Internal consistency and quantum decoherence in surface hopping.

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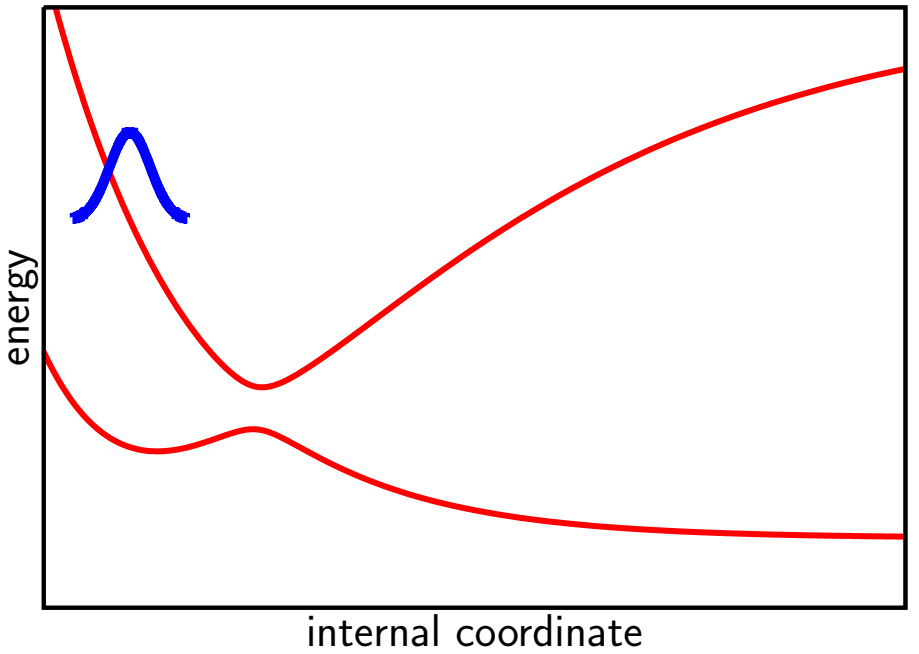
The surface hopping method.

- Many trajectories are run, starting in one or more excited electronic states.
- The initial conditions (nuclear coordinates $\mathbf{Q}$ and momenta $\mathbf{P}$) are sampled from a suitable distribution.
- The potential energy for a trajectory $\mathbf{Q}^{(j)}(t)$ is provided by the PES of the "current" state, $K^{(j)}(t)$.
- The current state can change because of nonadiabatic transitions $K \rightarrow L$ (surface hops).
- In computing the time-dependent or final product properties, only the current state of each trajectory is taken into account. For instance, the electronic contribution to the total energy is given by the current PES, and the state population is the fraction of trajectories $\Pi_K(t)$ that are running on state K.

  The hopping probability depends on the computed state probabilities $P_L^{(j)}(t)$ and their rates of change $\dot{P}_K^{(j)}$.

Quantum wavepackets.



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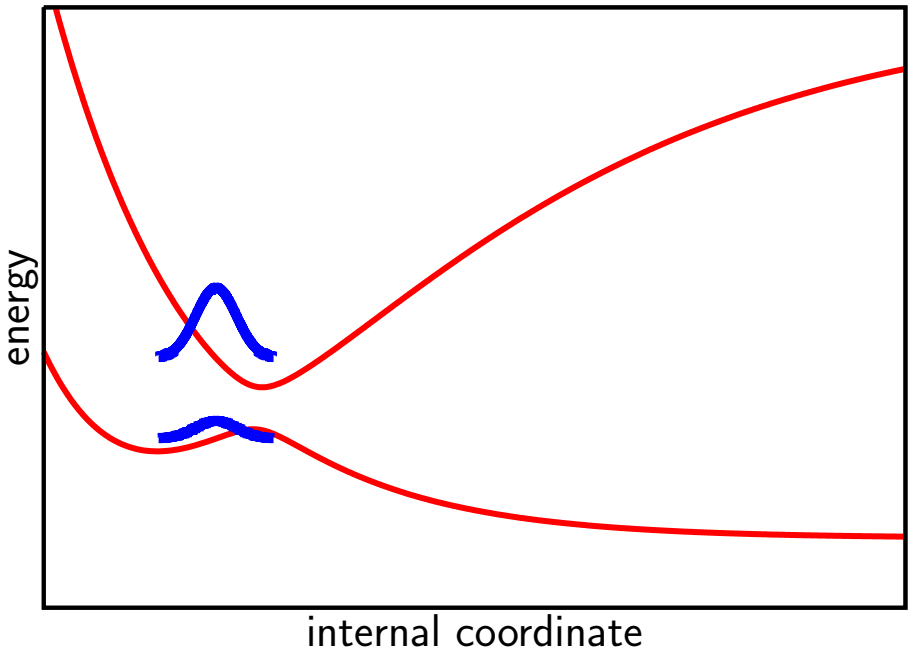

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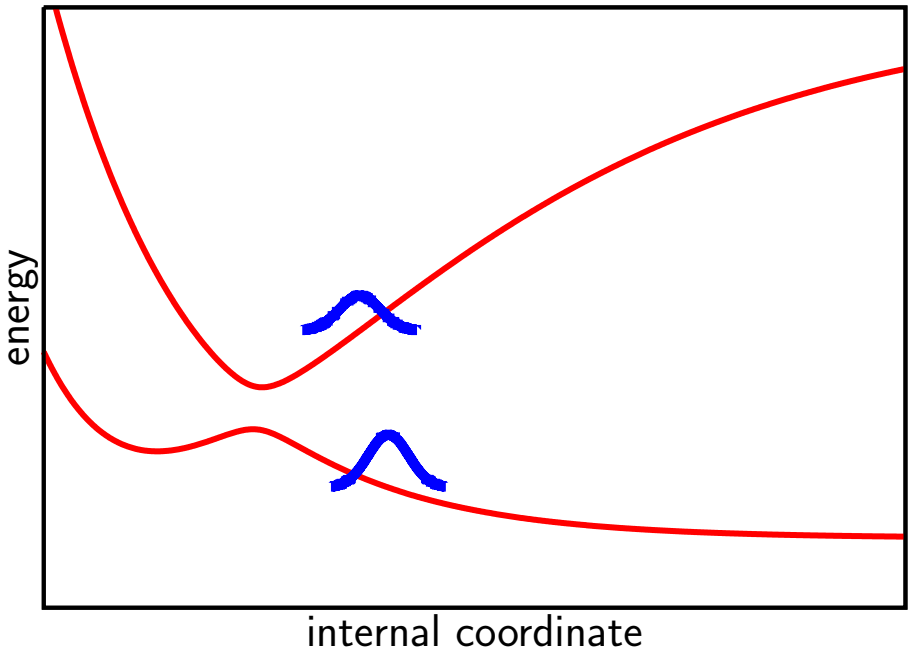

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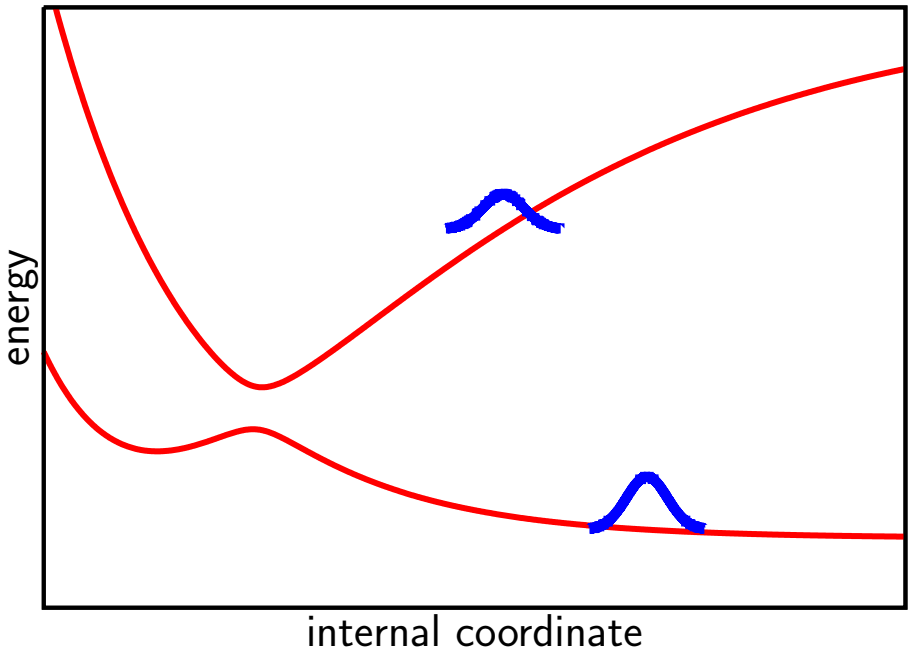

