HANDS-ON SESSION

Excited States Mixed Quantum-Classical Dynamics

Initial conditions sampling and Surface Hopping Dynamics

Josene M. Toldo
Université Claude Bernard Lyon1,
Laboratoire de Chimie, ENS de Lyon

LABORATOIRE DE CHIMIE ENS DE LYON

Université Claude Bernard Lyon 1

Overview of the Hands-on sessions

1. Initial conditions and Spectrum generation

Method overview

Generating a Wigner sampling

Simulating the absorption spectra

Selecting initial conditions for the dynamics

2. Surface hopping dynamics

Method overview

Setting up a CASPT2 dynamics with OpenMolcas

Setting up a TDDFT dynamics with ORCA

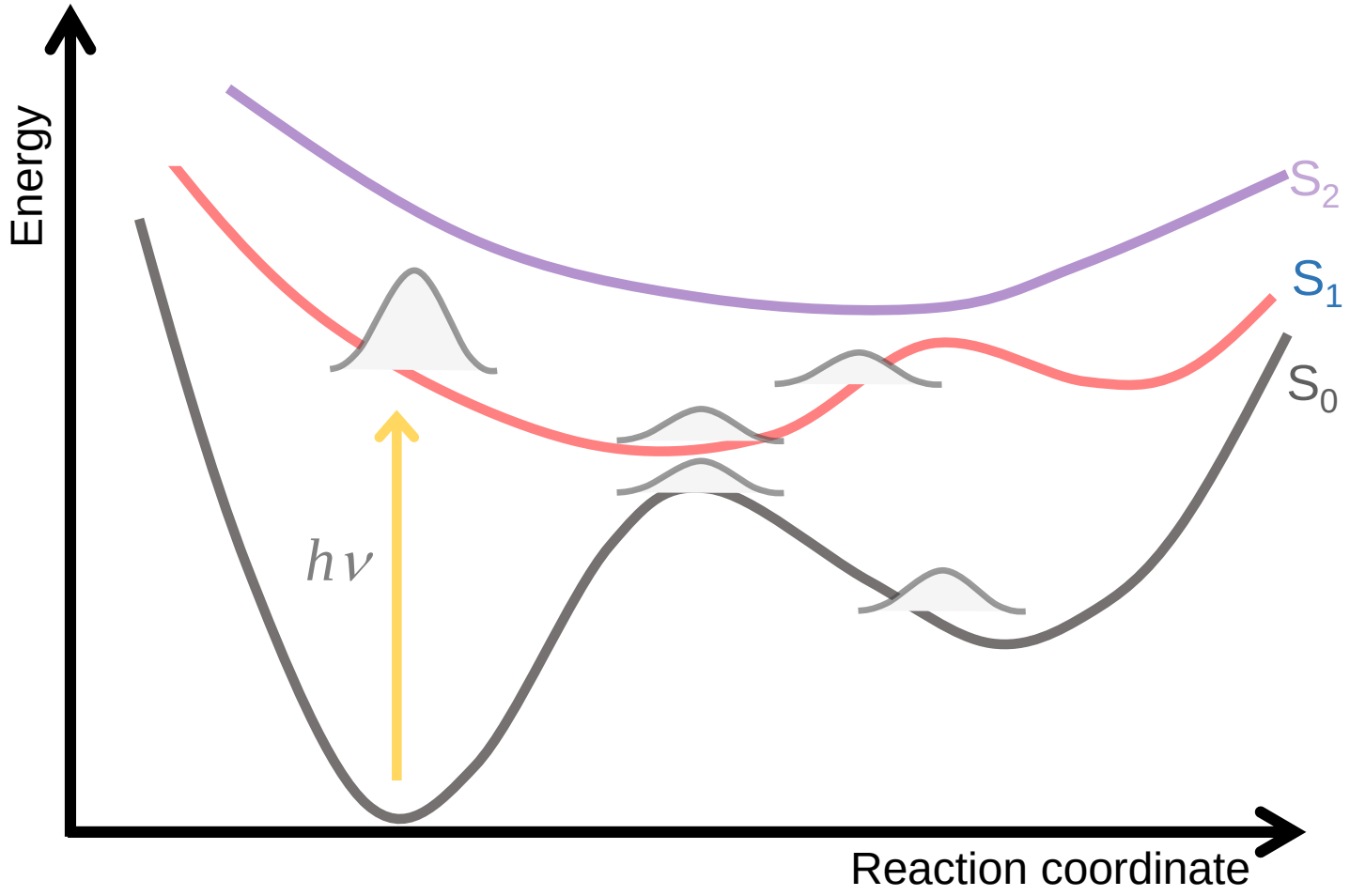
Running a TSH dynamics

3. Analysis

Running Ulamdyn for the statistical analysis

Analysing the results

Excited States Dynamics

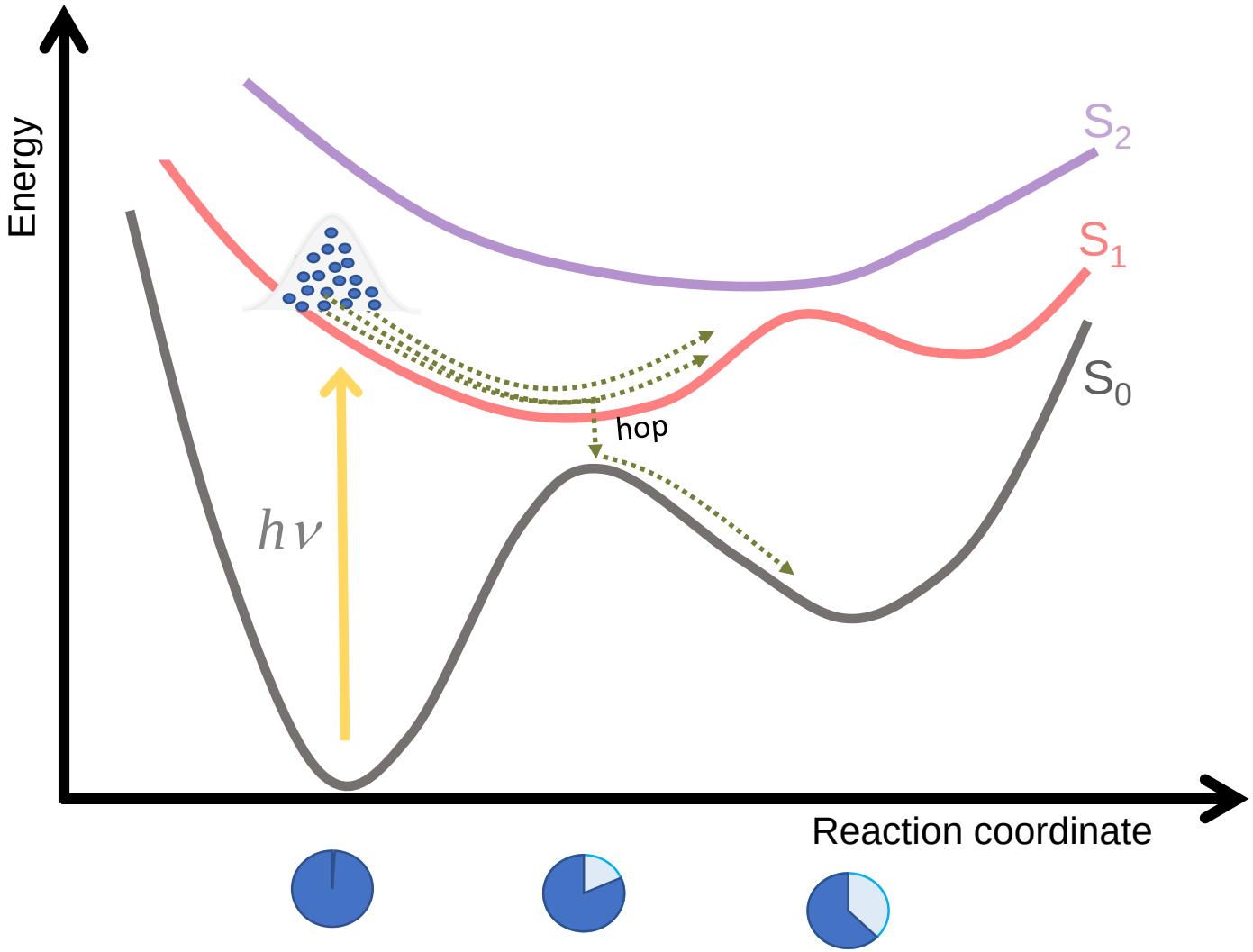


Photoinduced processes involves the **time evolution of the nuclear wavepacket** through a manifold of excited states.

Requires considering the coupling between electronic and nuclear motions.
Nonadiabatic regime

Breakdown of BO approximation.

Trajectory Surface hopping (TSH)



Core idea:

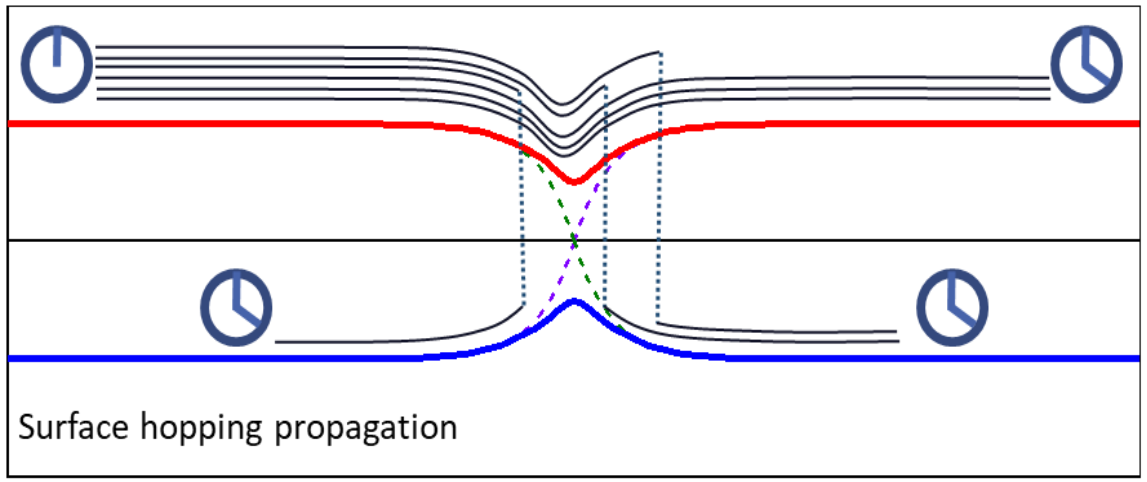
1. Nuclei are propagated via *classical trajectories*

