

L8

Methods for dynamics simulations I: Semi-classical propagation

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The semi-classical propagation

$$\varphi(\mathbf{r}, \mathbf{R}^c, t) = \sum_j c_j(t) \Phi_j(\mathbf{r}; \mathbf{R}^c(t)) \quad (\{\Phi_k\} | \langle \Phi_k | \Phi_l \rangle_{\mathbf{r}} = \delta_{kl})$$



$$\left(i\hbar \frac{\partial}{\partial t} - H_e \right) \varphi(\mathbf{r}, \mathbf{R}, t) = 0$$



$$i\hbar \frac{dc_k}{dt} + \sum_j \left(-H_{kj}^c + i\hbar \mathbf{F}_{kj}^c \cdot \mathbf{v}^c \right) c_j = 0$$

$$\frac{d^2 \mathbf{R}_m^c}{dt^2} - \frac{\mathfrak{F}_m^c}{M_m} = 0$$

$$\left[\begin{array}{l} \langle \Phi_k | \frac{\partial}{\partial t} | \Phi_j \rangle_{\mathbf{r}} = \mathbf{F}_{kj}^c \cdot \mathbf{v}^c \\ \mathbf{F}_{kj}^{c,m} \equiv \langle \Phi_k | \nabla_{\mathbf{R}_m} | \Phi_j \rangle_{\mathbf{r}} \\ A^c \equiv A(\mathbf{R}^c(t)) \end{array} \right.$$

$$\left(\{\Phi_k\} | H_{kj} = V_k \delta_{kj} \right) \quad \text{Adiabatic basis}$$

$$\left(\{\Phi_k^d\} | H_{kj} = W_{kj}, \mathbf{F}_{kj} = 0 \right) \quad \text{Diabatic basis}$$

$$\frac{d^2 \mathbf{R}_m^c}{dt^2} - \frac{\mathcal{F}_m^c}{M_m} = 0$$

$$\mathcal{F}_m^c = -\nabla_{\mathbf{R}_m} H_{ll}^c$$

Any standard method can be used in the integration of the Newton's equations.

A good one is the **Velocity Verlet**

For each nucleus m :
$$\mathbf{R}_m^c(t + \Delta t) = \mathbf{R}_m^c(t) + \mathbf{v}_m^c(t)\Delta t + \frac{1}{2}\mathbf{a}_m^c(t)\Delta t^2$$

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

$$\mathbf{a}_m^c(t) = -\frac{1}{M_m}\nabla_{\mathbf{R}} E\left[\mathbf{R}_m^c(t + \Delta t)\right]$$

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

- Swope et al. J. Chem. Phys. **76**, 637 (1982)

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
	2400	7.2 × 10 ¹³	13.9	4.5
O–C–O asymmetric stretch	2100	6.3 × 10 ¹³	15.9	5.1
C≡C, C≡N stretch	1700	5.1 × 10 ¹³	19.6	6.2
C=O (carbonyl) stretch	1600	4.8 × 10 ¹³	20.8	6.4
C=C stretch	1500	4.5 × 10 ¹³	22.2	7.1
H–O–H bend				
C–N–H bend				
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: $\Delta t < 2/\omega = 2/(2\pi\nu)$.

- Schlick, Barth and Mandziuk, Annu. Rev. Biophys. Struct. **26**, 181 (1997)

Table 1 Some typical vibrational modes^a

Vibrational mode	Wavelength of absorption [cm^{-1}] ($1/\lambda$)	Absorption frequency [s^{-1}] ($\nu = c/\lambda$)	Period [fs] ($1/\nu$)	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

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.

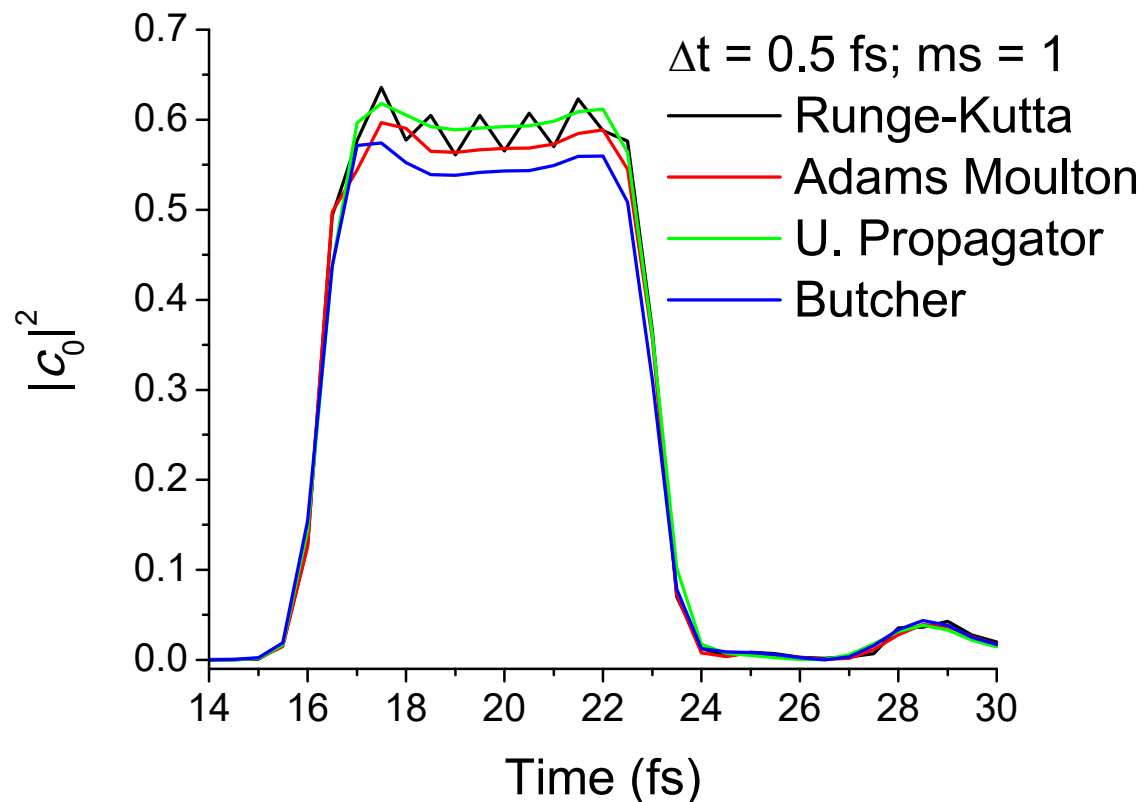
Exceptions:

- Dynamics close to the conical intersection may require 0.25 fs
- Dissociation processes may require even smaller time steps

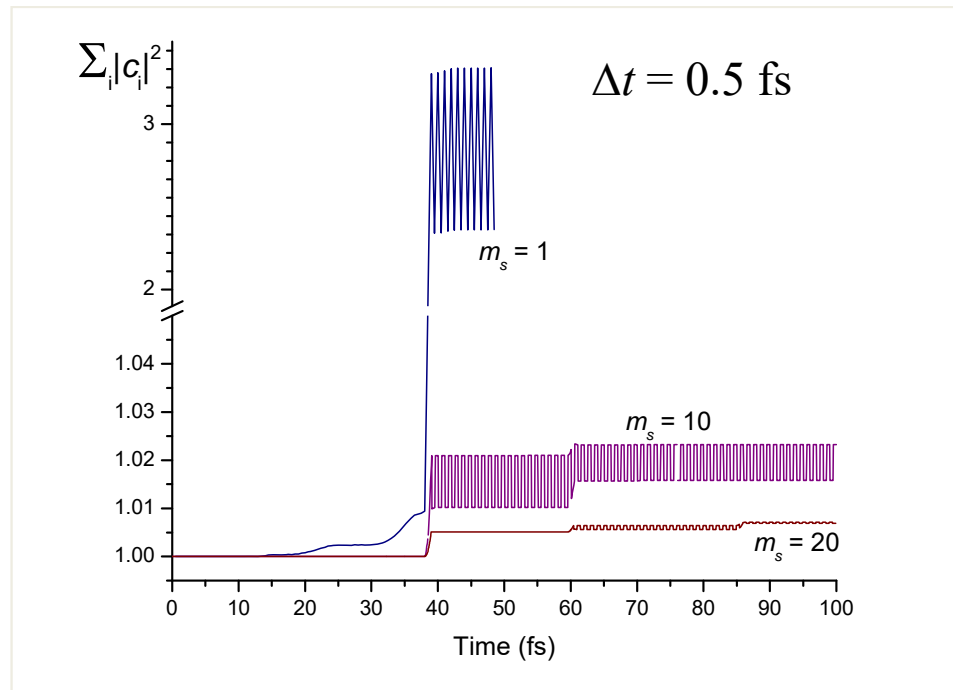
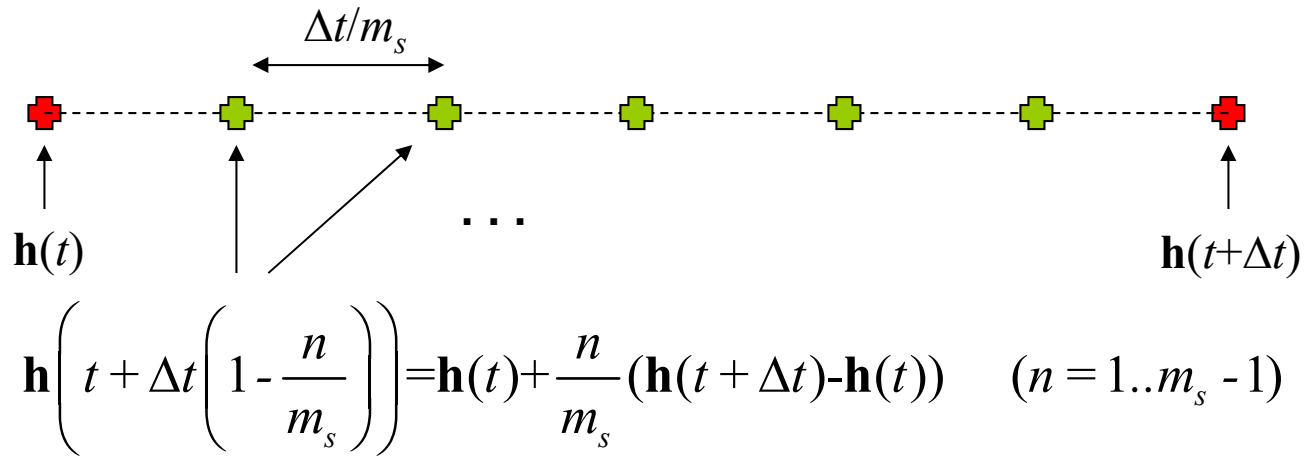
$$i\hbar \frac{dc_k}{dt} + \sum_j \left(-H_{kj}^c + i\hbar \mathbf{F}_{kj}^c \cdot \mathbf{v}^c \right) c_j = 0$$

SC-TDSE

The SC-TDSE is solved with standard methods
(Unitary Propagator, Adams Moulton 6th-order, Butcher 5th-oder)



