

SHARC: Surface Hopping in the Adiabatic Representation Including Arbitrary Couplings

Tutorial

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Contents

1	Before you Start	4
1.1	Description of the model system	4
2	Quick Tutorial	5
2.1	Input File	5
2.2	Geometry File	6
2.3	QM Run Script	6
2.4	MOLPRO Template	6
2.5	Interface Input	7
2.6	Running SHARC	7
2.7	Output	7
3	Full Tutorial	8
3.1	Important	8
3.2	Optimization and Frequency calculation	8
3.3	Sampling from Wigner distribution	12
3.4	Setting up the initial energy calculations	13
3.4.1	MOLPRO input template	13
3.4.2	Setup of initial calculations	14
3.5	Excited-state selection	18
3.6	Absorption spectra from Initial conditions files	21
3.6.1	Example	21
3.7	Setting up dynamics simulations	23
3.8	Analyzing a single trajectory	29
3.8.1	Data extraction and plotting	29
3.8.2	Analyzing internal coordinates	33
3.9	Analyzing the Ensemble	35
3.9.1	Ensemble Populations	35
3.9.2	Hopping Geometries	41
4	Specialized Tutorials	43
4.1	Using non-default atomic masses	43
4.2	Inactive states	44
4.3	Ionization spectra using <code>excite.py</code> and the COLUMBUS interface	44
4.3.1	<code>setup_init.py</code> Input	45
4.3.2	<code>excite.py</code> Input	45
5	Usage of the Interfaces	46
5.1	MOLPRO	46
5.2	MOLCAS	46
5.2.1	Template file	46
5.3	COLUMBUS	46
5.3.1	General steps in running COLUMBUS	47

5.3.2	COLUMBUS input for usage with the interface	47
5.4	Analytical expressions	48
5.4.1	One-dimensional case	48

1 Before you Start

In this tutorial, the steps necessary to perform non-adiabatic dynamics with SHARC are explained. The tutorial consists of three tutorial sections.

The first one is a quick tutorial, showing just the minimum steps necessary to run the dynamics code.

The second part contains the full tutorial presenting a complete dynamics study including initial condition generation and trajectory analysis (with plotting of the results and a brief discussion).

The third part is a collection of more specialized tutorials showing some advanced usage aspects in detail.

At the end of this document, some additional hints for the usage of the quantum chemistry interfaces are given.

1.1 Description of the model system

The task of the tutorial is to simulate the excited-state dynamics of ethylene. The employed method will be CASSCF(2,2)/6-31G*, using the MOLPRO program package. It is known that the excited-state manifold of ethylene necessitates a much more complex electronic structure treatment than CASSCF(2,2). Nevertheless, for the purposes of this tutorial it is sufficient to use the mentioned CASSCF method.

The main idea is to simulate the well-known excited-state dynamics of ethylene, which after excitation to the $\pi\pi^*$ state undergoes torsion around the double bond. This leads to a conical intersection with the ground state, allowing for ultra-fast relaxation. Additionally, we will also include the triplet $\pi\pi^*$ state, which is possible with the SHARC methodology. However, since spin-orbit coupling is very weak in this system (only light atoms, El-Sayed-forbidden), we do not expect ISC to occur.

In the following, an overview over the level of theory and the initial geometry are given:

Ab initio level of theory for ethylene.		6 Initial geometry ethylene		
Molecule	Ethylene	C	0.000000	0.000000
Charge	zero	C	0.000000	1.335000
Program	MOLPRO	H	0.943102	-0.544500
Method	SA-CASSCF(2,2)	H	0.943102	1.879500
Basis set	6-31G*	H	-0.943102	1.879500
Number of states	2 Singlets, 1 Triplet	H	-0.943102	-0.544500

2 Quick Tutorial

Here we just present how to prepare a single trajectory, using the equilibrium geometry as starting geometry and random velocities.

The goal is to prepare all input files for SHARC and the MOLPRO interface. The necessary files and directories are presented in figure 2.1. Note that the files **MOLPRO.template** and **SH2PRO.inp** are only necessary since we are using the SHARC-MOLPRO interface.

The contents of the files are given in the following.

2.1 Input File

The SHARC input file ("**input**") contains the dynamics settings and names of additional input files (geometry, velocity, coefficients). An example is given below:

```
geomfile "geom"
veloc random 0.1

nstates 2 0 1
state 2 mch
coeff auto

ezero -78.0814
tmax 10.0
stepsize 0.5

surf sharc
coupling ddr
```

The meaning of these keywords is: The geometry is read from file **geom**. The nuclear velocities are picked at random, with 0.1 eV kinetic energy per atom. Two singlet states and one triplet state (with

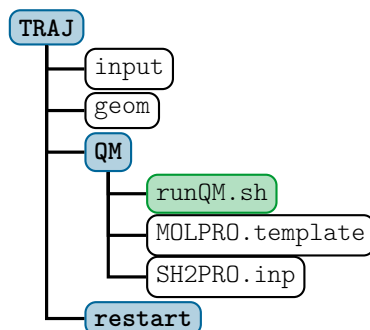


Figure 2.1: Input files for a SHARC dynamics simulation.

3 components) will be included in the simulation. The initial state is the second state (the S_1). The initial coefficients will be set automatically (the initial state will get a coefficient of 1.0, the remaining state zero). The diagonal elements of the Hamiltonian will be shifted by -78.0814 Hartree. The simulation will include 10 fs, with a 0.5 fs timestep. The SHARC formalism will be used (propagation on the diagonalized states). Vectorial non-adiabatic couplings will be used for the propagation.

2.2 Geometry File

The geometry file “**geom**” contains the chemical symbols, atomic charge, x , y and z coordinates and the relative atomic masses.

```
C 6.0  0.0 0.0  0.0 12.000
C 6.0  0.0 0.0  2.5 12.000
H 1.0  1.7 0.0 -1.2  1.008
H 1.0  1.7 0.0  3.7  1.008
H 1.0 -1.7 0.0  3.7  1.008
H 1.0 -1.7 0.0 -1.2  1.008
```

2.3 QM Run Script

At each timestep, SHARC writes the current geometry and different keywords to the file **QM/QM.in** and then calls **runQM.sh**. After this call is finished, SHARC reads the results of the quantum chemistry calculation from **QM.out**.

In most of the cases, in **runQM.sh** simply one of the SHARC-interfaces is called.

```
cd QM
$SHARC/SHARC_MOLPRO.py QM.in > QM.log
```

The interface will do all work necessary to produce the desired file **QM.out**.

2.4 MOLPRO Template

The MOLPRO interface needs as additional input file giving the settings for the electronic structure calculation. The file is called “**MOLPRO.template**”.

```
***
memory,12500,k
basis=6-31G*

{casscf
frozen,0
closed,7
occ,9
wf,16,1,0
state,2
weight,1,1
```

```
wf,16,1,2  
state,1  
weight,1  
};  
---
```

2.5 Interface Input

The interface additionally needs some paths, which are read from “SH2PRO.inp”.

```
molpro $MOLPRO/molpro  
scratchdir ./SCRA/  
savedir ../restart/
```

2.6 Running Sharc

The trajectory can then be started by simply executing:

```
$SHARC/sharc.x input
```

2.7 Output

SHARC produces four output files, **output.log**, **output.lis**, **output.dat** and **output.xyz**. The file **output.log** contains mainly a listing of the chosen options and the resulting dynamics settings. At higher print levels, the log file contains also information per timestep. **output.lis** contains a table with one line per timestep, giving active states, energies and expectation values. **output.dat** contains a list of all important matrices and vectors at each timestep. This information can be extracted with **data_extractor.x** to yield plottable table files. **output.xyz** contains the geometries of all timesteps (the comments to each geometry give the active state).

3 Full Tutorial

This tutorial presents all steps of a dynamics simulation. These steps include preparation steps like optimization and frequency calculation, generation of the Wigner distribution, calculation of the excited states of the Wigner distribution, initial state selection. It will be shown how to run the dynamics simulations. Also, trajectory analysis will be visited, including plotting of energies, populations, etc. of a single trajectory, calculation of internal coordinates, ensemble populations.

3.1 Important

Beyond the core dynamics program the SHARC suite contains a number of Python scripts allowing to perform various types of setup and analysis tasks. There are basically two types of these scripts. Non-interactive scripts can be controlled by command-line arguments and options. Every non-interactive script can be called with the command line option **-h** in order to get a description of the functionality and possible options. Interactive scripts ask the user for information about the task to be conducted (using features like auto-complete and default values), and only perform the task after the input has been completed.

In the tutorial, the output of the interactive scripts is shown as in this example. **Red bold text** gives the input which the user has to type.

```
Type of calculation: 2
Frequency calculation? [True] <ENTER>

Geometry filename: [geom.xyz] (autocomplete enabled) g<TAB>
Geometry filename: [geom.xyz] (autocomplete enabled) geom.xyz
```

During the interactive sessions, square brackets indicate that the question has a default answer, which can be used by just pressing ENTER. If filenames or directory paths need to be entered, auto-complete is active, which can be used by pressing TAB. Every interactive script upon completion also produces a file **KEYSTROKES.name**, which contains all user input for the last run.

Please make sure before starting that **\$SHARC** is set to the directory containing the SHARC scripts and executables.

It is also advisable to set **\$MOLPRO** to the MOLPRO executable.

3.2 Optimization and Frequency calculation

In general, the user is free to calculate the frequencies and normal modes with any quantum chemistry software and any method he sees fit. The user only has to provide a standard MOLDEN format file containing the results of the frequency calculation. However, usually it is advisable to

calculate the frequencies at the same level of theory as the dynamics calculation. For the ethylene example, we will use the quantum chemistry method specified above.

Create an empty directory. Prepare a geometry file called **geom.xyz** containing the given geometry.

```
user@host> mkdir Ethylene
user@host> cd Ethylene
user@host> vi geom.xyz
```

The SHARC suite comes with an input generator for MOLPRO, which produces input for single-point calculations, optimizations and frequency calculations. It can be invoked with

```
user@host> $SHARC/molpro_input.py
```

The script is interactive. Start the script and prepare an optimization plus frequency calculation on SA-CASSCF level. The script can also generate a Bash-script to instantly launch the MOLPRO calculation.

```
=====
||                                     ||
||               MOLPRO Input file generator               ||
||                                     ||
||               Author: Sebastian Mai                     ||
||                                     ||
||               Version:0.2                               ||
||               04.06.14                                   ||
||                                     ||
||=====

This script allows to quickly create MOLPRO input files for single-points calculations,
ground state optimizations, frequency calculations and SA-CASSCF calculations.
It also generates MOLPRO.template files to be used with the SHARC-MOLPRO Interface.

-----Type of calculation-----

This script generates input for the following types of calculations:
 1      Single point calculations (HF, DFT, MP2, SS/SA-CASSCF)
 2      Optimizations & Frequency calculations (HF, DFT, MP2, SS/SA-CASSCF)
 3      MOLPRO.template file for dynamics (SA-CASSCF)
Please enter the number corresponding to the type of calculation.

Type of calculation: 2                                # Anything after # is a comment
Frequency calculation? [True] <ENTER>                 # Opt + Freq

-----Geometry-----

Please specify the geometry file (xyz format, Angstroms):
Geometry filename: [geom.xyz] (autocomplete enabled) <ENTER> # use default "geom.xyz"
Number of atoms: 6
Nuclear charge: 16

Enter the total (net) molecular charge:
Charge: [0] <ENTER>
Number of electrons: 16

Use standard masses (most common isotope)? [True] <ENTER>

-----Level of theory-----

Supported by this script are:
 1      HF
```

```

2      DFT (Only numerical frequencies)
3      MP2 (Only numerical frequencies)
4      SS-CASSCF
5      SA-CASSCF (Only numerical frequencies)

Level of theory: 5      # SA-CASSCF

Please enter the basis set.
For SA-CASSCF Optimizations/Frequencies and SS-CASSCF Frequencies,
only segmented basis sets are allowed.
Common available basis sets:
  Pople:      6-31G**, 6-311G, 6-31+G, 6-31G(d,p), ...
  Dunning:    cc-pVXZ, aug-cc-pVXZ, cc-pVXZ-DK, ...    not available
  Turbomole:  def2-SV(P), def2-SVP, def2-TZVP, ...
  ANO:        ROOS                                     not available
Basis set: 6-31G*
Douglas-Kroll scalar-relativistic integrals? [True] <ENTER>

-----CASSCF Settings-----

Number of active electrons: 2
Number of active orbitals: 2
Please enter the number of states as a list of integers
e.g. 3 0 3 for three singlets, zero doublets and three triplets.
Number of states: 2 0 1
Accepted number of states: 2 0 1

Please specify the state to optimize
e.g. 3 2 for the second triplet state.
Root: [1 1] <ENTER>      # first singlet state

-----Memory-----

Memory in MB: 300

#####Full input#####          # this output is for debugging

ltype      5
DK          True
basis      6-31g*
mem         300
cas.norb    2
maxmult     3
cas.nact    2
ctype      2
nelec       16
cas.nstates [2, 0, 1]
geom        [['C', 0.0, 0.0, -0.002313],
              ['C', -0.0, 0.0, 1.337313],
              ['H', 0.931545, 0.0, -0.572106],
              ['H', 0.931545, 0.0, 1.907105],
              ['H', -0.931545, 0.0, 1.907105],
              ['H', -0.931545, 0.0, -0.572106]]
cas.root    [1, 1]
natom       6
ncharge     16
freq        True
nondefmass  False