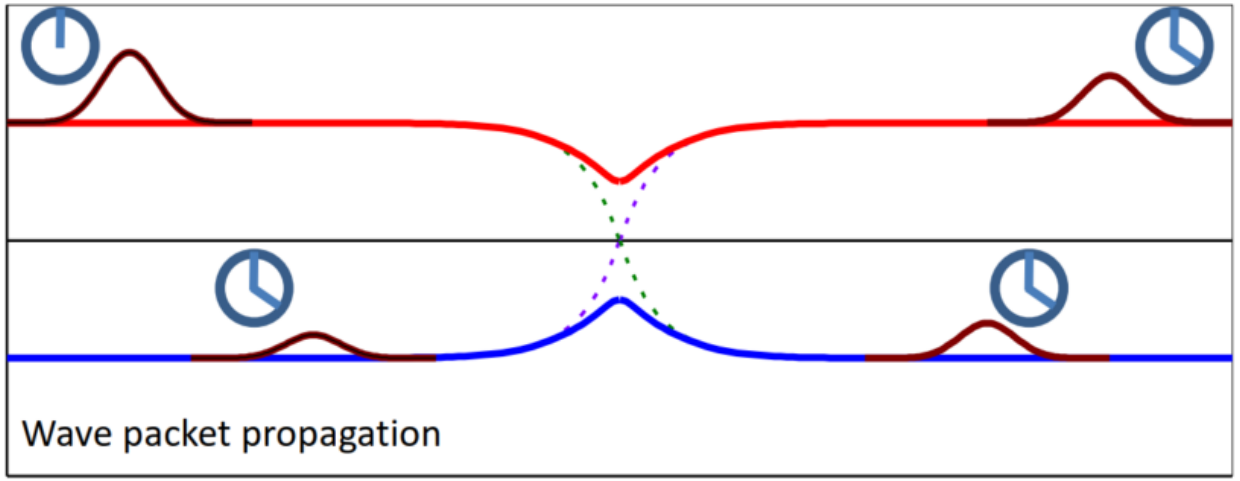
2. Electrons are treated *quantum mechanically*

3. Changes between surfaces are controlled by a nonadiabatic algoritm which introduces the post BO effects.

Crespo-Otero and Barbatti, Chem. Rev. **2018**, *118*, 7026.

Trajectory Surface hopping (TSH)

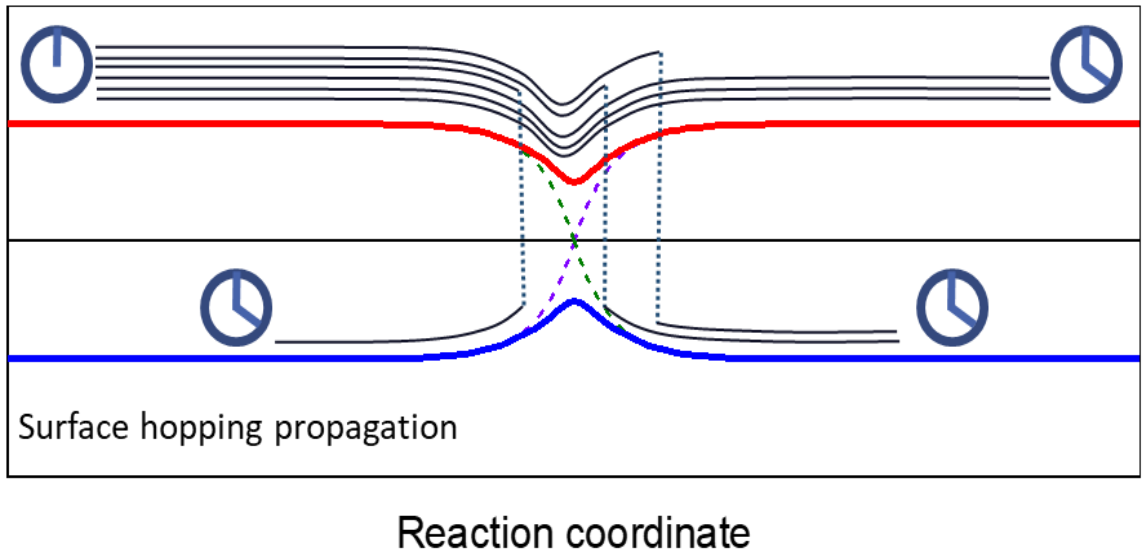


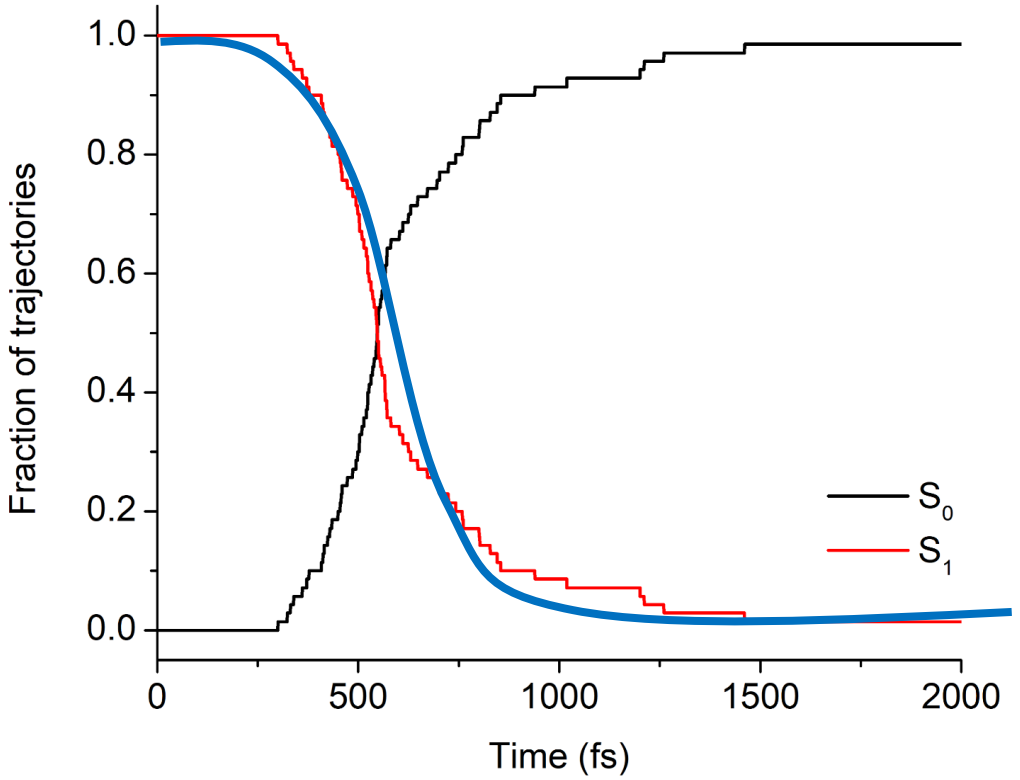


A swarm of independent trajectories are propagated adiabatically to mimic the wavepacket.

Crespo-Otero and Barbatti, Chem. Rev. **2018**, *118*, 7026.

Trajectory Surface hopping (TSH)





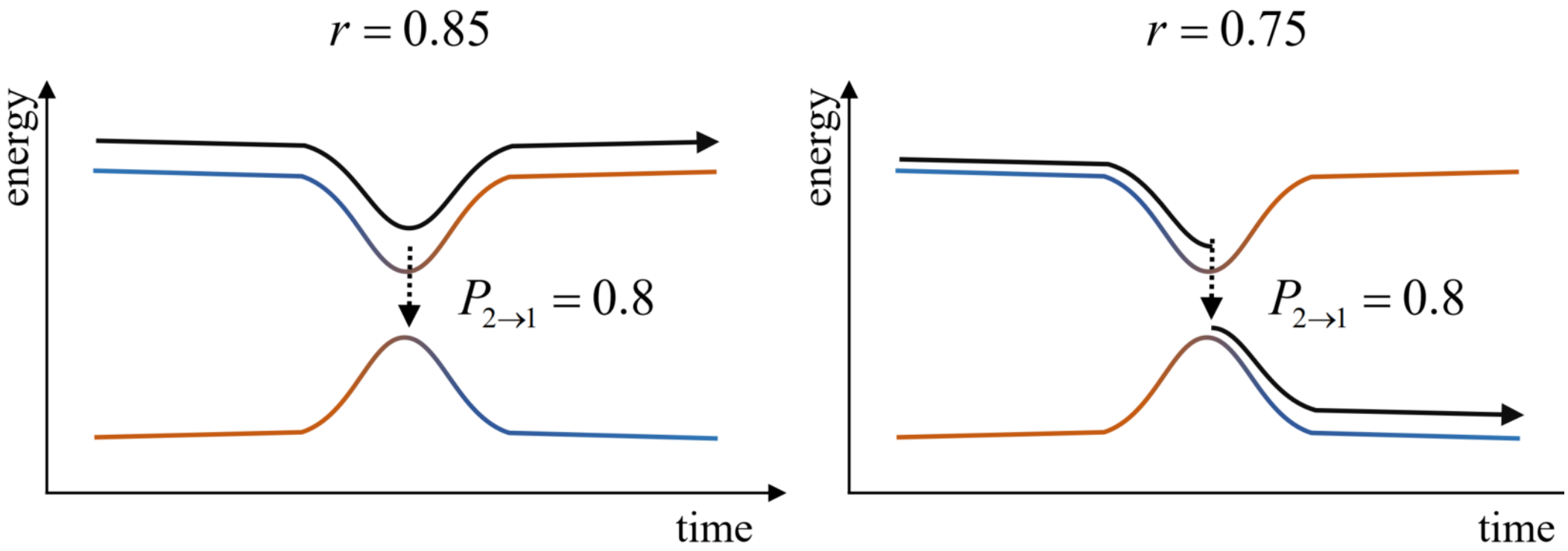
Ensemble of independent trajectories

Statistical treatment to get electronic populations

Crespo-Otero and Barbatti, Chem. Rev. **2018**, *118*, 7026.