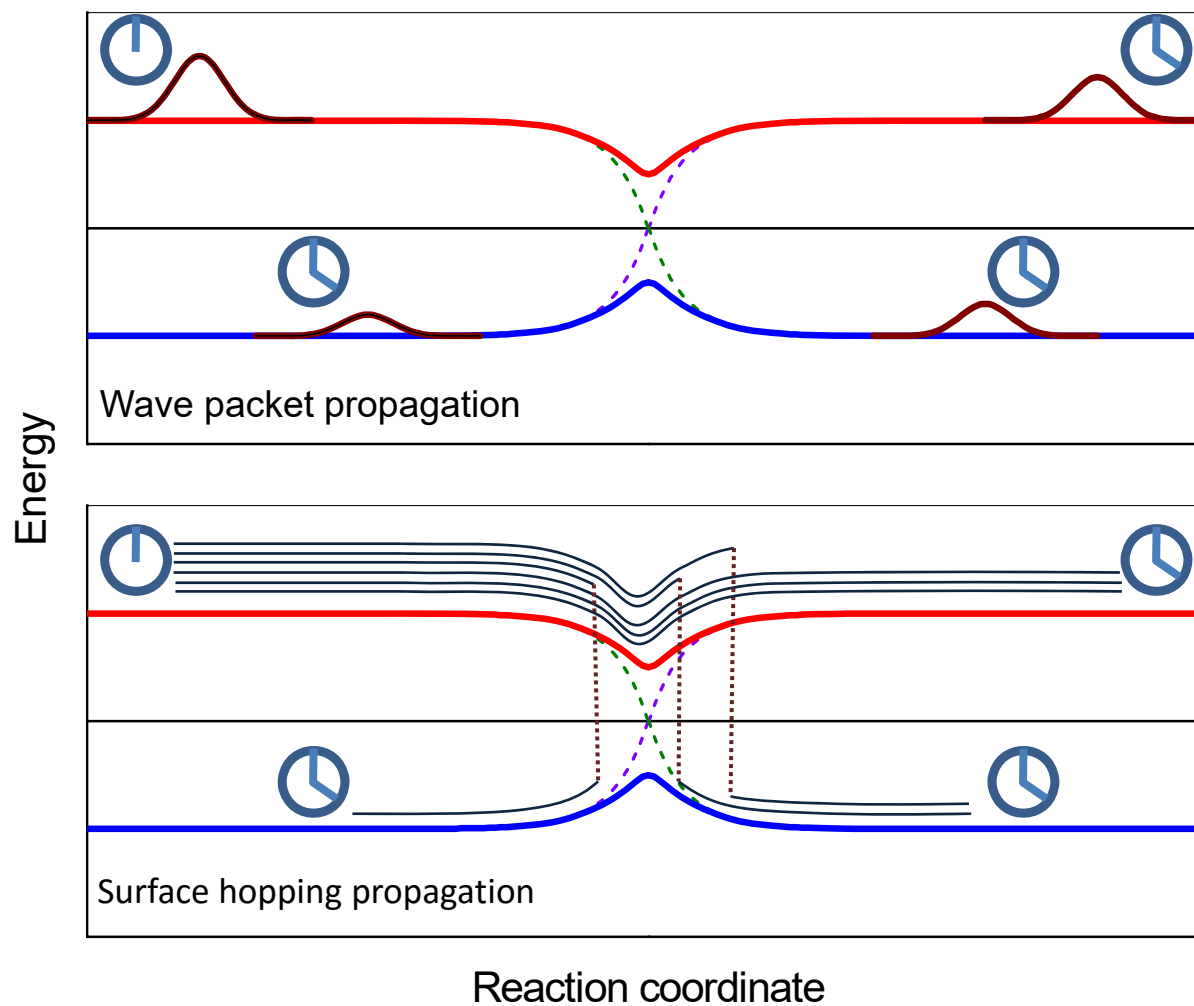
Time-step for the SC-TDSE





Surface hopping

Surface hopping



- Tully, Preston, JCP **55**, 562 (1971)

$$P_{l \rightarrow k} = \frac{\text{Population increment in } k \text{ due to flux from } l \text{ during } \Delta t}{\text{Population of } l}$$

$$\rho_{lk}(t) = c_l c_k^*$$

$$P_{l \rightarrow k} = \max \left[0, \frac{2\Delta t}{\rho_{ll}} \left(\hbar^{-1} \text{Im}(\rho_{kl}) H_{lk}^c - \text{Re}(\rho_{kl}) \mathbf{F}_{kl}^c \cdot \mathbf{v}^c \right) \right]$$

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

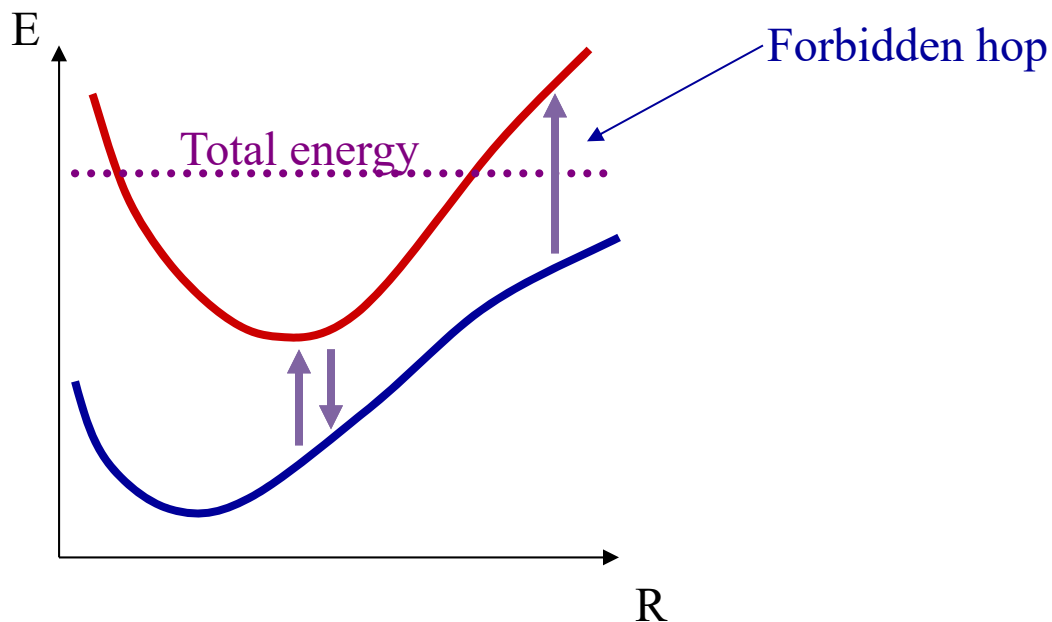
A hopping will take place if two conditions are satisfied:

1) A uniformly selected random number r_t in the $[0, 1]$ interval is such that

$$\sum_{n=1}^{k-1} P_{l \rightarrow n}(t) < r_t \leq \sum_{n=1}^k P_{l \rightarrow n}(t)$$

2) The energy gap between the final and initial states satisfies

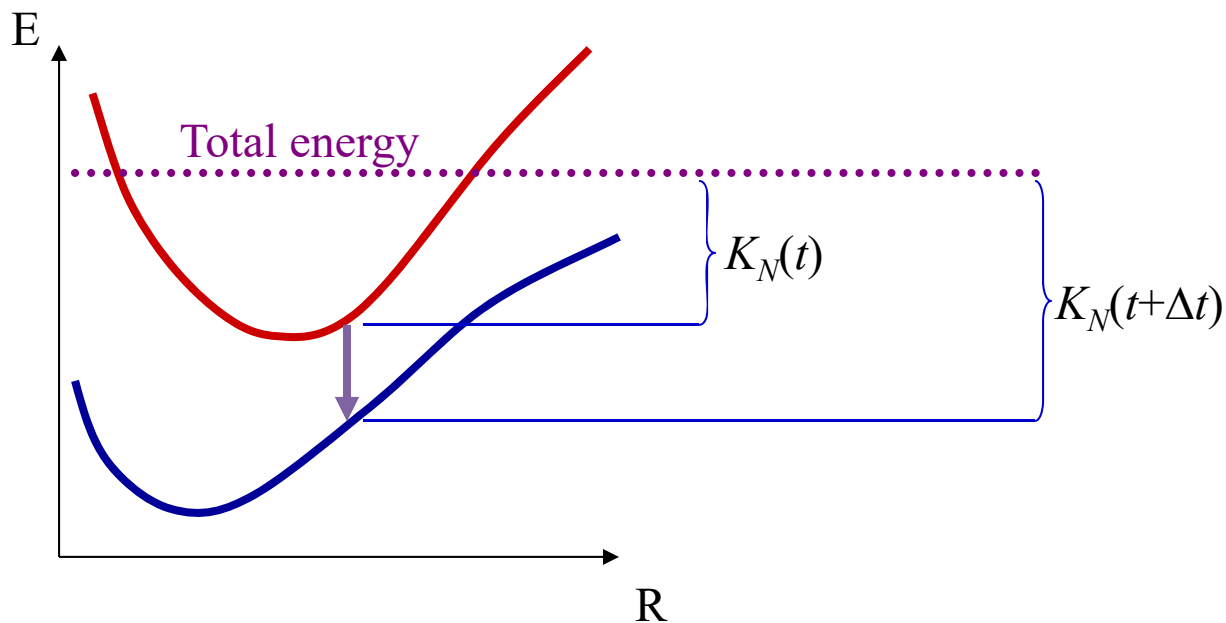
$$V_k(\mathbf{R}^c(t)) - V_l(\mathbf{R}^c(t)) \leq \frac{\left(\sum_m^{N_{at}} \mathbf{v}_m^c \cdot \mathbf{F}_{kl}^{c,m} \right)^2}{2 \sum_m^{N_{at}} M_m^{-1} \left(\mathbf{F}_{kc}^{c,m} \right)^2}$$



How to treat such situations:

- Reject all classically forbidden hop and keep the momentum
- Reject all classically forbidden hop and invert the momentum
- Use the time uncertainty principle to search for a point where the hop is allowed

• Jasper, Stechmann, Truhlar, J. Chem. Phys. **116**, 5424 (2002)



After hop, what are the new nuclear velocities?

- Redistribute the energy excess equally among all degrees
- Adjust velocities components in the direction of the nonadiabatic coupling \mathbf{h}_{12}
- Adjust velocities components in the direction of the difference gradient vector \mathbf{g}_{12}

- Pechukas, Phys. Rev. **181**, 174 (1969)
- Fabiano, Keal, Thiel, Chem. Phys. **349**, 334 (2008)

Surface hopping: fewest-switches

1. Solve SE for \mathbf{R}^c

$$H_e \Phi_k(r; \mathbf{R}^c) = V_k \Phi_k(r; \mathbf{R}^c) \Rightarrow V_k, \nabla V_k, \mathbf{F}_{kj} \equiv \langle \Phi_k | \nabla | \Phi_j \rangle$$

2. Solve Newton's equation on one surface

$$\frac{d^2 \mathbf{R}_m^c}{dt^2} + \frac{\nabla_m V_l^c}{M_m} = 0$$

3. Integrate the SC-TDSE

$$i\hbar \frac{dc_k}{dt} + \sum_j \left(-V_k^c \delta_{kj} + i\hbar \mathbf{F}_{kj}^c \cdot \mathbf{v}^c \right) c_j = 0$$

4. Compute transition probability

$$P_{l \rightarrow k} = \max \left[0, \frac{-2\Delta t}{|c_l|^2} \operatorname{Re}(c_k c_l^*) \mathbf{F}_{kl}^c \cdot \mathbf{v}^c \right]$$

5. Decide surface for next time step

$$\sum_{n=1}^{k-1} P_{l \rightarrow n}(t) < r_t \leq \sum_{n=1}^k P_{l \rightarrow n}(t), \quad r_t = \text{random}[0,1]$$

Step 1 is the
computational
bottleneck

- If it hops, then **adjust momentum**
- **Repeat** procedure until the end of the trajectory
- Compute **many** trajectories



Surface hopping: overview

Simple implementation

- Propagation in Cartesian coordinates
- Trivial connection to different quantum chemical methods, including QM/MM (regarding these methods can provide excited state energies, energy gradients and nonadiabatic couplings)
- Independent trajectories: trivial parallelization

Local approximation

- No need of precomputing multidimensional potential energy surfaces
- Straightforward on-the-fly implementation
- All nuclear degrees of freedom are propagated

Simple implementation

- High computational costs in the on-the fly approach

Local approximation

- Inconsistent treatment of zero point energy
- No treatment of tunneling effects
- Wrong coherence between states

Comparison to other methods

- Cattaneo and Persico, J. Phys. Chem. A **101**, 3454 (1997)
- Worth, Hunt, Robb, J. Phys. Chem. A **107**, 621 (2003)

