

Mixed quantum-classical dynamics.

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## Outline of this talk.

- The nuclear coordinates as parameters in the time-dependent Schroedinger equation.
- Mean-field and surface hopping methods.
- Tully's fewest switches algorithm.
- Quantum decoherence corrections.
- The sampling of initial conditions.

# Mixed Quantum-Classical (MQC) Dynamics.

The MQC 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].

# Mixed quantum-classical dynamics

Nuclear motion: Newton equations

Electronic motion: Schrödinger equation

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

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

$$|\psi_{el}(t)\rangle = \sum_L A_L(t) e^{-i\gamma_L(t)} |\psi_L(Q(t))\rangle \quad \text{with} \quad \gamma_L(t) = \int_0^t U_L(Q(t')) dt'$$

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

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

$$\hat{\mathcal{H}}_{el} |\psi_{el}\rangle = \sum_L A_L(t) e^{-i\gamma_L(t)} U_L |\psi_L\rangle$$

$$\dot{A}_K = \sum_{L(\neq K)} A_L(t) e^{i(\gamma_K - \gamma_L)} \sum_r \dot{Q}_r g_{KL}^{(r)} \quad \text{with} \quad g_{KL}^{(r)} = \left\langle \psi_K \left| \frac{\partial}{\partial Q_r} \right| \psi_L \right\rangle$$

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

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

that are specific of each trajectory.

We can go through the same steps in the diabatic representation:

$$|\psi_{el}(t)\rangle = \sum_J D_J(t) e^{-\frac{i}{\hbar} \int_0^t H_{JJ}(t') dt'} |\eta_J\rangle$$

$$\dot{D}_I = -\frac{i}{\hbar} \sum_{J(\neq I)} e^{-\frac{i}{\hbar} \int_0^t (H_{JJ} - H_{II}) dt'} H_{IJ}(t) D_J(t)$$

# Landau-Zener model

Two state, one coordinate model.

Two diabatic potentials cross each other at  $Q = Q^*$ :

$$H_{22} - H_{11} = F(Q - Q^*) \quad H_{12} = \text{constant} \quad \dot{Q} = \text{constant}$$

Before going through the crossing we choose the diabatic representation to coincide with the adiabatic one. The state probabilities are

$$P_1^{(dia)} = |D_1|^2 = P_1^{(adia)} = |A_1|^2 = 1$$

$$P_2^{(dia)} = |D_2|^2 = P_2^{(adia)} = |A_2|^2 = 0$$

After the crossing:

$$P_2^{(dia)} = 1 - e^{-2\pi H_{12}^2/\hbar|\dot{Q}F|} \simeq \frac{2\pi H_{12}^2}{\hbar|\dot{Q}F|}$$

$$P_2^{(adia)} = e^{-2\pi H_{12}^2/\hbar|\dot{Q}F|} \simeq 1 - \frac{2\pi H_{12}^2}{\hbar|\dot{Q}F|}$$

Approximations valid for  $\frac{H_{12}^2}{\hbar|\dot{Q}F|} \ll 1$ .

Transition probabilities for neutral/ionic avoided crossings.  
 Energies in atomic units.  $H_{12}=0.00065$  for LiF and  $0.00015$  for NaCl.

	LiF	NaCl
cold collision, $T = 10^{-3}$ K		
kinetic energy, $E_K = K_B T/2$	$1.58 \cdot 10^{-9}$	$1.58 \cdot 10^{-9}$
$P_{1 \rightarrow 2}$ neutral $\rightarrow$ ionic	1.000	1.000
$P_{1 \rightarrow 2}$ between adiabatic states	0.000	0.000
thermal collision, $T = 300$ K		
kinetic energy, $E_K = K_B T/2$	$4.75 \cdot 10^{-4}$	$4.75 \cdot 10^{-4}$
$P_{1 \rightarrow 2}$ neutral $\rightarrow$ ionic	0.789	0.217
$P_{1 \rightarrow 2}$ between adiabatic states	0.211	0.783
vertical excitation		
kinetic energy, $E_K = U_2(R_e) - U_2(R^*)$	0.0475	0.0410
$P_{1 \rightarrow 2}$ neutral $\rightarrow$ ionic	0.144	0.026
$P_{1 \rightarrow 2}$ between adiabatic states	0.856	0.974
collision between ions		
kinetic energy, $E_K = IP - EA$	0.0732	0.0559
$P_{1 \rightarrow 2}$ ionic $\rightarrow$ neutral	0.118	0.022
$P_{1 \rightarrow 2}$ between adiabatic states	0.882	0.978

# The Newton equations for the nuclei

Connection between quantum dynamics (electrons) and classical dynamics (nuclei): the forces acting on the nuclei.

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

Energy conservation:

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

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

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

$r$  component of the force in mean-field (Ehrenfest) formulation:

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

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

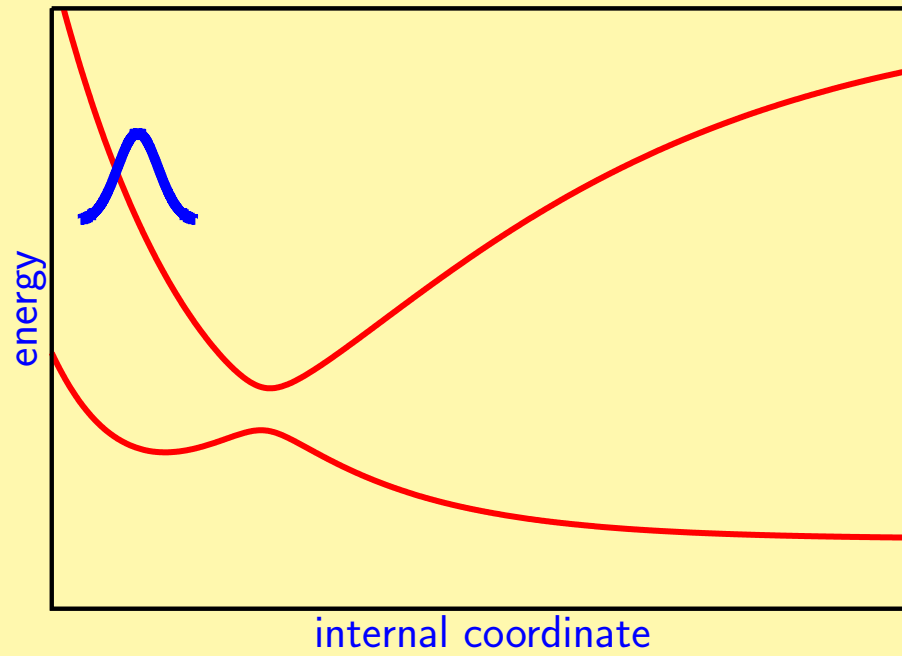
$$F_r^{(1)} = - \sum_K |A_K|^2 \frac{\partial U_K}{\partial Q_r}$$

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

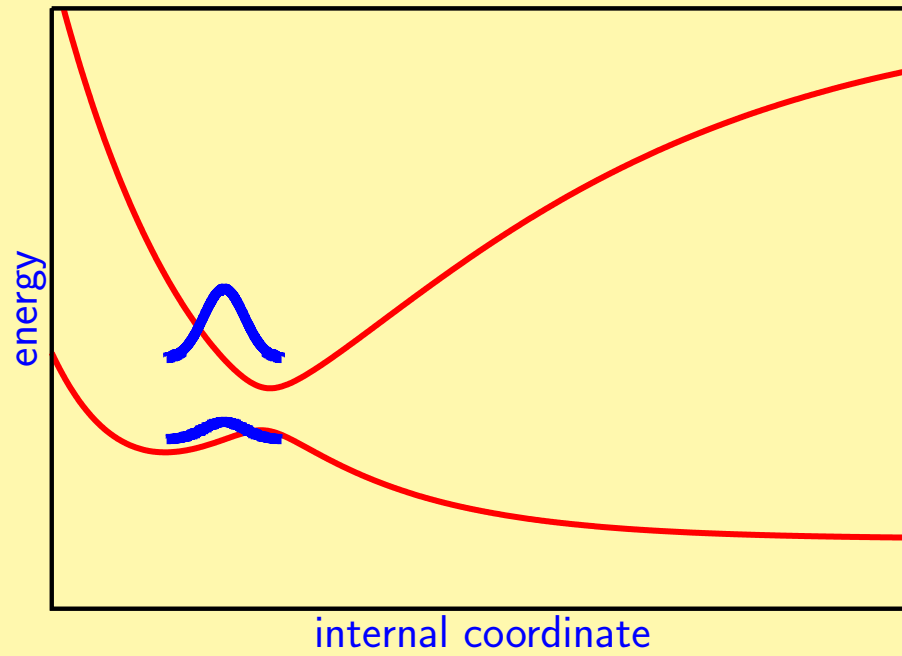
$$F_r^{(2)} = - \sum_K \sum_{L(\neq K)} \Re \left( A_K^* A_L e^{i(\gamma_K - \gamma_L)} \right) (U_K - U_L) g_{KL}^{(r)}$$

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.