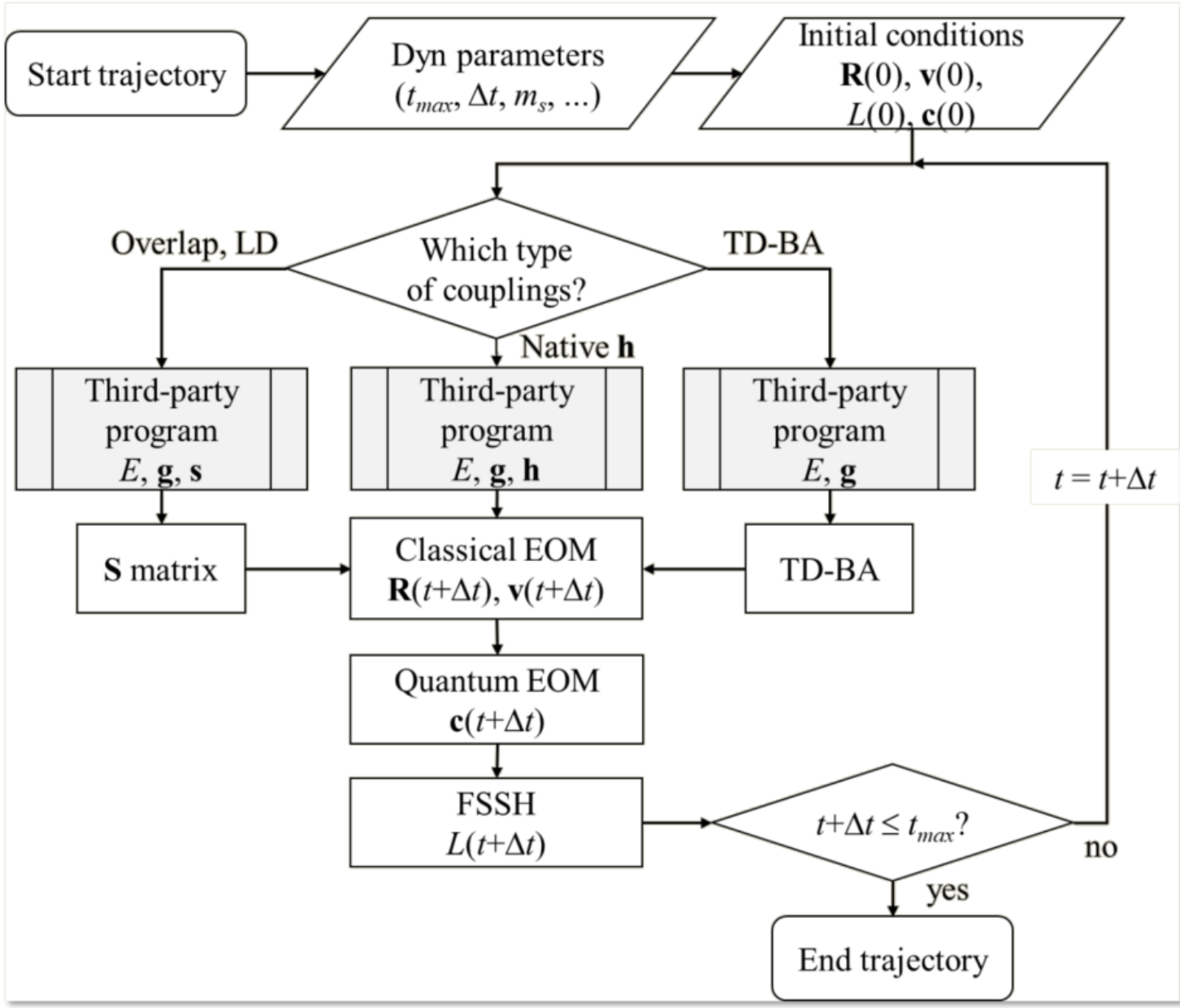
Trajectory Surface hopping (TSH)

Hops to a different potential surface in regions of near-degeneracy between surfaces.



The probability of these stochastic hops is governed by the magnitude of the non-adiabatic coupling.

How TSH works?



Initial conditions and Spectrum

https://newtonx.org/documentation-tutorials/

How to sample initial conditions?

To initiate the simulation of a trajectory we need initial conditions.

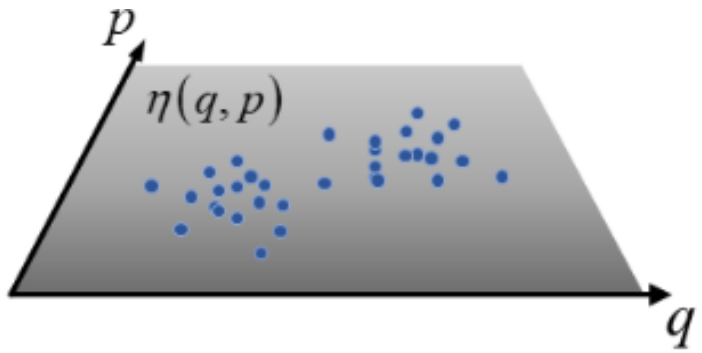
- Initial geometry — geom file
- Initial velocity — veloc file
- Initial electronic state — control.dyn: NSTATDYN
- Initial TDSE coefficients — wf.inp (optional)

To get them , we build an ensemble of nuclear points with coordinates and momenta {R, P}

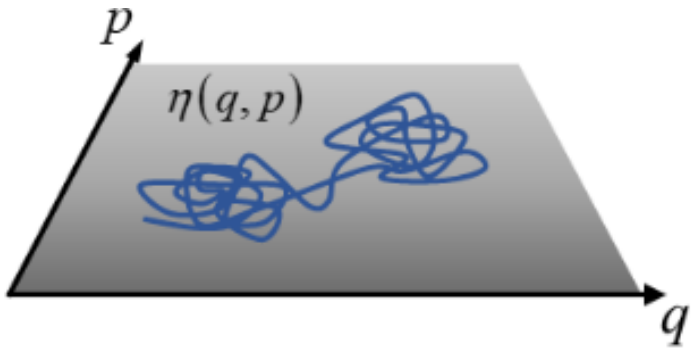
Sampling initial conditions

To initiate the simulation of a trajectory we need initial conditions.
They can be sampled using:

- Method 1: Probability distribution functions
  - Classical harmonic oscillator
  - **Uncorrelated Quantum Harmonic Oscillator (Wigner Distribution)**
  - Correlated quantum Harmonic Oscillator



- Method 2: Pick up points from previous long trajectory in the ground state



- Method 3: Random velocities

Barbatti; Sen. *Int J Quantum Chem* **2016,** *116*, 762

Sampling initial conditions

Wigner Distribution: link a wavefunction to a probability distribution in phase space (position, momenta)

$$W(x,p) = \frac{1}{\pi\hbar}\int_{-\infty}^{\infty} \psi^{\star}(x+y)\psi(x-y)e^{2ipy/\hbar}dy$$

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

Method 1: Probability distribution function

Uncorrelated sampling : Sample *qi* and *pi* randomly. `(Wigner)`

Sampling ground-state density at the initial time considering the **harmonic approximation** and employing the Wigner distribution :

$$P_W(\boldsymbol{q},\boldsymbol{p}) = \prod_{i=1}^{3N-6} \frac{\alpha_i}{\pi\hbar} exp\left(-\frac{2\alpha_i}{\hbar\omega_i}\left[\frac{\mu_i\omega_i^2 q_i^2}{2} + \frac{p_i^2}{2\mu_i}\right]\right); \qquad \alpha_i = tanh\left(\frac{\hbar\omega_i}{2k_BT}\right)$$

A stochastic algorithm generates an ensemble of N^* normal coordinates from the Wigner distribution and then they are converted to Cartesian geometries à {R, P} .
The distribution of energies:

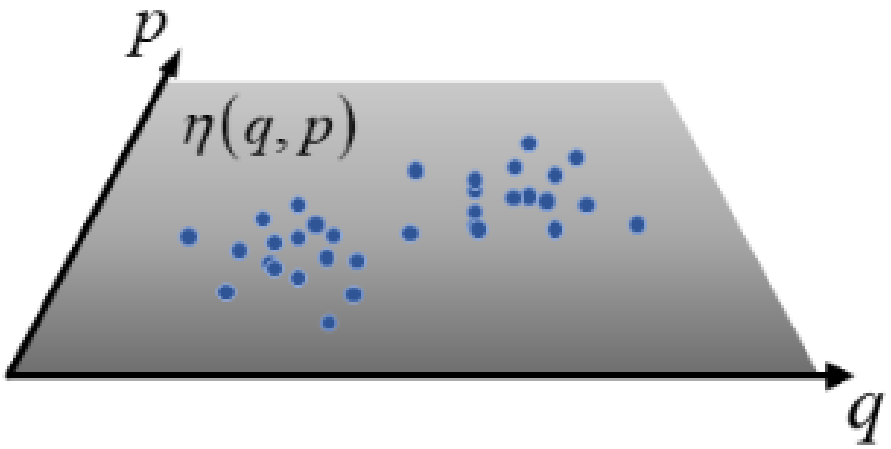
$$\langle E_{tot} \rangle \pm \sigma = \sum_{i=1}^{3N_{at}-6} \frac{\hbar\omega_i}{2\alpha_i} \pm \sqrt{\sum_{i=1}^{3N_{at}-6} \left(\frac{\hbar\omega_i}{2\alpha_i}\right)^2}$$

```
init_input:
NACT = 2
```

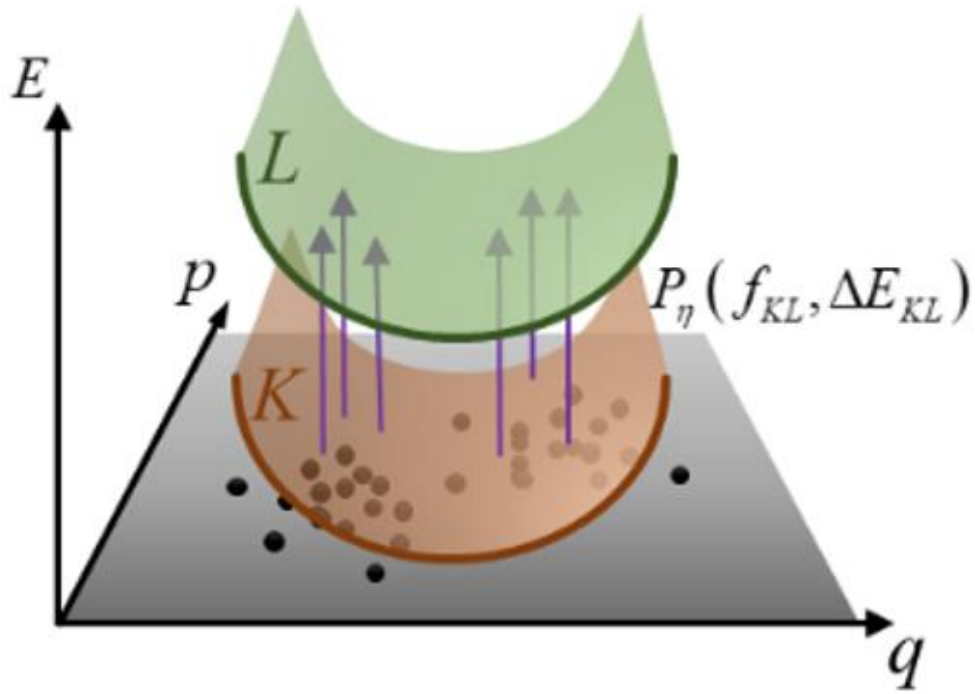
Crespo-Otero and Barbatti, Theor Chem Acc **131**, 1237 (2012).