Comparison between hopping algorithms

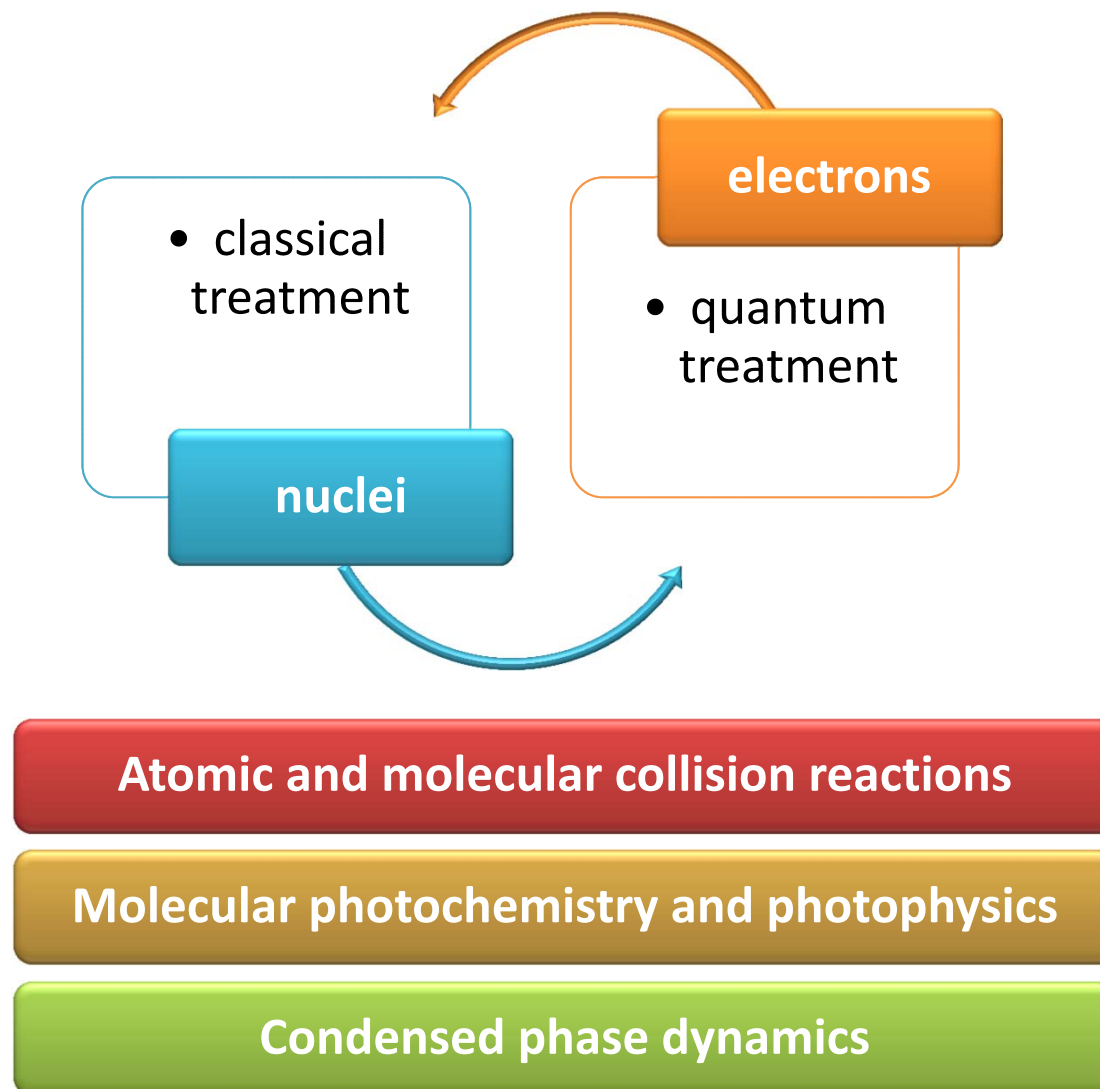
- Zhu, A. W. Jasper, and D. G. Truhlar, JCTC **1**, 527 (2005)
- Fabiano, Groenhof, Thiel, Chem. Phys. **351**, 111 (2008)

Conceptual background

- Herman, J. Chem. Phys. **103**, 8081 (1995)
- Schwartz, Bittner, Prezhdo, Rossky, J. Chem. Phys. **104**, 5942 (1996)
- Tully, Faraday Discuss. **110**, 407 (1998)
- Schmidt, Parandekar, Tully, J. Chem. Phys. **129**, 044104 (2008)

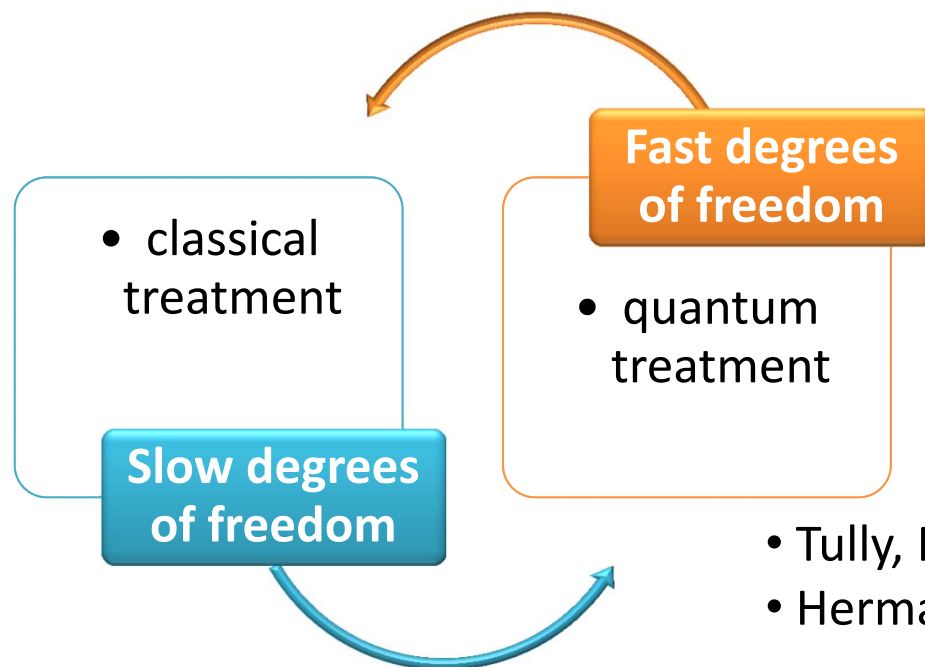
Surface hopping reviews

- Doltsinis, NIC series, 2002
- Barbatti, WIREs: Comp. Mol. Sci. **1**, 620 (2011)



See References in:

- Barbatti, WIREs: Comp. Mol. Sci. **1**, 620 (2011)



- Tully, Faraday Discuss. **110**, 407 (1998)
- Herman, J. Chem. Phys. **103**, 8081 (1995)

Singlet-triplet transitions

- Carbogno, Behler, Reuter, Gross, Phys. Rev. B **81**, 035410 (2010)

Electric field interactions

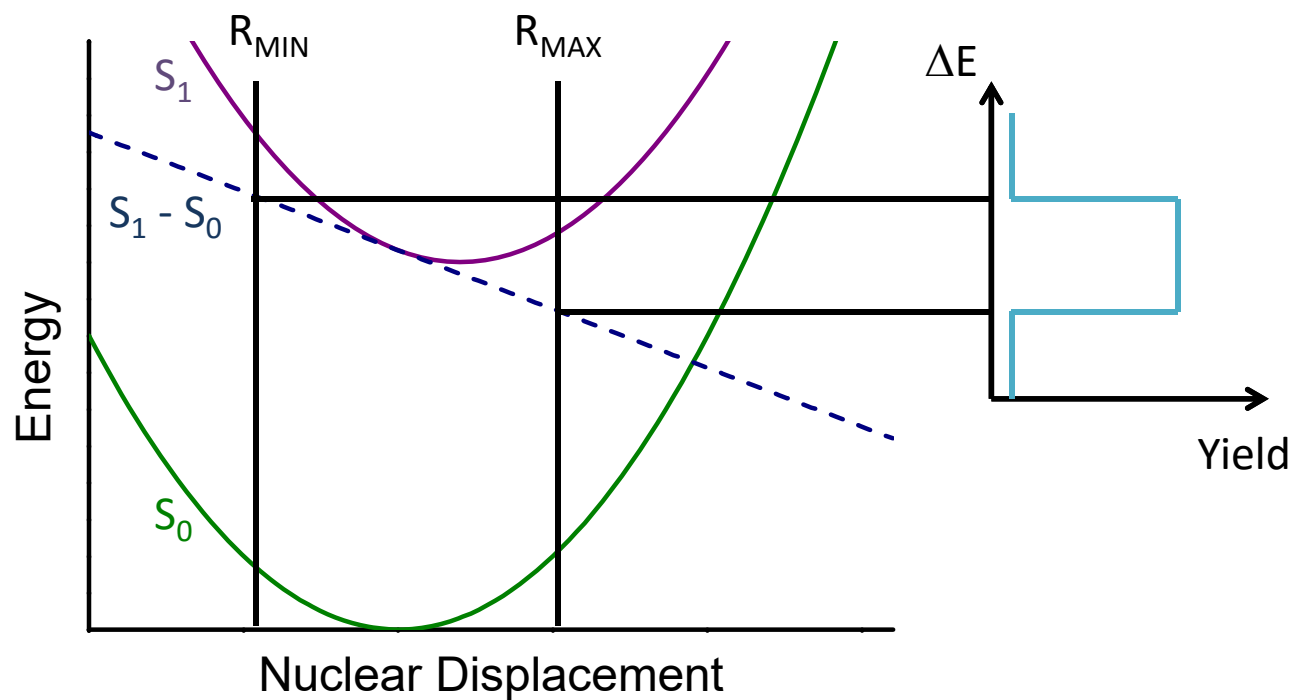
- Mitric, Petersen, Bonacic-Koutecky, Phys. Rev. A **79**, 053416 (2009)

Solvent-induced vibrational relaxation

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



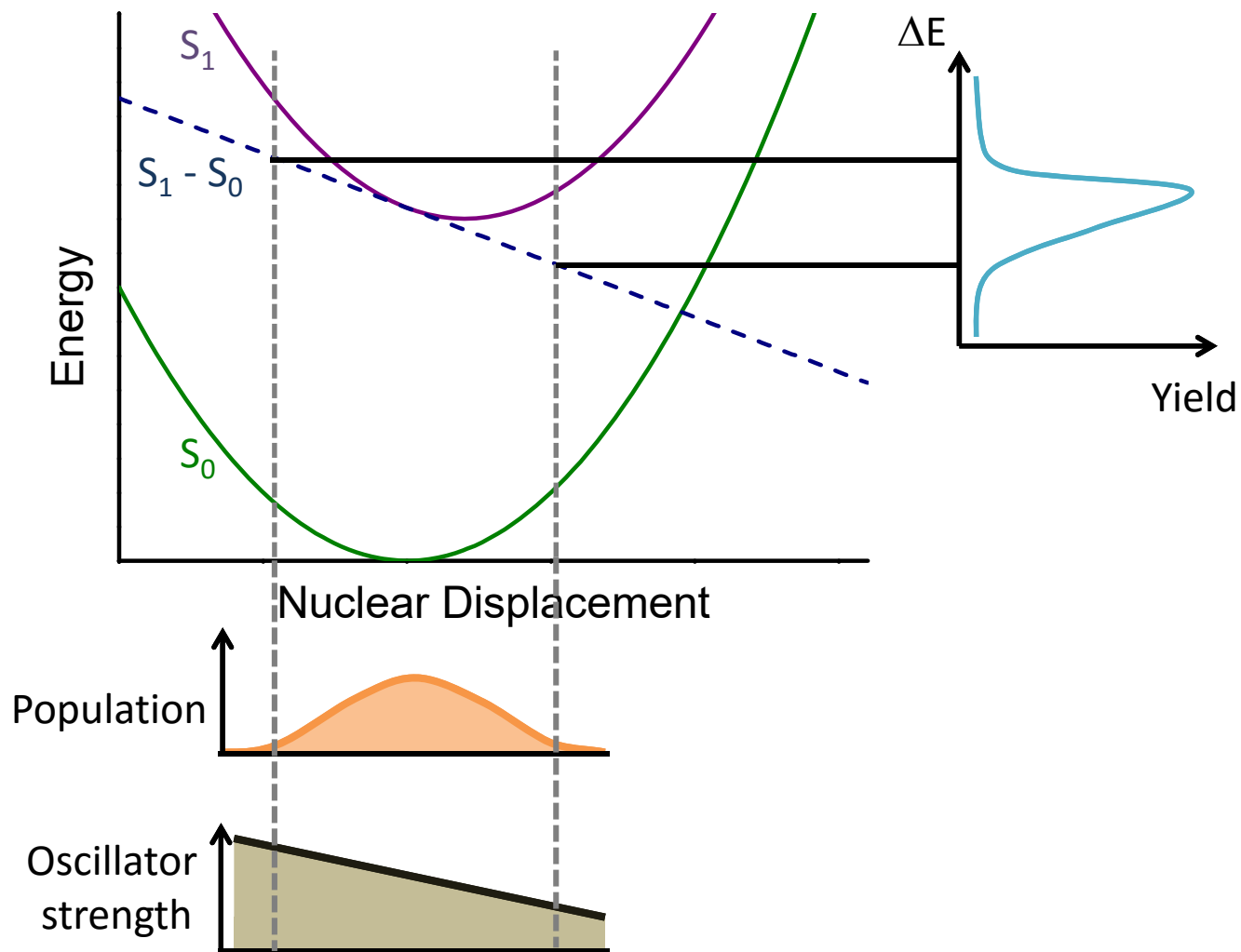
*An intuitive approach for
spectrum simulations*



Supposing that the excitation probability is constant between R_{MIN} and R_{MAX} and 0 otherwise.