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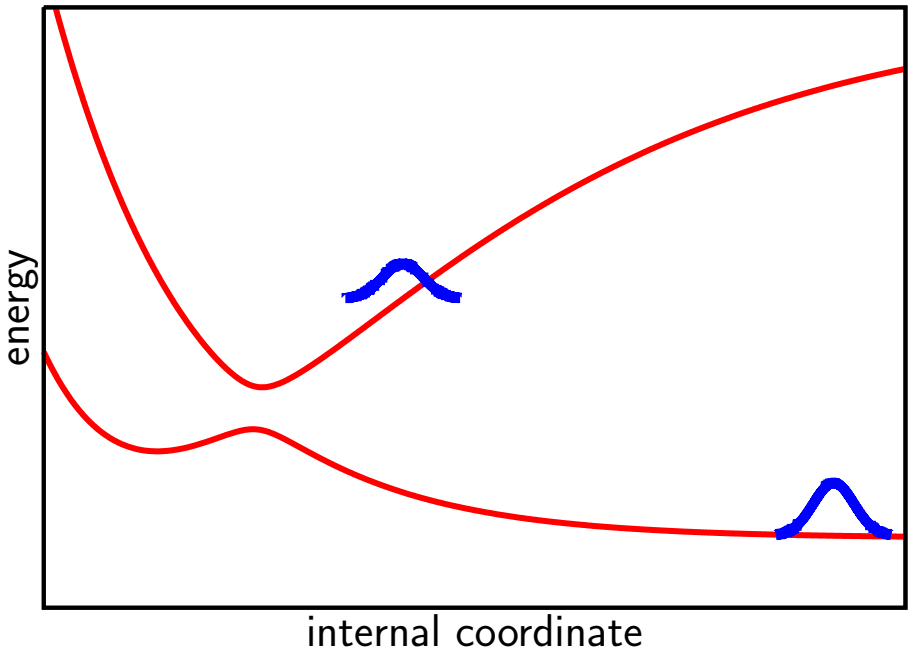
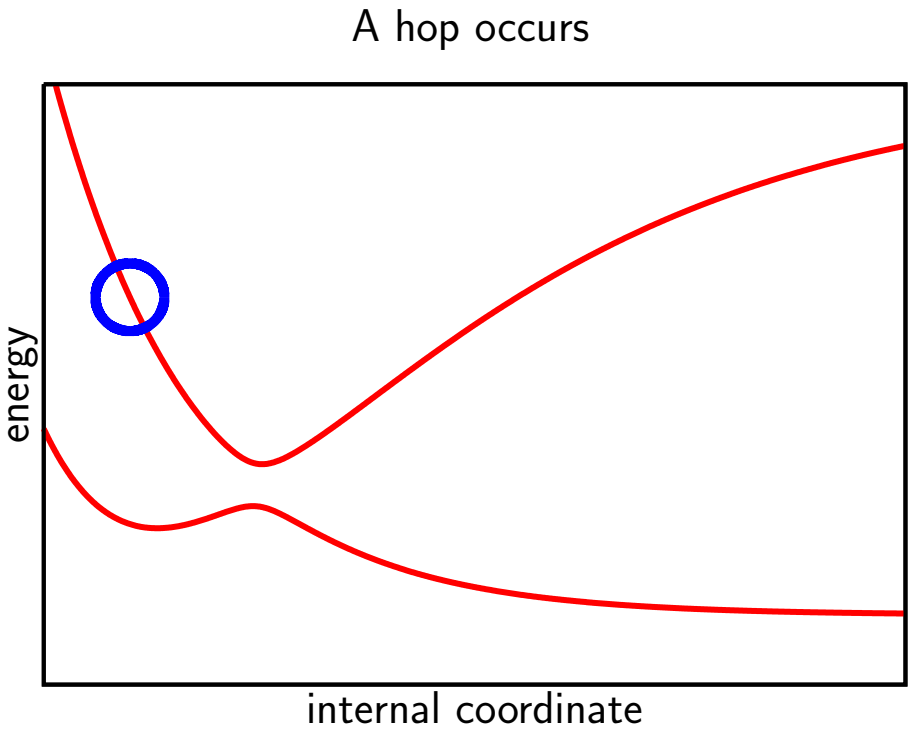


Semiclassical treatment: surface hopping.



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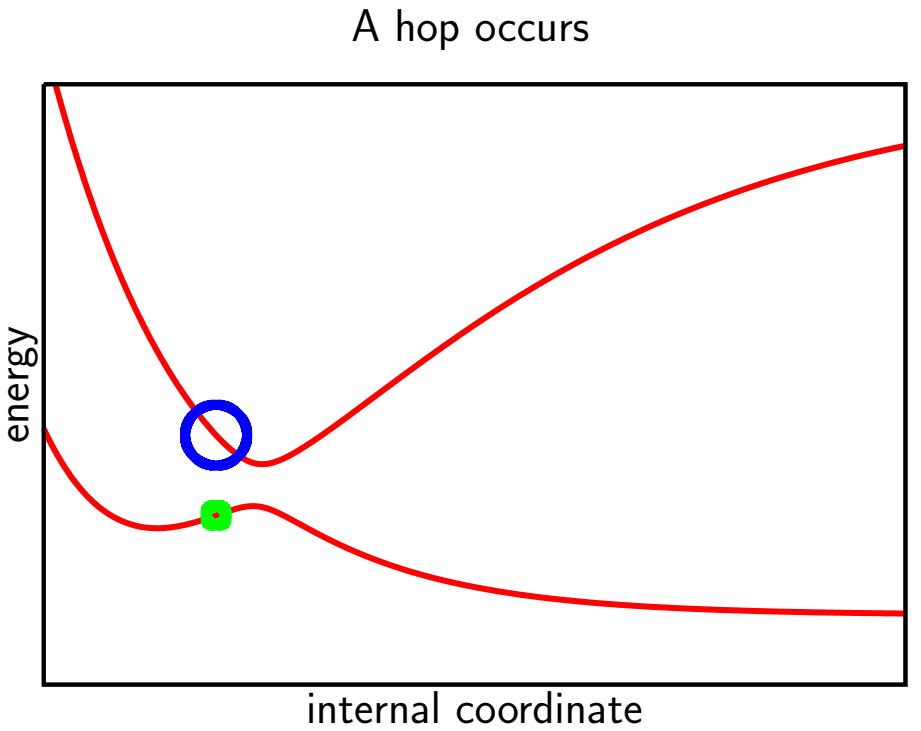

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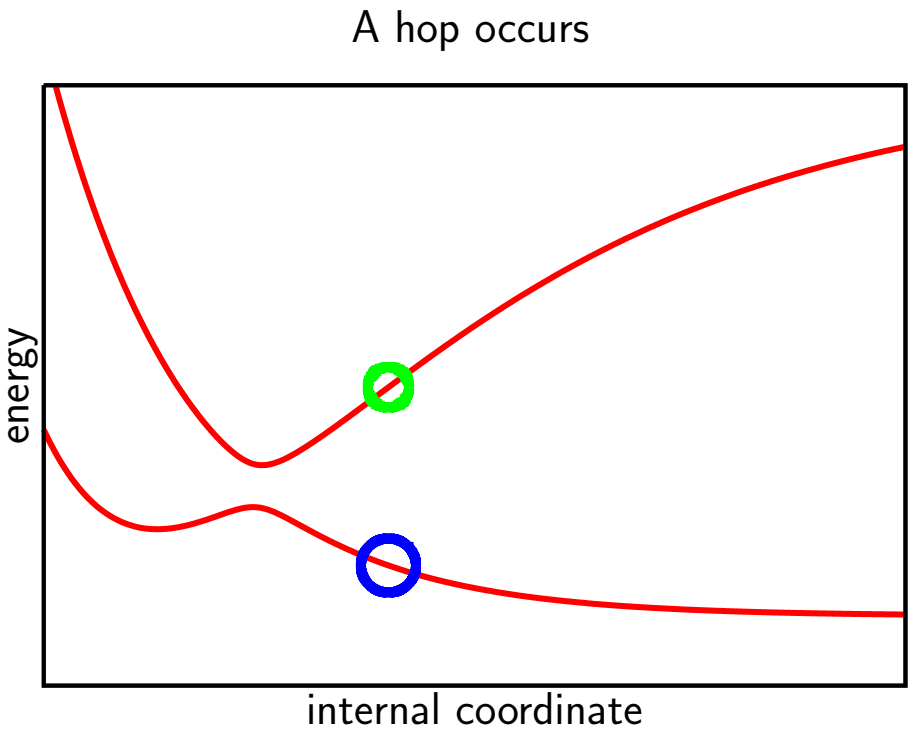

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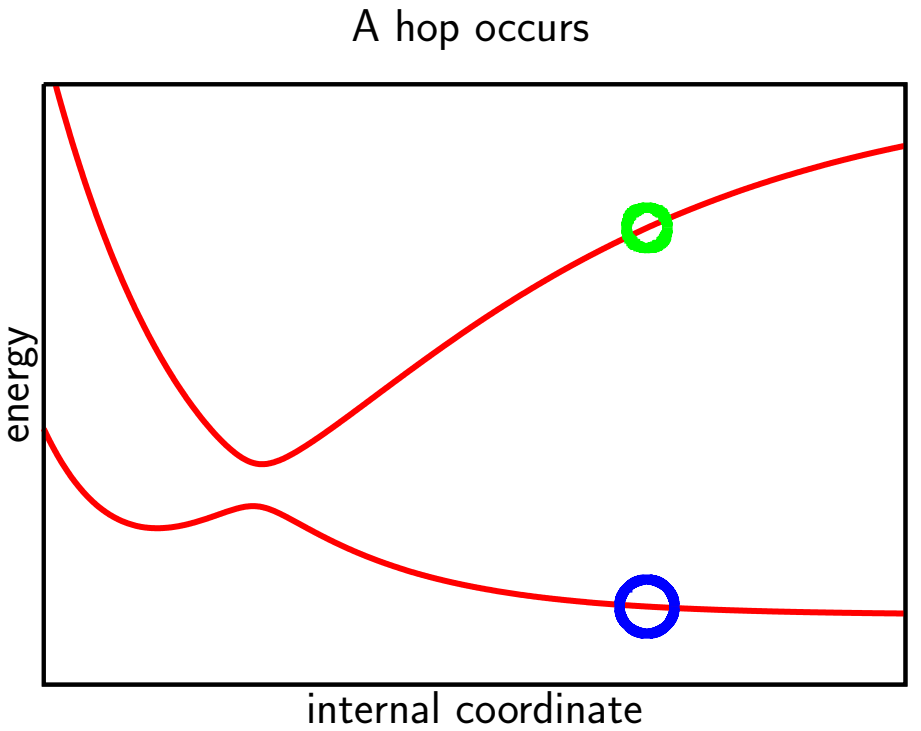

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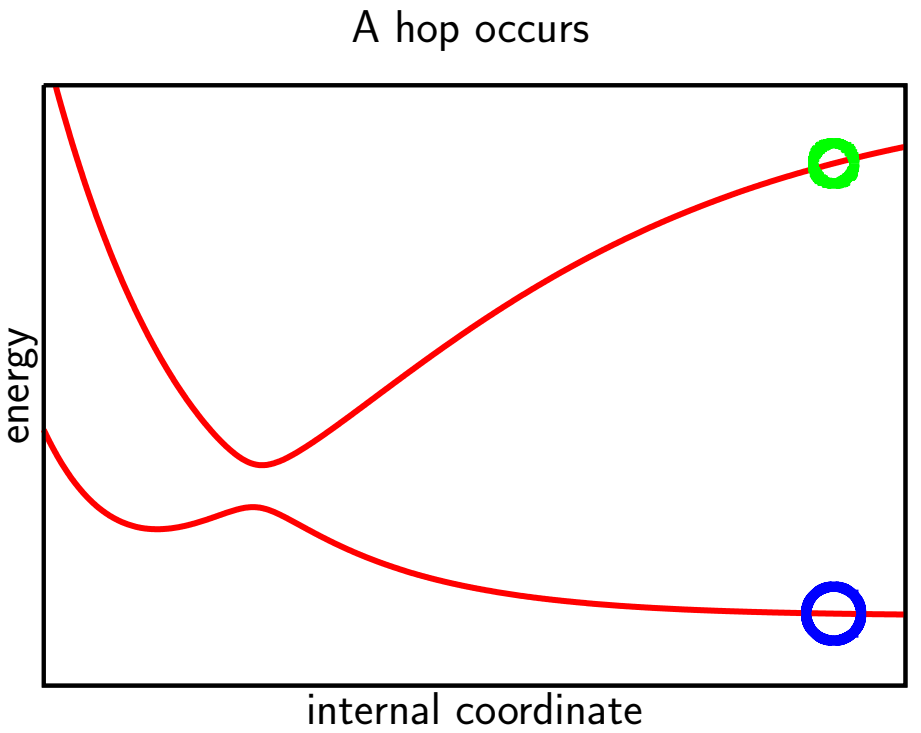

