HANDS-ON SESSION

Excited States Mixed Quantum-Classical Dynamics

Initial conditions sampling and Surface Hopping Dynamics

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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

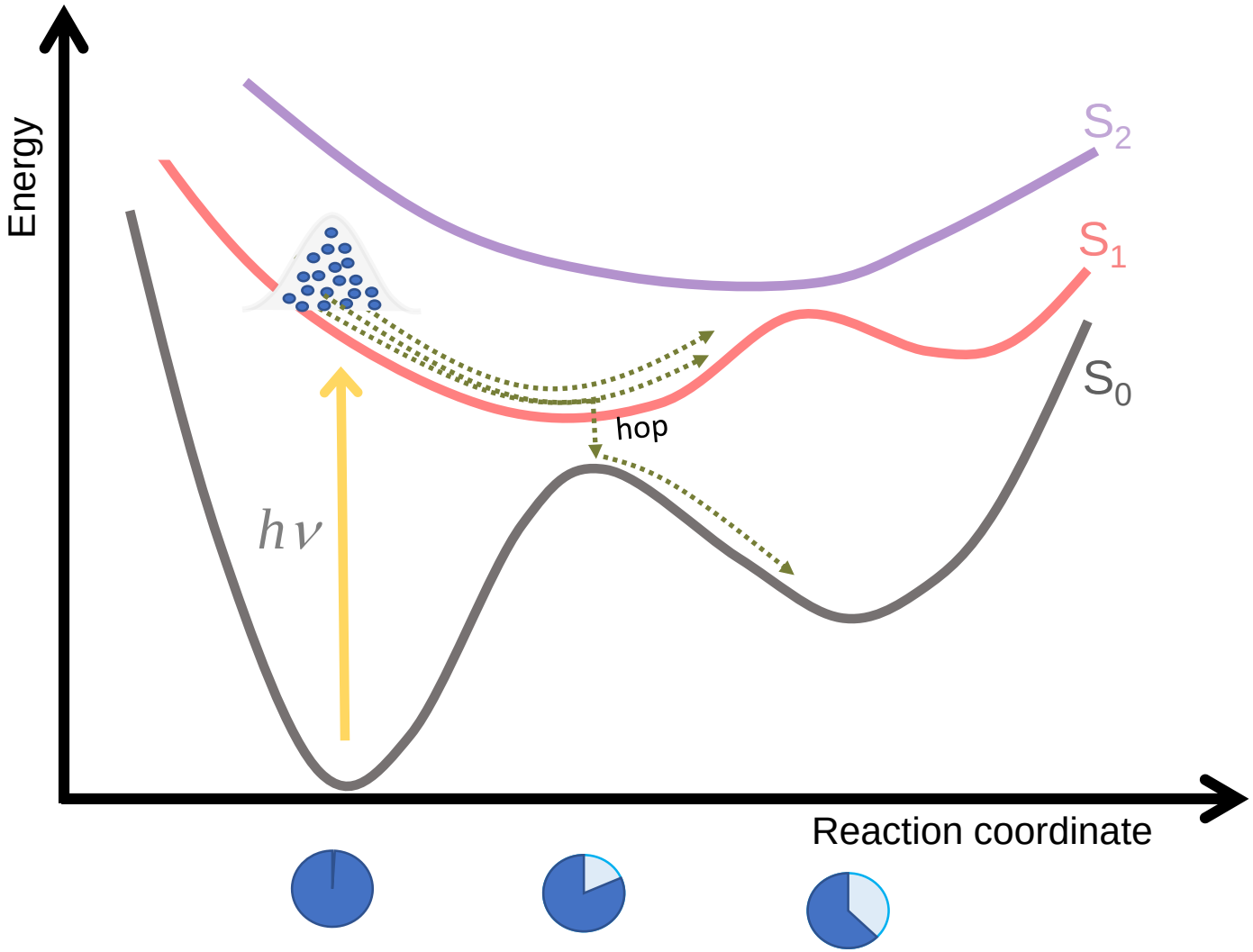
Running a TSH dynamics

3. Analysis

Running Ulamdyn for the statistical analysis

Analysing the results

Trajectory Surface hopping (TSH)



Core idea:

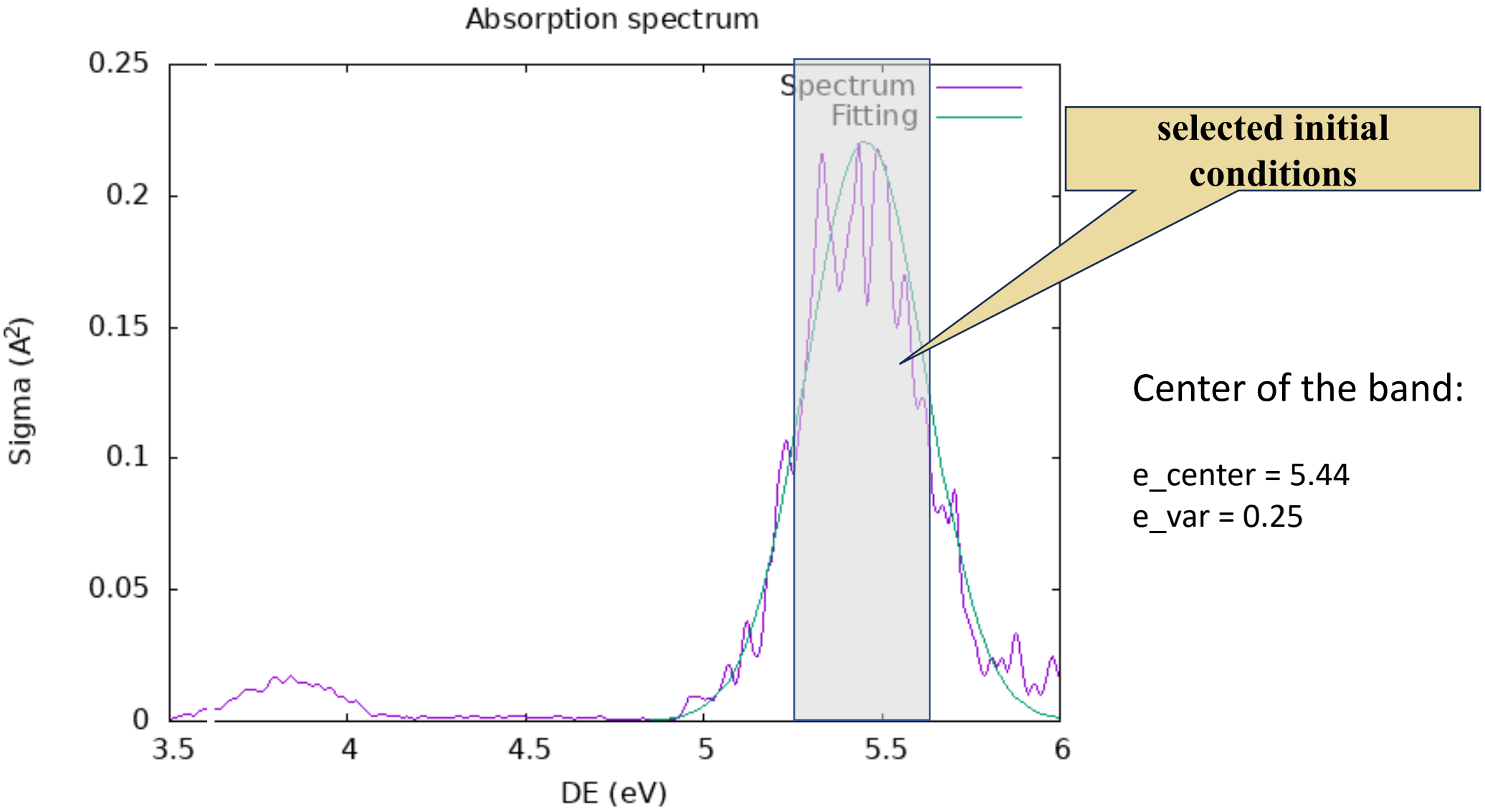
1. Nuclei are propagated via *classical trajectories*

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.