```

```

Writing input to MOLPRO.input

Run script? [True] <ENTER>

-----Path to MOLPRO-----

Environment variable $MOLPRO detected:
$MOLPRO=/usr/license/molpro/molpros_2012_1_5_Linux_x86_64_i8/bin/molpro

Do you want to use this MOLPRO installation? [True] <ENTER>

-----Scratch directory-----

Please specify an appropriate scratch directory. This will be used to temporally store the integrals.
The scratch directory will be deleted after the calculation. Remember that this script cannot check
whether the path is valid, since you may run the calculations on a different machine. The path will
not be expanded by this script.
Path to scratch directory: (autocomplete enabled) $TMPDIR/Ethylene/Opt

Writing run script run_MOLPRO.sh

Finished

```

Execute the run script.

```
user@host> sh run_MOLPRO.sh
```

This will produce the files **MOLPRO.out**, **freq.molden** and **wf**. The first file contains (among other things) the ground state minimum energy (should be -78.08139491 Hartree) and the vibrational wavenumbers. Check for any imaginary frequencies. There should be an output block like this in the output file:

Low Vibration	Wavenumber
Nr	[1/cm]
1	0.00
2	0.00
3	0.00
4	0.00
5	0.00
6	0.00
Vibration	Wavenumber
Nr	[1/cm]
1	885.91
2	970.08
3	1068.60
4	1299.39
5	1342.30
6	1439.73
7	1605.70
8	1774.83
9	3319.44
10	3339.21
11	3396.75
12	3422.73

The **wf** file contains the CASSCF orbitals and can be used as starting orbitals for subsequent CASSCF calculations. The **freq.molden** is needed in the next step.

3.3 Sampling from Wigner distribution

In the next step, the initial coordinates and velocities need to be calculated from the harmonic frequencies and normal modes. The corresponding SHARC script can be executed by typing

```
user@host> $SHARC/wigner.py -n 20 freq.molden
```

The **-n** option is necessary to specify the number of initial conditions to be generated. Here, we generate 20 initial conditions. The output should look like this:

```
Initial condition generation started...
MOLDEN file           = "freq.molden"
OUTPUT file           = "initconds"
Number of geometries   = 20
Random number generator seed = 16661

Geometry:
C   6.0  -0.000000000  0.000000000  -0.00760978  12.000000000
C   6.0   0.000000000  0.000000000   2.53039416  12.000000000
H   1.0   1.73012211  0.000000000  -1.07271869   1.00782503
H   1.0   1.73012212  0.000000000   3.59550308   1.00782503
H   1.0  -1.73012211  0.000000000   3.59550308   1.00782503
H   1.0  -1.73012212  0.000000000  -1.07271870   1.00782503
Assumed Isotopes: H-1 C-12
Isotopes with * are pure isotopes.

Frequencies (cm-1):
 1    885.9700
 2    970.0600
 3   1068.5700
 4   1299.2900
 5   1342.3400
 6   1439.6100
 7   1605.6600
 8   1774.6800
 9   3319.3700
10   3339.1300
11   3396.7200
12   3422.7000
```

The results of the sampling are written to the file **initconds**. This file contains all necessary information for subsequent steps.

3.4 Setting up the initial energy calculations

In the next step, for each geometry an excited-state calculation has to be conducted in order to obtain the excitation energies and oscillator strengths. This calculations can be setup using the script `setup_init.py`.

3.4.1 Molpro input template

However, first we need to prepare the input for the MOLPRO excited-state calculation. Again launch the MOLPRO input generator:

```
user@host> $SHARC/molpro_input.py
```

Prepare a template file for the SHARC-MOLPRO interface.

```
=====
||                                     ||
||               MOLPRO Input file generator               ||
||                                     ||
||               Author: Sebastian Mai                      ||
||                                     ||
||               Version:0.2                                ||
||               04.06.14                                   ||
||                                     ||
||=====

This script allows to quickly create MOLPRO input files for single-points calculations,
ground state optimizations, frequency calculations and SA-CASSCF calculations.
It also generates MOLPRO.template files to be used with the SHARC-MOLPRO Interface.

-----Type of calculation-----

This script generates input for the following types of calculations:
 1      Single point calculations (HF, DFT, MP2, SS/SA-CASSCF)
 2      Optimizations & Frequency calculations (HF, DFT, MP2, SS/SA-CASSCF)
 3      MOLPRO.template file for dynamics (SA-CASSCF)
Please enter the number corresponding to the type of calculation.

Type of calculation: 3          # MOLPRO.template generation

-----Geometry-----

No geometry necessary for MOLPRO.template generation

Number of electrons: [16] <ENTER>          # if MOLPRO.input is there, all following
                                           # input is auto-detected

-----Level of theory-----

Supported by this script are:
 1      HF
 2      DFT
 3      MP2
 4      SS-CASSCF
 5      SA-CASSCF

Choosing SA-CASSCF for MOLPRO.template generation.

Please enter the basis set.
```

For MOLPRO.template generation, only segmented basis sets are allowed.

Common available basis sets:

Pople: 6-31G**, 6-311G, 6-31+G, 6-31G(d,p), ...

Dunning: cc-pVXZ, aug-cc-pVXZ, cc-pVXZ-DK, ... not available

Turbomole: def2-SV(P), def2-SVP, def2-TZVP, ...

ANO: ROOS not available

Basis set: [6-31G*] **<ENTER>**

Douglas-Kroll scalar-relativistic integrals? [True] **<ENTER>**

-----CASSCF Settings-----

Number of active electrons: [2] **<ENTER>**

Number of active orbitals: [2] **<ENTER>**

Please enter the number of states as a list of integers

e.g. 3 0 3 for three singlets, zero doublets and three triplets.

Number of states: [2 0 1] **<ENTER>**

Accepted number of states: 2 0 1

-----Memory-----

Recommendation: for small systems: 100-300 MB, for medium-sized systems: 1000-2000 MB

Memory in MB: [300] **<ENTER>**

#####Full input#####

```
ltype      5
DK          True
basis      6-31G*
mem        300
cas.norb    2
maxmult     3
cas.nact    2
ctype      3
cas.nstates [2, 0, 1]
nelec      16
geom       None
freq       False
```

Writing input to MOLPRO.template

Finished

This will create a file called **MOLPRO.template**, which is needed for the following setup steps.

3.4.2 Setup of initial calculations

Now launch the setup script. Note that the subdirectory structure will be created in the directory where the script is run.

user@host> **\$SHARC/setup_init.py**

This script is also interactive.

||

||

```

||                               Setup initial conditions for SHARC dynamics                               ||
||                               Author: Sebastian Mai                                                  ||
||                               Version:0.2                                                            ||
||                               03.06.14                                                                ||
||=====||

This script automatizes the setup of excited-state calculations for initial conditions
for SHARC dynamics.

-----Initial conditions file-----

Initial conditions file "initconds" detected. Do you want to use this?
Use file "initconds"? [True] <ENTER>

File "initconds" contains 20 initial conditions.
Number of atoms is 6

-----Range of initial conditions-----

Please enter the range of initial conditions for which an excited-state calculation
should be performed as two integers separated by space.
Initial condition range: [1 20] 1 10 # not all initial conditions need to be calculated

Script will use initial conditions 1 to 10 (10 in total).

-----Number of states-----

Please enter the number of states as a list of integers
e.g. 3 0 3 for three singlets, zero doublets and three triplets.
Number of states: 2 0 1 # this can differ from the number of states in MOLPRO.template
Total number of states: 5

Spin-Orbit calculation? [True] <ENTER>
Will calculate spin-orbit matrix.

-----Choose the quantum chemistry interface-----

Please specify the quantum chemistry interface (enter any of the following numbers):
1      MOLPRO (only CASSCF)
2      COLUMBUS (CASSCF, RASSCF and MRCISD), using SEWARD integrals
3      Analytical PESs
4      MOLCAS (only CASSCF)

Interface number: 1

=====
||                               MOLPRO Interface setup                               ||
||=====||

-----Path to MOLPRO-----

Environment variable $MOLPRO detected:
$MOLPRO=/usr/license/molpro/molpros_2012_1_5_Linux_x86_64_i8/bin/molpro

```

Do you want to use this MOLPRO installation? [True] **<ENTER>**

-----Scratch directory-----

Please specify an appropriate scratch directory. This will be used to temporally store the integrals. The scratch directory will be deleted after the calculation. Remember that this script cannot check whether the path is valid, since you may run the calculations on a different machine. The path will not be expanded by this script.

Path to scratch directory: (autocomplete enabled) **\$TMPDIR/Init_WORK**

-----MOLPRO input template file-----

Please specify the path to the MOLPRO.template file. This file must be a valid MOLPRO input file for a CASSCF calculation. It should contain the following settings:

- memory settings
- Basis set (possibly also Douglas-Kroll settings etc.)
- CASSCF calculation with:
 - * Number of frozen, closed and occupied orbitals
 - * wf and state cards for the specification of the wavefunction

MOLPRO.template files can easily be created using molpro_input.py (Open a second shell if you need to create one now).

The MOLPRO interface will generate the remaining MOLPRO input automatically.

Valid file "MOLPRO.template" detected.

Use this template file? [True] **<ENTER>**

-----Initial wavefunction: MO Guess-----

Please specify the path to a MOLPRO wavefunction file containing suitable starting MOs for the CASSCF calculation. Please note that this script cannot check whether the wavefunction file and the Input template are consistent!

If you optimized your geometry with MOLPRO/CASSCF you can reuse the "wf" file from the optimization.

Do you have an initial wavefunction file? [True] **<ENTER>**

Initial wavefunction file: [wf.init] (autocomplete enabled) **wf**

```
=====
||                               Run mode setup                               ||
=====
```

-----Run script-----

This script can generate the run scripts for each initial condition in two modes:

- In the first mode, the calculation is run in subdirectories of the current directory.
- In the second mode, the input files are transferred to another directory (e.g. a local scratch directory), the calculation is run there, results are copied back and the temporary directory is deleted. Note that this temporary directory is not the same as the scratchdir employed by the interfaces.

Note that in any case this script will setup the input subdirectories in the current working directory.