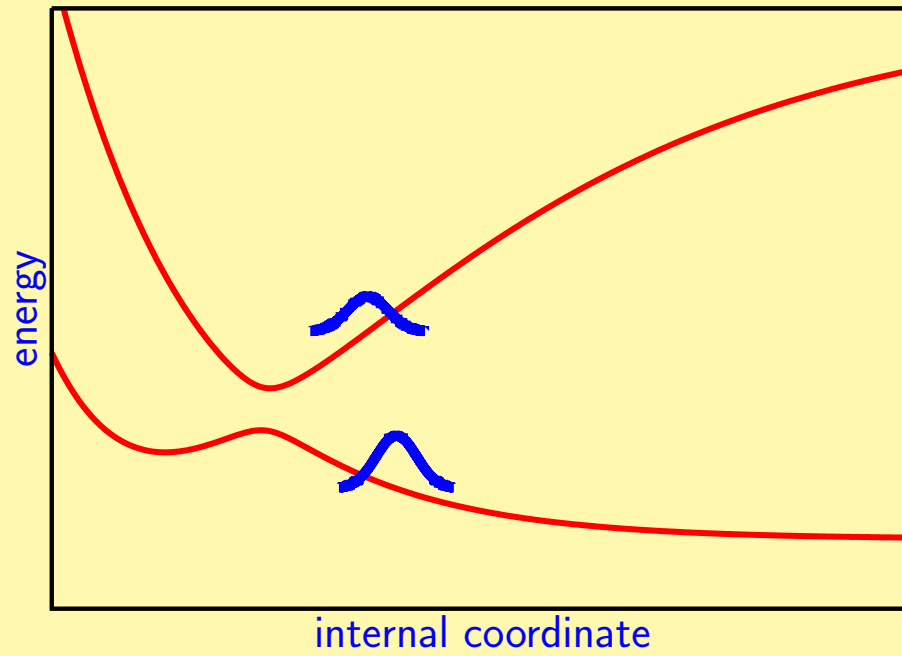
# Quantum wavepackets.



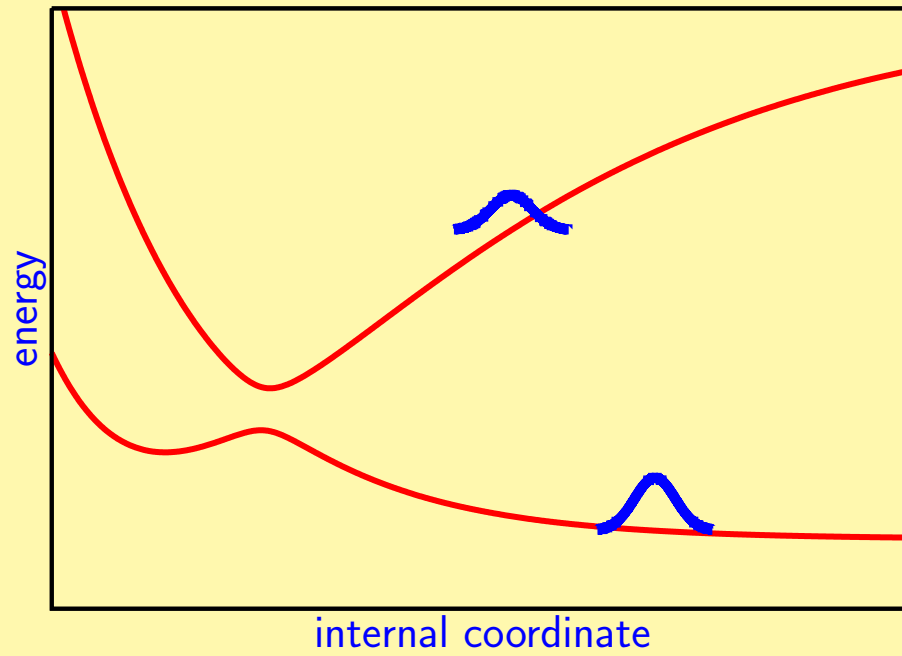
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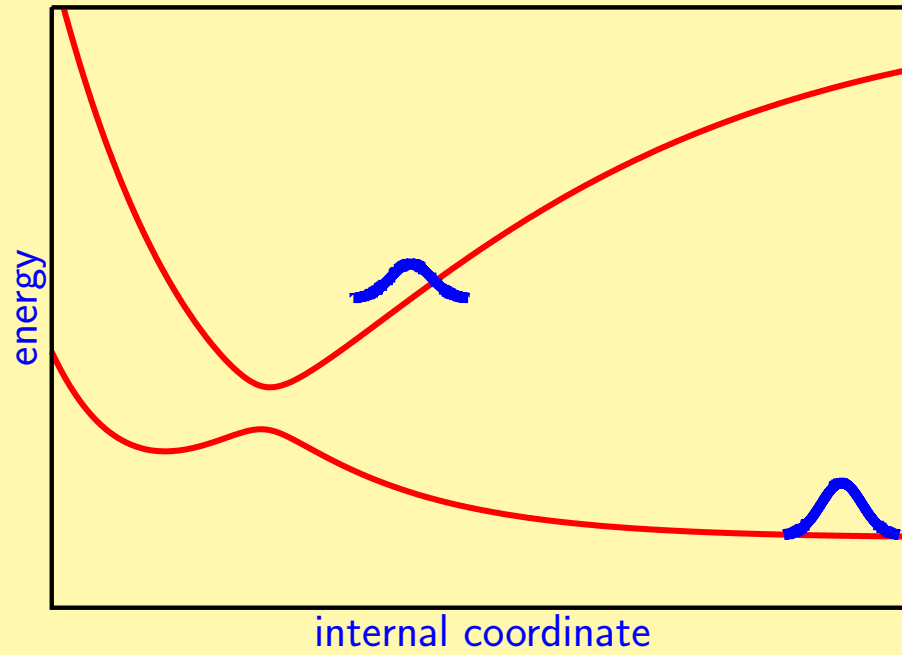
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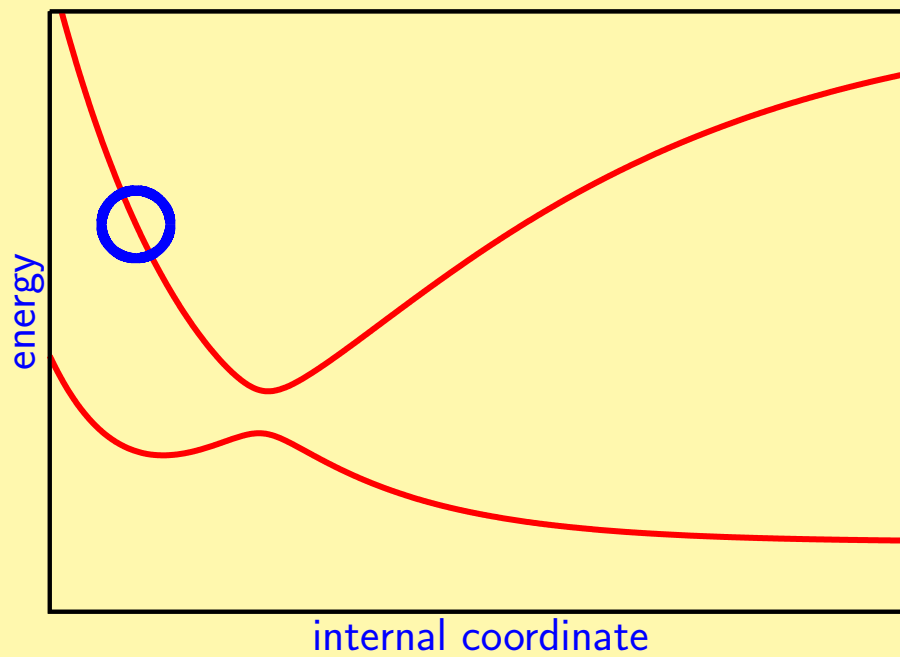
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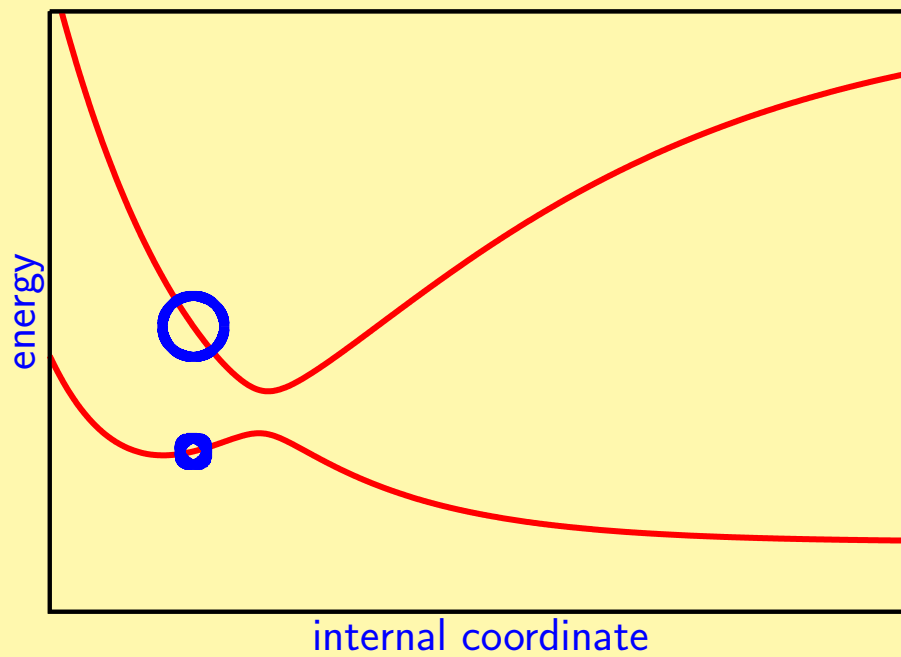
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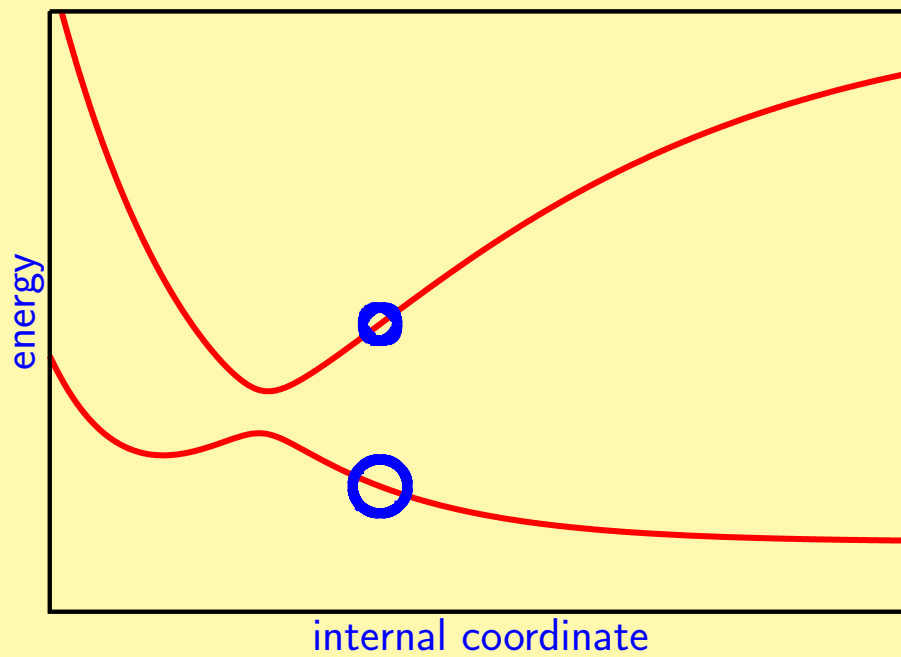
# MQC treatment: mean-field.