Select initial conditions



Center of the band:

e_center = 5.44
e_var = 0.25

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

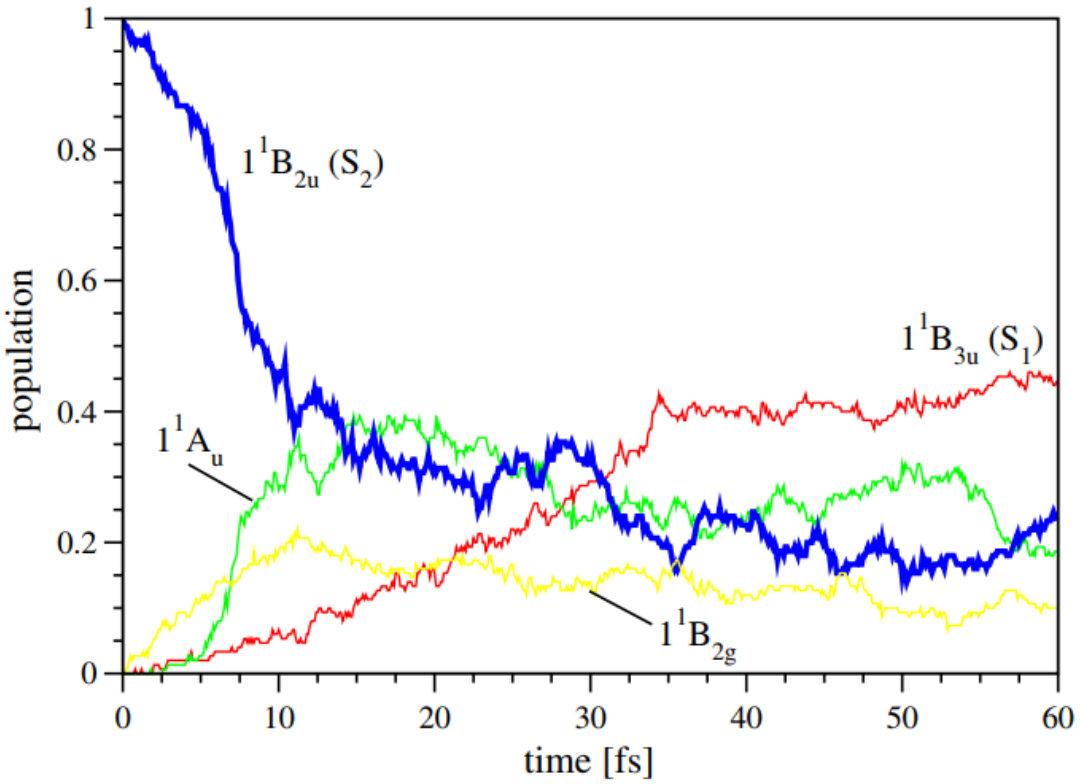
Nonadiabatic dynamics within the time dependent density functional theory: Ultrafast photodynamics in pyrazine

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



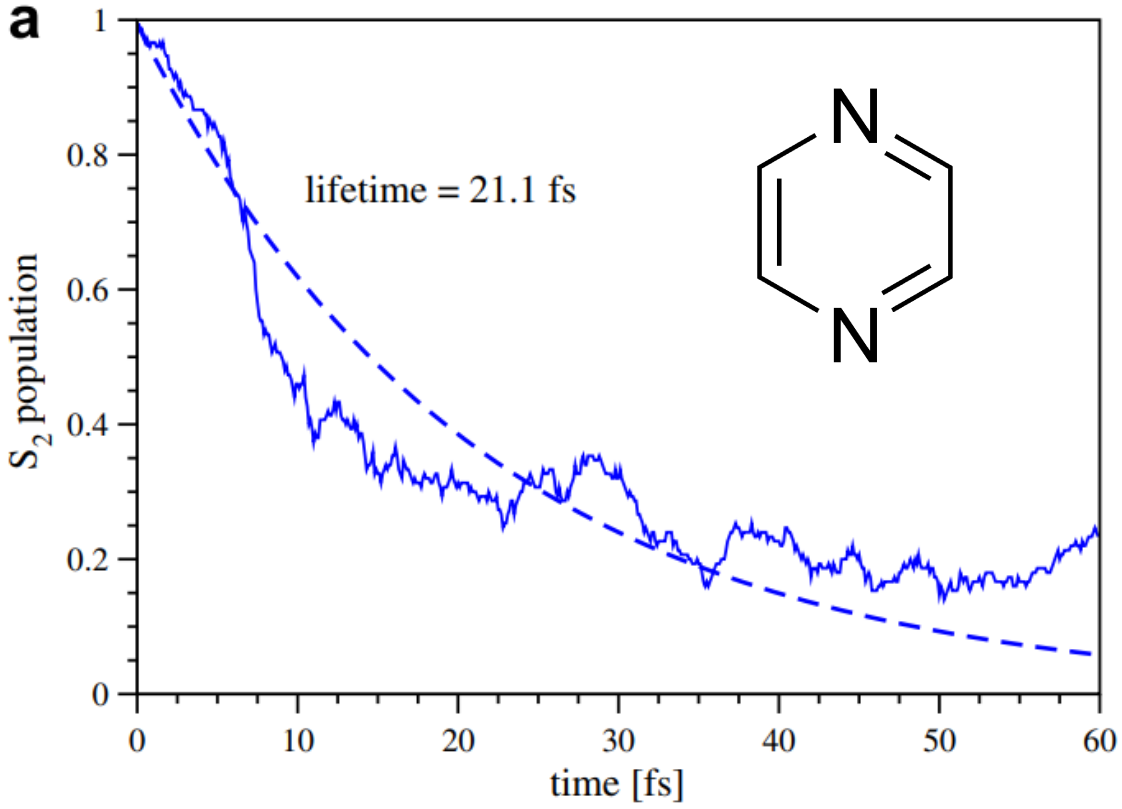
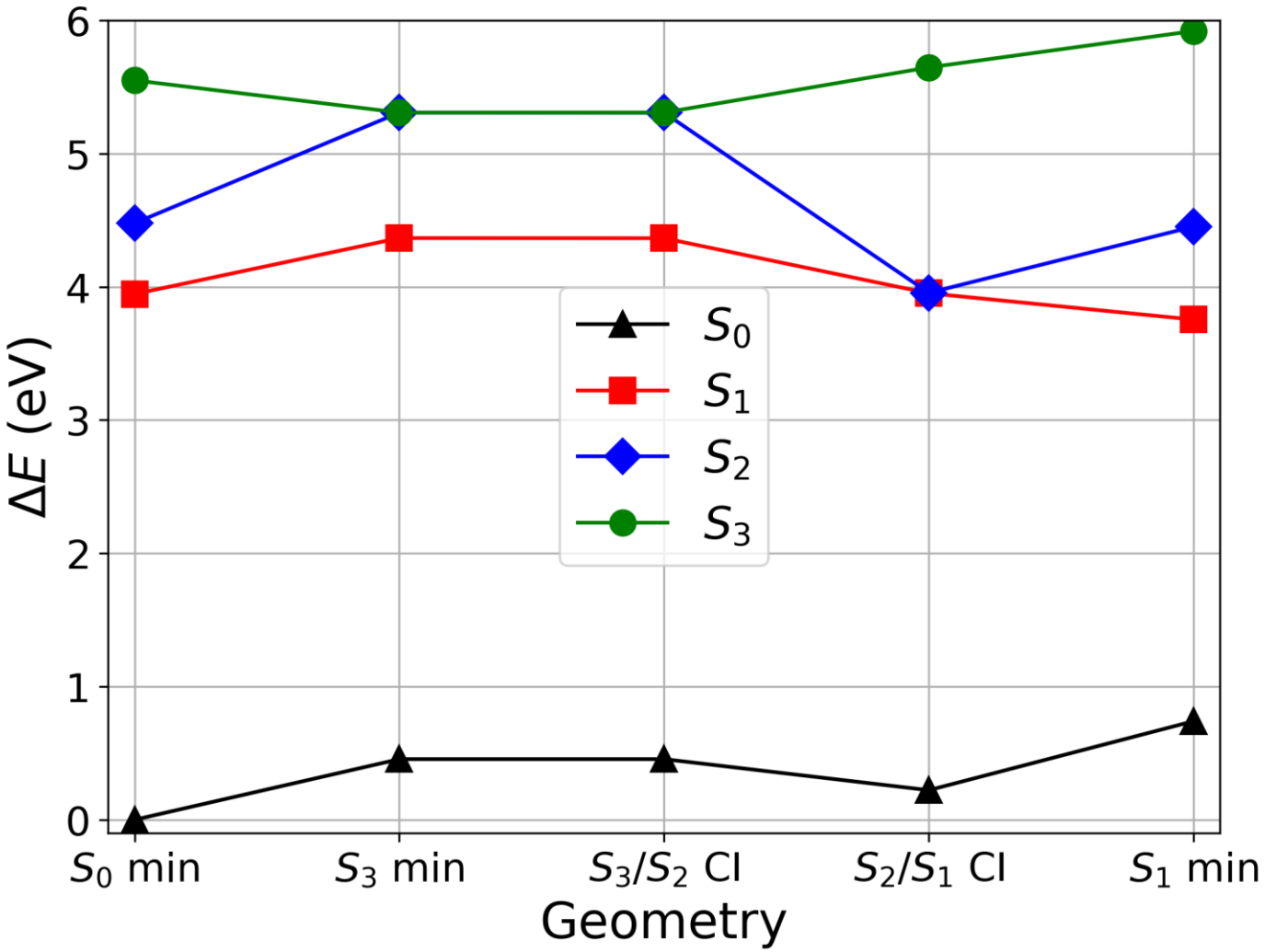
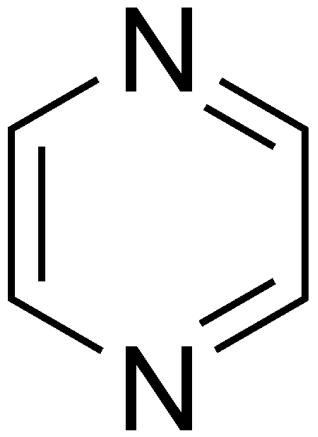


