_K(t)$  = state population = fraction of trajectories in state  $K$

Internal consistency requirement:  $\Pi_K(t) = \bar{P}_K(t)$

If  $T_{K \rightarrow L}$  is the  $K \rightarrow L$  hopping probability in a small time step  $\Delta t$ , the variation of  $\Pi_K$  is

$$\Delta \Pi_K = - \sum_L \Pi_K \bar{T}_{K \rightarrow L} + \sum_L \Pi_L \bar{T}_{L \rightarrow K}$$

where  $\bar{T}_{K \rightarrow L}$  and  $\bar{T}_{L \rightarrow K}$  are averages over all trajectories.

We want to define  $T_{K \rightarrow L}$  such that:

$$\Delta \Pi_K(t) = \dot{\bar{P}}_K(t) \Delta t \quad \forall K, t$$

From the TDSE we had  $\dot{A}_K = \sum_{L(\neq K)} A_L(t) e^{i(\gamma_K - \gamma_L)} \sum_r \dot{Q}_r g_{KL}^{(r)}$ , whence:

$$\dot{P}_K = \dot{A}_K A_K^* + A_K \dot{A}_K^* = - \sum_{L(\neq K)} B_{KL}$$

$$B_{KL} = 2\Re \left[ A_L A_K^* e^{i(\gamma_K - \gamma_L)} \right] \sum_r \dot{Q}_r g_{KL}^{(r)} \quad (\text{notice that } B_{LK} = -B_{KL})$$

Then:

$$\bar{T}_{K \rightarrow L} = \max \left\{ 0, \frac{\bar{B}_{KL}}{\Pi_K} \Delta t \right\}$$

This definition is both...

- ... unpractical, because it would force one to run all trajectories in parallel
- ... unphysical, because hopping events occurring on well separated reaction or scattering channels would influence each other [10].

Tully's "fewest switches" definition avoids the use of average quantities [1]:

$$T_{K \rightarrow L} = \frac{B_{KL} \Delta t}{P_K} \quad \text{only if } B_{KL} > 0$$

However, it cannot satisfy rigorously the internal consistency requirement.

## Decoherence correction.

- Integrating the TDSE for a single representative point on different PES is a good approximation of the quantum wavepacket dynamics, as far as the wavepackets occupy approximately the same positions in the phase space.
- When the average position and momentum of two wavepackets are very different, they evolve quite independently (**quantum decoherence**).
- To introduce quantum decoherence corrections in a mixed quantum-classical method, we should:
  - let the representative points travel independently on the different PES;
  - correct the probabilities and coefficients computed by the TDSE according to the distance between the representative points [5, 7, 8, 10].

## Our proposal.

- We associate a gaussian wavepacket to each representative point:

$$G_i(\mathbf{Q}, \mathbf{P}) = N \prod_{\alpha} \exp \left[ -\frac{m_{\alpha}^{1/2}(Q_{\alpha} - Q_{i,\alpha})^2}{4\sigma^2} + iP_{i,\alpha}Q_{\alpha} \right]$$

where  $Q_{\alpha}$  is a nuclear cartesian coordinate.

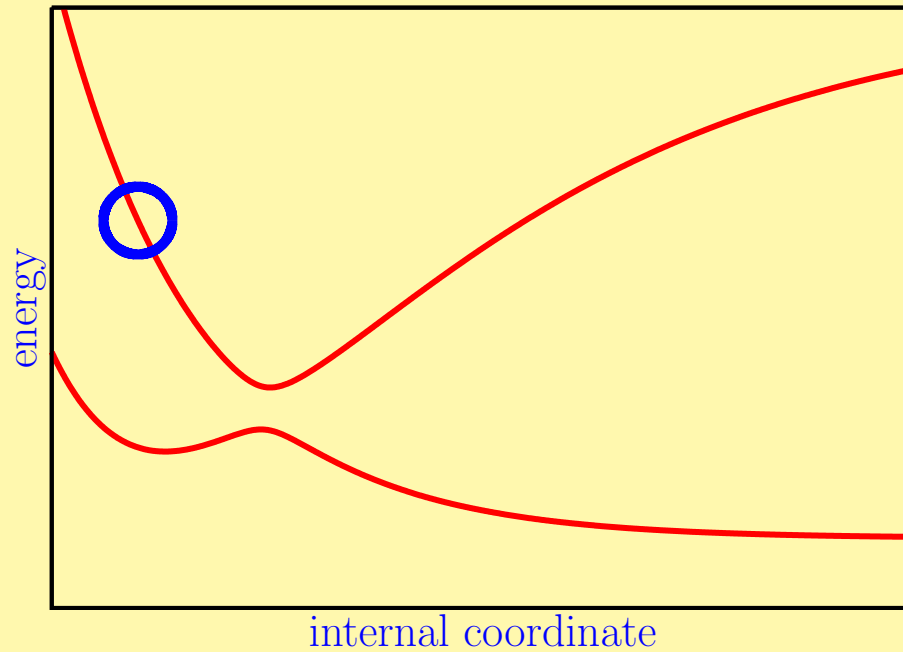
- One wavepacket  $G_0$  travels on the current PES,  $U_K$ .
- More wavepackets are created, every  $n_D$  time steps, on the other states  $L$ , if their probabilities  $P_L(t)$  have increased in time. Each new wavepacket  $G_i$  has initially the same  $\mathbf{Q}_i$  as  $G_0$ , and the module of  $\mathbf{P}_i$  is adjusted for energy conservation.
- The trajectories  $\mathbf{Q}_i(t)$ , with  $i \neq 0$ , are computed in a simplified way, to avoid performing electronic calculations at geometries different from the current one,  $\mathbf{Q}_0$ . All the momenta  $\mathbf{P}_i$  are updated every  $n_D$  steps, using only the information needed for energy conservation, computed at  $\mathbf{Q}_0$ .

- We compute the overlaps between  $G_0$  and the wavepackets travelling on the other PESs:

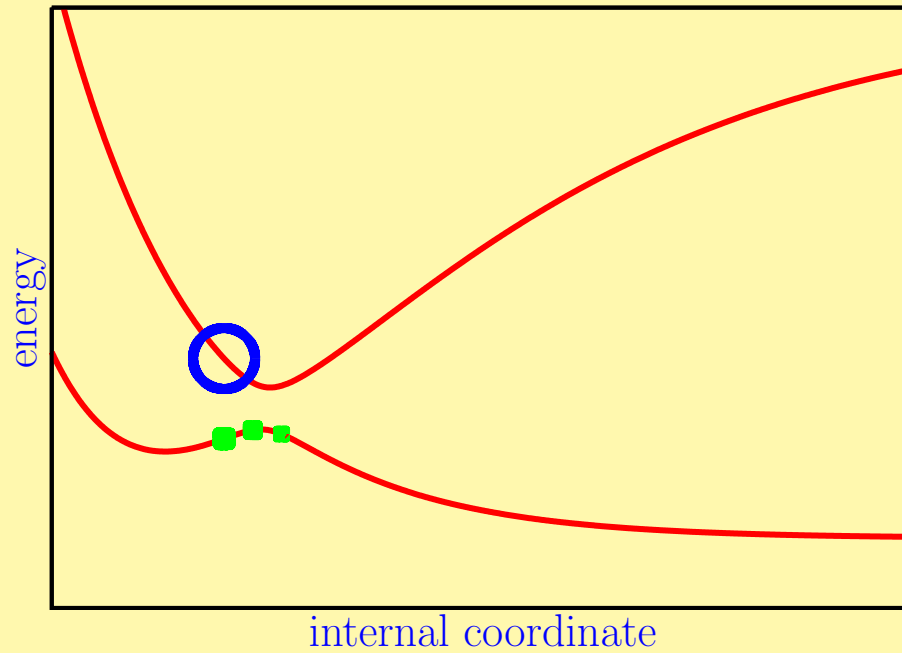
$$|\langle G_0 | G_i \rangle| = \prod_{\alpha} \exp \left[ -\frac{m_{\alpha}^{1/2}(Q_{0,\alpha} - Q_{i\alpha})^2}{8\sigma^2} - \frac{\sigma^2(P_{0,\alpha} - P_{i\alpha})^2}{2m_{\alpha}^{1/2}} \right]$$

- When the overlap  $|\langle G_0 | G_i \rangle|$  drops below a threshold  $s_{min}$ , the wavepacket  $G_i$  should not interfere any more with the time evolution of the current state: therefore it is suppressed, and the corresponding probability is attributed to  $G_0$ .
- When a surface hopping occurs, a new  $G_0$  is created, and all the other wavepackets on the same PES are suppressed.
- The decoherence correction (DC) depends on two parameters:
  - The overlap threshold,  $s_{min}$ .
  - The gaussian width,  $\sigma$ .