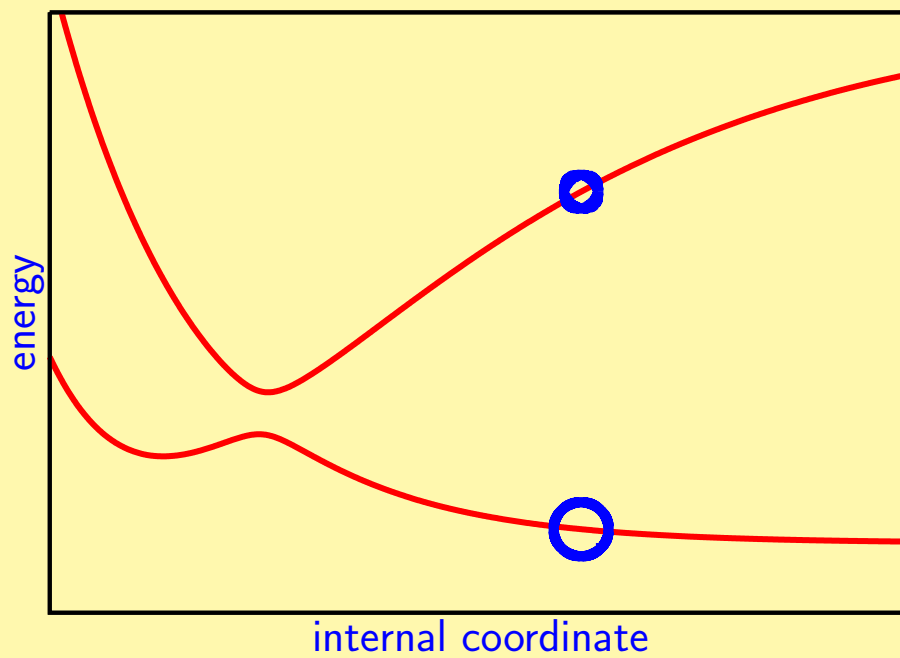
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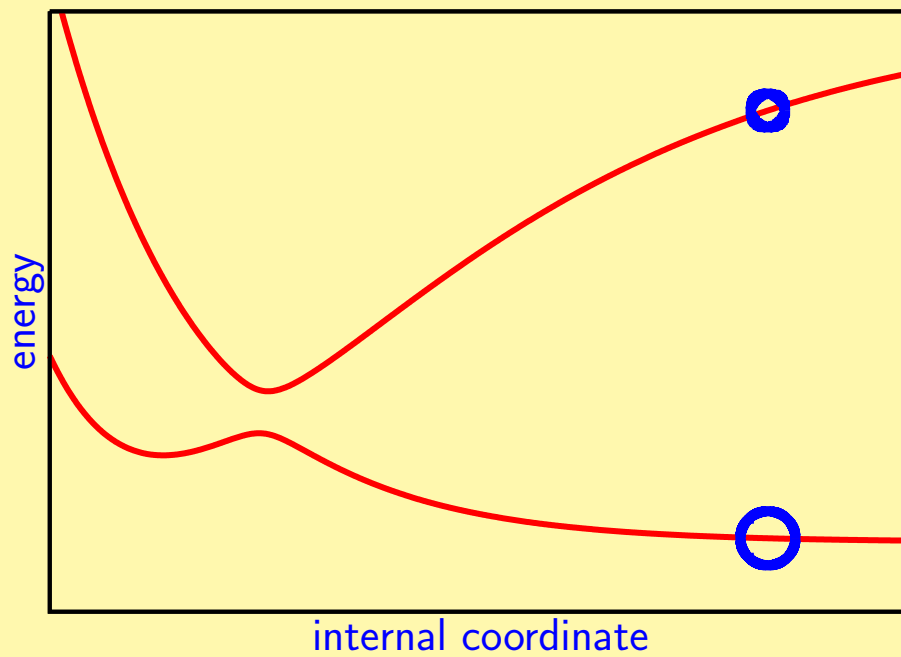
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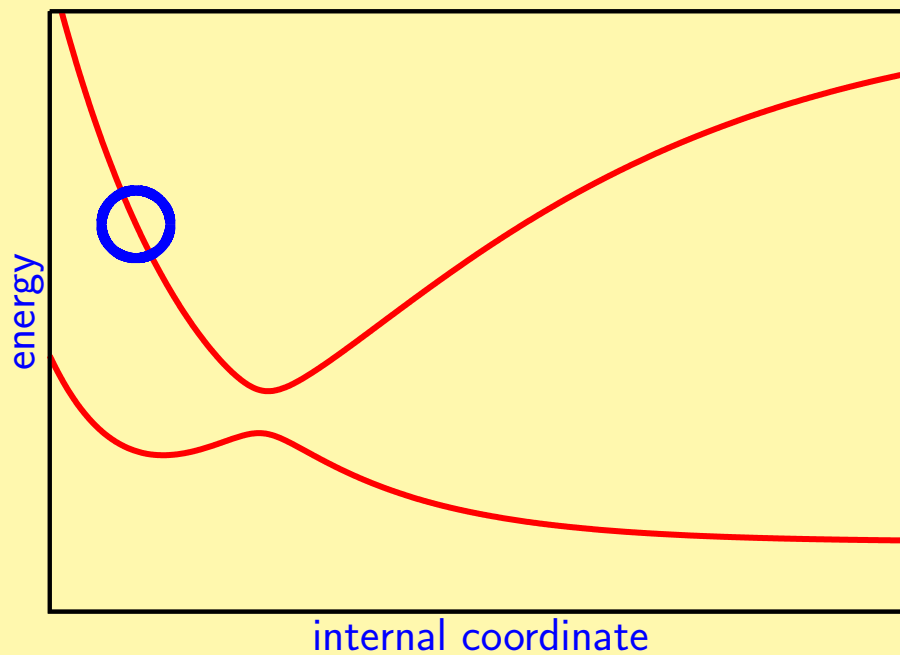