More realistic case

However, excitation probability depends on the population (how many molecules) and on the oscillator strength (transition intensity).



If we know:

1. The population distribution $\{\mathbf{R}\}$
2. The excitation energies as a function of the coordinates $\Delta E(\mathbf{R})$
3. And the oscillator strength as a function of the coordinates $f(\mathbf{R})$

Then the spectrum is given by:

$$\sigma(E) \propto \sum_l^{N_p} \Delta E(\mathbf{R}_l) f(\mathbf{R}_l) g(E - \Delta E(\mathbf{R}_l), \delta_n)$$

where g is a line-shape function (Gaussian, Lorentzian).

If f is assumed constant and equal $f(\mathbf{R}_0)$, we have the Condon approximation.

With the constants and summing over all electronic states:

$$\sigma(E) = \frac{\pi e^2 \hbar}{2mc\epsilon_0 n_r E} \sum_n^{N_{fs}} \frac{1}{N_p} \sum_l^{N_p} \Delta E_{0,n}(\mathbf{R}_l) f_{0n}(\mathbf{R}_l) g(E - \Delta E(\mathbf{R}_l), \delta_n)$$

In SI units, σ is in $\text{m}^2/\text{molecule}$

1. Compute the distribution $\{\mathbf{R}\}$
(Ensemble of molecules with different geometries \mathbf{R}_n)
2. For each \mathbf{R}_n in $\{\mathbf{R}\}$ compute ΔE and f
(This is the conventional quantum chemical calculation)

3. Compute the cross section

$$\sigma(E) = \frac{\pi e^2 \hbar}{2mc\epsilon_0 n_r E} \sum_n^{N_{fs}} \frac{1}{N_p} \sum_l^{N_p} \Delta E_{0,n}(\mathbf{R}_l) f_{0n}(\mathbf{R}_l) g(E - \Delta E(\mathbf{R}_l), \delta_n)$$

4. Compare to experiments

$$\sigma = 10^3 \ln(10) \frac{\epsilon}{N_A}$$

Pros:

- Easy to use
- Absolute heights
- Absolute widths
- Post-Condon Approximation:
 - ✓ Dark vibronic bands

Cons:

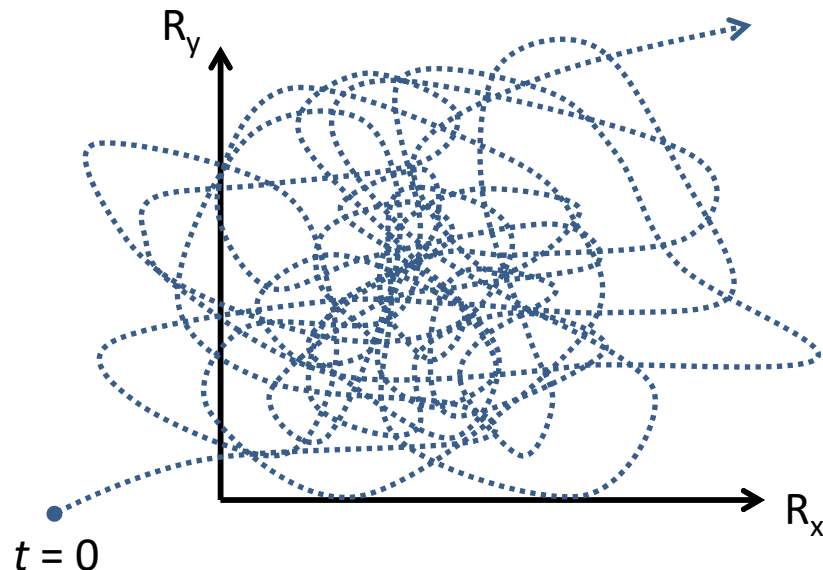
- No info on excited-state wave function:
 - ✓ No vibrational resolution
 - ✓ No nonadiabatic effects
- One arbitrary parameter
- It costs about 200-500 single point calculations



Computing the ensemble $\{\mathbf{R}\}$

Method 1: Trajectories

Run trajectories in the ground state.



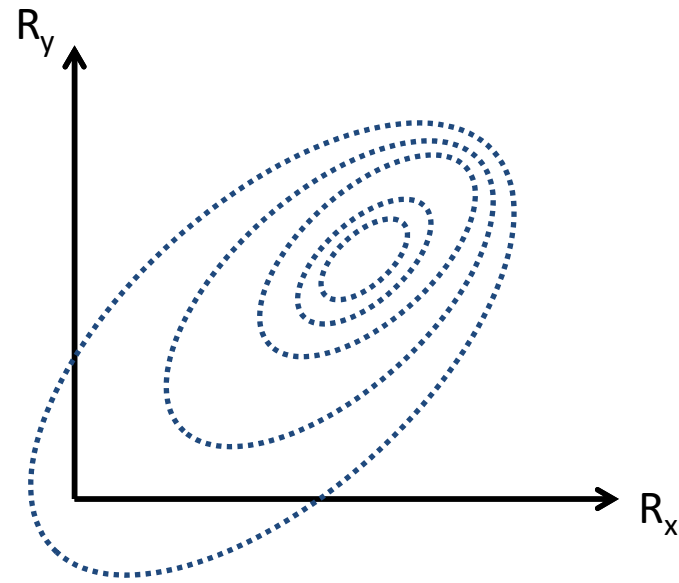
After a long time (~ 1 ns), the distribution of points will reflect the probability of finding the molecule with each \mathbf{R} .

Pick up ~ 500 points from the trajectories to compute σ .

Velocities are available too.

Method 2: Quantum distributions

If we know the nuclear wave function $\chi_{00}(\mathbf{R})$ in the ground state, we can sample $\{\mathbf{R}\}$ from the distribution $|\chi_{00}(\mathbf{R})|^2$.



It is particularly simple to use this method if we suppose that the nuclei vibrate harmonically along the normal modes \mathbf{q}

$$|\chi_{00}(\mathbf{q})|^2 \propto \prod_{i=1}^{3N-6} \exp(-\mu_i \omega_i q_i^2 / \hbar)$$

Velocities are not available.

Still Method 2: Wigner Distributions

According to Wigner, a quantum density can be projected on the classical phase space by

$$P_W(\mathbf{R}, \mathbf{P}) = (\pi\hbar)^{-3N_{at}} \int d\boldsymbol{\eta} \chi^*(\mathbf{R} + \boldsymbol{\eta}) \chi(\mathbf{R} - \boldsymbol{\eta}) \exp(2i\boldsymbol{\eta} \cdot \mathbf{P} / \hbar)$$

For a molecule represented as $3N_{at}-6$ quantum harmonic oscillators in the vibrational ground state, P_W is:

$$P_W(\mathbf{q}, \mathbf{p}) = \frac{1}{(\pi\hbar)^{3N_{at}-6}} \prod_{i=1}^{3N_{at}-6} \exp\left(\frac{-q_i^2}{2\sigma_{qi}^2}\right) \exp\left(\frac{-p_i^2}{2\sigma_{pi}^2}\right)$$
$$\sigma_{qi}^2 = \frac{\hbar}{2\mu_i\omega_i} \quad \sigma_{pi}^2 = \frac{\hbar\mu_i\omega_i}{2}$$

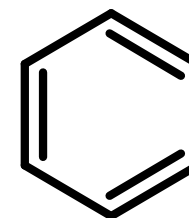
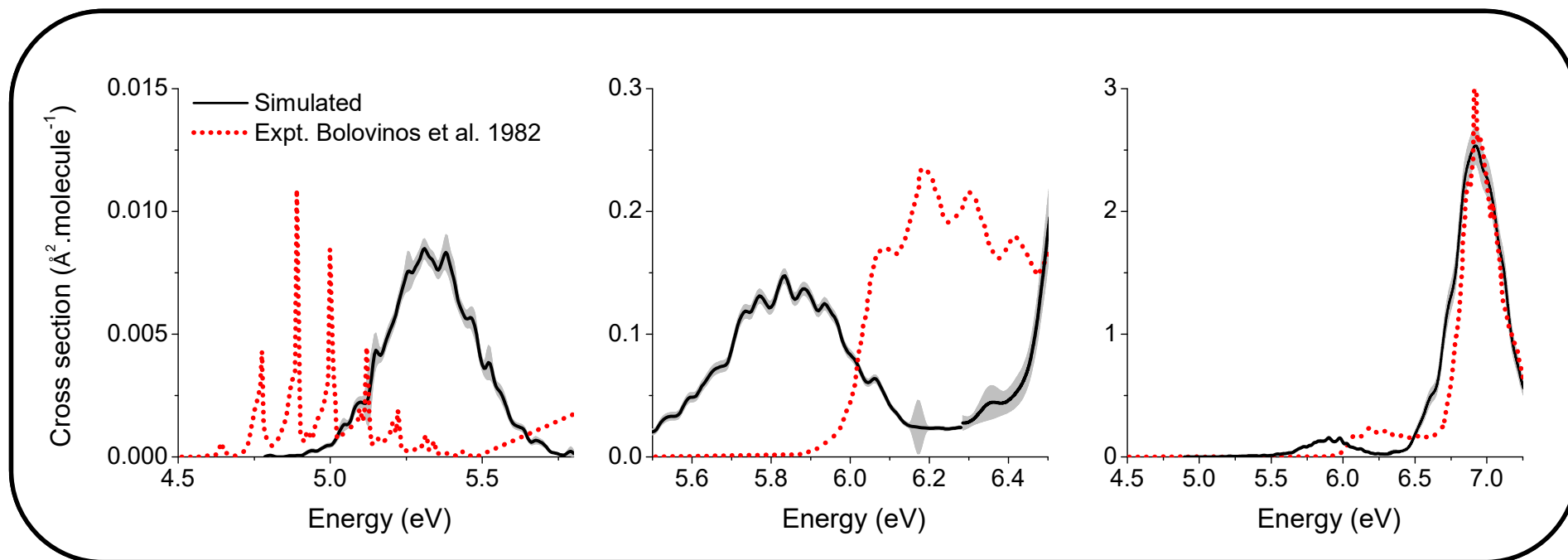
Velocities are available.

- Schinke, Photodissociation Dynamics, Cambridge, 1993.