Probability distribution function and Absorption cross section

Probability distribution



Transition probabilities



Absorption cross-section:

$$\sigma^{pa}(E)=\frac{\pi e^2\hbar}{2m_e c\varepsilon_0 E}\sum_{L}^{N_{fs}}\frac{1}{N_p}\sum_{n}^{N_p}\Delta E_{1L}(\mathbf{R}_n)\,f_{1L}(\mathbf{R}_n)\,w_s\left(E-\Delta E_{1L}(\mathbf{R}_n),\delta\right)$$

Absorption cross section

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

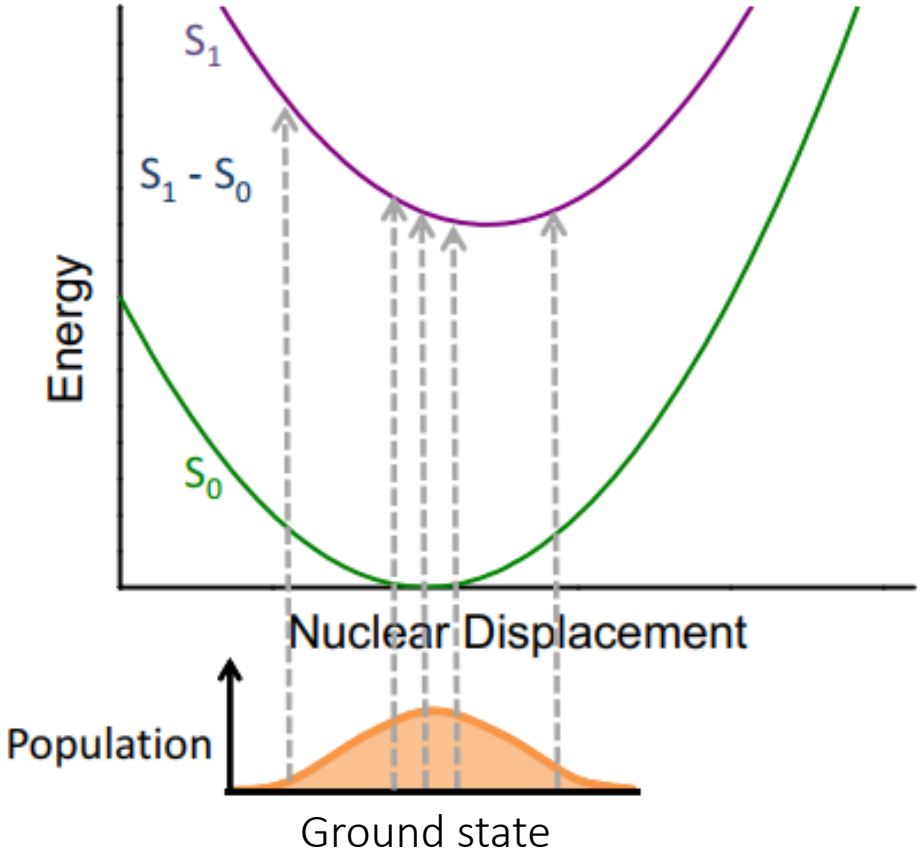


Photo excitation : time = 0

Barbatti; Sen. *Int J Quantum Chem* 2016, *116*, 762

Absorption cross section

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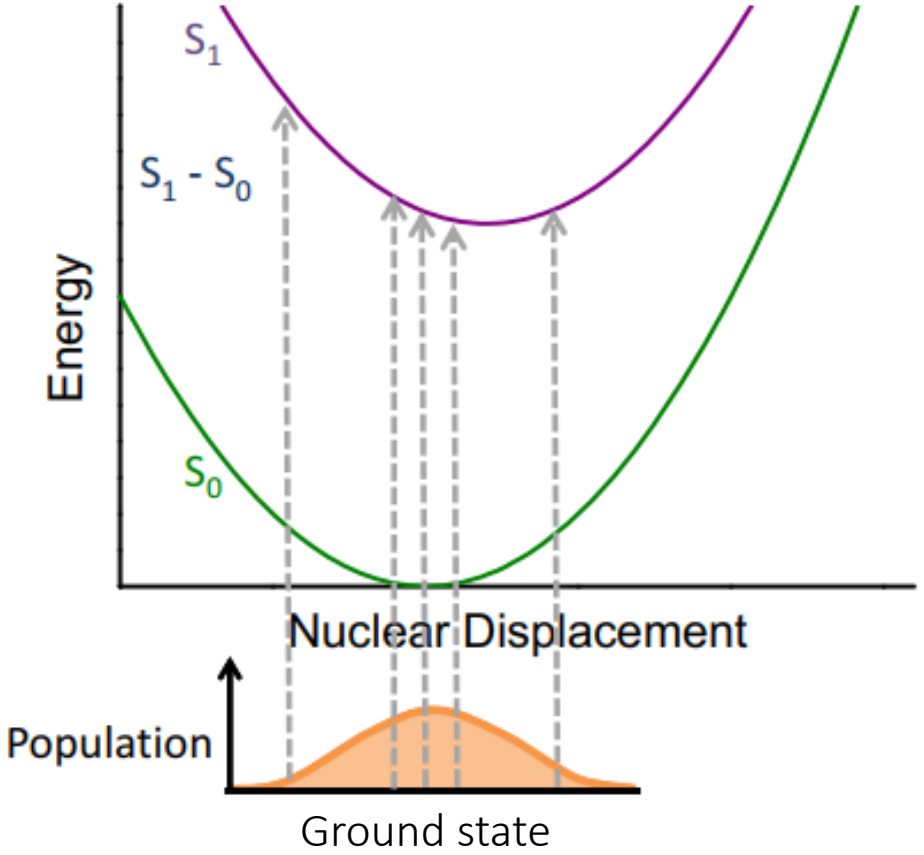
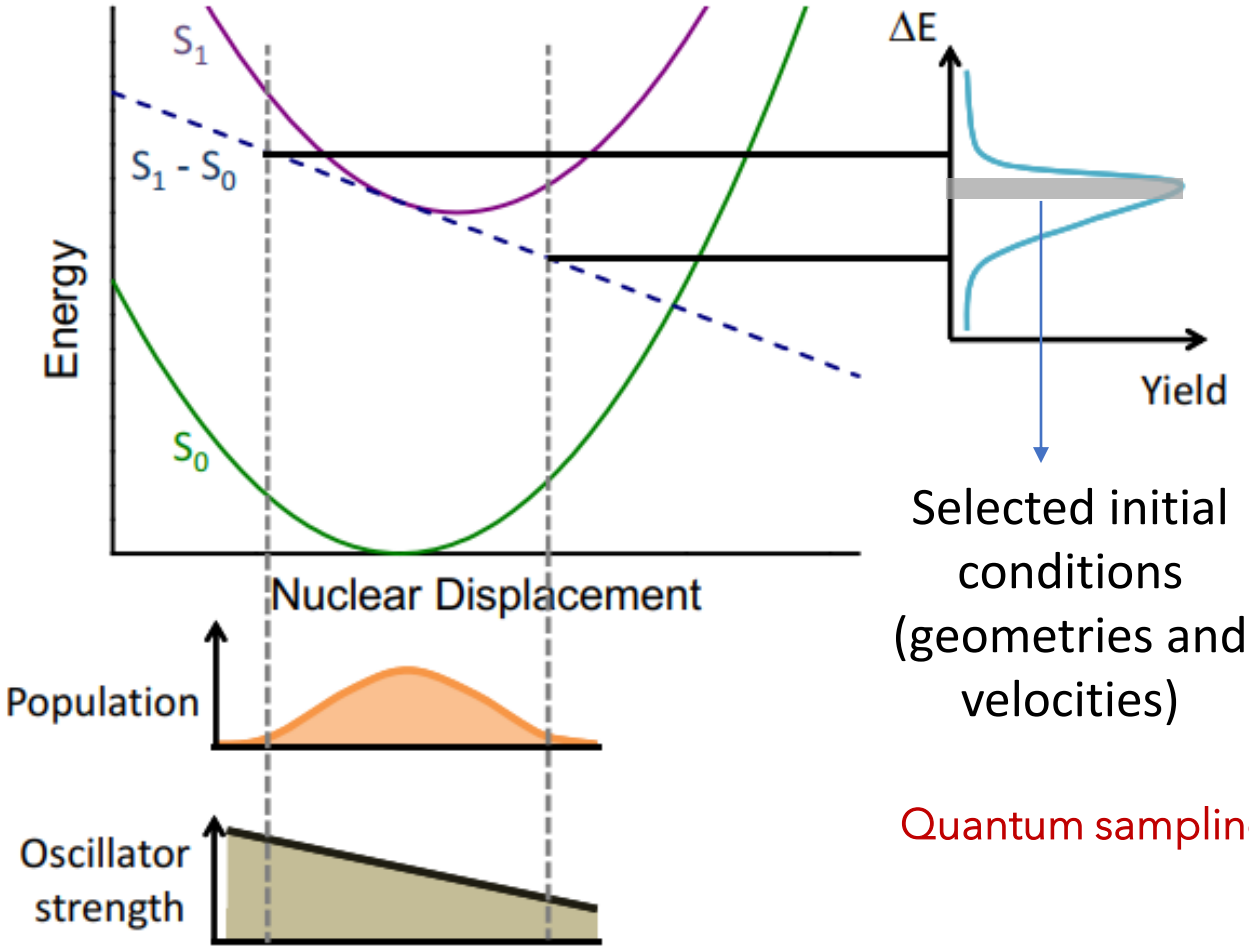


Photo excitation : time = 0



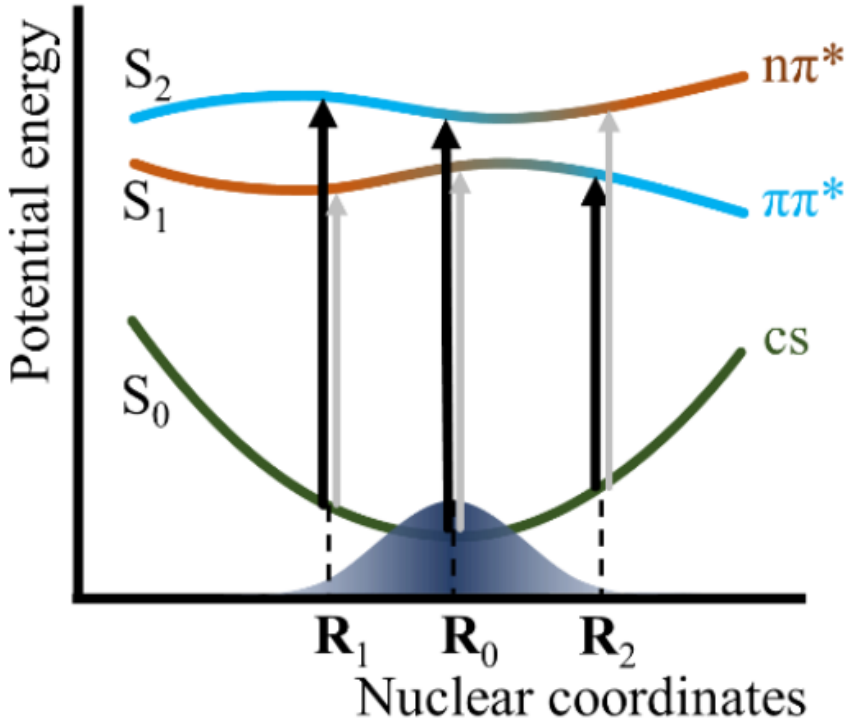
Selected initial conditions (geometries and velocities)

Quantum sampling

Barbatti; Sen. *Int J Quantum Chem* 2016, *116*, 762

Defining the initial state

To define the initial state, we should take care of state crossings.
In this example, geometry R1 should start in S2, while R2 should start in S1.