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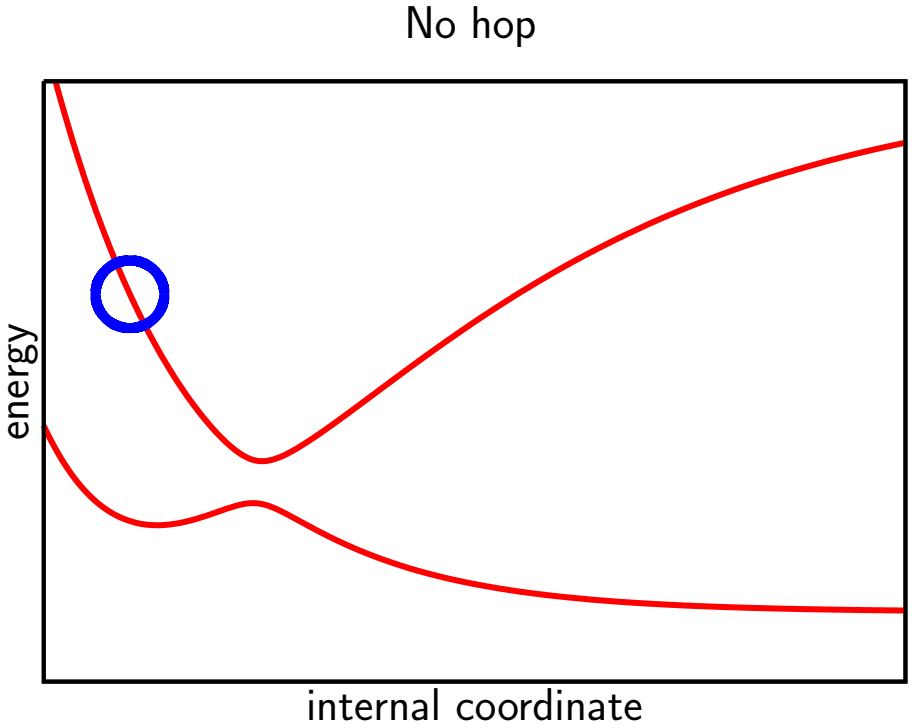

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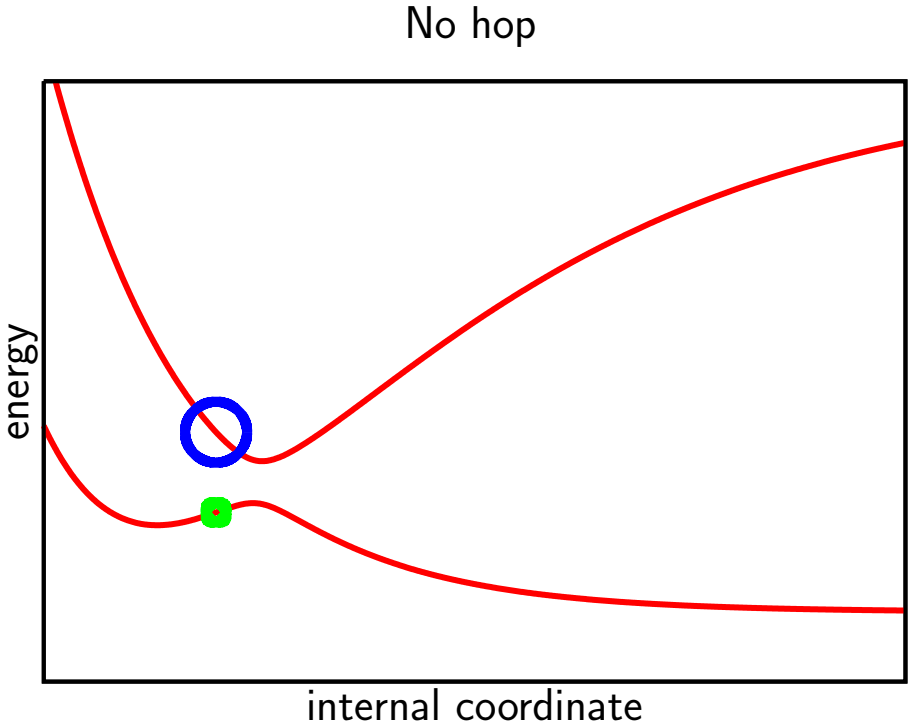

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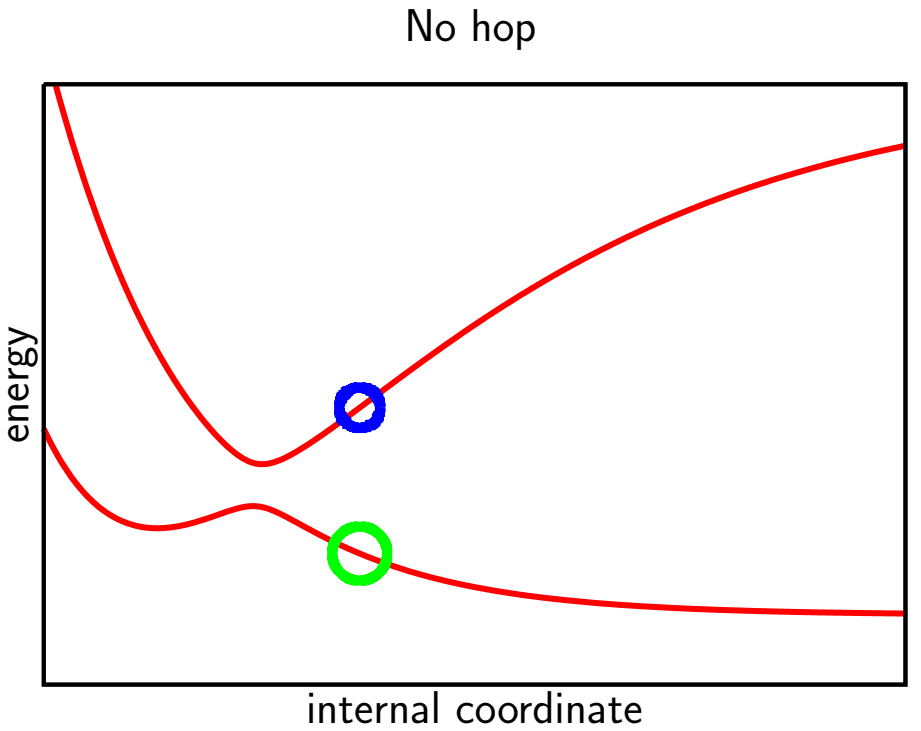

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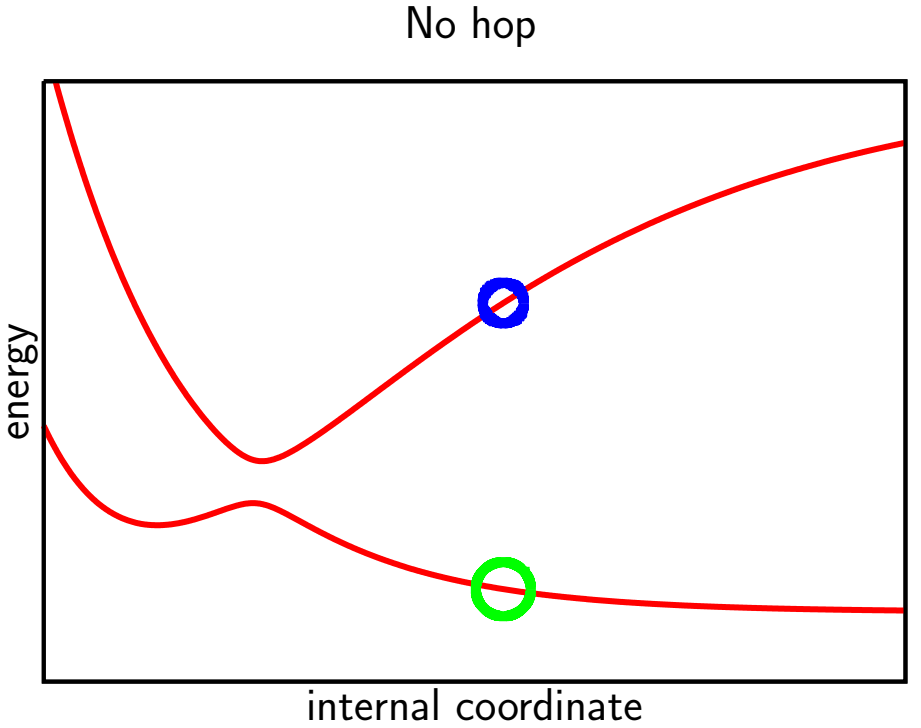