Examples



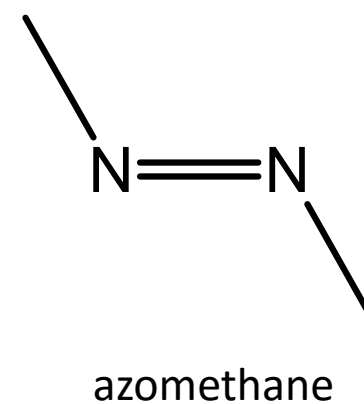
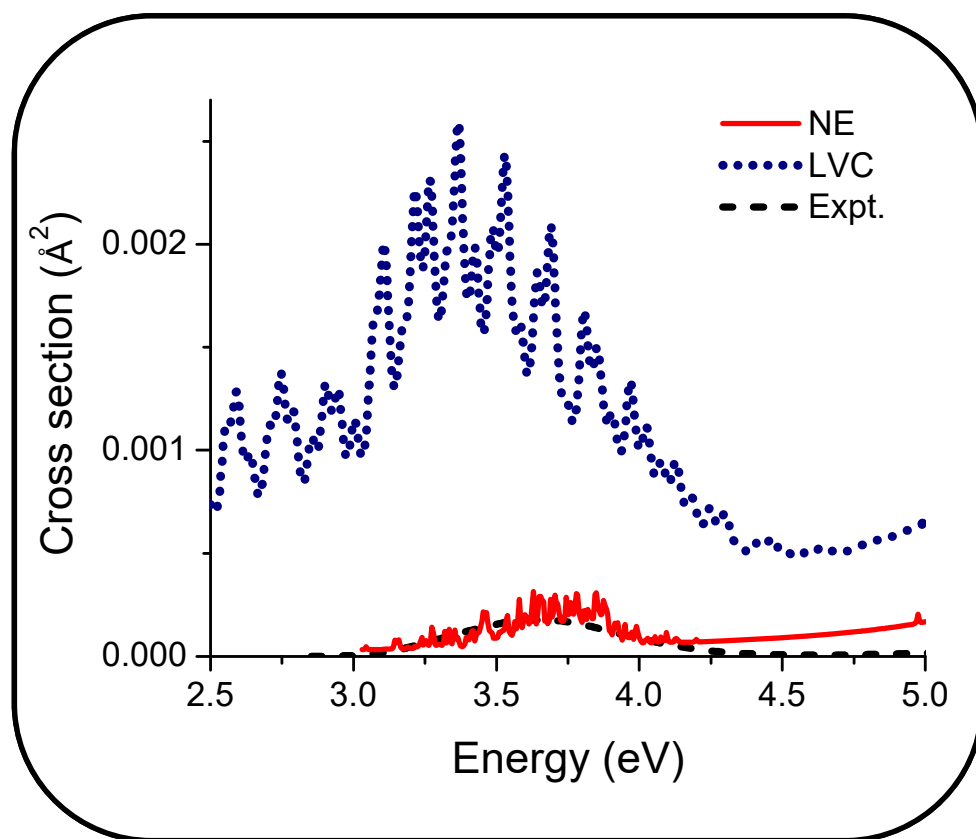
Several orders of magnitude



- Crespo-Otero, Barbatti, Theor Chem Acc **131**, 1237 (2012)

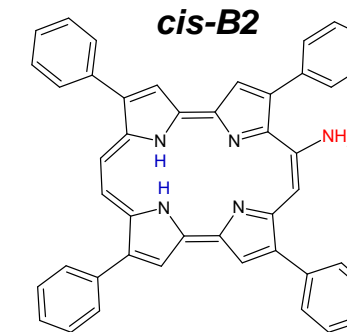
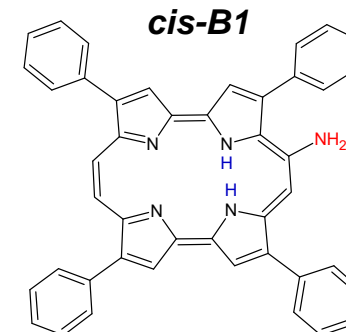
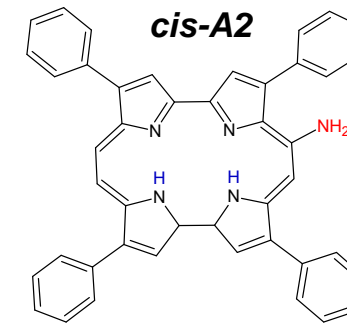
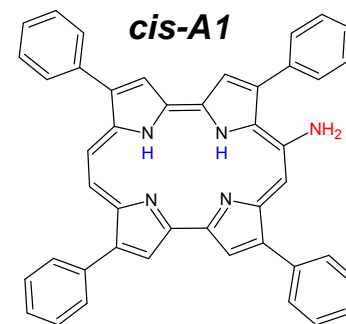
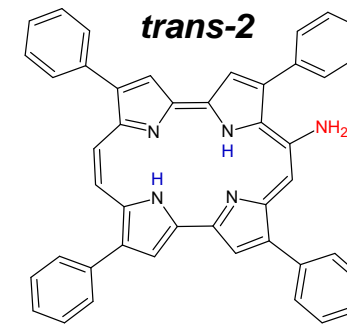
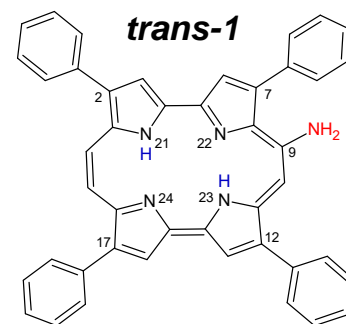
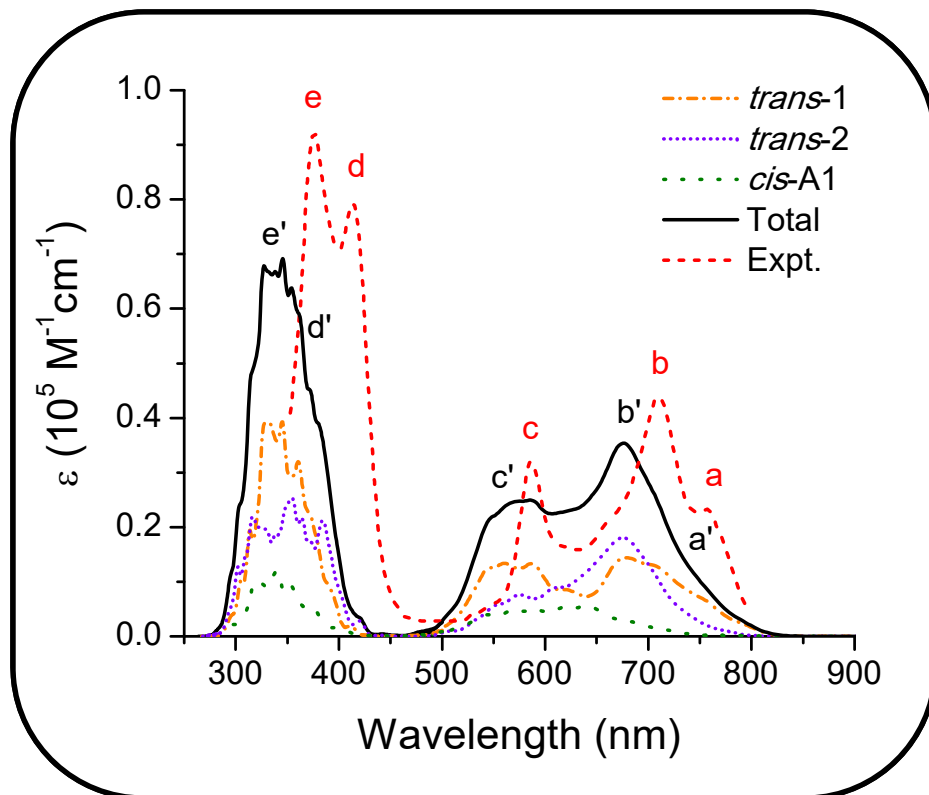
Dark bands, vibronic coupling

LIGHT AND
MOLECULES



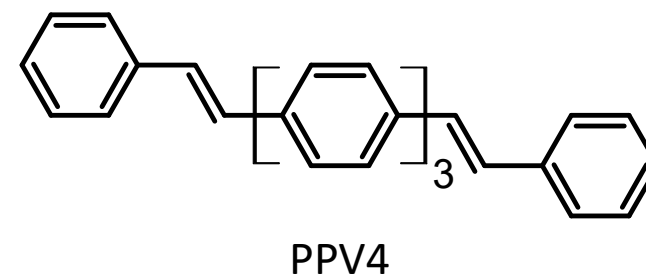
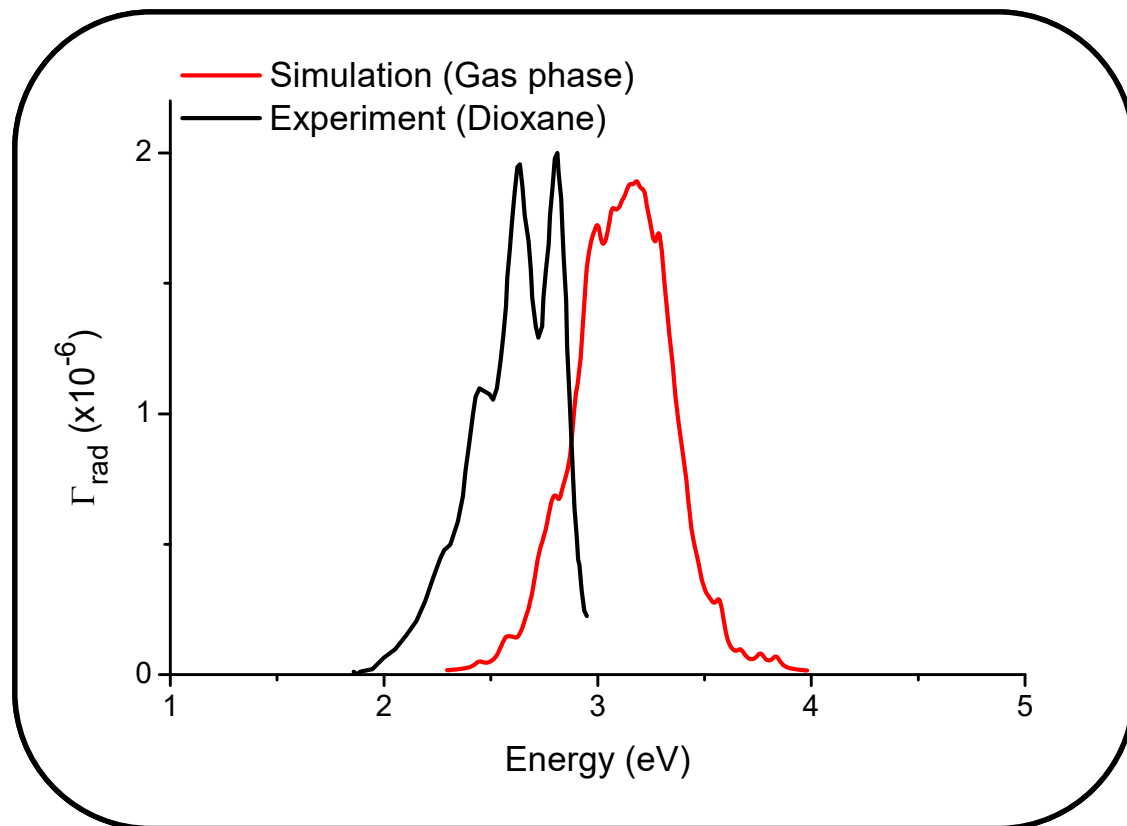
- Szalay, Aquino, Barbatti, Lischka, Chem Phys **380**, 9 (2011)