Accept initial condition if:

1. $\left|\Delta E_{1N}(\mathbf{R}_i) - \varepsilon\right| \leq \delta\varepsilon$
2. $r \leq \frac{f_{1N}(\mathbf{R}_i)}{f_{0N}^{\max}} \quad r = random(0,1)$

```
$NX/nxinp
```
<Select initial conditions for multiple excited states>

Barbatti; Sen. *Int J Quantum Chem* 2016, *116*, 762

Initial conditions and spectrum

Case study:
Pyrazine

Case study : Ultrafast photodynamics of Pyrazine

Chemical Physics 349 (2008) 319–324

Contents lists available at ScienceDirect

Chemical Physics

journal homepage: www.elsevier.com/locate/chemphys

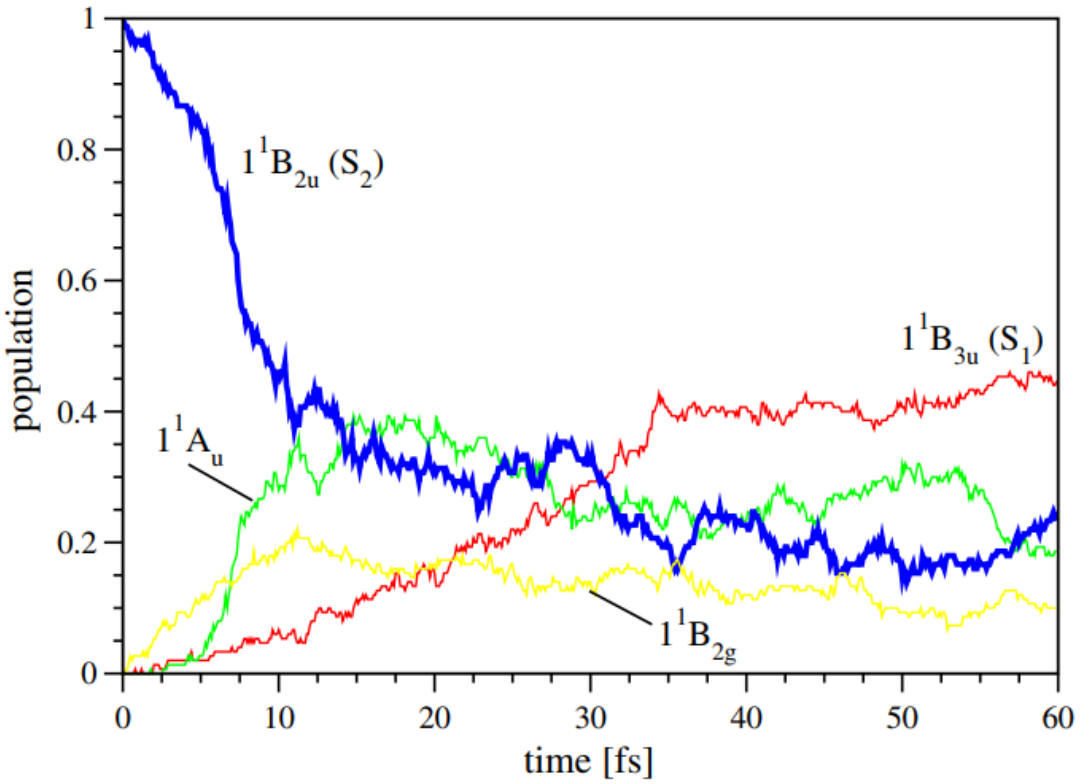
Nonadiabatic dynamics within the time dependent density functional theory: Ultrafast photodynamics in pyrazine

Ute Werner [a], Roland Mitrić [a], Toshinori Suzuki [b], Vlasta Bonačić-Koutecký [a,*]

[a] *Institut für Chemie, Humboldt-Universität zu Berlin, Brook-Taylor-Straße 2, 12489 Berlin, Germany*
[b] *Chemical Dynamics Laboratory, RIKEN, Hirosawa 2-1, Wako, Saitama 351-0198, Japan*

Werner, Mitric, Suzuki, Bonacic-Koutecky, *Chem. Phys.*, **2008**, *349*, 319.

Case study : Ultrafast photodynamics of Pyrazine



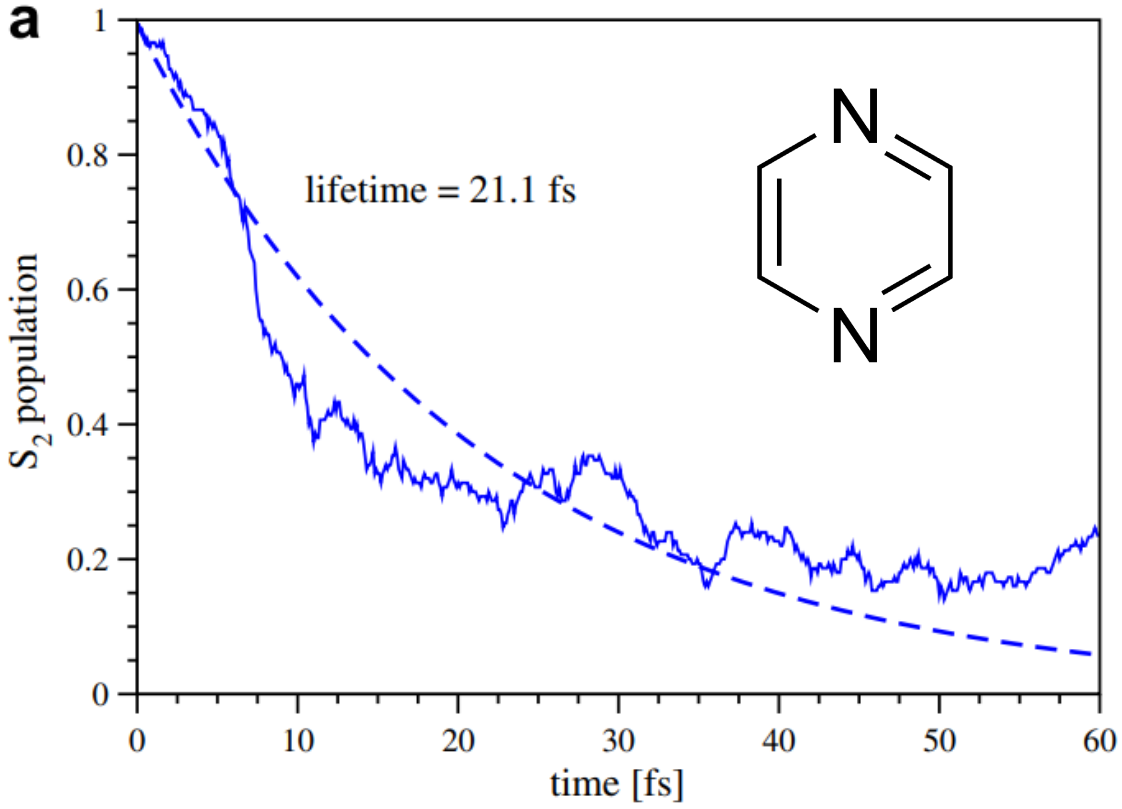
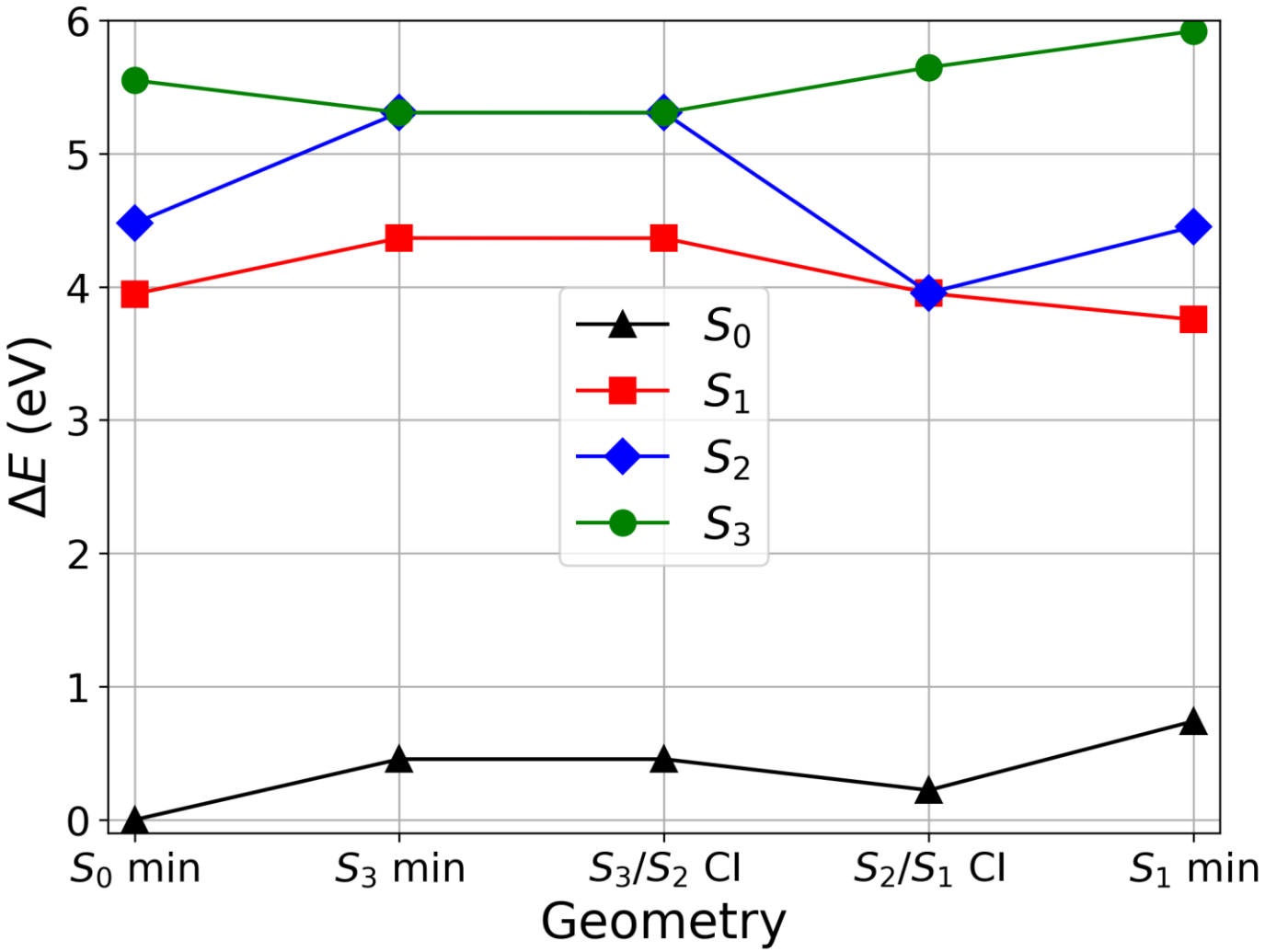
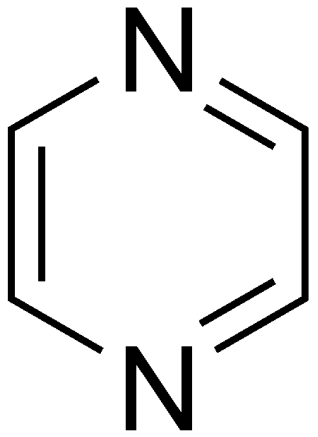