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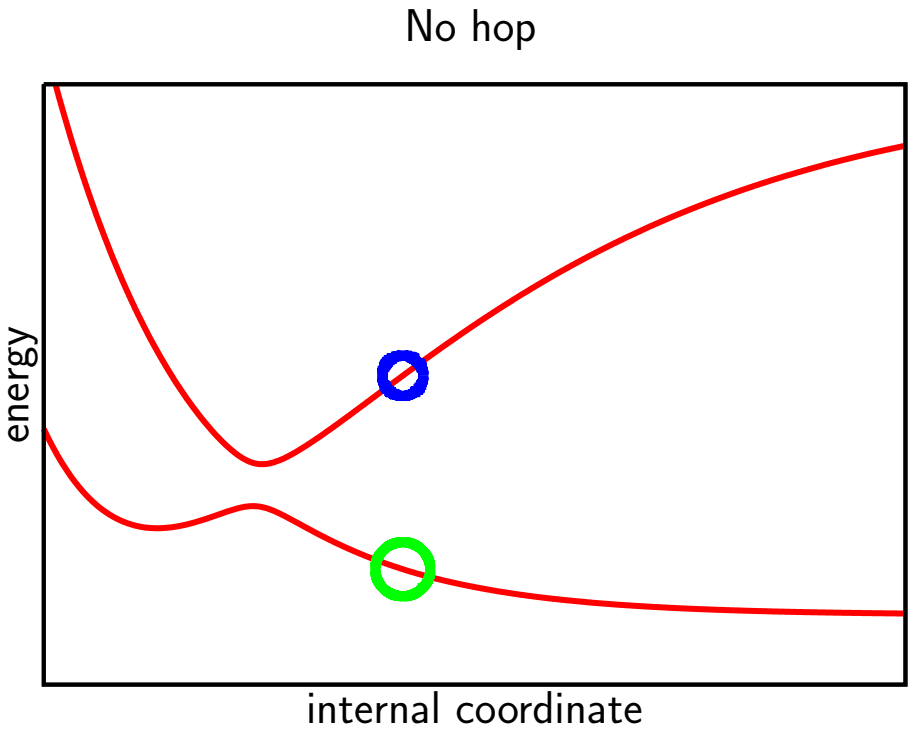


Tully's "fewest switches" algorithm for SH (1990)

Underlying assumptions:

- There is one representative point of the nuclear motion, $\mathbf{Q}^{(j)}(t)$, for all the electronic states.
- The electronic time-evolution for the j-th trajectory is expressed by a wave-function, that can be expanded on the adiabatic basis:
$$\left|\Psi^{(j)}(t)\right\rangle = \sum_L C_L^{(j)}(t) \left|\psi_L^{(j)}\right\rangle$$
- The $C_L^{(j)}(t)$ coefficients are determined by solving the TDSE:
$$i\hbar \frac{d\Psi^{(j)}}{dt} = \hat{\mathcal{H}}_{el}\Psi^{(j)}.$$
- The state probabilities for the trajectory j are: $P_L^{(j)}(t) = \left|C_L^{(j)}(t)\right|^2$.

  They can be averaged over N_T trajectories: $\overline{p}_L = \dfrac{1}{N_T}\sum_{j=1}^{N_T} P_L^{(j)}$

- For a two state system, the probability to make a transition from state K to state L for the j-th trajectory is:

$$\begin{aligned} T^{(j)}_{K\to L}(t) &= \max\left\{0, \frac{P^{(j)}_K(t) - P^{(j)}_K(t+\Delta t)}{P^{(j)}_K(t)}\Delta t\right\} \\ &\simeq \max\left\{0, \frac{-\dot{P}^{(j)}_K(t)}{P^{(j)}_K(t)}\Delta t\right\} \end{aligned}$$

- The number of state switches is minimized assuming that the flux of probability between the two states results from probability transferring in only one direction.
- Very easy to implement.
- Probably the most popular algorithm for SH.

Internal consistency

Internal consistency requirement: $\boxed{\Pi_K(t) = \overline{p}_K(t)}$

We want to define a $K \to L$ transition probability $T^{(j)}_{K\to L}(t)$, for a time step Δt, such that the above requirement is satisfied.

For a two state system $\{\psi_K, \psi_L\}$:

In a time step Δt: $\Delta\overline{p}_K = \dot{\overline{p}}_K \Delta t$
and $\Delta\Pi_K = -\Pi_K \overline{T}_{K\to L} + \Pi_L \overline{T}_{L\to K}$

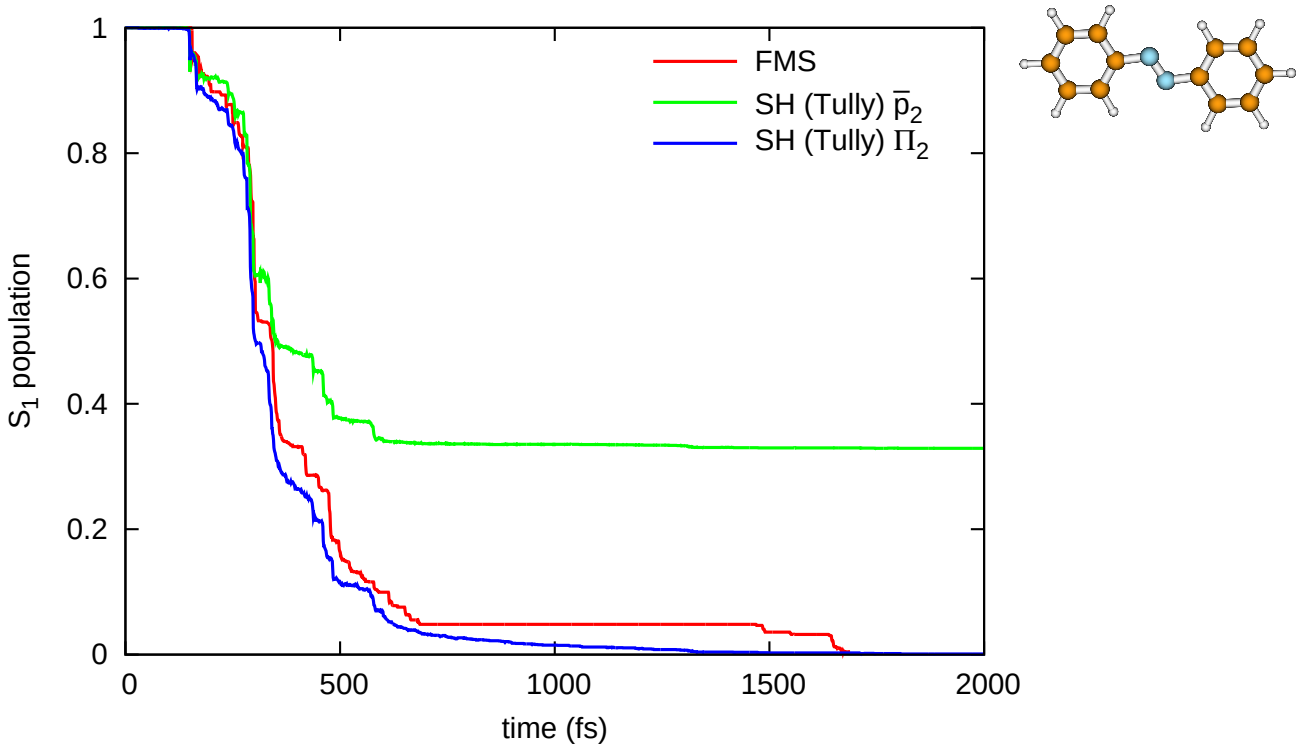
$$\text{So}: \quad \overline{T}_{K\to L} = \max\left\{0, \frac{-\dot{\overline{p}}_K}{\Pi_K}\Delta t\right\}$$

This condition is not easily implemented and may lead to artifacts in the case of swarms of trajectories corresponding to different channels.

$$\text{Tully's prescription}: \quad T^{(j)}_{K\to L} = \max\left\{0, \frac{-\dot{P}^{(j)}_K}{P^{(j)}_K}\Delta t\right\}$$

Comparison with quantum calculations

Excited state decay of $trans$-azobenzene, $n \longrightarrow \pi^*$ excitation.



See: Toniolo, Ciminelli, Persico, Martínez, J. Chem. Phys. **123**, 234308 (2005)

The coherence problem

- 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).
- Neglecting quantum decoherence in SH leads to discrepancies between $\Pi_K(t)$ and $\overline{p}_K(t)$. Decoherence and internal consistency are strongly connected.
- Usually the averaged state probabilities $\overline{p}_K(t)$ are just disregarded.

Low coupling regions

Consider a two state system ($\mathbf{1}$ and $\mathbf{2}$). Far from the strong interaction region, the state probabilities exhibit fast Rabi oscillations:

$$P_2(t) \simeq P_2(t_0) + \frac{2V}{|\Delta E|}[\Im\{C_1^*(t_0)C_2(t_0)\}\cos(\Omega t) - \Re\{C_1^*(t_0)C_2(t_0)\}\sin(\Omega t)]$$

where ΔE is the $\mathbf{1}-\mathbf{2}$ energy gap, V is the nonadiabatic coupling and $\Omega = \sqrt{\Delta E^2 + 4V^2}$.

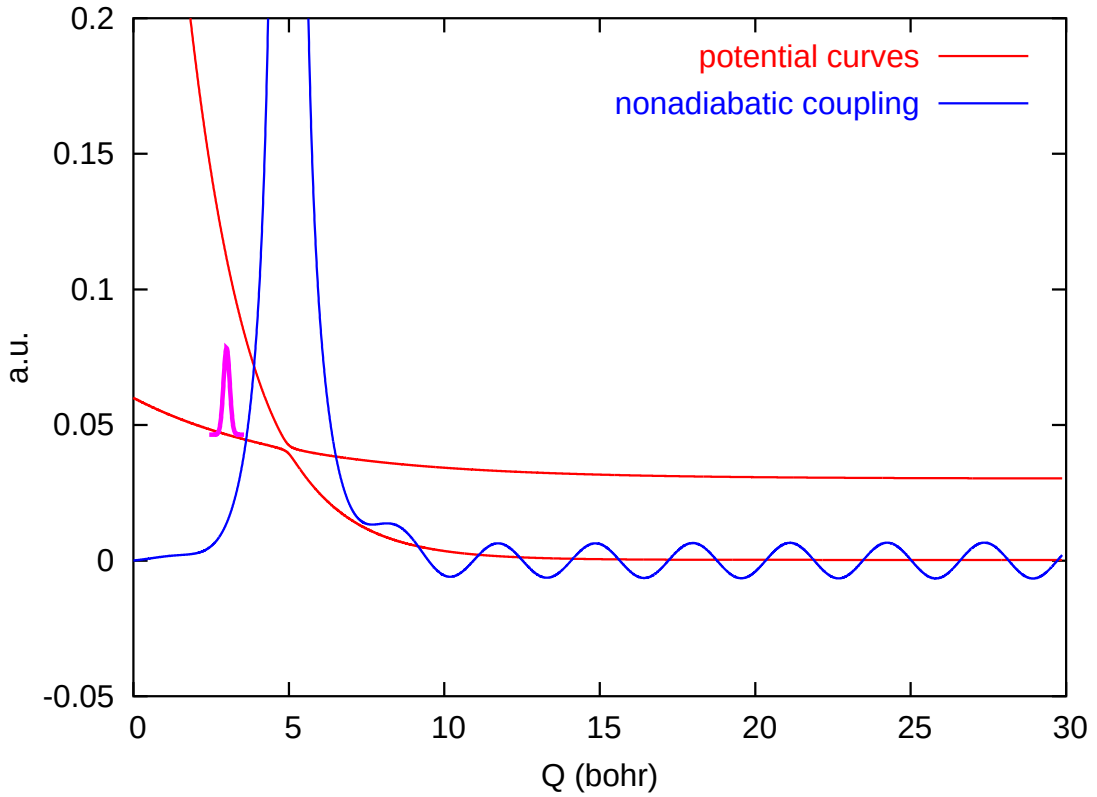
Such oscillations are due to the coherence of the $\mathbf{1}$ and $\mathbf{2}$ wavepackets, that should disappear as the wavepackets take different paths in the two PES, but is conserved in trajectory calculations.