Do you want to use mode 1

(actually perform the calculations in subdirectories of:

/user/mai/Documents/NewSHARC/SHARC_1.5/TESTS/Tutorial/MOLPRO_Ethylene/Init)


```

Calculate here? [False] yes

-----Submission script-----

During the setup, a script for running all initial conditions sequentially in batch mode
is generated. Additionally, a queue submission script can be generated for all initial conditions.

Generate submission script? [False] <ENTER>

#####Full input#####

initf          <open file 'initconds', mode 'r' at 0x7f64cdab9b70>
soc            True
ninit          20
scratchdir     $TMPDIR/Init_WORK
molpro.guess    wf
molpro         /usr/license/molpro/molpros_2012_1_5_Linux_x86_64_i8/bin/molpro
here           True
states         [2, 0, 1]
interface      1
irange         [1, 10]
natom          6
qsub           False
nstates        5
molpro.template MOLPRO.template
cwd            /user/sharc/Tutorial/Ethylene/

Do you want to setup the specified calculations? [True] <ENTER>

Progress: [=====] 100%

```

The script will create a directory **ICOND_005i** for each initial condition (and **ICOND_00000** for the equilibrium geometry), with the corresponding input for the quantum chemistry interface and a runscript. Additionally, the script **all_run_init.sh** is generated, which allows to run all excited-state calculations subsequently.

Run all initial conditions calculations:

```
user@host> sh all_run_init.sh
```

For larger calculations, you should send each **ICOND_****/run.sh** script to a queueing system.

After the calculations are finished, each subdirectory should contain a file called **QM.out** holding the Hamiltonian and transition dipole moment matrices.

3.5 Excited-state selection

In the next step, the results of the excited-state calculations have to be read, converted to excitation energies and oscillator strengths, and the brightest initial conditions selected for the dynamics simulation. This task is accomplished using

```
user@host> $SHARC/excite.py
```

This script is interactive, and input should be straight-forward. Per default, the script reads the ground state equilibrium energy from **ICOND_00000/QM.out**, if this file exists. Otherwise, the script asks for the ground states equilibrium energy.

```
=====
||                               ||
||           Excite initial conditions for SHARC           ||
||                               ||
||           Author: Sebastian Mai                         ||
||                               ||
||           Version:0.2                                    ||
||           03.06.14                                      ||
||                               ||
||=====
=====

This script automatizes to read-out the results of initial excited-state calculations for SHARC.
It calculates oscillator strength (in MCH and diagonal basis) and stochastically
determines whether a trajectory is bright or not.

-----Initial conditions file-----

Initial conditions file "initconds" detected. Do you want to use this?
Use file "initconds"? [True] <ENTER>

File "initconds" contains 20 initial conditions.
Number of atoms is 6

-----Generate excited state lists-----

Using the following options, excited state lists can be added to the initial conditions:

1      Generate a list of dummy states
2      Read excited-state information from ab initio calculations (from setup_init.py)

How should the excited-state lists be generated? [2] <ENTER>          # Read from ICOND_%05i/
Please enter the path to the directory containing the ICOND subdirectories.
Path to ICOND directories: (autocomplete enabled) .                  # "." is the current directory

/user/sharc/Tutorial/Ethylene/
Directory contains 11 subdirectories.
There are more initial conditions in initconds.

-----Excited-state representation-----

This script can calculate the excited-state energies and oscillator strengths in two
representations.
These representations are:
- MCH representation: Only the diagonal elements of the Hamiltonian are taken into account.
The states are the spin-free states as calculated in the quantum chemistry code. This option
is usually sufficient for systems with small SOC (below 300 cm-1).

```

- diagonal representation: The Hamiltonian including spin-orbit coupling is diagonalized. The states are spin-corrected, fully adiabatic. Note that for this the excited-state calculations have to include spin-orbit couplings. This is usually not necessary for systems with small SOC.

Do you want to use the diagonal representation (yes=diag, no=MCH)? **no**

-----Reference energy-----

Reference energy read from file
/user/sharc/Tutorial/Ethylene/ICOND_000000/QM.out
E_ref= -78.081394900000

-----Excited-state selection-----

Using the following options, the excited states can be flagged as valid initial states for dynamics:

- 1 Unselect all initial states
- 2 Provide a list of desired initial states
- 3 Simulate delta-pulse excitation based on excitation energies and oscillator strengths

How should the excited states be flagged? [3] **<ENTER>** # Use oscillator strengths

-----Excitation window-----

Enter the energy window for exciting the trajectories.
Range (eV): [0.0 10.0] 9 11

Script will allow excitations only between 9.000000 eV and 11.000000 eV.

-----Considered states-----

#State	Mult	M_s	Quant	# Here the states are listed, if known
1	1	0	1	
2	1	0	2	
3	3	-1	1	
4	3	0	1	
5	3	1	1	

Do you want to include all states in the selection? [True] **<ENTER>**

-----Random number seed-----

Please enter a random number generator seed (type "!" to initialize the RNG from the system time).
RNG Seed: [!] **1234**

#####Full input#####

```

initf          <open file 'initconds', mode 'r' at 0x153e390>
eharm          0.0543664278
ninit         20
diag          False
erange        [0.33074377942027749, 0.40424239706922804]
allowed       set([])
excite        3

```

```

repr          MCH
states        [2, 0, 1]
ion           False
iconddir      /user/sharc/Tutorial/Ethylene/
make_list     False
eref          -78.0813949
ncond         11
natom         6
read_QMout    True
gen_list      2

Do you want to continue? [True] <ENTER>

Number of initial conditions in file:      20
Number of initial conditions with QM.out:  10
Number of initial conditions excited:

State  Excited  InRange  Total
  1         0         0      10
  2        10        10      10    # we can setup 10 trajectories starting from state 2 (S1)
  3         0         0      10
  4         0         0      10
  5         0         0      10
Writing output to initconds.excited ...

```

excite.py will generate a new file called **initconds.excited**, which contains all information from the **initconds** file, as well as information about the ground state equilibrium energy, the state representation and the excited states for each initial condition. In order to calculate absorption spectra and to setup trajectories, this file is necessary.

If you later want to do another selection (with a different excitation window or with the exclusion of some states), you can tell **excite.py** to read from **initconds.excited**, instead of reading all **QM.out** files again.

From the **initconds.excited** file, also absorption spectra can be generated, see section 3.6.

3.6 Absorption spectra from Initial conditions files

The content of the file **initconds.excited** can be used to generate absorption spectra which go beyond the Condon approximation. The spectrum is the sum of the spectra of each initial condition, which is a line spectrum of the excitation energies versus the oscillator strengths. A Gaussian (or Lorentzian) convolution of the line spectra can be done as well.

The calculation of convoluted or line spectra is carried out by **spectrum.py**.

3.6.1 Example

Call the script by

```
user@host> $SHARC/spectrum.py -o spectrum.out -e 9 12 initconds.excited
```

Using command-line options it is possible to calculate only spectra for part of the initial condition set, to change the size and limits of the energy grid (here we plot from 9 eV to 12 eV) and to influence the line shape (Gaussian or Lorentzian, and FWHM). With the **-l** option, a line spectrum is produced instead.

The program also writes some information about the calculation to the screen:

```
Number of grid points: 500
Energy range: 9.000 to 12.000 eV
Lineshape: Gaussian
Number of initial conditions: 50
Reference energy -78.0813949000
Representation: MCH
Reading initial conditions 1 to 50

Number of states: 5
Number of initial conditions with excited-state information (per state):
10 10 10 10 10

Progress: [=====] 100%

Maximum of the absorption spectrum: 1.782352

Output spectrum written to "spectrum.out".
```

The results can be easily plotted using **GNUPLOT**. Just give the corresponding command-line flag and then call **GNUPLOT**:

```
user@host> $SHARC/spectrum.py -o spectrum.out -e 9 12
--gnuplot spectrum.gp initconds.excited
user@host> gnuplot spectrum.gp
```

In figure 3.1 the result of this convolution is shown. Note that on CASSCF level of theory, the excitation energy of ethylene is reproduced quite badly and the number of initial conditions is too low to reliably sample the ground state Wigner distribution.

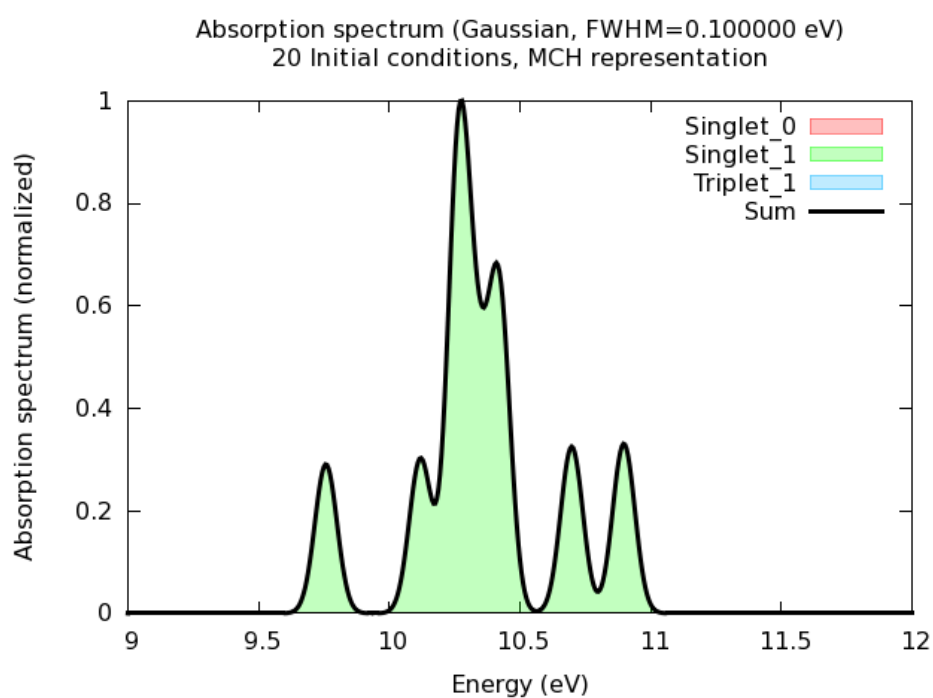


Figure 3.1: Absorption spectrum and based on 10 initial conditions (Since there are 20 initial conditions in `initconds.excited`, the title lists 20 instead of 10).

3.7 Setting up dynamics simulations

The last preparatory step towards dynamics simulations consists naturally in setting up the SHARC input files and run scripts. The interactive script **setup_traj.py** takes care of this step. Run the script in the directory where the trajectories should be set up. Make sure that you have all files required by the interface (**MOLPRO.template**, **wf**) at hand.

```
user@host> $SHARC/setup_traj.py
```

```
=====
||                                     ||
||           Setup trajectories for SHARC dynamics           ||
||                                     ||
||           Author: Sebastian Mai                          ||
||                                     ||
||           Version:0.2                                     ||
||           03.06.14                                       ||
||                                     ||
||=====

This script automatizes the setup of the input files for SHARC dynamics.

=====
||                                     ||
||           Initial conditions                             ||
||=====

This script reads the initial conditions (geometries, velocities, initial excited state)
from the initconds.excited files as provided by excite.py.

Initial conditions file "initconds.excited" detected. Do you want to use this?
Use file "initconds.excited"? [True] <ENTER>

File initconds.excited contains 20 initial conditions.
Number of atoms is 6
Reference energy -78.081394900000 a.u.
Excited states are in MCH representation.

Please enter the number of states as a list of integers
e.g. 3 0 3 for three singlets, zero doublets and three triplets.
Number of states: [2 0 1] <ENTER>          # a different number of states than in the
                                           # initial calculations could be used in the dynamics

Number of states: [2, 0, 1]
Total number of states: 5

Do you want all states to be active? [True] <ENTER>

Do you want to see the content of the initconds file? [True] <ENTER>

Number of initial conditions in file:      20
Contents of the initconds file:

Legend:
?      Geometry and Velocity
.      not selected
#      selected

State 1:      # we performed only 10 initial excitation calculations, hence the "?"
              10      20
```

```

      |      |
0 | ..... ?????????? # No initial conditions selected in S0
State 2:
      10      20
      |      |
0 | ##### ?????????? # Initial conditions 1 to 10 are selected
State 3:
      10      20
      |      |
0 | ..... ?????????? # No initial conditions selected in T1
State 4:
      10      20
      |      |
0 | ..... ??????????
State 5:
      10      20
      |      |
0 | ..... ??????????
Number of excited states and selections:
State   #InitCalc   #Selected
  1         10         0
  2         10        10 # we can setup 10 trajectories starting from state 2 (S1)
  3         10         0
  4         10         0
  5         10         0

Please enter a list specifying for which excited states trajectories should be set-up
e.g. 1 2 5 to select states 1, 2, and 5.
States to setup the dynamics: [2] <ENTER>

There can be 10 trajectories set up.

Please enter the index of the first initial condition in the initconds file to be setup.
Starting index: [1] <ENTER>

There can be 10 trajectories set up, starting in 1 states.

Please enter the total number of trajectories to setup.
Number of trajectories: [10] <ENTER>

Please enter a random number generator seed (type "!" to initialize the RNG from the system time).
RNG Seed: [!] 1234

=====
||                               Choose the quantum chemistry interface                               ||
=====

Please specify the quantum chemistry interface (enter any of the following numbers):
1      MOLPRO (only CASSCF)
2      COLUMBUS (CASSCF, RASSCF and MRCISD), using SEWARD integrals
3      Analytical PESs
4      MOLCAS (only CASSCF)

Interface number: 1