Fig. 2. Time dependent population of the excited states of pyrazine after excitation to the S_2 state: 1^1B_{3u} (S_1) (red), 1^1A_u (green), 1^1B_{2u} (S_2) (blue) and 1^1B_{2g} (yellow) (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.) .

Werner, Mitric, Suzuki, Bonacic-Koutecky, *Chem. Phys.*, **2008**, *349*, 319.

Pyrazine PES main points





Steps

1. Perform a **geometry optimization** in the ground electronic state (S0) (Orca)

2. Perform a **frequency calculation** at the optimized S0 configuration (Orca)

3. Using the optimized geometry and the frequencies:
    a. Generate an approximate **Wigner distribution** for uncoupled harmonic oscillators, that will be used to select initial conditions for TSH dynamics
    b. For each selected nuclear geometry, **perform a TDDFT calculation** to extract the energies and oscillator strengths for a subset of low-lying electronic states .
    c. Plot a **photoabsorption** cross-section based on the previous calculations

4. Based on the sampled initial conditions, **create a series of trajectories** and run them one after the other, independently

5. Collect the results and make an **statistical analysis**

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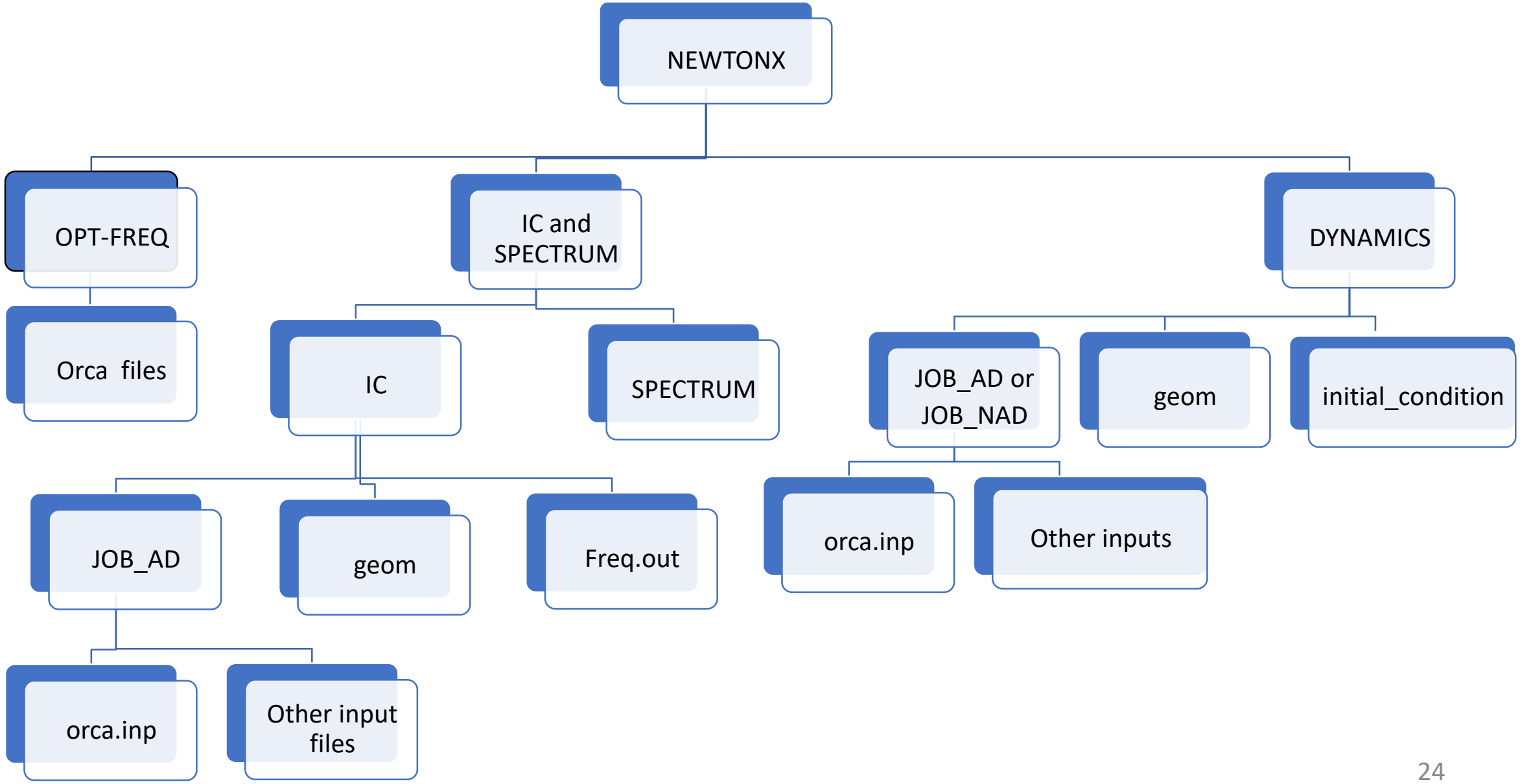
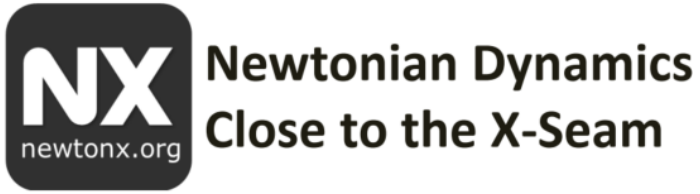
Input files tree



Overview

Surface hopping & Nuclear ensemble spectrum
Newton-X – Prof. Mario Barbatti, Aix-Marseille University
https://newtonx.org/



Electronic structure

TDDFT:
ORCA – Prof. Frank Neese, MPI Mulheim
https://www.faccts.de/orca/

XMS-CASPT2:
OpenMolcas – Prof. Roland Lindht
https://gitlab.com/Molcas/OpenMolcas

- Open source

Electronic structure and Dynamics

Program	Electronic structure
COLUMBUS	MRCI, MCSCF + MM
BAGEL	XMS-CASPT2
GAMESS	MCSCF
TURBOMOLE	ADC(2) + MM
	TDDFT, TDA + MM
GAUSSIAN	TDDFT, TDA, CIS
	TDDFT + AMOEBA
ORCA	TD-DFT / TDA
MOPAC (Pisa)	FOMO-CI, EXASH
MNDO	OMx/MRCI
DFTB+	TD-DFTB
OpenMolcas	CASSCF and CASPT2
MLatom	Machine learning
OpenQP	MR-SF-TDDFT

Before starting

1. Access BEM using
`ssh -X username@ui.wcss.pl`

2. Export NX
`export NX=/lustre/pd03/hpc-smukherjee-1743077499/SOFT/newtonx-cs/bin`
`and launch the command: $NX/nxinp`

3. Copy the files needed for the Tutorial to your /home directory:

```
mkdir TUTORIAL_3
cd TUTORIAL_3
cp -r /lustre/pd03/hpc-smukherjee-1743077499/MOLEX2025_TUTORIAL_FILES/TUTORIAL_3/IC_ORCA ~
```

Creating the input files

1. Go to the directory where you are running the initial conditions and copy the relevant files (optimized geometry and frequency file):

```
cd IC_ORCA
cp -r INPUTS/* .
```

2. Convert the optimized geometry from .xyz to NX format:

```
$NX/xyz2nx < opt.xyz
```

3. Check the JOB_AD folder containing the orca.inp file:

```
JOB_AD/orca.inp
```

ORCA input

JOB_AD/orca.inp:

```
! B3LYP def2-SVP DEFGRID3

%maxcore 1000 # Memory settings

%tddft
nroots 3
tda false
end

* xyzfile 0 1 geom.xyz
```

Creating the input files for NEA

4. To create the input of Newton-X to set the initial conditions, run
`$NX/nxinp`

Select `(1)GENERATE INITIAL CONDITIONS` and answer the questions.

```
============================================================
                        NEWTON-X
        Newtonian dynamics close to the crossing seam
                     www.newtonx.org
============================================================

                    MAIN MENU

                    1. GENERATE INITIAL CONDITIONS

                    2. SET BASIC INPUT

                    3. SET GENERAL OPTIONS

                    4. SET NONADIABATIC DYNAMICS

                    5. GENERATE TRAJECTORIES AND SPECTRUM

                    6. SET STATISTICAL ANALYSIS

                    7. EXIT
```

nact	Q/P-uncorrelated quantum harmonic oscillator (Wigner)	2
iprog	Read vibrational modes from ORCA output	11
numat	Number of atoms	[Enter]
n_points	Number of initial conditions to be generated	6
file_geom	File containing the geometry	[Enter]
file_nmodes	File containing normal modes	Orca.hess
anh_f		1
rescale	Rescale the kinetic energy to make the total energy of the initial state to match that of the equilibrium?	N
temp	Temperature	0.0
	Are these initial conditions for photoelectron spectrum?	N
chk_e	Check the energies between states NIS and NFS	1
nis	Ground state = 1	1
nfs	Total number of state including the GS	4
kvert	Use the vertical excitation energy of the equilibrium geometry	1
de	Width of restriction (center +/- de/2)	100
prog	ORCA TDDFT (or TDA)	5
iseed	Set random seed	-1
lvprt	Standard level	1
EXIT	Leave the menu	8