Due to the oscillations, we have $\mathbf{2} \rightarrow \mathbf{1}$ hops, much more frequently than viceversa, because: 1) once in the PES $\mathbf{1}$, ΔE increases and V decreases, and 2) some upward hops are frustrated.

This bias can significantly affect the simulation of slow decays.

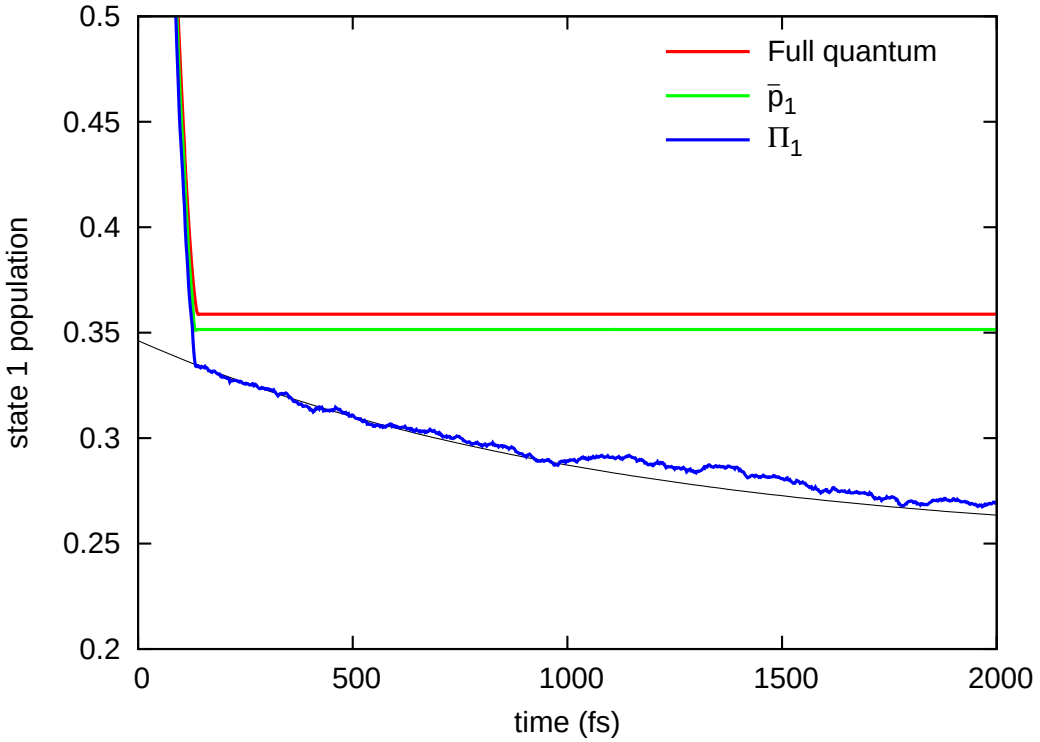
Avoided crossing with oscillatory coupling.

Potential energy curves and coupling.



Coherence effects after the crossing

After the passage through the avoided crossing, the probability oscillations cause an exponential decay with $\tau \simeq 7$ ps.



Decoherence correction

To introduce quantum decoherence corrections in a semiclassical method, we must:

- evaluate how far from each other the representative points would travel on the different PES;
- correct the probabilities and coefficients computed by the TDSE according to the distance between the representative points.

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_α 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.

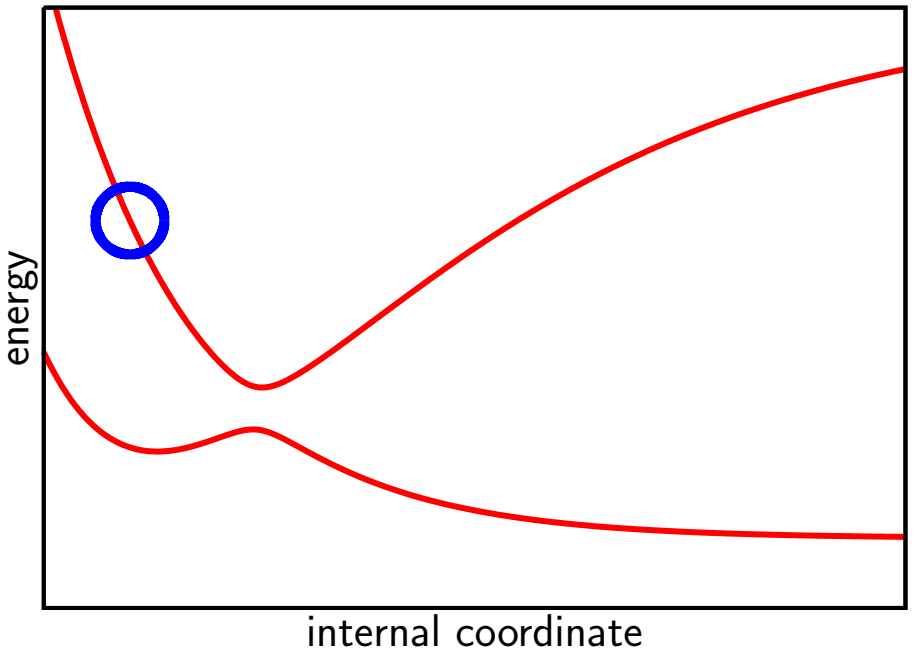
- The trajectories $\mathbf{Q}_i(t)$, with $i \neq 0$, are computed in a simplified way, to avoid performing electronic calculations at geometries different from the current one, $\mathbf{Q}_0$. All the momenta $\mathbf{P}_i$ are updated every n_D steps, using only the information needed for energy conservation, 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, which is chosen to be very small in the following applications ($s_{min} = 10^{-9}$).
  - The gaussian width σ, which is varied to test its influence on the results.

Surface hopping with decoherence correction.



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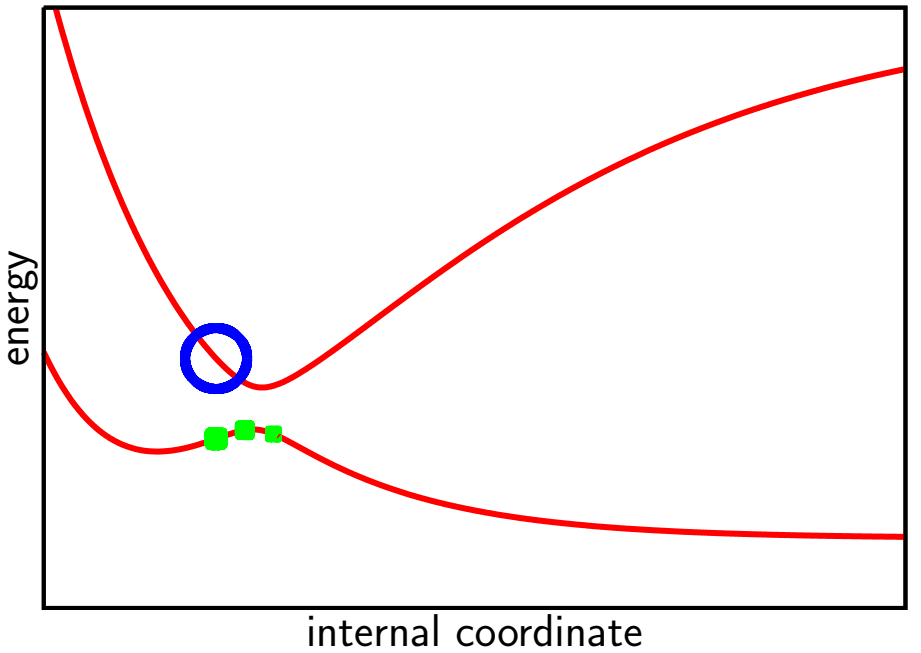

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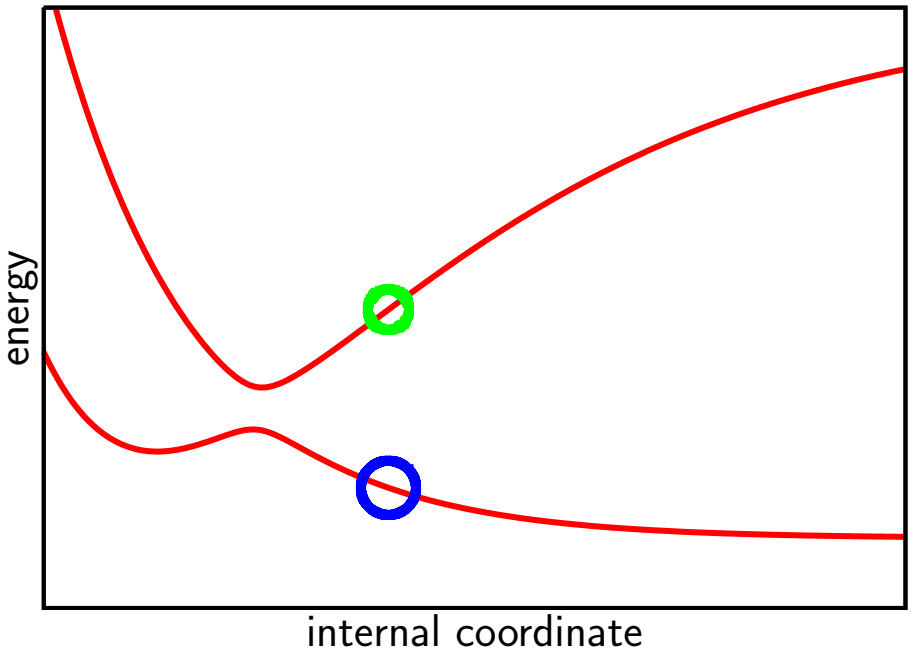