## MQC treatment: surface hopping

- We calculate many trajectories (a “swarm”)
- At any time, each trajectory runs on one adiabatic state,  $K$
- The force is only related to the potential energy  $U_K$
- A trajectory can hop from state  $K$  to  $L$ , according to a stochastic algorithm [1, 3, 4, 11] that takes into account the computed state probabilities  $P_K(t)$  and  $P_L(t)$ .

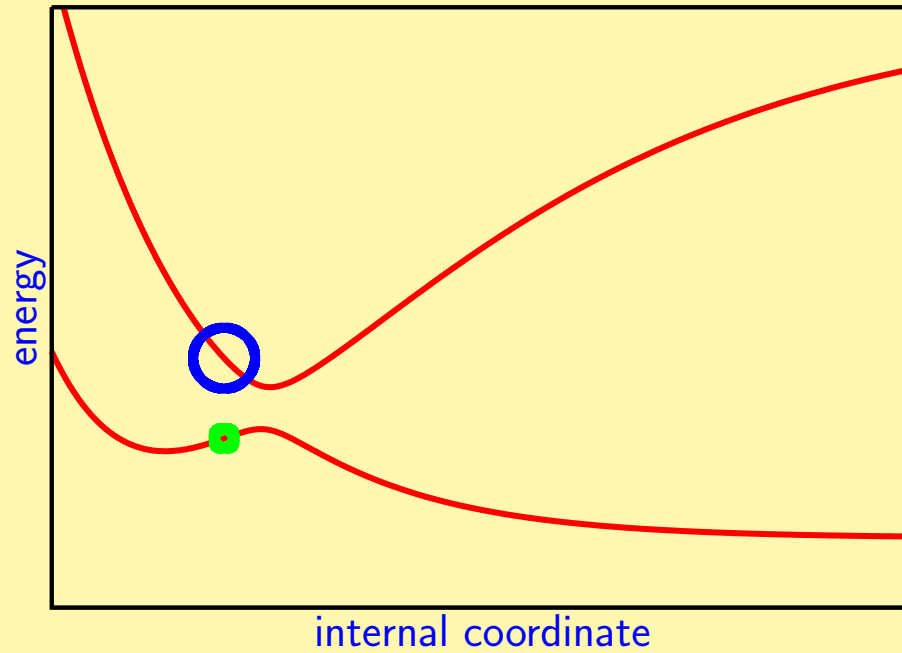
# MQC treatment: surface hopping.

A hop occurs



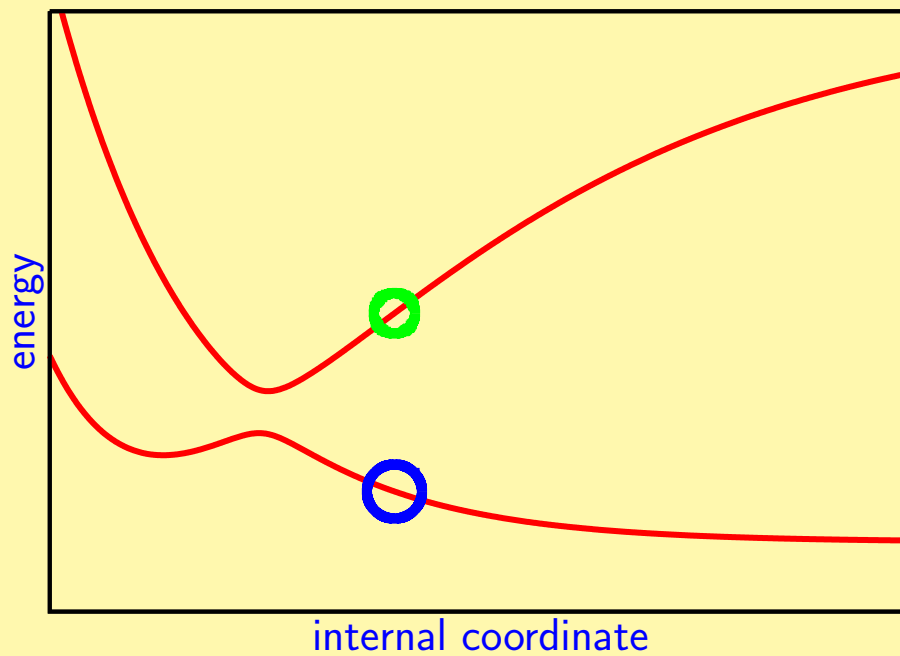
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A hop occurs



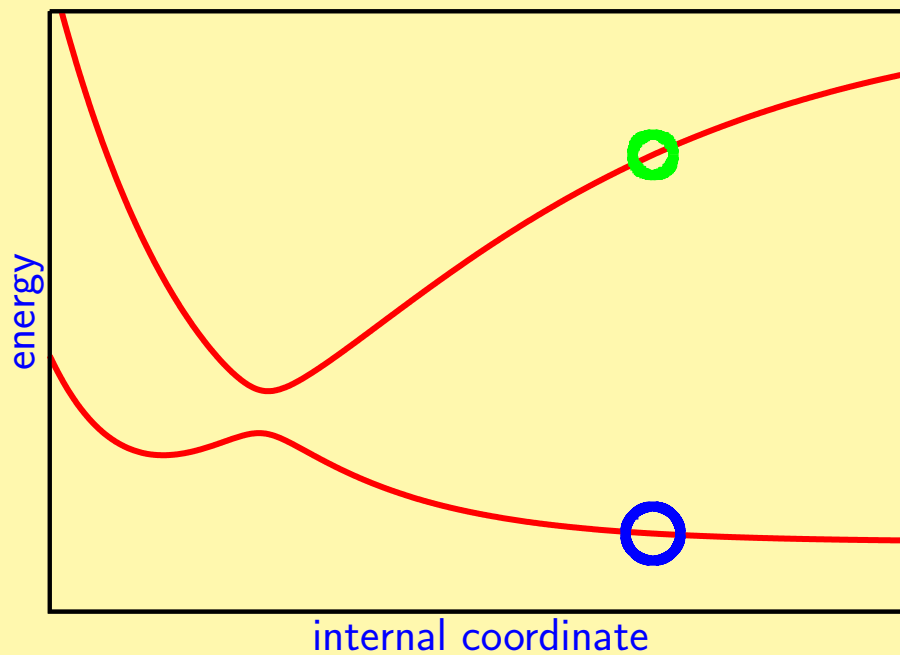
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A hop occurs