INPUT: initqp_input

For Orca:

```
&dat
 nact = 2
 iprog = 11
 numat = 10
 npoints = 10
 file_geom = geom
 file_nmodes = orca.hess
 anh_f = 1
 rescale = n
 temp = 0
 ics_flg = n
 chk_e = 1
 nis = 1
 nfs = 4
 kvert = 1
 de = 100
 prog = 5
 iseed = -1
 lvprt = 1
/
```

For OpenMolcas:

```
&dat
 nact = 2
 iprog = 5
 numat = 10
 npoints = 10
 file_geom = geom
 nm_flag = 2
 file_nmodes = freq.molden
 anh_f = 1
 rescale = n
 temp = 0
 ics_flg = n
 chk_e = 1
 nis = 1
 nfs = 4
 kvert = 1
 de = 100
 prog = 16.1
 iseed = -1
 lvprt = 1
/
```

Creating the input files for NEA

5. Split initial conditions:
$NX/split_initcond.pl

```
Number of directories to split the initial condition jobs: (default=2) 2
Will the job run in a batch system? (y/n) (default=y) n
```

6.Copy the submission file to each INITIAL_CONDITION/I* folder
cp submit_nxns-orca6.job INITIAL_CONDITION/I1
cp submit_nxns-orca6.job INITIAL_CONDITION/I2

5. Go to **each one of the folders** and run the submission script:
cd INITIAL_CONDITION/I1
sbatch submit_nxcs-orca6.job

✓ Note that command to run initial conditions is: $NX/initcond.pl > initcond.log

Creating the input files for NEA

✓ To check the queue:
squeue -u user

When the calculations finishes you will see in initialcond.log:

```
      ==========  Done 5 of 5 ============

End of initial conditions generation.
          ======================== NEWTON-X ends here ==================
```

6. Merge Initital conditions :
cd INITIAL_CONDITIONS

$NX/merge_initcond.pl
Number of initial_condition files to be merged: 2

OpenMolcas input

- Now, create initial conditions for XMS-CASPT2 calculations using OpenMolcas.

3. Copy the files needed for the Tutorial to your /home directory:

```
cd TUTORIAL_3

cp -r /lustre/pd03/hpc-smukherjee-1743077499/MOLEX2025_TUTORIAL_FILES/TUTORIAL_3/IC_OPENMOLCAS ~
```

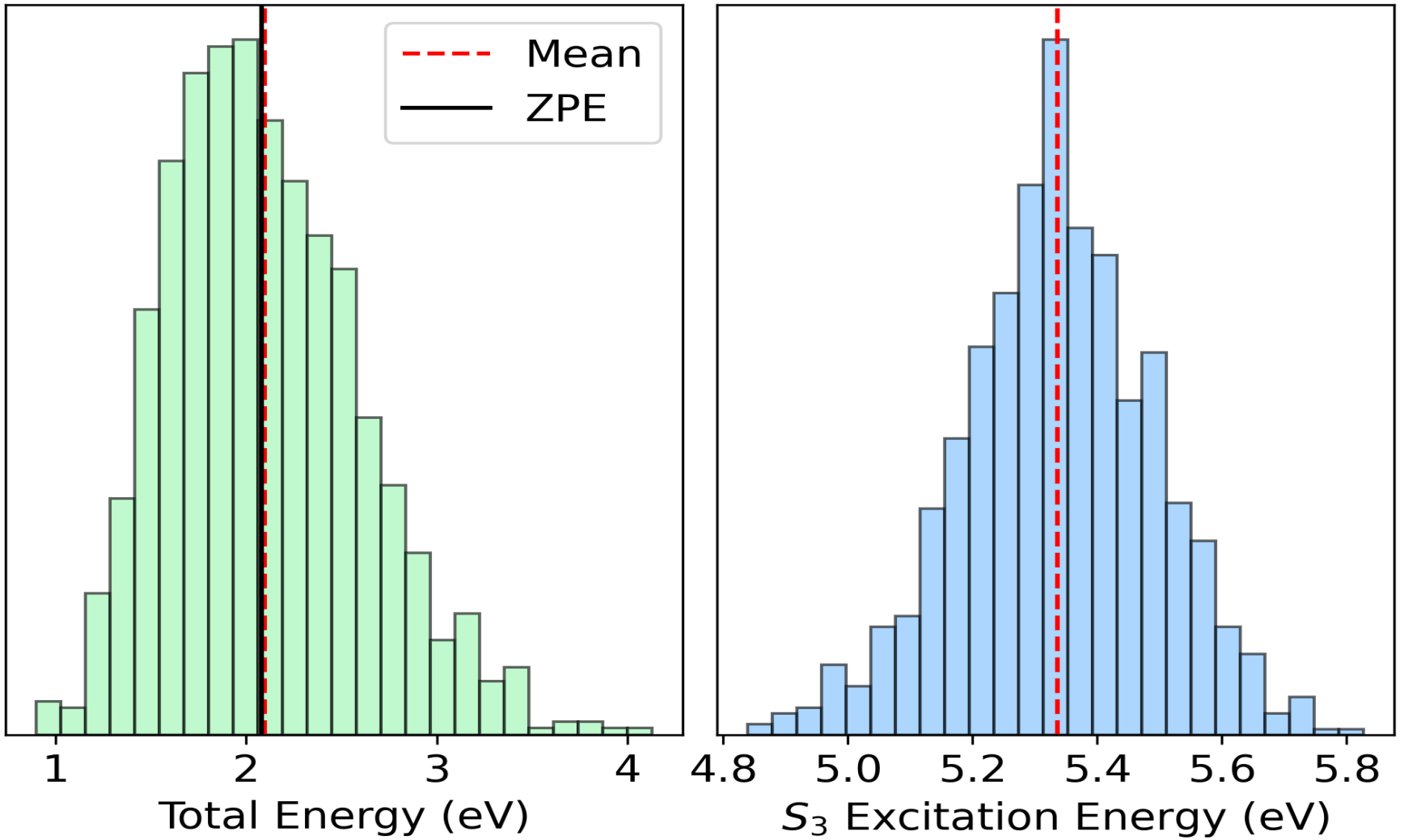
✓ In the JOB_AD folder you should have:

```
openmolcas.input
openmolcas.RasOrb
```

```
&GATEWAY
  Title= Pyrazine_caspt2
  coord = openmolcas.xyz
  basis = cc-pVDZ
  Group=NoSymm
  RICD

>>> EXPORT MOLCAS_MAXITER=100

&SEWARD
grid input
grid=ultrafine
end of grid input

&RASSCF
  FileOrb = $CurrDir/openmolcas.RasOrb
  Spin= 1
  Nactel= 10 0 0
  Inactive= 16
  Ras2= 8
  CiRoot= 4 4 1

&CASPT2
  XMultistate= 4 1 2 3 4

>>> COPY $Project.JobMix JOB001

&RASSI
  Nr of Job=1 4; 1 2 3 4
  EJob
  DIPR = 0
```

Wigner sampling

1000 Initial Conditions



Spectrum simulation

Spectrum simulation

1. Create a folder called SPECTRUM_ORCA and go there:

```
mkdir SPECTRUM_ORCA
cd SPECTRUM_ORCA
```

2. Copy the initial_condition1.* files from the RESULTS folder:

```
mkdir SPECTRUM_ORCA
cd SPECTRUM_ORCA
cp ../IC_ORCA/RESULTS/initial_condition.1.* .
```

- Login into an interactive node:

```
sub-interactive -t 6 -m 24
#module load Python/3.10.8-GCCcore-12.2.0
```

3. run :

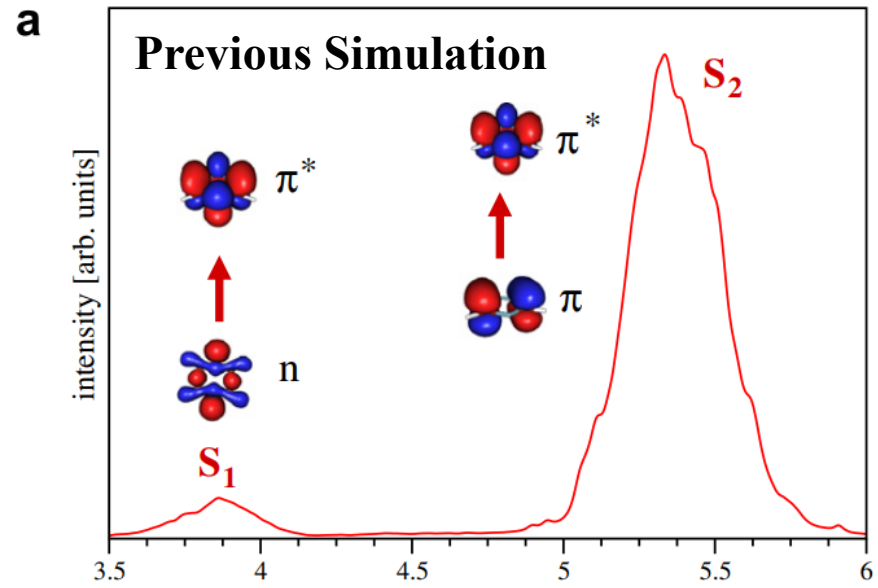
```
$NX/nxinp
```

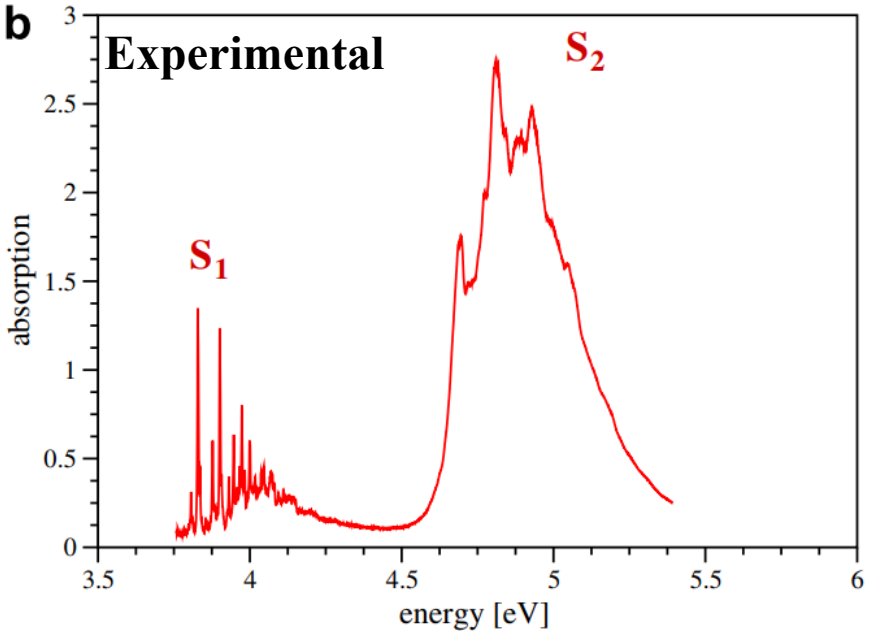
Select `6. GENERATE TRAJECTORIES AND SPECTRUM`