```



```

=====
||                               Surface Hopping dynamics settings                               ||
=====

-----Simulation time-----

Please enter the total simulation time.
Simulation time (fs): [1000.0] 100

Please enter the simulation timestep (0.5 fs recommended).
Simulation timestep (fs): [0.5] <ENTER>

Simulation will have 201 timesteps.

Please enter the number of substeps for propagation (25 recommended).
Nsubsteps: [25] <ENTER>

The trajectories can be prematurely terminated after they run for a certain time in
the lowest state.
Do you want to prematurely terminate trajectories? [False] <ENTER>

-----Dynamics settings-----

Do you want to perform the dynamics in the diagonal representation (SHARC dynamics)
or in the MCH representation (regular surface hopping)?
SHARC dynamics? [True] <ENTER>

Please choose the quantities to describe non-adiabatic effects between the states:
1      DDT      = < a|d/dt|b >      Hammes-Schiffer-Tully scheme
2      DDR      = < a|d/dR|b >      original Tully scheme
3      overlap  = < a(t0)|b(t) >    Local Diabatization scheme

Coupling number: 2

For SHARC dynamics, the evaluation of the mixed gradients necessitates to calculate
non-adiabatic coupling vectors (Recommended).
Include non-adiabatic couplings in the gradient transformation? [True] <ENTER>

During a surface hop, the kinetic energy has to be modified in order to conserve total
energy. There are several options to that:
1      Do not conserve total energy. Hops are never frustrated.
2      Adjust kinetic energy by rescaling the velocity vectors. Often sufficient.
3      Adjust kinetic energy only with the component of the velocity vector along the
      non-adiabatic coupling vector.
EkinCorrect: [2] <ENTER>

Do you want to apply decoherence to the diagonal states?
Decoherence? [True] <ENTER>

Do you want to scale the energies and gradients?
Scaling? [False] <ENTER>

Do you want to damp the dynamics (Kinetic energy is reduced at each timestep by a factor)?
Damping? [False] <ENTER>

-----Selection of Gradients and NACs-----

```

In order to speed up calculations, SHARC is able to select which gradients and NAC vectors it has to calculate at a certain timestep. The selection is based on the energy difference between the state under consideration and the classical occupied state.

Select gradients? [False] **yes** # this and
 Select non-adiabatic couplings? [False] **yes** # this strongly speeds up the calculation

Please enter the energy difference threshold for the selection of gradients and non-adiabatic couplings (in eV). (0.5 eV recommended, or even larger if SOC is strong in this system.)

Selection threshold (eV): [0.5] **<ENTER>**

-----Laser file-----

Do you want to include a laser field in the simulation? [False] **<ENTER>**

```
=====
||                               MOLPRO Interface setup                               ||
=====
```

-----Path to MOLPRO-----

Environment variable \$MOLPRO detected:

\$MOLPRO=/usr/license/molpro/molpros_2012_1_5_Linux_x86_64_i8/bin/molpro

Do you want to use this MOLPRO installation? [True] **<ENTER>**

-----Scratch directory-----

Please specify an appropriate scratch directory. This will be used to temporally store the integrals. The scratch directory will be deleted after the calculation. Remember that this script cannot check whether the path is valid, since you may run the calculations on a different machine. The path will not be expanded by this script.

Path to scratch directory: (autocomplete enabled) **\$TMPDIR/Traj_WORK**

-----MOLPRO input template file-----

Please specify the path to the MOLPRO.template file. This file must be a valid MOLPRO input file for a CASSCF calculation. It should contain the following settings:

- memory settings
- Basis set (possibly also Douglas-Kroll settings etc.)
- CASSCF calculation with:
 - * Number of frozen, closed and occupied orbitals
 - * wf and state cards for the specification of the wavefunction

MOLPRO.template files can easily be created using molpro_input.py (Open a second shell if you need to create one now).

The MOLPRO interface will generate the remaining MOLPRO input automatically.

Valid file "MOLPRO.template" detected.

Use this template file? [True] **<ENTER>**

-----Initial wavefunction: MO Guess-----

Please specify the path to a MOLPRO wavefunction file containing suitable starting MOs for the CASSCF calculation. Please note that this script cannot check whether the wavefunction file and the Input template are consistent!

If you optimized your geometry with MOLPRO/CASSCF you can reuse the "wf" file from the optimization.

Do you have an initial wavefunction file? [True] **<ENTER>**

Initial wavefunction file: [wf.init] (autocomplete enabled) **wf**

```
=====
||                               Run mode setup                               ||
=====
```

-----Run script-----

This script can generate the run scripts for each trajectory in two modes:

- In the first mode, the calculation is run in subdirectories of the current directory.
- In the second mode, the input files are transferred to another directory (e.g. a local scratch directory), the calculation is run there, results are copied back and the temporary directory is deleted. Note that this temporary directory is not the same as the scratchdir employed by the interfaces.

Note that in any case this script will setup the input subdirectories in the current working directory.

Do you want to use mode 1

(actually perform the calculations in subdirectories of:

/user/mai/Documents/NewSHARC/SHARC_1.5/TESTS/Tutorial/MOLPRO_Ethylene)

Calculate here? [False] **yes**

-----Submission script-----

During the setup, a script for running all initial conditions sequentially in batch mode is generated. Additionally, a queue submission script can be generated for all initial conditions.

Generate submission script? [False] **<ENTER>**

#####Full input#####

```
ntraj          10
ninit          20
molpro.gradaccdefault 1e-07
states         [2, 0, 1]
kill           False
nstates        5
molpro.guess    wf
show_content   True
eharm          0.0543664278
n_issel        [0, 10, 0, 0, 0]
nsubstep       25
diag           False
actstates      [2, 0, 1]
ekinincorrect   2
scratchdir     $TMPDIR/Traj_WORK
eselect        0.5
eref           -78.0813949
```

```

damping                False
firstindex             1
cwd                   /user/sharc/Tutorial/Ethylene/
surf                   sharc
initf                  <open file 'initconds.excited', mode 'r' at 0x7f9c3f39d030>
dtstep                 0.5
repr                  MCH
here                   True
scaling                False
statemap              {1: [1, 1, 0.0],
                       2: [1, 2, 0.0],
                       3: [3, 1, -1.0],
                       4: [3, 1, 0.0],
                       5: [3, 1, 1.0]}

interface              1
qsub                   False
laser                  False
coupling               2
sel_g                  True
tmax                   100.0
molpro                 /usr/license/molpro/molpros_2012_1_5_Linux_x86_64_i8/bin/molpro
molpro.gradaccumax     0.01
sel_t                  True
setupstates            set([2])
printlevel             2
natom                  6
gradcorrect            True
decoherence            0.1
molpro.template        MOLPRO.template
isactive               [True, True, True, True, True]

```

Do you want to setup the specified calculations? [True] **<ENTER>**

```

=====
||                               Setting up directories...                               ||
=====

```

Progress: [=====] 100%

10 trajectories setup, last initial condition was 10 in state 2.

The script creates for each of the initial states (“States to setup the dynamics”) a directory called **<Mult>_<Num>**, e.g., **Singlet_1**, which contains the input for all trajectories starting in the S_1 . Each of these directories contains subdirectories named **TRAJ_00001**, **TRAJ_00002**, etc. Note that these numbers are not consecutive: if an initial condition has not been selected, the number will be missing. Each subdirectory contains the SHARC input (consisting of the files **input**, **geom**, and **veloc**), the directories **QM** and **restart**, and the run script for the trajectory, **run.sh**.

For the purposes of the tutorial it is sufficient to only calculate one trajectory. Change to the subdirectory of one of the trajectories and execute it.

```

user@host> cd Singlet_1/TRAJ_00001
user@host> sh run.sh&
user@host> tailf output.lis

```

While the trajectory is running, you can watch its progress in the file **output.lis** (short output listing). For each timestep, it contains the currently occupied diagonal state (and approximate MCH

state), the kinetic, potential and total energy, the RMS gradient, the state dipole and spin expectation values of the currently occupied diagonal state and the time needed for this step. Surface hopping events are also mentioned in this file.

Besides the **output.lis** file, SHARC creates the files **output.log**, **output.xyz** and **output.dat**. The file **output.log** contains mainly parsing information of the input file parsing and a list of internal steps of the dynamics simulation. With sufficiently high **printlevel** in the SHARC input file, the log file may also contain debug information in various detail. The file **output.dat** contains for each timestep the most important matrices and vectors. This information can be used to calculate the excited-state energies, populations, hopping probabilities and a large number of expectation values. See below for the usage of **data_extractor.x** and **make_gnuplot.py**, which can be used for plotting the mentioned quantities. Finally, **output.xyz** contains the cartesian coordinates of all atoms for each timestep. This file can be opened with any program capable of processing xyz files, like Molden, Molekel and Gabedit. Additionally, the SHARC suite contains the program **geo.py**, which is a command line tool to extract internal coordinates from such an xyz file.

We will first cover the analysis of a single trajectory based on the output files. Later we will also analyze ensemble properties. For these analysis the tutorial assumes that you ran trajectories **TRAJ_00001** to **TRAJ_00005**.

3.8 Analyzing a single trajectory

3.8.1 Data extraction and plotting

The file **output.dat** contains the Hamiltonian, transformation matrix, dipole matrices, coefficients, hopping probabilities, kinetic energy and random number from the surface hopping procedure in a compressed form. The program **data_extractor.x** can be used to generate data tables, which can then be plotted.

```
user@host> $SHARC/data_extractor.x output.dat
```

The program creates a subdirectory called **output_data**. Currently, the following files will be created:

- **coeff_diag.out** contains the coefficients in the diagonal representation.
- **coeff_MCH.out** contains the coefficients in the MCH representation.
- **energy.out** contains kinetic, current potential, total and potential energy of all excited states.
- **fosc.out** contains the oscillator strengths of the current state and all excited states.
- **spin.out** contains the total spin expectation values of the current state and all excited states.
- **expec.out** contains the content of **energy.out**, **fosc.out** and **spin.out** in one file (for plotting).
- **prob.out** contains the surface hopping random number and the hopping probabilities in the diagonal representation.

In order to plot the content of these files in an efficient manner, **gnuplot** can be used. Use

```
user@host> $SHARC/make_gnuscript.py 2 0 1 > trajectory.gp
```

to create a **gnuplot** script with the correct state numbering and labeling. Execute

```
user@host> gnuplot trajectory.gp
```

in the **output_data** directory to plot energies, populations and hopping probabilities (Use **<ENTER>** to continue with the next plot). In figures 3.2, 3.3, 3.4 and 3.5 the output for ethylene trajectory **TRAJ_00001** for the first 100 fs is given.