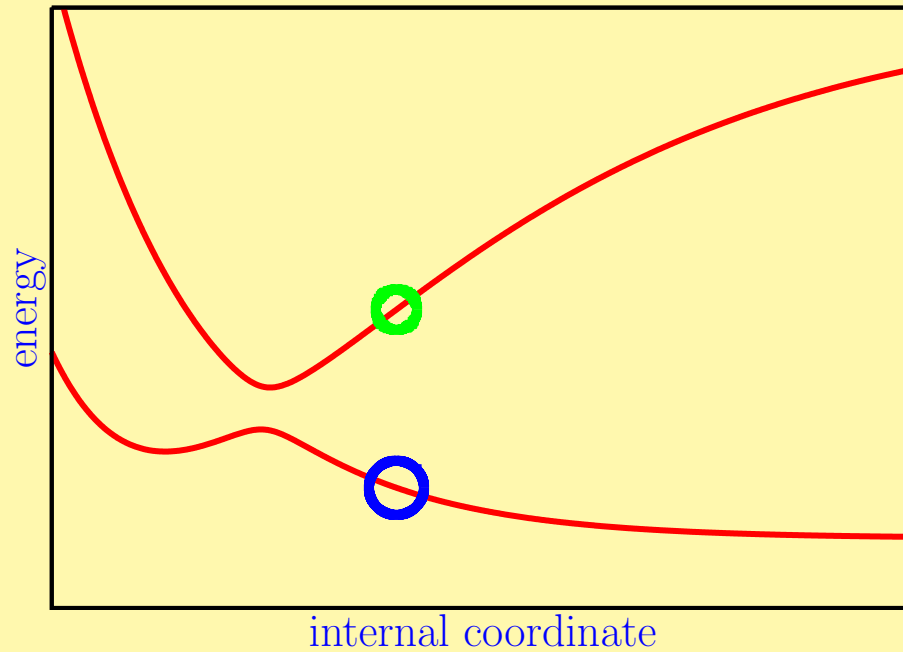
# Surface hopping with decoherence correction.



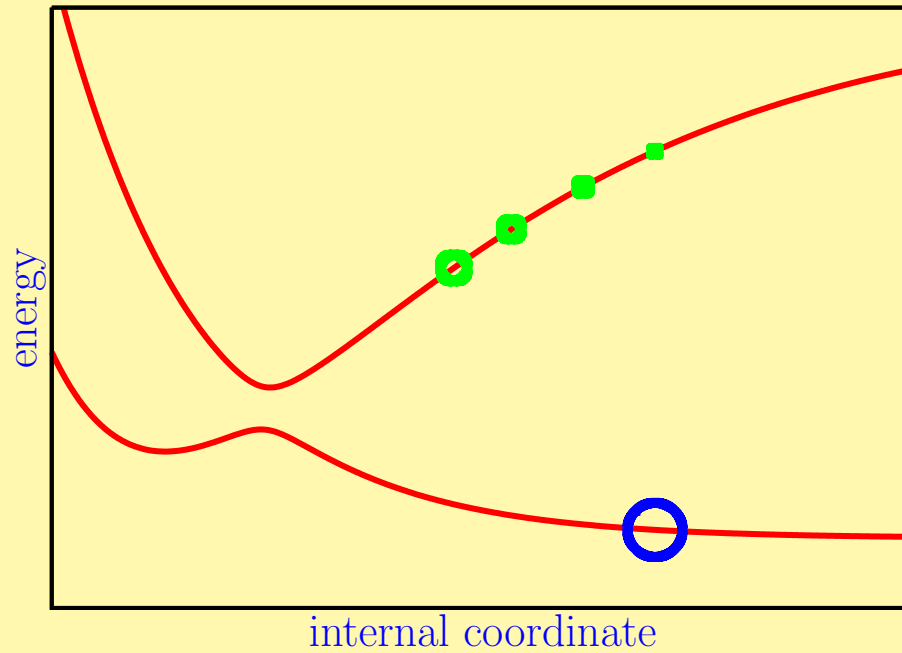
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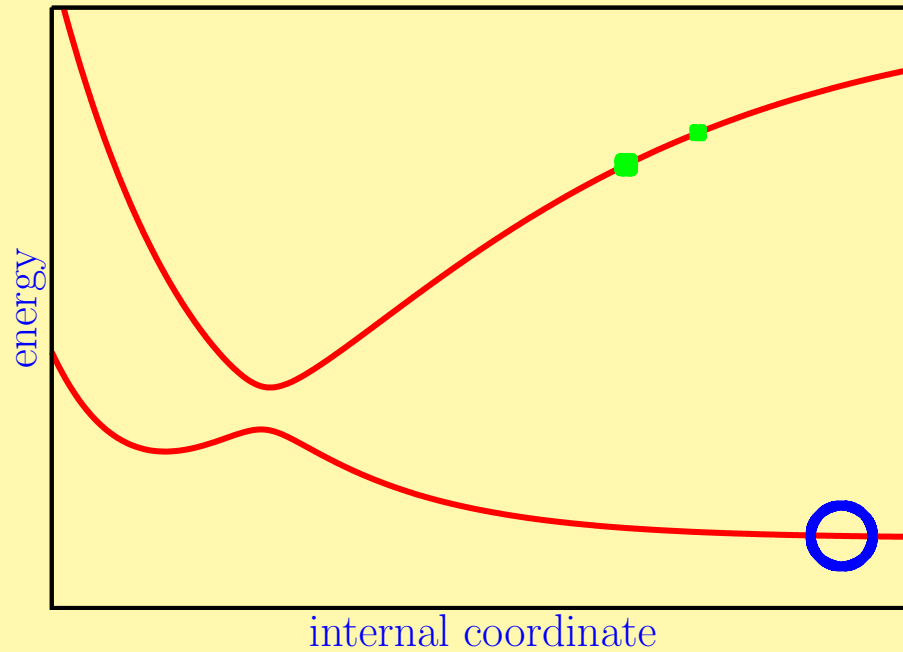
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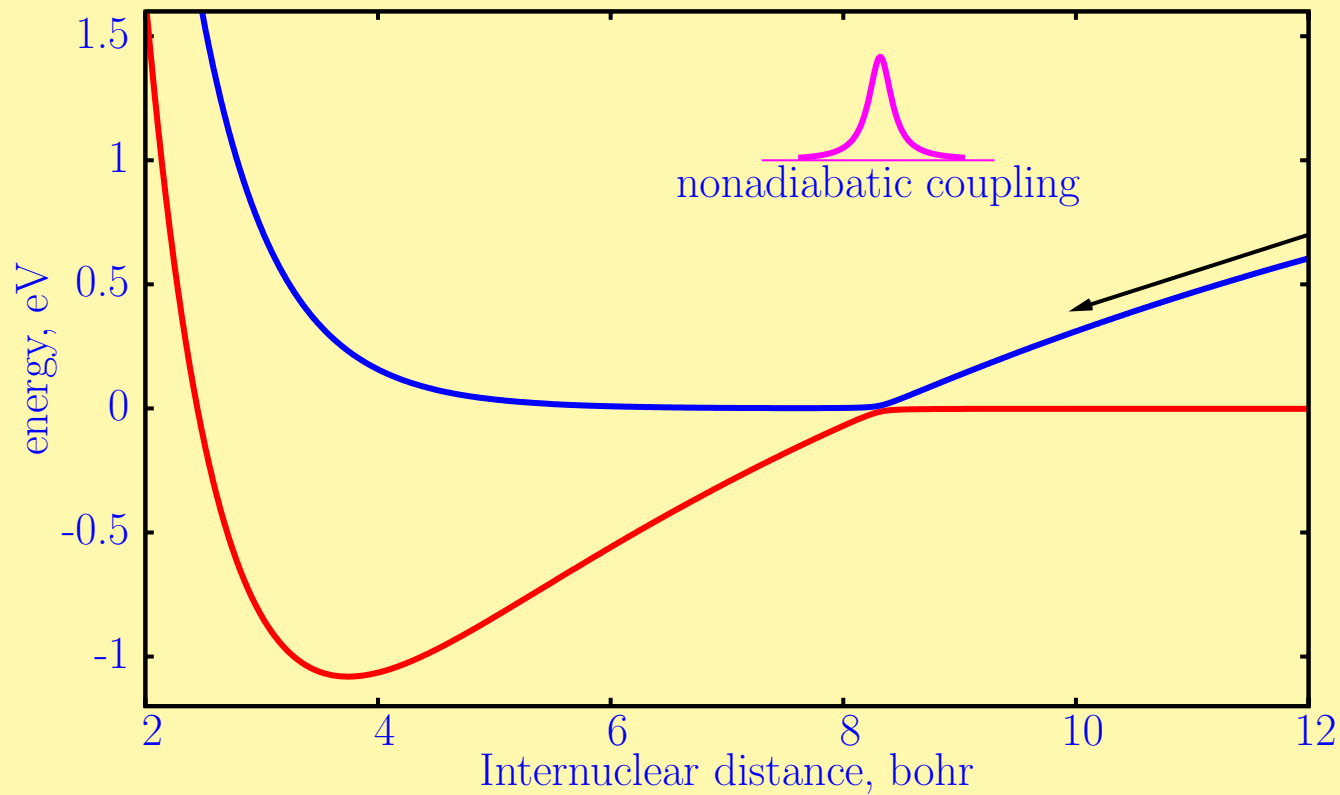