Fig. 2. Time dependent population of the excited states of pyrazine after excitation to the S_2 state: 1^1B_{3u} (S_1) (red), 1^1A_u (green), 1^1B_{2u} (S_2) (blue) and 1^1B_{2g} (yellow) (For interpretation of the references to colour in this figure legend, the reader is referred to the web version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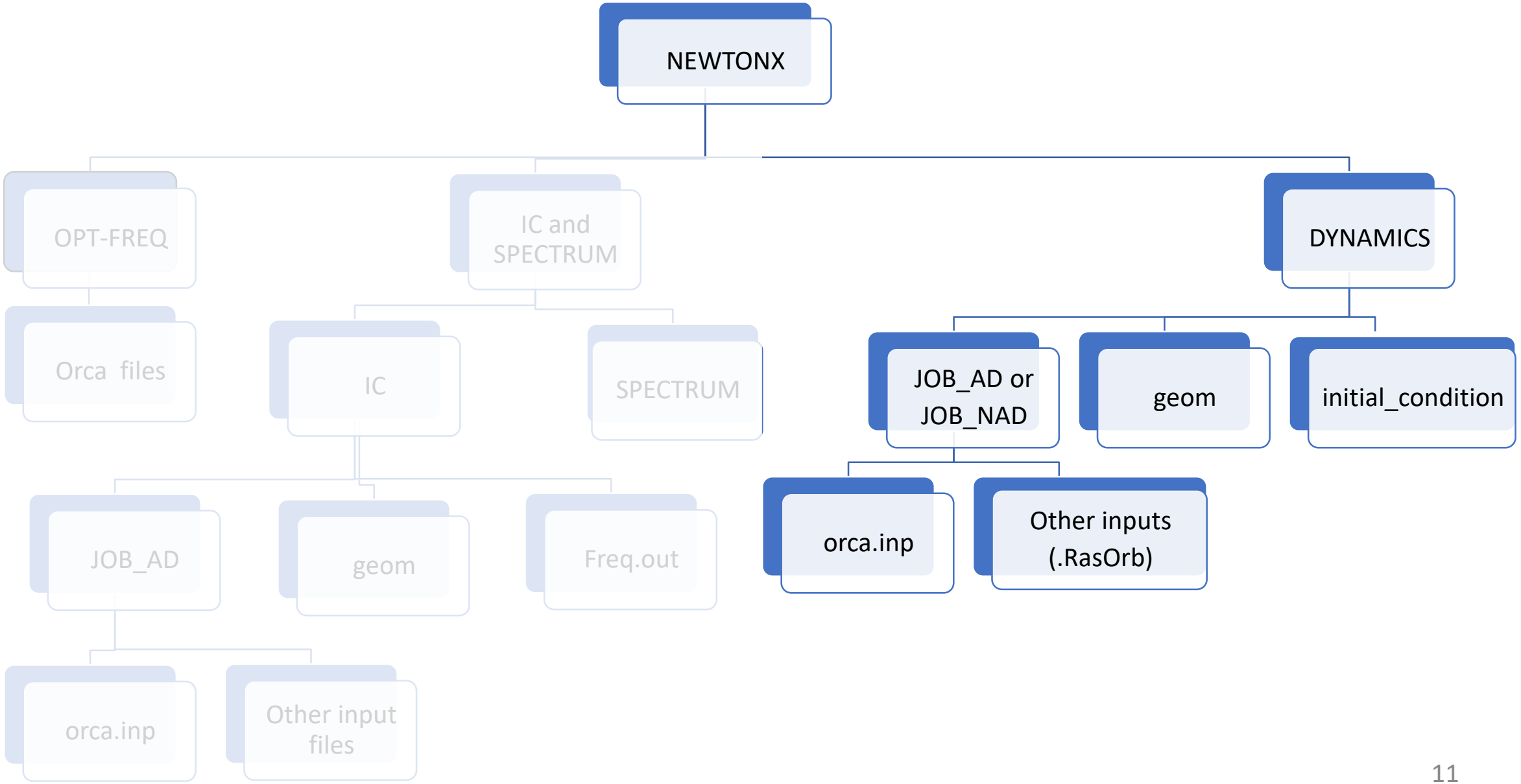
Input files tree



PART 2

Surface Hopping dynamics

Fewest Switching trajectory surface hopping evolution

Nuclear evolution

$$\frac{d^2\bar{\mathbf{R}}}{dt^2} = \frac{1}{M_\alpha}\mathbf{F}\left(\bar{\mathbf{R}}\right) = \frac{1}{M_\alpha}\frac{\partial \mathbf{E}_K}{\partial \bar{\mathbf{R}}}$$

TDSE in the adiabatic representation

$$\frac{dc_J}{dt} = \sum_K -c_K\left(\frac{i}{\hbar}H_{JK} + \sigma_{JK}^{NAC}\right)$$

Hopping probabilities

$$P_{J\to K}^{FSSH} = \max\left[0, -\frac{2\Delta t}{|C_L|^2}\Re\left(\sigma_{JK}^{NAC}C_K C_J^*\right)\right]$$

- ✓ Initial Geometries
- ✓ Initial Velocities
- ✓ Initial Electronic State
- ✓ Initial TDSE coefficients

At every classical time step we need to compute energies, gradients and σ_{JK}^{NAC}

Baeck-An couplings (TDBA) dynamics

The coupling terms between any pair of states are

$$\sigma_{JK}^{NAC}\left(\bar{\mathbf{R}}\right) \equiv \left\langle \psi_J \left| \frac{\partial \psi_K}{\partial t} \right\rangle = \mathbf{d}_{JK} \cdot \bar{\mathbf{v}} \right.$$

$$\mathbf{d}_{JK} \equiv \left\langle \psi_J \left| \nabla \psi_K \right\rangle \right.$$

When explicit nonadiabatic coupling vectors are not available the coupling terms can be computed by finite differences (time-derivative couplings).