Discussion of Figure 3.2 In figure 3.2, the potential energies of all states included in the dynamics depending on time is given. The currently occupied state is marked with black circles. Each line

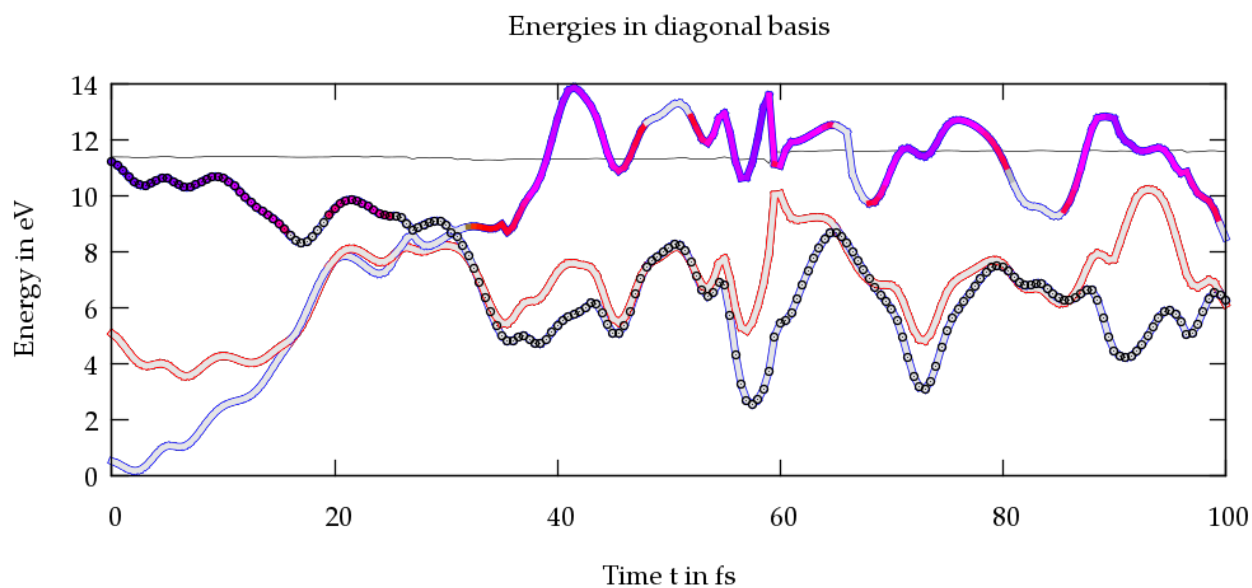


Figure 3.2: Plot of the potential energies for an ethylene trajectory with 2 singlet and 1 triplet states.

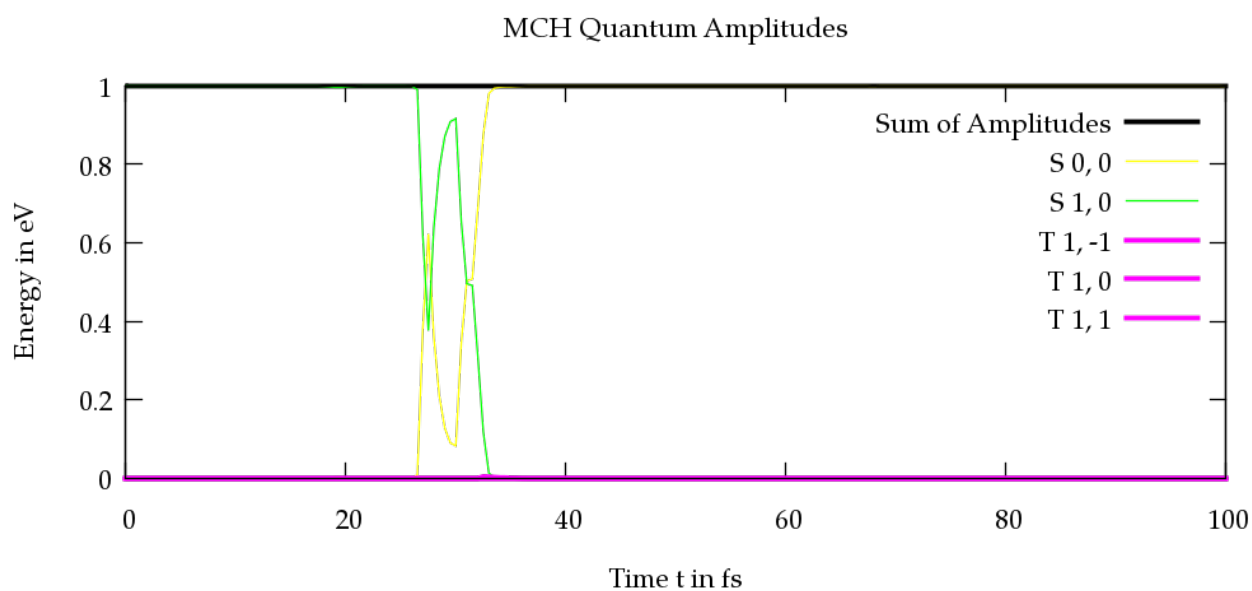


Figure 3.3: Plot of the excited-state populations in the MCH representation.

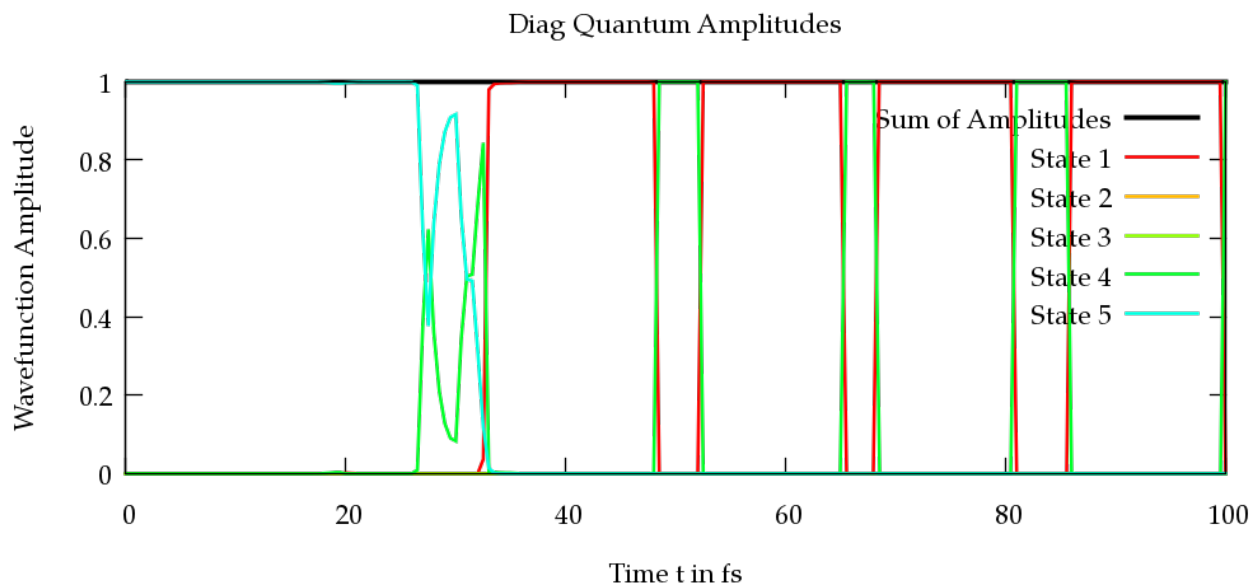


Figure 3.4: Plot of the excited-state populations in the diagonal representation.

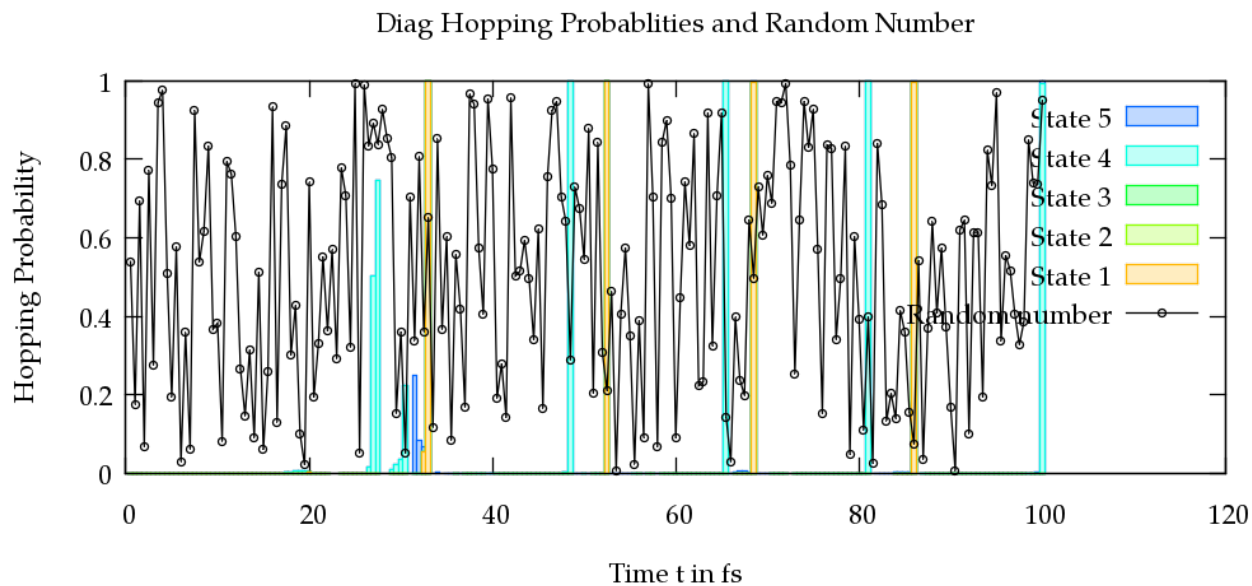


Figure 3.5: Plot of the hopping probabilities in the diagonal representation. Additionally, the random number for the surface hopping procedure is given.

is colored and additionally has a colored contour. The inner color encodes the oscillator strength of the state at each instant of time. Dark states are light grey, while brighter states are given in grey, dark grey, orange, red, magenta or blue, in order of increasing oscillator strength. The outer color encodes the total spin expectation value. Singlets are blue, triplets red and states with mixed singlet-triplet character are green. Since in ethylene spin-orbit coupling is negligible, in the example only blue and red lines are visible.

In the figure, the trajectory starts in the highest excited state, which is singlet and very bright, according to the coloring. After some oscillations, at 30 fs it crosses with the lower singlet state and changes non-adiabatically to the lower state. For later times, the system oscillates with a lot of kinetic energy in the S_0 . It also crosses with the T_1 on several occasions, notably around 50 fs, 65 fs and 80 fs. The thin black line at around 11 eV is the total energy of the system. It stays nearly constant, but fluctuates because the system has a lot of kinetic energy and the timestep is comparably large.

Discussion of Figure 3.3 In figure 3.3, the MCH populations are given depending on time. The system starts with 100% of the population in the upper singlet state S_1 . Around 30 fs, population is transferred to S_0 . The population transfer is complete at approximately 33 fs. In figure 3.2 at the same time it can be seen that the trajectory switches to the lower singlet surface. In figure 3.3, after the hop nearly 100% of the population is in S_0 . The triplet state does not get populated at all during the dynamics, which was expected, since the spin-orbit coupling is extremely weak and the singlet and triplet states do not stay close for long periods of time.

Discussion of Figure 3.4 In figure 3.4, the diagonal populations are given depending on time. It can be seen nicely that the populated diagonal state changes several times during the simulation because the S_0 crosses with the T_1 . In the diagonal representation, this leads to near-complete population transfer as T_1 becomes the lower state and S_0 the higher state (and vice versa).

Discussion of Figure 3.5 Figure 3.5 shows the surface hopping probabilities and the corresponding random numbers depending on time. In a nutshell, a surface hop happens whenever the random number lies within one of the colored bars. The color of the bar corresponds to the state into which the trajectory will hop. In the diagram, there are several hopping probabilities close to unity. This corresponds to the near-complete population transfer during the crossing of the S_0 and T_1 states.