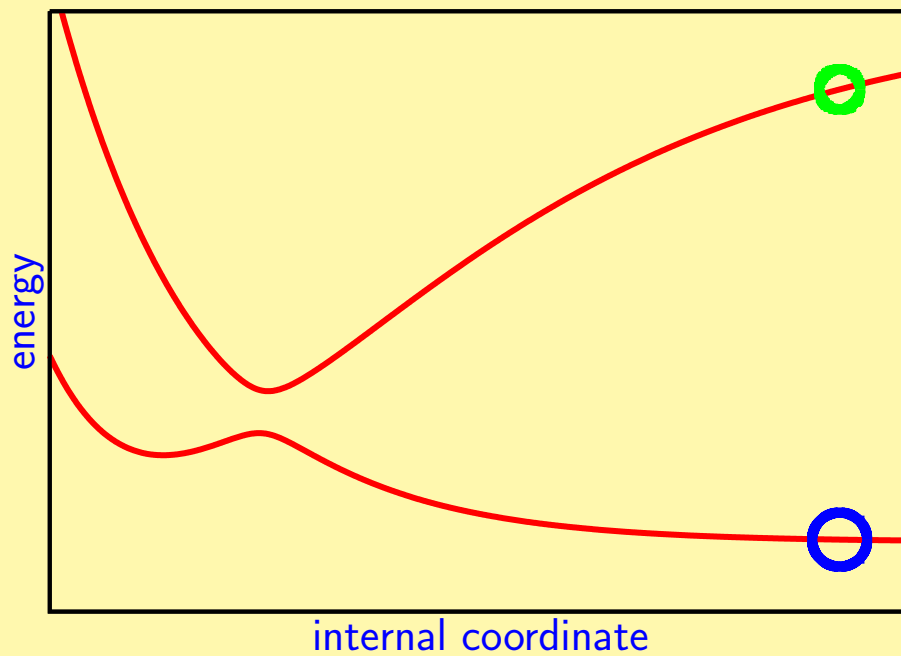
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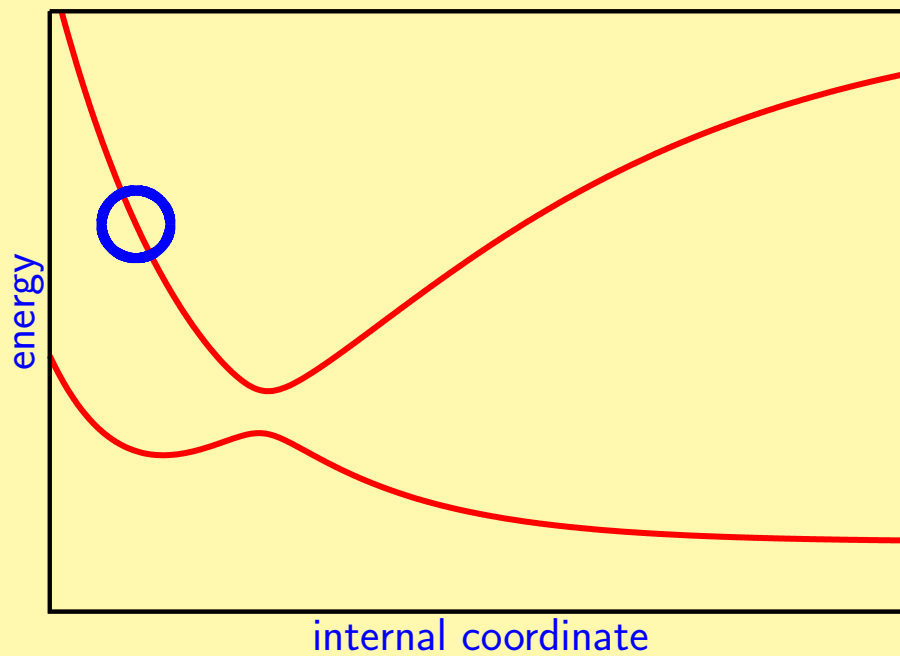
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A hop occurs



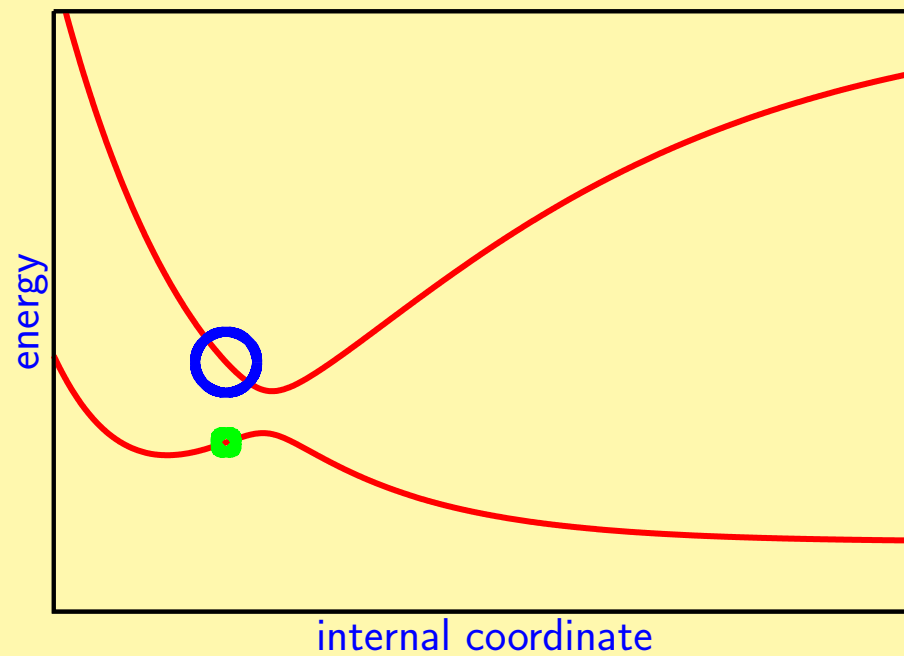
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No hop



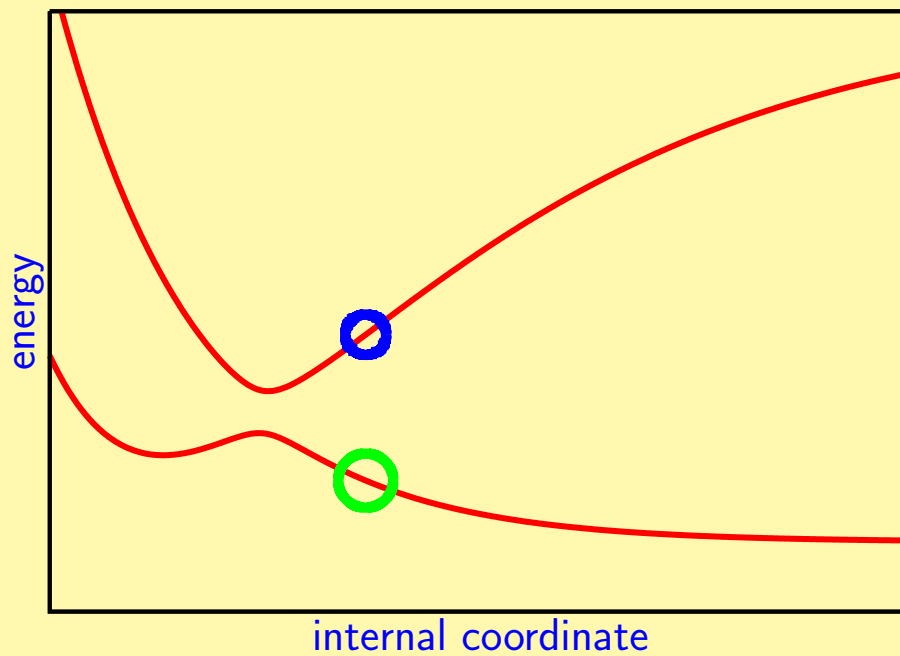
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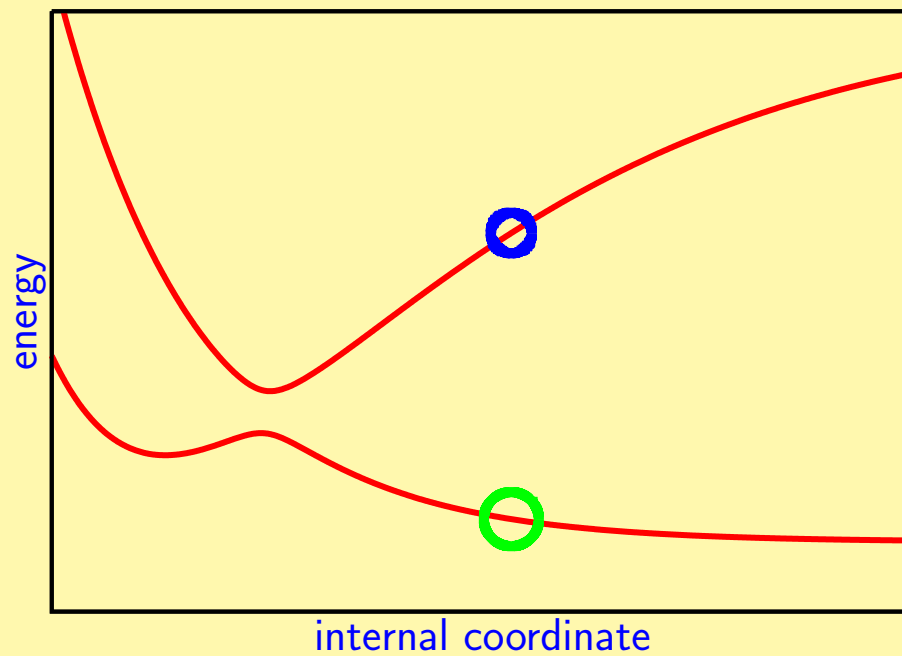
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No hop