Instead σ_{LJ}^{NAC}, we can use Baeck-An couplings.[1] The BA couplings only depend on the energy difference between the states.

$$\sigma_{JL} \approx v_Q h_{JL} = \frac{\mathrm{sgn}\left(\Delta E_{JL}\right)}{2} \sqrt{\frac{1}{\Delta E_{JL}} \frac{d^2 \Delta E_{JL}}{dt^2}}$$

do Casal.; Toldo,; Pinheiro .; Barbatti,. Fewest Switches Surface Hopping with Baeck-An Couplings. *Open Research Europe* 2021, *1*, 49.

TSH Dynamics

ORCA/TDDFT with Baeck An couplings

Step 0 – Before starting

1. Access BEM using

```
ssh -X username@ui.wcss.pl
```

2. Export NXCS and NXNS

```
export NX=/lustre/pd03/hpc-smukherjee-1743077499/SOFT/newtonx-cs/bin
export NXHOME=/lustre/pd03/hpc-smukherjee-1743077499/SOFT/newtonx
```

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

```
cp -r /lustre/pd03/hpc-smukherjee-1743077499/MOLEX2025_TUTORIAL_FILES/TUTORIAL_4 ~
cd TUTORIAL_4
```

4. Create a folder called DYN_ORCA and move to this directory

```
mkdir DYN_ORCA && cd DYN_ORCA
```

Preparing the inputs

5. Copy the selected initial conditions to DYN_ORCA directory and rename it

```
cp ~/TUTORIAL_3/SPECTRUM_ORCA/SELECTED_INITIAL_CONDITIONS/initial_condition.1.4  .
mv initial_condition.1.4 initial_condition
```

6. Copy the geom file and JOB_AD from the IC_ORCA folder (from yesterday):

```
cp ~/TUTORIAL_3/IC_ORCA/geom .
cp -r ~/TUTORIAL_3/IC_ORCA/JOB_AD .
```

7.Edit the orca.inp file inside JOB_AD

```
vi JOB_AD/orca.inp
```

Preparing the inputs

JOB_AD/orca.inp:

```
%pal nprocs 6
     end

! B3LYP def2-SVP ENGRAD DEFGRID3

%maxcore 1000 # Memory settings

%tddft
nroots 3
tda false
end

* xyzfile 0 1 geom.xyz
```

The input is similar to the one for the initial conditions, but it needs the ENGRAD keyword for the calculation of the excited state gradients, required for the dynamics.

Preparing the inputs

In this tutorial, we are going to use **NewtonX-NS** to run the TSH dynamics.

8. To create the inputs for NX-NS TSH, run:
`$NXHOME/bin/nx_geninp`

This command is analogous to the nxinp in NewtonX-CS:
`$NX/nxinp`

Select `(1) GENERATE A BASIC INPUT`

```
============================================================
                        NEWTON-X NS 3
            Newtonian dynamics close to the crossing seam
                        www.newtonx.org
============================================================

Please select the task to be performed:


1. Generate a basic input

2. Set up a non-adiabatic dynamics

3. Create trajectories

4. Save configuration and exit

Enter the desired choice: <1>
```

	1- Generate a basic input	
Nat	Number of atoms	[Enter]
Nstat	Number of states	4
Nstatdyn	State on which the dynamics will start	4
progname	QM program and method to use	4.1
dt	Time step of the classical equations	0.5
tmax	Maximum duration of the simulation	10
dc_method	Original algorithm from Tully	1
Baeck-An	Do you want to use approximated Baeck-An couplings ?	y
	Press any key to go back to the General Option menu.	

In the main nx_geninp menu you have the option to set more general options if you select option **2. Set up a non-adiabatic dynamics**.
Normally, this is not necessary; only if you want to change to some nondefault options.

In the Menu `2. Set up a non-adiabatic` dynamics, you will see:

1. Set TDSE integration method and Surface Hopping algorithm
2. Define which non-adiabatic couplings (NAC) will be computed
3. Define how to compute time-derivative couplings
4. Return to main menu

The following options can be accessed through this menu:

```
&sh
  integrator = 1
  ms = 20
  getphase = 1
  nohop = 0
  nrelax = 0
  seed = -1
  probmin = 0.00
  popdev = 0.05
  tully = 1
  decay = 0.10
  mom = 1
  adjmom = 0
/
```

```
&nad_setup
  kross = 1
  cascade = 0
  current = 1
  never_state = 1
  include_pair = 0
/

&auxnac
  model = 0
  ba_smooth = 0
  ba_dh = 0.100000000000
  ba_de = 0.073498644351
  ba_dv = 0.100000000000
/
```

```
&nxconfig
  nat = 10
  nstat = 4
  nstatdyn = 4
  progname = orca
  methodname =
tddft
  dt = 0.50
  tmax = 500.00
  dc_method = 3
  use_locdiab = F
  epot_diff = 0.20
/
```

Control file : user_config.nml

Now we are ready to generate the trajectories. Run:
$NXHOME/bin/nx_geninp

Type	3- Create trajectories	3
nis	Lowest state considered	1
screen	Energy restriction criterion. Do not apply	0
read_os_from_file	Read oscillator strengths from initial_condition file	-1
norm	Use the energy-restricted data set	local
seed	A randomized seed is used	-1
run_is:	Will you compute the dynamical observables	n
proceed	Proceed to trajectory generation	1
	Save configuration and exit	4

Running the trajectories

- Copy the submission file to each TRAJ directory.
  You can find the submission file inside the DYN-ORCA folder that you copied earlier.

5. Go to **each one of the folders** and run the submission script:
   cd TRAJECTORIES/TRAJ1
   sbatch submit_nxns-orca6.job

✓ Note that command to run initial conditions is:
   $NXHOME/bin/nx_moldyn > md.log 2>&1

TSH Dynamics

OPENMOLCAS/XMS-CASPT2 with NACS

Step 0 – Before starting

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

2. Export NXCS and NXNS
export NX=/lustre/pd03/hpc-smukherjee-1743077499/SOFT/newtonx-cs/bin
export NXHOME=/lustre/pd03/hpc-smukherjee-1743077499/SOFT/newtonx

3. Copy the files needed for the Tutorial to your /home directory:
`cp -r /lustre/pd03/hpc-smukherjee-1743077499/MOLEX2025_TUTORIAL_FILES/TUTORIAL_4 ~`
`cd TUTORIAL_4`

4. Create a folder called DYN_MOLCAS and move to this directory
mkdir DYN_MOLCAS && cd DYN_MOLCAS

Preparing the inputs

In the makedir.log in SELECTED_INIIAL_CONDITIONS we have for the XMS-CASPT2 job:

```
The number of initial conditions selected for transitions
from state 1 into states (2 3 4) is 0:374:149.
```

5. Copy the selected initial conditions to DYN_CASPT2 directory and rename it

```
cp ~/TUTORIAL_3/SPECTRUM_ORCA/SELECTED_INITIAL_CONDITIONS/initial_condition.1.3  .
cp ~/TUTORIAL_3/SPECTRUM_ORCA/SELECTED_INITIAL_CONDITIONS/initial_condition.1.4  .
```

6. Now, create one folder to start the dynamics in State 3 and another in state 4 and move the respective initial_condition.1.x to each folder.

```
mkdir state_3
mkdir state_4
mv initial_condition.1.3 state_3
mv initial_condition.1.4 state_4
```

Preparing the inputs

7. In each folder, rename the initial_conditions file, like in the example:

```
cd state_4
mv initial_condition.1.4 initial_condition
```

8. Copy the geom file and JOB_AD from the IC_OPENMOLCAS folder (from yesterday):

```
cp ~/TUTORIAL_3/IC_OPENMOLCAS/geom .
cp -r ~/TUTORIAL_3/IC_OPENMOLCAS/JOB_AD .
```