3.8.2 Analyzing internal coordinates

The file **output.xyz** contains the cartesian coordinates of all timesteps. Oftentimes, one is interested in the variation of certain internal coordinates (like bond lengths, angles, etc.) during the dynamics. The SHARC tool **geo.py** can quickly calculate these values. Invoke the program and enter the internal coordinate specifications:

```
user@host> $SHARC/geo.py -g output.xyz -t 0.5
```

```
Enter the internal coordinate specifications:
```

```
r 1 2
```

```
d 6 1 2 5
```

```
end
```

```
Number of internal coordinate requests: 2
```

```
Number of geometries: 200
```

```
FINISHED!
```

The **-g** option specifies the filename of the input xyz geometry file, while the **-t** option specifies the timestep. **geo.py** writes the results to standard out, so redirect the output to some file:

```
user@host> $SHARC/geo.py -g output.xyz -t 0.5 > Geo.out
```

The file **Geo.out** contains a table with the specified internal coordinates:

#	1	2	3
#	time	r 1 2	d 6 1 2 5
	0.0000	1.3073	11.0993
	0.5000	1.3157	10.1916
	1.0000	1.3283	9.1573
	:	:	:

Use GNUPLOT to plot this table.

```
user@host> gnuplot
```

The file **Geo.out** contains a table with the specified internal coordinates:

```
gnuplot> p "Geo.out" u 1:2 w l      # Plot column 2 versus 1
gnuplot> p "Geo.out" u 1:3 w l      # Plot column 3 versus 1
```

The results are shown in figures 3.6 and 3.7.

Discussion of the internal coordinates In figures 3.6 the C=C bond length is plotted over time. It can be easily seen that after excitation to the $\pi\pi^*$ state, the C=C bond stretches strongly and starts to oscillate around the average bond length of a single C–C bond (1.5 Å).

In figure 3.7, the dihedral angle H–C=C–H is plotted in degrees (confined to the interval $[0, 180^\circ]$). It can be seen that after excitation the molecule undergoes torsion around the double bond. This (together with pyramidalization of the carbon atoms) leads to the well-known conical intersection of the $\pi\pi^*$ state and the ground state. In this trajectory, the conical intersection was reached after about 30 fs (recall figure 3.2).

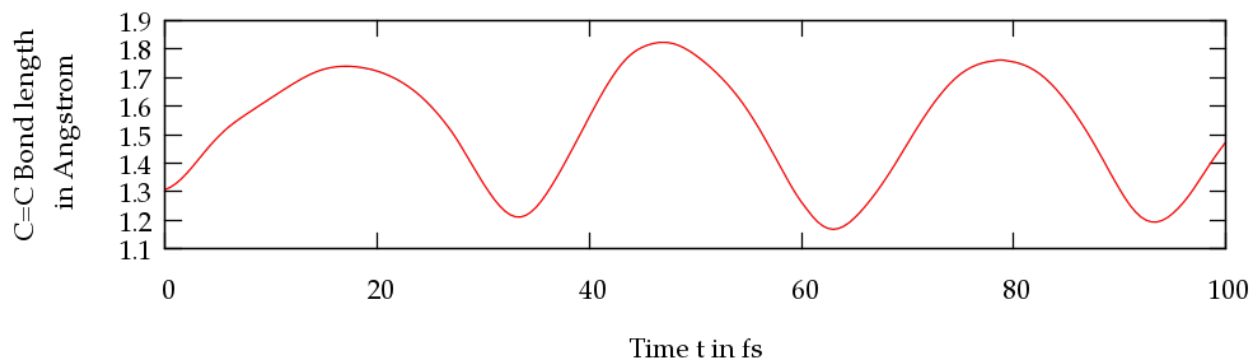


Figure 3.6: Value of the C=C bond length during the simulation.

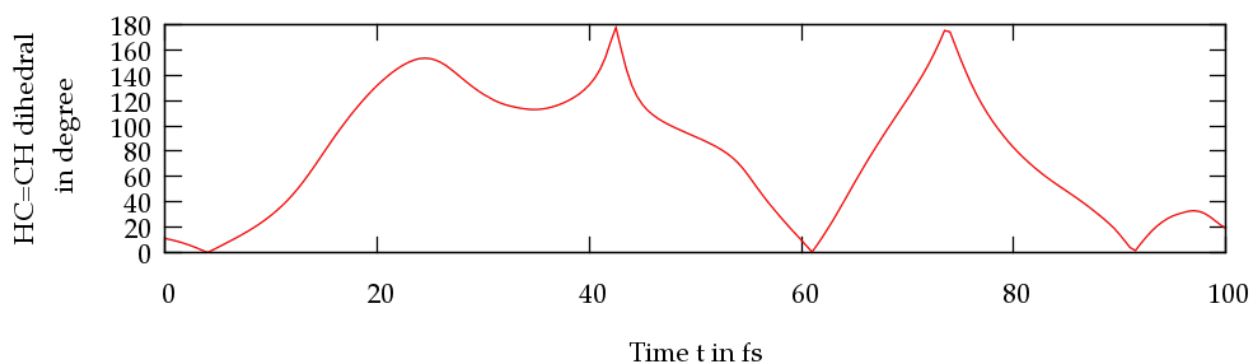


Figure 3.7: Value of one of the H-C=C-H dihedrals during the simulation.

3.9 Analyzing the Ensemble

3.9.1 Ensemble Populations

Among the main results of a SHARC simulation are the time-dependent excited-state populations within the simulated ensemble. In order to obtain these populations, the populations of all trajectories have to be summed up and normalized to the number of trajectories.

The script **populations.py** can be used to calculate various excited-state populations. There are several concepts:

- Count for each timestep the number of trajectories in each classical state. These are the “classical” populations.
- For each timestep calculate the sum of the squares of the quantum amplitudes of each state. These sums are called the “quantum” populations.
- Count for each timestep the number of trajectories whose expectation values are within a certain interval. This can be used to obtain populations which correspond to certain classes of states (e.g. count all trajectories with large oscillator strength \Rightarrow Approximate $\pi\pi^*$ population).

In the following, an example is given on the usage of **populations.py**, and afterwards the results of using the different concepts are discussed.

```
user@host> $SHARC/populations.py
```

=====

Reading populations from SHARC dynamics

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Version:0.1
12.03.14

This script reads output.lis files and calculates ensemble populations (e.g. based on the classically occupied state or based on the quantum amplitudes).

-----Paths to trajectories-----

Please enter the paths to all directories containing the "TRAJ_0XXXX" directories.
E.g. S_2 and S_3.

Please enter one path at a time, and type "end" to finish the list.

Path: [end] (autocomplete enabled) **Singlet 1**

```
[ 'TRAJ_00005', 'TRAJ_00004', 'TRAJ_00008', 'TRAJ_00001', 'TRAJ_00009',  
  'TRAJ_00002', 'TRAJ_00006', 'TRAJ_00010', 'TRAJ_00007', 'TRAJ_00003']
```

```
Found 10 subdirectories in total.
```

Path: [end] (autocomplete enabled) **<ENTER>**

Total number of subdirectories: 10

-----Analyze Mode-----

This script can analyze the classical populations in different ways:

- ```

1 Number of trajectories in each diagonal state
 from output.lis
2 Number of trajectories in each MCH state

```

```

 from output.lis
3 Number of trajectories in each MCH state (multiplets summed up)
 from output.lis
4 Number of trajectories whose total spin value falls into certain intervals
 from output.lis
5 Number of trajectories whose dipole moment falls into certain intervals
 from output.lis
6 Number of trajectories whose oscillator strength falls into certain intervals
 from output_data/fosc.out

```

It can also sum the quantum amplitudes:

```

7 Quantum amplitudes in diagonal picture
 from output_data/coeff_diag.out
8 Quantum amplitudes in MCH picture
 from output_data/coeff_MCH.out
9 Quantum amplitudes in MCH picture (multiplets summed up)
 from output_data/coeff_MCH.out

```

Analyze mode: **3**

-----Number of states-----

Please enter the number of states as a list of integers  
e.g. 3 0 3 for three singlets, zero doublets and three triplets.

Number of states: [2 0 1] **<ENTER>**

-----Normalization-----

Normalize the populations? [True] **<ENTER>**

-----Simulation time-----

Up to which simulation time should the analysis be performed? (Trajectories  
which are shorter are continued with their last values.)

Simulation time (in fs): [1000.0] **100**

-----Gnuplot script-----

Gnuplot script? [False] **yes**

Gnuplot script filename? [populations.gp] (autocomplete enabled) **pop\_class.gp**

#####Full input#####

```

normalize True
paths ['Singlet_1/']
gnuplot_out pop_class.gp
gnuplot True
run_extractor False
states [2, 0, 1]
mode 3
maxtime 100.0
nstates 3
nmstates 5

```

Do you want to do the specified analysis? [True] **<ENTER>**

Checking the directories...

# If not all trajectories were run, this will be detected here

Singlet\_1//TRAJ\_00005 OK

```

Singlet_1//TRAJ_00004 OK
Singlet_1//TRAJ_00008 Singlet_1//TRAJ_00008/output.lis NOT FOUND
Singlet_1//TRAJ_00001 OK
Singlet_1//TRAJ_00009 Singlet_1//TRAJ_00009/output.lis NOT FOUND
Singlet_1//TRAJ_00002 OK
Singlet_1//TRAJ_00006 Singlet_1//TRAJ_00006/output.lis NOT FOUND
Singlet_1//TRAJ_00010 Singlet_1//TRAJ_00010/output.lis NOT FOUND
Singlet_1//TRAJ_00007 Singlet_1//TRAJ_00007/output.lis NOT FOUND
Singlet_1//TRAJ_00003 OK
Number of trajectories: 5
Found dt=0.500000, nsteps=2001, nstates=3

Singlet_1//TRAJ_00005/output.lis 200 # Number of steps read
Singlet_1//TRAJ_00004/output.lis 200
Singlet_1//TRAJ_00001/output.lis 200
Singlet_1//TRAJ_00002/output.lis 200
Singlet_1//TRAJ_00003/output.lis 200
Shortest trajectory: 100.000000
Longest trajectory: 100.000000

Writing to pop.out ...

```

The incoherent sum of the quantum amplitudes can be calculated with mode 9. Rerun **populations.py**.  
 user@host> **\$SHARC/populations.py**

```

: : : : : :
-----Analyze Mode-----

This script can analyze the classical populations in different ways:
1 Number of trajectories in each diagonal state
 from output.lis
2 Number of trajectories in each MCH state
 from output.lis
3 Number of trajectories in each MCH state (multiplets summed up)
 from output.lis
4 Number of trajectories whose total spin value falls into certain intervals
 from output.lis
5 Number of trajectories whose dipole moment falls into certain intervals
 from output.lis
6 Number of trajectories whose oscillator strength falls into certain intervals
 from output_data/fosc.out

It can also sum the quantum amplitudes:
7 Quantum amplitudes in diagonal picture
 from output_data/coeff_diag.out
8 Quantum amplitudes in MCH picture
 from output_data/coeff_MCH.out
9 Quantum amplitudes in MCH picture (multiplets summed up)
 from output_data/coeff_MCH.out

Analyze mode: 9

Run data_extractor.x for each trajectory prior to performing the analysis?
For many or long trajectories, this might take some time.
Run data_extractor.x? [True] <ENTER>

```

```

: : : : : :
-----Gnuplot script-----

Gnuplot script? [False] yes
Gnuplot script filename? [populations.gp] (autocomplete enabled) pop_quant.gp

: : : : : :

Overwrite pop.out? [False] <ENTER>

Please enter the output filename: (autocomplete enabled) pop_quant.out
Writing to pop_quant.out ...

```

Third, we obtain the number of trajectories whose oscillator strength falls into one of these intervals:  $0 < f_{\text{osc}} < 10^{-4}$ ,  $10^{-4} < f_{\text{osc}} < 10^{-1}$  and  $10^{-1} < f_{\text{osc}}$ . Rerun **populations.py** again.

user@host> **\$SHARC/populations.py**

```

: : : : : :
-----Analyze Mode-----

This script can analyze the classical populations in different ways:
1 Number of trajectories in each diagonal state
 from output.lis
2 Number of trajectories in each MCH state
 from output.lis
3 Number of trajectories in each MCH state (multiplets summed up)
 from output.lis
4 Number of trajectories whose total spin value falls into certain intervals
 from output.lis
5 Number of trajectories whose dipole moment falls into certain intervals
 from output.lis
6 Number of trajectories whose oscillator strength falls into certain intervals
 from output_data/fosc.out

It can also sum the quantum amplitudes:
7 Quantum amplitudes in diagonal picture
 from output_data/coeff_diag.out
8 Quantum amplitudes in MCH picture
 from output_data/coeff_MCH.out
9 Quantum amplitudes in MCH picture (multiplets summed up)
 from output_data/coeff_MCH.out

Analyze mode: 6

Run data_extractor.x for each trajectory prior to performing the analysis?
For many or long trajectories, this might take some time.
Run data_extractor.x? [True] no # Was already done above

: : : : : :
-----Gnuplot script-----

```

```

Gnuplot script? [False] yes
Gnuplot script filename? [populations.gp] (autocomplete enabled) pop_fosc.gp

-----Intervals-----

Please enter the interval limits, all on one line.
Interval limits: 1e-4 1e-1 # Outer limits 0 and infinity are automatically assumed

: : : : : : :
: : : : : : :

Overwrite pop.out? [False] <ENTER>

Please enter the output filename: (autocomplete enabled) pop_fosc.out
Writing to pop_quant.out ...