Tautomeric effects

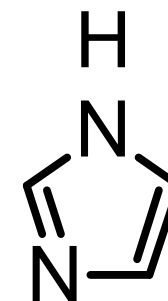
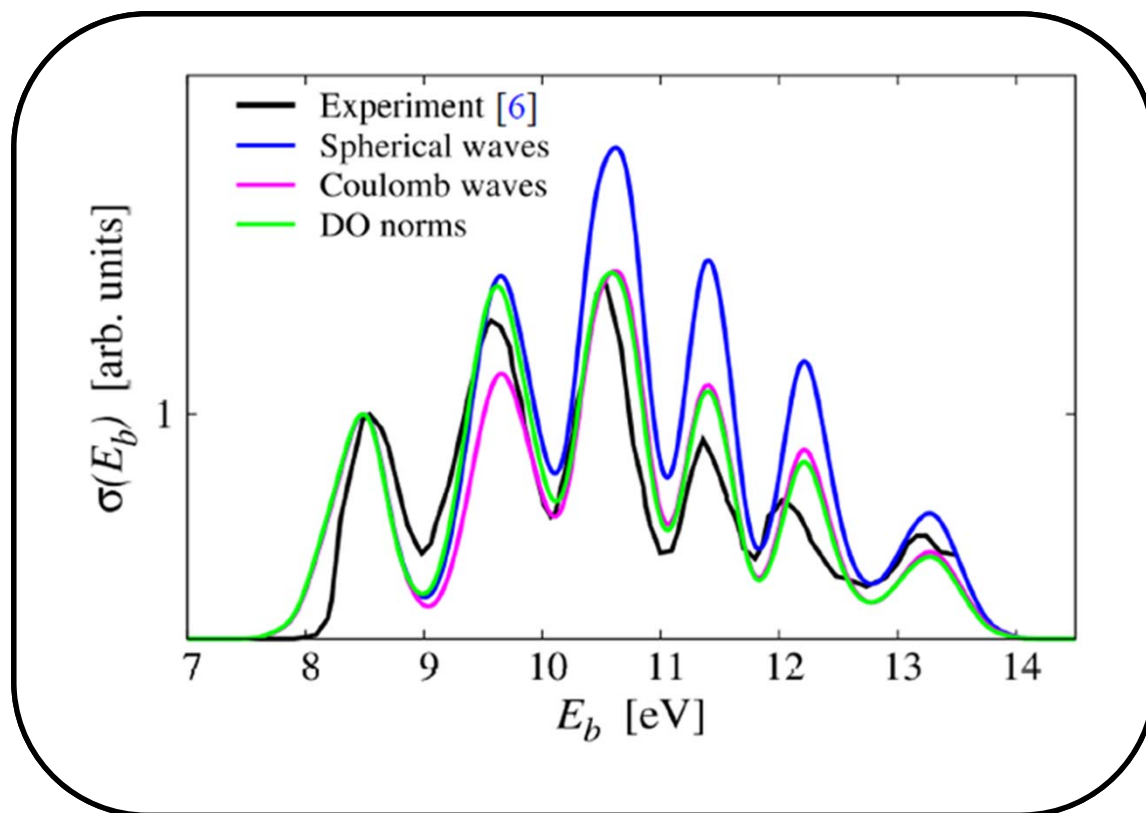


- Lan, Nonell, Barbatti, J Phys Chem A **116**, 3366 (2012)

Porphycene



- Cardozo, Aquino, Barbatti, Borges Jr., Lischka, J Phys Chem A **119**, 1787 (2015)



imidazole

- Arbelo-González, Crespo-Otero, Barbatti, in preparation (2015)



*Nuclear Ensemble Approach:
Formal Aspects*

First order of the time-dependent perturbation theory

$$\sigma(E) = \frac{\pi}{3\hbar c \epsilon_0 n_r E} \sum_{n,k} \int |\Delta E_{00,nk}(\mathbf{R}) \chi_{00}^*(\mathbf{R}) \langle \phi_0 | \mu(\mathbf{r}, \mathbf{R}) | \phi_n \rangle_{\mathbf{r}} \chi_{nk}(\mathbf{R})|^2 \delta(\Delta E_{00,nk}(\mathbf{R}) - E) d\mathbf{R}$$

$$\Delta E_{00,nk} = E_{nk} - E_{00} + \Delta E_{0,n}$$

The problem can be recast in the time domain:

$$\sigma(E) = \frac{1}{6\hbar^2 c \epsilon_0 n_r E} \sum_n \text{Re} \int \Delta E_{0,n}^2(\mathbf{R}) M_{0n}^2(\mathbf{R}) \left[\int \chi_{00}^*(\mathbf{R}) \chi_n(\mathbf{R}, t) e^{i(E+E_{00})t/\hbar} dt \right] d\mathbf{R}$$

$$M_{0n}(\mathbf{R}) = \langle \phi_0 | \mu_e(\mathbf{r}; \mathbf{R}) | \phi_n \rangle_{\mathbf{r}} \quad \Delta E_{0,n} \approx \langle \Delta E_{00,nk} \rangle_k$$

$$|\chi_n(t)\rangle = e^{-iH_n t/\hbar} |\chi_{00}\rangle$$

- Sakurai (1994) Modern Quantum Mechanics
- Tannor, Heller, J Chem Phys 77, 202 (1982)

The core of the method is to compute the overlap

$$\varphi(\mathbf{R}, t) = \chi_{00}^*(\mathbf{R}) \chi_n(\mathbf{R}, t)$$

needed to integrate

$$\sigma(E) = \frac{1}{6\hbar^2 c \epsilon_0 n_r E} \sum_n \operatorname{Re} \int \Delta E_{0,n}^2(\mathbf{R}) M_{0n}^2(\mathbf{R}) \left[\int \chi_{00}^*(\mathbf{R}) \chi_n(\mathbf{R}, t) e^{i(E+E_{00})t/\hbar} dt \right] d\mathbf{R}$$

Tannor and Heller proposed an analytical solution based on harmonic oscillators

$$\langle \chi_{00} | \chi_n(t) \rangle = \exp \left[\sum_j \left(\frac{-\Delta_{nj}^2}{2} (1 - e^{-i\omega_j t}) - \frac{i\omega_j t}{2} \right) + \frac{i}{\hbar} \Delta E_{0,n}^a t \right]$$

But we want to go beyond the Condon approximation.

Starting from Tannor-Heller equation:

$$\langle \chi_{00} | \chi_n(t) \rangle = \exp \left[\sum_j \left(\frac{-\Delta_{nj}^2}{2} (1 - e^{-i\omega_j t}) - \frac{i\omega_j t}{2} \right) + \frac{i}{\hbar} \Delta E_{0,n}^a t \right]$$

The expansion to second order is

$$\langle \chi_{00} | \chi_n(t) \rangle \approx \exp \left[-i \left(\frac{1}{2} \sum_j (\Delta_{nj}^2 + 1) \omega_j + \omega_{0n}^a \right) t - \frac{1}{2} \left(\sum_j \Delta_{nj}^2 \omega_j^2 \right) t^2 \right]$$

This motivates to introduce the following functional:

$$\chi_{00}^* \chi_n(\mathbf{R}, t) = |\chi_{00}(\mathbf{R})|^2 \exp \left[-\frac{i}{\hbar} \Delta E_{0,n}(\mathbf{R}) t - \frac{i}{\hbar} \varepsilon_n t - \frac{i}{\hbar} E_{00} t - \frac{1}{8\hbar^2} \delta_n^2 t^2 \right]$$

- Crespo-Otero, Barbatti, Theor Chem Acc **131**, 1237 (2012)

$$\chi_{00}^* \chi_n(\mathbf{R}, t) = |\chi_{00}(\mathbf{R})|^2 \exp \left[-\frac{i}{\hbar} \Delta E_{0,n}(\mathbf{R}) t - \frac{i}{\hbar} \varepsilon_n t - \frac{i}{\hbar} E_{00} t - \frac{1}{8\hbar^2} \delta_n^2 t^2 \right]$$



$$\sigma(E) = \frac{1}{6\hbar^2 c \varepsilon_0 n_r E} \sum_n \text{Re} \int \Delta E_{0,n}^2(\mathbf{R}) M_{0n}^2(\mathbf{R}) \left[\int \chi_{00}^*(\mathbf{R}) \chi_n(\mathbf{R}, t) e^{i(E+E_{00})t/\hbar} dt \right] d\mathbf{R}$$



$$\sigma(E) = \frac{\pi \hbar e^2}{2mc \varepsilon_0 n_r E} \sum_n \int |\chi_{00}(\mathbf{R})|^2 \Delta E_{0,n}(\mathbf{R}) f_{0n}(\mathbf{R}) g_{Gauss}(E - \Delta E_{0,n}(\mathbf{R}) - \varepsilon_n(\mathbf{R}), \delta_n) d\mathbf{R}$$

$$g_{Gauss}(E - \Delta E_{0,n}(\mathbf{R}) + \varepsilon_n(\mathbf{R}), \delta_n) = \frac{1}{(2\pi(\delta_n/2)^2)^{1/2}} \exp \left(\frac{-(E - \Delta E_{0,n}(\mathbf{R}) - \varepsilon_n)^2}{2(\delta_n/2)^2} \right)$$

$$\sigma(E) = \frac{\pi \hbar e^2}{2mc\varepsilon_0 n_r E} \sum_n \int |\chi_{00}(\mathbf{R})|^2 \Delta E_{0,n}(\mathbf{R}) f_{0n}(\mathbf{R}) g(E - \Delta E_{0,n}(\mathbf{R}) - \varepsilon_n(\mathbf{R}), \delta_n) d\mathbf{R}$$

If we have a ground-state distribution of points $\{\mathbf{R}_l\}$

We can integrate the cross section by Monte-Carlo and get:

$$\sigma(E) = \frac{\pi e^2 \hbar}{2mc\varepsilon_0 n_r E} \sum_n \frac{1}{N_p} \sum_l \Delta E_{0,n}(\mathbf{R}_l) f_{0n}(\mathbf{R}_l) g(E - \Delta E(\mathbf{R}_l), \delta_n)$$

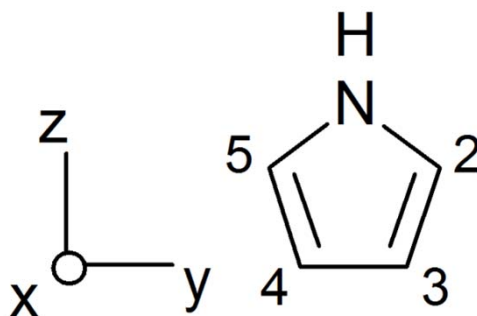


Effects of different samplings

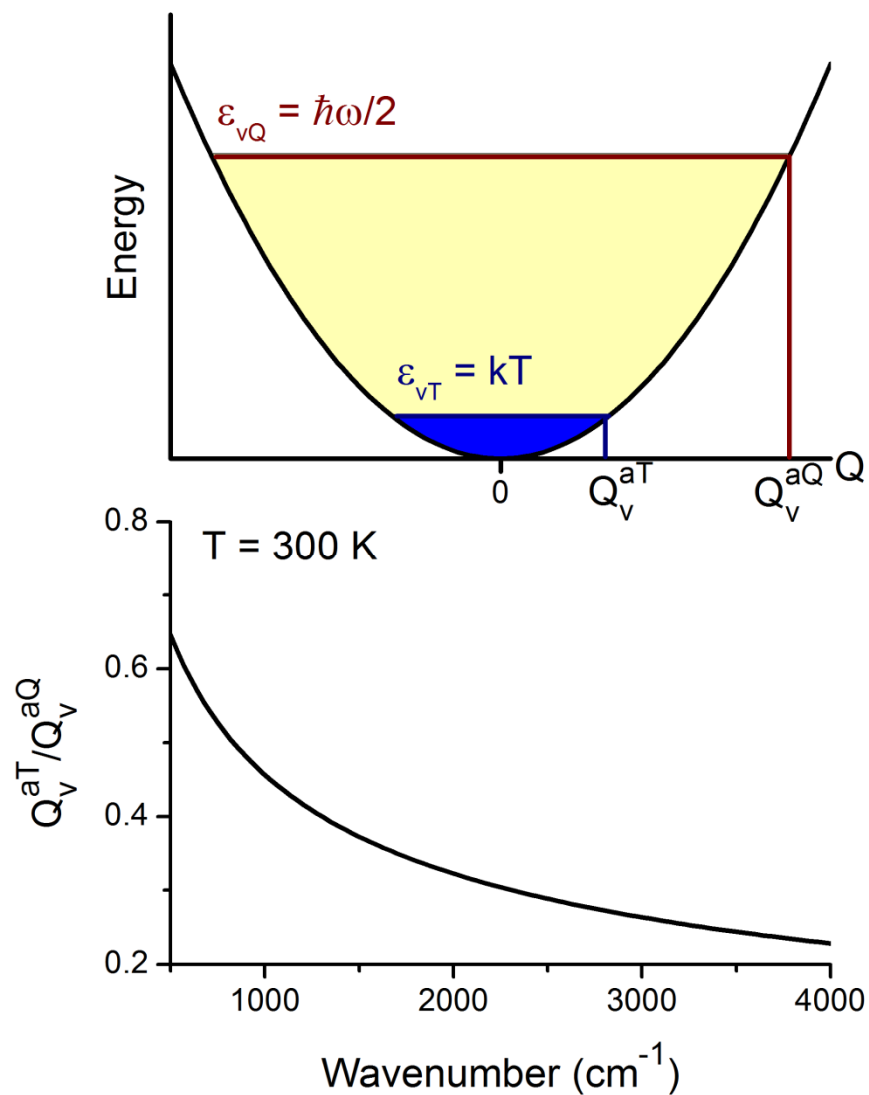
To make spectrum and select initial conditions for excited state dynamics, we need an ensemble of geometries and velocities representing the ground state distribution.