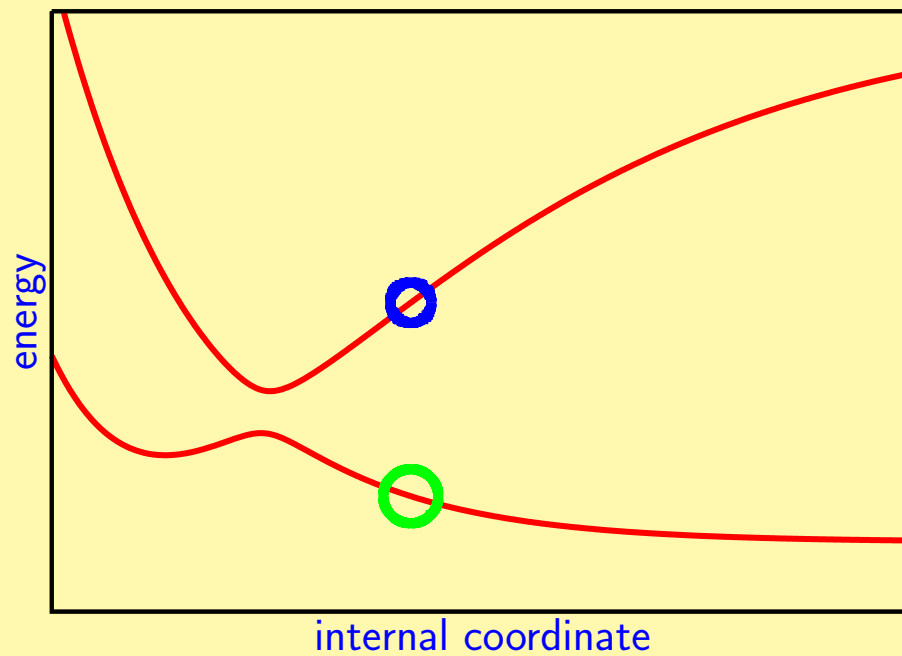
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No hop



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No hop



# Internal consistency of surface hopping

Definitions:

$P_K^{(j)}(t)$  = computed probability of state  $K$  for the trajectory  $j$

$\langle P_K \rangle$  = average over all trajs. of  $P_K^{(j)}(t)$

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

Internal consistency requirement:  $\Pi_K(t) = \langle P_K \rangle$

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

$$\Delta \Pi_K = - \sum_L \Pi_K \langle T_{K \rightarrow L} \rangle + \sum_L \Pi_L \langle T_{L \rightarrow K} \rangle$$

where  $\langle T_{K \rightarrow L} \rangle$  and  $\langle T_{L \rightarrow K} \rangle$  are averages over all trajectories.

We want to define  $T_{K \rightarrow L}^{(j)}$  such that:

$$\Delta \Pi_K(t) = \frac{\langle P_K \rangle}{dt} \Delta t \quad \forall K, t$$

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:

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

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

Then:

$$\langle T_{K \rightarrow L} \rangle = \max \left\{ 0, \frac{\langle B_{KL} \rangle}{\Pi_K} \Delta t \right\}$$

This definition is both...

- ... unpractical, because it would force us 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]:

$$T_{K \rightarrow L}^{(j)} = \max \left\{ 0, \frac{B_{KL}^{(j)}}{P_K^{(j)}} \Delta t \right\}$$

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.

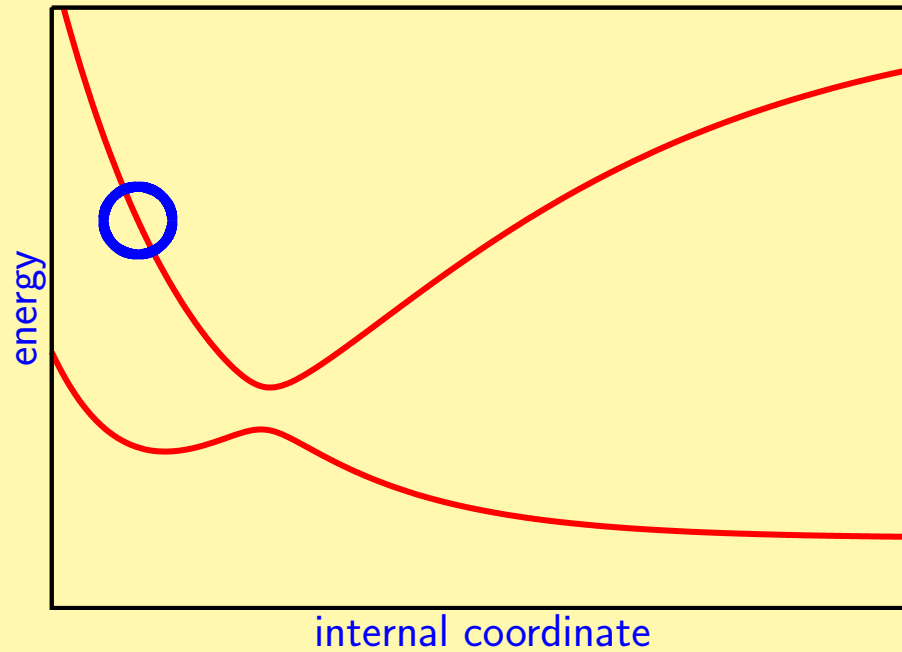
- One wavepacket  $G_0$  travels on the current PES,  $U_K$ .
- More wavepackets are created, every  $n_D$  time steps, on the other states  $L$ , if their probabilities  $P_L(t)$  have increased in time. Each new wavepacket  $G_i$  has initially the same  $\mathbf{Q}_i$  as  $G_0$ , and the module of  $\mathbf{P}_i$  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:

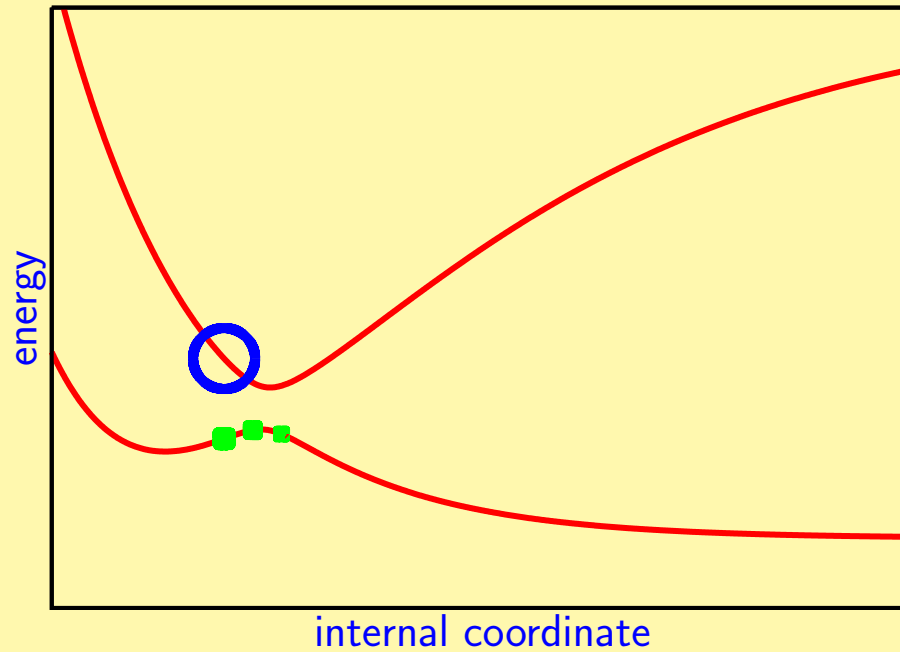
$$|\langle G_0 | G_i \rangle| = \prod_{\alpha} \exp \left[ -\frac{m_{\alpha}^{1/2} (Q_{0,\alpha} - Q_{i\alpha})^2}{8\sigma^2} - \frac{\sigma^2 (P_{0,\alpha} - P_{i\alpha})^2}{2m_{\alpha}^{1/2}} \right]$$

- 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,  $\sigma$ .

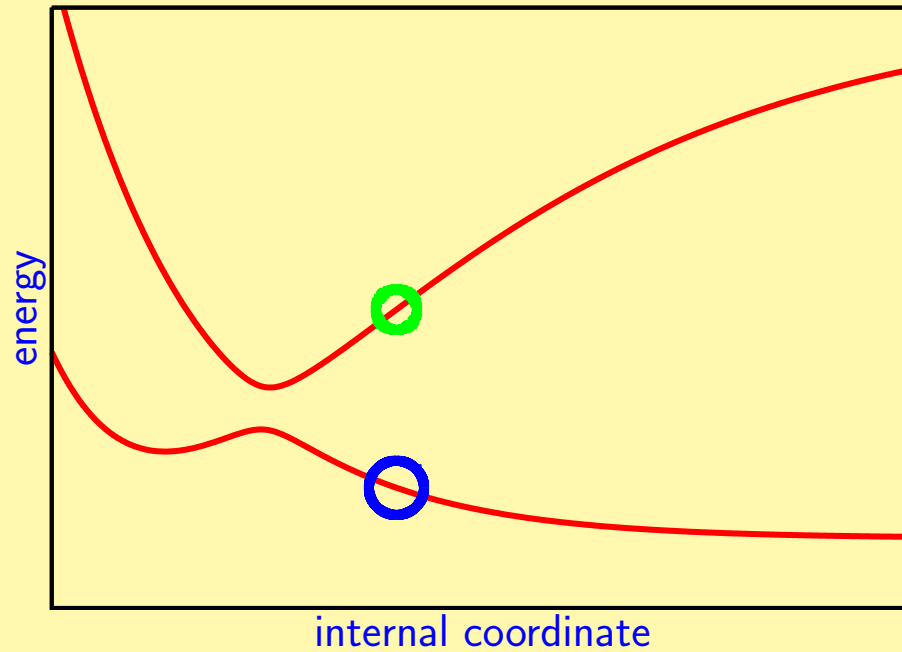
# Surface hopping with decoherence correction.



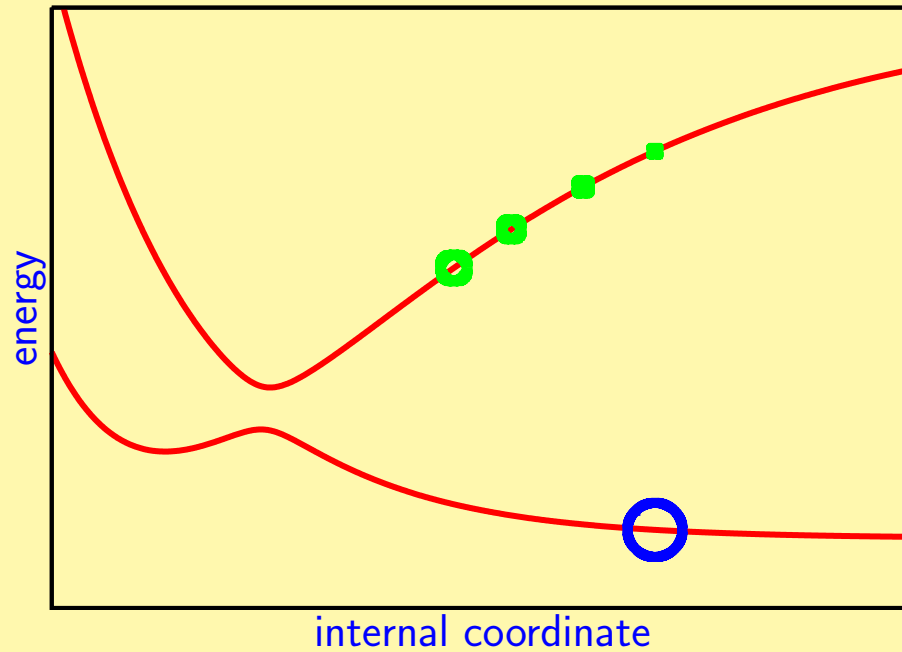
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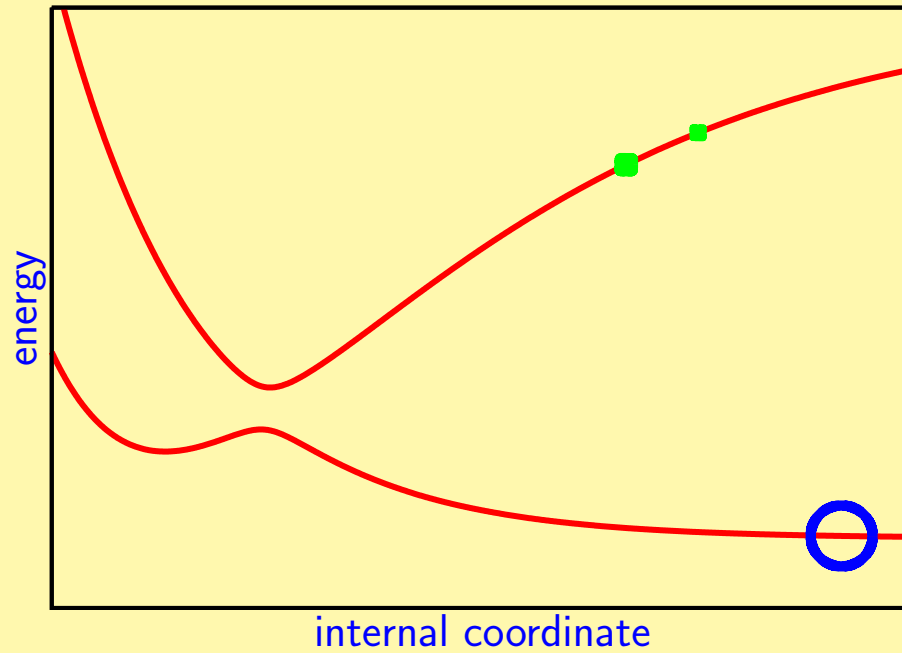
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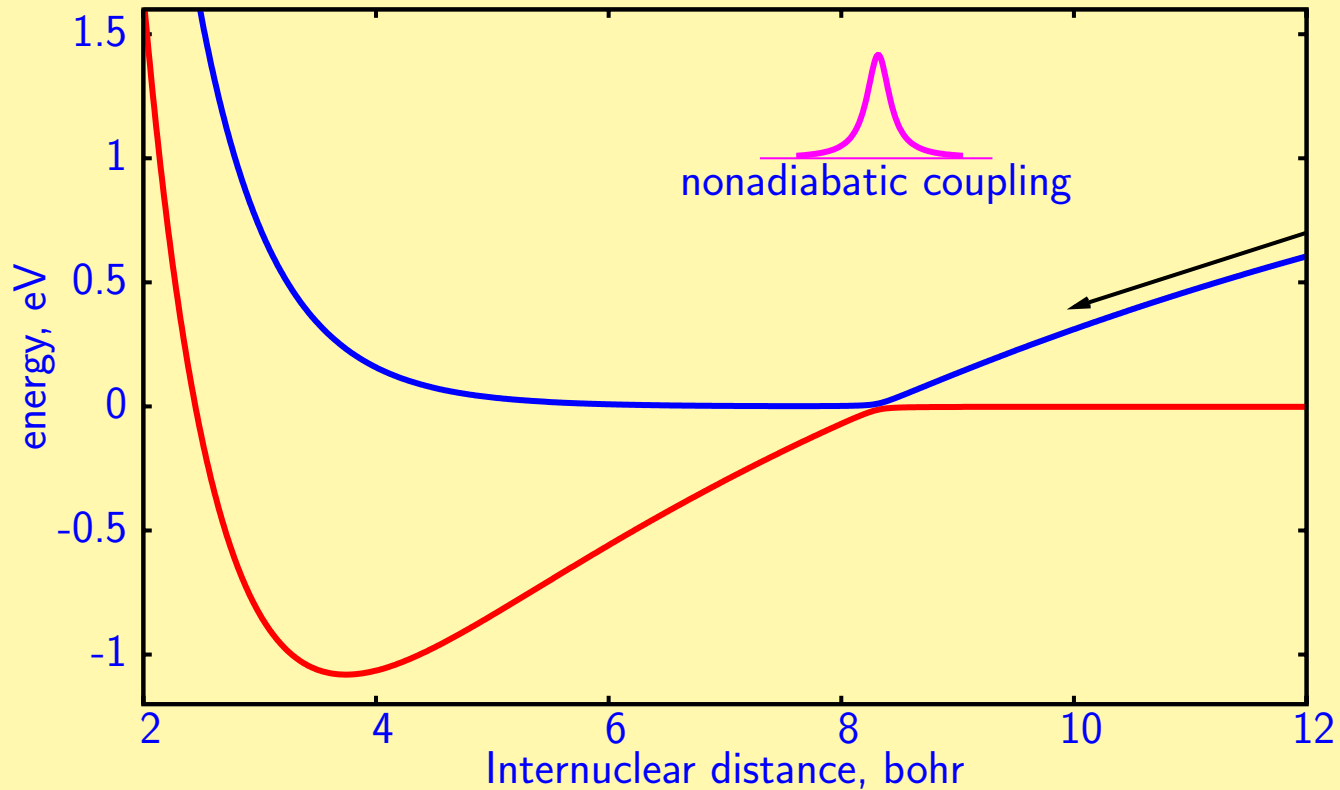