9. Rename JOB_AD and check openmolcas.inp file inside JOB_NAD

```
mv JOB_AD mv JOB_NAD
```

XMS-CASPT2 - input

JOB_NAD/openmolcas.inp:

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

>>> EXPORT MOLCAS_MAXITER=100

&SEWARD
 DoAnalyticalDoAnalytical
 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=all
 Imagin = 0.1
```

Preparing the inputs

In this tutorial, we are going to use **NewtonX-NS** to run the TSH dynamics.

8. To create the inputs for NX-NS TSH, run:
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This command is analogous to the nxinp in NewtonX-CS:
`$NX/nxinp`

Select `(1) GENERATE A BASIC INPUT`

```
============================================================
                        NEWTON-X NS 3
          Newtonian dynamics close to the crossing seam
                        www.newtonx.org
============================================================

Please select the task to be performed:


1. Generate a basic input

2. Set up a non-adiabatic dynamics

3. Create trajectories

4. Save configuration and exit

Enter the desired choice: <1>
```

Control file : user_config.nml

	1- Generate a basic input	
Nat	Number of atoms	[Enter]
Nstat	Number of states	4
Nstatdyn	State on which the dynamics will start	4
progname	QM program and method to use : OM / XMS-CASPT2	6.2
dt	Time step of the classical equations	0.5
tmax	Maximum duration of the simulation	10
dc_method	Original algorithm from Tully	1
Baeck-An	Do you want to use approximated Baeck-An couplings ?	n
	Press any key to go back to the General Option menu.	

In the Menu `2. Set up a non-adiabatic` dynamics, you will see:

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  getphase = 1
  nohop = 0
  nrelax = 0
  seed = -1
  probmin = 0.00
  popdev = 0.05
  tully = 1
  decay = 0.10
  mom = 1
  adjmom = 2
  adjtheta = 0
/
```

```
&nad_setup
  kross = 1
  cascade = 0
  current = 1
  never_state = 0
  include_pair = 0
/
```

```
&openmolcas
 mocoef = 1
 prt_mo = 20
 all_grads = 0
/
```

```
&nxconfig
  nat = 10
  nstat = 4
  nstatdyn = 4
  progname = openmolcas
  methodname = caspt2
  dt = 0.50
  tmax = 10.00
  dc_method = 1
  use_locdiab = F
  /
```

Control file : user_config.nml

Now we are ready to generate the trajectories. Run:
$NXHOME/bin/nx_geninp

Type	3- Create trajectories	3
nis	Lowest state considered	1
screen	Energy restriction criterion. Do not apply	0
read_os_from_file	Read oscillator strengths from initial_condition file	-1
norm	Use the energy-restricted data set	local
seed	A randomized seed is used	-1
run_is:	Will you compute the dynamical observables	n
proceed	Proceed to trajectory generation	1
	Save configuration and exit	4

Running the trajectories

- Copy the submission file to each TRAJ directory.
  You can find the submission file inside the DYN-ORCA folder that you copied earlier.

5. Go to **each one of the folders** and run the submission script:
   cd TRAJECTORIES/TRAJ1
   sbatch submit_nxns-orca6.job

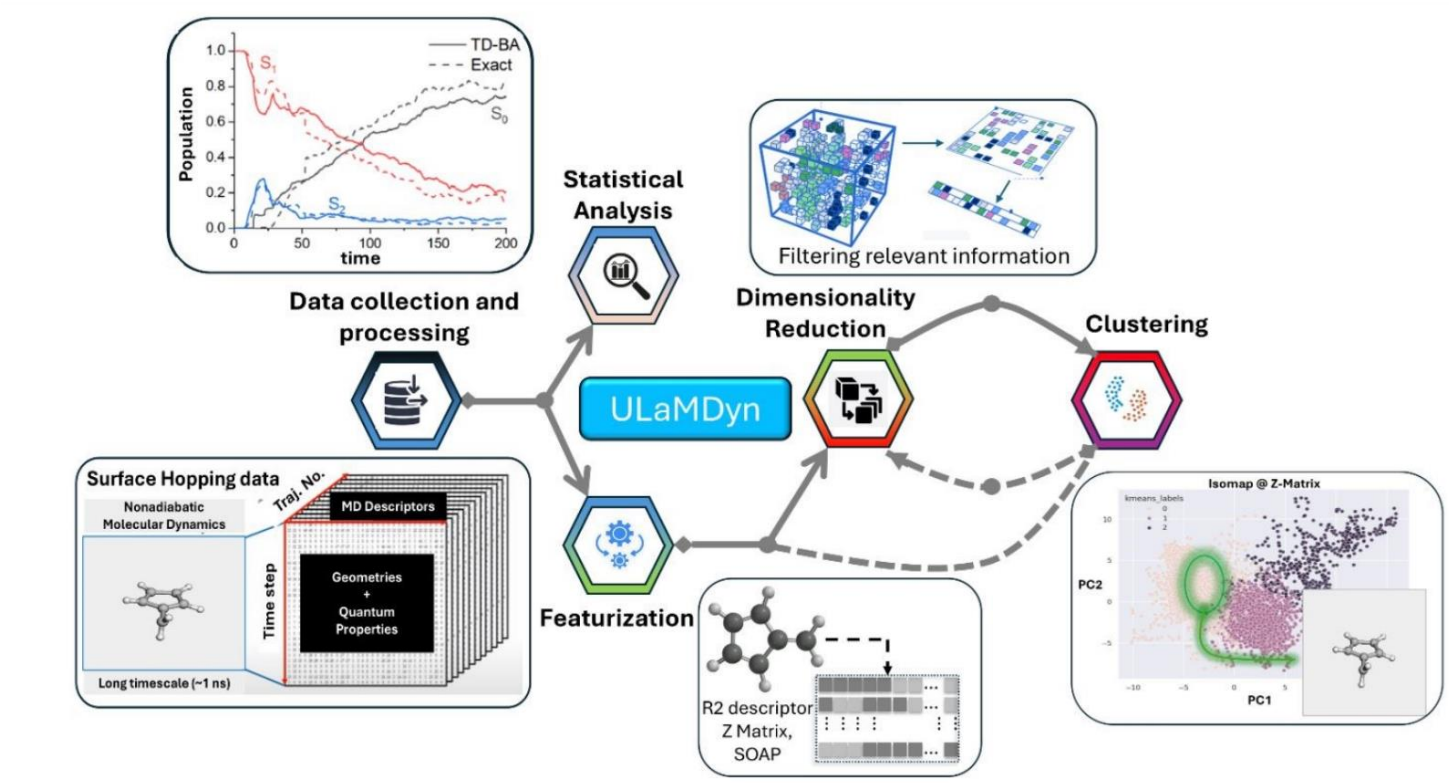
✓ Note that command to run initial conditions is:
   $NXHOME/bin/nx_moldyn > md.log 2>&1

Part 3

Analysis of TSH results

ULaMDyn: Enhancing Excited-State Dynamics Analysis Through Streamlined Unsupervised Learning