```

Use the produced GNUPLOT scripts to plot the obtained populations.

```

user@host> gnuplot pop_class.gp
user@host> gnuplot pop_quant.gp
user@host> gnuplot pop_fosc.gp

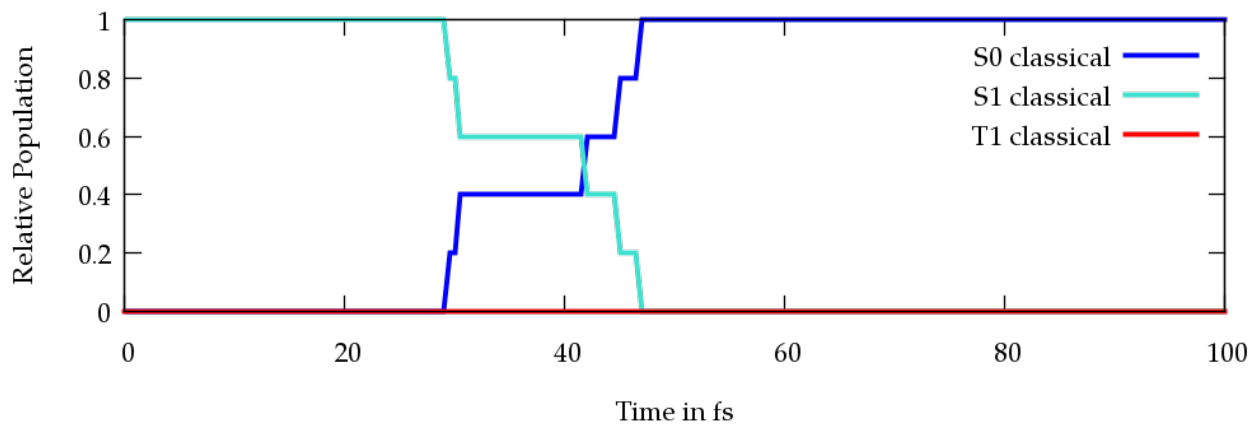
```

This will create the files **pop\_class.gp.png**, **pop\_quant.gp.png** and **pop\_fosc.gp.png**. They are shown in figures 3.8, 3.9 and 3.10. In 3.8, the classical populations are given. In figure 3.9, the incoherent sum of the quantum amplitudes is given (obtained by using mode 9 in **populations.py**). In figure 3.10, the 5 trajectories are classified depending on their oscillator strengths.

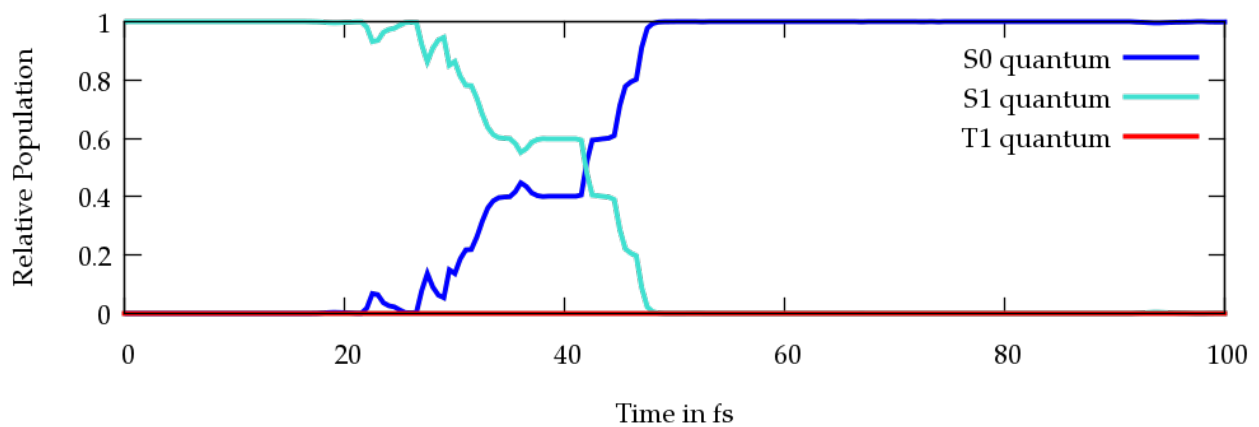
**Discussion of Figure 3.8** In figure 3.8 it can be seen that between 30 and 50 fs simulation time, all ethylene trajectories changed from the initial  $S_1$  state to the  $S_0$  ground state. Two trajectories performed the surface hop at about 30 fs, while the remaining three trajectories switched between 40 and 50 fs. The  $T_1$  state remained completely unpopulated.

**Discussion of Figure 3.9** In figure 3.9 the quantum populations are shown. For sufficiently large ensembles, figure 3.8 should closely follow figure 3.9. Consistency between the classical and quantum populations can be improved by using the decoherence correction (Input option in **setup\_traj.py**).

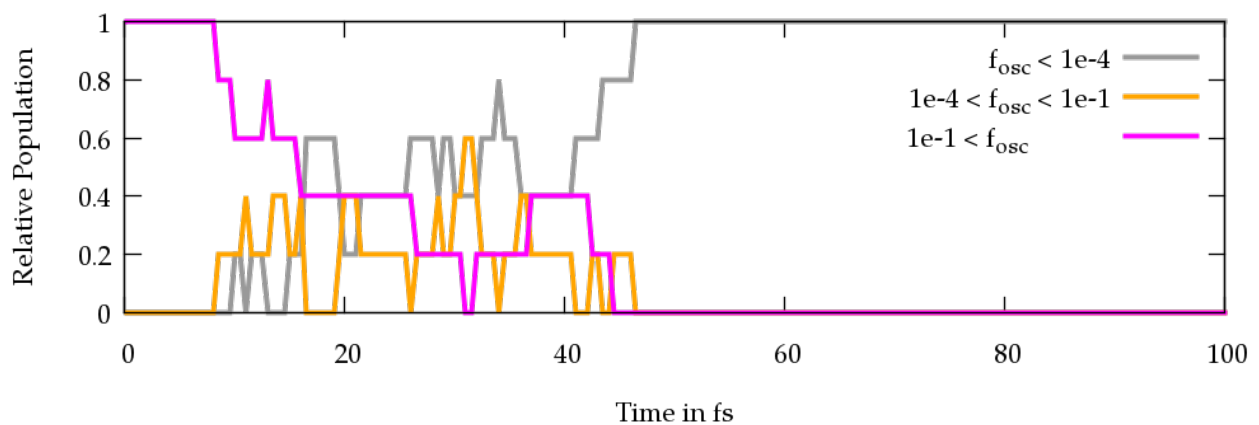
**Discussion of Figure 3.10** In figure 3.10 the ensemble population was classified according to the oscillator strength of the classically populated state. The chosen interval limits were 0.0001 and 0.1, giving three classes of states (below 0.0001, between 0.0001 and 0.1, and above 0.1). Initially, all trajectories are in the bright  $\pi\pi^*$  state and are thus classified into the third class. During the dynamics, the induced torsion around the double bond reduces the oscillator strength, so that the trajectories are classified into the intermediate class. Later, the trajectories decay to the ground state, which has by definition an oscillator strength of zero (since  $f_{osc}$  is proportional to the excitation energy). Note that in this example the ground state cannot be distinguished from the triplet state, which has negligible oscillator strength and thus would also be classified into the first class. In general, however, classifying the population according to oscillator strength sometimes allows to approximately obtain populations of  $\pi\pi^*$  and  $n\pi^*$  states.



**Figure 3.8:** Classical populations for an ensemble of 5 trajectories.



**Figure 3.9:** Quantum populations for an ensemble of 5 trajectories.



**Figure 3.10:** Populations classified based on oscillator strength for an ensemble of 5 trajectories.



### 3.9.2 Hopping Geometries

Often, one is also interested in geometries which fulfill certain criteria, e.g., geometries where surface hops occurred. **crossing.py** is a script to collect those geometries from all trajectories. Its usage is comparable to **populations.py**.

```
user@host> $SHARC/crossing.py
```

```
=====
||
||
|| Reading hopping geometries from SHARC dynamics
||
||
|| Author: Sebastian Mai
||
||
|| Version:0.2
|| 04.06.14
||
||
```

This script reads output.lis files and output.xyz files to produce a list of all geometries where certain surface hops (or other events) occurred.

-----Paths to trajectories-----

Please enter the paths to all directories containing the "TRAJ\_0XXXX" directories.

E.g. S\_2 and S\_3.

Please enter one path at a time, and type "end" to finish the list.

Path: [end] (autocomplete enabled) Singlet\_1

```
['TRAJ_00005', 'TRAJ_00004', 'TRAJ_00008', 'TRAJ_00001', 'TRAJ_00009',
 'TRAJ_00002', 'TRAJ_00006', 'TRAJ_00010', 'TRAJ_00007', 'TRAJ_00003']
```

Found 10 subdirectories in total.

Path: [end] (autocomplete enabled) **ENTER**

Total number of subdirectories: 10

-----Analyze Mode-----

This script can find geometries where:

```
1 A change of MCH state occurred (ignoring hops within one multiplet)
 from output.lis
```

Analyze mode: 1

-----Number of states-----

Please enter the number of states as a list of integers

e.g. 3 0 3 for three singlets, zero doublets and three triplets.

Number of states: [2 0 1] **<ENTER>**

-----States involved in surface hop-----

In this analysis mode, all geometries are fetched where a trajectory switches from a given MCH state to another given MCH state.

Please enter the first MCH state involved (mult state):

State 1: 1 2 # Only hops from S1

Please enter the second MCH state involved (mult state):

State 2: 1 1 # to S0

```

Direction:
1 Forwards # Only hops S1 -> S0
2 Backwards # Only hops S0 -> S1
3 Two-way # Hops S0 -> S1 and S1 -> S0

Direction mode: [3] 1

#####Full input#####

paths ['Singlet_1/']
tostates [[1, 1]]
run_extractor False
states [2, 0, 1]
mode 1
dirmode 1
nstates 3
fromstates [[1, 2]]
nmstates 5

Do you want to do the specified analysis? [True] <ENTER>

Checking the directories...
Singlet_1//TRAJ_00001 OK
Singlet_1//TRAJ_00002 OK
Singlet_1//TRAJ_00003 OK
Singlet_1//TRAJ_00004 OK
Singlet_1//TRAJ_00005 OK
Singlet_1//TRAJ_00006 Singlet_1//TRAJ_00006/output.lis NOT FOUND
Singlet_1//TRAJ_00007 Singlet_1//TRAJ_00007/output.lis NOT FOUND
Singlet_1//TRAJ_00008 Singlet_1//TRAJ_00008/output.lis NOT FOUND
Singlet_1//TRAJ_00009 Singlet_1//TRAJ_00009/output.lis NOT FOUND
Singlet_1//TRAJ_00010 Singlet_1//TRAJ_00010/output.lis NOT FOUND
Number of trajectories: 5

Writing to crossing.xyz ...

```

The output file **crossing.xyz** in turn can also be analyzed with **geo.py** in order to calculate internal coordinates.

## 4 Specialized Tutorials

### 4.1 Using non-default atomic masses

Sometimes, in dynamics simulations one is interested in isotope effects. This necessitates the modification of the atomic mass of the corresponding atoms. The atomic masses are included in the geometry file, which is read by SHARC during initialization of the dynamics.