	6 - Generate absorption or emission spectrum	1
nis	Initial state	1
Nfs	Array of final states	2-4
Prob_kind	F - Absorption (photoabsorption cross-section)	F
Screen	0 - don't apply any restriction	0
os_condon	-1 - try to read from initial_condition file	-1
Norm	local - Use energy-restricted data set	local
Seed	1 - a randomized seed is used	1
L_shape	gauss - Normalized Gaussian function.	gauss
Delta	Phenomenological broadening of the spectrum.	0.02
Temp	Temperature	0
Nref	Refraction index	1
Eps	Distance between consecutive points in the spectrum.	0.005
Kappa	The range of the spectrum is defined between	0
run_IS	Will you compute the spectrum for a target distribution different from the sampling distribution?	0

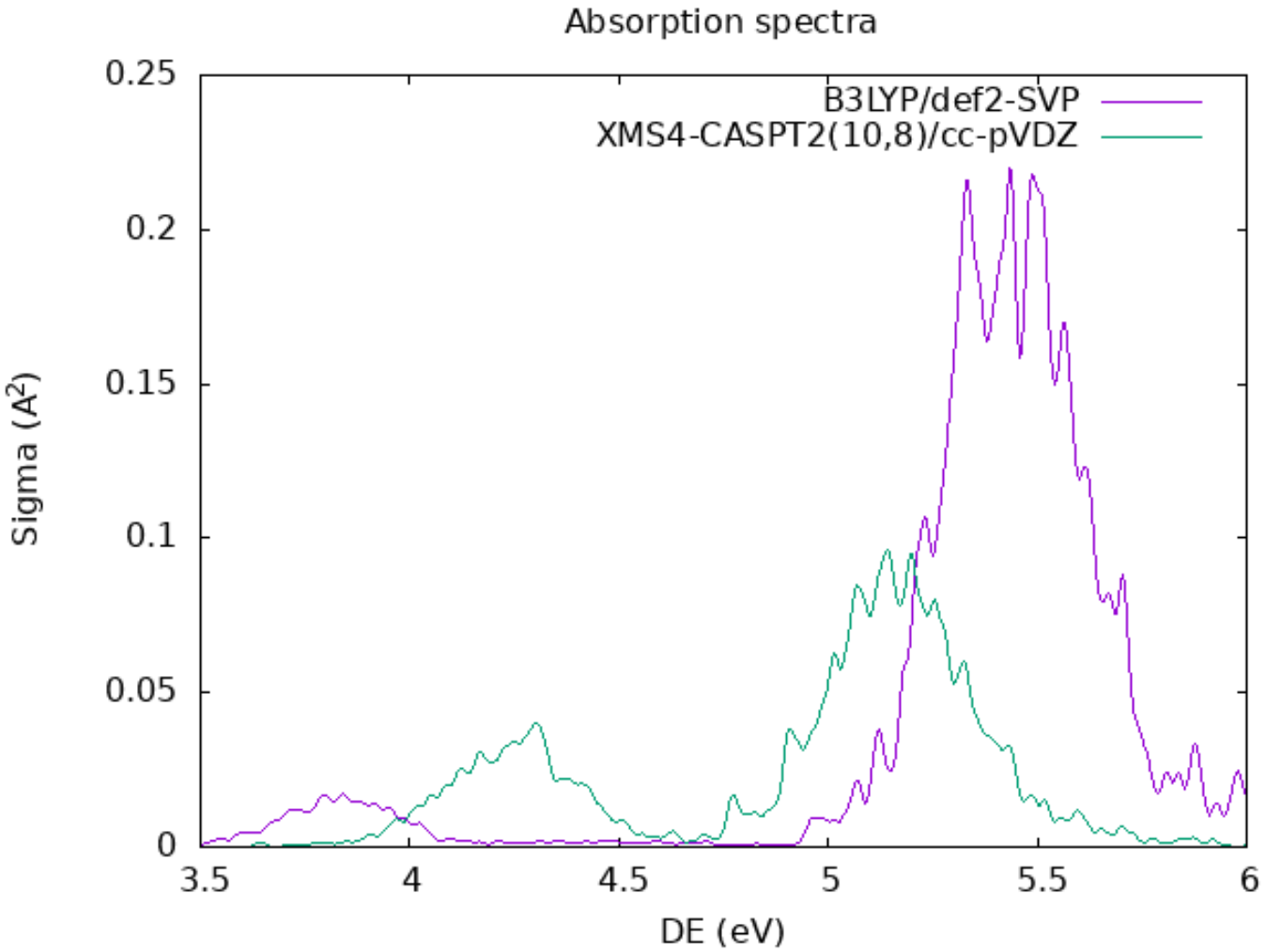
- To visualize the spectrum and get the maximum:

```
gnuplot spectrum.gnu
```



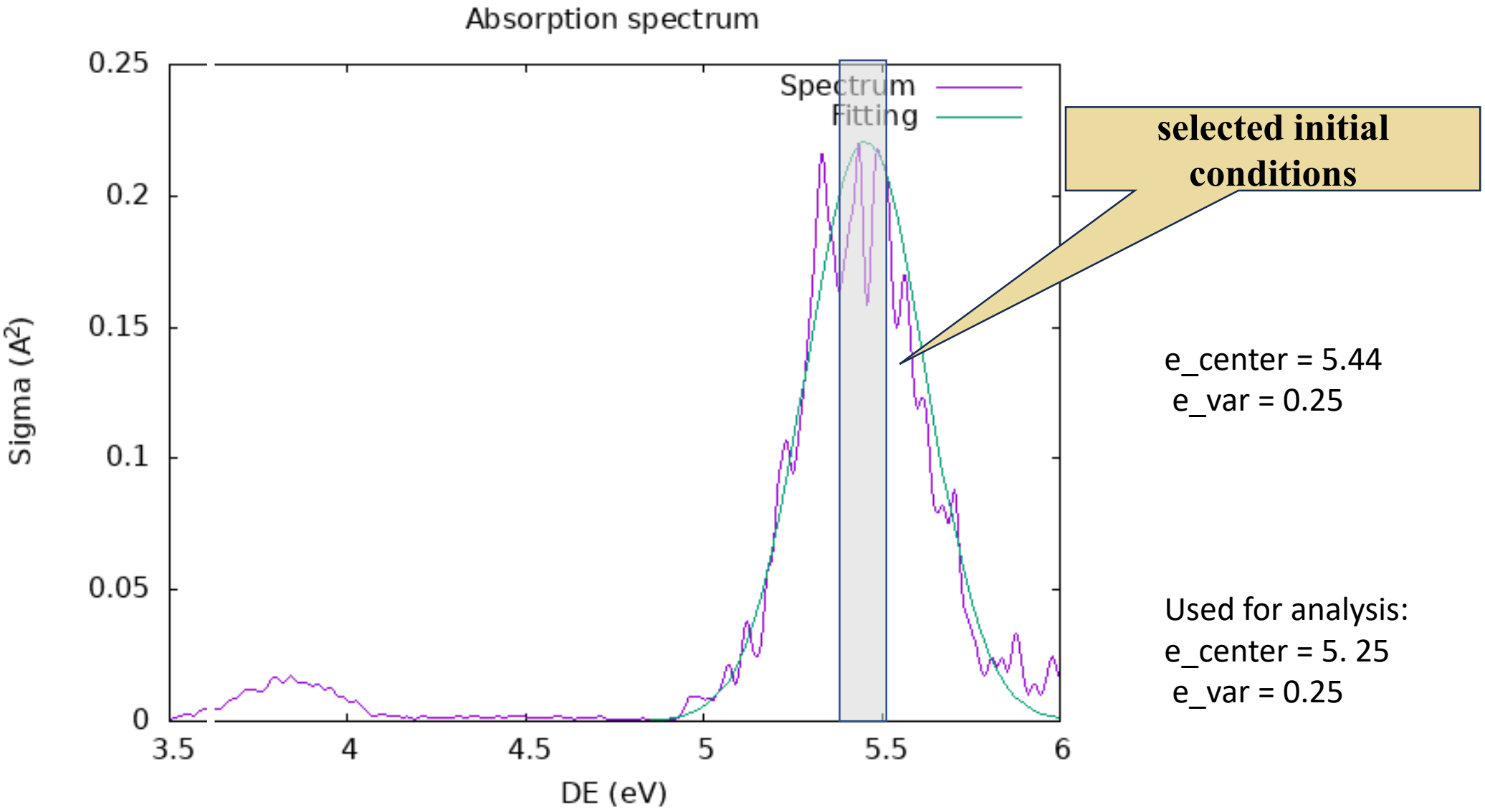


Current simulation



Werner, Mitric, Suzuki, Bonacic-Koutecky, *Chem. Phys.*, **2008**, *349*, 319.

Select initial conditions



e_center = 5.44
e_var = 0.25

Used for analysis:
e_center = 5. 25
e_var = 0.25

Select initial conditions for multiple states

```
$NX/nxinp

6       ! Generate trajectories and spectrum
yes     ! To delete previous input files
3       ! Select initial conditions for multiple initial states
1       ! nis:  Initial state
2-4     !nfs:  Array of final states
F       ! prob_kind: Absorption spectra
2       ! Screen: apply new energy restriction
5.44    ! e_center:  Center of the energy restriction
0.25    !  e_var:  Width of the energy restriction
-1      ! os_condon: Read oscillator strength from final_output
local   ! Use de highest oscillator strenght in the selected width to
normalize
1       ! Randomized seed
0       ! run_IS = compute observable only for the target distribution
7       ! EXIT
```

Select initial conditions for multiple states

Now, check the end of the makedir.log file

✓ you will see the proportion of trajectories starting from each one of the states. For ORCA job, you will see something like:

```
The number of initial conditions selected for transitions
      from state 1 into states (2 3 4) is 0:1:349.
```

Select initial conditions for multiple states

Now, check the end of the makedir.log file

✓ you will see the proportion of trajectories starting from each one of the states. For ORCA job, you will see something like:

```
The number of initial conditions selected for transitions
      from state 1 into states (2 3 4) is 0:1:349.
```

This procedure will create a folder called: `SELECTED_INITIAL_CONDITIONS`
containing the selected initial conditions for the states selected:

```
initial_condition.1.2
initial_condition.1.3
initial_condition.1.4     <---- this is the state we are going to start the dynamics
```

This files will be used tomorrow to initiate the TSH dynamics!