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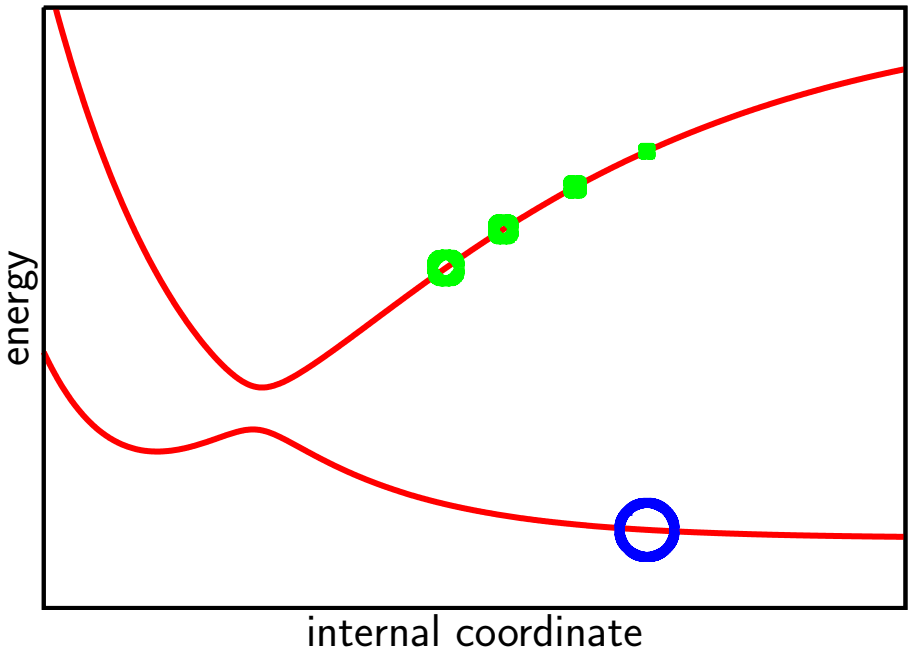

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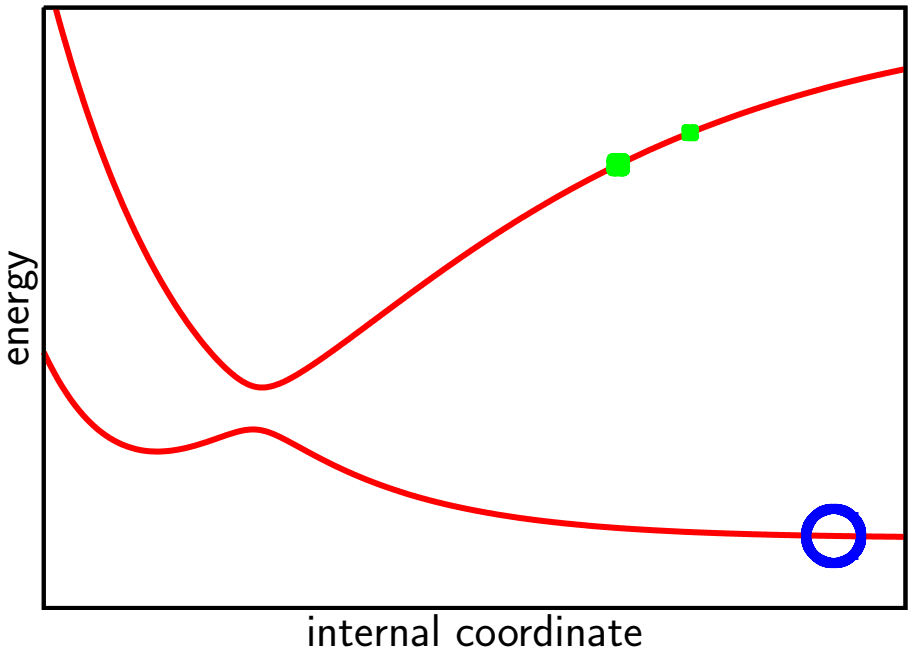
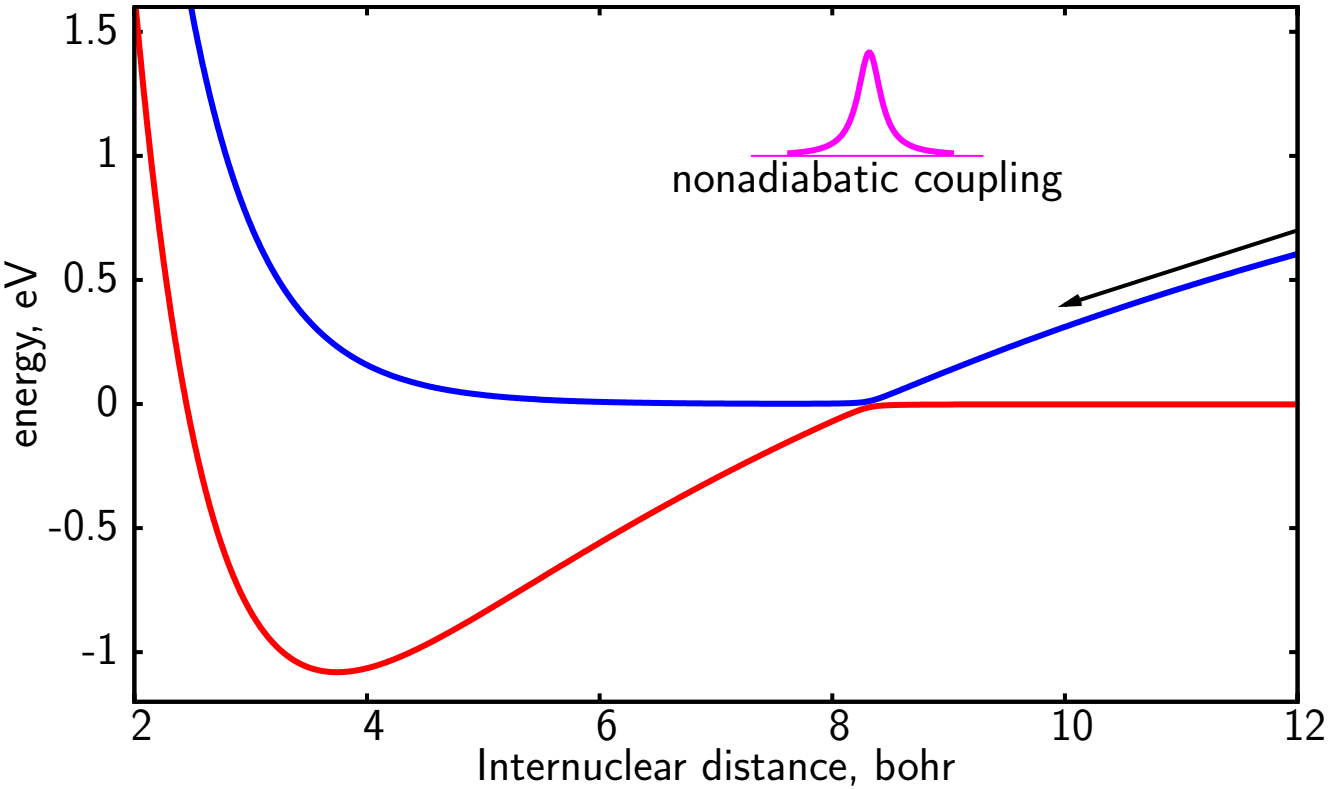


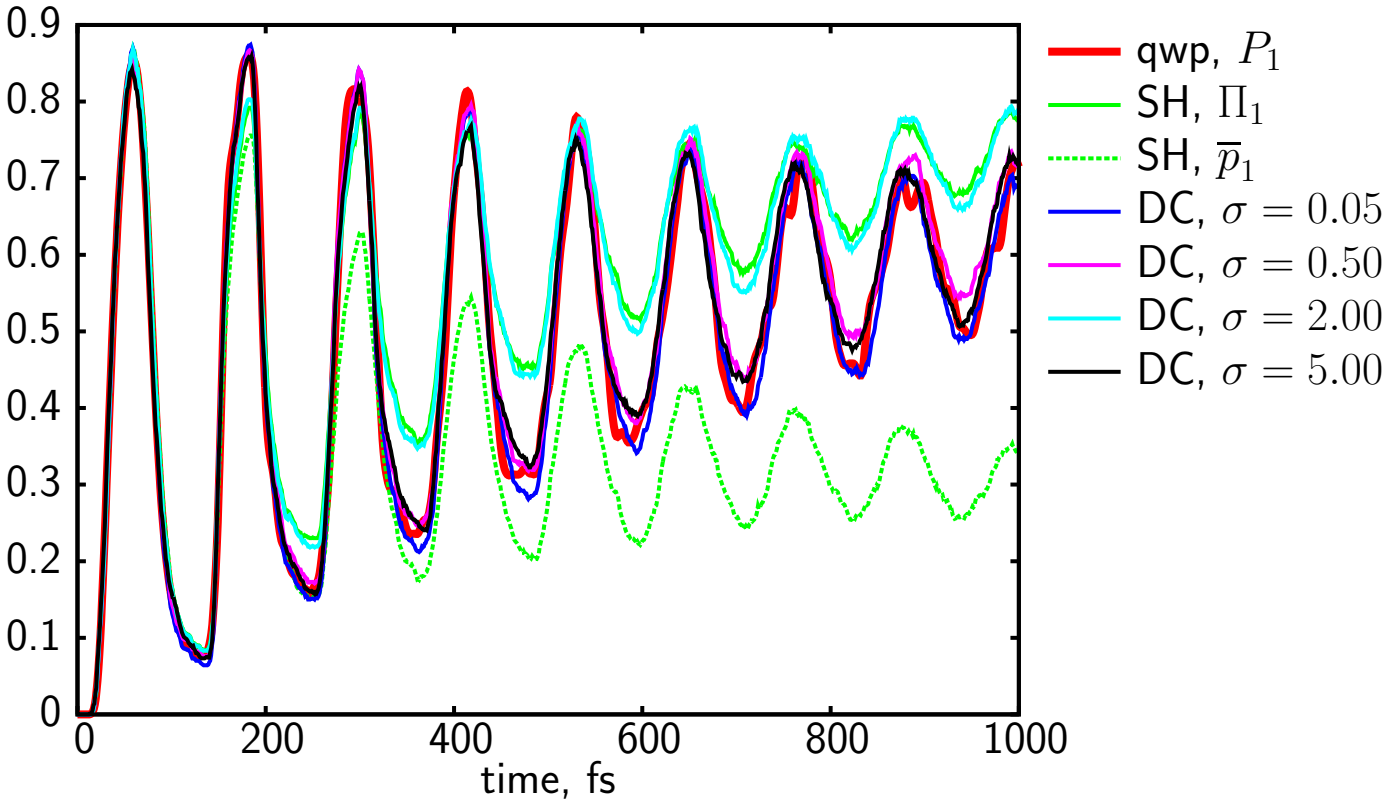
1D model:
ionic/neutral crossing, many passages.