How much different is to sample them either with a Quantum distribution (Wigner) or with a Thermal distribution (trajectory)?

Let's check that for pyrrole.



- Barbatti and Sen, Int J Quantum Chem (2015)

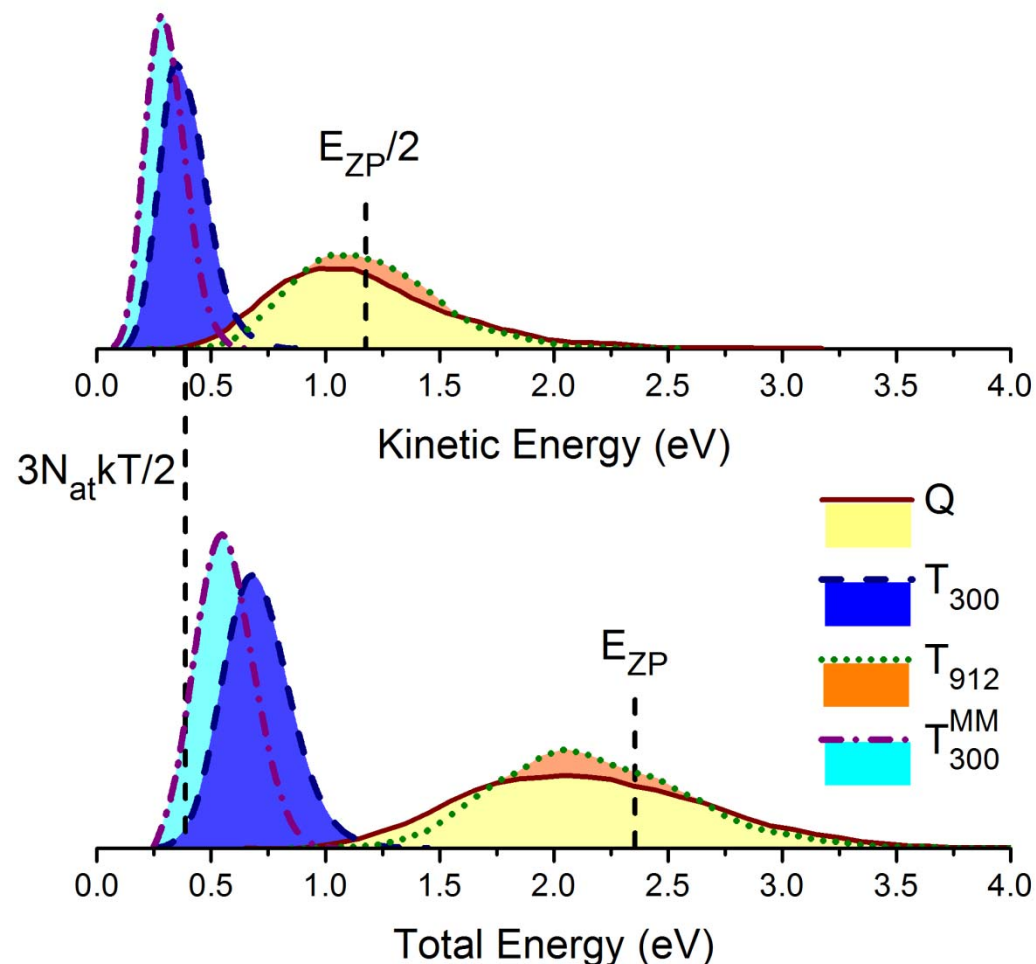


Thermal amplitudes at 300 K are much smaller than quantum amplitudes with zero-point energy.

This difference is specially important for large wavenumbers.

TxQ Ground-state energies in the ensemble

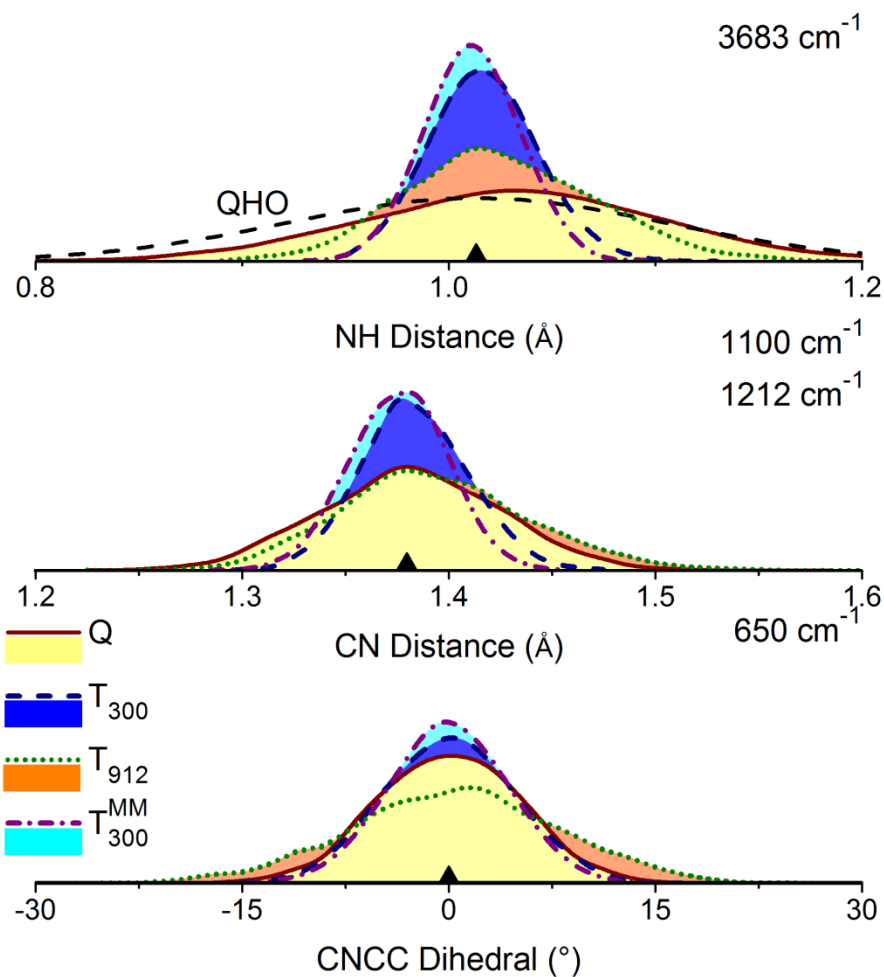
LIGHT AND
MOLECULES



The ground state energy distribution in a Q ensemble and in a T ensemble are completely different.

We could raise the temperature until it matches ZPE. For pyrrole, this happens at ~900 K. The distribution looks good.

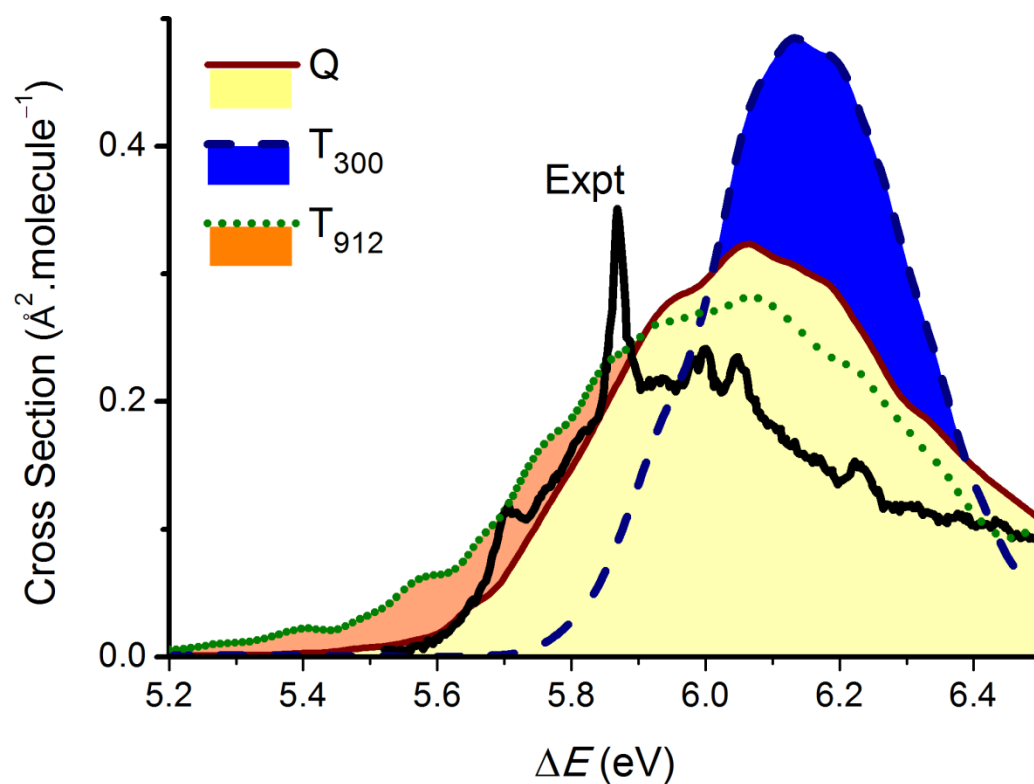
TxQ geometries in the ensemble



The Q distribution of geometries is much broader than the T.

The effect is larger for bigger wavenumbers.

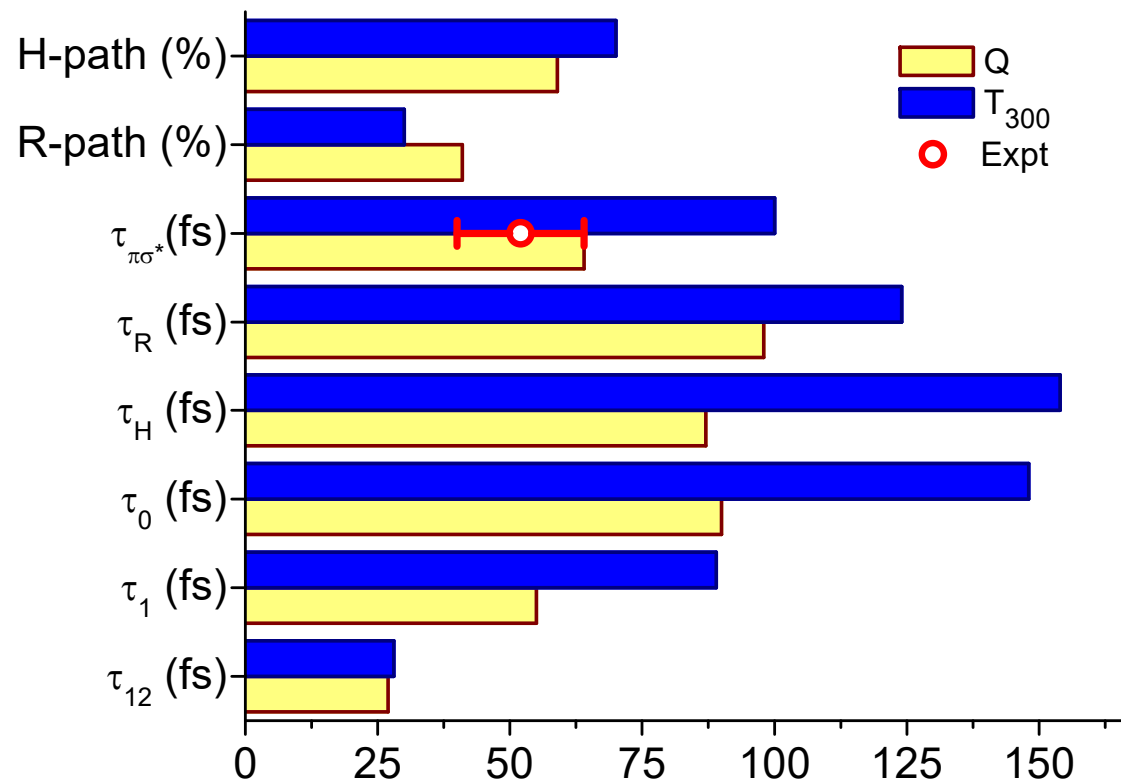
The 900 K distribution has artifacts for small and large wavenumbers.