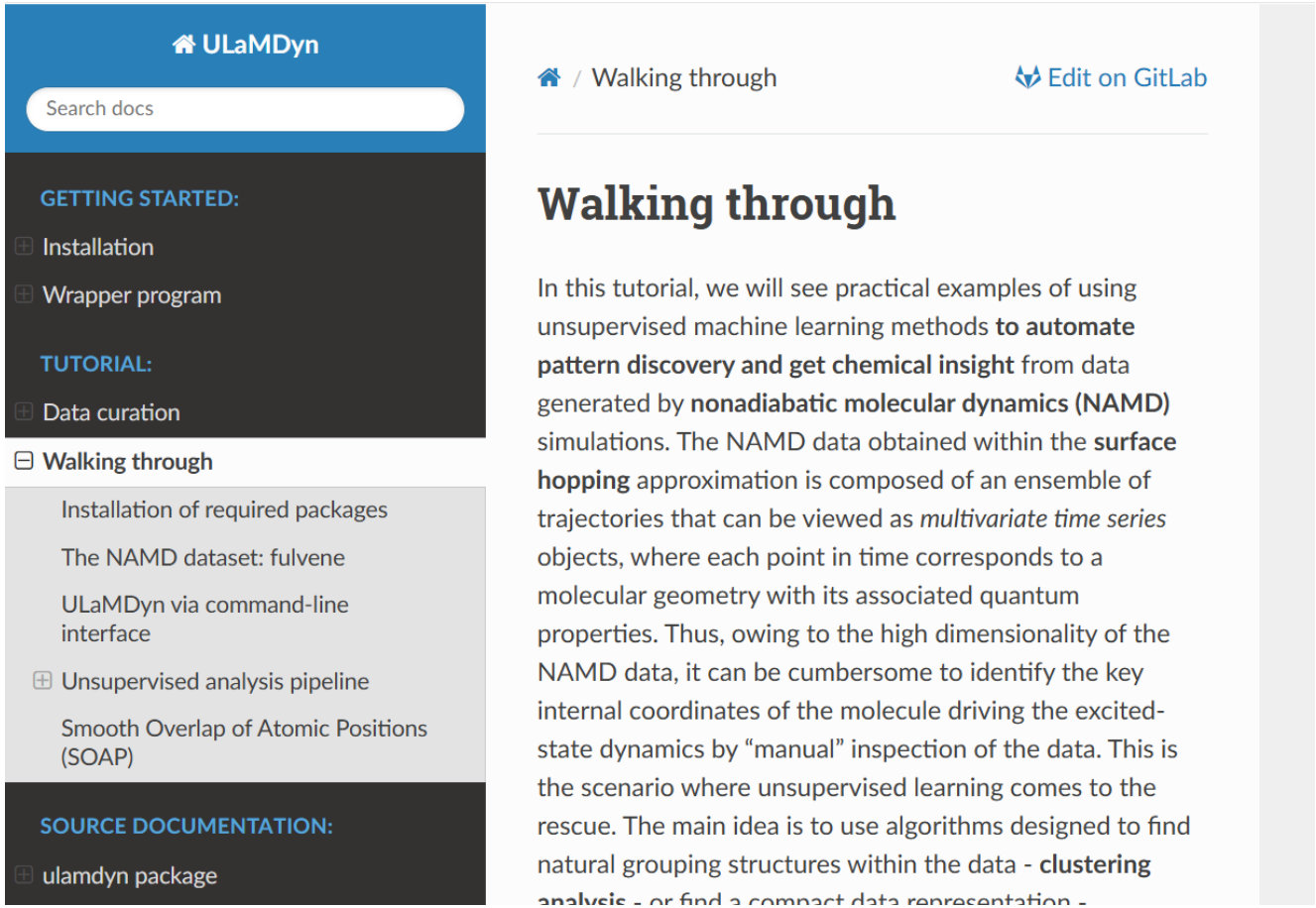
Max Pinheiro, Jr., Matheus de Oliveira Bispo, Rafael Souza Mattos, Mariana Telles do Casal, Bidhan Chandra Garain, Josene M Toldo, SAIKAT MUKHERJEE and Mario Barbatti



Pinheiro et al, Digital Discovery, 2024, Accepted. DOI /10.1039/D4DD00374H

https://ulamdyn.com/

https://ulamdyn.com/ulamdyn_walking-through.html



Jupyter notebook available at:
https://gitlab.com/light-and-molecules/ulamdyn_paper-2025

Before starting

1. Load interactive environment and visualization modules

```
sub-interactive -t 6 -m 24
# module load Molden/7.3-GCCcore-12.3.0
# module load VMD/1.9.4a57-foss-2022a
```

2. Load modules and environment:

```
module load Python/3.10.8-GCCcore-12.2.0
source /lustre/pd03/hpc-smukherjee-1743077499/SOFT/ULAMDYN/myenv/bin/activate
```

3. Run Ulamdyn helper:

```
run-ulamdyn --help
```

4. Copy the files to your home:

```
cp -r MOLEX2025/MOLEX2025_TUTORIAL_FILES/TUTORIAL_5 ~
```

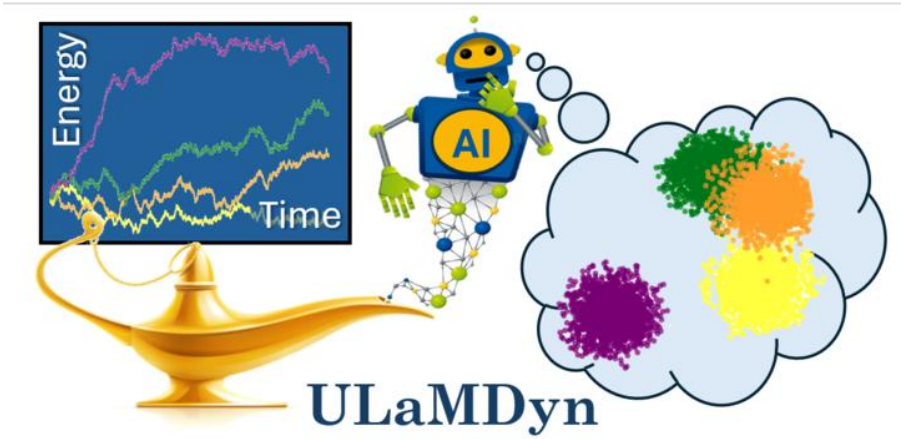
and go to `/ANALYSIS_ORCA/TRAJECTORIES`

Running ULaMDyn

- Create trajs_tmax.dat:

```
cd TRAJECTORIES
./get_lasttime.sh

You should have the file geom.xyz .
(copy geom and run $NX/nx2xyz)
```



- Ulamdyn basic command lines:

```
run-ulamdyn --save_dataset=all
run-ulamdyn --create_stats=all
run-ulamdyn --save_xyz=geoms,"hops,S43"
```

- Run BootStrap:

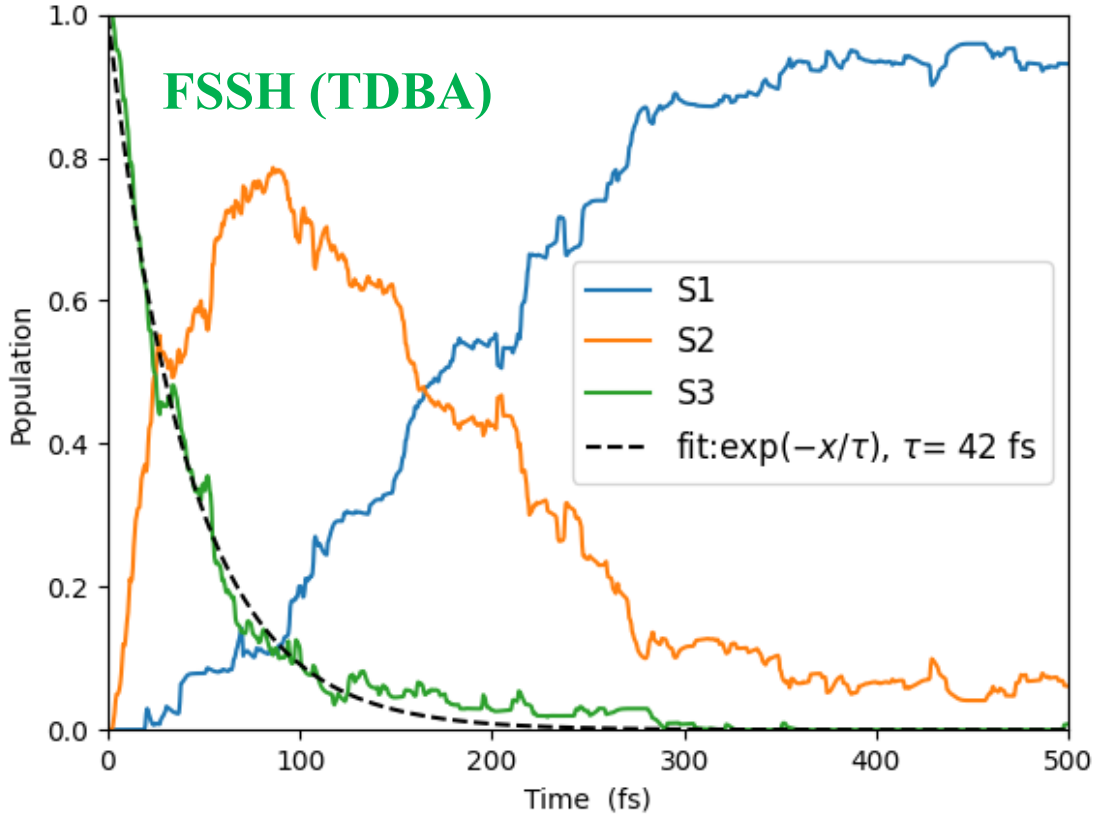
```
run-ulamdyn --bootstrap=1000
```

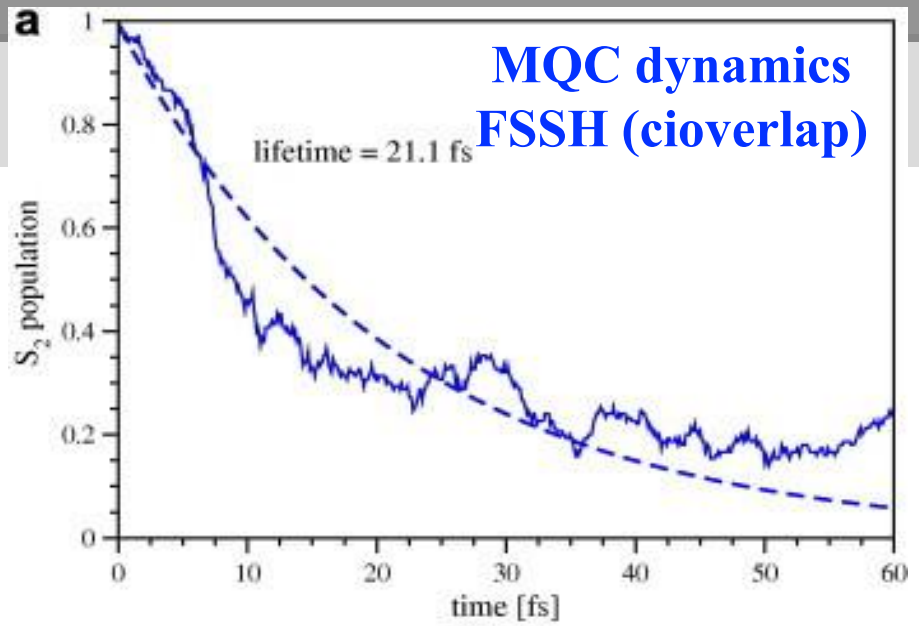
Plotting the population

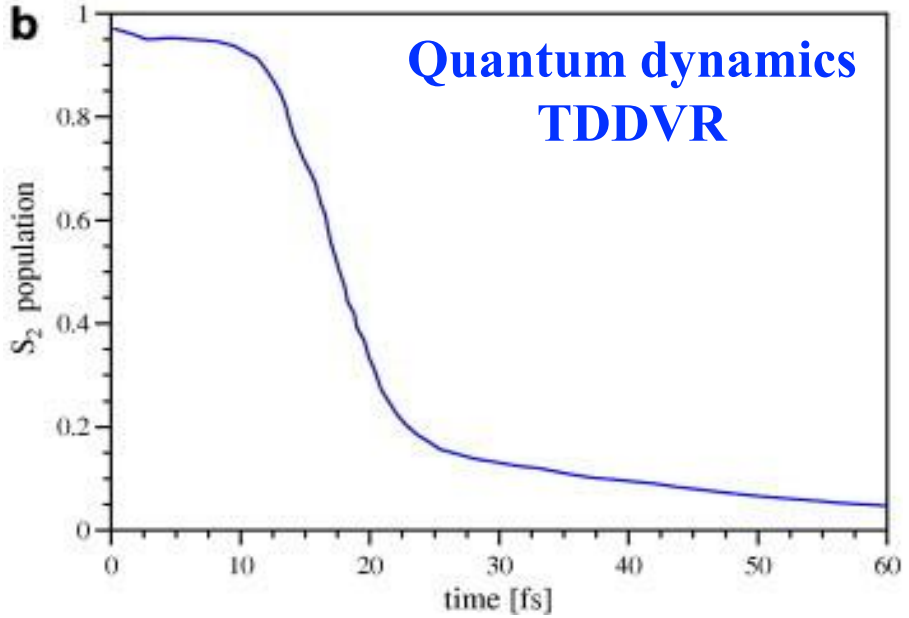
- Plot the population:

```
python plot-pop.py
```