Potential energy curves and coupling.



Ionic/neutral crossing.

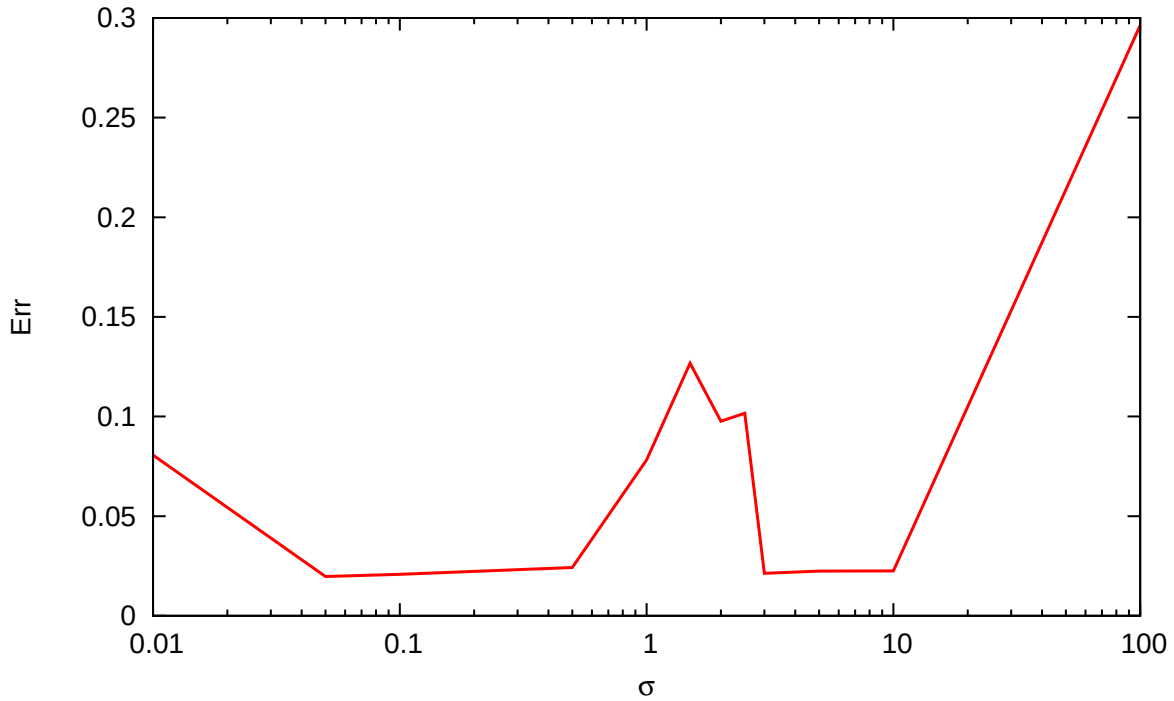
Time dependent population of the first electronic state.



Ionic/neutral crossing.

Accumulated error $Err(t)$ for t=1000 fs

$$Err(t) = \frac{1}{t}\int_o^t \left|\overline{p}_1(t') - P_1^{quant}(t')\right| dt'$$



Avoided crossing with oscillatory coupling.

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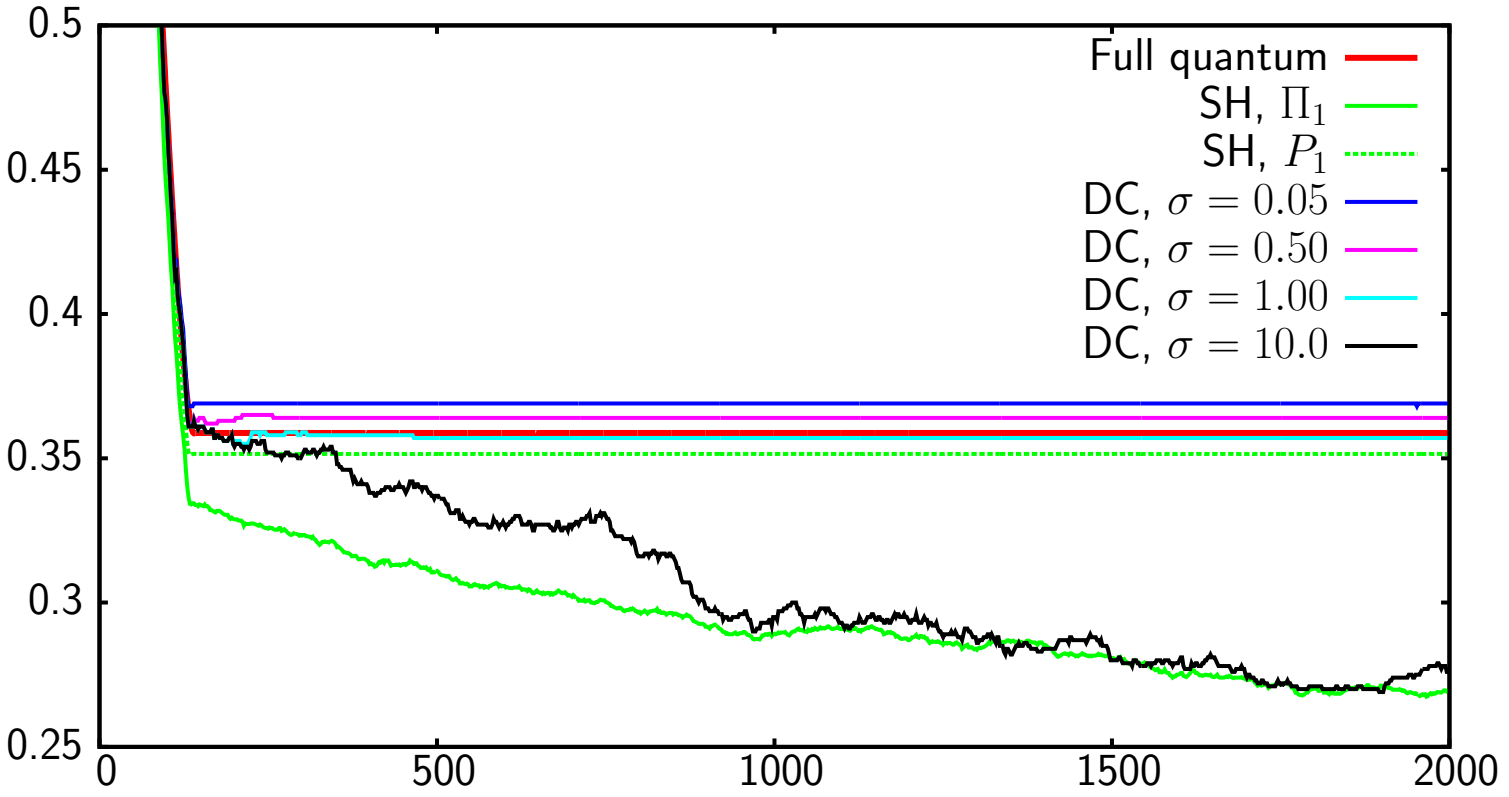
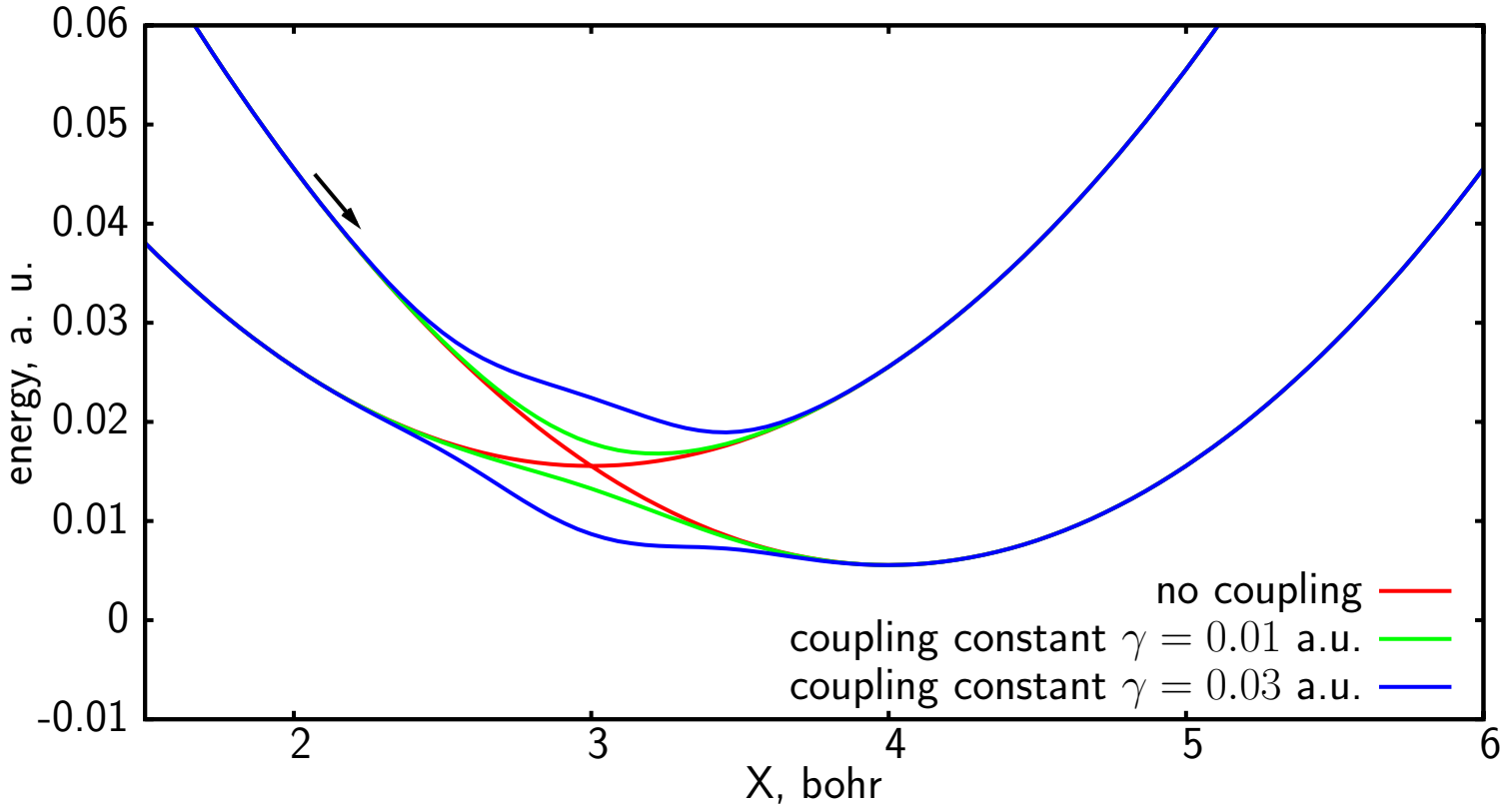