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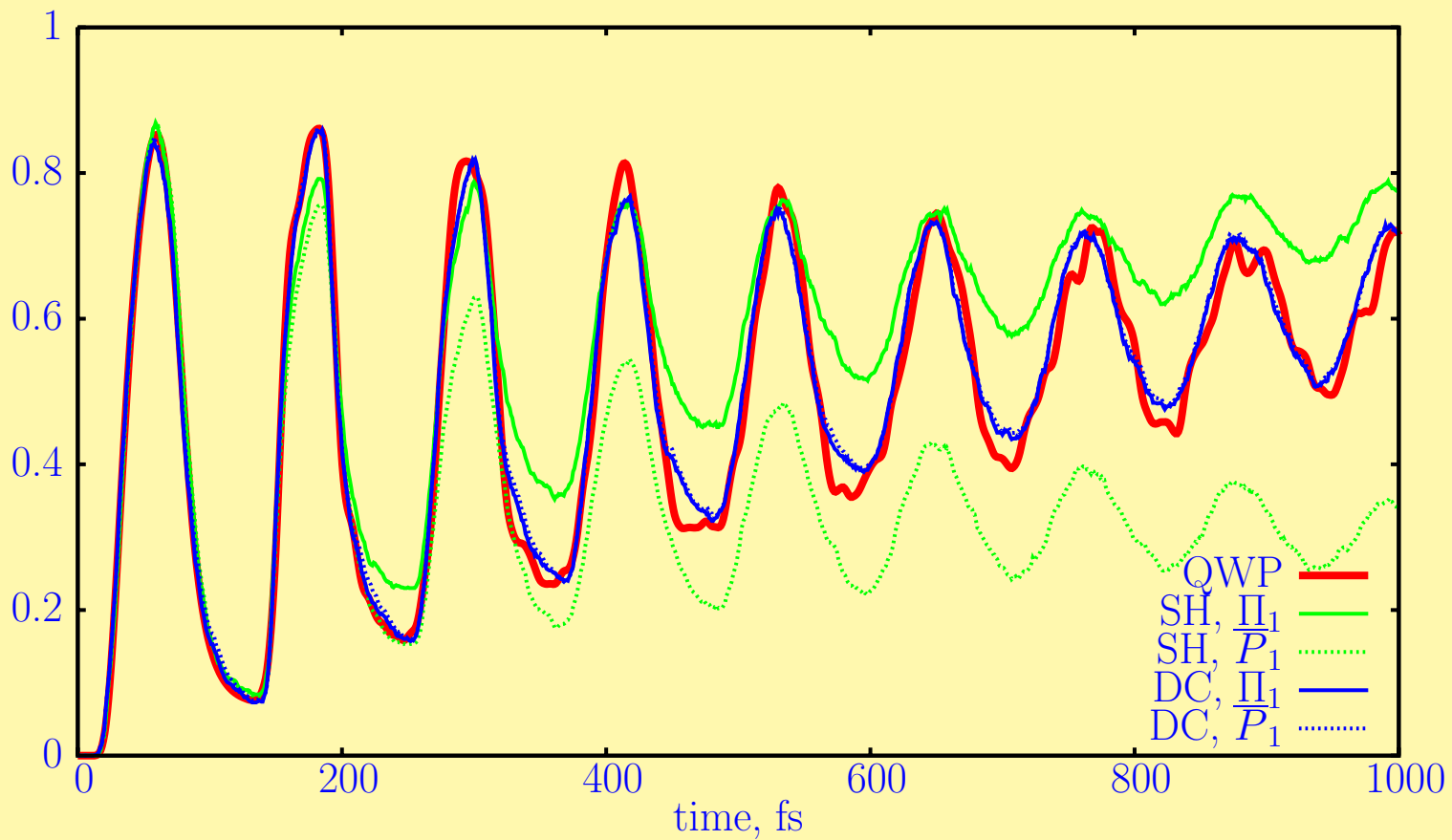
# 1D model: ionic/neutral crossing, many passages.

Potential energy curves and coupling.



# Ionic/neutral crossing.

Time dependent population of the first electronic state.



## A bit of statistics

$N_T \equiv$  total number of trajectories

$P \equiv$  probability of “interesting” event

Average number of interesting events:  $X \simeq N_T P$

Standard deviation on  $X$ :  $\sigma = \sqrt{N_T P(1 - P)}$

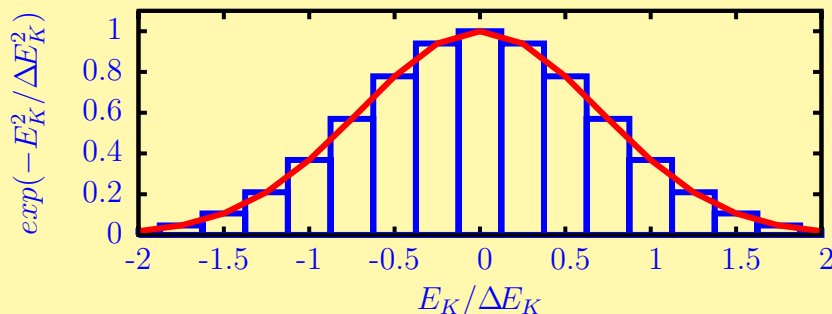
Relative error:  $\frac{\sigma}{X} = \sqrt{\frac{1-P}{N_T P}} = \sqrt{\frac{1-P}{X}}$

Example:  $\Phi \equiv$  quantum yield of a photodissociation,  $\Delta\Phi = \sqrt{\Phi(1 - \Phi)/N_T}$

If  $\Phi = 0.2$ ,  $N_T=100$  yields  $\Delta\Phi = 0.04$ , and  $N_T=1000$ ,  $\Delta\Phi = 0.013$ .

Now we make a histogram of the final kinetic energy of a photofragment.

Suppose the distribution is a gaussian and we choose the box width of the histogram as in the figure. The central box contains about 7% of the reactive trajectories, i.e. 1.4% of  $N_T$ . The relative error is then 0.85 with  $N_T=100$  and 0.27 with  $N_T=1000$ .



# Sampling of initial conditions

Two alternatives:

- Quantum mechanical distribution of coordinates and momenta in a given vibrational state.
- Thermal distribution according to classical statistics.

Vibrational ground state in a normal coordinate treatment:

$$\text{normal coordinate} \equiv Q_\sigma = \sum_r L_{r\sigma} \sqrt{m_r} \Delta Q_r$$

$$\text{cartesian displacement} \equiv \Delta Q_r = m_r^{-1/2} \sum_\sigma L_{r\sigma} Q_\sigma$$

We sample independently each  $Q_\sigma$  and  $P_\sigma$  from the distributions:

$$W(Q_\sigma) = \sqrt{\frac{\omega_\sigma}{\pi}} e^{-\omega_\sigma Q_\sigma^2} \quad W(P_\sigma) = \frac{1}{\sqrt{\pi \omega_\sigma}} e^{-P_\sigma^2 / \omega_\sigma}$$

Problems:

- The classical total energy is not constant (it averages to the ZPE)
- The zero point energy is there and available
- We did not take into account temperature and anharmonicity

## The zero point energy problem.

Zero point energy in the ground electronic state  $\equiv E_{ZP} = \frac{1}{2} \sum_r^{N_{vib}} \hbar\omega_r$

Minimum-to-minimum transition energy  $\equiv \Delta E_{eq}$

Vibrational energy in the excited state  $\equiv E_{vib} = E_{ZP} + h\nu - \Delta E_{eq}$

In quantum mechanics, the zero point energy cannot be disposed of, whereas a classical trajectory can transfer the ZPE of one or several modes to other modes, a forbidden process that can make easier to overcome a barrier or to dissociate a bond. We can reduce  $E_{ZP}$  by freezing  $N_{high}$  modes with high frequency in the sampling procedure.

In the QM statistical limit, the average energy content of mode  $Q_r$  is

$$\overline{E}_r(\text{QM}) = \frac{\hbar\omega_r}{2} + \frac{\hbar\omega_r}{e^{\hbar\omega_r/K_B T} - 1}$$

with the effective temperature  $T$  such that  $\sum_r^{N_{vib}} \overline{E}_r(\text{QM}) = E_{vib}$ .