Furthermore, modification of the atomic masses influences the Wigner distribution of initial conditions. **wigner.py** has a facility to adjust the atomic mass during initial condition generation. Call **wigner.py** as usual, but include the **-m** option:

```
user@host> $SHARC/wigner.py freq.molden -m
```

Instead of directly producing the initial conditions file, **wigner.py** will start a dialog, where the user can modify the atomic masses. Initially, all atoms are assumed to use the default mass (the mass of the most common isotope). The user can then add atoms to the list of atoms with non-default masses, thereby specifying the mass.

```
Initial condition generation started...
MOLDEN file = "freq.molden"
OUTPUT file = "initconds"
Number of geometries = 20
Random number generator seed = 16661

Option -m used, please enter non-default masses:
+ number mass add non-default mass <mass> for atom <number>
- number remove non-default mass for atom <number> (default mass will be used)
show show non-default atom masses
end finish input for non-default masses

+ 1 14.054321 # Give atom number 1 the mass 14.054321
show

Atom Mass
 1 14.054321000000

- 1 # Give atom number 1 the default mass
+ 2 16.054321 # Give atom number 2 the mass 16.054321
+ 2 15.054321 # Give atom number 2 the mass 15.054321
end

Geometry:
C 6.0 -0.000000000 0.000000000 -0.00760978 12.000000000
C 6.0 0.000000000 0.000000000 2.53039416 15.05432100
H 1.0 1.73012211 0.000000000 -1.07271869 1.00782503
H 1.0 1.73012212 0.000000000 3.59550308 1.00782503
H 1.0 -1.73012211 0.000000000 3.59550308 1.00782503
H 1.0 -1.73012212 0.000000000 -1.07271870 1.00782503
Assumed Isotopes: H-1 C-12
Isotopes with * are pure isotopes.
```

Frequencies (cm<sup>-1</sup>):

|    |           |
|----|-----------|
| 1  | 885.9700  |
| 2  | 970.0600  |
| 3  | 1068.5700 |
| 4  | 1299.2900 |
| 5  | 1342.3400 |
| 6  | 1439.6100 |
| 7  | 1605.6600 |
| 8  | 1774.6800 |
| 9  | 3319.3700 |
| 10 | 3339.1300 |
| 11 | 3396.7200 |
| 12 | 3422.7000 |

Note that with the **+** command the mass of an already specified atom can also be changed.

**Frequency calculation** Please also note that the preceding frequency calculation also has to use the same atomic masses as the run of **wigner.py**. For MOLPRO, **molpro.input.py** can setup frequency calculations with non-standard atomic masses. For COLUMBUS, the user can edit the **geom** before starting the frequency calculation.

## 4.2 Inactive states

Sometimes, states should be included in the dynamics simulation in order to calculate transient absorption spectra, transient ionization spectra or simply in order to see how these states evolve during the dynamics. When it is not expected that these states are actually occupied during the simulation, SHARC has a mechanism to neglect all couplings between these states (called inactive henceforth) and the occupied states. This allows also to neglect the gradients and non-adiabatic couplings involving these states, thereby saving considerable amounts of computation time.

It is only possible to make the highest states in each multiplicity inactive. With **states 3 0 3** and **actstates 2 0 1** in the SHARC input, one would include  $S_0$ ,  $S_1$ ,  $S_2$ ,  $T_1$ ,  $T_2$  and  $T_3$  in the simulation, but restrict the actual dynamics to  $S_0$ ,  $S_1$  and  $T_1$ .

It is advisable to make inactive all states which do not show any couplings with the occupied states (e.g., ionic states in a dynamics simulation of a neutral molecule).

**Inactive states in excite.py** **excite.py** also allows to exclude states in the excitation process. Note, however, that this is unrelated to the inactive states in the dynamics. It would be possible to exclude a state in the excitation process but still keep it in the dynamics simulation. An example would be to excite to dark  $n\pi^*$  states, which would not be selected if bright  $\pi\pi^*$  states are present.

## 4.3 Ionization spectra using excite.py and the Columbus interface

When using the COLUMBUS interface, it is possible to calculate Dyson norms between pairs of neutral and ionic states. These norms are an estimate for the single-photon ionization probability. **setup\_init.py** and **excite.py** can be used to calculate ionization spectra based on a Wigner distribution of geometries, essentially in the same way as absorption spectra are calculated.

### 4.3.1 setup\_init.py Input

First, obtain the **initconds** file as usual. Then setup the initial excited-state calculations. Use the COLUMBUS interface. The last interface-related question will be whether Dyson norms should be calculated. Enter the path to the Dyson program of Matthias Ruckebauer and to the Dyson-compatible version of **civeconsolidate**.

```
-----Ionization probability by Dyson norms-----

Dyson norms? [False] yes
Path to dyson executable: (autocomplete enabled) $DYSON/dyson.x
Path to civeconsolidate executable: [$COLUMBUS/civeconsolidate] (autocomplete enabled) <ENTER>
c2 threshold for Dyson: [0.0001] <ENTER>
```

Finish the setup as usual and run the calculations.

### 4.3.2 excite.py Input

Use **excite.py** as usual to read the results of the excited-state calculations. Near the end, the following question is asked:

```
Use Dyson norms instead of dipole moments? [False] yes
```

The script will use the Dyson norms in the place of the  $x$  component of the transition dipole moments, while the  $y$  and  $z$  components will be set to zero. The remaining usage is identical to the regular case (transition dipole moments). **spectrum.py** can be used to obtain plottable spectra.

## 5 Usage of the Interfaces

All of the SHARC scripts are in principal compatible with the interfaces to MOLPRO, MOLCAS and COLUMBUS. However, depending on the interface, some details of the preparation of the dynamics change. In the following, these details are addressed.

### 5.1 MOLPRO

See the full tutorial in chapter 3. In combination with `molpro_input.py` and the setup scripts, usage should be relatively straight-forward.

### 5.2 MOLCAS

Instead of the `MOLPRO.template` file needed for MOLPRO, usage of MOLCAS requires a `MOLCAS.template` file, which has a different structure. The template file can be setup with the script `molcas_input.py`.

#### 5.2.1 Template file

An exemplary template file looks like:

```
basis cc-pvdz
ras2 3
nactel 4
inactive 6
spin 1 roots 4
spin 3 roots 3
```

Currently, there are no more keywords than the ones given in this example. **basis** defines the basis set, **ras2** is the number of active orbitals, **nactel** is the number of active electrons and **inactive** is the number of doubly occupied orbitals. The lines with **spin** and **roots** keywords defines the number of states per multiplicity, in this case 4 singlet states and 3 triplet states.

### 5.3 COLUMBUS

Since COLUMBUS is a complex suite of many independent programs (each with own input files), input preparation is conducted with COLUMBUS' interactive input facility `colinp`. In order to perform single-point calculations and optimizations/frequency calculations, please refer to the [COLUMBUS online documentation](#) and the [standard tutorial](#).

### 5.3.1 General steps in running COLUMBUS

In order to use COLUMBUS, whether via its driver script **runc** or through the SHARC-COLUMBUS interface, you have to set the environment variable **\$COLUMBUS** to the directory containing the COLUMBUS executables (like **runc**, **mcscf.x**, **ciudg.x**, etc.).

In order to prepare a calculation, first convert the standard xyz file containing the molecular geometry to COLUMBUS format:

```
user@host> $COLUMBUS/xyz2col.x < geom.xyz
```

which will create the file **geom**. Then, start **colinp**

```
user@host> $COLUMBUS/colinp
```

Go through the input sections, starting with the integral section, followed by SCF, CASSCF, MRCI and finally the run setup. After the preparation of the input, start COLUMBUS via

```
user@host> $COLUMBUS/runc -m [MEMORY in MB] > runls&
```

An optimization can be carried out directly with **runc** – just use the corresponding options in **colinp**. For a (numerical) frequency calculation, use **colinp** to generate the internal coordinates and the **DISPLACEMENT** directories. Then, a calculation needs to be carried out in each of the **DISPLACEMENT** subdirectories, a task which is accomplished by the **calc.pl** script. The script **forceconst.pl** collects the results and produces the file **suscalls**, which is compatible with the MOLDEN format (and can be used with **wigner.py**).

### 5.3.2 COLUMBUS input for usage with the interface

Instead of a template file as in the MOLPRO case, for COLUMBUS a template directory is needed. The directory contains one subdirectory with input for each multiplicity (singlets, doublets, triplets, ...). However, even-electron wavefunctions of different multiplicities can be computed together in the same job if spin-orbit couplings are desired. Otherwise independent multiple-DRT inputs (ISC keyword) are also acceptable. Note that symmetry is not allowed when using the interface.

In order to prepare the input for the SHARC-COLUMBUS interface, you can furthermore see the [tutorial on spin-orbit coupling calculations](#).

**Integral input** The interface is only able to use input for calculations using MOLPRO/SEWARD integrals. No symmetry is allowed here. Make sure that you include scalar-relativistic and spin-orbit (AMFI) effects in the integral input.

**MCSCF input** The MCSCF section can use any desired state-averaging scheme. However, frozen core orbitals in the MCSCF step are not possible. Prepare the MCSCF input for CI gradients. It is advisable to use very tight MCSCF convergence criteria.

**MRCI input** Either prepare a single-DRT input without SOCI (to cover a single multiplicity), a single-DRT input with SOCI and a sufficient maximum multiplicity for spin-orbit couplings or a independent multiple-DRT input (ISC case). Make sure that all multiplicities are covered with all input directories.

In the MRCI input, make sure to use sequential **ciudg**. Also take care to setup gradient input on MRCI level.

**Job control** Setup a single-point calculation with the following steps:

- SCF
- MCSCF
- MR-CISD (serial operation) or SO-CI coupled to non-rel CI (for SOCI DRT inputs)
- one-electron properties for all methods
- transition moments for MR-CISD
- nonadiabatic couplings (and/or gradients)

Request first transition moments and interstate couplings in the following dialogues. Analysis in internal coordinates and intersection slope analysis are not required.

## 5.4 Analytical expressions

For the interface using analytical expressions for the potential energy surfaces, only one input file (**SH2Ana.inp**) is needed. This file contains the definitions of all analytical expressions. See below for an example of this file.

The remaining procedure with the analytical potential interface is analogue to the usage of the other interfaces.

### 5.4.1 One-dimensional case

In the following, we will prepare the input for a single particle moving in one dimension on two states.

The file **SH2Ana.inp** consists of a file header and a file body. The header for the one-dimensional case and for two states could look as follows:

```
1
2
H x 0 0
```

The first line defines the number of atoms to be one, the second line gives the number of states. The third line is a mapping of the cartesian coordinates of the atom to variable names. In this case, the  $x$  component of the coordinate of the atom is linked to the actual variable called **x**. The variable can then be used in the file body in the definitions of the potentials.

Below the file header (with  $n_{\text{atom}} + 2$  lines), different blocks can be put. Variable blocks define can be used to define constants:

```
Variables
k 2.0
D12 10.0
Re 2.0
omega 13.
mu 1.0
End
```

Most importantly, matrix blocks define the potential energies, couplings and gradients. A matrix block could look like:



```
Hamiltonian
0.5*k*x**2+omega,
0, 0.5*k*(x-Re)**2+D12,
```

Note the keyword **Hamiltonian**, which defines the type of matrix given.

Another matrix block gives the derivatives of the Hamiltonian with respect to the variable **x**:

```
Derivatives x
k*x,
0, k*(x-Re),
```

The user has to provide the correct derivatives of the Hamiltonian manually.

Put together, the complete input for the example might look like:

```
1
2
H x 0 0

Variables
k 2.0
D12 10.0
Re 2.0
mu 1.0
End

Hamiltonian
0.5*k*x**2,
0, 0.5*k*(x-Re)**2+D12,

Derivatives x # Derivatives with respect to x
k*x, # Derivatives need to be given manually
0, k*(x-Re),

Dipole 1
0.0,
0.5*mu, 0.0,
```

Only the **Hamiltonian** block and one **Derivatives** block for each variable needs to be present. Optional blocks are **SpinOrbit**, **Dipole** and **Dipolederivaties**.

For more details please refer to the manual.