The spectrum is qualitatively wrong
for T.

It is much better for Q.

900 K is not bad.



Qualitatively, the results are similar.

However, T dynamics is slower than Q.

The distribution of paths is also different.

Q matches better the experiments.

Initial conditions

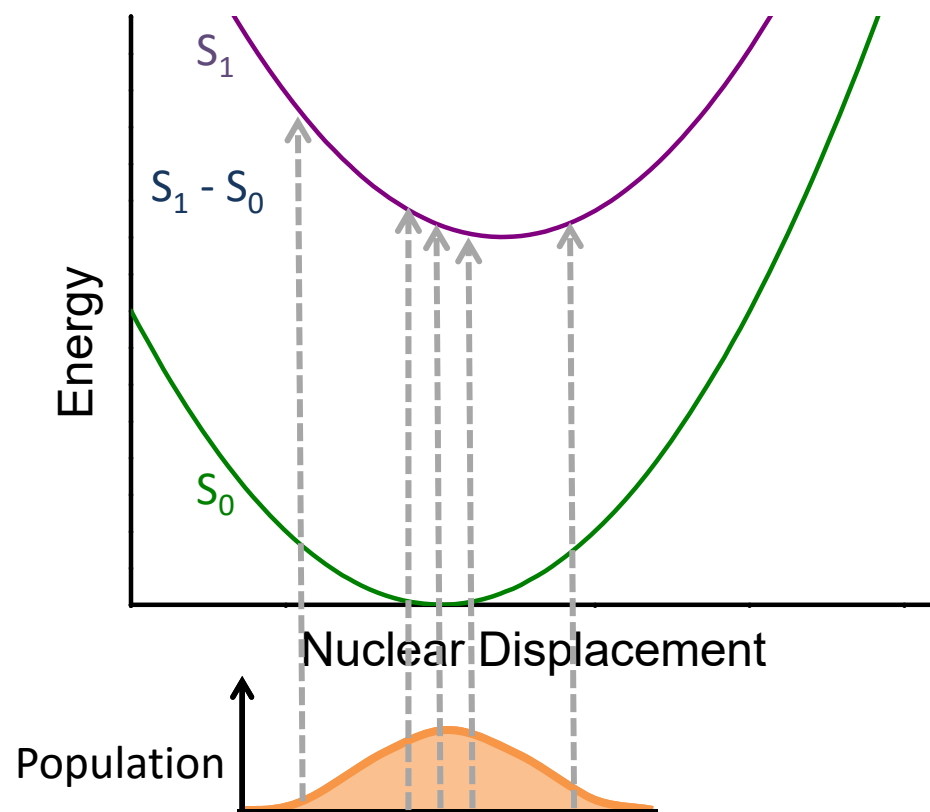


To initiate the simulation of a trajectory we need initial coordinates and initial velocities of the nuclei.

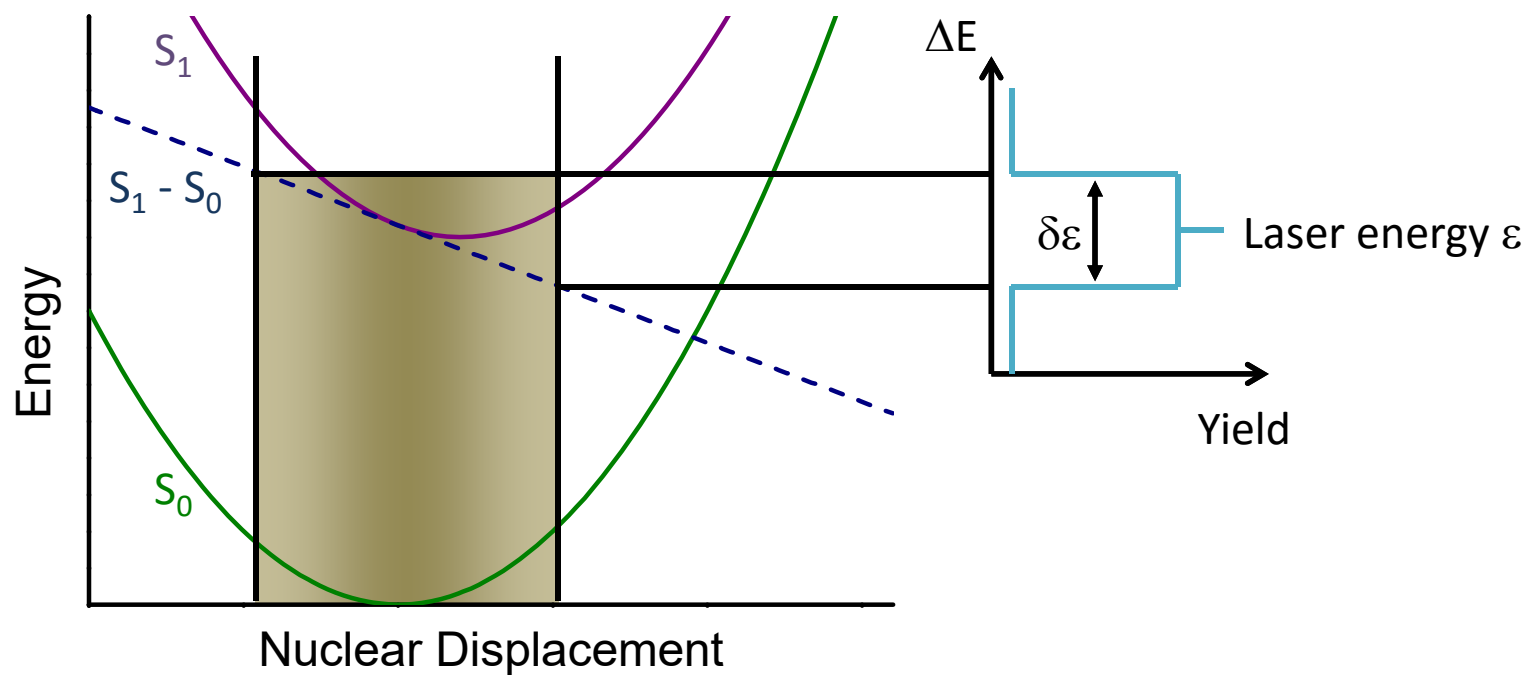
To get them, we may use the same methods that we have discussed for spectrum simulations.

Using either trajectories or quantum distributions, we can build an ensemble of $\{\mathbf{R}, \mathbf{P}\}$ points.

Simulations of excited-state trajectories have a very clear starting point: The photo excitation, which is taken as instantaneous and defining $t = 0$.

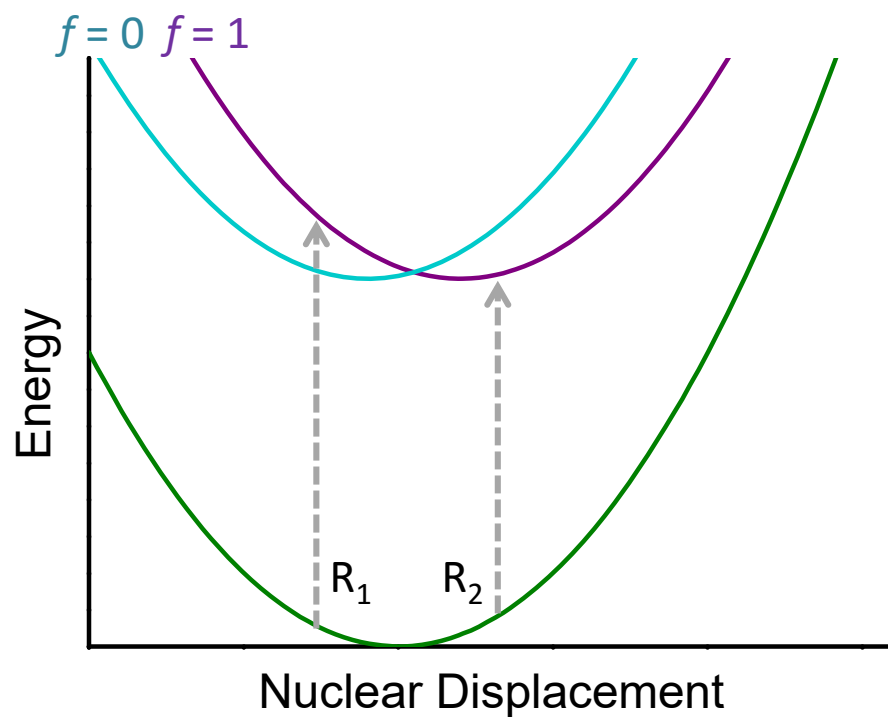


A monochromatic excitation may be set by accepting only **(R,P)** points for which $\varepsilon - \delta\varepsilon < \Delta E < \varepsilon + \delta\varepsilon$

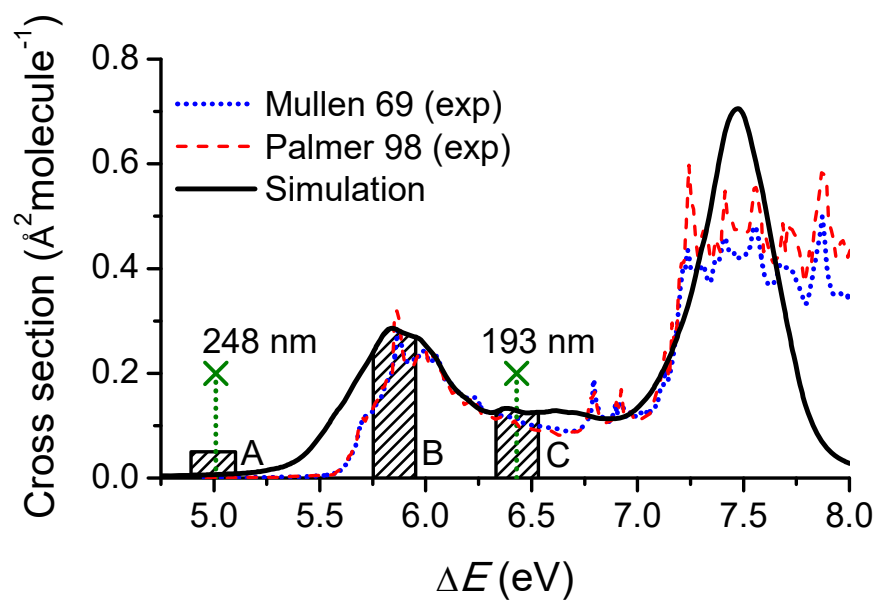


We should take care of state crossings.

In this example, geometry R_1 should start in S_2 , while R_2 should start in S_1 .



Example: Pyrrole



Number of trajectories starting in each state and in each energy window.

State	Window A 4.90-5.10 eV	Window B 5.75-5.95 eV	Window C 6.33-6.53 eV
S_1	15	0	0
S_2	0	5	0
S_3	0	6	0
S_4	0	31	0
S_5	0	13	2
S_6	0	0	8
S_7	0	0	8
S_8	0	0	15
S_9	0	0	12
S_{10}	0	0	1
Total	15	55	46

- Barbatti, Pittner, Pederzoli, Werner, Mitric, Bonacic-Koutecky, Lischka, Chem Phys **375**, 26 (2010)

- Surface hopping is one of the most used approach for nonadiabatic dynamics simulations of molecules.
- It describes internal conversion well.
- It fails for global quantum effects.