Classically:

$$\overline{E}(\text{class.}) = \frac{E_{vib}}{N_{vib}} = \frac{1}{N_{vib}} \left[ h\nu - \Delta E_{eq} + \frac{1}{2} \sum_r^{N_{vib} - N_{high}} \hbar\omega_r \right]$$

## Example: azomethane, $\text{CH}_3\text{-N}=\text{N-CH}_3$ .

Frequencies and energies in  $\text{cm}^{-1}$ .

mode	frequency	ZPE	<u>QM energy</u>	<u>class. energy</u>
$N_{vib}$			per mode	$E_{vib}/N_{vib}$
1	214	107	626	213
2	222	111	627	217
3	312	156	633	224
4	353	176	637	231
5	591	296	666	244
6	919	460	730	263
...	...	...	...	...
17	1447	724	879	553
18	1583	792	925	586
19	2925	1462	1489	647
20	2926	1463	1489	708
21	2977	1488	1513	770
22	2981	1490	1515	832
23	2989	1494	1519	894
24	2988	1494	1518	957

## Thermal distribution of the initial conditions

When one or more low frequency coordinates ( $\hbar\omega < K_B T$ ) are important, one needs to consider a thermal distribution of initial conditions. Most often, in such cases the normal coordinate approximation is not valid because of the anharmonicity of the ground state PES. Computing several vibrational states and levels in a QM treatment is therefore very difficult for the most of the large systems of photochemical interest.

The alternative is to rely on classical mechanics also for the sampling of the initial conditions. A practical way to generate a Boltzmann distribution of coordinates and momenta is to sample from a sufficiently long Brownian trajectory. This is done by integrating the Langevin equations:

$$m_r \ddot{Q}_r = -\frac{\partial V}{\partial Q_r} - \gamma_r m_r \dot{Q}_r + X_r(t)$$

Here  $\gamma_r$  is the friction coefficient for the atom to which the  $r$  coordinate belongs.  $X_r(t)$  is a gaussian random white noise, with the properties:  $\langle X_r \rangle = 0$ ,  $\langle X_r(0) X_s(t) \rangle = 2m_r \gamma_r K_B T \delta_{rs} \delta(t)$ .

## Excitation!!!

Once a QM or a classical distribution in the nuclear phase space has been defined, we must apply to it an excitation process.

In QM wavepacket dynamics, one can treat explicitly the molecule-radiation interaction. There seems to be no sensible way to do it in a mixed MQCD approach. Within the Ehrenfest philosophy, any excitation probability short of a full swap from the ground to the excited state leads to serious artifacts: the most obvious is that the trajectory is stuck near the minimum of the ground state PES, which dominates the mean-field potential.

According to the surface hopping philosophy, we jump on the excited PES  $U_K$  by a vertical excitation (no change in the nuclear coordinates and momenta), and we start integrating Newton's and Schrödinger's equations with  $P_K = 1$  and  $P_L = 0 \quad \forall L \neq K$ . We want to combine the chosen distribution in the nuclear phase space,  $W(\mathbf{Q}, \mathbf{P})$  with the optical transition probability, which is proportional to the squared transition dipole:

$$P_{exc} = \langle 0 | \vec{\mu} | K \rangle^2 = \vec{\mu}_{0K}^2(\mathbf{Q})$$

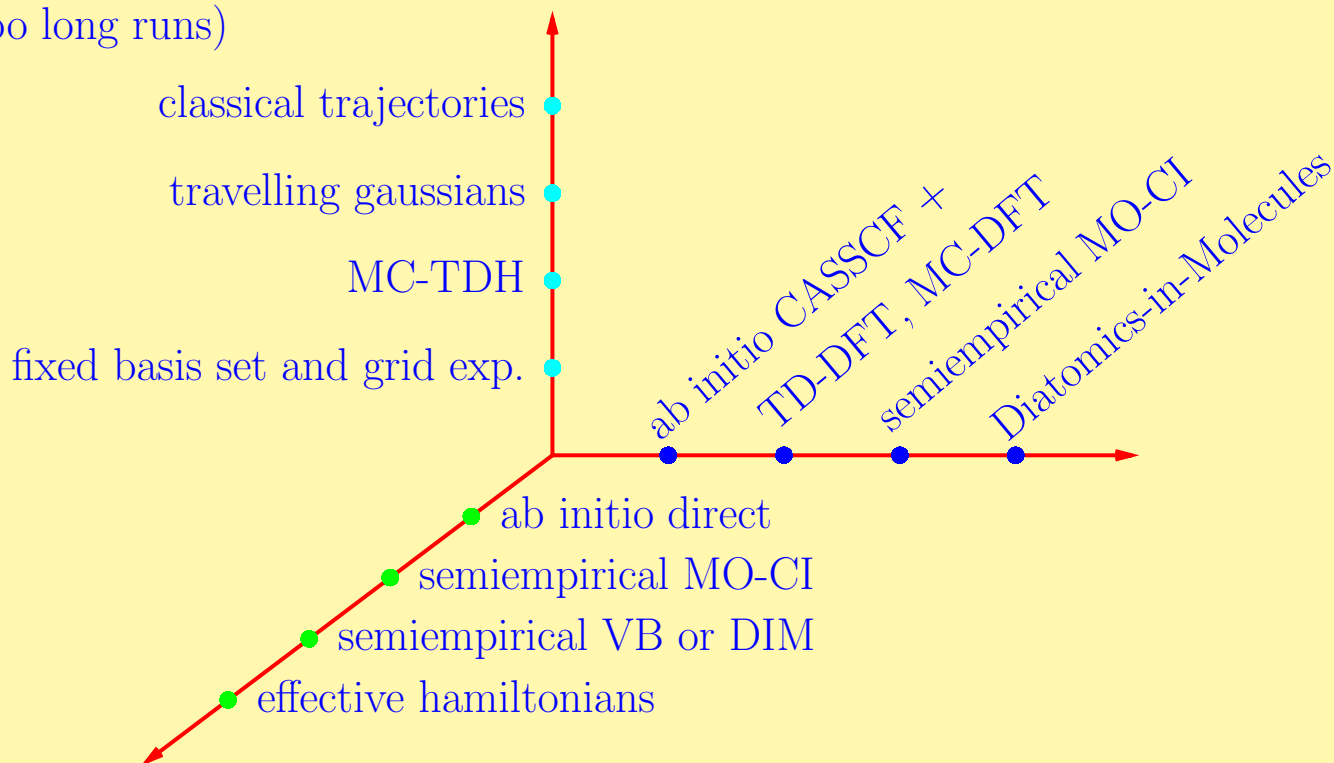
The full stochastic procedure to sample the initial conditions (positions, momenta and electronic state) consists of the following steps [11, 12]:

- (1) We set a transition energy window  $[\Delta E_{min}, \Delta E_{max}]$ , that can be narrowed to simulate an approximately monochromatic exciting light.
- (2) We also set a parameter  $\mu_{ref}^2$ , with the same order of magnitude as the square transition dipoles for the transitions we are interested in.
- (3) We sample from the  $W(\mathbf{Q}, \mathbf{P})$  distribution a set of points  $(\mathbf{Q}_i, \mathbf{P}_i)$  in the nuclear phase space, without any bias. For each point  $(\mathbf{Q}_i, \mathbf{P}_i)$ , we go through steps (4) to (7).
- (4) We calculate the transition energies  $\Delta E_{0K}$  from the ground state to the other singlets, and the corresponding transition dipoles  $\vec{\mu}_{0K}$ .
- (5) If none of the  $\Delta E_{0K}$  transition energies falls within the chosen window  $[\Delta E_{min}, \Delta E_{max}]$ , no trajectory is started from the current point  $(\mathbf{Q}_i, \mathbf{P}_i)$ .
- (6) If one or more states, from  $K_1$  to  $K_2$ , fall within the window, we define the sums:  $S_K = \sum_{L=K_1}^K \mu_{0L}^2$ . Then, we define  $N_{max}$  as the next integer value of  $S_{K_2}/\mu_{ref}^2$ . At most  $N_{max}$  trajectories will start from the current point  $(\mathbf{Q}_i, \mathbf{P}_i)$ .
- (7) For  $N_{max}$  times, we extract a random number  $R$  in the interval  $[0, N_{max}\mu_{ref}^2]$ . If  $S_{K-1} < R \leq S_K$ , we start a trajectory in state  $K$ , otherwise, if  $R > S_{K_2}$ , no trajectory is launched.