Analysis: S_3 Lifetime

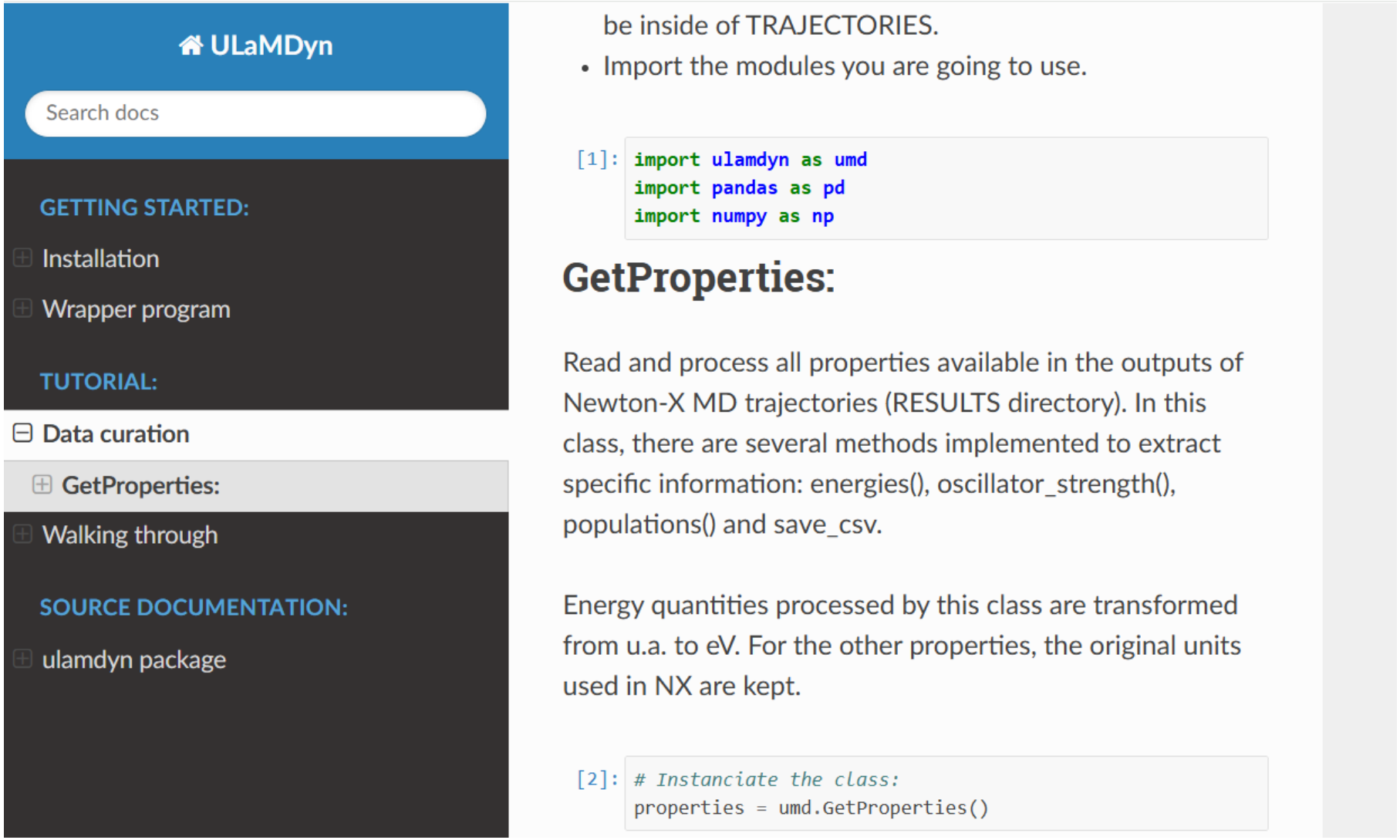






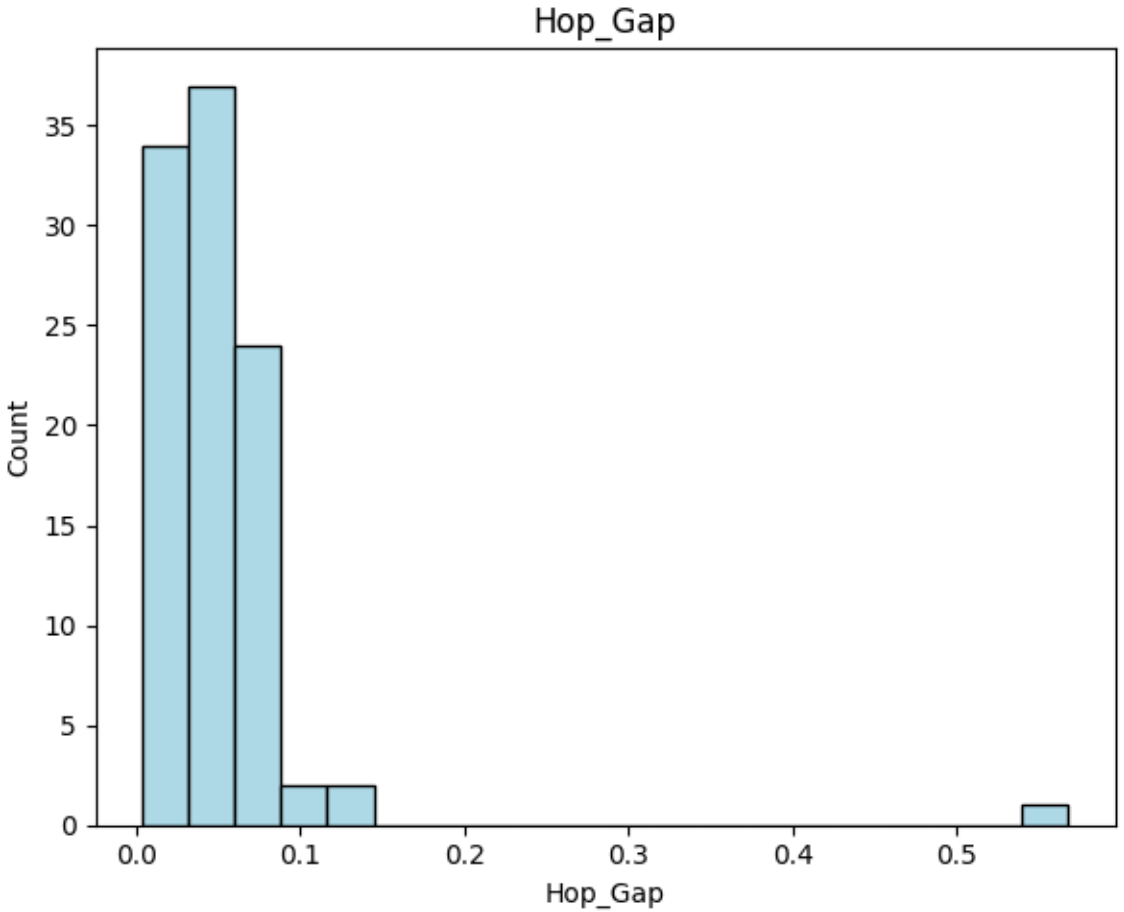
FSSH: U. Werner, R. Mitric, T. Suzuki, V. Bonacic-Koutecky, *Chem. Phys.* **349**, 319 (2008).
QD: P. Puzari, R. S. Swathi, B. Sarkar, S. Adhikari, *J. Chem. Phys.* **123**, 134317 (2005).

Running Ulamdyn

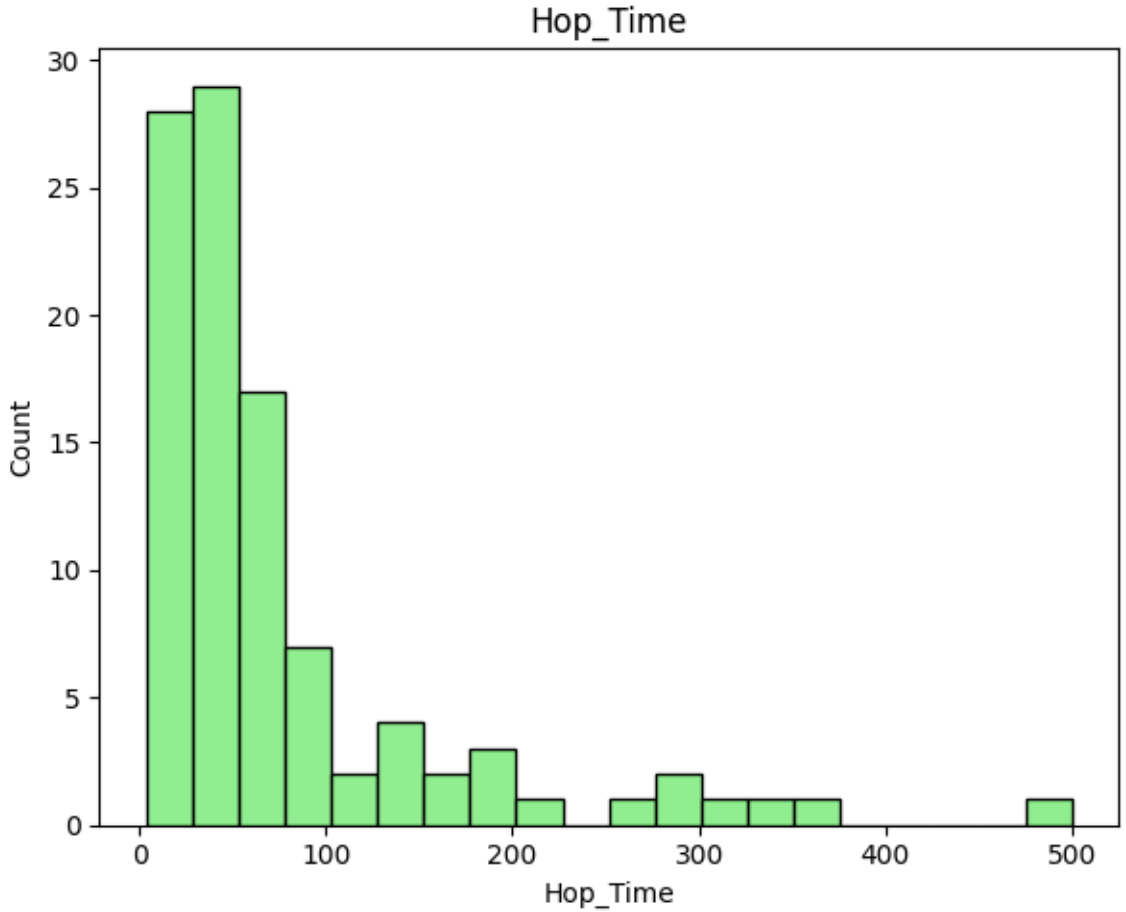


https://ulamdyn.com/data_curation.html

Analysis: Hopping



HOPS S43 : GAP



HOPS S43 : Times