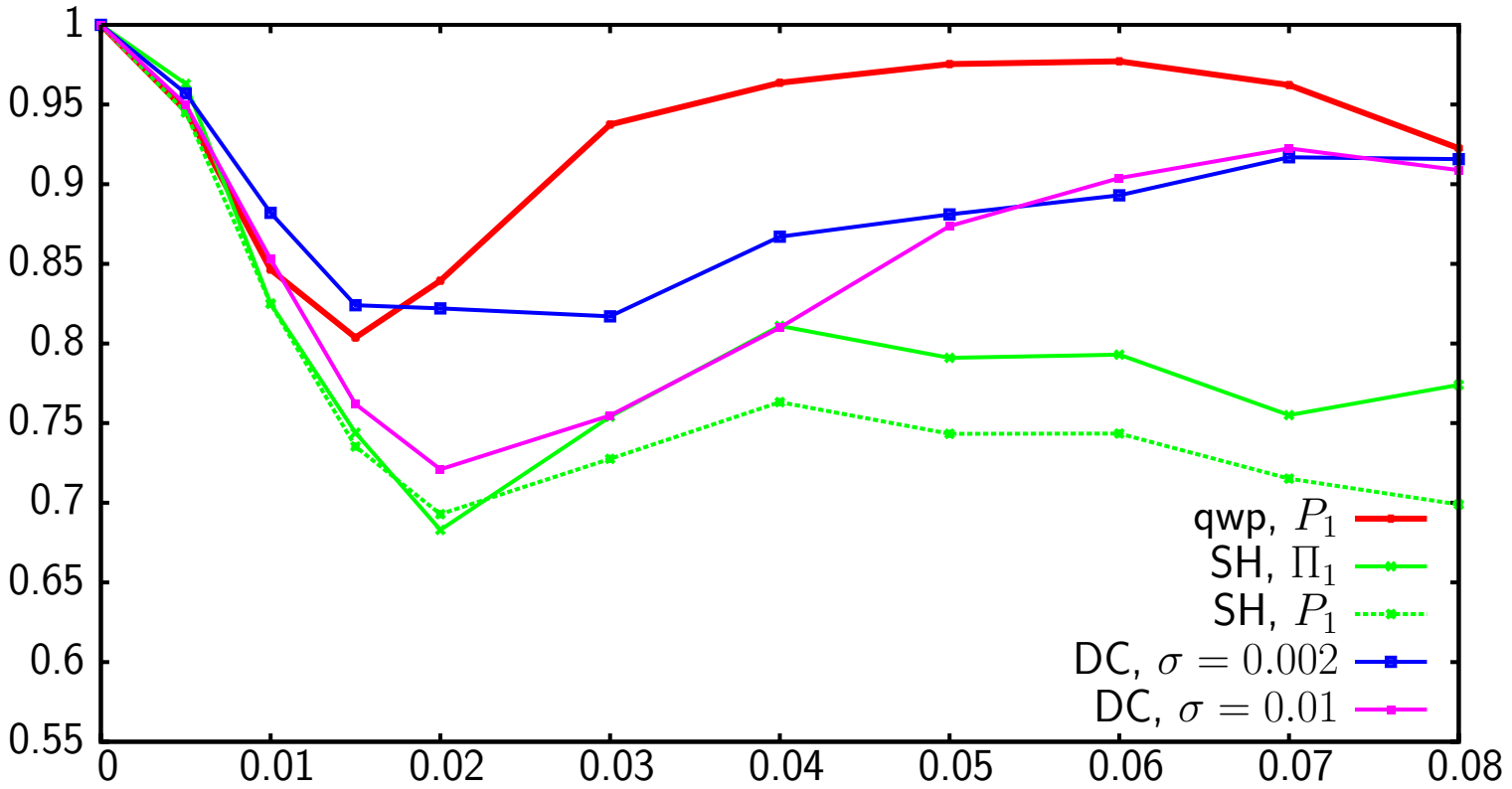
2D model: conical intersection.

Potential energy curves with different couplings.



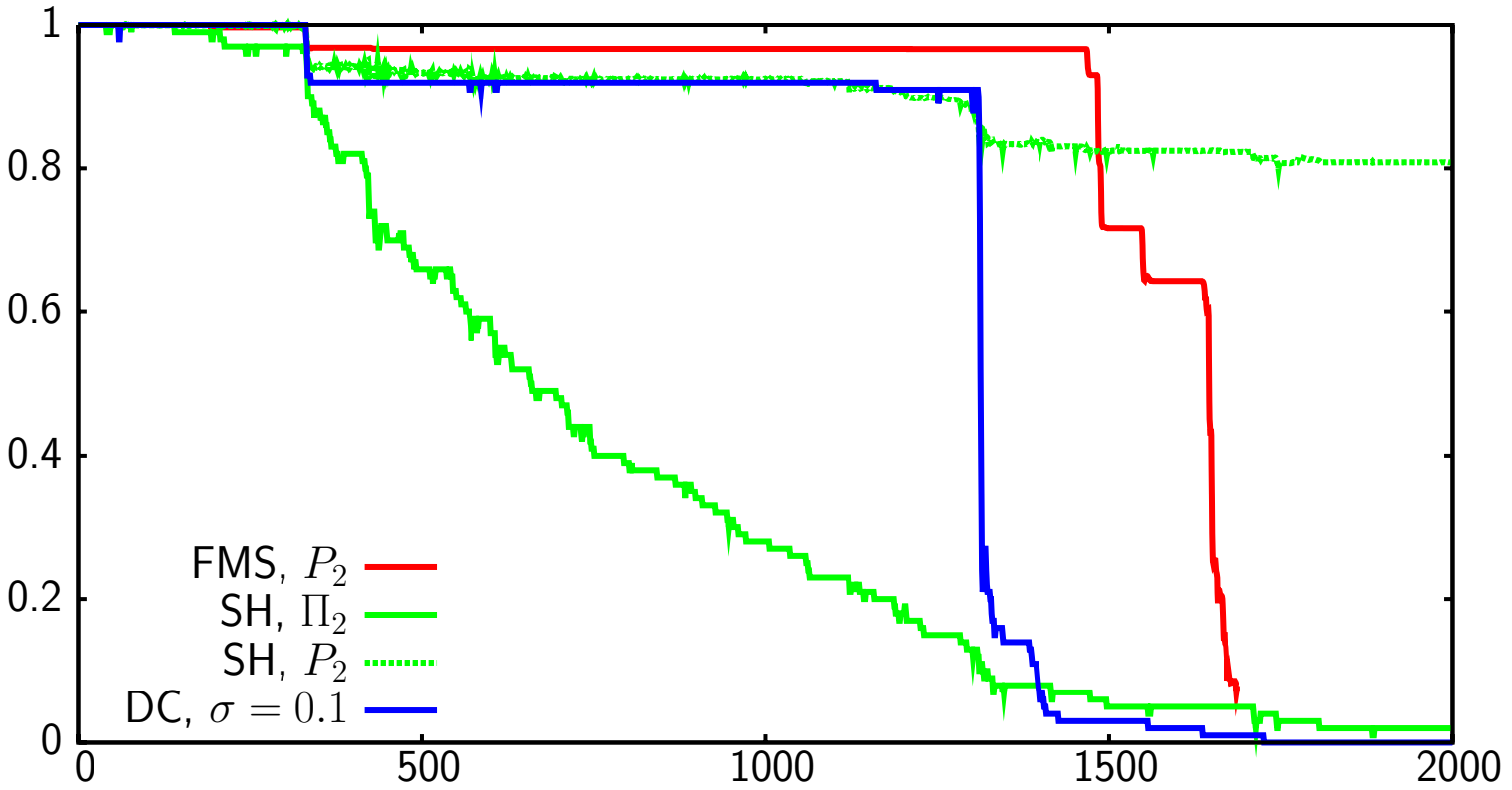
Conical intersection.

Transition probability for one passage through the intersection region, as a function of the coupling strength γ.



Excited state decay of $trans$-azobenzene, $n \longrightarrow \pi^*$ excitation.

A long lasting wavepacket.



Perspectives

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Cut-throat savings

In an attempt to boost its struggling economy, Italy's government is focusing on easy, but unwise, targets.

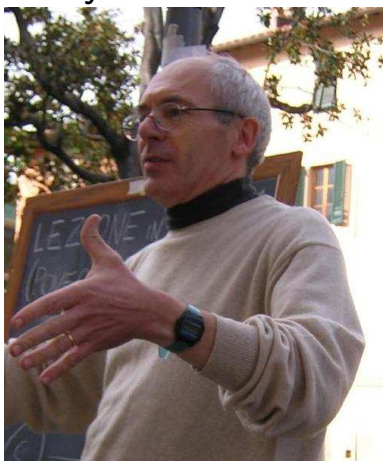
It is a dark and angry time for scientists in Italy, faced as they are with a government acting out its own peculiar cost-cutting philosophy. Last week, tens of thousands of researchers took to the streets to register their opposition to a proposed bill designed to control civil-service spending (see page 840). If passed, as expected, the bill would dispose of nearly 2,000 temporary research staff, who are the backbone of the country's grossly understaffed research institutions — and about half of whom had already been selected for permanent jobs.

Even as the scientists were marching, Silvio Berlusconi's centre-right government, which took office in May, decreed that the budgets of both universities and research could be used as funds to shore up Italy's banks and credit institutes. This is not the first time that Berlusconi has targeted universities. In August, he signed a decree that cut

- Turn-over: one recruitment for five retirements.
- In 2010 the University of Pisa will not have enough money to pay the salaries of the permanent staff.

This work was done in collaboration with

Prof. Maurizio Persico, University of Pisa



Alberto Zoccante, currently at University of Aarhus, PhD student