# Direct methods for nonadiabatic dynamics

Two strategies:

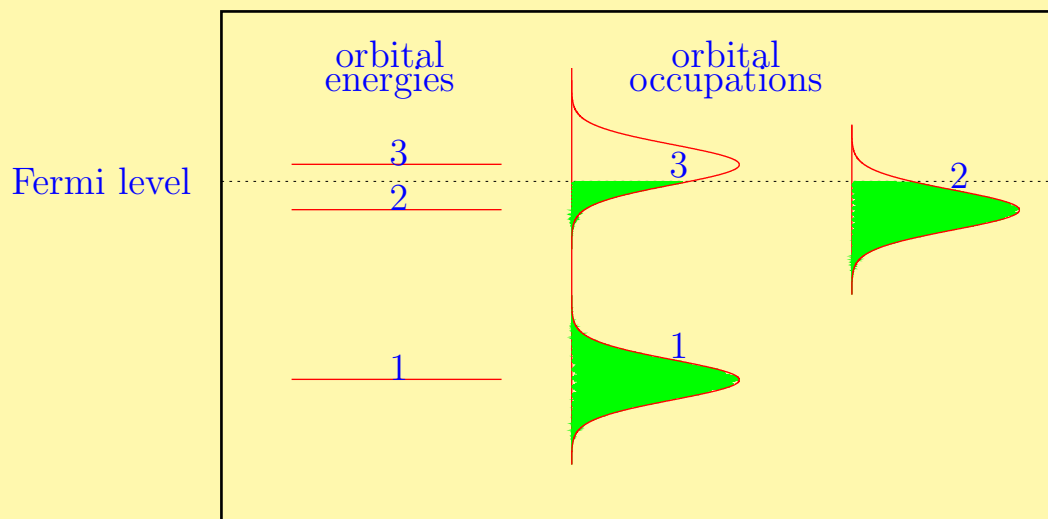
- Compute PES and couplings before starting the dynamics and represent them analytically (good for not too complicated surfaces and long runs)
- Compute PES and couplings “on the fly” (good for large systems and not too long runs)



# Semiempirical method for direct dynamics

Our choice: semiempirical NDO methods (MNDO, AM1, PM3...) with CI wavefunctions, based on floating occupation SCF orbitals [11, 13].

$$\text{occupation number} \equiv N_K = \frac{\sqrt{2}}{\sqrt{\pi}w} \int_{-\infty}^{\varepsilon_F} \exp \left[ -\frac{(\varepsilon - \varepsilon_K)^2}{2w^2} \right] d\varepsilon$$

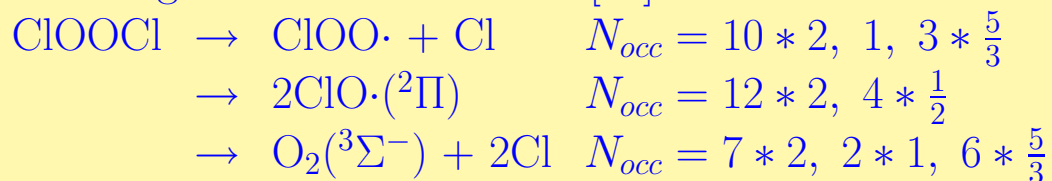


- Homolytic dissociation is correctly represented
- Degenerate orbitals are equally occupied
- The lowest virtuals are partially optimized

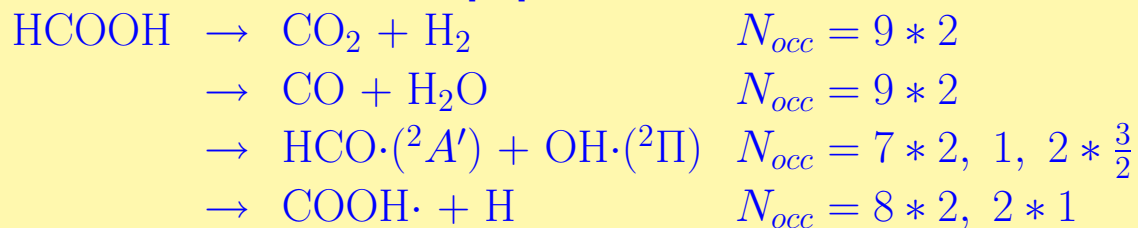
Some examples of variable orbital occupation.

- Photoisomerizations by twisting of double bonds, diradical and zwitterionic states: 2 electrons in 2 orbitals. For ethylene,  $N_{occ} = 5 * 2, 2 * 1$ .

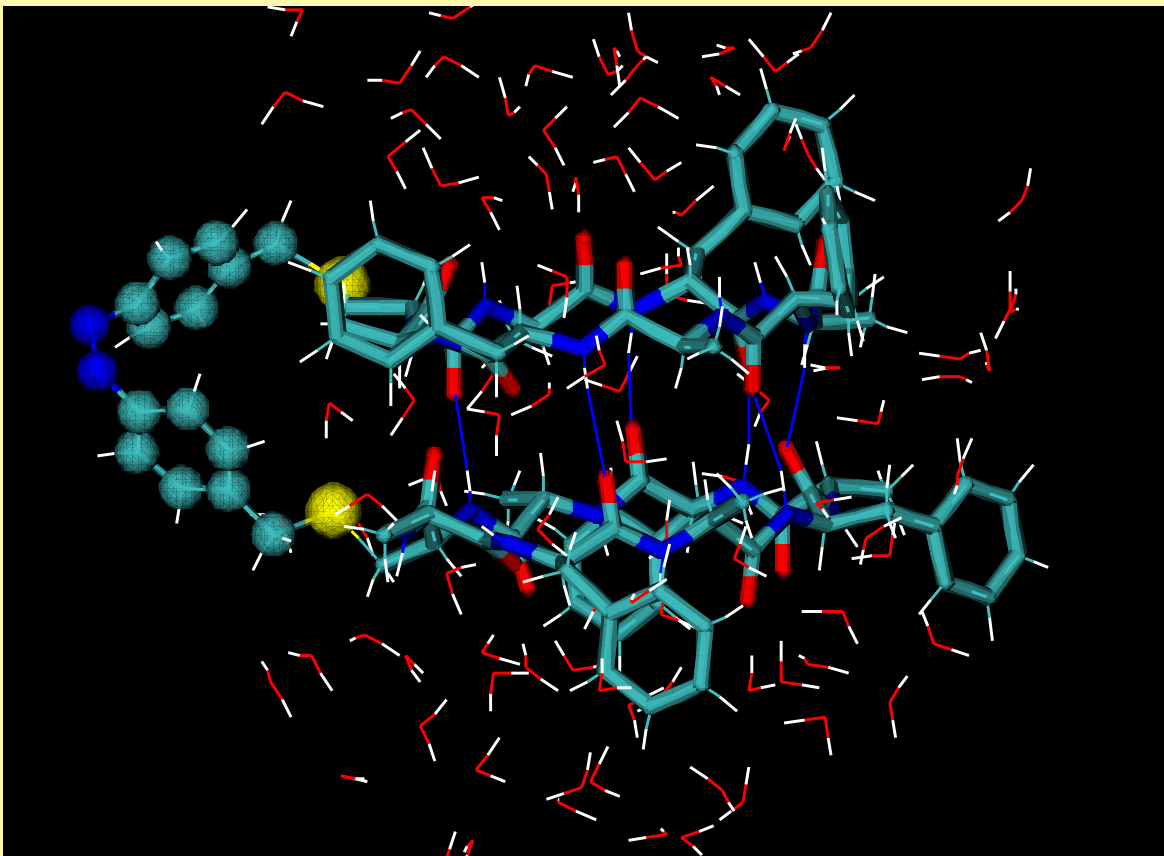
- Photofragmentation of ClOOCl [14]:



- Photolysis of formic acid [15]:



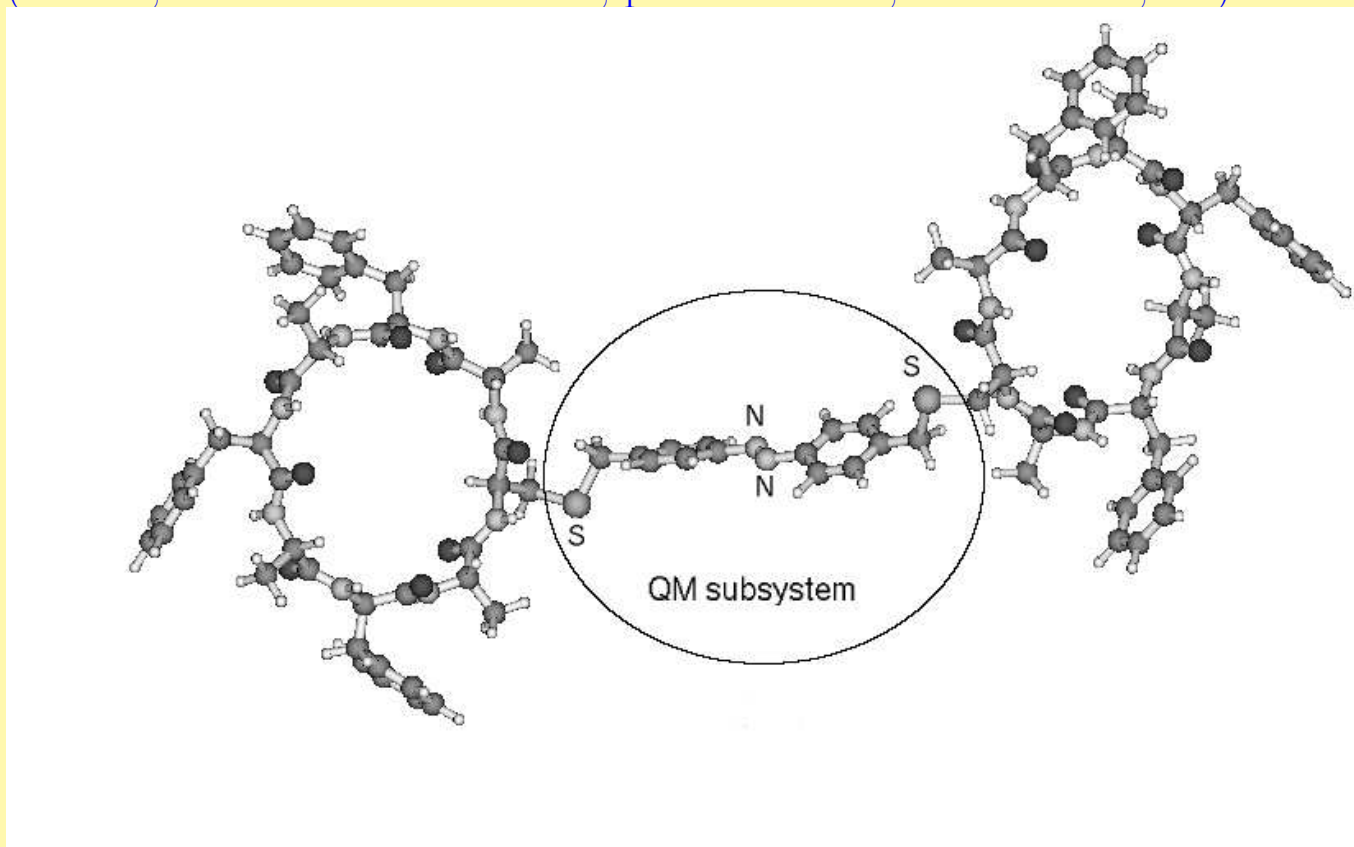
## Hybrid QM/MM methods



What can we do with this?

The whole system is partitioned into two subsystems [16–18]:

- the QM (Quantum mechanics) one, containing the chromophore and the reactive center;
- the MM (Molecular Mechanics) one, which is the “chemical environment” (solvent, unreactive substituents, proteic matrix, solid surface, etc).



The hamiltonian contains three terms:

$$\hat{\mathcal{H}}_{el} = \hat{\mathcal{H}}_{QM} + \hat{\mathcal{H}}_{MM} + \hat{\mathcal{H}}_{QM/MM}$$

Total energy for state  $K$ :

$$U_K = \langle \psi_K | \hat{\mathcal{H}}_{QM} + \hat{\mathcal{H}}_{QM/MM} | \psi_K \rangle + U_{MM}$$

QM/MM interaction:

$$\hat{\mathcal{H}}_{QM/MM} = - \sum_{i,m} \frac{q_m}{R_{im}} + \sum_{\alpha,m} \frac{Z_\alpha q_m}{R_{\alpha m}} + \sum_{\alpha,m} \epsilon_{\alpha m} \left[ \left( \frac{\sigma_{\alpha m}}{R_{\alpha m}} \right)^{12} - \left( \frac{\sigma_{\alpha m}}{R_{\alpha m}} \right)^6 \right]$$

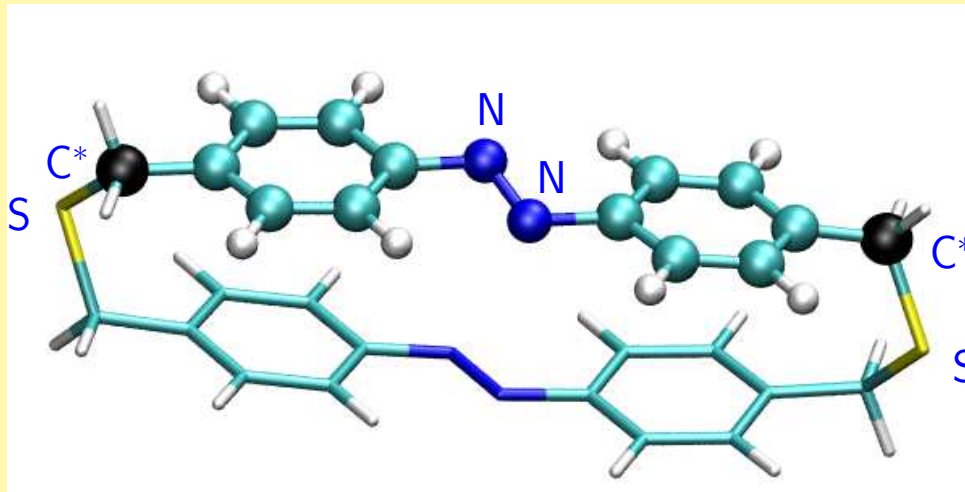
The index  $i$  numbers the electrons,  $\alpha$  the QM atoms/nuclei,  
 $m$  the MM ones.

$q_m \equiv$  atomic charge of MM atom  $m$

$Z_\alpha \equiv$  core charge of QM atom  $\alpha$

# Covalent bonding between the QM and MM subsystems

Azobenzenophane [13]. The QM atoms are represented with balls-and-sticks, the MM atoms with sticks only.



Most proposals assign a special status to an atom that is at the boundary between the QM and MM subsystems, as the carbon atoms marked with C\* in the figure. The semiempirical methods offer more degrees of freedom than the *ab initio* ones, which makes easier to combine them with Molecular Mechanics.

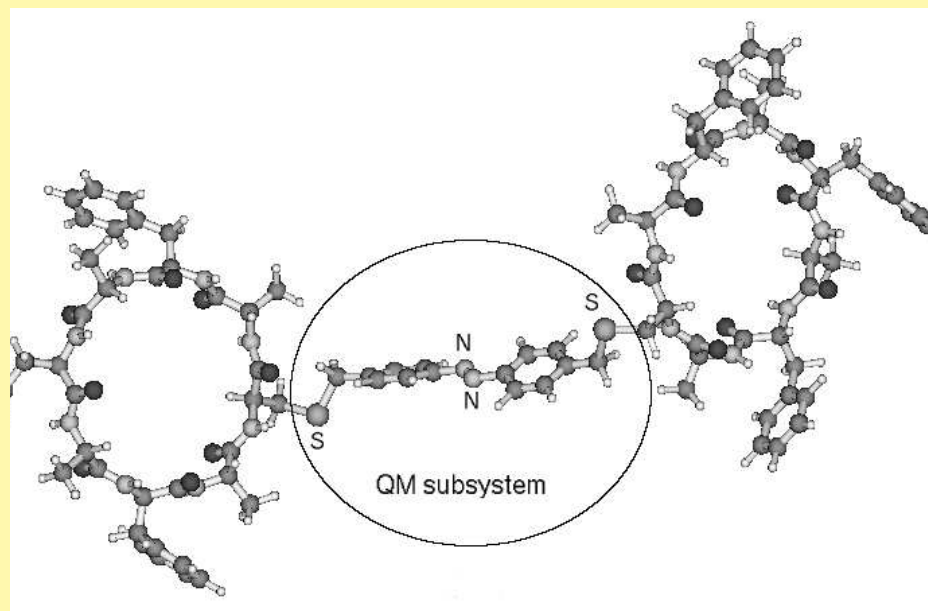
## Thiel's connection atom (CA)

- The connection atom is placed at the boundary between the QM and MM subsystems.
- It bears one basis function of  $s$  type, therefore it can only form one  $\sigma$  bond with the nearest QM atom.
- The strength and polarity of this bond are adjusted by choosing the semiempirical parameters of the connection atom (core charge,  $U_{ss}$ ,  $\beta_s$  etc).
- The MM potential must include some terms, functions of bond angles and dihedral angles, depending on the position of the connection atom and its neighbours, both on the QM and on the MM side. This is necessary because the single bond made with an  $s$  orbital on the CA cannot provide the correct behaviour of the angular potential [17, 19].