# Surface hopping with decoherence correction.



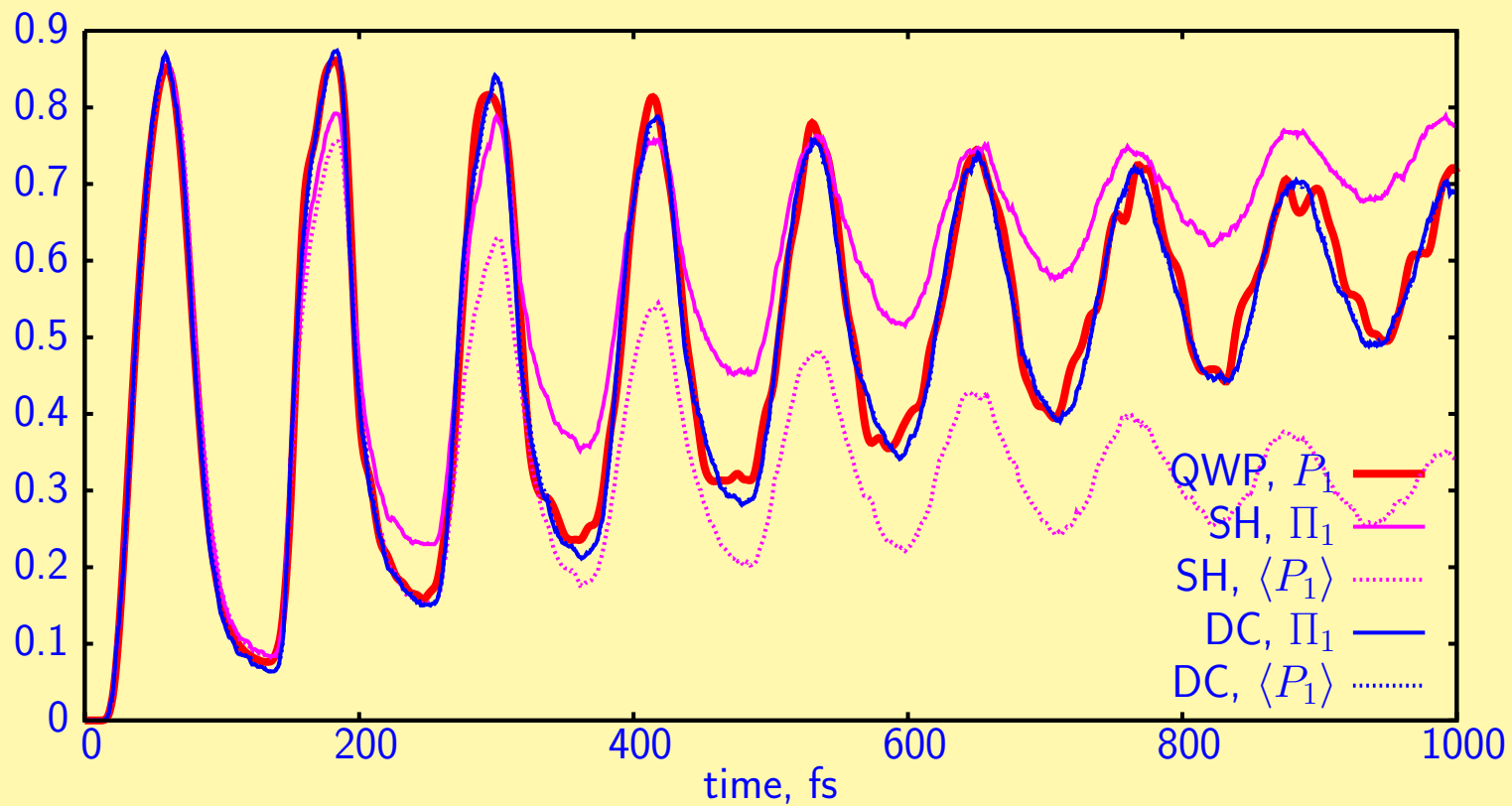
# 1D model: ionic/neutral crossing, many passages.

Potential energy curves and coupling.



# Ionic/neutral crossing.

Time dependent population of the first electronic state.



# 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:

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

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	$\overline{\text{QM energy}}$	$\overline{\text{class. energy}}$
$N_{vib}$			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 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:

$$P_{exc} \propto \langle \psi_0 | \vec{\mu} | \psi_K \rangle^2 = \vec{\mu}_{0K}^2(\mathbf{Q})$$

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 excited states, 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:  $S_K = \sum_{L=K_1}^K \mu_{0L}^2$ , with  $K_1 \leq K \leq K_2$ . 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.

## References

- [1] J. C. Tully, *J. Chem. Phys.* **93**, 1061 (1990).
- [2] P. Cattaneo and M. Persico, *J. Phys. Chem. A* **101**, 3454 (1997).
- [3] J. C. Tully, *Faraday Discuss.* **110**, 407 (1998).
- [4] K. Drukker, *J. Comput. Phys.* **153**, 225 (1999).
- [5] J.-Y. Fang and S. Hammes-Schiffer, *J. Phys. Chem. A* **103**, 9399 (1999).
- [6] N. L. Doltsinis and D. Marx, *J. Theor. Comp. Chem.* **1**, 319 (2002).
- [7] C. Zhu, S. Nangia, A. W. Jasper and D. G. Truhlar, *J. Chem. Phys.* **121**, 7658 (2004).
- [8] C. Zhu, A. W. Jasper and D. G. Truhlar, *J. Chem. Theory Comput.* **1**, 527 (2005).
- [9] G. Stock and M. Toss, *Adv. Chem. Phys.* **131**, 243 (2005).
- [10] G. Granucci and M. Persico, *J. Chem. Phys.* **126**, 134114 (2007).
- [11] G. Granucci, M. Persico and A. Toniolo, *J. Chem. Phys.* **114**, 10608 (2001).

[12] L. Creatini, T. Cusati, G. Granucci and M. Persico, Chem. Phys. 347, 492 (2008).