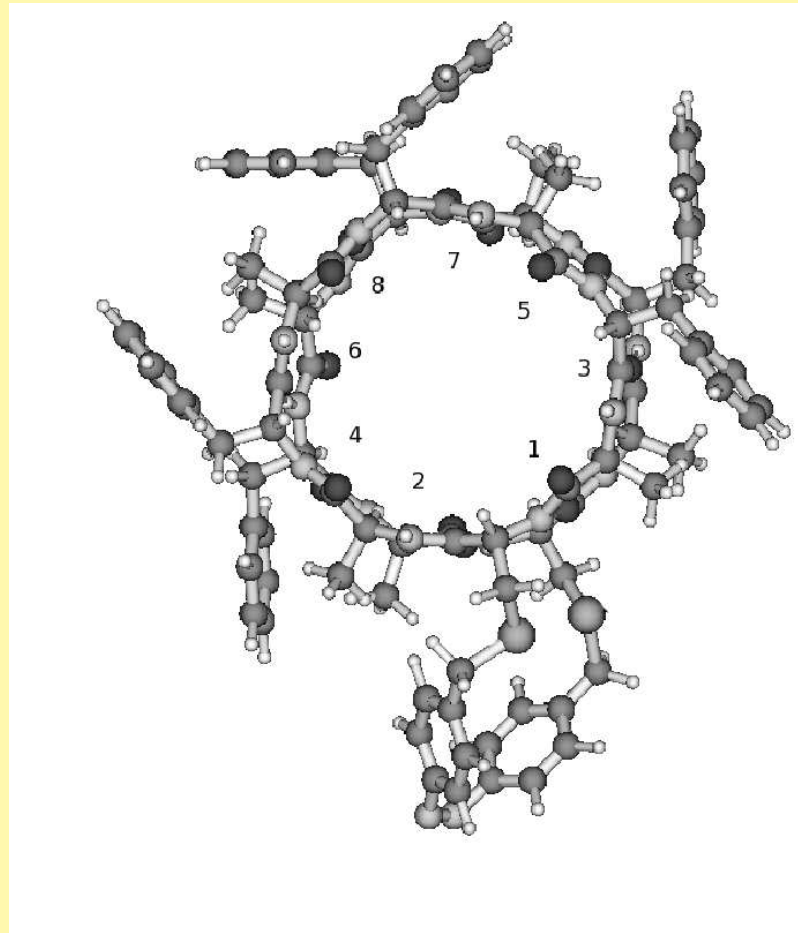
## A peptidic derivative of azobenzene (ABCP).

Reza Ghadiri and coworkers demonstrated the reversible photoswitching of *cis* and *trans*-ABCP [20,21]. The two isomers have remarkably different self-assembling behaviours, because they form intra- and inter-molecular H-bonds, respectively.

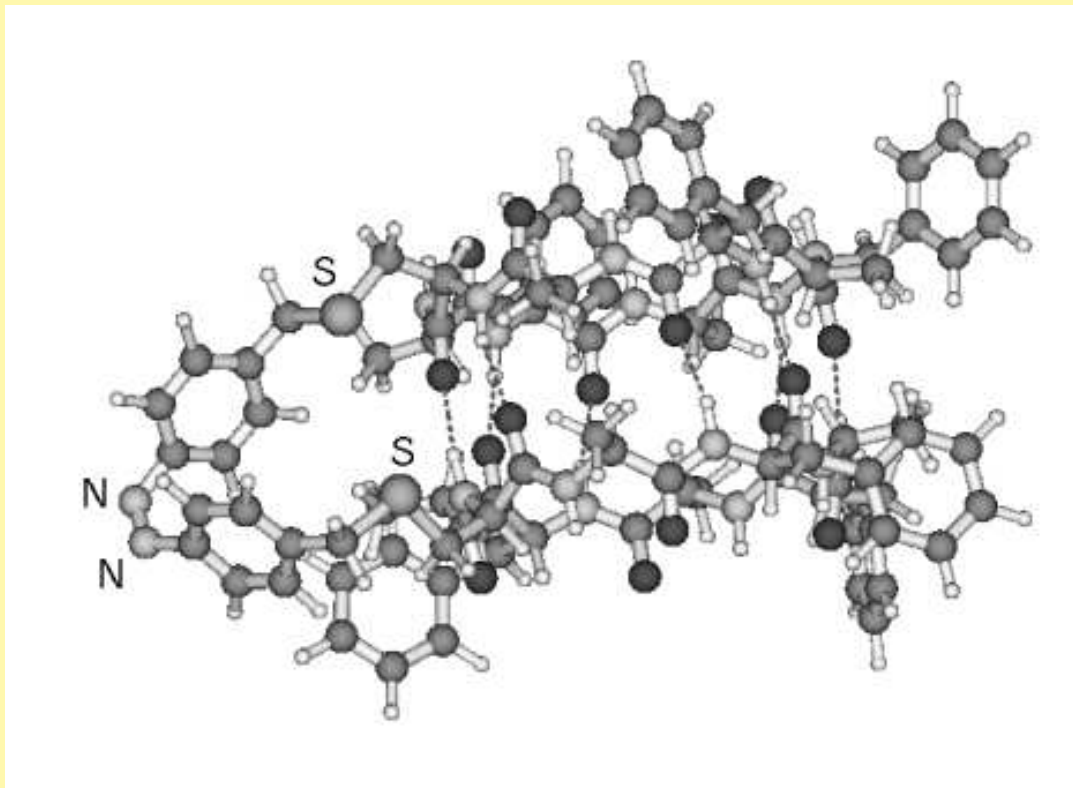
One may think that the H-bonds would hinder the photoisomerization. However, we computed a *cis*  $\rightarrow$  *trans* quantum yield of 0.59 [18].



The *trans* isomer. An elliptic line encloses the QM atoms.

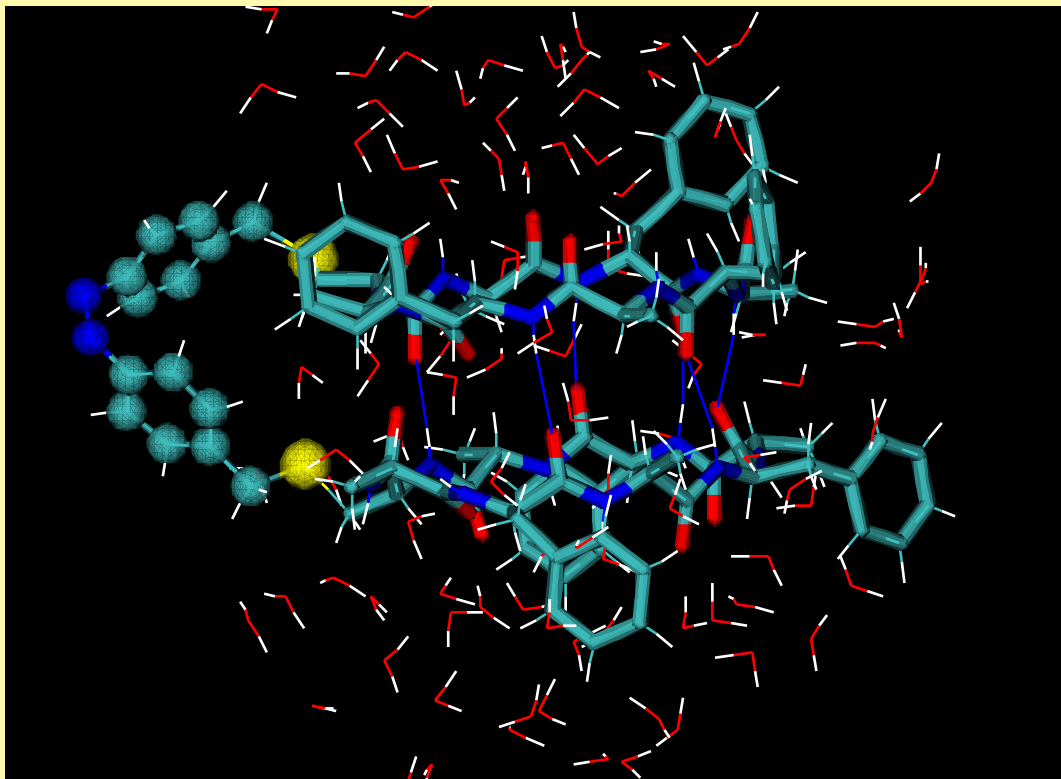


Top view of the *cis* isomer. The aminoacid residues are numbered.



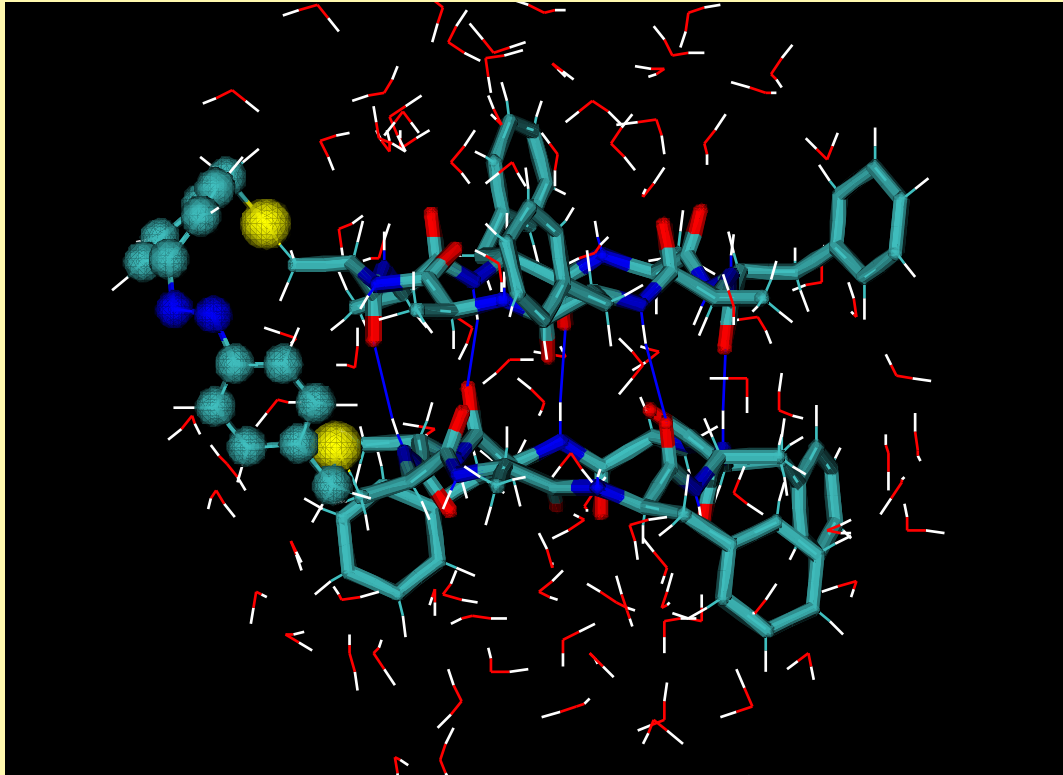
Lateral view of the *cis* isomer.

Ready to start.



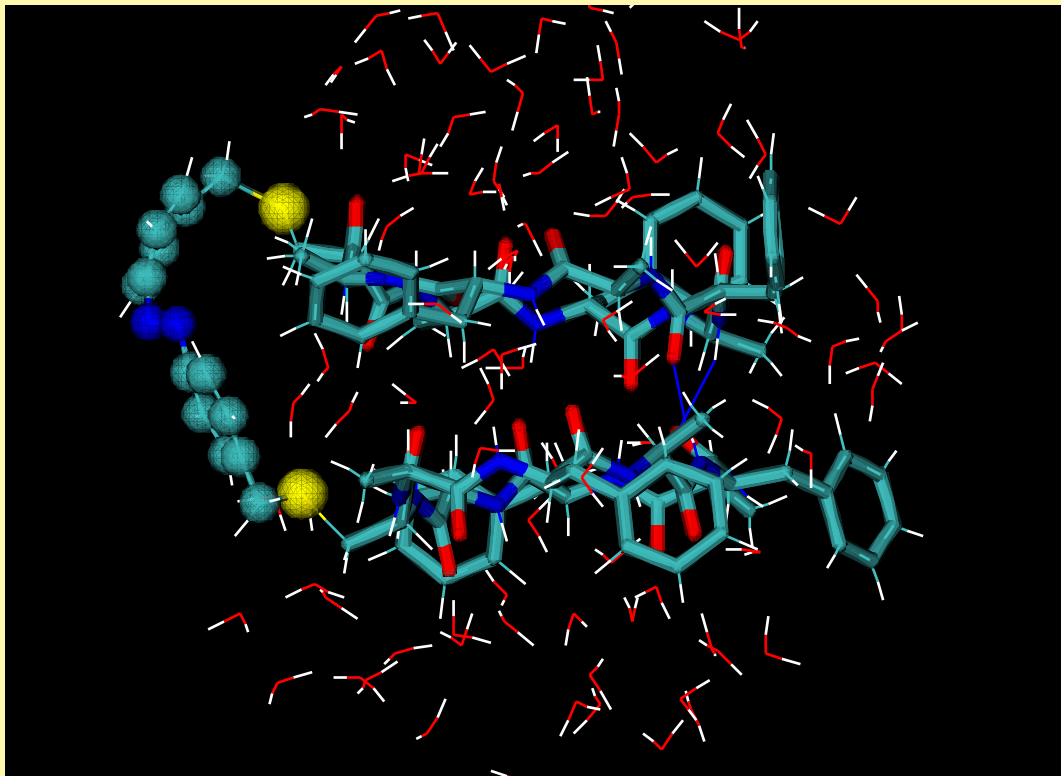
A typical initial configuration for a trajectory describing the *cis*  $\rightarrow$  *trans* photoisomerization of ABCP. The H-bonds are wetted by 103 water molecules.

250 fs: the isomerization is done.

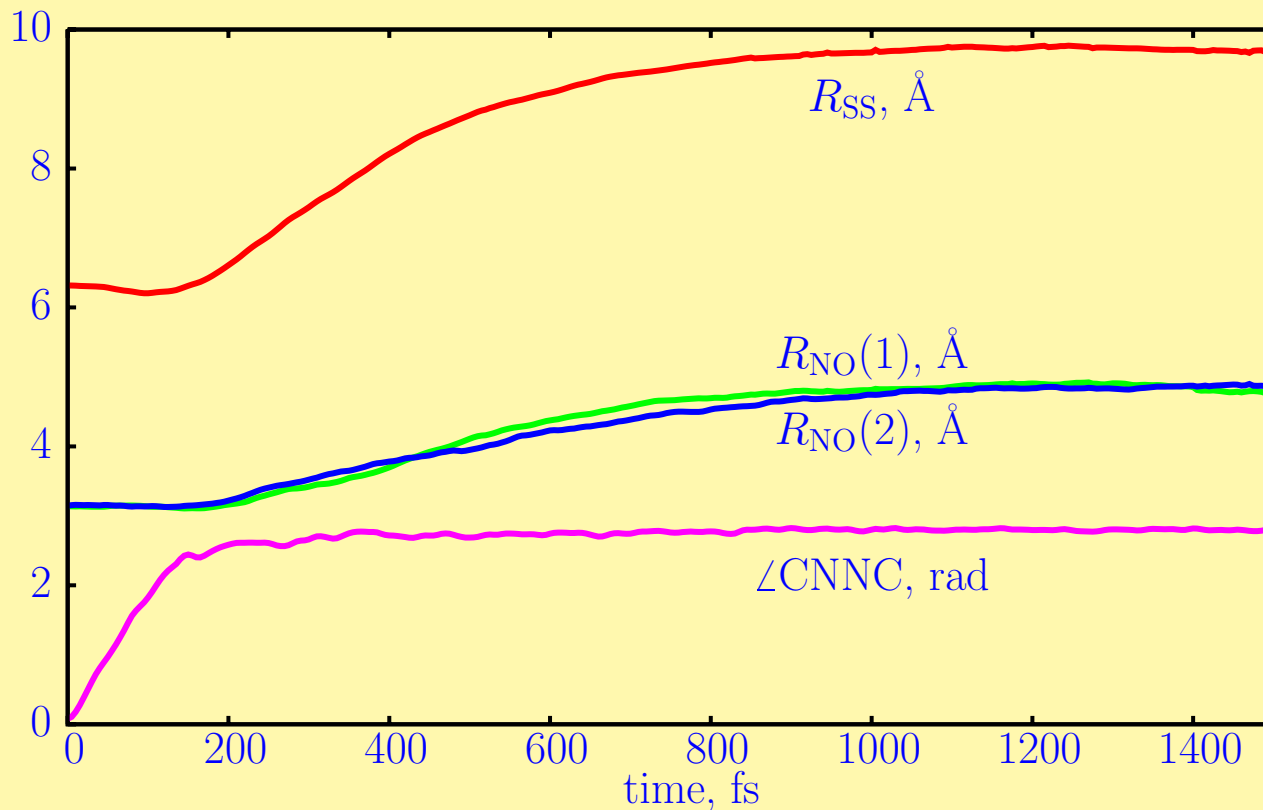


The trans isomer is distorted out of planarity.

1500 fs: little more to be seen.



The photoisomerization is fast ( $\approx 100$  fs), but the structural changes propagate in the supramolecular structure in much longer times.



Geometrical changes in the photoisomerization of ABCP: CNNC torsion angle, distance between the sulphur atoms of the bridges, and N...H-O distances for the two H-bonds closest to azobenzene.

## References

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